Supporting Information

Copper-Catalyzed 1,4-Alkylarylation of 1,3-Enynes Masked Alkyl Electrophiles

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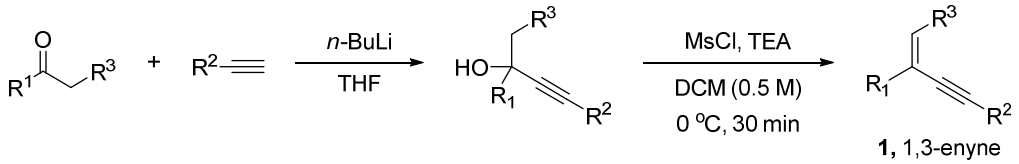
Materials and methods 3
Synthesis of 1,3-enynes 4
Characterization data for 1,3-enynes 5
Synthesis of alkyl diacyl peroxides 9
Characterization data for diacyl peroxides 10
Optimization of the reaction conditions 12
General procedure for Table S1: 12
General procedure for 1,4-alkylarylation of 1,3-enynes 13
General procedure A 13
General procedure B 13
Characterization data for products 14
Synthetic applications 29
a) Synthesis of indenyl iodide 7 with NIS 29
b) Synthesis of 1*H*-indene 8 30
c) Synthesis of 2*H*-pyran 9 31
d) Synthesis of 2*H*-pyran 10 31
Preliminary mechanism study 33
a) Radical trapping experiment 33
b) Radical clock experiments 33
c) Radical dimerization 36
Single crystal data of 20 37
Reference 38
NMR spectra 39

Materials and methods

All reactions were carried out under an atmosphere of nitrogen in an flame-dried glassware with magnetic stirring unless otherwise indicated. Commercially obtained reagents were used as received. Solvents were dried by Innovative Technology Solvent Purification System. Liquids and solutions were transferred via syringe. All reactions were monitored by thin-layer chromatography. GC-MS data were recorded on Thermo ISQ QD. ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded on Bruker-BioSpin AVANCE III HD and JEOL ECZ600S. Data for ^{1}H NMR spectra are reported relative to TMS as an internal standard (0.00 ppm) and are reported as follows: chemical shift (ppm), multiplicity, coupling constant (Hz), and integration. Data for ^{13}C NMR spectra are reported relative to chloroform as an internal standard (77.16 ppm) and are reported in terms of chemical shift (ppm). HRMS data were recorded on Thermo Fisher Scientific LTQ FTICR-MS, Waters Micromass GCT Premier or Thermo Finnigan DECAX-30000 LCQ Deca XP.

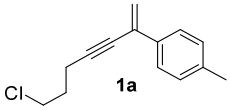
Synthesis of 1,3-enynes



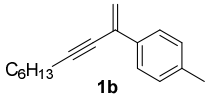
To a 50 mL round bottomed flask was charged with terminal alkyne (5 mmol, 1 equiv) and 10 mL of THF. The solution was cooled to -78 °C and *n*-BuLi (2.5 M in THF, 2 mL, 5 mmol, 1 equiv) was added. The resulting solution was stirred for 20 minutes at room temperature and then cooled to -78 °C again. Ketone (5 mmol, 1 equiv) in THF solution was added dropwise. The reaction mixture was then allowed to warm to room temperature and was monitored by TLC for completion. On completion the reaction was quenched with saturated aqueous NH_4Cl (40 mL). The aqueous layer was extracted with ethyl acetate and the combined organic layers were washed with brine (30 mL), dried over $MgSO_4$ and filtered. Then concentrated under reduced pressure to afford the crude propargyl alcohol[1].

The resulting crude propargyl alcohol was dissolved in dry DCM (40 mL), and the mixture was cooled to 0 °C with a cooling bath. To this solution was added TEA (25 mmol, 5 equiv) and methylsulfonyl chloride (12.5 mmol, 2.5 equiv) sequentially. After 30 min the reaction was monitored by TLC for completion. Once completion the reaction was quenched with saturated aqueous NH_4Cl (40 mL). The aqueous layer was extracted with ethyl acetate and the combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude material was purified by flash chromatography to yield the 1,3-enyne[2].

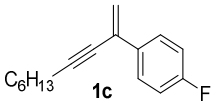
Characterization data for 1,3-enynes



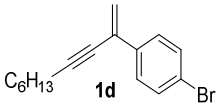
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 5.82 (s, 1H), 5.54 (s, 1H), 3.70 (t, *J* = 6.4 Hz, 2H), 2.61 (t, *J* = 6.8 Hz, 2H), 2.35 (s, 3H), 2.05 (p, *J* = 6.6 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.15, 134.78, 130.47, 129.05, 125.91, 119.14, 89.42, 80.90, 43.81, 31.43, 21.20, 16.88. HRMS (EI+) calcd for $[C_{14}H_{15}Cl]^+$ ($[M]^+$): 218.0862, found: 218.0867.



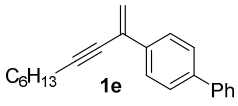
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 5.79 (s, 1H), 5.52 (s, 1H), 2.40 (t, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 1.66 – 1.54 (m, 2H), 1.51 – 1.39 (m, 2H), 1.37 – 1.27 (m, 4H), 0.94 – 0.86 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.98, 135.03, 130.77, 128.96, 125.97, 118.47, 91.88, 79.88, 31.39, 28.74, 28.68, 22.61, 21.18, 19.44, 14.10. HRMS (EI+) calcd for $[C_{17}H_{22}]^+$ ($[M]^+$): 226.1722, found: 226.1730.



^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.66 – 7.57 (m, 2H), 7.06 – 6.97 (m, 2H), 5.76 (s, 1H), 5.54 (s, 1H), 2.40 (t, *J* = 7.1 Hz, 2H), 1.64 – 1.54 (m, 2H), 1.48 – 1.41 (m, 2H), 1.35 – 1.29 (m, 4H), 0.91 – 0.88 (m, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 162.81 (d, *J* = 247.5 Hz), 134.01 (d, *J* = 3.0 Hz), 130.01, 127.86 (d, *J* = 8.1 Hz), 119.10, 115.16 (d, *J* = 21.5 Hz), 92.42, 79.67, 31.42, 28.76, 28.73, 22.66, 19.47, 14.13. HRMS (EI+) calcd for $[C_{16}H_{19}F]^+$ ($[M]^+$): 230.1471, found: 230.1474.

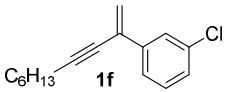


^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.55 – 7.50 (m, 2H), 7.48 – 7.43 (m, 2H), 5.82 (s, 1H), 5.59 (s, 1H), 2.41 (t, *J* = 7.2 Hz, 2H), 1.64 – 1.56 (m, 2H), 1.48 – 1.41 (m, 2H), 1.36 – 1.30 (m, 4H), 0.91 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 136.85, 131.44, 130.11, 127.80, 122.28, 119.80, 92.68, 79.39, 31.46, 28.77, 22.70, 19.50, 14.18. HRMS (EI+) calcd for $[C_{16}H_{19}Br]^+$ ($[M]^+$): 290.0670, found: 290.0675.



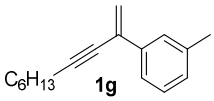
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.69 (m, 2H), 7.63 – 7.54 (m, 4H), 7.46 – 7.39 (m, 2H), 7.37 – 7.30 (m, 1H), 5.88 (s, 1H), 5.60 (s, 1H), 2.42 (t, *J* = 7.1 Hz, 2H), 1.67 – 1.57 (m, 2H), 1.52 – 1.42 (m, 2H), 1.37 – 1.29 (m, 4H), 0.95 – 0.86 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*)

δ 140.92, 140.68, 136.83, 130.59, 128.81, 127.41, 127.05, 126.99, 126.53, 119.25, 92.24, 79.75, 31.40, 28.76, 28.71, 22.63, 19.48, 14.11. The spectrum data matches previously reported values[3].



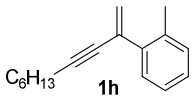
1f

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (s, 1H), 7.55 – 7.48 (m, 1H), 7.27 – 7.23 (m, 2H), 5.83 (s, 1H), 5.60 (s, 1H), 2.40 (t, *J* = 7.1 Hz, 2H), 1.63 – 1.56 (m, 2H), 1.48 – 1.41 (m, 2H), 1.35 – 1.30 (m, 4H), 0.90 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 139.67, 134.31, 129.87, 129.47, 128.09, 126.37, 124.15, 120.31, 92.70, 79.19, 31.40, 28.70, 28.67, 22.63, 19.42, 14.10. HRMS (EI+) calcd for $[C_{16}H_{19}Cl]^+$ ($[M]^+$): 246.1175, found: 246.1185.



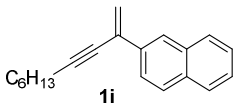
1g

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.57 – 7.39 (m, 2H), 7.26 – 7.21 (m, 1H), 7.14 – 7.09 (m, 1H), 5.83 (d, *J* = 1.3 Hz, 1H), 5.57 (d, *J* = 1.2 Hz, 1H), 2.42 (t, *J* = 7.1 Hz, 2H), 2.38 (s, 3H), 1.65 – 1.59 (m, 2H), 1.51 – 1.45 (m, 2H), 1.36 – 1.30 (m, 4H), 0.92 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 137.91, 137.89, 131.15, 128.96, 128.26, 126.91, 123.30, 119.32, 92.04, 79.98, 31.48, 28.81, 28.76, 22.70, 21.57, 19.53, 14.17. HRMS (EI+) calcd for $[C_{17}H_{22}]^+$ ($[M]^+$): 226.1722, found: 226.1719.



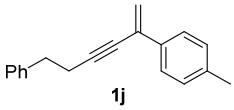
1h

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 – 7.23 (m, 1H), 7.23 – 7.16 (m, 3H), 5.69 (d, *J* = 1.9 Hz, 1H), 5.39 (d, *J* = 2.0 Hz, 1H), 2.45 (s, 3H), 2.34 (t, *J* = 7.1 Hz, 2H), 1.58 – 1.53 (m, 2H), 1.44 – 1.38 (m, 2H), 1.33 – 1.28 (m, 4H), 0.90 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 140.10, 135.52, 132.36, 130.39, 128.76, 127.75, 125.88, 123.91, 92.07, 80.71, 31.44, 28.74, 22.65, 20.28, 19.56, 14.13. HRMS (EI+) calcd for $[C_{17}H_{22}]^+$ ($[M]^+$): 226.1722, found: 226.1729.



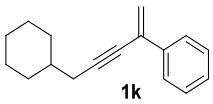
1i

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 7.90 – 7.72 (m, 4H), 7.46 (m, 2H), 5.98 (s, 1H), 5.67 (s, 1H), 2.47 (t, *J* = 7.0 Hz, 2H), 1.72 – 1.59 (m, 2H), 1.55 – 1.47 (m, 2H), 1.40 – 1.31 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 135.08, 133.28, 133.15, 130.91, 128.42, 127.82, 127.55, 126.22, 126.16, 125.91, 123.46, 119.69, 92.31, 79.78, 31.41, 28.76, 28.71, 22.63, 19.51, 14.10. The spectrum data matches previously reported values[3].



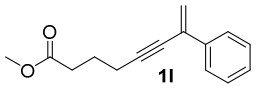
1j

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.53 – 7.43 (m, 2H), 7.36 – 7.32 (m, 2H), 7.30 – 7.24 (m, 3H), 7.16 – 7.11 (m, 2H), 5.82 (d, *J* = 1.2 Hz, 1H), 5.54 (d, *J* = 1.2 Hz, 1H), 2.95 (t, *J* = 7.5 Hz, 2H), 2.74 (t, *J* = 7.5 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 140.76, 138.09, 134.89, 130.73, 129.05, 128.69, 128.53, 126.44, 126.07, 118.79, 90.88, 80.77, 35.18, 21.69, 21.27. HRMS (EI+) calcd for $[C_{19}H_{18}]^+$ ($[M]^+$): 246.1409, found: 246.1413.



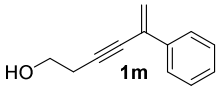
1k

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.59 (m, 2H), 7.36 – 7.26 (m, 3H), 5.83 (d, *J* = 1.2 Hz, 1H), 5.58 (d, *J* = 1.1 Hz, 1H), 2.31 (d, *J* = 6.6 Hz, 2H), 1.90 – 1.84 (m, 2H), 1.77 – 1.64 (m, 4H), 1.31 – 1.10 (m, 5H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.87, 131.04, 128.26, 128.08, 126.08, 119.32, 90.97, 80.61, 37.52, 32.84, 27.26, 26.31, 26.18. HRMS (EI+) calcd for $[C_{17}H_{20}]^+$ ($[M]^+$): 224.1565, found: 224.1574.



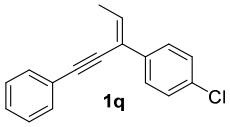
1l

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.66 – 7.61 (m, 2H), 7.35 – 7.32 (m, 2H), 7.30 – 7.27 (m, 1H), 5.85 (d, *J* = 1.1 Hz, 1H), 5.59 (d, *J* = 1.1 Hz, 1H), 3.67 (s, 3H), 2.51 – 2.47 (m, 4H), 1.95 – 1.90 (m, 2H).^{13}C NMR (150 MHz, Chloroform-*d*) δ 173.69, 137.68, 130.83, 128.41, 128.28, 126.11, 119.93, 90.51, 80.71, 51.70, 33.01, 24.00, 18.96. HRMS (ESI) calcd for $[C_{15}H_{26}O_2Na]^+$ ($[M+Na]^+$): 251.1043, found: 251.1042.



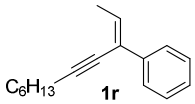
1m

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.55 (m, 2H), 7.36 – 7.24 (m, 3H), 5.85 (s, 1H), 5.61 (s, 1H), 3.82 – 3.69 (m, 2H), 2.83 – 2.73 (m, 1H), 2.63 (t, *J* = 6.5 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.49, 130.60, 128.43, 128.34, 126.08, 120.34, 88.30, 81.46, 61.13, 23.75. HRMS (EI+) calcd for $[C_{12}H_{12}O]^+$ ($[M]^+$): 172.0888, found: 172.0894.



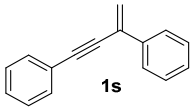
1q

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.45 (m, 4H), 7.38 – 7.23 (m, 5H), 6.46 (q, *J* = 6.9 Hz, 1H), 2.12 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 136.81, 133.70, 133.23, 131.60, 128.55, 128.48, 128.44, 127.24, 123.51, 123.37, 96.02, 86.26, 17.19. HRMS (EI+) calcd for $[C_{17}H_{13}Cl]^+$ ($[M]^+$): 252.0706, found: 252.0698.



1r

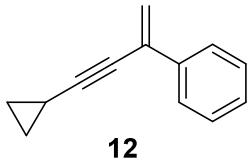
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.49 (m, 2H), 7.35 – 7.27 (m, 2H), 7.26 – 7.19 (m, 1H), 6.39 (q, *J* = 6.9 Hz, 1H), 2.46 (t, *J* = 7.0 Hz, 2H), 2.04 (d, *J* = 6.9 Hz, 3H), 1.66 – 1.57 (m, 2H), 1.53 – 1.46 (m, 2H), 1.35 – 1.29 (m, 4H), 0.93 – 0.88 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.94, 131.52, 128.21, 127.14, 125.87, 124.77, 96.85, 77.71, 31.38, 28.95, 28.64, 22.61, 19.64, 16.78, 14.07. The spectrum data matches previously reported values[3].



1s

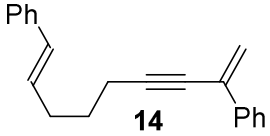
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.69 (m, 2H), 7.58 – 7.50 (m, 2H), 7.41 – 7.31 (m, 6H), 5.98 (s, 1H), 5.76 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.28, 131.68, 130.62,

128.42, 128.36, 126.11, 123.11, 120.68, 90.78, 88.56. The spectrum data matches previously reported values[3].



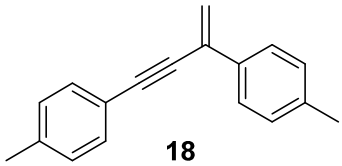
12

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.55 (m, 2H), 7.39 – 7.25 (m, 3H), 5.81 (d, *J* = 1.1 Hz, 1H), 5.55 (d, *J* = 1.2 Hz, 1H), 1.53 – 1.33 (m, 1H), 0.87 – 0.77 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.89, 130.96, 128.36, 128.21, 126.14, 119.55, 95.20, 75.10, 8.77, 0.30. The spectrum data matches previously reported values[4].



14

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.47 (m, 2H), 7.39 – 7.23 (m, 7H), 7.22 – 7.15 (m, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 6.22 (dt, *J* = 15.9, 7.0 Hz, 1H), 5.85 (s, 1H), 5.60 (s, 1H), 2.46 (t, *J* = 7.1 Hz, 2H), 2.41 – 2.33 (m, 2H), 1.84 – 1.73 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.79, 137.70, 130.94, 130.80, 129.75, 128.58, 128.37, 128.22, 127.04, 126.13, 126.05, 119.64, 91.58, 80.26, 32.23, 28.41, 18.96. MS (EI+) calcd for $[C_{21}H_{20}Cl]^{+}$ ($[M]^{+}$): 272.1, found: 272.3.



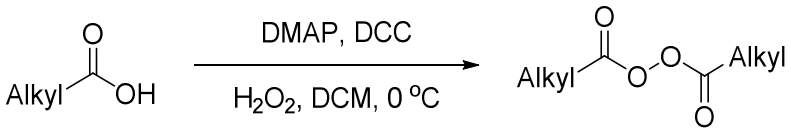
18

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.64 – 7.61 (m, 2H), 7.45 – 7.41 (m, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 5.92 (d, *J* = 1.1 Hz, 1H), 5.69 (d, *J* = 1.3 Hz, 1H), 2.37 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 138.62, 138.32, 134.70, 131.68, 130.62, 129.22, 129.18, 126.12, 120.19, 119.57, 90.89, 88.20, 21.63, 21.30. The spectrum data matches previously reported values[5].

Synthesis of alkyl diacyl peroxides

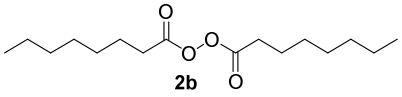
Alkyl diacyl peroxides have potentials to explode. Any alkyl diacyl peroxides involved reaction (as product or substrate) should be carried out with precautions!

Lauroyl peroxide (LPO) **2a** was purchased from Admas. Other peroxides were prepared according to our previous work[6].

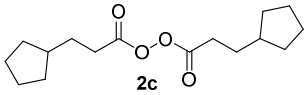


A solution of DMAP (0.6 mmol), 30% hydrogen peroxide (8 mmol), and acid (6 mmol) in DCM (8 mL) was cooled to -15 ^{o}C for about 10 min, then DCC (6.72 mmol) was added. After stirring at -15~-10 ^{o}C for 1.5 h, DCM (15 mL) was added into the reaction solution and the solution was filtered through a short pad of silica gel. Then washed the pad of silica gel by additional 40 mL of DCM. The combined solution was concentrated on a rotary evaporator under vacuum at 10~15 ^{o}C and then purified by flash column chromatography on silica gel to give the alkyl diacyl peroxide.

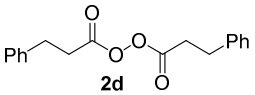
Characterization data for diacyl peroxides



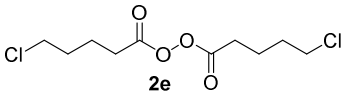
^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.42 (t, *J* = 7.5 Hz, 4H), 1.76 – 1.66 (m, 4H), 1.41 – 1.24 (m, 16H), 0.93 – 0.83 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.25, 31.54, 30.00, 28.87, 28.75, 24.81, 22.55, 14.00. The spectrum data matches previously reported values[7].



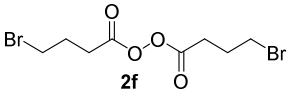
^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.49 – 2.40 (m, 4H), 1.87 – 1.69 (m, 10H), 1.65 – 1.48 (m, 8H), 1.19 – 1.02 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.40, 39.47, 32.29, 30.94, 29.36, 25.10. The spectrum data matches previously reported values[6].



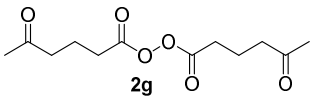
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.26 (m, 4H), 7.26 – 7.17 (m, 6H), 3.02 (t, *J* = 7.8 Hz, 4H), 2.80 – 2.68 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.42, 139.33, 128.71, 128.29, 126.71, 31.70, 30.70. The spectrum data matches previously reported values[6].



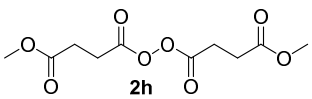
^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.67 – 3.47 (m, 4H), 2.57 – 2.45 (m, 4H), 1.95 – 1.81 (m, 8H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.77, 44.23, 31.42, 29.20, 22.15. The spectrum data matches previously reported values[6].



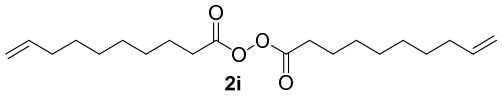
^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.68 – 3.30 (m, 4H), 2.73 – 2.50 (m, 4H), 2.36 – 2.11 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.19, 31.80, 28.39, 27.60. The spectrum data matches previously reported values[6].



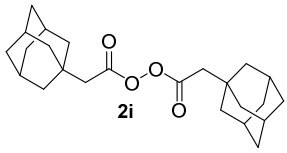
^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.60 (t, *J* = 7.0 Hz, 4H), 2.49 (t, *J* = 7.0 Hz, 4H), 2.16 (s, 6H), 1.97 (p, *J* = 6.9 Hz, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 207.44, 168.76, 41.60, 29.95, 28.88, 18.64. The spectrum data matches previously reported values[6].



^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.72 (s, 6H), 2.81 – 2.69 (m, 8H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.80, 168.21, 52.25, 28.72, 25.34. The spectrum data matches previously reported values[6].



^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.89 – 5.72 (m, 2H), 5.06 – 4.88 (m, 4H), 2.42 (t, *J* = 7.4 Hz, 4H), 2.07 – 2.00 (m, 4H), 1.75 – 1.67 (m, 4H), 1.40 – 1.29 (m, 16H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.30, 139.09, 114.33, 33.81, 30.07, 29.02, 28.94, 28.90, 28.88, 24.88. The spectrum data matches previously reported values[6].

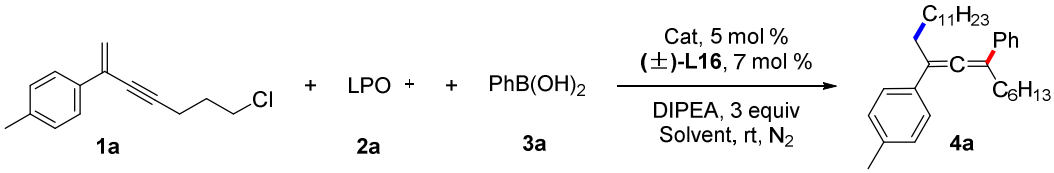


^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.19 (s, 4H), 2.00 (s, 6H), 1.74 – 1.63 (m, 24H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.72, 44.46, 42.11, 36.53, 32.99, 28.55. The spectrum data matches previously reported values[7].

Optimization of the reaction conditions

General procedure for Table S1: In a flame-dried Schlenk tube, Cat. (0.01 mmol, 5 mol%) and Py-Box ligand **(±)-L16** (0.014 mmol, 7 mol%) were dissolved in THF (1 mL) under a nitrogen atmosphere, and the mixture was stirred at room temperature for 30 minutes. Then 1,3-enyne **1a** (0.2 mmol, 1.0 equiv), peroxide **2a** (0.3 mmol, 1.5 equiv), $PhB(OH)_2$ (0.6 mmol, 3 equiv) and base (0.6 mmol, 3 equiv) were sequentially added. The reaction mixture was stirred at rt for 5 h. Upon completion of the reaction as monitored by TLC, the solvent was concentrated under vacuum. The crude residue was purified by flash column chromatography on silica gel to give the product.

Table S1. Optimized reaction conditions[a]



1a 2a 3a 4a

entry	cat.	solvent	base	yield (%)
1	CuTc	THF	DIPEA	69%
2	$Cu(OAc)_2$	THF	DIPEA	67%
3	$Cu(OTf)_2$	THF	DIPEA	51%
4	$Cu(TFA)_2$	THF	DIPEA	66%
5	$Pd(OAc)_2$	THF	DIPEA	trace
6	$NiCl_2$	THF	DIPEA	trace
7	$CoCl_2$	THF	DIPEA	trace
8	$Cu(CH_3CN)_4BF_4$	THF	DIPEA	70%
9	$Cu(CH_3CN)_4BF_4$	DCM	DIPEA	50%
10	$Cu(CH_3CN)_4BF_4$	TBME	DIPEA	21%
11	$Cu(CH_3CN)_4BF_4$	1,4-dioxane	DIPEA	18%
12	$Cu(CH_3CN)_4BF_4$	DMF	DIPEA	Trace
13	$Cu(CH_3CN)_4BF_4$	DME	DIPEA	47%
14	$Cu(CH_3CN)_4BF_4$	THF	KF	18%
15	$Cu(CH_3CN)_4BF_4$	THF	DMAP	trace
16	$Cu(CH_3CN)_4BF_4$	THF	K_2CO_3	trace
17	$Cu(CH_3CN)_4BF_4$	THF	Et_3N	65%
18[b]	$Cu(CH_3CN)_4BF_4$	THF	DIEPA	53%
19[c]	$Cu(CH_3CN)_4BF_4$	THF	DIEPA	trace

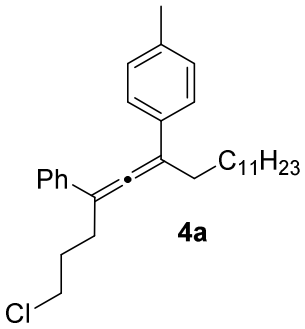
[a] Reaction conditions: **1a** (0.2 mmol, 1 equiv), **2a** (0.3 mmol, 1.5 equiv), **3a** (0.6 mmol, 3 equiv), Cat. (5 mol%), **(±)-L16** (7 mol%), base (0.6 mmol, 3 equiv), solvent (1 mL), rt. [b] 2,4,6-Triphenyloroxin instead of $PhB(OH)_2$. [c] PhBpin instead of $PhB(OH)_2$. [d] Isolated yield.

General procedure for 1,4-alkylarylation of 1,3-enynes

General procedure A: In a flame-dried Schlenk tube, $Cu(CH_3CN)_4BF_4$ (0.01 mmol, 5 mol%) and Py-Box ligand **(±)-L16** (0.014 mmol, 7 mol%) were dissolved in THF (1 mL) under a nitrogen atmosphere, and the mixture was stirred at room temperature for 30 minutes. Then 1,3-enyne (0.2 mmol, 1.0 equiv), peroxide (0.3 mmol, 1.5 equiv), $PhB(OH)_2$ (0.6 mmol, 3 equiv) and DIPEA (0.6 mmol, 3 equiv) were sequentially added. The reaction mixture was stirred at rt for 5 h. Upon completion of the reaction as monitored by TLC, the solvent was concentrated under vacuum. The crude residue was purified by flash column chromatography on silica gel to give the product.

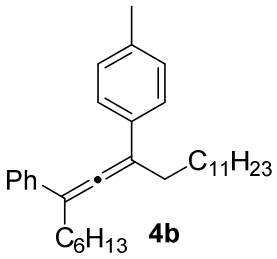
General procedure B: In a flame-dried Schlenk tube, $Cu(CH_3CN)_4BF_4$ (0.01 mmol, 5 mol%) and Py-Box ligand **(±)-L16** (0.014 mmol, 7 mol%) were dissolved in THF (1 mL) under a nitrogen atmosphere, and the mixture was stirred at room temperature for 30 minutes. Then 1,3-enyne (0.2 mmol, 1.0 equiv), peroxide (0.3 mmol, 1.5 equiv), $PhB(OH)_2$ (0.6 mmol, 3 equiv) and DMF (1 mL) were sequentially added. The reaction mixture was stirred at rt for 5 h. Upon completion of the reaction as monitored by TLC, the solvent was concentrated under vacuum. The crude residue was purified by flash column chromatography on silica gel to give the product.

Characterization data for products



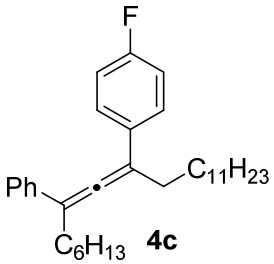
4a

Following the general procedure **A**, **4a** was obtained as a liquid (63 mg, 70% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.30 (m, 4H), 7.28 – 7.21 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 3.63 (t, *J* = 6.4 Hz, 2H), 2.74 (t, *J* = 7.5 Hz, 2H), 2.56 (t, *J* = 7.6 Hz, 2H), 2.36 (s, 3H), 2.15 – 2.01 (m, 2H), 1.66 – 1.54 (m, 2H), 1.40 (p, *J* = 7.6, 7.1 Hz, 2H), 1.37 – 1.22 (m, 16H), 0.91 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 204.80, 136.79, 133.71, 129.38, 128.63, 126.95, 125.95, 110.04, 107.78, 45.06, 32.07, 31.10, 30.58, 29.88, 29.82, 29.78, 29.68, 29.51, 28.30, 27.65, 22.85, 21.22, 14.28. HRMS (DART) calcd for $[C_{31}H_{44}Cl]^{+}$([M+H]$^{+}$): 451.3126, found: 451.3123.



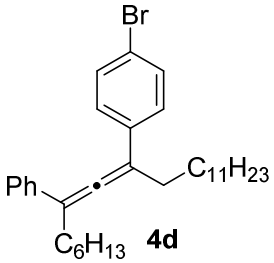
4b

Following the general procedure A, **4b** was obtained as a liquid (58 mg, 63% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 8.3 Hz, 2H), 2.56 (q, *J* = 7.2 Hz, 4H), 2.35 (s, 3H), 1.67 – 1.57 (m, 4H), 1.45 – 1.39 (m, 4H), 1.32 – 1.25 (m, 20H), 0.92 – 0.87 (m, 6H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 205.15, 137.36, 136.42, 134.18, 129.25, 128.49, 126.62, 126.03, 125.95, 109.00, 32.07, 31.93, 30.53, 29.88, 29.82, 29.79, 29.71, 29.58, 29.51, 28.28, 28.26, 22.84, 21.20, 14.27, 14.22. HRMS (DART) calcd for $[C_{34}H_{51}]^{+}$ ([M+H]$^{+}$): 459.3985, found: 459.3981.



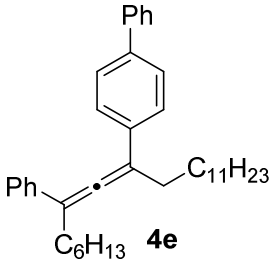
4c

Following the general procedure A, **4c** was obtained as a liquid (43 mg, 46% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 7.7 Hz, 2H), 7.40 – 7.34 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 6.99 (t, *J* = 8.7 Hz, 2H), 2.72 – 2.38 (m, 4H), 1.63 – 1.51 (m, 4H), 1.42 – 1.34 (m, 4H), 1.30 – 1.21 (m, 20H), 0.90 – 0.83 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.98 (d, *J* = 1.9 Hz), 161.78 (d, *J* = 245.7 Hz), 133.04 (d, *J* = 3.2 Hz), 128.45, 127.38 (d, *J* = 7.8 Hz), 126.71, 125.91, 115.23 (d, *J* = 21.3 Hz), 109.23, 108.26, 31.96, 31.80, 30.59, 30.40, 29.73, 29.71, 29.70, 29.67, 29.58, 29.44, 29.40, 28.13, 28.08, 22.73, 14.16, 14.11. HRMS (DART) calcd for $[C_{33}H_{48}F]^{+}$ ($[M+H]^{+}$): 463.3735, found: 463.3731.



4d

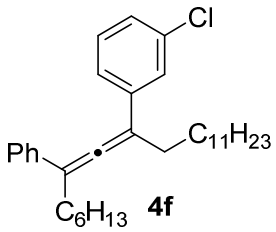
Following the general procedure A, **4d** was obtained as a liquid (68 mg, 65% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.45 – 7.41 (m, 4H), 7.34 – 7.29 (m, 4H), 7.24 – 7.20 (m, 1H), 2.56 (t, *J* = 7.6 Hz, 2H), 2.52 (t, *J* = 7.6 Hz, 2H), 1.64 – 1.53 (m, 4H), 1.43 – 1.36 (m, 4H), 1.32 – 1.24 (m, 20H), 0.92 – 0.87 (m, 6H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 205.39, 136.80, 136.23, 131.54, 128.57, 127.62, 126.90, 126.02, 120.46, 109.63, 108.45, 32.03, 31.87, 30.43, 30.38, 29.78, 29.75, 29.64, 29.51, 29.48, 28.19, 28.14, 22.80, 14.23, 14.18. HRMS (DART) calcd for $[C_{33}H_{48}Br]^{+}$ ($[M+H]^{+}$): 523.2934, found: 523.2931.



4e

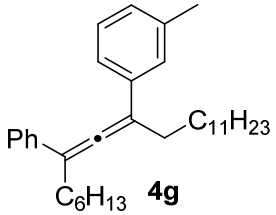
Following the general procedure A, **4e** was obtained as a liquid (76 mg, 73% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 7.6 Hz, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 3H), 7.26 (t, *J* = 7.5 Hz, 1H), 2.74 – 2.37 (m, 4H), 1.72 – 1.62 (m, 4H), 1.50 – 1.42 (m, 4H), 1.36 – 1.28 (m, 20H), 0.95 – 0.90 (m, 6H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 205.71, 141.03, 139.56, 137.16, 136.22, 128.91, 128.58, 127.28, 127.15, 127.08, 126.81, 126.47, 126.10, 109.36, 108.95, 32.10, 31.96, 30.57,

30.53, 29.93, 29.87, 29.83, 29.75, 29.63, 29.55, 28.34, 28.30, 22.88, 14.31, 14.26. HRMS (DART) calcd for $[C_{39}H_{53}]^+$ ($[M+H]^+$): 521.4142, found: 521.4136.



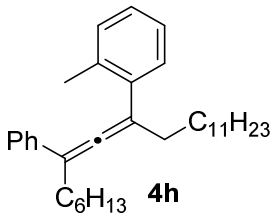
4f

Following the general procedure A, **4f** was obtained as a liquid (53 mg, 55% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.43 – 7.39 (m, 2H), 7.39 – 7.36 (m, 1H), 7.34 – 7.28 (m, 3H), 7.24 – 7.18 (m, 2H), 7.18 – 7.14 (m, 1H), 2.54 (t, *J* = 8.4 Hz, 2H), 2.50 (t, *J* = 7.8 Hz, 2H), 1.60 – 1.52 (m, 4H), 1.42 – 1.36 (m, 4H), 1.27 – 1.22 (m, 20H), 0.88 – 0.85 (m, 6H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 205.51, 139.37, 136.72, 134.51, 129.63, 128.57, 126.93, 126.66, 126.06, 125.95, 124.19, 109.73, 108.35, 32.03, 31.87, 30.44, 30.38, 29.79, 29.76, 29.74, 29.63, 29.51, 29.47, 28.16, 28.10, 22.80, 14.24, 14.18. HRMS (DART) calcd for $[C_{33}H_{48}Cl]^+$ ($[M+H]^+$): 479.3439, found: 479.3435.



4g

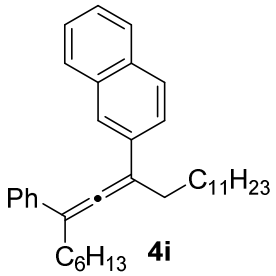
Following the general procedure A, **4g** was obtained as a liquid (65 mg, 71% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.41 (m, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.16 (m, 4H), 7.01 (d, *J* = 7.3 Hz, 1H), 2.65 – 2.42 (m, 4H), 2.33 (s, 3H), 1.66 – 1.53 (m, 4H), 1.45 – 1.34 (m, 4H), 1.30 – 1.19 (m, 20H), 0.91 – 0.83 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.30, 137.96, 137.20, 137.05, 128.42, 128.34, 127.47, 126.63, 126.58, 125.97, 123.11, 109.09, 108.89, 32.00, 31.86, 30.48, 30.42, 29.80, 29.76, 29.72, 29.63, 29.51, 29.44, 28.19, 28.17, 22.78, 21.65, 14.21, 14.16. HRMS (DART) calcd for $[C_{34}H_{51}]^+$ ($[M+H]^+$): 459.3985, found: 459.3981.



4h

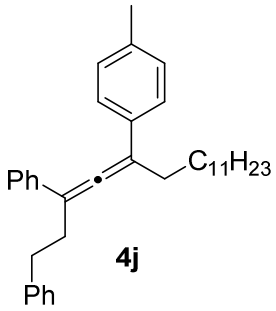
Following the general procedure A, **4h** was obtained as a liquid (50 mg, 54% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.39 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.24 (m, 1H), 7.21 – 7.11 (m, 4H), 2.50 – 2.38 (m, 4H), 2.33 (s, 3H), 1.61 – 1.47 (m, 4H), 1.42 – 1.33 (m, 4H), 1.31 – 1.23 (m, 20H), 0.91 – 0.86 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.77, 138.50, 137.67,

135.78, 130.39, 128.35, 128.25, 126.73, 126.34, 126.15, 125.68, 108.21, 106.00, 34.50, 31.97, 31.88, 30.55, 29.73, 29.69, 29.67, 29.59, 29.41, 29.39, 28.30, 28.15, 22.75, 20.71, 14.18, 14.16. HRMS (DART) calcd for $[C_{34}H_{51}]^+$ ($[M+H]^+$): 459.3985, found: 459.3982.



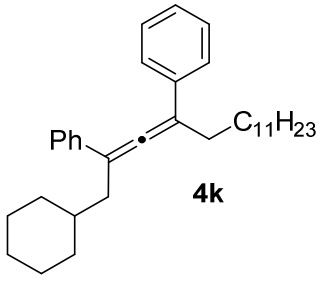
4i

Following the general procedure A, **4i** was obtained as a liquid (53 mg, 54% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.76 (m, 3H), 7.71 (d, *J* = 8.7 Hz, 1H), 7.59 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.48 – 7.39 (m, 4H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 2.67 (t, *J* = 7.6 Hz, 2H), 2.58 (t, *J* = 7.6 Hz, 2H), 1.71 – 1.57 (m, 4H), 1.46 – 1.38 (m, 4H), 1.32 – 1.23 (m, 20H), 0.89 – 0.82 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.04, 137.05, 134.51, 133.73, 132.46, 128.46, 128.01, 127.78, 127.56, 126.69, 126.05, 125.99, 125.55, 125.43, 123.39, 109.38, 31.96, 31.81, 30.45, 30.35, 29.82, 29.73, 29.69, 29.62, 29.48, 29.41, 28.17, 22.74, 22.72, 14.17, 14.11. HRMS (DART) calcd for $[C_{37}H_{51}]^+$ ($[M+H]^+$): 495.3985, found: 495.3980.



4j

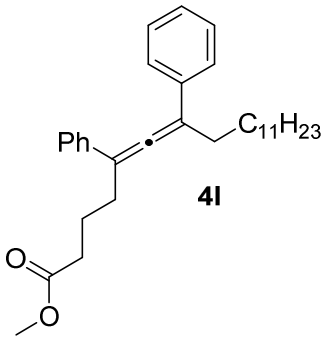
Following the general procedure A, **4j** was obtained as a liquid (43 mg, 45% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.49 – 7.44 (m, 2H), 7.35 – 7.31 (m, 2H), 7.31 – 7.27 (m, 4H), 7.24 – 7.19 (m, 4H), 7.13 (d, *J* = 8.4 Hz, 2H), 2.96 – 2.86 (m, 4H), 2.56 – 2.45 (m, 2H), 2.35 (s, 3H), 1.55 – 1.50 (m, 2H), 1.41 – 1.24 (m, 18H), 0.92 – 0.89 (m, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 205.11, 142.19, 137.05, 136.56, 133.93, 129.28, 128.58, 128.46, 126.79, 126.01, 125.98, 109.68, 108.41, 34.42, 32.33, 32.05, 30.54, 29.87, 29.82, 29.77, 29.68, 29.50, 28.22, 22.83, 21.21, 14.27. HRMS (DART) calcd for $[C_{36}H_{47}]^+$ ($[M+H]^+$): 479.3672, found: 479.3669.



4k

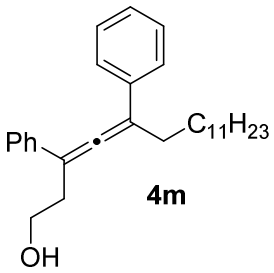
Following the general procedure **A**, **4k** was obtained as a liquid (61 mg, 67% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.40 (m, 4H), 7.30 (t, *J* = 7.6 Hz, 4H), 7.22 – 7.15 (m, 2H),

2.54 (t, *J* = 7.6 Hz, 2H), 2.44 (d, *J* = 6.9 Hz, 2H), 1.90 – 1.74 (m, 3H), 1.71 – 1.56 (m, 6H), 1.31 – 1.19 (m, 22H), 0.89 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 205.96, 137.22, 137.10, 128.41, 126.58, 126.17, 126.07, 107.97, 107.18, 38.54, 36.41, 33.73, 33.68, 31.98, 30.63, 29.80, 29.74, 29.72, 29.70, 29.59, 29.42, 28.30, 26.57, 26.32, 26.27, 22.76, 14.20. HRMS (DART) calcd for $[C_{34}H_{49}]^+$ ($[M+H]^+$): 457.3829, found: 457.3826.



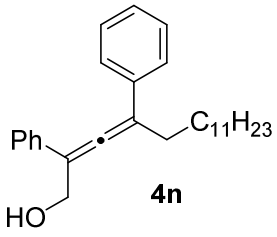
4l

Following the general procedure A, **4l** was obtained as a liquid (64 mg, 69% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.49 – 7.43 (m, 4H), 7.36 – 7.30 (m, 4H), 7.23 – 7.18 (m, 2H), 3.66 (s, 3H), 2.61 (t, *J* = 7.7 Hz, 2H), 2.57 (t, *J* = 7.6 Hz, 2H), 2.43 (t, *J* = 7.4 Hz, 2H), 1.99 – 1.89 (m, 2H), 1.64 – 1.54 (m, 2H), 1.42 – 1.36 (m, 2H), 1.31 – 1.24 (m, 16H), 0.90 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 205.21, 174.04, 136.90, 136.74, 128.60, 128.58, 126.90, 126.06, 125.98, 109.85, 108.37, 51.61, 33.91, 32.05, 30.53, 29.87, 29.80, 29.77, 29.67, 29.49, 28.28, 23.48, 22.83, 14.26. HRMS (DART) calcd for $[C_{32}H_{45}O_2]^+$ ($[M+H]^+$): 461.3414, found: 461.3411.



4m

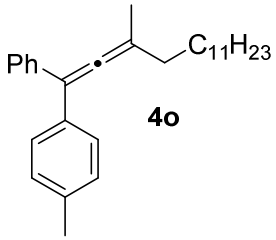
Following the general procedure **A**, **4m** was obtained as a liquid (26 mg, 32% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 7.7 Hz, 4H), 7.34 – 7.26 (m, 4H), 7.23 – 7.17 (m, 2H), 3.87 (t, *J* = 6.5 Hz, 2H), 2.94 – 2.74 (m, 2H), 2.55 (t, *J* = 7.6 Hz, 2H), 2.31 (t, *J* = 7.5 Hz, 1H), 1.64 – 1.53 (m, 2H), 1.43 – 1.34 (m, 2H), 1.32 – 1.24 (m, 16H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.82, 136.34, 136.28, 128.67, 128.60, 127.10, 127.06, 125.90, 125.84, 110.19, 105.80, 61.39, 33.47, 31.95, 30.41, 29.75, 29.69, 29.66, 29.63, 29.55, 29.39, 28.18, 22.73, 14.17. HRMS (DART) calcd for $[C_{29}H_{41}O]^+$ ($[M+H]^+$): 405.3152, found: 405.3149.



4n

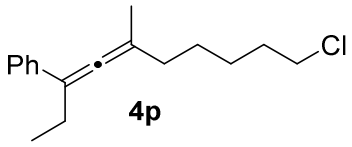
Following the general procedure **A**, **4n** was obtained as a liquid (33 mg, 42% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.47 – 7.42 (m, 4H), 7.36 – 7.31 (m, 4H), 7.27 – 7.22 (m, 2H),

4.72 – 4.61 (m, 2H), 2.64 – 2.55 (m, 2H), 1.62 – 1.55 (m, 2H), 1.42 – 1.36 (m, 2H), 1.32 – 1.21 (m, 17H), 0.88 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 203.57, 136.15, 134.54, 128.82, 128.70, 127.43, 127.40, 126.23, 126.12, 112.40, 110.07, 61.86, 32.03, 30.53, 29.77, 29.74, 29.72, 29.62, 29.47, 28.20, 22.81, 14.25. HRMS (EI+) calcd for $[C_{28}H_{38}O]^+$ ($[M]^+$): 390.2923, found: 390.2931.



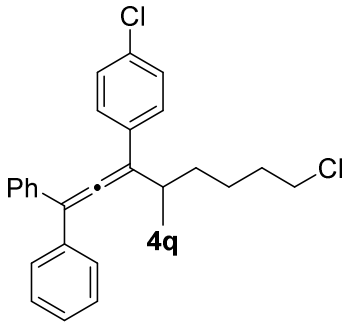
4o

Following the general procedure A, **4o** was obtained as a liquid (38 mg, 49% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.27 (m, 4H), 7.25 – 7.20 (m, 3H), 7.13 (d, *J* = 7.9 Hz, 2H), 2.35 (s, 3H), 2.12 (t, *J* = 7.5 Hz, 2H), 1.85 (s, 3H), 1.55 – 1.47 (m, 2H), 1.29 – 1.18 (m, 18H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 203.08, 138.38, 136.39, 135.23, 128.96, 128.37, 128.33, 128.19, 126.62, 108.57, 102.87, 34.42, 31.98, 29.75, 29.72, 29.70, 29.68, 29.58, 29.48, 29.43, 27.66, 22.76, 21.19, 19.08, 14.19. HRMS (DART) calcd for $[C_{29}H_{41}]^+$ ($[M+H]^+$): 389.3203, found: 389.3200.



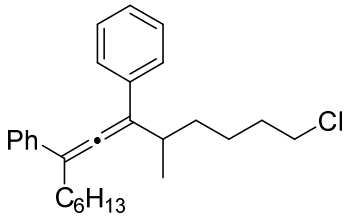
4p

Following the general procedure A, **4p** was obtained as a liquid (13 mg, 27% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.35 (m, 2H), 7.32 – 7.27 (m, 2H), 7.19 – 7.15 (m, 1H), 3.47 (t, *J* = 6.8 Hz, 2H), 2.41 (q, *J* = 7.3 Hz, 2H), 2.14 – 2.04 (m, 2H), 1.80 (s, 3H), 1.77 – 1.71 (m, 2H), 1.52 – 1.43 (m, 4H), 1.10 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 200.98, 138.38, 128.23, 126.11, 125.78, 106.70, 103.35, 45.15, 34.17, 32.54, 26.97, 26.74, 23.18, 19.12, 12.77. HRMS (EI+) calcd for $[C_{17}H_{23}Cl]^+$ ($[M]^+$): 262.1488, found: 262.1485.



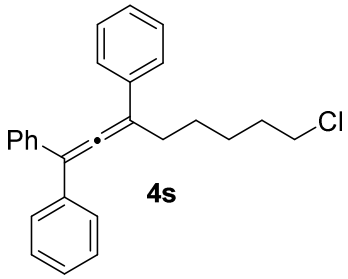
4q

Following the general procedure A, **4q** was obtained as a liquid (27 mg, 32% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.26 (m, 14H), 3.37 – 3.22 (m, 2H), 2.84 – 2.74 (m, 1H), 1.71 – 1.54 (m, 4H), 1.52 – 1.38 (m, 2H), 1.36 – 1.22 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 206.11, 136.68, 136.49, 134.78, 132.76, 128.81, 128.54, 128.53, 128.25, 128.15, 127.77, 127.49, 127.45, 114.30, 114.14, 44.93, 35.59, 34.45, 32.81, 25.00, 20.61. HRMS (DART) calcd for $[C_{27}H_{27}Cl_2]^+$ ($[M+H]^+$): 421.1484, found: 421.1481.



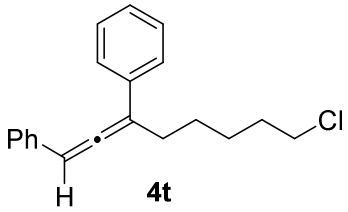
4r

Following the general procedure A, **4r** was obtained as a liquid (16 mg, 20% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.38 (m, 4H), 7.35 – 7.26 (m, 4H), 7.24 – 7.16 (m, 2H), 3.51 (t, *J* = 6.7 Hz, 1.5 H), 3.35 (t, *J* = 6.7, Hz, 0.5H), 2.88 – 2.74 (m, 1H), 2.54 (t, *J* = 7.6 Hz, 2H), 1.77 (m, 1.5H), 1.61 – 1.54 (m, 3.5H), 1.43 – 1.36 (m, 3H), 1.29 – 1.24 (m, 6H), 1.19 (dd, *J* = 6.8, 1.8 Hz, 3H), 0.87 – 0.84 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.53, 136.98, 136.83, 128.51, 128.45, 126.70, 126.66, 126.40, 125.77, 45.11, 35.79, 34.13, 32.89, 31.80, 30.50, 29.55, 28.41, 24.96, 22.72, 20.25, 14.12. HRMS (DART) calcd for $[C_{27}H_{36}Cl]^{+}$ ($[M+H]^{+}$): 395.2500, found: 395.2497.



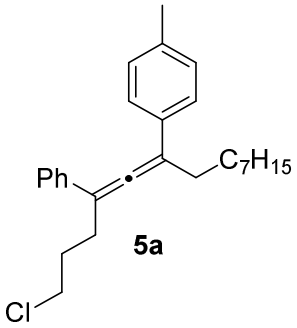
4s

Following the general procedure A, **4s** was obtained as a liquid (34 mg, 46% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.46 (m, 2H), 7.44 – 7.37 (m, 4H), 7.37 – 7.30 (m, 6H), 7.30 – 7.20 (m, 3H), 3.36 (t, *J* = 6.8 Hz, 2H), 2.64 (t, *J* = 7.4 Hz, 2H), 1.82 – 1.60 (m, 4H), 1.52 – 1.41 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 206.99, 136.85, 136.11, 128.65, 128.51, 128.32, 127.38, 127.17, 126.05, 113.12, 108.77, 45.05, 32.57, 30.18, 27.23, 26.87. HRMS (DART) calcd for $[C_{26}H_{26}Cl]^{+}$ ($[M+H]^{+}$): 373.1718, found: 373.1714.



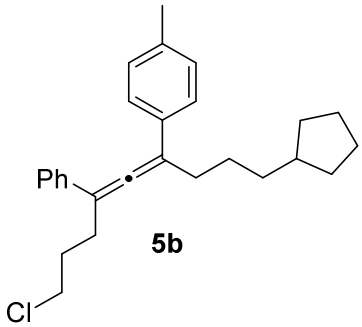
4t

Following the general procedure **A**, **4t** was obtained as a liquid (19 mg, 32% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.41 (m, 2H), 7.36 – 7.29 (m, 6H), 7.24 – 7.18 (m, 2H), 6.54 (t, *J* = 3.2 Hz, 1H), 3.48 (t, *J* = 6.7 Hz, 2H), 2.65 – 2.52 (m, 2H), 1.84 – 1.72 (m, 2H), 1.69 – 1.51 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.42, 136.06, 134.54, 128.78, 128.57, 127.15, 127.12, 126.79, 126.10, 109.65, 98.15, 45.11, 32.49, 29.93, 27.17, 26.81. HRMS (DART) calcd for $[C_{20}H_{22}Cl]^{+}$ ($[M+H]^{+}$): 297.1405, found: 297.1403.



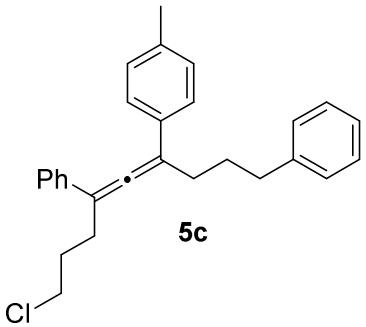
5a

Following the general procedure A, **5a** was obtained as a liquid (50 mg, 63% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.40 (m, 2H), 7.37 – 7.25 (m, 4H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 3.60 (t, *J* = 6.4 Hz, 2H), 2.71 (t, *J* = 7.5 Hz, 2H), 2.52 (d, *J* = 8.0 Hz, 2H), 2.33 (s, 3H), 2.11 – 1.97 (m, 2H), 1.63 – 1.49 (m, 2H), 1.43 – 1.33 (m, 2H), 1.32 – 1.19 (m, 8H), 0.86 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.71, 136.70, 133.62, 129.29, 128.54, 126.86, 125.86, 109.94, 107.69, 44.99, 31.89, 31.02, 30.50, 29.79, 29.55, 29.39, 28.22, 27.56, 22.72, 21.14, 14.17. HRMS (DART) calcd for $[C_{27}H_{36}Cl]^{+}$ ($[M+H]^{+}$): 395.2500, found: 395.2498.



5b

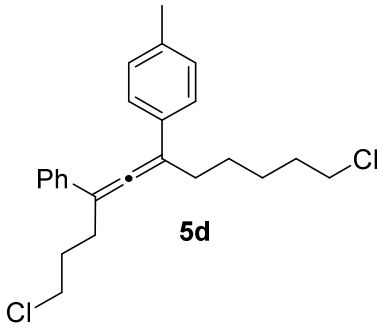
Following the general procedure **A**, **5b** was obtained as a liquid (48 mg, 61% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.40 (m, 2H), 7.36 – 7.26 (m, 4H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 2H), 3.60 (t, *J* = 6.5 Hz, 2H), 2.71 (t, *J* = 7.5 Hz, 2H), 2.53 (t, *J* = 7.6 Hz, 2H), 2.32 (s, 3H), 2.10 – 1.98 (m, 2H), 1.79 – 1.63 (m, 3H), 1.62 – 1.43 (m, 6H), 1.41 – 1.35 (m, 2H), 1.09 – 0.94 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.74, 136.70, 133.63, 129.30, 128.55, 126.87, 125.88, 125.87, 109.92, 107.71, 44.99, 39.98, 36.27, 32.75, 32.71, 31.03, 30.72, 27.58, 27.32, 25.22, 21.15. HRMS (DART) calcd for $[C_{27}H_{34}Cl]^{+}$ ($[M+H]^{+}$): 393.2344, found: 393.2341.



5c

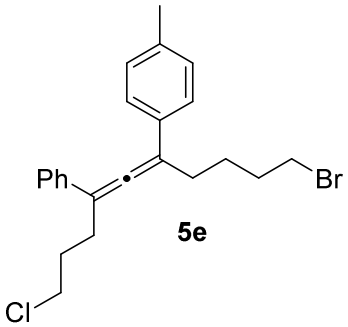
Following the general procedure A, **5c** was obtained as a liquid (41 mg, 51% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.49 – 7.44 (m, 2H), 7.36 – 7.29 (m, 4H), 7.29 – 7.25 (m, 2H), 7.25 – 7.21 (m, 1H), 7.18 (t, *J* = 6.8 Hz, 1H), 7.16 – 7.10 (m, 4H), 3.60 (t, *J* = 6.4 Hz, 2H), 2.79 – 2.67 (m, 4H), 2.60 (t, *J* = 7.6 Hz, 2H), 2.34 (s, 3H), 2.11 – 2.01 (m, 2H), 1.98 – 1.87 (m, 2H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 204.72, 142.29, 136.89, 136.64, 133.54, 129.40, 128.69, 128.58,

128.43, 127.06, 125.96, 125.90, 109.70, 108.15, 45.02, 35.92, 31.08, 30.04, 29.88, 27.66, 21.20. HRMS (DART) calcd for $[C_{28}H_{30}Cl]^+$ ($[M+H]^+$): 401.2031, found: 401.2027.



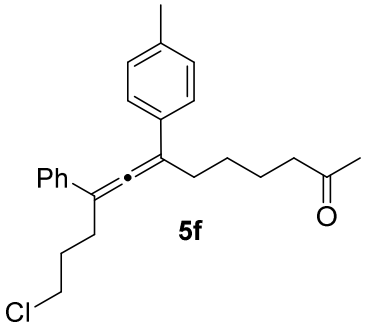
5d

Following the general procedure A, **5d** was obtained as a liquid (56 mg, 72% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.38 (m, 2H), 7.37 – 7.26 (m, 4H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 3.61 (t, *J* = 6.4 Hz, 2H), 3.46 (t, *J* = 6.7 Hz, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.56 (t, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 2.13 – 1.98 (m, 2H), 1.80 – 1.70 (m, 2H), 1.65 – 1.47 (m, 5H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.62, 136.86, 136.55, 133.39, 129.35, 128.60, 126.98, 125.85, 125.81, 109.56, 107.99, 45.13, 44.96, 32.55, 31.01, 30.30, 27.57, 27.42, 27.00, 21.15. HRMS (DART) calcd for $[C_{24}H_{29}Cl_2]^+$ ($[M+H]^+$): 387.1641, found: 387.1638.



5e

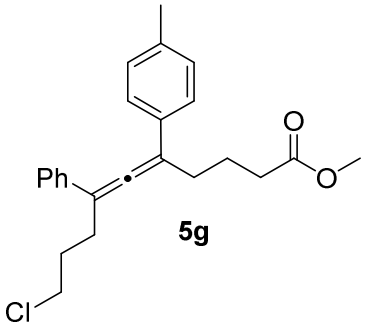
Following the general procedure **A**, **5e** was obtained as a liquid (51 mg, 54% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.39 (m, 2H), 7.37 – 7.27 (m, 4H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 3.61 (t, *J* = 6.4 Hz, 2H), 3.37 (t, *J* = 6.8 Hz, 2H), 2.72 (t, *J* = 7.5 Hz, 2H), 2.57 (t, *J* = 7.6 Hz, 2H), 2.33 (s, 3H), 2.11 – 2.00 (m, 2H), 1.99 – 1.90 (m, 2H), 1.79 – 1.65 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.60, 136.94, 136.44, 133.24, 129.39, 128.64, 127.06, 125.88, 125.81, 109.25, 108.22, 44.94, 33.57, 32.64, 31.02, 29.57, 27.63, 26.65, 21.16. HRMS (EI+) calcd for $[C_{23}H_{26}ClBr]^+$ ($[M]^+$): 416.0906, found: 416.0904.



5f

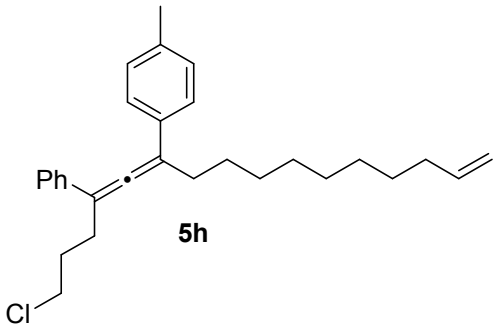
Following the general procedure A, **5f** was obtained as a liquid (40 mg, 52% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.45 – 7.42 (m, 2H), 7.34 – 7.29 (m, 4H), 7.24 – 7.20 (m, 1H), 7.13 (d, *J* = 8.1 Hz, 2H), 3.61 (t, *J* = 6.4 Hz, 2H), 2.72 (t, *J* = 7.5 Hz, 2H), 2.56 (t, *J* = 7.5 Hz, 2H), 2.41 (t, *J* = 7.5 Hz, 2H), 2.34 (s, 3H), 2.08 – 2.01 (m, 5H), 1.71 – 1.65 (m, 2H), 1.62 – 1.51 (m, 2H). ^{13}C NMR

(150 MHz, Chloroform-*d*) δ 209.10, 204.67, 136.93, 136.61, 133.41, 129.42, 128.68, 127.06, 125.91, 125.88, 109.58, 108.06, 45.02, 43.69, 31.06, 30.36, 29.92, 27.69, 27.63, 23.89, 21.20. HRMS (DART) calcd for $[C_{25}H_{30}OCl]^+$ ($[M+H]^+$): 381.1980, found: 381.1977.



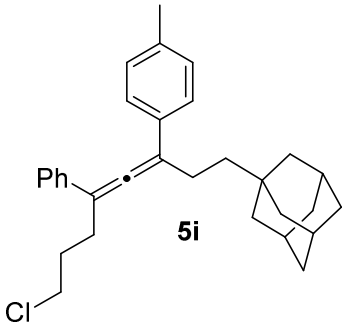
5g

Following the general procedure **A**, **5g** was obtained as a liquid (46 mg, 60% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.46 – 7.43 (m, 2H), 7.35 – 7.31 (m, 4H), 7.25 – 7.21 (m, 1H), 7.14 (d, *J* = 8.2 Hz, 2H), 3.65 (s, 3H), 3.62 (t, *J* = 6.5 Hz, 2H), 2.73 (t, *J* = 7.5 Hz, 2H), 2.60 (t, *J* = 7.7 Hz, 2H), 2.42 (t, *J* = 7.3 Hz, 2H), 2.34 (s, 3H), 2.11 – 2.02 (m, 2H), 1.96 – 1.87 (m, 2H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 204.62, 173.99, 137.01, 136.47, 133.25, 129.44, 128.69, 127.12, 125.96, 125.88, 109.21, 108.44, 51.67, 45.01, 33.88, 31.06, 29.94, 27.68, 23.49, 21.21. HRMS (DART) calcd for $[C_{24}H_{28}O_2Cl]^+$ ($[M+H]^+$): 383.1772, found: 383.1769.



5h

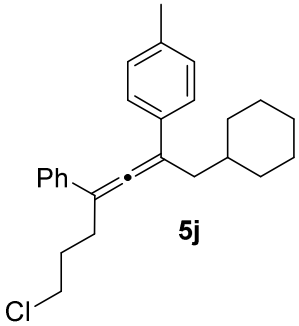
Following the general procedure **A**, **5h** was obtained as a liquid (53 mg, 63% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.48 – 7.44 (m, 2H), 7.35 – 7.31 (m, 4H), 7.25 – 7.21 (m, 1H), 7.17 – 7.11 (m, 2H), 5.86 – 5.77 (m, 1H), 5.04 – 4.97 (m, 1H), 4.97 – 4.90 (m, 1H), 3.63 (t, *J* = 6.5 Hz, 2H), 2.73 (t, *J* = 7.5 Hz, 2H), 2.55 (d, *J* = 7.8 Hz, 2H), 2.35 (s, 3H), 2.14 – 1.99 (m, 4H), 1.65 – 1.50 (m, 2H), 1.42 – 1.34 (m, 4H), 1.31 – 1.24 (m, 6H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 204.79, 139.39, 139.37, 136.80, 136.77, 133.68, 129.38, 128.63, 126.95, 125.94, 114.24, 110.01, 107.79, 45.06, 33.92, 31.09, 30.56, 29.83, 29.60, 29.21, 29.03, 28.27, 27.63, 21.21. HRMS (DART) calcd for $[C_{29}H_{38}Cl]^+$ ($[M+H]^+$): 421.2657, found: 421.2654.



5i

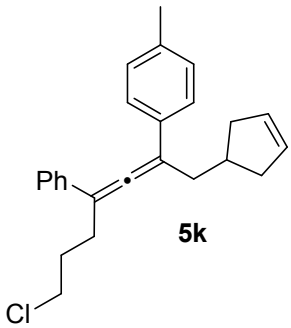
Following the general procedure **A**, **5i** was obtained as a liquid (44 mg, 49% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.40 (m, 2H), 7.36 – 7.26 (m, 4H), 7.23 – 7.18 (m, 1H), 7.12 (d, *J* =

7.9 Hz, 2H), 3.61 (t, *J* = 6.4 Hz, 2H), 2.72 (t, *J* = 7.2 Hz, 2H), 2.55 – 2.47 (m, 2H), 2.33 (s, 3H), 2.12 – 2.00 (m, 2H), 1.96 (s, 3H), 1.76 – 1.60 (m, 6H), 1.58 -1.48 (m, 6H), 1.39 – 1.33 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.59, 136.72, 136.68, 133.58, 129.28, 128.55, 126.83, 125.88, 125.85, 110.41, 107.54, 44.98, 42.89, 42.42, 37.27, 32.43, 30.96, 28.77, 27.46, 23.77, 21.14. HRMS (DART) calcd for $[C_{31}H_{38}Cl]^+$ ($[M+H]^+$): 445.2657, found: 445.2654.



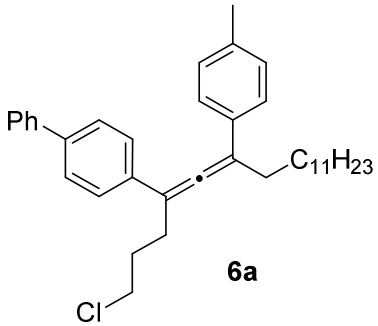
5j

Following the general procedure A, **5j** was obtained as a liquid (45 mg, 60% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.47 – 7.41 (m, 2H), 7.37 – 7.28 (m, 4H), 7.24 – 7.20 (m, 1H), 7.18 – 7.09 (m, 2H), 3.61 (t, *J* = 6.5 Hz, 2H), 2.80 – 2.66 (m, 2H), 2.52 – 2.39 (m, 2H), 2.35 (s, 3H), 2.15 – 2.02 (m, 2H), 1.88 – 1.78 (m, 2H), 1.72 – 1.65 (m, 2H), 1.64 – 1.53 (m, 2H), 1.23 – 1.10 (m, 3H), 1.03 – 0.89 (m, 2H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 205.50, 136.80, 136.75, 133.83, 129.36, 128.60, 126.89, 126.16, 126.05, 108.12, 106.59, 45.05, 38.73, 36.49, 33.78, 33.73, 31.20, 27.86, 26.60, 26.35, 26.33, 21.21. HRMS (DART) calcd for $[C_{26}H_{32}Cl]^+$ ($[M+H]^+$): 379.2187, found: 379.2184.



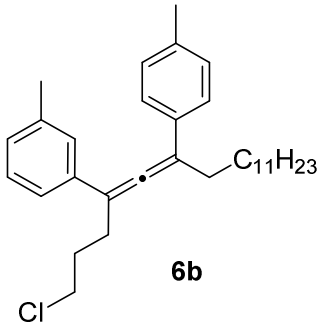
5k

Following the general procedure A, **5k** was obtained as a liquid (14 mg, 19% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.41 (m, 2H), 7.37 – 7.29 (m, 4H), 7.24 – 7.19 (m, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 5.69 – 5.56 (m, 2H), 3.61 (t, *J* = 6.5 Hz, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.67 – 2.60 (m, 2H), 2.59 – 2.41 (m, 3H), 2.33 (s, 3H), 2.17 – 1.99 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 205.29, 136.80, 136.46, 133.69, 129.90, 129.70, 129.30, 128.54, 126.89, 125.88, 125.81, 109.15, 107.65, 45.01, 39.59, 39.56, 37.66, 35.61, 31.02, 27.68, 21.12. HRMS (DART) calcd for $[C_{25}H_{28}Cl]^+$ ($[M+H]^+$): 363.1874, found: 363.1871.



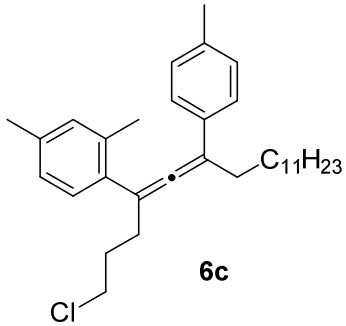
6a

Following the general procedure **B**, **6a** was obtained as a liquid (63 mg, 60% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.64 – 7.61 (m, 2H), 7.60 – 7.57 (m, 2H), 7.57 – 7.52 (m, 2H), 7.47 – 7.43 (m, 2H), 7.39 – 7.33 (m, 3H), 7.17 (d, *J* = 7.9 Hz, 2H), 3.66 (t, *J* = 6.4 Hz, 2H), 2.78 (t, *J* = 7.5 Hz, 2H), 2.62 – 2.55 (m, 2H), 2.37 (s, 3H), 2.17 – 2.07 (m, 2H), 1.68 – 1.58 (m, 2H), 1.46 – 1.40 (m, 2H), 1.34 – 1.26 (m, 16H), 0.91 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 205.09, 140.90, 139.78, 136.86, 135.78, 133.68, 129.44, 128.91, 127.35, 127.06, 126.36, 126.01, 110.20, 107.55, 45.05, 32.06, 31.15, 30.63, 29.90, 29.84, 29.80, 29.70, 29.52, 28.34, 27.69, 22.85, 21.23, 14.27. HRMS (DART) calcd for $[C_{37}H_{48}Cl]^{+}$ ($[M+H]^{+}$): 527.3439, found: 727.3434.



6b

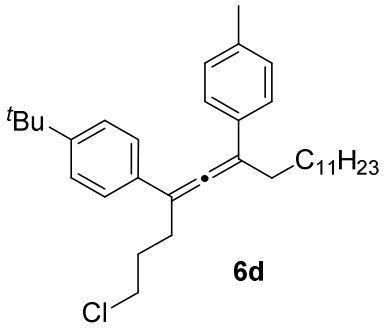
Following the general procedure A, **6b** was obtained as a liquid (64 mg, 69% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.27 – 7.17 (m, 3H), 7.12 (d, *J* = 7.9 Hz, 2H), 7.03 (d, *J* = 7.2 Hz, 1H), 3.60 (t, *J* = 6.5 Hz, 2H), 2.70 (t, *J* = 7.5 Hz, 2H), 2.59 – 2.47 (m, 2H), 2.33 (s, 6H), 2.09 – 1.98 (m, 2H), 1.62 – 1.50 (m, 2H), 1.43 – 1.34 (m, 2H), 1.30 – 1.21 (m, 16H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.70, 138.09, 136.64, 136.63, 133.71, 129.28, 128.45, 127.69, 126.52, 125.88, 123.02, 109.74, 107.69, 45.01, 31.99, 31.04, 30.49, 29.81, 29.75, 29.71, 29.62, 29.44, 28.21, 27.64, 22.77, 21.65, 21.14, 14.21. HRMS (DART) calcd for $[C_{32}H_{46}Cl]^{+}$ ($[M+H]^{+}$): 465.3283, found: 465.3279.



6c

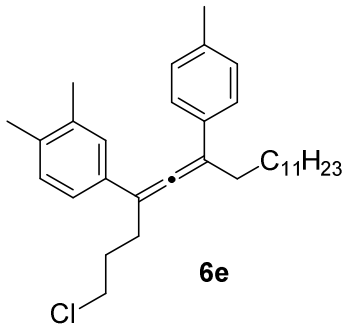
Following the general procedure **A**, **6c** was obtained as a liquid (53 mg, 55% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.04 – 6.92 (m, 2H), 3.58 (t, *J* = 6.5 Hz, 2H), 2.56 (d, *J* = 7.6 Hz, 2H), 2.43 (d, *J* = 7.6 Hz, 2H), 2.33 (s, 3H), 2.29 (s, 6H), 2.04 – 1.94 (m, 2H), 1.59 – 1.49 (m, 2H), 1.38 – 1.23 (m, 18H), 0.88 (t,

J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 202.53, 136.57, 136.27, 135.64, 135.01, 134.30, 131.37, 129.09, 128.16, 126.54, 126.08, 106.58, 106.53, 44.86, 32.00, 31.62, 31.02, 30.68, 29.77, 29.73, 29.72, 29.65, 29.44, 28.34, 22.77, 21.13, 21.04, 20.69, 14.21. HRMS (DART) calcd for $[C_{33}H_{48}Cl]^+$ ($[M+H]^+$): 479.3439, found: 479.3434.



