Supporting Information

Visible Light-Induced Photoredox-Catalyzed Assembly-Point Di/Trifunctionalization of Diazomethyl Radicals

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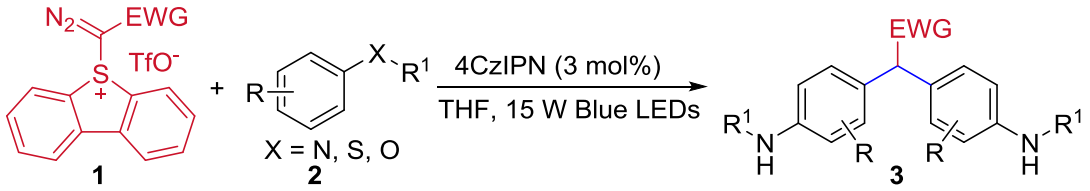
I. General Information

All reagents were commercial and were used without further purification. The substrates were prepared according to the previous method reported. Chromatography was carried on flash silica gel (300-400 mesh). All reactions were monitored by TLC, which was performed on percolated aluminum sheets of silica gel 60 (F254). Unless noted, the ^{1}H NMR spectra were recorded at 500 MHz, 600 MHz in $CDCl_3$, the ^{13}C NMR spectra were recorded at 151 MHz in $CDCl_3$ with TMS as internal standard, and the ^{19}F NMR spectra were recorded at 565MHz in $CDCl_3$. All coupling constants (*J* values) were reported in Hertz (Hz). High-resolution mass spectra (HRMS) were obtained using a Bruker micro TOF II focus spectrometer (ESI). The α-diazosulfonium triflates **1**[1] and ethene-1,1-diyldibenzene **7**[2] were prepared according to the reported literature procedures. All of the α-diazosulfonium triflates and ethene-1,1-diyldibenzene are known compounds. Compounds **2** and **5** are commercially available drugs from Energy Chemistry. The compound **6a** and **9e** were glued on glass fiber, respectively. Data were collected at 293 K on a Bruker SMART APEX II CCD diffractometer using graphite-monochromated Mo Kradiation (λ = 0.71073Å) and IP technique in the range $2.19° < \theta < 27.48°$. Empirical absorption correction was applied. The structures were solved by the direct method and refined by the full-matrix least-squares method on F2 using the SHELXS 97 crystallographic software package. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Hydrogen atoms were located from difference Fourier maps. Blue LEDs (15 W, λ = 465 nm) was purchased from Sigma-Aldrich (SynLED parallel photoreactor Z742680). Quartz tube (10 mL) was used as the irradiation vessel. Density functional theory (DFT) calculations were performed using the Gaussian 09 package[3] to calculate the structures and energies of complexes. All of the molecular structures were optimized at a theoretical level of (U)B3LYP-D3[4]/6-3lg(d,p)[5]. The calculations were carried out with the implicit universal solvation model based on Solute Electron Density (SMD)[6]. Frequency calculations were carried out at the same level to confirm all the optimized structures as minima (no imaginary frequency) or transition states (only one imaginary frequency), and provided the thermal relative Gibbs free energy correction. Marcus theory has been used to investigate the kinetics for the SET reaction pathway for radical and non-radical bimolecular reactions.[7]

II. Synthetic Procedures and Analytical Data of Compounds 3

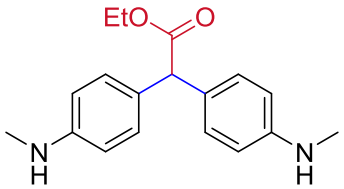


Substituted arenes **2a**-**r** (0.6 mmol, 3.0 equiv), α-diazosulfonium triflates **1** (0.2 mmol, 1.0 equiv), 4CzIPN (0.006 mmol, 3.0 mol%) and THF (2.0 mL) were added to a 10 mL Schlenk tube. The mixture was then stirred at room temperature under N_2 atmosphere and irradiated with 15 W blue LEDs for 24 h. After **1** were consumed (monitored by TLC), the reaction mixture was concentrated, and the residue was purified by silica gel column chromatography to give the desired product **3**.

A gram-scale synthesis of compound 3aa:

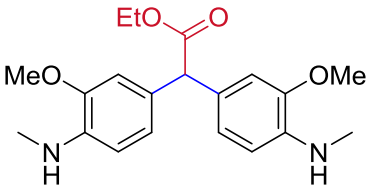
Substituted aniline **2a** (1.61 g, 15.0 mmol), α-diazosulfonium triflates **1a** (2.23 g, 5.0 mmol), 4CzIPN (0.12 g, 0.15 mmol) and THF (50 mL) were added to a round-bottomed flask. The mixture was then stirred at room temperature under N_2 atmosphere and irradiated with 15 W blue LEDs for 36 h. After **1** were consumed (monitored by TLC), the reaction mixture was concentrated, and the residue was purified by silica gel column chromatography (EA/PE = 3/10) to give the desired product **3aa** (0.97 g, 65%) as yellow oil.

Ethyl 2,2-bis(4-(methylamino)phenyl)acetate (3aa):



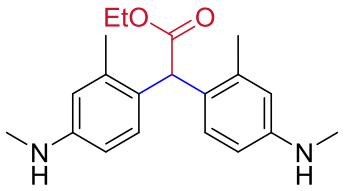
Following the general procedure, **3aa** was isolated by flash chromatography on silica (EA/PE = 3/10) as yellow oil (45.4 mg, 76% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.3 Hz, 4H), 6.45 (d, *J* = 8.6 Hz, 4H), 4.70 (s, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 2.71 (s, 6H), 1.14 (t, *J* = 7.2 Hz, 3H) ; ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.60, 148.24, 129.30, 128.21, 112.41, 60.79, 55.53, 30.80, 14.20; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{23}N_2O_2^+$ 299.1754; Found 299.1756. The NMR data are consistent with the reported values.[8]

Ethyl 2,2-bis(3-methoxy-4-(methylamino)phenyl)acetate (3ab):



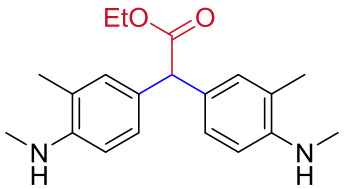
Following the general procedure, **3ab** was isolated by flash chromatography on silica (EA/PE = 3/10) as yellow oil (53.8 mg, 75% yield);^{1}H NMR (500 MHz, $CDCl_3$) δ 6.82 (dd, *J* = 8.1, 1.9 Hz, 2H), 6.74 (d, *J* = 1.9 Hz, 2H), 6.51 (d, *J* = 8.1 Hz, 2H), 4.83 (s, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 6H), 2.83 (s, 6H), 1.25 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.58, 146.83, 138.37, 127.32, 121.23, 109.76, 108.96, 60.78, 56.22, 55.43, 30.40, 14.24; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{27}N_2O_4^+$ 359.1965; Found 359.1974.

Ethyl 2,2-bis(2-methyl-4-(methylamino)phenyl)acetate (3ac):



Following the general procedure, **3ac** was isolated by flash chromatography on silica (EA/PE = 3/10) as yellow oil (46.4 mg, 71% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.89 (d, *J* = 8.3 Hz, 2H), 6.43 (d, *J* = 1.8 Hz, 2H), 6.39 (dd, *J* = 8.3, 2.7 Hz, 2H), 5.06 (s, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.80 (s, 6H), 2.17 (s, 6H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.88, 148.17, 137.13, 129.10, 126.12, 114.59, 109.99, 60.77, 49.62, 30.77, 19.80, 14.28; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{27}N_2O_2^+$ 327.2067; Found 327.2070.

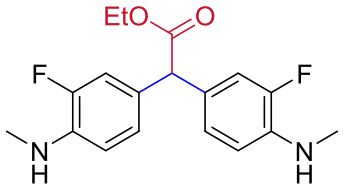
Ethyl 2,2-bis(3-methyl-4-(methylamino)phenyl)acetate (3ad):



Following the general procedure, **3ad** was isolated by flash chromatography on silica (EA/PE = 3/10) as yellow oil (42.4 mg, 65% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.4 Hz, 2H), 7.00 (s, 2H), 6.54 (d, *J* = 8.3 Hz, 2H), 4.78 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.54 (s, 2H), 2.86 (s, 6H), 2.08 (s, 6H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.75, 146.14, 130.13, 127.85, 127.08, 121.99, 109.12,

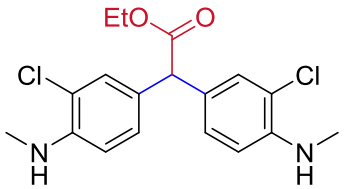
60.73, 55.60, 30.87, 17.50, 14.22; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{27}N_2O_2^+$ 327.2067; Found 327.2070.

Ethyl 2,2-bis(3-fluoro-4-(methylamino)phenyl)acetate (3ae):



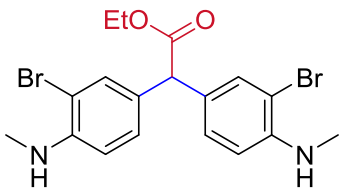
Following the general procedure, **3ae** was isolated by flash chromatography on silica (EA/PE = 3/10) as yellow oil (40.1 mg, 60% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.94 (s, 2H), 6.93 – 6.91 (m, 2H), 6.60 (t, *J* = 8.6 Hz, 2H), 4.76 (s, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 2H), 2.85 (s, 6H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.80, 151.36 (d, *J* = 239.1 Hz), 136.85 (d, *J* = 11.6 Hz), 127.30 (d, *J* = 6.3 Hz), 124.47 (d, *J* = 3.2 Hz), 114.45 (d, *J* = 19.6 Hz), 111.24 (d, *J* = 3.8 Hz), 61.09, 55.05, 30.26, 14.16. ^{19}F NMR (565 MHz, $CDCl_3$) δ -136.48; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{21}F_2N_2O_2^+$ 335.1566; Found 335.1565.

Ethyl 2,2-bis(3-chloro-4-(methylamino)phenyl)acetate (3af):



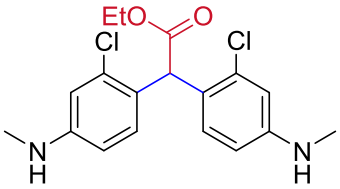
Following the general procedure, **3af** was isolated by flash chromatography on silica (EA/PE = 3/10) as yellow oil (42.6 mg, 58% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 2.1 Hz, 2H), 7.08 (dd, *J* = 8.4, 2.1 Hz, 2H), 6.58 (d, *J* = 8.4 Hz, 2H), 4.73 (s, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.87 (s, 6H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.73, 144.07, 128.92, 127.86, 127.68, 119.03, 110.56, 61.12, 54.81, 30.44, 14.16; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{21}Cl_2N_2O_2^+$ 367.0975; Found 367.0964.

Ethyl 2,2-bis(3-bromo-4-(methylamino)phenyl)acetate (3ag):



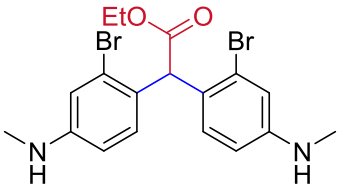
Following the general procedure, **3ag** was isolated by flash chromatography on silica (EA/PE = 3/10) as yellow oil (48.4 mg, 53% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 2.1 Hz, 2H), 7.13 (dd, *J* = 8.4, 2.1 Hz, 2H), 6.56 (d, *J* = 8.4 Hz, 2H), 4.72 (s, 1H), 4.31 (s, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.87 (s, 6H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.70, 145.05, 132.11, 128.54, 128.14, 110.57, 109.51, 61.13, 54.63, 30.63, 14.17; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{21}Br_2N_2O_2^+$ 454.9964; Found 454.9963.

Ethyl 2,2-bis(2-chloro-4-(methylamino)phenyl)acetate (3ah):



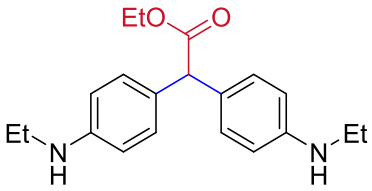
Following the general procedure, **3ah** was isolated by flash chromatography on silica (EA/PE = 3/10) as yellow oil (36.7 mg, 50% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.83 (d, *J* = 8.5 Hz, 2H), 6.58 (d, *J* = 2.4 Hz, 2H), 6.39 (dd, *J* = 8.5, 2.5 Hz, 2H), 5.49 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.74 (s, 6H), 1.18 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.69, 149.32, 135.15, 130.10, 123.98, 112.76, 111.17, 61.16, 50.03, 30.55, 14.19; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{21}Cl_2N_2O_2^+$ 367.0975; Found 367.0966.

Ethyl 2,2-bis(2-bromo-4-(methylamino)phenyl)acetate (3ai):



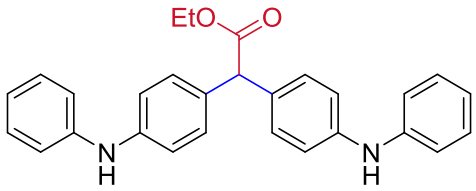
Following the general procedure, **3ai** was isolated by flash chromatography on silica (EA/PE = 3/10) as yellow oil (43.8 mg, 48% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.85 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 2.5 Hz, 2H), 6.47 (dd, *J* = 8.5, 2.5 Hz, 2H), 5.50 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 2H), 2.79 (s, 6H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.64, 149.35, 130.11, 126.02, 125.77, 116.08, 111.70, 61.19, 55.20, 30.54, 14.22; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{21}Br_2N_2O_2^+$ 454.9964; Found 454.9965.

Ethyl 2,2-bis(4-(ethylamino)phenyl)acetate (3aj):



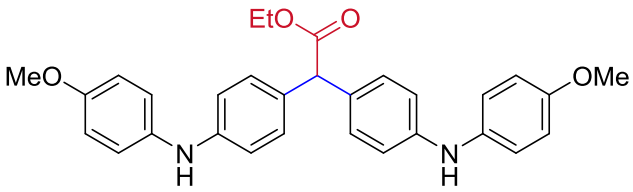
Following the general procedure, **3aj** was isolated by flash chromatography on silica (EA/PE = 3/10) as yellow oil (49.0 mg, 75% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.6 Hz, 4H), 6.53 (d, *J* = 8.5 Hz, 4H), 4.78 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.52 (s, 2H), 3.12 (q, *J* = 7.1 Hz, 4H), 1.24 – 1.21 (m, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.62, 147.36, 129.32, 128.10, 112.66, 60.78, 55.51, 38.53, 14.93, 14.21; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{26}N_2NaO_2^+$ 349.1886; Found 349.1893. The NMR data are consistent with the reported values.[8]

Ethyl 2,2-bis(4-(phenylamino)phenyl)acetate (3ak):



Following the general procedure, **3ak** was isolated by flash chromatography on silica (EA/PE = 3/10) as yellow oil (44.8 mg, 53% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.23 (m, 4H), 7.21 (d, *J* = 8.5 Hz, 4H), 7.05 (d, *J* = 7.5 Hz, 4H), 7.02 (d, *J* = 8.5 Hz, 4H), 6.91 (t, *J* = 7.4 Hz, 2H), 5.68 (s, 2H), 4.88 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 1.31 – 1.18 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.07, 142.99, 142.20, 131.52, 129.45, 129.34, 121.04, 117.89, 117.70, 61.10, 55.80, 14.22; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{27}N_2O_2^+$ 423.2067; Found 423.2059. The NMR data are consistent with the reported values.[8]

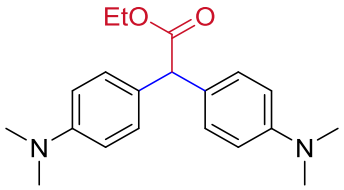
Ethyl 2,2-bis(4-((4-methoxyphenyl)amino)phenyl)acetate (3al):



Following the general procedure, **3al** was isolated by flash chromatography on silica (EA/PE = 3/10) as yellow oil (51.2 mg, 53% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.6 Hz, 4H), 6.97 (d, *J* = 8.9 Hz, 4H), 6.78 (d, *J* = 2.1 Hz, 4H), 6.76 (d, *J* = 2.3 Hz, 4H), 5.40 (s, 2H), 4.76 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.71 (s, 6H), 1.18 (t,

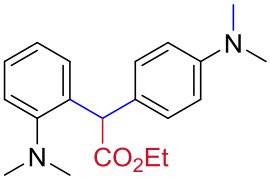
J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.24, 155.27, 144.14, 135.68, 130.27, 129.39, 122.14, 115.62, 114.67, 60.97, 55.67, 55.59, 14.20; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{30}N_2NaO_4^+$ 505.2098; Found 505.2090.

Ethyl 2,2-bis(4-(dimethylamino)phenyl)acetate (3am-I):



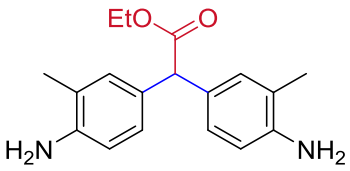
Following the general procedure, **3am-I** was isolated by flash chromatography on silica (EA/PE = 1/5) as yellow oil (25.5 mg, 39% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.5 Hz, 4H), 6.68 (d, *J* = 8.6 Hz, 4H), 4.83 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.91 (s, 12H), 1.24 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.58, 149.60, 129.13, 127.50, 112.63, 60.77, 55.35, 40.64, 14.22; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{27}N_2O_2^+$ 327.2067; Found 327.2076. The NMR data are consistent with the reported values.[8]

Ethyl 2-(2-(dimethylamino)phenyl)-2-(4-(dimethylamino)phenyl)acetate (3am-II):



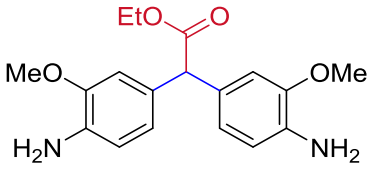
Following the general procedure, **3am-II** was isolated by flash chromatography on silica (EA/PE = 1/5) as yellow oil (22.9 mg, 35% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 – 7.20 (m, 4H), 7.11 (d, *J* = 7.7 Hz, 1H), 7.03 (t, *J* = 6.5 Hz, 1H), 6.71 (d, *J* = 8.7 Hz, 2H), 5.36 (s, 1H), 4.27 – 4.16 (m, 1H), 4.13 – 4.07 (m, 1H), 2.93 (s, 6H), 2.63 (s, 6H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.78, 152.70, 149.62, 136.33, 129.76, 129.49, 127.76, 126.31, 124.25, 120.82, 112.63, 60.54, 50.94, 45.18, 40.60, 14.32; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{27}N_2O_2^+$ 327.2067; Found 327.2076.

Ethyl 2,2-bis(4-amino-3-methylphenyl)acetate (3an):



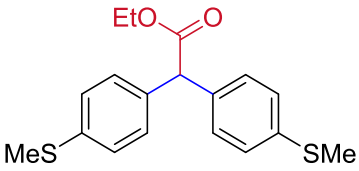
Following the general procedure, **3an** was isolated by flash chromatography on silica (EA/PE = 1/5) as yellow oil (43.6 mg, 73% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 – 6.87 (m, 4H), 6.60 (d, *J* = 7.9 Hz, 2H), 4.76 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.54 (s, 4H), 2.12 (s, 6H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.57, 143.50, 130.54, 129.48, 126.96, 122.37, 114.96, 60.84, 55.61, 17.49, 14.21; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{23}N_2O_2^+$ 299.1754; Found 299.1754. The NMR data are consistent with the reported values.[8]

Ethyl 2,2-bis(4-amino-3-methoxyphenyl)acetate (3ao):



Following the general procedure, **3ao** was isolated by flash chromatography on silica (EA/PE = 1/5) as yellow oil (50.2 mg, 76% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.76 (d, *J* = 1.8 Hz, 2H), 6.71 (d, *J* = 8.2 Hz, 2H), 6.64 (d, *J* = 8.0 Hz, 2H), 4.81 (s, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 6H), 3.74 (s, 4H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.37, 147.24, 135.13, 129.39, 121.04, 114.70, 110.81, 60.90, 56.24, 55.46, 14.23; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{23}N_2O_4^+$ 331.1652; Found 331.1652. The NMR data are consistent with the reported values.[8]

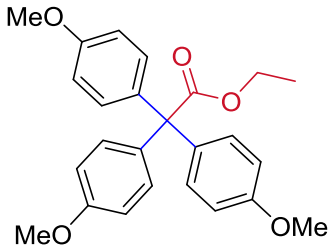
Ethyl 2,2-bis(4-(methylthio)phenyl)acetate (3ap):



Following the general procedure, **3ap** was isolated by flash chromatography on silica (EA/PE = 1/10) as yellow oil (34.6 mg, 52% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (d, *J* = 2.3 Hz, 8H), 4.81 (s, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.36 (s, 6H), 1.15 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.31, 137.51, 135.54, 128.98, 126.77,

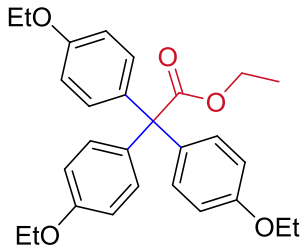
61.28, 56.05, 15.83, 14.15; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{20}NaO_2S_2^+$ 355.0797; Found 355.0790.

Ethyl 2,2,2-tris(4-methoxyphenyl)acetate (3aq):



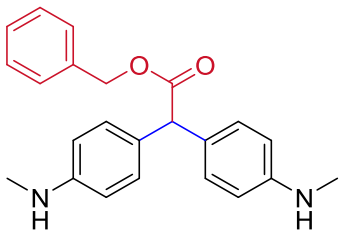
Following the general procedure, **3aq** was isolated by flash chromatography on silica (EA/PE = 1/10) as yellow oil (66.7 mg, 82% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.97 (d, *J* = 8.9 Hz, 6H), 6.71 (d, *J* = 8.9 Hz, 6H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.70 (s, 9H), 1.12 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.16, 158.21, 135.68, 131.28, 112.91, 65.44, 61.56, 55.20, 14.02; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{26}NaO_5^+$ 429.1672; Found 429.1673.

Ethyl 2,2,2-tris(4-ethoxyphenyl)acetate (3ar):



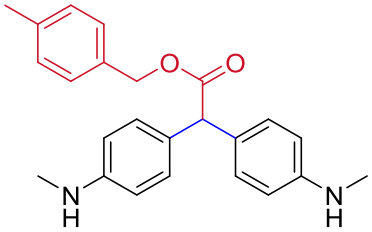
Following the general procedure, **3ar** was isolated by flash chromatography on silica (EA/PE = 1/10) as yellow oil (69.1 mg, 77% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.9 Hz, 6H), 6.77 (d, *J* = 8.9 Hz, 6H), 4.26 (q, *J* = 7.1 Hz, 2H), 4.01 (q, *J* = 7.0 Hz, 6H), 1.39 (t, *J* = 7.0 Hz, 9H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.70, 143.47, 142.28, 138.84, 129.66, 128.11, 128.07, 127.68, 127.48, 127.14, 124.93, 61.00, 47.06, 14.22; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{32}NaO_5^+$ 471.2142; Found 471.2131.

Benzyl 2,2-bis(4-(methylamino)phenyl)acetate (3ba):



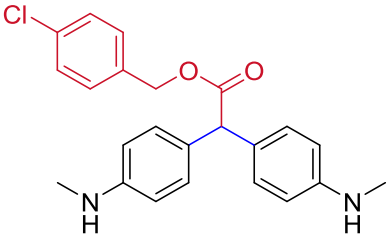
Following the general procedure, **3ba** was isolated by flash chromatography on silica (EA/PE = 3/10) as yellow oil (50.5 mg, 70% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 5H), 7.10 (d, *J* = 8.5 Hz, 4H), 6.53 (d, *J* = 8.5 Hz, 4H), 5.15 (s, 2H), 4.87 (s, 1H), 3.66 (s, 2H), 2.80 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.44, 148.30, 136.07, 129.34, 128.44, 128.10, 128.02, 127.97, 112.39, 66.54, 55.44, 30.80; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{24}N_2NaO_2^+$ 383.1730; Found 383.1733.

4-Methylbenzyl 2,2-bis(4-(methylamino)phenyl)acetate (3ca)



Following the general procedure, **3ca** was isolated by flash chromatography on silica (EA/PE = 3/10) as yellow oil (50.9 mg, 68% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 7.8 Hz, 2H), 7.13 – 7.09 (m, 6H), 6.53 (d, *J* = 8.6 Hz, 4H), 5.11 (s, 2H), 4.85 (s, 1H), 3.65 (s, 2H), 2.80 (s, 6H), 2.33 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.48, 148.27, 137.83, 133.04, 129.34, 129.12, 128.26, 128.04, 112.38, 66.53, 55.43, 30.81, 21.21; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{26}N_2NaO_2^+$ 397.1886; Found 397.1893.

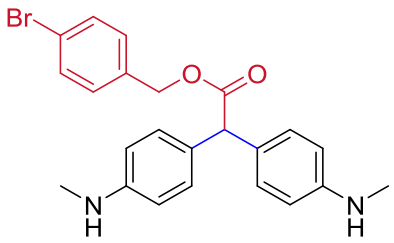
4-Chlorobenzyl 2,2-bis(4-(methylamino)phenyl)acetate (3da):



Following the general procedure, **3da** was isolated by flash chromatography on silica (EA/PE = 3/10) as yellow oil (53.7 mg, 68% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 4H), 6.53 (d, *J* = 8.5 Hz, 4H), 5.10 (s, 2H), 4.85 (s, 1H), 3.67 (s, 2H), 2.80 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.29, 147.31, 133.57, 132.84, 128.43, 128.28, 127.57, 126.71,

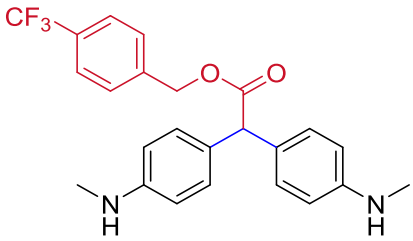
111.35, 64.62, 54.39, 29.75; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{23}ClN_2NaO_2^+$ 417.1340; Found 417.1330.

4-Bromobenzyl 2,2-bis(4-(methylamino)phenyl)acetate (3ea):



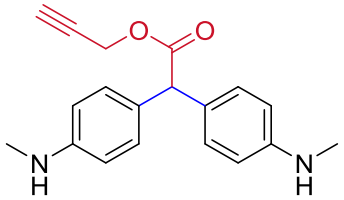
Following the general procedure, **3ea** was isolated by flash chromatography on silica (EA/PE = 3/10) as yellow oil (58.9 mg, 67% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.6 Hz, 4H), 6.53 (d, *J* = 8.5 Hz, 4H), 5.09 (s, 2H), 4.85 (s, 1H), 3.70 (s, 2H), 2.80 (s, 6H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.28, 147.31, 134.09, 130.53, 128.71, 128.28, 126.69, 120.99, 111.35, 64.64, 54.38, 29.75; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{24}BrN_2O_2^+$ 439.1016; Found 439.1011.

4-(Trifluoromethyl)benzyl 2,2-bis(4-(methylamino)phenyl)acetate (3fa):



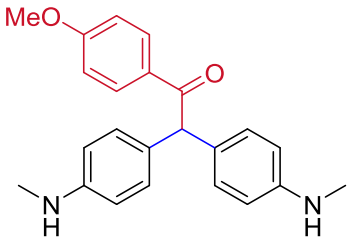
Following the general procedure, **3fa** was isolated by flash chromatography on silica (EA/PE = 3/10) as yellow oil (53.1 mg, 62% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 4H), 6.54 (d, *J* = 8.5 Hz, 4H), 5.19 (s, 2H), 4.88 (s, 1H), 3.68 (s, 2H), 2.80 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.25, 148.39, 140.10, 129.31, 127.95, 127.58, 125.39 (q, *J* = 3.5 Hz), 112.39, 65.47, 55.42, 30.76. ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.59; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{24}F_3N_2O_2^+$ 429.1784; Found 429.1789.

Prop-2-yn-1-yl 2,2-bis(4-(methylamino)phenyl)acetate (3ga):



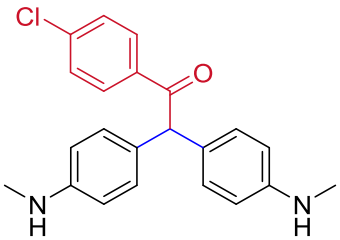
Following the general procedure, **3ga** was isolated by flash chromatography on silica (EA/PE = 3/10) as yellow oil (46.3 mg, 75% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (d, *J* = 8.5 Hz, 4H), 6.48 (d, *J* = 8.6 Hz, 4H), 4.79 (s, 1H), 4.64 (d, *J* = 2.4 Hz, 2H), 3.62 (s, 2H), 2.74 (s, 6H), 2.37 (t, *J* = 2.5 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.75, 147.35, 128.27, 126.49, 111.37, 76.69, 73.86, 54.04, 51.27, 29.74; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{21}N_2O_2^+$ 309.1598; Found 309.1589.

1-(4-Methoxyphenyl)-2,2-bis(4-(methylamino)phenyl)ethan-1-one (3ha):



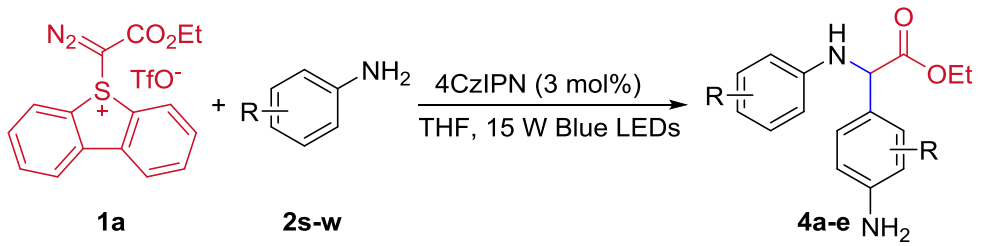
Following the general procedure, **3ha** was isolated by flash chromatography on silica (EA/PE = 3/10) as yellow oil (46.9 mg, 65% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.9 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 4H), 6.85 (d, *J* = 8.9 Hz, 2H), 6.54 (d, *J* = 8.5 Hz, 4H), 5.77 (s, 1H), 3.81 (s, 3H), 3.67 (s, 2H), 2.79 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.92, 163.04, 148.11, 131.22, 130.23, 129.83, 128.76, 113.61, 112.58, 57.56, 55.41, 30.80; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{25}N_2O_2^+$ 361.1911; Found 361.1913.

1-(4-Chlorophenyl)-2,2-bis(4-(methylamino)phenyl)ethan-1-one (3ia):



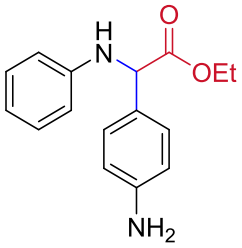
Following the general procedure, **3ia** was isolated by flash chromatography on silica (EA/PE = 3/10) as yellow oil (43.1 mg, 59% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.04 (d, *J* = 8.5 Hz, 4H), 6.55 (d, *J* = 8.5 Hz, 4H), 5.74 (s, 1H), 2.80 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.17, 148.27, 138.93, 135.53, 130.36, 129.81, 128.74, 127.97, 112.63, 58.05, 30.74; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{22}ClN_2O^+$ 365.1415; Found 365.1415.

Ⅲ. Synthetic Procedures and Analytical Data of Compounds 4



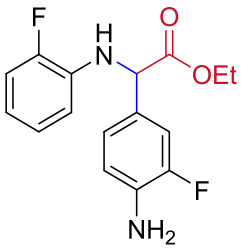
Substituted anilines **2s-w** (0.6 mmol, 3.0 equiv), α-diazosulfonium triflates **1a** (0.2 mmol, 1.0 equiv), 4CzIPN (0.006 mmol, 3.0 mol%) and THF (2.0 mL) were added to a 10 mL Schlenk tube. The mixture was then stirred at room temperature under N_2 atmosphere and irradiated with 15 W blue LEDs for 18 h. After **1** were consumed (monitored by TLC), the reaction mixture was concentrated, and the residue was purified by silica gel column chromatography to give the desired product **4**.

Ethyl 2-(4-aminophenyl)-2-(phenylamino)acetate (4a):



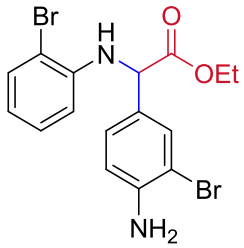
Following the general procedure, **4a** was isolated by flash chromatography on silica (EA/PE = 1/5) as yellow oil (41.1 mg, 76% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.3 Hz, 2H), 7.12 (t, *J* = 7.7 Hz, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 8.2 Hz, 2H), 6.56 (d, *J* = 7.9 Hz, 2H), 4.94 (s, 1H), 4.83 (s, 1H), 4.27 – 4.16 (m, 1H), 4.15 – 4.09 (m, 1H), 3.67 (s, 2H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.34, 146.40, 146.22, 129.18, 128.26, 127.35, 117.87, 115.30, 113.38, 61.59, 60.28, 14.11; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{19}N_2O_2^+$ 271.1441; Found 271.1441. The NMR data are consistent with the reported values.[8]

Ethyl 2-(4-amino-3-fluorophenyl)-2-((2-fluorophenyl)amino)acetate (4b):



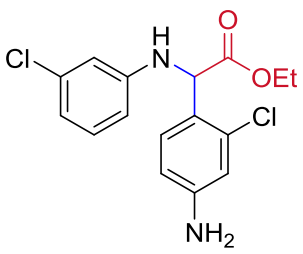
Following the general procedure, **4b** was isolated by flash chromatography on silica (EA/PE = 1/5) as yellow oil (31.9 mg, 52% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (d, *J* = 11.7 Hz, 1H), 7.06 (d, *J* = 8.2 Hz, 1H), 7.02 – 6.93 (m, 1H), 6.85 (t, *J* = 7.7 Hz, 1H), 6.73 (t, *J* = 8.6 Hz, 1H), 6.66 – 6.56 (m, 1H), 6.42 (t, *J* = 8.2 Hz, 1H), 5.13 (s, 1H), 4.93 (d, *J* = 5.9 Hz, 1H), 4.26 – 4.21 (m, 1H), 4.18 – 4.13 (m, 1H), 3.73 (s, 2H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.35, 152.39 (d, *J* = 239.8 Hz), 150.81 (d, *J* = 240.1 Hz), 134.60 (d, *J* = 13.0 Hz), 134.42 (d, *J* = 11.5 Hz), 127.69 (d, *J* = 5.7 Hz), 124.41 (d, *J* = 3.6 Hz), 123.22 (d, *J* = 3.3 Hz), 117.56 (d, *J* = 6.9 Hz), 116.92 (d, *J* = 3.9 Hz), 114.62 (d, *J* = 18.3 Hz), 114.08 (d, *J* = 19.7 Hz), 112.98 (d, *J* = 3.0 Hz), 61.90, 59.69, 14.06. ^{19}F NMR (565 MHz, $CDCl_3$) δ -134.27, -135.46; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{17}F_2N_2O_2^+$ 307.1253; Found 307.1251.

Ethyl 2-(4-amino-3-bromophenyl)-2-((2-bromophenyl)amino)acetate (4c):



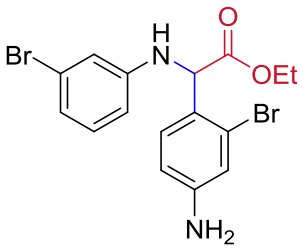
Following the general procedure, **4c** was isolated by flash chromatography on silica (EA/PE = 1/5) as yellow oil (49.7 mg, 58% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.20 (d, *J* = 8.3 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 8.3 Hz, 1H), 6.56 (t, *J* = 7.5 Hz, 1H), 6.35 (d, *J* = 8.0 Hz, 1H), 5.65 (d, *J* = 5.6 Hz, 1H), 4.91 (d, *J* = 5.5 Hz, 1H), 4.27 – 4.21 (m, 1H), 4.19 – 4.13 (m, 1H), 4.11 (s, 2H), 1.23 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.13, 144.16, 142.85, 132.50, 131.22, 128.34, 127.96, 127.07, 118.56, 115.84, 112.23, 110.11, 109.38, 62.04, 59.71, 14.07; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{16}Br_2N_2NaO_2^+$ 448.9471; Found 448.9467.

Ethyl 2-(4-amino-2-chlorophenyl)-2-((3-chlorophenyl)amino)acetate (4d):



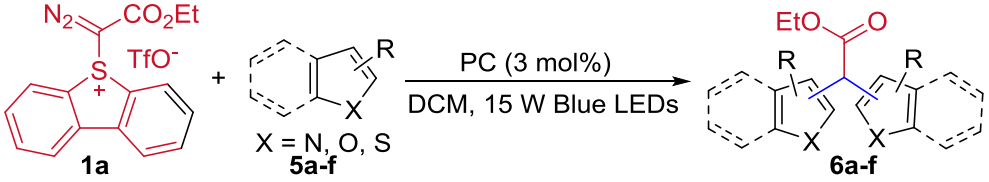
Following the general procedure, **4d** was isolated by flash chromatography on silica (EA/PE = 1/5) as yellow oil (46.8 mg, 69% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.4 Hz, 1H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 2.4 Hz, 1H), 6.64 (d, *J* = 7.7 Hz, 1H), 6.55 (s, 1H), 6.51 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.41 (d, *J* = 8.0 Hz, 1H), 5.40 (d, *J* = 5.5 Hz, 1H), 5.02 (d, *J* = 6.0 Hz, 1H), 4.26 – 4.19 (m, 1H), 4.16 – 4.10 (m, 1H), 3.75 (s, 2H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.55, 147.38, 146.97, 134.88, 134.70, 130.18, 128.75, 124.39, 117.93, 115.65, 114.20, 113.32, 111.50, 61.94, 56.34, 14.02; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{17}Cl_2N_2O_2^+$ 339.0662; Found 339.0667.

Ethyl 2-(4-amino-2-bromophenyl)-2-((3-bromophenyl)amino)acetate (4e):



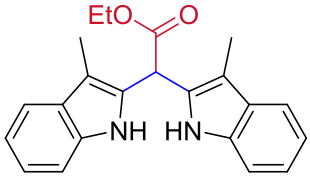
Following the general procedure, **4e** was isolated by flash chromatography on silica (EA/PE = 1/5) as yellow oil (53.9 mg, 63% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.4 Hz, 1H), 6.95 (t, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 2.4 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 6.73 (s, 1H), 6.55 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.44 (d, *J* = 8.2 Hz, 1H), 5.38 (d, *J* = 5.6 Hz, 1H), 5.03 (d, *J* = 5.9 Hz, 1H), 4.26 – 4.19 (m, 1H), 4.1– 4.10 (m, 1H), 3.73 (s, 2H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.51, 147.49, 147.08, 130.48, 128.71, 125.94, 124.99, 123.10, 120.83, 118.88, 116.35, 114.79, 111.95, 61.96, 58.65, 14.02; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{16}Br_2N_2NaO_2^+$ 448.9471; Found 448.9475.

IV. Synthetic Procedures and Analytical Data of Compounds 6



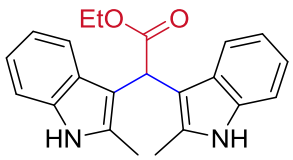
Substituted heteroarenes **5a-f** (0.6 mmol, 3.0 equiv), α-diazosulfonium triflates **1a** (0.2 mmol, 1.0 equiv), PC (0.006 mmol, 3.0 mol%) and DCM (2.0 mL) were added to a 10 mL Schlenk tube. The mixture was then stirred at room temperature under N_2 atmosphere and irradiated with 15 W blue LEDs for 24 h. After **1** were consumed (monitored by TLC), the reaction mixture was concentrated, and the residue was purified by silica gel column chromatography to give the desired product **6**.

Ethyl 2,2-bis(3-methyl-1*H*-indol-2-yl)acetate (6a):



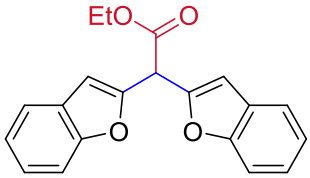
Following the general procedure, **6a** was isolated by flash chromatography on silica (EA/PE = 3/10) as yellow solid (47.8 mg, 69% yield); mp 150.5-151.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (s, 2H), 7.51 (d, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 2H), 5.53 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.29 (s, 6H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.54, 135.50, 128.94, 128.45, 122.20, 119.54, 118.67, 111.05, 109.23, 62.16, 40.50, 14.13, 8.51; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{23}N_2O_2^+$ 347.1754; Found 347.1761.

Ethyl 2,2-bis(2-methyl-1*H*-indol-3-yl)acetate (6b):



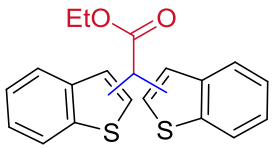
Following the general procedure, **6b** was isolated by flash chromatography on silica (EA/PE = 3/10) as yellow solid (41.6 mg, 60% yield); mp 178.0-178.8 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (s, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.07 (t, *J* = 7.5 Hz, 2H), 6.97 (t, *J* = 7.5 Hz, 2H), 5.45 (s, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.18 (s, 6H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.51, 133.83, 131.13, 127.32, 119.86, 118.38, 117.74, 109.10, 107.73, 59.98, 39.12, 13.24, 11.34; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{22}N_2NaO_2^+$ 369.1573; Found 369.1564.

Ethyl 2,2-di(benzofuran-2-yl)acetate (6c):



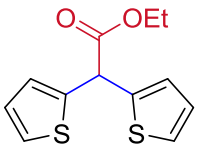
Following the general procedure, **6c** was isolated by flash chromatography on silica (EA/PE = 1/10) as colorless oil (43.6 mg, 68% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 2H), 6.76 (s, 2H), 5.39 (s, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.68, 155.00, 151.40, 128.17, 124.40, 122.95, 121.10, 111.30, 105.65, 62.32, 46.41, 14.08; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{17}O_4^+$ 321.1121; Found 321.1116.

Ethyl 2,2-bis(benzo[*b*]thiophen-2(3)-yl)acetate (6d):



Following the general procedure, **6d** was isolated by flash chromatography on silica (EA/PE = 1/10) as colorless oil (41.6 mg, 59% yield, 1:0.6 (2:3)); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 – 7.72 (m, 4H), 7.71 – 7.56 (m, 1H), 7.39 – 7.32 (m, 4H), 7.29 (dt, *J* = 18.5, 7.3 Hz, 1H), 5.66 (d, *J* = 34.7 Hz, 1H), 4.33 – 4.17 (m, 2H), 1.28 (dt, *J* = 11.7, 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.12, 170.55, 140.64, 140.50, 140.35, 139.90, 139.41, 137.93, 137.69, 131.76, 131.58, 125.16, 125.13, 124.63, 124.58, 124.35, 124.32, 123.52, 123.27, 122.99, 122.97, 122.18, 121.65, 121.61, 61.95, 61.69, 47.14, 45.43, 14.22, 14.15; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{16}NaO_2S_2^+$ 375.0484; Found 375.0481.

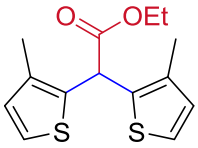
Ethyl 2,2-di(thiophen-2-yl)acetate (6e):



Following the general procedure, **6e** was isolated by flash chromatography on silica (EA/PE = 1/10) as colorless oil (21.7 mg, 43% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17 (dd, *J* = 5.2, 1.2 Hz, 2H), 6.97 (dd, *J* = 2.7, 1.8 Hz, 2H), 6.88 (dd, *J* = 5.1, 3.5 Hz, 2H), 5.38 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151

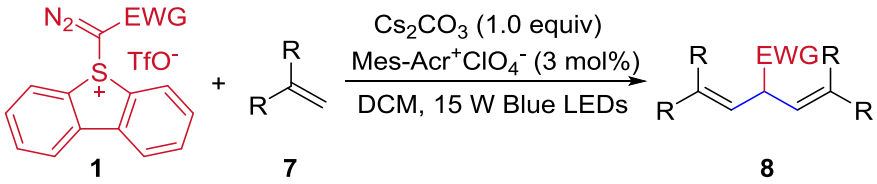
MHz, $CDCl_3$) δ 170.69, 140.77, 126.62, 126.27, 125.42, 61.90, 47.70, 14.06; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{12}NaO_2S_2^+$ 275.0171; Found 275.0169.

Ethyl 2,2-bis(3-methylthiophen-2-yl)acetate (6f):



Following the general procedure, **6f** was isolated by flash chromatography on silica (EA/PE = 1/10) as colorless oil (22.4 mg, 40% yield); ^1H NMR (500 MHz, $CDCl_3$) δ 7.14 (d, *J* = 5.1 Hz, 2H), 6.79 (d, *J* = 5.2 Hz, 2H), 5.43 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.20 (s, 6H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.97, 134.63, 134.41, 129.66, 123.77, 61.76, 44.47, 14.12, 13.99; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{16}NaO_2S_2^+$ 303.0484; Found 303.0484.

Ⅴ. Synthetic Procedures and Analytical Data of Compounds 8

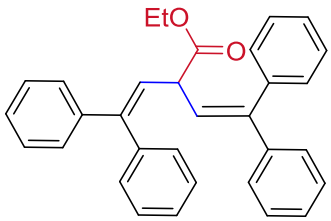


Substituted alkenes **7** (0.6 mmol, 3.0 equiv), α-diazosulfonium triflates **1** (0.2 mmol, 1.0 equiv), Mes-Acr^{+}ClO$_4^{-}$ (0.006 mmol, 3.0 mol%), Cs_2CO_3 (0.2 mmol, 1.0 equiv) and DCM (2.0 mL) were added to a 10 mL Schlenk tube. The mixture was then stirred at room temperature under N_2 atmosphere and irradiated with 15 W blue LEDs for 18 h. After **1** were consumed (monitored by TLC), the reaction mixture was concentrated, and the residue was purified by silica gel column chromatography to give the desired product **8**.

A gram-scale synthesis of compound 8a:

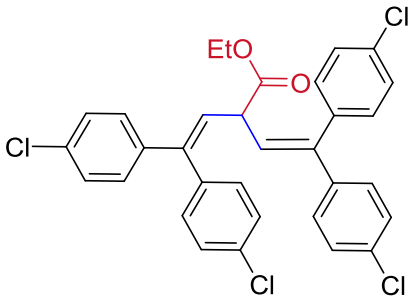
Substituted ethene-1,1-diyldibenzene **7a** (2.70 g, 15.0 mmol), α-diazosulfonium triflates **1a** (2.23 g, 5.0 mmol), Mes-Acr^{+}ClO$_4^{-}$ (0.09 g, 0.15 mmol), Cs_2CO_3 (1.63 g, 5.0 mmol) and DCM (50 mL) were added to a round-bottomed flask. The mixture was then stirred at room temperature under N_2 atmosphere and irradiated with 15 W blue LEDs for 36 h. After **1** were consumed (monitored by TLC), the reaction mixture was concentrated, and the residue was purified by silica gel column chromatography (EA/PE = 1/10) to give the desired product **8a** (1.56 g, 70%) as colorless oil.

Ethyl 2-(2,2-diphenylvinyl)-4,4-diphenylbut-3-enoate (8a):



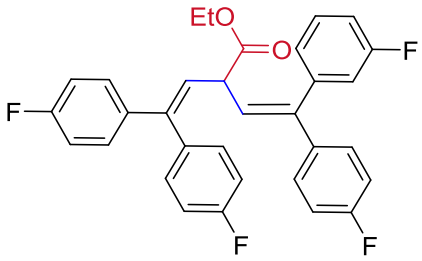
Following the general procedure, **8a** was isolated by flash chromatography on silica (EA/PE = 1/10) as colorless oil (64.0 mg, 72% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 9H), 7.23 – 7.18 (m, 3H), 7.15 (t, *J* = 7.4 Hz, 4H), 6.97 (d, *J* = 7.1 Hz, 4H), 6.20 (d, *J* = 10.1 Hz, 2H), 4.20 (t, *J* = 10.0 Hz, 1H), 4.16 (q, *J* = 7.0 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.70, 143.46, 142.27, 138.82, 129.65, 128.10, 128.05, 127.67, 127.46, 127.12, 124.91, 60.99, 47.05, 14.20; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{28}NaO_2^+$ 467.1982; Found 467.1981. The NMR data are consistent with the reported values.[9]

Ethyl 2-(2,2-bis(4-chlorophenyl)vinyl)-4,4-bis(4-chlorophenyl)but-3-enoate (8b):



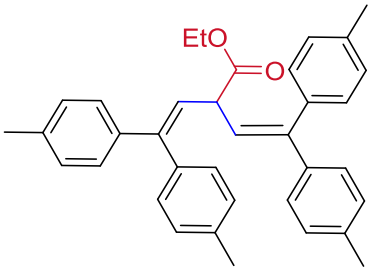
Following the general procedure, **8b** was isolated by flash chromatography on silica (EA/PE = 1/10) as colorless oil (96.7 mg, 83% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.5 Hz, 4H), 7.16 (d, *J* = 8.4 Hz, 4H), 7.10 (d, *J* = 8.6 Hz, 4H), 6.84 (d, *J* = 8.4 Hz, 4H), 6.14 (d, *J* = 10.1 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 4.07 (t, *J* = 10.2 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.03, 141.69, 139.86, 136.60, 133.80, 133.76, 130.79, 128.79, 128.50, 128.43, 125.07, 61.41, 47.05, 14.22; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{24}Cl_4NaO_2^+$ 603.0423; Found 603.0429.

Ethyl 2-(2,2-bis(4-fluorophenyl)vinyl)-4-(3-fluorophenyl)-4-(4-fluorophenyl)but-3-enoate (8c):



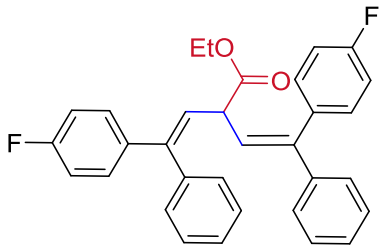
Following the general procedure, **8c** was isolated by flash chromatography on silica (EA/PE = 1/10) as colorless oil (90.9 mg, 88% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (dd, *J* = 8.8, 5.4 Hz, 4H), 6.95 (t, *J* = 8.7 Hz, 4H), 6.91 (dd, *J* = 8.5, 5.8 Hz, 4H), 6.87 (t, *J* = 8.7 Hz, 4H), 6.11 (d, *J* = 10.2 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 4.09 (t, *J* = 10.2 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.36, 163.12 (d, *J* = 247.8 Hz), 161.48 (d, *J* = 247.3 Hz), 141.69, 137.93 (d, *J* = 3.4 Hz), 134.48 (d, *J* = 3.4 Hz), 131.21 (d, *J* = 7.9 Hz), 129.19 (d, *J* = 8.1 Hz), 124.65, 115.19 (d, *J* = 7.5 Hz), 115.05 (d, *J* = 7.6 Hz), 61.26, 47.09, 14.21. ^{19}F NMR (565 MHz, $CDCl_3$) δ -114.34, -114.49; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{24}F_4NaO_2^+$ 539.1605; Found 539.1596.

Ethyl 2-(2,2-di-*p*-tolylvinyl)-4,4-di-p-tolylbut-3-enoate (8d):



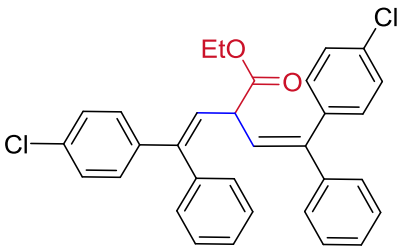
Following the general procedure, **8d** was isolated by flash chromatography on silica (EA/PE = 1/10) as colorless oil (68.1 mg, 68% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.1 Hz, 4H), 7.06 (d, *J* = 8.0 Hz, 4H), 6.93 (d, *J* = 7.7 Hz, 4H), 6.83 (d, *J* = 7.7 Hz, 4H), 6.10 (d, *J* = 10.1 Hz, 2H), 4.17 (t, *J* = 10.0 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.32 (d, *J* = 6.6 Hz, 12H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.03, 143.03, 139.74, 137.17, 136.45, 136.11, 129.60, 128.77, 128.61, 127.60, 124.10, 60.88, 47.11, 21.25, 21.10, 14.23; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{36}H_{36}NaO_2^+$ 523.2608; Found 523.2615.

