Supplementary Information

Activation of Alkynes by Chalcogen Bonding: A Se···π Interaction Catalyzed Intramolecular Cyclization of 1,6–Diynes

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Table of Contents:

1. General Information

All the chemicals were either purchased from commercial suppliers or purified by standard procedures as specified in *Purification of Laboratory Chemicals*, 7th Ed (Armarego, W. L. F.; Chai, C. L. L. Butterworth Heinemann: 2013). All manipulations were carried out by using standard Schlenk techniques. All solvents were purified and degassed prior to use. Analytical thin-layer chromatography (TLC) was performed on silica gel plates and analyzed by UV light or by potassium permanganate stains followed by heating. Flash chromatography was carried out utilizing silica gel (200-300 mesh). ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, ^{19}F NMR, ^{77}Se NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 at 298K on a Bruker AM-400 spectrometer (400 MHz ^{1}H, 100 MHz ^{13}C, 162 MHz ^{31}P NMR, 376 MHz ^{19}F NMR, 76 MHz ^{77}Se NMR). The chemical shifts are reported in ppm relative to either the residual solvent peak (^{13}C) (δ = 77.00 ppm for $CDCl_3$; δ = 53.84 ppm for CD_2Cl_2), (^{1}H) (δ = 7.26 ppm for $CDCl_3$; δ = 5.30 ppm for CD_2Cl_2; δ = 0 ppm for TMS) as an internal standard. (^{31}P) (δ = 0 ppm for 85% H_3PO_4 aqueous solution), as an external standard. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet doublet, q = quartet), coupling constant (Hz), integration. Data for ^{13}C NMR are reported as chemical shift. HRMS were performed on a Bruker Apex II mass instrument (ESI).

2. Experimental procedures

2.1 Catalysts **PCH1-9** as depicted below were evaluated in this work:

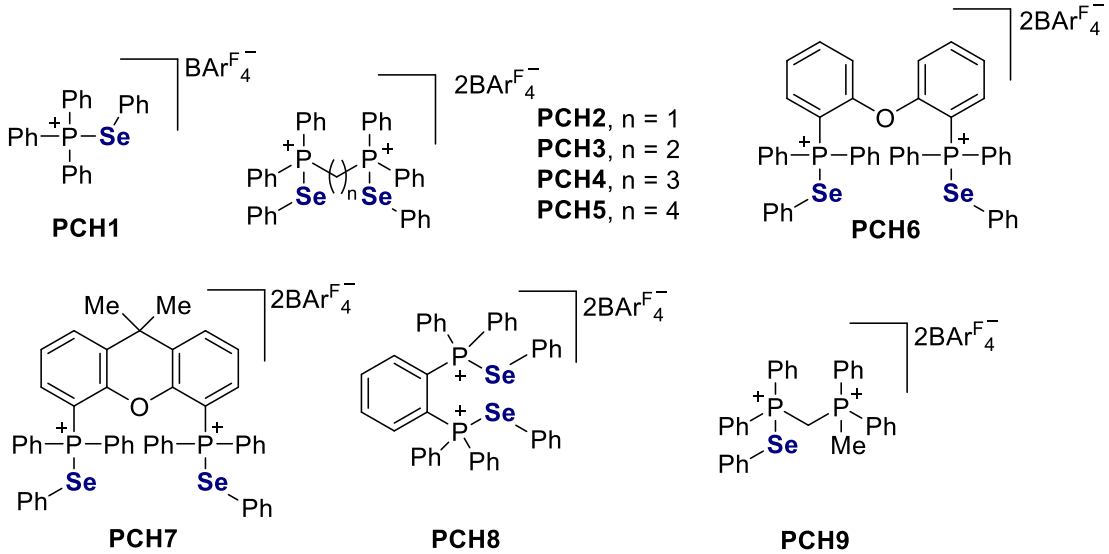
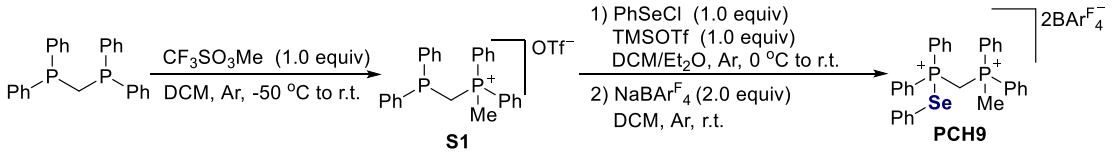


Figure S1. Catalysts **PCH1-PCH9**.

Catalysts **PCH1-PCH8** were prepared according to the reported procedures.[1-5] Catalyst P**CH9** was prepared using the following procedure:[6]



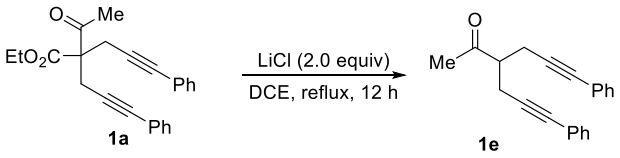
To a solution of CF_3SO_3Me (3.0 mmol, 1.0 equiv) in dry CH_2Cl_2 (5.0 mL) was added bis(diphenylphosphino)methane (3.0 mmol, 1.0 equiv) dissolved in dry CH_2Cl_2 (5.0 mL) dropwise under argon over 30 minutes at –50 °C. The reaction mixture was stirred at –50 °C for another 1 h. The above reaction system was allowed to warm up to room temperature and stand for 12 h. The solid precipitate was filtered, washed by anhydrous diethyl ether and dried in vacuo to give **S1** as a white solid in 90% yield.

To a red solution of PhSeCl (1.0 mmol, 1.0 equiv) in dry Et_2O (6.0 mL) at 0 °C under argon was added TMSOTf (1.0 mmol, 1.0 equiv) slowly. The reaction mixture was allowed to warm to room temperature and stirred for 40 minutes to give a dark orange solution. Then **S1** (1.0 mmol) in dry CH_2Cl_2 (4.0 mL) was added over 5 minutes at 0 °C. The reaction mixture was allowed to warm to room temperature and stand for 1 h. The white solid suspension was filtered and washed with anhydrous diethyl ether. Then sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (2.0 mmol, 2.0 equiv) was added to a solution of the above white solid (1.0 mmol) in dry CH_2Cl_2 (10.0 mL) under argon, and the reaction mixture was stirred at room temperature for 24 h. Then the reaction mixture was filtered and the filtrate was concentrated to give a saturated solution under reduced pressure and then 10.0 mL *n*-hexane was slowly added. The two-phase solution was then placed at room temperature under argon and the desirable product precipitates out as a white solid. Then the precipitated white solid was collected by filtration and recrystallized twice from CH_2Cl_2 and *n*-hexane to afford pure catalyst **PCH9** in 71% yield.

2.2 Synthesis of substrates

Compounds **1a, 1b**, **1e, 1f** and **1i** are known compounds and the spectral data are in agreement with the literature report.[7-9]

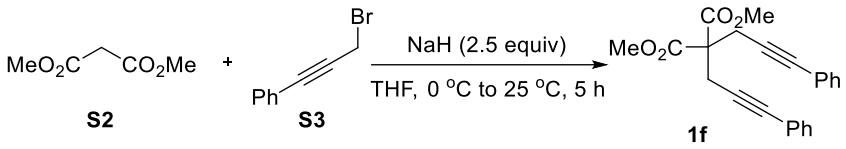
2.2.1 Synthesis of 1e:



A solution of diyne **1a** (5.0 mmol) and LiCl (10.0 mmol, 2.0 equiv) in DMF (25.0 mL) was heated at reflux. After stirring for 12 h, the reaction mixture was cooled and diluted with water (50.0 mL) and ethyl acetate (100.0 mL). Then the reaction mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated in vacuo after filtration, and the residue

was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 20:1) to afford compound **1e** as a yellow oil in 62% yield.

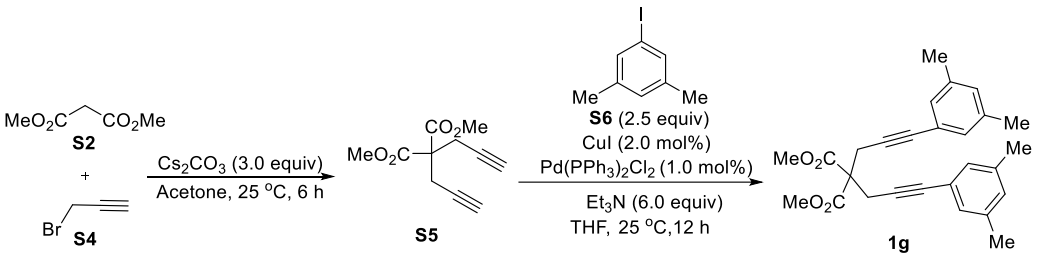
2.2.2 Synthesis of 1f:



NaH (500.0 mg, 60% dispersion in mineral oil, 12.5 mmol, 2.5 equiv) was added slowly to a solution of dimethyl malonate **S2** (660.0 mg, 5.0 mmol) in THF (25.0 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min. Then (3-bromoprop-1-yn-1-yl) benzene **S3** (2.4 g, 12.5 mmol, 2.5 equiv) was added dropwise, and the reaction mixture was stirred at 25 °C for 5 h. After the completion of reaction as judged by TLC analysis, H_2O (10.0 mL) was added slowly to quench the reaction, and the aqueous layer was extracted with ethyl acetate (3×20 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated in vacuo after filtration, and the residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 15:1) to afford compound **1f** as a light oil in 83% yield.

Note: Compounds **1a-1d** and **1f** were synthesized according to the above experimental procedures.

2.2.3 Synthesis of 1g:



Procedure for synthesis of S5:

Cs_2CO_3 (9.78 g, 30.0 mmol, 3.0 equiv) was added to a solution of dimethyl malonate **S2** (1.2 g, 10.0 mmol, 1.0 equiv) in acetone at 25 °C, and the reaction mixture was stirred for 15 minutes. Then 3-bromoprop-1-yne **S4** (3.57 g, 3.0 mmol, 3.0 equiv) was added to the above reaction mixture. The resulting mixture was stirred under this condition for 6 h. After the completion of reaction as judged by TLC analysis, the solvent was removed under reduced pressure. The residue was dissolved in water and extracted using ethyl acetate and dried over anhydrous Na_2SO_4. The solvent was evaporated in vacuo after filtration, and the residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 20:1) to afford compound dimethyl 2,2-di(prop-2-yn-1-yl)malonate **S5** as a white

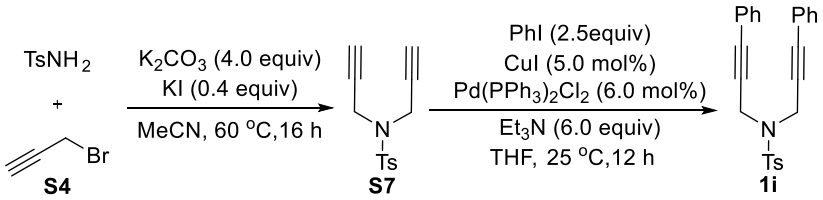
solid in 65% yield.

Procedure for synthesis of 1g:

Dimethyl 2,2-di(prop-2-yn-1-yl)malonate **S5** (1.35 g, 6.5 mmol, 1.0 equiv) and 1-iodo-3,5-dimethylbenzene **S6** (3.77 g, 16.25 mmol, 2.5 equiv) were dissolved in dry THF in a dried Schlenk flask. Then $Pd(PPh_3)_2Cl_2$ (45.6 mg, 0.065 mmol, 1.0 mol%), CuI (24.8 mg, 0.13 mmol, 2.0 mol%) and freshly distilled Et_3N (4.0 g, 39.0 mmol, 6.0 equiv) were added to the reaction mixture under argon atmosphere. The resulting mixture was stirred at 25 °C for 12 h under argon atmosphere until the reaction was completed as judged by TLC analysis. Then the reaction mixture was diluted with water and extracted with ethyl acetate. The combined organic layer was dried over Na_2SO_4, filtered and concentrated to give crude material. The crude material was purified via column chromatography on silica gel (*n*-hexane/ethyl acetate = 20:1) to afford compound dimethyl 2,2-bis(3-(3,5-dimethylphenyl)prop-2-yn-1-yl)malonate **1g** as a white solid in 76% yield.

Note: Compounds **1g** and **1h** were synthesized from above experimental procedures.

2.2.4 Procedure for synthesis of 1i: [7]



2.5.1. Procedure for synthesis of 4-methyl-*N,N*-di(prop-2-yn-1-yl)benzenesulfonamide (S7)

K_2CO_3 (1.93 g, 28.07 mmol, 4.0 equiv), potassium iodide (464.0 mg, 2.80 mmol, 0.4 equiv) and 3-bromoprop-1-yne **S5** (2.08 g, 7.71 mmol, 2.5 equiv) were added to a solution of 4-methylbenzenesulfonamide (1.2 g, 7.01 mmol, 1.0 equiv) in MeCN at 25 °C. The resulting mixture was heated at 60 °C for 12 h. The reaction mixture was cooled to 25 °C and the solvent was removed under reduced pressure. Then the resulting solid was dissolved in ethyl acetate, and washed with water and brine and then dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the crude product was purified via column chromatography using *n*-hexane/ethyl acetate (*n*-hexane/ethyl acetate = 20:1) as an eluent to afford compound 4-methyl-*N,N*-di(prop-2-yn-1-yl) benzenesulfonamide **S7** as a brown solid (1.1 g, 64% yield).

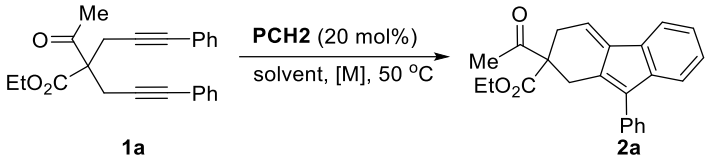
2.5.2. Procedure for synthesis of 4-methyl-*N,N*-bis(3-phenylprop-2-yn-1 yl)benzenesulfonamide (1i)

$Pd(PPh_3)_2Cl_2$ (187.0 mg, 0.26 mmol, 6.0 mol%), CuI (42.0 mg, 0.22 mmol, 5.0 mol%) and freshly distilled Et_3N (2.69 g, 26.72 mmol, 6.0 equiv) were added to a solution of 4-methyl-*N,N*-di(prop-2-yn-1-yl)benzenesulfonamide **S7** (1.1 g, 4.45 mmol, 1.0 equiv) and iodobenzene (2.27 g, 11.13 mmol, 2.5 equiv) in dry THF under argon

atmosphere. The resulting mixture was stirred at 25 °C for 12 h. After the completion of reaction as judged by TLC analysis, the reaction mixture was diluted with water and extracted with ethyl acetate. The combined organic layer was dried over Na_2SO_4, filtered and concentrated to give crude material. The crude material was purified via column chromatography using *n*-hexane/ethyl acetate (*n*-hexane/ethyl acetate = 20:1) as an eluent to afford 4-methyl-*N,N*-bis(3-phenylprop-2-yn-1-yl)benzenesulfonamide **1i** as a yellow solid (1.53 g, 86% yield).

2.6. Optimization of reaction condition

Table S1. Optimization of reaction condition.[a]



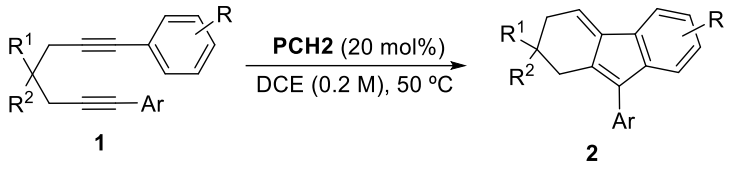
1a **2a**

Entry	Solvent (mL)[b]	Concentration (mol/L)	Time (h)	Yield (%)[c]
1	DCE	0.1	24	47
2	DCE	0.125	20	56
3	DCE	0.2	20	73
4	DCE	0.3	48	54
5	DCE	0.5	48	51
6	acetone	0.2	48	n.r.
7	THF	0.2	48	n.r.
8	MeOH	0.2	48	n.r.
9	1,4-dioxane	0.2	48	n.r.
10	toluene	0.2	48	35
11	DMF	0.2	48	n.r.
12	DMSO	0.2	48	n.r.

[a] Unless otherwise noted, all the experiments were carried out with **1a** (0.2 mmol) and **PCH2** (20.0 mol %) at 50 °C in 1.0 mL solvent under argon atmosphere. [b] DCE = 1,2-dichloroethane, THF = tetrahydrofuran, DMF = *N,N*-Dimethylformamide, DMSO = Dimethyl sulfoxide. [c] Isolated yield. n.r. = no reaction.

General procedure for optimization: Substrate **1a** (0.2 mmol, 1.0 equiv) was added to a solution of catalyst **PCH2** (20.0 mol %) in freshly dried solvent (1.0 mL) in a 10 mL-Schlenk tube under argon atmosphere. The reaction mixture was stirred at 50 °C for the indicated reaction time. Then the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel to give the desired product **2a**.

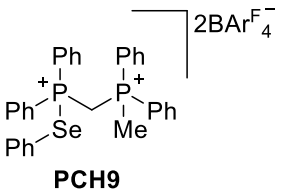
2.7. Optimized Procedure



General Method: Substrate 1,6-diyne **1** (0.2 mmol, 1.0 equiv) was added to a solution of catalyst **PCH2** (20 mol %) in DCE (1.0 mL) in a 10 mL-Schlenk tube under argon atmosphere. The above reaction mixture was stirred at 50 °C until the completion of the reaction as judged by TLC analysis. Then the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel to give the desired product **2**.

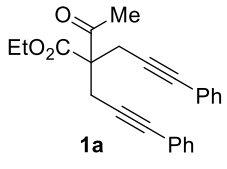
3. Compound characterization

PCH9 was prepared according to the corresponding procedure. White solid (71% yield). **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 8.08 – 7.42 (m, 44H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.14 – 6.88 (m, 4H), 4.96 (t, *J* = 14.9 Hz, 2H), 2.16 (d, *J* = 13.4 Hz, 3H); **^{13}C NMR** (100 MHz, CD_2Cl_2) δ 162.29 (q, *J* = 49.51 Hz), 138.55, 137.58, 135.33, 133.53 (d, *J* = 11.26 Hz), 133.43, 132.46 (d, *J* = 10.87 Hz), 132.13 (dd, *J* = 19.8, 13.54 Hz), 131.91, 130.92 (d, *J* = 13.04 Hz), 130.72 (d, *J* = 10.31 Hz), 129.43 (qq, *J* = 31.3, 2.8 Hz), 125.12 (q, *J* = 270.8 Hz), 118.11 - 117.95 (m), 117.47 (d, *J* = 5.7 Hz), 115.35 (d, *J* = 14.33 Hz), 114.54 (d, *J* = 27.45 Hz), 25.02 (t, *J* = 41.86 Hz) 9.71 (d, *J* = 56.09 Hz); **^{31}P NMR** (162 MHz, CD_2Cl_2) δ 30.34 (d, P^+Ph_2SePh, $^2J_{P^+-P^+}$ = 14.4 Hz), 19.92 (d, P^+Ph_2Me, $^2J_{P^+-P^+}$ = 14.7 Hz); **^{77}Se NMR** (76 MHz, CD_2Cl_2) δ 316.10 (d, J_{Se-P} = 484.1 Hz); **^{19}F NMR** (376 MHz, CD_2Cl_2) δ -62.67; **HRMS** (ESI+) exact mass calculated for $[M]^{2+}$ ($C_{32}H_{30}P_2Se$) requires m/z 278.0489, found m/z 278.0490.



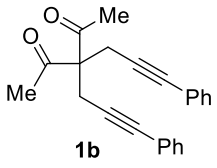
ethyl 2-acetyl-5-phenyl-2-(3-phenylprop-2-yn-1-yl)pent-4-ynoate (1a):

Compound **1a** was synthesized according to the corresponding procedure as a white solid in 58% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 6.7, 3.1 Hz, 4H), 7.27 (dd, *J* = 4.8, 2.0 Hz, 6H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.28 – 3.17 (m, 4H), 2.28 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.24, 169.51, 131.64, 128.19, 128.05, 122.99, 84.12, 83.93, 63.08, 62.13, 26.24, 22.98, 14.09; **HRMS** (ESI+) exact mass calculated for $[M+H]^+$ ($C_{24}H_{23}O_3$) requires m/z 359.1642, found m/z 359.1633.



