BEILSTEIN JOURNAL OF ORGANIC CHEMISTRY

# Supporting Information

for

# Fritsch–Buttenberg–Wiechell rearrangement of magnesium alkylidene carbenoids leading to the formation of alkynes

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*Beilstein J. Org. Chem.* **2021,** *17,* 1352–1359. doi:10.3762/bjoc.17.94

## Characterization data, copies of NMR spectra, and computational details

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**Experimental**

Sulfoxides **2b** [1], (*E*)-**2e** and (*Z*)-**2e** [1], (*E*)-**2f** and (*Z*)-**2f** [2], and (*E*)-**2g** and (*Z*)-**2g** [3], alkynes **4b** [4], **4d** [5], **4e** [6], **4f** [7], and **4g** [8], and alkenes **9d** [9] and **9e** [10] are known compounds. Characterization data were in agreement with those reported in the literature.

**4,4'-[2-Fluoro-2-(*p*-tolylsulfinyl)ethene-1,1-diyl]bis(methoxybenzene) (5).** $R_f$ = 0.45 (hexane/EtOAc, 1:1); colorless solid; mp 110.3–111.1 ºC; IR (ATR) 2964, 2927, 2841, 1605, 1507, 1250, 1175, 1106, 1032 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.79 (s, 3H), 3.88 (s, 3H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H); $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 21.5, 55.3, 55.4, 113.7, 114.1, 125.3, 127.1 (d, *J* = 4.8 Hz), 127.4 (d, *J* = 2.4 Hz), 130.0, 131.0 (d, *J* = 6.0 Hz), 131.7 (d, *J* = 6.0 Hz), 132.3 (d, *J* = 2.4 Hz), 137.4, 141.9, 154.4 (d, *J* = 323.9 Hz), 160.2, 160.3; MS ($FAB^+$) *m/z* (%) 397 ($[M+H]^+$, 100), 380 (13), 348 (17), 273 (20); HRMS ($FAB^+$) calcd for $C_{23}H_{22}FO_3S$ ($[M+H]^+$): 397.1274, found: 397.1275.

**4,4'-[2-Bromo-2-(*p*-tolylsulfinyl)ethene-1,1-diyl]bis(methoxybenzene) (6).** A solution of sulfoxide **8** (189 mg, 0.499 mmol) in THF (1 mL) was added dropwise to a solution of LDA (1.3 mmol) in THF (4.5 mL) over a period of 4 min at −78 °C, and the mixture was stirred at −78 °C for 10 min. A solution of 1,2-dibromo-1,1,2,2-tetrachloroethane (814 mg, 2.50 mmol) in THF (2.5 mL) was added to the mixture at −78 °C, and the reaction mixture was warmed to 0 °C over a period of 30 min. The reaction mixture was stirred at 0 °C for 1 h, and the reaction was quenched with aq sat $NH_4Cl$ (1 mL). The mixture was extracted with $CHCl_3$ (10 mL) and water (10 mL), and the aqueous layer was extracted with $CHCl_3$ (2 × 3 mL). The combined organic layer was dried over $Na_2SO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc 2:1 to 1:1) to give sulfoxide **6** [158 mg, 0.345 mmol, 69%, $R_f$ = 0.60 (hexane/EtOAc 1:1)]. Yellow solid; mp 143.5–144.4 ºC; IR (ATR) 3024, 2955, 2904, 2838, 1604, 1503, 1460, 1302, 1250, 1172, 1083, 1058, 1025, 808 $cm^{-1}$; 1H NMR (301 MHz, $CDCl_3$) δ 2.42 (s, 3H), 3.81 (s, 3H), 3.85 (s, 3H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 7.20–7.33 (m, 6H), 7.48 (d, *J* = 8.3 Hz, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 21.5, 55.3, 55.4, 113.5, 114.0, 125.0, 129.7, 130.1, 131.3, 131.5, 131.8, 132.8, 140.2, 141.4, 152.9, 160.1, 160.4; MS ($FAB^+$) *m/z* (%) 459 (100), 457 ($[M+H]^+$, 98), 238 (68); HRMS ($FAB^+$) calcd for $C_{23}H_{22}{}^{79}BrO_3S$ ($[M+H]^+$): 457.0473, found: 457.0476.

**4,4'-[2-Methoxy-2-(*p*-tolylsulfinyl)ethene-1,1-diyl]bis(methoxybenzene) (7).** A 1.0 mol/L solution of *sec*-BuLi in cyclohexane and hexane (1.3 mL, 1.3 mmol) was added to a solution of 1,10-phenanthroline (5.1 mg, 0.028 mmol), TMEDA (125 mg, 1.08 mmol), and methoxy(*p*-tolylthio)(trimethylsilyl)methane (244 mg, 1.01 mmol) in THF (2.5 mL) at −78 °C, and the mixture was stirred at −78 °C for 2.5 h. Then, 4,4'-dimethoxybenzophenone (268 mg, 1.11 mmol) was added to the mixture at −78 °C, and the reaction mixture was stirred at 26 °C for 22 h. The reaction was quenched with sat. aq. $NH_4Cl$ (5 mL) and extracted with $CHCl_3$ (15 mL) and water (5 mL). The aqueous layer was extracted with $CHCl_3$ (3 × 15 mL), and the combined organic layer was washed with brine (5 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc 20:1) to give 1-methoxyvinyl *p*-tolyl sulfide (374 mg, 0.952 mmol, 94%). *m*CPBA (containing water, >65% purity, 192 mg, approximately 1.1 mmol) was added to a solution of 1-methoxyvinyl *p*-tolyl sulfide (374 mg, 0.952 mmol) in $CHCl_3$ (4.8 mL) portionwise at 0 °C over a period of 2 h. The reaction was quenched with sat. aq. $Na_2SO_3$ (15 mL) and extracted with toluene (15 mL). The organic layer was washed with aq NaOH (5%, 2 × 15 mL), and the combined aqueous layer was extracted with toluene (3 × 15 mL). The combined organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc 1:1) to give **7** [366 mg, 0.896 mmol, 94%, $R_f$ = 0.30 (hexane/EtOAc 1:1)] as a yellow oil. IR (ATR) 2934, 2835, 1604, 1508, 1461, 1246, 1208, 1173, 1105, 1029, 834, 808 $cm^{-1}$; $^1H$ NMR (399 MHz, $CDCl_3$) δ 2.40 (s, 3H), 3.63 (s, 3H), 3.79 (s, 3H), 3.86 (s, 3H), 6.80 (d, *J* = 8.9 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 7.22–7.34 (m, 6H), 7.51 (d, *J* = 8.2 Hz, 2H); $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 21.4, 55.2, 55.3, 63.4, 113.6, 113.9, 124.8, 129.6, 129.8, 130.1, 131.5, 132.2, 135.3, 139.2, 140.8, 155.9, 159.6, 159.8; MS ($FAB^+$) *m/z* (%) , 431 ($[M+Na]^+$, 25), 409 ($[M+H]^+$, 100), 285 (70), 254 (42), 154 (71), 136 (49); HRMS ($FAB^+$) calcd for $C_{24}H_{25}O_4S$ ($[M+H]^+$): 409.1474, found: 409.1472.

**4,4'-[2-(*p*-Tolylsulfinyl)ethene-1,1-diyl]bis(methoxybenzene) (8).** $R_f$ = 0.30 (hexane/EtOAc 1:1); colorless oil; IR (ATR) 2963, 2936, 2838, 1604, 1584, 1507, 1460, 1444, 1300, 1287, 1248, 1173, 1027, 835, 799, 750 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 2.42 (s, 3H), 3.81 (s, 3H), 3.88 (s, 3H), 6.64 (s, 1H), 6.83 (d, *J* = 9.0 Hz, 2H), 6.98 (d, *J* = 9.0 Hz, 2H), 7.21 (d, *J* = 9.0 Hz, 2H), 7.30–7.33 (m, 4H), 7.57 (d, *J* = 8.0 Hz, 2H); $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 21.4, 55.4, 113.7, 113.8, 124.6, 129.6, 130.0, 130.1, 131.2, 131.8, 131.9, 141.0, 142.4, 152.1, 160.3, 160.9; MS ($FAB^+$) *m/z* (%) 379 ($[M+H]^+$, 100), 362 (17), 330 (23); HRMS ($FAB^+$) calcd for $C_{23}H_{23}O_3S$ ($[M+H]^+$): 379.1368, found: 379.1369.

**[2-Chloro-2-(*p*-tolylsulfinyl)ethene-1,1-diyl]dibenzene (2b).** Colorless solid; mp 149.9–150.7 °C; IR (ATR) 3054, 1595, 1489, 1443, 1081, 1053, 1033, 843, 808, 767, 758, 701, 623 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 2.42 (s, 3H), 7.26–7.28 (m, 2H), 7.32–7.35 (m, 5H), 7.37–7.39 (m, 2H), 7.42–7.47 (m, 3H), 7.51 (d, *J* = 8.2 Hz, 2H); $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 21.5, 124.9, 128.3, 128.7, 129.1, 129.2, 129.4, 129.8, 130.0, 137.5, 138.3, 138.4, 138.8, 141.8, 149.5; MS (FAB$^+$) *m/z* (%) 353 ([M+H]$^+$, 100); HRMS (FAB$^+$) calcd for $C_{21}H_{18}{}^{35}ClOS$ ([M+H]$^+$): 353.0767, found: 353.0767.

**{3-[Chloro(*p*-tolylsulfinyl)methylene]pentane-1,5-diyl}dibenzene (2c).** $R_f$ = 0.38 (hexane/EtOAc 1:1); colorless solid; mp 65.9–66.8 °C; IR (ATR) 3025, 2929, 1599, 1494, 1453, 1086, 1054, 804, 746, 694 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 2.41 (s, 3H), 2.63–2.99 (m, 8H), 7.16–7.35 (m, 14H); $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 21.5, 32.9, 34.9, 35.3, 35.9, 124.7, 126.4, 126.6, 128.3, 128.4, 128.6, 128.8, 129.7, 135.5, 138.2, 140.0, 140.4, 141.5, 150.2; MS (FAB$^+$) *m/z* (%) 409 ([M+H]$^+$, 100), 91 (20); HRMS (FAB$^+$) calcd for $C_{25}H_{26}{}^{35}ClOS$ ([M+H]$^+$): 409.1393, found: 409.1390.

**[4-Chloro-4-(*p*-tolylsulfinyl)but-3-en-1-yne-1,3-diyl]dibenzene (2d).** *L*-**2d** [$R_f$ = 0.47 (hexane/EtOAc 3:1)]: colorless solid; mp 78.3–79.2 °C; IR (ATR) 3054, 3022, 2921, 2195, 1488, 1442, 1086, 1061, 1027, 1016, 925, 807, 754, 732, 688 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 2.41 (s, 3H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.37–7.43 (m, 6H), 7.55–7.57 (m, 2H) , 7.62–7.65 (m, 2H), 7.74 (d, *J* = 8.3 Hz, 2H); $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 21.5, 85.7, 101.0, 121.8, 124.3, 127.9, 128.3, 128.6, 128.9, 129.5, 129.6, 130.0, 131.7, 134.9, 139.1, 142.1, 145.6; MS (FAB$^+$) *m/z* (%) 377 ([M+H]$^+$, 100), 254 (24), 154 (26), 137 (19), 93 (31); HRMS (FAB$^+$) calcd for $C_{23}H_{18}{}^{35}ClOS$ ([M+H]$^+$): 377.0767, found: 377.0767. *M*-**2d** [$R_f$ = 0.44 (hexane/EtOAc, 3:1)]: colorless solid; mp 113.8-114.4 °C; IR (ATR) 3055, 3003, 2195, 1488, 1442, 1085, 1057, 905, 807, 752, 688, 641 $cm^{-1}$; $^1H$ NMR (399 MHz, $CDCl_3$) δ 2.40 (s, 3H), 7.29–7.38 (m, 5H), 7.44–7.51 (m, 7H), 7.57–7.60 (m, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 21.5, 86.8, 102.3, 121.8, 124.9, 128.4, 128.8, 129.4, 129.6, 129.7, 129.9, 132.0, 132.6, 134.9, 138.4, 142.1, 144.7; MS (FAB$^+$) *m/z* (%) 377 ([M+H]$^+$, 100), 202 (17), 154 (18), 136 (15), 93 (19); HRMS (FAB$^+$) calcd for $C_{23}H_{18}{}^{35}ClOS$ ([M+H]$^+$): 377.0767, found: 377.0766.

**(*E*)-1-[(1-Chloro-2-phenylprop-1-en-1-yl)sulfinyl]-4-methylbenzene [(*E*)-2e].** (*E*)-**2e**: Colorless solid; mp 79.7–80.4 °C; IR (ATR) 3054, 3000, 2920, 1594, 1489, 1432, 1083, 1050, 1031, 1015, 900, 813, 761, 702 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 2.32 (s, 3H), 2.40 (s, 3H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.34–7.36 (m, 2H), 7.39–7.48 (m, 5H); $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 21.5, 24.2, 125.0, 128.1,

128.80, 128.81, 129.7, 136.7, 138.7, 138.9, 141.7, 147.8; MS (FAB$^+$) *m/z* (%) 291 ([M+H]$^+$, 100); HRMS (FAB$^+$) calcd for $C_{16}H_{16}{}^{35}ClOS$ ([M+H]$^+$): 291.0610, found: 291.0609. [$^{13}$C]-(*E*)-**2e**: $^1$H NMR (500 MHz, $CDCl_3$) δ 2.32 (d, *J* = 6.3 Hz, 3H), 2.40 (s, 3H), 7.29 (d, *J* = 8.6 Hz, 2H), 7.34–7.37 (m, 2H), 7.40–7.47 (m, 5H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 21.4, 24.1 (d, *J* = 42.0 Hz), 124.9, 128.1, 128.7, 128.8, 129.7, 136.6 (d, *J* = 81.6 Hz), 138.6 (d, *J* = 2.4 Hz), 138.8 (d, *J* = 52.8 Hz), 141.6, 147.7 ($^{13}$C-labeled, *J* = 42.0, 52.8, 81.6 Hz).

**(*Z*)-1-[(1-Chloro-2-phenylprop-1-en-1-yl)sulfinyl]-4-methylbenzene [(*Z*)-2e].** (*Z*)-**2e**: Colorless solid; mp 88.3–89.2 °C; IR (ATR) 3060, 2956, 1490, 1435, 1087, 1054, 893 807, 704 cm$^{-1}$; $^1$H NMR (301 MHz, $CDCl_3$) δ 2.43 (s, 3H), 2.61 (s, 3H), 7.23–7.41 (m, 7H), 7.57 (d, *J* = 8.3 Hz, 2H); $^{13}$C NMR (76 MHz, $CDCl_3$) δ 21.5, 22.7, 124.5, 127.3, 128.4, 128.6, 129.9, 134.9, 138.6, 139.6, 141.8, 145.2; MS (FAB$^+$) *m/z* (%) 291 ([M+H]$^+$, 100); HRMS (FAB$^+$) calcd for $C_{16}H_{16}{}^{35}ClOS$ ([M+H]$^+$): 291.0610, found: 291.0609. [$^{13}$C]-(*Z*)-**2e**: $^1$H NMR (500 MHz, $CDCl_3$) δ 2.42 (s, 3H), 2.61 (d, *J* = 6.9 Hz, 3H), 7.24–7.26 (m, 2H), 7.31–7.38 (m, 5H), 7.57 (d, *J* = 8.6 Hz, 2H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 21.5, 22.6 (d, *J* = 42.0 Hz), 124.5, 127.2, 128.4 (d, *J* = 3.6 Hz), 128.5, 129.9, 134.8 (d, *J* = 82.2 Hz), 138.5, 139.5 (d, *J* = 52.8 Hz), 141.8, 145.2 ($^{13}$C-labeled, *J* = 42.0, 52.8, 82.2 Hz).

**(*E*)-1-[(1-Chloro-2-methyl-4-phenylbut-1-en-3-yn-1-yl)sulfinyl]-4-methylbenzene [(*E*)-2f].** Yellow solid; mp 94.0–95.0 °C; IR (ATR) 3061, 2921, 2186, 1594, 1574, 1492, 1446, 1083, 1063, 925, 815, 759, 687 cm$^{-1}$; $^1$H NMR (500 MHz, $CDCl_3$) δ 2.18 (s, 3H), 2.41 (s, 3H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.37–7.43 (m, 3H), 7.53–7.55 (m, 2H), 7.63 (d, *J* = 8.0 Hz, 2H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 21.4, 21.5, 85.7, 99.8, 121.9, 124.3, 125.9, 128.6, 129.5, 129.9, 131.7, 139.0, 141.9, 145.1; MS (FAB$^+$): *m/z* (%) 315 [(M+H)$^+$, 100], 192 (26); HRMS (FAB$^+$) calcd for $C_{18}H_{16}{}^{35}ClOS$ ([M+H]$^+$): 315.0610, found: 315.0608.

**(*Z*)-1-[(1-Chloro-2-methyl-4-phenylbut-1-en-3-yn-1-yl)sulfinyl]-4-methylbenzene [(*Z*)-2f].** Colorless solid; mp 109.0–110.0 °C; IR (ATR) 3019, 2923, 2232, 2187, 1568, 1489, 1442, 1084, 1053, 1027, 1014, 896, 813, 756, 687 cm$^{-1}$; $^1$H NMR (399 MHz, $CDCl_3$) δ 2.41 (s, 3H), 2.49 (s, 3H), 7.31–7.39 (m, 5H), 7.46–7.49 (m, 2H), 7.53 (d, *J* = 8.2 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 20.5, 21.5, 87.0, 100.0, 121.8, 124.5, 127.3, 128.5, 129.5, 130.0, 132.0, 138.2, 142.0, 142.1; MS (FAB$^+$): *m/z* (%) 315 [(M+H)$^+$, 100]; HRMS (FAB$^+$) calcd for $C_{18}H_{16}{}^{35}ClOS$ ([M+H]$^+$): 315.0610, found: 315.0609.

**1,1-Bis(4-methoxyphenyl)-3-methyl-1-butene (10).** $R_f$ = 0.25 (hexane/EtOAc 30:1); yellow oil; IR (ATR) 2958, 2932, 2835, 1606, 1509, 1463, 1283, 1240, 1172, 1034, 827, 756 $cm^{-1}$; $^1H$ NMR (399 MHz, $CDCl_3$) δ 1.00 (d, *J* = 6.6 Hz, 6H), 2.45 (d of sepet, *J* = 10.0, 6.6 Hz, 1H), 3.78 (s, 3H), 3.83 (s, 3H), 5.75 (d, *J* = 10.0 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 7.09 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 8.8 Hz, 2H); $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 23.4, 28.7, 55.2, 55.3, 113.4, 113.5, 128.3, 130.8, 133.1, 135.6, 135.9, 138.1, 158.4, 158.6; MS ($EI^+$) *m/z* (%) 282 ($M^+$, 100), 267 (30), 251 (21); HRMS ($EI^+$) calcd for $C_{19}H_{22}O_2$: 282.1620, found: 282.1621.

**1,2-Diphenylethyne (4b).** Colorless solid; mp 57.2–57.8 °C; IR (ATR) 3064, 1600, 1493, 1443, 1070, 1026, 918, 754, 688 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.32–7.37 (m, 6H), 7.52–7.54 (m, 4H); $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 89.4, 123.3, 128.3, 128.4, 131.6; MS (EI): *m/z* (%) 178 ($M^+$, 100); HRMS (EI) calcd for $C_{14}H_{10}$: 178.0783, found: 178.0783.

**5-Methyl-1-phenyl-3-(2-phenylethyl)hex-3-ene (11).** $R_f$ = 0.57 (hexane/EtOAc 30:1); colorless oil; IR (ATR) 3063, 3029, 2954, 2932, 2864, 1603, 1496, 1453, 744, 696 $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 0.85 (d, *J* = 6.6 Hz, 6H), 2.27–2.30 (m, 2H), 2.33–2.37 (m, 4H), 2.46 (d of sepet, *J* = 9.5, 6.6 Hz, 1H), 2.66–2.73 (m, 4H), 4.96 (d, *J* = 9.5 Hz, 1H), 7.17–7.19 (m, 6H), 7.25–7.30 (m, 4H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 23.4, 27.0, 32.6, 35.0, 35.3, 38.6, 125.7, 125.8, 128.2, 128.3, 128.4, 128.5, 134.1, 135.2, 142.4, 142.5; MS ($EI^+$) *m/z* (%) 91 ($M^+$, 100), 278 (58); HRMS ($EI^+$) calcd for $C_{21}H_{26}$: 278.2035, found: 278.2034.

**1,4-Diphenylbuta-1,3-diyne (4d).** iPrMgCl (2.5 equiv) and *t*-BuMgCl (2.5 equiv) were used. Yellow solid; mp 83.1–83.7 °C; IR (ATR) 3049, 2925, 2852, 2150, 1593, 1570, 1485, 1439, 1178, 1157, 1068, 1025, 916, 752, 683 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.31–7.39 (m, 6H), 7.52–7.55 (m, 4H); $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 73.9, 81.6, 121.8, 128.5, 129.2, 132.5; MS (EI): *m/z* (%) 202 ($M^+$, 100); HRMS (EI) calcd for $C_{16}H_{10}$: 202.0783, found: 202.0783.

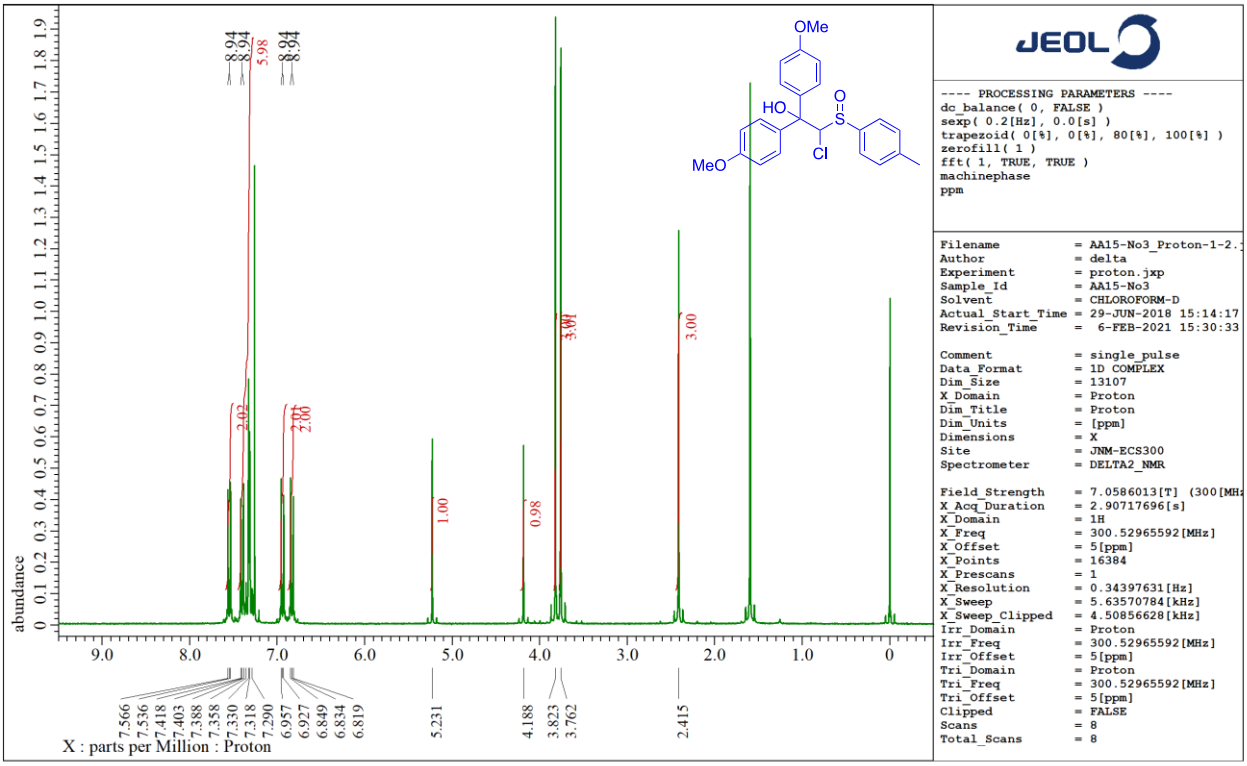
**Prop-1-yn-1-ylbenzene (4e). 4e**: Yellow oil; IR (ATR) 2919, 2855, 1726, 1599, 1490, 1441, 1276, 754, 690 $cm^{-1}$; $^1H$ NMR (301 MHz, $CDCl_3$) δ 2.05 (s, 3H), 7.26–7.30 (m, 3H), 7.37–7.40 (m, 2H); $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 4.4, 79.7, 85.8, 124.0, 127.5, 128.2, 131.5; MS (EI): *m/z* (%) 116 ($M^+$, 100); HRMS (EI) calcd for $C_9H_8$: 116.0626, found: 116.0626. [2-$^{13}C$]-**4e**: $^1H$ NMR (500 MHz, $CDCl_3$) δ 2.05 (d, *J* = 10.9 Hz, 3H), 7.24–7.29 (m, 3H), 7.38–7.39 (m, 2H); $^{13}C$ NMR (126 MHz, $CDCl_3$) δ 4.3 (d, *J* = 68.4 Hz), 79.6 (d, *J* = 180.5 Hz), 85.8 ($^{13}C$-labeled, *J* = 68.4, 180.5 Hz), 124.1

(d, $J$ = 13.2 Hz), 127.5, 128.2, 131.5 (d, $J$ = 2.4 Hz). Position of $^{13}$C-labelled carbon was confirmed by hydogenation of 2-$^{13}$C-1-propyn-1-ylbenzene [2-$^{13}$C]-**4e** in the presence of Pd/C. 2-$^{13}$C-propylbenzene: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 0.94 (dt, $J$ = 4.2, 7.4 Hz, 3H), 1.65 (d of sextet, $J$ = 126.6, 7.4 Hz, 2H), 2.58 (dt, $J$ = 4.2, 7.4 Hz, 2H), 7.15–7.18 (m, 3H), 7.24–7.28 (m, 2H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 13.9 (d, $J$ = 33.6 Hz), 24.6 ($^{13}$C-labeled, $J$ = 33.6 Hz), 38.1 ($J$ = 33.6 Hz), 125.6, 128.2, 128.5, 142.7.

