Electronic Supplementary Information

Fe(II)-Catalyzed Alkenylation of Benzylic C-H Bond with Diazo Compounds

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1. General Information

1.1 Analytic methods

^{1}H NMR and ^{13}C NMR data were obtained on AVANCE III Bruker 400 M Hz nuclear resonance spectrometers unless otherwise noted. $CDCl_3$ was used as solvent and tetramethylsilane (TMS) was used as the internal standard. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^{1}H NMR spectrum as 0.00 ppm. The data of ^{1}H NMR was reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant (*J* values) in Hz and integration. Chemical shifts for ^{13}C NMR spectra were recorded in ppm from TMS using the central peak of $CDCl_3$ (77.0 ppm) as the internal standard. Flash chromatography was performed using 200-300 mesh silica gel with the indicated eluent according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm) unless otherwise noted. High-resolution mass spectral (HRMS) data were recorded on Bruker APEX IV Fourier transform ion cyclotron resonance mass spectrometer using electrospray ionization (ESI and EI) by the analytical center in Peking University.

1.2 Reagents

Anhydrous $FeCl_2$ (98%) was purchased from Stream. DCE was used after distillation from petroleum ether. Other reagents were purchased and used directly without further purification otherwise noted.

Toluene, 1,2-dichloroethane were degassed by purging with nitrogen for 25 min and purified using an MBRAUN SPS-800 solvent purification system, which contained 75 ppm H_2O (measured by Karl-Fischer method).

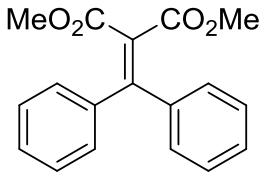
2. Experiments

General procedure for the oxidative alkenylation of Diazo Compounds 1c and diarylmethane 1a: An oven-dried Schlenk tube was charged with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 0.5 mmol), $FeCl_2$ (0.1 mmol), diphenylmethane and its derivatives (0.4 mmol), and diazoester**s** (0.2 mmol). Then dry dichloroethane（DCE, 1.0 mL）was added by syringe. The tube was degassed and refilled with N_2 for three times. The sealed reaction mixture was stirred at 90 ^{o}C for 24 h. The mixture was cooled to room temperature and was added saturated brine (15.0 mL). Then the mixture was washed with dichloromethane (3 x 20 mL). The organic layer was collected and washed with water (2 x 30 mL) and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by flash column chromatography eluting with petroleum ether to afford the desired products.

General procedure for the oxidative alkenylation of Diazo Compounds 2a and

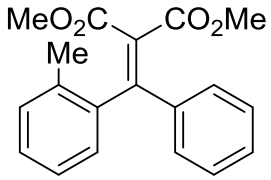
diarylmethane 1a: An oven-dried Schlenk tube was charged with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 0.5 mmol), $FeCl_2$ (0.1 mmol), diphenylmethane and its derivatives (0.4 mmol), Then dry dichloroethane（DCE, 0.4 mL）was added by syringe. The tube was degassed and refilled with N_2 for three times. The sealed reaction mixture was stirred at 90 ^oC for 0.5 h. Subsequently, the diazoester **2a** (0.2 mmol in DCE, 0.6 mL) was added with syringe pump over a period of 30 min. The mixture was cooled to room temperature and was added saturated brine (15.0 mL). Then the mixture was washed with dichloromethane (3 x 20 mL). The organic layer was collected and washed with water (2 x 30 mL) and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by flash column chromatography eluting with petroleum ether to afford the desired product **4c**.

3. ^{1}H and ^{13}C NMR and HRMS Data



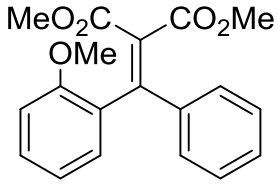
Dimethyl 2-(diphenylmethylene)malonate (3a)

Yield: 52.2 mg (88%), pink oil, R_f = 0.6 (PE:EA = 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.16-7.19 (m, 4H), 7.30-7.37 (m, 6H), 3.60 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 156.6, 139.9, 129.3, 129.1, 128.2, 52.2; HRMS (ESI): Anal. cacld. for $C_{18}H_{17}O_4$ ($[M+H]^+$) 297.1121, found: 297.1119.



Dimethyl 2-(phenyl(*o*-tolyl)methylene)malonate (3b)

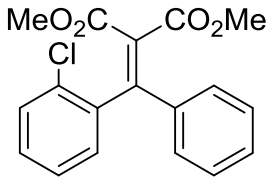
Yield: 57.9 mg (93%), red oil, R_f = 0.6 (PE:EA = 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.27-7.33 (m, 3H), 7.13-7.24 (m, 6H), 3.64 (s, 3H), 3.52 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 165.2, 156.5, 139.4, 138.7, 135.7, 130.4, 129.4, 128.6, 128.5, 128.3, 128.1, 126.5, 125.5, 52.4, 52.2, 19.7; HRMS (ESI): Anal. cacld. for $C_{19}H_{19}O_4$ ($[M+H]^+$) 311.1278, found: 311.1276.



Dimethyl 2-((*o*-methoxyphenyl)(phenyl)methylene)malonate (3c)

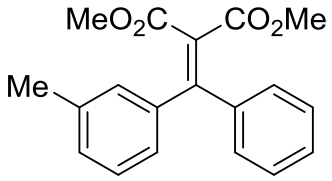
Yield: 55.1 mg (85%), red oil, R_f = 0.5 (PE:EA = 8:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ

7.27-7.34 (m, 4H), 7.19-7.21 (m, 2H), 7.00-7.02 (m, 1H), 6.89-6.94 (m, 2H), 3.69 (s, 3H), 3.60 (s, 3H), 3.58 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 165.4, 156.5, 152.8, 140.2, 130.3, 130.2, 129.0, 128.9, 128.4, 128.0, 126.8, 120.4, 111.2, 77.2, 55.6, 52.2, 52.0; HRMS (ESI): Anal. cacld. for $C_{19}H_{18}O_5$ ($[M+H]^+$) 326.1151, found: 326.1149.



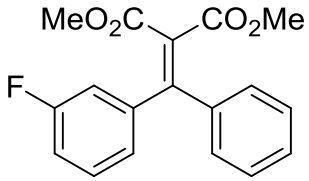
Dimethyl 2-((*o*-chlorophenyl)(phenyl)methylene)malonate (3d)

Yield: 55.0 mg (83%), colorless oil, R_f = 0.6 (PE:EA = 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38-7.41 (m, 1H), 7.27-7.30 (m, 5H), 7.23-7.25 (m, 2H), 7.19-7.21 (m, 1H), 3.64 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 164.3, 153.4, 138.7, 138.3, 132.4, 129.8, 129.7, 129.6, 129.5, 128.4, 128.3, 127.6, 126.6, 52.5, 52.3; HRMS (ESI): Anal. cacld. for $C_{18}H_{16}ClO_4$ ($[M+H]^+$) 331.0732, found: 331.0722.



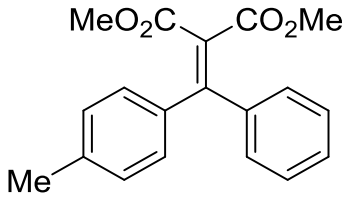
Dimethyl 2-(phenyl(*m*-tolyl)methylene)malonate (3e)

Yield: 47.6 mg (77%), red oil, R_f = 0.6 (PE:EA = 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.30-7.38 (m, 3H), 7.16-7.25 (m, 4H), 6.96-7.00 (m, 2H), 7.19-7.21 (m, 1H), 3.60 (s, 3H), 3.59 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 164.3, 153.4, 138.7, 138.3, 132.4, 129.8, 129.7, 129.6, 129.5, 128.4, 128.3, 127.6, 126.6, 52.5, 52.3; HRMS (ESI): Anal. cacld. for $C_{19}H_{19}O_4$ ($[M+H]^+$) 311.1278, found: 311.1239.



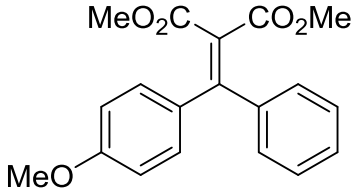
Dimethyl 2-((3-fluorophenyl)(phenyl)methylene)malonate (3f)

Yield: 37.0 mg (59%), colorless oil, R_f = 0.6 (PE:EA = 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28-7.39 (m, 4H), 7.15-7.18 (m, 2H), 7.04-7.08 (m, 1H), 7.68-7.00 (m, 1H), 6.85-6.89 (m, 1H), 3.63 (s, 3H), 3.61 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 165.9, 163.7, 161.2, 154.9, 142.0, 141.9, 139.3, 129.9, 129.8, 129.6, 129.0, 128.4, 126.2, 124.7, 124.7, 116.4, 116.2, 116.1, 116.0, 52.4, 52.4; HRMS (EI): Anal. cacld. for $C_{18}H_{15}O_4F$ ($[M]^+$) 314.0953, Found: 314.0949.



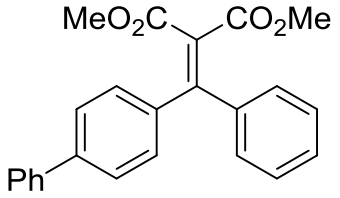
Dimethyl 2-(phenyl(*p*-tolyl)methylene)malonate (3g)

Yield: 59.6 mg (96%), red liquid, R_f = 0.6 (PE:EA = 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.29-7.36 (m, 3H), 7.12-7.18 (m, 4H), 7.05-7.07 (m, 2H), 3.63 (s, 3H), 3.58 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 166.6, 166.5, 156.8, 140.2, 139.7, 137.0, 129.3, 129.2, 129.1, 129.0, 128.2, 124.83, 52.3, 52.2, 21.4; HRMS (EI): Anal. cacld. for $C_{19}H_{18}O_4$ ($[M]^+$) 310.1203, found: 310.1200.



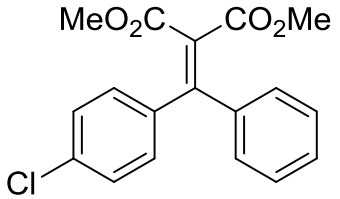
Dimethyl 2-((*p*-methoxyphenyl)(phenyl)methylene)malonate (3h)

Yield: 50.2 mg (77%), colorless liquid, R_f = 0.5 (PE:EA = 8:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.30-7.39 (m, 3H), 7.16-7.18 (m, 2H), 7.09-7.12 (m, 2H), 6.82-6.86 (m, 2H), 3.81 (s, 3H), 3.65 (s, 3H), 3.58 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 166.6, 160.7, 156.6, 140.3, 132.1, 131.0, 129.3, 129.3, 128.12, 124.1, 113.6, 55.3, 52.3, 52.2; HRMS (EI): Anal. Cacld. for $C_{19}H_{18}O_5$ ($[M]^+$) 326.1150, found: 326.1149.



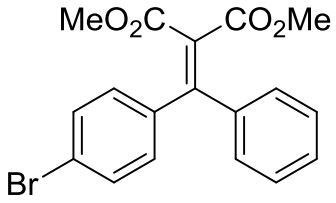
Dimethyl 2-([1,1'-biphenyl]-4-yl(phenyl)methylene)malonate (3i)

Yield: 68.5 mg (92%), white solid, R_f = 0.5 (PE:EA = 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55-7.61 (m, 4H), 7.41-7.45 (m, 2H), 7.32-7.36 (m, 4H), 7.20-7.26 (m, 4H), 3.64 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 166.5, 166.4, 156.3, 142.2, 140.2, 140.0, 138.8, 129.8, 129.4, 129.2, 128.9, 128.3, 127.8, 127.1, 126.9, 125.3, 52.4, 52.3; HRMS (EI): Anal. cacld. for $C_{24}H_{20}O_4$ ($[M]^+$) 372.1357, found: 372.1356.



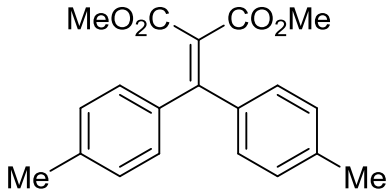
Dimethyl 2-((*p*-chlorophenyl)(phenyl)methylene)malonate (3j)

Yield: 58.8 mg (89%), colorless oil, R_f = 0.5 (PE:EA = 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.29-7.38 (m, 5H), 7.10-7.17 (m, 4H), 3.64 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 166.0, 155.2, 139.5, 138.3, 135.5, 130.5, 129.6, 129.0, 128.6, 128.4, 125.8, 52.4, 52.3; HRMS (EI): Anal. cacld. for $C_{18}H_{15}O_4Cl$ ($[M]^+$) 330.0657, found: 330.0653.



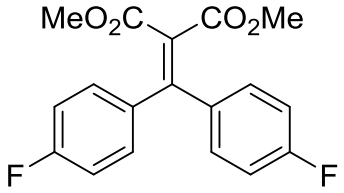
Dimethyl 2-((*p*-bromophenyl)(phenyl)methylene)malonate (3k)

Yield: 51.0 mg (68%), colorless solid, R_f = 0.6 (PE:EA = 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.45-7.47 (m, 2H), 7.31-7.36 (m, 3H), 7.14-7.16 (m, 2H), 7.03-7.06 (m, 2H), 3.64 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 166.2, 166.0, 155.2, 139.4, 138.8, 131.5, 130.7, 129.6, 129.0, 128.7, 128.4, 128.3, 126.6, 125.8, 123.9, 52.4, 52.3; HRMS (EI): Anal. cacld. for $C_{18}H_{15}O_4Br$ ($[M]^+$) 374.0151, found: 374.0148.



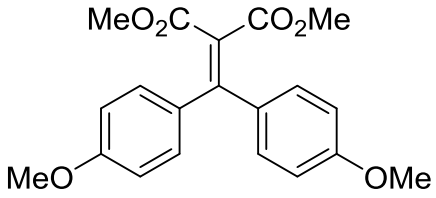
Dimethyl 2-(di-*p*-tolylmethylene)malonate (3l)

Yield: 63.4 mg (98%), yellow solid, R_f = 0.6 (PE:EA = 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.11-7.13 (dd, 4H), 7.04-7.06 (dd, 4H), 3.62 (s, 6H), 2.35 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 157.0, 139.6, 137.2, 129.3, 128.9, 124.3, 52.2, 21.4; HRMS (EI): Anal. cacld. for $C_{20}H_{20}O_4$ ($[M]^+$) 324.1359, found: 324.1356.



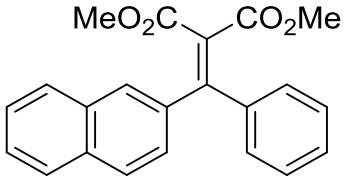
Dimethyl 2-(bis(*p*-fluorophenyl)methylene)malonate (3m)

Yield: 50.0 mg (75%), yellow solid, R_f = 0.6 (PE:EA = 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.13-7.17 (m, 4H), 7.01-7.05 (m, 4H), 3.63 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 164.7, 162.2, 154.3, 135.7, 135.7, 131.2, 131.1, 125.6, 115.6, 115.4, 52.4; HRMS (EI): Anal. cacld. for $C_{18}H_{14}O_4F_2$ ($[M]^+$) 332.0857, found: 332.0855.



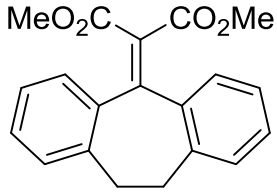
Dimethyl 2-(bis(*p*-methoxyphenyl)methylene)malonate (3n)

Yield: 39.2 mg (55%), white solid, R_f = 0.6 (PE:EA = 6:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.09-7.12 (dd, 4H), 6.86-6.85 (dd, 4H), 3.80 (s, 6H), 3.61 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 160.8, 156.6, 132.5, 131.2, 122.9, 113.6, 55.3, 52.1; HRMS (EI): Anal. cacld. for $C_{20}H_{20}O_6$ ([M]$^+$) 356.1258, found: 356.1254.



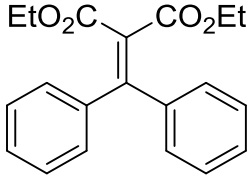
Dimethyl 2-(naphthalen-2-yl(phenyl)methylene)malonate (3o)

Yield: 58.3 mg (84%), white solid, R_f = 0.6 (PE:EA = 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.77-7.84 (m, 3H), 7.68 (s, 1H), 7.46-7.53 (m, 2H), 7.32-7.38 (m, 3H), 7.20-7.26 (m, 3H), 3.63 (s, 3H), 3.57 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 166.4, 156.5, 134.0, 137.4, 133.5, 132.8, 129.5, 129.2, 128.9, 128.5, 128.3, 127.9, 127.8, 127.1, 126.5, 126.5, 125.7, 52.3, 52.3; HRMS (EI): Anal. cacld. for $C_{22}H_{18}O_4$ ([M]$^+$) 346.1201, found: 346.1200.



Dimethyl 2-(10,11-dihydro-5*H*-dibenzo[*a,d*][7]annulen-5-ylidene)malonate (3p)

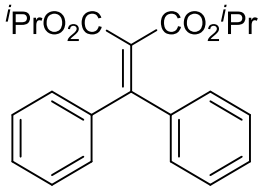
Yield: 58.0 mg (90%), white solid, Rf = 0.6 (PE:EA = 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.20-7.23 (m, 4H), 7.11-7.15 (m, 4H), 3.58 (s, 6H), 3.39-3.46 (m, 2H), 2.85-2.91 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 158.0, 138.4, 136.8, 129.4, 128.8, 126.8, 126.0, 125.6, 52.2, 32.0; HRMS (EI): Anal. cacld. for $C_{20}H_{18}O_4$ ([M]$^+$) 322.1201, found: 322.1120.



Diethyl 2-(diphenylmethylene)malonate (4a)

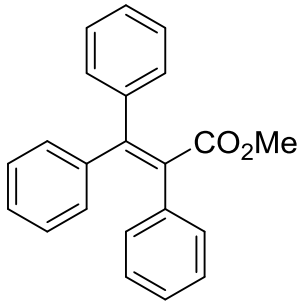
Yield: 40.0 mg (62%), red oil, R_f = 0.6 (PE:EA = 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ

7.29-7.38 (m, 6H), 7.18-7.20 (m, 4H), 4.07 (q, J = 0.40 Hz, 4H), 1.02 ((t, J = 0.40 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 157.0, 139.6, 137.2, 129.3, 128.9, 124.3, 52.2, 21.4; HRMS (EI): Anal. cacld. for $C_{20}H_{20}O_4$ ([M]$^+$) 324.1359, found: 324.1356.



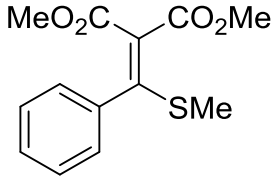
Diisopropyl 2-(diphenylmethylene)malonate (4b)

Yield: 49.1 mg (70%), red oil, R_f = 0.6 (PE:EA = 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31 (m, 6H), 7.19 (d, J = 6.9 Hz, 4H), 4.94 (dt, J = 12.2, 6.1 Hz, 2H), 1.07 (d, J = 6.1 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 154.6, 140.2, 129.1, 129.0, 128.1, 68.9, 21.3; HRMS (EI): Anal. cacld. for $C_{22}H_{24}O_4$ ([M]$^+$) 352.1672, found: 352.1669.



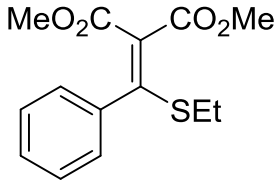
Methyl 2,3,3-triphenylacrylate (4c)

Yield: 45.2 mg (72%), yellow solid, R_f = 0.6 (PE:EA = 20:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32-7.33 (m, 3H), 7.26-7.28 (m, 2H), 7.09-7.19 (m, 8H), 6.99-7.01 (m, 2H), 3.55 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 140.1, 129.1, 129.1, 128.1, 61.2, 13.6; HRMS (ESI): Anal. cacld. for $C_{22}H_{19}O_2$ ([M+H]$^+$) 315.1380, found: 315.1380.



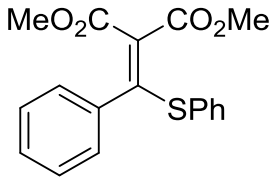
Dimethyl 2-((methylthio)(phenyl)methylene)malonate (6a)

Yield: 37.2 mg (70%), yellow oil, R_f = 0.6 (PE:EA = 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33-7.42 (m, 3H), 7.17-7.19 (m, 2H), 3.82 (s, 3H), 3.38 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 164.3, 163.8, 135.3, 128.9, 128.4, 127.8, 120.7, 52.1, 52.0, 16.2; HRMS (EI): Anal. cacld. for $C_{13}H_{14}O_4S$ ([M]$^+$) 266.0611, found: 266.0607.



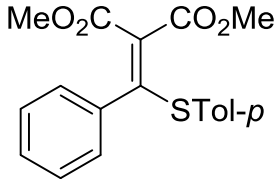
Dimethyl 2-((ethylthio)(phenyl)methylene)malonate (6b)

Yield: 19.6 mg (35%), yellow oil, R_f = 0.6 (PE:EA = 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43-7.33 (m, 3H), 7.23 (dd, J = 7.6, 1.5 Hz, 2H), 3.82 (s, 3H), 3.38 (s, 3H), 2.26 (q, J = 7.5 Hz, 2H), 1.07 (t, J = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 164.4, 162.9, 135.7, 128.9, 128.3, 127.9, 121.0, 52.1, 52.0, 27.1, 14.1; HRMS (EI): Anal. cacld. for $C_{14}H_{16}O_4S$ ($[M]^+$) 280.0769, found: 280.0764.



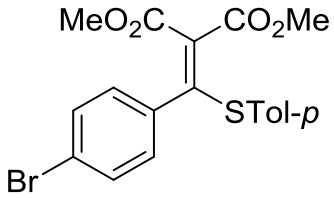
Dimethyl 2-(phenyl(phenylthio)methylene)malonate (6c)

Yield: 46.6 mg (71%), red solid, R_f = 0.6 (PE:EA = 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.15-7.17 (m, 2H), 7.08-7.12 (m, 1H), 6.97-7.05 (m, 7H), 3.85 (s, 3H), 3.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 164.2, 162.4, 135.5, 135.3, 130.6, 128.7, 128.7, 128.5, 128.4, 127.4, 120.9, 52.3, 52.2; HRMS (EI): Anal. cacld. for $C_{18}H_{16}O_4S$ ($[M]^+$) 328.0769, found: 328.0764.



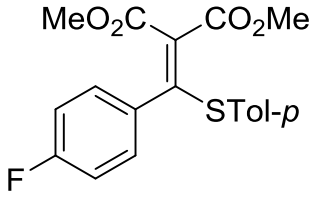
Dimethyl 2-(phenyl(*p*-tolylthio)methylene)malonate (6d):

Yield: 36.9 mg (54%), purple solid, R_f = 0.6 (PE:EA = 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.99-7.06 (m, 5H), 6.97-6.98 (m, 2H), 6.84 (d, J = 8.0 Hz, 2H), 3.85 (s, 3H), 3.38 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 164.3, 163.0, 138.9, 135.4, 129.2, 128.7, 128.3, 127.4, 126.9, 120.6, 52.3, 52.1, 21.1; HRMS (EI): Anal. cacld. for $C_{19}H_{18}O_4S$ ($[M]^+$) 342.0927, found: 342.0920.

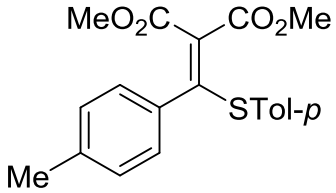


Dimethyl 2-((4-bromophenyl)(*p*-tolylthio)methylene)malonate (6e)

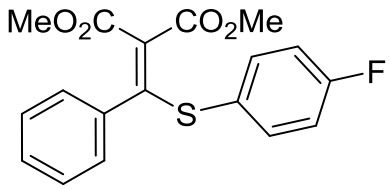
Yield: 43.7 mg (52%), yellow solid, R_f = 0.6 (PE:EA = 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.20 (d, J = 8.4 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 6.86-6.90 (m, 4H), 3.85 (s, 3H), 3.44 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 164.2, 161.0, 139.3, 135.4, 134.4, 130.7, 130.3, 129.5, 126.6, 122.7, 121.4, 52.4, 52.3, 21.2; HRMS (EI): Anal. cacld. for $C_{19}H_{17}O_4BrS$ ($[M]^+$) 420.0030, found: 420.0025.