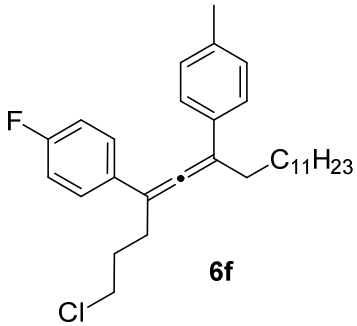
6d

Following the general procedure **B**, **6d** was obtained as a liquid (35 mg, 35% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.21 (m, 6H), 7.03 (d, *J* = 7.7 Hz, 2H), 3.52 (t, *J* = 6.4 Hz, 2H), 2.62 (t, *J* = 7.4 Hz, 2H), 2.49 – 2.40 (m, 2H), 2.24 (s, 3H), 2.02 – 1.91 (m, 2H), 1.53 – 1.45 (m, 2H), 1.36 – 1.26 (m, 2H), 1.23 (s, 9H), 1.21 – 1.14 (m, 16H), 0.80 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.57, 149.85, 136.59, 133.76, 133.66, 129.25, 125.86, 125.54, 125.48, 109.85, 107.37, 45.03, 34.52, 31.99, 31.36, 31.05, 30.54, 29.84, 29.75, 29.71, 29.61, 29.43, 28.26, 27.53, 22.77, 21.14, 14.20. HRMS (DART) calcd for $[C_{35}H_{52}Cl]^+$ ($[M+H]^+$): 507.3752, found: 507.3748.



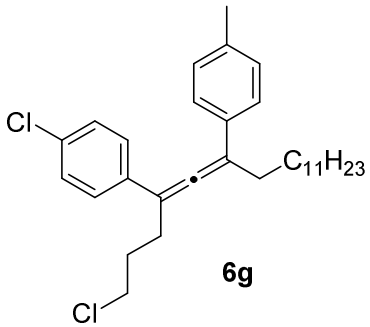
6e

Following the general procedure **B**, **6e** was obtained as a liquid (34 mg, 36% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.28 (m, 2H), 7.22 – 7.15 (m, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 1H), 3.60 (t, *J* = 6.5 Hz, 2H), 2.68 (t, *J* = 7.5 Hz, 2H), 2.57 – 2.48 (m, 2H), 2.33 (s, 3H), 2.24 (s, 6H), 2.09 – 1.98 (m, 2H), 1.60 – 1.51 (m, 3H), 1.41 – 1.34 (m, 2H), 1.30 – 1.21 (m, 16H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.41, 136.65, 136.53, 135.34, 133.86, 129.83, 129.23, 127.08, 125.85, 123.29, 109.57, 107.50, 45.03, 31.98, 31.05, 30.49, 29.80, 29.74, 29.70, 29.61, 29.42, 28.20, 27.64, 22.75, 21.12, 20.01, 19.47, 14.19. HRMS (DART) calcd for $[C_{33}H_{48}Cl]^+$ ($[M+H]^+$): 479.3439, found: 479.3434.



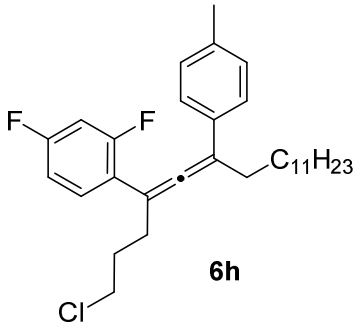
6f

Following the general procedure A, **6f** was obtained as a liquid (58 mg, 62% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.35 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.99 (t, *J* = 8.7 Hz, 2H), 3.60 (t, *J* = 6.4 Hz, 2H), 2.68 (t, *J* = 7.5 Hz, 2H), 2.53 (t, *J* = 7.6 Hz, 2H), 2.33 (s, 3H), 2.09 – 1.97 (m, 2H), 1.61 – 1.48 (m, 2H), 1.41 – 1.33 (m, 2H), 1.31 – 1.21 (m, 16H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.39 (d, *J* = 2.0 Hz), 161.92 (d, *J* = 246.1 Hz), 136.82, 133.47, 132.69, 132.65, 129.32, 127.32 (d, *J* = 7.9 Hz), 125.83, 115.38 (d, *J* = 21.4 Hz), 110.15, 106.93, 44.91, 31.97, 30.93, 30.48, 29.76, 29.73, 29.70, 29.68, 29.58, 29.42, 28.20, 27.73, 22.75, 21.13, 14.19. HRMS (DART) calcd for $[C_{31}H_{43}ClF]^{+}$ ($[M+H]^{+}$): 469.3032, found: 469.3028.



6g

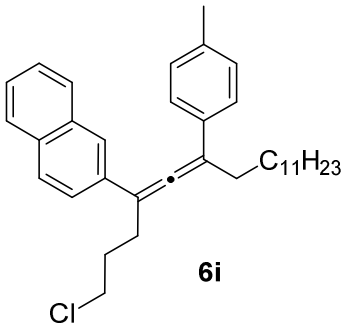
Following the general procedure **B**, **6g** was obtained as a liquid (42 mg, 43% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 – 7.33 (m, 2H), 7.32 – 7.25 (m, 4H), 7.16 – 7.11 (m, 2H), 3.61 (t, *J* = 6.4 Hz, 2H), 2.68 (t, *J* = 7.5 Hz, 2H), 2.53 (t, *J* = 7.6 Hz, 2H), 2.34 (s, 3H), 2.10 – 1.97 (m, 2H), 1.62 – 1.49 (m, 2H), 1.40 – 1.34 (m, 2H), 1.31 – 1.22 (m, 16H), 0.88 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 204.79, 137.00, 135.33, 133.35, 132.61, 129.42, 128.71, 127.15, 125.92, 110.47, 107.04, 44.92, 32.04, 30.97, 30.52, 29.81, 29.79, 29.77, 29.75, 29.63, 29.48, 28.24, 27.59, 22.82, 21.20, 14.25. HRMS (DART) calcd for $[C_{31}H_{43}Cl_2]^{+}$ ($[M+H]^{+}$): 485.2736, found: 485.2732.



6h

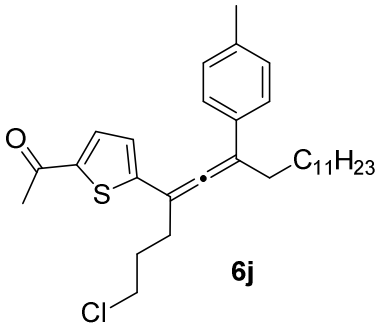
Following the general procedure **B**, **6h** was obtained as a liquid (75 mg, 77% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.36 – 7.27 (m, 3H), 7.15 (d, *J* = 7.9 Hz, 2H), 6.88 – 6.76 (m, 2H), 3.59 (t,

J = 6.5 Hz, 2H), 2.67 (d, *J* = 7.2 Hz, 2H), 2.49 (t, *J* = 7.8 Hz, 2H), 2.35 (s, 3H), 2.06 – 1.93 (m, 2H), 1.63 – 1.51 (m, 2H), 1.39 – 1.24 (m, 18H), 0.90 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 204.91, 161.93 (dd, *J* = 267.5, 11.5 Hz), 160.28 (dd, *J* = 270.9, 12.2 Hz), 136.82, 133.56, 130.26 (dd, *J* = 8.8, 5.3 Hz), 129.33, 126.07, 121.82 (dd, *J* = 12.9, 2.9 Hz), 121.82 (dd, *J* = 12.9, 2.9 Hz), 108.11, 104.47 (t, *J* = 25.9 Hz), 102.58, 44.71, 32.05, 31.11, 30.45, 29.91, 29.80, 29.77, 29.72, 29.66, 29.49, 28.12, 22.82, 21.19, 14.24. HRMS (DART) calcd for $[C_{31}H_{42}ClF_2]^+$ ($[M+H]^+$): 487.2938, found: 487.2932.



6i

Following the general procedure **B**, **6i** was obtained as a liquid (61 mg, 61% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.86 – 7.83 (m, 2H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 8.6 Hz, 1H), 7.62 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.38 – 7.36 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 3.67 (t, *J* = 6.4 Hz, 2H), 2.87 (t, *J* = 7.5 Hz, 2H), 2.61 (t, *J* = 7.2 Hz, 2H), 2.36 (s, 3H), 2.19 – 2.11 (m, 2H), 1.67 – 1.57 (m, 2H), 1.45 – 1.39 (m, 2H), 1.31 – 1.23 (m, 16H), 0.90 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 205.54, 136.88, 134.20, 133.83, 133.67, 132.64, 129.45, 129.40, 128.14, 128.03, 127.67, 126.26, 126.03, 125.98, 125.81, 125.33, 123.47, 110.33, 108.12, 45.11, 32.05, 31.14, 30.62, 29.87, 29.79, 29.76, 29.68, 29.49, 28.31, 27.63, 22.83, 21.22, 14.26. HRMS (DART) calcd for $[C_{35}H_{46}Cl]^+$ ($[M+H]^+$): 501.3283, found: 501.3278.

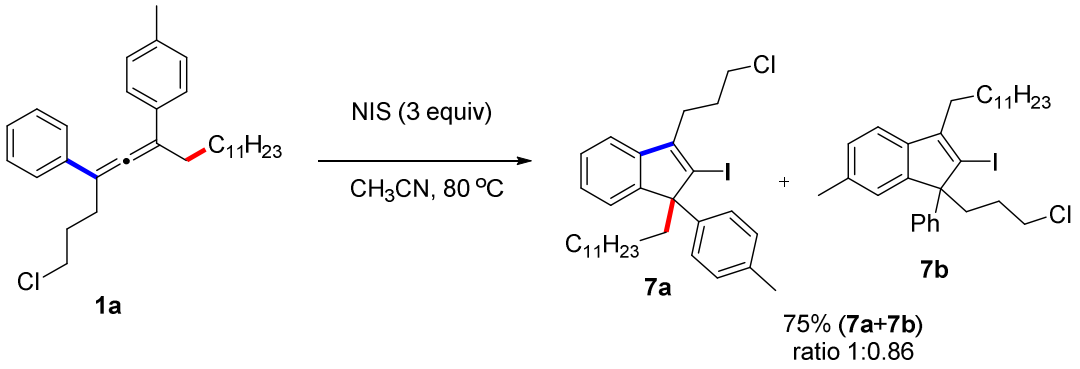


6j

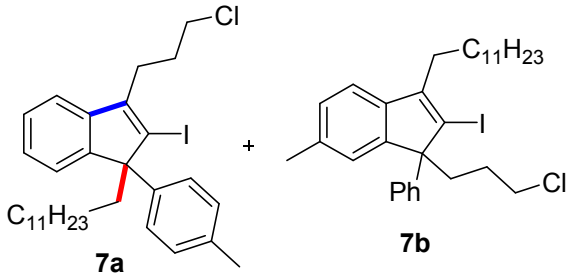
Following the general procedure **B**, **6j** was obtained as a liquid (69 mg, 69% yield). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 4.0 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 4.0 Hz, 1H), 3.59 (t, *J* = 6.4 Hz, 2H), 2.70 – 2.64 (m, 2H), 2.56 – 2.52 (m, 2H), 2.50 (s, 3H), 2.33 (s, 3H), 2.09 – 2.01 (m, 2H), 1.58 – 1.52 (m, 2H), 1.41 – 1.36 (m, 2H), 1.29 – 1.23 (m, 16H), 0.87 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 205.25, 190.63, 151.59, 142.28, 137.49, 133.38, 132.60, 129.46, 126.27, 123.62, 111.90, 103.73, 44.60, 32.03, 30.92, 30.76, 29.78, 29.76, 29.61, 29.48, 28.43, 28.13, 26.56, 22.81, 21.23, 14.24. HRMS (DART) calcd for $[C_{31}H_{44}OClS]^+$ ($[M+H]^+$): 499.2796, found: 499.2792.

Synthetic applications

a) Synthesis of indenyl iodide 7 with NIS

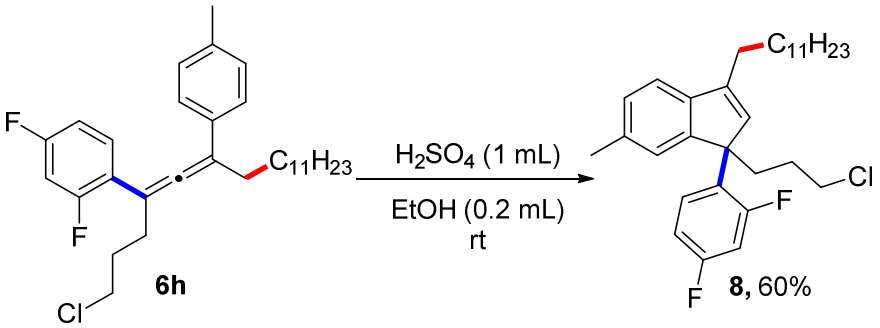


In a flame-dried Schlenk tube was charged with allene (**1a**, 0.2 mmol), NIS (0.6 mmol) and CH_3CN (1 mL). The resulting suspension was stirred at 80 °C for 10 h. Upon completion of the reaction as monitored by TLC, the solvent was concentrated under vacuum. The crude residue was purified by flash column chromatography on silica gel to give the products **7a** and **7b** as a mixture in 75% yield.

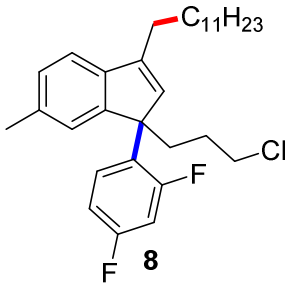


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.18 (m, 3H), 7.14 – 6.78 (m, 5H), 3.70 – 3.34 (m, 2H), 2.88 – 2.53 (m, 2H), 2.51 – 2.00 (m, 6H), 1.77 – 1.55 (m, 1H), 1.46 – 1.05 (m, 20H), 0.89 – 0.85 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 152.40, 151.95, 148.43, 146.03, 143.01, 141.73, 140.75, 138.66, 136.45, 135.74, 129.20, 128.47, 127.59, 126.90, 126.69, 126.65, 126.55, 125.82, 124.13, 123.33, 118.79, 118.74, 116.58, 112.66, 63.58, 62.88, 45.58, 44.62, 34.55, 32.01, 31.99, 31.96, 31.15, 29.92, 29.90, 29.76, 29.72, 29.71, 29.68, 29.66, 29.62, 29.60, 29.44, 29.42, 29.39, 28.16, 27.20, 26.30, 22.78, 22.70, 21.56, 21.11, 14.23. HRMS (DART) calcd for $[C_{31}H_{42}ClI]^+$ ($[M+H]^+$): 576.2014, found: 576.2008.

b) Synthesis of 1*H*-indene 8

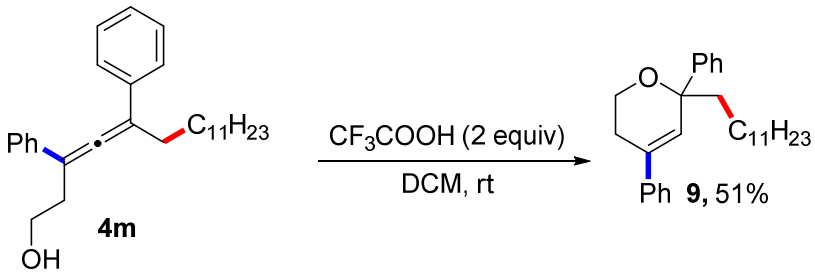


In a flame-dried Schlenk tube was charged with allene (**6i**, 0.1 mmol), H_2SO_4 (1 mL) and CH_3CH_2OH (0.2 mL). The resulting suspension was stirred at room temperature for 1 h. Upon completion of the reaction as monitored by TLC, the solvent was concentrated under vacuum. The crude residue was purified by flash column chromatography on silica gel to give the product **8** in 60% yield.

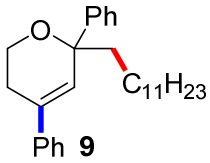


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 (s, 1H), 7.22 – 7.15 (m, 2H), 7.12 (d, *J* = 8.0 Hz, 1H), 6.85 – 6.75 (m, 1H), 6.72 – 6.60 (m, 1H), 6.25 (s, 1H), 3.40 (t, *J* = 6.7 Hz, 2H), 2.58 – 2.43 (m, 3H), 2.41 (s, 3H), 2.22 – 2.07 (m, 1H), 1.70 – 1.56 (m, 3H), 1.42 – 1.23 (m, 19H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.17 (dd, *J* = 250.2, 11.5 Hz), 161.80 (dd, *J* = 247.8, 12.3 Hz), 149.40, 143.33, 142.02, 134.14 (d, *J* = 3.0 Hz), 134.12, 129.00 (dd, *J* = 9.1, 6.7 Hz), 127.90, 125.81 (dd, *J* = 12.3, 3.8 Hz), 124.59 (d, *J* = 2.8 Hz), 119.60, 110.61 (dd, *J* = 20.3, 3.4 Hz), 104.68 (dd, *J* = 28.0, 25.0 Hz), 57.28 (d, *J* = 3.2 Hz), 45.50, 33.87, 33.81, 31.96, 29.72, 29.69, 29.67, 29.53, 29.40, 28.17, 27.90, 27.52, 22.74, 21.72, 14.17. HRMS (DART) calcd for $[C_{31}H_{42}ClF_2]^+$ ($[M+H]^+$): 487.2938, found: 487.2934.

c) Synthesis of 2*H*-pyran 9

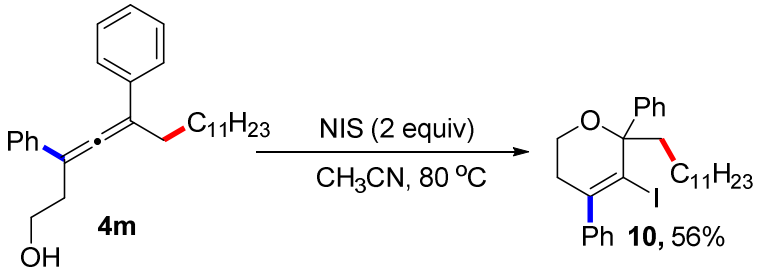


In a flame-dried Schlenk tube was charged with allene (**4m**, 0.1 mmol), CF_3COOH (2 equiv) and DCM (0.2 mL). The resulting suspension was stirred at room temperature for 1 h. Upon completion of the reaction as monitored by TLC, the solvent was concentrated under vacuum. The crude residue was purified by flash column chromatography on silica gel to give the product **9** in 51% yield.

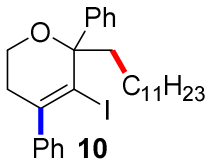


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 7.3 Hz, 4H), 7.33 – 7.24 (m, 4H), 7.24 – 7.20 (m, 1H), 7.20 – 7.15 (m, 1H), 6.44 (s, 1H), 3.99 – 3.86 (m, 1H), 3.57 (td, *J* = 11.1, 3.6 Hz, 1H), 2.75 – 2.56 (m, 1H), 2.23 – 2.14 (m, 1H), 1.87 – 1.66 (m, 2H), 1.24 – 1.12 (m, 20H), 0.80 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 145.95, 140.62, 134.90, 128.48, 128.21, 127.46, 126.74, 126.19, 125.10, 78.34, 60.47, 43.98, 31.95, 30.03, 29.67, 29.60, 29.39, 27.25, 23.90, 22.73, 14.17. HRMS (DART) calcd for $[C_{29}H_{41}O]^+$ ($[M+H]^+$): 405.3152, found: 405.3149.

d) Synthesis of 2*H*-pyran 10



In a flame-dried Schlenk tube was charged with allene (**4m**, 0.1 mmol), NIS (2 equiv) and CH_3CN (0.2 mL). The resulting suspension was stirred at room temperature for 10 h. Upon completion of the reaction as monitored by TLC, the solvent was concentrated under vacuum. The crude residue was purified by flash column chromatography on silica gel to give the product **10** in 56% yield.

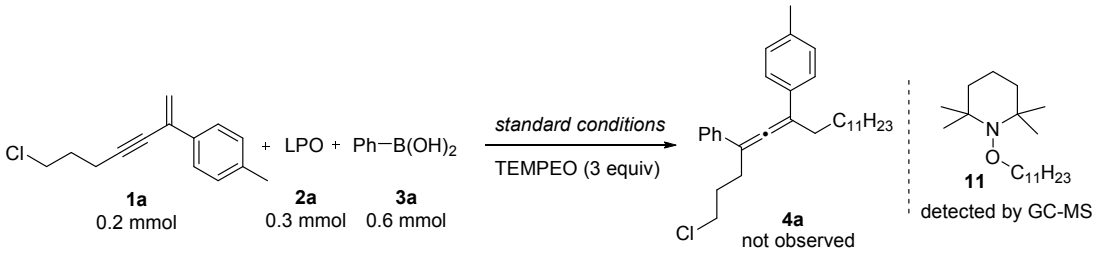


10

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.60 (m, 2H), 7.44 – 7.31 (m, 6H), 7.25 – 7.20 (m, 2H), 3.78 – 3.68 (m, 1H), 3.67 – 3.58 (m, 1H), 2.88 – 2.74 (m, 1H), 2.43 – 2.33 (m, 2H), 2.27 – 2.18 (m, 1H), 1.76 – 1.63 (m, 1H), 1.61 – 1.50 (m, 1H), 1.42 – 1.26 (m, 18H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 146.25, 146.24, 142.31, 128.50, 128.33, 128.00, 127.85, 127.80, 127.56, 105.63, 81.80, 58.73, 40.83, 35.03, 31.98, 30.00, 29.79, 29.76, 29.74, 29.72, 29.69, 29.42, 23.36, 22.75, 14.19. HRMS (DART) calcd for $[C_{29}H_{40}OI]^{+}$ ($[M+H]^{+}$): 531.2118, found: 531.2114.

Preliminary mechanism study

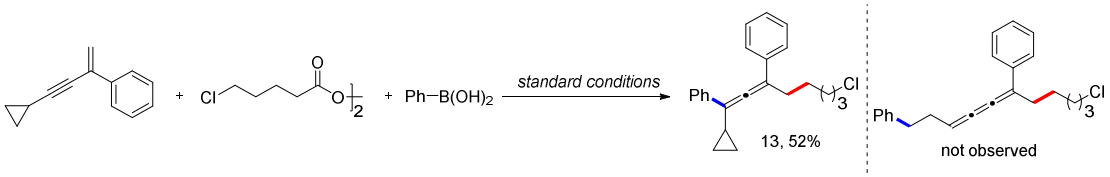
a) Radical trapping experiment



In a flame-dried Schlenk tube, $Cu(CH_3CN)_4BF_4$ (0.01 mmol, 5 mol %) and Py-Box ligand **(±)-L16** (0.014 mmol, 7 mol %) were dissolved in THF (1 mL) under a nitrogen atmosphere, and the mixture was stirred at room temperature for 30 minutes. Then 1,3-enyne (0.2 mmol, 1.0 equiv), peroxide (0.3 mmol, 1.5 equiv), $PhB(OH)_2$ (0.6 mmol, 3 equiv), DIPEA (0.6 mmol, 3 equiv) and TEMPO (3 mmol) were sequentially added. The reaction mixture was stirred at rt for 5 hours. The solution was filtrated with ethyl acetate on silica gel, and then detected by GC-MS. No desired coupling product was detected, but compound **11** was detected by GC-MS analysis.

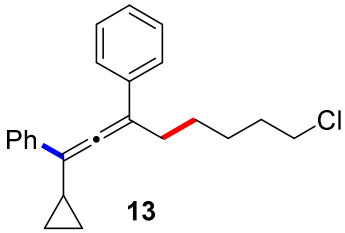
b) Radical clock experiments

Ring-opening reaction:



In a flame-dried Schlenk tube, $Cu(CH_3CN)_4BF_4$ (0.01 mmol, 5 mol %) and Py-Box ligand **(±)-L16** (0.014 mmol, 7 mol %) were dissolved in THF (1 mL) under a nitrogen atmosphere, and the mixture was stirred at room temperature for 30 minutes. Then 1,3-enyne **12** (0.2 mmol, 1.0 equiv), peroxide **2e** (0.3 mmol, 1.5 equiv), $PhB(OH)_2$ (0.6 mmol, 3 equiv) and DIPEA (0.6 mmol, 3 equiv) were sequentially added. The reaction mixture was stirred at rt for 5 hours. Upon completion of the reaction as monitored by TLC, the solvent was concentrated under vacuum. The crude residue was purified by flash column chromatography on silica gel to give the product **13** in

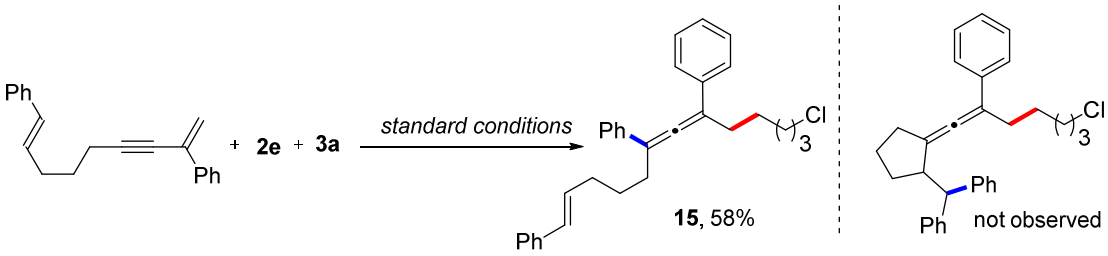
52% yield.



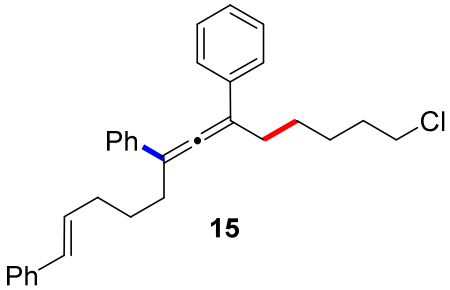
13

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 7.7 Hz, 2H), 7.46 – 7.26 (m, 6H), 7.26 – 7.17 (m, 2H), 3.46 (t, *J* = 6.7 Hz, 2H), 2.55 (t, *J* = 6.8 Hz, 2H), 1.82 – 1.67 (m, 3H), 1.59 – 1.49 (m, 4H), 0.89 – 0.85 (m, 2H), 0.64 – 0.40 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.22, 137.23, 136.54, 128.54, 128.44, 126.95, 126.93, 126.17, 125.80, 112.60, 110.03, 45.10, 32.56, 30.09, 27.28, 26.90, 11.33, 6.96, 6.90. HRMS (DART) calcd for $[C_{23}H_{26}Cl]^+$ ($[M+H]^+$): 337.1718, found: 337.1715.

Ring closing reaction

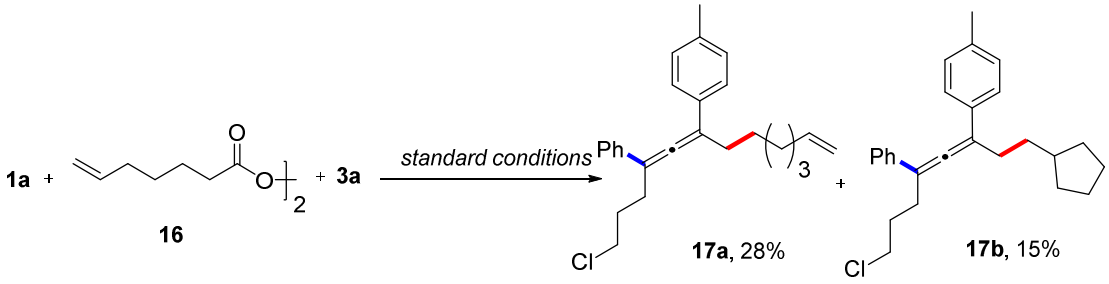


In a flame-dried Schlenk tube, $Cu(CH_3CN)_4BF_4$ (0.01 mmol, 5 mol %) and Py-Box ligand **(±)-L16** (0.014 mmol, 7 mol %) were dissolved in THF (1 mL) under a nitrogen atmosphere, and the mixture was stirred at room temperature for 30 minutes. Then 1,3-enyne **14** (0.2 mmol, 1.0 equiv), peroxide **2e** (0.3 mmol, 1.5 equiv), $PhB(OH)_2$ (0.6 mmol, 3 equiv) and DIPEA (0.6 mmol, 3 equiv) were sequentially added. The reaction mixture was stirred at rt for 5 hours. Upon completion of the reaction as monitored by TLC, the solvent was concentrated under vacuum. The crude residue was purified by flash column chromatography on silica gel to give the product **15** in 58% yield.

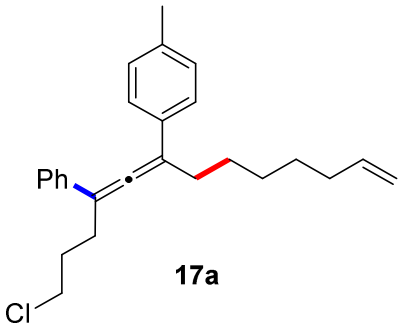


15

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.41 (m, 4H), 7.34 – 7.15 (m, 11H), 6.32 (d, *J* = 15.9 Hz, 1H), 6.20 (dt, *J* = 15.8, 6.8 Hz, 1H), 3.43 (t, *J* = 6.7 Hz, 2H), 2.67 – 2.53 (m, 4H), 2.30 (q, *J* = 6.9 Hz, 2H), 1.82 – 1.69 (m, 4H), 1.65 – 1.47 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 205.21, 137.78, 136.86, 136.82, 130.50, 130.33, 128.61, 128.58, 128.56, 126.95, 126.92, 126.01, 125.97, 109.21, 109.12, 45.16, 33.07, 32.61, 30.26, 29.90, 27.92, 27.45, 27.03. HRMS (DART) calcd for $[C_{31}H_{34}Cl]^+$ ($[M+H]^+$): 441.2344, found: 441.2340.

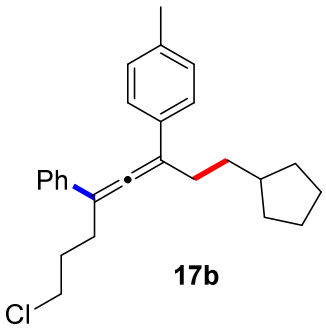


In a flame-dried Schlenk tube, $Cu(CH_3CN)_4BF_4$ (0.01 mmol, 5 mol %) and Py-Box ligand **(±)-L16** (0.014 mmol, 7 mol %) were dissolved in THF (1 mL) under a nitrogen atmosphere, and the mixture was stirred at room temperature for 30 minutes. Then 1,3-enyne **1a** (0.2 mmol, 1.0 equiv), peroxide **16** (0.3 mmol, 1.5 equiv), $PhB(OH)_2$ (0.6 mmol, 3 equiv) and DIPEA (0.6 mmol, 3 equiv) were sequentially added. The reaction mixture was stirred at rt for 5 hours. Upon completion of the reaction as monitored by TLC, the solvent was concentrated under vacuum. The crude residue was purified by flash column chromatography on silica gel to give the products **17a** and **17b** in 28% and 15% yields.



17a

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.41 (m, 2H), 7.35 – 7.28 (m, 4H), 7.24 – 7.19 (m, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 5.85 – 5.68 (m, 1H), 5.02 – 4.85 (m, 2H), 3.61 (t, *J* = 6.4 Hz, 2H), 2.70 (t, *J* = 7.4 Hz, 2H), 2.53 (t, *J* = 7.6 Hz, 2H), 2.33 (s, 3H), 2.11 – 1.96 (m, 4H), 1.62 – 1.56 (m, 2H), 1.45 – 1.36 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.66, 139.07, 136.73, 136.64, 133.53, 129.28, 128.54, 126.87, 125.83, 114.29, 109.84, 107.74, 44.98, 33.82, 30.98, 30.42, 29.23, 28.81, 28.01, 27.53, 21.13. HRMS (EI+) calcd for $[C_{26}H_{31}Cl]^+$ ($[M]^+$): 378.2114, found: 378.2108.

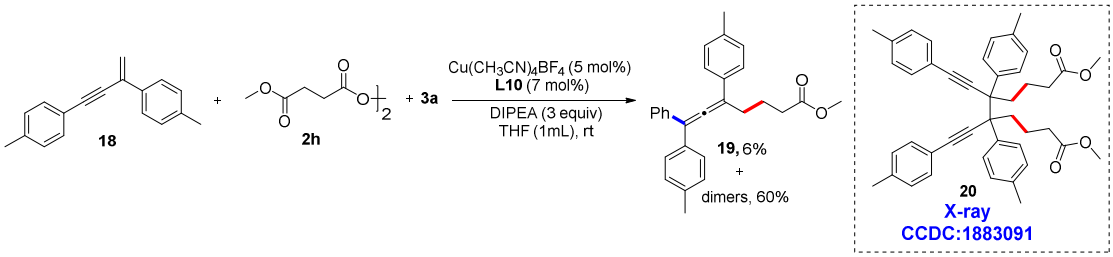


17b

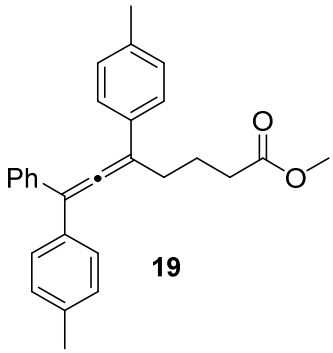
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.39 (m, 2H), 7.37 – 7.26 (m, 4H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 3.61 (t, *J* = 6.4 Hz, 2H), 2.71 (t, *J* = 7.5 Hz, 2H), 2.60 – 2.44 (m, 2H), 2.33 (s, 3H), 2.11 – 1.99 (m, 2H), 1.90 – 1.70 (m, 3H), 1.58 (td, *J* = 11.4, 10.3, 3.3 Hz, 4H),

1.53 – 1.40 (m, 2H), 1.17 – 1.03 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.65, 136.70, 133.56, 129.27, 128.52, 126.83, 125.84, 125.82, 110.02, 107.60, 44.99, 40.21, 34.58, 32.73, 32.67, 30.97, 29.74, 27.51, 25.20, 21.13. HRMS (EI+) calcd for $[C_{26}H_{31}Cl]^+$ ($[M]^+$): 378.2114, found: 378.2110.

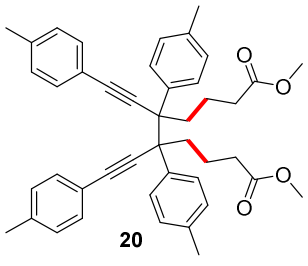
c) Radical dimerization



In a flame-dried Schlenk tube, $Cu(CH_3CN)_4BF_4$ (0.01 mmol, 5 mol%) and Py-Box ligand **L10** (0.014 mmol, 7 mol%) were dissolved in THF (1 mL) under a nitrogen atmosphere, and the mixture was stirred at room temperature for 30 minutes. Then 1,3-enyne **18** (0.2 mmol, 1.0 equiv), peroxide **2h** (0.3 mmol, 1.5 equiv), $PhB(OH)_2$ (0.6 mmol, 3 equiv) and DIPEA (0.6 mmol, 3 equiv) were sequentially added. The reaction mixture was stirred at rt for 5 h. Upon completion of the reaction as monitored by TLC, the solvent was concentrated under vacuum. The crude residue was purified by flash column chromatography on silica gel to give the products **19** in 28% yields, and a mixture of homocoupling dimers in 60% yield.



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.27 (m, 4H), 7.29 – 7.15 (m, 6H), 7.06 (dd, *J* = 8.1, 4.1 Hz, 4H), 3.55 (s, 3H), 2.57 (t, *J* = 7.6 Hz, 2H), 2.34 – 2.21 (m, 8H), 2.02 – 1.83 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 206.46, 173.96, 137.10, 137.03, 136.93, 133.84, 132.97, 129.35, 129.19, 128.43, 128.32, 128.22, 127.25, 125.92, 113.07, 108.06, 51.55, 33.70, 29.83, 23.27, 21.23, 21.16. HRMS (ESI) calcd for $[C_{28}H_{28}O_2Na]^+$ ($[M+Na]^+$): 419.1982, found: 419.1981.



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 7.8 Hz, 4H), 7.36 (d, *J* = 7.9 Hz, 4H), 7.14 (t, *J* = 8.9 Hz, 8H), 3.54 (s, 6H), 2.60 – 2.44 (m, 2H), 2.37 (s, 6H), 2.36 (s, 6H), 2.24 – 2.14 (m, 4H), 1.65 – 1.57 (m, 4H), 1.43 – 1.32 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.99, 137.97, 136.52, 136.00, 131.32, 129.08, 127.80, 120.65, 91.79, 87.88, 54.69, 51.36, 35.65, 34.31, 21.52, 21.12, 21.07. HRMS (ESI) calcd for $[C_{44}H_{46}O_4Na]^+$ ($[M+Na]^+$): 661.3288, found: 661.3289.

Single crystal data of 20

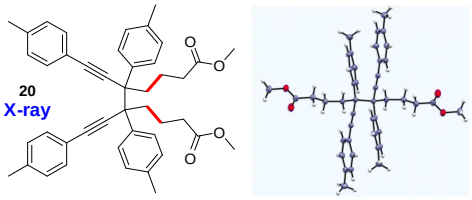


Table S2. Crystal data and structure refinement for data.

Identification code	Compound-20	
Empirical formula	C44 H46 O4	
Formula weight	638.81	
Temperature	99.99(10) K	
Wavelength	1.3405 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.8484(4) Å	α= 76.980(4)°.
	b = 11.0591(5) Å	β= 84.293(3)°.
	c = 15.2489(6) Å	γ = 86.909(3)°.
Volume	1772.66(13) Å^3	
Z	2	
Density (calculated)	1.197 Mg/m^3	
Absorption coefficient	0.374 mm^{-1}	
F(000)	684	
Crystal size	0.15 x 0.08 x 0.07 mm^3	
Theta range for data collection	2.596 to 60.549°.	
Index ranges	-13<=h<=14, -14<=k<=14, -18<=l<=19	
Reflections collected	24617	
Independent reflections	7932 [R(int) = 0.0281]	
Completeness to theta = 53.543°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.81422	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7932 / 0 / 439	
Goodness-of-fit on F^2	1.085	

Final R indices [I>2sigma(I)]	R1 = 0.0449, wR2 = 0.1234
R indices (all data)	R1 = 0.0516, wR2 = 0.1283
Extinction coefficient	n/a
Largest diff. peak and hole	0.401 and -0.291 e.Å^{-3}

Reference

1. X.-R. Song, Y.-P. Han, Y.-F. Qiu, Z.-H. Qiu, X.-Y. Liu, P.-F. Xu, Y.-M. Liang, *Chem. Eur. J.* 2014, **20**, 12046.
2. M. Wakayama, H. Nemoto, M. Shibuya, *Tetrahedron Lett.* 1996, **37**, 5397.
3. X. Zhu, W. Deng, M. F. Chiou, C. Ye, W. Jian, Y. Zeng, Y. Jiao, L. Ge, Y. Li, X. Zhang and H. Bao, *J. Am. Chem. Soc.* 2019, **141**, 548.
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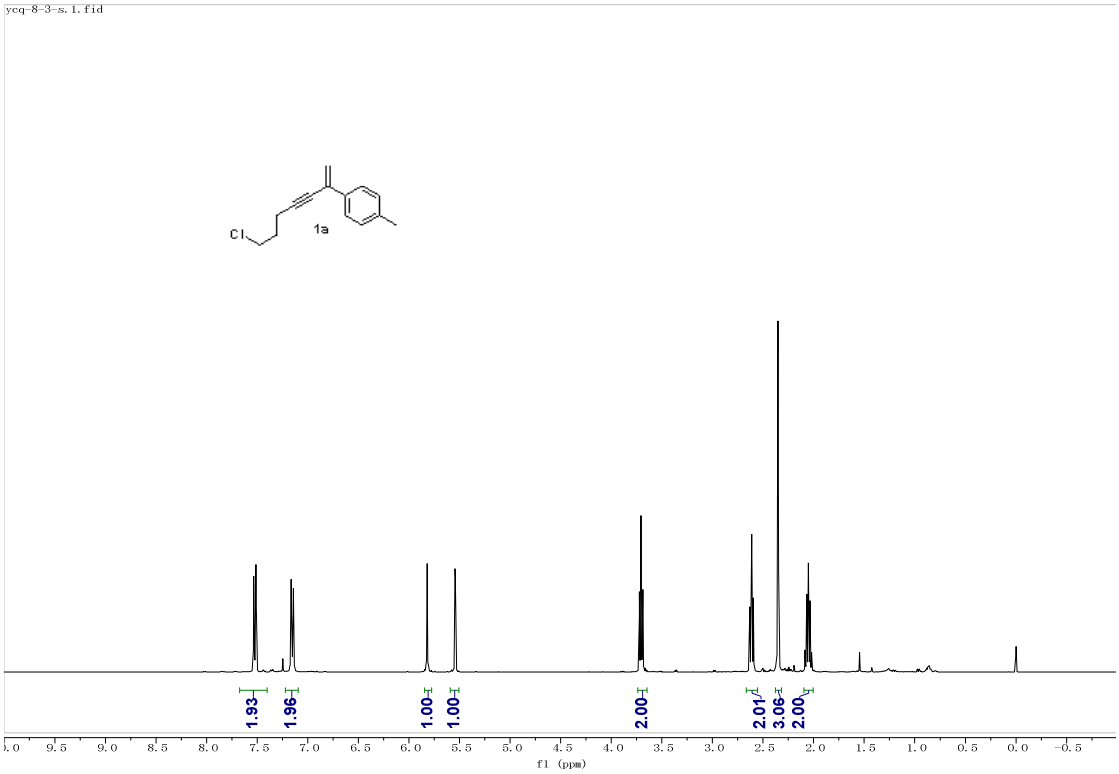
5. T. Chen, C. Guo, M. Goto and L. B. Han, *Chem. Commun.* 2013, **49**, 7498.
6. C. Ye, B. Qian, Y. Li, M. Su, D. Li and H. Bao, *Org. Lett.* 2018, **20**, 3202.
7. H. Zhou, L. Ge, J. Song, W. Jian, Y. Li, C. Li and H. Bao, *iScience*, 2018, **3**, 255.

