Supporting Information

for

One-pot preparation of 4-aryl-3-bromocoumarins from 4-aryl-2-propynoic acids with diaryliodonium salts, TBAB, and $Na_2S_2O_8$

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NMR charts of all coumarin derivatives 3Aa–3Ap, 3Ba–3Ea, and 4Aa–9Aa, and X-ray analytical data of 3Da

Table of contents

General

^{1}H NMR spectra were measured on 400 MHz spectrometers. Chemical shifts were recorded as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad), coupling constant (Hz), integration, and assignment. ^{13}C NMR spectra were measured on 100 MHz spectrometers. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard (deuterochloroform at 77.0 ppm). Characteristic peaks in the infrared (IR) spectra were recorded in wave number, cm^{-1}. High-resolution mass spectra were recorded by Thermo Fisher Scientific Exactive Orbitrap mass spectrometers. Melting points were uncorrected. Thin-layer chromatography (TLC) was performed using 0.25 mm silica gel plates (60F-254). The products were purified by column chromatography on neutral silica gel 60N (63–210 mesh).

Typical procedure for the one-pot conversion of 3-aryl-2-propynoic acids 1 into 4-aryl-3-bromocoumarins 3

To a mixture of 3-phenyl-2-propynoic acid (**1a**, 0.5 mmol, 73.1 mg), CuCl (5 mol %, 2.5 mg), and K_2CO_3 (0.25 mmol, 34.6 mg) in CH_2Cl_2 (7.5 mL) was added diphenyliodonium trifluoromethanesulfonate (0.5 mmol, 215.1 mg). The flask was flushed with argon gas, and then the obtained mixture was stirred for 3 h at 50 °C. The solvent was removed, and TBAB (1.0 mmol, 322.4 mg), $Na_2S_2O_8$ (1.0 mmol, 238.1 mg), and DCE/H_2O (1:1, 5.0 mL) were added to the residue. The obtained mixture was stirred for 19 h at 90 °C. Water (5.0 mL) was added to the reaction mixture and the product was extracted with $CHCl_3$ (15 mL × 3). The organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica-gel column chromatography (eluent: *n*-hexane/EtOAc = 9:1) to give 3-bromo-4-phenylcoumarin (**3Aa**, 81.5 mg, 54% yield).

3-Bromo-4-phenylcoumarin (3Aa)[1]: Yield: 81.5 mg (54%); white solid; Mp: 146-147 °C; IR (neat) 1725, 1273, 1034 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.08 (dd, 1H, *J* = 8.0, 1.6 Hz), 7.20 (td, 1H, *J* = 7.8, 1.1 Hz), 7.29-7.32 (m, 2H), 7.42 (dd, 1H, *J* = 8.3, 0.9 Hz), 7.52-7.60 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 112.5, 116.7, 120.2, 124.7, 127.6, 128.0, 128.8, 129.3, 132.0, 135.2, 152.4, 154.6, 157.3; HRMS (APCI) Calcd for $C_{15}H_{10}O_2Br$ $[M+H]^+$ = 300.9859, Found = 300.9857.

3-Bromo-4-(2'-methylphenyl)coumarin (3Ab): Yield: 90.3 mg (57%); white solid; Mp: 99-100 °C; IR (neat) 1729, 1275, 1035 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.12 (s, 3H), 6.93 (dd, 1H, *J* = 7.9, 1.4 Hz), 7.10 (d, 1H, *J* = 7.9 Hz), 7.18 (td, 1H, *J* = 7.4, 1.1 Hz), 7.35-7.46 (m, 4H), 7.57 (td, 1H, *J* = 7.6, 1.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 19.2, 112.9, 116.8, 119.9, 124.9, 126.3, 127.1, 127.4, 129.4, 130.6, 132.1, 134.8, 134.9, 152.4, 155.0, 157.3; HRMS (APCI) Calcd for $C_{16}H_{12}O_2Br$ $[M+H]^+$ = 315.0015, Found = 315.0015.

3-Bromo-4-(3'-methylphenyl)coumarin (3Ac): Yield: 85.3 mg (54%); colorless oil; IR (neat) 1725, 1276, 1037 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.45 (s, 3H), 7.10 (d, 1H, *J* = 8.7 Hz), 7.10 (d, 1H, *J* = 7.9 Hz), 7.10 (s, 1H), 7.19 (td, 1H, *J* = 7.9, 1.1 Hz), 7.34 (d, 1H, *J* = 7.5 Hz), 7.41 (dd, 1H, *J* = 8.4, 0.9 Hz), 7.45 (t, 1H, *J* = 7.9 Hz), 7.56 (td, 1H, *J* = 7.8, 1.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.5, 112.4, 116.7, 120.3, 124.6, 125.0, 127.7, 128.4, 128.7, 130.0, 132.0, 135.1, 138.6, 152.4, 154.8, 157.4; HRMS (APCI) Calcd for $C_{16}H_{12}O_2Br$ $[M+H]^+$ = 315.0015, Found = 315.0015.

3-Bromo-4-(4'-methylphenyl)coumarin (3Ad)[2]: Yield: 91.4 mg (58%); white solid; Mp: 163-164 °C; IR (neat) 1721, 1273, 1038 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.48 (s, 3H), 7.12 (dd, 1H, *J* = 7.9, 1.6 Hz), 7.16-7.51 (m, 3H), 7.37 (d, 2H, *J* = 7.9 Hz), 7.41 (dd, 1H, *J* = 8.4, 0.9 Hz), 7.56 (td, 1H, *J* = 7.7, 1.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.4, 112.6, 116.8, 120.4, 124.6, 127.7, 128.0, 129.5, 132.0, 132.3, 139.4, 152.4, 154.8, 157.5; HRMS (APCI) Calcd for $C_{16}H_{12}O_2Br$ $[M+H]^+$ = 315.0015, Found = 315.0015.

3-Bromo-4-(4'-methoxyphenyl)coumarin (3Ae)[2]: Yield: 86.2 mg (52%); pale yellow solid; Mp: 167-168 °C; IR (neat) 1730, 1251, 1034 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.91 (s, 3H), 7.08 (d, 2H, *J* = 8.8 Hz), 7.16 (dd, 1H, *J* = 8.2, 1.8 Hz), 7.20 (td, 1H, *J* = 7.6, 1.1 Hz), 7.26 (d, 2H, *J* = 8.8 Hz), 7.41 (d, 1H, *J* = 8.4 Hz), 7.56 (td, 1H, *J* = 7.6, 2.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 55.3, 112.7, 114.1, 116.7, 120.4, 124.6, 127.2, 127.7, 129.7, 131.9, 152.3, 134.4, 157.4, 160.2; HRMS (APCI) Calcd for $C_{16}H_{12}O_3Br$ $[M+H]^+$ = 330.9964, Found = 330.9962.

3-Bromo-4-(4'-fluorophenyl)coumarin (3Af)[2]: Yield: 82.3 mg (52%); white solid; Mp: 124-125 °C; IR (neat) 1710, 1275, 1038 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.07 (dd, 1H, *J* = 8.0, 1.4 Hz), 7.21 (td, 1H, *J* = 7.6, 1.1 Hz), 7.23-7.33 (m, 4H), 7.42 (dd, 1H, *J* = 8.4, 0.9 Hz), 7.58 (td, 1H, *J* = 7.8, 1.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ

= 113.1, 116.2 ($J_{C\text{-}F}$ = 21.9 Hz), 116.9, 120.2, 124.8, 127.4, 130.2 ($J_{C\text{-}F}$ = 8.6 Hz), 131.1 ($J_{C\text{-}F}$ = 3.8 Hz), 132.2, 152.4, 153.7, 157.2, 163.1 ($J_{C\text{-}F}$ = 249.9 Hz); HRMS (APCI) Calcd for $C_{15}H_9O_2BrF$ $[M+H]^+$ = 318.9764, Found = 318.9764

3-Bromo-4-(4'-chlorophenyl)coumarin (3Ag)[2]: Yield: 152.2 mg (50%); white solid; Mp: 152-153 °C; IR (neat) 1717, 1277, 1037 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.06 (dd, 1H, *J* = 8.2, 1.6 Hz), 7.21 (td, 1H, *J* = 7.6, 1.1 Hz), 7.25-7.28 (m, 2H), 7.42 (dd, 1H, *J* = 8.4, 1.1 Hz), 7.56 (d, 2H, *J* = 8.4 Hz), 7.58 (td, 1H, *J* = 7.8, 1.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ =112.9, 117.0, 120.0, 124.8, 127.3, 129.3, 129.6, 132.3, 133.5, 135.6, 152.4, 153.5, 157.1; HRMS (APCI) Calcd for $C_{15}H_9O_2BrCl$ $[M+H]^+$ = 334.9469, Found = 334.9468.

3-Bromo-4-(2'-chlorophenyl)coumarin (3Ah): Yield: 106.7 mg (64%); white solid; Mp: 162-163 °C; IR (neat) 1732, 1277, 1036 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.94 (dd, 1H, *J* = 7.9, 1.4 Hz), 7.21 (t, 1H, *J* = 7.7 Hz), 7.25 (dd, 1H, *J* = 7.3, 2.0 Hz) , 7.43 (d, 1H, *J* = 8.4 Hz), 7.45-7.53 (m, 2H), 7.56-7.62 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 113.6, 116.8, 119.4, 124.9, 126.8, 127.4, 129.4, 130.0, 130.8, 132.0, 132.1, 134.2, 152.3, 152.4, 157.1; HRMS (APCI) Calcd for $C_{15}H_9O_2BrCl$ $[M+H]^+$ = 334.9469, Found = 334.9468.

3-Bromo-4-(3'-chlorophenyl)coumarin (3Ai): Yield: 95.2 mg (57%); white solid; Mp: 138-139 °C; IR (neat) 1715, 1276, 1038 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.06 (dd, 1H, *J* = 8.0, 1.6 Hz), 7.18-7.25 (m, 2H), 7.32 (s, 1H), 7.42 (d, 1H, *J* = 8.4 Hz), 7.49-7.55 (m, 2H), 7.59 (td, 1H, *J* = 8.0, 1.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 112.8, 116.8, 119.7, 124.8, 126.3, 127.2, 128.0, 129.5, 130.3, 132.2, 134.8, 136.7, 152.2, 152.9, 156.9; HRMS (APCI) Calcd for $C_{15}H_9O_2BrCl$ $[M+H]^+$ = 334.9469, Found = 334.9468.

3-Bromo-4-(4'-bromophenyl)coumarin (3Aj): Yield: 95.2 mg (51%); white solid; Mp: 154-155 °C; IR (neat) 1718, 1276, 1037 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.06 (dd, 1H, *J* = 7.9, 1.6 Hz), 7.18-7.23 (m, 3H), 7.42 (dd, 1H, *J* = 8.4, 1.1 Hz), 7.58 (td, 1H, *J* = 7.9, 1.6 Hz), 7.72 (d, 2H, *J* = 8.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 112.8, 116.9, 119.9, 123.8, 124.8, 127.2, 129.8, 132.2, 132.2, 134.0, 152.4, 153.4, 157.1; HRMS (APCI) Calcd for $C_{15}H_9O_2Br_2$ $[M+H]^+$ = 378.8964, Found = 378.8966.

4-(Biphenyl-4'-yl)-3-bromocoumarin (3Ak): Yield: 107.6 mg (57%); yellow solid;

Mp: 199-200 °C; IR (neat) 1733, 1275, 1036 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.18 (dd, 1H, *J* = 8.0, 1.8 Hz), 7.22 (td, 1H, *J* = 7.4, 1.1 Hz), 7.39 (d, 2H, *J* = 8.4 Hz), 7.43 (d, 2H, *J* = 8.6 Hz), 7.51 (t, 2H, *J* = 7.3 Hz), 7.58 (td, 1H, *J* = 7.6, 2.0 Hz), 7.69 (d, 2H, *J* = 7.5 Hz), 7.79 (d, 2H, *J* = 8.4 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 112.6, 116.8, 120.2, 124.7, 127.1, 127.4, 127.6, 127.9, 128.6, 128.9, 132.0, 134.0, 139.9, 142.1, 152.4, 154.4, 157.3; HRMS (APCI) Calcd for $C_{21}H_{14}O_2Br$ $[M+H]^+$ = 377.0172, Found = 377.0170.

3-Bromo-4-(naphthalen-2'-yl)coumarin (3Al): Yield: 88.3 mg (50%); white solid; Mp: 180-181 °C; IR (neat) 1721, 1275, 1038 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.11 (dd, 1H, *J* = 8.0, 1.6 Hz), 7.17 (td, 1H, *J* = 7.6, 1.1 Hz), 7.40 (dd, 1H, *J* = 8.4, 1.8 Hz), 7.44 (dd, 1H, *J* = 8.3, 0.7 Hz), 7.55-7.65 (m, 3H), 7.81 (s, 1H), 7.90-7.99 (m, 2H), 8.04 (d, 1H, *J* = 8.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 112.8, 116.8, 120.3, 124.7, 125.3, 126.9, 127.2, 127.7, 127.7, 127.9, 128.3, 128.7, 132.1, 132.5, 132.8, 133.2, 152.4, 154.6, 157.4; HRMS (APCI) Calcd for $C_{19}H_{12}O_2Br$ $[M+H]^+$ = 351.0015, Found = 351.0013.

3-Bromo-4-(naphthalen-1'-yl)coumarin (3Am): Yield: 98.3 mg (56%); white solid; Mp: 106-107 °C; IR (neat) 1731, 1277, 1035 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.83 (dd, 1H, *J* = 8.0, 1.6 Hz), 7.08 (dt, 1H, *J* = 7.6, 1.1 Hz), 7.39 (dd, 1H, *J* = 7.0, 1.1 Hz), 7.44-7.48 (m, 3H), 7.54-7.58 (m, 2H), 7.65 (t, 1H, *J* = 7.6 Hz), 7.99 (d, 1H, *J* = 8.2 Hz), 8.04 (d, 1H, *J* = 8.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 114.1, 116.8, 120.6, 124.6, 124.8, 125.4, 126.0, 126.7, 127.2, 127.7, 128.7, 129.6, 129.7, 132.1, 132.8, 133.5, 152.3, 154.1, 157.3; HRMS (APCI) Calcd for $C_{19}H_{12}O_2Br$ $[M+H]^+$ = 351.0015, Found = 351.0014.

4-(Benzo[*b*]thiophen-2'-yl)-3-bromocoumarin (3An): Yield: 82.7 mg (46%); red solid; Mp: 214-215 °C; IR (neat) 1722, 1272, 1038 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.23 (td, 1H, *J* = 7.7, 0.9 Hz), 7.39 (dd, 1H, *J* = 8.0, 1.4 Hz), 7.39 (s, 1H), 7.43 (d, 1H, *J* = 8.4 Hz), 7.45-7.51 (m, 2H), 7.59 (td, 1H, *J* = 7.8, 1.6 Hz), 7.88-7.96 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 115.2, 116.8, 120.2, 122.4, 124.4, 124.9, 125.0, 125.5, 125.8, 127.4, 132.3, 134.8, 139.1, 140.6, 148.5, 152.1, 156.9; HRMS (APCI) Calcd for $C_{17}H_{10}O_2BrS$ $[M+H]^+$ = 356.9579, Found = 356.9579.

4-(Benzofuran-2'-yl)-3-bromocoumarin (3Ao): Yield: 73.0 mg (43%); white solid; Mp: 129-130 °C; IR (neat) 1739, 1278, 1038 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ =

7.28-7.31 (m, 2H), 7.37 (t, 1H, *J* = 7.7 Hz), 7.41-7.48 (m, 2H), 7.57-7.64 (m, 3H), 7.75 (d, 1H, *J* = 7.9 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 111.7, 111.8, 114.3, 117.0, 118.8, 122.0, 123.8, 124.9, 126.1, 127.1, 127.4, 132.3, 143.5, 148.1, 152.3, 155.0, 157.1; HRMS (APCI) Calcd for $C_{17}H_{10}O_3Br$ $[M+H]^+$ = 340.9808, Found = 340.9808.

3-Bromo-4-propylcoumarin (3Ap): Yield: 55.6 mg (42%); white solid; Mp: 58-59 °C; IR (neat) 2931, 1720, 1272, 1036 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.13 (s, 3H, *J* = 7.3 Hz), 1.72 (sextet, 2H, *J* = 8.2 Hz), 3.03 (t, 2H, *J* = 8.2 Hz), 7.34 (td, 1H, *J* = 7.7, 1.1 Hz), 7.37 (d, 1H, *J* = 8.2 Hz), 7.57 (td, 1H, *J* = 7.7, 1.4 Hz), 7.66 (dd, 1H, *J* = 8.2, 1.4 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 14.3, 21.5, 34.6, 112.7, 117.2, 118.9, 124.8, 124.8, 131.8, 152.1, 154.7, 157.1; HRMS (APCI) Calcd for $C_{12}H_{12}O_2Br$ $[M+H]^+$ = 267.0015, Found = 267.0015.

3-Bromo-7-methyl-4-phenycoumarin (3Ba): Yield: 95.2 mg (60%); white solid; Mp: 186-187 °C; IR (neat) 1722, 1255, 1022 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.44 (s, 3H), 6.95 (d, 1H, *J* = 8.2 Hz), 7.00 (dd, 1H, *J* = 8.2, 0.9 Hz), 7.21 (s, 1H), 7.29 (dd, 2H, *J* = 7.6, 1.4 Hz), 7.51-7.59 (m, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.6, 111.2, 116.8, 117.9, 125.9, 127.2, 128.0, 128.7, 129.2, 135.3, 143.5, 152.4, 154.6, 157.6; HRMS (APCI) Calcd for $C_{16}H_{12}O_2Br$ $[M+H]^+$ = 315.0015, Found = 315.0014.

3-Bromo-7-(*tert*-butyl)-4-phenylcoumarin (3Ca): Yield: 124.6 mg (70%); white solid; Mp: 132-133 °C; IR (neat) 2951, 1718, 1281, 1031 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.34 (s, 9H), 7.01 (d, 1H, *J* = 8.4 Hz), 7.22 (dd, 1H, *J* = 8.4, 1.8 Hz), 7.27-7.33 (m, 2H), 7.41 (d, 1H, *J* = 1.8 Hz), 7.50-7.58 (m, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 30.8, 35.1, 111.3, 113.4, 117.7, 122.2, 127.1, 127.9, 128.7, 129.2, 135.2, 152.3, 154.4, 156.6, 157.6; HRMS (APCI) Calcd for $C_{19}H_{18}O_2Br$ $[M+H]^+$ = 357.0485, Found = 357.0484.

3-Bromo-7-chloro-4-phenylcoumarin (3Da): Yield: 77.6 mg (46%); white solid; Mp: 191-192 °C; IR (neat) 1731, 1237, 1034 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.01 (d, 1H, *J* = 8.6 Hz), 7.16 (dd, 1H, *J* = 8.7, 1.8 Hz), 7.27-7.30 (m, 2H), 7.42 (s, 1H), 7.52-7.60 (m, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 112.5, 117.0, 118.9, 125.3, 127.9, 128.4, 128.9, 129.5, 134.8, 137.9, 152.5, 153.9, 156.7; HRMS (APCI) Calcd for $C_{15}H_9O_2BrCl$ $[M+H]^+$ = 334.9469, Found = 334.9469.

Crystal Data for 3-Bromo-7-chloro-4-phenylcoumarin 3Da: Formula $C_{15}H_8BrClO_2$, colorless, crystal dimensions 0.20 × 0.20 × 0.10 mm^3, Plate, space group P 1 21/c 1', a = 9.6791(10) Å, b = 15.5782(17) Å, c = 8.9056(10) Å, α = 90°, β = 102.9168(15)°, γ = 90°, V = 1308.8(2) $Å^3$, Z = 4, ρ_{calc} = 1.269 g cm^{-3}, F(000) = 664, μ(MoKα) = 3.337 mm^{-1}, T = 173 K. 7298 reflections collected, 2994 independent reflections with $I > 2\sigma(I)$ ($2\theta_{max}$ = 27.56°), and 172 parameters were used for the solution of structure. The non-hydrogen atoms were refined anisotropically. R_1 = 0.0286 and wR_2 = 0.0657. GOF = 1.053. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1587945. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

3,7-Dibromo-4-phenylcoumarin (3Ea): Yield: 79.5 mg (42%); white solid; Mp: 186-187 °C; IR (neat) 1730, 1235, 1069 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.94 (d, 1H, J = 8.6 Hz), 7.27-7.33 (m, 3H), 7.54-7.61 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 112.7, 119.3, 119.9, 125.9, 127.9, 128.1, 128.6, 129.0, 129.5, 134.7, 152.4, 154.0, 156.7; HRMS (APCI) Calcd for $C_{15}H_9O_2Br_2$ $[M+H]^+$ = 378.8964, Found = 378.8964.

Preparation of 4-phenylcoumarin (4Aa)

To a mixture of 3-bromo-4-phenylcoumarin (**3Aa**, 0.5 mmol, 150.6 mg) in EtOH (7.5 mL) was added Zn powder (5 mmol, 363.3 mg). Under argon atmosphere, the obtained mixture was stirred for 16 h at refluxing temperature. The cooled mixture was filtered through celite, and then the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: *n*-hexane/AcOEt = 9:1) to afford 4-phenylcoumarin (**4Aa**, 89.9 mg, 81% yield).

4-Phenylcoumarin (4Aa)[3]: Yield: 89.9 mg (81%); white solid; IR (neat) 1722, 1277, 1034 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.39 (s, 1H), 7.24 (td, 1H, J = 7.7, 0.9 Hz), 7.42 (dd, 1H, J = 8.3, 0.9 Hz), 7.45-7.59 (m, 7H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 115.2, 117.3, 119.0, 124.1, 127.0, 128.4, 128.8, 129.7, 131.9, 135.2, 154.2, 155.7, 160.8; HRMS (APCI) Calcd for $C_{15}H_{11}O_2$ $[M+H]^+$ = 223.0754, Found = 223.0753.

Preparation of 4-phenyl-3-(4'-methylbenzenesulfenyl)coumarin (5Aa)

To a mixture of 3-bromo-4-phenylcoumarin (**3Aa**, 0.5 mmol, 150.6 mg) and K_2CO_3 (1.5 mmol, 103.7 mg), CuI (0.010 mmol, 9.6 mg), and DMEDA (0.020 mmol, 10μL) in

toluene (2.0 mL) was added *p*-toluenethiol (1.2 mmol, 74.6 mg). Under argon atmosphere, the obtained mixture was stirred for 2 h at 135 °C. Saturated $NaHCO_3$ aqueous solution (5.0 mL) was added to the reaction mixture, and the product was extracted with $CHCl_3$ (15 mL × 3). The organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica-gel column chromatography (eluent: *n*-hexane/EtOAc = 9:1) to give 4-phenyl-3-(4'-methylbenzenesulfenyl)coumarin (**5Aa**, 106.6 mg, 62% yield).

4-Phenyl-3-(4'-methylbenzenesulfenyl)coumarin (5Aa): Yield: 106.6 mg (62%); yellow oil; IR(neat) 1719, 1276, 1036 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.28 (s, 3H), 7.02 (d, 2H, *J* = 7.9 Hz), 7.08-7.20 (m, 3H), 7.18 (td, 1H, *J* = 7.8, 1.1 Hz) , 7.24-7.28 (m, 1H), 7.39 (dd, 1H, *J* = 8.4, 0.9 Hz), 7.47-7.60 (m, 5H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.0, 116.7, 120.4, 122.3, 124.2, 128.0, 128.3, 128.4, 128.9, 129.7, 129.8, 131.0, 132.0, 134.8, 136.8, 153.2, 158.3, 159.1; HRMS (APCI) Calcd for $C_{22}H_{17}O_2S$ $[M+H]^+$ = 345.0944, Found = 345.0943.