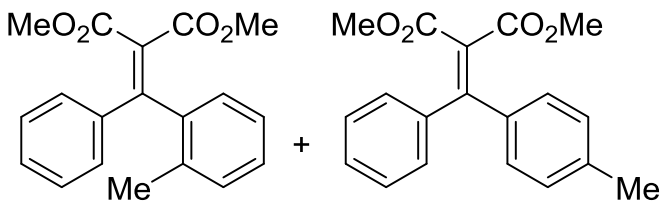
Dimethyl 2-((4-fluorophenyl)(*p*-tolylthio)methylene)malonate (6f):
Yield: 37.7 mg (52%), purple solid, R_f = 0.6 (PE:EA = 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.04 (d, J = 8.0 Hz, 2H), 7.01-6.94 (m, 2H), 6.87 (d, J = 7.9 Hz, 2H), 6.76 (t, J = 8.7 Hz, 2H), 3.85 (s, 3H), 3.43 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 164.2, 163.6, 161.6, 161.1, 139.2, 135.4, 131.5, 131.4, 130.7, 130.6, 129.8, 129.4, 129.4, 129.3, 128.6, 126.7, 126.6, 121.2, 114.7, 114.5, 52.4, 52.2, 21.1; HRMS (EI): Anal. cacld. for $C_{19}H_{17}O_4FS$ ($[M]^+$) 360.0831, found: 360.0826.



Dimethyl 2-((4-methylphenyl)(*p*-tolylthio)methylene)malonate (6g)
Yield: 41.3 mg (58%), red solid, R_f = 0.6 (PE:EA = 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.04 (d, J = 8.0 Hz, 2H), 6.93 – 6.81 (m, 6H), 3.82 (s, 3H), 3.41 (s, 3H), 2.18 (d, J = 3.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 164.4, 162.8, 138.7, 138.3, 135.1, 132.6, 129.2, 128.7, 128.1, 127.3, 120.8, 52.2, 52.1, 21.2, 21.1; HRMS (EI): Anal. cacld. for $C_{20}H_{20}O_4S$ ($[M]^+$) 356.1081, found: 356.1077.

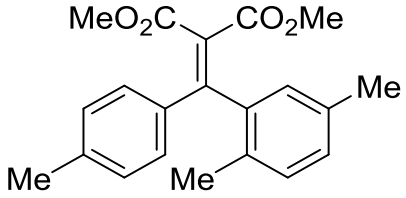


Dimethyl 2-(((4-fluorophenyl)thio)(phenyl)methylene)malonate (6h)
Yield: 35.3 mg (51%), white solid, R_f = 0.6 (PE:EA = 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.12-7.16 (m, 2H), 7.06-7.08 (m, 3H), 6.94-6.98 (m, 2H), 6.70-6.76 (m, 2H), 3.86 (s, 3H), 3.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 164.2, 164.2, 162.3, 161.7, 137.7, 137.6, 135.1, 128.6, 128.5, 127.6, 125.9, 125.9, 120.9, 115.8, 115.6, 52.4, 52.2; HRMS (EI): Anal. cacld. for $C_{18}H_{15}O_4FS$ ($[M]^+$) 346.0676, found: 346.0670.



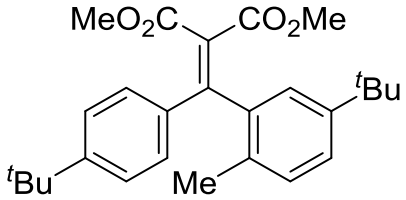
Dimethyl 2-(phenyl(*o*-tolyl)methylene)malonate (8a+8b)

Yield: 29.2 mg (47%), red oil, R_f = 0.6 (PE:EA = 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.27-7.37 (m, 6H), 7.12-7.23 (m, 10H), 7.05-7.07 (d, 2H), 3.64 (d, 6H), 3.58 (d, 3H), 2.35 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 166.6, 166.5, 165.2, 156.8, 156.5, 140.2, 139.6, 139.4, 138.7, 137.0, 135.7, 130.4, 129.4, 129.3, 129.2, 129.1, 129.1, 129.0, 128.6, 128.5, 128.3, 128.2, 128.1, 126.5, 125.5, 124.9, 52.4, 52.3, 52.2, 52.1, 21.4, 19.7; HRMS (EI): Anal. cacld. for $C_{19}H_{18}O_4$ ($[M]^+$) 310.1204, found: 310.1120.



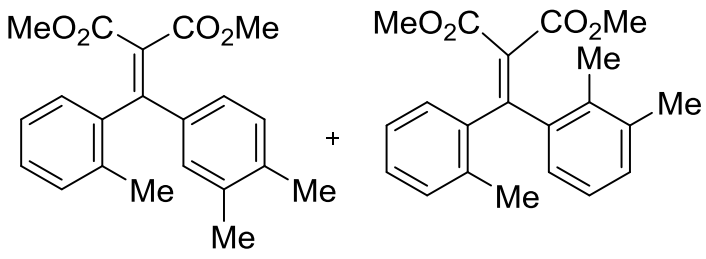
Dimethyl 2-((2,5-dimethylphenyl)(*p*-tolyl)methylene)malonate (9a)

Yield: 54.8 mg (81%), white solid, R_f = 0.6 (PE:EA = 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.09 (s, 4H), 7.05 (s, 2H), 6.93 (s, 1H), 3.67 (s, 3H), 3.54 (s, 3H), 2.33 (s, 3H), 2.30 (s, 3H), 2.03 (s, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 165.4, 156.8, 139.6, 139.5, 135.9, 134.9, 132.6, 130.2, 129.2, 129.0, 128.6, 128.6, 125.7, 52.3, 52.0, 21.4, 20.9, 19.2; HRMS (EI): Anal. cacld. for $C_{21}H_{22}O_4$ ($[M]^+$) 338.1516, found: 338.1513.

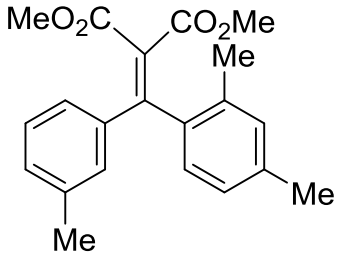


Dimethyl 2-((5-(*tert*-butyl)-2-methylphenyl)(*p*-(*tert*-butyl)phenyl)methylene)malonate (9b)

Yield: 82.8 mg (98%), yellow oil, R_f = 0.6 (PE:EA = 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.29-7.31 (m, 2H), 7.24-27 (m, 1H), 7.17 (d, 1H), 7.11-7.13 (m, 2H), 7.05-7.07 (m, 1H), 3.68 (s, 3H), 3.48 (s, 3H), 1.30 (s, 9H), 1.29 (s, 9H) ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 165.8, 157.1, 152.6, 148.3, 139.2, 135.4, 133.0, 130.0, 128.5, 125.6, 125.5, 125.2, 125.1, 52.2, 52.0, 34.7, 34.4, 31.4, 31.2, 19.2; HRMS (ESI): Anal. cacld. for $C_{27}H_{35}O_4$ ($[M+H]^+$) 423.2530, found: 423.2527.

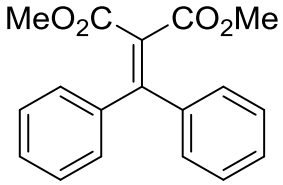


Dimethyl 2-((*m,p*-dimethylphenyl)(*o*-tolyl)methylene)malonate (10a+10b, ratio = 4.3:1**)**
Yield: 54.5 mg (81%), yellow solid, R_f = 0.6 (PE:EA = 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.08-7.25 (m, 5.7H), 7.01-7.05 (m, 1.4H), 6.93-6.95 (d, 2.3H), 3.67 (s, 3H), 3.55 (d, 1.3H), 3.52 (s, 3H), 2.23 (s, 3H), 2.25 (s, 0.7H), 2.18 (s, 3H), 2.20 (s, 0.7H), 2.16 (s, 0.7H), 2.08 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 165.7, 165.3, 156.7, 139.7, 138.4, 136.5, 136.2, 135.8, 130.6, 130.3, 129.6, 129.5, 128.9, 128.4, 128.1, 126.7, 126.2, 125.7, 125.5, 125.1, 52.3, 52.2, 52.0, 20.5, 19.8, 19.7, 19.7; HRMS (EI): Anal. cacld. for $C_{21}H_{22}O_4$ ($[M]^+$) 338.1503, found: 338.1513.

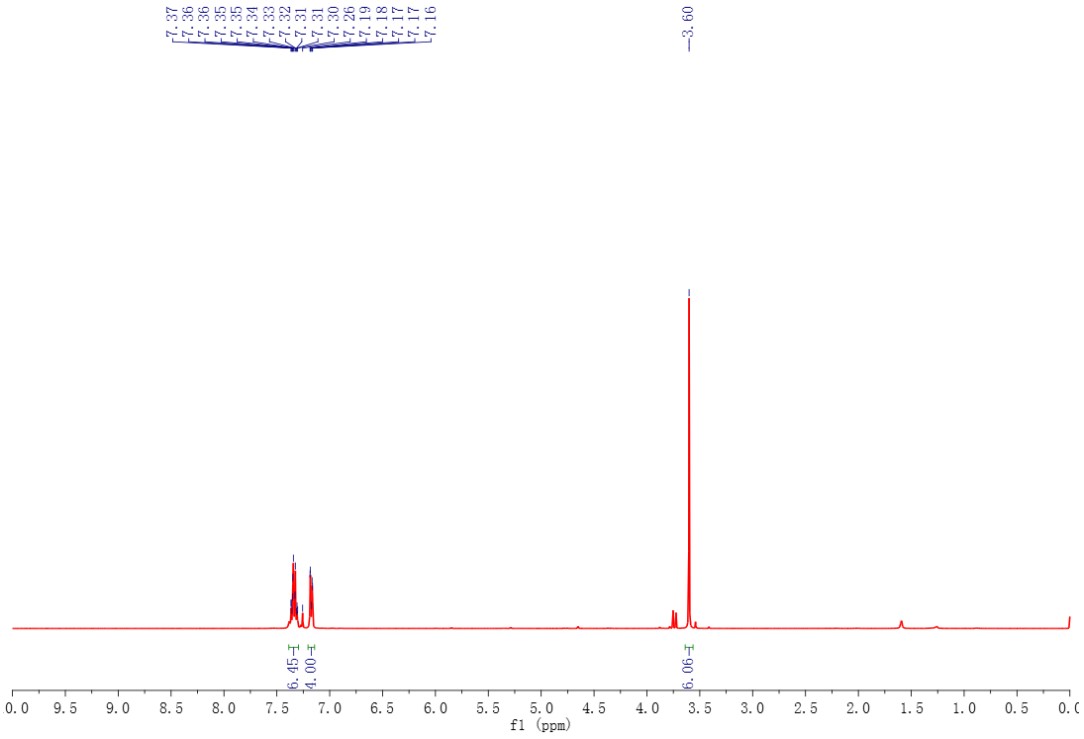


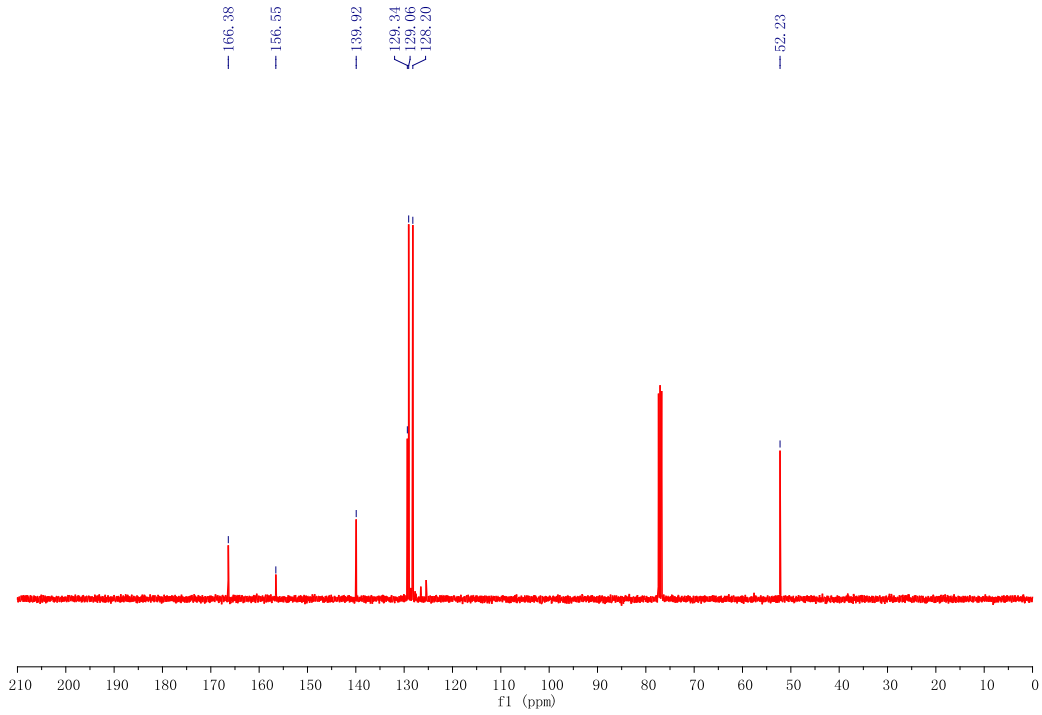
Dimethyl 2-((*m,p*-dimethylphenyl)(*o*-tolyl)methylene)malonate (11a)
Yield: 54.5 mg (81%), red oil, R_f = 0.6 (PE:EA = 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12-7.20 (m, 2H), 6.99-7.03 (m, 5H), 3.64 (s, 3H), 3.56 (s, 3H), 2.33 (s, 3H), 2.29 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 165.3, 157.1, 139.0, 138.3, 137.8, 136.6, 135.5, 131.2, 130.2, 129.0, 128.1, 128.1, 126.2, 125.7, 52.3, 52.1, 21.4, 21.3, 19.7; HRMS (EI): Anal. cacld. for $C_{21}H_{22}O_4$ ($[M]^+$) 338.1519, found: 338.1513.

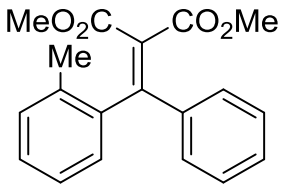
4. ^{1}H and ^{13}C NMR Spectra



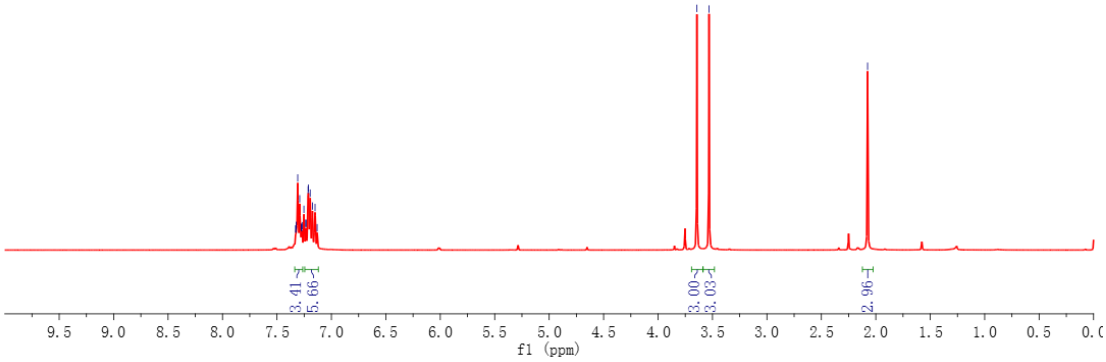
Dimethyl 2-(diphenylmethylene)malonate (3a)

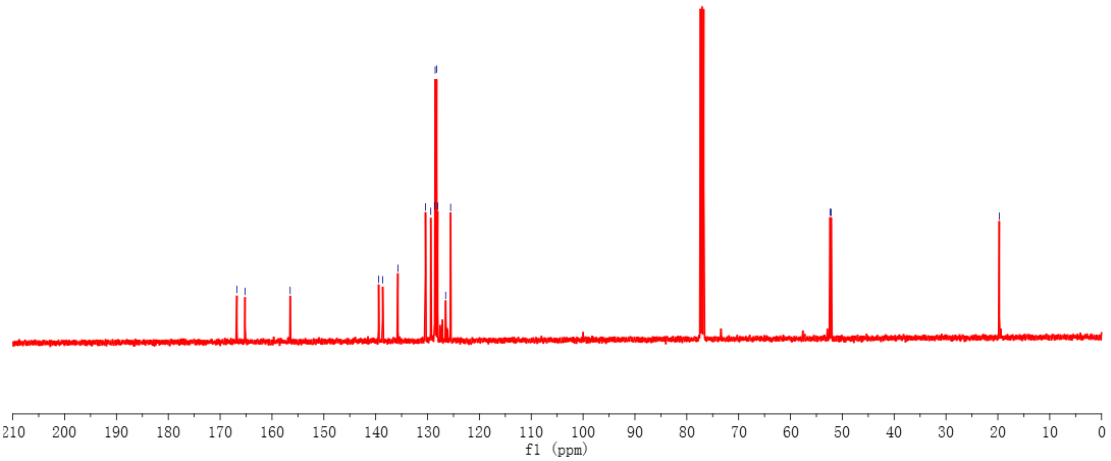


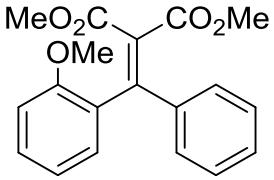




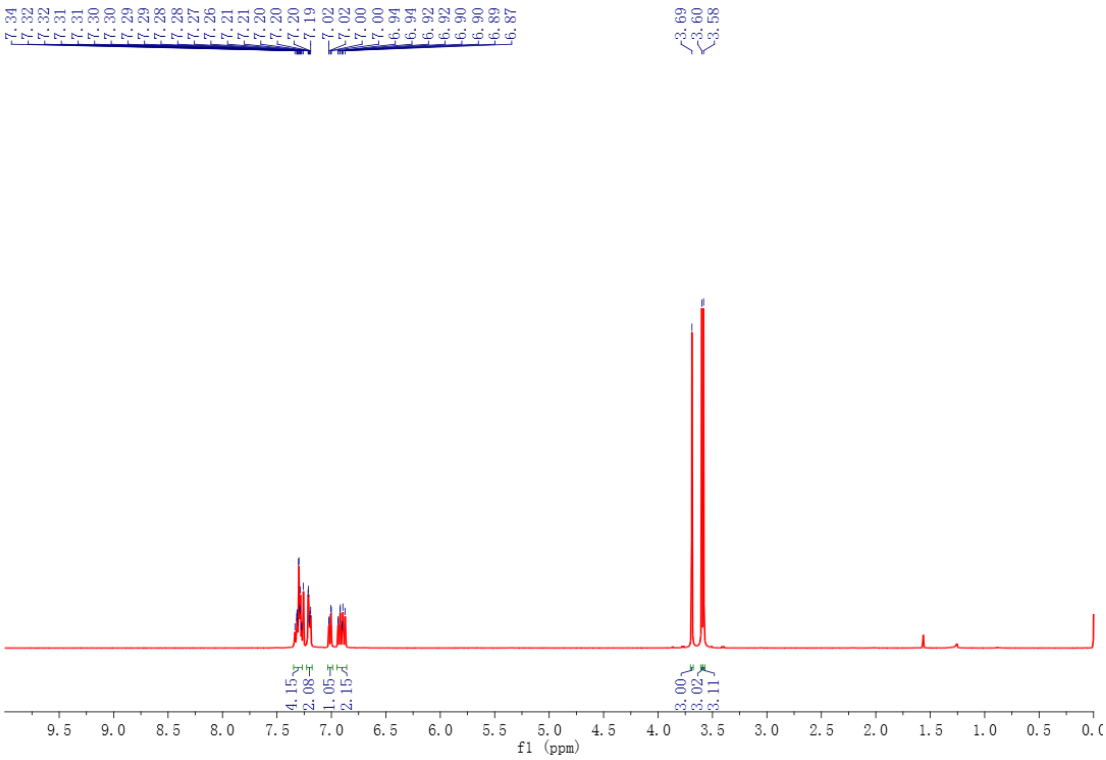
Dimethyl 2-(phenyl(*o*-tolyl)methylene)malonate (3b)

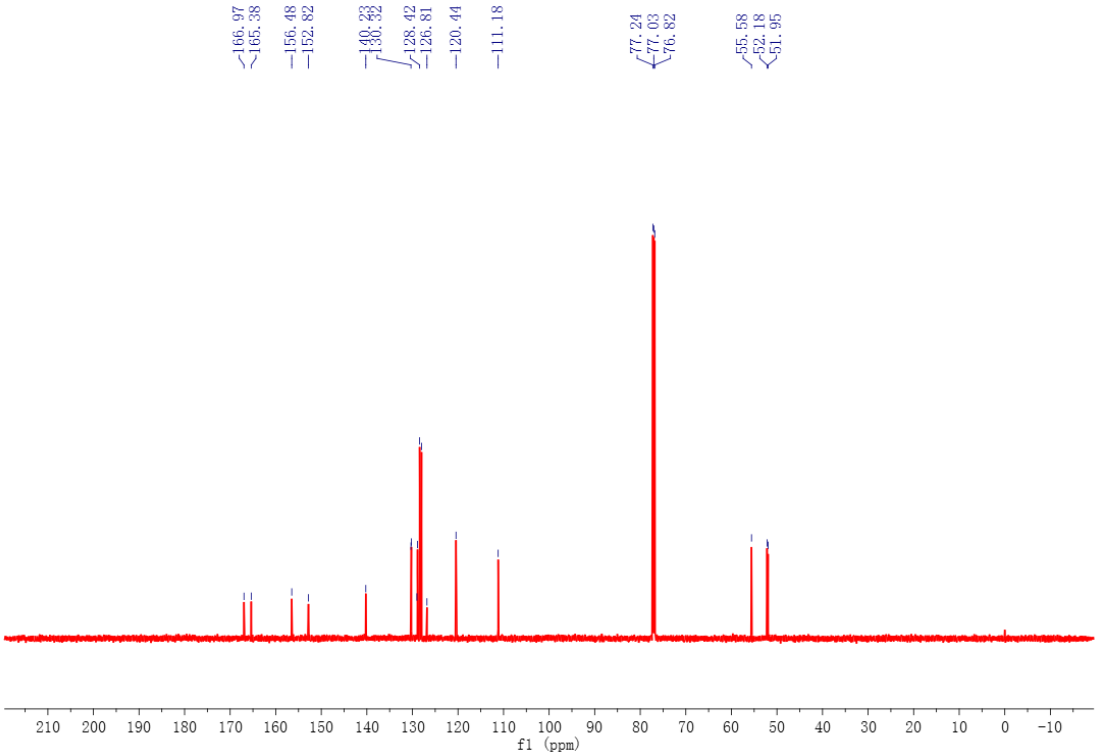


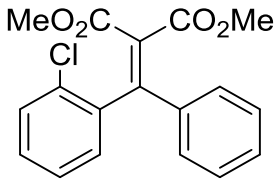




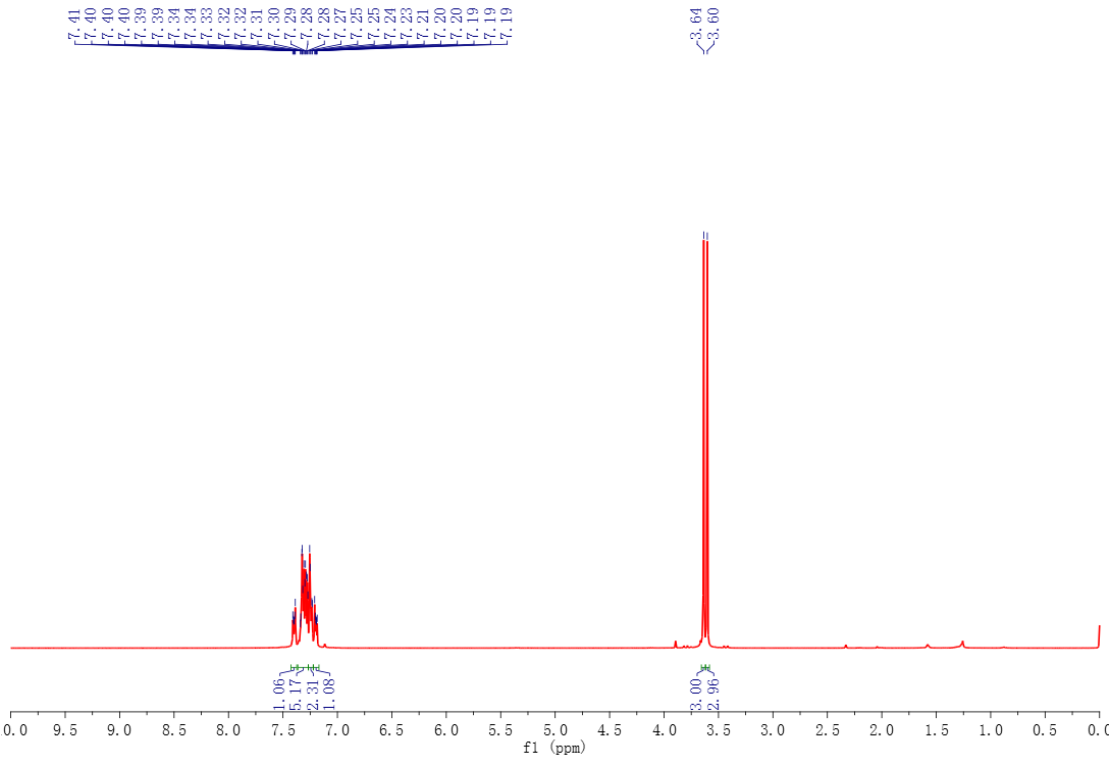
Dimethyl 2-((*o*-methoxyphenyl)(phenyl)methylene)malonate (3c)