NMR spectra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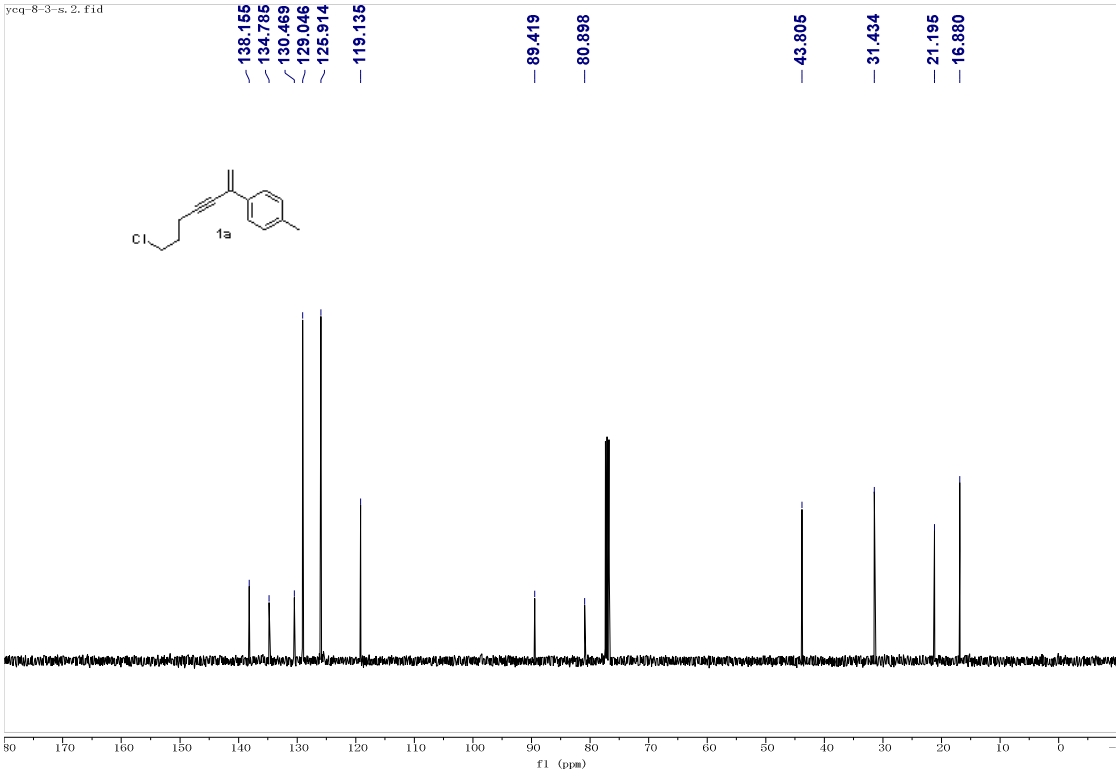
1.00
2.00
2.01
3.06
2.00
f1 (ppm)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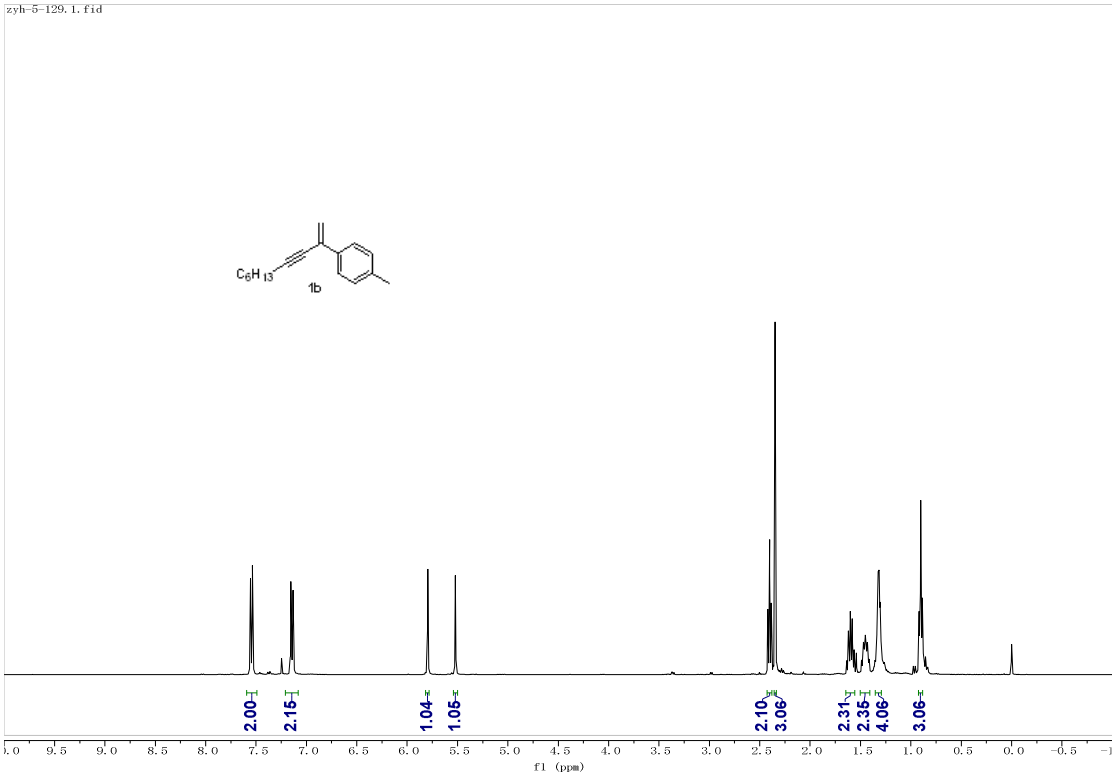
21.195
16.880
Cl
1a
f1 (ppm)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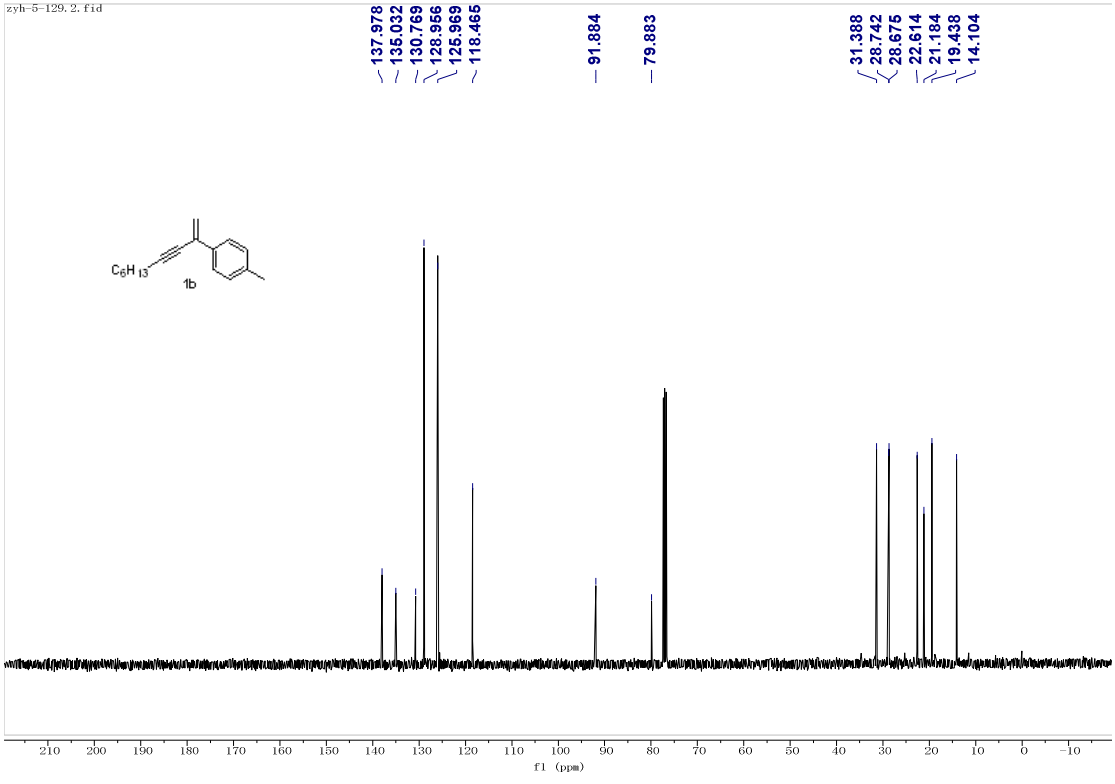
2.15
1.04
1.05
2.10
3.06
2.31
2.35
4.06
3.06
f1 (ppm)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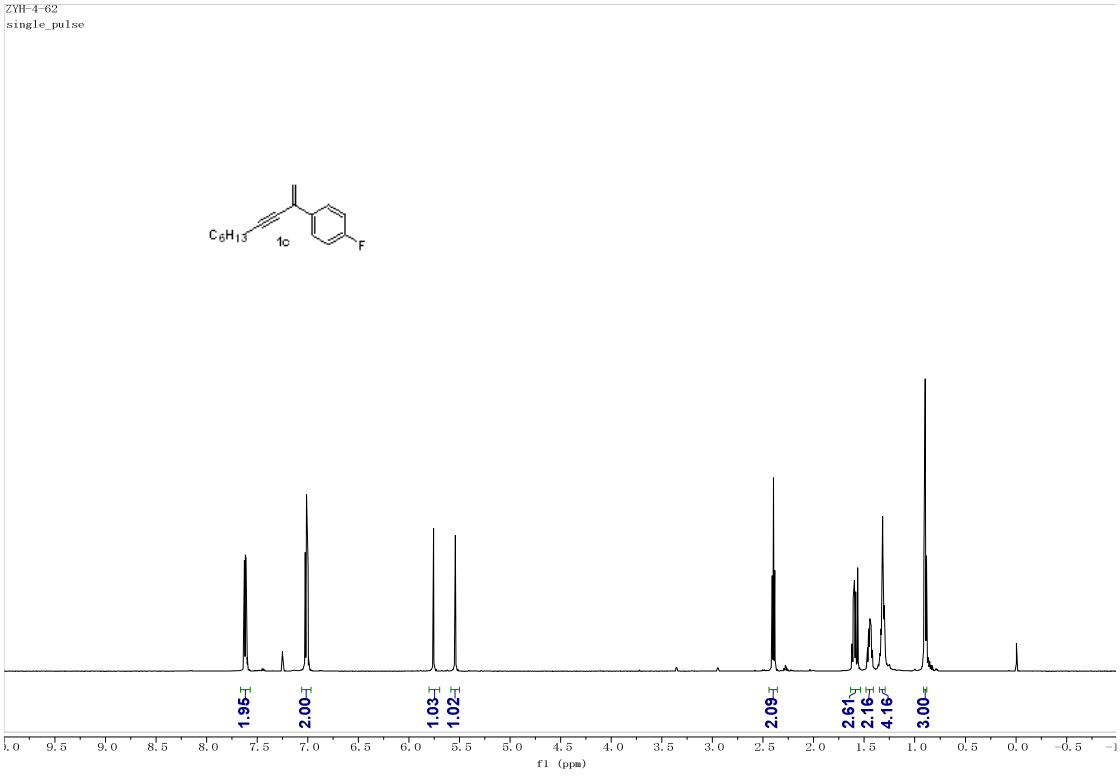
21.184
19.438
14.104
C6H13
1b
f1 (ppm)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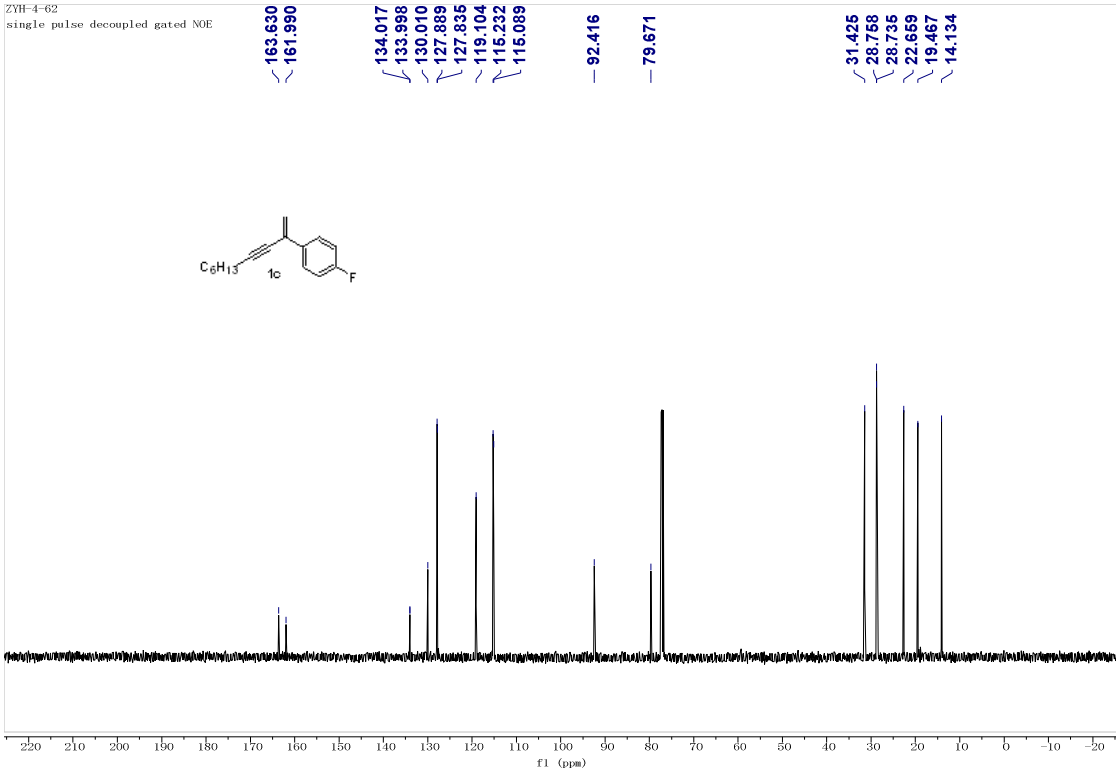
1.03
1.02
2.09
2.61
2.16
4.16
3.00
f1 (ppm)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161.990
134.017
133.998
130.010
127.889
127.835
119.104
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115.089
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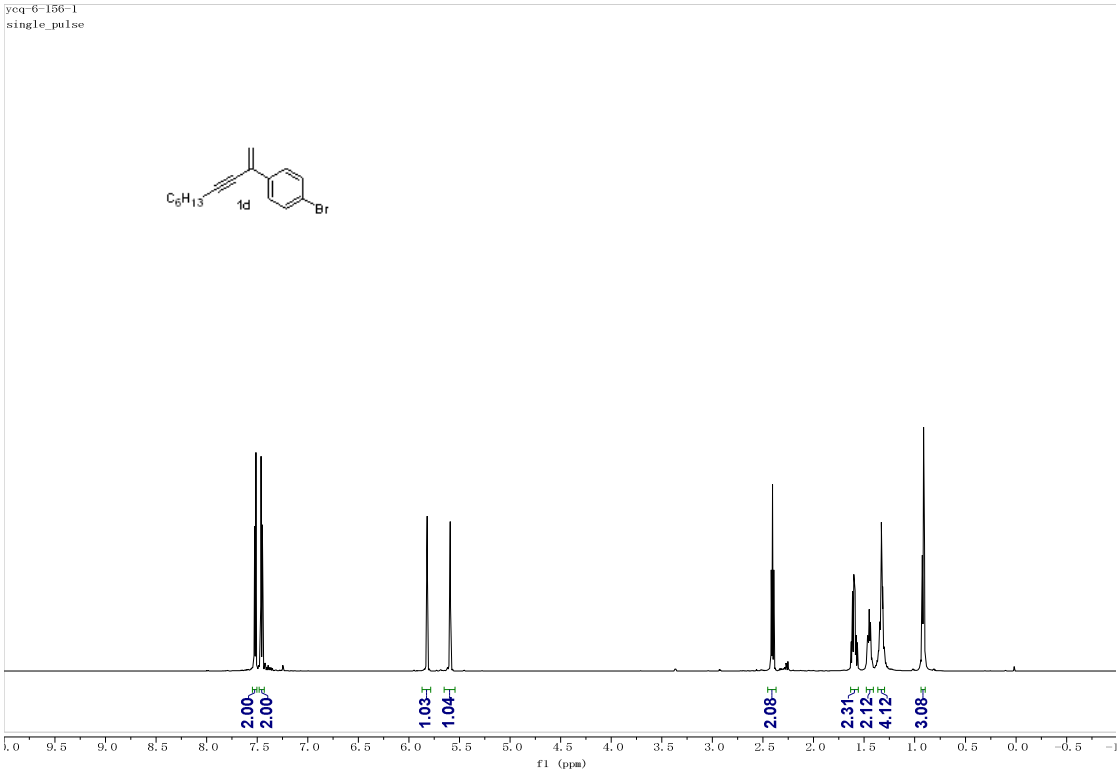
14.134
C6H13
1c
F
f1 (ppm)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1d
Br
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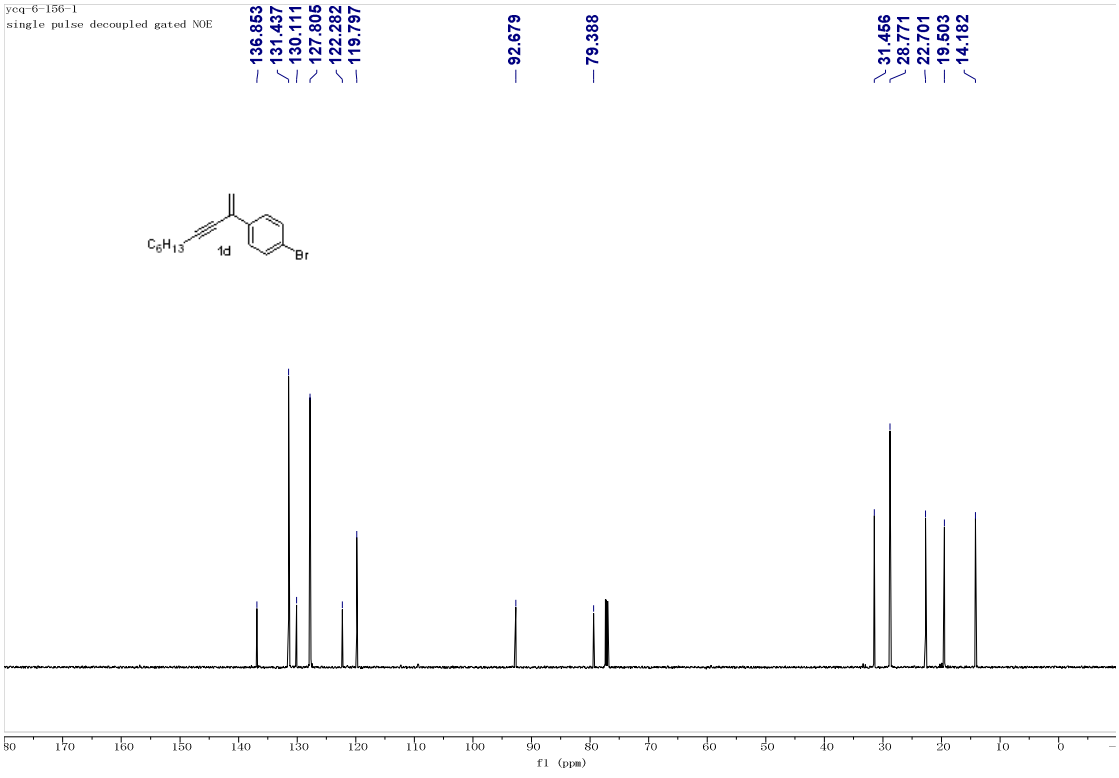
2.00
1.03
1.04
2.08
2.31
2.12
4.12
3.08
f1 (ppm)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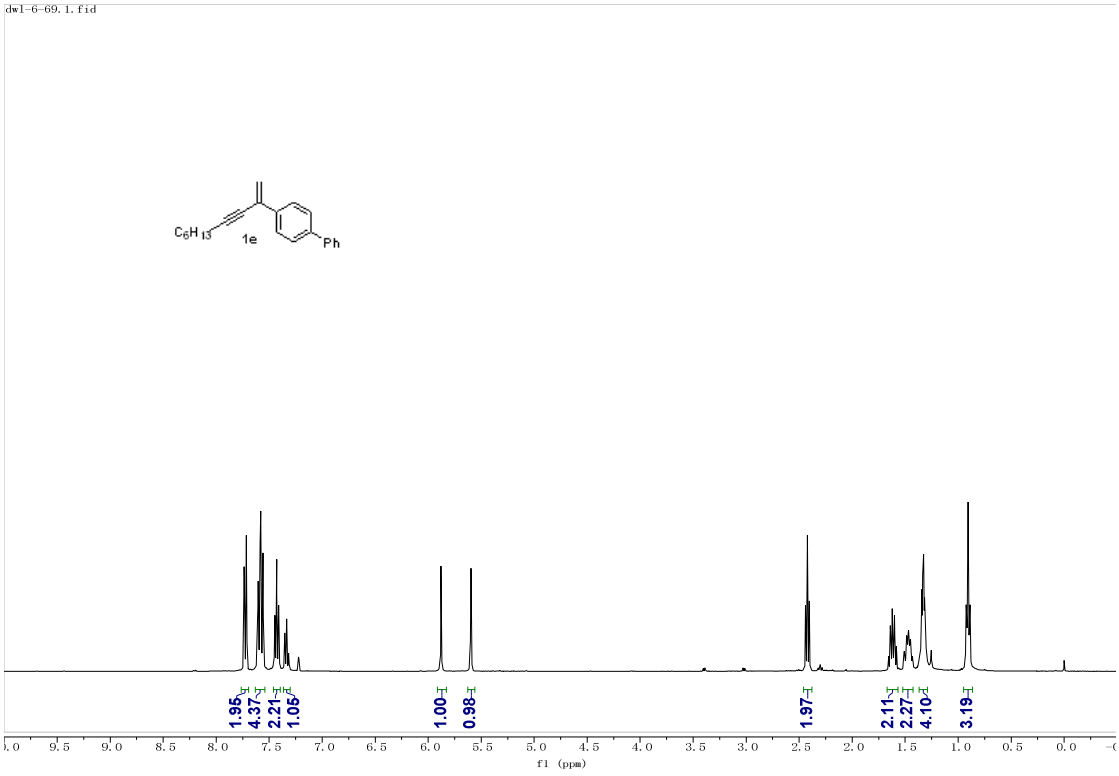
31.456
28.771
22.701
19.503
14.182
C_6H_{13}
1d
Br
f1 (ppm)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1e
Ph
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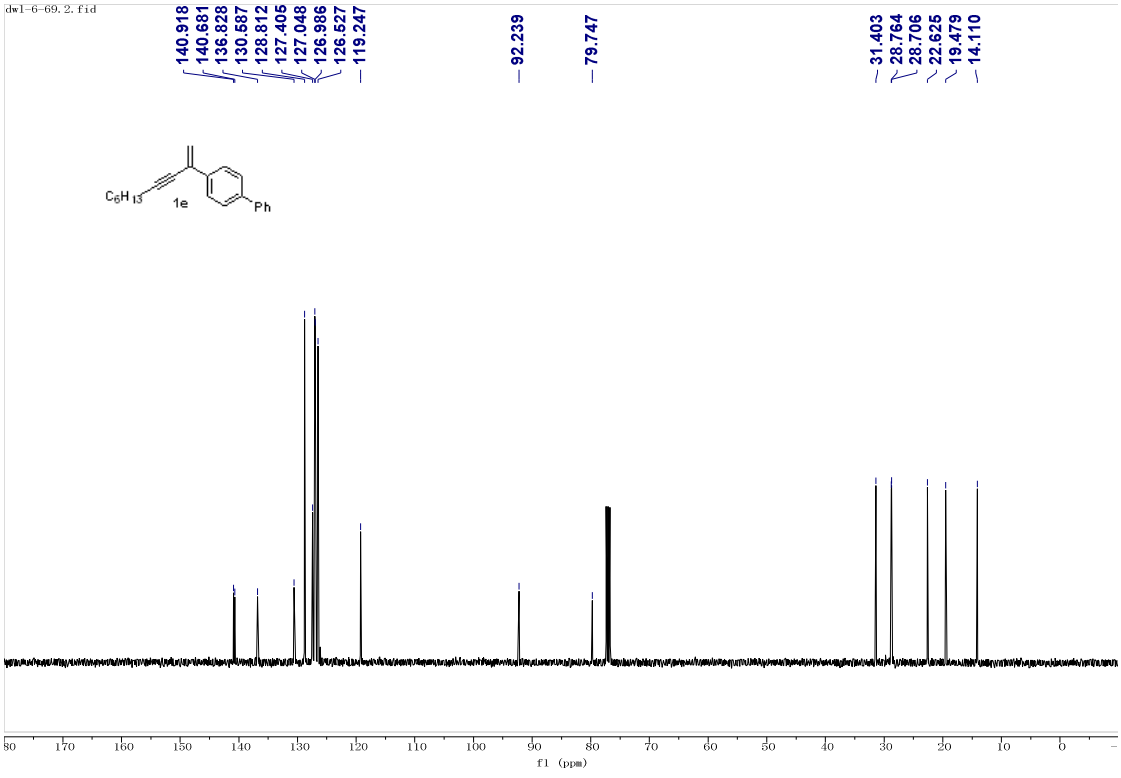
2.21
1.05
1.00
0.98
1.97
2.11
2.27
4.10
3.19
f1 (ppm)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130.587
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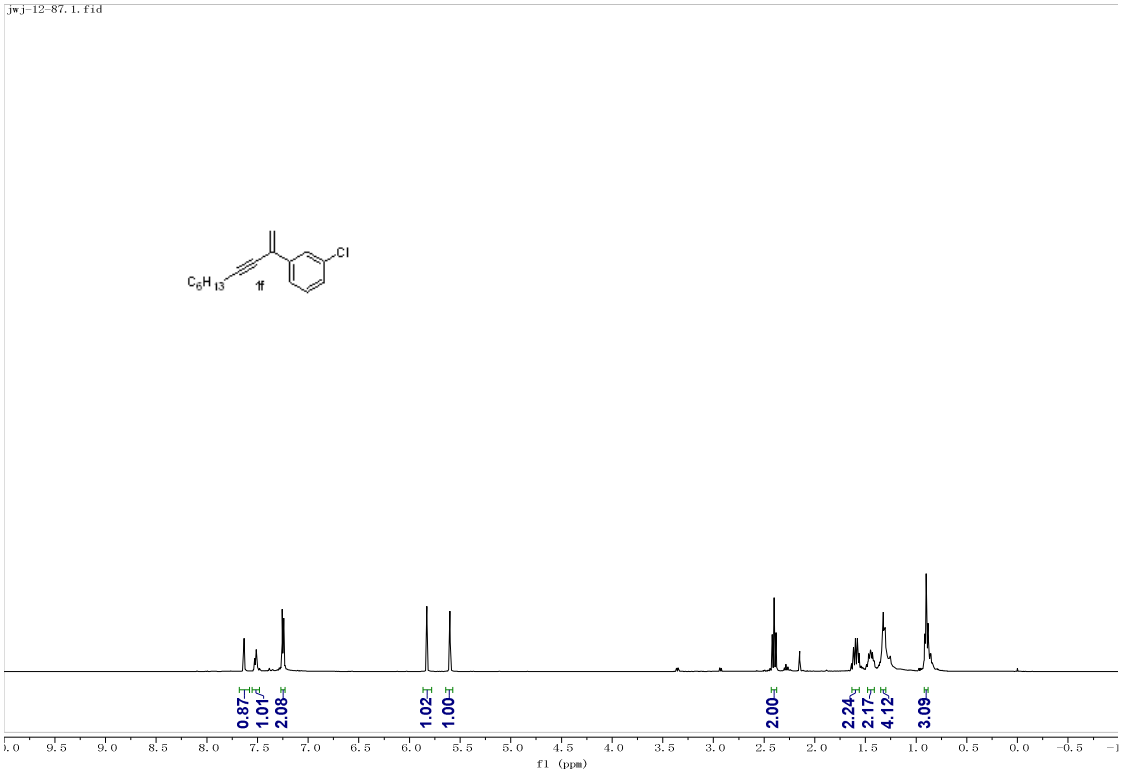
126.986
126.527
119.247
92.239
79.747
31.403
28.764
28.706
22.625
19.479
14.110
C6H13
1e
Ph
f1 (ppm)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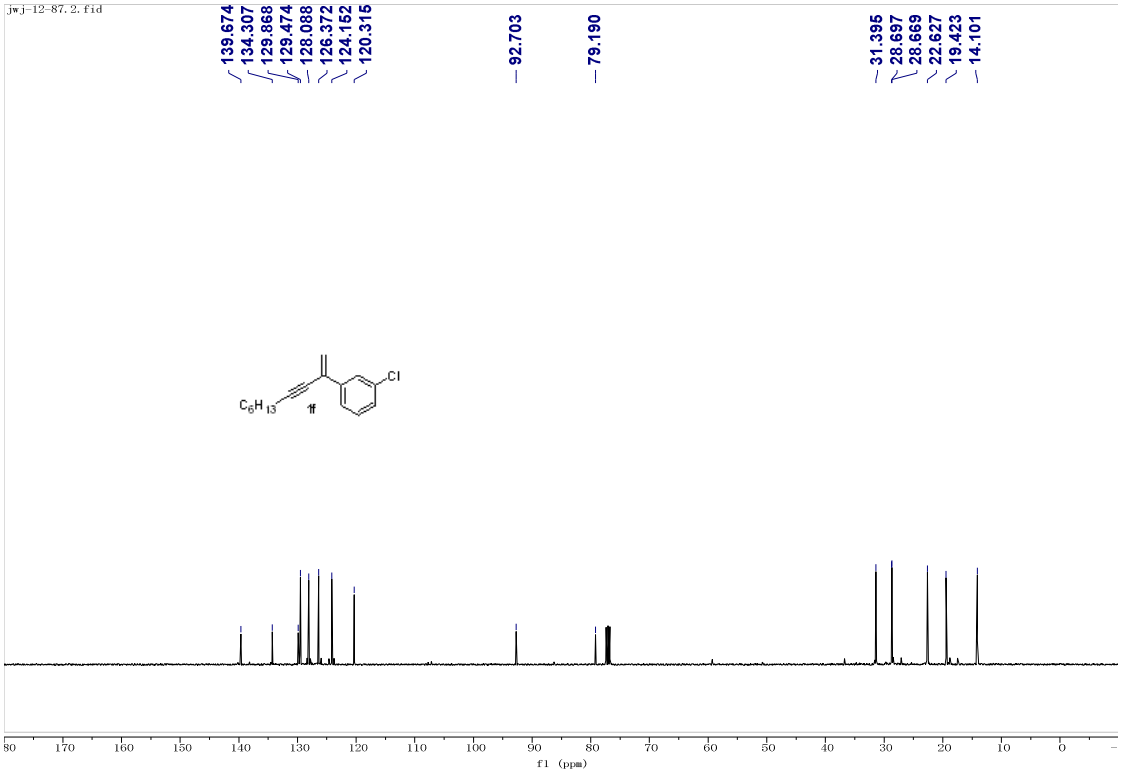
1.00
2.00
2.24
2.17
4.12
3.09
f1 (ppm)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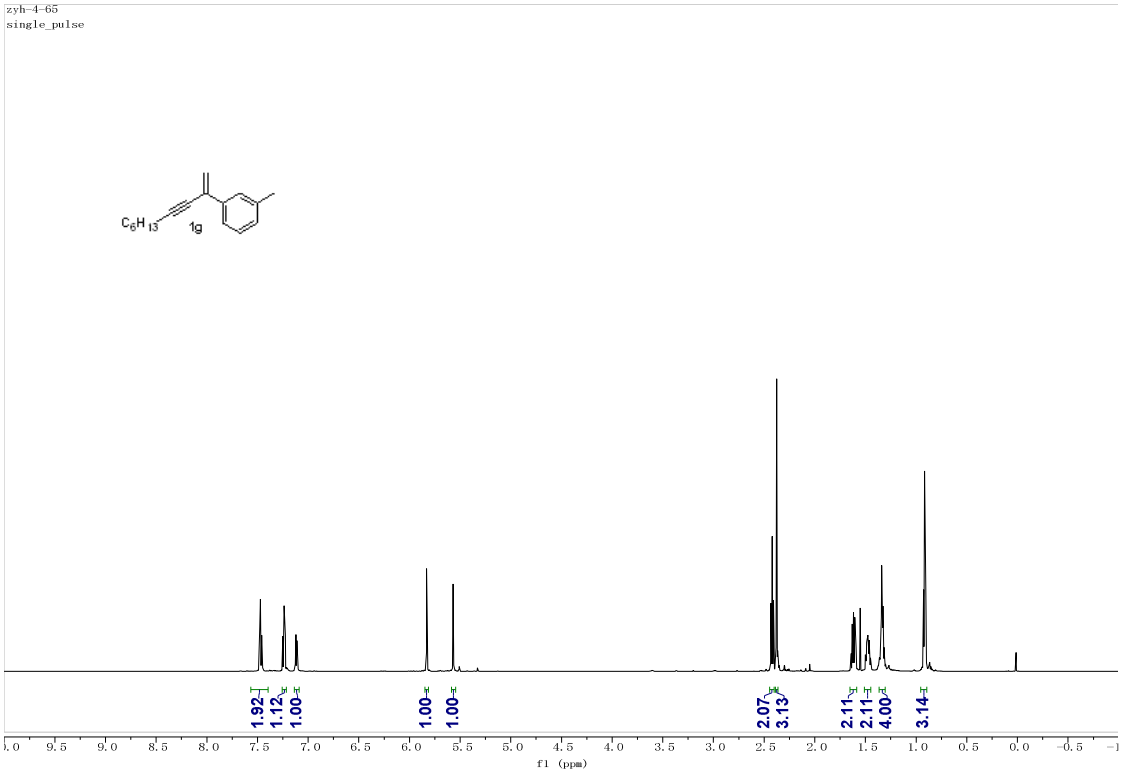
14.101
Cl
C_6H_{13}
1f
f1 (ppm)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C6H13
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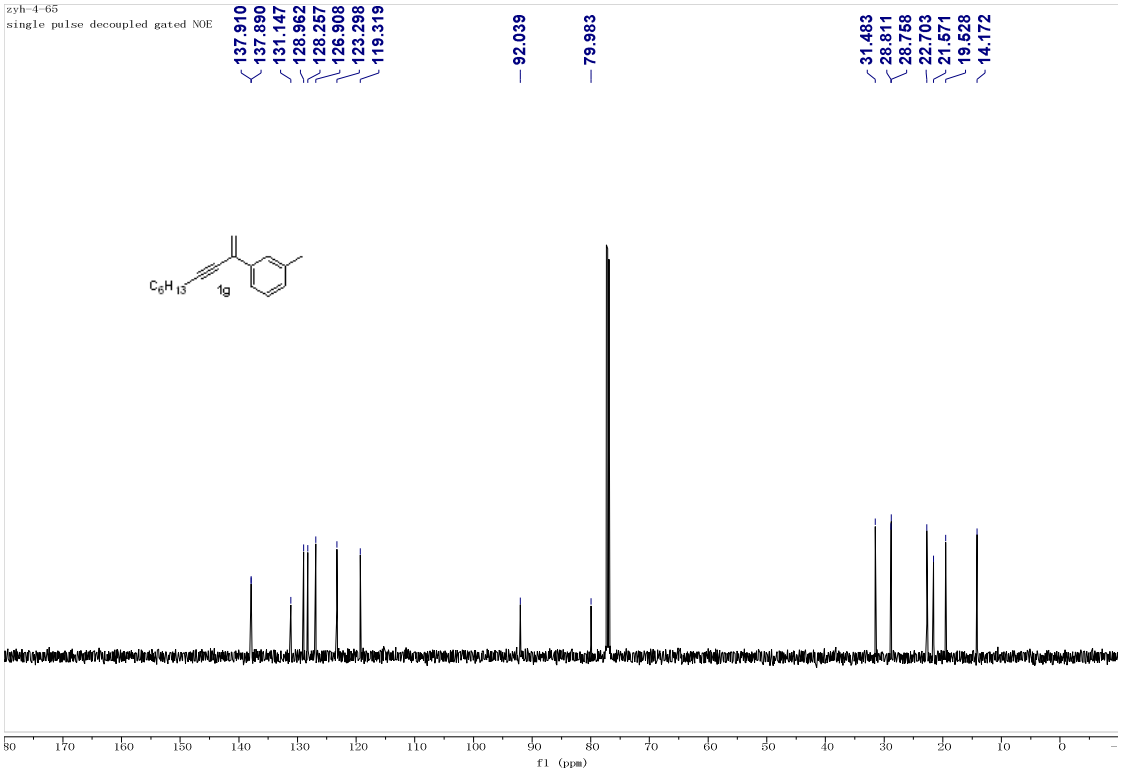
1.00
1.00
2.07
3.13
2.11
2.11
4.00
3.14
f1 (ppm)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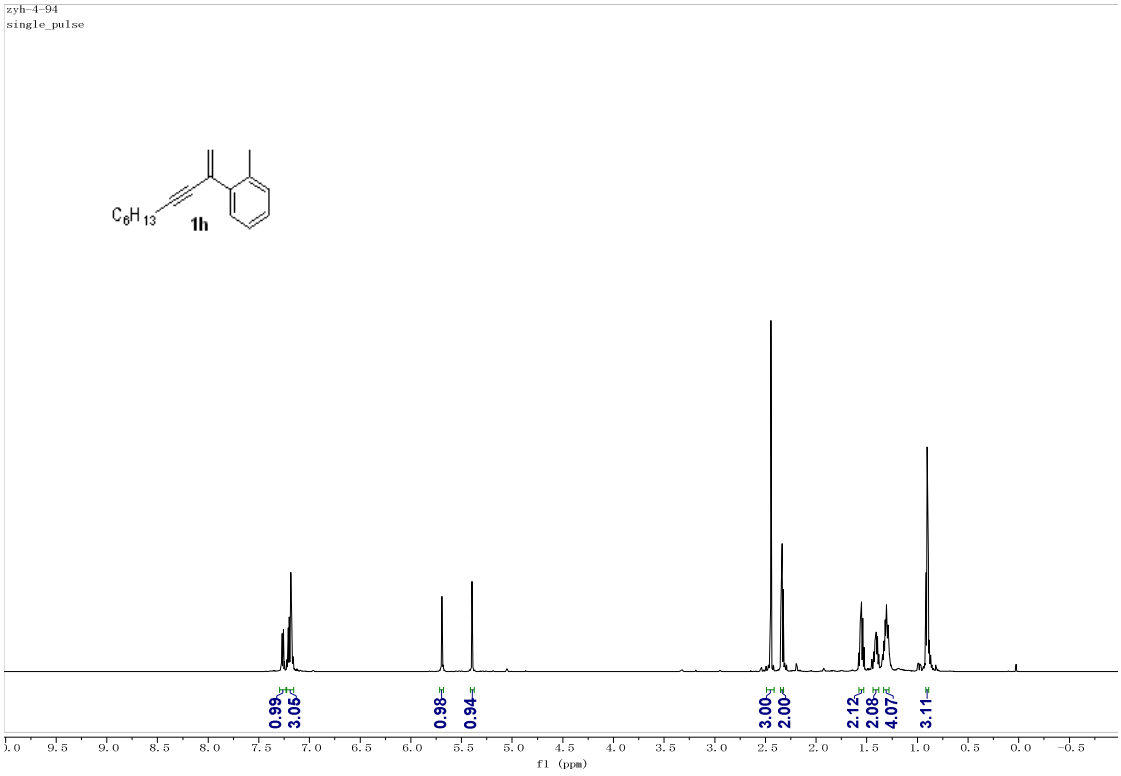
1g
f1 (ppm)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0.94
3.00
2.00
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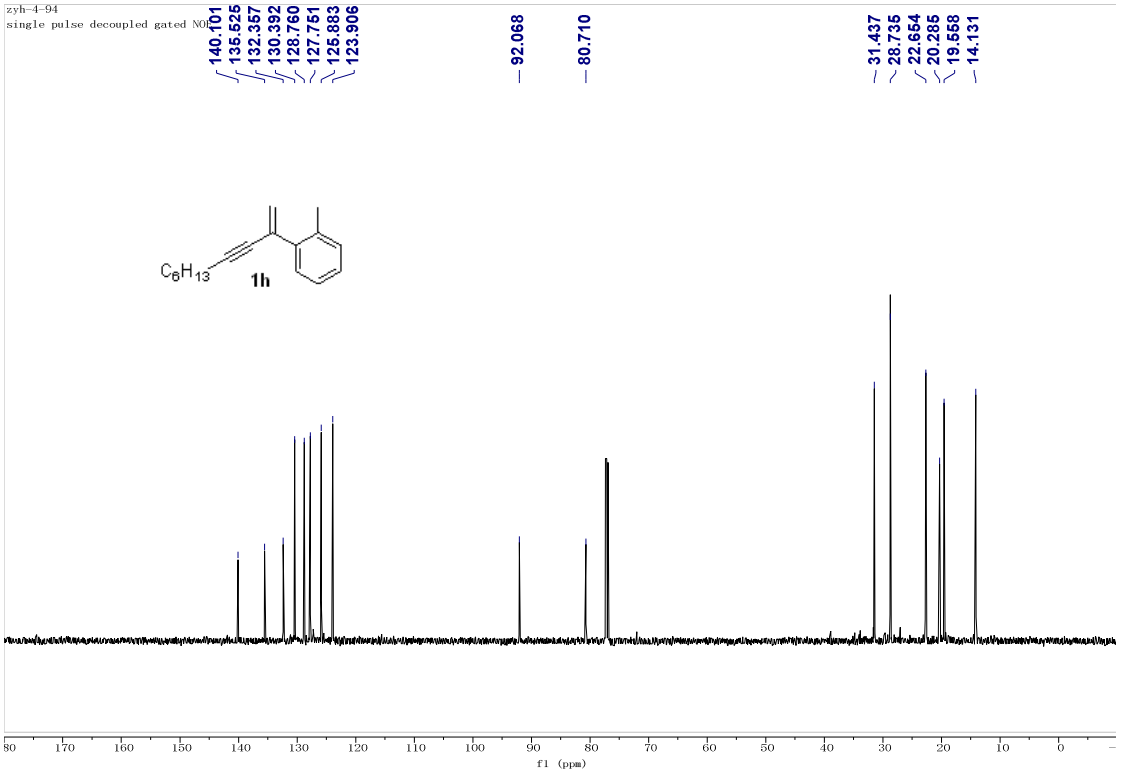
2.08
4.07
3.11
f1 (ppm)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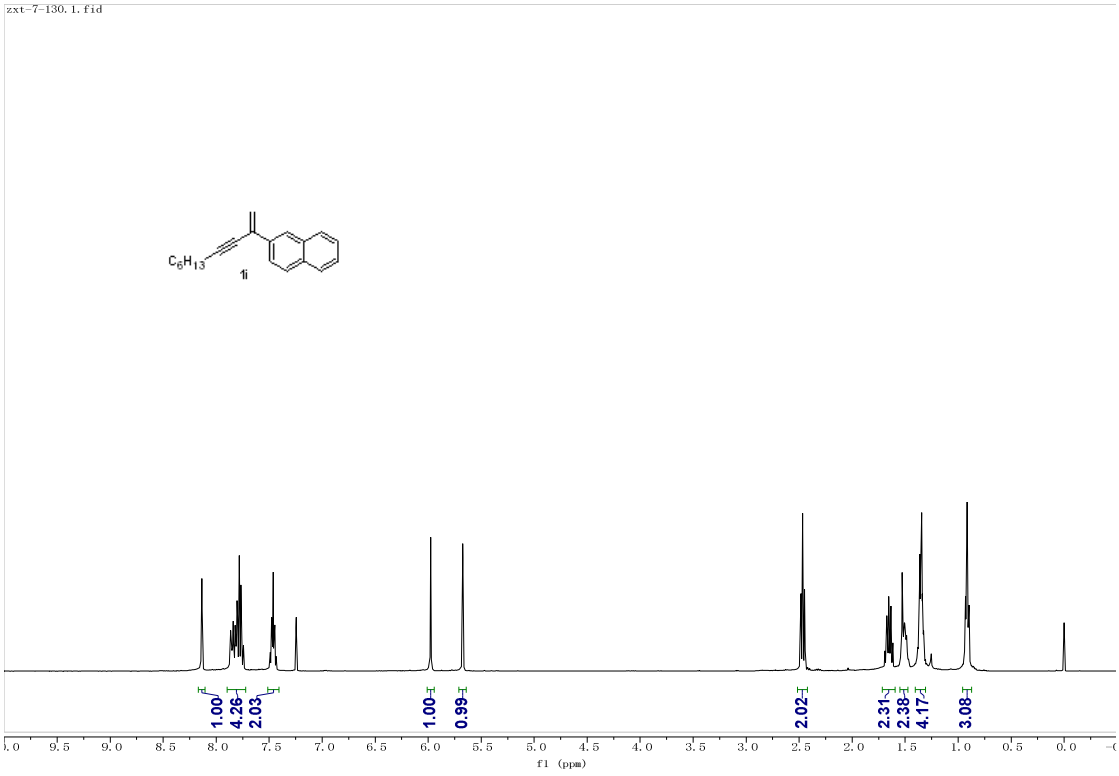
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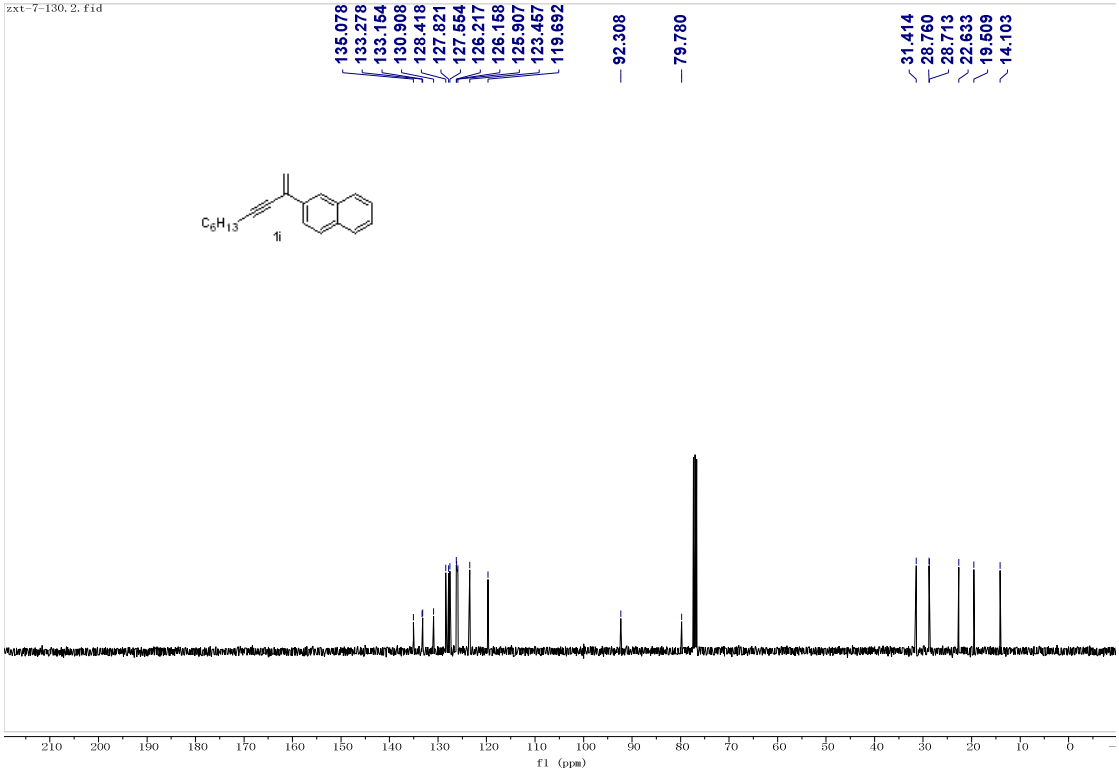
f1 (ppm)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123.457
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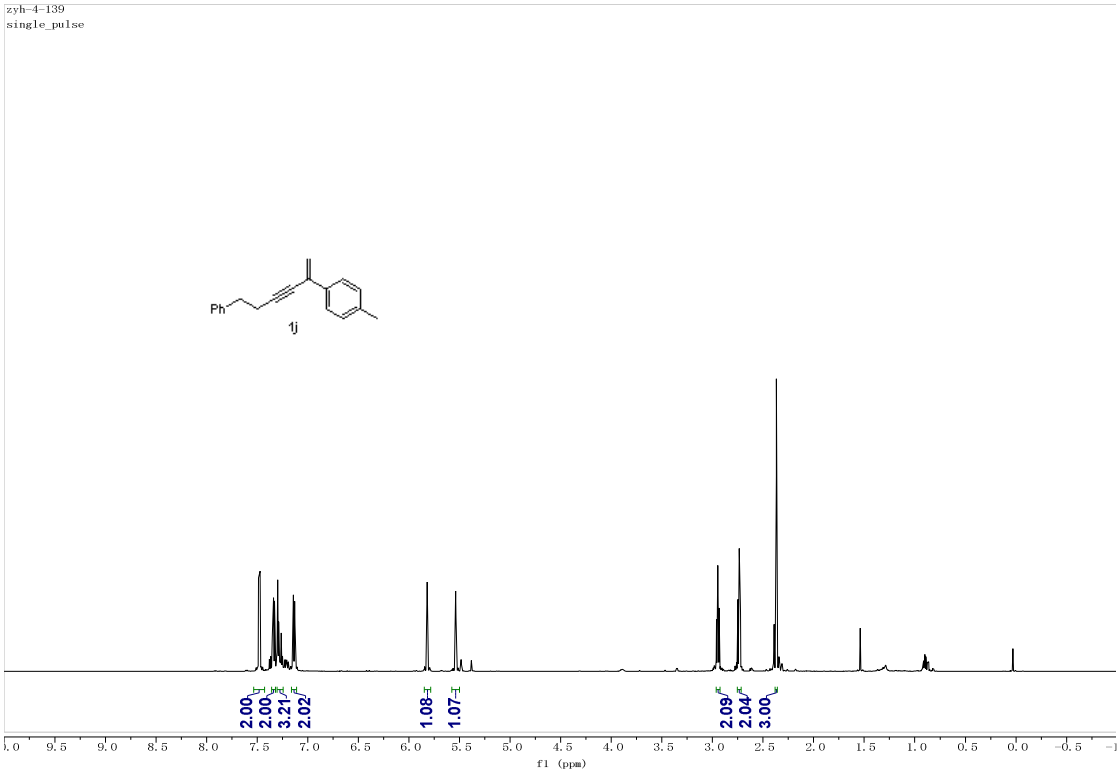
1i
f1 (ppm)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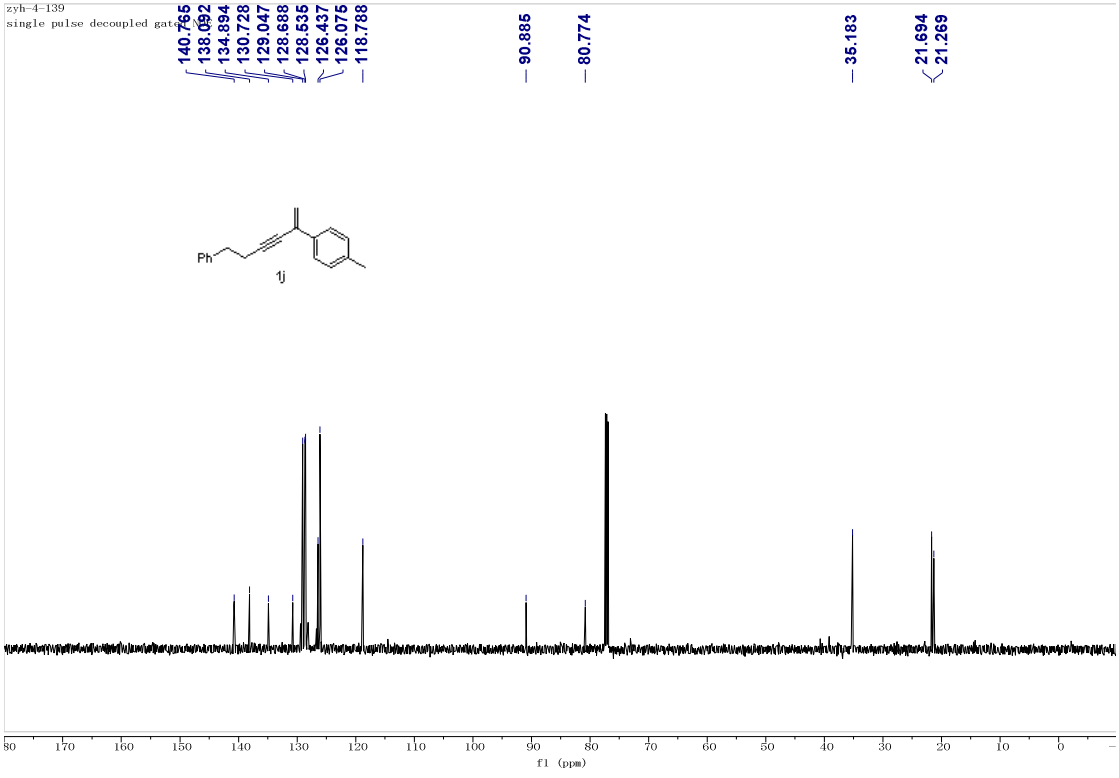
1.08
1.07
2.09
2.04
3.00
f1 (ppm)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35.183
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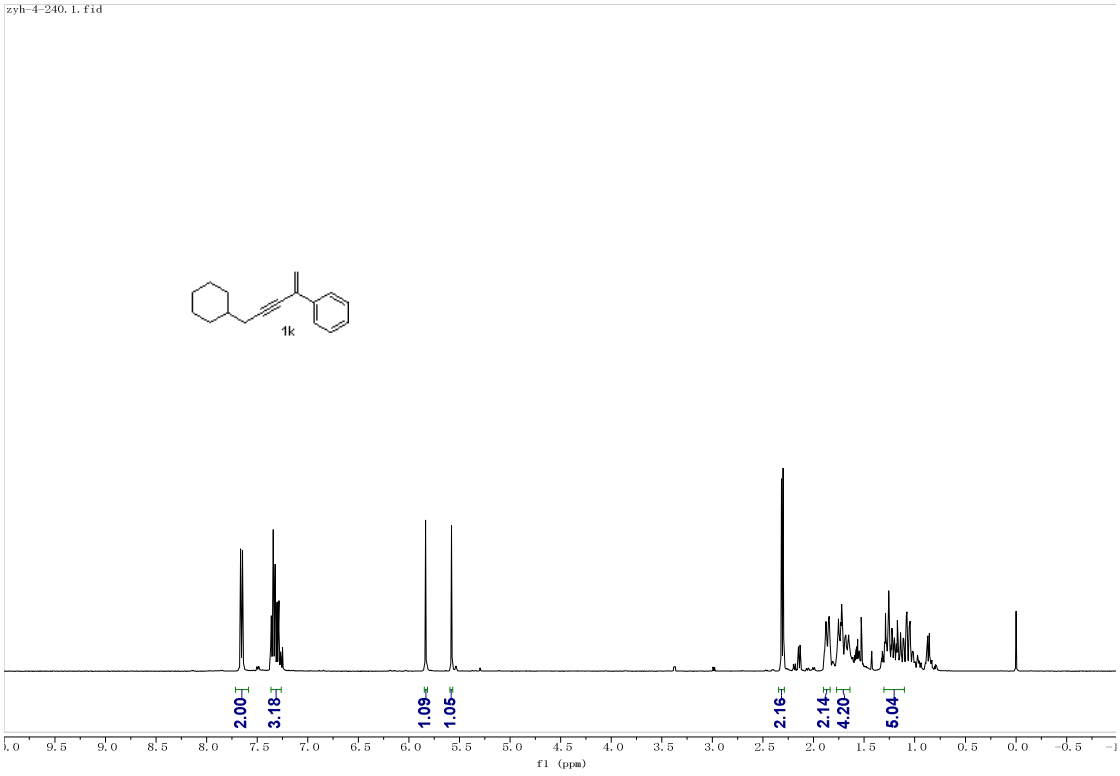
21.269
Ph
1j
f1 (ppm)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2.14
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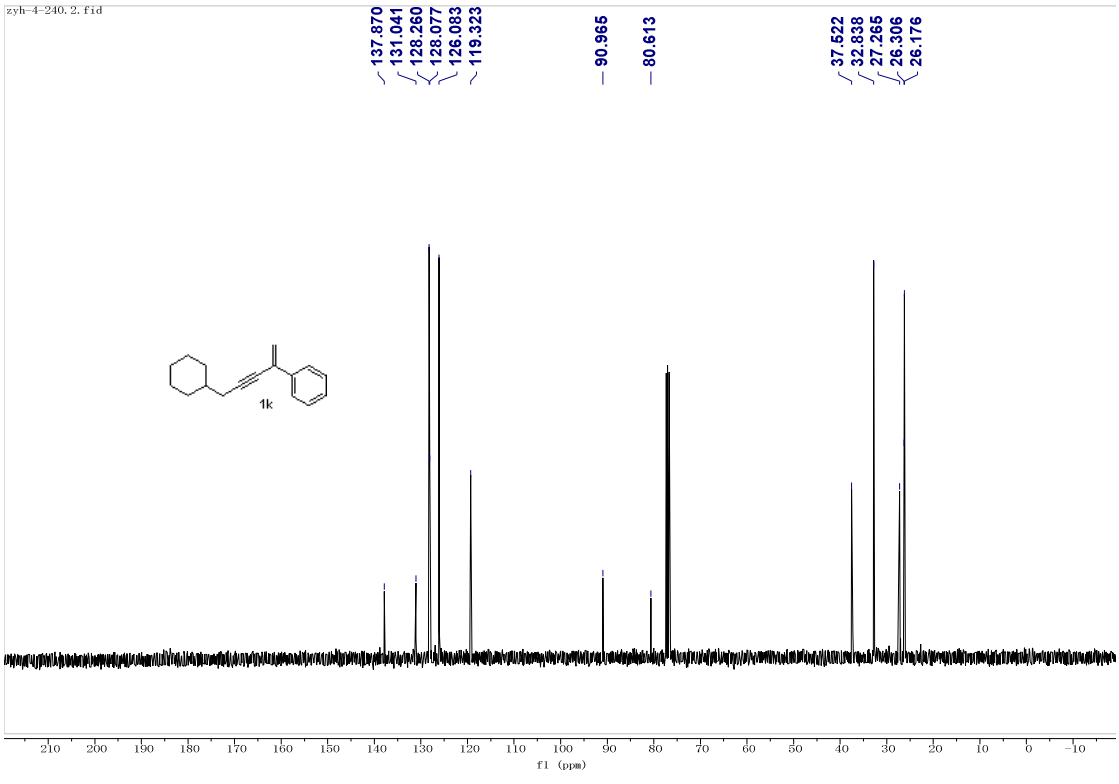
5.04
f1 (ppm)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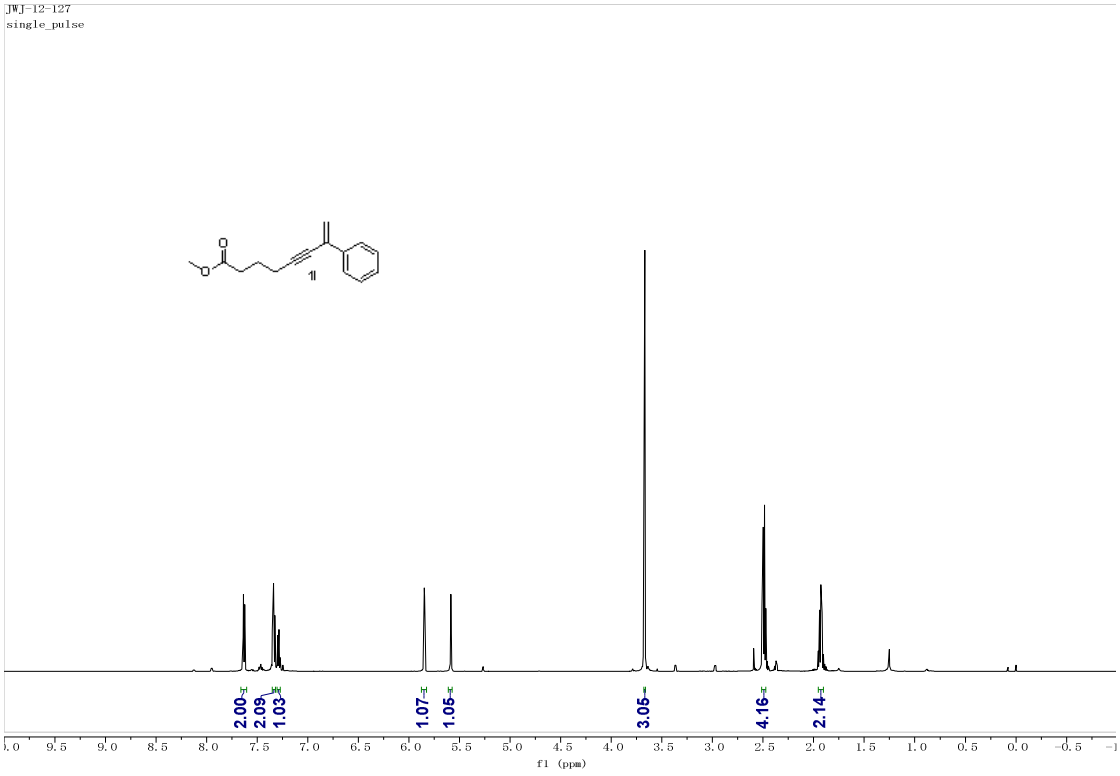
1k
f1 (ppm)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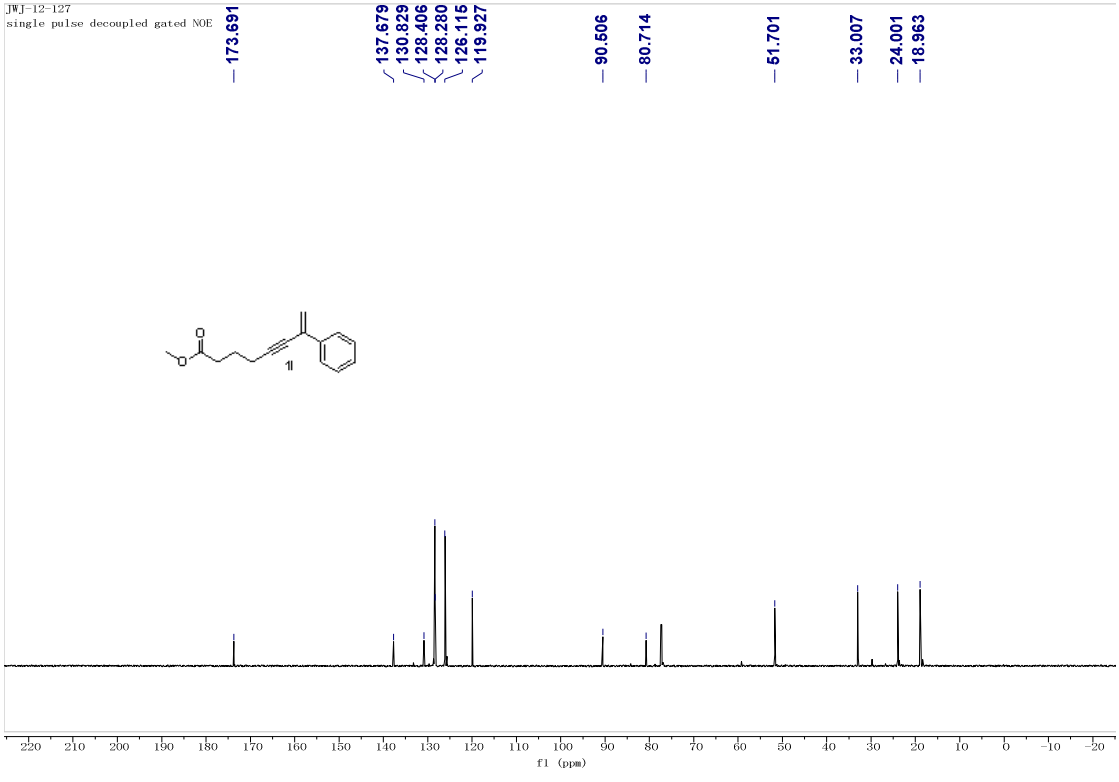
1.03
1.07
1.05
3.05
4.16
2.14
f1 (ppm)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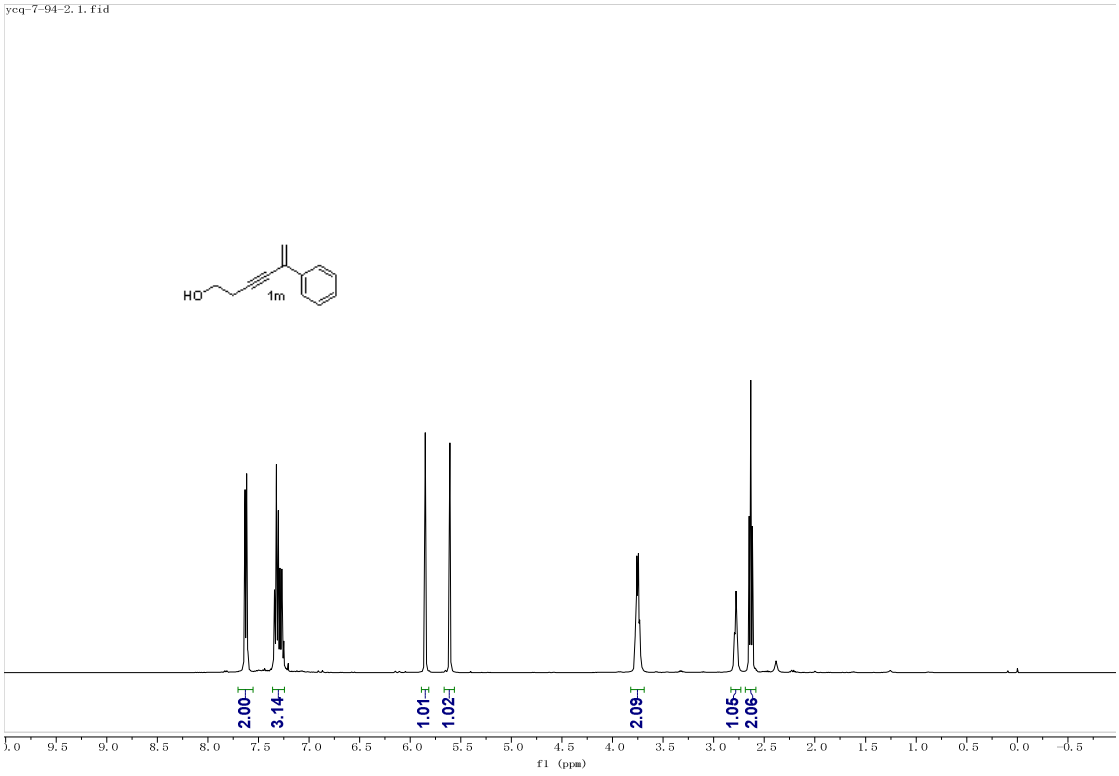
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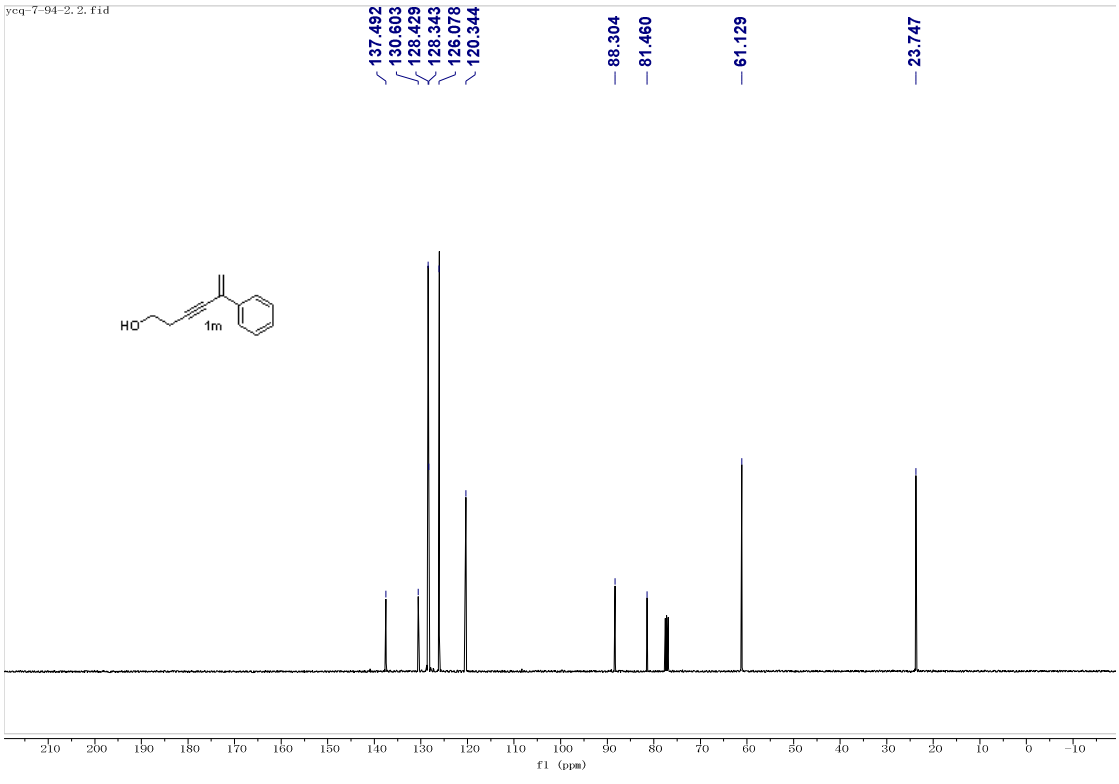
f1 (ppm)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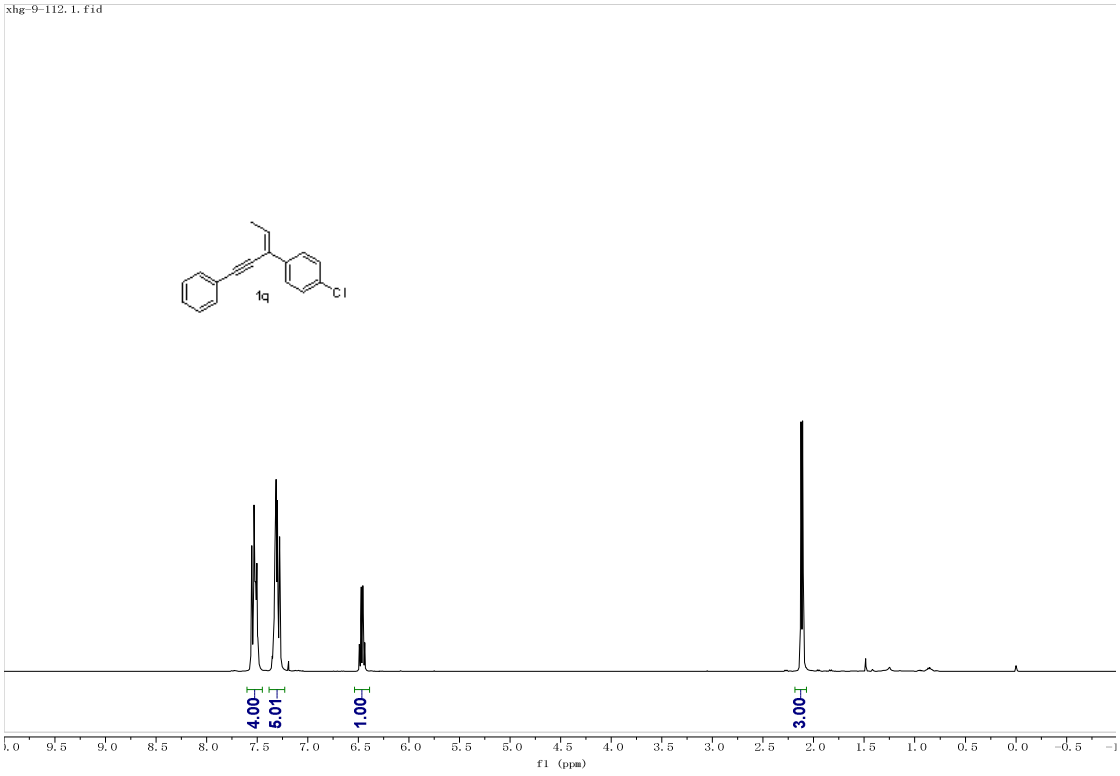
HO
1m
f1 (ppm)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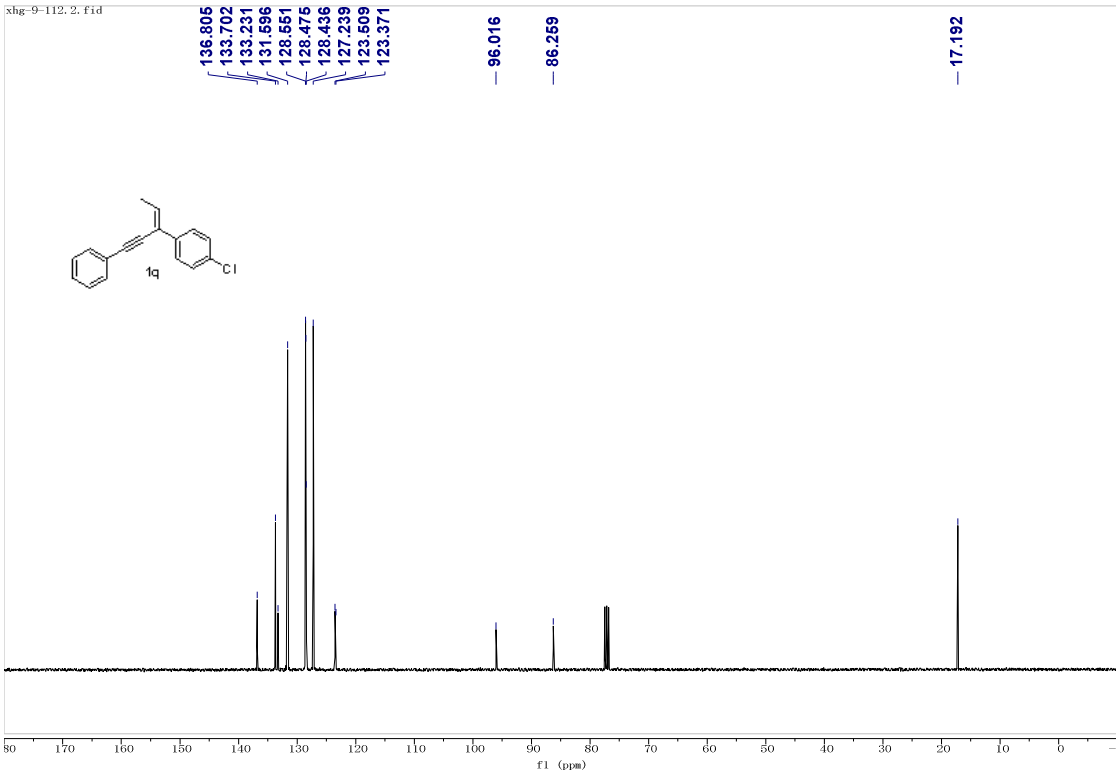
f1 (ppm)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127.239
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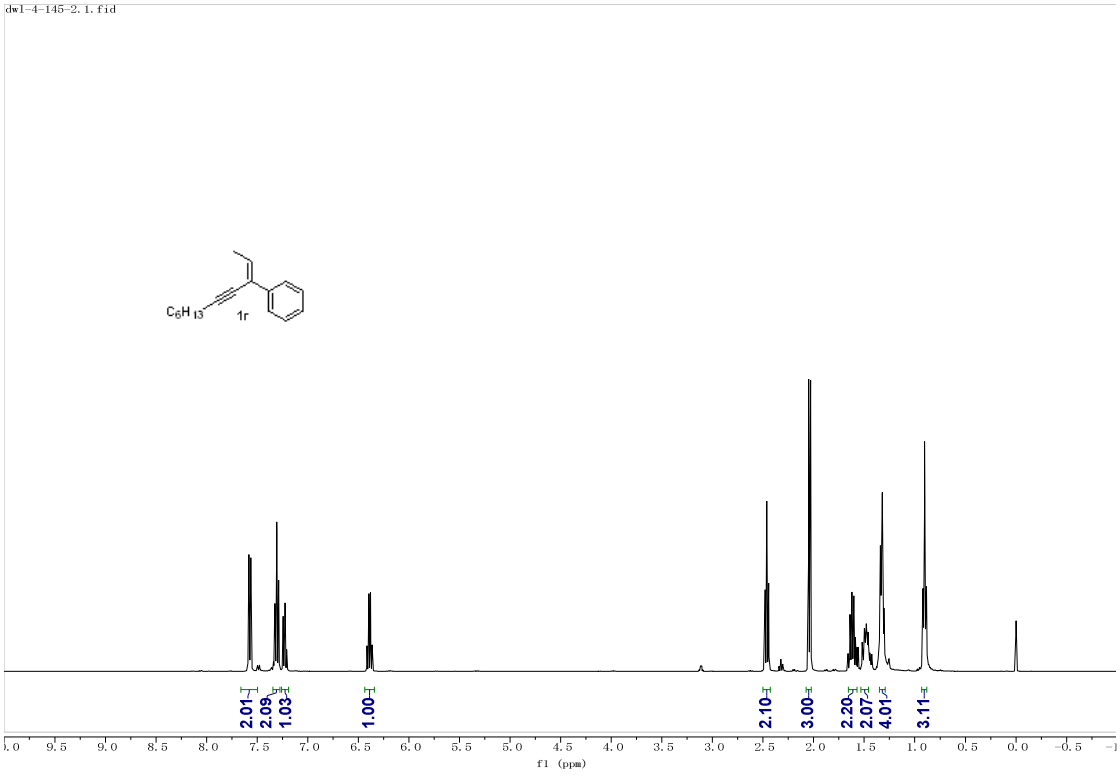
123.371
96.016
86.259
17.192
1q
Cl
f1 (ppm)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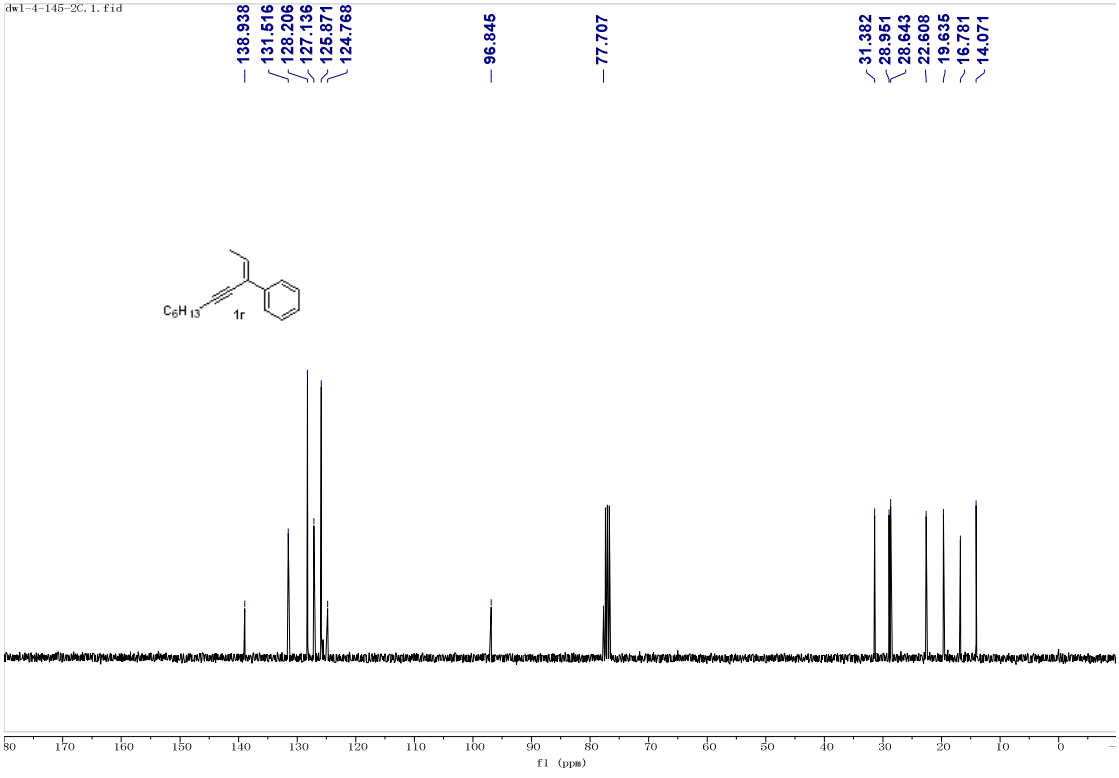
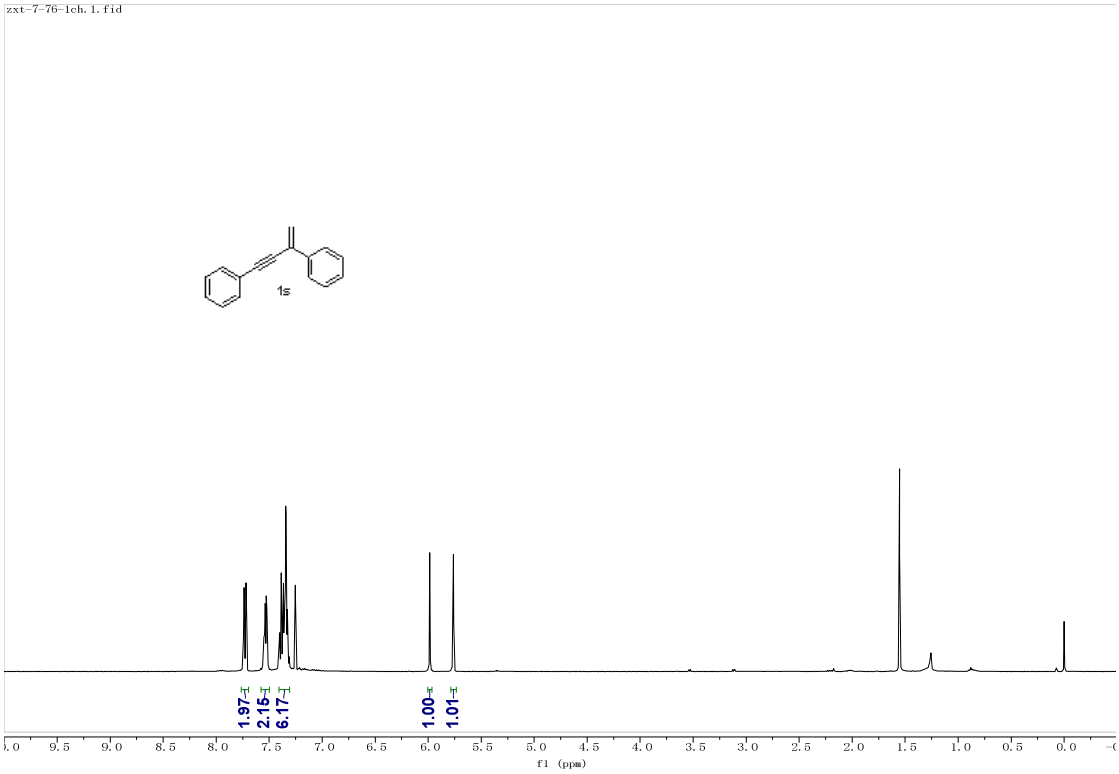
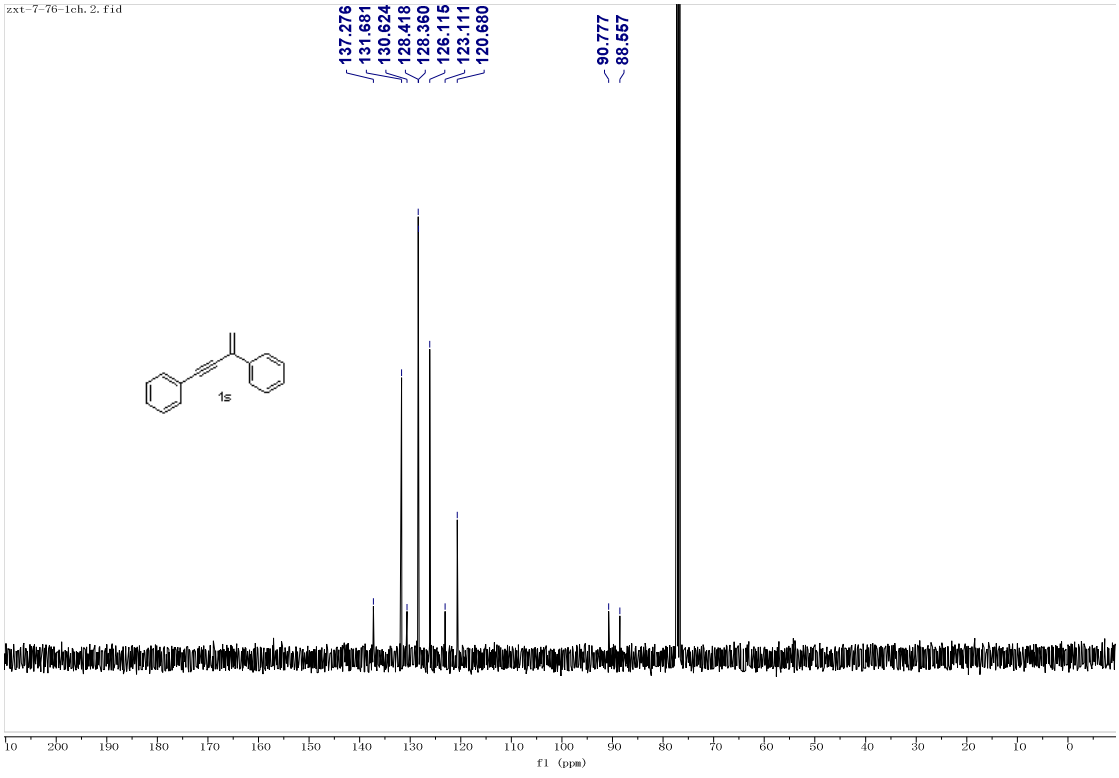
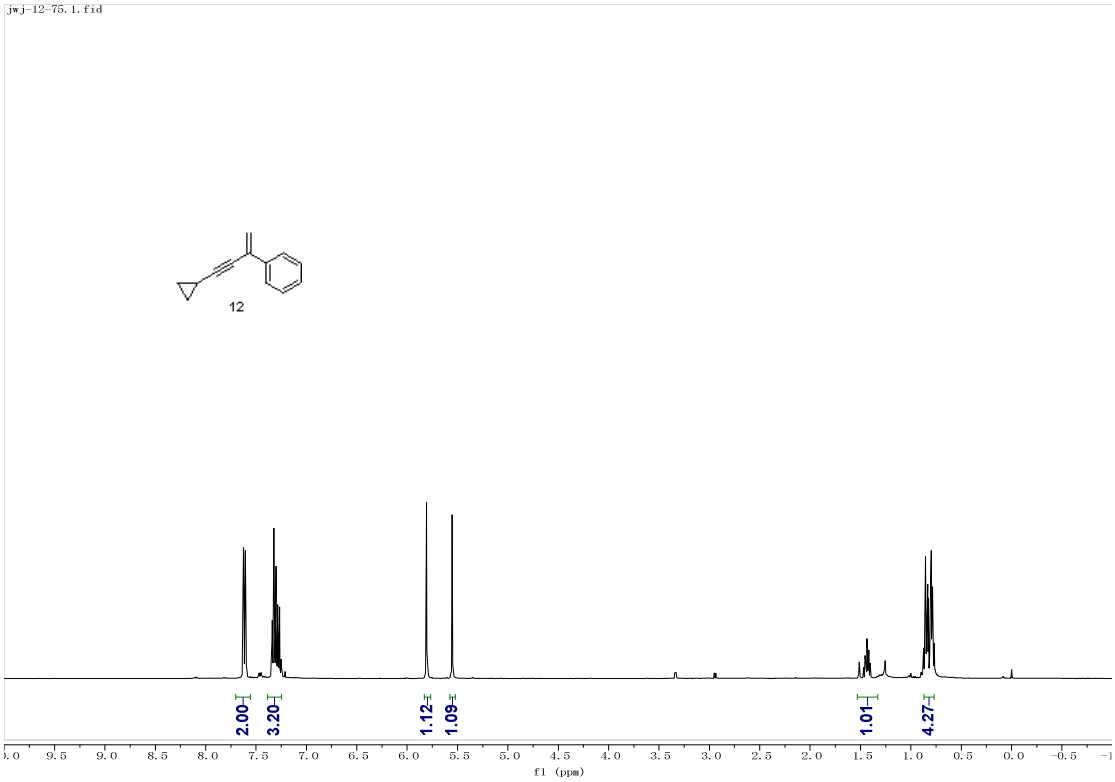
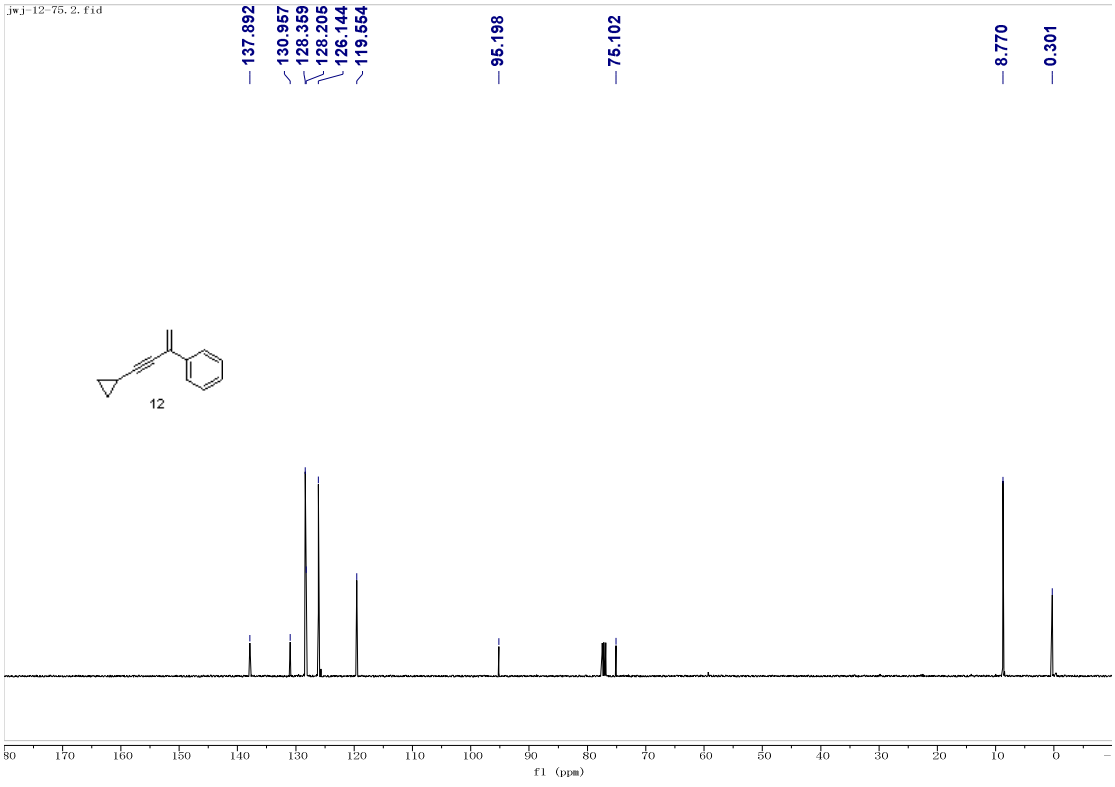
3.00
2.20
2.07
4.01
3.11
f1 (ppm)

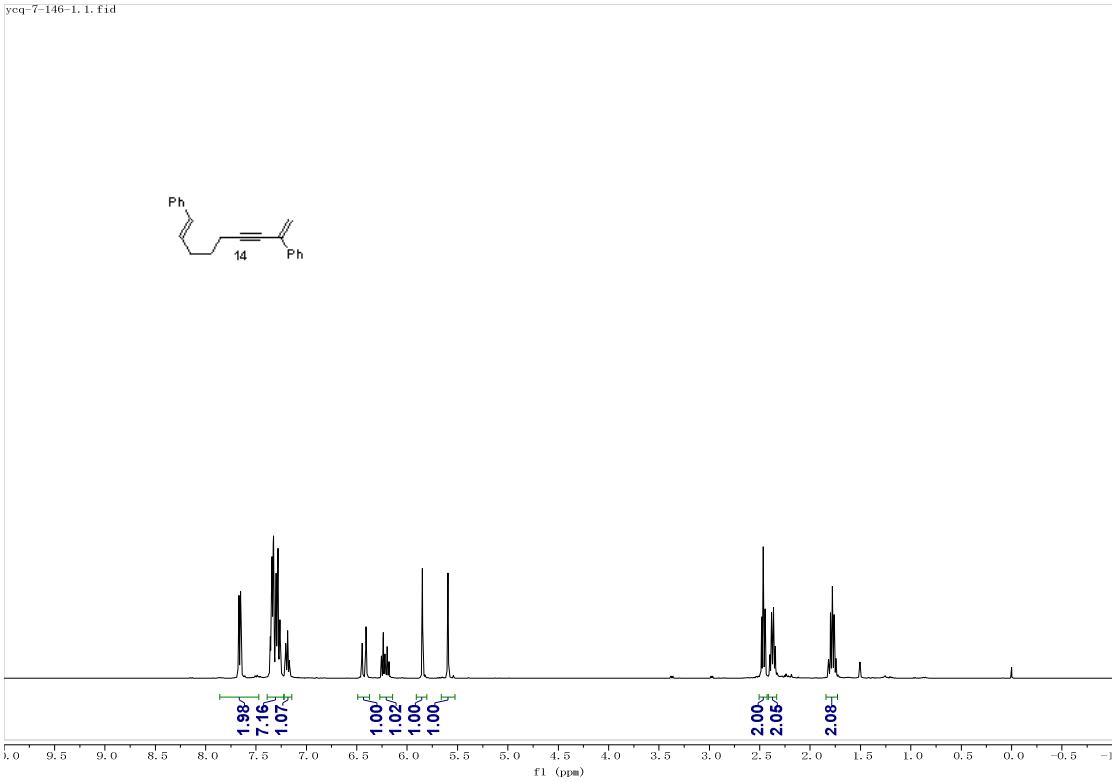

dw1-4-145-2C.1.fid
138.938
131.516
128.206
127.136
125.871
124.768
96.845
77.707
31.382
28.951
28.643
22.608
19.635
16.781
14.071
C6H13
1r
f1 (ppm)

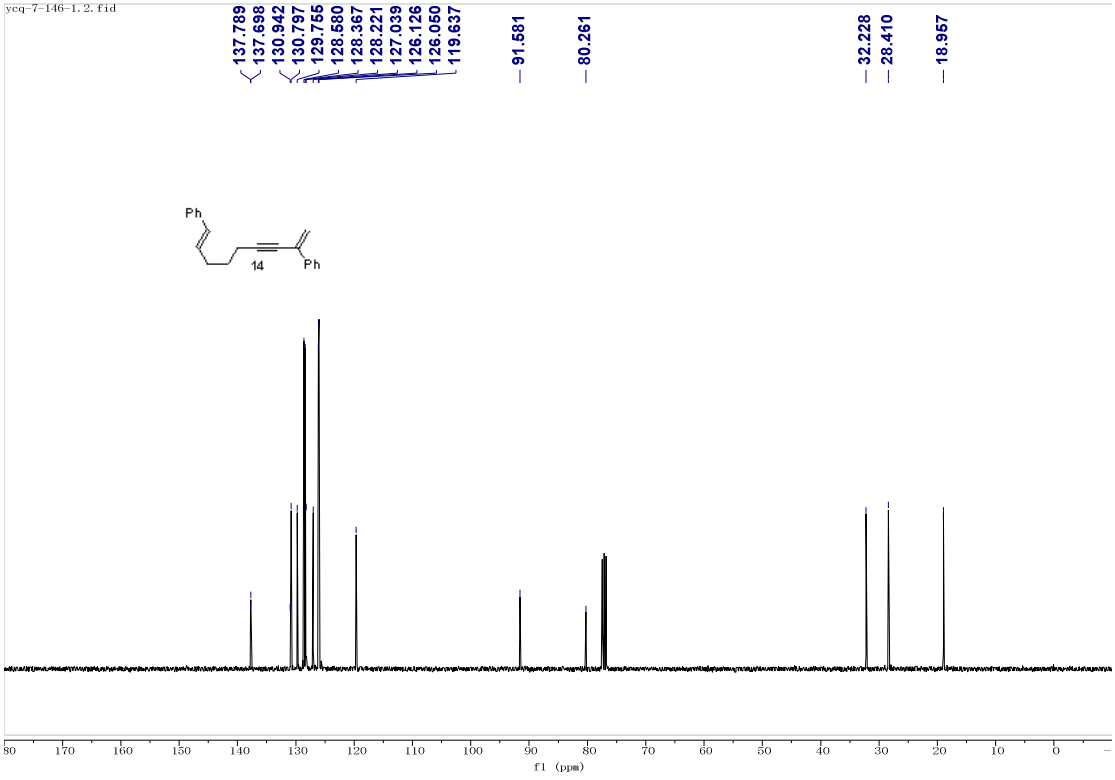

zxt-7-76-1ch.1.fid
1s
1.97
2.15
6.17
1.00
1.01
f1 (ppm)

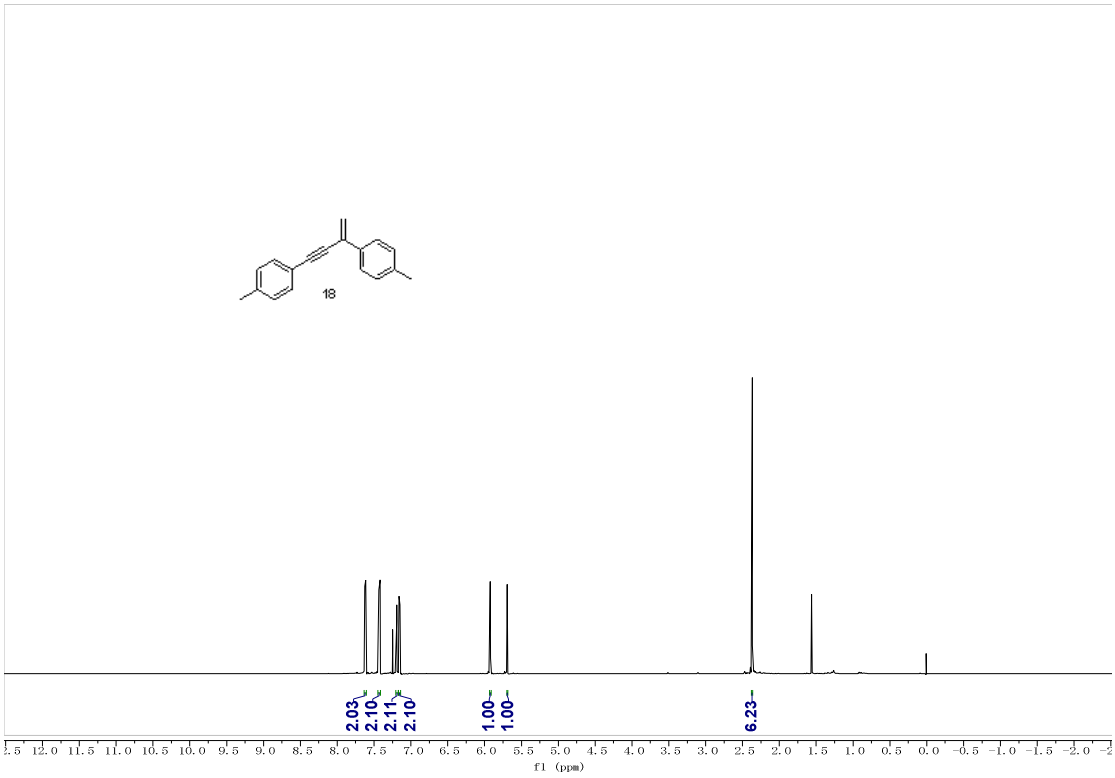

zxt-7-76-1ch.2.fid
137.276
131.681
130.624
128.418
128.360
126.115
123.111
120.680
90.777
88.557
1s
f1 (ppm)