3,3-bis(3-phenylprop-2-yn-1-yl)pentane-2,4-dione (1b):

Compound **1b** was synthesized according to the corresponding procedure as a white solid in 74% yield; **^{1}H NMR**

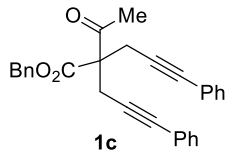


1b

(400 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 4H), 7.28 (dd, *J* = 5.2, 2.0 Hz, 6H), 3.27 (s, 4H), 2.27 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 203.10, 131.63, 128.22, 128.17, 122.76, 84.25, 84.18, 70.62, 26.55, 22.21; **HRMS** (ESI+) exact mass calculated for $[M+H]^+$ ($C_{23}H_{21}O_2$) requires m/z 329.1537, found m/z 329.1535.

benzyl 2-acetyl-5-phenyl-2-(3-phenylprop-2-yn-1-yl)pent-4-ynoate (1c):

Compound **1c** was synthesized according to the corresponding procedure as a light oil in 64% yield; **^{1}H NMR** (400

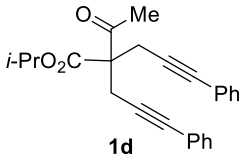


1c

MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 15H), 5.24 (s, 2H), 3.30 – 3.18 (m, 4H), 2.21 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.05, 169.44, 134.99, 131.69, 128.59, 128.48, 128.31, 128.17, 128.08, 122.92, 84.08, 84.01, 67.76, 63.17, 26.31, 23.02; **HRMS** (ESI+) exact mass calculated for $[M+H]^+$ ($C_{29}H_{25}O_3$) requires m/z 421.1799, found m/z 421.1794.

isopropyl 2-acetyl-5-phenyl-2-(3-phenylprop-2-yn-1-yl)pent-4-ynoate (1d):

Compound **1d** was synthesized according to the corresponding procedure as a white solid in 70% yield; **^{1}H NMR**

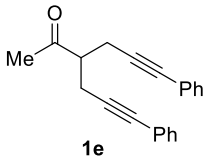


1d

(400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 6.7, 3.2 Hz, 4H), 7.30 – 7.24 (m, 6H), 5.13 (p, *J* = 6.3 Hz, 1H), 3.27 – 3.15 (m, 4H), 2.27 (s, 3H), 1.27 (d, *J* = 6.3 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.30, 168.99, 131.64, 128.18, 128.03, 123.02, 84.21, 83.85, 69.84, 63.07, 26.14, 22.91, 21.53; **HRMS** (ESI+) exact mass calculated for $[M+H]^+$ ($C_{25}H_{25}O_3$) requires m/z 373.1799, found m/z 373.1801.

6-phenyl-3-(3-phenylprop-2-yn-1-yl)hex-5-yn-2-one (1e):

Compound **1e** was synthesized according to the corresponding procedure as a yellow oil in 62% yield; **^{1}H NMR**

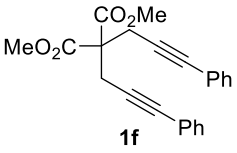


1e

(400 MHz, $CDCl_3$) δ 7.41 – 7.38 (m, 4H), 7.30 – 7.28 (m, 6H), 3.06 - 2.99 (m, 1H), 2.88 – 2.77 (m, 4H), 2.36 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 208.43, 131.60, 128.23, 127.96, 123.23, 86.33, 82.75, 50.50, 29.81, 20.81; **HRMS** (ESI+) exact mass calculated for $[M+H]^+$ ($C_{21}H_{19}O$) requires m/z 287.1431, found m/z 287.1435.

dimethyl 2,2-bis(3-phenylprop-2-yn-1-yl)malonate (1f):

Compound **1f** was synthesized according to the corresponding procedure as a light oil in 83% yield; **^{1}H NMR** (400

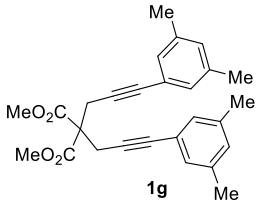


1f

MHz, $CDCl_3$) δ 7.39 (dd, *J* = 6.8, 3.1 Hz, 4H), 7.30 – 7.27 (m, 6H), 3.81 (s, 6H), 3.28 (s, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.38, 131.68, 128.19, 128.05, 123.03, 83.87, 83.79, 57.27, 53.09, 23.83; **HRMS** (ESI+) exact mass calculated for $[M+H]^+$ ($C_{23}H_{21}O_4$) requires m/z 361.1435, found m/z 361.1436.

dimethyl 2,2-bis(3-(3,5-dimethylphenyl)prop-2-yn-1-yl)malonate (1g):

Compound **1g** was synthesized according to the corresponding procedure as a white solid in 76% yield; **^{1}H NMR**

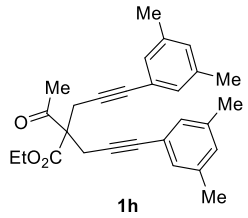


1g

(400 MHz, $CDCl_3$) δ 7.02 (s, 4H), 6.93 (s, 2H), 3.81 (s, 6H), 3.27 (s, 4H), 2.28 (s, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.40, 137.70, 129.92, 129.32, 122.63, 84.00, 83.01, 57.24, 53.04, 23.76, 21.01; **HRMS** (ESI+) exact mass calculated for $[M+H]^+$ ($C_{27}H_{29}O_4$) requires m/z 417.2061, found m/z 417.2065.

ethyl 2-acetyl-5-(3,5-dimethylphenyl)-2-(3-(3,5-dimethylphenyl)prop-2-yn-1-yl)pent-4-ynoate (1h):

Compound **1h** was synthesized according to the corresponding procedure as a colorless oil in 55% yield; **^{1}H NMR**

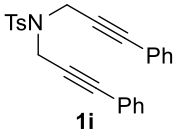


1h

(400 MHz, $CDCl_3$) δ 7.02 (s, 4H), 6.93 (s, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.29 – 3.18 (m, 4H), 2.30 (s, 3H), 2.28 (s, 12H), 1.31 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.31, 169.50, 137.68, 129.91, 129.28, 122.59, 84.14, 83.26, 63.07, 62.04, 26.20, 22.92, 20.97, 14.04; **HRMS** (ESI+) exact mass calculated for $[M+H]^+$ ($C_{28}H_{31}O_3$) requires m/z 415.2268, found m/z 415.2264.

4-methyl-N,N-bis(3-phenylprop-2-yn-1-yl)benzenesulfonamide (1i):

Compound **1i** was synthesized according to the corresponding procedure as a yellow solid in 86% yield; **^{1}H NMR**

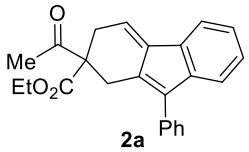


1i

(400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.29 – 7.19 (m, 12H), 4.44 (s, 4H), 2.31 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.80, 135.36, 131.64, 129.56, 128.47, 128.13, 127.96, 122.18, 85.75, 81.62, 37.47, 21.37; **HRMS** (ESI+) exact mass calculated for $[M+H]^+$ ($C_{25}H_{22}NO_2S$) requires m/z 400.1366, found m/z 400.1363.

ethyl 2-acetyl-9-phenyl-2,3-dihydro-1H-fluorene-2-carboxylate (2a):

Compound **2a** was synthesized according to the corresponding procedure as a yellow solid in 73% yield; **^{1}H NMR**

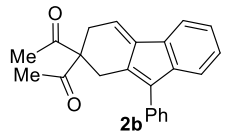


2a

(400 MHz, $CDCl_3$) δ 7.57 – 7.48 (m, 5H), 7.42 – 7.37 (m, 1H), 7.32 – 7.30 (m, 1H), 7.23 (td, *J* = 7.4, 1.3 Hz, 1H), 7.17 (td, *J* = 7.4, 1.3 Hz, 1H), 6.82 (t, *J* = 4.5 Hz, 1H), 4.18 – 4.14 (m, 2H), 3.43 – 3.22 (m, 2H), 3.09 (t, *J* = 4.5 Hz, 2H), 2.17 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 203.81, 171.10, 143.43, 139.89, 137.74, 134.29, 134.26, 130.05, 128.56, 128.55, 127.48, 124.91, 124.72, 119.47, 119.40, 62.82, 61.76, 31.41, 29.14, 26.17, 13.90; **HRMS** (ESI+) exact mass calculated for $[M+H]^+$ ($C_{24}H_{23}O_3$) requires m/z 359.1642, found m/z 359.1638.

1,1'-(9-phenyl-2,3-dihydro-1H-fluorene-2,2-diyl)bis(ethan-1-one) (2b):

Compound **2b** was synthesized according to the corresponding procedure as a yellow solid in 67% yield; **^{1}H NMR**

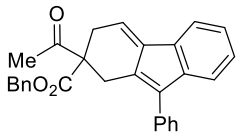


2b

(400 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 5H), 7.44 – 7.40 (m, 1H), 7.31 (d, *J* = 6.9 Hz, 1H), 7.24 (td, *J* = 7.4, 1.3 Hz, 1H), 7.18 (td, *J* = 7.4, 1.3 Hz, 1H), 6.82 (t, *J* = 4.5 Hz, 1H), 3.35 (s, 2H), 3.10 (d, *J* = 4.5 Hz, 2H), 2.10 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 205.25, 143.39, 140.41, 138.07, 134.18, 134.07, 130.06, 128.68, 128.56, 127.63, 124.85, 124.80, 119.52, 119.51, 70.24, 31.07, 28.67, 26.44; **HRMS** (ESI+) exact mass calculated for $[M+H]^+$ ($C_{23}H_{21}O_2$) requires m/z 329.1537, found m/z 329.1532.

benzyl 2-acetyl-9-phenyl-2,3-dihydro-1H-fluorene-2-carboxylate (2c):

Compound **2c** was synthesized according to the corresponding procedure as a yellow oil in 51% yield; **^{1}H NMR**

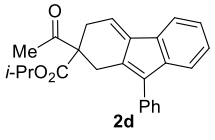


2c

(400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.4 Hz, 1H), 7.44 (d, *J* = 4.4 Hz, 4H), 7.36 (dt, *J* = 8.7, 4.2 Hz, 1H), 7.29 – 7.26 (m, 2H), 7.24 – 7.19 (m, 3H), 7.16 (td, *J* = 7.6, 1.5 Hz, 3H), 6.80 (t, *J* = 4.5 Hz, 1H), 5.16 – 5.04 (m, 2H), 3.46 – 3.04 (m, 4H), 2.10 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 203.66, 171.10, 143.49, 140.01, 137.91, 135.05, 134.30, 134.21, 129.91, 128.58, 128.50, 128.31, 127.99, 127.55, 127.51, 124.81, 124.79, 119.54, 119.49, 67.49, 63.13, 31.53, 29.17, 26.21; **HRMS** (ESI+) exact mass calculated for $[M+H]^+$ ($C_{29}H_{25}O_3$) requires m/z 421.1799, found m/z 421.1810.

isopropyl 2-acetyl-9-phenyl-2,3-dihydro-1H-fluorene-2-carboxylate (2d):

Compound **2d** was synthesized according to the corresponding procedure as a yellow solid in 68% yield; **^{1}H NMR**



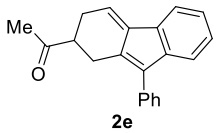
2d

(400 MHz, $CDCl_3$) δ 7.57 – 7.48 (m, 5H), 7.39 (ddt, *J* = 8.7, 6.4, 1.7 Hz, 1H), 7.31 (dt, *J* = 7.5, 0.9 Hz, 1H), 7.22 (td, *J* = 7.4, 1.3 Hz, 1H), 7.16 (td, *J* = 7.3, 1.3 Hz, 1H), 6.82 (t, *J* = 4.5 Hz, 1H), 5.00 (p, *J* = 6.3 Hz, 1H), 3.42 – 3.18 (m, 2H), 3.09 – 3.04 (m, 2H), 2.17 (s, 3H), 1.18 (d, *J* = 6.3 Hz,

3H), 1.11 (d, *J* = 6.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 203.88, 170.60, 143.40, 139.88, 137.65, 134.31, 134.27, 130.18, 128.56, 128.55, 127.47, 127.45, 124.99, 124.70, 119.46, 119.39, 69.34, 63.00, 31.45, 29.07, 26.12, 21.40, 21.36; **HRMS** (ESI+) exact mass calculated for $[M+H]^+$ ($C_{25}H_{25}O_3$) requires m/z 373.1799, found m/z 373.1804.

1-(9-phenyl-2,3-dihydro-1H-fluoren-2-yl)ethan-1-one (2e):

Compound **2e** was synthesized according to the corresponding procedure as a yellow oil in 53% yield; **^{1}H NMR**

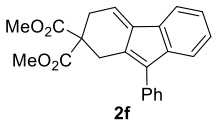


2e

(400 MHz, $CDCl_3$) δ 7.58 – 7.56 (m, 1H), 7.49 – 7.47 (m, 4H), 7.38 – 7.33 (m, 2H), 7.25 – 7.16 (m, 2H), 6.89 – 6.87 (m, 1H), 3.07 (dd, *J* = 15.8, 3.9 Hz, 1H), 3.05 – 2.85 (m, 1H), 2.82 (dd, *J* = 15.8, 11.5 Hz, 1H), 2.73 – 2.70 (m, 2H), 2.19 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 209.88, 143.28, 140.20, 136.68, 134.46, 134.44, 132.08, 128.65, 128.53, 127.47, 127.40, 126.54, 124.63, 119.40, 119.31, 49.75, 28.37, 28.14, 25.99; **HRMS** (ESI+) exact mass calculated for $[M+H]^+$ ($C_{21}H_{19}O$) requires m/z 287.1431, found m/z 287.1431.

dimethyl 9-phenyl-1,3-dihydro-2H-fluorene-2,2-dicarboxylate (2f):

Compound **2f** was synthesized according to the corresponding procedure as a yellow solid in 56% yield; **^{1}H NMR**

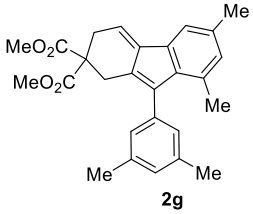


2f

(400 MHz, $CDCl_3$) δ 7.56 – 7.46 (m, 5H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.16 (t, *J* = 7.3 Hz, 1H), 6.80 (t, *J* = 4.5 Hz, 1H), 3.70 (s, 6H), 3.34 (s, 2H), 3.14 (d, *J* = 4.5 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.12, 143.56, 139.80, 137.76, 134.37, 134.31, 129.88, 128.60, 128.57, 127.53, 127.49, 124.71, 124.47, 119.52, 119.43, 56.58, 52.96, 32.12, 29.78; **HRMS** (ESI+) exact mass calculated for $[M+H]^+$ ($C_{23}H_{21}O_4$) requires m/z 361.1435, found m/z 361.1437.

Dimethyl 9-(3,5-dimethylphenyl)-6,8-dimethyl-1,3-dihydro-2H-fluorene-2,2-dicarboxylate (2g):

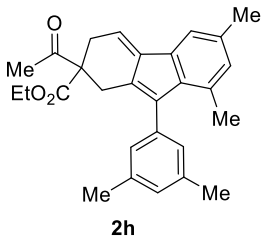
Compound **2g** was synthesized according to the corresponding procedure as a yellow oil in 62% yield; **^{1}H NMR**



2g

(400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 1.6 Hz, 1H), 6.99 – 6.98 (m, 1H), 6.92 (d, *J* = 1.7 Hz, 2H), 6.76 (s, 1H), 6.69 (t, *J* = 4.5 Hz, 1H), 3.69 (s, 6H), 3.08 (d, *J* = 4.5 Hz, 2H), 3.05 (s, 2H), 2.36 (s, 6H), 2.33 (s, 3H), 1.88 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.21, 139.93, 139.64, 139.03, 137.38, 136.96, 134.81, 134.12, 131.28, 130.36, 129.82, 128.70, 126.65, 123.09, 118.11, 56.65, 52.78, 32.16, 29.42, 21.39, 21.13, 19.82; **HRMS** (ESI+) exact mass calculated for $[M+H]^+$ ($C_{27}H_{29}O_4$) requires m/z 417.2061 found m/z 417.2058.

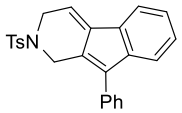
ethyl 2-acetyl-9-(3,5-dimethylphenyl)-6,8-dimethyl-2,3-dihydro-1H-fluorene-2-carboxylate (2h):



2h

Compound **2h** was synthesized according to the corresponding procedure as a yellow oil in 52% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 1.6 Hz, 1H), 7.00 (s, 1H), 6.93 – 6.92 (m, 2H), 6.76 (s, 1H), 6.71 (t, *J* = 4.5 Hz, 1H), 4.14 (qd, *J* = 7.2, 1.6 Hz, 2H), 3.13 – 2.96 (m, 4H), 2.36 (s, 6H), 2.33 (s, 3H), 2.15 (s, 3H), 1.88 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 204.12, 171.29, 139.90, 139.64, 138.95, 137.46, 136.92, 134.79, 134.19, 131.25, 130.36, 129.81, 128.77, 126.64, 126.52, 123.70, 118.10, 62.76, 61.67, 31.39, 28.81, 26.23, 21.36, 21.13, 19.80, 13.95; **HRMS** (ESI+) exact mass calculated for $[M+H]^+$ ($C_{28}H_{31}O_3$) requires m/z 415.2268 found m/z 415.2272.

9-phenyl-2-tosyl-2,3-dihydro-1H-indeno[2,1-c]pyridine (2i):



2i

Compound **2i** was synthesized according to the corresponding procedure as a yellow solid in 33% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.59 (m, 2H), 7.57 – 7.46 (m, 3H), 7.42 (td, *J* = 6.9, 1.6 Hz, 3H), 7.33 – 7.30 (m, 1H), 7.25 – 7.21 (m, 1H), 7.19 – 7.14 (m, 3H), 6.62 (t, *J* = 4.1 Hz, 1H), 4.46 (s, 2H), 4.18 (d, *J* = 4.1 Hz, 2H), 2.30 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.63, 142.73, 138.83, 137.38, 134.10, 133.71, 133.54, 129.47, 128.84, 128.30, 128.04, 127.99, 127.58, 127.27, 125.16, 121.72, 119.89, 119.68, 45.22, 43.86, 21.38; **HRMS** (ESI+) exact mass calculated for $[M+H]^+$ ($C_{25}H_{22}NO_2S$) requires m/z 400.1366, found m/z 400.1359.

Note: Compounds **2a, 2f** and **2i** are known compounds and the spectral data are in agreement with the literature report.[7]

4. Mechanistic study

4.1 Tracing the reaction process of 1a using ^{31}P NMR

To a reaction mixture of catalyst **PCH2** (20.0 mol %) and **1a** (0.01 mmol) in a 10 mL-Schlenk tube was added DCE (0.5 mL) under argon atmosphere. The reaction mixture was stirred at 50 °C until the reaction was completed as judged by TLC analysis. Then the reaction mixture was transferred to an NMR tube and 0.2 mL CD_2Cl_2 was added. The reaction mixture was traced by ^{31}P NMR using 85% H_3PO_4 aqueous solution as an external standard. NMR experiments reveal that only one ^{31}P signal (δ 30.89 ppm) assigned to catalyst **PCH2** was observed. It shows that the catalyst was stable during the reaction process.

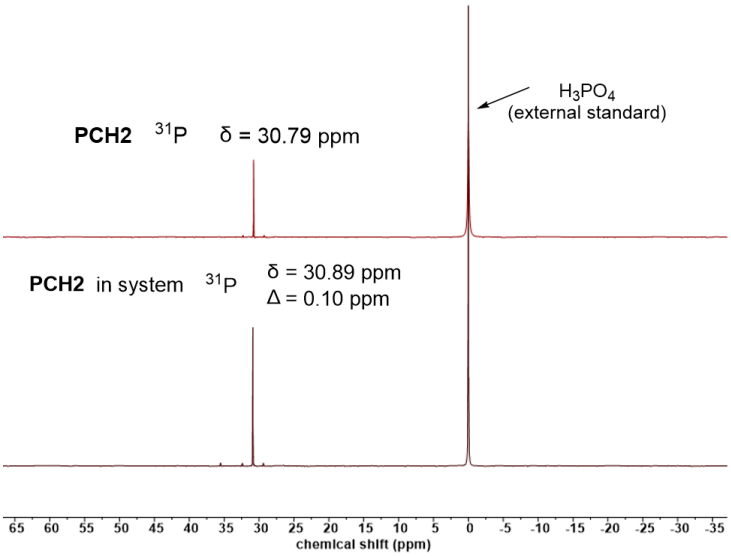
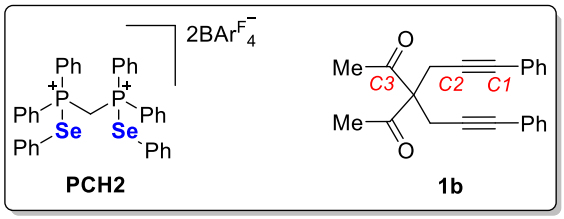


Figure S2. Tracing the reaction process of **1a** using ^{31}P NMR.

4.2 ^{13}C NMR titration experiment.



Substrate **1b** (1.0 equiv, 0.061 mmol) and different equivalent catalyst **PCH2** (0.1 equiv, 0.4 equiv, 0.6 equiv, 0.8 equiv, 1.0 equiv, 1.5 equiv, 2.0 equiv) were dissolved in 0.6 mL CD_2Cl_2. The binding constant of 3.49 ± 0.01 M^{-1} was calculated by http://supramolecular.org[10-12] using the collected data, assuming a coordination mode of 1:1. The horizontal axis is the ratio of the concentration of catalyst **PCH2** and substrate **1b**, while the vertical axis is the ^{13}C NMR chemical shift.

Table S2. The chemical shift of ^{13}C NMR of **1b** upon addition of **PCH2**.

