Supporting Information

Rhodium-Catalyzed Homocoupling of γ-Alkylated *tert*-Propargylic Alcohols

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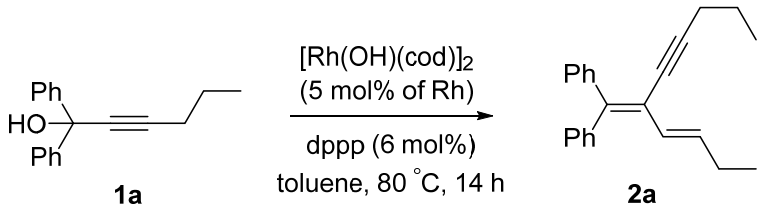
1. General information

All air-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or argon. NMR spectra were recorded on Bruker AVANCE AV-500 spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C) or Bruker AVANCE AV-300 spectrometer (300 MHz for ^{1}H, 75 MHz for ^{13}C). Chemical shifts were reported in δ (ppm) referenced to the residual solvent peak of $CDCl_3$ (δ 7.26) for ^{1}H NMR and $CDCl_3$ (δ 77.0) for ^{13}C NMR. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). Coupling constants were reported in Hertz (Hz). High resolution mass spectra (HRMS) were obtained on an Agilent 1100 LC/DAD/MSD spectrometer (ESI) or Waters GCT Premier mass spectrometer (EI). For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with $KMnO_4$ followed by heating. Flash column chromatography was performed with silica gel (300–400 mesh).

2. Materials

Toluene, THF, and 1,4-dioxane were distilled over benzophenone ketyl under N_2. Rhodium complex $[Rh(OH)(cod)]_2$[1] was prepared according to the reported procedure. Bisphosphine ligands were purchased and used as received. Propargylic alcohols were prepared according to the reported procedures.[2]

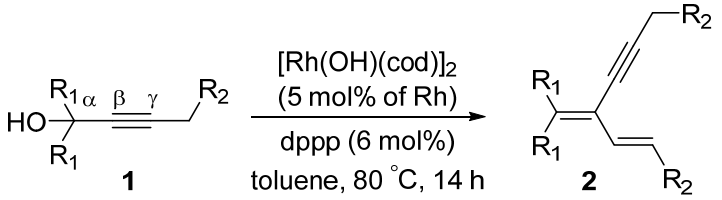
3. A typical procedure for the synthesis of 2a (Table 1, entry 3)



$[Rh(OH)(cod)]_2$ (2.3 mg, 5.0 μmol, 5 mol % Rh) and dppp (4.9 mg, 12 μmol, 6 mol %) were placed in an oven-dried Schlenk tube under nitrogen. Anhydrous toluene (0.4 mL) was added and the resulting mixture was stirred at 35 °C for 10 min. Substrate **1a** (50.0 mg, 0.20 mmol) and another portion of anhydrous toluene (0.6 mL) were added successively, and the mixture was stirred at 80 °C for 14 h. Upon completion, the reaction mixture was passed

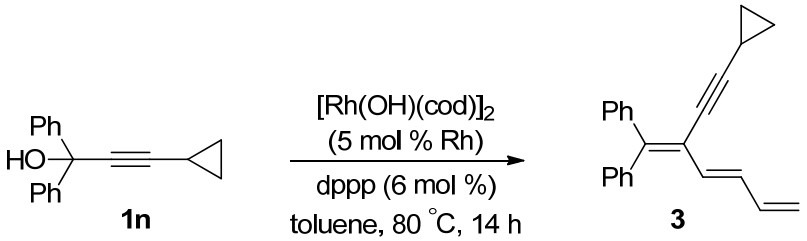
through a short column of silica gel with EtOAc as eluent. The solvent was removed on a rotary evaporator, and the crude product was subjected to silica gel chromatography with petroleum ether to give **2a** (25.8 mg, 86% yield) as a colorless oil.

4. A general procedure for Scheme 2



$[Rh(OH)(cod)]_2$ (2.3 mg, 5.0 μmol, 5 mol % Rh) and dppp (4.9 mg, 12 μmol, 6 mol %) were placed in an oven-dried Schlenk tube under nitrogen. Anhydrous toluene (0.4 mL) was added and the resulting mixture was stirred at 35 °C for 10 min. Substrate **1** (0.20 mmol) and another portion of anhydrous toluene (0.6 mL) were added successively, and the mixture was stirred at 80 °C for 14 h. Upon completion, the reaction mixture was passed through a short column of silica gel with EtOAc as eluent. The solvent was removed on a rotary evaporator, and the crude product was subjected to silica gel chromatography with petroleum ether to give **2** (13 examples, 56–93% yield).

5. <u>The procedure for Scheme 4</u>

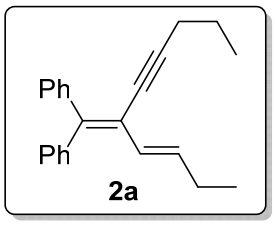


$[Rh(OH)(cod)]_2$ (2.3 mg, 5.0 μmol, 5 mol % Rh) and dppp (4.9 mg, 12 μmol, 6 mol %) were placed in an oven-dried Schlenk tube under nitrogen. Anhydrous toluene (0.4 mL) was added and the resulting mixture was stirred at 35 °C for 10 min. Substrate **1n** (49.6 mg, 0.20 mmol) and another portion of anhydrous toluene (0.6 mL) were added successively, and the mixture was stirred at 80 °C for 14 h. Upon completion, the reaction mixture was passed through a short column of silica gel with EtOAc as eluent. The solvent was removed on a

rotary evaporator, and the crude product was subjected to silica gel chromatography with petroleum ether to give product **3** as a colorless oil (22.2 mg, 75% yield).

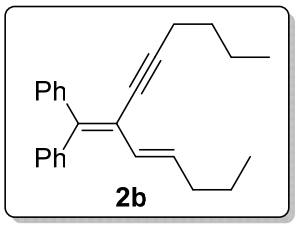
6. Characterization of the products

(*E*)-(2-(But-1-en-1-yl)hept-1-en-3-yne-1,1-diyl)dibenzene (**2a**)



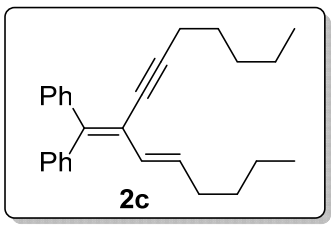
Compound 2a. (86% yield at a 0.20 mmol scale, 25.8 mg; 83% yield at a 1.0 mmol scale, 124.6 mg). Purification by flash chromatography with petroleum ether as the eluent, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.93 (t, *J* = 7.3 Hz, 3H), 1.02 (t, *J* = 7.4 Hz, 3H), 1.44–1.61 (m, 2H), 2.07–2.21 (m, 2H), 2.31 (t, *J* = 6.8 Hz, 2H), 6.23 (d, *J* = 15.4 Hz, 1H), 6.38 (dt, *J* = 17.2 Hz, 6.7 Hz, 1H), 7.19 (d, *J* = 7.3 Hz, 2H), 7.25–7.40 (m, 6H), 7.44 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.5, 13.6, 21.6, 22.0, 25.8, 79.0, 95.6, 120.1, 127.1, 127.2, 127.4, 127.7, 127.9, 130.3, 130.6, 136.9, 141.3, 142.5, 145.5; HRMS (EI) calcd for $C_{23}H_{24}$ $[M]^+$ 300.1873, found 300.1877.

(*E*)-(2-(Pent-1-en-1-yl)oct-1-en-3-yne-1,1-diyl)dibenzene (**2b**)



Compound 2b. (76% yield at a 0.20 mmol scale, 24.9 mg). Purification by flash chromatography with petroleum ether as the eluent, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.84–0.92 (m, 6H), 1.26–1.44 (m, 6H), 2.03–2.10 (m, 2H), 2.30 (t, *J* = 6.8 Hz, 2H), 6.21 (d, *J* = 15.3 Hz, 1H), 6.34 (dt, *J* = 17.2 Hz, 6.9 Hz, 1H), 7.17 (d, *J* = 6.6 Hz, 2H), 7.20–7.34 (m, 6H), 7.42 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.6, 13.7, 19.3, 21.9, 22.5, 29.7, 30.6, 78.9, 95.7, 120.2, 127.1, 127.2, 127.4, 127.9, 128.7, 130.3, 130.6, 135.3, 141.3, 142.5, 145.4; HRMS (EI) calcd for $C_{25}H_{28}$ $[M]^+$ 328.2186, found 328.2191.

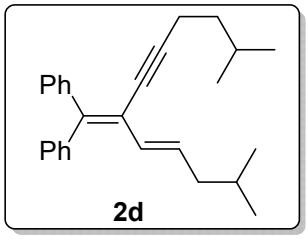
(*E*)-(2-(Hex-1-en-1-yl)non-1-en-3-yne-1,1-diyl)dibenzene (**2c**)



Compound 2c. (73% yield at a 0.20 mmol scale, 26.0 mg). Purification by flash chromatography with petroleum ether as the eluent, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.8 (t, *J* = 6.3 Hz, 6H), 1.18–1.31 (m, 8H), 1.32–1.42 (m, 2H), 1.98–2.05 (m, 2H), 2.23 (t, *J* = 6.9 Hz, 2H), 6.12 (d, *J* = 15.3 Hz, 1H), 6.22 (dt, *J* = 15.1 Hz, 7.5 Hz, 1H), 7.08 (d, *J* = 7.4 Hz, 2H), 7.14–7.28 (m, 6H), 7.33 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.90, 13.95, 19.6, 22.3, 28.2, 29.7, 31.0, 31.5, 32.4, 79.0,

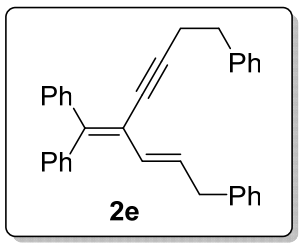
95.7, 120.2, 127.1, 127.2, 127.4, 127.9, 128.6, 130.3, 130.6, 135.5, 141.3, 142.5, 145.4; $C_{27}H_{32}$ $[M]^+$ 356.2499, found 356.2503.

(*E*)-(7-Methyl-2-(4-methylpent-1-en-1-yl)oct-1-en-3-yne-1,1-diyl)dibenzene (**2d**)



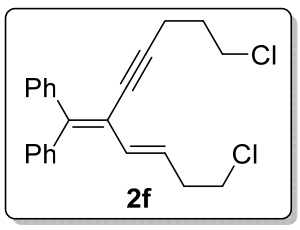
Compound 2d. (75% yield at a 0.20 mmol scale, 26.7 mg). Purification by flash chromatography with petroleum ether as the eluent, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.84–0.90 (m, 12H), 1.37 (t, *J* = 7.1 Hz, 2H), 1.55–1.70 (m, 2H), 1.97 (t, *J* = 6.8 Hz, 2H), 2.31 (t, *J* = 7.2 Hz, 2H), 6.17 (d, *J* = 15.2 Hz, 1H), 6.31 (dt, *J* = 15.1 Hz, 7.6 Hz, 1H), 7.15 (d, *J* = 6.5 Hz, 2H), 7.21–7.41 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.5, 22.1, 22.3, 26.9, 28.6, 37.3, 42.0, 78.9, 95.6, 120.1, 127.1, 127.2, 127.3, 127.8, 129.6, 130.2, 130.6, 134.2, 141.3, 142.4, 145.4; HRMS (EI) calcd for $C_{27}H_{32}$ $[M]^+$ 356.2499, found 356.2505.

(*E*)-(2-(4-Phenylbut-1-yn-1-yl)penta-1,3-diene-1,1,5-triyl)tribenzene (**2e**)



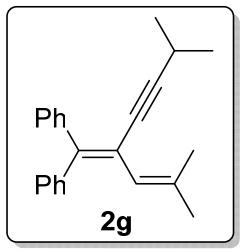
Compound 2e. (85% yield at a 0.20 mmol scale, 36.0 mg). Purification by flash chromatography with petroleum ether as the eluent, yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.57 (t, *J* = 7.4 Hz, 2H), 2.75 (t, *J* = 7.3 Hz, 2H), 3.39 (d, *J* = 6.0 Hz, 2H), 6.25 (d, *J* = 15.3 Hz, 1H), 6.31–6.38 (m, 1H), 7.14 (d, *J* = 7.0 Hz, 8H), 7.32–7.22 (m, 10H), 7.38 (d, *J* = 5.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 34.7, 39.0, 79.5, 94.7, 119.6, 126.0, 126.1, 127.3, 127.4, 127.9, 128.3, 128.4, 128.6, 129.9, 130.3, 130.6, 140.3, 140.7, 141.1, 142.3, 146.5; HRMS (EI) calcd for $C_{33}H_{28}$ $[M]^+$ 424.2186, found 424.2191.

(*E*)-(7-Chloro-2-(4-chlorobut-1-en-1-yl)hept-1-en-3-yne-1,1-diyl)dibenzene (**2f**)



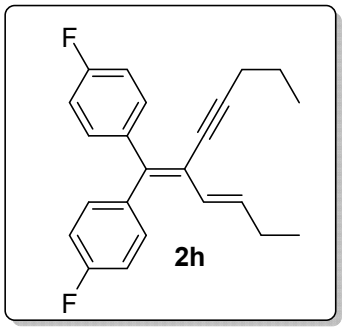
Compound 2f. (91% yield at a 0.20 mmol scale, 33.5 mg). Purification by flash chromatography with petroleum ether as the eluent, yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.83–1.91 (m, 2H), 2.50–2.56 (m, 4H), 3.42 (t, *J* = 6.4 Hz, 2H), 3.53 (t, *J* = 7.0 Hz, 2H), 6.20–6.35 (m, 2H), 7.14 (d, *J* = 6.2 Hz, 2H), 7.24–7.39 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.0, 31.2, 35.8, 43.5, 43.9, 79.7, 93.5, 119.3, 127.56, 127.59, 128.0, 129.9, 130.1, 130.5, 131.1, 140.7, 142.3, 147.6; HRMS (EI) calcd for $C_{23}H_{22}Cl_2$ $[M]^+$ 368.1093, found 368.1097.

(5-Methyl-2-(2-methylprop-1-en-1-yl)hex-1-en-3-yne-1,1-diyl)dibenzene (**2g**)



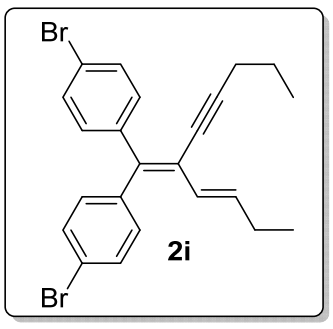
Compound 2g. (56% yield at a 0.20 mmol scale, 16.8 mg). Purification by flash chromatography with petroleum ether as the eluent, white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.06 (d, *J* = 6.8 Hz, 6H), 1.70 (s, 3H), 1.89 (s, 3H), 2.60 (hept, *J* = 6.8 Hz, 1H), 5.7 (s, 1H), 7.14 (d, *J* = 6.9 Hz, 2H), 7.20–7.28 (m, 6 H), 7.40 (d, *J* = 7.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.8, 21.4, 22.4, 26.9, 80.9, 100.2, 118.4, 123.7, 126.98, 126.99, 127.3, 127.6, 130.4, 130.6, 136.7, 141.7, 142.4, 147.4; HRMS (EI) calcd for $C_{23}H_{24}$ $[M]^+$ 300.1873, found 300.1879.

(*E*)-4,4'-(2-(But-1-en-1-yl)hept-1-en-3-yne-1,1-diyl)bis(fluorobenzene) (**2h**)



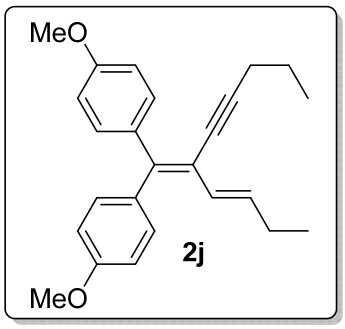
Compound 2h. (87% yield at a 0.20 mmol scale, 29.2 mg). Purification by flash chromatography with petroleum ether as the eluent, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.92 (t, *J* = 7.4 Hz, 3H), 0.99 (t, *J* = 7.4 Hz, 3H), 1.51 (sext, *J* = 7.2 Hz, 2H), 2.13 (quint, *J* = 7.2 Hz, 2H), 2.30 (t, *J* = 7.0 Hz, 2H), 6.15 (d, *J* = 15.2 Hz, 1H), 6.36 (dt, *J* = 15.2 Hz, 6.7 Hz, 1H), 6.95 (t, *J* = 8.7 Hz, 2H), 7.02 (t, *J* = 8.7 Hz, 2H), 7.10–7.13 (m, 2 H), 7.36–7.39 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.47, 13.50, 21.6, 22.0, 25.8, 78.8, 95.9, 114.3, 114.4, 114.9, 115.1, 120.5, 127.3, 131.95, 132.02, 132.2, 132.3, 137.0, 137.5, 138.3, 143.1, 161.0, 161.1, 163.0, 163.1; HRMS (EI) calcd for $C_{23}H_{22}F_2$ $[M]^+$ 336.1684, found 336.1693.

(*E*)-4,4'-(2-(But-1-en-1-yl)hept-1-en-3-yne-1,1-diyl)bis(fluorobenzene) (**2i**)



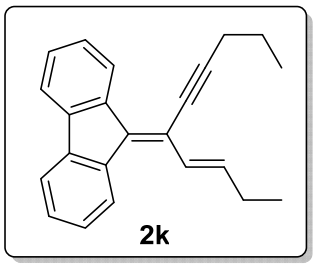
Compound 2i. (70% yield at a 0.20 mmol scale, 32.1 mg). Purification by flash chromatography with petroleum ether as the eluent, yellowish oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.92 (t, *J* = 7.4 Hz, 3H), 0.98 (d, *J* = 7.5 Hz, 3H), 1.27 (d, *J* = 9.4 Hz, 2H), 1.50–1.57 (m, 2H), 2.04–2.19 (m, 2H), 2.30 (t, *J* = 6.9 Hz, 2H), 6.14 (d, *J* = 15.2 Hz, 1H), 6.33–6.44 (m, 1H), 7.01 (d, *J* = 8.3 Hz, 2H), 7.23–7.28 (m, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.5, 21.6, 21.9, 25.8, 30.9, 78.7, 96.6, 121.2, 121.4, 121.7, 127.2, 130.7, 131.3, 132.0, 132.3, 138.3, 139.7, 140.9, 142.6; HRMS (EI) calcd for $C_{23}H_{22}{}^{79}Br_2$ $[M]^+$ 456.0083, found 456.0087; calcd for $C_{23}H_{22}{}^{81}Br_2$ $[M]^+$ 460.0045, found 460.0050.