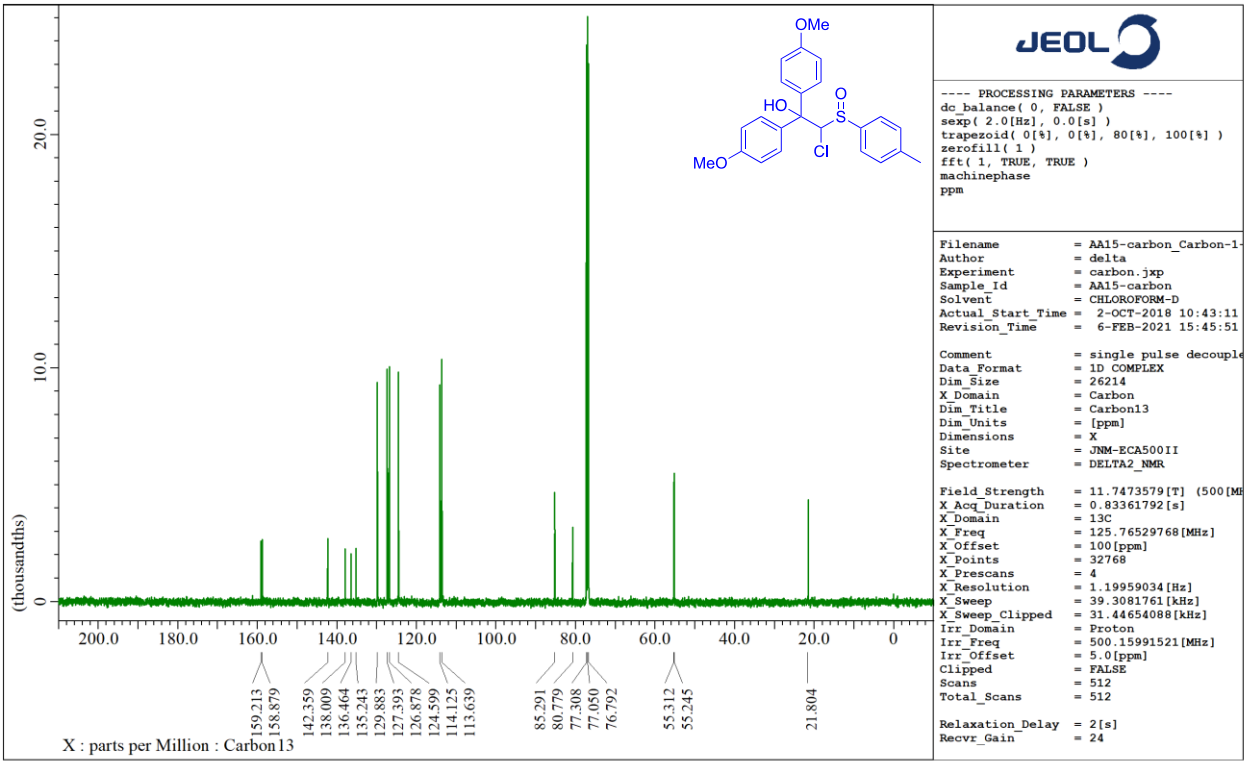
**Penta-1,3-diyn-1-ylbenzene (4f).** iPrMgCl (2.5 equiv) and *t*-BuMgCl (2.5 equiv) were used. Colorless oil; IR (ATR) 3057, 2914, 2250, 1595, 1490, 1443, 1375, 1070, 1025, 916, 755, 689 cm$^{-1}$; $^{1}$H NMR (399 MHz, $CDCl_3$) δ 2.02 (s, 3H), 7.27–7.35 (m, 3H), 7.46–7.48 (m, 2H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 4.6, 64.3, 74.2, 74.4, 80.4, 122.1, 128.4, 128.8, 132.5; MS (EI): *m*/*z* (%) 140 ($M^+$, 100); HRMS (EI) calcd for $C_{11}H_8$: 140.0626, found: 140.0625.

**1-Chloro-4-ethynylbenzene (4g).** Yellow solid; mp 43.2–43.8 °C; IR (ATR) 3263, 1591, 1487, 1397, 1088, 1014, 823 cm$^{-1}$; $^{1}$H NMR (400 MHz, $CDCl_3$) δ 3.11 (s, 1H), 7.30 (d, $J$ = 8.8 Hz, 2H), 7.42 (d, $J$ = 8.8 Hz, 2H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 78.2, 82.5, 120.6, 128.7, 133.4, 134.9; MS (EI): *m/z* (%) 136 ($M^+$, 100), 101 (19); HRMS (EI) calcd for $C_8H_5{}^{35}Cl$: 136.0080, found: 136.0080.

