BEILSTEIN JOURNAL OF ORGANIC CHEMISTRY

# Supporting Information

for

# Regioselective alkylation of a versatile indazole: Electrophile scope and mechanistic insights from density functional theory calculations

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# Characterization of all compounds ($^{1}$H NMR, $^{13}$C NMR, LC–MS, IR), and crystallographic methods and data for products P1 and P2

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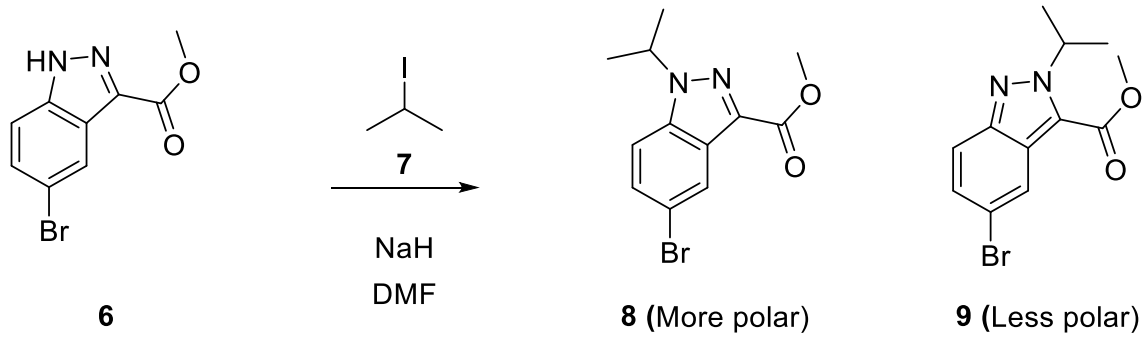
**Scheme S1 Procedure.**

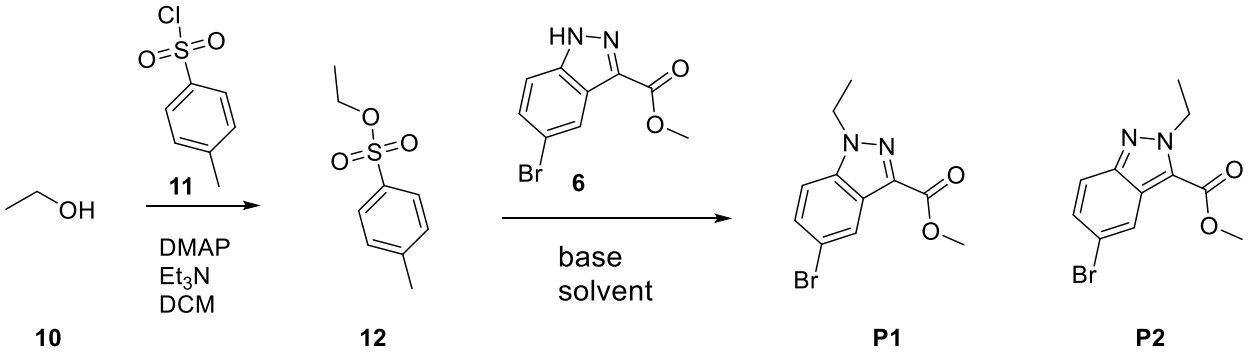



**6** **8 (**More polar) **9 (**Less polar)

To a solution of methyl 5-bromo-1*H*-indazole-3-carboxylate (**6,** 1 g, 3.92 mmol) in DMF (Volume: 10 mL) at 0 ℃ was treated with sodium hydride (0.172 g, 60% dispersion, 4.31 mmol). After 15 min, 2-iodopropane (1.187 mL, 11.76 mmol) was added at 0 °C and the reaction was warmed slowly in the ice bath to RT and stirred for 15 h. The mixture was poured into EtOAc and washed with water and brine. The organic layer was dried and concentrated, and the obtained residue was purified by chromatography [silica gel (40 g), eluting with EtOAc in hexane from 0–50%] to give methyl 5-bromo-1-isopropyl-1*H*-indazole-3-carboxylate (**8**, 0.45 g, 1.514 mmol, 38.6% yield) as a white solid and methyl 5-bromo-2-isopropyl-2*H*-indazole-3-carboxylate (**9**, 0.54 g, 1.817 mmol, 46.4% yield) as a white solid. Characterization is consistent with **15c** and **16c** (vide infra).

**Table S1. Conditions screening**.

To a solution of methyl 5-bromo-1*H*-indazole-3-carboxylate (0.500 g, 1.960 mmol) in [solvent] (20 mL) at RT was added [base, equiv] followed by ethyl 4-methylbenzenesulfonate (**12,** equiv). The resulting mixture was stirred for [#] hours at [#] °C. The mixture was poured into EtOAc 500 mL and washed with water 100 mL and brine. The organic layer was dried and concentrated, the obtained residue was purified by chromatography [silica gel (24 g), eluting with EtOAc in hexane from 0–70%] to give ## P1 and ## P2 as white solids. Characterization is consistent with **15b** and **16b** (vide infra).




10 12 P1 P2

| Entry | Eq. of 12 | Eq. of 6 | Base (eq.) | Solvent | Temperature (°C) | Time (h) | P1 % (Isolated) |
|---|---|---|---|---|---|---|---|
| 1 | 1.0 | 1.0 | $Cs_2CO_3$ (2.0) | DMF | 90 | 2 | 52 |
| 2 | 1.1 | 1.0 | $Cs_2CO_3$ (2.0) | DMF | 90 | 2 | 54 |
| 3 | 1.2 | 1.0 | $Cs_2CO_3$ (2.0) | DMF | 90 | 2 | 54 |
| 4 | 1.3 | 1.0 | $Cs_2CO_3$ (2.0) | DMF | 90 | 2 | 54 |
| 5 | 1.4 | 1.0 | $Cs_2CO_3$ (2.0) | DMF | 90 | 2 | 55 |
| 6 | 1.5 | 1.0 | $Cs_2CO_3$ (2.0) | DMF | 90 | 2 | 60 |
| 7 | 2.0 | 1.0 | $Cs_2CO_3$ (2.0) | DMF | 90 | 2 | 54 |
| 8 | 2.5 | 1.0 | $Cs_2CO_3$ (2.0) | DMF | 90 | 2 | 53 |
| 9 | 3.0 | 1.0 | $Cs_2CO_3$ (2.0) | DMF | 90 | 2 | 54 |
| 10 | 1.5 | 1.0 | $Cs_2CO_3$ (2.0) | DMF | 110 | 2 | 48 |
| 11 | 1.5 | 1.0 | $Cs_2CO_3$ (2.0) | DMF | 100 | 2 | 51 |
| 12 | 1.5 | 1.0 | $Cs_2CO_3$ (2.0) | DMF | 80 | 2 | 51 |
| 13 | 1.5 | 1.0 | $Cs_2CO_3$ (2.0) | DMF | 70 | 2 | 54 |
| 14 | 1.5 | 1.0 | $Cs_2CO_3$ (2.0) | DMF | 60 | 2 | 49 |
| 15 | 1.5 | 1.0 | $Cs_2CO_3$ (2.0) | DMF | 50 | 2 | 52 |
| 16 | 1.5 | 1.0 | $Cs_2CO_3$ (2.0) | DMF | 40 | 2 | 45 |
| 17 | 1.5 | 1.0 | $Cs_2CO_3$ (1.0) | DMF | RT | 24 | 49 |
| 18 | 1.5 | 1.0 | $Cs_2CO_3$ (1.0) | DMF | 90 | 2 | 54 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 19 | 1.5 | 1.0 | $Cs_2CO_3$ (1.5) | DMF | 90 | 2 | 54 |
| 20 | 1.5 | 1.0 | $Cs_2CO_3$ (2.5) | DMF | 90 | 2 | 53 |
| 21 | 1.5 | 1.0 | $Cs_2CO_3$ (3.0) | DMF | 90 | 2 | 51 |
| 22 | 1.5 | 1.0 | $Cs_2CO_3$ (4.0) | DMF | 90 | 2 | 53 |
| 23 | 1.5 | 1.0 | NaH (1.0) | DMF | 25 | 24 | 31 |
| 24 | 1.5 | 1.0 | NaH (2.0) | DMF | 25 | 24 | 35 |
| 25 | 1.5 | 1.0 | NaH (3.0) | DMF | 25 | 24 | 35 |

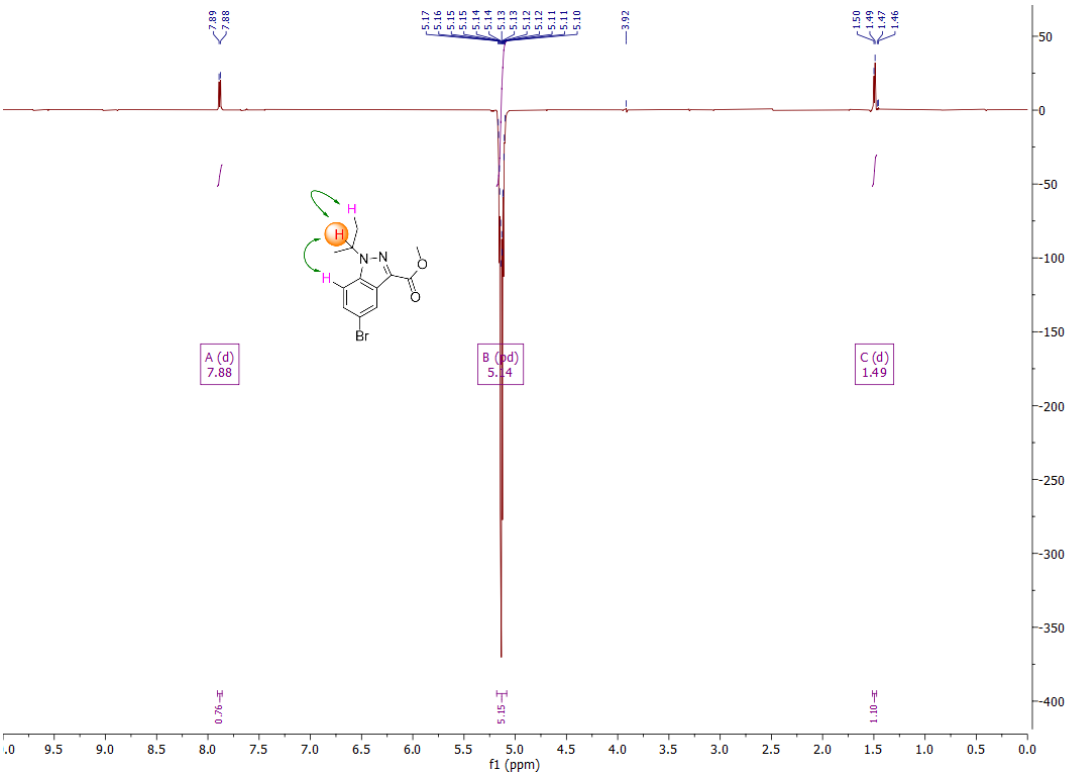



**Figure S1. 1D NOE of 8.**

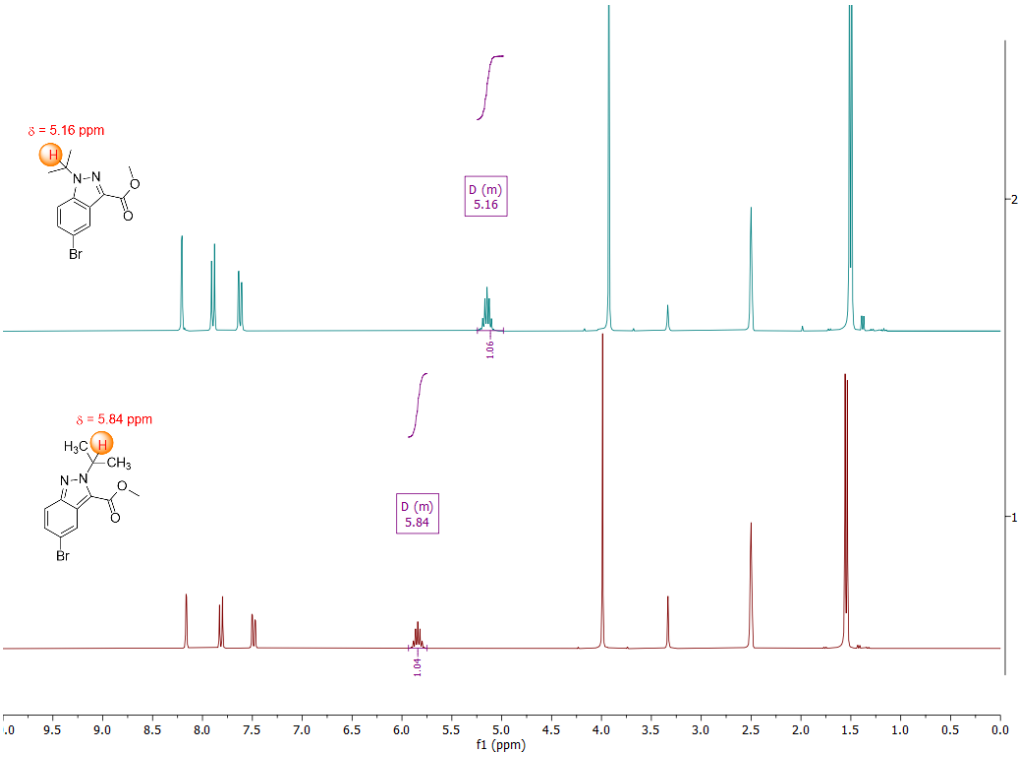
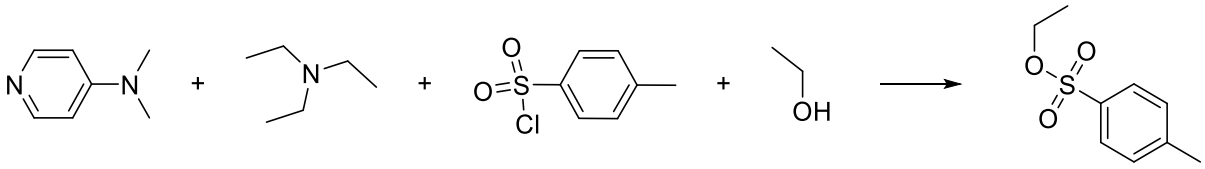



**Figure S2. NMR comparison of 8 and 9.**

**Synthesis of compounds 12, 14a, c–l.**

Alkyl sulfonates **12** and **14d–p** were prepared according to the procedure described by Marco, J. L. *J. **Heterocyclic Chem**.*, **23,** 1059 **(1986)**. Our specific procedures and characterization are provided below. Alkyl sulfonates **14a**, **c**, and **q** were purchased from Sigma-Aldrich.

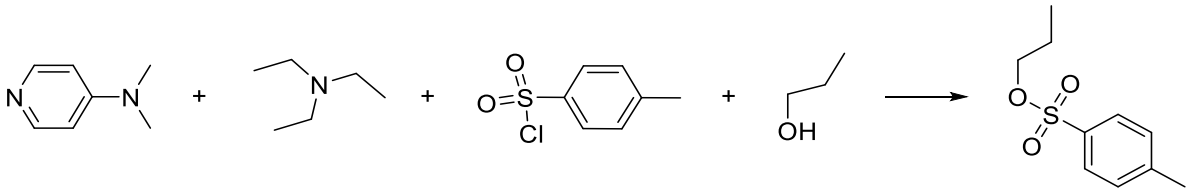
**Preparation of ethyl 4-methylbenzenesulfonate (12).**



To a mixture of ethanol (10 mL, 171 mmol), DMAP (1.046 g, 8.56 mmol) and TEA (35.8 mL, 257 mmol) in anhydrous DCM (450 mL) was added *p*-toluenesulfonyl chloride (35.9 g, 188 mmol) at 0 °C. The mixture was stirred briskly at 20 °C for 16 h and later diluted with brine (20 mL) and water (20 mL). The organic layer was separated, washed with brine (20 mL), dried over $MgSO_4$ and evaporated on a rotary evaporator. The residue obtained was purified by flash column chromatography [silica gel (80 g), eluting with EtOAc in hexane from 0–

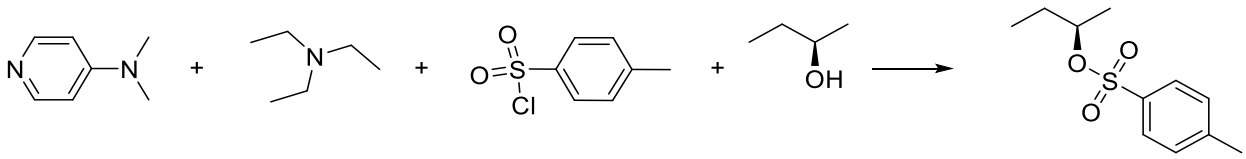
100%] to give ethyl 4-methylbenzenesulfonate (23.4 g, 117 mmol, 68.2% yield) as a clear oil; $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 7.91 – 7.81 (m, 2H), 7.61 – 7.51 (m, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.50 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); $^{13}$C{H} NMR (75 MHz, DMSO-$d_6$) δ 144.8, 132.7, 130.2, 127.5, 67.3, 21.1, 14.5; IR (KBr disk) 3025, 1354, 1189, 1176, 1004, 915, 8616, 804, 778, 663, 555 cm$^{-1}$; HRMS (ESI) m/z: $[M + H_2O]^+$ calculated for $C_9H_{14}O_4S$ 218.0613, found 218.0808.

**Preparation of propyl 4-methylbenzenesulfonate (14d).**



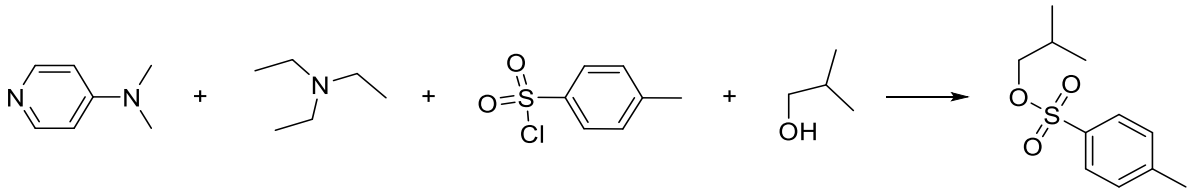

To a mixture of 4-methylbenzenesulfonyl chloride (3.49 g, 18.30 mmol), *N*,*N*-dimethylpyridin-4-amine (0.102 g, 0.832 mmol) and propan-1-ol (1 g, 16.64 mmol) in anhydrous DCM (10 mL) was added 4-methylbenzenesulfonyl chloride (3.49 g, 18.30 mmol) at 0 ℃. The mixture was stirred briskly at 20 ℃ for 16 h and later diluted with brine (50 mL) and water (50 mL). The organic layer was separated, washed with brine (50 mL), dried over $MgSO_4$ and evaporated on a rotary evaporator. The residue obtained was purified by flash column chromatography [silica gel (40 g), eluting with EtOAc in hexane from 0–100%] to give propyl 4-methylbenzenesulfonate (3.2 g, 14.93 mmol, 90% yield) as a clear oil; $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 7. 7.78 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 3.97 (t, J = 6.4 Hz, 2H), 2.42 (s, 3H), 1.56 (h, J = 7.4 Hz, 2H), 0.80 (t, J = 7.4 Hz, 3H); $^{13}$C{H} NMR (75 MHz, DMSO-$d_6$) δ 144.8, 132.6, 130.1, 127.5, 72.4, 21.8, 21.1, 9.7; HRMS (ESI+) m/z: calculated for $C_{10}H_{14}NaO_3S^+$ 237.0561, ion source failed; LCMS mass found: 237.10.

**Preparation of (*R*)-sec-butyl 4-methylbenzenesulfonate (14e).**



To a mixture of (*R*)-butan-2-ol (1 g, 13.49 mmol), *N*,*N*-dimethylpyridin-4-amine (0.082 g, 0.675 mmol) and triethylamine (2.82 mL, 20.24 mmol) in anhydrous DCM (20 mL) was added 4-methylbenzenesulfonyl chloride (2.83 g, 14.84 mmol)at 0 °C. The mixture was stirred briskly at 20 °C for 16 h and later diluted with brine (50 mL) and water (50 mL). The organic layer was separated, washed with brine (50 mL), dried over $MgSO_4$ and evaporated on a rotary evaporator. The residue obtained was purified by flash column chromatography [silica gel (40 g), eluting with EtOAc in hexane from 0–100%] to give (*R*)-sec-butyl 4-methylbenzenesulfonate (2.98 g, 13.05 mmol, 97% yield) as a clear oil; $^1$H NMR (300 MHz, DMSO-$d_6$) δ 7.83 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.3 Hz, 2H), 4.93 (s, 1H), 4.74 – 4.46 (m, 1H), 1.71 – 1.47 (m, 2H), 1.25 (dd, J = 6.2, 2.2 Hz, 3H), 0.83 (t, J = 7.4 Hz, 3H); $^{13}$C{H} NMR (75 MHz, DMSO-$d_6$) δ 144.6, 133.8, 130.1, 127.4, 81.8, 28.7, 21.1, 20.0, 9.0; IR (KBr disk) 2979, 2939, 1599, 1463, 1382, 1362, 1306, 1189, 1176, 1110, 1094, 1020 cm$^{-1}$; HRMS (ESI) m/z: $[M + Na]^+$ calculated for $C_{11}H_{20}NO_3S^+$ 246.1158 found 246.1162.

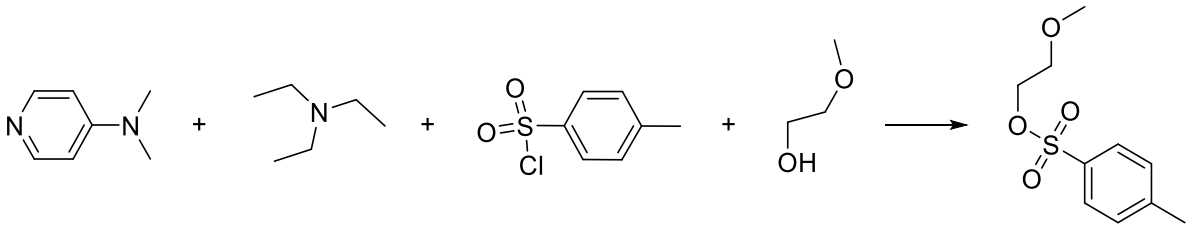
**Preparation of isobutyl 4-methylbenzenesulfonate (14f).**



To a mixture of 2-methylpropan-1-ol (1 g, 13.49 mmol), *N*,*N*-dimethylpyridin-4-amine (0.082 g, 0.675 mmol) and triethylamine (2.82 mL, 20.24 mmol) in anhydrous DCM (10 mL) was added 4-methylbenzenesulfonyl chloride (2.83 g, 14.84 mmol) at 0 °C. The mixture was stirred briskly at 20 °C for 16 h and later diluted with brine (50 mL) and water (50 mL). The organic layer was separated, washed with brine (50 mL), dried over $MgSO_4$

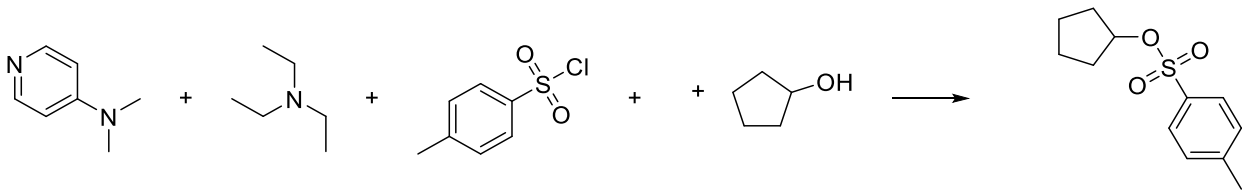
and evaporated on a rotary evaporator. The residue obtained was purified by flash column chromatography [silica gel (40 g), eluting with EtOAc in hexane from 0–100%] to give isobutyl 4-methylbenzenesulfonate (2.66 g, 11.65 mmol, 86% yield) as a clear oil; $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 6.97 (d, J = 8.3 Hz, 2H), 6.64 (d, J = 8.3 Hz, 2H), 2.98 (d, J = 6.3 Hz, 2H), 1.65 (s, 3H), 1.07 (hept, J = 13.2, 6.6 Hz, 1H), 0.06 (d, J = 6.8 Hz, 6H); $^{13}$C{H} NMR (75 MHz, DMSO-$d_6$) δ 144.8, 132.5, 130.1, 127.5, 76.2, 27.4, 21.0, 18.2; IR (KBr disk) 2967, 1470, 1395, 1360, 1189, 1175, 1097 cm$^{-1}$; HRMS (ESI) m/z: $[M + H_2O]^+$ calculated for $C_{11}H_{18}O_4S^+$ 246.0926, found 246.1139.

**Preparation of 2-methoxyethyl 4-methylbenzenesulfonate (14g).**



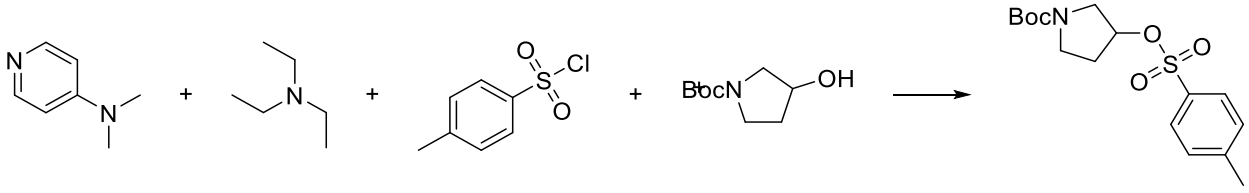
To a mixture of 2-methoxyethan-1-ol (1 g, 13.14 mmol), *N*,*N*-dimethylpyridin-4-amine (0.080 g, 0.657 mmol) and triethylamine (2.75 mL, 19.71 mmol) in anhydrous DCM (20 mL) was added 4-methylbenzenesulfonyl chloride (2.76 g, 14.46 mmol) at 0 ℃. The mixture was stirred briskly at 20 ℃ for 16 h and later diluted with brine (50 mL) and water (50 mL). The organic layer was separated, washed with brine (50 mL), dried over $MgSO_4$ and evaporated on a rotary evaporator. The residue obtained was purified by flash column chromatography [silica gel (40 g), eluting with EtOAc in hexane from 0–100%] to give 2-methoxyethyl 4-methylbenzenesulfonate (2.62 g, 11.38 mmol, 87% yield) as a clear oil. $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 7.83 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 8.3 Hz, 2H), 4.22 – 4.11 (m, 2H), 3.58 (dd, J = 5.1, 3.8 Hz, 2H), 3.35 (s, 3H), 3.31 (s, 3H); $^{13}$C{H} NMR (75 MHz, DMSO-$d_6$) δ 144.9, 132.4, 130.1, 127.6, 69.7, 69.3, 57.9, 21.1, 21.1; IR (KBr disk) 1598, 1451, 1356, 1189, 1176, 1131, 1097, 1019 cm$^{-1}$; HRMS (ESI) m/z: $[M + H_2O]^+$ calculated for $C_{10}H_{16}O_5S^+$ 248.0718, found 248.0940.

**Preparation of cyclopentyl 4-methylbenzenesulfonate (14h).**



To a mixture of 4-methylbenzenesulfonyl chloride (2.435 g, 12.77 mmol), *N*,*N*-dimethylpyridin-4-amine (0.071 g, 0.580 mmol) and triethylamine (2.427 mL, 17.41 mmol) in anhydrous DCM (20 mL) was 4-methylbenzenesulfonyl chloride (2.435 g, 12.77 mmol) at 0 °C. The mixture was stirred briskly at 20 °C for 16 h and later diluted with brine (50 mL) and water (50 mL). The organic layer was separated, washed with brine (50 mL), dried over MgSO4 and evaporated on a rotary evaporator. The residue obtained was purified by flash column chromatography [silica gel (40 g), eluting with EtOAc in hexane from 0–100%] to give cyclopentyl 4-methylbenzenesulfonate (1.54 g, 6.41 mmol, 55.2% yield) as a clear oil; $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 7.82 (dq, J = 8.5, 1.8 Hz, 2H), 7.48 (d, J = 7.9 Hz, 2H), 4.98 (q, J = 3.8 Hz, 1H), 4.94 (d, J = 3.3 Hz, 2H), 1.85 – 1.67 (m, 7H), 1.62 (s, 2H); $^{13}$C{H} NMR (75 MHz, DMSO-$d_6$) δ 144.7, 133.8, 130.1, 127.4, 85.6, 32.5, 22.6, 21.1; IR (KBr disk) ~3000, ~1300, 1163 cm$^{-1}$; HRMS (ESI) m/z: $[M + NH_4]^+$ calculated for $C_{12}H_{20}NO_3S^+$ 258.1158, found 258.1164.

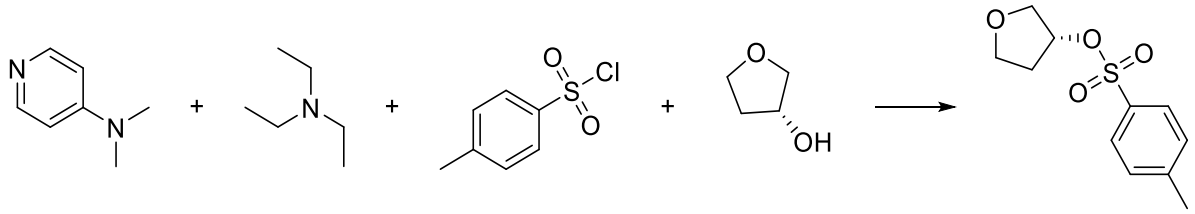
**Preparation of *tert*-butyl 3-(tosyloxy)pyrrolidine-1-carboxylate (14i).**



To a mixture of *tert*-butyl 3-hydroxypyrrolidine-1-carboxylate (1 g, 5.34 mmol), *N*,*N*-dimethylpyridin-4-amine (0.033 g, 0.267 mmol) and triethylamine (1.117 mL, 8.01 mmol) in anhydrous DCM (20 mL) was added 4-

methylbenzenesulfonyl chloride (1.120 g, 5.87 mmol) at 0 ℃. The mixture was stirred briskly at 20 ℃ for 16 h and later diluted with brine (50 mL) and water (50 mL). The organic layer was separated, washed with brine (50 mL), dried over $MgSO_4$ and evaporated on a rotary evaporator. The residue obtained was purified by flash column chromatography [silica gel (40 g), eluting with EtOAc in hexane from 0–100%] to give *tert*-butyl 3-(tosyloxy)pyrrolidine-1-carboxylate as a mixture of rotomers (1.76 g, 5.15 mmol, 97% yield) as a clear oil; $^1$H NMR (300 MHz, DMSO-$d_6$) δ 7.85 (d, J = 8.3 Hz, 2H), 7.50 (d, J = 8.2 Hz, 2H), 5.14 – 5.05 (m, 1H), 4.92 (s, 2H), 3.56 – 3.26 (m, 7H), 2.06 (d, J = 9.7 Hz, 2H), 1.47 (d, J = 7.2 Hz, 8H); $^{13}$C{H} NMR (75 MHz, DMSO-$d_6$) δ 153.3, 153.2, 145.1, 133.2, 133.1, 130.3, 127.5, 81.7, 80.8, 78.7, 51.4, 51.4, 43.4, 43.1, 31.4, 30.6, 28.0, 21.1; IR (KBr disk) 2972, 1683, 1412, 1356, 1198, 1189, 1167, 1119 cm$^{-1}$; HRMS (ESI) m/z: $[M + Na]^+$ calculated for $C_{16}H_{23}NNaO_5S^+$ 364.1195, found 364.1221.

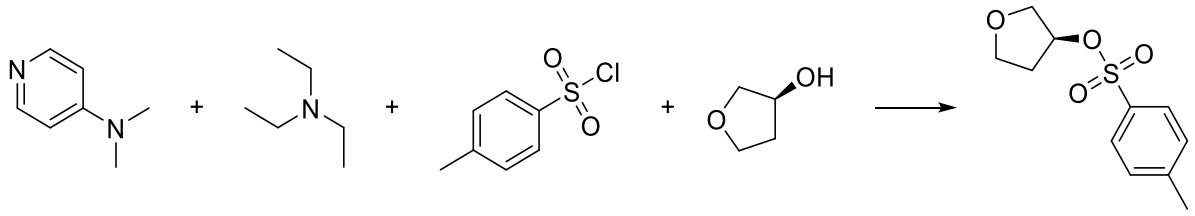
**Preparation of (*R*)-tetrahydrofuran-3-yl 4-methylbenzenesulfonate (14j).**




To a mixture of (*R*)-tetrahydrofuran-3-ol (1 g, 11.35 mmol), *N*,*N*-dimethylpyridin-4-amine (0.069 g, 0.567 mmol) and triethylamine (2.373 mL, 17.02 mmol) in anhydrous DCM (20 mL) was added 4-methylbenzenesulfonyl chloride (2.380 g, 12.48 mmol) at 0 °C. The mixture was stirred briskly at 20 ℃ for 16 h and later diluted with brine (50 mL) and water (50 mL). The organic layer was separated, washed with brine (50 mL), dried over $MgSO_4$ and evaporated on a rotary evaporator. The residue obtained was purified by flash column chromatography [silica gel (40 g), eluting with EtOAc in hexane from 0–100%] to give (*R*)-tetrahydrofuran-3-yl 4-methylbenzenesulfonate (2.175 g, 8.98 mmol, 79% yield) as a clear oil; $^1$H NMR (300 MHz, DMSO-$d_6$) δ 7.87 – 7.78 (m, 2H), 7.49 (d, J = 8.1 Hz, 2H), 5.16 (ddt, J = 6.0, 3.9, 1.8 Hz, 1H), 4.92 (s, 2H), 3.95 – 3.70 (m, 4H), 2.22 – 2.09 (m, 1H), 2.04 (td, J = 11.4, 4.6 Hz, 1H); $^{13}$C{H} NMR (75 MHz, DMSO-$d_6$) δ 145.1, 133.2, 130.3, 127.5,

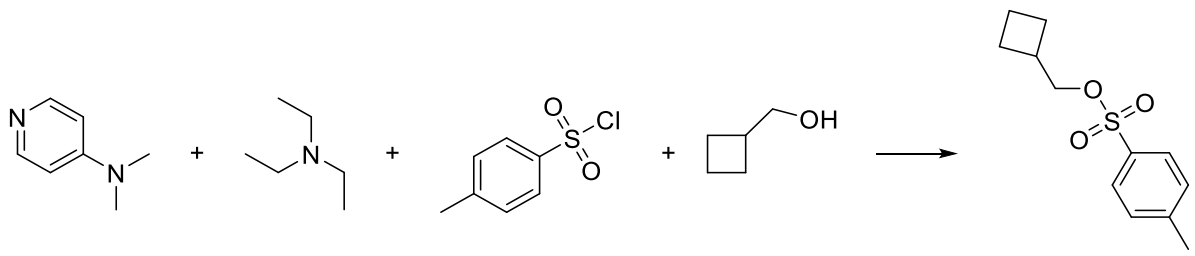
82.4, 72.1, 66.0, 32.5, 21.1; IR (KBr disk) 2984, 2874, 1598, 1364, 1189, 1175, 1093, 1079 $cm^{-1}$; HRMS (ESI) m/z: $[M + H_2O]^+$ calculated for $C_{11}H_{16}O_5S^+$ 260.0718, found 260.0946.

**Preparation of (*S*)-tetrahydrofuran-3-yl 4-methylbenzenesulfonate (14k).**



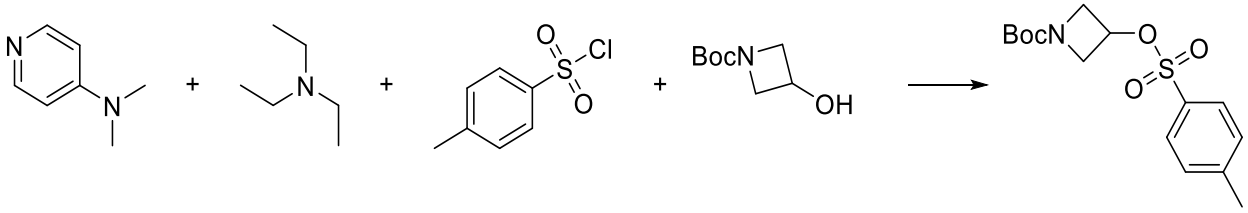
To a mixture of (*S*)-tetrahydrofuran-3-ol (1 g, 11.35 mmol), *N*,*N*-dimethylpyridin-4-amine (0.069 g, 0.567 mmol) and triethylamine (2.373 mL, 17.02 mmol) in anhydrous DCM (20 mL) was added 4-methylbenzenesulfonyl chloride (2.380 g, 12.48 mmol) at 0 °C. The mixture was stirred briskly at 20 ℃ for 16 h and later diluted with brine (50 mL) and water (50 mL). The organic layer was separated, washed with brine (50 mL), dried over $MgSO_4$ and evaporated on a rotary evaporator. The residue obtained was purified by flash column chromatography [silica gel (40 g), eluting with EtOAc in hexane from 0–100%] to give (*S*)-tetrahydrofuran-3-yl 4-methylbenzenesulfonate (2.45 g, 10.11 mmol, 89% yield) as a clear oil; $^1$H NMR (300 MHz, DMSO-$d_6$) δ 7.89 – 7.78 (m, 2H), 7.49 (dt, J = 8.5, 2.7 Hz, 2H), 5.16 (ddt, J = 6.0, 4.1, 2.0 Hz, 1H), 4.92 (d, J = 2.5 Hz, 1H), 3.97 – 3.71 (m, 5H), 2.27 – 1.89 (m, 2H); $^{13}$C{H} NMR (75 MHz, DMSO-$d_6$) δ 145.1, 133.2, 130.3, 127.5, 82.4, 72.1, 66.0, 32.5, 21.1; IR (KBr disk) 2984, 2956, 2874, 1598, 1360, 1189, 1176, 1093 $cm^{-1}$; HRMS (ESI) m/z: $[M + H_2O]^+$ calculated for $C_{11}H_{16}O_5S^+$ 260.0718, found 260.0948.

**Preparation of (*S*)-tetrahydrofuran-3-yl 4-methylbenzenesulfonate (14l).**



To a mixture of cyclobutylmethanol (1 g, 11.61 mmol), *N*,*N*-dimethylpyridin-4-amine (0.071 g, 0.580 mmol) and triethylamine (2.427 mL, 17.41 mmol) in anhydrous DCM (20 mL) was added 4-methylbenzenesulfonyl chloride (2.435 g, 12.77 mmol)at 0 ℃. The mixture was stirred briskly at 20 ℃ for 16 h and later diluted with brine (50 mL) and water (50 mL). The organic layer was separated, washed with brine (50 mL), dried over MgSO4 and evaporated on a rotary evaporator. The residue obtained was purified by flash column chromatography [silica gel (40 g), eluting with EtOAc in hexane from 0–100%] to give cyclobutylmethyl 4-methylbenzenesulfonate (2.45 g, 10.19 mmol, 88% yield) as a clear oil; $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 7.94 – 7.65 (m, 2H), 7.49 (d, J = 7.9 Hz, 2H), 4.93 (s, 2H), 4.01 (d, J = 6.6 Hz, 2H), 2.63 (p, J = 7.3 Hz, 1H), 2.04 (ddd, J = 10.9, 6.1, 2.5 Hz, 2H), 1.94 (d, J = 8.7 Hz, 1H), 1.87 (dd, J = 10.2, 5.2 Hz, 1H), 1.76 (q, J = 8.3 Hz, 2H); $^{13}$C{H} NMR (75 MHz, DMSO-$d_6$) δ 144.7, 132.6, 130.1, 127.5, 74.0, 33.3, 23.6, 21.0, 17.6; IR (KBr disk) 2980, 2945, 2891, 2868, 1623, 1616, 1599, 1576, 1559, 1360, 1189, 1176, 1097 cm$^{-1}$; HRMS (ESI) m/z: $[M + NH_4]^+$ calculated for $C_{12}H_{20}NO_3S^+$ 258.1158, found 258.1160.

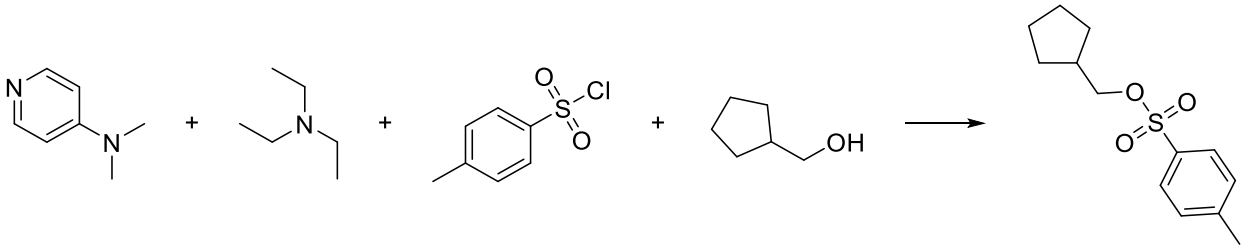
**Preparation of *tert*-butyl 3-(tosyloxy)azetidine-1-carboxylate (14m).**




To a mixture of *tert*-butyl 3-hydroxyazetidine-1-carboxylate (1 g, 5.77 mmol), *N*,*N*-dimethylpyridin-4-amine (0.035 g, 0.289 mmol) and triethylamine (1.207 mL, 8.66 mmol) in anhydrous DCM (20 mL) was added 4-methylbenzenesulfonyl chloride (1.211 g, 6.35 mmol) at 0 ℃. The mixture was stirred briskly at 20 ℃ for 16 h and later diluted with brine (50 mL) and water (50 mL). The organic layer was separated, washed with brine (50 mL), dried over MgSO4 and evaporated on a rotary evaporator. The residue obtained was purified by flash column chromatography [silica gel (40 g), eluting with EtOAc in hexane from 0–100%] to give *tert*-butyl 3-(tosyloxy)azetidine-1-carboxylate (1.6 g, 85% yield) as a clear oil. $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 7.81 (d, J = 8.5 Hz, 2H), 7.51 (d, J = 7.9 Hz, 2H), 5.08 (tt, J = 6.6, 3.9 Hz, 1H), 4.17 – 3.86 (m, 2H), 3.73 (s, 2H), 2.43 (s,

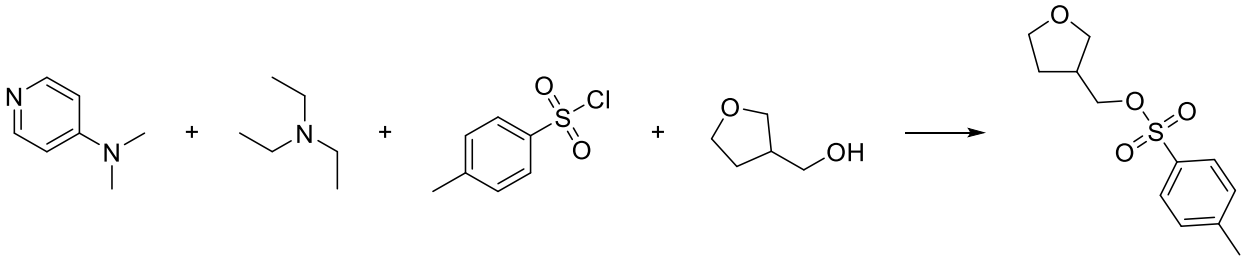
3H), 1.34 (s, 9H); $^{13}C\{H\}$ NMR (75 MHz, DMSO-$d_6$) δ 155.3, 145.5, 132.2, 130.3, 127.7, 79.2, 68.6, 55.9, 27.9, 21.1; IR (KBr disk) 2978, 2933, 2886, 1705, 1598, 1495, 1479, 1456, 1401, 1367, 1299, 1256, 1210, 1192, 1179, 1091, 1022 $cm^{-1}$; HRMS (ESI) m/z: $[M + Na]^+$ calculated for $C_{15}H_{21}NNaO_5S^+$ 350.1033, found 350.1043.

**Preparation of cyclopentylmethyl 4-methylbenzenesulfonate (14n).**



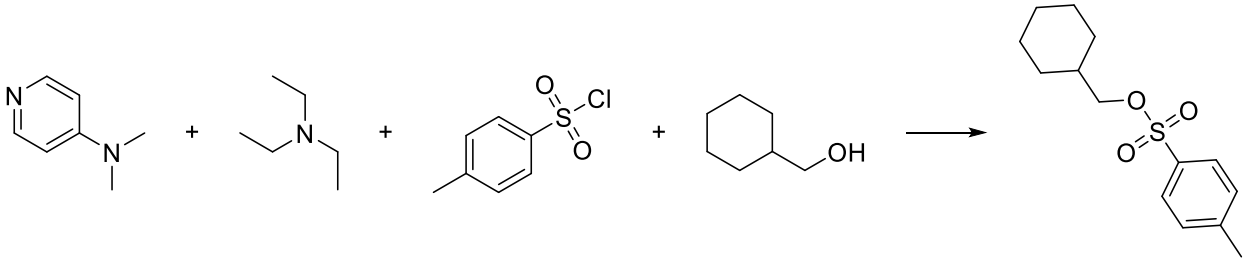
To a mixture of cyclopentylmethanol (1 g, 9.98 mmol), *N*,*N*-dimethylpyridin-4-amine (0.061 g, 0.499 mmol) and triethylamine (2.087 mL, 14.98 mmol) in anhydrous DCM (20 mL) was added 4-methylbenzenesulfonyl chloride (2.094 g, 10.98 mmol) at 0 °C. The mixture was stirred briskly at 20 °C for 16 h and later diluted with brine (50 mL) and water (50 mL). The organic layer was separated, washed with brine (50 mL), dried over MgSO4 and evaporated on a rotary evaporator. The residue obtained was purified by flash column chromatography [silica gel (40 g), eluting with EtOAc in hexane from 0–100%] to give cyclopentylmethyl 4-methylbenzenesulfonate (2.2 g, 8.65 mmol, 87% yield) as a clear oil; $^1H$ NMR (300 MHz, DMSO-$d_6$) δ 7.82 (dt, J = 8.8, 2.4 Hz, 2H), 7.53 – 7.43 (m, 2H), 4.93 (d, J = 2.6 Hz, 3H), 3.99 – 3.84 (m, 2H), 2.29 – 2.13 (m, 1H), 1.75 (d, J = 11.4 Hz, 2H), 1.65 – 1.51 (m, 4H), 1.34 – 1.14 (m, 2H); $^{13}C\{H\}$ NMR (75 MHz, DMSO-$d_6$) δ 144.7, 132.6, 130.0, 127.5, 74.0, 38.0, 28.3, 24.7, 21.0; IR (KBr disk) 2956, 2870, 1599, 1495, 1454, 1362, 1190, 1097, 1020 $cm^{-1}$; HRMS (ESI) m/z: $[M + NH_4]^+$ calculated for $C_{13}H_{22}NO_3S^+$ 272.1315, found 272.1324.

**Preparation of (tetrahydrofuran-3-yl)methyl 4-methylbenzenesulfonate (14o).**



To a mixture of (tetrahydrofuran-3-yl)methanol (1 g, 9.79 mmol), *N*,*N*-dimethylpyridin-4-amine (0.060 g, 0.490 mmol) and triethylamine (2.047 mL, 14.69 mmol) in anhydrous DCM (20 mL) was added 4-methylbenzenesulfonyl chloride (2.053 g, 10.77 mmol)at 0 °C. The mixture was stirred briskly at 20 ℃ for 16 h and later diluted with brine (50 mL) and water (50 mL). The organic layer was separated, washed with brine (50 mL), dried over MgSO4 and evaporated on a rotary evaporator. The residue obtained was purified by flash column chromatography [silica gel (40 g), eluting with EtOAc in hexane from 0–100%] to give (tetrahydrofuran-3-yl)methyl 4-methylbenzenesulfonate (2.215 g, 8.64 mmol, 88% yield) as a clear oil; $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 7.90 – 7.75 (m, 2H), 7.49 (dd, *J* = 8.4, 2.4 Hz, 2H), 4.09 – 3.89 (m, 2H), 3.87 – 3.62 (m, 3H), 3.50 (dd, *J* = 9.0, 5.2 Hz, 1H), 2.61 (q, *J* = 7.1 Hz, 1H), 2.50 (d, *J* = 2.7 Hz, 3H), 2.03 (dtd, *J* = 13.1, 8.0, 5.5 Hz, 1H), 1.69 – 1.51 (m, 1H); $^{13}$C{H} NMR (75 MHz, DMSO-$d_6$) δ 145.1, 132.4, 130.3, 127.7, 72.0, 69.1, 66.9, 37.9, 28.0, 21.1; IR (KBr disk) 2974, 2871, 1779, 1599, 1495, 1360, 1190, 1097 cm$^{-1}$; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{12}H_{17}O_4S^+$ 257.0842, found 257.0854.

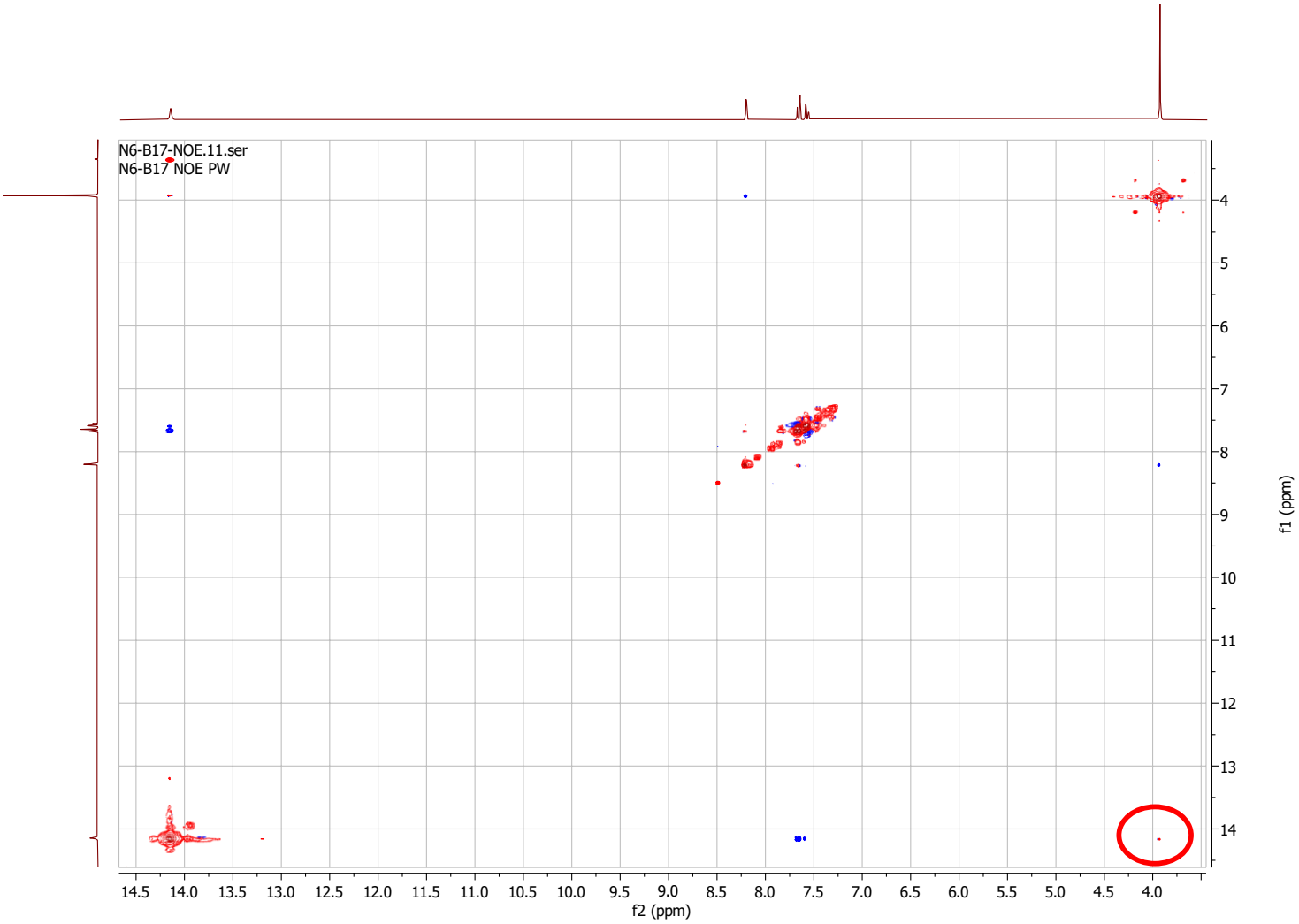
**Preparation of cyclohexylmethyl 4-methylbenzenesulfonate (14p).**



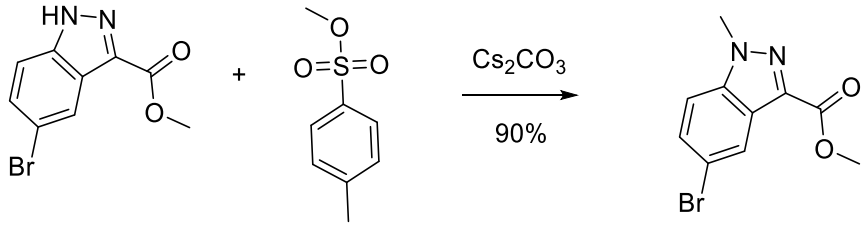

To a mixture of cyclohexylmethanol (1 g, 8.76 mmol), *N*,*N*-dimethylpyridin-4-amine (0.053 g, 0.438 mmol) and triethylamine (1.831 mL, 13.14 mmol) in anhydrous DCM (20 mL) was added 4-methylbenzenesulfonyl chloride (1.836 g, 9.63 mmol) at 0 ℃. The mixture was stirred briskly at 20 °C for 16 h and later diluted with brine (50 mL) and water (50 mL). The organic layer was separated, washed with brine (50 mL), dried over $MgSO_4$ and evaporated on a rotary evaporator. The residue obtained was purified by flash column chromatography [silica gel (40 g), eluting with EtOAc in hexane from 0–100%] to give cyclohexylmethyl 4-methylbenzenesulfonate (850mg, 3.17 mmol, 36.2% yield) as a clear oil; $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 7.81 (dt, J = 8.4, 2.0 Hz, 2H), 7.49 (d,

J = 7.9 Hz, 2H), 4.93 (d, J = 1.6 Hz, 4H), 3.85 (dt, J = 6.1, 2.0 Hz, 2H), 1.69 (d, J = 13.1 Hz, 6H), 1.34 – 1.13 (m, 3H), 0.97 (t, J = 11.6 Hz, 2H); $^{13}C\{H\}$ NMR (75 MHz, DMSO-$d_6$) δ 144.8, 132.5, 130.1, 127.5, 75.2, 36.5, 28.4, 25.6, 24.9, 21.1; IR (KBr disk) 2950, 2875, 1599, 1494, 1450, 1360, 1306, 1291, 1189, 1176, 1097, 1019 $cm^{-1}$; HRMS (ESI) m/z: $[M + H_2O]^+$ calculated for $C_{14}H_{22}O_4S^+$ 286.1239, found 286.1476.

**Figure S3. 2D NOE of 6. Circled in-phase correlation is between CH3 and NH.**



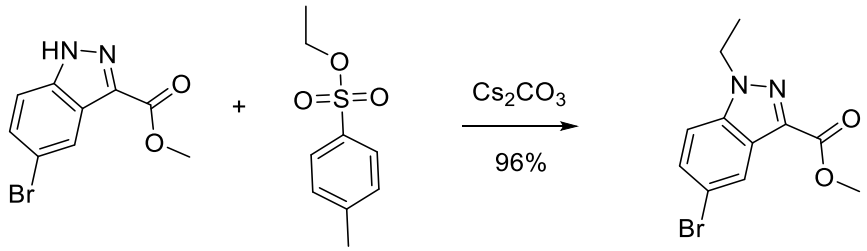
**Preparation of methyl 5-bromo-1-methy-1*H*-indazole-3-carboxylate (15a)**




**6** **14a** **15a**

To a solution of methyl 5-bromo-1*H*-indazole-3-carboxylate (**6**, 300 mg, 1.176 mmol) in dioxane (10 mL) at RT was added cesium carbonate (766 mg, 2.352 mmol) followed by tosylate **14a**. The resulting mixture was stirred for 2 h at 90 °C. The mixture was poured into EtOAc (500 mL) and washed with water (100 mL) and brine. The organic layer was dried and concentrated, the obtained residue was purified by chromatography [silica gel (24 g), eluting with EtOAc in hexane from 0–70%] to give methyl 5-bromo-1-methyl-1*H*-indazole-3-carboxylate, **15a**, (285 mg, 1.059 mmol, 90% yield) as a white solid; melting point = 141.3 °C. 1H NMR (300 MHz, DMSO-$d_6$) δ 8.19 (dd, *J* = 1.9, 0.7 Hz, 1H), 7.82 (dd, *J* = 9.0, 0.7 Hz, 1H), 7.65 (dd, *J* = 8.9, 1.9 Hz, 1H), 4.17 (s, 3H), 3.92 (s, 3H); $^{13}$C{1H} NMR (75 MHz, DMSO-$d_6$) δ 161.8, 139.4, 132.7, 129.4, 124.1, 123.0, 116.0, 113.0, 51.8, 36.6; IR (KBr disk) 1708, 1459, 1442, 1392, 1326, 1252, 1196 cm$^{-1}$; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{10}H_{10}BrN_2O_2^+$ 268.9921, found 268.9902. **16a** isolated yield: n.d.

**Preparation of methyl 5-bromo-1-ethyl-1*H*-indazole-3-carboxylate (15b)**

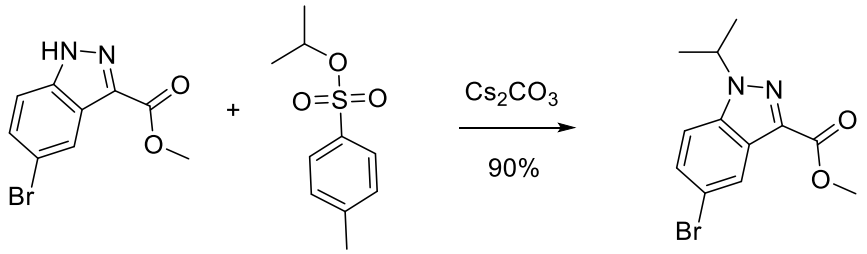



**6** **12** **15b**

The compound was prepared from **6** (500 mg, 1.96 mmol) using similar procedure as compound **15a** with 96% yield (532 mg, 1.879 mmol) as a white solid as a white solid: melting point = 78.4 °C; $^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.21 (d, *J* = 1.8 Hz, 1H), 7.87 (d, *J* = 8.9 Hz, 1H), 7.64 (dd, *J* = 8.9, 1.9 Hz, 1H), 4.56 (q, *J* = 7.2 Hz,

2H), 3.93 (s, 3H), 1.43 (t, $J$ = 7.2 Hz, 3H); $^{13}$C{1H} NMR (75 MHz, DMSO-$d_6$) δ 162.0, 138.3, 132.9, 129.3, 124.3, 123.2, 116.0, 112.9, 51.8, 50.9, 21.9; IR (KBr disk) 1705, 1466, 1196, 1183, 1086, 1067, 1041 cm$^{-1}$; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{11}H_{11}BrN_2O_2^+$ 282.0077, found 282.0092. **16b** isolated yield, 25 mg, 5%.

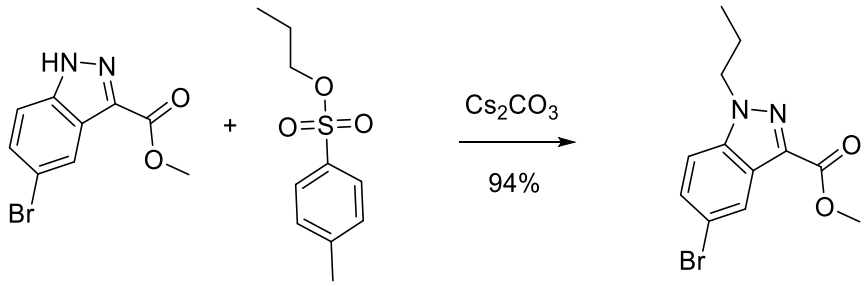
**Preparation of methyl 5-bromo-1-propyl-1*H*-indazole-3-carboxylate (15c)**




**6** **14c** **15c**

The compound was prepared from **6** (0.238 g, 0.933 mmol) using similar procedure as compound **15a** with 90% yield (249 mg, 0.838 mmol) as a white solid; melting point = 106.9 °C; $^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.21 (d, $J$ = 1.9, 0.7 Hz, 1H), 7.90 (d, $J$ = 9.1, 0.7 Hz, 1H), 7.63 (dd, $J$ = 9.0, 1.9 Hz, 1H), 5.15 (hept, $J$ = 6.6 Hz, 1H), 3.93 (s, 3H), 1.50 (d, $J$ = 6.6 Hz, 6H); $^{13}$C{1H} NMR (75 MHz, DMSO-$d_6$) δ 162.0, 138.3, 132.9, 129.3, 124.3, 123.2, 116.0, 112.9, 51.8, 50.9, 21.9; IR (KBr disk) 1485, 1462, 1436, 1392, 1332, 1196 cm$^{-1}$; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{12}H_{13}BrN_2O_2^+$ 296.0233, found 296.0254. **16c** isolated yield: n.d.

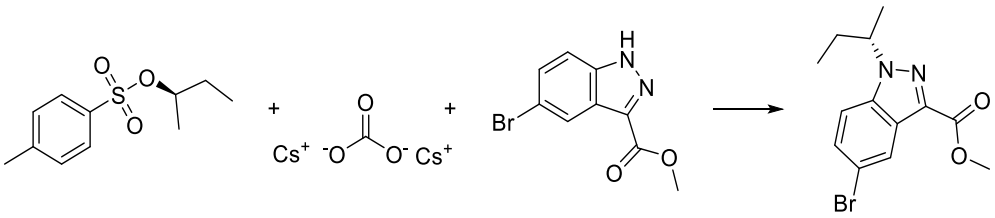
**Preparation of methyl 5-bromo-1-propyl-1*H*-indazole-3-carboxylate (15d)**




**6** **14d** **15d**

The compound was prepared from **6** (238 mg, 0.933 mmol) using similar procedure as compound **15a** with 94% yield (261 mg, 0.878 mmol) as a white solid; melting point = 63.8 °C; $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 8.21 (d, $J$ = 1.9, 0.7 Hz, 1H), 7.88 (d, $J$ = 9.0, 0.7 Hz, 1H), 7.63 (d, $J$ = 9.0, 1.9 Hz, 1H), 4.49 (t, $J$ = 6.9 Hz, 2H), 3.93 (s, 3H), 1.87 (h, $J$ = 7.3 Hz, 2H), 0.82 (t, $J$ = 7.4 Hz, 3H). $^{13}$C{1H} NMR (75 MHz, DMSO-$d_6$) δ 161.9, 139.2, 133.0, 129.4, 124.1, 123.2, 116.0, 112.9, 51.8, 50.7, 22.7, 10.9; IR (KBr disk) 1725, 1464, 1190, 1175, 1149, 1118 cm$^{-1}$; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{12}H_{13}BrN_2O_2^+$ 296.0233, found 296.0245. **16d** isolated yield: 10 mg, 0.034 mmol, 3.61%.

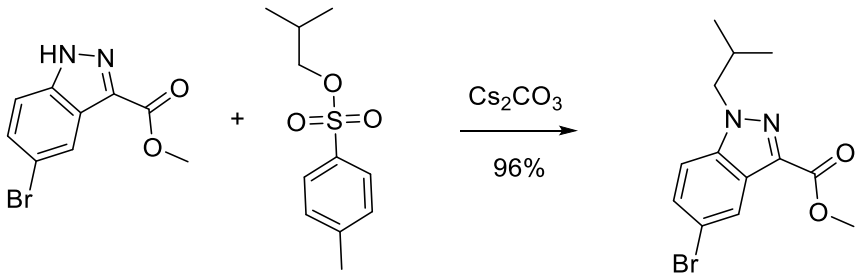
**Preparation of methyl (*S*)-5-bromo-1-(sec-butyl)-1*H*-indazole-3-carboxylate (15e)**



This compound was prepared from **6** (0.223 g, 0.876 mmol) using similar procedure as compound **15a** in 95% yield (259 mg, 0.832 mmol) as a white solid; m.p. = 68.4 °C; $^{1}$H NMR (300 MHz, DMSO-$d6$) δ 8.22 (d, $J$ = 1.8 Hz, 1H), 7.92 (d, $J$ = 9.0 Hz, 1H), 7.62 (dd, $J$ = 9.0, 1.9 Hz, 1H), 4.98 – 4.85 (m, 1H), 3.93 (s, 3H), 2.05 – 1.76 (m, 2H), 1.50 (d, $J$ = 6.6 Hz, 3H), 0.66 (t, $J$ = 7.4 Hz, 3H); $^{13}$C{H} NMR (75 MHz, DMSO-$d_6$) δ 162.0, 139.3, 133.2, 129.4, 124.0, 123.3, 116.0, 112.9, 56.5, 51.8, 29.2, 20.2, 10.5; IR (KBr disk) 2965, 2937, 2875, 1701, 1451, 1377, 1244, 1205 cm$^{-1}$; HRMS (ESI) m/z: $[M^+]$ calculated for $C_{13}H_{15}BrN_2O_2^+$ 310.0390, found 310.0399.

**16e** isolated yield: 6 mg, 0.019 mmol, 2.201% yield.

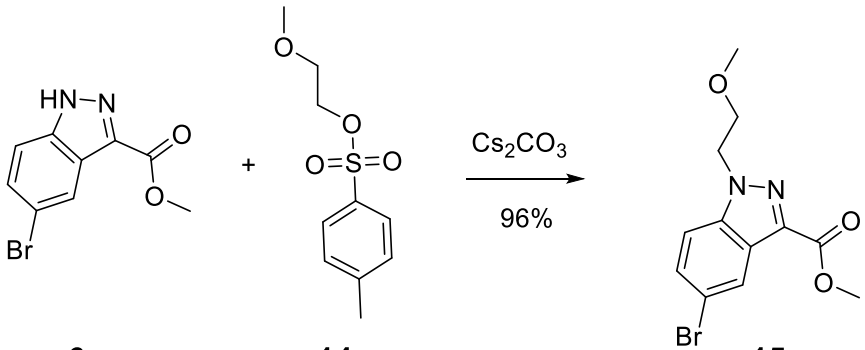
**Preparation of methyl 5-bromo-1-isobutyl-1*H*-indazole-3-carboxylate (15f)**




**6** **14e** **15e**

The compound was prepared from **6** (0.223 g, 0.876 mmol) using a similar procedure as compound **15a** with 96% yield (261 mg, 0.839 mmol) as a white solid; melting point = 98.4 °C; $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 8.20 (d, $J$ = 1.9, 0.7 Hz, 1H), 7.89 (d, $J$ = 9.0, 0.7 Hz, 1H), 7.63 (dd, $J$ = 9.0, 1.9 Hz, 1H), 4.35 (d, $J$ = 7.3 Hz, 2H), 3.93 (s, 3H), 2.31 – 2.13 (m, 1H), 0.85 (d, $J$ = 6.7 Hz, 6H). $^{13}$C{1H} NMR (75 MHz, DMSO-$d_6$) δ 162.0, 139.8, 133.1, 129.6, 124.0, 123.2, 116.0, 113.3, 55.0, 51.8, 29.9, 25.8, 25.1; IR (KBr disk) 2961, 1733, 1717, 1482, 1466, 1229, 1194, 1122 cm$^{-1}$; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{13}H_{15}BrN_2O_2^+$ 310.0399, found 310.0394. **16f** isolated yield: 3 mg, 9.64 µmol, 1.101%.

**Preparation of methyl 5-bromo-1-(2-methoxyethyl)-1*H*-indazole-3-carboxylate (15g)**

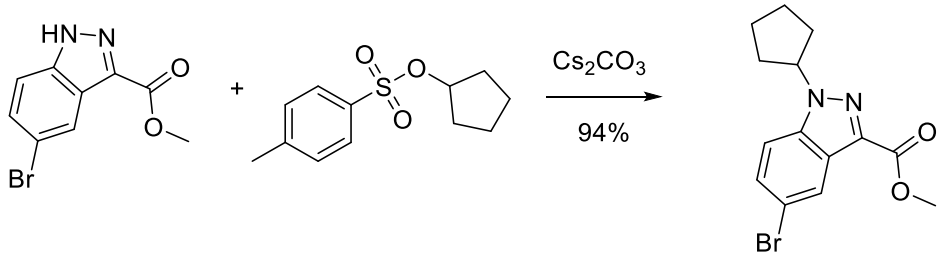



**6** **14g** **15g**

The compound was prepared from **6** (0.222 g, 0.869 mmol) using a similar procedure as compound **15a** with 96% yield (260 mg, 0.830 mmol) as a white solid; melting point = 111.5 °C; $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 8.21 (d, $J$ = 1.9, 0.7 Hz, 1H), 7.85 (d, $J$ = 9.0, 0.7 Hz, 1H), 7.64 (dd, $J$ = 9.0, 1.9 Hz, 1H), 4.71 (t, $J$ = 5.1 Hz, 2H), 3.94

(s, 3H), 3.79 (t, $J$ = 5.1 Hz, 2H), 3.18 (s, 3H); $^{13}$C{1H} NMR (75 MHz, DMSO-$d_6$) δ 161.9, 139.9, 133.3, 129.5, 124.1, 123.1, 116.0, 113.4, 70.4, 58.1, 51.8, 49.4; IR (KBr disk) 1718, 1483, 1461, 1395, 1228, 1198, 1164, 1112, 1011 cm$^{-1}$; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{12}H_{13}BrN_2O_3^+$ 312.0182, found 312.0189. **16f** isolated yield: 5 mg, 0.016 mmol, 1.838%.

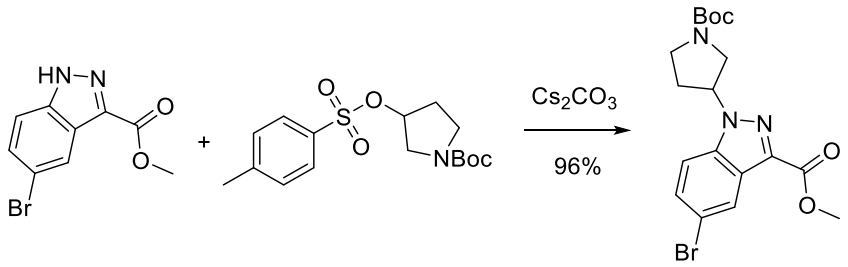
**Preparation of methyl 5-bromo-1-cyclopentyl-1*H*-indazole-3-carboxylate (15h)**




**6** **14h** **15h**

The compound was prepared from **6** (0.212 g, 0.832 mmol) using a similar procedure as compound **15a** with 94% yield (252 mg, 0.780 mmol) as a white solid; melting point = 84.6 °C; $^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.21 (d, $J$ = 1.9, 0.7 Hz, 1H), 7.89 (d, $J$ = 9.0, 0.7 Hz, 1H), 7.63 (dd, $J$ = 9.0, 1.9 Hz, 1H), 5.39 – 5.22 (m, 1H), 3.93 (s, 3H), 2.25 – 2.12 (m, 2H), 2.07 – 1.94 (m, 2H), 1.95 – 1.81 (m, 2H), 1.79 – 1.66 (m, 2H). $^{13}$C{1H} NMR (75 MHz, DMSO-$d_6$) δ 162.0, 138.9, 132.8, 129.4, 124.4, 123.2, 123.2, 116.0, 113.0, 59.6, 51.8, 32.0, 24.2; IR (KBr disk) 2950, 2871, 1712, 1477, 1399, 1231, 1194, 1155, 1131, 1097 cm$^{-1}$; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{14}H_{15}BrN_2O_2^+$ 322.0390, found 322.0404. **16g** isolated yield: 12 mg, 0.037 mmol, 4.46%.

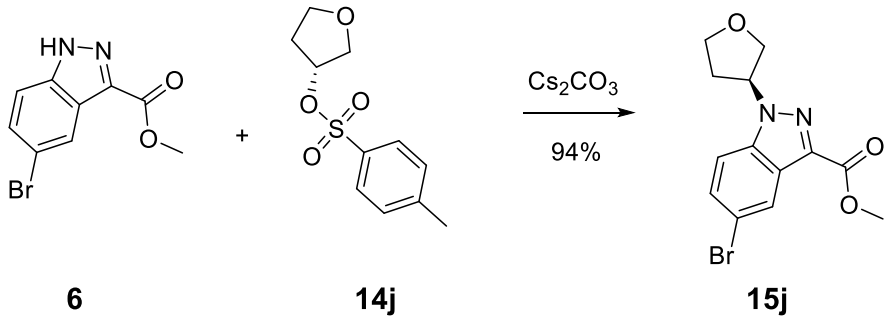
**Preparation of methyl 5-bromo-1-(1-(*tert*-butoxycarbonyl)pyrrolidin-3-yl)-1*H*-indazole-3-carboxylate (15i).**




**6** **14i** **15i**

The compound was prepared from **6** (0.149 g, 0.586 mmol) as a mixture of rotomers using a similar procedure as compound **15a** with 96% yield (239 mg, 0.563 mmol) as a white solid; melting point = 106.8 °C; $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 8.22 (d, $J$ = 1.8 Hz, 1H), 7.92 (d, $J$ = 9.0 Hz, 1H), 7.67 (dd, $J$ = 9.0, 1.9 Hz, 1H), 5.59 (d, $J$ = 6.4 Hz, 1H), 3.93 (s, 3H), 3.88 – 3.78 (m, 1H), 3.65 – 3.54 (m, 2H), 3.46 (d, $J$ = 7.1 Hz, 1H), 2.39 (s, 2H), 1.40 (d, $J$ = 8.8 Hz, 9H); $^{13}$C{1H} NMR (75 MHz, DMSO-$d_6$) δ 161.8, 153.5, 153.4, 139.1, 133.5, 129.8, 124.3, 123.3, 116.3, 113.0, 78.7, 57.5, 56.8, 56.8, 51.9, 50.4, 50.4, 44.7, 44.4, 31.0, 30.2, 28.1; IR (KBr disk) 2980, 2955, 2933, 2886, 1718, 1684, 1481, 1412, 1219, 1173, 1116, 1100 cm$^{-1}$; HRMS (ESI) m/z: $[M + Na]^+$ calculated for $C_{18}H_{22}BrN_3O_4^+$ 423.0866, found 446.0707. **16i** isolated yield: 3 mg, 7.07 µmol, 1.207%.

**Preparation of methyl (*S*)-5-bromo-1-(tetrahydrofuran-3-yl)-1*H*-indazole-3-carboxylate (15j).**

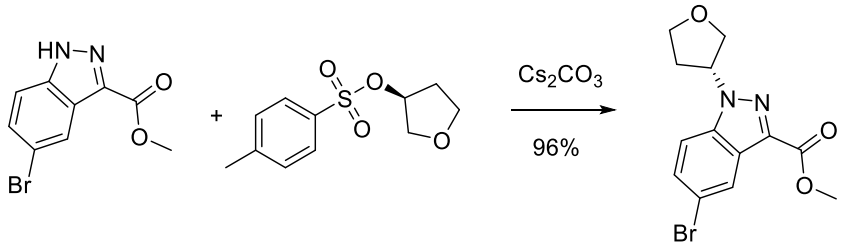



**6** **14j** **15j**

The compound was prepared from **6** (0.211 g, 0.825 mmol) using a similar procedure as compound **15a** with 94% yield (253 mg, 0.778 mmol) as a white solid; melting point = 108.8 °C; $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 8.23

(d, *J* = 1.9, 0.7 Hz, 1H), 7.91 (d, *J* = 9.0, 0.7 Hz, 1H), 7.66 (dd, *J* = 9.0, 1.9 Hz, 1H), 5.68 – 5.59 (m, 1H), 4.14 – 4.04 (m, 2H), 3.98 (d, *J* = 3.8 Hz, 1H), 3.93 (s, 3H), 3.91 – 3.82 (m, 1H), 2.49 – 2.44 (m, 1H), 2.40 – 2.28 (m, 1H); $^{13}$C{1H} NMR (75 MHz, DMSO-$d_6$) δ 161.8, 138.9, 133.2, 129.6, 124.5, 123.3, 116.2, 113.0, 71.6, 67.4, 59.0, 51.9, 32.1; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{13}H_{13}BrN_2O_3^+$ 324.0182, found 324.0187. **16j** isolated yield: 5 mg, 0.015 mmol, 1.863%.

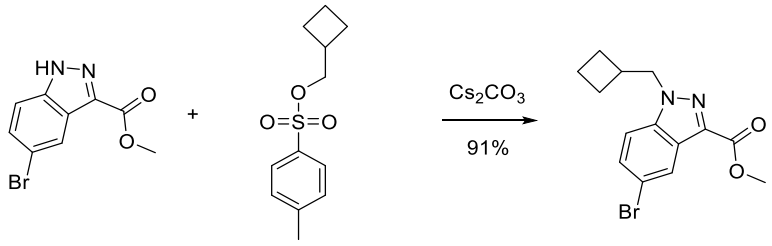
**Preparation of methyl (*R*)-5-bromo-1-(tetrahydrofuran-3-yl)-1*H*-indazole-3-carboxylate (15k).**




**6** **14k** **15k**

The compound was prepared from **6** (0.211 g, 0.825 mmol) using a similar procedure as compound **15a** with 96% yield (257 mg, 0.790 mmol) as a white solid; melting point = 89.9 °C; $^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.23 (d, *J* = 1.8 Hz, 1H), 7.92 (d, 1H), 7.67 (dd, *J* = 9.0, 1.9 Hz, 1H), 5.70 – 5.59 (m, 1H), 4.15 – 4.05 (m, 2H), 3.99 (d, *J* = 3.8 Hz, 1H), 3.94 (s, 3H), 3.88 (td, *J* = 8.1, 5.9 Hz, 1H), 2.56 (d, *J* = 7.6 Hz, 1H), 2.41 – 2.25 (m, 1H); $^{13}$C{1H} NMR (75 MHz, DMSO-$d_6$) δ 161.9, 138.9, 133.2, 129.6, 124.5, 123.3, 116.2, 113.0, 71.6, 67.4, 59.0, 51.9, 32.1; IR (KBr disk) 1701, 1459, 1435, 1399, 1230, 1209, 1168 cm$^{-1}$; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{13}H_{13}BrN_2O_3^+$ 324.0182, found 324.0196. **16k** isolated yield: 4 mg, 0.012 mmol, 1.49%.

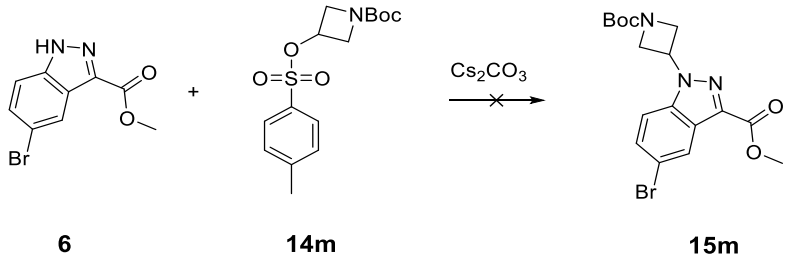
**Preparation of methyl 5-bromo-1-(cyclobutylmethyl)-1*H*-indazole-3-carboxylate (15l).**




**6** **14l** **15l**

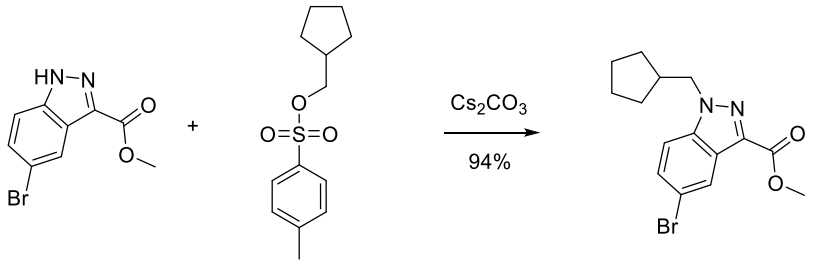
The compound was prepared from **6** (0.212 g, 0.832 mmol using a similar procedure as compound **15a** in 91% yield (245 mg, 0.758 mmol) as a white solid; m.p. = 88.9 °C; $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 8.20 (d, $J$ = 1.9, 0.7 Hz, 1H), 7.90 (d, $J$ = 9.0, 0.7 Hz, 1H), 7.63 (dd, $J$ = 9.0, 1.9 Hz, 1H), 4.56 (d, $J$ = 7.2 Hz, 2H), 3.93 (s, 3H), 2.85 (p, $J$ = 7.4 Hz, 1H), 1.99 – 1.87 (m, 2H), 1.87 – 1.73 (m, 4H); $^{13}$C{H} NMR (75 MHz, DMSO-$d_6$) δ 162.0, 139.4, 133.1, 129.5, 124.1, 123.2, 116.0, 113.1, 53.8, 51.8, 35.2, 25.3, 17.7; IR (KBr disk) 2953, 2933, 1718, 1466, 1449, 1433, 1407, 1317, 1244, 1205, 1170 cm$^{-1}$; HRMS (ESI) m/z: [M$^{+}$] calculated for $C_{14}H_{15}BrN_2O_2^{+}$ 322.0390, found 322.0393.**16l** isolated yield: 4 mg, 0.012 mmol, 1.487% yield.

**Preparation of methyl 5-bromo-1-((1-(*tert*-butoxycarbonyl)azetidin-3-yl)methyl)-1*H*-indazole-3-carboxylate (15m). No reaction.**




**6** **14m** **15m**

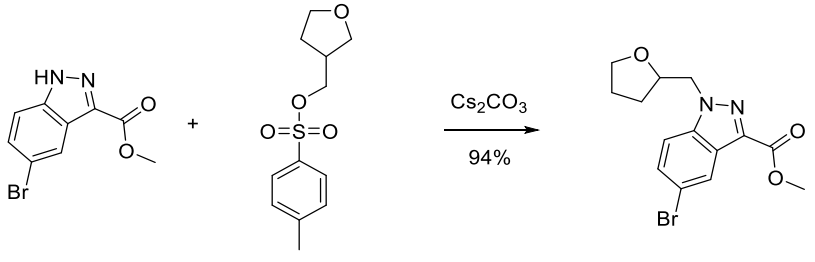
**Preparation of methyl 5-bromo-1-(cyclopentylmethyl)-1*H*-indazole-3-carboxylate (15n).**




**6** **14n** **15n**

The compound was prepared from **6** (0.201 g, 0.786 mmol) in 94% yield (248 mg, 0.735 mmol) as a white solid; m.p. = 111.4 °C; $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 8.21 (d, $J$ = 1.8 Hz, 1H), 7.90 (d, $J$ = 8.7 Hz, 1H), 7.63 (dd, $J$ = 9.0, 1.9 Hz, 1H), 4.46 (d, $J$ = 7.5 Hz, 2H), 3.93 (s, 3H), 2.48 – 2.44 (m, 1H), 1.68 – 1.43 (m, 6H), 1.35 – 1.20 (m, 2H); $^{13}$C{1H} NMR (75 MHz, DMSO-$d_6$) δ 162.0, 139.3, 133.0, 129.5, 124.1, 123.2, 116.0, 113.1, 53.6, 51.8, 29.6, 24.4; IR (KBr disk) 2950, 2864, 1722, 1457, 1435, 1405, 1358, 1321, 1231, 1194, 1157, 1123 cm$^{-1}$; HRMS (ESI) m/z: [M$^{+}$] calculated for $C_{15}H_{17}BrN_2O_2^{+}$ 336.0546, found 336.0567. **16n** isolated yield: 5 mg, 0.015 mmol, 1.886% yield.

**Preparation of methyl 5-bromo-1-((tetrahydrofuran-2-yl)methyl)-1*H*-indazole-3-carboxylate (15o).**

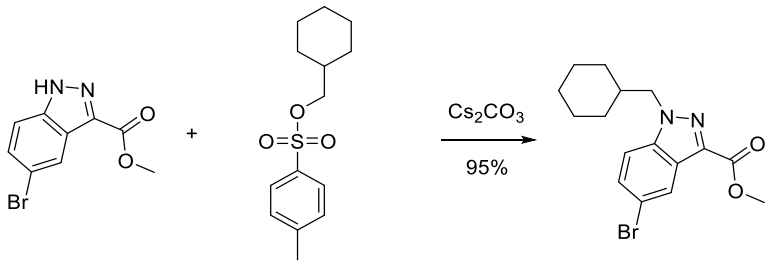



**6** **14o** **15o**

The compound was prepared from **6** (0.199 g, 0.780 mmol) in 94% yield (248 mg, 0.735 mmol) as a white solid; m.p. = 74.5 °C; $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 8.23 (d, 1H), 7.93 (d, $J$ = 9.0, 0.7 Hz, 1H), 7.66 (dd, $J$ = 9.0, 1.9 Hz, 1H), 4.54 (d, $J$ = 7.5 Hz, 2H), 3.94 (s, 3H), 3.88 – 3.74 (m, 1H), 3.71 – 3.57 (m, 2H), 3.48 (dd, $J$ = 8.7, 5.6 Hz, 1H), 2.83 (p, $J$ = 6.6 Hz, 1H), 1.98 – 1.81 (m, 1H), 1.72 – 1.55 (m, 1H); $^{13}$C{H} NMR (75 MHz,

DMSO-$d_6$) δ 162.3, 139.8, 133.7, 130.1, 124.6, 123.7, 116.6, 113.4, 70.4, 67.2, 52.3, 51.9, 29.8; IR (KBr disk) 2950, 2866, 1732, 1713, 1483, 1224, 1166, 1123 $cm^{-1}$; HRMS (ESI) m/z: [$M^+$] calculated for $C_{14}H_{15}BrN_2O_3^+$ 338.0339, found 338.0355. **16o** isolated yield: 5 mg, 0.015 mmol, 2% yield.

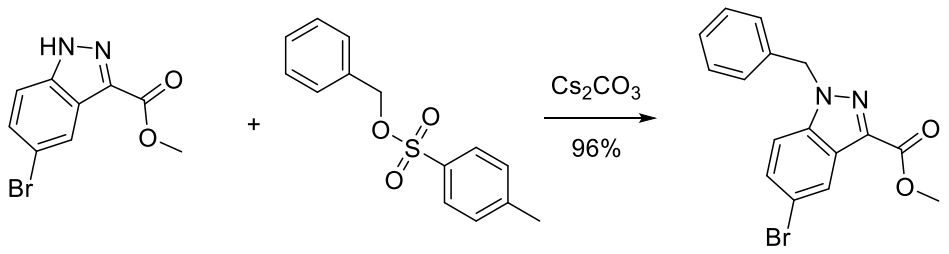
**Preparation of methyl 5-bromo-1-(cyclohexylmethyl)-1*H*-indazole-3-carboxylate (15p).**




**6** **14p** **15p**

The compound was prepared from **6** (0.190 g, 0.745 mmol) using a similar procedure as compound **15a** with 95% yield (249 mg, 0.709 mmol) as a white solid; melting point = 136.5 °C; $^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.21 (d, *J* = 1.9, 0.6 Hz, 1H), 7.89 (d, *J* = 9.0, 0.7 Hz, 1H), 7.63 (dd, *J* = 9.0, 1.9 Hz, 1H), 4.38 (d, *J* = 7.2 Hz, 2H), 3.94 (s, 3H), 2.00 – 1.83 (m, 1H), 1.63 (s, 3H), 1.46 (d, *J* = 12.1 Hz, 2H), 1.14 (t, *J* = 9.9 Hz, 3H), 1.02 (d, *J* = 11.2 Hz, 2H). $^{13}$C{1H} NMR (75 MHz, DMSO-$d_6$) δ 162.0, 139.8, 133.1, 129.6, 124.0, 123.2, 116.0, 113.3, 55.0, 51.8, 29.9, 25.8, 25.1; IR (KBr disk) 2927, 2849, 1727, 1477, 1462, 1447, 1435, 1323, 1219, 1166, 1152, 1125 $cm^{-1}$; HRMS (ESI) m/z: [M + H]$^+$ calculated for $C_{16}H_{19}BrN_2O_2^+$ 350.0703, found 350.0709. **16p** isolated yield: 7 mg, 0.020 mmol, 2.67%.

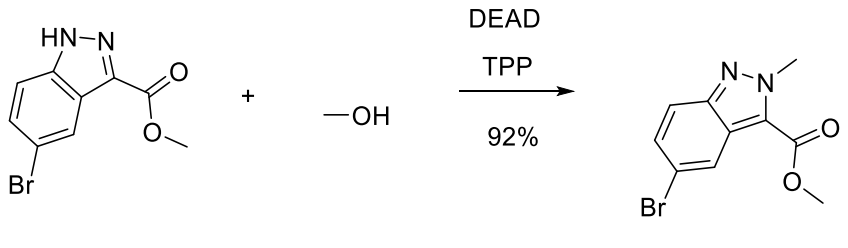
**Preparation of methyl 1-benzyl-5-bromo-1*H*-indazole-3-carboxylate (15q).**




**6** **14q** **15q**

The compound was prepared from **6** (0.194 g, 0.762 mmol) using a similar procedure as compound **15a** with 96% yield (253 mg, 0.733 mmol) as a white solid; melting point = 122 °C; $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 8.22 (d, $J$ = 1.8 Hz, 1H), 7.90 (d, $J$ = 9.0 Hz, 1H), 7.65 (dd, $J$ = 9.0, 1.9 Hz, 1H), 7.39 – 7.21 (m, 5H), 5.80 (s, 2H), 3.93 (s, 3H). $^{13}$C{1H} NMR (75 MHz, DMSO-$d_6$) δ 161.9, 139.2, 136.2, 133.6, 129.9, 128.7, 127.9, 127.5, 124.4, 123.3, 116.2, 113.1, 52.9, 51.9; IR (KBr disk) 1735, 1455, 1325, 1298, 1220, 1153 cm$^{-1}$; HRMS (ESI) m/z: [M + H]$^{+}$ calculated for $C_{16}H_{13}BrN_2O_2^{+}$ 344.0233, found 344.0249. **16q** isolated yield: n.d.

**Preparation of methyl 5-bromo-2-methyl-2*H*-indazole-3-carboxylate (16a).**

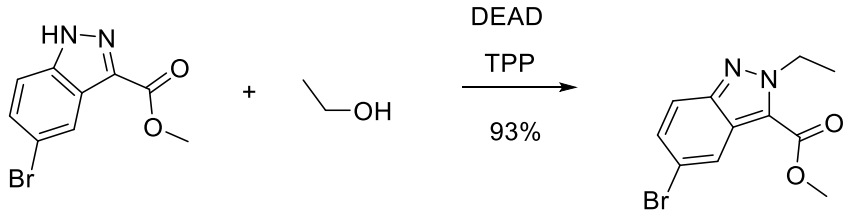



**6** **13a** **16a**

To a solution of methanol (631 µL, 15.60 mmol) in THF (15 mL) was added triphenylphosphine (8186 mg, 31.2 mmol) and methyl 5-bromo-1*H*-indazole-3-carboxylate (**6**, 3980 mg, 15.60 mmol) at 0 ℃, followed by adding DEAD (4941 µL, 31.2 mmol). The resulting mixture was stirred for 10 min at 0 ℃ and warmed to 50 ℃ and stirred for 2 h. After TLC showed completion, solvent was removed, the residue was purified by chromatography [silica gel (24 g), eluting with EA in hexane from 0–60%] to give methyl 5-bromo-2-methyl-2*H*-indazole-3-

carboxylate, **16a**, (3.850 g, 14.31 mmol, 92% yield) as a light pink solid; melting point = 110.7 °C; $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 8.14 (d, $J$ = 2.0 Hz, 1H), 7.77 (dd, $J$ = 9.1, 0.7 Hz, 1H), 7.49 (dd, $J$ = 9.0, 1.9 Hz, 1H), 4.42 (s, 3H), 3.98 (s, 3H); $^{13}$C{1H} NMR (75 MHz, DMSO-$d_6$) δ 159.4, 144.7, 129.3, 123.6, 123.2, 122.8, 120.0, 118.0, 52.2, 41.4; IR (KBr disk) 1708, 1459, 1442, 1392, 1326, 1252, 1196 cm$^{-1}$; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{10}H_{10}BrN_2O_2^+$ 268.9921, found 268.9918.

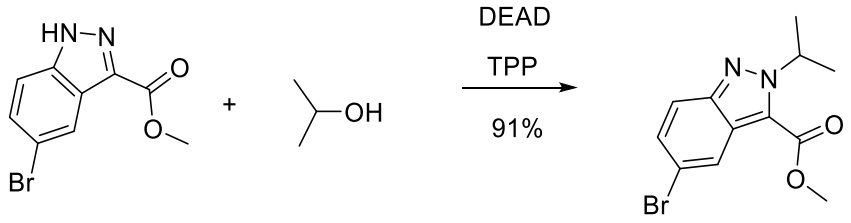
**Preparation of methyl 5-bromo-2-ethyl-2*H*-indazole-3-carboxylate (16b).**




**6** **13b** **16b**

The compound was prepared from **6** (1.384 g, 5.43 mmol) using a similar procedure as compound **16a** with 93% yield (1.422 g, 5.02 mmol) as a white solid; melting point = 98.8 °C; $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 8.16 (dd, $J$ = 1.9, 0.8 Hz, 1H), 7.80 (dd, $J$ = 9.1, 0.8 Hz, 1H), 7.50 (dd, $J$ = 9.1, 1.9 Hz, 1H), 4.86 (q, $J$ = 7.2 Hz, 2H), 4.00 (s, 3H), 1.48 (t, $J$ = 7.2 Hz, 3H). $^{13}$C{1H} NMR (75 MHz, DMSO-$d_6$) δ 8.16 (dd, J = 1.9, 0.8 Hz, 1H), 7.80 (dd, J = 9.1, 0.8 Hz, 1H), 7.50 (dd, J = 9.1, 1.9 Hz, 1H), 4.86 (q, J = 7.2 Hz, 2H), 4.00 (s, 3H), 1.48 (t, J = 7.2 Hz, 3H); IR (KBr disk) 1708, 1459, 1436, 1325, 1200, 1120, 1069, 1030 cm$^{-1}$; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{11}H_{11}BrN_2O_2^+$ 282.0077, found 282.0093.

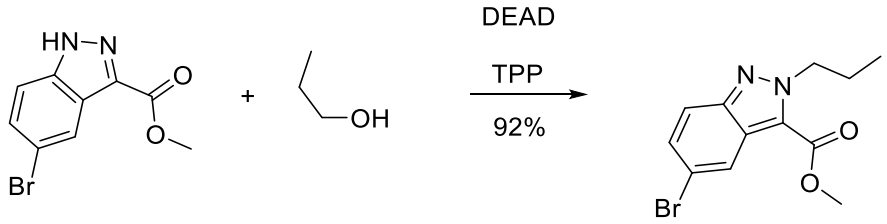
**Preparation of methyl 5-bromo-2-isopropyl-2*H*-indazole-3-carboxylate (16c).**




**6** **13c** **16c**

The compound was prepared from **6** (1061 mg, 4.16 mmol) using a similar procedure as compound **16a** with 91% yield (1.141 g, 3.84 mmol) as a white solid; melting point = 103.3 °C; $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 8.17 (d, $J$ = 1.9 Hz, 1H), 7.82 (d, $J$ = 9.0 Hz, 1H), 7.49 (dd, $J$ = 9.1, 1.9 Hz, 1H), 5.84 (hept, $J$ = 6.6 Hz, 1H), 3.99 (s, 3H), 1.55 (d, $J$ = 6.6 Hz, 6H). $^{13}$C{1H} NMR (75 MHz, DMSO-$d_6$) δ 160.0, 145.4, 129.8, 124.3, 123.7, 122.9, 120.9, 118.5, 54.2, 52.7, 23.1; IR (KBr disk) 1703, 1455, 1433, 1382, 1248, 1200, 1168 cm$^{-1}$; HRMS (ESI) m/z: [M + H]$^{+}$ calculated for $C_{12}H_{13}BrN_2O_2^{+}$ 296.0233, found 296.0232.

**Preparation of methyl 5-bromo-2-propyl-2*H*-indazole-3-carboxylate (16d).**

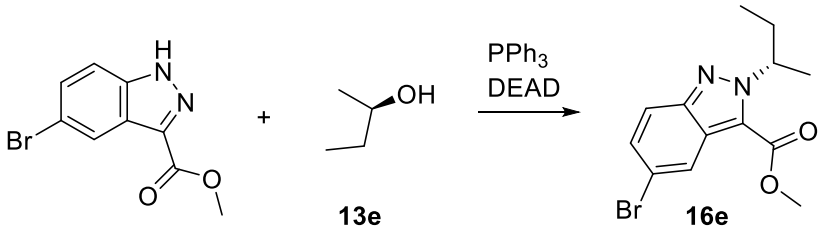



**6** **13d** **16d**

The compound was prepared from **6** (1,061 mg, 4.16 mmol) using a similar procedure as compound **16a** with 92% yield (1.141 g, 3.84 mmol) as a white solid; melting point = 77.7 °C; $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 8.17 (dd, $J$ = 1.9, 0.8 Hz, 1H), 7.80 (dd, $J$ = 9.1, 0.8 Hz, 1H), 7.50 (dd, $J$ = 9.1, 1.9 Hz, 1H), 4.80 (t, $J$ = 7.2 Hz, 2H), 1.92 (h, $J$ = 7.4 Hz, 2H), 0.87 (t, $J$ = 7.4 Hz, 3H); $^{13}$C{1H} NMR (75 MHz, DMSO-$d_6$) δ 159.4, 144.9, 129.5, 123.8,

123.1, 122.9, 120.3, 118.1, 54.6, 52.3, 23.5, 10.8; IR (KBr disk) 1701, 1462, 1325, 1218, 1202, 1185 $cm^{-1}$; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{12}H_{13}BrN_2O_2^+$ 296.0233, found 296.0245.

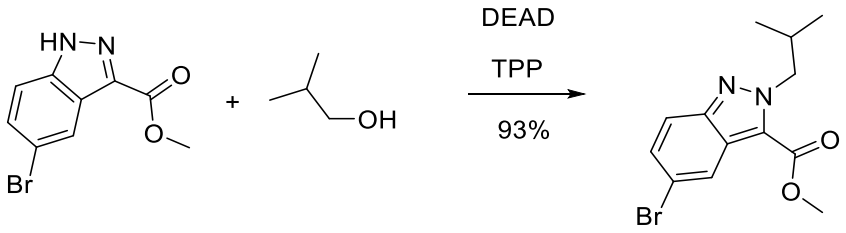
**Preparation of methyl (*S*)-5-bromo-2-(sec-butyl)-2*H*-indazole-3-carboxylate (16e).**




13e 16e

The compound was prepared from **6** (860 mg, 3.37 mmol) using a similar procedure as compound **16a** 97% yield as a white solid (1.020 g, 97% yield); m.p. = 70.3 °C; $^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.17 (d, *J* = 1.9, 0.8 Hz, 1H), 7.82 (d, *J* = 9.1, 0.8 Hz, 1H), 7.49 (dd, *J* = 9.1, 1.9 Hz, 1H), 5.78 – 5.61 (m, 1H), 3.99 (s, 3H), 2.13 – 1.79 (m, 2H), 1.54 (d, *J* = 6.6 Hz, 3H), 0.70 (t, *J* = 7.4 Hz, 3H); $^{13}$C{H} NMR (75 MHz, DMSO-$d_6$) δ 159.7, 145.2, 129.4, 123.6, 123.3, 120.4, 118.1, 58.9, 52.3, 29.6, 20.9, 10.3; IR (KBr disk) 2981, 2965, 2937, 2875, 1708, 1490, 1462, 1454, 1380, 1255, 1247, 1209, 1195 $cm^{-1}$; HRMS (ESI) m/z: $[M^+]$ calculated for $C_{13}H_{15}BrN_2O_2^+$ 310.0390, found 310.0399.