(*E*)-4,4'-(2-(But-1-en-1-yl)hept-1-en-3-yne-1,1-diyl)bis(methoxybenzene) (**2j**)



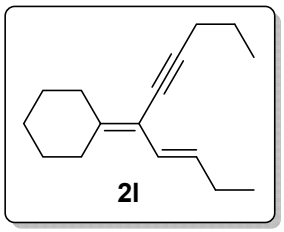
Compound 2j. (93% yield at a 0.20 mmol scale, 33.5 mg). Purification by flash chromatography with petroleum ether as the eluent, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7.4 Hz, 3H), 1.00 (t, *J* = 7.4 Hz, 3H), 1.46–1.54 (m, 2H), 2.07–2.17 (m, 2H), 2.31 (t, *J* = 6.9 Hz, 2H), 3.80 (s, 3H), 3.83 (s, 3H), 6.22 (d, *J* = 15.3 Hz, 1H), 6.26–6.37 (m, 1H), 6.79 (d, *J* = 8.3 Hz, 2H), 6.86 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.7, 13.8, 21.7, 22.1, 25.9, 55.2, 79.5, 95.0, 112.7, 113.3, 118.4, 128.1, 131.0, 131.8, 133.9, 135.3, 135.9, 145.0, 158.8, 158.8; HRMS (EI) calcd for $C_{25}H_{28}O_2$ $[M]^+$ 360.2084, found 360.2094.

(*E*)-9-(Dec-3-en-6-yn-5-ylidene)-9H-fluorene (**2k**)



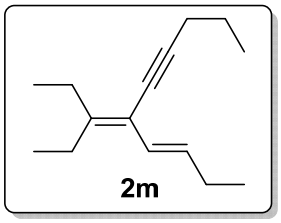
Compound 2k. (71% yield at a 0.20 mmol scale, 21.2 mg). Purification by flash chromatography with petroleum ether as the eluent, yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.14 (t, *J* = 7.4 Hz, 3H), 1.18 (t, *J* = 7.4 Hz, 3H), 1.78 (sext, *J* = 7.2 Hz, 2H), 2.39 (quint, *J* = 7.2 Hz, 2H), 2.64 (t, *J* = 7.1 Hz, 2H), 6.67 (dt, *J* = 15.2 Hz, 6.6 Hz, 1H), 7.24–7.33 (m, 5H), 7.68–7.72 (m, 2H), 7.89 (d, *J* = 7.7 Hz, 1H), 8.78 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.4, 13.8, 22.1, 22.2, 26.2, 80.2, 103.0, 122.1, 124.8, 126.2, 126.8, 126.9, 127.5, 127.7, 127.8, 137.0, 138.0, 139.0, 139.7, 140.2, 141.4; HRMS (EI) calcd for $C_{23}H_{22}$ $[M]^+$ 298.1716, found 298.1724.

(*E*)-Dec-3-en-6-yn-5-ylidenecyclohexane (**2l**)



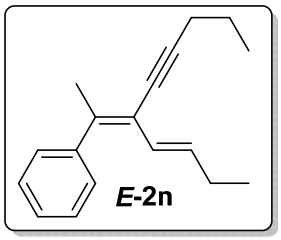
Compound 2l. (73% yield at a 0.20 mmol scale, 15.8 mg). Purification by flash chromatography with petroleum ether as the eluent, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.04 (t, *J* = 7.4 Hz, 6H), 1.40–1.71 (m, 8H), 2.12–2.22 (m, 2H), 2.31–2.44 (m, 4H), 2.53 (d, *J* = 5.5 Hz, 2H), 6.08–6.21 (m, 1H), 6.40 (d, *J* = 15.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.6, 13.8, 21.5, 22.5, 25.8, 26.7, 27.8, 27.9, 29.9, 34.4, 77.8, 94.1, 114.3, 124.2, 134.3, 146.9; HRMS (EI) calcd for $C_{16}H_{24}$ $[M]^+$ 216.1873, found 216.1878.

(*E*)-5-(Pentan-3-ylidene)dec-3-en-6-yne (**2m**)



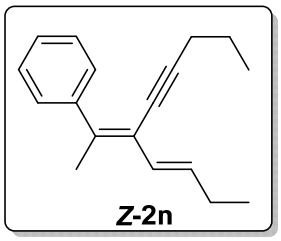
Compound 2m. (68% yield at a 0.20 mmol scale, 13.9 mg). Purification by flash chromatography with petroleum ether as the eluent, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.04 (t, *J* = 7.6 Hz, 12H), 1.56–1.65 (m, *J* = 12.8, 2H), 2.10–2.30 (m, 4H), 2.32–2.45 (m, 4H), 6.04–6.23 (m, 1H), 6.30 (d, *J* = 15.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.7, 13.3, 13.6, 13.8, 21.6, 22.5, 24.1, 25.9, 28.6, 77.8, 94.1, 116.5, 124.7, 134.1, 150.7; HRMS (EI) calcd for $C_{15}H_{24}$ $[M]^+$ 204.1873, found 204.1884.

((*E*)-3-((*E*)-But-1-en-1-yl)oct-2-en-4-yn-2-yl)benzene (***E*-2n**)



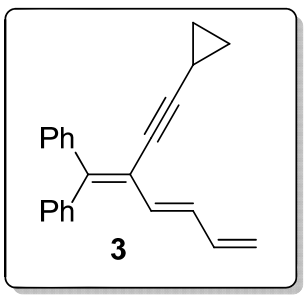
Compound *E*-2n. (45% yield at a 0.40 mmol scale, 21.4 mg). Purification by flash chromatography with petroleum ether/CH_2Cl_2 (30:1, v/v) as the eluent, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.00 (t, *J* = 7.4 Hz, 3H), 1.14 (t, *J* = 7.4 Hz, 3H), 1.73 (sext, *J* = 7.2 Hz, 2H), 2.11 (quint, *J* = 7.2 Hz, 2H), 2.39 (s, 3H), 2.52 (t, *J* = 7.0 Hz, 2H), 6.12 (d, *J* = 15.3 Hz, 1H), 6.20 (dt, *J* = 15.2 Hz, 6.5 Hz, 1H), 7.24 (d, *J* = 7.1 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.6, 13.7, 21.6, 22.5, 24.2, 25.6, 78.1, 96.5, 119.5, 126.4, 126.9, 128.0, 128.4, 134.8, 142.2, 142.3; HRMS (EI) calcd for $C_{18}H_{22}$ $[M]^+$ 238.1716, found 238.1714.

((*Z*)-3-((*E*)-But-1-en-1-yl)oct-2-en-4-yn-2-yl)benzene (***Z*-2n**)



Compound *Z*-2n. (27% yield at a 0.40 mmol scale, 13.0 mg). Purification by flash chromatography with petroleum ether/CH_2Cl_2 (30:1, v/v) as the eluent, colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.4 Hz, 3H), 1.14 (t, *J* = 7.4 Hz, 3H), 1.46 (sext, *J* = 7.2 Hz, 2H), 2.21 – 2.33 (m, 7H), 6.37 (dt, *J* = 13.3 Hz, 6.6 Hz, 1H), 6.52 (d, *J* = 15.1 Hz, 1H), 7.27 (t, *J* = 7.3 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.48 (d, *J* = 7.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.4, 13.7, 20.0, 21.4, 22.0, 25.9, 78.6, 93.7, 118.8, 125.6, 126.7, 127.5, 128.3, 136.4, 140.7, 144.2; HRMS (EI) calcd for $C_{18}H_{22}$ $[M]^+$ 238.1716, found 238.1714.

(*E*)-(2-(Cyclopropylethynyl)hexa-1,3,5-triene-1,1-diyl)dibenzene (**3**)



Compound 3. (75% yield at a 0.20 mmol scale, 22.2 mg). Purification by flash chromatography with petroleum ether as the eluent, colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.60–0.64 (m,2H), 0.70 – 0.83 (m, 2H), 1.30 – 1.46 (m, 1H), 5.11 (d, *J* = 10.1

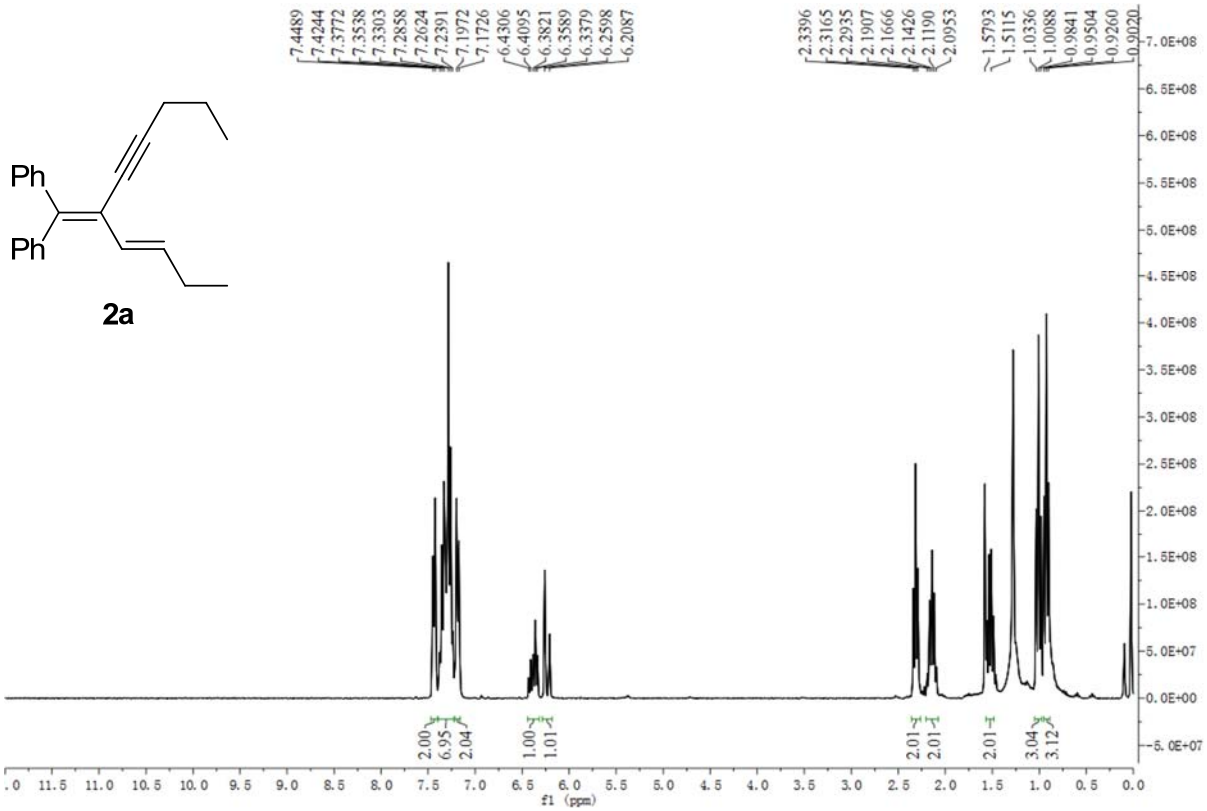
Hz, 1H), 5.31 (d, *J* = 16.9 Hz, 1H), 6.20–6.51 (m, 2H), 6.81 (dd, *J* = 14.9, 10.9 Hz, 1H), 7.14 (d, *J* = 7.3 Hz, 2H), 7.22–7.35 (m, 6H), 7.39 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.5, 29.8, 73.7, 99.0, 118.0, 119.9, 127.4, 127.6, 119.9, 130.4, 130.7, 131.9, 133.5, 137.1, 141.0, 142.2, 147.9; HRMS (EI) calcd for $C_{23}H_{20}$ $[M]^+$ 296.1560, found 296.1559.

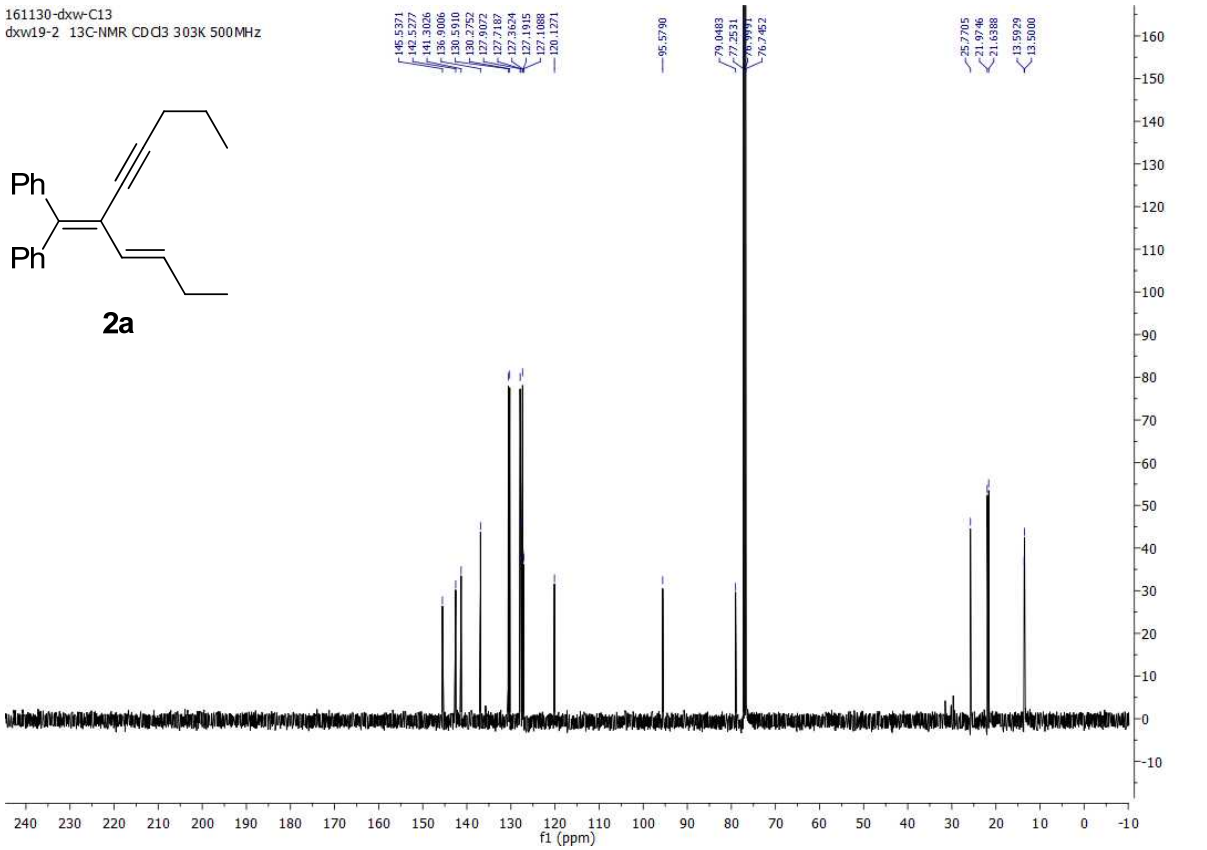
7. References

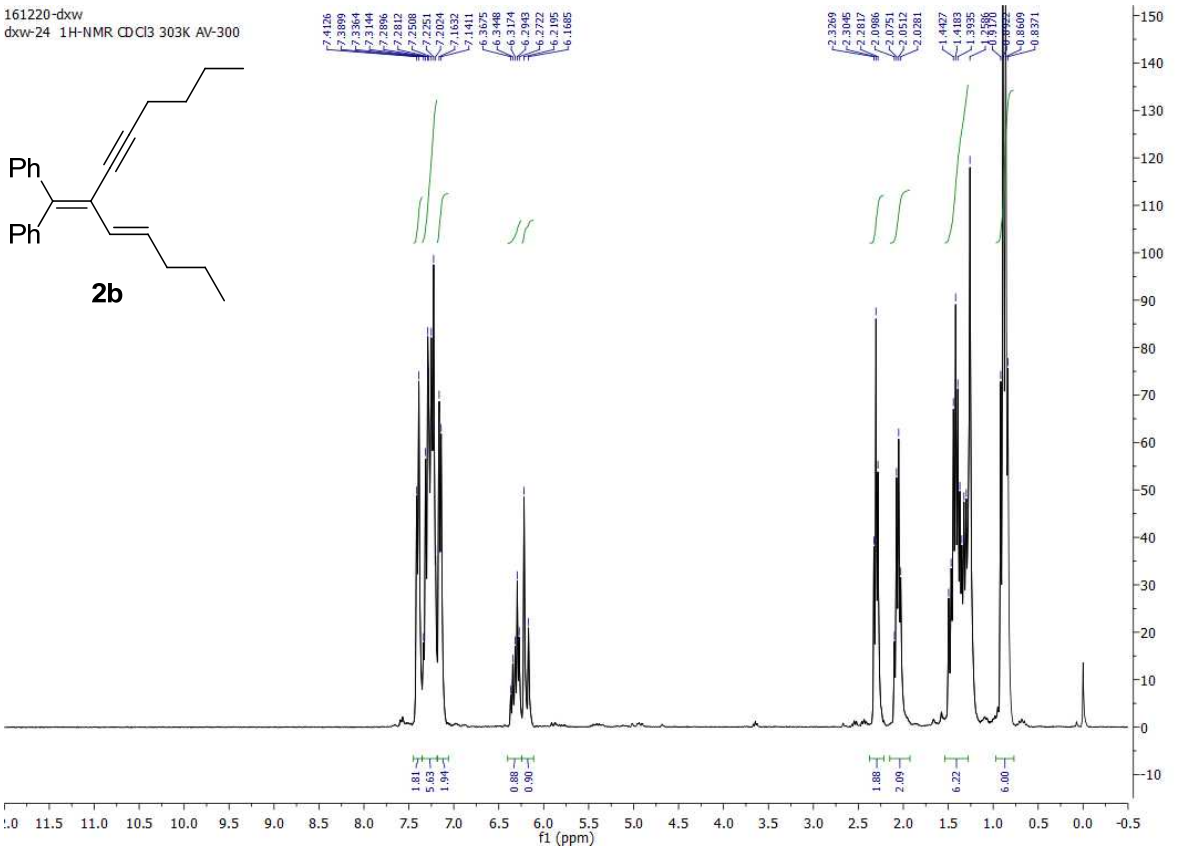
[1] Uson, R.; Oro, L. A.; Cabeza, J. A. *Inorg. Synth.* **1985**, *23*, 126.