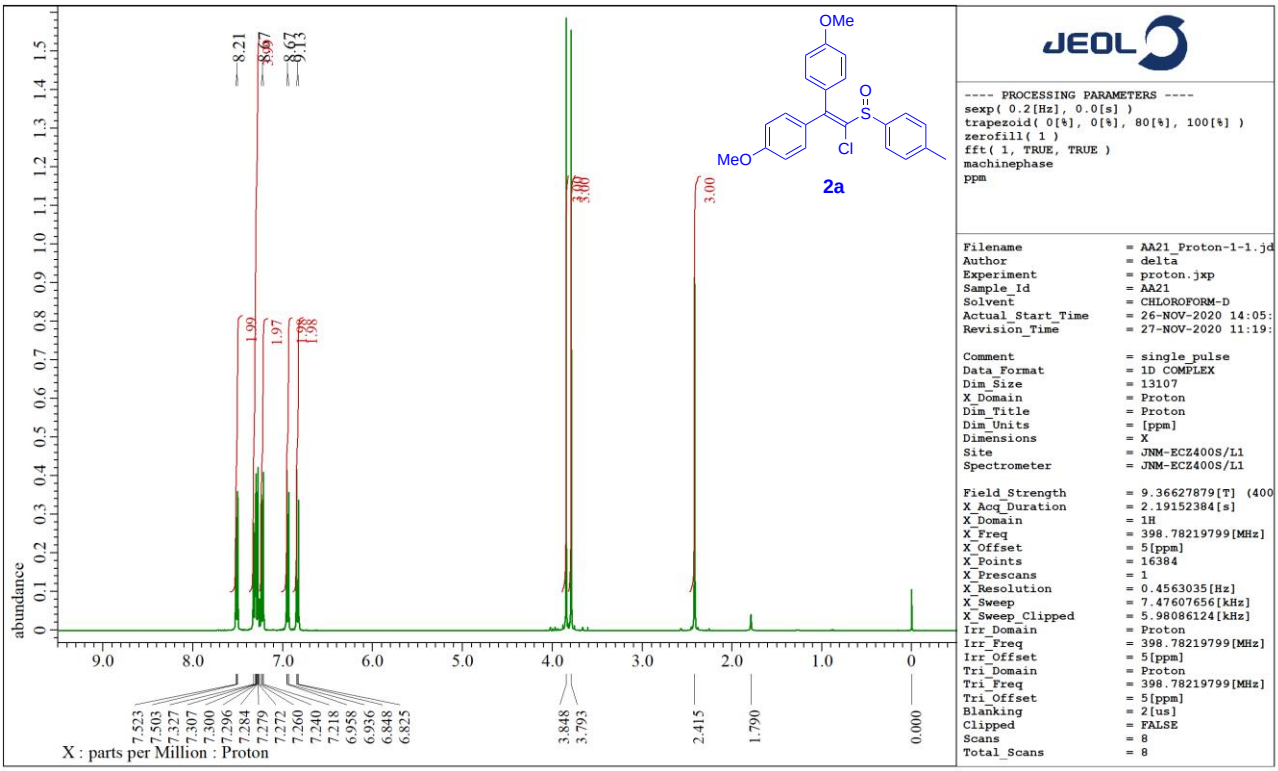
$^{1}$H NMR



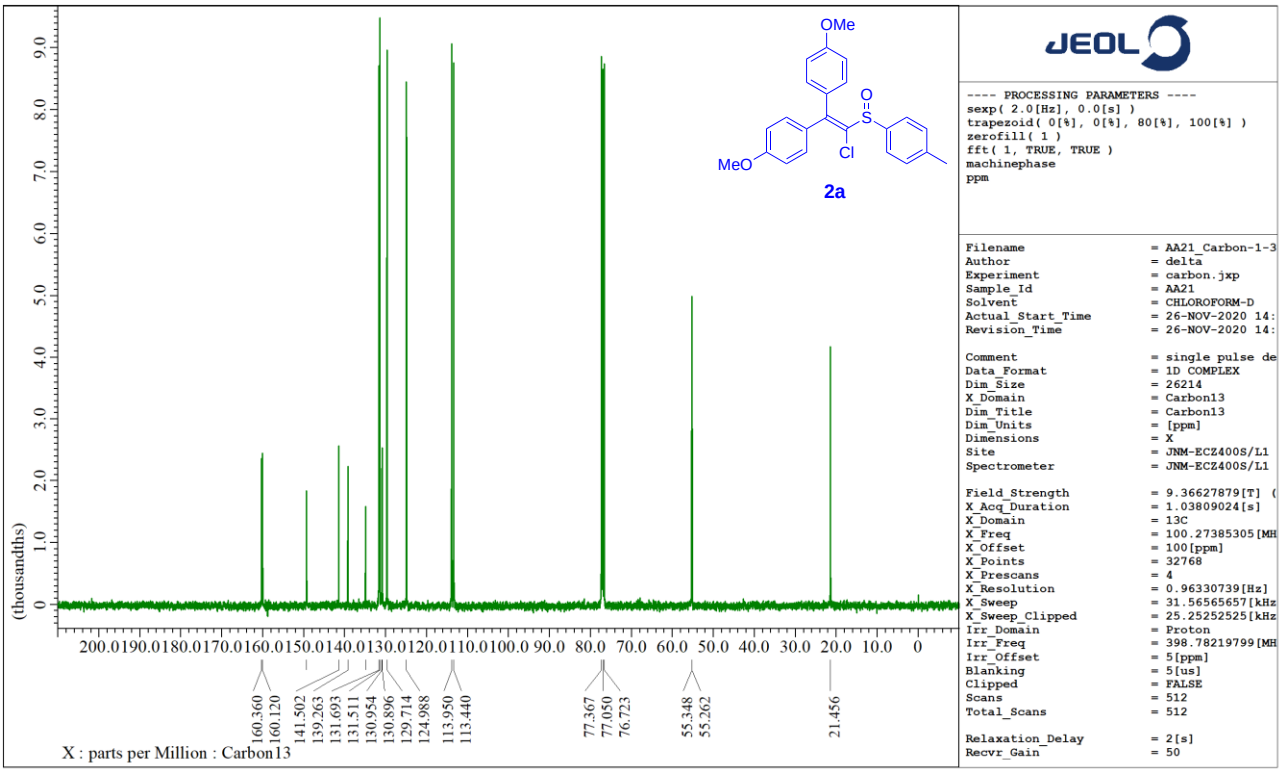

$^{13}$C NMR



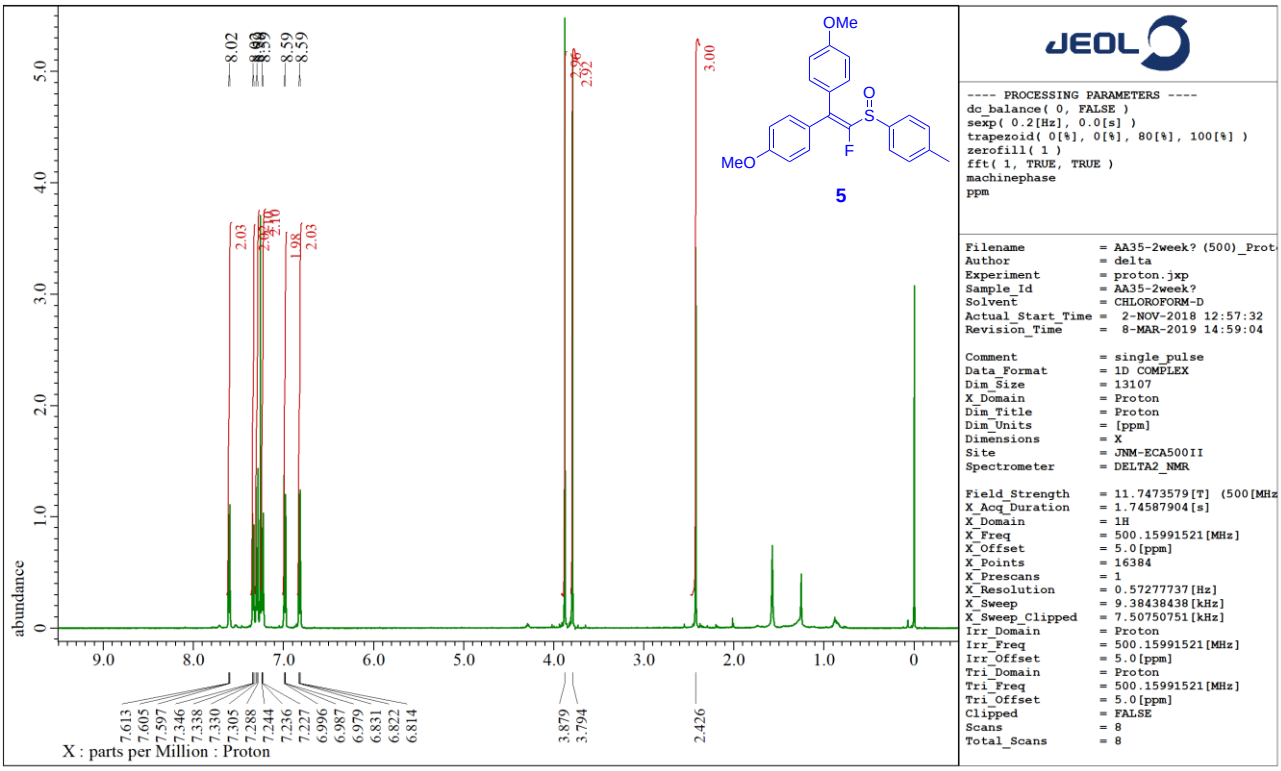
$^{1}$H NMR of **2a**



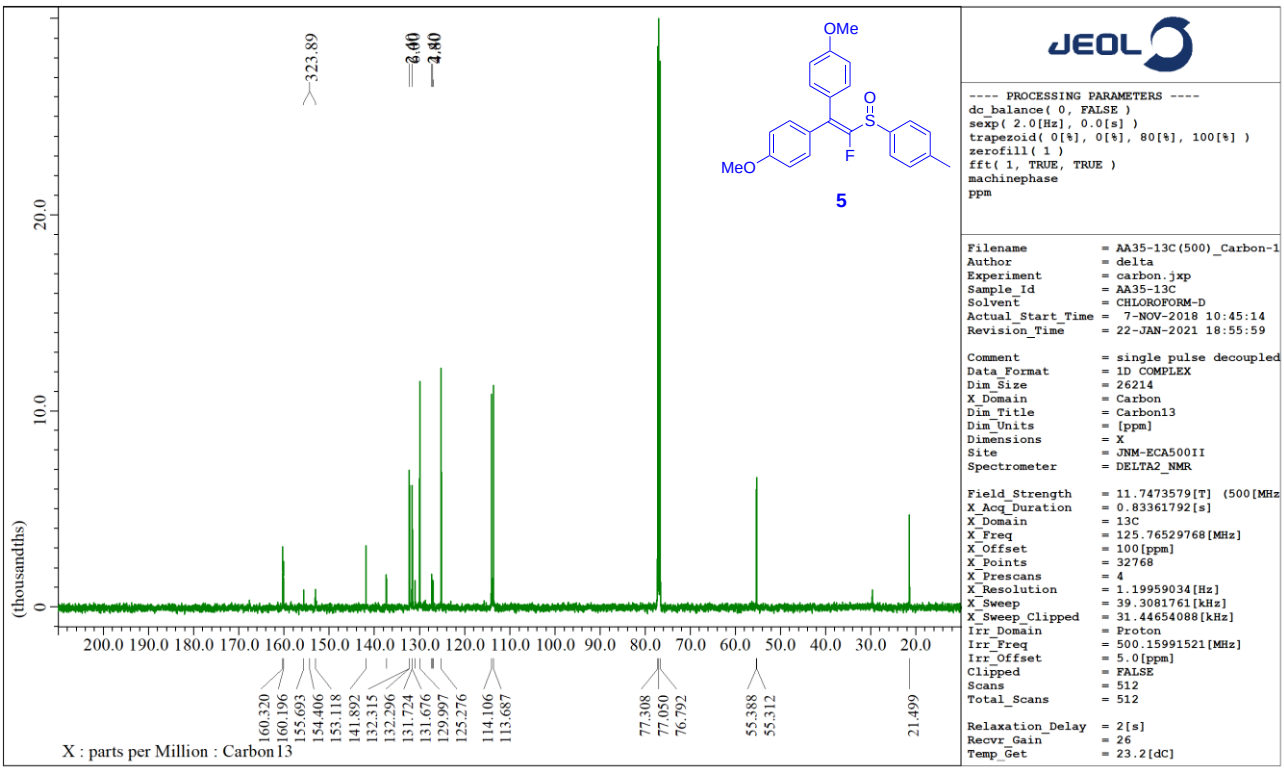

$^{13}$C NMR of **2a**



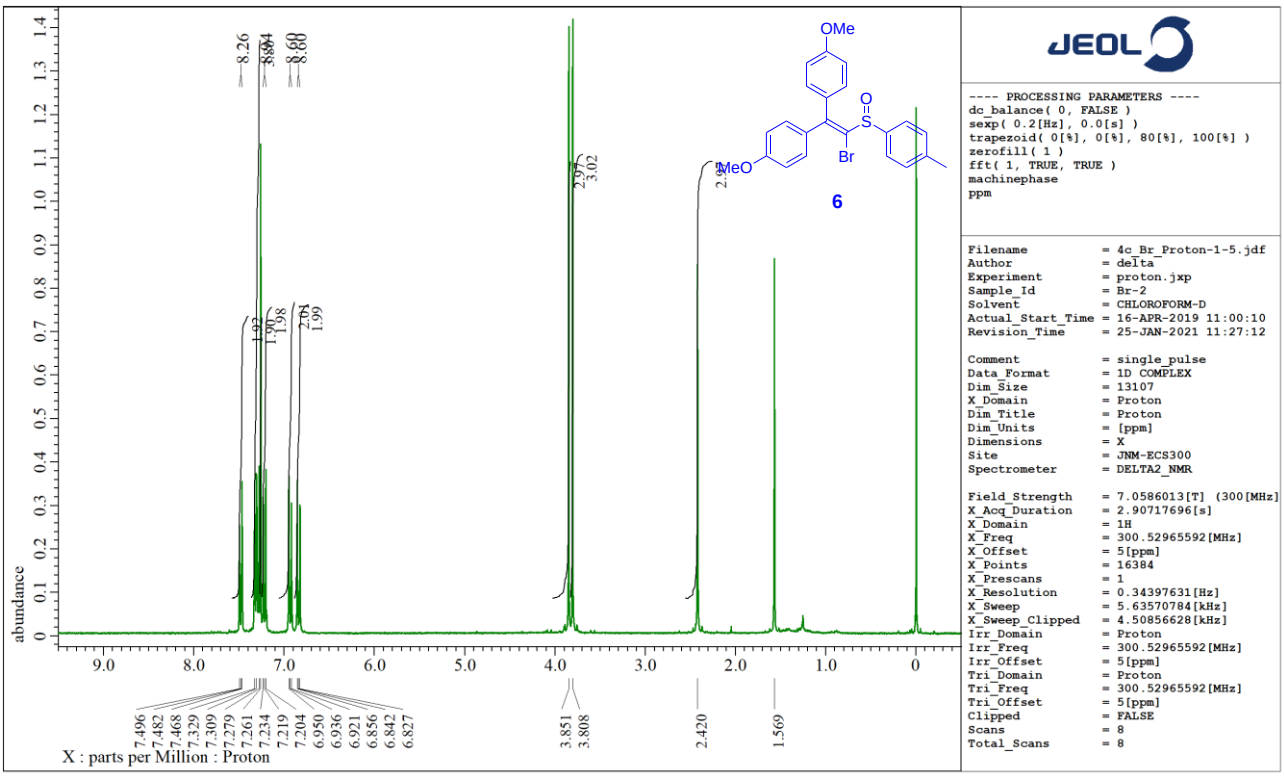
$^{1}$H NMR of **5**



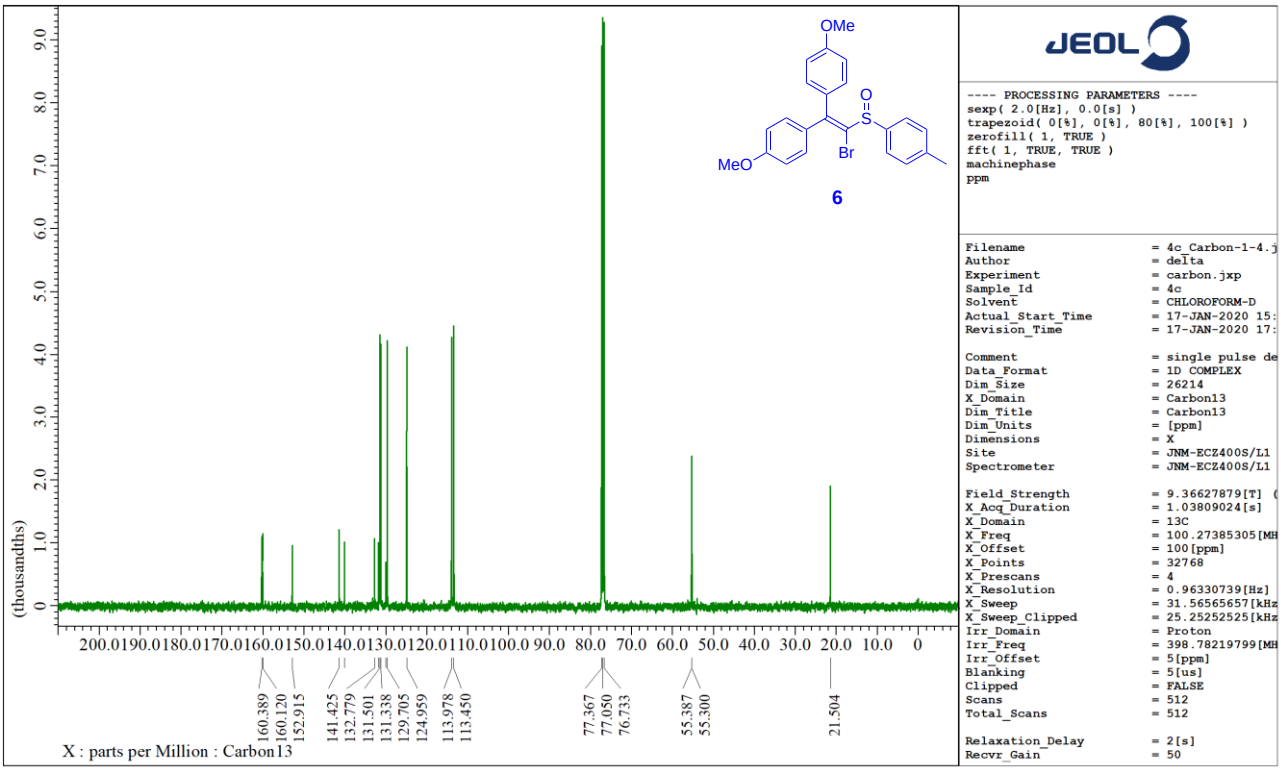

$^{13}$C NMR of **5**



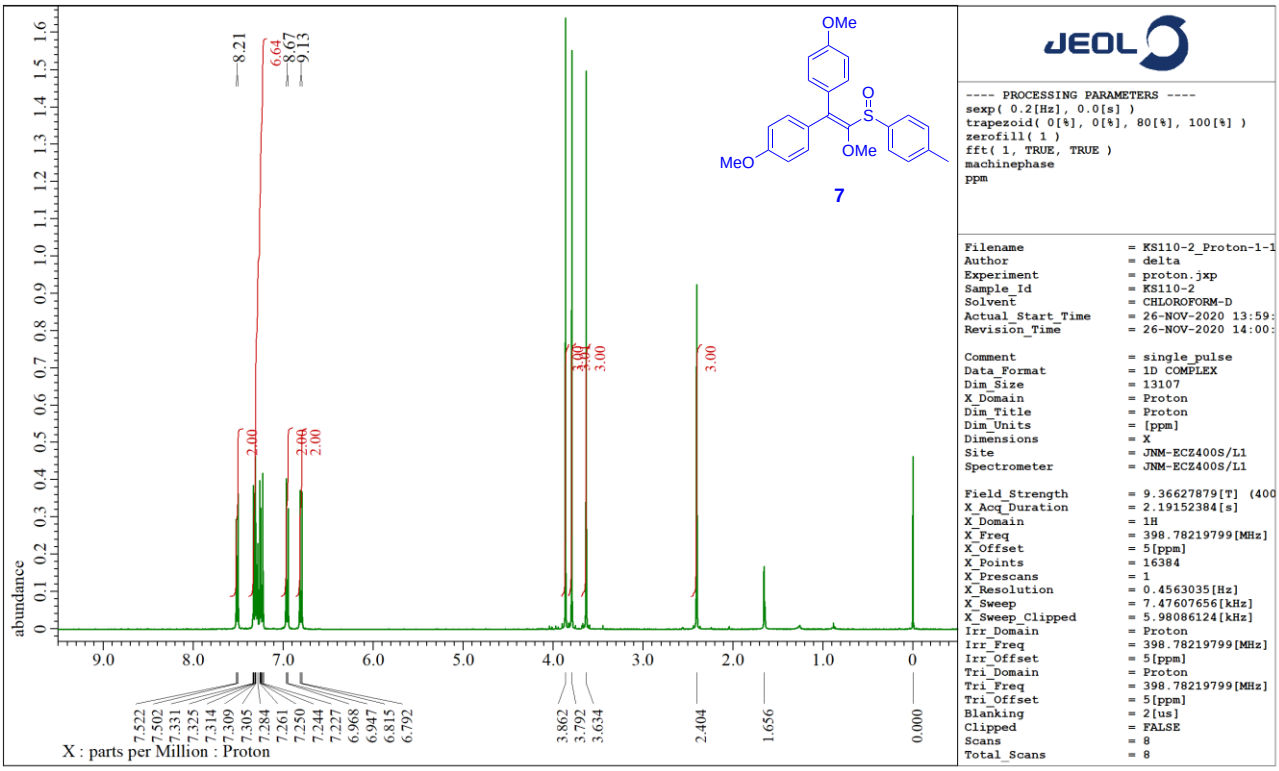
$^{1}$H NMR of **6**



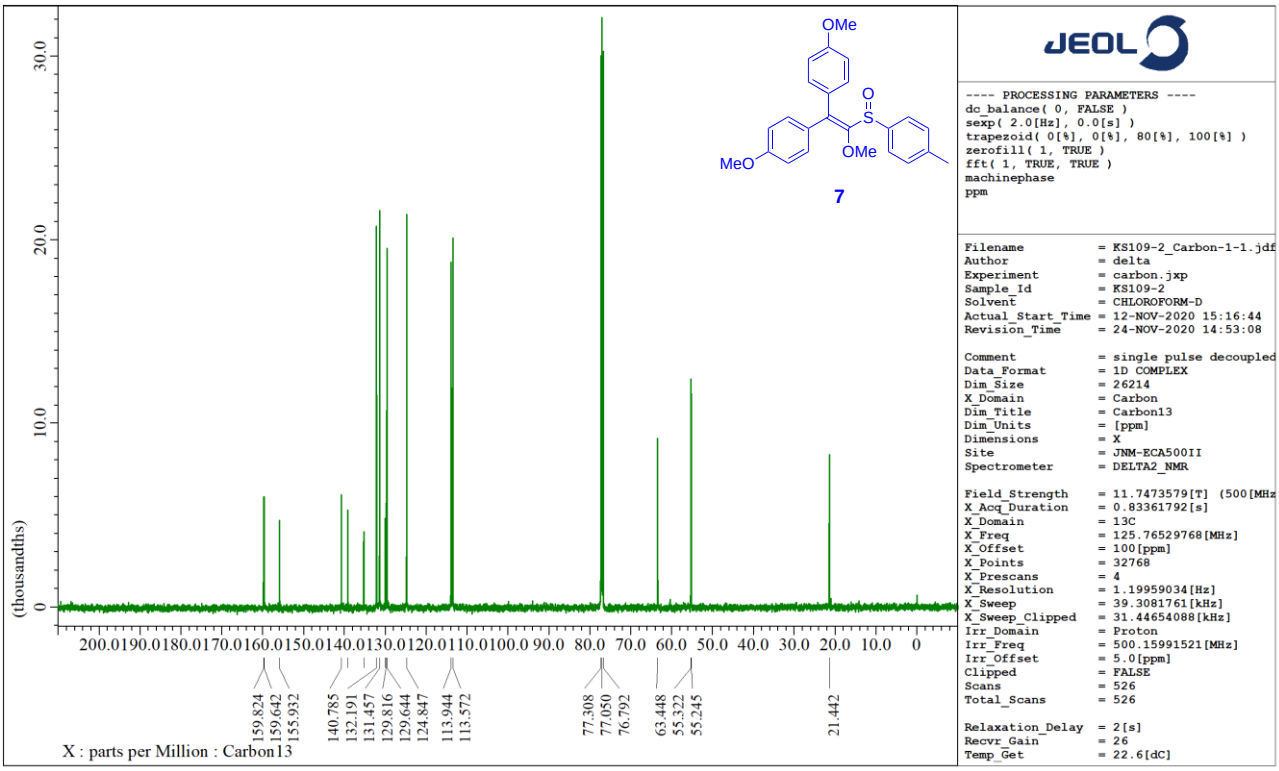

$^{13}$C NMR of **6**



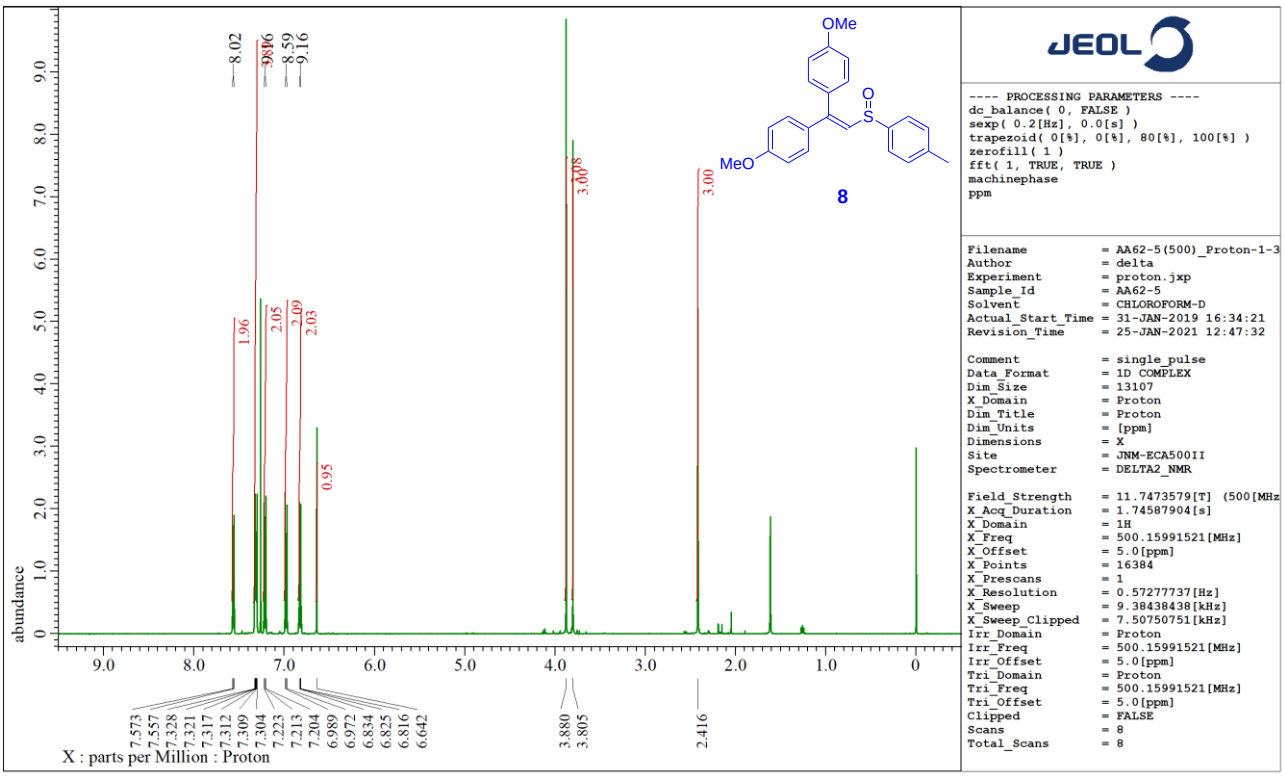
$^{1}$H NMR of **7**



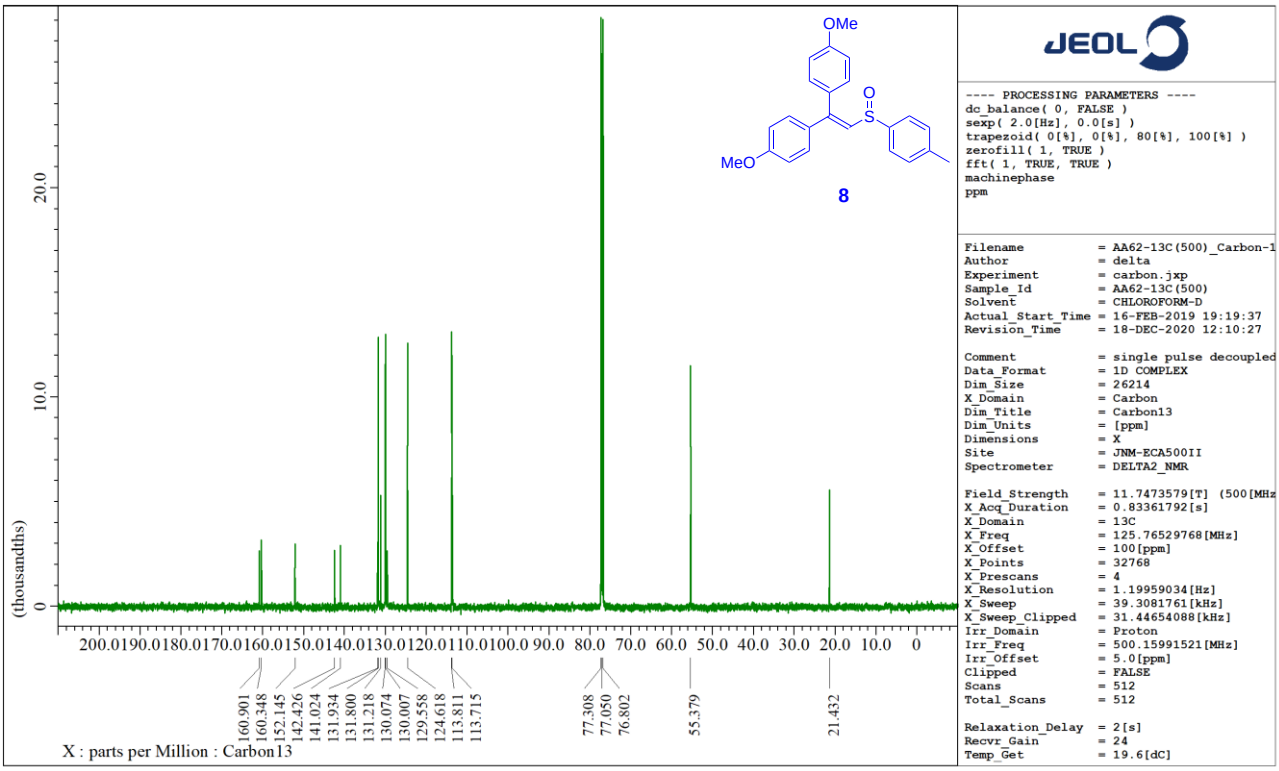

$^{13}$C NMR of **7**



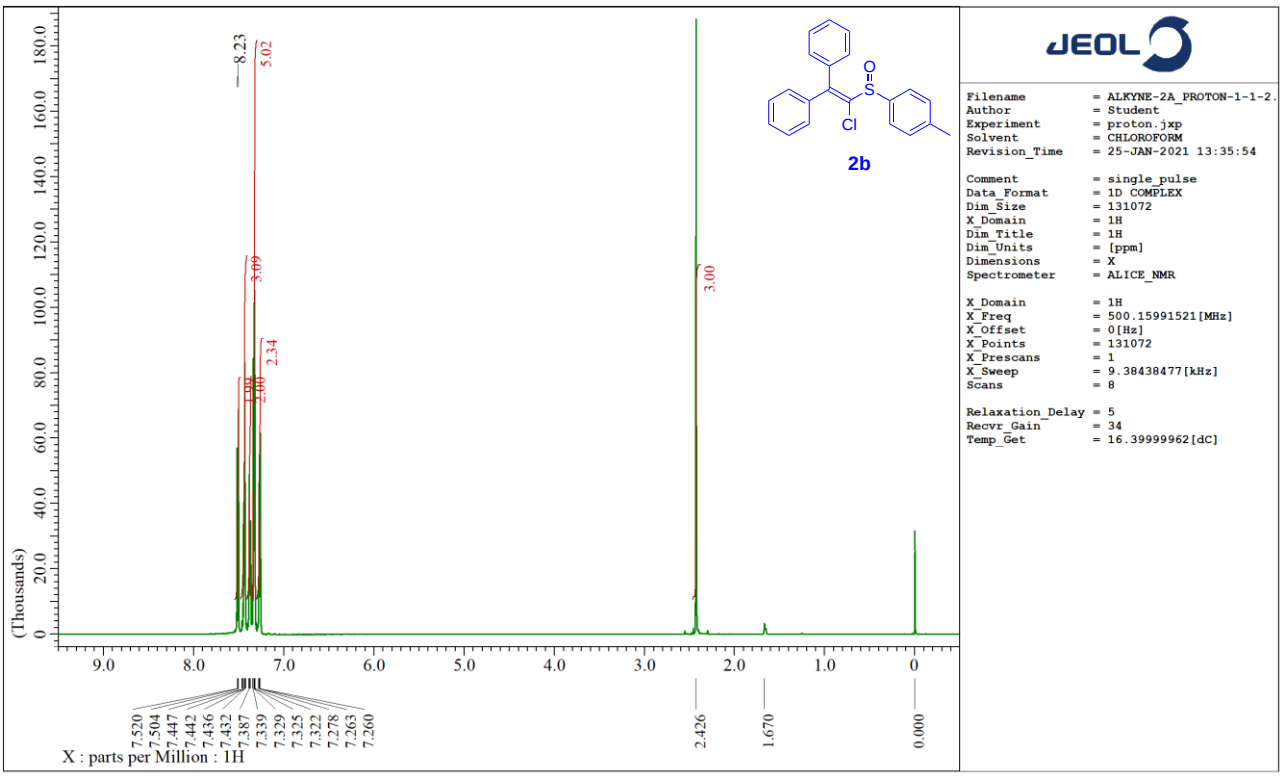
$^{1}$H NMR of **8**



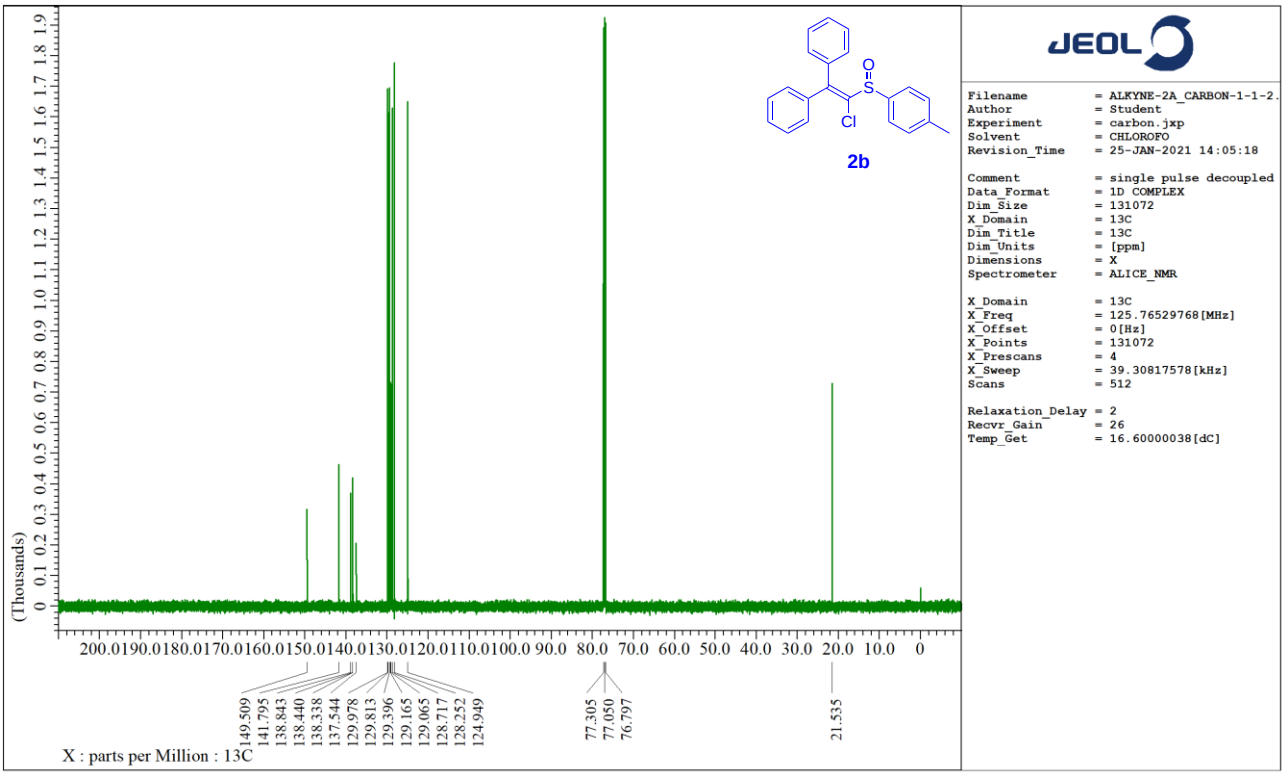

