Supporting Information

Asymmetric Michael Addition of *N-tert*-Butanesulfinyl Imidate with *α,β*-unsaturated Diesters: Scope and Application to the Synthesis of Indanone Derivatives

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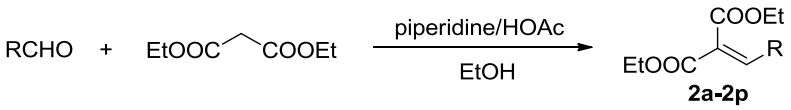
1. General Information

Tetrahydrofuran (THF) was freshly distilled under nitrogen atmosphere from sodium/benzophenone ketyl. LDA was freshly prepared. All other chemicals were of commercial grade and used without further purification. Petroleum ether refers to the 40-60 ℃ boiling fraction. ^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz) spectra were recorded on a Mercury 300 spectrometer (300 MHz for ^{1}H), and Variant MR-400 (100 MHz for ^{13}C) in deuterated solvents with tetramethylsilane (TMS, d = 0.0 ppm) as internal standard unless specified otherwise. All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or argon. Column Chromatography was performed with Combi*Flash*® companion system (Teledyne Isco. cn), silica gel was purchased from qingdaohaiyang (300-400 mesh). HPLC was performed on a JASCO 2000 instrument by using Daicel columns. LC-MS was performed on an Agilent 1100 instrument by column Eclipse XDB-C_{18} (4.6 × 150 mm, 5 μm) or Extend-C_{18} (4.6 × 150 mm, 5 μm).

2. Preparation and characterization of compounds

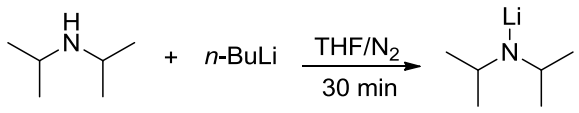
2.1 General procedure for the synthesis of 2a-2p



2a-2p

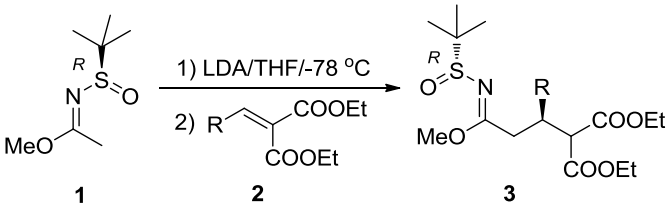
To a solution of diethyl malonate (5.0 mmol, 1.0 equiv) in EtOH was added the corresponding aldehyde (5.0 mmol, 1.0 equiv), then a catalytic amount of HOAc and piperidine were added, the resulting mixture was heated to reflex overnight. The solvent of the reaction mixture was evaporated in vacuo, the crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 20:1) to obtain **2a-2p**.

2.2 General procedure for the synthesis of LDA



Under nitrogen atmosphere, to the solution of diisopropylamine (11 mmol, 1.1 equiv) in THF (20 ml) was added *n*-butyllithium (10 mmol, 1.0 equiv) slowly at -78 ^{o}C, the resulted solution was stirred for another 30 min to obtain freshly prepared LDA.

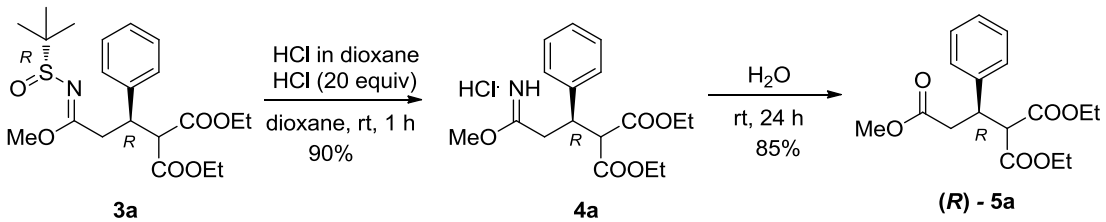
2.3 General procedure for the synthesis of 3a to 3p



1 2 3

Under nitrogen atmosphere, a solution of *N*-*tert*-butanesulfinyl imidate **1** (1.0 equiv, 0.2 mmol) in THF (5.0 mL) was cooled to -78 ^{o}C, a solution of LDA (1.2 equiv, 0.24 mmol, 0.25 mol/L) in THF was added slowly. And the resulting solution was stirred for 45 min at -78 ^{o}C. After deprotonation, a solution of **2** (1.5 equiv, 0.3 mmol) in THF (1.0 mL) was added dropwise, and the reaction mixture was stirred for another 2 h at -78 ^{o}C. To the reaction mixture was added a saturated solution of NH_4Cl (0.5 mL), followed by an aqueous solution of NaOH (2.0 mL, 1.0 N). The aqueous phase was extracted with EtOAc (3 × 20 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and evaporated in vacuo. The crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 4:1) to yield pure **3**.

2.4 General procedure for the synthesis of 5a

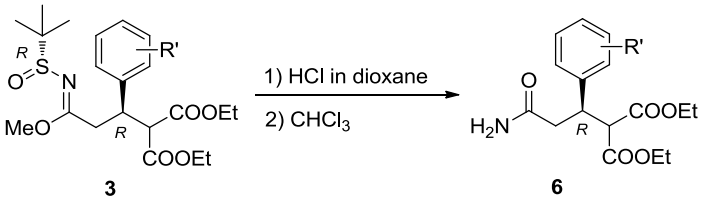


3a **4a** **(*R*) - 5a**

To a solution of **3a** (0.43 g, 1.0 mmol) in dioxane (10 mL) was added dropwise freshly prepared saturated HCl in dioxane (15 mL, ~20 equiv HCl), the mixture was allowed to stir for 1 h. Then the reaction mixture was concentrated in vacuo. Precipitation in diethyl ether afforded 0.3 g (0.9 mmol) of pure **4a**. Hydrochloride **4a** (0.8 mmol) was dissolved in H_2O (10 mL). The reaction mixture was stirred for 24 h at room temperature, subsequently poured into a saturated aqueous solution of

$NaHCO_3$ (15 mL), and extracted with diethyl ether (3 × 15 mL). The combined organic phases were dried ($MgSO_4$), filtered, and evaporated in vacuo. The crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 5:1) to yield pure **5a**.

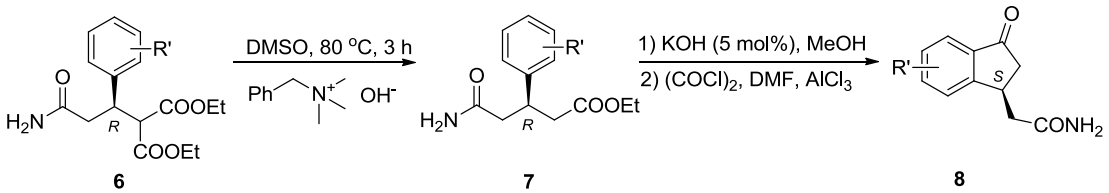
2.5 General procedure for the synthesis of 6



3 **6**

To a solution of **3** (1.0 mmol) in dioxane (10 mL) was added dropwise freshly prepared saturated dioxane/HCl (15 mL, ~20 equiv HCl). The mixture was allowed to stir for 1 h. Then the reaction mixture was concentrated in vacuo. Precipitation in diethyl ether afforded pure imidate hydrochloride. The hydrochloride was immediately dissolved in chloroform (10 mL). The reaction mixture was stirred for 16 h at reflux temperature and subsequently evaporated in vacuo. The crude product was purified by flash chromatography (petroleum ether/ethyl acetate = 2:1) to yield pure **6**.

2.6 General procedure for the synthesis of 8

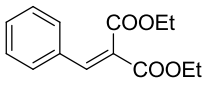


6 **7** **8**

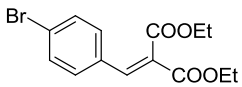
Anhydrous benzene (35 mL) was added to a solution of Triton-B (40% w/w) in methanol (1.19 mmol) and the solution was concentrated under reduced pressure almost to dryness. Compound **6** (1.0 mmol) in 3.5 mL of anhydrous DMSO was added to the solution obtained previously and the mixture was stirred at 80 ^oC for 3 h, then poured into water (5.5 mL), dried over anhydrous $MgSO_4$, filtered and concentrated. The residue was submitted to chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to yield the de-ethoxycarbonylated product **7**. To the solution of 5% KOH in CH_3OH-H_2O was added compound **7** (100 mg) and the reaction system was stirred at reflux temperature. After the end of reaction, CH_3OH was evaporated in vacuo. Water was added to the residue, then

alkali solution was added to the mixture to regulate pH value until it was less than 7, the aqueous phase was extracted with EtOAc (3 × 20 mL). The combined organic phases were dried ($MgSO_4$), filtered and evaporated in vacuo. To the crude product was added 10 mL of HOAc, 7 mL of H_2O and 1.5 mL of H_2SO_4 and the mixture was refluxed overnight, then cooled to room temperature, extracted with EtOAc and washed with water, saturated NaCl acqueous solution, the organic phases were dried over anhydrous $MgSO_4$, evaporated in vacuo. The crude product was obtained and immediately used in the next step without purification. To a solution of the product obtained previously in dry CH_2Cl_2 (5.0 mL) was added oxalyl chloride (90 μL) and DMF (50 μL) at 0 ^oC, the mixture was stirred at room temperture for 30 min, and then evaporated in vacuo. Dry CH_2Cl_2 (5.0 mL) and $AlCl_3$ (138 mg) were added to the residue and stirred for another 5 h. The reaction mixture was poured into ice water, filtered and extracted with EtOAc, washed with saturated acqueous NaCl solution, the organic phases were dried over $MgSO_4$, evaporated in vacuo. The residue was submitted to chromatography on silica gel to yield (petroleum ether/ethyl acetate = 2:1) product **8**.

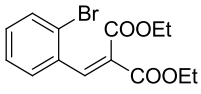
2.7 Characterization data of 2a-2p



2a 80% yield, oil; ^1H NMR (300 MHz, $CDCl_3$): δ 1.26-1.35 (m, 6H), 4.27-4.36 (m, 4H), 7.34-7.40 (m, 3H), 7.43-7.46 (m, 2H), 7.73 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.3, 15.6, 63.1, 63.2, 127.7, 130.2, 130.9, 132.0, 134.3, 143.6, 165.6, 168.2; HRMS (ESI) for $C_{14}H_{16}O_4$ $[M+H]^+$: calcd 249.1127, found 249.1117.

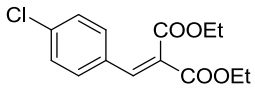


2b 72% yield, oil; ^1H NMR (300 MHz, $CDCl_3$): δ 1.27-1.35 (m, 6H), 4.26-4.36 (m, 4H), 7.29-7.34 (m, 2H), 7.48-7.53 (m, 2H), 7.65 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 14.1, 61.8, 61.9, 125.0, 126.9, 130.8, 131.8, 132.0, 140.7, 163.9, 166.4; HRMS (ESI) for $C_{14}H_{15}BrO_4$ $[M+Na]^+$: calcd 349.0035, found 349.0051.