[2] (a) Liu, N.; Zhi, Y.; Yao, J.; Xing, J.; Lu, T.; Dou, X. *Adv. Synth. Catal.* 10.1002/adsc.201701263. (b) Dou, X.; Huang, Y.; Hayashi, T. *Angew. Chem. Int. Ed.* **2016**, *55*, 1133.

8. NMR spectra



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Ph
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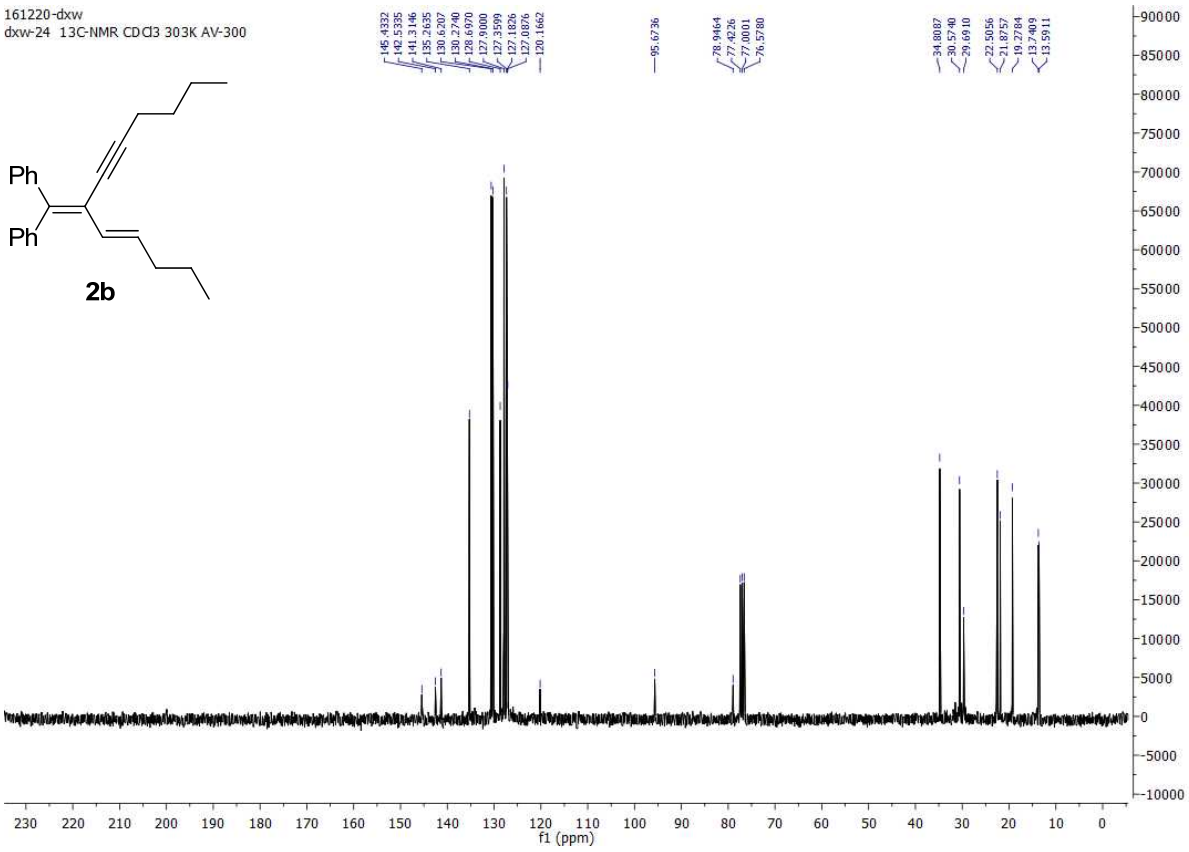
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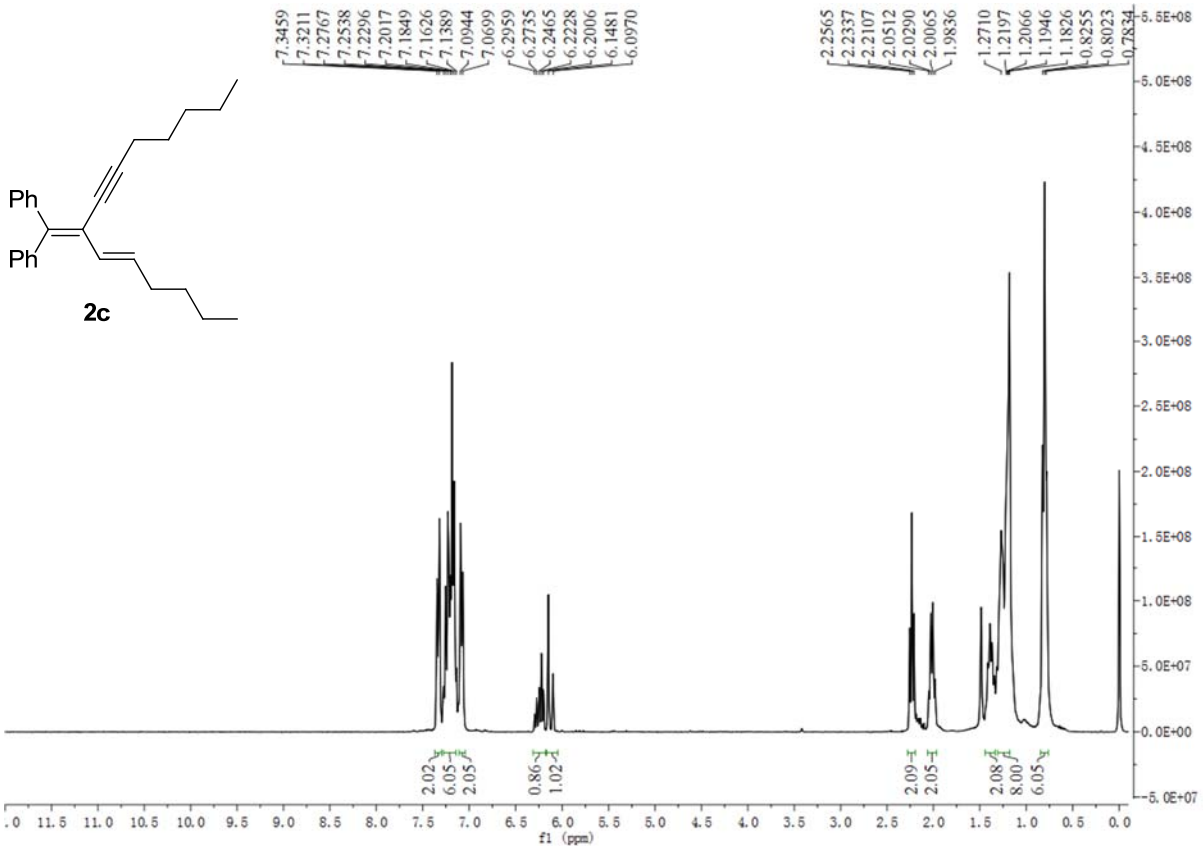
Ph
2b
f1 (ppm)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7.0944
7.0699
6.2959
6.2735
6.2465
6.2228
6.2006
6.1481
6.0970
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2.2337
2.2107
2.0512
2.0290
2.0065
1.9836
1.2710
1.2197
1.2066
1.1946
1.1826
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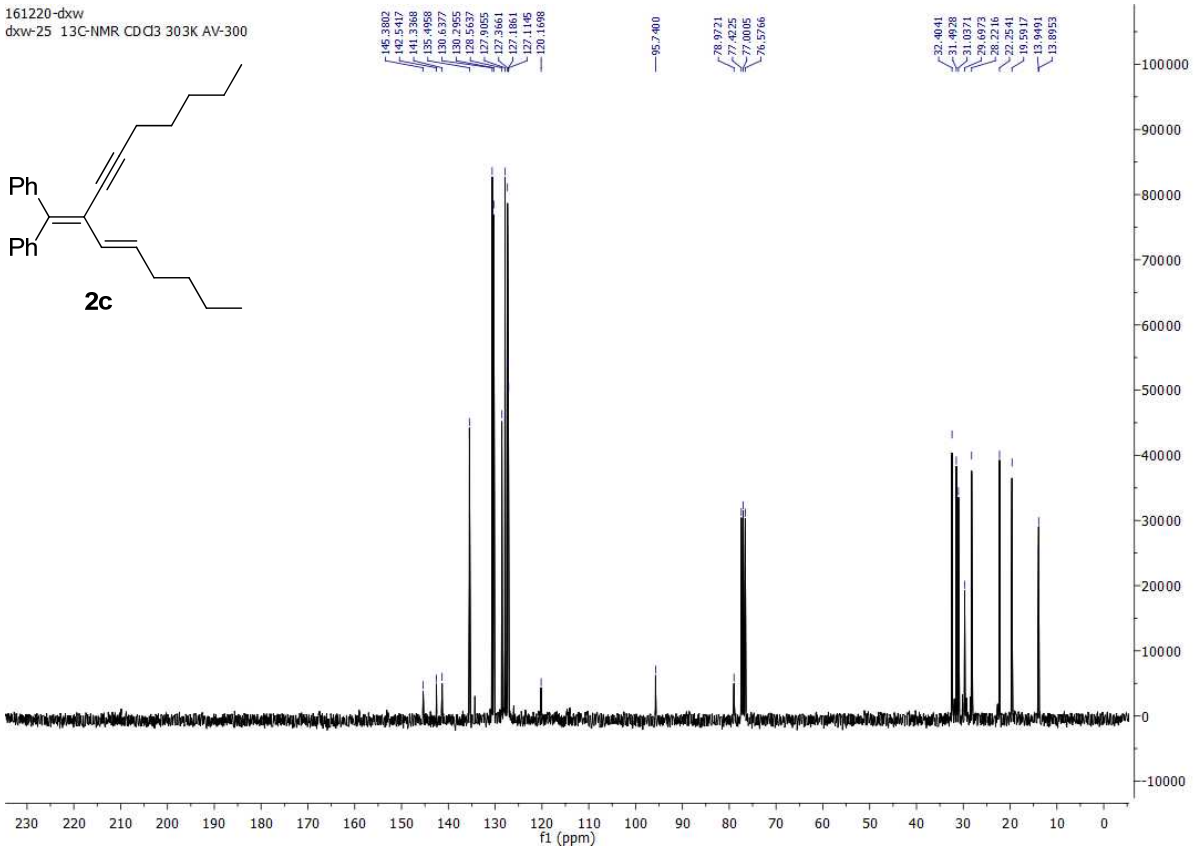