$^{13}$C NMR of **8**



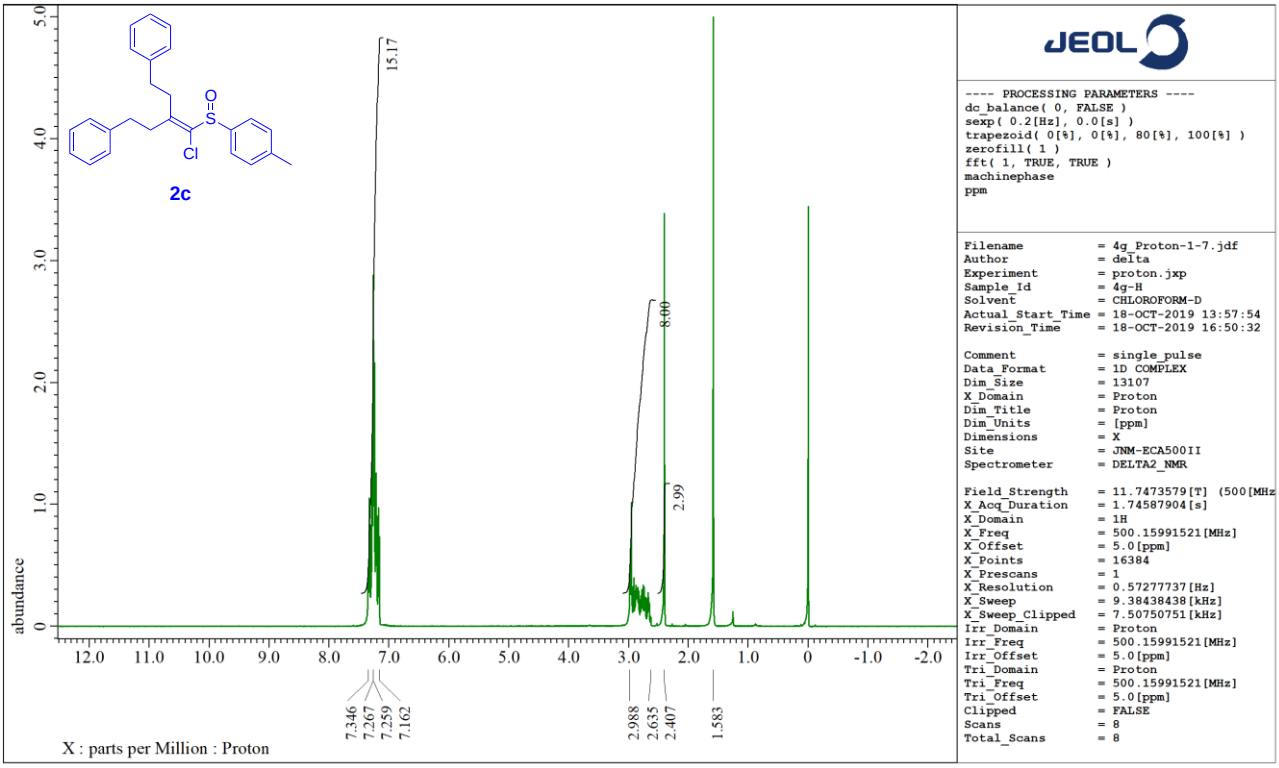
$^{1}$H NMR of **2b**



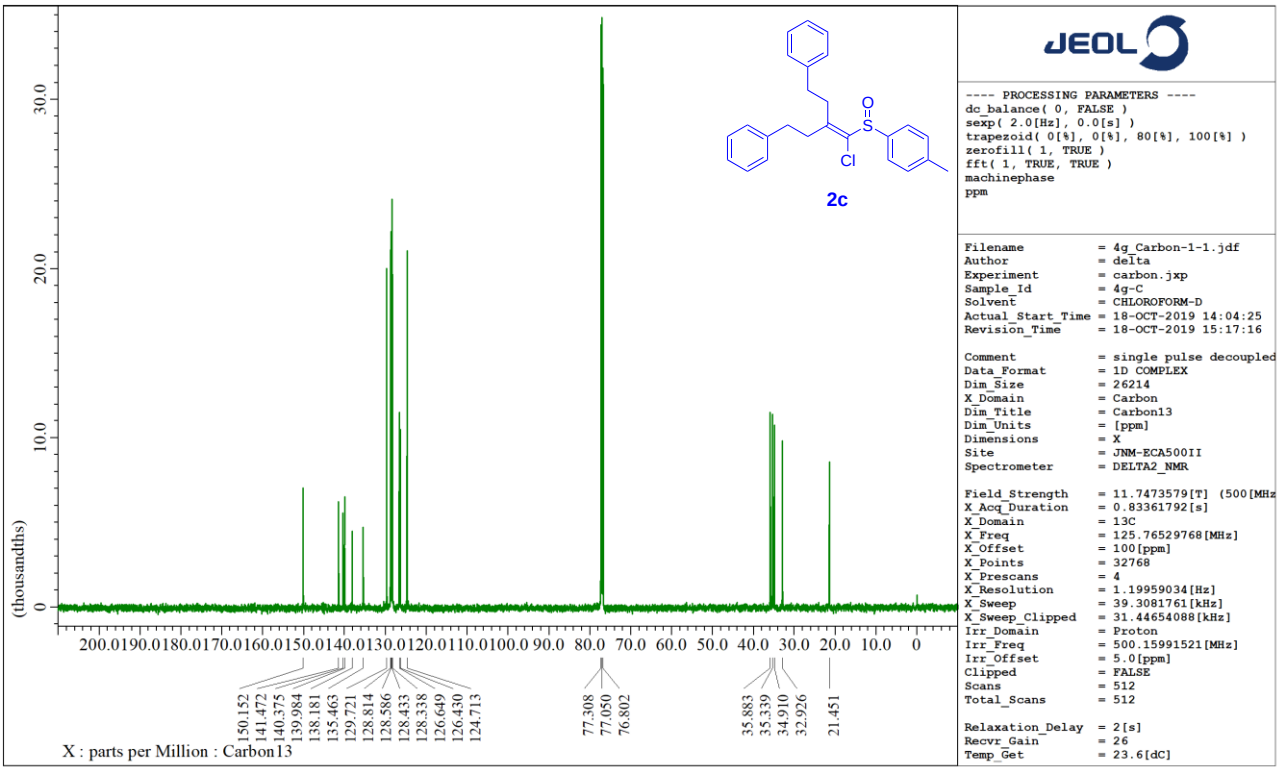

$^{13}$C NMR of **2b**



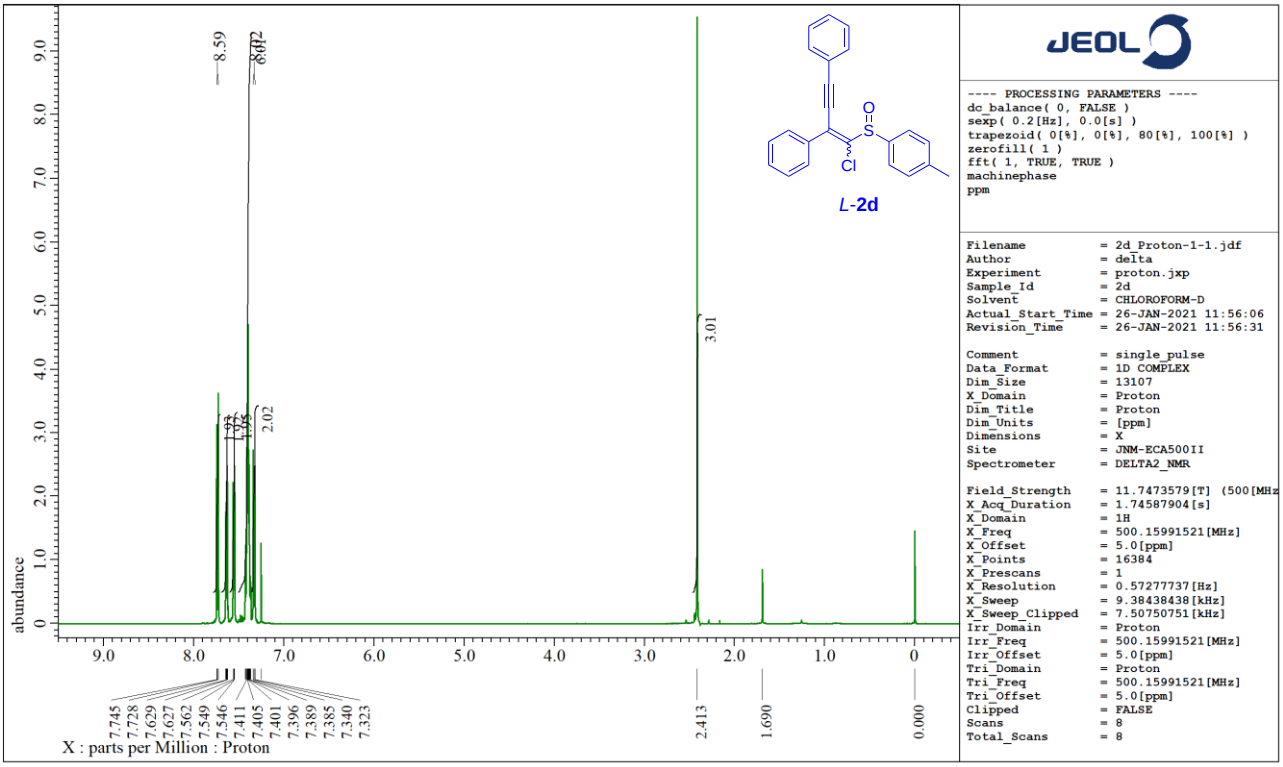
$^{1}$H NMR of **2c**



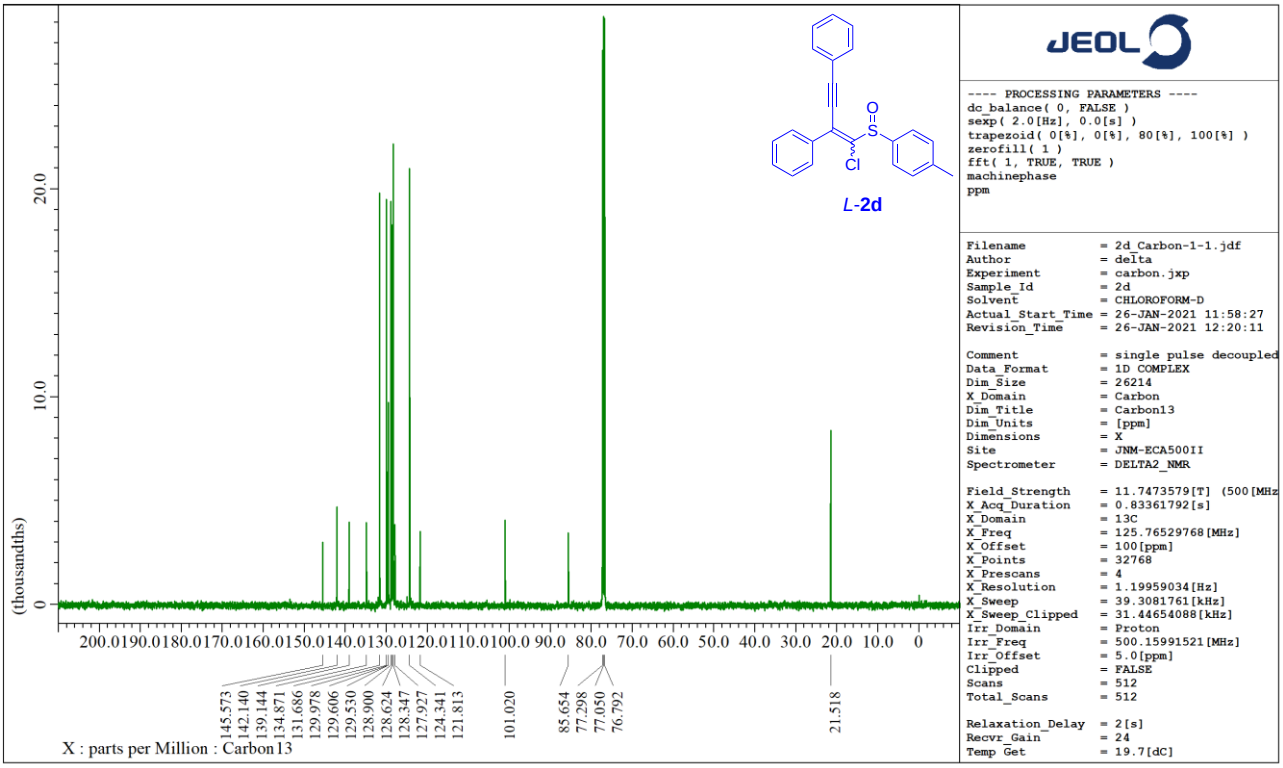

$^{13}$C NMR of **2c**



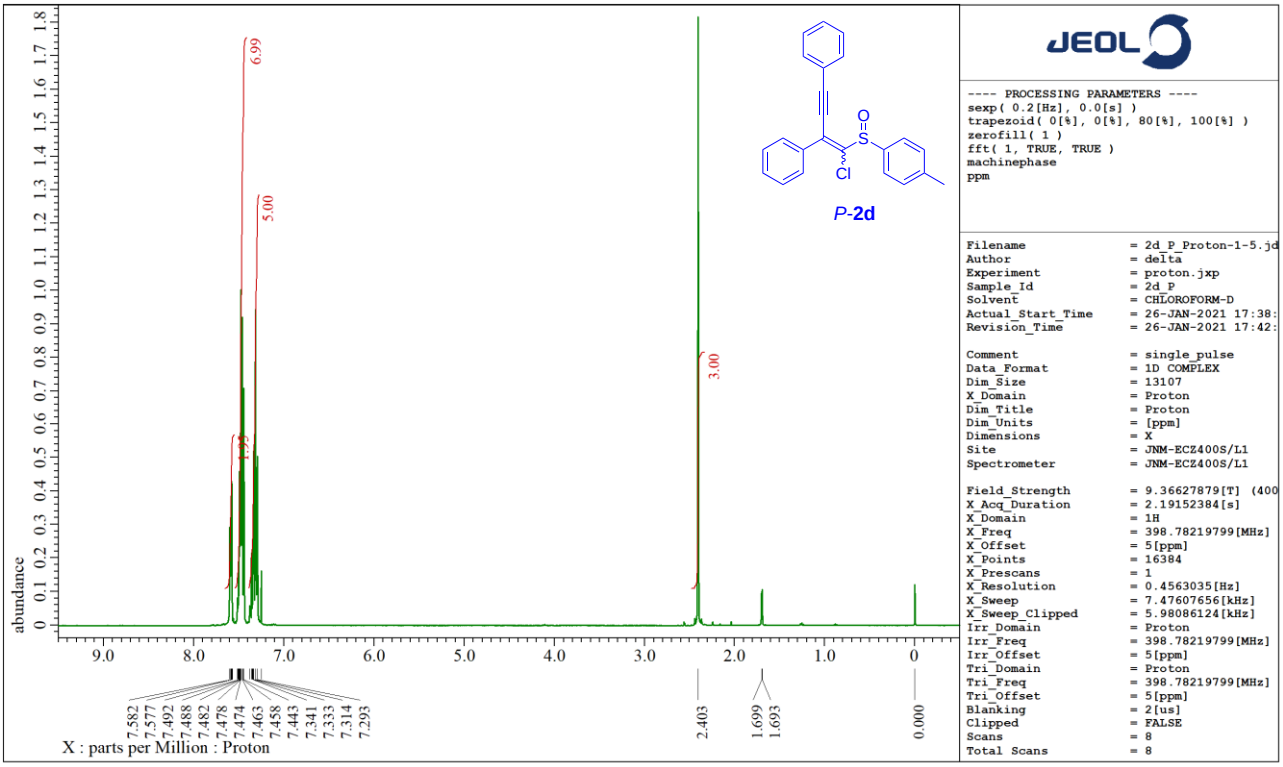
$^{1}$H NMR of *L*-**2d**



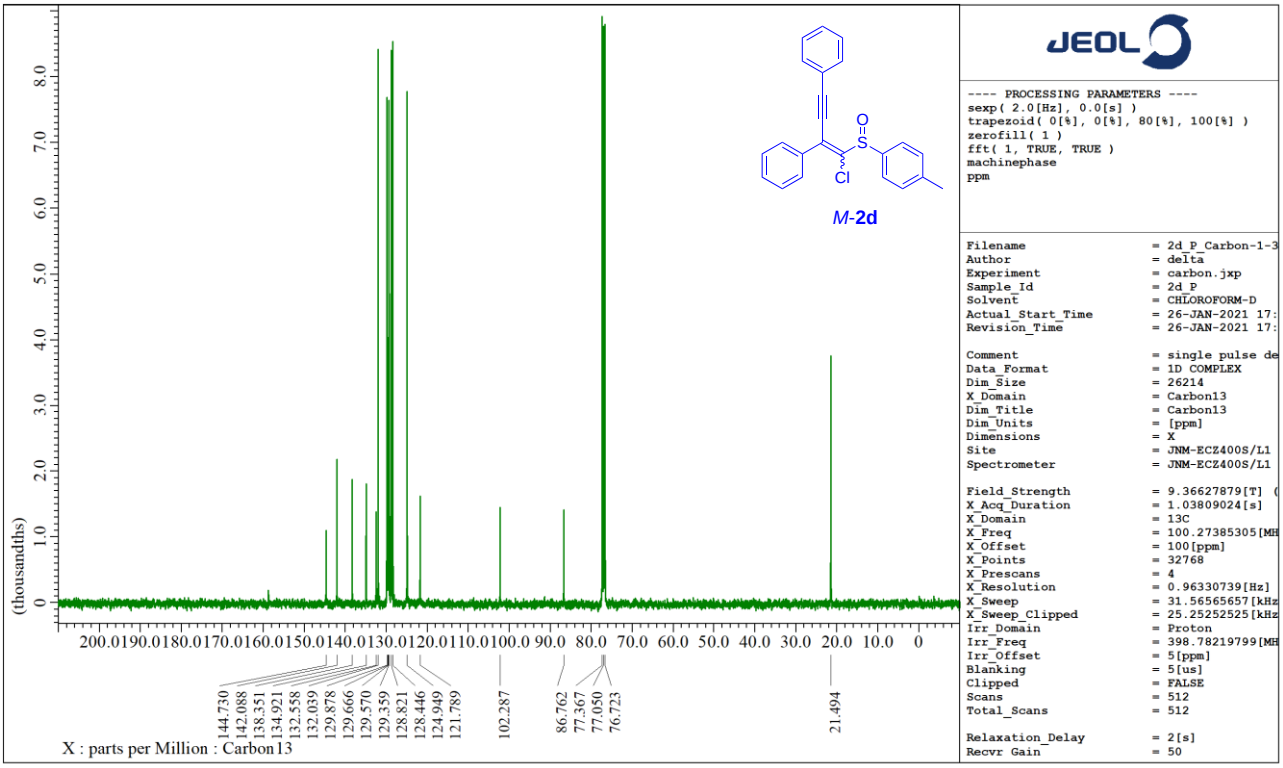

$^{13}$C NMR of *L*-**2d**



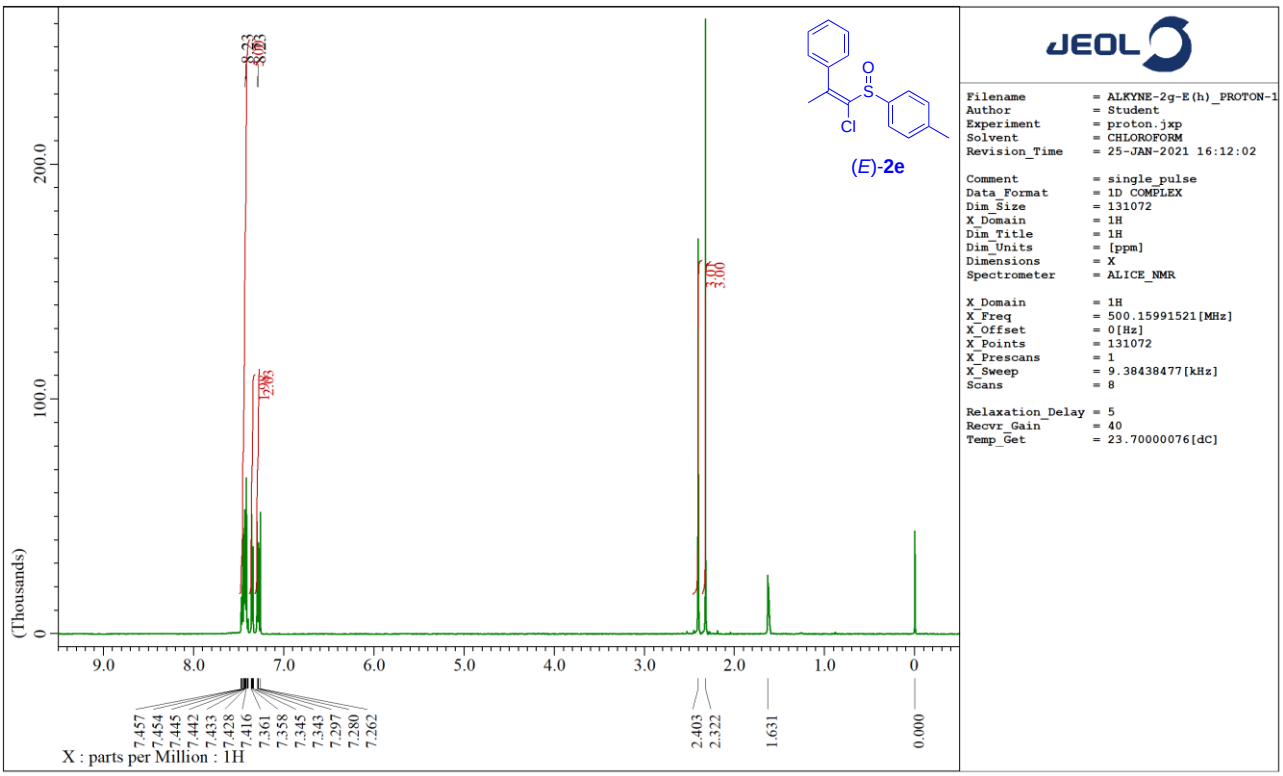
$^{1}$H NMR of *P*-**2d**



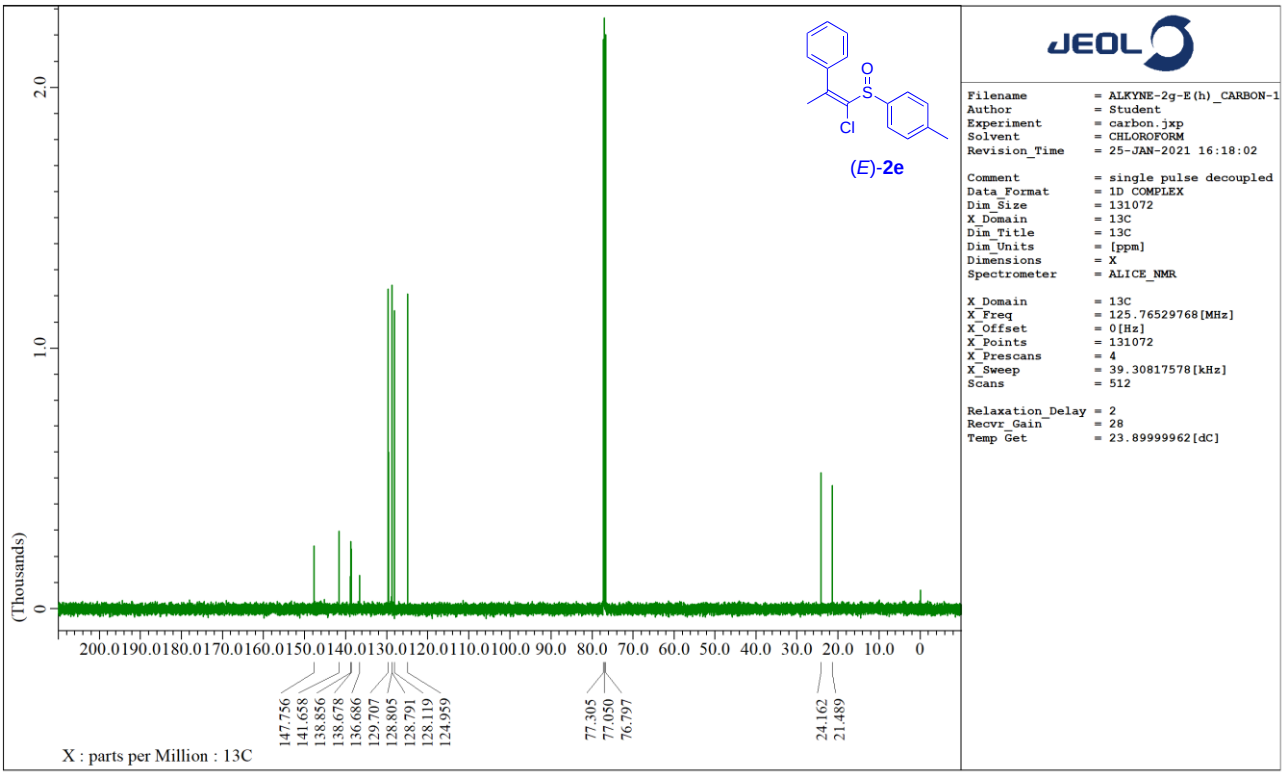

$^{13}$C NMR of *P*-**2d**



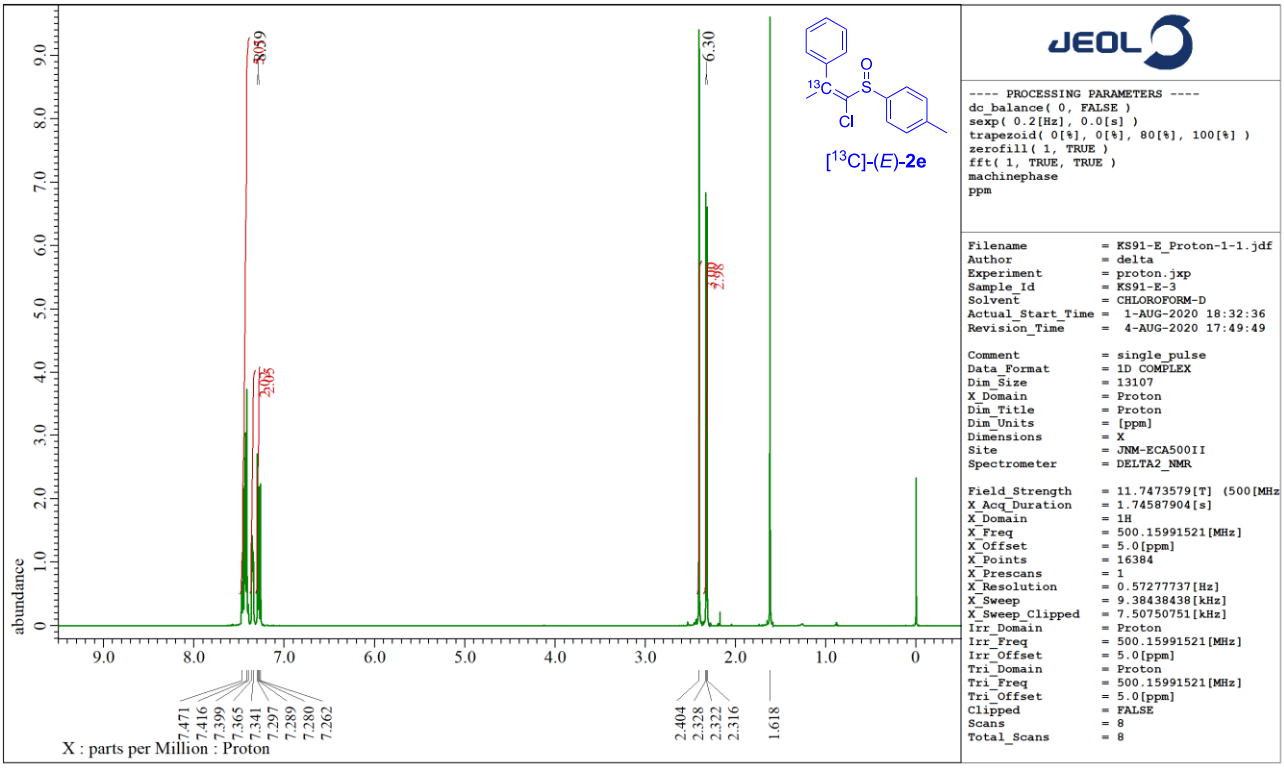
$^{1}$H NMR of (*E*)-**2e**



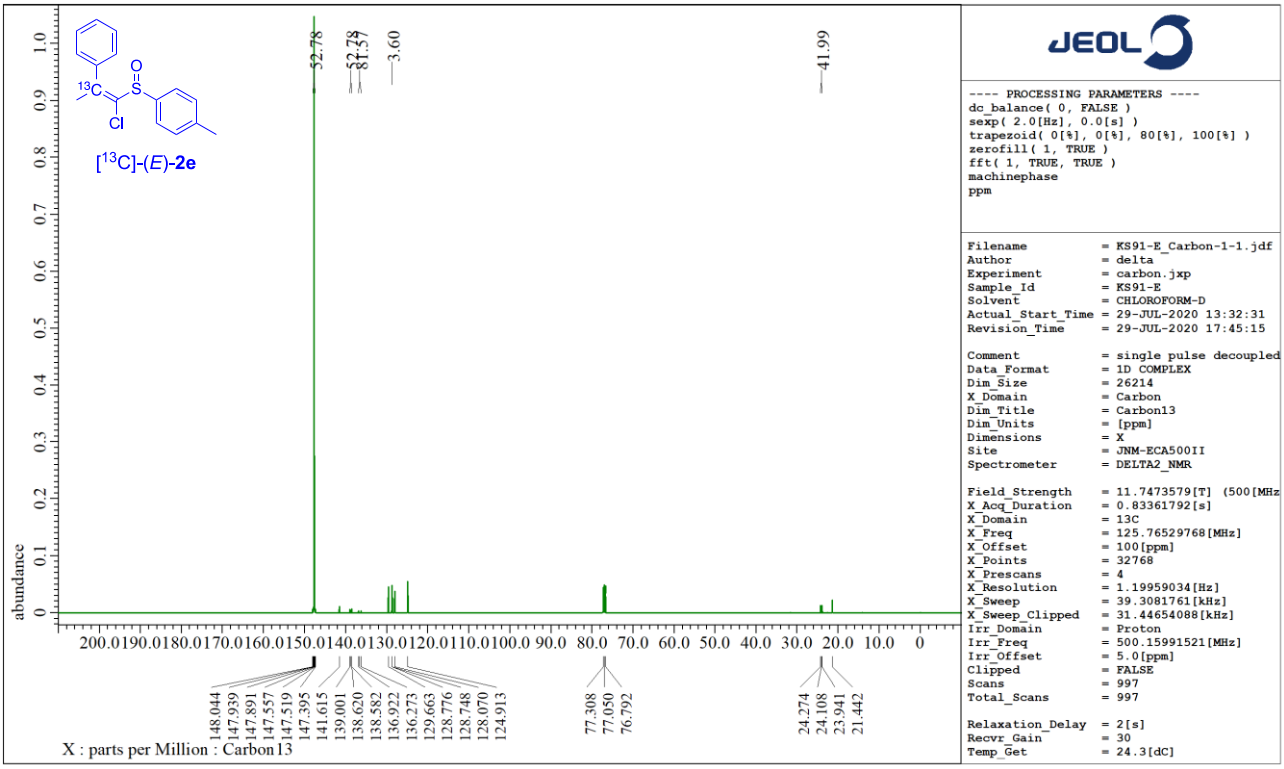

$^{13}$C NMR of (*E*)-**2e**



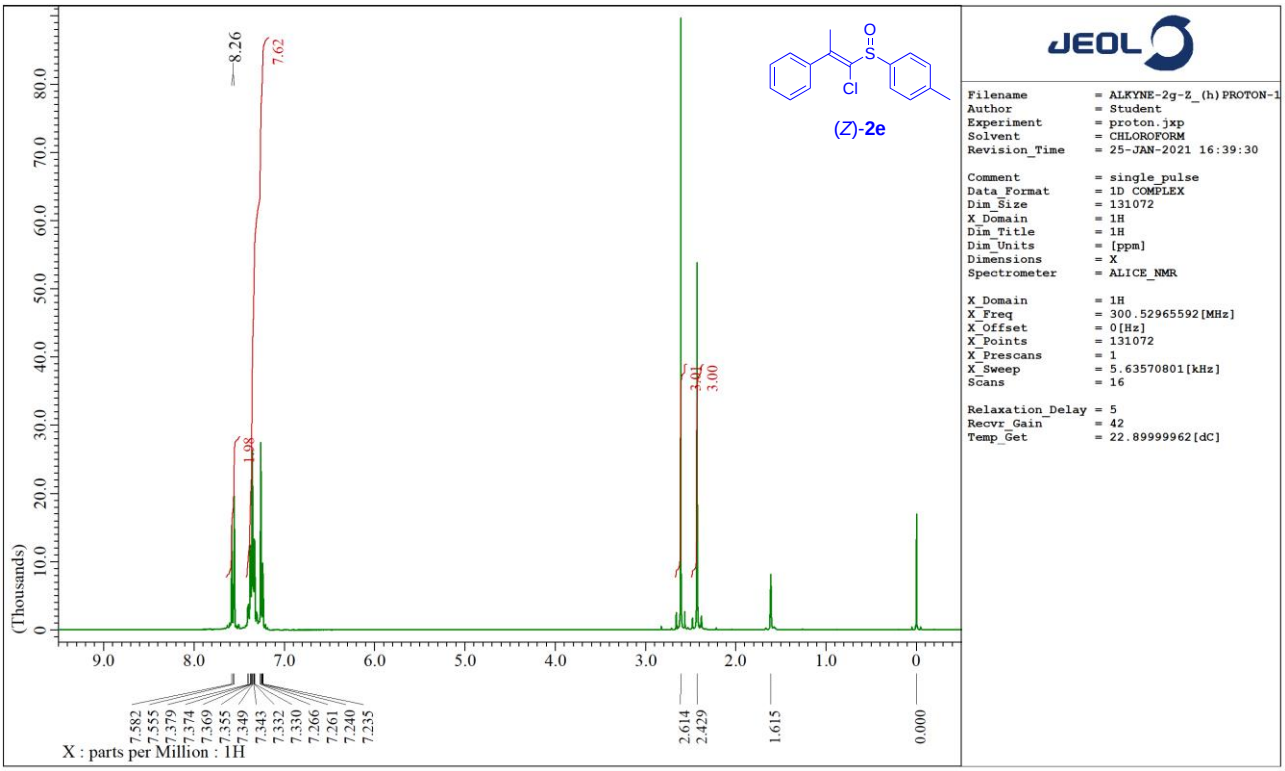