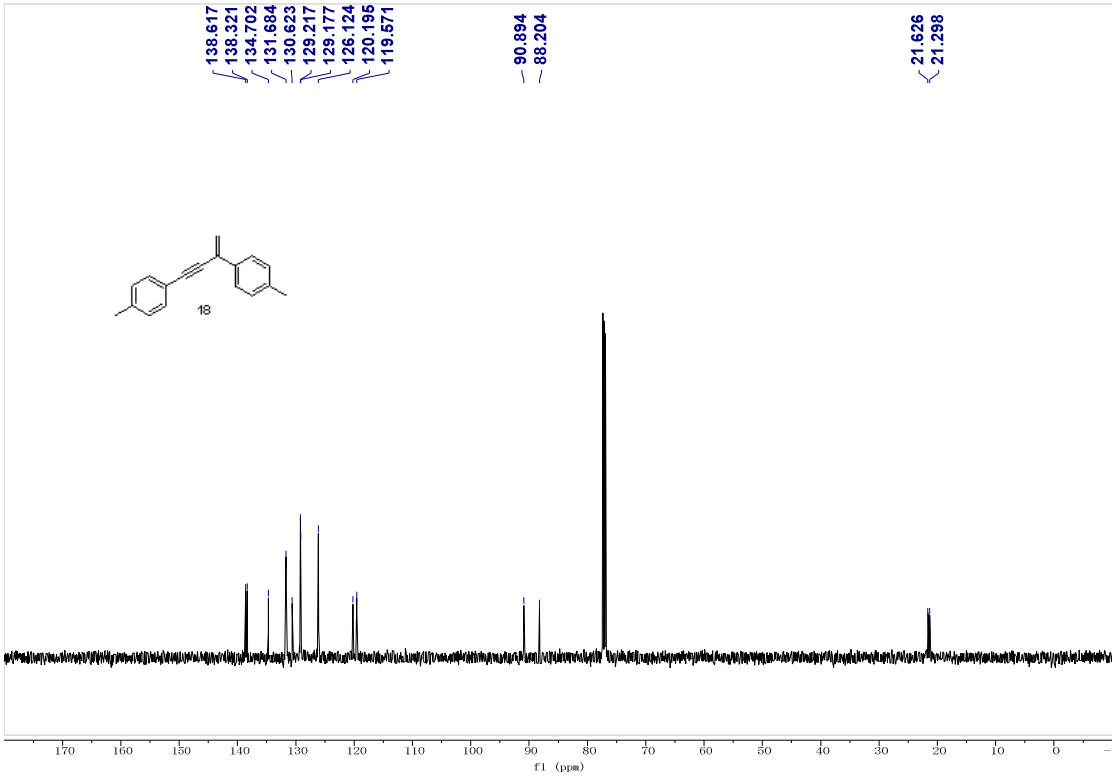

jwj-12-75.1.fid
12
2.00
3.20
1.12
1.09
1.01
4.27
f1 (ppm)

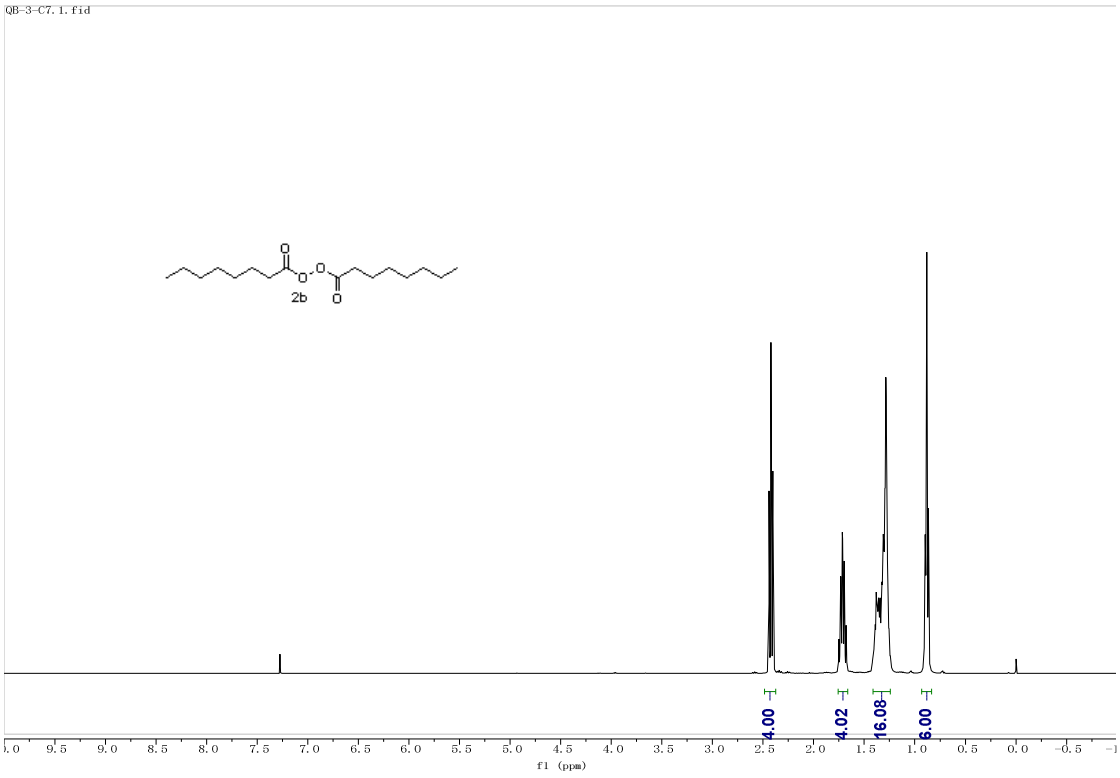

jwj-12-75.2.fid
137.892
130.957
128.359
128.205
126.144
119.554
95.198
76.102
8.770
0.301
12
f1 (ppm)

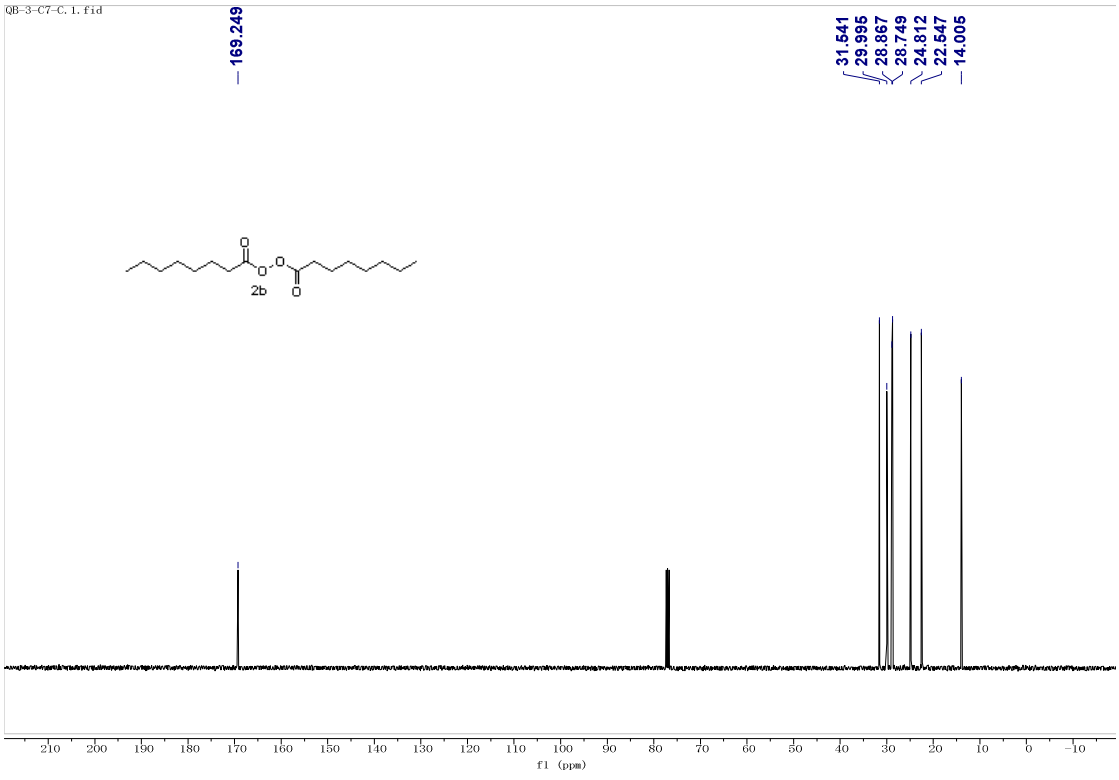

ycq-7-146-1.1.fid
Ph
14
Ph
1.98
7.16
1.07
1.00
1.02
1.00
1.00
2.00
2.05
2.08
f1 (ppm)

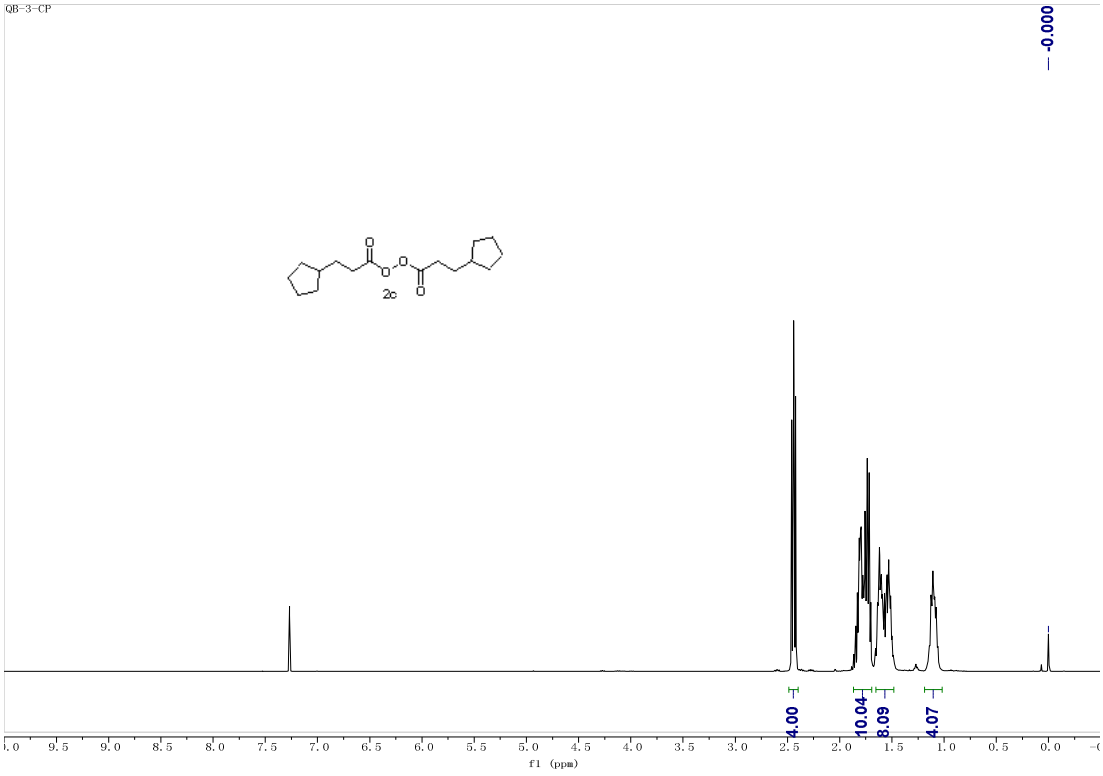

ycq-7-146-1.2.fid
137.789
137.698
130.942
130.797
129.755
128.580
128.367
128.221
127.039
126.126
126.050
119.637
91.581
80.261
32.228
28.410
18.957
Ph
14
Ph
f1 (ppm)

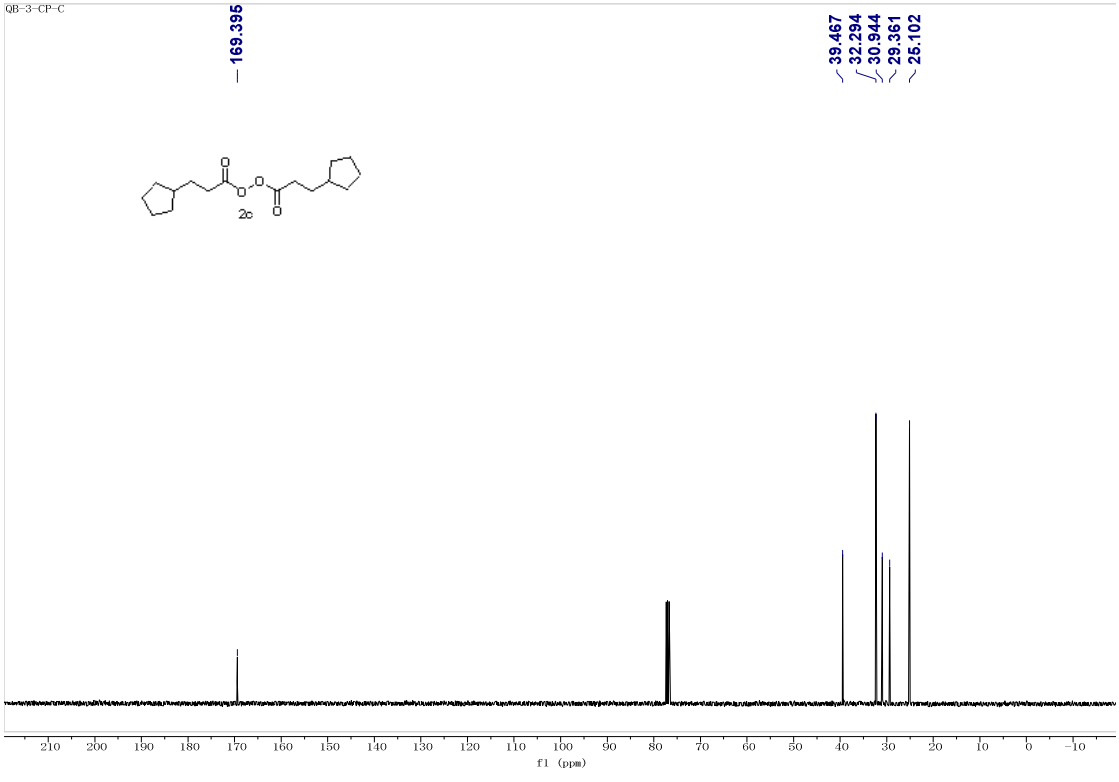

18
2.03
2.10
2.11
2.10
1.00
1.00
6.23
f1 (ppm)

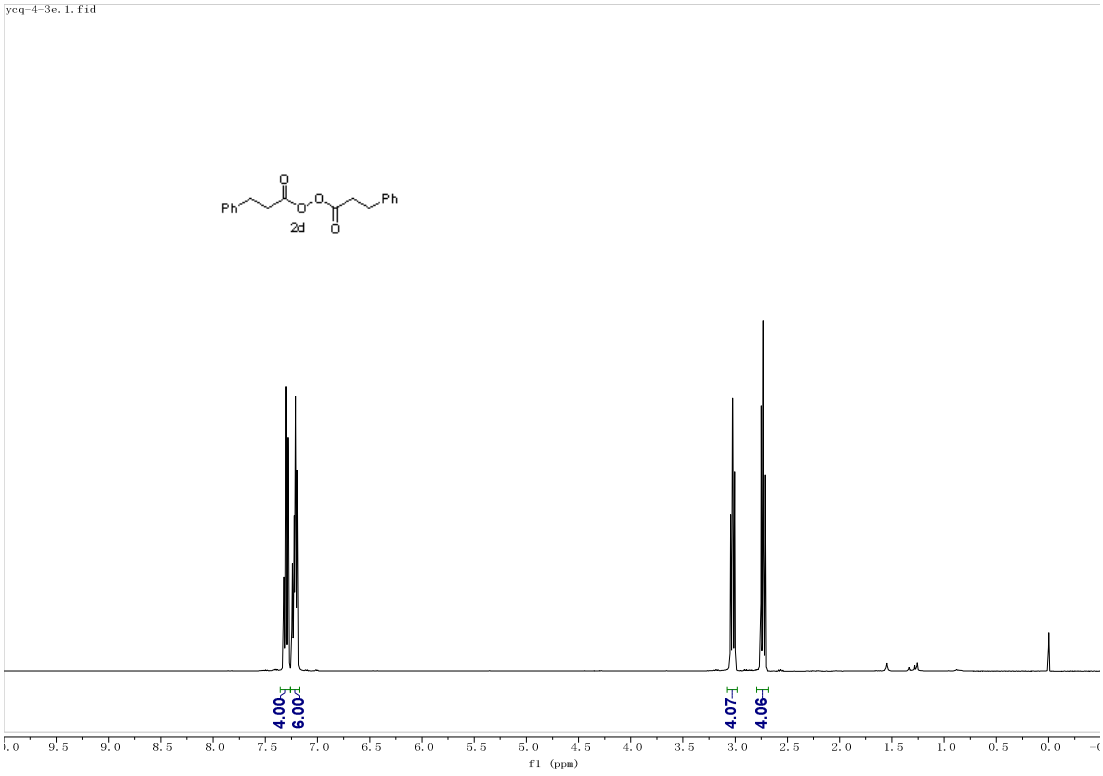

138.617
138.321
134.702
131.684
130.623
129.217
129.177
126.124
120.195
119.671
90.894
88.204
21.626
21.298
18
f1 (ppm)

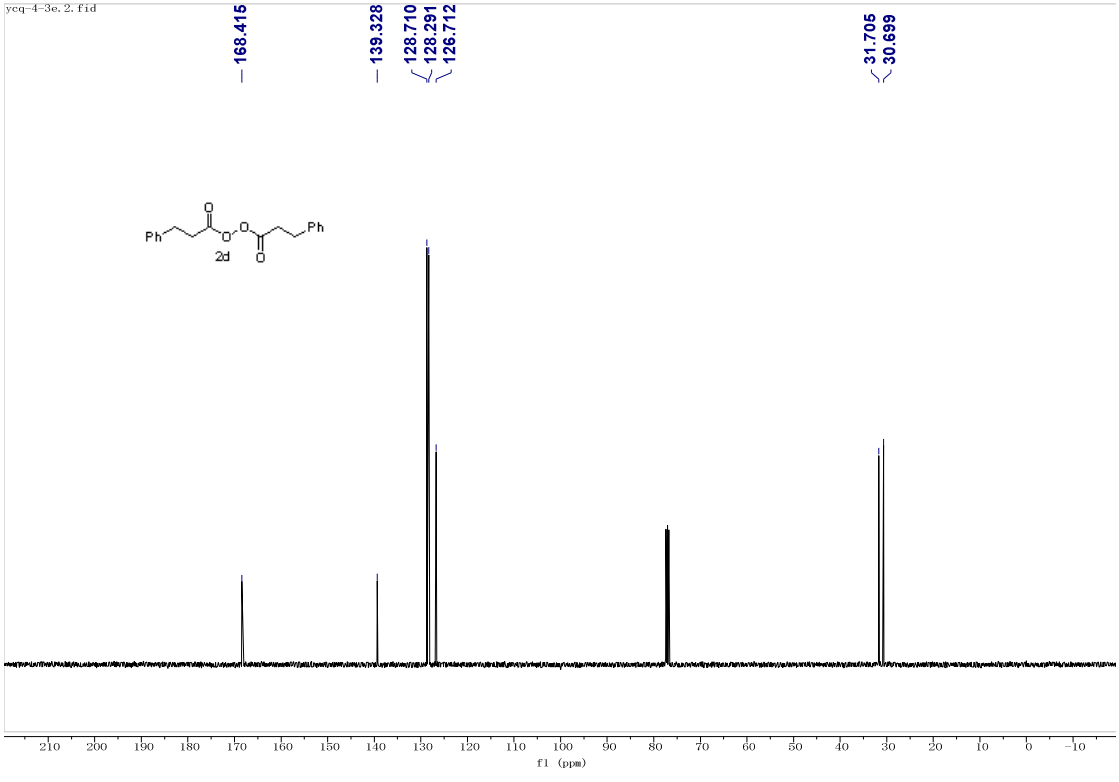

QB-3-C7.1.fid
2b
4.00
4.02
16.08
6.00
f1 (ppm)

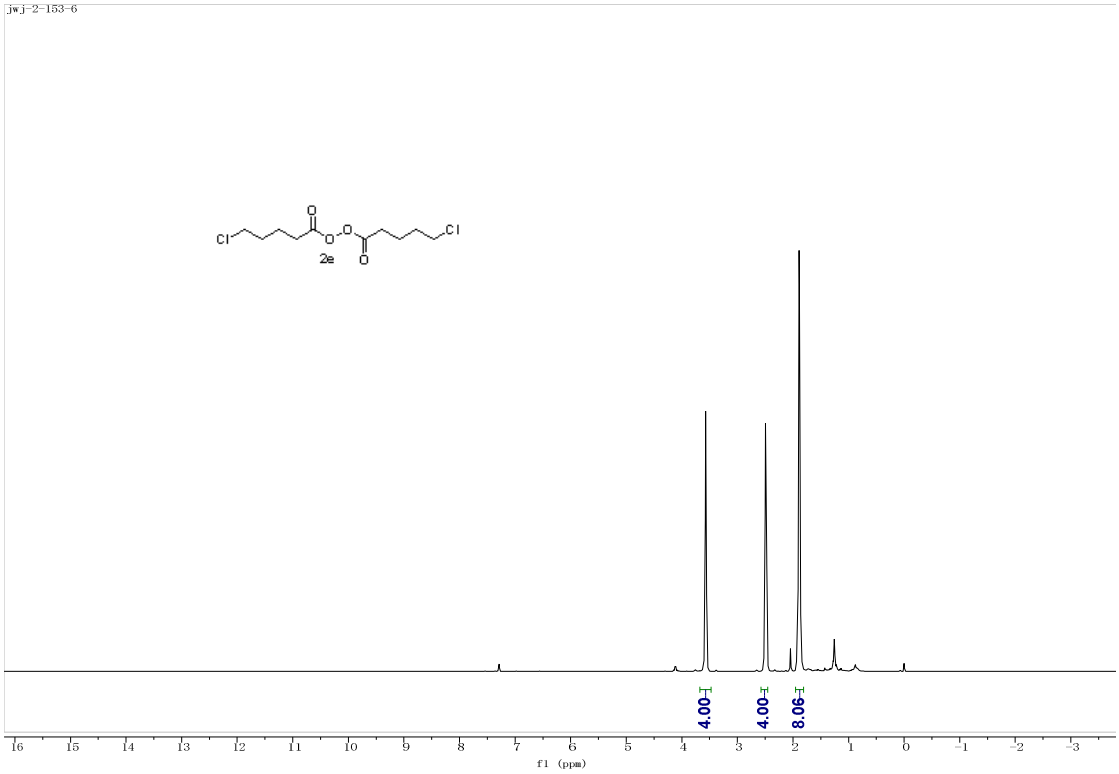

QB-3-C7-C.1.fid
169.249
31.541
29.995
28.867
28.749
24.812
22.547
14.005
2b
f1 (ppm)

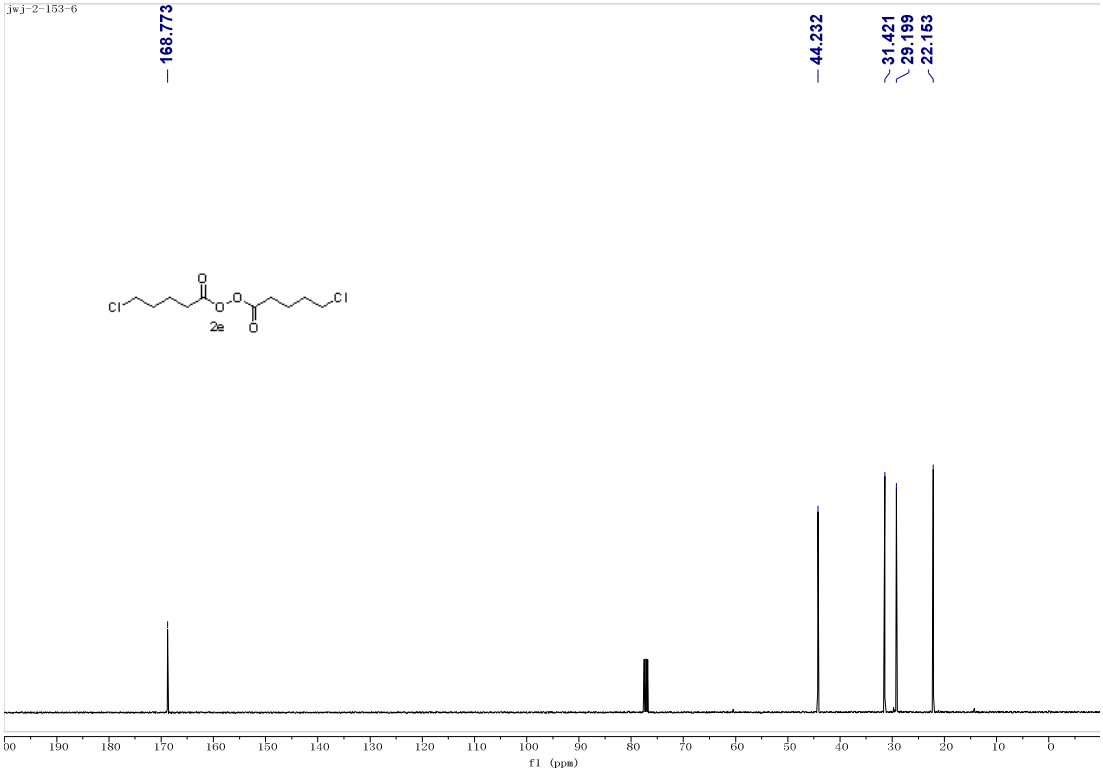

QB-3-CP
-0.000
2c
4.00
10.04
8.09
4.07
f1 (ppm)

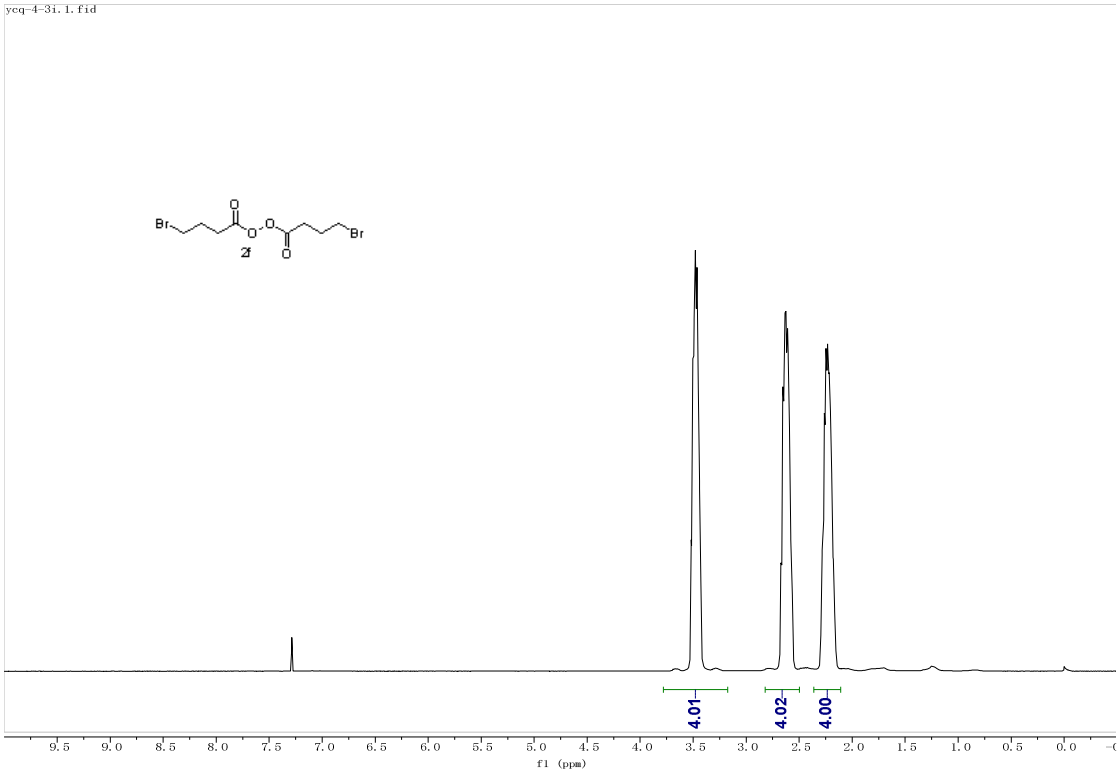

QB-3-CP-C
169.395
39.467
32.294
30.944
29.361
25.102
2c
f1 (ppm)

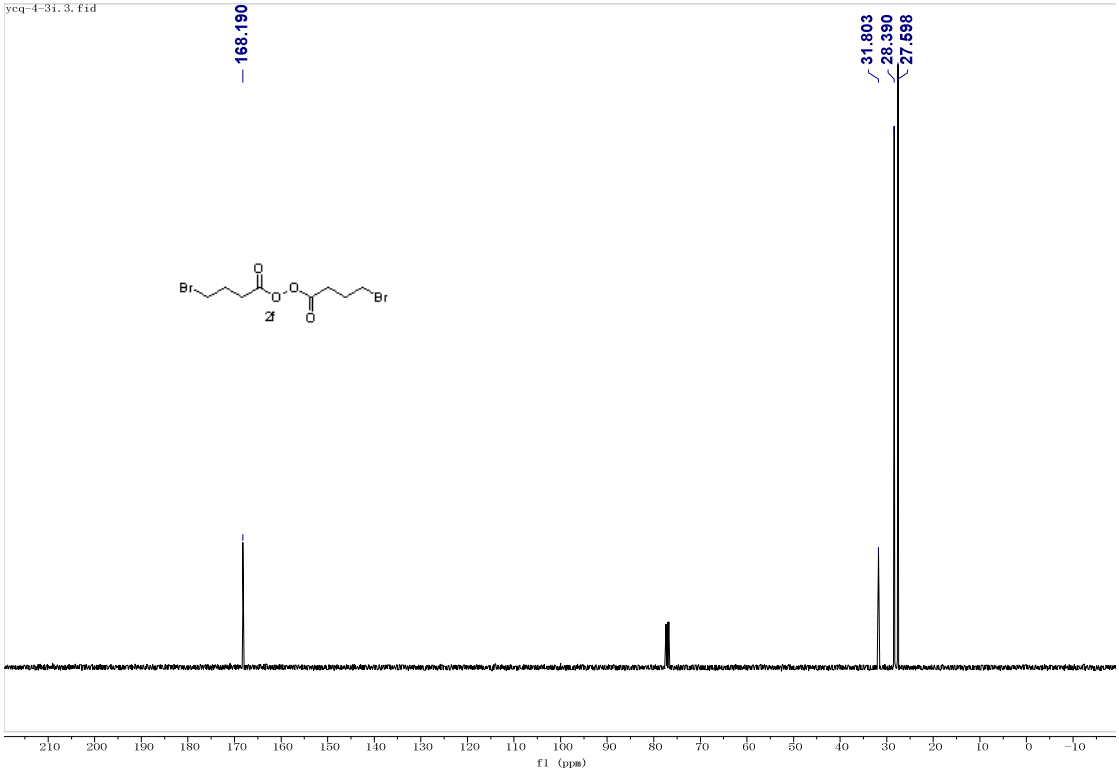

ycq-4-3e.1.fid
Ph
O
O
O
O
Ph
2d
4.00
6.00
4.07
4.06
f1 (ppm)

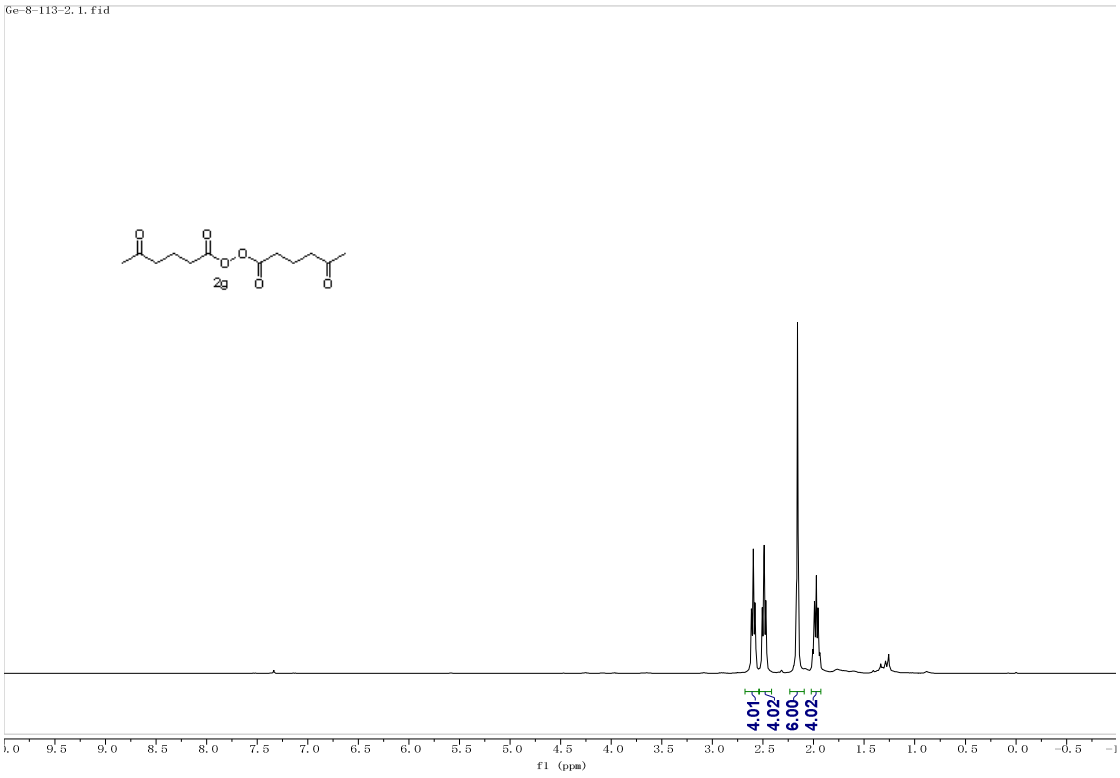

ycq-4-3e.2.fid
168.415
139.328
128.710
128.291
126.712
31.705
30.699
Ph
O
O
O
O
Ph
2d
f1 (ppm)

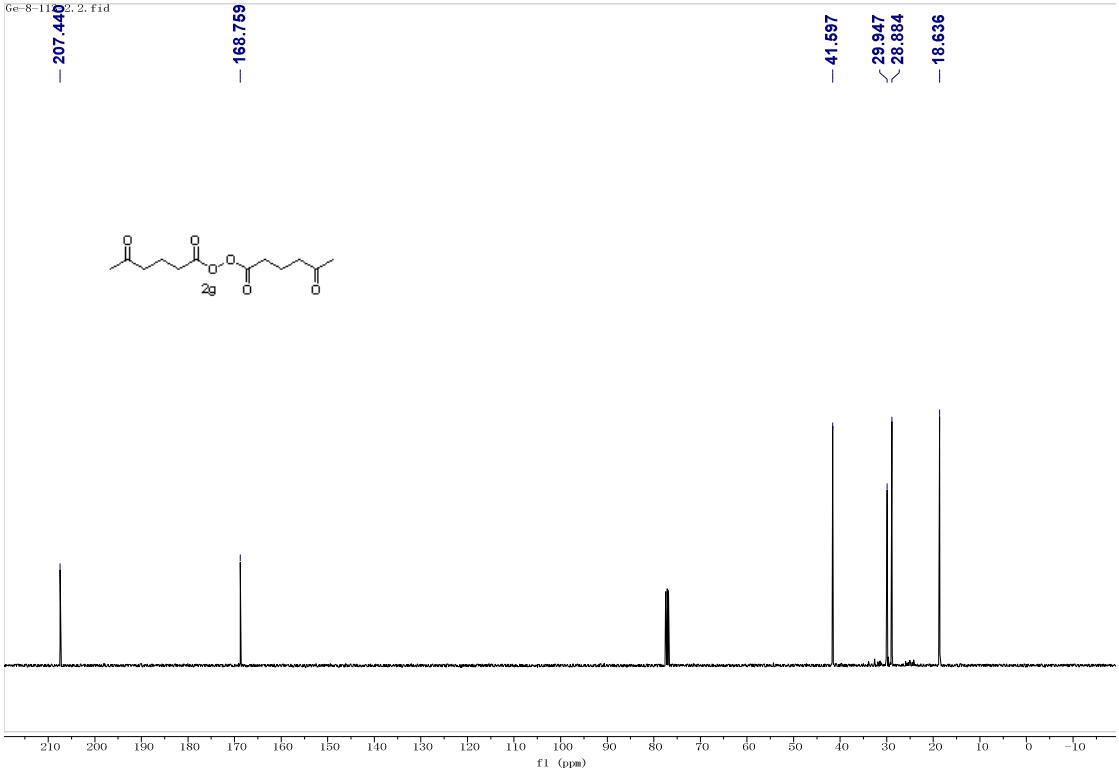

jwj-2-153-6
Cl
O
O
O
O
Cl
2e
4.00
4.00
8.06
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

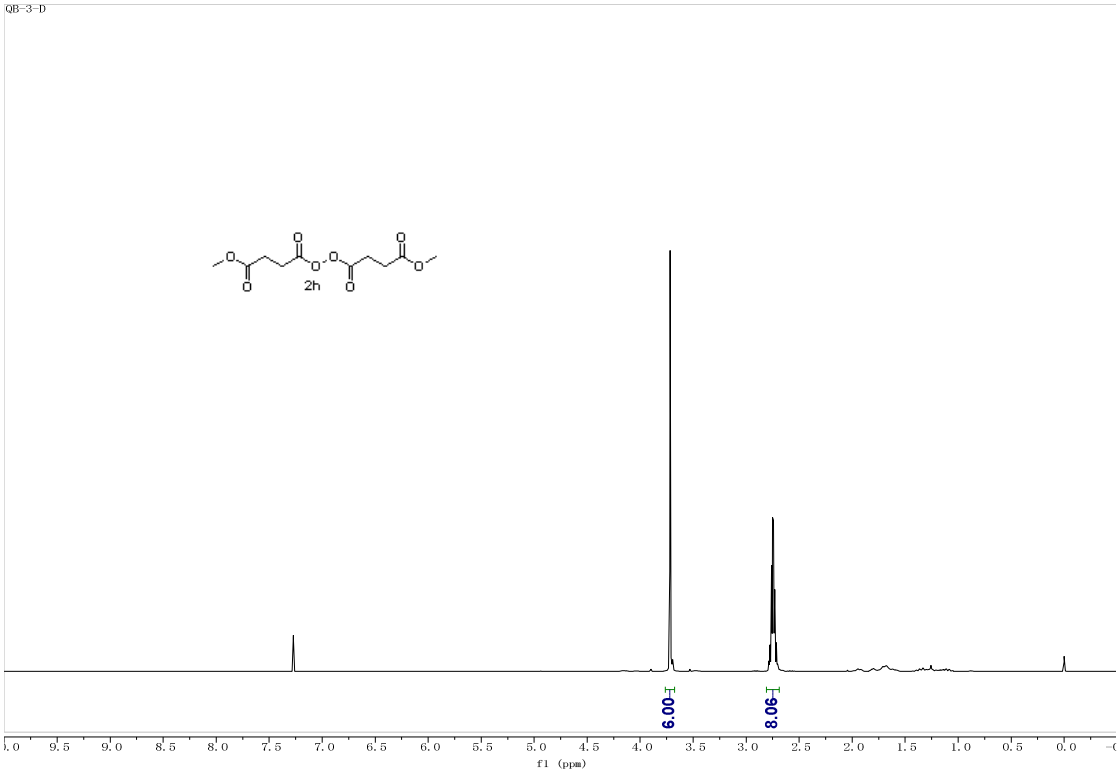

jwj-2-153-6
168.773
44.232
31.421
29.199
22.153
Cl
O
O
O
O
Cl
2e
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

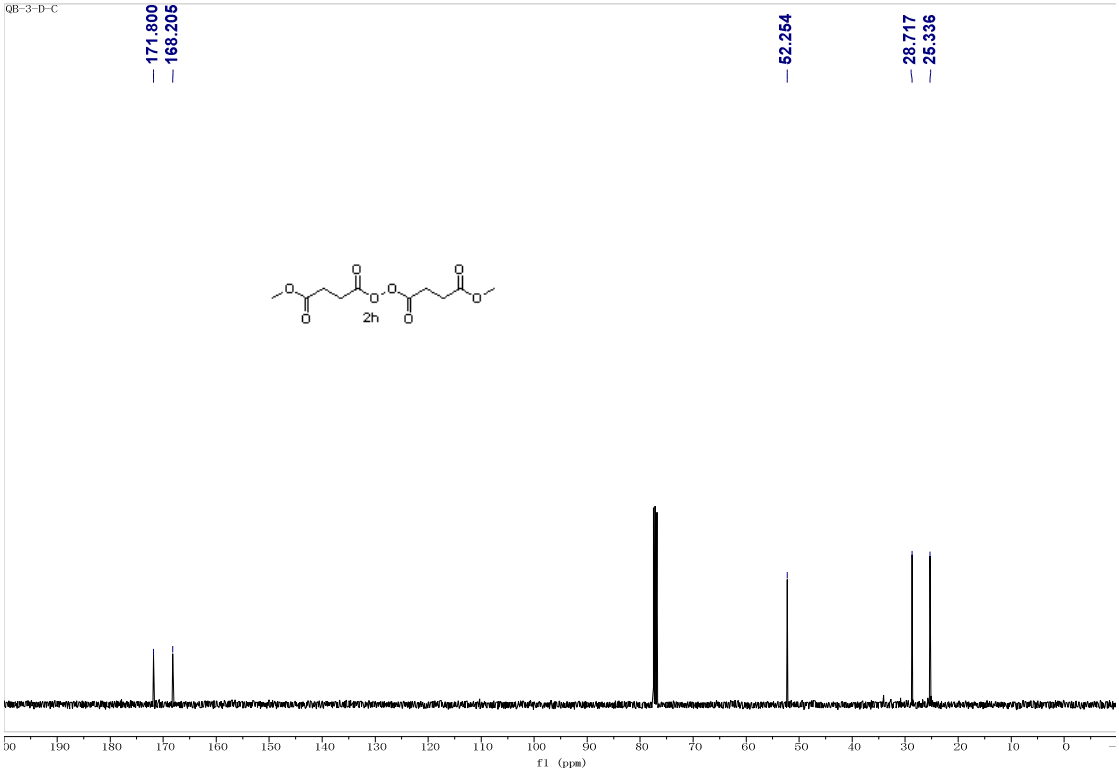

ycq-4-3i.1.fid
Br
Br
2f
4.01
4.02
4.00
f1 (ppm)

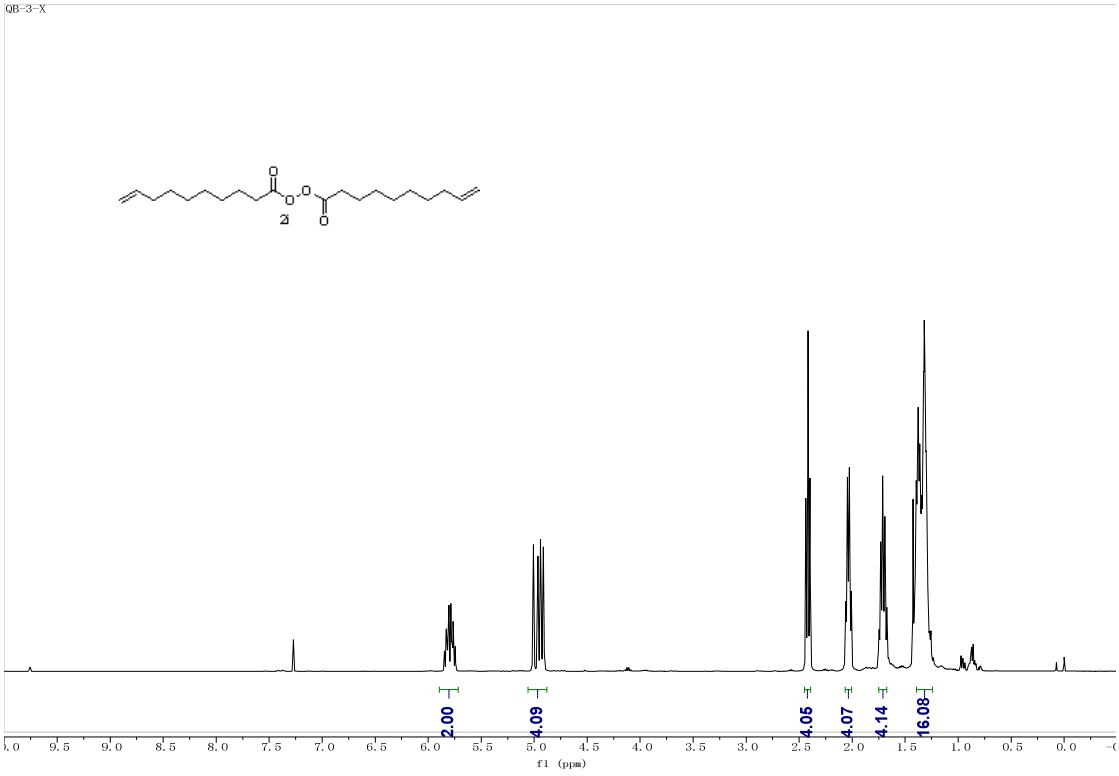

ycq-4-3i.3.fid
168.190
31.803
28.390
27.698
Br
Br
2f
f1 (ppm)

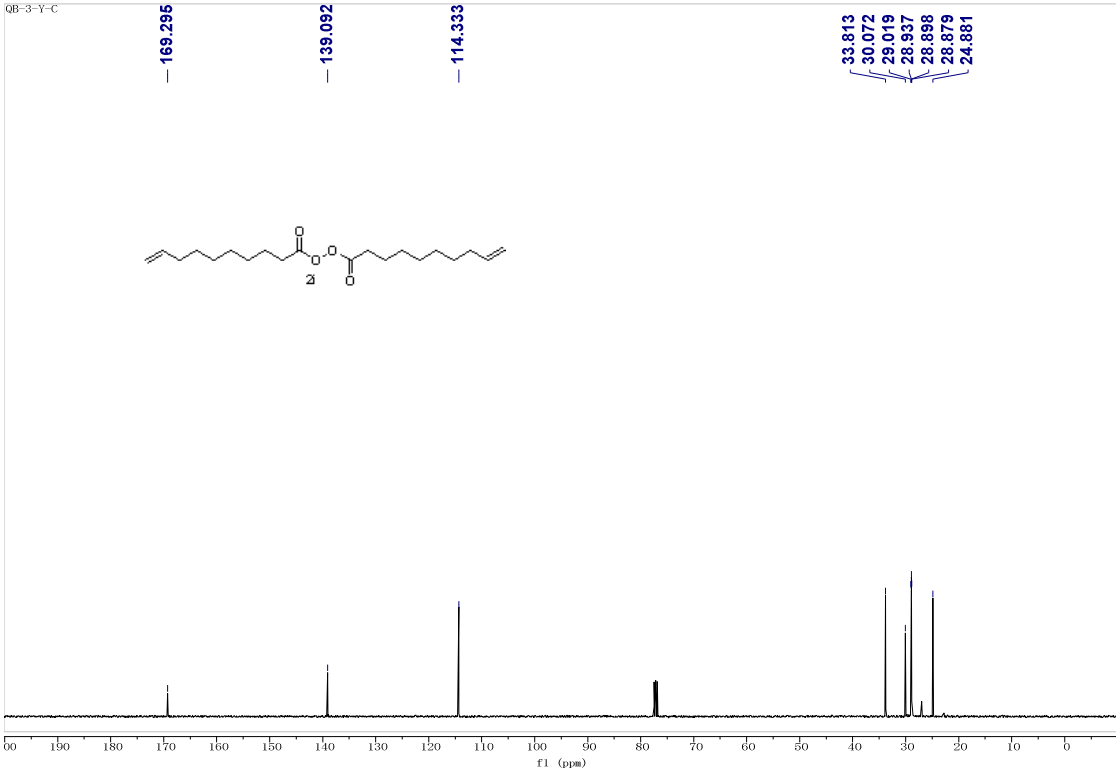

Ge-8-113-2.1.fid
2g
4.01
4.02
6.00
4.02
f1 (ppm)

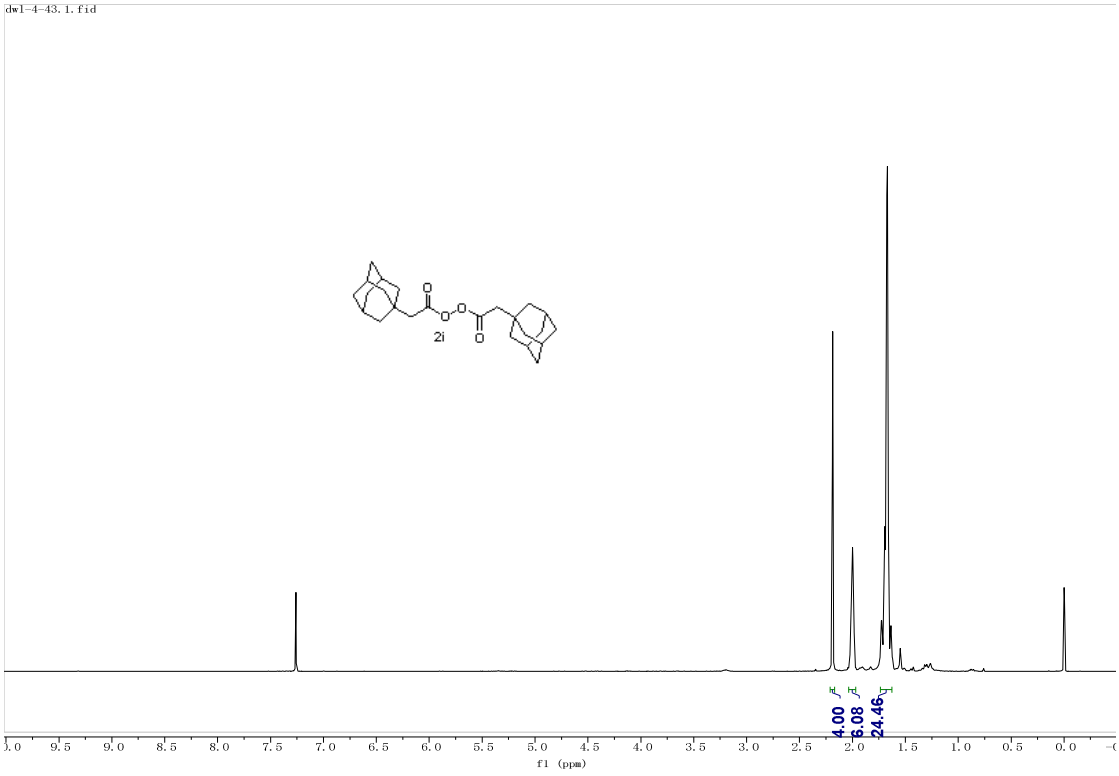

Ge-8-113-2.2.fid
207.448
168.759
41.597
29.947
28.884
18.636
2g
f1 (ppm)

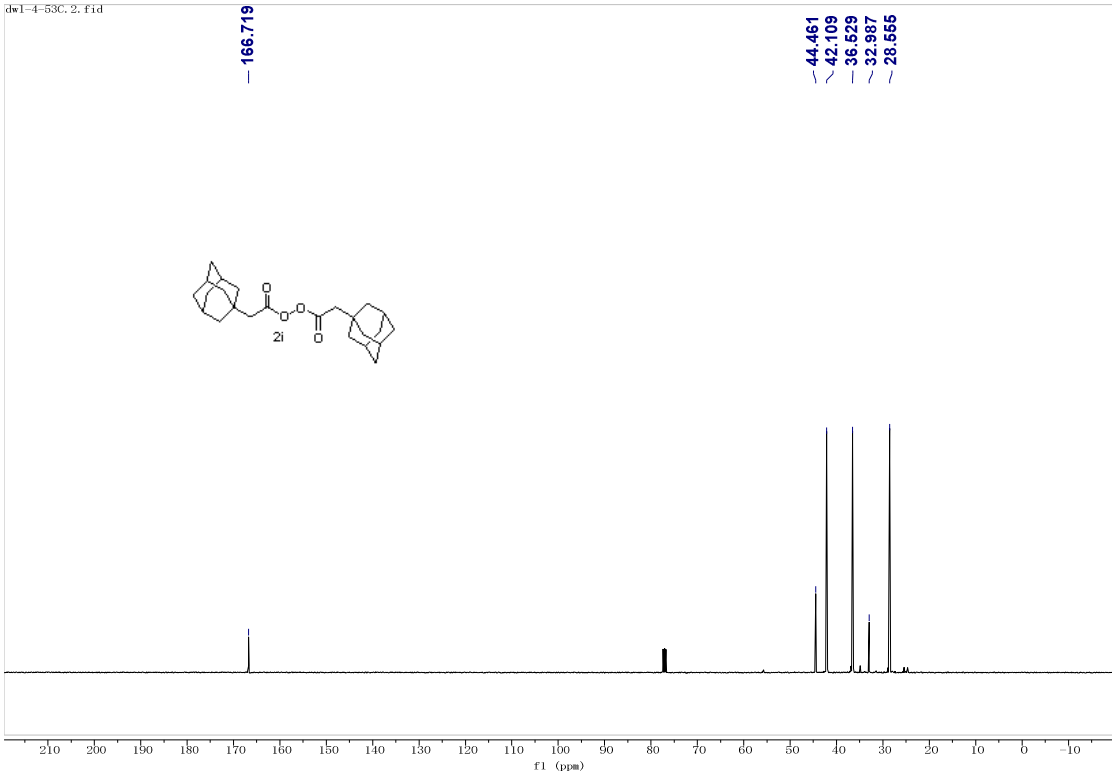

QB-3-D
2h
6.00
8.06
f1 (ppm)

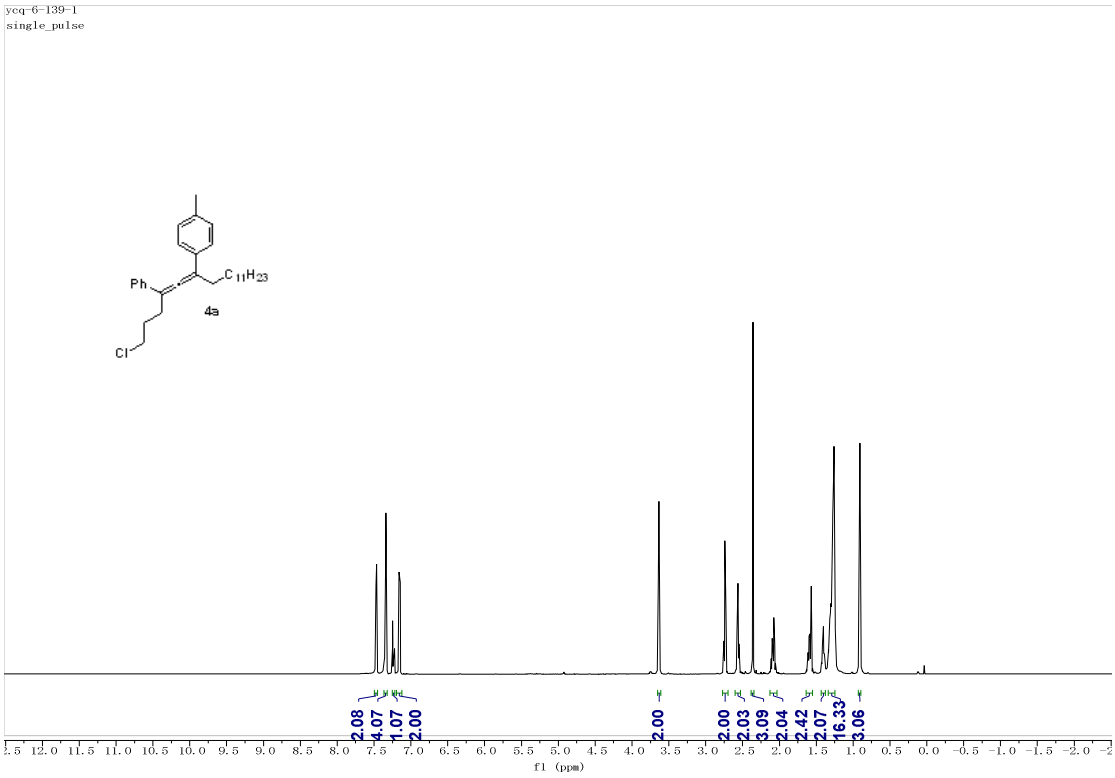

QB-3-D-C
171.800
168.205
52.254
28.717
25.336
2h
f1 (ppm)

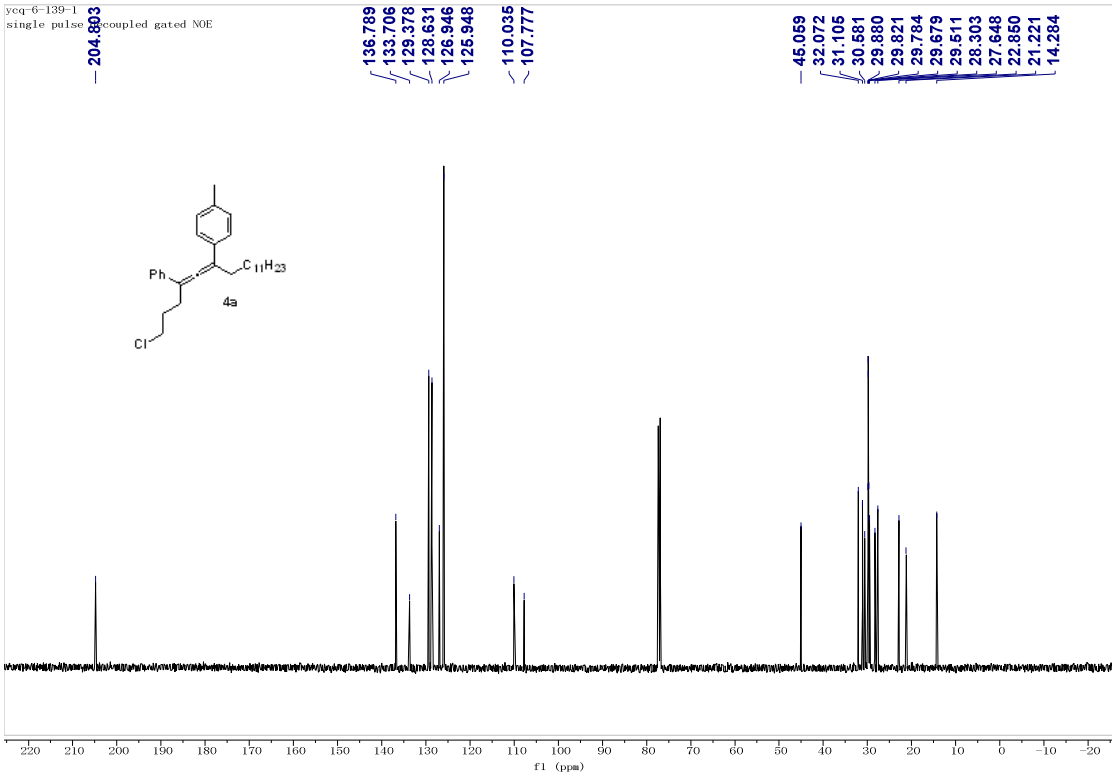

QB-3-X
2.00
4.09
4.05
4.07
4.14
16.08
f1 (ppm)

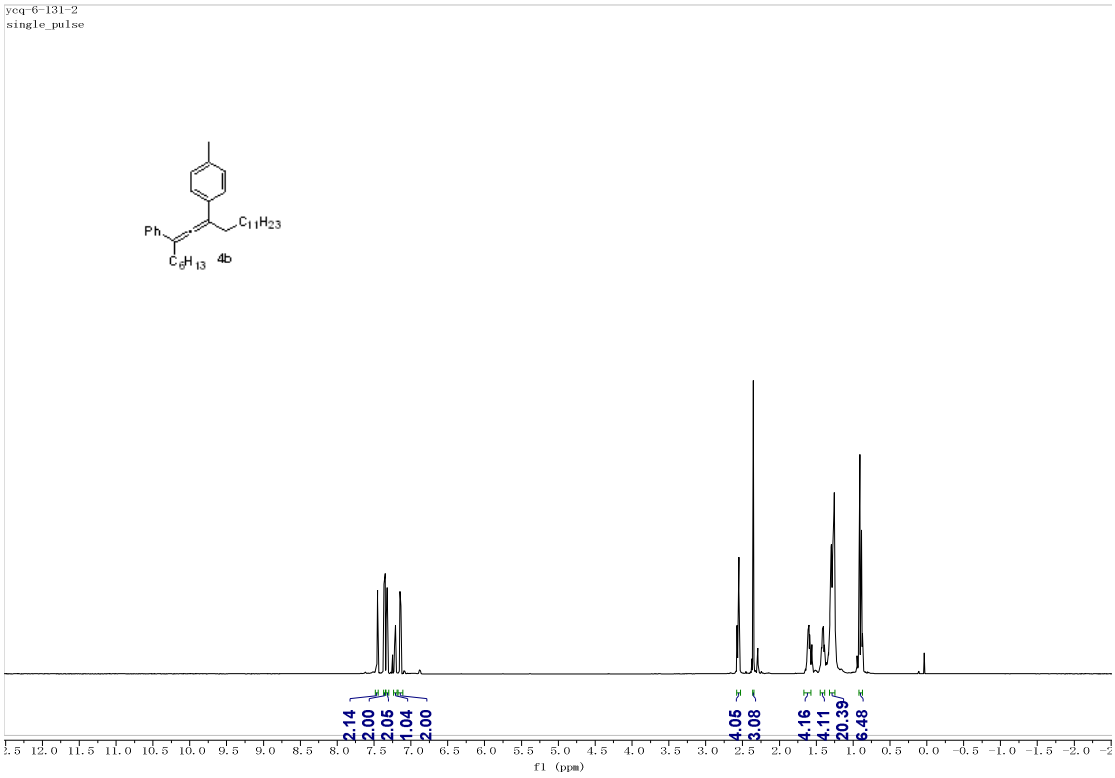

QB-3-Y-C
169.295
139.092
114.333
33.813
30.072
29.019
28.937
28.898
28.879
24.881
f1 (ppm)

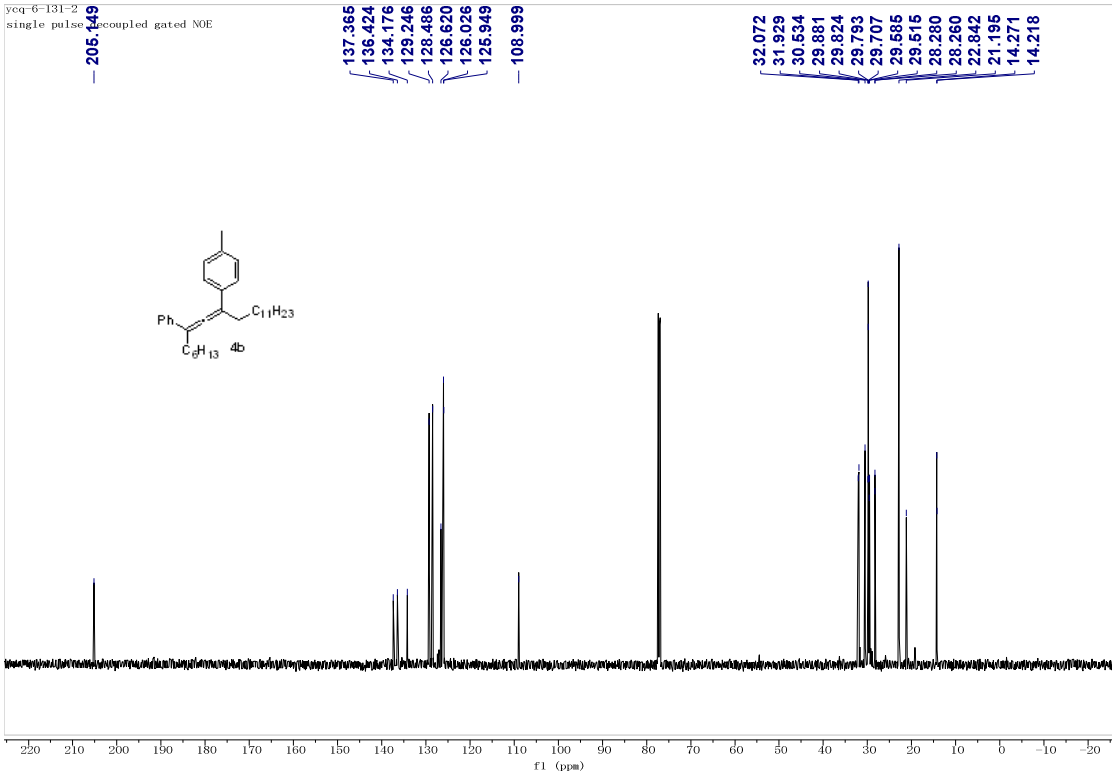

dwl-4-43.1.fid
2i
4.00
6.08
24.46
f1 (ppm)

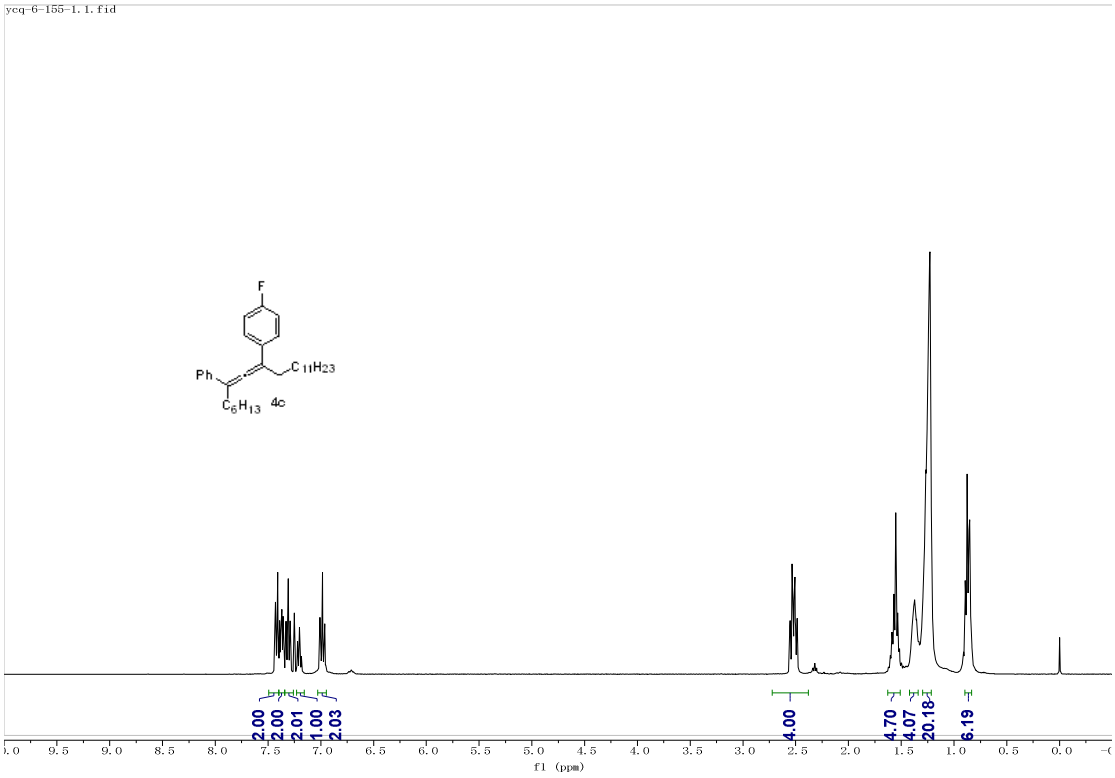

dwl-4-53C.2.fid
166.719
44.461
42.109
36.529
32.987
28.555
2i
f1 (ppm)

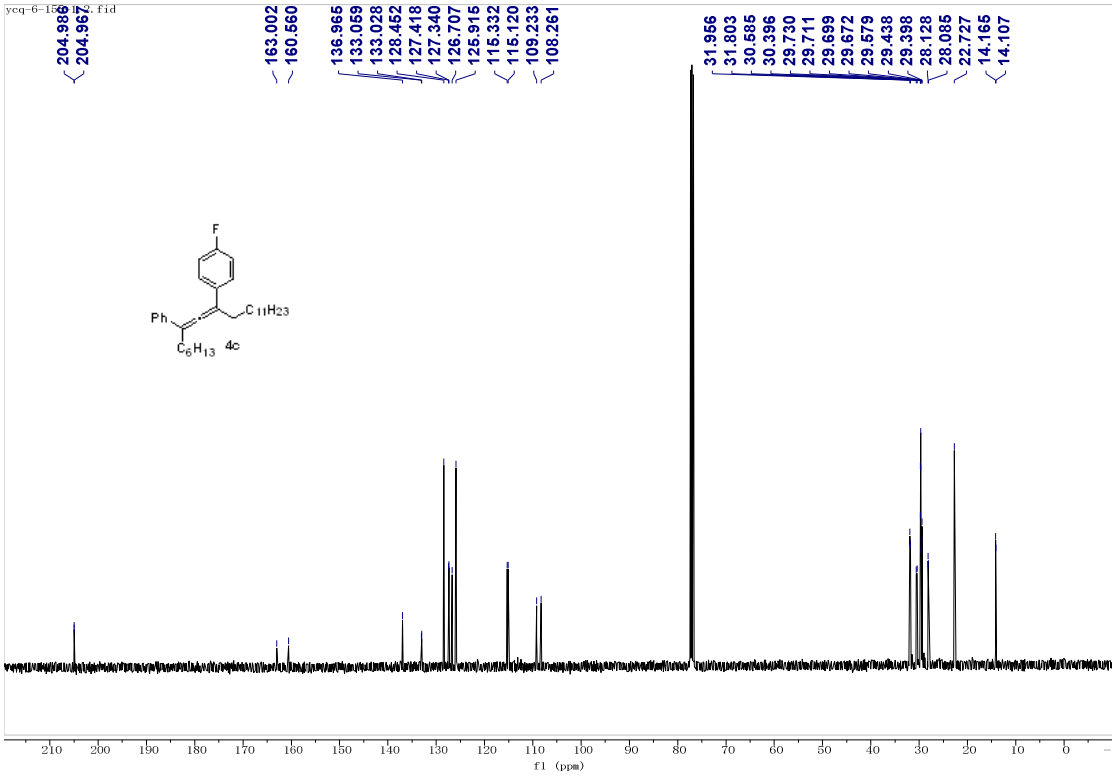

ycq-6-139-1
single_pulse
Ph
C11H23
Cl
4a
2.08
4.07
1.07
2.00
2.00
2.00
2.03
3.09
2.04
2.42
2.07
16.33
3.06
f1 (ppm)

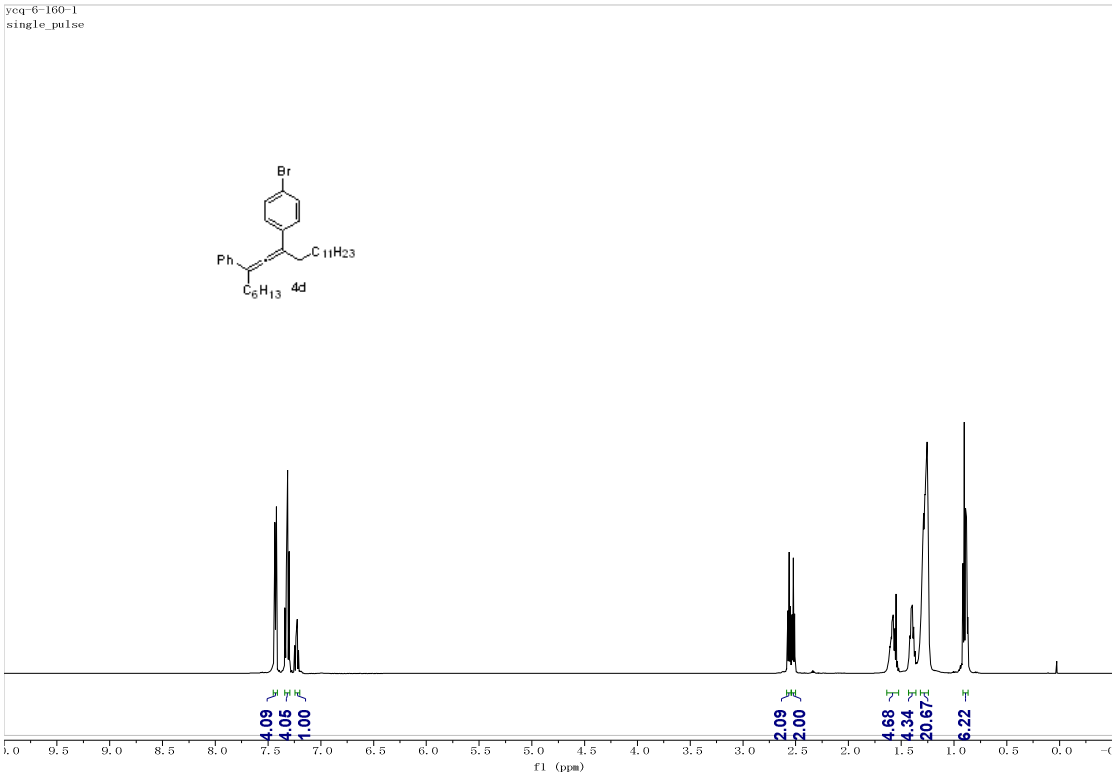

ycq-6-139-1
single pulse decoupled gated NOE
204.803
136.789
133.706
129.378
128.631
126.946
125.948
110.035
107.777
45.059
32.072
31.105
30.581
29.880
29.821
29.784
29.679
29.511
28.303
27.648
22.850
21.221
14.284
Ph
C11H23
Cl
4a
f1 (ppm)