f1 (ppm)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127.1145
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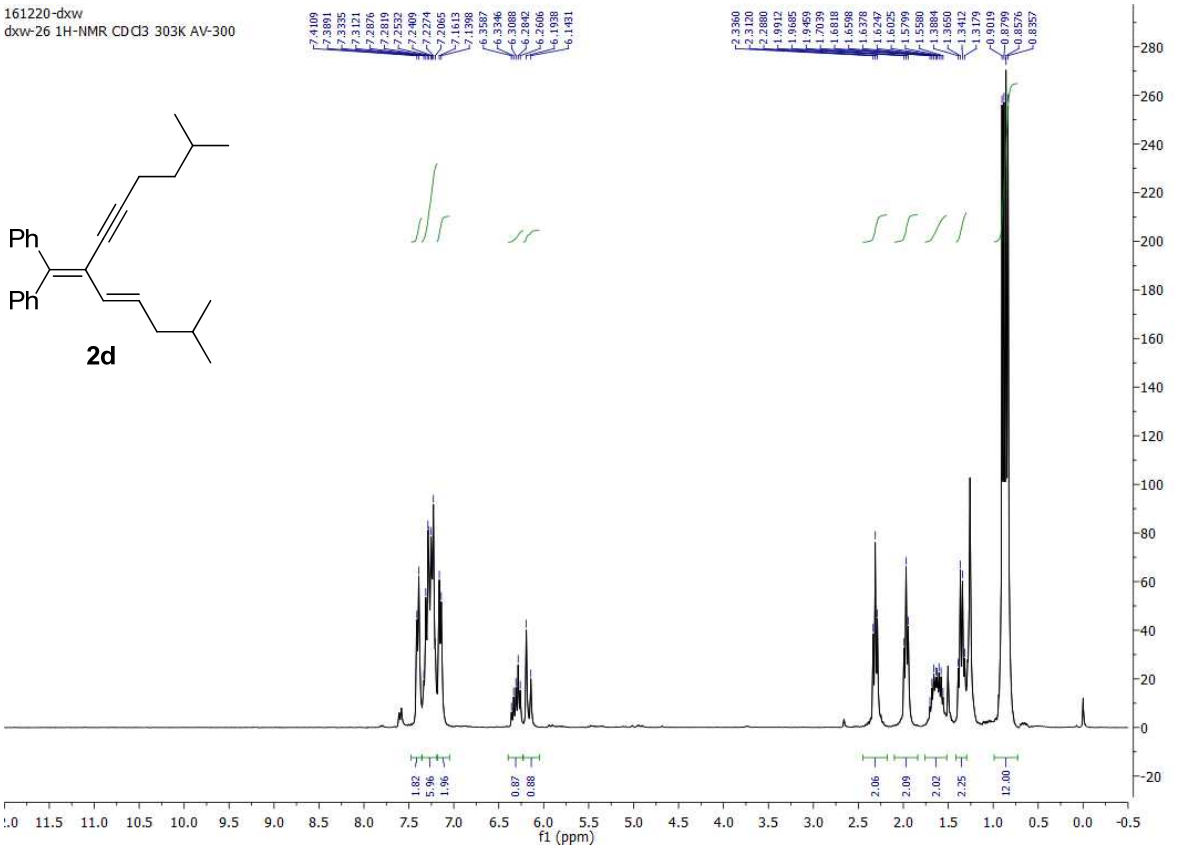
f1 (ppm)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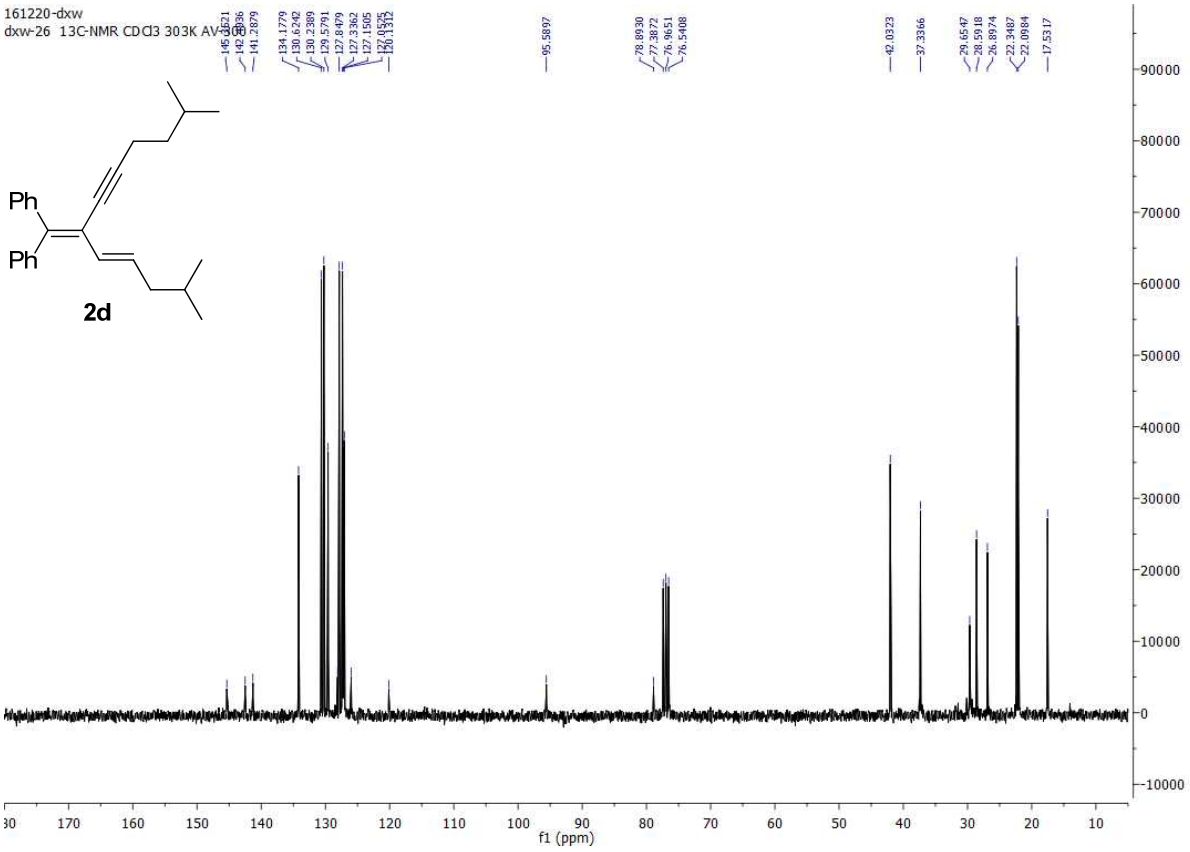
Ph
2d
f1 (ppm)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dxw-26 13C-NMR CDCl3 303K AV-300
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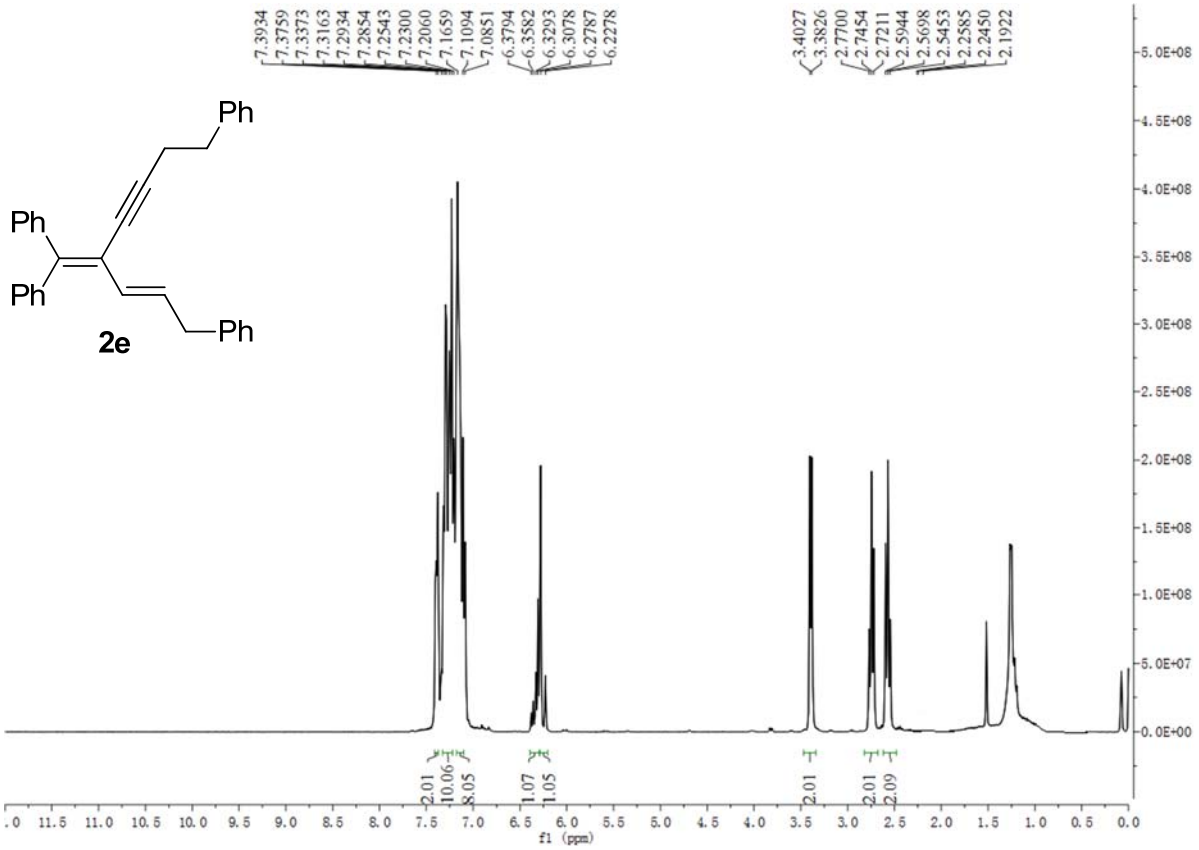
Ph
2d
f1 (ppm)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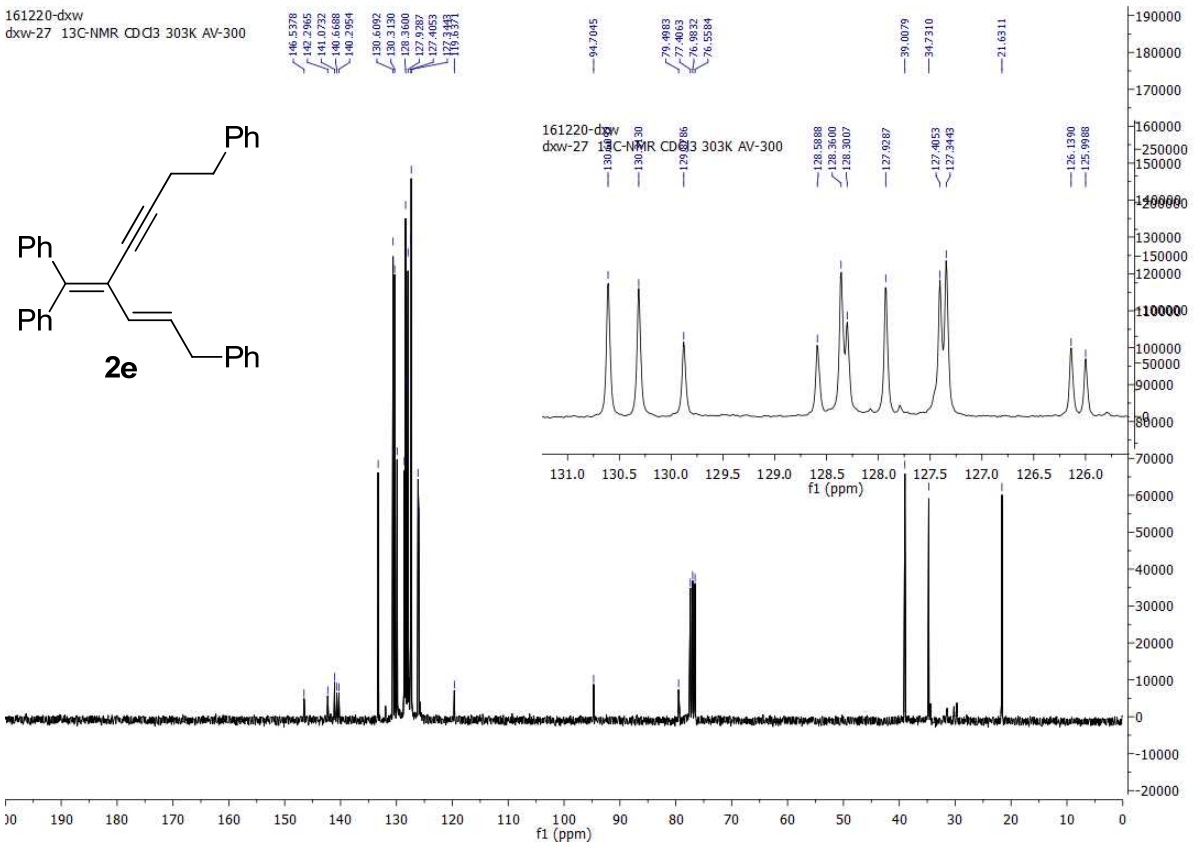
Ph
Ph
2e
f1 (ppm)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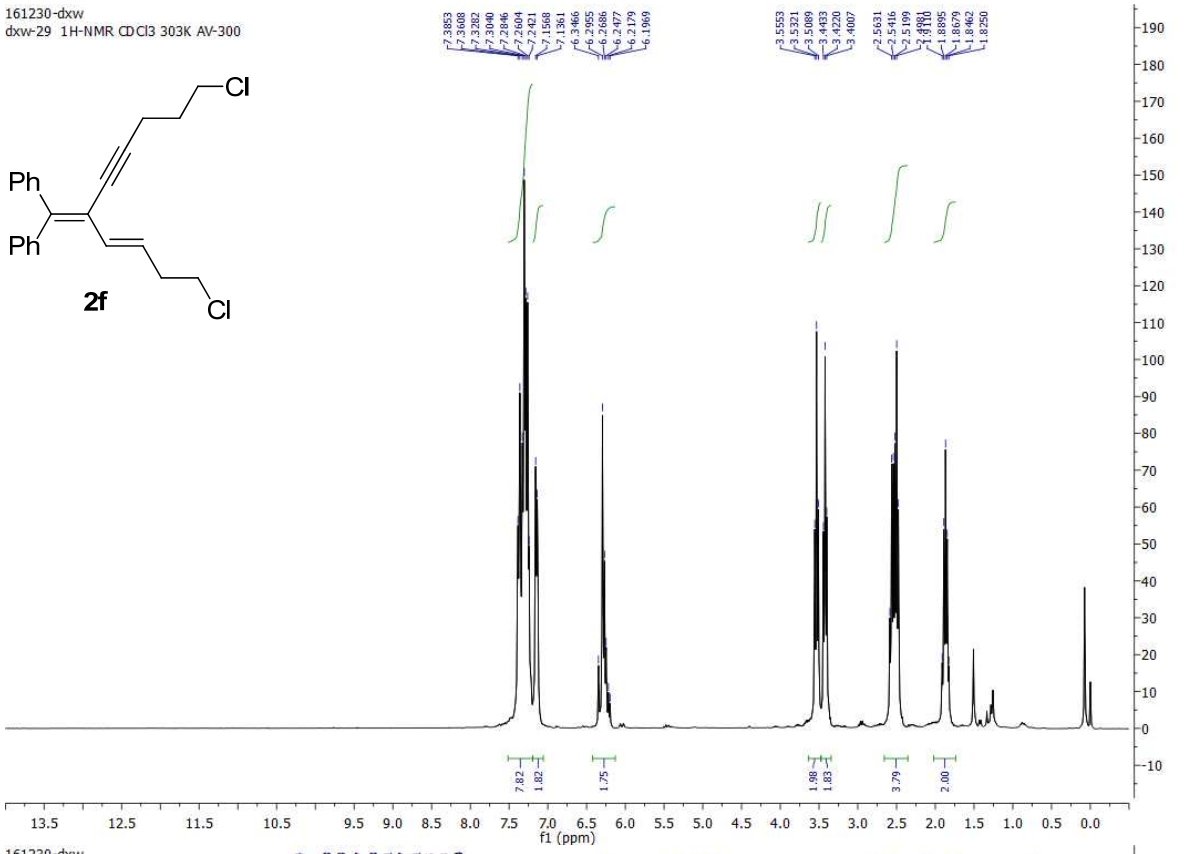
Ph
Ph
Ph
2e