Preparation of 3-(4'-methoxybenzoylamino)-4-phenylcoumarin (6Aa)

To a mixture of 3-bromo-4-phenylcoumarin (**3Aa**, 0.5 mmol, 150.6 mg) and K_2CO_3 (1.5 mmol, 103.7 mg), CuI (0.010 mmol, 9.6 mg), and DMEDA (0.020 mmol, 10μL) in toluene (2.0 mL) was added *p*-methoxybenzamide (1.2 mmol, 90.7 mg). Under argon atmosphere, the obtained mixture was stirred for 2 h at 135 °C. Saturated $NaHCO_3$ aqueous solution (5.0 mL) was added to the reaction mixture, and the product was extracted with $CHCl_3$ (15 mL × 3). The organic layer was dried over Na_2SO_4. The organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica-gel column chromatography (eluent: *n*-hexane/EtOAc = 1:1) to give *N*-(4'-phenylcoumarin-3'-yl)-4-methoxybenzamide (**6Aa**, 95.2 mg, 51% yield).

3-(4'-Methoxybenzoylamino)-4-phenylcoumarin (6Aa): Yield: 95.2 mg (51%); white solid; Mp: 234-235 °C; IR(neat) 1718, 1654, 1605, 1254, 1029 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.83 (s, 3H), 6.87 (d, 2H, *J* = 8.8 Hz) , 7.23 (td, 1H, *J* = 7.6, 1.1 Hz), 7.33 (dd, 1H, *J* = 8.0, 1.4 Hz) , 7.37-7.49 (m, 6H), 7.54 (td, 1H, *J* = 7.6, 1.6 Hz), 7.64 (d, 2H, *J* = 8.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 55.4, 113.7, 116.8, 120.2, 120.8, 124.6, 125.7, 127.2, 128.4, 128.5, 128.9, 129.3, 131.2, 133.1, 147.2, 151.9, 160.0, 162.6, 165.3; HRMS (APCI) Calcd for $C_{23}H_{18}O_4N$ $[M+H]^+$ = 372.1230, Found = 372.1228.

Preparation of (*E*)-3-(4'-methylstyryl)-4-phenylcoumarin (7Aa)

To a mixture of 3-bromo-4-phenylcoumarin **(3Aa)** (0.5 mmol, 150.6 mg), K_2CO_3 (1.0 mmol, 138.2 mg), and $PdCl_2(PPh_3)_2$ (0.010 mmol, 7.0 mg) in DMF (5.0 mL) was added 4-methylstyrene (1.0 mmol, 68 μL). Under argon atmosphere, the obtained mixture was stirred for 3 h at 90 °C. Saturated $NaHCO_3$ aqueous solution (5.0 mL) was added to the reaction mixture, and the product was extracted with EtOAc (15 mL × 3), and washed with brine (15 mL). The organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica-gel column chromatography (eluent: *n*-hexane:EtOAc = 9:1) to give (*E*)-3-(4'-methylstyryl)-4-phenylcoumarin (**7Aa**) (133.4 mg, 79% yield).

(*E*)-3-(4'-Methylstyryl)-4-phenylcoumarin (7Aa): Yield: 133.4 mg (79%); light yellow solid; Mp: 129-130 °C; IR (neat) 3067, 1715, 1256, 969 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.30 (s, 3H), 6.65 (d, 1H, *J* = 16.2 Hz), 7.04-7.08 (m, 3H), 7.12-7.17 (m, 3H), 7.29-7.33 (m, 2H), 7.38 (dd, 1H, *J* = 8.2, 1.1 Hz), 7.48 (td, 1H, *J* = 7.8, 1.6 Hz), 7.52-7.60 (m, 3H), 7.91 (d, 1H, *J* = 16.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ =21.3, 116.4, 120.8, 120.9, 121.6, 124.1, 126.8, 127.4, 128.8, 128.9, 129.0, 129.3, 130.9, 134.7, 134.9, 135.6, 138.1, 149.8, 152.1, 160.0; HRMS (APCI) Calcd for $C_{24}H_{19}O_2$ $[M+H]^+$ = 339.1380, Found = 339.1377.

Preparation of 4-phenyl-3-(phenylethynyl)coumarin (8Aa)

To a mixture of 3-bromo-4-phenylcoumarin (**3Aa**, 0.5 mmol, 150.6 mg) and CuI (0.010 mmol, 1.9 mg) and $PdCl_2(PPh_3)_2$ (0.010 mmol, 7.0 mg) in Et_3N (2.5 mL) was added ethynylbenzene (0.6 mmol, 66 μL). Under argon atmosphere, the obtained mixture was stirred for 3 h at 60 °C. Water (2.5 mL) was added to the reaction mixture, and the product was extracted with EtOAc (15 mL × 3), and washed with brine (15 mL). The organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica-gel column chromatography (eluent: *n*-hexane:EtOAc = 9:1) to give 4-phenyl-3-(phenylethynyl)coumarin (**8Aa**, 96.4 mg, 60% yield).

4-Phenyl-3-(phenylethynyl)coumarin (8Aa): Yield: 96.4 mg (60%); yellow solid; Mp: 159-160 °C; IR (neat) 2207, 1716, 1246, 1064 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.19-7.33 (m, 7H), 7.42 (dd, 1H, *J* = 8.4, 0.9 Hz), 7.48-7.61 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 83.7, 98.7, 111.1, 117.0, 119.7, 122.4, 124.5, 127.6, 128.2, 128.4, 128.8, 129.1, 129.4, 131.7, 132.0, 134.3, 152.8, 156.2, 159.5; HRMS (APCI) Calcd for

$C_{23}H_{15}O_2$ $[M+H]^+$ = 323.1067, Found = 323.1064.

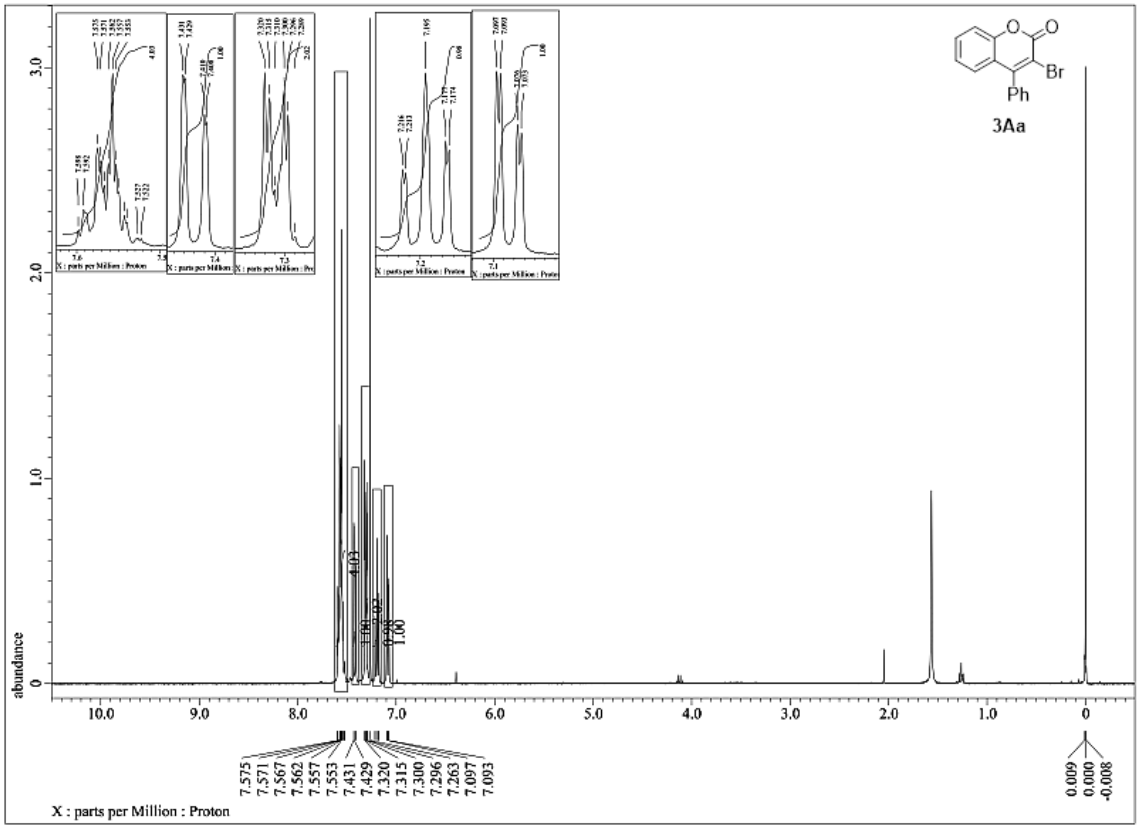
Preparation of 3,4-diphenylcoumarin (9Aa)

To a mixture of 3-bromo-4-phenylcoumarin **(3Aa**, 0.5 mmol, 150.6 mg) and $PhB(OH)_2$ (1.0 mmol, 121.9 mg) in DMF (10 mL) was added $PdCl_2(PPh_3)_2$ (0.025 mmol, 17.5 mg). Under the argon atmosphere, the obtained mixture was stirred for 30 min at room temperature. Then, K_2CO_3 (1.0 mmol, 138.2 mg) in H_2O (2 mL) was added to the mixture, and the obtained mixture was stirred for 1.5 h at 60 °C. Water (5 mL) was added to the reaction mixture, and the product was extracted with CH_2Cl_2 (15 mL × 3), and washed with brine (15 mL × 2). The organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica-gel column chromatography (eluent: *n*-hexane/EtOAc = 9:1) to give 3,4-diphenylcoumarin (**9Aa**, 113.7 mg, 76% yield).

3,4-Diphenylcoumarin (9Aa)*[1]*: Yield: 113.7 mg (76%); white solid; Mp: 223-224 °C; IR (neat) 1711, 1297, 1038 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.10-7.25 (m, 9H), 7.28-7.35 (m, 3H), 7.44 (dd, 1H, *J* = 8.3, 0.7 Hz), 7.54 (td, 1H, *J* = 7.4, 2.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 116.7, 120.4, 124.1, 126.9, 127.6, 127.7, 127.8, 128.2, 128.3, 129.3, 130.5, 131.4, 133.8, 134.4, 151.6, 153.2, 161.3; HRMS (APCI) Calcd for $C_{21}H_{15}O_2$ $[M+H]^+$ = 299.1067, Found = 299.1065.