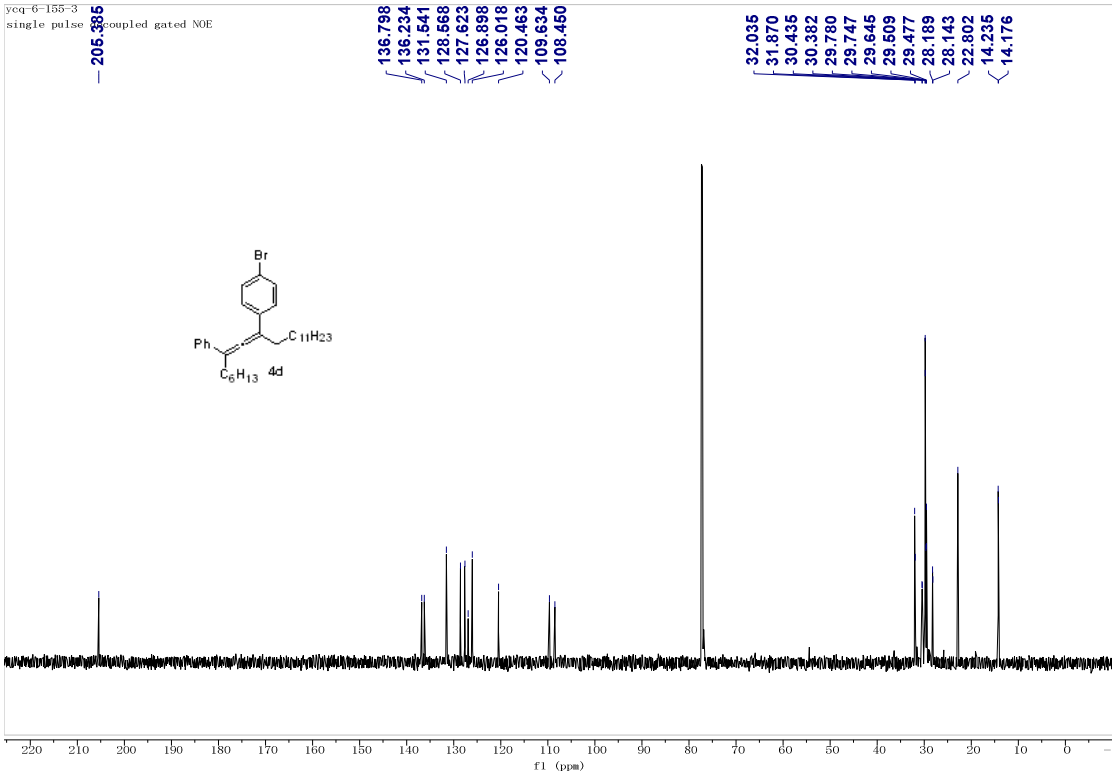

ycq-6-131-2
single_pulse
Ph
C11H23
C6H13
4b
2.14
2.00
2.05
1.04
2.00
4.05
3.08
4.16
4.11
20.39
6.48
f1 (ppm)

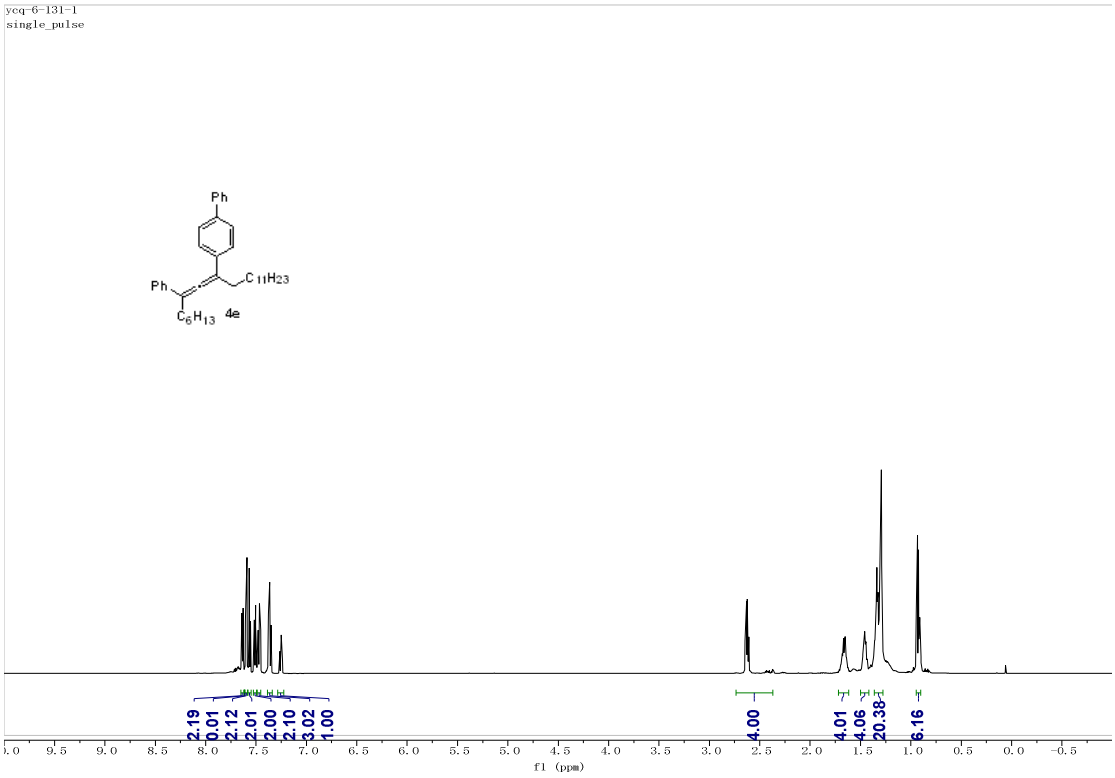

ycq-6-131-2
single pulse decoupled gated NOE
205.149
137.365
136.424
134.176
129.246
128.486
126.620
126.026
125.949
108.999
32.072
31.929
30.534
29.881
29.824
29.793
29.707
29.585
29.515
28.280
28.260
22.842
21.195
14.271
14.218
Ph
C11H23
C6H13
4b
f1 (ppm)

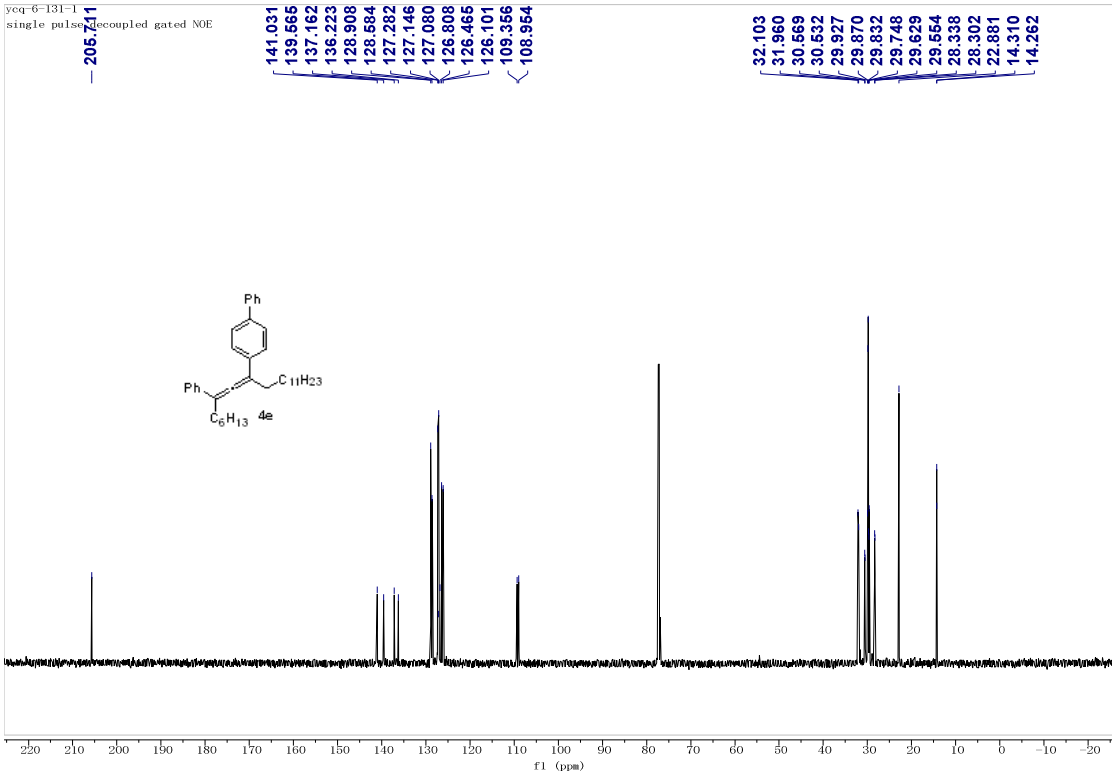

ycq-6-155-1.1.fid
F
Ph
C11H23
C6H13
4c
2.00
2.00
2.01
1.00
2.03
4.00
4.70
4.07
20.18
6.19
f1 (ppm)

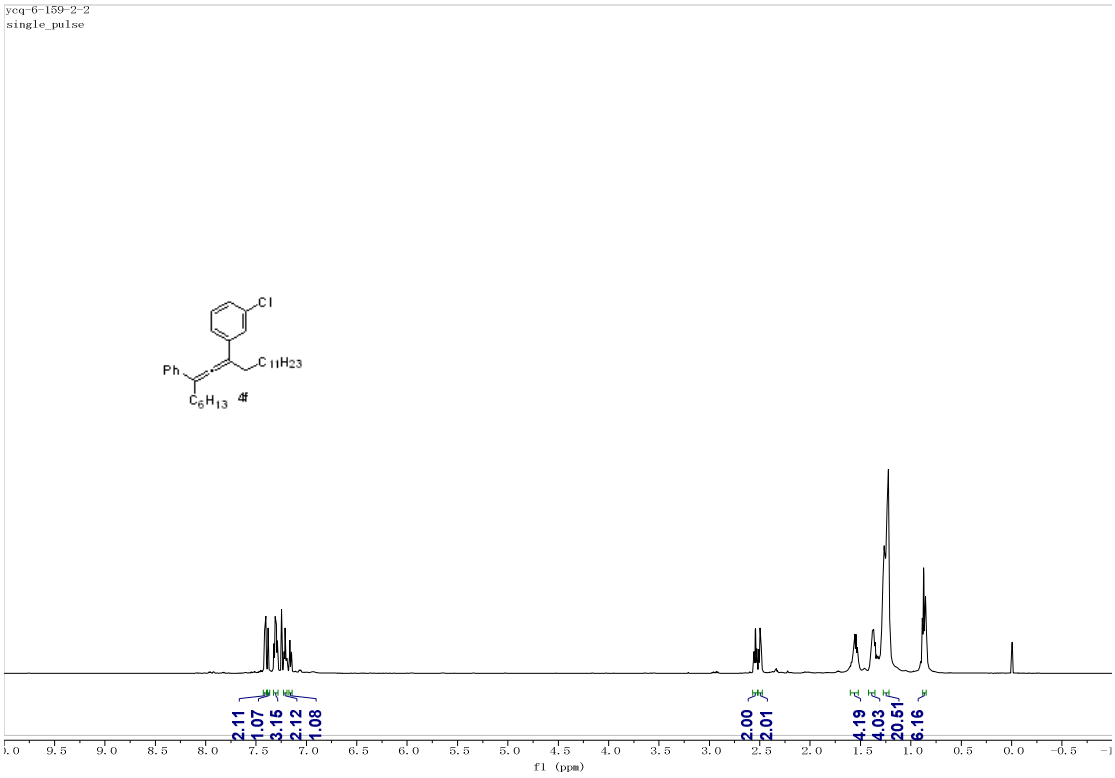

ycq-6-155-2.1.fid
204.986
204.967
163.002
160.560
136.965
133.059
133.028
128.452
127.418
127.340
126.707
125.915
115.332
116.120
109.233
108.261
31.956
31.803
30.585
30.396
29.730
29.711
29.699
29.672
29.579
29.438
29.398
28.128
28.085
22.727
14.165
14.107
F
Ph
C11H23
C6H13
4c
f1 (ppm)

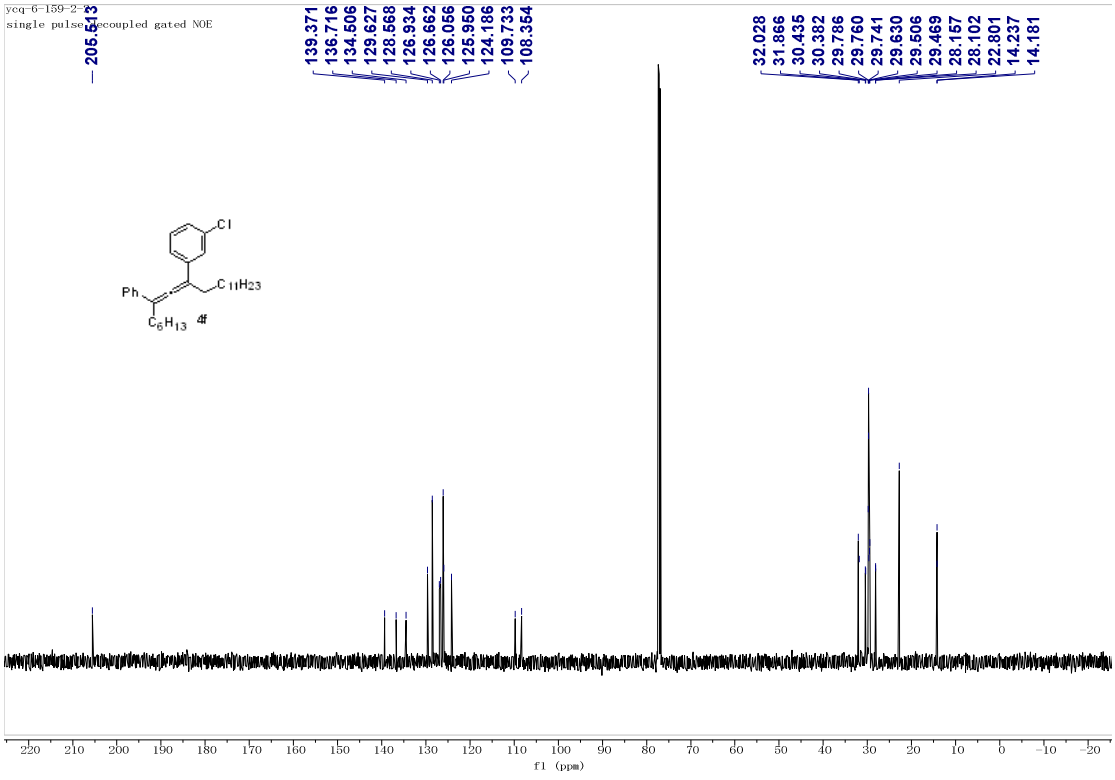

ycq-6-160-1
single_pulse
Br
Ph
C11H23
C6H13
4d
4.09
4.05
1.00
2.09
2.00
4.68
4.34
20.67
6.22
f1 (ppm)

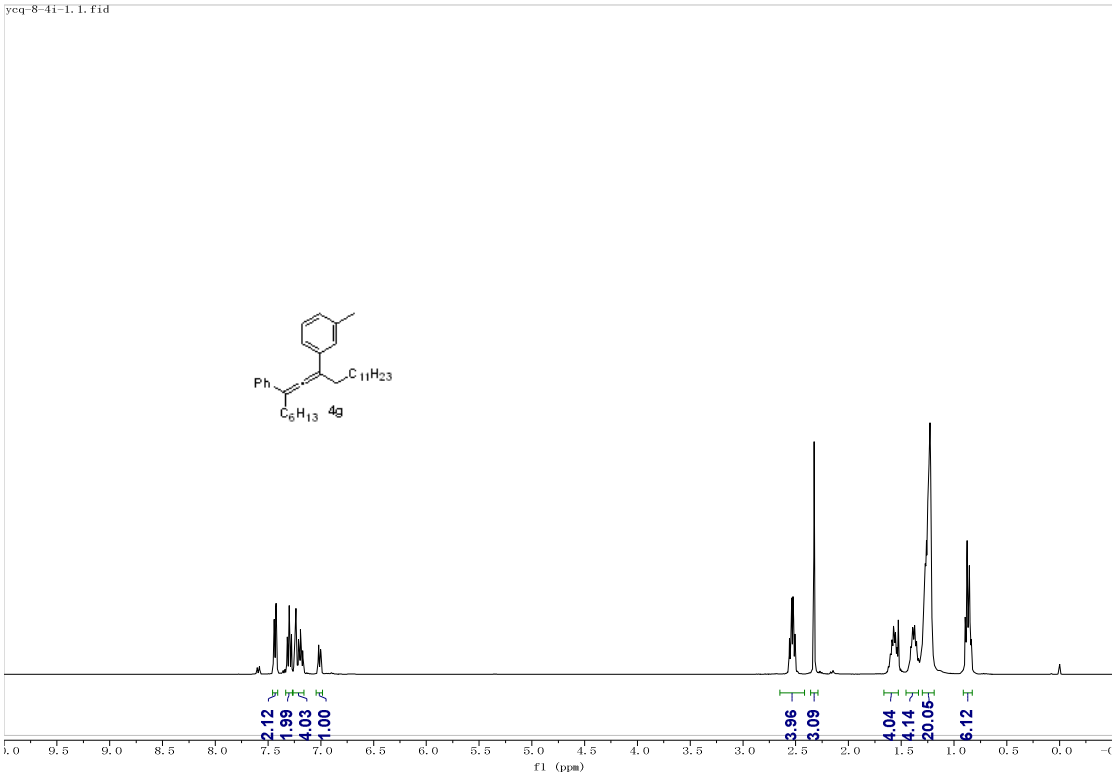

ycq-6-155-3
single pulse decoupled gated NOE
205.385
136.798
136.234
131.541
128.568
127.623
126.898
126.018
120.463
109.634
108.450
32.035
31.870
30.435
30.382
29.780
29.747
29.645
29.509
29.477
28.189
28.143
22.802
14.235
14.176
Br
Ph
C11H23
C6H13
4d
f1 (ppm)

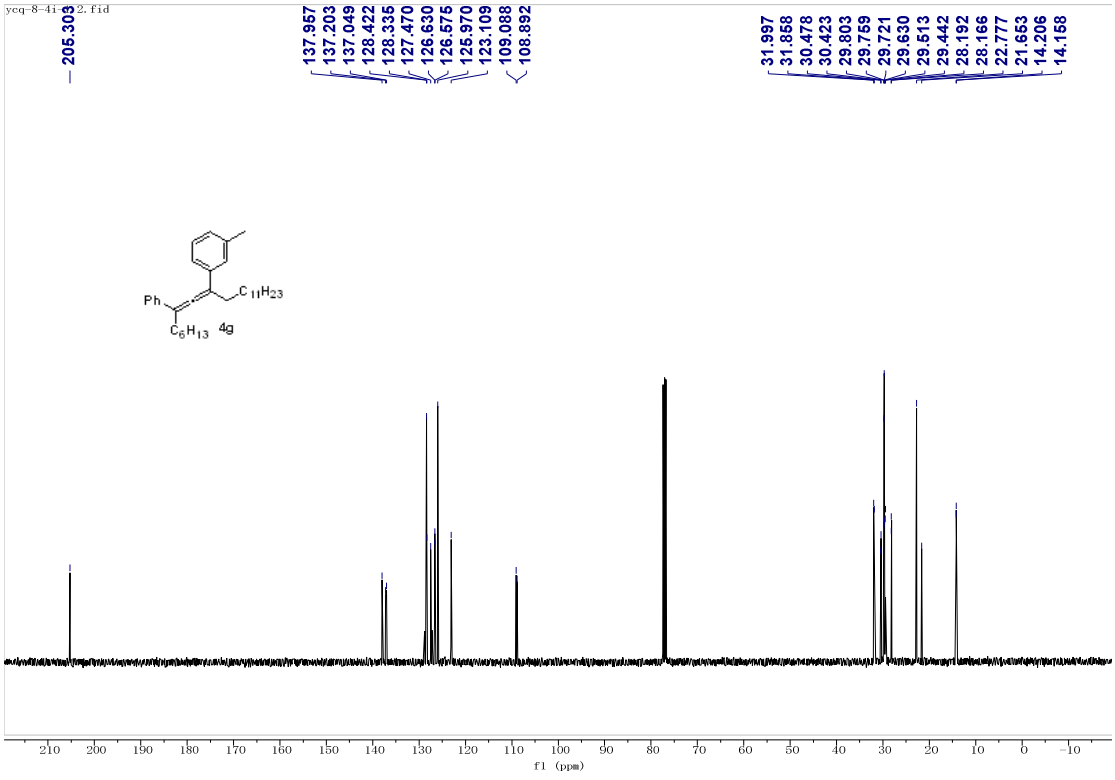

ycq-6-131-1
single_pulse
Ph
Ph
C11H23
C6H13
4e
2.19
0.01
2.12
2.01
2.00
2.10
3.02
1.00
4.00
4.01
4.06
20.38
6.16
f1 (ppm)

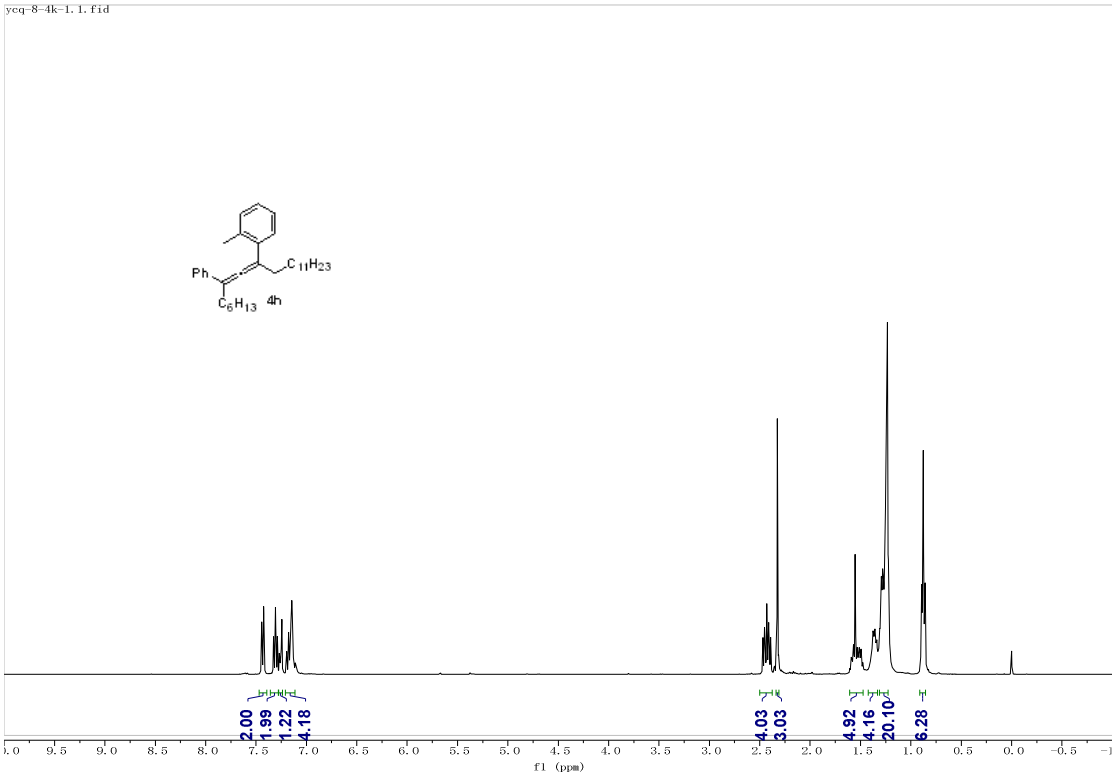

ycq-6-131-1
single pulse decoupled gated NOE
205.711
141.031
139.565
137.162
136.223
128.908
128.584
127.282
127.146
127.080
126.808
126.465
126.101
109.356
108.954
32.103
31.960
30.569
30.532
29.927
29.870
29.832
29.748
29.629
29.554
28.338
28.302
22.881
14.310
14.262
Ph
Ph
C11H23
C6H13
4e
f1 (ppm)

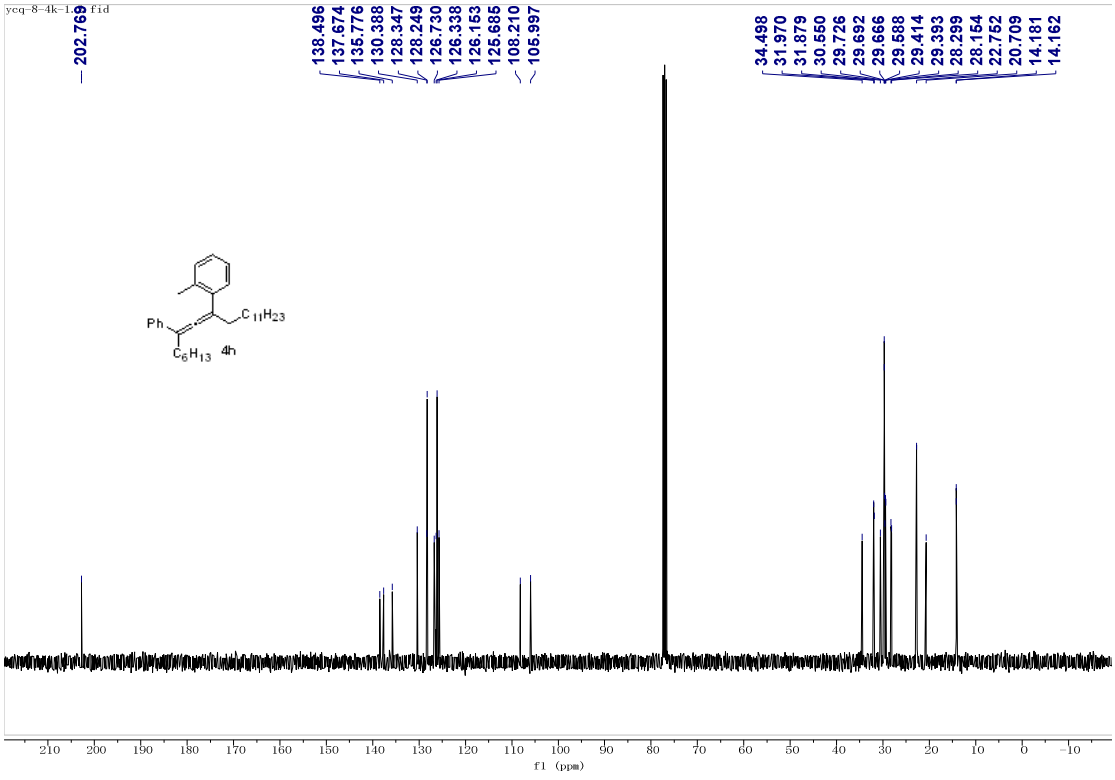

ycq-6-159-2-2
single_pulse
Cl
Ph
C11H23
C6H13
4f
2.11
1.07
3.15
2.12
1.08
2.00
2.01
4.19
4.03
20.51
6.16
f1 (ppm)

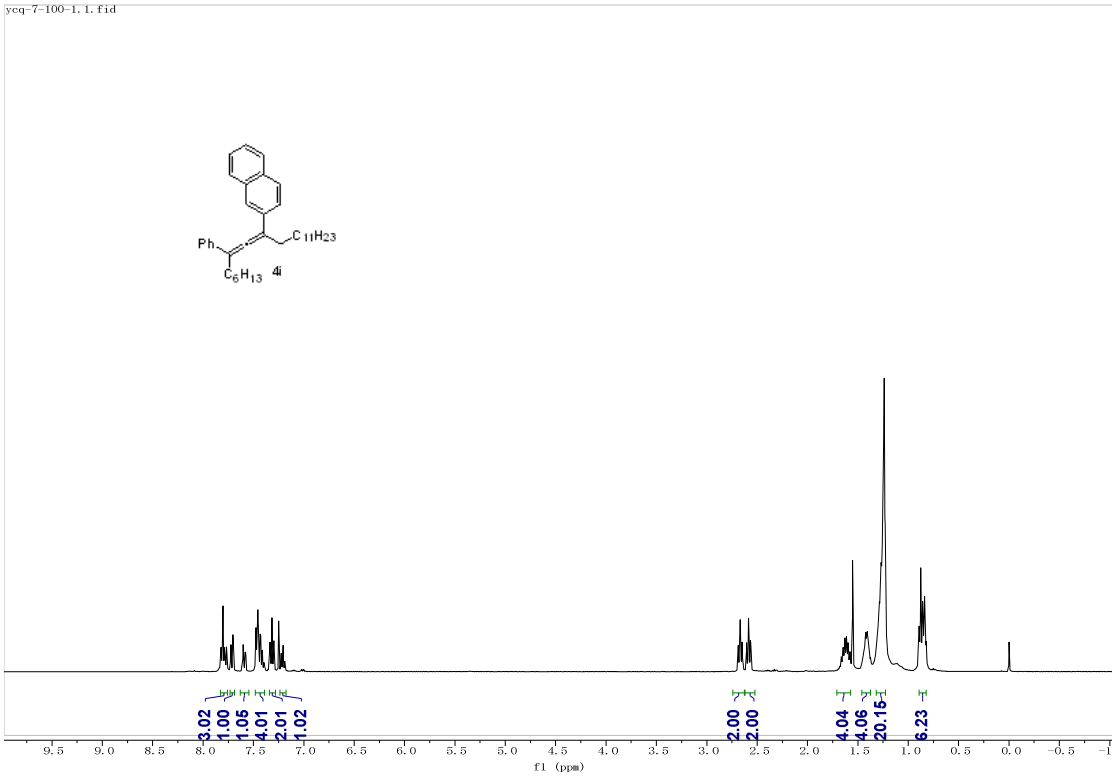

ycq-6-159-2-2
single pulse decoupled gated NOE
205.513
139.371
136.716
134.506
129.627
128.568
126.934
126.662
126.056
125.950
124.186
109.733
108.354
32.028
31.866
30.435
30.382
29.786
29.760
29.741
29.630
29.606
29.469
28.157
28.102
22.801
14.237
14.181
Cl
Ph
C11H23
C6H13
4f
f1 (ppm)

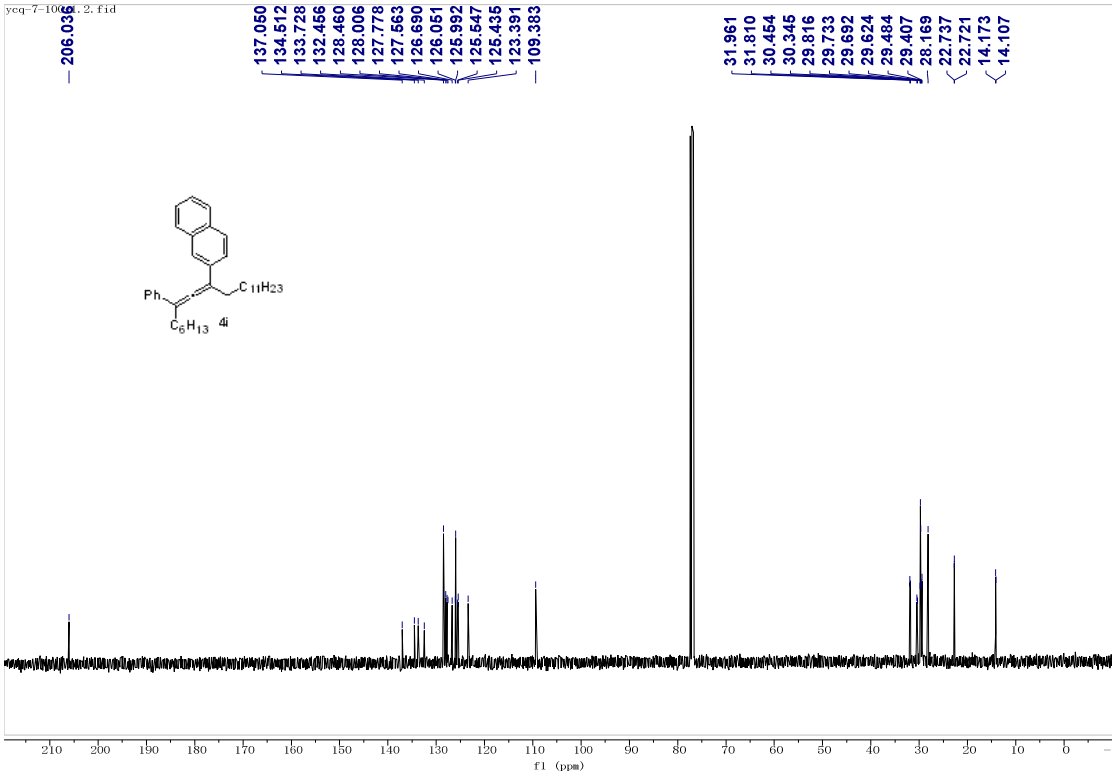

ycq-8-4i-1.1.fid
Ph
C11H23
C6H13
4g
2.12
1.99
4.03
1.00
3.96
3.09
4.04
4.14
20.05
6.12
f1 (ppm)

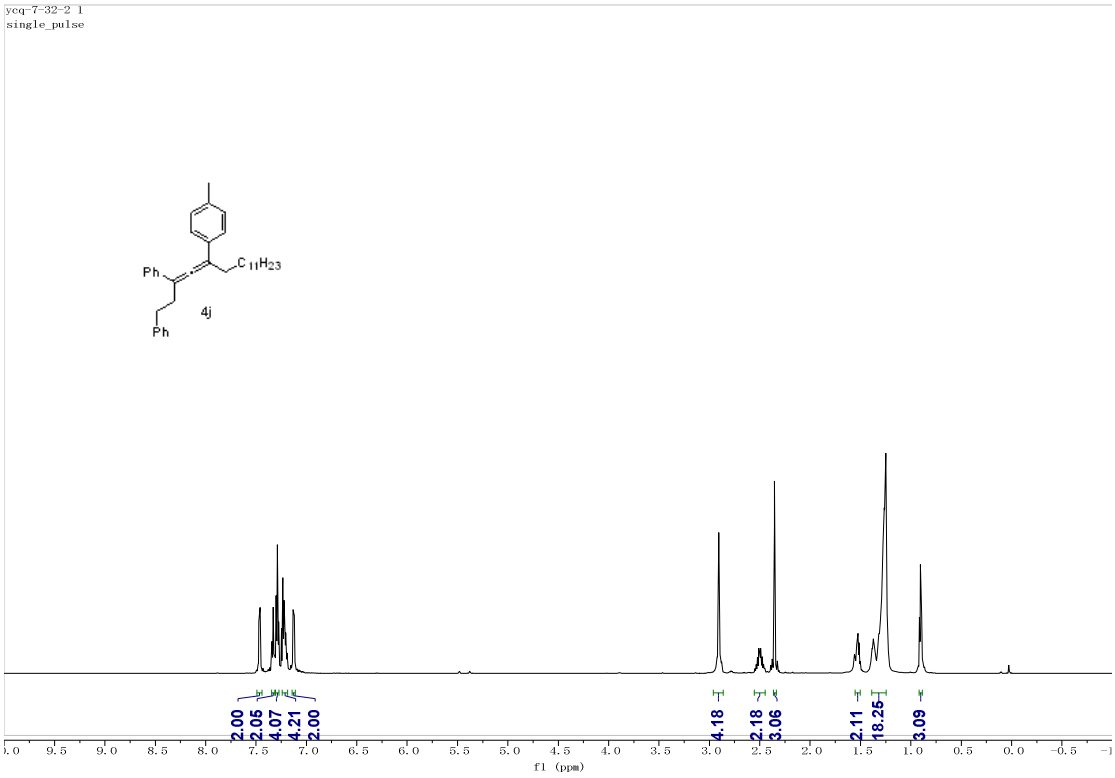

ycq-8-4i-2.fid
205.303
137.957
137.203
137.049
128.422
128.335
127.470
126.630
126.575
125.970
123.109
109.088
108.892
31.997
31.858
30.478
30.423
29.803
29.759
29.721
29.630
29.513
29.442
28.192
28.166
22.777
21.653
14.206
14.158
Ph
C11H23
C6H13
4g
f1 (ppm)

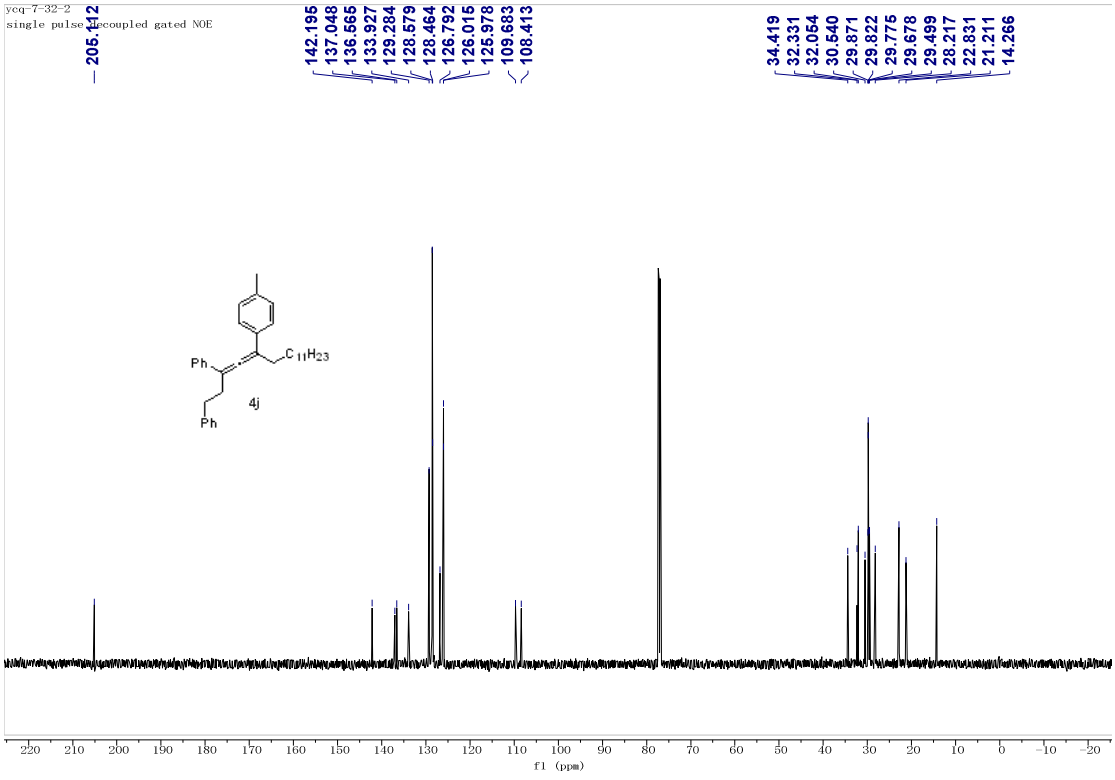

ycq-8-4k-1.1.fid
Ph
C6H13
C11H23
4h
2.00
1.99
1.22
4.18
4.03
3.03
4.92
4.16
20.10
6.28
f1 (ppm)

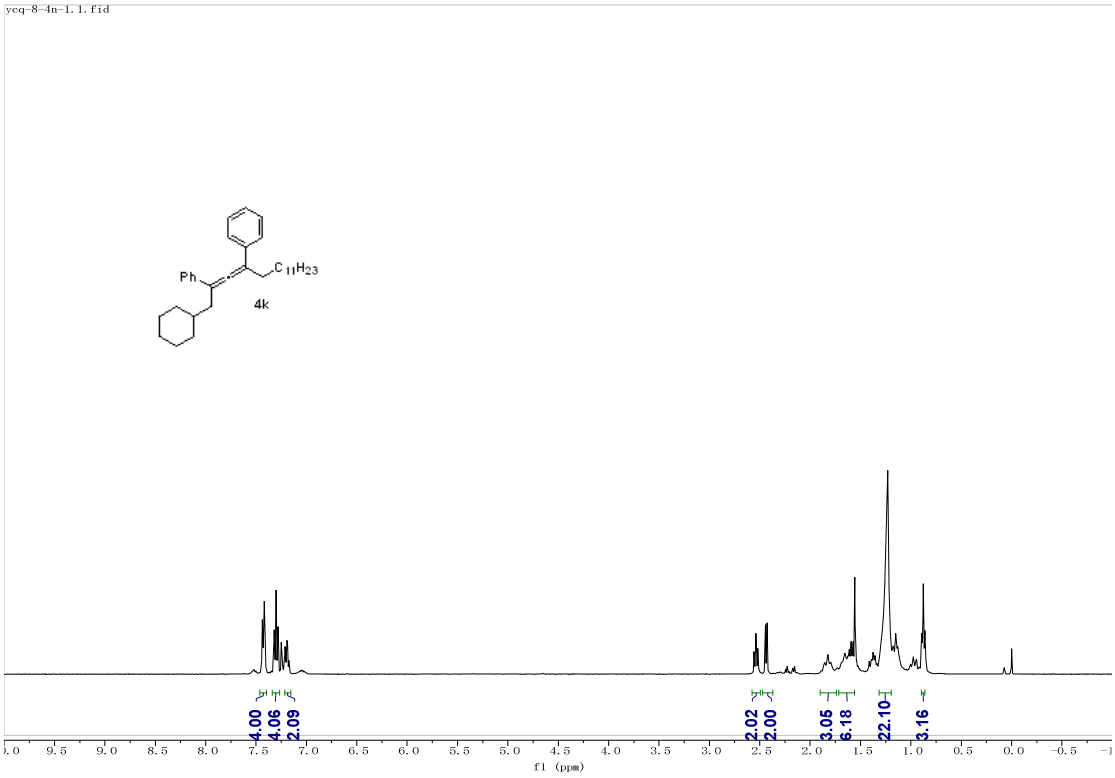

ycq-8-4k-1.2.fid
202.769
138.496
137.674
135.776
130.388
128.347
128.249
126.730
126.338
126.153
125.685
108.210
105.997
34.498
31.970
31.879
30.550
29.726
29.692
29.666
29.588
29.414
29.393
28.299
28.154
22.752
20.709
14.181
14.162
Ph
C6H13
C11H23
4h
f1 (ppm)

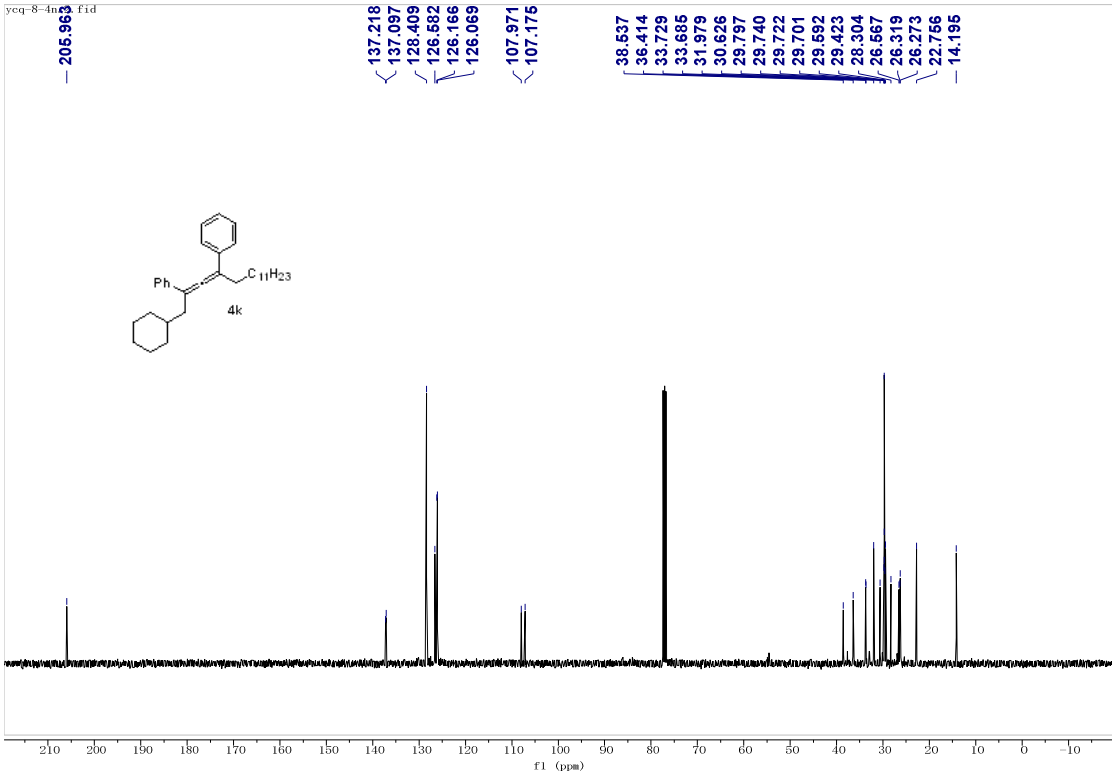

yeq-7-100-1.1.fid
Ph
C11H23
C6H13
4i
3.02
1.00
1.05
4.01
2.01
1.02
2.00
2.00
4.04
4.06
20.15
6.23
f1 (ppm)

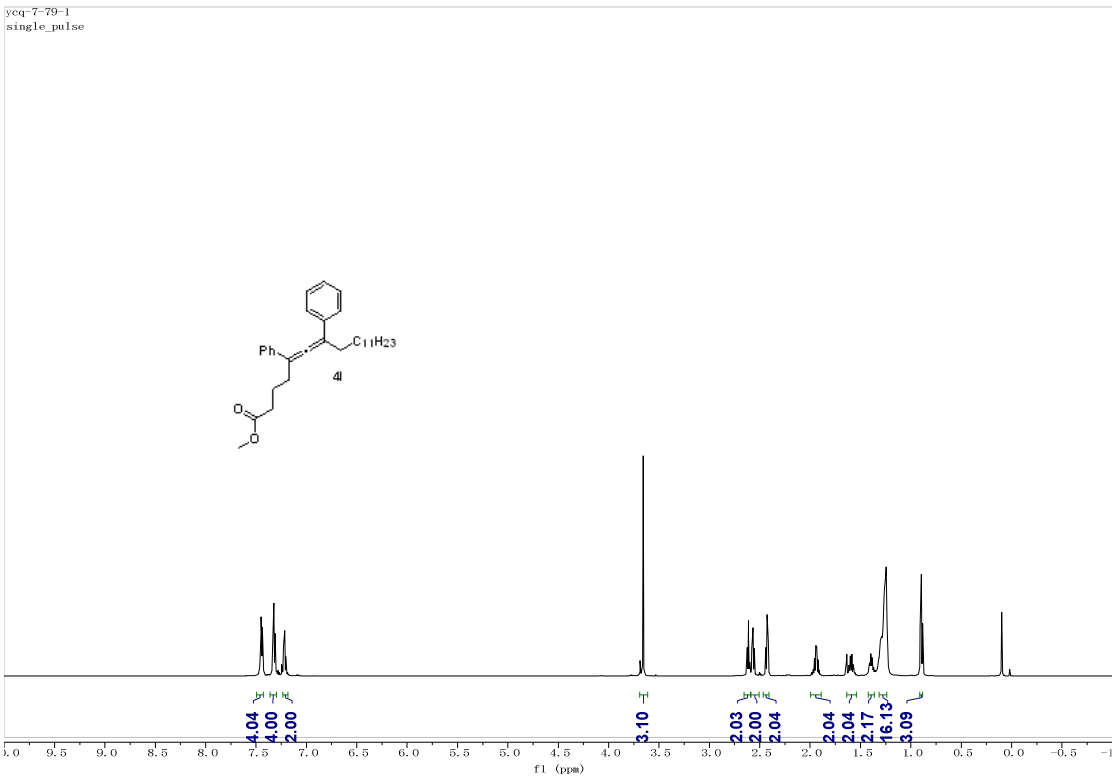

yeq-7-100-1.2.fid
206.036
137.050
134.512
133.728
132.456
128.460
128.006
127.778
127.563
126.690
126.051
125.992
125.547
125.435
123.391
109.383
31.961
31.810
30.454
30.345
29.816
29.733
29.692
29.624
29.484
29.407
28.169
22.737
22.721
14.173
14.107
Ph
C11H23
C6H13
4i
f1 (ppm)

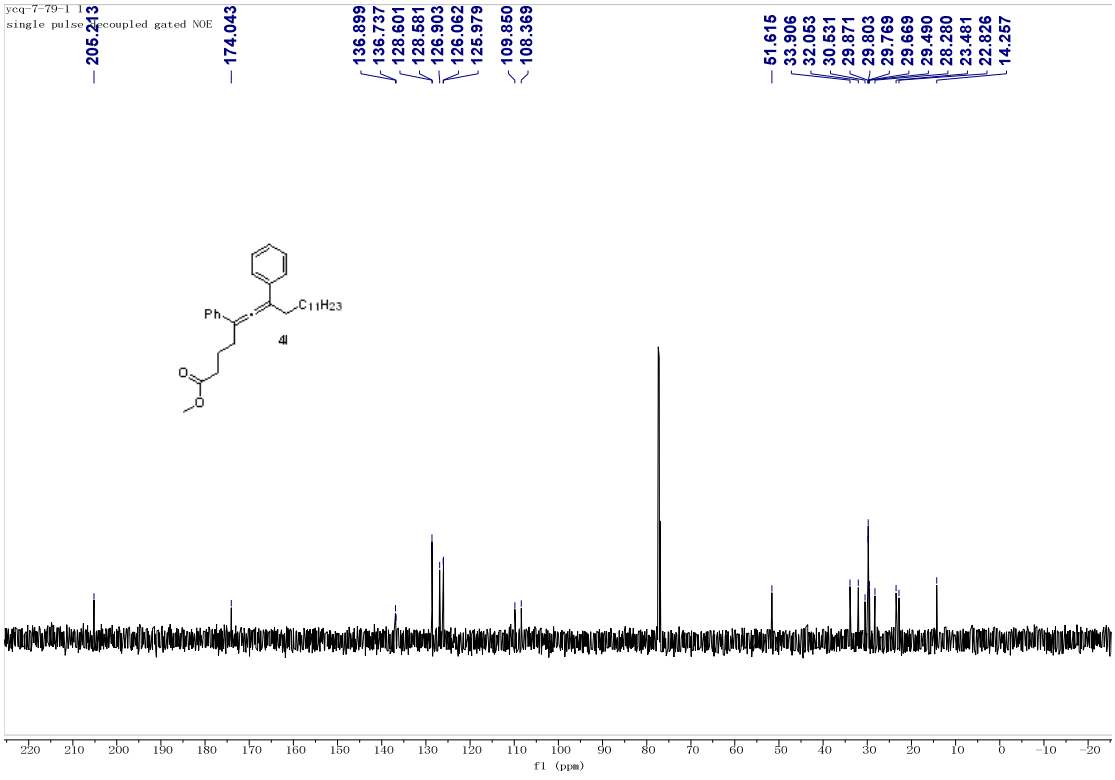

ycq-7-32-2 1
single_pulse
Ph
C11H23
Ph
4j
2.00
2.05
4.07
4.21
2.00
4.18
2.18
3.06
2.11
18.25
3.09
f1 (ppm)

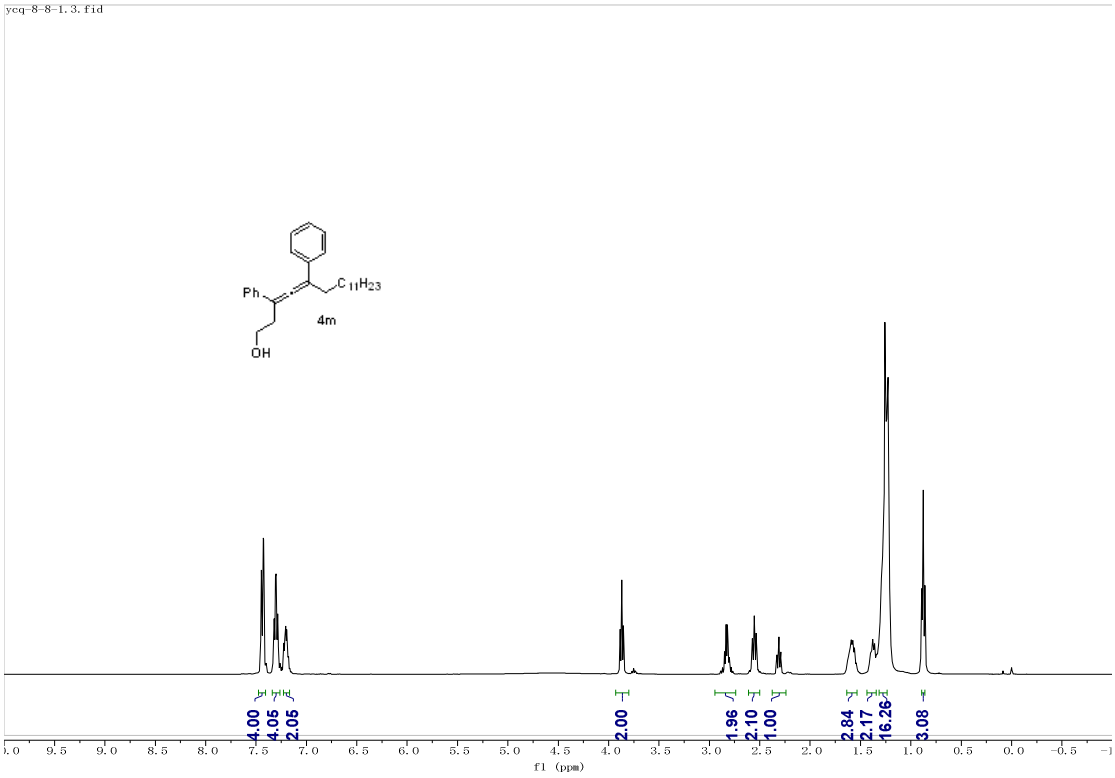

ycq-7-32-2
single pulse decoupled gated NOE
206.112
142.195
137.048
136.565
133.927
129.284
128.579
128.464
126.792
126.015
125.978
109.683
108.413
34.419
32.331
32.054
30.540
29.871
29.822
29.775
29.678
29.499
28.217
22.831
21.211
14.266
Ph
C11H23
Ph
4j
f1 (ppm)

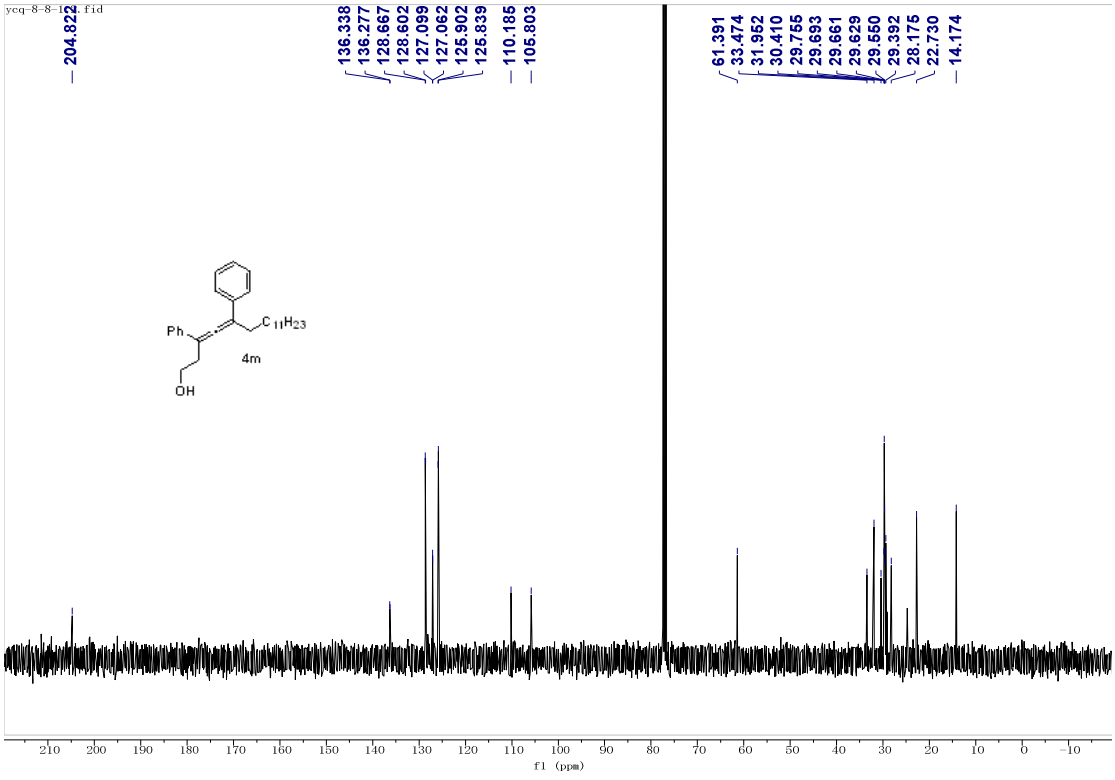

ycq-8-4n-1.1.fid
Ph
C11H23
4k
4.00
4.06
2.09
2.02
2.00
3.05
6.18
22.10
3.16
f1 (ppm)

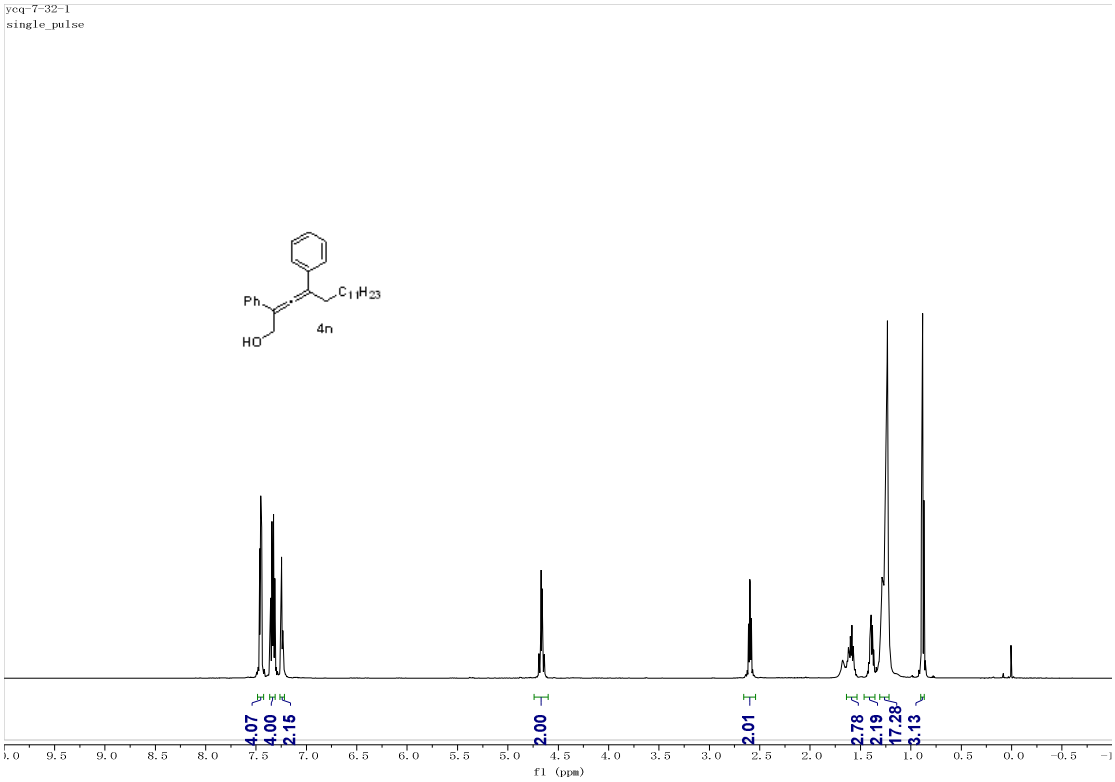

ycq-8-4n-13.fid
206.963
137.218
137.097
128.409
126.582
126.166
126.069
107.971
107.175
38.537
36.414
33.729
33.685
31.979
30.626
29.797
29.740
29.722
29.701
29.592
29.423
28.304
26.567
26.319
26.273
22.756
14.195
Ph
C11H23
4k
f1 (ppm)

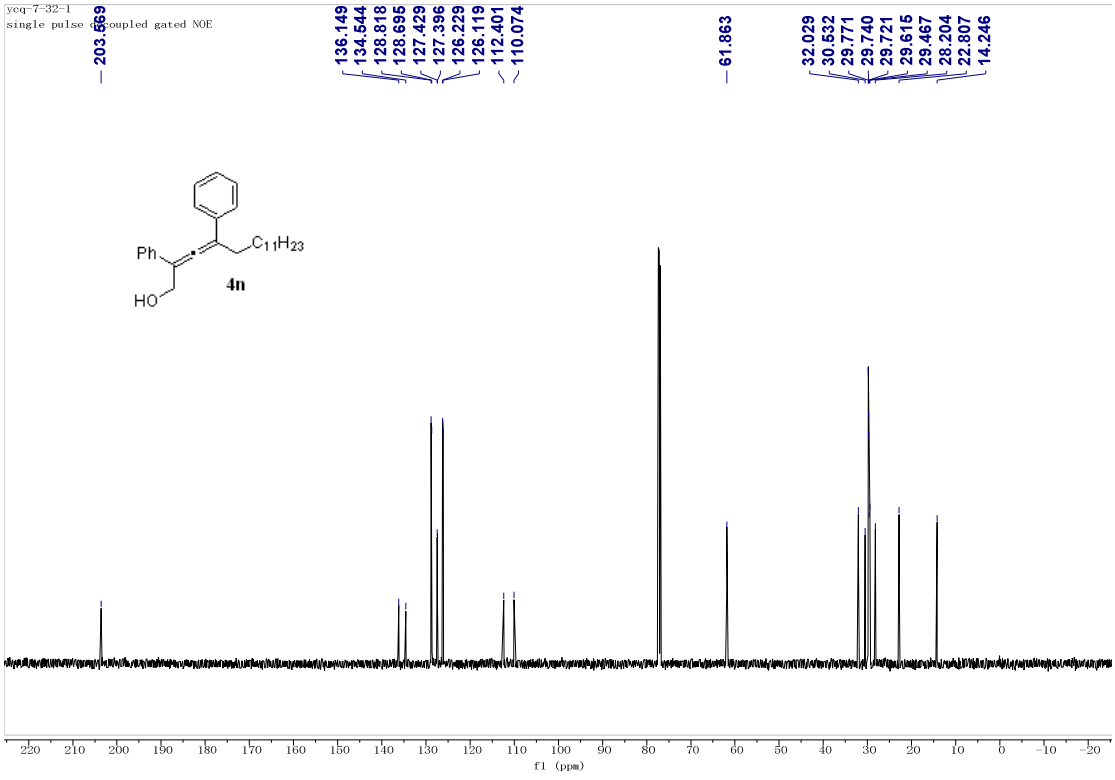

ycq-7-79-1
single_pulse
Ph
C11H23
4l
O
O
4.04
4.00
2.00
3.10
2.03
2.00
2.04
2.04
2.04
2.17
16.13
3.09
f1 (ppm)

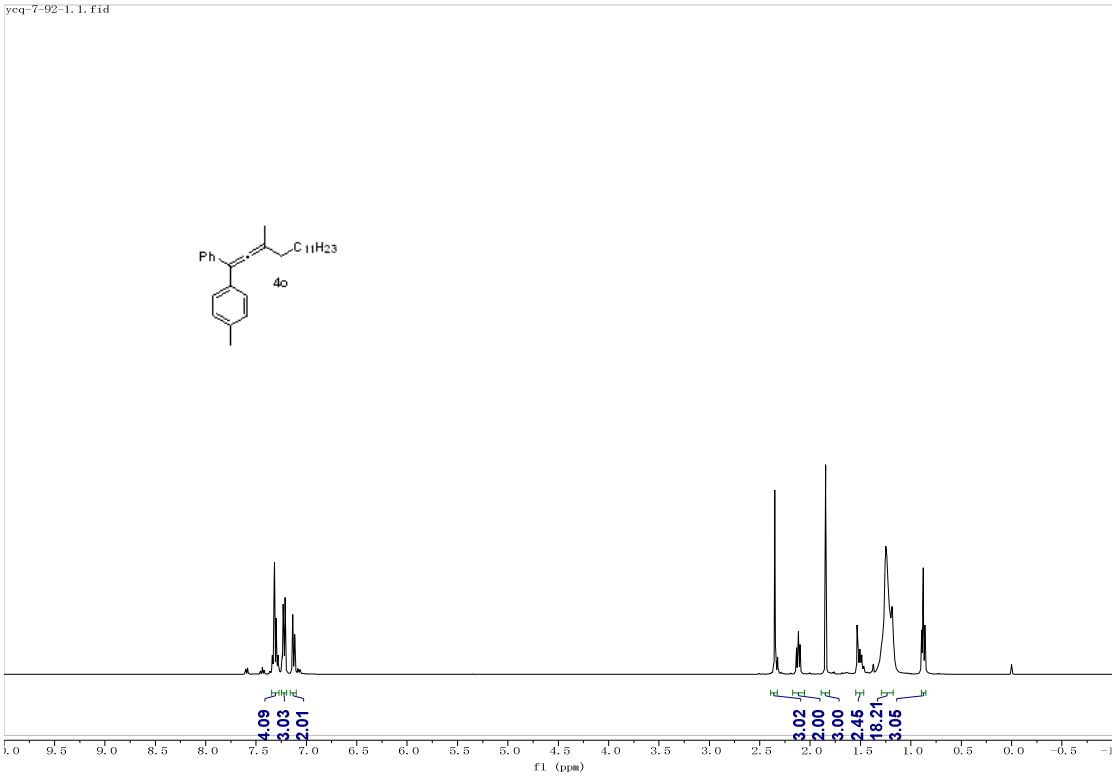

ycq-7-79-1 1
single pulse decoupled gated NOE
205.213
174.043
136.899
136.737
128.601
128.581
126.903
126.062
125.979
109.850
108.369
61.615
33.906
32.053
30.531
29.871
29.803
29.769
29.669
29.490
28.280
23.481
22.826
14.257
Ph
C11H23
4l
O
O
f1 (ppm)

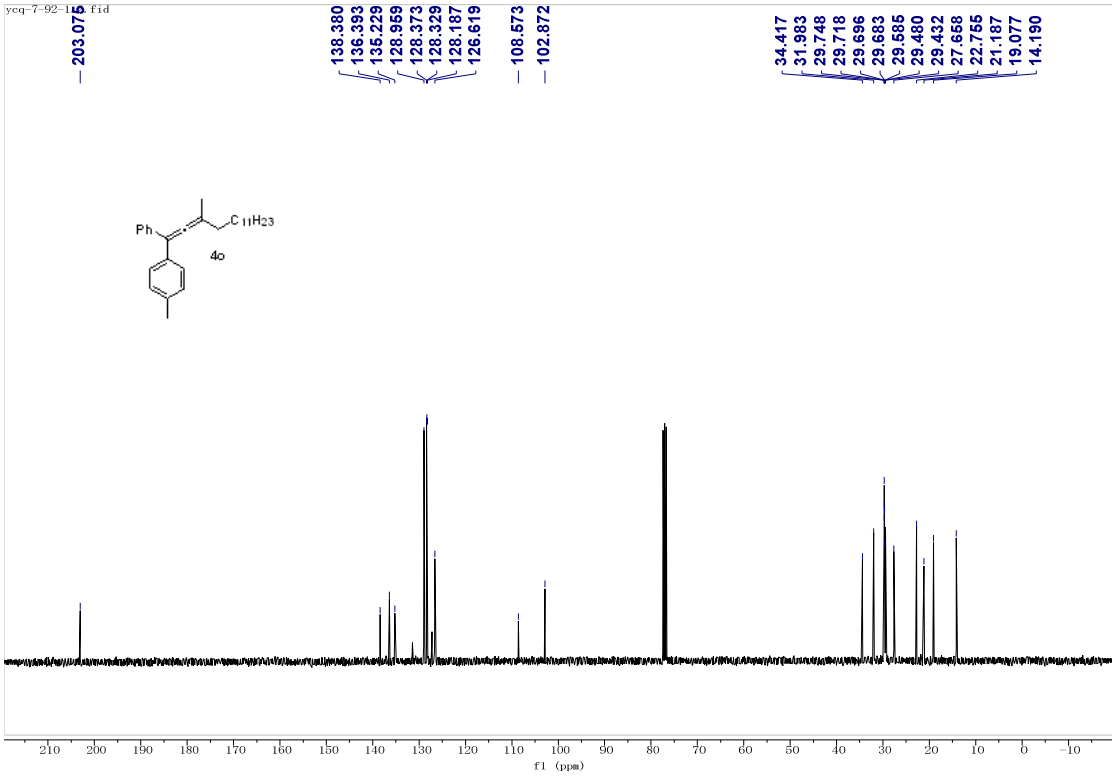

ycq-8-8-1.3.fid
Ph
C11H23
4m
OH
4.00
4.05
2.05
2.00
1.96
2.10
1.00
2.84
2.17
16.26
3.08
f1 (ppm)

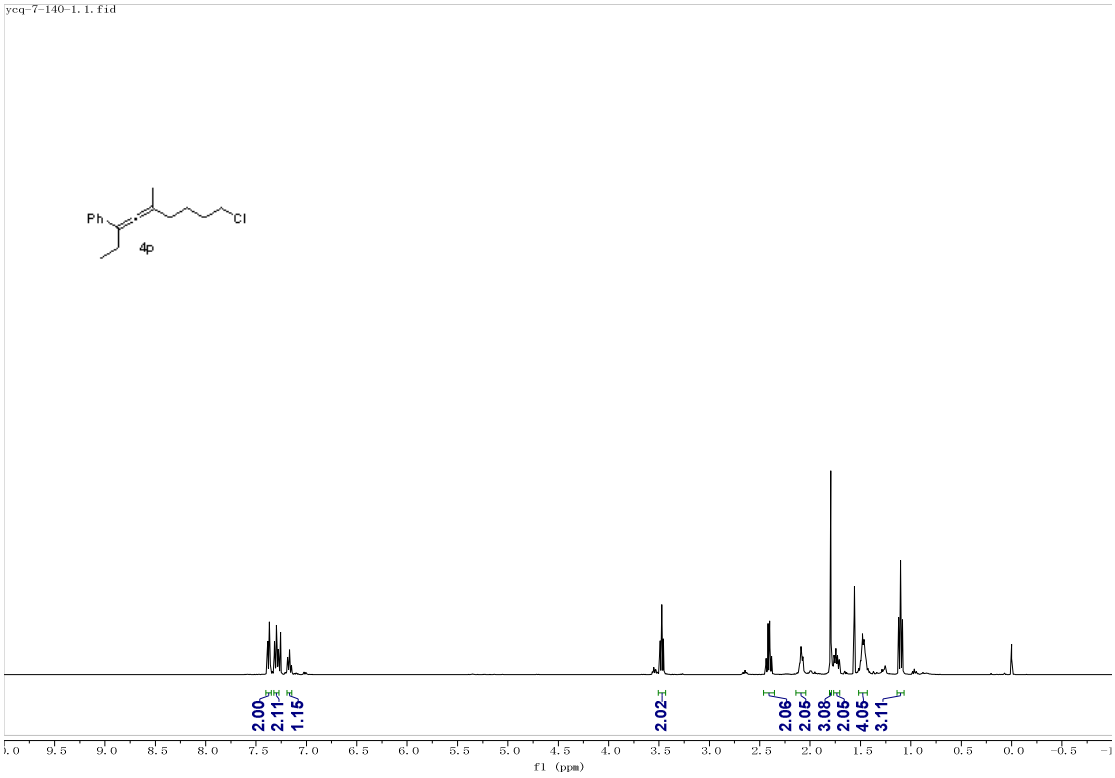

ycq-8-8-1.4.fid
204.822
136.338
136.277
128.687
128.602
127.099
127.062
125.902
125.839
110.185
105.803
61.391
33.474
31.952
30.410
29.755
29.693
29.661
29.629
29.550
29.392
28.175
22.730
14.174
Ph
C11H23
4m
OH
f1 (ppm)