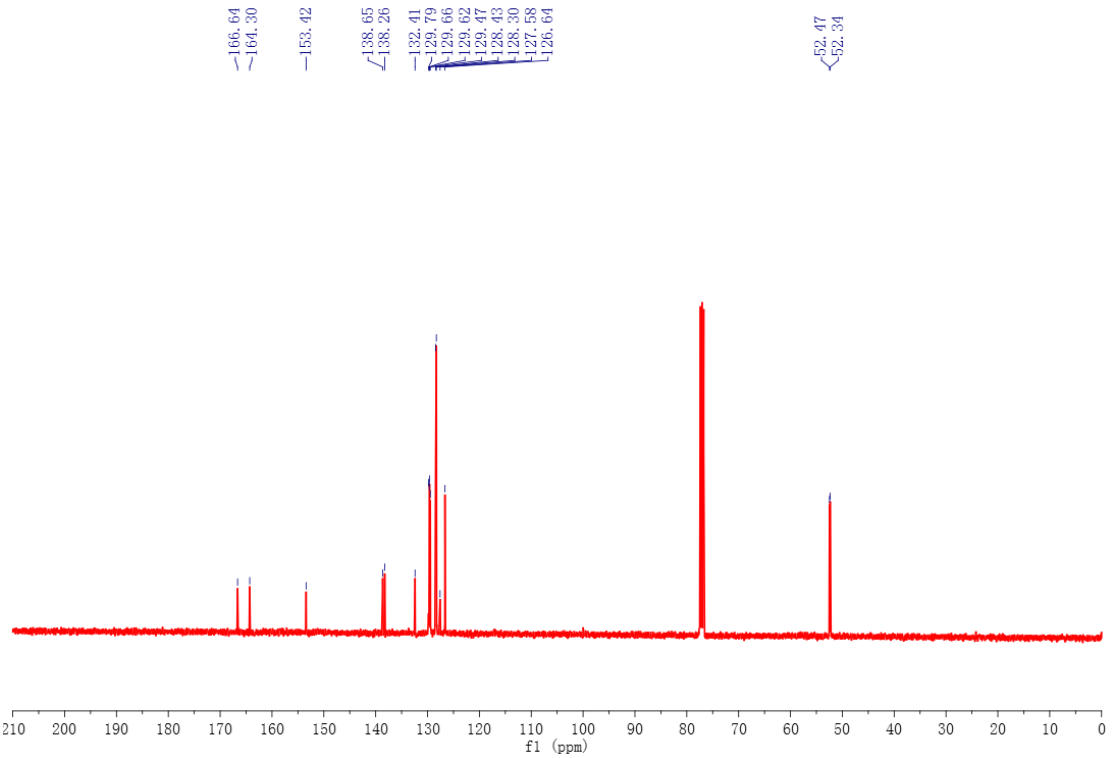


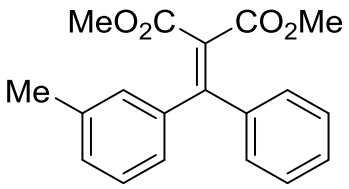




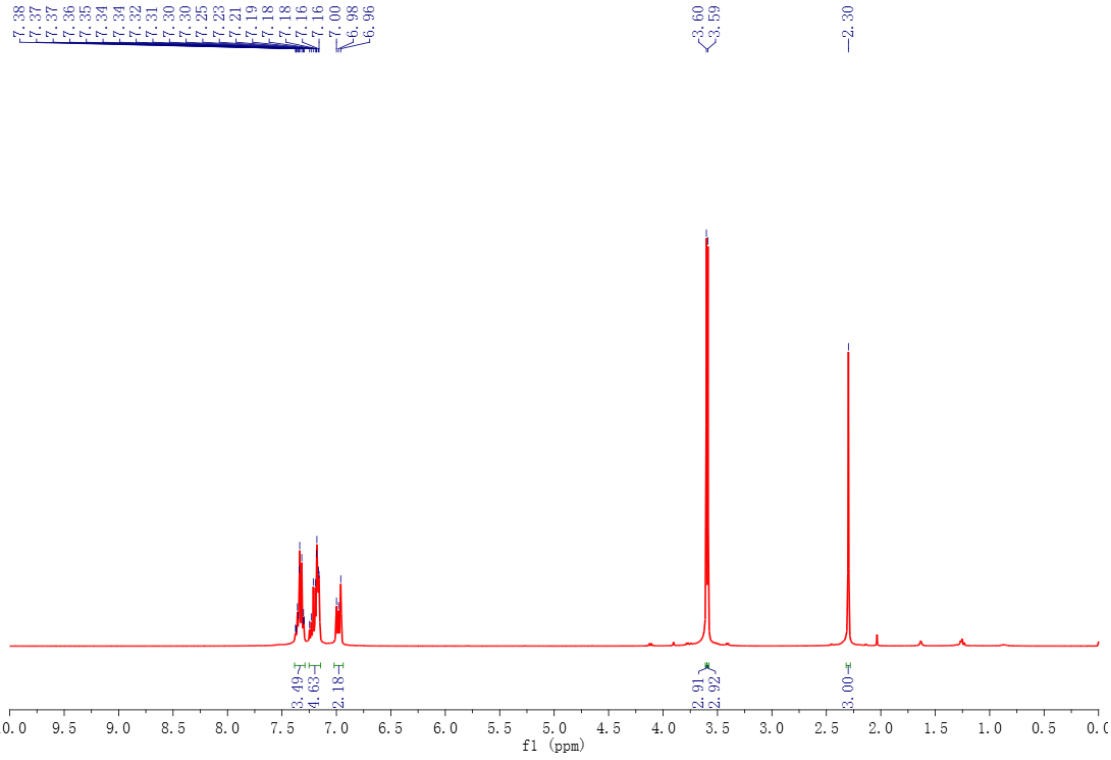
Dimethyl 2-((*o*-chlorophenyl)(phenyl)methylene)malonate (3d)

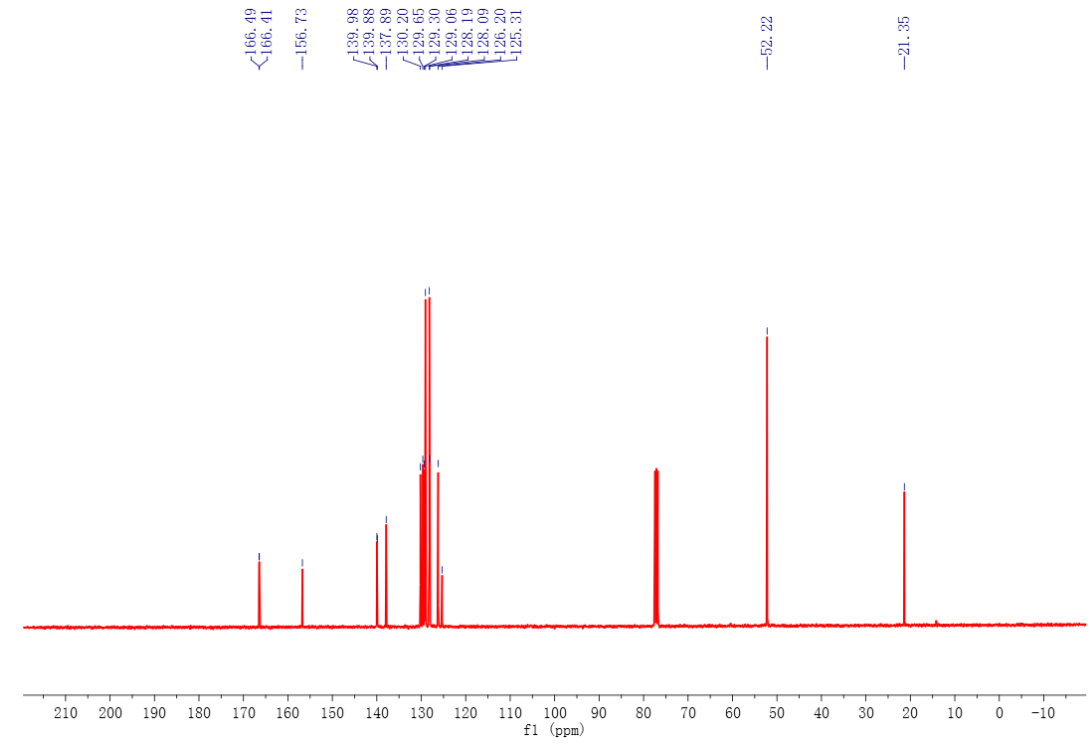


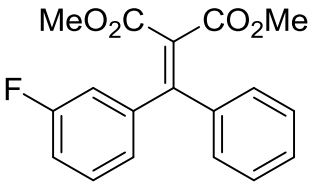




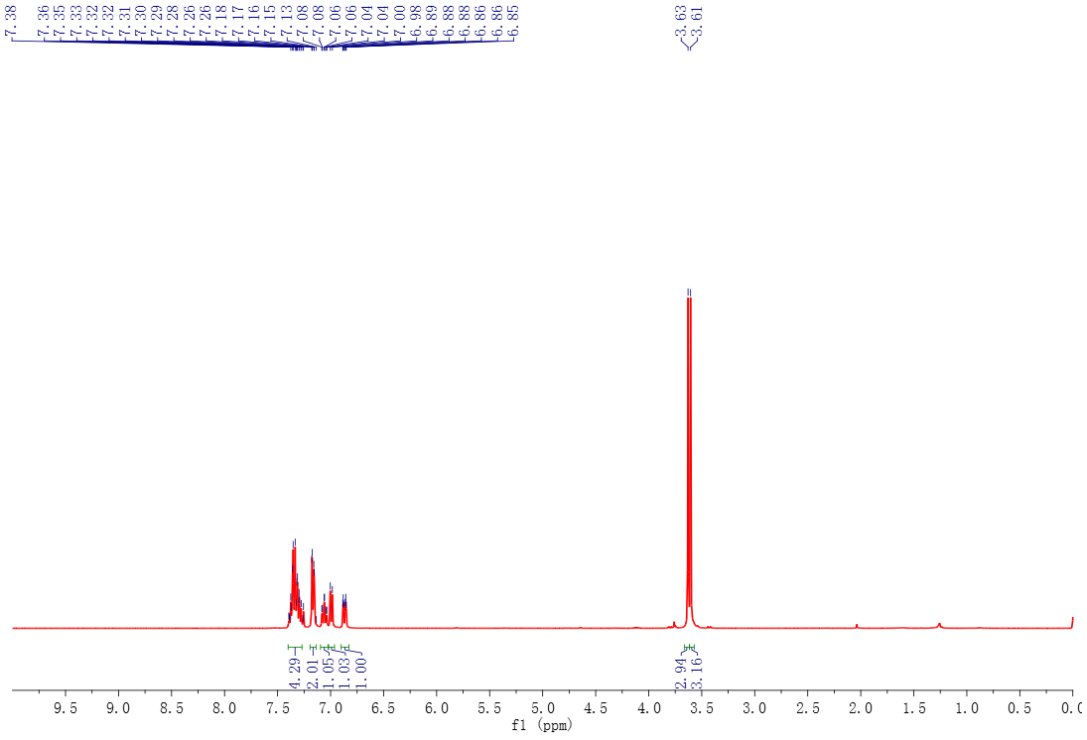
Dimethyl 2-(phenyl(*m*-tolyl)methylene)malonate (3e)

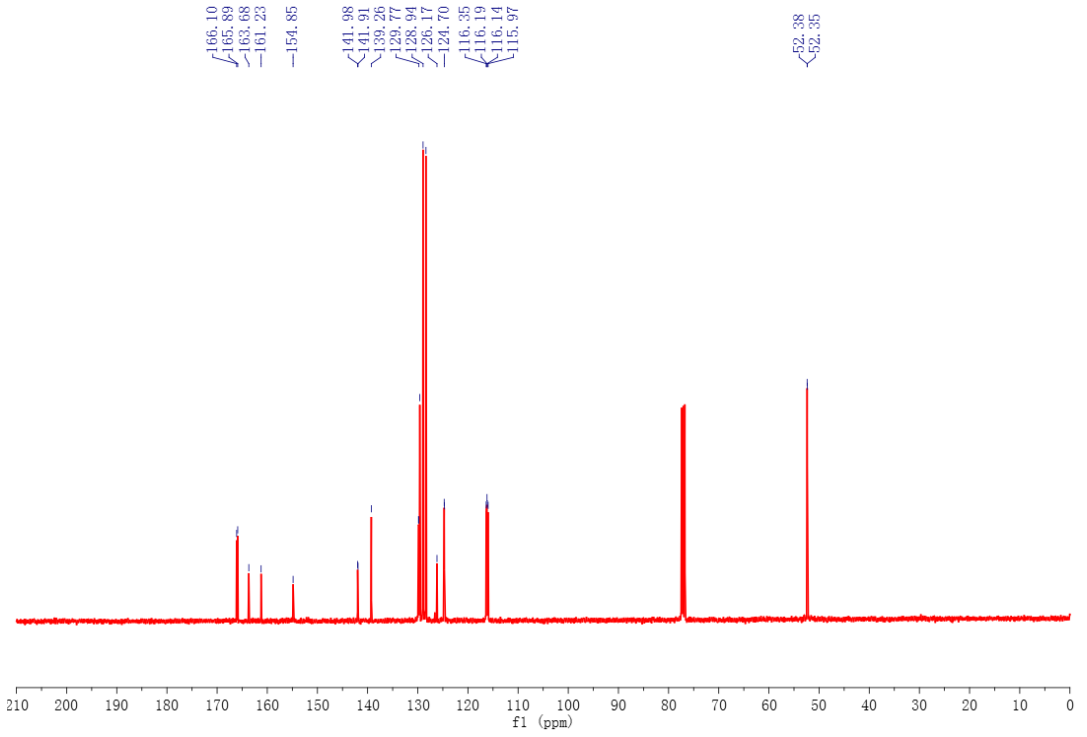


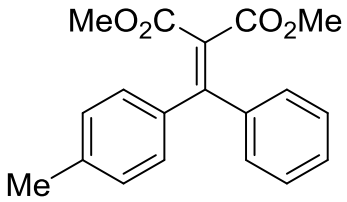




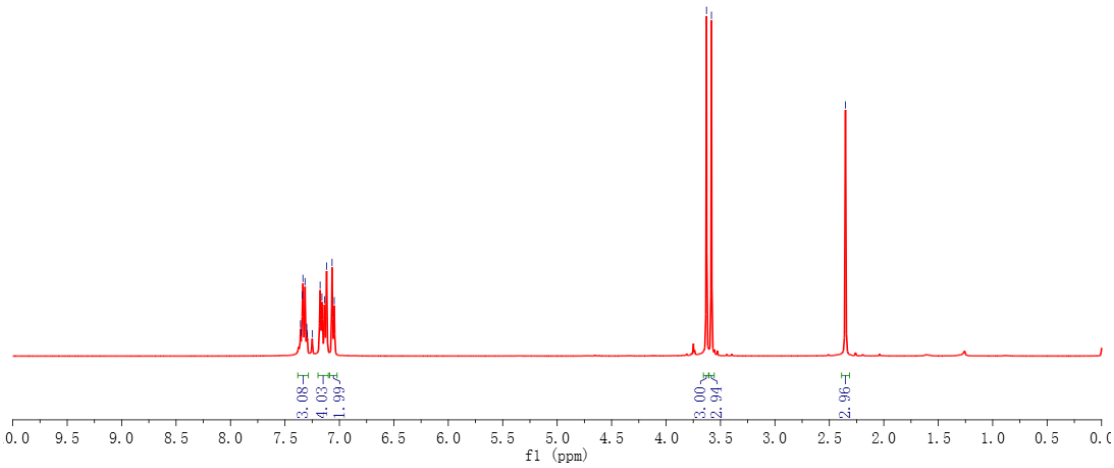
Dimethyl 2-((*m*-fluorophenyl)(phenyl)methylene)malonate (3f)

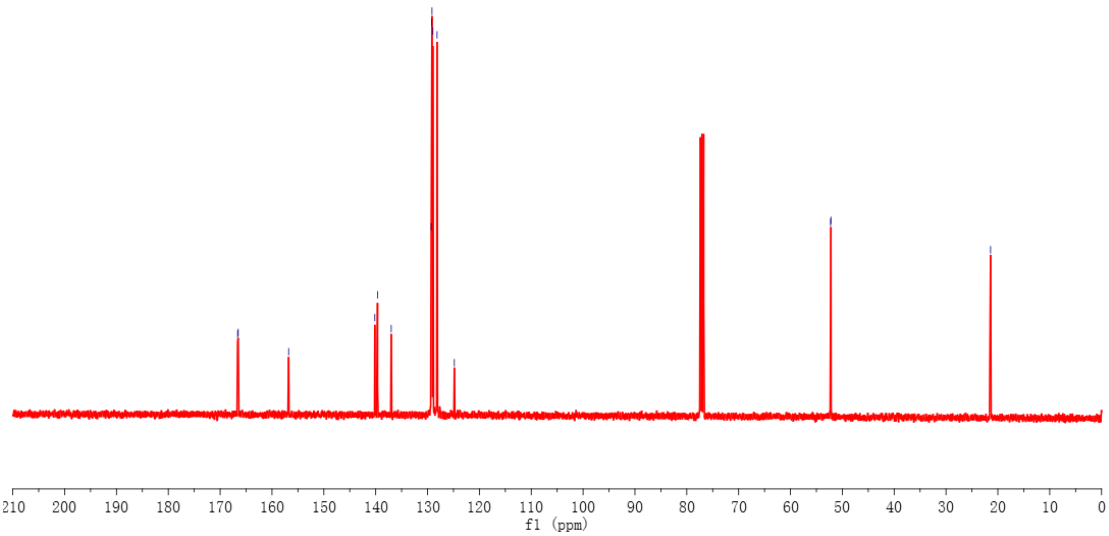


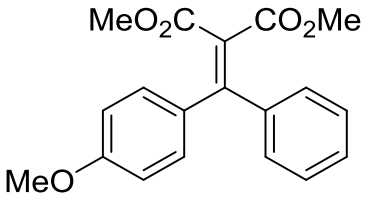




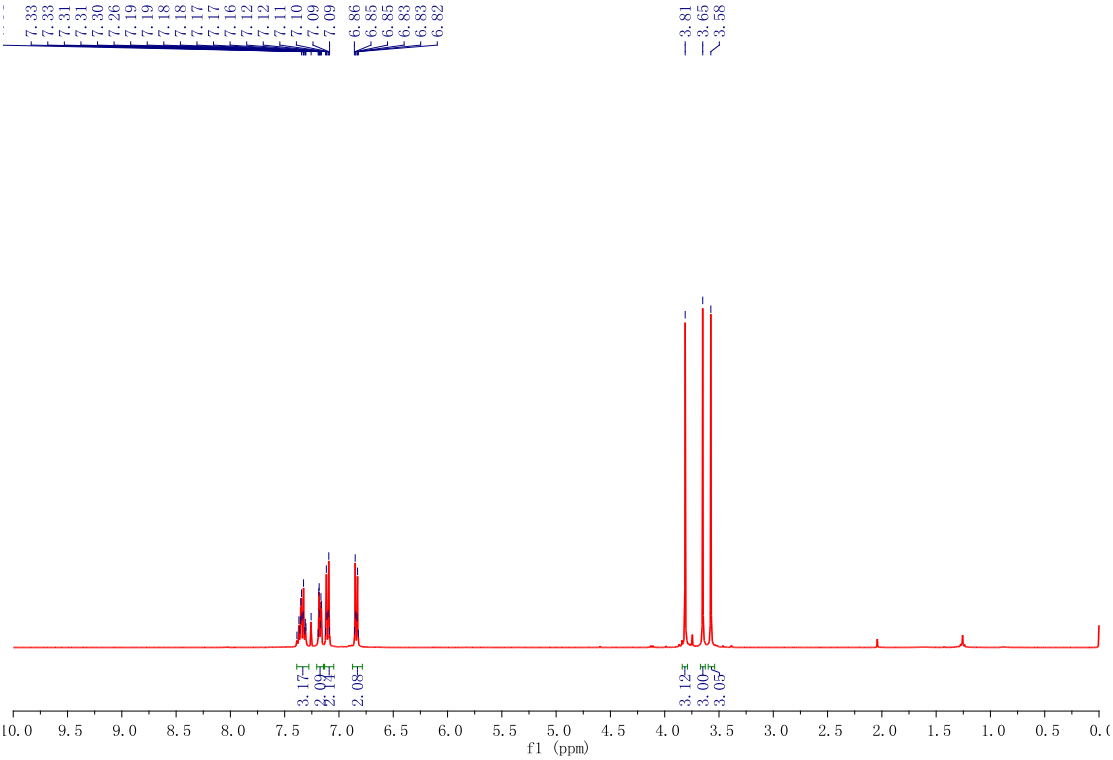
Dimethyl 2-(phenyl(*p*-tolyl)methylene)malonate (3g)