References

1. Zhang, L.; Meng, T.; Fan, T.; Wu, J. *J. Org. Chem*. **2007**, *72*, 7279-7286.
2. Qiu, G.; Liu, T.; Ding, Q. *Org. Chem. Front.* **2016**, *3*, 510-515.
3. Sasaki, T.; Miyagi, K.; Moriyama, K.; Togo, H. *Org. Lett*. **2016**, *18*, 944-947.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abundance
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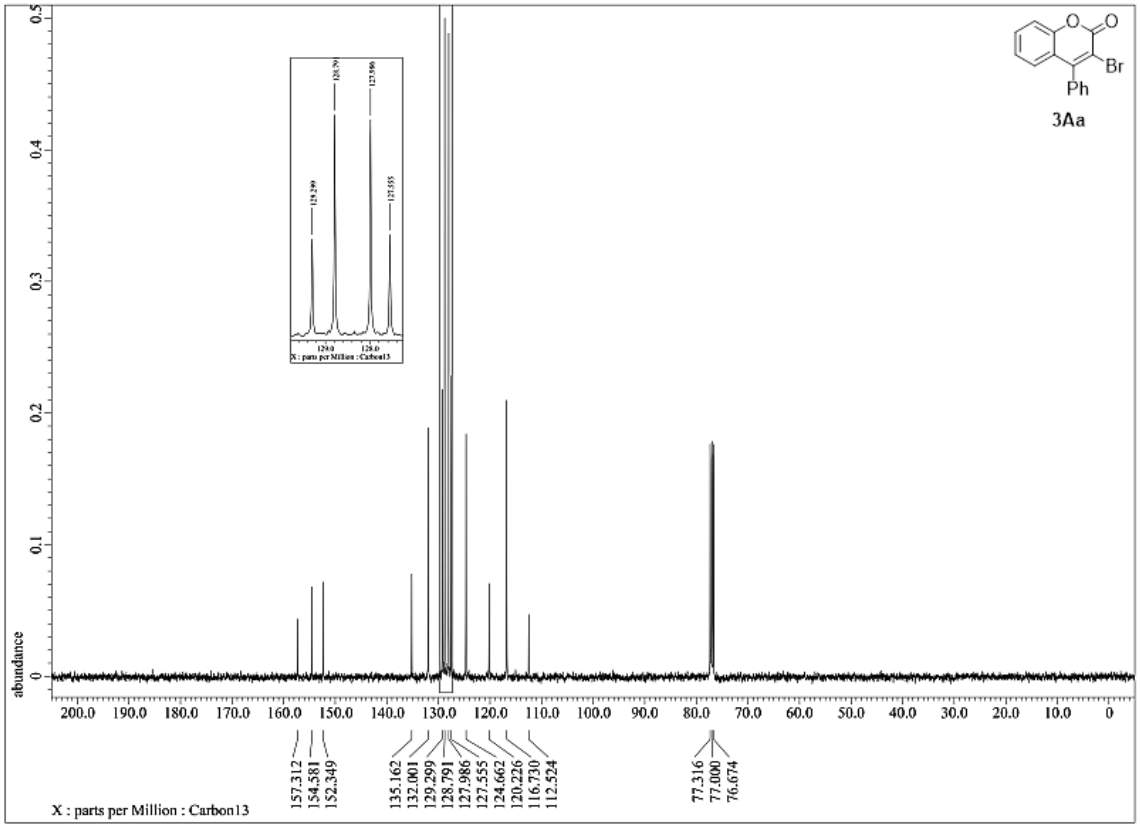
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abundance
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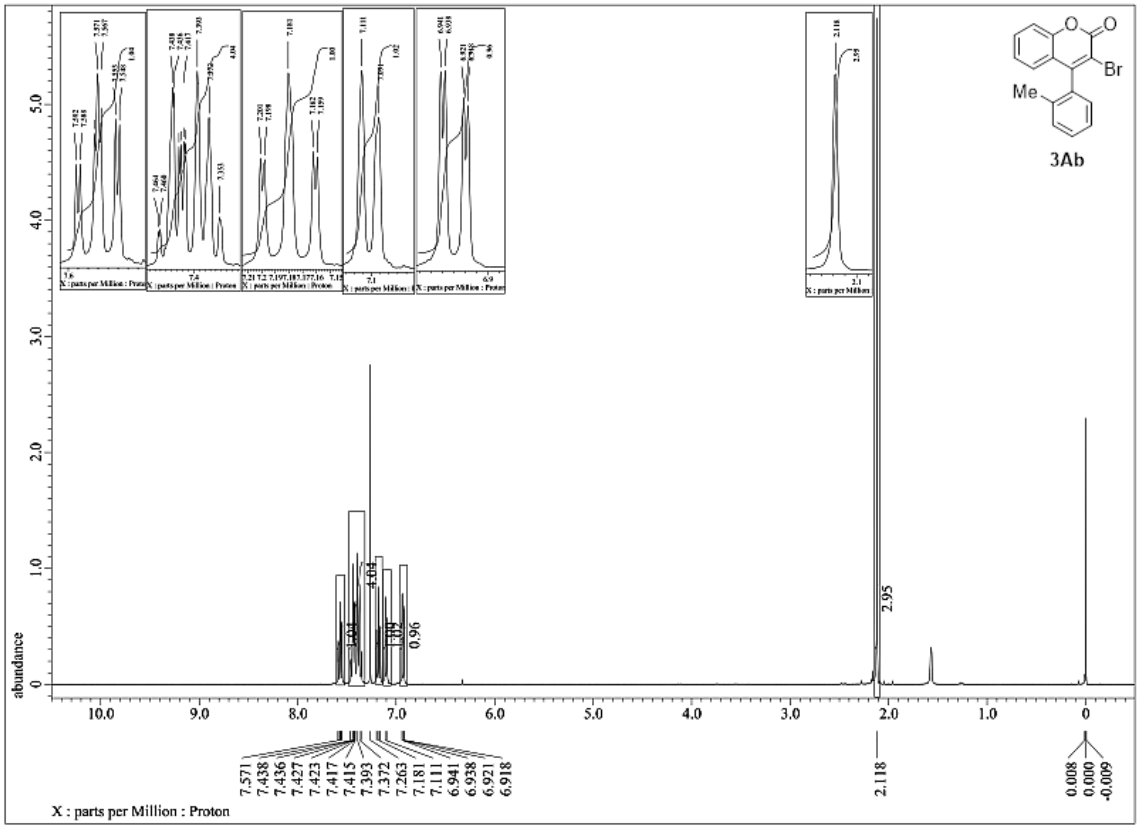
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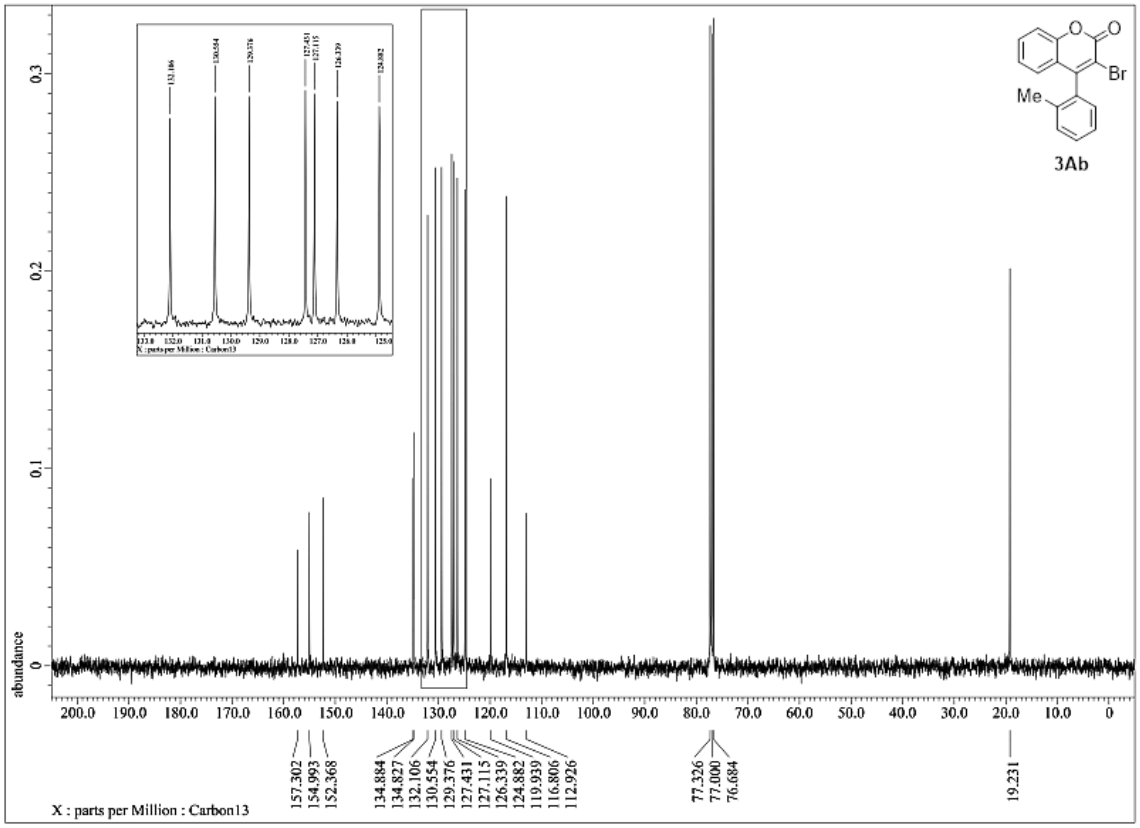
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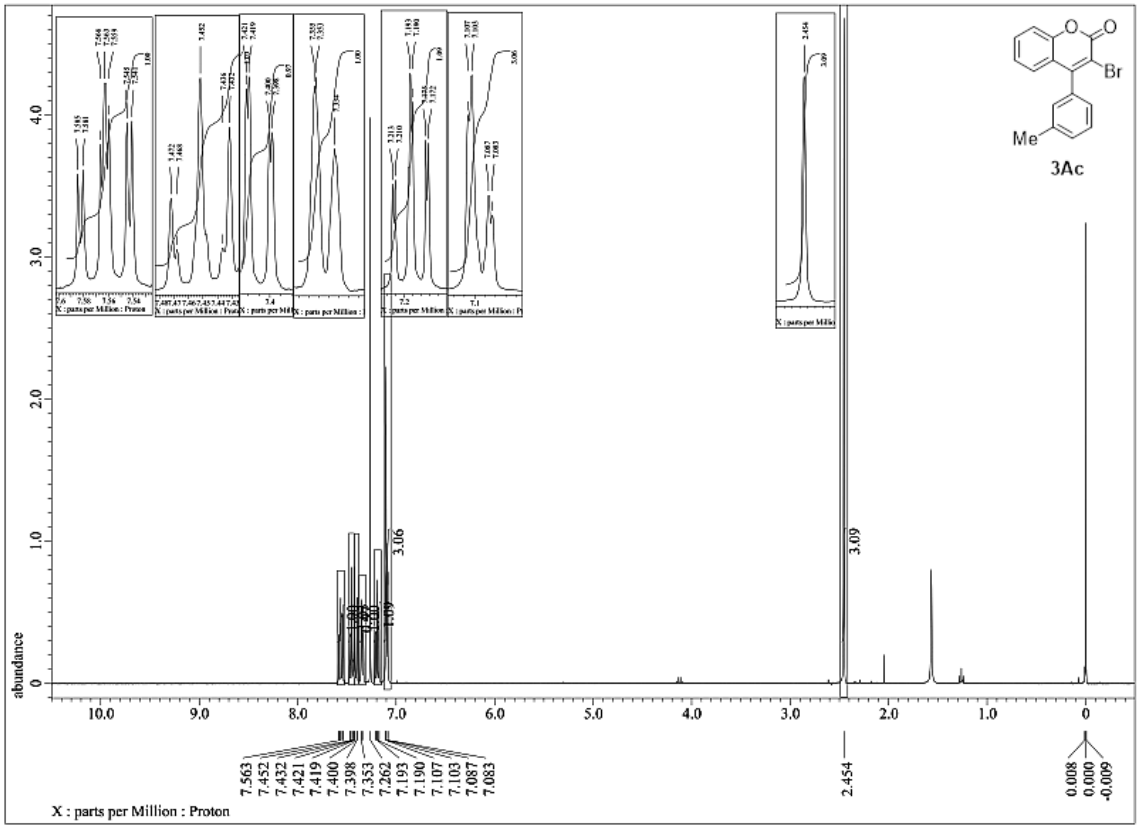
X : parts per Million : Carbon13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7.400
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7.103
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7.083
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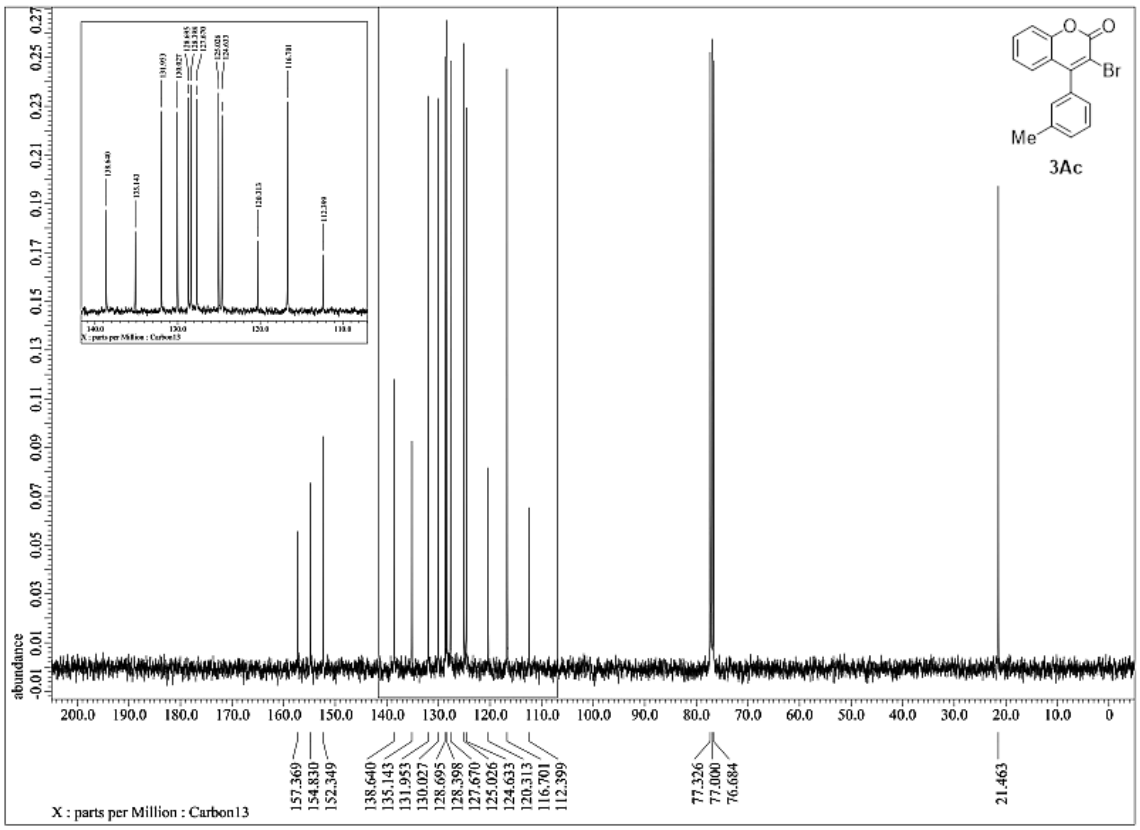
X : parts per Million : Proton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abundance
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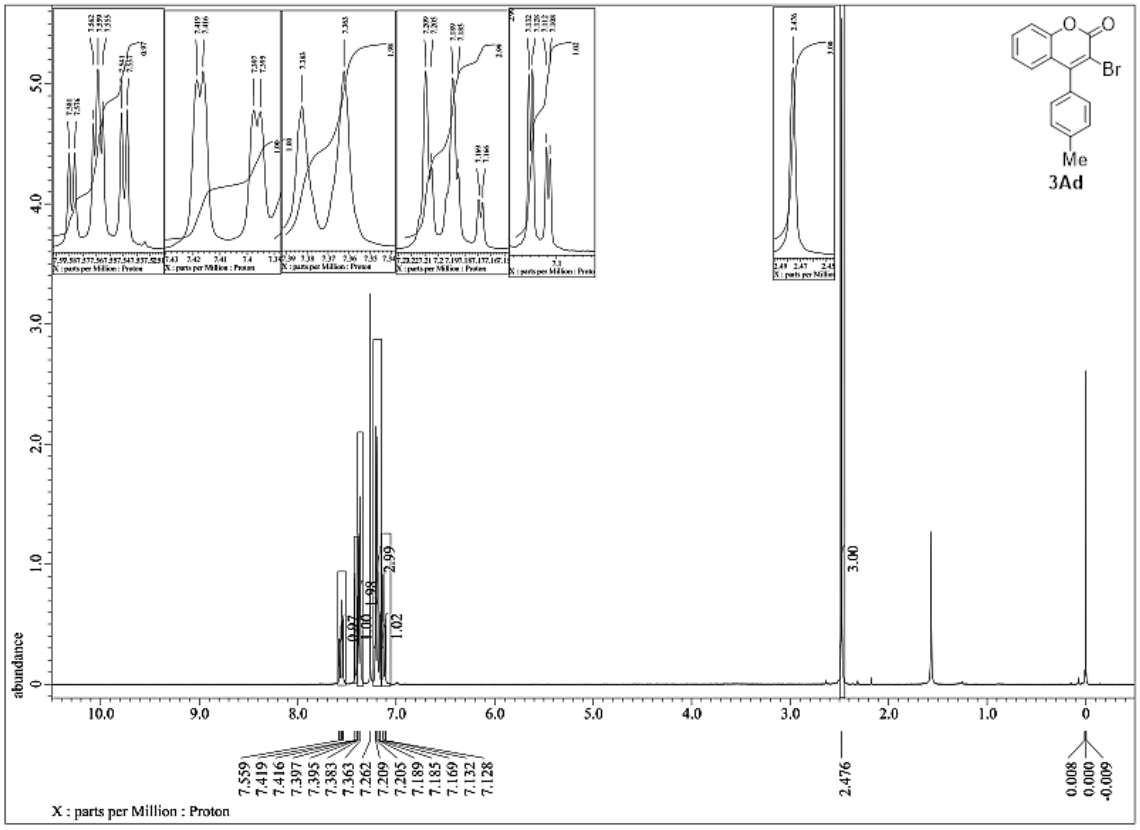
77.000
76.684
21.463
X : parts per Million : Carbon13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abundance