Host concentration / M	Guest concentration / M	C1	C2	C3
0.101666667	0	84.35	84.85	203.40
0.101666667	0.013887968	84.39	84.82	203.54
0.101666667	0.040082601	84.47	84.79	203.79
0.101666667	0.061052058	84.52	84.77	203.94
0.101666667	0.081674384	84.58	84.75	204.10
0.101666667	0.10175343	84.62	84.74	204.23
0.101666667	0.152630145	84.74	84.70	204.56
0.101666667	0.203369356	84.83	84.68	204.82

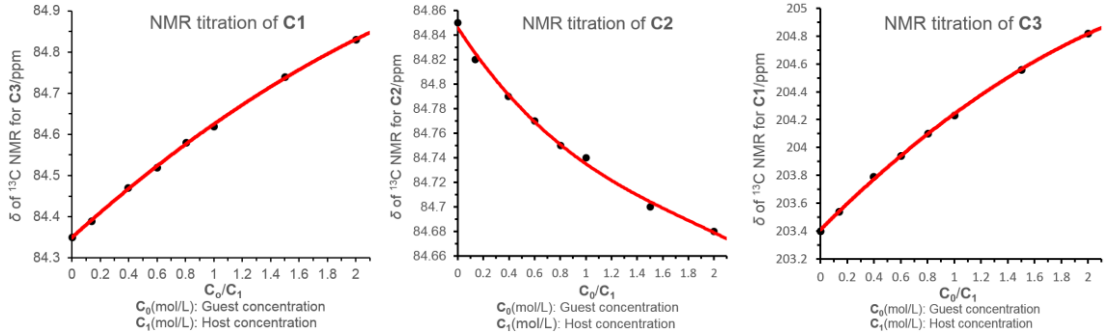


Figure S3. The ^{13}C NMR chemical shift of **1b** upon addition of **PCH2.**

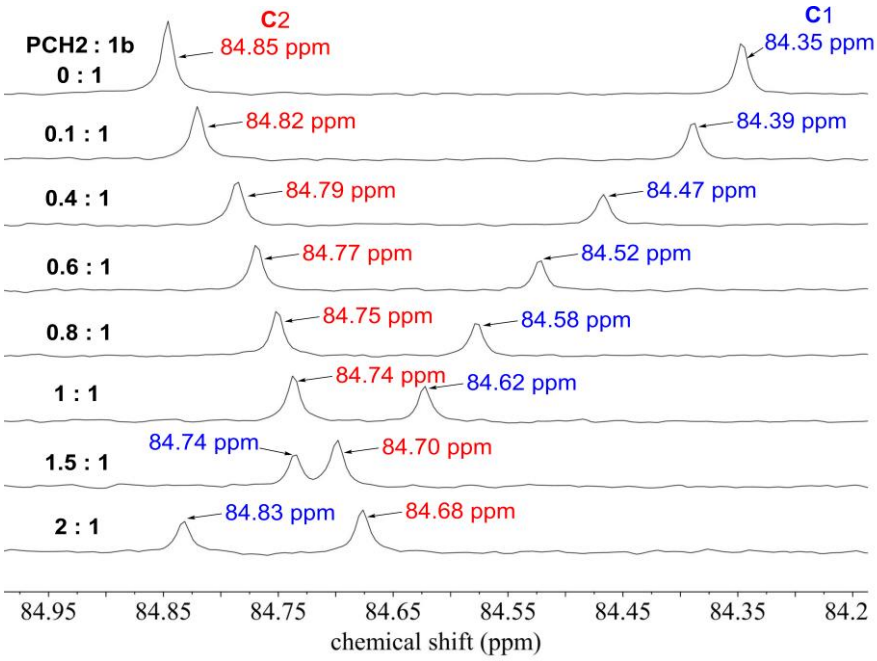


Figure S4. The ^{13}C NMR chemical shift of C1 and C2.

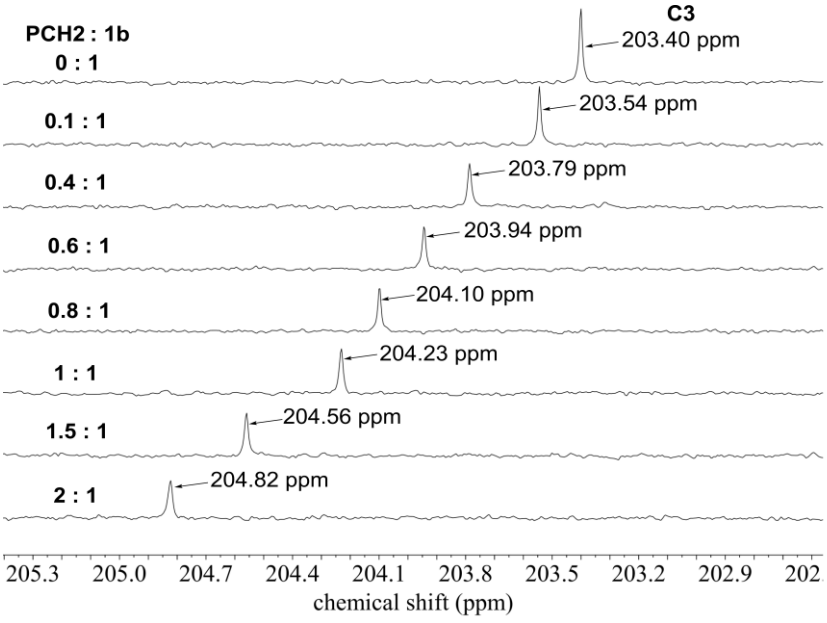
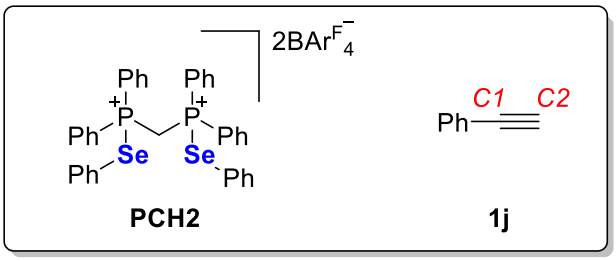


Figure S5. The ^{13}C NMR chemical shift of C3.



Substrate **1j** (1.0 equiv, 0.122 mmol) and catalyst **PCH2** (1.0 equiv) were dissolved in 0.6 mL CD_2Cl_2. A downfield shift of the signals of the carbons of alkynes in phenylacetylene was detected by ^{13}C NMR analysis, which indicates that there is a weak Se···π interaction between **PCH2** and phenylacetylene **1j**.

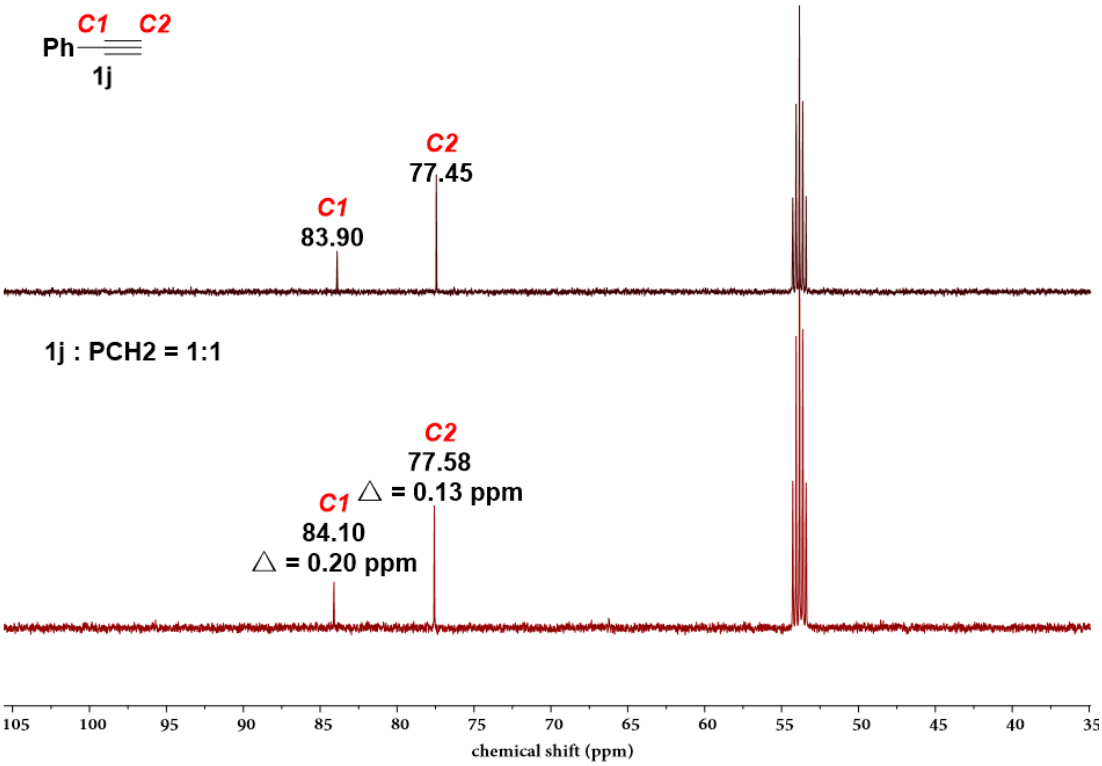
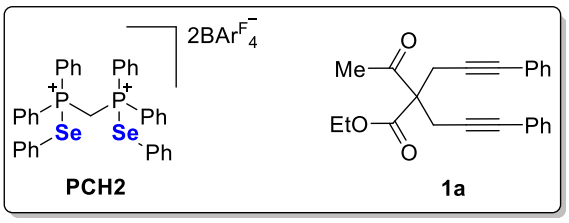


Figure S6. The ^{13}C NMR chemical shift of phenylacetylene **1j** upon addition of **PCH2.**

4.3 ^{31}P NMR experiment.



Catalyst **PCH2** (1 equiv, 0.01 mmol) and substrate **1a** (1.0 equiv, 0.01 mmol) were dissolved in 0.6 mL CD_2Cl_2. The

^{31}P NMR experiment was carried out using 85% H_3PO_4 aqueous solution as an external standard. The chemical shift of ^{31}P signal of **PCH2** almost remains unchanged, thus excluding the possible interaction of **1a** with phosphorus part.

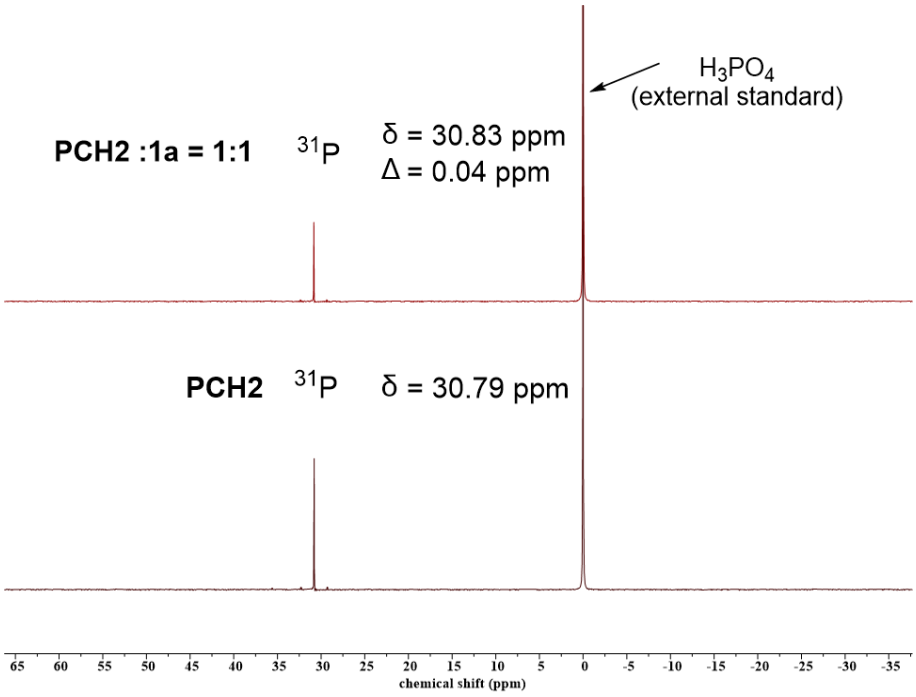
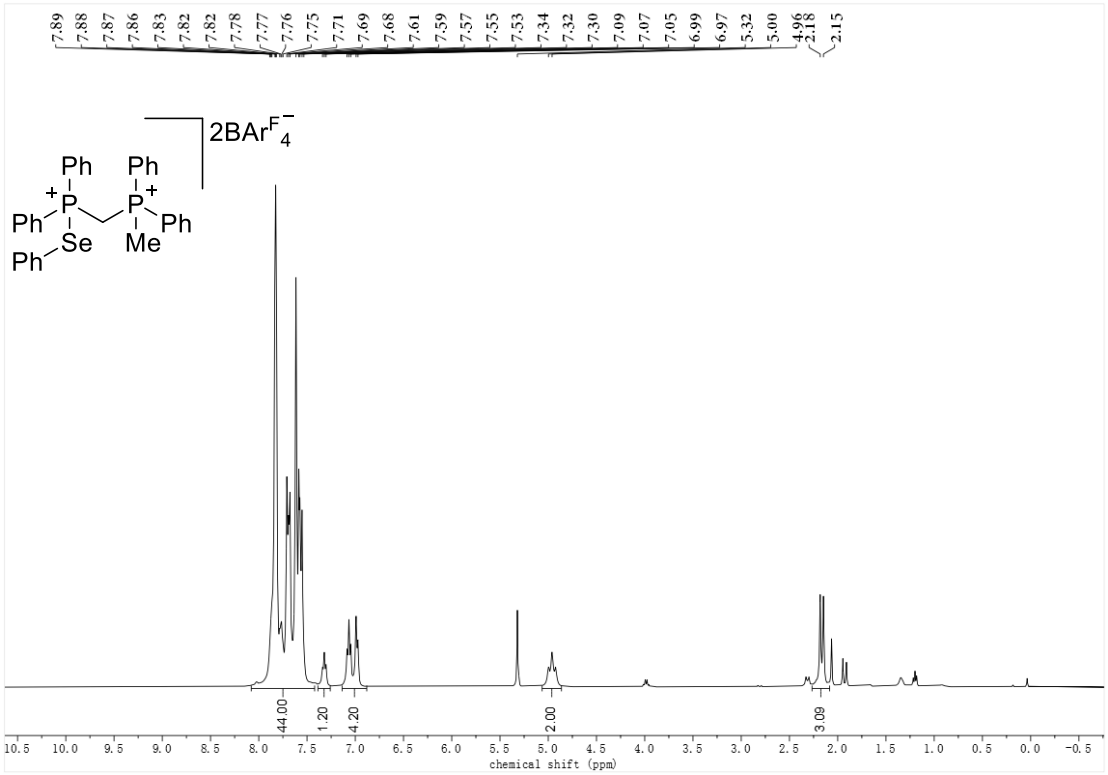


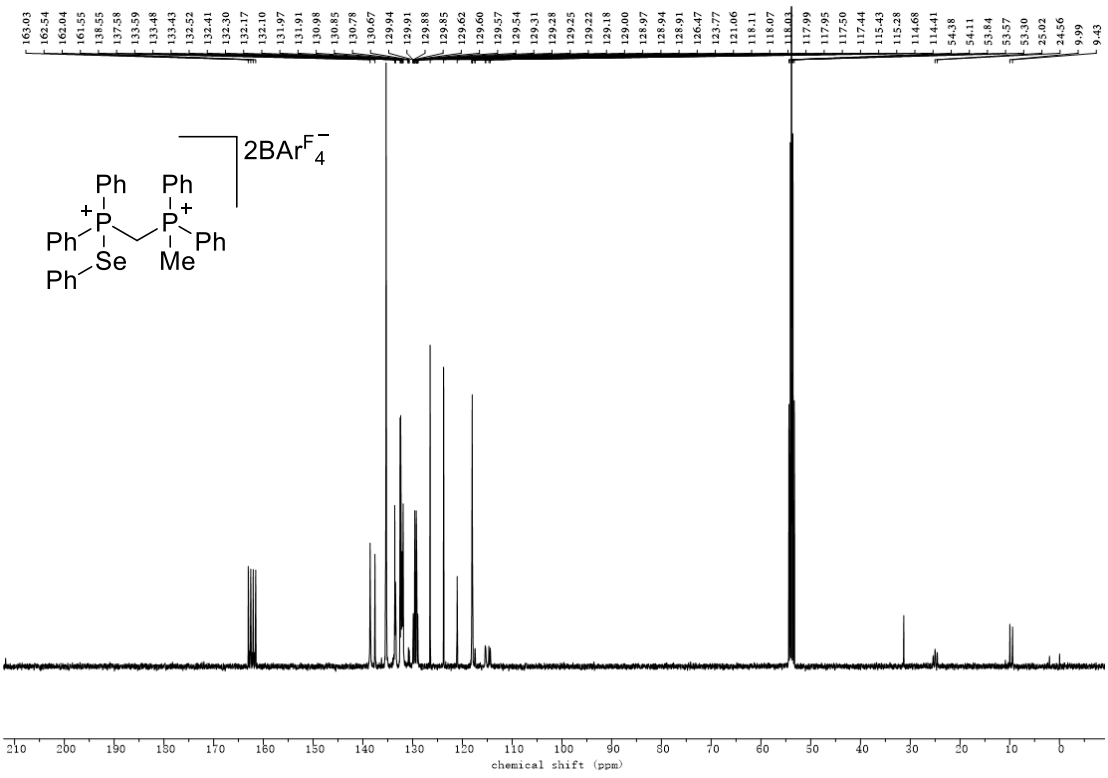
Figure S7. The ^{31}P NMR chemical shift of **PCH2** upon addition of **1a.**

5. Copies of NMR spectra

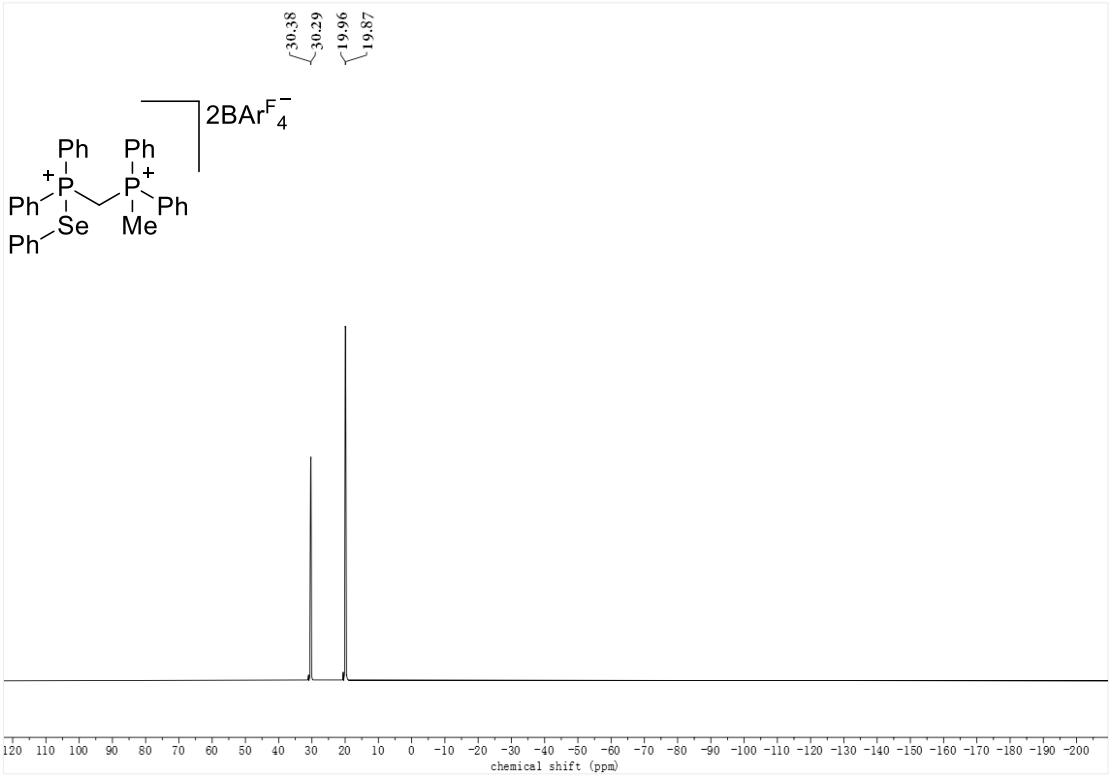
^{1}H NMR spectrum of compound **PCH9** (CD_2Cl_2, 400MHz)