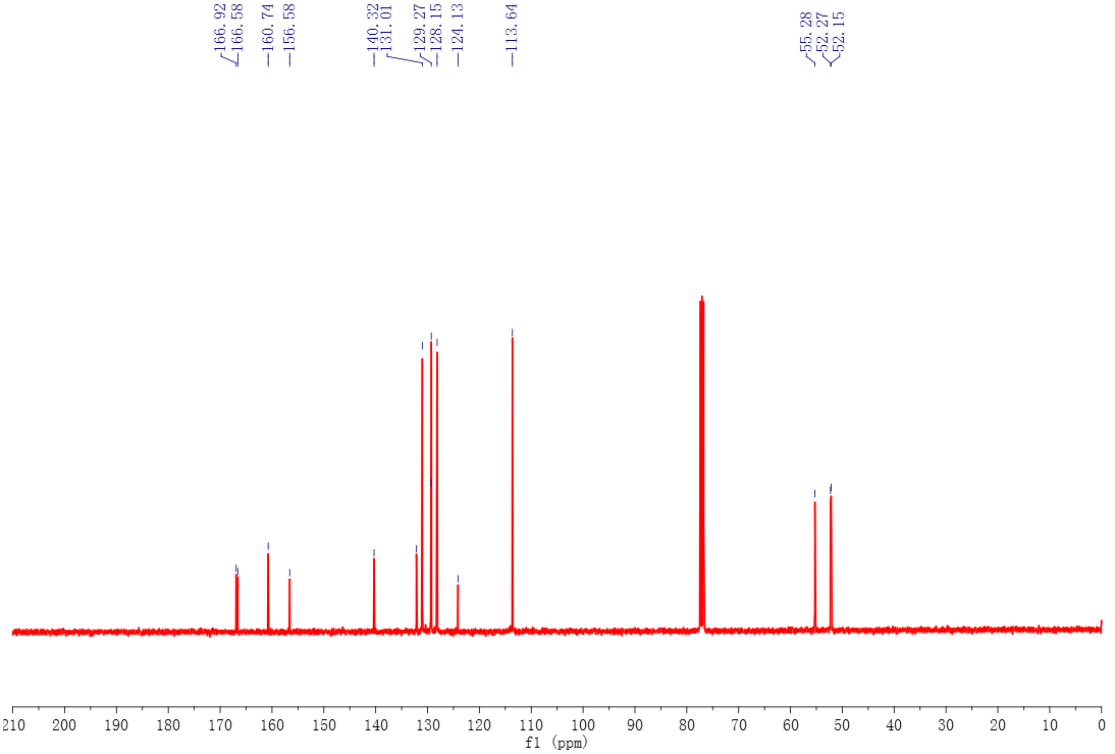


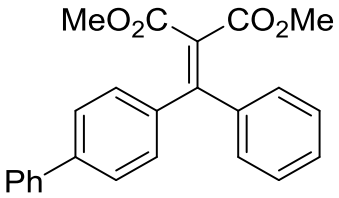




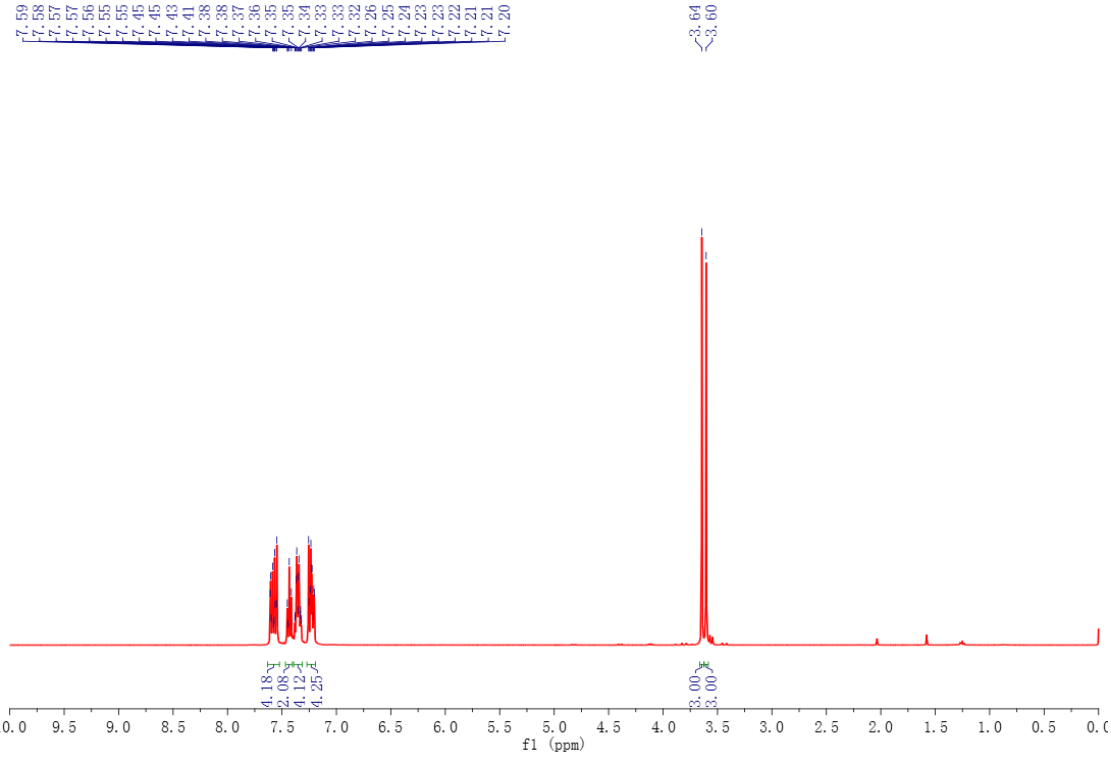
Dimethyl 2-((*p*-methoxyphenyl)(phenyl)methylene)malonate (3h)

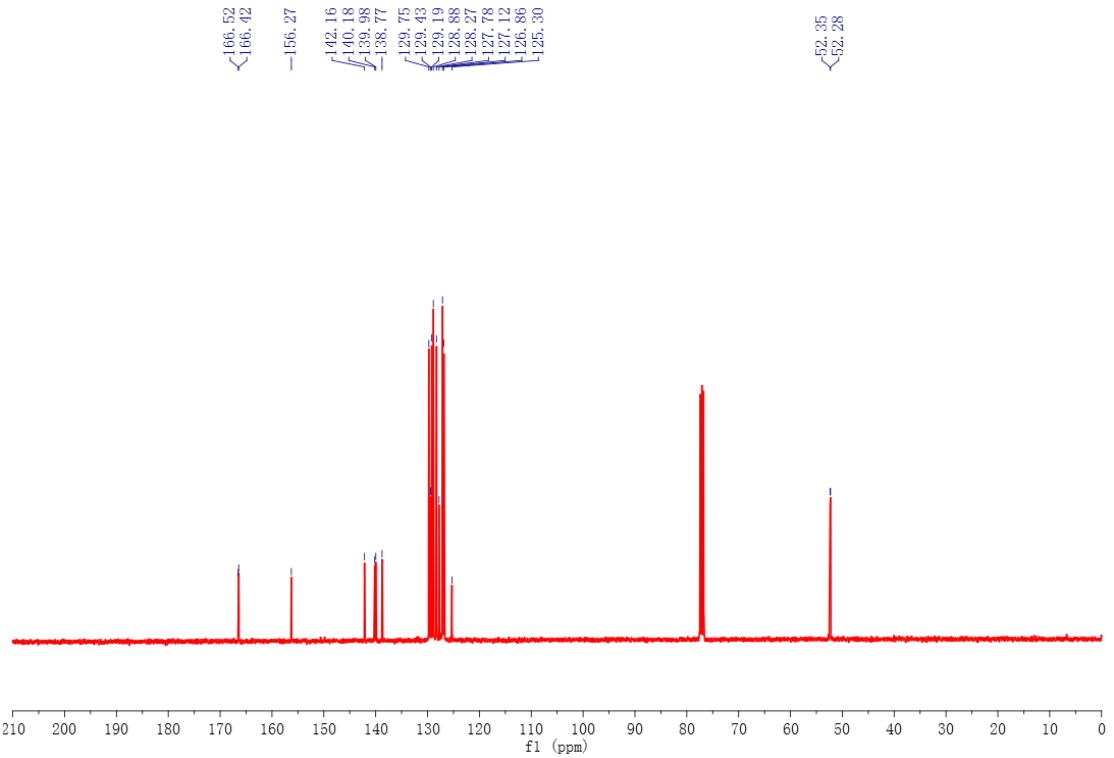


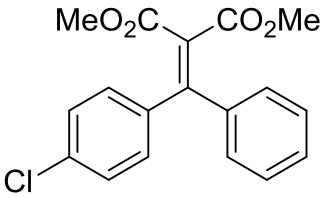




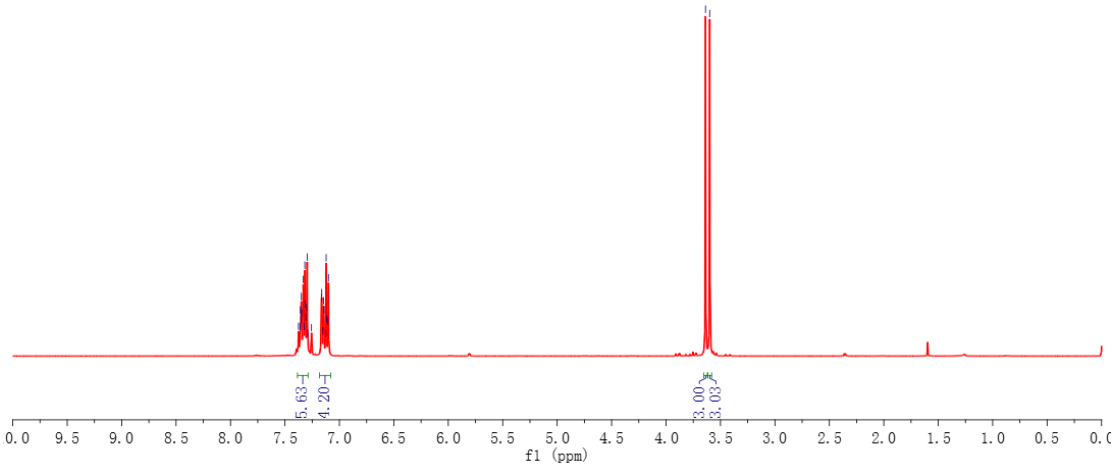
Dimethyl 2-([1,1'-biphenyl]-4-yl(phenyl)methylene)malonate (3i)

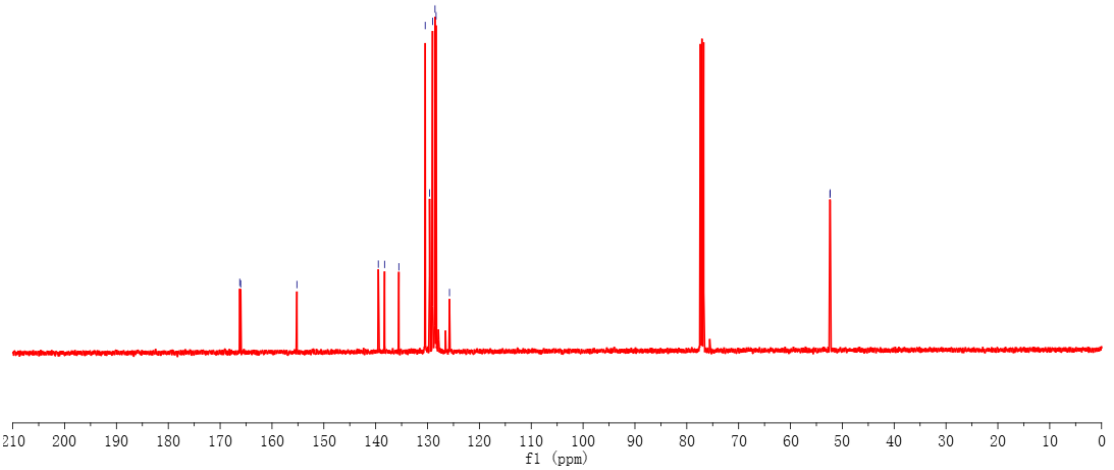


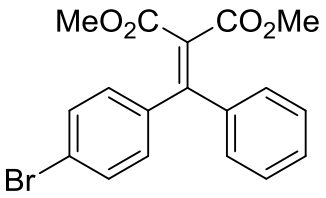




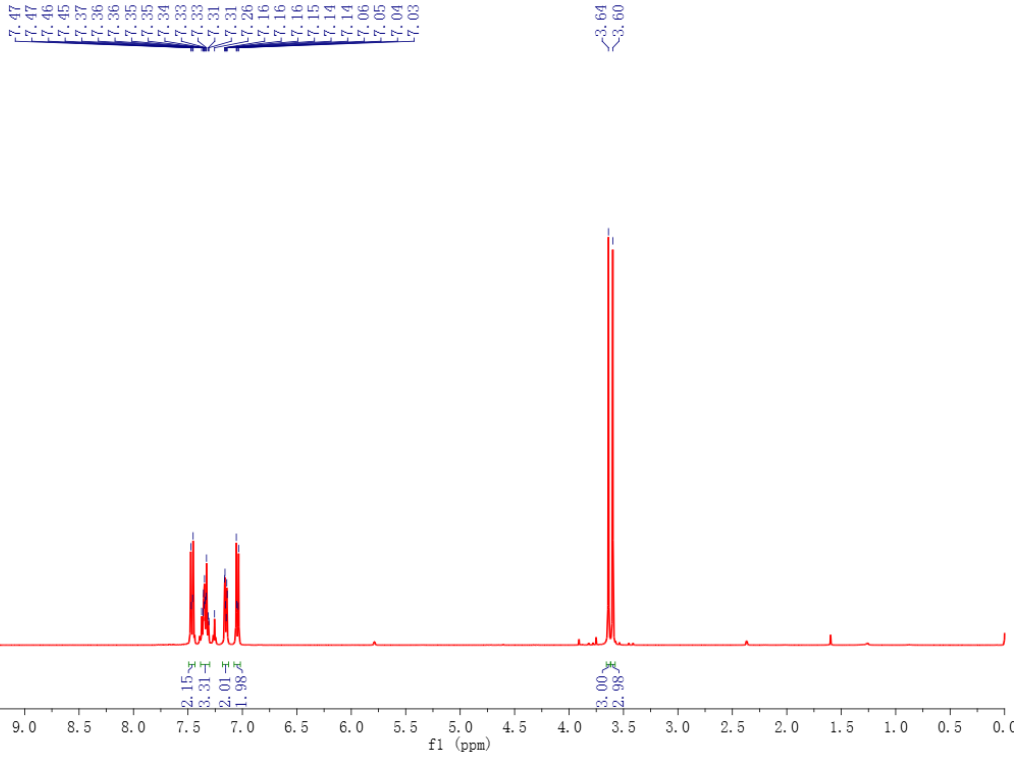
Dimethyl 2-((*p*-chlorophenyl)(phenyl)methylene)malonate (3j)

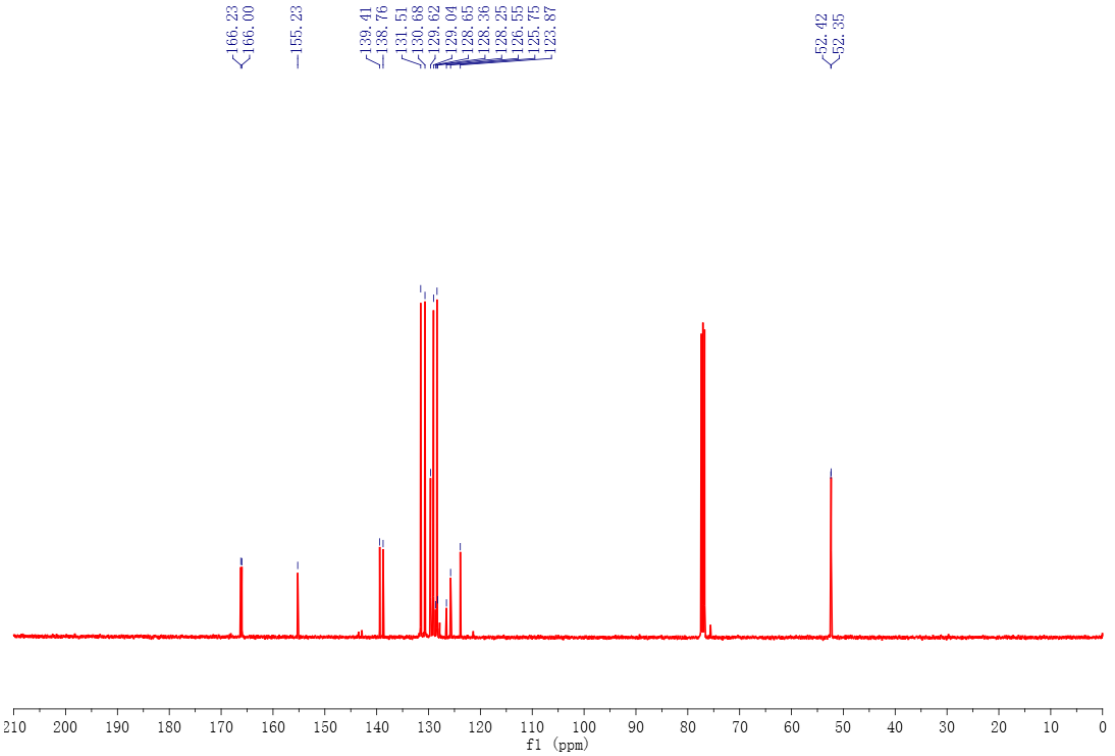


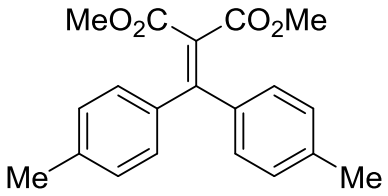




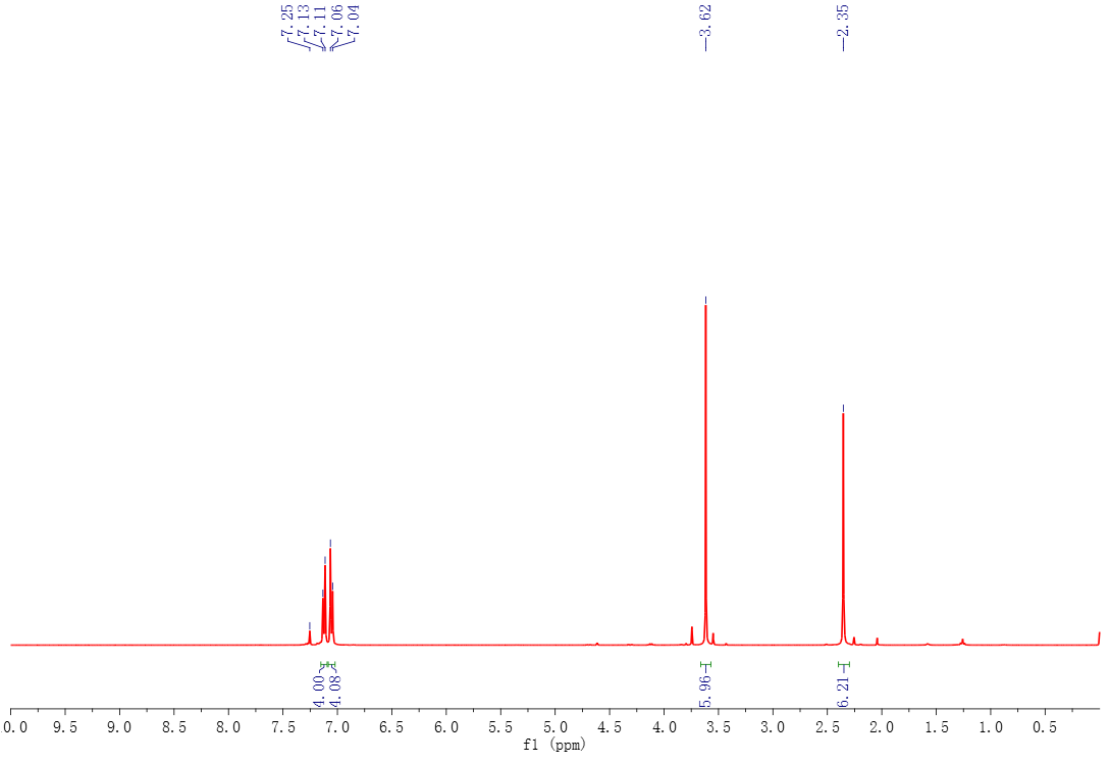
Dimethyl 2-((*p*-bromophenyl)(phenyl)methylene)malonate (3k)

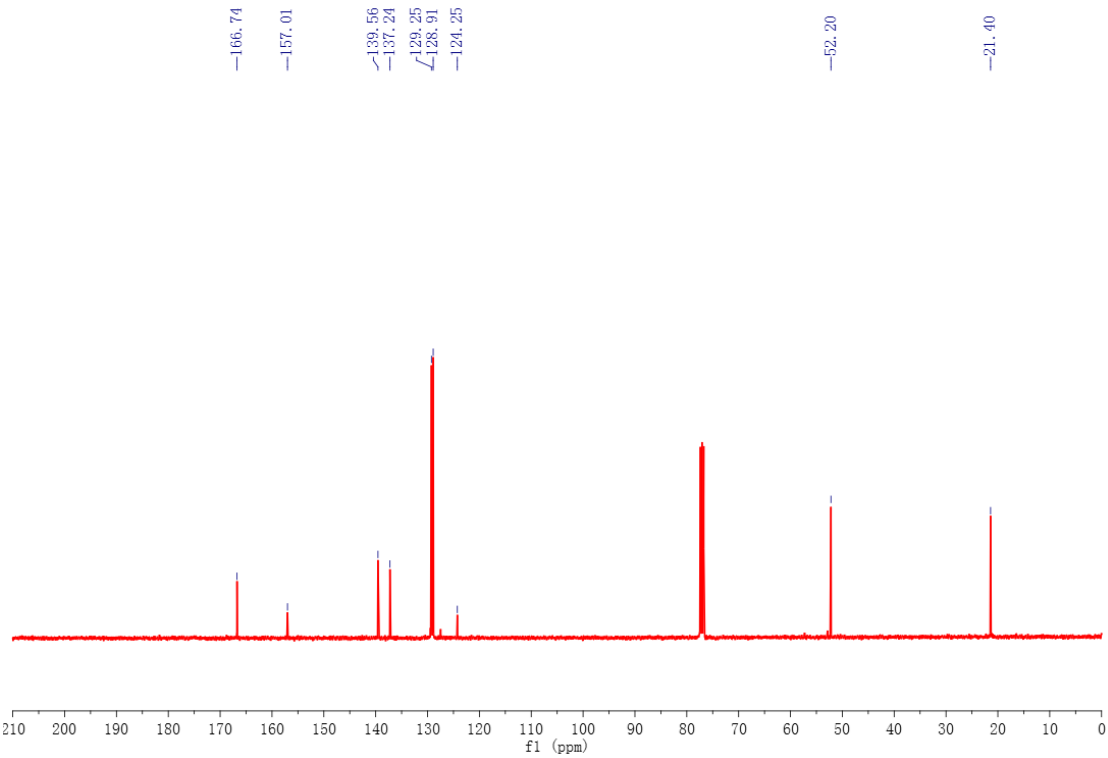


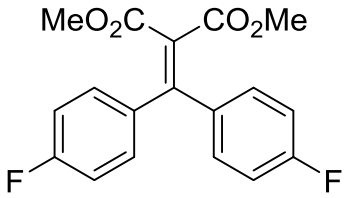




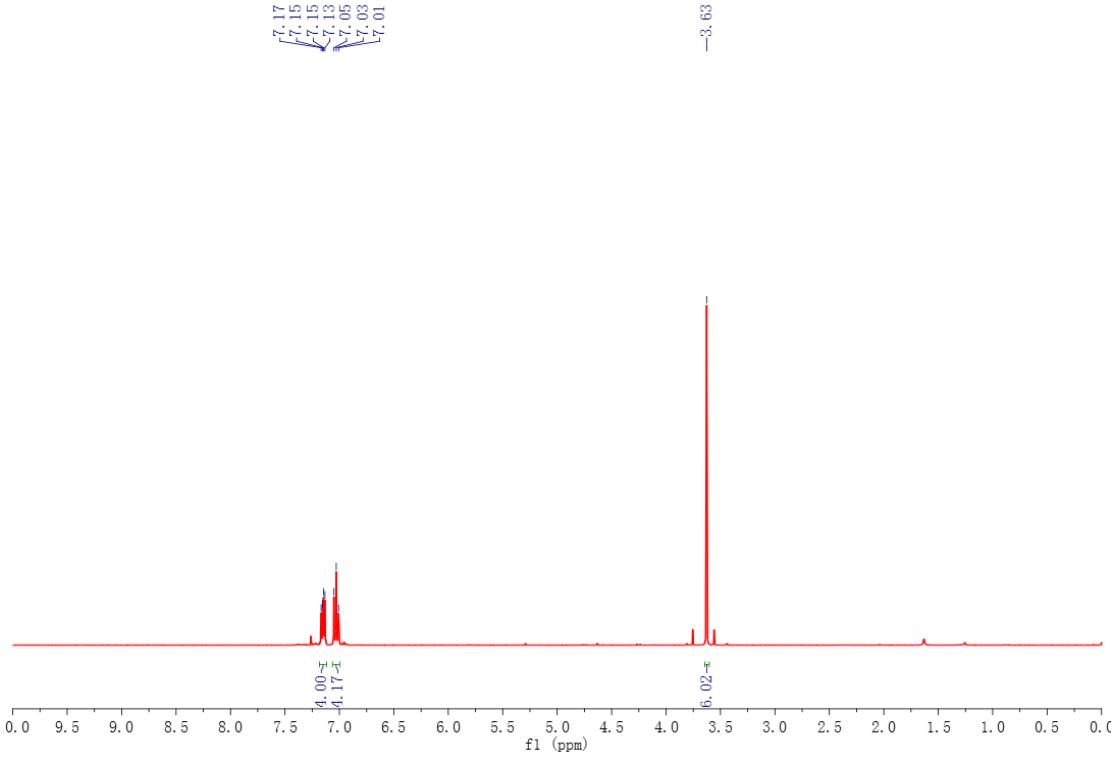
Dimethyl 2-(di-*p*-tolylmethylene)malonate (3l)