f1 (ppm)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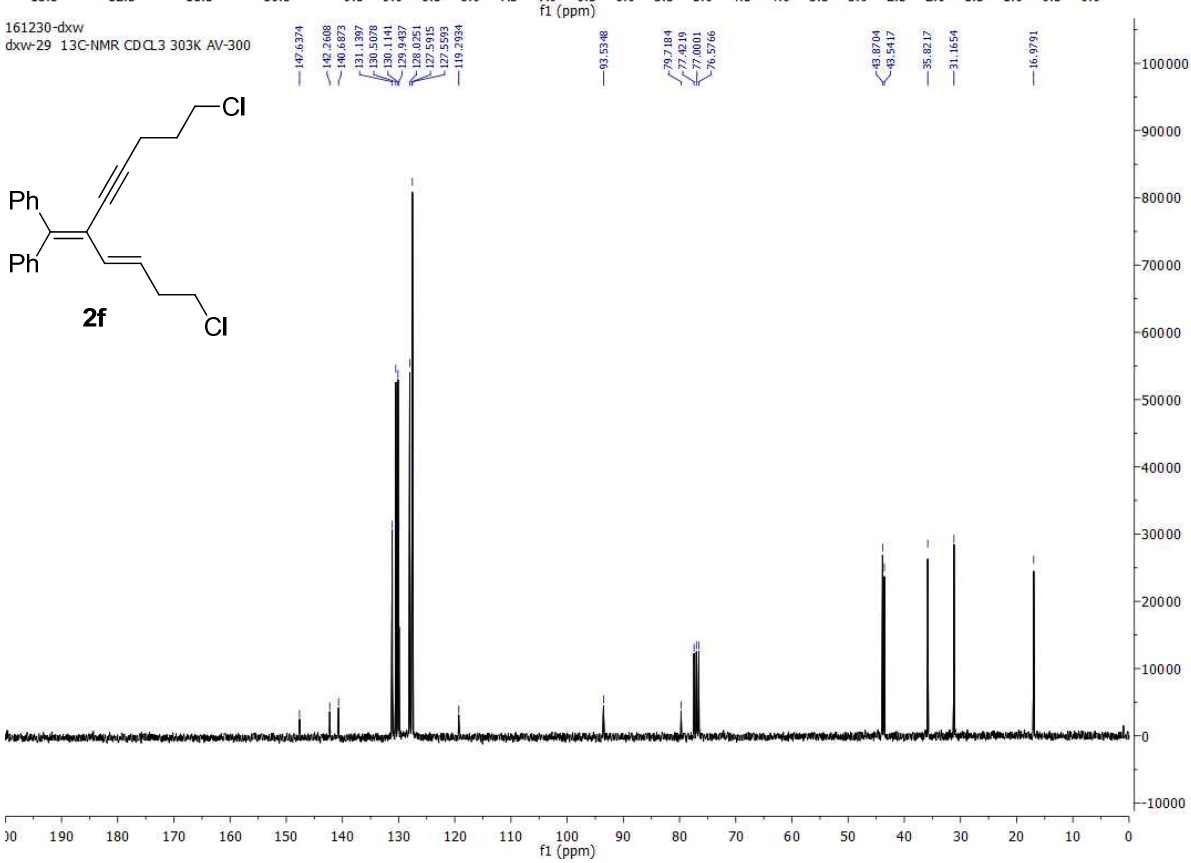
Ph
2f
Cl
f1 (ppm)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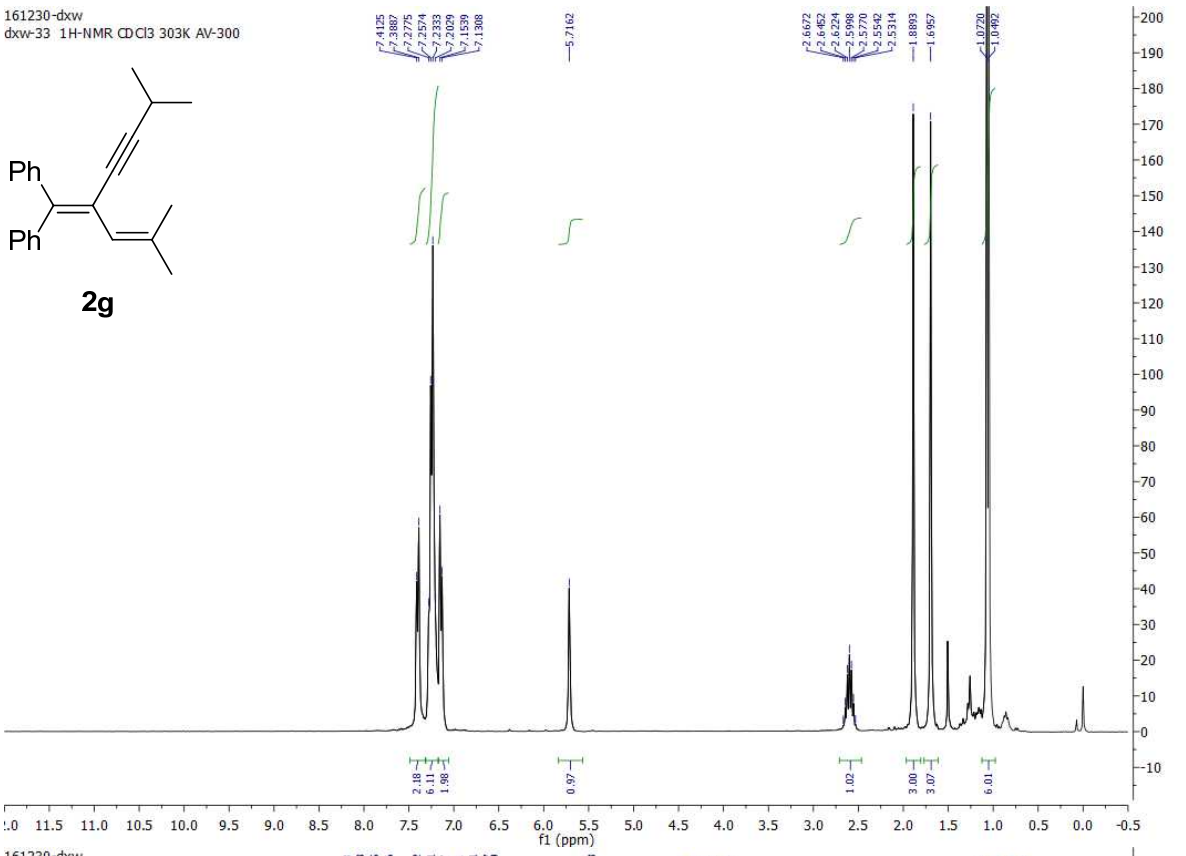
Ph
Ph
2f
Cl
f1 (ppm)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Ph
2g
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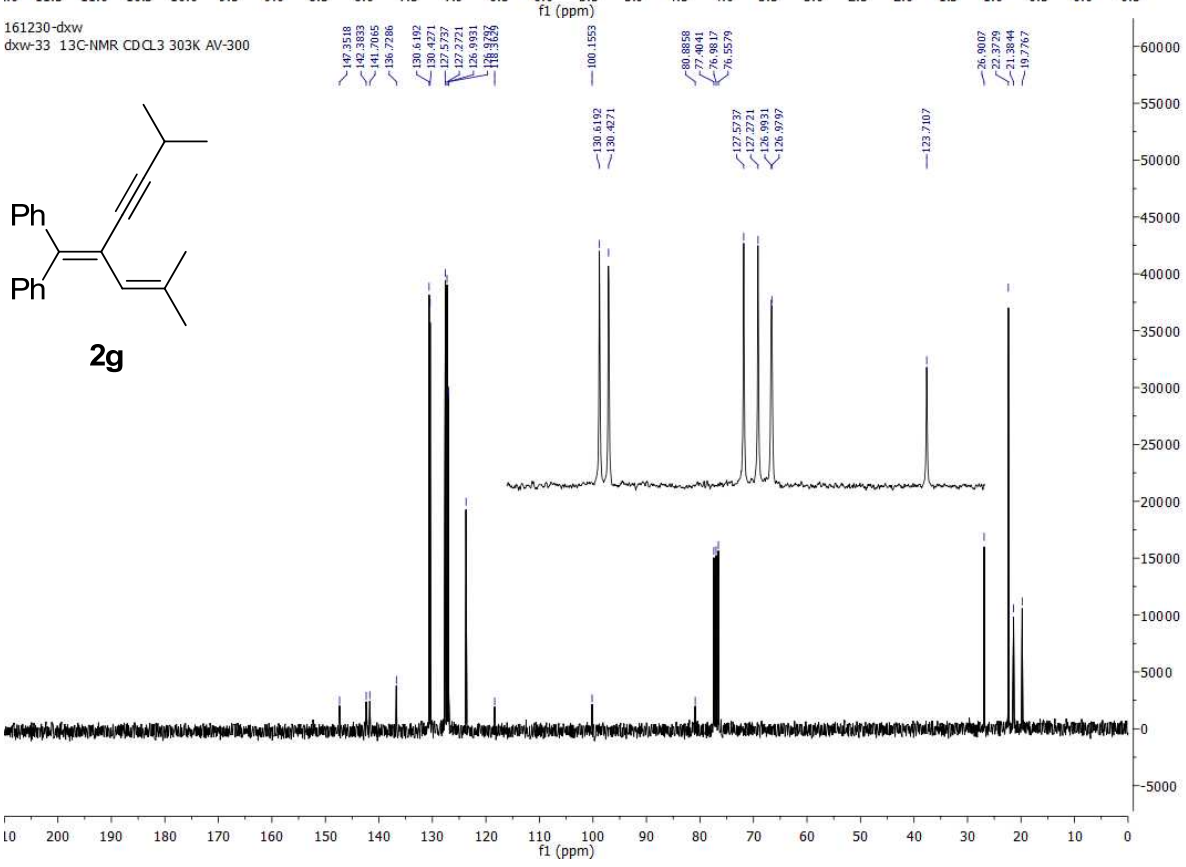
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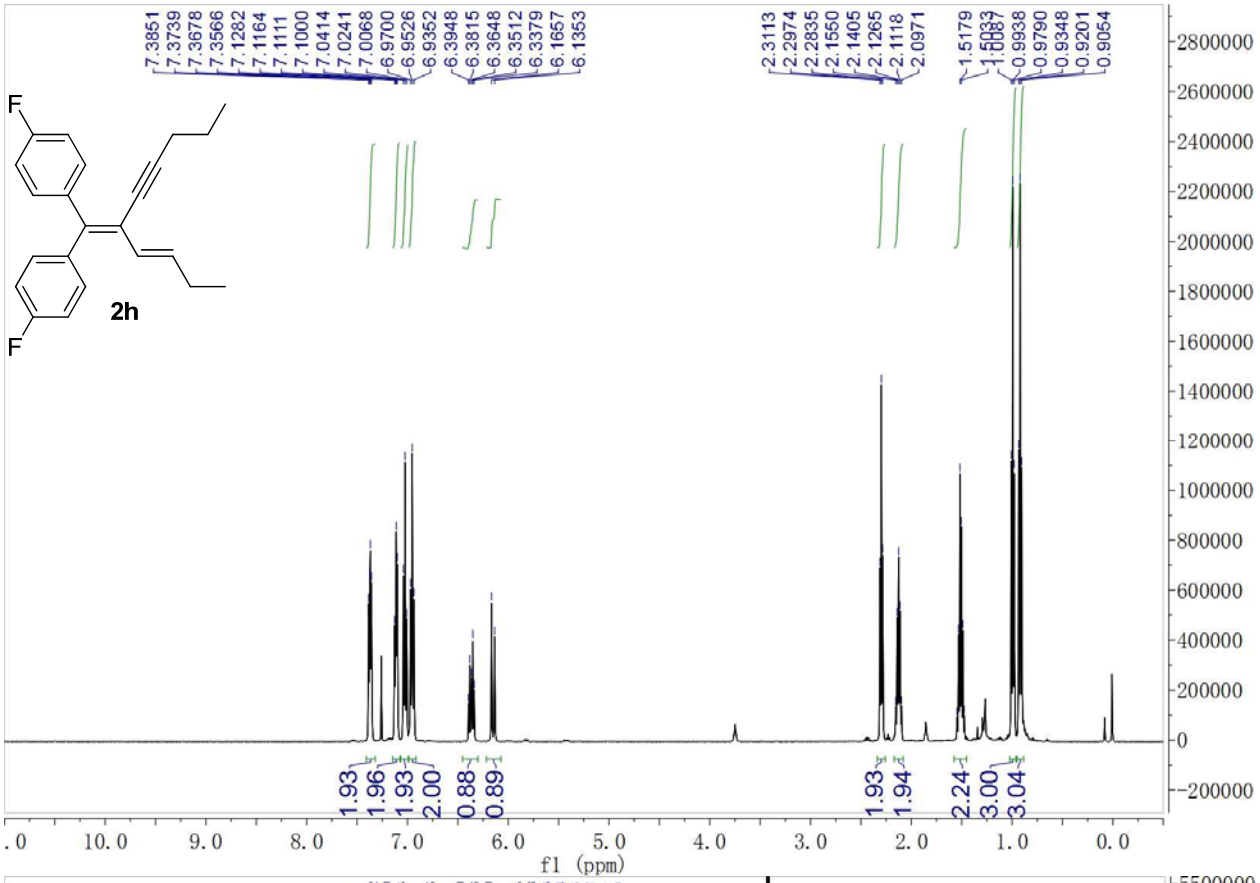
Ph
Ph
2g
f1 (ppm)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2.1405
2.1265
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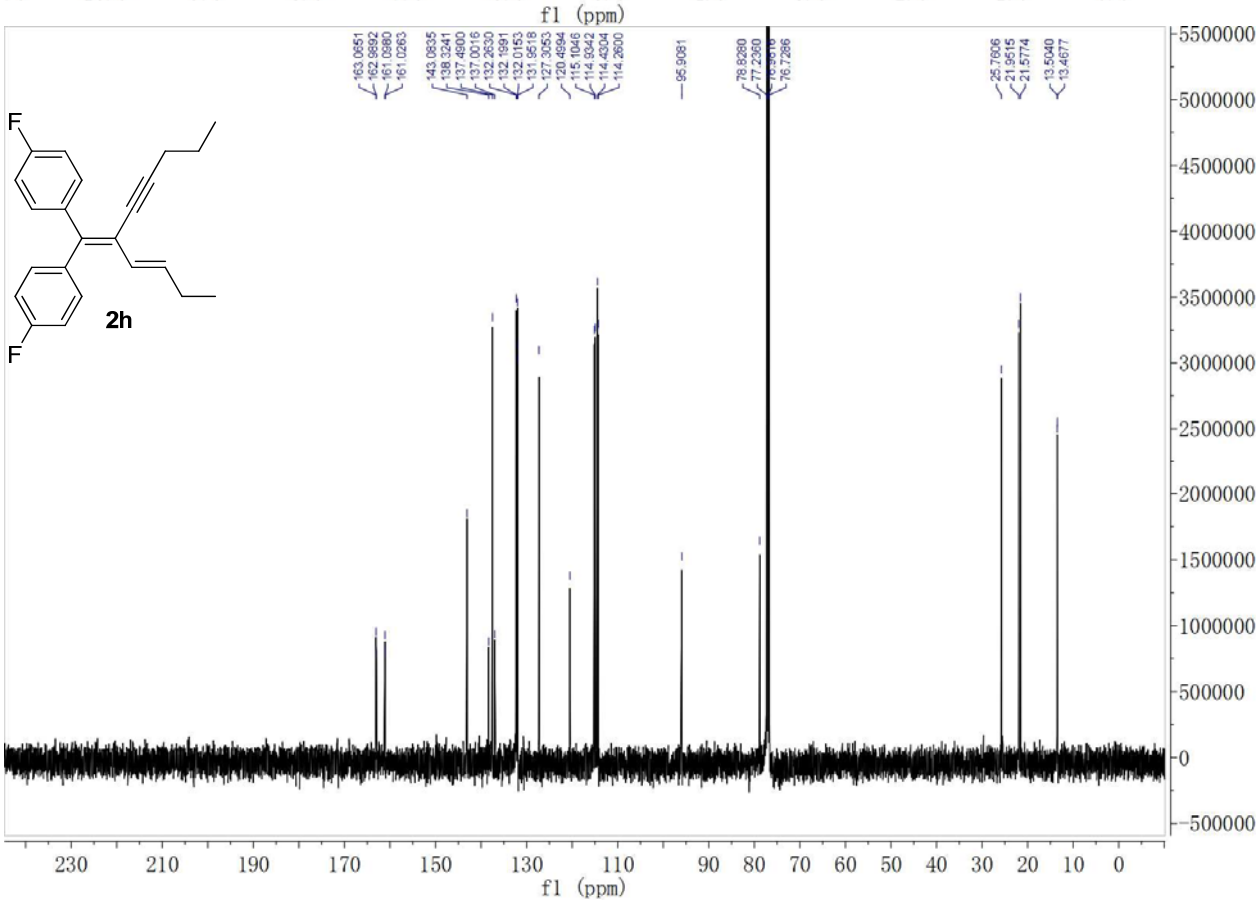
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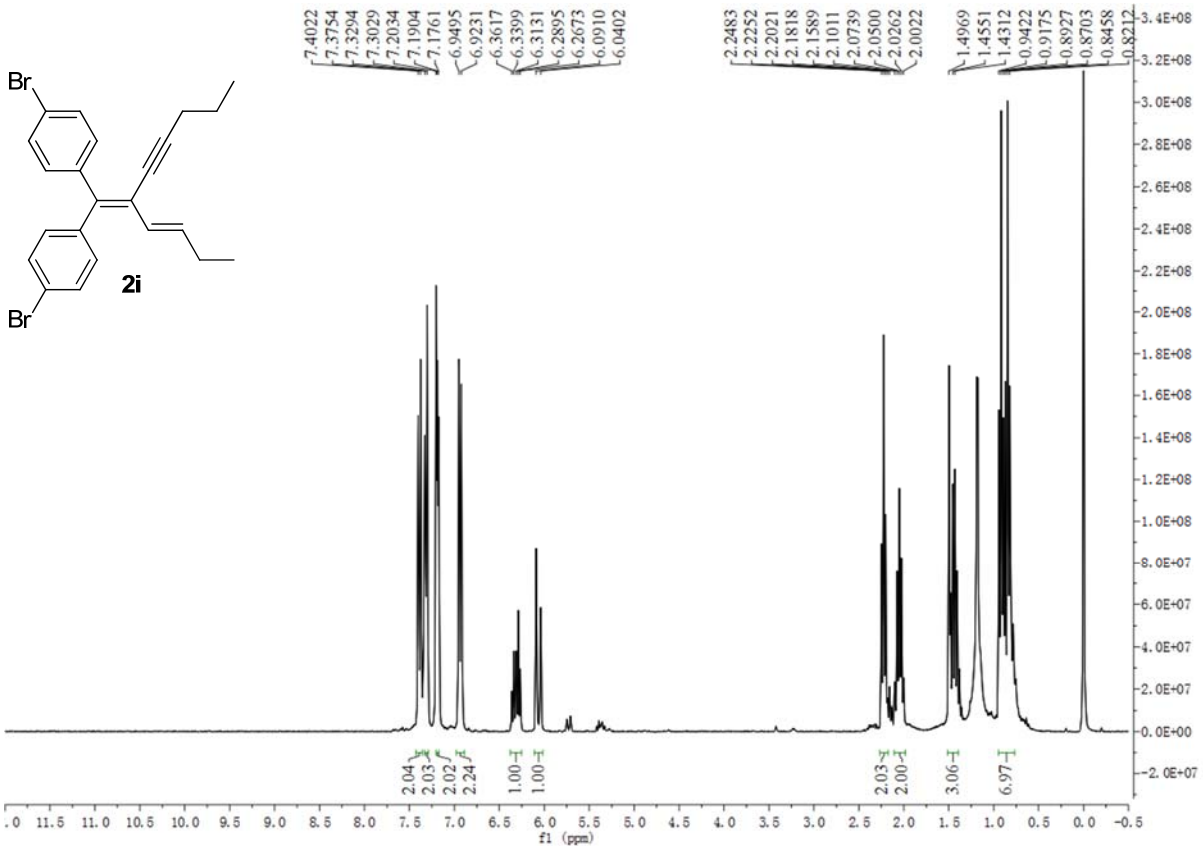