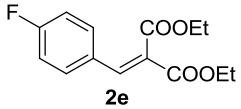
2c

77% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.14 (t, J = 5.4 Hz, 3H), 1.32 (t, J = 5.4 Hz, 3H), 4.17-4.22 (m, 2H), 4.27-4.33 (m, 2H), 7.18-7.28 (m, 2H), 7.38-7.41 (m, 1H), 7.58-7.60 (m,1H), 7.94 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 14.1, 61.6, 61.8, 124.5, 127.4, 128.8, 129.4, 131.2, 133.0, 133.9, 141.6, 163.6, 165.6; HRMS (ESI) for $C_{14}H_{15}BrO_4$ $[M+Na]^+$: calcd 349.0051, found 349.0039.



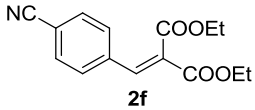
2d

80% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.31 (m, 6H), 4.31 (m, 4H), 7.35 (m, 4H), 7.67 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.3, 15.6, 63.2, 63.3, 128.3, 130.5, 132.1, 132.8, 138.1, 142.1, 165.4, 167.9; HRMS (ESI) for $C_{14}H_{15}ClO_4$ $[M+Na]^+$: calcd 305.0557, found 305.0545.



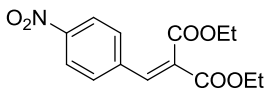
2e

85% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.31 (m, 6H), 4.20 (m, 4H), 7.08 (m, 2H), 7.50 (m, 2H), 7.68 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 14.1, 61.7, 61.8, 116.0 (d, $^{2}J_{CF}$ = 17 Hz), 126.1, 129.1, 131.6 (d, $^{3}J_{CF}$ = 7 Hz), 140.8, 163.9 (d, $^{1}J_{CF}$ = 200 Hz), 164.1, 166.6; HRMS (ESI) for $C_{14}H_{15}FO_4$ $[M+Na]^+$: calcd 289.0852, found 289.0861.



2f

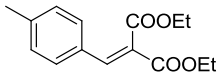
78% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.26 (t, J = 5.4 Hz, 3H), 1.33 (t, J = 5.4 Hz, 3H), 4.31 (m, 4H), 7.53 (d, J = 6.3 Hz, 2H), 7.66 (d, J = 6.3 Hz, 2H), 7.70 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.6, 14.8, 62.76, 62.81, 114.3, 118.9, 130.2, 130.4, 133.2, 138.1, 140.3, 164.1, 166.5; HRMS (ESI) for $C_{15}H_{15}NO_4$ $[M+Na]^+$: calcd 296.0899, found 296.0903.



2g

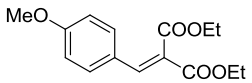
85% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.27 (t, J = 5.8 Hz, 3H), 1.33 (t, J = 5.4 Hz, 3H), 4.16 (q, J = 5.4 Hz, 2H), 3.7 (q, J = 7.2 Hz, 2H),

7.58-7.61 (m, 2H), 7.74 (s, 1H), 8.20-8.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 14.1, 62.08, 62.12, 123.9, 129.93, 129.98, 139.1, 139.2, 148.4, 163.3, 165.6; HRMS (ESI) for $C_{14}H_{15}NO_6$ $[M+Na]^+$: calcd 316.0797, found 316.0787.



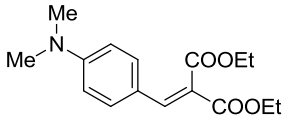
2h

75% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.27-1.33 (m, 6H), 2.35 (s, 3H), 4.25-4.36 (m, 4H), 7.16 (d, J = 6.0 Hz, 2H), 7.34 (d, J = 6.3 Hz, 2H), 7.69 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.6, 14.9, 22.2, 62.3, 62.4, 125.9, 130.3, 130.8, 141.9, 142.9, 165.0, 167.7; HRMS (ESI) for $C_{15}H_{18}O_4$ $[M+Na]^+$: calcd 285.1103, found 285.1108.



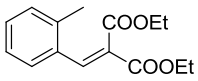
2i

81% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.30-1.34 (m, 6H), 3.82 (s, 3H), 4.26-4.39 (m, 4H), 6.86-6.91 (m, 2H), 7.40-7.44 (m, 2H), 7.67 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.6, 14.9, 56.0, 62.1, 62.3, 114.98, 124.3, 126.1, 132.3, 142.5, 162.3, 165.2, 167.9; HRMS (ESI) for $C_{15}H_{18}O_5$ $[M+Na]^+$: calcd 301.1052, found 301.1064.



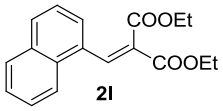
2j

80% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.28-1.35 (m, 6H), 3.00 (s, 6H), 4.26 (q, J = 5.4 Hz, 2H), 4.6 (q, J = 5.4 Hz, 2H), 6.59-6.63 (m, 2H), 7.35 (d, J = 6.9 Hz, 2H), 7.62 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 14.2, 40.0, 61.1, 61.4, 111.5, 119.9, 120.1, 131.9, 142.7, 151.8, 165.1, 168.0; HRMS (ESI) for $C_{16}H_{21}NO_4$ $[M+Na]^+$: calcd 314.1368, found 314.1382.



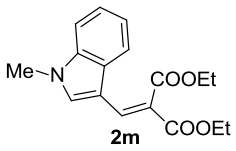
2k

74% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.15 (t, J = 5.4 Hz, 3H), 1.33 (t, J = 5.4 Hz, 3H), 2.36 (s, 3H), 4.20 (q, J = 5.4 Hz, 2H), 4.30 (q, J = 5.4 Hz, 2H), 7.11-7.33 (m, 4H), 7.96 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.5, 14.8, 20.6, 62.2, 62.3, 126.7, 128.5, 128.5, 130.7, 131.1, 133.4, 138.3, 142.4, 164.8, 167.0; HRMS (ESI) for $C_{15}H_{18}O_4$ $[M+Na]^+$: calcd 285.1103, found 285.1092.



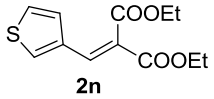
2l

75% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.06 (t, J = 7.5 Hz, 3H), 1.38 (t, J = 7.2 Hz, 3H), 4.16 (q, J = 7.2 Hz, 2H), 3.7 (q, J = 7.2 Hz, 2H), 7.41-7.46 (m, 1H), 7.51-7.59 (m, 3H), 7.86-7.89 (m, 2H), 7.99-8.02 (m, 1H), 8.48 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 14.2, 61.5, 61.8, 124.1, 125.2, 126.40, 126.42, 126.9, 128.7, 129.3, 130.5, 130.8, 131.4, 133.4, 141.3, 164.0, 166.2; HRMS (ESI) for $C_{18}H_{18}O_4$ $[M+Na]^+$: calcd 321.1103, found 321.1111.



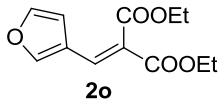
2m

83% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.35 (m, 6H), 3.81 (s, 3H), 4.31 (q, J = 5.4 Hz, 2H), 4.38 (q, J = 5.4 Hz, 2H), 7.23-7.35 (m, 4H), 7.71 (s, 1H), 7.80 (m, 1H), 8.10 (d, J = 0.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 14.3, 33.5, 61.1, 61.4, 109.1, 109.9, 118.6, 121.4, 123.0, 128.5, 132.2, 134.9, 136.8, 165.5, 168.1; HRMS (ESI) for $C_{17}H_{19}NO_4$ $[M+Na]^+$: calcd 324.1212, found 324.1228.



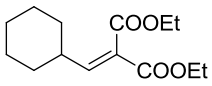
2n

80% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.33 (m, 6H), 4.29 (q, J = 5.4 Hz, 2H), 4.37 (q, J = 5.4 Hz, 2H), 7.18-7.20 (m, 1H), 7.32-7.34 (m, 1H), 7.62-7.64 (m, 1H), 7.71 (d, J = 0.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 14.1, 61.5, 61.7, 124.3, 126.9, 127.0, 130.8, 134.8, 135.3, 164.4, 166.9; HRMS (ESI) for $C_{12}H_{14}O_4S$ $[M+Na]^+$: calcd 277.0511, found 277.0497.



2o

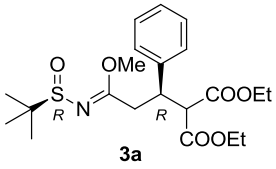
77% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.31 (m, 6H), 4.25 (q, J = 5.4 Hz, 2H), 4.37 (q, J = 5.4 Hz, 2H), 6.45-6.47 (m, 1H), 6.32 (d, J = 2.7 Hz, 1H), 7.42 (s, 1H), 7.48 (d, J = 1.2 Hz ,1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 14.1, 61.5, 61.6, 112.6, 117.9, 122.0, 127.5, 146.1, 149.0, 164.2, 166.3; HRMS (ESI) for $C_{12}H_{14}O_5$ $[M+Na]^+$: calcd 261.0739, found 261.0792.



2p

81% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.08-1.33 (m, 11H), 1.63-1.75 (m, 5H), 2.32-2.42 (m, 1H), 4.21 (q, J = 5.4 Hz, 2H), 4.90 (q, J = 5.4 Hz, 2H), 6.79 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.8, 14.9, 25.9, 26.3, 32.4, 39.7, 61.8, 61.9, 127.5, 154.3, 165.0, 166.5; HRMS (ESI) for $C_{14}H_{22}O_4$ $[M+Na]^+$: calcd 277.1416, found 277.1427.

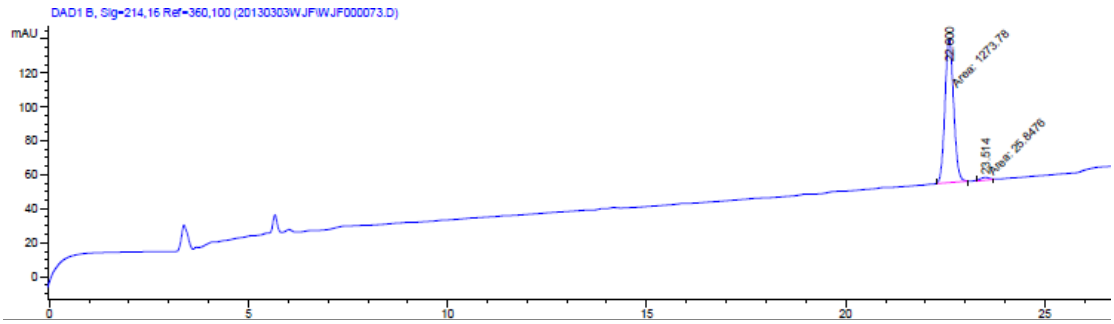
2.8 Characterization data and HPLC of addition products 3a-3p



3a

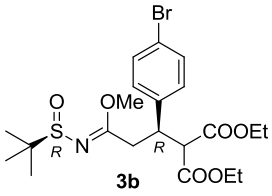
94% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.91 (t, J = 7.5 Hz, 3H), 0.97 (s, 9H), 1.27 (t, J = 6.9 Hz, 3H), 2.90 (dd, J = 4.5 Hz, 17.4 Hz, 1H), 3.35-3.44 (m, 1H), 3.59 (s, 3H), 3.69 (d, J = 10.8 Hz, 1H), 3.83-3.96 (m, 3H), 4.22 (q, J = 7.2 Hz, 2H), 7.13-7.26 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.6, 14.0, 21.6, 36.6, 42.5, 53.9, 55.5, 57.4, 61.3, 61.8, 127.4, 128.2, 128.3, 138.8, 167.2, 167.8, 173.7; IR (KBr): v = 2981, 2947, 1751, 1734, 1614, 1456, 1367, 1254, 1157, 1078, 702 cm^{-1}; HRMS (ESI) for $C_{21}H_{31}NO_6S$ $[M+Na]^+$: calcd 448.1770, found 448.1759.