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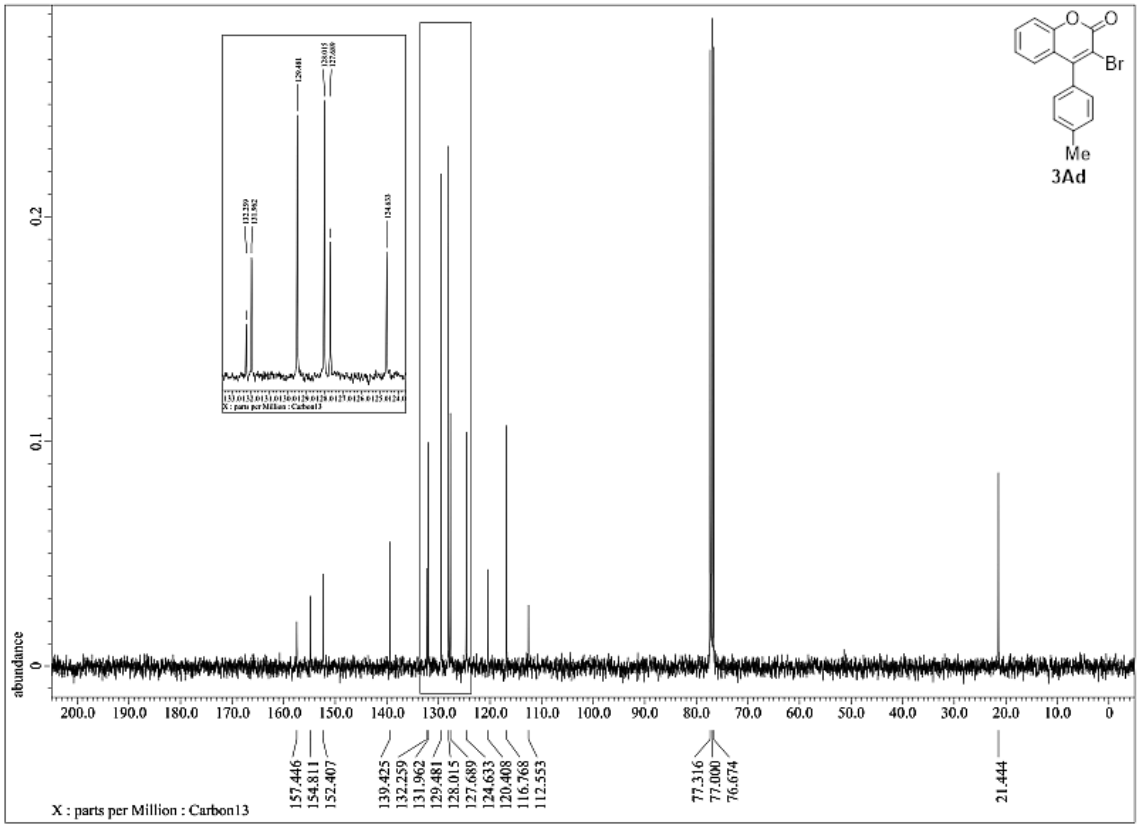
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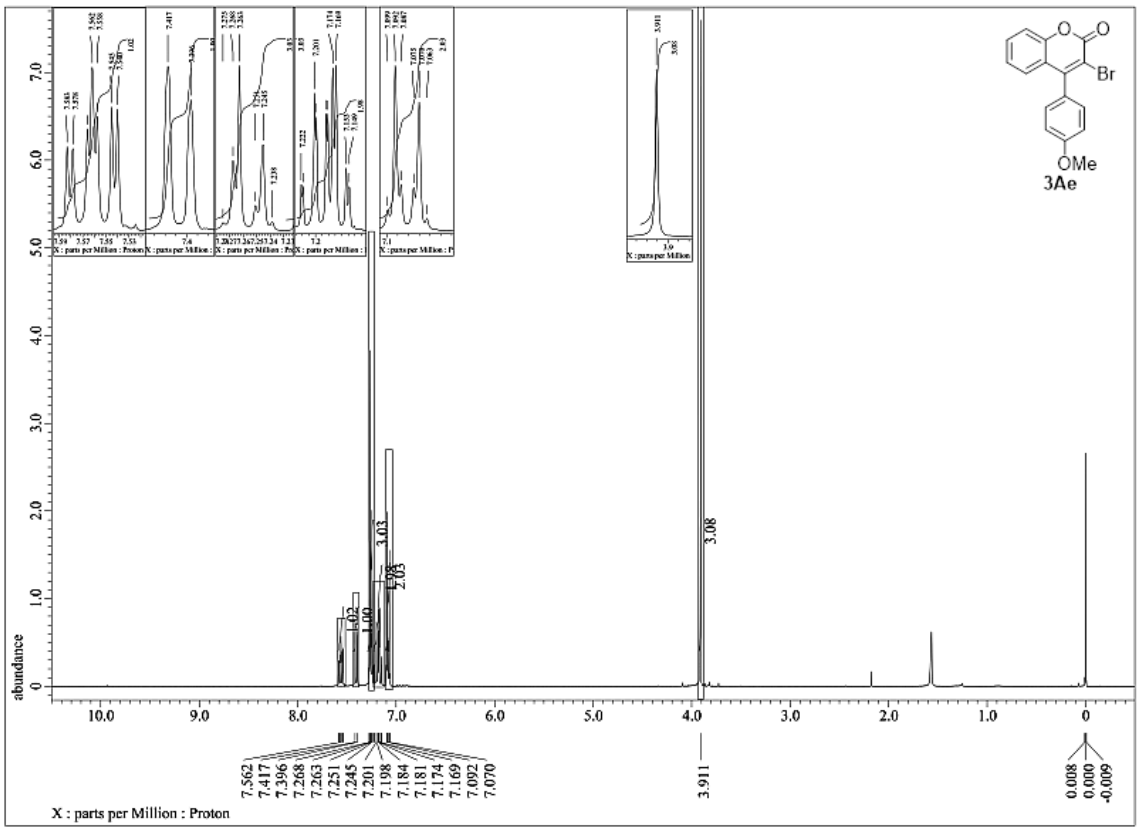
3Ae
abundance
X : parts per Million : Proton
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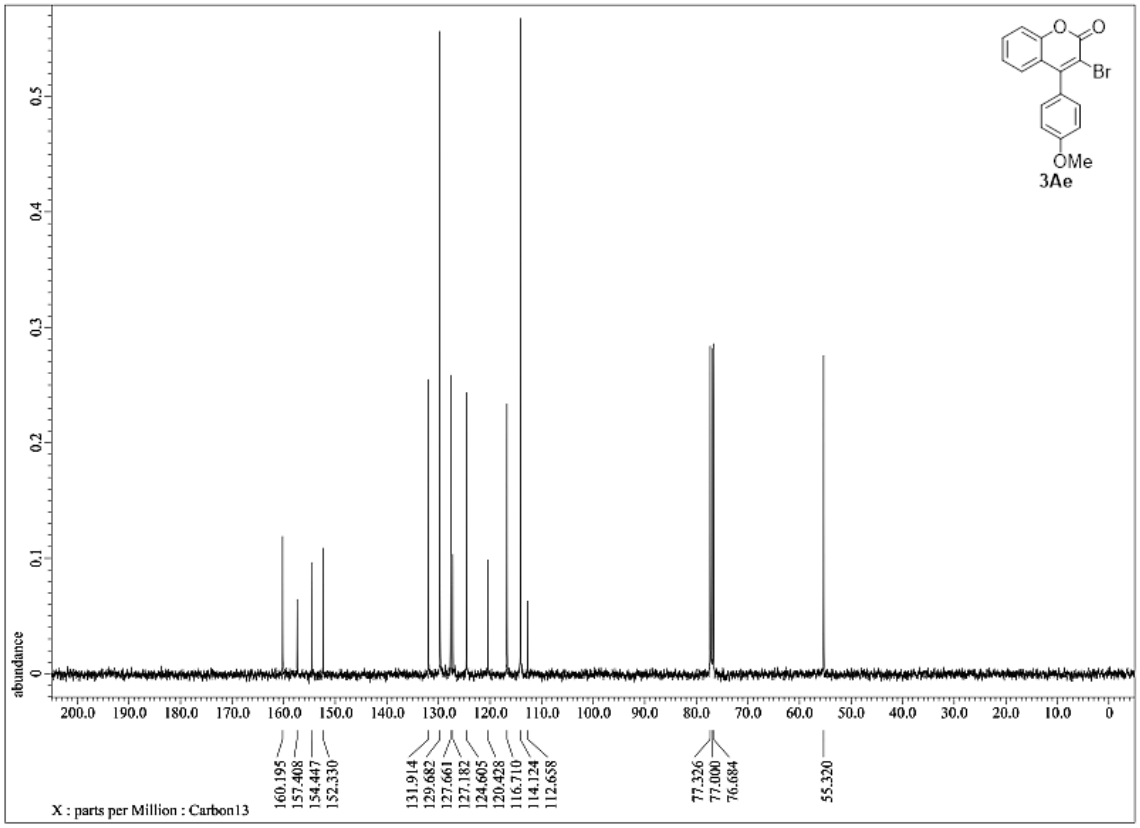
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abundance
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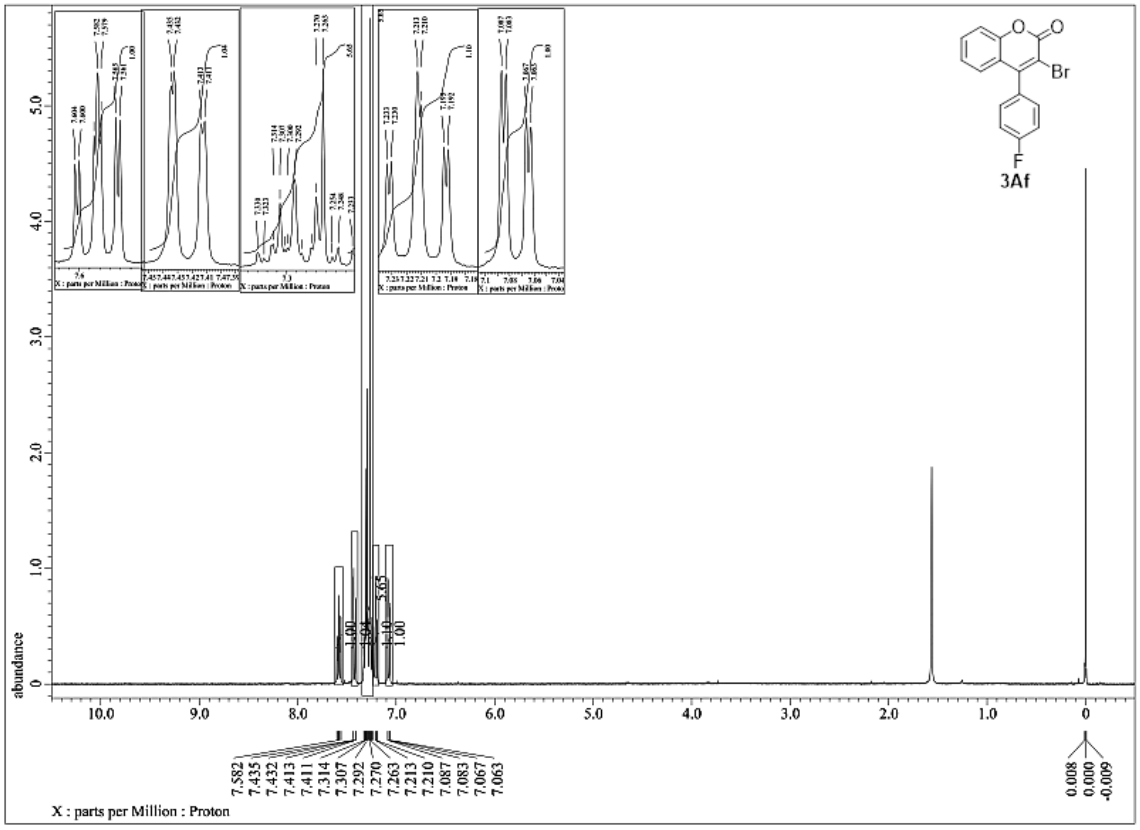
77.000
76.684
55.320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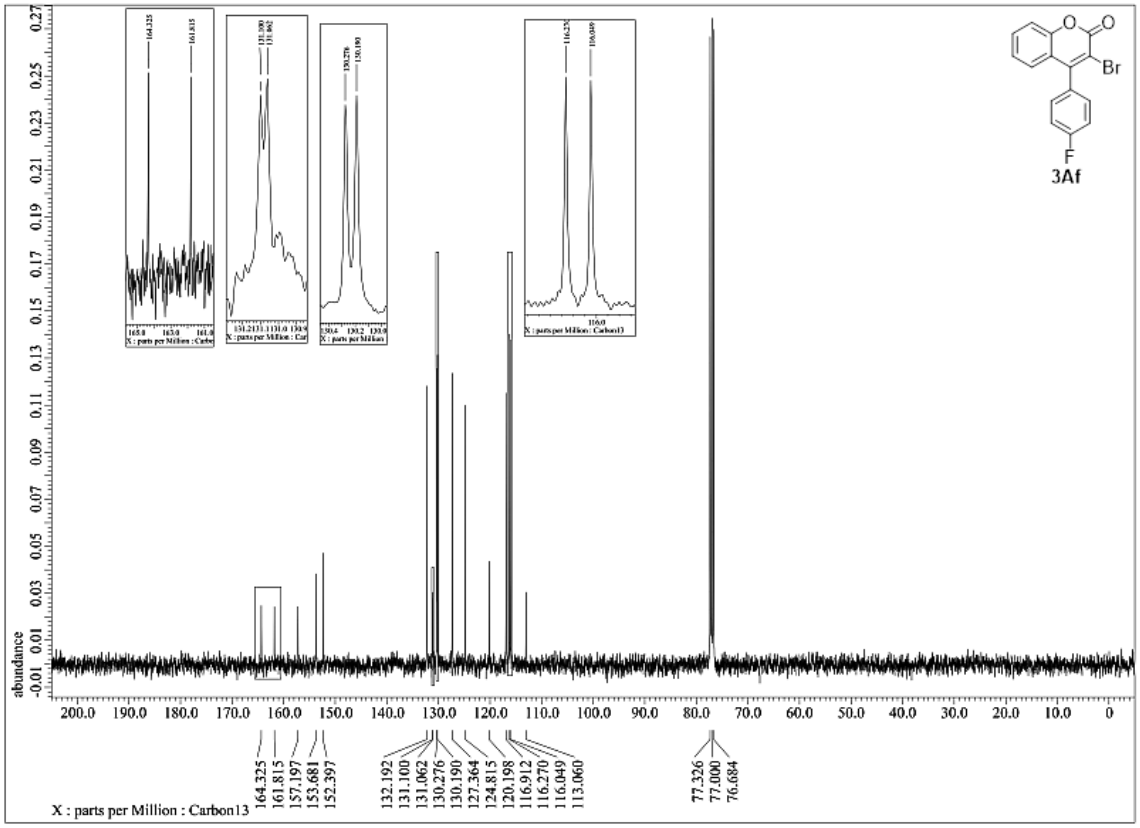
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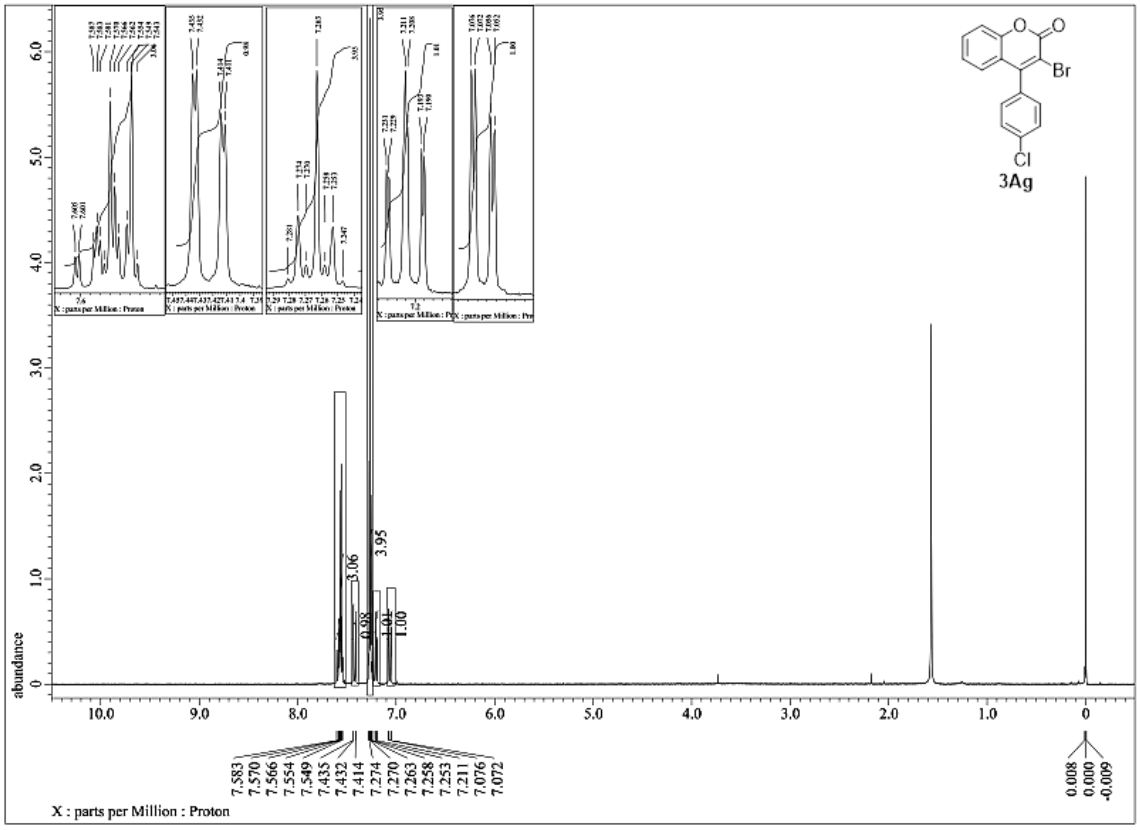
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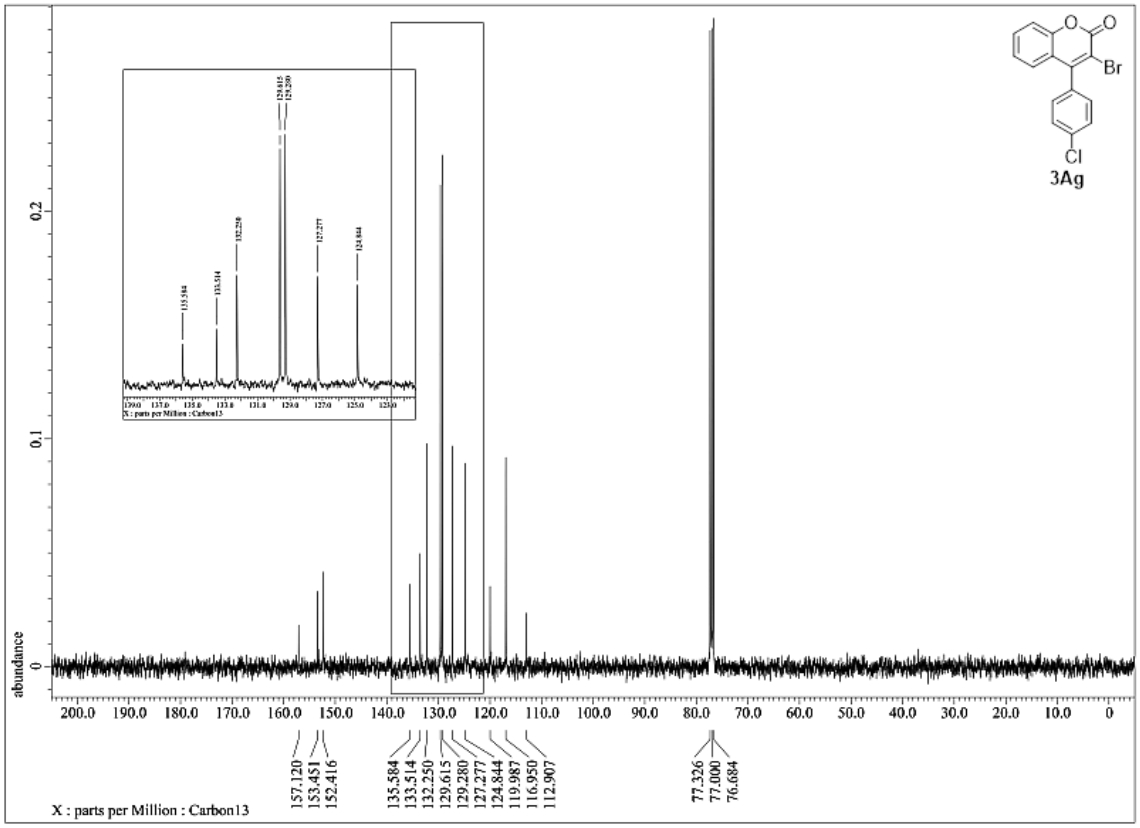
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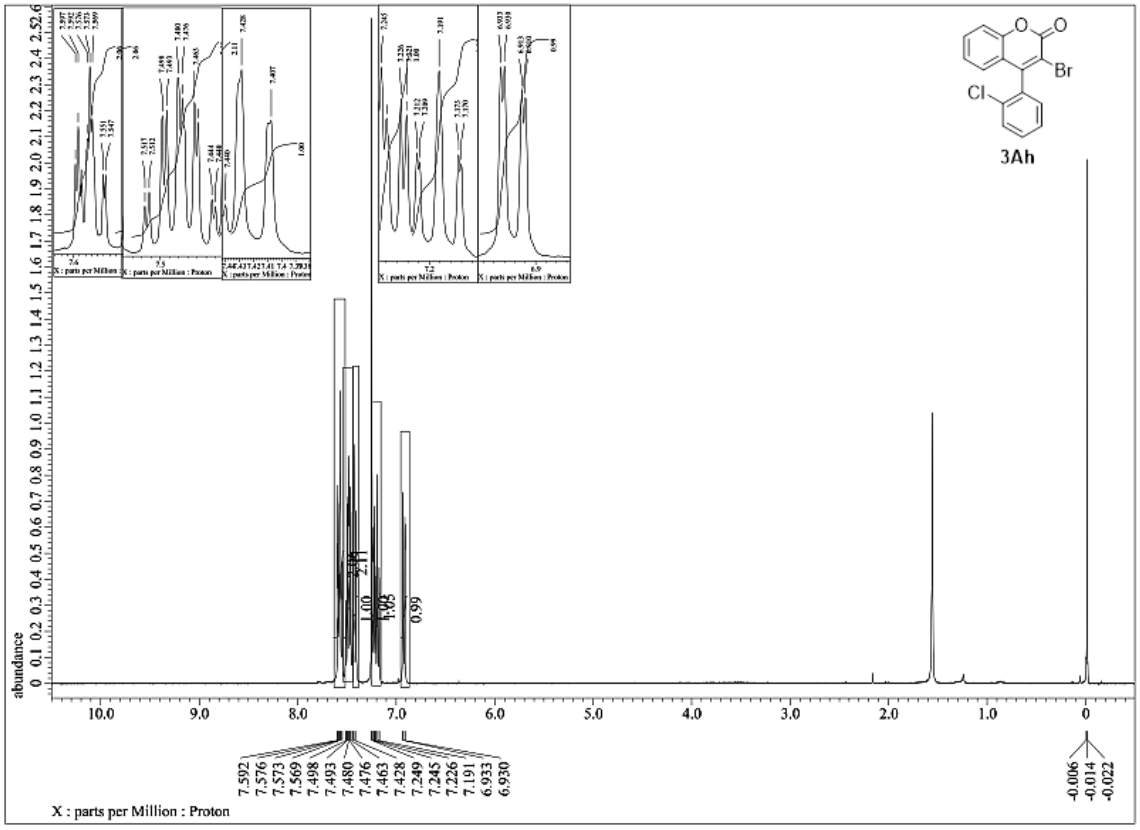
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abundance
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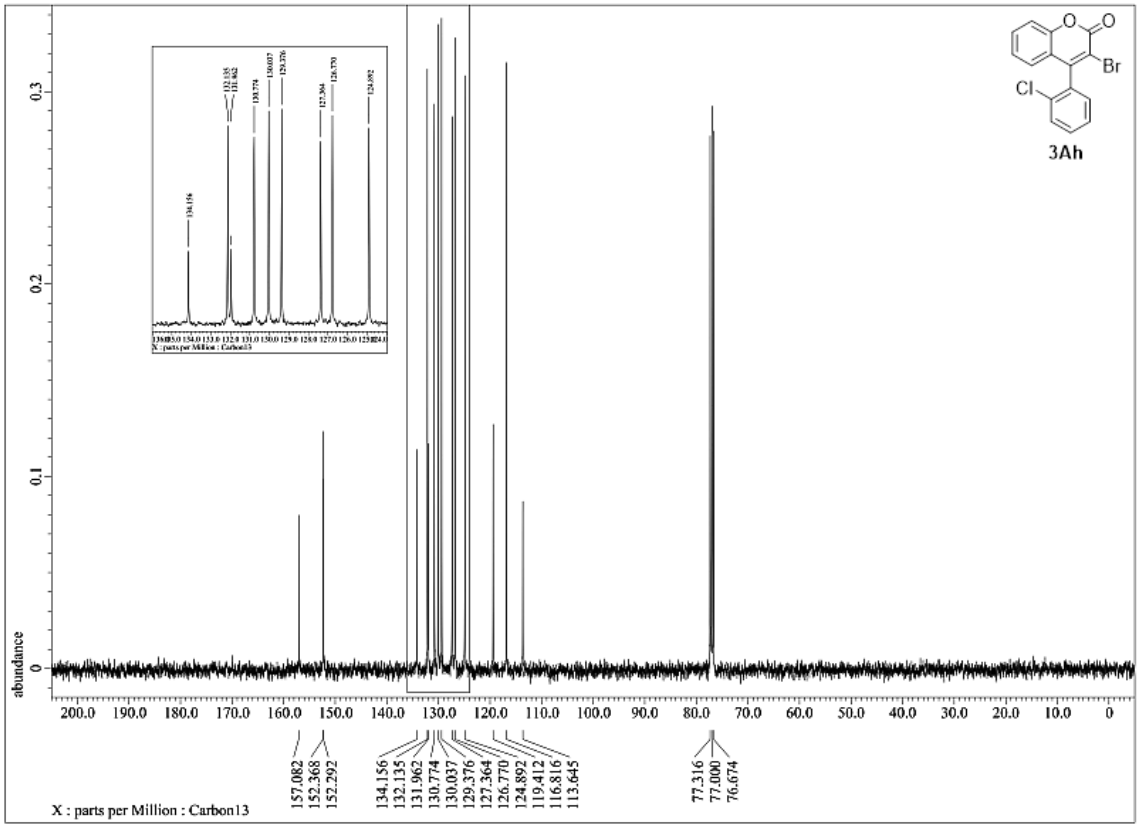
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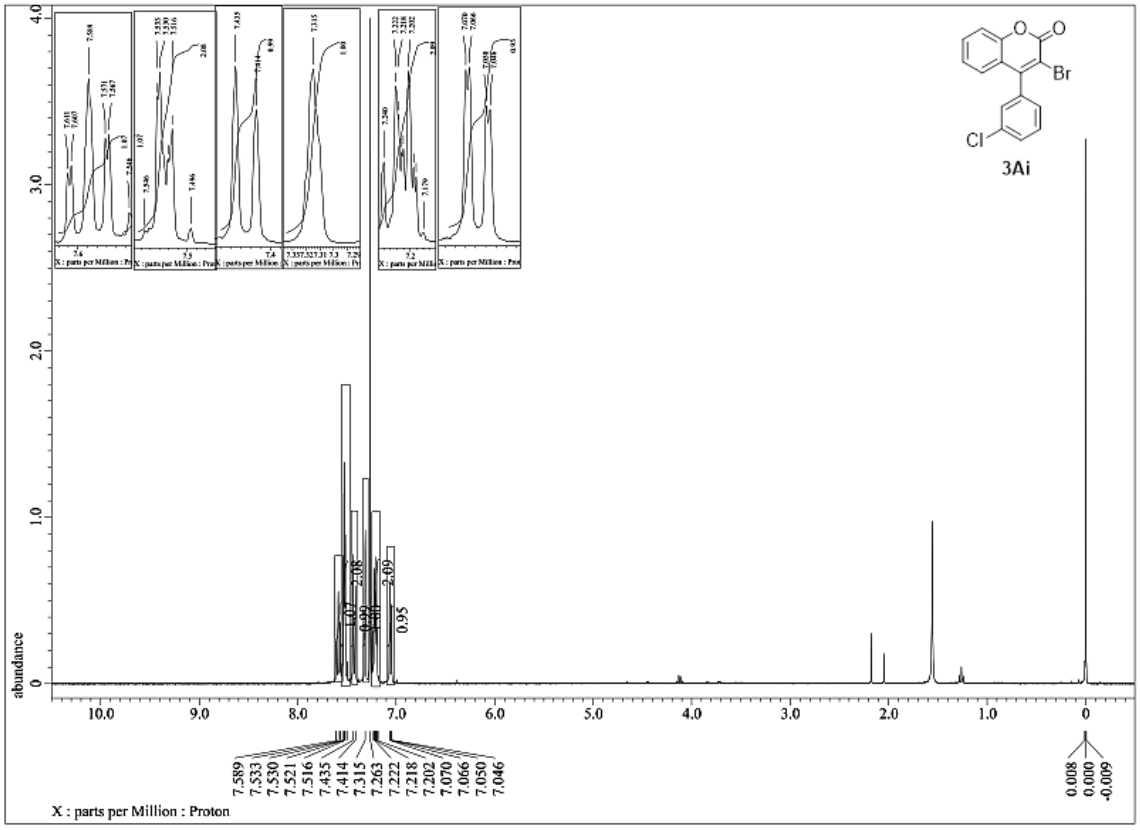
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abundance
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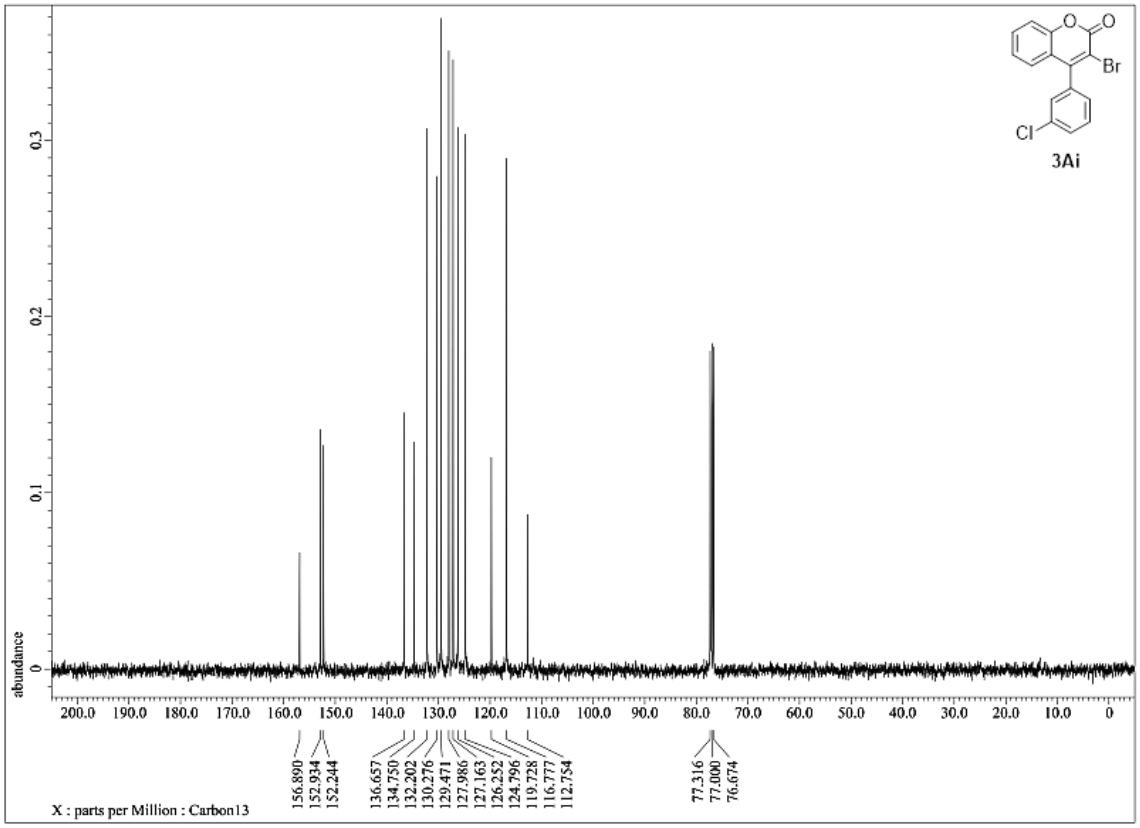
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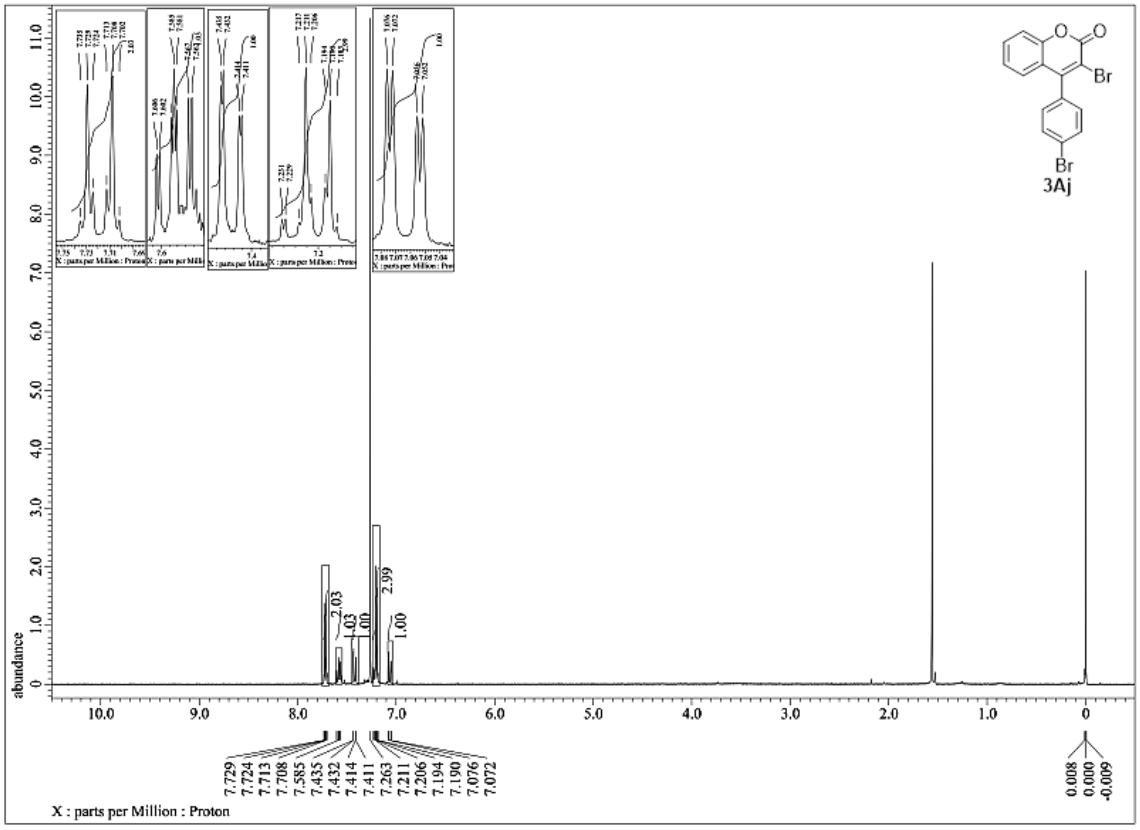
abundance