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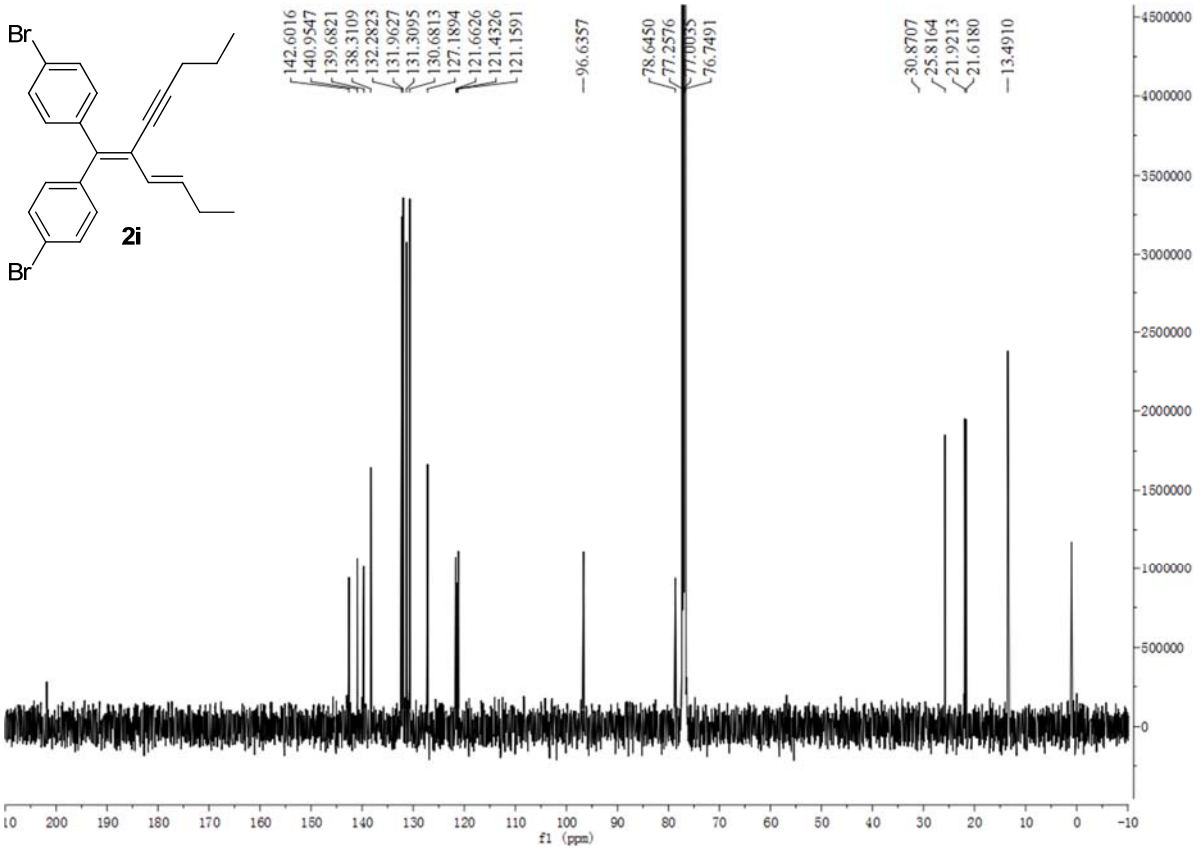
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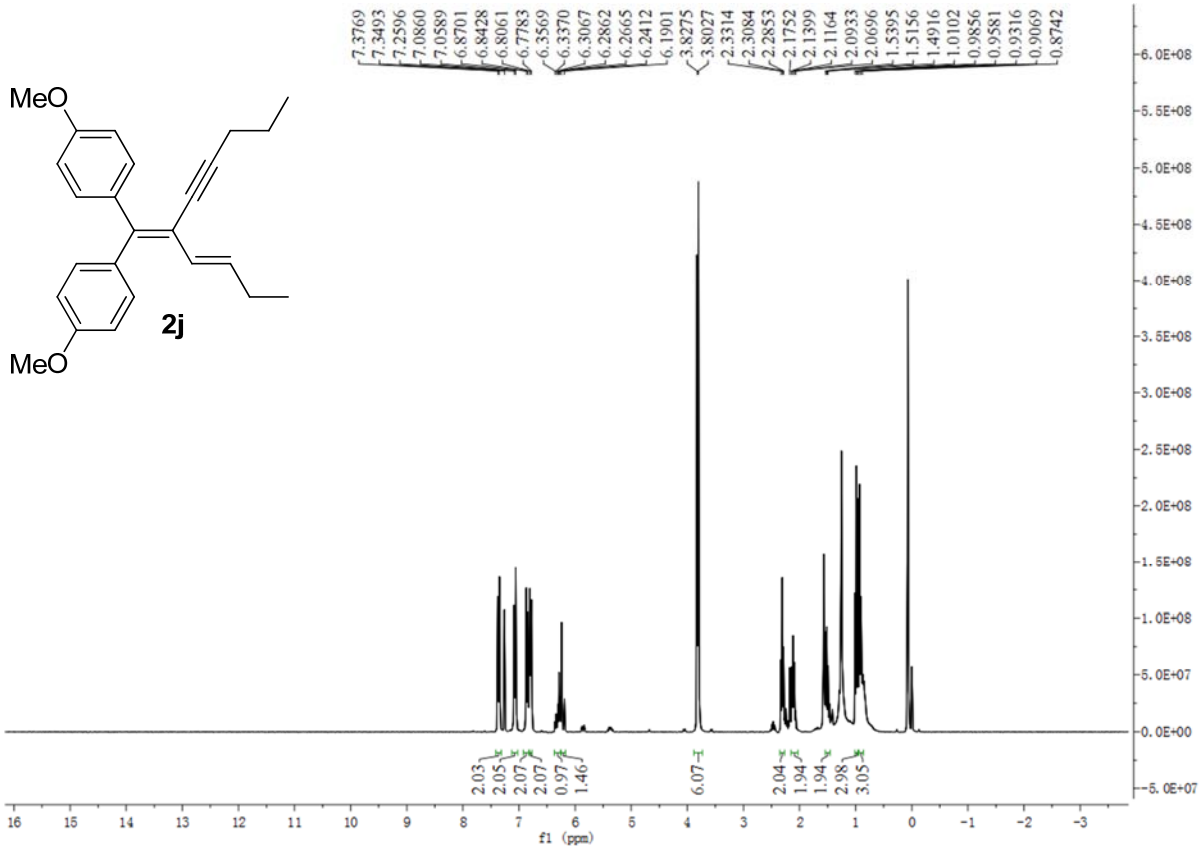
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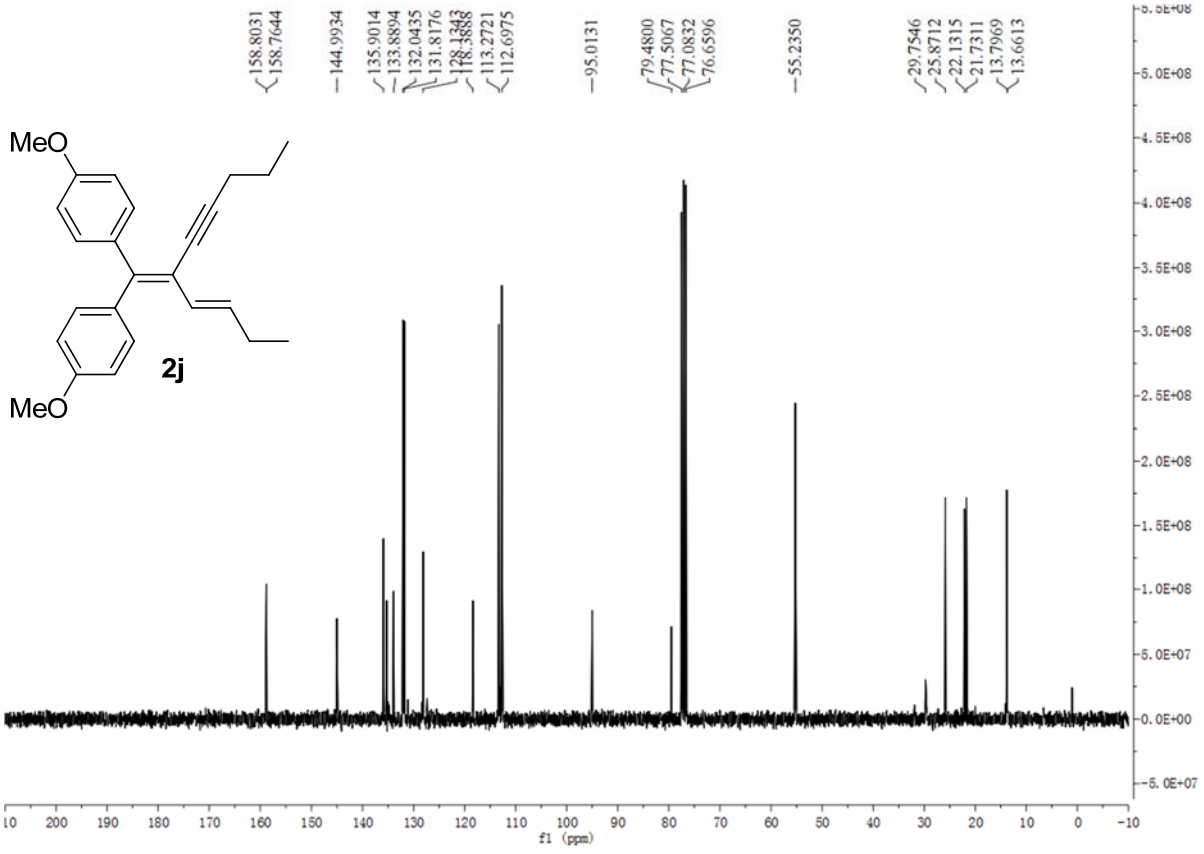
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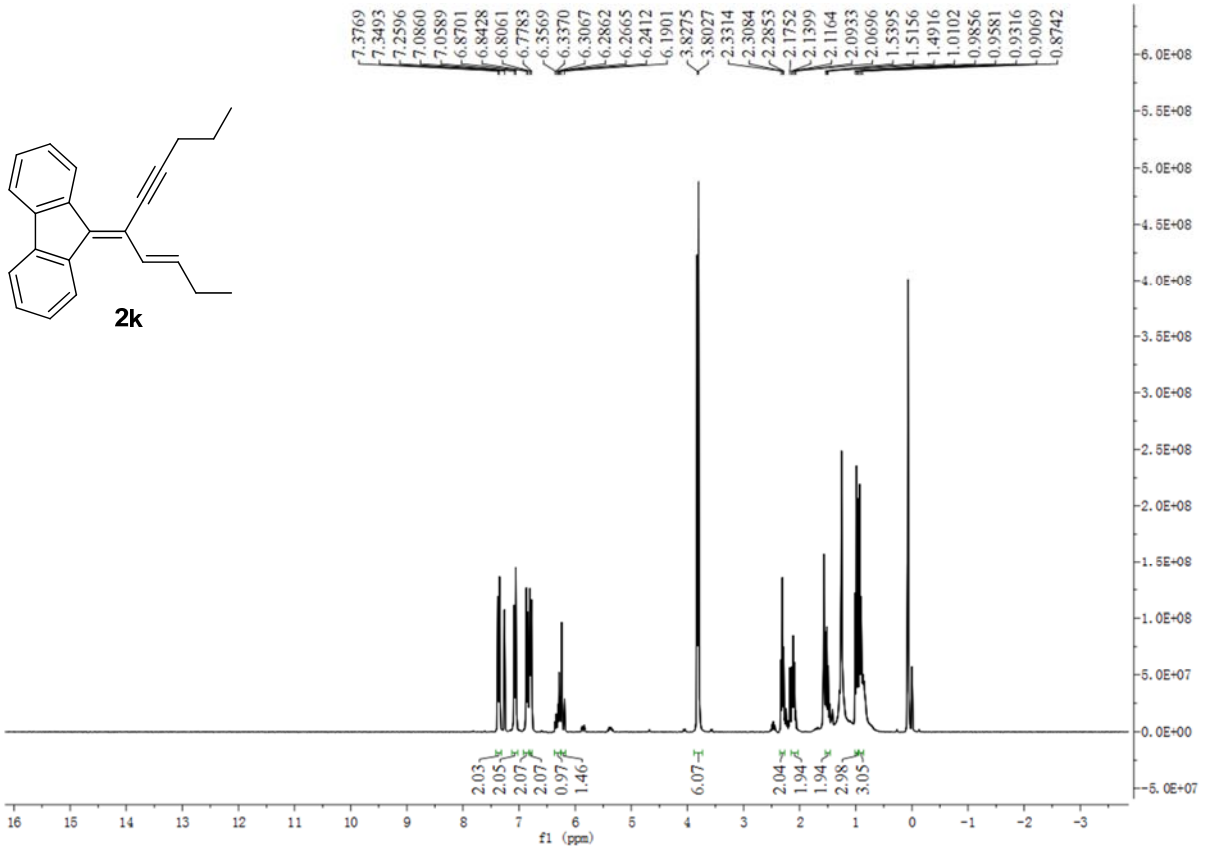
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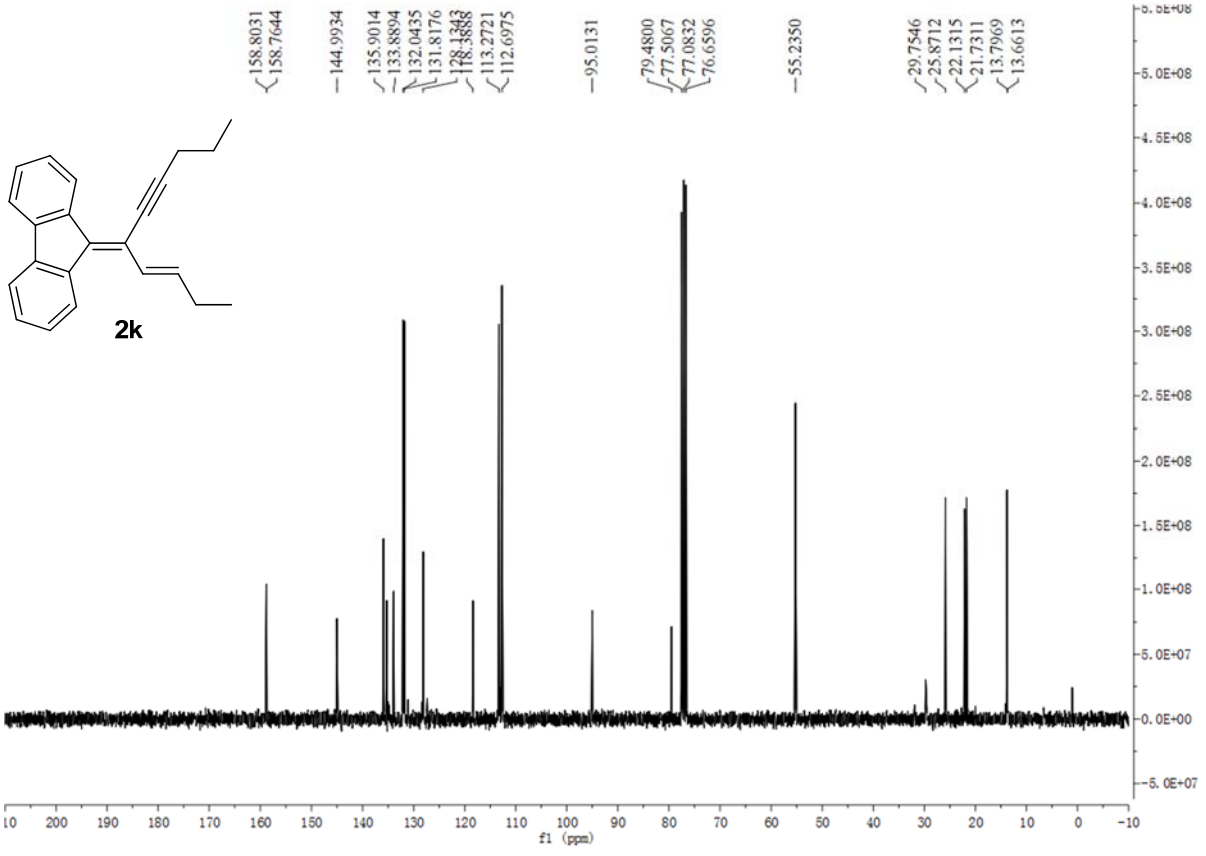
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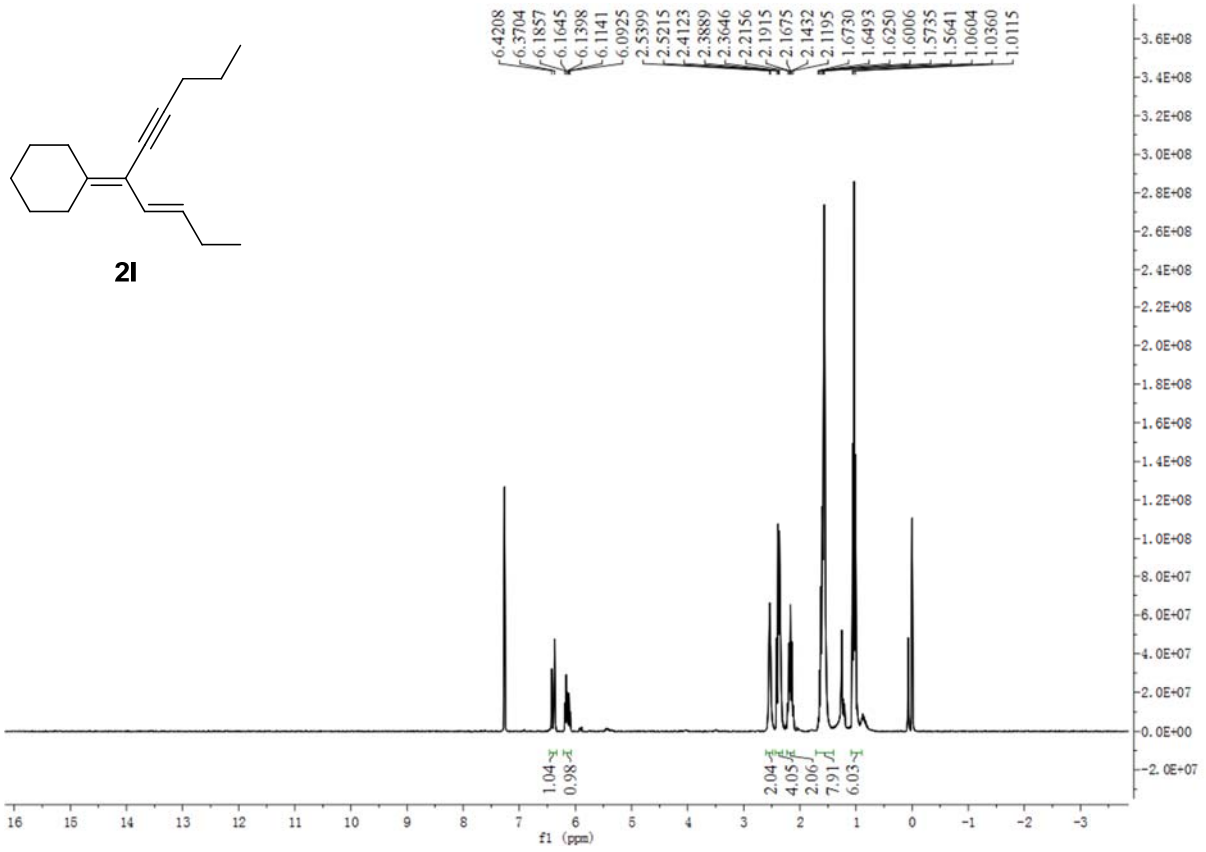
f1 (ppm)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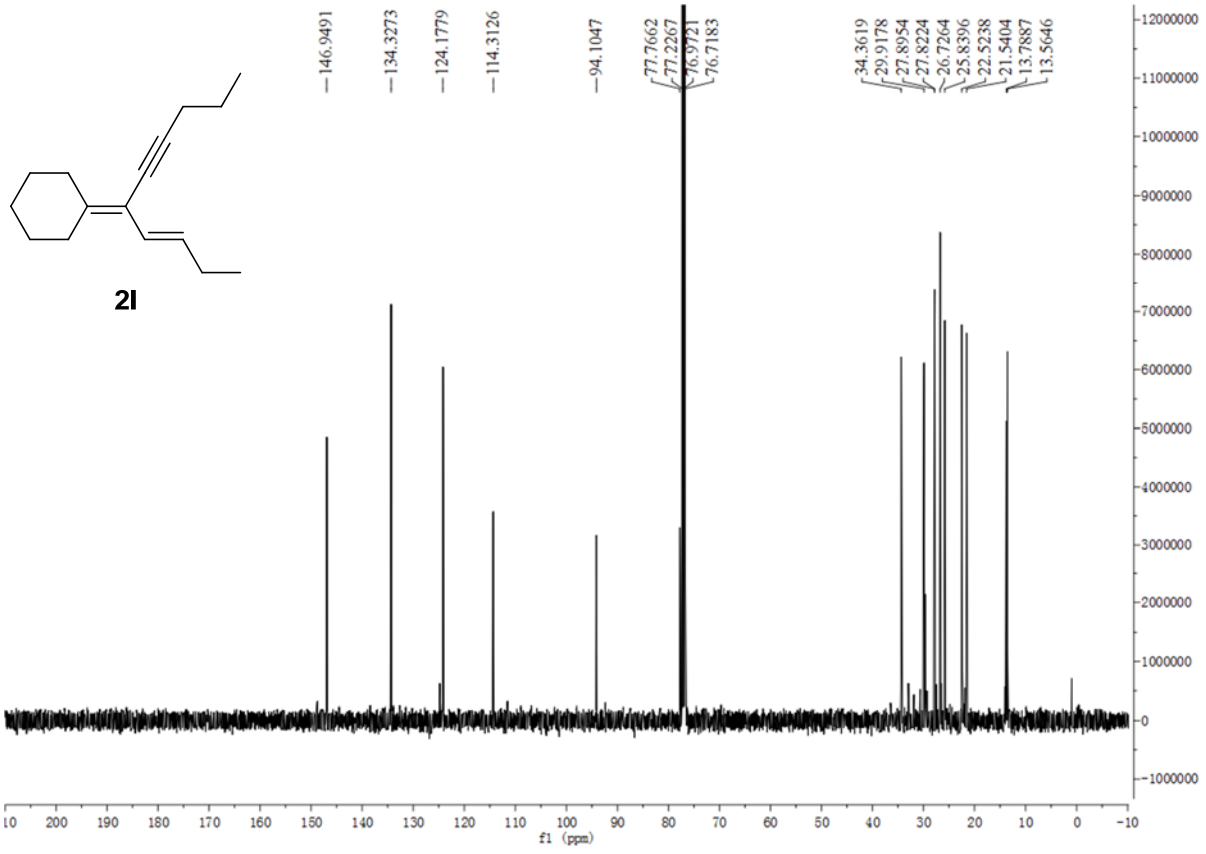
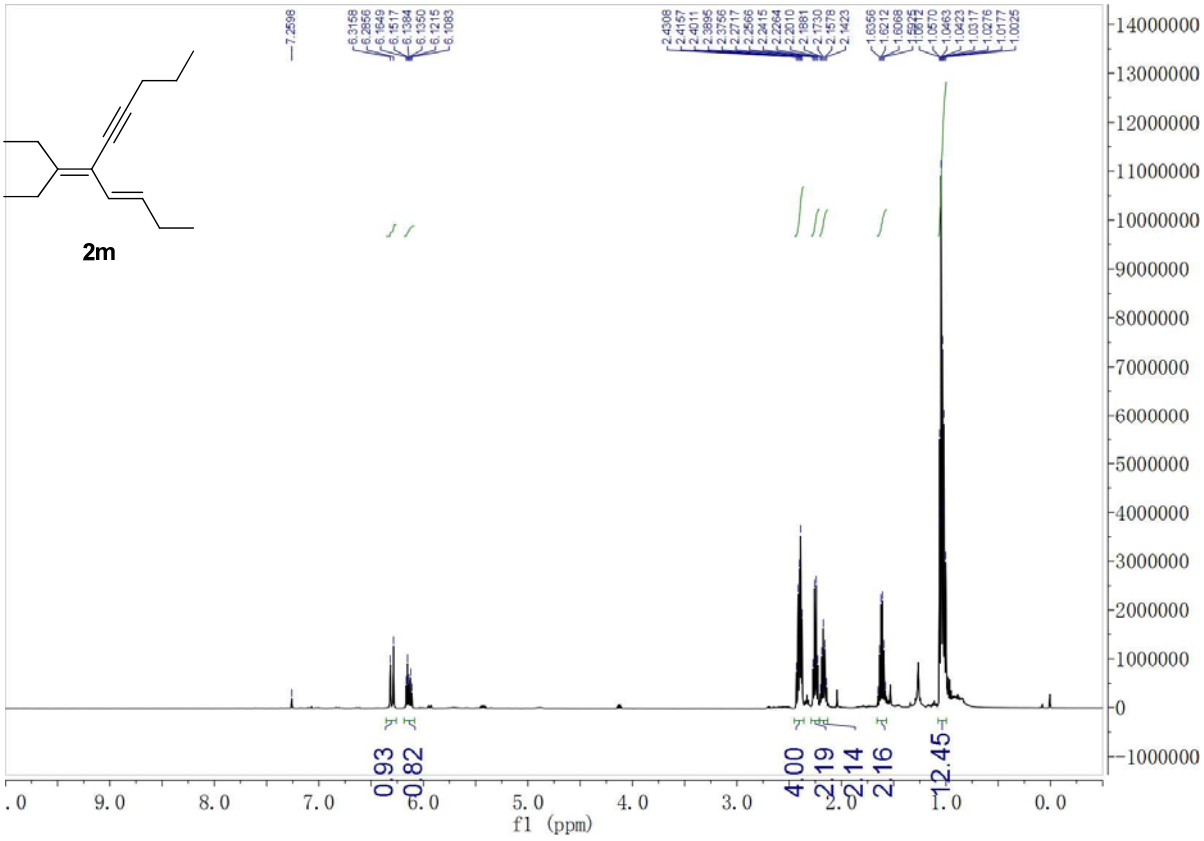
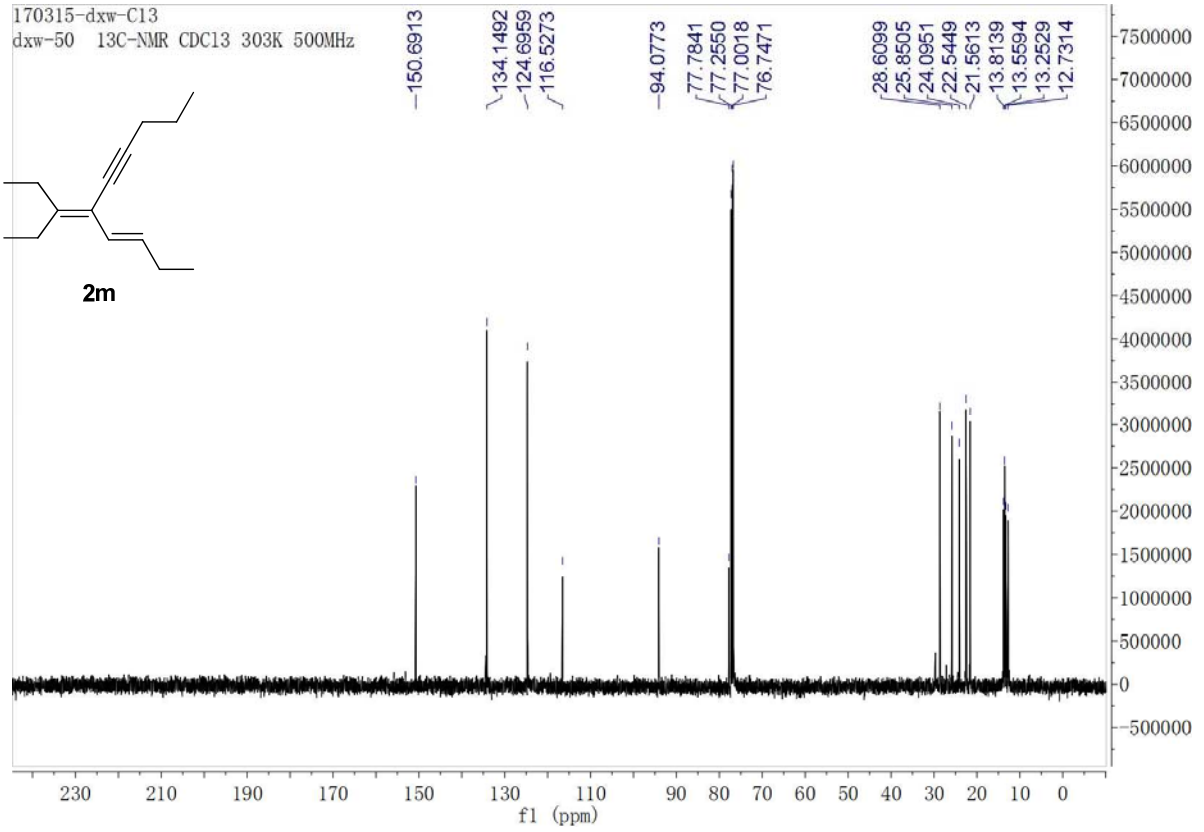
1.04
0.98
2.04
4.05
2.06
7.91
6.03
f1 (ppm)