Analytical HPLC: Agilent 1200 series, Extend-C_{18} Column (4.6×150 mm, 5 micron particle size), mobile phase H_2O/CH_3OH (the gradient of CH_3OH is from 5% to 90% during 0-40 min); Flow = 0.8 mL/min; Detected by UV at 214 nm; Retention time: 22.60 min (maj), 23.51 min.



Signal 1: DAD1 B, Sig=214,16 Ref=360,100

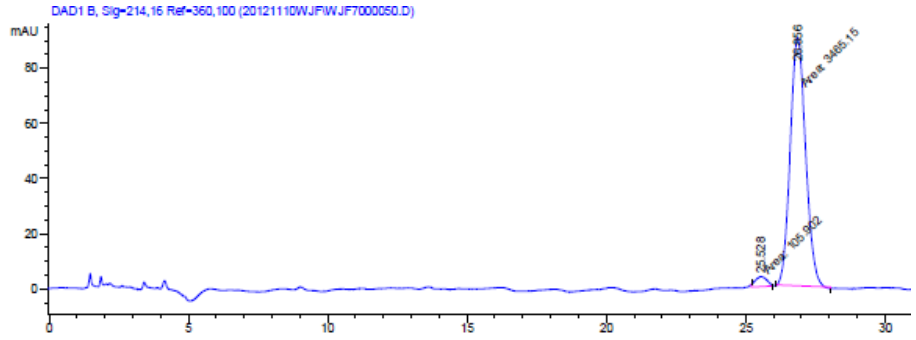
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.600	MM	0.2504	1273.78381	84.79194	98.0112
2	23.514	MM	0.2802	25.84759	1.53772	1.9888



3b

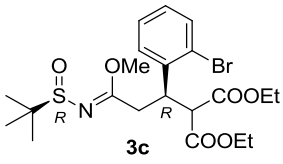
90% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.98 (t, J = 7.2 Hz, 3H), 1.03 (s, 9H), 1.28 (t, J = 7.2 Hz, 3H), 2.91 (dd, J = 4.2 Hz, 15.2 Hz, 1H), 3.34-3.42 (m, 1H), 3.59 (s, 3H), 3.65 (d, J = 10.8 Hz, 1H), 3.87-3.95 (m, 3H), 4.19-4.26 (m, 2H), 7.09-7.13 (m, 2H), 7.37-7.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 14.0, 21.7, 36.4, 41.9, 54.0, 55.9, 57.2, 61.5, 62.0, 121.4, 130.0, 131.5, 138.0, 167.0, 167.5, 172.9; IR (KBr): v = 2981, 2947, 1751, 1734, 1612, 1489, 1288, 1254, 1178, 1074, 1010 cm^{-1}; HRMS (ESI) for $C_{21}H_{30}BrNO_6S$ $[M+H]^+$: calcd 504.1055, found 504.1048.

Analytical HPLC: Agilent 1200 series, Eclipse XDB-C_{18} Column (4.6×150 mm, 5 micron particle size), mobile phase H_2O/CH_3OH (40:60); Flow = 0.8 mL/min; Detected by UV at 214 nm; Retention time: 25.53 min, 26.86 min (maj).



Signal 1: DAD1 B, Sig=214,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.528	MM	0.4913	105.90210	3.59236	2.9656
2	26.856	MM	0.6424	3465.15137	89.90769	97.0344

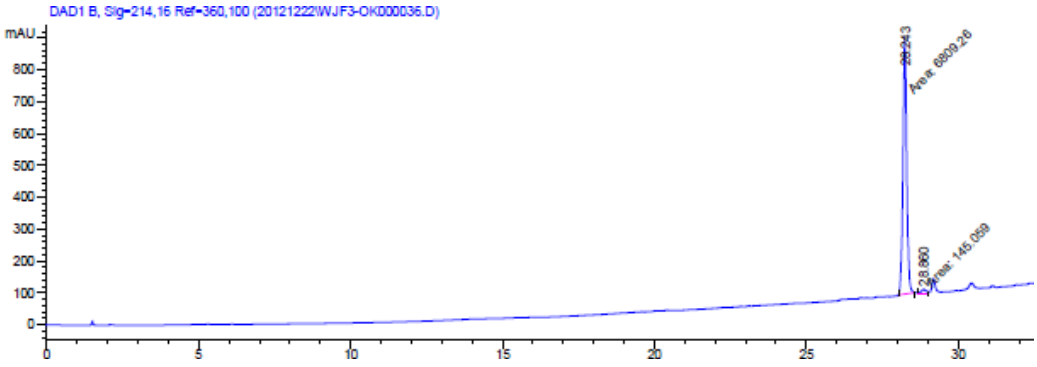


3c

90% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.978-1.025 (m, 12H), 1.27 (t, J = 7.2 Hz, 3H), 2.61 (dd, J = 4.2 Hz, 14.4 Hz, 1H), 3.50 (s, 1H), 3.65 (s, 3H), 3.77 (s, 1H), 3.91-3.98 (m, 2H), 4.18-4.28 (m, 2H), 4.54 (s, 1H), 7.02-7.08 (m, 1H), 7.24-7.34 (m, 2H), 7.48-7.51 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 14.0, 21.7, 29.7, 35.7, 40.4, 54.0, 55.7, 61.5, 61.9, 125.2, 127.6, 128.8, 129.7, 133.2, 138.5,

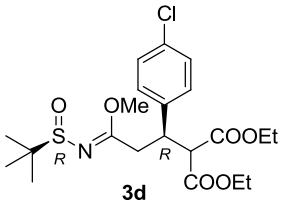
167.1, 167.6, 173.3; IR (KBr): ν = 2964, 2921, 1734, 1612, 1440, 1259, 1086, 1020, 796 cm^{-1}; HRMS (ESI) for $C_{21}H_{30}BrNO_6S$ $[M+H]^+$: calcd 504.1055, found 504.1051.

Analytical HPLC: Agilent 1200 series, Extend-C_{18} Column (4.6×150 mm, 5 micron particle size), mobile phase H_2O/CH_3OH (the gradient of CH_3OH is from 5% to 90% during 0-40 min); Flow = 0.8 mL/min; Detected by UV at 214 nm; Retention time: 28.24 min (maj), 28.86 min.



Signal 1: DAD1 B, Sig=214,16 Ref=360,100

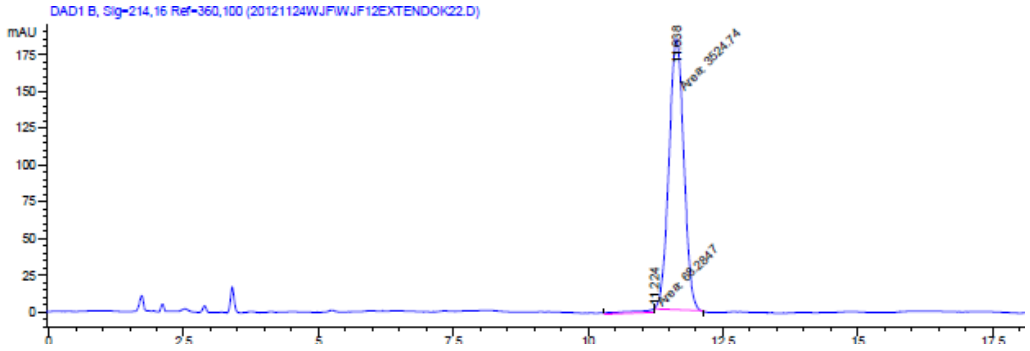
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.243	MM	0.1425	6809.26025	796.45758	97.9141
2	28.860	MM	0.2002	145.05910	12.07778	2.0859



3d

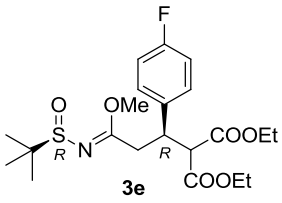
94% yield, oil; ^1H NMR (300 MHz, $CDCl_3$): δ 0.95 (t, J = 7.2 Hz, 3H), 1.01 (s, 9H), 1.25 (t, J = 5.4 Hz, 3H), 2.88 (dd, J = 3.6 Hz, 10.8 Hz, 1H), 3.32-3.39 (m, 1H), 3.57 (s, 3H), 3.63 (d, J = 8.1 Hz, 1H), 3.86-3.93 (m, 3H), 4.17-4.23 (m, 2H), 7.13-7.16 (m, 2H), 7.19-7.22 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.6, 14.0, 21.6, 36.4, 41.8, 53.9, 55.8, 57.2, 61.4, 61.9, 128.5, 129.6, 133.2, 137.5, 167.0, 167.5, 172.9; IR (KBr): ν = 2981, 2925, 1751, 1612, 1493, 1442, 1367, 1290, 1178, 1074, 756 cm^{-1}; HRMS (ESI) for $C_{21}H_{30}ClNO_6S$ $[M+Na]^+$: calcd 482.1380, found 482.1360.

Analytical HPLC: Agilent 1200 series, Eclipse XDB-C_{18} Column (4.6×150 mm, 5 micron particle size), mobile phase H_2O/CH_3OH (40:60); Flow = 0.8 mL/min; Detected by UV at 214 nm; Retention time: 11.22 min, 11.63 min (maj).



Signal 1: DAD1 B, Sig=214,16 Ref=360,100

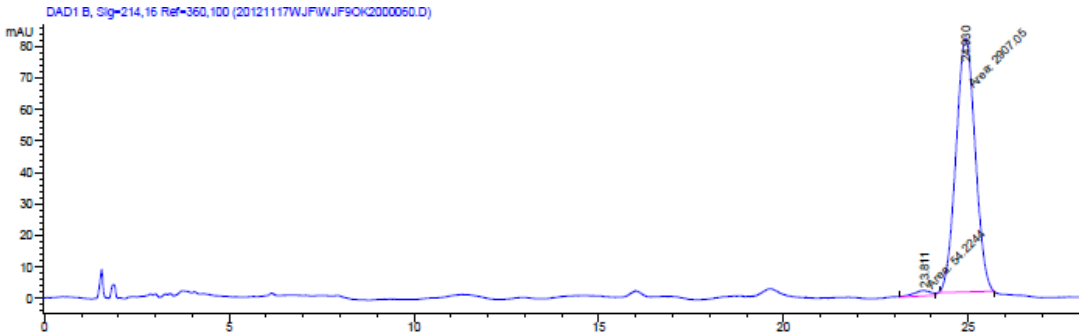
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.224	MM	0.4656	68.28474	2.44439	1.9005
2	11.638	MM	0.3195	3524.73682	183.86060	98.0995



3e

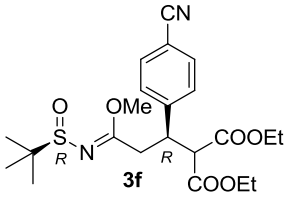
95% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.96 (t, J = 5.4 Hz, 3H), 1.03 (s, 9H), 1.28 (t, J = 5.4 Hz, 3H), 2.90 (dd, J = 3.3 Hz, 10.5 Hz, 1H), 3.35-3.41 (m, 1H), 3.59 (s, 3H), 3.65 (d, J = 8.1 Hz, 1H), 3.86-3.96 (m, 3H), 4.19-4.26 (m, 2H), 6.92-6.98 (m, 2H), 7.17-7.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 14.0, 21.7, 36.6, 41.8, 53.9, 55.8, 57.5, 61.4, 61.9, 115.2 (d, $^{2}J_{CF}$ = 22 Hz), 129.9 (d, $^{3}J_{CF}$ = 8 Hz), 134.7(d, $^{4}J_{CF}$ = 4 Hz), 162.0 (d, $^{1}J_{CF}$ = 244 Hz), 167.2, 167.7, 173.1; IR (KBr): ν = 2922, 2852, 1741, 1600, 1513, 1369, 1255, 1165, 1078, 845, 748 cm^{-1}; HRMS (ESI) for $C_{21}H_{30}FNO_6S$ $[M+H]^+$: calcd 444.1856, found 444.1856.