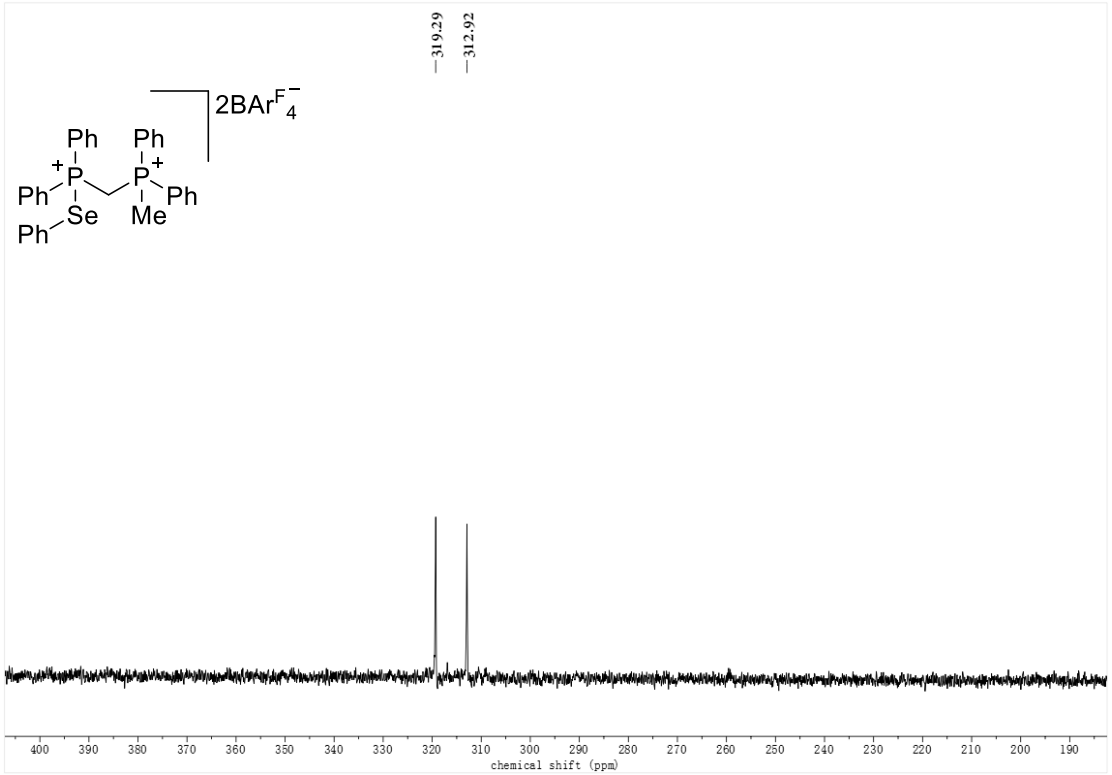
^{13}C NMR spectrum of compound **PCH9** (CD_2Cl_2, 100MHz)



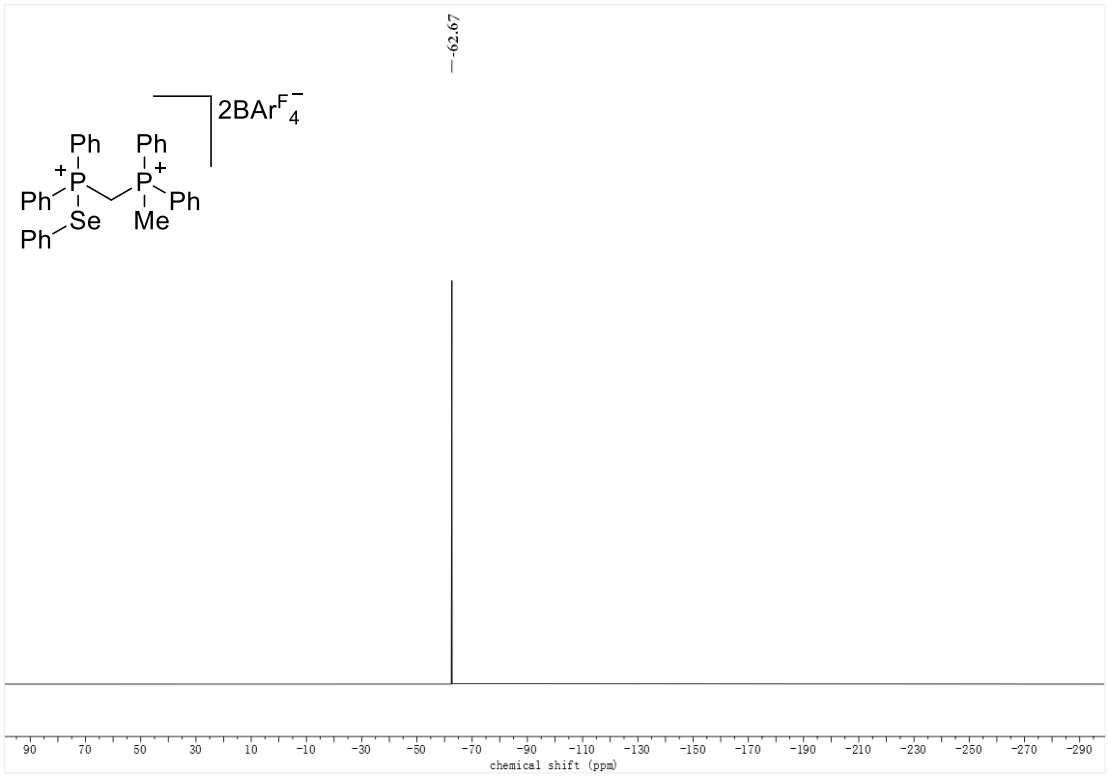
^{31}P NMR spectrum of compound **PCH9** (CD_2Cl_2, 162MHz)



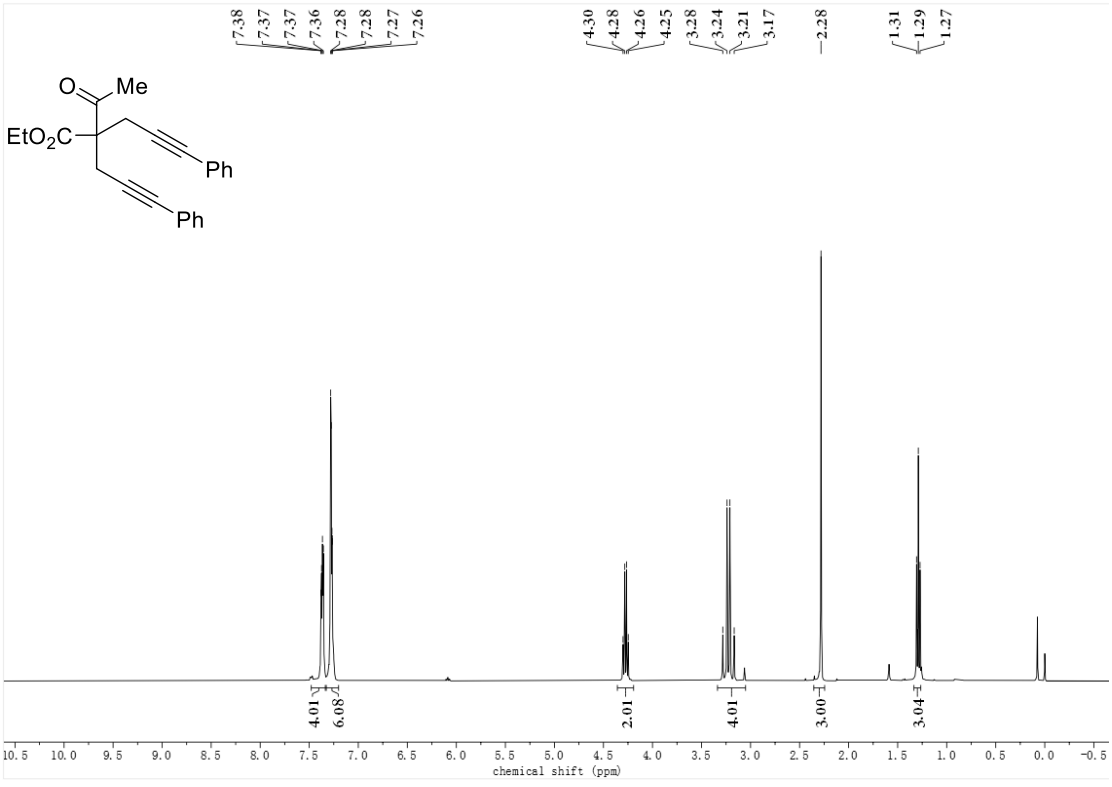
^{77}Se NMR spectrum of compound **PCH9** (CD_2Cl_2, 76MHz)



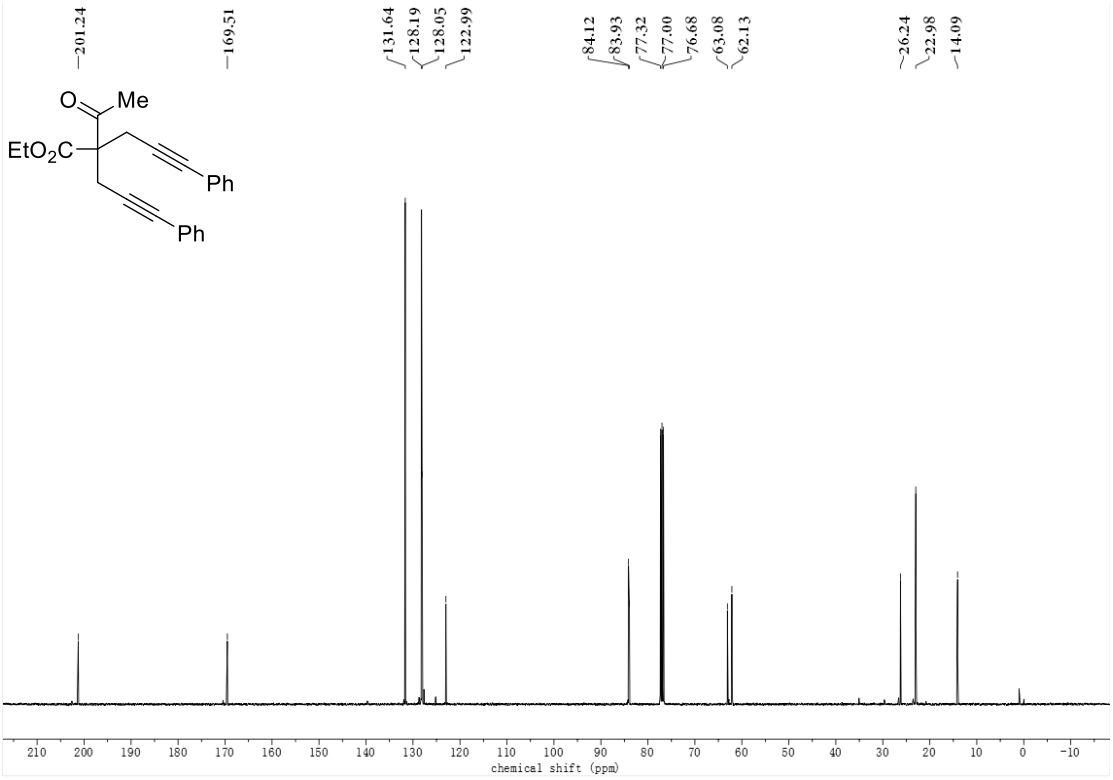
^{19}F NMR spectrum of compound **PCH9** (CD_2Cl_2, 376MHz)



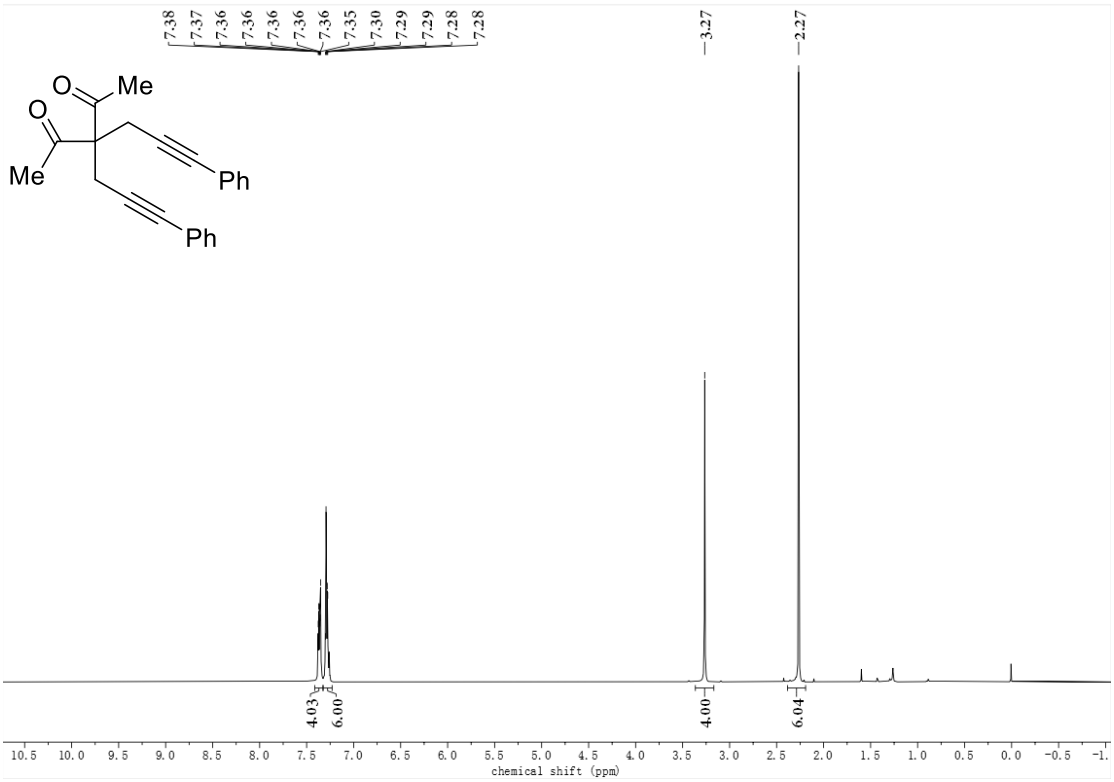
^{1}H NMR spectrum of compound **1a** ($CDCl_3$, 400MHz)



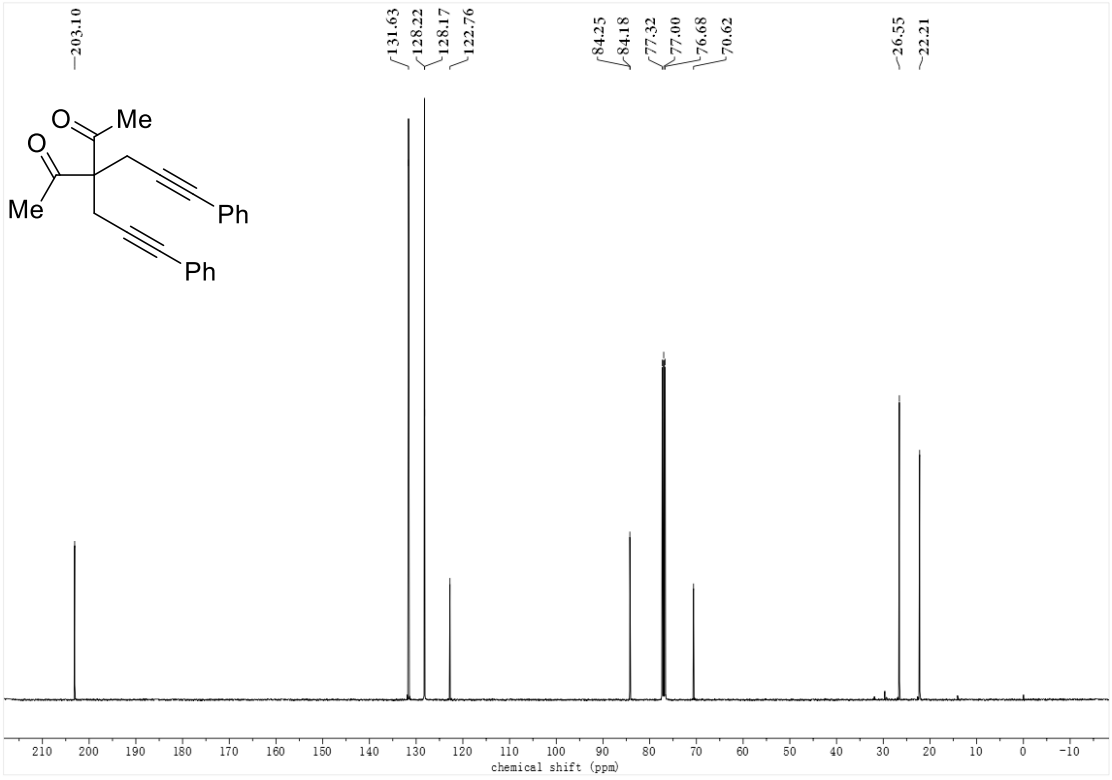
^{13}C NMR spectrum of compound **1a** ($CDCl_3$, 100MHz)



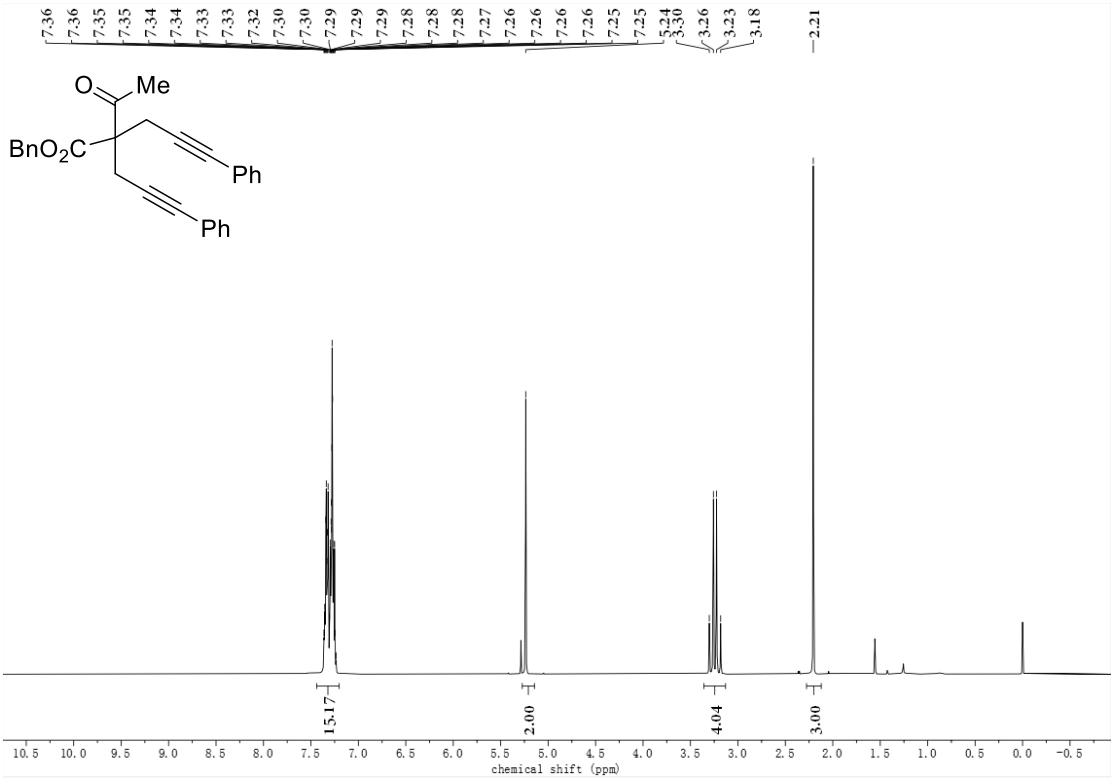
^{1}H NMR spectrum of compound **1b** ($CDCl_3$, 400MHz)



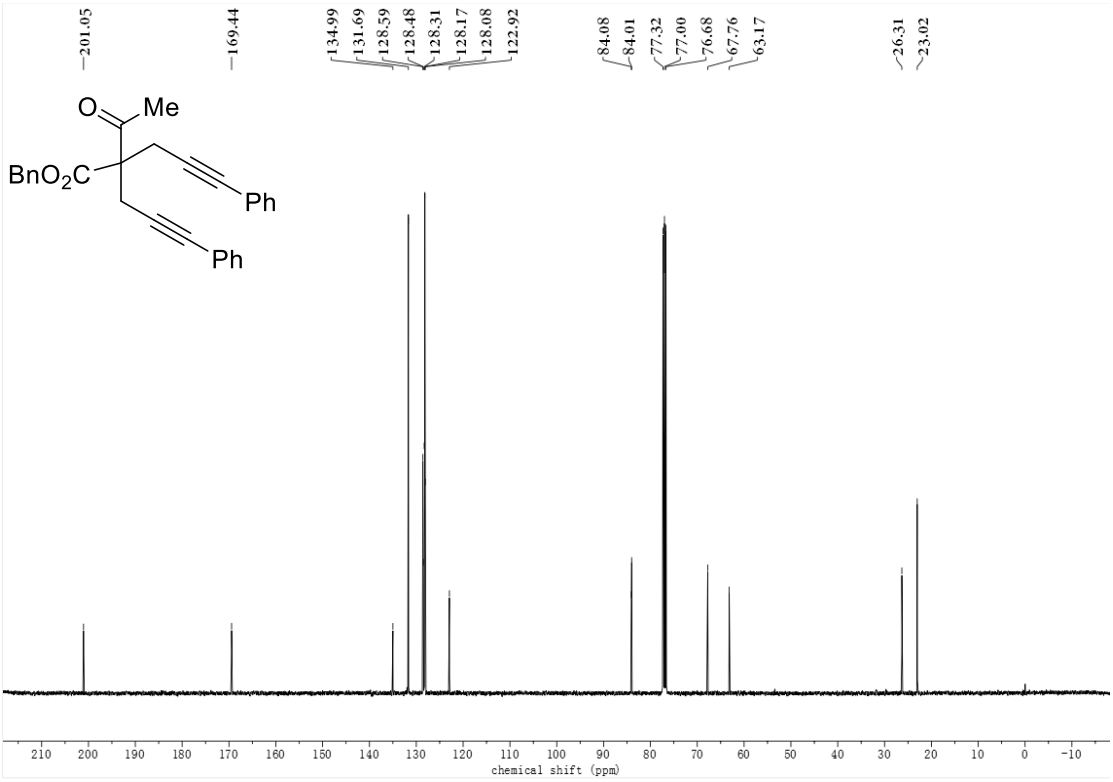
^{13}C NMR spectrum of compound **1b** ($CDCl_3$, 100MHz)