Ethyl 4-(4-fluorophenyl)-2-(2-(4-fluorophenyl)-2-phenylvinyl)-4-phenylbut-3-enoate (8e):



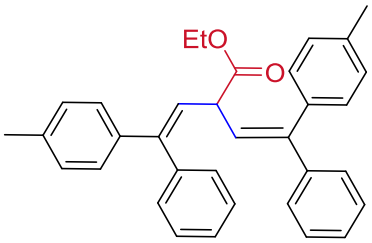
Following the general procedure, **8e** was isolated by flash chromatography on silica (EA/PE = 1/10) as colorless oil (75.0 mg, 78% yield, *E/Z:E/E:Z/Z* = 22:60:18 (determined by ^{1}H NMR)); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 3H), 7.21 – 7.12 (m, 7H), 6.96 – 6.90 (m, 6H), 6.89 – 6.85 (m, 1H), 6.80 (t, *J* = 8.7 Hz, 1H), 6.14 (ddd, *J* =10.5, 10.5, 10.0 Hz, 2H), 4.22 – 4.07 (m, 3H), 1.29 – 1.25 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.61, 172.53, 172.45, 163.21 (d, *J* = 247.3 Hz), 162.87 (d, *J* = 246.7 Hz), 162.78 (d, *J* = 246.3 Hz), 142.57, 142.55, 141.89 (d, *J* = 11.7 Hz), 138.63, 138.62, 138.34 (d, *J* = 3.3 Hz), 138.24 (d, *J* = 3.1 Hz), 134.67, 134.65, 131.32, 131.29, 131.27, 131.23, 129.54, 129.29, 129.23, 128.21, 128.19, 128.16, 127.70, 127.67, 127.58, 127.42, 127.31, 125.06, 124.93, 124.63, 124.44, 115.09 (d, *J* = 21.4 Hz), 115.07 (d, *J* = 21.3 Hz), 115.05 (d, *J* = 21.4 Hz), 115.03 (d, *J* = 21.3 Hz), 61.18, 61.13, 61.07, 47.16, 47.08, 46.98, 14.21, 14.20. ^{19}F NMR (565 MHz, $CDCl_3$) δ -114.75, -114.97, -115.12; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{26}F_2NaO_2^+$ 503.1793; Found 503.1793.

Ethyl 4-(4-chlorophenyl)-2-(2-(4-chlorophenyl)-2-phenylvinyl)-4-phenylbut-3-enoate (8f):



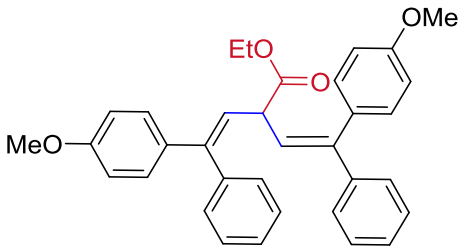
Following the general procedure, **8f** was isolated by flash chromatography on silica (EA/PE = 1/10) as colorless oil (75.0 mg, 73% yield, *E/Z:E/E:Z/Z* = 23:62:15 (determined by ^{1}H NMR)); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 4H), 7.24 – 7.20 (m, 3H), 7.20 – 7.17 (m, 2H), 7.16 – 7.15 (m, 1H), 7.13 (d, *J* = 8.5 Hz, 3H), 7.08 (d, *J* = 8.4 Hz, 1H), 6.92 (d, *J* = 7.9 Hz, 2H), 6.86 (t, *J* = 8.6 Hz, 2H), 6.16 (ddd, *J* = 10.0, 10.5, 10.0 Hz, 2H), 4.25 – 4.01 (m, 3H), 1.38 – 1.17 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.41, 172.38, 172.33, 142.61, 142.56, 142.54, 141.55, 141.50, 140.65, 140.52, 138.29, 138.26, 137.16, 133.46, 133.44, 133.16, 130.91, 129.53, 129.51, 128.92, 128.90, 128.34, 128.33, 128.28, 128.26, 128.24, 128.20, 127.79, 127.77, 127.55, 127.49, 127.41, 125.04, 124.93, 124.84, 61.25, 61.20, 61.15, 47.11, 47.07, 46.99, 14.22, 14.19; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{26}Cl_2NaO_2^+$ 535.1202; Found 535.1202.

Ethyl 4-phenyl-2-(2-phenyl-2-(*p*-tolyl)vinyl)-4-(*p*-tolyl)but-3-enoate (8g):



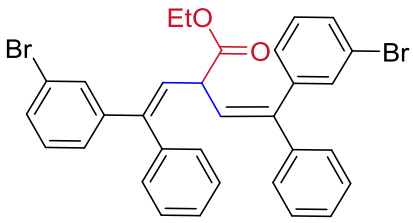
Following the general procedure, **8g** was isolated by flash chromatography on silica (EA/PE = 1/10) as colorless oil (61.4 mg, 65% yield, *E/Z:E/E:Z/Z* = 25:55:20 (determined by ^{1}H NMR)); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.21 (m, 5H), 7.15 – 7.11 (m, 3H), 7.10 – 7.04 (m, 4H), 6.94 (d, *J* = 8.0 Hz, 4H), 6.84 (dd, *J* = 8.0, 8.0 Hz, 2H), 6.14 (dt, *J* = 10.5, 10.0 Hz, 2H), 4.27 – 4.06 (m, 3H), 2.33 (d, *J* = 6.8 Hz, 6H), 1.28 – 1.24 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.86, 143.34, 143.31, 143.17, 142.49, 142.45, 139.52, 139.01, 137.26, 136.64, 136.56, 135.92, 135.87, 129.69, 129.65, 129.58, 129.52, 129.12, 128.80, 128.75, 128.65, 128.05, 128.00, 127.93, 127.71, 127.67, 127.55, 127.37, 127.02, 126.86, 124.80, 124.76, 124.24, 124.18, 60.94, 60.92, 47.16, 47.06, 46.98, 21.24, 21.22, 21.09, 14.21; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{32}NaO_2^+$ 495.2295; Found 495.2287.

Ethyl 4-(4-methoxyphenyl)-2-(2-(4-methoxyphenyl)-2-phenylvinyl)-4-phenylbut-3-enoate (8h):



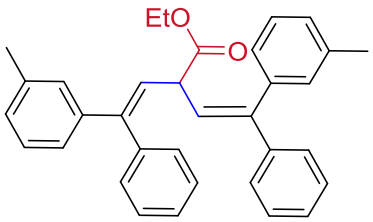
Following the general procedure, **8h** was isolated by flash chromatography on silica (EA/PE = 1/10) as colorless oil (53.5 mg, 53% yield, *E/Z:E/E:Z/Z* = 31:53:16 (determined by ^{1}H NMR)); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.26 (m, 2H), 7.25 – 7.24 (m, 2H), 7.23 – 7.22 (m, 3H), 7.20 – 7.17 (m, 1H), 7.16 – 7.13 (m, 2H), 6.99 – 6.84 (m, 4H), 6.82 – 6.61 (m, 4H), 6.27 – 6.00 (m, 2H), 4.35 – 4.03 (m, 3H), 3.79 (d, *J* = 7.1 Hz, 6H), 1.35 – 1.19 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.93, 172.90, 159.16, 158.67, 158.65, 142.94, 142.91, 142.74, 142.65, 139.16, 134.96, 131.23, 130.90, 130.83, 129.71, 128.80, 128.05, 127.99, 127.78, 127.75, 127.40, 127.38, 126.98, 124.77, 124.62, 123.36, 113.48, 113.44, 113.38, 60.97, 60.92, 55.29, 55.18, 55.05, 47.22, 47.09, 14.24, 14.22, 14.12; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{32}NaO_4^+$ 527.2193; Found 527.2192.

Ethyl 4-(3-bromophenyl)-2-(2-(3-bromophenyl)-2-phenylvinyl)-4-phenylbut-3-enoate (8i):



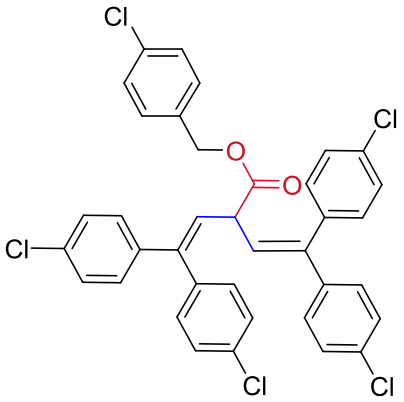
Following the general procedure, **8i** was isolated by flash chromatography on silica (EA/PE = 1/10) as colorless oil (87.9 mg, 73% yield, *E/Z:E/E:Z/Z* = 23:56:21 (determined by ^{1}H NMR)); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 3H), 7.27 (d, *J* = 7.0 Hz, 3H), 7.23 – 7.16 (m, 4H), 7.16 – 7.08 (m, 4H), 7.06 – 6.96 (m, 1H), 6.93 – 6.85 (m, 3H), 6.17 (ddd, *J* = 10.0, 10.0, 10.0 Hz, 2H), 4.23 – 4.15 (m, 2H), 4.15 – 4.02 (m, 1H), 1.33 – 1.25 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.32, 172.28, 172.25, 144.34, 144.14, 142.61, 142.54, 142.49, 142.42, 141.31, 141.20, 140.89, 140.84, 137.99, 137.95, 132.47, 132.34, 130.53, 130.49, 130.42, 130.38, 129.64, 129.62, 129.51, 129.35, 128.31, 128.29, 128.27, 128.19, 127.84, 127.61, 127.56, 127.51, 126.43, 126.34, 125.75, 125.69, 125.29, 125.24, 122.43, 122.42, 122.26, 61.35, 61.29, 61.23, 60.41, 47.05, 46.97, 31.61, 29.73, 22.68, 21.08, 14.25, 14.23, 14.21, 14.15; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{32}H_{26}Br_2NaO_2^+$ 623.0192; Found 623.0191.

Ethyl 4-phenyl-2-(2-phenyl-2-(*m*-tolyl)vinyl)-4-(*m*-tolyl)but-3-enoate (8j):



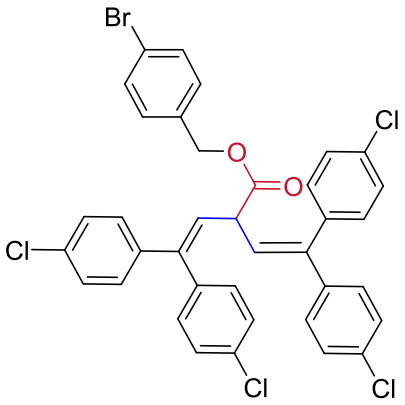
Following the general procedure, **8j** was isolated by flash chromatography on silica (EA/PE = 1/10) as colorless oil (59.6 mg, 63% yield, *E/Z:E/E:Z/Z* = 30:48:22 (determined by ^{1}H NMR)); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 – 7.20 (m, 5H), 7.19 – 7.16 (m, 1H), 7.15 – 7.10 (m, 3H), 7.07 – 7.04 (m, 2H), 7.04 – 6.97 (m, 3H), 6.95 (d, *J* = 7.0 Hz, 1H), 6.92 (d, *J* = 6.9 Hz, 1H), 6.80 (d, *J* = 13.8 Hz, 1H), 6.75 (dd, *J* = 16.8, 16.8 Hz, 1H), 6.16 (dd, *J* = 10.2, 10.2 Hz, 2H), 4.24 – 4.09 (m, 3H), 2.29 (s, 3H), 2.23 (d, *J* = 7.2 Hz, 3H), 1.28 – 1.25 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.92, 172.85, 172.78, 143.64, 143.59, 143.52, 143.48, 142.35, 142.33, 142.26, 138.93, 138.80, 138.78, 137.67, 137.66, 137.46, 137.38, 130.26, 130.18, 129.65, 129.58, 128.27, 128.24, 128.23, 128.21, 128.07, 128.01, 127.98, 127.96, 127.94, 127.90, 127.82, 127.64, 127.61, 127.39, 127.37, 127.06, 126.99, 126.79, 126.73, 124.96, 124.91, 124.88, 60.96, 60.93, 60.91, 47.02 (2C), 47.00, 21.43, 21.42, 21.40, 14.21; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{32}NaO_2^+$ 495.2295; Found 495.2296.

4-Chlorobenzyl 2-(2,2-bis(4-chlorophenyl)vinyl)-4,4-bis(4-chlorophenyl)but-3-en oate (8k):



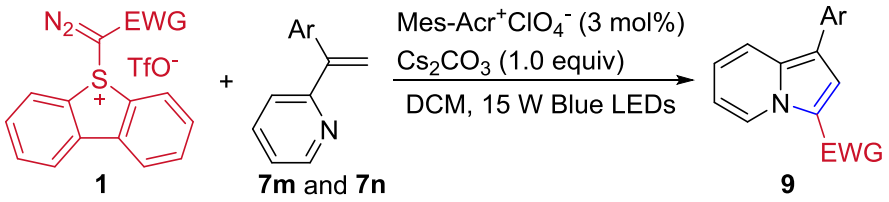
Following the general procedure, **8k** was isolated by flash chromatography on silica (EA/PE = 1/10) as colorless oil (81.5 mg, 60% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.4 Hz, 2H), 7.23 (dd, *J* = 8.4, 6.2 Hz, 6H), 7.12 (d, *J* = 8.3 Hz, 4H), 7.07 (d, *J* = 8.5 Hz, 4H), 6.78 (d, *J* = 8.3 Hz, 4H), 6.11 (d, *J* = 10.1 Hz, 2H), 5.11 (s, 2H), 4.11 (t, *J* = 10.1 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.72, 142.10, 139.67, 136.49, 134.39, 134.05, 133.92, 133.83, 130.71, 129.49, 128.86, 128.76, 128.54, 128.47, 124.59, 66.16, 47.00; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{37}H_{26}Cl_5O_2^+$ 677.0370; Found 677.0363.

4-Bromobenzyl 2-(2,2-bis(4-chlorophenyl)vinyl)-4,4-bis(4-chlorophenyl)but-3-en oate (8l):



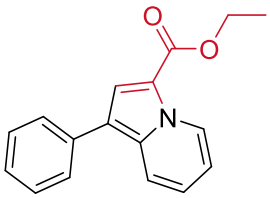
Following the general procedure, **8l** was isolated by flash chromatography on silica (EA/PE = 1/10) as colorless oil (96.9 mg, 67% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 4H), 7.17 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 4H), 7.07 (d, *J* = 8.6 Hz, 4H), 6.78 (d, *J* = 8.4 Hz, 4H), 6.11 (d, *J* = 10.1 Hz, 2H), 5.09 (s, 2H), 4.11 (t, *J* = 10.2 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.70, 142.11, 139.66, 136.49, 134.56, 133.92, 133.84, 131.82, 130.71, 129.76, 128.76, 128.54, 128.47, 124.57, 122.52, 66.19, 46.99; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{37}H_{26}BrCl_4O_2^+$ 720.9865; Found 720.9863.

Ⅵ. Synthetic Procedures and Analytical Data of Compounds 9



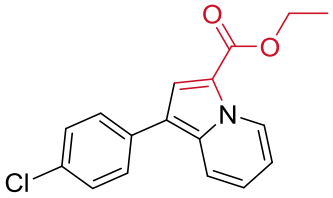
Substituted 2-(1-arylvinyl)pyridines **7** (0.3mmol, 1.5 equiv), α-diazosulfonium triflates **1** (0.2 mmol, 1.0 equiv), Mes-Acr^{+}ClO$_4^{-}$ (0.006 mmol, 3.0 mol%), Cs_2CO_3 (0.2 mmol, 1.0 equiv) and DCM (2.0 mL) were added to a 10 mL Schlenk tube. The mixture was then stirred at room temperature under N_2 atmosphere and irradiated with 15 W blue LEDs for 18 h. After **1** were consumed (monitored by TLC), the reaction mixture was concentrated, and the residue was purified by silica gel column chromatography to give the desired product **9**.

Ethyl-1-phenylindolizine-3-carboxylate (9a):



Following the general procedure, **9a** was isolated by flash chromatography on silica (EA/PE = 1/10) as white solid (37.7 mg, 71% yield); mp 89.0-89.6 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.48 (d, *J* = 7.2 Hz, 1H), 7.82 (d, *J* = 9.1 Hz, 1H), 7.67 (s, 1H), 7.58 (d, *J* = 7.7 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.11 – 7.03 (m, 1H), 6.83 (t, *J* = 6.9 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.43, 135.15, 134.78, 128.82, 127.89, 127.59, 126.23, 122.30, 120.68, 117.79, 116.31, 113.98, 113.05, 59.88, 14.61; HRMS (ESI) m/z: [M + H]$^{+}$ Calcd for $C_{17}H_{16}NO_2^{+}$ 266.1176; Found 266.1177. The NMR data are consistent with the reported values.[10]

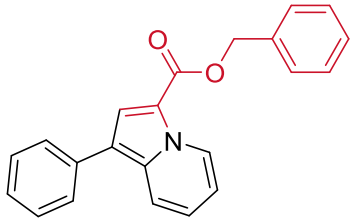
Ethyl 1-(4-chlorophenyl)indolizine-3-carboxylate (9b):



Following the general procedure, **9b** was isolated by flash chromatography on silica (EA/PE = 1/10) as white solid (43.8 mg, 73% yield); mp 93.4-94.8 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.41 (d, *J* = 7.1 Hz, 1H), 7.68 (d, *J* = 9.0 Hz, 1H), 7.56 (s, 1H), 7.43

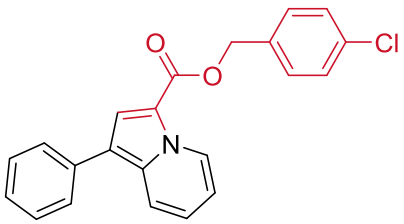
(d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.01 (ddd, *J* = 9.0, 6.6, 1.1 Hz, 1H), 6.77 (t, *J* = 6.9 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.33, 134.65, 133.64, 131.95, 129.00, 128.97, 127.66, 122.61, 120.57, 117.50, 114.97, 114.14, 113.18, 59.97, 14.61; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{14}ClNNaO_2^+$ 322.0605; Found 322.0610. The NMR data are consistent with the reported values.[10]

Benzyl-1-phenylindolizine-3-carboxylate (9c):



Following the general procedure, **9c** was isolated by flash chromatography on silica (EA/PE = 1/10) as white solid (21.0 mg, 32% yield); mp 90.0-90.8 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.43 (d, *J* = 7.1 Hz, 1H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.64 (s, 1H), 7.51 (d, *J* = 7.1 Hz, 2H), 7.41 (d, *J* = 7.0 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 15.4 Hz, 1H), 6.79 (t, *J* = 6.9 Hz, 1H), 5.33 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.09, 136.64, 135.02, 128.83, 128.58, 128.08, 128.00, 127.90, 127.65, 126.31, 122.56, 120.97, 117.83, 116.52, 113.58, 113.20, 65.52; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{18}NO_2^+$ 328.1332; Found 328.1332.

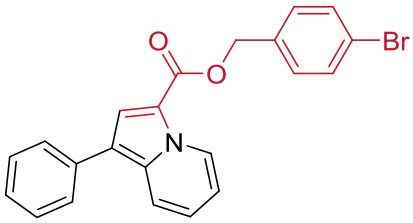
4-Chlorobenzyl 1-phenylindolizine-3-carboxylate (9d):



Following the general procedure, **9d** was isolated by flash chromatography on silica (EA/PE = 1/10) as white solid (49.2 mg, 68% yield); mp 92.3-92.9 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.40 (d, *J* = 7.1 Hz, 1H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.62 (s, 1H), 7.50 (d, *J* = 6.8 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.02 (ddd, *J* = 9.0, 6.6, 1.2 Hz, 1H), 6.79 (t, *J* = 6.9 Hz, 1H), 5.28 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.91, 135.17, 134.94, 133.95, 129.40, 128.86, 128.77, 127.90, 127.63, 126.38, 122.72, 120.97, 117.86, 116.62,

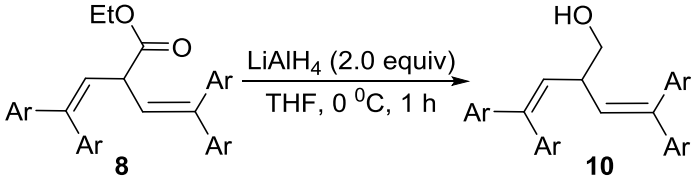
113.32, 64.70; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{17}ClNO_2^+$ 362.0942; Found 362.0938.

4-Bromobenzyl 1-phenylindolizine-3-carboxylate (9e):



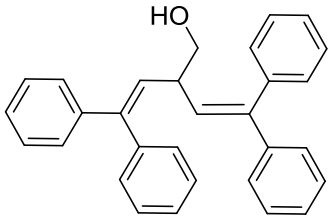
Following the general procedure, **9e** was isolated by flash chromatography on silica (EA/PE = 1/10) as white solid (52.8 mg, 65% yield); mp 98.2-98.8 ^oC; ^1H NMR (600 MHz, $CDCl_3$) δ 9.40 (d, *J* = 7.2 Hz, 1H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.62 (s, 1H), 7.50 (d, *J* = 7.1 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.05 – 6.97 (m, 1H), 6.79 (t, *J* = 6.8 Hz, 1H), 5.26 (s, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.70, 142.11, 139.66, 136.49, 134.56, 133.92, 133.84, 131.82, 130.71, 129.76, 128.76, 128.54, 128.47, 124.57, 122.52, 66.19, 46.99; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{17}BrNO_2^+$ 406.0437; Found 406.0435.

VII. Synthetic Procedures and Analytical Data of Compounds 10



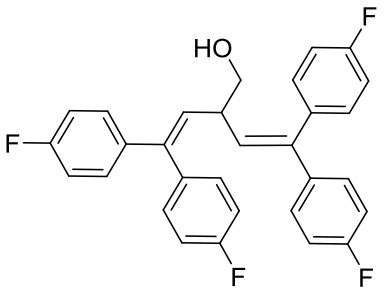
A 10 mL Schlenk tube was charged with **8** (0.2 mmol, 1.0 equiv), THF (1.0 mL) and a stir bar under N_2, then a solution of $LiAlH_4$ (0.4 mmol, 2.0 equiv) was added at 0 ^oC. The mixture was stirred for 1 h. Then the resulting mixture was quenched by H_2O, extracted with DCM (20 mL × 3), dried with anhydrous Na_2SO_4, concentrated in vacuo, and purified by silica column chromatography (EA/PE = 1/5) to give **10**.

2-(2,2-Diphenylvinyl)-4,4-diphenylbut-3-en-1-ol (10a):



Following the general procedure, **10a** was isolated by flash chromatography on silica (EA/PE = 1/5) as colorless oil (76.5 mg, 95% yield); ^1H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.20 (m, 12H), 7.16 (t, *J* = 7.4 Hz, 4H), 6.96 (d, *J* = 7.3 Hz, 4H), 5.97 (d, *J* = 9.8 Hz, 2H), 3.62 (d, *J* = 6.9 Hz, 2H), 3.60 – 3.52 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.86, 142.46, 139.33, 129.61, 128.17, 128.13, 127.61, 127.42, 127.34, 127.00, 66.46, 43.05; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{30}H_{27}O^+$ 403.2056; Found 403.2055.

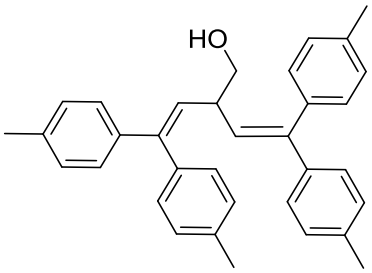
2-(2,2-Bis(4-fluorophenyl)vinyl)-4,4-bis(4-fluorophenyl)but-3-en-1-ol (10c):



Following the general procedure, **10c** was isolated by flash chromatography on silica (EA/PE = 1/5) as colorless oil (88.3 mg, 93% yield); ^1H NMR (500 MHz, $CDCl_3$) δ 7.14 (dd, *J* = 8.7, 5.5 Hz, 4H), 6.94 (t, *J* = 8.7 Hz, 4H), 6.91 – 6.84 (m, 8H), 5.87 (d, *J*

= 10.1 Hz, 2H), 3.64 (d, *J* = 5.6 Hz, 2H), 3.49 – 3.42 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.35 (d, *J* = 247.187 Hz), 162.01 (d, *J* = 247.187 Hz), 141.90, 138.23 (d, *J* = 3.0 Hz), 134.98 (d, *J* = 3.5 Hz), 131.14 (d, *J* = 8.0 Hz), 128.95 (d, *J* = 7.8 Hz), 127.44, 115.19 (d, *J* = 14.3 Hz), 115.05 (d, *J* = 14.5 Hz), 66.27, 43.02. ^{19}F NMR (565 MHz, $CDCl_3$) δ -114.65, -114.80; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{30}H_{23}F_4O^+$ 475.1680; Found 475.1688.

2-(2,2-Di-*p*-tolylvinyl)-4,4-di-*p*-tolylbut-3-en-1-ol (10d):



Following the general procedure, **10d** was isolated by flash chromatography on silica (EA/PE = 1/5) as colorless oil (85.3 mg, 93% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.1 Hz, 4H), 7.06 (d, *J* = 8.0 Hz, 4H), 6.95 (d, *J* = 7.7 Hz, 4H), 6.83 (d, *J* = 7.7 Hz, 4H), 5.87 (d, *J* = 9.7 Hz, 2H), 3.59 (d, *J* = 7.0 Hz, 2H), 3.57 – 3.48 (m, 1H), 2.33 (d, *J* = 14.4 Hz, 12H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.56, 139.86, 137.04, 136.58, 136.34, 129.51, 128.79, 128.73, 127.32, 126.68, 66.51, 43.06, 21.24, 21.09; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{34}H_{35}O^+$ 459.2682; Found 459.2678.

VIII. The Crystal Structure of Compounds 6a and 9e

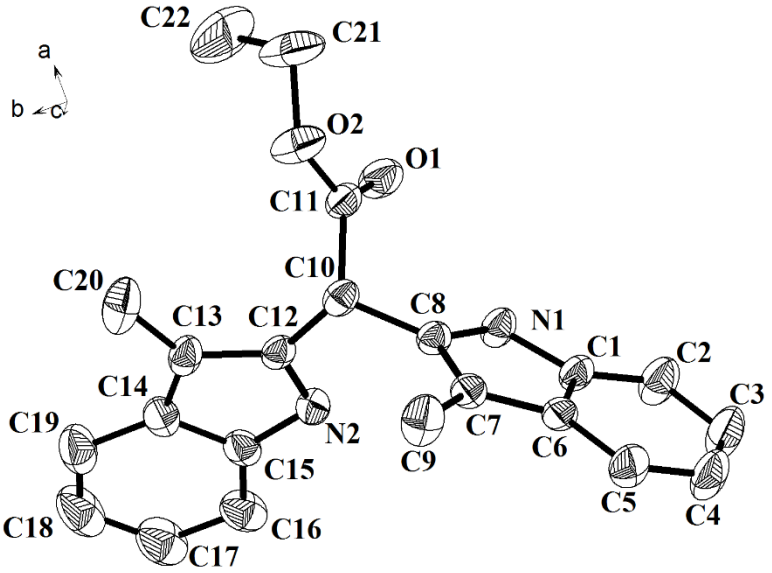


Figure 1. The ORTEP drawing of crystal. Method of Crystallization: The **6a** was recrystallized from mixed solvents of ethyl acetate and petroleum ether at 25 ˚C.

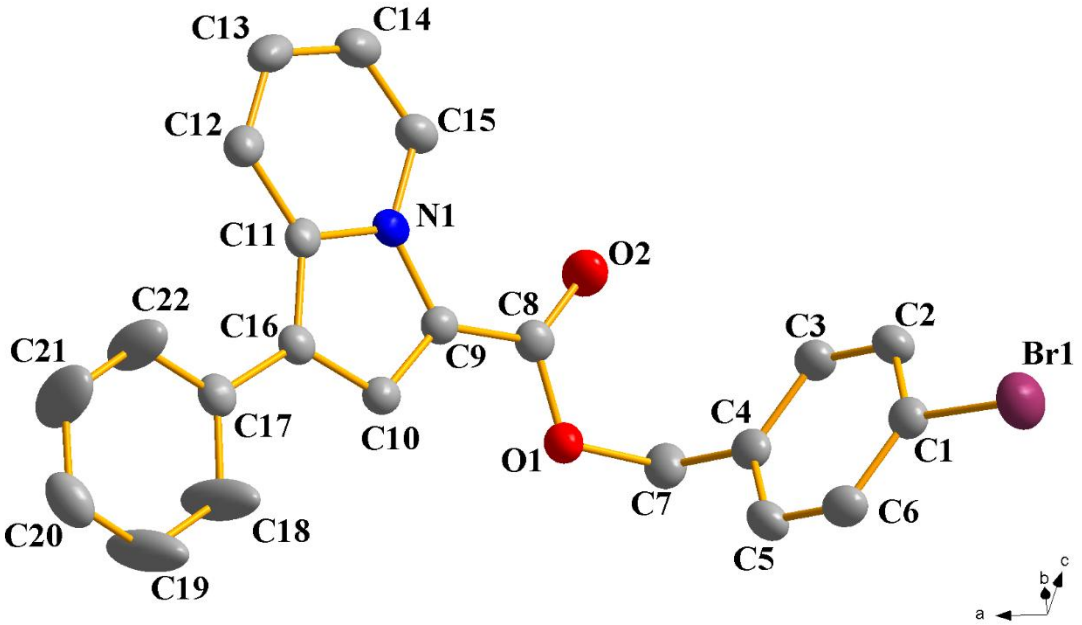


Figure 2. The ORTEP drawing of crystal. Method of Crystallization: The **9e** was recrystallized from mixed solvents of ethyl acetate and petroleum ether at 25 ˚C.

IX. Stern Volmer Analysis

Fluorescence quenching experiments were performed on Fluorescence quenching experiments were performed on Edinburgh FLS920P010404 Fluorescence Spectrometer. All solutions were irradiated at 400 nm and the emission intensity at 552 nm was observed. Stern-Volmer analysis on the quenching of fluorescence lifetime was carried out in MeCN (5 mL) with detection at 552 nm, where the concentration of 4CzIPN was 0.00005 M. The emission spectrums of 4CzIPN with varying the quencher of α-diazosulfonium triflate **1a** and *N*-methylaniline **2a** were determined with quencher concentrations in the range of 0 mM to 50 mM, respectively. Stern-Volmer plots were constructed according to the Stern-Volmer equation.

Table 1. Stern-Volmer raw data.

entry	4CzIPN concentration (M)	**1a** concentration (M)	I (cd)	I_0/I
1	0.000050	0	845.008	1.000
2	0.000050	0.01	357.410	2.364
3	0.000050	0.02	187.633	4.504
4	0.000050	0.03	132.887	6.359
5	0.000050	0.04	85.097	9.930
6	0.000050	0.05	58.739	14.386

entry	4CzIPN concentration (M)	**2a** concentration (M)	I (cd)	I_0/I
1	0.000050	0	845.008	1.000
2	0.000050	0.01	537.590	1.572
3	0.000050	0.02	427.358	1.977
4	0.000050	0.03	371.325	2.275
5	0.000050	0.04	325.387	2.597
6	0.000050	0.05	267.575	3.158

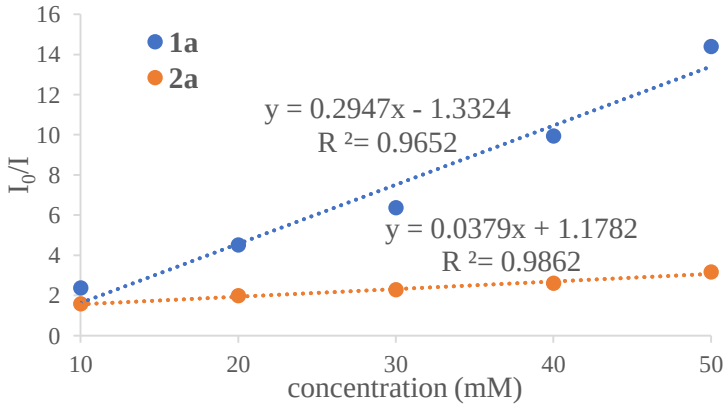


Figure 3. Stern-Volmer plots of 4CzIPN quenching with varying the quencher concentrations of **1a** and **2a** in the range of 10 mM to 50 mM.

X. References

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XI. Computational Details (Cartesian Coordinates of Optimized Structures)

1a

S	-0.14093000	0.00668300	-1.14181000
C	-1.32870800	-1.22436900	-0.57573600
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C	-2.31726700	0.84792900	0.12115600
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C	-2.90662400	3.12948900	0.61988100
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H	-2.89750600	-1.70017000	-0.72251900

2a

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TS1

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XII. Copies of ^{1}H NMR and ^{13}C NMR Spectra