X : parts per Million : Carbon13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abundance
X : parts per Million : Proton
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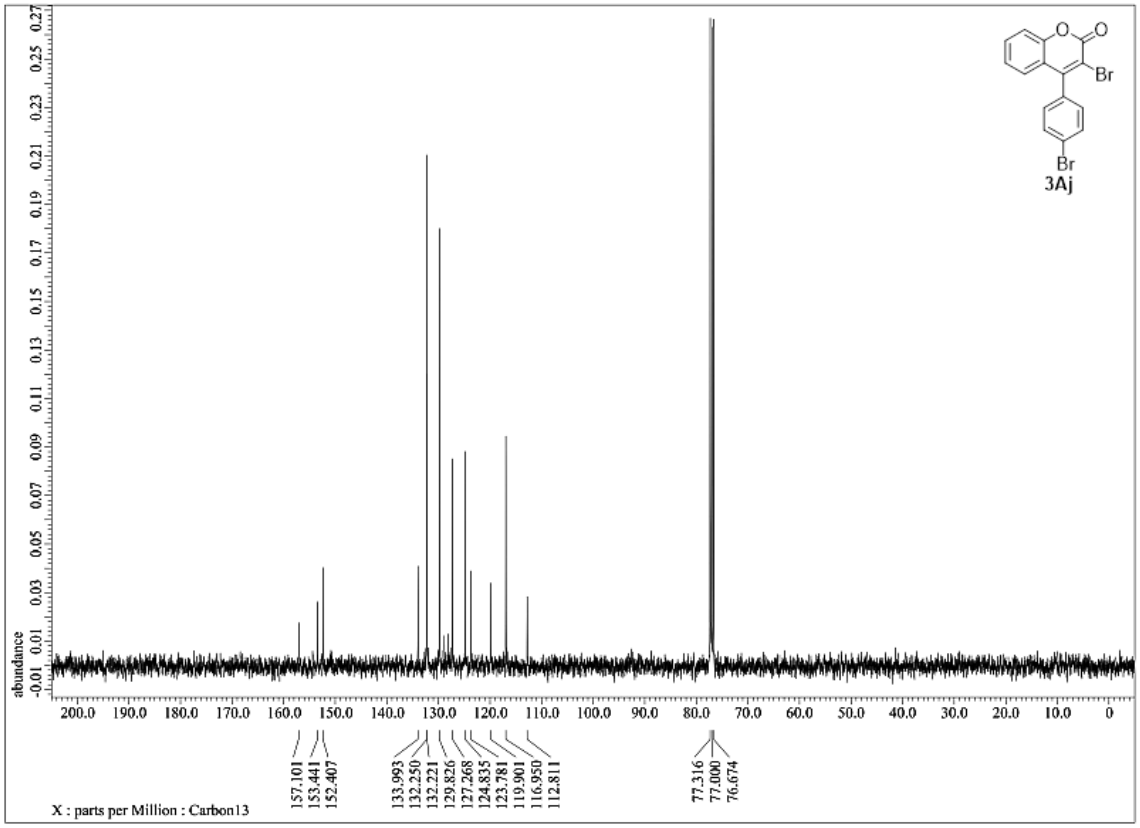
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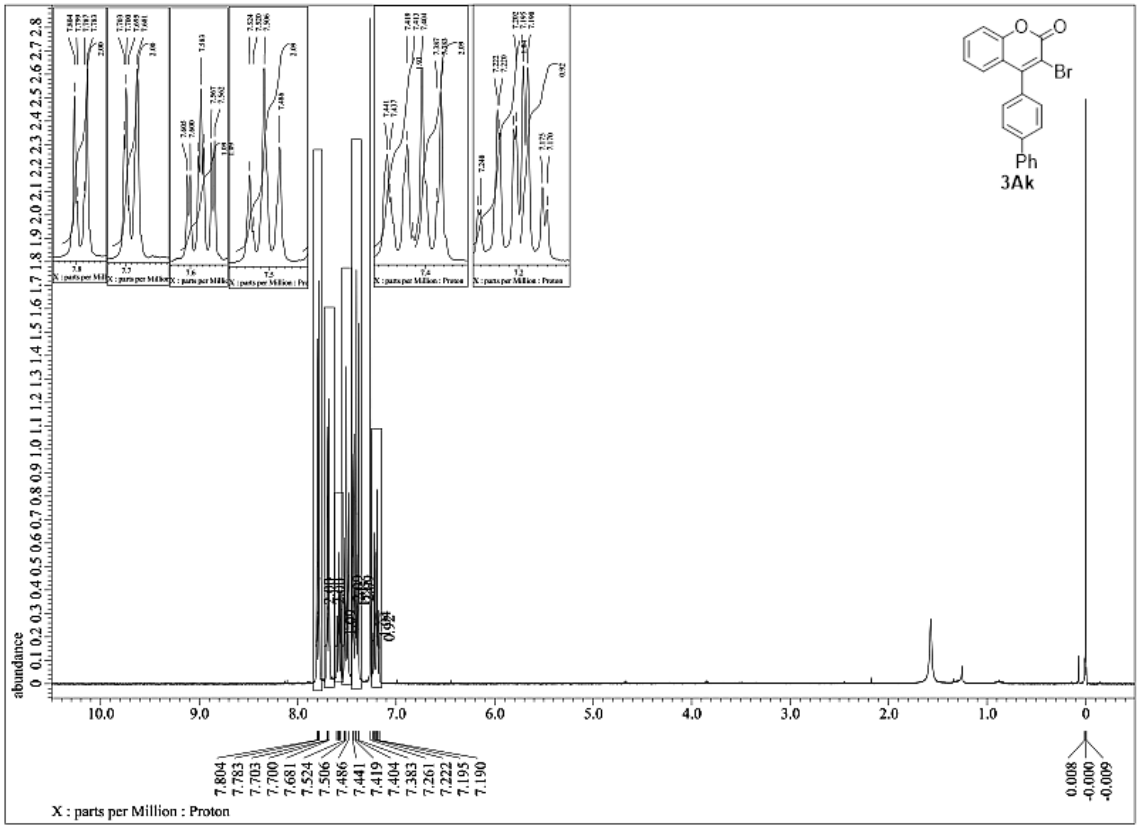
Br
Ph
3Ak
abundance
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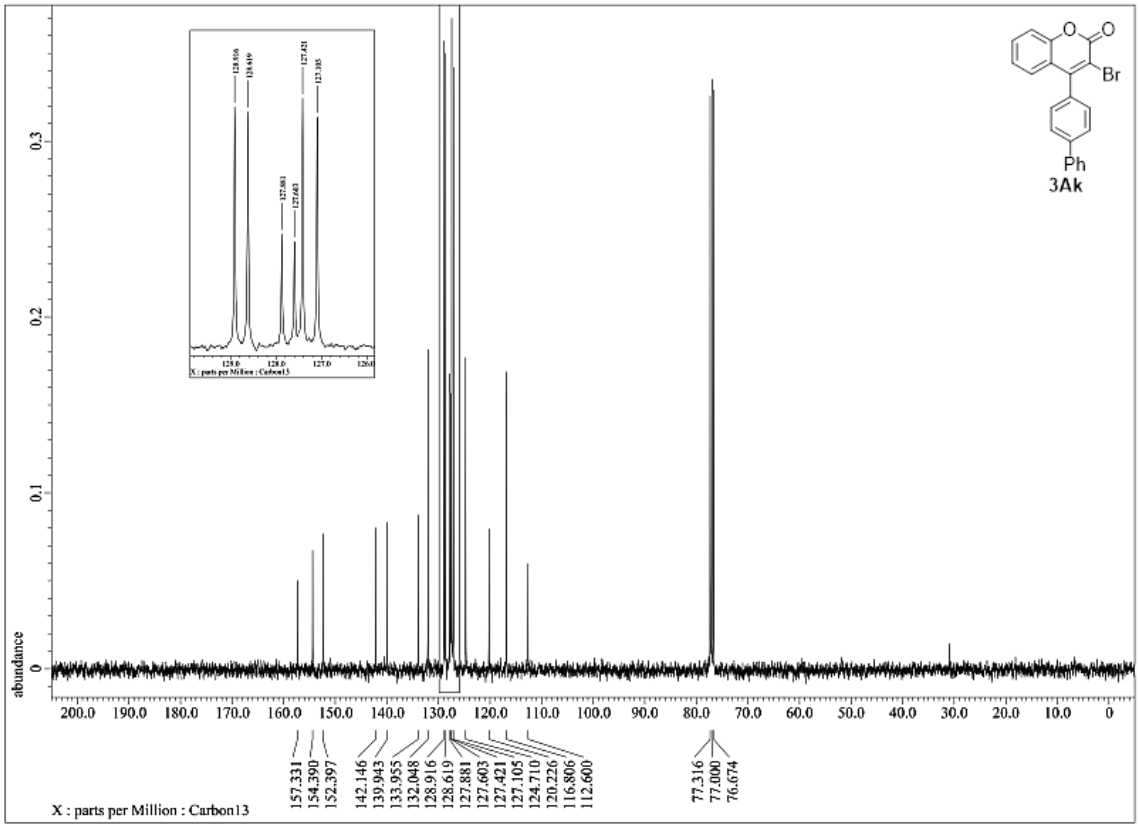
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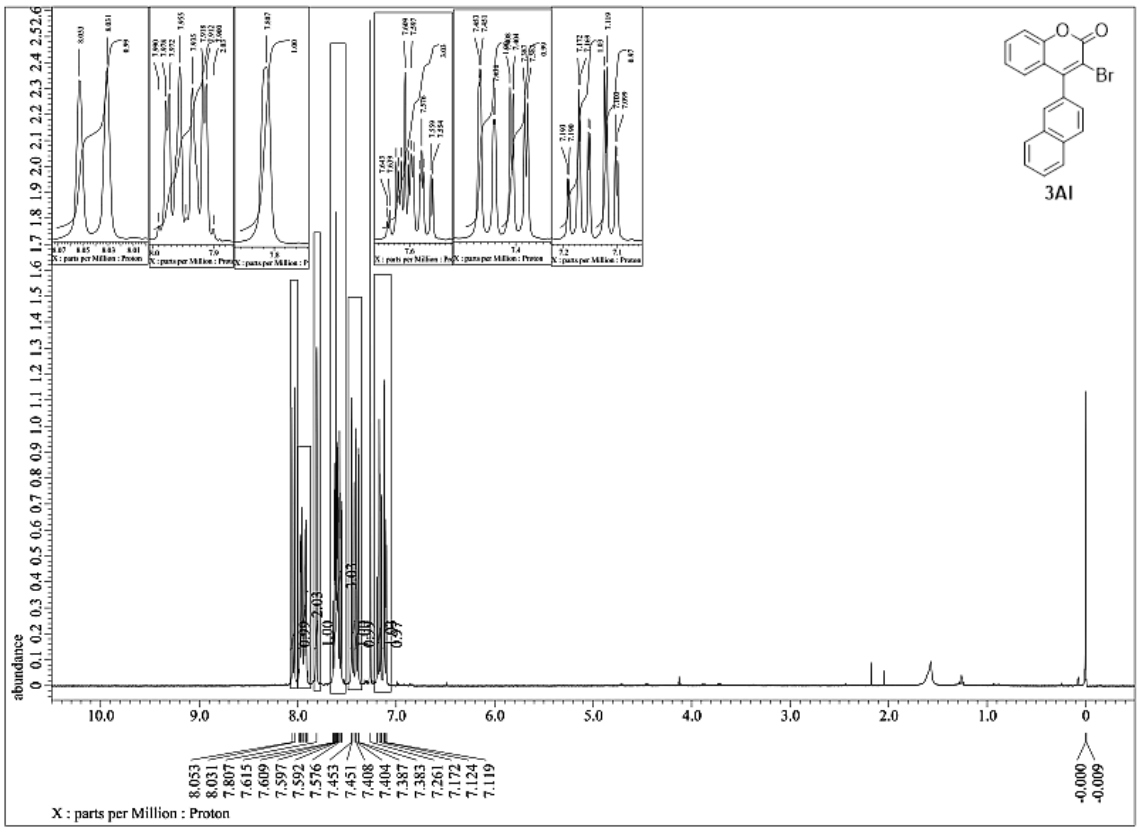
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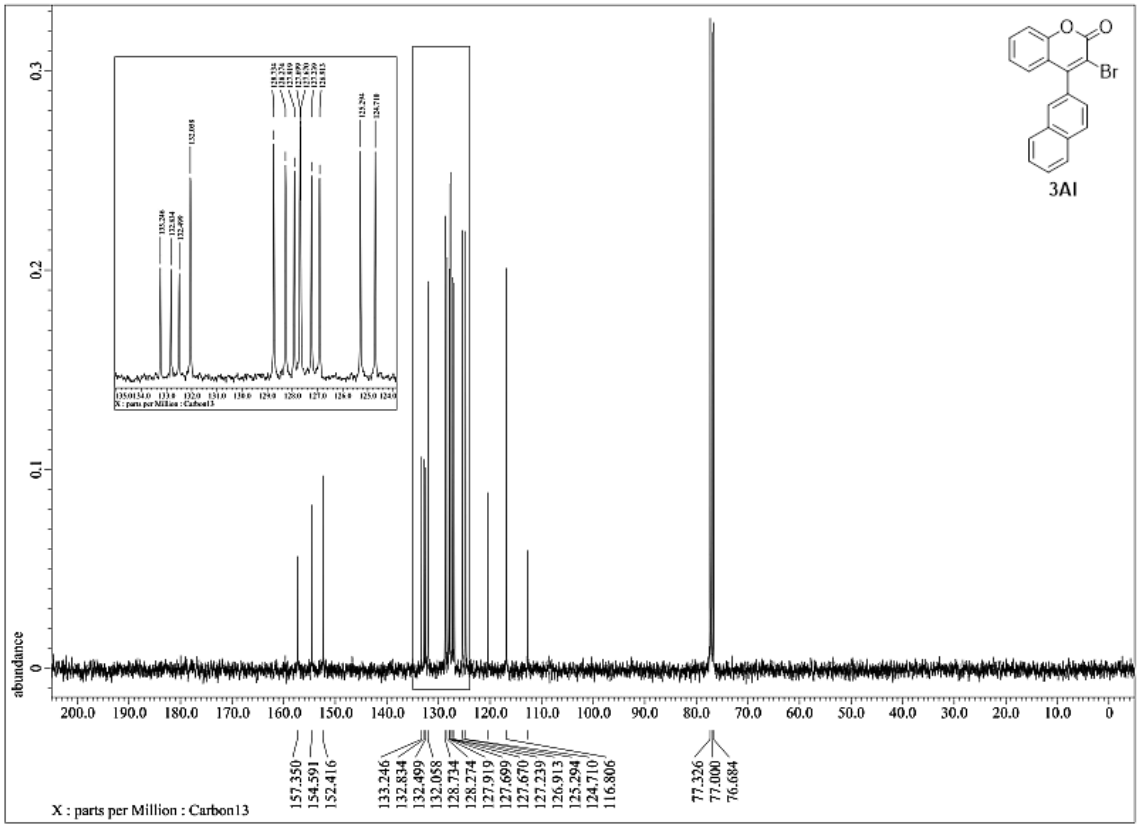
X : parts per Million : Proton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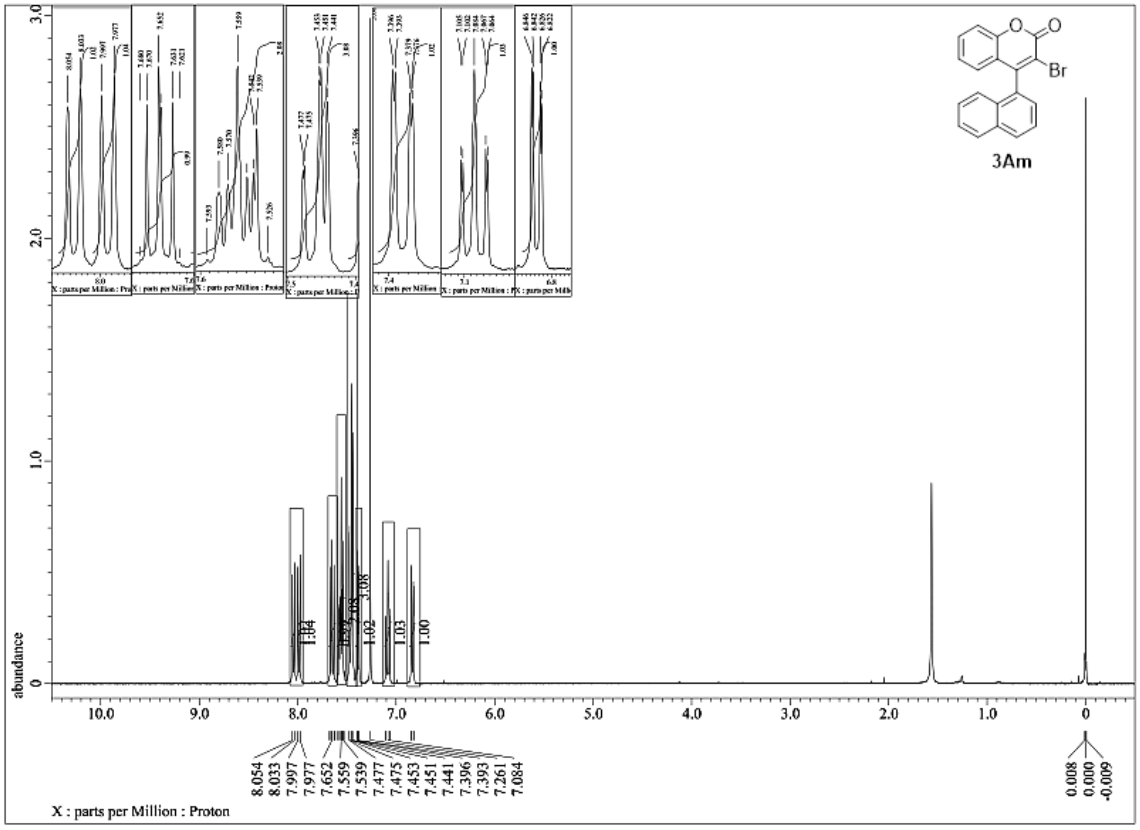
X : parts per Million : Carbon13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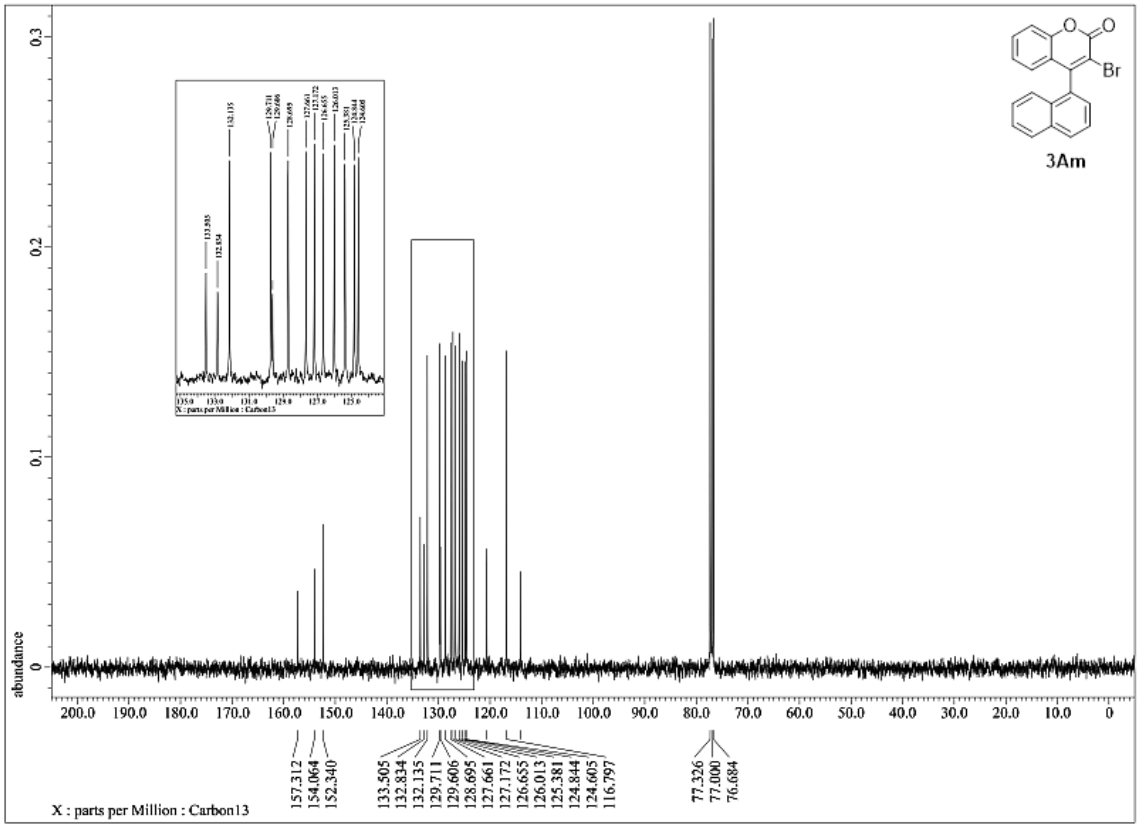
abundance
X : parts per Million : Proton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abundance
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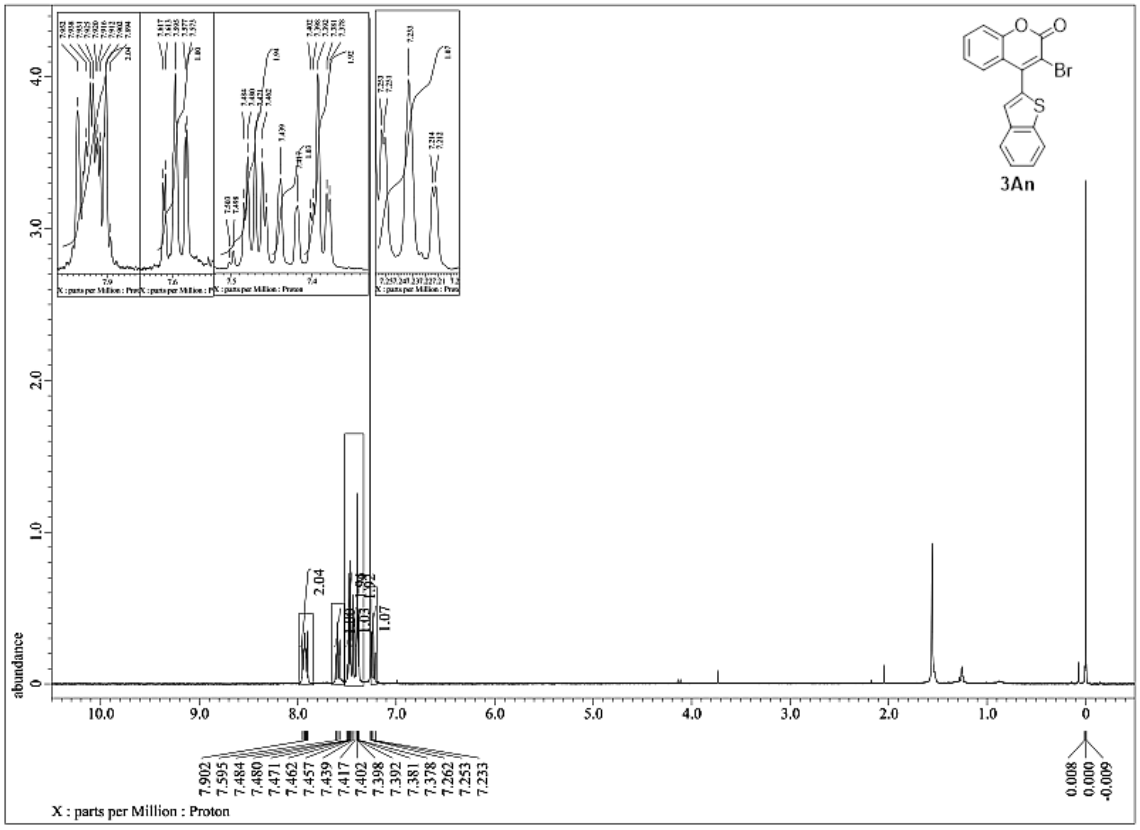
3An
abundance
X : parts per Million : Proton
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7.402
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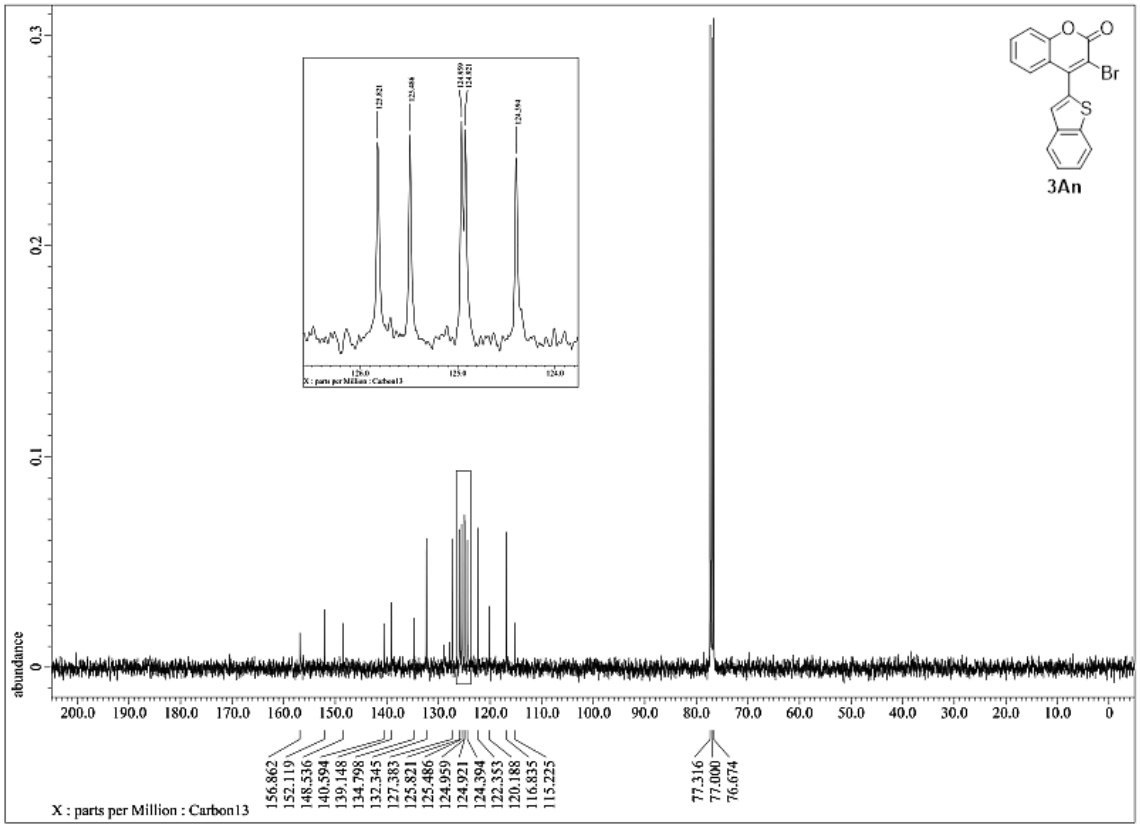
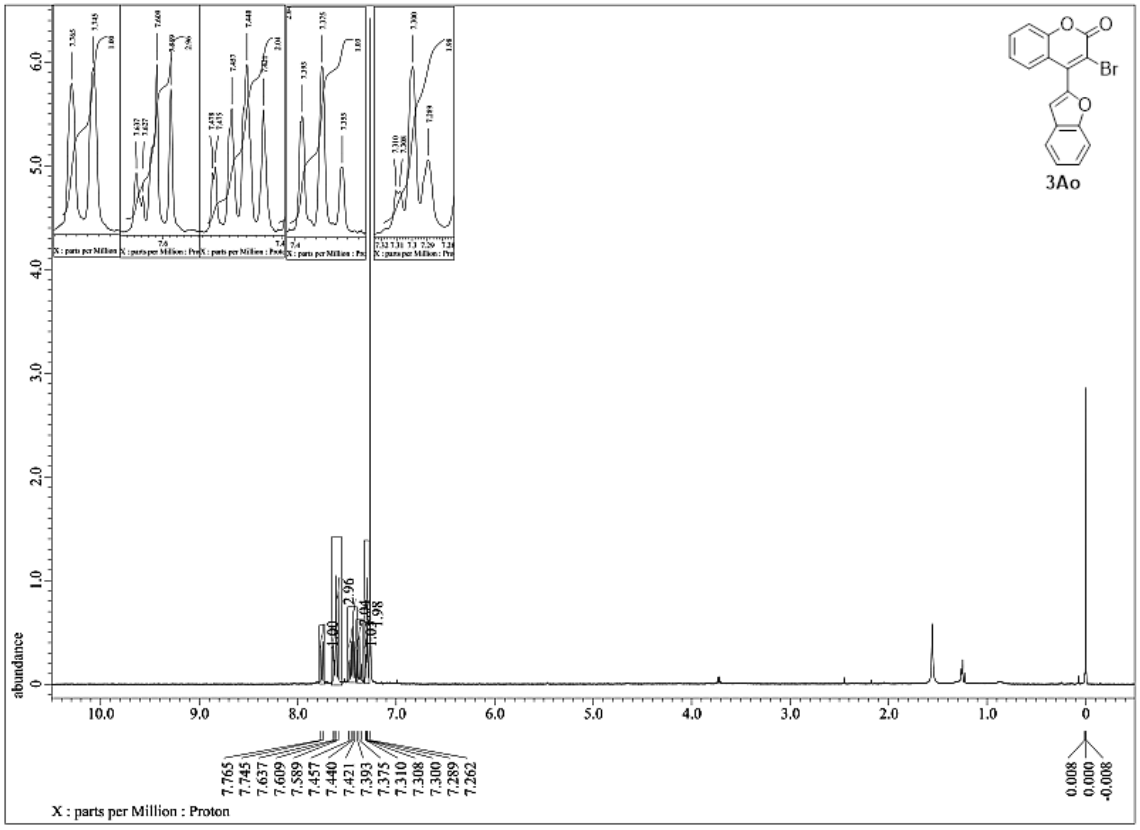
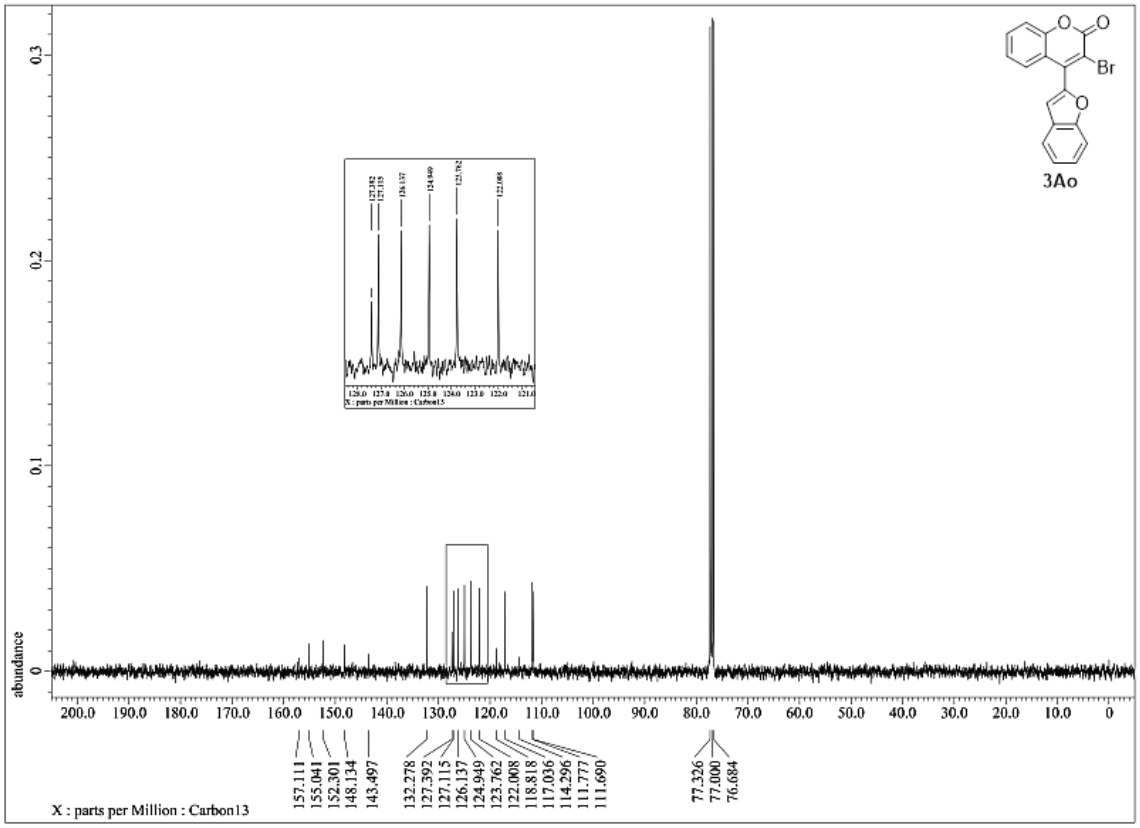
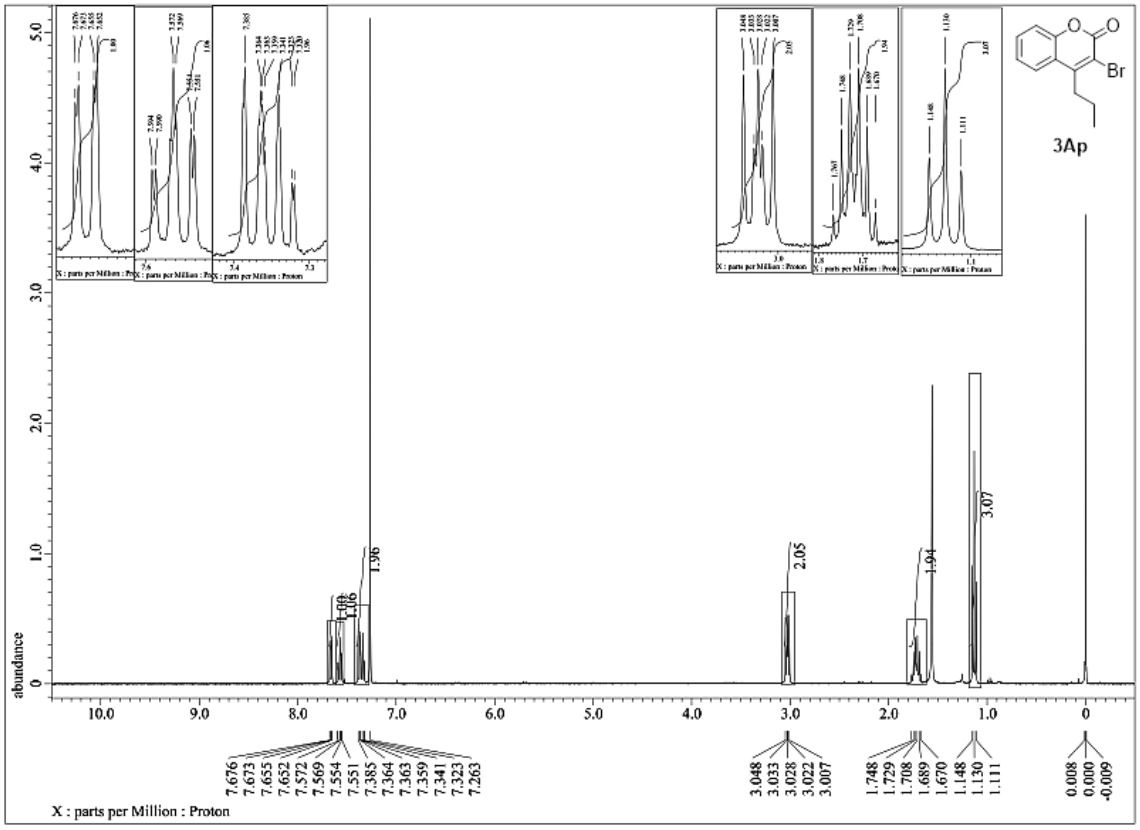
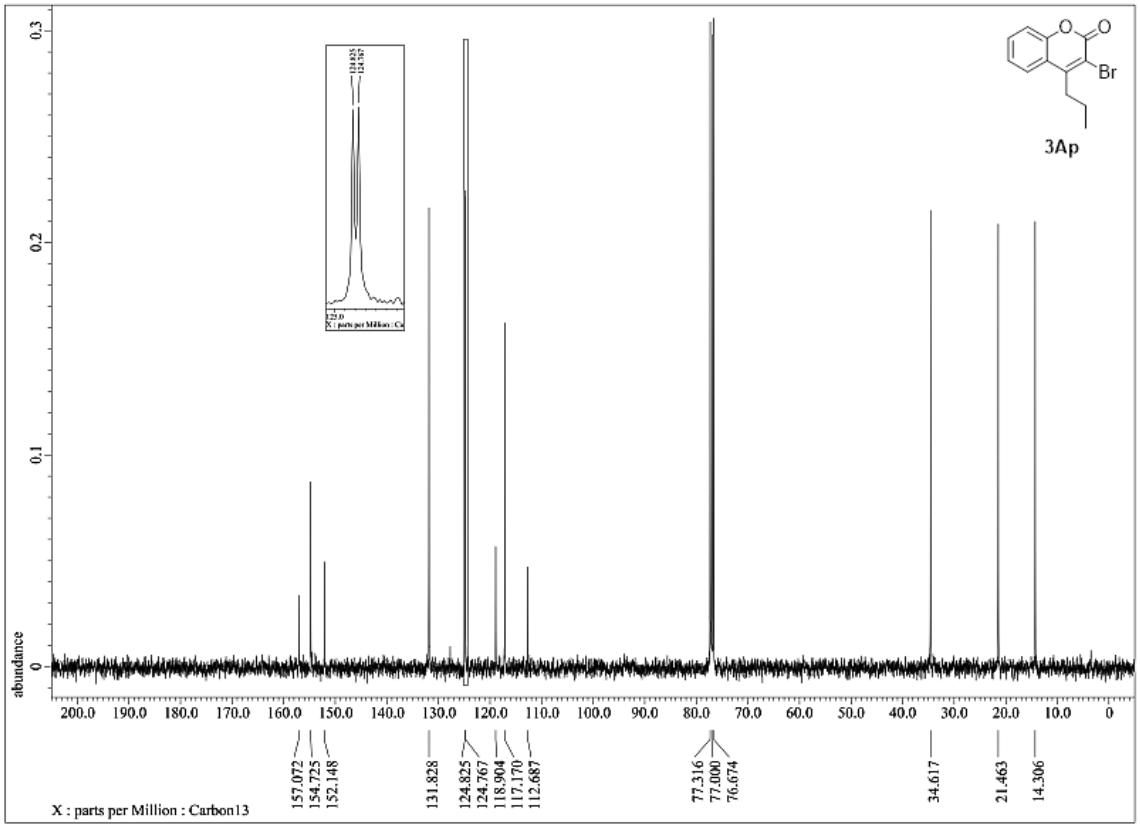
1.07