$^{1}$H NMR of [$^{13}$C]-(*E*)-**2e**



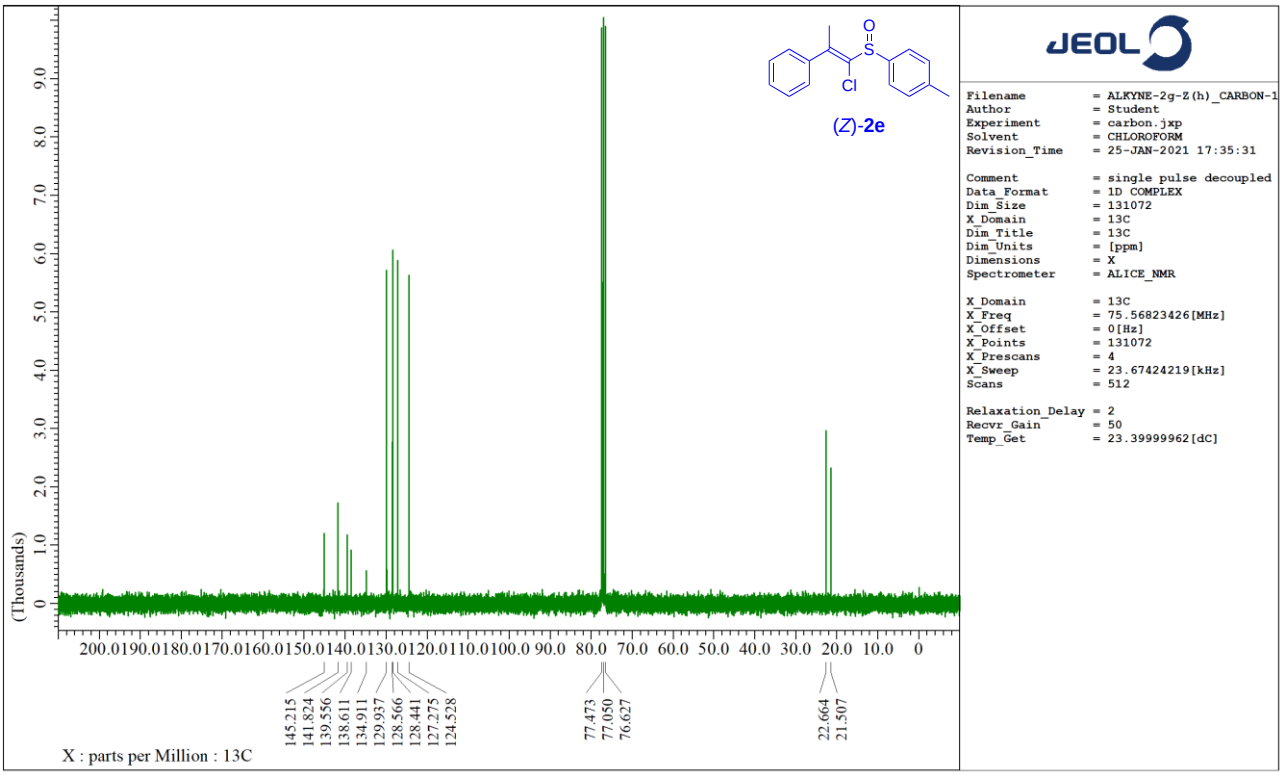

$^{13}$C NMR of [$^{13}$C]-(*E*)-**2e**



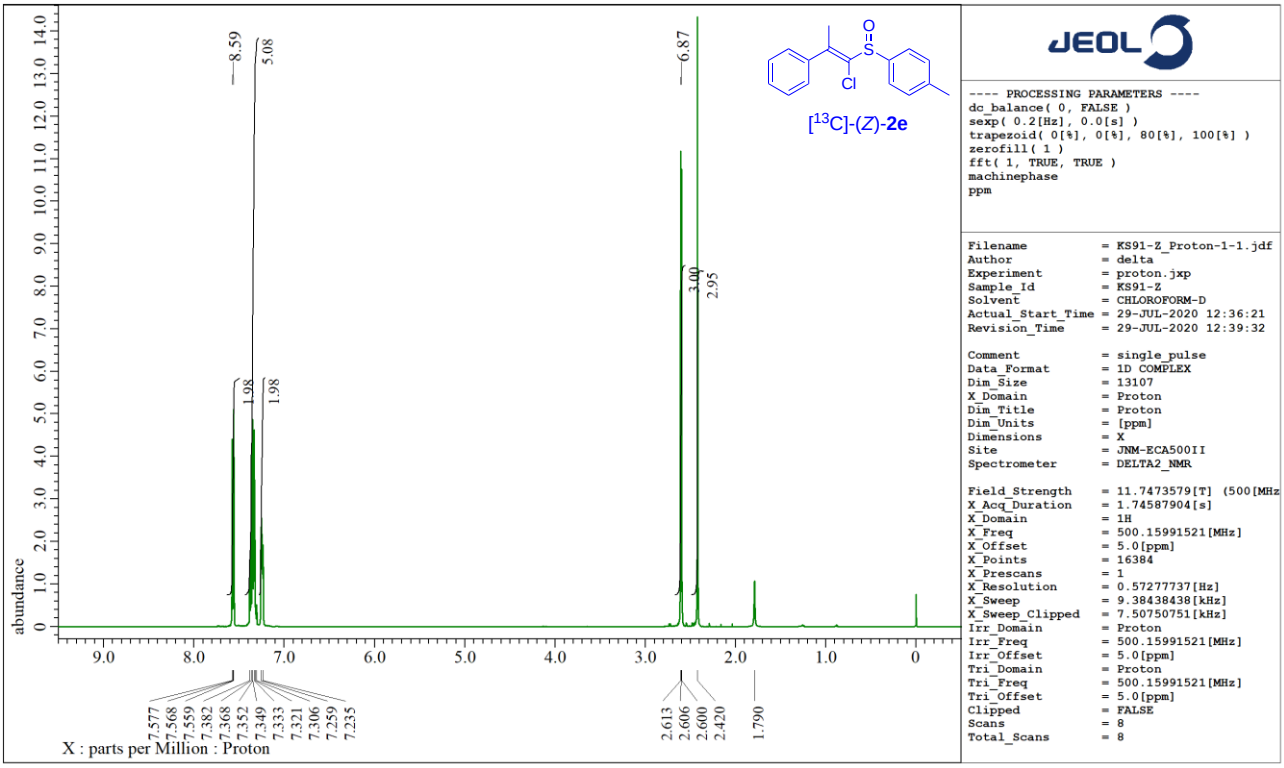
$^{1}$H NMR of (*Z*)-**2e**



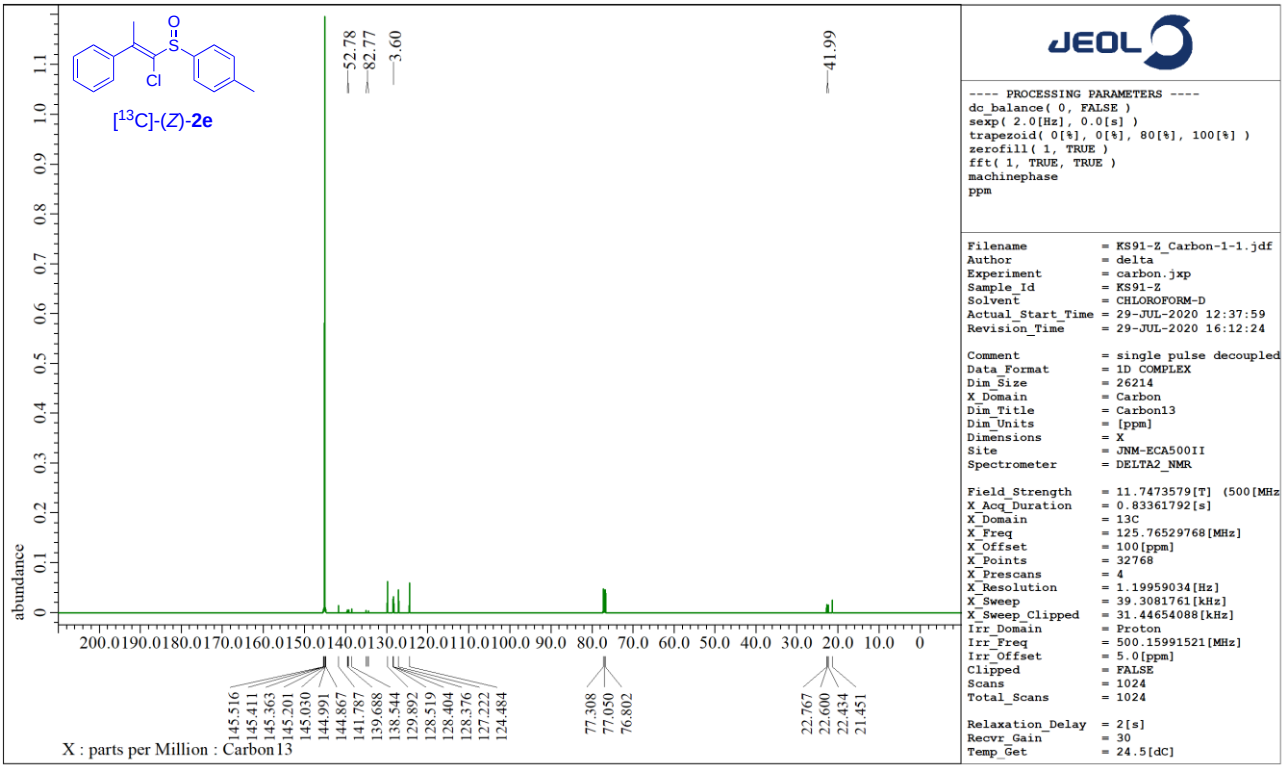

$^{13}$C NMR of (*Z*)-**2e**



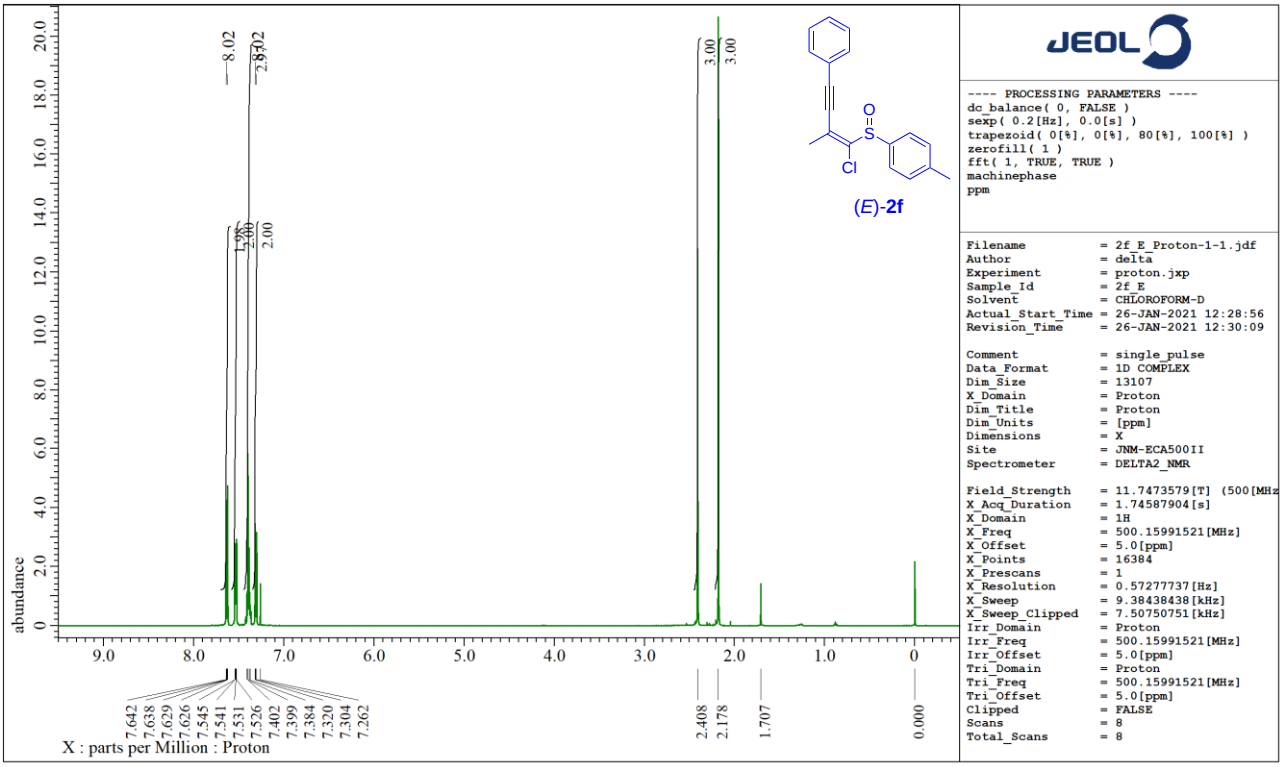
$^{1}$H NMR of [$^{13}$C]-(*Z*)-**2e**



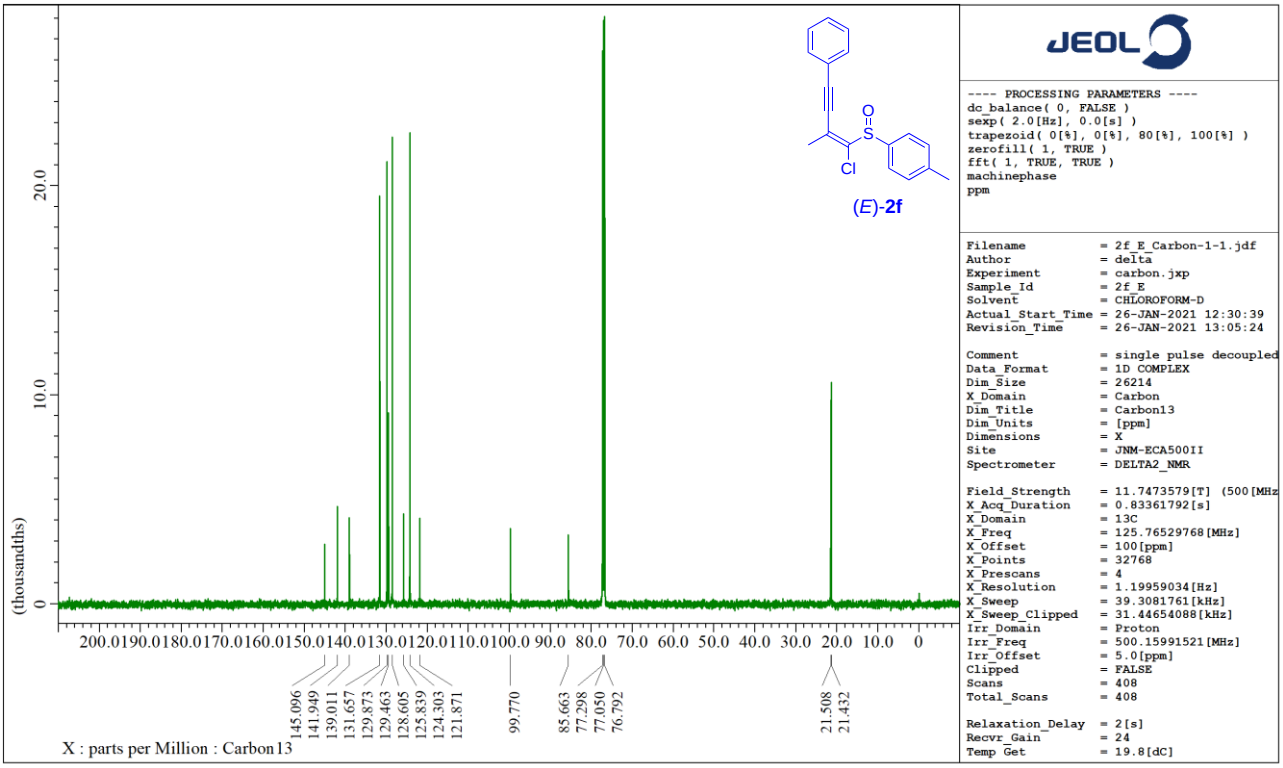

$^{13}$C NMR of [$^{13}$C]-(*Z*)-**2e**



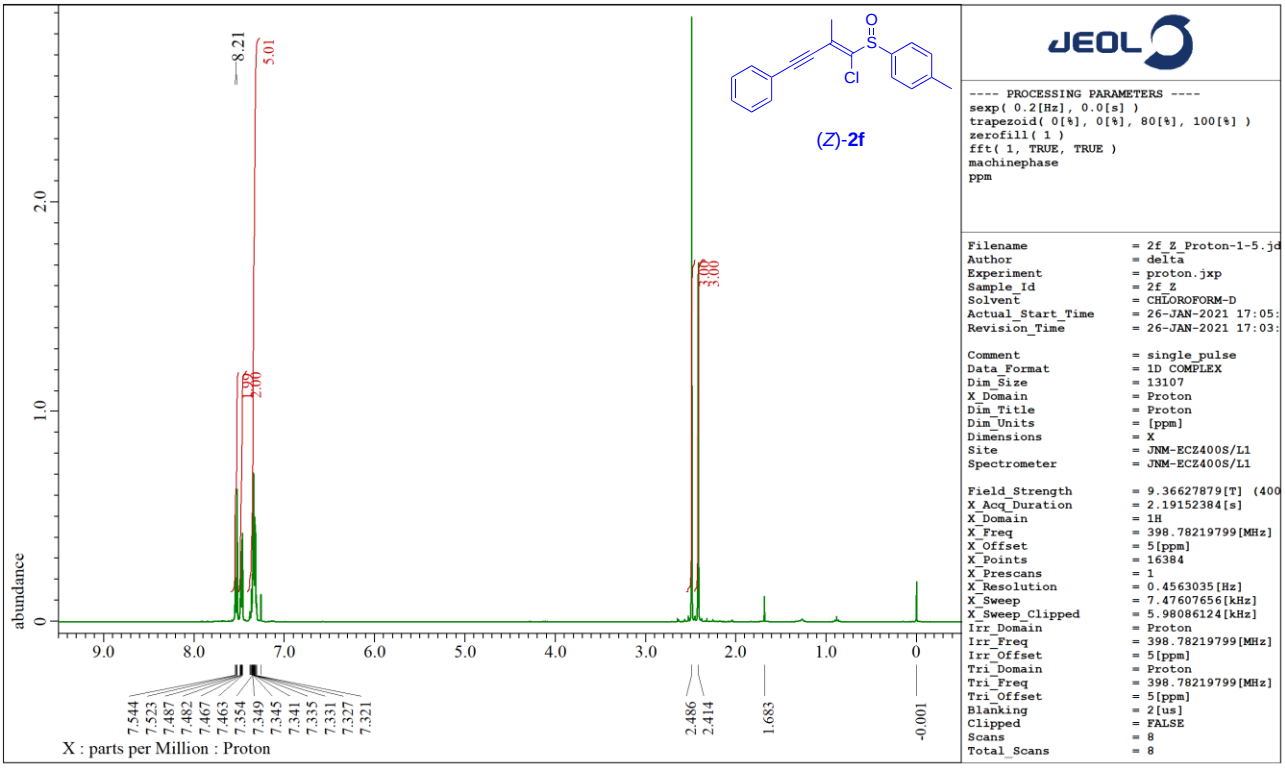
$^{1}$H NMR of (*E*)-**2f**



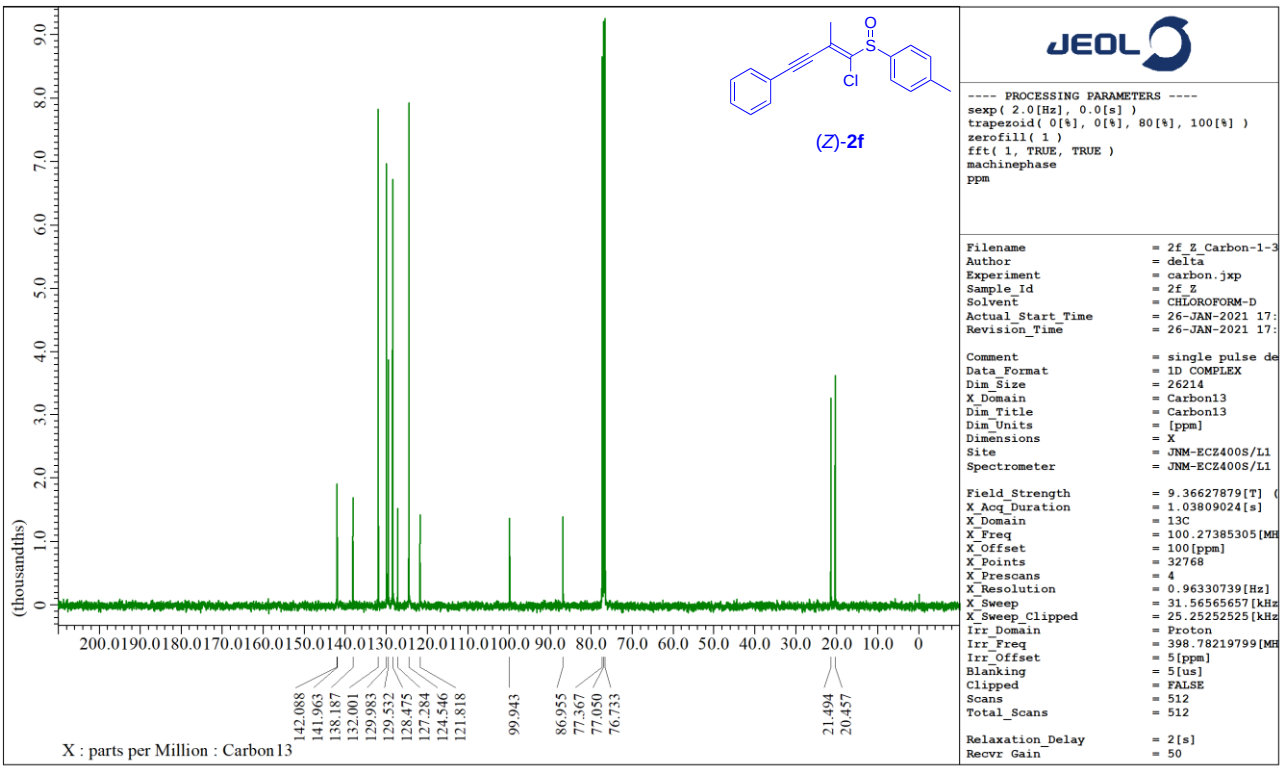

$^{13}$C NMR of (*E*)-**2f**



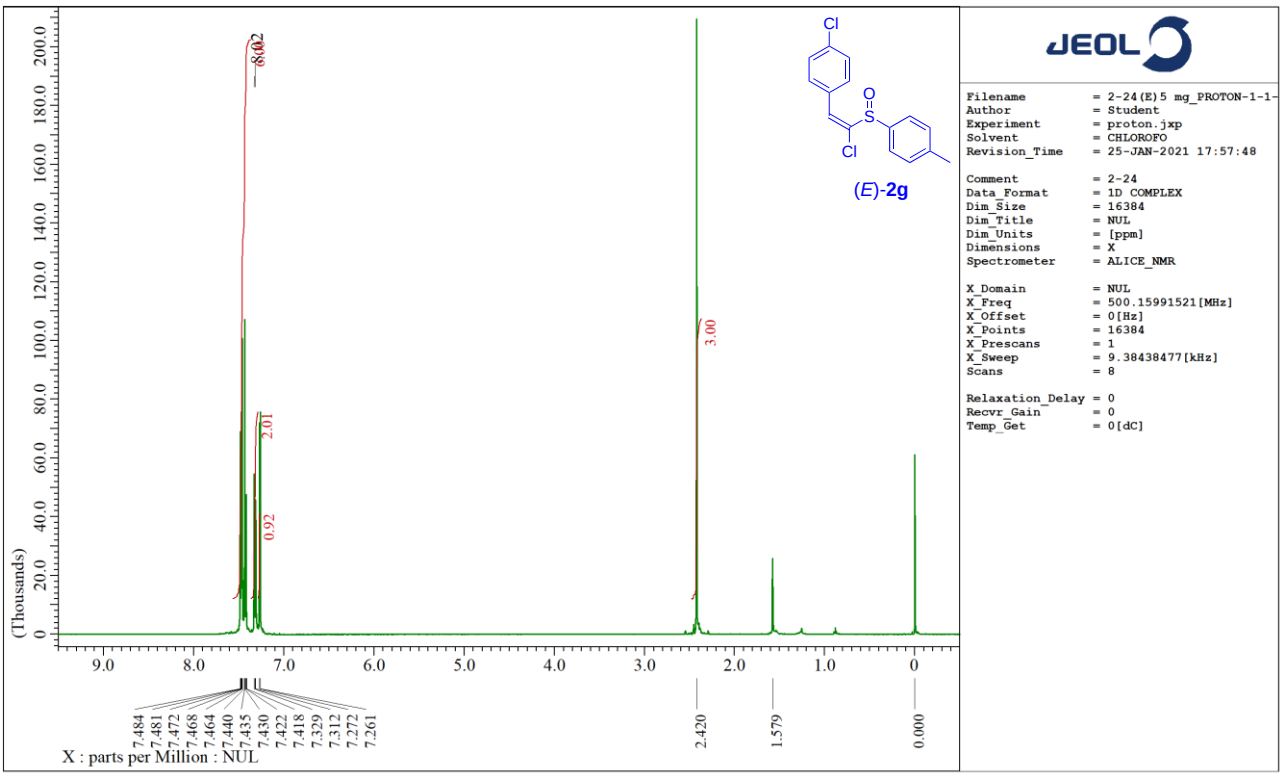
$^{1}$H NMR of (*Z*)-**2f**



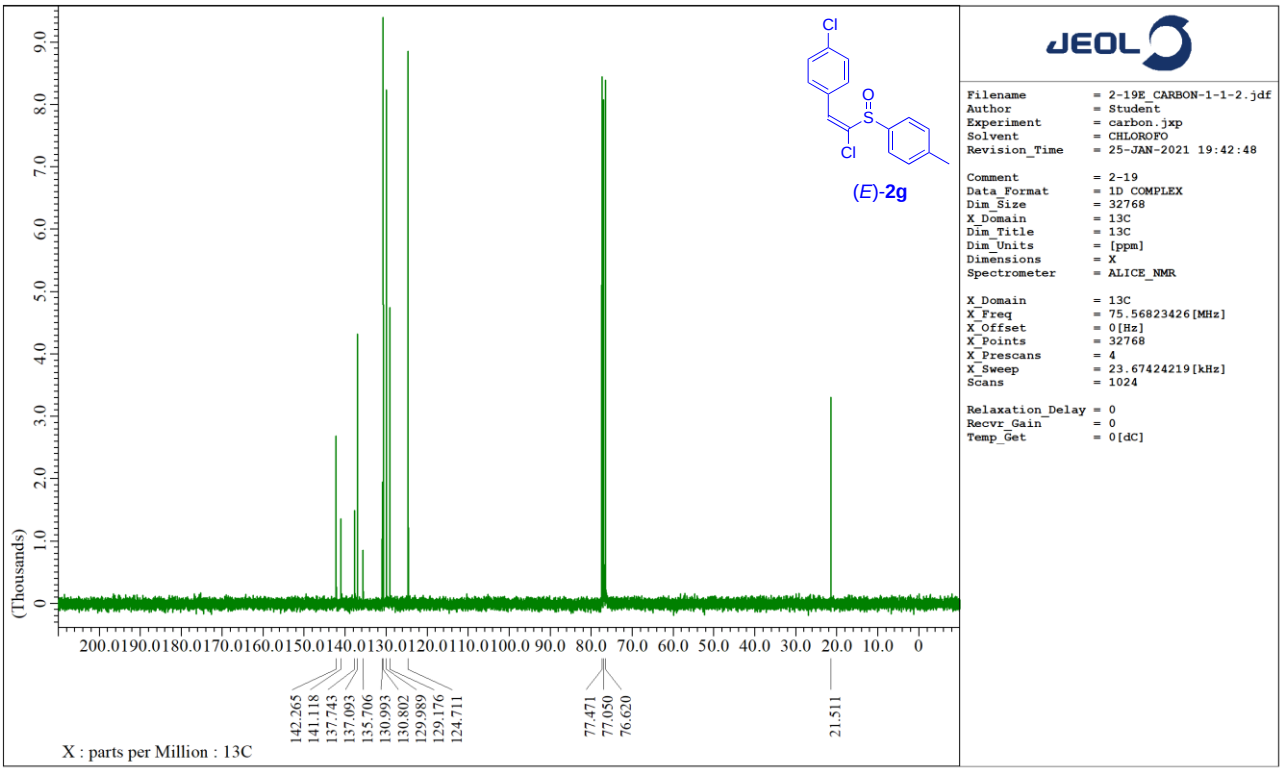

$^{13}$C NMR of (*Z*)-**2f**