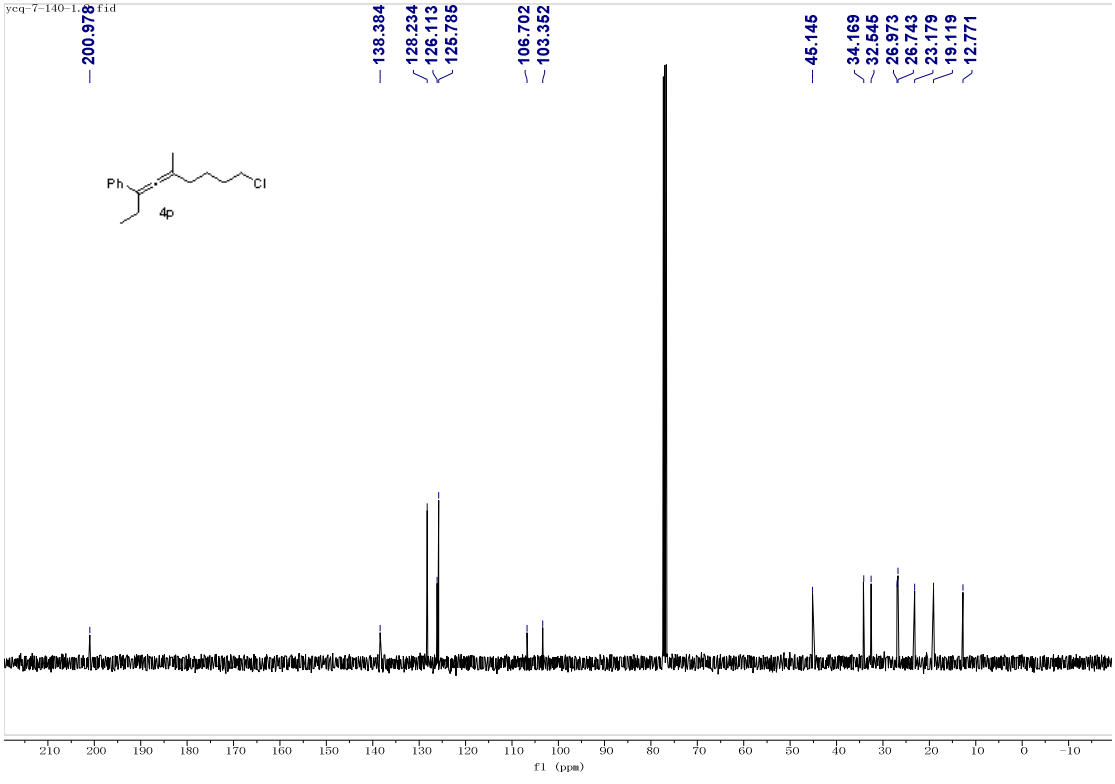

ycq-7-32-1
single_pulse
Ph
HO
C11H23
4n
4.07
4.00
2.15
2.00
2.01
2.78
2.19
17.28
3.13
f1 (ppm)

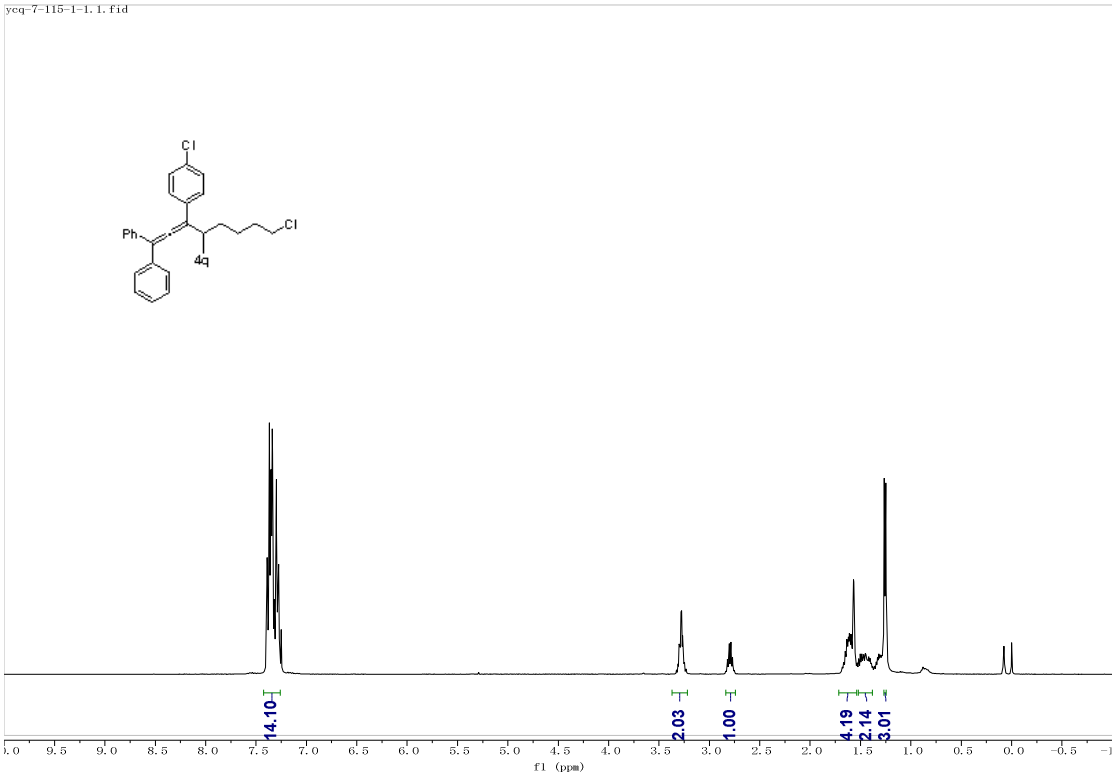

ycq-7-32-1
single pulse decoupled gated NOE
203.669
136.149
134.544
128.818
128.695
127.429
127.396
126.229
126.119
112.401
110.074
61.863
32.029
30.532
29.771
29.740
29.721
29.615
29.467
28.204
22.807
14.246
Ph
HO
C11H23
4n
f1 (ppm)

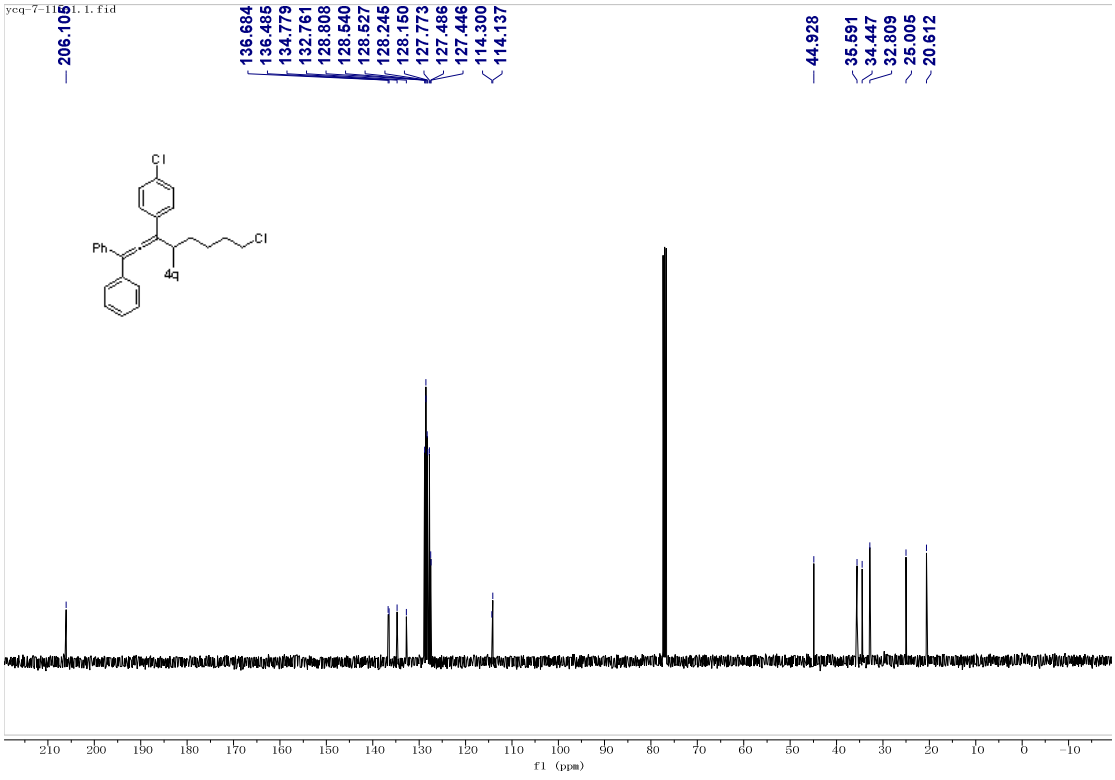

ycq-7-92-1.1.fid
Ph
C11H23
4o
4.09
3.03
2.01
3.02
2.00
3.00
2.45
18.21
3.05
f1 (ppm)

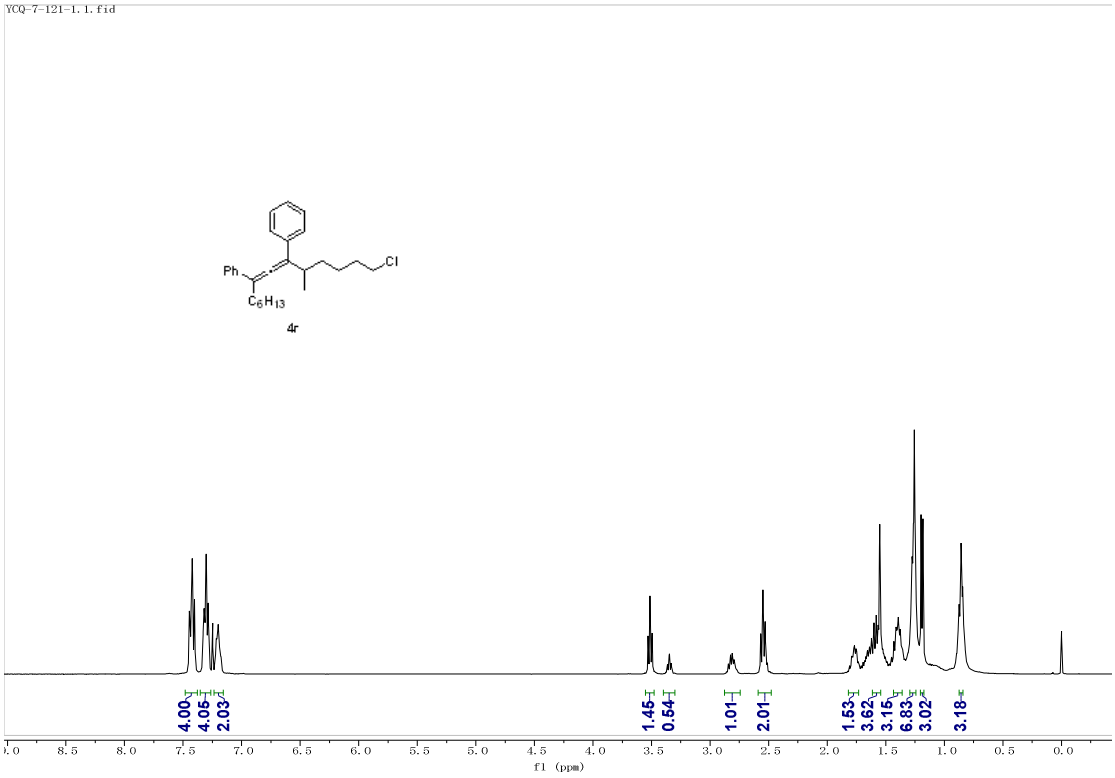

ycq-7-92-1
203.076
138.380
136.393
135.229
128.959
128.373
128.329
128.187
126.619
108.573
102.872
34.417
31.983
29.748
29.718
29.696
29.683
29.585
29.480
29.432
27.658
22.755
21.187
19.077
14.190
Ph
C11H23
4o
f1 (ppm)

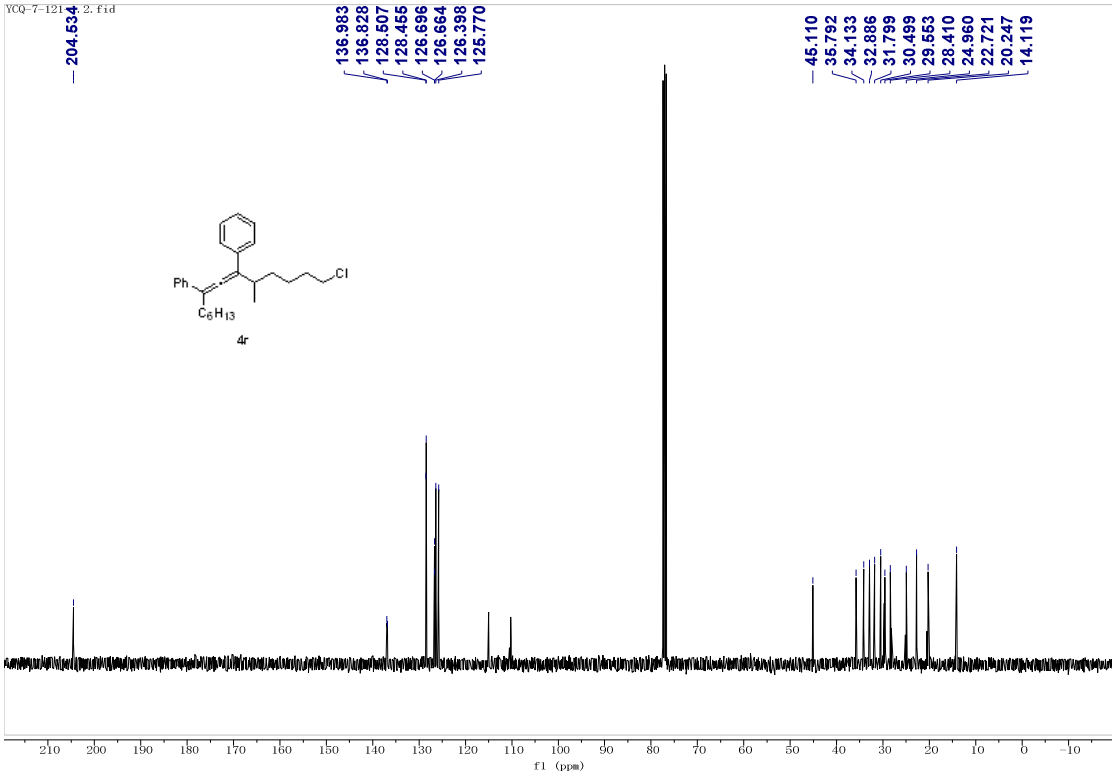

ycq-7-140-1.1.fid
Ph
Cl
4p
2.00
2.11
1.15
2.02
2.06
2.05
3.08
2.05
4.05
3.11
f1 (ppm)

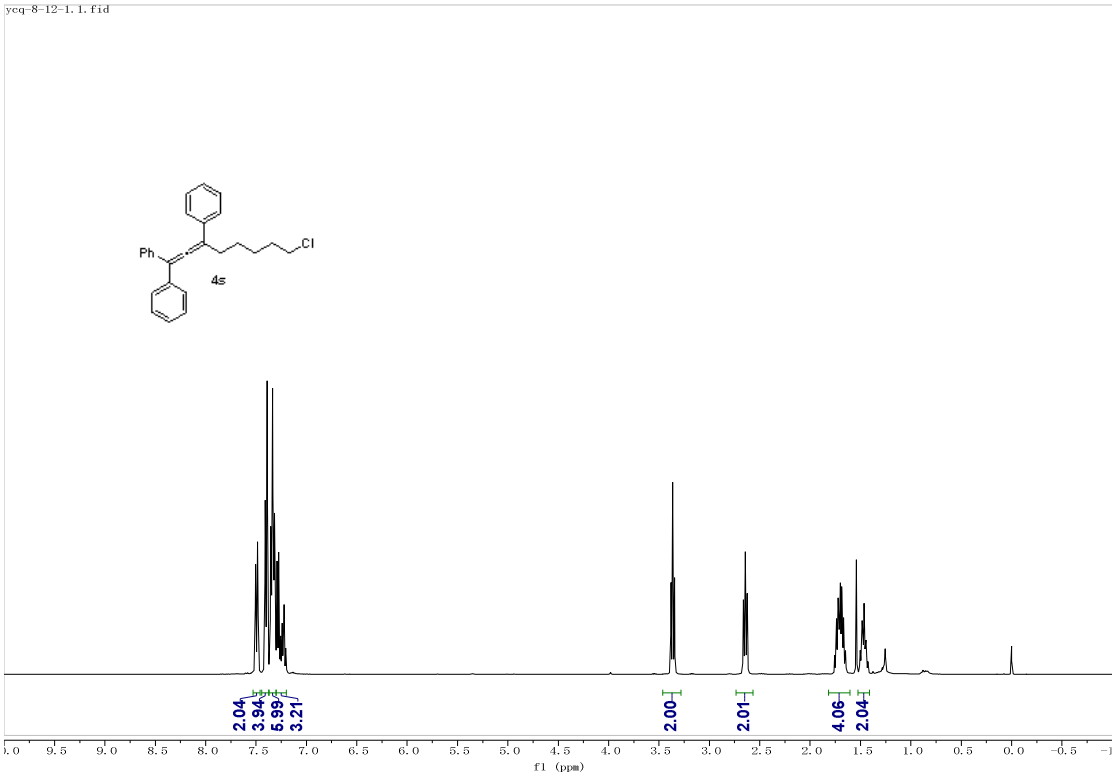

ycq-7-140-1.2.fid
200.978
138.384
128.234
126.113
125.785
106.702
103.352
45.145
34.169
32.545
26.973
26.743
23.179
19.119
12.771
Ph
Cl
4p
f1 (ppm)

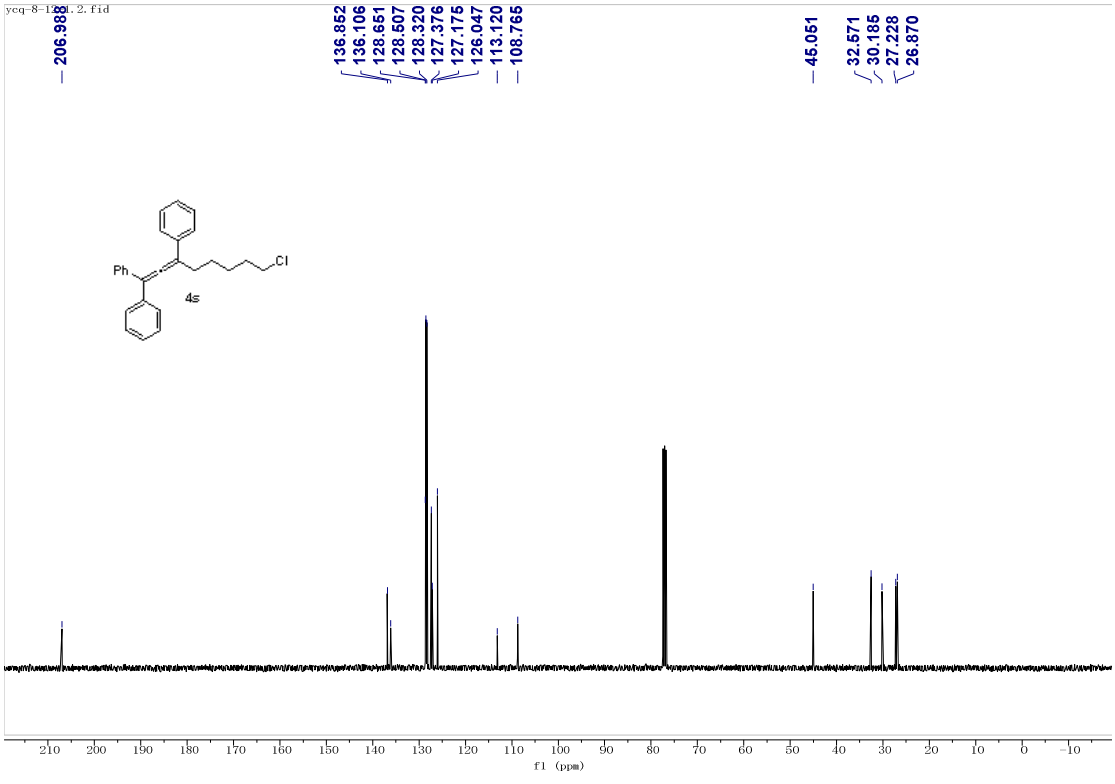

ycq-7-115-1-1.1.fid
Cl
Ph
Cl
4q
14.10
2.03
1.00
4.19
2.14
3.01
f1 (ppm)

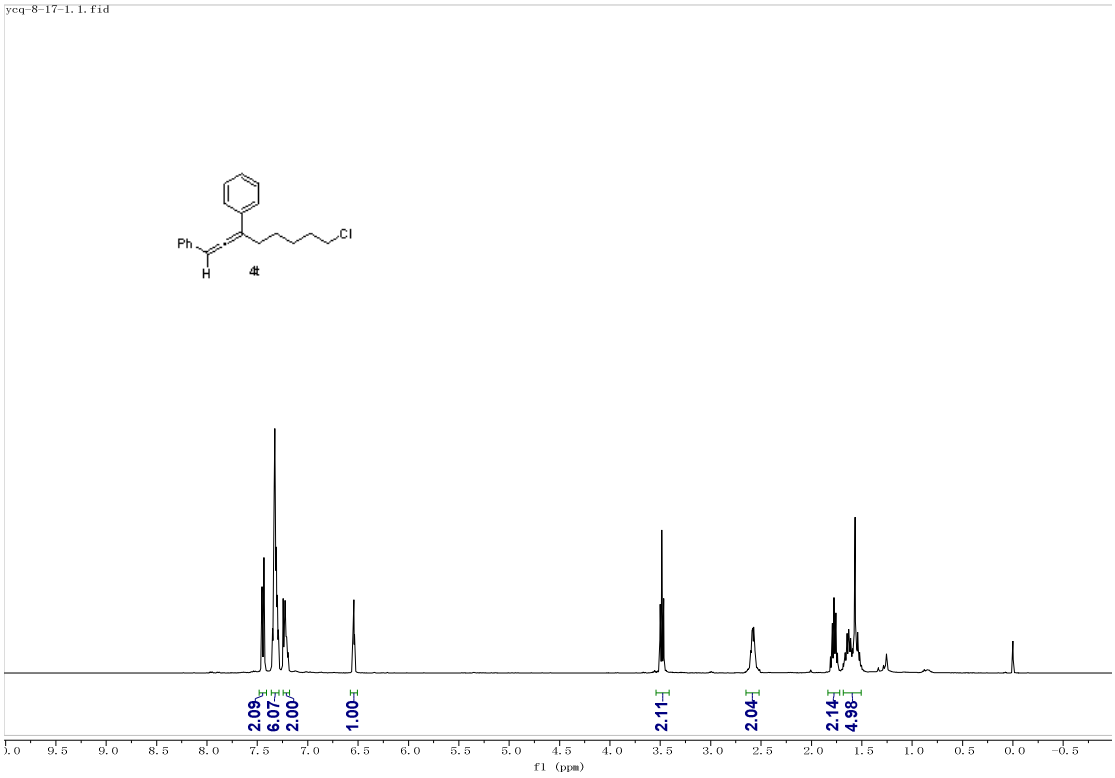

ycq-7-115-1.1.fid
206.105
136.684
136.485
134.779
132.761
128.808
128.540
128.527
128.245
128.150
127.773
127.486
127.446
114.300
114.137
44.928
35.591
34.447
32.809
25.005
20.612
Cl
Ph
Cl
4q
f1 (ppm)

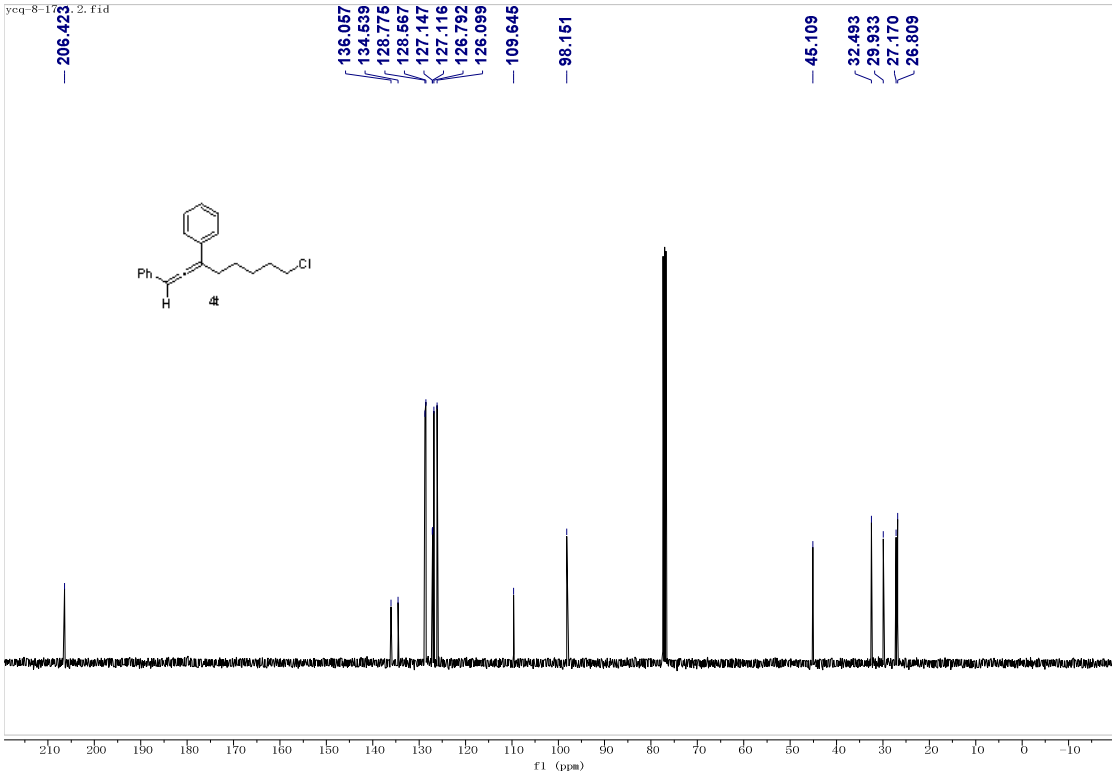

YCQ-7-121-1.1.fid
Ph
C6H13
Cl
4r
4.00
4.05
2.03
1.45
0.54
1.01
2.01
1.53
3.62
3.15
6.83
3.02
3.18
f1 (ppm)

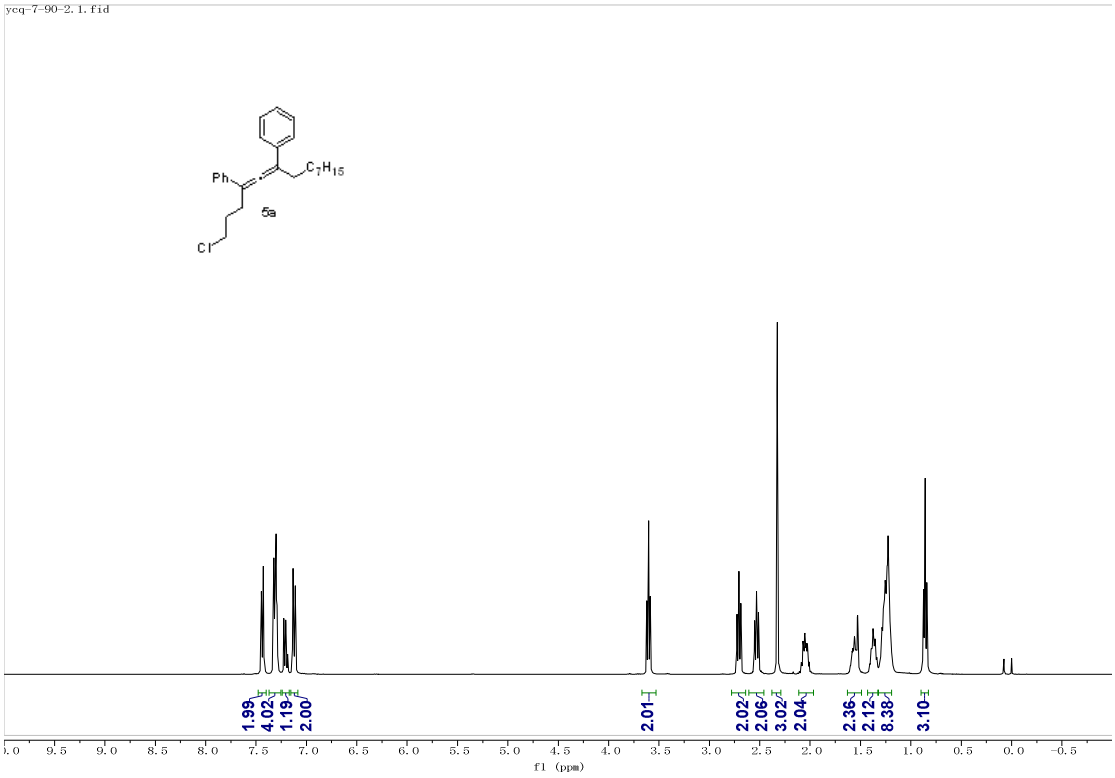

YCQ-7-121-2.fid
204.534
136.983
136.828
128.507
128.455
126.696
126.664
126.398
125.770
45.110
35.792
34.133
32.886
31.799
30.499
29.553
28.410
24.960
22.721
20.247
14.119
Ph
C6H13
Cl
4r
f1 (ppm)

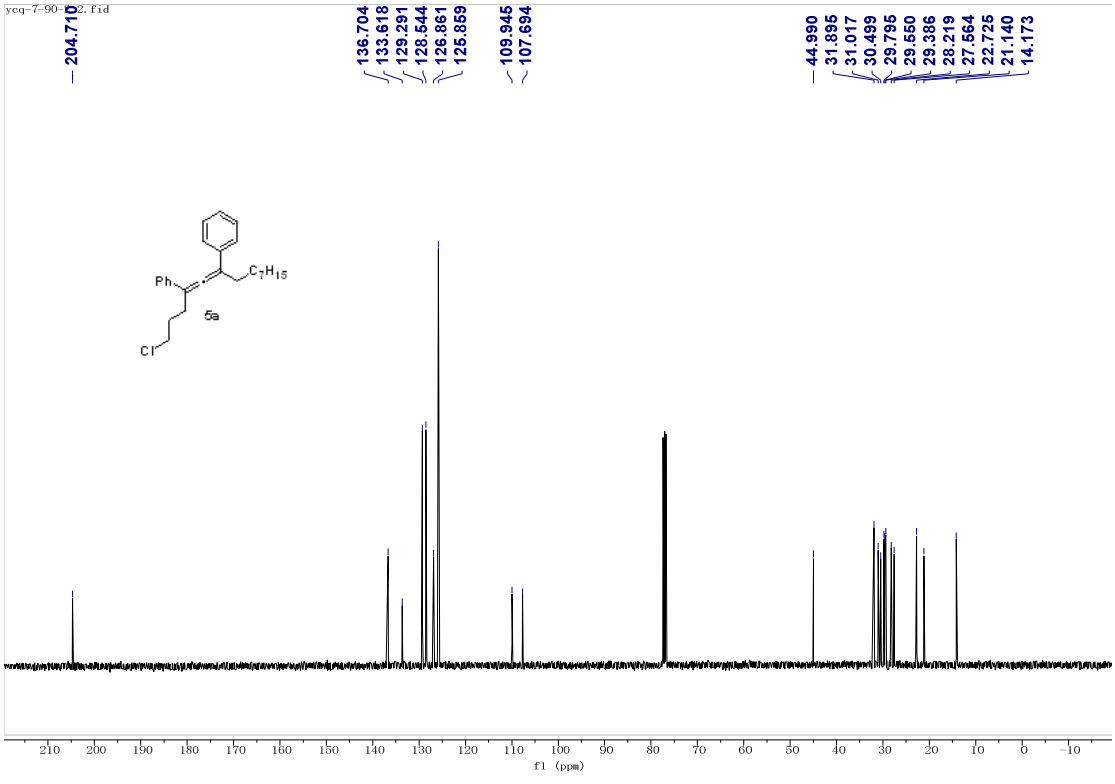

ycq-8-12-1.1.fid
Ph
Cl
4s
2.04
3.94
5.99
3.21
2.00
2.01
4.06
2.04
f1 (ppm)

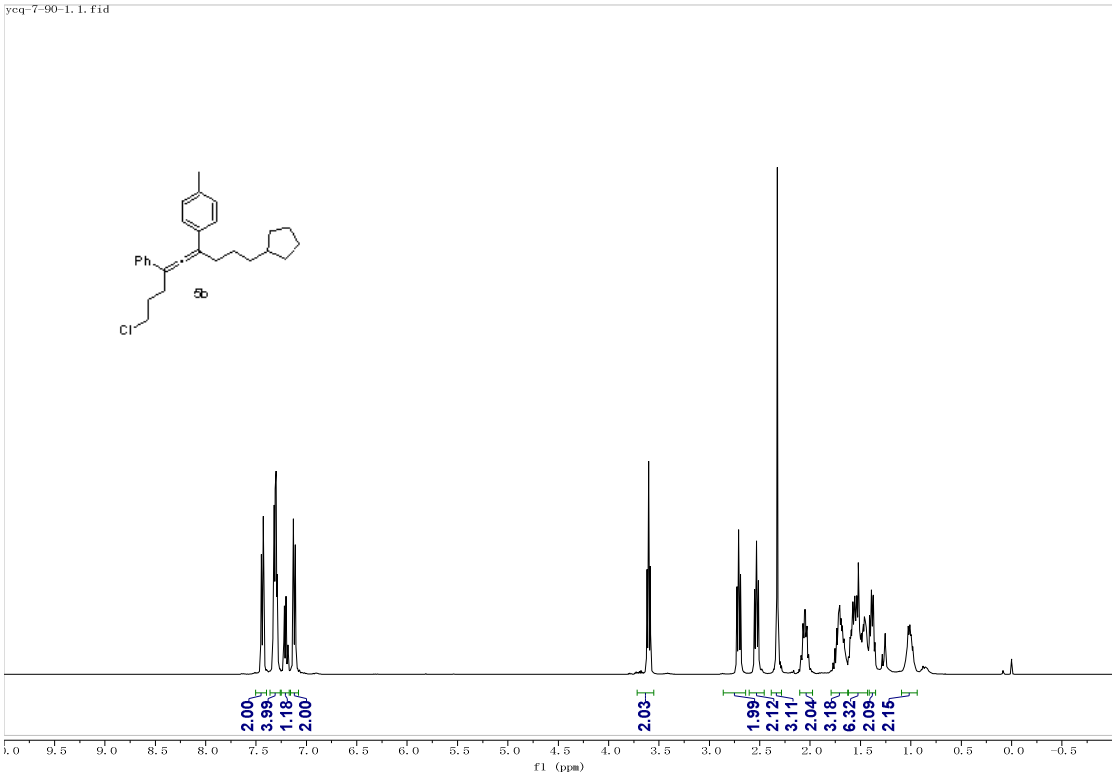

ycq-8-12-1.2.fid
206.988
136.852
136.106
128.651
128.507
128.320
127.376
127.175
126.047
113.120
108.765
45.051
32.571
30.185
27.228
26.870
Ph
Cl
4s
f1 (ppm)

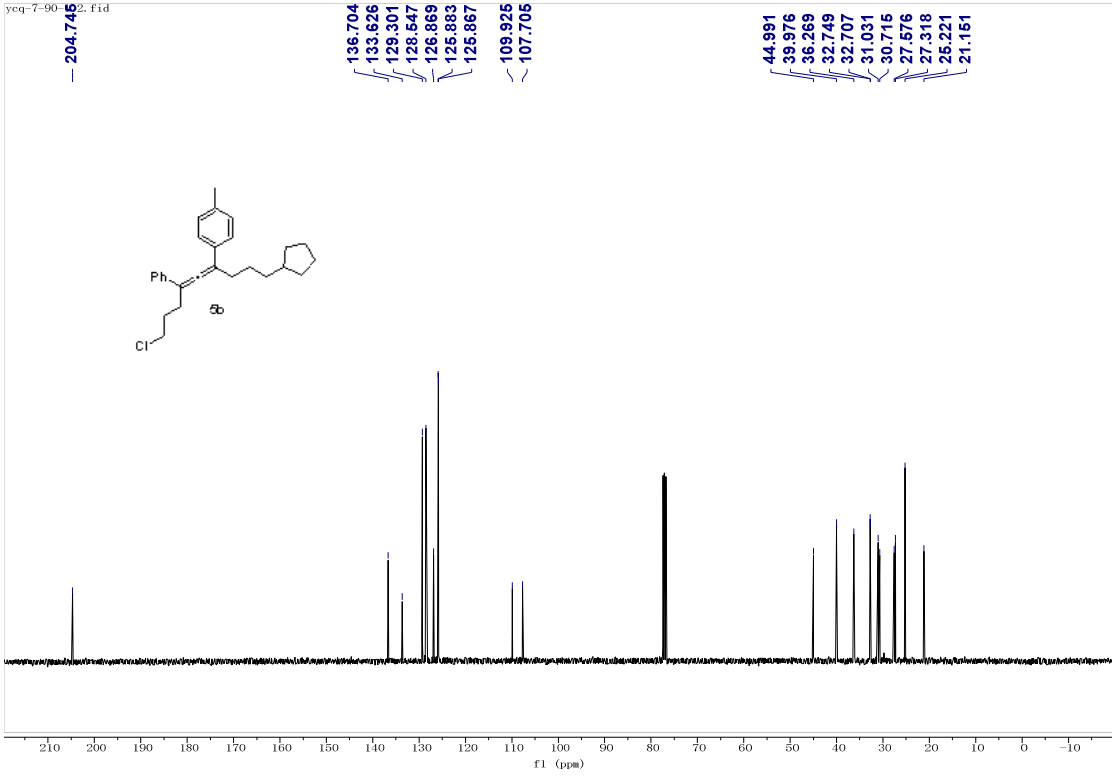

ycq-8-17-1.1.fid
Ph
H
Cl
4t
2.09
6.07
2.00
1.00
2.11
2.04
2.14
4.98
f1 (ppm)

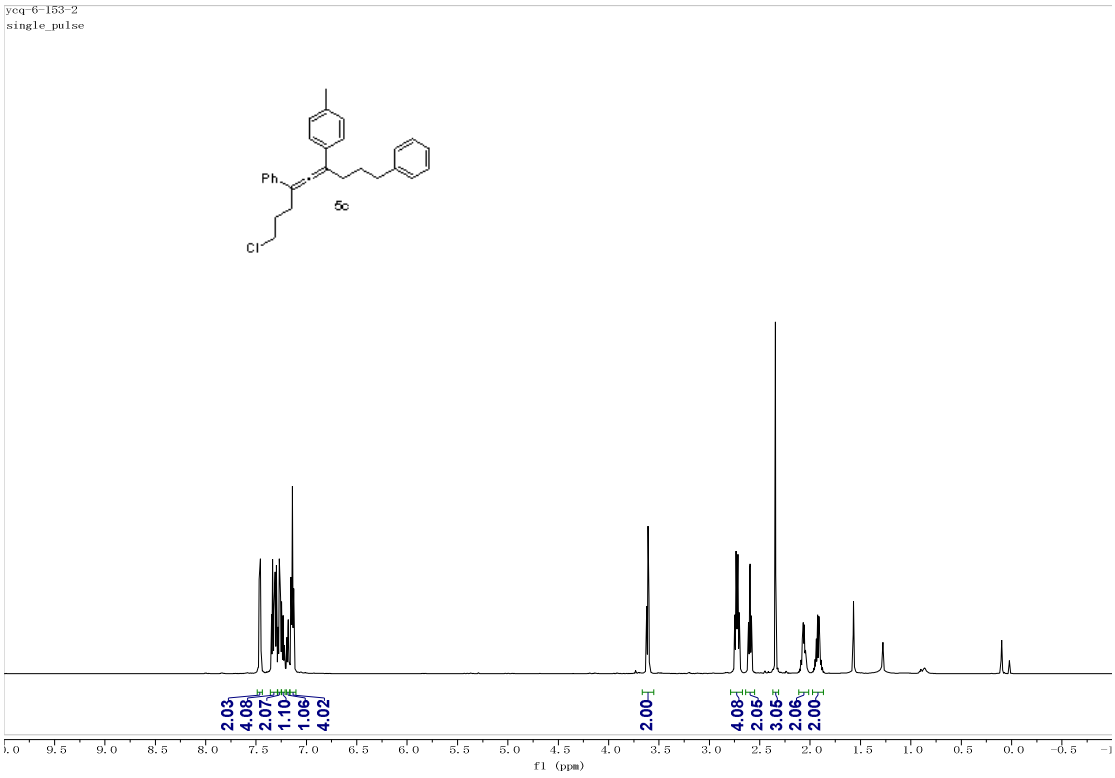

ycq-8-17-1.2.fid
206.423
136.057
134.539
128.775
128.567
127.147
127.116
126.792
126.099
109.645
98.151
45.109
32.493
29.933
27.170
26.809
Ph
H
Cl
4t
f1 (ppm)

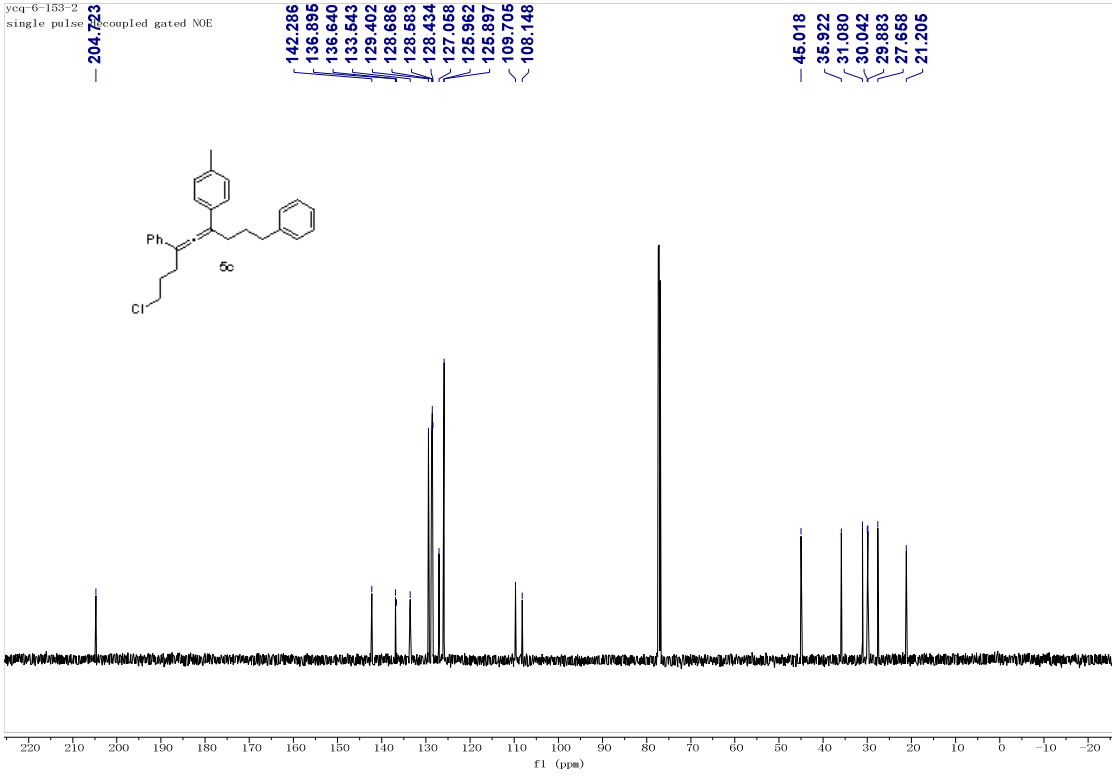

ycq-7-90-2.1.fid
Ph
C7H15
5a
Cl
1.99
4.02
1.19
2.00
2.01
2.02
2.06
3.02
2.04
2.36
2.12
8.38
3.10
f1 (ppm)

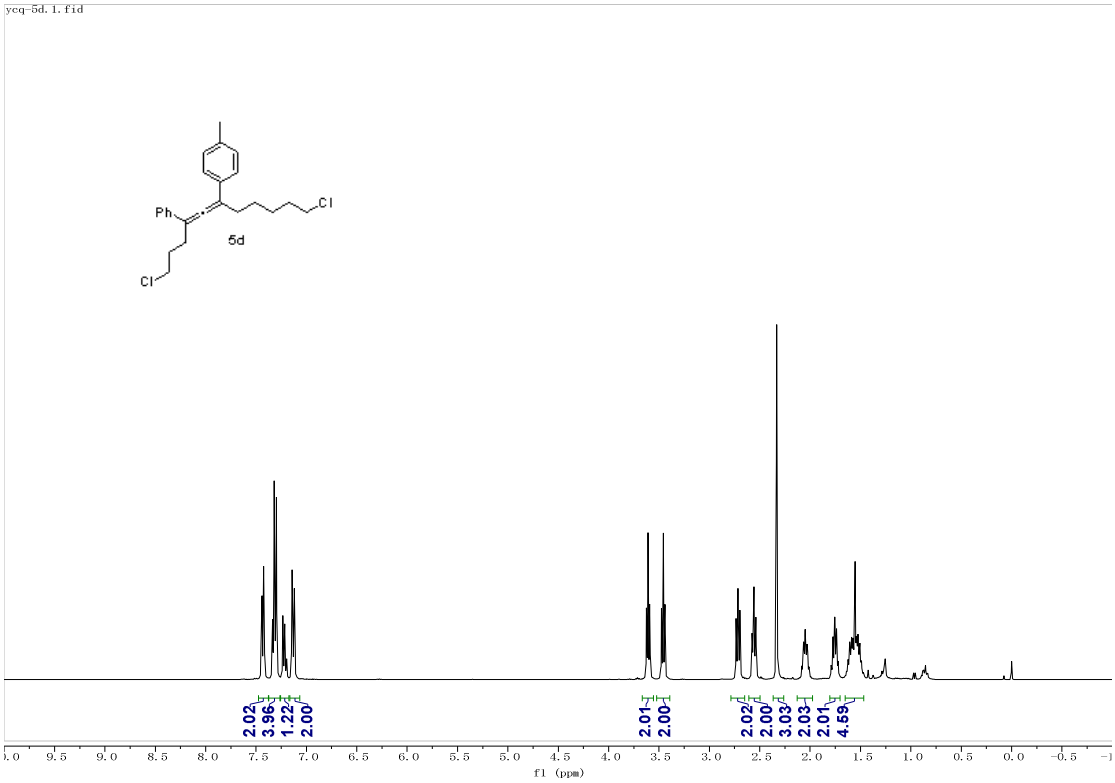

ycq-7-90-2.fid
204.710
136.704
133.618
129.291
128.544
126.861
125.859
109.945
107.694
44.990
31.895
31.017
30.499
29.795
29.550
29.386
28.219
27.564
22.725
21.140
14.173
Ph
C7H15
5a
Cl
f1 (ppm)

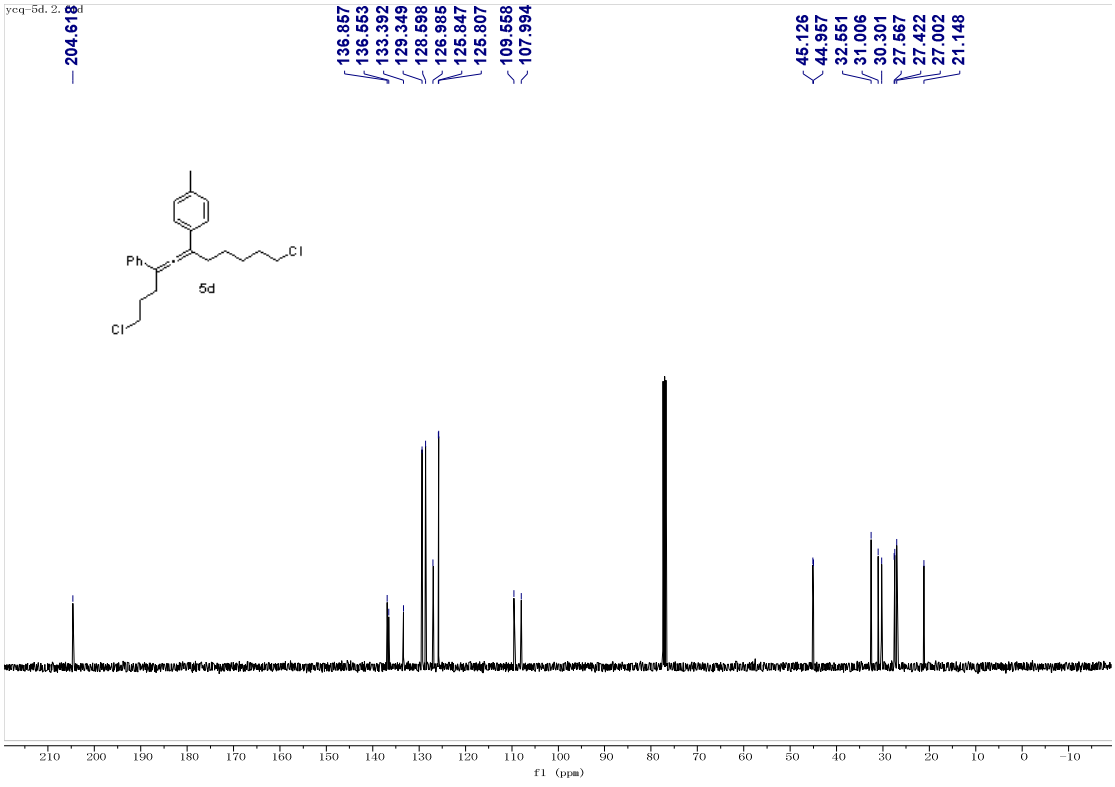

ycq-7-90-1.1.fid
Ph
5b
Cl
2.00
3.99
1.18
2.00
2.03
1.99
2.12
3.11
2.04
3.18
6.32
2.09
2.15
f1 (ppm)

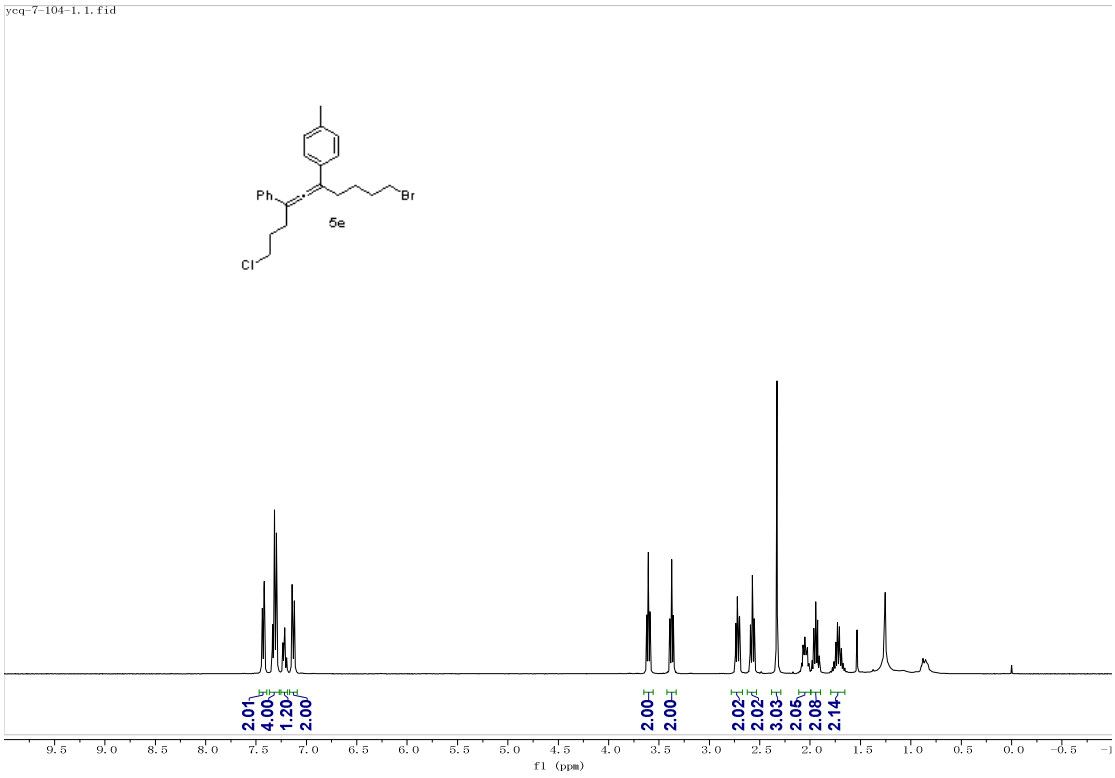

ycq-7-90-2.fid
204.745
136.704
133.626
129.301
128.547
126.869
125.883
125.867
109.925
107.705
44.991
39.976
36.269
32.749
32.707
31.031
30.715
27.676
27.318
25.221
21.151
Ph
5b
Cl
f1 (ppm)

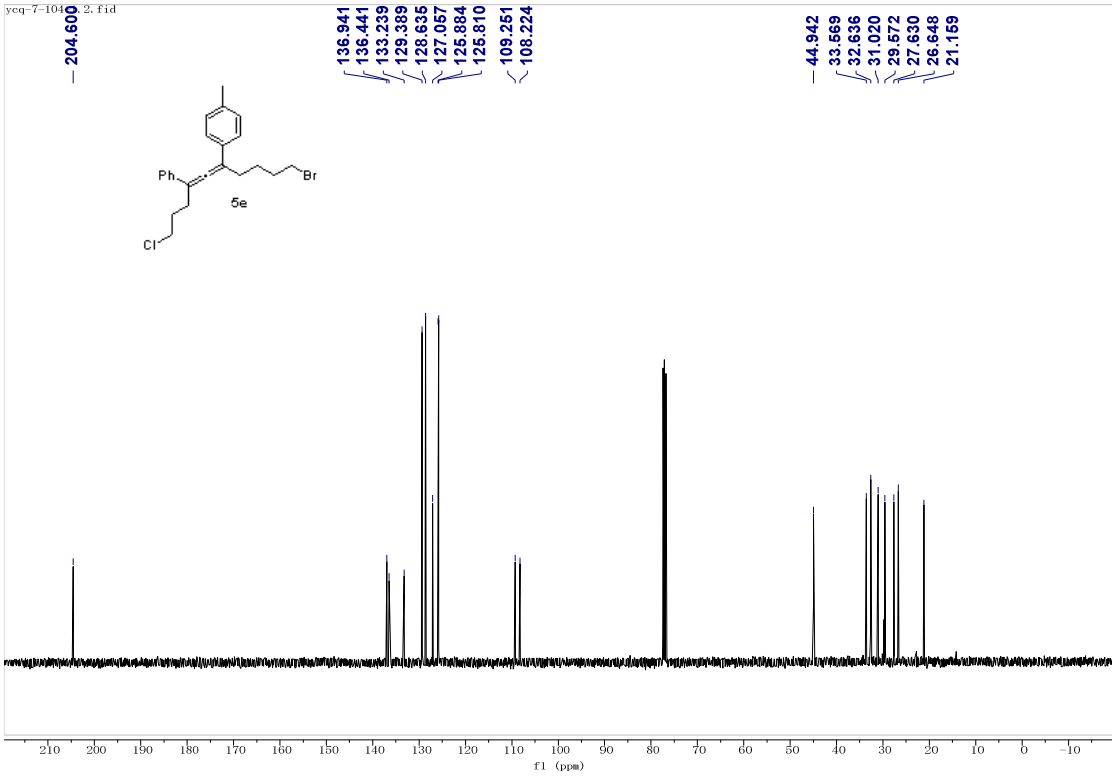

ycq-6-153-2
single_pulse
Ph
Cl
5c
2.03
4.08
2.07
1.10
1.06
4.02
2.00
4.08
2.05
3.05
2.06
2.00
f1 (ppm)

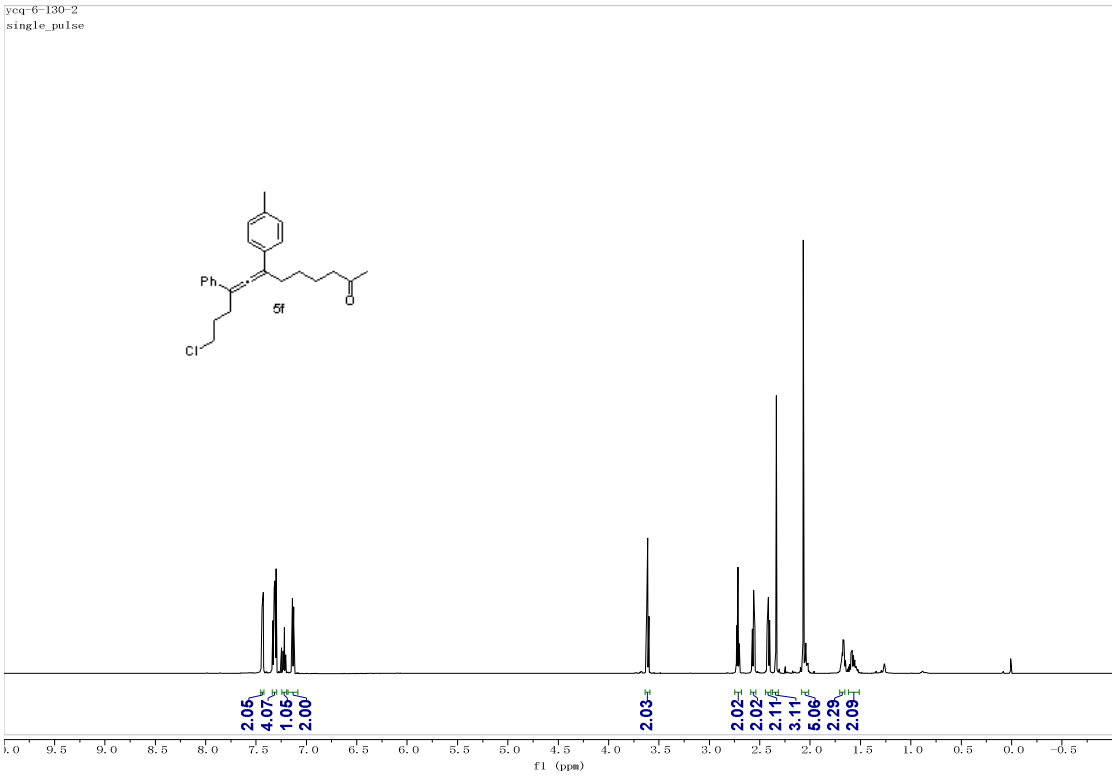

ycq-6-153-2
single pulse decoupled gated NOE
204.723
142.286
136.895
136.640
133.543
129.402
128.686
128.583
128.434
127.058
125.962
125.897
109.705
108.148
45.018
35.922
31.080
30.042
29.883
27.658
21.205
Ph
Cl
5c
f1 (ppm)

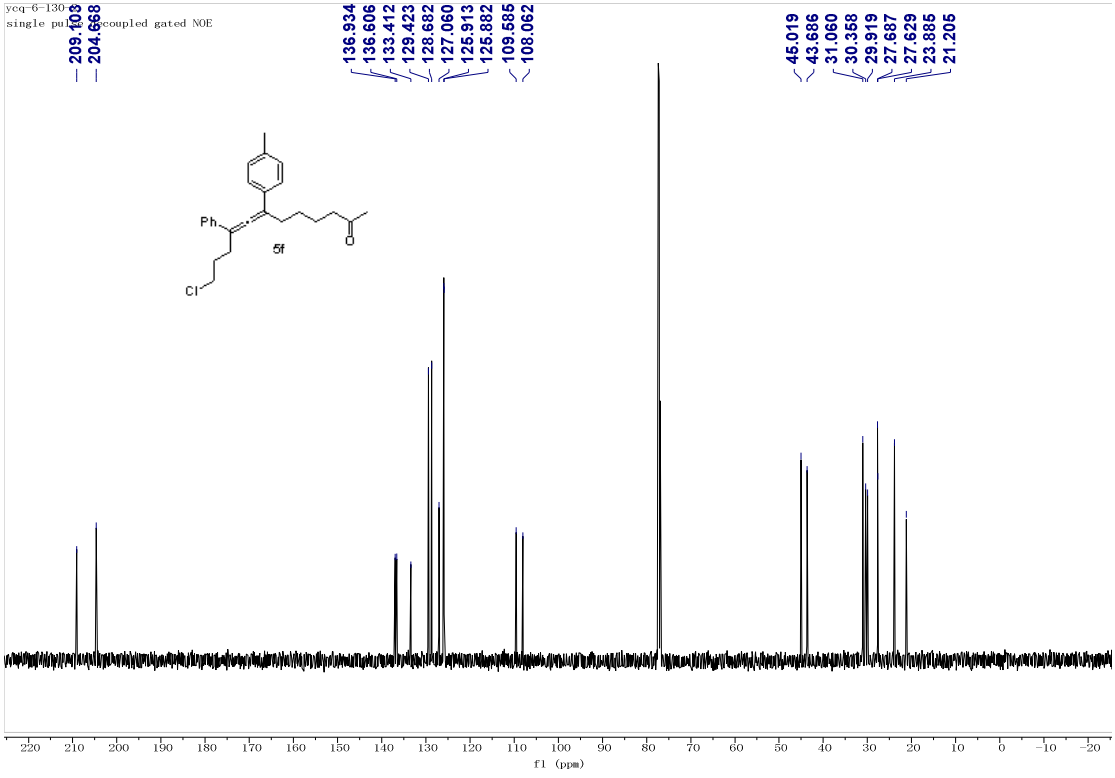

ycq-5d.1.fid
Ph
Cl
Cl
5d
2.02
3.96
1.22
2.00
2.01
2.00
2.02
2.00
3.03
2.03
2.01
4.59
f1 (ppm)

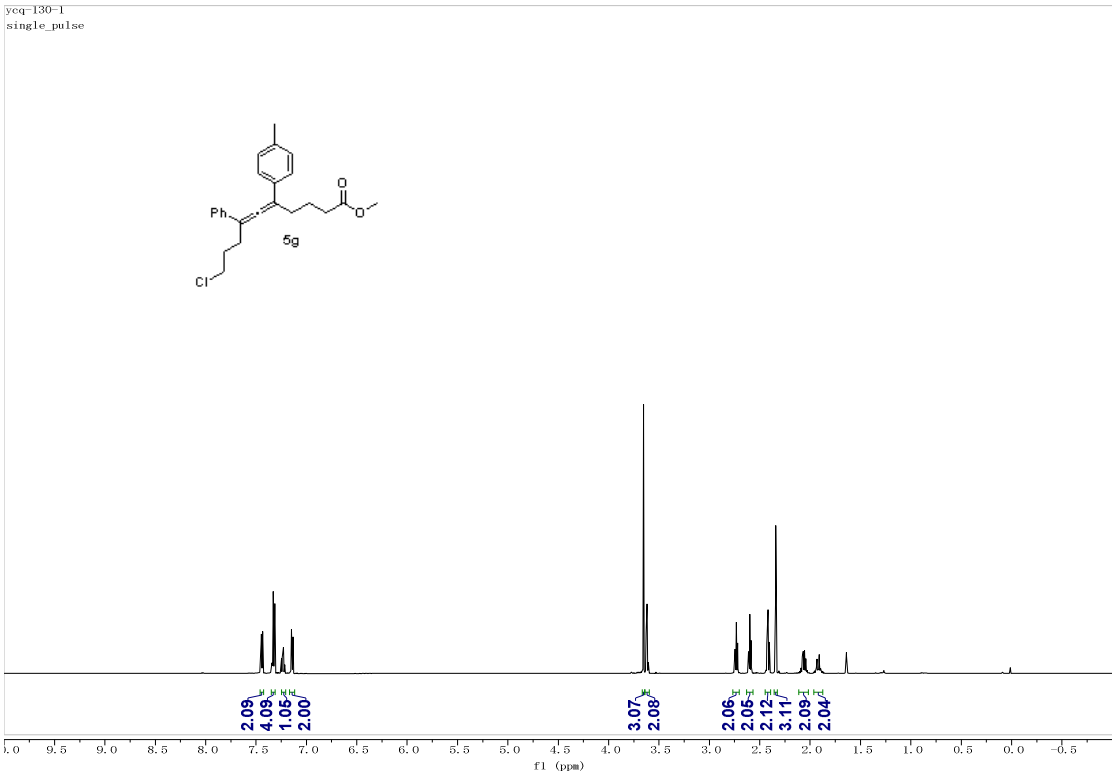

ycq-5d.2.fid
204.618
136.857
136.553
133.392
129.349
128.598
126.985
125.847
125.807
109.558
107.994
45.126
44.957
32.551
31.006
30.301
27.567
27.422
27.002
21.148
Ph
Cl
Cl
5d
f1 (ppm)

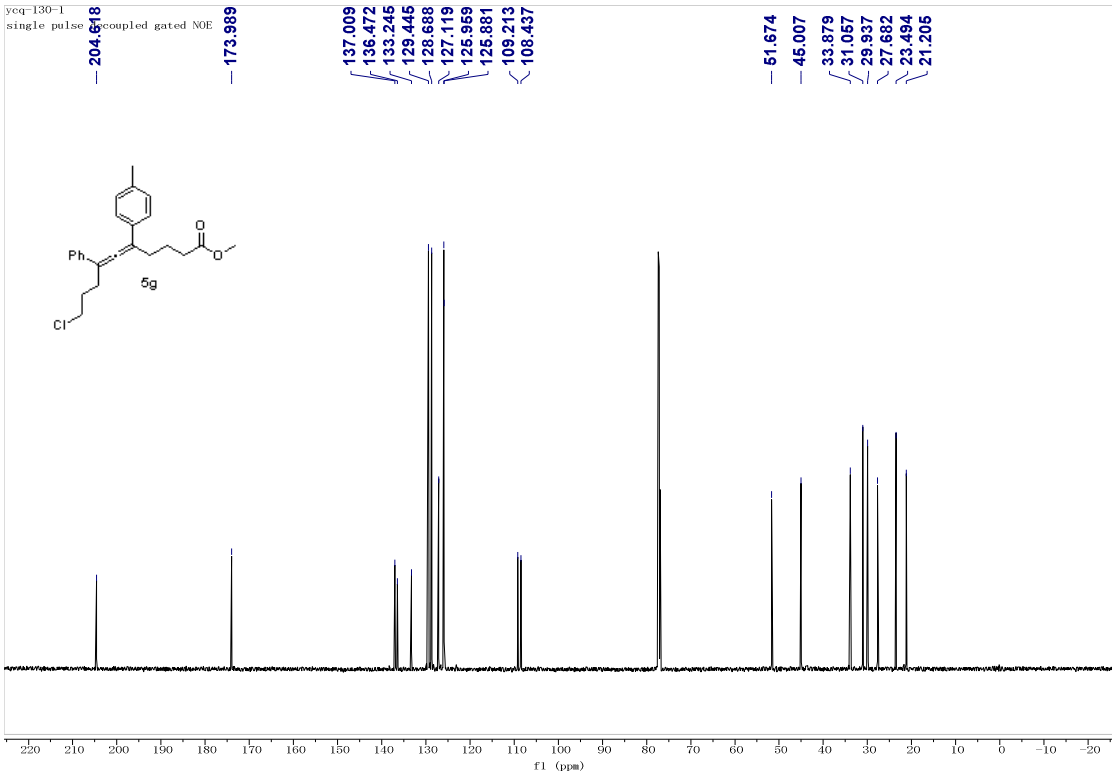

ycq-7-104-1.1.fid
Ph
Br
Cl
5e
2.01
4.00
1.20
2.00
2.00
2.00
2.02
2.02
3.03
2.05
2.08
2.14
f1 (ppm)

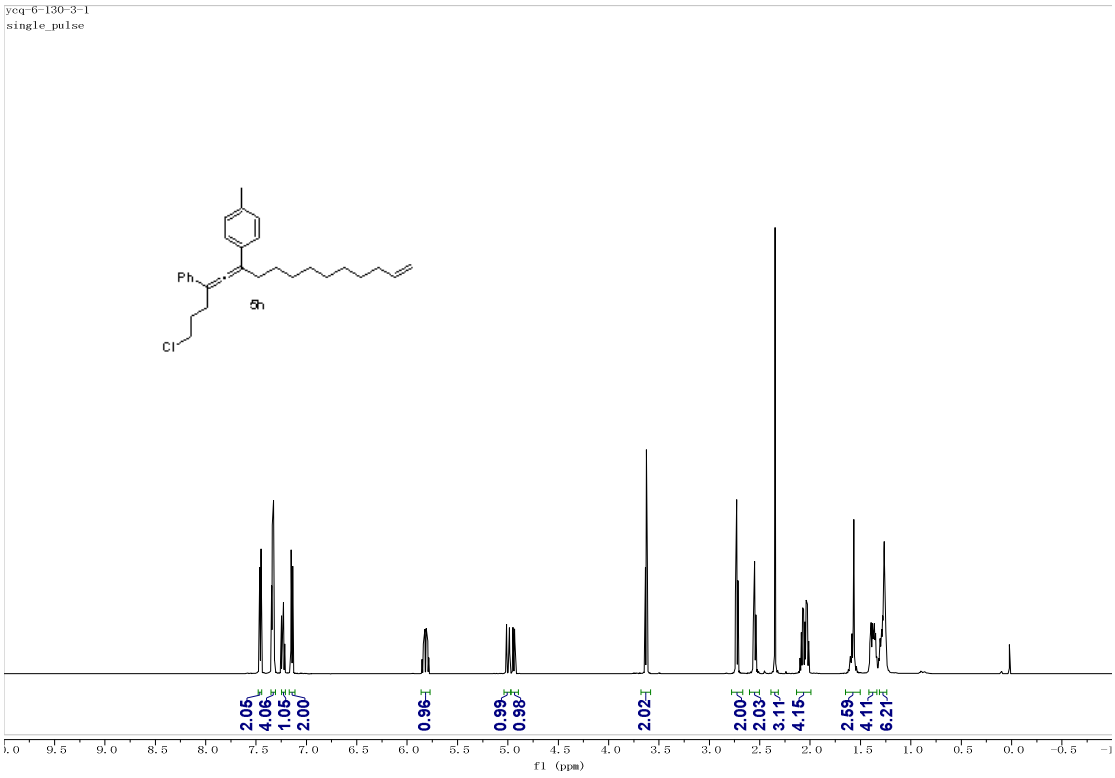

ycq-7-104-2.2.fid
204.609
136.941
136.441
133.239
129.389
128.635
127.057
125.884
125.810
109.251
108.224
44.942
33.669
32.636
31.020
29.572
27.630
26.648
21.159
Ph
Br
Cl
5e
f1 (ppm)