**Preparation of methyl 5-bromo-2-isobutyl-2*H*-indazole-3-carboxylate (16f).**

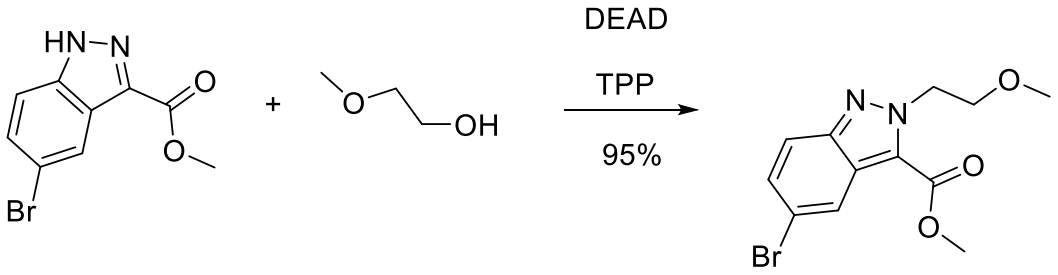



6 13f 16f

The compound was prepared from **6** (860 mg, 3.37 mmol) using a similar procedure as compound **16a** with 93% yield (981 mg, 3.15 mmol) as a white solid; melting point = 100.6 °C; $^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.17 (d,

*J* = 1.9, 0.8 Hz, 1H), 7.80 (d, *J* = 9.1, 0.7 Hz, 1H), 7.50 (dd, *J* = 9.1, 1.9 Hz, 1H), 4.67 (d, *J* = 7.3 Hz, 2H), 3.99 (s, 3H), 2.35 – 2.18 (m, 1H), 0.87 (d, *J* = 6.7 Hz, 6H). $^{13}$C{1H} NMR (75 MHz, DMSO-$d_6$) δ 159.5, 144.9, 129.5, 123.8, 123.2, 123.1, 120.3, 118.2, 59.7, 52.3, 29.6, 19.6; IR (KBr disk) 2953, 2909, 2871, 1705, 1459, 1323, 1254, 1205, 1192, 1082 cm$^{-1}$; HRMS (ESI) m/z: [M + H]$^+$ calculated for $C_{13}H_{15}BrN_2O_2^+$ 310.0399, found 310.0396.

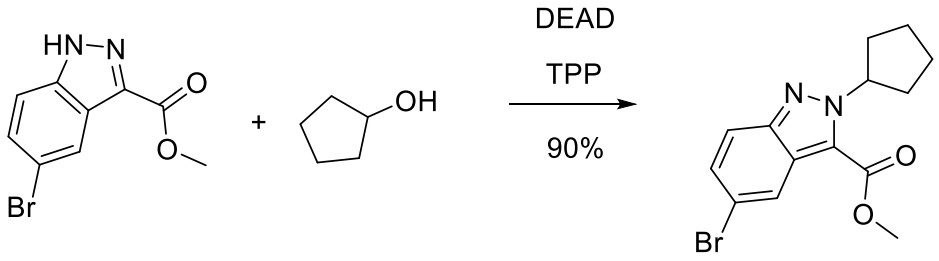
**Preparation of methyl 5-bromo-2-(2-methoxyethyl)-2*H*-indazole-3-carboxylate (16g).**




**6** **13g** **16g**

The compound was prepared from **6** (838 mg, 3.29 mmol) using similar procedure as compound **16a** with 95% yield (981 mg, 3.13 mmol) as a white solid; melting point = 74 °C; $^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.17 (dd, *J* = 1.9, 0.8 Hz, 1H), 7.80 (dd, *J* = 9.1, 0.8 Hz, 1H), 7.51 (dd, *J* = 9.1, 1.9 Hz, 1H), 5.04 (t, *J* = 5.5 Hz, 2H), 4.00 (s, 3H), 3.85 (t, *J* = 5.5 Hz, 2H), 3.21 (s, 3H). $^{13}$C{1H} NMR (75 MHz, DMSO-$d_6$) δ 159.5, 145.1, 129.6, 123.8, 123.5, 123.1, 120.3, 118.2, 70.5, 58.0, 52.3, 52.3; IR (KBr disk) 1705, 1487, 1459, 1435, 1407, 1326, 1304, 1256, 1220, 1205 cm$^{-1}$; HRMS (ESI) m/z: [M + H]$^+$ calculated for $C_{12}H_{13}BrN_2O_3^+$ 312.0182, found 312.0181.

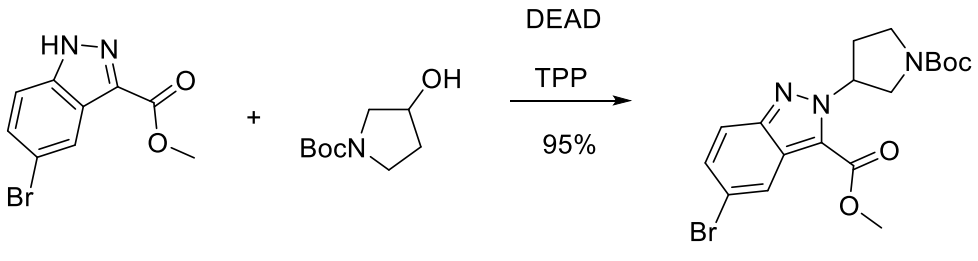
**Preparation of methyl 5-bromo-2-cyclopentyl-2*H*-indazole-3-carboxylate (16h).**




**6** **13h** **16h**

The compound was prepared from **6** (740 mg, 2.90 mmol) using a similar procedure as compound **16a** with 90% yield (845 mg, 2.61 mmol) as a white solid; melting point = 101.8 °C; $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 8.17 (d, $J$ = 1.9, 0.8 Hz, 1H), 7.81 (dd, $J$ = 9.1, 0.8 Hz, 1H), 7.49 (dd, $J$ = 9.1, 1.9 Hz, 1H), 6.04 – 5.88 (m, 1H), 4.00 (s, 3H), 2.29 – 2.17 (m, 2H), 2.16 – 2.04 (m, 2H), 1.98 – 1.84 (m, 2H), 1.79 – 1.63 (m, 2H). $^{13}$C{1H} NMR (75 MHz, DMSO-$d_6$) δ 159.6, 144.8, 129.4, 124.0, 123.1, 120.5, 118.0, 62.6, 52.3, 33.2, 24.5; IR (KBr disk) 2952, 2866, 1712, 1490, 1466, 1457, 1434, 1376, 1324, 1308, 1257, 1213, 1098 cm$^{-1}$; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{14}H_{15}BrN_2O_2^+$ 322.0390, found 322.0408.

**Preparation of methyl 5-bromo-2-(1-(*tert*-butoxycarbonyl)pyrrolidin-3-yl)-2*H*-indazole-3-carboxylate (16i).**

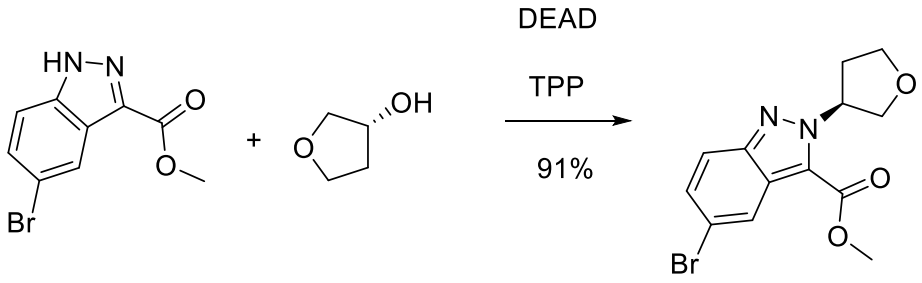



**6** **13i** **16i**

The compound was prepared from **6** (341 mg, 1.335 mmol) as a mixture of rotamers using a similar procedure as compound **16a** with 95% yield (541 mg, 1.275 mmol) as a white solid; melting point = 148.8 °C; $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 8.19 (d, $J$ = 1.9, 0.7 Hz, 1H), 7.81 (d, $J$ = 9.1, 0.8 Hz, 1H), 7.51 (dd, $J$ = 9.1, 1.9 Hz, 1H), 6.12

(s, 1H), 4.01 (s, 3H), 3.90 – 3.79 (m, 1H), 3.72 (dd, *J* = 12.1, 3.2 Hz, 1H), 3.57 (s, 1H), 3.49 (s, 1H), 2.45 (d, *J* = 8.3 Hz, 2H), 1.41 (dd, *J* = 6.9, 2.6 Hz, 9H). $^{13}$C{1H} NMR (75 MHz, DMSO-$d_6$) δ 159.6, 153.5, 153.4, 144.9, 129.7, 123.9, 123.4, 123.1, 120.5, 118.4, 78.6, 61.2, 60.5, 52.4, 51.8, 44.9, 44.7, 31.7, 30.9, 28.1; IR (KBr disk) 1708, 1679, 1403, 1375, 1243, 1205, 1189, 1162 cm$^{-1}$; HRMS (ESI) m/z: [M + Na]$^+$ calculated for $C_{18}H_{22}BrN_3O_4Na^+$ 446.0691, found 446.0705.

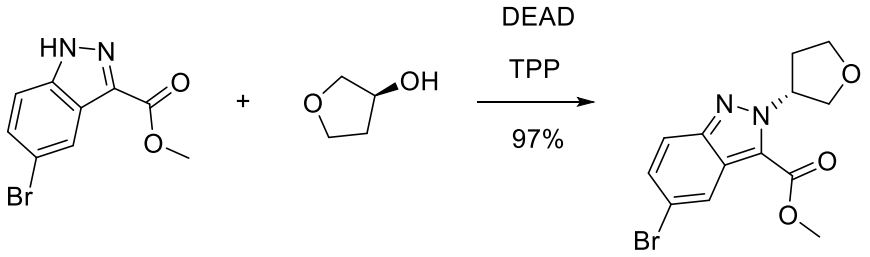
**Preparation of methyl (*S*)-5-bromo-2-(tetrahydrofuran-3-yl)-2*H*-indazole-3-carboxylate (16j).**




**6** **13j** **16j**

The compound was prepared from **6** (724 mg, 2.84 mmol) using a similar procedure as compound **16a** with 91% yield (841 mg, 2.59 mmol) as a white solid; melting point = 141.2 °C; $^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.17 (d, *J* = 1.9, 0.8 Hz, 1H), 7.82 (d, *J* = 9.1, 0.7 Hz, 1H), 7.50 (dd, *J* = 9.1, 1.9 Hz, 1H), 6.22 – 6.11 (m, 1H), 4.18 – 4.05 (m, 2H), 4.02 (d, *J* = 3.2 Hz, 1H), 3.99 (s, 3H), 3.95 – 3.85 (m, 1H), 2.59 – 2.52 (m, 1H), 2.47 (d, *J* = 2.4 Hz, 1H). $^{13}$C{1H} NMR (75 MHz, DMSO-$d_6$) δ 159.7, 144.8, 129.6, 124.1, 123.4, 123.1, 120.6, 118.3, 73.1, 67.5, 62.2, 52.4, 32.4; IR (KBr disk) 1705, 1455, 1257, 1215, 1092, 1067 cm$^{-1}$; HRMS (ESI) m/z: [M + H]$^+$ calculated for $C_{13}H_{13}BrN_2O_3^+$ 324.0182, found 324.0182.

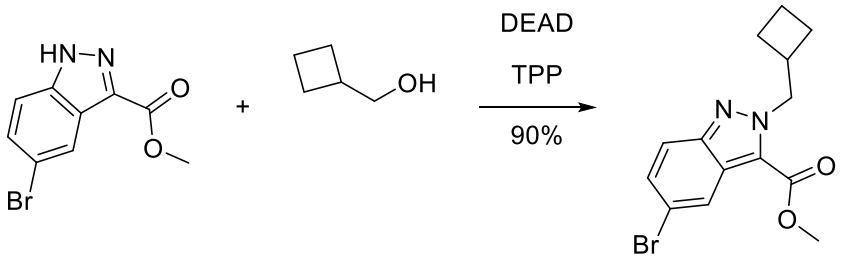
**Preparation of methyl (*R*)-5-bromo-2-(tetrahydrofuran-3-yl)-2*H*-indazole-3-carboxylate (16k).**




**6** **13k** **16k**

The compound was prepared from **6** (724 mg, 2.84 mmol) using a similar procedure as compound **16a** with 97% yield (898 mg, 2.76 mmol) as a white solid; melting point = 126.2 °C; $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 8.18 (d, $J$ = 1.9, 0.7 Hz, 1H), 7.83 (d, $J$ = 9.1, 0.8 Hz, 1H), 7.51 (dd, $J$ = 9.1, 1.9 Hz, 1H), 6.22 – 6.12 (m, 1H), 4.21 – 4.06 (m, 2H), 4.03 (d, $J$ = 3.0 Hz, 1H), 4.00 (s, 3H), 3.96 – 3.86 (m, 1H), 2.59 – 2.54 (m, 1H), 2.49 – 2.41 (m, 1H); $^{13}$C{1H} NMR (75 MHz, DMSO-$d_6$) δ 159.6, 144.8, 129.6, 124.0, 123.3, 123.1, 120.5, 118.3, 73.1, 67.5, 62.2, 52.3, 32.4; IR (KBr disk) 1701, 1455, 1256, 1213, 1090, 1067, 1036 cm$^{-1}$; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{13}H_{13}BrN_2O_3^+$ 324.0182, found 324.0182.

**Preparation of methyl 5-bromo-2-(cyclobutylmethyl)-2*H*-indazole-3-carboxylate (16l).**

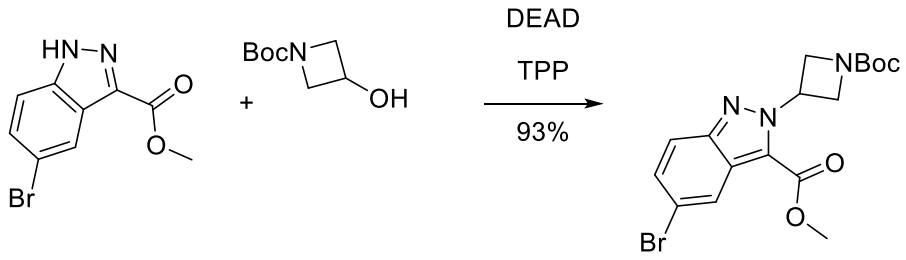



**6** **13l** **16l**

The compound was prepared from **6** (740 mg, 2.90 mmol) using a similar procedure as compound **16a** with 90% yield (844 mg, 2.61 mmol) as a white solid; m.p. = °87.5; $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 8.16 (d, $J$ = 1.9, 0.8 Hz, 1H), 7.79 (d, $J$ = 9.0, 0.7 Hz, 1H), 7.49 (dd, $J$ = 9.1, 1.9 Hz, 1H), 4.88 (d, $J$ = 7.3 Hz, 2H), 3.99 (s, 3H), 2.90 (p, $J$ = 7.4 Hz, 1H), 1.98 – 1.90 (m, 2H), 1.88 – 1.78 (m, 4H); $^{13}$C{H} NMR (75 MHz, DMSO-$d_6$) δ 159.5, 144.9,

129.4, 123.7, 123.0, 122.7, 120.2, 118.1, 57.3, 52.2, 35.6, 25.1, 17.7; IR (KBr disk) 2942, 1705, 1462, 1321, 1252, 1205 $cm^{-1}$; HRMS (ESI) m/z: $[M^+]$ calculated for $C_{14}H_{15}BrN_2O_2^+$ 322.0390, found 322.0398.

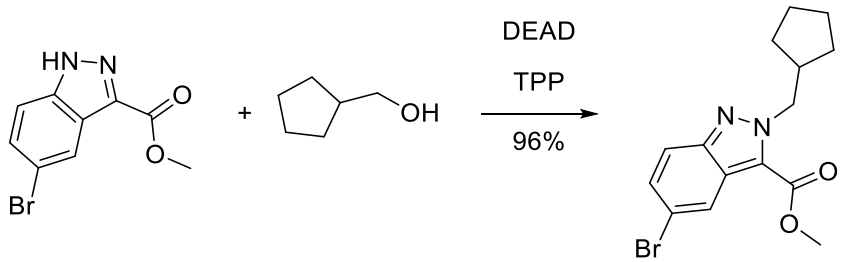
**Preparation of methyl 5-bromo-2-(1-(*tert*-butoxycarbonyl)azetidin-3-yl)-2*H*-indazole-3-carboxylate (16m).**




**6** **13m** **16m**

The compound was prepared as a mixture of rotamers from **6** (368 mg, 1.443 mmol) using a similar procedure as compound **16a** with 93% yield (551 mg, 1.343 mmol) as a white solid; $^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.17 (s, 1H), 7.88 (d, J = 8.8 Hz, 1H), 7.54 (d, J = 9.1 Hz, 1H), 6.22 – 6.08 (m, 1H), 4.41 (q, J = 7.7 Hz, 4H), 4.13 (q, J = 7.0 Hz, 1H), 3.98 (s, 3H), 1.41 (d, J = 1.2 Hz, 9H); $^{13}$C{H} NMR (75 MHz, DMSO-$d_6$) δ 159.3, 155.5, 155.4, 153.5, 145.0, 130.0, 124.0, 123.9, 123.0, 120.6, 118.5, 79.0, 79.0, 65.9, 64.0, 52.4, 50.9, 28.02, 27.96, 14.0; IR (KBr disk) 3060, 2976, 2966, 2930, 2892, 1748, 1709, 1494, 01468, 1439, 1394, 1368, 1332, 1307, 1259, 1248, 1215, 1171, 1157, 1140, 1101, 1084, 1035, 1003 $cm^{-1}$; HRMS (ESI) m/z: $[M\text{-}C_4H_8{}^1 + H]^+$ calculated for $C_{13}H_{13}BrN_3O_4^+$ 354.0084, found 354.0094.

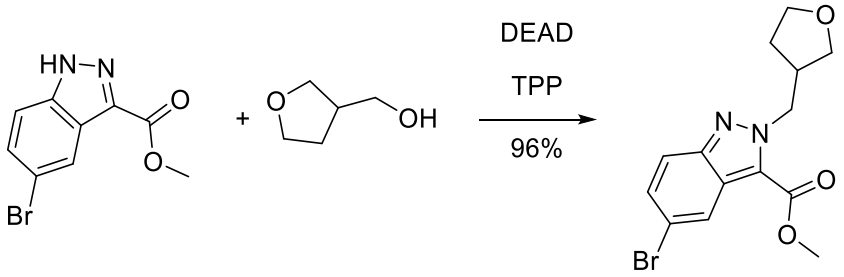
**Preparation of methyl 5-bromo-2-(cyclopentylmethyl)-2*H*-indazole-3-carboxylate (16n).**




**6** **13n** **16n**

The compound was prepared from **6** (637 mg, 2.496 mmol) using a similar procedure as compound **16a** with 96% yield (810 mg, 2.42 mmol) as a white solid; m.p. = 101.7 °C; $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 8.17 (d, J = 1.9 Hz, 1H), 7.80 (d, J = 9.1 Hz, 1H), 7.50 (dd, J = 9.1, 1.9 Hz, 1H), 4.78 (d, J = 7.6 Hz, 2H), 3.99 (s, 3H), 2.58 – 2.52 (m, 1H), 1.67 – 1.45 (m, 6H), 1.39 – 1.24 (m, 2H); $^{13}$C{1H} NMR (75 MHz, DMSO-$d_6$) δ 159.6, 144.9, 129.5, 123.9, 123.2, 122.9, 120.4, 118.2, 57.1, 52.3, 29.4, 24.4; IR (KBr disk) 2946, 2868, 1705, 1485, 1459, 1420, 1325, 1302, 1254, 1203 cm$^{-1}$; HRMS (ESI) m/z: [M$^{+}$] calculated for $C_{15}H_{17}BrN_2O_2^{+}$ 336.0546, found 336.0560.

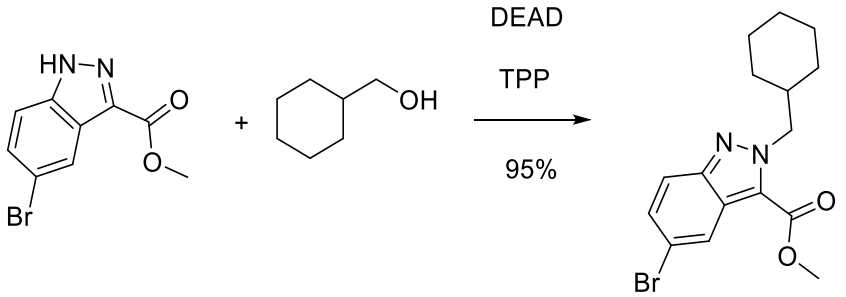
**Preparation of methyl 5-bromo-2-((tetrahydrofuran-3-yl)methyl)-2*H*-indazole-3-carboxylate (16o).**




**6** **13o** **16o**

The compound was prepared from **6** (624 mg, 2.448 mmol) using a similar procedure as compound **16a** with 98% yield (810 mg, 2.388 mmol) as a white solid; m.p. = 69.1 °C; $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 8.18 (d, 1H), 7.82 (d, J = 9.1, 0.8 Hz, 1H), 7.51 (dd, J = 9.1, 1.9 Hz, 1H), 4.93 – 4.73 (m, 2H), 4.00 (s, 3H), 3.81 (td, J = 8.1, 5.6 Hz, 1H), 3.69 – 3.60 (m, 2H), 3.60 – 3.52 (m, 1H), 2.91 (h, J = 13.2, 6.8, 6.3 Hz, 1H), 1.99 – 1.85 (m, 1H), 1.76 – 1.58 (m, 1H); $^{13}$C{H} NMR (75 MHz, DMSO-$d_6$) δ 159.5, 145.0, 129.7, 123.8, 123.2, 120.4, 118.3, 69.9, 66.7, 55.2, 52.4, 29.1; IR (KBr disk) 2953, 2853, 1708, 1492, 1459, 1254, 1205 cm$^{-1}$; HRMS (ESI) m/z: [M + H$^{+}$] calculated for $C_{14}H_{16}BrN_2O_3^{+}$ 339.0339, found 339.0367.

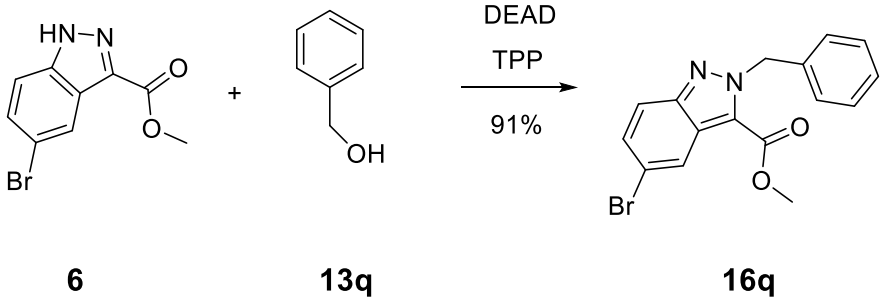
**Preparation of methyl 5-bromo-2-(cyclohexylmethyl)-2*H*-indazole-3-carboxylate (16p).**




**6** **13p** **16p**

The compound was prepared from **6** (558 mg, 2.189 mmol) using a similar procedure as compound **16a** with 95% yield (730 mg, 2.078 mmol) as a white solid; melting point = 98.8 °C; $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 8.17 (d, $J$ = 1.9, 0.8 Hz, 1H), 7.79 (d, $J$ = 9.1, 0.8 Hz, 1H), 7.49 (dd, $J$ = 9.1, 1.9 Hz, 1H), 4.70 (d, $J$ = 7.2 Hz, 2H), 3.99 (s, 3H), 2.03 – 1.89 (m, 1H), 1.61 (d, $J$ = 17.2 Hz, 3H), 1.47 (d, $J$ = 11.8 Hz, 2H), 1.20 – 1.08 (m, 3H), 1.04 (d, $J$ = 11.5 Hz, 2H); $^{13}$C{1H} NMR (75 MHz, DMSO-$d_6$) δ 159.6, 159.5, 144.9, 133.4, 129.6, 123.8, 123.2, 120.3, 118.2, 58.5, 52.3, 29.9, 25.8, 25.1; IR (KBr disk) 2916, 2847, 1701, 1466, 1446, 1323, 1209 cm$^{-1}$; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{16}H_{19}BrN_2O_2^+$ 350.0703, found 350.0716.

**Preparation of methyl 2-benzyl-5-bromo-2*H*-indazole-3-carboxylate (16q).**

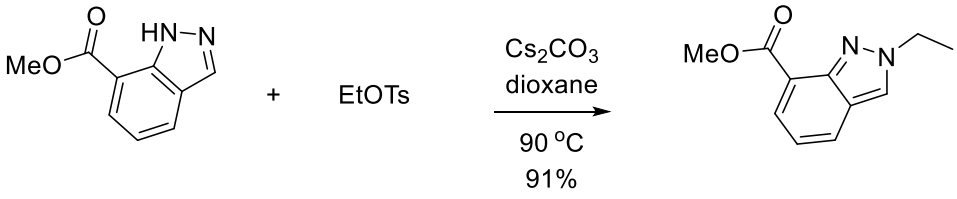



**6** **13q** **16q**

The compound was prepared from **6** (500 mg, 4.62 mmol) using a similar procedure as compound **16a** in 91% yield (723 mg, 2.094 mmol) as a white solid; melting point = 122.6 °C; $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ 8.18 (d, $J$ = 1.9, 0.8 Hz, 1H), 7.82 (d, $J$ = 9.1, 0.8 Hz, 1H), 7.52 (dd, $J$ = 9.1, 1.9 Hz, 1H), 7.39 – 7.20 (m, 5H), 6.07 (s, 2H), 3.98 (s, 3H); $^{13}$C{1H} NMR (75 MHz, DMSO-$d_6$) δ 159.5, 145.4, 136.3, 129.9, 128.6, 127.9, 127.5, 123.9,

123.3, 123.1, 120.5, 118.5, 56.1, 52.4; IR (KBr disk) 1708, 1470, 1300, 1256, 1216, 1093 $cm^{-1}$; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{16}H_{13}BrN_2O_2^+$ 344.0233, found 344.0249.

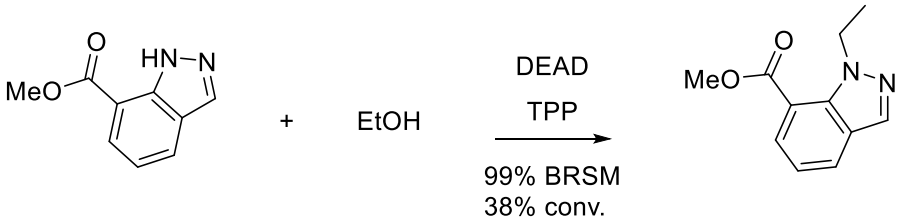
**Preparation of methyl 2-ethyl-2*H*-indazole-7-carboxylate (19).**




**18** **12** **19**

This compounds was prepared from methyl 1*H*-indazole-7-carboxylate (**18**, 176 mg, 1.0 mmol) using a similar procedure as **15a** in 93% yield (190 mg, 0.93 mmol) as a viscous oil; $^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.57 (s, 1H), 8.02 (d, $J$ = 8.3 Hz, 1H), 7.92 (d, $J$ = 7.1 Hz, 1H), 7.14 (t, $J$ = 7.7 Hz, 1H), 4.51 (q, $J$ = 7.3 Hz, 2H), 3.88 (s, 3H), 1.52 (t, $J$ = 7.3 Hz, 3H); $^{13}$C{1H} NMR (75 MHz, DMSO-$d_6$) δ 166.1, 144.8, 129.7, 126.6, 124.2, 123.2, 119.9, 118.5, 51.8, 48.0, 15.7; IR (KBr disk) 1729, 1606, 1575, 1505, 1455, 1435, 1375, 1304, 1271, 1235, 1202, 1176, 1138, 1116, 1065, 1032 $cm^{-1}$; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{11}H_{13}N_2O_2^+$ 205.0977, found 205.0923.

**Preparation of methyl 1-ethyl-1*H*-indazole-7-carboxylate (20).**

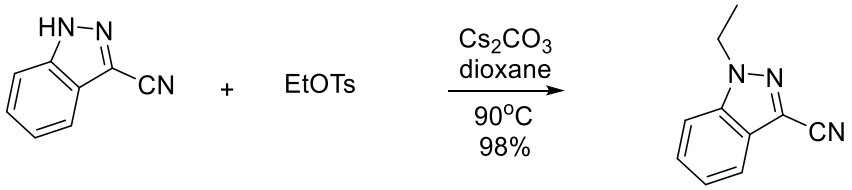



**18** **20**

This compound was prepared from methyl 1*H*-indazole-7-carboxylate (**18**, 1.912 g, 10.85 mmol) using a similar procedure as **16a** in >99% (852 mg, 4.17 mmol) yield as a viscous oil based on recovered starting material **18** (1.190 g, 6.7 mmol); $^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.25 (s, 1H), 8.05 (d, $J$ = 8.0 Hz, 1H), 7.87 (d, $J$ = 7.3 Hz, 1H), 7.23 (t, $J$ = 7.6 Hz, 1H), 4.59 (q, $J$ = 7.1 Hz, 2H), 3.94 (s, 3H), 1.30 (t, $J$ = 7.2 Hz, 3H); $^{13}$C{1H} NMR (75 MHz, DMSO-$d_6$) δ 166.4, 135.2, 133.9, 129.4, 126.3, 126.1, 119.7, 115.0, 52.4, 46.6, 15.1; IR (KBr disk) 1710,

1617, 1555, 1522, 1436, 1380, 1318, 1280, 1203, 1140, 1039, 1005 $cm^{-1}$; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{11}H_{13}N_2O_2^+$ 205.0977, found 205.0993.

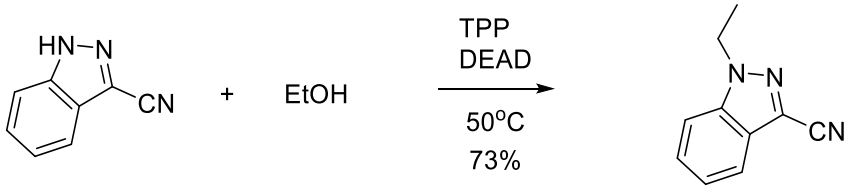
**Preparation of 1-ethyl-1*H*-indazole-3-carbonitrile (22), method A.**




**21** **12** **22**

This compound was prepared from 1*H*-indazole-3-carbonitrile (**21**, 143 mg, 1 mmol) using a similar procedure to **15a** in 98% yield (167 mg, 0.98 mmol) as a viscous oil; 1H NMR (300 MHz, DMSO-$d_6$) δ 7.92 (dd, *J* = 20.4, 8.5 Hz, 2H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 4.60 (q, *J* = 6.9 Hz, 2H), 1.45 (t, *J* = 7.2 Hz, 3H); $^{13}C\{1H\}$ NMR (75 MHz, DMSO-$d_6$) δ 138.9, 127.7, 124.5, 123.9, 118.8, 115.8, 113.8, 111.3, 44.6, 14.5; IR (KBr disk) 2230, 1466, 1352, 1235, 1223 $cm^{-1}$; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{10}H_{10}N_3^+$ 172.0875, found 172.0775.

**Preparation of 1-ethyl-1*H*-indazole-3-carbonitrile (22), method B.**



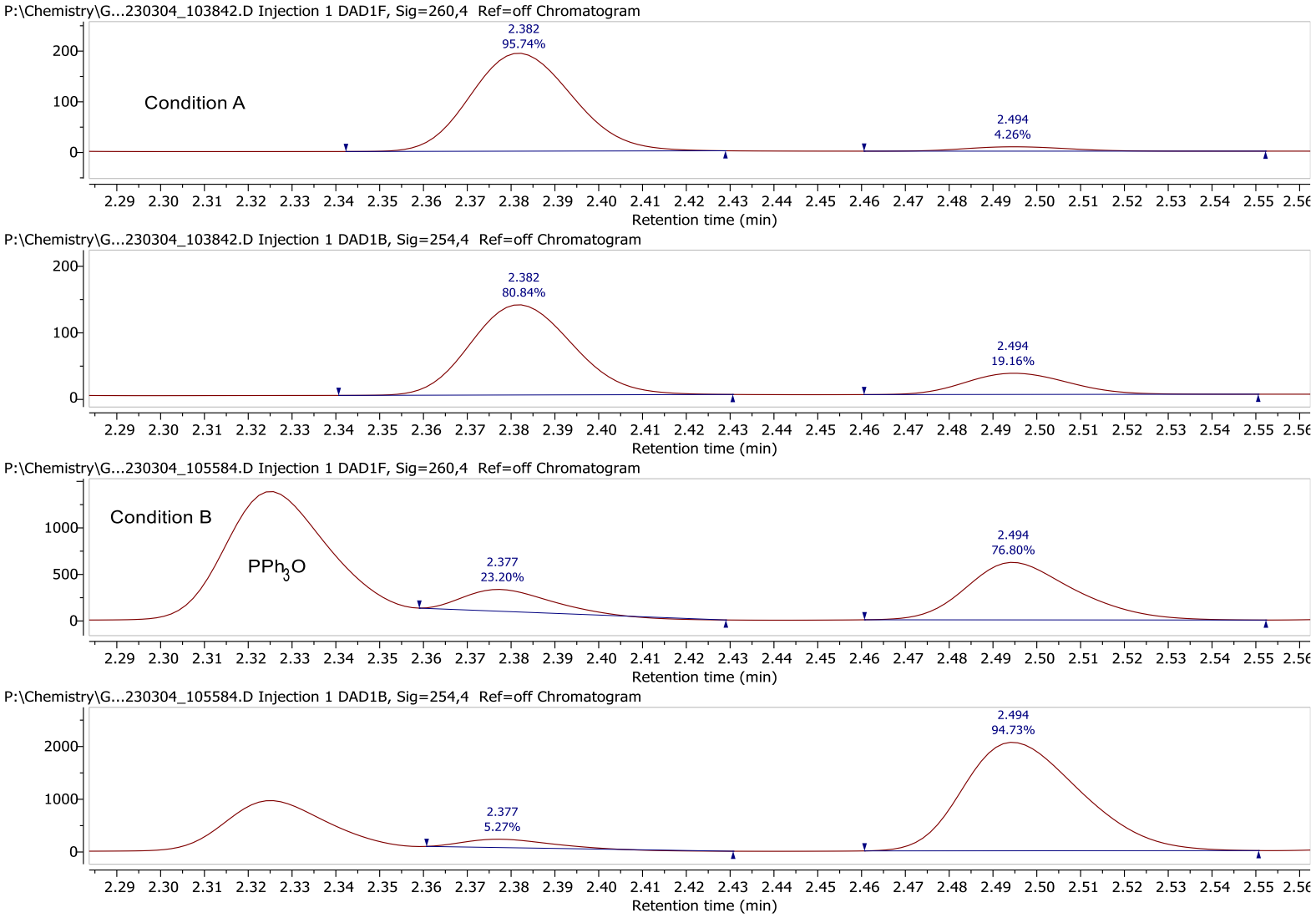

**21** **22**

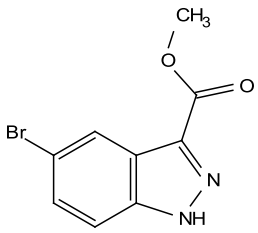
This compound was prepared from 1*H*-indazole-3-carbonitrile (**21**, 777 mg, 5.43 mmol) using a similar procedure to **16a** in 73% yield (679 mg, 3.97 mmol) as a viscous oil; $^1H$ NMR (300 MHz, DMSO-$d_6$) δ 7.92 (dd, *J* = 20.4, 8.5 Hz, 2H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 4.60 (q, *J* = 6.9 Hz, 2H), 1.45 (t, *J* = 7.2 Hz, 3H); $^{13}C\{1H\}$ NMR (75 MHz, DMSO-$d_6$) δ 138.9, 127.7, 124.5, 123.9, 118.8, 115.8, 113.8, 111.3, 44.6, 14.5; IR (KBr

disk) 2230, 1466, 1352, 1235, 1223 $cm^{-1}$; HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{10}H_{10}N_3^+$ 172.0875, found 172.0779.

**Crude LCMS data. Condition A (top), Condition B (bottom). $N^1$ Product has shorter Rt for a-q.**

**a (zoom)**

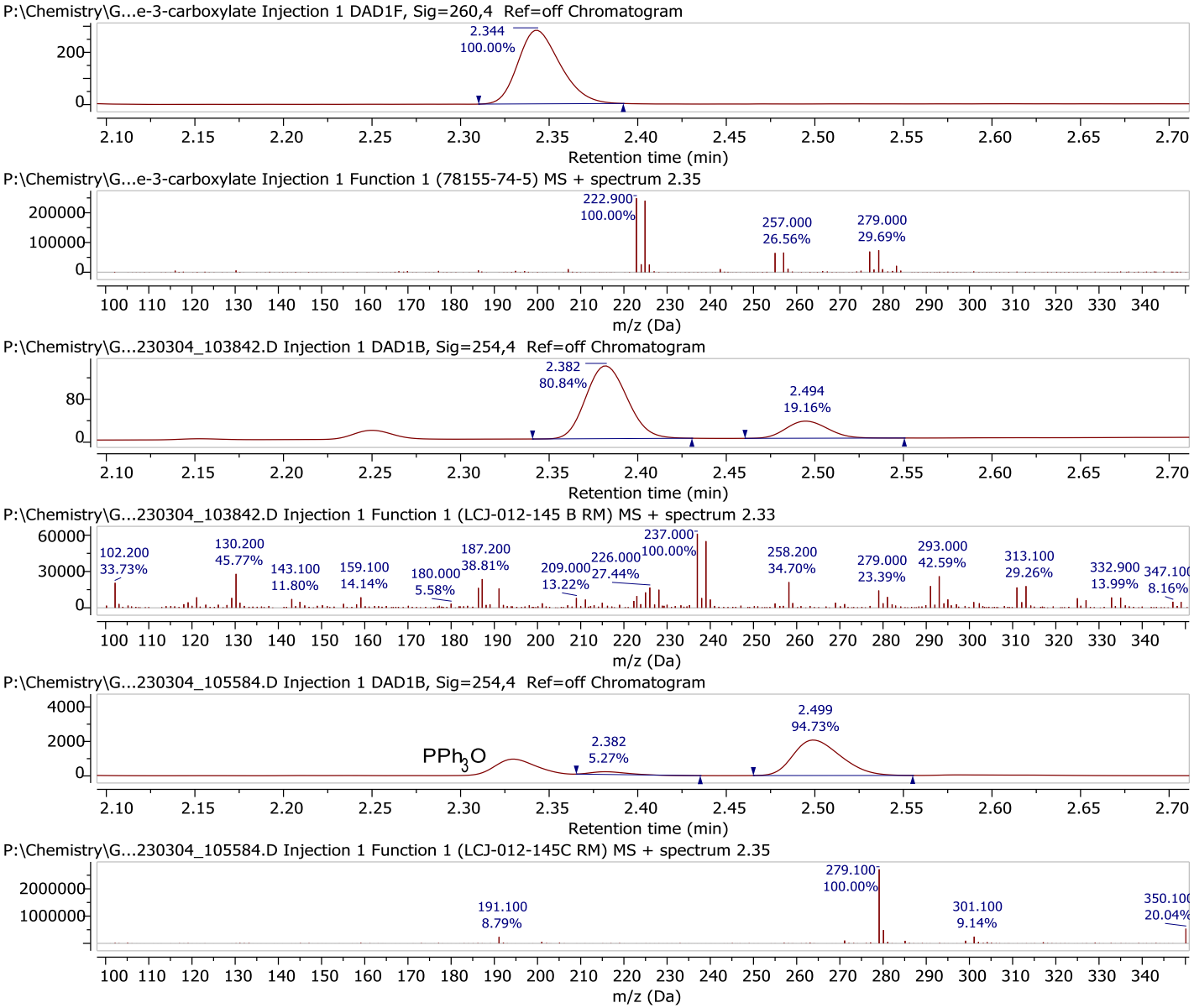




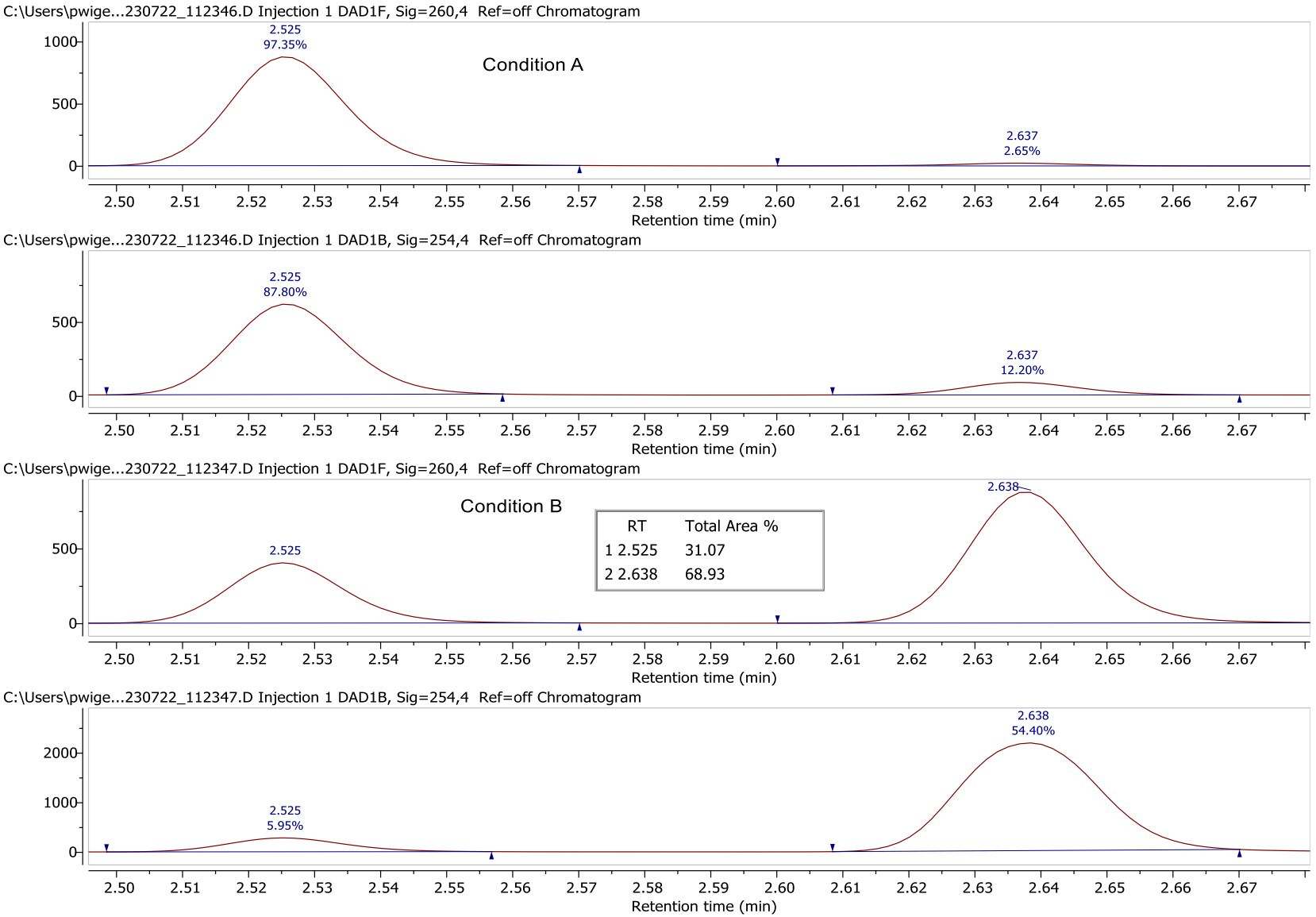

6

Condition A
R=$CH_3$

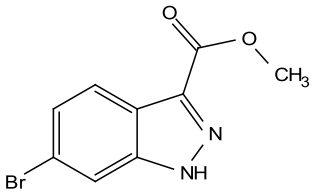
Condition B
R=$CH_3$



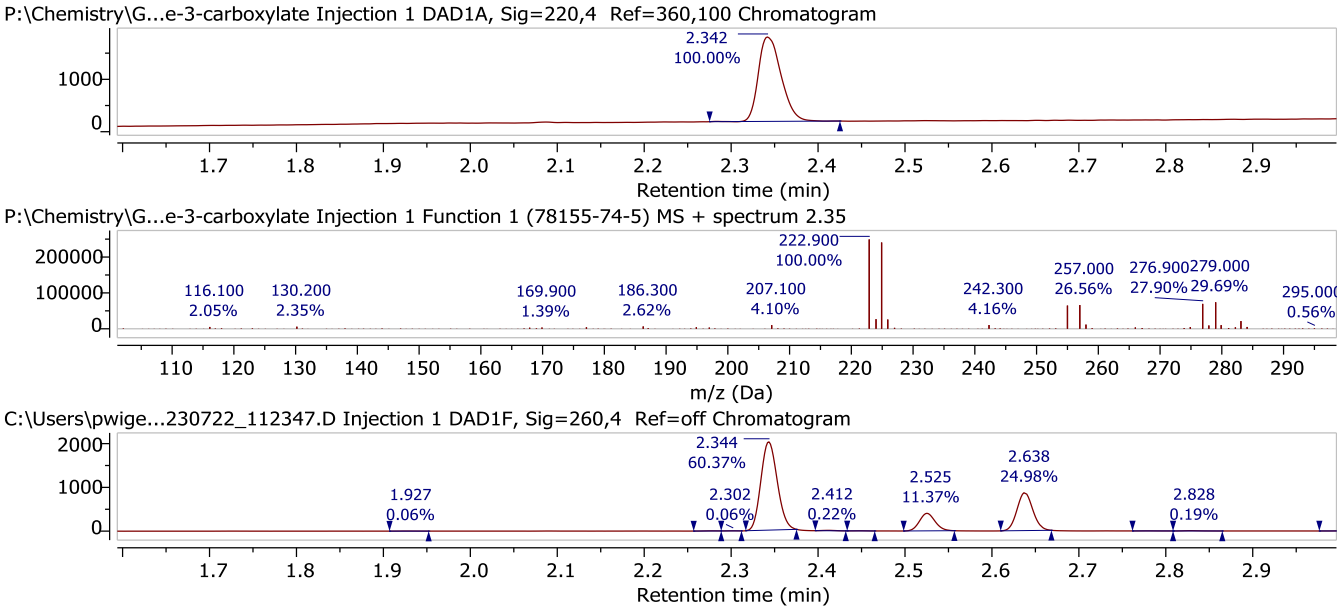

**a: R = $CH_3$, 6 versus reaction mixtures. Mass spectra for reaction mixtures at 2.344 minutes for each condition.**


C:\Users\pwige...230722_112346.D Injection 1 DAD1F, Sig=260,4 Ref=off Chromatogram
2.525
97.35%
Condition A
2.637
2.65%
Retention time (min)
C:\Users\pwige...230722_112346.D Injection 1 DAD1B, Sig=254,4 Ref=off Chromatogram
2.525
87.80%
2.637
12.20%
Retention time (min)
C:\Users\pwige...230722_112347.D Injection 1 DAD1F, Sig=260,4 Ref=off Chromatogram
Condition B
2.638
2.525
RT Total Area %
1 2.525 31.07
2 2.638 68.93
Retention time (min)
C:\Users\pwige...230722_112347.D Injection 1 DAD1B, Sig=254,4 Ref=off Chromatogram
2.638
54.40%
2.525
5.95%
Retention time (min)

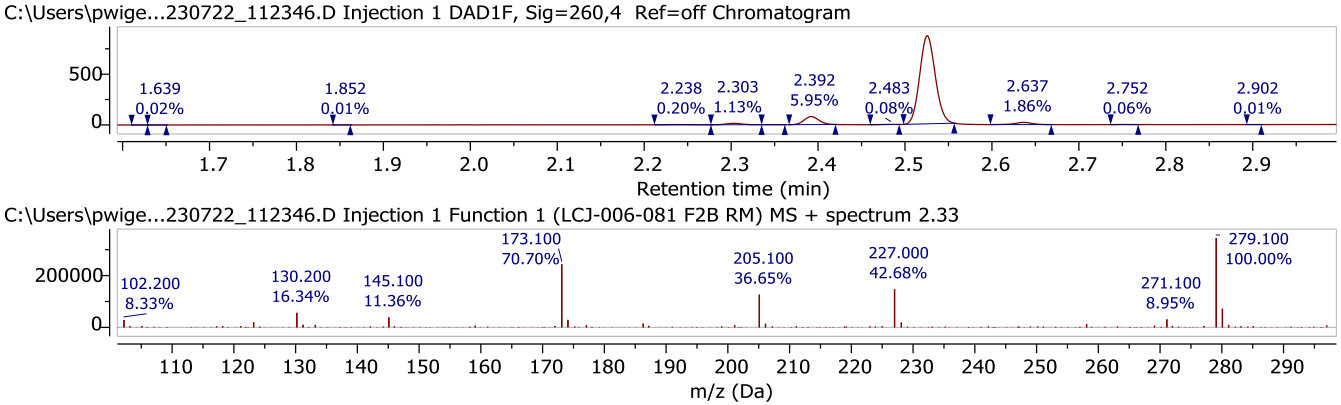
**b (zoom)**



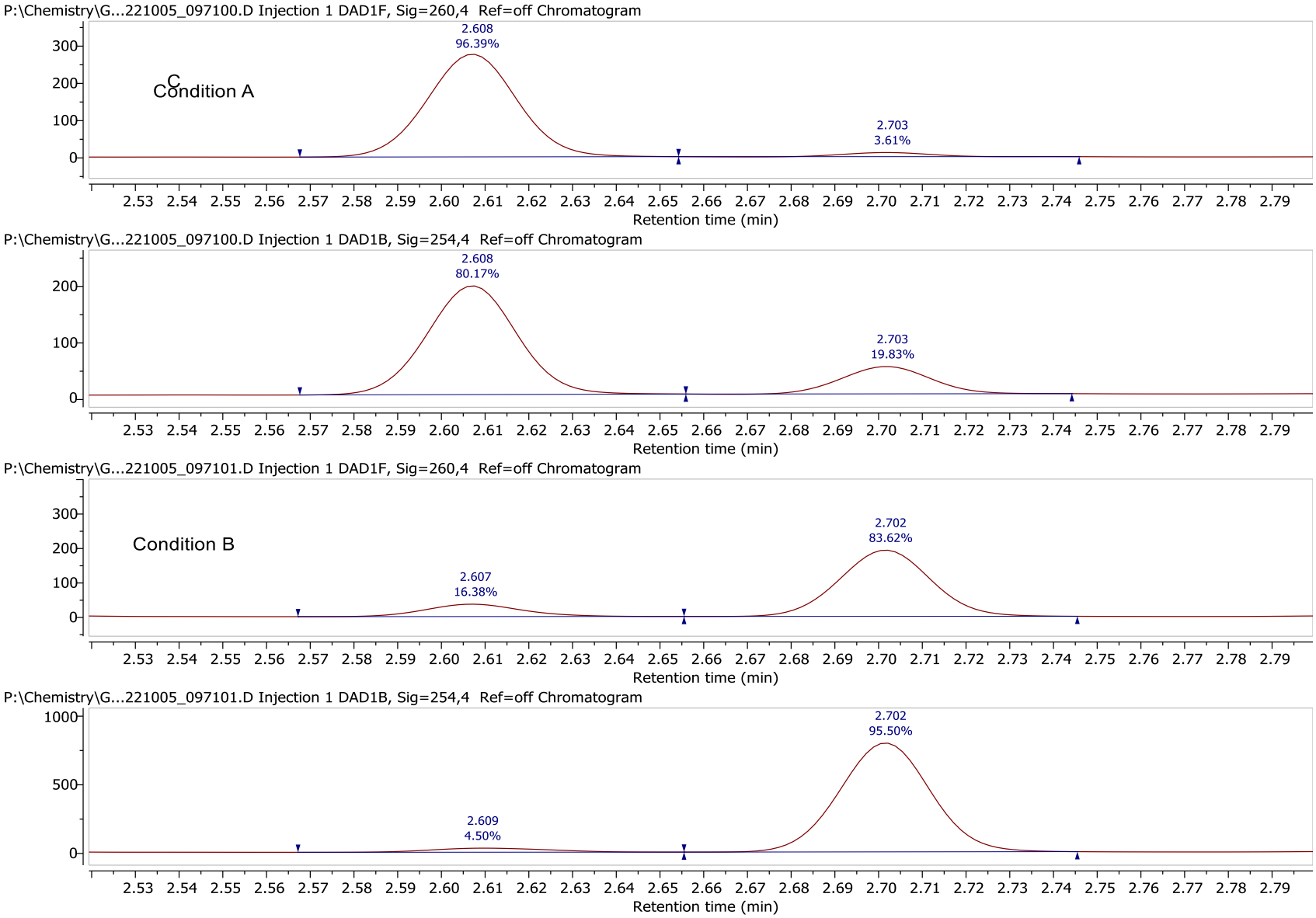

Condition A



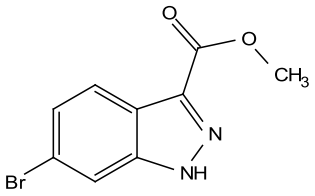

Condition B



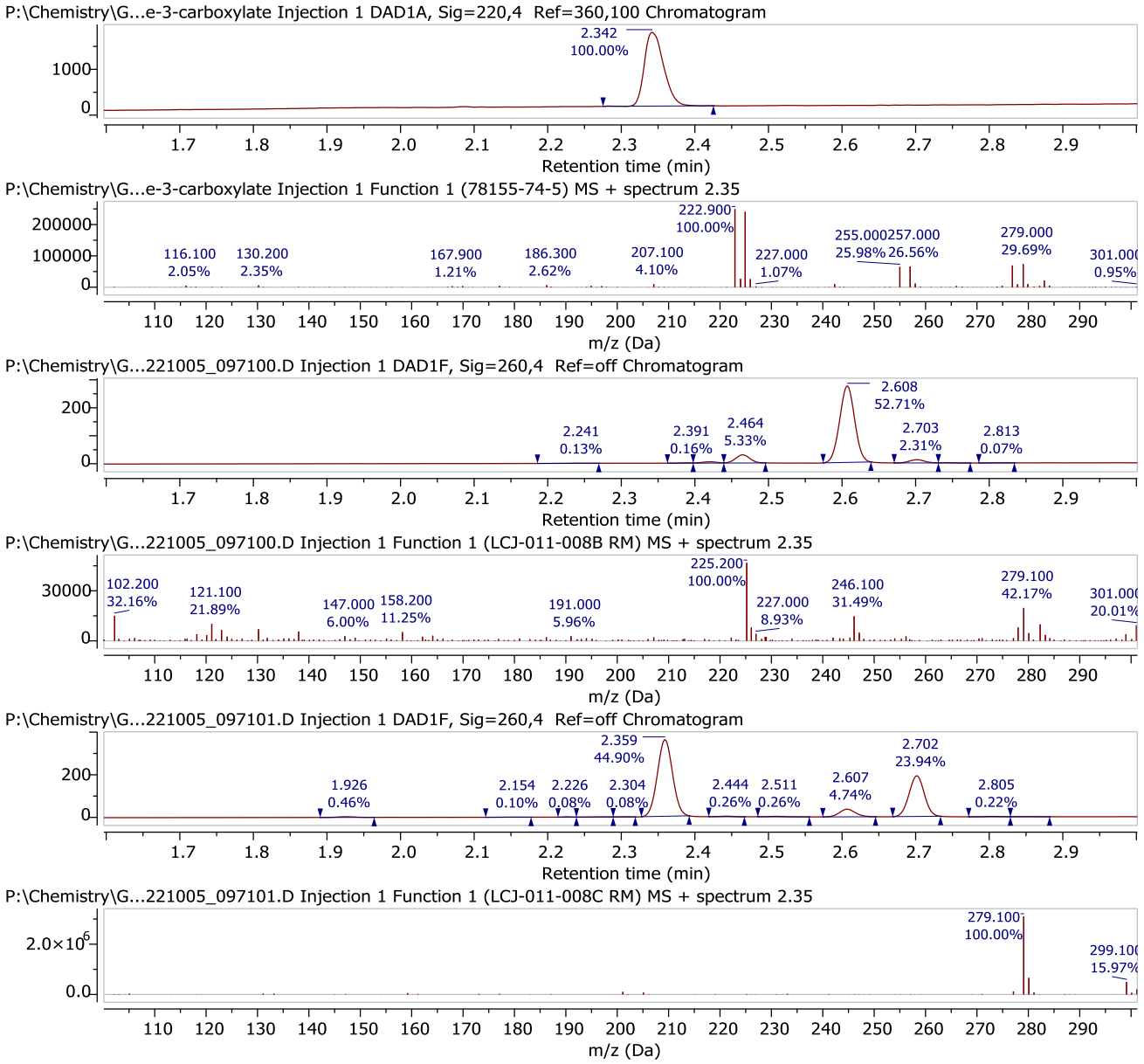

**b: R = Et, 6 versus reaction mixtures. Mass spectra for reaction mixtures at 2.344 minutes for each condition.**


P:\Chemistry\G...221005_097100.D Injection 1 DAD1F, Sig=260,4 Ref=off Chromatogram
2.608
96.39%
C
Condition A
2.703
3.61%
Retention time (min)
P:\Chemistry\G...221005_097100.D Injection 1 DAD1B, Sig=254,4 Ref=off Chromatogram
2.608
80.17%
2.703
19.83%
Retention time (min)
P:\Chemistry\G...221005_097101.D Injection 1 DAD1F, Sig=260,4 Ref=off Chromatogram
Condition B
2.702
83.62%
2.607
16.38%
Retention time (min)
P:\Chemistry\G...221005_097101.D Injection 1 DAD1B, Sig=254,4 Ref=off Chromatogram
2.702
95.50%
2.609
4.50%
Retention time (min)

**c**



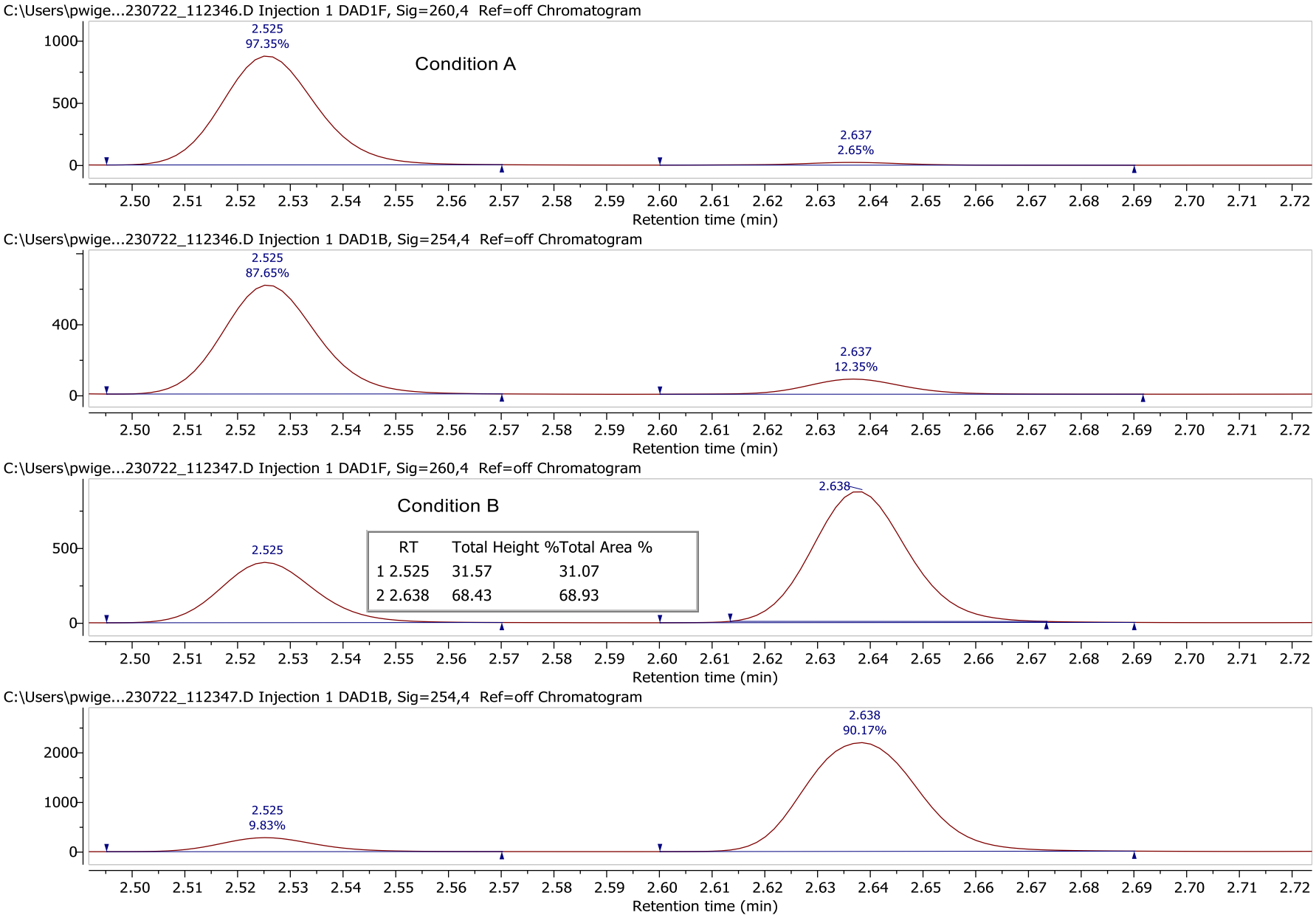

Condition A



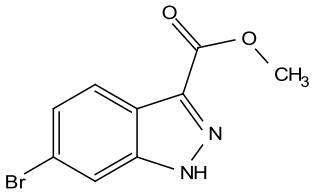

Condition B



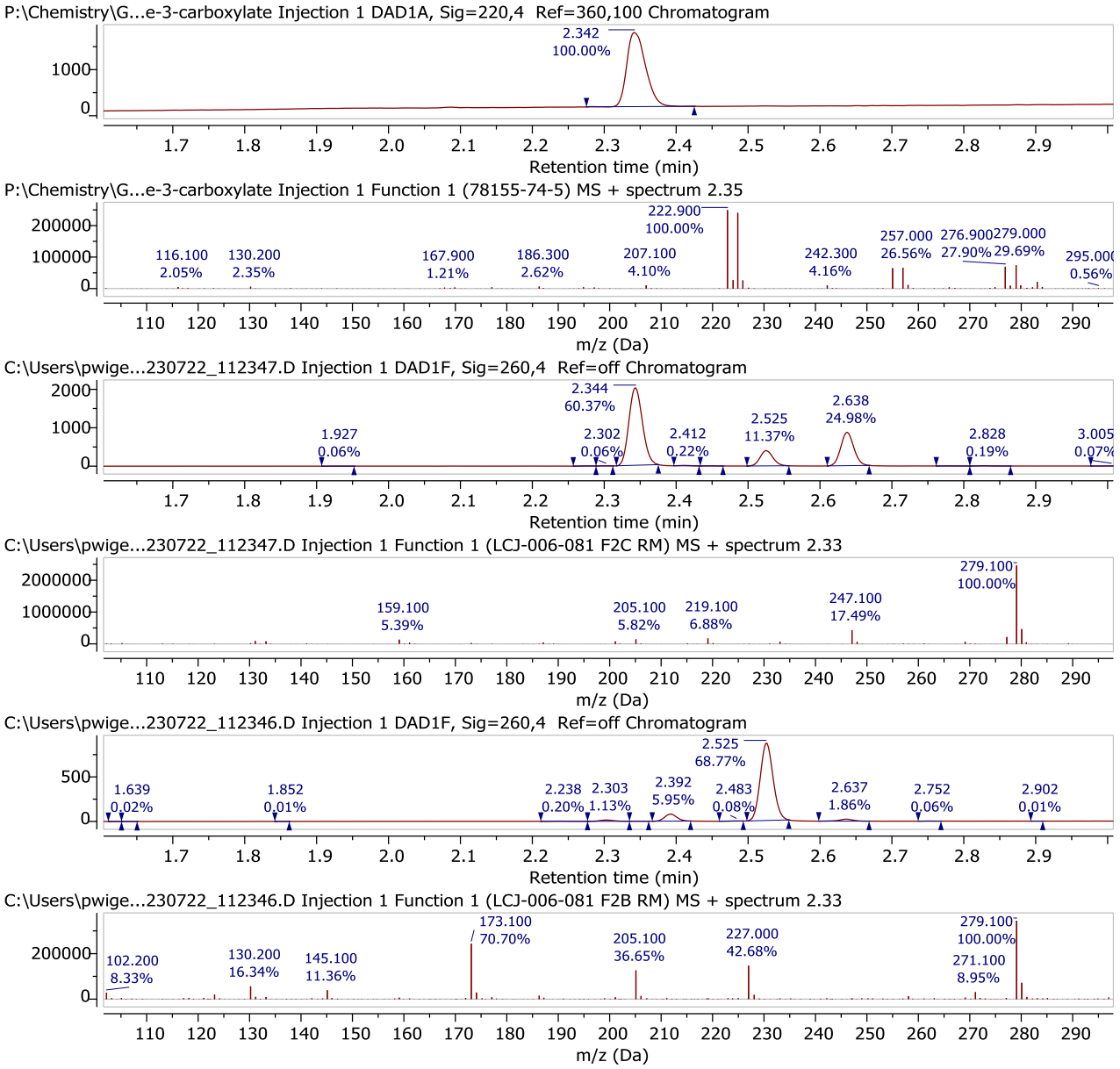

**c: R = iPr, 6 versus reaction mixtures. Mass spectra for reaction mixtures at 2.344 minutes for each condition.**


C:\Users\pwige...230722_112346.D Injection 1 DAD1F, Sig=260,4 Ref=off Chromatogram
2.525
97.35%
Condition A
2.637
2.65%
Retention time (min)
C:\Users\pwige...230722_112346.D Injection 1 DAD1B, Sig=254,4 Ref=off Chromatogram
2.525
87.65%
2.637
12.35%
Retention time (min)
C:\Users\pwige...230722_112347.D Injection 1 DAD1F, Sig=260,4 Ref=off Chromatogram
Condition B
2.638
2.525
RT Total Height % Total Area %
1 2.525 31.57 31.07
2 2.638 68.43 68.93
Retention time (min)
C:\Users\pwige...230722_112347.D Injection 1 DAD1B, Sig=254,4 Ref=off Chromatogram
2.638
90.17%
2.525
9.83%
Retention time (min)

**d**



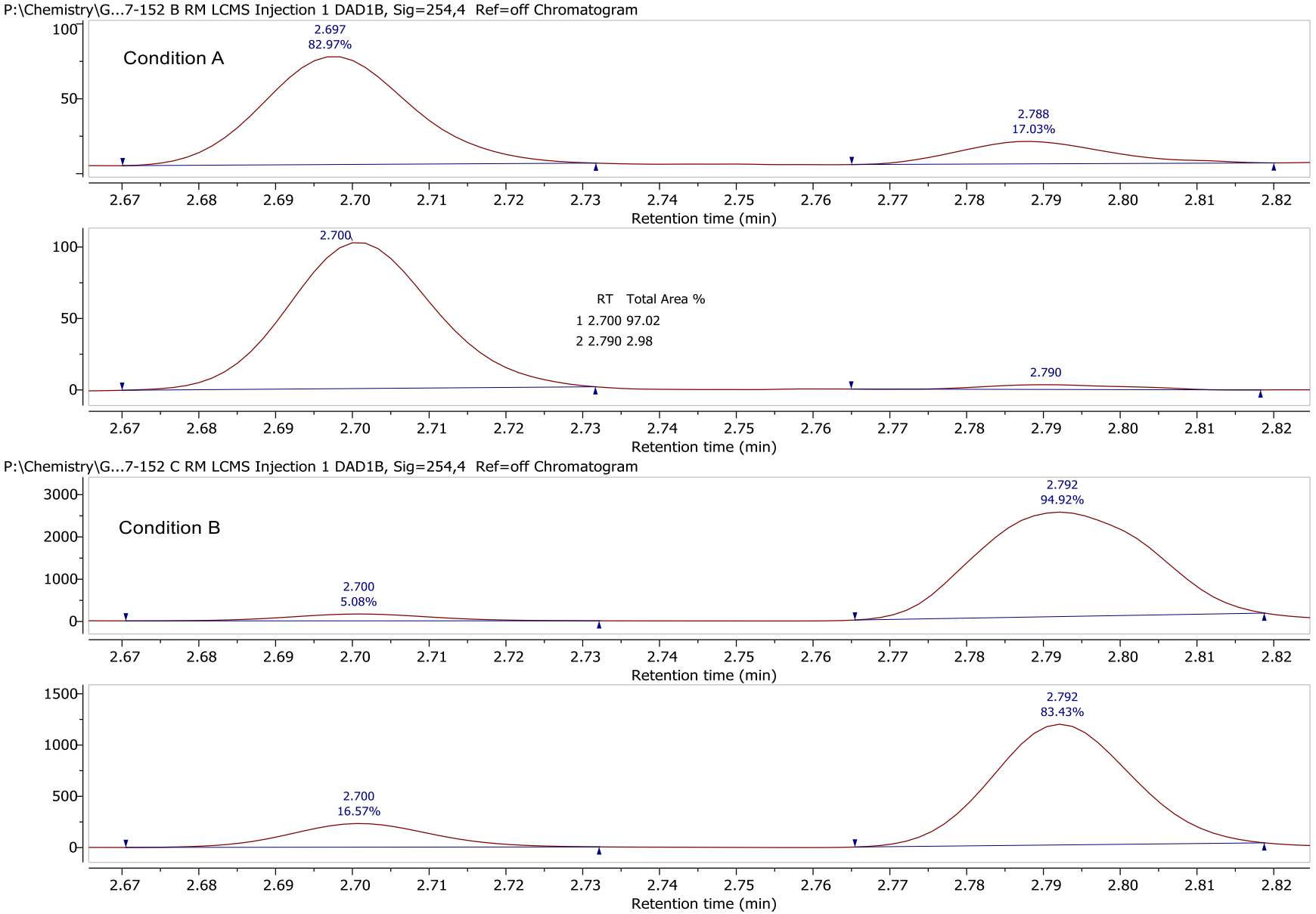

Condition A



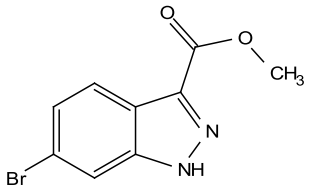

Condition B



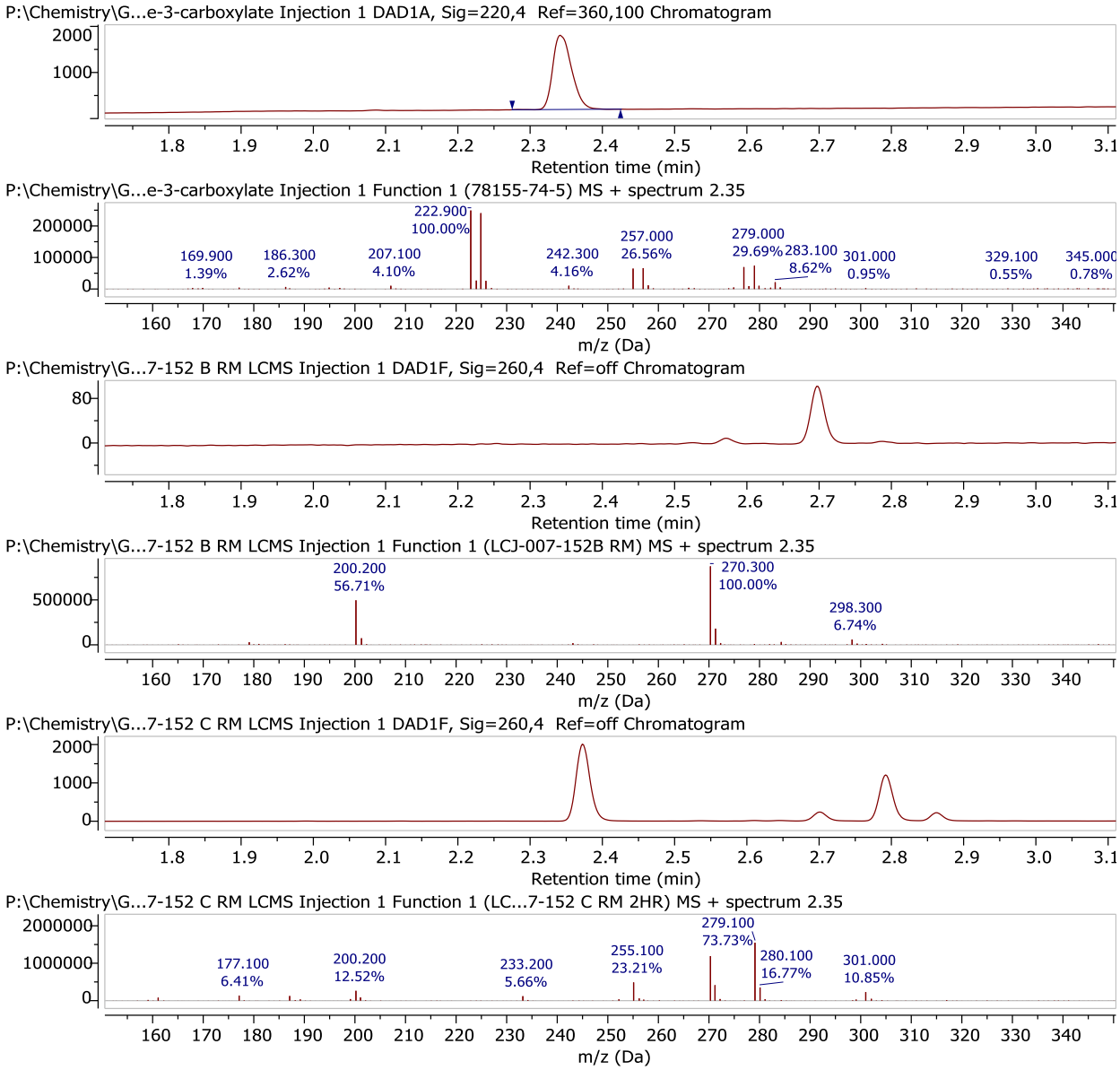

**d: R = Pr, 6 versus reaction mixtures. Mass spectra for reaction mixtures at 2.344 minutes for each condition.**


P:\Chemistry\G...7-152 B RM LCMS Injection 1 DAD1B, Sig=254,4 Ref=off Chromatogram
Condition A
2.697
82.97%
2.788
17.03%
Retention time (min)
2.700
RT Total Area %
1 2.700 97.02
2 2.790 2.98
2.790
Retention time (min)
P:\Chemistry\G...7-152 C RM LCMS Injection 1 DAD1B, Sig=254,4 Ref=off Chromatogram
Condition B
2.792
94.92%
2.700
5.08%
Retention time (min)
2.792
83.43%
2.700
16.57%
Retention time (min)

**e**



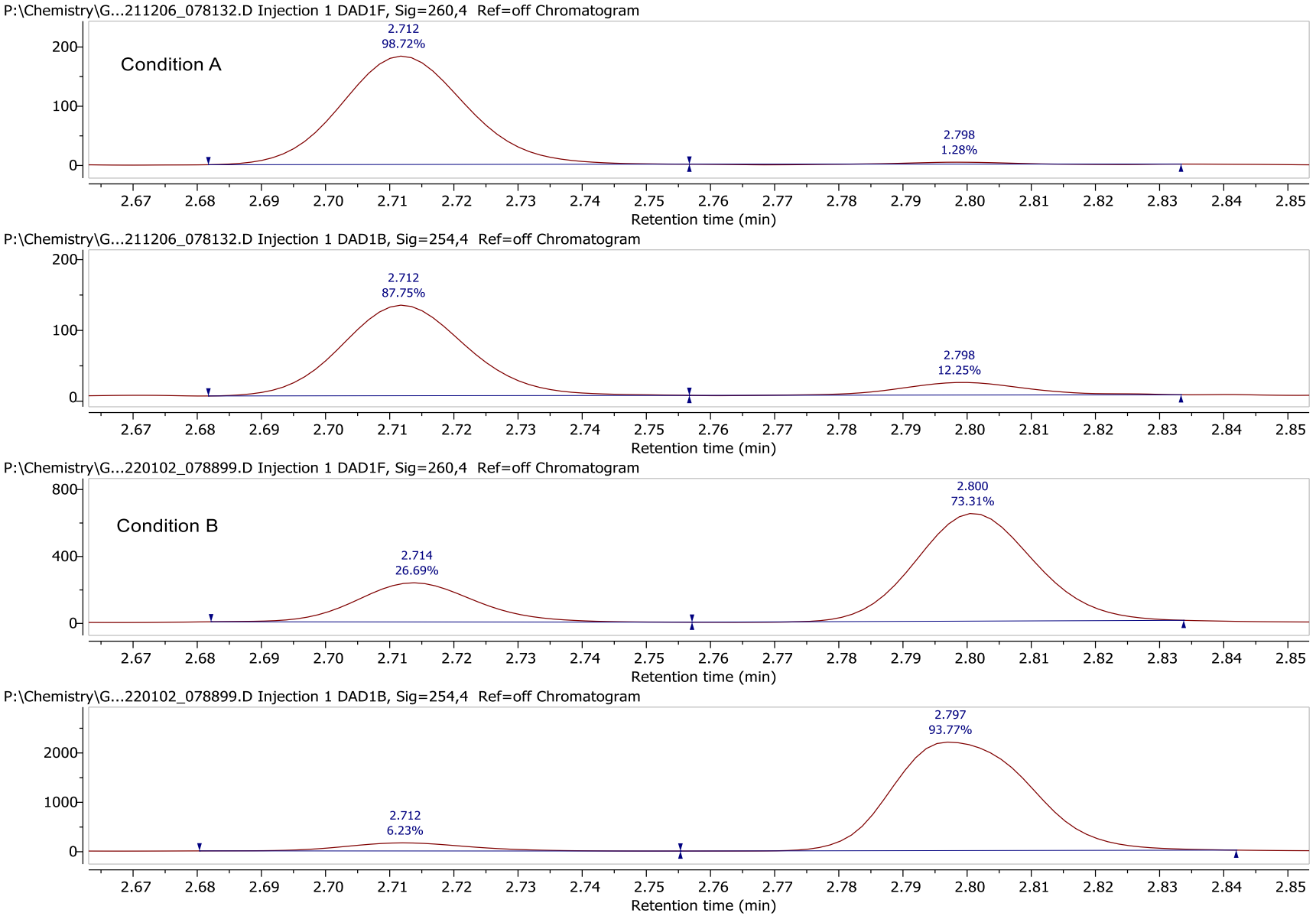

Condition A



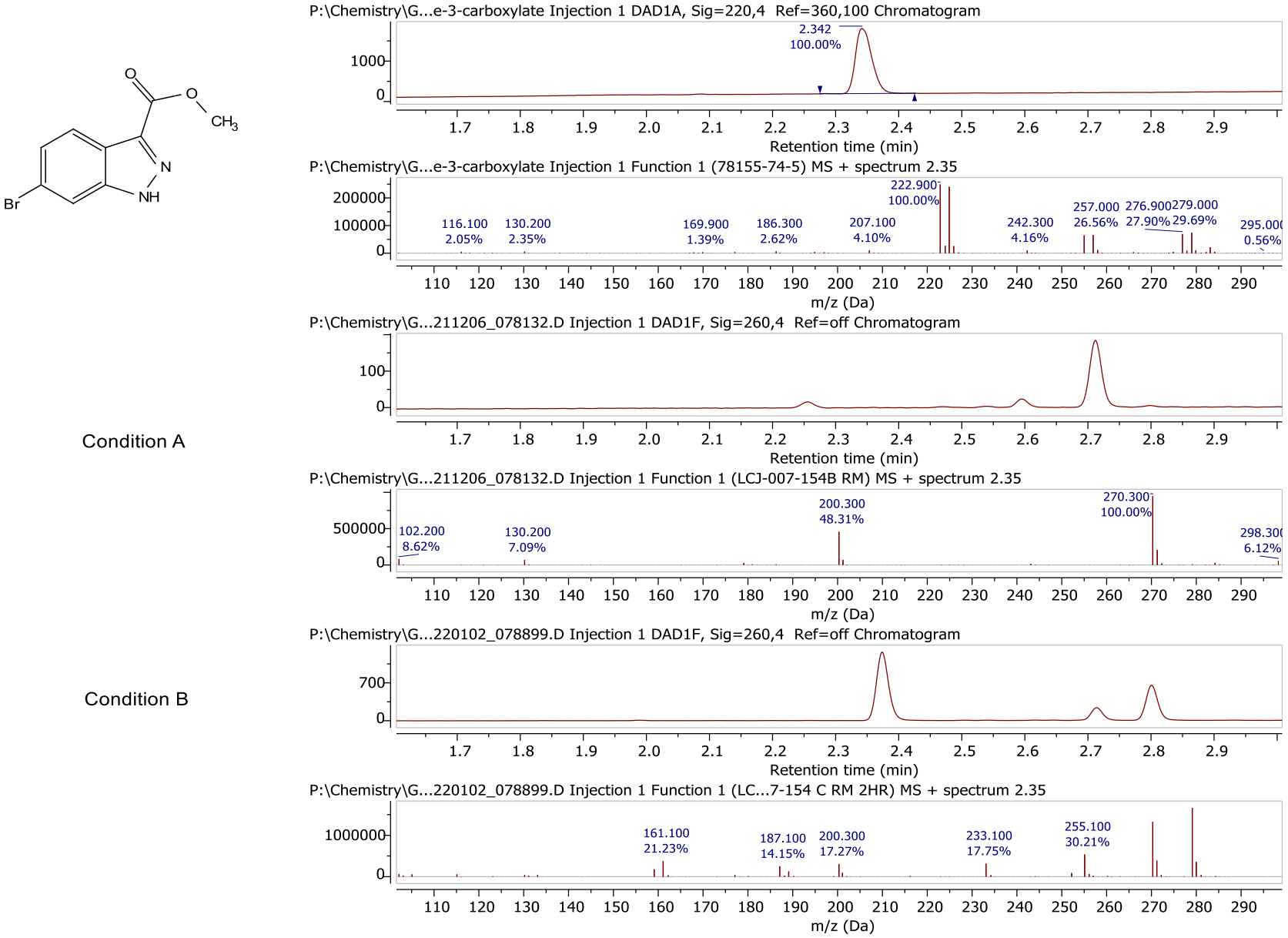

Condition B



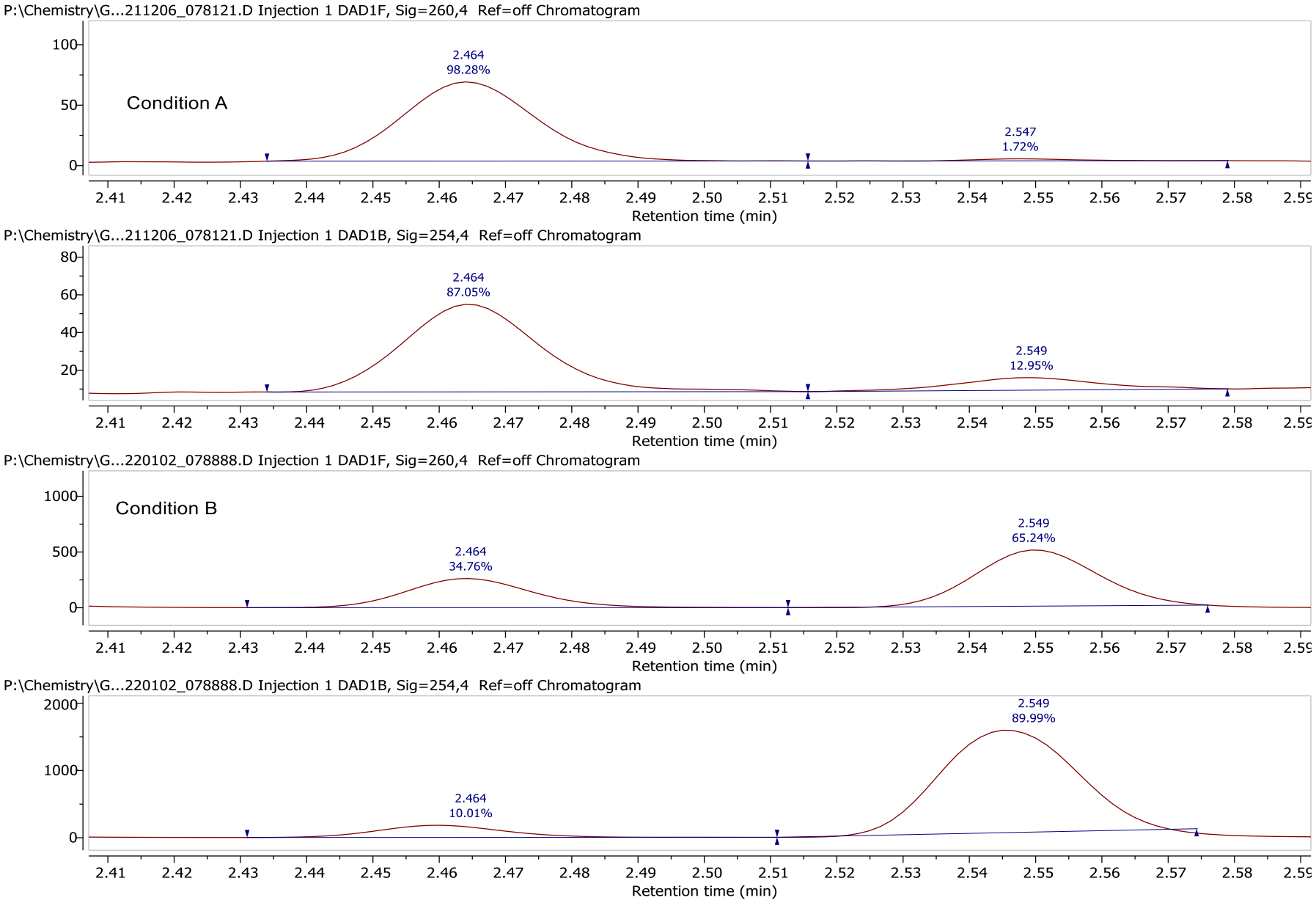

**e: R = (R)- *sec*-butyl, 6 versus reaction mixtures. Mass spectra for reaction mixtures at 2.35 minutes for each condition**


P:\Chemistry\G...211206_078132.D Injection 1 DAD1F, Sig=260,4 Ref=off Chromatogram
Condition A
2.712
98.72%
2.798
1.28%
Retention time (min)
P:\Chemistry\G...211206_078132.D Injection 1 DAD1B, Sig=254,4 Ref=off Chromatogram
2.712
87.75%
2.798
12.25%
Retention time (min)
P:\Chemistry\G...220102_078899.D Injection 1 DAD1F, Sig=260,4 Ref=off Chromatogram
Condition B
2.714
26.69%
2.800
73.31%
Retention time (min)
P:\Chemistry\G...220102_078899.D Injection 1 DAD1B, Sig=254,4 Ref=off Chromatogram
2.712
6.23%
2.797
93.77%
Retention time (min)

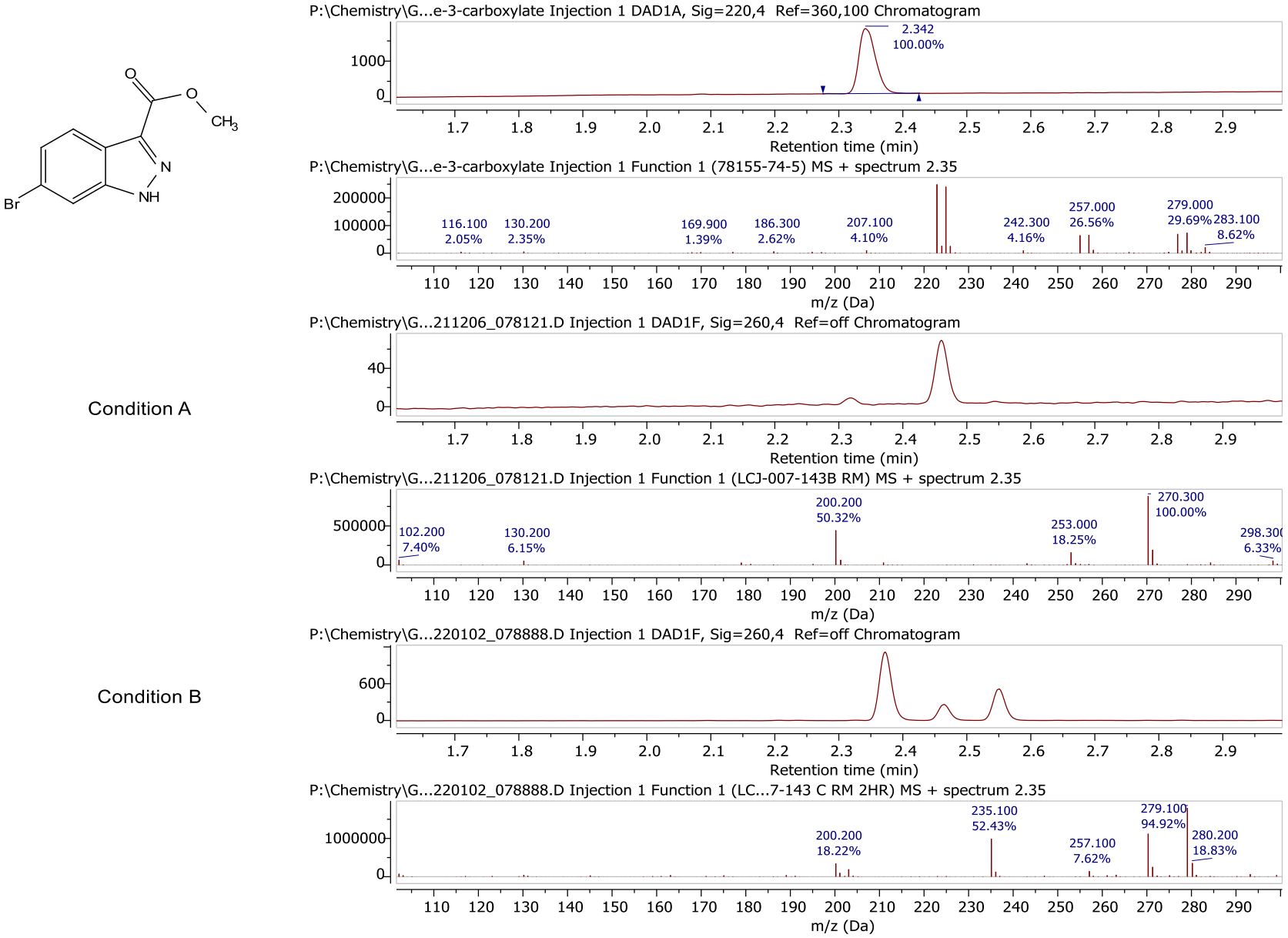
**f**



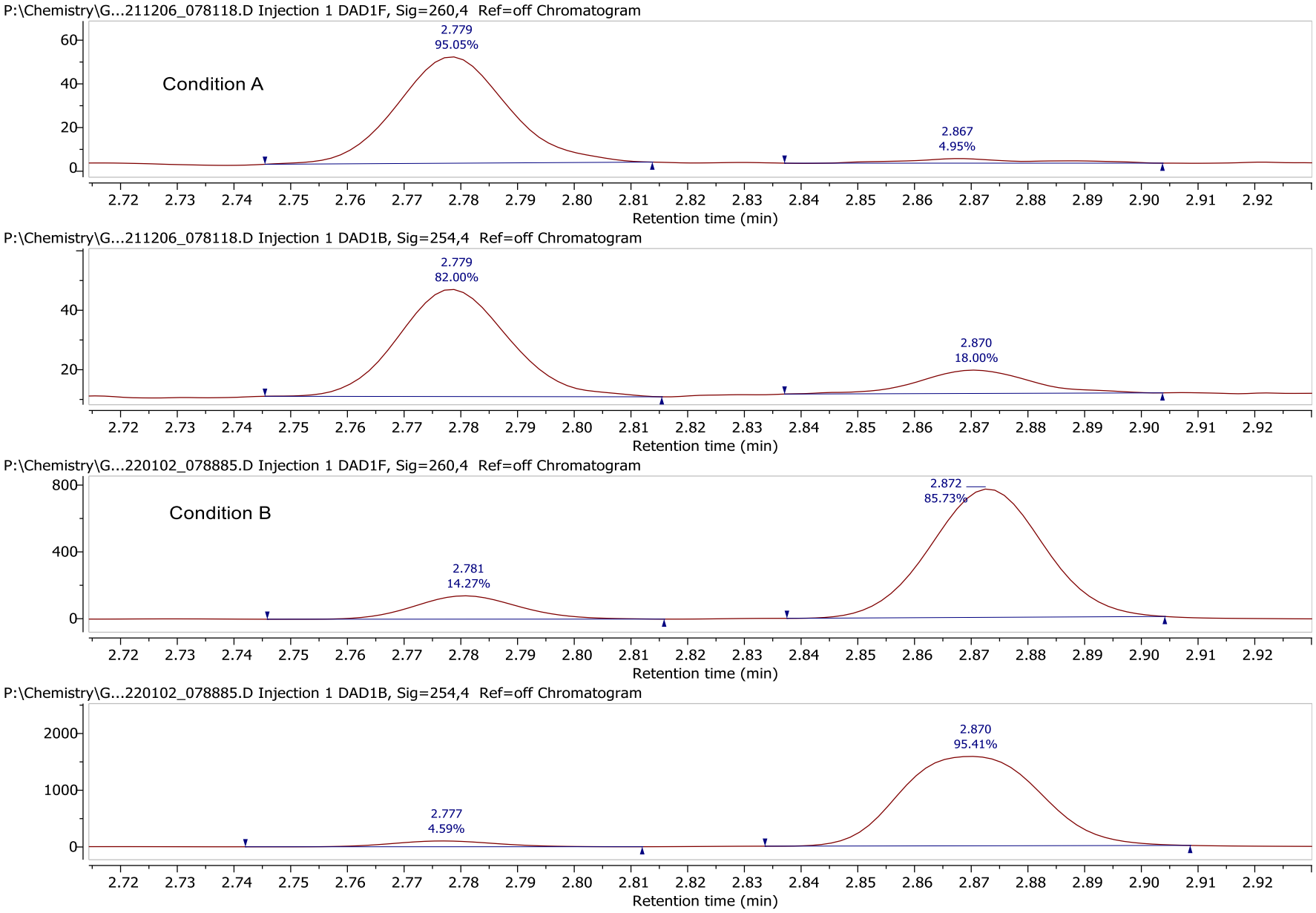

**f: R = iBu, 6 versus reaction mixtures. Mass spectra for reaction mixtures at 2.35 minutes for each condition.**


P:\Chemistry\G...211206_078121.D Injection 1 DAD1F, Sig=260,4 Ref=off Chromatogram
Condition A
2.464
98.28%
2.547
1.72%
Retention time (min)
P:\Chemistry\G...211206_078121.D Injection 1 DAD1B, Sig=254,4 Ref=off Chromatogram
2.464
87.05%
2.549
12.95%
Retention time (min)
P:\Chemistry\G...220102_078888.D Injection 1 DAD1F, Sig=260,4 Ref=off Chromatogram
Condition B
2.464
34.76%
2.549
65.24%
Retention time (min)
P:\Chemistry\G...220102_078888.D Injection 1 DAD1B, Sig=254,4 Ref=off Chromatogram
2.464
10.01%
2.549
89.99%
Retention time (min)

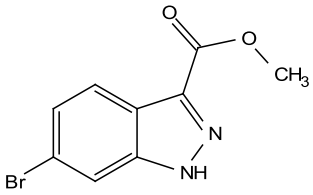
**g**



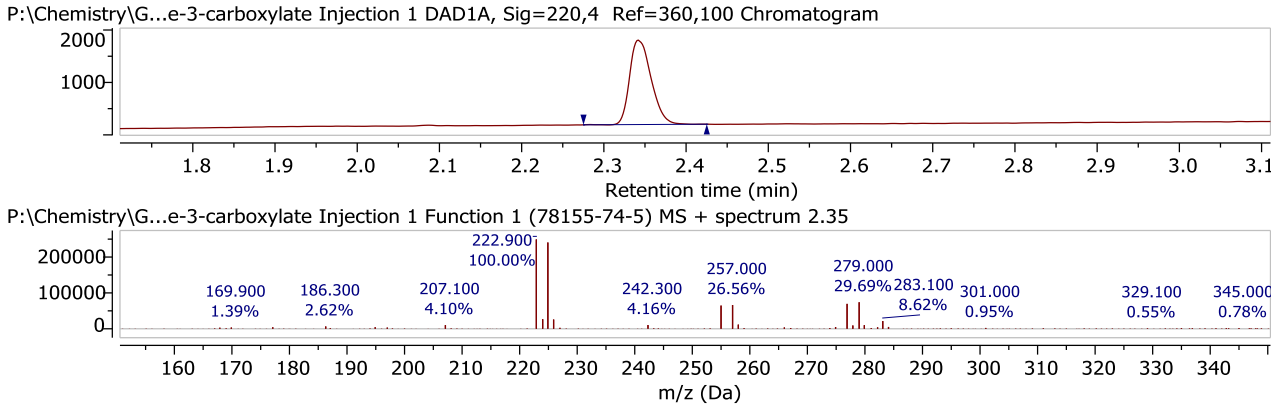

**g: R = 2-OMeEt, 6 versus reaction mixtures. Mass spectra for reaction mixtures at 2.35 minutes for each condition.**


P:\Chemistry\G...211206_078118.D Injection 1 DAD1F, Sig=260,4 Ref=off Chromatogram
Condition A
2.779
95.05%
2.867
4.95%
Retention time (min)
P:\Chemistry\G...211206_078118.D Injection 1 DAD1B, Sig=254,4 Ref=off Chromatogram
2.779
82.00%
2.870
18.00%
Retention time (min)
P:\Chemistry\G...220102_078885.D Injection 1 DAD1F, Sig=260,4 Ref=off Chromatogram
Condition B
2.872
85.73%
2.781
14.27%
Retention time (min)
P:\Chemistry\G...220102_078885.D Injection 1 DAD1B, Sig=254,4 Ref=off Chromatogram
2.870
95.41%
2.777
4.59%
Retention time (min)