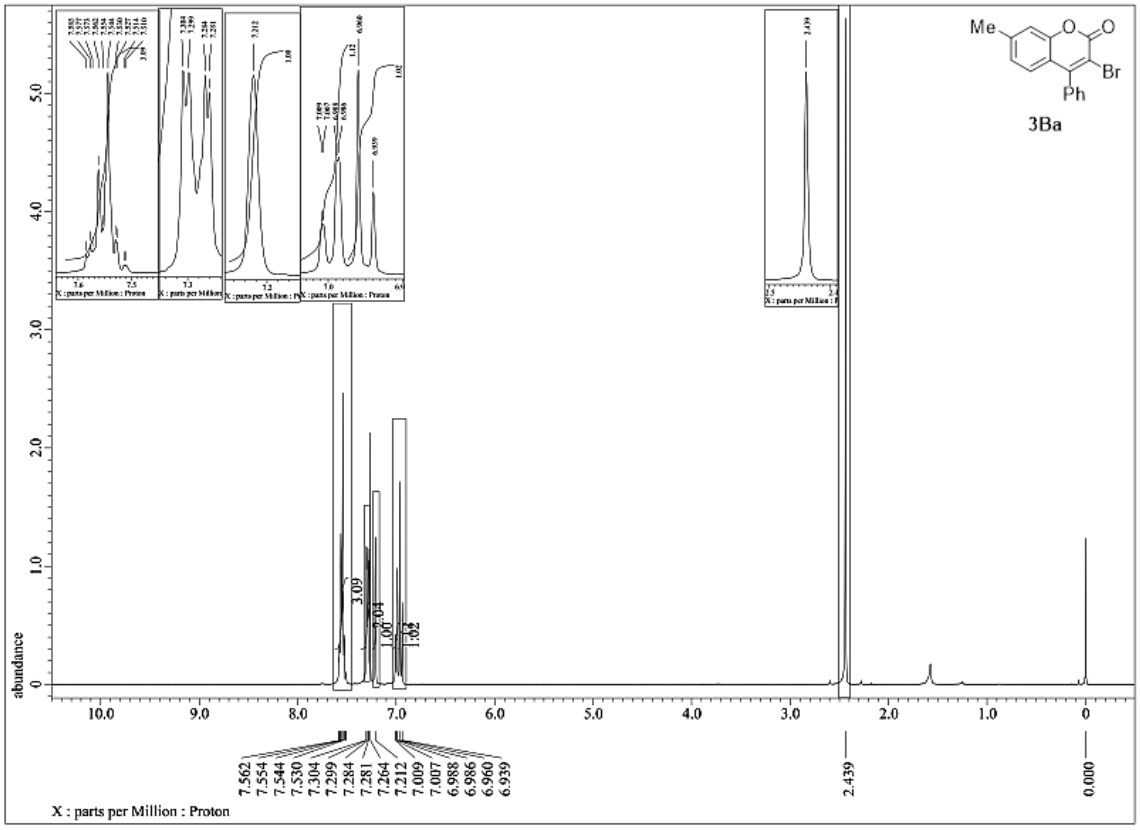

3An
abundance
X : parts per Million : Carbon13
156.862
152.119
148.536
140.594
139.148
134.798
132.345
127.383
125.821
125.486
124.959
124.921
124.394
122.353
120.188
116.835
115.225
77.316
77.000
76.674

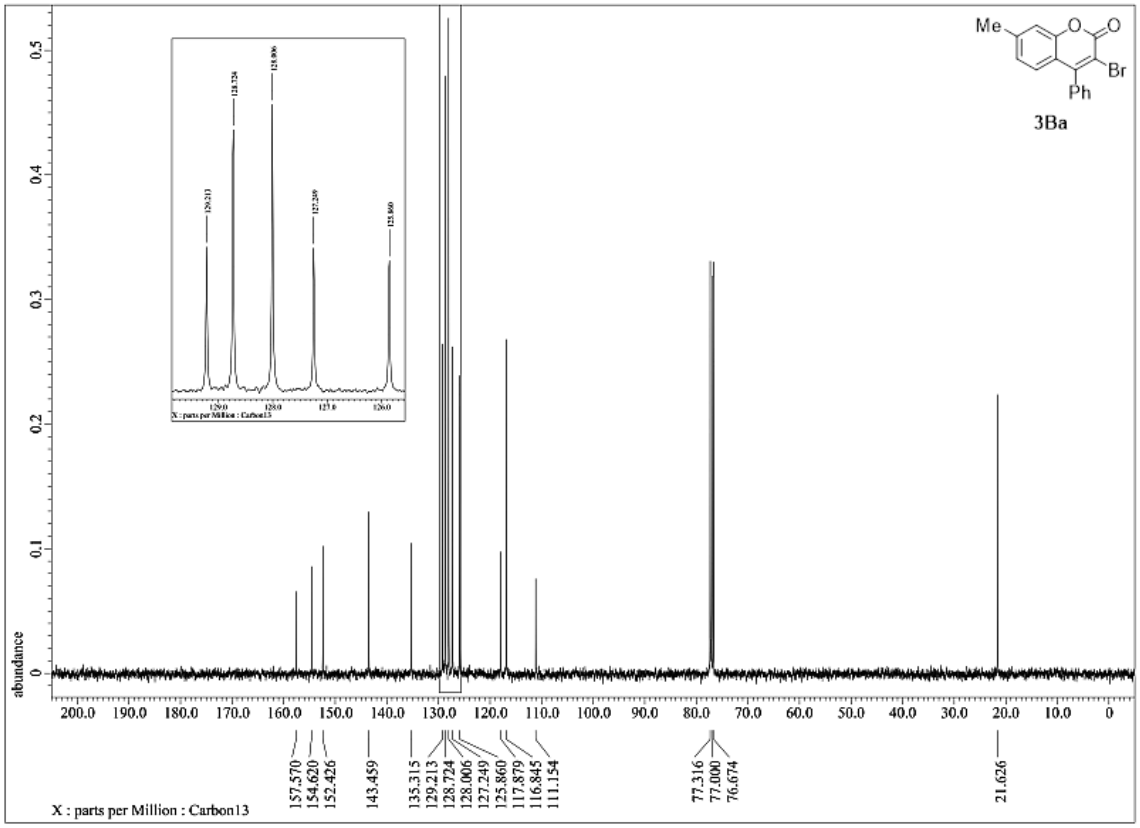

3Ao
abundance
X : parts per Million : Proton

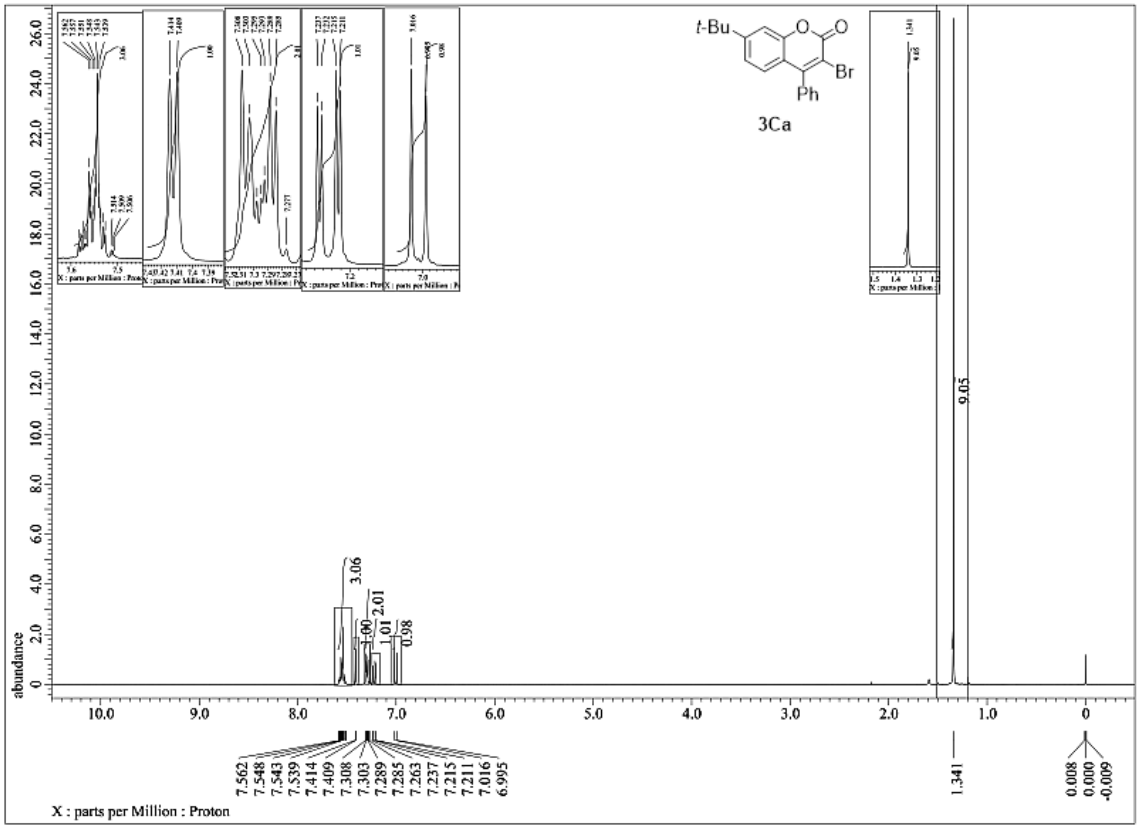

3Ao
abundance
X : parts per Million : Carbon13

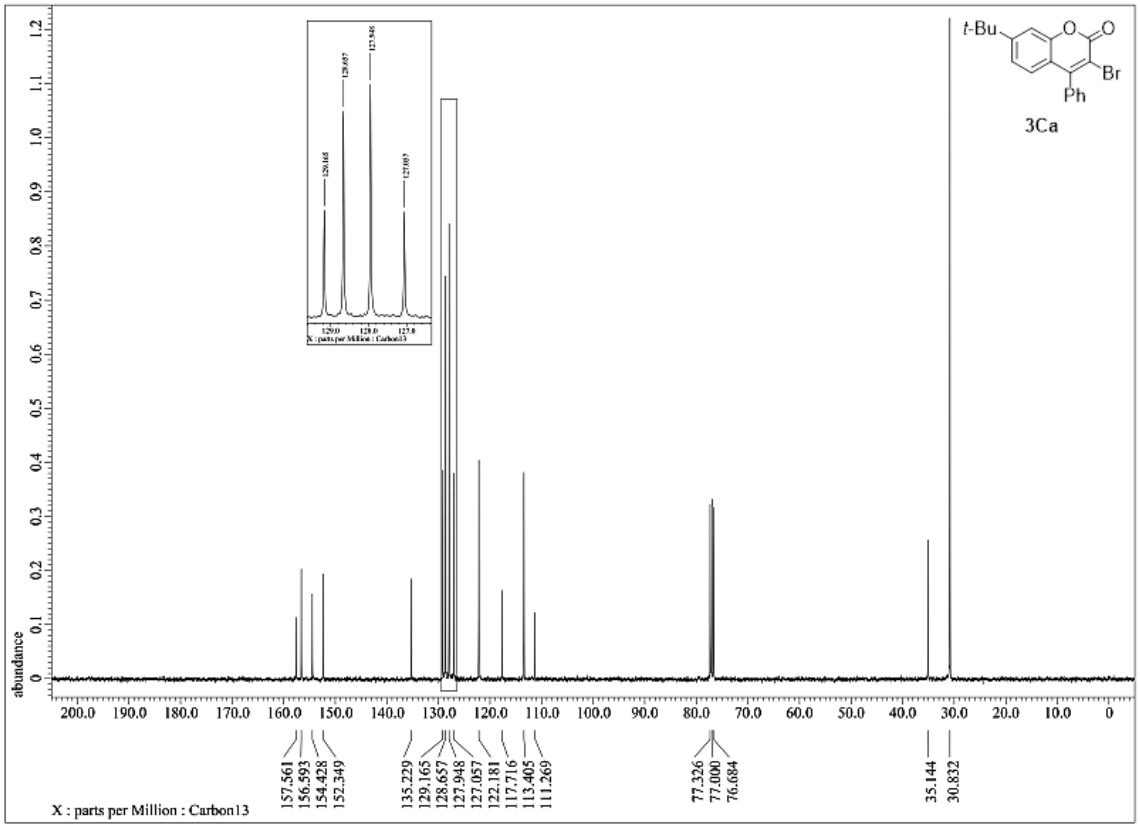

3Ap
abundance
X : parts per Million : Proton
7.676
7.673
7.655
7.652
7.572
7.569
7.554
7.551
7.385
7.364
7.363
7.359
7.341
7.323
7.263
3.048
3.033
3.028
3.022
3.007
1.748
1.729
1.708
1.689
1.670
1.148
1.130
1.111
0.008
0.000
-0.009
1.96
1.06
1.06
2.05
1.94
3.07

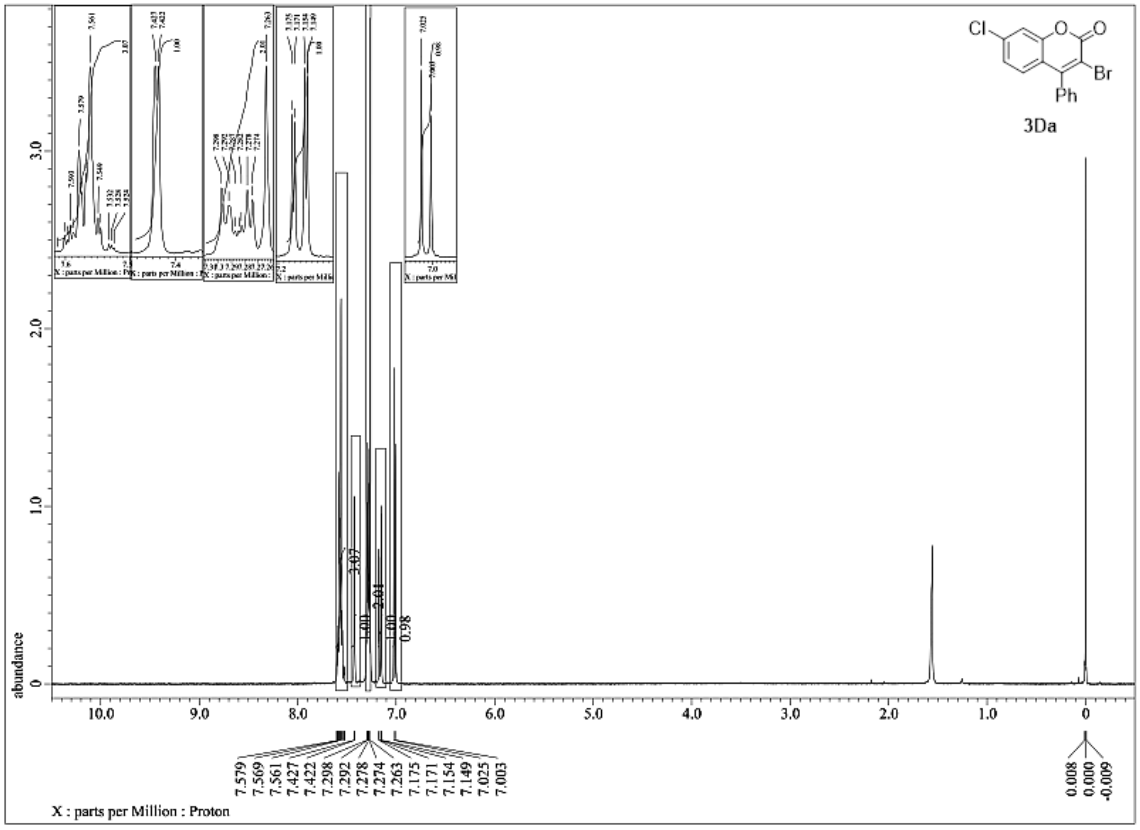

3Ap
abundance
X : parts per Million : Carbon13
157.072
154.725
152.148
131.828
124.825
124.767
118.904
117.170
112.687
77.316
77.000
76.674
34.617
21.463
14.306