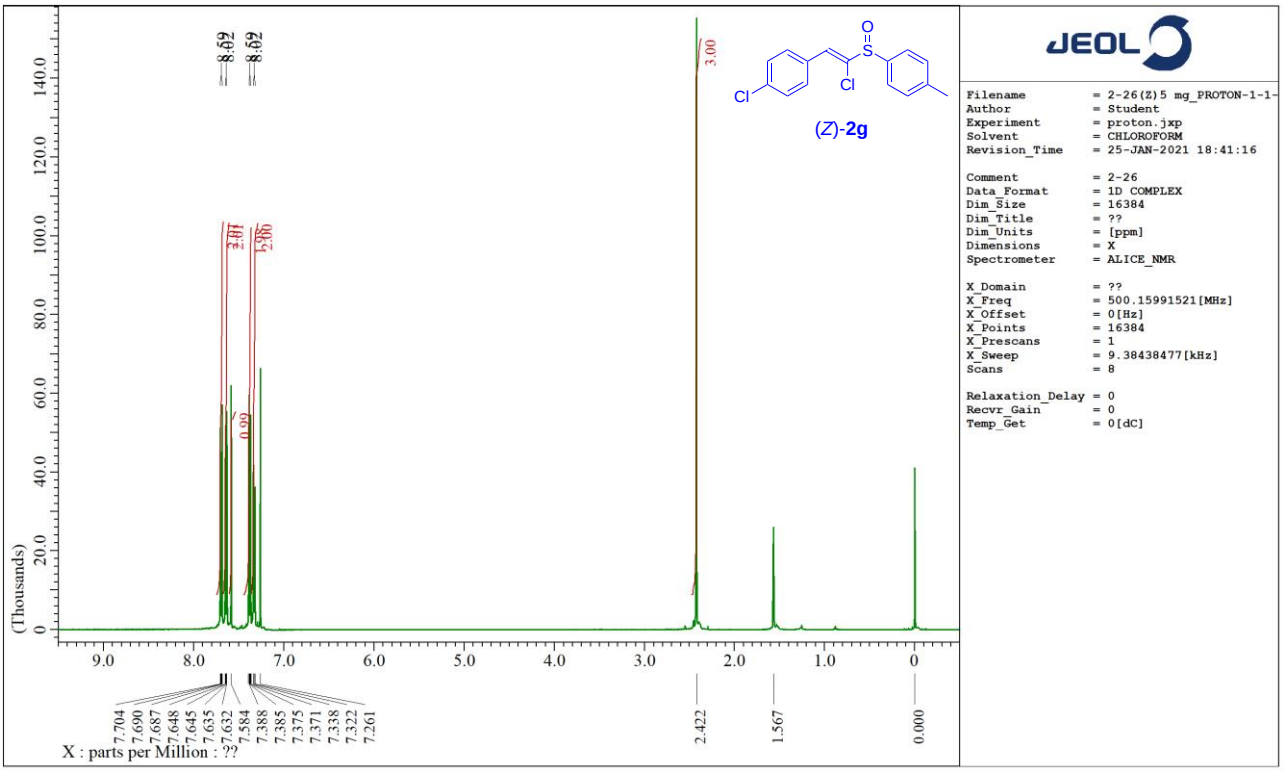
$^{1}$H NMR of (*E*)-**2g**



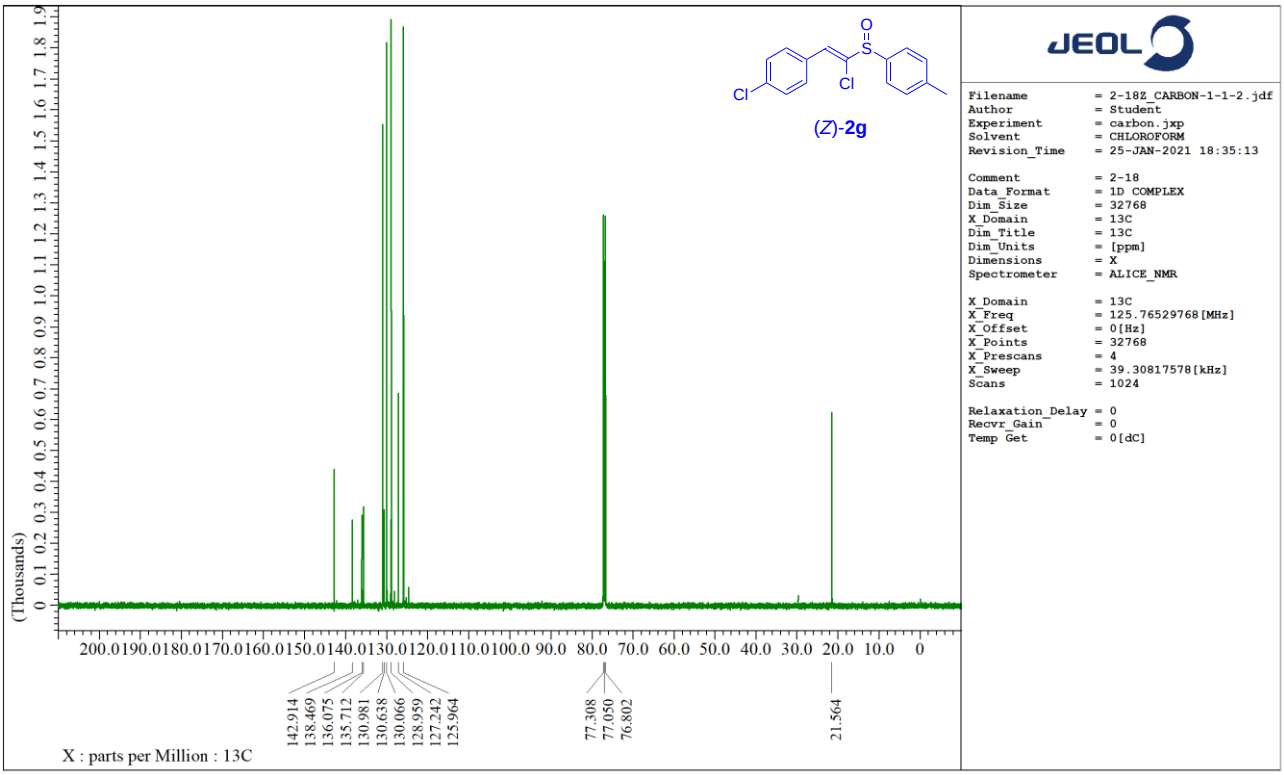

$^{13}$C NMR of (*E*)-**2g**



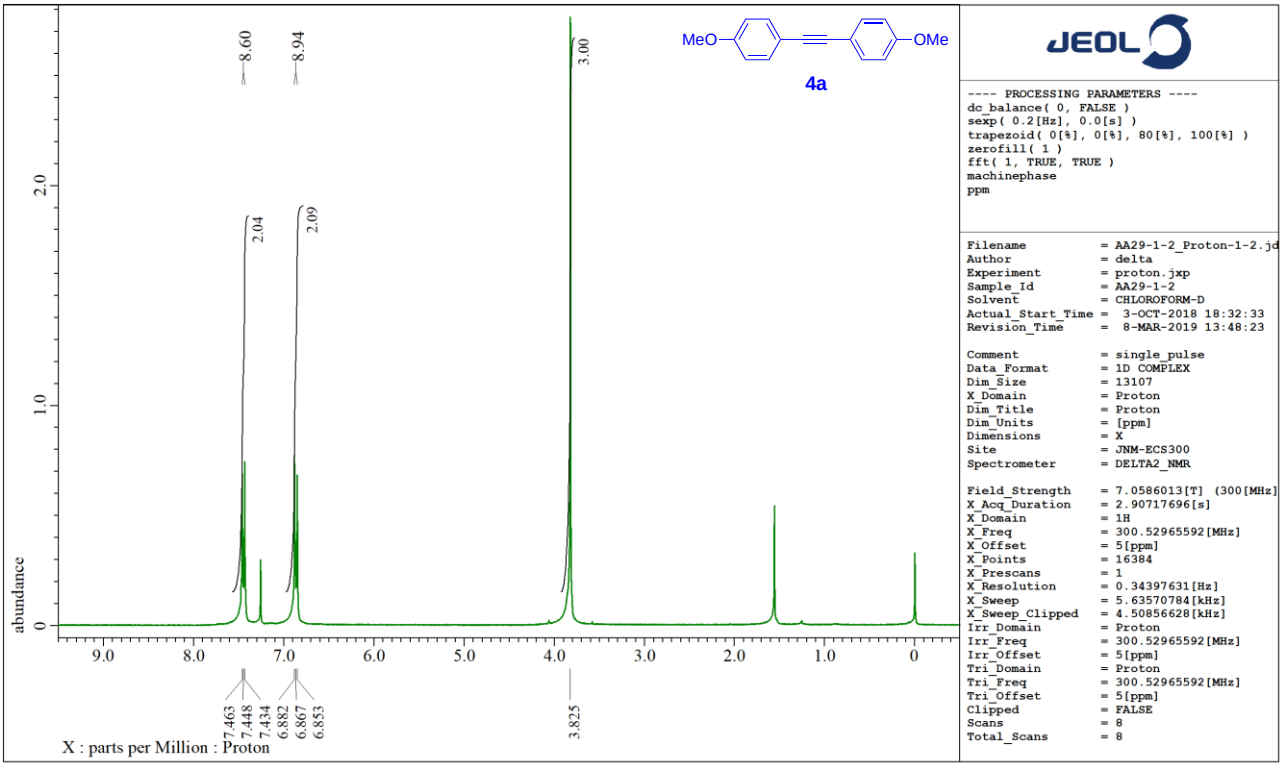
$^{1}$H NMR of (*Z*)-**2g**



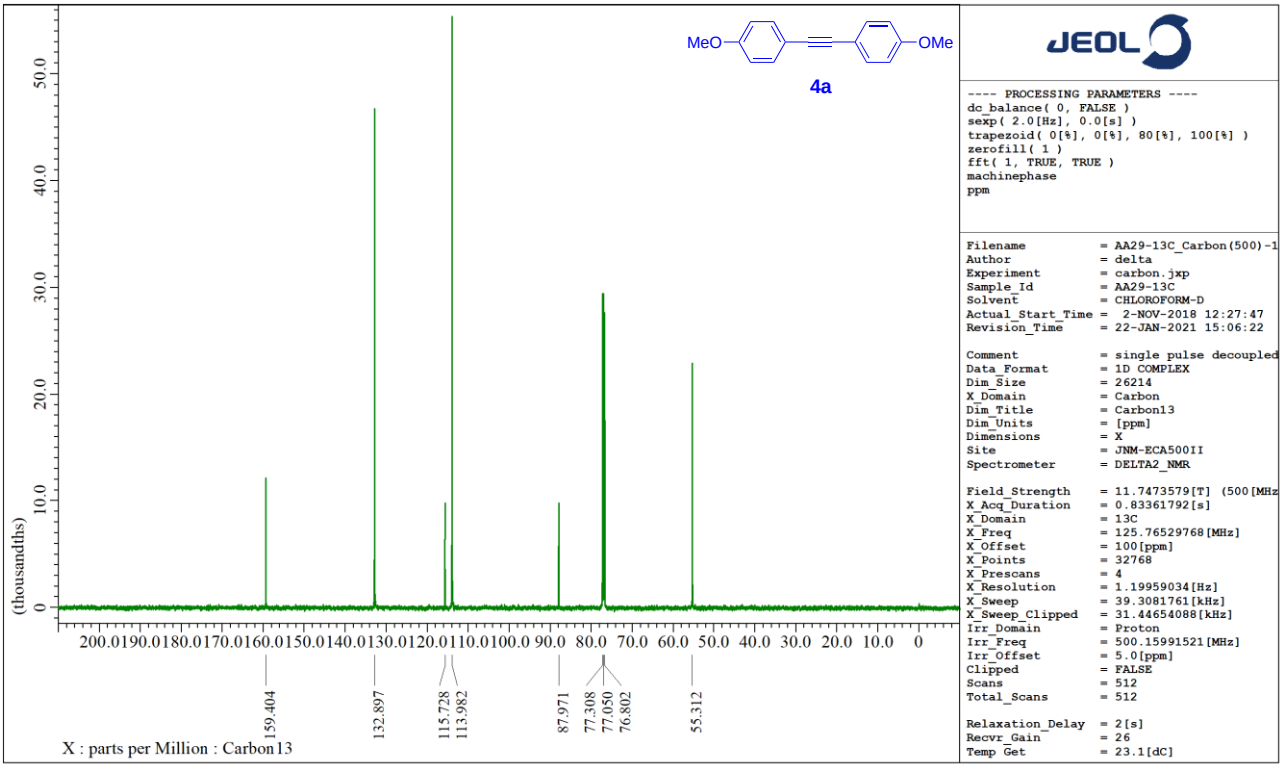

$^{13}$C NMR of (*Z*)-**2g**



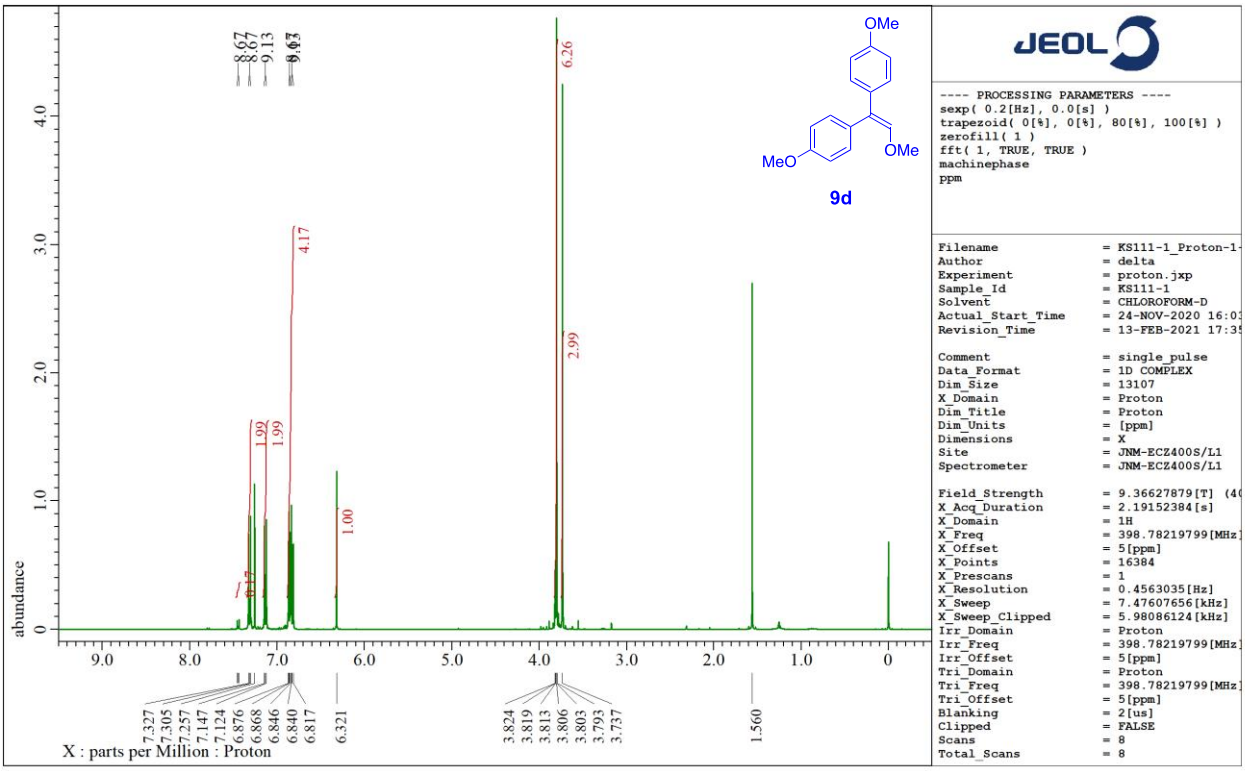
$^{1}$H NMR of **4a**



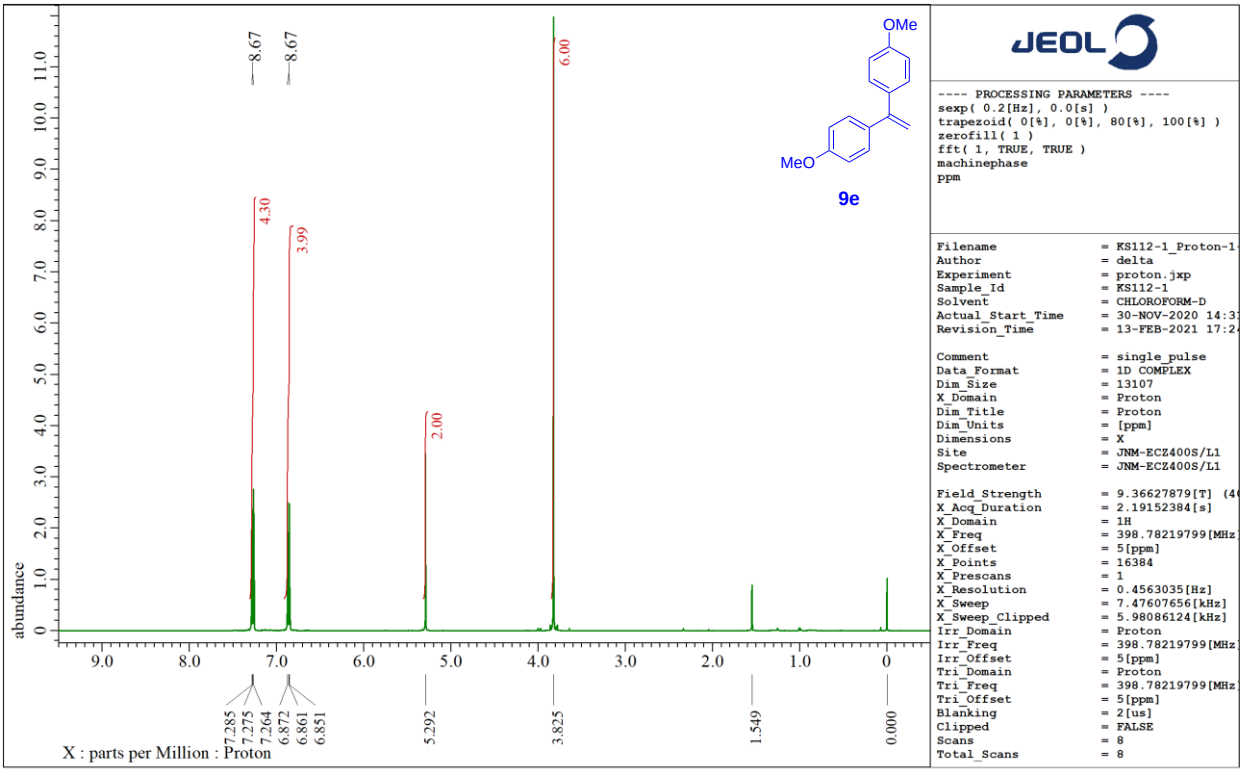

$^{13}$C NMR of **4a**



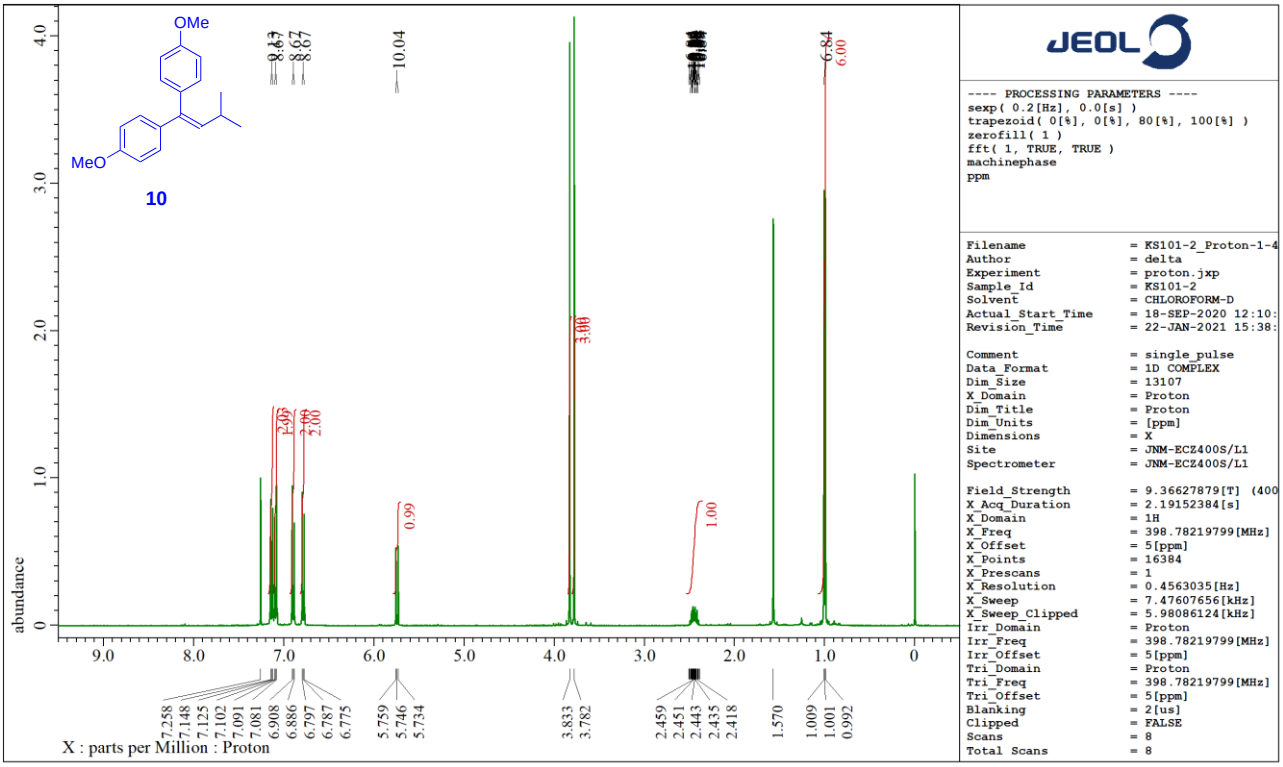
$^1$H NMR of **9d**



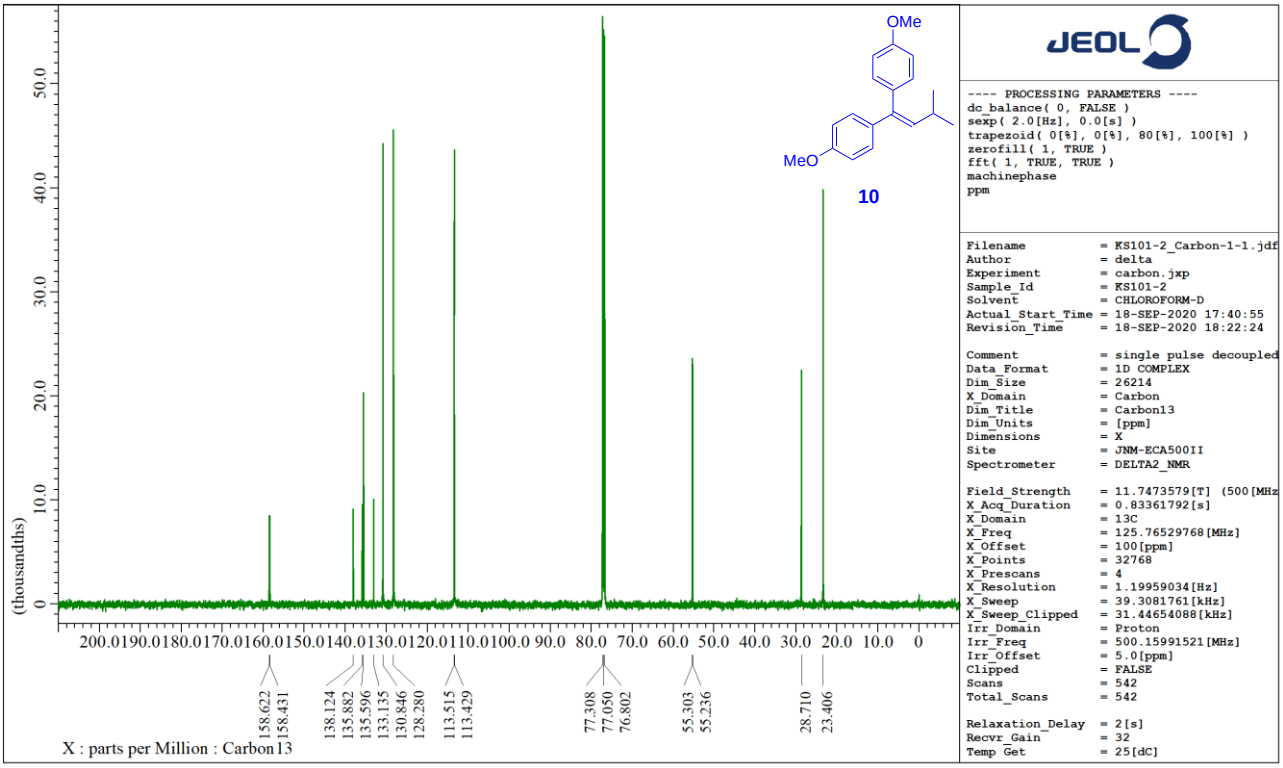

$^1$H NMR of **9e**



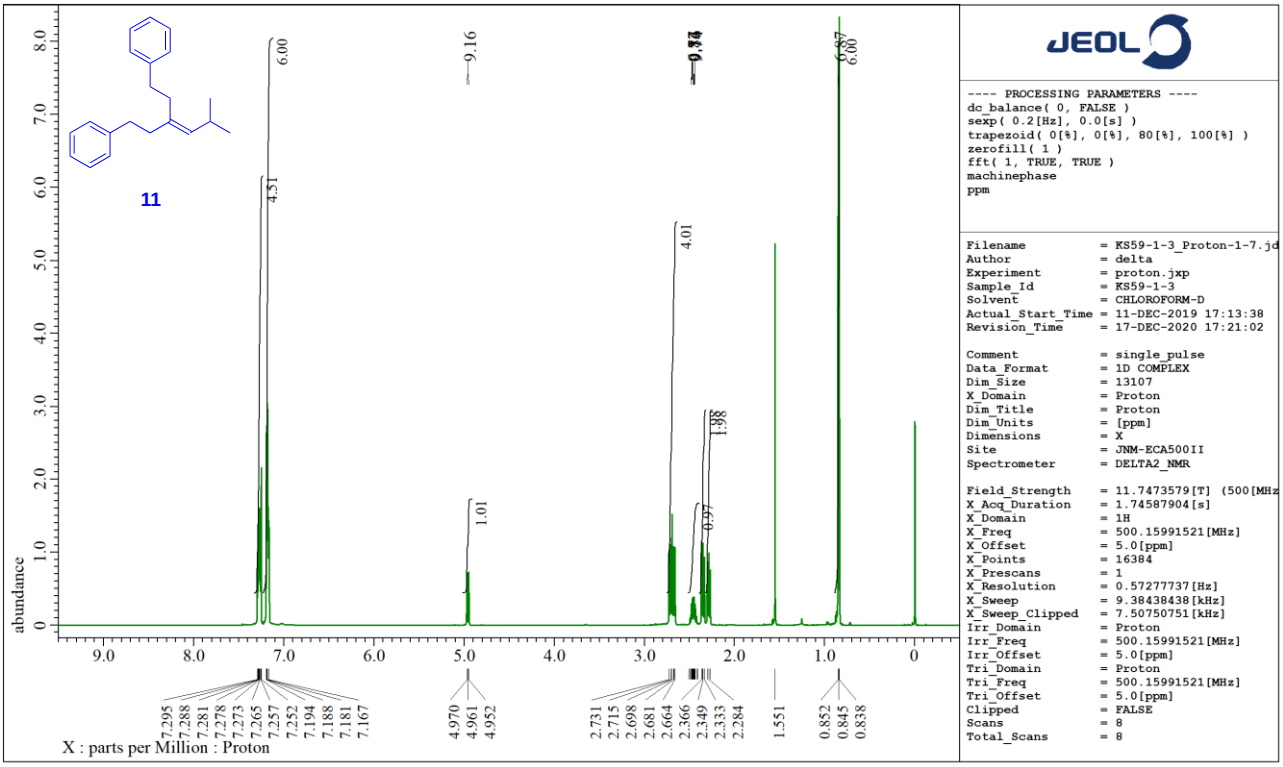
$^{1}$H NMR of **10**



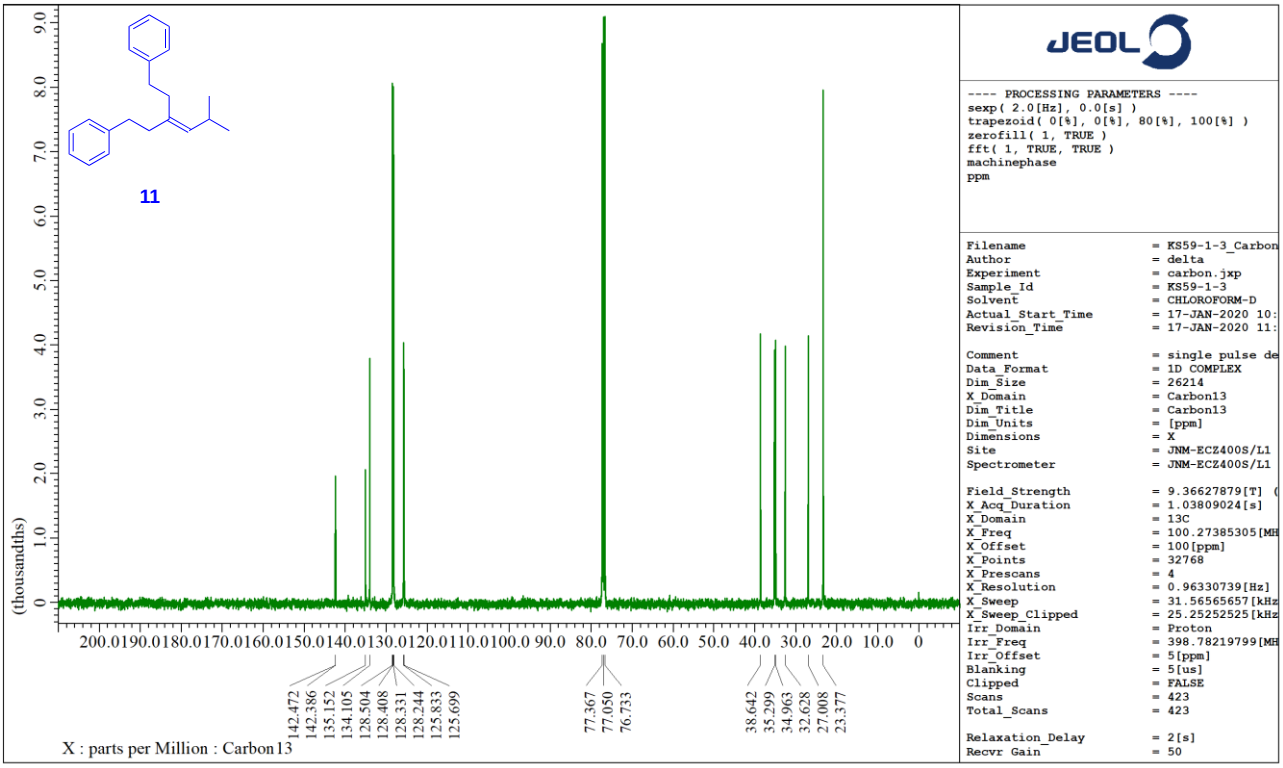

$^{13}$C NMR of **10**



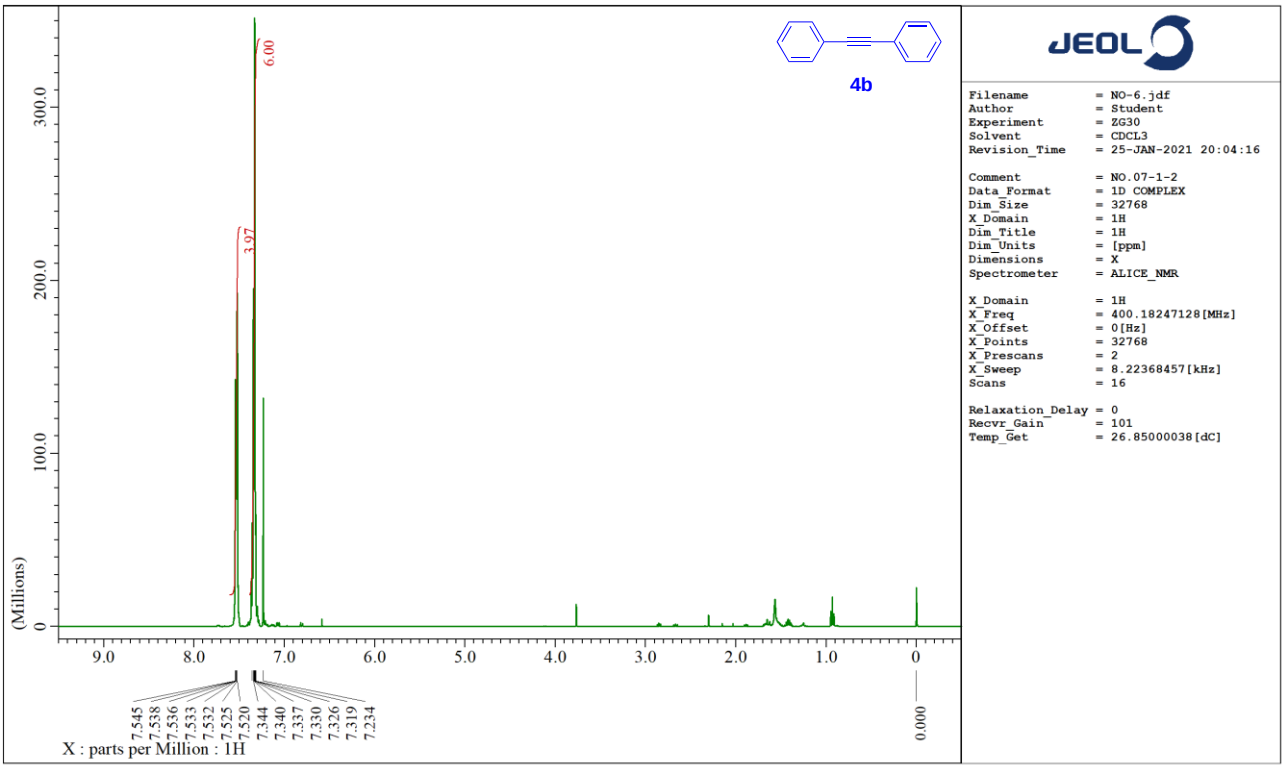
$^{1}$H NMR of **11**