**h**

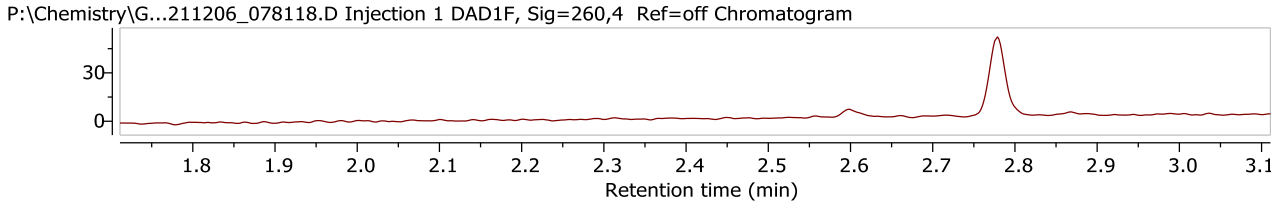


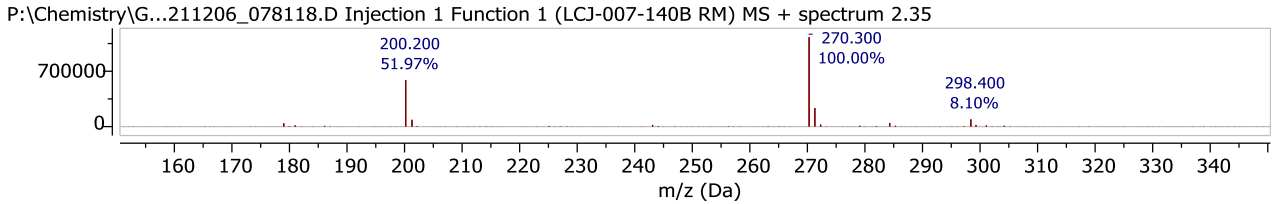

Condition A



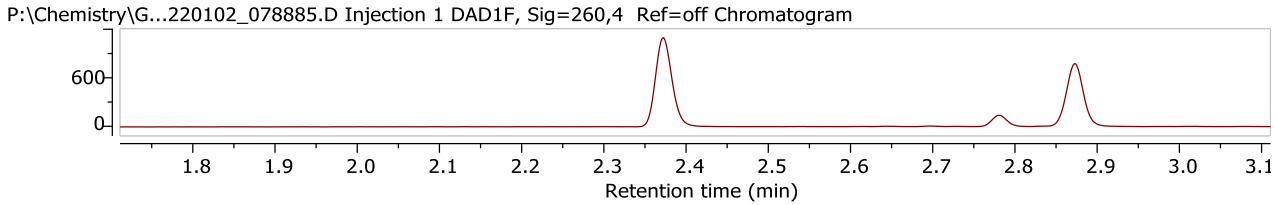


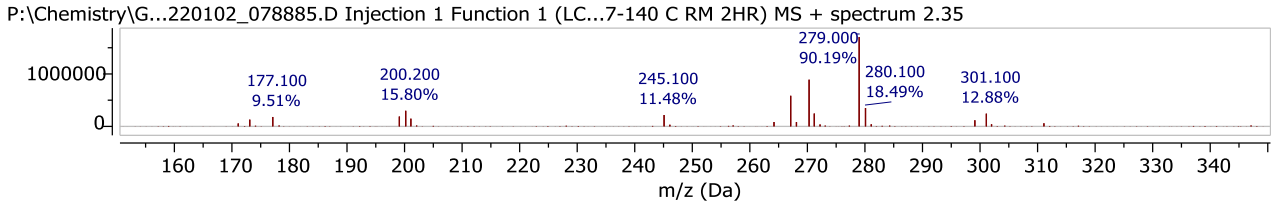




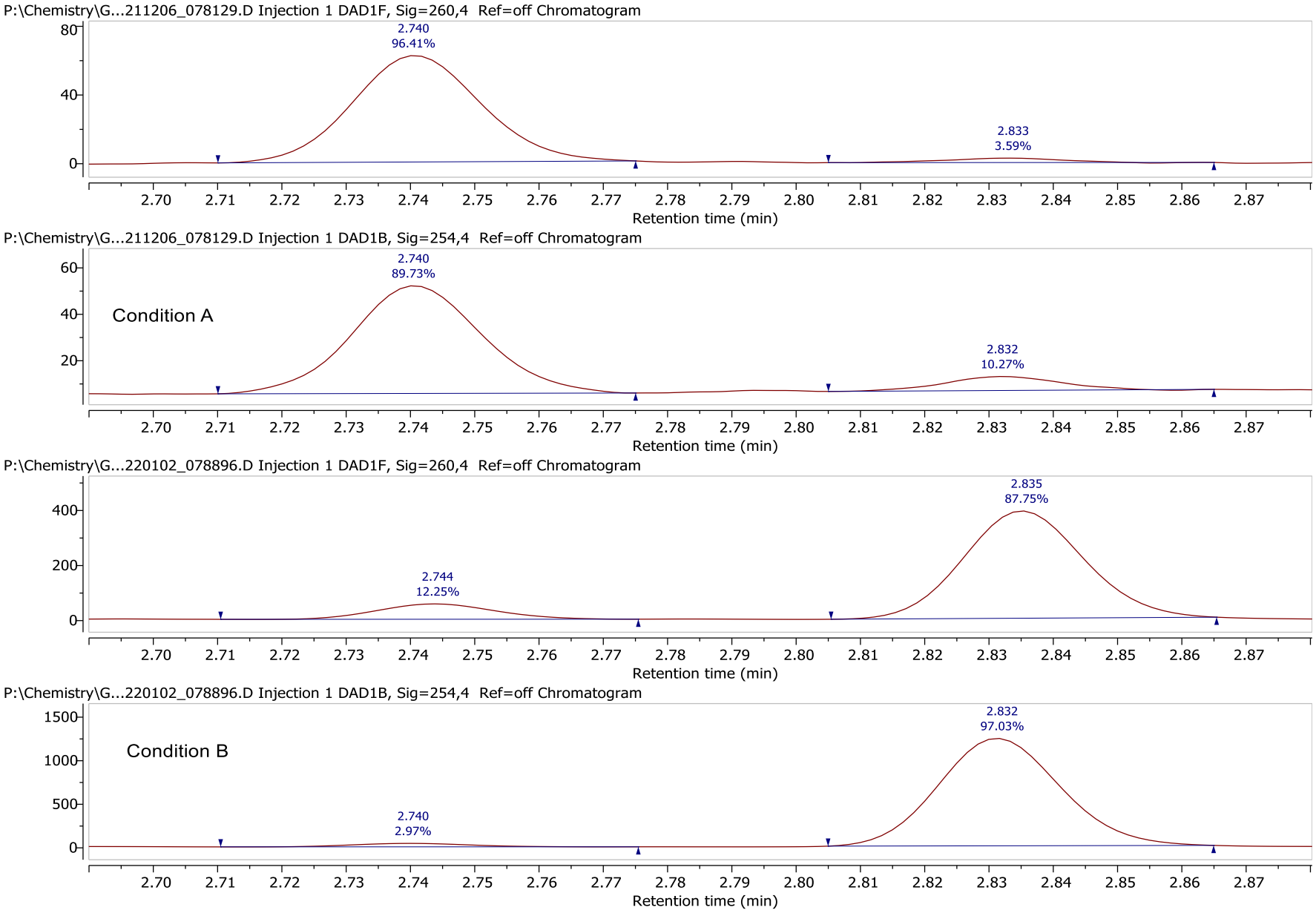




Condition B

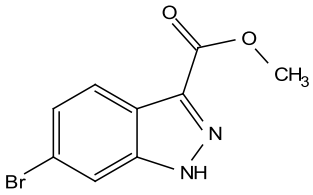


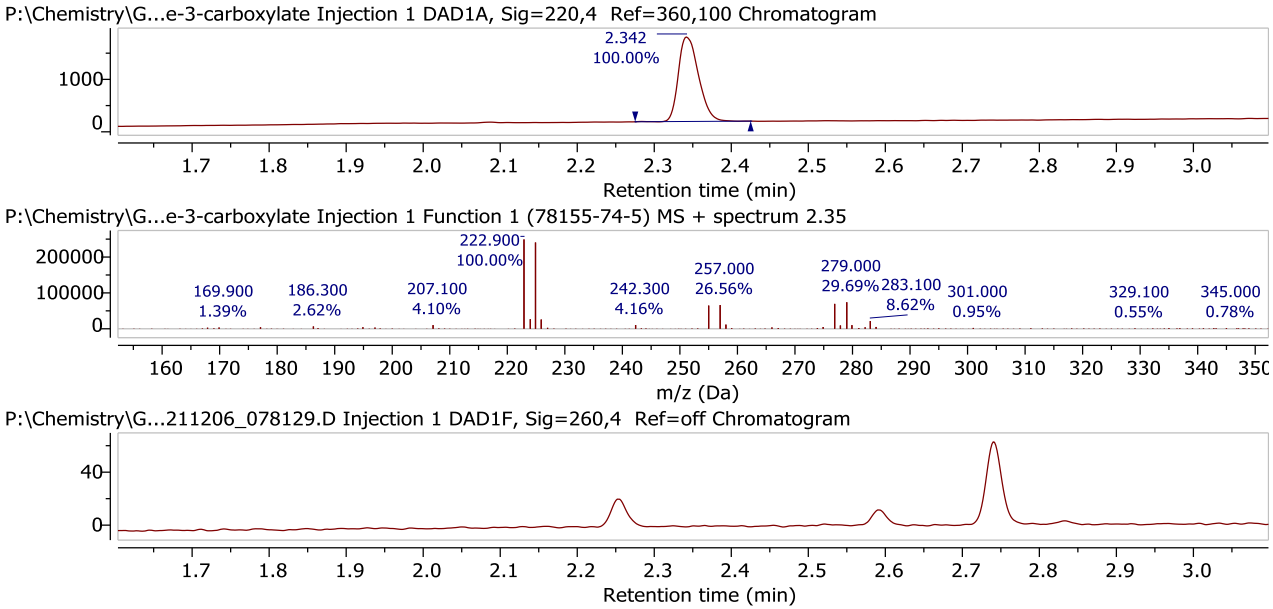

**h: R = cC5H9, 6 versus reaction mixtures. Mass spectra for reaction mixtures at 2.35 minutes for each condition.**


P:\Chemistry\G...211206_078129.D Injection 1 DAD1F, Sig=260,4 Ref=off Chromatogram
2.740
96.41%
2.833
3.59%
Retention time (min)
P:\Chemistry\G...211206_078129.D Injection 1 DAD1B, Sig=254,4 Ref=off Chromatogram
Condition A
2.740
89.73%
2.832
10.27%
Retention time (min)
P:\Chemistry\G...220102_078896.D Injection 1 DAD1F, Sig=260,4 Ref=off Chromatogram
2.744
12.25%
2.835
87.75%
Retention time (min)
P:\Chemistry\G...220102_078896.D Injection 1 DAD1B, Sig=254,4 Ref=off Chromatogram
Condition B
2.740
2.97%
2.832
97.03%
Retention time (min)

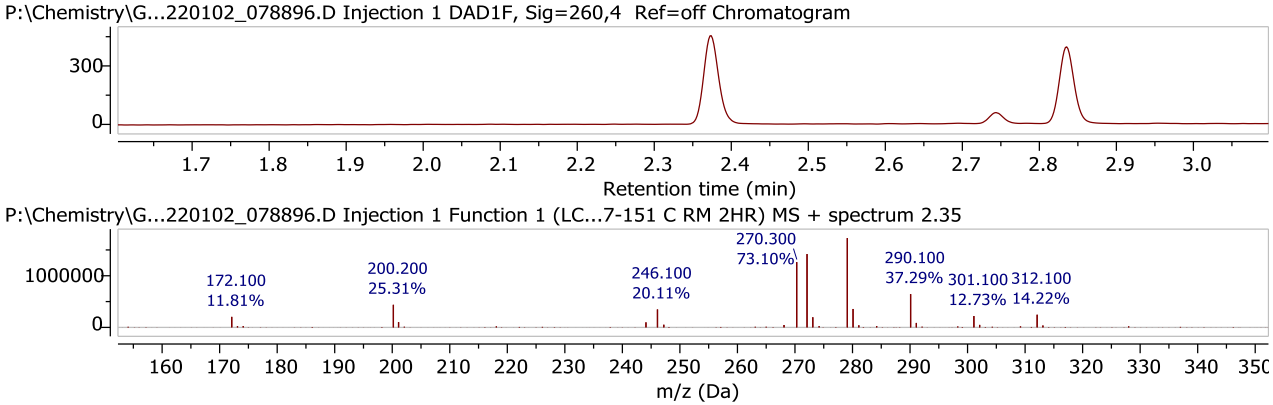
**i**



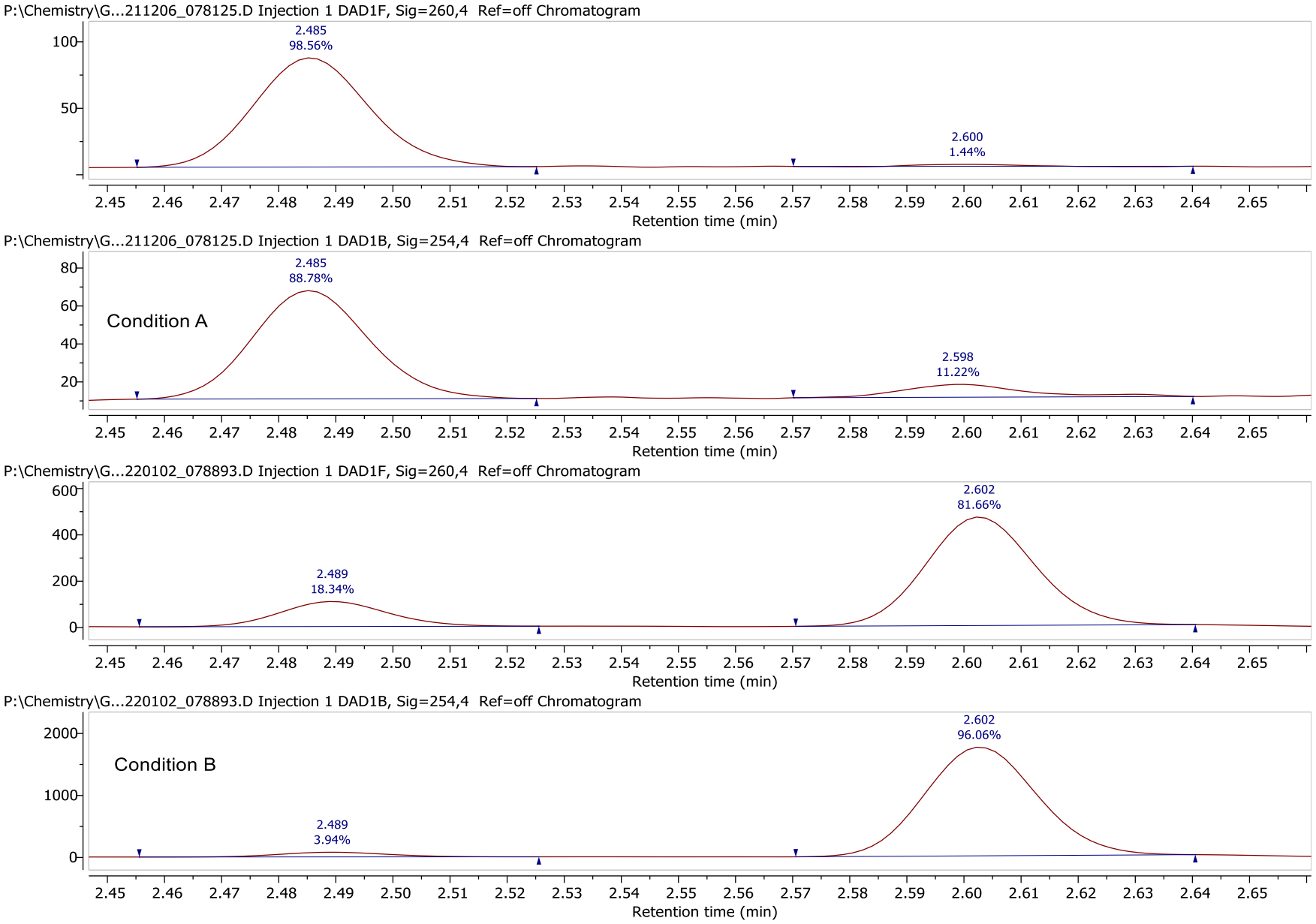

Condition A



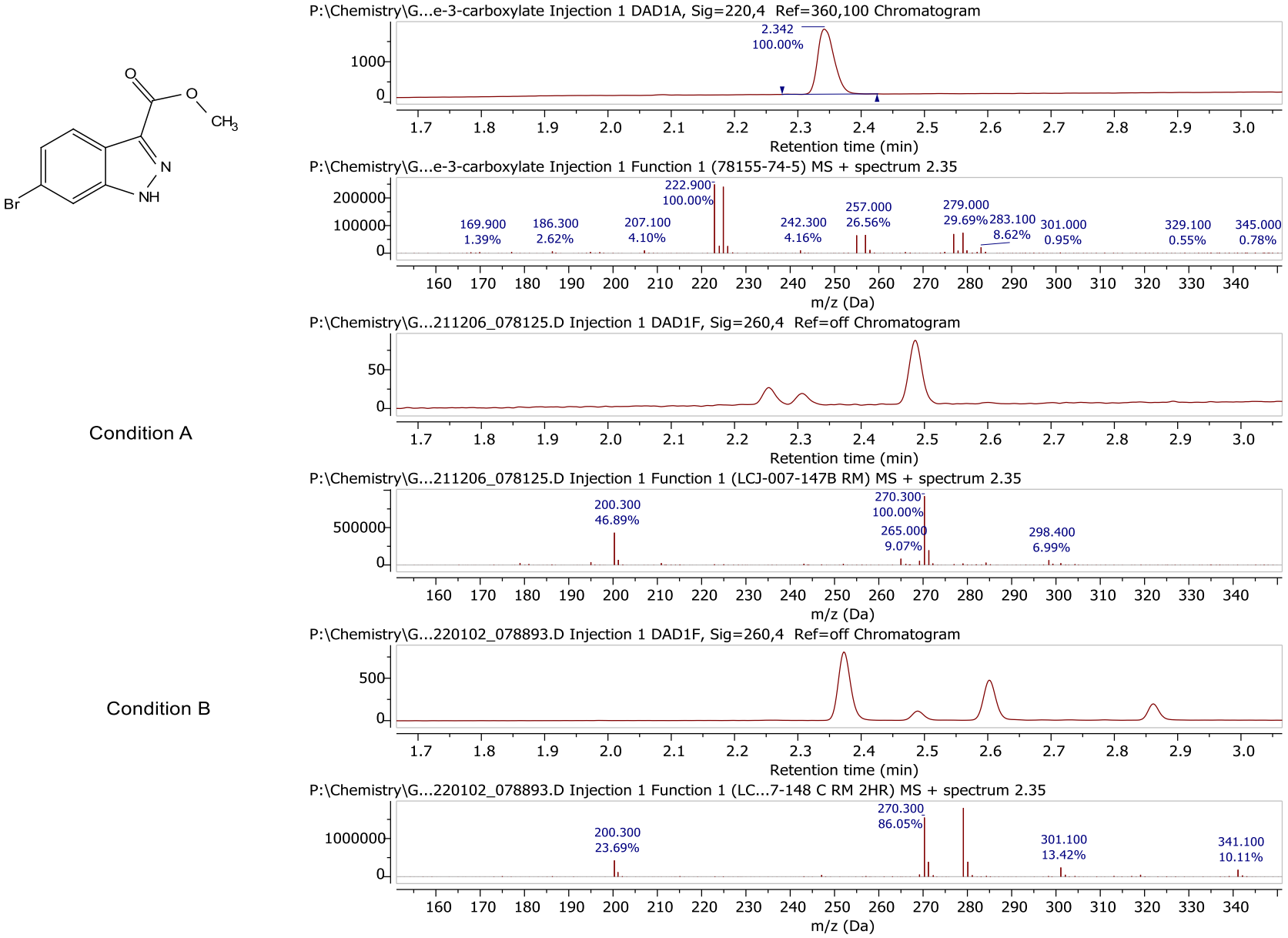

Condition B



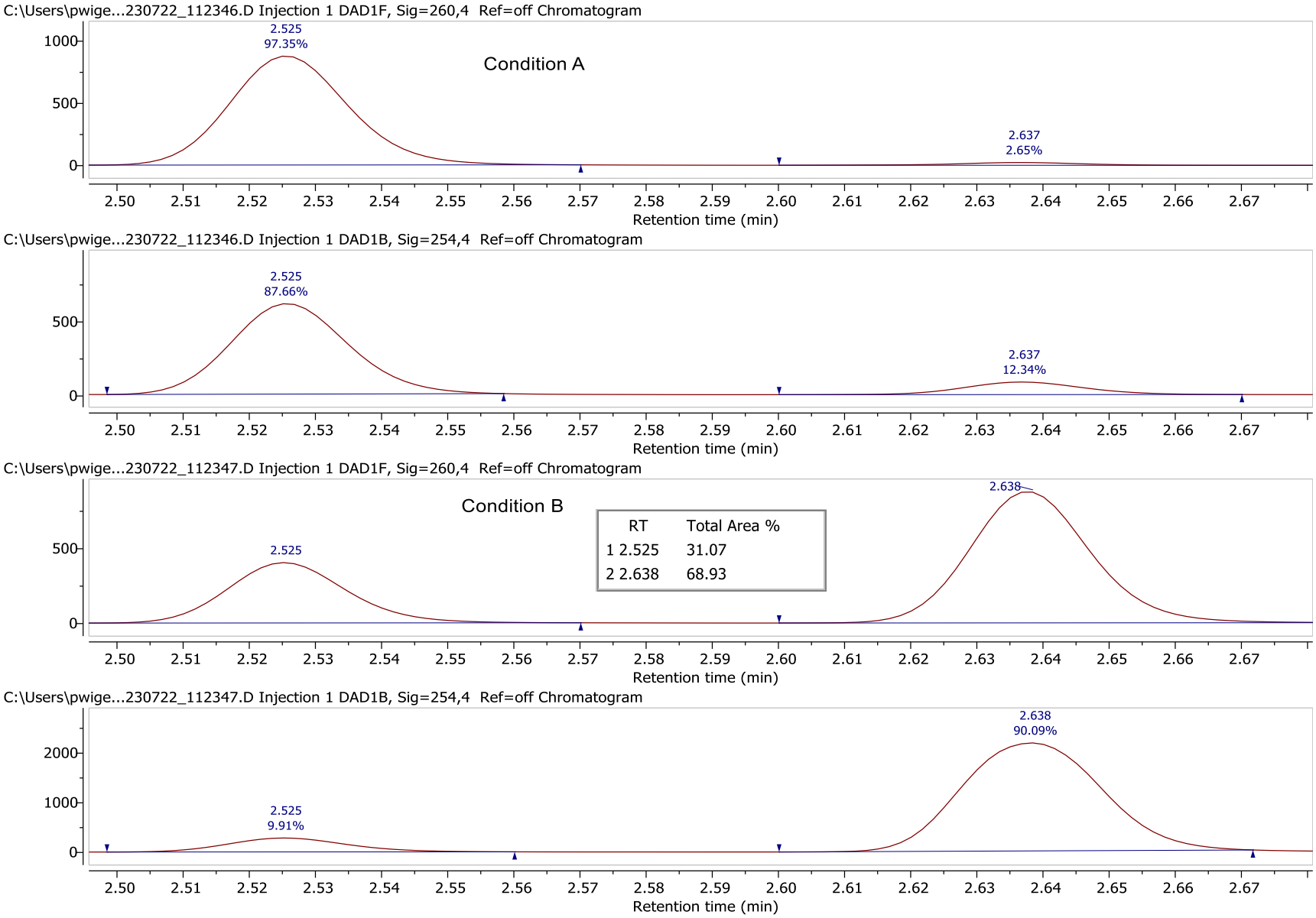

**i: R = *N*-Boc-3-pyrrolidine, 6 versus reaction mixtures. Mass spectra for reaction mixtures at 2.35 minutes for each condition.**


P:\Chemistry\G...211206_078125.D Injection 1 DAD1F, Sig=260,4 Ref=off Chromatogram
2.485
98.56%
2.600
1.44%
Retention time (min)
P:\Chemistry\G...211206_078125.D Injection 1 DAD1B, Sig=254,4 Ref=off Chromatogram
Condition A
2.485
88.78%
2.598
11.22%
Retention time (min)
P:\Chemistry\G...220102_078893.D Injection 1 DAD1F, Sig=260,4 Ref=off Chromatogram
2.489
18.34%
2.602
81.66%
Retention time (min)
P:\Chemistry\G...220102_078893.D Injection 1 DAD1B, Sig=254,4 Ref=off Chromatogram
Condition B
2.489
3.94%
2.602
96.06%
Retention time (min)

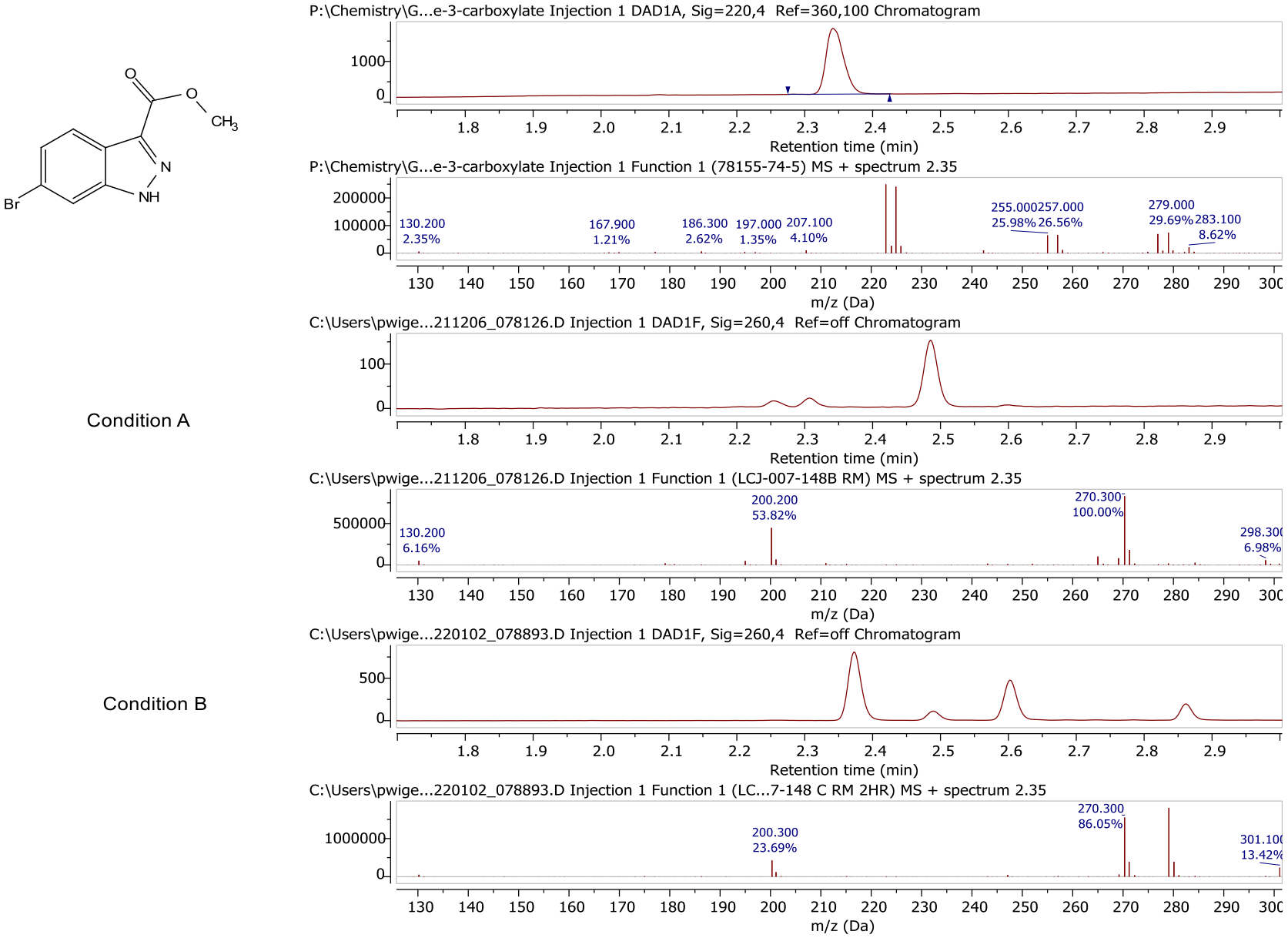
**j**



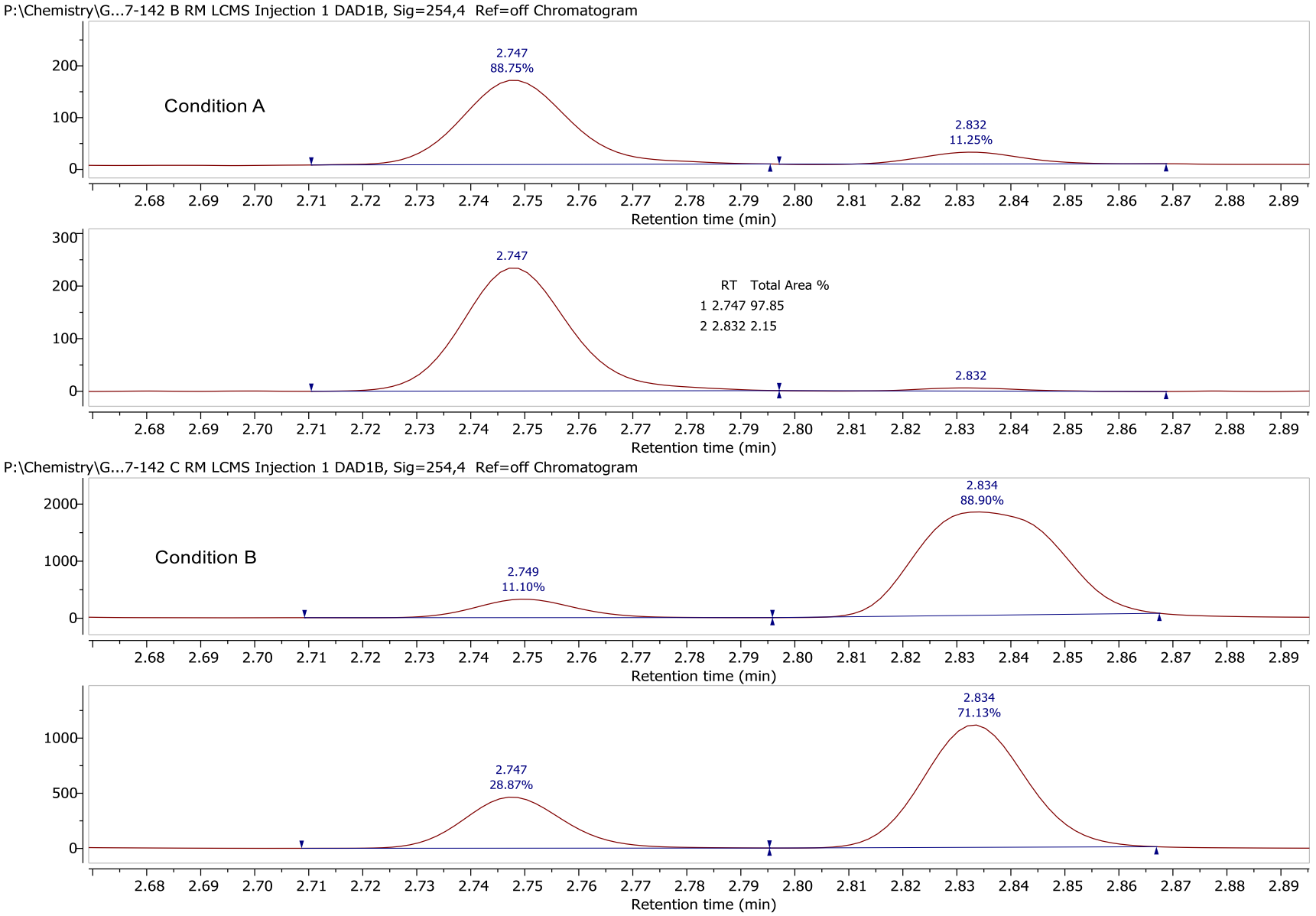

**j: R = (*S*)-3-THF, 6 versus reaction mixtures. Mass spectra for reaction mixtures at 2.35 minutes for each condition.**


C:\Users\pwige...230722_112346.D Injection 1 DAD1F, Sig=260,4 Ref=off Chromatogram
2.525
97.35%
Condition A
2.637
2.65%
Retention time (min)
C:\Users\pwige...230722_112346.D Injection 1 DAD1B, Sig=254,4 Ref=off Chromatogram
2.525
87.66%
2.637
12.34%
Retention time (min)
C:\Users\pwige...230722_112347.D Injection 1 DAD1F, Sig=260,4 Ref=off Chromatogram
Condition B
RT Total Area %
1 2.525 31.07
2 2.638 68.93
2.525
2.638
Retention time (min)
C:\Users\pwige...230722_112347.D Injection 1 DAD1B, Sig=254,4 Ref=off Chromatogram
2.525
9.91%
2.638
90.09%
Retention time (min)

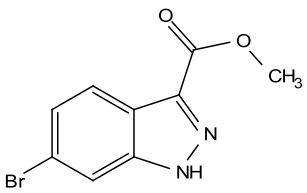
**k**



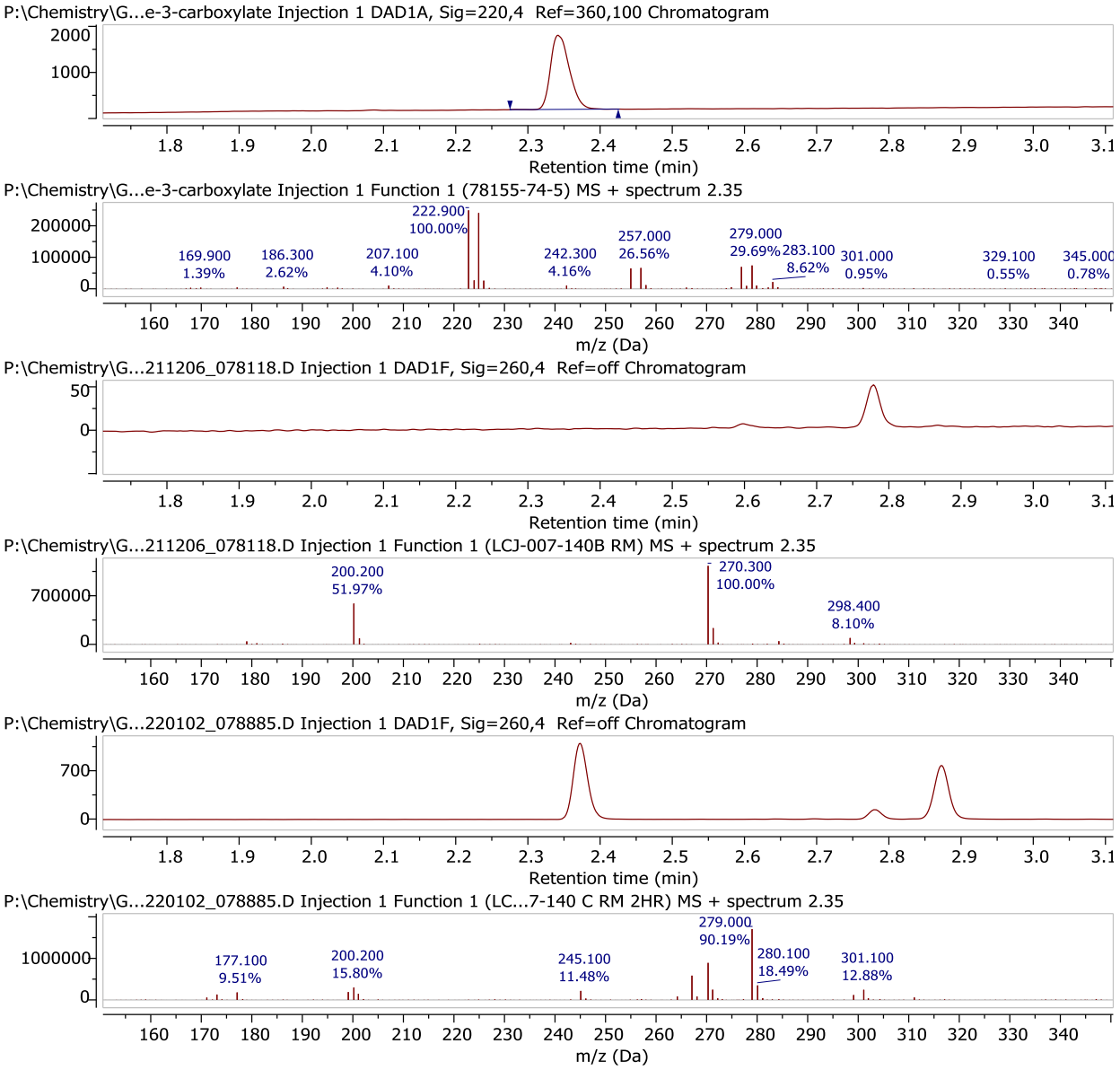

**k: R = (*R*)-3-THF, 6 versus reaction mixtures. Mass spectra for reaction mixtures at 2.35 minutes for each condition.**


P:\Chemistry\G...7-142 B RM LCMS Injection 1 DAD1B, Sig=254,4 Ref=off Chromatogram
Condition A
2.747
88.75%
2.832
11.25%
Retention time (min)
2.747
RT Total Area %
1 2.747 97.85
2 2.832 2.15
2.832
Retention time (min)
P:\Chemistry\G...7-142 C RM LCMS Injection 1 DAD1B, Sig=254,4 Ref=off Chromatogram
Condition B
2.834
88.90%
2.749
11.10%
Retention time (min)
2.834
71.13%
2.747
28.87%
Retention time (min)

I

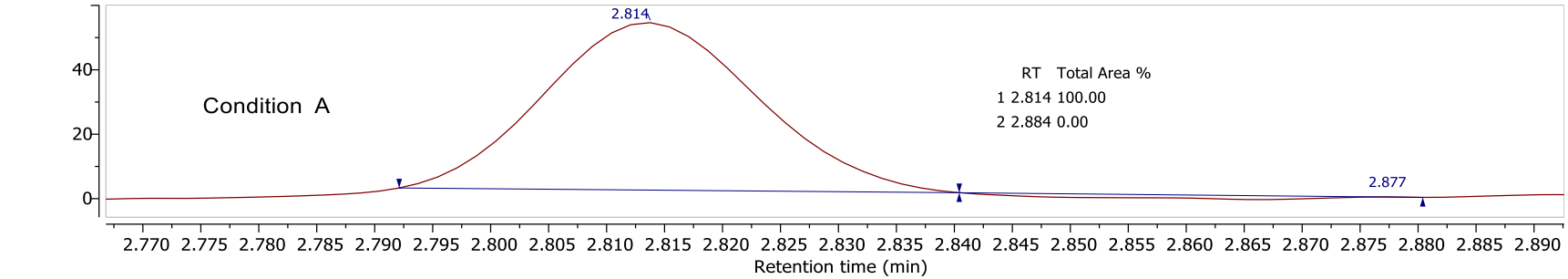



Condition A

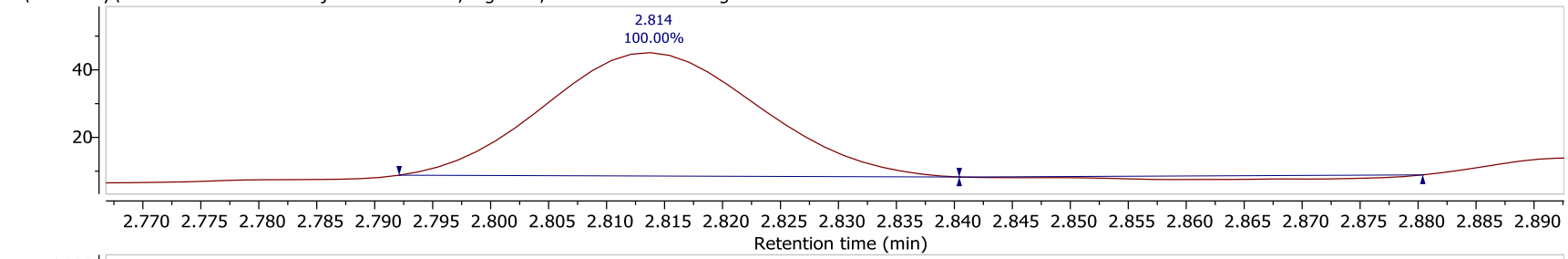


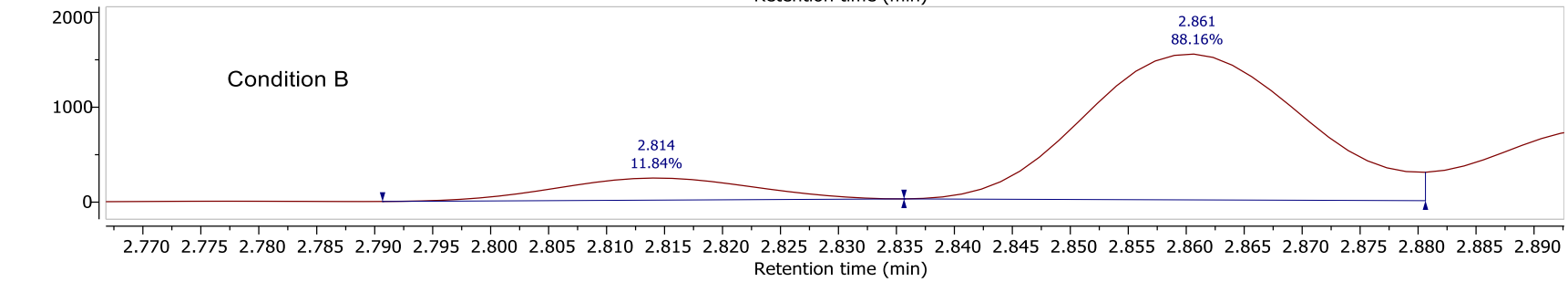

Condition B

**l: R = $CH_2cC_4H_7$, 6 versus reaction mixtures. Mass spectra for reaction mixtures at 2.35 minutes for each condition.**

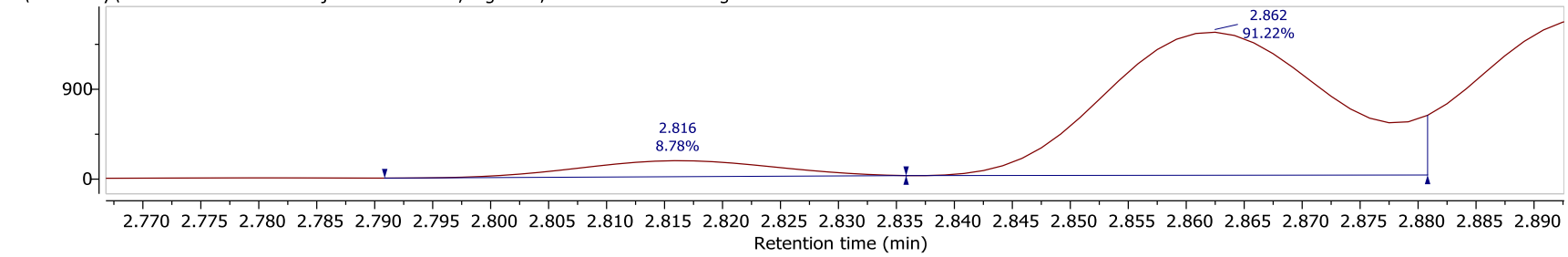



P:\Chemistry\G...7-141 B RM LCMS Injection 1 DAD1B, Sig=254,4 Ref=off Chromatogram

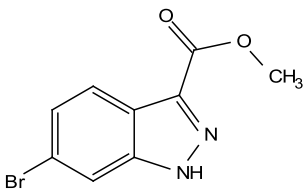


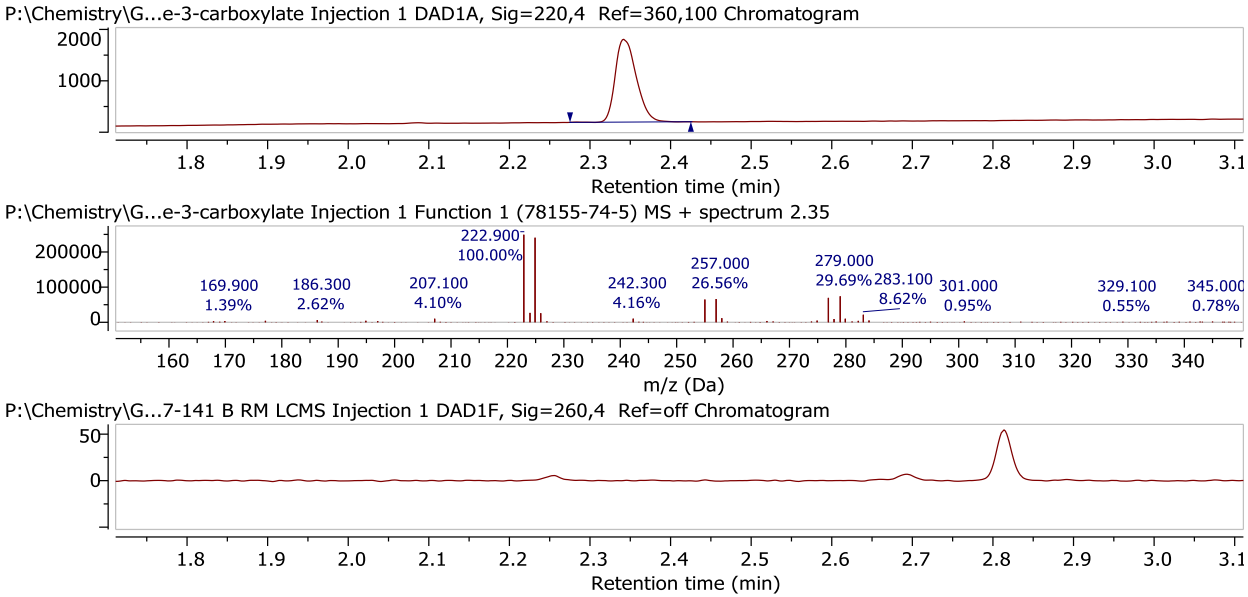

P:\Chemistry\G...7-141 C RM LCMS Injection 1 DAD1B, Sig=254,4 Ref=off Chromatogram



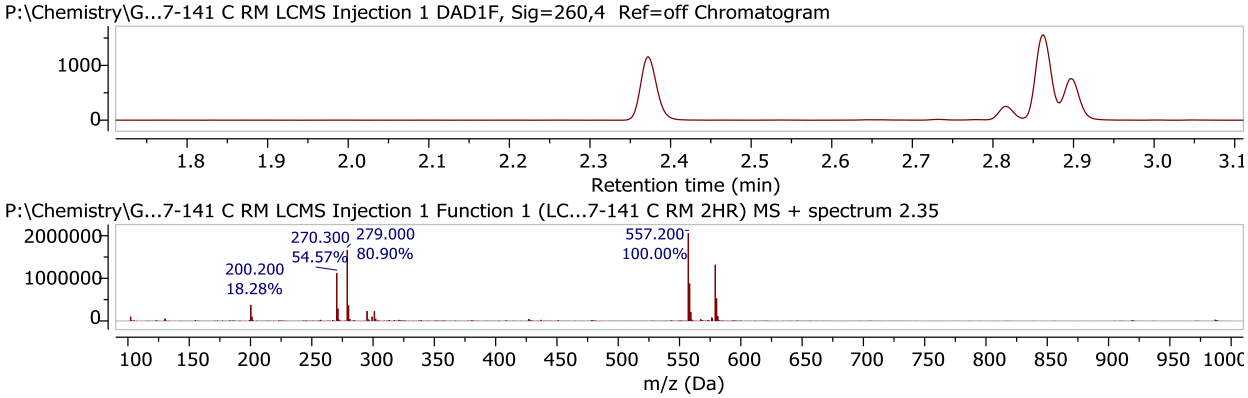

**n**



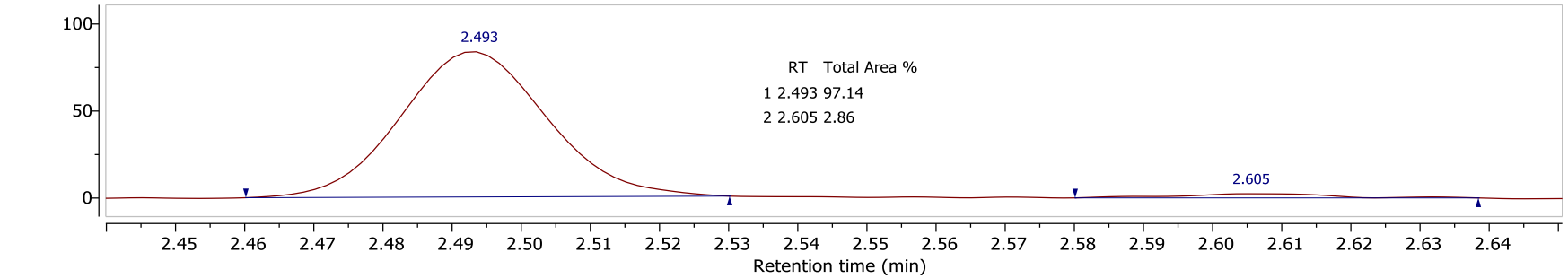

Condition A



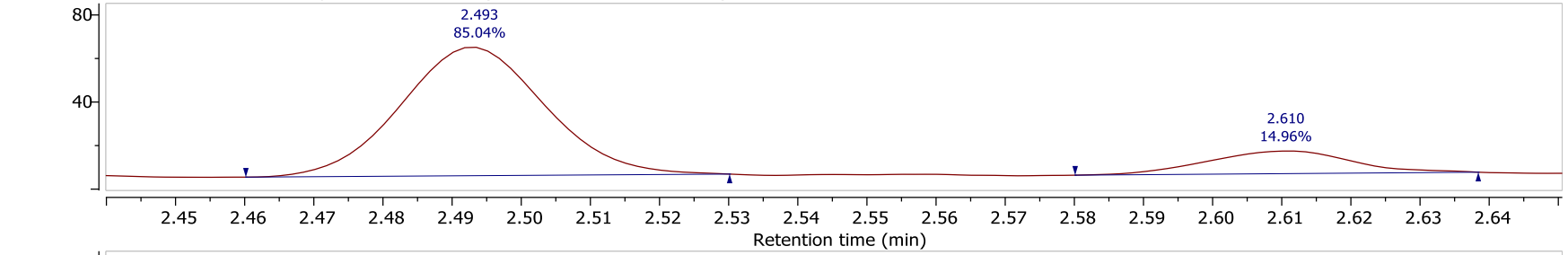

Condition B

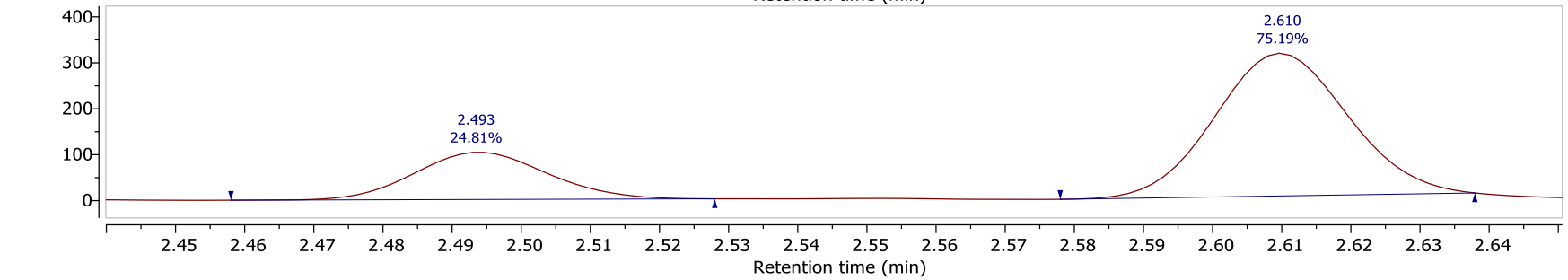



**n: R = $CH_2cC_5H_9$, 6 versus reaction mixtures. Mass spectra for reaction mixtures at 2.35 minutes for each condition.**

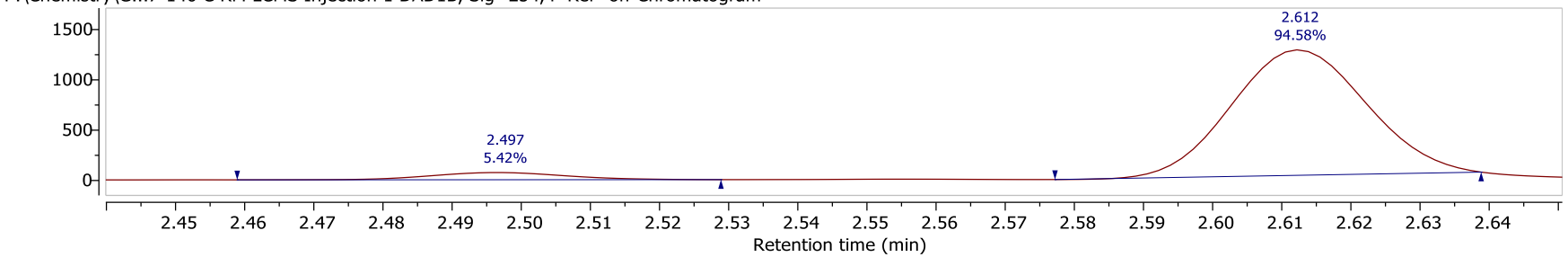



P:\Chemistry\G...7-146 B RM LCMS Injection 1 DAD1B, Sig=254,4 Ref=off Chromatogram

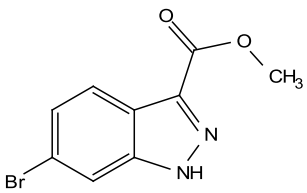


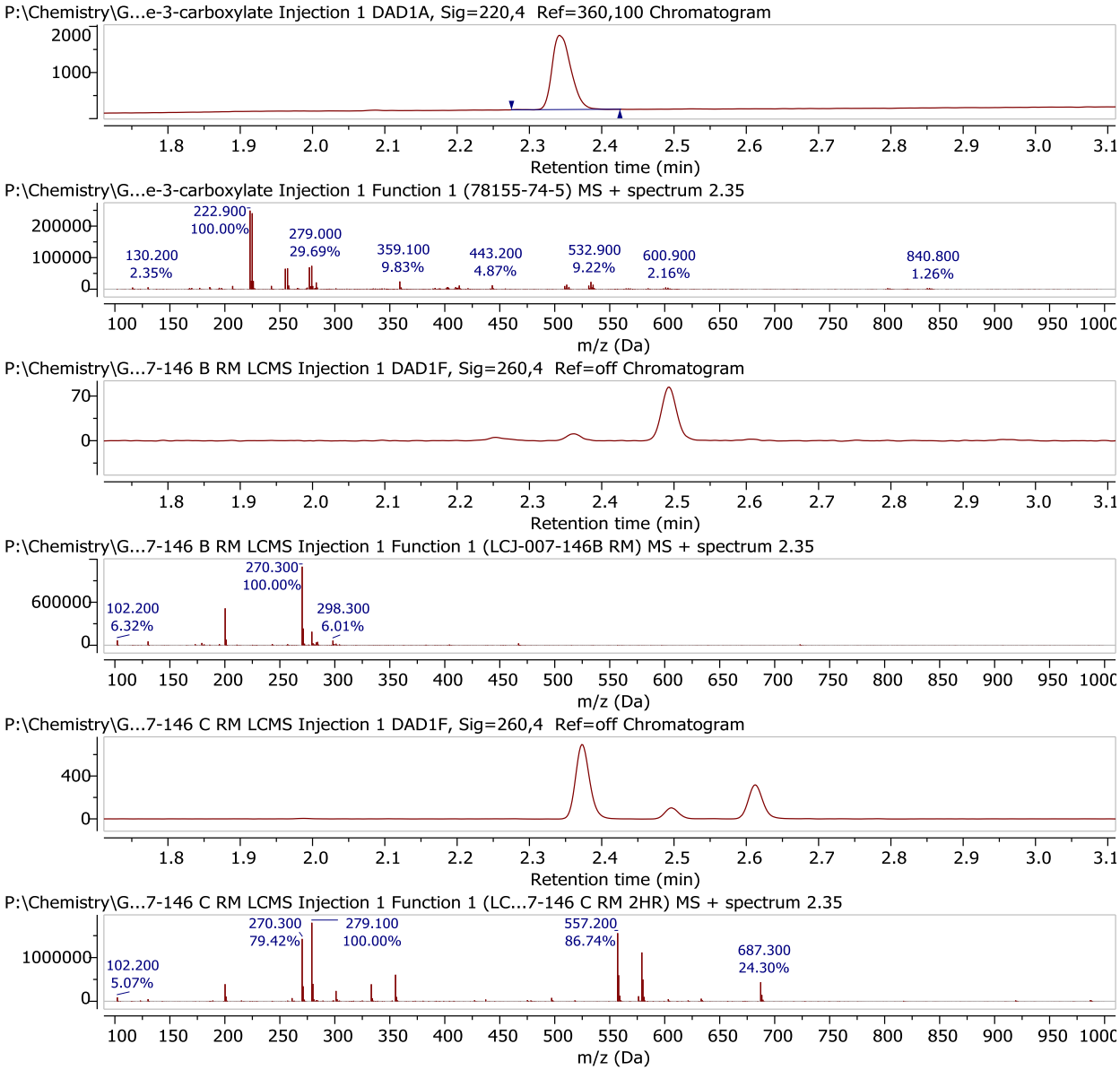

P:\Chemistry\G...7-146 C RM LCMS Injection 1 DAD1B, Sig=254,4 Ref=off Chromatogram




**o**



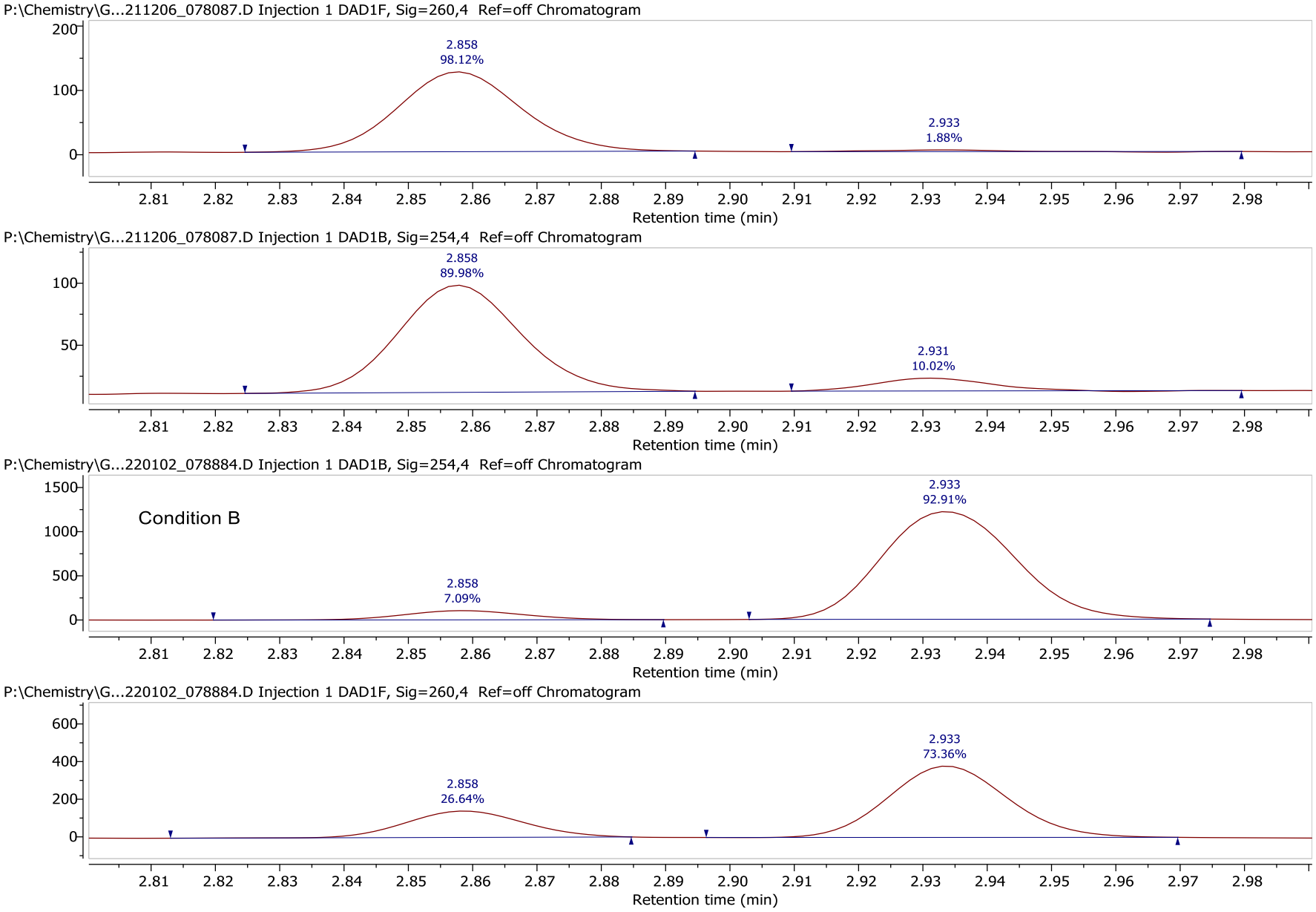

Condition A



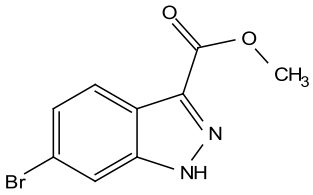

Condition B



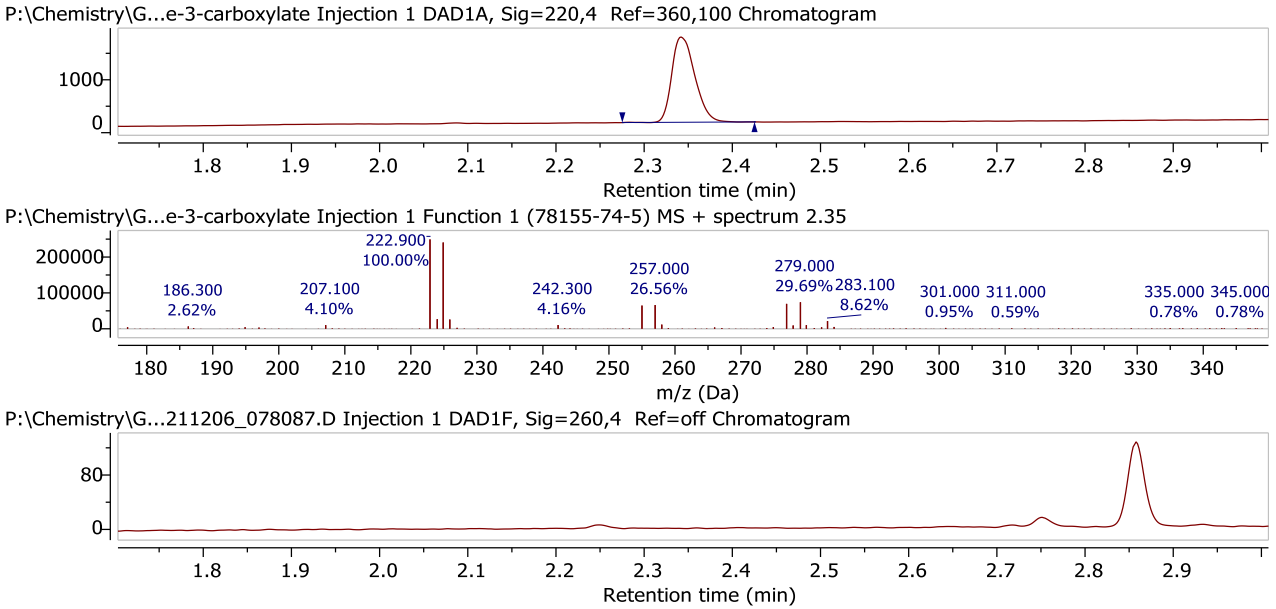

**o: R = $CH_2cC_4H_7O$, 6 versus reaction mixtures. Mass spectra for reaction mixtures at 2.35 minutes for each condition.**


P:\Chemistry\G...211206_078087.D Injection 1 DAD1F, Sig=260,4 Ref=off Chromatogram
2.858
98.12%
2.933
1.88%
Retention time (min)
P:\Chemistry\G...211206_078087.D Injection 1 DAD1B, Sig=254,4 Ref=off Chromatogram
2.858
89.98%
2.931
10.02%
Retention time (min)
P:\Chemistry\G...220102_078884.D Injection 1 DAD1B, Sig=254,4 Ref=off Chromatogram
Condition B
2.933
92.91%
2.858
7.09%
Retention time (min)
P:\Chemistry\G...220102_078884.D Injection 1 DAD1F, Sig=260,4 Ref=off Chromatogram
2.933
73.36%
2.858
26.64%
Retention time (min)

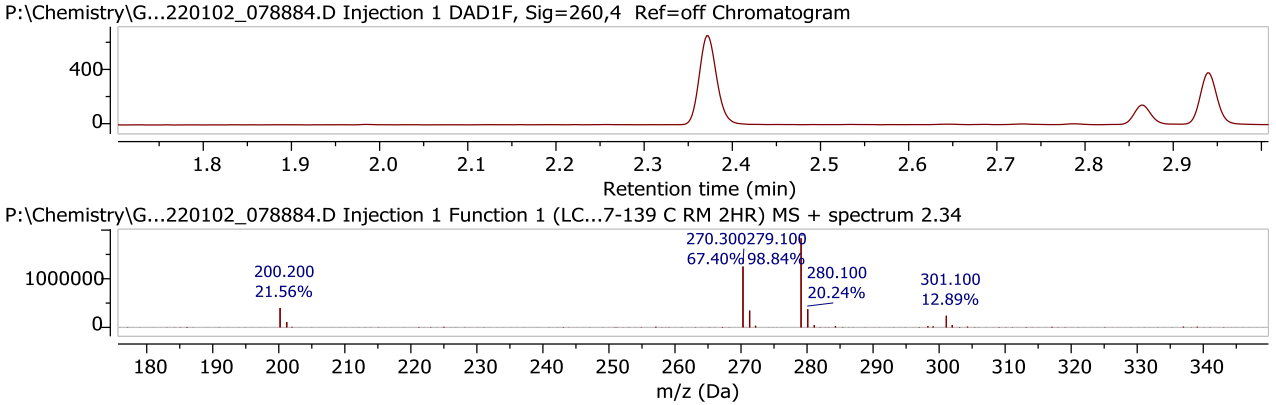
**p**



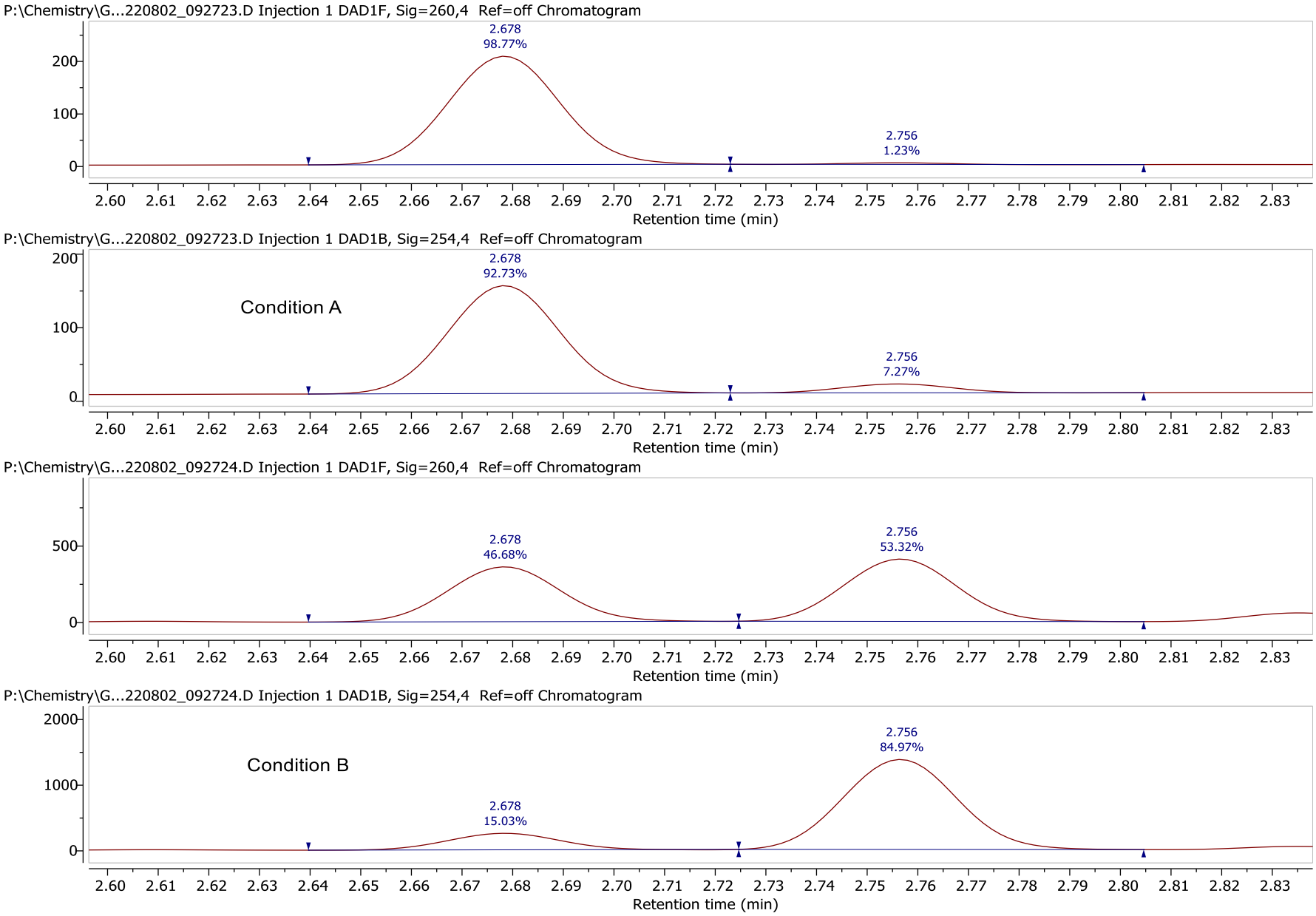

Condition A



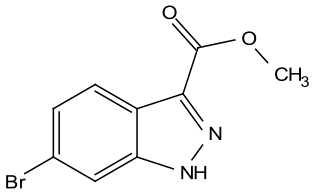

Condition B



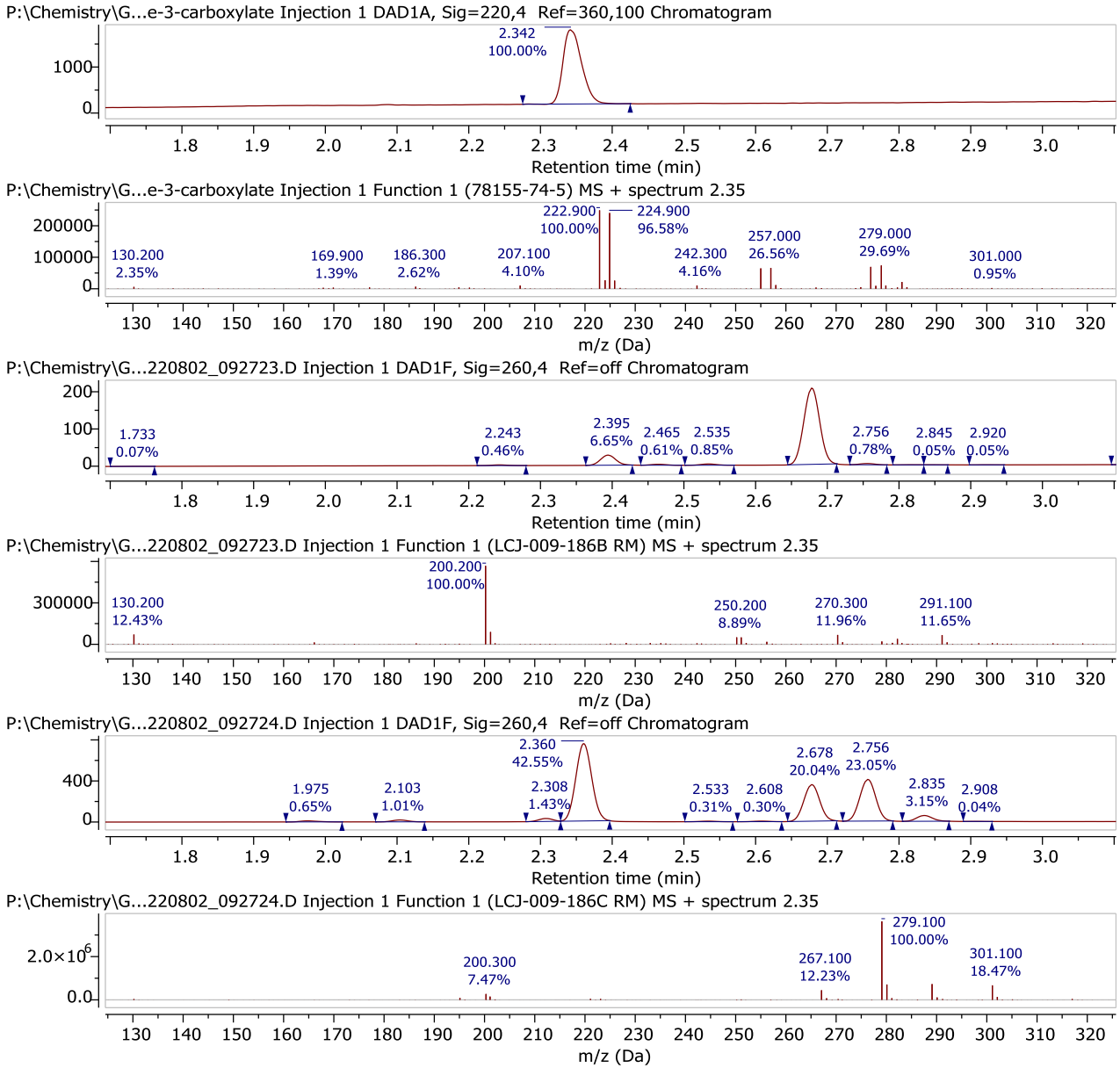

**p: R = $CH_2cC_6H_{11}$, 6 versus reaction mixtures. Mass spectra for reaction mixtures at 2.35 minutes for each condition.**


P:\Chemistry\G...220802_092723.D Injection 1 DAD1F, Sig=260,4 Ref=off Chromatogram
2.678
98.77%
2.756
1.23%
Retention time (min)
P:\Chemistry\G...220802_092723.D Injection 1 DAD1B, Sig=254,4 Ref=off Chromatogram
Condition A
2.678
92.73%
2.756
7.27%
Retention time (min)
P:\Chemistry\G...220802_092724.D Injection 1 DAD1F, Sig=260,4 Ref=off Chromatogram
2.678
46.68%
2.756
53.32%
Retention time (min)
P:\Chemistry\G...220802_092724.D Injection 1 DAD1B, Sig=254,4 Ref=off Chromatogram
Condition B
2.678
15.03%
2.756
84.97%
Retention time (min)

**q**




Condition A

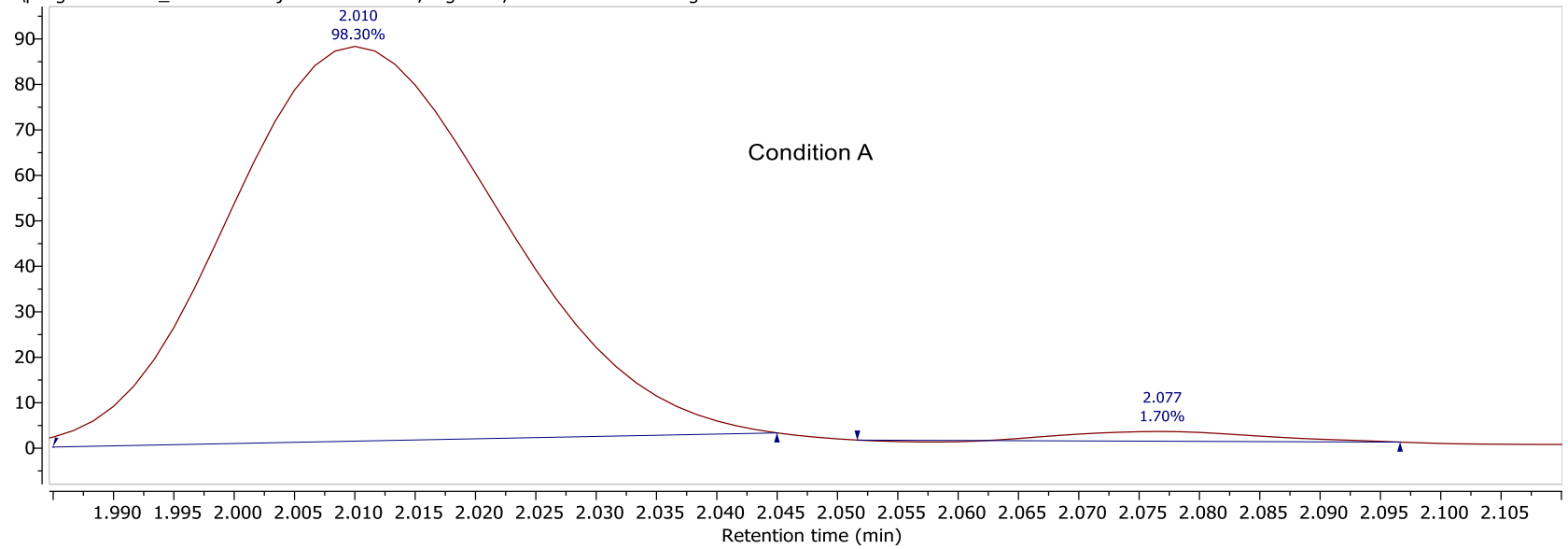



Condition B

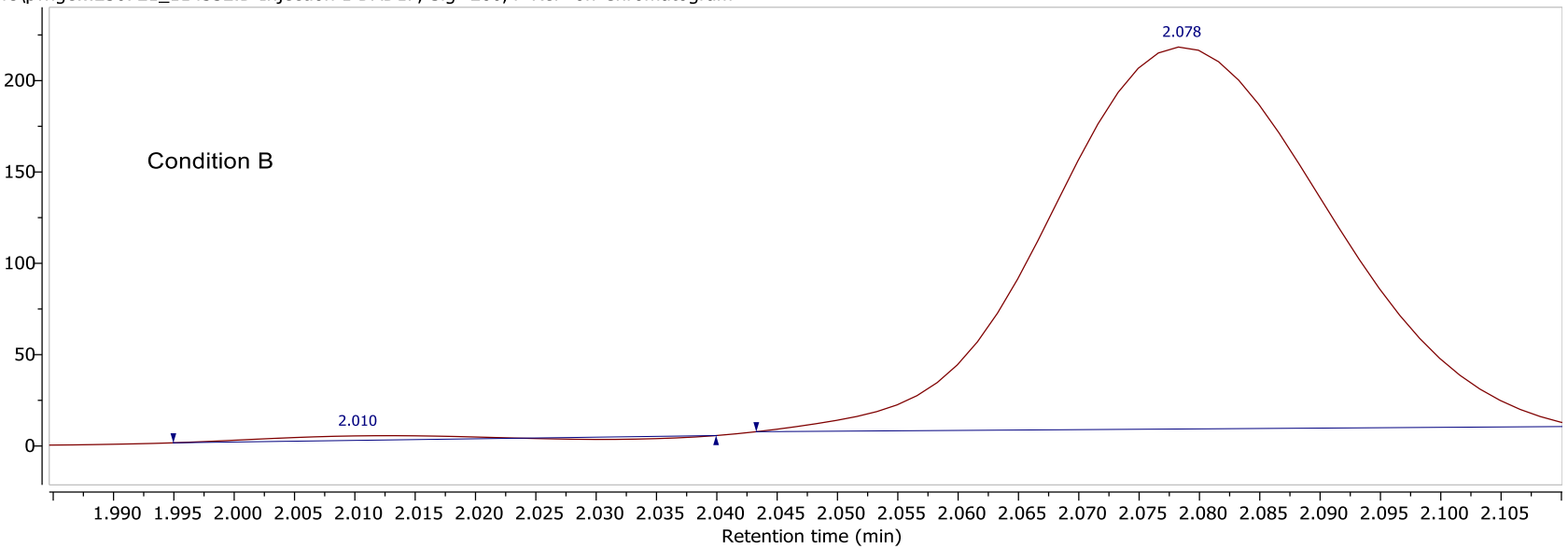



**q: R = Bn, 6 versus reaction mixtures. Mass spectra for reaction mixtures at 2.35 minutes for each condition**

C:\Users\pwige...230721_114581.D Injection 1 DAD1F, Sig=260,4 Ref=off Chromatogram

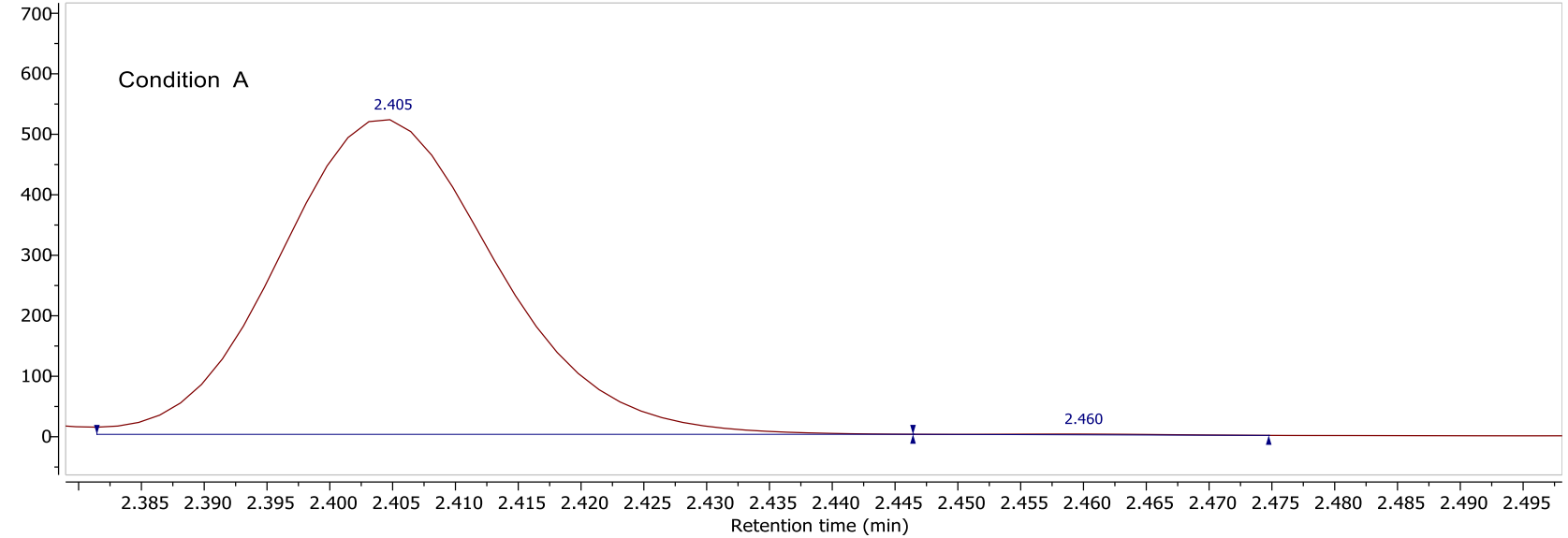



C:\Users\pwige...230721_114532.D Injection 1 DAD1F, Sig=260,4 Ref=off Chromatogram

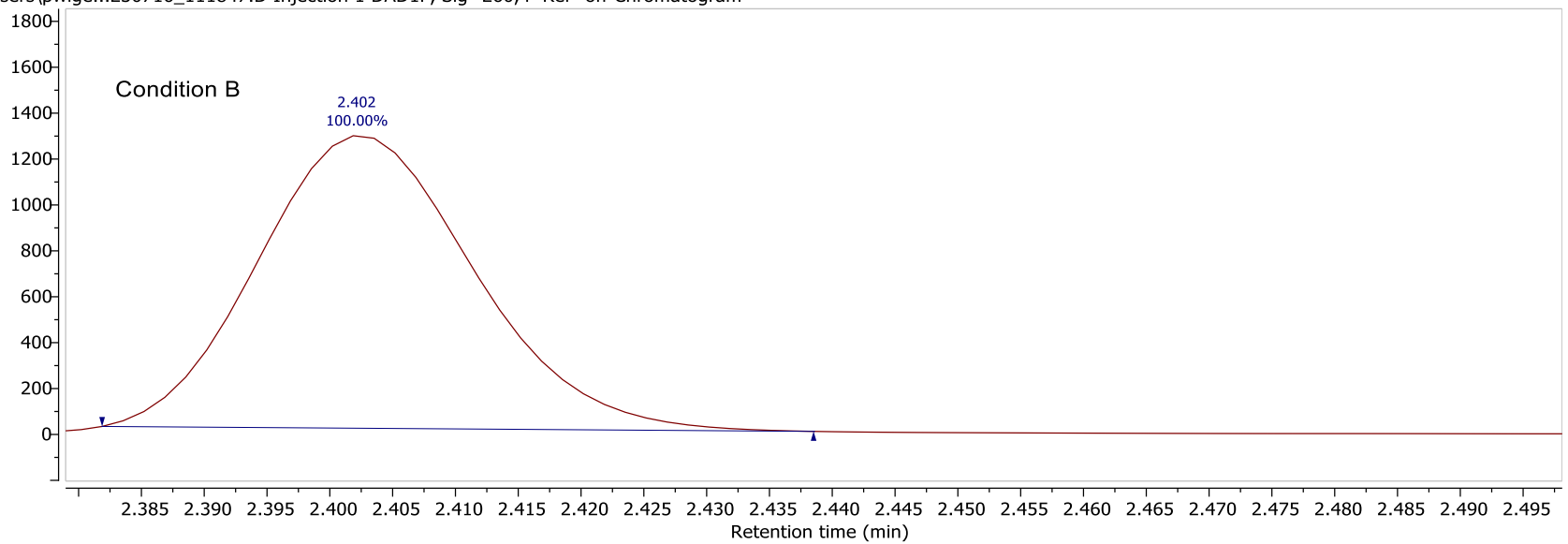



**19 /20**

C:\Users\pwige...230716_111844.D Injection 1 DAD1F, Sig=260,4 Ref=off Chromatogram



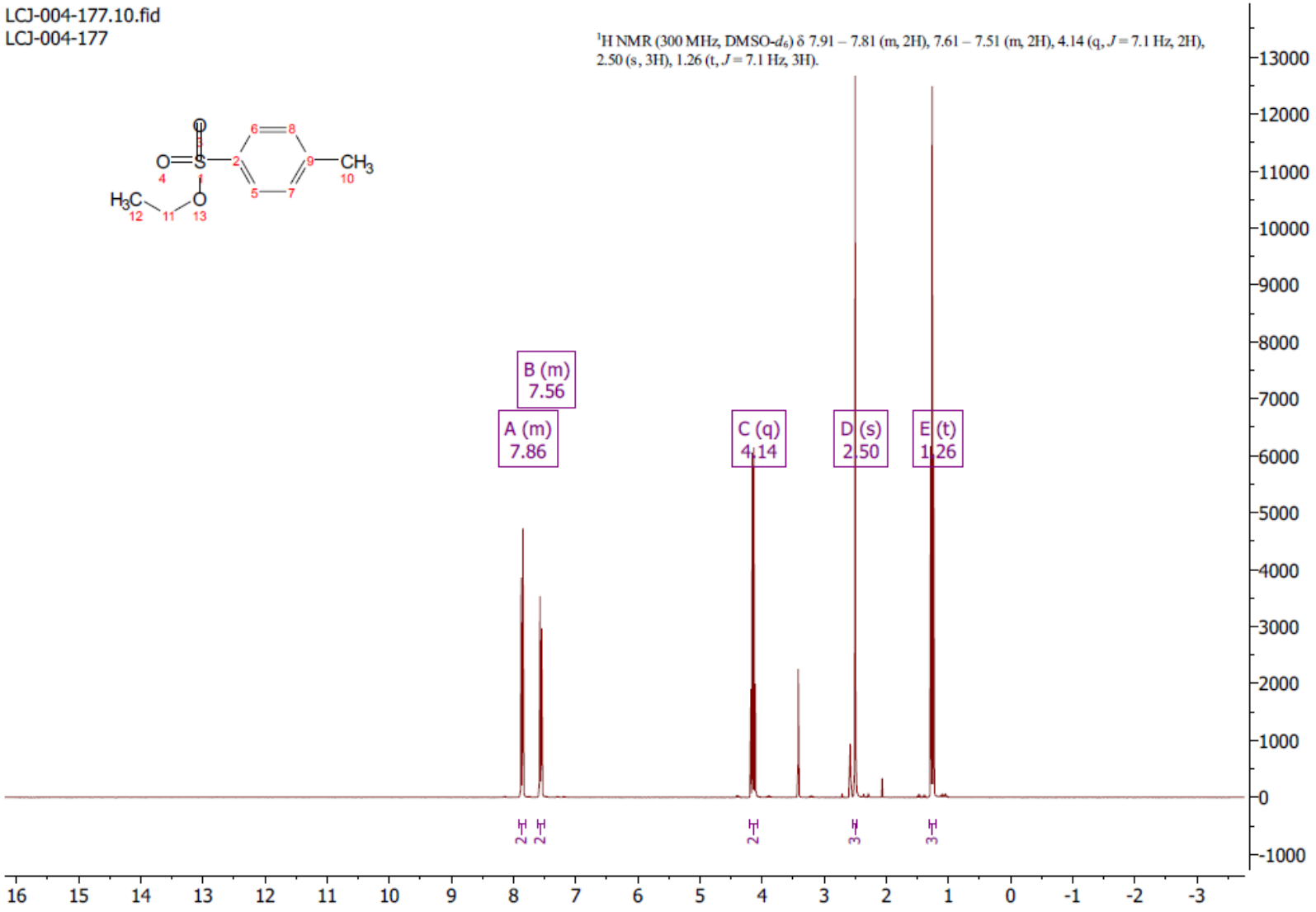

C:\Users\pwige...230716_111847.D Injection 1 DAD1F, Sig=260,4 Ref=off Chromatogram

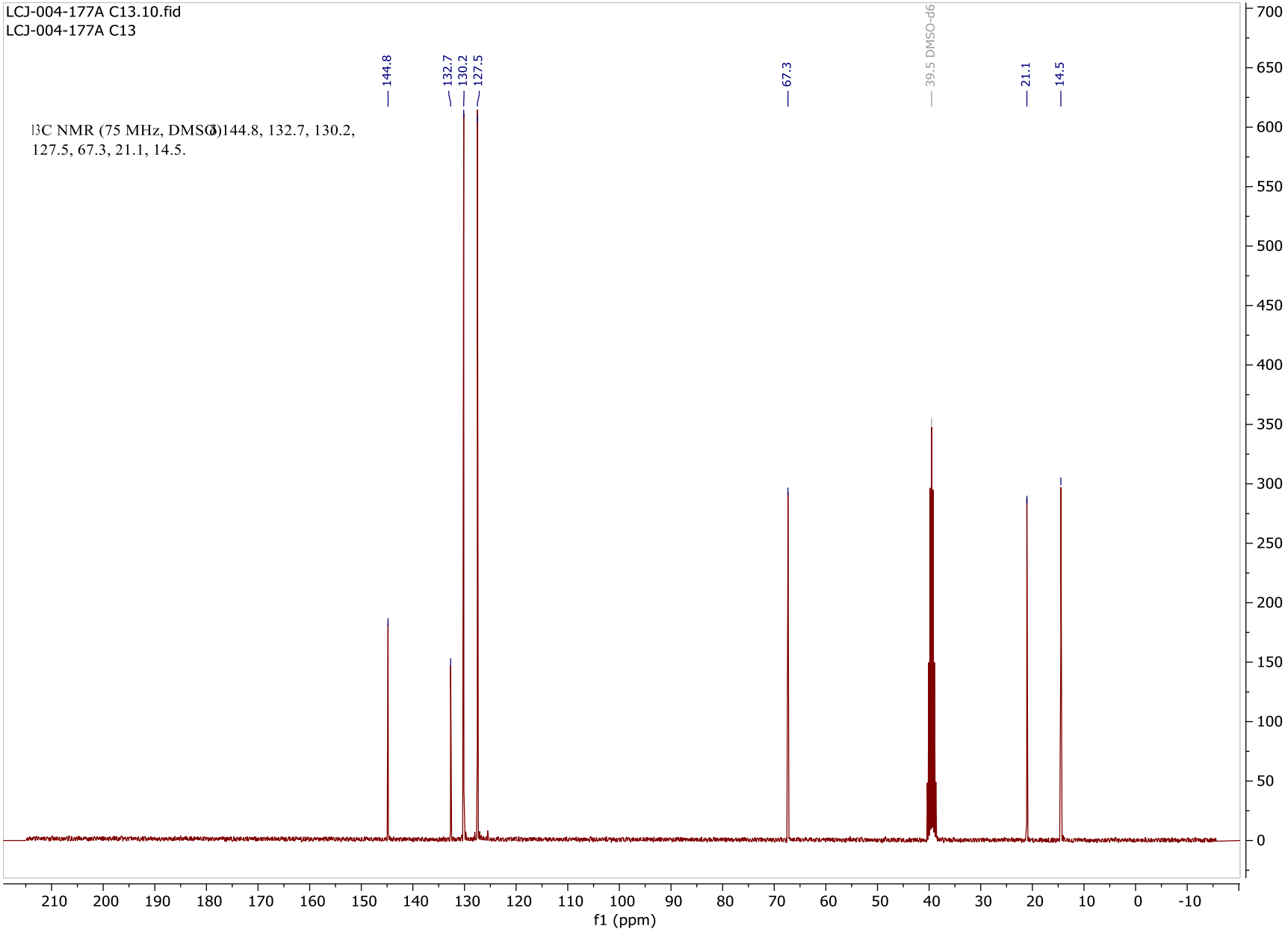



**22**

**NMR Spectra of synthesized compounds.**

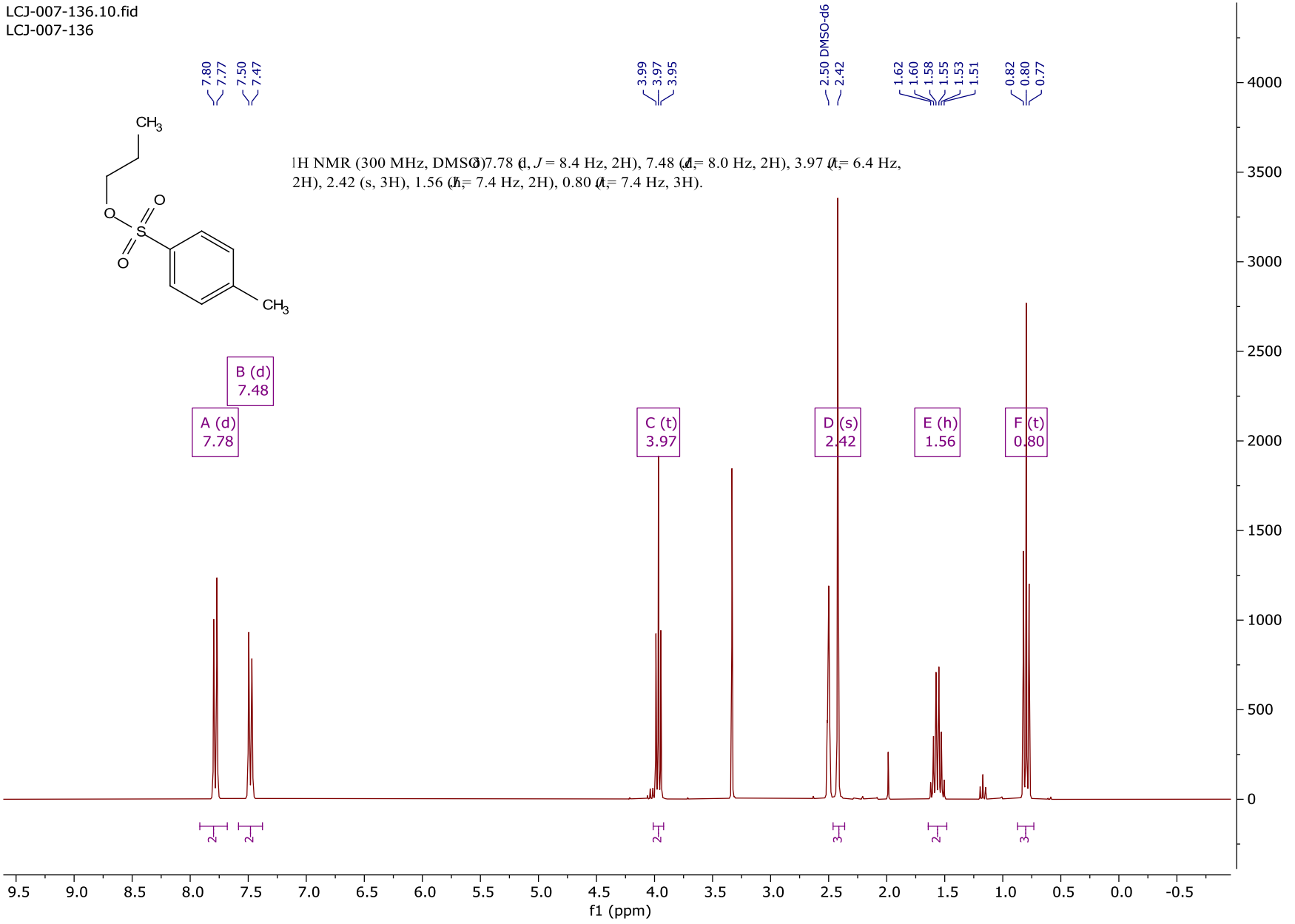
**14b**-$^{1}$H



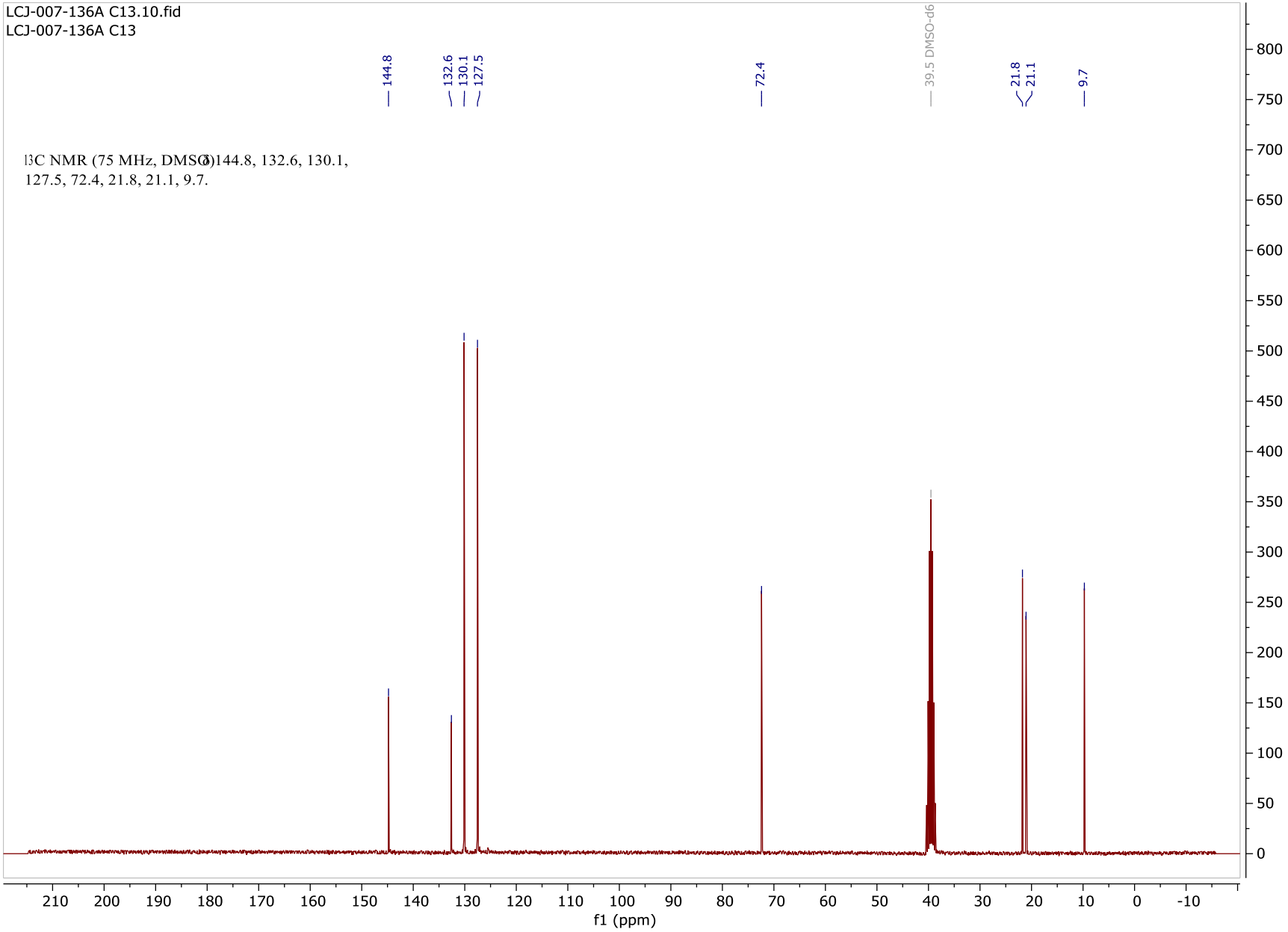

LCJ-004-177A C13.10.fid
LCJ-004-177A C13
144.8
132.7
130.2
127.5
67.3
39.5 DMSO-d6
21.1
14.5
13C NMR (75 MHz, DMSO-d6) δ 144.8, 132.7, 130.2, 127.5, 67.3, 21.1, 14.5.
f1 (ppm)