Analytical HPLC: Agilent 1200 series, Eclipse XDB-C_{18} Column (4.6×150 mm, 5 micron particle size), mobile phase H_2O/CH_3OH (40:60); Flow = 0.8 mL/min; Detected by UV at 214 nm; Retention time: 23.81 min, 24.93 min (maj).



Signal 1: DAD1 B, Sig=214,16 Ref=360,100

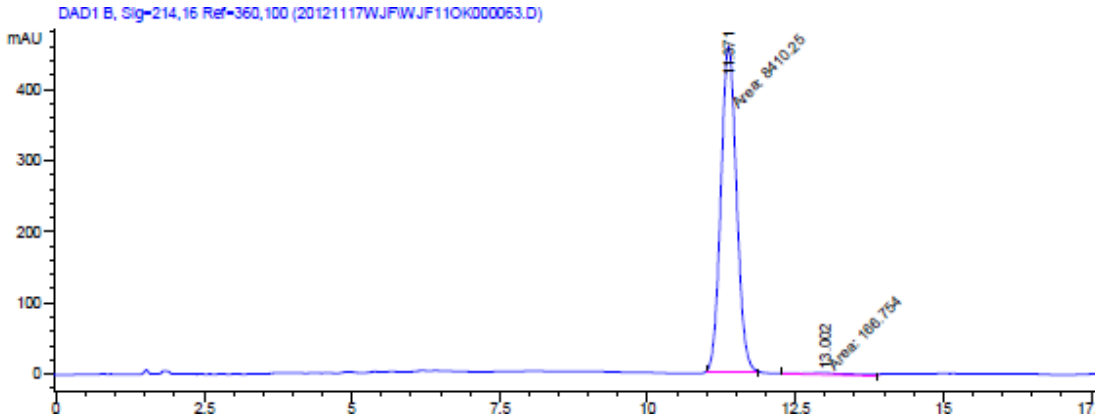
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.811	MM	0.5300	54.22445	1.70509	1.8311
2	24.930	MM	0.6023	2907.05444	80.44553	98.1689



3f

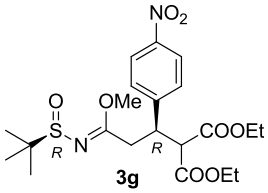
93% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.96 (t, J = 5.4 Hz, 3H), 1.03 (s, 9H), 1.26 (t, J = 5.4 Hz, 3H), 2.94 (dd, J = 3.3 Hz, 10.8 Hz, 1H), 3.38-3.45 (m, 1H), 3.55 (s, 3H), 3.67 (d, J = 8.4 Hz, 1H), 3.85-3.93 (m, 2H), 3.96-4.02 (m, 1H), 4.17-4.25 (m, 2H), 7.36 (d, J = 6.3 Hz, 2H), 7.60 (d, J = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 14.0, 21.7, 36.1, 42.4, 54.0, 56.1, 56.9, 61.6, 62.1, 110.9, 119.0, 129.2, 132.2, 144.1, 166.8, 167.3, 172.5; IR (KBr): ν = 2962, 2925, 1753, 1734, 1618, 1460, 1259, 1176, 1076, 1026, 798 cm^{-1}; HRMS (ESI) for $C_{22}H_{30}N_2O_6S$ $[M+H]^+$: calcd 451.1903, found 451.1913.

Analytical HPLC: Agilent 1200 series, Extend- C_{18} Column (4.6×150 mm, 5 micron particle size), mobile phase H_2O/CH_3OH (40:60); Flow = 0.8 mL/min; Detected by UV at 214 nm; Retention time: 11.37 min (maj), 13.00 min.



Signal 1: DAD1 B, Sig=214,16 Ref=360,100

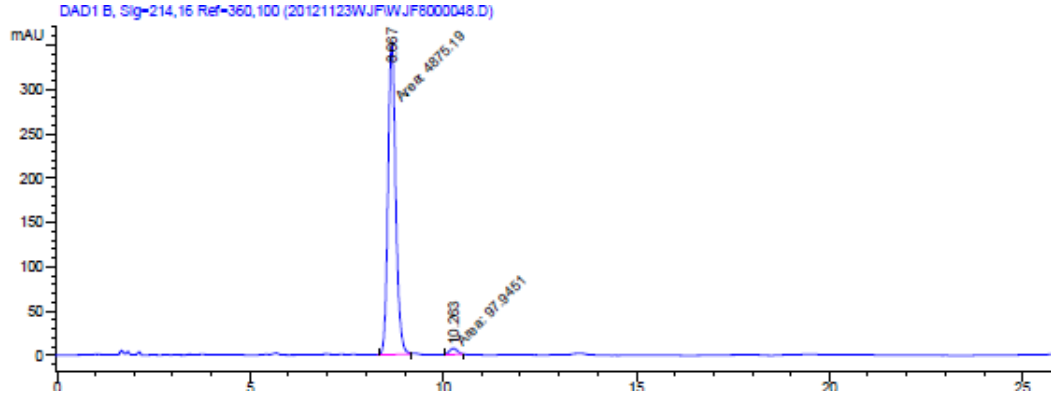
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.371	MM	0.3068	8410.25000	456.81848	98.0558
2	13.002	MM	0.9428	166.75404	2.94788	1.9442



3g

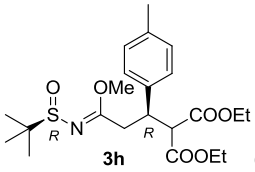
92% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.99 (t, J = 5.4 Hz, 3H), 1.05 (s, 9H), 1.29 (t, J = 5.4 Hz, 3H), 2.98 (dd, J = 3.3 Hz, 10.8 Hz, 1H), 3.44-3.50 (m, 1H), 3.57 (s, 3H), 3.71 (d, J = 8.1 Hz, 1H), 3.86-3.97 (m, 2H), 4.05-4.12 (m, 1H), 4.20-4.28 (m, 2H), 7.45 (d, J = 6.6 Hz, 2H), 7.39 (d, J = 6.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 21.8, 29.7, 36.1, 42.2, 54.1, 56.3, 57.0, 61.7, 62.2, 123.6, 129.4, 147.0, 147.3, 166.9, 167.3, 171.6; IR (KBr): v = 2962, 2924, 1732, 1637, 1523, 1348, 1259, 1076, 799 cm^{-1}; HRMS (ESI) for $C_{21}H_{30}N_2O_8S$ $[M+Na]^+$: calcd 493.1621, found 493.1617.

Analytical HPLC: Agilent 1200 series, Extend-C_{18} Column (4.6×150 mm, 5 micron particle size), mobile phase H_2O/CH_3OH (40:60); Flow = 0.8 mL/min; Detected by UV at 214 nm; Retention time: 8.67 min (maj), 10.26 min.



Signal 1: DAD1 B, Sig=214,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.667	MM	0.2309	4875.18604	351.82318	98.0305
2	10.263	MM	0.2448	97.94510	6.66785	1.9695

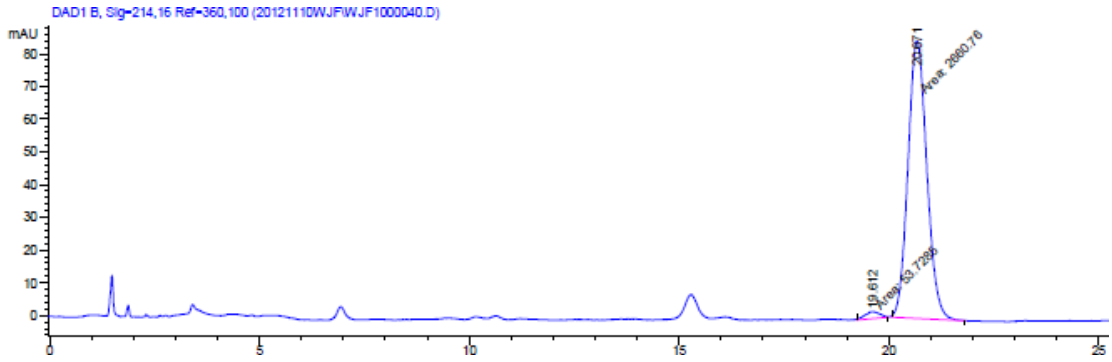


3h

91% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.94 (t, J = 6.9 Hz, 3H), 0.97 (s, 9H), 1.26 (t, J = 6.9 Hz, 3H), 2.24 (s, 3H), 2.69 (dd, J = 4.5 Hz, 14.4 Hz, 1H), 3.31-3.39 (m, 1H), 3.59 (s, 3H), 3.54 (d, J = 10.8 Hz, 1H), 3.83-3.92 (m, 3H), 4.17-4.24 (m, 2H), 7.00-7.08 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.6, 14.0, 20.9, 21.6, 36.6, 42.0, 53.8, 55.5, 57.5, 61.2, 61.7, 128.0, 129.0, 135.7, 136.9, 167.2,

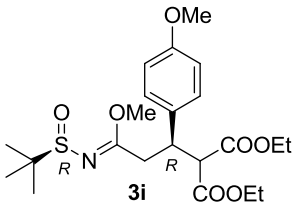
167.8, 173.9; IR (KBr): ν = 2981, 2923, 2852, 1751, 1734, 1612, 1442, 1296, 1157, 1076, 756 cm^{-1}; HRMS (ESI) for $C_{22}H_{33}NO_6S$ $[M+H]^+$: calcd 440.2107, found 440.2105.

Analytical HPLC: Agilent 1200 series, Eclipse XDB-C_{18} Column (4.6×150 mm, 5 micron particle size), mobile phase H_2O/CH_3OH (40:60); Flow = 0.8 mL/min; Detected by UV at 214 nm; Retention time: 19.61 min, 20.67 min (maj).