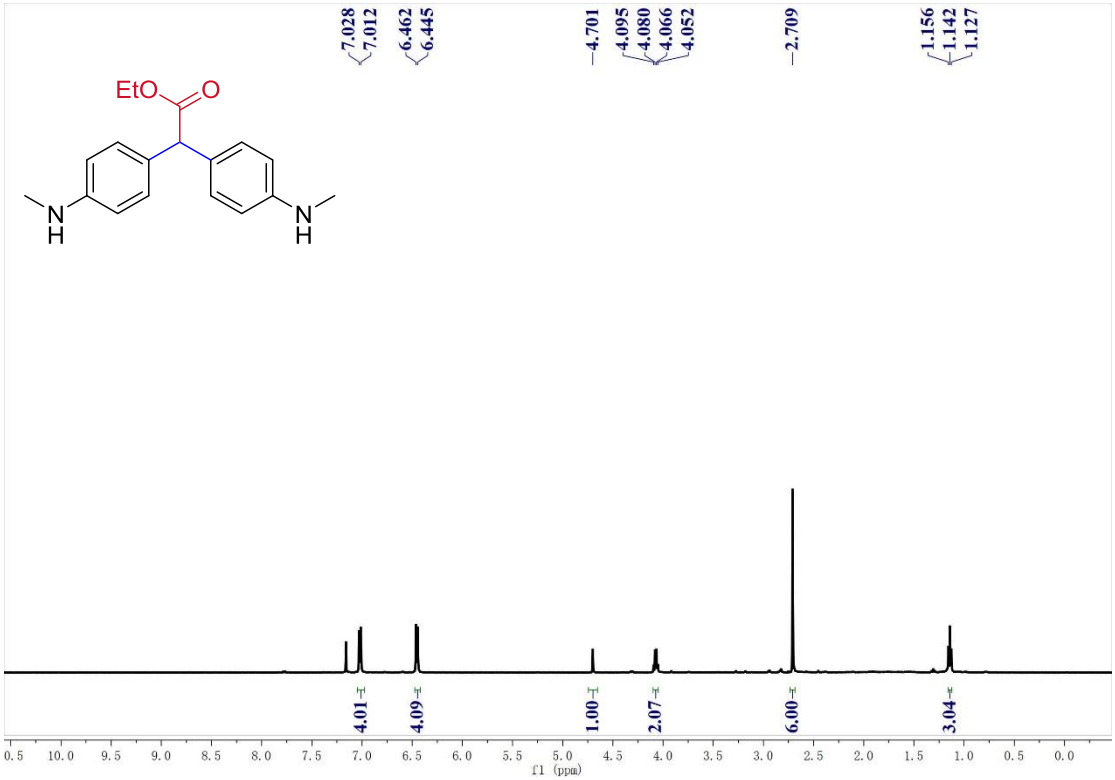

Figure 4. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3aa**

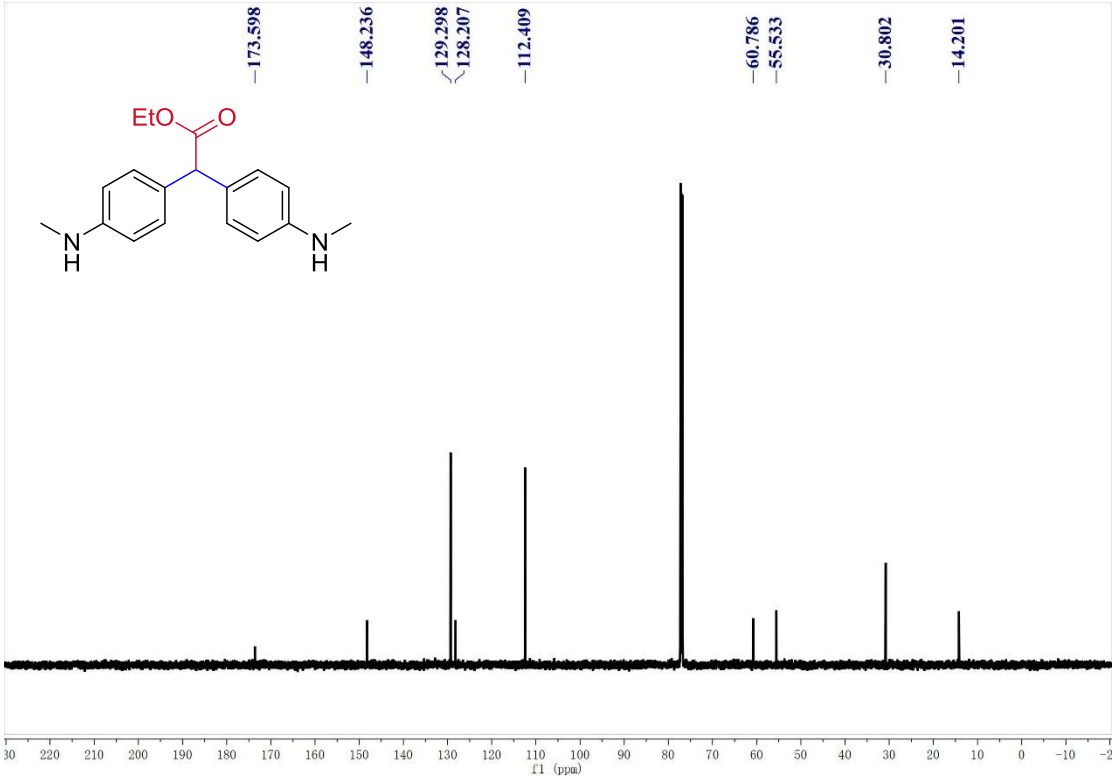

Figure 5. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3aa**

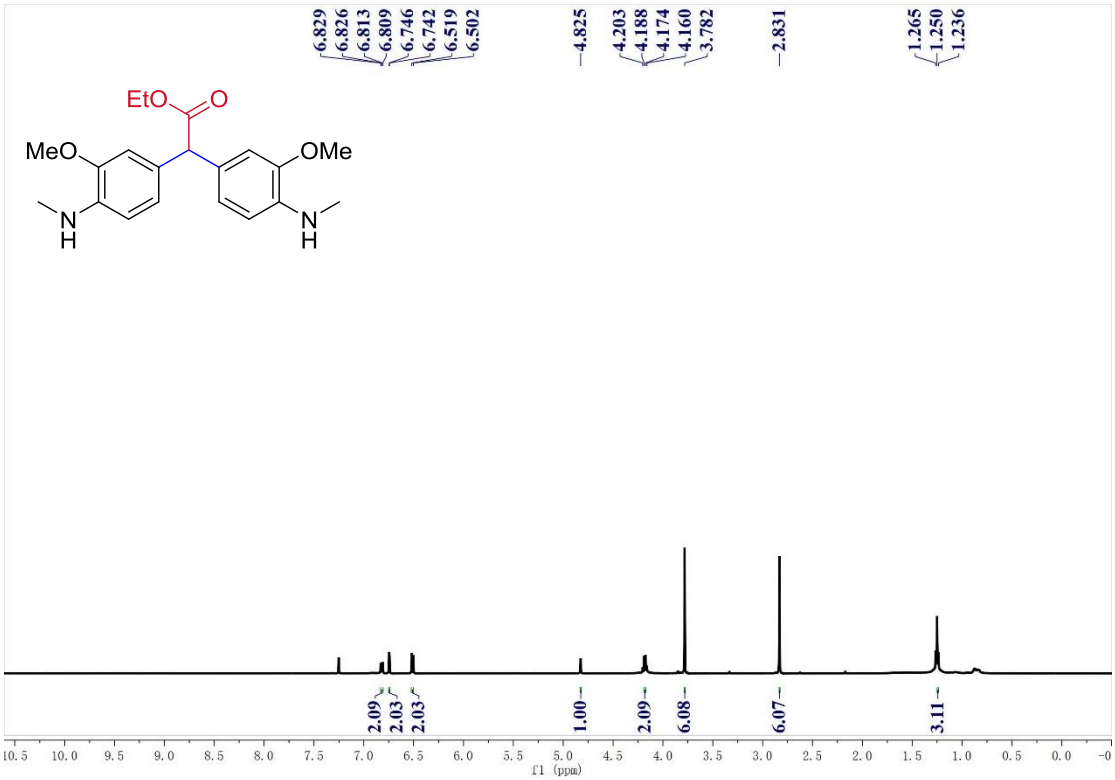

Figure 6. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3ab**

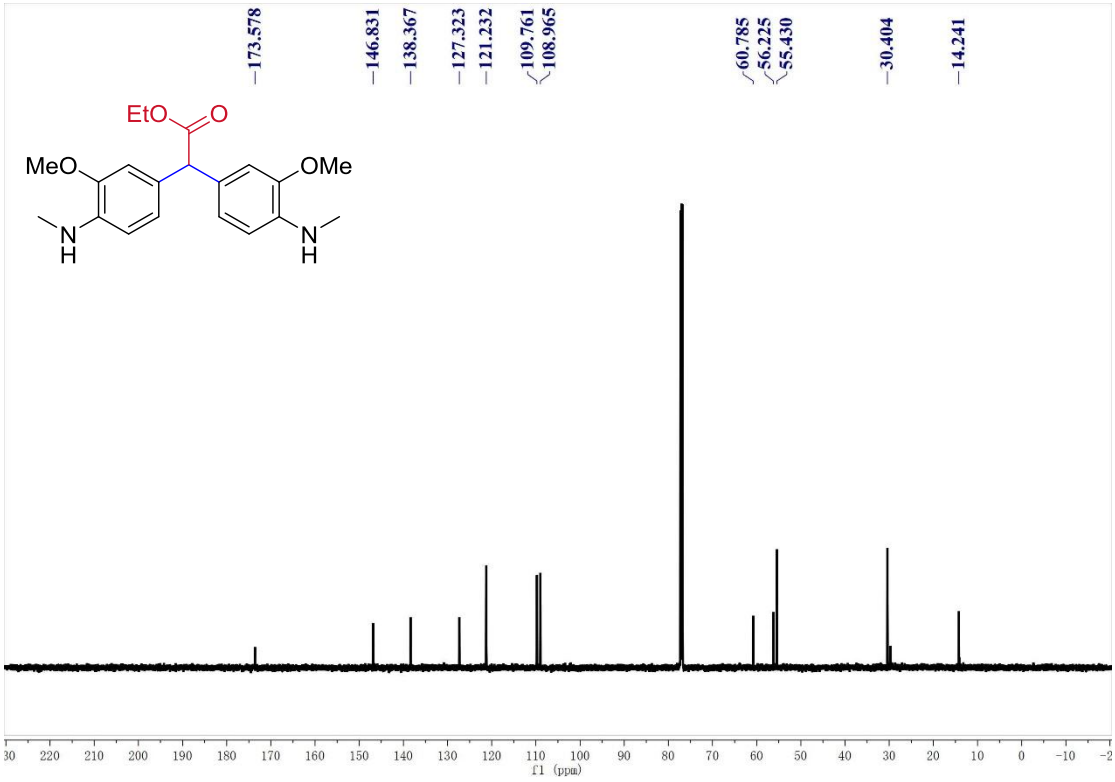

Figure 7. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ab**

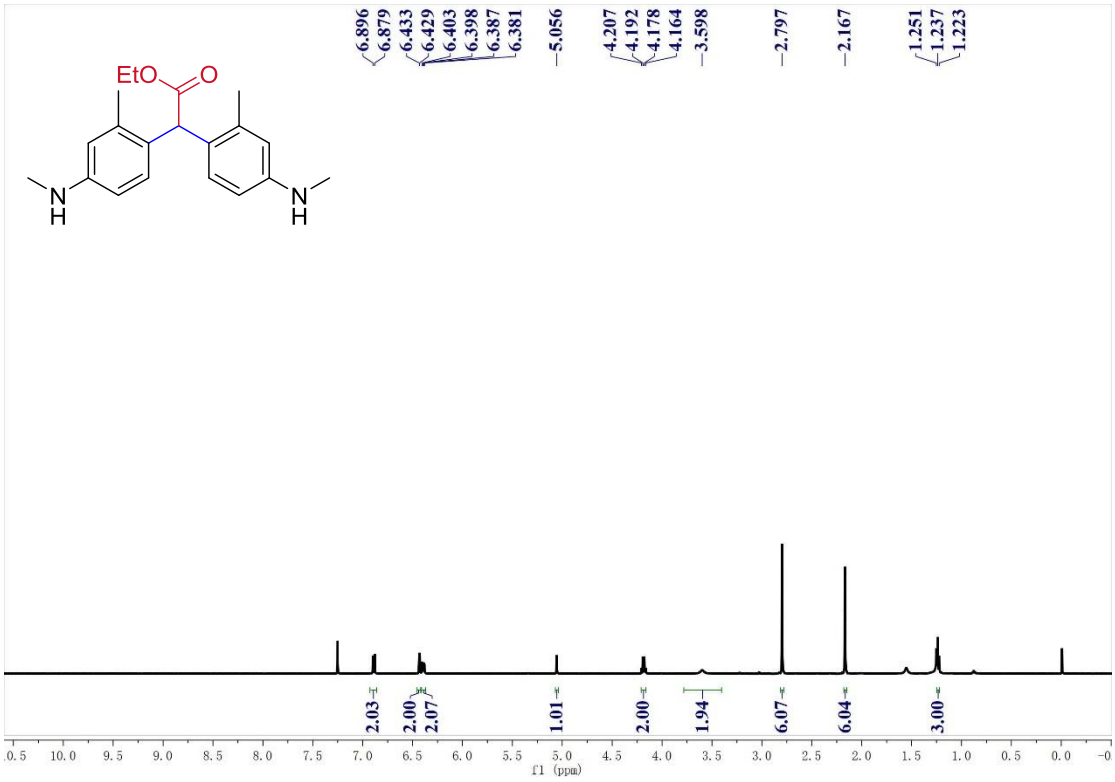

Figure 8. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3ac**

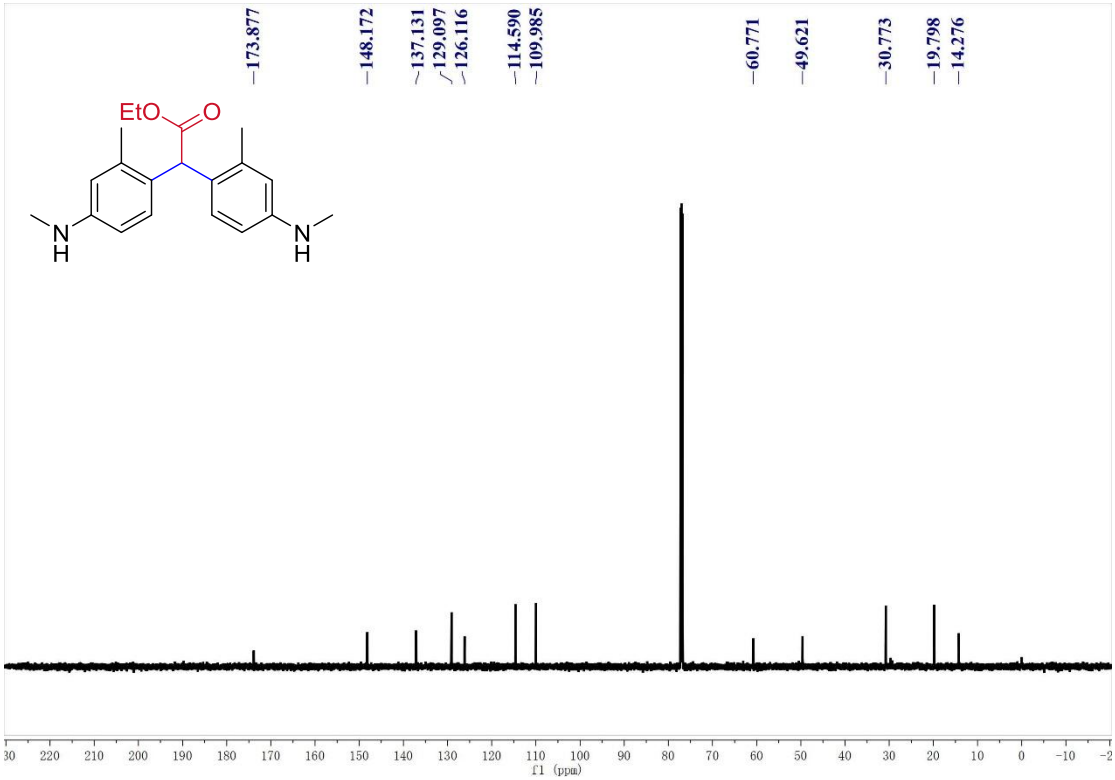

Figure 9. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ac**

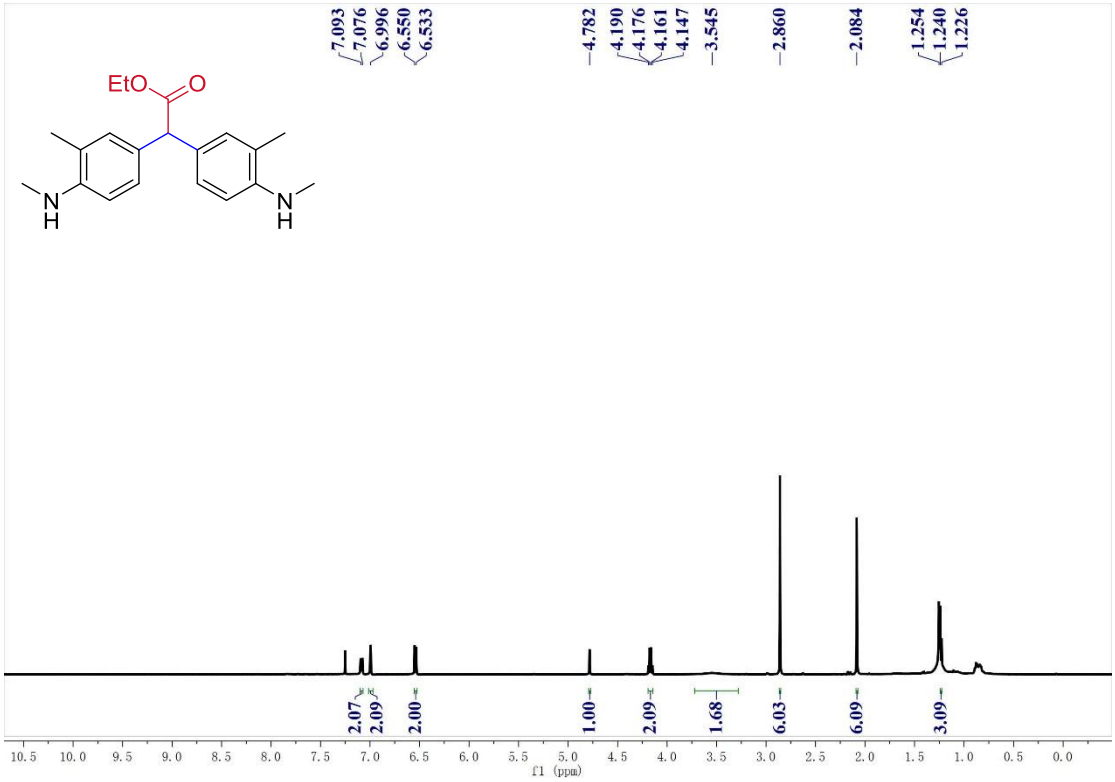

Figure 10. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3ad**

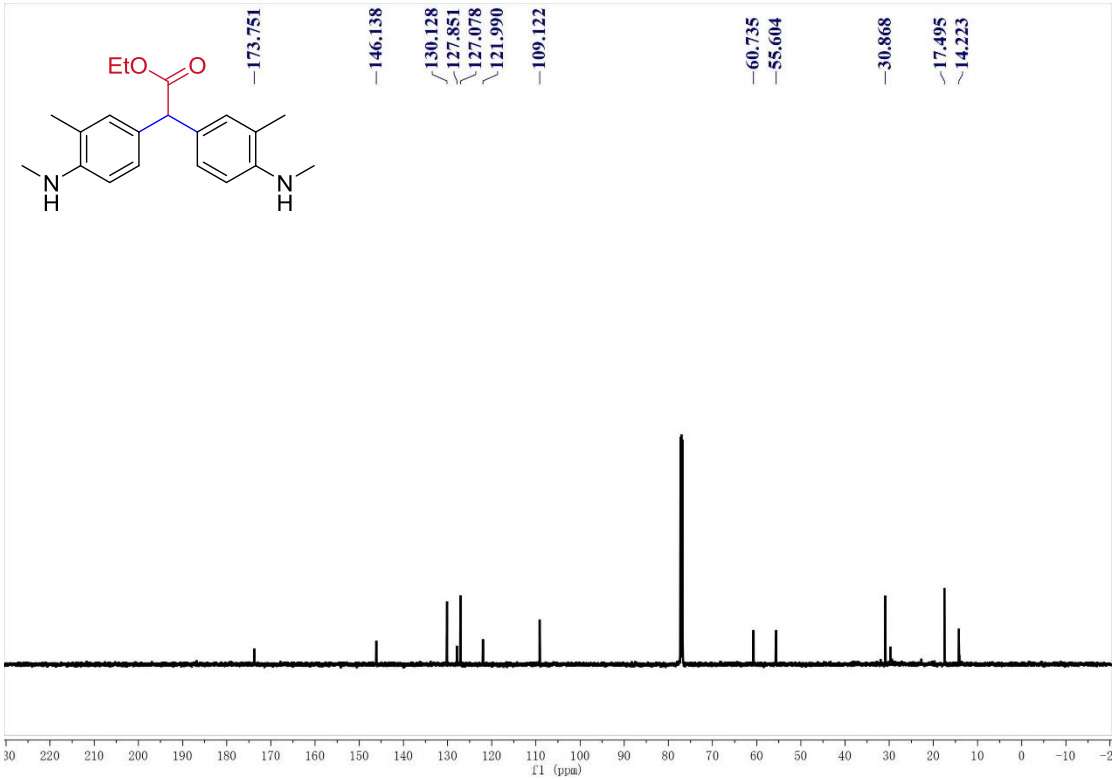

Figure 11. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ad**

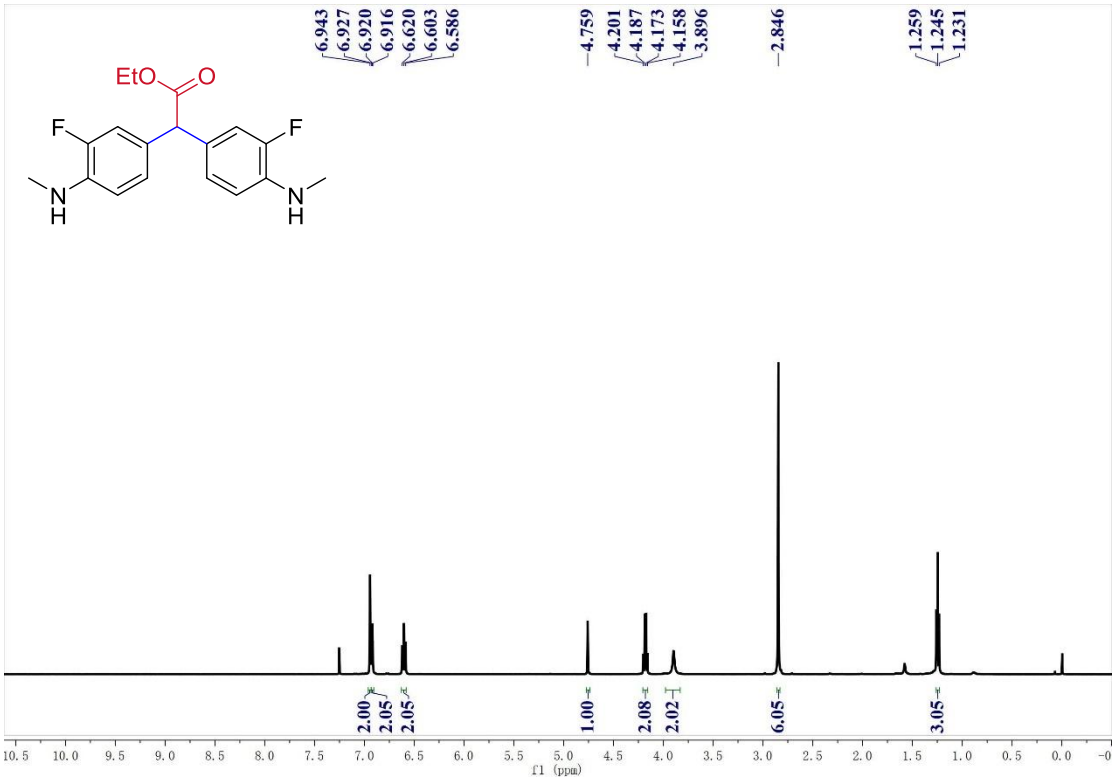

Figure 12. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3ae**

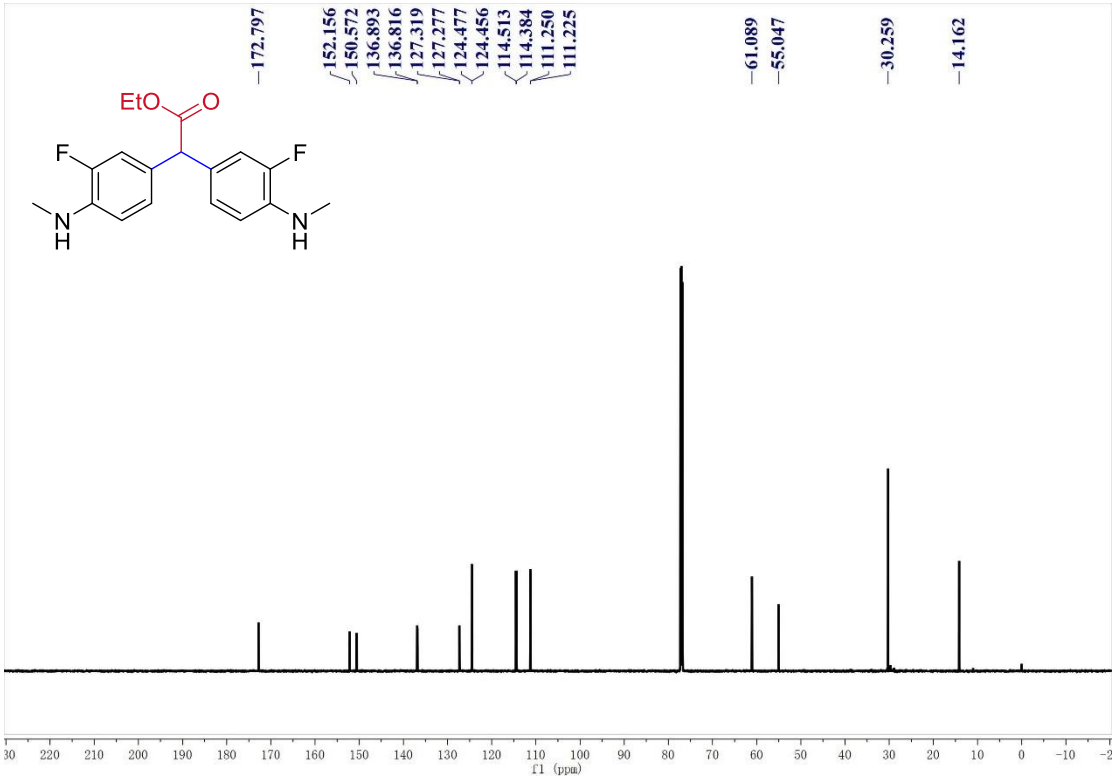

Figure 13. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ae**

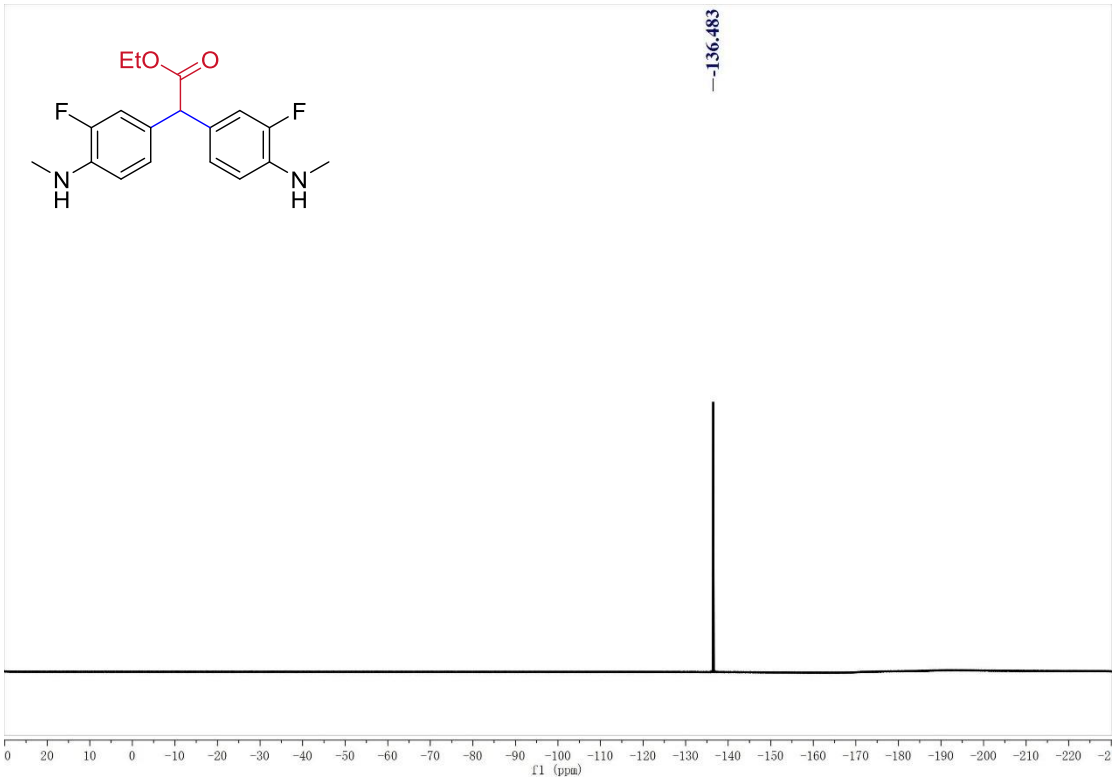

Figure 14. ^{19}F NMR (565 MHz, $CDCl_3$) spectra of compound **3ae**

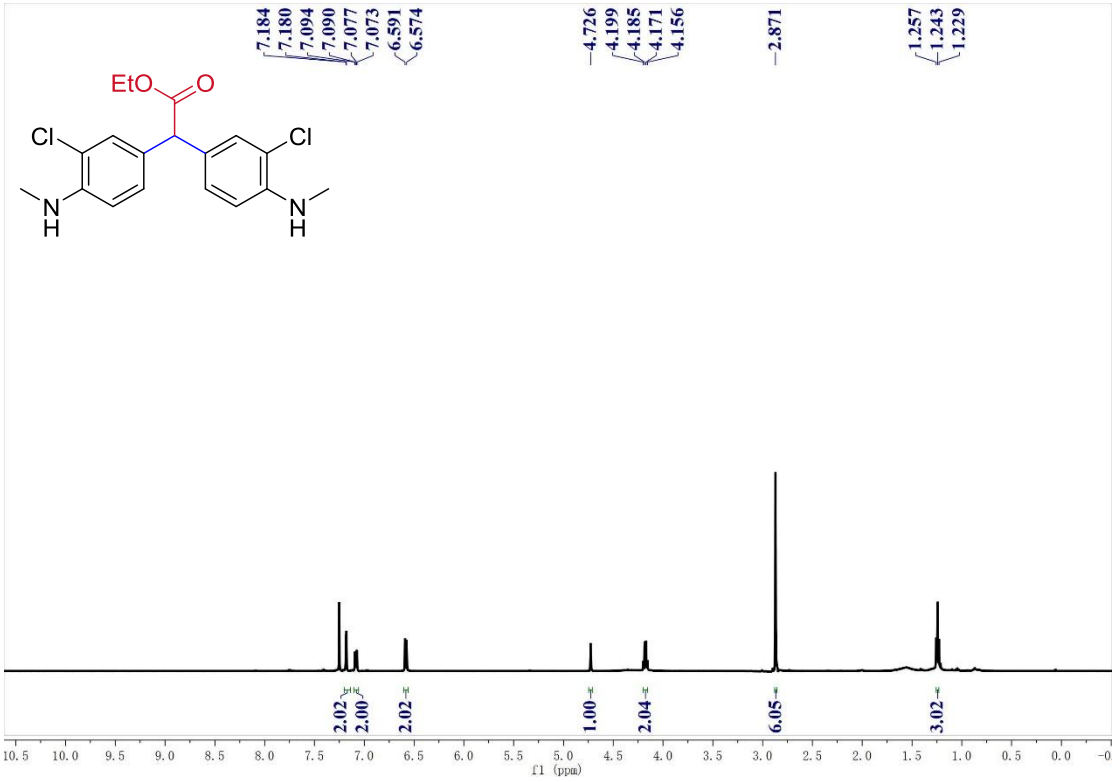

Figure 15. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3af**

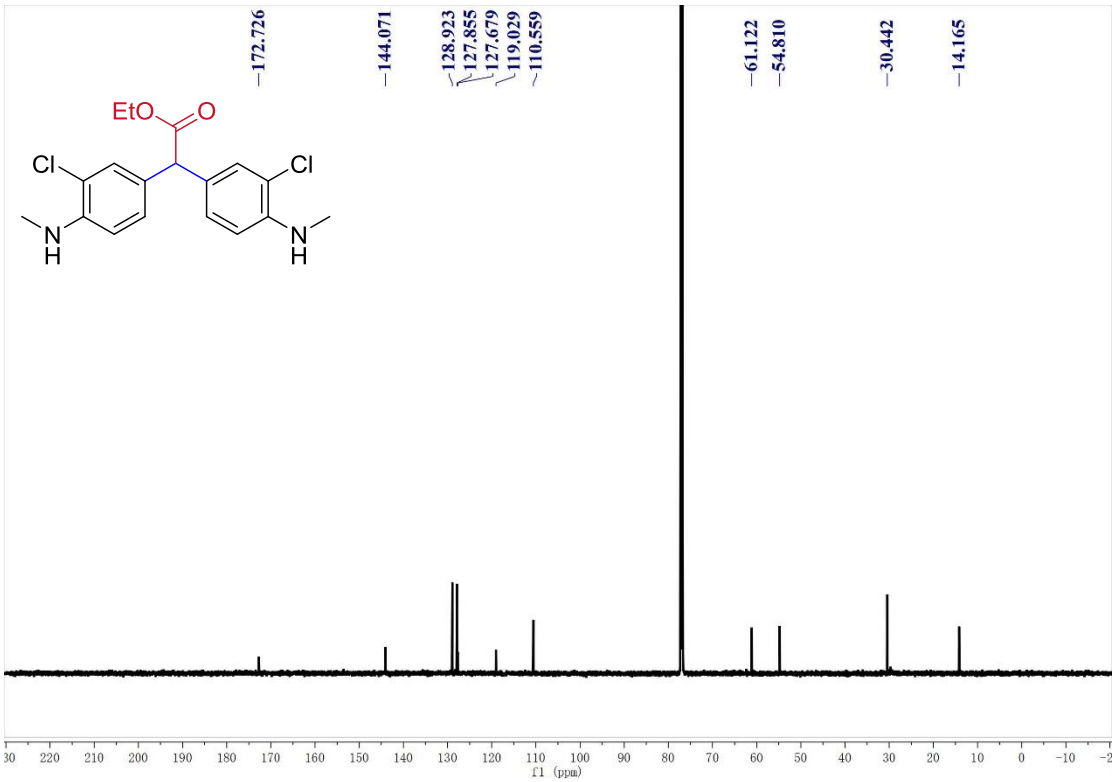

Figure 16. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3af**

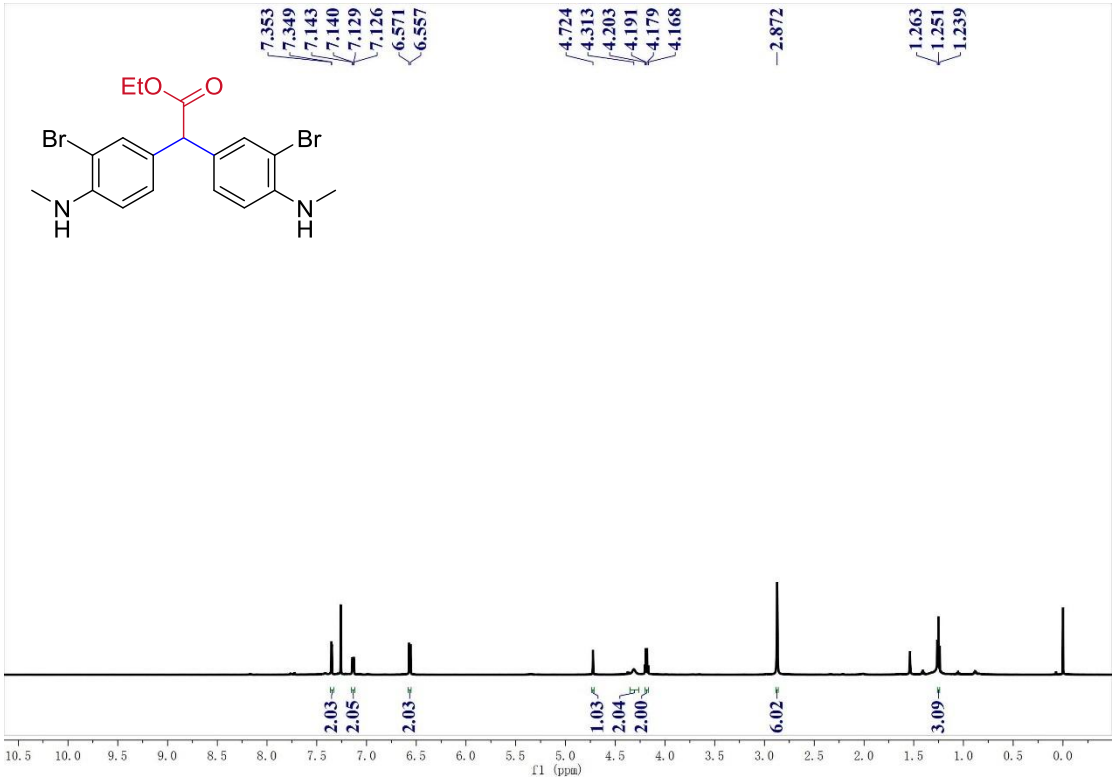

Figure 17. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3ag**

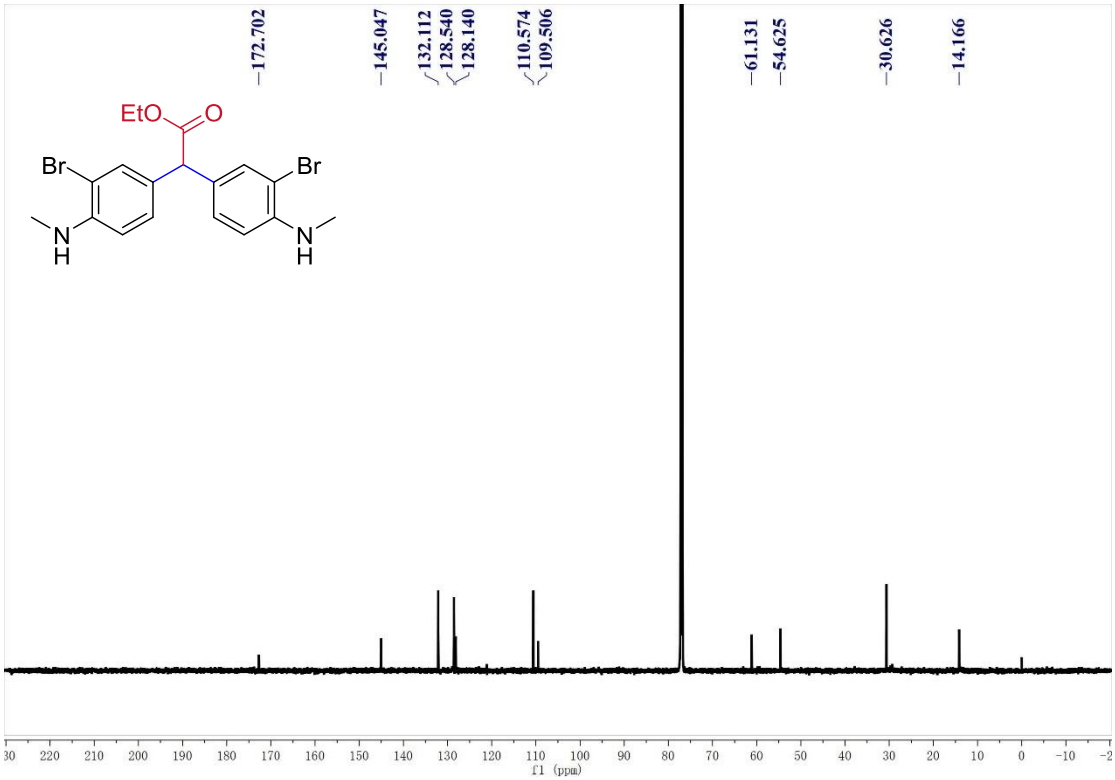

Figure 18. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ag**

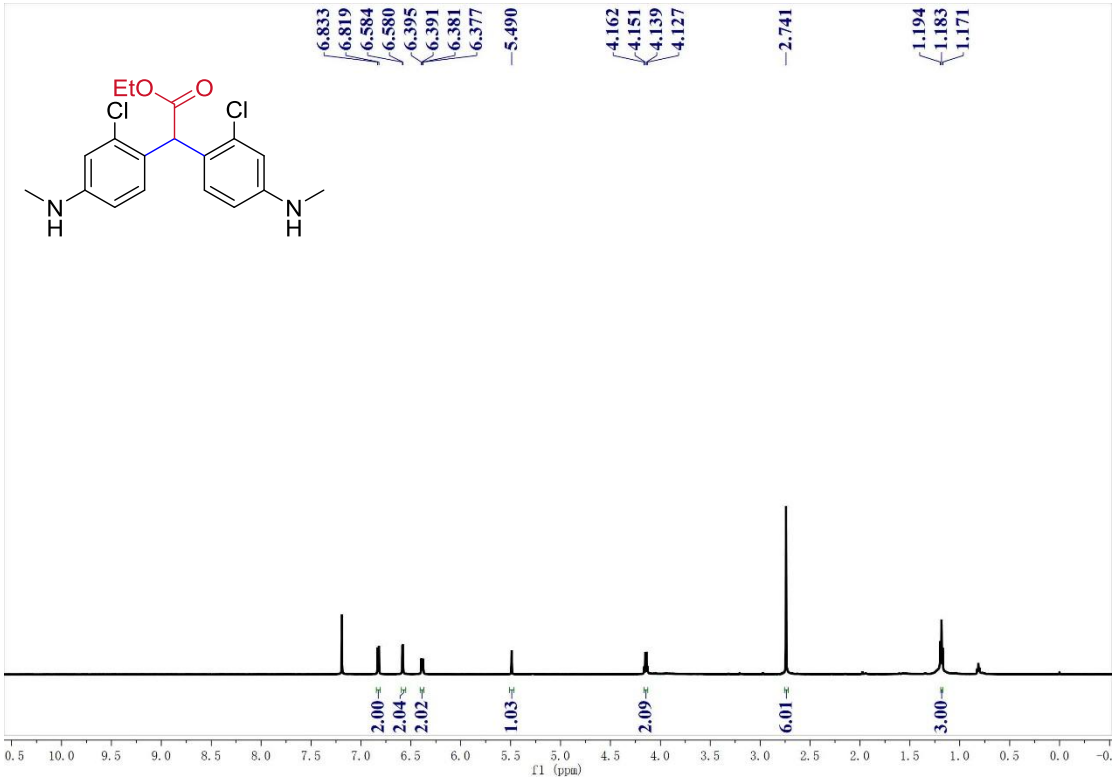

Figure 19. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3ah**

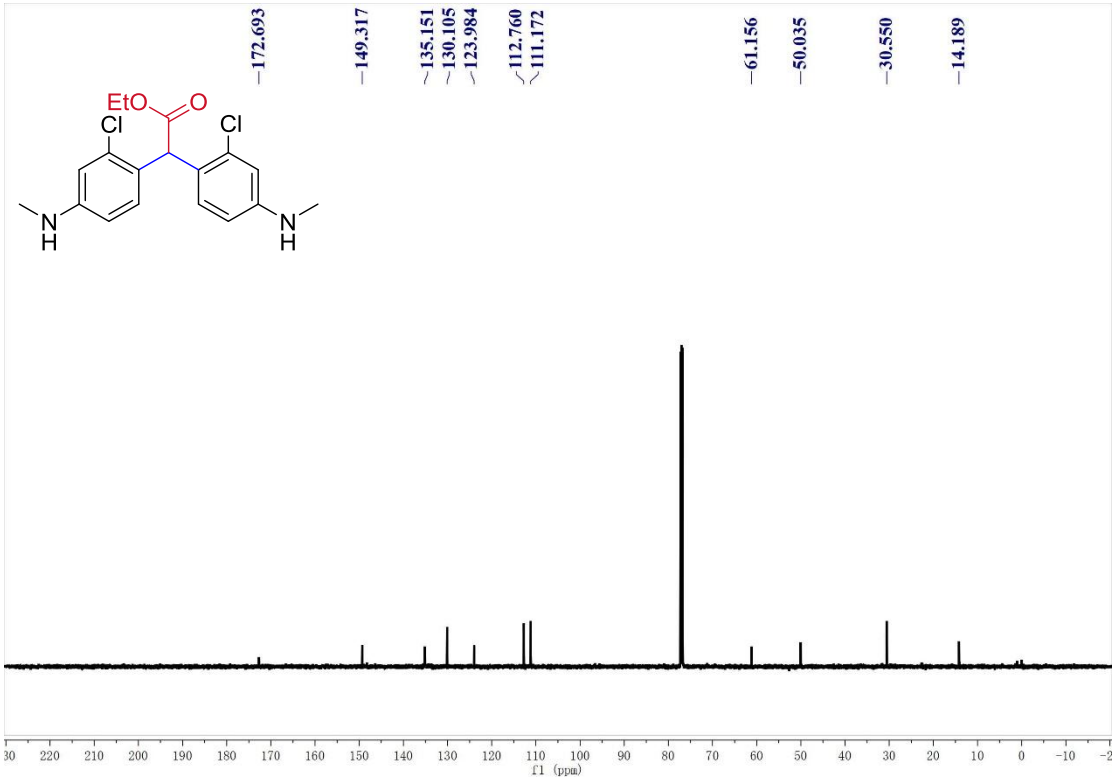

Figure 20. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ah**

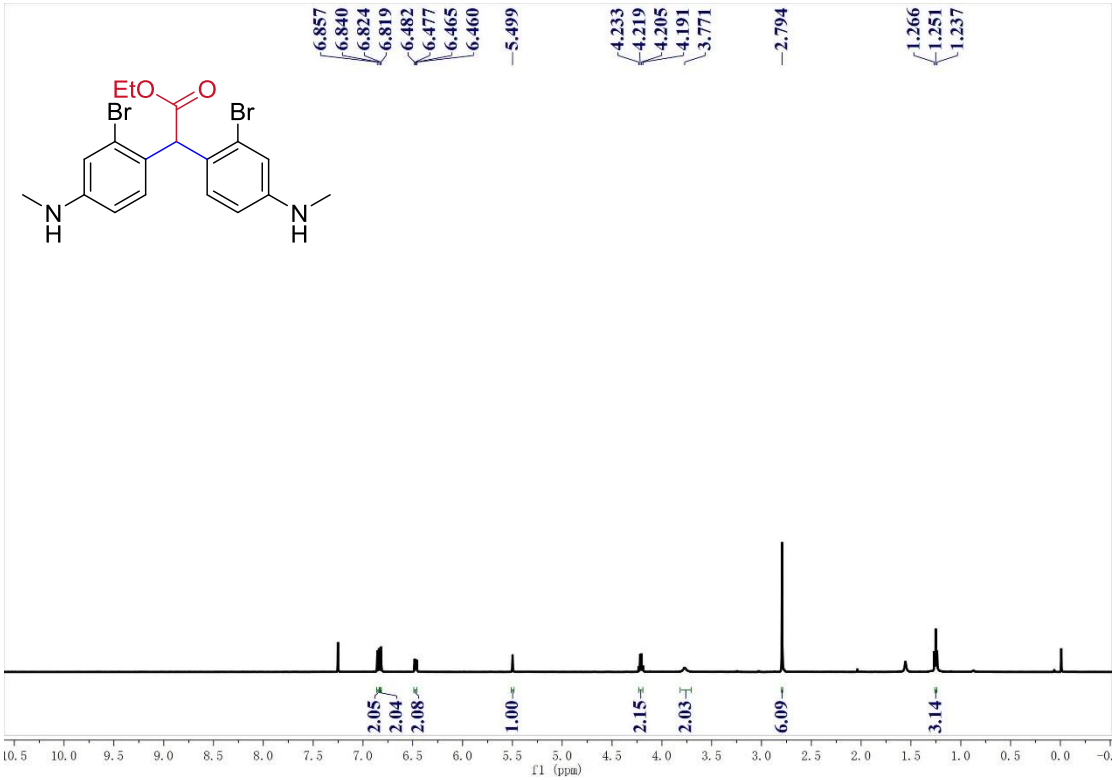

Figure 21. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3ai**

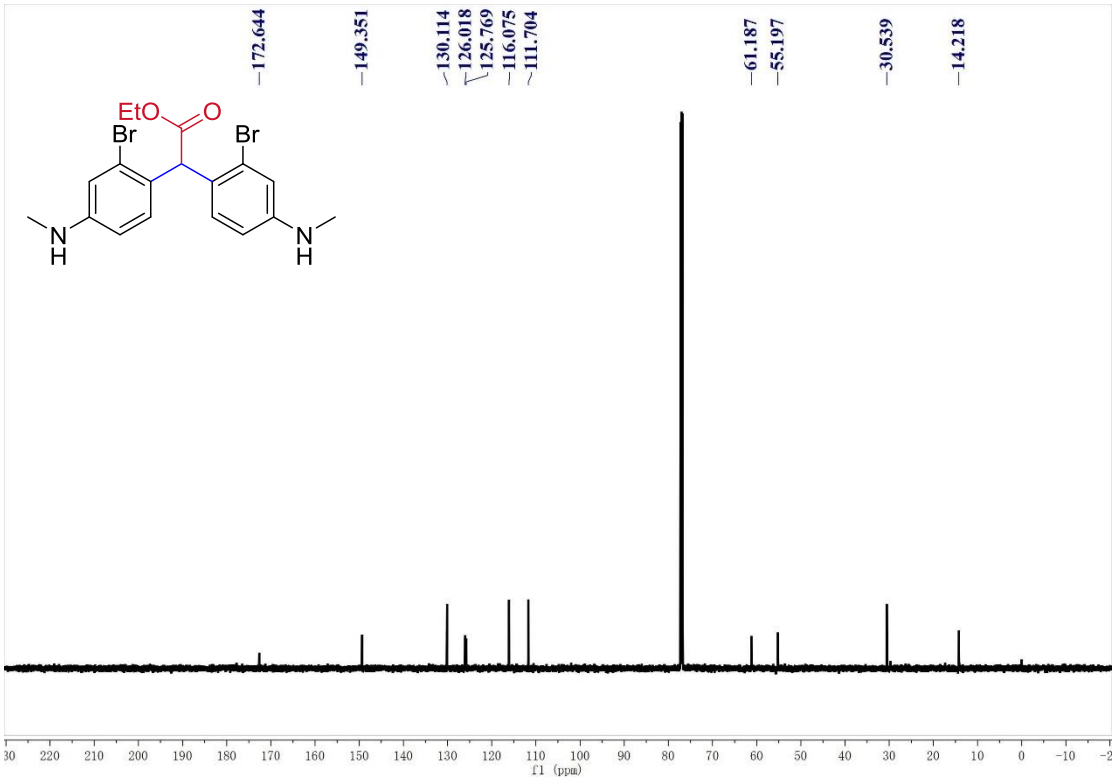

Figure 22. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ai**

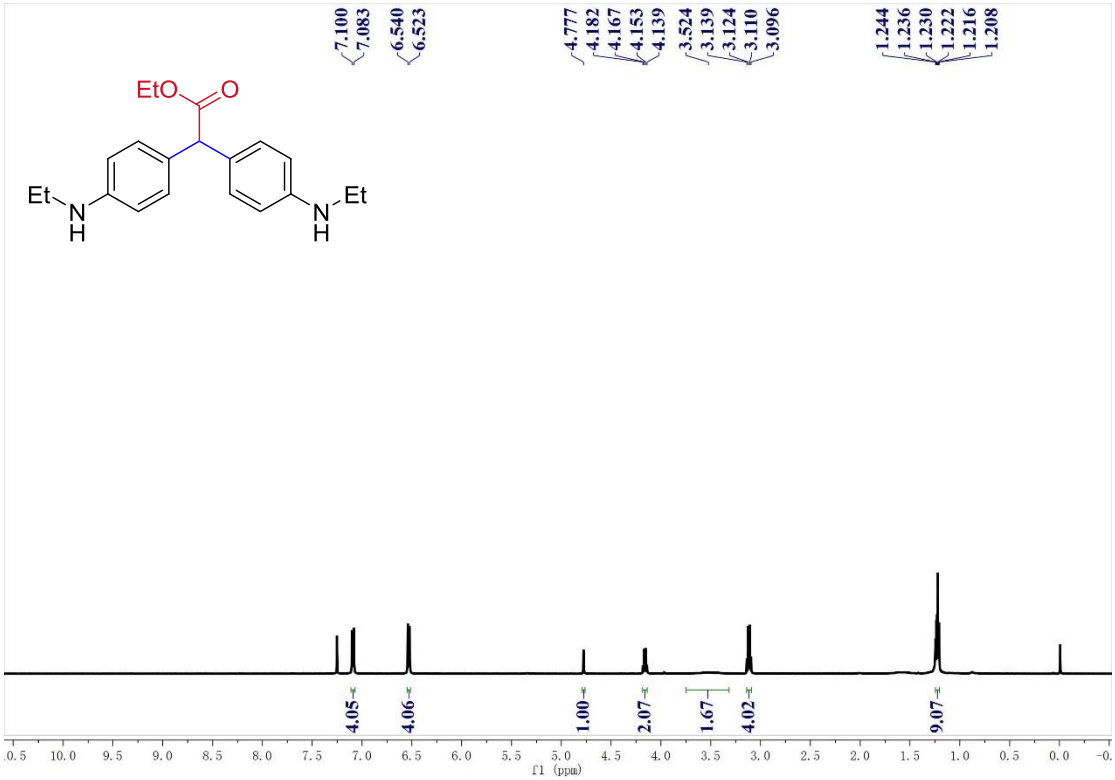

Figure 23. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3aj**

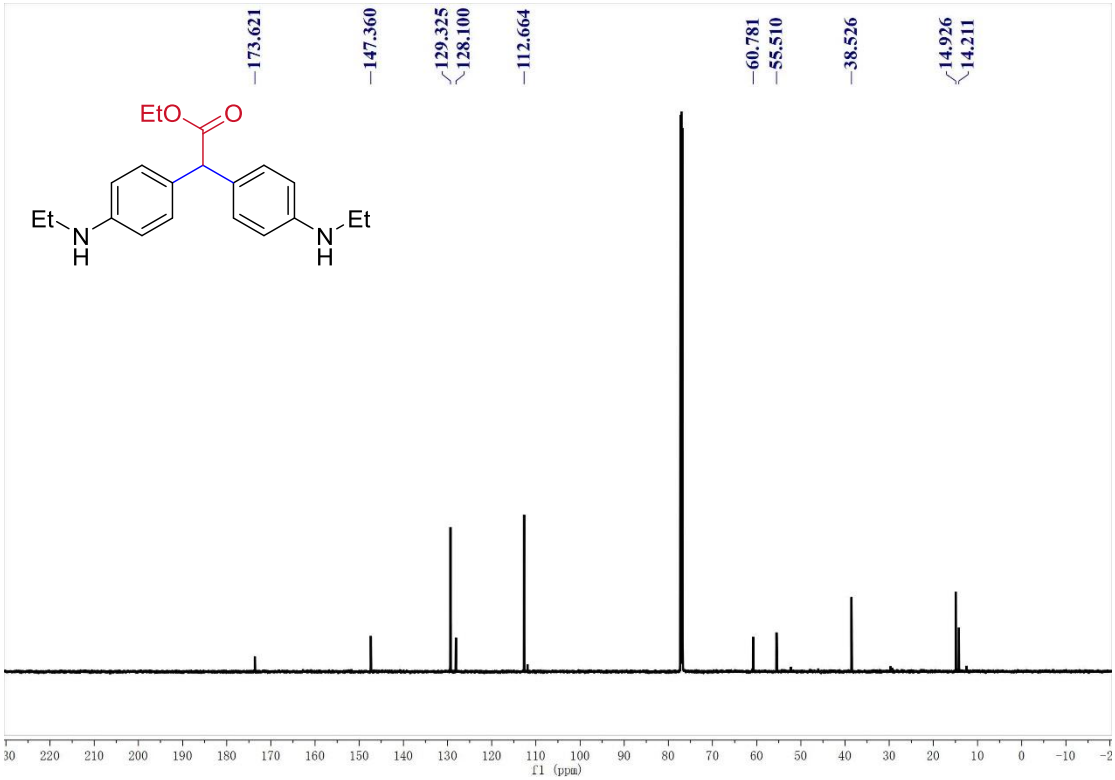

Figure 24. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3aj**