**14b**-$^{13}$C

LCJ-007-136.10.fid
LCJ-007-136

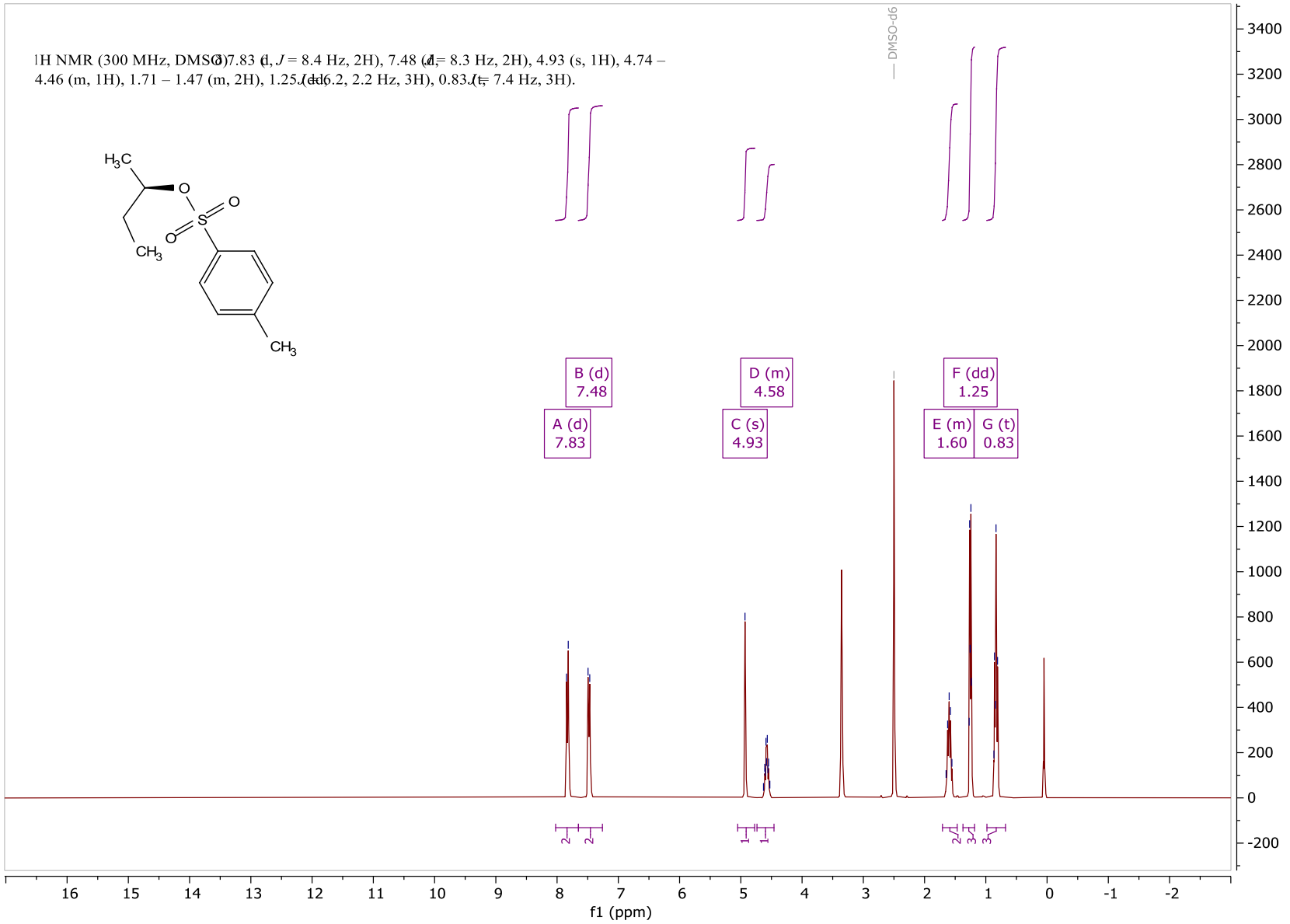


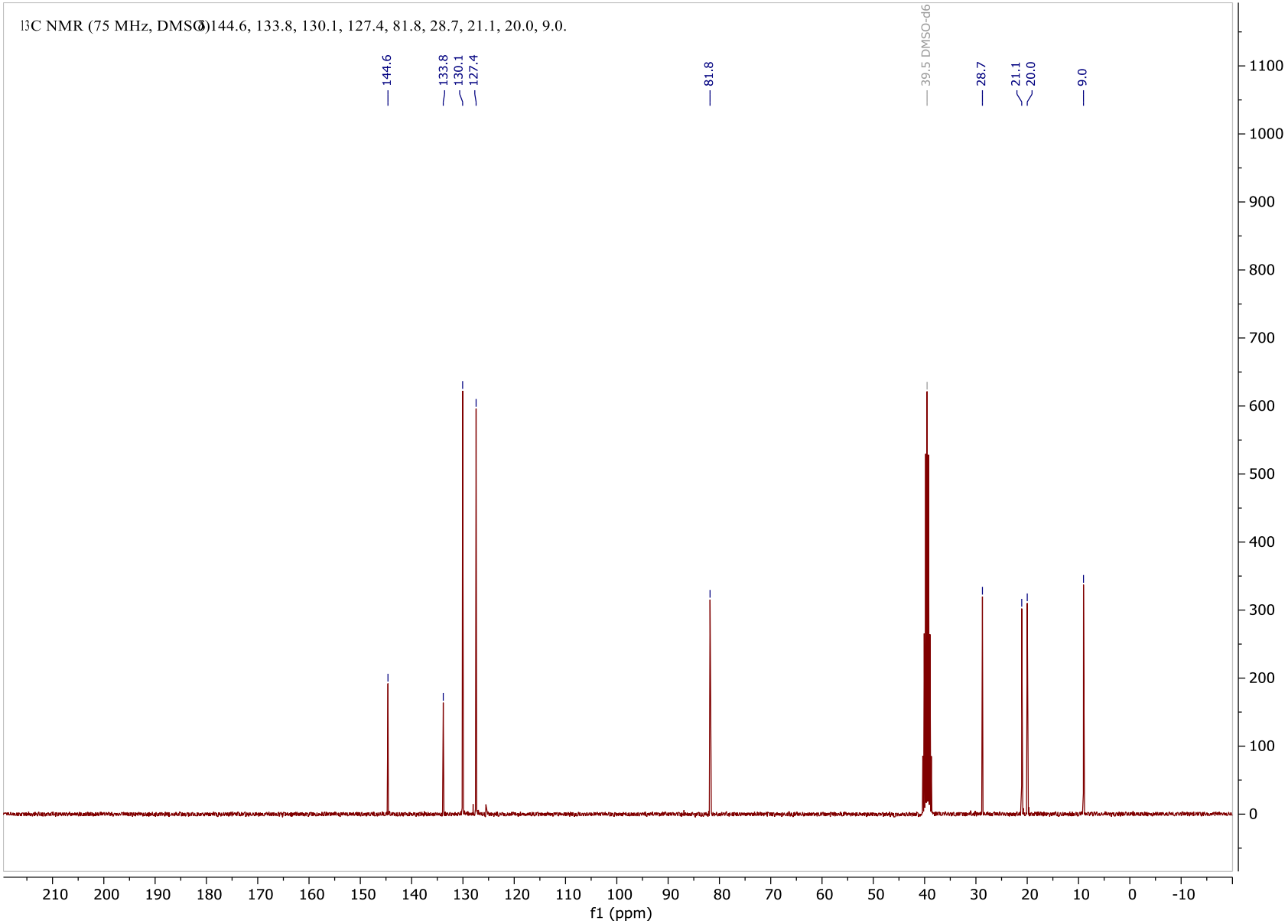

**14d**-$^{1}$H


LCJ-007-136A C13.10.fid
LCJ-007-136A C13
144.8
132.6
130.1
127.5
72.4
39.5 DMSO-d6
21.8
21.1
9.7
13C NMR (75 MHz, DMSO) δ 144.8, 132.6, 130.1,
127.5, 72.4, 21.8, 21.1, 9.7.
f1 (ppm)

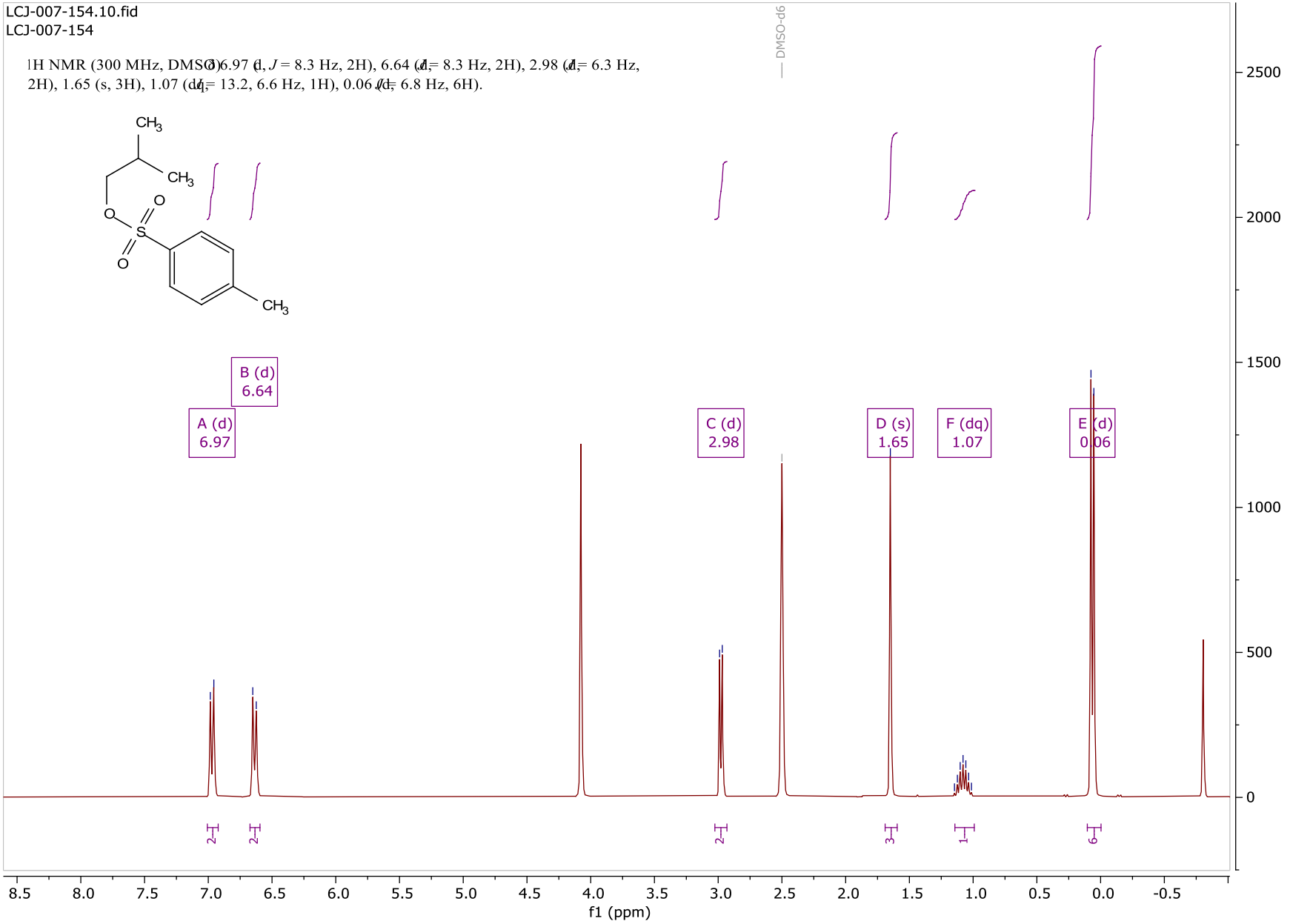
**14d**-$^{13}$C

**14e**-$^{1}$H

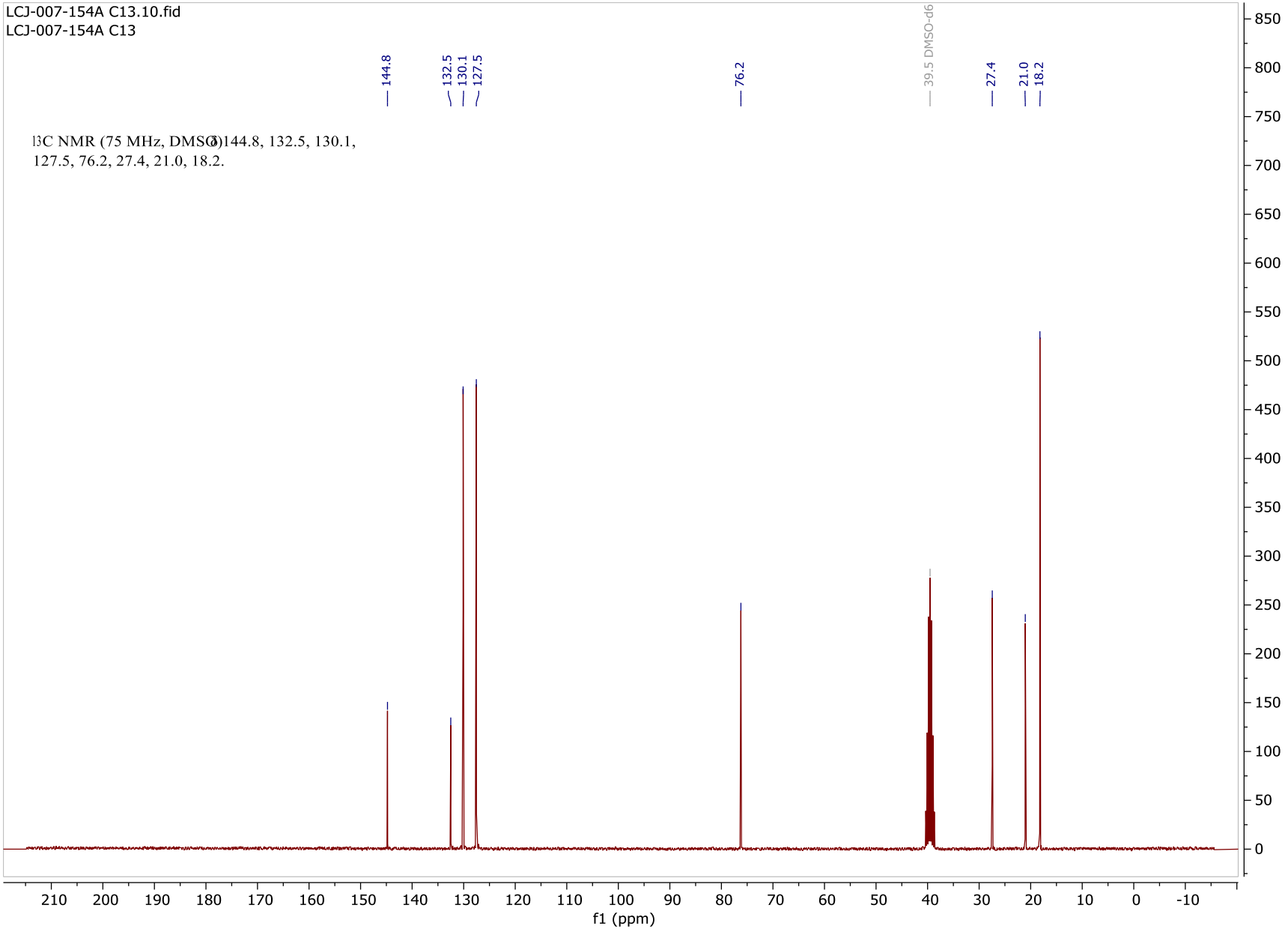

1H NMR (300 MHz, DMSO) δ 7.83 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.3 Hz, 2H), 4.93 (s, 1H), 4.74 – 4.46 (m, 1H), 1.71 – 1.47 (m, 2H), 1.25 (dd, J = 6.2, 2.2 Hz, 3H), 0.83 (t, J = 7.4 Hz, 3H).
DMSO-d6
B (d) 7.48
A (d) 7.83
D (m) 4.58
C (s) 4.93
F (dd) 1.25
E (m) 1.60
G (t) 0.83
f1 (ppm)


13C NMR (75 MHz, DMSO) δ 144.6, 133.8, 130.1, 127.4, 81.8, 28.7, 21.1, 20.0, 9.0.
144.6
133.8
130.1
127.4
81.8
39.5 DMSO-d6
28.7
21.1
20.0
9.0
f1 (ppm)

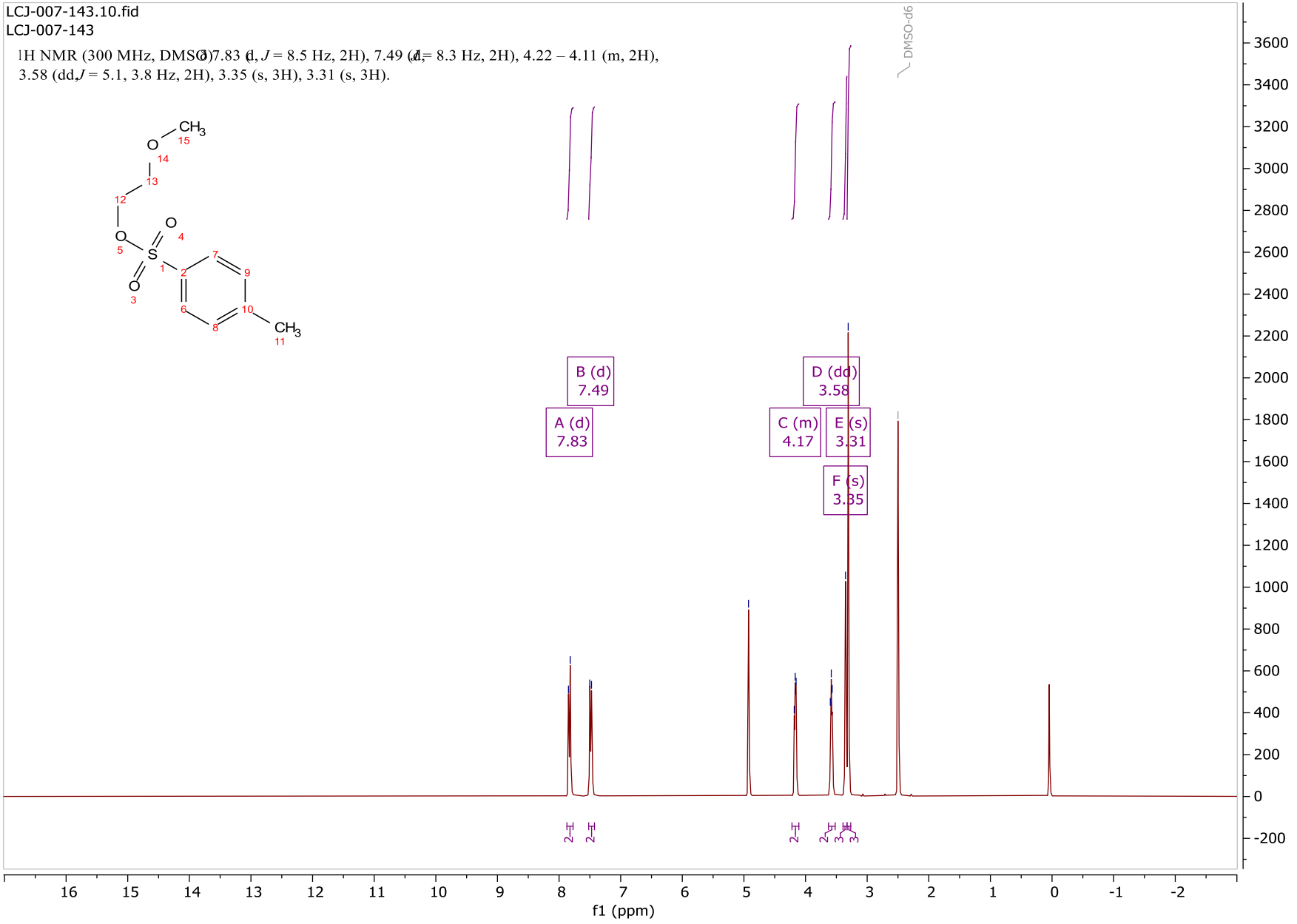
14e-$^{13}$C


LCJ-007-154.10.fid
LCJ-007-154
1H NMR (300 MHz, DMSO-d6) δ 6.97 (d, J = 8.3 Hz, 2H), 6.64 (d, J = 8.3 Hz, 2H), 2.98 (d, J = 6.3 Hz, 2H), 1.65 (s, 3H), 1.07 (dq, J = 13.2, 6.6 Hz, 1H), 0.06 (d, J = 6.8 Hz, 6H).
DMSO-d6
A (d) 6.97
B (d) 6.64
C (d) 2.98
D (s) 1.65
F (dq) 1.07
E (d) 0.06
2-H
2-H
2-H
3-H
1-H
6-H
f1 (ppm)

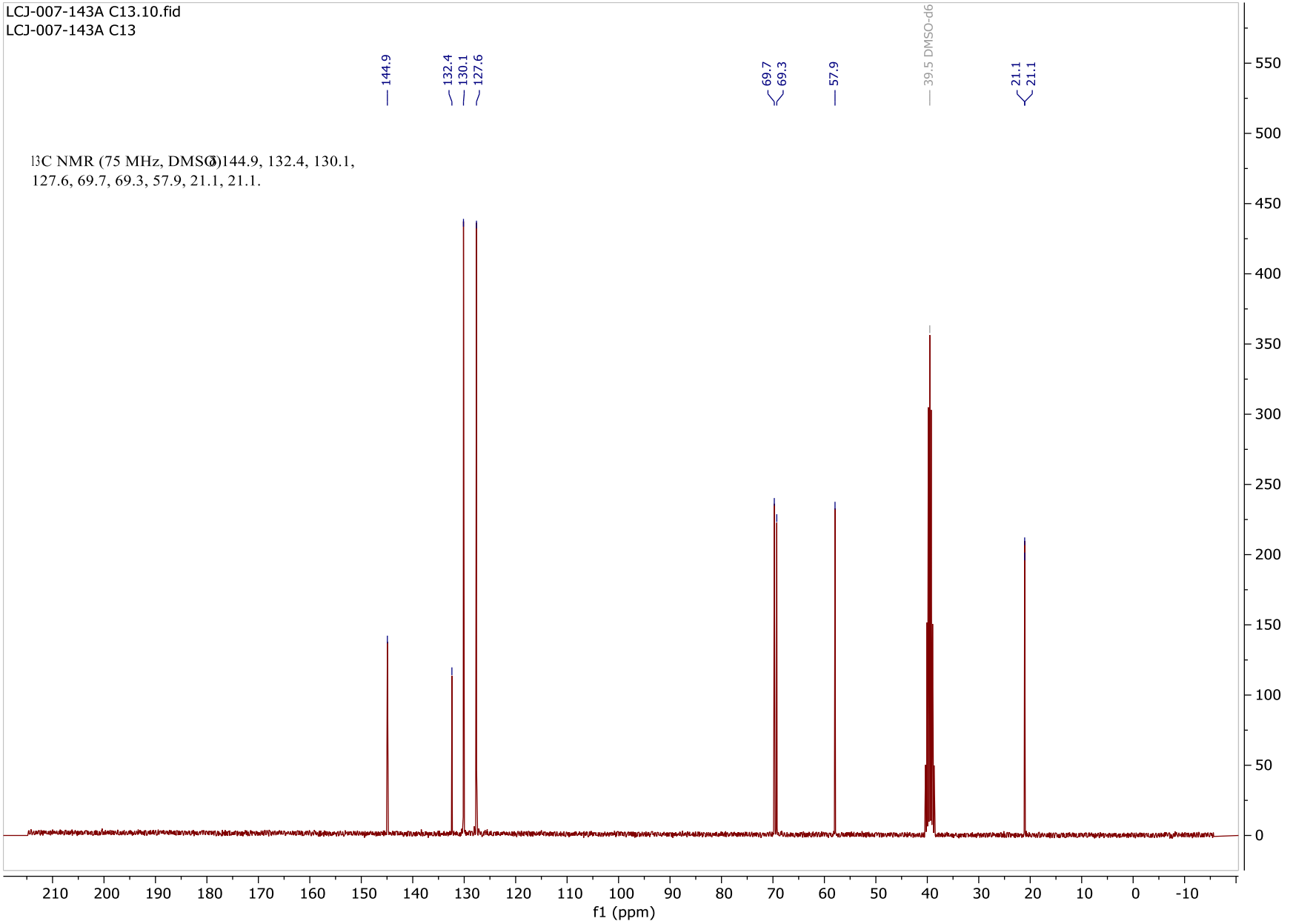
**14f**-$^{1}$H


LCJ-007-154A C13.10.fid
LCJ-007-154A C13
144.8
132.5
130.1
127.5
76.2
39.5 DMSO-d6
27.4
21.0
18.2
13C NMR (75 MHz, DMSO-d6) δ 144.8, 132.5, 130.1, 127.5, 76.2, 27.4, 21.0, 18.2.
f1 (ppm)

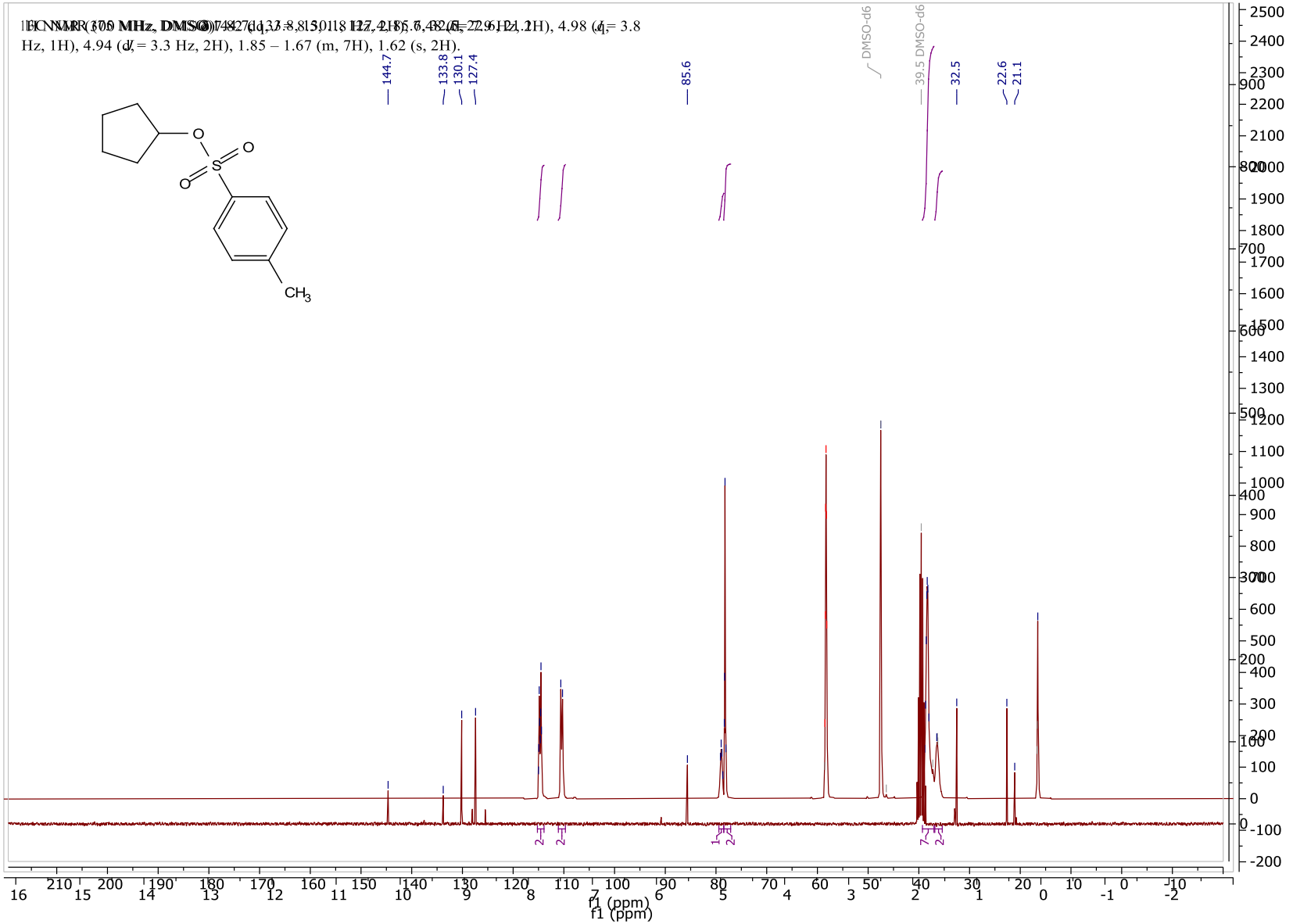
**14f**-$^{13}$C


LCJ-007-143.10.fid
LCJ-007-143
1H NMR (300 MHz, DMSO-d6) δ 7.83 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 8.3 Hz, 2H), 4.22 – 4.11 (m, 2H), 3.58 (dd, J = 5.1, 3.8 Hz, 2H), 3.35 (s, 3H), 3.31 (s, 3H).
DMSO-d6
B (d) 7.49
A (d) 7.83
D (dd) 3.58
C (m) 4.17
E (s) 3.31
F (s) 3.35
f1 (ppm)

**14g**-$^{1}$H

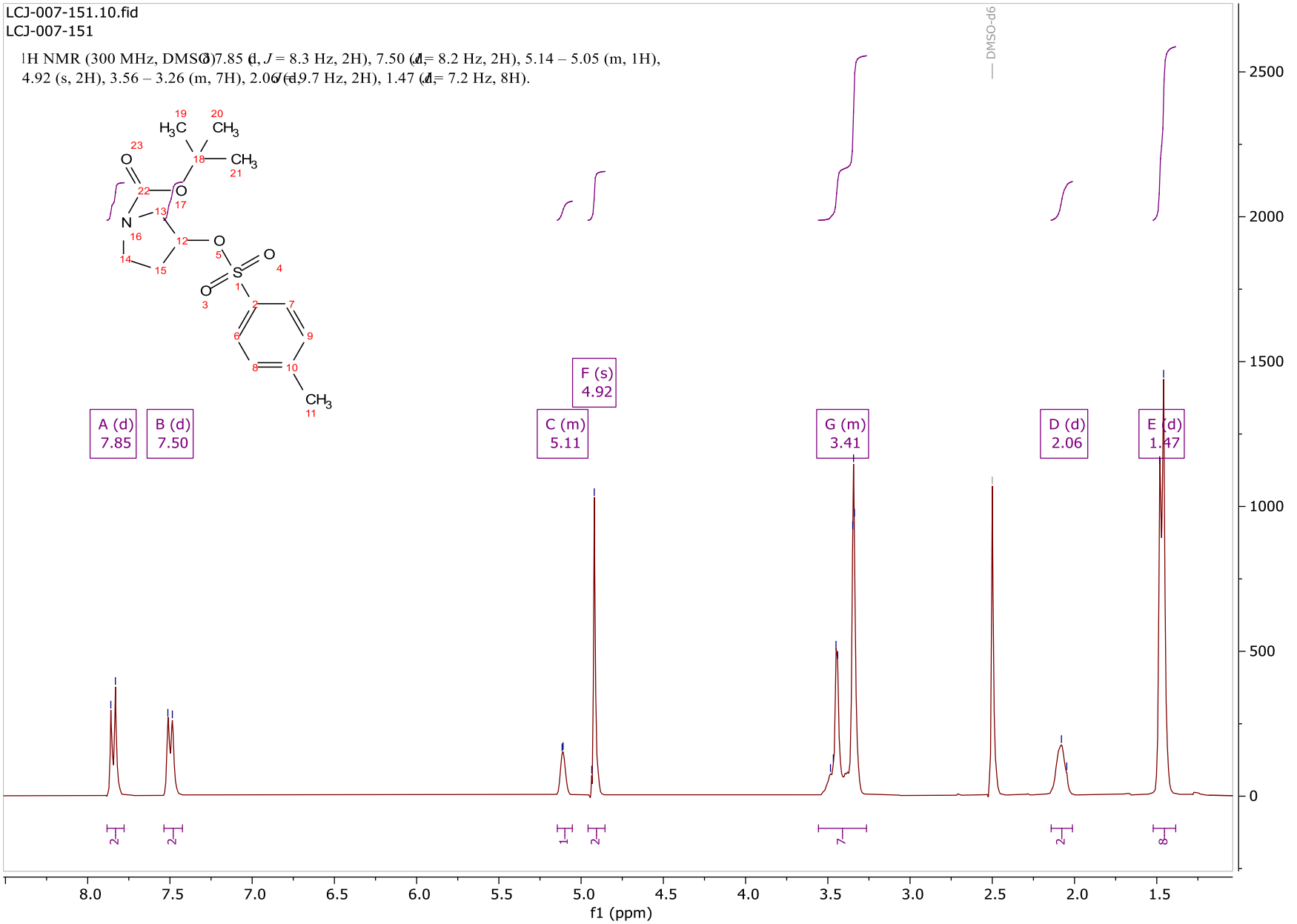

LCJ-007-143A C13.10.fid
LCJ-007-143A C13
144.9
132.4
130.1
127.6
69.7
69.3
57.9
39.5 DMSO-d6
21.1
21.1
13C NMR (75 MHz, DMSO) δ 144.9, 132.4, 130.1,
127.6, 69.7, 69.3, 57.9, 21.1, 21.1.
f1 (ppm)

**14g**-$^{13}$C

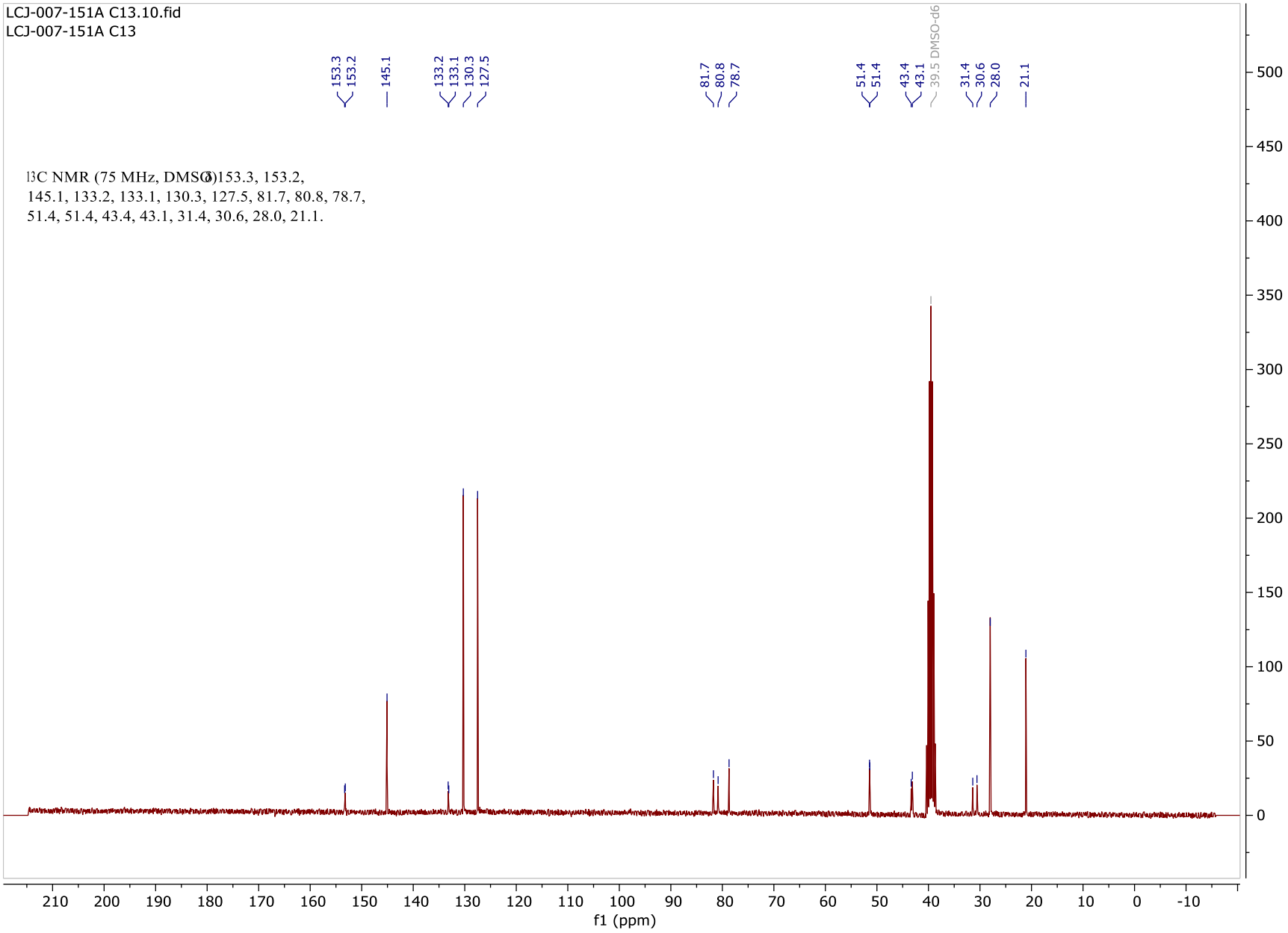



**14h**-$^{1}$H

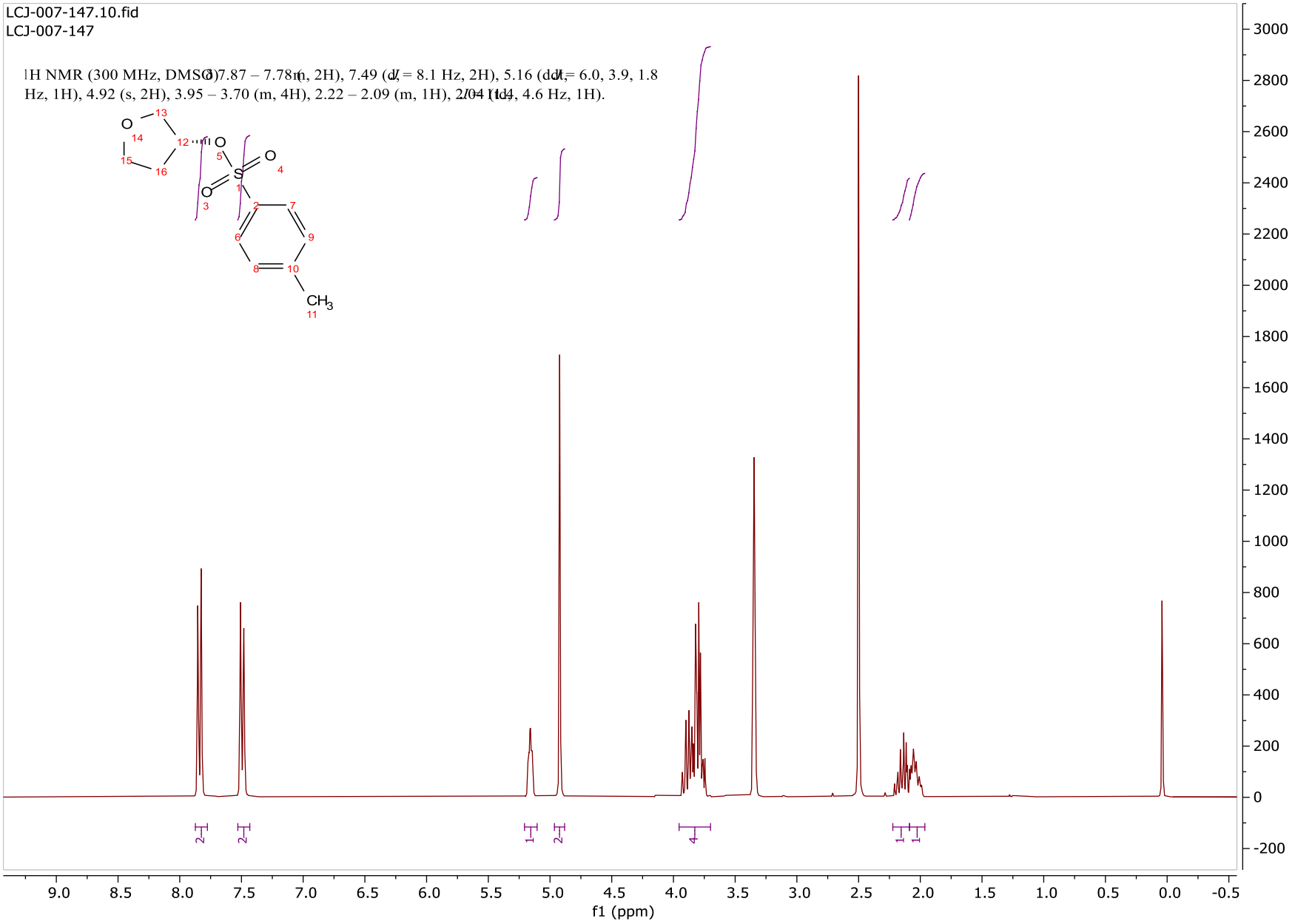
**14h**-$^{13}$C


LCJ-007-151.10.fid
LCJ-007-151
1H NMR (300 MHz, DMSO-d6) 7.85 (d, J = 8.3 Hz, 2H), 7.50 (d, J = 8.2 Hz, 2H), 5.14 – 5.05 (m, 1H), 4.92 (s, 2H), 3.56 – 3.26 (m, 7H), 2.06 (d, J = 9.7 Hz, 2H), 1.47 (d, J = 7.2 Hz, 8H).
DMSO-d6
A (d) 7.85
B (d) 7.50
C (m) 5.11
F (s) 4.92
G (m) 3.41
D (d) 2.06
E (d) 1.47
f1 (ppm)

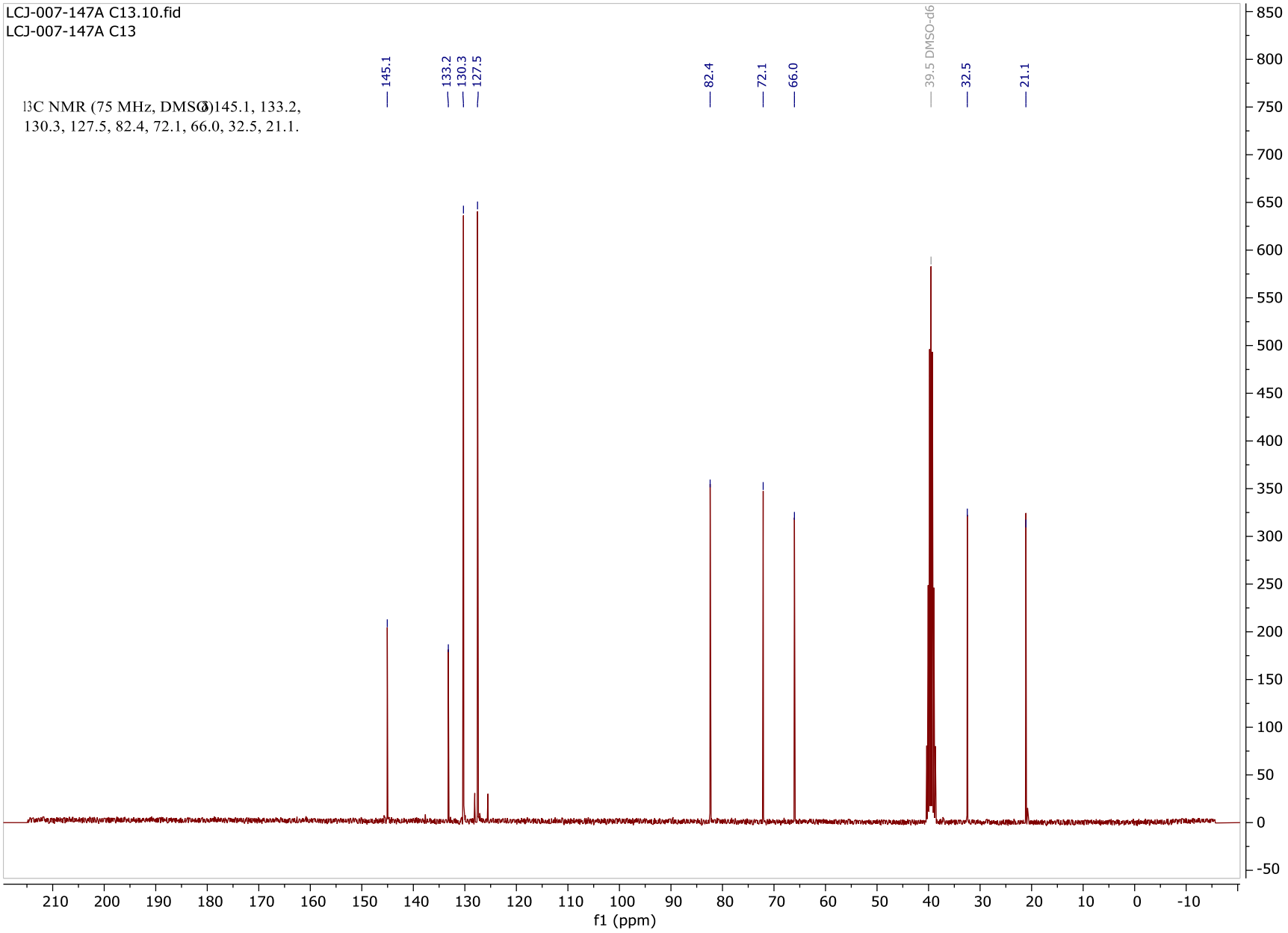
**14i**-$^{1}$H


LCJ-007-151A C13.10.fid
LCJ-007-151A C13
153.3
153.2
145.1
133.2
133.1
130.3
127.5
81.7
80.8
78.7
51.4
51.4
43.4
43.1
39.5 DMSO-d6
31.4
30.6
28.0
21.1
13C NMR (75 MHz, DMSO) δ 153.3, 153.2,
145.1, 133.2, 133.1, 130.3, 127.5, 81.7, 80.8, 78.7,
51.4, 51.4, 43.4, 43.1, 31.4, 30.6, 28.0, 21.1.
f1 (ppm)

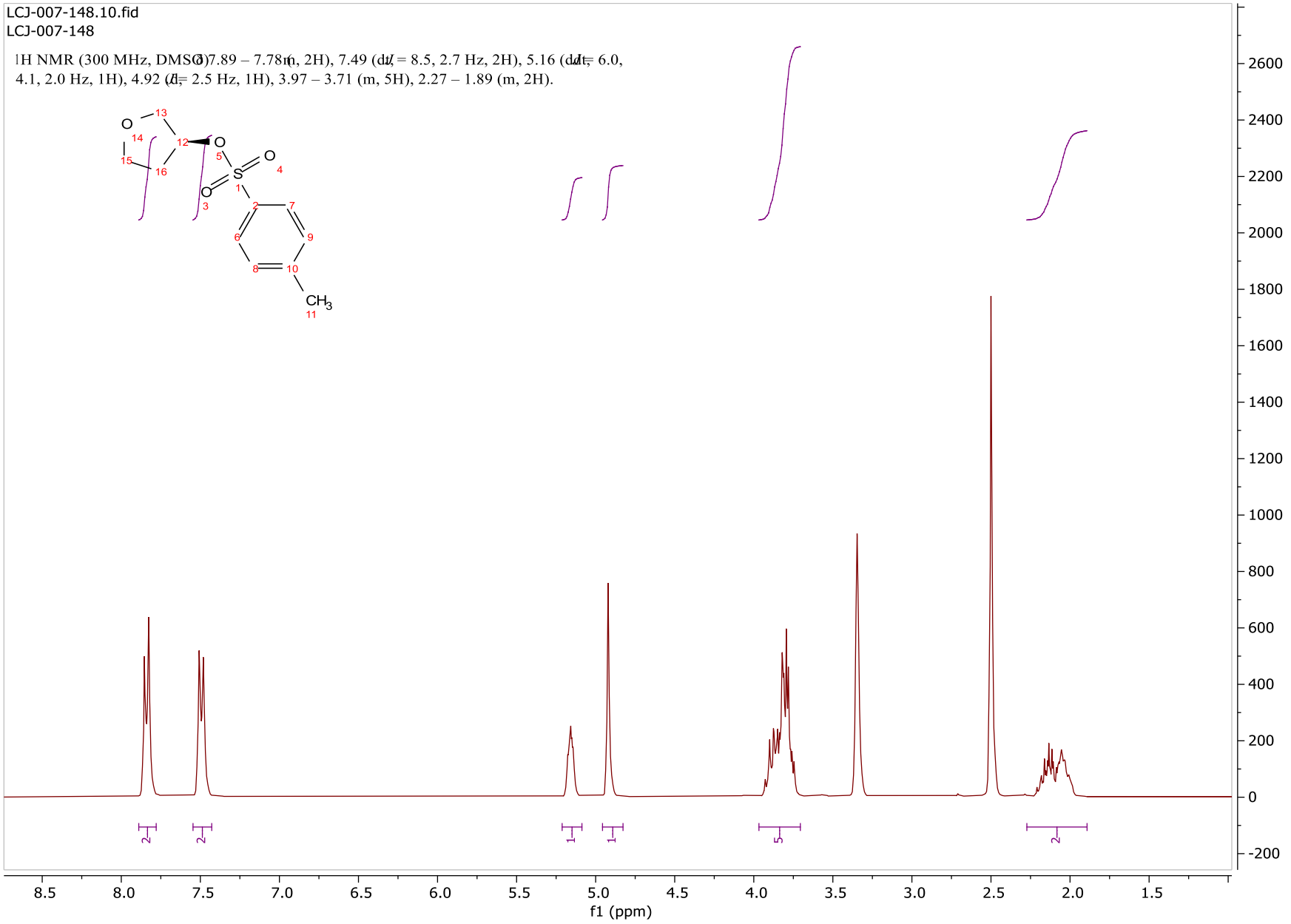
**14i**-$^{13}$C


LCJ-007-147.10.fid
LCJ-007-147
1H NMR (300 MHz, DMSO) 7.87 – 7.78 (m, 2H), 7.49 (d, J = 8.1 Hz, 2H), 5.16 (dd, J = 6.0, 3.9, 1.8 Hz, 1H), 4.92 (s, 2H), 3.95 – 3.70 (m, 4H), 2.22 – 2.09 (m, 1H), 2.04 (td, J = 14.4, 4.6 Hz, 1H).
O
13
14
12
15
16
O
5
O
4
S
1
O
3
2
7
6
9
8
10
CH3
11
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
2-I
2-I
1-I
2-I
4-I
1-I
1-I
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

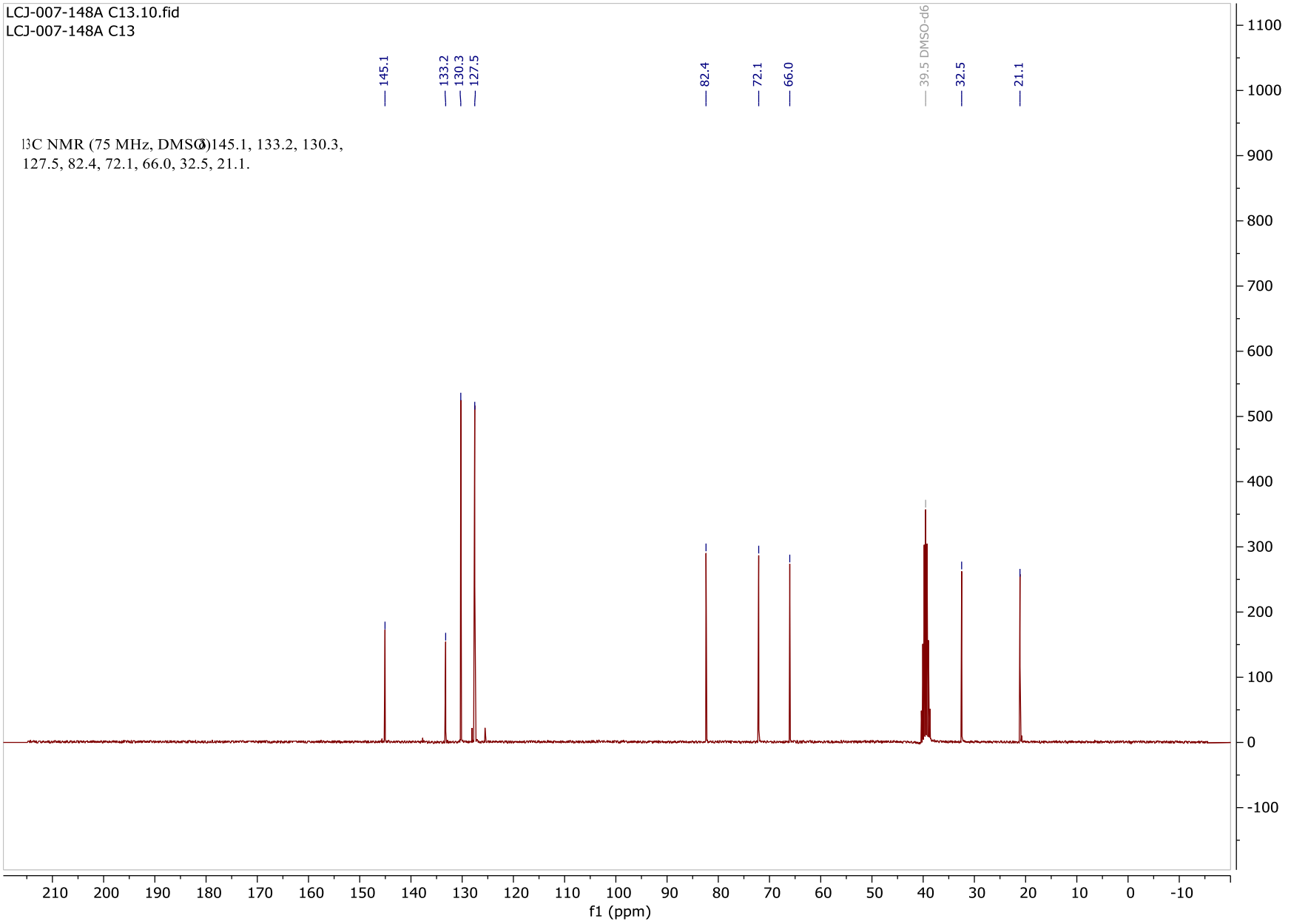
**14j**-$^{1}$H


LCJ-007-147A C13.10.fid
LCJ-007-147A C13
13C NMR (75 MHz, DMSO) δ 145.1, 133.2, 130.3, 127.5, 82.4, 72.1, 66.0, 32.5, 21.1.
145.1
133.2
130.3
127.5
82.4
72.1
66.0
39.5 DMSO-d6
32.5
21.1
f1 (ppm)

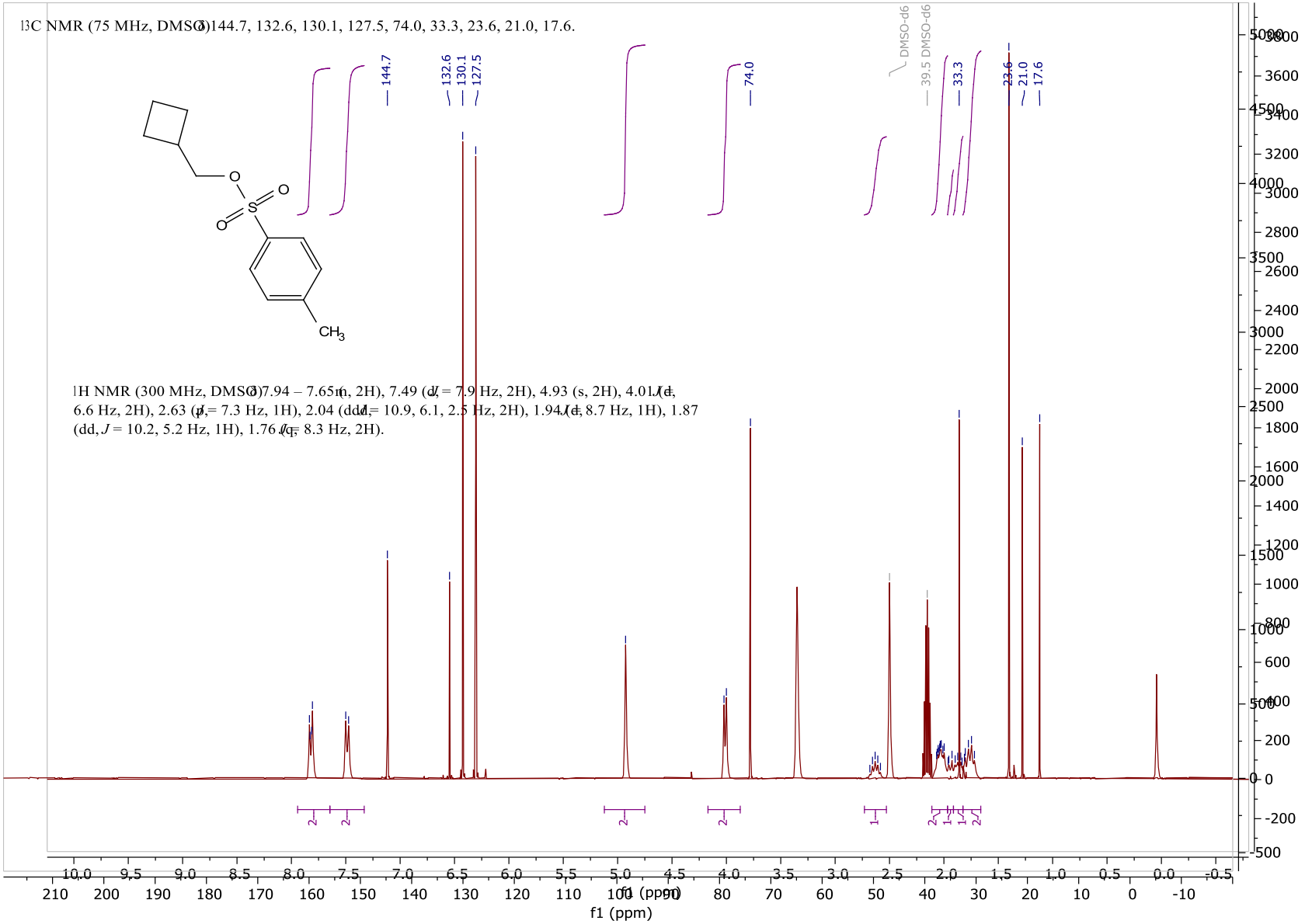
**14j**-$^{13}$C


LCJ-007-148.10.fid
LCJ-007-148
1H NMR (300 MHz, DMSO) 7.89 – 7.78 (m, 2H), 7.49 (dd, J = 8.5, 2.7 Hz, 2H), 5.16 (dd, J = 6.0, 4.1, 2.0 Hz, 1H), 4.92 (d, J = 2.5 Hz, 1H), 3.97 – 3.71 (m, 5H), 2.27 – 1.89 (m, 2H).
f1 (ppm)

**14k**-$^{1}$H

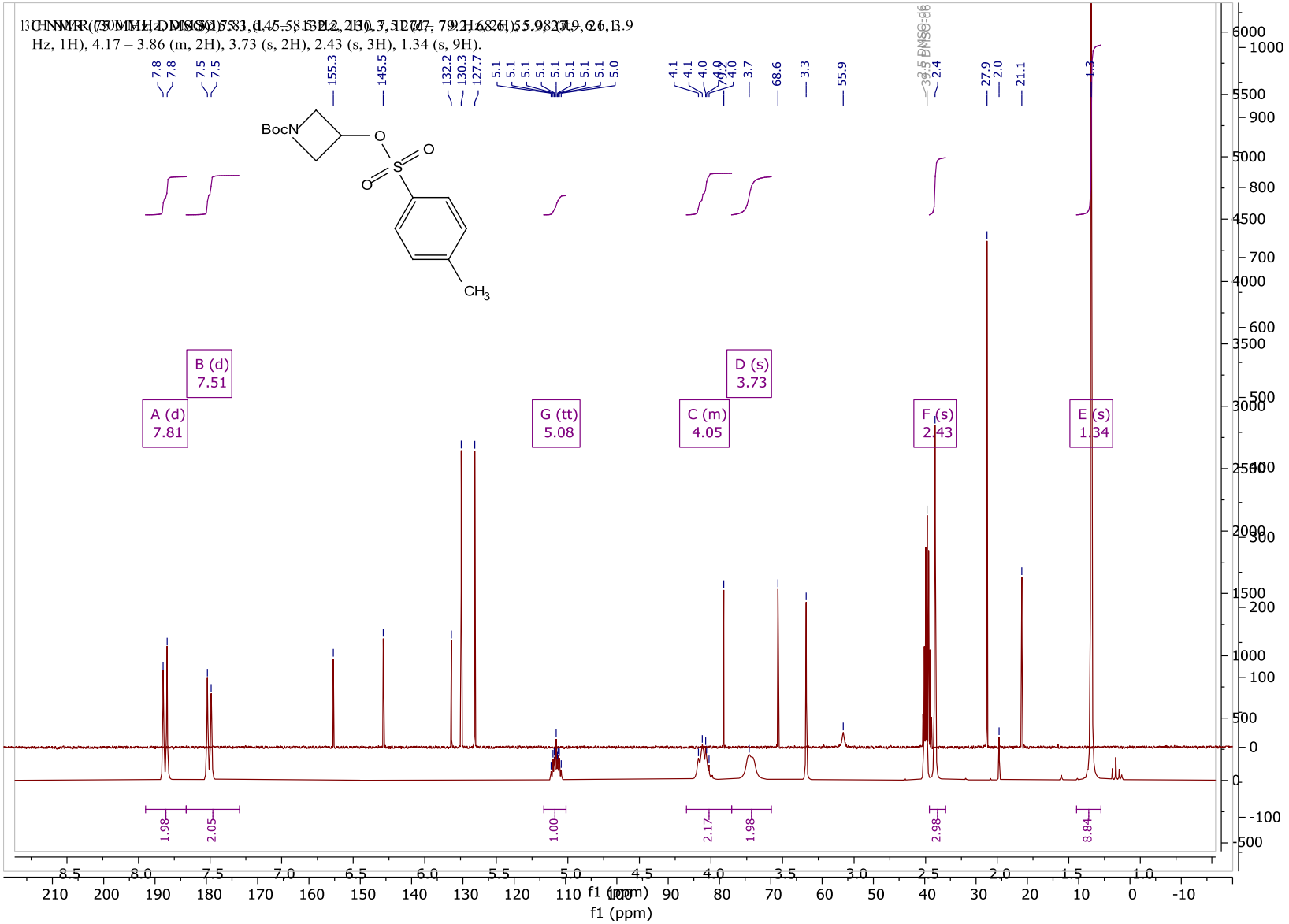

LCJ-007-148A C13.10.fid
LCJ-007-148A C13
145.1
133.2
130.3
127.5
82.4
72.1
66.0
39.5 DMSO-d6
32.5
21.1
13C NMR (75 MHz, DMSO) δ 145.1, 133.2, 130.3, 127.5, 82.4, 72.1, 66.0, 32.5, 21.1.
f1 (ppm)

**14k**-$^{13}$C



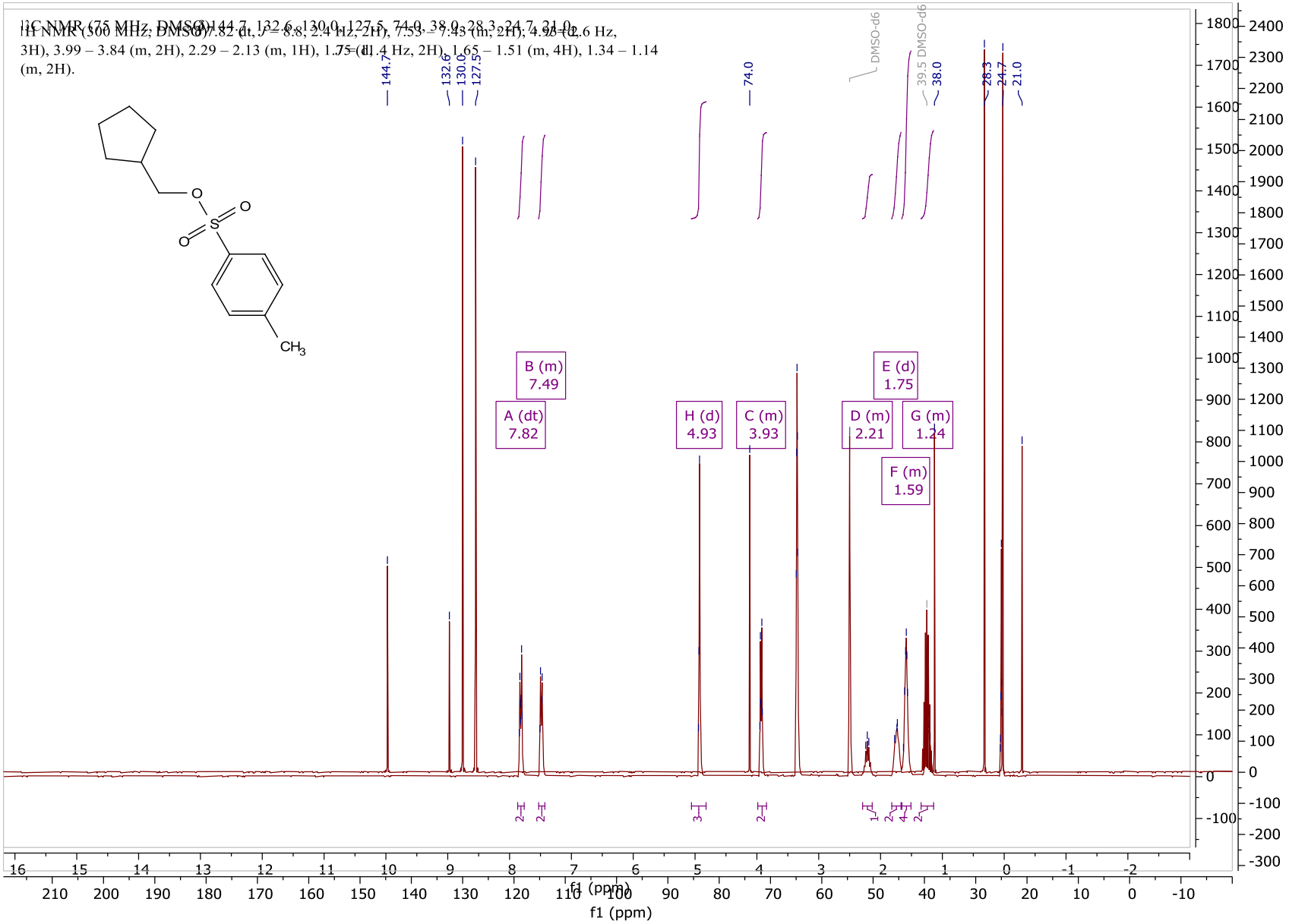

**14l**-$^{1}$H

**14l**-$^{13}$C



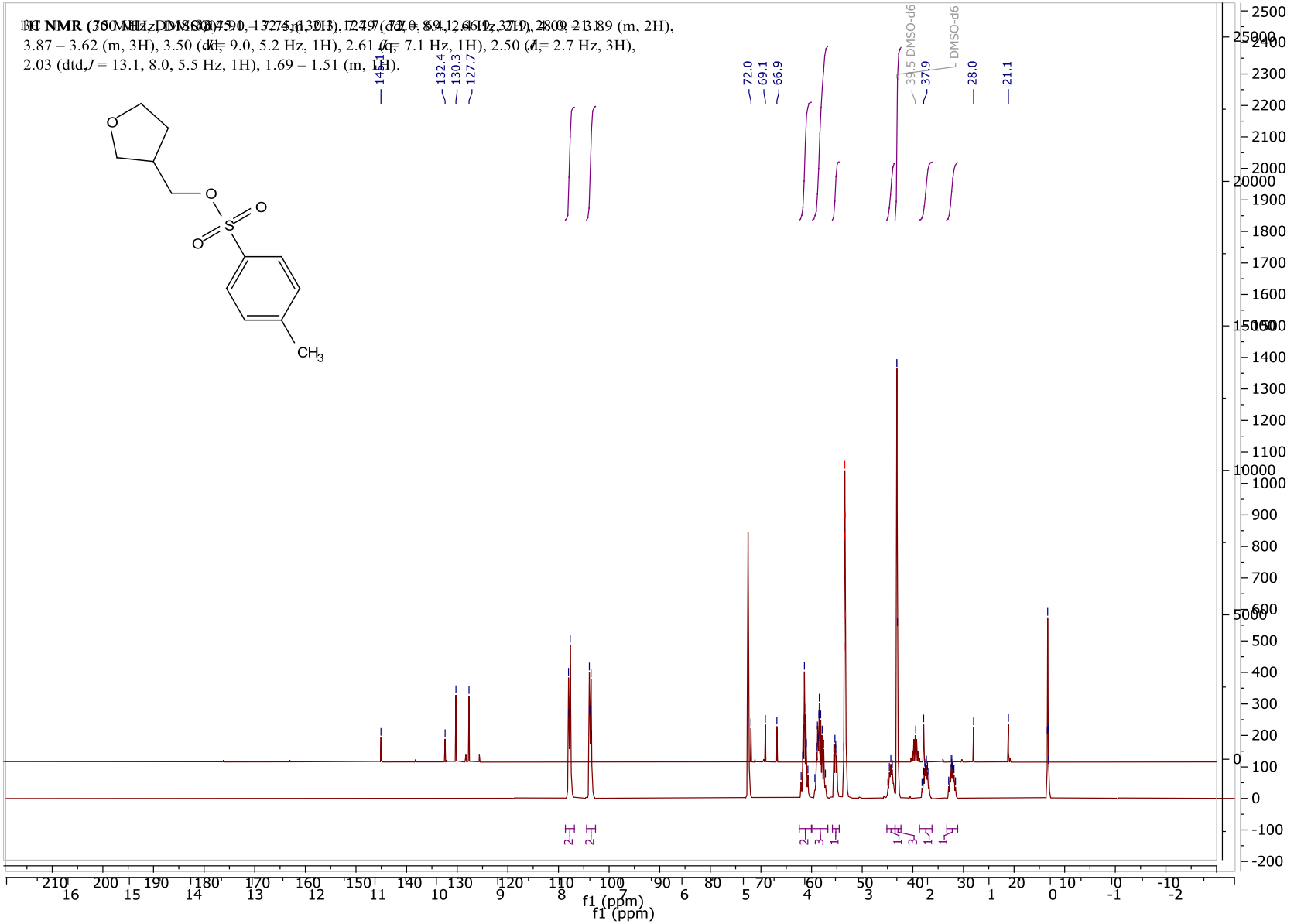

**14m**-$^{1}$H

**14m**-$^{13}$C



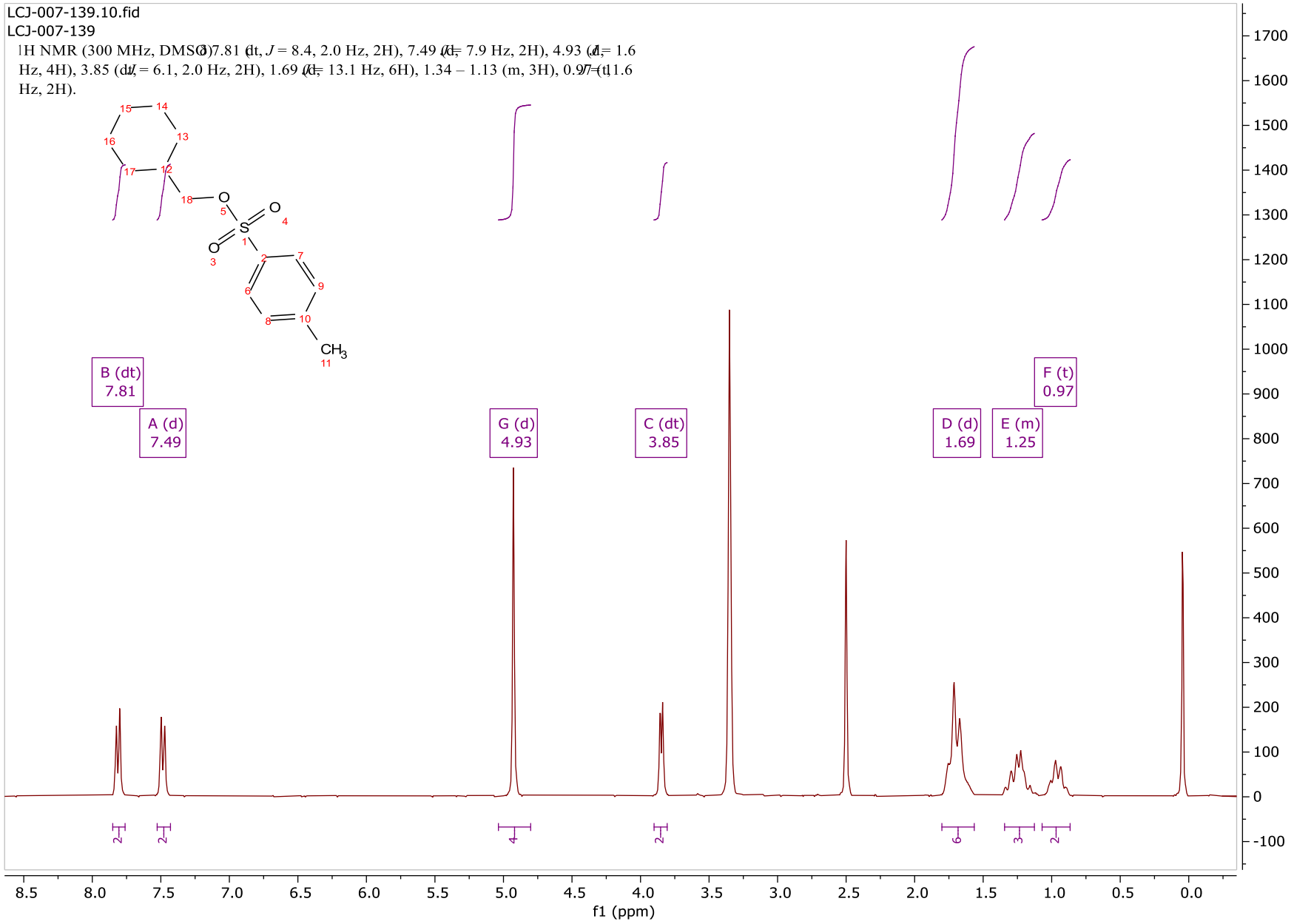

**15n**-$^{1}$H

**15n**-$^{13}$C

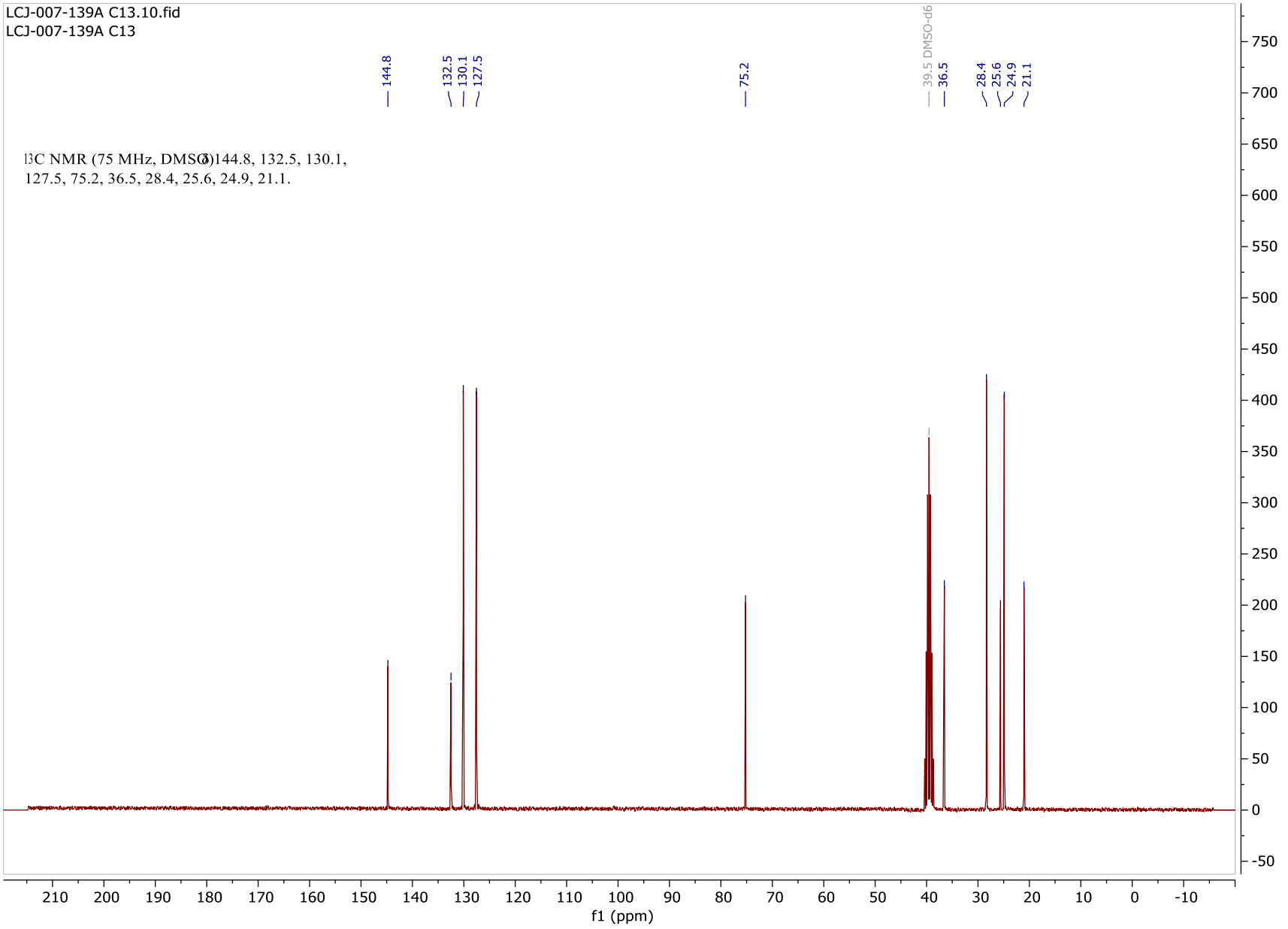



**15o**-$^{1}$H

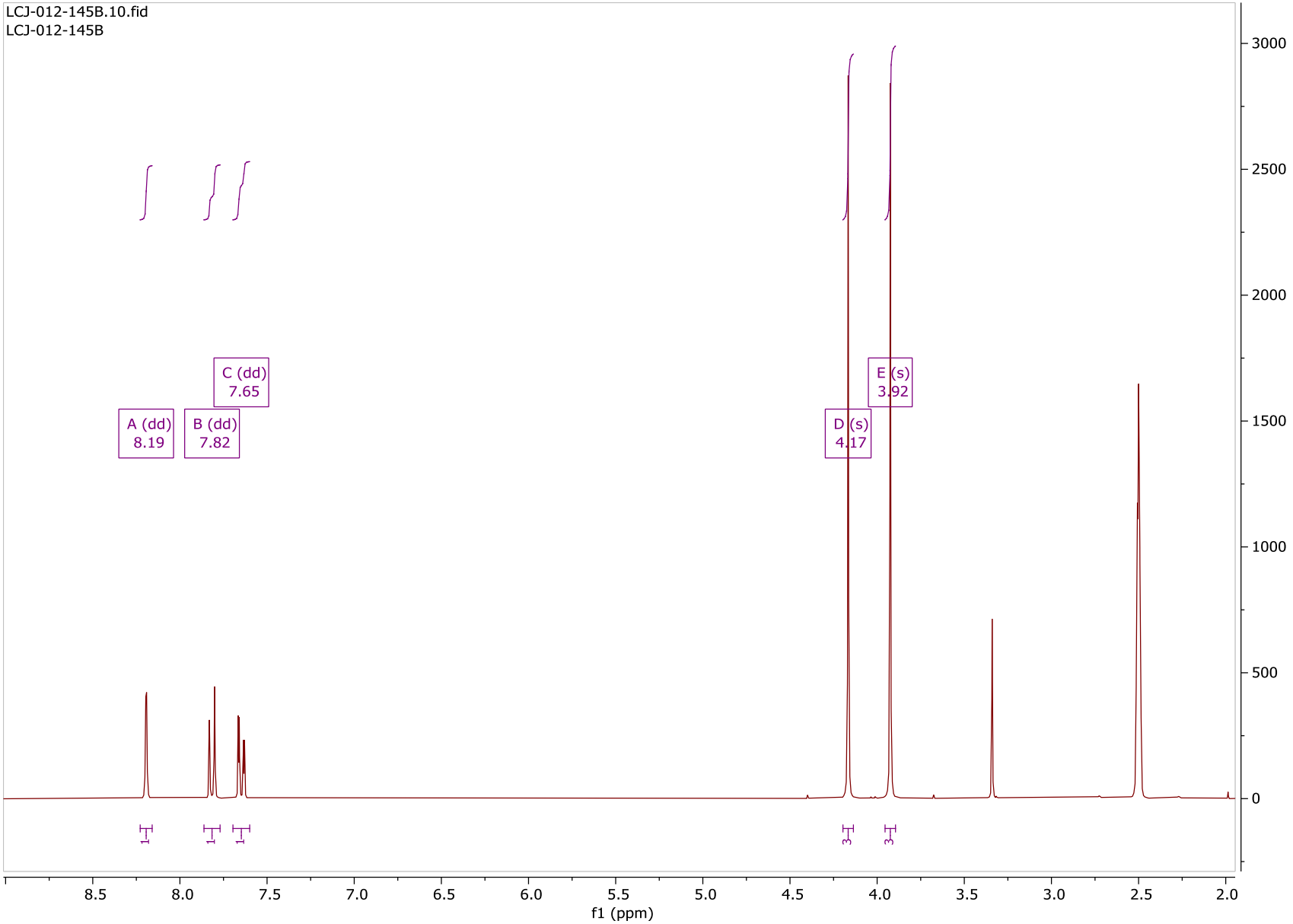
**15o**-$^{13}$C


LCJ-007-139.10.fid
LCJ-007-139
1H NMR (300 MHz, DMSO) δ 7.81 (dt, J = 8.4, 2.0 Hz, 2H), 7.49 (d, J = 7.9 Hz, 2H), 4.93 (d, J = 1.6 Hz, 4H), 3.85 (dt, J = 6.1, 2.0 Hz, 2H), 1.69 (d, J = 13.1 Hz, 6H), 1.34 – 1.13 (m, 3H), 0.97 (t, J = 1.6 Hz, 2H).
B (dt) 7.81
A (d) 7.49
G (d) 4.93
C (dt) 3.85
D (d) 1.69
E (m) 1.25
F (t) 0.97
f1 (ppm)

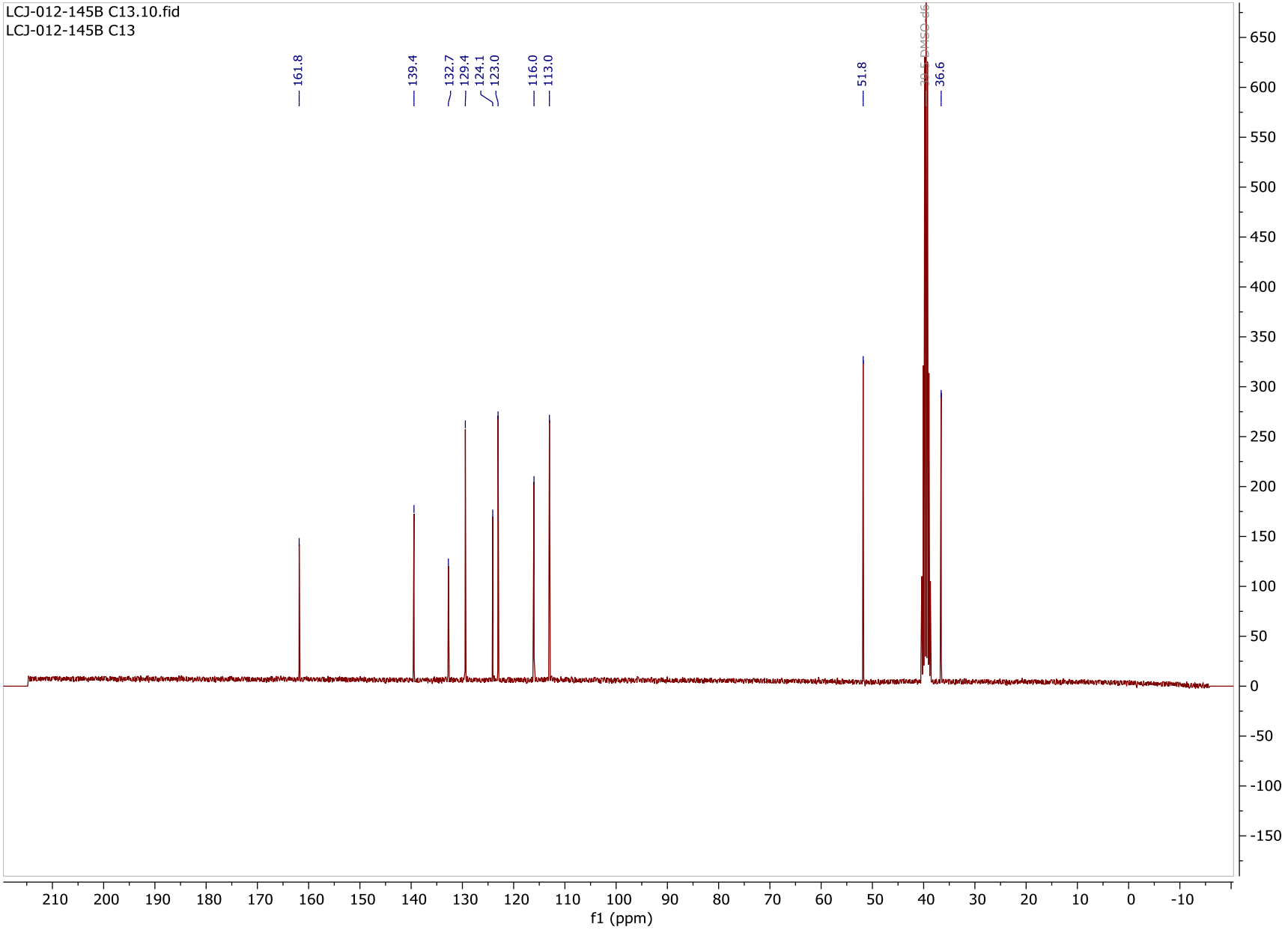
**14p**-$^{1}$H


LCJ-007-139A C13.10.fid
LCJ-007-139A C13
144.8
132.5
130.1
127.5
75.2
39.5 DMSO-d6
36.5
28.4
25.6
24.9
21.1
13C NMR (75 MHz, DMSO) δ 144.8, 132.5, 130.1, 127.5, 75.2, 36.5, 28.4, 25.6, 24.9, 21.1.
f1 (ppm)

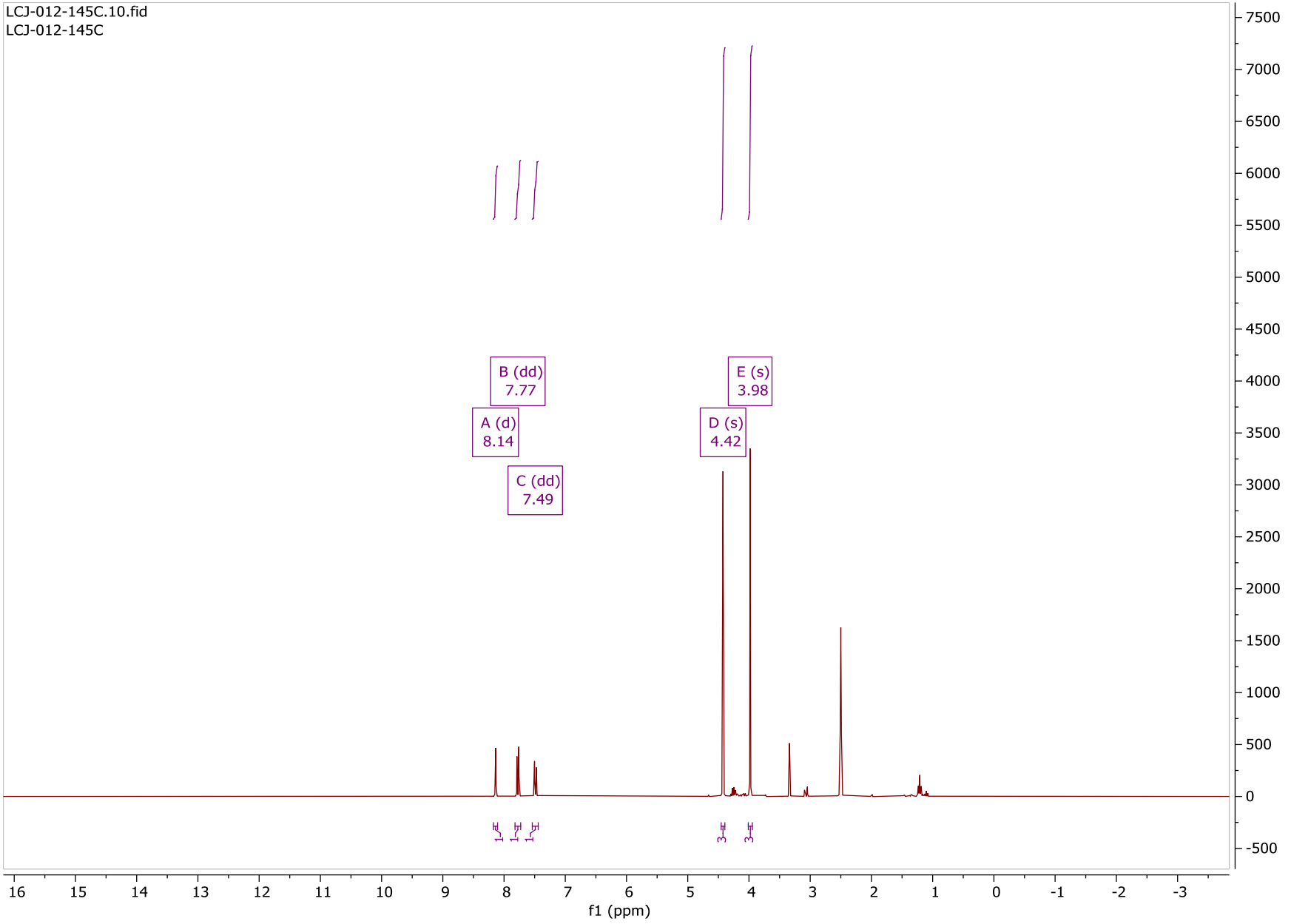
**14p**-$^{13}$C


LCJ-012-145B.10.fid
LCJ-012-145B
A (dd)
8.19
B (dd)
7.82
C (dd)
7.65
D (s)
4.17
E (s)
3.92
1H
1H
1H
3H
3H
3000
2500
2000
1500
1000
500
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

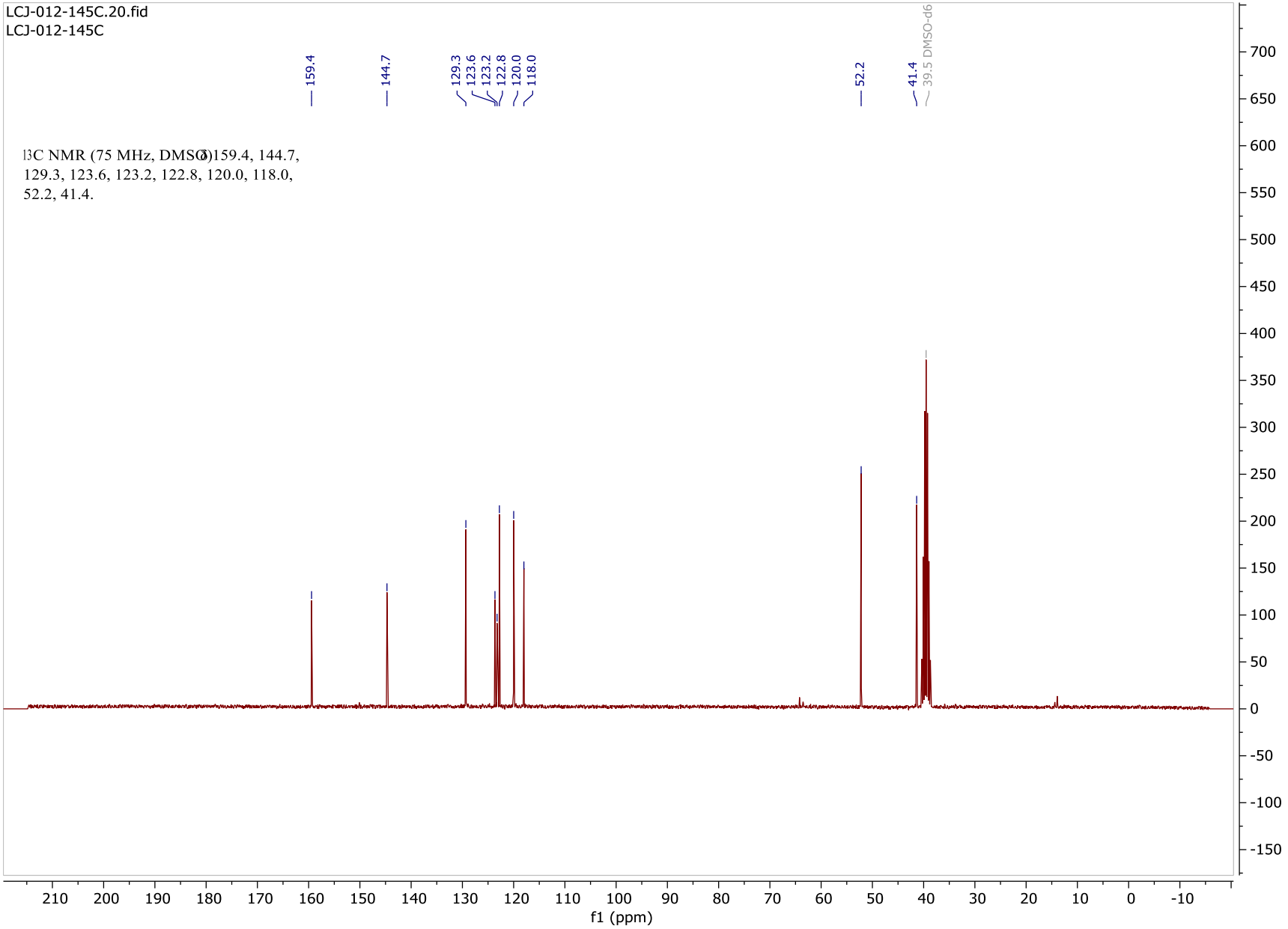
**15a**-$^{1}$H


LCJ-012-145B C13.10.fid
LCJ-012-145B C13
161.8
139.4
132.7
129.4
124.1
123.0
116.0
113.0
51.8
39.5 DMSO-d6
36.6
f1 (ppm)

**15a**-$^{13}$C


LCJ-012-145C.10.fid
LCJ-012-145C
B (dd)
7.77
A (d)
8.14
C (dd)
7.49
E (s)
3.98
D (s)
4.42
f1 (ppm)

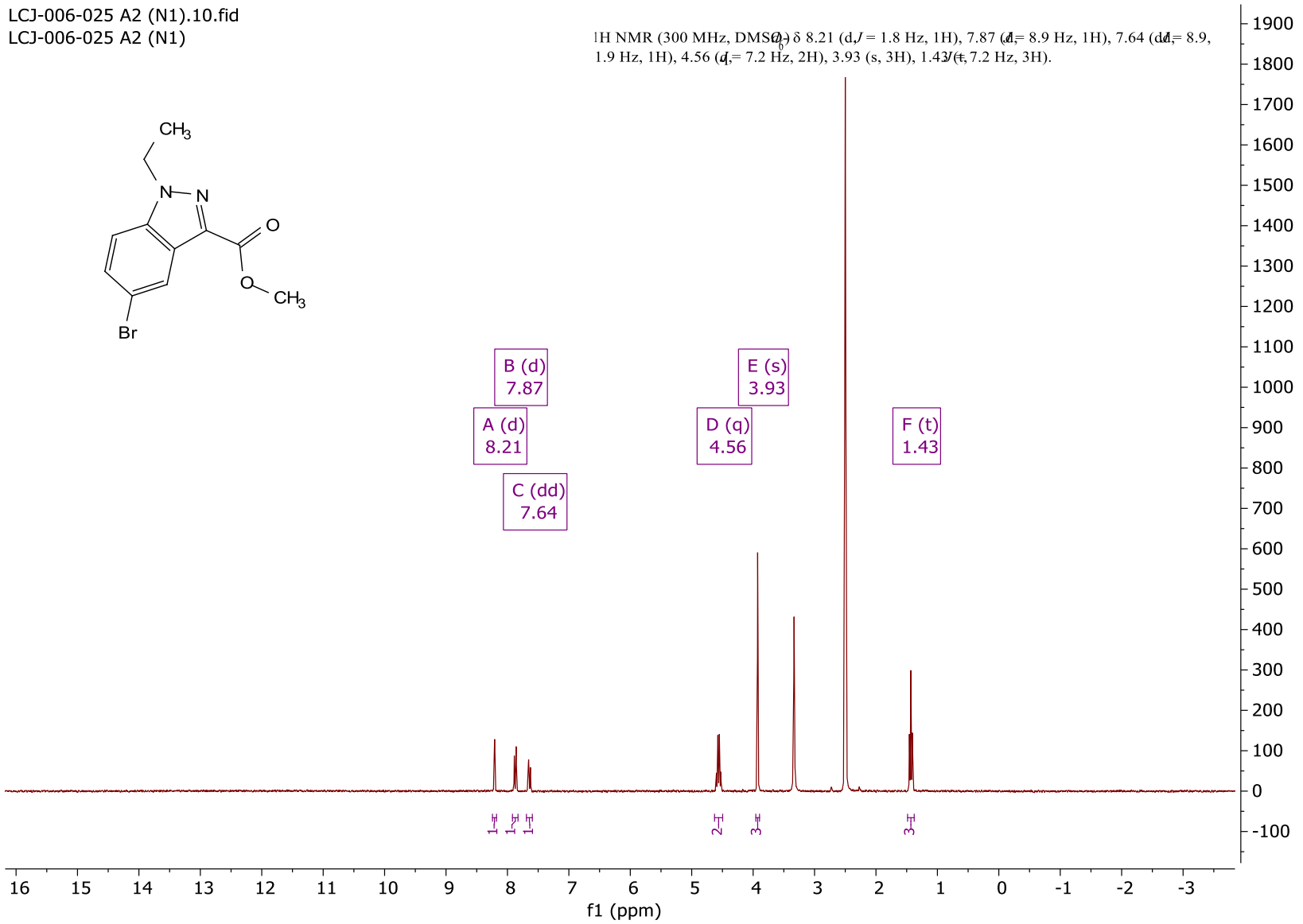
**16a**-$^{1}$H


LCJ-012-145C.20.fid
LCJ-012-145C
159.4
144.7
129.3
123.6
123.2
122.8
120.0
118.0
52.2
41.4
39.5 DMSO-d6
13C NMR (75 MHz, DMSO-d6) δ 159.4, 144.7, 129.3, 123.6, 123.2, 122.8, 120.0, 118.0, 52.2, 41.4.
f1 (ppm)

**16a**-$^{13}$C

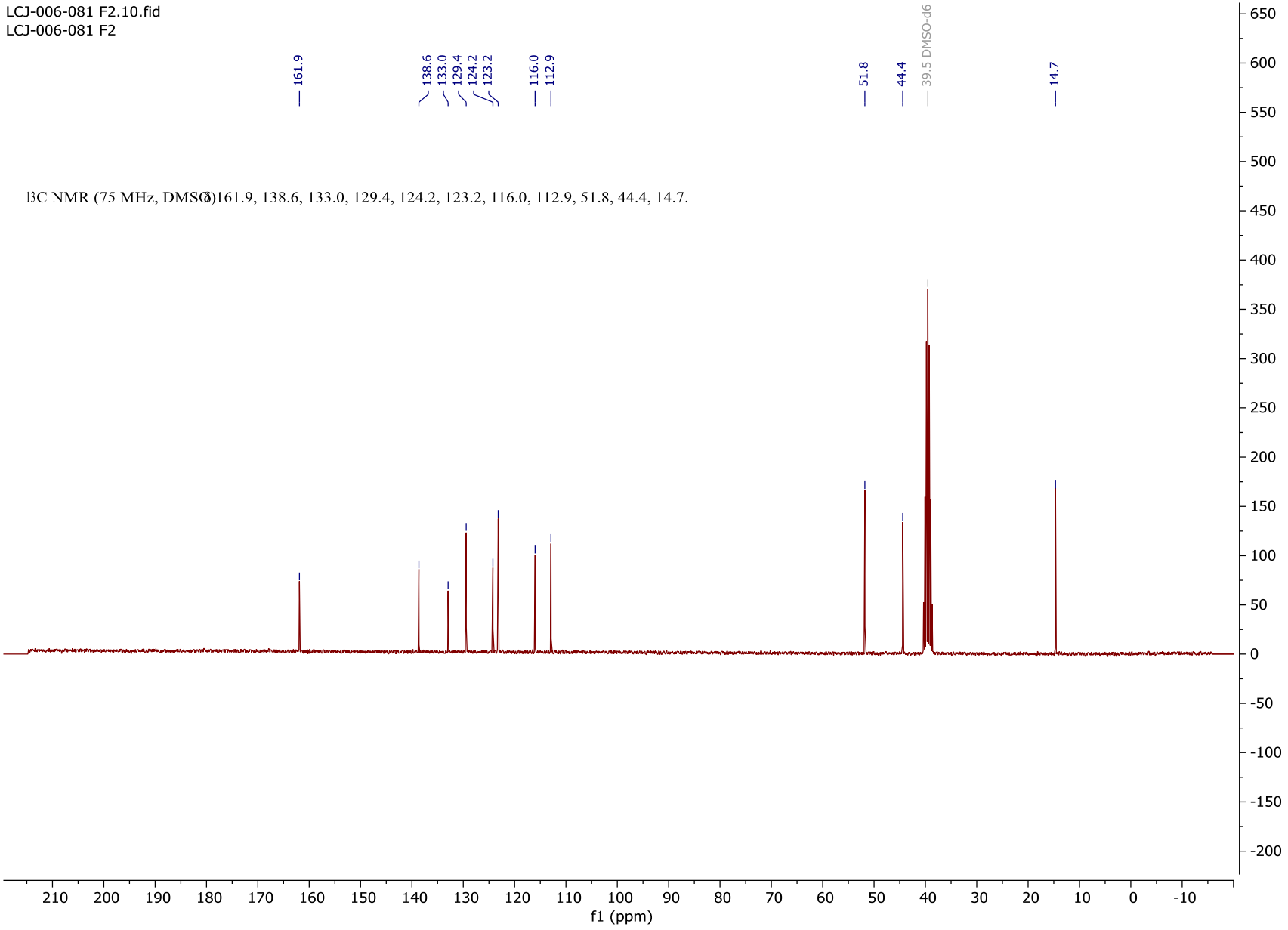
LCJ-006-025 A2 (N1).10.fid
LCJ-006-025 A2 (N1)

$^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.21 (d, $J$ = 1.8 Hz, 1H), 7.87 (d, $J$ = 8.9 Hz, 1H), 7.64 (dd, $J$ = 8.9, 1.9 Hz, 1H), 4.56 (q, $J$ = 7.2 Hz, 2H), 3.93 (s, 3H), 1.43 (t, $J$ = 7.2 Hz, 3H).