Signal 1: DAD1 B, Sig=214,16 Ref=360,100

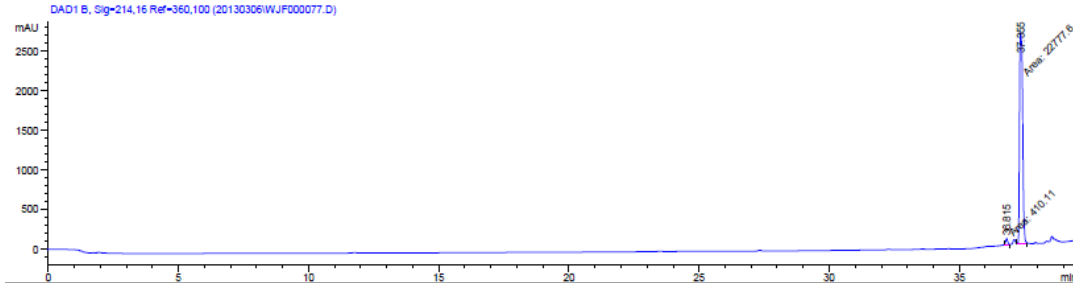
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.612	MM	0.4047	53.72846	2.21250	1.9793
2	20.671	MM	0.5222	2660.75537	84.92070	98.0207



3i

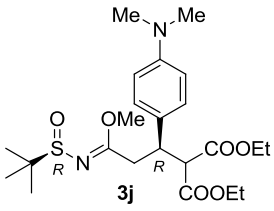
93% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.96 (t, J = 6.9 Hz, 3H), 1.00 (s, 9H), 1.27 (t, J = 6.9 Hz, 3H), 2.87 (dd, J = 4.2 Hz, 14.1 Hz, 1H), 3.31-3.40 (m, 1H), 3.59 (s, 3H), 3.64 (d, J = 10.8 Hz, 1H), 3.74 (s, 3H), 3.83-3.92 (m, 3H), 4.18-4.25 (m, 2H), 6.74-6.79 (m, 2H), 7.09-7.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 14.0, 21.7, 36.7, 41.7, 53.9, 55.2, 57.6, 61.3, 61.8, 113.7, 129.3, 130.8, 158.8, 167.3, 167.8, 173.8; IR (KBr): ν = 2980, 2933, 1749, 1732, 1641, 1253, 1159, 1077, 735 cm^{-1}; HRMS (ESI) for $C_{22}H_{33}NO_7S$ $[M+H]^+$: calcd 456.2056, found 456.2056, found. 456.2056, found 456.2058.

Analytical HPLC: Agilent 1200 series, Eclipse XDB-C_{18} Column (4.6×150 mm, 5 micron particle size), mobile phase H_2O/CH_3OH (the gradient of CH_3OH is from 5% to 90% during 0-40 min); Flow = 0.8 mL/min; Detected by UV at 214 nm; Retention time: 36.81 min, 37.35 min (maj).



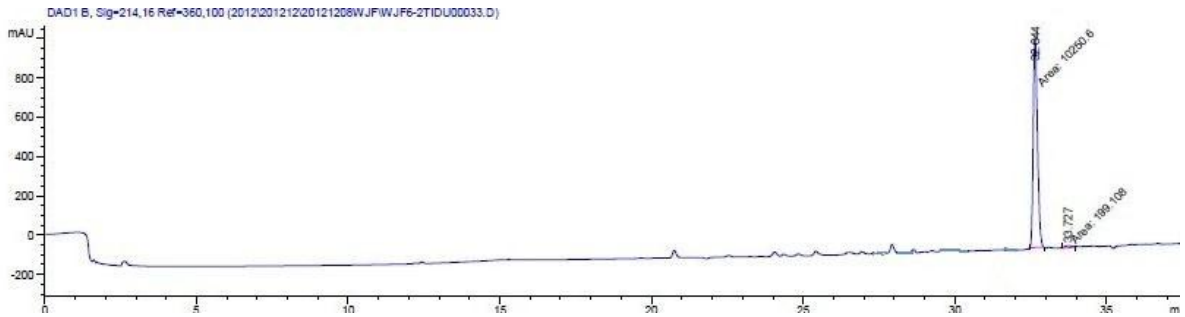
Signal 1: DAD1 B, Sig=214,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.815	MM	0.0920	410.11038	74.33292	1.7687
2	37.355	MM	0.1426	2.27776e4	2662.08008	98.2313



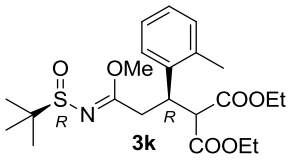
3j 92% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.96 (t, J = 6.9 Hz, 3H), 1.00 (s, 9H), 1.27 (t, J = 6.9 Hz, 3H), 2.87 (dd, J = 4.2 Hz, 14.1 Hz, 1H), 3.31-3.40 (m, 1H), 3.59 (s, 3H), 3.64 (d, J = 10.8 Hz, 1H), 3.74 (s, 3H), 3.83-3.92 (m, 3H), 4.18-4.25 (m, 2H), 6.74-6.79 (m, 2H), 7.09-7.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 14.0, 21.7, 36.7, 41.7, 53.9, 55.2, 57.6, 61.3, 61.8, 113.7, 129.3, 130.8, 158.8, 167.3, 167.8, 173.8; IR (KBr): v = 2962, 2925, 2854, 1733, 1614, 1458, 1259, 1092, 1018, 798 cm^{-1}; HRMS (ESI) for $C_{23}H_{36}N_2O_6S$ $[M+Na]^+$: calcd 491.2192, found 491.2174.

Analytical HPLC: Agilent 1200 series, Extend-C_{18} Column (4.6×150 mm, 5 micron particle size), mobile phase H_2O/CH_3OH (the gradient of CH_3OH is from 5% to 90% during 0-40 min); Flow = 0.8 mL/min; Detected by UV at 214 nm; Retention time: 32.64 min (maj), 33.73 min.



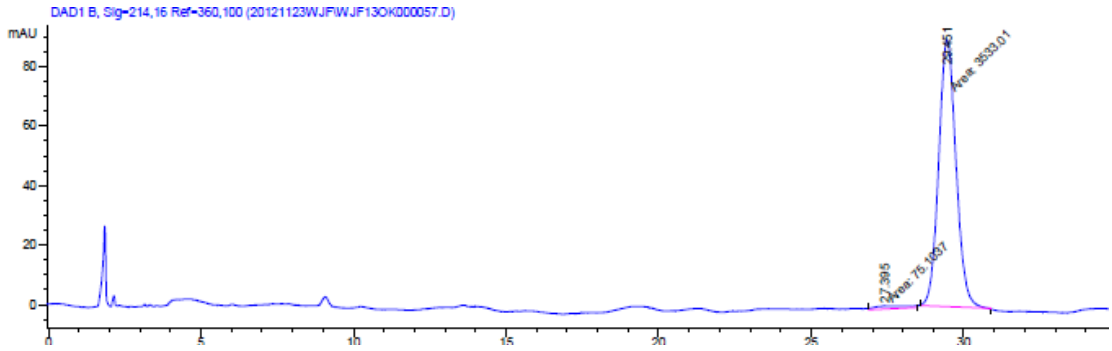
Signal 1: DAD1 B, Sig=214,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.644	MM	0.1616	1.04076e4	1073.48352	97.0753
2	33.727	MM	0.4029	313.56223	12.96986	2.9247



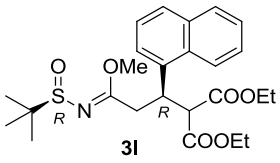
3k 91% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (t, J = 5.4 Hz, 3H), 0.97 (s, 9H), 1.27 (t, J = 5.4 Hz, 3H), 2.35 (s, 3H), 2.90 (dd, J = 3.3 Hz, 10.5 Hz, 1H), 3.37-3.43 (m, 1H), 3.59 (s, 3H), 3.69 (d, J = 8.4 Hz, 1H), 3.80-3.86 (m, 2H), 4.19-4.28 (m, 3H), 7.03 (d, J = 3.0 Hz, 2H), 7.10-7.13 (m, 1H), 7.21 (d, J = 5.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.5, 14.0, 19.4, 21.6, 29.6, 36.5, 53.7, 55.5, 61.2, 61.8, 126.1, 127.0, 130.4, 136.8, 137.2, 167.3, 167.9, 173.9; IR (KBr): v = 2981, 2947, 1751, 1734, 1614, 1460, 1367, 1253, 1157, 1078, 764 cm^{-1}; HRMS (ESI) for $C_{22}H_{33}NO_6S$ $[M+Na]^+$: calcd 462.1926, found 462.1946.

Analytical HPLC: Agilent 1200 series, Eclipse XDB-C_{18} Column (4.6×150 mm, 5 micron particle size), mobile phase H_2O/CH_3OH (40:60); Flow = 0.8 mL/min; Detected by UV at 214 nm; Retention time: 27.40 min, 29.45 min (maj).



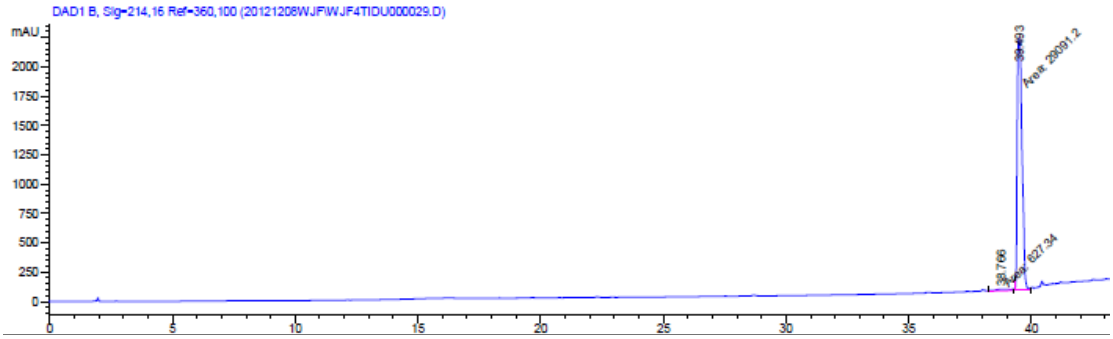
Signal 1: DAD1 B, Sig=214,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.395	MM	1.0837	75.10366	1.15502	2.0815
2	29.451	MM	0.6580	3533.00610	89.48875	97.9185



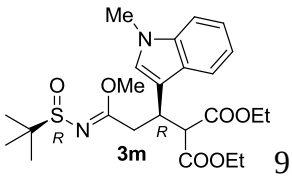
3l 88% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.66 (t, J = 7.2 Hz, 3H), 0.87 (s, 9H), 1.30 (t, J = 7.2 Hz, 3H), 3.07 (dd, J = 4.5 Hz, 14.4 Hz, 1H), 3.37 (s, 3H), 3.53-3.61 (m, 1H), 3.65-3.72 (m, 2H), 3.90 (d, J = 10.8 Hz, 1H), 4.23-4.30 (m, 2H), 4.91-4.99 (m, 1H), 7.40-7.55 (m, 4H), 7.70 (d, J = 7.8 Hz, 1H), 7.78 (d, J = 8.7 Hz, 1H), 8.27 (d, J = 8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.3, 13.1, 20.5, 34.6, 36.1, 52.7, 54.5, 57.0, 60.3, 60.9, 122.4, 123.9, 124.2, 124.6, 125.0, 126.9, 127.5, 130.8, 132.8, 134.8, 166.2, 167.0, 172.8; IR (KBr): ν = 2962, 2918, 1456, 1377, 1259, 1090, 1018, 798 cm^{-1}; HRMS (ESI) for $C_{25}H_{33}NO_6S$ $[M+H]^+$: calcd 476.2107, found 476.2110.