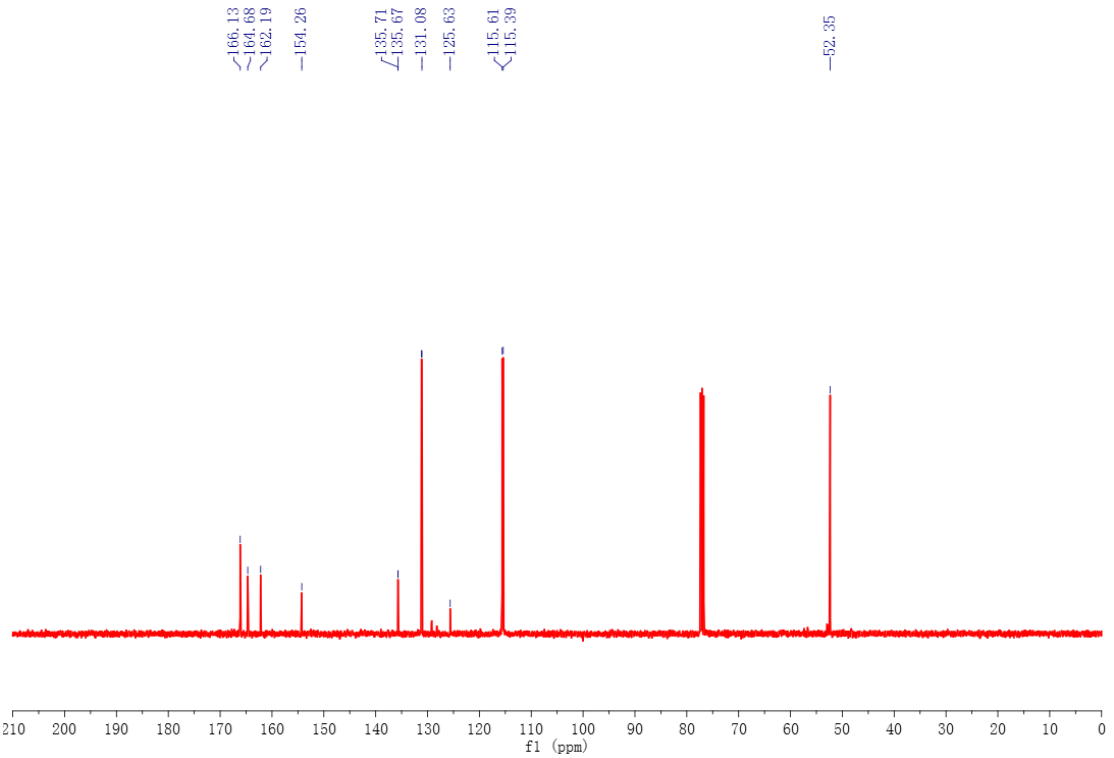


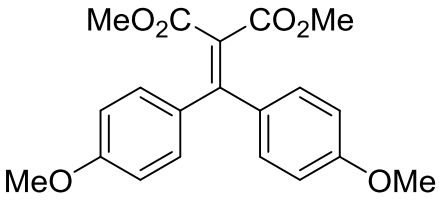




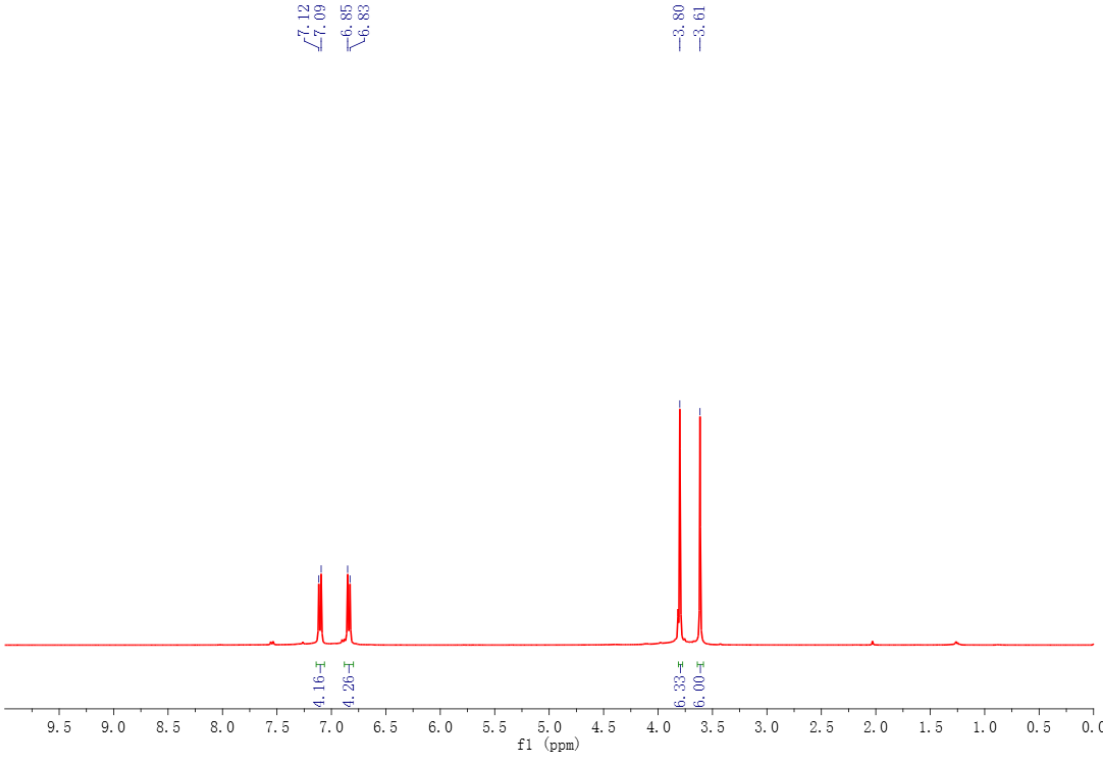
Dimethyl 2-(bis(*p*-fluorophenyl)methylene)malonate (3m)

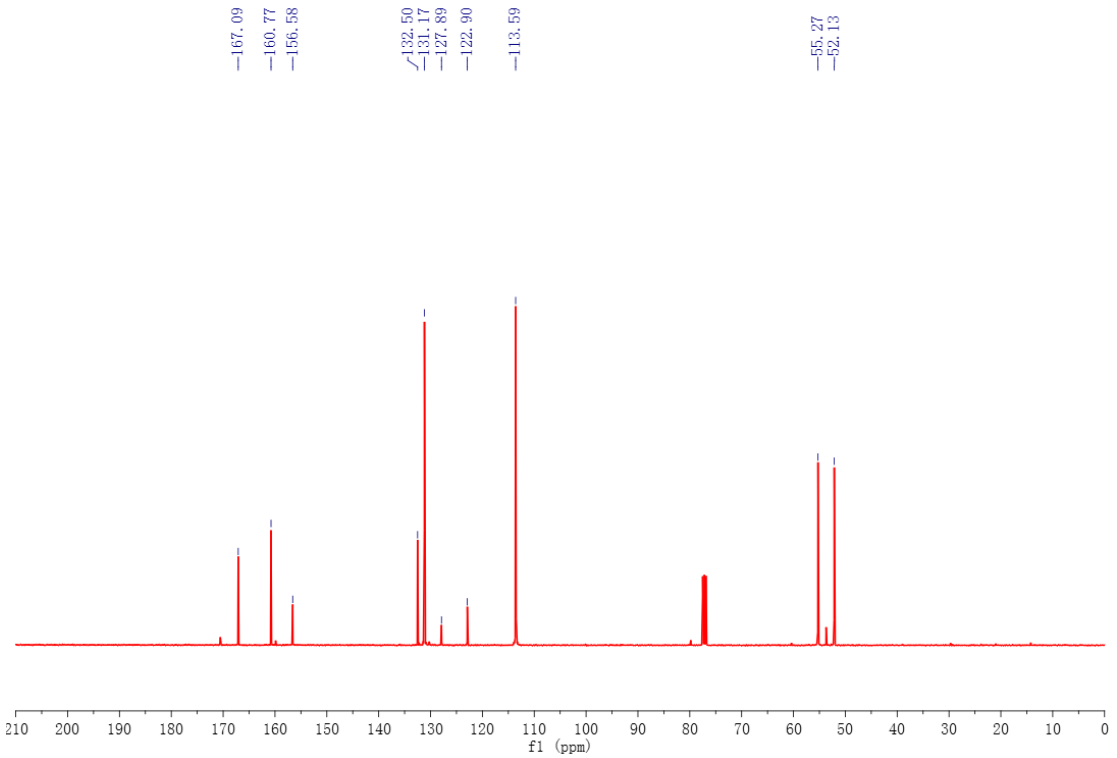


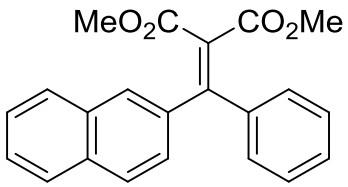




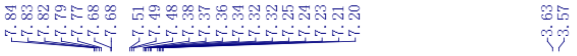
Dimethyl 2-(bis(*p*-methoxyphenyl)methylene)malonate (3n)

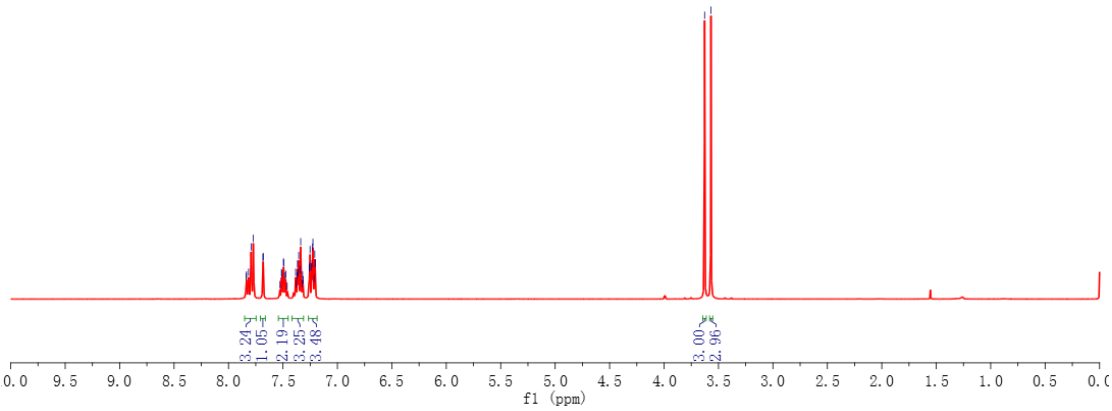


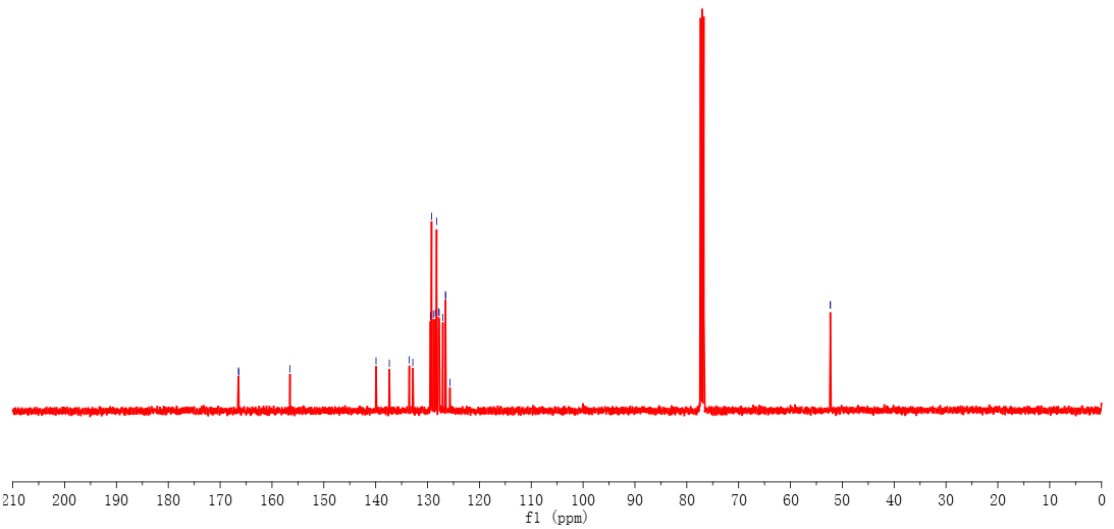


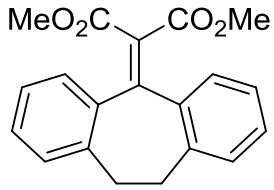


Dimethyl 2-(naphthalen-2-yl(phenyl)methylene)malonate (3o)

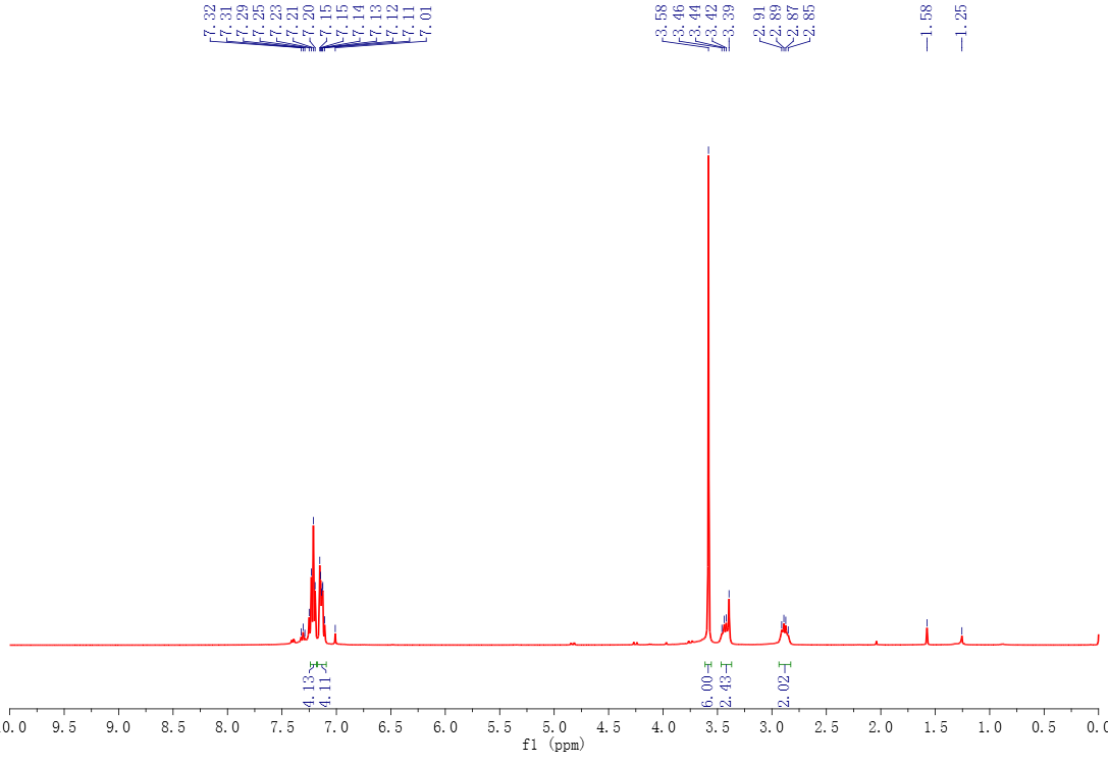


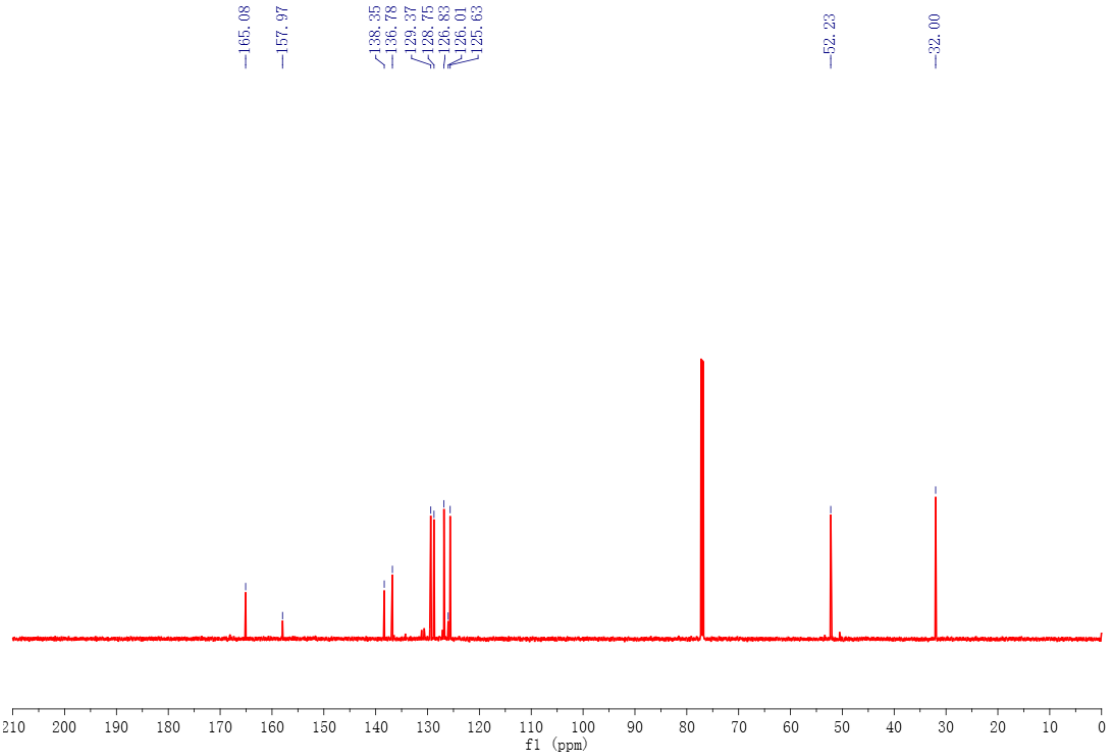


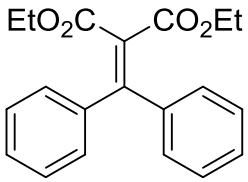




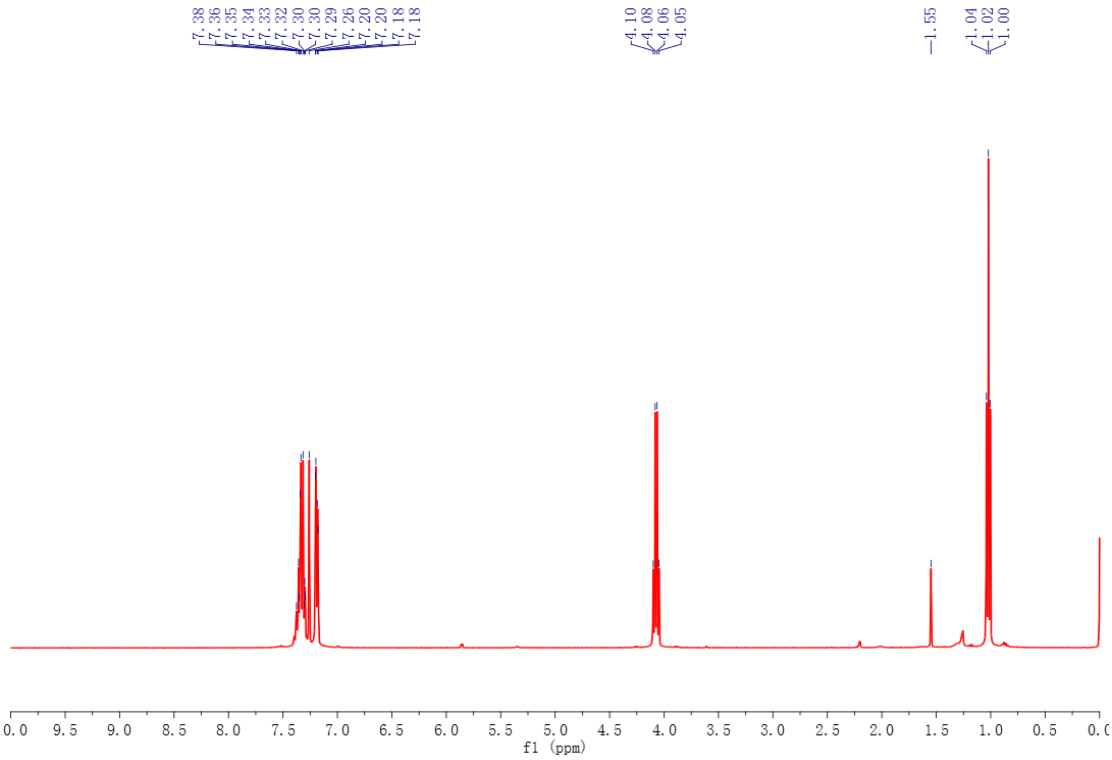
Dimethyl 2-(10,11-dihydro-5*H*-dibenzo[*a*,*d*][7]annulen-5-ylidene)malonate (3p)

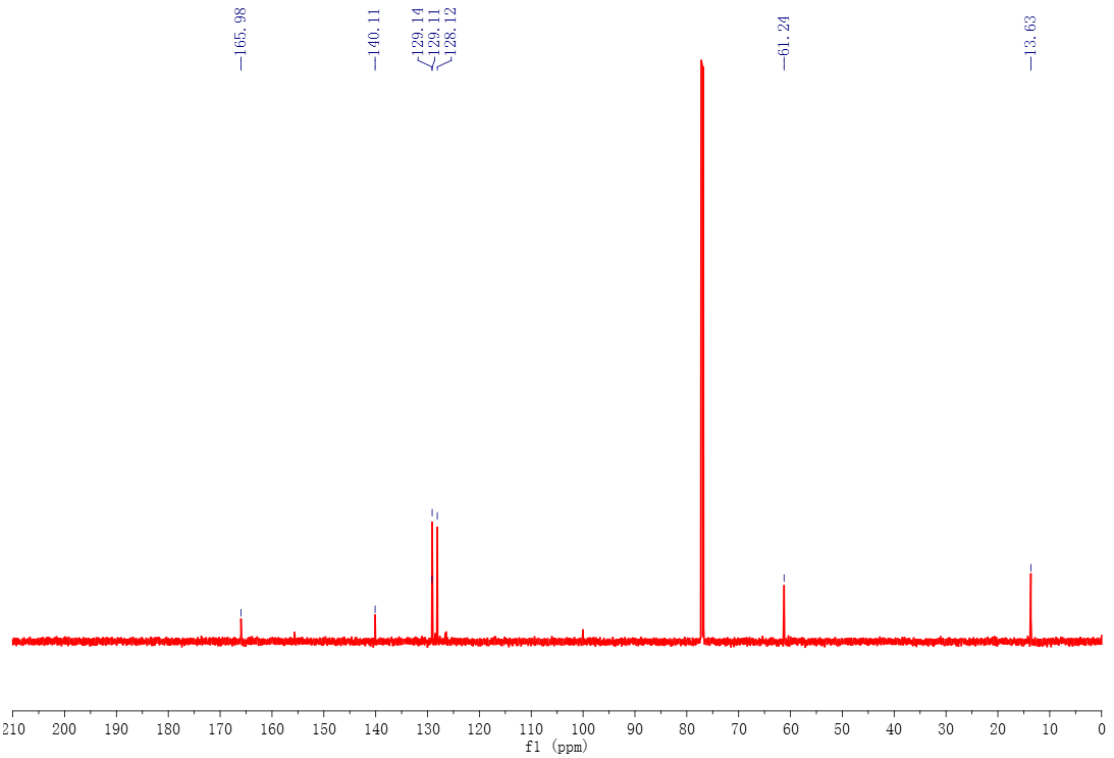


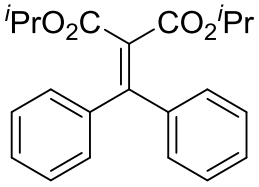




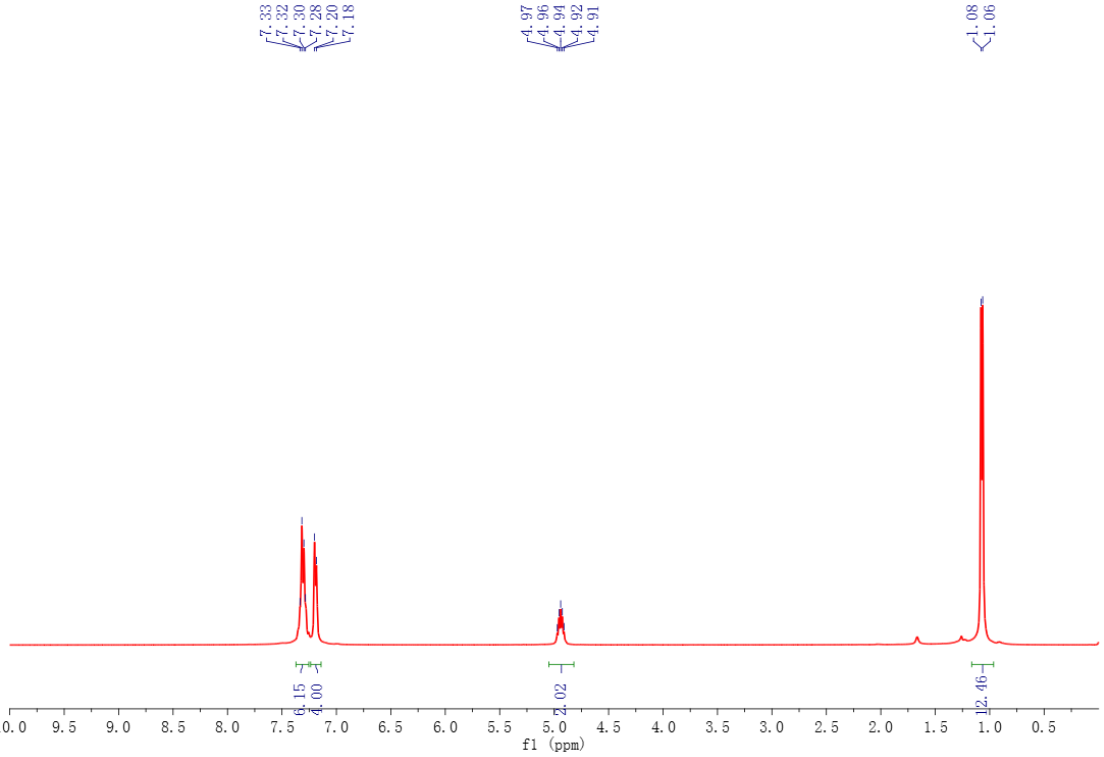
Diethyl 2-(diphenylmethylene)malonate (4a)