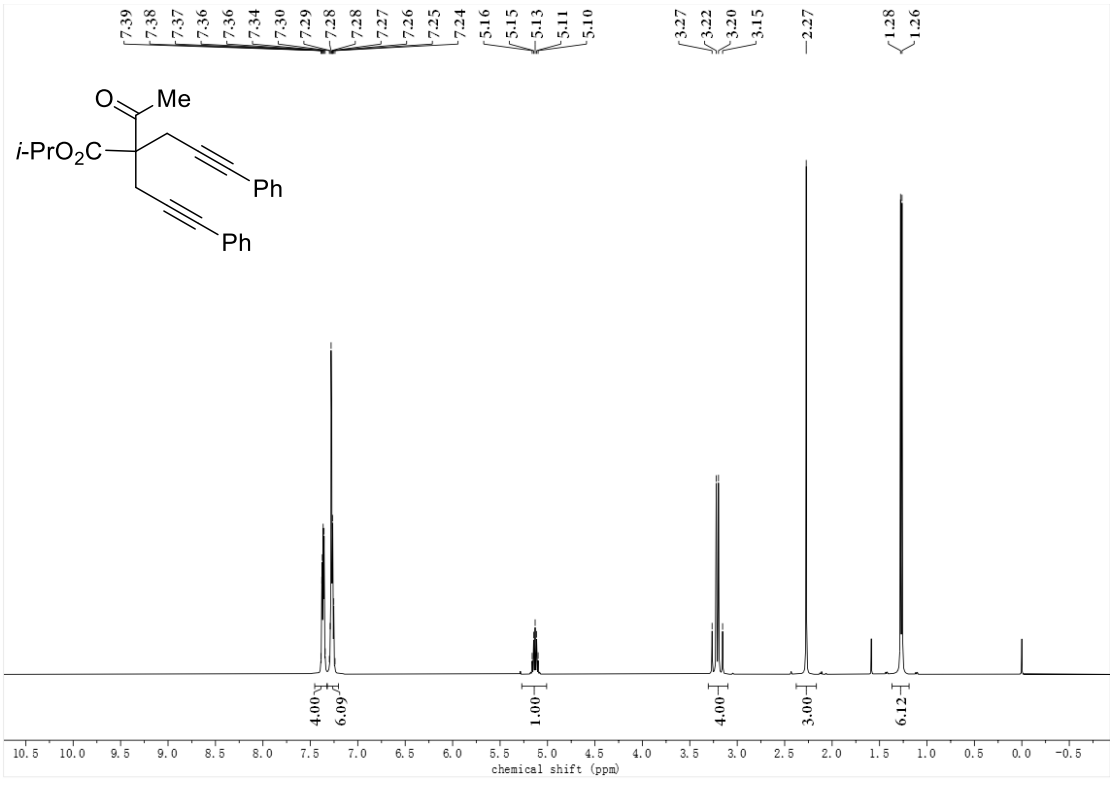
^{1}H NMR spectrum of compound **1c** ($CDCl_3$, 400MHz)



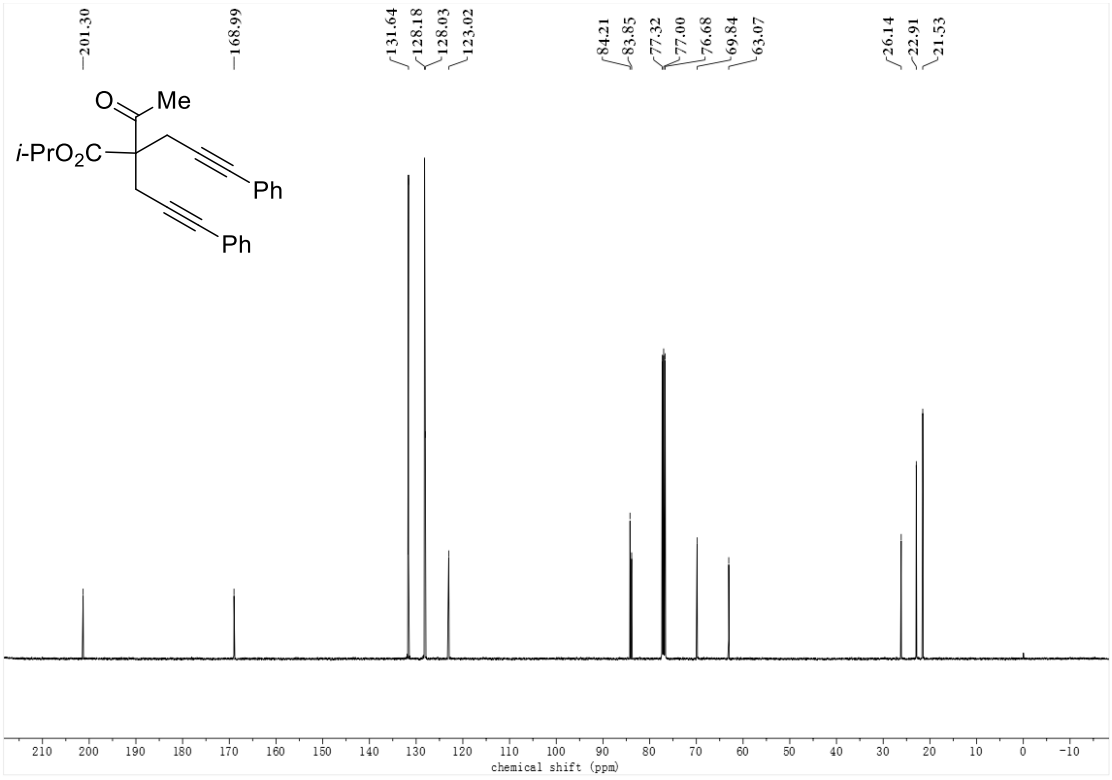
^{13}C NMR spectrum of compound **1c** ($CDCl_3$, 100MHz)



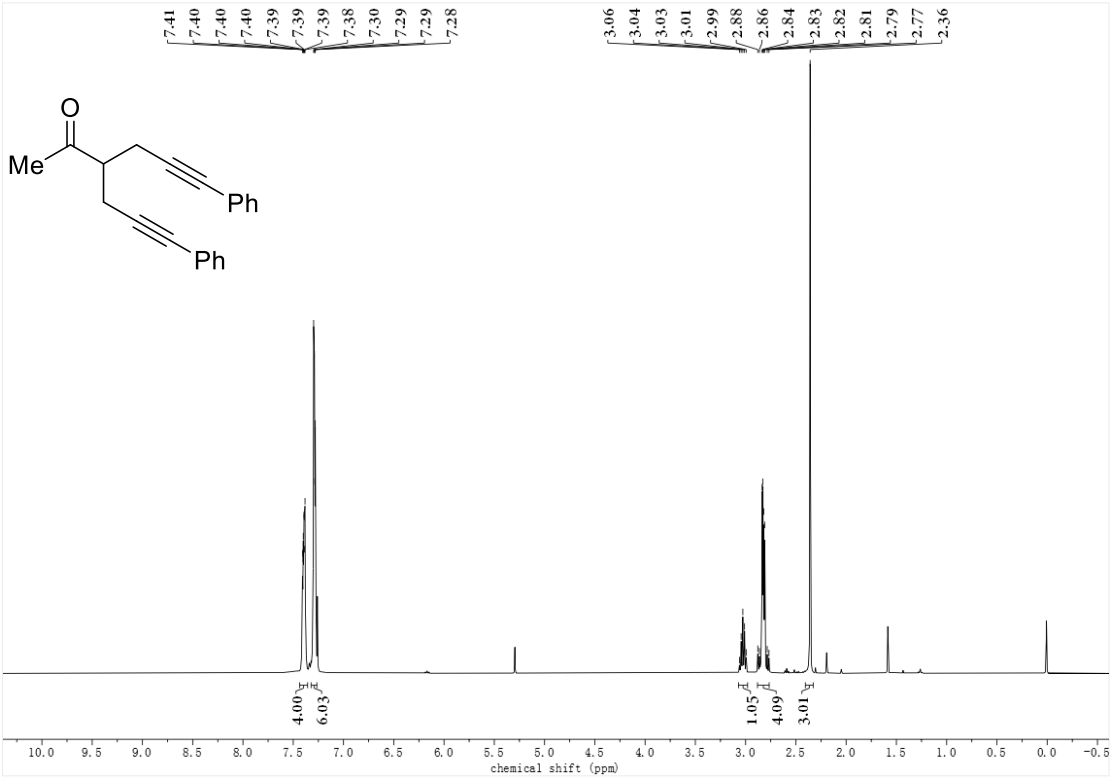
^{1}H NMR spectrum of compound **1d** ($CDCl_3$, 400MHz)



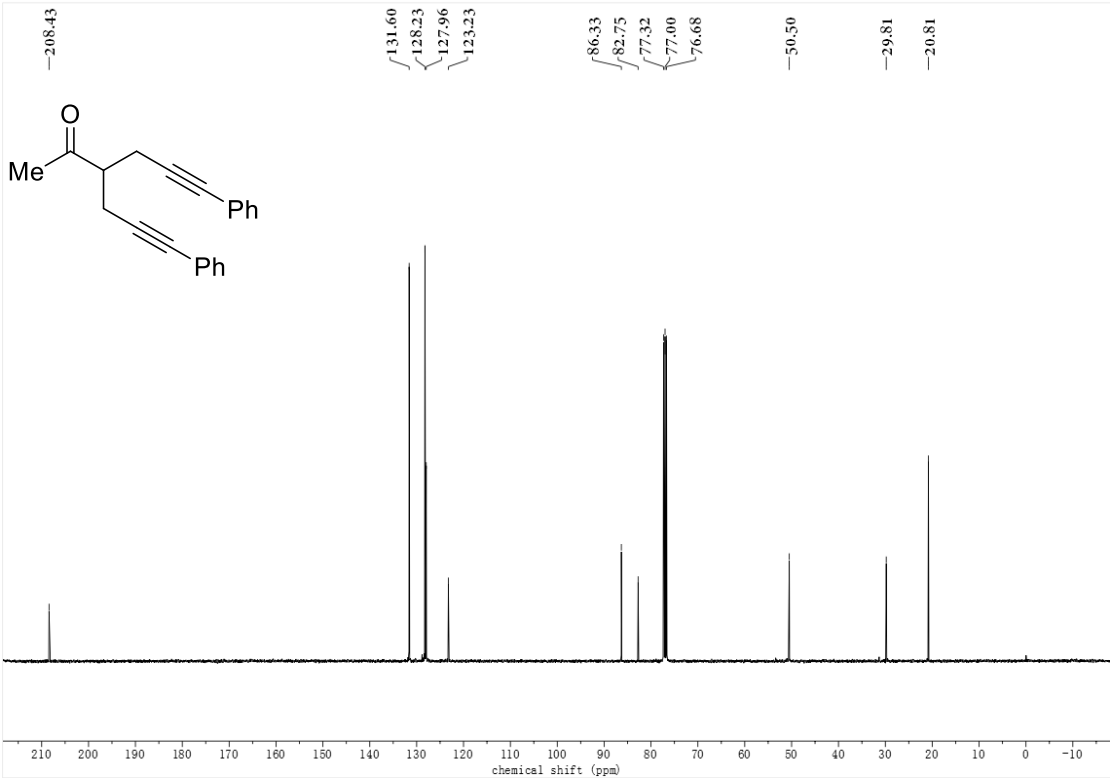
^{13}C NMR spectrum of compound **1d** ($CDCl_3$, 100MHz)



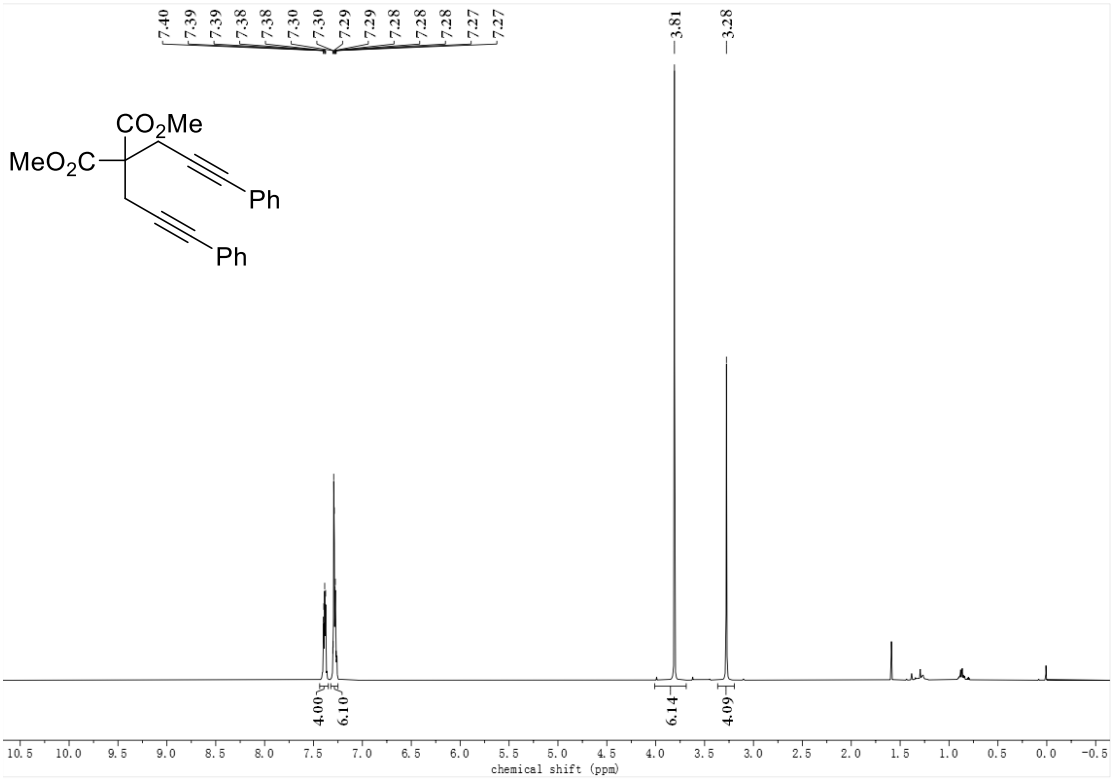
^{1}H NMR spectrum of compound **1e** ($CDCl_3$, 400MHz)



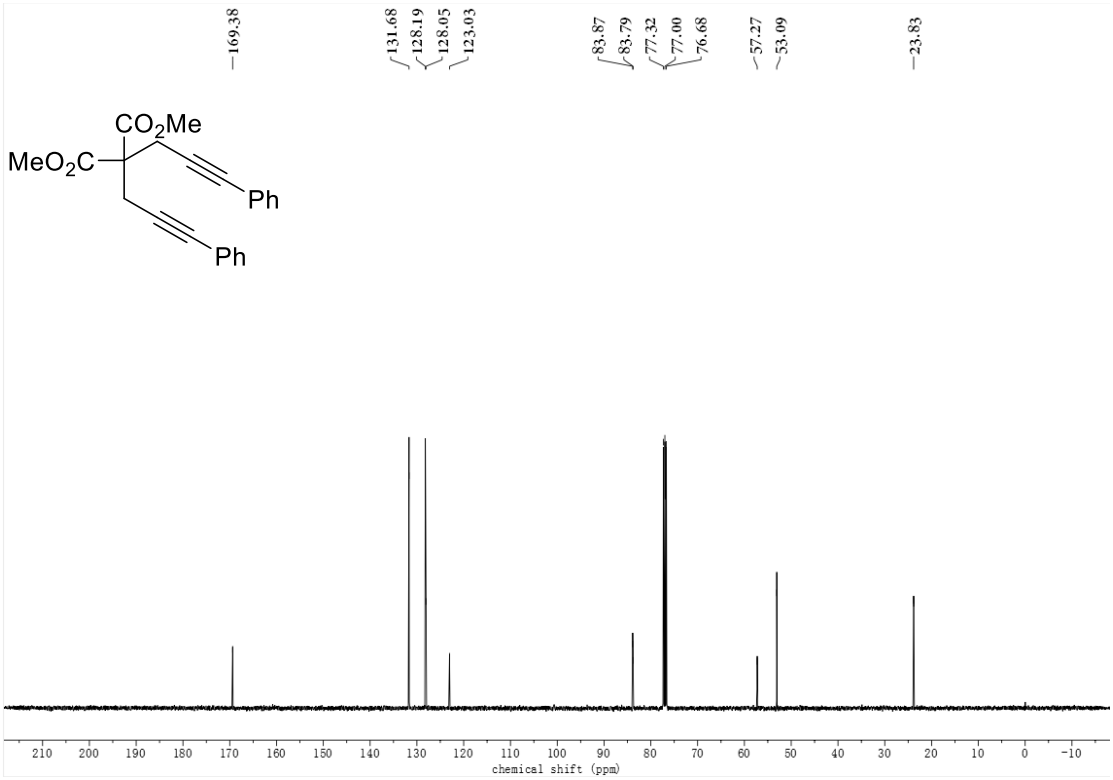
^{13}C NMR spectrum of compound **1e** ($CDCl_3$, 100MHz)



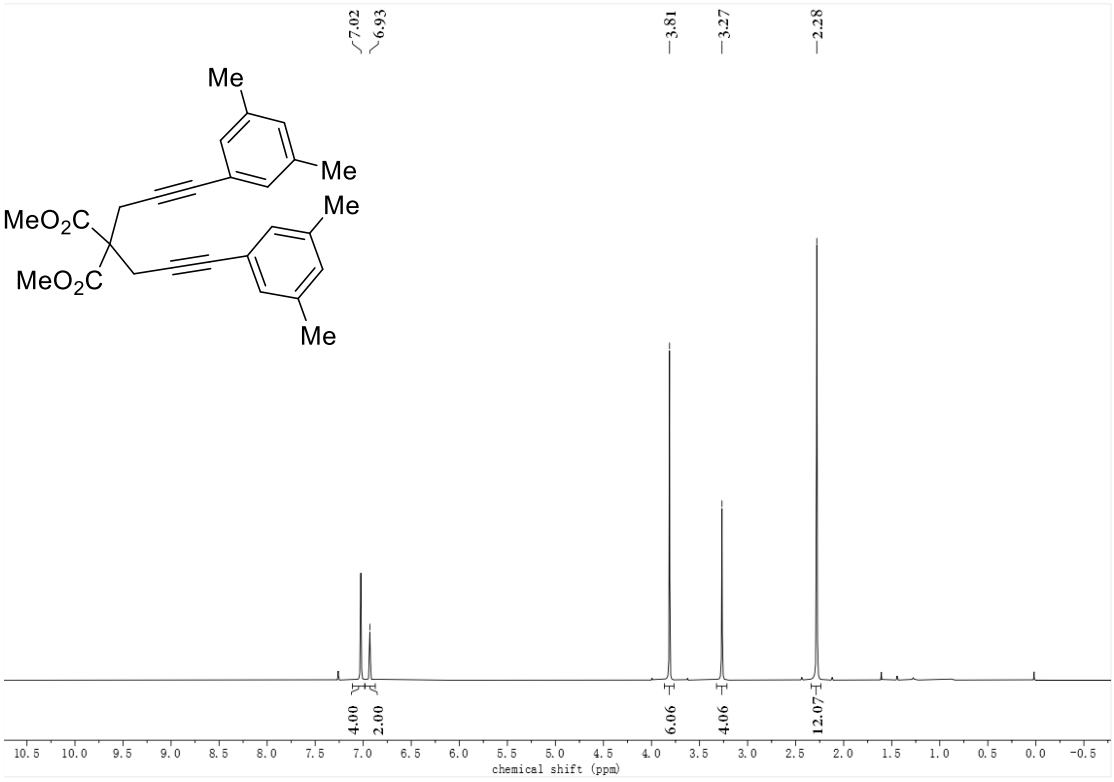
^{1}H NMR spectrum of compound **1f** ($CDCl_3$, 400MHz)