Analytical HPLC: Agilent 1200 series, Elipse XDB-C_{18} Column (4.6×150 mm, 5 micron particle size), mobile phase H_2O/CH_3OH (the gradient of CH_3OH is from 5% to 90% during 0-40 min); Flow = 0.8 mL/min; Detected by UV at 214 nm; Retention time: 38.77 min, 39.49 min (maj).



Signal 1: DAD1 B, Sig=214,16 Ref=360,100

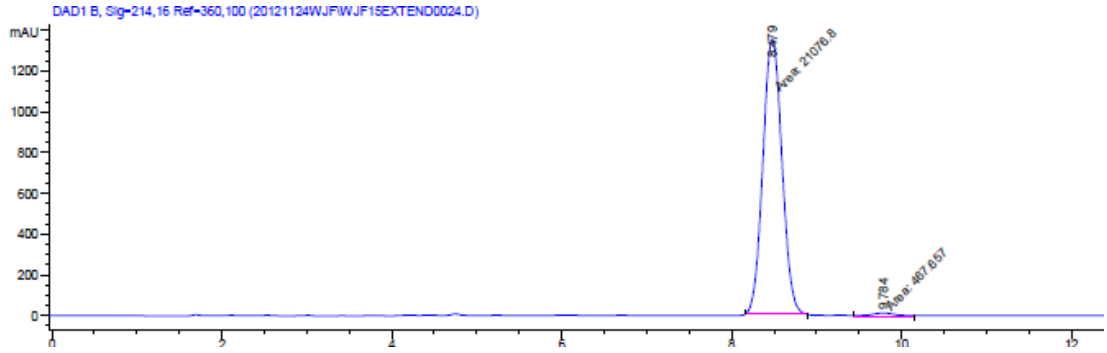
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.766	MM	0.7249	627.34045	14.42304	2.1109
2	39.493	MM	0.2271	2.90912e4	2135.00610	97.8891



3m 91% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.84 (m, 12H), 1.26 (t, J = 5.4 Hz, 3H), 2.94 (dd, J = 3.0 Hz, 10.2 Hz, 1H), 3.51-3.57 (m, 5H), 3.69 (s, 3H), 3.80-3.88 (m, 3H), 4.17-4.31 (m, 3H), 6.98 (s, 1H), 7.05-7.20 (m, 3H), 7.61 (d, J = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.5, 14.0, 21.4, 32.7, 33.9, 36.8, 53.9,

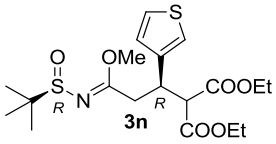
55.3, 57.4, 61.2, 61.6, 109.0, 112.2, 119.0, 121.5, 127.0, 127.2, 136.6, 167.6, 168.8, 174.6; IR (KBr): ν = 2981, 2921, 1732, 1610, 1473, 1282, 1241, 1068, 1027, 742 cm^{-1}; HRMS (ESI) for $C_{24}H_{34}N_2O_6S$ $[M+H]^+$: calcd 479.2216, found 479.2202.

Analytical HPLC: Agilent 1200 series, Extend-C_{18} Column (4.6×150 mm, 5 micron particle size), mobile phase H_2O/CH_3OH (40:60); Flow = 0.8 mL/min; Detected by UV at 214 nm; Retention time: 8.48 min (maj), 9.78 min.



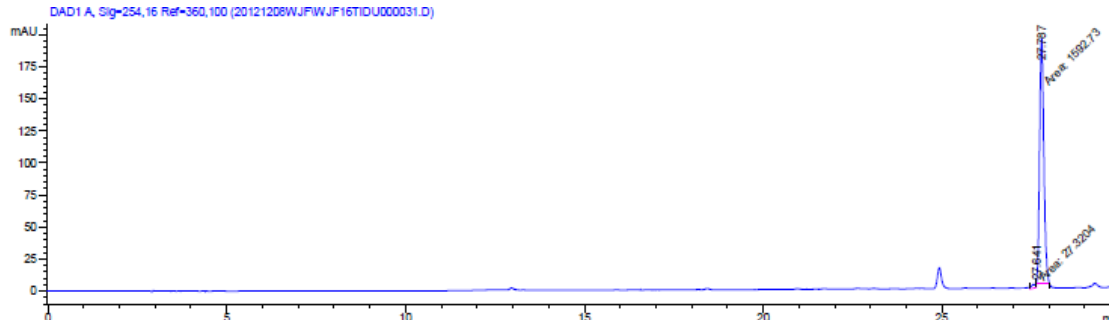
Signal 1: DAD1 B, Sig=214,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.479	MM	0.2605	2.10768e4	1348.27454	97.8293
2	9.784	MM	0.4078	467.65677	19.11308	2.1707



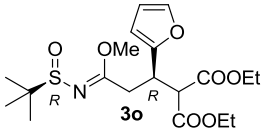
89% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.00 (t, J = 5.4 Hz, 3H), 1.04 (s, 9H), 1.26 (t, J = 5.4 Hz, 3H), 2.88 (dd, J = 3.3 Hz, 10.8 Hz, 1H), 3.33-3.39 (m, 1H), 3.62-3.65 (m, 4H), 3.91-3.97 (m, 2H), 4.05-4.12 (m, 1H), 4.17-4.23 (m, 2H), 6.96-6.97 (m, 1H), 7.05-7.06 (m, 1H), 7.18-7.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 14.0, 21.7, 36.6, 37.9, 54.0, 55.7, 57.4, 61.4, 61.8, 122.6, 125.6, 127.0, 139.5, 167.3, 167.6, 173.5; IR (KBr): ν = 3084, 2979, 2924, 1739, 1599, 1369, 1290, 1157, 1072, 1032 cm^{-1}; HRMS (ESI) for $C_{19}H_{29}NO_6S_2$ $[M+H]^+$: calcd 432.1515, found 432.1516.

Analytical HPLC: Agilent 1200 series, Elipse XDB-C_{18} Column (4.6×150 mm, 5 micron particle size), mobile phase H_2O/CH_3OH (40:60); Flow = 0.8 mL/min; Detected by UV at 214 nm; Retention time: 27.64 min, 27.79 min (maj).



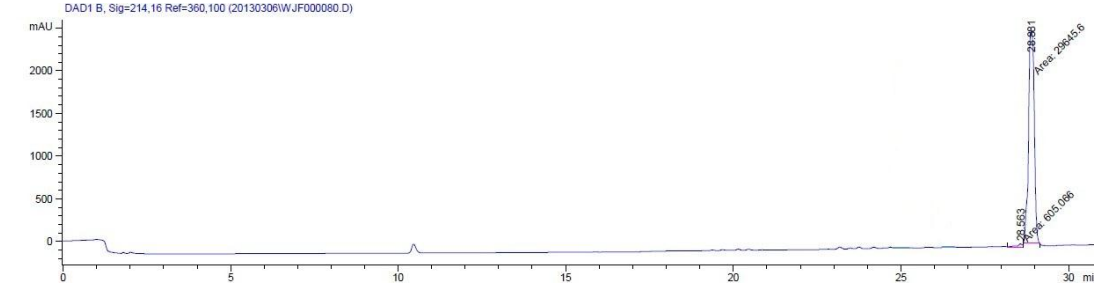
Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.641	MM	0.1392	27.32037	3.27062	1.6864
2	27.787	MM	0.1386	1592.73035	191.57603	98.3136



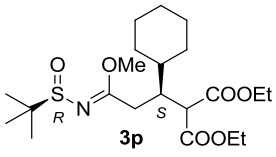
3o 88% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.08-1.10 (m, 12H), 1.26 (t, J = 5.4 Hz, 3H), 2.89 (dd, J = 3.3 Hz, 10.8 Hz, 1H), 3.37-3.43 (m, 1H), 3.67 (s, 3H), 3.74 (d, J = 7.5 Hz, 1H), 3.99-4.10 (m, 3H), 4.16-4.24 (m, 2H), 6.07-6.08 (m, 1H), 6.20-6.21 (m, 1H), 7.27-7.28 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 14.0, 21.7, 34.7, 36.0, 54.1, 55.5, 55.6, 61.5, 61.8, 107.4, 110.1, 141.9, 152.2, 167.2, 167.4, 173.5; IR (KBr): ν = 2981, 1734, 1612, 1442, 1367, 1288, 1155, 1078, 1031, 739 cm^{-1}; HRMS (ESI) for $C_{19}H_{29}NO_7S$ $[M+Na]^+$: calcd 438.1562, found 438.1578.

Analytical HPLC: Agilent 1200 series, Elipse XDB-C_{18} Column (4.6×150 mm, 5 micron particle size), mobile phase H_2O/CH_3OH (the gradient of CH_3OH is from 5% to 90% during 0-40 min); Flow = 0.8 mL/min; Detected by UV at 214 nm; Retention time: 28.56 min, 28.88 min (maj).



Signal 1: DAD1 B, Sig=214,16 Ref=360,100

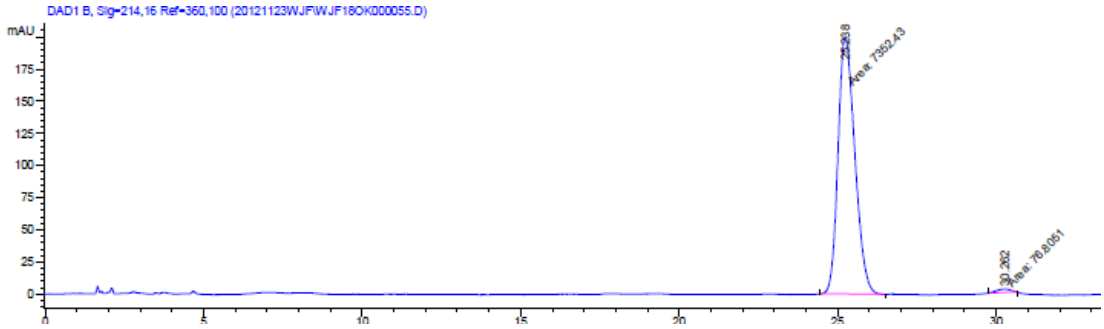
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.563	MM	0.2366	605.06635	42.62391	2.0002
2	28.881	MM	0.1989	2.96456e4	2484.74219	97.9998



3p

93% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.00-1.10 (m, 3H), 1.19 (s, 9H), 1.23-1.27 (m, 6H), 1.32-1.39 (m, 1H), 1.60-1.80 (m, 7H), 2.68-2.75 (m, 2H), 2.95-3.01 (m, 1H), 3.51 (d, J = 5.4 Hz, 1H), 3.75 (s, 3H), 4.10-4.22 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.7, 14.8, 22.6, 27.0, 27.4, 29.5, 41.1, 41.3, 54.5, 54.9, 56.7, 62.1, 62.2, 169.4, 169.7, 176.0; IR (KBr): ν = 2962, 2929, 1753, 1732, 1606, 1448, 1259, 1079, 1020, 796 cm^{-1}; HRMS (ESI) for $C_{21}H_{37}NO_6S$ $[M+Na]^+$: calcd 454.2239, found 454.2222.