**15b**-$^1$H

LCJ-006-081 F2.10.fid
LCJ-006-081 F2

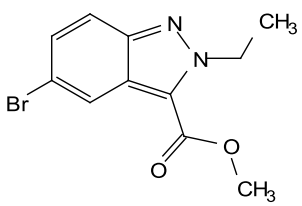



$^{13}$C NMR (75 MHz, DMSO) δ 161.9, 138.6, 133.0, 129.4, 124.2, 123.2, 116.0, 112.9, 51.8, 44.4, 14.7.

**15b**-$^{13}$C

LCJ-006-081 F2C.10.fid
LCJ-006-081 F2C

$^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.16 (dd, $J$ = 1.9, 0.8 Hz, 1H), 7.80 (dd, $J$ = 9.1, 0.8 Hz, 1H), 7.50 (dd, $J$ = 9.1, 1.9 Hz, 1H), 4.86 (q, $J$ = 7.2 Hz, 2H), 4.00 (s, 3H), 1.48 (t, $J$ = 7.2 Hz, 3H).

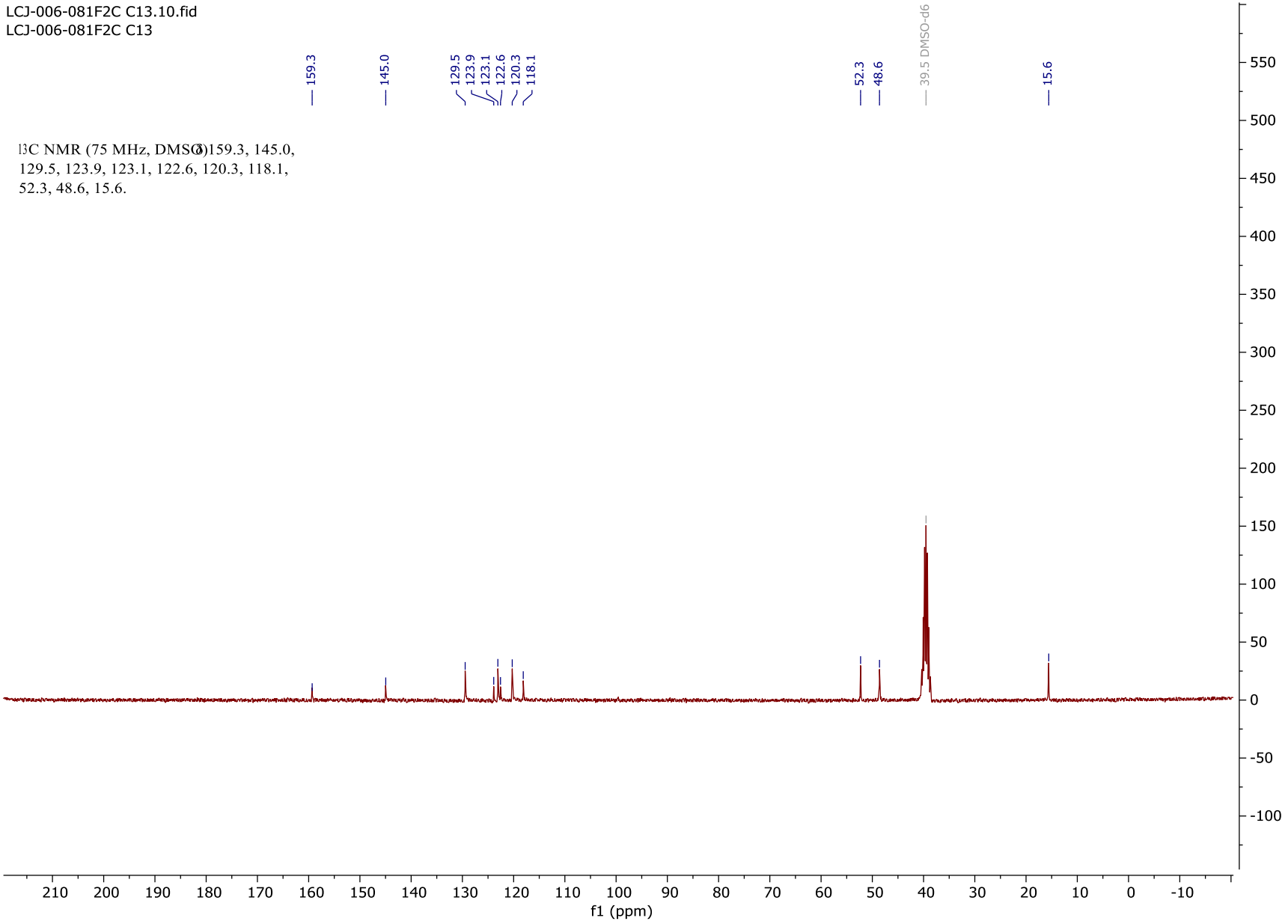






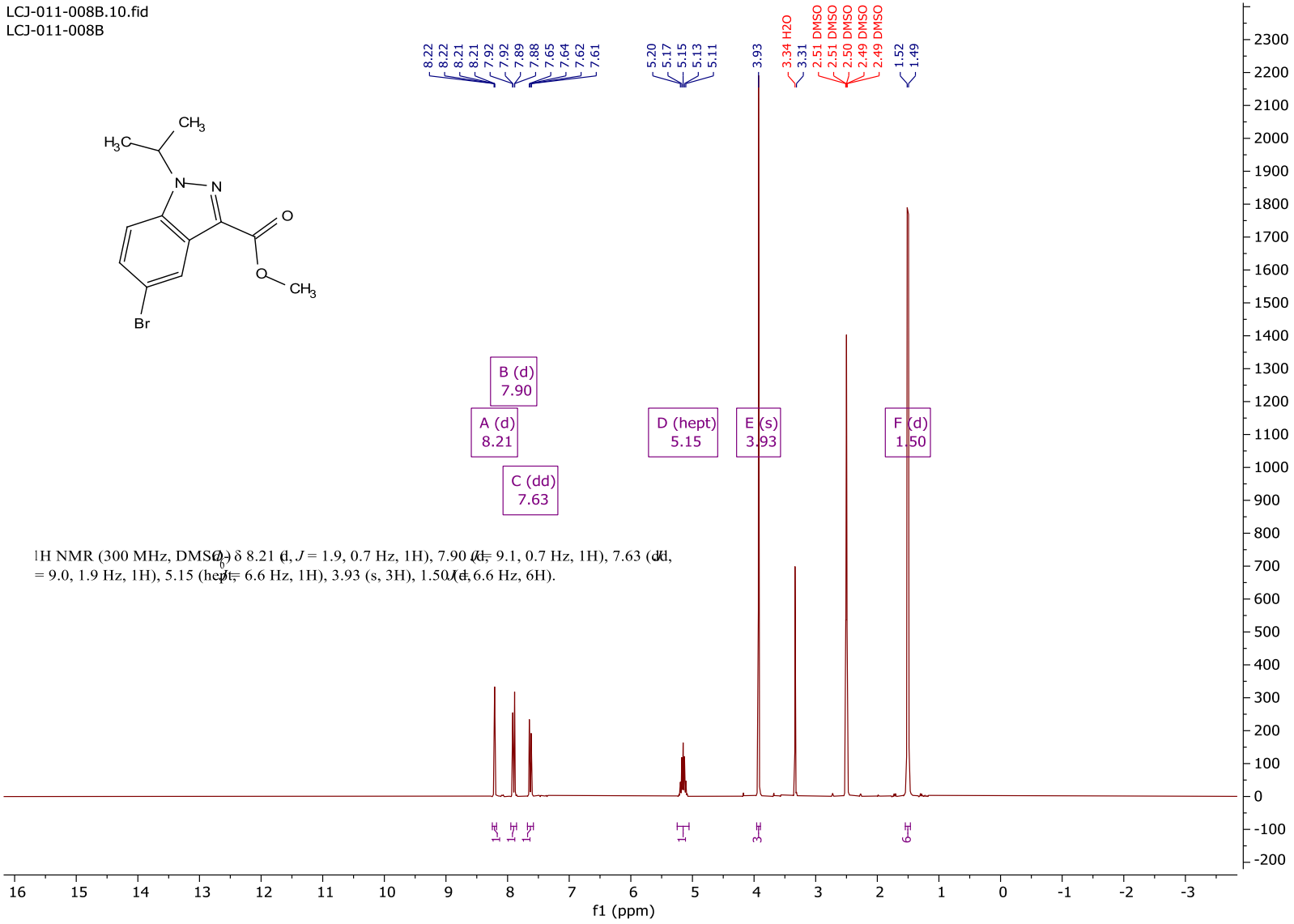
**16b**-$^1$H

LCJ-006-081F2C C13.10.fid
LCJ-006-081F2C C13

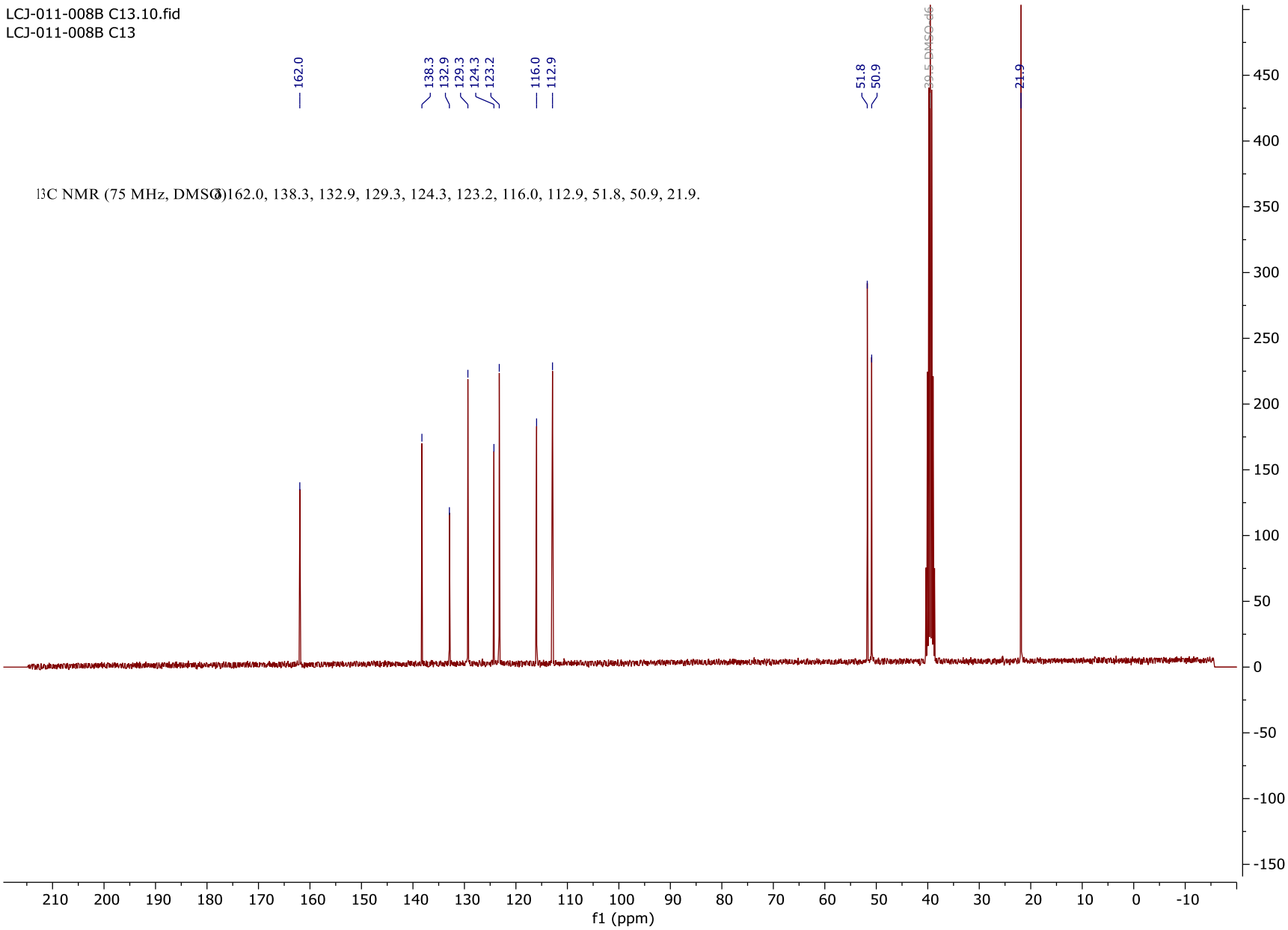



$^{13}$C NMR (75 MHz, DMSO) 159.3, 145.0, 129.5, 123.9, 123.1, 122.6, 120.3, 118.1, 52.3, 48.6, 15.6.

**16b**-$^{13}$C


LCJ-011-008B.10.fid
LCJ-011-008B
8.22 8.22 8.21 8.21 7.92 7.92 7.89 7.88 7.65 7.64 7.62 7.61
5.20 5.17 5.15 5.13 5.11
3.93
3.34 H2O
3.31
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.49 DMSO
2.49 DMSO
1.52
1.49
B (d) 7.90
A (d) 8.21
C (dd) 7.63
D (hept) 5.15
E (s) 3.93
F (d) 1.50
1H NMR (300 MHz, DMSO-d6) δ 8.21 (d, J = 1.9, 0.7 Hz, 1H), 7.90 (d, J = 9.1, 0.7 Hz, 1H), 7.63 (dd, J = 9.0, 1.9 Hz, 1H), 5.15 (hept, J = 6.6 Hz, 1H), 3.93 (s, 3H), 1.50 (d, J = 6.6 Hz, 6H).
1.00 1.00 1.00 1.00 3.00 6.00
f1 (ppm)

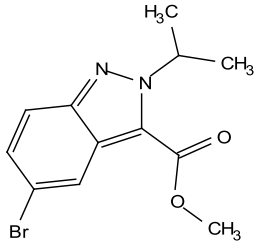
**15c**-$^{1}$H


LCJ-011-008B C13.10.fid
LCJ-011-008B C13
162.0
138.3
132.9
129.3
124.3
123.2
116.0
112.9
51.8
50.9
39.5 DMSO-d6
21.9
13C NMR (75 MHz, DMSO) δ 162.0, 138.3, 132.9, 129.3, 124.3, 123.2, 116.0, 112.9, 51.8, 50.9, 21.9.
f1 (ppm)

**15c**-$^{13}$C

LCJ-011-008C.10.fid
LCJ-011-008C

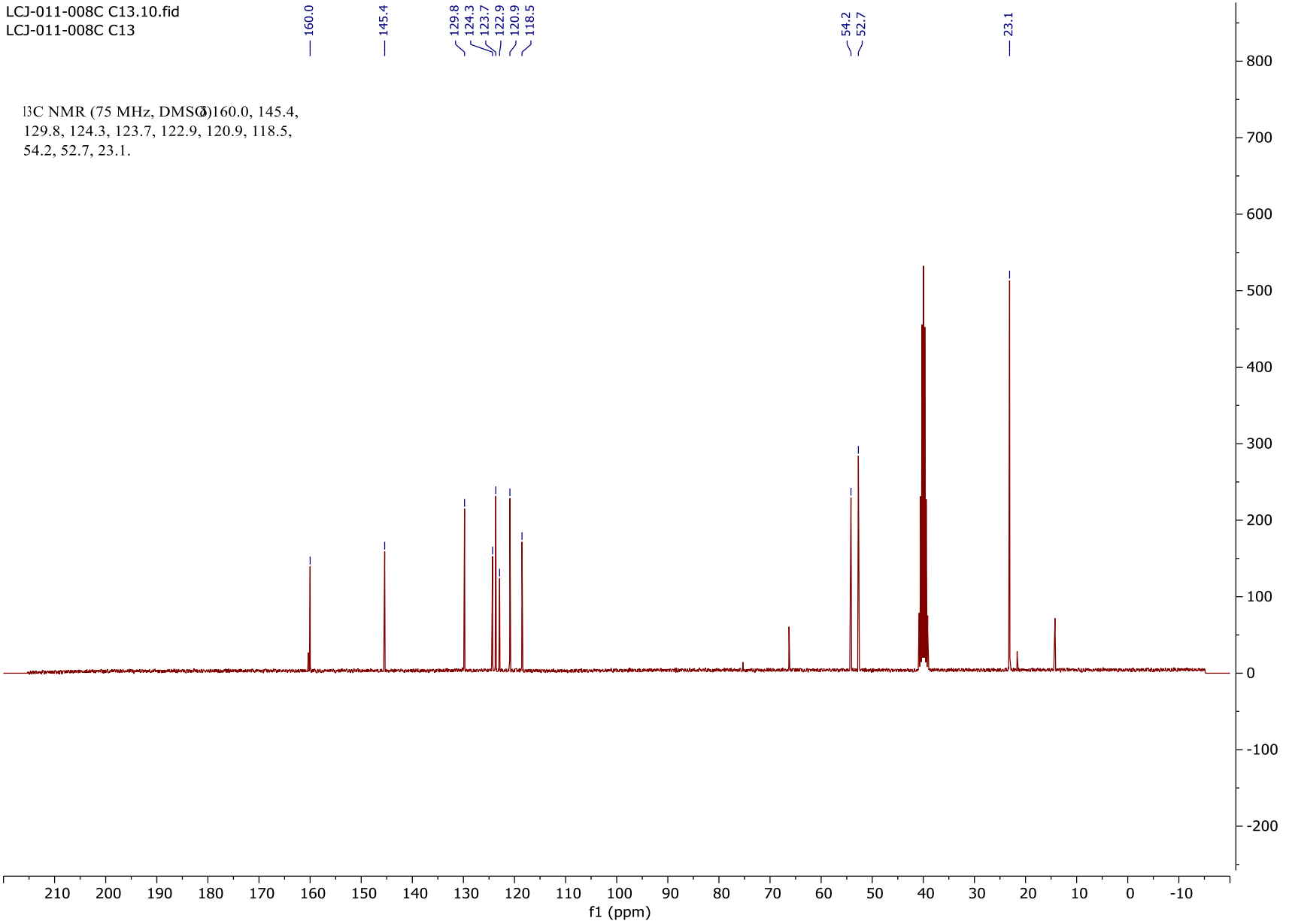
$^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.17 (d, $J$ = 1.9 Hz, 1H), 7.82 (d, $J$ = 9.0 Hz, 1H), 7.49 (dd, $J$ = 9.1, 1.9 Hz, 1H), 5.84 (hept, $J$ = 6.6 Hz, 1H), 3.99 (s, 3H), 1.55 (d, $J$ = 6.6 Hz, 6H).







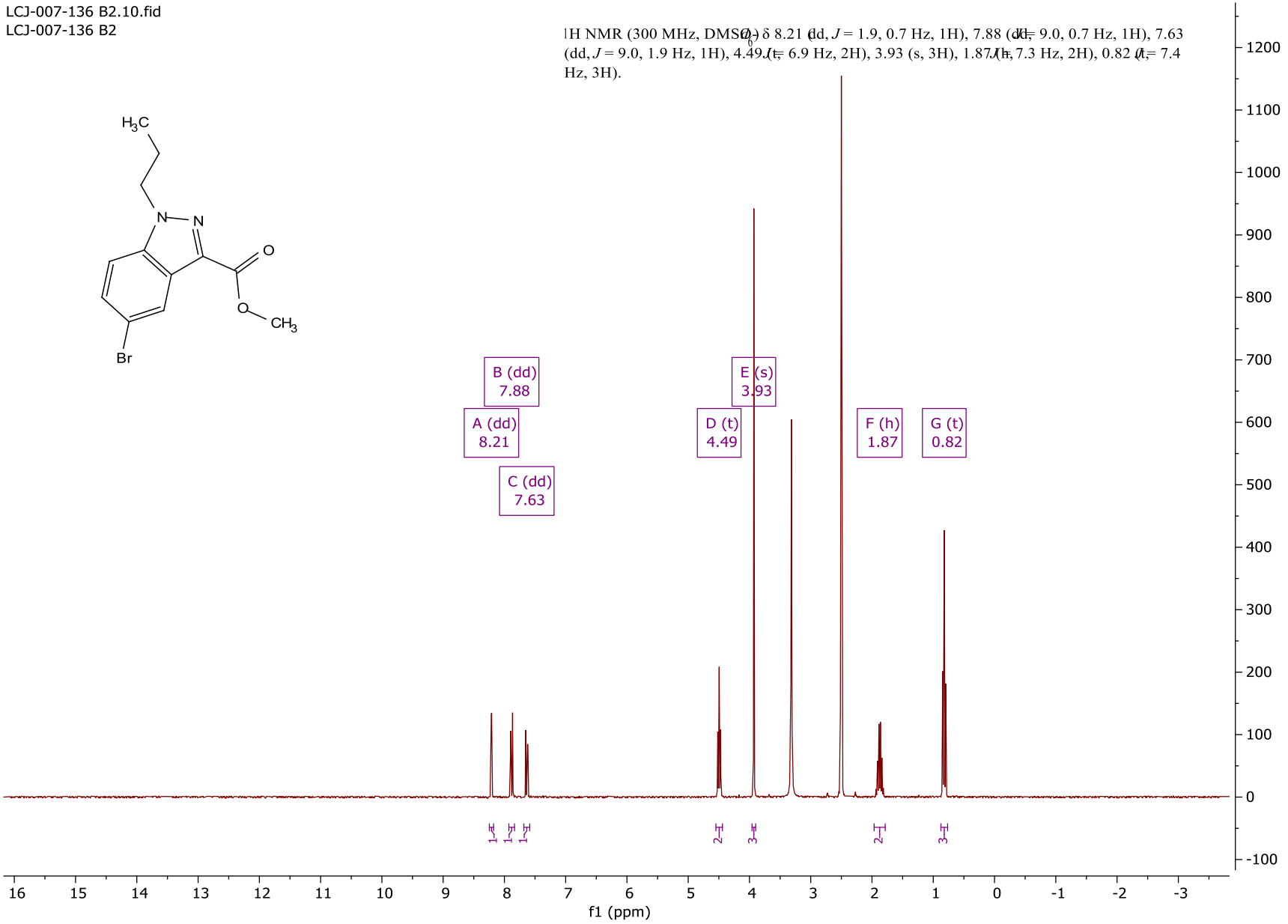
**16c**-$^1$H


LCJ-011-008C C13.10.fid
LCJ-011-008C C13
160.0
145.4
129.8
124.3
123.7
122.9
120.9
118.5
54.2
52.7
23.1
13C NMR (75 MHz, DMSO) δ 160.0, 145.4,
129.8, 124.3, 123.7, 122.9, 120.9, 118.5,
54.2, 52.7, 23.1.
800
700
600
500
400
300
200
100
0
-100
-200
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

**16c**-$^{13}$C

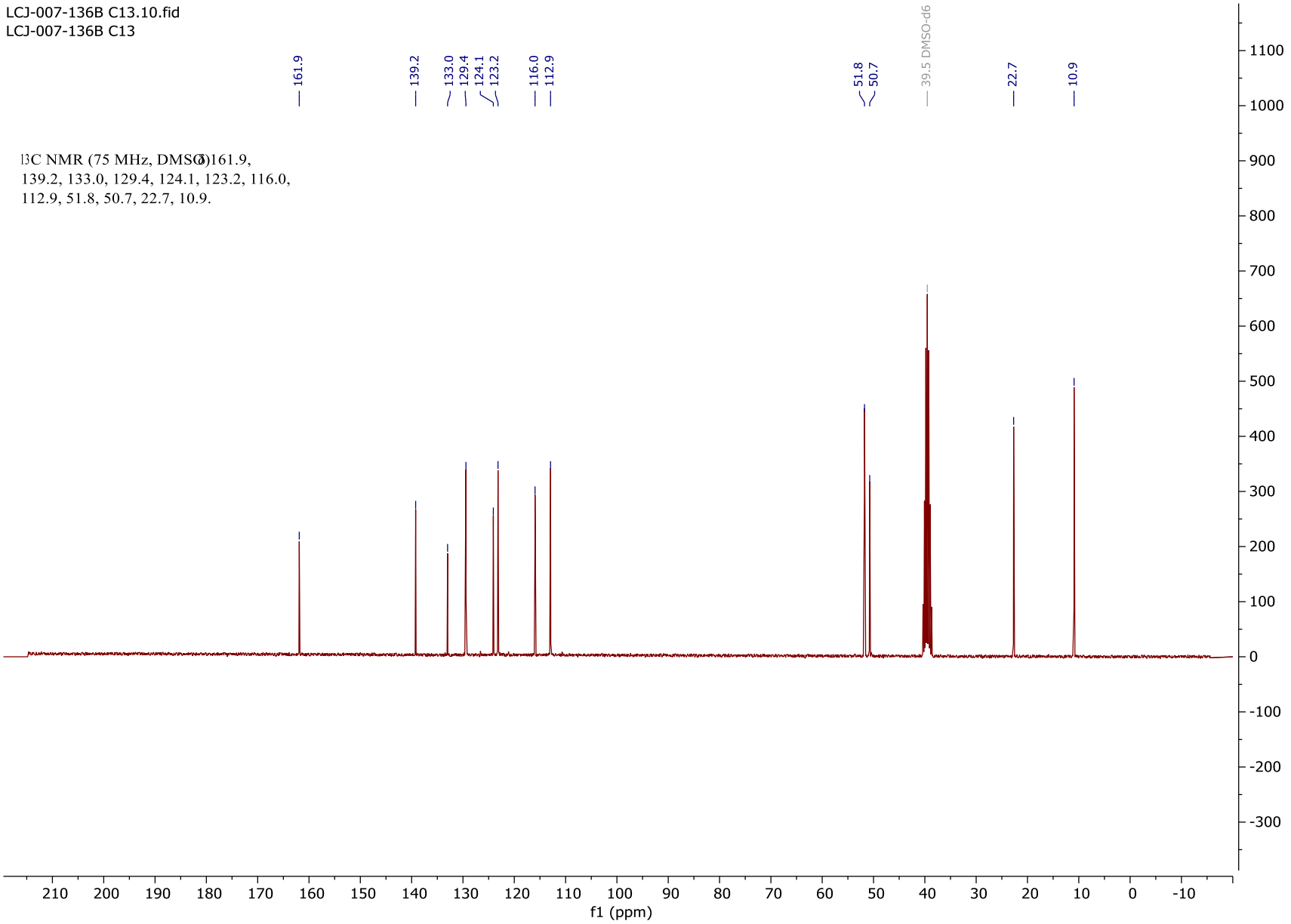
LCJ-007-136 B2.10.fid
LCJ-007-136 B2

$^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.21 (dd, $J$ = 1.9, 0.7 Hz, 1H), 7.88 (dd, $J$ = 9.0, 0.7 Hz, 1H), 7.63 (dd, $J$ = 9.0, 1.9 Hz, 1H), 4.49 (t, $J$ = 6.9 Hz, 2H), 3.93 (s, 3H), 1.87 (h, $J$ = 7.3 Hz, 2H), 0.82 (t, $J$ = 7.4 Hz, 3H).




**15d**-$^1$H

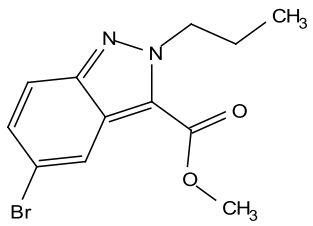
LCJ-007-136B C13.10.fid
LCJ-007-136B C13




$^{13}$C NMR (75 MHz, DMSO) $\delta$ 161.9, 139.2, 133.0, 129.4, 124.1, 123.2, 116.0, 112.9, 51.8, 50.7, 22.7, 10.9.

**15d**-$^{13}$C

LCJ-007-136 C1.10.fid
LCJ-007-136 C1




$^1$H NMR (300 MHz, DMSO) $\delta$ 8.17 (dd, $J$ = 1.9, 0.8 Hz, 1H), 7.80 (dd, $J$ = 9.1, 0.8 Hz, 1H), 7.50 (dd, $J$ = 9.1, 1.9 Hz, 1H), 4.80 (t, $J$ = 7.2 Hz, 2H), 1.92 (h, $J$ = 7.4 Hz, 2H), 0.87 (t, $J$ = 7.4 Hz, 3H).

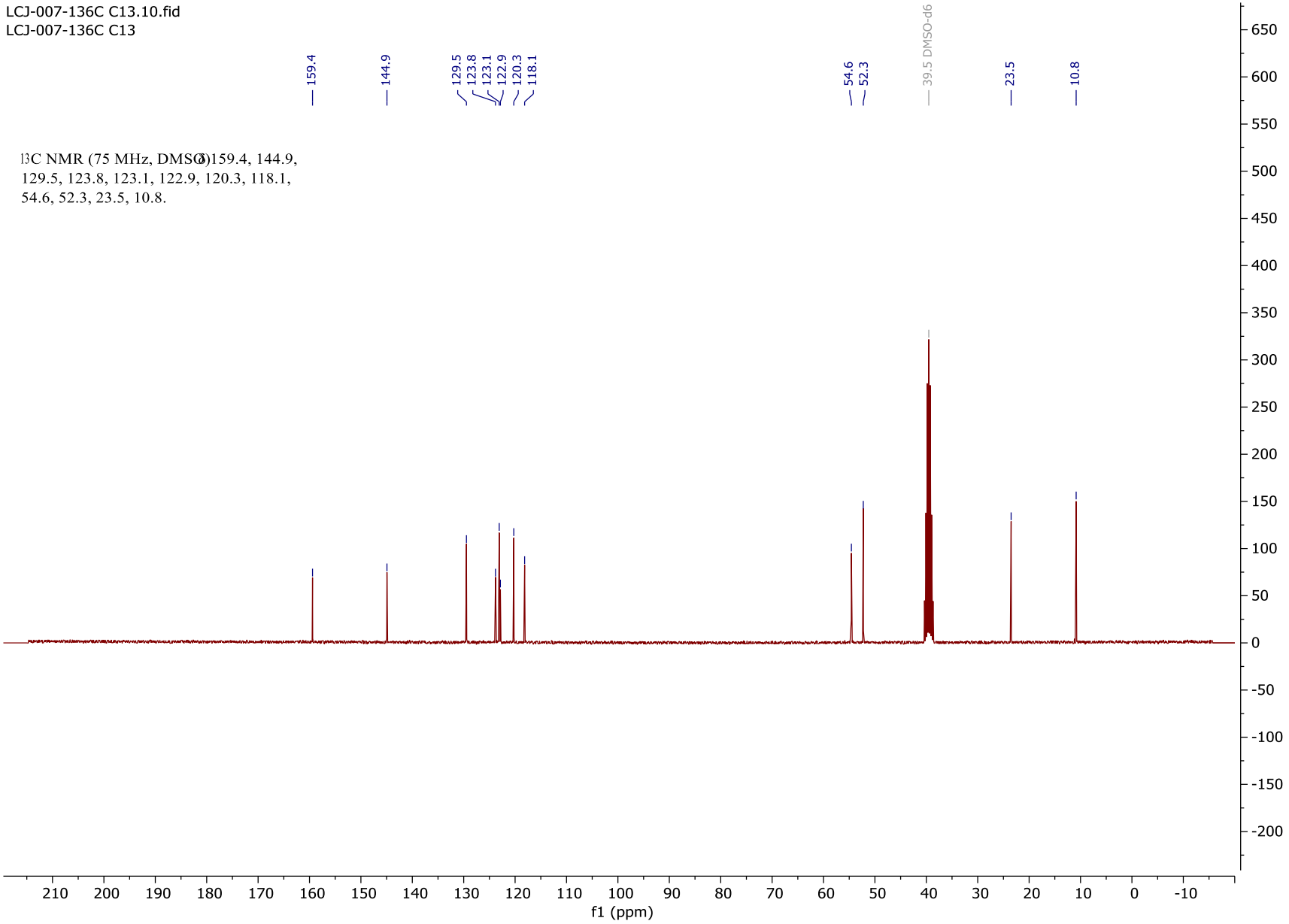



**16d**-$^1$H

LCJ-007-136C C13.10.fid
LCJ-007-136C C13

159.4
144.9
129.5
123.8
123.1
122.9
120.3
118.1
54.6
52.3
39.5 DMSO-d6
23.5
10.8

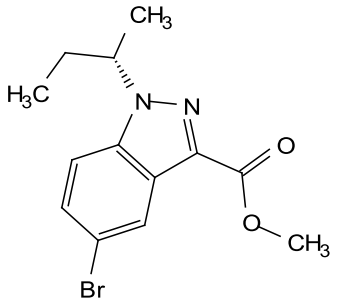
$^{13}$C NMR (75 MHz, DMSO) 159.4, 144.9, 129.5, 123.8, 123.1, 122.9, 120.3, 118.1, 54.6, 52.3, 23.5, 10.8.




**16d**-$^{13}$C

LCJ-007-152B.10.fid
LCJ-007-152B

$^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.22 (d, $J$ = 1.8 Hz, 1H), 7.92 (d, $J$ = 9.0 Hz, 1H), 7.62 (dd, $J$ = 9.0, 1.9 Hz, 1H), 4.98 – 4.85 (m, 1H), 3.93 (s, 3H), 2.05 – 1.76 (m, 2H), 1.50 (d, $J$ = 6.6 Hz, 3H), 0.66 (t, $J$ = 7.4 Hz, 3H).

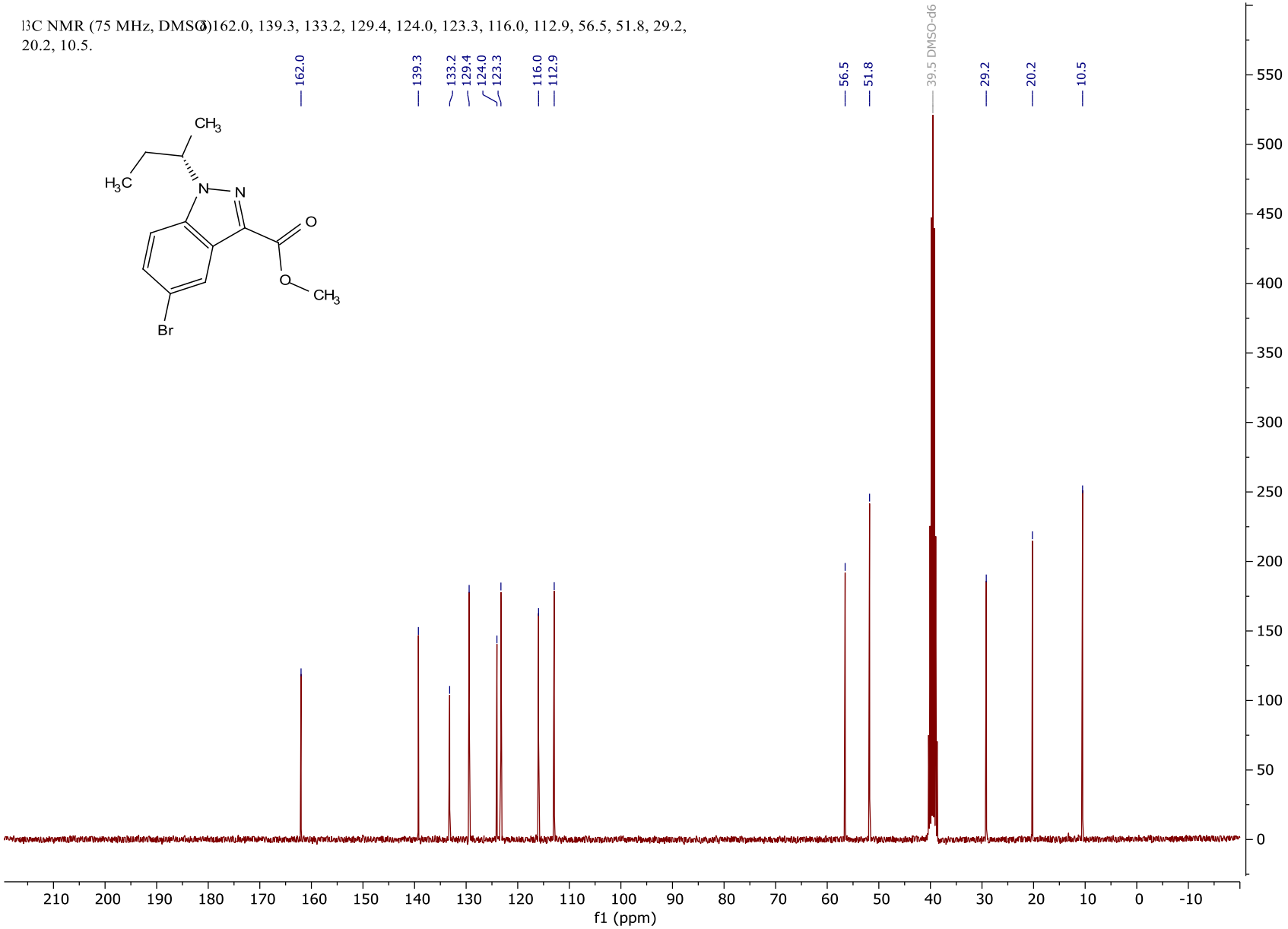






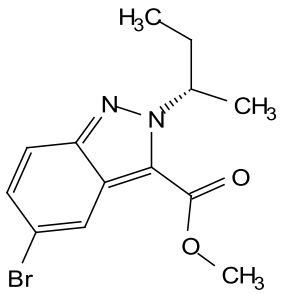
**15e**-$^1$H

13C NMR (75 MHz, DMSO) δ 162.0, 139.3, 133.2, 129.4, 124.0, 123.3, 116.0, 112.9, 56.5, 51.8, 29.2, 20.2, 10.5.




**15e**-$^{13}$C

LCJ-007-152 C1.10.fid
LCJ-007-152 C1

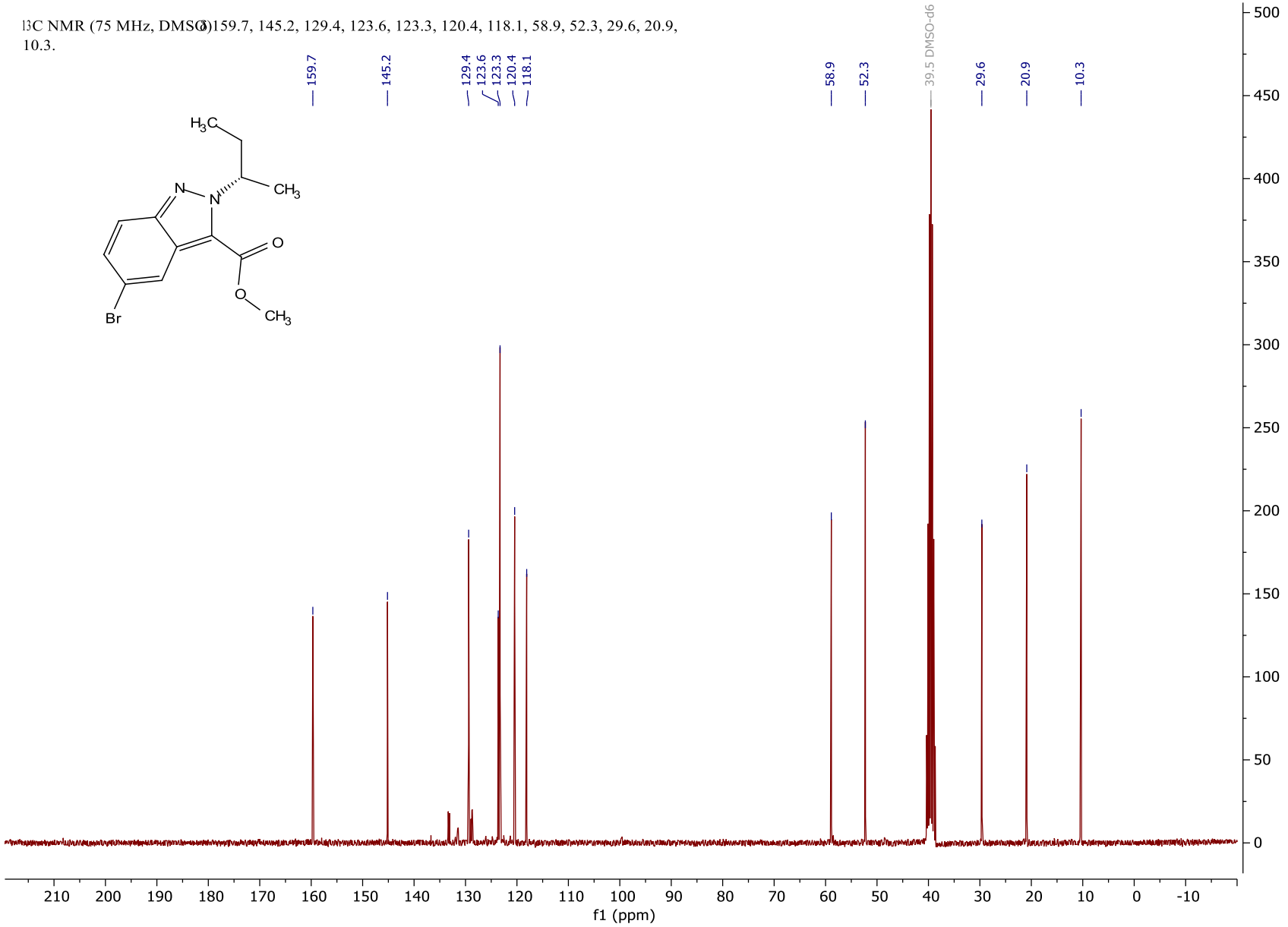



$^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.17 (d, $J$ = 1.9, 0.8 Hz, 1H), 7.82 (d, $J$ = 9.1, 0.8 Hz, 1H), 7.49 (dd, $J$ = 9.1, 1.9 Hz, 1H), 5.78 – 5.61 (m, 1H), 3.99 (s, 3H), 2.13 – 1.79 (m, 2H), 1.54 (d, $J$ = 7.4 Hz, 3H), 0.70 (t, $J$ = 7.4 Hz, 3H).



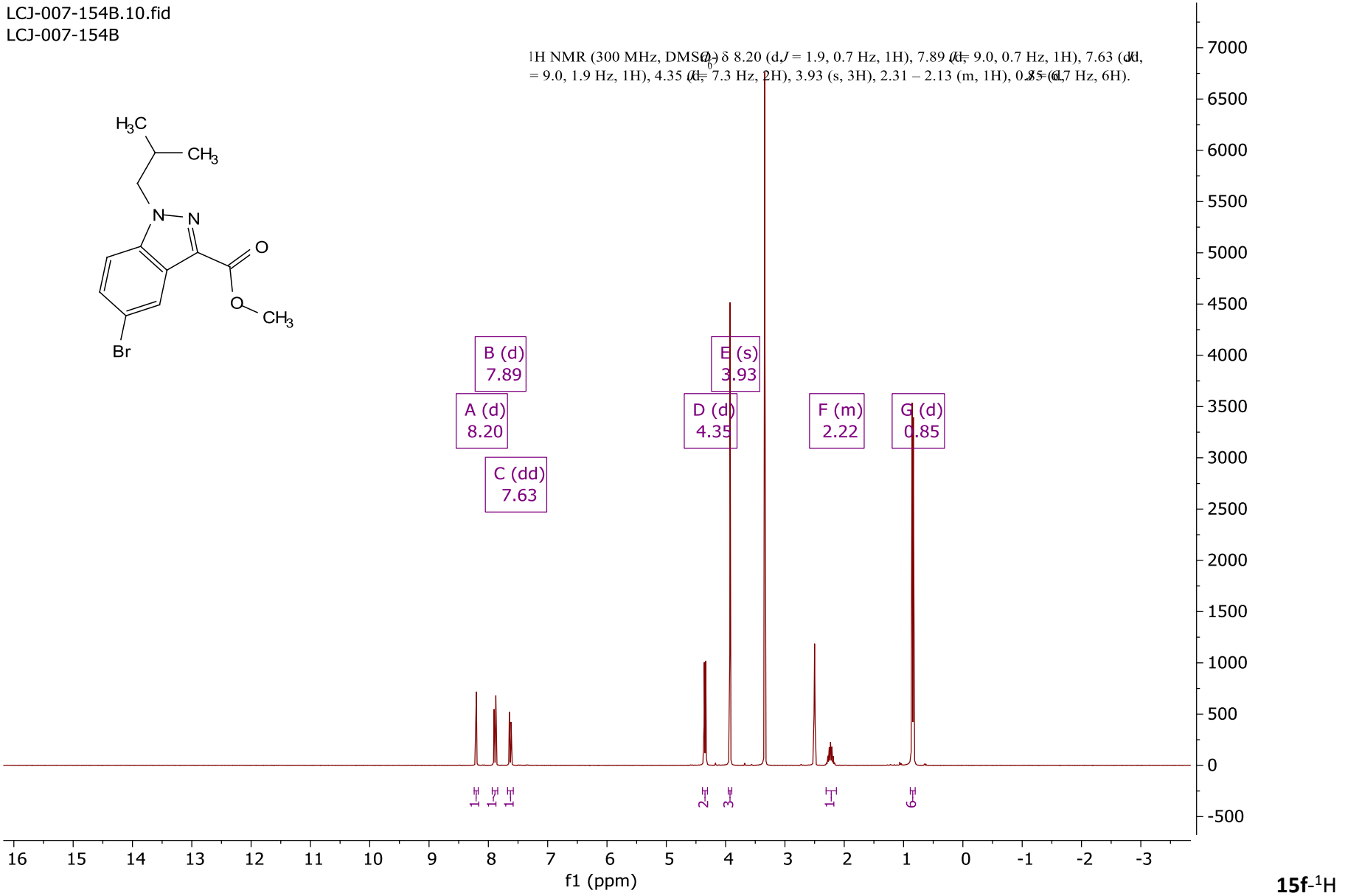

**16e**-$^1$H

13C NMR (75 MHz, DMSO) δ 159.7, 145.2, 129.4, 123.6, 123.3, 120.4, 118.1, 58.9, 52.3, 29.6, 20.9, 10.3.

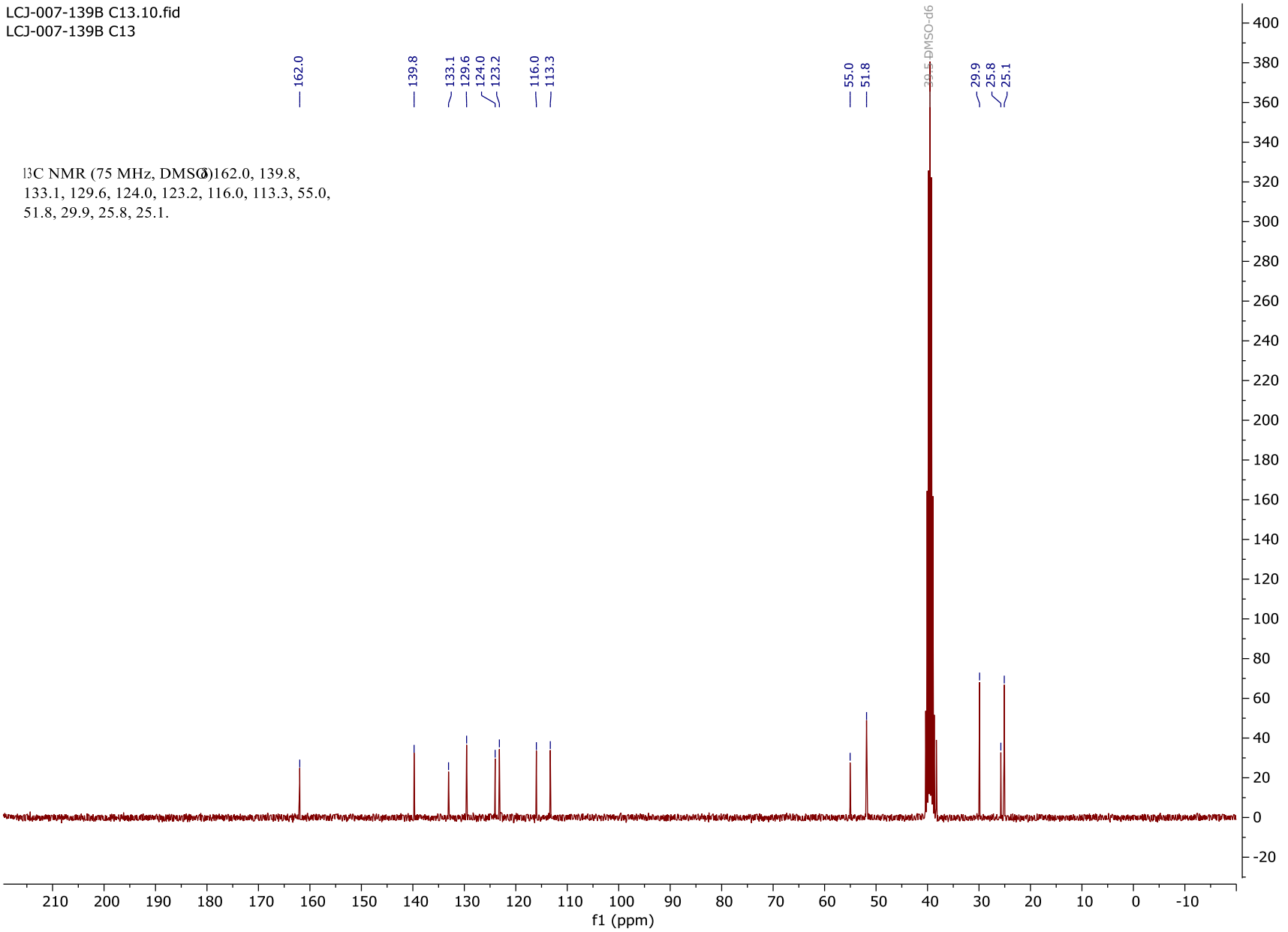



**16e**-$^{13}$C

LCJ-007-154B.10.fid
LCJ-007-154B

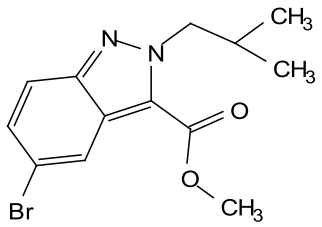



**15f**-$^{1}$H


LCJ-007-139B C13.10.fid
LCJ-007-139B C13
162.0
139.8
133.1
129.6
124.0
123.2
116.0
113.3
55.0
51.8
39.5 DMSO-d6
29.9
25.8
25.1
13C NMR (75 MHz, DMSO-d6) δ 162.0, 139.8, 133.1, 129.6, 124.0, 123.2, 116.0, 113.3, 55.0, 51.8, 29.9, 25.8, 25.1.
f1 (ppm)

**15f-$^{13}$C**

LCJ-007-154 C1.10.fid
LCJ-007-154 C1



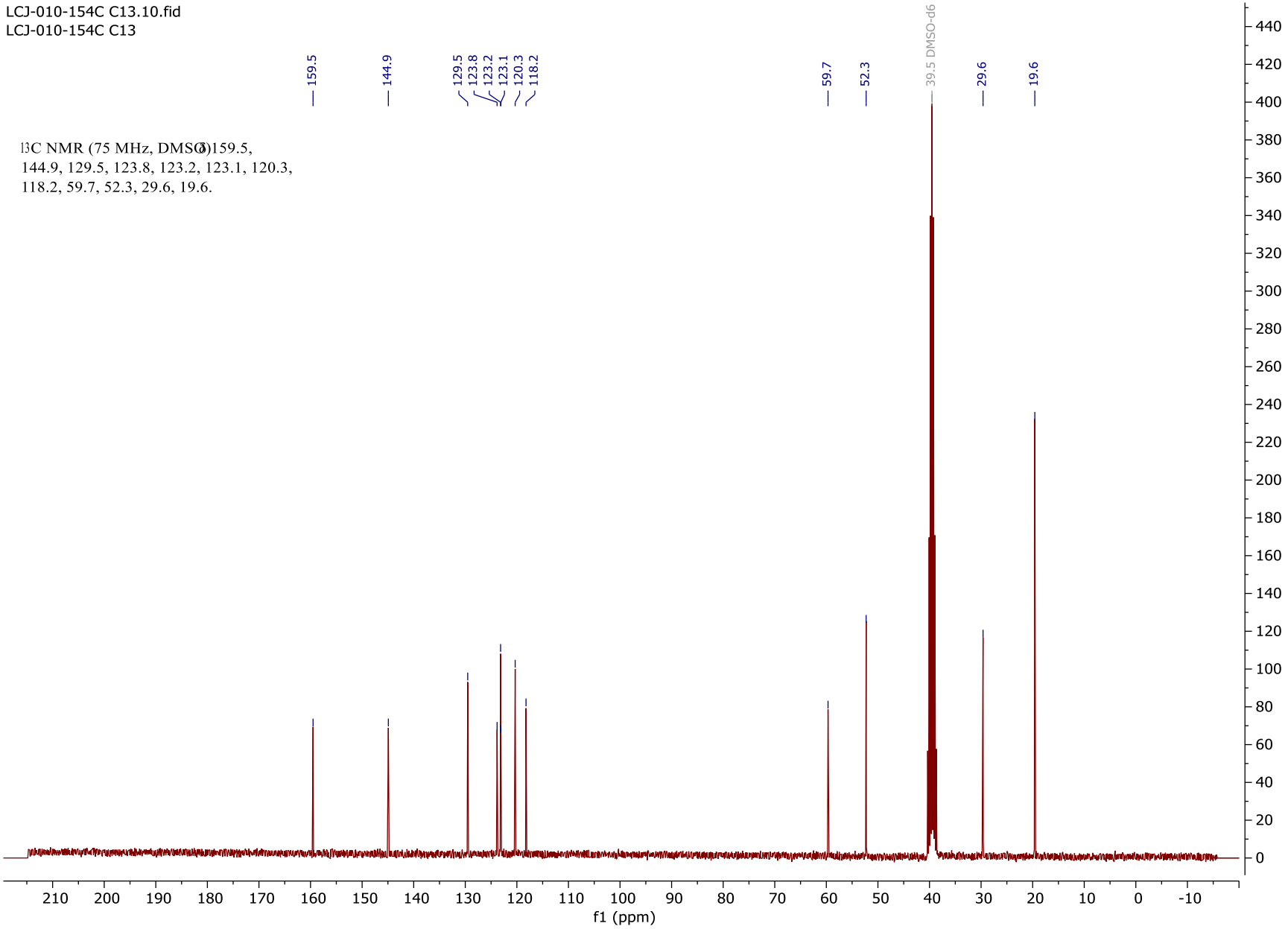

$^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.17 (d, $J$ = 1.9, 0.8 Hz, 1H), 7.80 (d, $J$ = 9.1, 0.7 Hz, 1H), 7.50 (dd, $J$ = 9.1, 1.9 Hz, 1H), 4.67 (d, $J$ = 7.3 Hz, 2H), 3.99 (s, 3H), 2.35 – 2.18 (m, 1H), 0.87 (d, $J$ = 6.7 Hz, 6H).




**16f**-$^1$H

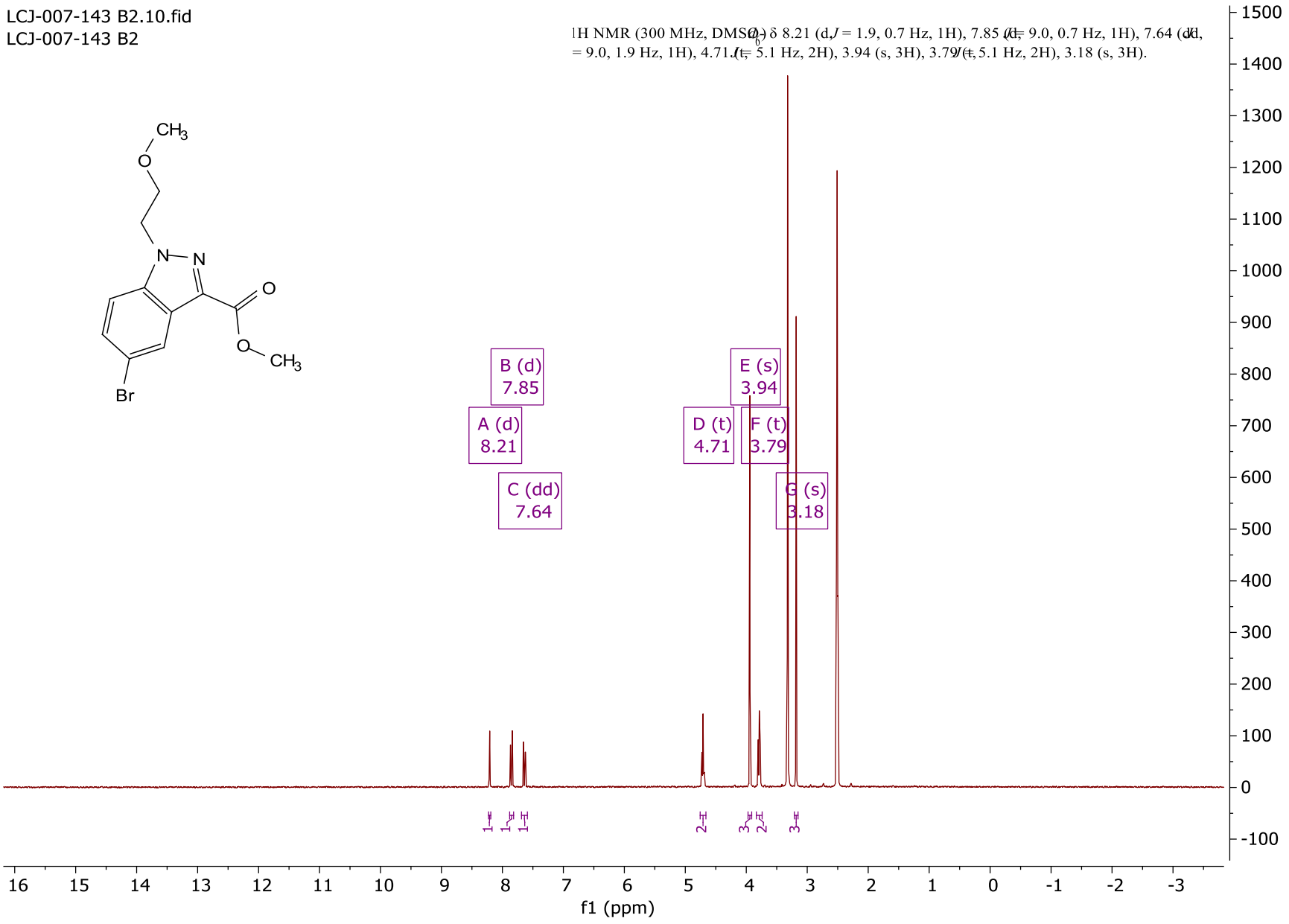
LCJ-010-154C C13.10.fid
LCJ-010-154C C13

13C NMR (75 MHz, DMSO) 159.5, 144.9, 129.5, 123.8, 123.2, 123.1, 120.3, 118.2, 59.7, 52.3, 29.6, 19.6.



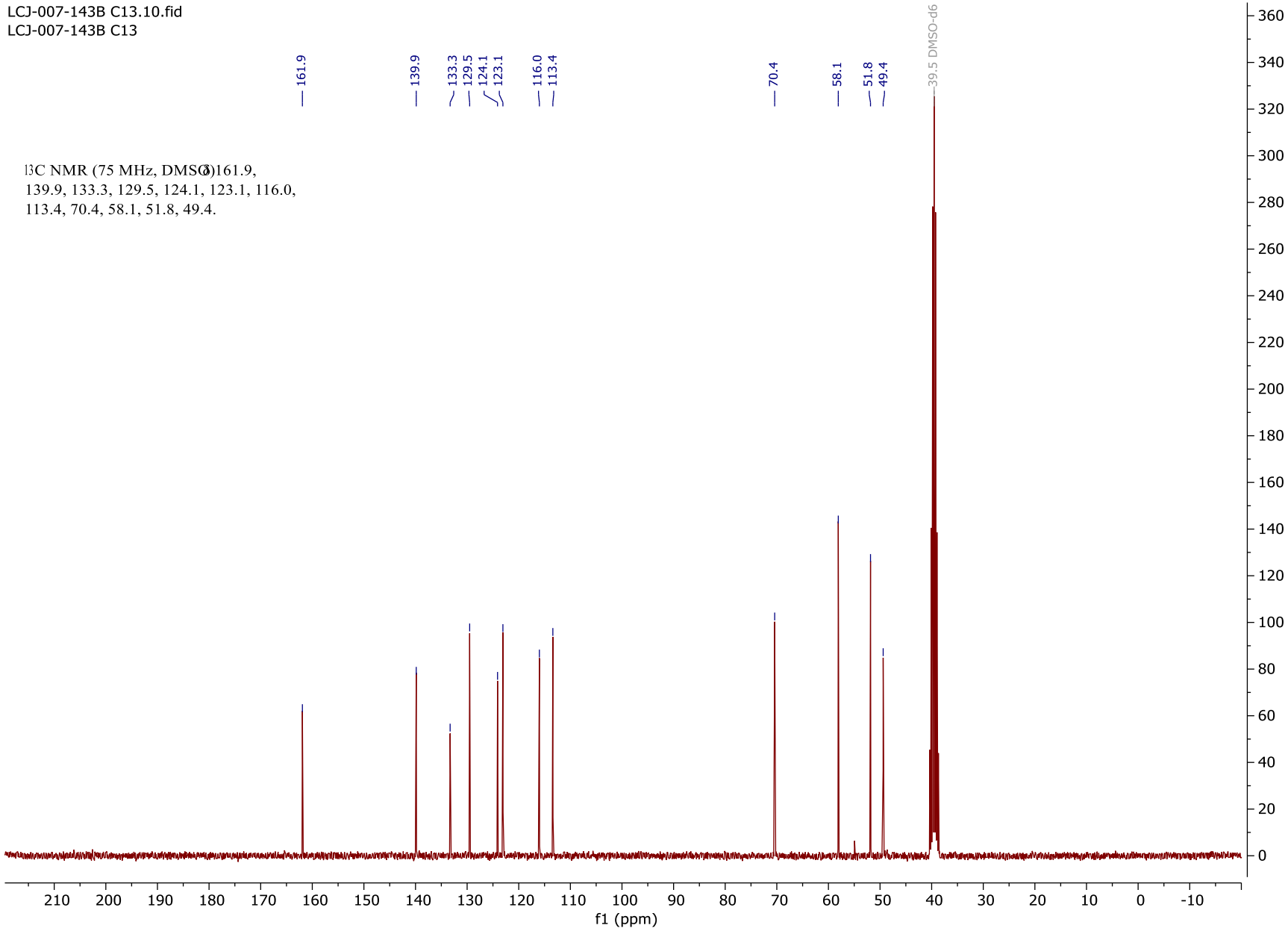

**16f**-$^{13}$C

LCJ-007-143 B2.10.fid
LCJ-007-143 B2




**15g**-$^1$H

LCJ-007-143B C13.10.fid
LCJ-007-143B C13

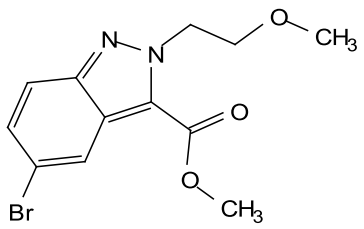



$^{13}$C NMR (75 MHz, DMSO-$d_6$) 161.9, 139.9, 133.3, 129.5, 124.1, 123.1, 116.0, 113.4, 70.4, 58.1, 51.8, 49.4.

**15g**-$^{13}$C

LCJ-007-143 C1.10.fid
LCJ-007-143 C1

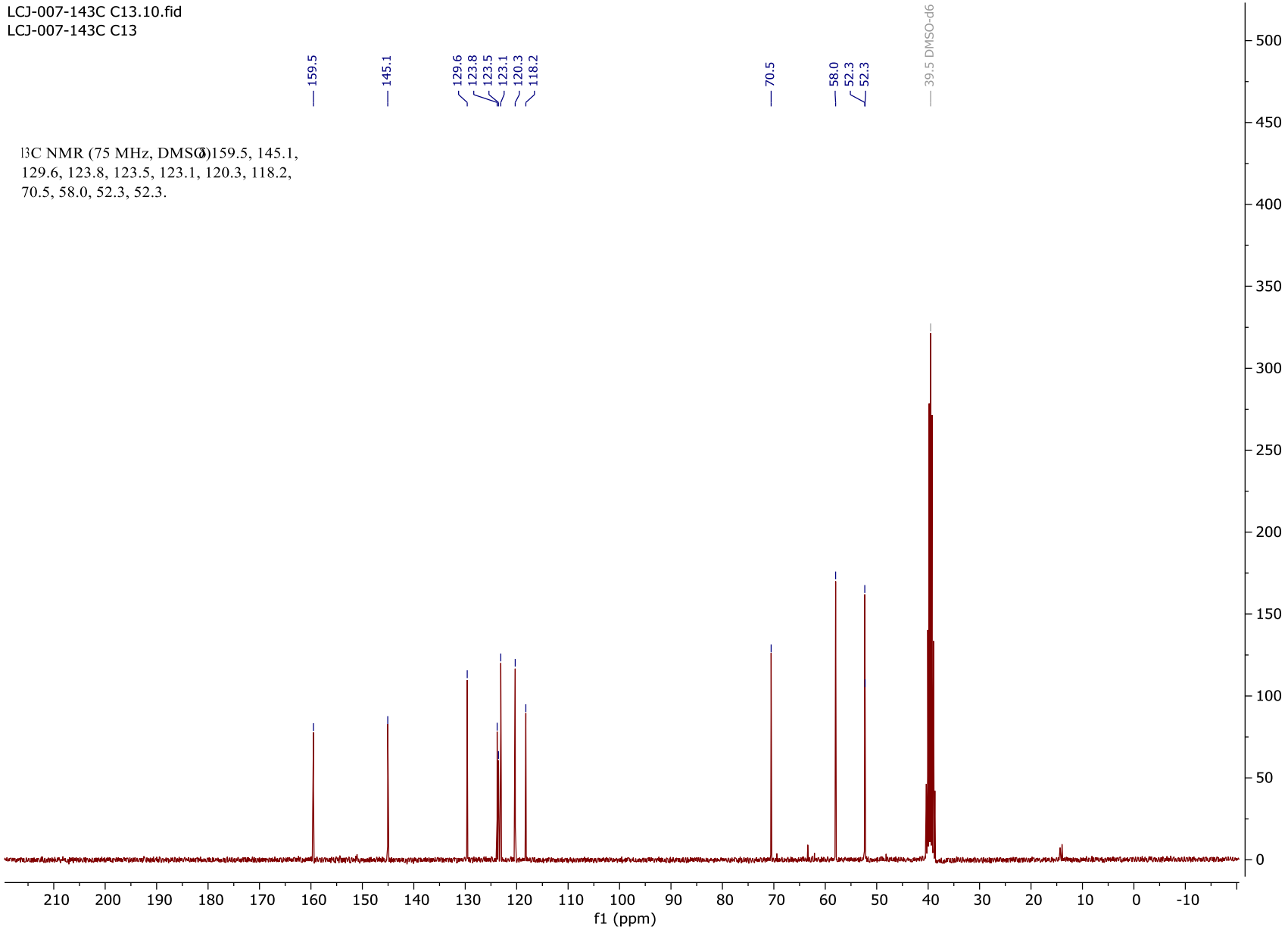
$^1$H NMR (300 MHz, $DMSO_{d_6}$) δ 8.17 (dd, $J$ = 1.9, 0.8 Hz, 1H), 7.80 (dd, $J$ = 9.1, 0.8 Hz, 1H), 7.51 (dd, $J$ = 9.1, 1.9 Hz, 1H), 5.04 ($J$ = 5.5 Hz, 2H), 4.00 (s, 3H), 3.85 ($J$ = 5.5 Hz, 2H), 3.21 (s, 3H).



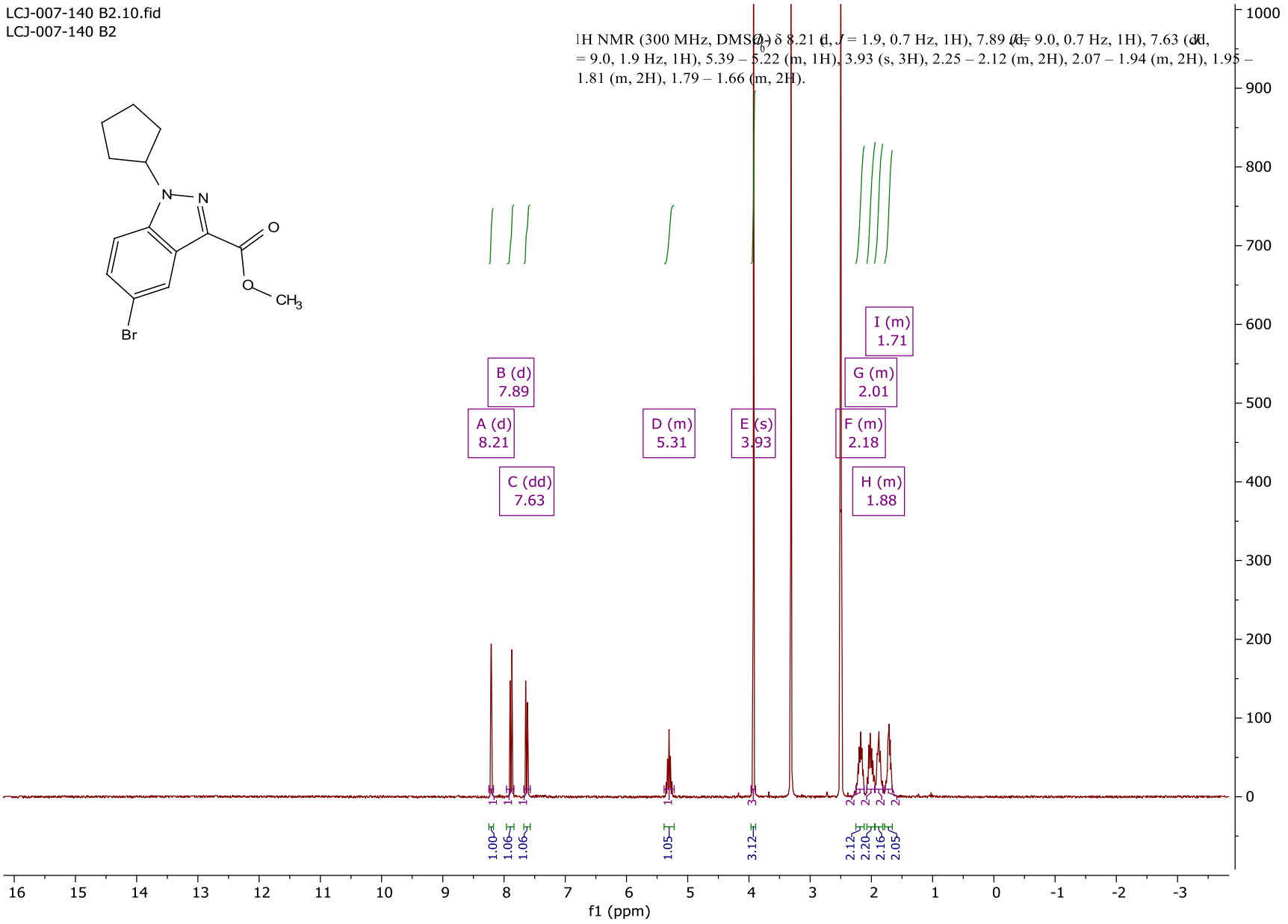




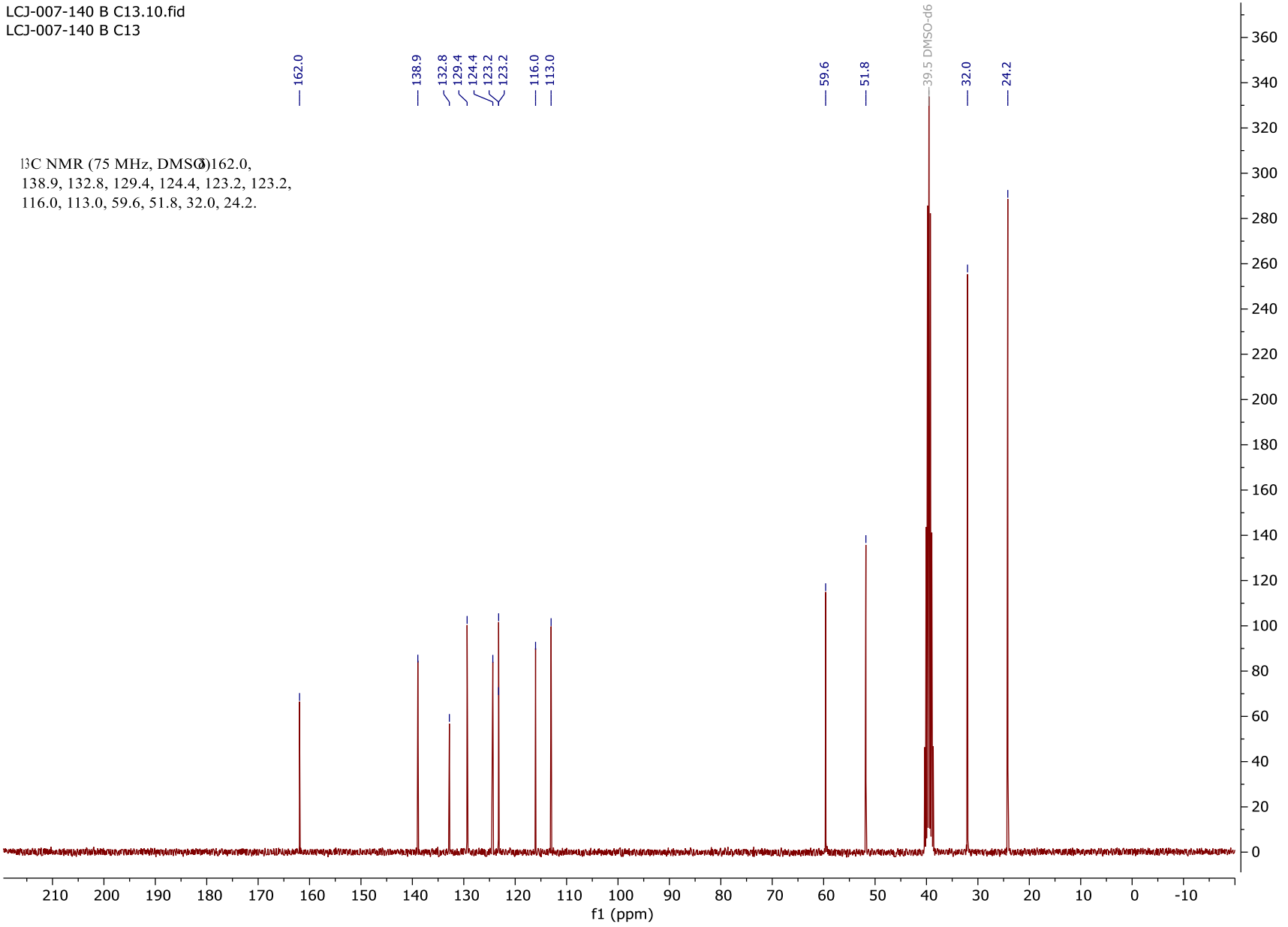
**16g**-$^1$H


LCJ-007-143C C13.10.fid
LCJ-007-143C C13
159.5
145.1
129.6
123.8
123.5
123.1
120.3
118.2
70.5
58.0
52.3
52.3
39.5 DMSO-d6
13C NMR (75 MHz, DMSO) δ 159.5, 145.1,
129.6, 123.8, 123.5, 123.1, 120.3, 118.2,
70.5, 58.0, 52.3, 52.3.
f1 (ppm)

**16g**-$^{13}$C


LCJ-007-140 B2.10.fid
LCJ-007-140 B2
1H NMR (300 MHz, DMSO-d6) δ 8.21 (d, J = 1.9, 0.7 Hz, 1H), 7.89 (d, J = 9.0, 0.7 Hz, 1H), 7.63 (dd, J = 9.0, 1.9 Hz, 1H), 5.39 – 5.22 (m, 1H), 3.93 (s, 3H), 2.25 – 2.12 (m, 2H), 2.07 – 1.94 (m, 2H), 1.95 – 1.81 (m, 2H), 1.79 – 1.66 (m, 2H).
N
N
O
O
CH3
Br
A (d) 8.21
B (d) 7.89
C (dd) 7.63
D (m) 5.31
E (s) 3.93
F (m) 2.18
G (m) 2.01
H (m) 1.88
I (m) 1.71
1.00
1.06
1.06
1.05
3.12
2.12
2.20
2.16
2.05
f1 (ppm)

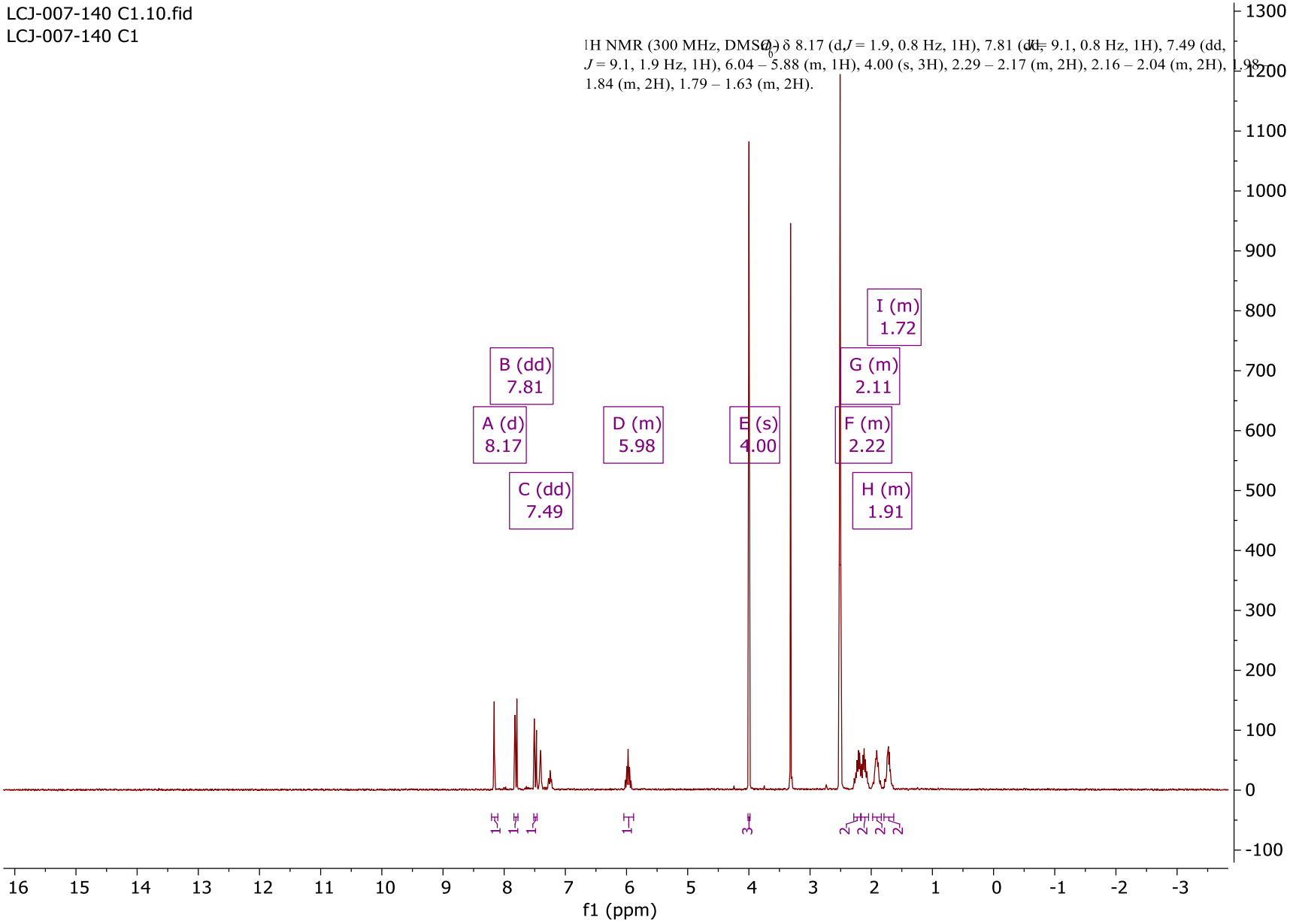
**15h**-$^{1}$H


LCJ-007-140 B C13.10.fid
LCJ-007-140 B C13
162.0
138.9
132.8
129.4
124.4
123.2
123.2
116.0
113.0
59.6
51.8
39.5 DMSO-d6
32.0
24.2
13C NMR (75 MHz, DMSO) δ 162.0,
138.9, 132.8, 129.4, 124.4, 123.2, 123.2,
116.0, 113.0, 59.6, 51.8, 32.0, 24.2.
f1 (ppm)

**15h**-$^{13}$C

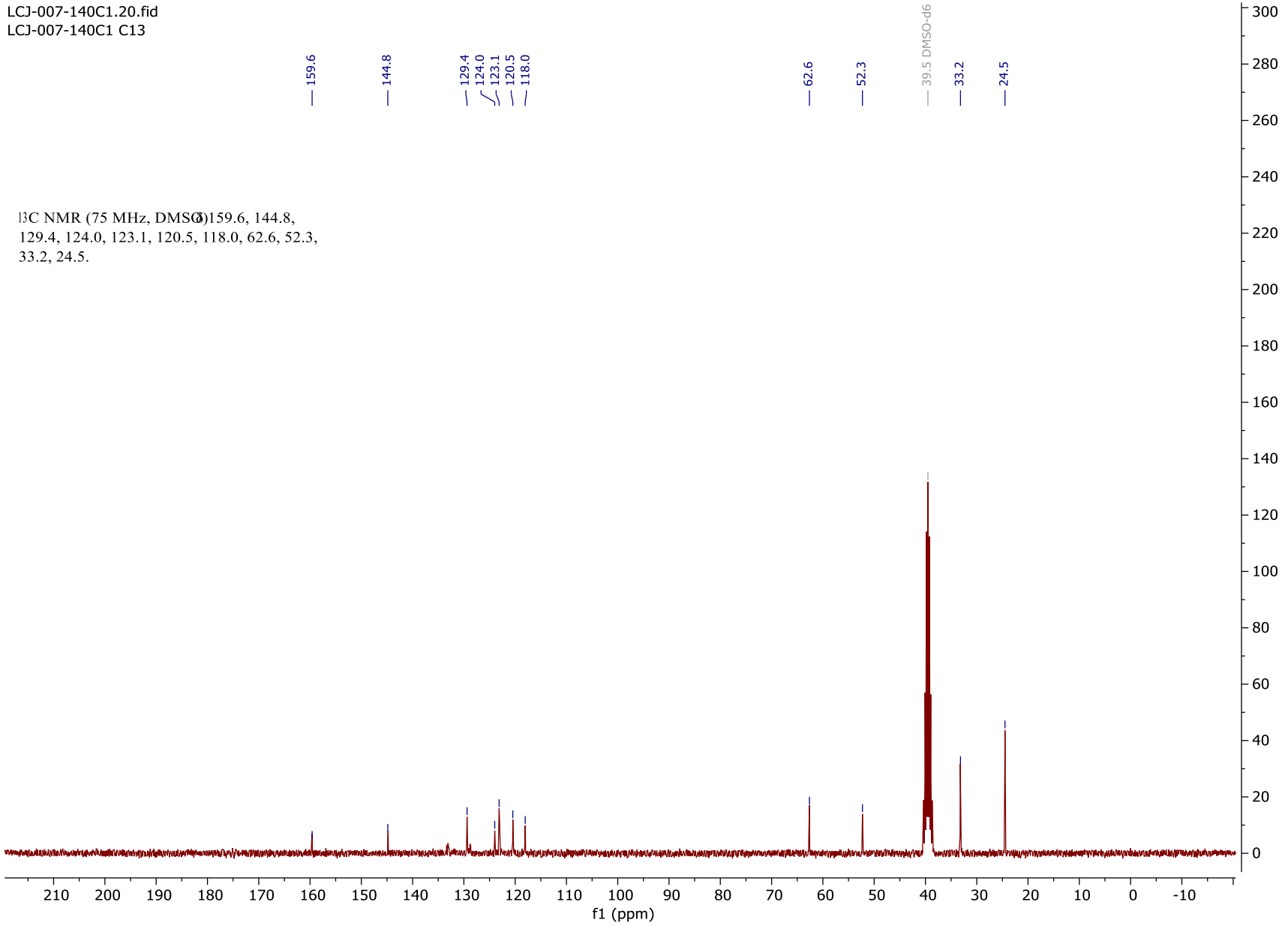
LCJ-007-140 C1.10.fid
LCJ-007-140 C1

$^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.17 (d, $J$ = 1.9, 0.8 Hz, 1H), 7.81 (dd, $J$ = 9.1, 0.8 Hz, 1H), 7.49 (dd, $J$ = 9.1, 1.9 Hz, 1H), 6.04 – 5.88 (m, 1H), 4.00 (s, 3H), 2.29 – 2.17 (m, 2H), 2.16 – 2.04 (m, 2H), 1.98 – 1.84 (m, 2H), 1.79 – 1.63 (m, 2H).




**16h**-$^1$H

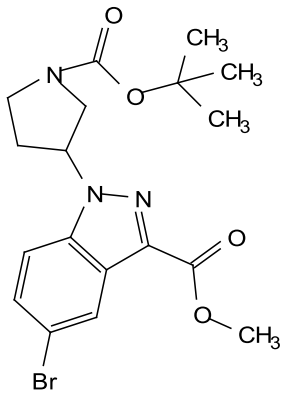
LCJ-007-140C1.20.fid
LCJ-007-140C1 C13




$^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ 159.6, 144.8, 129.4, 124.0, 123.1, 120.5, 118.0, 62.6, 52.3, 33.2, 24.5.

**16h**-$^{13}$C

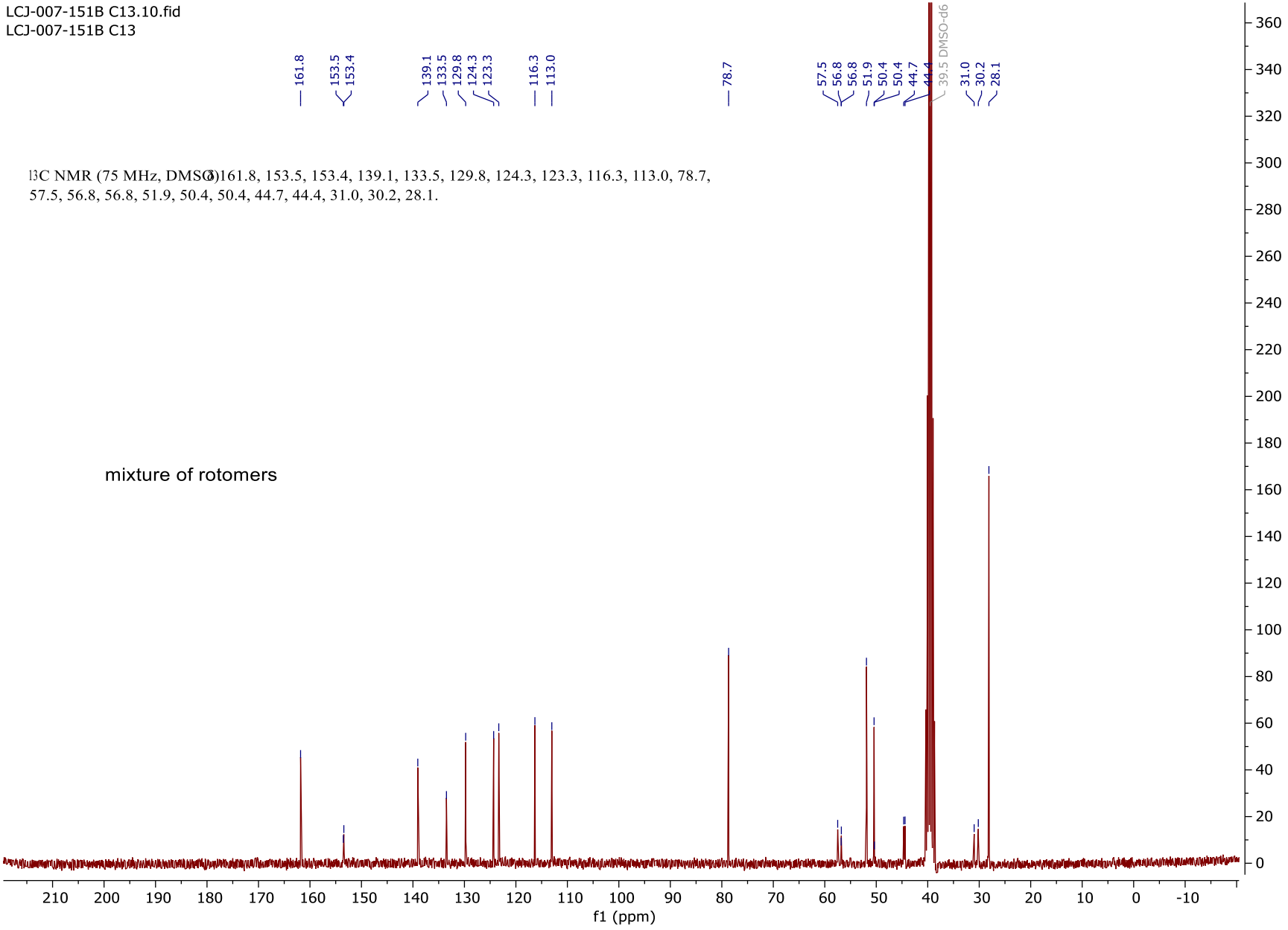
LCJ-007-151B.10.fid
LCJ-007-151 B



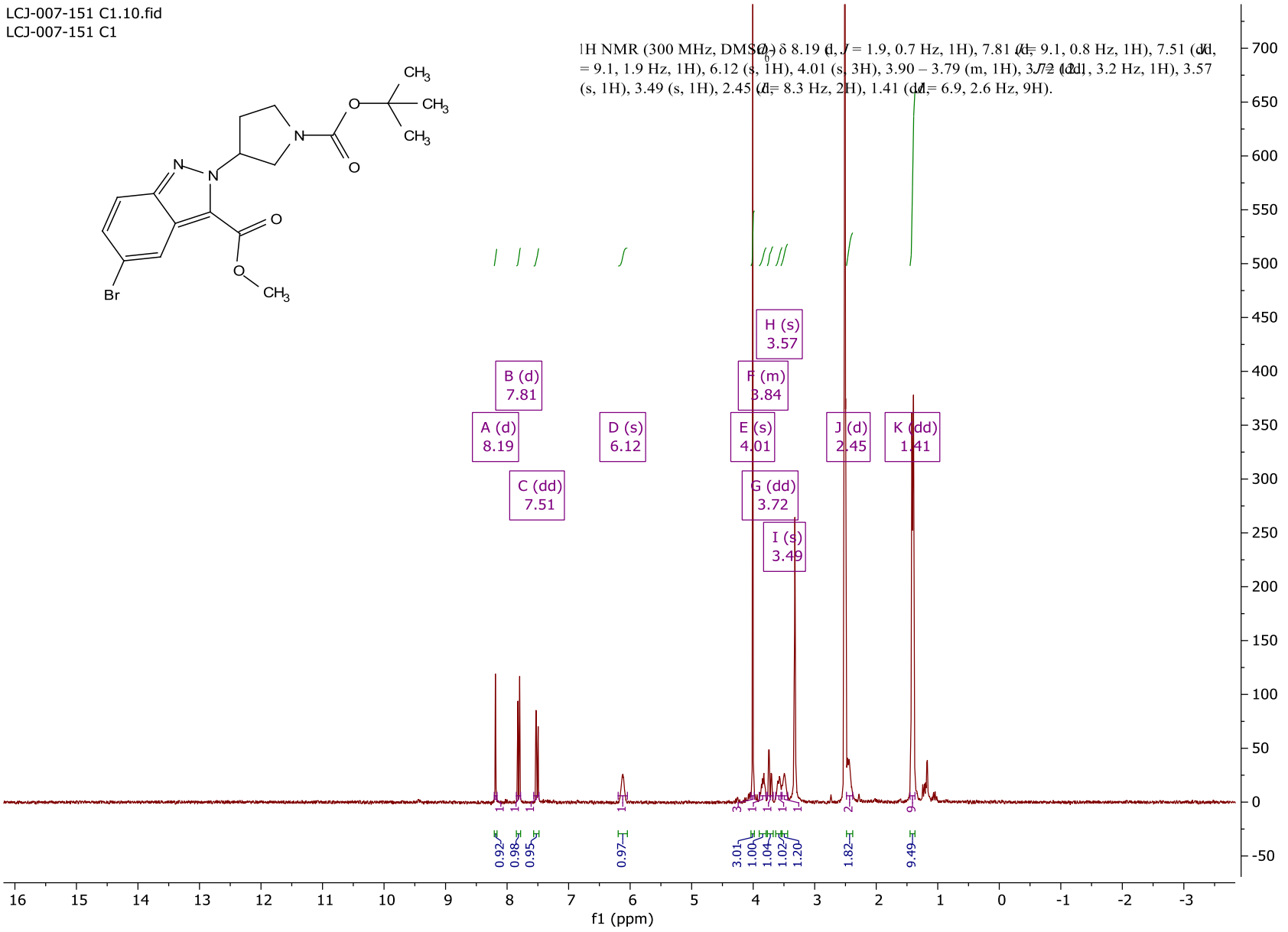

$^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.22 (d, $J$ = 1.8 Hz, 1H), 7.92 (d, $J$ = 9.0 Hz, 1H), 7.67 (dd, $J$ = 9.0, 1.9 Hz, 1H), 5.59 (d, $J$ = 6.4 Hz, 1H), 3.93 (s, 3H), 3.88 – 3.78 (m, 1H), 3.65 – 3.54 (m, 2H), 3.46 (d, $J$ = 7.1 Hz, 1H), 2.39 (s, 2H), 1.40 (s, 9H).