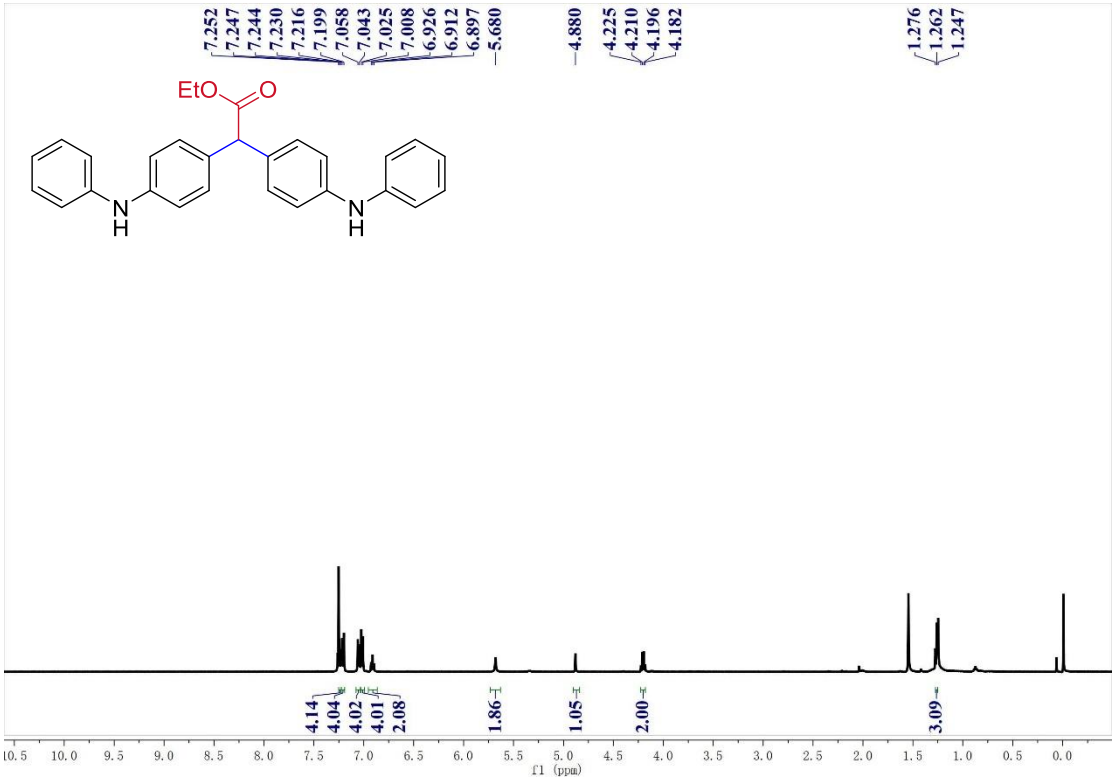

Figure 25. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3ak**

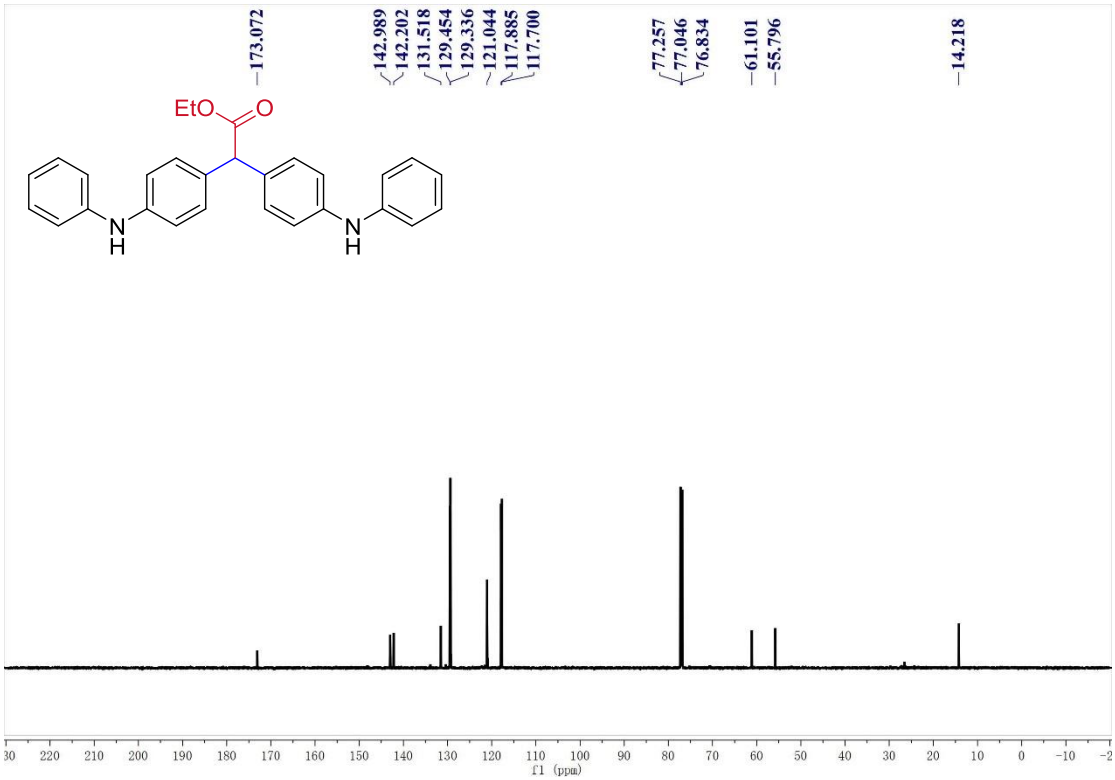

Figure 26. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ak**

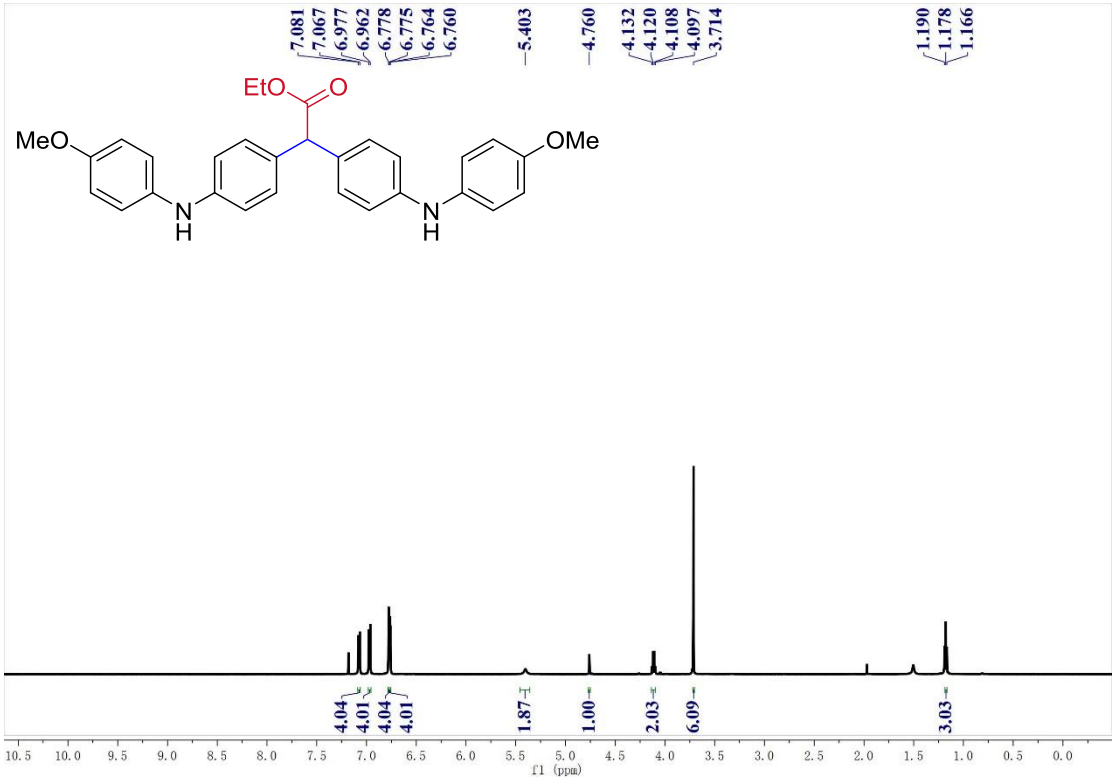

Figure 27. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3al**

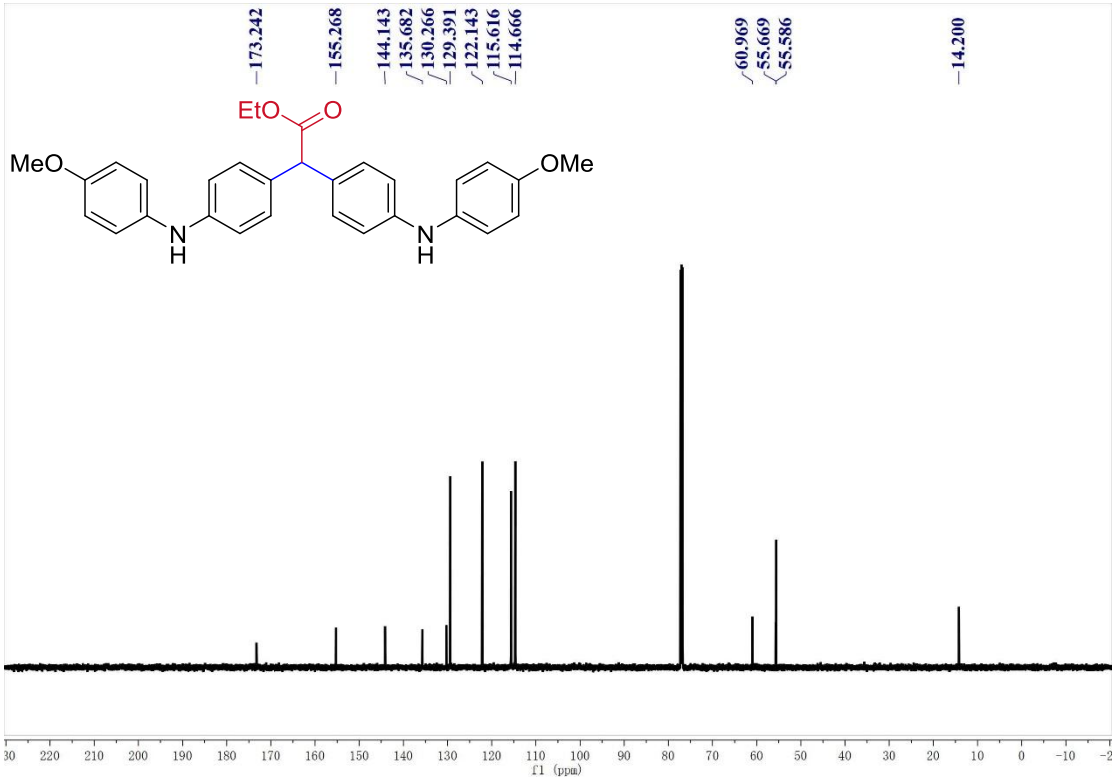

Figure 28. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3al**

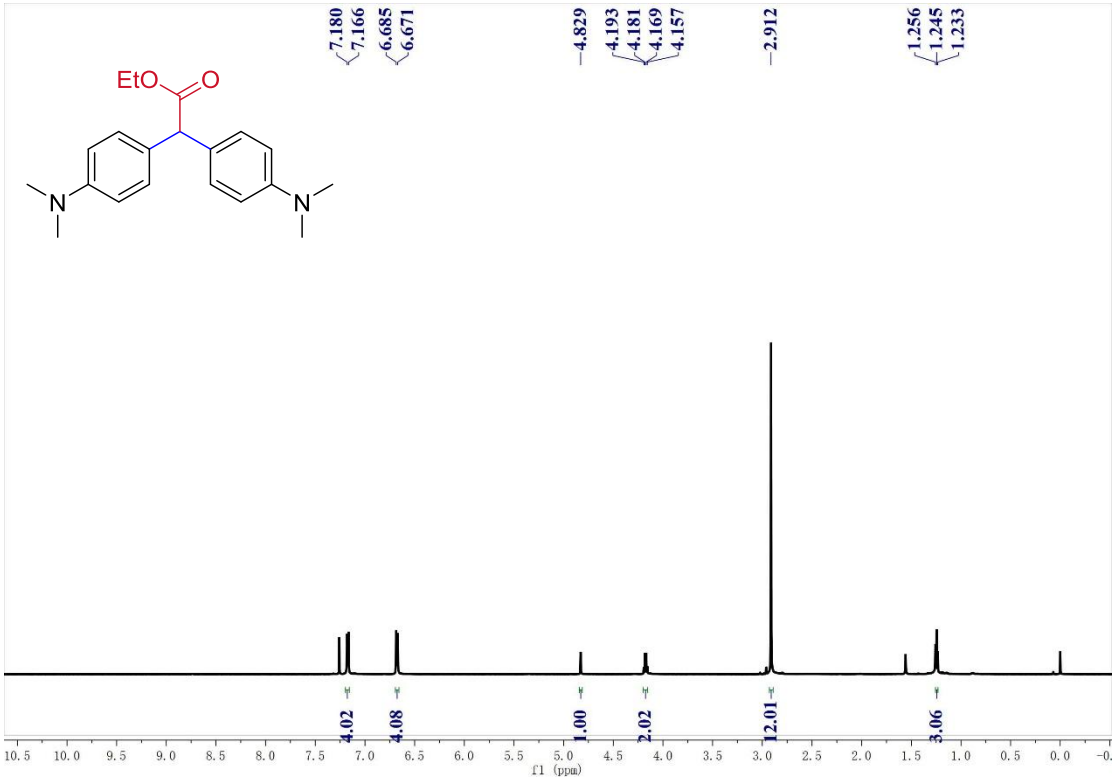

Figure 29. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3am-I**

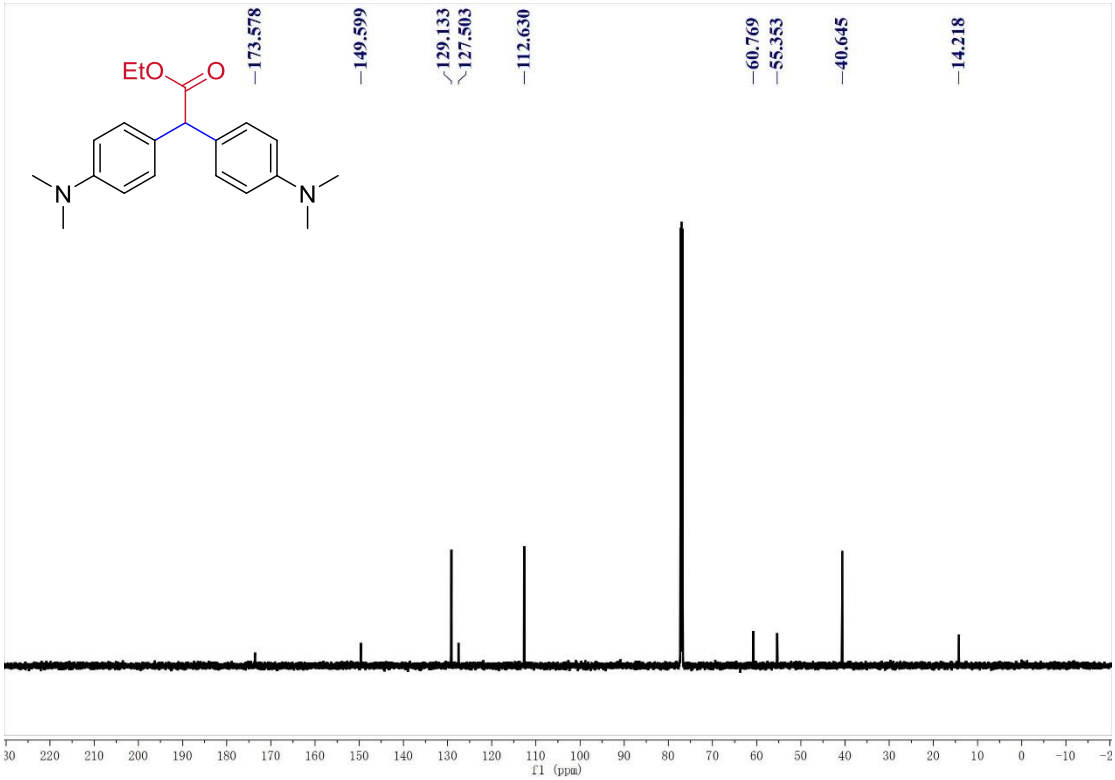

Figure 30. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3am-I**

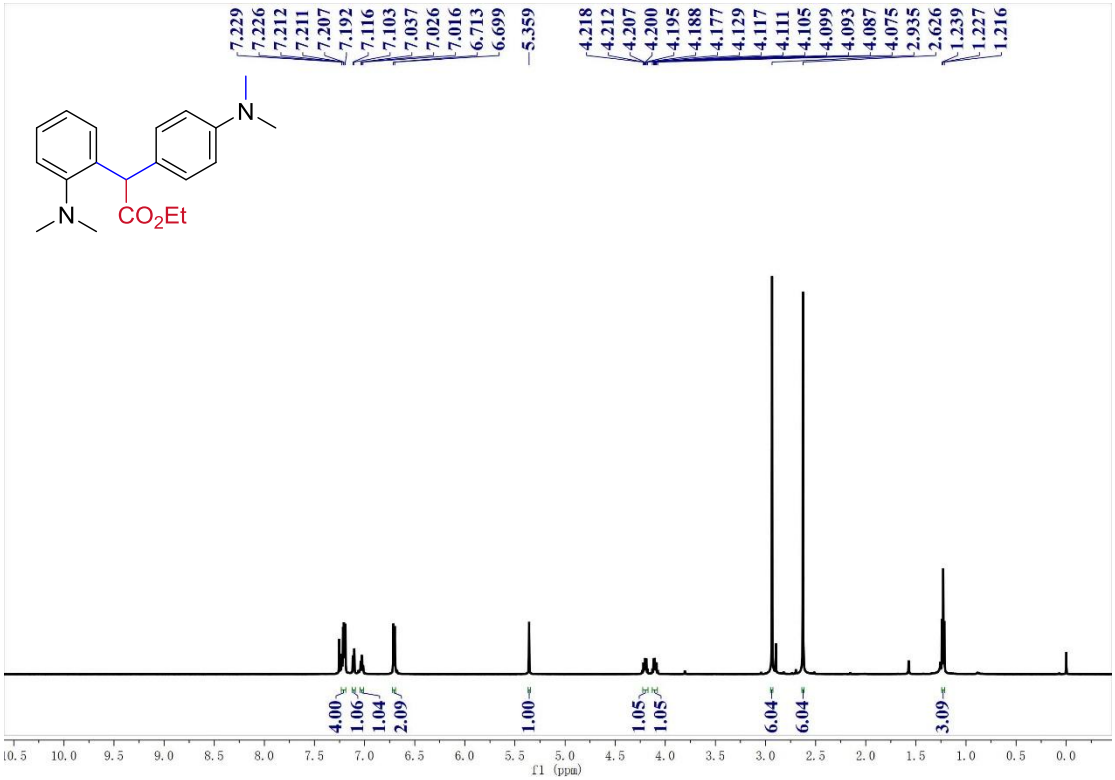

Figure 31. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3am-II**

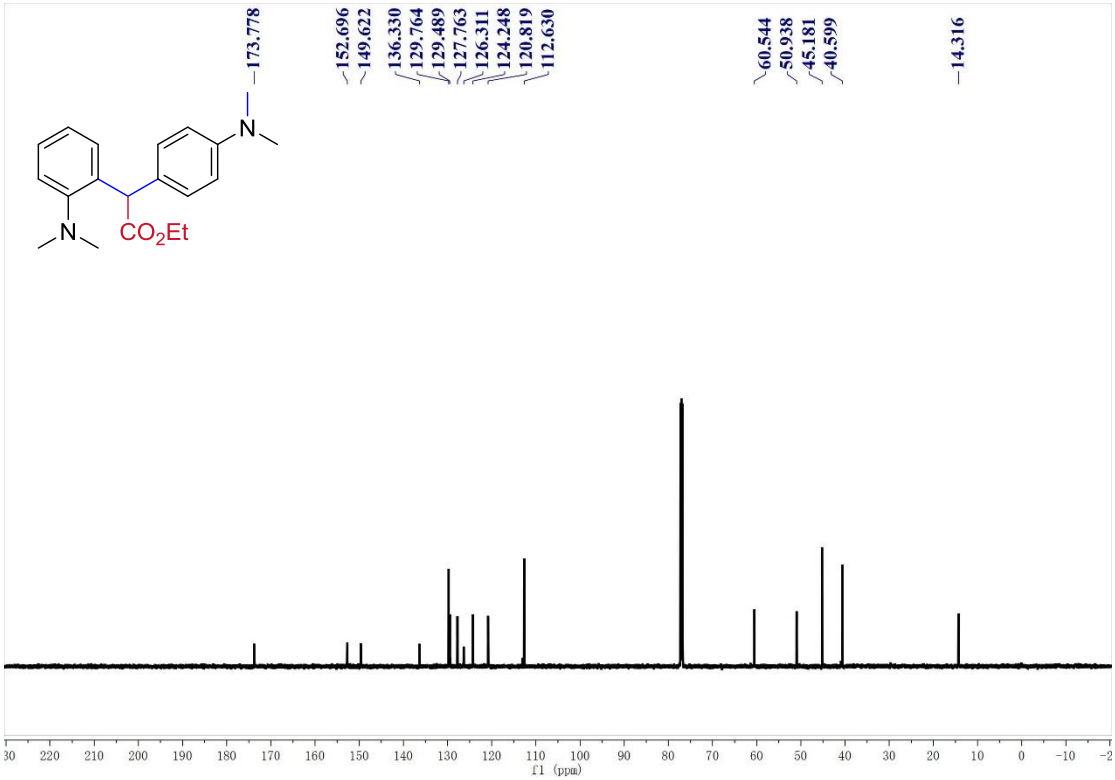

Figure 32. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3am-II**

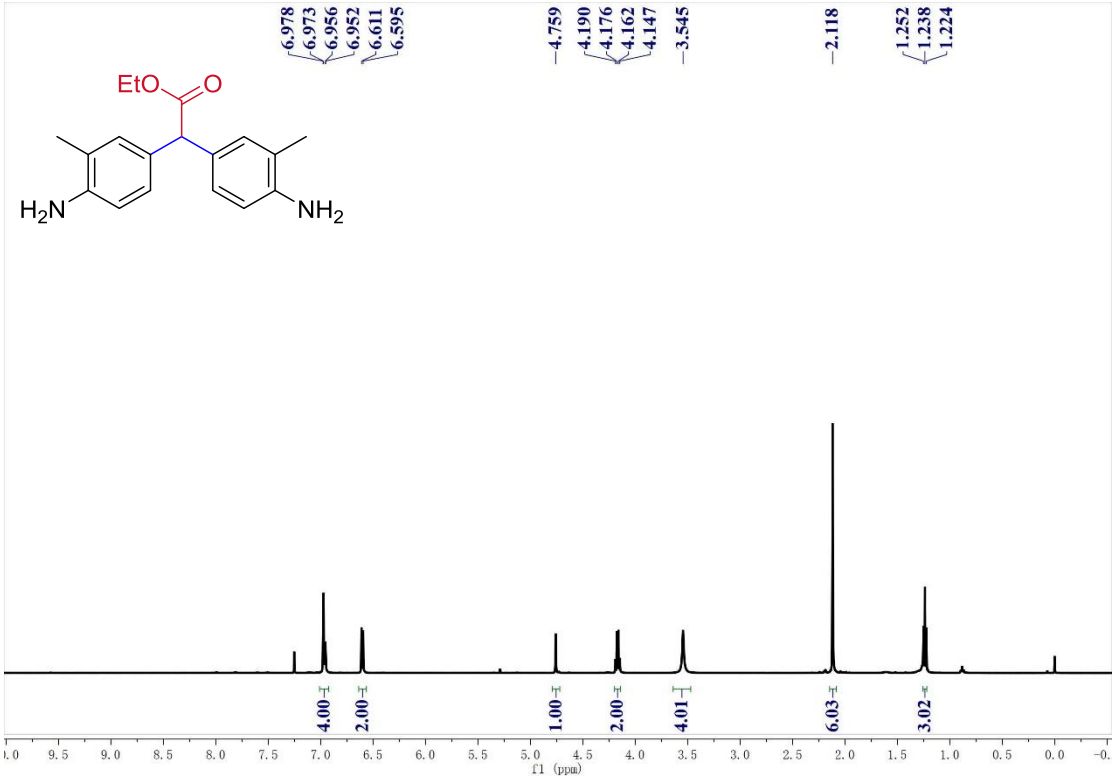

Figure 33. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3an**

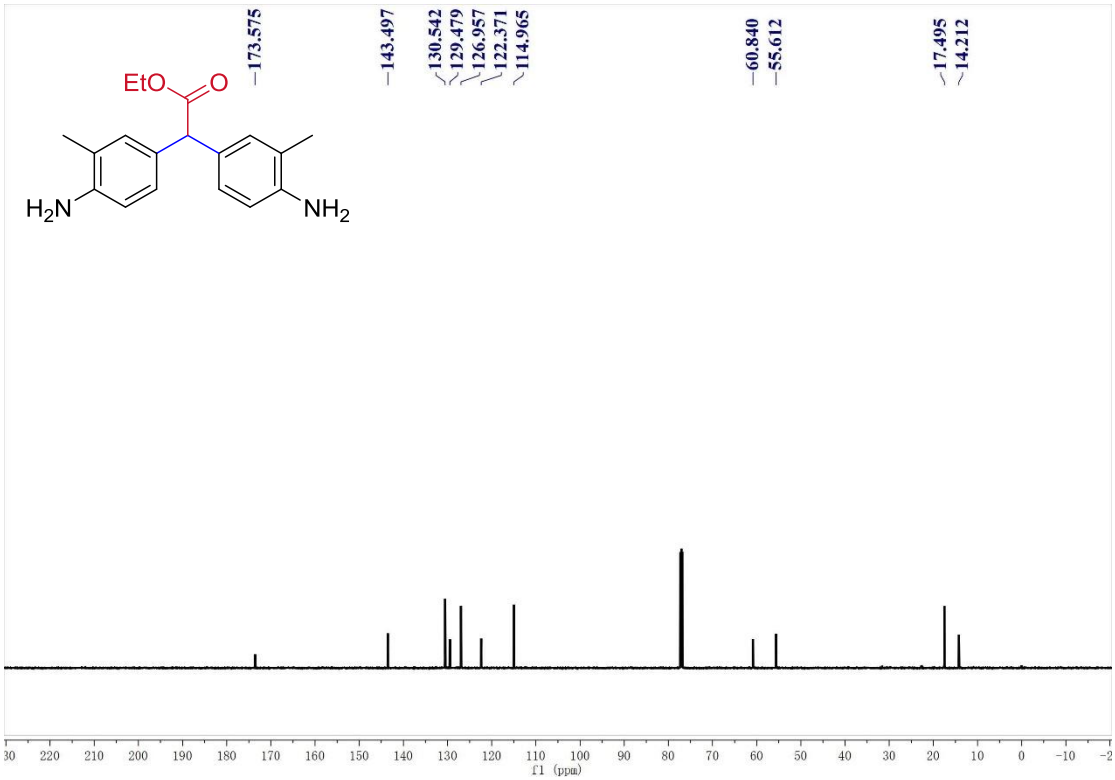

Figure 34. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3an**

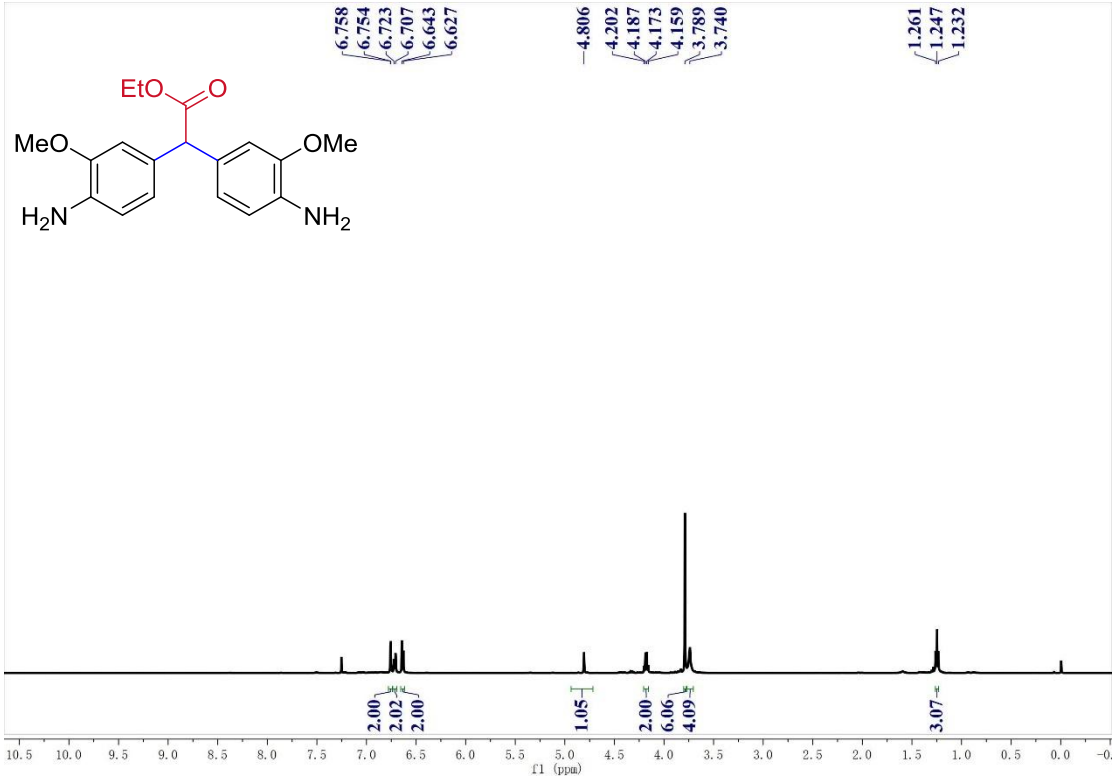

Figure 35. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3ao**

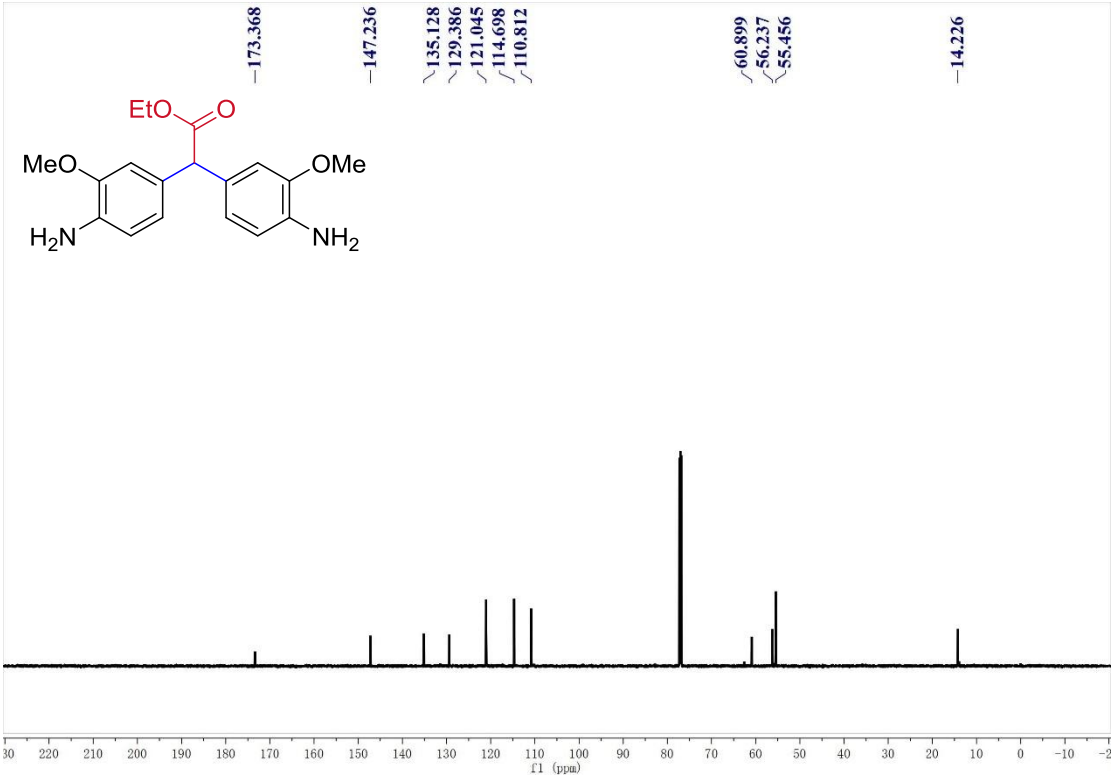

Figure 36. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ao**

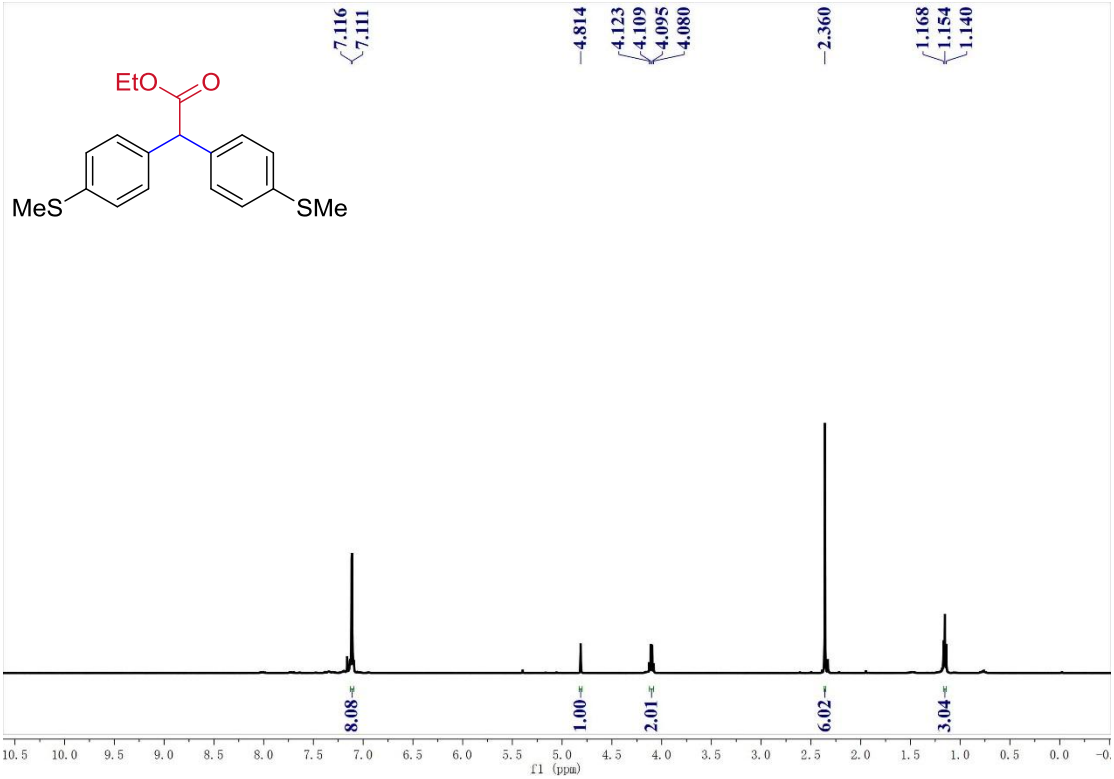

Figure 37. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3ap**

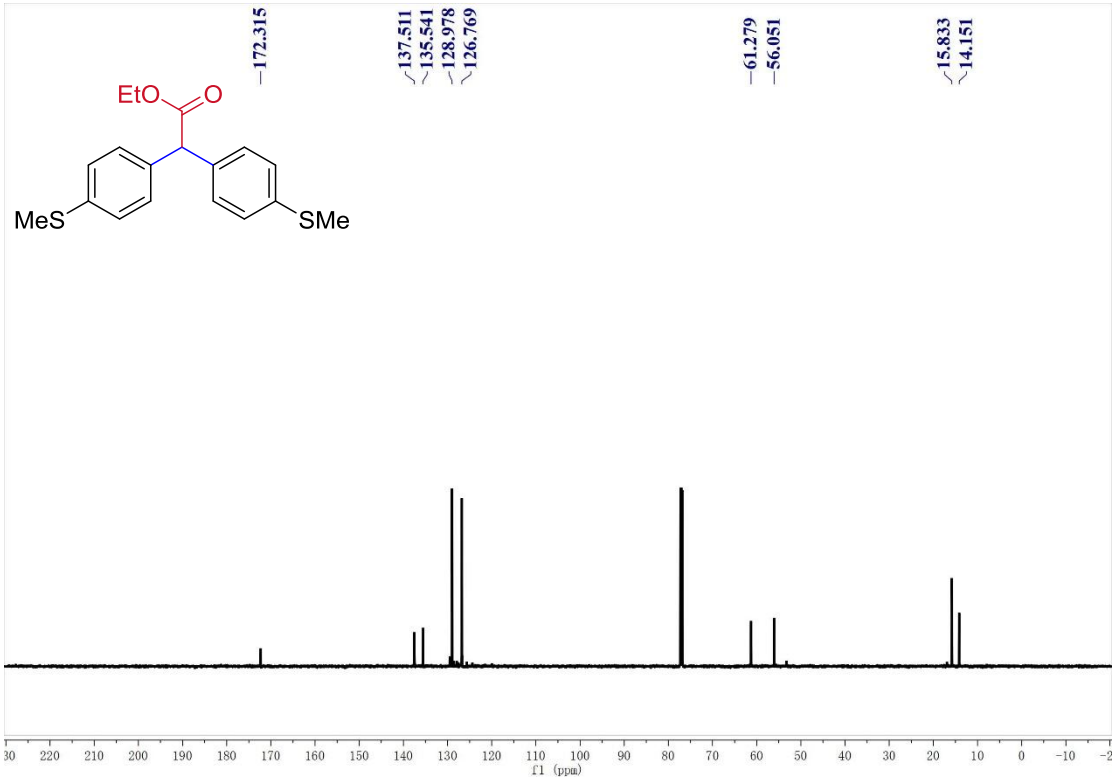

Figure 38. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ap**

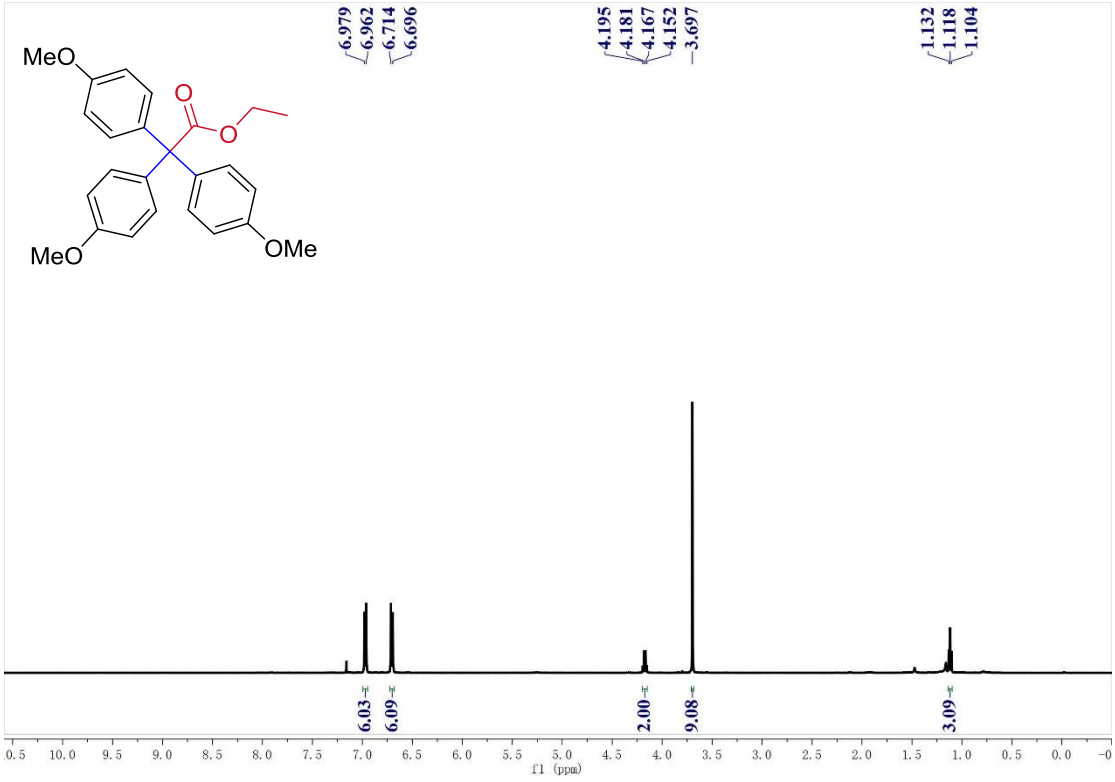

Figure 39. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3aq**

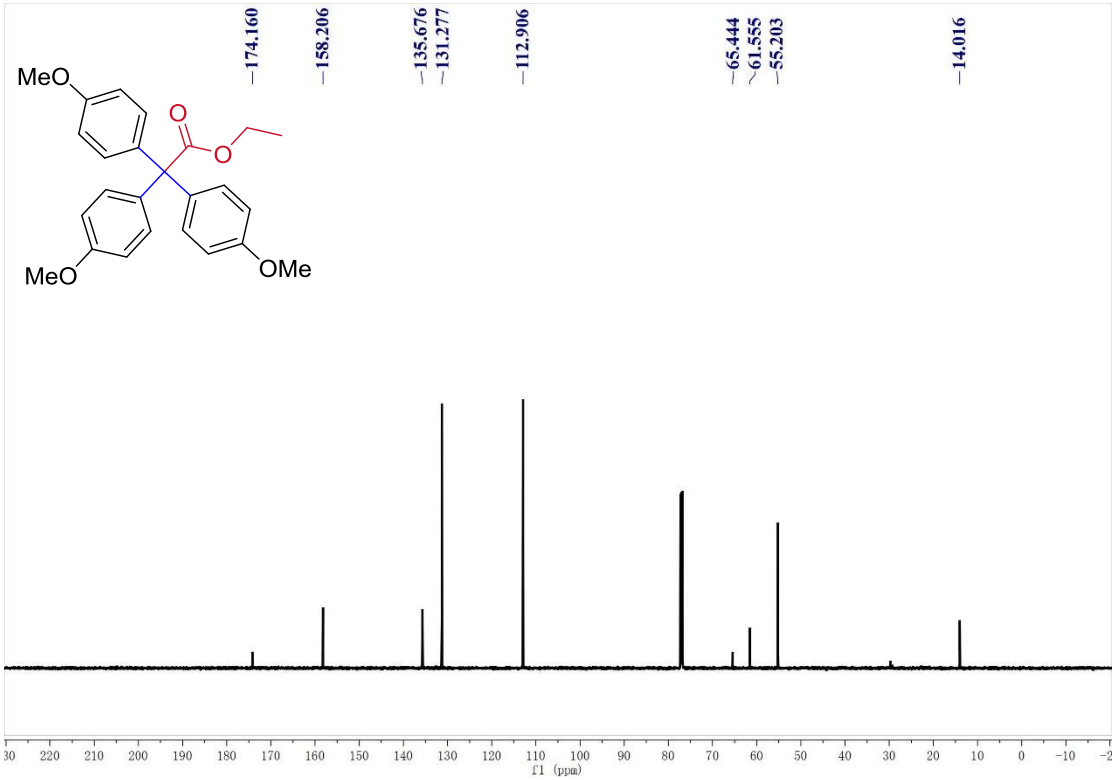

Figure 40. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3aq**

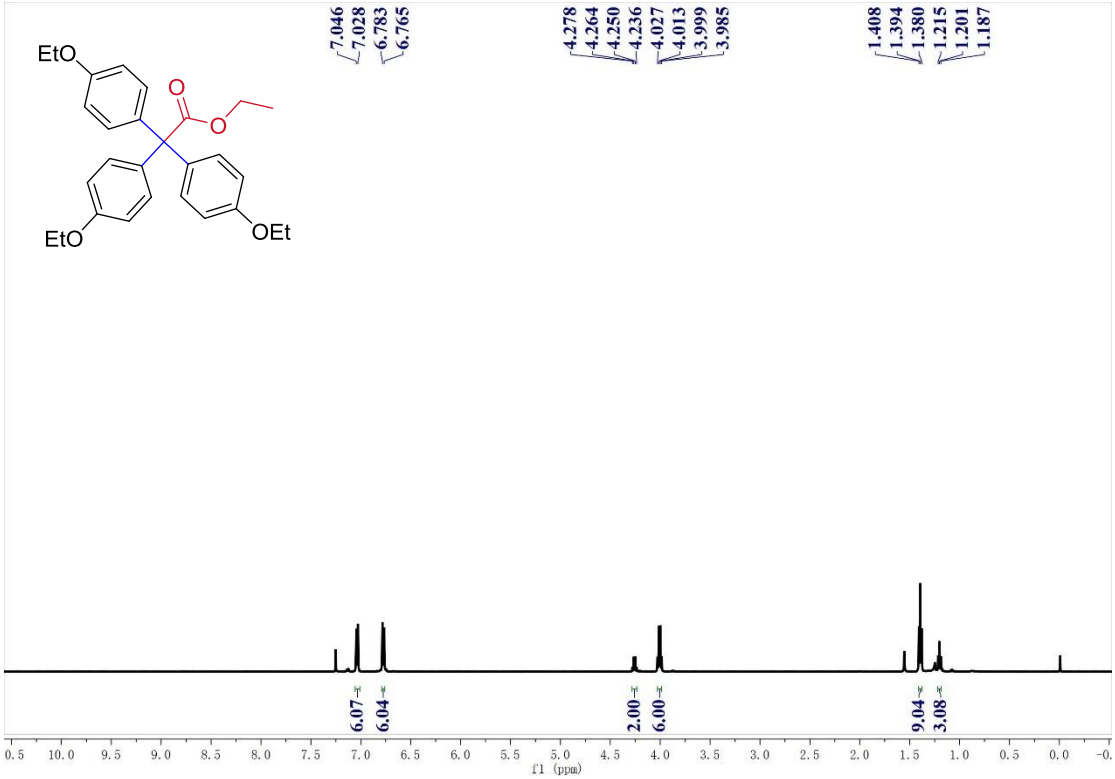

Figure 41. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3ar**

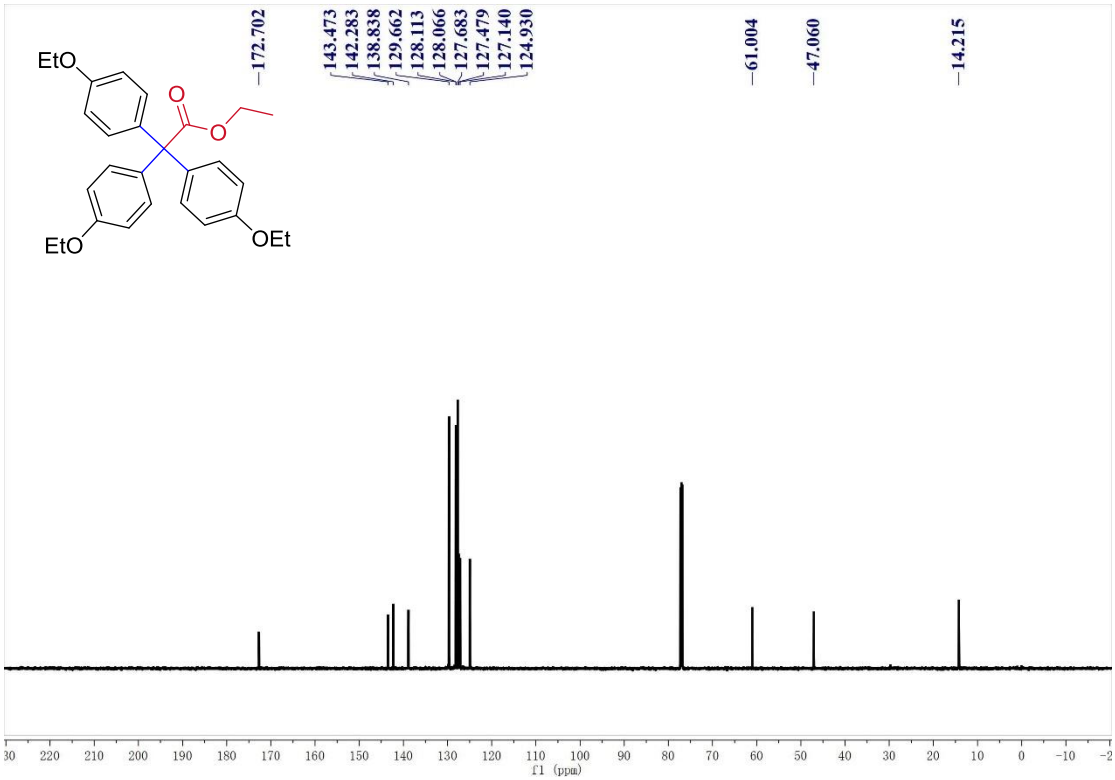

Figure 42. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ar**

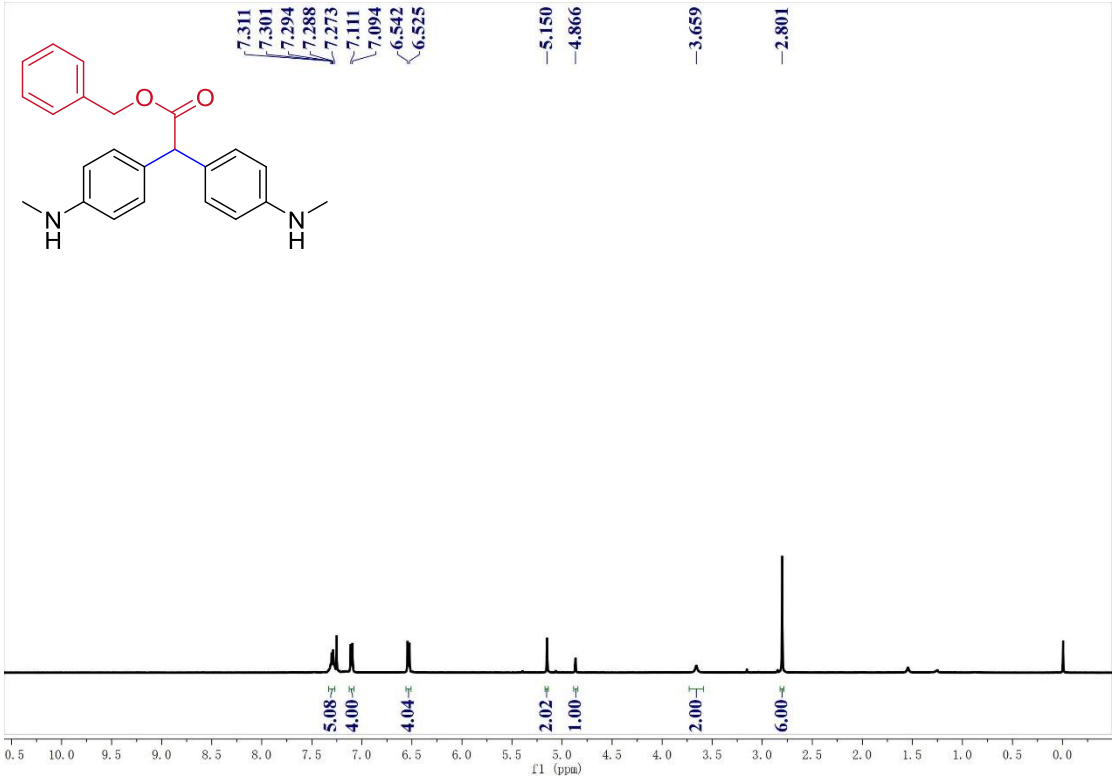

Figure 43. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3ba**

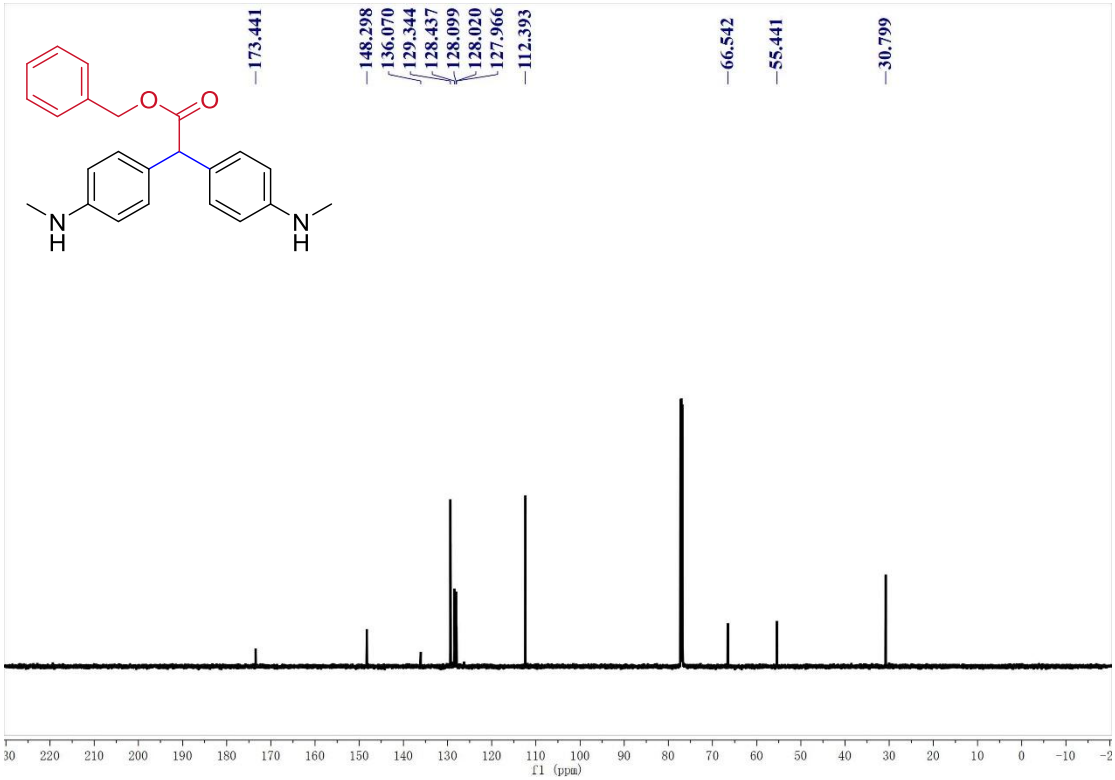

Figure 44. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ba**

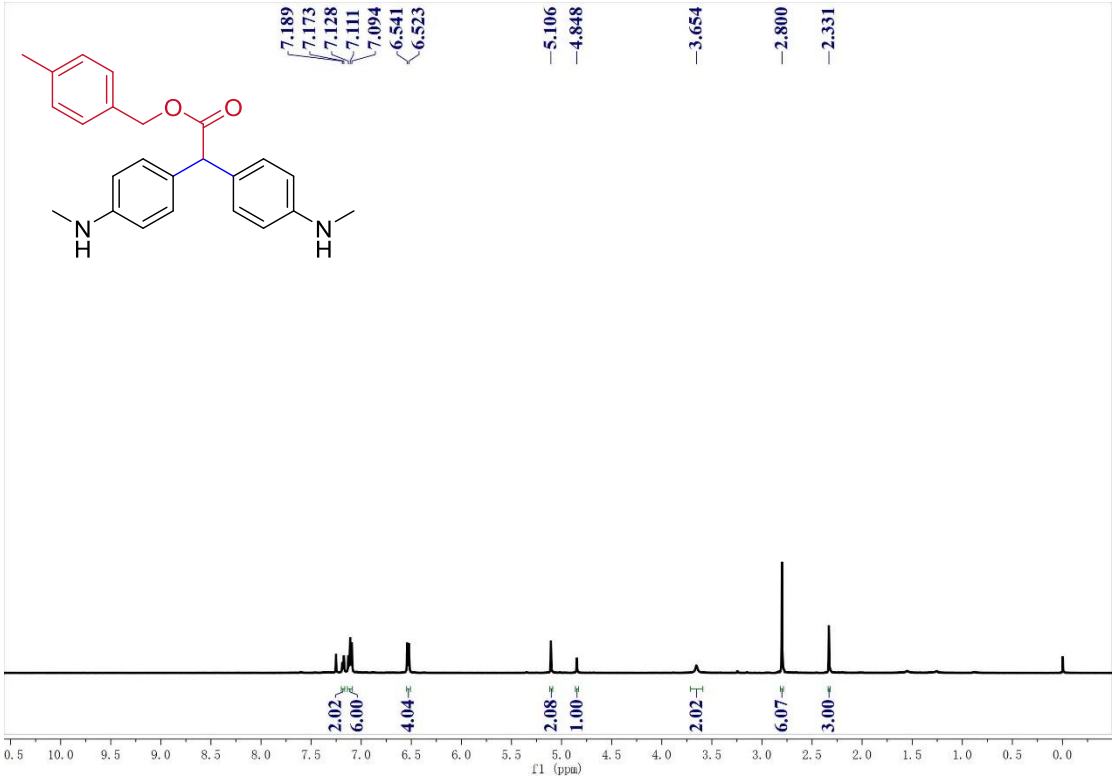