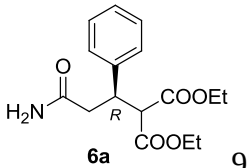
Analytical HPLC: Agilent 1200 series, Extend-C_{18} Column (4.6×150 mm, 5 micron particle size), mobile phase H_2O/CH_3OH (40:60); Flow = 0.8 mL/min; Detected by UV at 214 nm; Retention time: 25.24 min (maj), 30.26 min.



Signal 1: DAD1 B, Sig=214,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.238	MM	0.6136	7352.43213	199.71094	98.9662
2	30.262	MM	0.5042	76.80513	2.53890	1.0338

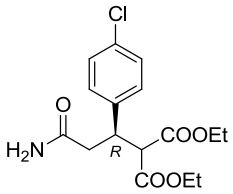
2.9 Characterization data of 6a, 6d, 6e and 6i



6a

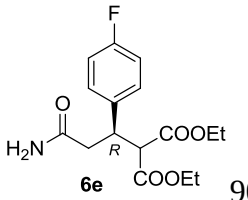
92% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.94 (t, J = 5.4 Hz,

3H), 1.20 (t, *J* = 5.4 Hz, 3H), 2.56 (dd, *J* = 7.2 Hz, 10.8 Hz, 1H), 2.67 (dd, *J* = 3.3 Hz, 10.8 Hz, 1H), 3.73 (d, *J* = 7.5 Hz, 1H), 3.81-3.3.90 (m, 3H), 4.14 (dd, *J* = 5.4 Hz, 10.5 Hz, 2H), 5.79 (d, *J* = 10.5 Hz, 2H), 7.15-7.26 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 14.0, 39.9, 41.9, 57.3, 61.4, 61.7, 127.3, 128.2, 128.5, 140.0, 167.7, 168.3, 173.2; IR (KBr): ν = 3420, 3258, 2980, 1744, 1670, 1501, 1257, 1150, 1044, 810 cm^{-1}; HRMS (ESI) for $C_{16}H_{21}NO_5$ $[M+Na]^+$: calcd 330.1317, found 330.1342.



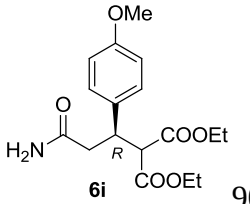
6d

88% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.01 (t, *J* = 5.4 Hz, 3H), 1.23 (t, *J* = 5.4 Hz, 3H), 2.55 (dd, *J* = 7.2 Hz, 10.8 Hz, 1H), 2.71 (dd, *J* = 3.3 Hz, 11.1 Hz, 1H), 3.73 (d, *J* = 7.5 Hz, 1H), 3.83-3.89 (m, 1H), 3.94 (dd, *J* = 5.4 Hz, 10.5 Hz, 2H), 4.14-4.20 (m, 2H), 5.69 (s, 1H), 5.76 (s, 1H), 5.79 (dd, *J* = 1.5 Hz, 4.8 Hz, 2H), 7.15-7.26 (dd, *J* = 1.8 Hz, 5.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 13.9, 39.7, 41.1, 56.9, 61.4, 61.7, 128.5, 129.5, 133.0, 138.5, 167.4, 168.0, 172.6; IR (KBr): ν = 3448, 3315, 2985, 1741, 1662, 1490, 1315, 1254, 1159, 1026, 835 cm^{-1}; HRMS (ESI) for $C_{16}H_{20}ClNO_5$ $[M+Na]^+$: calcd 364.0928, found 364.0922.



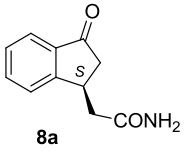
6e

90% yield, oil; H NMR (300 MHz, $CDCl_3$): δ 1.01 (t, *J* = 5.4 Hz, 3H), 1.24 (t, *J* = 5.1 Hz, 3H), 2.57 (dd, *J* = 7.5 Hz, 11.1 Hz, 1H), 2.71 (dd, *J* = 3.3 Hz, 11.1 Hz, 1H), 3.74 (d, *J* = 7.5 Hz, 1H), 3.85-3.97 (m, 3H), 4.16-4.22 (m, 2H), 5.90 (d, *J* = 9.9 Hz, 2H), 6.95 (t, *J* = 6.6 Hz, 2H), 7.21-7.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 13.9, 39.9, 41.1, 57.2, 61.4, 61.7, 115.2 (d, $^2J_{CF}$ = 17 Hz), 129.7 (d, $^3J_{CF}$ = 7 Hz), 135.6 (d, $^4J_{CF}$ = 3 Hz), 161.8 (d, $^1J_{CF}$ = 195 Hz), 167.5, 168.0, 172.9; IR (KBr): ν = 3446, 3278, 2989, 1747, 1660, 1510, 1301, 1255, 1160, 1024, 840 cm^{-1}; HRMS (ESI) for $C_{16}H_{20}FNO_5$ $[M+H]^+$: calcd 326.1404, found 326.1403.



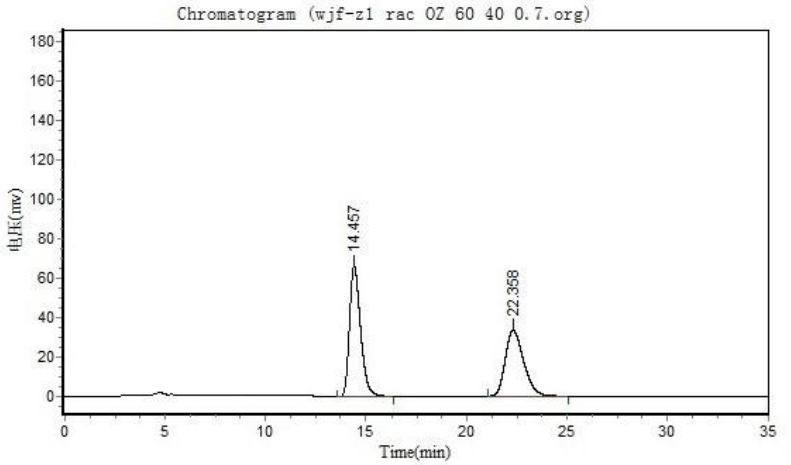
6i 90% yield, oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.01 (t, J = 5.4 Hz, 3H), 1.23 (t, J = 5.4 Hz, 3H), 2.55 (dd, J = 7.5 Hz, 10.8 Hz, 1H), 2.71 (dd, J = 3.3 Hz, 10.8 Hz, 1H), 3.69-3.84 (m, 5H), 3.93 (dd, J = 5.4 Hz, 10.8 Hz, 2H), 4.17 (dd, J = 5.4 Hz, 10.5 Hz, 2H), 5.58 (s, 1H), 5.62 (s, 1H), 6.76-6.80 (m, 2H), 7.15-7.26 (dd, J = 1.2 Hz, 4.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 13.9, 40.2, 41.1, 55.1, 57.4, 61.3, 61.6, 113.8, 129.1, 131.7, 158.6, 167.6, 168.2, 172.9; IR (KBr): ν = 3408, 3192, 2985, 1745, 1655, 1520, 1255, 1182, 1029 cm^{-1}; HRMS (ESI) for $C_{17}H_{23}NO_6$ $[M+Na]^+$: calcd 360.1423, found 360.1431.

2.10 Characterization data and HPLC of 3-subsituted indanone derivatives 8a, 8d, 8e and 8i



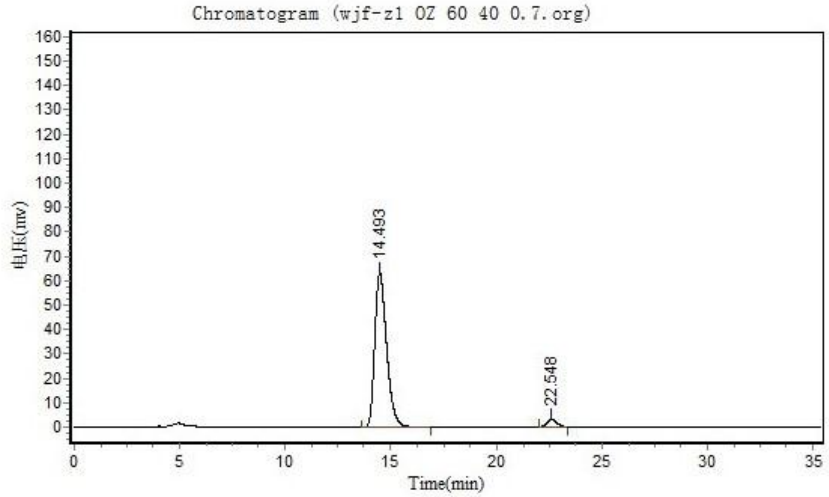
8a 75% yield, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.38-2.47 (m, 2H), 2.75 (dd, J = 4.5 Hz, 10.8 Hz, 1H), 3.01 (dd, J = 5.4 Hz, 14.4 Hz, 1H), 3.88-3.95 (m, 1H), 5.58 (s, 1H), 5.69 (s, 1H), 7.40 (t, J = 5.4 Hz, 1H), 7.54 (dd, J = 0.6 Hz, 6.0 Hz, 1H), 7.59-7.63 (m, 1H), 7.73 (d, J = 5.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 34.6, 42.0, 43.2, 123.7, 125.5, 128.0, 135.0, 136.7, 157.1, 173.1, 205.5; IR (KBr): ν = 3320, 2922, 2544, 2378, 1701, 1635, 1464, 1423, 1288, 756 cm^{-1}; HRMS (EI) for $C_{11}H_{11}NO_2$ $[M]^+$: calcd 189.0790, found 189.0788.

HPLC: Chiral OZ column (250 mm); detected at 214 nm; hexane/*i*-propanol = 60/40; flow = 0.7 mL/min; Retention time: 14.49 min (maj), 22.55 min.