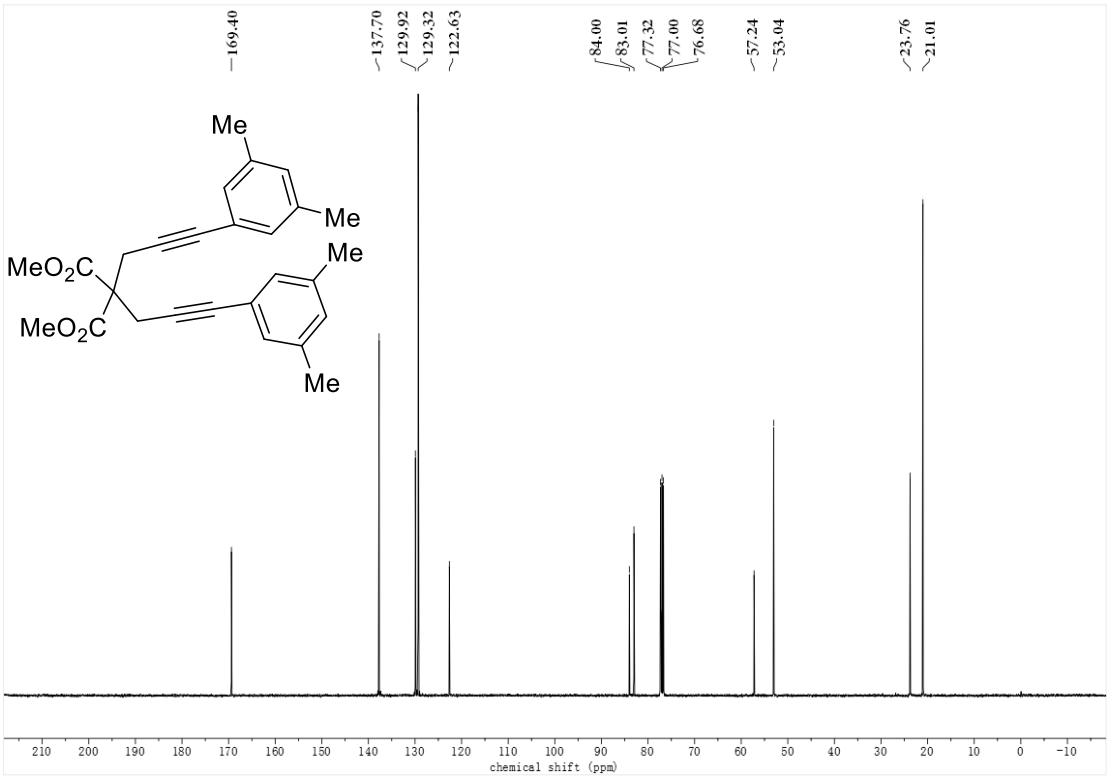
^{13}C NMR spectrum of compound **1f** ($CDCl_3$, 100MHz)



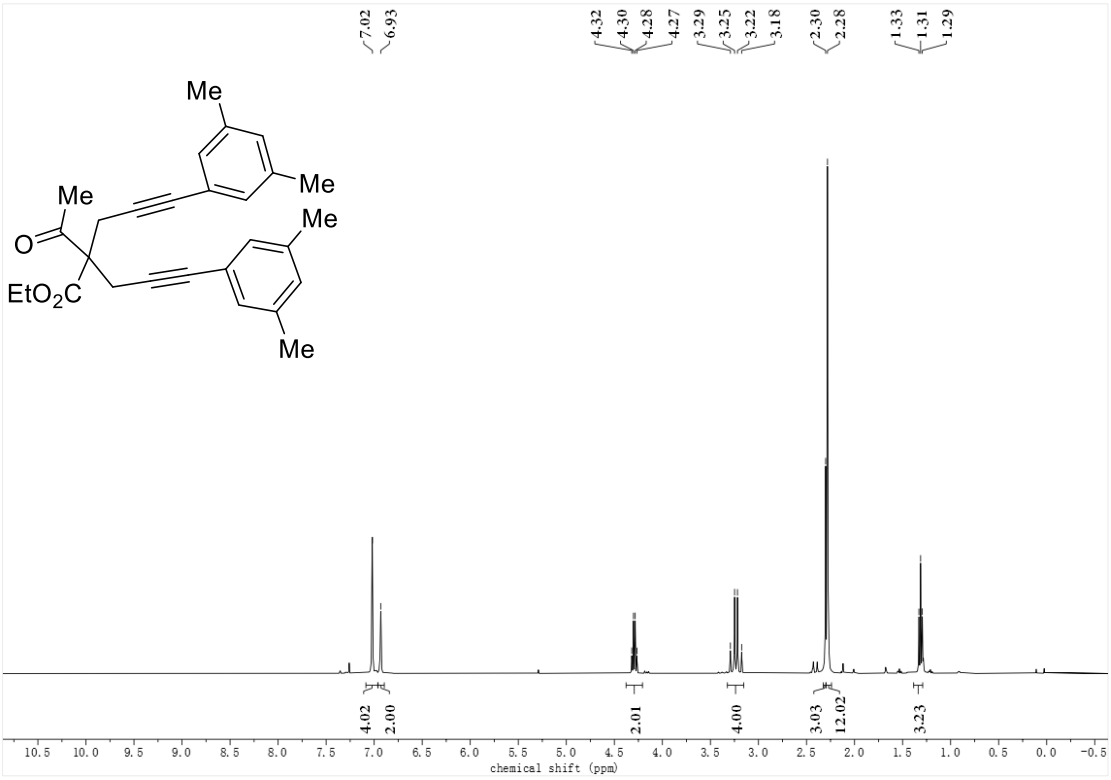
^{1}H NMR spectrum of compound **1g** ($CDCl_3$, 400MHz)



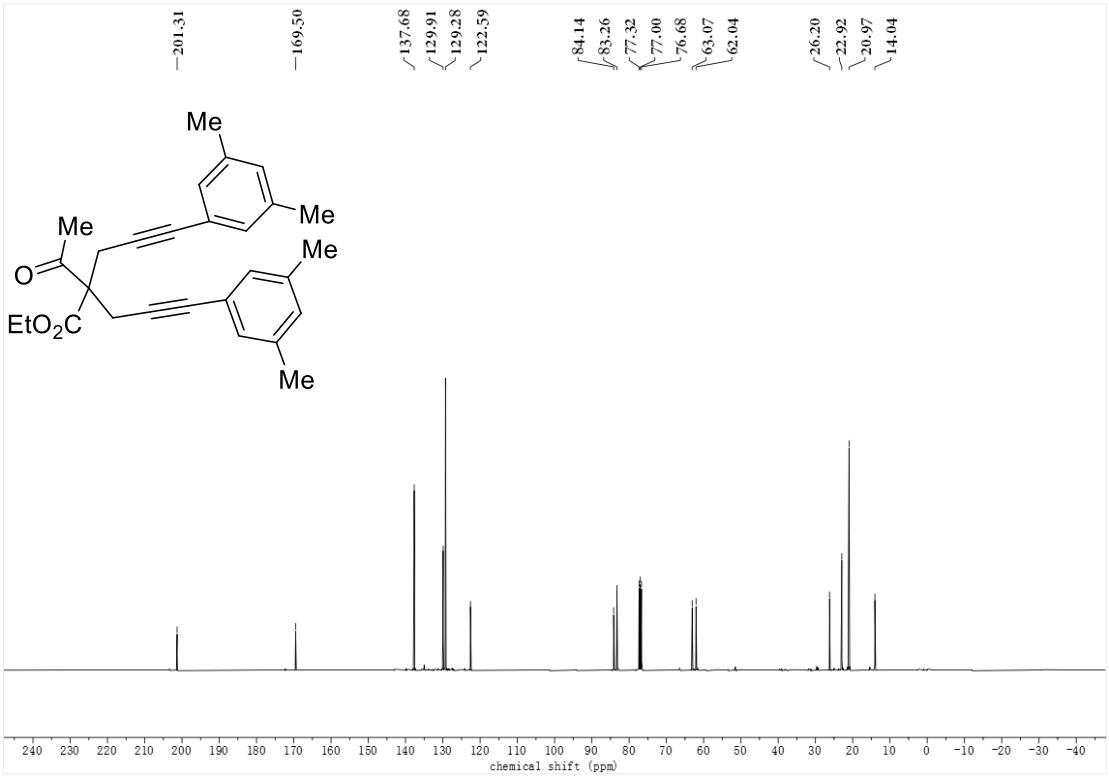
^{13}C NMR spectrum of compound **1g** ($CDCl_3$, 100MHz)



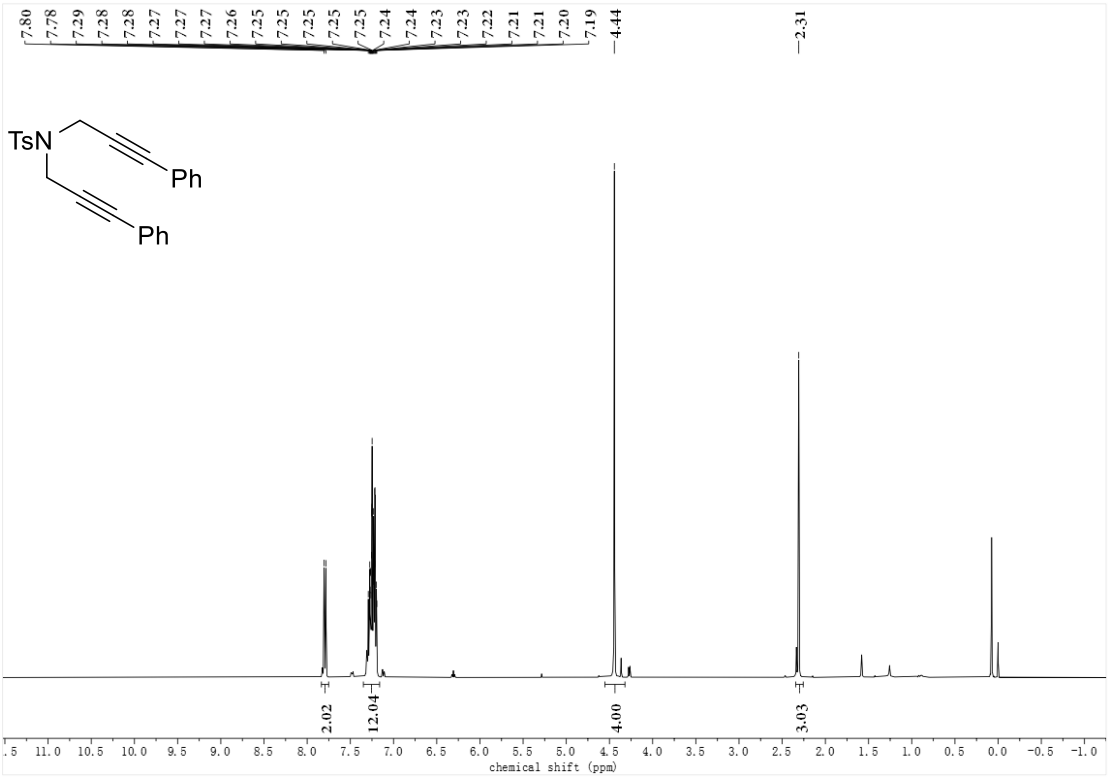
^{1}H NMR spectrum of compound **1h** ($CDCl_3$, 400MHz)



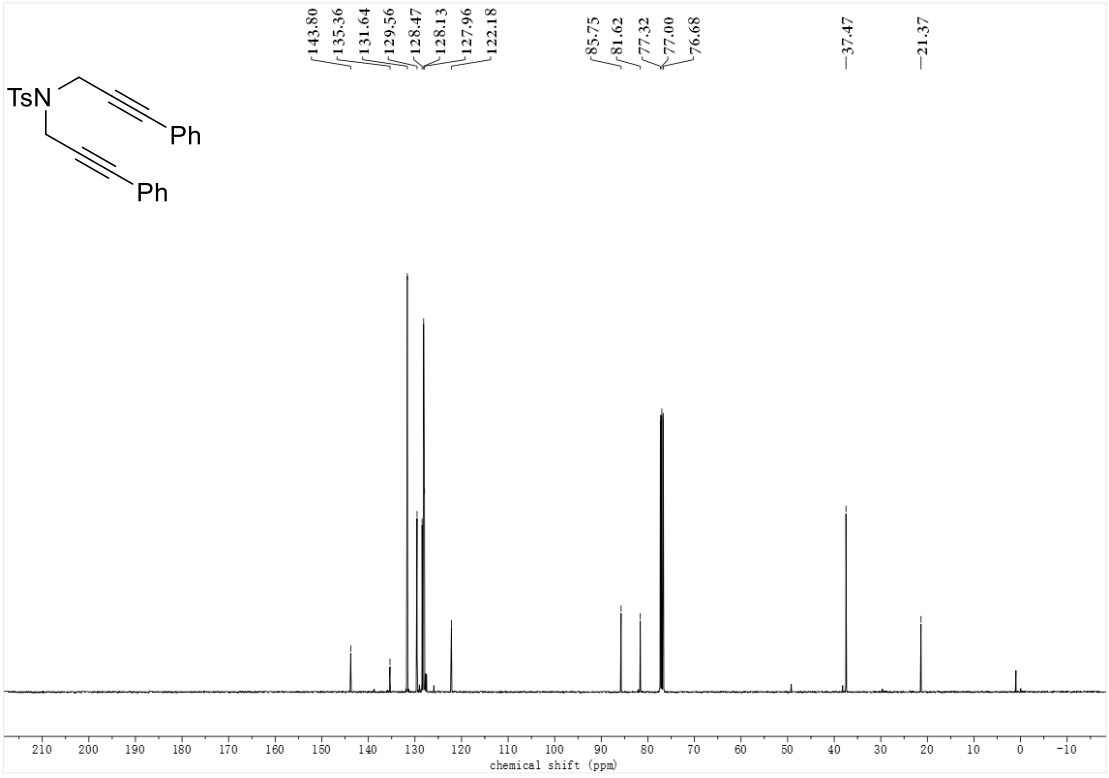
^{13}C NMR spectrum of compound **1h** ($CDCl_3$, 100MHz)



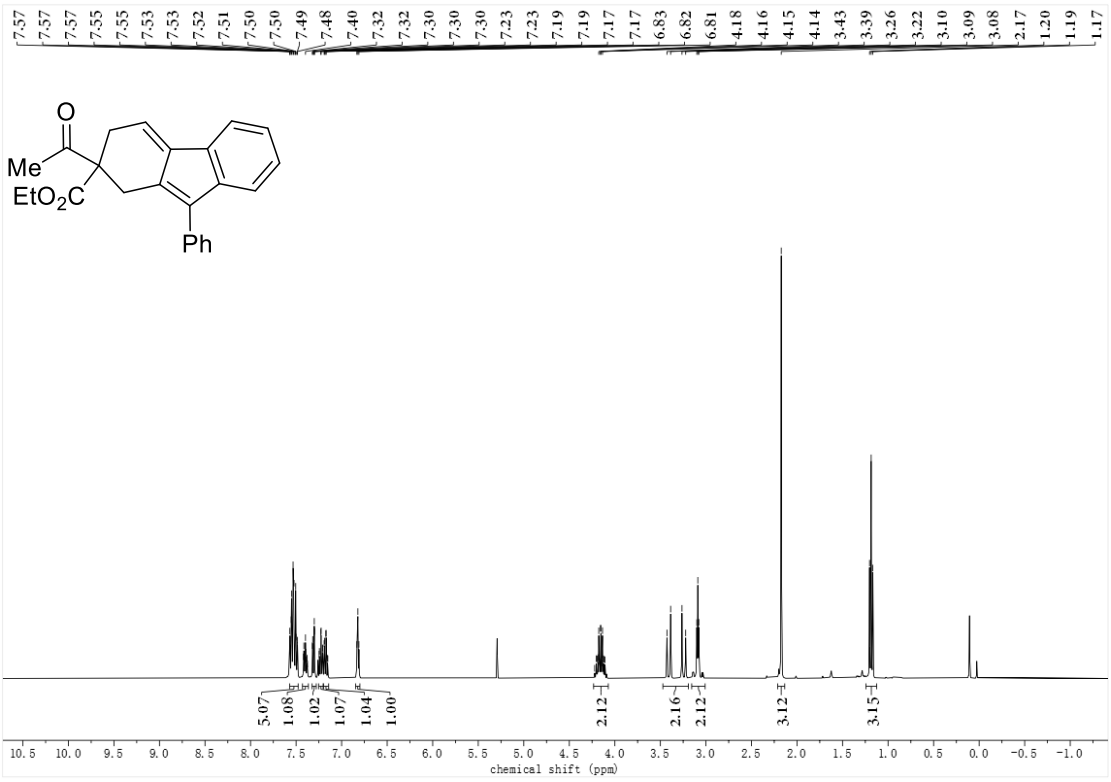
^{1}H NMR spectrum of compound **1i** ($CDCl_3$, 400MHz)



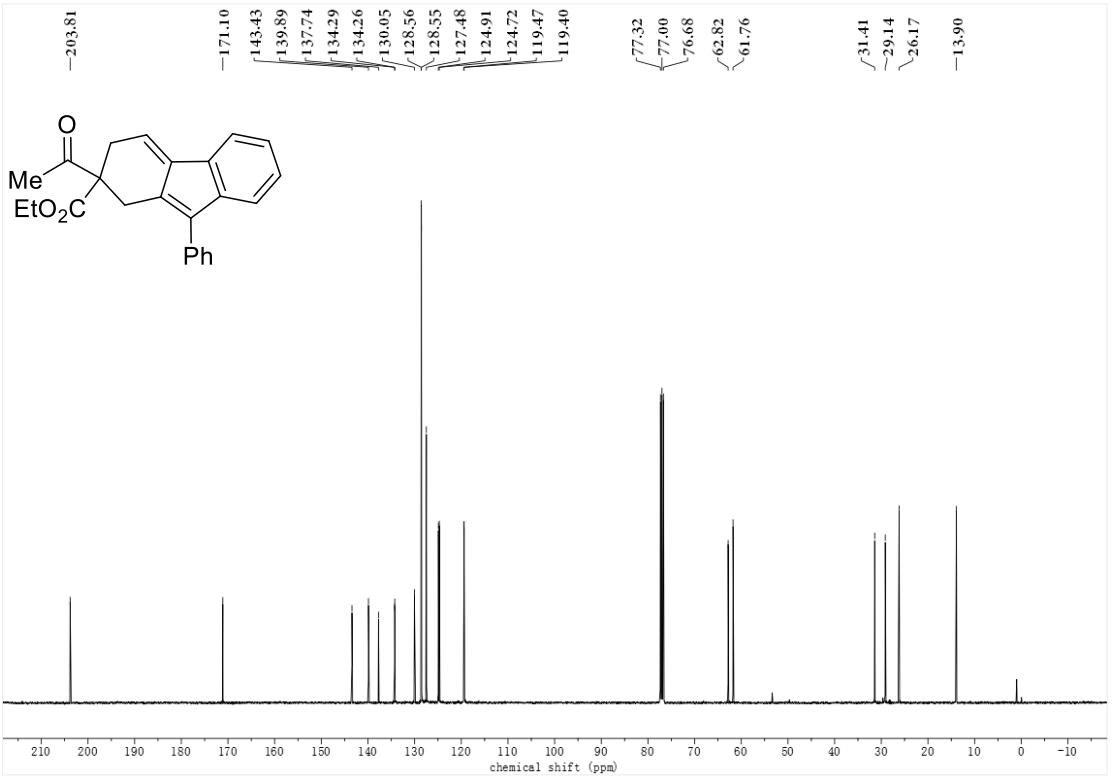
^{13}C NMR spectrum of compound **1i** ($CDCl_3$, 100MHz)



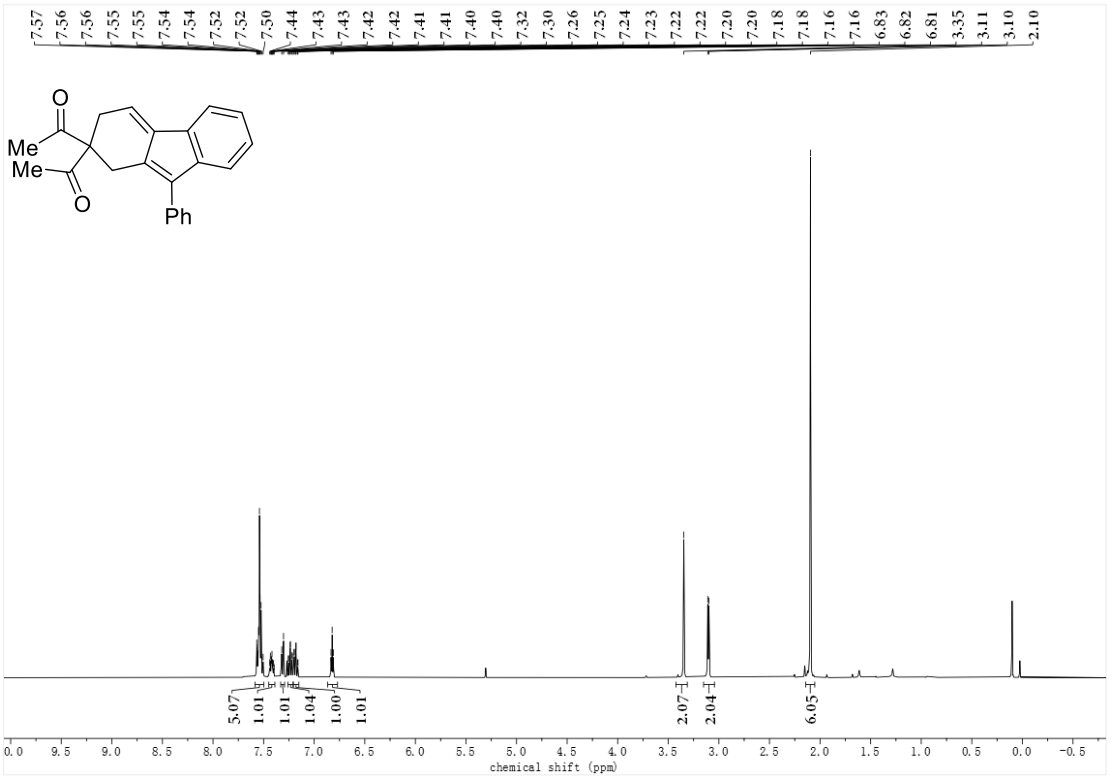
^{1}H NMR spectrum of compound **2a** ($CDCl_3$, 400MHz)