Figure 45. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3ca**

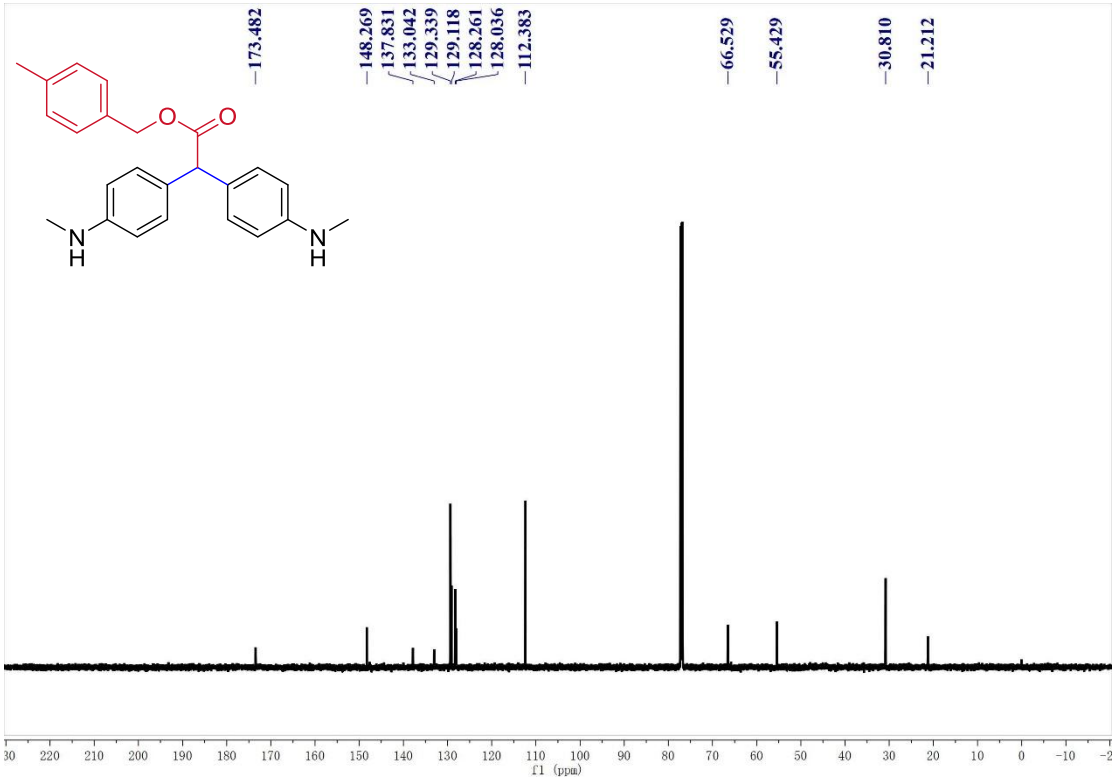

Figure 46. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ca**

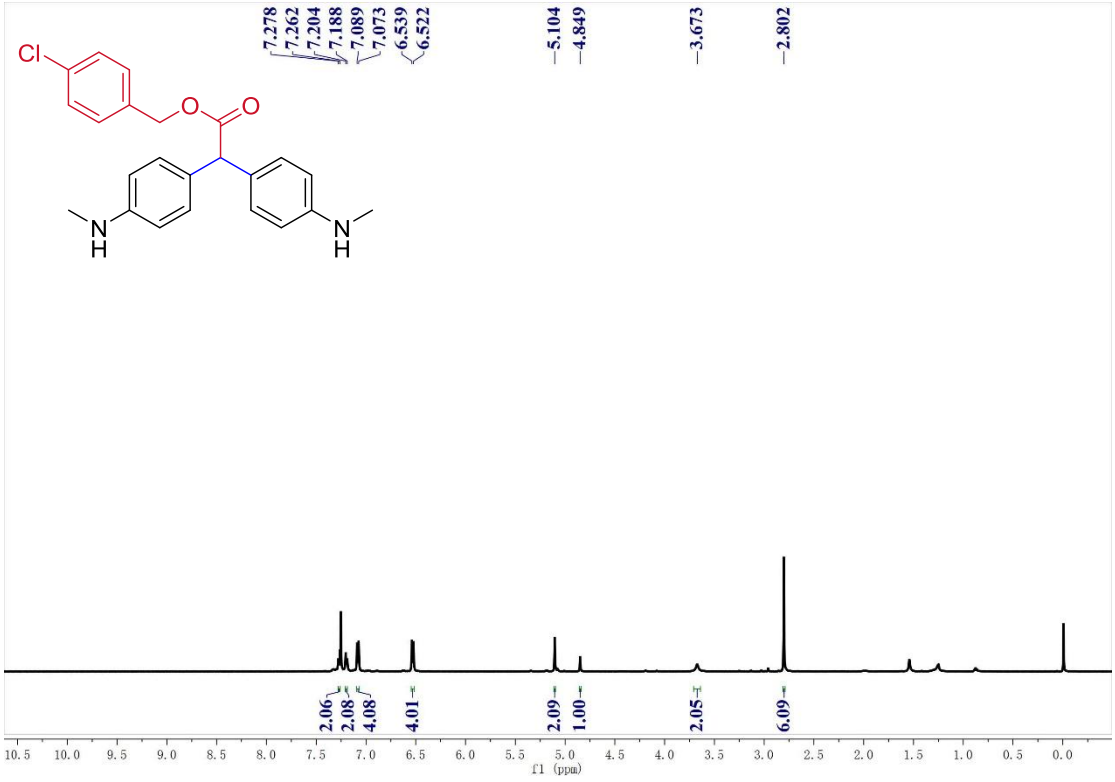

Figure 47. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3da**

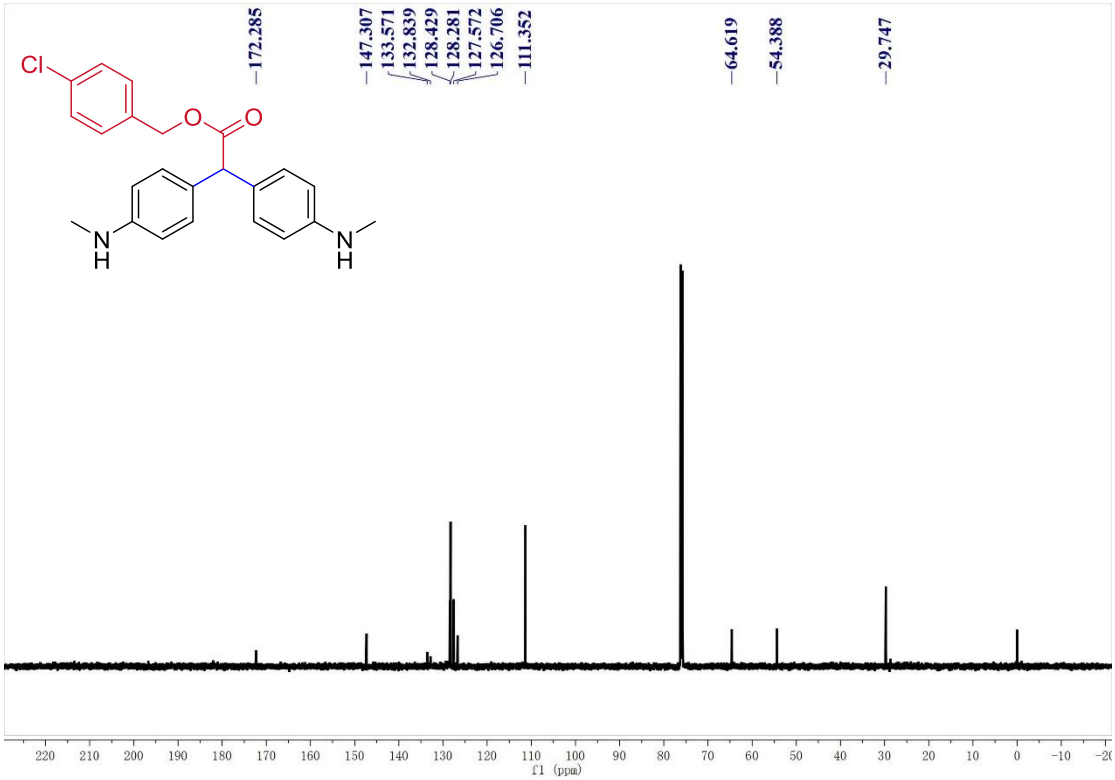

Figure 48. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3da**

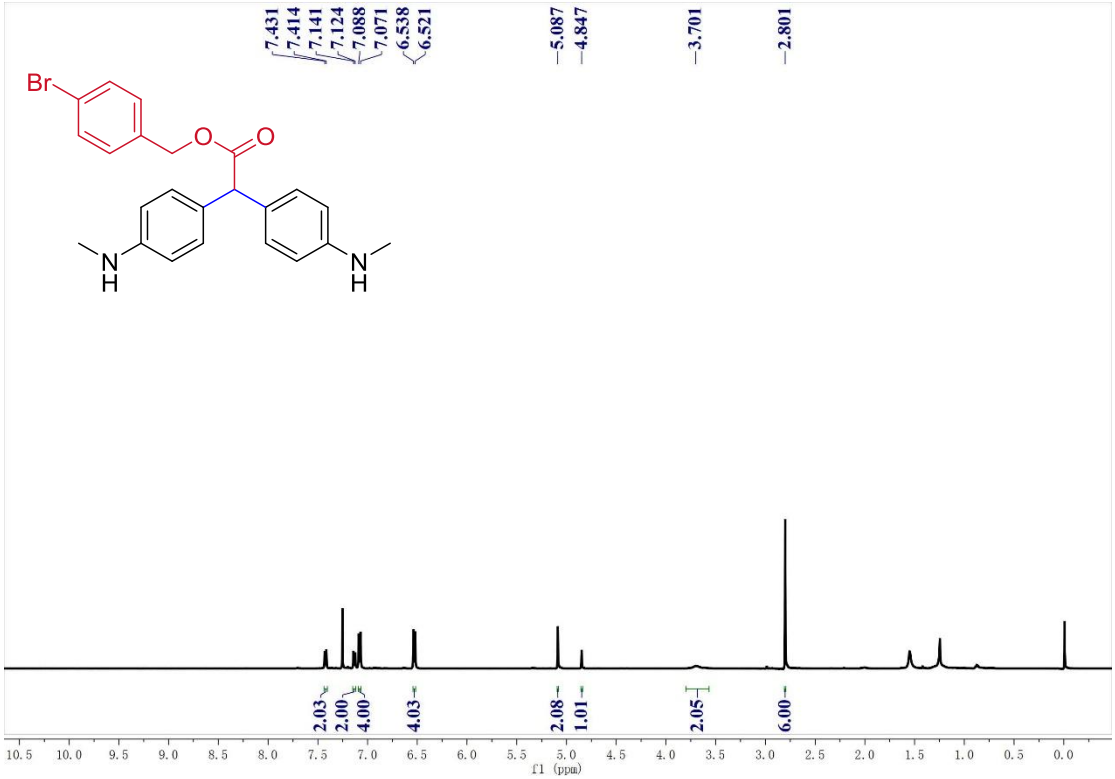

Figure 49. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3ea**

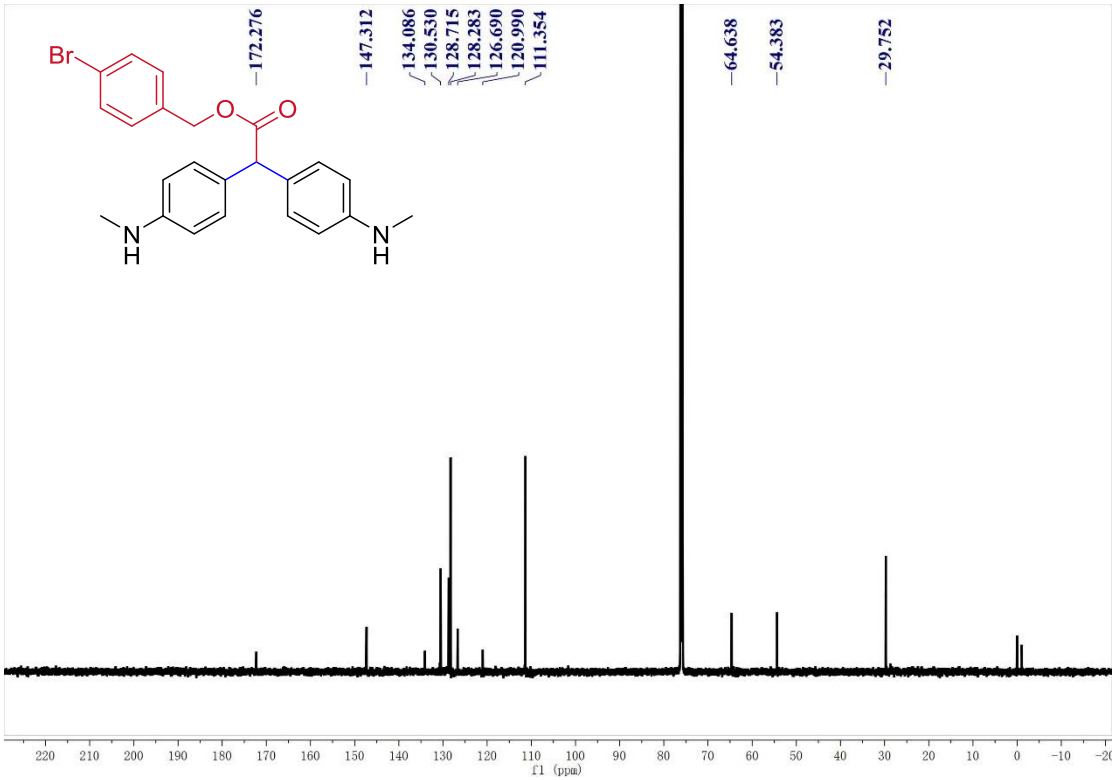

Figure 50. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ea**

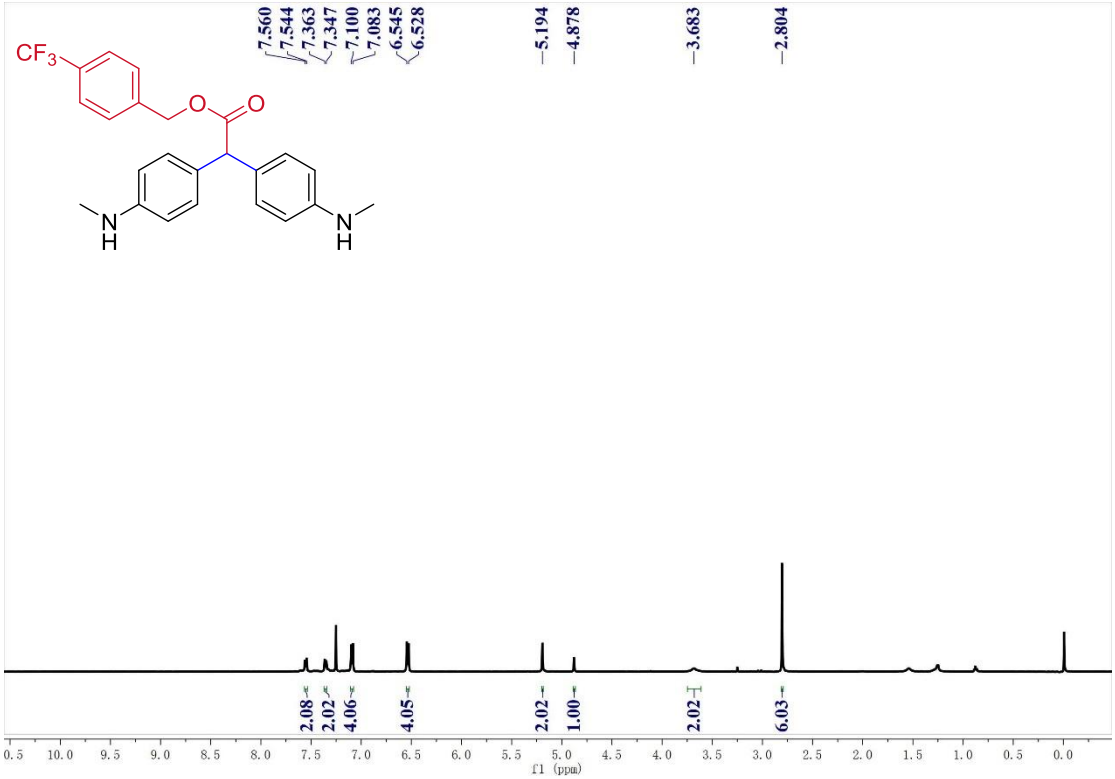

Figure 51. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3fa**

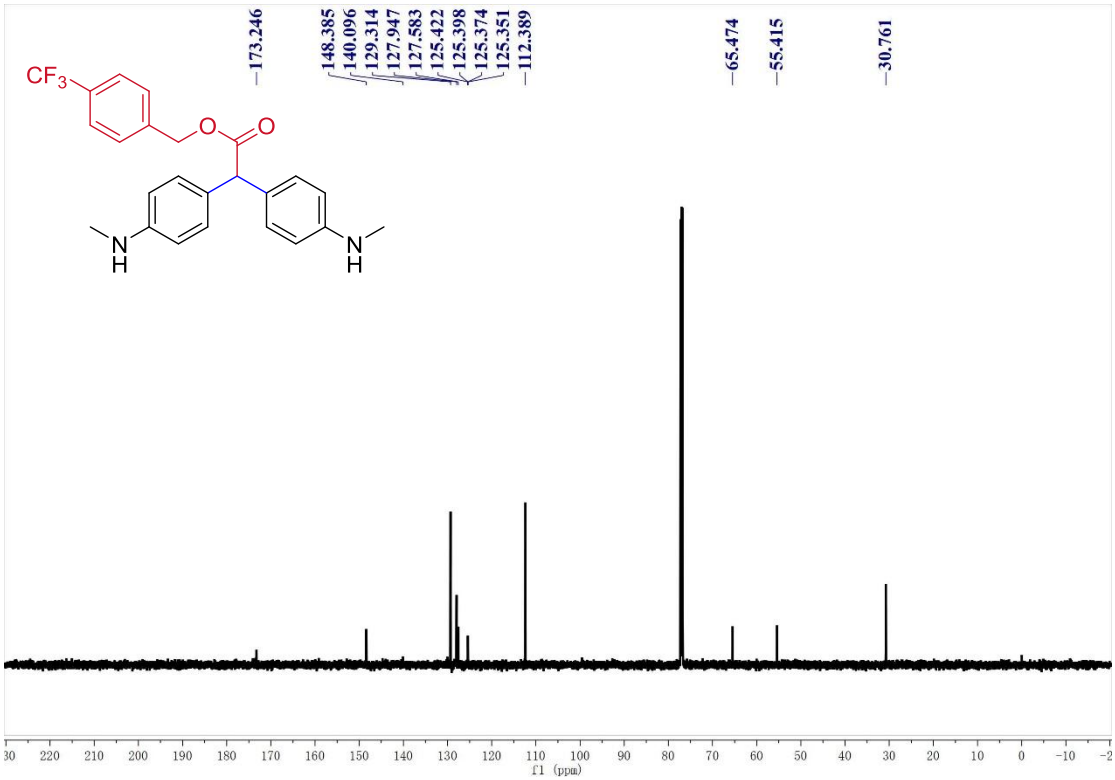

Figure 52. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3fa**

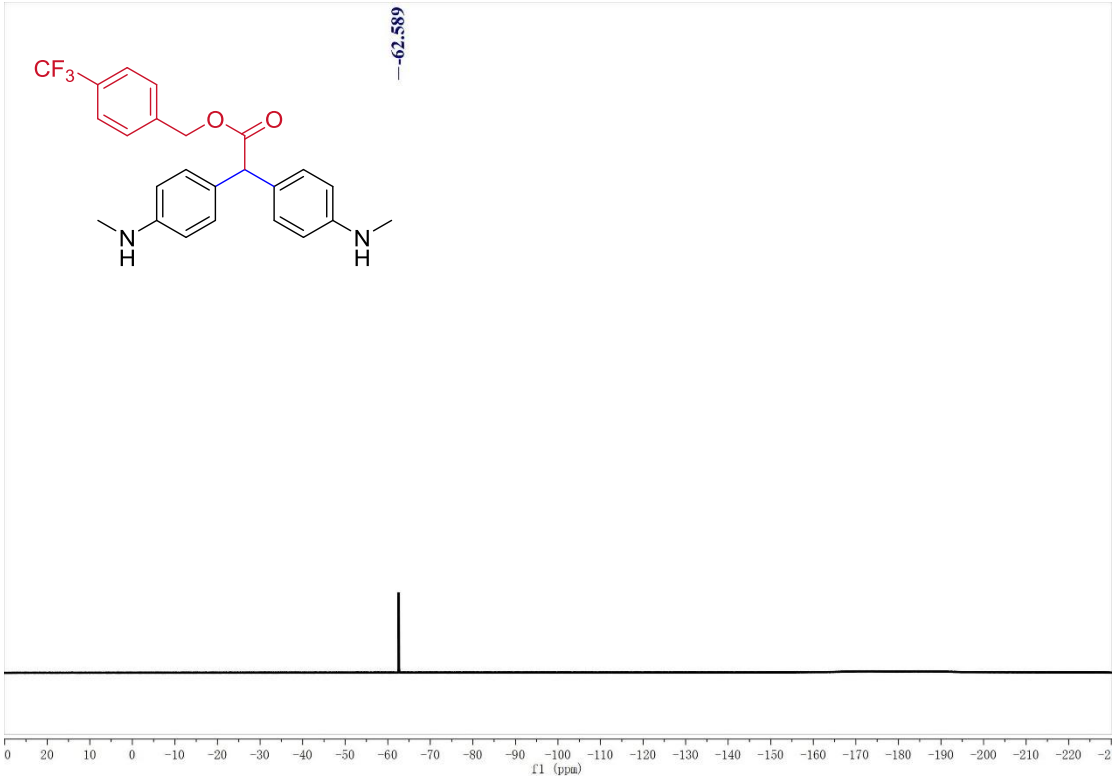

Figure 53. ^{19}F NMR (565 MHz, $CDCl_3$) spectra of compound **3fa**

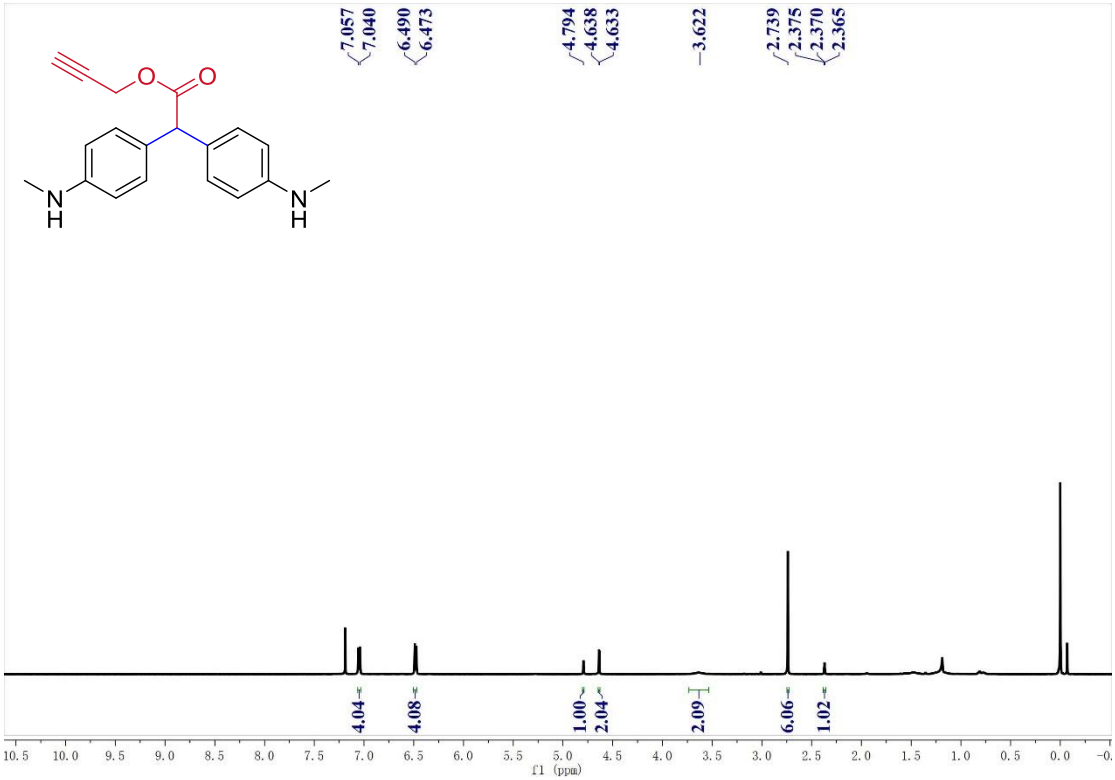

Figure 54. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3ga**

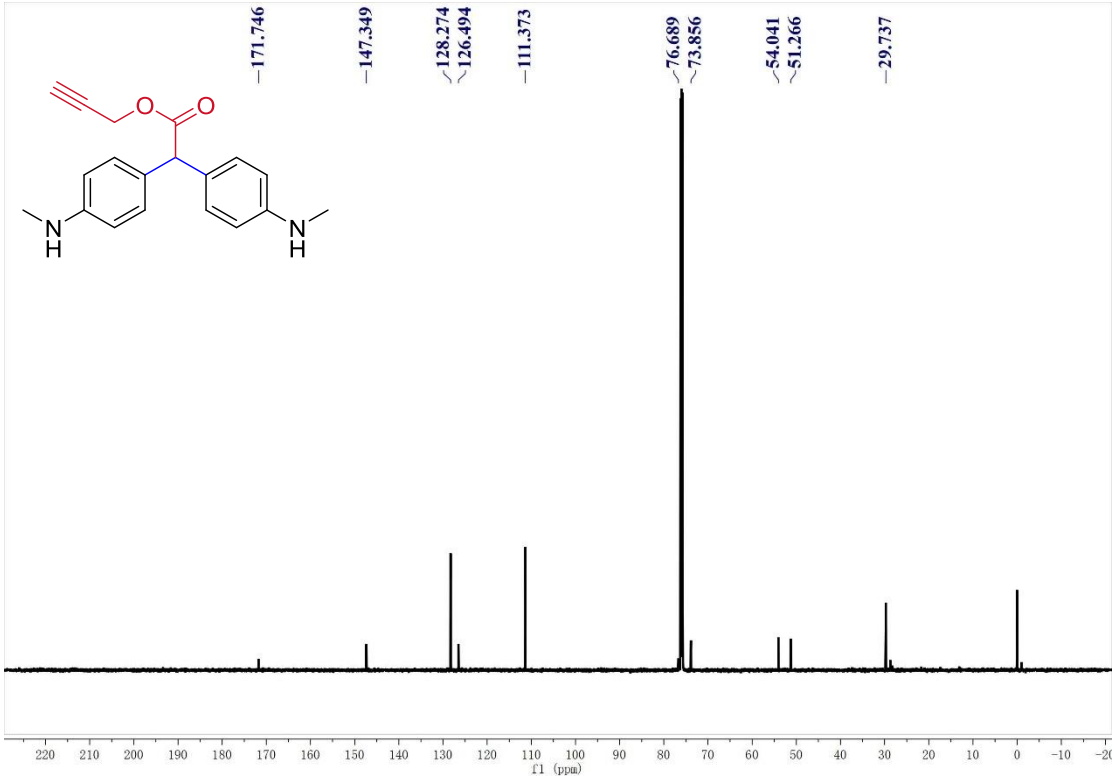

Figure 55. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ga**

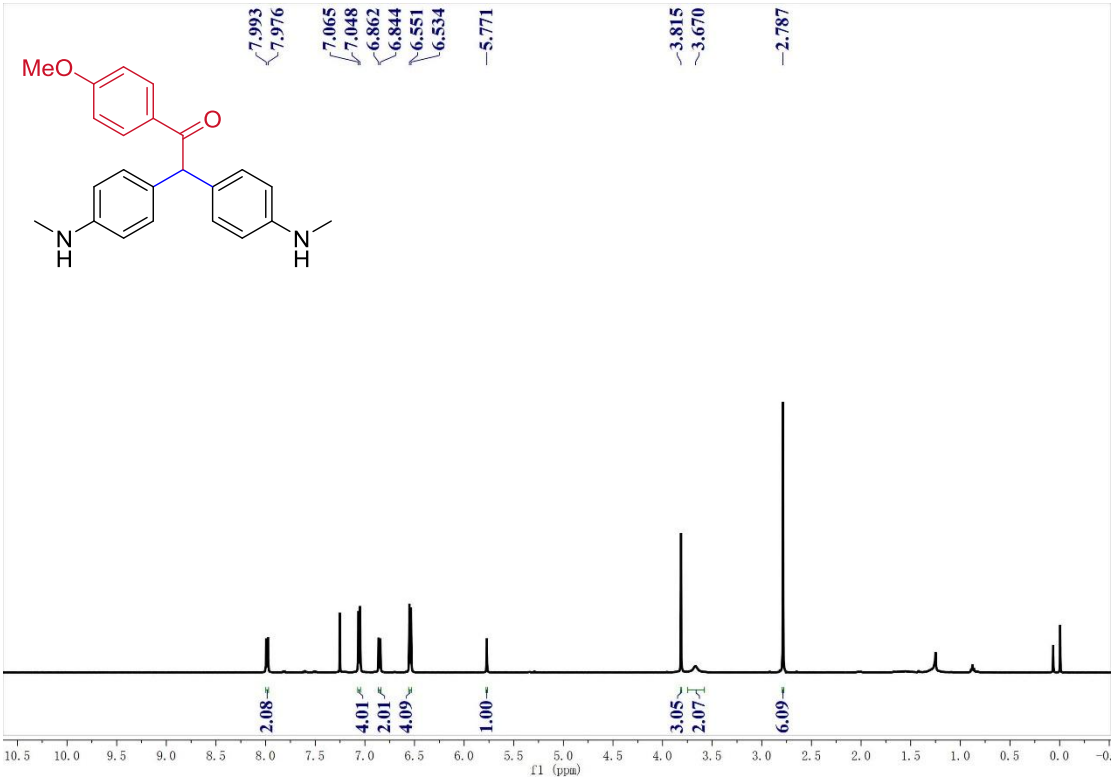

Figure 56. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3ha**

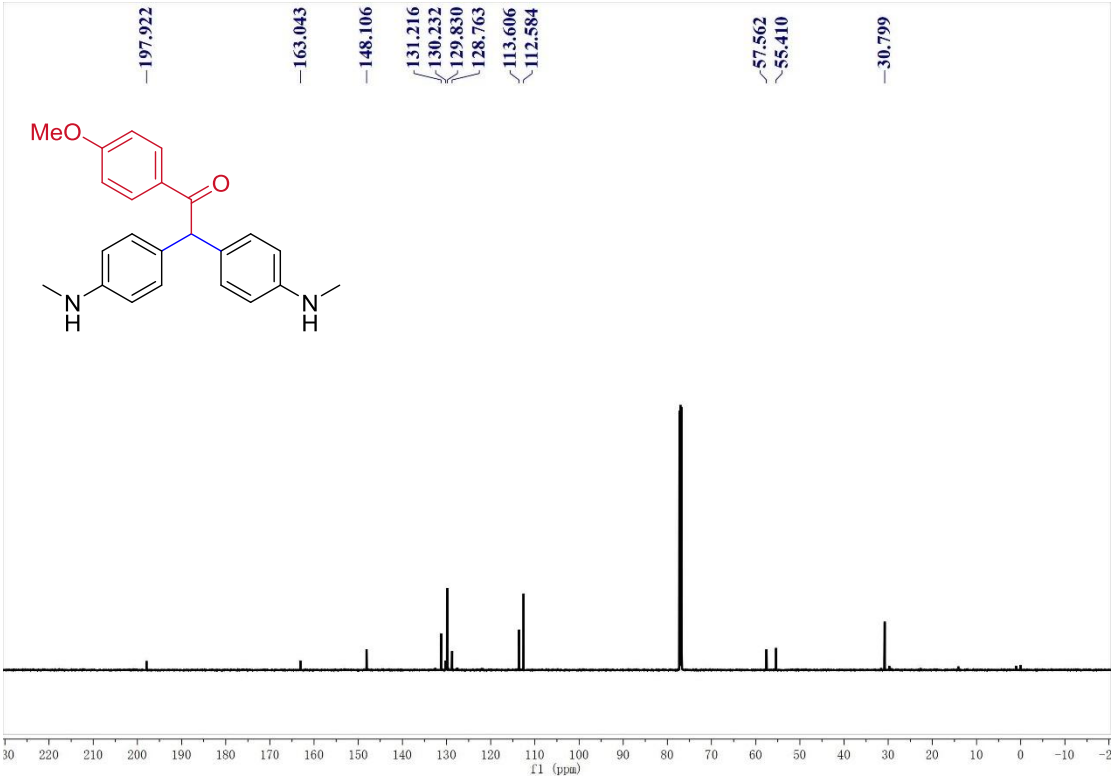

Figure 57. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ha**

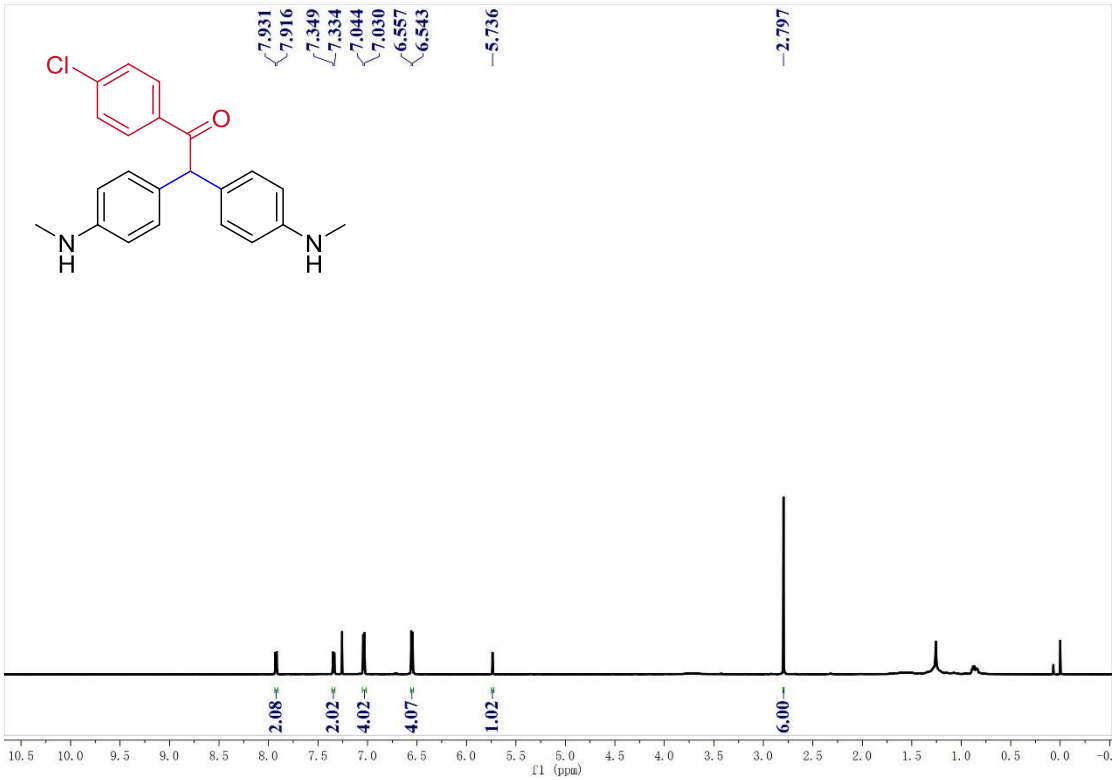

Figure 58. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3ia**

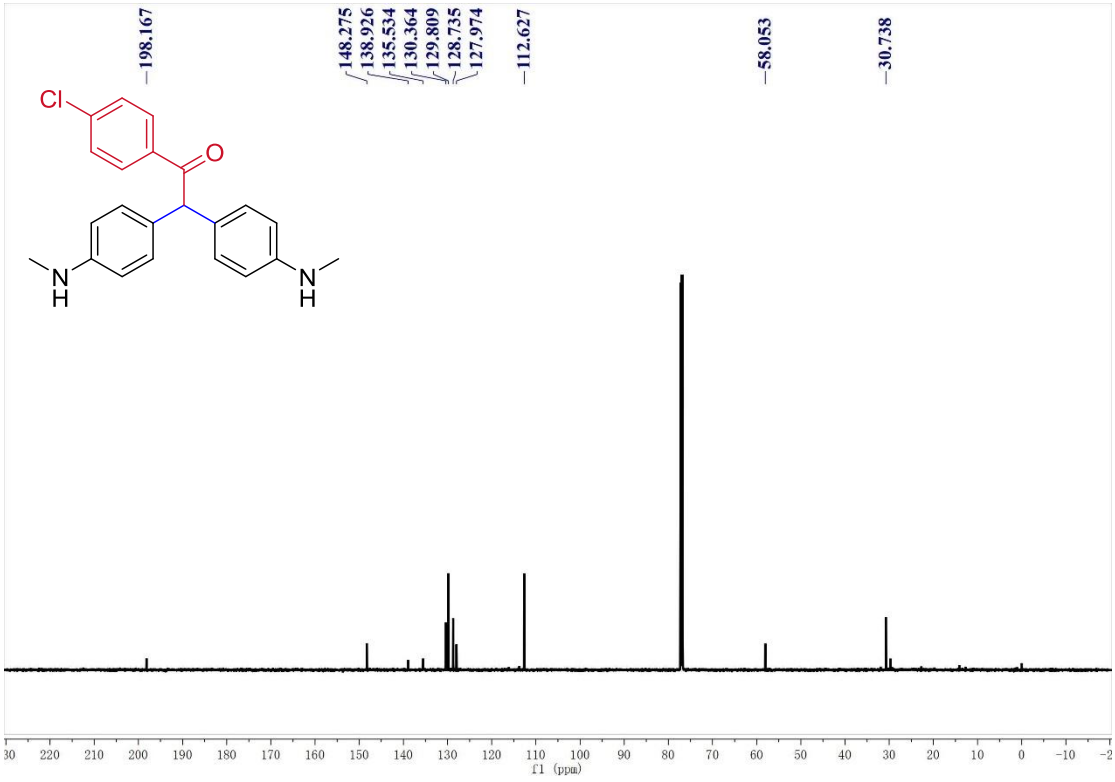

Figure 59. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3ia**

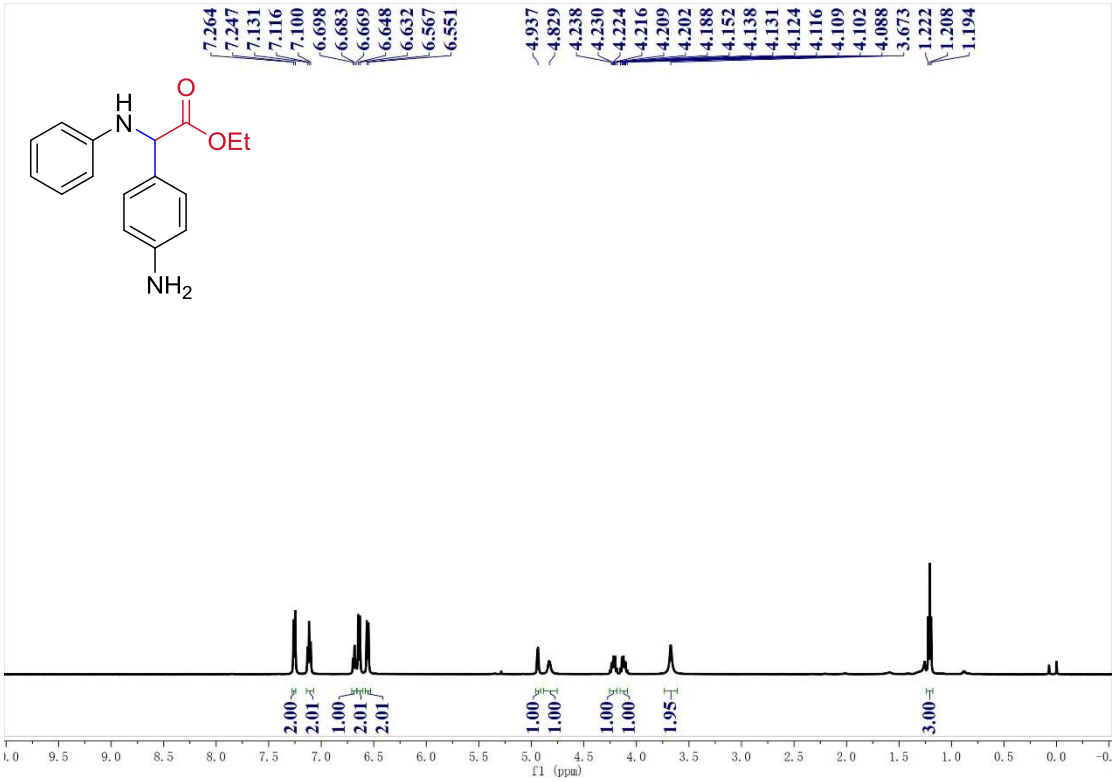

Figure 60. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **4a**

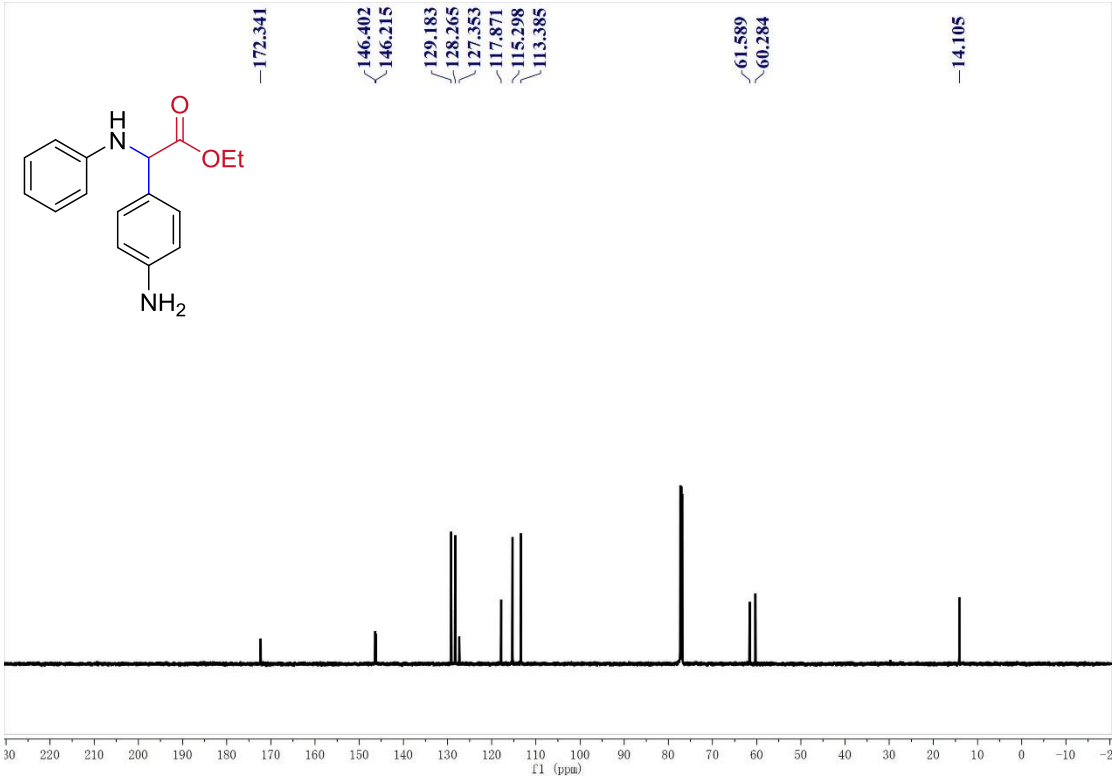

Figure 61. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **4a**

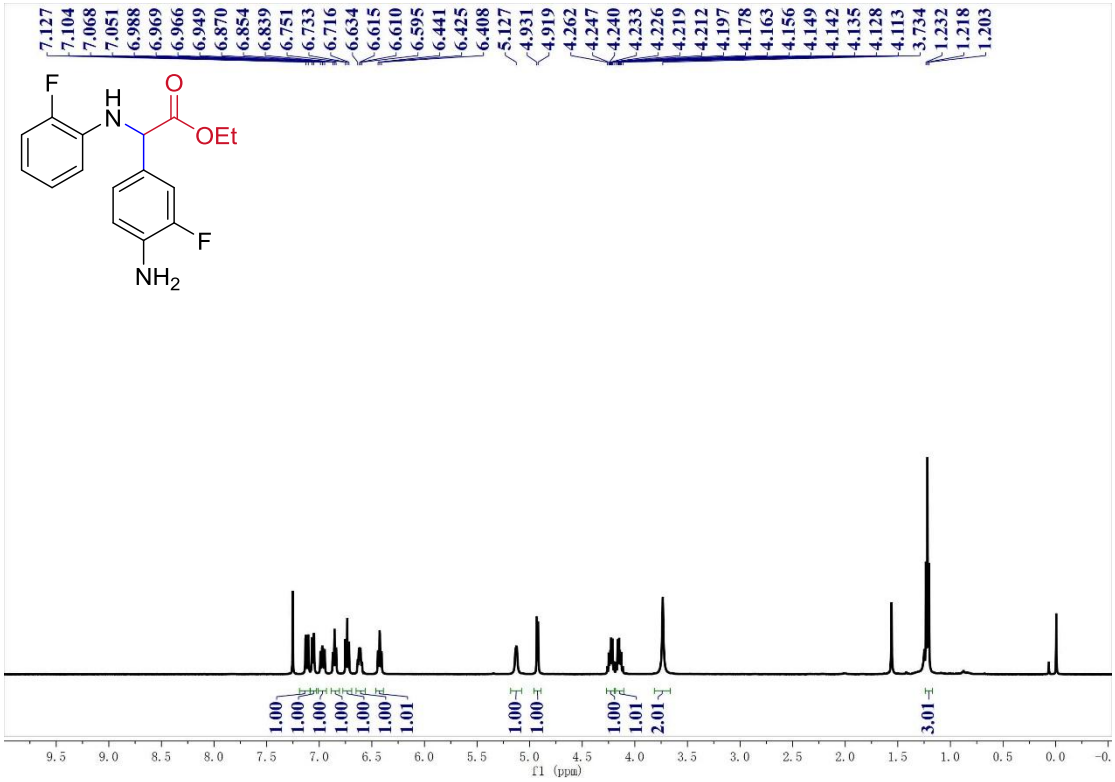

Figure 62. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **4b**

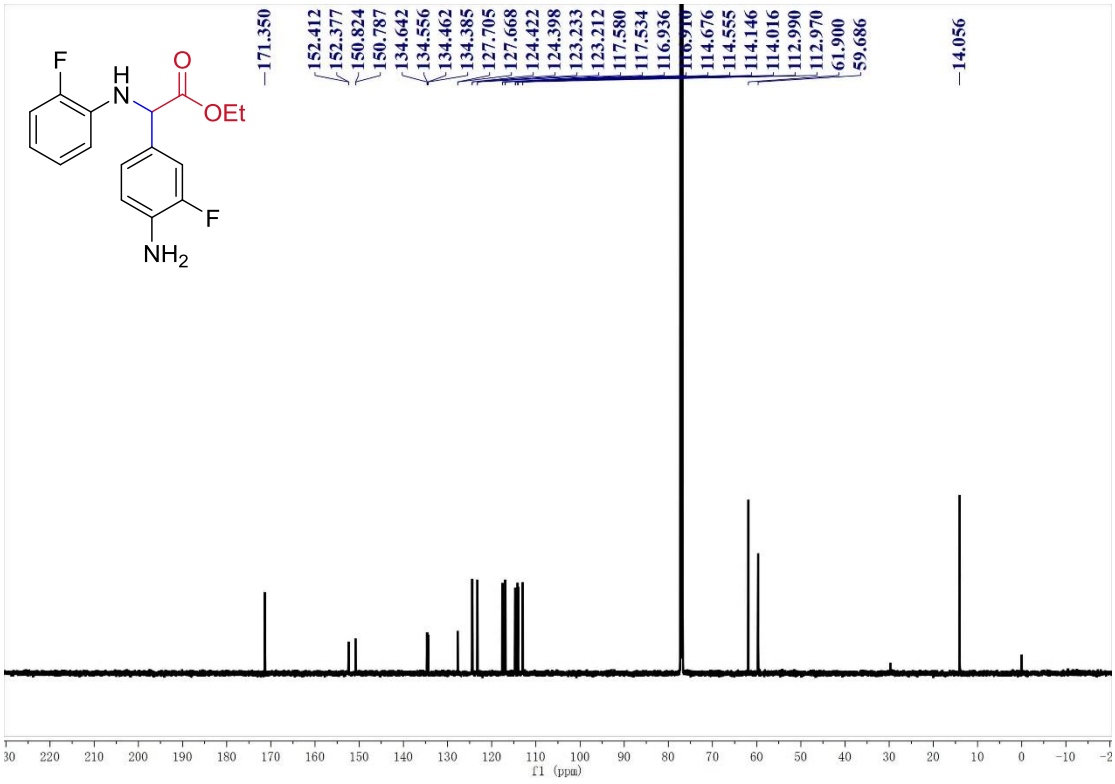

Figure 63. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **4b**

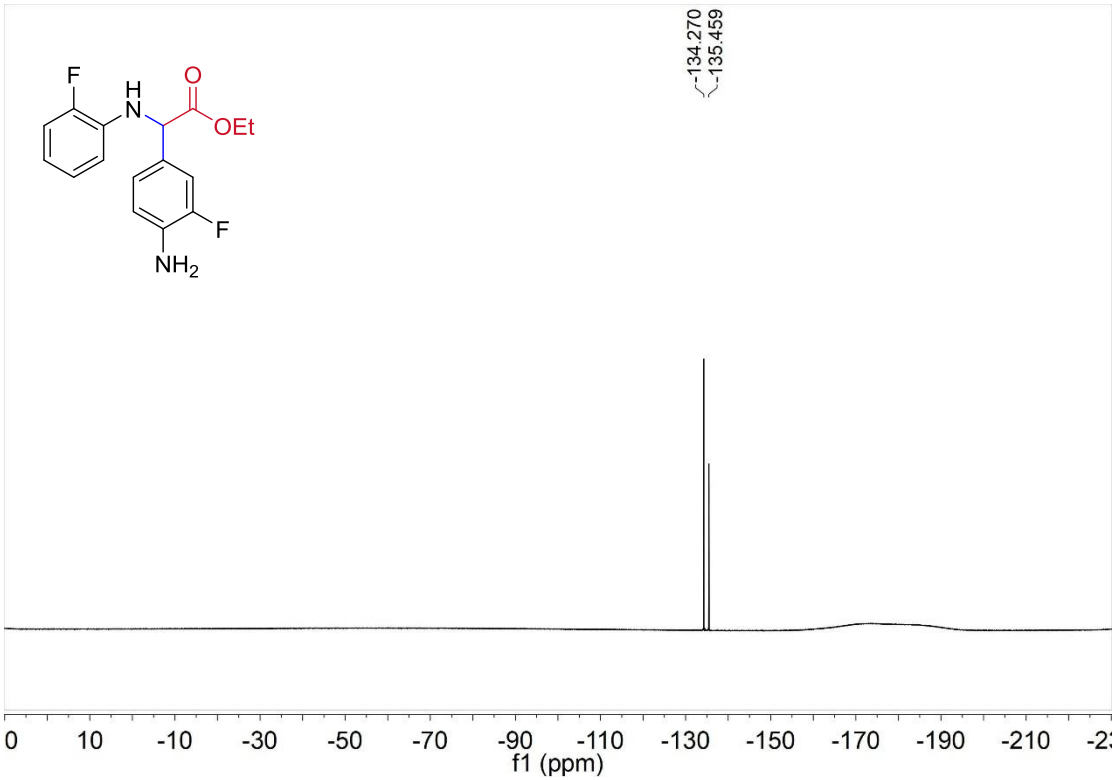

Figure 64. ^{19}F NMR (565 MHz, $CDCl_3$) spectra of compound **4b**

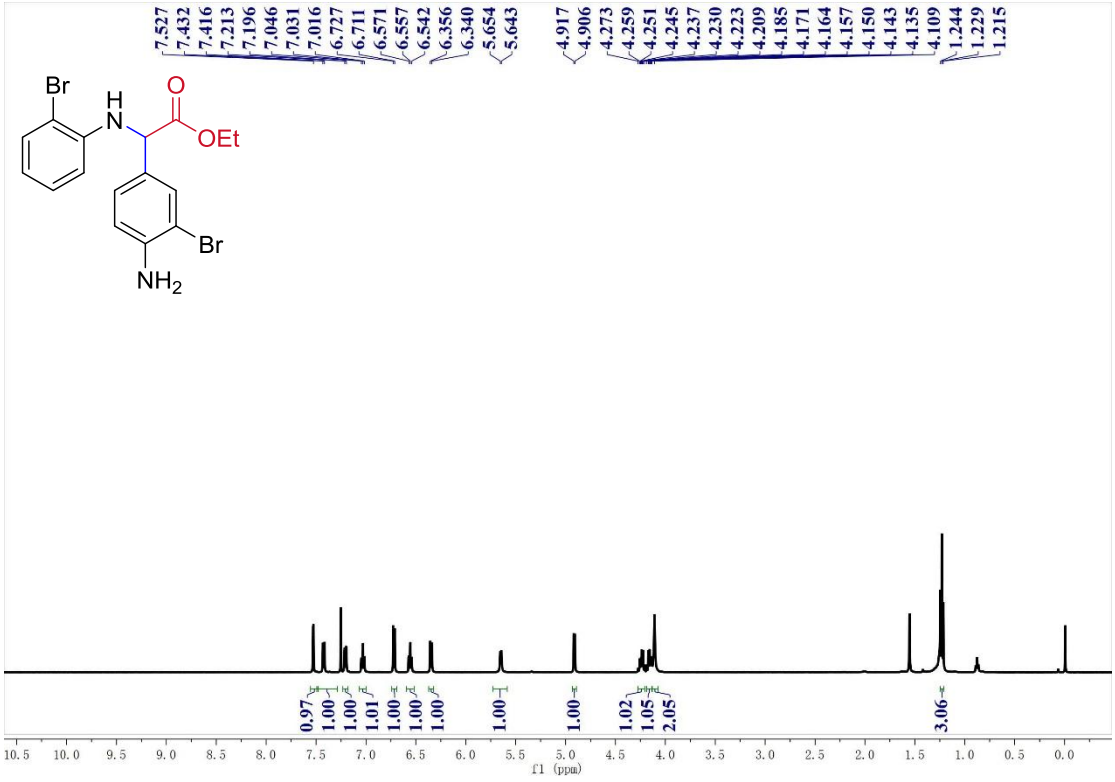

Figure 65. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **4c**