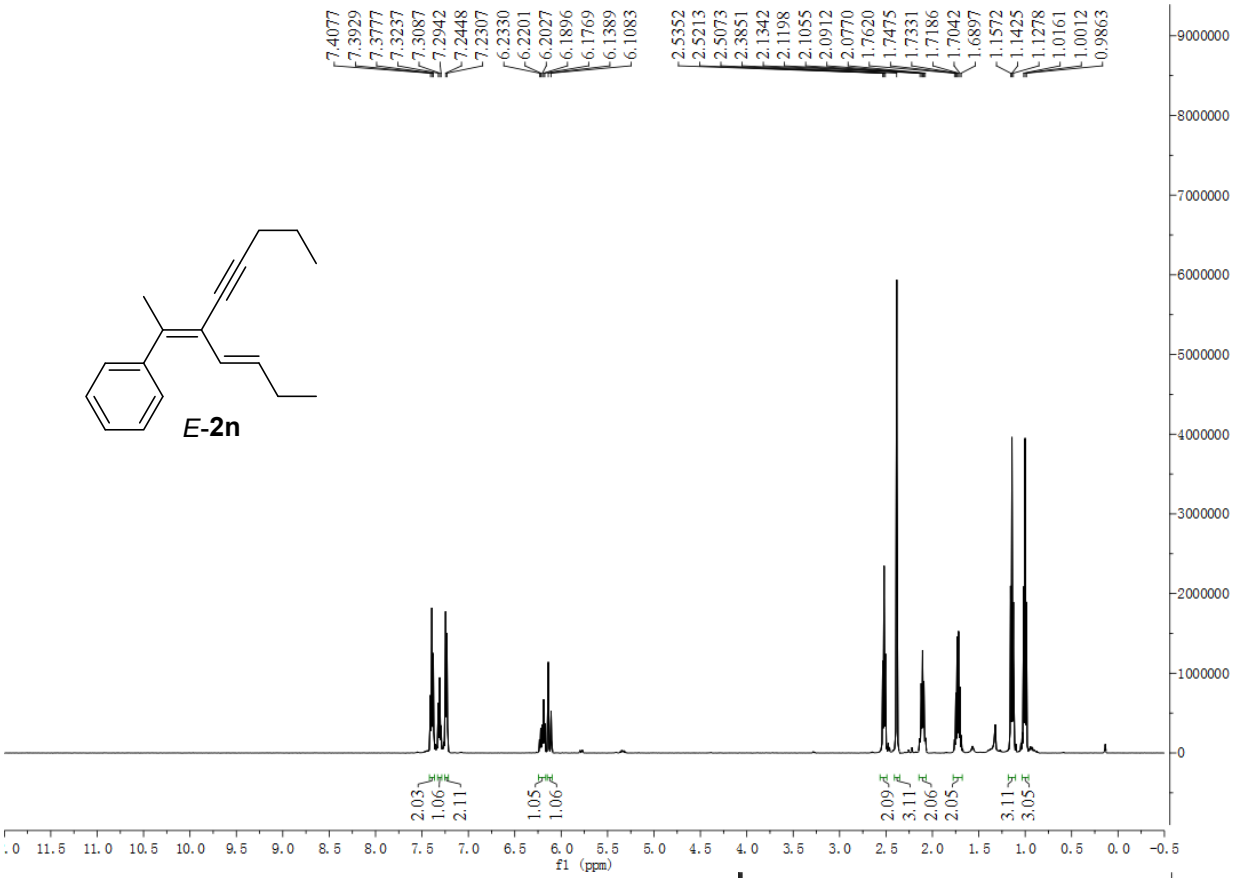
2l

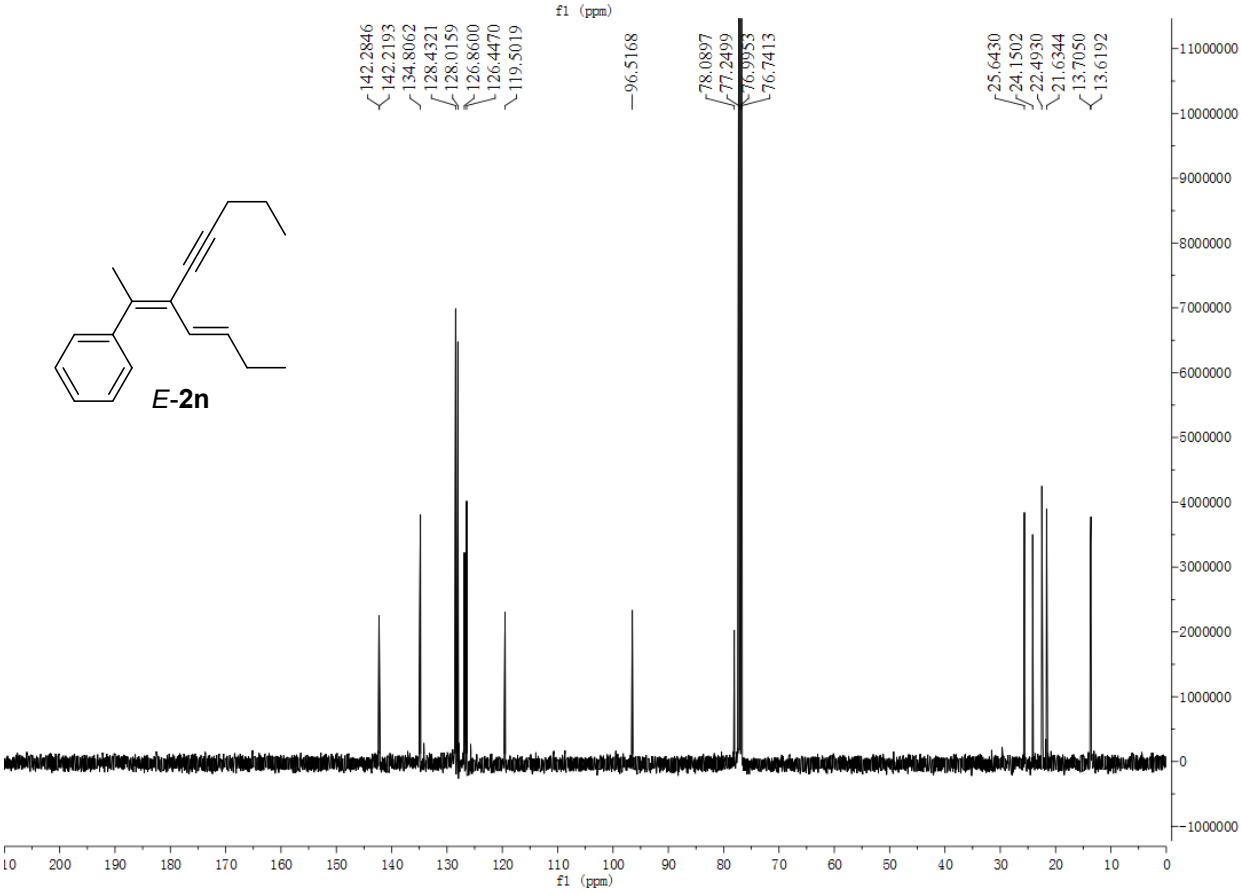

146.9491
134.3273
124.1779
114.3126
94.1047
77.7662
77.2267
76.9721
76.7183
34.3619
29.9178
27.8954
27.8224
26.7264
25.8396
22.5238
21.5404
13.7887
13.5646
f1 (ppm)

2l

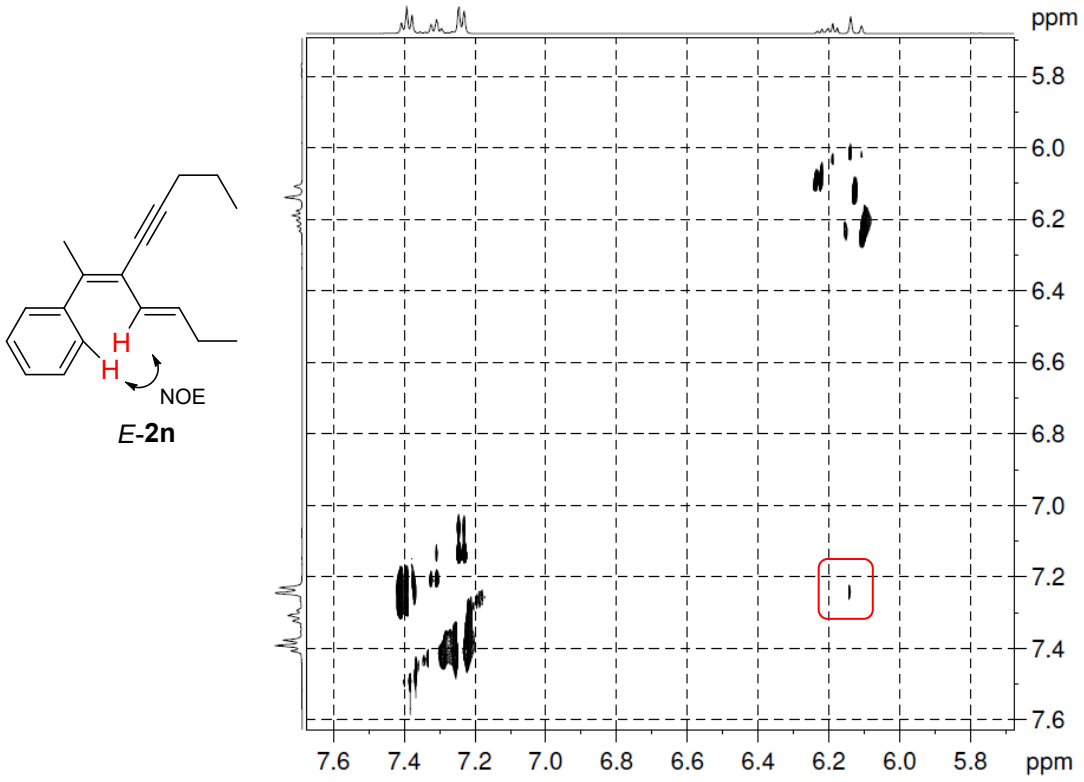

2m
f1 (ppm)


170315-dxw-C13
dxw-50 13C-NMR CDCl3 303K 500MHz
2m
f1 (ppm)


7.4077
7.3929
7.3777
7.3237
7.3087
7.2942
7.2448
7.2307
6.2330
6.2201
6.2027
6.1896
6.1769
6.1389
6.1083
2.5352
2.5213
2.5073
2.3851
2.1342
2.1198
2.1055
2.0912
2.0770
1.7620
1.7475
1.7331
1.7186
1.7042
1.6897
1.1572
1.1425
1.1278
1.0161
1.0012
0.9863
E-2n
2.03
1.06
2.11
1.05
1.06
2.09
3.11
2.06
2.05
3.11
3.05
f1 (ppm)

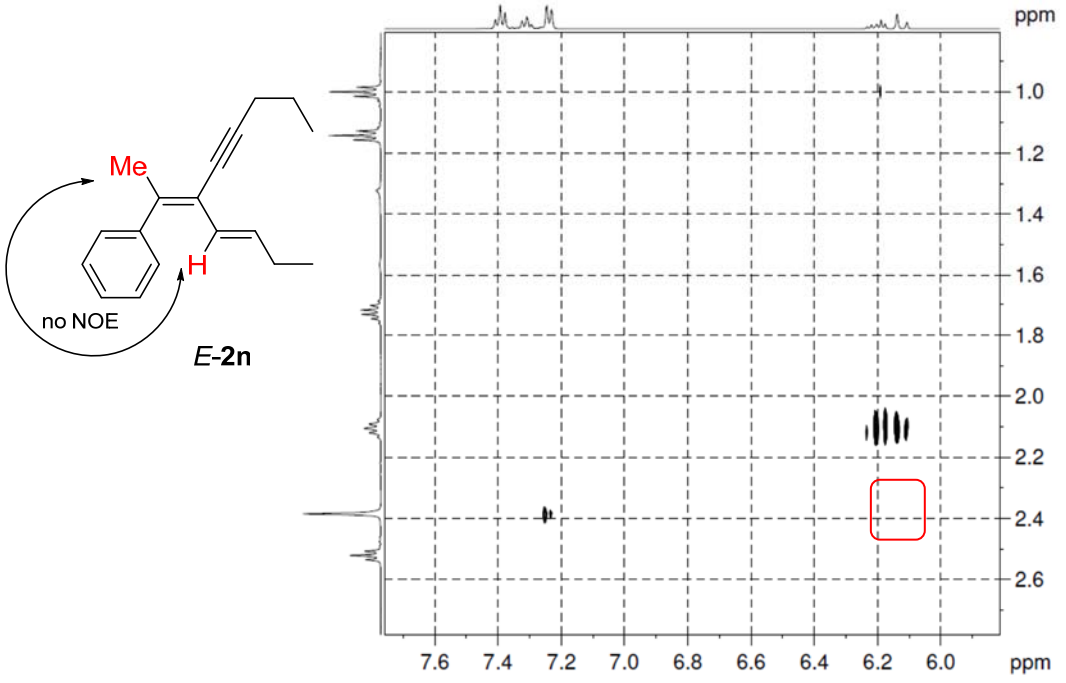

142.2846
142.2193
134.8062
128.4321
128.0159
126.8600
126.4470
119.5019
96.5168
78.0897
77.2499
76.9953
76.7413
25.6430
24.1502
22.4930
21.6344
13.7050
13.6192
E-2n
f1 (ppm)