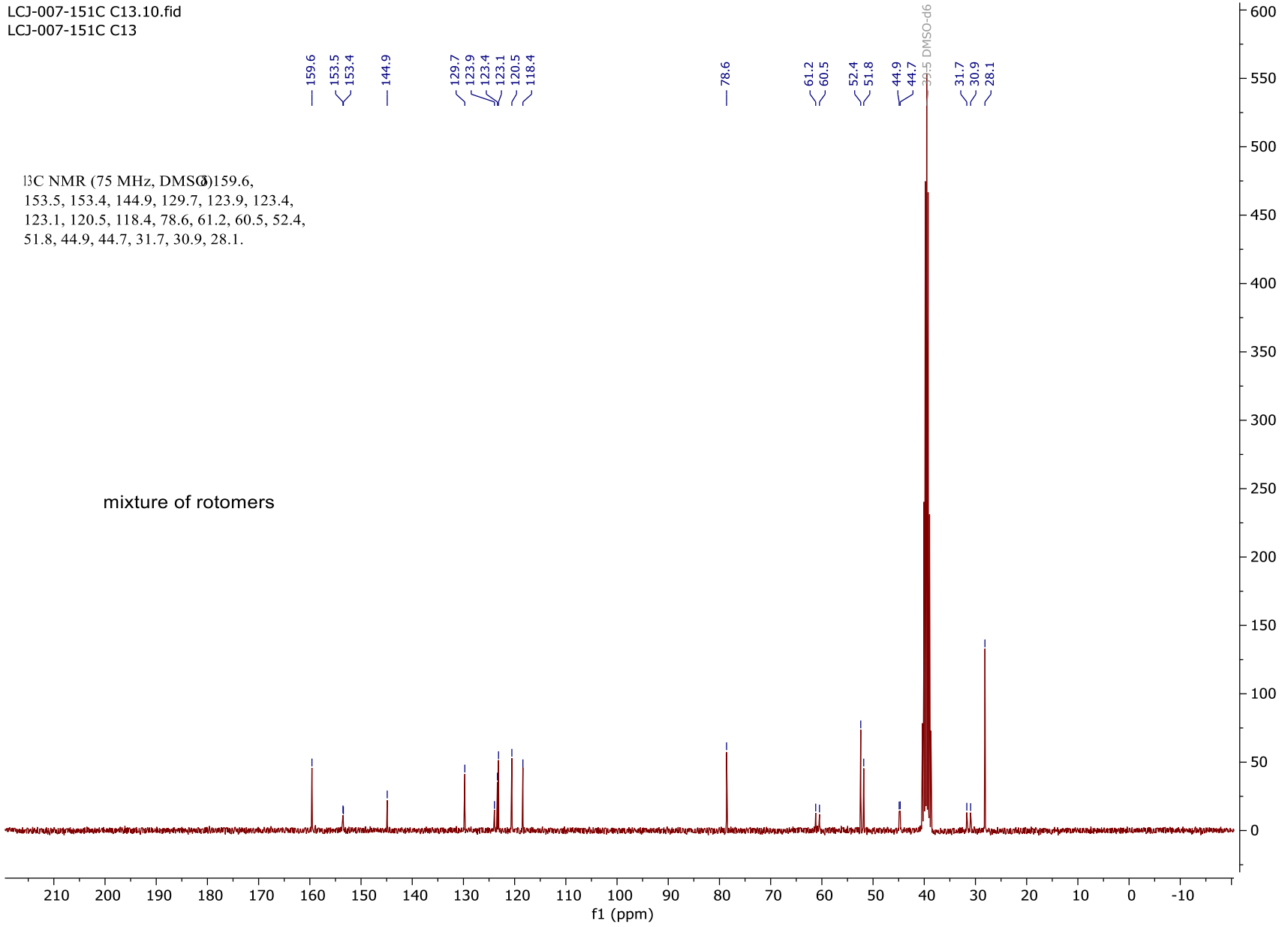

**15i**-$^1$H


LCJ-007-151B C13.10.fid
LCJ-007-151B C13
161.8
153.5
153.4
139.1
133.5
129.8
124.3
123.3
116.3
113.0
78.7
57.5
56.8
56.8
51.9
50.4
50.4
44.7
44.4
39.5 DMSO-d6
31.0
30.2
28.1
13C NMR (75 MHz, DMSO) δ 161.8, 153.5, 153.4, 139.1, 133.5, 129.8, 124.3, 123.3, 116.3, 113.0, 78.7, 57.5, 56.8, 56.8, 51.9, 50.4, 50.4, 44.7, 44.4, 31.0, 30.2, 28.1.
mixture of rotomers
f1 (ppm)

**15i**-$^{13}$C


LCJ-007-151 C1.10.fid
LCJ-007-151 C1
1H NMR (300 MHz, DMSO-d6) δ 8.19 (d, J = 1.9, 0.7 Hz, 1H), 7.81 (d, J = 9.1, 0.8 Hz, 1H), 7.51 (dd, J = 9.1, 1.9 Hz, 1H), 6.12 (s, 1H), 4.01 (s, 3H), 3.90 – 3.79 (m, 1H), 3.72 (dd, J = 11.1, 3.2 Hz, 1H), 3.57 (s, 1H), 3.49 (s, 1H), 2.45 (d, J = 8.3 Hz, 2H), 1.41 (dd, J = 6.9, 2.6 Hz, 9H).
A (d) 8.19
B (d) 7.81
C (dd) 7.51
D (s) 6.12
E (s) 4.01
F (m) 3.84
G (dd) 3.72
H (s) 3.57
I (s) 3.49
J (d) 2.45
K (dd) 1.41
0.92
0.98
0.95
0.97
3.01
1.00
1.04
1.02
1.20
1.82
9.49
f1 (ppm)

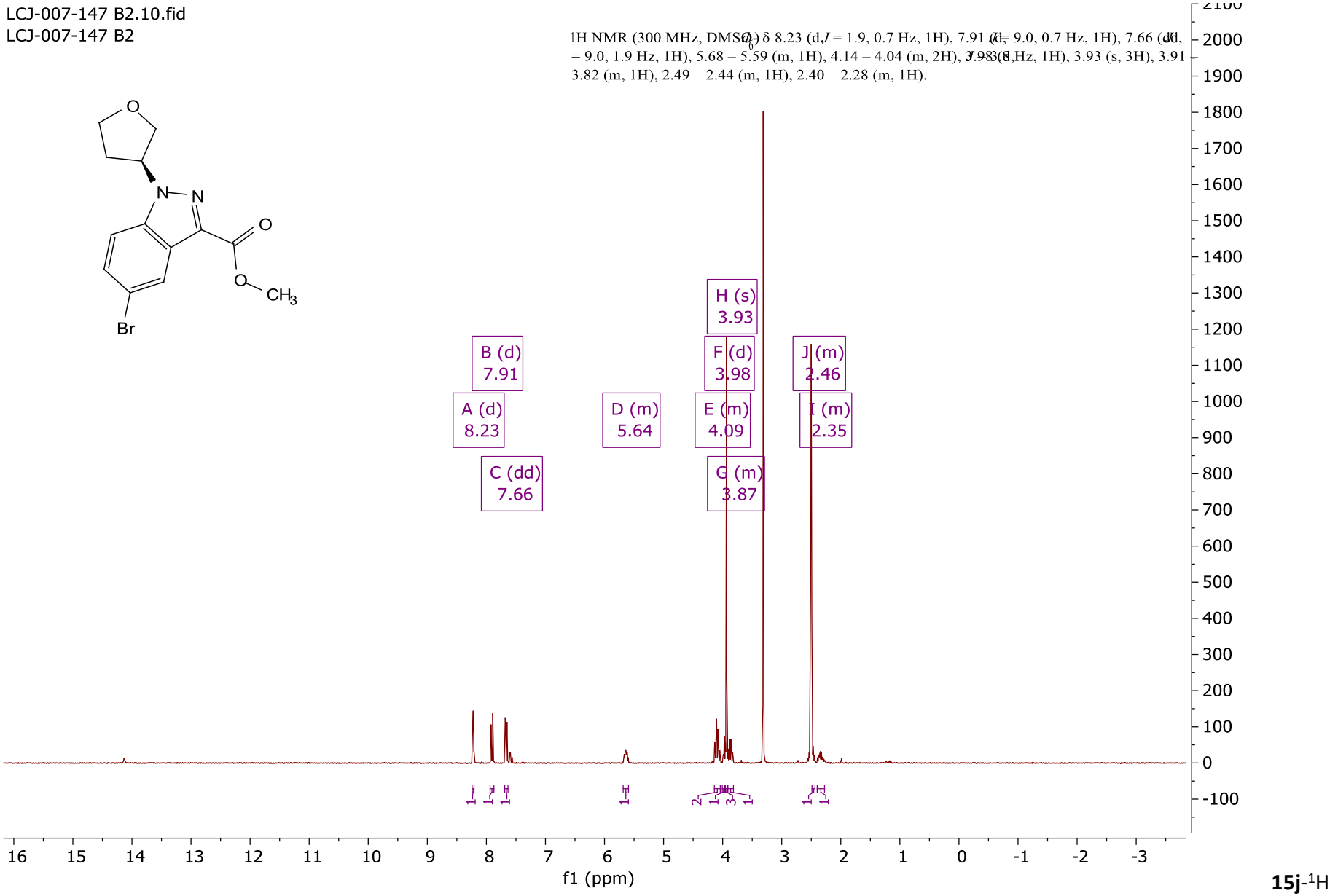
**16i**-$^{1}$H


LCJ-007-151C C13.10.fid
LCJ-007-151C C13
159.6
153.5
153.4
144.9
129.7
123.9
123.4
123.1
120.5
118.4
78.6
61.2
60.5
52.4
51.8
44.9
44.7
39.5 DMSO-d6
31.7
30.9
28.1
13C NMR (75 MHz, DMSO) δ 159.6,
153.5, 153.4, 144.9, 129.7, 123.9, 123.4,
123.1, 120.5, 118.4, 78.6, 61.2, 60.5, 52.4,
51.8, 44.9, 44.7, 31.7, 30.9, 28.1.
mixture of rotomers
f1 (ppm)

**16i**-$^{13}$C

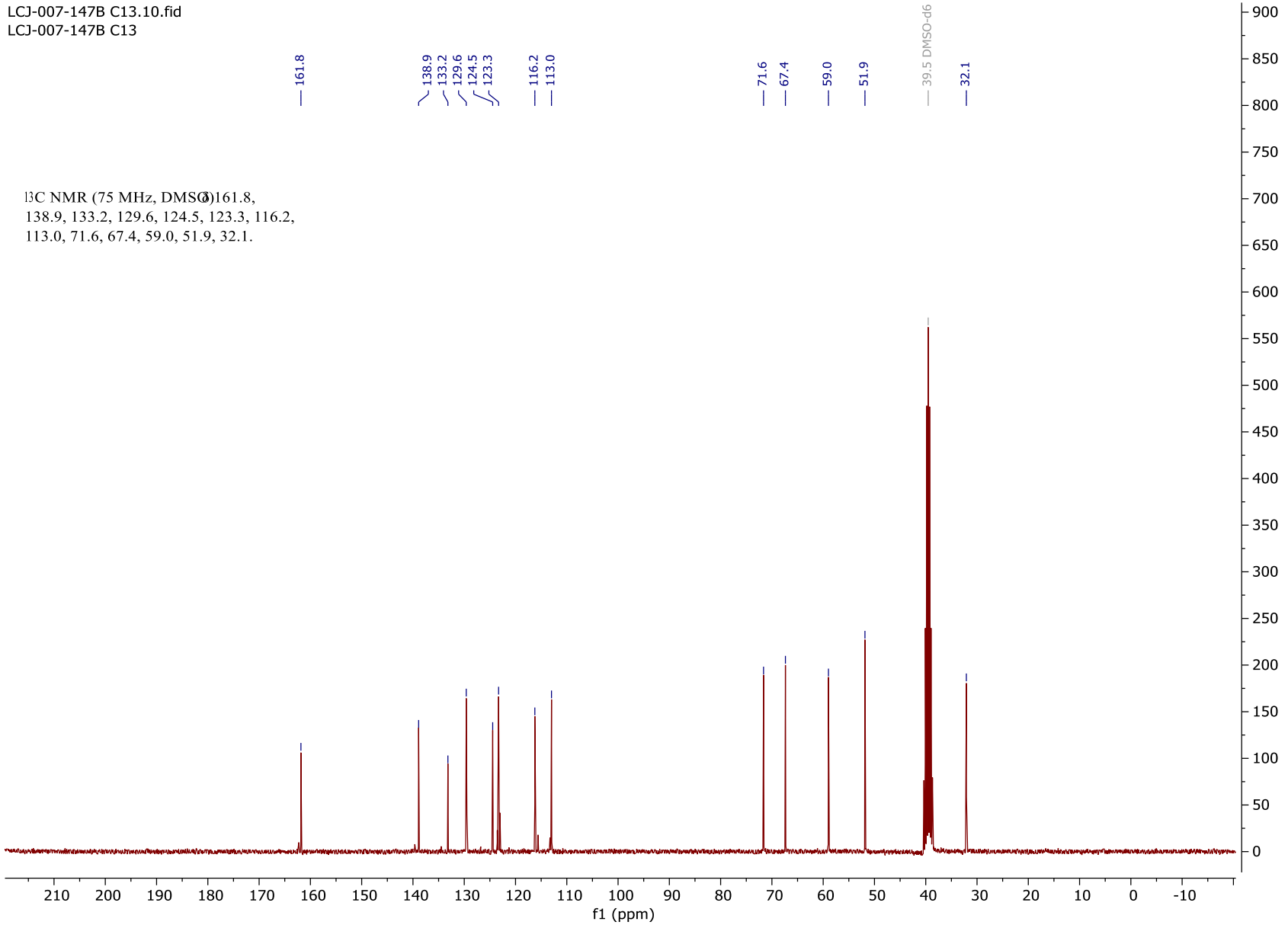
LCJ-007-147 B2.10.fid
LCJ-007-147 B2

$^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.23 (d, $J$ = 1.9, 0.7 Hz, 1H), 7.91 (d, $J$ = 9.0, 0.7 Hz, 1H), 7.66 (dd, $J$ = 9.0, 1.9 Hz, 1H), 5.68 – 5.59 (m, 1H), 4.14 – 4.04 (m, 2H), 3.98 (d, $J$ = 8.3 Hz, 1H), 3.93 (s, 3H), 3.91 – 3.82 (m, 1H), 2.49 – 2.44 (m, 1H), 2.40 – 2.28 (m, 1H).




**15j**-$^1$H

LCJ-007-147B C13.10.fid
LCJ-007-147B C13

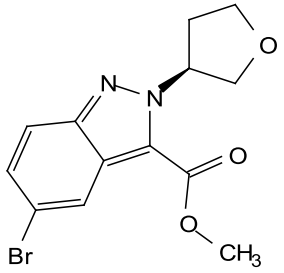



$^{13}$C NMR (75 MHz, DMSO) 161.8, 138.9, 133.2, 129.6, 124.5, 123.3, 116.2, 113.0, 71.6, 67.4, 59.0, 51.9, 32.1.

**15j**-$^{13}$C

LCJ-007-147 C1.10.fid
LCJ-007-147 C1

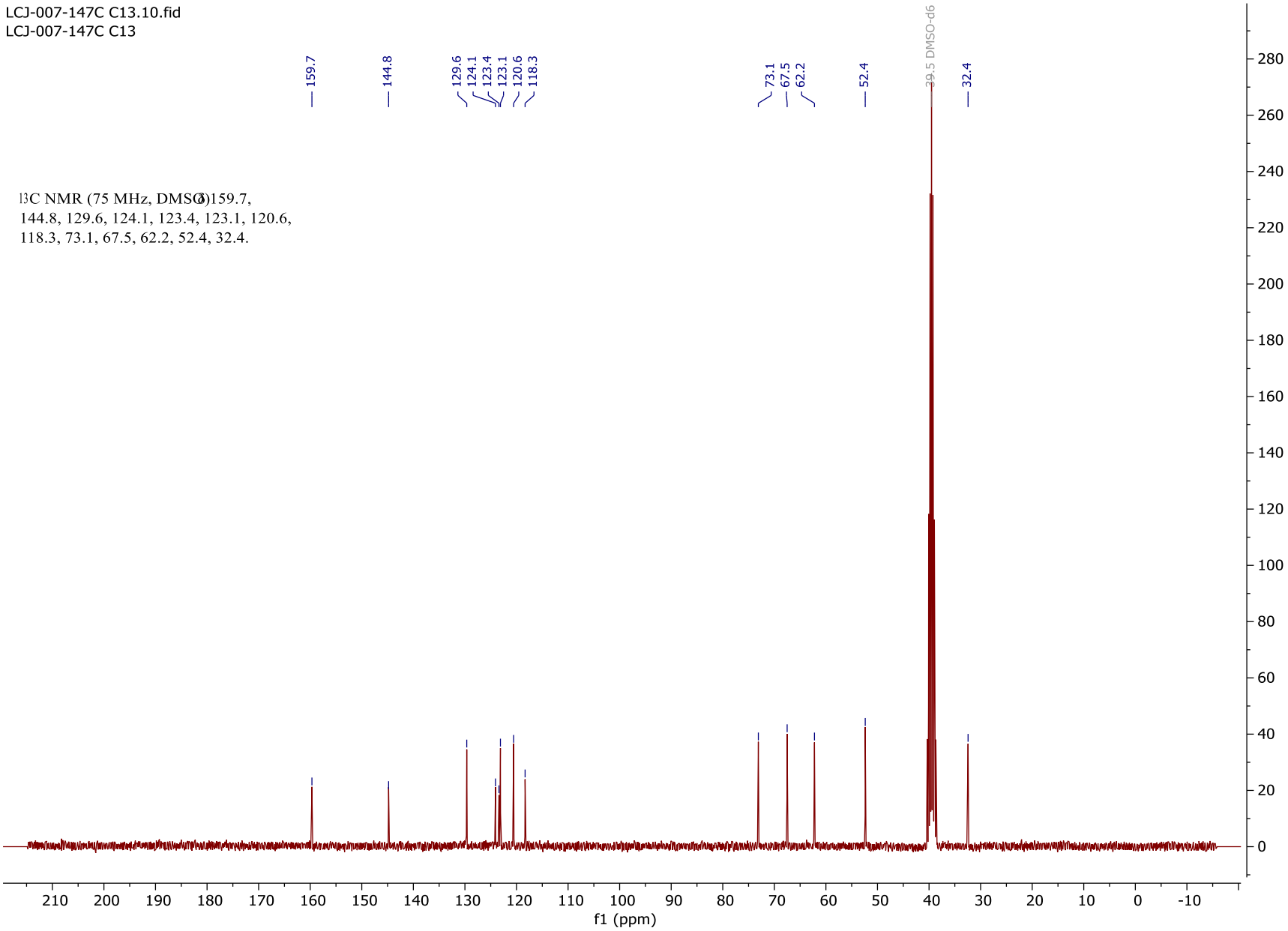
$^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.17 (d, $J$ = 1.9, 0.8 Hz, 1H), 7.82 (d, $J$ = 9.1, 0.7 Hz, 1H), 7.50 (dd, $J$ = 9.1, 1.9 Hz, 1H), 6.22 – 6.11 (m, 1H), 4.18 – 4.05 (m, 2H), 4.02 (d, $J$ = 2.4 Hz, 1H), 3.99 (s, 3H), 3.95 – 3.85 (m, 1H), 2.59 – 2.52 (m, 1H), 2.47 (d, $J$ = 2.4 Hz, 1H).







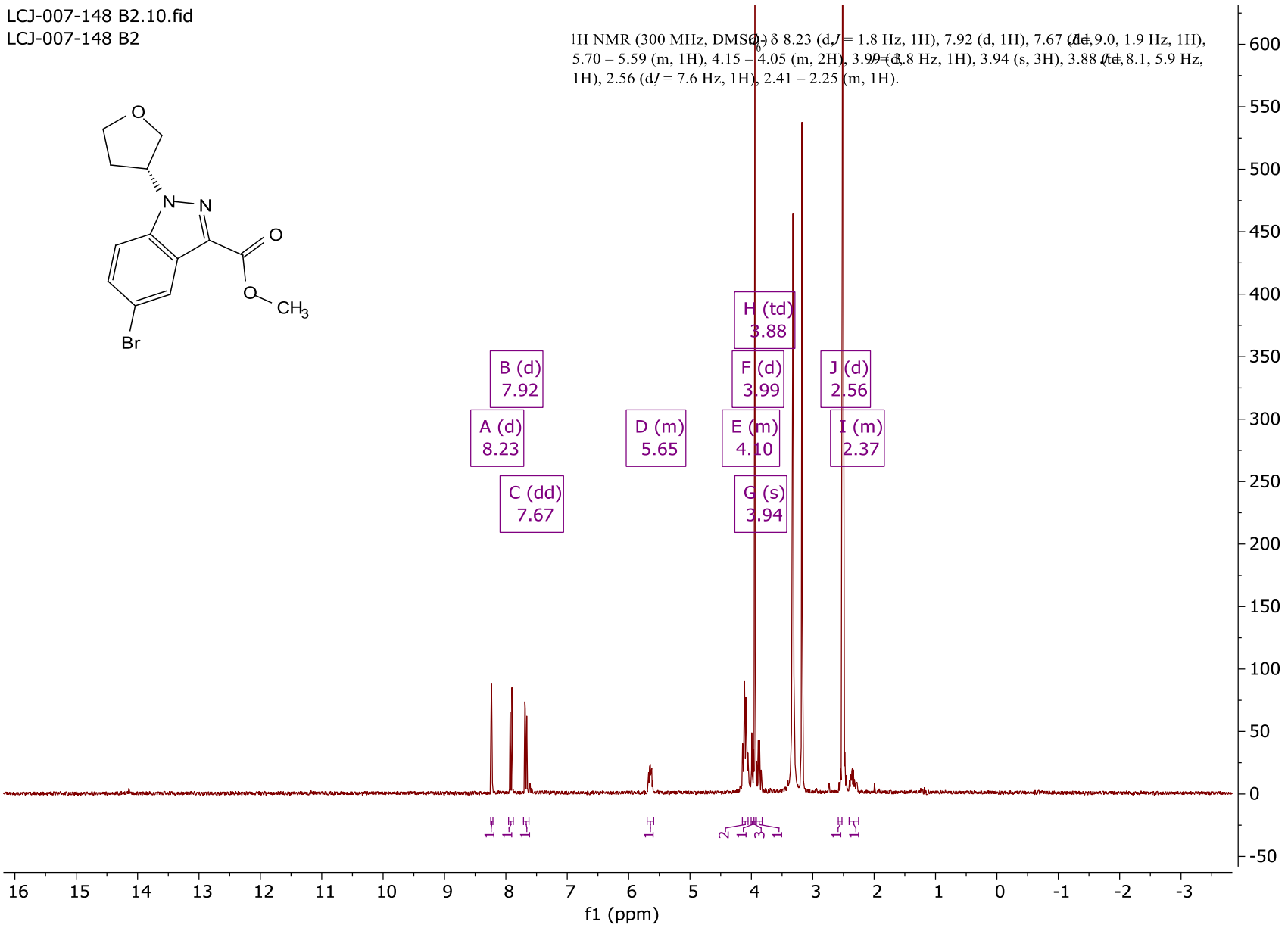
**16j**-$^1$H




$^{13}$C NMR (75 MHz, DMSO) $\delta$ 159.7, 144.8, 129.6, 124.1, 123.4, 123.1, 120.6, 118.3, 73.1, 67.5, 62.2, 52.4, 32.4.

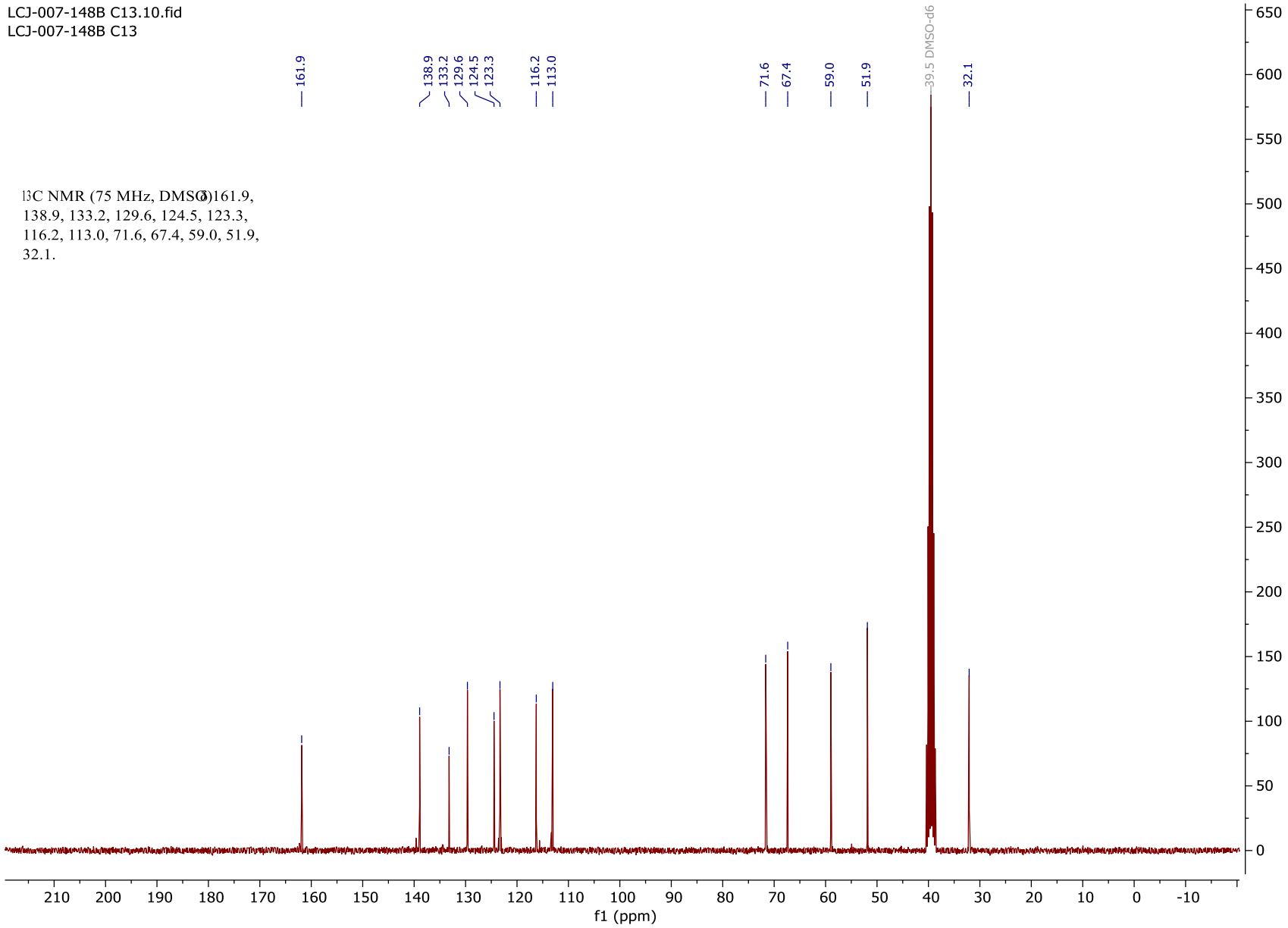
**16j**-$^{13}$C

LCJ-007-148 B2.10.fid
LCJ-007-148 B2




**15k**-$^{1}$H

LCJ-007-148B C13.10.fid
LCJ-007-148B C13

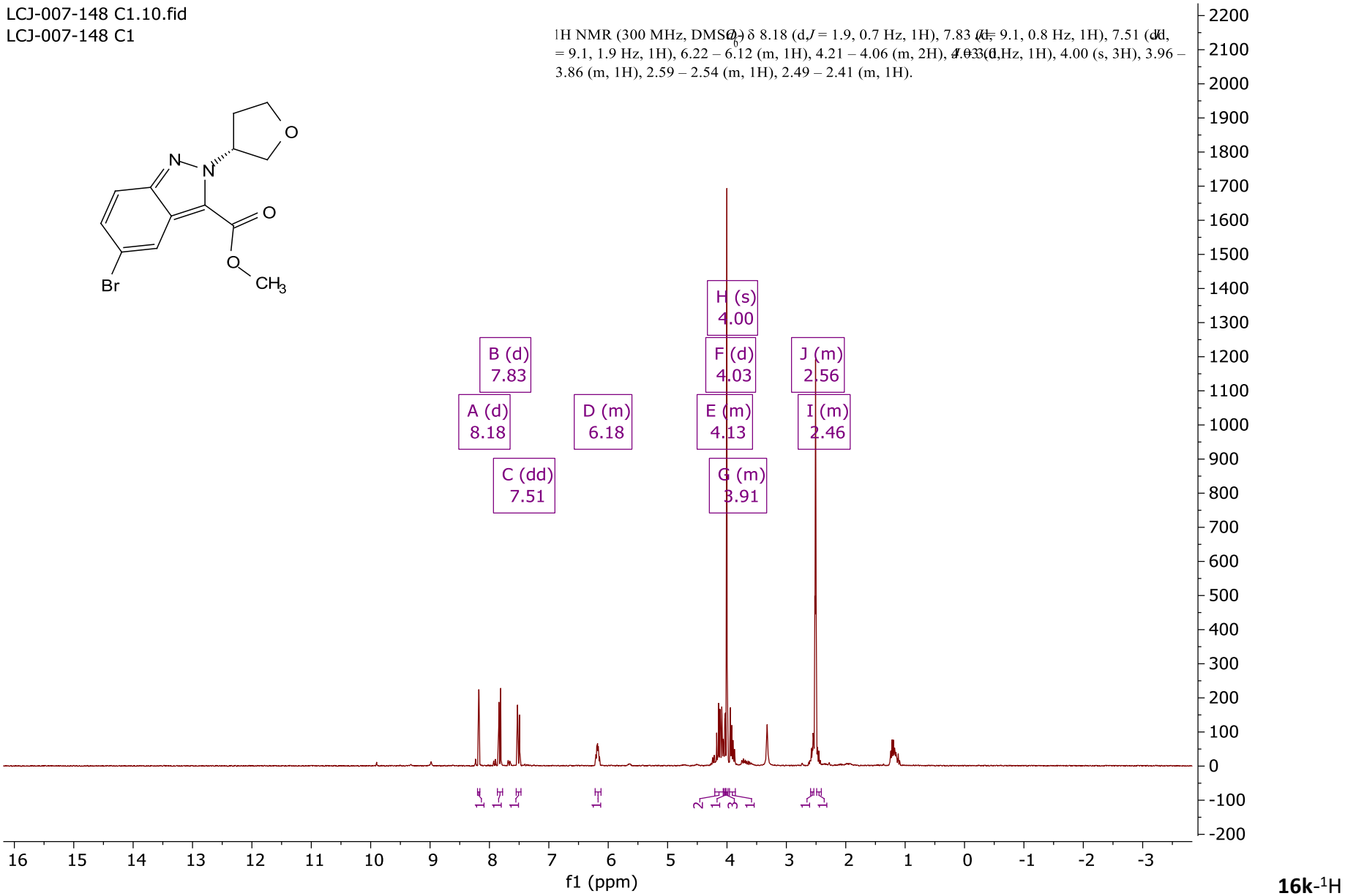



$^{13}$C NMR (75 MHz, DMSO-$d_6$) 161.9, 138.9, 133.2, 129.6, 124.5, 123.3, 116.2, 113.0, 71.6, 67.4, 59.0, 51.9, 32.1.

**15k**-$^{13}$C

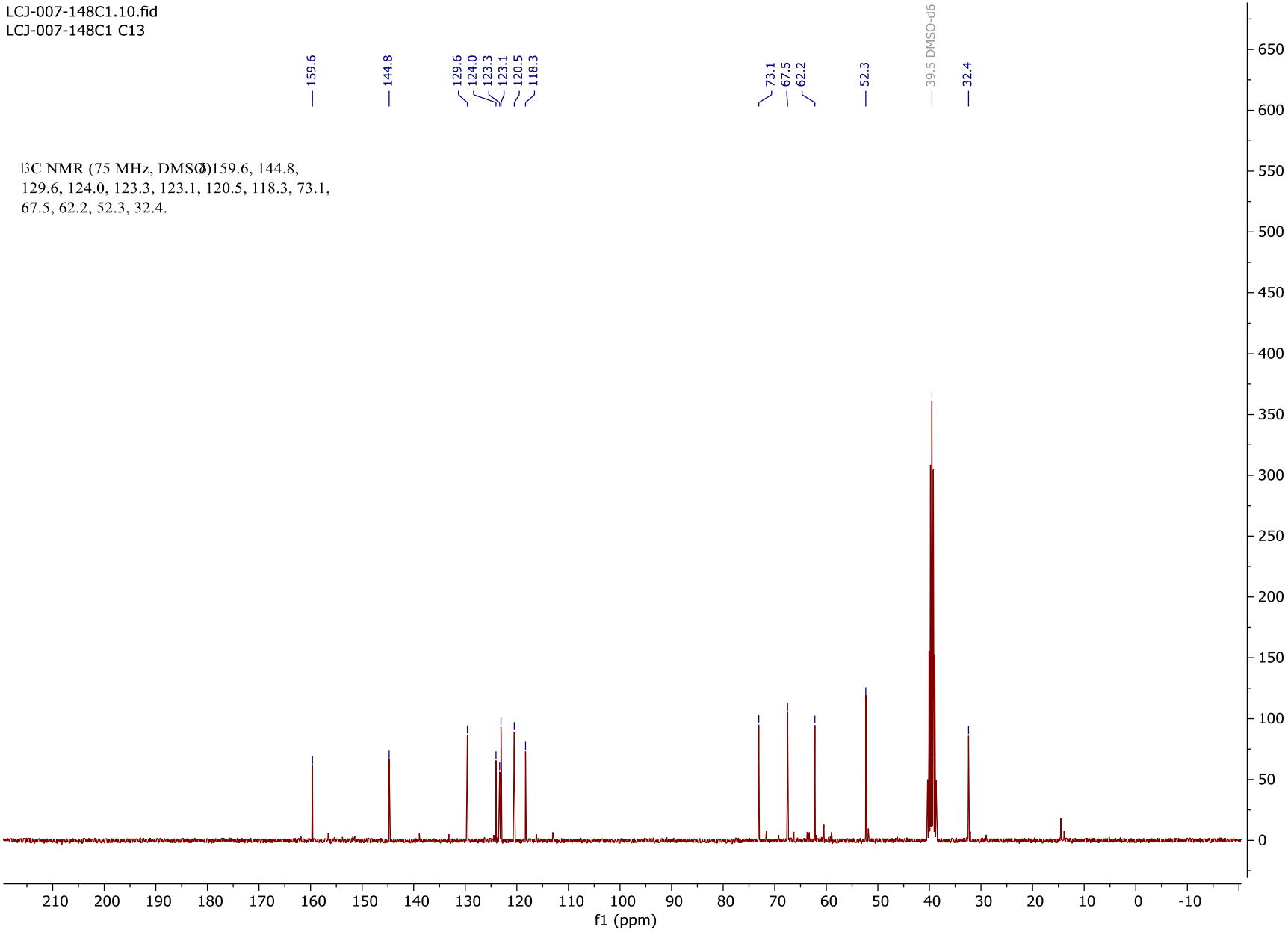
LCJ-007-148 C1.10.fid
LCJ-007-148 C1

$^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.18 (d, $J$ = 1.9, 0.7 Hz, 1H), 7.83 (d, $J$ = 9.1, 0.8 Hz, 1H), 7.51 (dd, $J$ = 9.1, 1.9 Hz, 1H), 6.22 – 6.12 (m, 1H), 4.21 – 4.06 (m, 2H), 4.03 (d, $J$ = 0.7 Hz, 1H), 4.00 (s, 3H), 3.96 – 3.86 (m, 1H), 2.59 – 2.54 (m, 1H), 2.49 – 2.41 (m, 1H).




**16k**-$^1$H

LCJ-007-148C1.10.fid
LCJ-007-148C1 C13

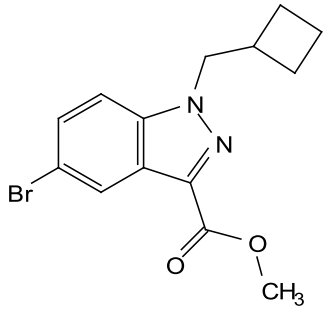



$^{13}$C NMR (75 MHz, DMSO-$d_6$) 159.6, 144.8, 129.6, 124.0, 123.3, 123.1, 120.5, 118.3, 73.1, 67.5, 62.2, 52.3, 32.4.

**16k**-$^{13}$C

LCJ-007-142 B2.10.fid
LCJ-007-142 B2

$^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.20 (d, $J$ = 1.9, 0.7 Hz, 1H), 7.90 (d, $J$ = 9.0, 0.7 Hz, 1H), 7.63 (dd, $J$ = 9.0, 1.9 Hz, 1H), 4.56 (d, $J$ = 7.2 Hz, 2H), 3.93 (s, 3H), 2.85 (p, $J$ = 7.4 Hz, 1H), 1.99 – 1.87 (m, 2H), 1.87 – 1.73 (m, 4H).

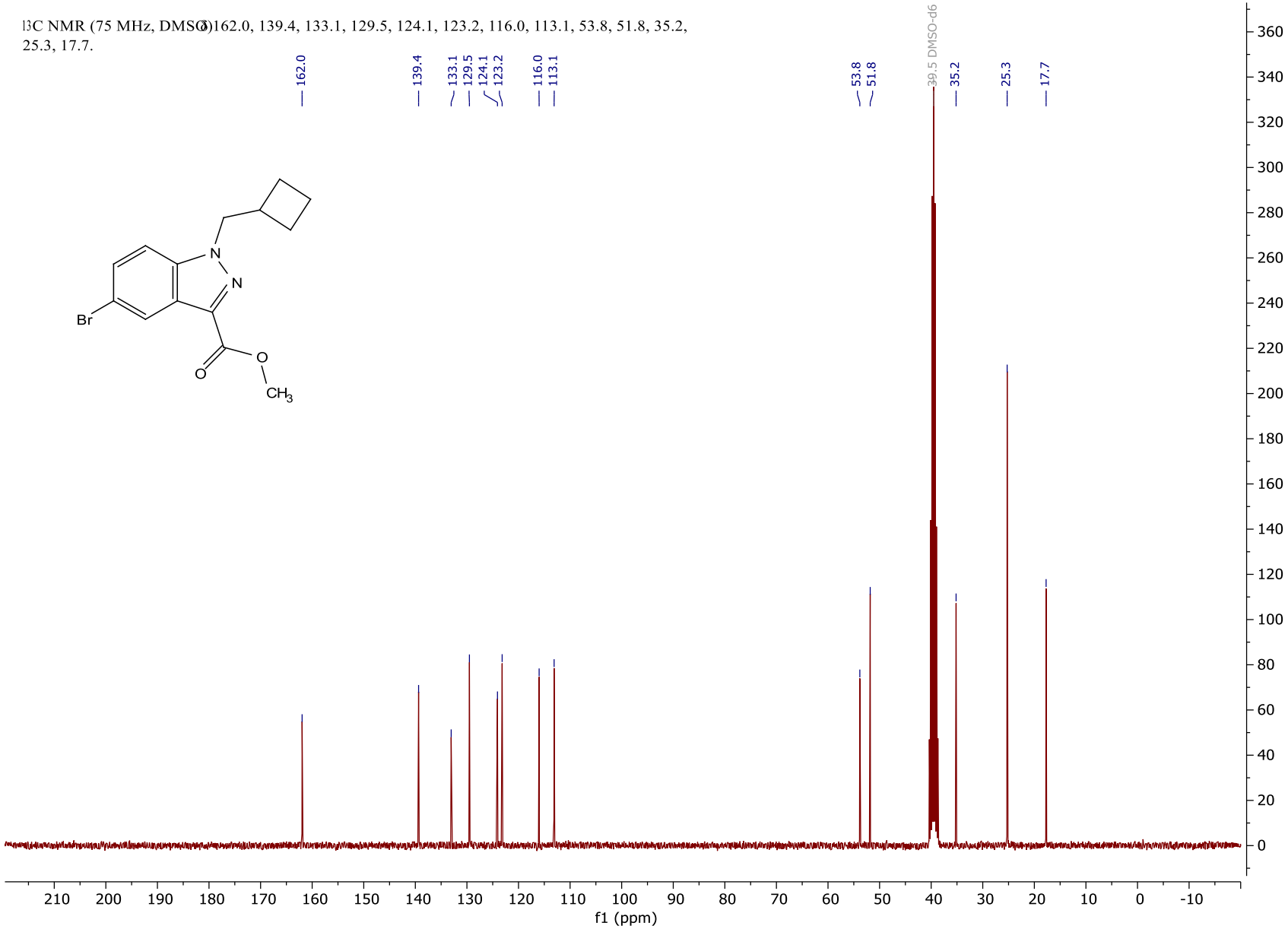






**15l**-$^1$H

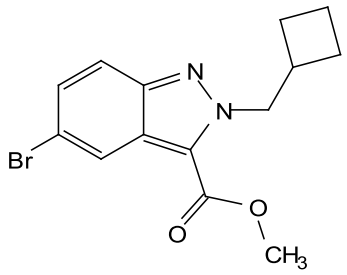
$^{13}$C NMR (75 MHz, DMSO) δ 162.0, 139.4, 133.1, 129.5, 124.1, 123.2, 116.0, 113.1, 53.8, 51.8, 35.2, 25.3, 17.7.




**15l**-$^{13}$C

LCJ-007-142 C1.10.fid
LCJ-007-142 C1

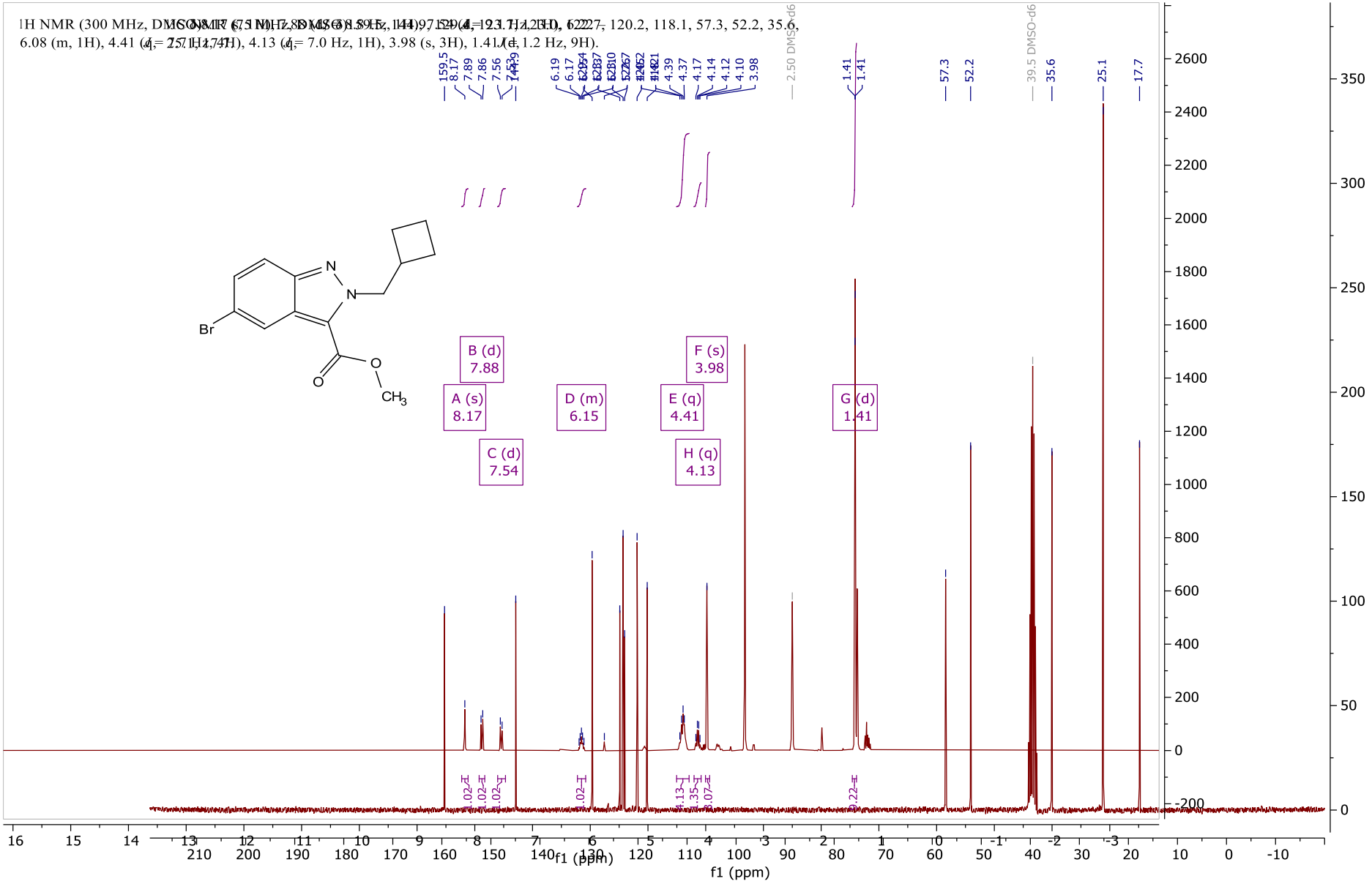
$^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.16 (d, $J$ = 1.9, 0.8 Hz, 1H), 7.79 (d, $J$ = 9.0, 0.7 Hz, 1H), 7.49 (dd, $J$ = 9.1, 1.9 Hz, 1H), 4.88 (d, $J$ = 7.3 Hz, 2H), 3.99 (s, 3H), 2.90 (p, $J$ = 7.4 Hz, 1H), 1.98 – 1.90 (m, 2H), 1.88 – 1.78 (m, 4H).





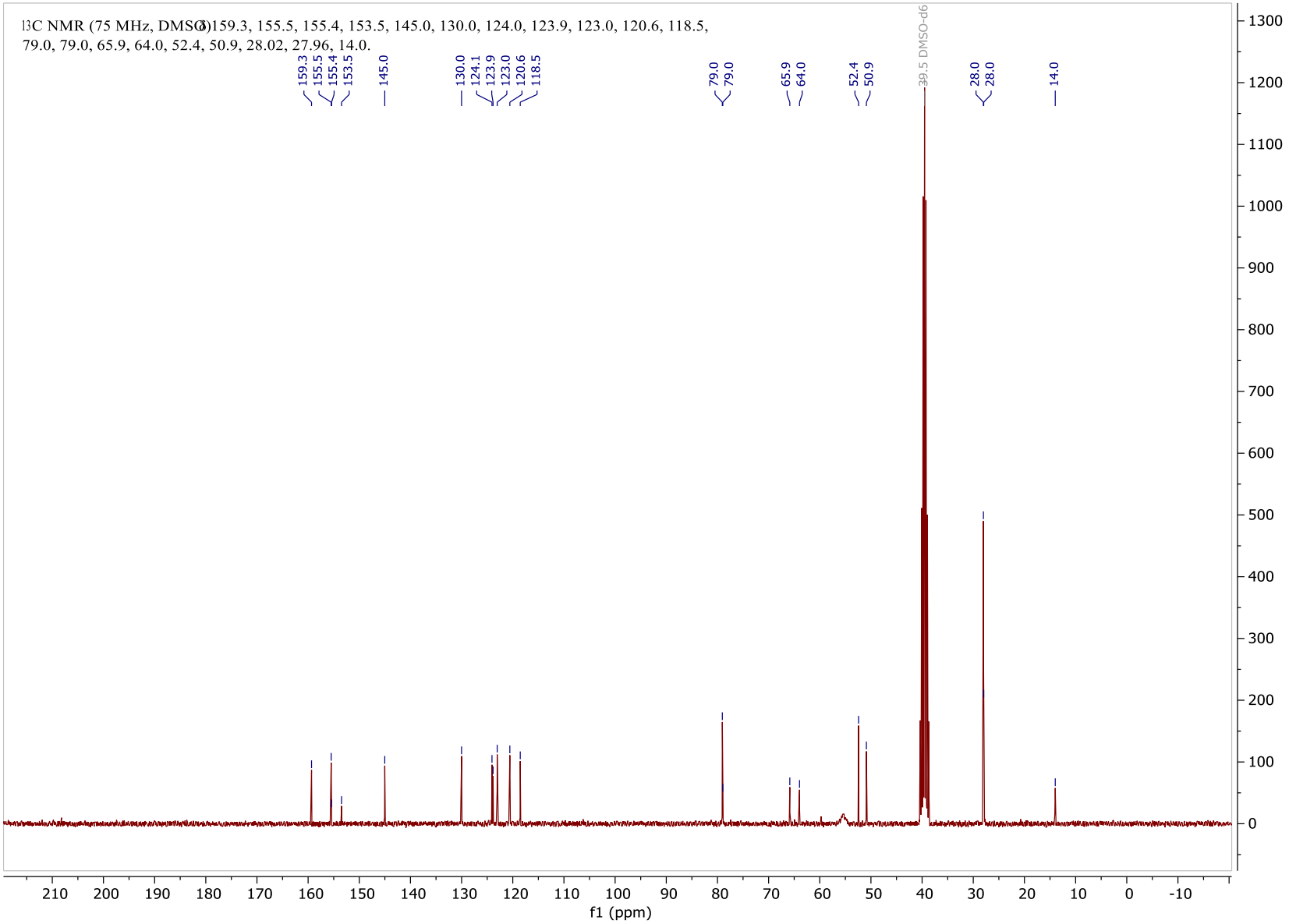


**16l**-$^1$H

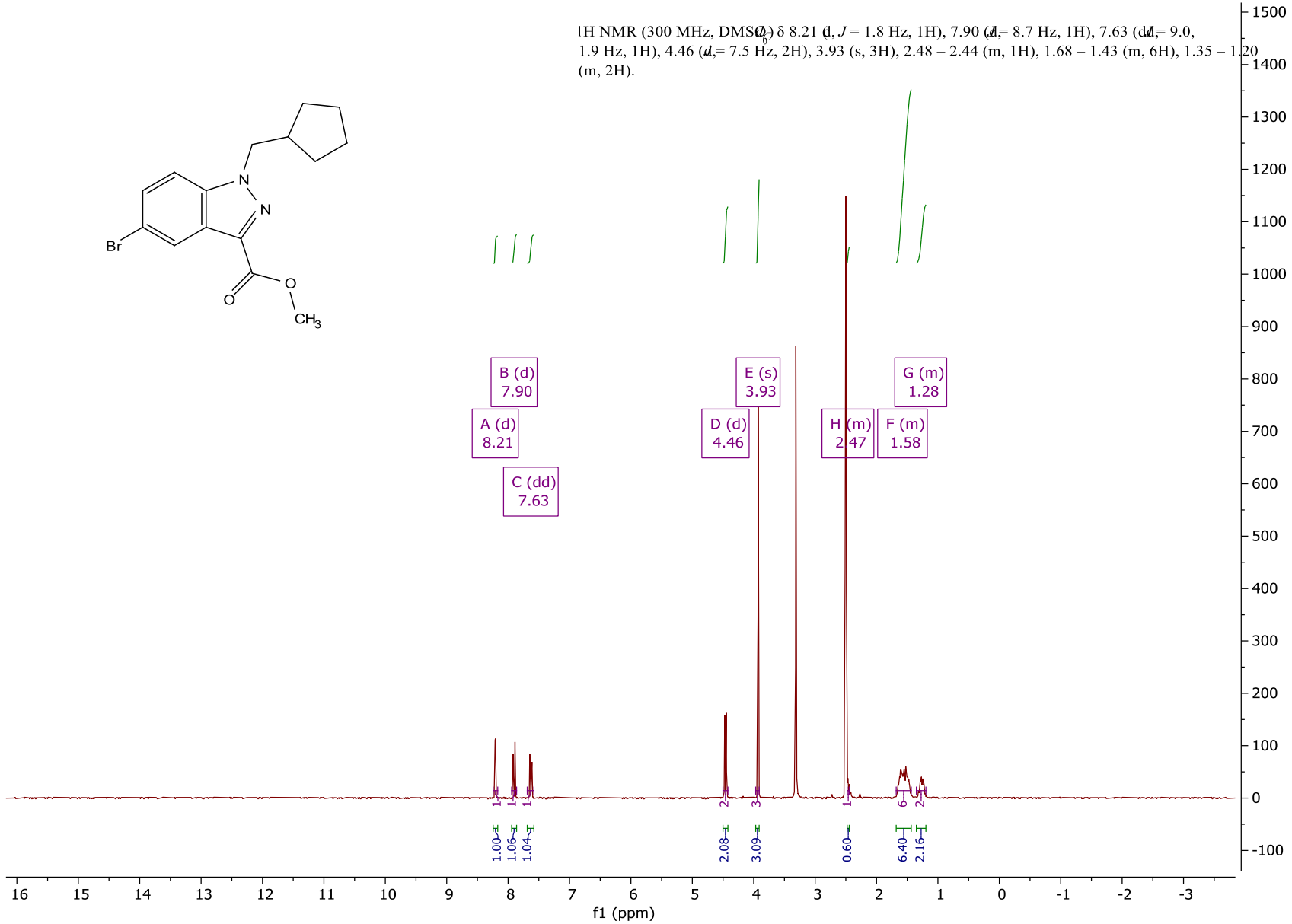



**16l**-$^{13}$C

**16m**-$^{1}$H

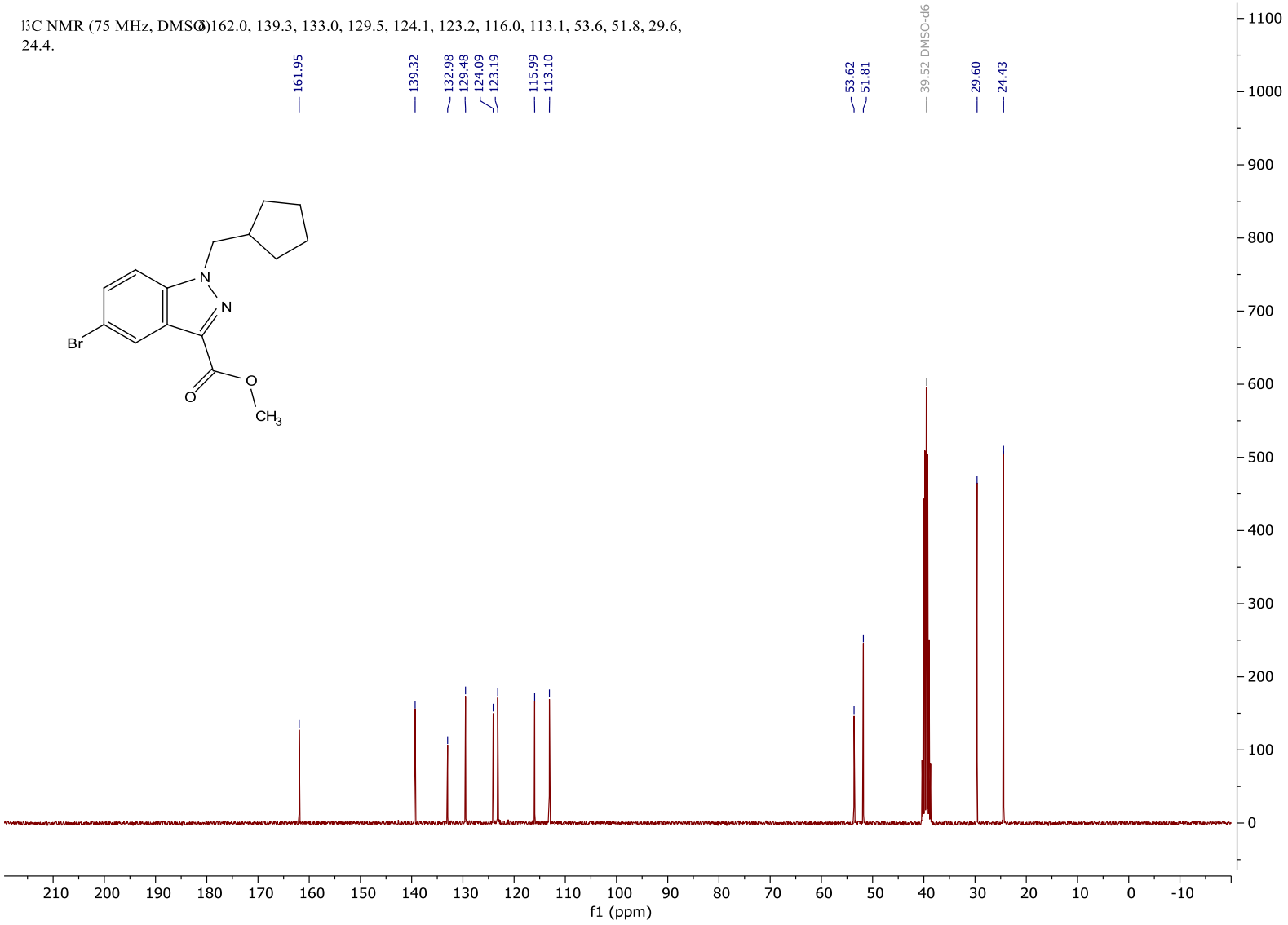

13C NMR (75 MHz, DMSO) δ 159.3, 155.5, 155.4, 153.5, 145.0, 130.0, 124.0, 123.9, 123.0, 120.6, 118.5, 79.0, 79.0, 65.9, 64.0, 52.4, 50.9, 28.02, 27.96, 14.0.
159.3
155.5
155.4
153.5
145.0
130.0
124.1
123.9
123.0
120.6
118.5
79.0
79.0
65.9
64.0
52.4
50.9
39.5 DMSO-d6
28.0
28.0
14.0
f1 (ppm)

**16m**-$^{13}$C

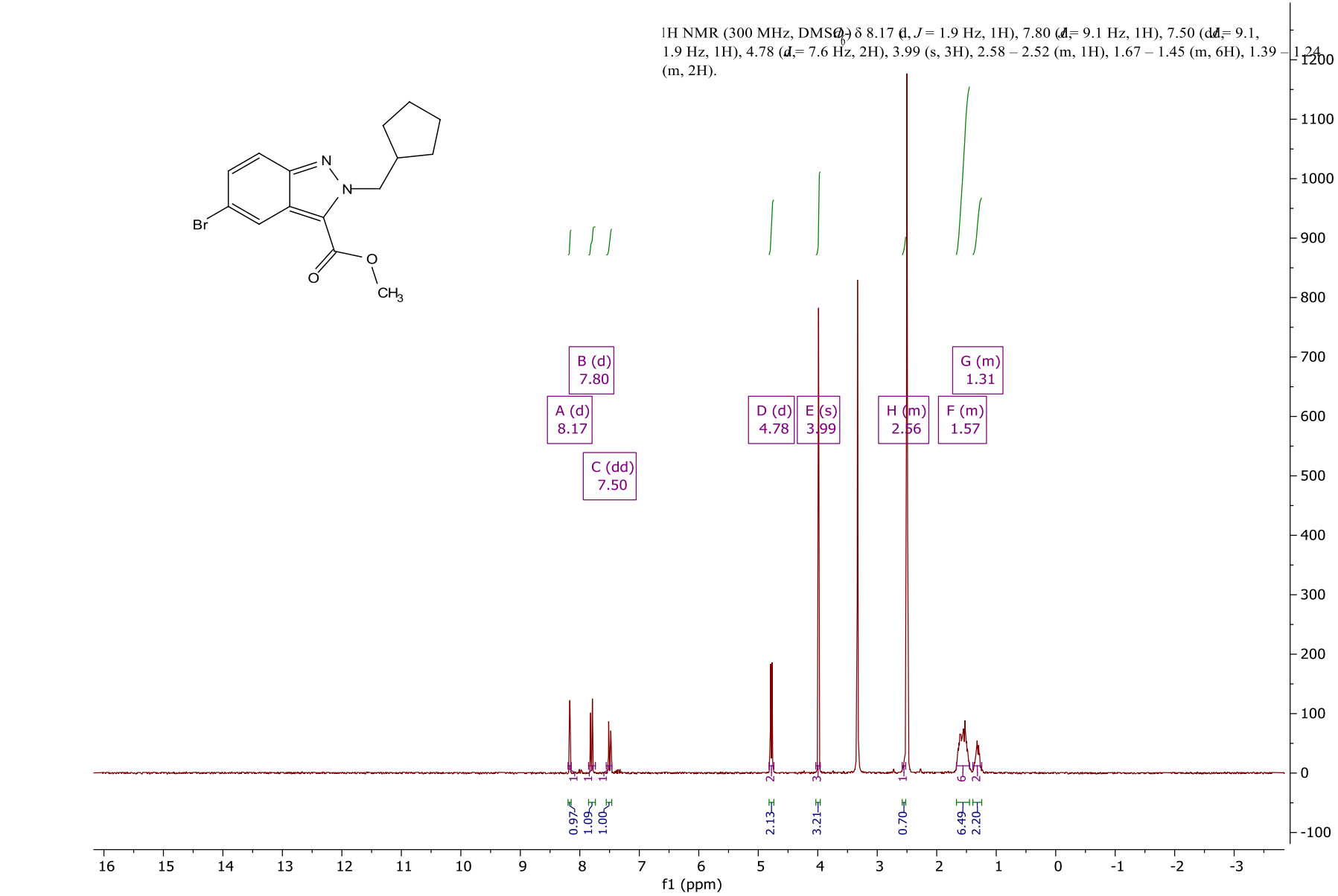

1H NMR (300 MHz, DMSO-d6) δ 8.21 (d, J = 1.8 Hz, 1H), 7.90 (d, J = 8.7 Hz, 1H), 7.63 (dd, J = 9.0, 1.9 Hz, 1H), 4.46 (d, J = 7.5 Hz, 2H), 3.93 (s, 3H), 2.48 – 2.44 (m, 1H), 1.68 – 1.43 (m, 6H), 1.35 – 1.20 (m, 2H).
Br
N
N
O
O
CH3
B (d) 7.90
A (d) 8.21
C (dd) 7.63
D (d) 4.46
E (s) 3.93
H (m) 2.47
F (m) 1.58
G (m) 1.28
1.00
1.06
1.04
2.08
3.09
0.60
6.40
2.16
f1 (ppm)

**15n**-1H

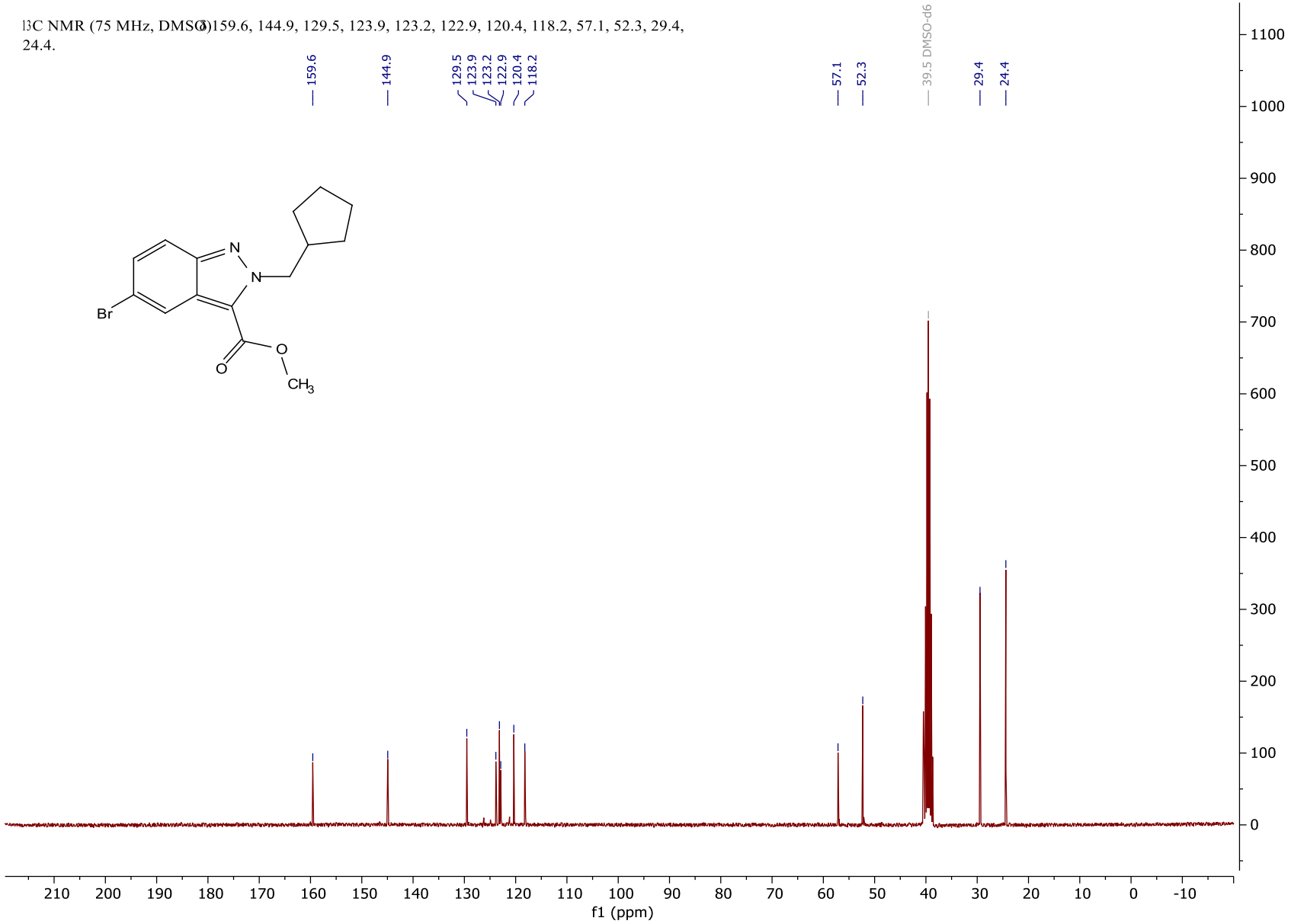
$^{13}$C NMR (75 MHz, DMSO) δ 162.0, 139.3, 133.0, 129.5, 124.1, 123.2, 116.0, 113.1, 53.6, 51.8, 29.6, 24.4.



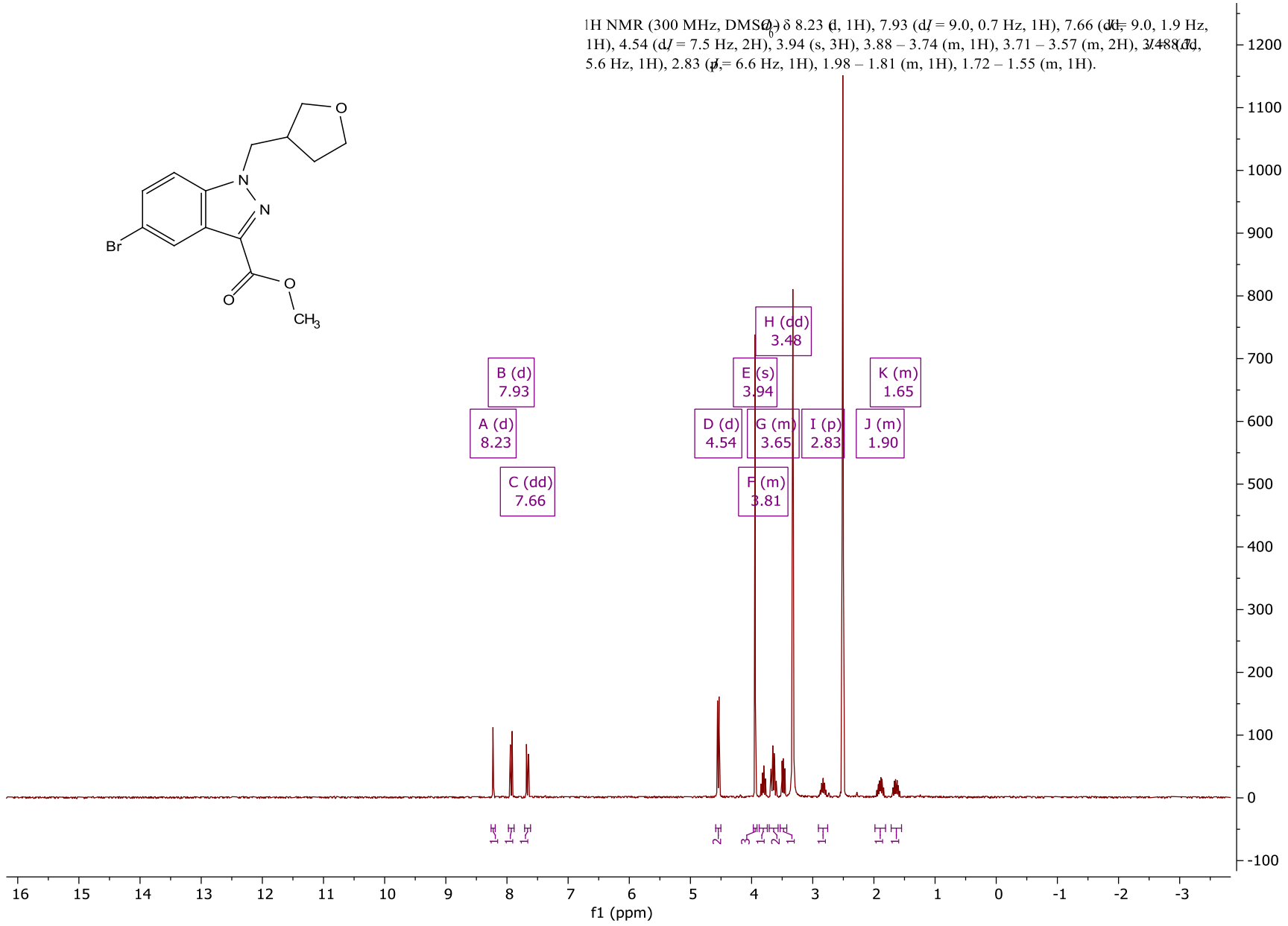

15n-$^{13}$C


1H NMR (300 MHz, DMSO-d6) δ 8.17 (d, J = 1.9 Hz, 1H), 7.80 (d, J = 9.1 Hz, 1H), 7.50 (dd, J = 9.1, 1.9 Hz, 1H), 4.78 (d, J = 7.6 Hz, 2H), 3.99 (s, 3H), 2.58 – 2.52 (m, 1H), 1.67 – 1.45 (m, 6H), 1.39 – 1.24 (m, 2H).
Br
N
N
O
O
CH3
A (d) 8.17
B (d) 7.80
C (dd) 7.50
D (d) 4.78
E (s) 3.99
H (m) 2.56
F (m) 1.57
G (m) 1.31
0.97
1.09
1.00
2.13
3.21
0.70
6.49
2.20
f1 (ppm)

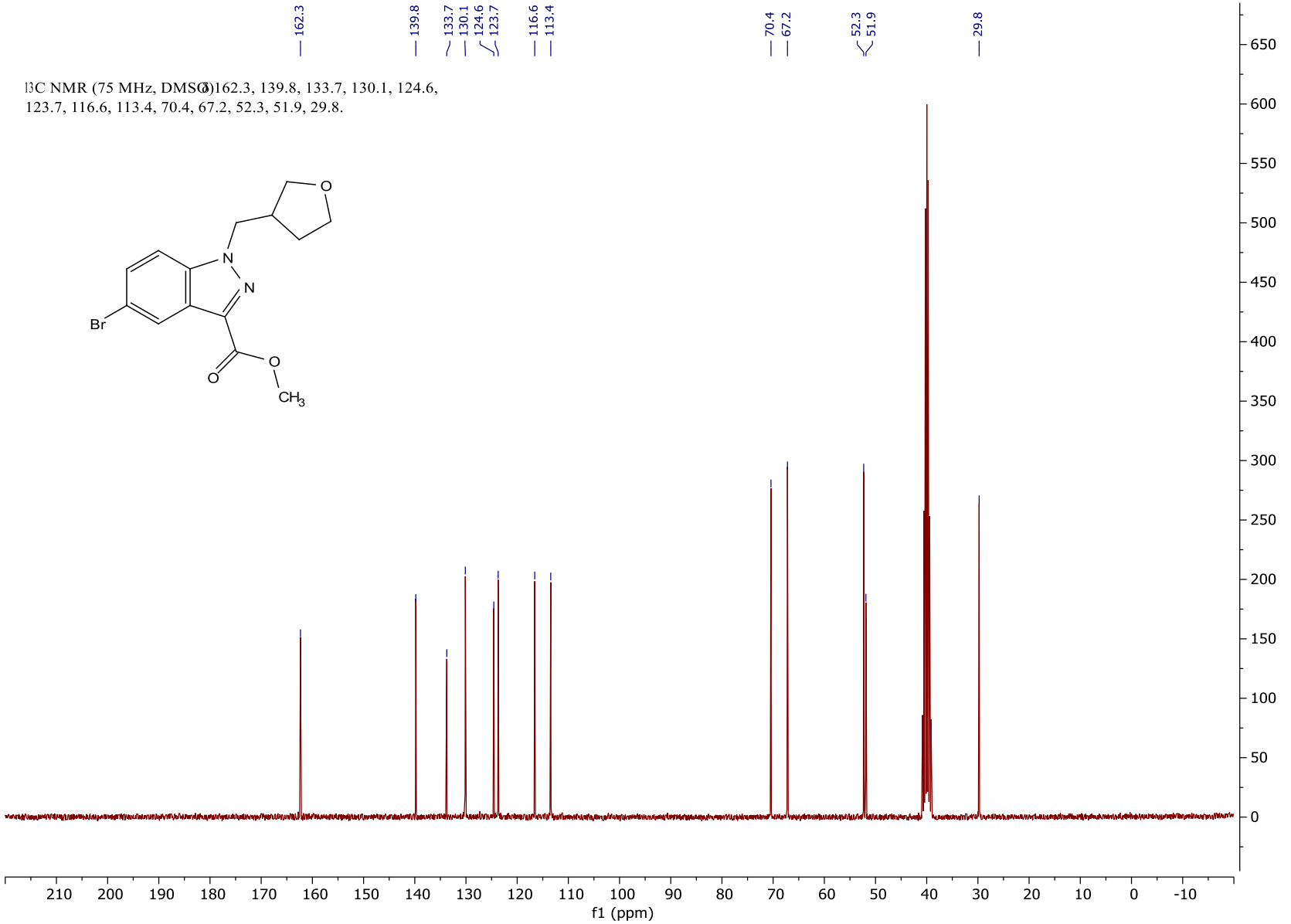
16n-$^{1}$H


13C NMR (75 MHz, DMSO) δ 159.6, 144.9, 129.5, 123.9, 123.2, 122.9, 120.4, 118.2, 57.1, 52.3, 29.4, 24.4.
159.6
144.9
129.5
123.9
123.2
122.9
120.4
118.2
57.1
52.3
39.5 DMSO-d6
29.4
24.4
Br
N
N
O
O
CH3
f1 (ppm)

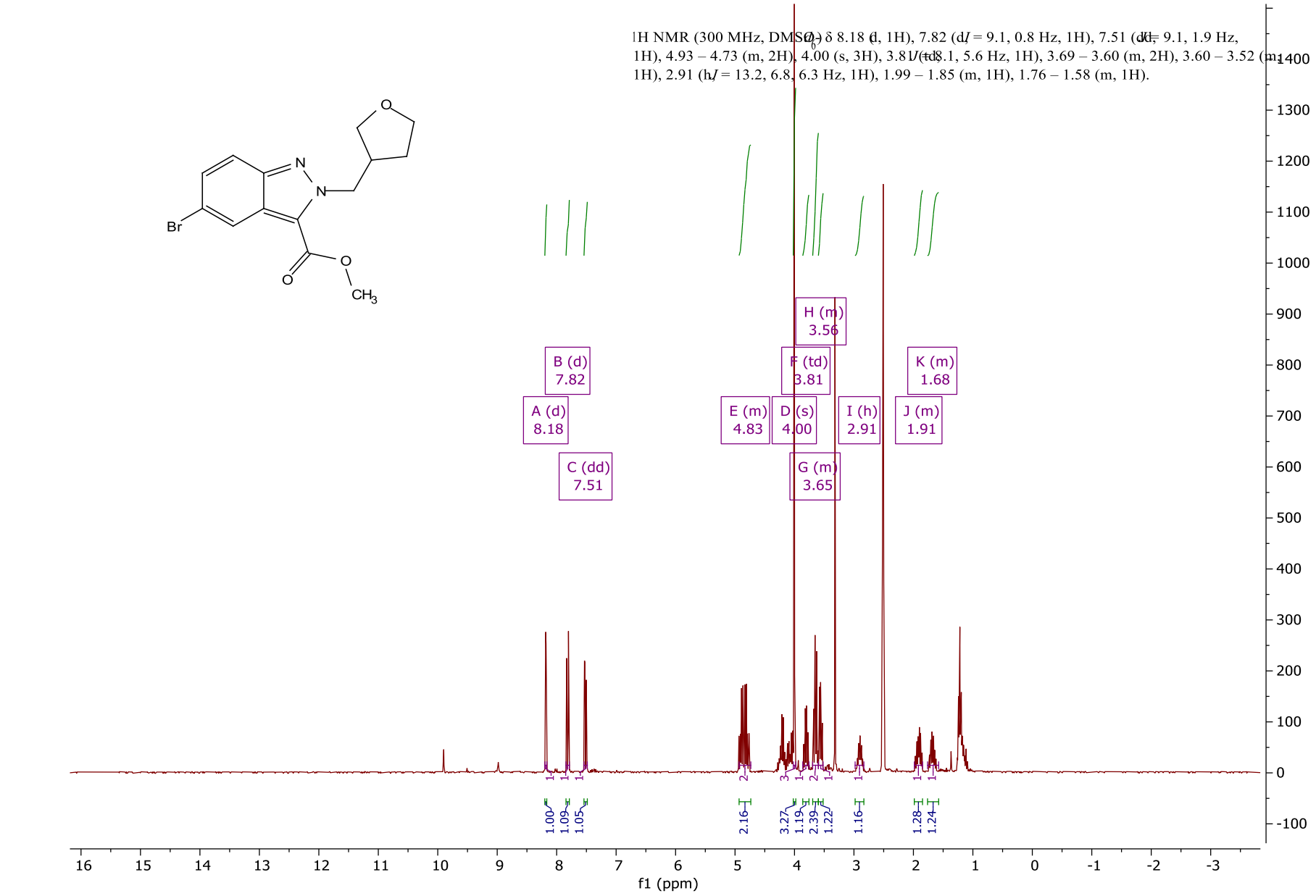
16n-$^{13}$C


1H NMR (300 MHz, DMSO-d6) δ 8.23 (d, 1H), 7.93 (d, J = 9.0, 0.7 Hz, 1H), 7.66 (dd, J = 9.0, 1.9 Hz, 1H), 4.54 (d, J = 7.5 Hz, 2H), 3.94 (s, 3H), 3.88 – 3.74 (m, 1H), 3.71 – 3.57 (m, 2H), 3.48 (dd, 5.6 Hz, 1H), 2.83 (p, J = 6.6 Hz, 1H), 1.98 – 1.81 (m, 1H), 1.72 – 1.55 (m, 1H).
Br
N
N
O
O
O
CH3
B (d) 7.93
A (d) 8.23
C (dd) 7.66
H (dd) 3.48
E (s) 3.94
D (d) 4.54
G (m) 3.65
I (p) 2.83
J (m) 1.90
K (m) 1.65
F (m) 3.81
f1 (ppm)

**15o**-$^{1}$H

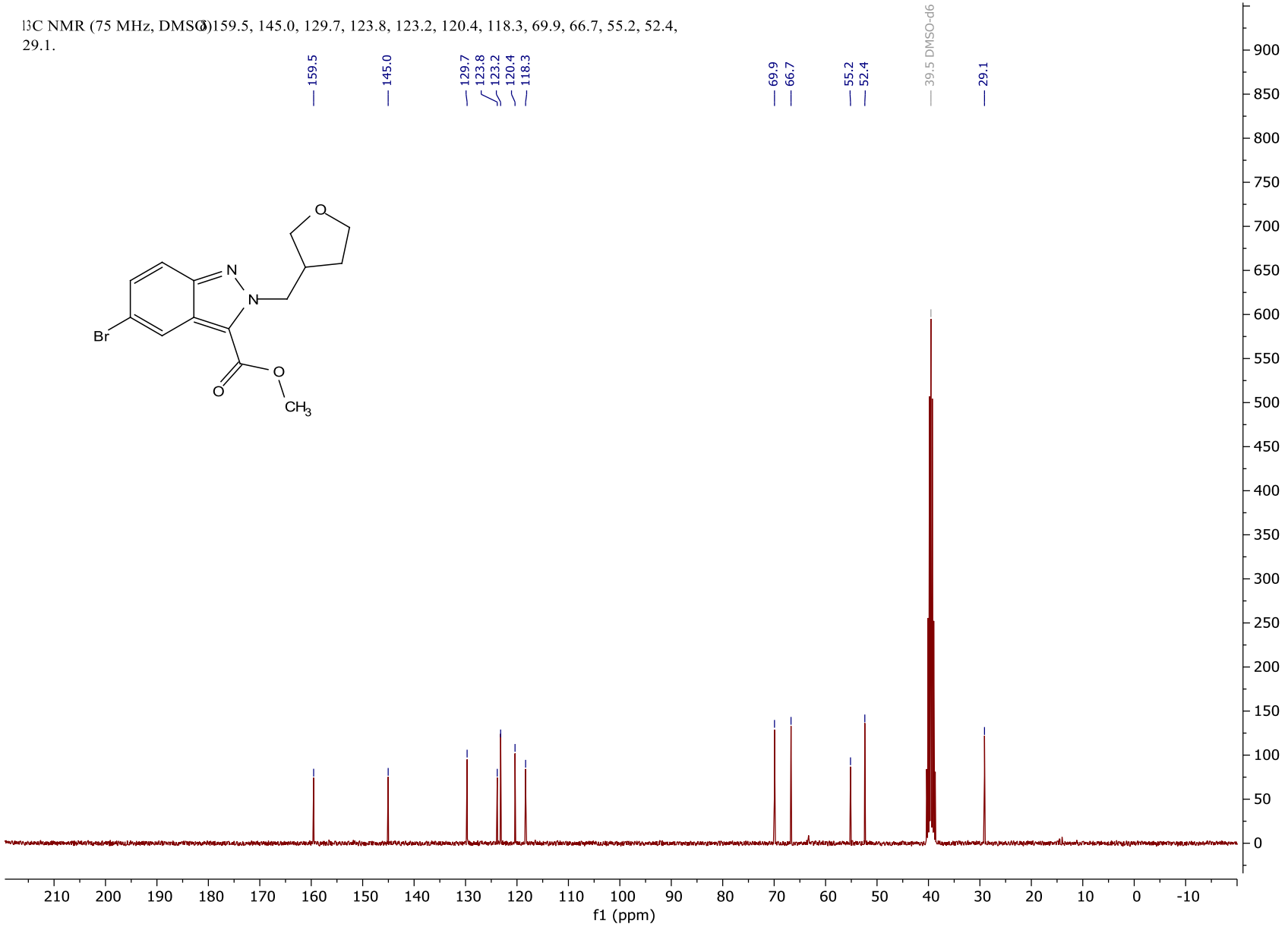

162.3
139.8
133.7
130.1
124.6
123.7
116.6
113.4
70.4
67.2
52.3
51.9
29.8
13C NMR (75 MHz, DMSO) 162.3, 139.8, 133.7, 130.1, 124.6, 123.7, 116.6, 113.4, 70.4, 67.2, 52.3, 51.9, 29.8.
Br
N
N
O
O
O
CH3
f1 (ppm)

**15o**-$^{13}$C


1H NMR (300 MHz, DMSO-d6) δ 8.18 (d, 1H), 7.82 (d, J = 9.1, 0.8 Hz, 1H), 7.51 (dd, J = 9.1, 1.9 Hz, 1H), 4.93 – 4.73 (m, 2H), 4.00 (s, 3H), 3.81 (td, J = 8.1, 5.6 Hz, 1H), 3.69 – 3.60 (m, 2H), 3.60 – 3.52 (m, 1H), 2.91 (h, J = 13.2, 6.8, 6.3 Hz, 1H), 1.99 – 1.85 (m, 1H), 1.76 – 1.58 (m, 1H).
Br
N
N
O
O
O
CH3
A (d) 8.18
B (d) 7.82
C (dd) 7.51
D (s) 4.00
E (m) 4.83
F (td) 3.81
G (m) 3.65
H (m) 3.56
I (h) 2.91
J (m) 1.91
K (m) 1.68
1.00
1.09
1.05
2.16
3.27
1.19
2.39
1.22
1.16
1.28
1.24
f1 (ppm)

**16o**-$^{1}$H

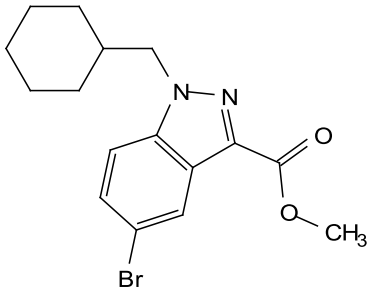
13C NMR (75 MHz, DMSO) δ 159.5, 145.0, 129.7, 123.8, 123.2, 120.4, 118.3, 69.9, 66.7, 55.2, 52.4, 29.1.




**16o**-$^{13}$C

LCJ-007-139 B2.10.fid
LCJ-007-139 B2

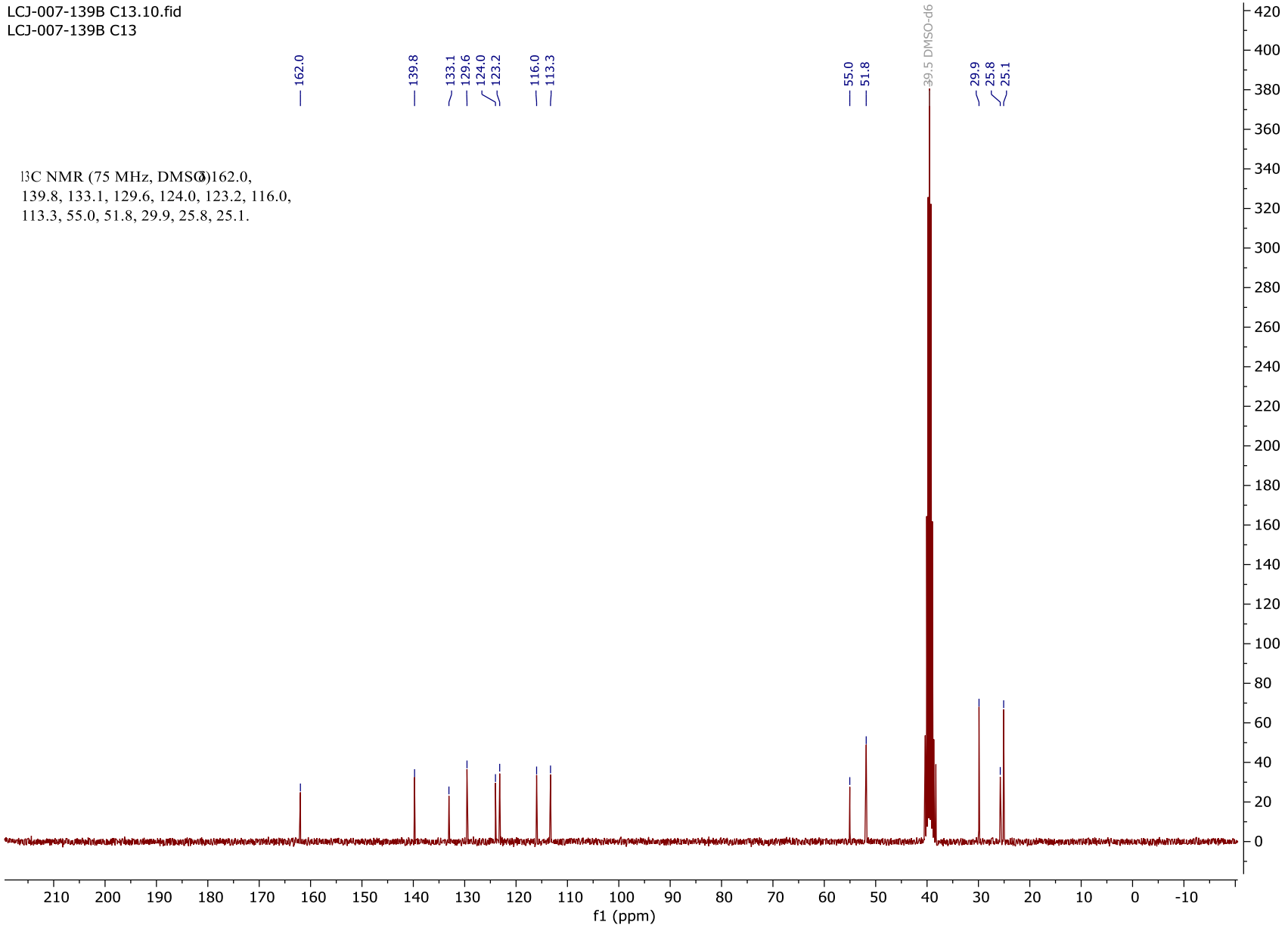
$^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.21 (d, $J$ = 1.9, 0.6 Hz, 1H), 7.89 (d, $J$ = 9.0, 0.7 Hz, 1H), 7.63 (dd, $J$ = 9.0, 1.9 Hz, 1H), 4.38 (d, $J$ = 7.2 Hz, 2H), 3.94 (s, 3H), 2.00 – 1.83 (m, 1H), 1.63 (s, 3H), 1.46 (d, $J$ = 12.1 Hz, 2H), 1.14 (t, $J$ = 9.9 Hz, 3H), 1.02 (d, $J$ = 11.2 Hz, 2H).







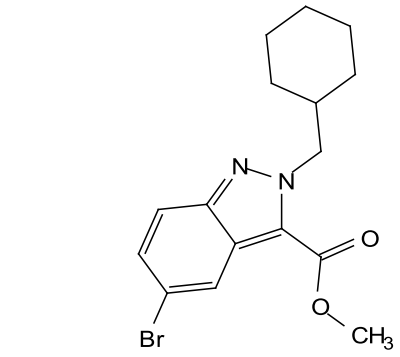
**15p**-$^1$H


LCJ-007-139B C13.10.fid
LCJ-007-139B C13
162.0
139.8
133.1
129.6
124.0
123.2
116.0
113.3
55.0
51.8
39.5 DMSO-d6
29.9
25.8
25.1
13C NMR (75 MHz, DMSO) δ 162.0,
139.8, 133.1, 129.6, 124.0, 123.2, 116.0,
113.3, 55.0, 51.8, 29.9, 25.8, 25.1.
f1 (ppm)

**15p**-$^{13}$C

LCJ-007-139 C1.10.fid
LCJ-007-139 C1

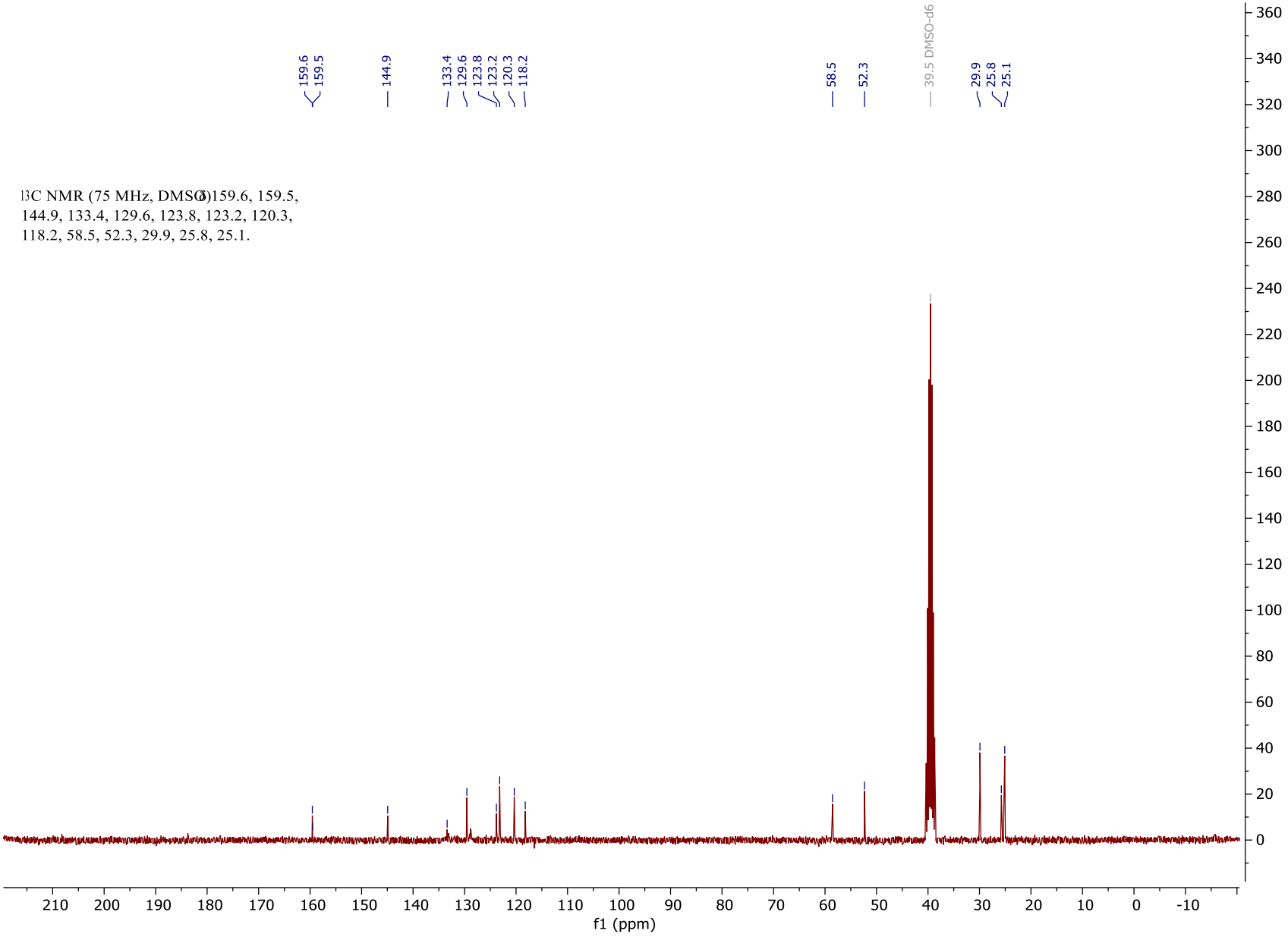
$^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.17 (d, $J$ = 1.9, 0.8 Hz, 1H), 7.79 (d, $J$ = 9.1, 0.8 Hz, 1H), 7.49 (dd, $J$ = 9.1, 1.9 Hz, 1H), 4.70 (d, $J$ = 7.2 Hz, 2H), 3.99 (s, 3H), 2.03 – 1.89 (m, 1H), 1.61 (d, $J$ = 7.2 Hz, 3H), 1.47 (d, $J$ = 11.8 Hz, 2H), 1.20 – 1.08 (m, 3H), 1.04 (d, $J$ = 11.5 Hz, 2H).







**16p**-$^1$H

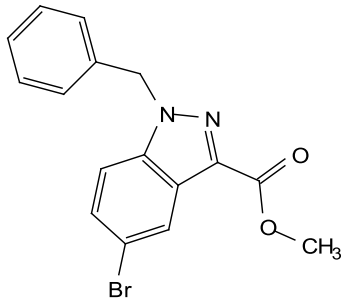



$^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ 159.6, 159.5, 144.9, 133.4, 129.6, 123.8, 123.2, 120.3, 118.2, 58.5, 52.3, 29.9, 25.8, 25.1.

**16p**-$^{13}$C

LCJ-009-186B2.10.fid
LCJ-009-186B2

$^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.22 (d, $J$ = 1.8 Hz, 1H), 7.90 (d, $J$ = 9.0 Hz, 1H), 7.65 (dd, $J$ = 9.0, 1.9 Hz, 1H), 7.39 – 7.21 (m, 5H), 5.80 (s, 2H), 3.93 (s, 3H).

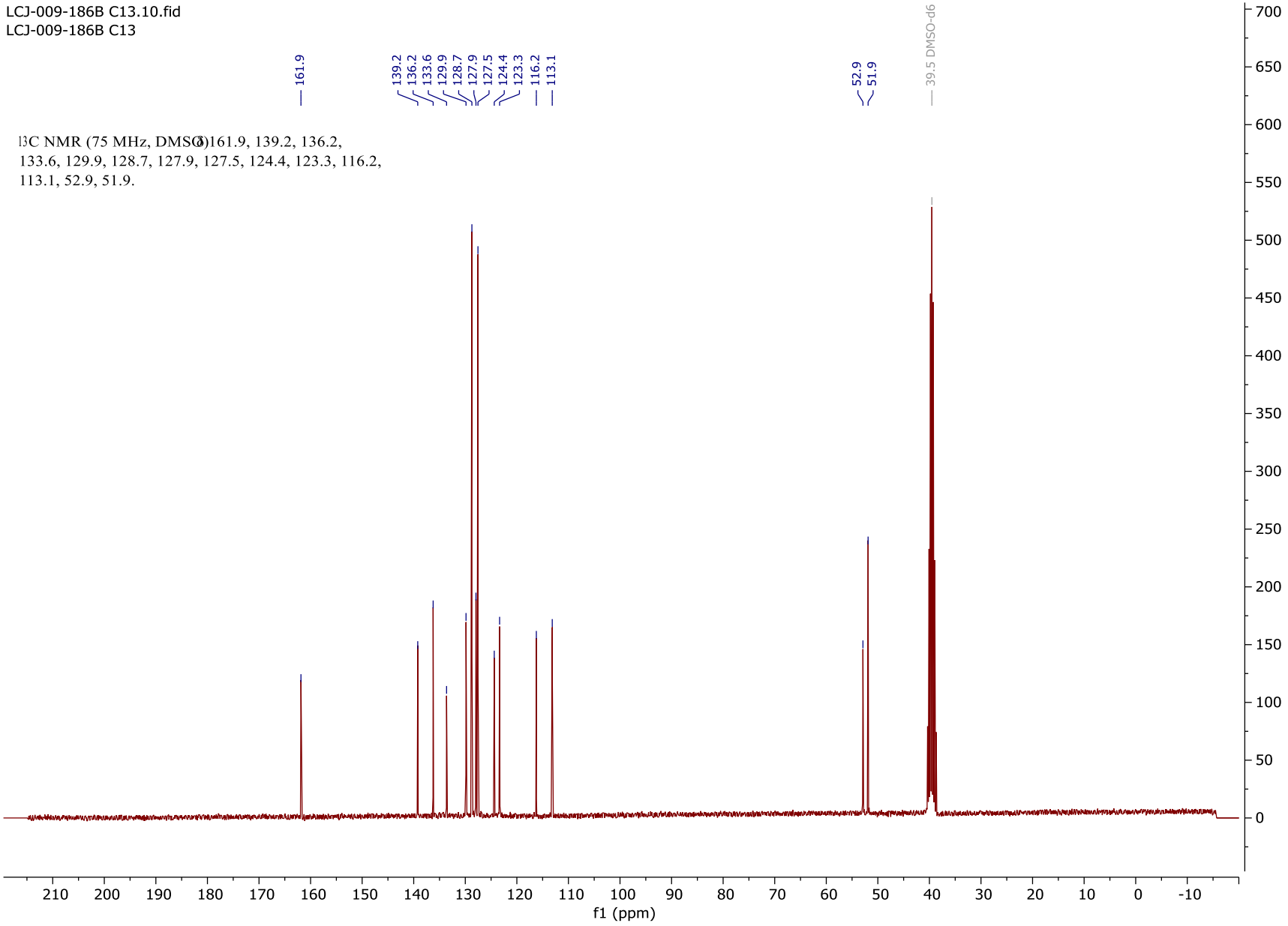






**15q**-$^1$H

LCJ-009-186B C13.10.fid
LCJ-009-186B C13

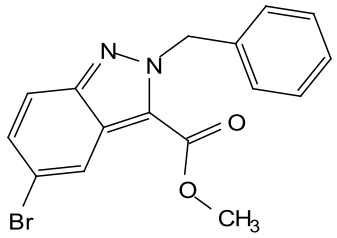



$^{13}$C NMR (75 MHz, DMSO-$d_6$) 161.9, 139.2, 136.2, 133.6, 129.9, 128.7, 127.9, 127.5, 124.4, 123.3, 116.2, 113.1, 52.9, 51.9.