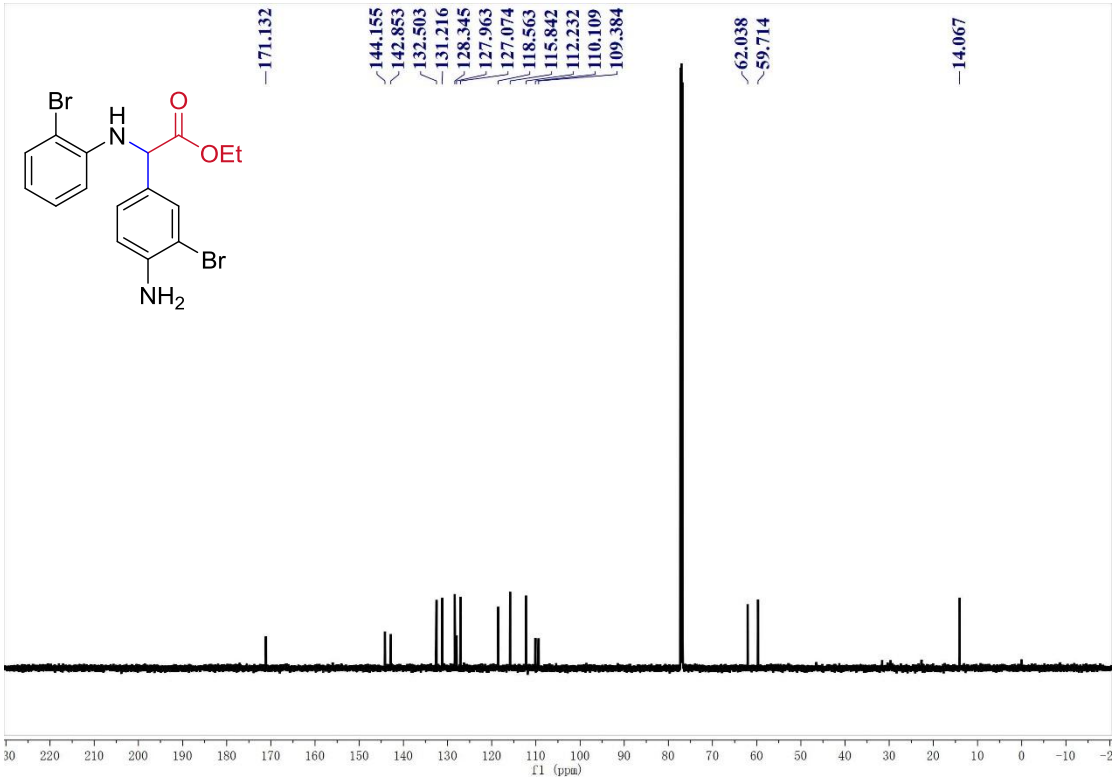

Figure 66. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **4c**

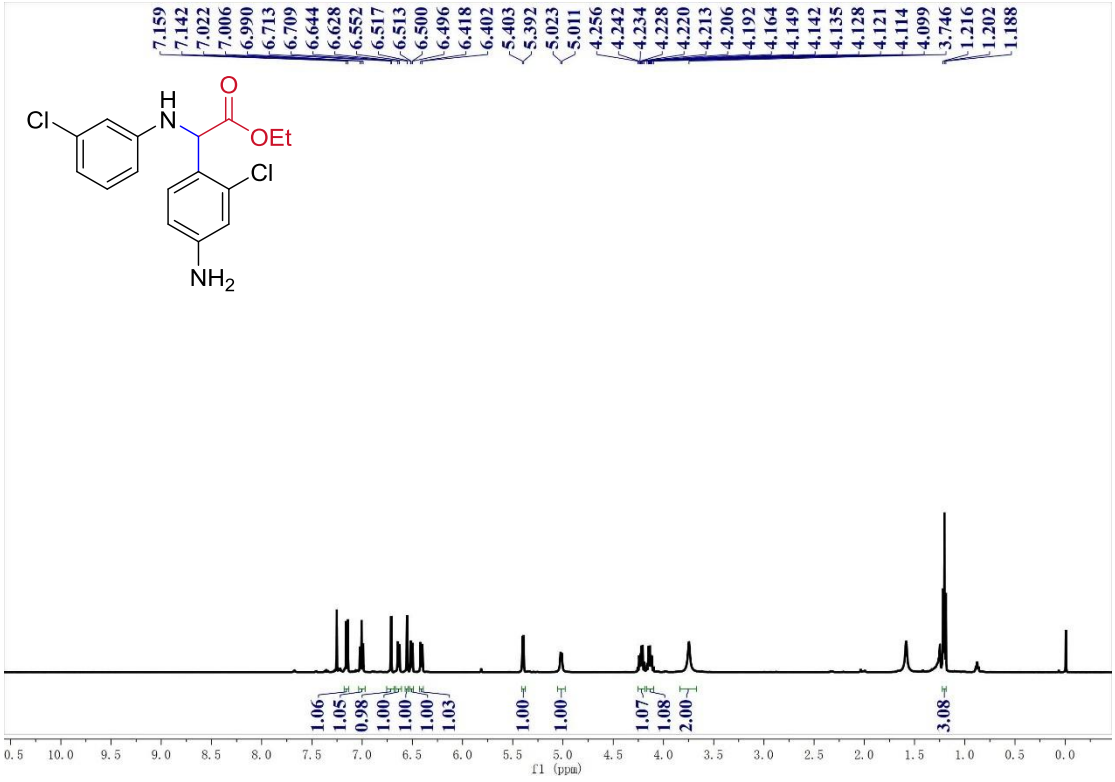

Figure 67. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **4d**

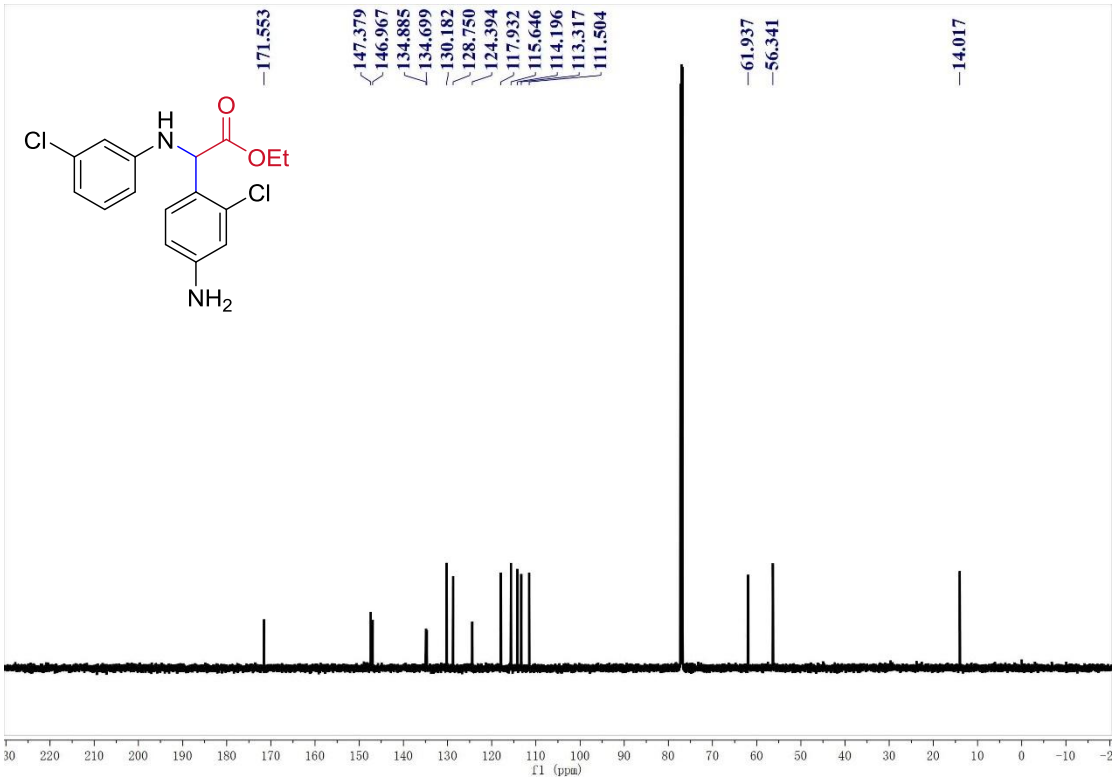

Figure 68. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **4d**

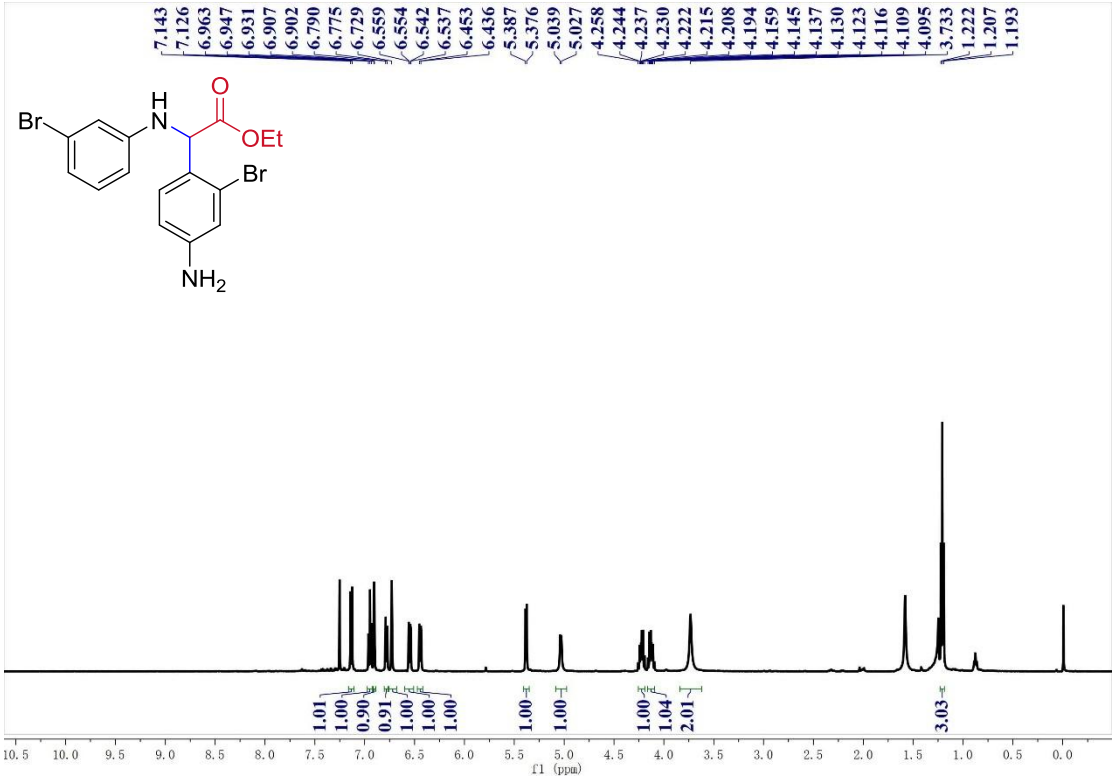

Figure 69. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **4e**

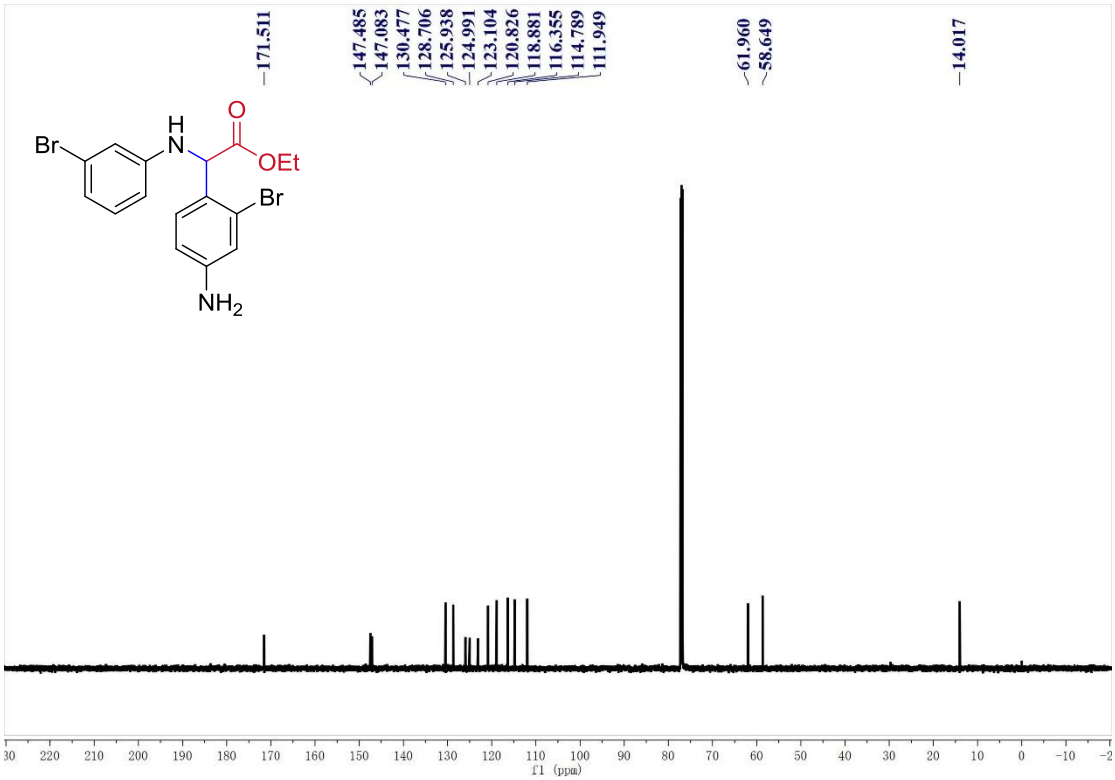

Figure 70. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **4e**

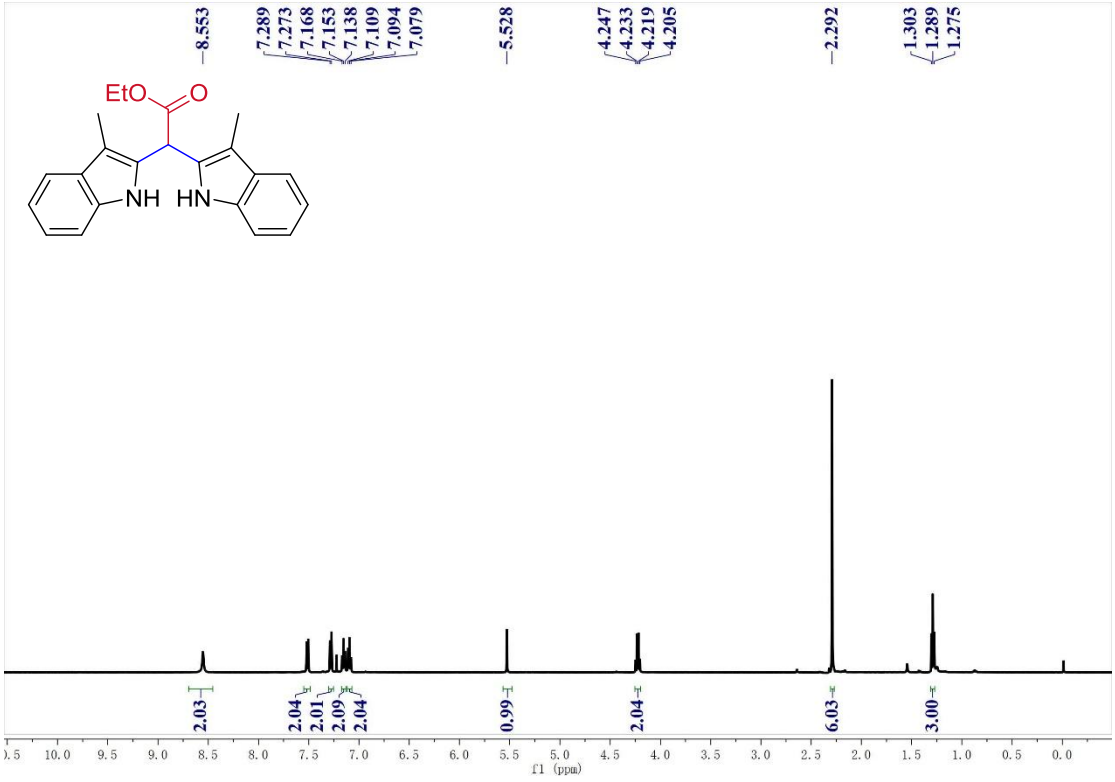

Figure 71. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **6a**

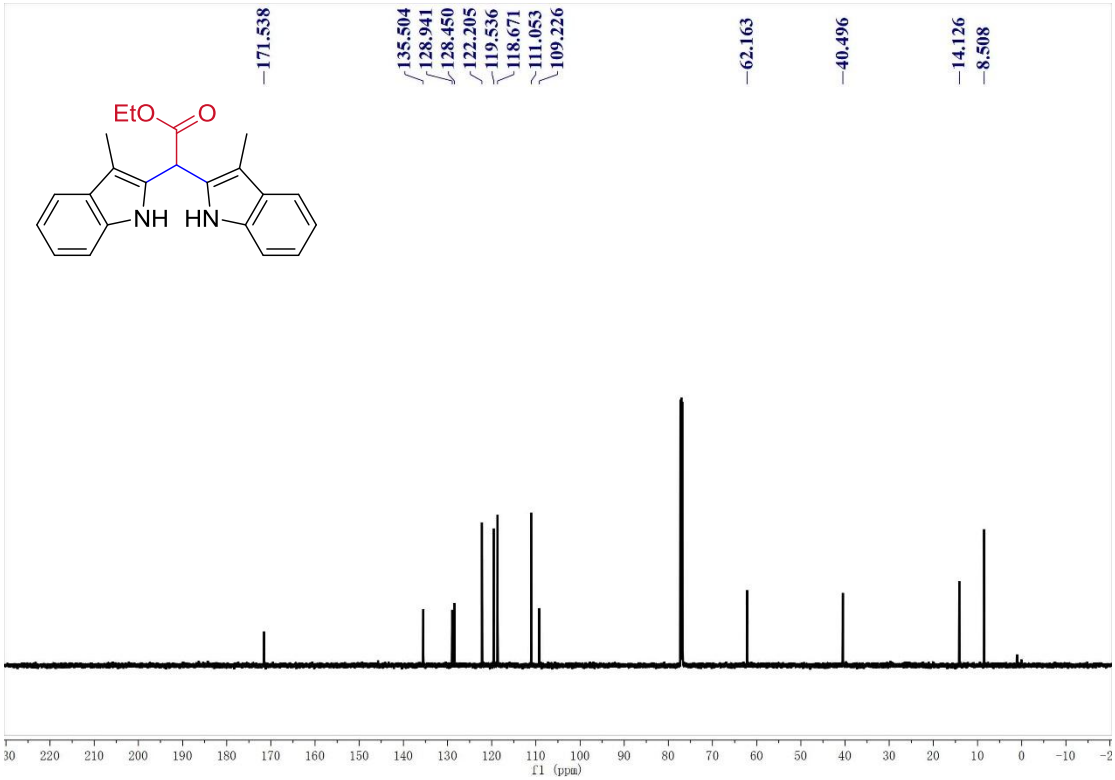

Figure 72. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **6a**

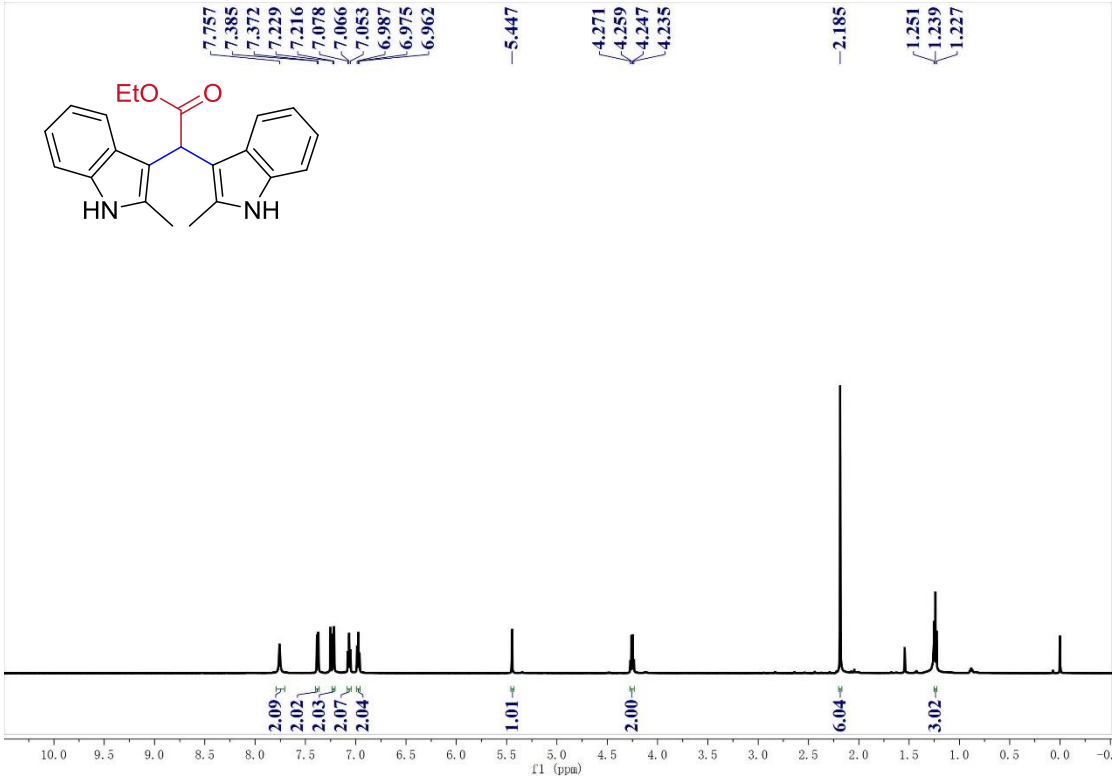

Figure 73. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **6b**

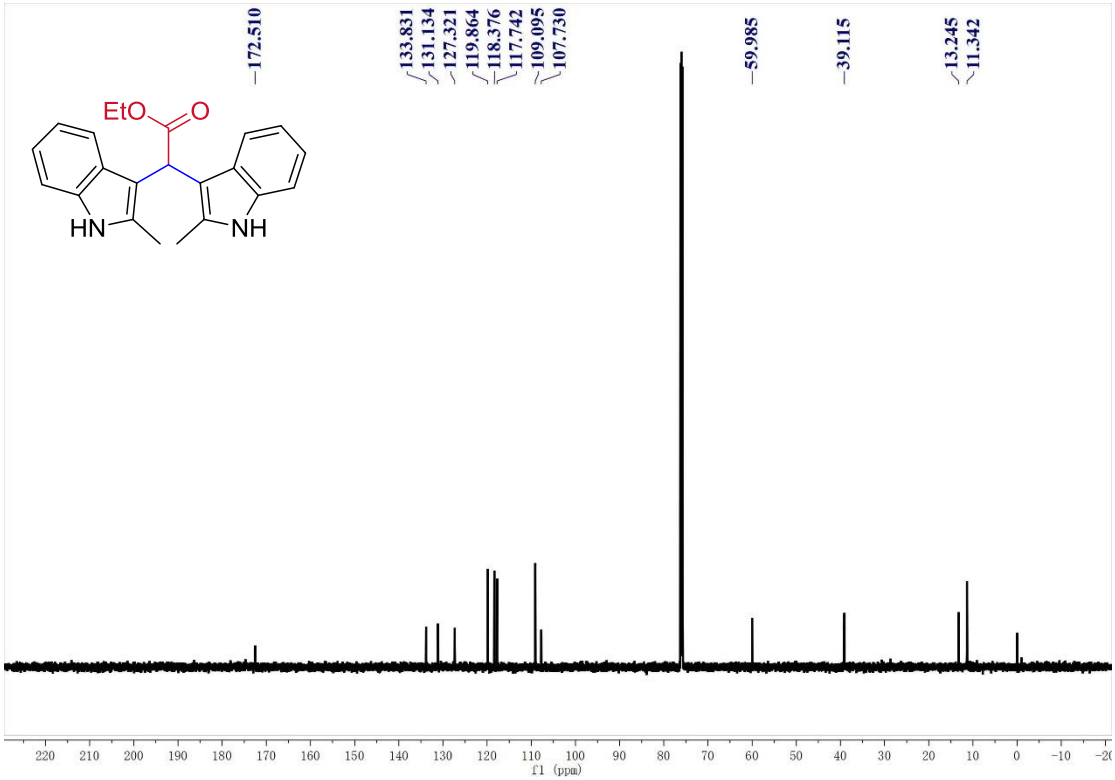

Figure 74. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **6b**

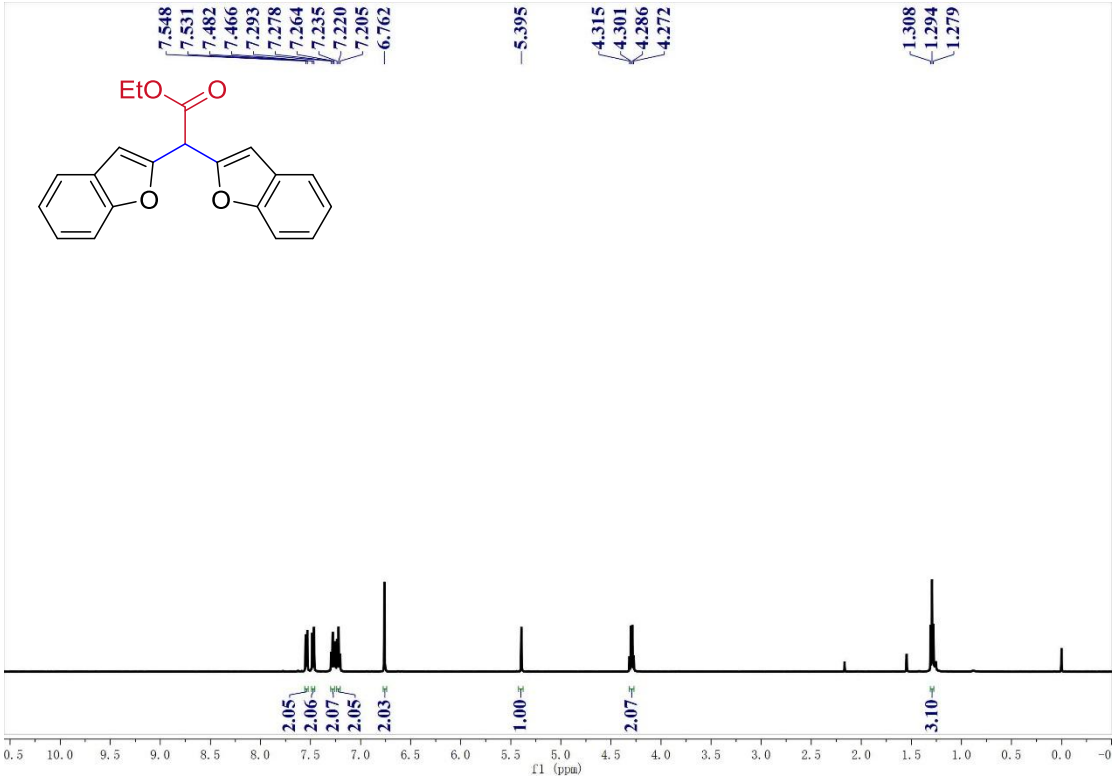

Figure 75. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **6c**

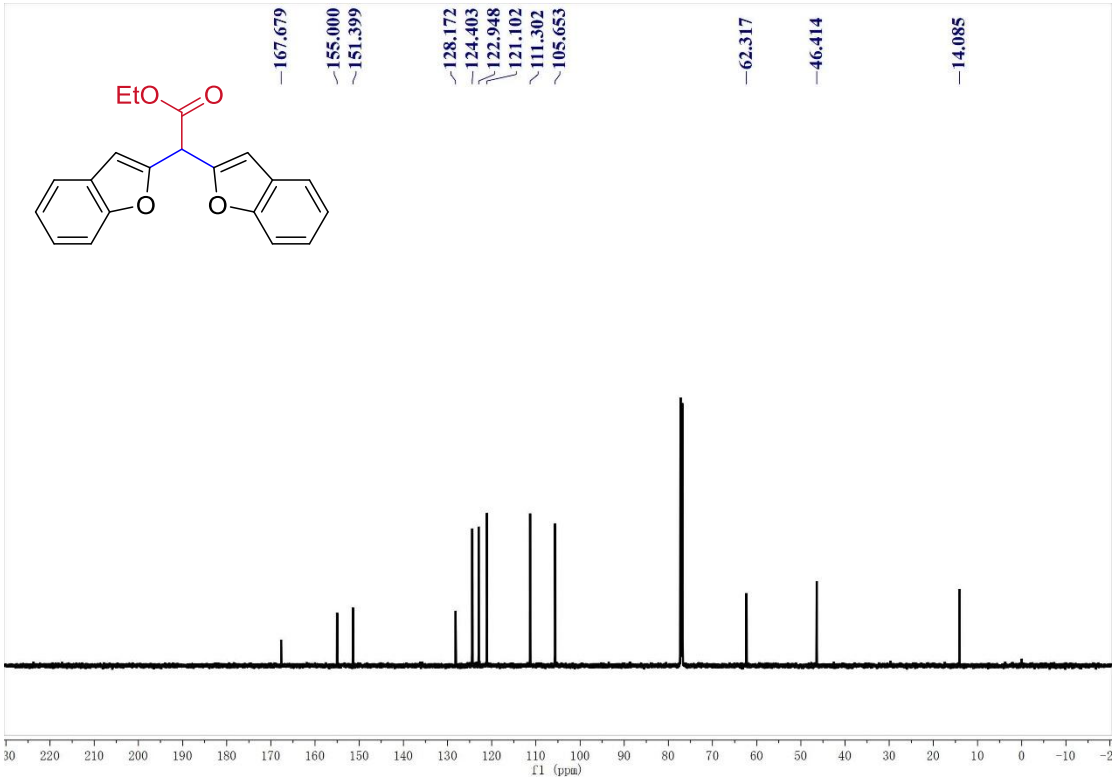

Figure 76. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **6c**

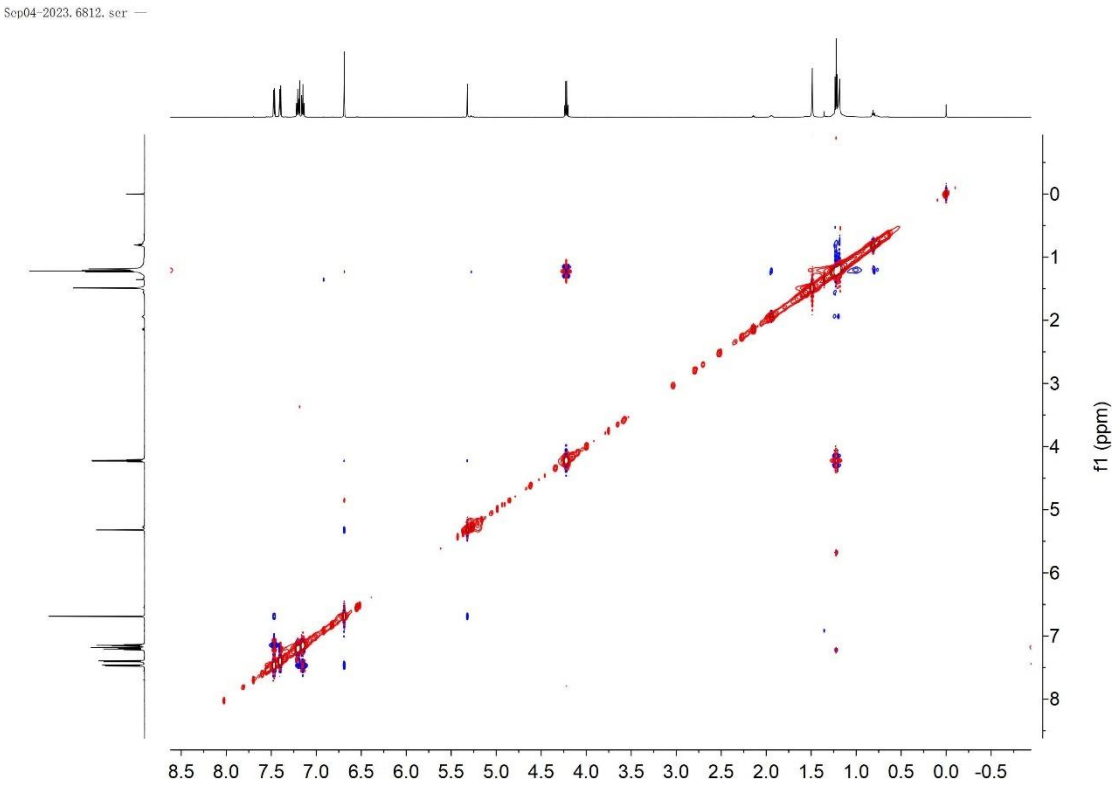

Figure 77. NOESY spectra of compound **6c**

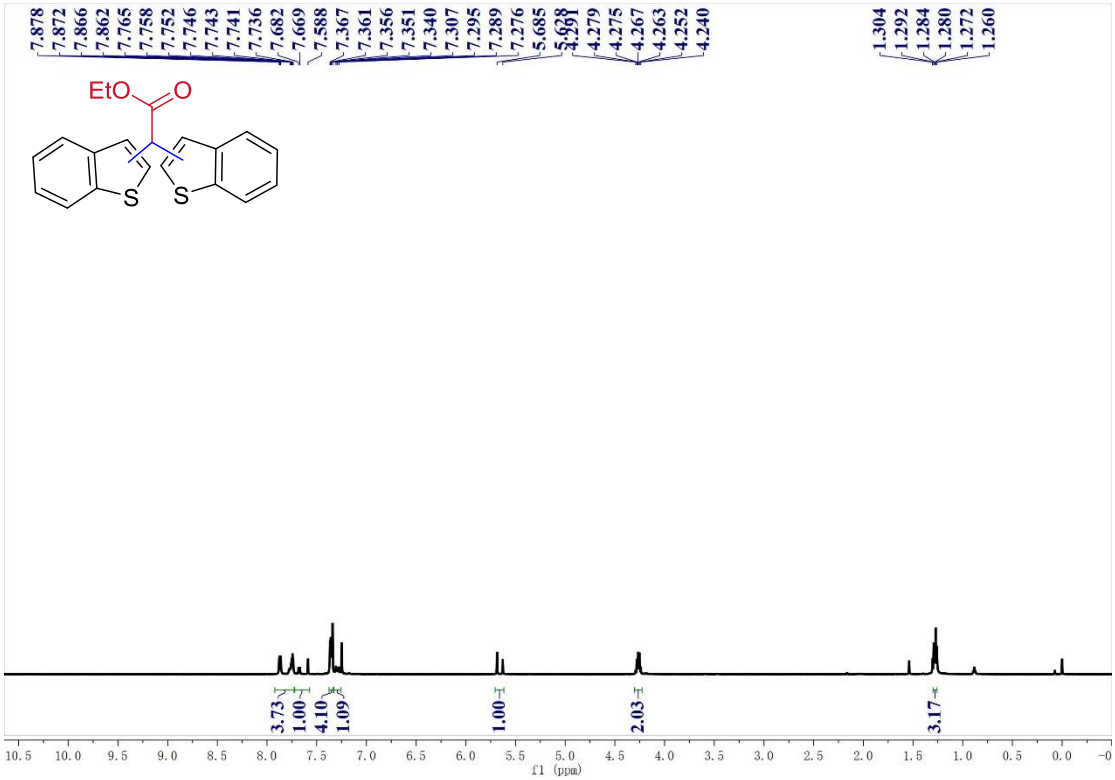

Figure 78. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **6d**

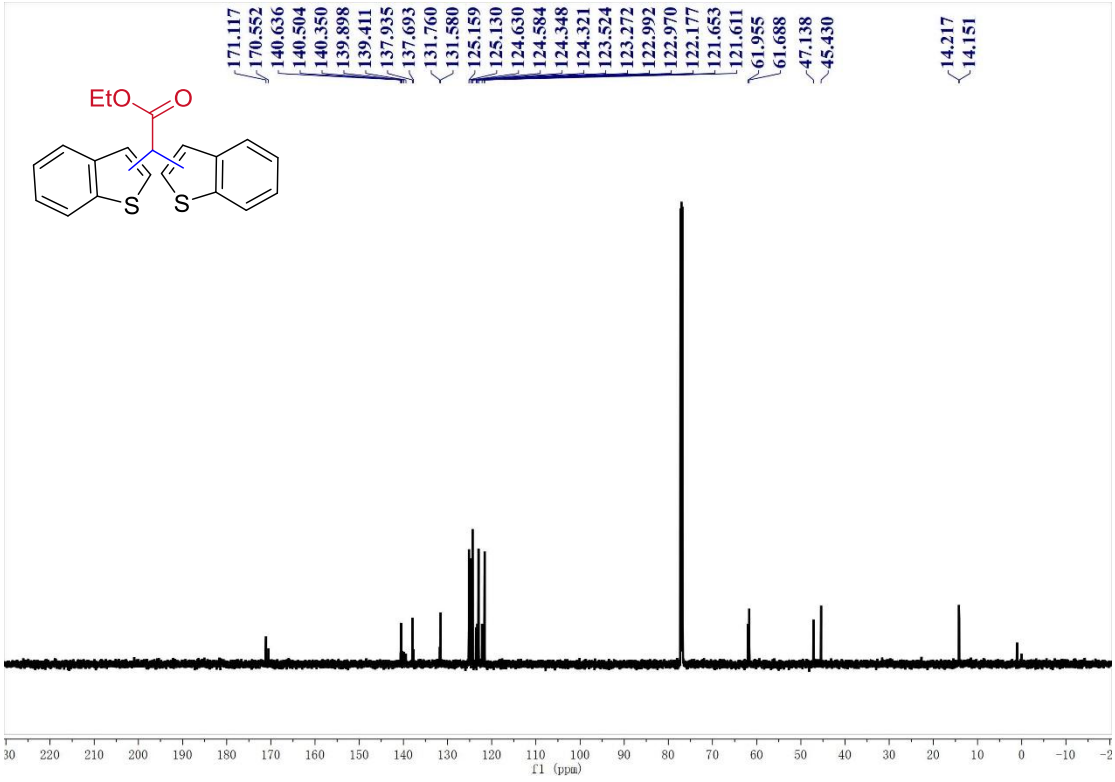

Figure 79. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **6d**

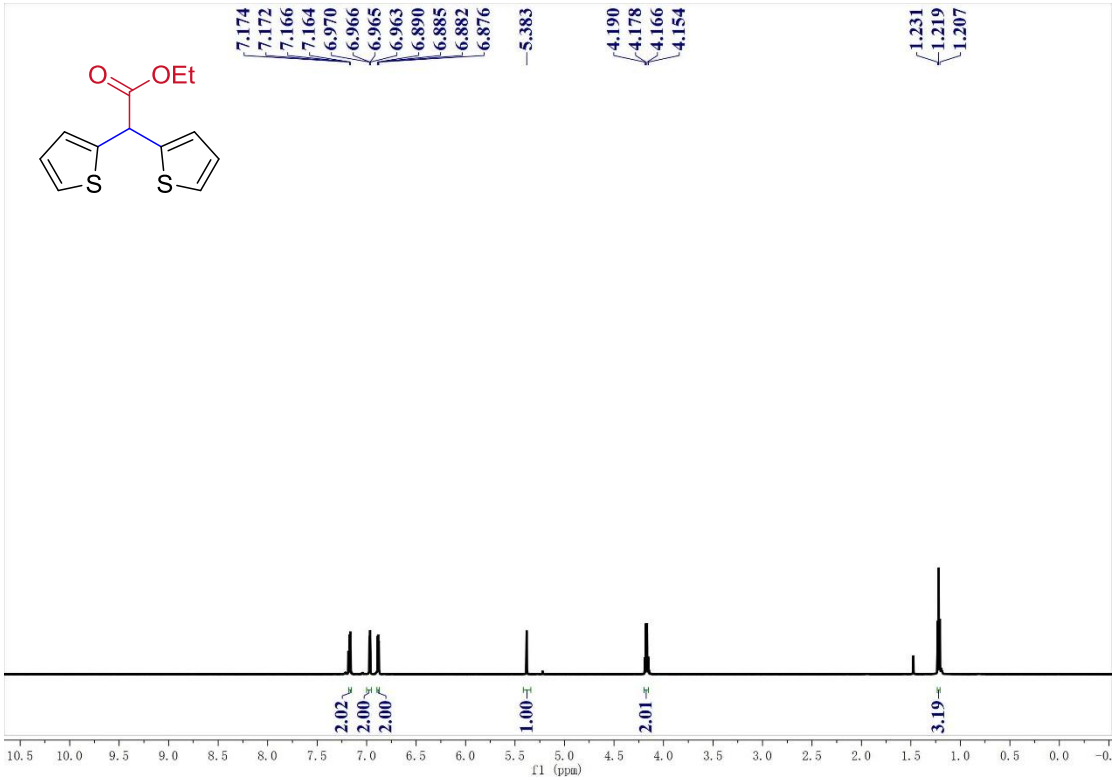

Figure 80. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **6e**

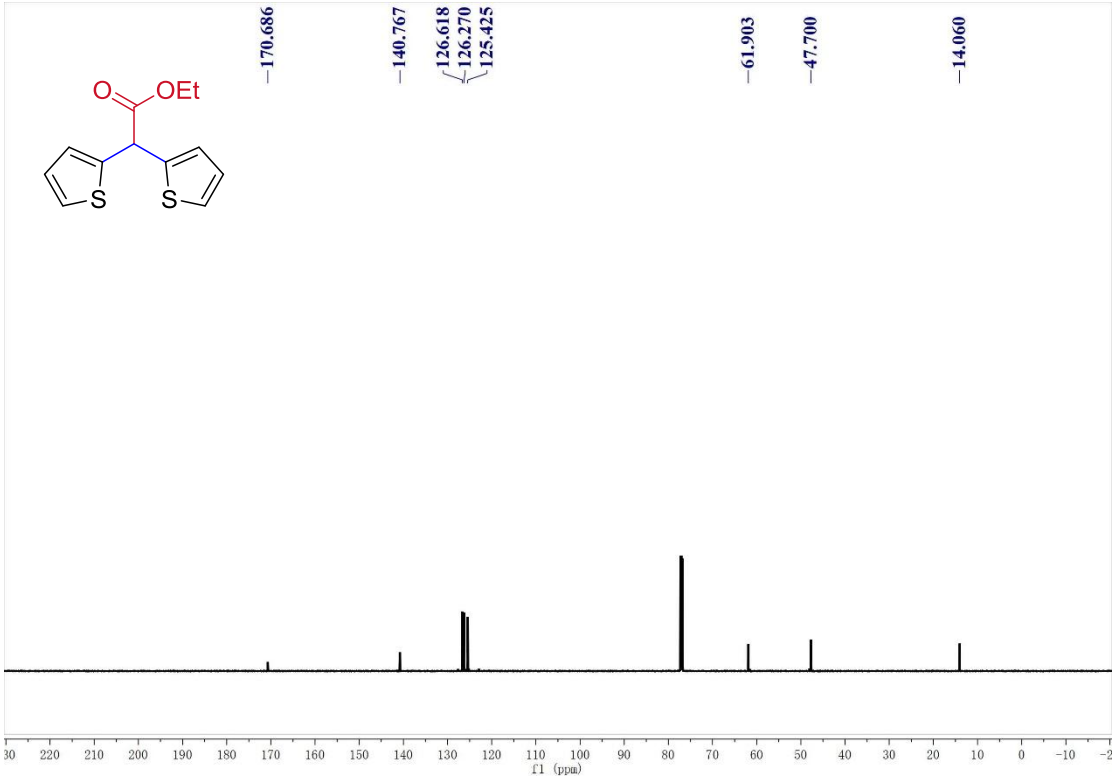

Figure 81. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **6e**

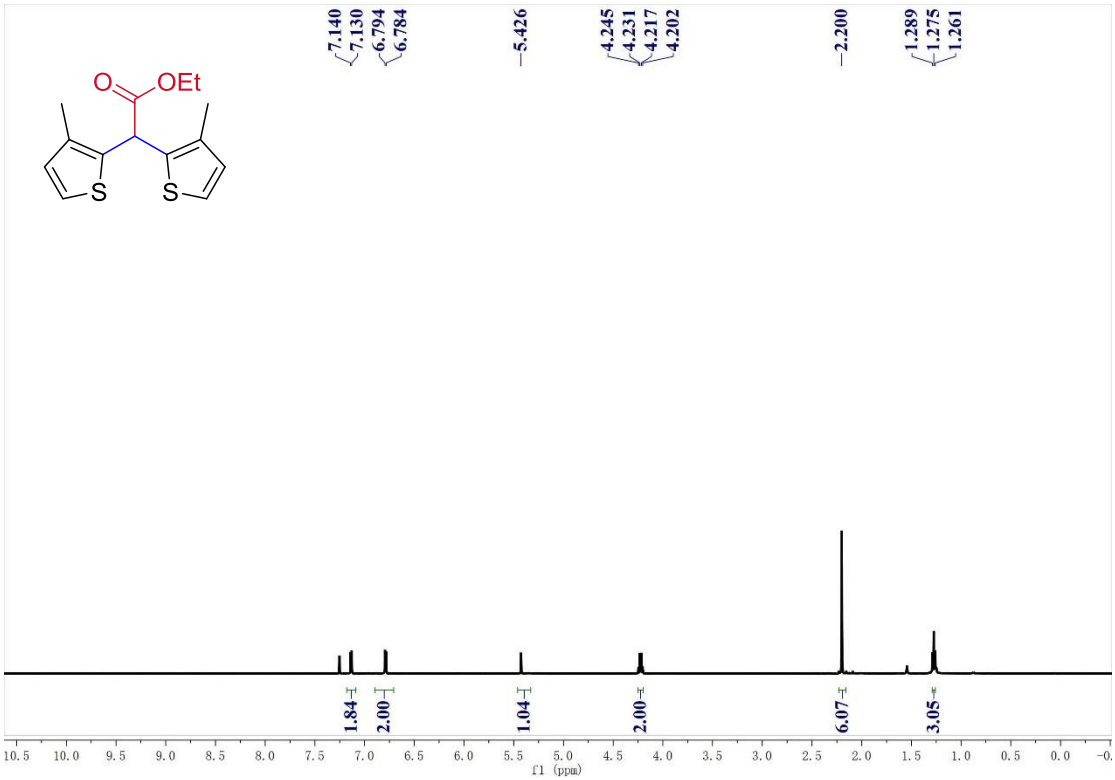

Figure 82. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **6f**

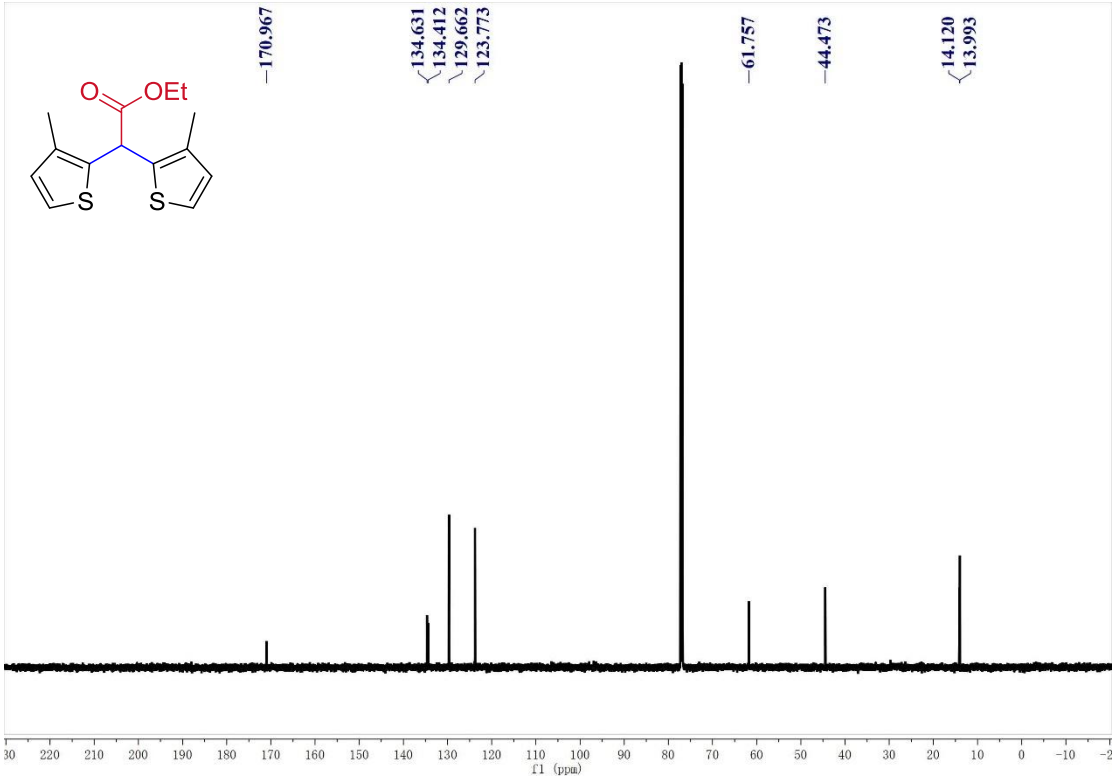

Figure 83. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **6f**

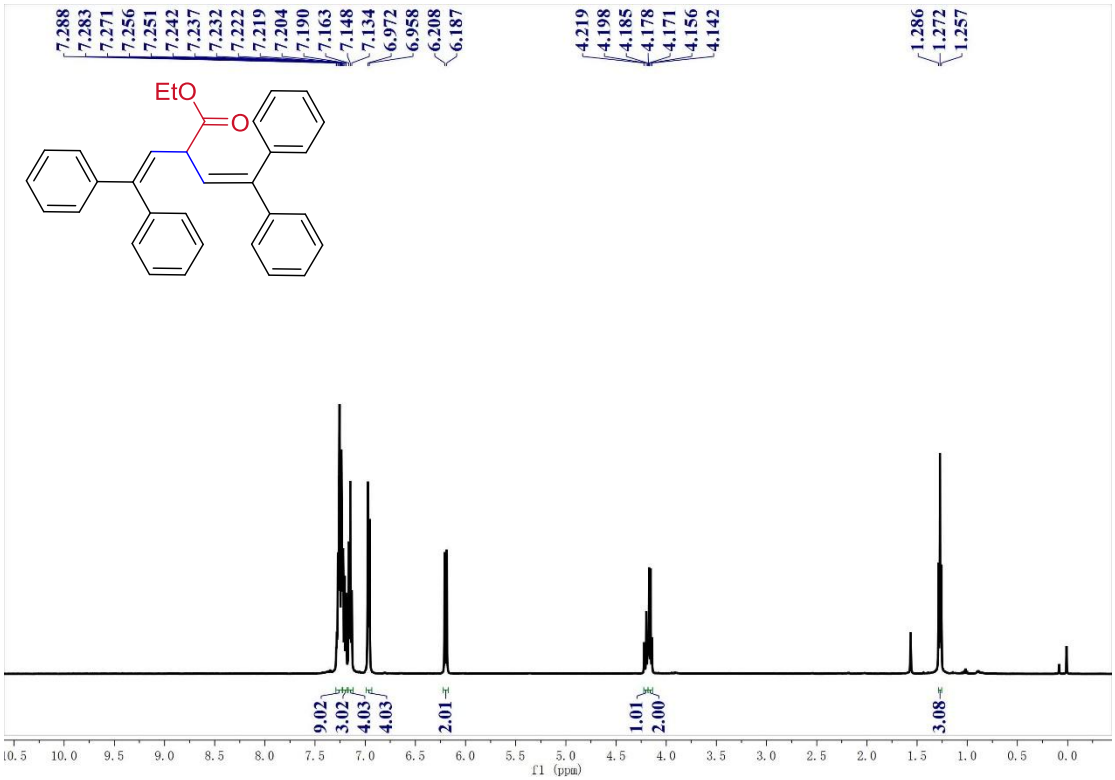

Figure 84. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **8a**

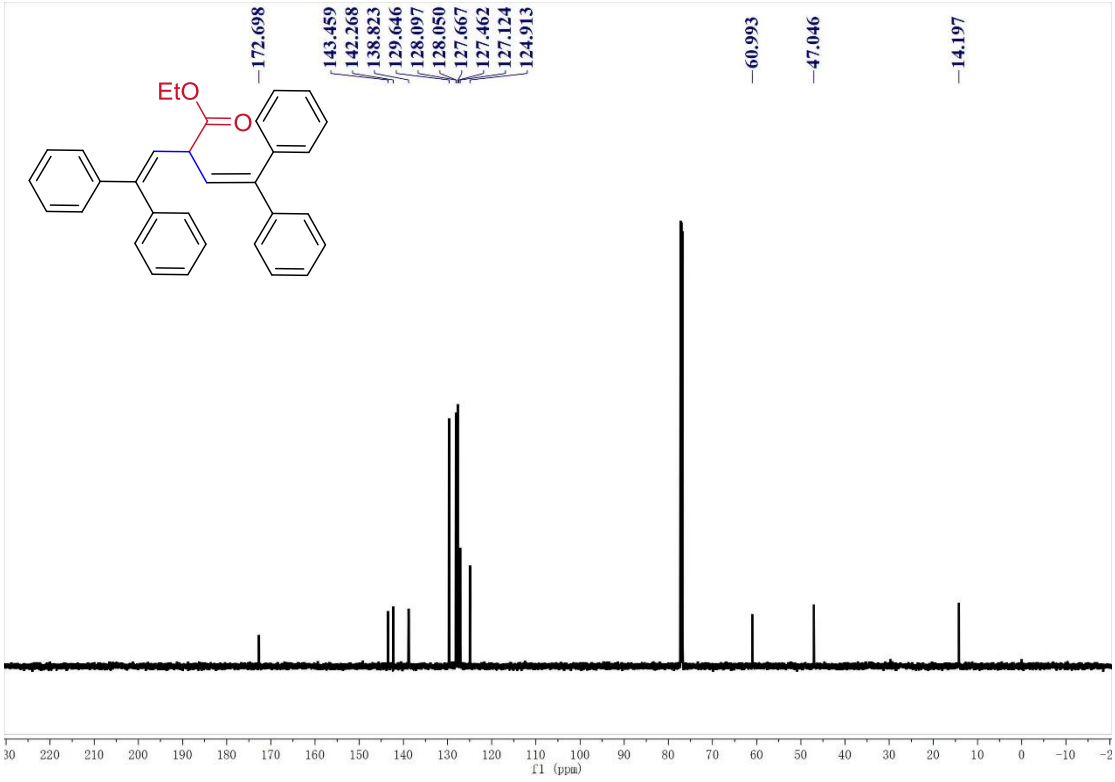

Figure 85. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **8a**

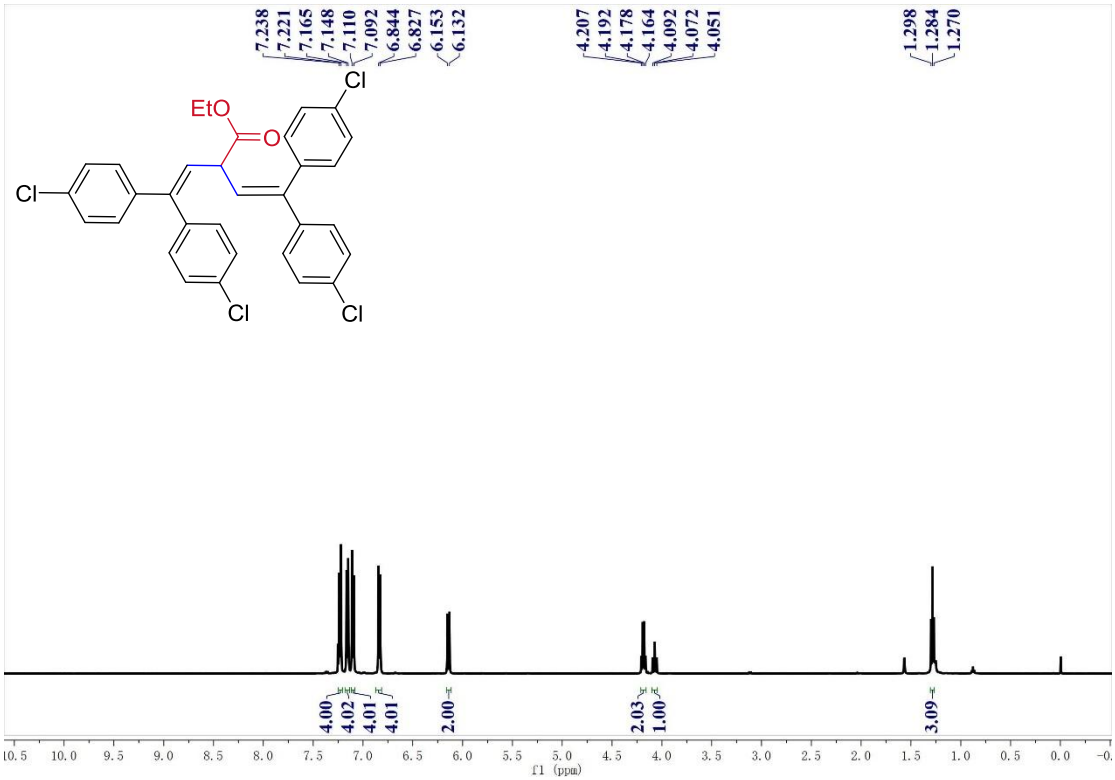