273–1 NOESY CDCl3 303K 500MHz

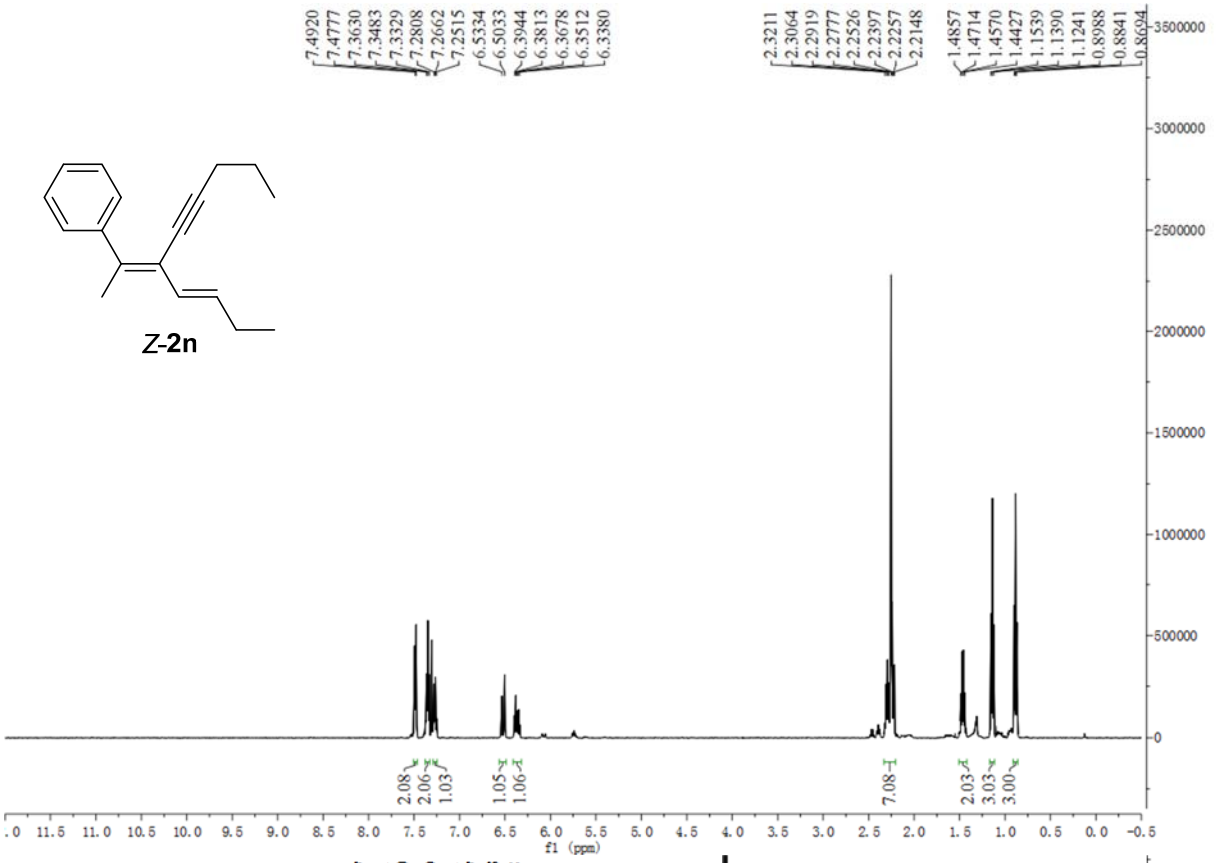


E-**2n**

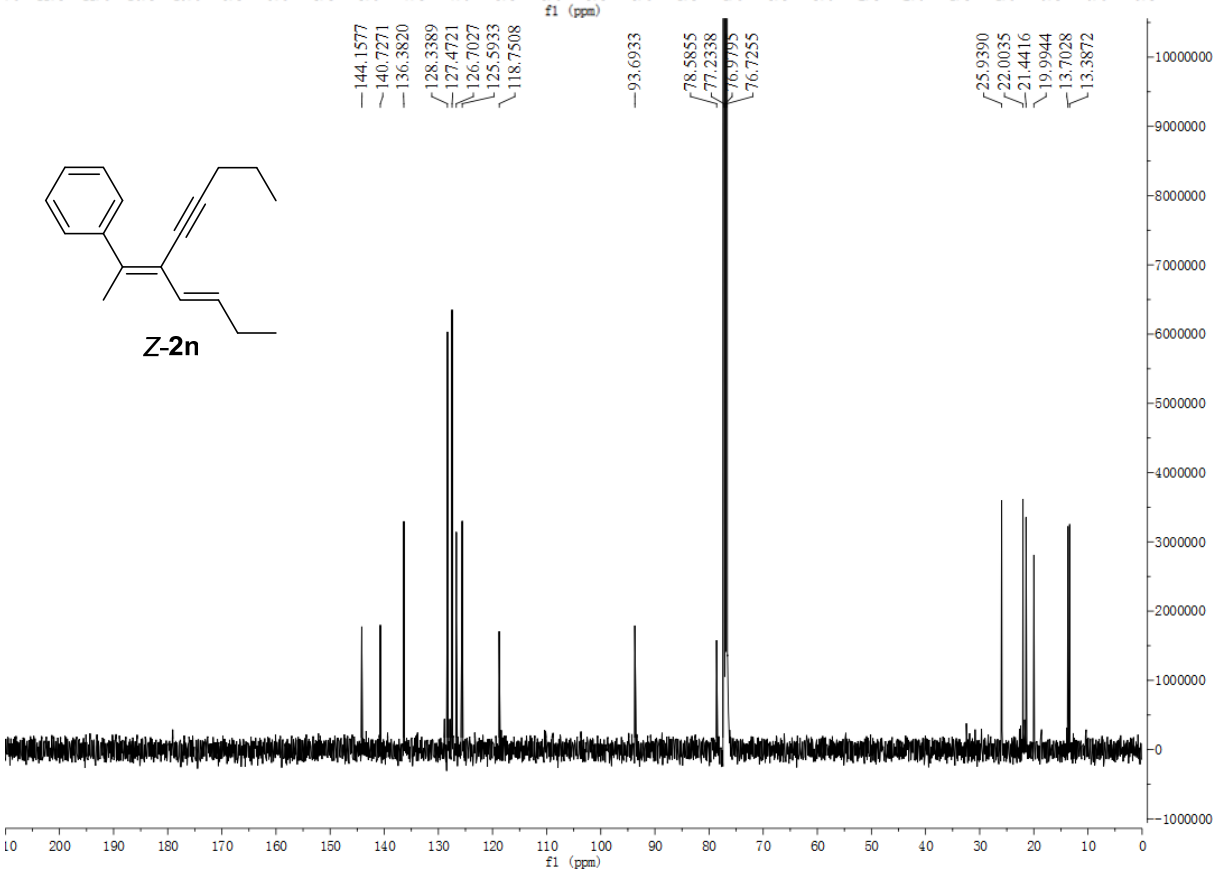
273–1 NOESY CDCl3 303K 500MHz



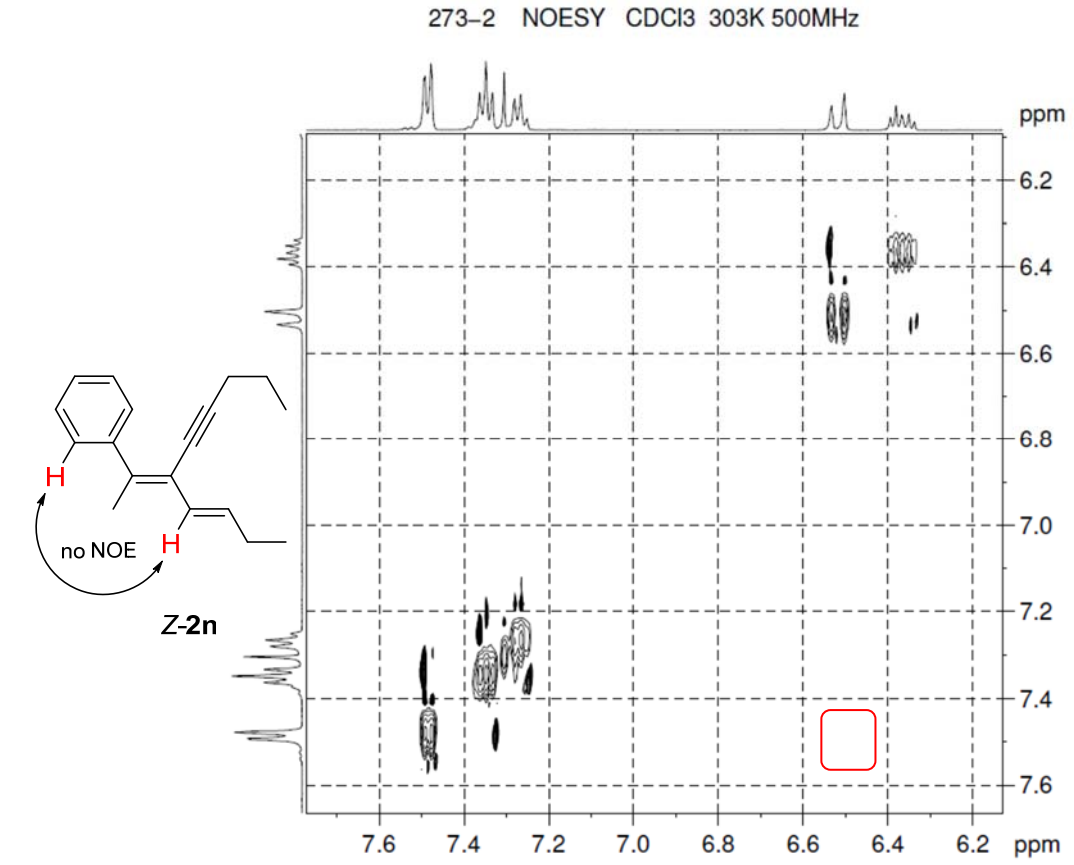
E-**2n**

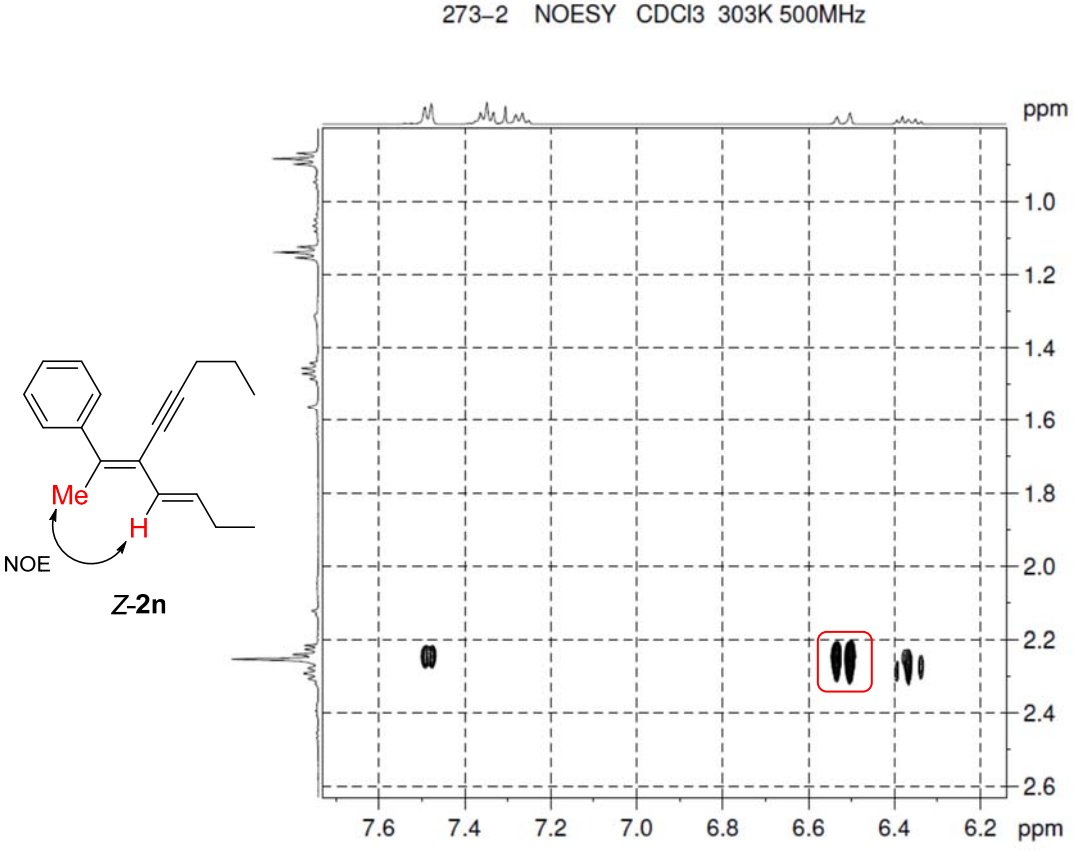

7.4920
7.4777
7.3630
7.3483
7.3329
7.2808
7.2662
7.2515
6.5334
6.5033
6.3944
6.3813
6.3678
6.3512
6.3380
2.3211
2.3064
2.2919
2.2777
2.2526
2.2397
2.2257
2.2148
1.4857
1.4714
1.4570
1.4427
1.1539
1.1390
1.1241
0.8988
0.8841
0.8694
2.08
2.06
1.03
1.05
1.06
7.08
2.03
3.03
3.00
f1 (ppm)

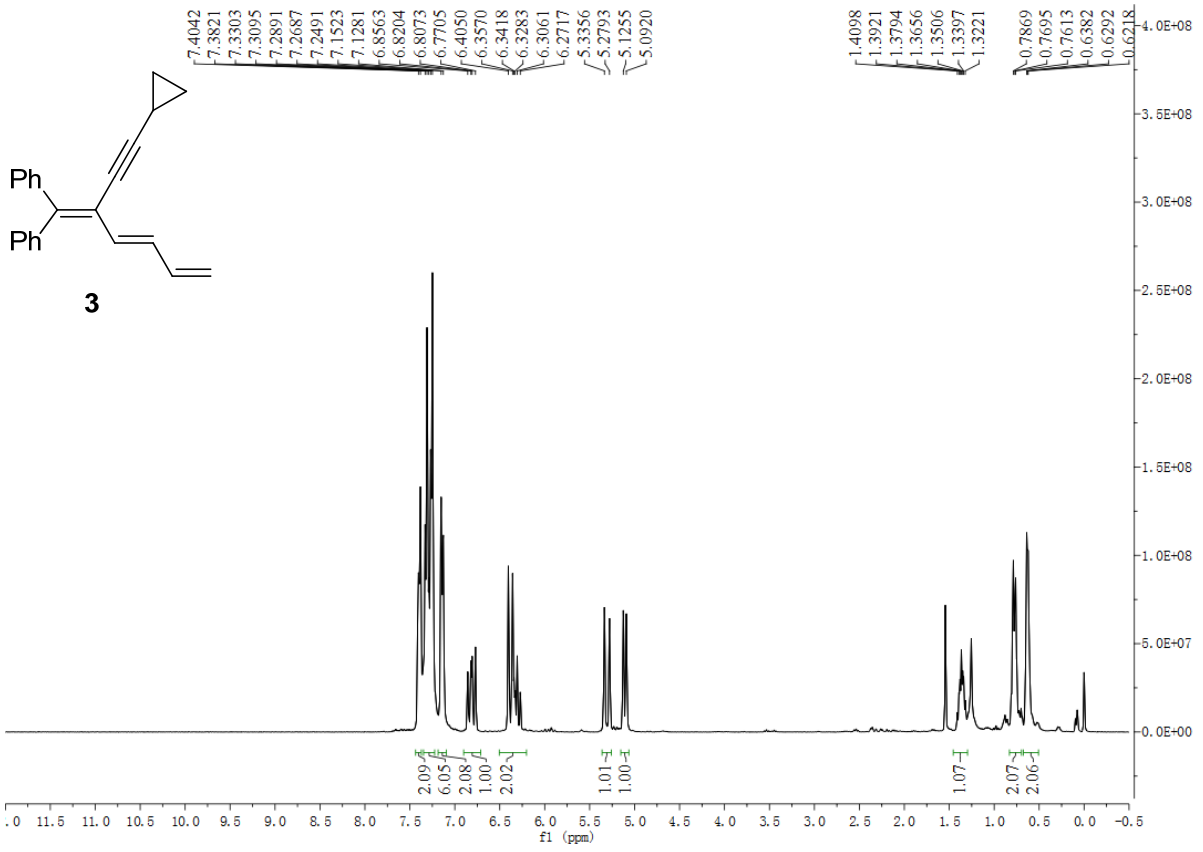
Z-**2n**

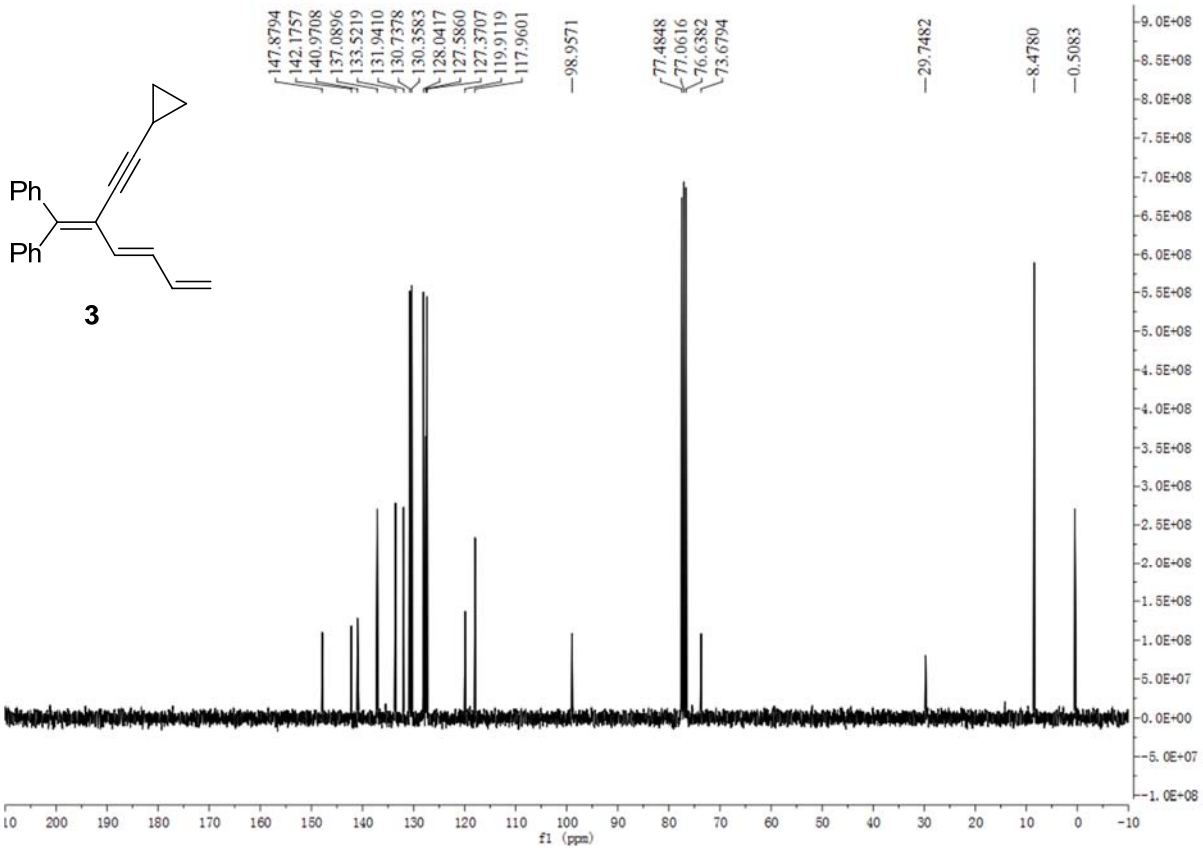

144.1577
140.7271
136.3820
128.3389
127.4721
126.7027
125.5933
118.7508
93.6933
78.5855
77.2338
76.9795
76.7255
25.9390
22.0035
21.4416
19.9944
13.7028
13.3872
f1 (ppm)

Z-**2n**


273–2 NOESY CDCl3 303K 500MHz
ppm
6.2
6.4
6.6
6.8
7.0
7.2
7.4
7.6
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 ppm
H
no NOE
H
Z-2n


273–2 NOESY CDCl3 303K 500MHz
ppm
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 ppm
Me
H
NOE
Z-2n


Ph
Ph
3
7.4042
7.3821
7.3303
7.3095
7.2891
7.2687
7.2491
7.1523
7.1281
6.8563
6.8204
6.8073
6.7705
6.4050
6.3570
6.3418
6.3283
6.3061
6.2717
5.3356
5.2793
5.1255
5.0920
1.4098
1.3921
1.3794
1.3656
1.3506
1.3397
1.3221
0.7869
0.7695
0.7613
0.6382
0.6292
0.6218
2.09
6.05
2.08
1.00
2.02
1.01
1.00
1.07
2.07
2.06
f1 (ppm)


Ph
Ph
3
147.8794
142.1757
140.9708
137.0896
133.5219
131.9410
130.7378
130.3583
128.0417
127.5860
127.3707
119.9119
117.9601
98.9571
77.4848
77.0616
76.6382
73.6794
29.7482
8.4780
0.5083
f1 (ppm)