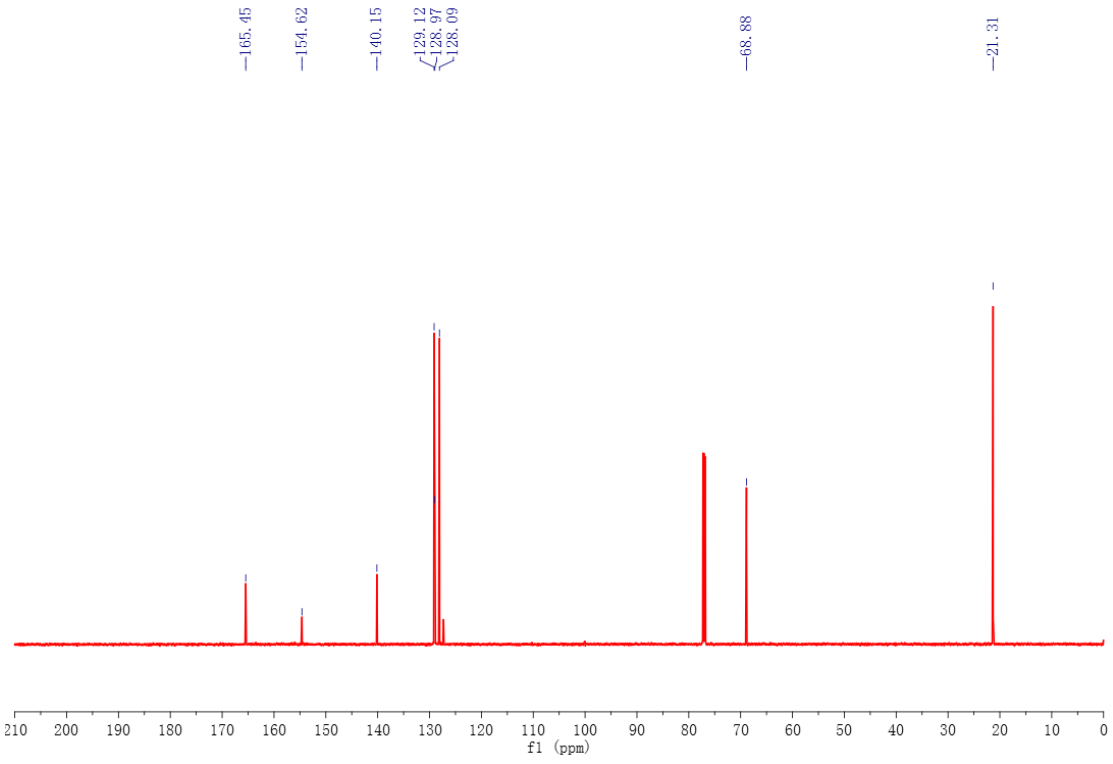






Diisopropyl 2-(diphenylmethylene)malonate (4b)





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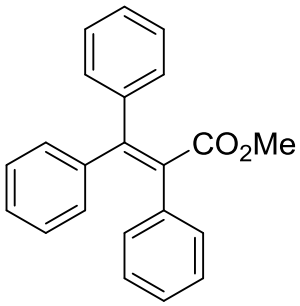
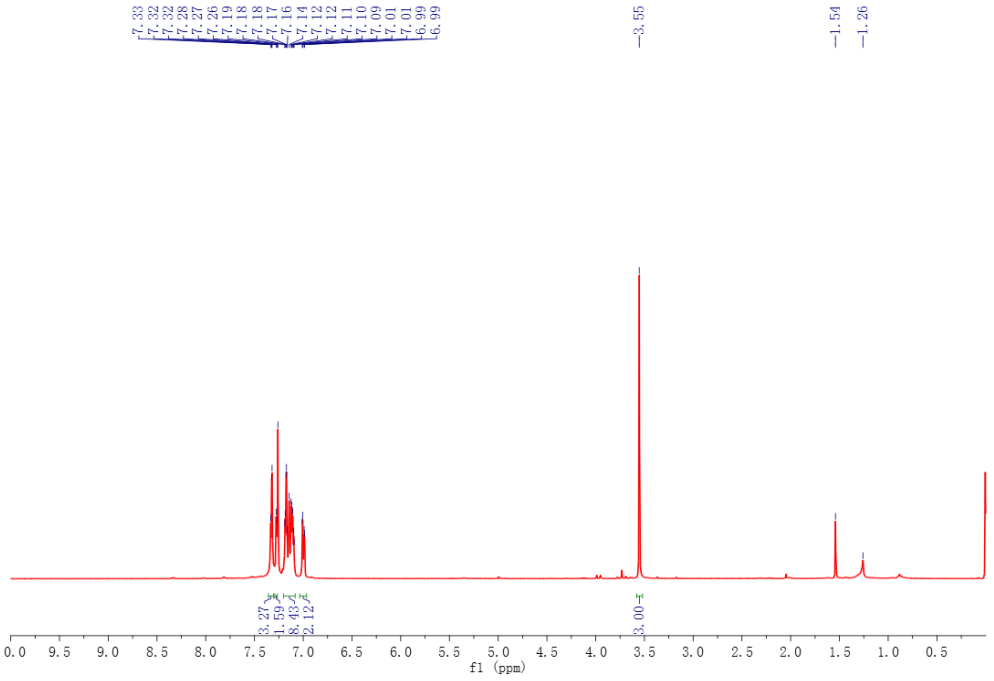
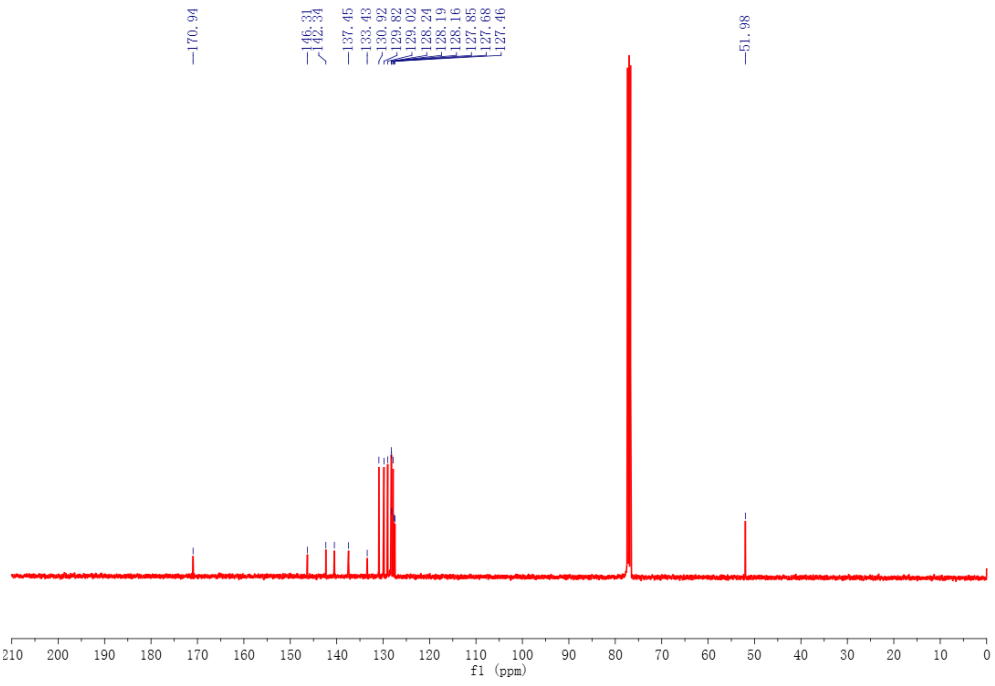
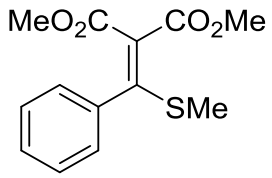


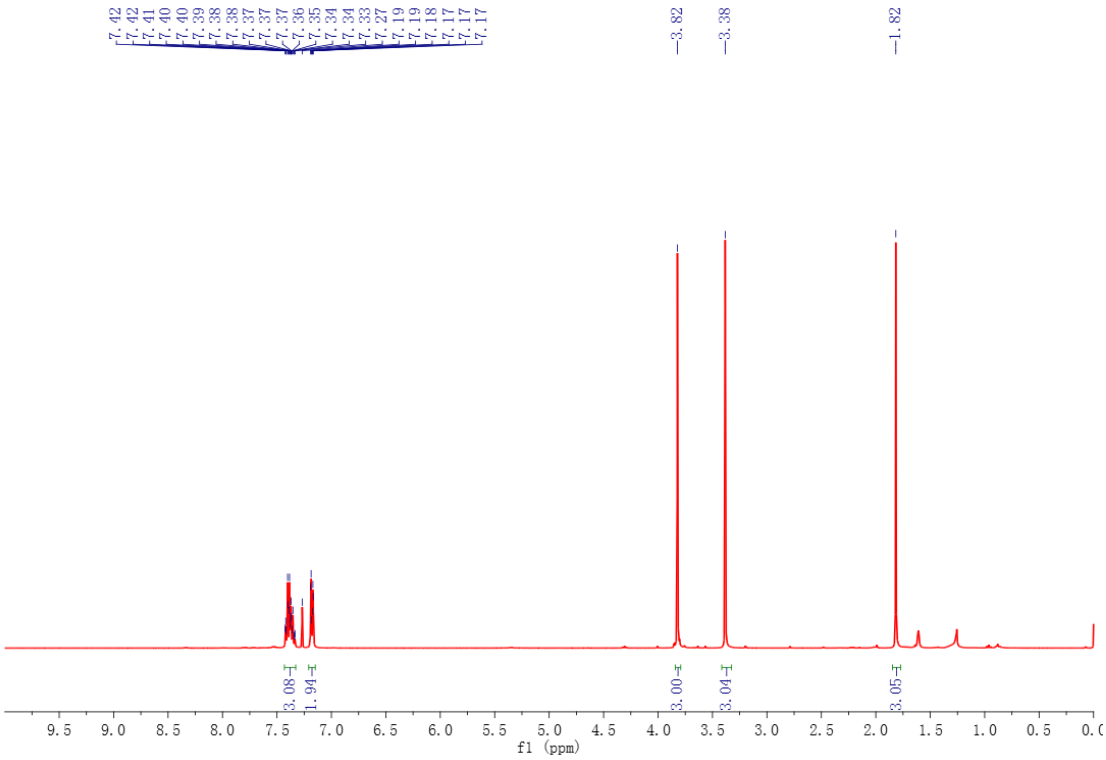
Methyl 2,3,3-triphenylacrylate (4c)

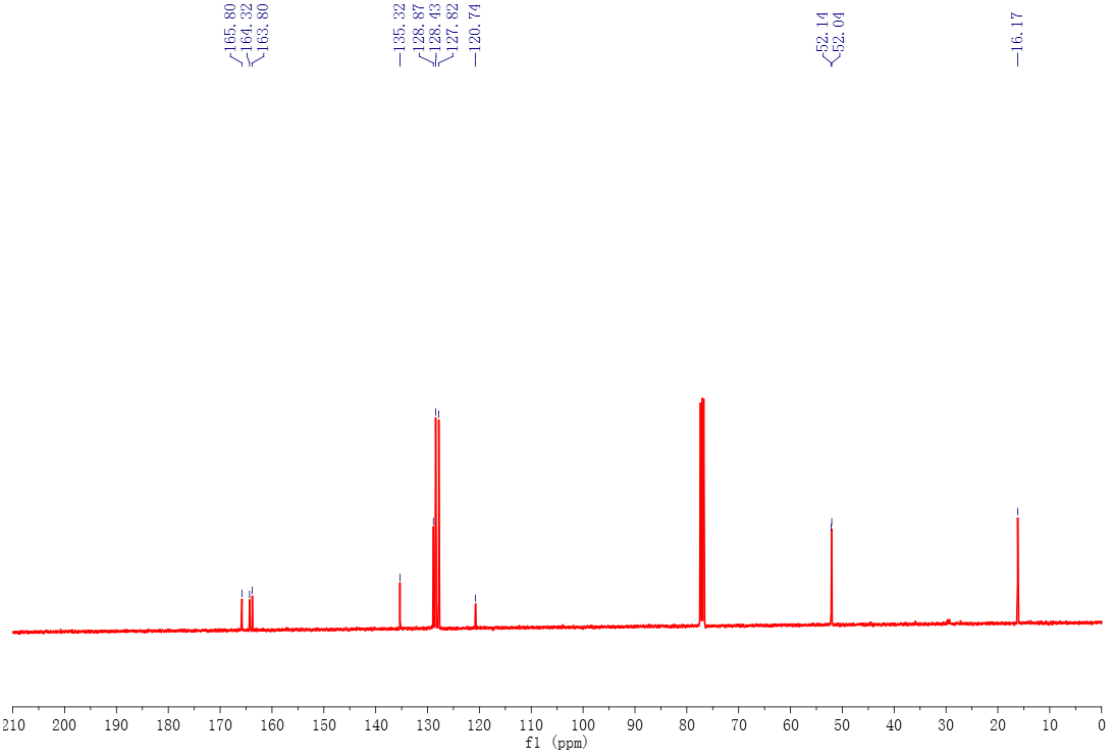


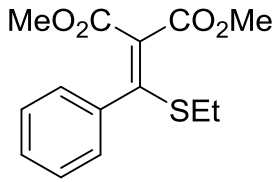




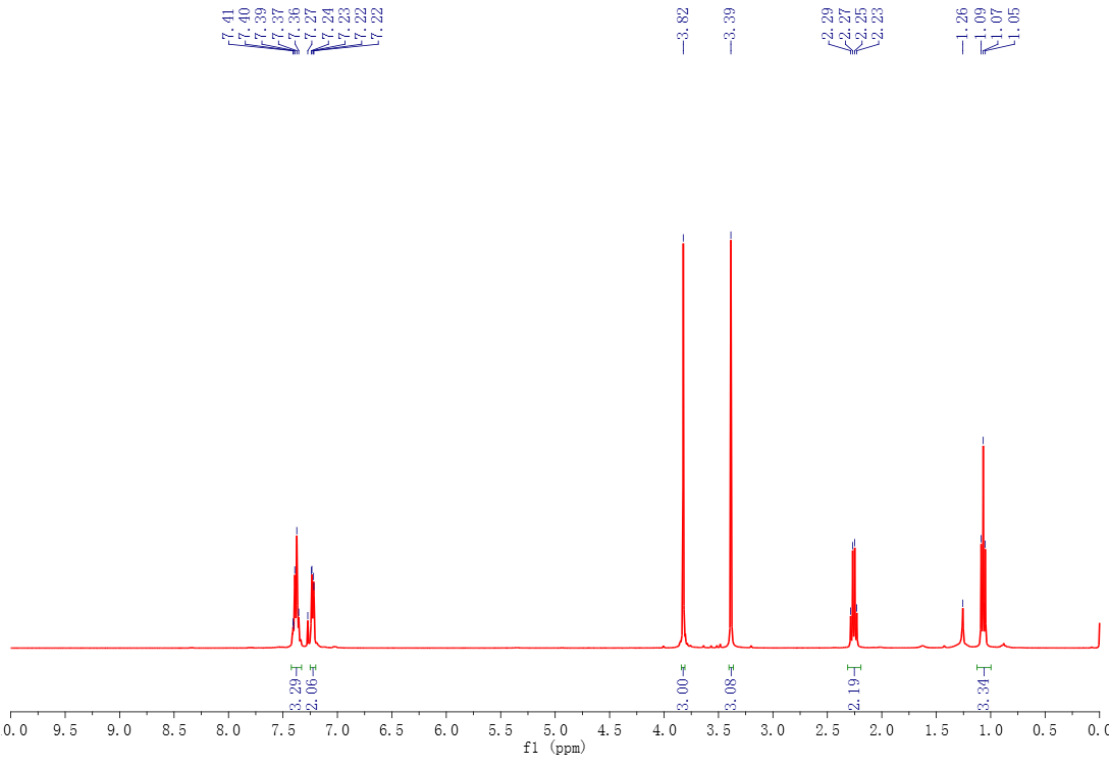
Dimethyl 2-((methylthio)(phenyl)methylene)malonate (6a)

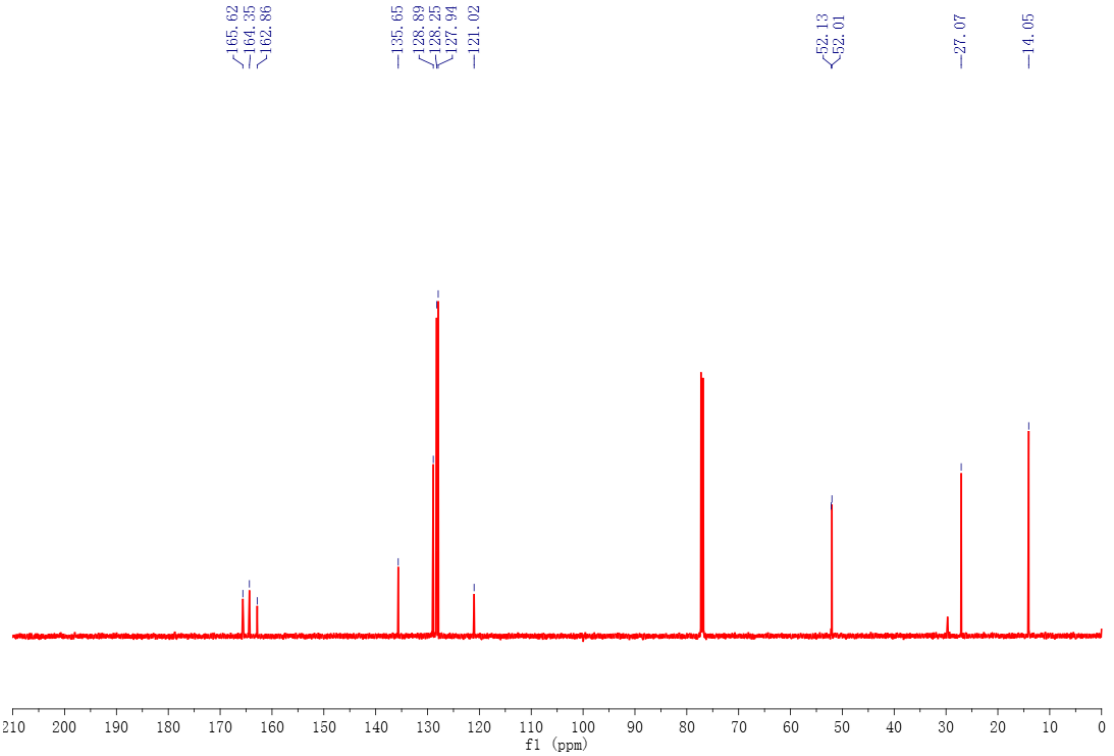


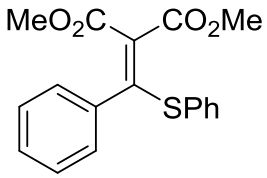




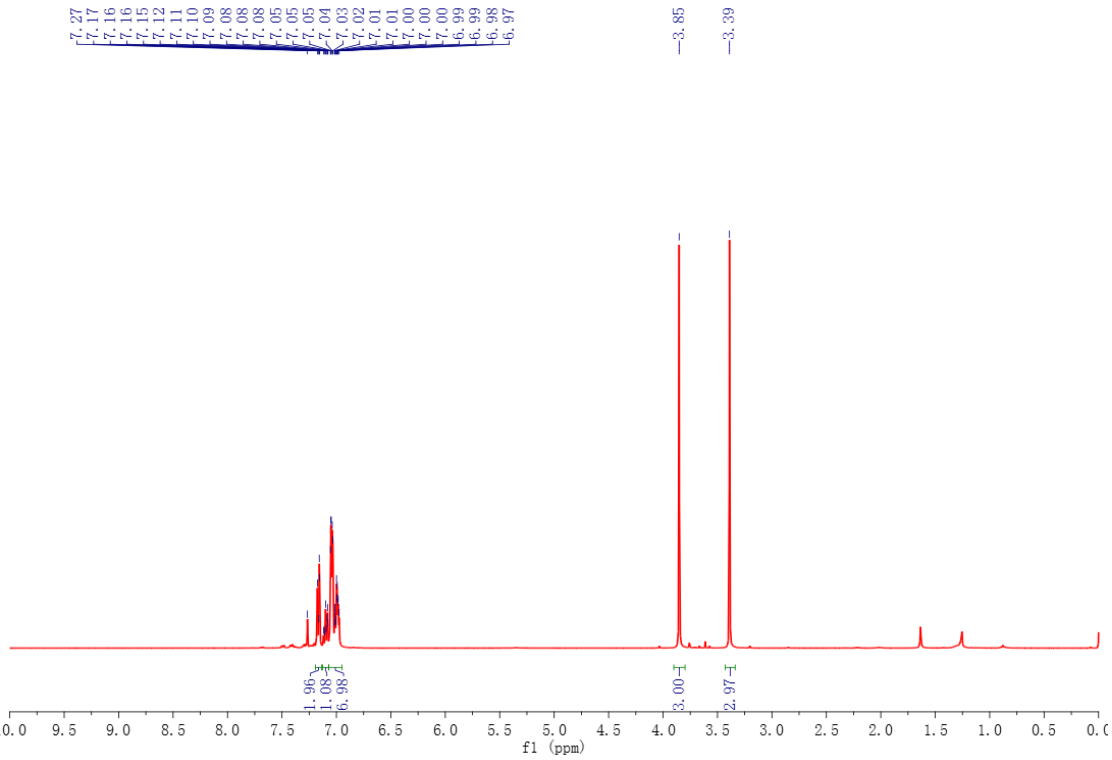
Dimethyl 2-((ethylthio)(phenyl)methylene)malonate (6b)