Figure 86. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **8b**

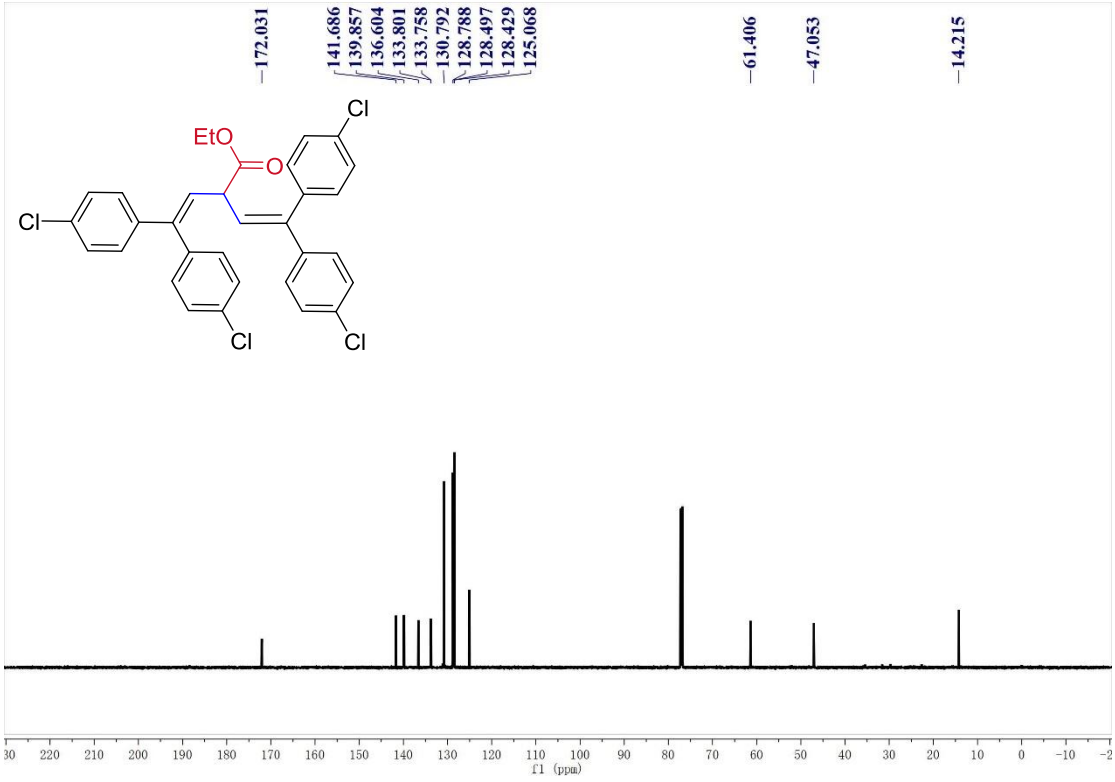

Figure 87. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **8b**

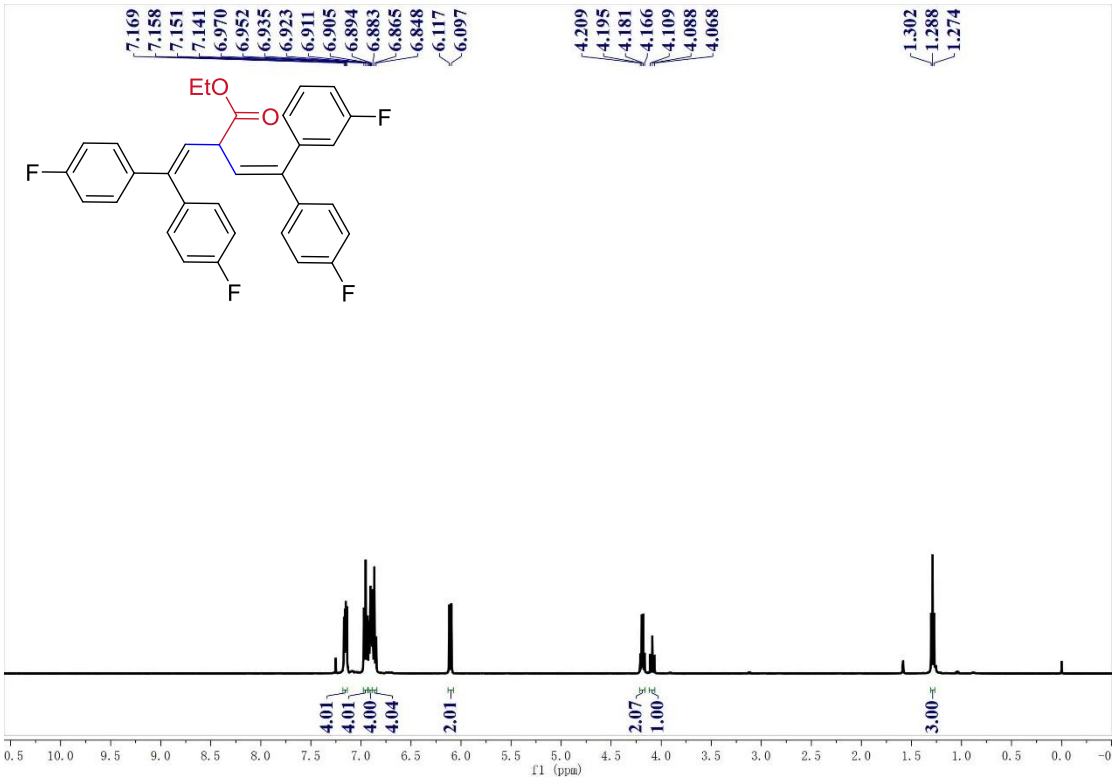

Figure 88. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **8c**

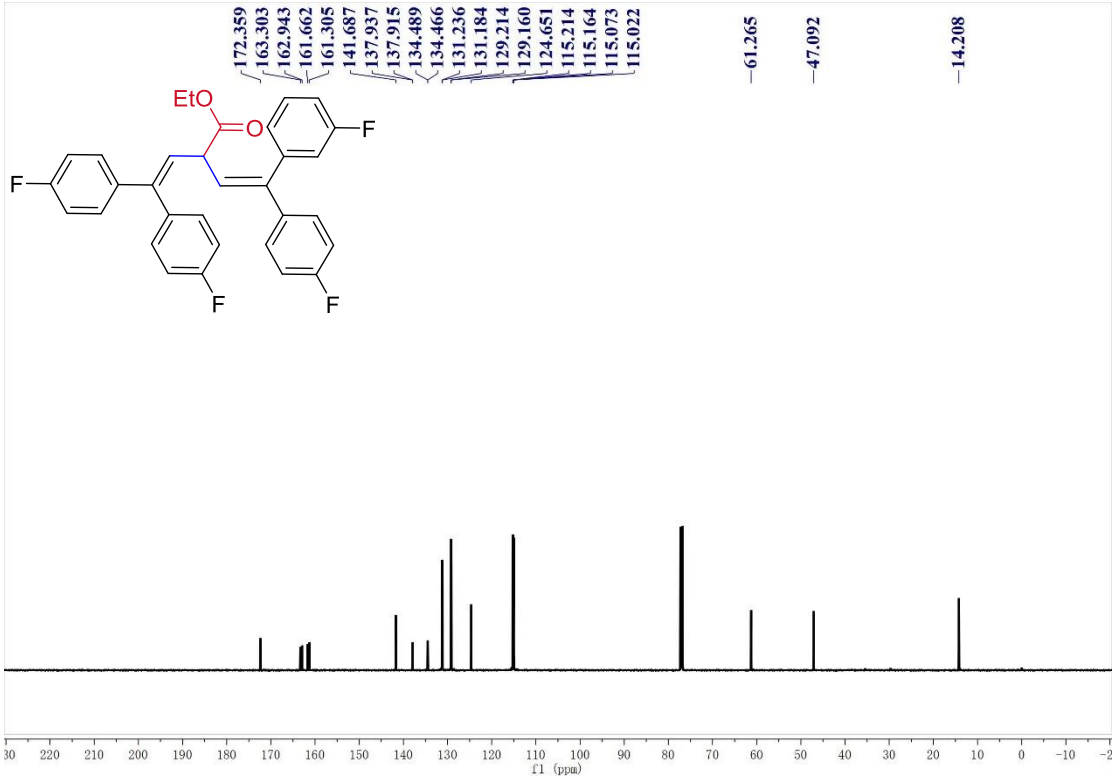

Figure 89. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **8c**

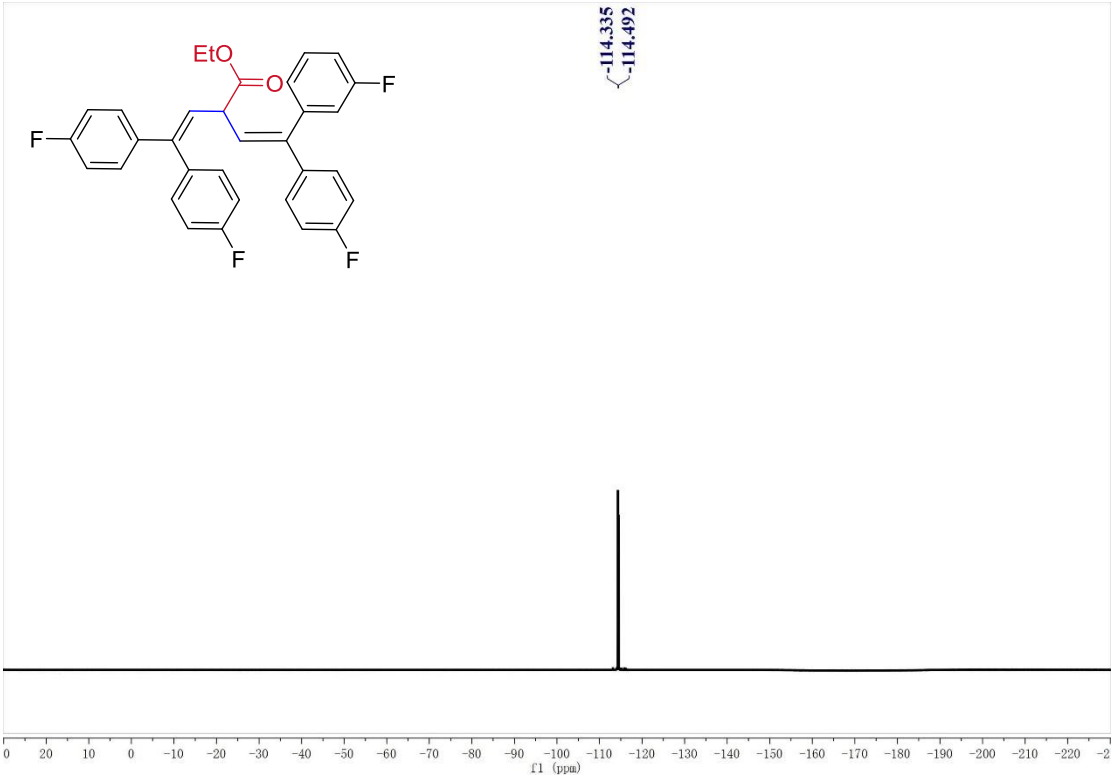

Figure 90. ^{19}F NMR (565 MHz, $CDCl_3$) spectra of compound **8c**

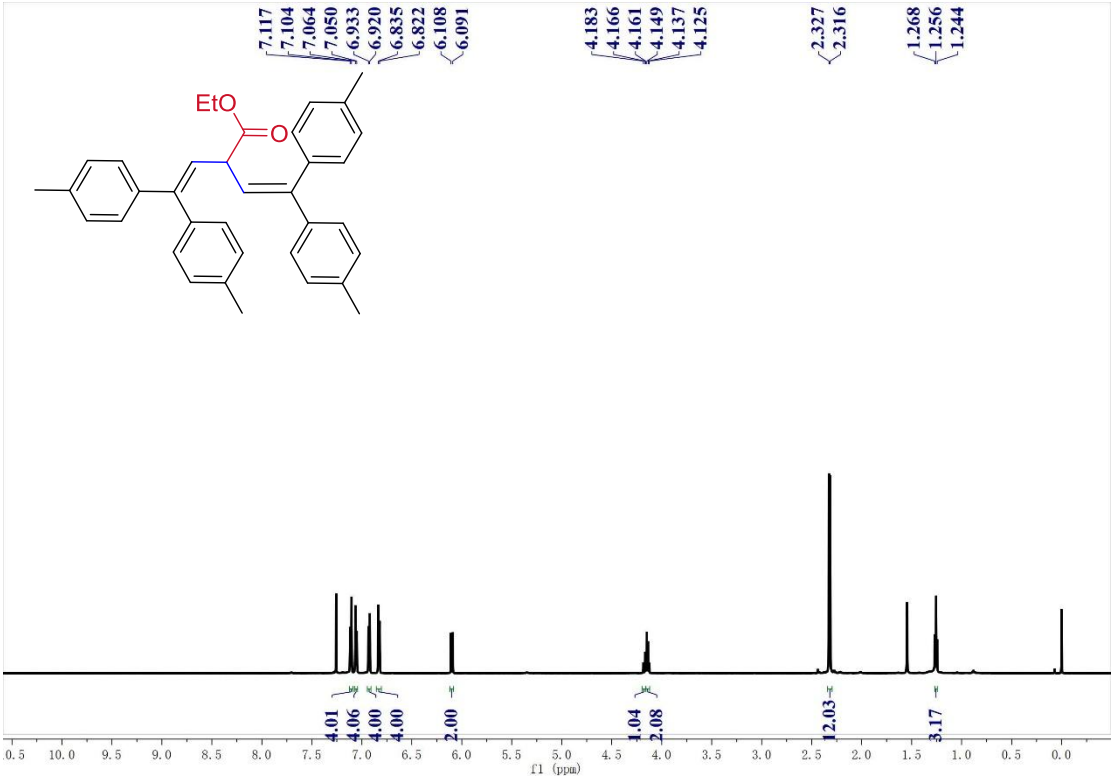

Figure 91. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **8d**

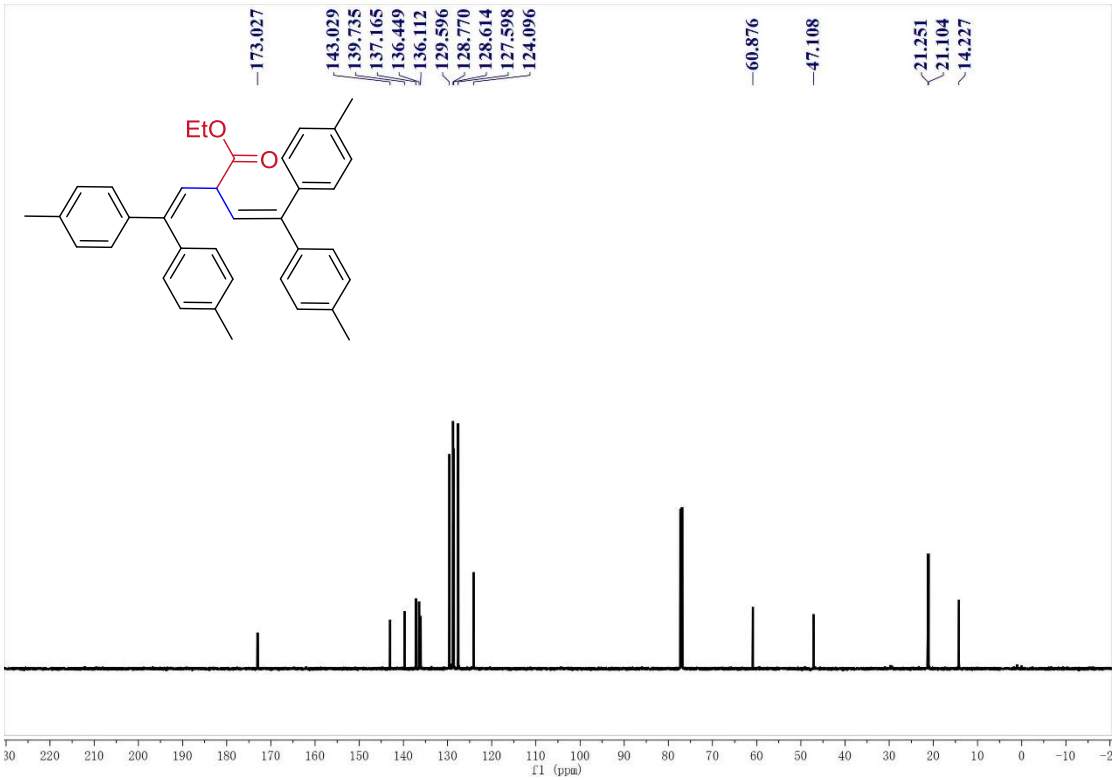

Figure 92. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **8d**

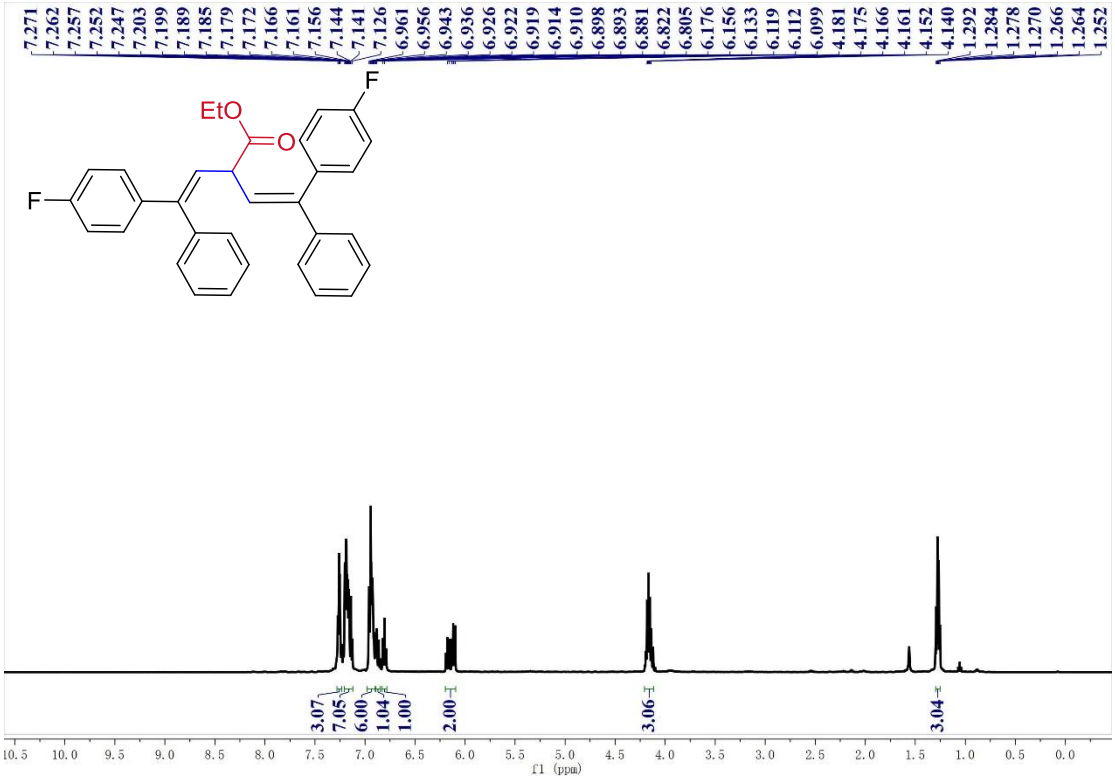

Figure 93. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **8e**

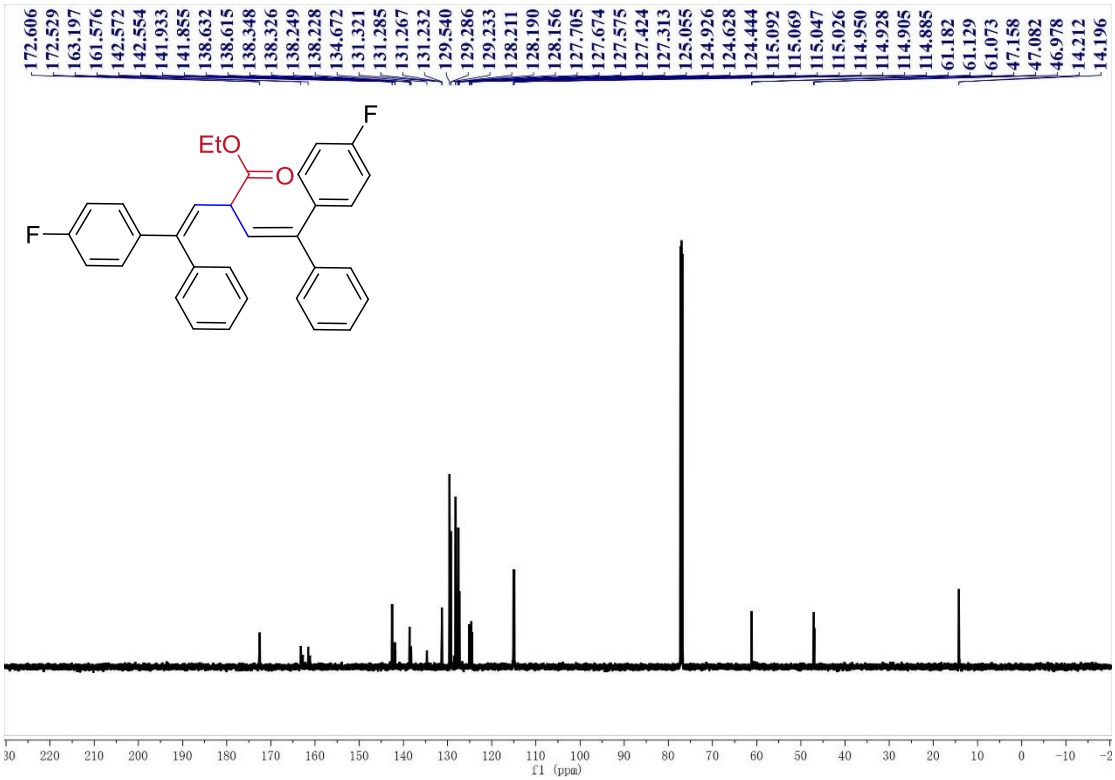

Figure 94. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **8e**

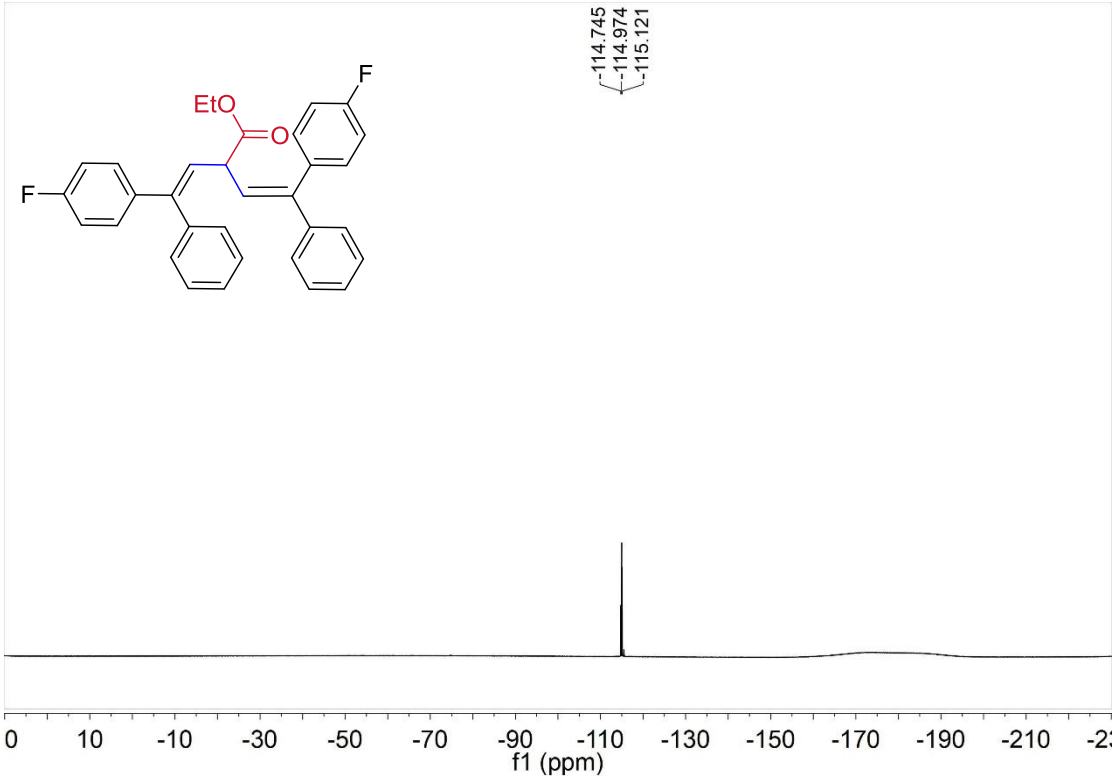

Figure 95. ^{19}F NMR (565 MHz, $CDCl_3$) spectra of compound **8e**

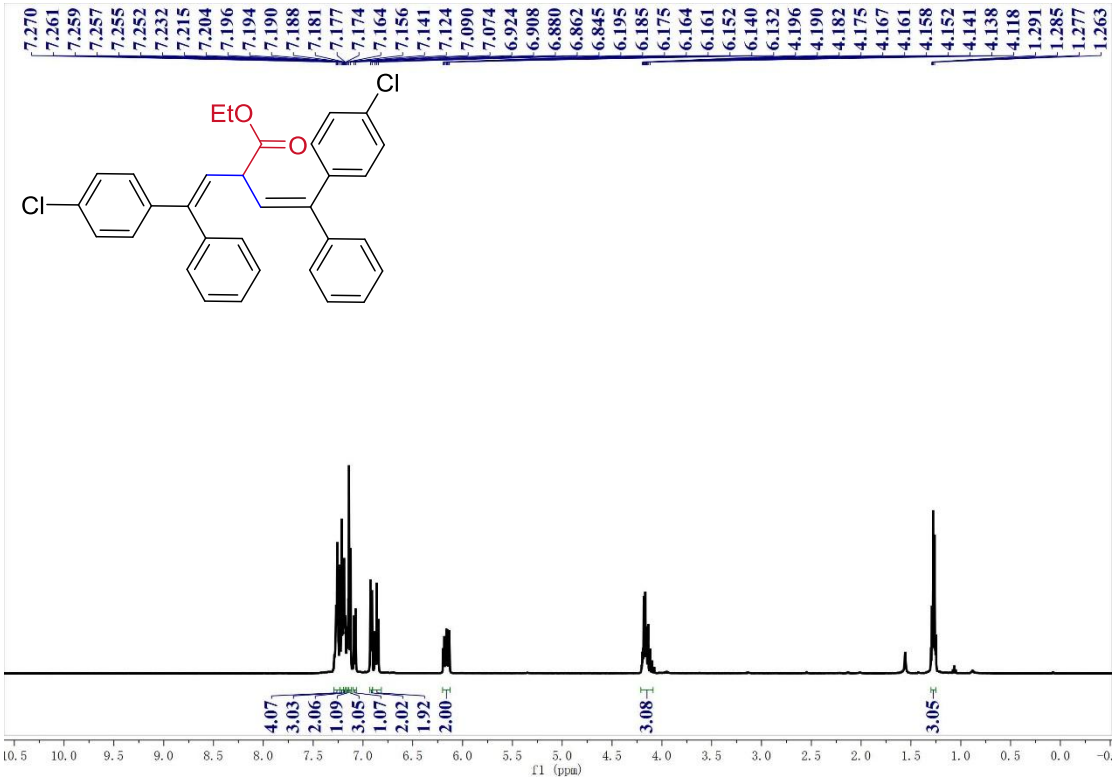

Figure 96. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **8f**

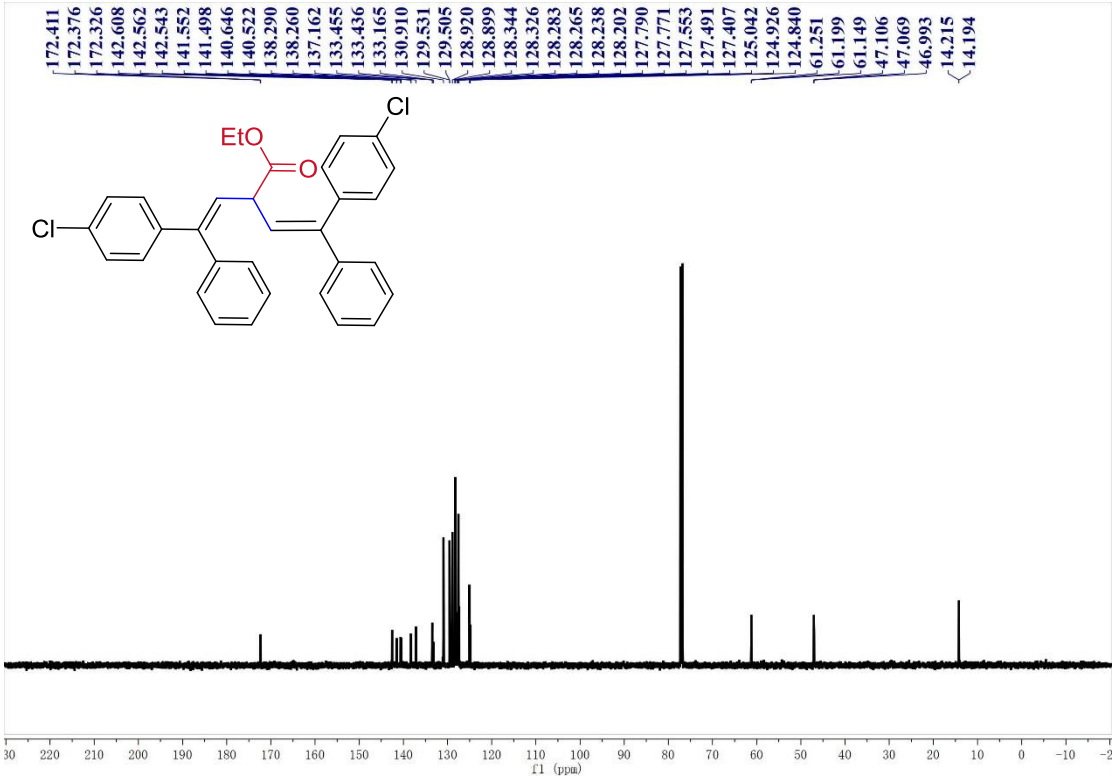

Figure 97. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **8f**

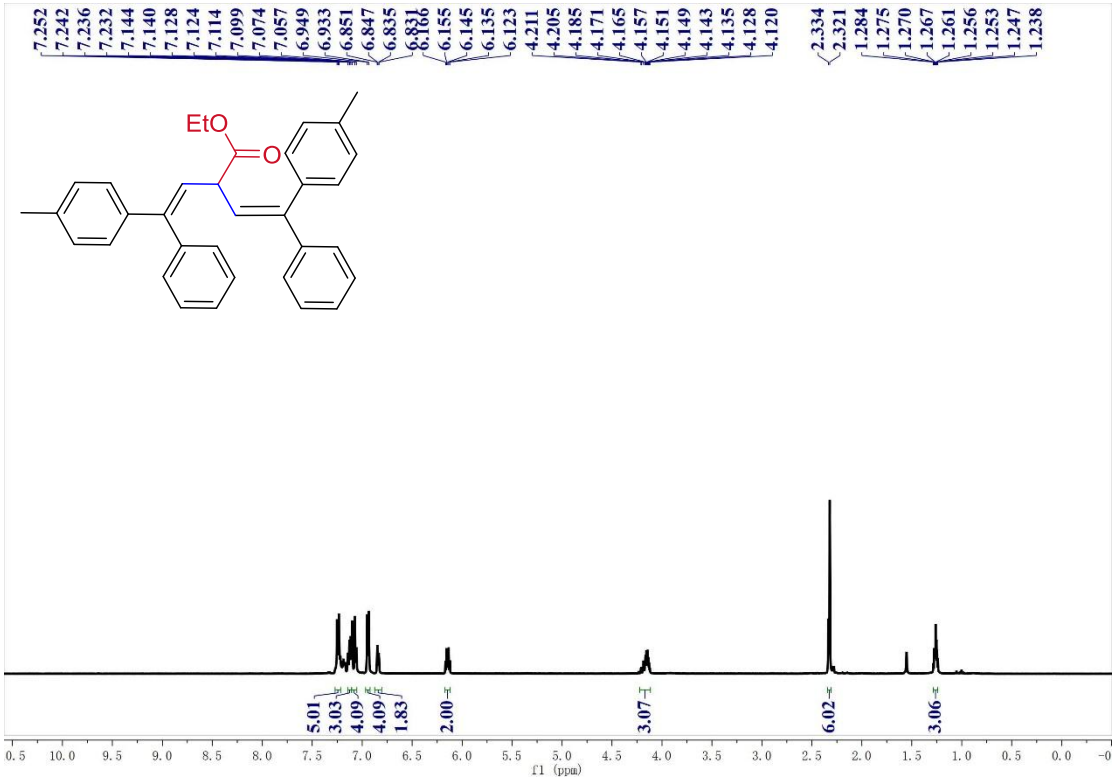

Figure 98. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **8g**

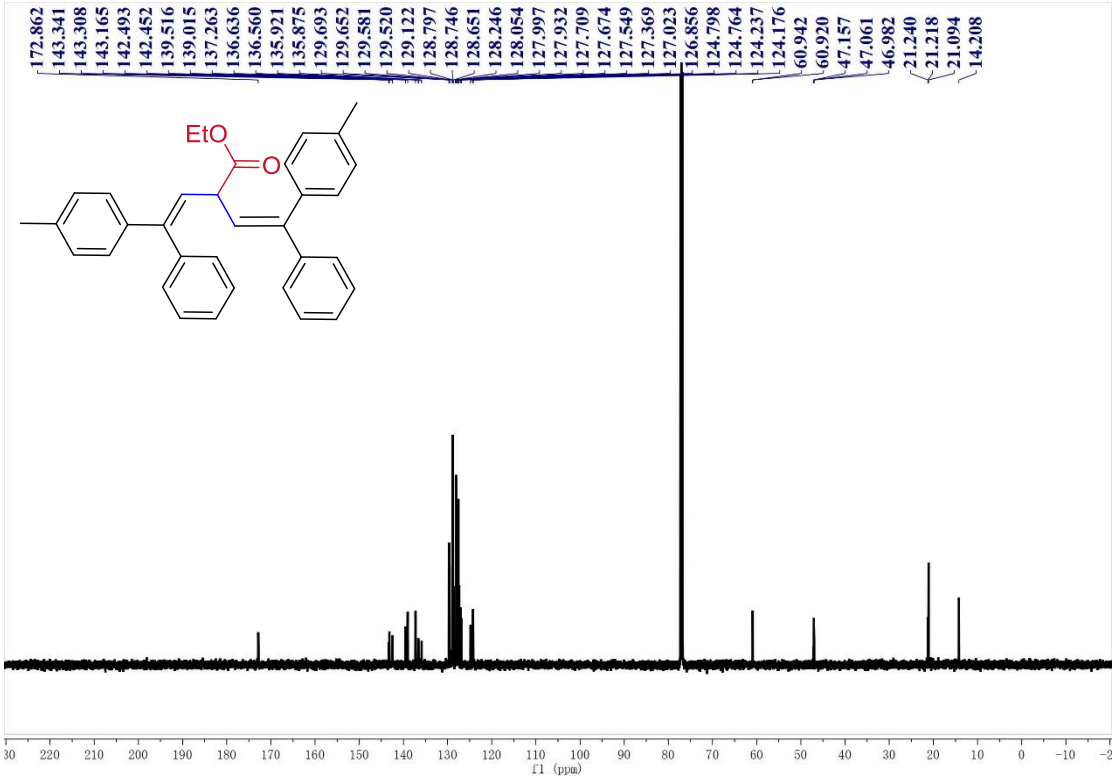

Figure 99. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **8g**

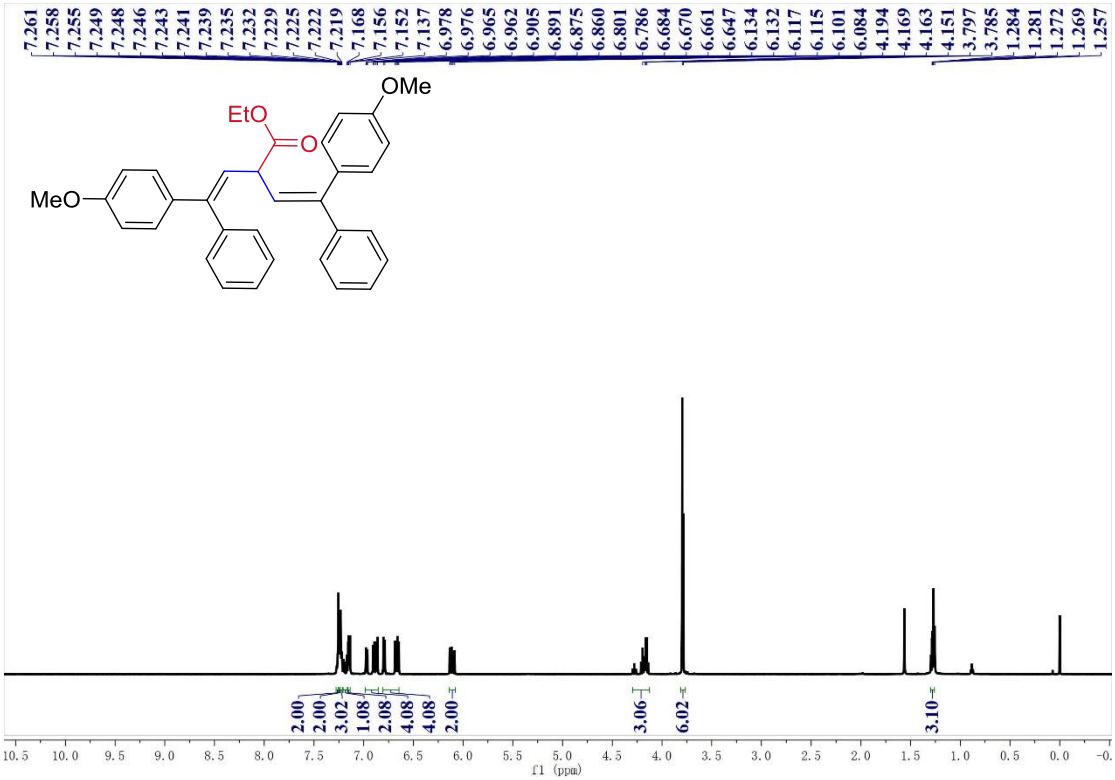

Figure 100. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **8h**

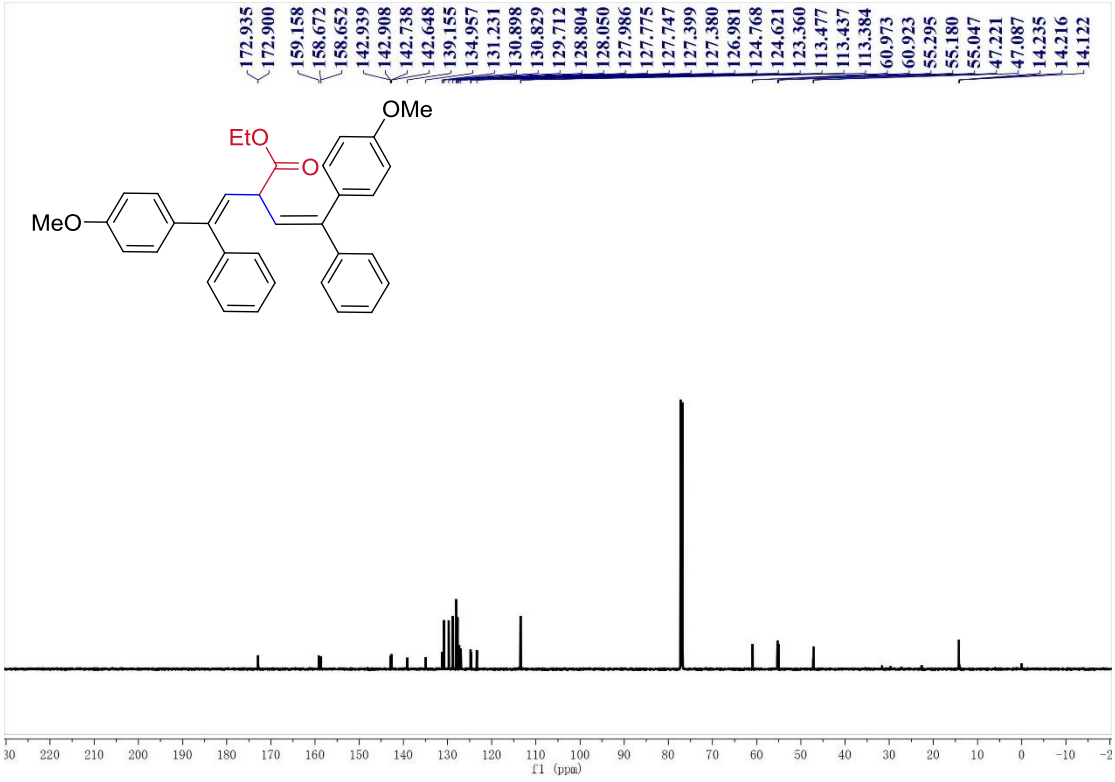

Figure 101. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **8h**

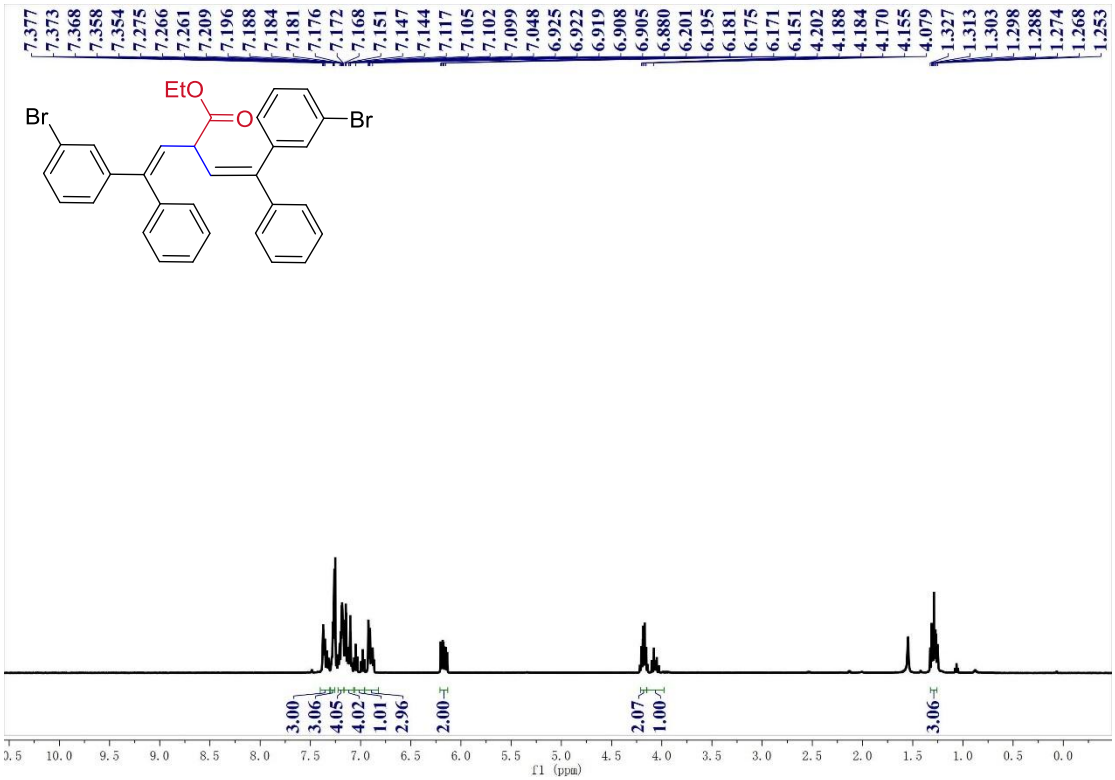

Figure 102. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **8i**

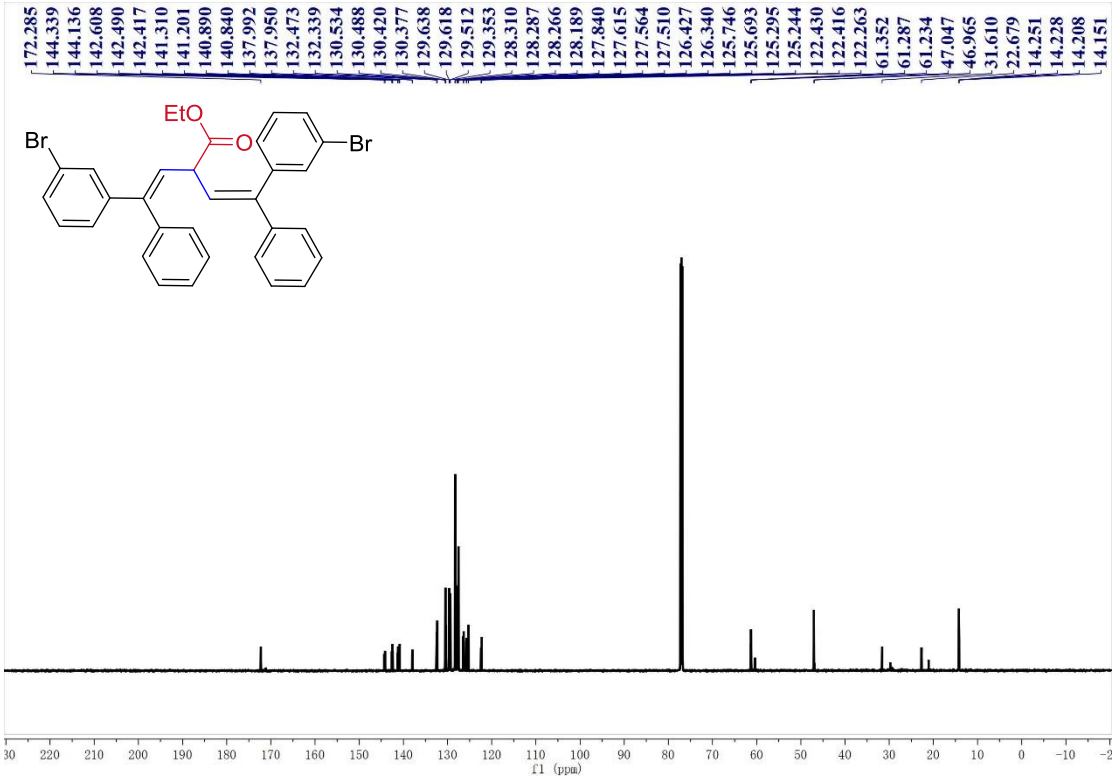

Figure 103. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **8i**

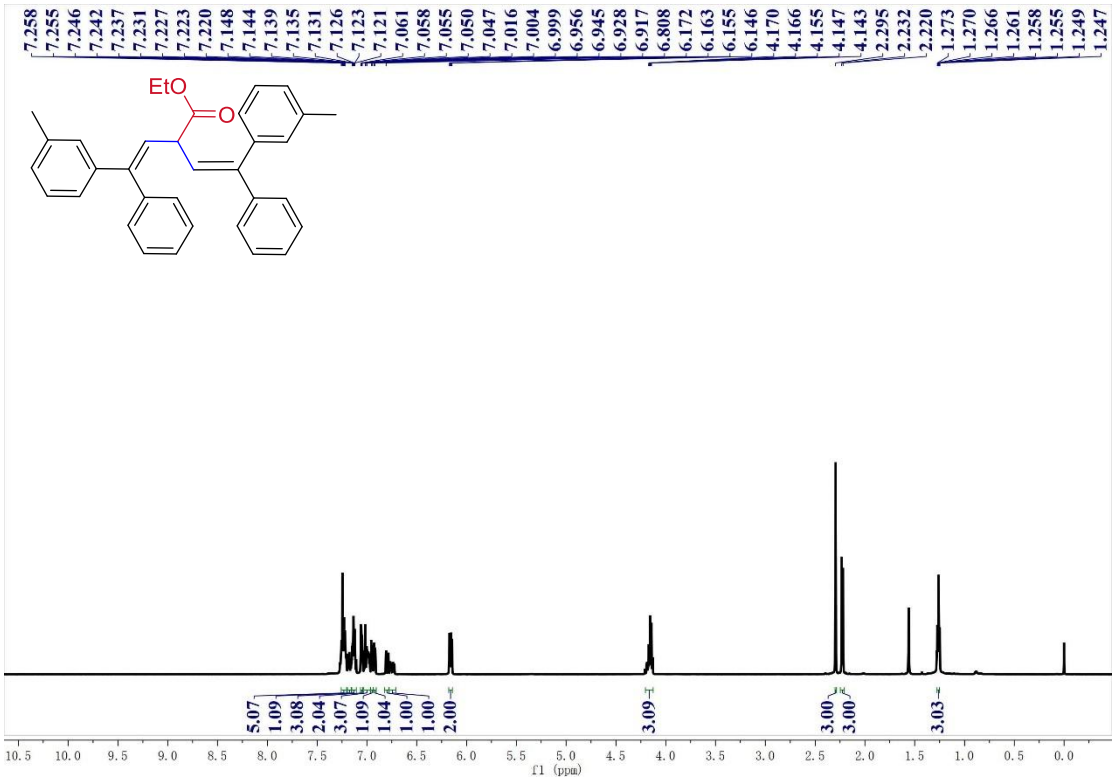

Figure 104. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **8j**

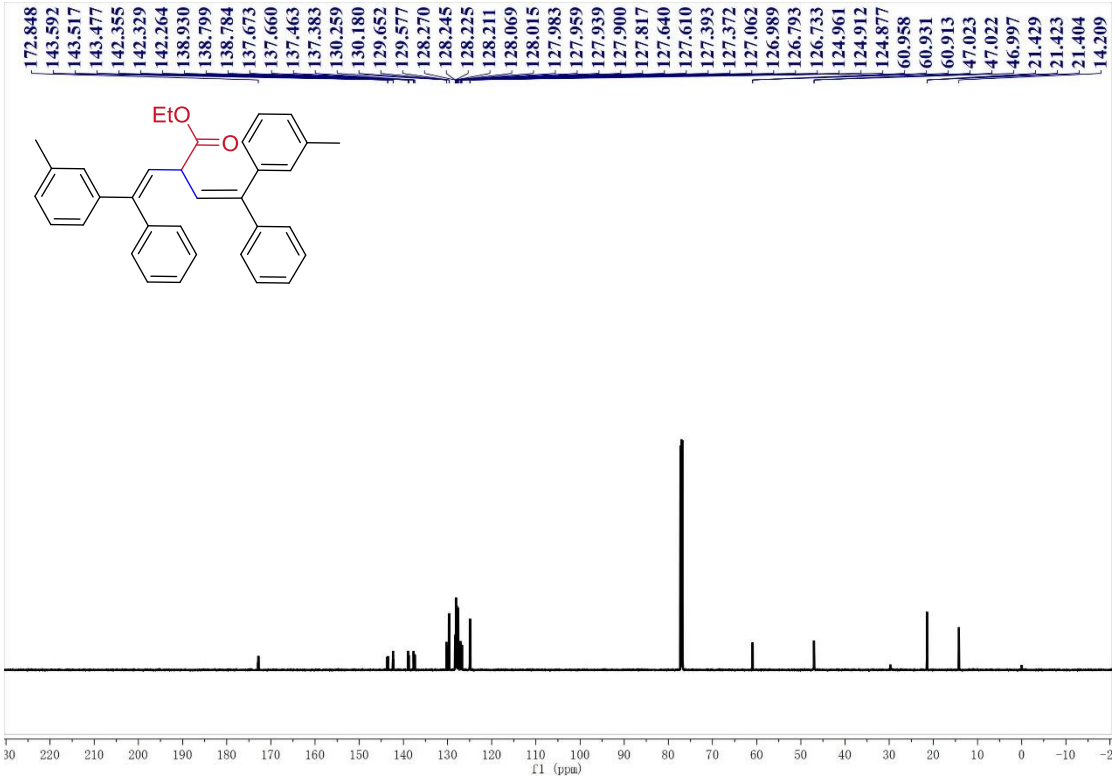

Figure 105. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **8j**

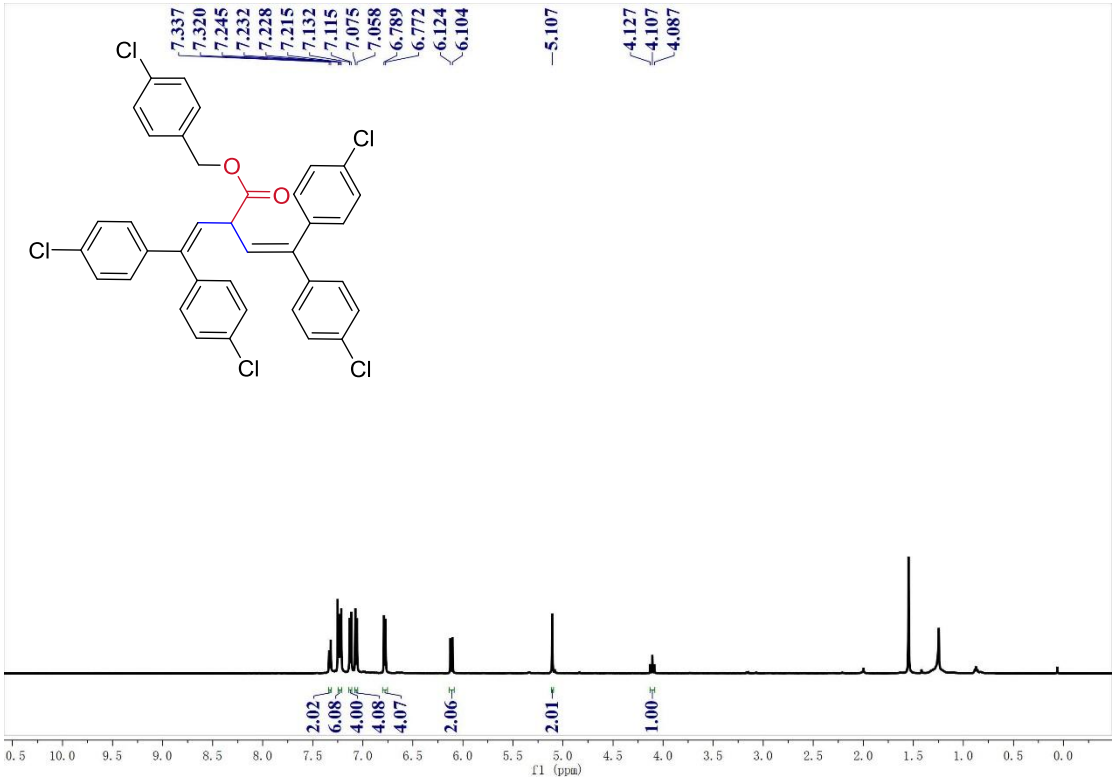

Figure 106. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **8k**