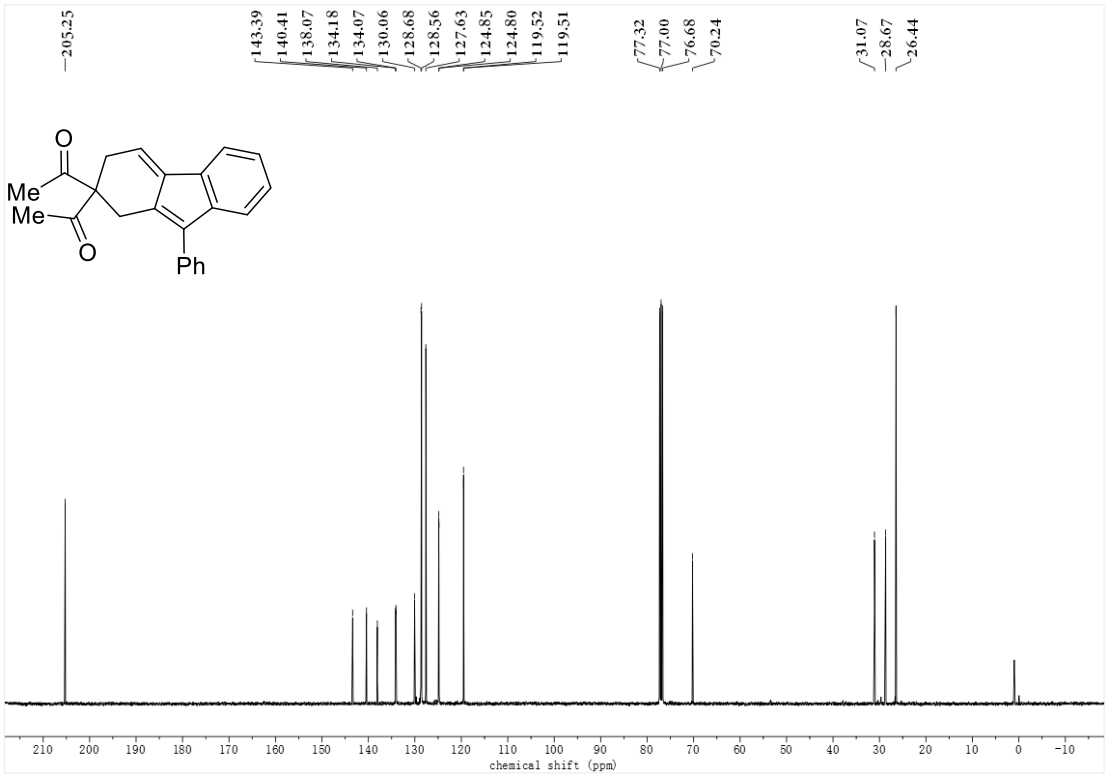
^{13}C NMR spectrum of compound **2a** ($CDCl_3$, 100MHz)



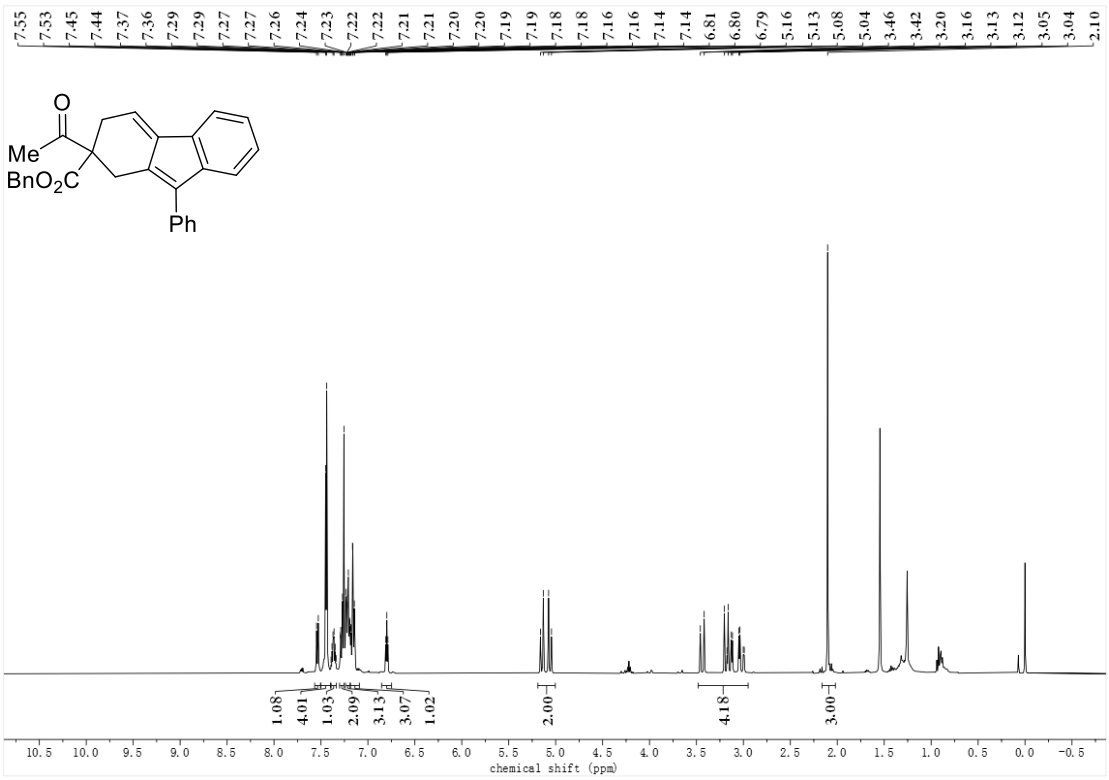
^{1}H NMR spectrum of compound **2b** ($CDCl_3$, 400MHz)



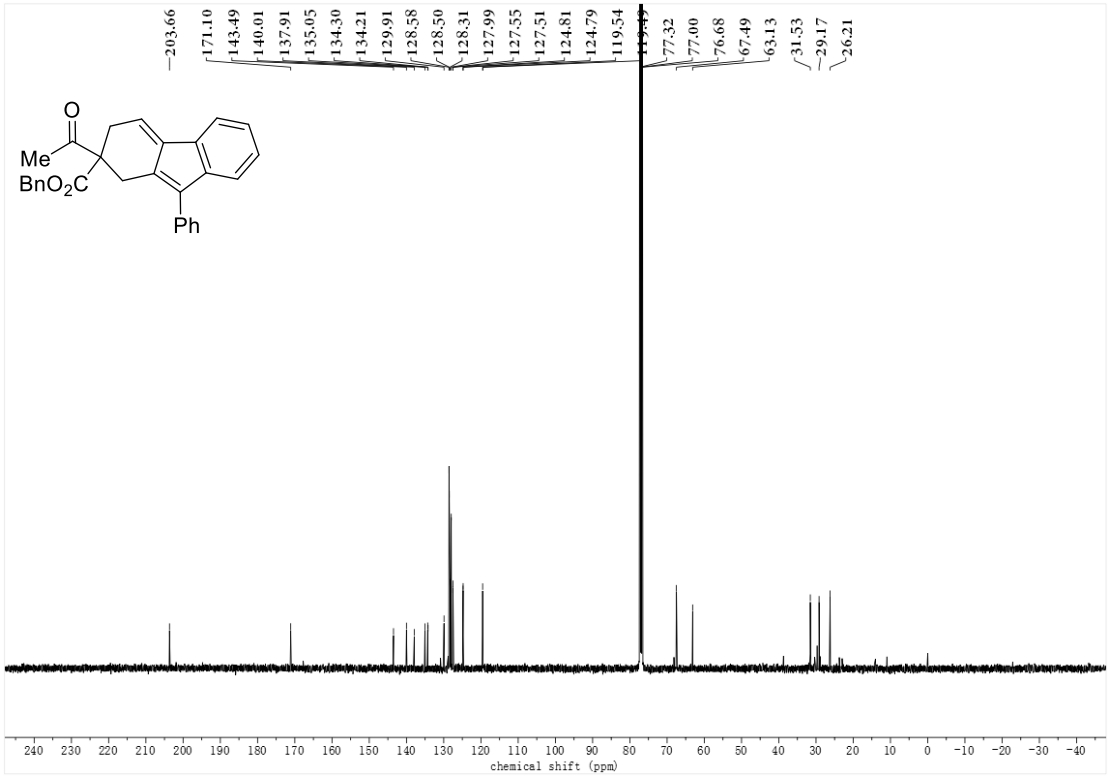
^{13}C NMR spectrum of compound **2b** ($CDCl_3$, 100MHz)



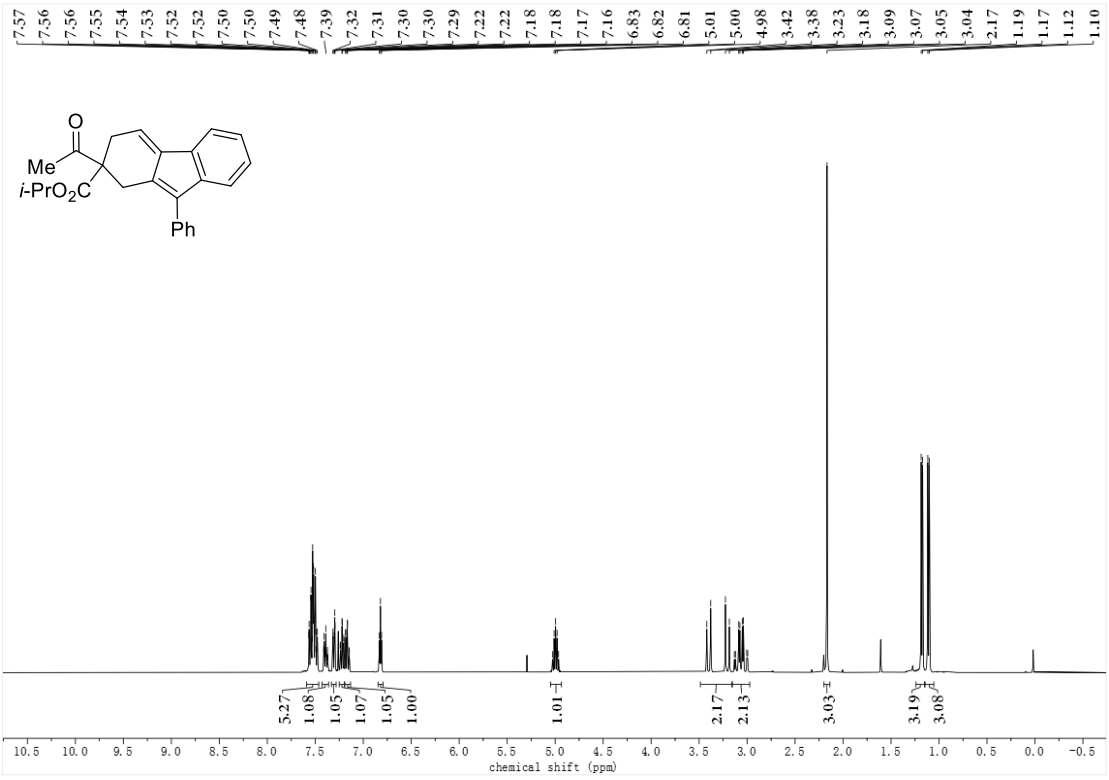
^{1}H NMR spectrum of compound **2c** ($CDCl_3$, 400MHz)



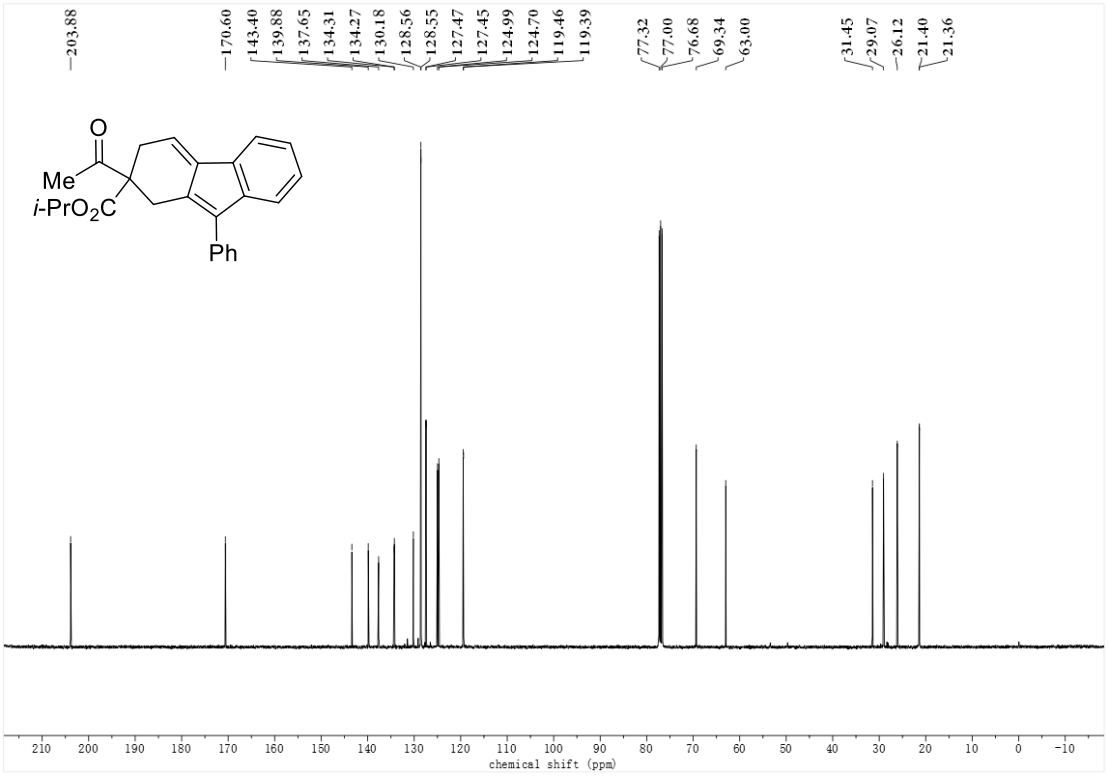
^{13}C NMR spectrum of compound **2c** ($CDCl_3$, 100MHz)



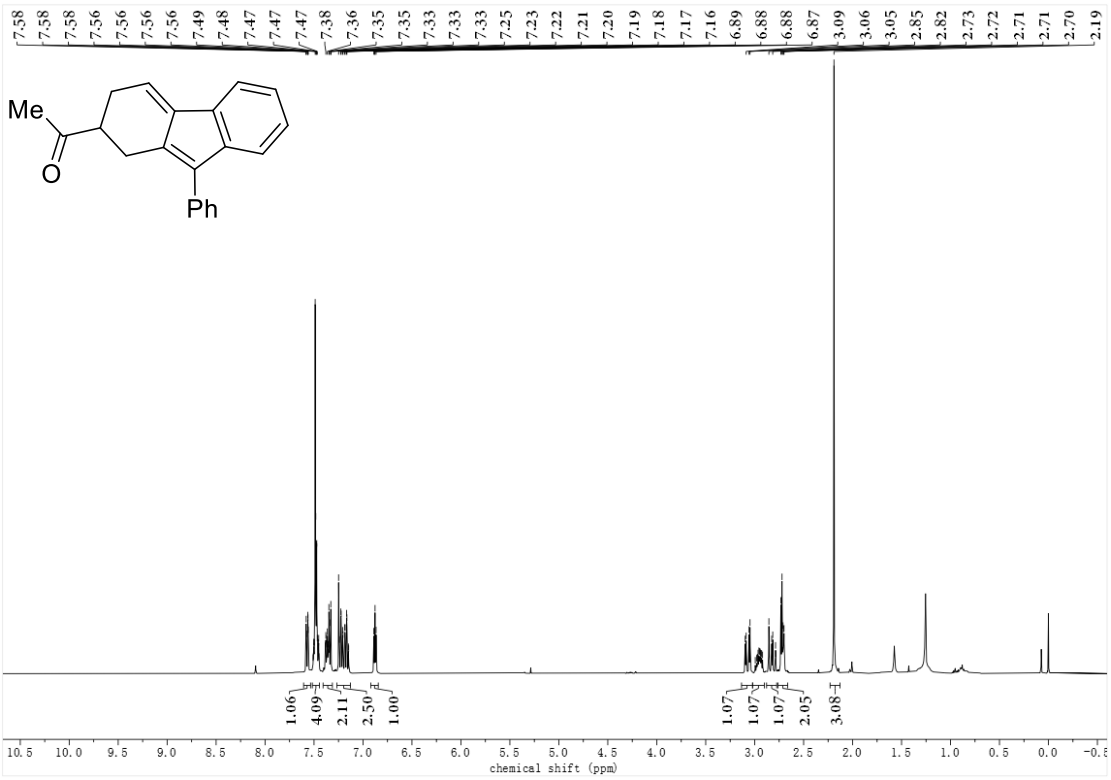
^{1}H NMR spectrum of compound **2d** ($CDCl_3$, 400MHz)



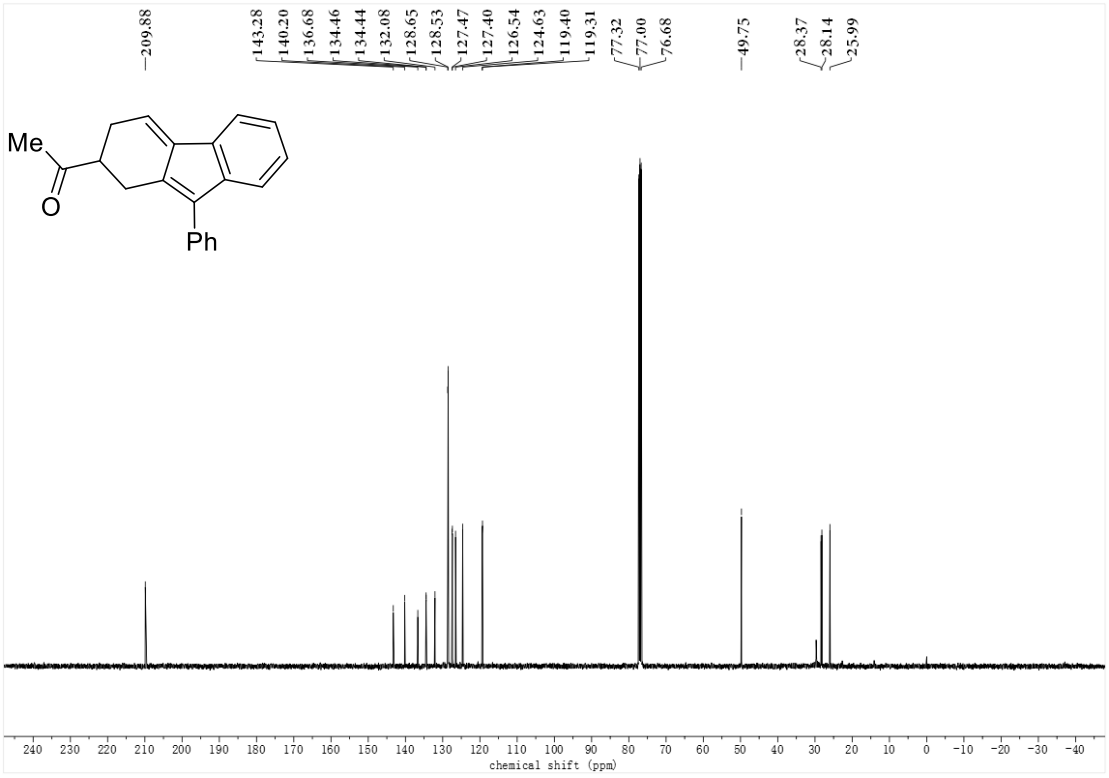
^{13}C NMR spectrum of compound **2d** ($CDCl_3$, 100MHz)



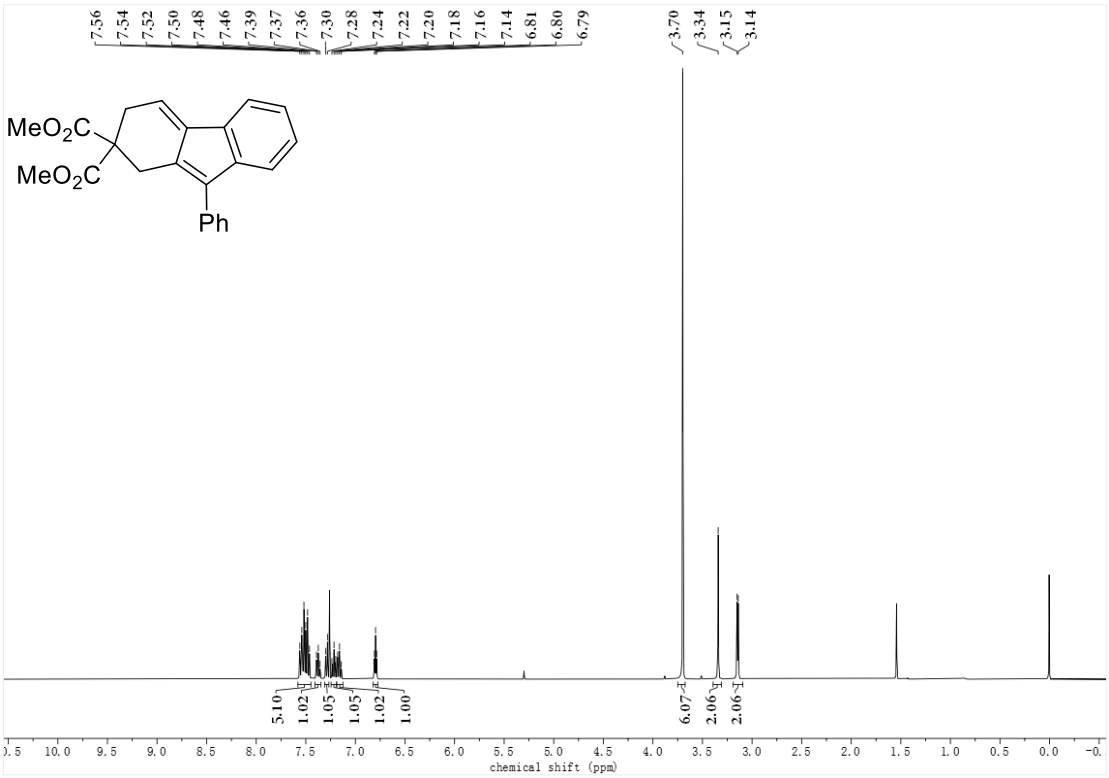
^{1}H NMR spectrum of compound **2e** ($CDCl_3$, 400MHz)