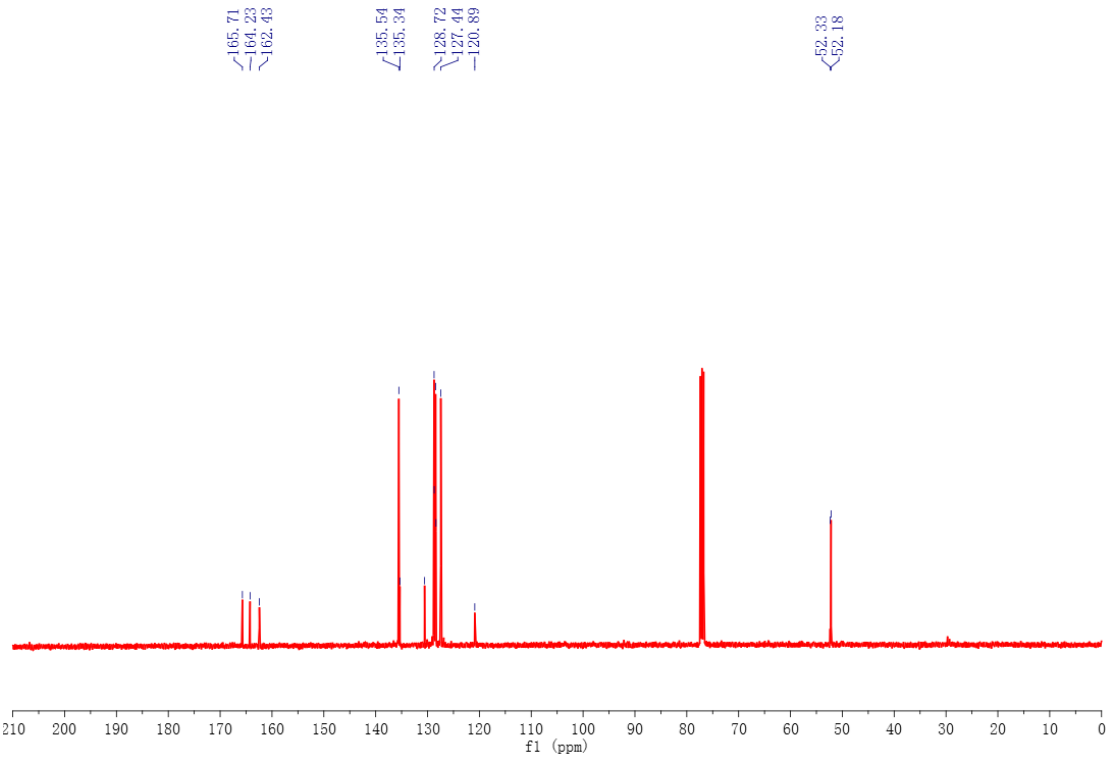


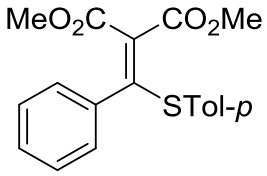




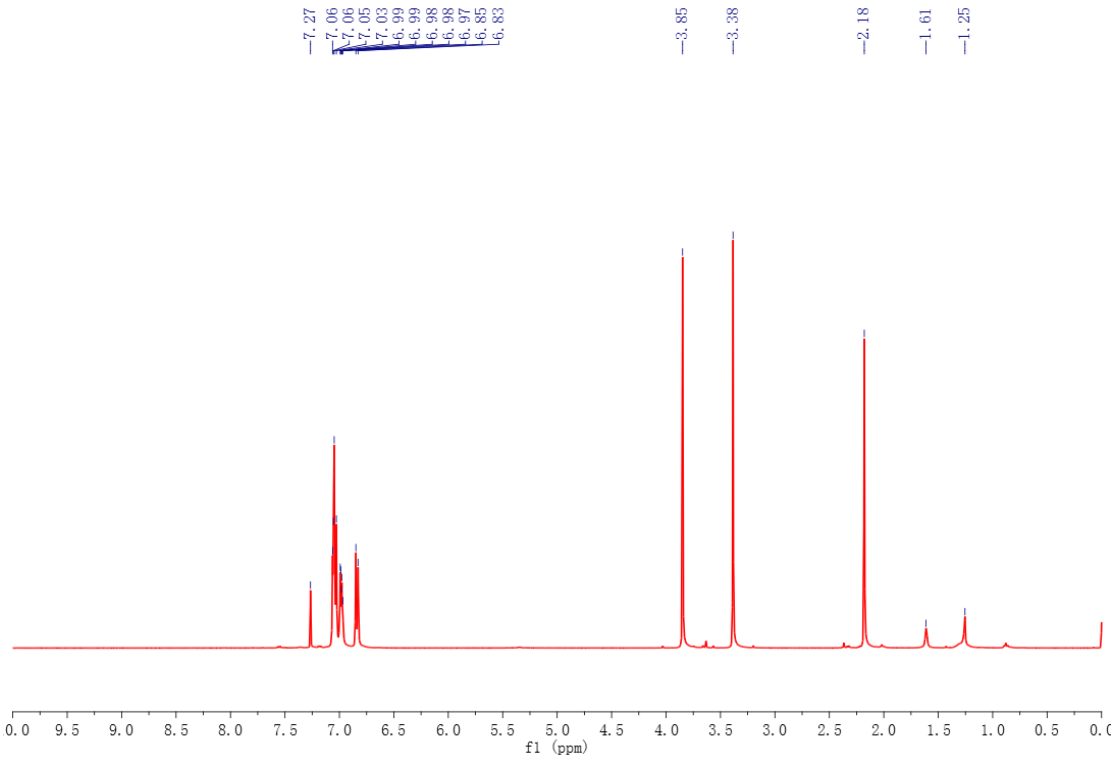
Dimethyl 2-(phenyl(phenylthio)methylene)malonate (6c)

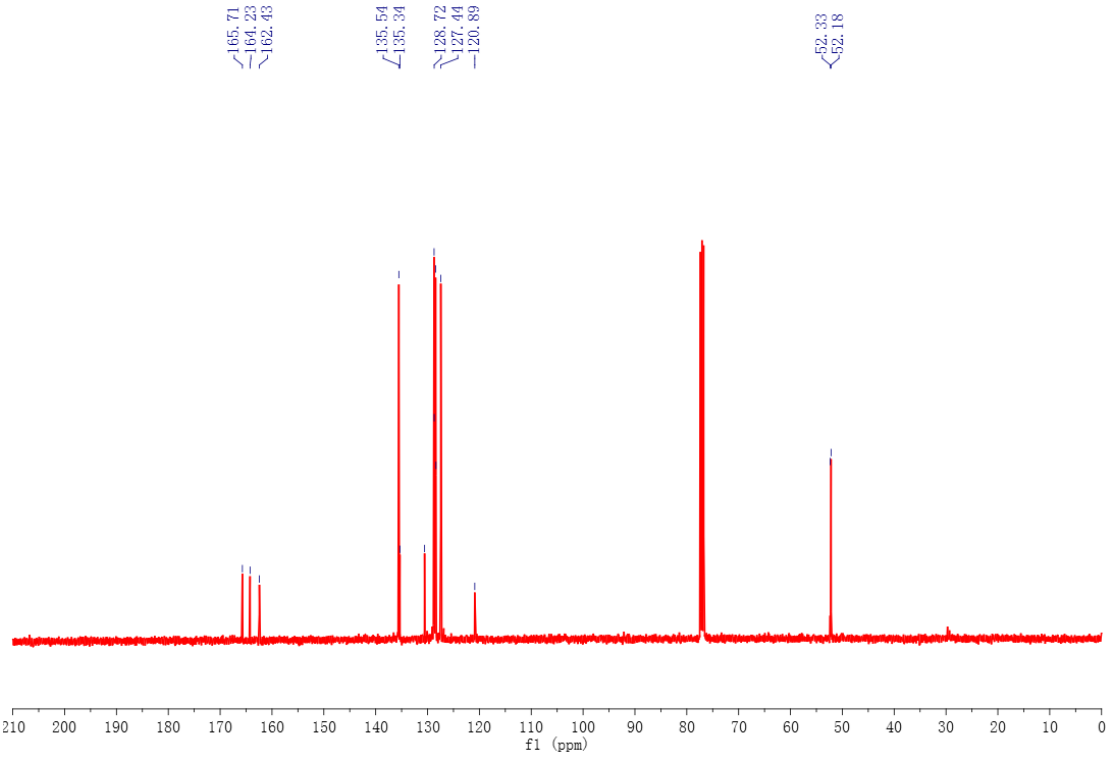


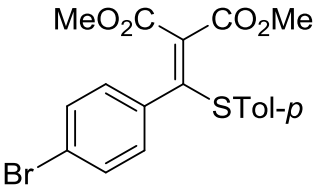




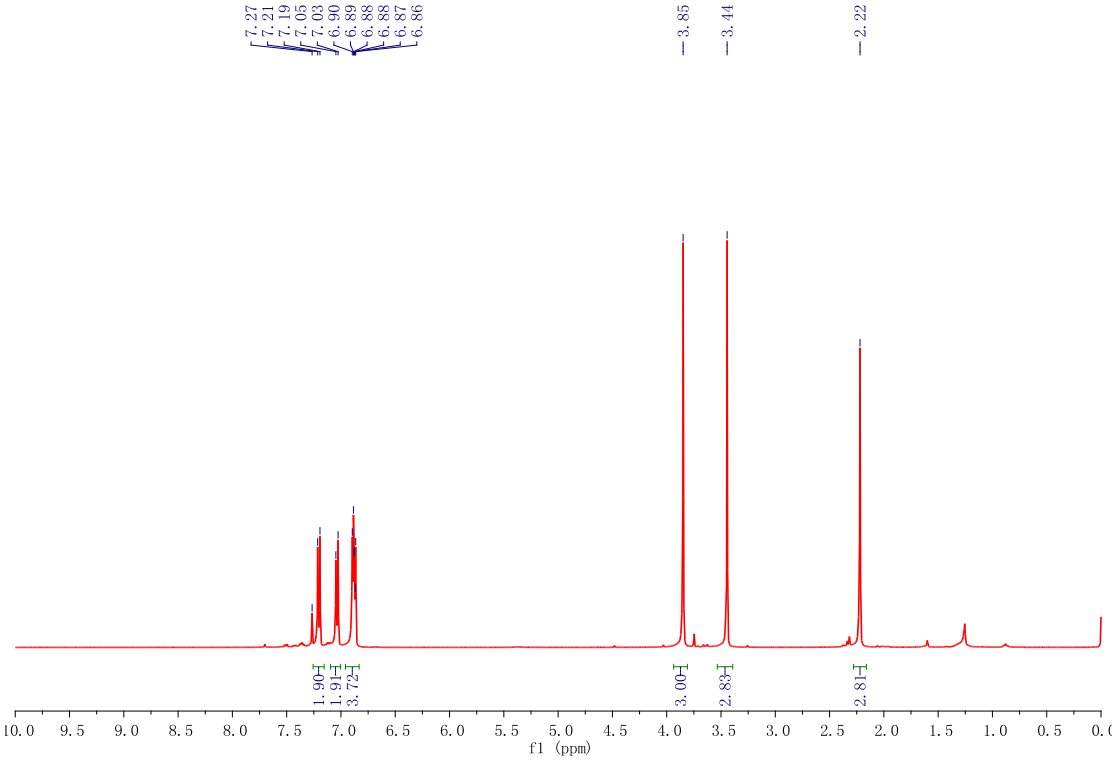
Dimethyl 2-(phenyl(*p*-tolylthio)methylene)malonate (6d)

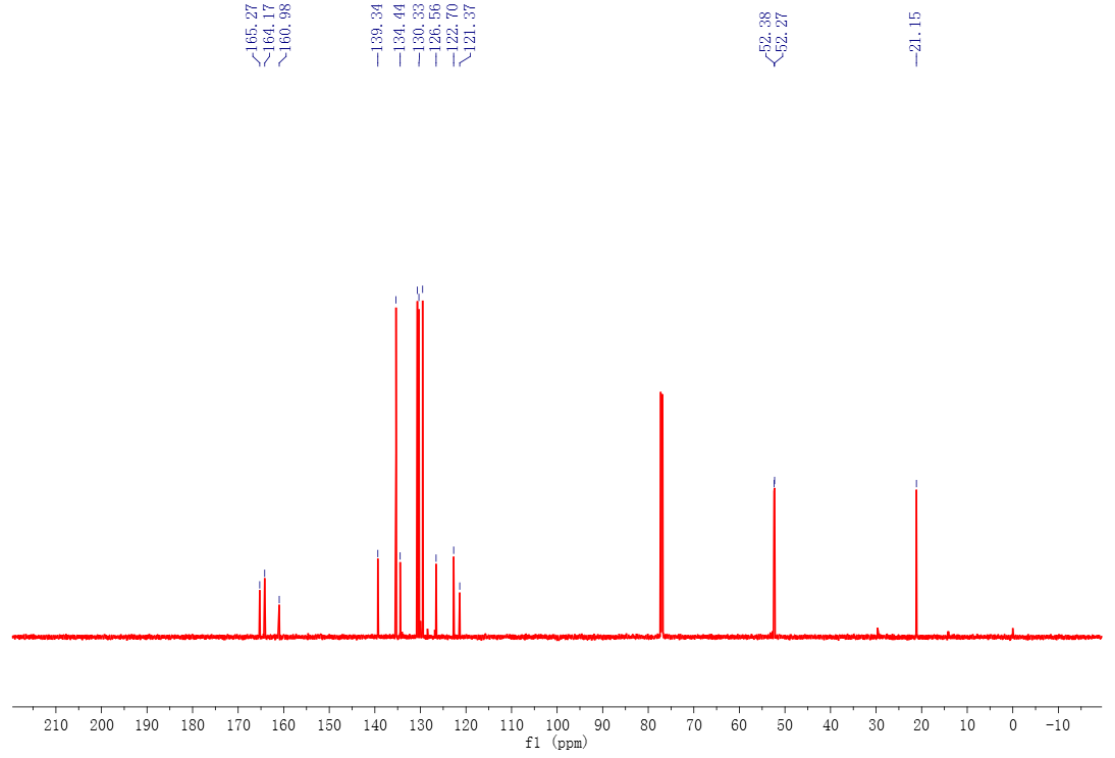


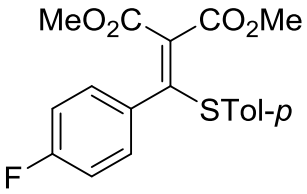




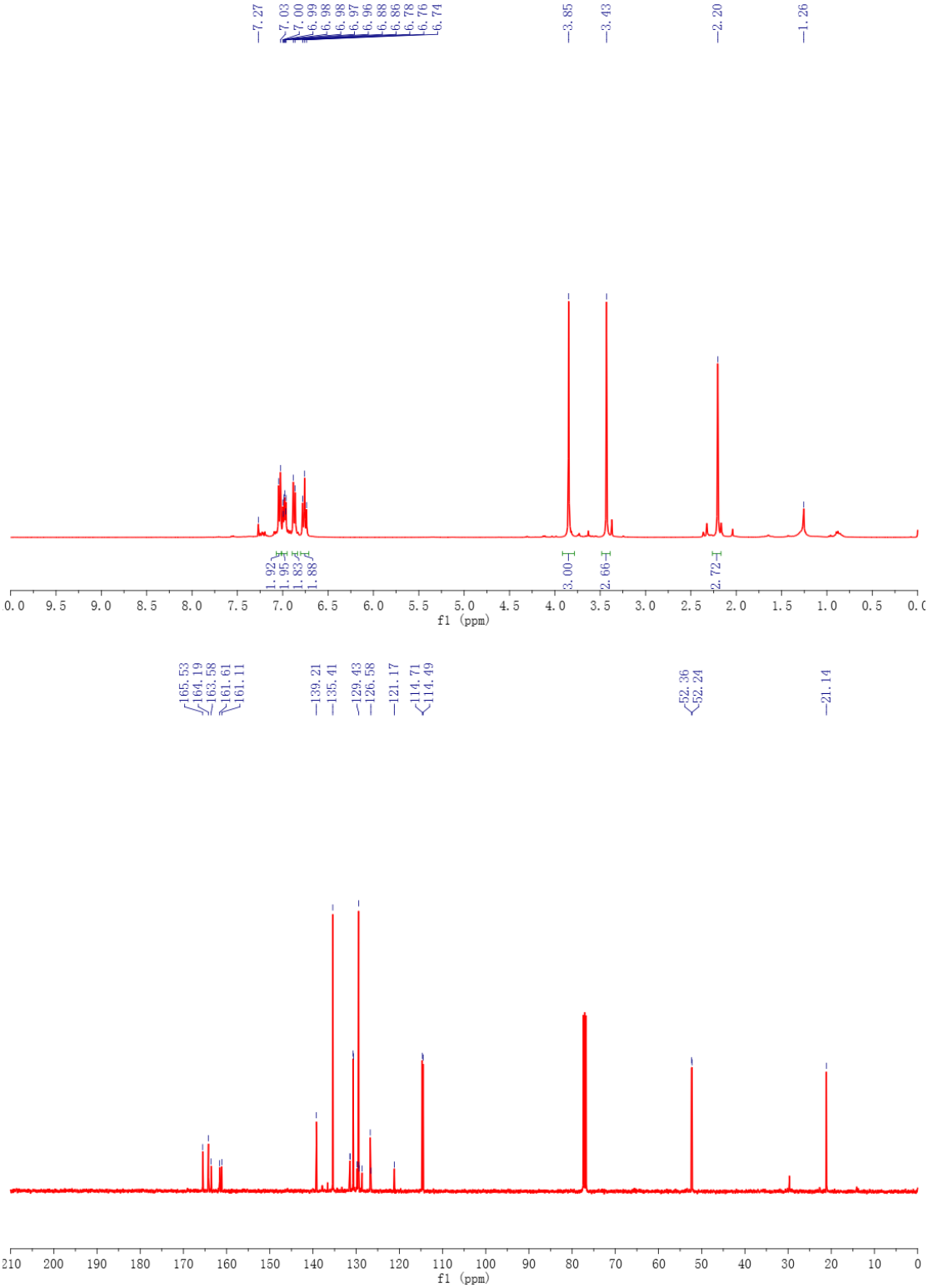
Dimethyl 2-((*p*-bromophenyl)(*p*-tolylthio)methylene)malonate (6e)

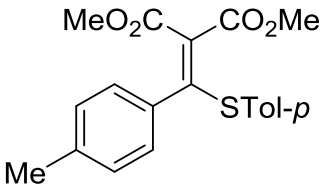




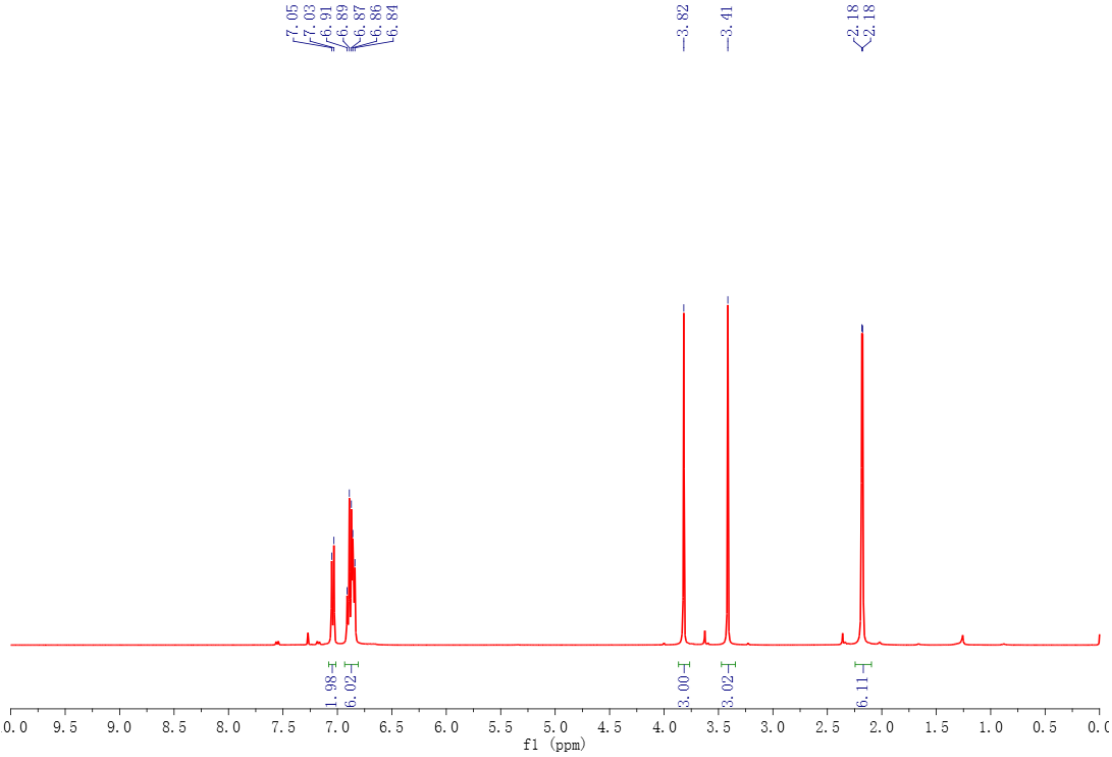


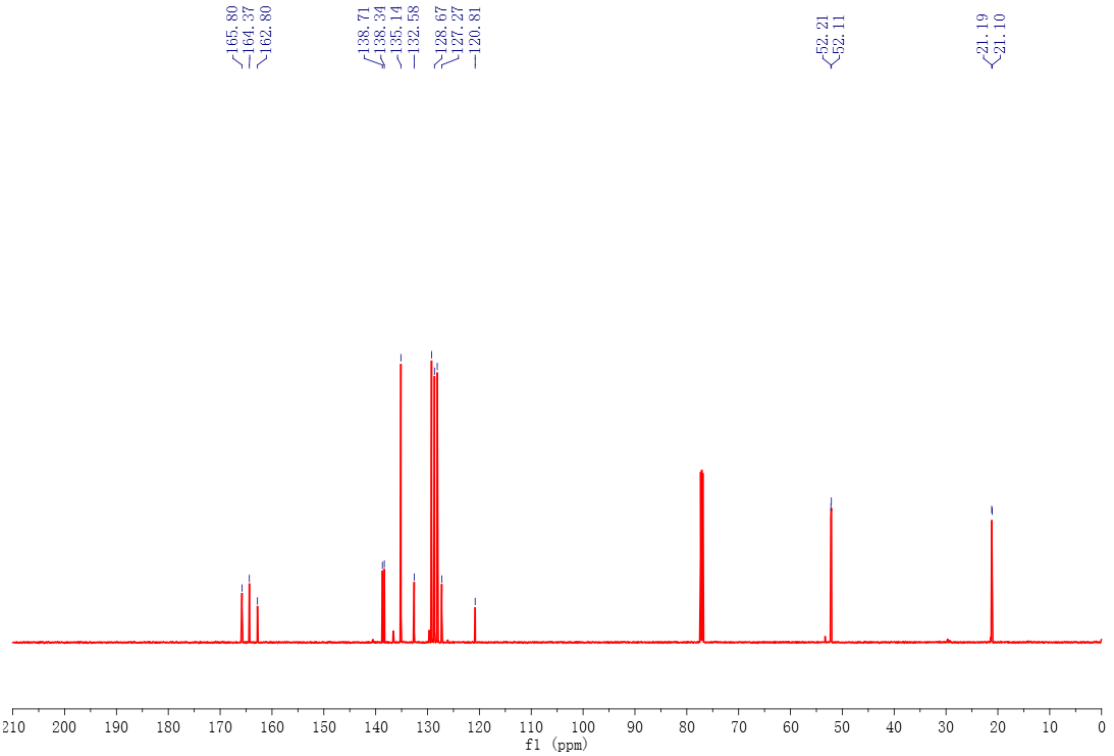
Dimethyl 2-((*p*-fluorophenyl)(*p*-tolylthio)methylene)malonate (6f)

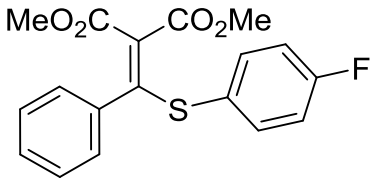




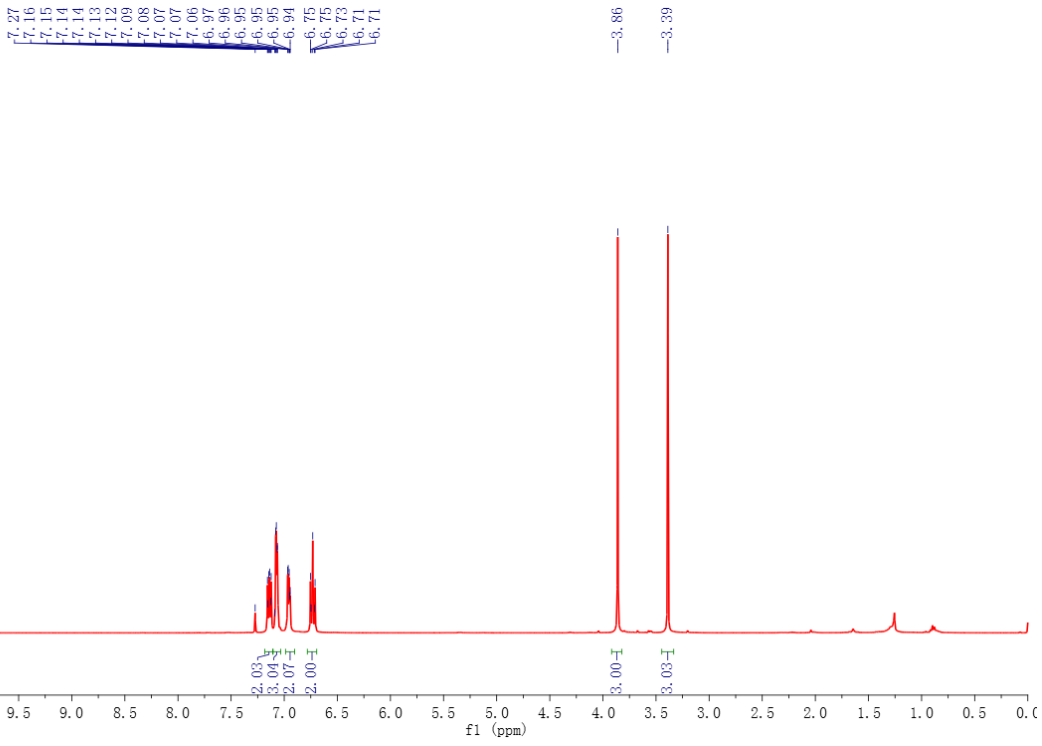
Dimethyl 2-((*p*-Methylphenyl)(*p*-tolylthio)methylene)malonate (6g)