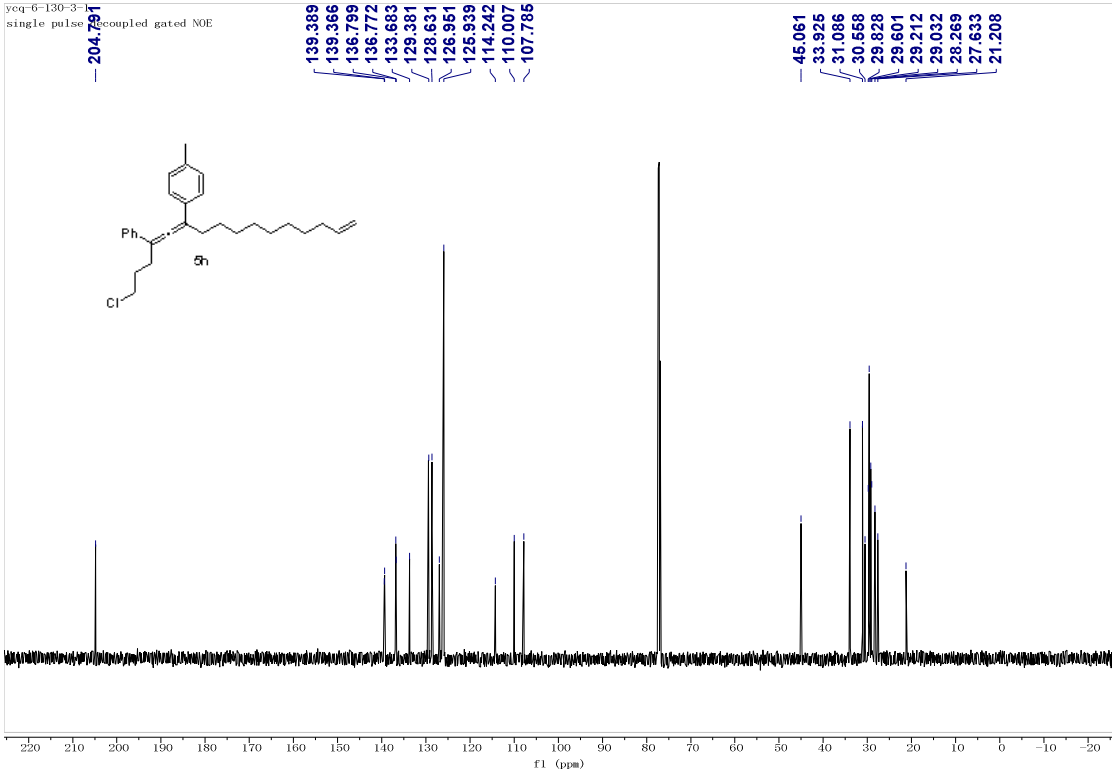

ycq-6-130-2
single_pulse
Ph
Cl
O
5f
2.05
4.07
1.05
2.00
2.03
2.02
2.02
2.11
3.11
5.06
2.29
2.09
f1 (ppm)

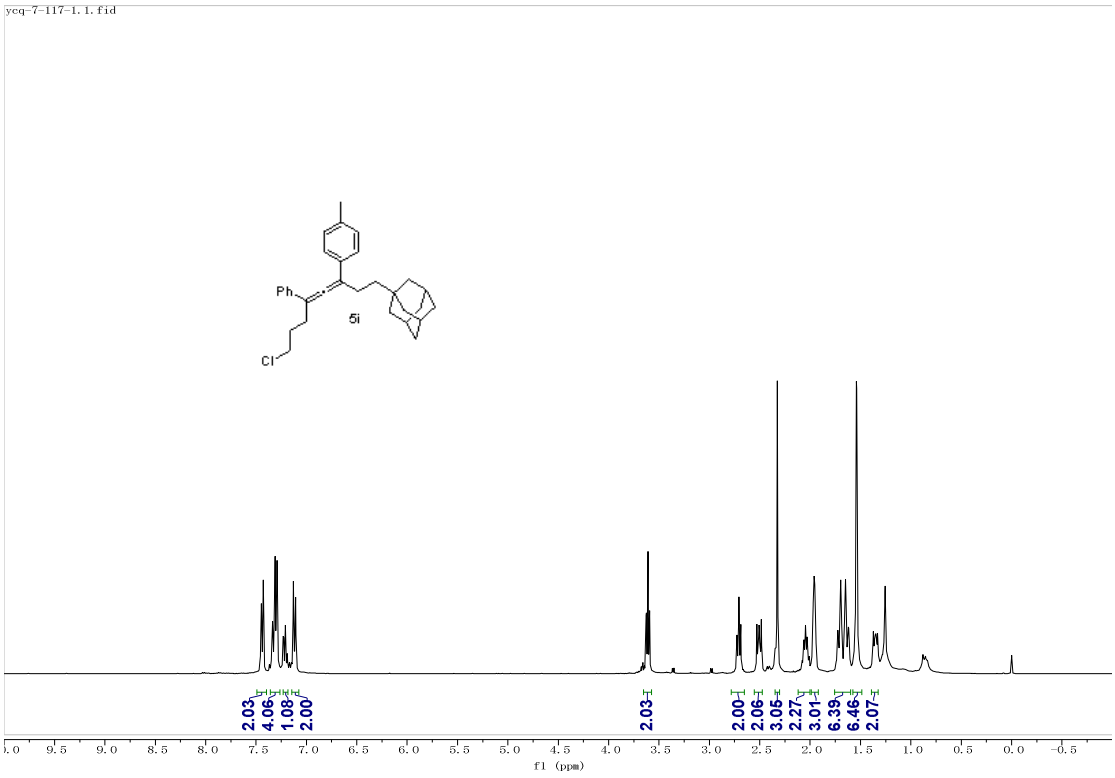

ycq-6-130-3
single pulse decoupled gated NOE
209.403
204.668
136.934
136.606
133.412
129.423
128.682
127.060
125.913
125.882
109.585
108.062
45.019
43.686
31.060
30.358
29.919
27.687
27.629
23.885
21.205
Ph
Cl
O
5f
f1 (ppm)

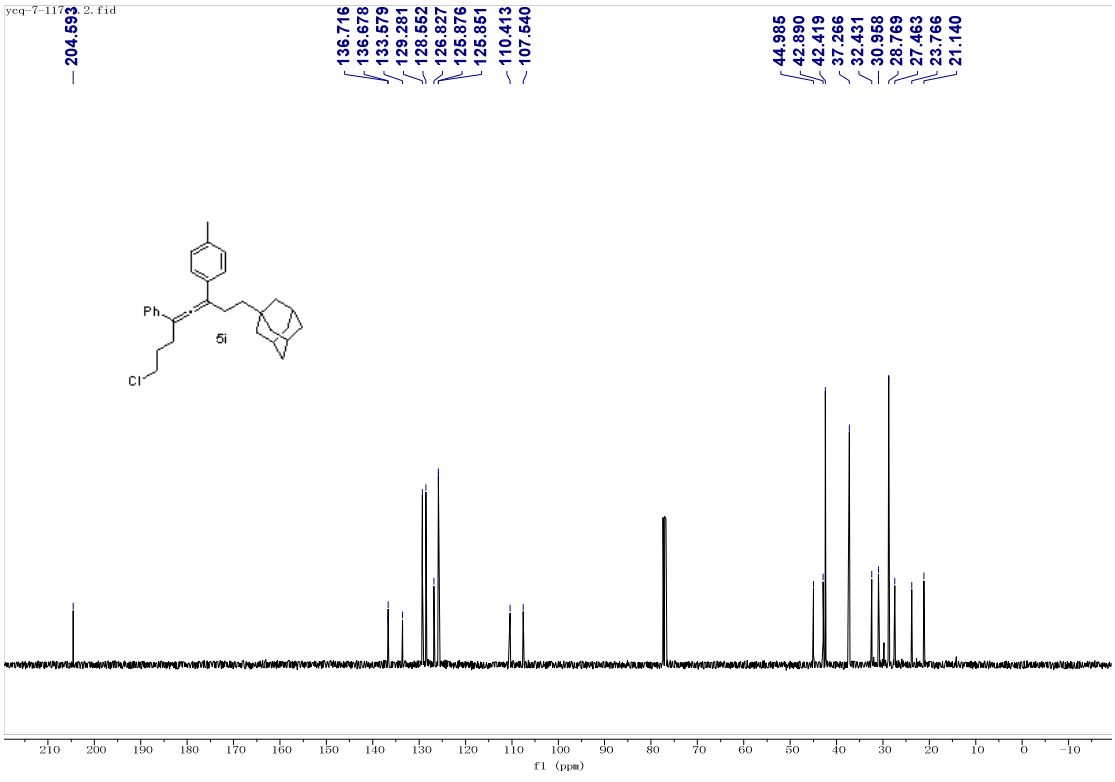

ycq-130-1
single_pulse
Ph
O
O
5g
Cl
2.09
4.09
1.05
2.00
3.07
2.08
2.06
2.05
2.12
3.11
2.09
2.04
f1 (ppm)

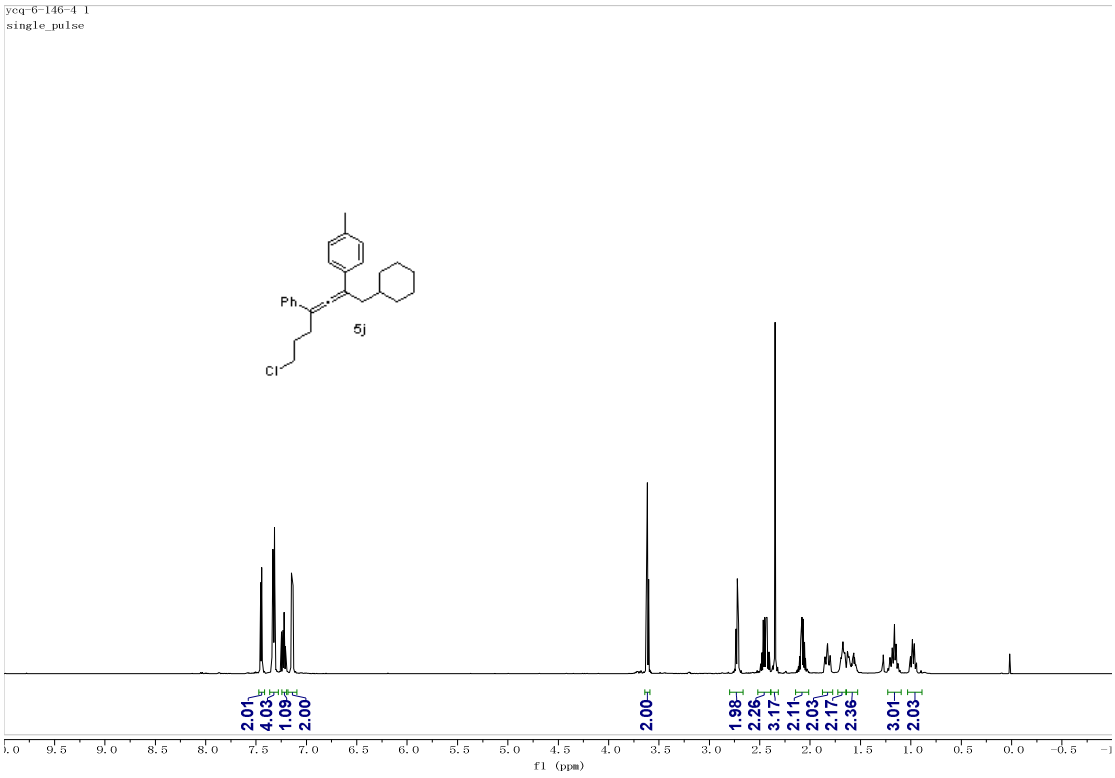

ycq-130-1
single pulse decoupled gated NOE
204.618
173.989
137.009
136.472
133.245
129.445
128.688
127.119
125.959
125.881
109.213
108.437
51.674
45.007
33.879
31.057
29.937
27.682
23.494
21.205
Ph
O
O
5g
Cl
f1 (ppm)

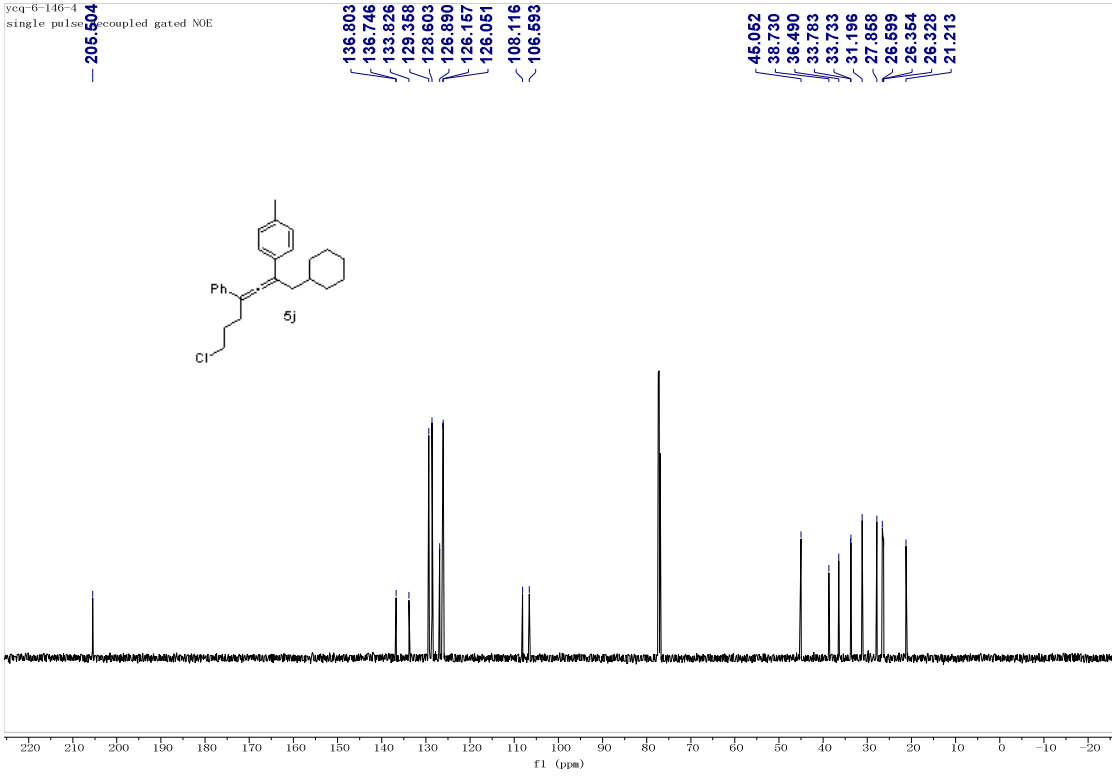

ycq-6-130-3-1
single_pulse
Ph
Cl
5h
2.05
4.06
1.05
2.00
0.96
0.99
0.98
2.02
2.00
2.03
3.11
4.15
2.59
4.11
6.21
f1 (ppm)

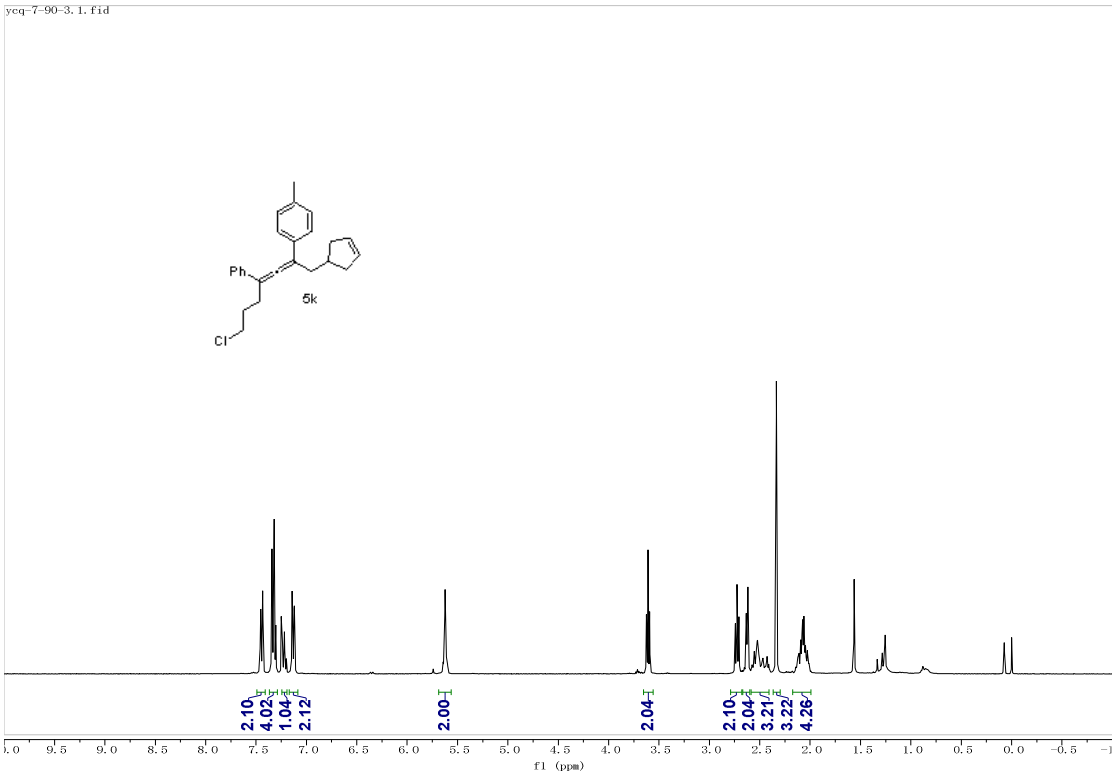

ycq-6-130-3-1
single pulse decoupled gated NOE
204.791
139.389
139.366
136.799
136.772
133.683
129.381
128.631
126.951
125.939
114.242
110.007
107.785
45.061
33.925
31.086
30.558
29.828
29.601
29.212
29.032
28.269
27.633
21.208
Ph
Cl
5h
f1 (ppm)

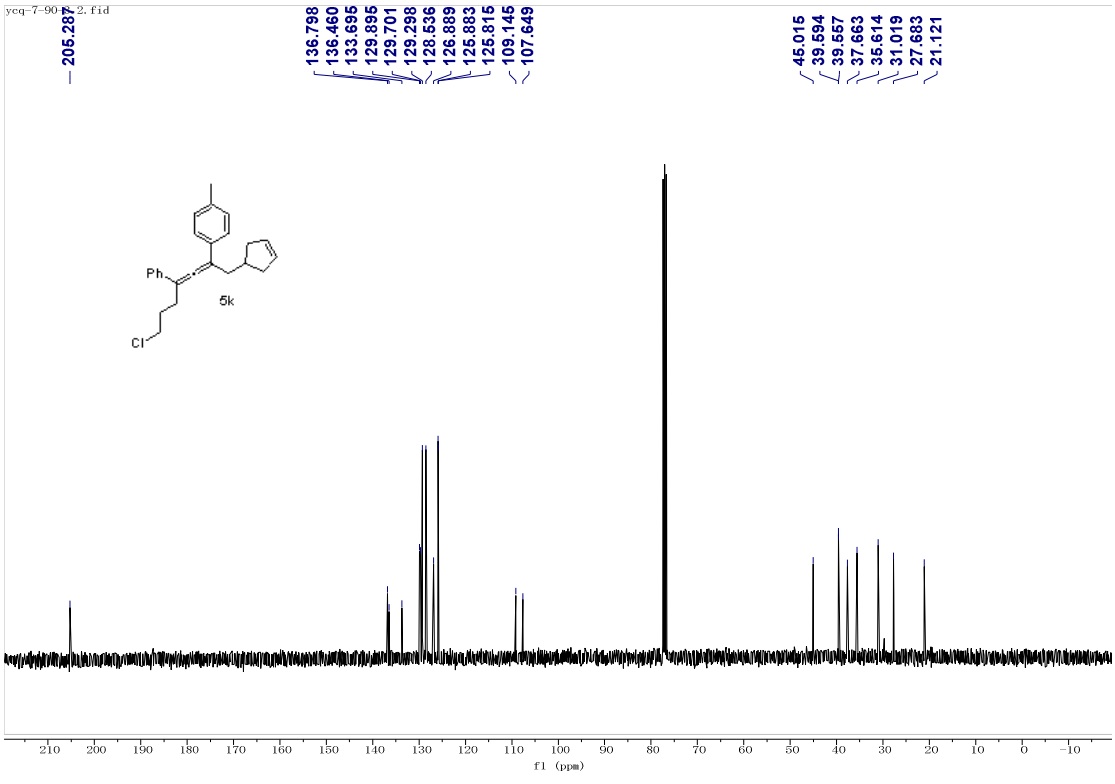

ycq-7-117-1.1.fid
Ph
5i
Cl
2.03
4.06
1.08
2.00
2.03
2.00
2.06
3.05
2.27
3.01
6.39
6.46
2.07
f1 (ppm)

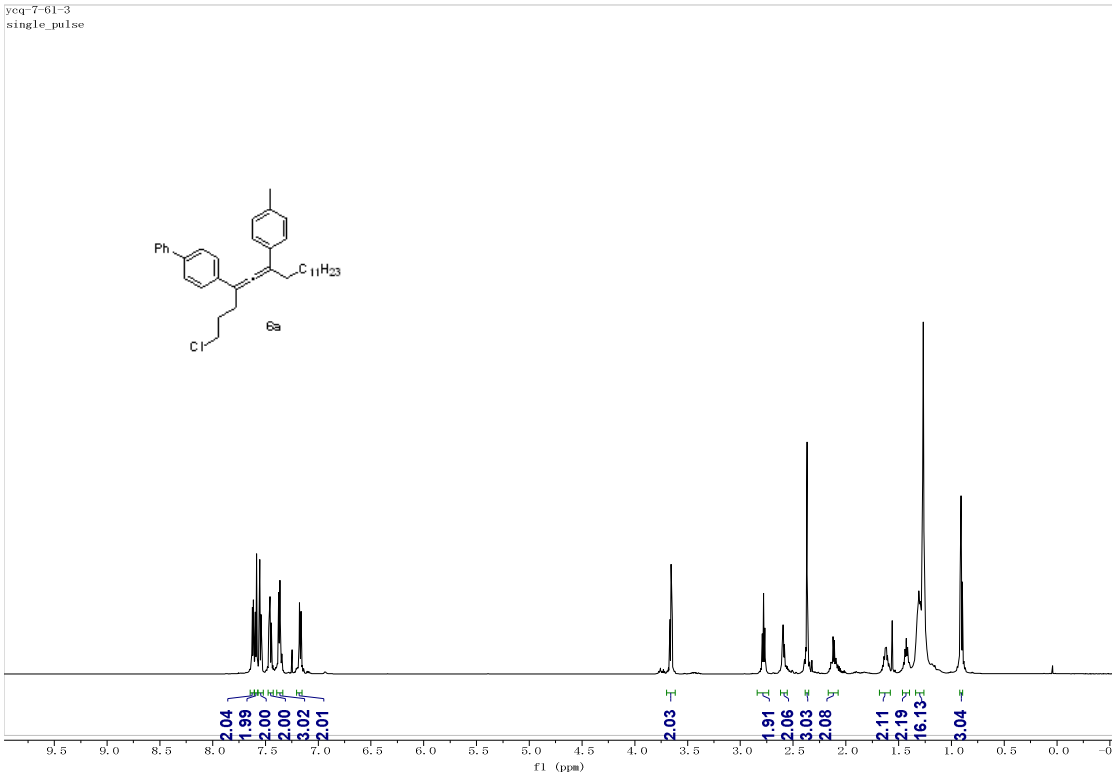

ycq-7-117-2.fid
204.593
136.716
136.678
133.579
129.281
128.552
126.827
125.876
125.851
110.413
107.540
44.985
42.890
42.419
37.266
32.431
30.958
28.769
27.463
23.766
21.140
Ph
5i
Cl
f1 (ppm)

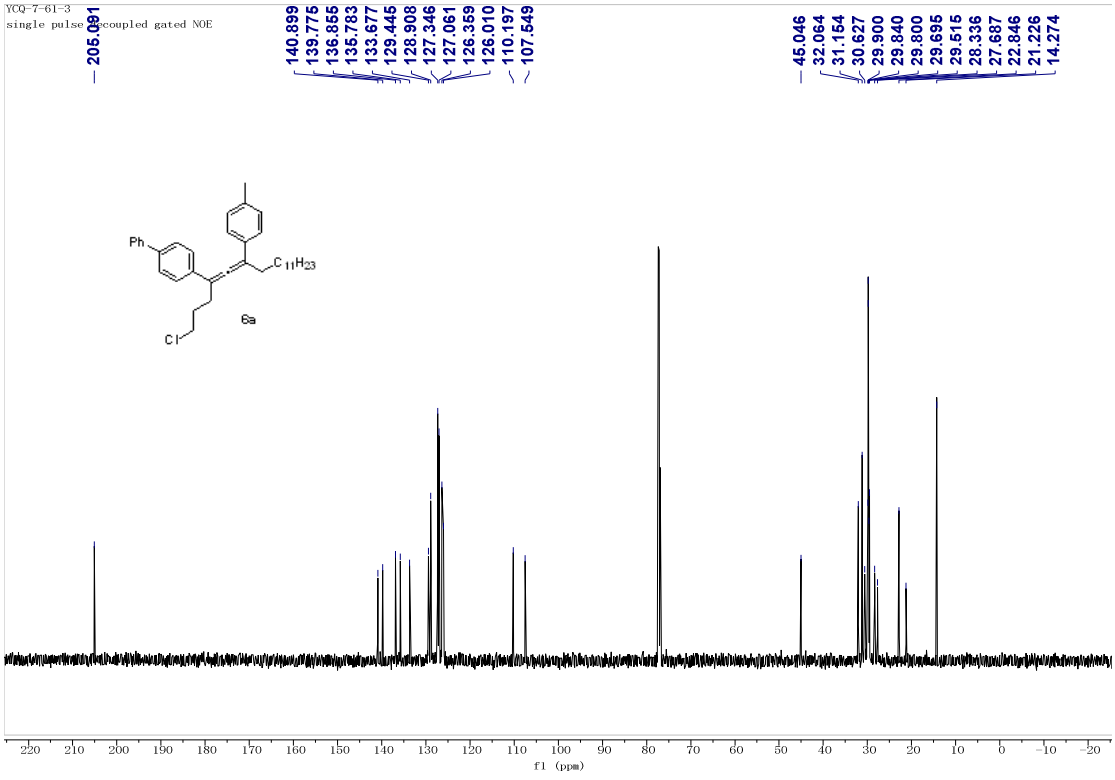

ycq-6-146-4 1
single_pulse
Ph
5j
Cl
2.01
4.03
1.09
2.00
2.00
1.98
2.26
3.17
2.11
2.03
2.17
2.36
3.01
2.03
f1 (ppm)

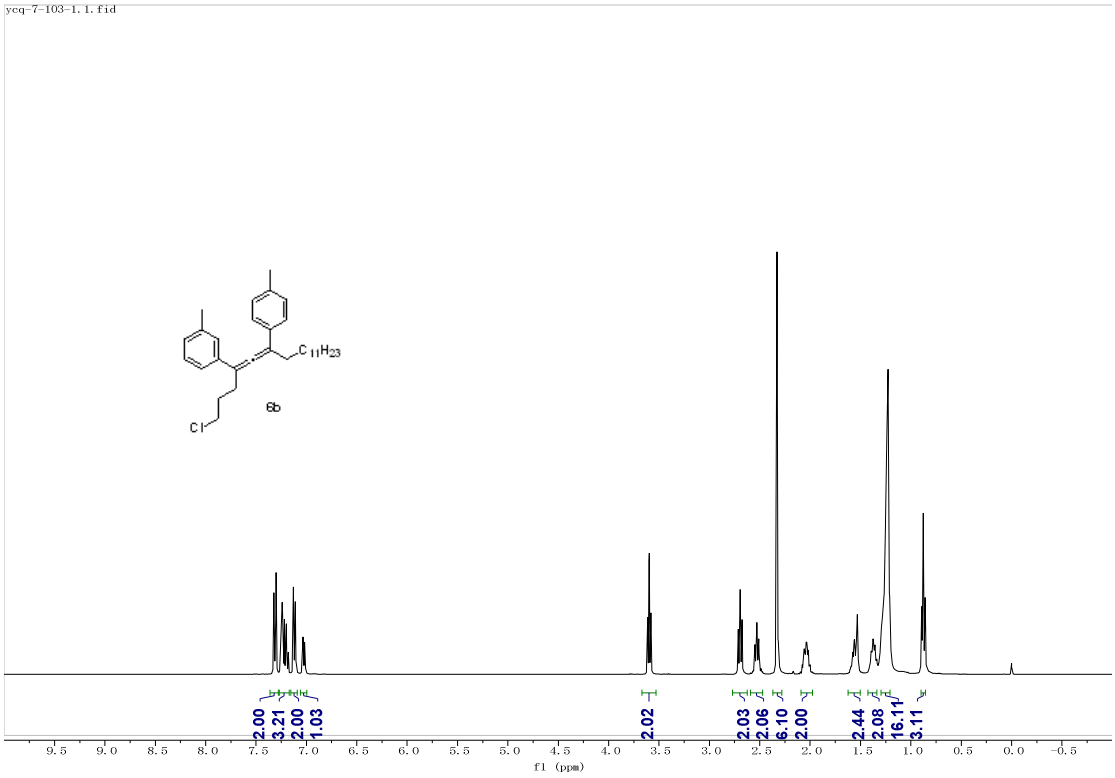

ycq-6-146-4
single pulse decoupled gated NOE
205.504
136.803
136.746
133.826
129.358
128.603
126.890
126.157
126.051
108.116
106.593
45.052
38.730
36.490
33.783
33.733
31.196
27.858
26.599
26.354
26.328
21.213
Ph
5j
Cl
f1 (ppm)

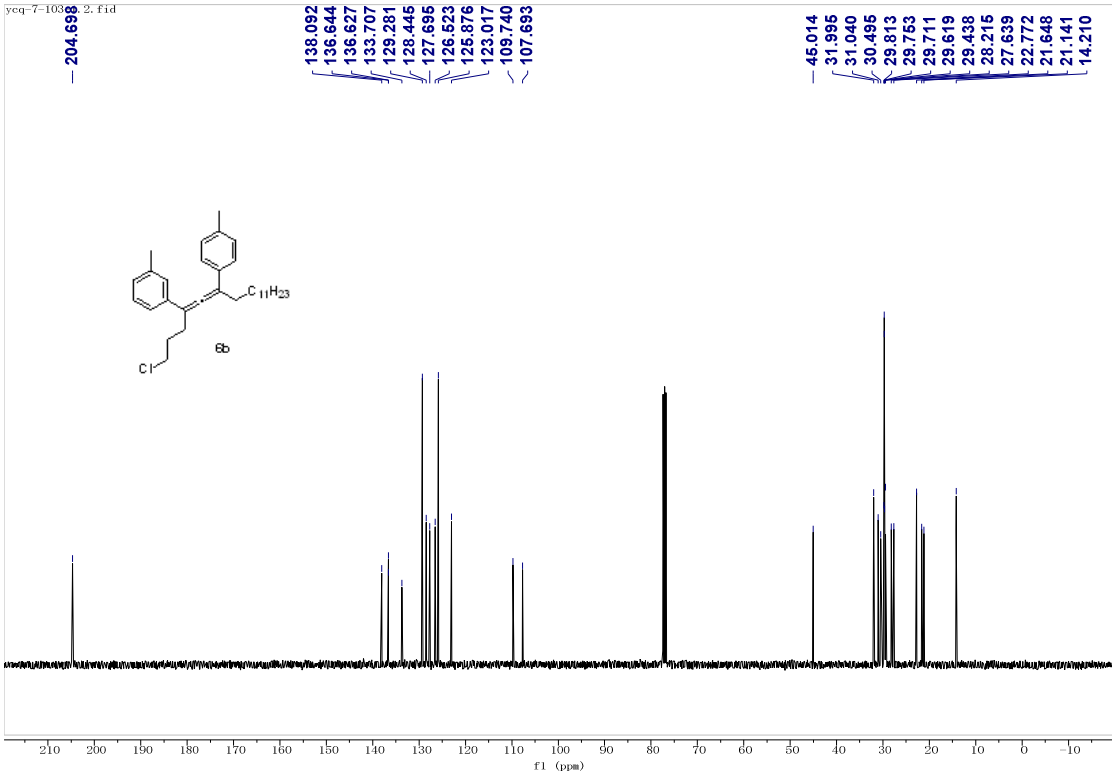

ycq-7-90-3.1.fid
Ph
5k
Cl
2.10
4.02
1.04
2.12
2.00
2.04
2.10
2.04
3.21
3.22
4.26
f1 (ppm)

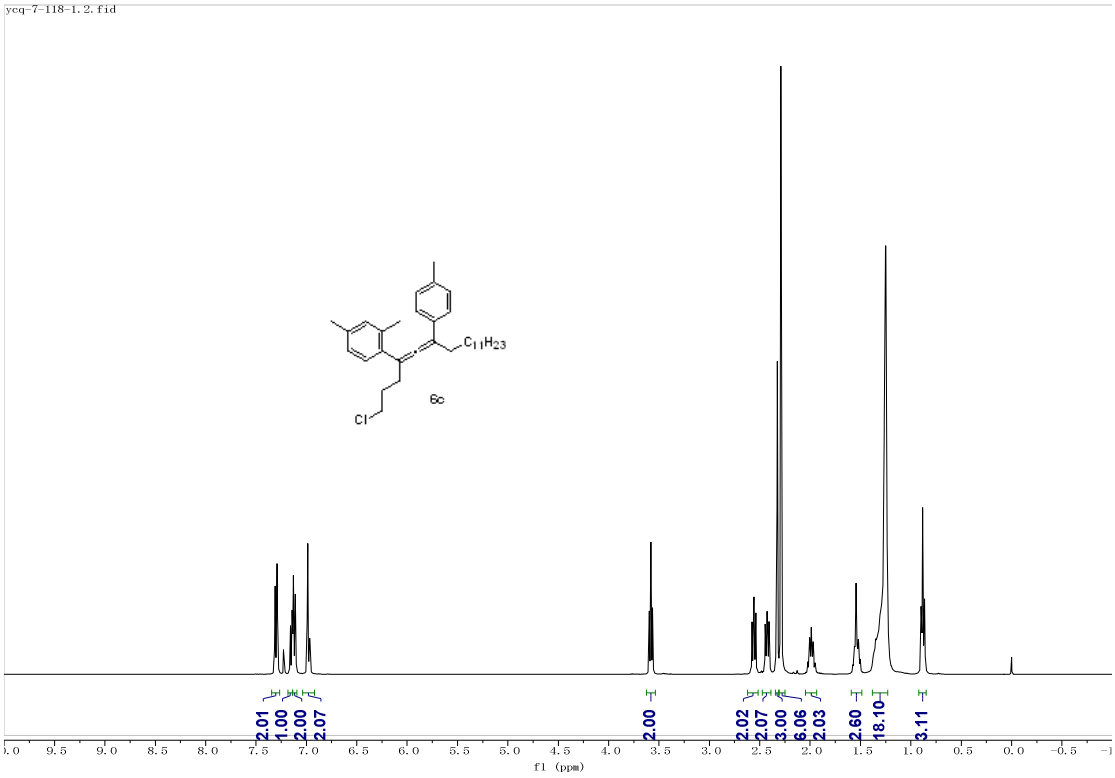

ycq-7-90-2.fid
205.287
136.798
136.460
133.695
129.895
129.701
129.298
128.536
126.889
125.883
125.815
109.145
107.649
45.015
39.694
39.557
37.663
35.614
31.019
27.683
21.121
Ph
5k
Cl
f1 (ppm)

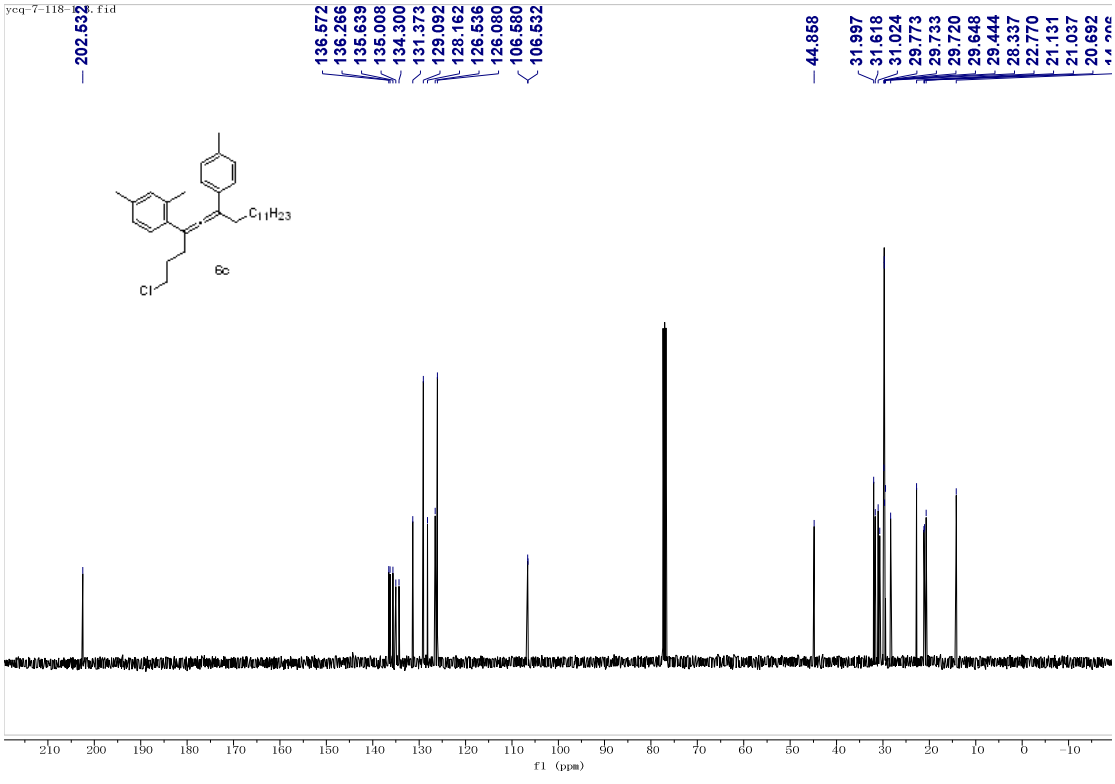

ycq-7-61-3
single_pulse
Ph
C11H23
Cl
6a
2.04
1.99
2.00
2.00
3.02
2.01
2.03
1.91
2.06
3.03
2.08
2.11
2.19
16.13
3.04
f1 (ppm)

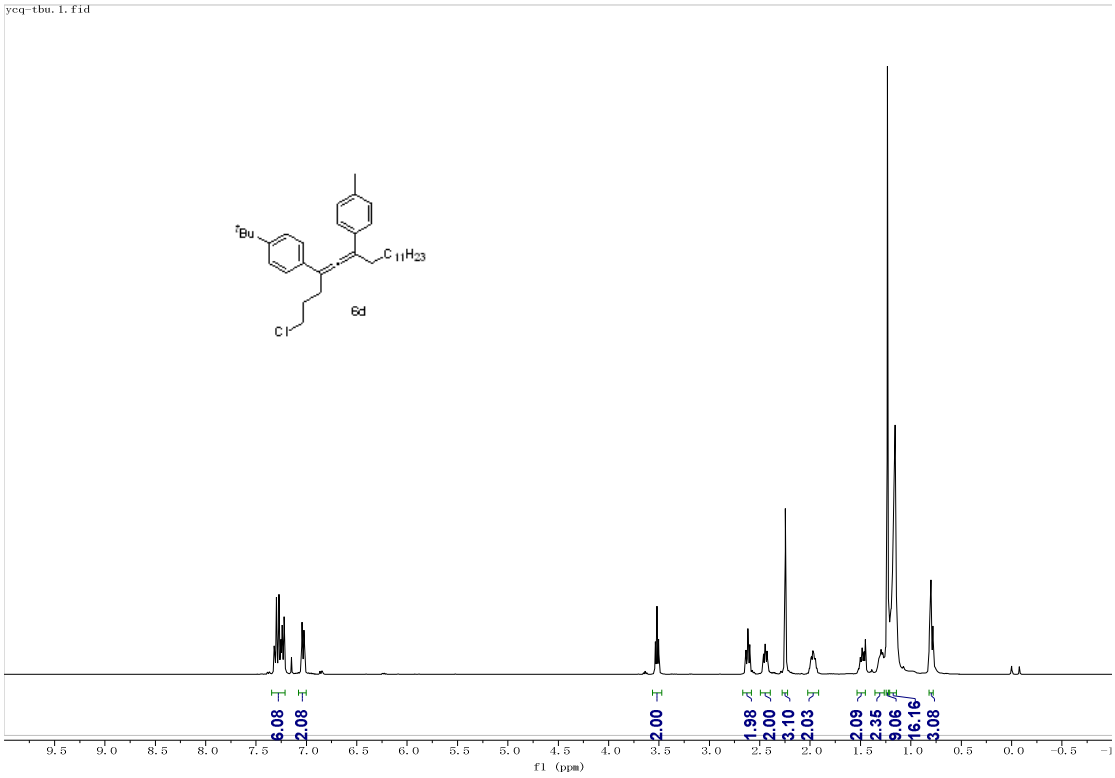

YCQ-7-61-3
single pulse decoupled gated NOE
205.091
140.899
139.775
136.855
135.783
133.677
129.445
128.908
127.346
127.061
126.359
126.010
110.197
107.549
45.046
32.064
31.154
30.627
29.900
29.840
29.800
29.695
29.515
28.336
27.687
22.846
21.226
14.274
Ph
C11H23
Cl
6a
f1 (ppm)

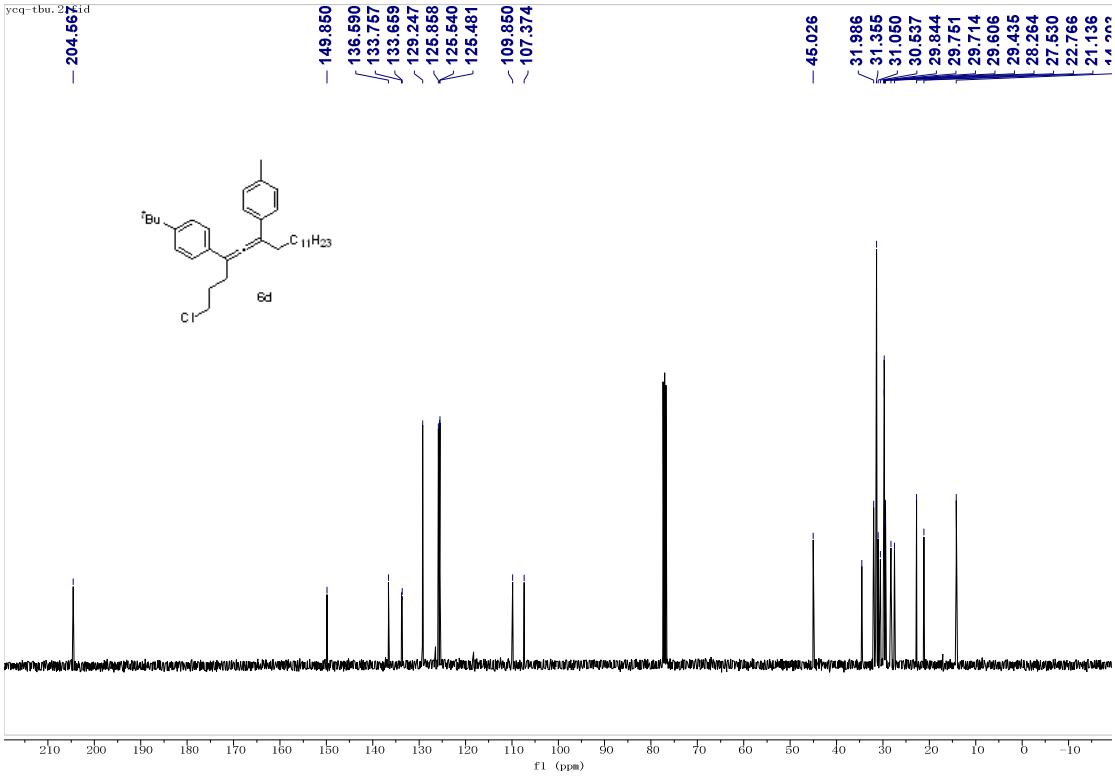

ycq-7-103-1.1.fid
6b
2.00
3.21
2.00
1.03
2.02
2.03
2.06
6.10
2.00
2.44
2.08
16.11
3.11
f1 (ppm)

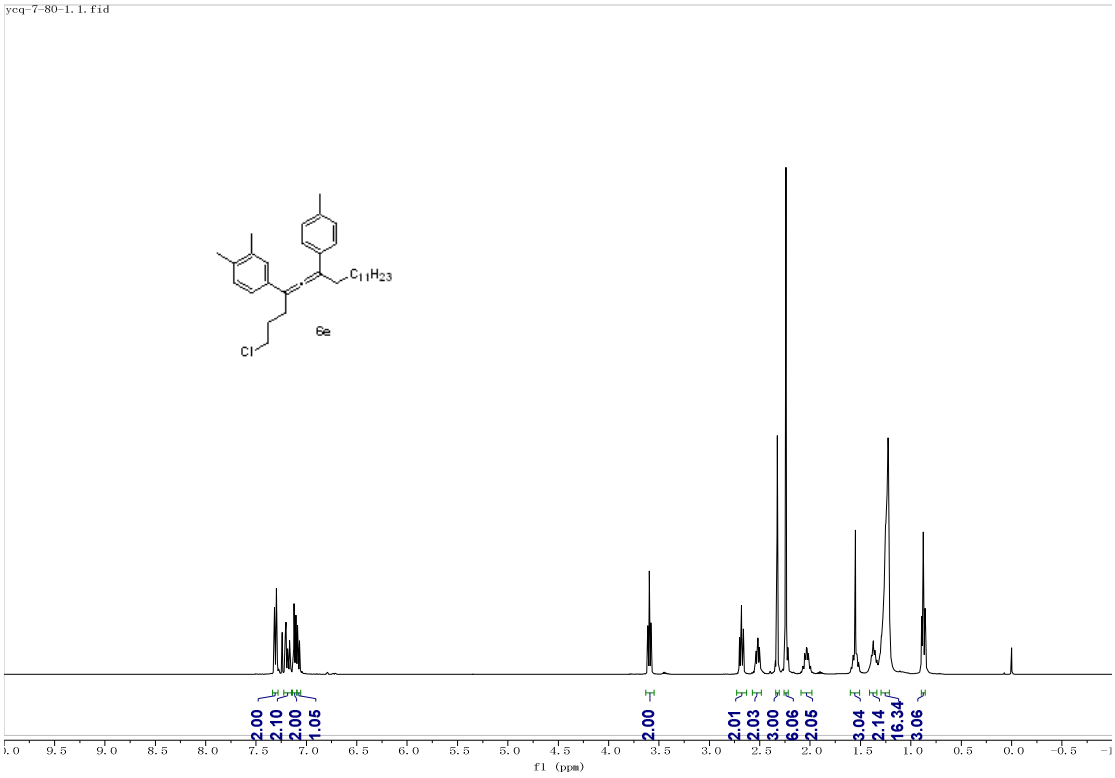

ycq-7-103-2.fid
204.698
138.092
136.644
136.627
133.707
129.281
128.445
127.695
126.523
125.876
123.017
109.740
107.693
45.014
31.995
31.040
30.495
29.813
29.753
29.711
29.619
29.438
28.215
27.639
22.772
21.648
21.141
14.210
6b
f1 (ppm)

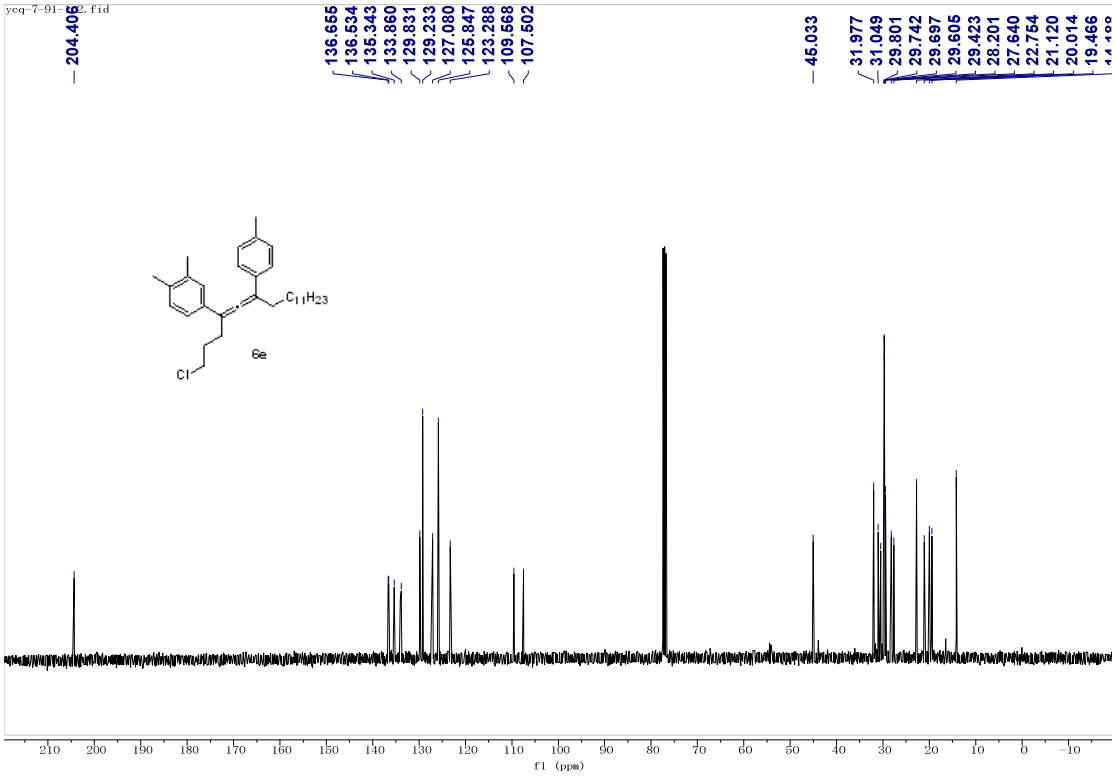

ycq-7-118-1.2.fid
2.01
1.00
2.00
2.07
2.00
2.02
2.07
3.00
6.06
2.03
2.60
18.10
3.11
f1 (ppm)
6c

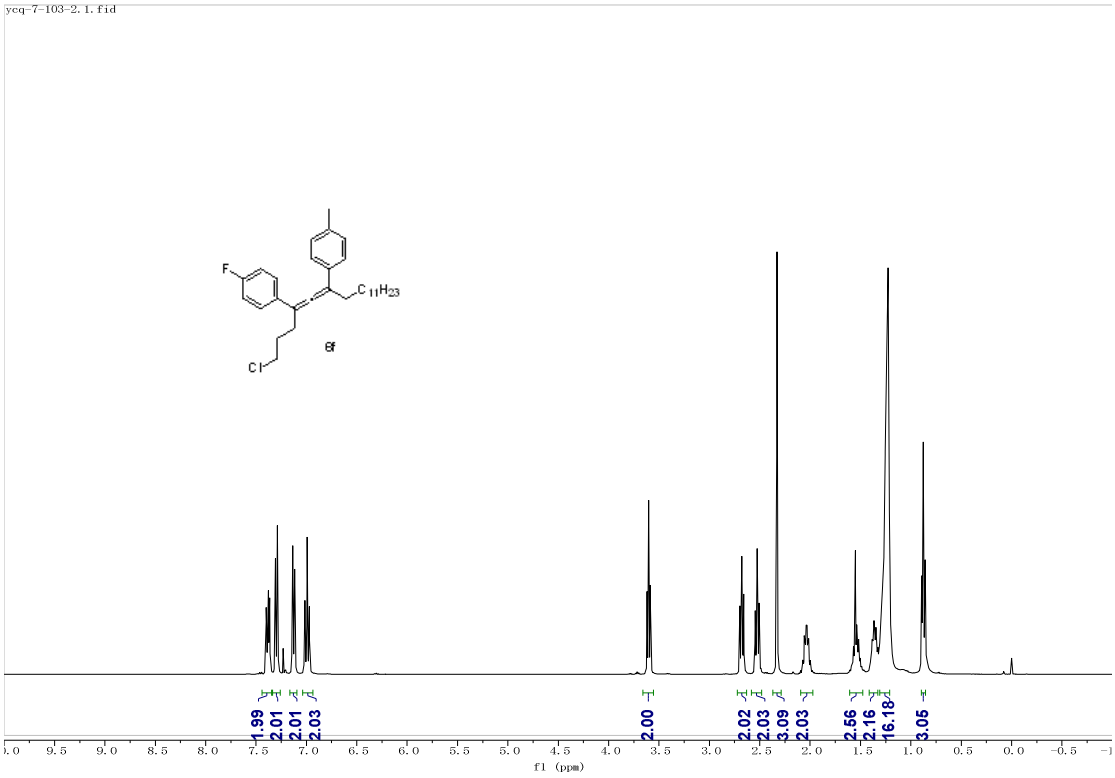

ycq-7-118-1.3.fid
202.532
136.572
136.266
135.639
135.008
134.300
131.373
129.092
128.162
126.536
126.080
106.580
106.532
44.858
31.997
31.618
31.024
29.773
29.733
29.720
29.648
29.444
28.337
22.770
21.131
21.037
20.692
f1 (ppm)
6c

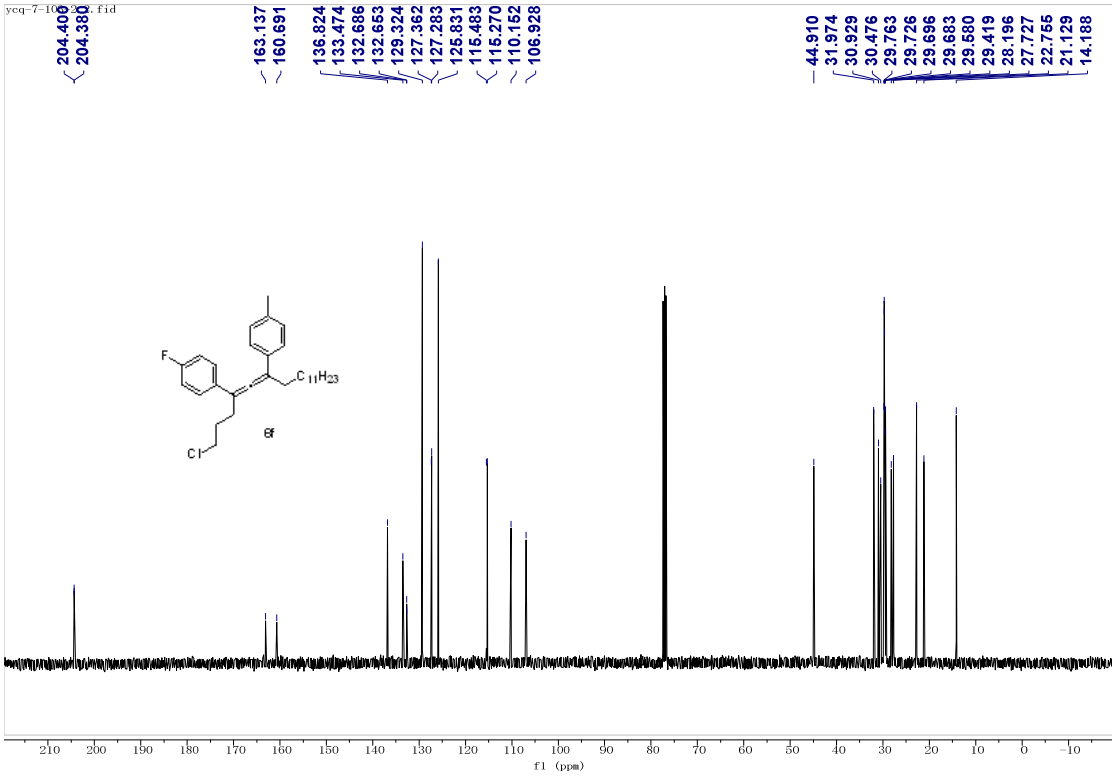

ycq-tbu.1.fid
tBu
C11H23
Cl
6d
6.08
2.08
2.00
1.98
2.00
3.10
2.03
2.09
2.35
9.06
16.16
3.08
f1 (ppm)

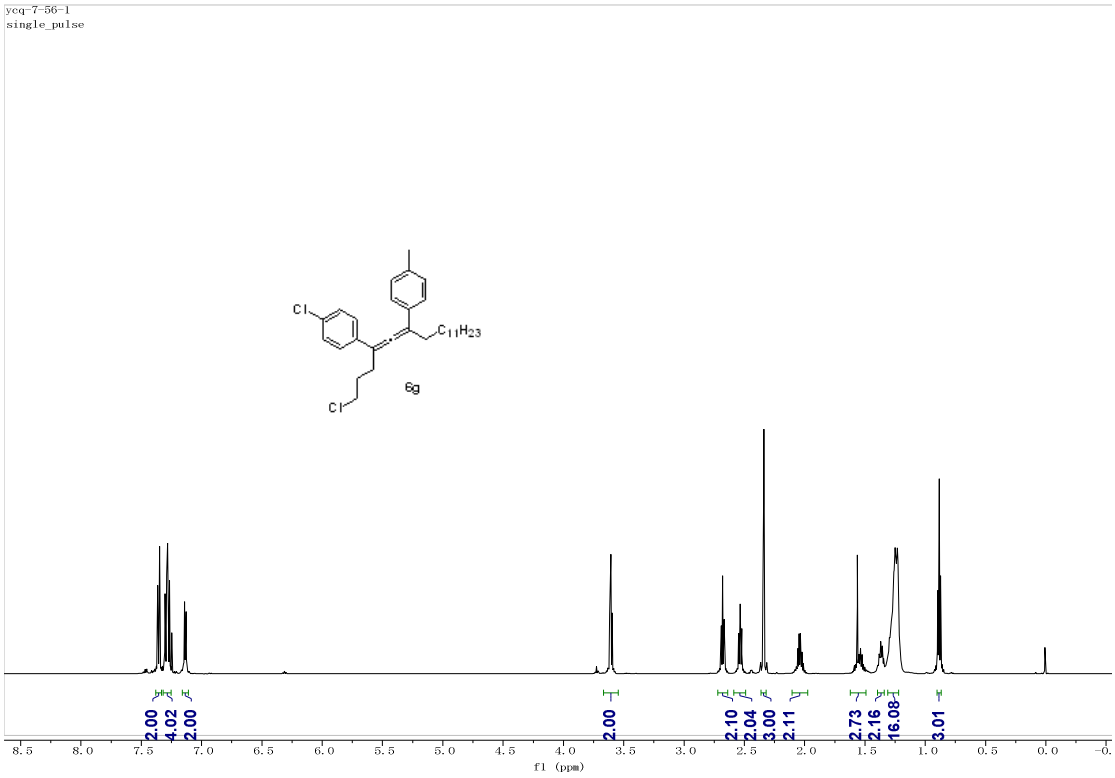

ycq-tbu.2.fid
204.566
149.850
136.590
133.757
133.659
129.247
125.858
125.540
125.481
109.850
107.374
45.026
31.986
31.355
31.050
30.537
29.844
29.751
29.714
29.606
29.435
28.264
27.530
22.766
21.136
tBu
C11H23
Cl
6d
f1 (ppm)

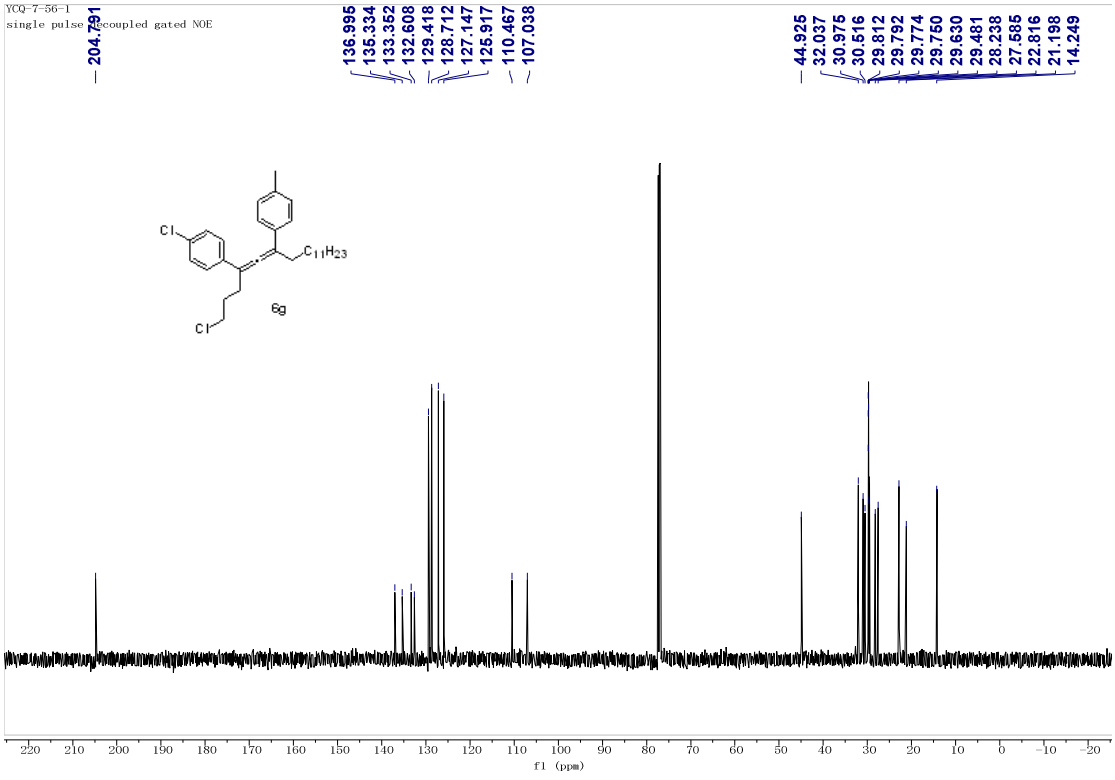

ycq-7-80-1.1.fid
$C_{11}H_{23}$
Cl
6e
2.00
2.10
2.00
1.05
2.00
2.01
2.03
3.00
6.06
2.05
3.04
2.14
16.34
3.06
f1 (ppm)

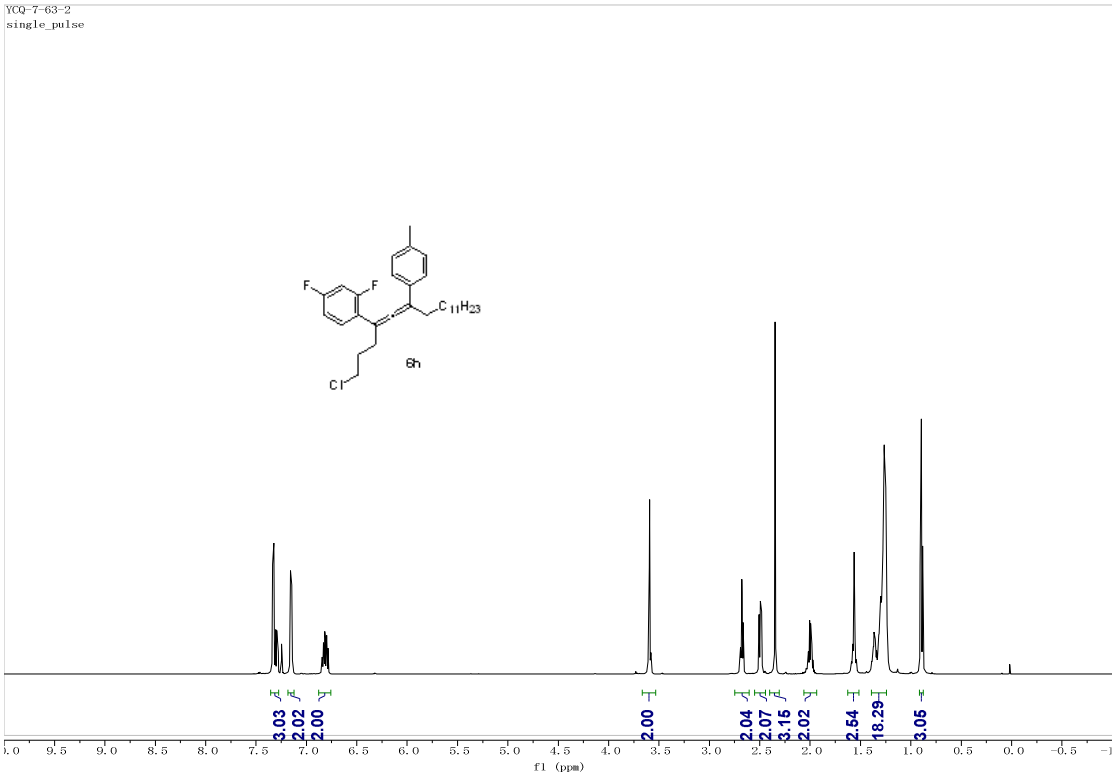

ycq-7-91-13C.fid
204.405
136.655
136.534
135.343
133.860
129.831
129.233
127.080
125.847
123.288
109.568
107.502
45.033
31.977
31.049
29.801
29.742
29.697
29.605
29.423
28.201
27.640
22.754
21.120
20.014
19.466
$C_{11}H_{23}$
Cl
6e
f1 (ppm)

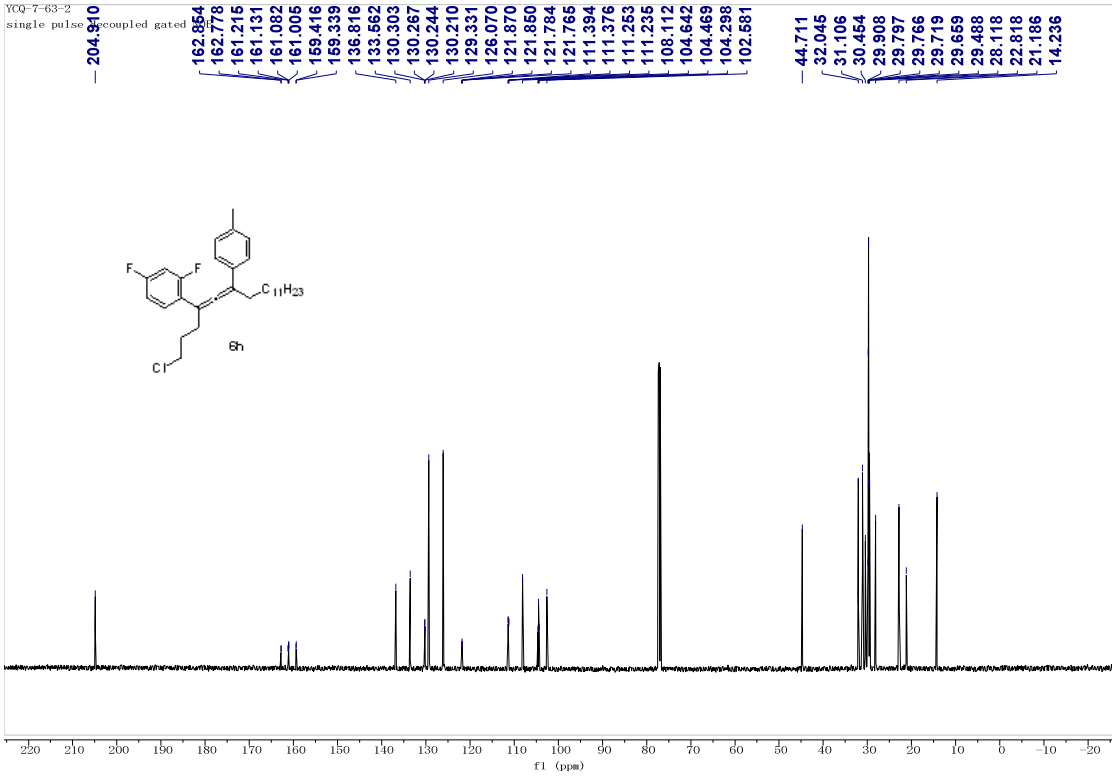

ycq-7-103-2.1.fid
F
C11H23
Br
Cl
1.99
2.01
2.01
2.03
2.00
2.02
2.03
3.09
2.03
2.56
2.16
16.18
3.05
f1 (ppm)

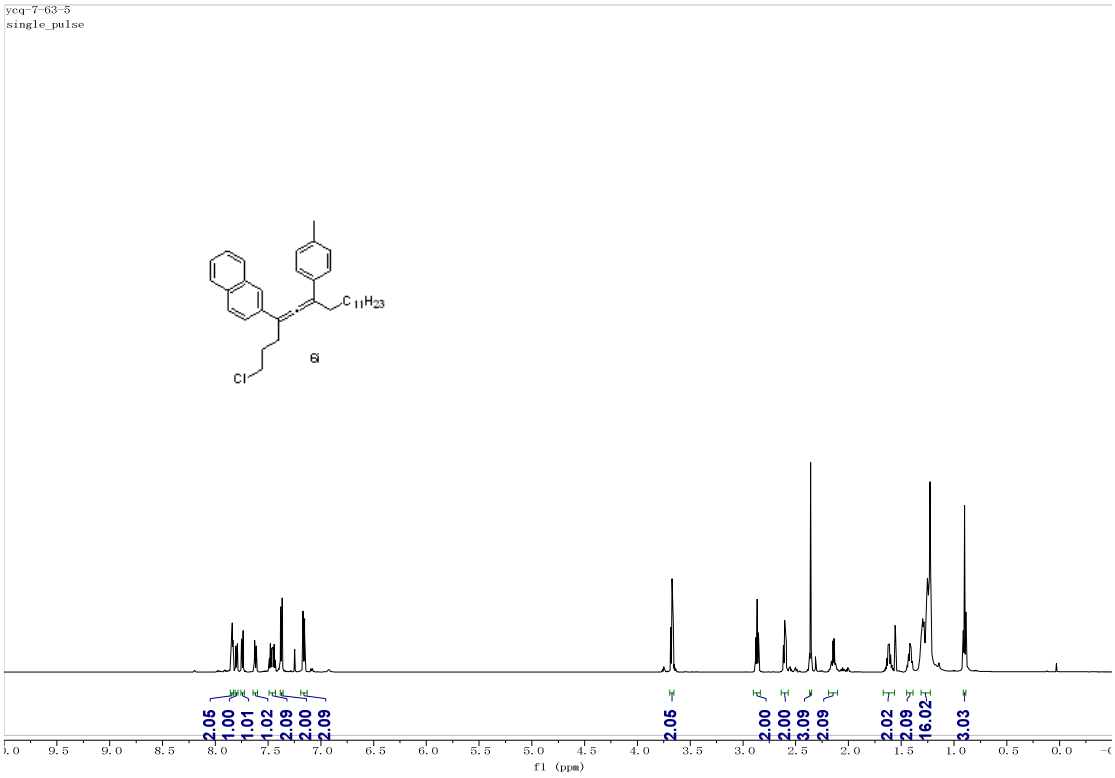

ycq-7-103-2.1.fid
204.400
204.380
163.137
160.691
136.824
133.474
132.686
132.653
129.324
127.362
127.283
125.831
115.483
115.270
110.152
106.928
44.910
31.974
30.929
30.476
29.763
29.726
29.696
29.683
29.580
29.419
28.196
27.727
22.755
21.129
14.188
F
C11H23
Br
Cl
f1 (ppm)