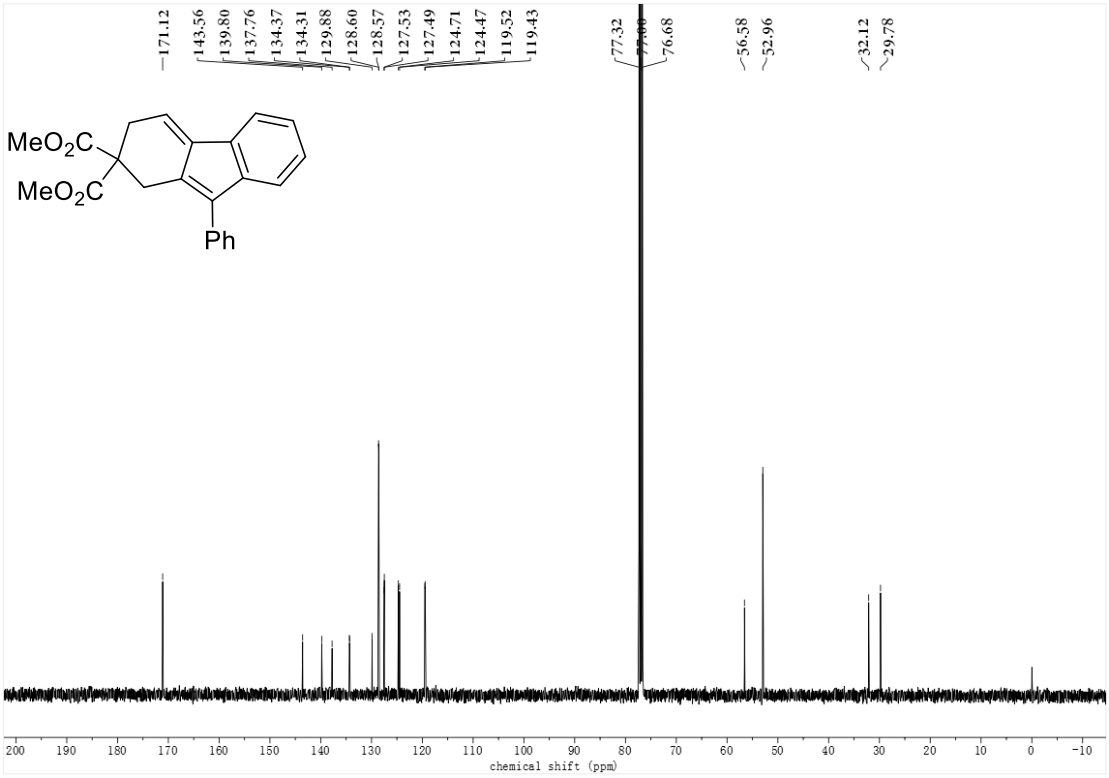
^{13}C NMR spectrum of compound **2e** ($CDCl_3$, 100MHz)



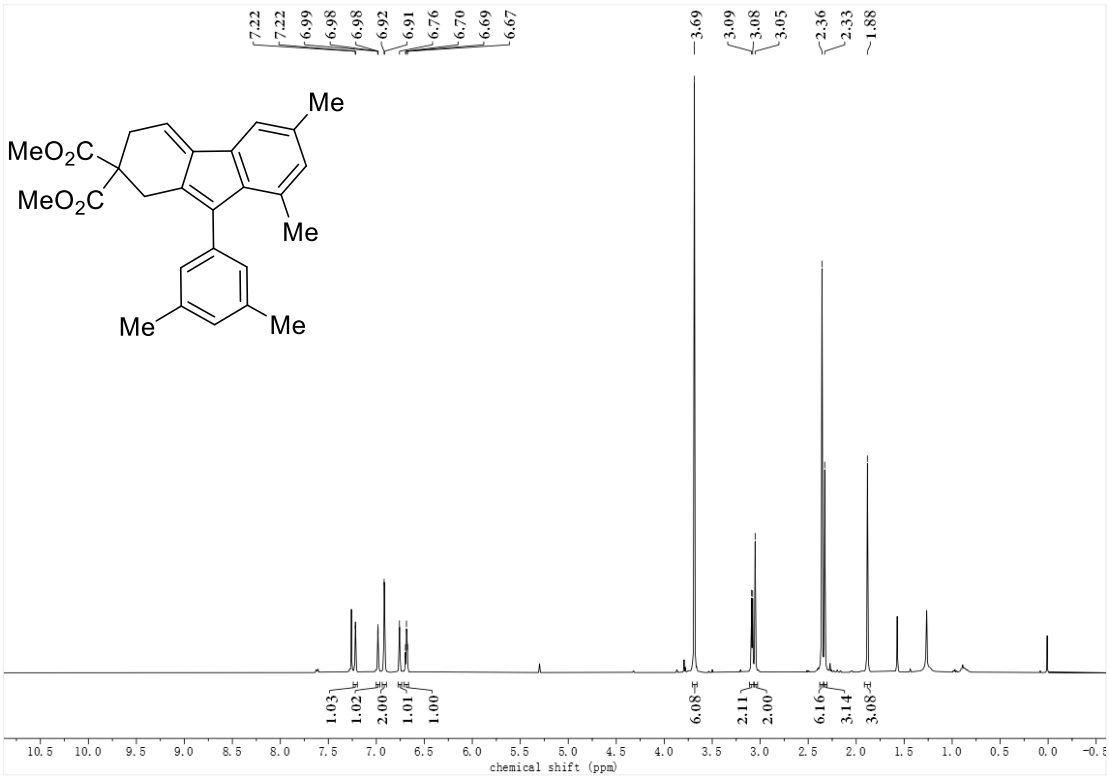
^{1}H NMR spectrum of compound **2f** ($CDCl_3$, 400MHz)



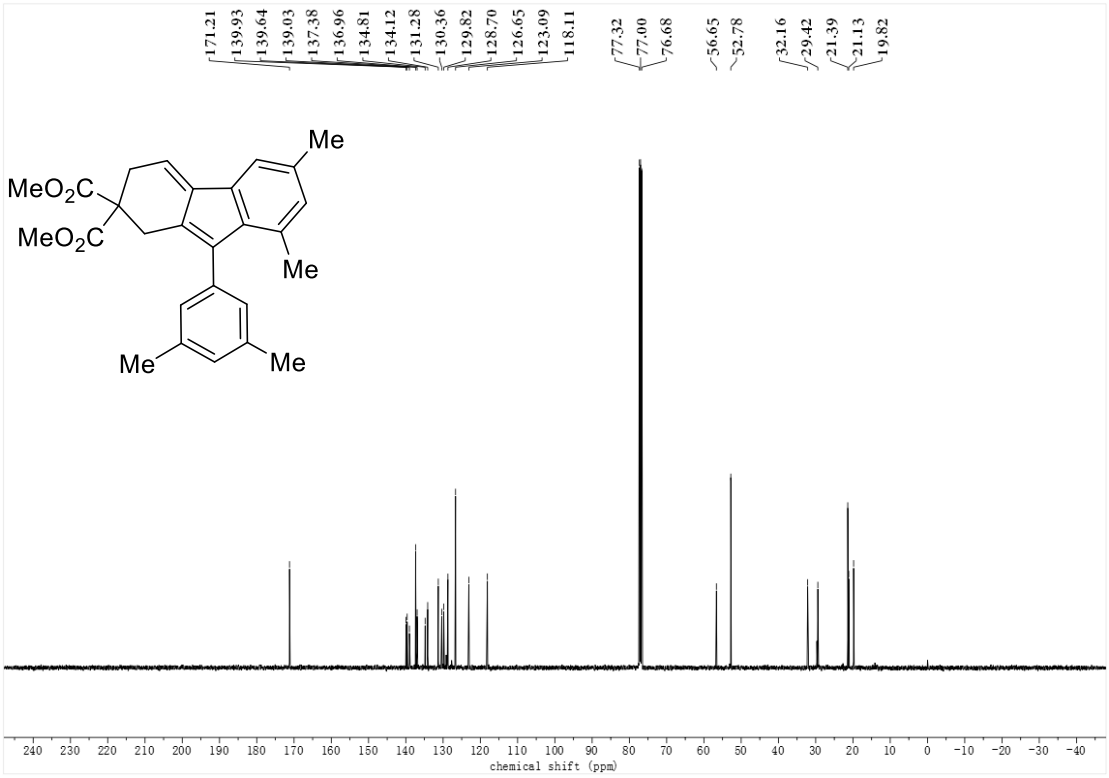
^{13}C NMR spectrum of compound **2f** ($CDCl_3$, 100MHz)



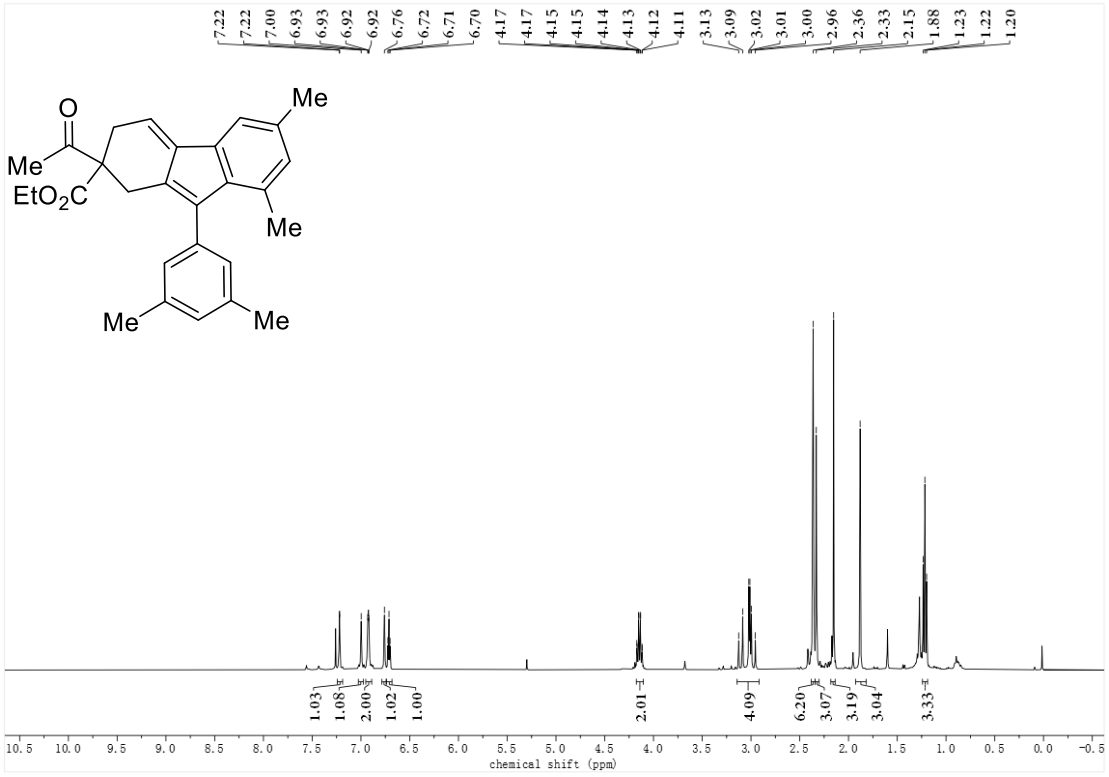
^{1}H NMR spectrum of compound **2g** ($CDCl_3$, 400MHz)



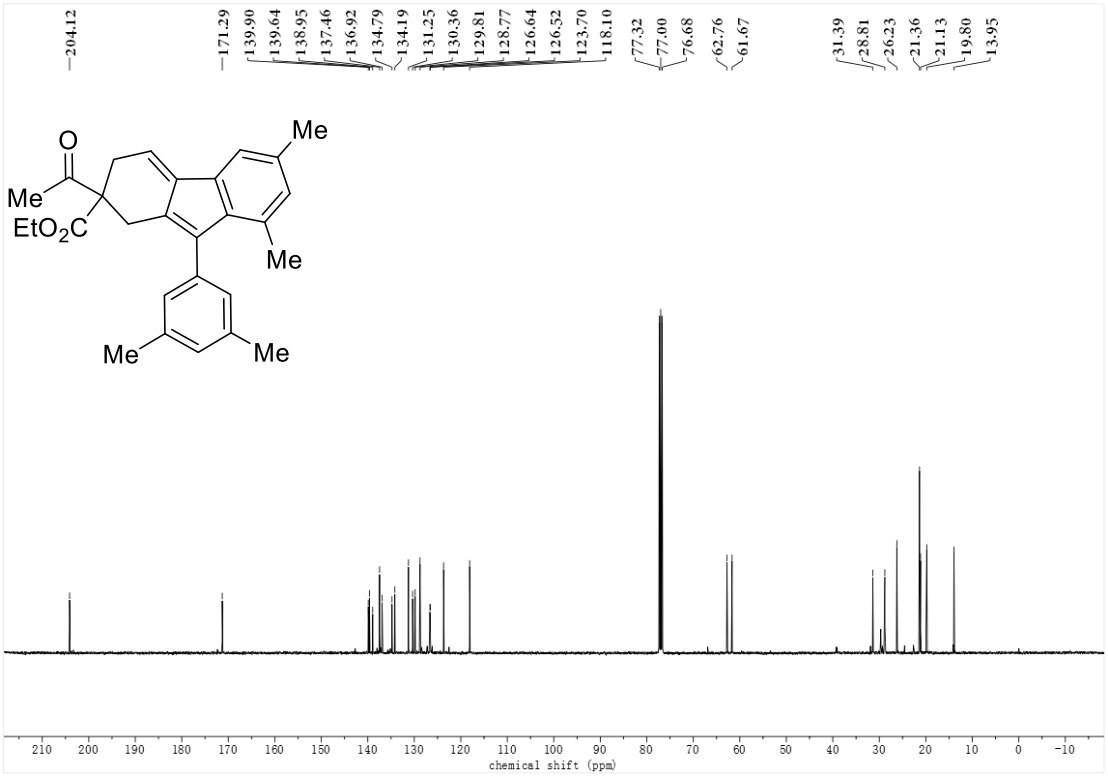
^{13}C NMR spectrum of compound **2g** ($CDCl_3$, 100MHz)



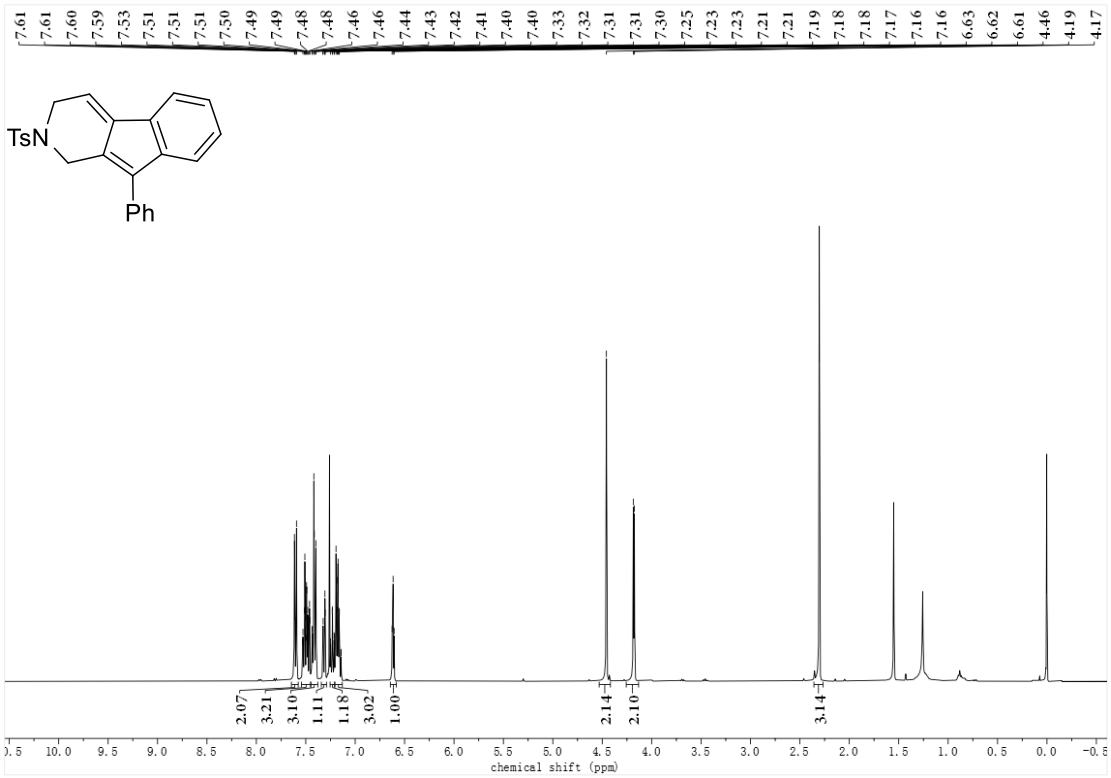
^{1}H NMR spectrum of compound **2h** ($CDCl_3$, 400MHz)



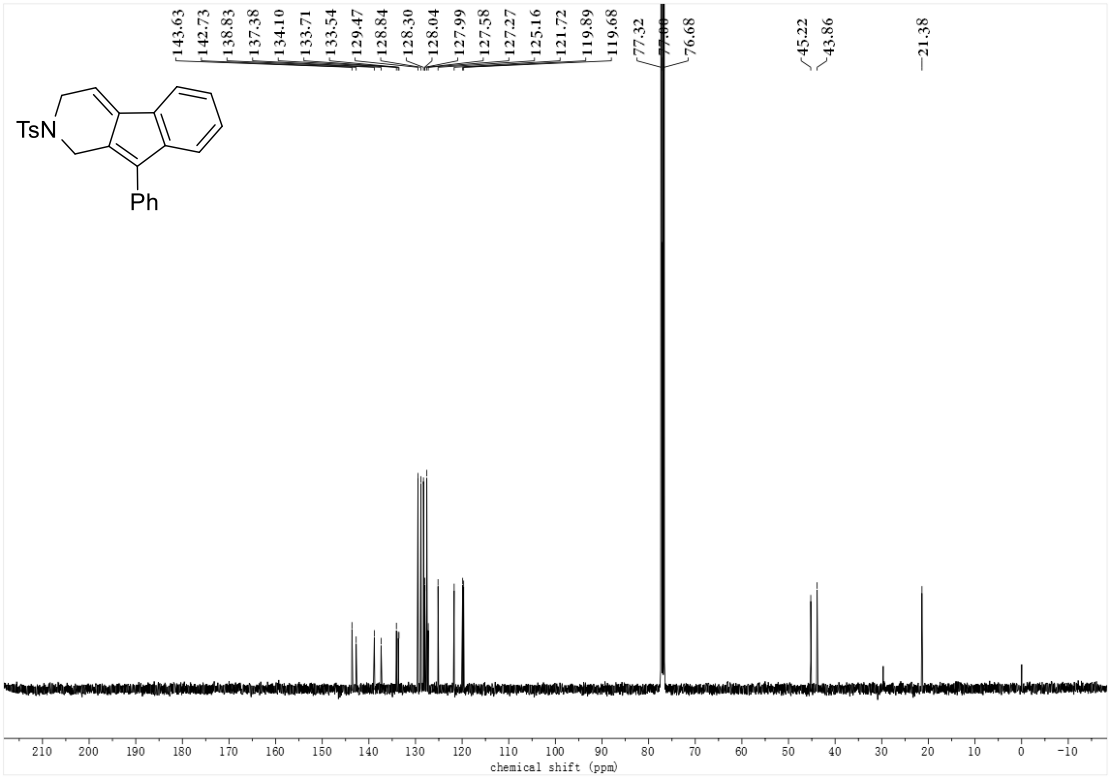
^{13}C NMR spectrum of compound **2h** ($CDCl_3$, 100MHz)



^{1}H NMR spectrum of compound **2i** ($CDCl_3$, 400MHz)



^{13}C NMR spectrum of compound **2i** ($CDCl_3$, 100MHz)



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