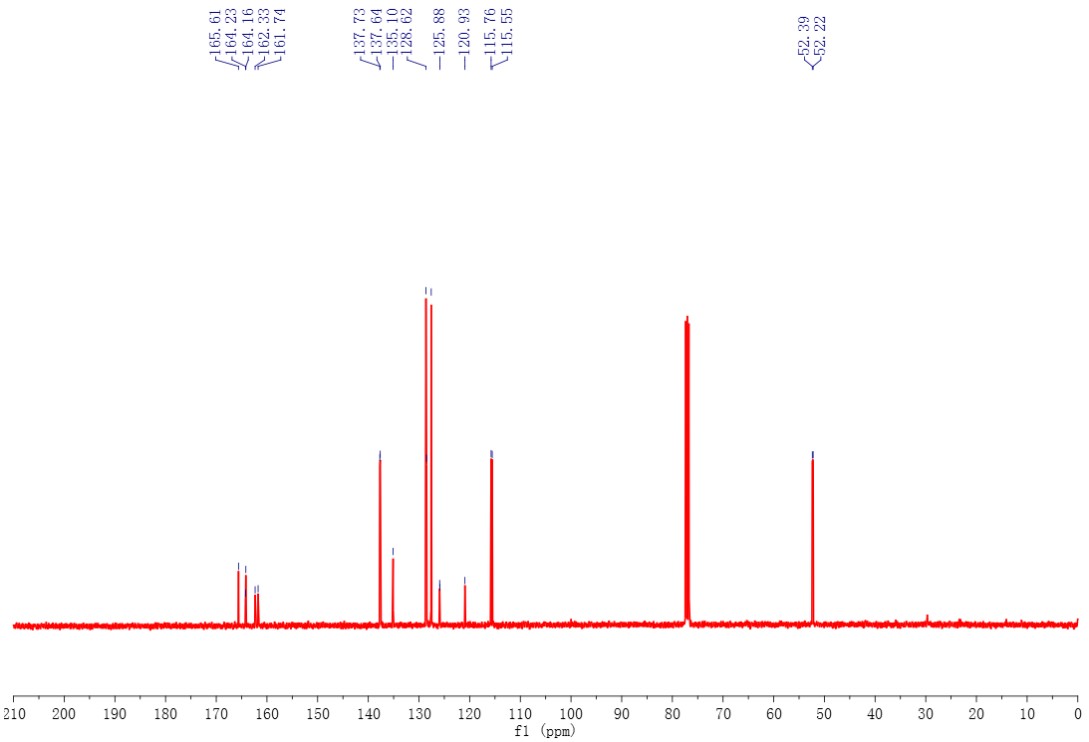


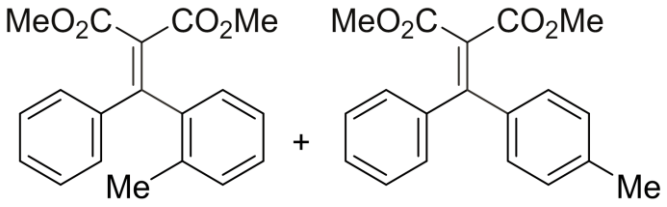




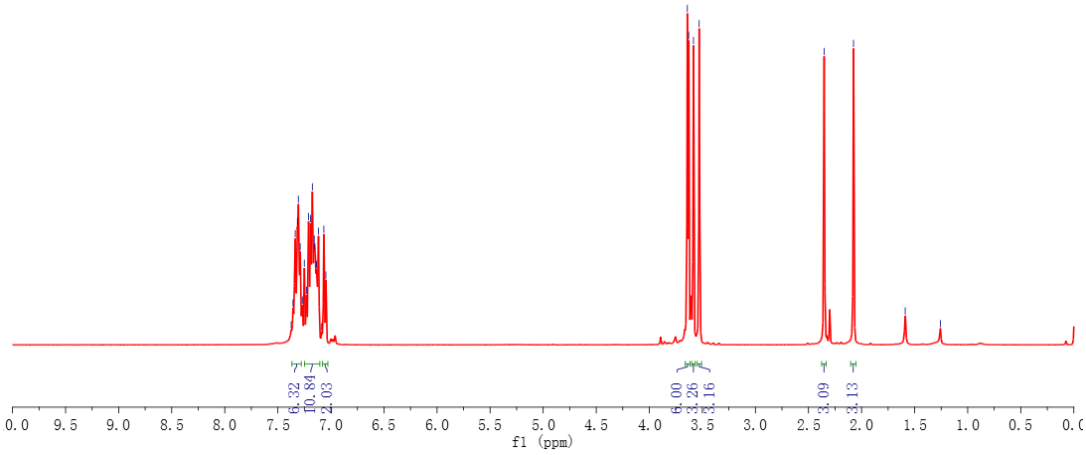
Dimethyl 2-(((*p*-fluorophenyl)thio)(phenyl)methylene)malonate (6h)

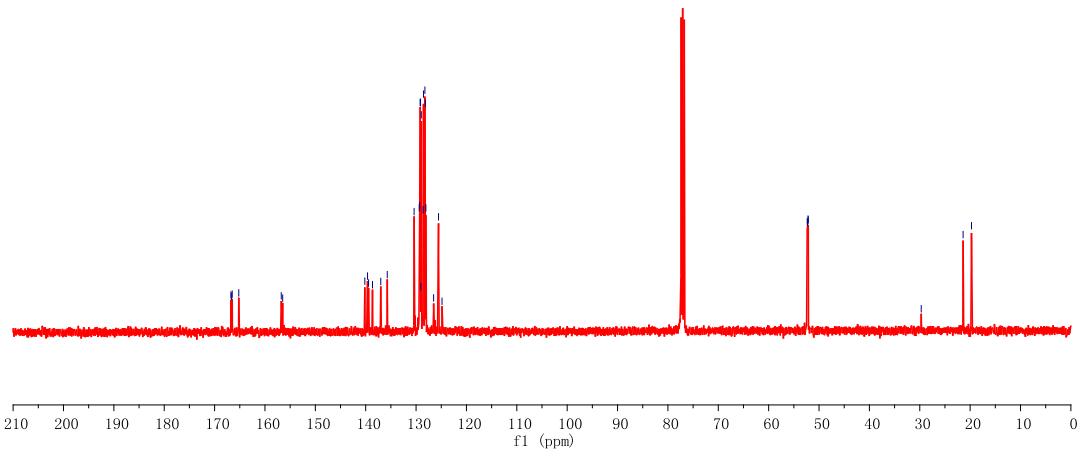


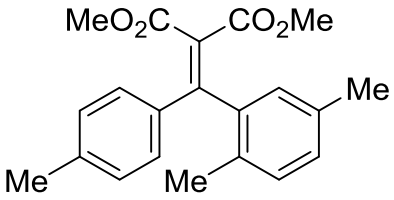




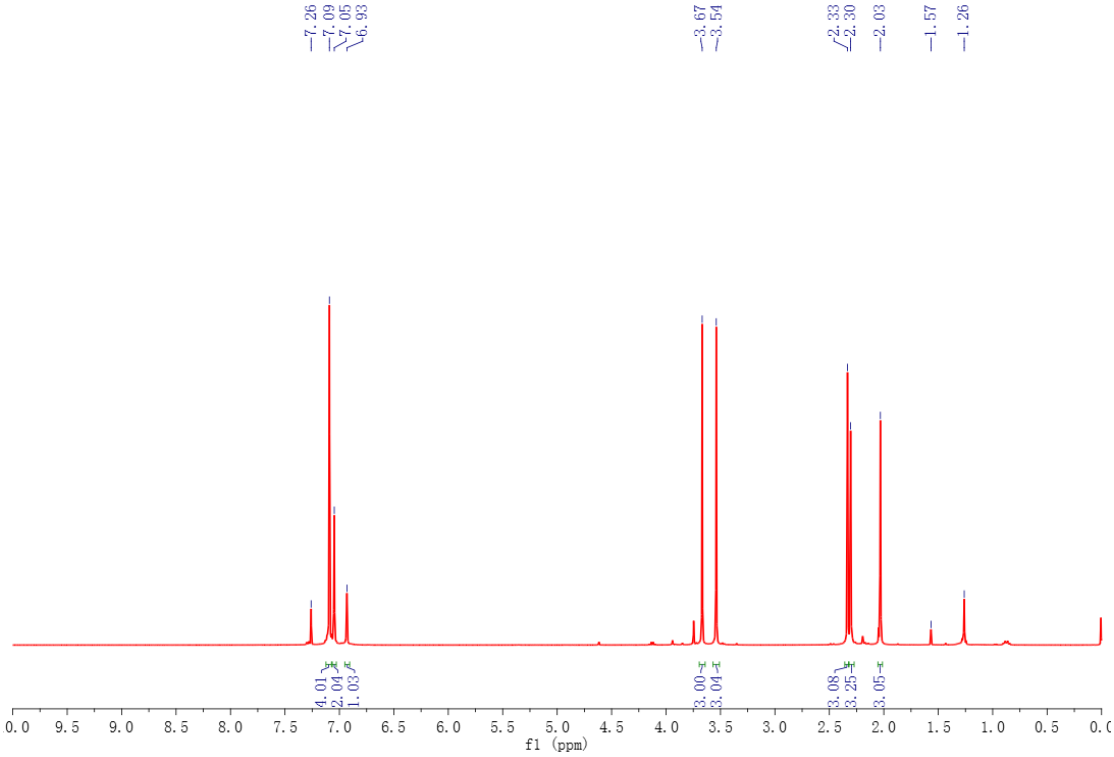
Dimethyl 2-(phenyl(*o*-tolyl)methylene)malonate (8a+8b)

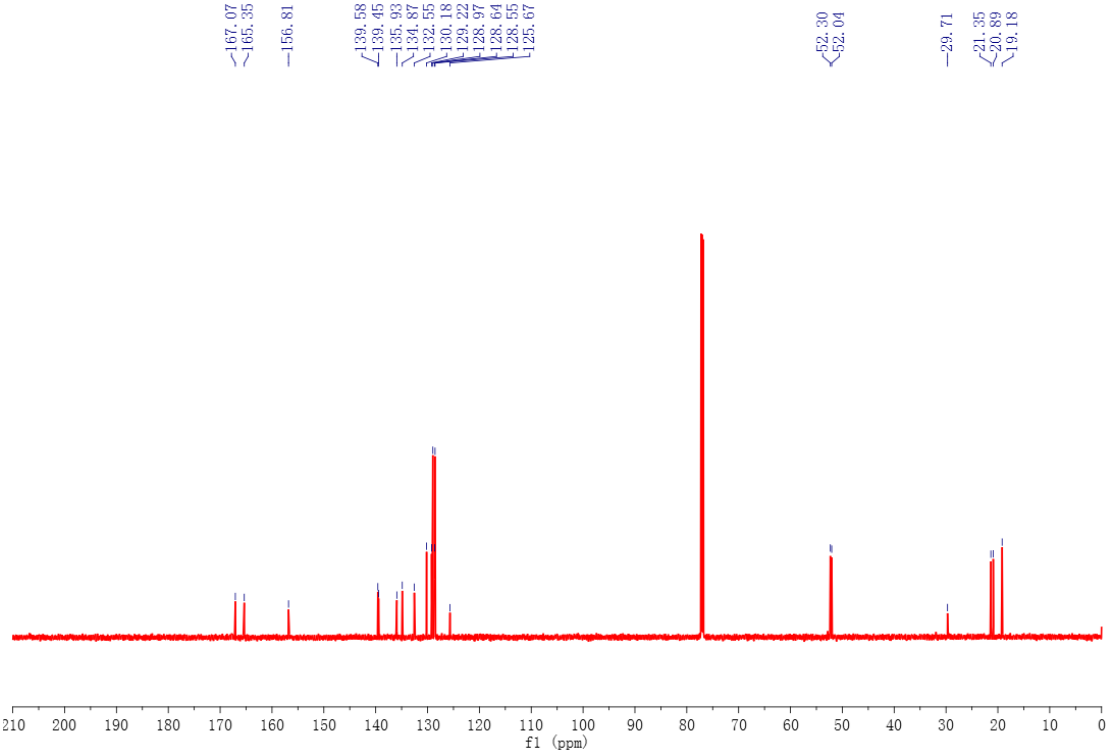


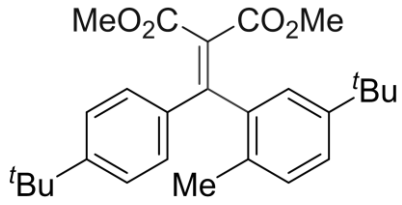




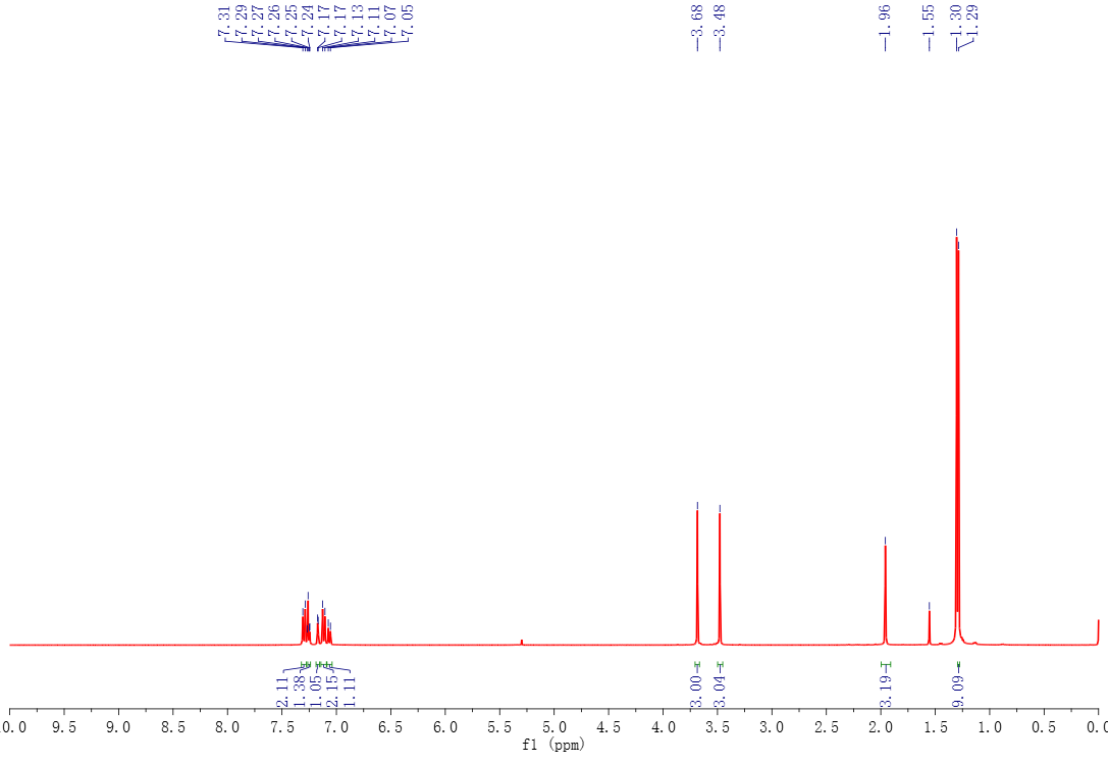
Dimethyl 2-((2,5-dimethylphenyl)(*p*-tolyl)methylene)malonate (9a)

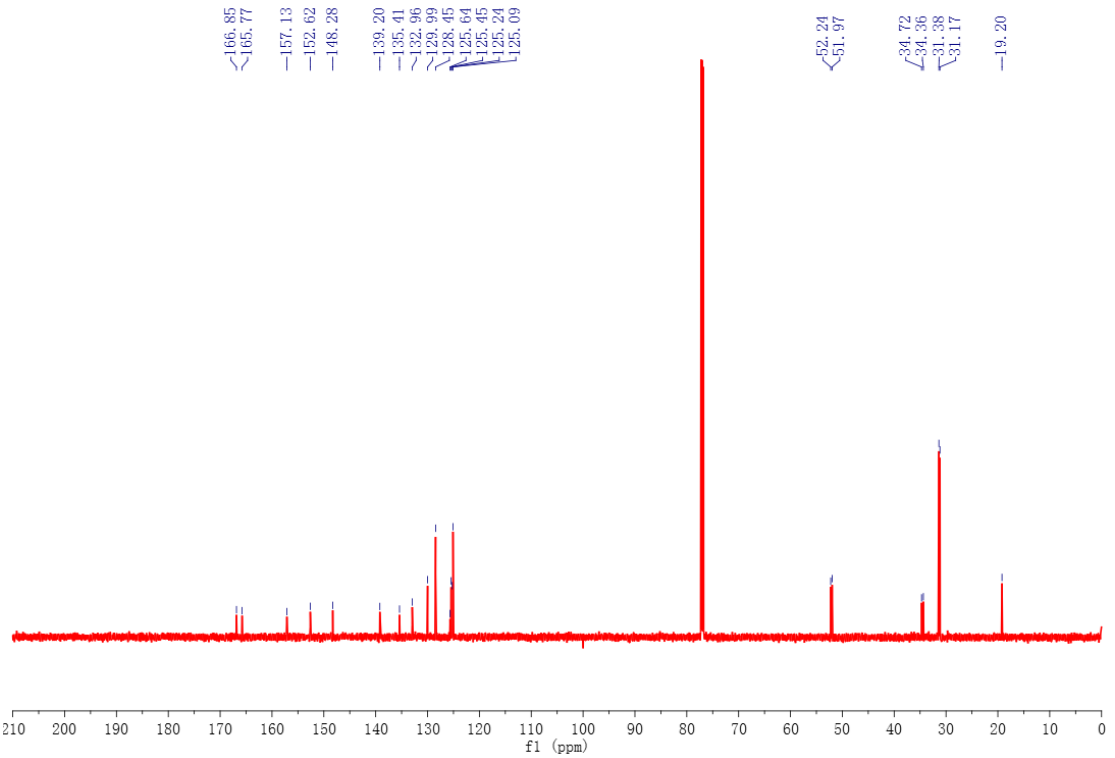


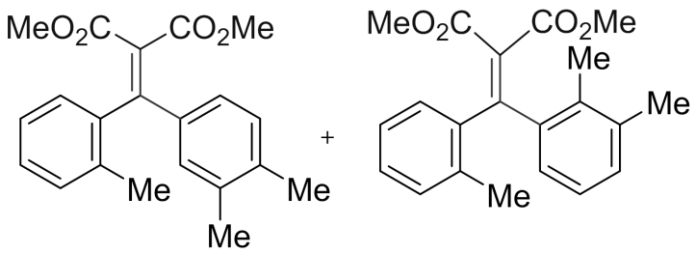




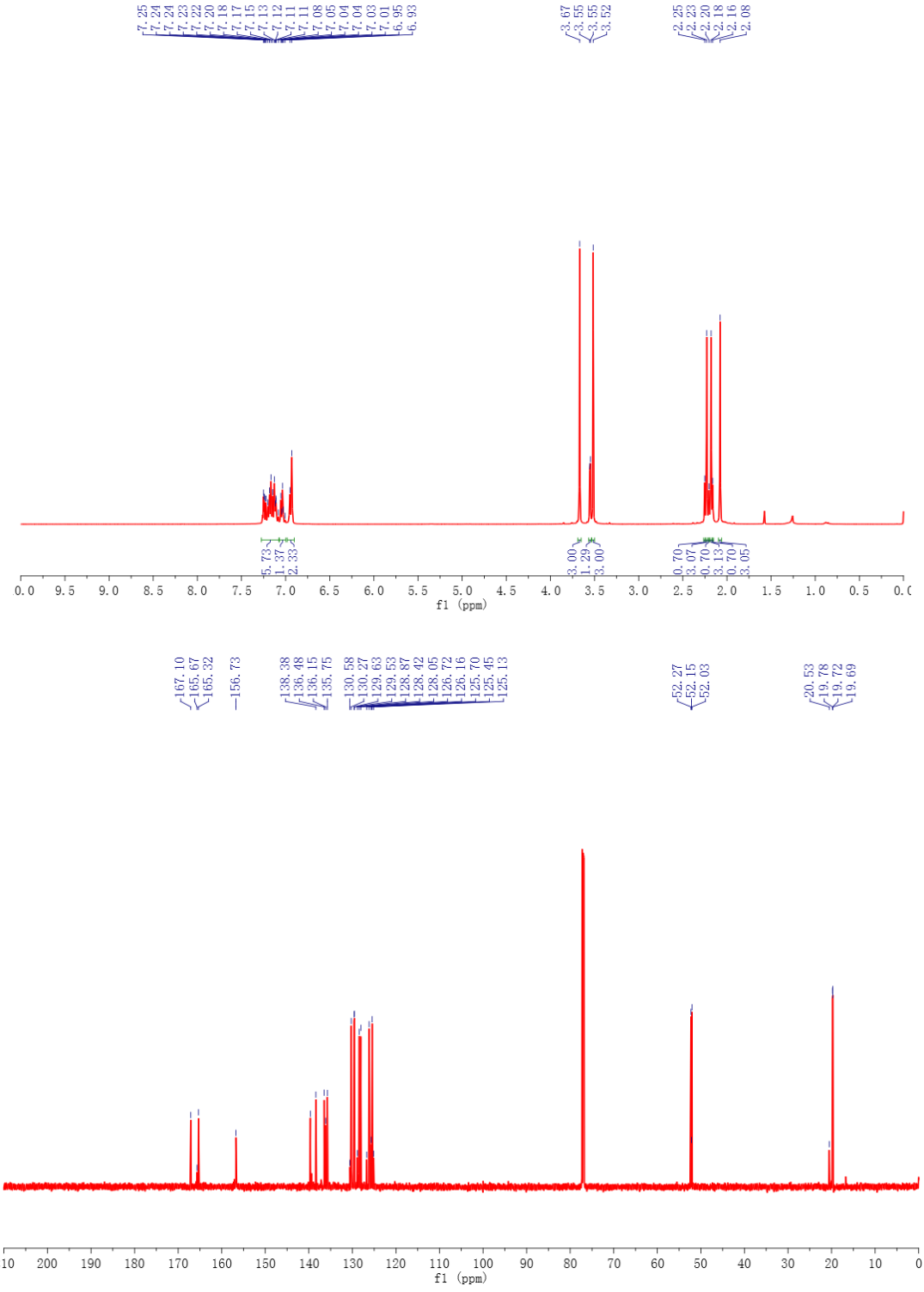
Dimethyl 2-((5-(*tert*-butyl)-2-methylphenyl)(4-(*tert*-butyl)phenyl)methylene)malonate (9b)

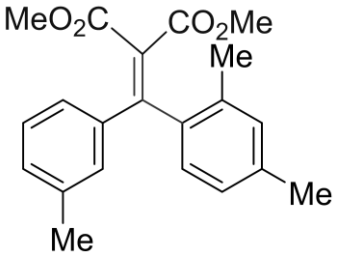






Dimethyl 2-((*m,p*-dimethylphenyl)(*o*-tolyl)methylene)malonate (10a+10b, ratio = 4.3:1**)**:





Dimethyl 2-((*m*,*p*-dimethylphenyl)(*o*-tolyl)methylene)malonate (11a)