**15q**-$^{13}$C

LCJ-009-186C1.10.fid
LCJ-009-186C1

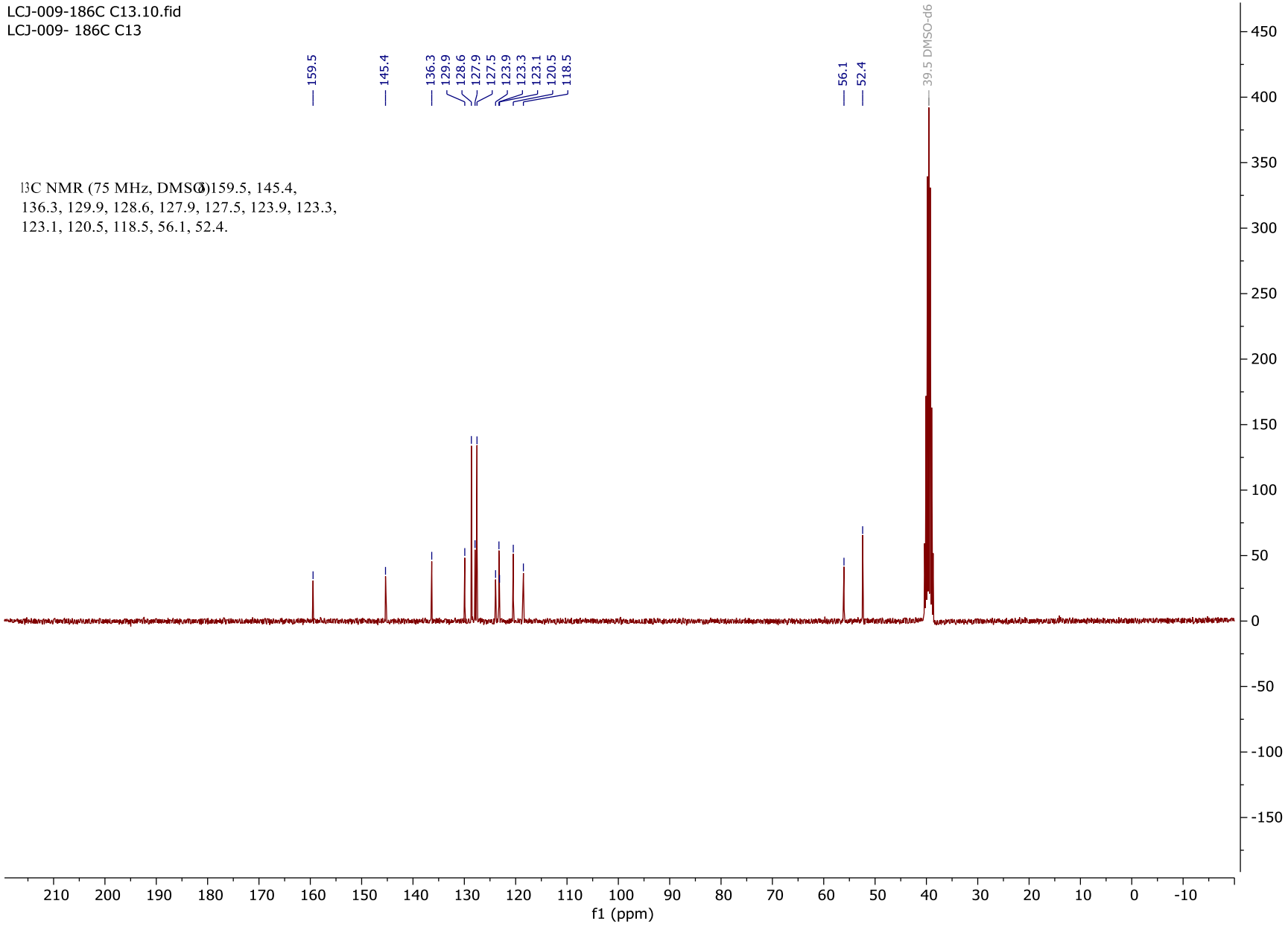
$^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.18 (d, $J$ = 1.9, 0.8 Hz, 1H), 7.82 (d, $J$ = 9.1, 0.8 Hz, 1H), 7.52 (dd, $J$ = 9.1, 1.9 Hz, 1H), 7.39 – 7.20 (m, 5H), 6.07 (s, 2H), 3.98 (s, 3H).





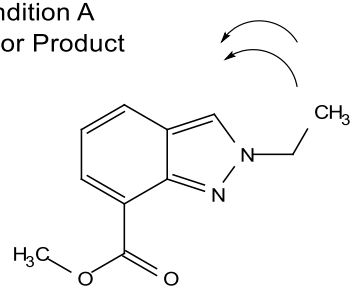


**16q**-$^1$H

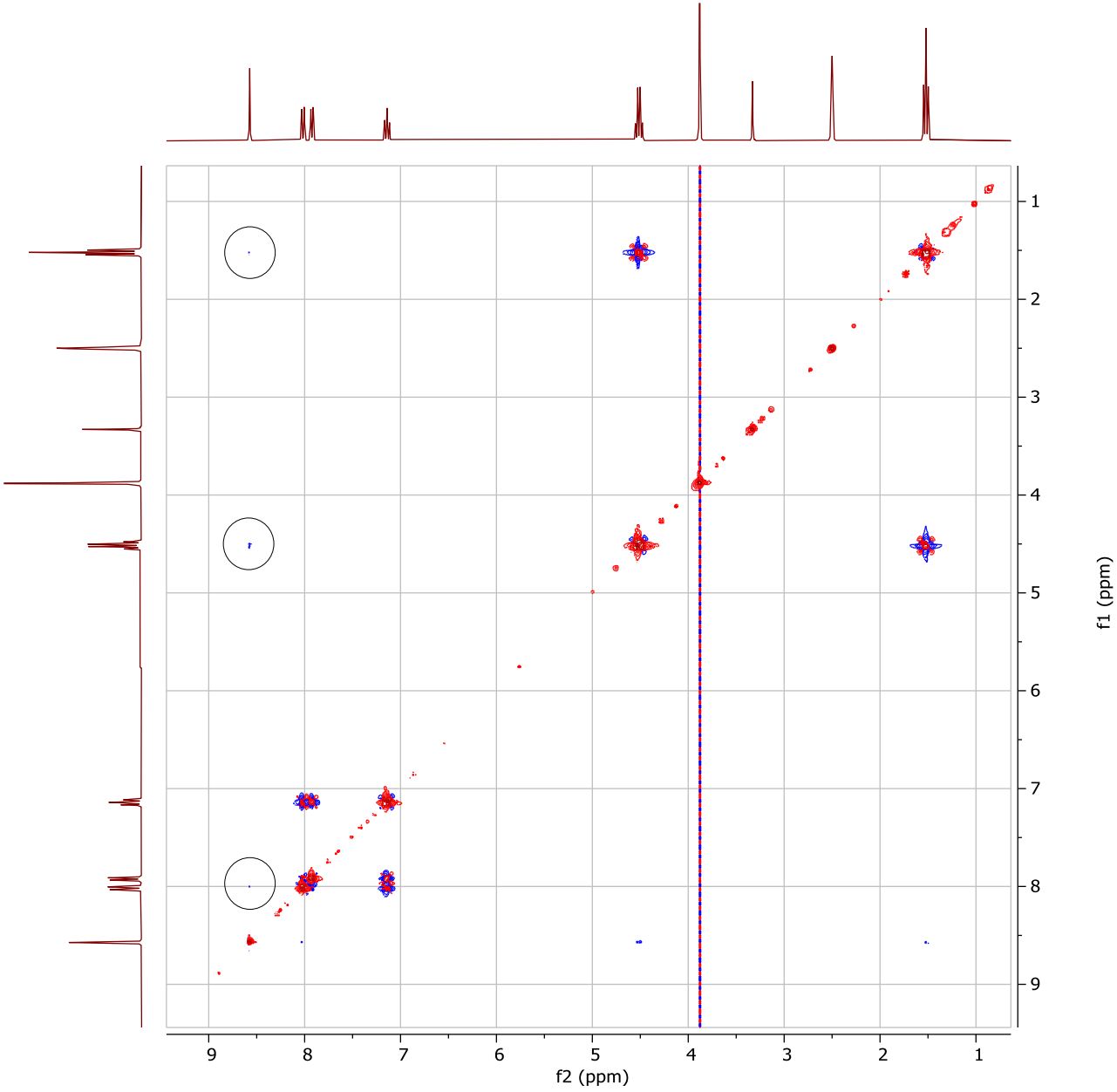

LCJ-009-186C C13.10.fid
LCJ-009- 186C C13
159.5
145.4
136.3
129.9
128.6
127.9
127.5
123.9
123.3
123.1
120.5
118.5
56.1
52.4
39.5 DMSO-d6
13C NMR (75 MHz, DMSO) δ 159.5, 145.4,
136.3, 129.9, 128.6, 127.9, 127.5, 123.9, 123.3,
123.1, 120.5, 118.5, 56.1, 52.4.
f1 (ppm)

**16q**-$^{13}$C

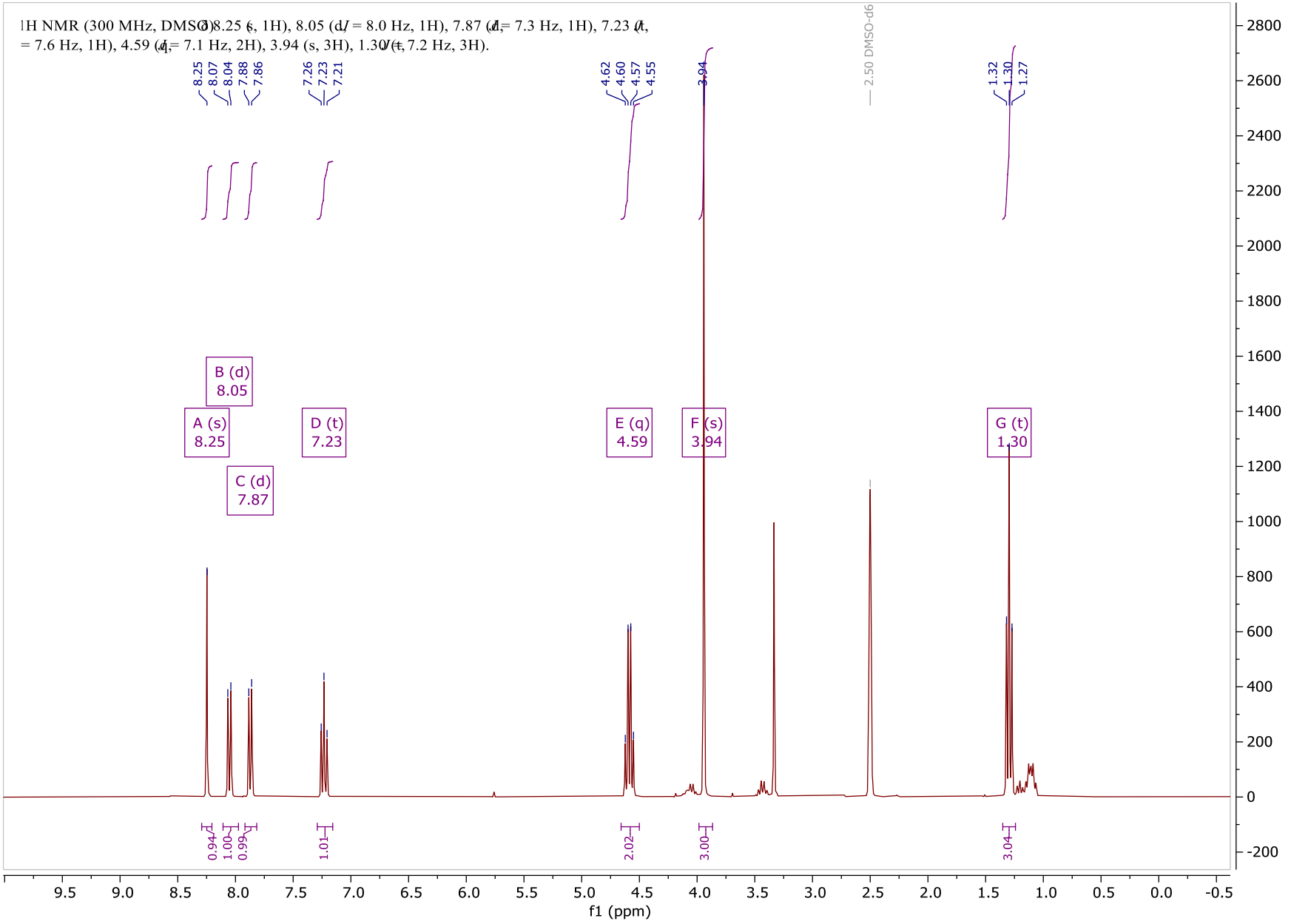
Condition A
Major Product



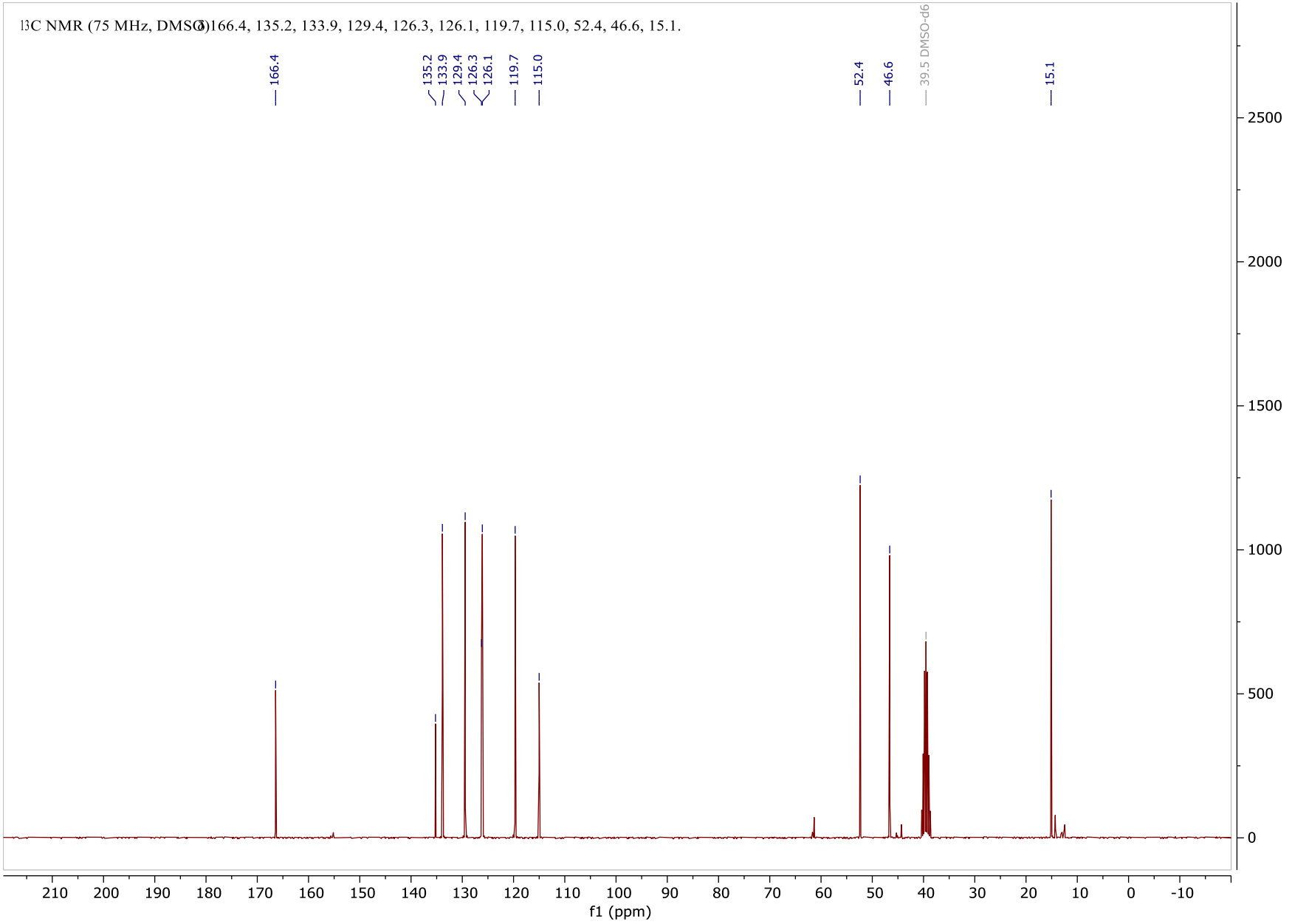

| | Parameter | Value |
|---|---|---|
| 1 | Solvent | DMSO |
| 2 | Temperature | 295.5 |
| 3 | Pulse Sequence | noesygpphpp |
| 4 | Experiment | NOESY |
| 5 | Probe | Z104275_0395 (PA BBO 300S1 BBF-H-D-05 Z) |
| 6 | Number of Scans | 32 |
| 7 | Receiver Gain | 210.0 |
| 8 | Relaxation Delay | 1.9541 |
| 9 | Pulse Width | 14.0000 |
| 10 | Presaturation Frequency | |
| 11 | Acquisition Time | 0.3871 |
| 12 | Acquisition Date | 2023-07-17T23:14:13 |
| 13 | Modification Date | 2023-07-18T05:22:11 |
| 14 | Class | |
| 15 | Spectrometer Frequency | (300.13, 300.13) |
| 16 | Spectral Width | (2645.5, 2645.5) |
| 17 | Lowest Frequency | (188.0, 188.0) |
| 18 | Nucleus | (1H, 1H) |
| 19 | Acquired Size | (1024, 256) |
| 20 | Spectral Size | (1024, 1024) |
| 21 | Digital Resolution | (2.58, 2.58) |



**20**-$^{1}$H

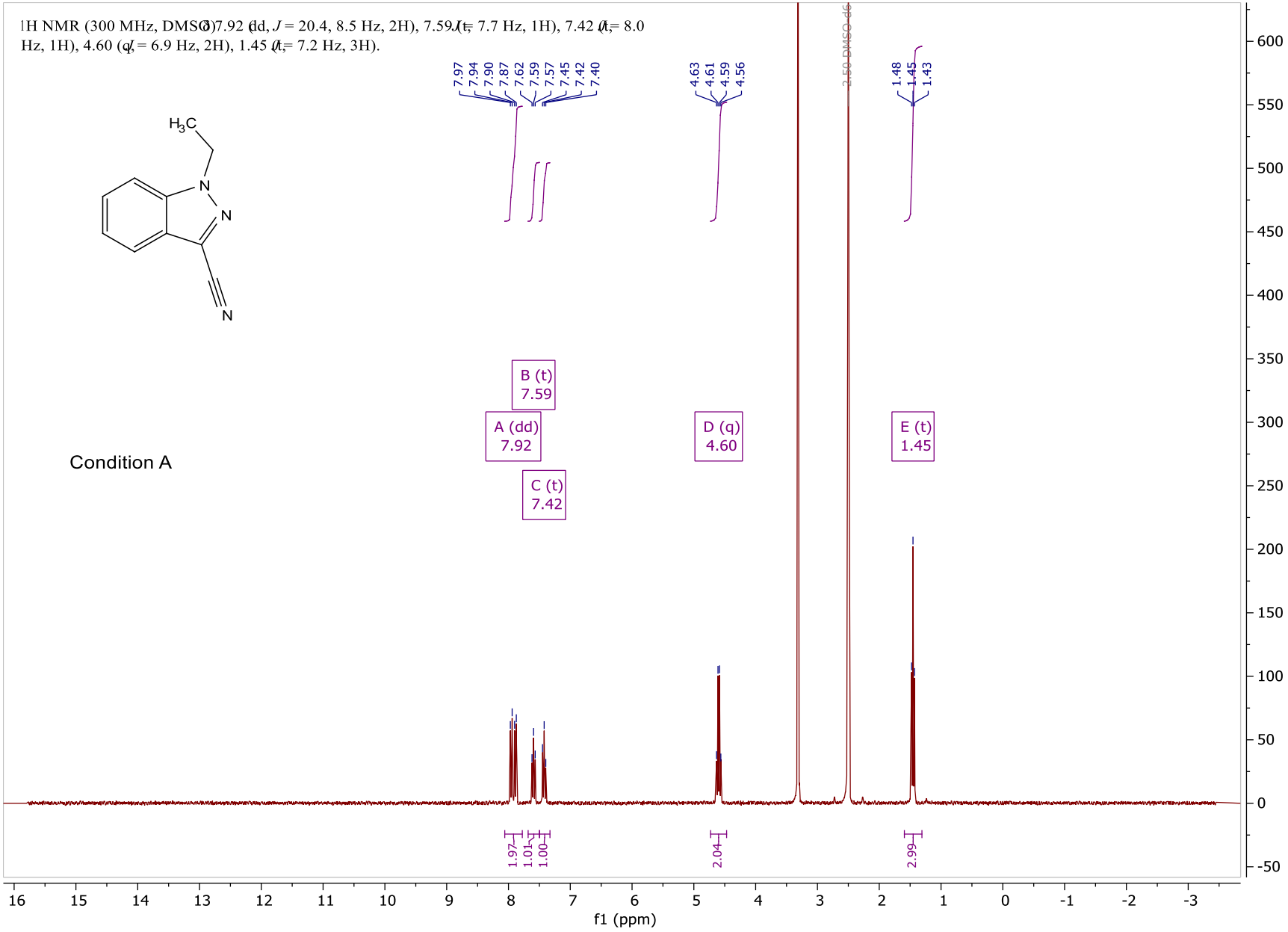

1H NMR (300 MHz, DMSO) δ 8.25 (s, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 7.3 Hz, 1H), 7.23 (t, J = 7.6 Hz, 1H), 4.59 (q, J = 7.1 Hz, 2H), 3.94 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H).
8.25
8.07
8.04
7.88
7.86
7.26
7.23
7.21
4.62
4.60
4.57
4.55
3.94
2.50 DMSO-d6
1.32
1.30
1.27
B (d) 8.05
A (s) 8.25
C (d) 7.87
D (t) 7.23
E (q) 4.59
F (s) 3.94
G (t) 1.30
0.94
1.00
0.99
1.01
2.02
3.00
3.04
f1 (ppm)

**20**-$^{13}$C


13C NMR (75 MHz, DMSO) δ 166.4, 135.2, 133.9, 129.4, 126.3, 126.1, 119.7, 115.0, 52.4, 46.6, 15.1.
166.4
135.2
133.9
129.4
126.3
126.1
119.7
115.0
52.4
46.6
39.5 DMSO-d6
15.1
2500
2000
1500
1000
500
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

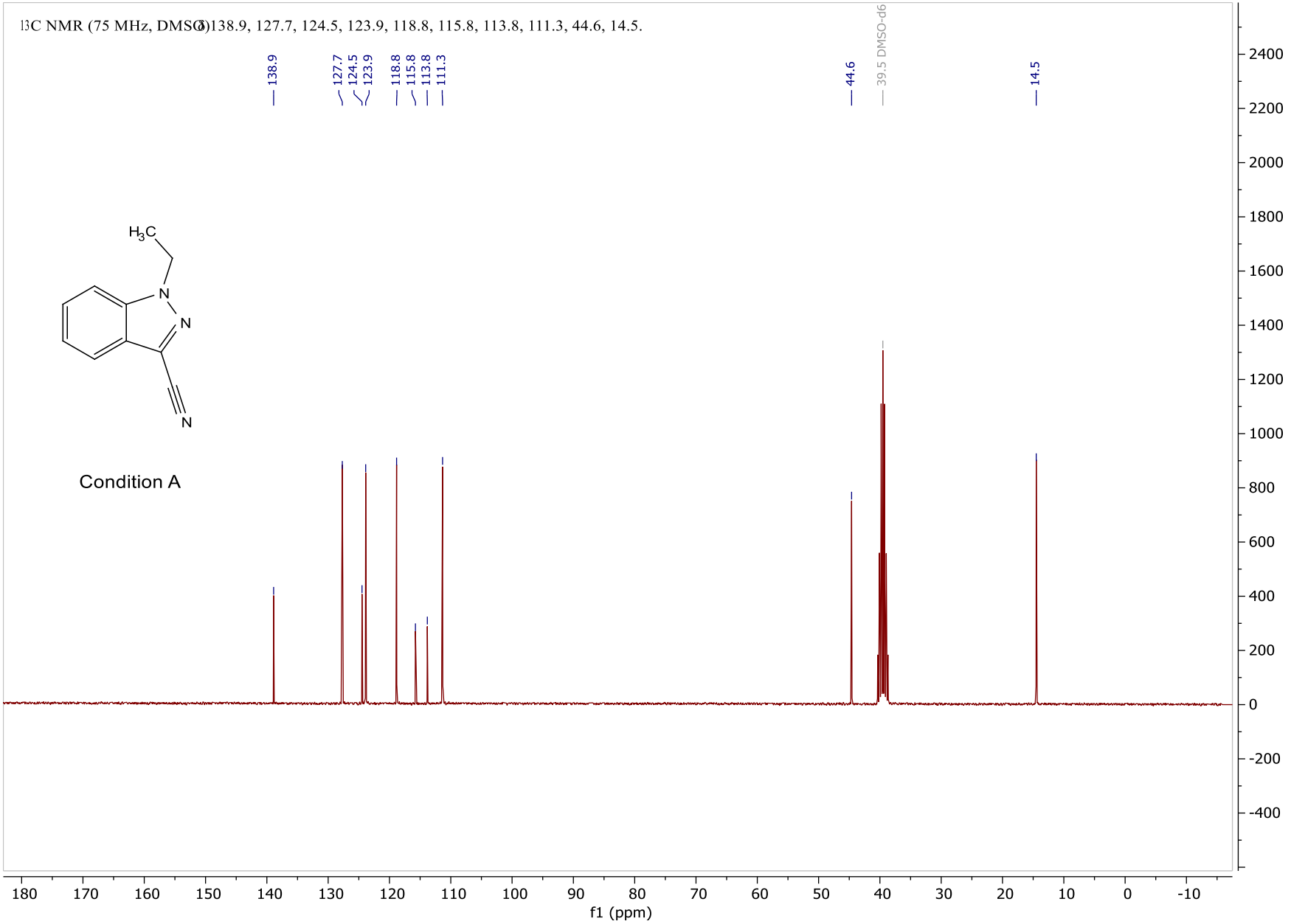
**22-**$^{1}$H

Cond. A


1H NMR (300 MHz, DMSO) δ 7.92 (dd, J = 20.4, 8.5 Hz, 2H), 7.59 (t, J = 7.7 Hz, 1H), 7.42 (t, J = 8.0 Hz, 1H), 4.60 (q, J = 6.9 Hz, 2H), 1.45 (t, J = 7.2 Hz, 3H).
7.97
7.94
7.90
7.87
7.62
7.59
7.57
7.45
7.42
7.40
4.63
4.61
4.59
4.56
2.50 DMSO-d6
1.48
1.45
1.43
H3C
N
N
N
B (t) 7.59
A (dd) 7.92
C (t) 7.42
D (q) 4.60
E (t) 1.45
Condition A
1.97
1.01
1.00
2.04
2.99
f1 (ppm)

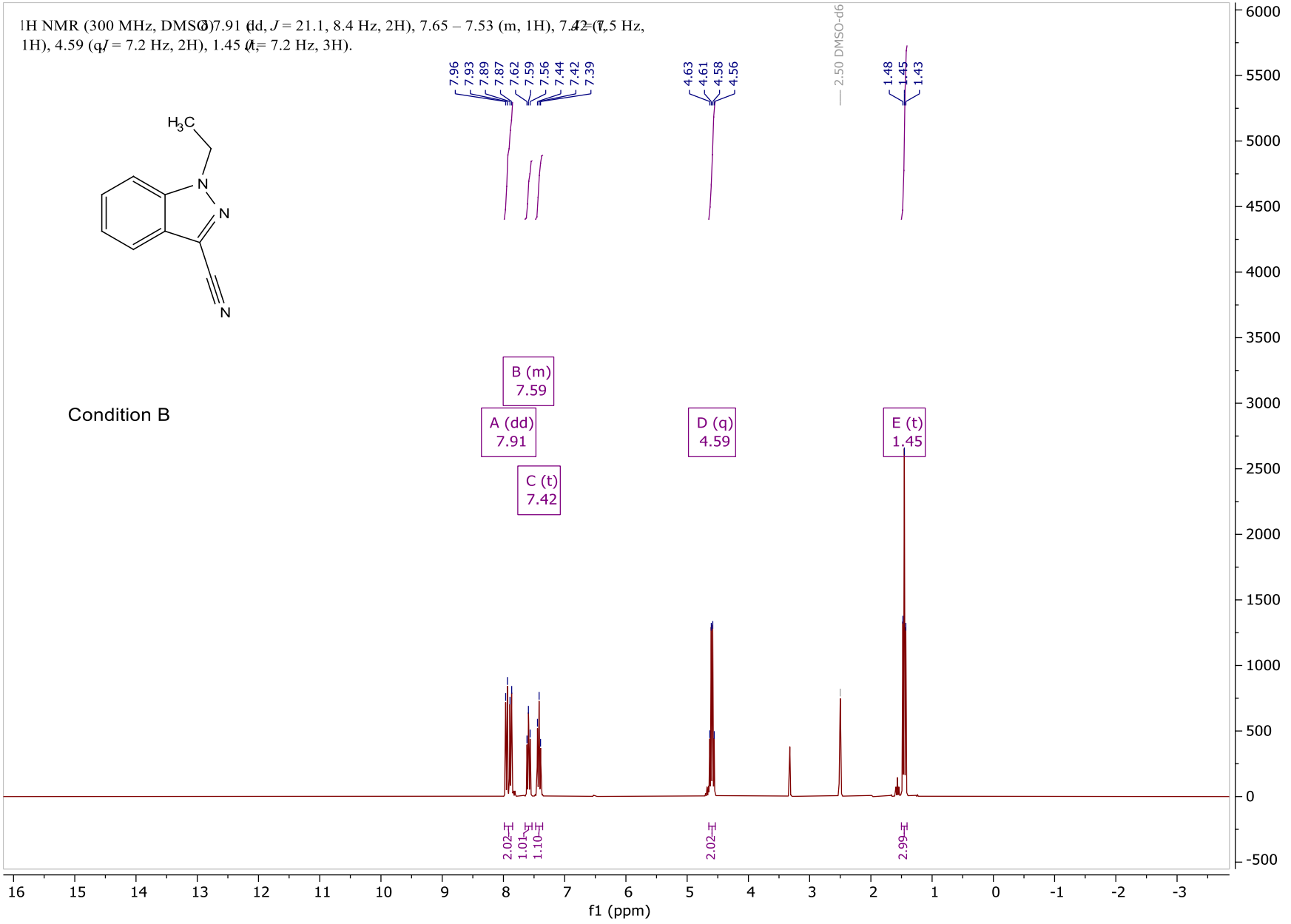
**22**-$^{13}$C

Cond. A


13C NMR (75 MHz, DMSO-d6) δ 138.9, 127.7, 124.5, 123.9, 118.8, 115.8, 113.8, 111.3, 44.6, 14.5.
138.9
127.7
124.5
123.9
118.8
115.8
113.8
111.3
44.6
39.5 DMSO-d6
14.5
H3C
N
N
N
Condition A
f1 (ppm)

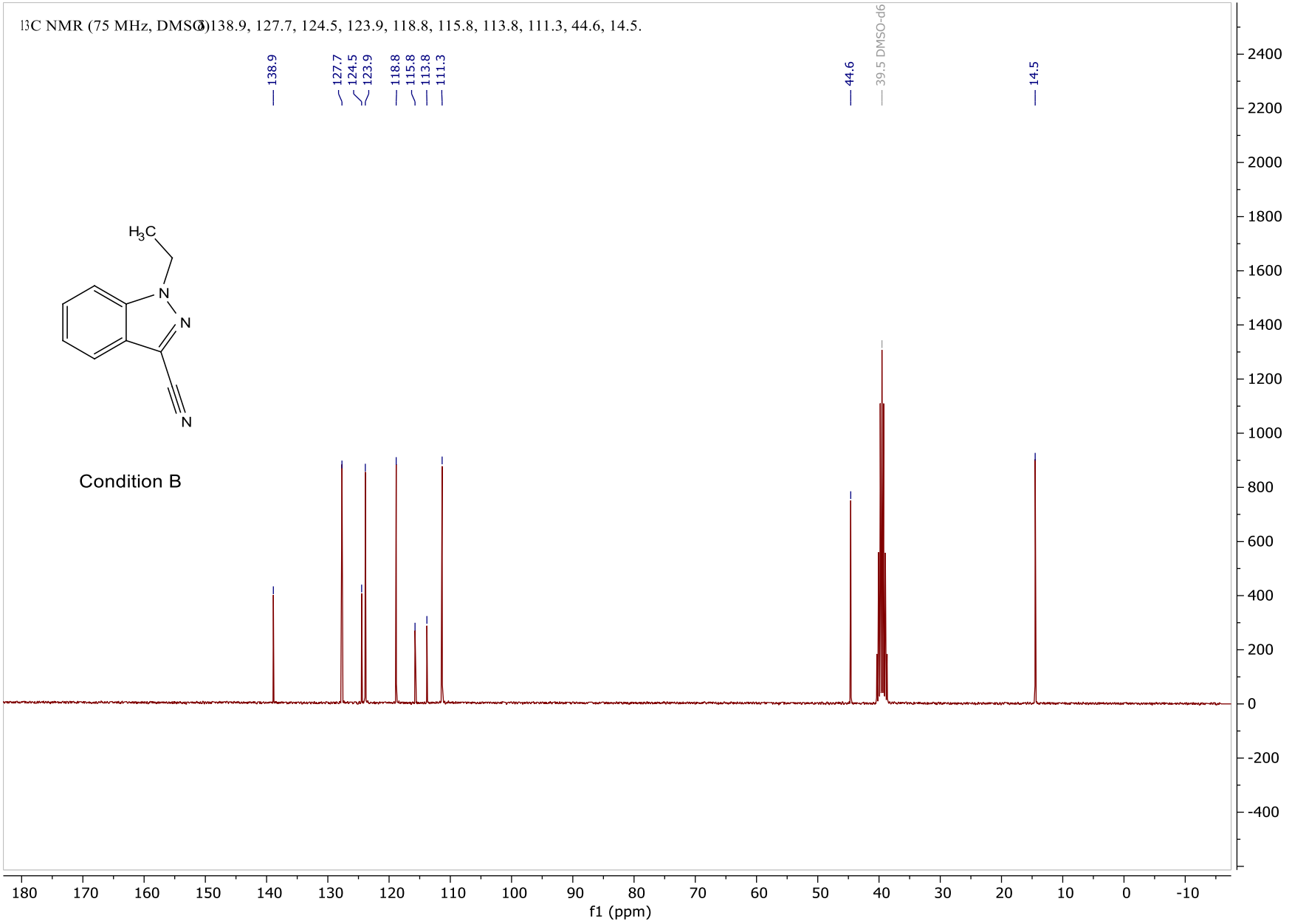
**22**-$^1$H

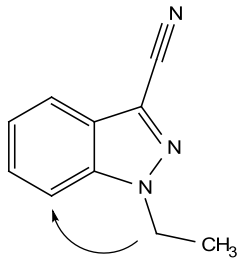
Cond. B


1H NMR (300 MHz, DMSO) δ 7.91 (dd, J = 21.1, 8.4 Hz, 2H), 7.65 – 7.53 (m, 1H), 7.42 (t, J = 7.5 Hz, 1H), 4.59 (q, J = 7.2 Hz, 2H), 1.45 (t, J = 7.2 Hz, 3H).
Condition B
B (m) 7.59
A (dd) 7.91
C (t) 7.42
D (q) 4.59
E (t) 1.45
2.50 DMSO-d6
f1 (ppm)

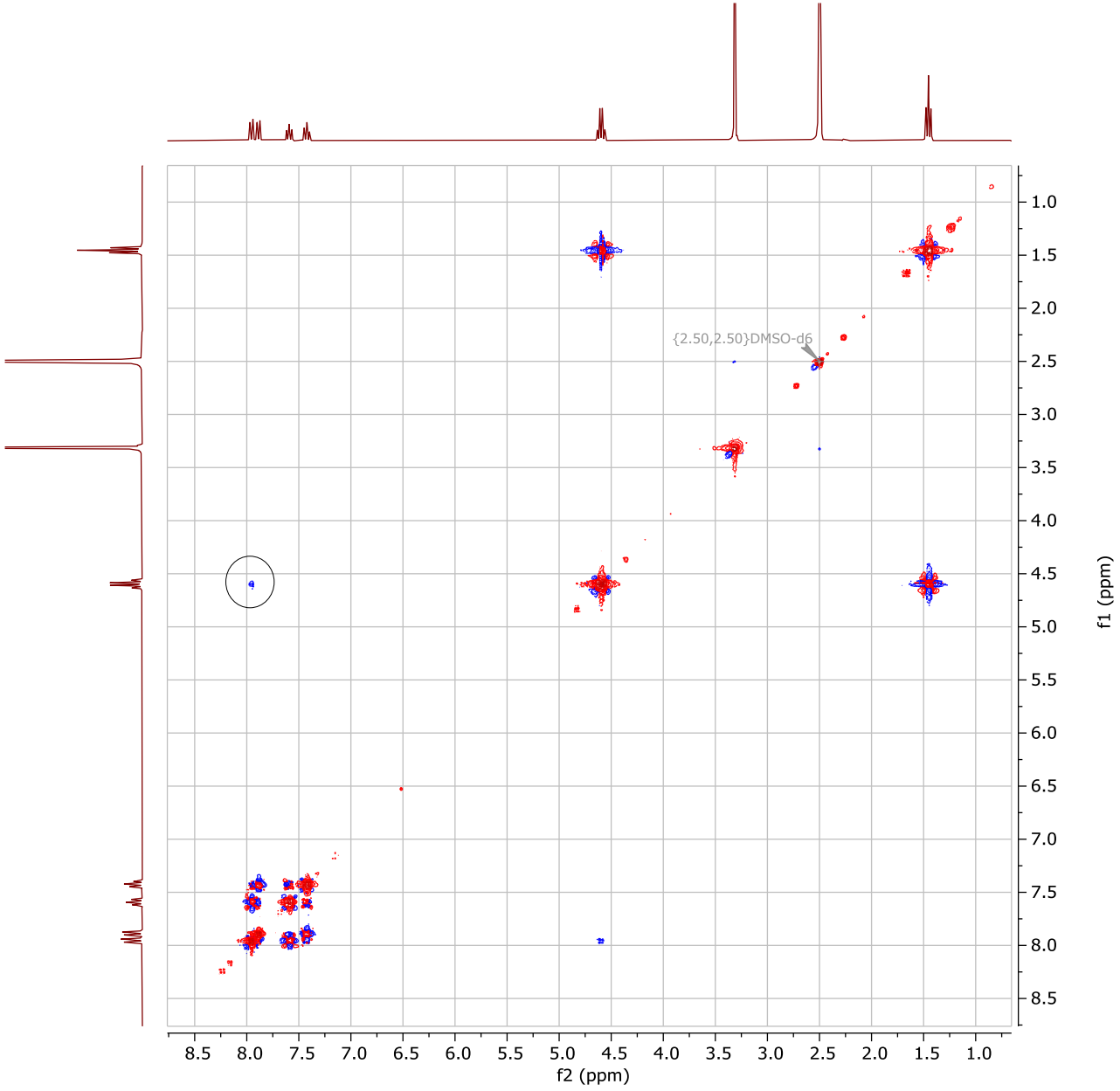
**22**-$^{1}$H

Cond. B


13C NMR (75 MHz, DMSO) δ 138.9, 127.7, 124.5, 123.9, 118.8, 115.8, 113.8, 111.3, 44.6, 14.5.
138.9
127.7
124.5
123.9
118.8
115.8
113.8
111.3
44.6
39.5 DMSO-d6
14.5
H3C
N
N
N
Condition B
f1 (ppm)




| | Parameter | Value |
|---|---|---|
| 1 | Solvent | DMSO |
| 2 | Temperature | -4.4 |
| 3 | Pulse Sequence | noesygpphpp |
| 4 | Experiment | NOESY |
| 5 | Probe | Z104275_0395 (PA BBO 300S1 BBF-H-D-05 Z) |
| 6 | Number of Scans | 32 |
| 7 | Receiver Gain | 210.0 |
| 8 | Relaxation Delay | 1.9214 |
| 9 | Pulse Width | 14.0000 |
| 10 | Presaturation Frequency | |
| 11 | Acquisition Time | 0.4198 |
| 12 | Acquisition Date | 2023-07-19T21:15:45 |
| 13 | Modification Date | 2023-07-20T03:24:00 |
| 14 | Class | |
| 15 | Spectrometer Frequency | (300.13, 300.13) |
| 16 | Spectral Width | (2439.0, 2439.0) |
| 17 | Lowest Frequency | (190.9, 190.6) |
| 18 | Nucleus | (1H, 1H) |
| 19 | Acquired Size | (1024, 256) |
| 20 | Spectral Size | (1024, 1024) |
| 21 | Digital Resolution | (2.38, 2.38) |



**Crystallography data and collection information.**

Crystals were grown by liquid-liquid diffusion using acetone and water with a small amount of compound initially dissolved in acetone.

**Data collection**

A Leica MZ 75 microscope was used to identify a suitable colorless needle with very well-defined faces with dimensions (max, intermediate, and min) 0.471 × 0.141 × 0.085 $mm^3$ from a representative sample of crystals of the same habit. The crystal mounted on a nylon loop was then placed in a cold nitrogen stream (Oxford) maintained at 110 K.

A BRUKER Quest X-ray (fixed-Chi geometry) diffractometer with a PHOTON II detector was employed for crystal screening, unit cell determination, and data collection. The goniometer was controlled using the APEX3 software suite.[1] The sample was optically centered with the aid of a video camera such that no translations were observed as the crystal was rotated through all positions. The X-ray radiation employed was generated from a Mo-Iμs X-ray tube ($K_\alpha$ = 0.71073Å).

45 data frames were taken at widths of 1°. These reflections were used to determine the unit cell. The unit cell was verified by examination of the *h k l* overlays on several frames of data. No super-cell or erroneous reflections were observed.

After careful examination of the unit cell, an extended data collection procedure (4 sets) was initiated using omega and phi scans.

**Data reduction, structure solution, and refinement**

Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX3.[1] The integration method employed a three-dimensional profiling algorithm, and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects. Finally, the data were merged and scaled

to produce a suitable data set. The absorption correction program SADABS[2] was employed to correct the data for absorption effects.

Systematic reflection conditions and statistical tests of the data suggested the space group $P2_1/c$. A solution was obtained readily using XT/XS in APEX3.[1,3] Hydrogen atoms were placed in idealized positions and were set riding on the respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. Absence of additional symmetry and voids were confirmed using PLATON (ADDSYM). The structure was refined (weighted least squares refinement on $F^2$) to convergence.[3,4]

Olex2 was employed for the final data presentation and structure plots.[4]

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[1] APEX3 "Program for Data Collection on Area Detectors" BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373 USA.

[2] SADABS, Sheldrick, G.M. "Program for Absorption Correction of Area Detector Frames", BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373 USA.

[3] Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122. Sheldrick, G. M. (2015), Acta Cryst. A71, 3-8. Sheldrick, G. M. (2015). Acta Cryst. C71, 3-8. XT, XS, BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373 USA.

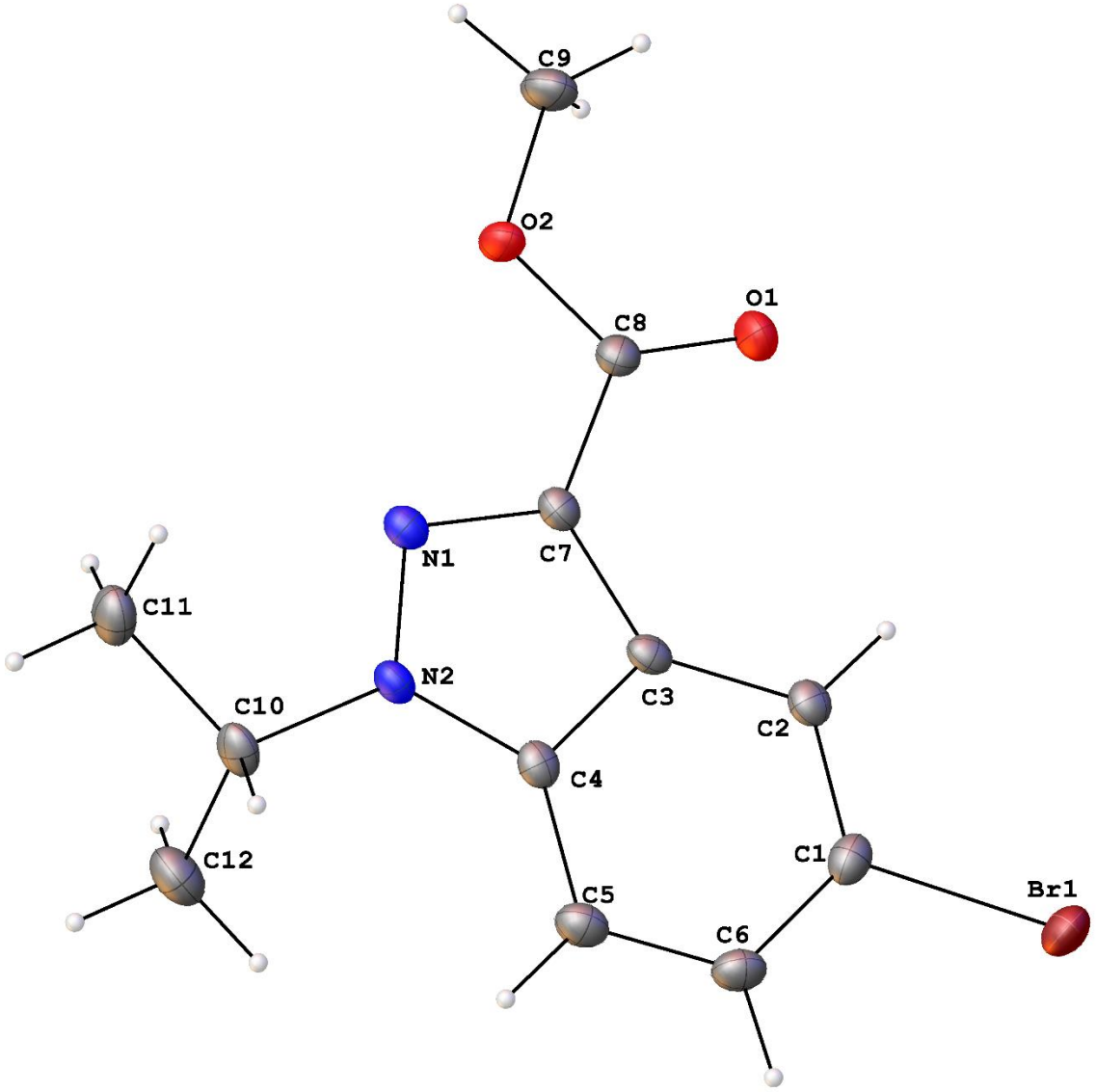
[4] Dolomanov, O. V, Bourhis, L. J., Gildea, R. J., Howard, J. A. K., and Puschmann, H. "OLEX2: A Complete Structure Solution, Refinement and Analysis Program", *J. Appl. Cryst.* **2009**, *42*, 339-341.

**Compound 8 crystal data.**

Bond precision: C-C = 0.0030 A Wavelength=0.71073
Cell: a=4.3946(8) b=20.075(3) c=13.610(3)
alpha=90 beta=92.840(7) gamma=90
Temperature: 110 K

| | Calculated | Reported |
|---|---|---|
| Volume | 1199.2(4) | 1199.2(4) |
| Space group | P 21/c | P 1 21/c 1 |
| Hall group | -P 2ybc | -P 2ybc |
| Moiety formula | C12 H13 Br N2 O2 | C12 H13 Br N2 O2 |
| Sum formula | C12 H13 Br N2 O2 | C12 H13 Br N2 O2 |
| Mr | 297.14 | 297.15 |
| Dx,g cm-3 | 1.646 | 1.646 |
| Z | 4 | 4 |
| Mu (mm-1) | 3.419 | 3.419 |
| F000 | 600.0 | 600.0 |
| F000’ | 599.10 | |
| h,k,lmax | 5,26,17 | 5,26,17 |
| Nref | 2768 | 2757 |
| Tmin,Tmax | 0.659,0.756 | 0.244,0.431 |
| Tmin’ | 0.230 | |

Correction method= # Reported T Limits: Tmin=0.244 Tmax=0.431
AbsCorr = MULTI-SCAN
Data completeness= 0.996 Theta(max)= 27.533
R(reflections)= 0.0263( 2422) wR2(reflections)= 0.0594( 2757)
S = 1.051 Npar= 157



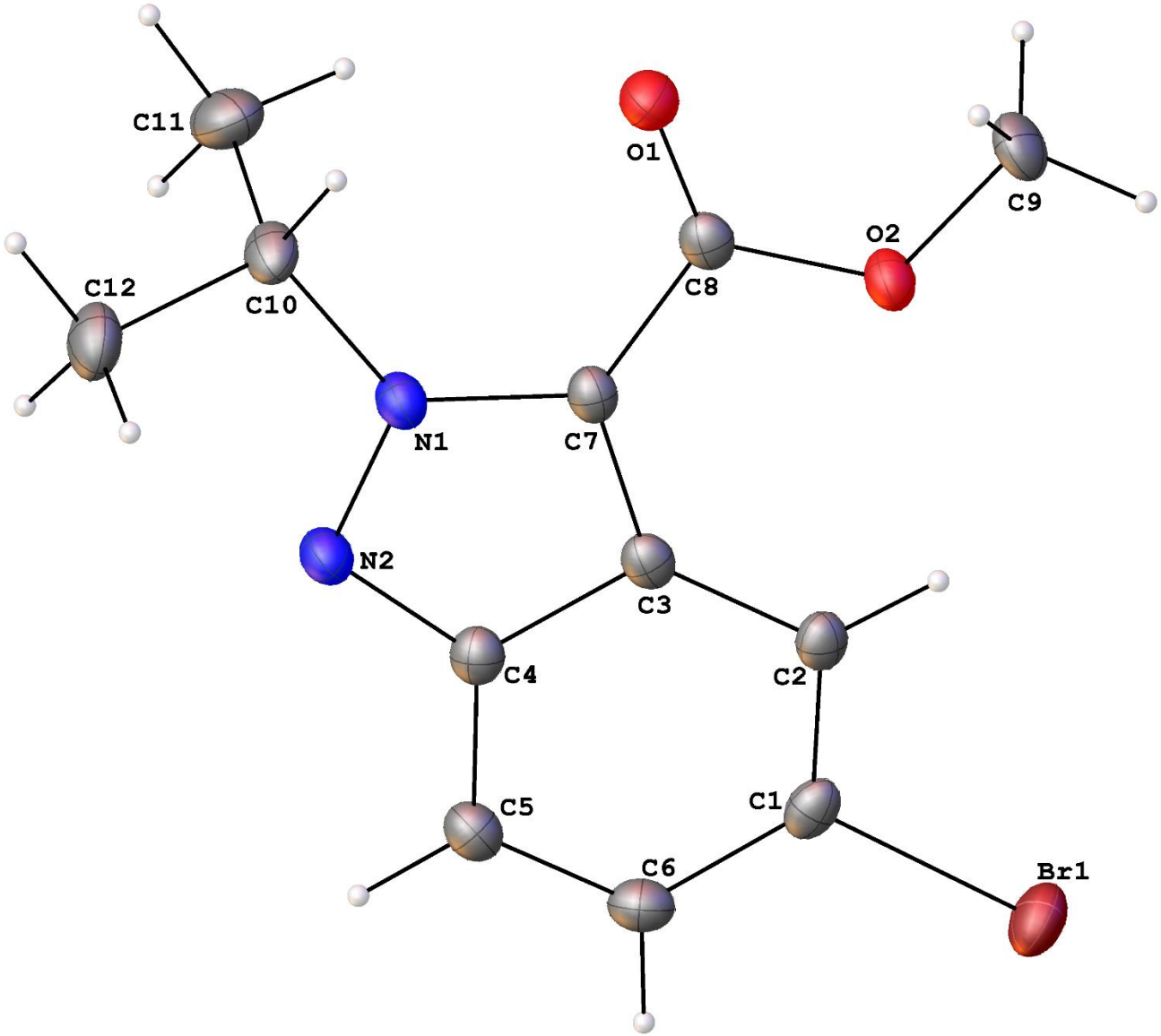

**8**. Thermal Ellipsoids at 50%

**Compound 9 crystal data.**

Bond precision: C-C = 0.0030 A Wavelength=0.71073
Cell: a=14.6240(13) b=4.6101(4) c=18.9039(18)
alpha=90 beta=109.153(3) gamma=90
Temperature: 110 K

| | Calculated | Reported |
|---|---|---|
| Volume | 1203.92(19) | 1203.92(19) |
| Space group | P 21/c | P 1 21/c 1 |
| Hall group | -P 2ybc | -P 2ybc |
| Moiety formula | C12 H13 Br N2 O2 | C12 H13 Br N2 O2 |
| Sum formula | C12 H13 Br N2 O2 | C12 H13 Br N2 O2 |
| Mr | 297.14 | 297.15 |
| Dx,g cm-3 | 1.639 | 1.639 |
| Z | 4 | 4 |
| Mu (mm-1) | 3.406 | 3.406 |
| F000 | 600.0 | 600.0 |
| F000’ | 599.10 | |
| h,k,lmax | 18,5,24 | 18,5,24 |
| Nref | 2743 | 2741 |
| Tmin,Tmax | 0.568,0.749 | 0.439,0.746 |
| Tmin’ | 0.199 | |

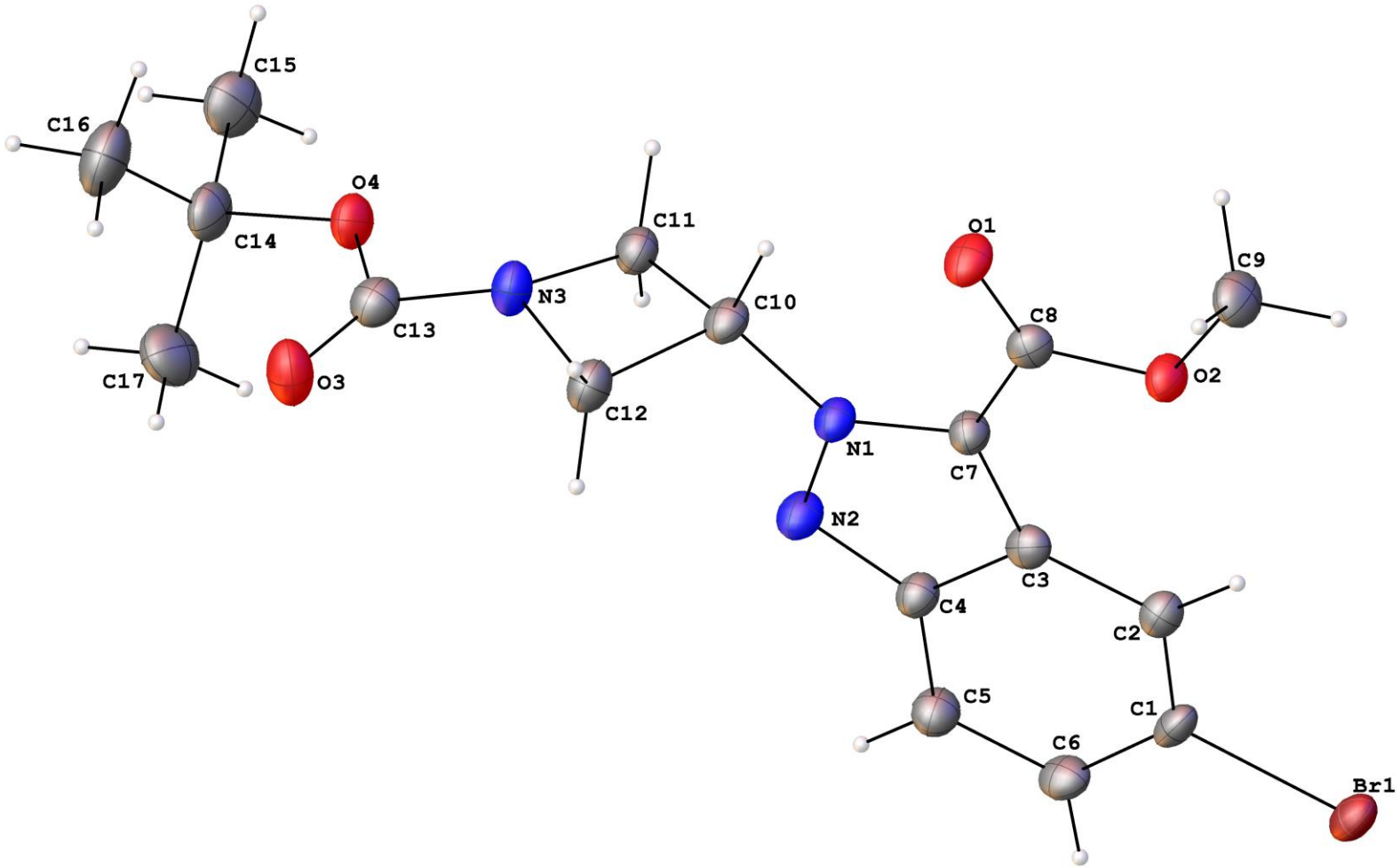
Correction method= # Reported T Limits: Tmin=0.439 Tmax=0.746
AbsCorr = MULTI-SCAN
Data completeness= 0.999 Theta(max)= 27.473
R(reflections)= 0.0273( 2252) wR2(reflections)= 0.0662( 2741)
S = 1.037 Npar= 157




**9**. Thermal ellipsoids drawn at 50%.

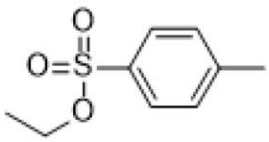
**Compound 16m crystal data**

| | |
|---|---|
| Empirical formula | C17 H20 Br N3 O4 |
| Formula weight | 410.27 |
| Temperature | 110.0 K |
| Wavelength | 1.54178 Å |
| Crystal system | Triclinic |
| Space group | P-1 |
| Unit cell dimensions | a = 6.7985(4) Å □= 98.920(3)°. |
| | b = 10.3761(5) Å □= 94.802(3)°. |
| | c = 13.0352(5) Å □ = 93.714(3)°. |
| Volume | 902.39(8) Å3 |
| Z | 2 |
| Density (calculated) | 1.510 Mg/m3 |
| Absorption coefficient | 3.341 mm-1 |
| F(000) | 420 |
| Crystal size | 0.249 x 0.041 x 0.033 mm3 |
| Theta range for data collection | 3.448 to 64.998°. |
| Index ranges | -7<=h<=7, -12<=k<=12, -15<=l<=15 |
| Reflections collected | 13661 |
| Independent reflections | 3034 [R(int) = 0.0290] |
| Completeness to theta = 64.998° | 99.4% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.3810 and 0.2211 |
| Refinement method | Full-matrix least-squares on F2 |
| Data / restraints / parameters | 3034 / 0 / 230 |
| Goodness-of-fit on F2 | 1.123 |
| Final R indices [I>2sigma(I)] | R1 = 0.0467, wR2 = 0.1412 |
| R indices (all data) | R1 = 0.0472, wR2 = 0.1417 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 2.056 and -0.424 e.Å-3 |




**16m.** Thermal ellipsoids drawn at 50%.

**IR Spectra of all compounds**



MW 21 July 23

Sample ID:LCJ-004-177A

Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\400-CM.a2m

Sample Scans:32

User:admin

Background Scans:32

Date/Time:07/21/2023 8:42:01 AM

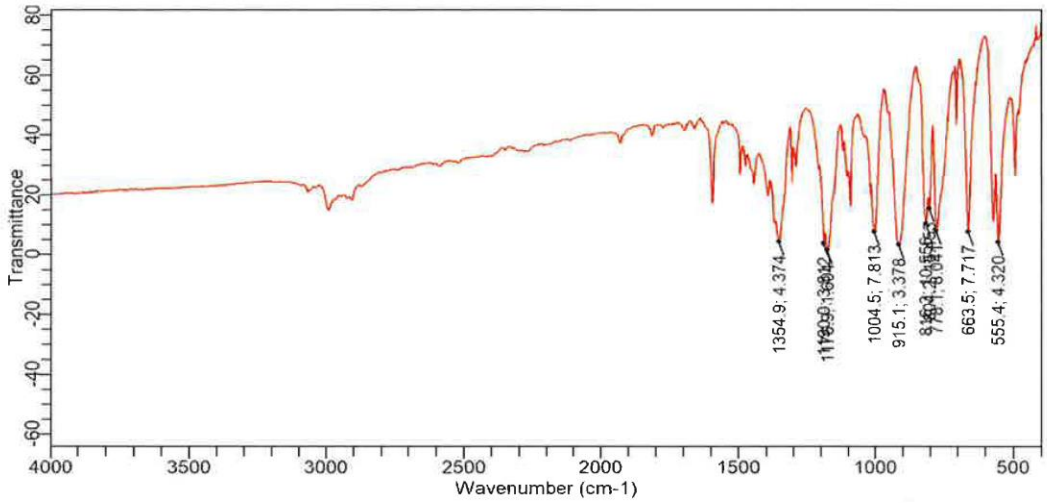
Resolution:2

Range:4000 - 400

System Status:Good

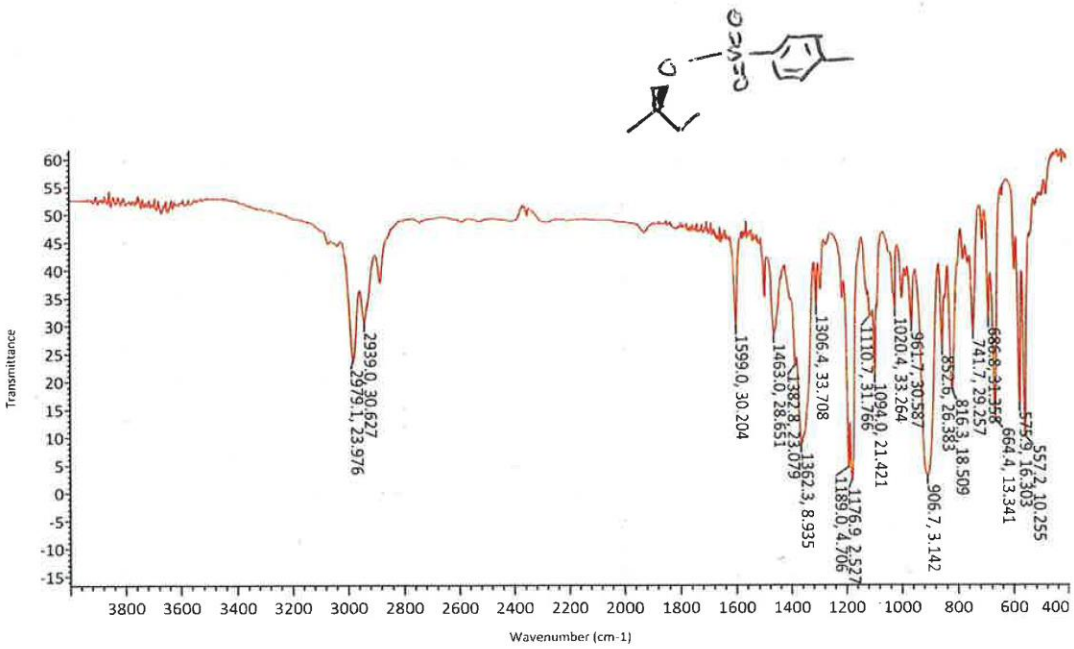
Apodization:Happ-Genzel

File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\\LCJ-004-177A_2023-07-21T08-42-01.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 555.37334 | 4.32017 |
| 2 | 663.46614 | 7.71654 |
| 3 | 778.08177 | 8.04144 |
| 4 | 804.17314 | 15.45306 |
| 5 | 816.28699 | 10.55550 |

| | | |
|---|---|---|
| 6 | 915.06144 | 3.37847 |
| 7 | 1004.51755 | 7.81263 |
| 8 | 1176.90692 | 1.60432 |
| 9 | 1189.95260 | 3.81152 |
| 10 | 1354.88730 | 4.37407 |



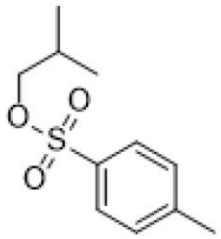

| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 557.2 | 10.255 |
| 2 | 575.9 | 16.303 |
| 3 | 664.4 | 13.341 |
| 4 | 686.8 | 31.358 |
| 5 | 741.7 | 29.257 |
| 6 | 816.3 | 18.509 |
| 7 | 852.6 | 26.383 |
| 8 | 906.7 | 3.142 |
| 9 | 961.7 | 30.587 |
| 10 | 1020.4 | 33.264 |
| 11 | 1094.0 | 21.421 |
| 12 | 1110.7 | 31.766 |

| | | |
|---|---|---|
| 13 | 1176.9 | 2.527 |
| 14 | 1189.0 | 4.706 |
| 15 | 1306.4 | 33.708 |
| 16 | 1362.3 | 8.935 |
| 17 | 1382.8 | 23.079 |
| 18 | 1463.0 | 28.651 |
| 19 | 1599.0 | 30.204 |
| 20 | 2939.0 | 30.627 |
| 21 | 2979.1 | 23.976 |

**E-SIGNATURES**

| **Signature** |
|---|

EB 21 July 2023



Sample ID:LCJ-7-154A

Method Name:C:\Users\Public\Documents\A_b\Methods\400-CM.a2m

Sample Scans:32

User:admin

Background Scans:32

Date/Time:07/21/2023 12:27:22 PM

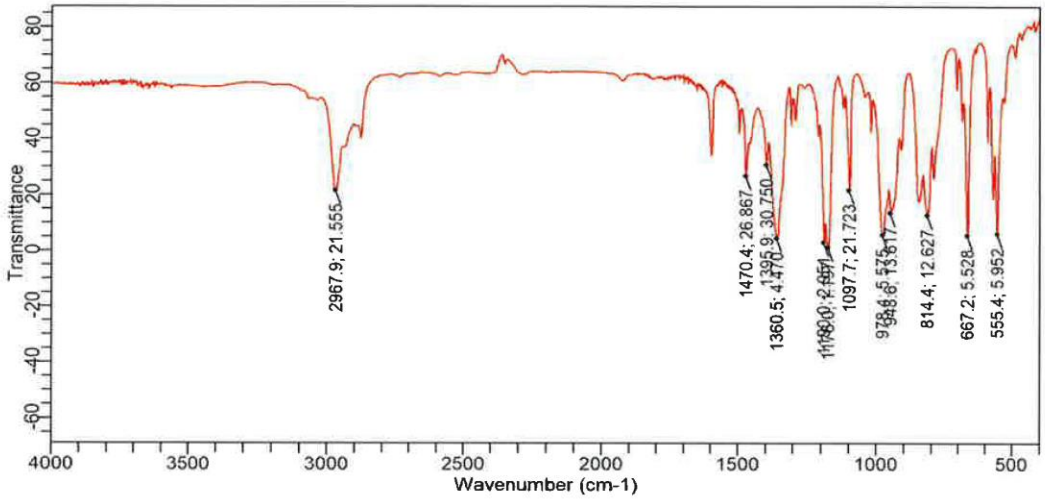
Resolution:2

Range:4000 - 400

System Status:Good

Apodization:Happ-Genzel

File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\\LCJ-7-154A_2023-07-21T12-27-22.a2r

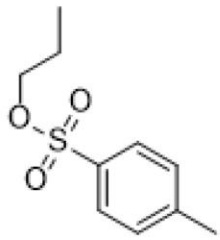



| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 555.37334 | 5.95184 |
| 2 | 667.19347 | 5.52762 |
| 3 | 814.42332 | 12.62689 |
| 4 | 948.60748 | 13.61750 |
| 5 | 978.42618 | 5.57532 |

| | | |
|---|---|---|
| 6 | 1097.70099 | 21.72255 |
| 7 | 1175.97509 | 1.19730 |
| 8 | 1189.95260 | 2.95069 |
| 9 | 1360.47831 | 4.47008 |
| 10 | 1395.88802 | 30.74959 |
| 11 | 1470.43478 | 26.86714 |
| 12 | 2967.89275 | 21.55489 |

bio cryst

MW 21 July 23



Sample ID:LCJ-007-136A

Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\400-CM.a2m

Sample Scans:32

User:admin

Background Scans:32

Date/Time:07/21/2023 9:17:12 AM

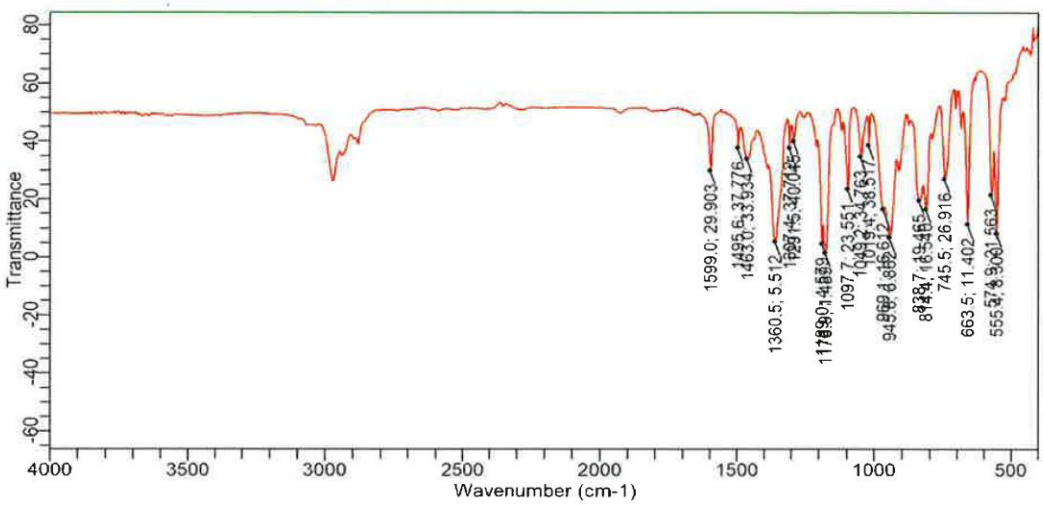
Resolution:2

Range:4000 - 400

System Status:Good

Apodization:Happ-Genzel

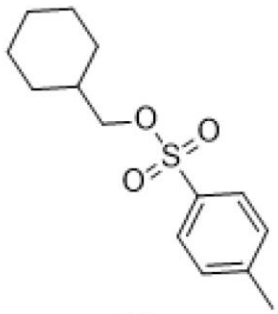
File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\\LCJ-007-136A_2023-07-21T09-17-12.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 555.37334 | 8.29953 |
| 2 | 574.94186 | 21.56274 |
| 3 | 663.46614 | 11.40194 |
| 4 | 745.46757 | 26.91646 |
| 5 | 814.42332 | 16.54014 |

| | | |
|---|---|---|
| 6 | 838.65101 | 19.46462 |
| 7 | 945.81198 | 6.86168 |
| 8 | 969.10784 | 16.61207 |
| 9 | 1019.42690 | 38.51664 |
| 10 | 1049.24560 | 34.76292 |
| 11 | 1097.70099 | 23.55116 |
| 12 | 1176.90692 | 1.48874 |
| 13 | 1189.02077 | 4.57866 |
| 14 | 1291.52256 | 40.04533 |
| 15 | 1307.36375 | 37.71186 |
| 16 | 1360.47831 | 5.51195 |
| 17 | 1462.98010 | 33.93383 |
| 18 | 1495.59431 | 37.77560 |
| 19 | 1599.02793 | 29.90264 |

MW 21 July 23



Sample ID:LCJ-007-139A

Method Name:C:\Users\Public\Documents\b\Methods\400-CM.a2m

Sample Scans:32

User:admin

Background Scans:32

Date/Time:07/21/2023 9:31:21 AM

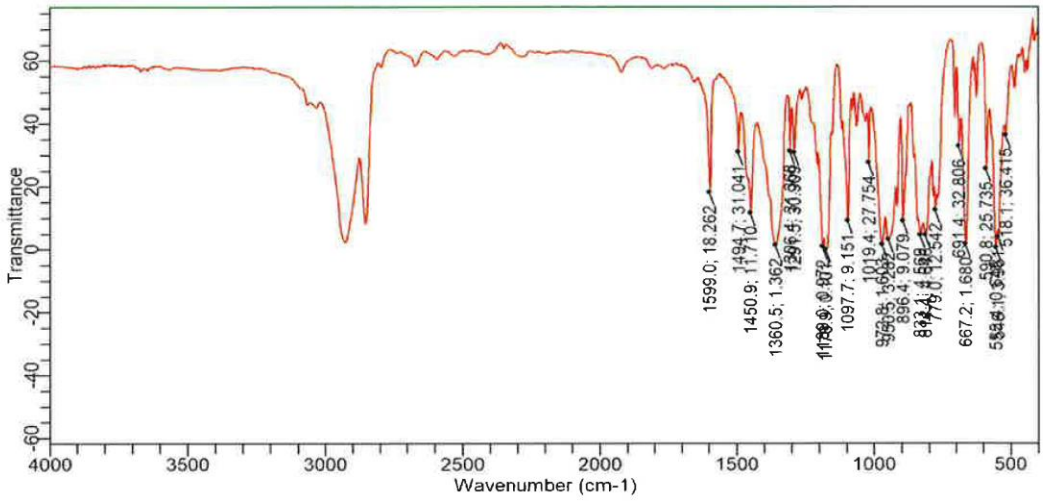
Resolution:2

Range:4000 - 400

System Status:Good

Apodization:Happ-Genzel

File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\\LCJ-007-139A_2023-07-21T09-31-21.a2r

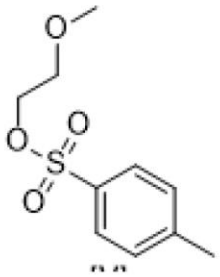



| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 518.09996 | 36.41539 |
| 2 | 546.05499 | 3.96116 |
| 3 | 555.37334 | 0.64514 |
| 4 | 590.78305 | 25.73509 |
| 5 | 667.19347 | 1.67954 |

| | | |
|---|---|---|
| 6 | 691.42117 | 32.80607 |
| 7 | 779.01361 | 12.54196 |
| 8 | 814.42332 | 4.64590 |
| 9 | 833.06001 | 4.56896 |
| 10 | 896.42475 | 9.07888 |
| 11 | 950.47115 | 3.28187 |
| 12 | 972.83518 | 1.60309 |
| 13 | 1019.42690 | 27.75373 |
| 14 | 1097.70099 | 9.15143 |
| 15 | 1176.90692 | 0.10147 |
| 16 | 1189.02077 | 0.97163 |
| 17 | 1291.52256 | 30.90919 |
| 18 | 1306.43191 | 31.36757 |
| 19 | 1360.47831 | 1.36246 |
| 20 | 1450.86625 | 11.70978 |
| 21 | 1494.66247 | 31.04129 |
| 22 | 1599.02793 | 18.26150 |

bio cryst

MW 21 July 23



Sample ID:LCJ-007-143A

Method Name:C:\Users\Public\Documents\Agile b\Methods\400-CM.a2m

Sample Scans:32

User:admin

Background Scans:32

Date/Time:07/21/2023 11:16:54 AM

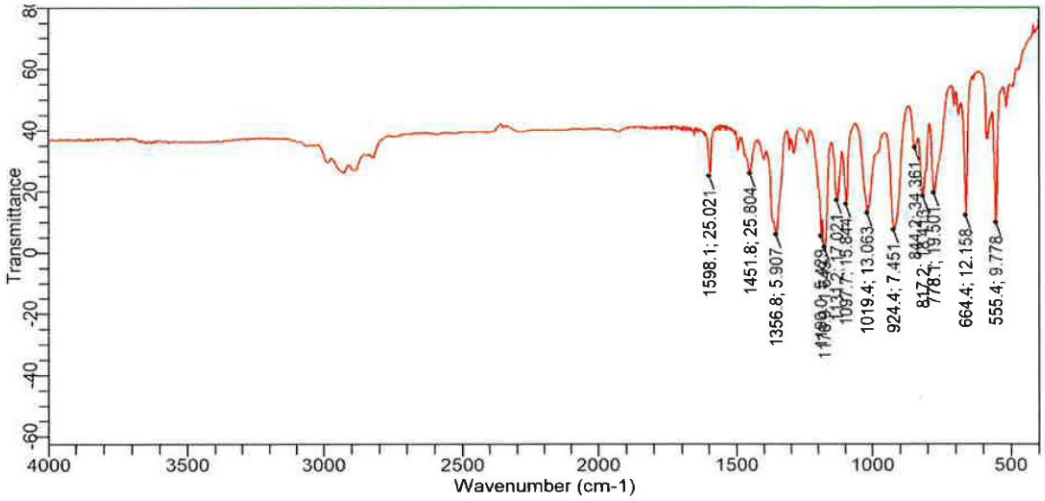
Resolution:2

Range:4000 - 400

System Status:Good

Apodization:Happ-Genzel

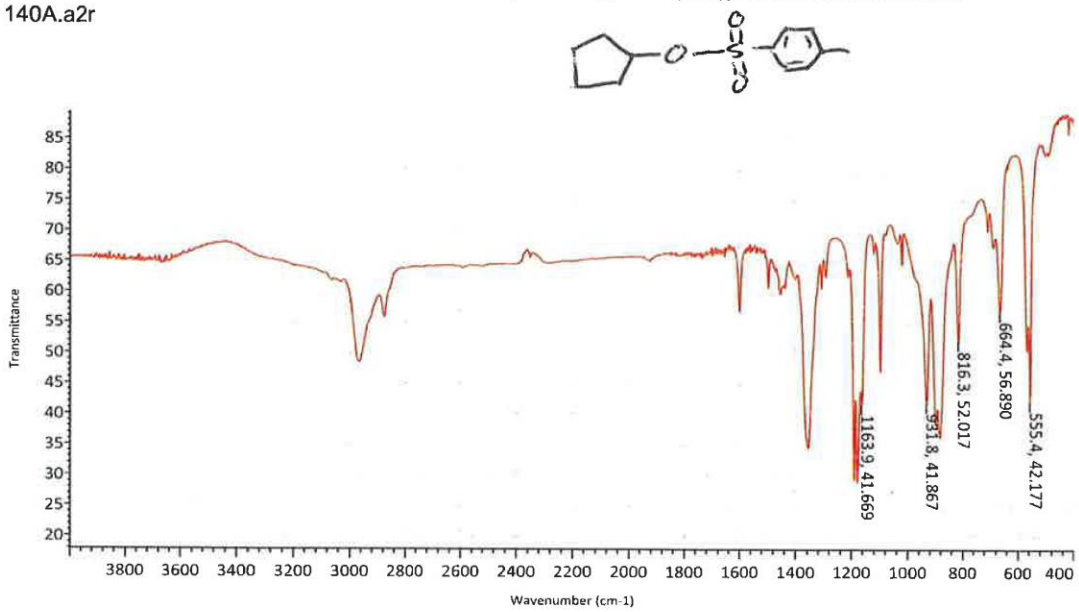
File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\\LCJ-007-143A_2023-07-21T11-16-54.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 555.37334 | 9.77778 |
| 2 | 664.39797 | 12.15797 |
| 3 | 778.08177 | 19.50105 |
| 4 | 817.21882 | 18.41314 |
| 5 | 844.24202 | 34.36130 |

| | | |
|---|---|---|
| 6 | 924.37978 | 7.45086 |
| 7 | 1019.42690 | 13.06254 |
| 8 | 1097.70099 | 15.84414 |
| 9 | 1131.24703 | 17.02116 |
| 10 | 1176.90692 | 1.64900 |
| 11 | 1189.95260 | 5.42944 |
| 12 | 1356.75097 | 5.90657 |
| 13 | 1451.79809 | 25.80354 |
| 14 | 1598.09610 | 25.02067 |

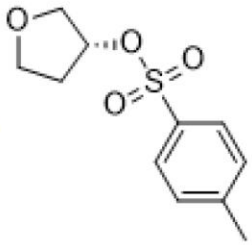
File Location:NAPLBBHPC2L810D\SQLEXPRESS|VAIMDB_Public(000)|Public Results\LCJ-007-140A.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 555.4 | 42.177 |
| 2 | 664.4 | 56.890 |
| 3 | 816.3 | 52.017 |
| 4 | 931.8 | 41.867 |
| 5 | 1163.9 | 41.669 |

**E-SIGNATURES**

| Signature |
|---|



MW 21 July 2

Sample ID:LCJ-007-147A

Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\400-CM.a2m

Sample Scans:32

User:admin

Background Scans:32

Date/Time:07/21/2023 11:29:15 AM

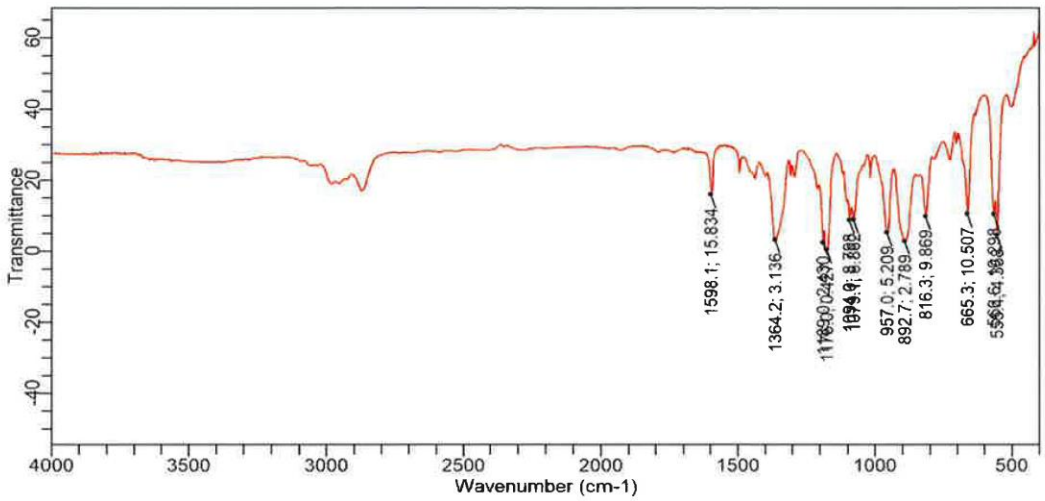
Resolution:2

Range:4000 - 400

System Status:Good

Apodization:Happ-Genzel

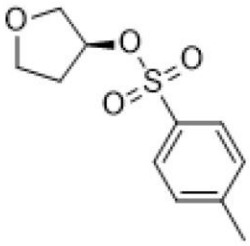
File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\\LCJ-007-147A_2023-07-21T11-29-15.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 555.37334 | 4.35797 |
| 2 | 566.55535 | 10.29819 |
| 3 | 665.32980 | 10.50725 |
| 4 | 816.28699 | 9.86903 |
| 5 | 892.69741 | 2.78888 |

| | | |
|---|---|---|
| 6 | 956.99399 | 5.20898 |
| 7 | 1079.06430 | 8.86190 |
| 8 | 1093.97366 | 8.79848 |
| 9 | 1175.97509 | 0.42671 |
| 10 | 1189.02077 | 2.43020 |
| 11 | 1364.20565 | 3.13606 |
| 12 | 1598.09610 | 15.83364 |

EB 21 July 2023



Sample ID:LCJ-7-148A

Method Name:C:\Users\Public\Docb\Methods\400-CM.a2m

Sample Scans:32

User:admin

Background Scans:32

Date/Time:07/21/2023 12:4

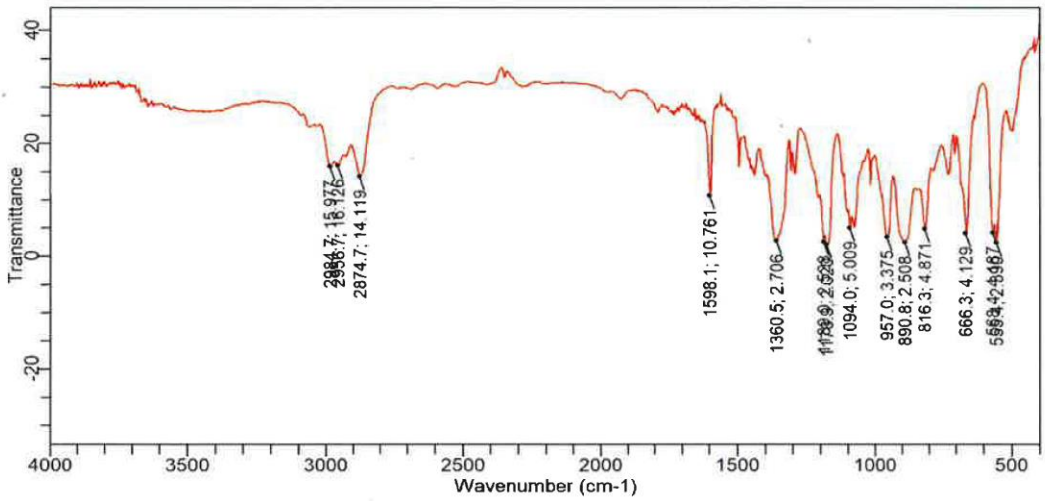
Resolution:2

Range:4000 - 400

System Status:Good

Apodization:Happ-Genzel

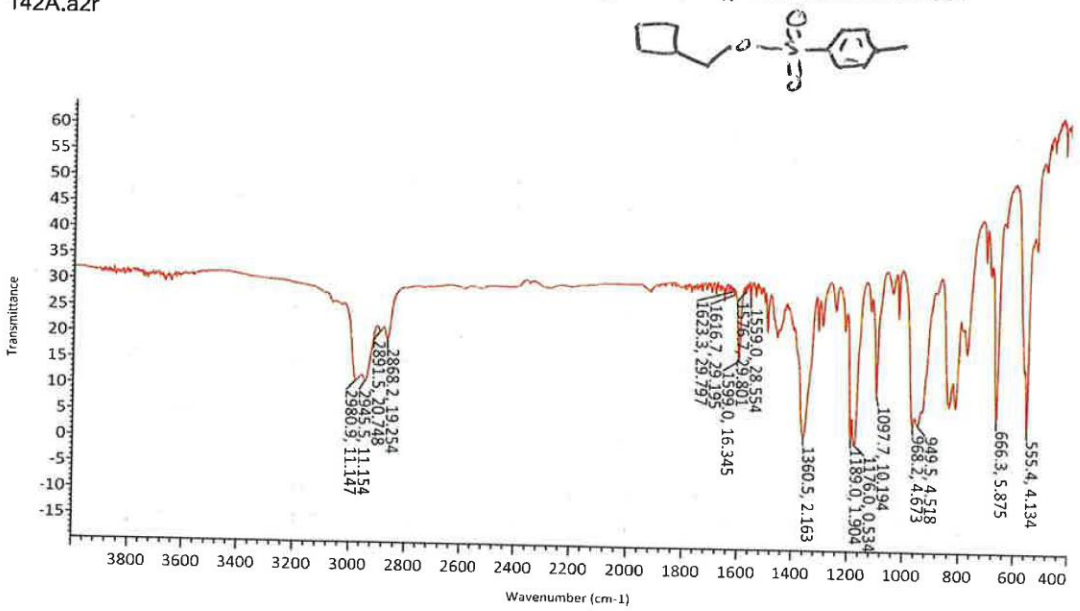
File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\LCJ-7-148A_2023-07-21T12-40-48.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 555.37334 | 2.39007 |
| 2 | 568.41902 | 4.18682 |
| 3 | 666.26164 | 4.12900 |
| 4 | 816.28699 | 4.87060 |
| 5 | 890.83374 | 2.50783 |

| | | |
|---|---|---|
| 6 | 956.99399 | 3.37456 |
| 7 | 1093.97366 | 5.00907 |
| 8 | 1176.90692 | 2.02001 |
| 9 | 1189.02077 | 2.52788 |
| 10 | 1360.47831 | 2.70644 |
| 11 | 1598.09610 | 10.76052 |
| 12 | 2874.70931 | 14.11903 |
| 13 | 2956.71074 | 16.12599 |
| 14 | 2984.66577 | 15.97663 |

File Location:NAPLBBHPC2L810D\SQLEXPRESS|VAIMDB_Public(000)|Public Results\LJC-004-142A.a2r

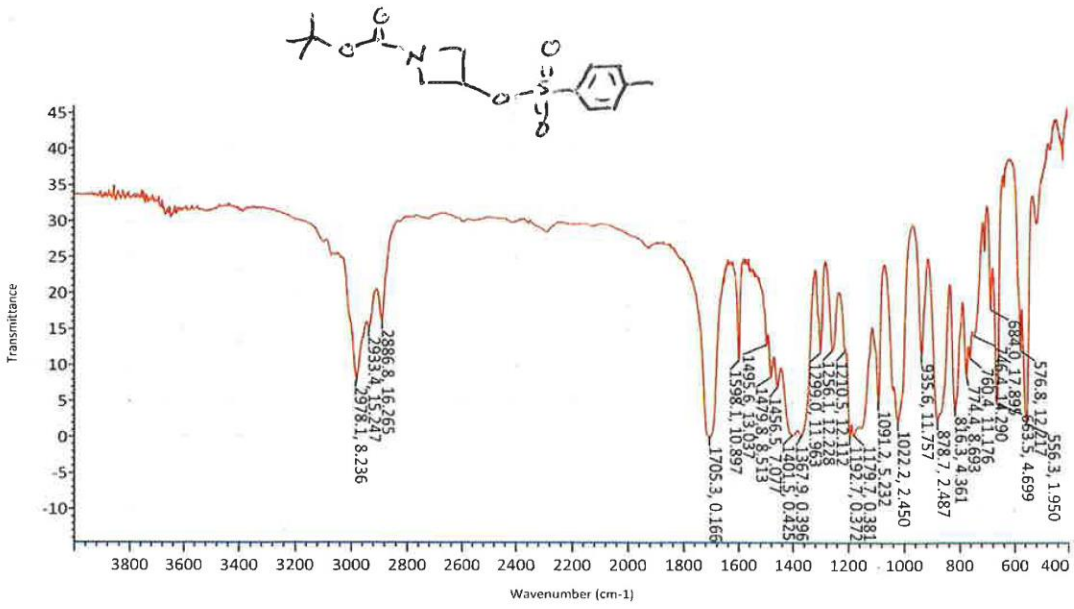



| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 555.4 | 4.134 |
| 2 | 666.3 | 5.875 |
| 3 | 949.5 | 4.518 |
| 4 | 968.2 | 4.673 |
| 5 | 1097.7 | 10.194 |
| 6 | 1176.0 | 0.534 |
| 7 | 1189.0 | 1.904 |
| 8 | 1360.5 | 2.163 |
| 9 | 1559.0 | 28.554 |
| 10 | 1576.7 | 29.801 |
| 11 | 1599.0 | 16.345 |

| | | |
|---|---|---|
| 12 | 1616.7 | 29.195 |
| 13 | 1623.3 | 29.797 |
| 14 | 2868.2 | 19.254 |
| 15 | 2891.5 | 20.748 |
| 16 | 2945.5 | 11.154 |
| 17 | 2980.9 | 11.147 |

**E-SIGNATURES**

| Signature |
|---|

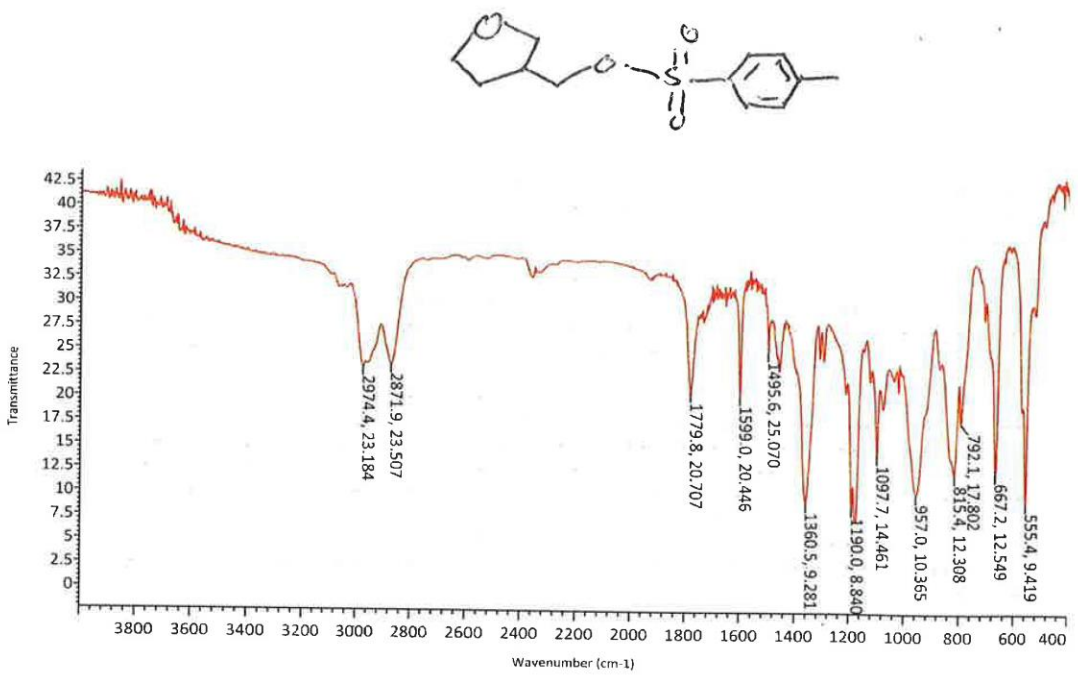



| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 556.3 | 1.950 |
| 2 | 576.8 | 12.217 |
| 3 | 663.5 | 4.699 |
| 4 | 684.0 | 17.895 |
| 5 | 746.4 | 14.290 |
| 6 | 760.4 | 11.176 |
| 7 | 774.4 | 8.693 |
| 8 | 816.3 | 4.361 |
| 9 | 878.7 | 2.487 |
| 10 | 935.6 | 11.757 |
| 11 | 1022.2 | 2.450 |
| 12 | 1091.2 | 5.232 |

| | | |
|---|---|---|
| 13 | 1179.7 | 0.381 |
| 14 | 1192.7 | 0.372 |
| 15 | 1210.5 | 12.112 |
| 16 | 1256.1 | 12.228 |
| 17 | 1299.0 | 11.963 |
| 18 | 1367.9 | 0.396 |
| 19 | 1401.5 | 0.425 |
| 20 | 1456.5 | 7.077 |
| 21 | 1479.8 | 8.513 |
| 22 | 1495.6 | 13.037 |
| 23 | 1598.1 | 10.897 |
| 24 | 1705.3 | 0.166 |
| 25 | 2886.8 | 16.265 |
| 26 | 2933.4 | 15.247 |
| 27 | 2978.1 | 8.236 |

**E-SIGNATURES**

| **Signature** |
|---|




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 555.4 | 9.419 |
| 2 | 667.2 | 12.549 |
| 3 | 792.1 | 17.802 |
| 4 | 815.4 | 12.308 |
| 5 | 957.0 | 10.365 |
| 6 | 1097.7 | 14.461 |
| 7 | 1190.0 | 8.840 |
| 8 | 1360.5 | 9.281 |
| 9 | 1495.6 | 25.070 |
| 10 | 1599.0 | 20.446 |
| 11 | 1779.8 | 20.707 |
| 12 | 2871.9 | 23.507 |

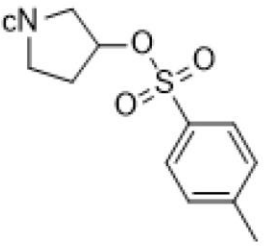
| | | |
|---|---|---|
| 13 | 2974.4 | 23.184 |

**E-SIGNATURES**

| Signature |
|---|

bio cryst

EB 21 July 2




Sample ID:LCJ-7-151A

Method Name:C:\Users\Public\Docum
b\Methods\400-CM.a2m

Sample Scans:32

User:admin

Background Scans:32

Date/Time:07/21/2023 12:02:10 PM

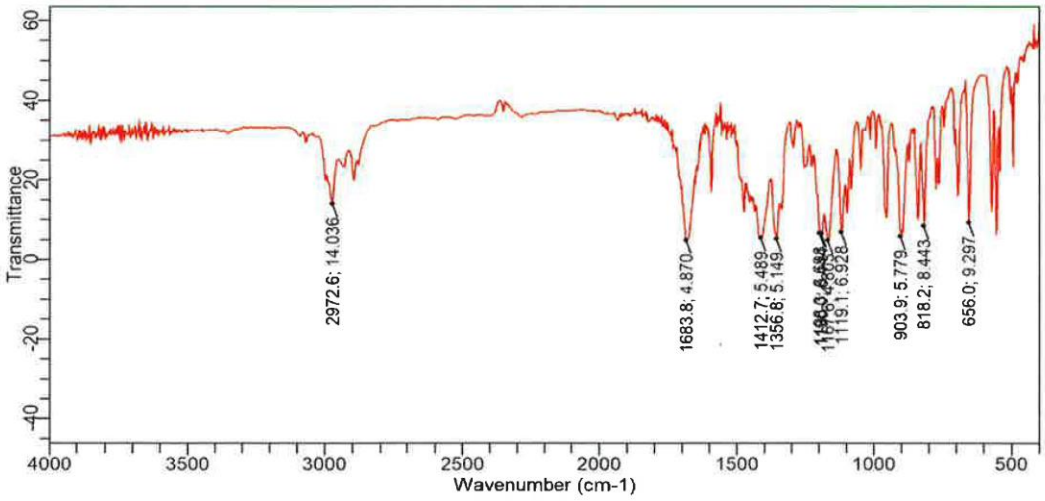
Resolution:2

Range:4000 - 400

System Status:Good

Apodization:Happ-Genzel

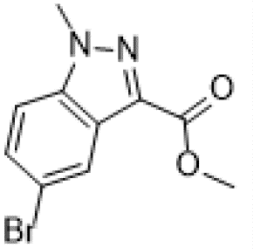
File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\\LCJ-7-151A_2023-07-21T12-02-10.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 656.01146 | 9.29742 |
| 2 | 818.15066 | 8.44256 |
| 3 | 903.87943 | 5.77865 |
| 4 | 1119.13319 | 6.92768 |
| 5 | 1167.58858 | 4.80282 |

| | | |
|---|---|---|
| 6 | 1189.95260 | 6.44371 |
| 7 | 1198.33911 | 6.69798 |
| 8 | 1356.75097 | 5.14927 |
| 9 | 1412.66104 | 5.48889 |
| 10 | 1683.82487 | 4.87042 |
| 11 | 2972.55193 | 14.03594 |