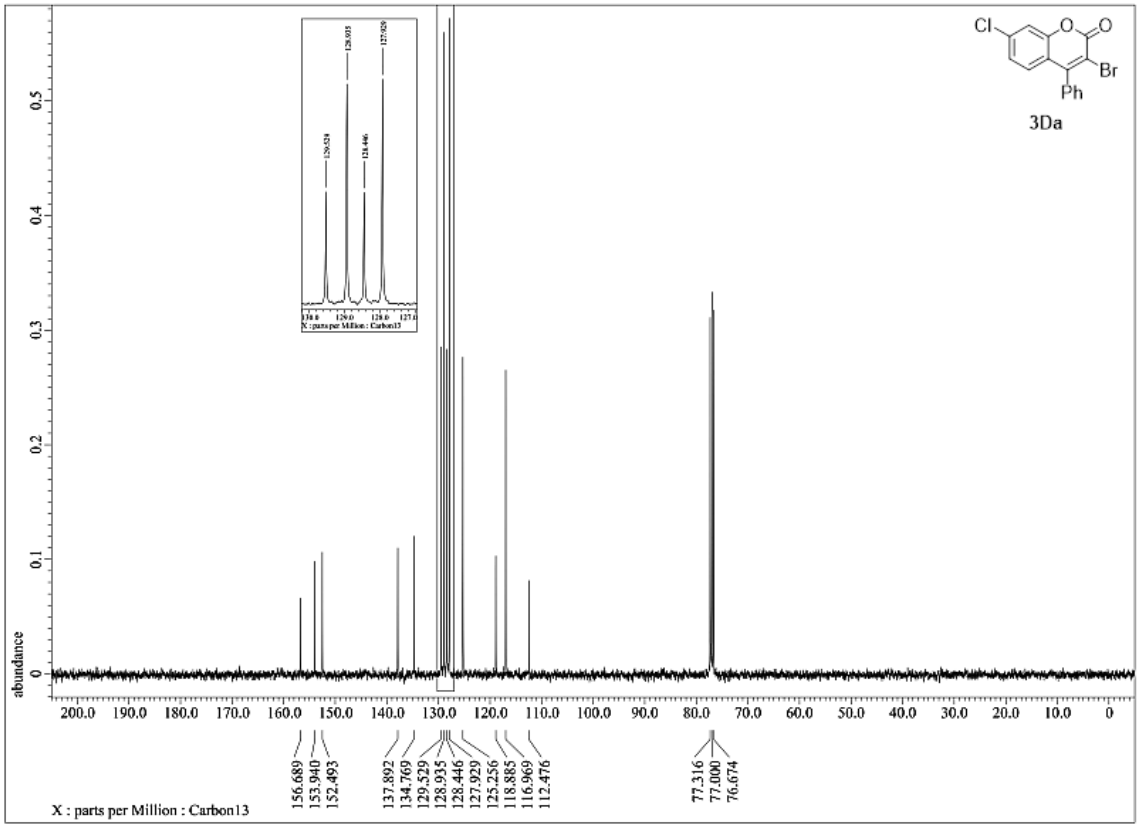

Me
O
O
Br
Ph
3Ba
abundance
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.562
7.554
7.544
7.530
7.304
7.299
7.284
7.281
7.264
7.212
7.009
7.007
6.988
6.986
6.960
6.939
2.439
0.000
X : parts per Million : Proton

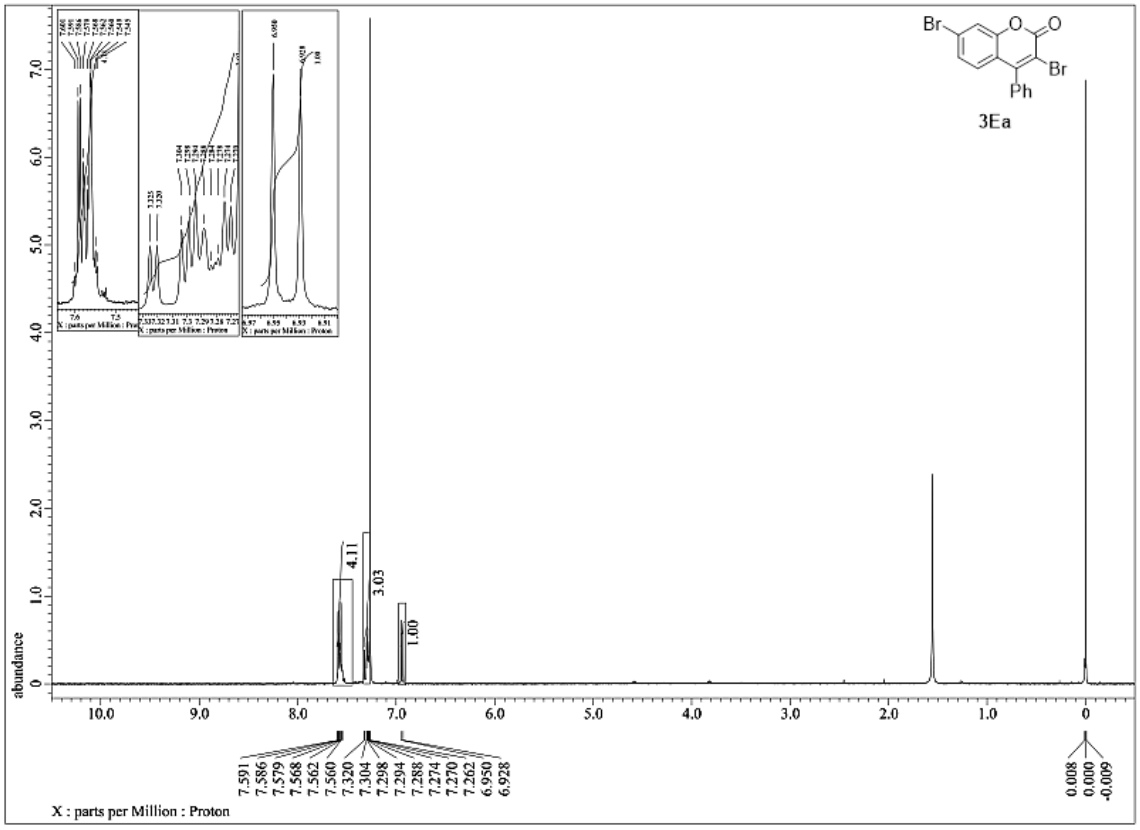

Me
O
O
Br
Ph
3Ba
abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
157.570
154.620
152.426
143.459
135.315
129.213
128.724
128.006
127.249
125.860
117.879
116.845
111.154
77.316
77.000
76.674
21.626
X : parts per Million : Carbon13

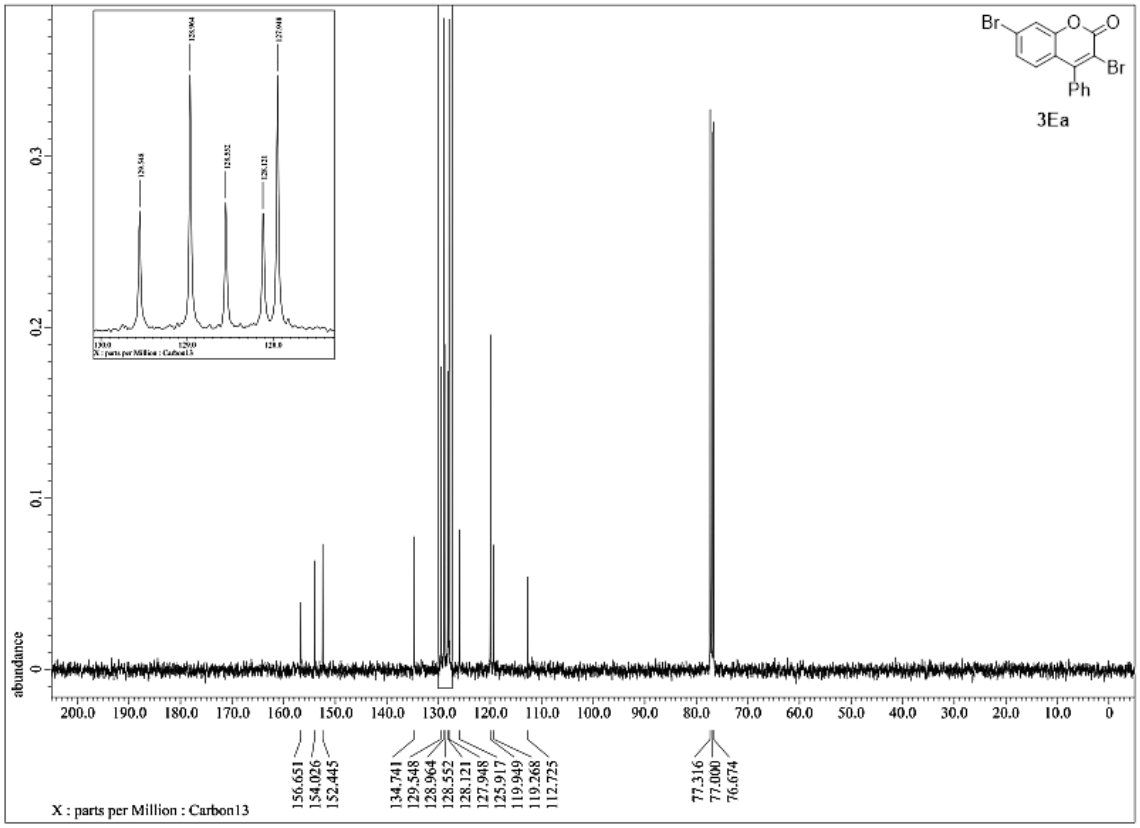

t-Bu
O
O
Br
Ph
3Ca
abundance
3.06
2.01
1.00
1.01
0.98
9.05
7.562
7.548
7.543
7.539
7.414
7.409
7.308
7.303
7.289
7.285
7.263
7.237
7.215
7.211
7.016
6.995
1.341
0.008
0.000
-0.009
X : parts per Million : Proton

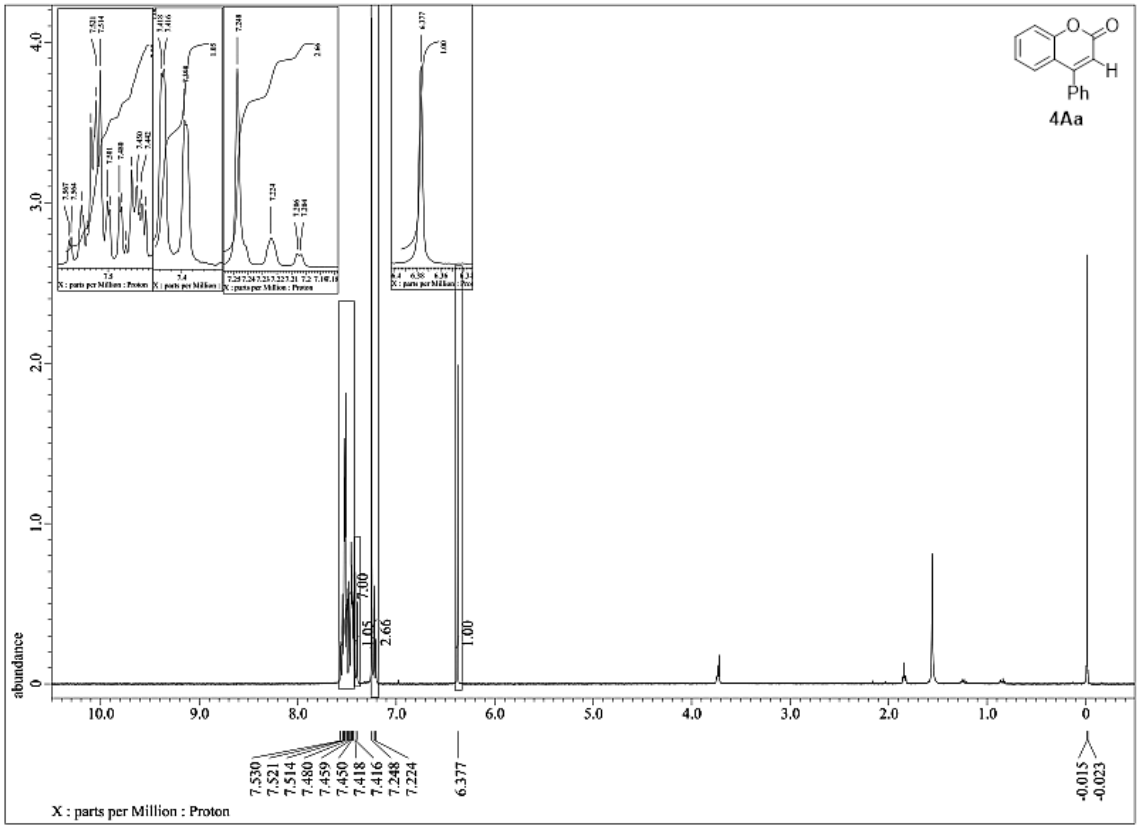

t-Bu
O
O
Br
Ph
3Ca
abundance
157.561
156.593
154.428
152.349
135.229
129.165
128.657
127.948
127.057
122.181
117.716
113.405
111.269
77.326
77.000
76.684
35.144
30.832
X : parts per Million : Carbon13

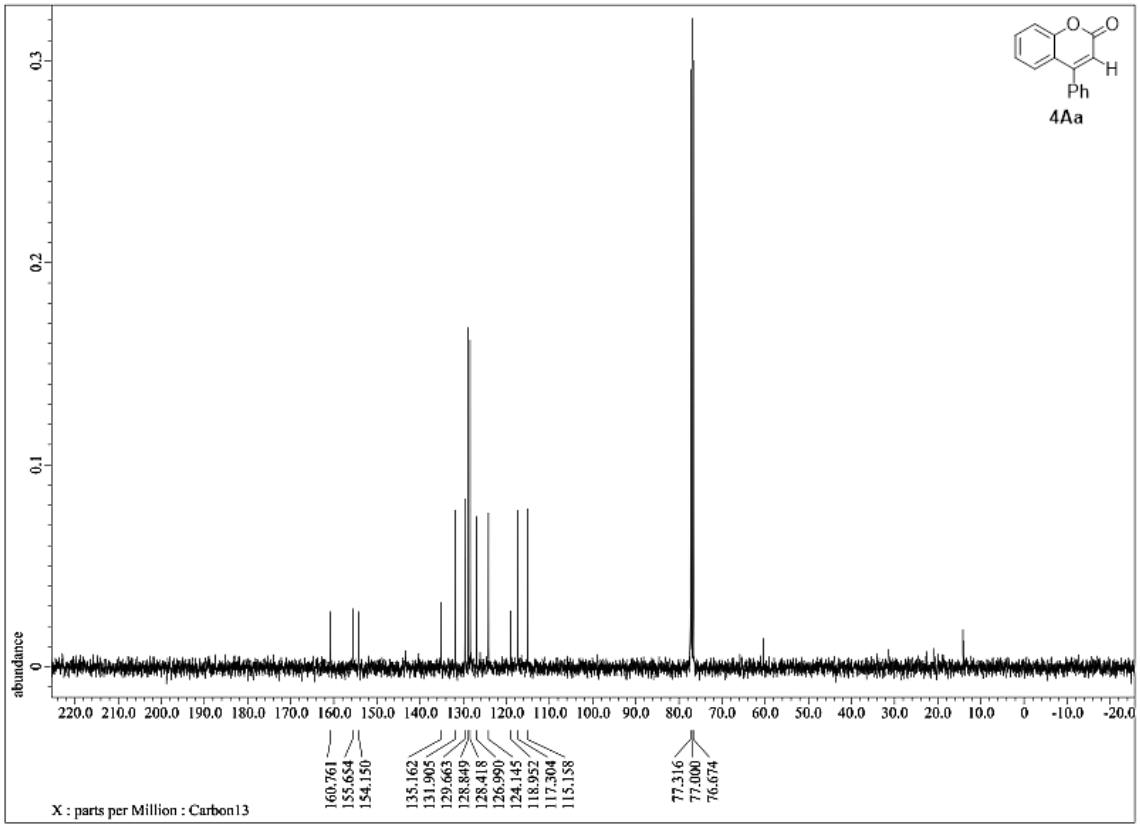

Cl
O
O
Br
Ph
3Da
abundance
3.07
1.01
2.01
1.01
0.98
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.579
7.569
7.561
7.427
7.422
7.298
7.292
7.278
7.274
7.263
7.175
7.171
7.154
7.149
7.025
7.003
0.008
0.000
-0.009
X : parts per Million : Proton

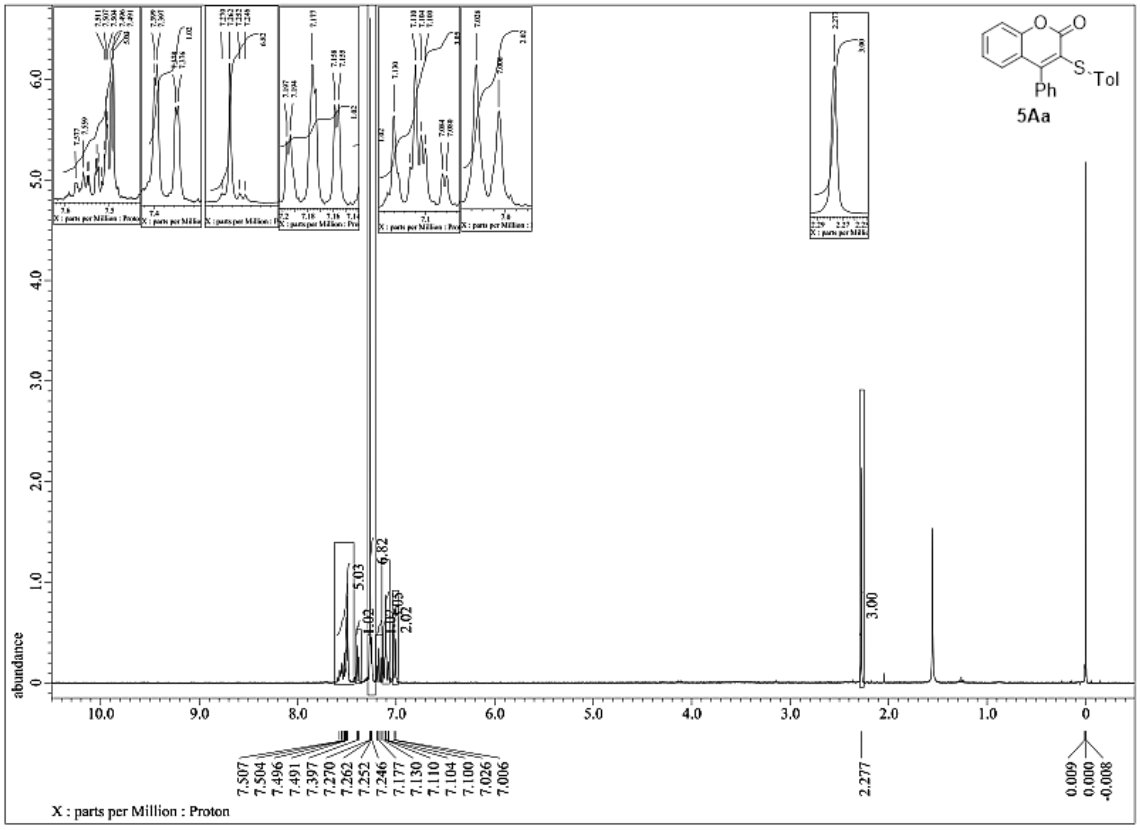

Cl
O
O
Br
Ph
3Da
abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
156.689
153.940
152.493
137.892
134.769
129.529
128.935
128.446
127.929
125.256
118.885
116.969
112.476
77.316
77.000
76.674
X : parts per Million : Carbon13

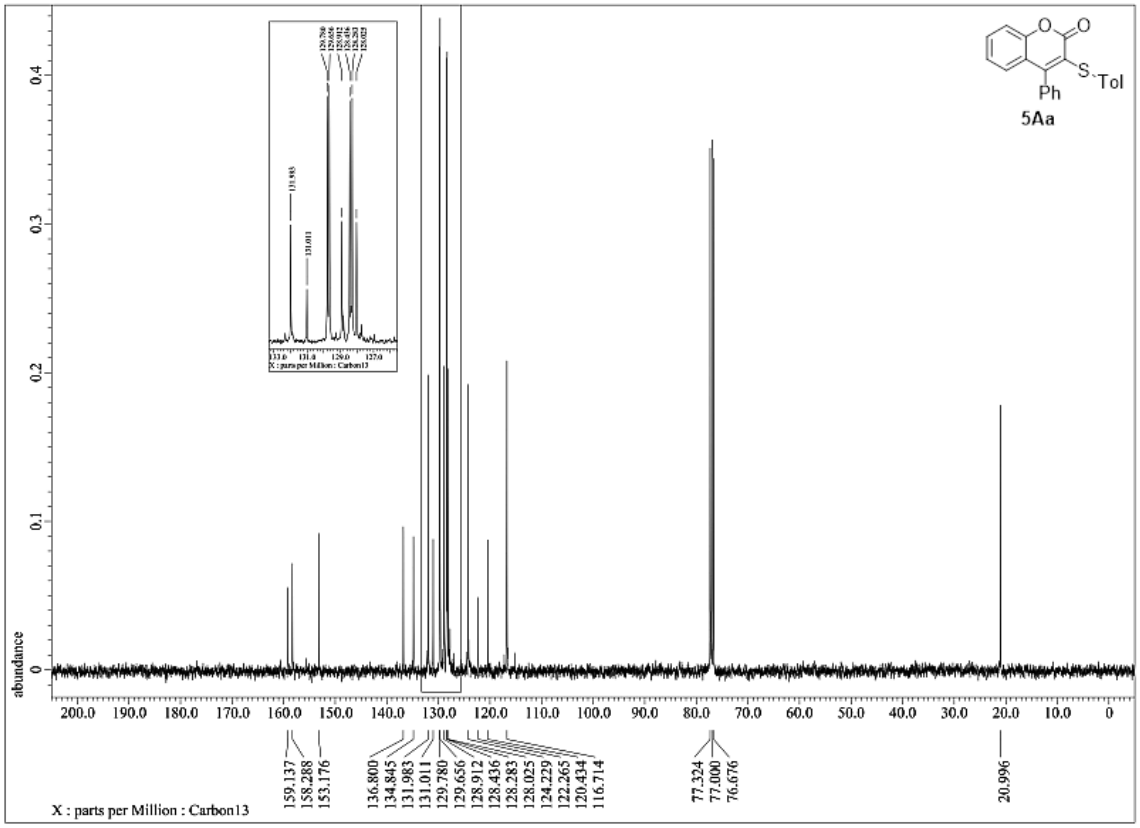

Br
O
O
Br
Ph
3Ea
abundance
4.11
3.03
1.00
7.591
7.586
7.579
7.568
7.562
7.560
7.320
7.304
7.298
7.294
7.288
7.274
7.270
7.262
6.950
6.928
0.008
0.000
-0.009
X : parts per Million : Proton

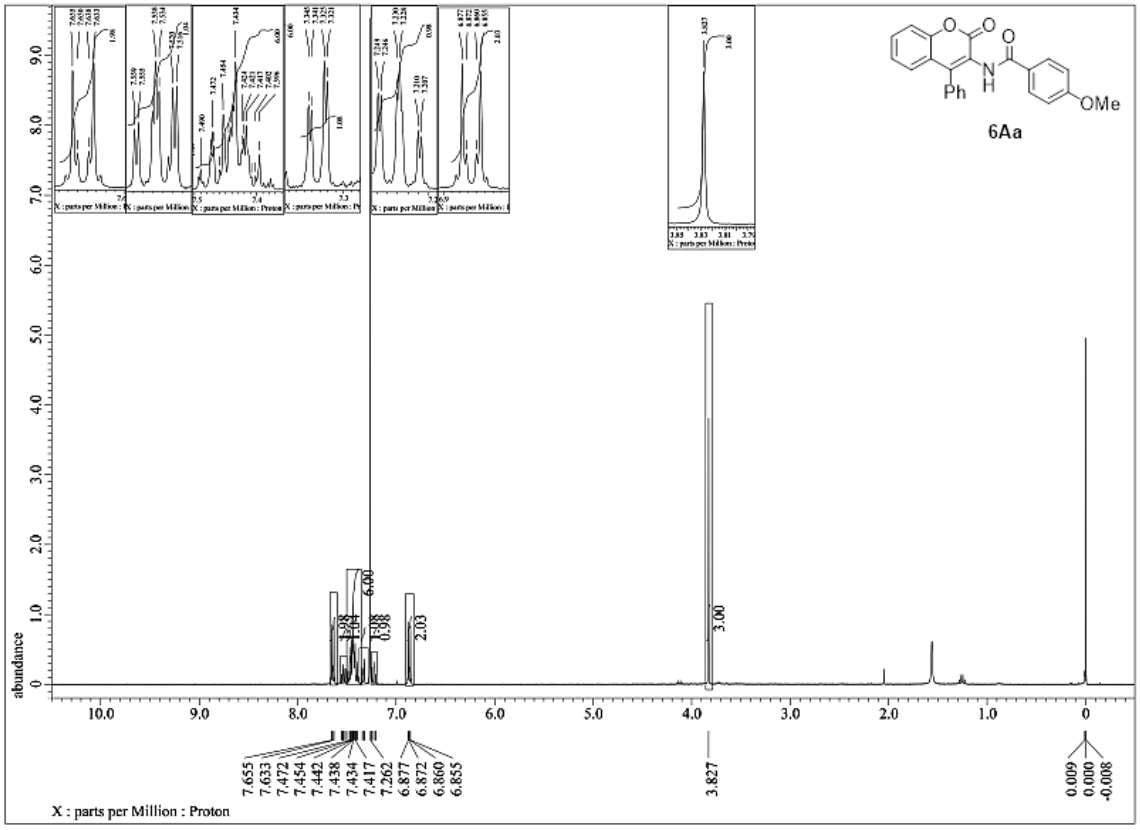

Br
O
O
Br
Ph
3Ea
abundance
156.651
154.026
152.445
134.741
129.548
128.964
128.552
128.121
127.948
125.917
119.949
119.268
112.725
77.316
77.000
76.674
X : parts per Million : Carbon13