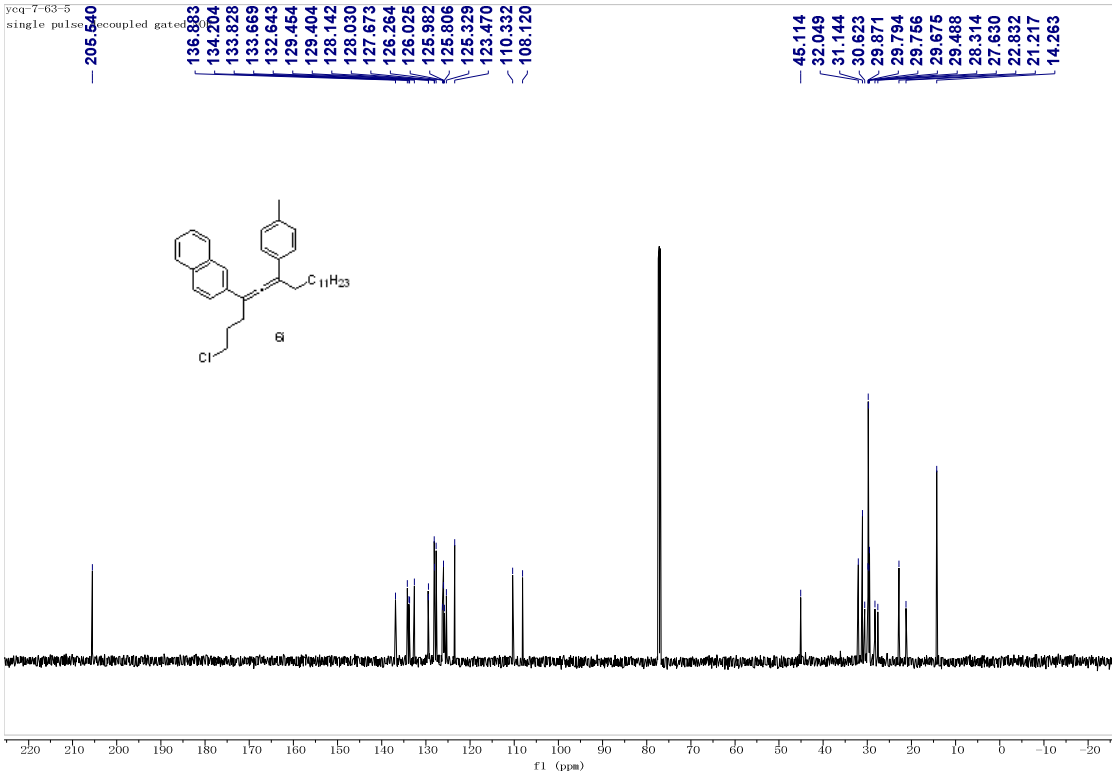

ycq-7-56-1
single_pulse
Cl
$C_{11}H_{23}$
Cl
6g
2.00
4.02
2.00
2.00
2.10
2.04
3.00
2.11
2.73
2.16
16.08
3.01
f1 (ppm)

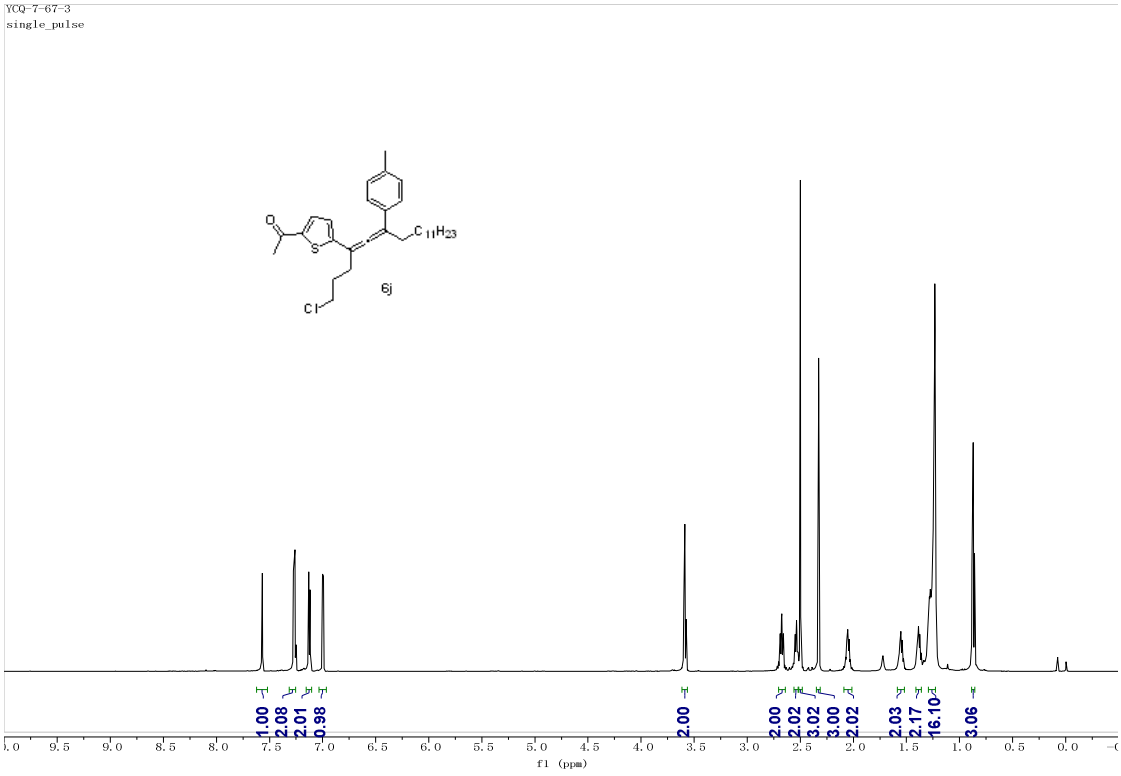

YCQ-7-56-1
single pulse decoupled gated NOE
204.791
136.995
135.334
133.352
132.608
129.418
128.712
127.147
125.917
110.467
107.038
44.925
32.037
30.975
30.516
29.812
29.792
29.774
29.750
29.630
29.481
28.238
27.585
22.816
21.198
14.249
Cl
$C_{11}H_{23}$
Cl
6g
f1 (ppm)

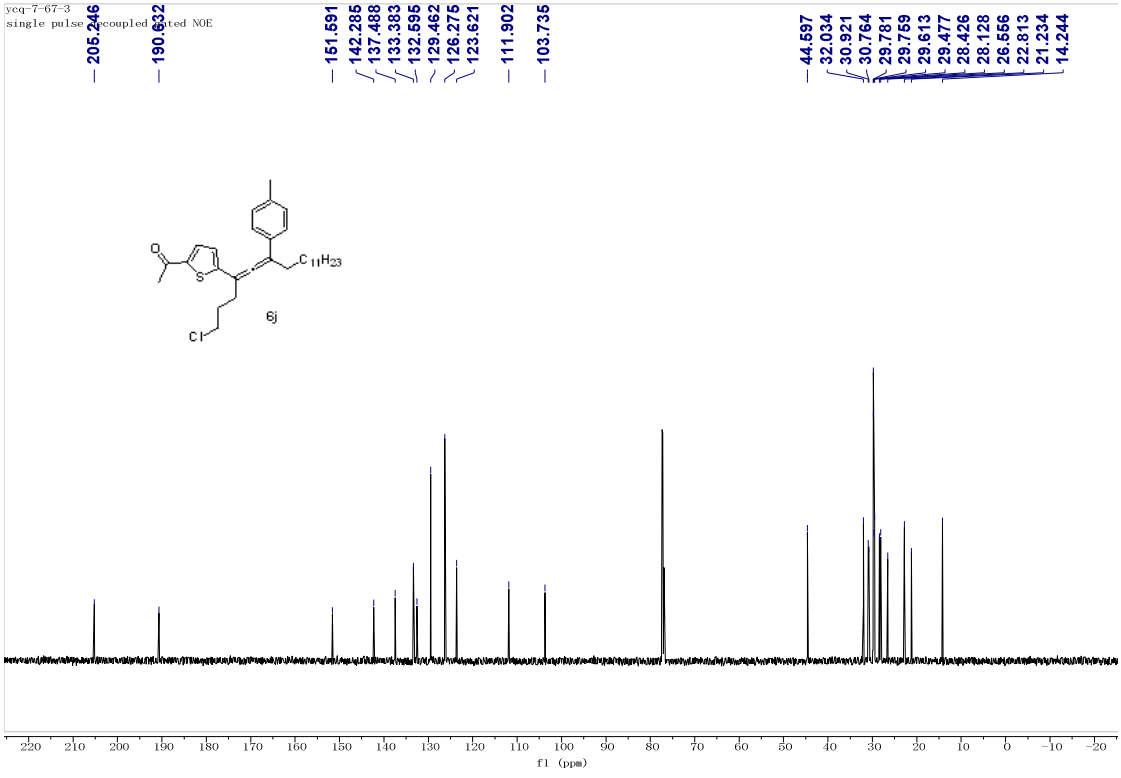

YCQ-7-63-2
single_pulse
F
F
C11H23
Cl
6h
3.03
2.02
2.00
2.00
2.04
2.07
3.15
2.02
2.54
18.29
3.05
f1 (ppm)

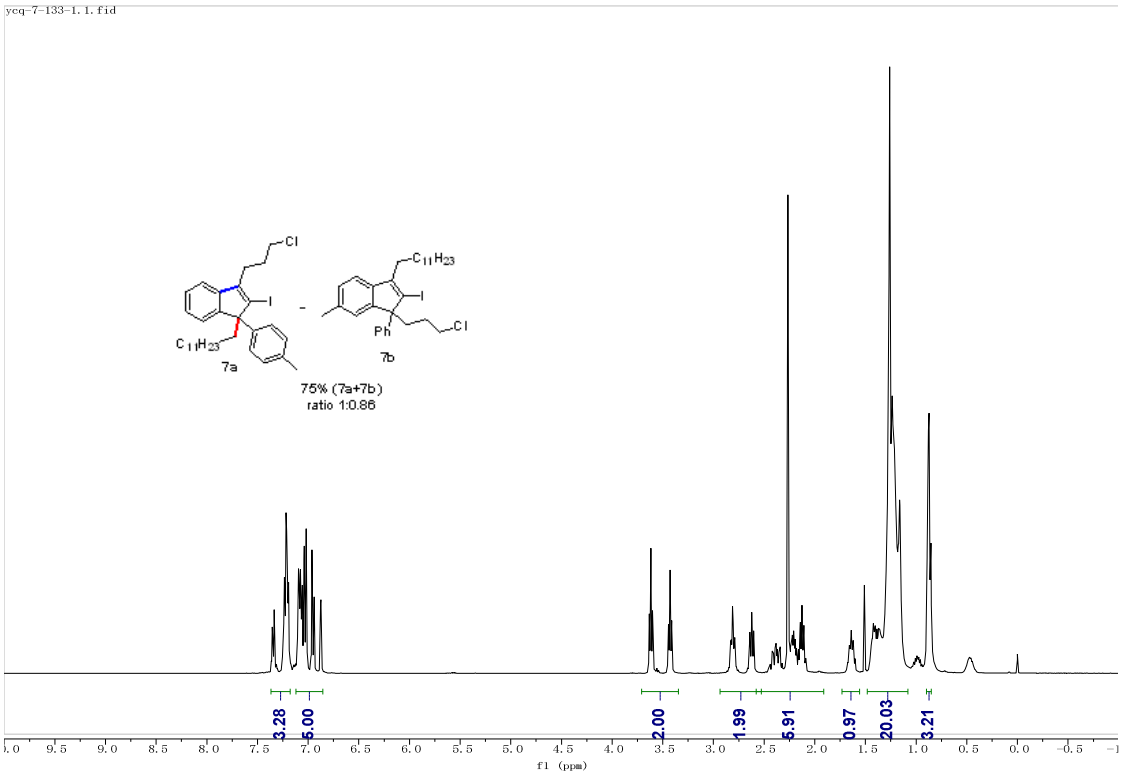

YCQ-7-63-2
single pulse decoupled gated DEPT
204.310
162.854
162.778
161.215
161.131
161.082
161.005
159.416
159.339
136.816
133.562
130.303
130.267
130.244
130.210
129.331
126.070
121.870
121.850
121.784
121.765
111.394
111.376
111.253
111.235
108.112
104.642
104.469
104.298
102.581
44.711
32.045
31.106
30.454
29.908
29.797
29.766
29.719
29.659
29.488
28.118
22.818
21.186
14.236
F
F
C11H23
Cl
6h
f1 (ppm)

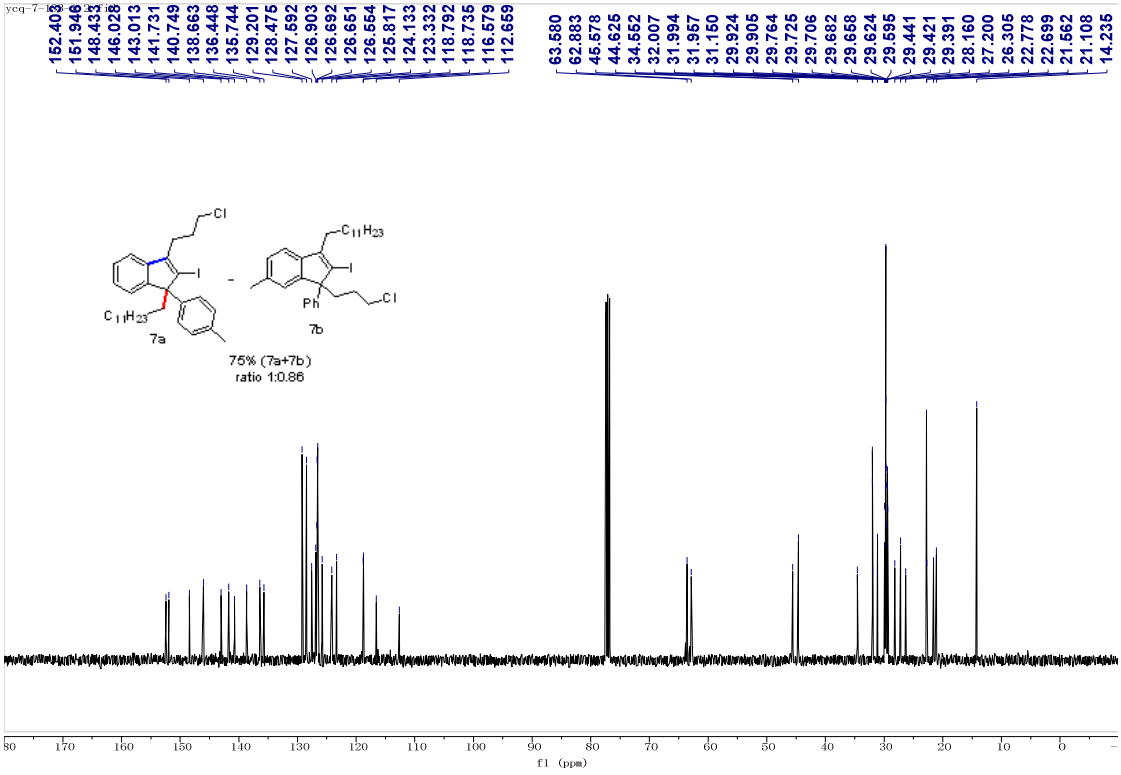

ycq-7-63-5
single_pulse
C11H23
Si
Cl
2.05
1.00
1.01
1.02
2.09
2.00
2.09
2.05
2.00
2.00
3.09
2.09
2.02
2.09
16.02
3.03
f1 (ppm)

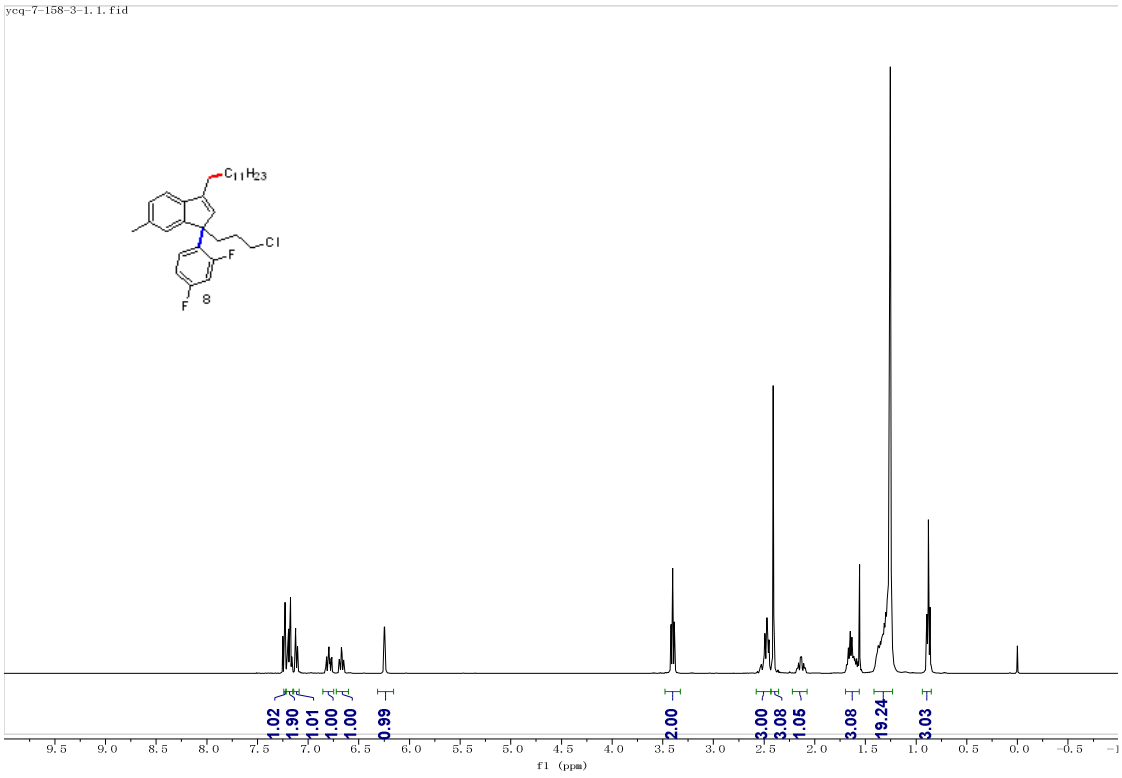

ycq-7-63-5
single pulse decoupled gated 13C
205.540
136.883
134.204
133.828
133.669
132.643
129.454
129.404
128.142
128.030
127.673
126.264
126.025
125.982
125.806
125.329
123.470
110.332
108.120
45.114
32.049
31.144
30.623
29.871
29.794
29.756
29.675
29.488
28.314
27.630
22.832
21.217
14.263
C11H23
Si
Cl
f1 (ppm)

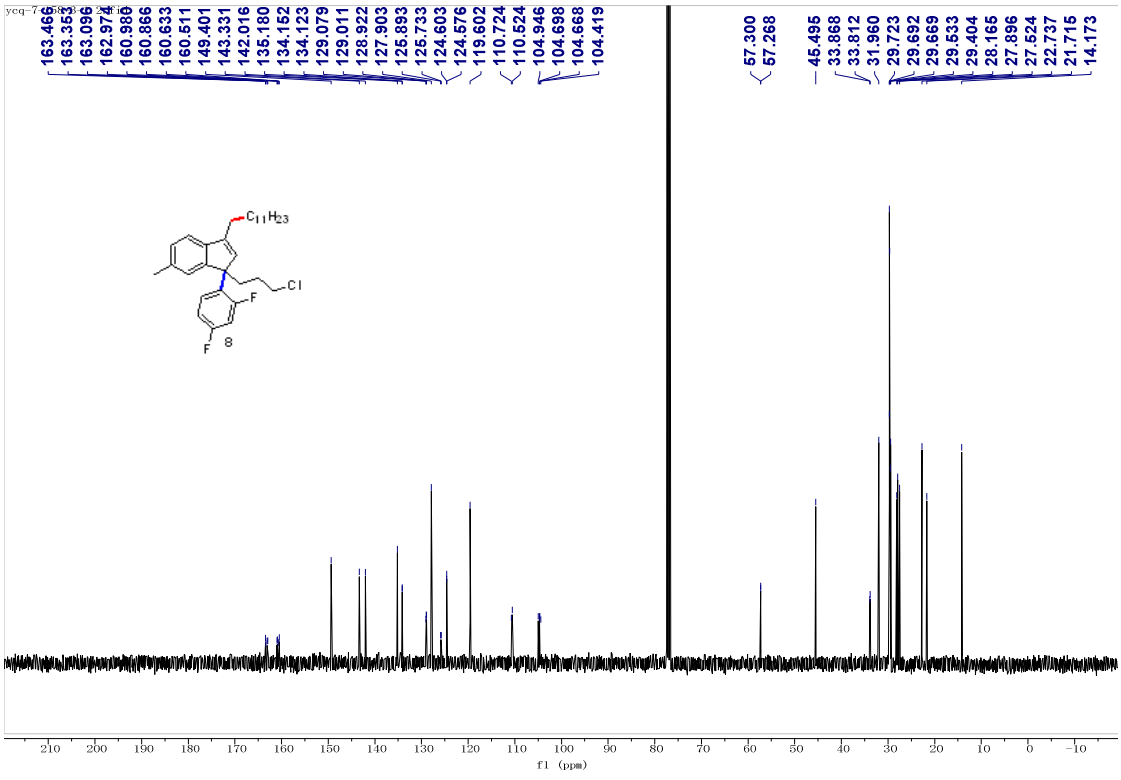

YCQ-7-67-3
single_pulse
6j
1.00
2.08
2.01
0.98
2.00
2.00
2.02
3.02
3.00
2.02
2.03
2.17
16.10
3.06
f1 (ppm)

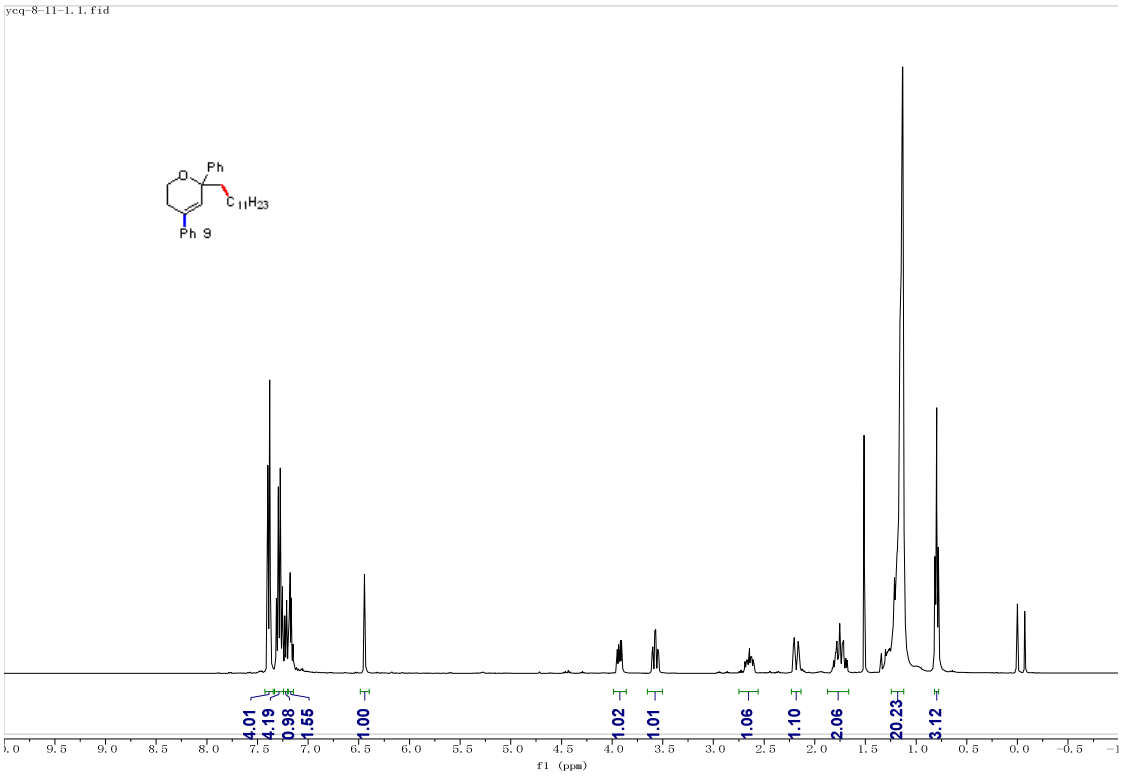

ycq-7-67-3
single pulse decoupled gated NOE
206.246
190.632
151.591
142.285
137.488
133.383
132.595
129.462
126.275
123.621
111.902
103.735
44.597
32.034
30.921
30.764
29.781
29.759
29.613
29.477
28.426
28.128
26.556
22.813
21.234
14.244
6j
f1 (ppm)

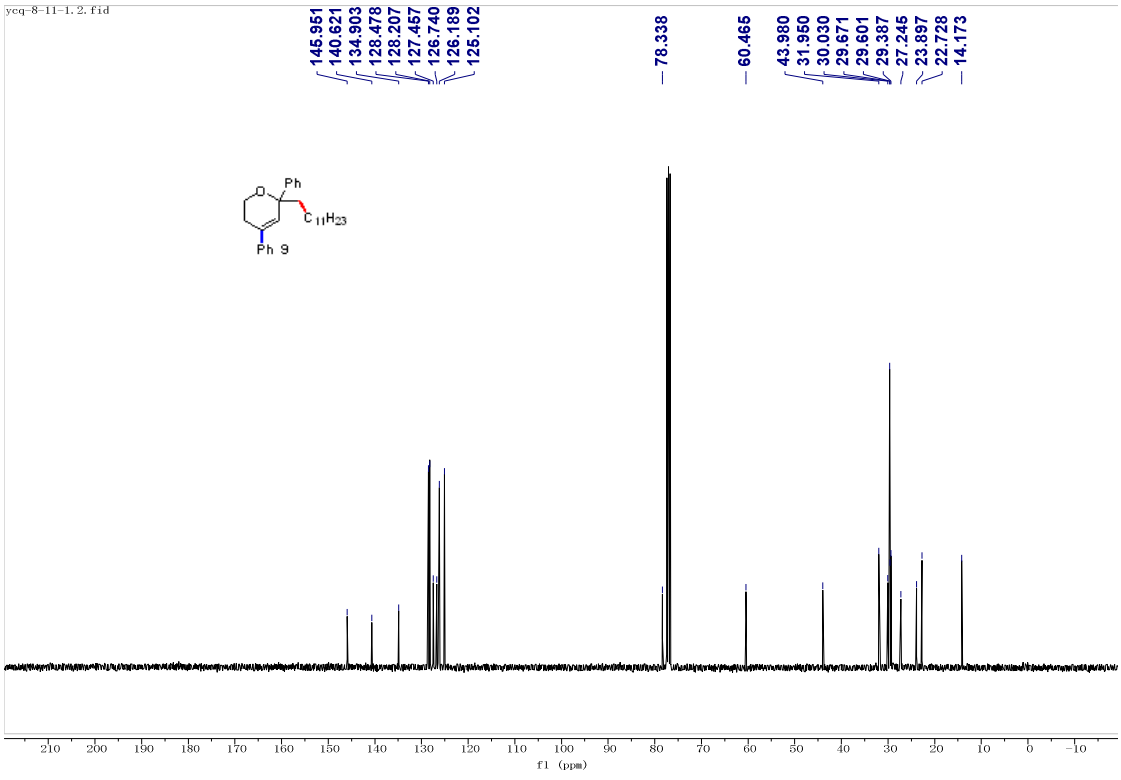

ycq-7-133-1.1.fid
Cl
I
$C_{11}H_{23}$
7a
$C_{11}H_{23}$
I
Ph
Cl
7b
75% (7a+7b)
ratio 1:0.86
3.28
5.00
2.00
1.99
5.91
0.97
20.03
3.21
f1 (ppm)

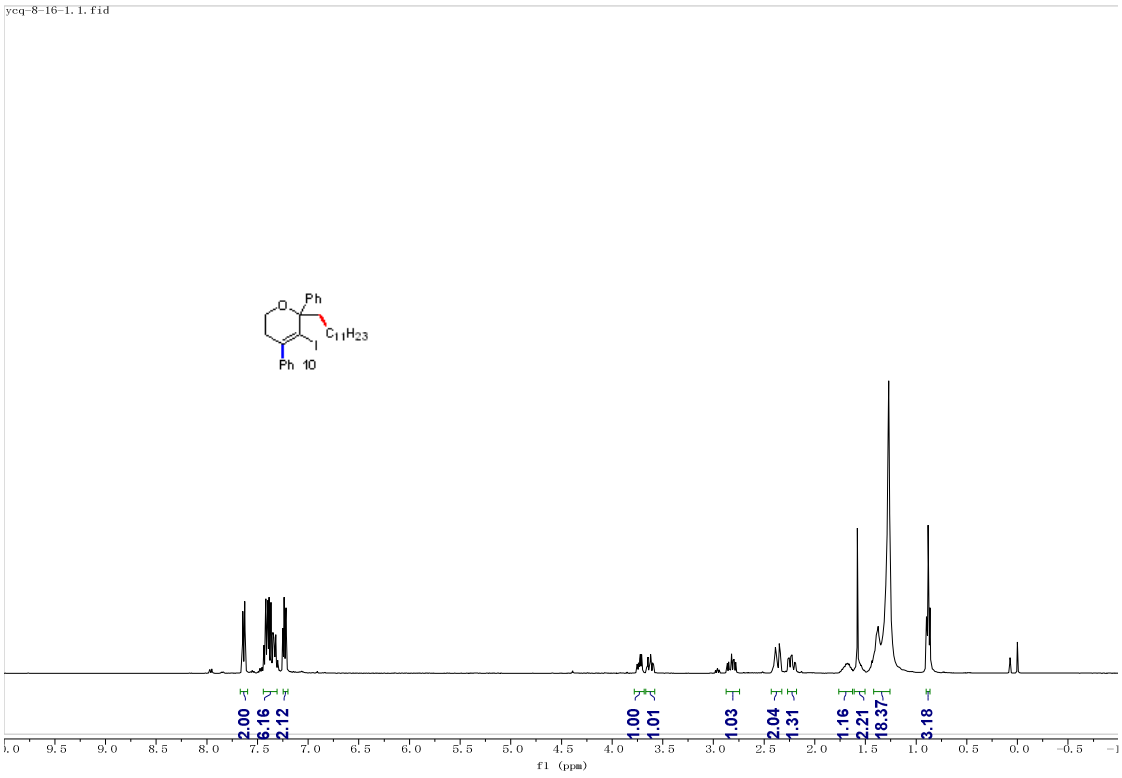

ycq-7-
152.403
151.946
148.433
146.028
143.013
141.731
140.749
138.663
136.448
135.744
129.201
128.475
127.592
126.903
126.692
126.651
126.564
125.817
124.133
123.332
118.792
118.735
116.579
112.659
63.580
62.883
45.678
44.625
34.552
32.007
31.994
31.957
31.150
29.924
29.905
29.764
29.725
29.706
29.682
29.668
29.624
29.595
29.441
29.421
29.391
28.160
27.200
26.305
22.778
22.699
21.562
21.108
14.235
Cl
I
$C_{11}H_{23}$
7a
$C_{11}H_{23}$
I
Ph
Cl
7b
75% (7a+7b)
ratio 1:0.86
f1 (ppm)

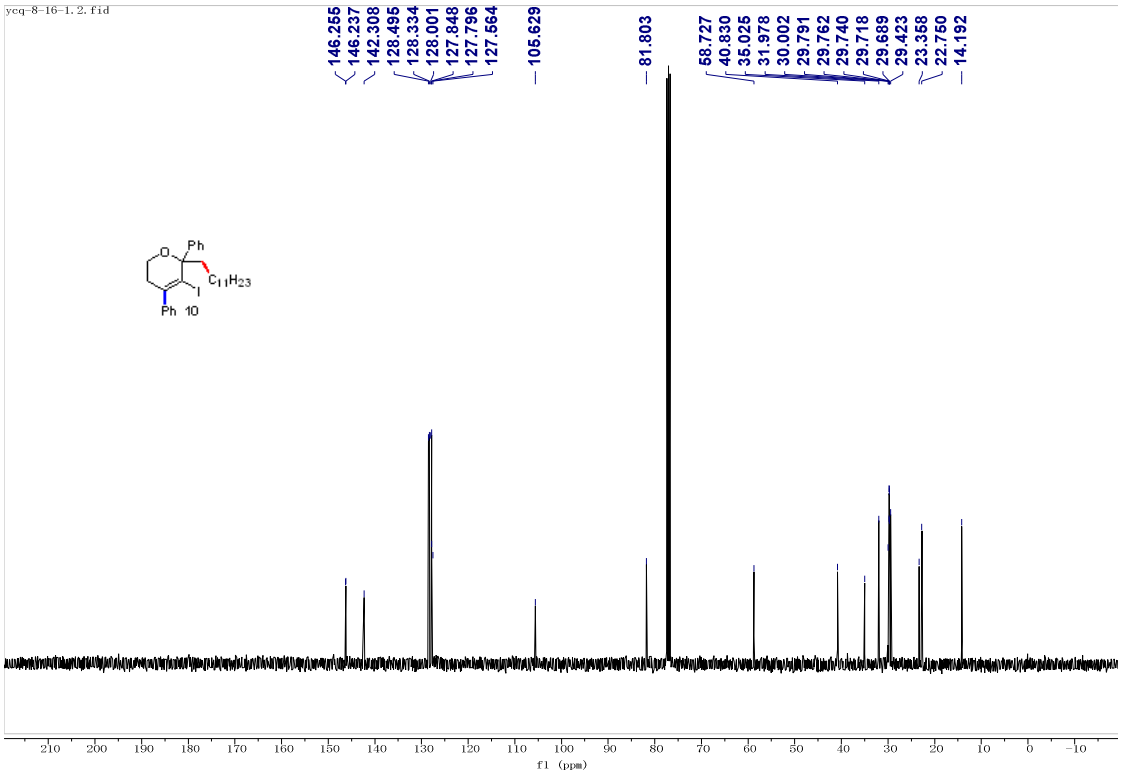

ycq-7-158-3-1.1.fid
$C_{11}H_{23}$
Cl
F
F
8
1.02
1.90
1.01
1.00
1.00
0.99
2.00
3.00
3.08
1.05
3.08
19.24
3.03
f1 (ppm)

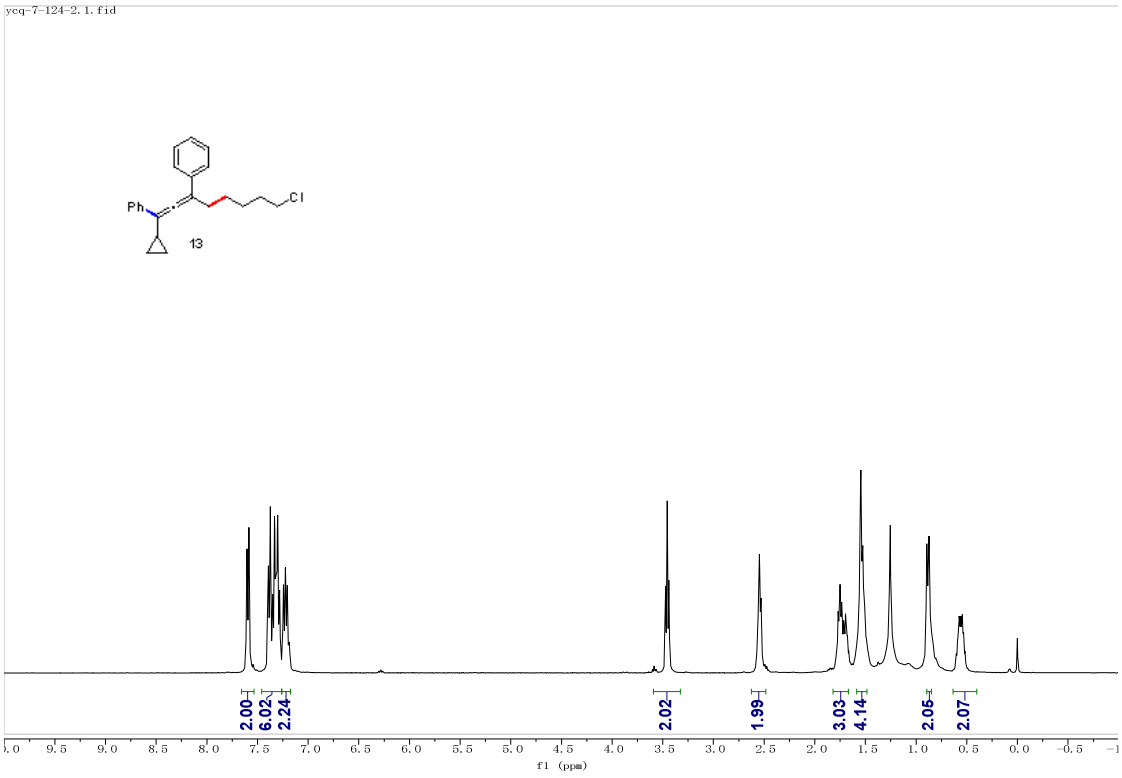

163.466
163.353
163.096
162.974
160.985
160.866
160.633
160.511
149.401
143.331
142.016
135.180
134.152
134.123
129.079
129.011
128.922
127.903
125.893
125.733
124.603
124.576
119.602
110.724
110.524
104.946
104.698
104.668
104.419
67.300
67.268
45.495
33.868
33.812
31.960
29.723
29.692
29.669
29.533
29.404
28.165
27.896
27.524
22.737
21.715
14.173
$C_{11}H_{23}$
Cl
F
F
8
f1 (ppm)

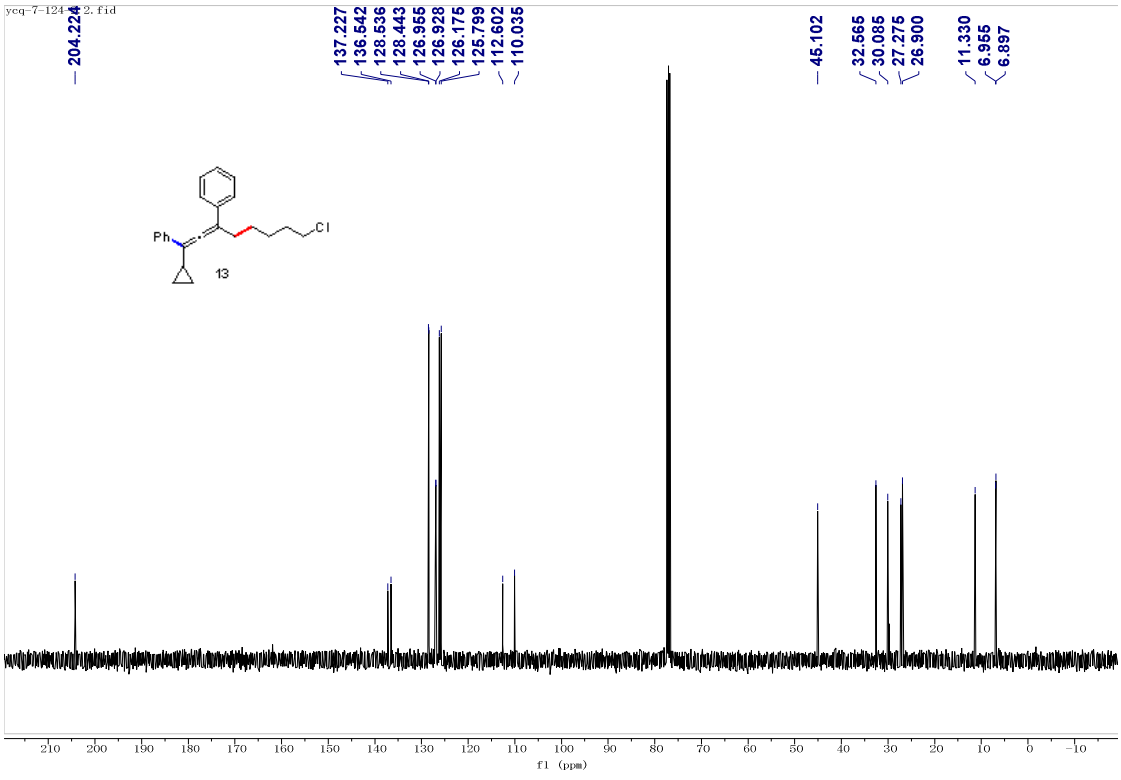

ycq-8-11-1.1.fid
Ph
C11H23
Ph 9
4.01
4.19
0.98
1.55
1.00
1.02
1.01
1.06
1.10
2.06
20.23
3.12
f1 (ppm)

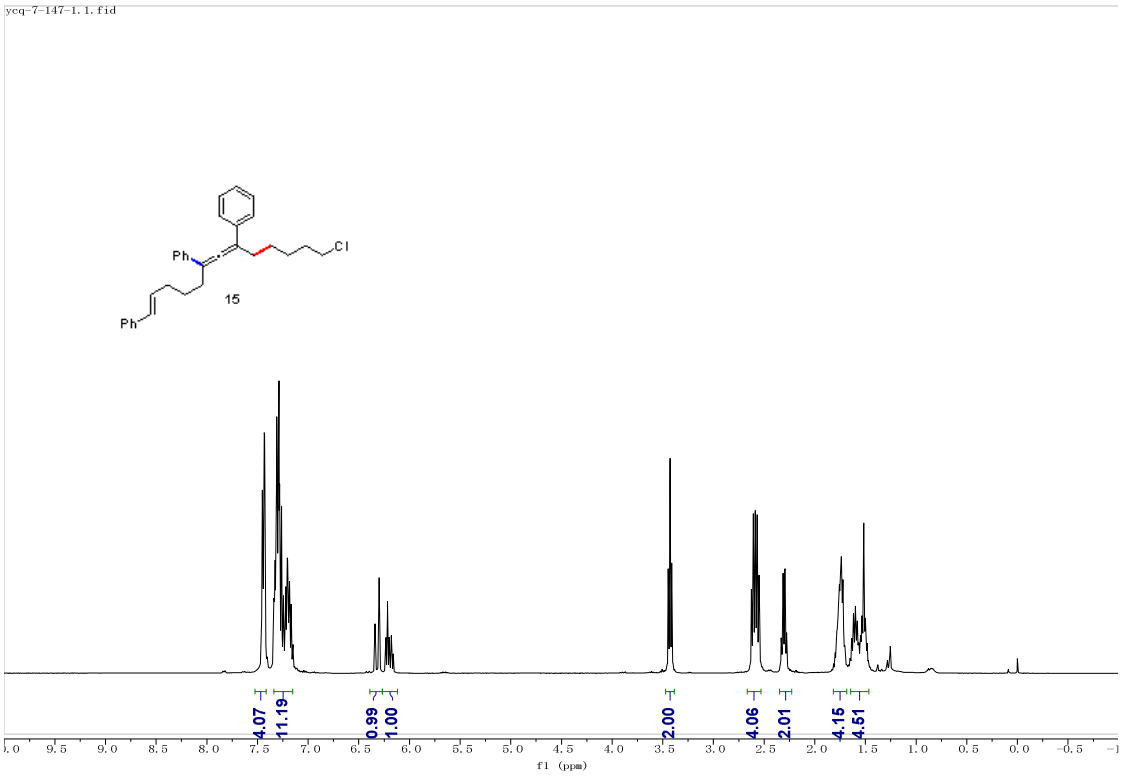

ycq-8-11-1.2.fid
145.951
140.621
134.903
128.478
128.207
127.457
126.740
126.189
125.102
78.338
60.465
43.980
31.950
30.030
29.671
29.601
29.387
27.245
23.897
22.728
14.173
Ph
C11H23
Ph 9
f1 (ppm)

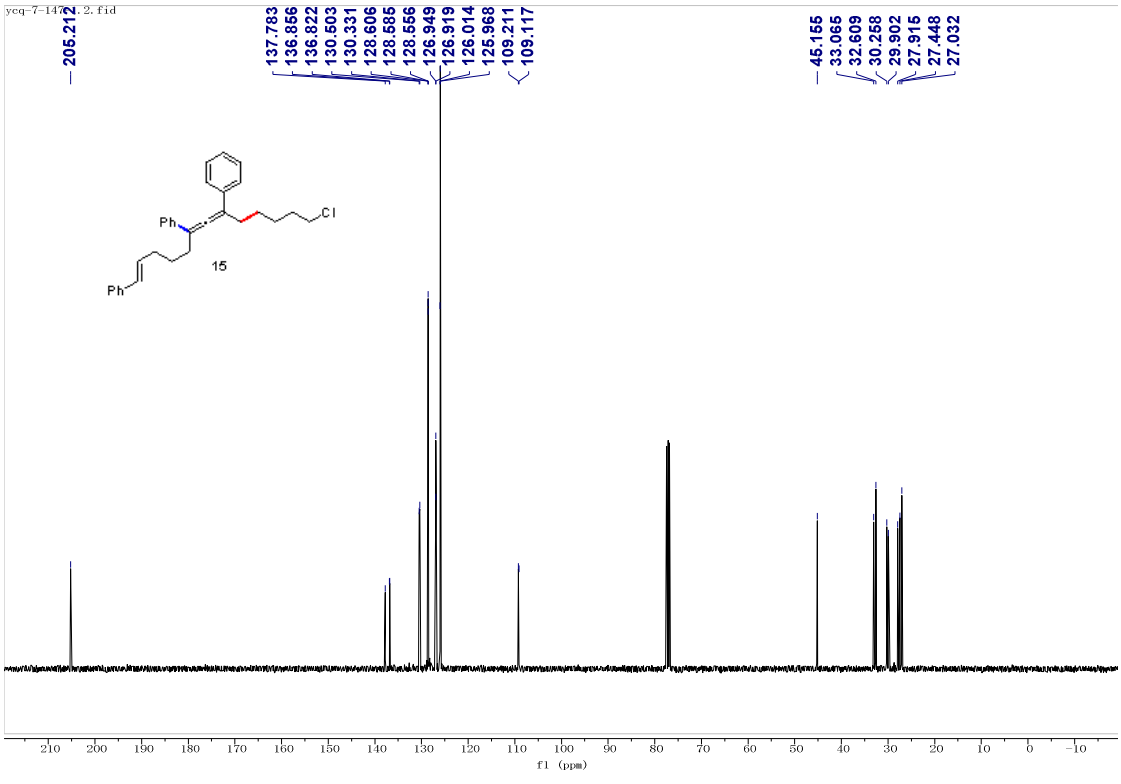

ycq-8-16-1.1.fid
Ph
O
$C_{11}H_{23}$
I
Ph 10
2.00
6.16
2.12
1.00
1.01
1.03
2.04
1.31
1.16
2.21
18.37
3.18
f1 (ppm)

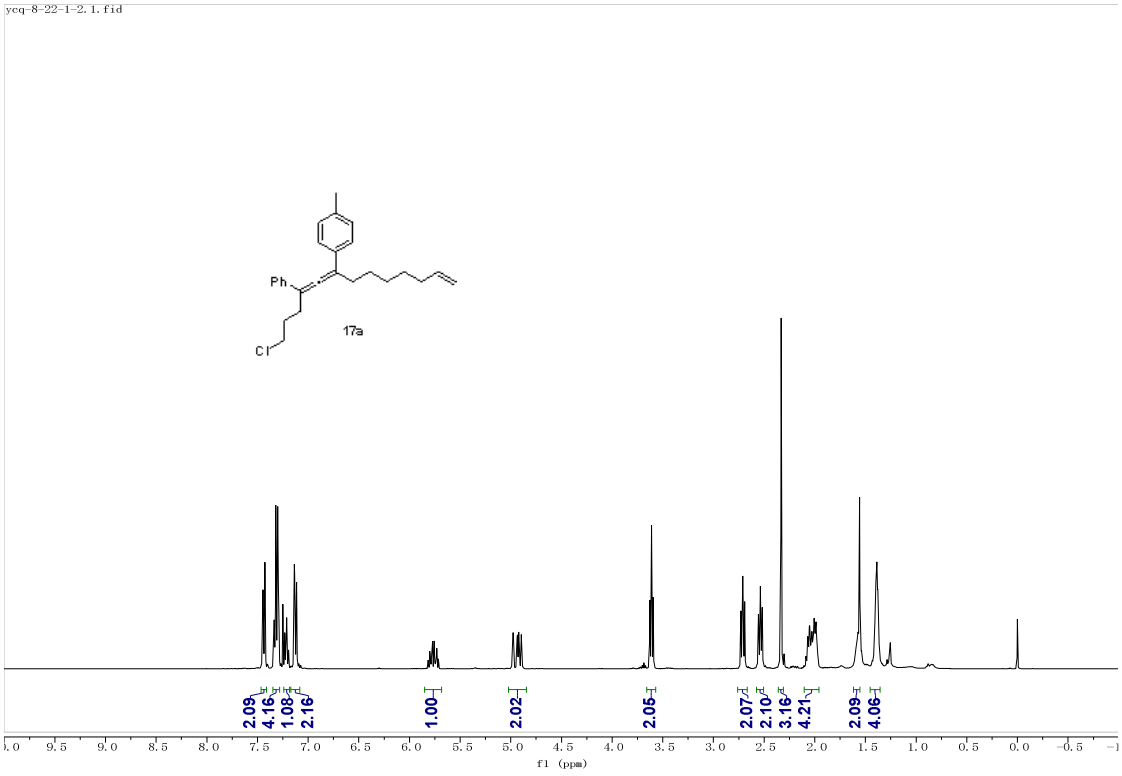

ycq-8-16-1.2.fid
146.255
146.237
142.308
128.495
128.334
128.001
127.848
127.796
127.564
105.629
81.803
58.727
40.830
35.025
31.978
30.002
29.791
29.762
29.740
29.718
29.689
29.423
23.358
22.750
14.192
Ph
O
$C_{11}H_{23}$
I
Ph 10
f1 (ppm)

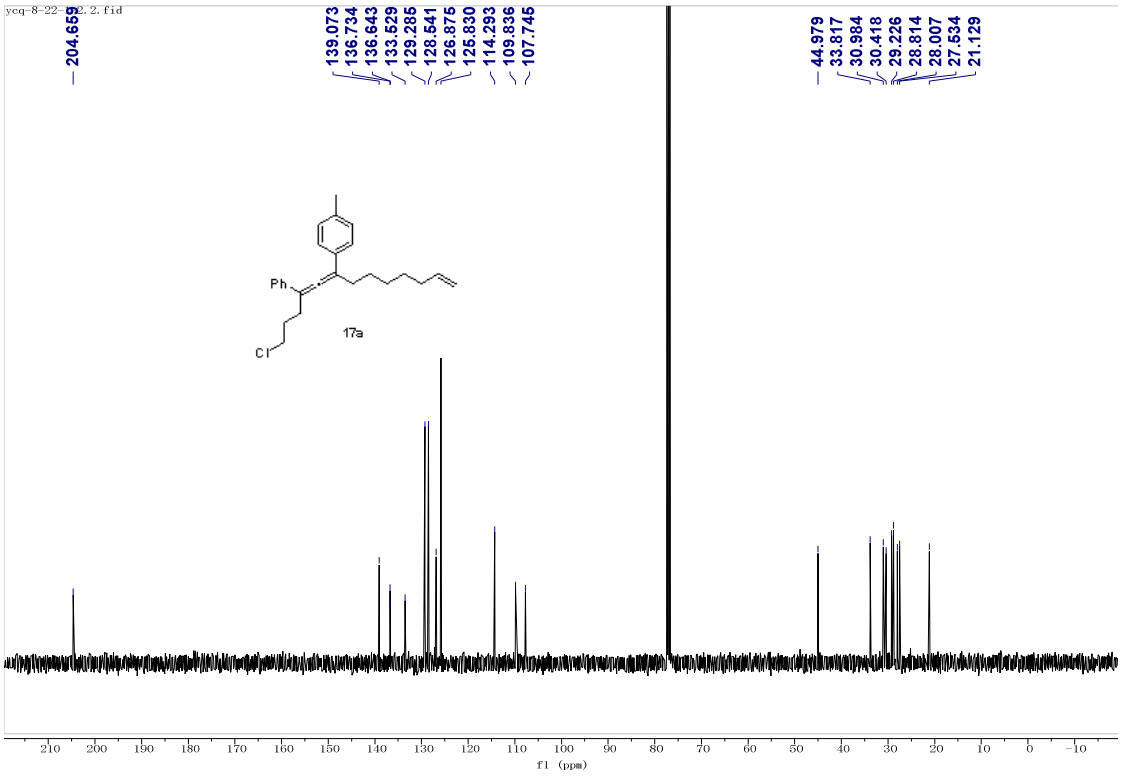

ycq-7-124-2.1.fid
Ph
Cl
13
2.00
6.02
2.24
2.02
1.99
3.03
4.14
2.05
2.07
f1 (ppm)

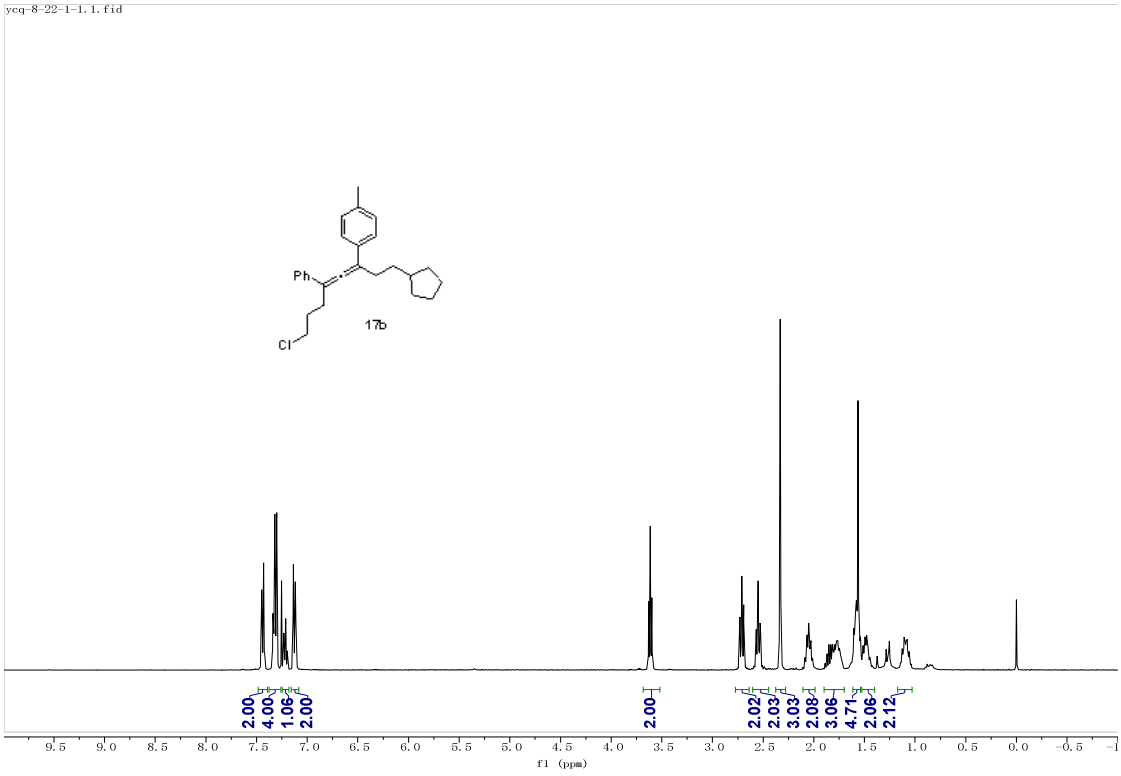

ycq-7-124-2.2.fid
204.224
137.227
136.542
128.536
128.443
126.955
126.928
126.175
125.799
112.602
110.035
45.102
32.565
30.085
27.275
26.900
11.330
6.955
6.897
Ph
Cl
13
f1 (ppm)

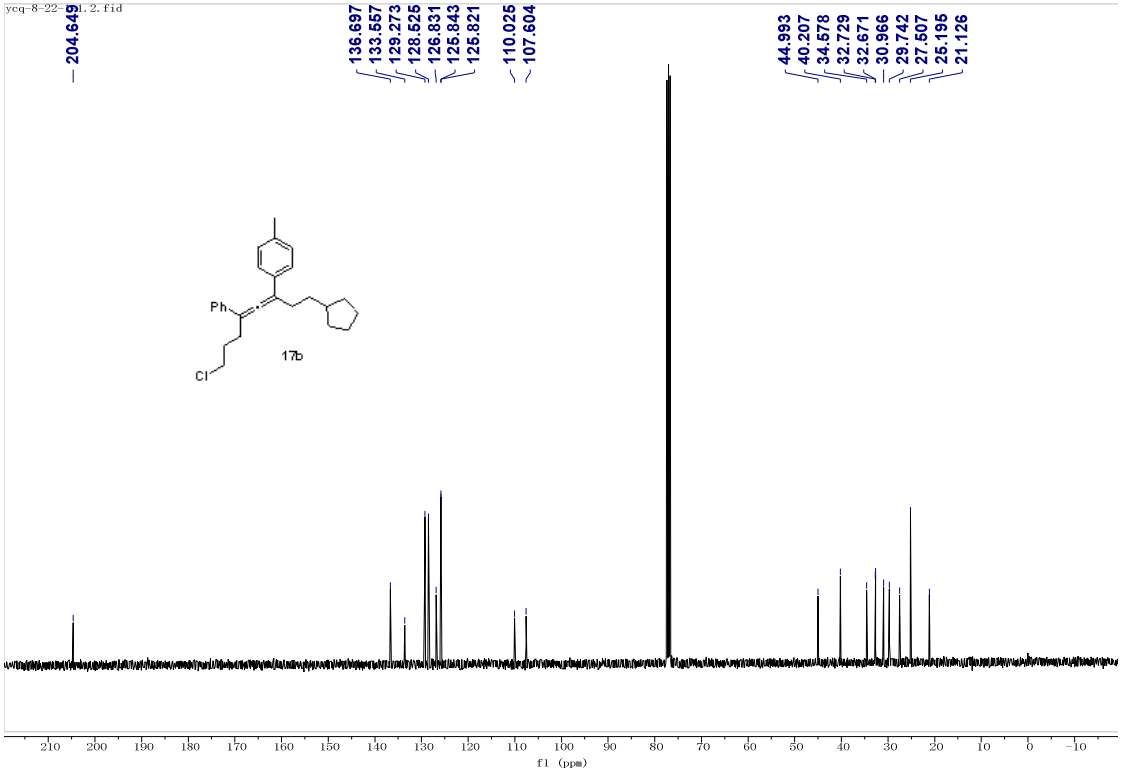

ycq-7-147-1.1.fid
Ph
Cl
Ph
15
4.07
11.19
0.99
1.00
2.00
4.06
2.01
4.15
4.51
f1 (ppm)

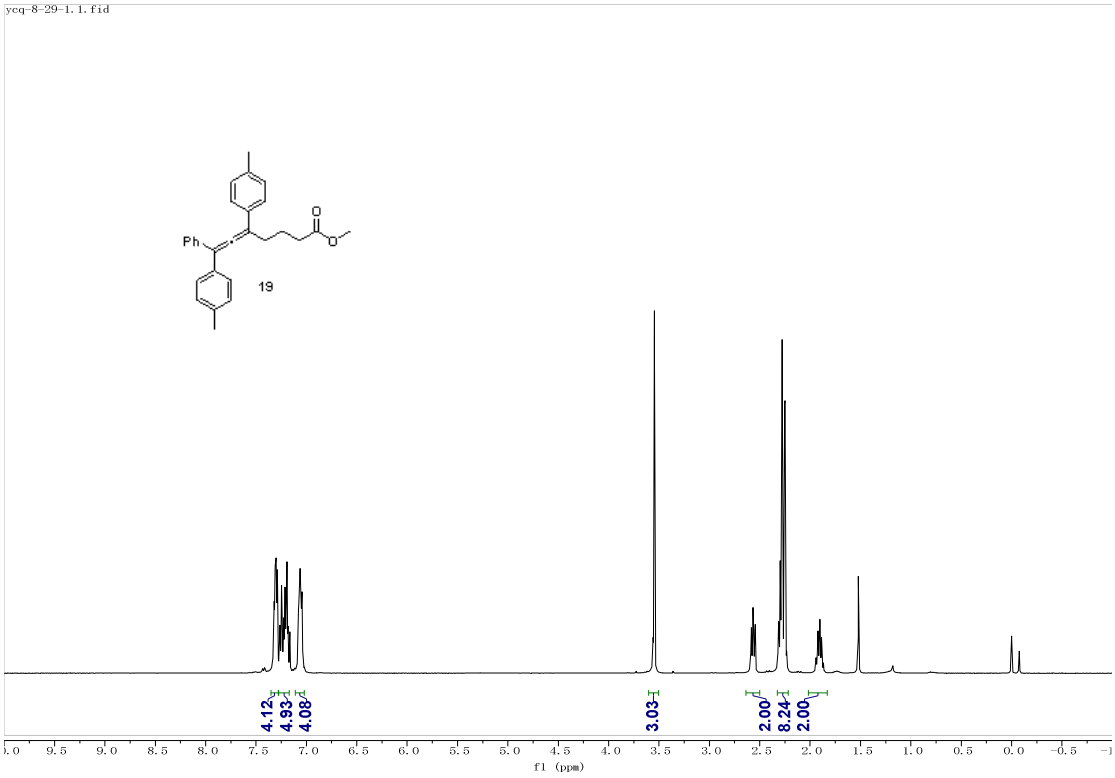

ycq-7-147-1.2.fid
205.212
137.783
136.856
136.822
130.503
130.331
128.606
128.585
128.556
126.949
126.919
126.014
125.968
109.211
109.117
45.155
33.065
32.609
30.258
29.902
27.915
27.448
27.032
Ph
Cl
Ph
15
f1 (ppm)

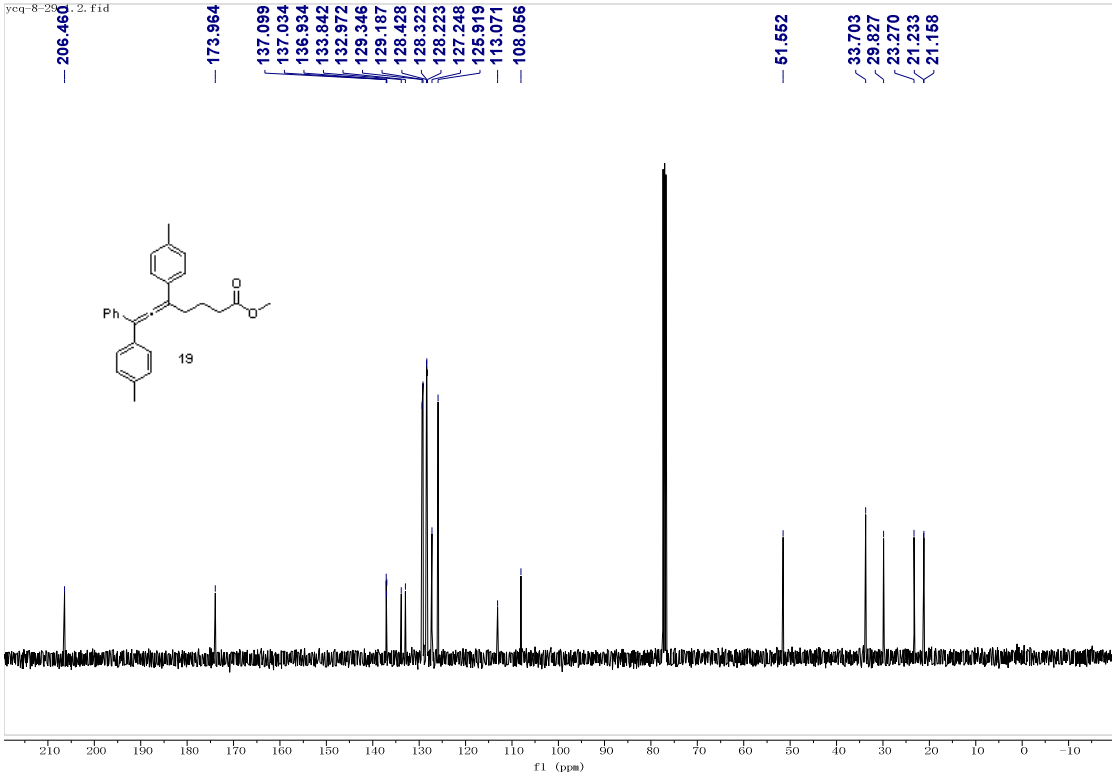

ycq-8-22-1-2.1.fid
Ph
Cl
17a
2.09
4.16
1.08
2.16
1.00
2.02
2.05
2.07
2.10
3.16
4.21
2.09
4.06
f1 (ppm)

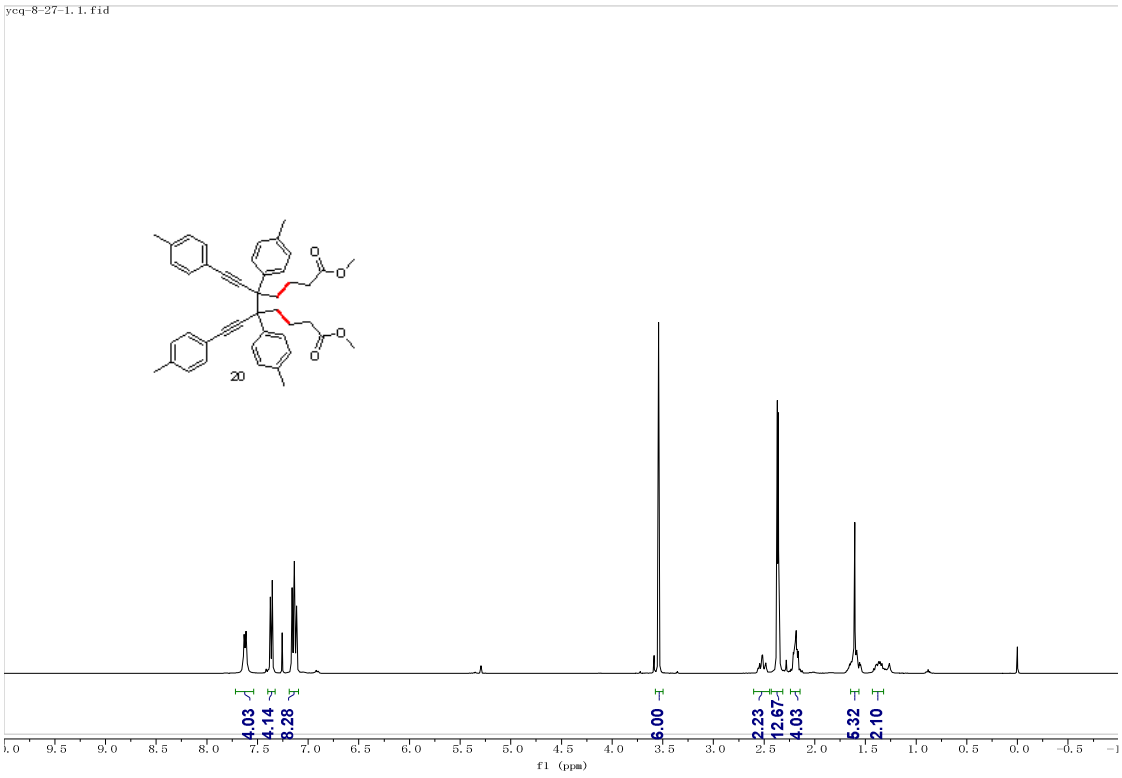

ycq-8-22-2.2.fid
204.659
139.073
136.734
136.643
133.529
129.285
128.541
126.875
125.830
114.293
109.836
107.745
44.979
33.817
30.984
30.418
29.226
28.814
28.007
27.534
21.129
Ph
Cl
17a
f1 (ppm)

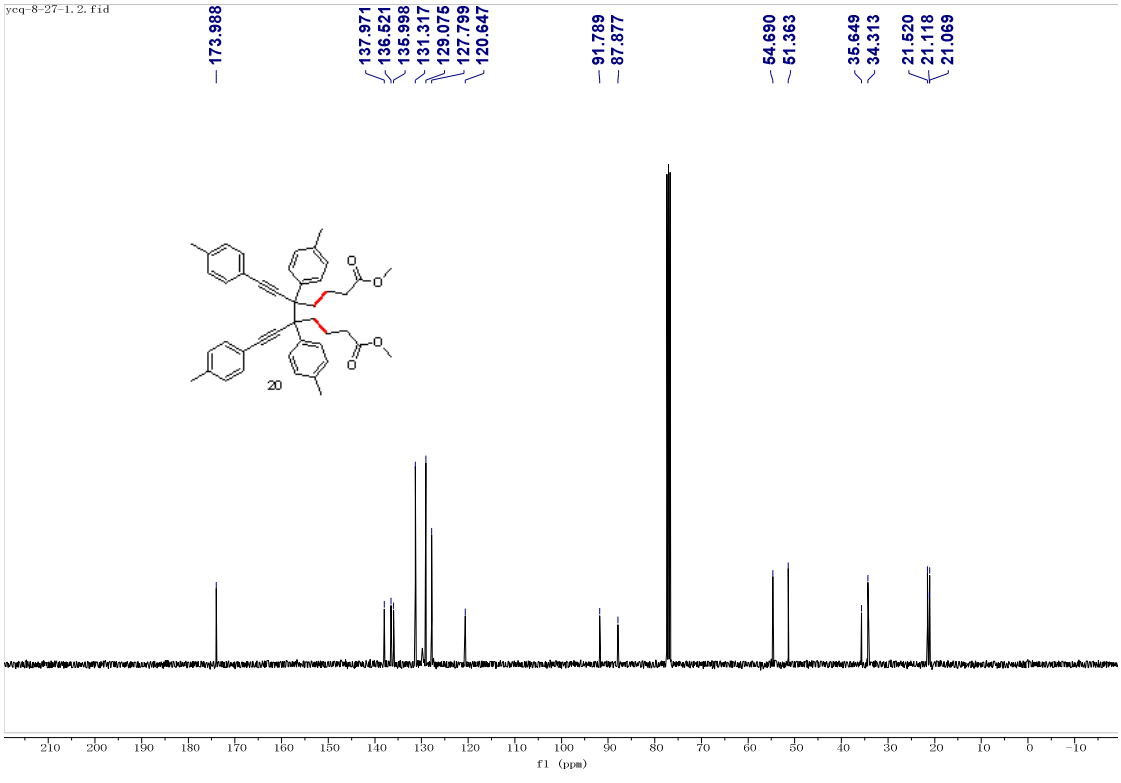

ycq-8-22-1-1.1.fid
Ph
Cl
17b
2.00
4.00
1.06
2.00
2.00
2.02
2.03
3.03
2.08
3.06
4.71
2.06
2.12
f1 (ppm)


ycq-8-22-1.2.fid
204.649
136.697
133.557
129.273
128.525
126.831
125.843
125.821
110.025
107.604
44.993
40.207
34.678
32.729
32.671
30.966
29.742
27.507
25.195
21.126
Ph
Cl
17b
f1 (ppm)


ycq-8-29-1.1.fid
Ph
O
O
19
4.12
4.93
4.08
3.03
2.00
8.24
2.00
f1 (ppm)


ycq-8-29-1.2.fid
206.460
173.964
137.099
137.034
136.934
133.842
132.972
129.346
129.187
128.428
128.322
128.223
127.248
125.919
113.071
108.056
51.552
33.703
29.827
23.270
21.233
21.158
Ph
O
O
19
f1 (ppm)


ycq-8-27-1.1.fid
20
4.03
4.14
8.28
6.00
2.23
12.67
4.03
5.32
2.10
f1 (ppm)


ycq-8-27-1.2.fid
173.988
137.971
136.521
135.998
131.317
129.075
127.799
120.647
91.789
87.877
64.690
61.363
35.649
34.313
21.520
21.118
21.069
20
f1 (ppm)