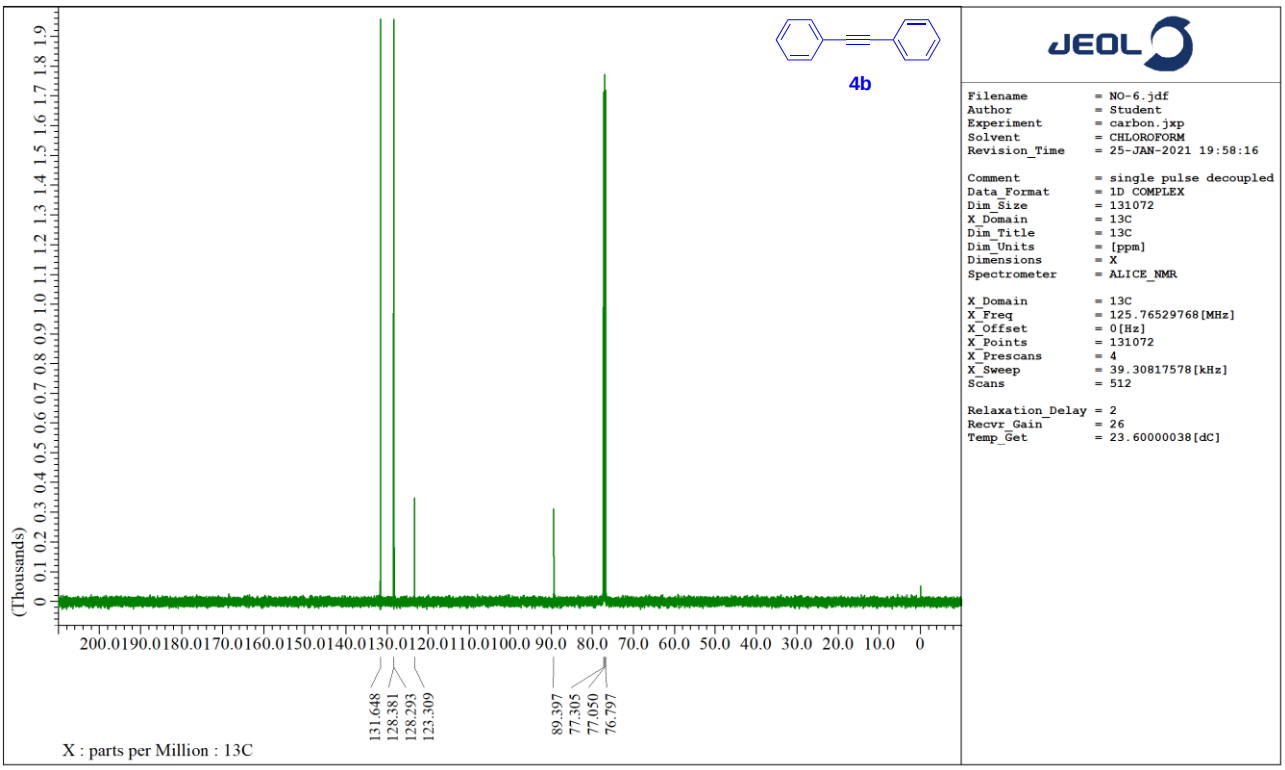

$^{13}$C NMR of **11**



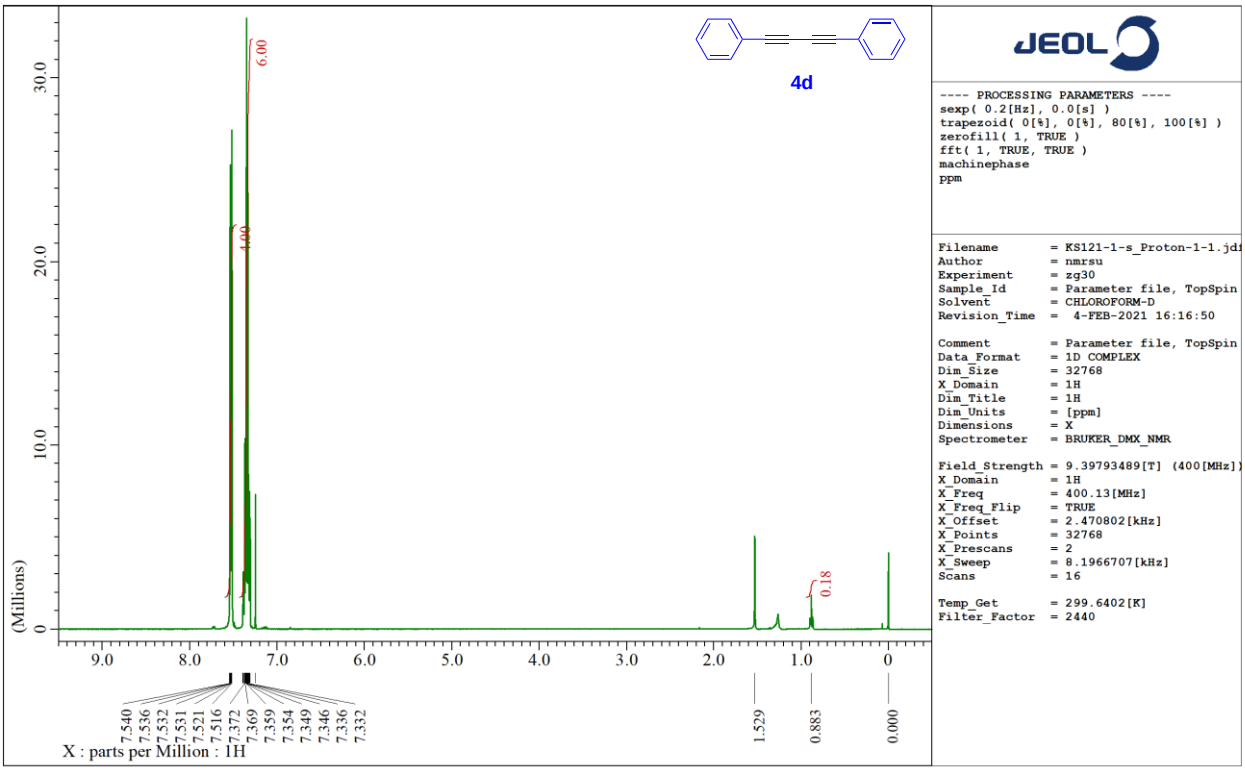
$^{1}$H NMR of **4b**




$^{13}$C NMR of **4b**



$^{1}$H NMR of **4d**

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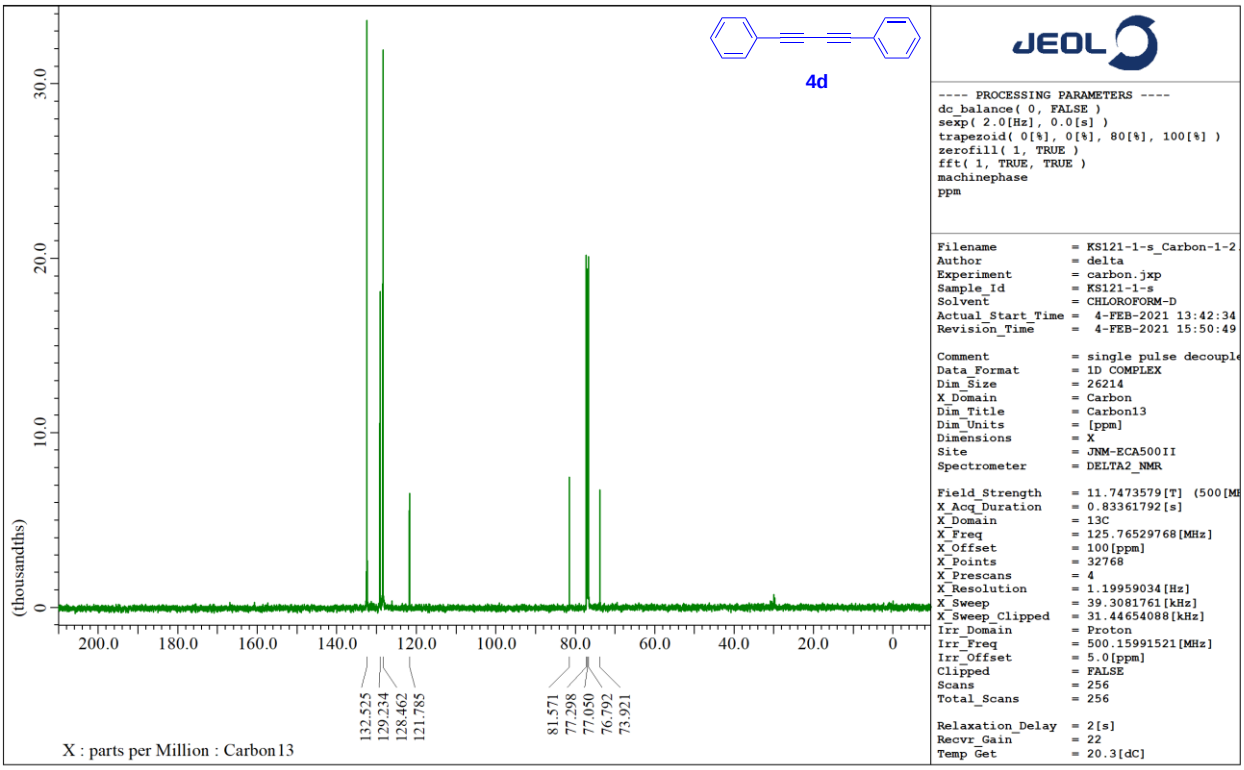

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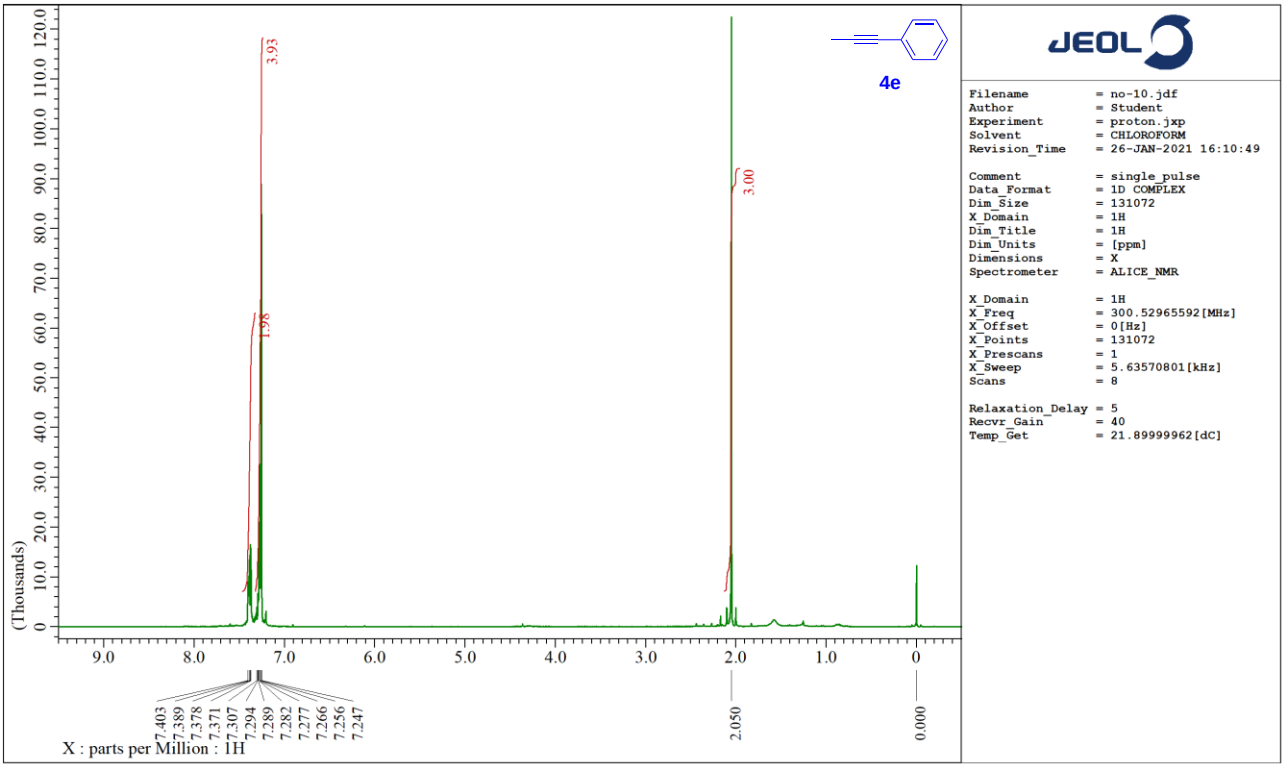
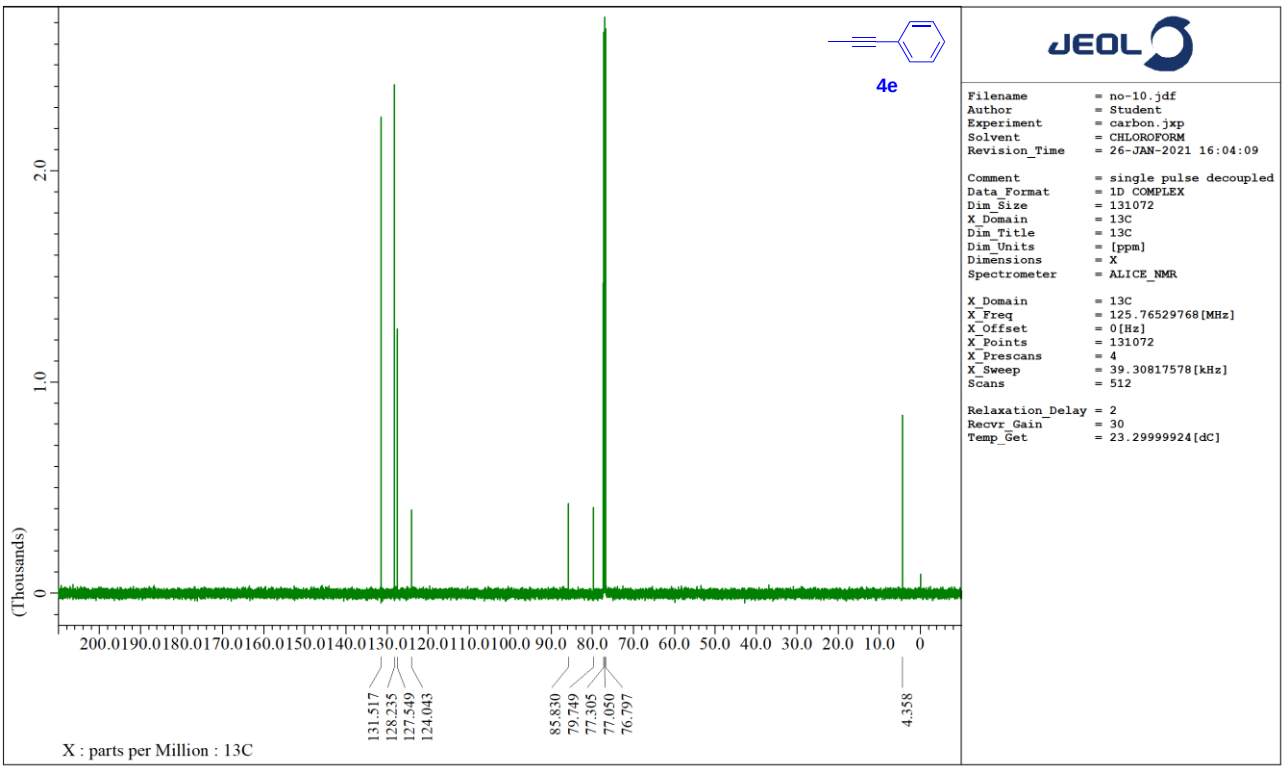
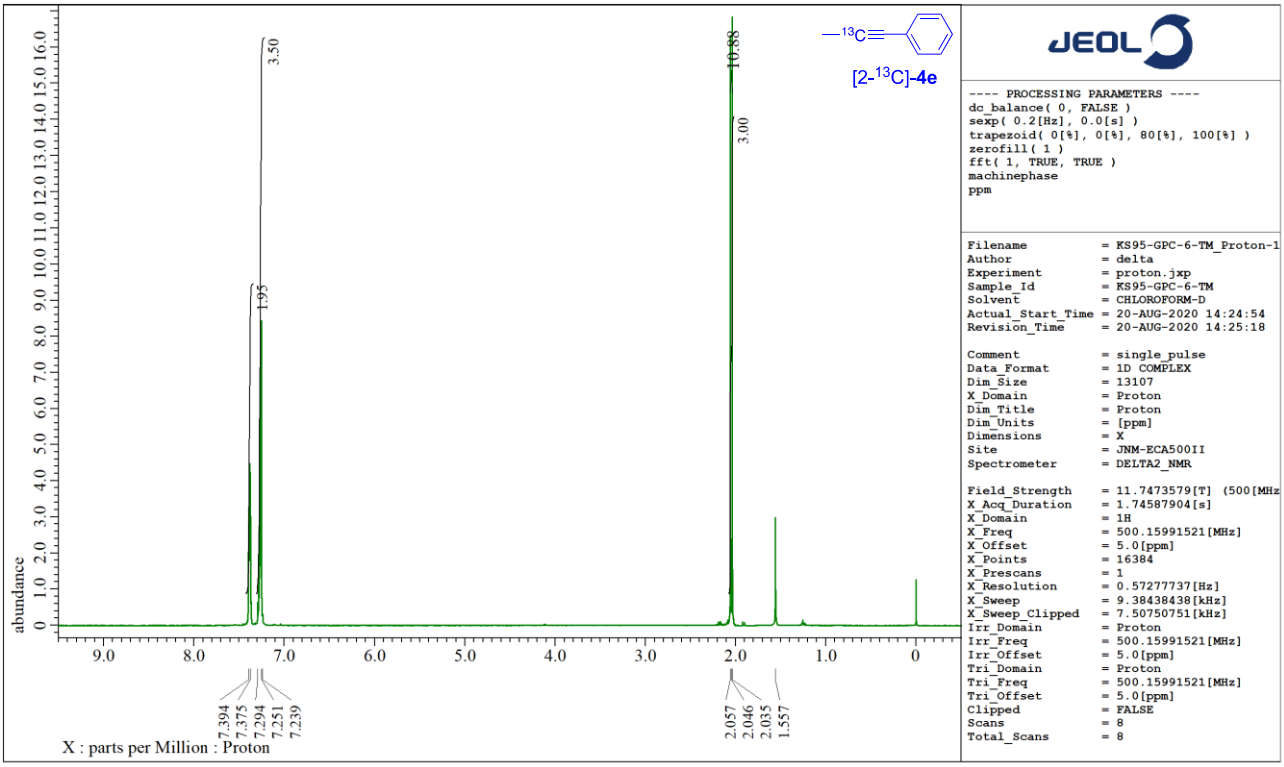


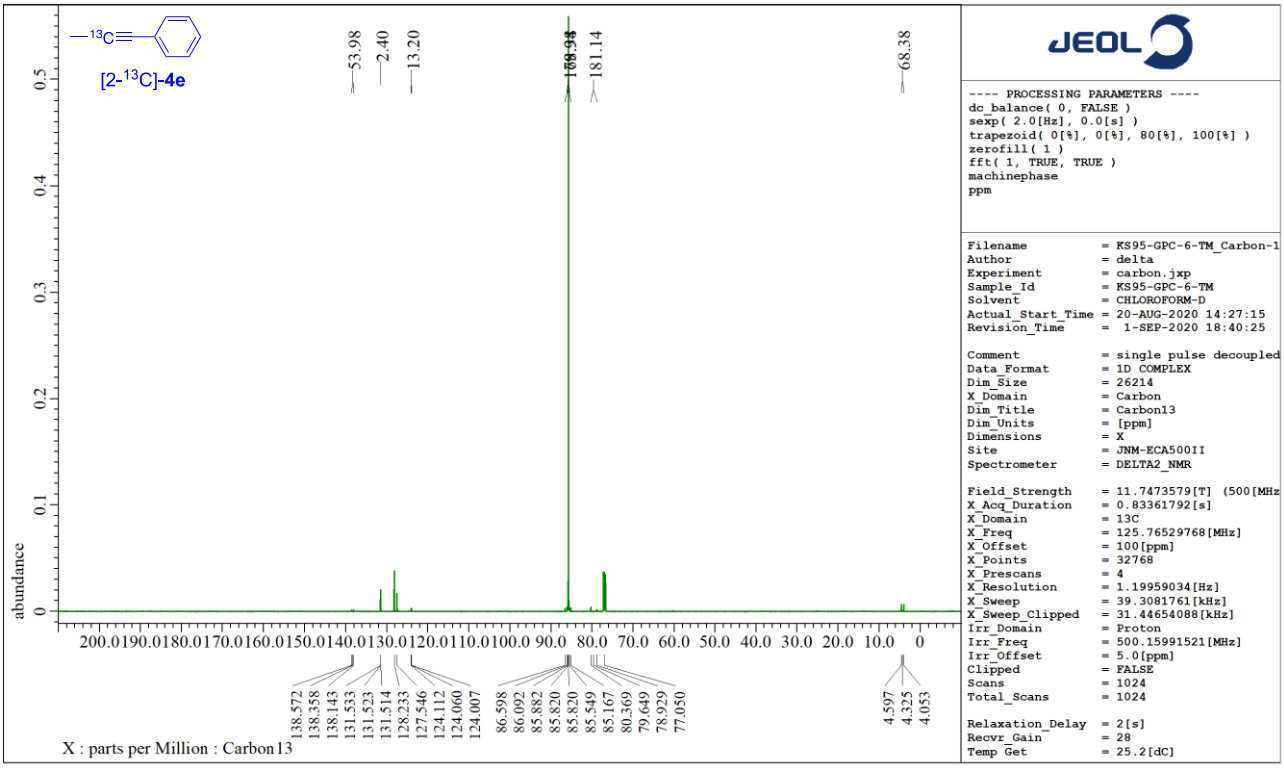

$^{13}$C NMR of **4e**



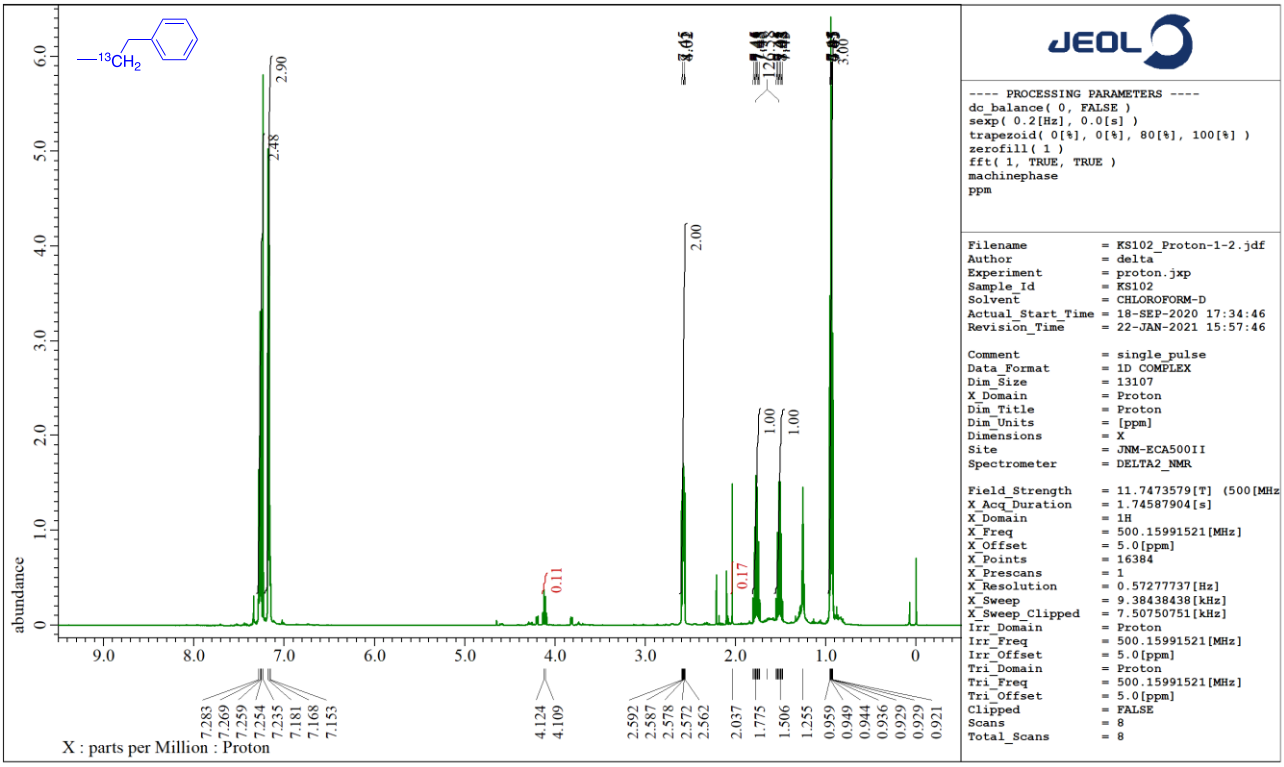
$^{1}$H NMR of [2-$^{13}$C]-**4e**



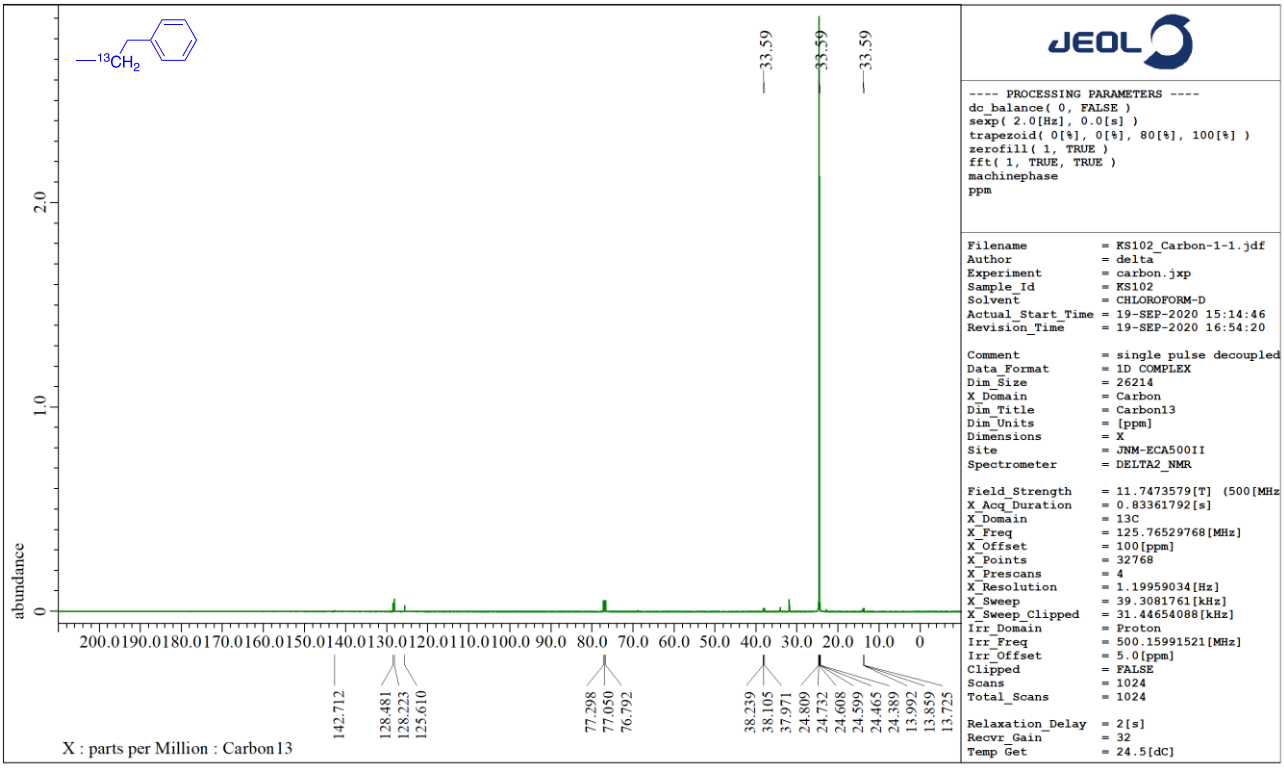

$^{13}$C NMR of [2-$^{13}$C]-**4e**



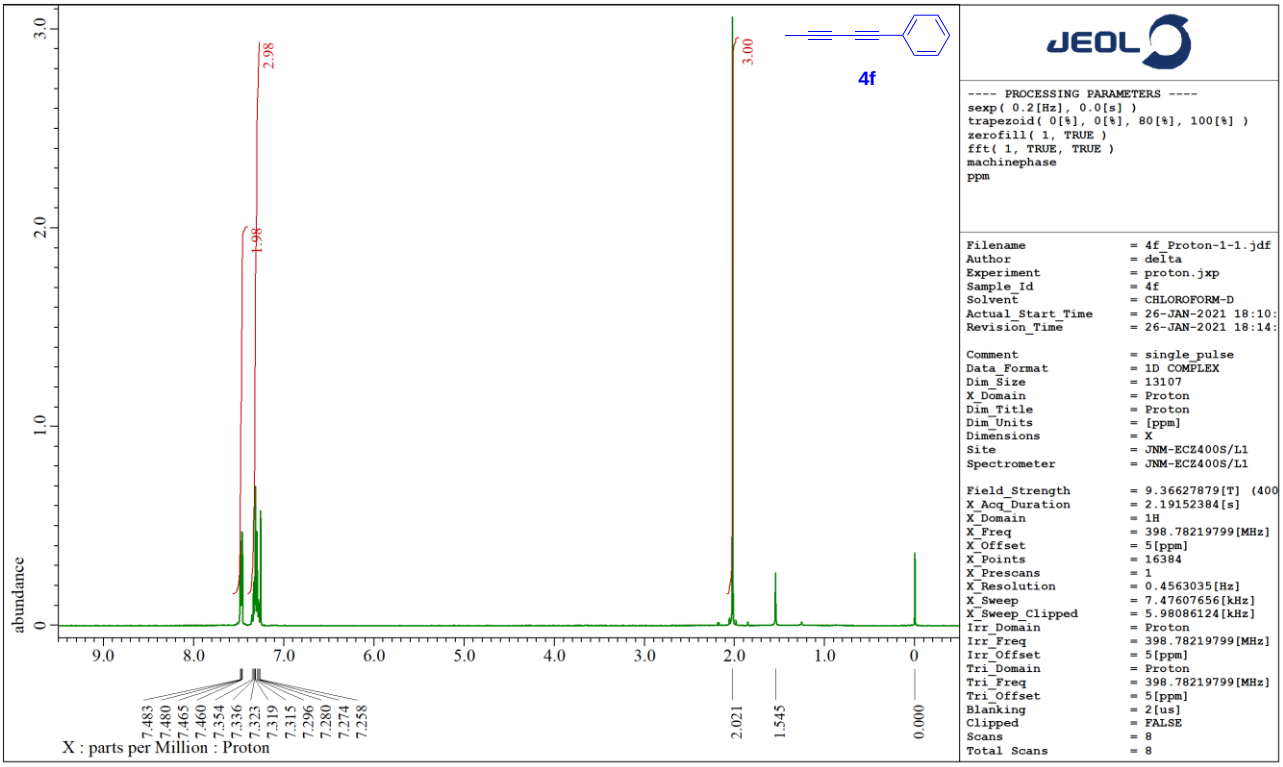
$^{1}$H NMR of [2-$^{13}$C]-propylbenzene