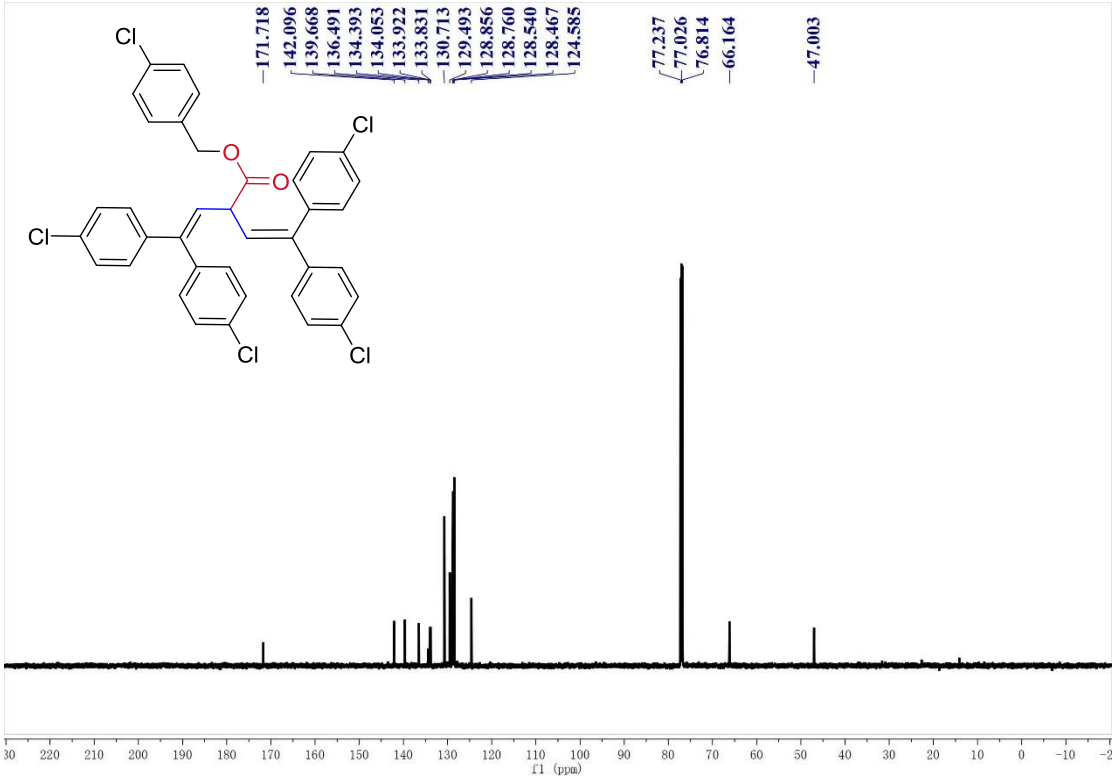

Figure 107. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **8k**

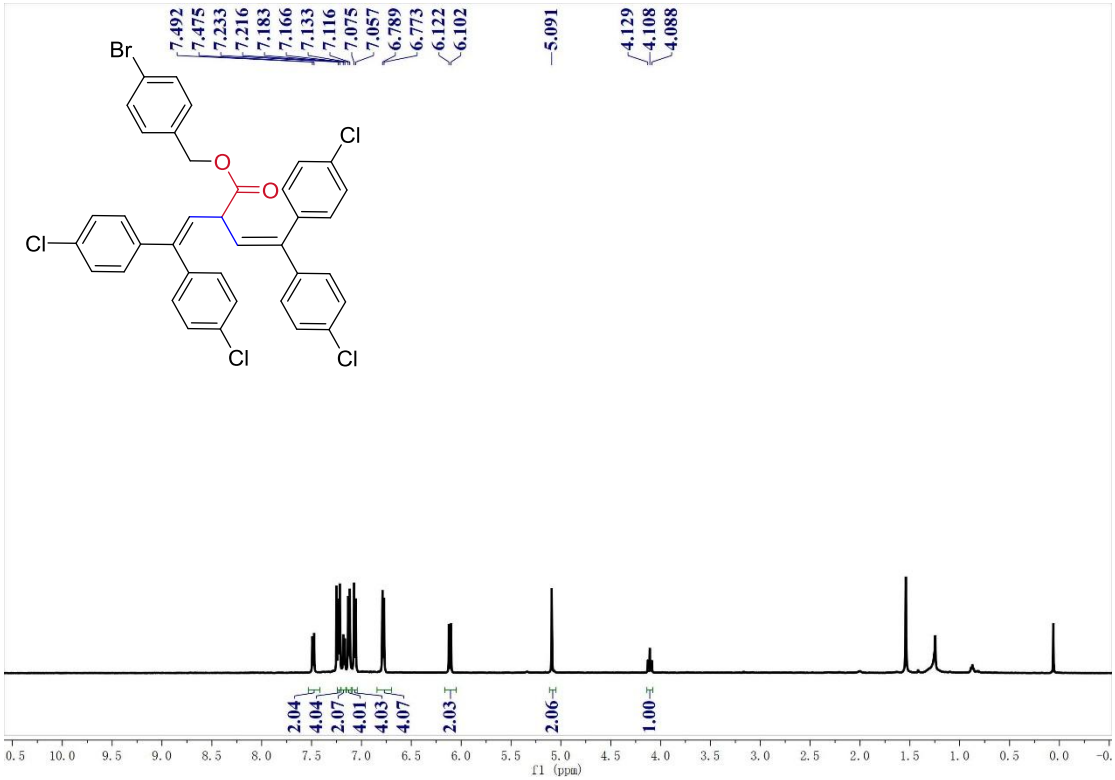

Figure 108. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **8l**

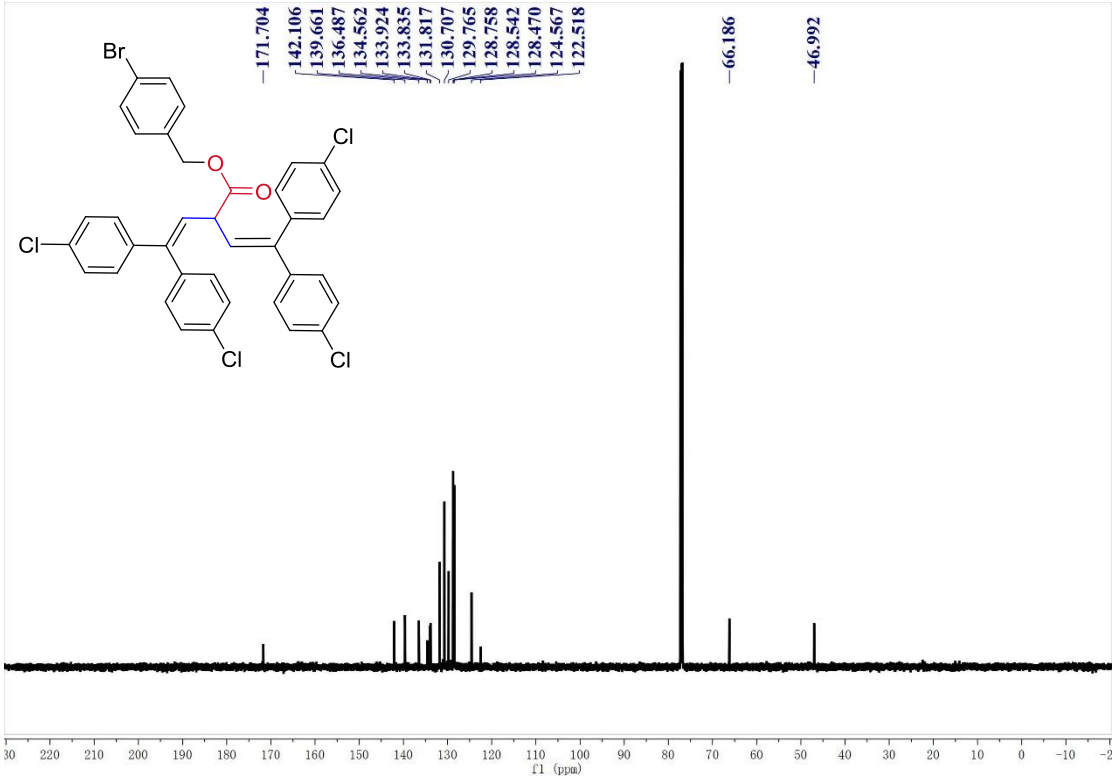

Figure 109. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **8l**

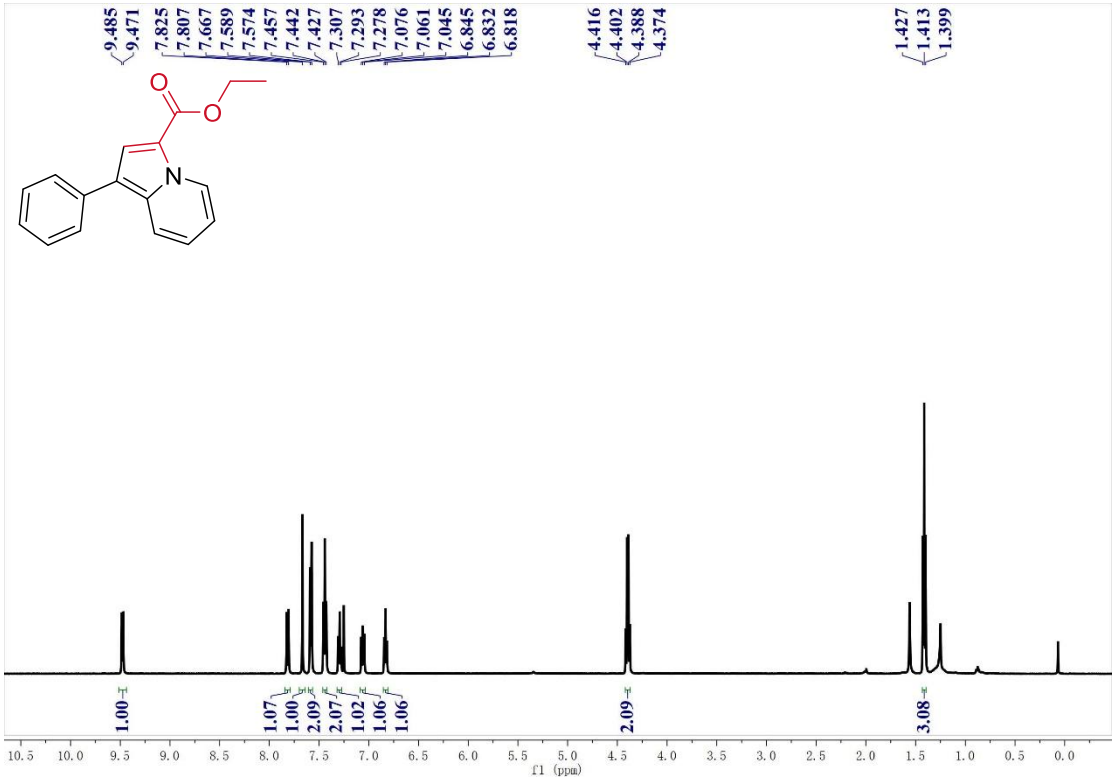

Figure 110. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **9a**

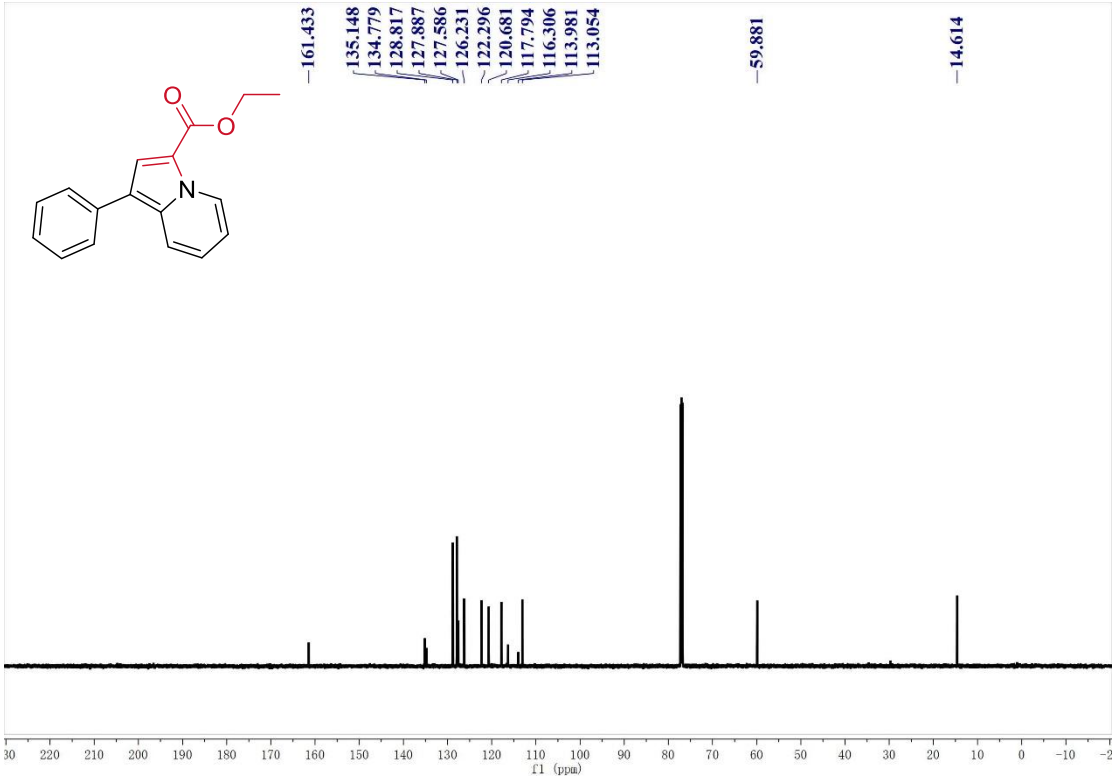

Figure 111. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **9a**

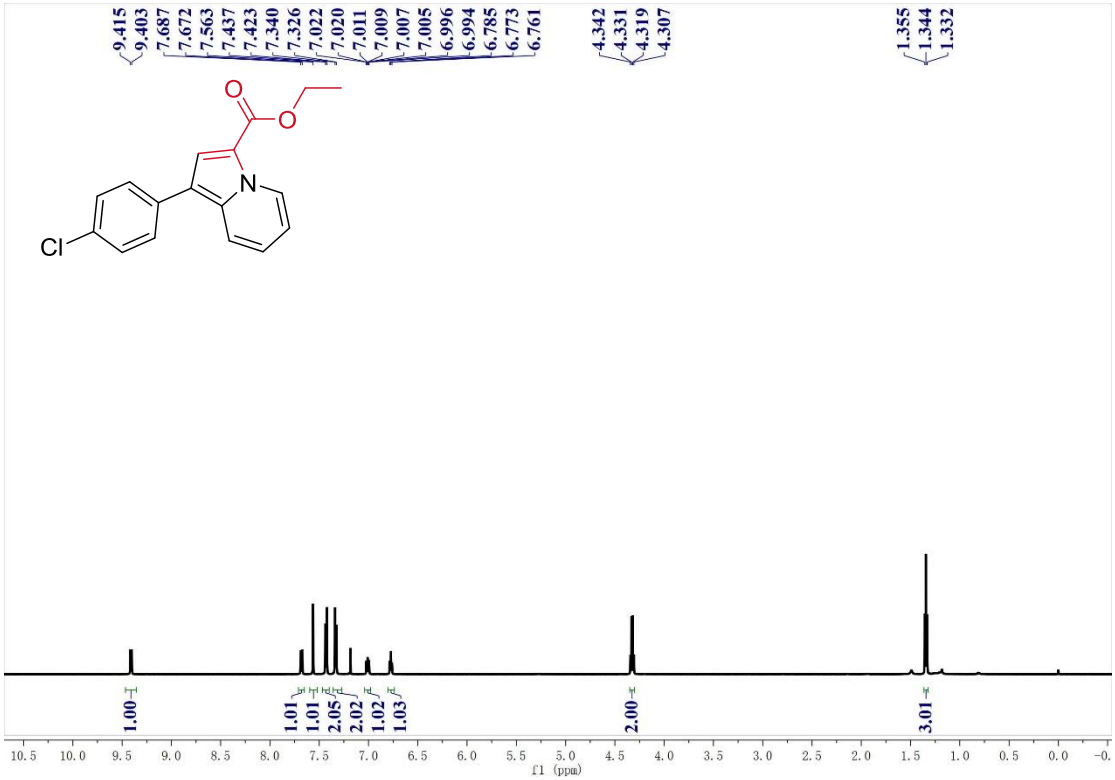

Figure 112. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **9b**

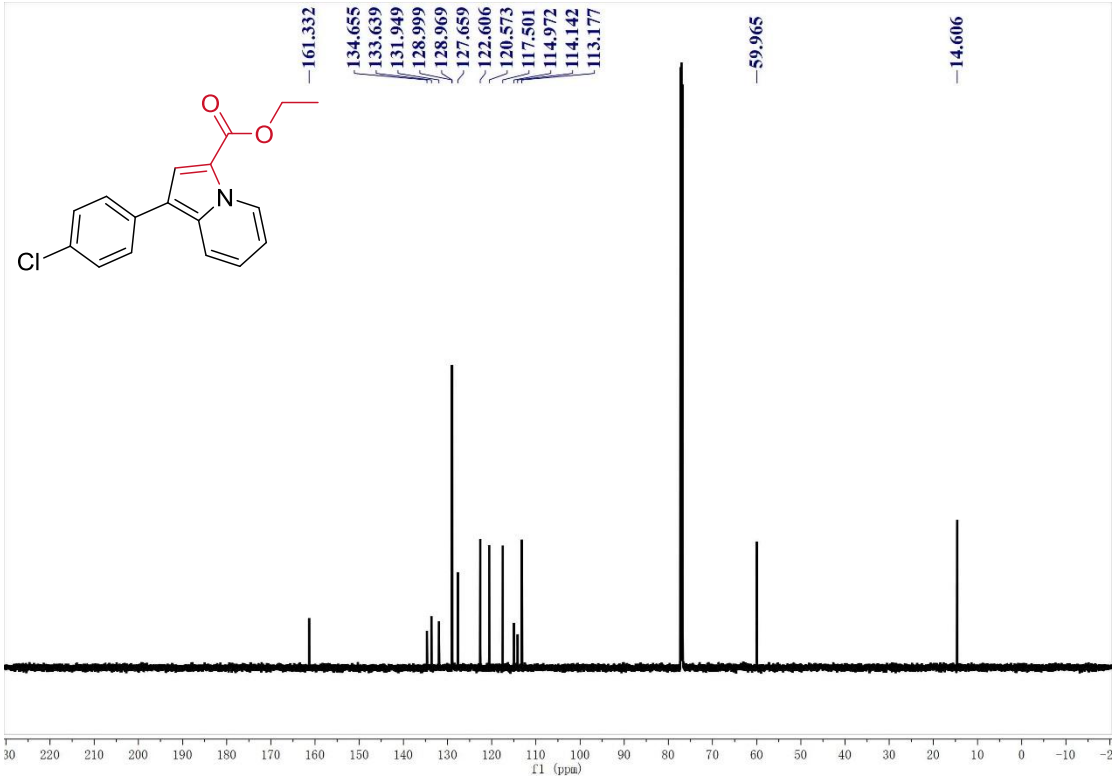

Figure 113. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **9b**

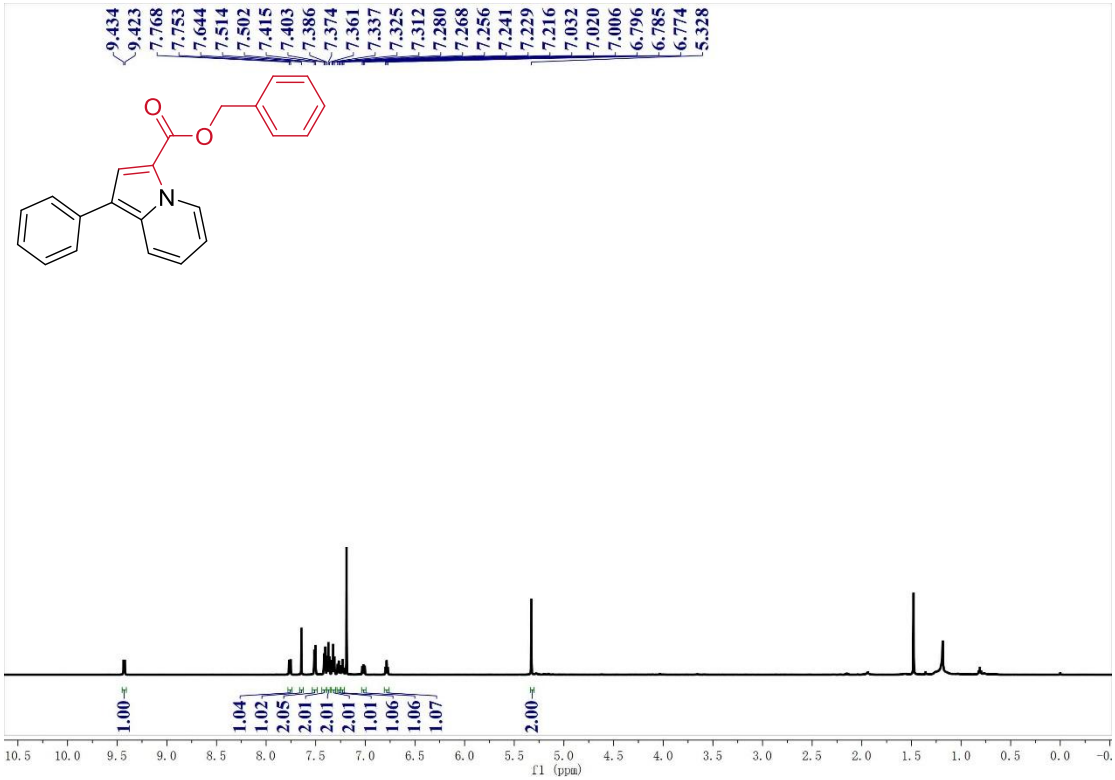

Figure 114. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **9c**

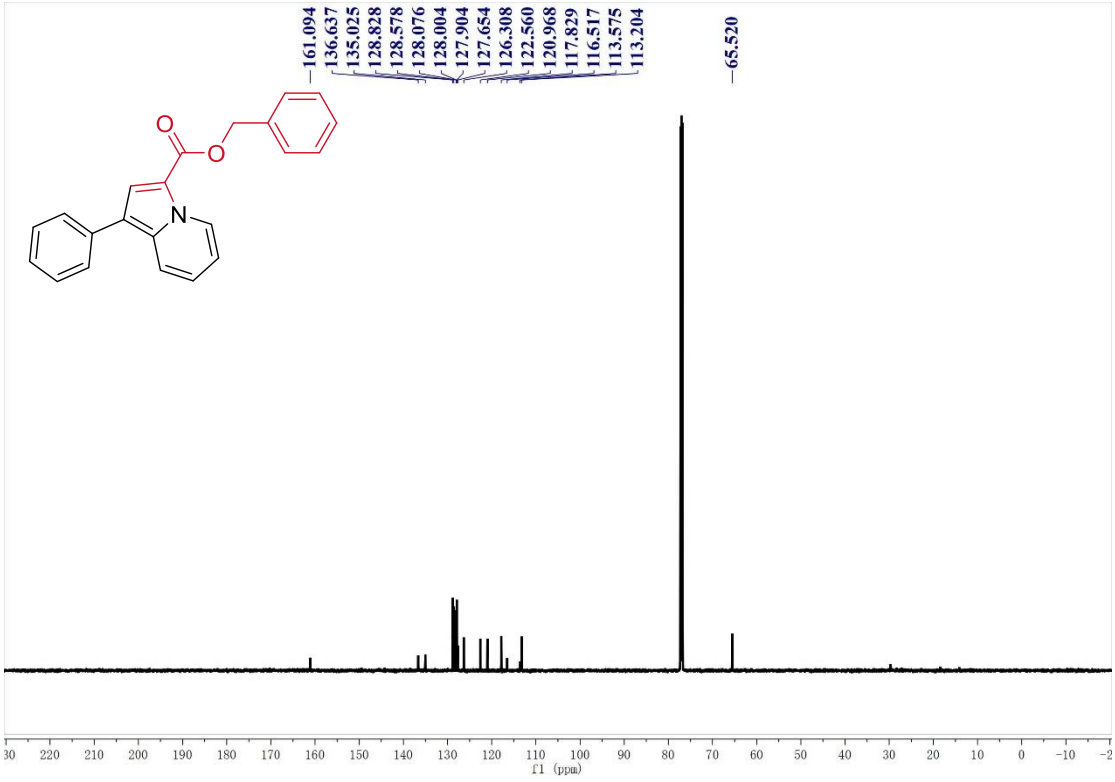

Figure 115. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **9c**

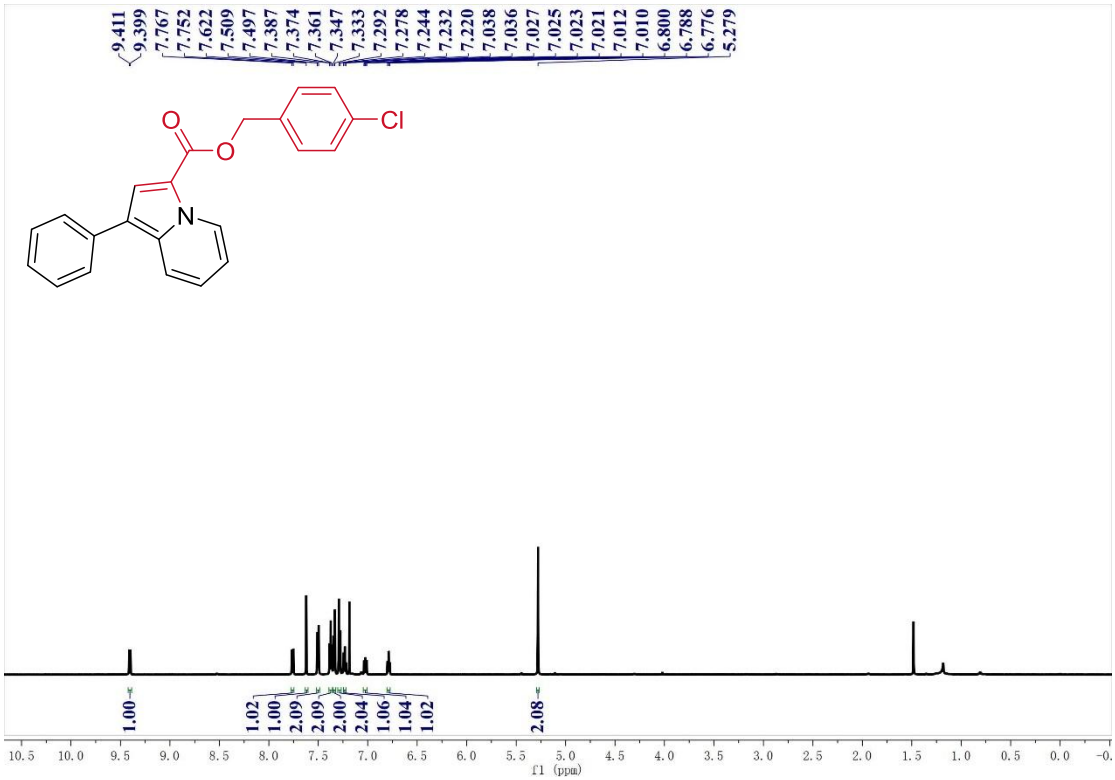

Figure 116. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **9d**

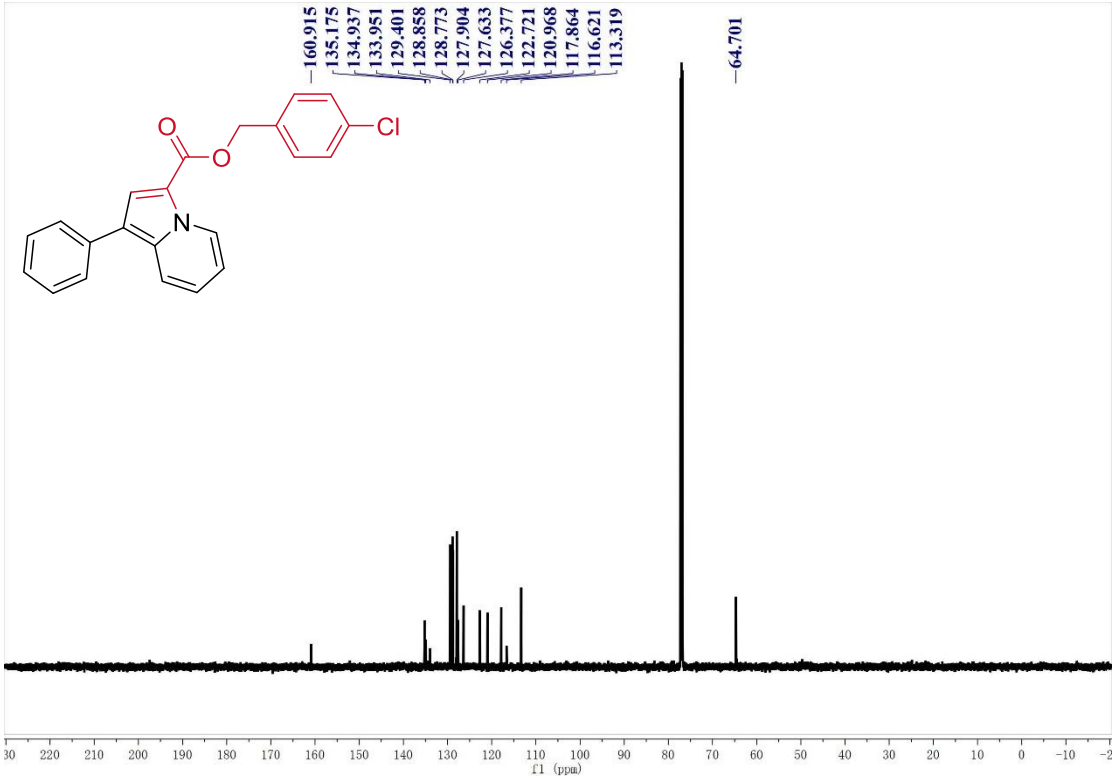

Figure 117. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **9d**

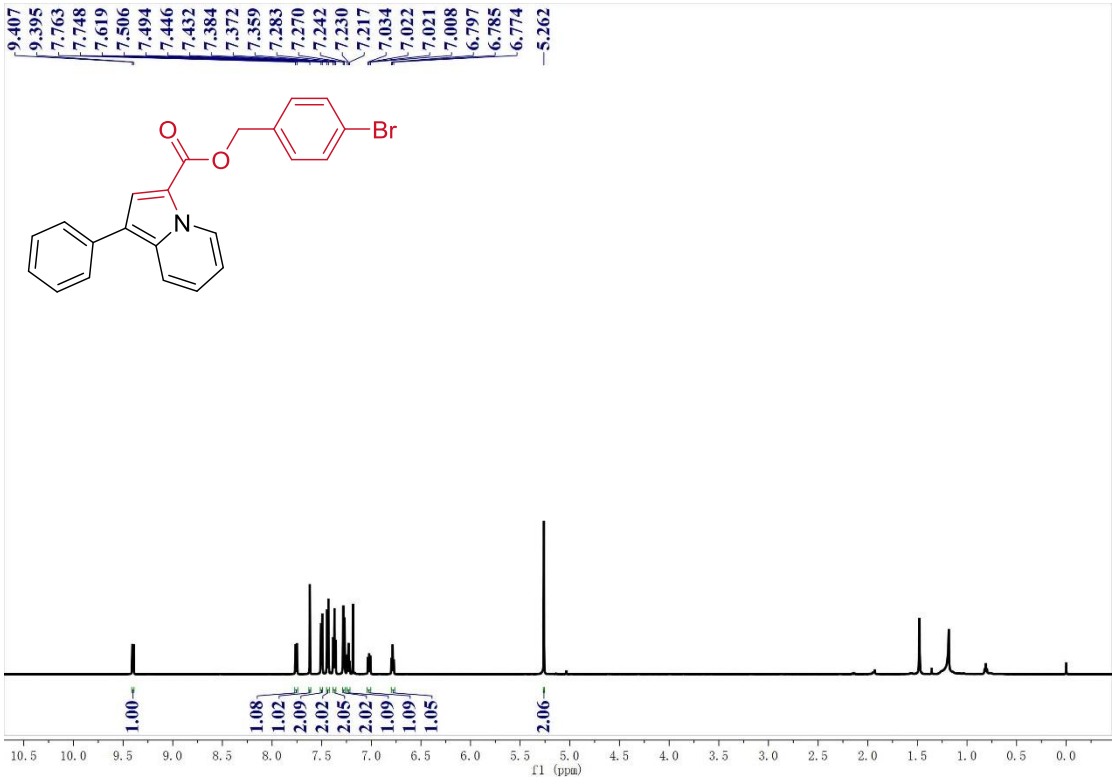

Figure 118. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **9e**

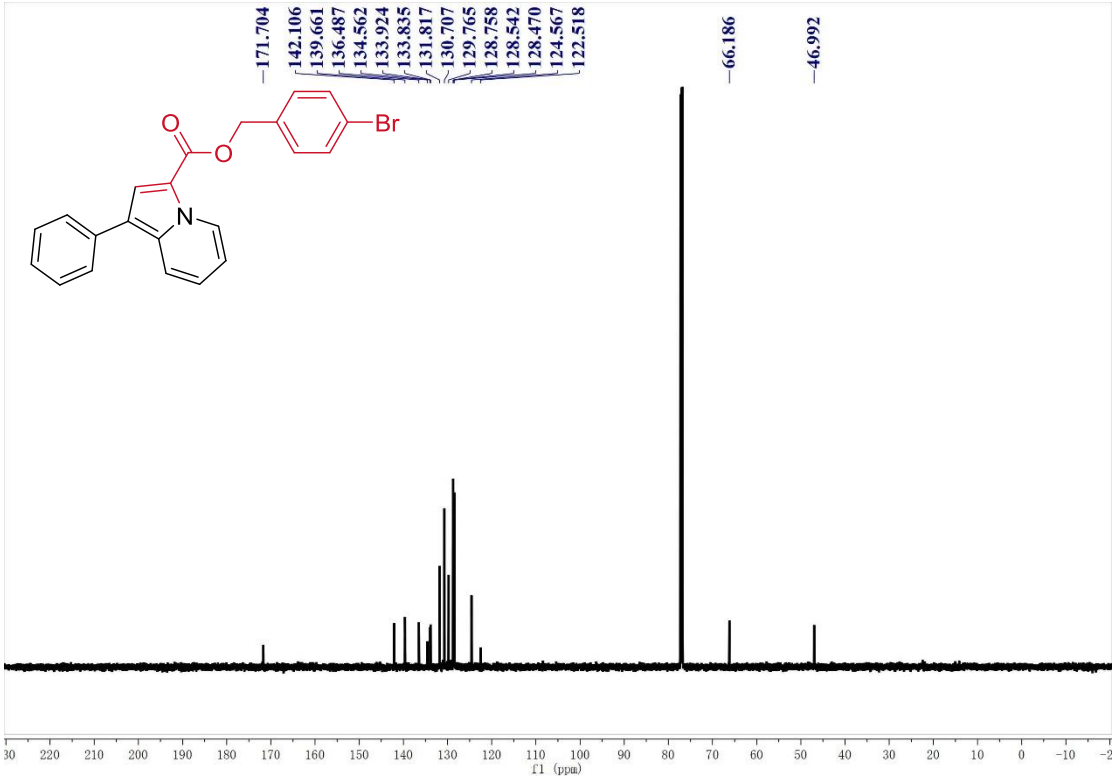

Figure 119. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **9e**

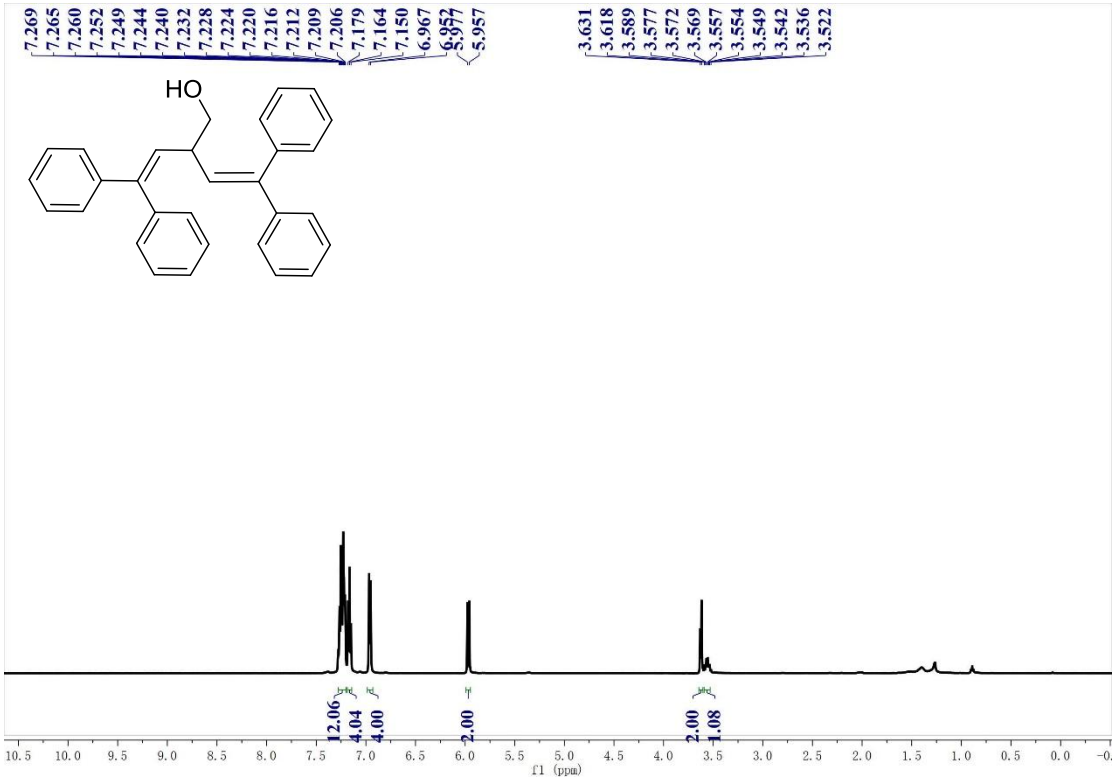

Figure 120. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **10a**

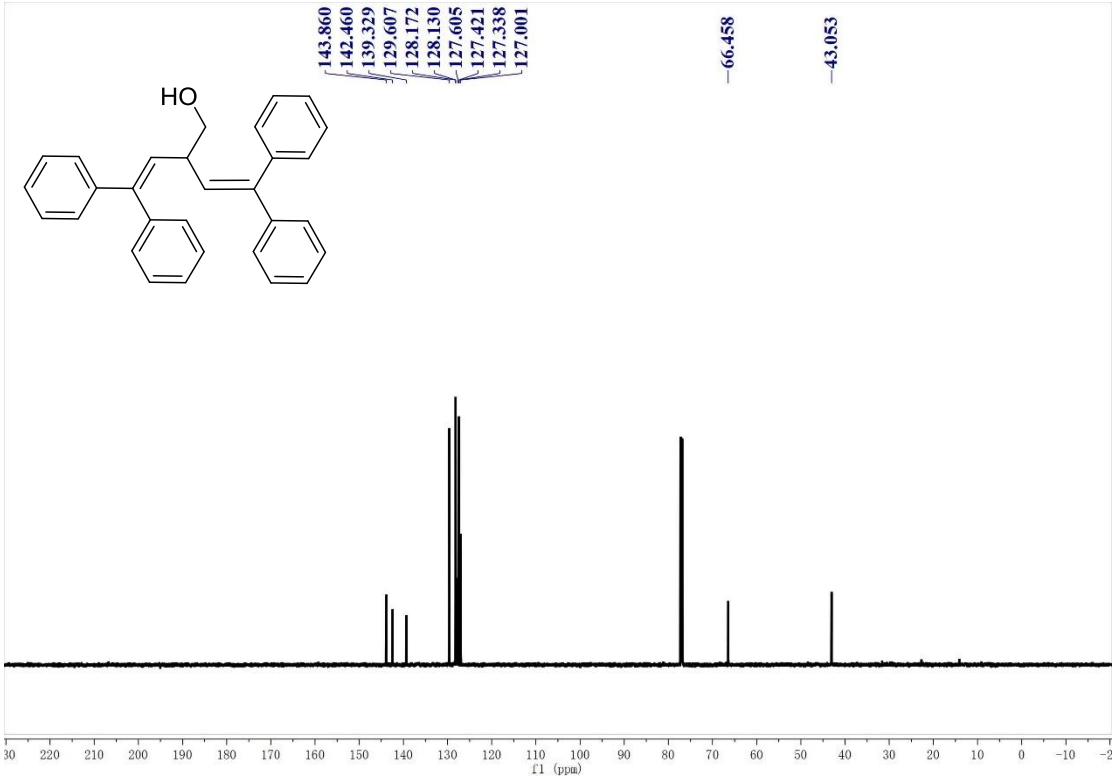

Figure 121. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **10a**

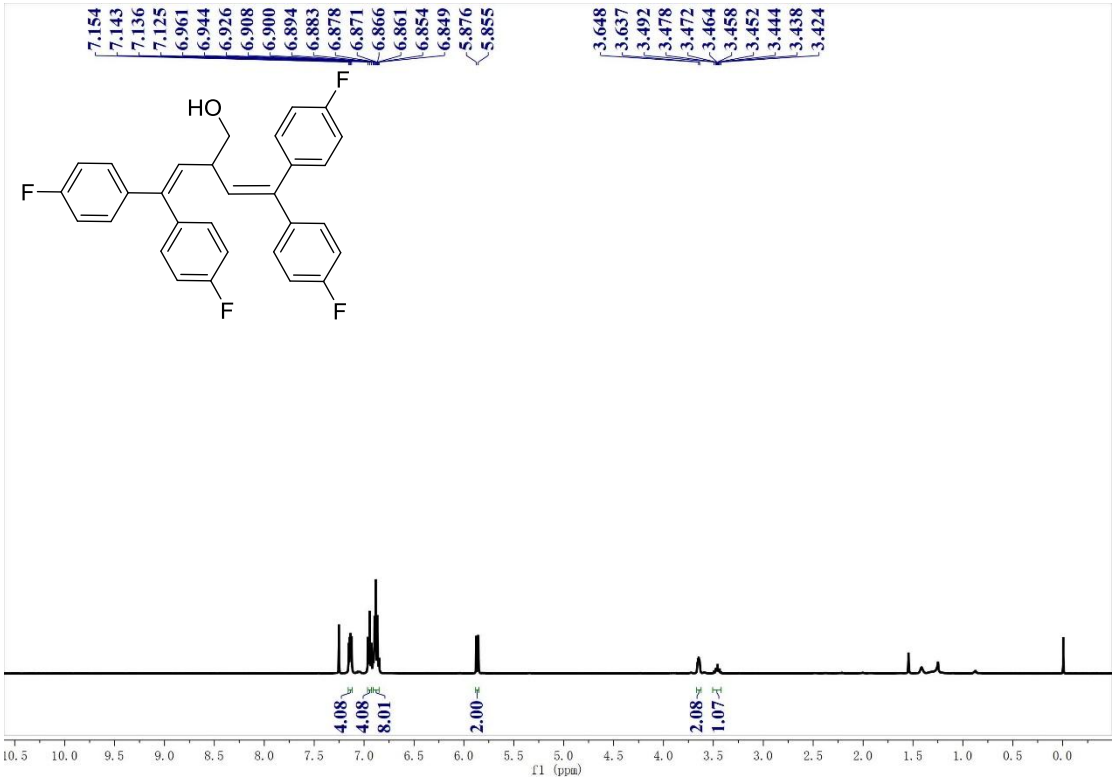

Figure 122. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **10c**

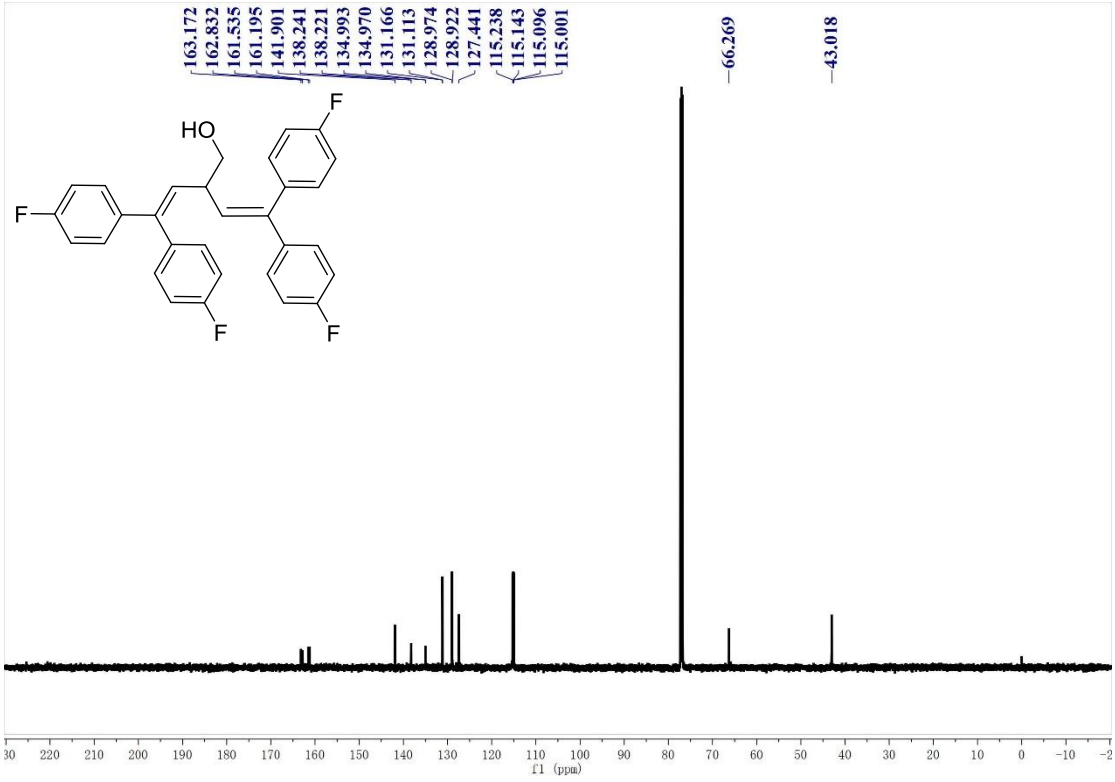

Figure 123. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **10c**

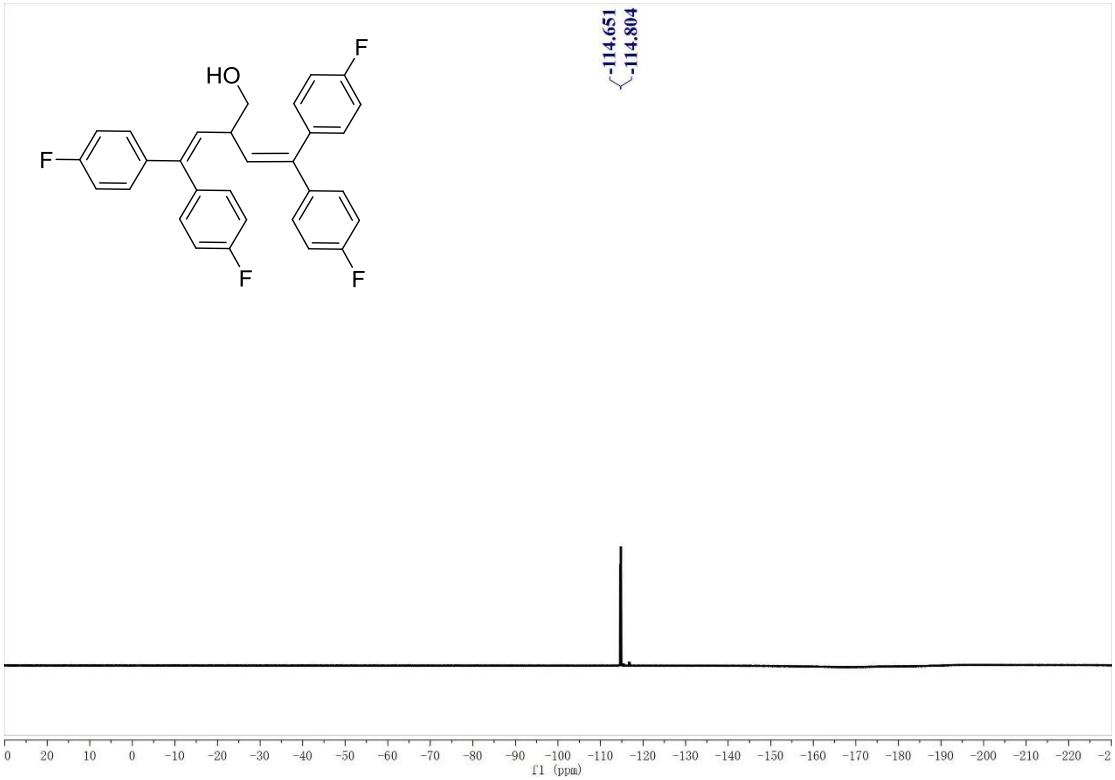

Figure 124. ^{19}F NMR (565 MHz, $CDCl_3$) spectra of compound **10c**

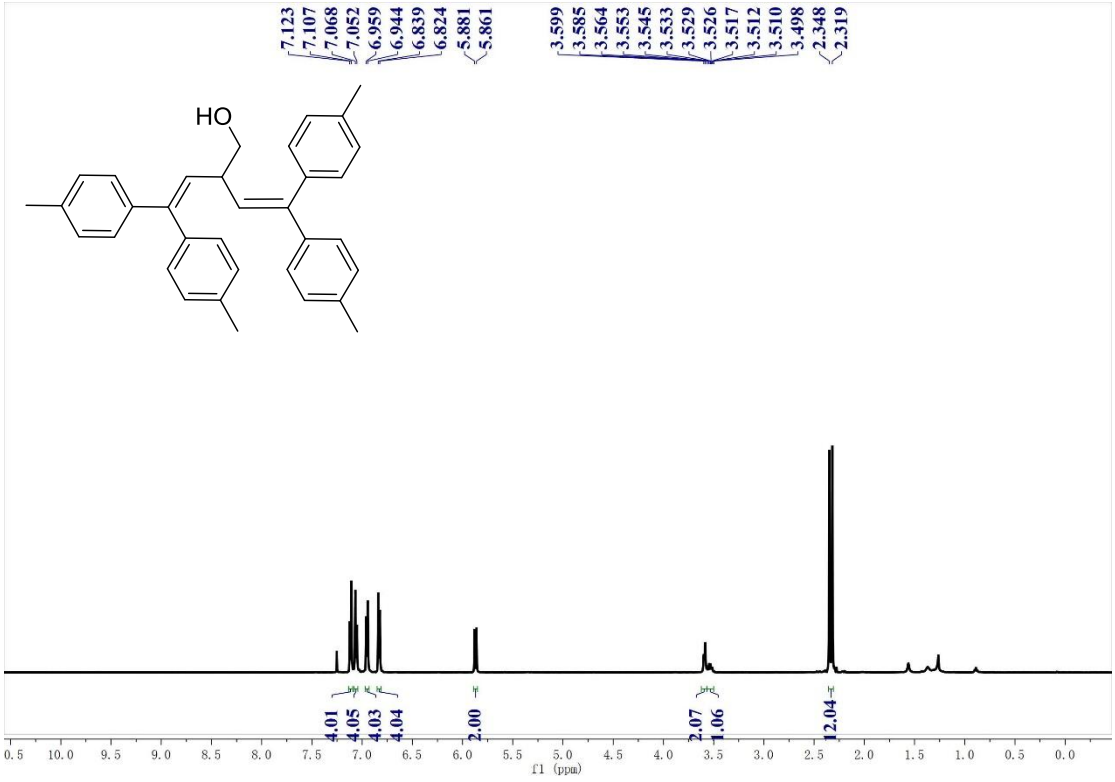

Figure 125. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **10d**

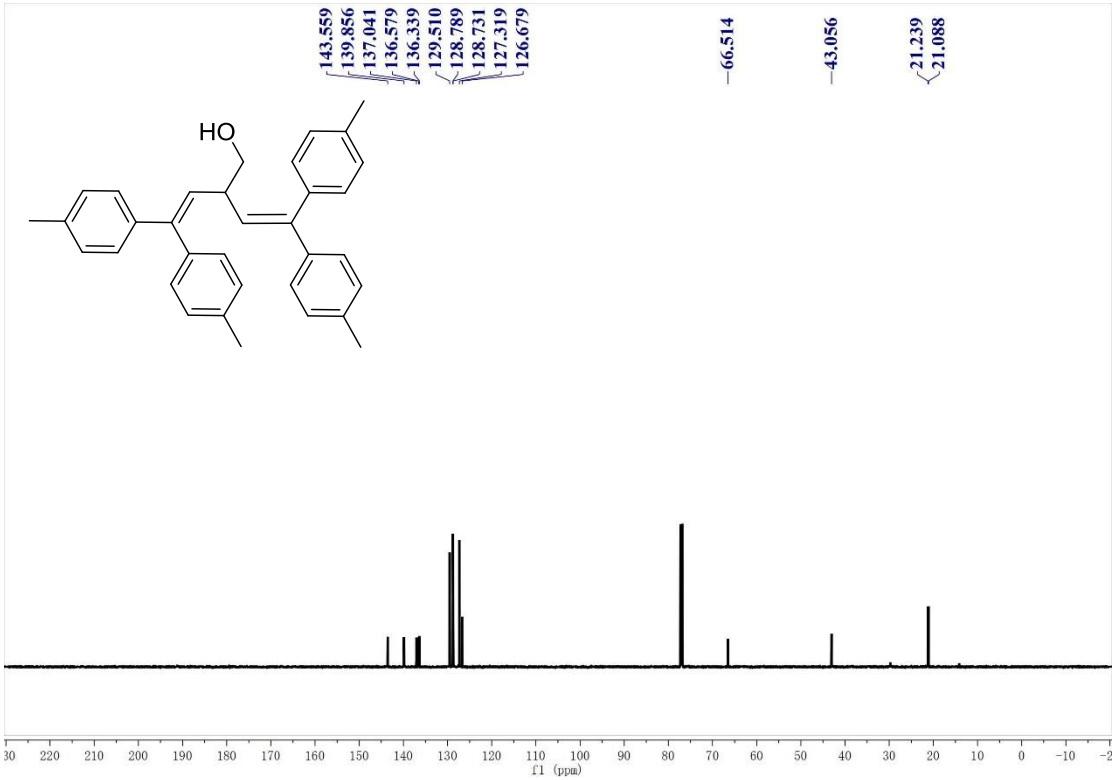

Figure 126. ^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **10d**