Sample ID:LCJ-012-145B




Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\ATR 128 Scans.a2m

Sample Scans:128

User:admin

Background Scans:32

Date/Time:03/13/2023 12:47:14 PM

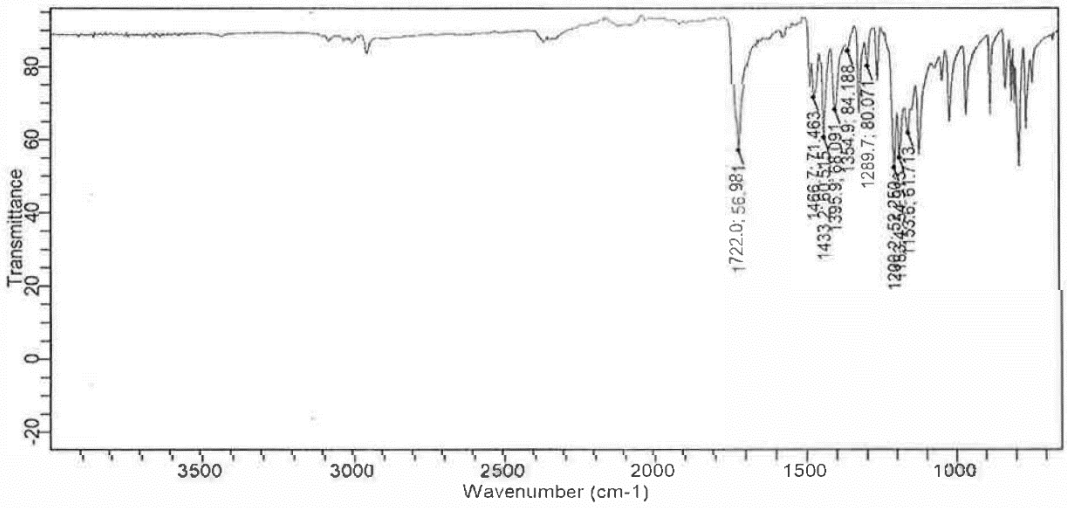
Resolution:4

Range:4000 - 650

System Status:Good

Apodization:Happ-Genzel

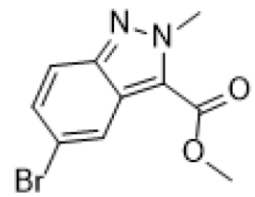
File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\\LCJ-012-145B_2023-03-13T12-47-14.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1153.61106 | 61.71313 |
| 2 | 1183.42976 | 54.91350 |
| 3 | 1200.20278 | 52.24999 |
| 4 | 1289.65889 | 80.07146 |
| 5 | 1354.88730 | 84.18800 |

| | | |
|---|---|---|
| 6 | 1395.88802 | 68.09095 |
| 7 | 1433.16140 | 60.51481 |
| 8 | 1466.70744 | 71.46253 |
| 9 | 1722.03008 | 56.98058 |

Sample ID:LCJ-012-145C

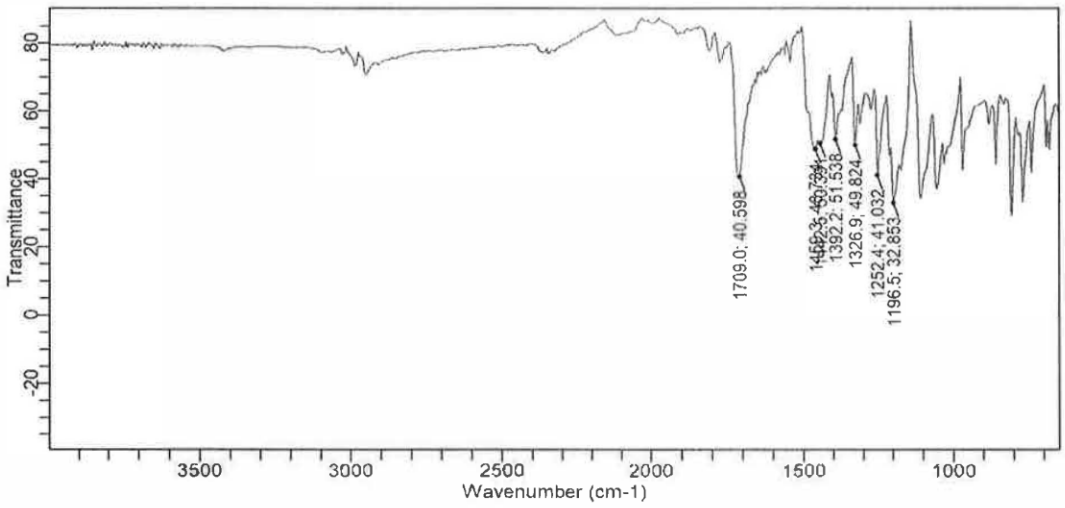



Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\ATR 128 Scans.a2m

Sample Scans:128
Background Scans:32
Resolution:4
System Status:Good

User:admin
Date/Time:03/13/2023 12:40:57 PM
Range:4000 - 650
Apodization:Happ-Genzel

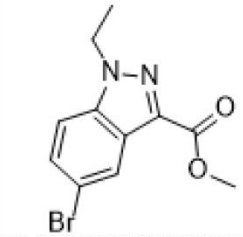
File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\LCJ-012-145C_2023-03-13T12-40-57.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1196.47545 | 32.85279 |
| 2 | 1252.38551 | 41.03164 |
| 3 | 1326.93227 | 49.82378 |
| 4 | 1392.16068 | 51.53811 |
| 5 | 1442.47974 | 50.39129 |

| | | |
|---|---|---|
| 6 | 1459.25276 | 48.73363 |
| 7 | 1708.98440 | 40.59753 |

Sample ID:LCJ-006-081B

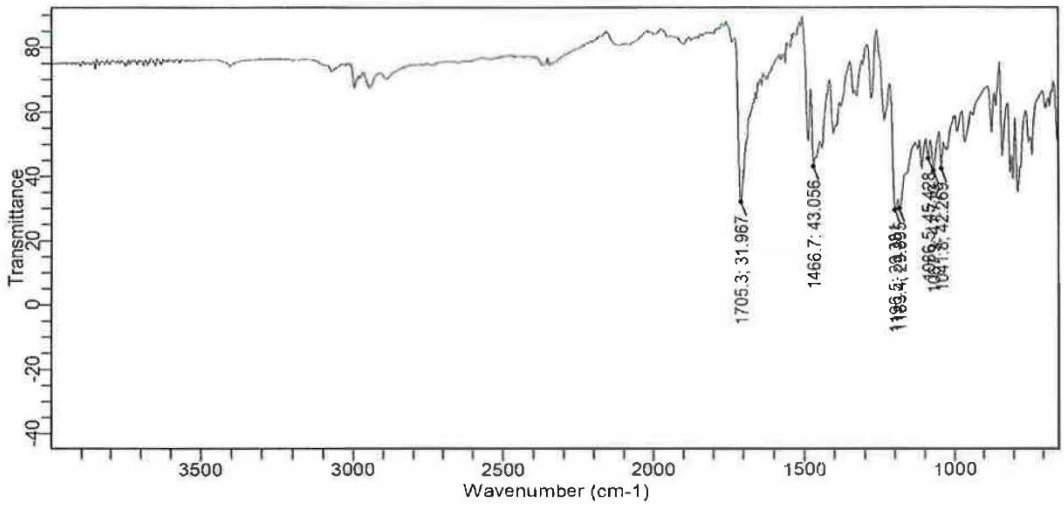



Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\ATR 128 Scans.a2m

Sample Scans:128
Background Scans:32
Resolution:4
System Status:Good

User:admin
Date/Time:03/13/2023 8:42:22 AM
Range:4000 - 650
Apodization:Happ-Genzel

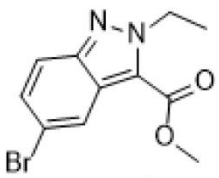
File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\LCJ-006-081B_2023-03-13T08-42-22.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1041.79093 | 42.26946 |
| 2 | 1067.88229 | 41.70964 |
| 3 | 1086.51898 | 45.42796 |
| 4 | 1183.42976 | 29.89476 |
| 5 | 1196.47545 | 29.38142 |

| | | |
|---|---|---|
| 6 | 1466.70744 | 43.05579 |
| 7 | 1705.25706 | 31.96682 |

Sample ID:LCJ-006-081C

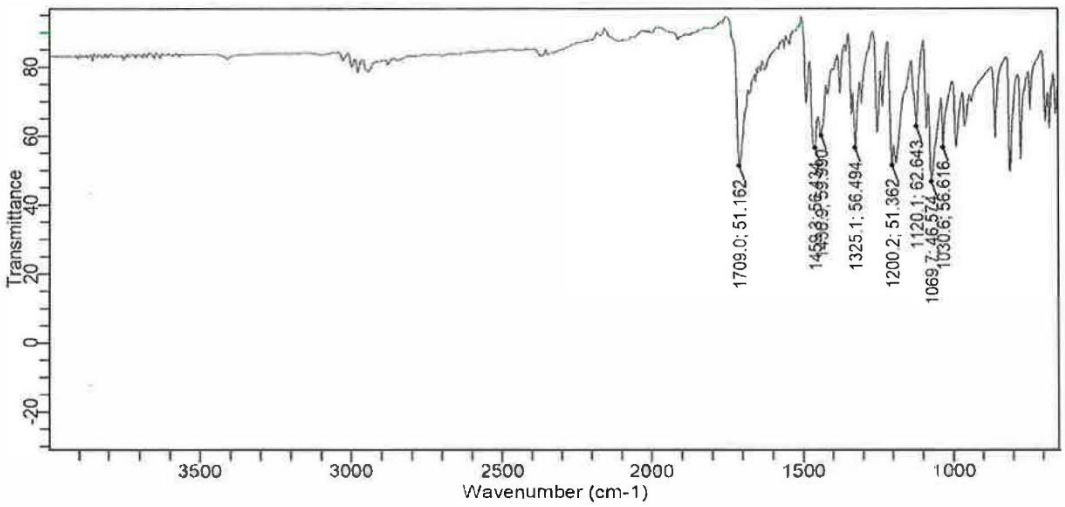



Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\ATR 128 Scans.a2m

Sample Scans:128
Background Scans:32
Resolution:4
System Status:Good

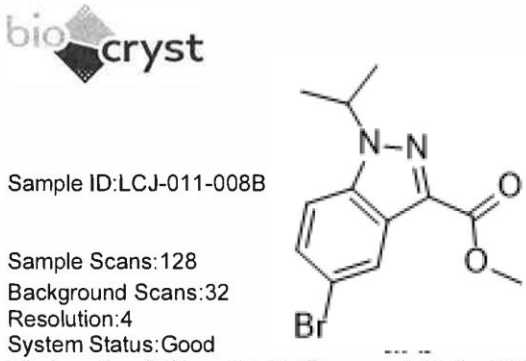
User:admin
Date/Time:03/13/2023 8:32:17 AM
Range:4000 - 650
Apodization:Happ-Genzel

File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\LCJ-006-081C_2023-03-13T08-32-17.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1030.60891 | 56.61588 |
| 2 | 1069.74596 | 46.57442 |
| 3 | 1120.06502 | 62.64288 |
| 4 | 1200.20278 | 51.36187 |
| 5 | 1325.06860 | 56.49372 |

| | | |
|---|---|---|
| 6 | 1436.88874 | 59.99048 |
| 7 | 1459.25276 | 56.43382 |
| 8 | 1708.98440 | 51.16249 |

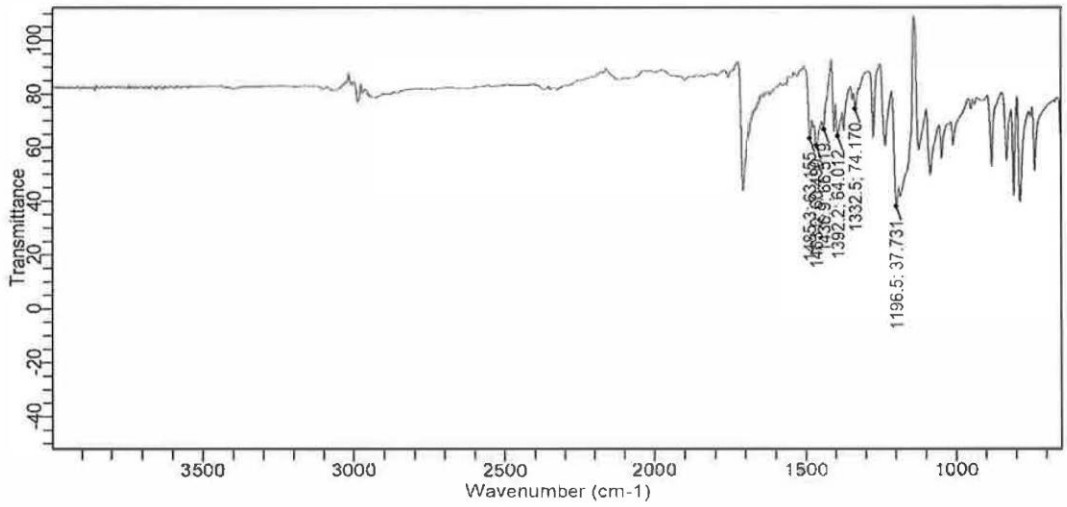


Sample ID:LCJ-011-008B

Sample Scans:128
Background Scans:32
Resolution:4
System Status:Good

Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\ATR 128 Scans.a2m
User:admin
Date/Time:03/13/2023 12:33:41 PM
Range:4000 - 650
Apodization:Happ-Genzel

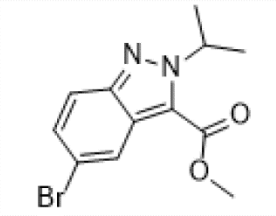
File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\\LCJ-011-008B_2023-03-13T12-33-41.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1196.47545 | 37.73147 |
| 2 | 1332.52328 | 74.16989 |
| 3 | 1392.16068 | 64.01244 |
| 4 | 1436.88874 | 66.51938 |
| 5 | 1462.98010 | 60.49031 |

| | | |
|---|---|---|
| 6 | 1485.34413 | 63.15505 |

Sample ID:LCJ-011-008C




Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\ATR 128 Scans.a2m

Sample Scans:128

User:admin

Background Scans:32

Date/Time:03/13/2023 12:24:30 PM

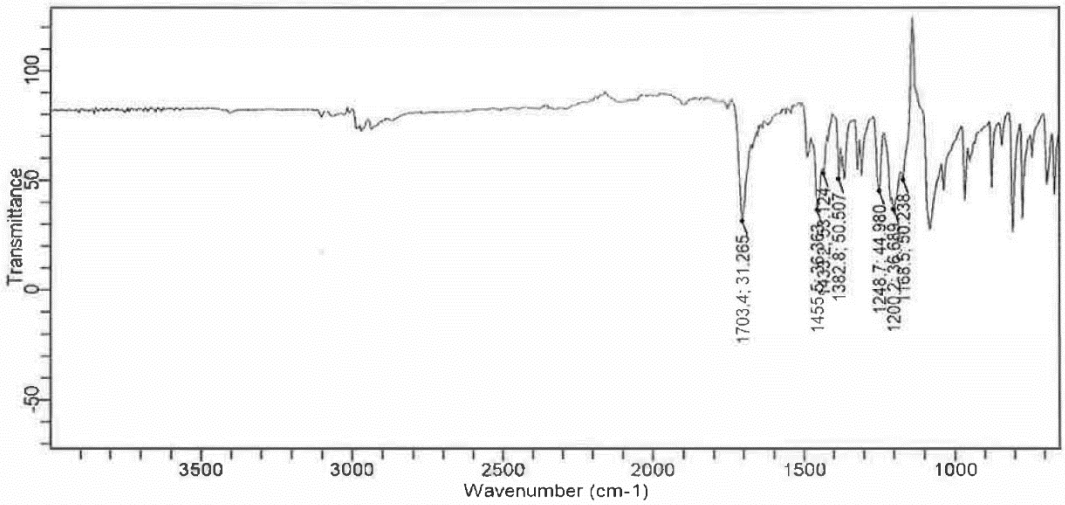
Resolution:4

Range:4000 - 650

System Status:Good

Apodization:Happ-Genzel

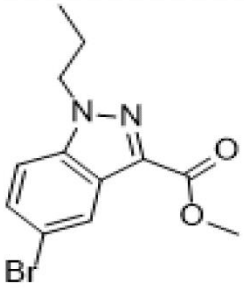
File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\\LCJ-011-008C_2023-03-13T12-24-30.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1168.52041 | 50.23774 |
| 2 | 1200.20278 | 36.68900 |
| 3 | 1248.65818 | 44.98000 |
| 4 | 1382.84234 | 50.50651 |
| 5 | 1433.16140 | 53.12354 |

| | | |
|---|---|---|
| 6 | 1455.52543 | 36.36317 |
| 7 | 1703.39339 | 31.26469 |

bio cryst

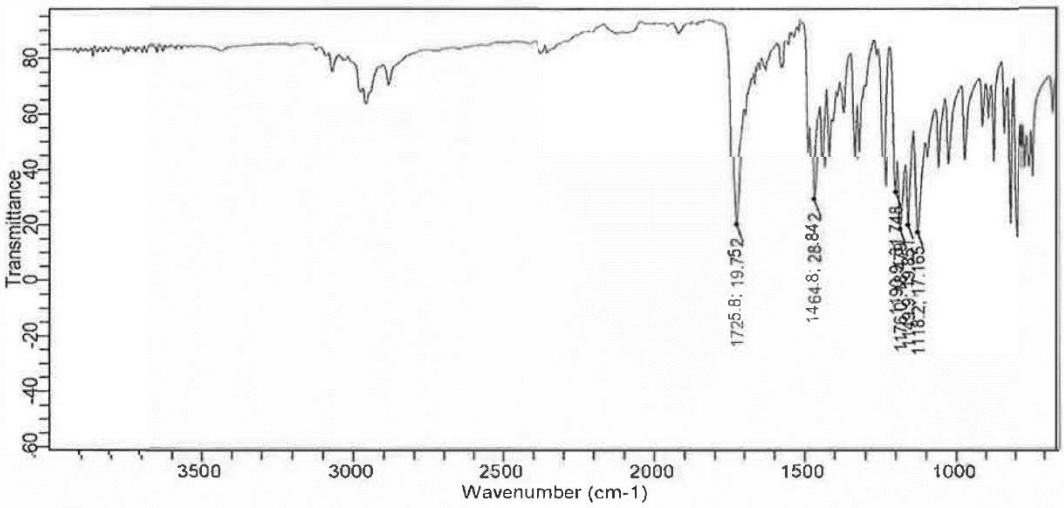



Sample ID:LCJ-007-136B

Sample Scans:128
Background Scans:32
Resolution:4
System Status:Good

Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\ATR 128 Scans.a2m
User:admin
Date/Time:03/13/2023 9:08:39 AM
Range:4000 - 650
Apodization:Happ-Genzel

File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\LCJ-007-136B_2023-03-13T09-08-39.a2r

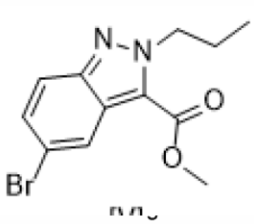



| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1118.20135 | 17.16486 |
| 2 | 1149.88372 | 19.85103 |
| 3 | 1175.97509 | 18.47925 |
| 4 | 1190.88444 | 31.74764 |
| 5 | 1464.84377 | 28.84161 |

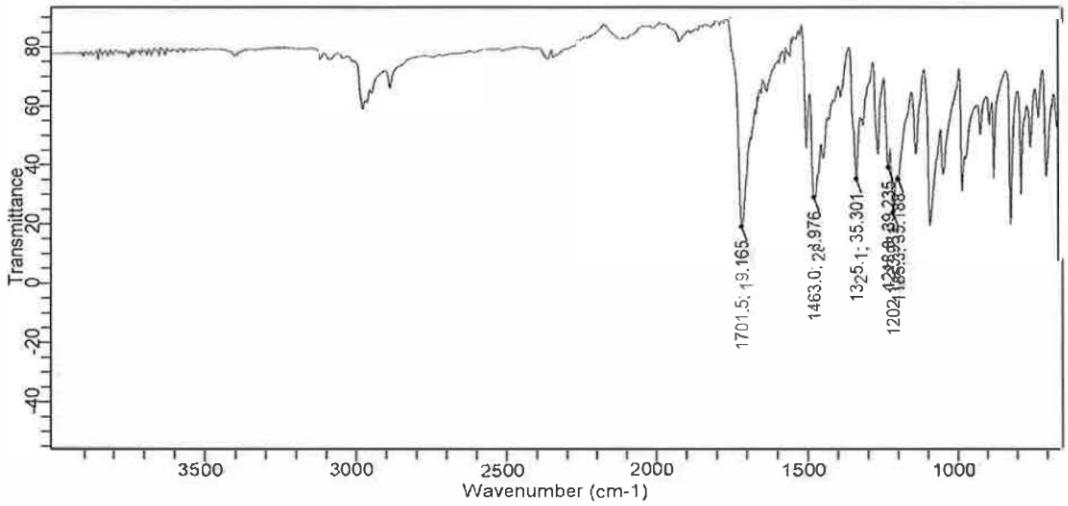
| | | |
|---|---|---|
| 6 | 1725.75742 | 19.75177 |

Sample ID:LCJ-007-136C

Sample Scans:128
Background Scans:32
Resolution:4
System Status:Good
File Location:C:\Users\Pul
42.a2r

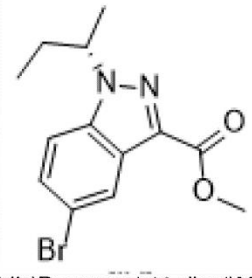



Method
Name:C:\Users\Public\Documents\Agilent\MicroLa
\Methods\ATR 128 Scans.a2m
User:admin
Date/Time:03/13/2023 8:57:42 AM
Range:4000 - 650
Apodization:Happ-Genzel
Lab\Results\LCJ-007-136C_2023-03-13T08-57-




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1185.29343 | 35.18787 |
| 2 | 1202.06645 | 23.93112 |
| 3 | 1218.83947 | 39.23543 |
| 4 | 1325.06860 | 35.30121 |
| 5 | 1462.98010 | 28.97583 |

| | | |
|---|---|---|
| 6 | 1701.52972 | 19.16455 |

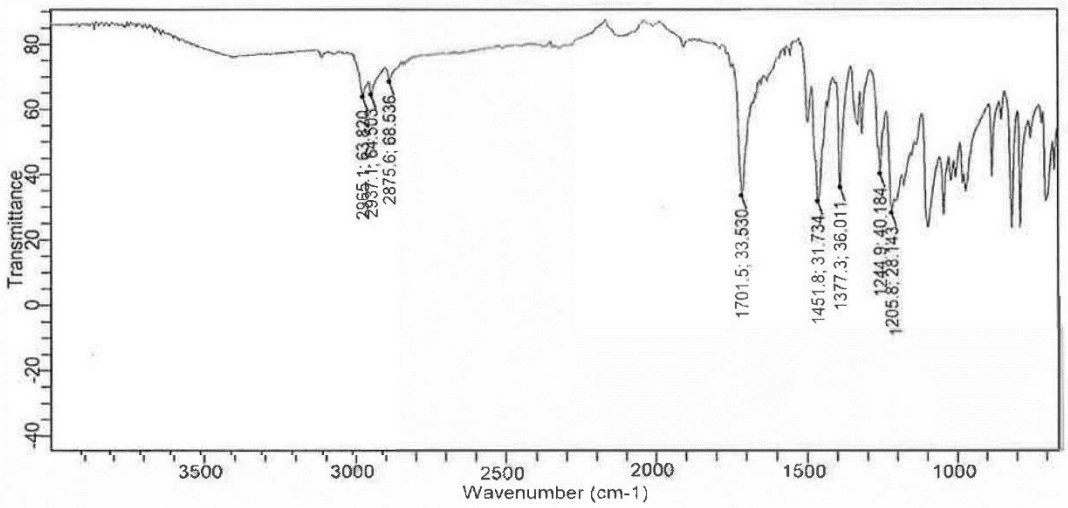


Sample ID:LCJ-007-152B

Sample Scans:128
Background Scans:32
Resolution:4
System Status:Good

Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\ATR 128 Scans.a2m
User:admin
Date/Time:03/13/2023 9:59:12 AM
Range:4000 - 650
Apodization:Happ-Genzel

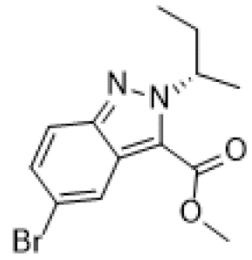
File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\\LCJ-007-152B_2023-03-13T09-59-12.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1205.79379 | 28.14339 |
| 2 | 1244.93084 | 40.18409 |
| 3 | 1377.25133 | 36.01087 |
| 4 | 1451.79809 | 31.73383 |
| 5 | 1701.52972 | 33.53023 |

| | | |
|---|---|---|
| 6 | 2875.64114 | 68.53643 |
| 7 | 2937.14222 | 64.50303 |
| 8 | 2965.09725 | 63.81967 |

Sample ID:LCJ-007-152C




Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\400-CM.a2m

Sample Scans:32

User:admin

Background Scans:32

Date/Time:03/13/2023 1:29:08 PM

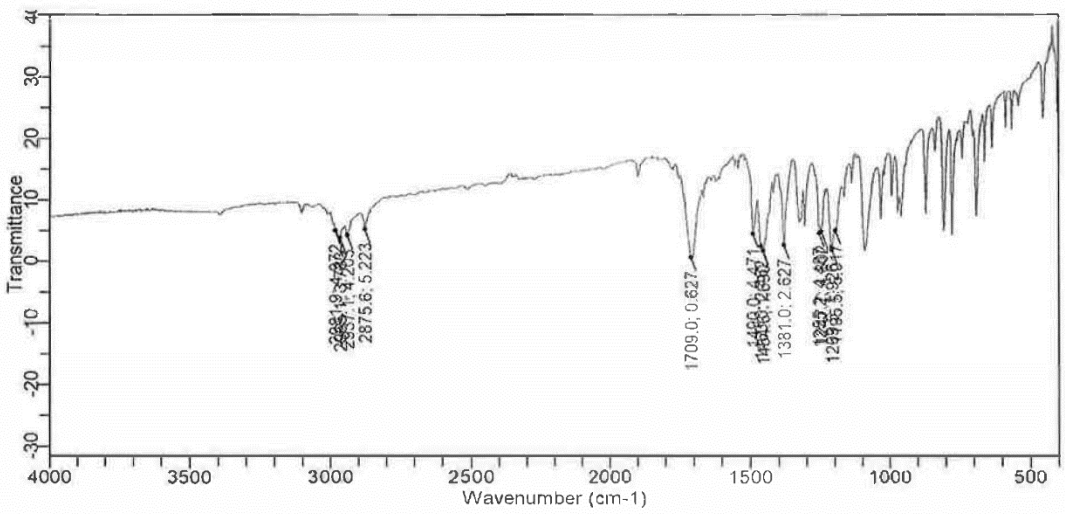
Resolution:2

Range:4000 - 400

System Status:Good

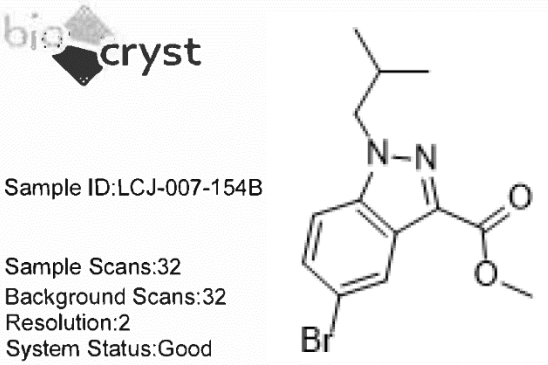
Apodization:Happ-Genzel

File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\LCJ-007-152C_2023-03-13T13-29-08.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1195.54361 | 5.01697 |
| 2 | 1209.52113 | 1.92555 |
| 3 | 1247.72634 | 4.80237 |
| 4 | 1255.18102 | 4.48735 |
| 5 | 1380.97867 | 2.62699 |

| | | |
|---|---|---|
| 6 | 1454.59359 | 1.68977 |
| 7 | 1462.98010 | 2.46233 |
| 8 | 1490.00330 | 4.47055 |
| 9 | 1708.98440 | 0.62685 |
| 10 | 2875.64114 | 5.22327 |
| 11 | 2937.14222 | 4.20273 |
| 12 | 2965.09725 | 3.78335 |
| 13 | 2981.87027 | 4.97185 |



Sample ID:LCJ-007-154B

Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\400-CM.a2m

Sample Scans:32

User:admin

Background Scans:32

Date/Time:03/13/2023 1:38:35 PM

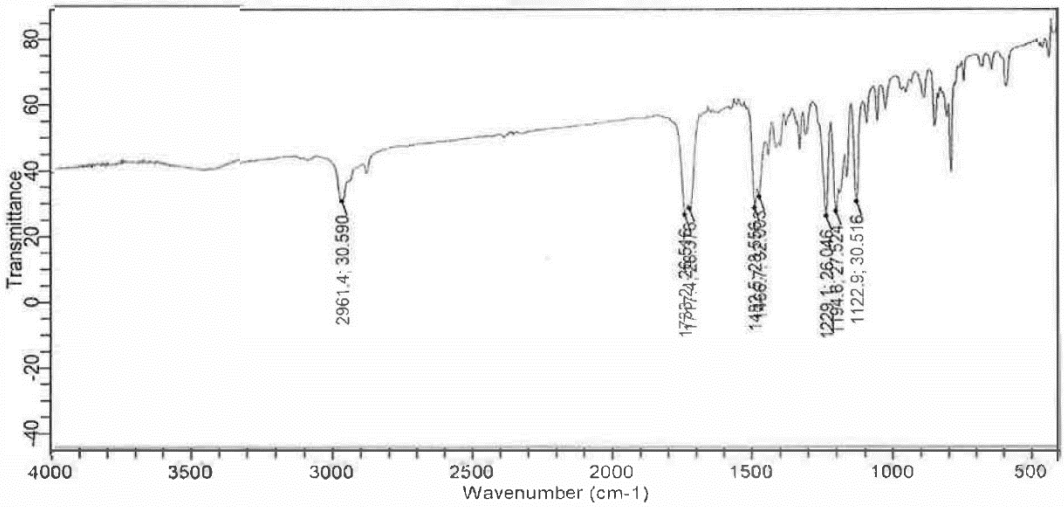
Resolution:2

Range:4000 - 400

System Status:Good

Apodization:Happ-Genzel

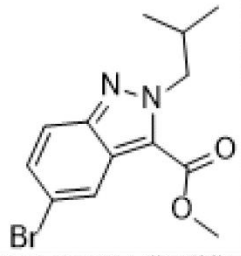
File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\\LCJ-007-154B_2023-03-13T13-38-35.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1122.86052 | 30.51611 |
| 2 | 1194.61178 | 27.52388 |
| 3 | 1229.08965 | 26.04618 |
| 4 | 1466.70744 | 32.00286 |
| 5 | 1482.54862 | 28.55584 |

| | | |
|---|---|---|
| 6 | 1717.37091 | 28.37635 |
| 7 | 1733.21209 | 26.51607 |
| 8 | 2961.36991 | 30.58969 |

Sample ID:LCJ-007-154C



Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\ATR 128 Scans.a2m

Sample Scans:128

User:admin

Background Scans:32

Date/Time:03/13/2023 10:12:54 AM

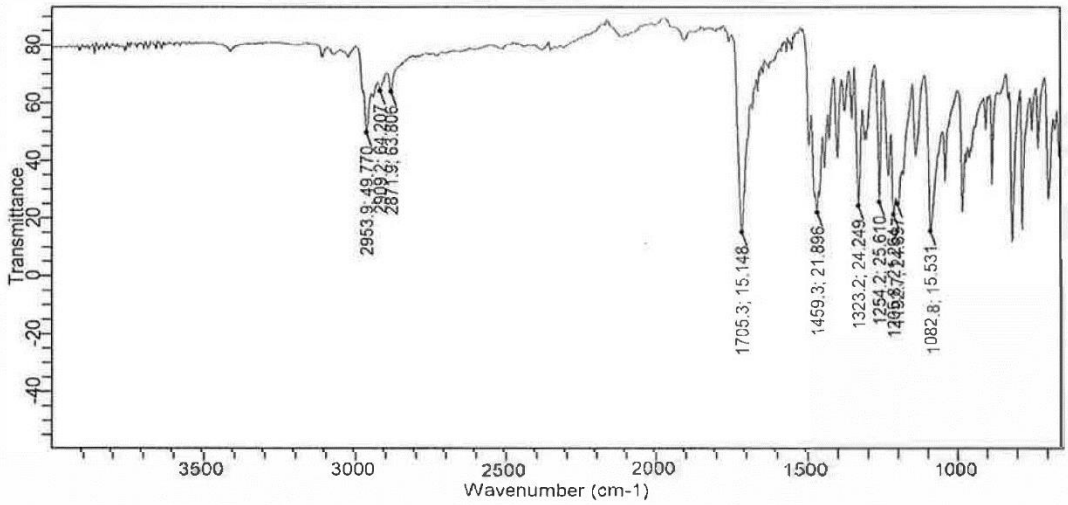
Resolution:4

Range:4000 - 650

System Status:Good

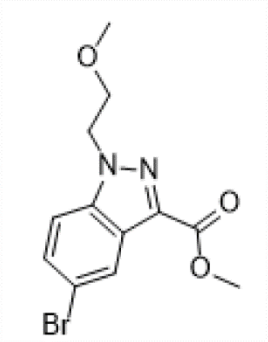
Apodization:Happ-Genzel

File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\\LCJ-007-154C_2023-03-13T10-12-54.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1082.79164 | 15.53131 |
| 2 | 1192.74811 | 24.89689 |
| 3 | 1205.79379 | 21.26395 |
| 4 | 1254.24918 | 25.61045 |
| 5 | 1323.20493 | 24.24895 |

| | | |
|---|---|---|
| 6 | 1459.25276 | 21.89565 |
| 7 | 1705.25706 | 15.14805 |
| 8 | 2871.91380 | 63.80600 |
| 9 | 2909.18718 | 64.20744 |
| 10 | 2953.91524 | 49.76992 |

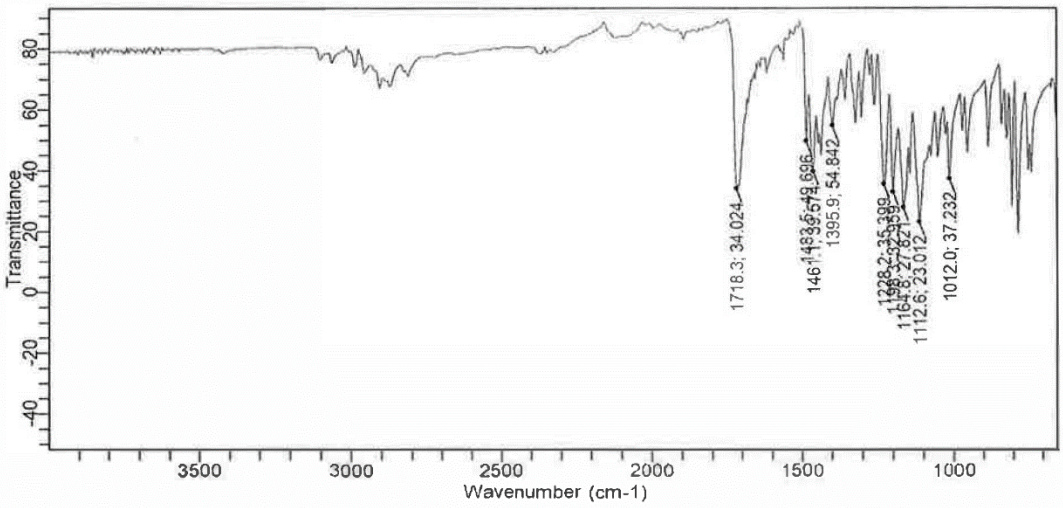


Sample ID:LCJ-007-143B

Sample Scans:128
Background Scans:32
Resolution:4
System Status:Good

Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\ATR 128 Scans.a2m
User:admin
Date/Time:03/13/2023 12:37:53 PM
Range:4000 - 650
Apodization:Happ-Genzel

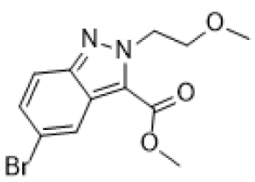
File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\LCJ-007-143B_2023-03-13T12-37-53.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1011.97222 | 37.23186 |
| 2 | 1112.61034 | 23.01163 |
| 3 | 1164.79307 | 27.82095 |
| 4 | 1198.33911 | 32.95888 |
| 5 | 1228.15782 | 35.39860 |

| | | |
|---|---|---|
| 6 | 1395.88802 | 54.84167 |
| 7 | 1461.11643 | 39.57371 |
| 8 | 1483.48046 | 49.69588 |
| 9 | 1718.30274 | 34.02357 |

Sample ID:LCJ-007-143C

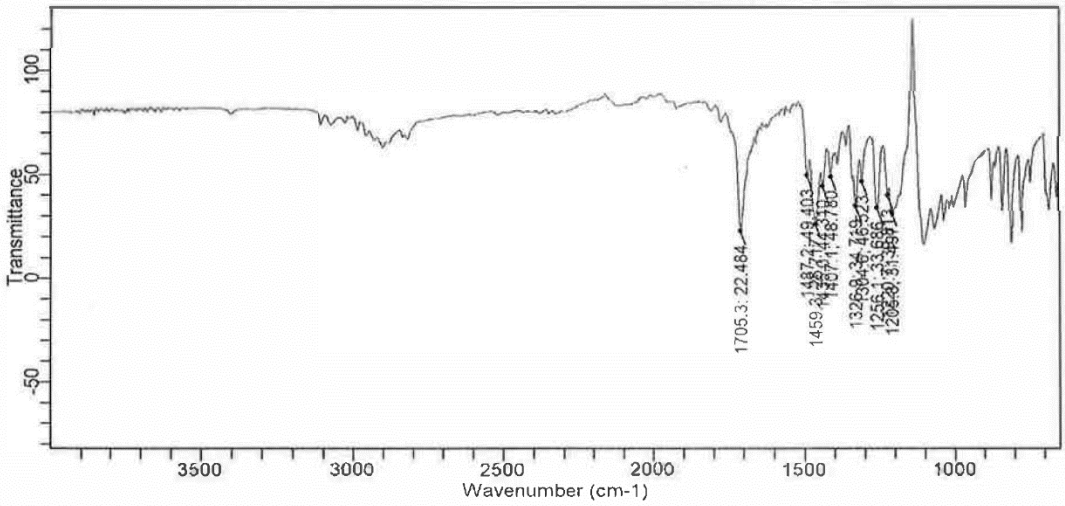


Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\ATR 128 Scans.a2m

Sample Scans:128
Background Scans:32
Resolution:4
System Status:Good

User:admin
Date/Time:03/13/2023 12:27:27 PM
Range:4000 - 650
Apodization:Happ-Genzel

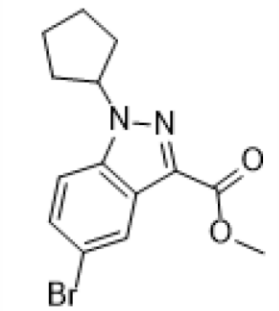
File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\LCJ-007-143C_2023-03-13T12-27-27.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1205.79379 | 31.49663 |
| 2 | 1220.70314 | 39.81252 |
| 3 | 1256.11285 | 33.68586 |
| 4 | 1304.56824 | 46.52315 |
| 5 | 1326.93227 | 34.71922 |

| | | |
|---|---|---|
| 6 | 1407.07003 | 48.77999 |
| 7 | 1435.02507 | 44.30999 |
| 8 | 1459.25276 | 25.71714 |
| 9 | 1487.20780 | 49.40263 |
| 10 | 1705.25706 | 22.48364 |

bio cryst




Sample ID:LCJ-007-140B

Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\ATR 128 Scans.a2m

Sample Scans:128

User:admin

Background Scans:32

Date/Time:03/13/2023 10:07:46 AM

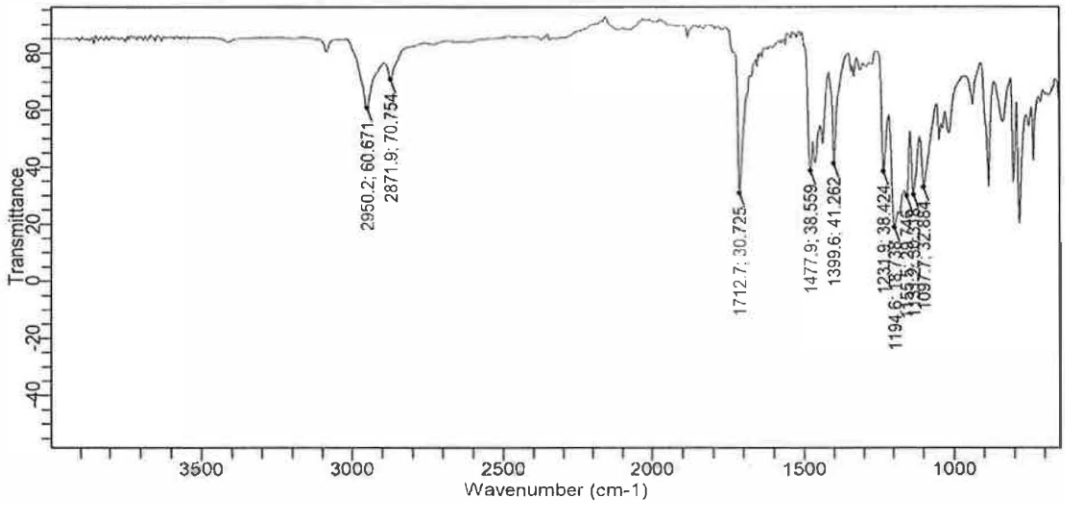
Resolution:4

Range:4000 - 650

System Status:Good

Apodization:Happ-Genzel

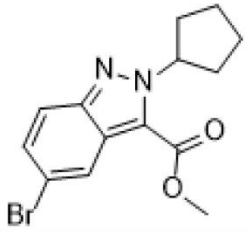
File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\LCJ-007-140B_2023-03-13T10-07-46.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1097.70099 | 32.88424 |
| 2 | 1131.24703 | 30.31772 |
| 3 | 1155.47473 | 29.74621 |
| 4 | 1194.61178 | 18.73827 |
| 5 | 1231.88516 | 38.42359 |

| | | |
|---|---|---|
| 6 | 1399.61536 | 41.26165 |
| 7 | 1477.88945 | 38.55933 |
| 8 | 1712.71174 | 30.72533 |
| 9 | 2871.91380 | 70.75439 |
| 10 | 2950.18790 | 60.67135 |

Sample ID:LCJ-007-140C




Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\400-CM.a2m

Sample Scans:32

User:admin

Background Scans:32

Date/Time:03/13/2023 1:34:08 PM

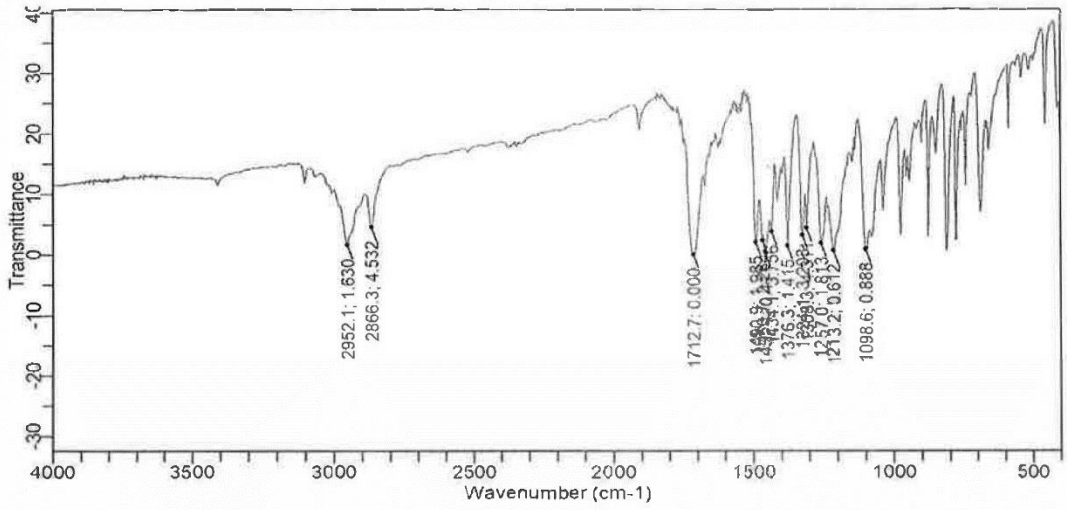
Resolution:2

Range:4000 - 400

System Status:Good

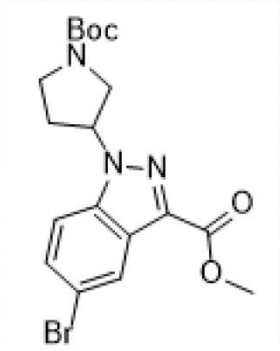
Apodization:Happ-Genzel

File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\LCJ-007-140C_2023-03-13T13-34-08.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1098.63283 | 0.88798 |
| 2 | 1213.24847 | 0.61244 |
| 3 | 1257.04469 | 1.81301 |
| 4 | 1308.29558 | 4.31137 |
| 5 | 1324.13677 | 3.20328 |

| | | |
|---|---|---|
| 6 | 1376.31950 | 1.41537 |
| 7 | 1434.09323 | 3.75614 |
| 8 | 1457.38909 | 0.41081 |
| 9 | 1466.70744 | 2.28432 |
| 10 | 1490.93513 | 1.98516 |
| 11 | 1712.71174 | 0.00001 |
| 12 | 2866.32280 | 4.53191 |
| 13 | 2952.05157 | 1.63012 |

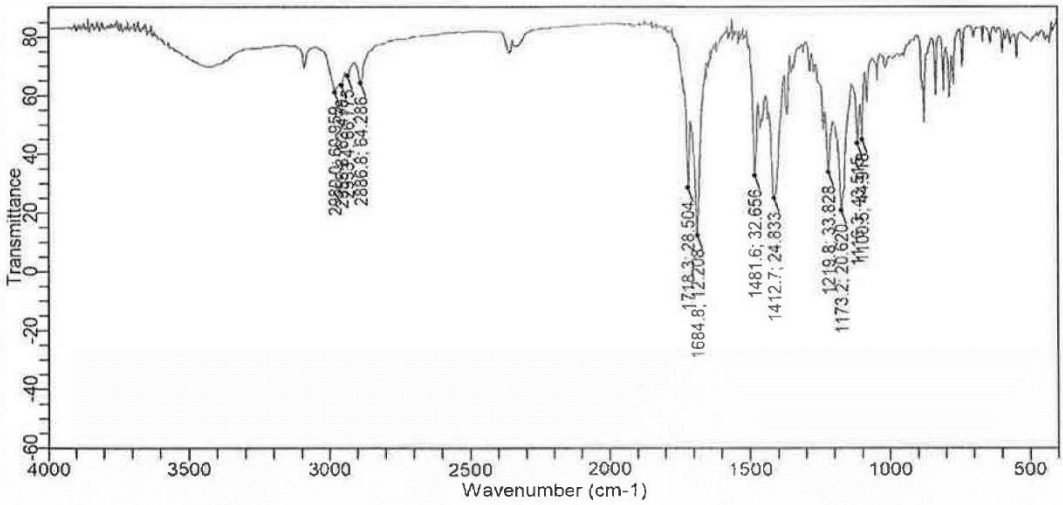



Sample ID:LCJ-007-151B

Sample Scans:32
Background Scans:32
Resolution:2
System Status:Good

Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\400-CM.a2m
User:admin
Date/Time:03/13/2023 1:13:03 PM
Range:4000 - 400
Apodization:Happ-Genzel

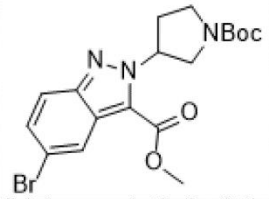
File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\\LCJ-007-151B_2023-03-13T13-13-03.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1100.49650 | 44.91764 |
| 2 | 1116.33768 | 43.51476 |
| 3 | 1173.17958 | 20.61996 |
| 4 | 1219.77131 | 33.82786 |
| 5 | 1412.66104 | 24.83296 |

| | | |
|---|---|---|
| 6 | 1481.61679 | 32.65622 |
| 7 | 1684.75670 | 12.20782 |
| 8 | 1718.30274 | 28.50403 |
| 9 | 2886.82315 | 64.28613 |
| 10 | 2933.41488 | 66.77500 |
| 11 | 2955.77890 | 63.47835 |
| 12 | 2980.00660 | 60.95887 |

Sample ID:LCJ-007-151C

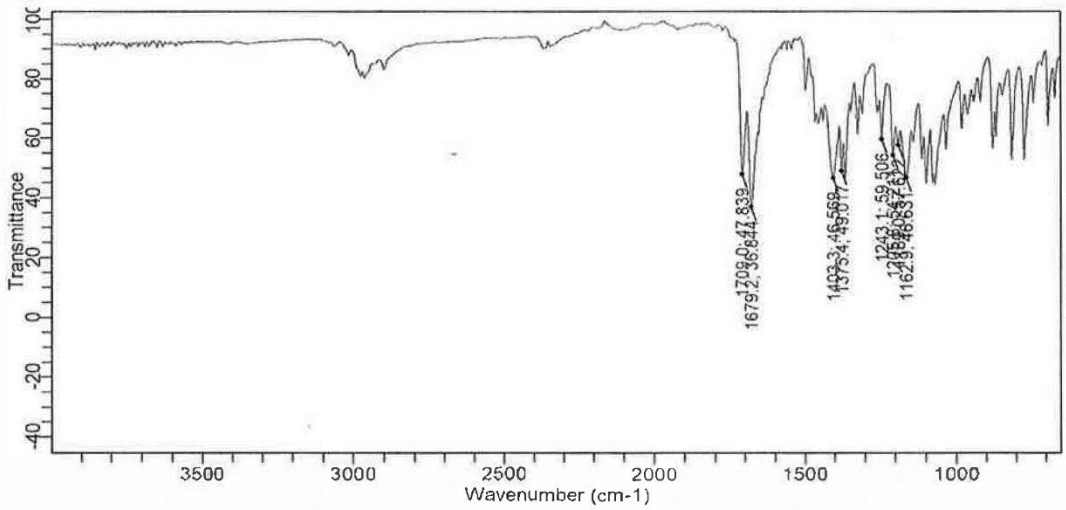



Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\ATR 128 Scans.a2m

Sample Scans:128
Background Scans:32
Resolution:4
System Status:Good

User:admin
Date/Time:03/13/2023 9:13:52 AM
Range:4000 - 650
Apodization:Happ-Genzel

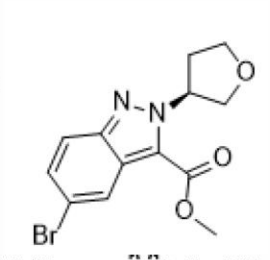
File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\\LCJ-007-151C_2023-03-13T09-13-52.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1162.92941 | 46.63055 |
| 2 | 1189.02077 | 57.62245 |
| 3 | 1205.79379 | 54.21115 |
| 4 | 1243.06717 | 59.50648 |
| 5 | 1375.38766 | 49.01651 |

| | | |
|---|---|---|
| 6 | 1403.34270 | 46.56858 |
| 7 | 1679.16570 | 36.84422 |
| 8 | 1708.98440 | 47.83945 |

Sample ID:LCJ-007-147C

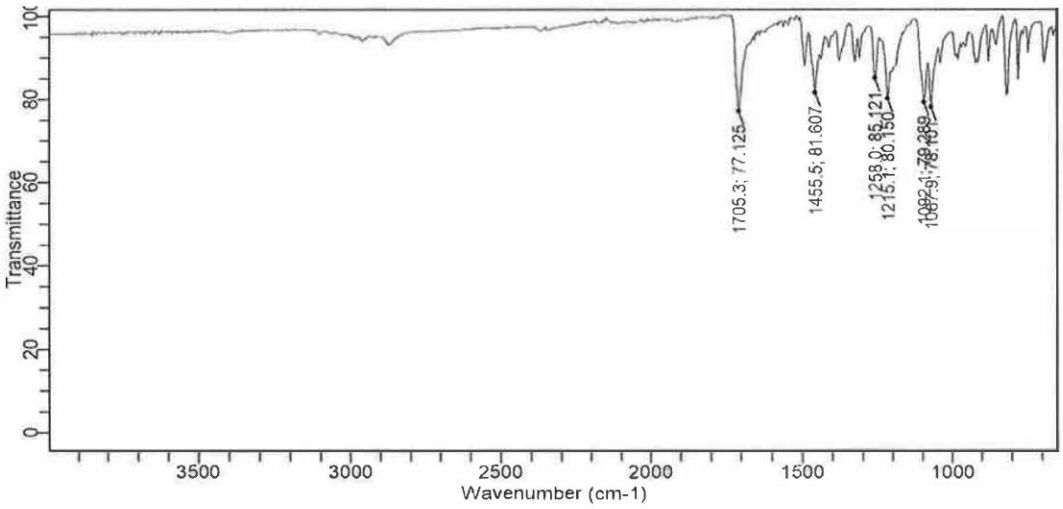


Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\ATR 128 Scans.a2m

Sample Scans:128
Background Scans:32
Resolution:4
System Status:Good

User:admin
Date/Time:03/13/2023 8:24:14 AM
Range:4000 - 650
Apodization:Happ-Genzel

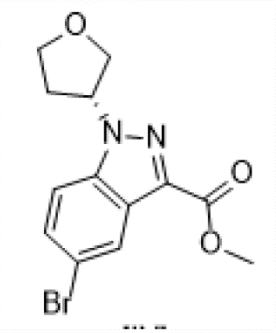
File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\LCJ-007-147C_2023-03-13T08-24-14.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1067.88229 | 78.10095 |
| 2 | 1092.10999 | 79.28906 |
| 3 | 1215.11213 | 80.15043 |
| 4 | 1257.97652 | 85.12144 |
| 5 | 1455.52543 | 81.60687 |

| | | |
|---|---|---|
| 6 | 1705.25706 | 77.12483 |

bio cryst

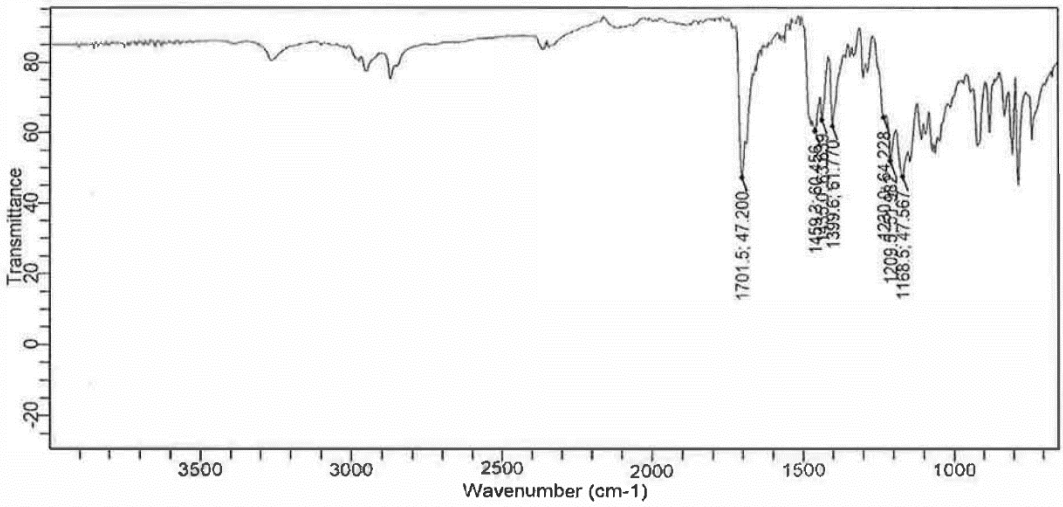


Sample ID:LCJ-007-148B

Sample Scans:128
Background Scans:32
Resolution:4
System Status:Good

Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\ATR 128 Scans.a2m
User:admin
Date/Time:03/13/2023 9:04:38 AM
Range:4000 - 650
Apodization:Happ-Genzel

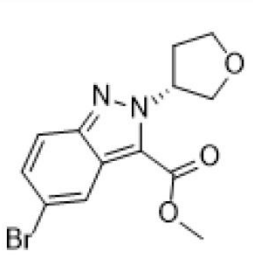
File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\LCJ-007-148B_2023-03-13T09-04-38.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1168.52041 | 47.56692 |
| 2 | 1209.52113 | 51.98202 |
| 3 | 1230.02149 | 64.22830 |
| 4 | 1399.61536 | 61.77011 |
| 5 | 1435.02507 | 63.63927 |

| | | |
|---|---|---|
| 6 | 1459.25276 | 60.45590 |
| 7 | 1701.52972 | 47.20011 |

Sample ID:LCJ-007-148C




Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\ATR 128 Scans.a2m

Sample Scans:128

User:admin

Background Scans:32

Date/Time:03/13/2023 8:54:01 AM

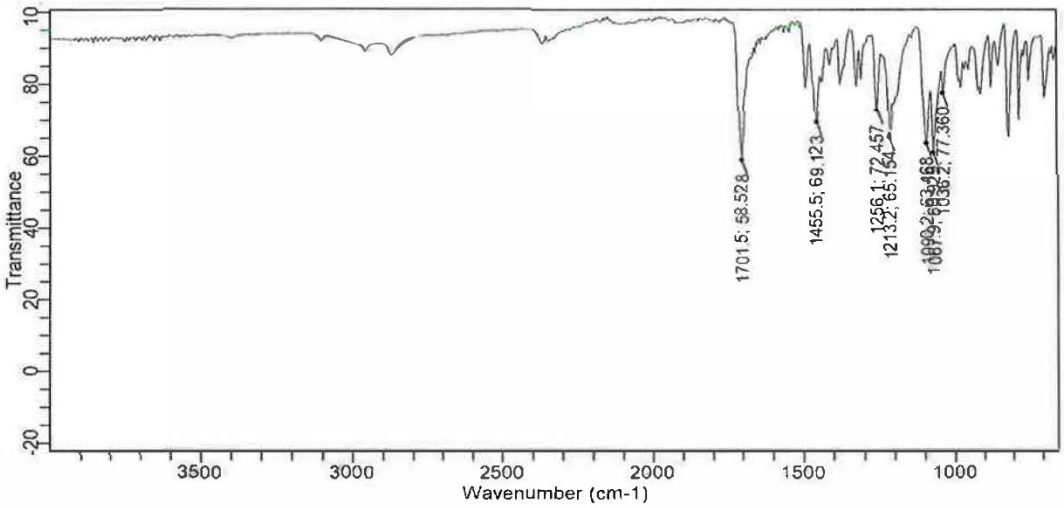
Resolution:4

Range:4000 - 650

System Status:Good

Apodization:Happ-Genzel

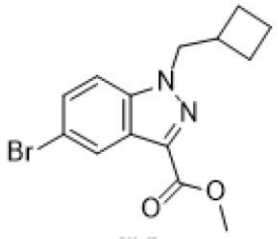
File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\LCJ-007-148C_2023-03-13T08-54-01.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1036.19992 | 77.35991 |
| 2 | 1067.88229 | 60.92893 |
| 3 | 1090.24632 | 63.46799 |
| 4 | 1213.24847 | 65.15430 |
| 5 | 1256.11285 | 72.45704 |

| | | |
|---|---|---|
| 6 | 1455.52543 | 69.12253 |
| 7 | 1701.52972 | 58.52757 |

Sample ID:LCJ-007-142B




Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\ATR 128 Scans.a2m

Sample Scans:128

User:admin

Background Scans:32

Date/Time:03/13/2023 12:06:34 PM

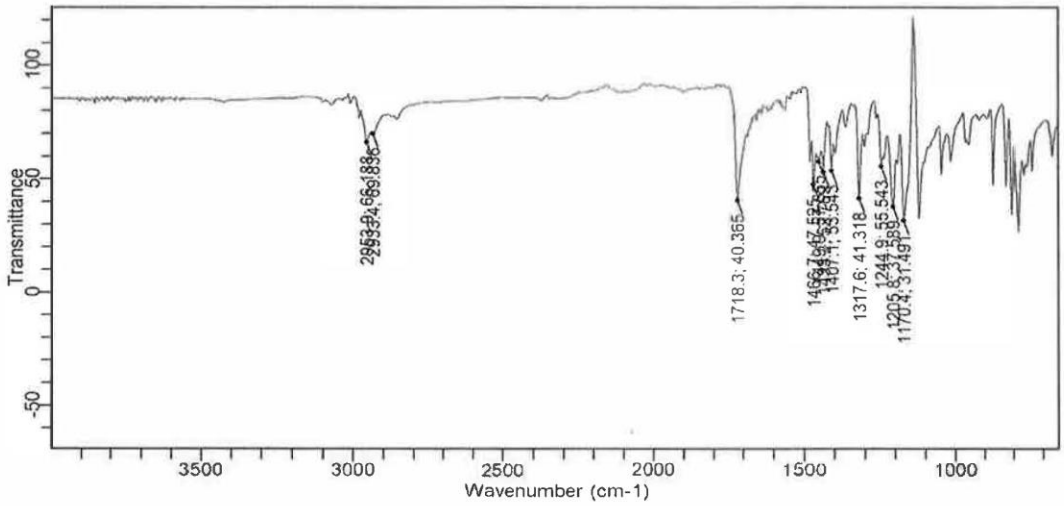
Resolution:4

Range:4000 - 650

System Status:Good

Apodization:Happ-Genzel

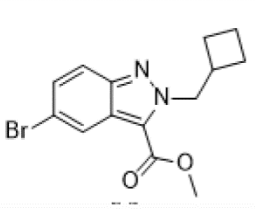
File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\\LCJ-007-142B_2023-03-13T12-06-34.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1170.38408 | 31.49126 |
| 2 | 1205.79379 | 37.58863 |
| 3 | 1244.93084 | 55.54266 |
| 4 | 1317.61393 | 41.31809 |
| 5 | 1407.07003 | 53.54253 |

| | | |
|---|---|---|
| 6 | 1433.16140 | 52.76884 |
| 7 | 1449.93442 | 57.65510 |
| 8 | 1466.70744 | 47.52462 |
| 9 | 1718.30274 | 40.36483 |
| 10 | 2933.41488 | 69.83553 |
| 11 | 2953.91524 | 66.18779 |

Sample ID:LCJ-007-142C

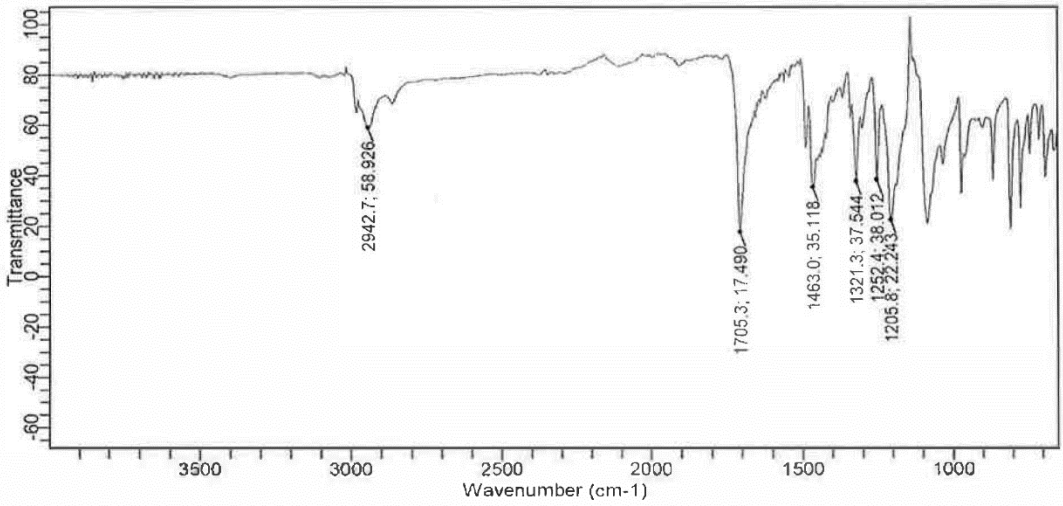



Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\ATR 128 Scans.a2m

Sample Scans:128
Background Scans:32
Resolution:4
System Status:Good

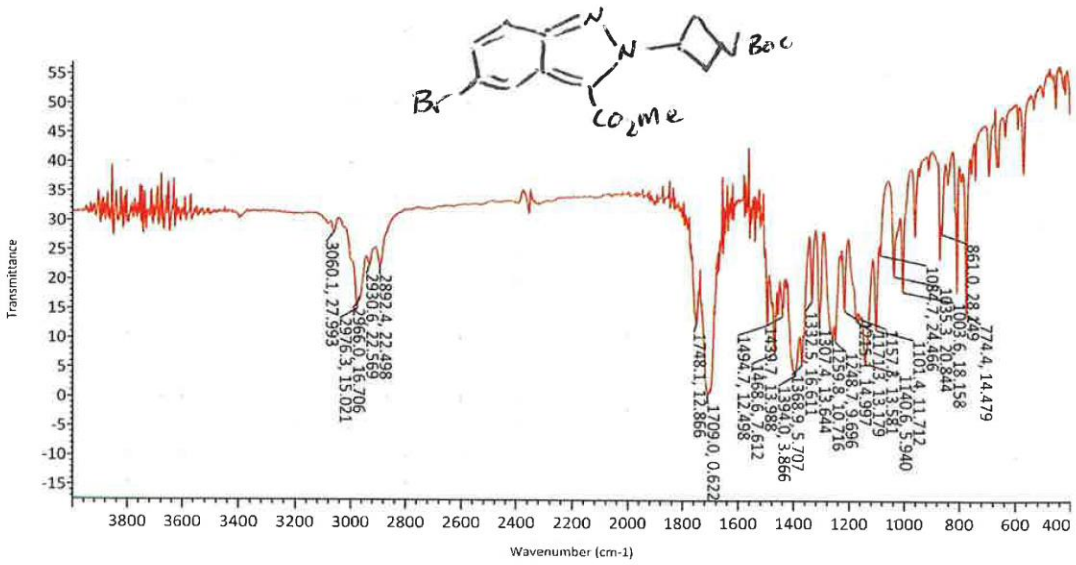
User:admin
Date/Time:03/13/2023 12:00:08 PM
Range:4000 - 650
Apodization:Happ-Genzel

File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\\LCJ-007-142C_2023-03-13T12-00-08.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1205.79379 | 22.24316 |
| 2 | 1252.38551 | 38.01169 |
| 3 | 1321.34126 | 37.54367 |
| 4 | 1462.98010 | 35.11781 |
| 5 | 1705.25706 | 17.49019 |

| | | |
|---|---|---|
| 6 | 2942.73322 | 58.92565 |



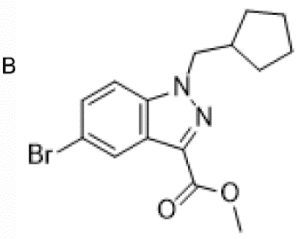

| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 774.4 | 14.479 |
| 2 | 861.0 | 28.149 |
| 3 | 1003.6 | 18.158 |
| 4 | 1035.3 | 20.844 |
| 5 | 1084.7 | 24.466 |
| 6 | 1101.4 | 11.712 |
| 7 | 1140.6 | 5.940 |
| 8 | 1157.3 | 13.581 |
| 9 | 1171.3 | 13.179 |
| 10 | 1215.1 | 14.997 |
| 11 | 1248.7 | 9.696 |
| 12 | 1259.8 | 10.716 |

| | | |
|---|---|---|
| 13 | 1307.4 | 13.644 |
| 14 | 1332.5 | 16.611 |
| 15 | 1368.9 | 5.707 |
| 16 | 1394.0 | 3.866 |
| 17 | 1439.7 | 13.988 |
| 18 | 1468.6 | 7.612 |
| 19 | 1494.7 | 12.498 |
| 20 | 1709.0 | 0.622 |
| 21 | 1748.1 | 12.866 |
| 22 | 2892.4 | 22.498 |
| 23 | 2930.6 | 22.569 |
| 24 | 2966.0 | 16.706 |
| 25 | 2976.3 | 15.021 |
| 26 | 3060.1 | 27.993 |

**E-SIGNATURES**

| **Signature** |
|---|

Sample ID:LCJ-007-141B

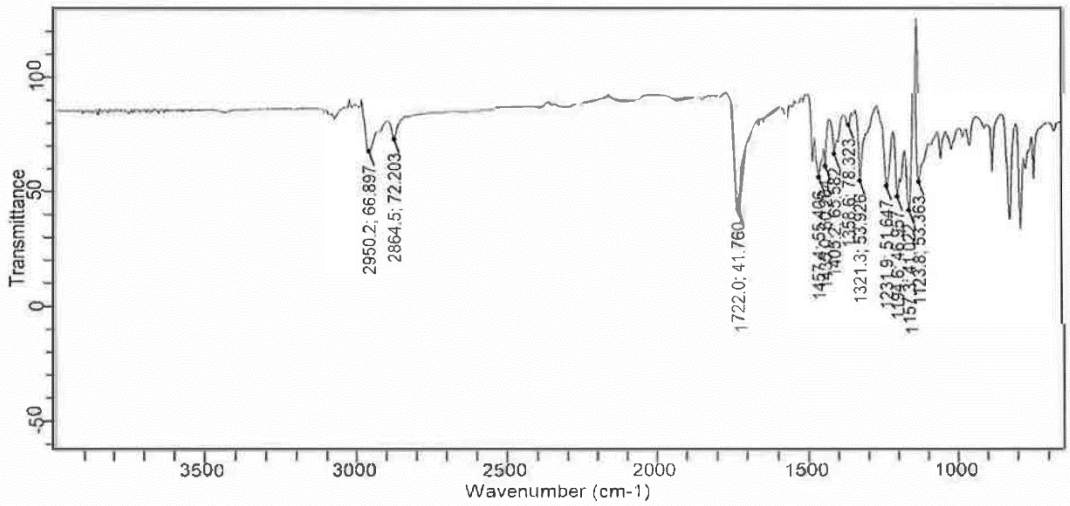



Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\ATR 128 Scans.a2m

Sample Scans:128
Background Scans:32
Resolution:4
System Status:Good

User:admin
Date/Time:03/13/2023 11:52:24 AM
Range:4000 - 650
Apodization:Happ-Genzel

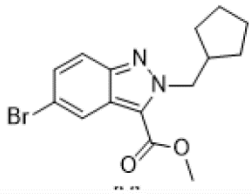
File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\\LCJ-007-141B_2023-03-13T11-52-24.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1123.79236 | 53.36288 |
| 2 | 1157.33840 | 41.02159 |
| 3 | 1194.61178 | 46.95675 |
| 4 | 1231.88516 | 51.64723 |
| 5 | 1321.34126 | 53.92642 |

| | | |
|---|---|---|
| 6 | 1358.61464 | 78.32318 |
| 7 | 1405.20636 | 65.58237 |
| 8 | 1435.02507 | 60.26444 |
| 9 | 1457.38909 | 55.40582 |
| 10 | 1722.03008 | 41.75959 |
| 11 | 2864.45913 | 72.20255 |
| 12 | 2950.18790 | 66.89715 |

Sample ID:LCJ-007-141C




Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\ATR 128 Scans.a2m

Sample Scans:128

User:admin

Background Scans:32

Date/Time:03/13/2023 11:48:38 AM

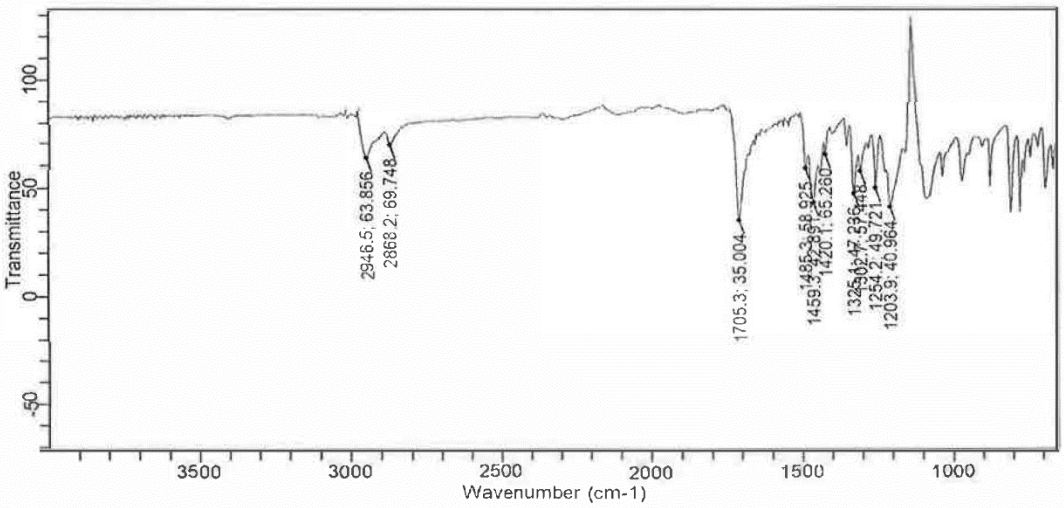
Resolution:4

Range:4000 - 650

System Status:Good

Apodization:Happ-Genzel

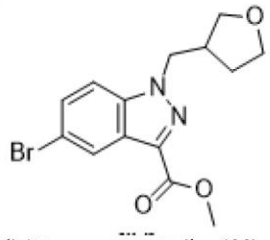
File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\\LCJ-007-141C_2023-03-13T11-48-38.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1203.93012 | 40.96397 |
| 2 | 1254.24918 | 49.72099 |
| 3 | 1302.70457 | 57.44787 |
| 4 | 1325.06860 | 47.23572 |
| 5 | 1420.11572 | 65.26002 |

| | | |
|---|---|---|
| 6 | 1459.25276 | 42.89111 |
| 7 | 1485.34413 | 58.92480 |
| 8 | 1705.25706 | 35.00428 |
| 9 | 2868.18647 | 69.74761 |
| 10 | 2946.46056 | 63.85648 |

Sample ID:LCJ-007-146B




Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\400-CM.a2m

Sample Scans:32

User:admin

Background Scans:32

Date/Time:03/13/2023 1:43:02 PM

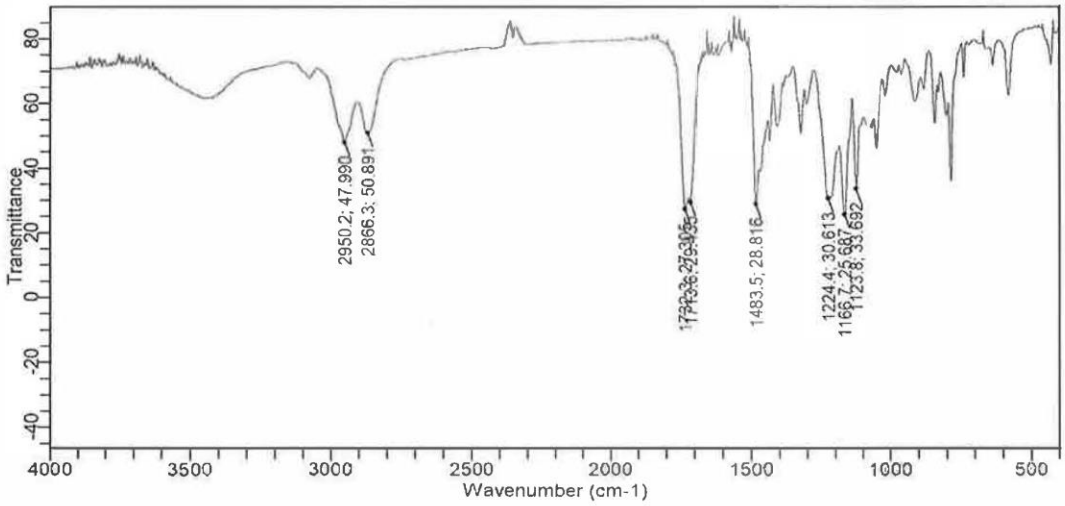
Resolution:2

Range:4000 - 400

System Status:Good

Apodization:Happ-Genzel

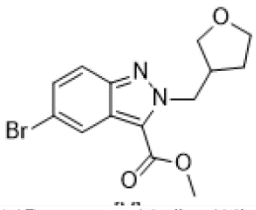
File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\\LCJ-007-146B_2023-03-13T13-43-02.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1123.79236 | 33.69202 |
| 2 | 1166.65674 | 25.68660 |
| 3 | 1224.43048 | 30.61295 |
| 4 | 1483.48046 | 28.81632 |
| 5 | 1713.64357 | 29.43483 |

| | | |
|---|---|---|
| 6 | 1732.28026 | 27.30534 |
| 7 | 2866.32280 | 50.89122 |
| 8 | 2950.18790 | 47.99018 |

Sample ID:LCJ-007-146C

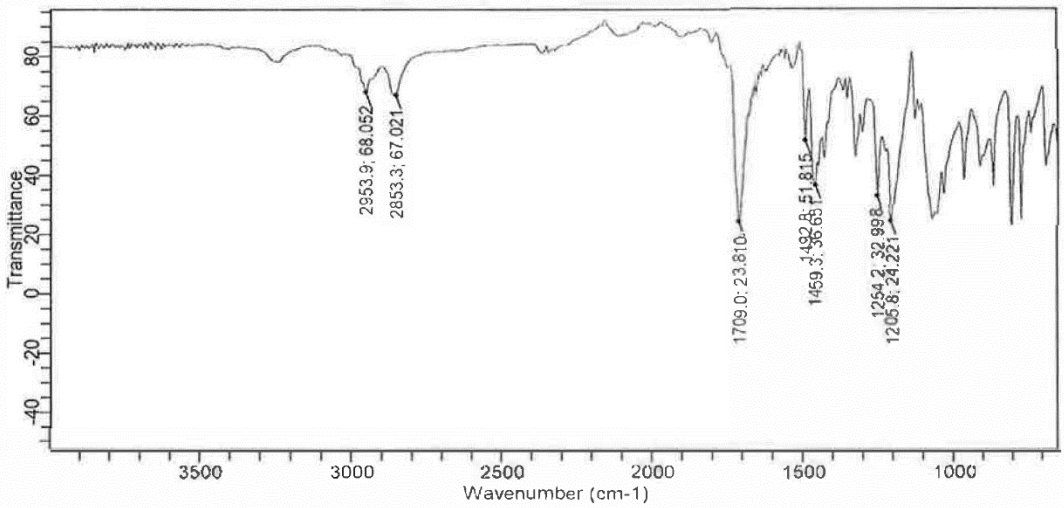


Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\ATR 128 Scans.a2m

Sample Scans:128
Background Scans:32
Resolution:4
System Status:Good

User:admin
Date/Time:03/13/2023 12:44:01 PM
Range:4000 - 650
Apodization:Happ-Genzel

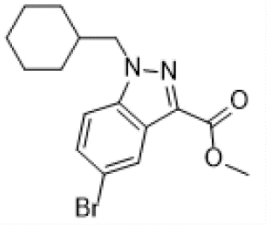
File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\\LCJ-007-146C_2023-03-13T12-44-01.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1205.79379 | 24.22135 |
| 2 | 1254.24918 | 32.99819 |
| 3 | 1459.25276 | 36.65103 |
| 4 | 1492.79880 | 51.81519 |
| 5 | 1708.98440 | 23.81042 |

| | | |
|---|---|---|
| 6 | 2853.27711 | 67.02071 |
| 7 | 2953.91524 | 68.05167 |

Sample ID:LCJ-007-139B

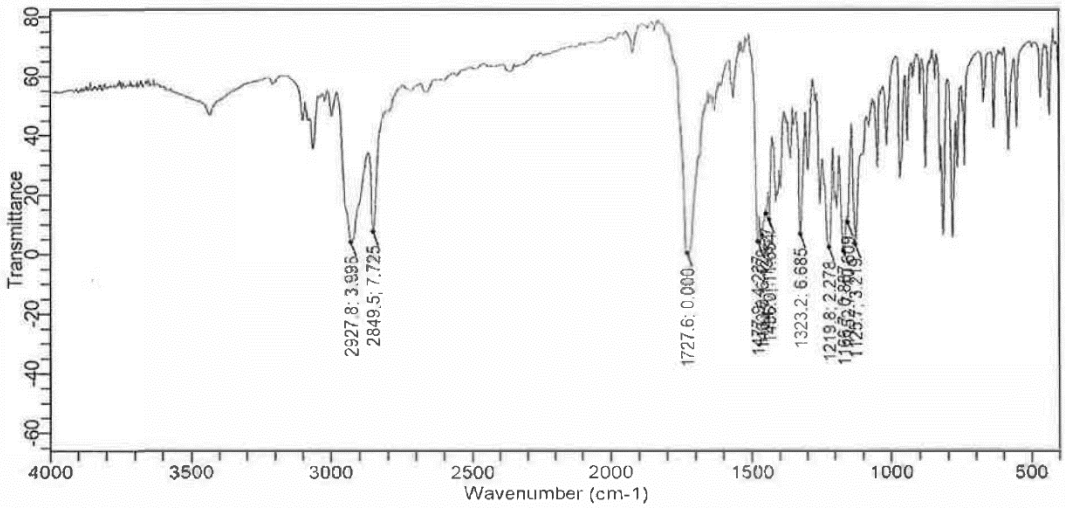



Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\400-CM.a2m

Sample Scans:32
Background Scans:32
Resolution:2
System Status:Good

User:admin
Date/Time:03/13/2023 1:19:20 PM
Range:4000 - 400
Apodization:Happ-Genzel

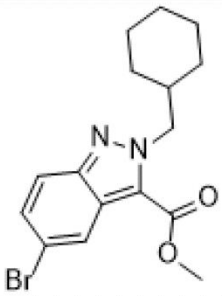
File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\\LCJ-007-139B_2023-03-13T13-19-20.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1125.65603 | 3.21879 |
| 2 | 1152.67923 | 10.60875 |
| 3 | 1166.65674 | 0.88655 |
| 4 | 1219.77131 | 2.27848 |
| 5 | 1323.20493 | 6.68505 |

| | | |
|---|---|---|
| 6 | 1435.95690 | 11.65402 |
| 7 | 1447.13892 | 13.57684 |
| 8 | 1462.98010 | 6.41979 |
| 9 | 1477.88945 | 4.23725 |
| 10 | 1727.62109 | 0.00001 |
| 11 | 2849.54978 | 7.72533 |
| 12 | 2927.82387 | 3.99554 |

Sample ID:LCJ-007-139C

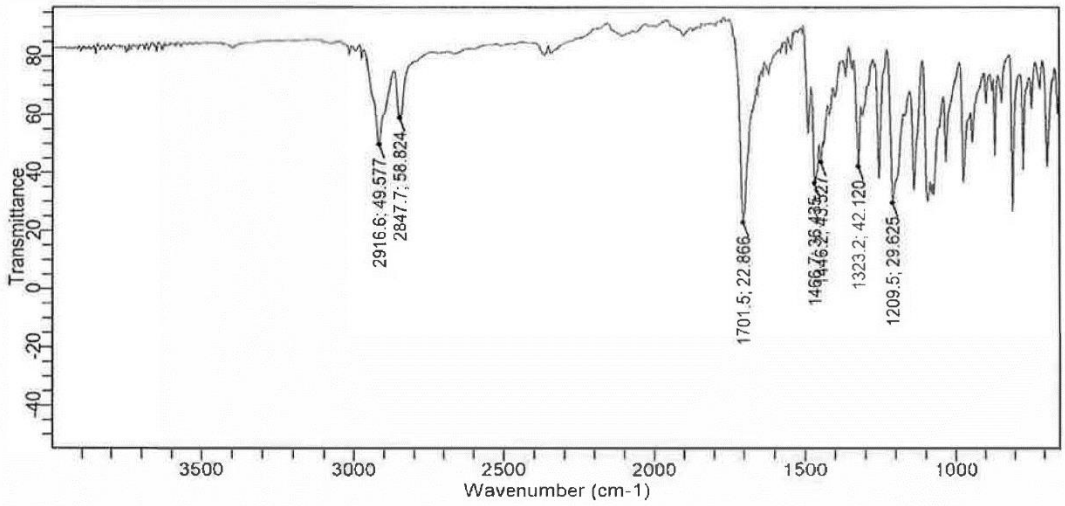


Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\ATR 128 Scans.a2m

Sample Scans:128
Background Scans:32
Resolution:4
System Status:Good

User:admin
Date/Time:03/13/2023 9:17:09 AM
Range:4000 - 650
Apodization:Happ-Genzel

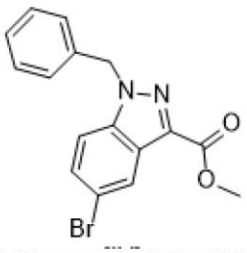
File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\\LCJ-007-139C_2023-03-13T09-17-09.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1209.52113 | 29.62499 |
| 2 | 1323.20493 | 42.11959 |
| 3 | 1446.20708 | 43.52681 |
| 4 | 1466.70744 | 36.43514 |
| 5 | 1701.52972 | 22.86613 |

| | | |
|---|---|---|
| 6 | 2847.68611 | 58.82384 |
| 7 | 2916.64186 | 49.57708 |

bio cryst




Sample ID:LCJ-009-186B

Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\ATR 128 Scans.a2m

Sample Scans:128

User:admin

Background Scans:32

Date/Time:03/13/2023 12:03:15 PM

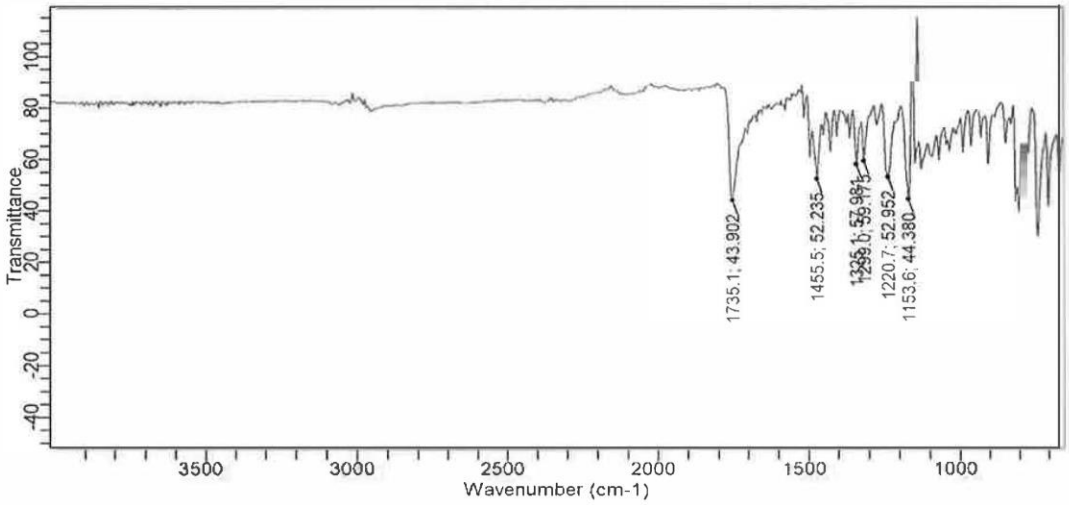
Resolution:4

Range:4000 - 650

System Status:Good

Apodization:Happ-Genzel

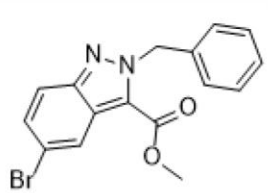
File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\LCJ-009-186B_2023-03-13T12-03-15.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1153.61106 | 44.38023 |
| 2 | 1220.70314 | 52.95247 |
| 3 | 1298.97724 | 59.17542 |
| 4 | 1325.06860 | 57.98121 |
| 5 | 1455.52543 | 52.23538 |

| | | |
|---|---|---|
| 6 | 1735.07576 | 43.90218 |

Sample ID:LCJ-009-186C



Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\ATR 128 Scans.a2m

Sample Scans:128

User:admin

Background Scans:32

Date/Time:03/13/2023 11:56:41 AM

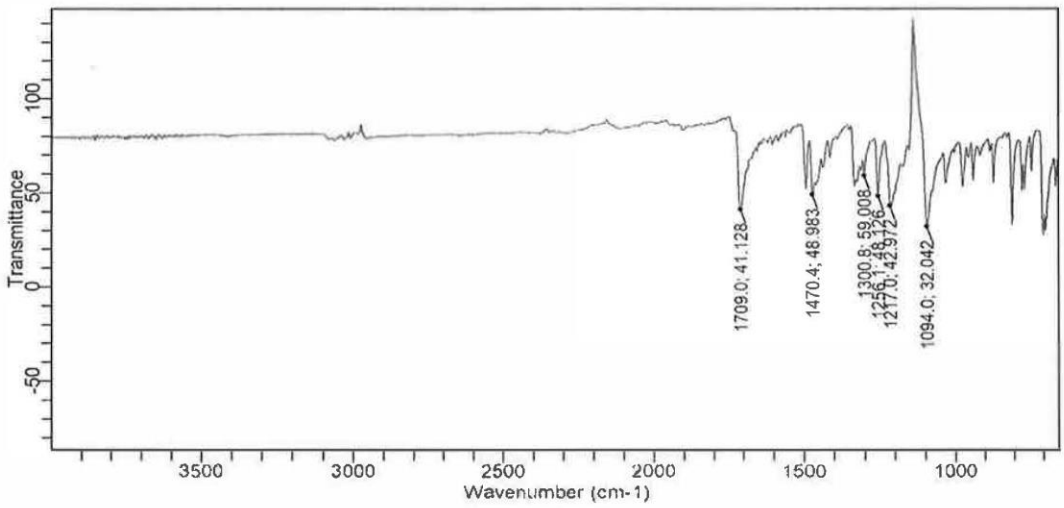
Resolution:4

Range:4000 - 650

System Status:Good

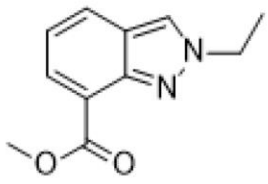
Apodization:Happ-Genzel

File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\LCJ-009-186C_2023-03-13T11-56-41.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 1093.97366 | 32.04191 |
| 2 | 1216.97580 | 42.97187 |
| 3 | 1256.11285 | 48.12629 |
| 4 | 1300.84091 | 59.00798 |
| 5 | 1470.43478 | 48.98330 |

| | | |
|---|---|---|
| 6 | 1708.98440 | 41.12782 |



MW 20 July 23

Sample ID:LCJ-013-121B

Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\400-CM.a2m

Sample Scans:32

User:admin

Background Scans:32

Date/Time:07/20/2023 1:20:47 PM

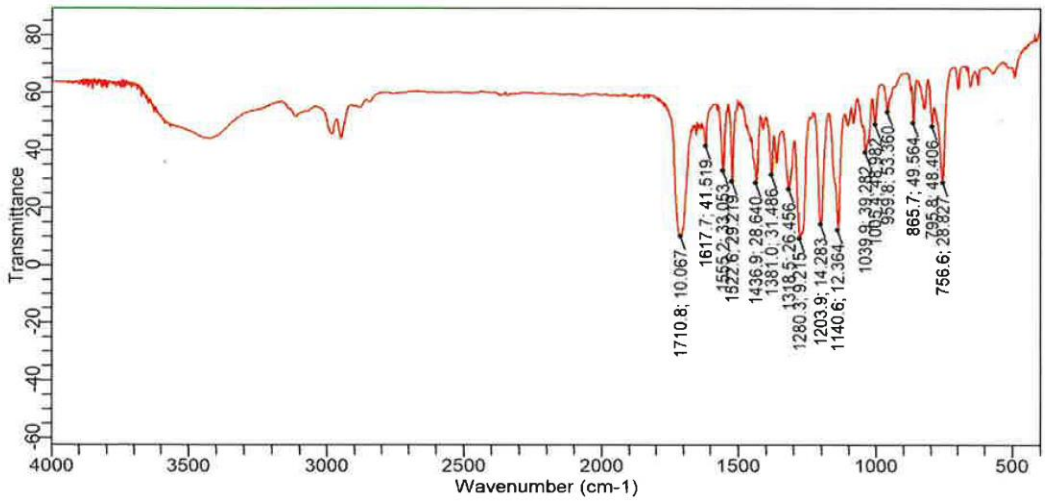
Resolution:2

Range:4000 - 400

System Status:Good

Apodization:Happ-Genzel

File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\LCJ-013-121B_2023-07-20T13-20-47.a2r

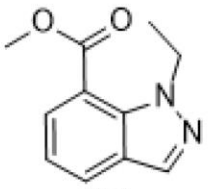



| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 756.64958 | 28.82692 |
| 2 | 795.78663 | 48.40602 |
| 3 | 865.67421 | 49.56427 |
| 4 | 959.78949 | 53.35960 |
| 5 | 1005.44938 | 48.98203 |

| | | |
|---|---|---|
| 6 | 1039.92726 | 39.28233 |
| 7 | 1140.56538 | 12.36356 |
| 8 | 1203.93012 | 14.28277 |
| 9 | 1280.34055 | 9.21451 |
| 10 | 1318.54576 | 26.45588 |
| 11 | 1380.97867 | 31.48569 |
| 12 | 1436.88874 | 28.63951 |
| 13 | 1522.61751 | 29.21877 |
| 14 | 1555.23171 | 33.05342 |
| 15 | 1617.66462 | 41.51938 |
| 16 | 1710.84807 | 10.06669 |

bio cryst

MW 27 July 23



[IV]

Exact Mass: 204.09

Sample ID:LCJ-013-121C

Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\400-CM.a2m

Sample Scans:32

User:admin

Background Scans:32

Date/Time:07/27/2023 10:26:50 AM

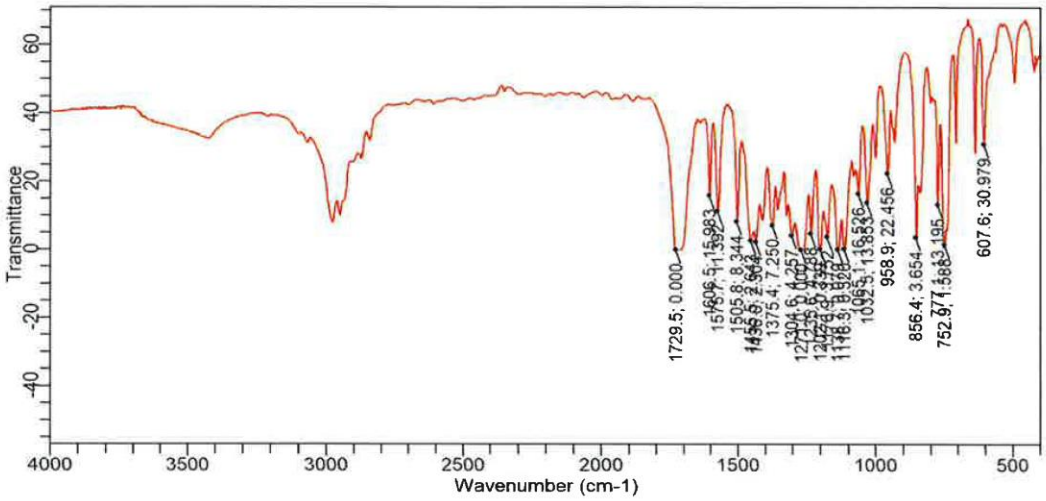
Resolution:2

Range:4000 - 400

System Status:Good

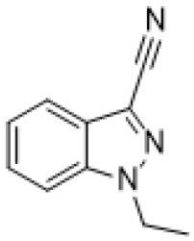
Apodization:Happ-Genzel

File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\LCJ-013-121C_2023-07-27T10-26-50.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 607.55607 | 30.97905 |
| 2 | 752.92224 | 1.58788 |
| 3 | 777.14994 | 13.19529 |
| 4 | 856.35587 | 3.65414 |
| 5 | 958.85766 | 22.45559 |

| | | |
|---|---|---|
| 6 | 1032.47258 | 13.85300 |
| 7 | 1065.08679 | 16.52627 |
| 8 | 1116.33768 | 0.31963 |
| 9 | 1138.70171 | 0.07853 |
| 10 | 1176.90692 | 3.75183 |
| 11 | 1202.06645 | 0.33912 |
| 12 | 1235.61249 | 4.78812 |
| 13 | 1271.02220 | 0.00001 |
| 14 | 1304.56824 | 4.25745 |
| 15 | 1375.38766 | 7.24957 |
| 16 | 1435.95690 | 2.30385 |
| 17 | 1455.52543 | 2.64266 |
| 18 | 1505.84449 | 8.34396 |
| 19 | 1575.73207 | 11.39162 |
| 20 | 1606.48261 | 15.98287 |
| 21 | 1729.48476 | 0.00001 |



MW 21 July 23

Sample ID:LCJ-013-123B

Method Name:C:\Users\Public\Documents\Agilent\MicroLab\Methods\400-CM.a2m

Sample Scans:32

User:admin

Background Scans:32

Date/Time:07/21/2023 7:59:50 AM

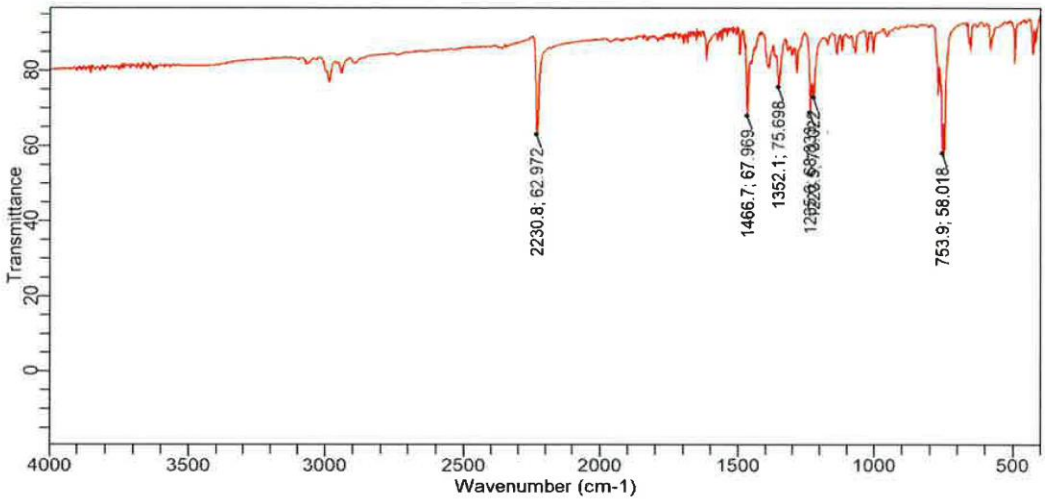
Resolution:2

Range:4000 - 400

System Status:Good

Apodization:Happ-Genzel

File Location:C:\Users\Public\Documents\Agilent\MicroLab\Results\LCJ-013-123B_2023-07-21T07-59-50.a2r




| Peak Number | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| 1 | 753.85408 | 58.01833 |
| 2 | 1223.49865 | 73.02160 |
| 3 | 1235.61249 | 68.83340 |
| 4 | 1352.09180 | 75.69780 |
| 5 | 1466.70744 | 67.96871 |

| | | |
|---|---|---|
| 6 | 2230.81170 | 62.97228 |

(1) a, C. W.; a, C. N. V.; b, P. G. C.; b, S. K.-G.; b, M. A. O.; b, G. T. Elucidation of the Presence and Location of T-Boc Protecting Groups in Amines and Dipeptides Using on-Column H/D Exchange HPLC/ESI/MS. *J. Am. Soc. Mass Spectrom.* **2005**, *16* (4), 553–564. https://doi.org/10.1016/j.jasms.2005.01.008.