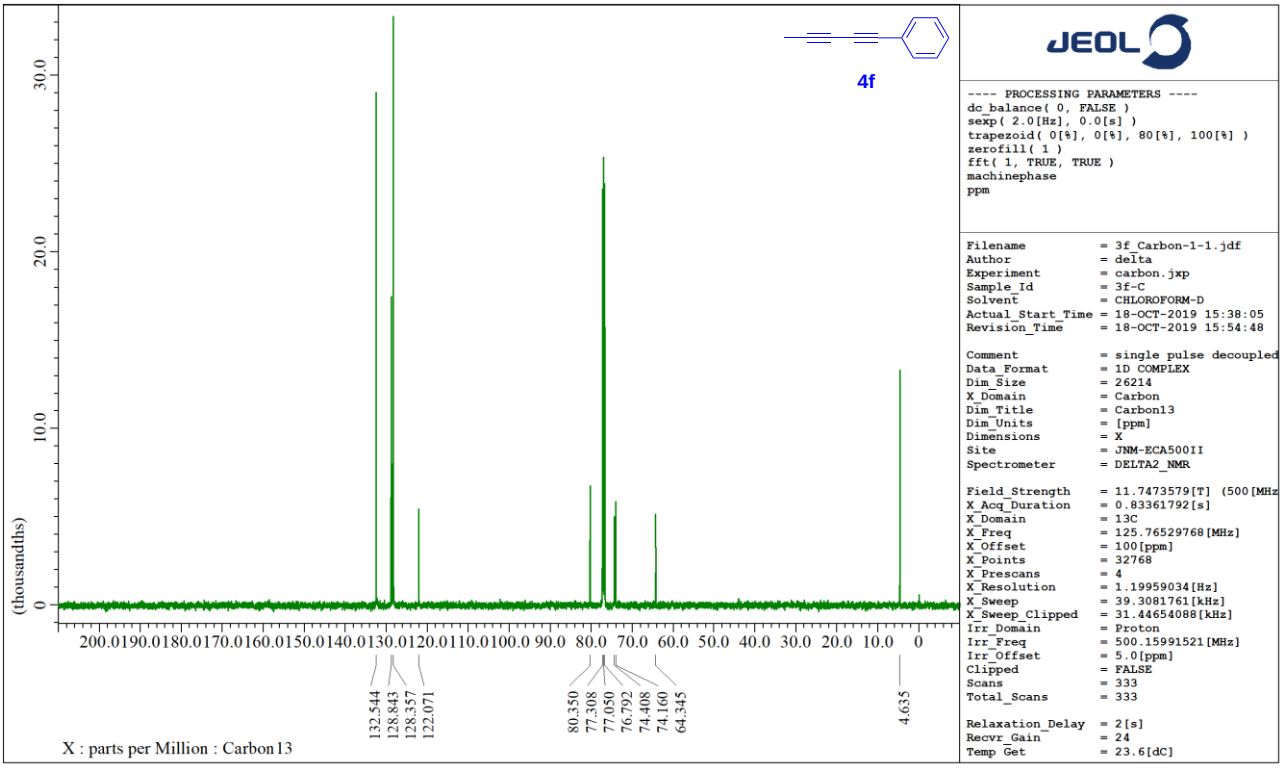

$^{13}$C NMR of [2-$^{13}$C]-propylbenzene



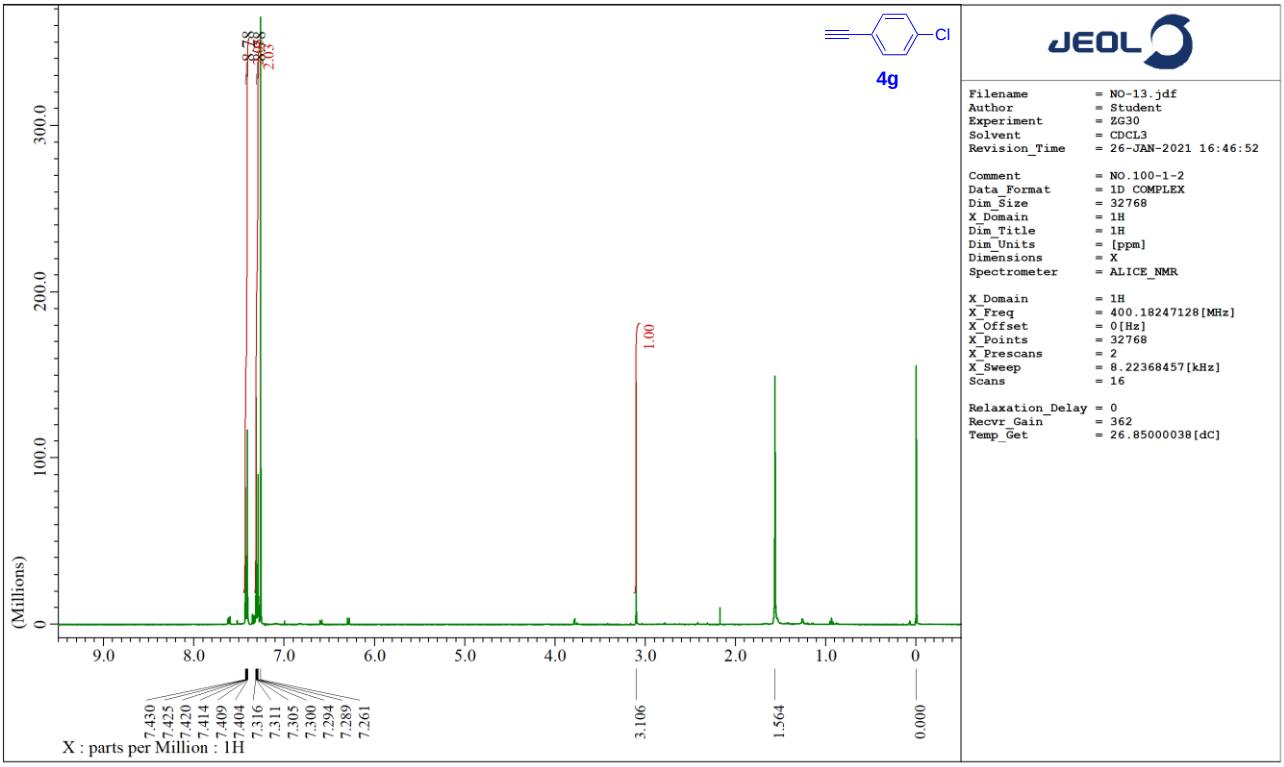
$^{1}$H NMR of **4f**



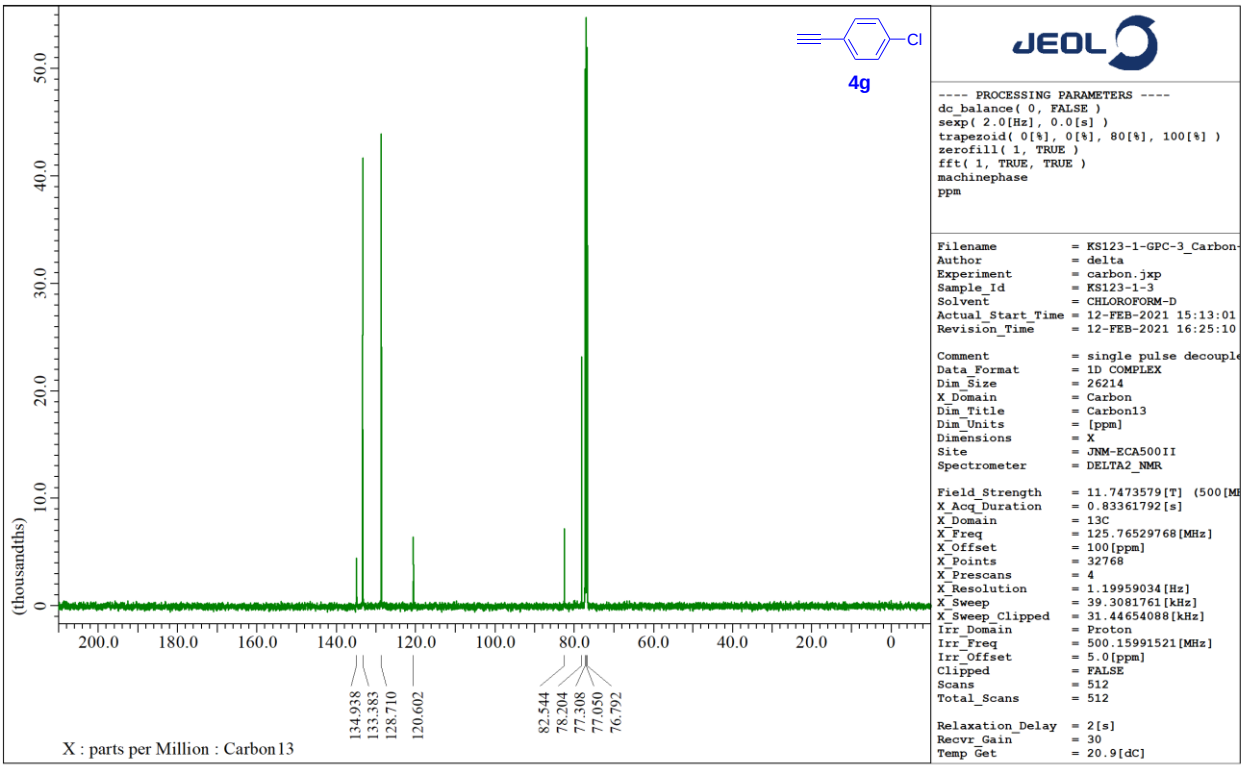

$^{13}$C NMR of **4f**



$^{1}$H NMR of **4g**




$^{13}$C NMR of **4g**



**Computational methods**

DFT calculations were performed using the Gaussian 09 software [11]. The geometries were fully optimized in the gas phase without symmetry constraints at the B3LYP/6-311++G(d,p) level of theory [12]. The QST3 method was used to locate transition states [13]. The frequency calculations were performed at the same level to confirm that the structures correspond to energy minima or transition states (zero or one imaginary frequencies, respectively). Starting from the transition-state structures, the reaction paths were followed using an intrinsic reaction coordinate (IRC) analysis [14]. The Jmol program was used to visualize the molecular structures [15].

**(*E*)-PhMeC=CClMgCl•2(OMe$_2$) [(*E*)-3e]**

No. of imaginary frequencies: 0

$E_0$: -1778.700728 hartree

$E_0 + E_{ZPE}$: -1778.395893 hartree

$E_0 + E_{tot}$: -1778.371287 hartree

$E_0 + H_{corr}$: -1778.370343 hartree

$E_0 + G_{corr}$: -1778.454738 hartree

| | | | |
|---|---|---|---|
| Mg | 0.987611 | -0.396165 | -0.143062 |
| C | -0.212418 | 1.375120 | -0.194129 |
| C | -1.534895 | 1.627638 | -0.179265 |
| Cl | 0.874153 | 2.881747 | -0.045386 |
| O | 1.455197 | -0.689261 | 1.890504 |
| O | 2.916193 | 0.143442 | -0.827449 |
| Cl | 0.958214 | -2.551221 | -0.940269 |
| C | -2.452730 | 0.449445 | -0.252205 |
| C | -3.545976 | 0.345330 | 0.625483 |
| C | -2.263206 | -0.578429 | -1.186720 |
| C | -4.396082 | -0.755899 | 0.585885 |
| H | -3.725510 | 1.127726 | 1.354302 |
| C | -3.110051 | -1.684963 | -1.223338 |
| H | -1.456041 | -0.501389 | -1.904883 |
| C | -4.179669 | -1.779891 | -0.337033 |
| H | -5.228470 | -0.816402 | 1.279007 |
| H | -2.930636 | -2.469270 | -1.949795 |
| H | -4.842289 | -2.637545 | -0.367935 |
| C | 3.053473 | 0.878634 | -2.055520 |
| H | 2.208453 | 1.560402 | -2.119643 |
| H | 3.981958 | 1.456002 | -2.033090 |
| H | 3.060522 | 0.189707 | -2.905834 |
| C | 4.015545 | -0.750026 | -0.596458 |
| H | 3.854109 | -1.220856 | 0.371214 |
| H | 4.049309 | -1.520118 | -1.371297 |
| H | 4.949149 | -0.179793 | -0.580090 |
| C | 1.409418 | -1.967970 | 2.549764 |
| H | 0.522353 | -2.023653 | 3.187652 |
| H | 1.357711 | -2.726470 | 1.771412 |
| H | 2.310505 | -2.100279 | 3.156577 |
| C | 1.506877 | 0.414378 | 2.811515 |
| H | 1.518437 | 1.332483 | 2.227392 |
| H | 0.624323 | 0.401841 | 3.457538 |
| H | 2.413602 | 0.342127 | 3.419813 |
| C | -2.204962 | 2.978331 | -0.048366 |
| H | -3.108418 | 3.019968 | -0.662207 |
| H | -2.507772 | 3.173255 | 0.987255 |
| H | -1.535948 | 3.783682 | -0.346614 |

**(*Z*)-PhMeC=CClMgCl•2(OMe$_2$) [(*Z*)-3e]**

No. of imaginary frequencies: 0

$E_0$: -1778.699864 hartree

$E_0 + E_{ZPE}$: -1778.395040 hartree

$E_0 + E_{tot}$: -1778.370499 hartree

$E_0 + H_{corr}$: -1778.369554 hartree

$E_0 + G_{corr}$: -1778.454657 hartree

| | | | |
|---|---|---|---|
| Mg | -1.687026 | -0.238196 | -0.308271 |
| C | 0.417804 | -0.007737 | -0.040541 |
| C | 1.480852 | -0.508109 | -0.689993 |
| Cl | 0.827268 | 1.090301 | 1.411375 |
| O | -2.624184 | 1.652167 | -0.469540 |
| O | -2.507911 | -0.902329 | 1.517747 |
| Cl | -2.903678 | -1.456067 | -1.832157 |
| C | 2.920682 | -0.248689 | -0.381522 |
| C | 3.730985 | -1.267870 | 0.134310 |
| C | 3.502617 | 0.997418 | -0.643370 |
| C | 5.081236 | -1.044010 | 0.396260 |
| H | 3.297388 | -2.240011 | 0.344076 |
| C | 4.854524 | 1.220359 | -0.391303 |
| H | 2.887246 | 1.795047 | -1.043412 |
| C | 5.648948 | 0.201060 | 0.131290 |
| H | 5.689880 | -1.843160 | 0.805507 |
| H | 5.287443 | 2.192364 | -0.601946 |
| H | 6.700519 | 0.375359 | 0.330433 |
| C | -1.745881 | -1.154587 | 2.711912 |
| H | -0.754842 | -0.732314 | 2.564625 |
| H | -2.231112 | -0.672612 | 3.566082 |
| H | -1.677676 | -2.232778 | 2.884534 |
| C | -3.854566 | -1.397512 | 1.606839 |

| | | | |
|---|---|---|---|
| H | -4.320517 | -1.254543 | 0.634457 |
| H | -3.841903 | -2.465393 | 1.842856 |
| H | -4.397395 | -0.850754 | 2.384073 |
| C | -3.712486 | 1.932348 | -1.369544 |
| H | -3.393284 | 2.669029 | -2.112700 |
| H | -3.974396 | 0.997280 | -1.859259 |
| H | -4.564675 | 2.322890 | -0.804596 |
| C | -2.166292 | 2.828773 | 0.219449 |
| H | -1.320403 | 2.542014 | 0.840695 |
| H | -1.846511 | 3.581177 | -0.507502 |
| H | -2.974637 | 3.232649 | 0.837063 |
| C | 1.246614 | -1.435491 | -1.868218 |
| H | 1.698558 | -1.021238 | -2.776285 |
| H | 1.721129 | -2.407820 | -1.695893 |
| H | 0.184999 | -1.605231 | -2.059327 |
| H | 2.925394 | -2.350989 | 0.242537 |
| H | 3.521341 | -2.239386 | -1.427021 |
| H | 4.658791 | -2.036274 | -0.051259 |
| C | 0.294764 | -1.912906 | 1.869310 |
| H | -0.565882 | -1.541391 | 2.434466 |
| H | -0.028477 | -2.272788 | 0.893566 |
| H | 0.780021 | -2.721606 | 2.426006 |
| C | 1.770195 | -0.285934 | 2.836952 |
| H | 2.418185 | 0.536524 | 2.539708 |
| H | 0.962144 | 0.096574 | 3.468842 |
| H | 2.340674 | -1.044302 | 3.382980 |
| C | -2.470742 | 3.161142 | -0.485982 |
| H | -2.945225 | 3.111938 | -1.469037 |
| H | -3.231320 | 3.405060 | 0.259570 |
| H | -1.722350 | 3.958524 | -0.496937 |

**[(*E*)-PhMeC=CClMgCl•2(OMe$_2$)]$^‡$ [(*E*)-3e$^‡$]**

No. of imaginary frequencies: 1 (243.2*i* cm$^{-1}$)

$E_0$: -1778.673338 hartree

$E_0 + E_{ZPE}$: -1778.371790 hartree

$E_0 + E_{tot}$: -1778.346635 hartree

$E_0 + H_{corr}$: -1778.345691 hartree

$E_0 + G_{corr}$: -1778.430985 hartree

| | | | |
|---|---|---|---|
| Mg | 1.242719 | 0.234796 | -0.182190 |
| C | -0.925405 | 1.022805 | 0.102293 |
| C | -1.773079 | 1.913911 | -0.165516 |
| Cl | 1.972811 | 2.423855 | 0.234005 |
| O | 1.230729 | -0.854597 | 1.636843 |
| O | 3.358677 | -0.452793 | -0.367278 |
| Cl | 0.603365 | -1.275566 | -1.864311 |
| C | -2.472955 | 0.349264 | -0.052184 |
| C | -3.257811 | 0.125465 | 1.093465 |
| C | -2.766248 | -0.338900 | -1.242126 |
| C | -4.320566 | -0.768301 | 1.047384 |
| H | -3.022379 | 0.659800 | 2.006754 |
| C | -3.825454 | -1.238731 | -1.277328 |
| H | -2.132103 | -0.189779 | -2.106644 |
| C | -4.603766 | -1.450919 | -0.138331 |
| H | -4.926784 | -0.936211 | 1.930279 |
| H | -4.039991 | -1.780048 | -2.191367 |
| H | -5.430683 | -2.151479 | -0.172320 |
| C | 4.288921 | 0.300780 | -1.157748 |
| H | 4.032869 | 1.350190 | -1.033636 |
| H | 5.307861 | 0.118374 | -0.799631 |
| H | 4.210957 | 0.009411 | -2.210883 |
| C | 3.639494 | -1.854591 | -0.410357 |

**MeC ≡ CPh•MgCl$_2$•2(OMe$_2$) (4e•MgCl$_2$)**

No. of imaginary frequencies: 0

$E_0$: -1778.752561 hartree

$E_0 + E_{ZPE}$: -1778.448488 hartree

$E_0 + E_{tot}$: -1778.422622 hartree

$E_0 + H_{corr}$: -1778.421678 hartree

$E_0 + G_{corr}$: -1778.511354 hartree

| | | | |
|---|---|---|---|
| Mg | 1.911076 | -0.013126 | -0.359925 |
| C | -2.538710 | 1.598971 | -0.372733 |
| C | -1.907650 | 2.616281 | -0.534134 |
| Cl | 2.446169 | 2.208557 | -0.382877 |
| O | 0.764243 | -0.231106 | 1.369374 |
| O | 3.728186 | -0.909960 | 0.186089 |
| Cl | 1.027031 | -1.538741 | -1.808075 |
| C | -3.278636 | 0.388791 | -0.200573 |
| C | -4.417578 | 0.352792 | 0.624645 |
| C | -2.881247 | -0.790358 | -0.857991 |
| C | -5.135767 | -0.827680 | 0.786498 |
| H | -4.732736 | 1.258656 | 1.129122 |
| C | -3.606190 | -1.966419 | -0.690622 |
| H | -2.001307 | -0.777888 | -1.490518 |
| C | -4.734374 | -1.991329 | 0.129643 |
| H | -6.013566 | -0.838285 | 1.423238 |
| H | -3.287493 | -2.865407 | -1.206398 |
| H | -5.298218 | -2.909031 | 0.254100 |
| C | 4.784309 | -0.197168 | 0.853480 |
| H | 4.448141 | 0.828887 | 0.986119 |
| H | 4.993137 | -0.665338 | 1.820375 |
| H | 5.684943 | -0.208635 | 0.233068 |
| C | 4.085668 | -2.265897 | -0.136222 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 3.249446 | -2.697533 | -0.681813 | H | -0.601672 | 1.126012 | 2.156195 |
| H | 4.979908 | -2.269722 | -0.766010 | H | 0.660427 | 0.547951 | 3.294168 |
| H | 4.277699 | -2.826137 | 0.784119 | C | -1.140102 | 3.834658 | -0.753980 |
| C | -0.007827 | -1.415709 | 1.644641 | H | -1.391885 | 4.281845 | -1.720662 |
| H | -1.073999 | -1.184818 | 1.586223 | H | -1.347376 | 4.577272 | 0.022169 |
| H | 0.241799 | -2.150064 | 0.881876 | H | -0.066632 | 3.623499 | -0.749686 |
| H | 0.244257 | -1.791454 | 2.641019 | | | | |
| C | 0.451187 | 0.853806 | 2.264611 | | | | |
| H | 1.079867 | 1.694929 | 1.981300 | | | | |

**Table S1.** Selected geometric parameters of model compounds

| compound | distance (Å) | | | | angle (°) | | |
|---|---|---|---|---|---|---|---|
| | C-Cl | C1-C2 | C2-C3 | C3-C1 | C1-C2-C3 | C2-C3-C1 | C3-C1-C2 |
| (*E*)-**3e** | 1.864 | 1.346 | 1.495 | 2.425 | 117.0 | 29.6 | 33.3 |
| (*E*)-**3e**$^{‡}$ | 3.222 | 1.259 | 1.718 | 1.695 | 67.4 | 43.3 | 69.3 |
| (*E*)-**4e**•$MgCl_2$ | 5.022 | 1.208 | 2.637 | 1.429 | 0.5 | 0.4 | 179.2 |

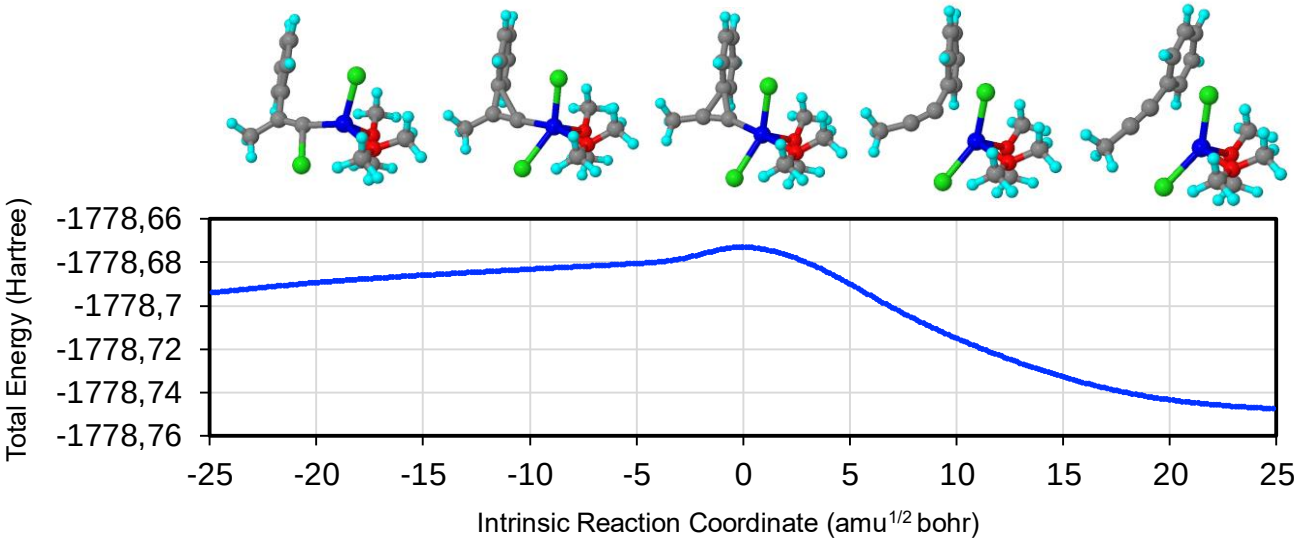



**Figure S1.** Intrinsic reaction coordinate for the FBW rearrangement of magnesium alkylidene carbenoid (*E*)-**3e**.

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