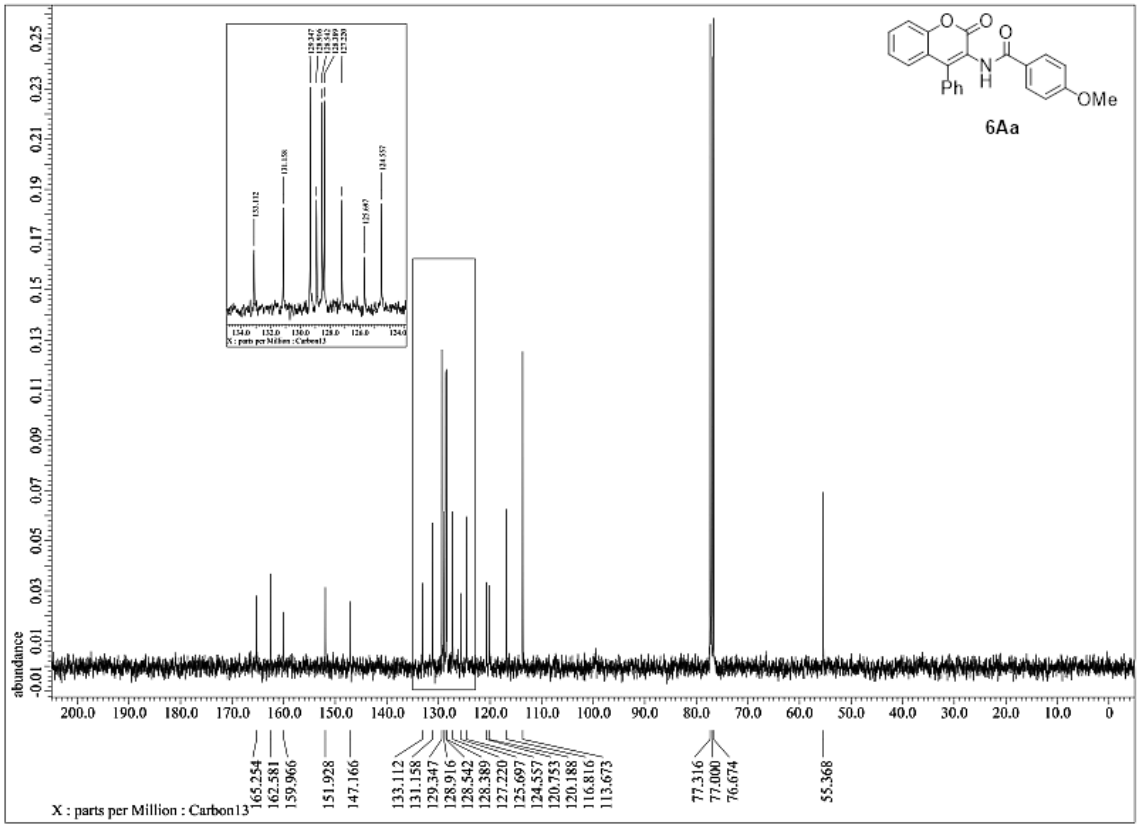

4Aa
abundance
X : parts per Million : Proton
7.530
7.521
7.514
7.480
7.459
7.450
7.418
7.416
7.248
7.224
6.377
-0.015
-0.023
7.00
1.05
2.66
1.00

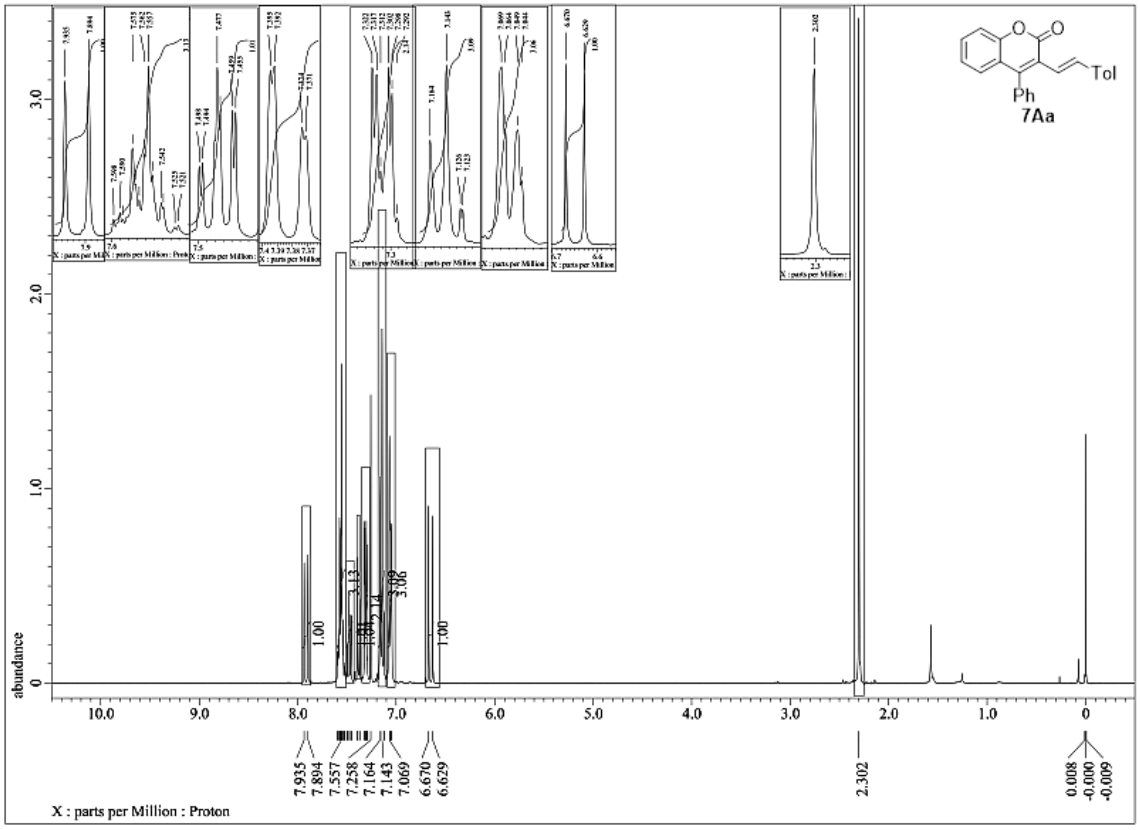

4Aa
abundance
X : parts per Million : Carbon13
160.761
155.654
154.150
135.162
131.905
129.663
128.849
128.418
126.990
124.145
118.952
117.304
115.158
77.316
77.000
76.674

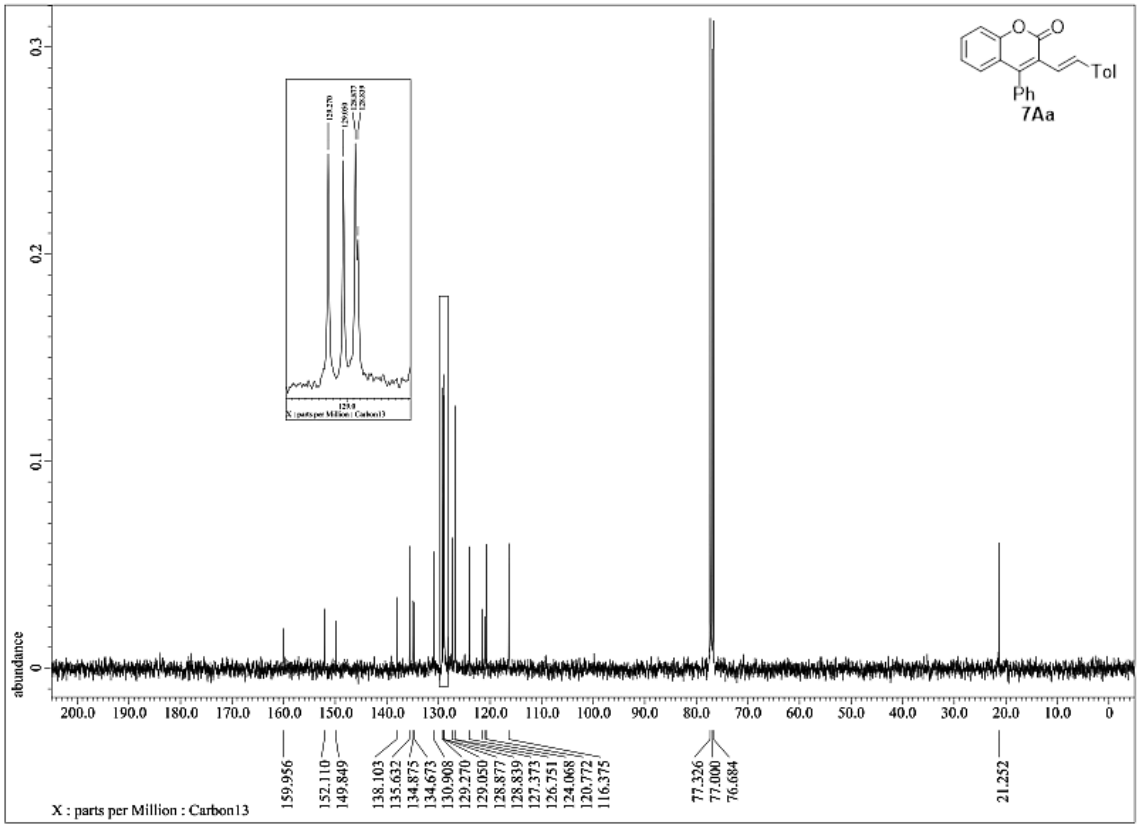

5Aa
abundance
X : parts per Million : Proton

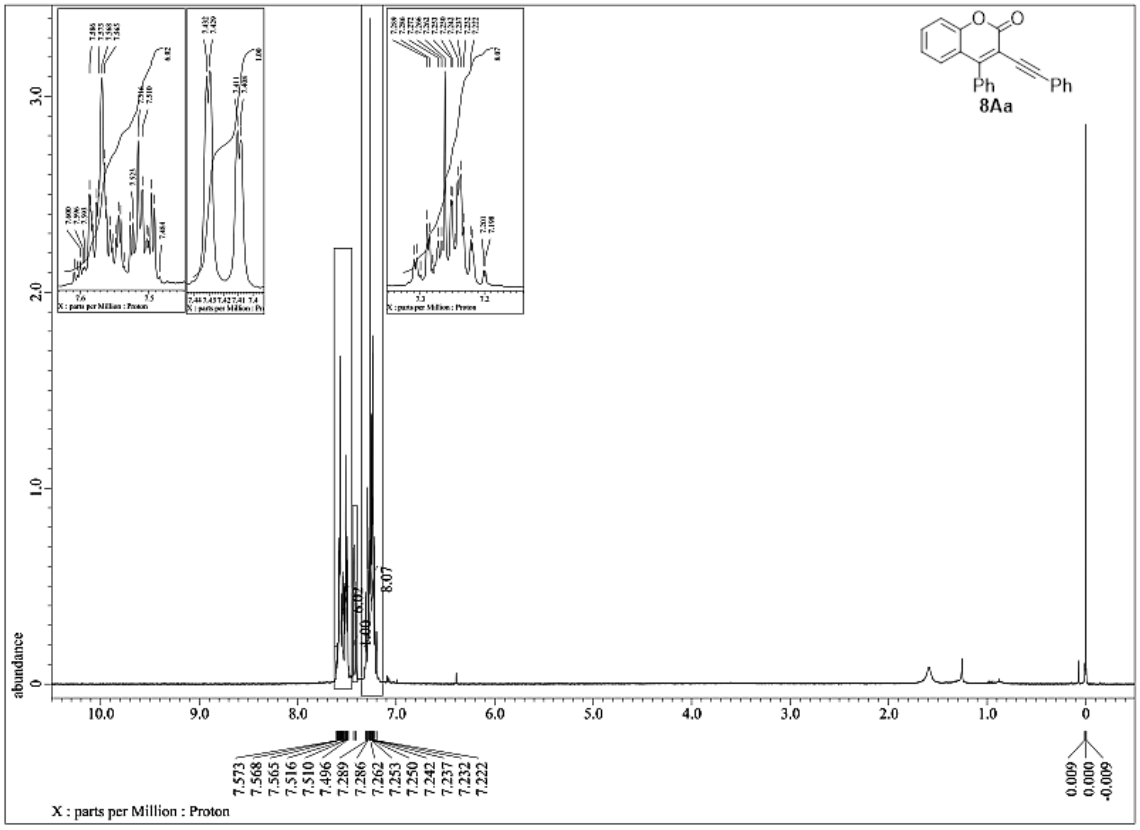

5Aa
abundance
X : parts per Million : Carbon13

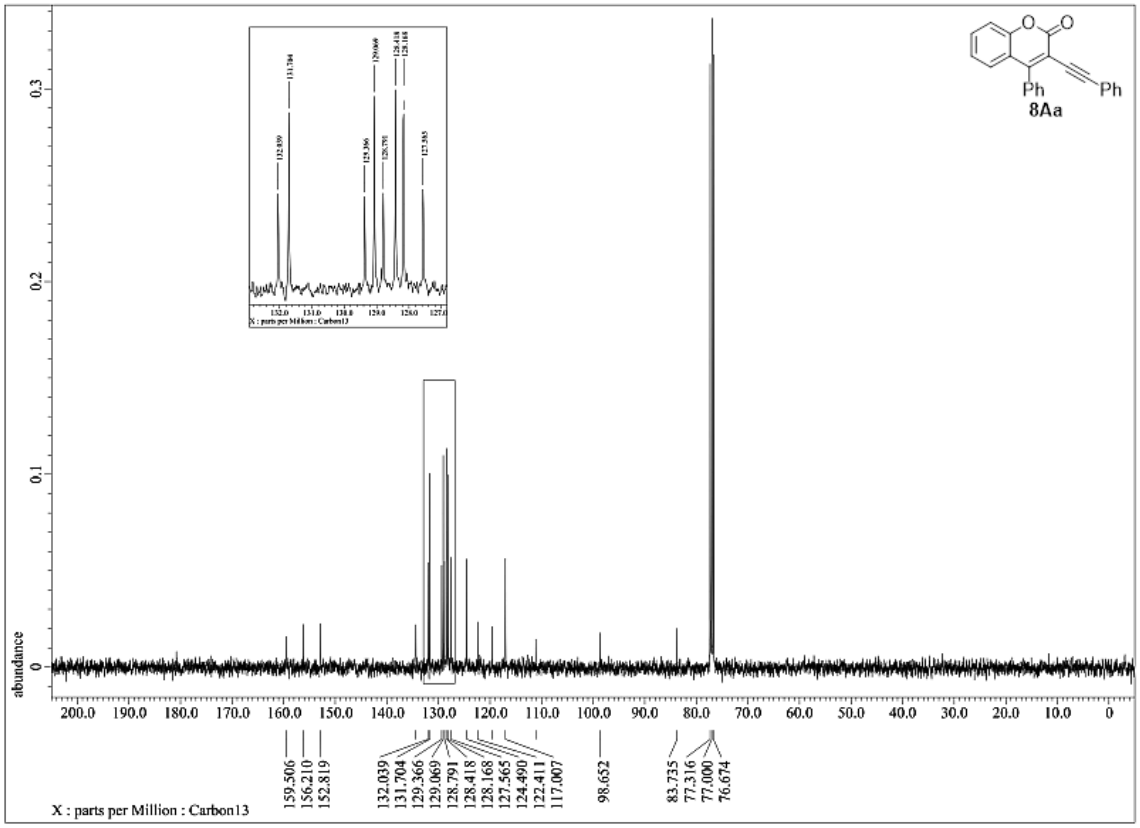

6Aa
abundance
6.00
1.04
1.08
0.98
2.03
3.00
7.655
7.633
7.472
7.454
7.442
7.438
7.434
7.417
7.262
6.877
6.872
6.860
6.855
3.827
0.009
0.000
-0.008
X : parts per Million : Proton

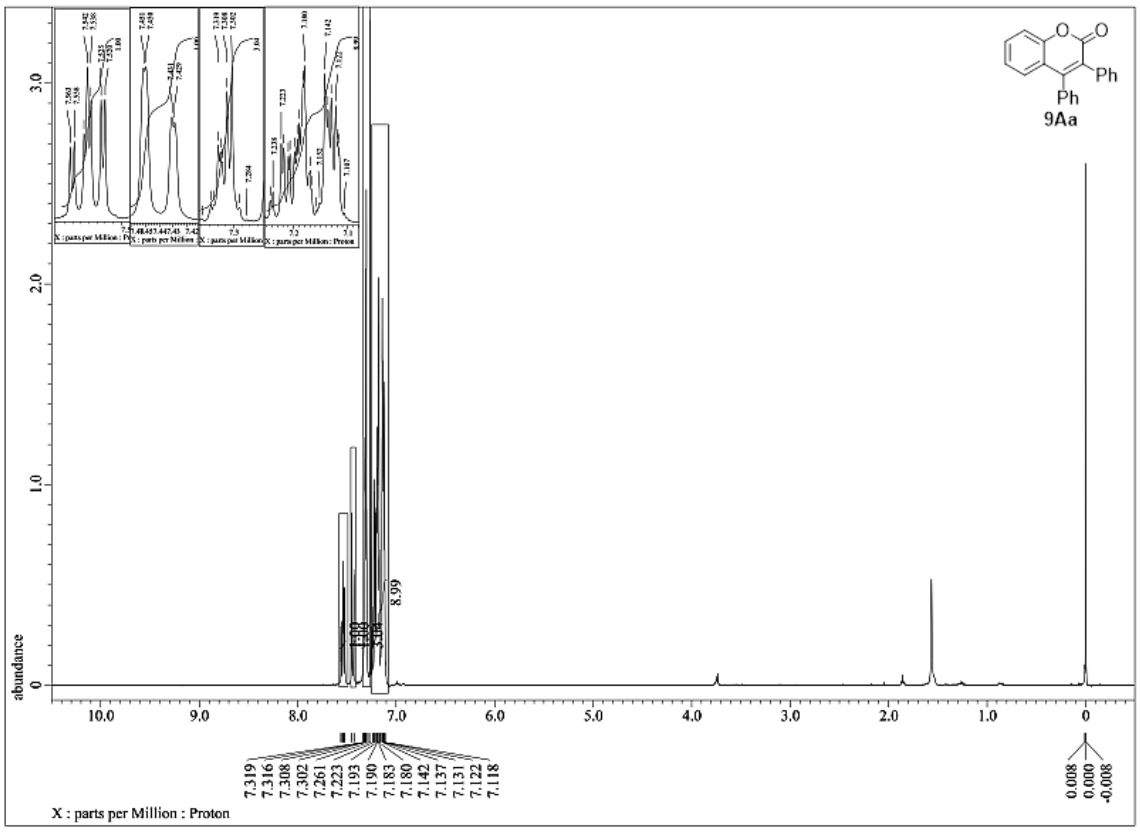

6Aa
abundance
165.254
162.581
159.966
151.928
147.166
133.112
131.158
129.347
128.916
128.542
128.389
127.220
125.697
124.557
120.753
120.188
116.816
113.673
77.316
77.000
76.674
55.368
X : parts per Million : Carbon13

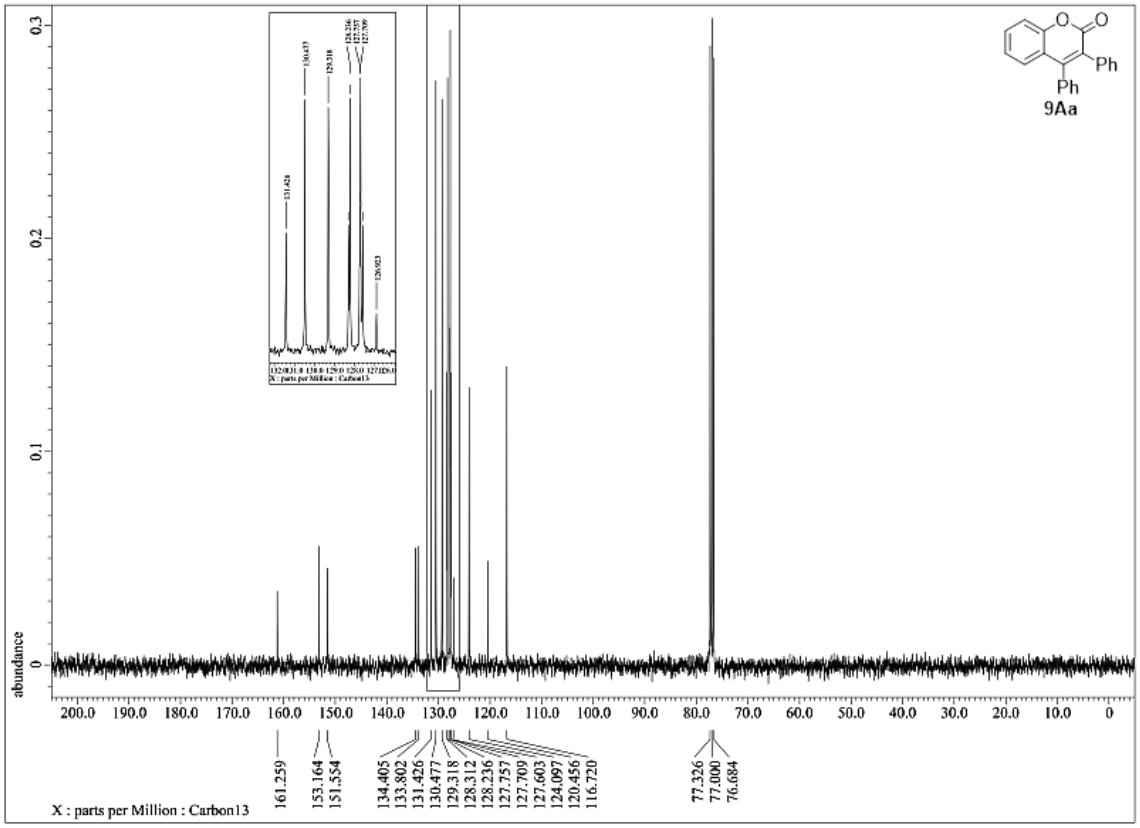

Tol
Ph
7Aa
abundance
X : parts per Million : Proton
7.935
7.894
7.557
7.258
7.164
7.143
7.069
6.670
6.629
2.302
0.008
-0.000
-0.009


Tol
Ph
7Aa
abundance
X : parts per Million : Carbon13
159.956
152.110
149.849
138.103
135.632
134.875
134.673
130.908
129.270
129.050
128.877
128.839
127.373
126.751
124.068
120.772
116.375
77.326
77.000
76.684
21.252


8Aa
abundance
X : parts per Million : Proton


8Aa
abundance
X : parts per Million : Carbon13


9Aa
abundance
X : parts per Million : Proton


9Aa
abundance
X : parts per Million : Carbon13