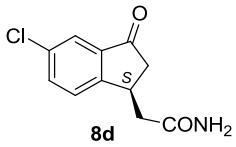
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.457	66221.453	2551007.750	50.7234
2		22.358	44874.676	2478248.500	49.2766
Total			111096.129	5029256.250	100.0000



Results

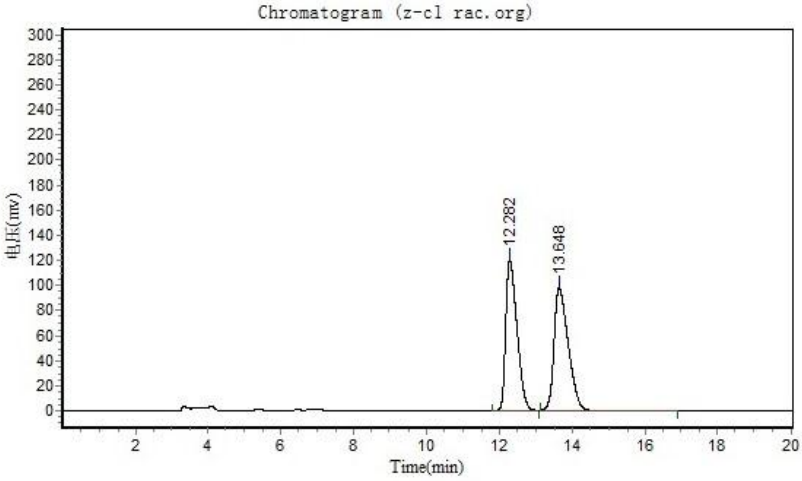
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.493	63188.426	2492024.250	97.0382
2		22.548	4823.975	76062.445	2.9618
Total			68012.400	2568086.695	100.0000



8d 77% yield, colorless oil; ^{1}H NMR (300 MHz, CD_3OD): δ 2.38-2.49 (m, 2H), 2.79 (dd, J = 4.2 Hz, 11.1 Hz, 1H), 2.94 (dd, J = 5.4 Hz, 14.4 Hz, 1H), 3.79-3.86 (m, 1H), 7.41-7.46 (m, 1H), 7.63-7.70 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD): δ 34.0, 39.9, 41.6, 121.9, 124.6, 126.7, 133.9, 135.3, 156.8, 174.3; IR (KBr): ν = 3323, 2921, 2459, 1700, 1630, 1460, 1421, 1289, 753 cm^{-1}; HRMS (EI) for

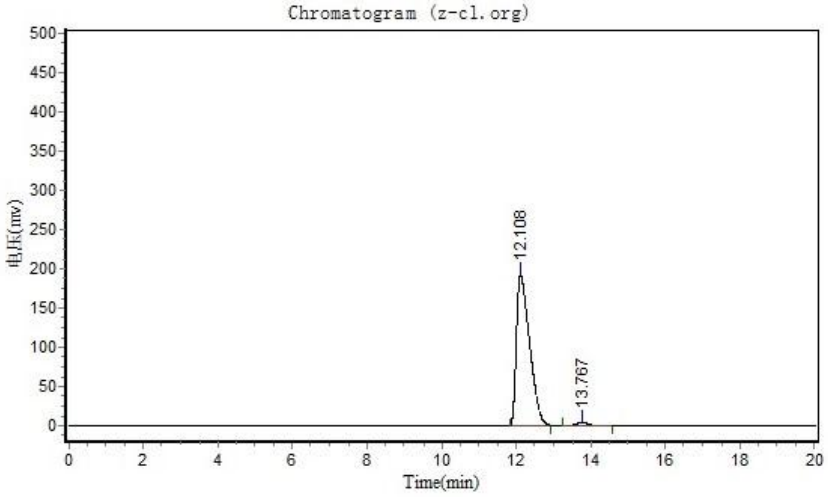
$C_{11}H_{10}ClNO_2$ $[M]^+$: calcd 223.0400, found 223.0398.

HPLC: Chiral OZ column (250 mm); detected at 214 nm; hexane/*i*-propanol = 60/40; flow = 0.7 mL/min; Retention time: 12.11 min (maj), 13.77 min.



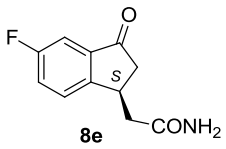
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.282	120269.242	2581285.000	49.2385
2		13.648	97777.430	2661126.250	50.7615
Total			218046.672	5242411.250	100.0000



Results

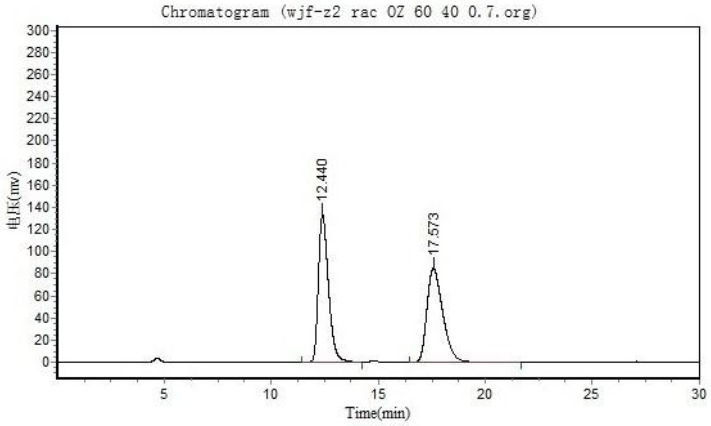
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.108	191682.031	4712815.000	97.7342
2		13.767	4549.515	109258.250	2.2658
Total			196231.546	4822073.250	100.0000



8e 85% yield, colorless oil; ^{1}H NMR (300 MHz, CD_3OD): δ 2.41-2.54 (m, 2H), 2.76 (dd, J = 4.5 Hz, 9.9 Hz, 1H), 2.98 (dd, J = 5.7 Hz, 14.4 Hz, 1H),

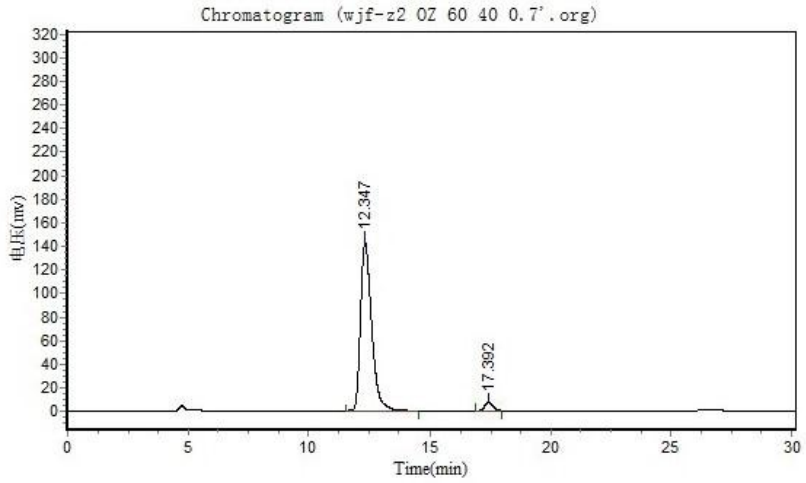
3.77-3.83 (m, 1H), 7.33 (dd, J = 2.1 Hz, 5.7 Hz, 1H), 7.40-7.45 (m, 1H), 7.73 (dd, J = 3.3 Hz, 6.3 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD): δ 34.5, 40.7, 43.2, 108.4 (d, $^2J_{CF}$ = 18 Hz), 122.2 (d, $^2J_{CF}$ = 19 Hz), 127.5 (d, $^3J_{CF}$ = 7 Hz), 138.34 (d, $^3J_{CF}$ = 6 Hz), 153.4, 162.6 (d, $^1J_{CF}$ = 196 Hz), 175.1, 205.3 (d, $^4J_{CF}$ = 2 Hz); IR (KBr): ν = 3321, 2923, 2542, 2370, 1703, 1638, 1452, 1420, 1288, 746 cm^{-1}; HRMS (EI) for $C_{11}H_{10}FNO_2$ $[M]^+$: calcd 207.0696, found 207.0696.

HPLC: Chiral OZ column (250 mm); detected at 214 nm; hexane/*i*-propanol = 60/40; flow = 0.7 mL/min; Retention time: 12.35 min (maj), 17.39 min.



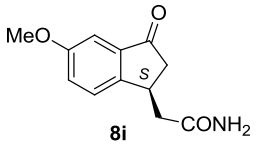
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.440	133515.203	4394888.000	49.8213
2		17.573	84465.469	4426413.500	50.1787
Total			217980.672	8821301.500	100.0000



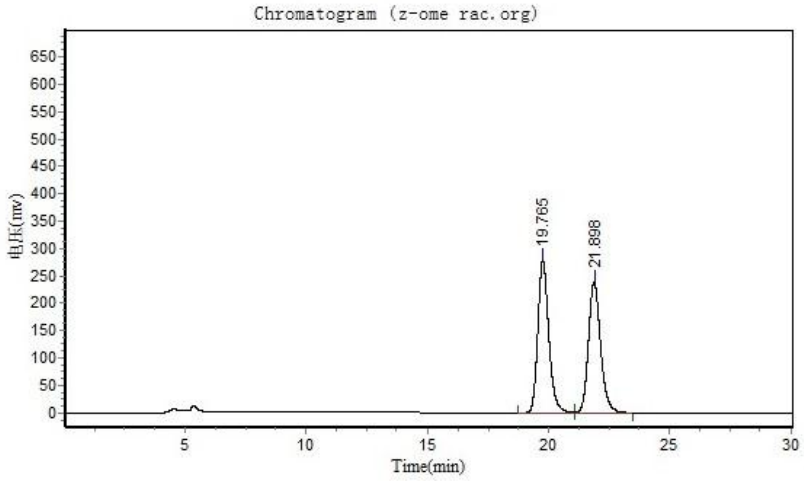
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.347	142075.953	4592370.000	97.1894
2		17.392	10289.347	132804.156	2.8106
Total			152365.300	4725174.156	100.0000



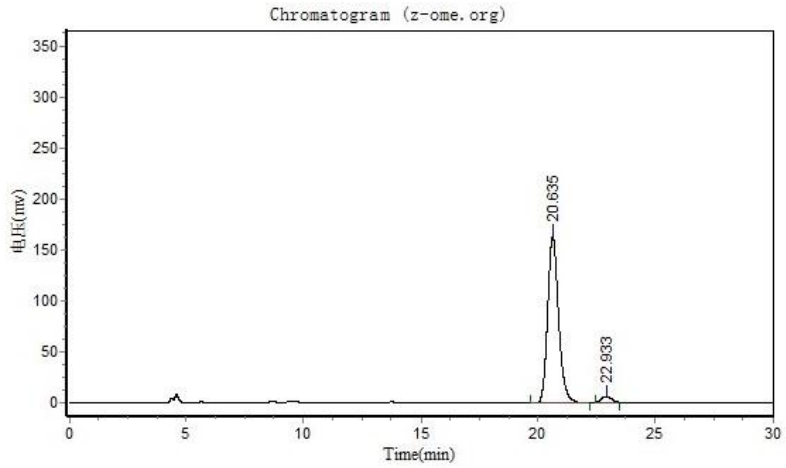
8i 82% yield, colorless oil; ^{1}H NMR (300 MHz, CD_3OD): δ 2.35-2.50 (m, 2H), 2.73 (dd, J = 4.2 Hz, 10.8 Hz, 1H), 2.95 (dd, J = 5.4 Hz, 14.4 Hz, 1H), 3.72-3.78 (m, 1H), 3.83 (s, 3H), 7.15 (d, J = 1.8 Hz, 1H), 7.26 (dd, J = 2.1 Hz, 6.3 Hz, 1H), 7.53 (d, J = 6.3 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD): δ 34.4, 41.1, 43.2, 54.7, 104.5, 123.6, 126.4, 137.6, 150.5, 160.0, 175.4; IR (KBr): ν = 3330, 2922, 2548, 2403, 1705, 1641, 1492, 1425, 1306, 1280, 1024, 850 cm^{-1}; HRMS (EI) for $C_{12}H_{13}NO_3$ $[M]^+$: calcd 219.0895, found 219.0889.

HPLC: Chiral OZ column (250 mm); detected at 214 nm; hexane/*i*-propanol = 60/40; flow = 0.7 mL/min; Retention time: 20.63 min (maj), 22.93 min.



Results

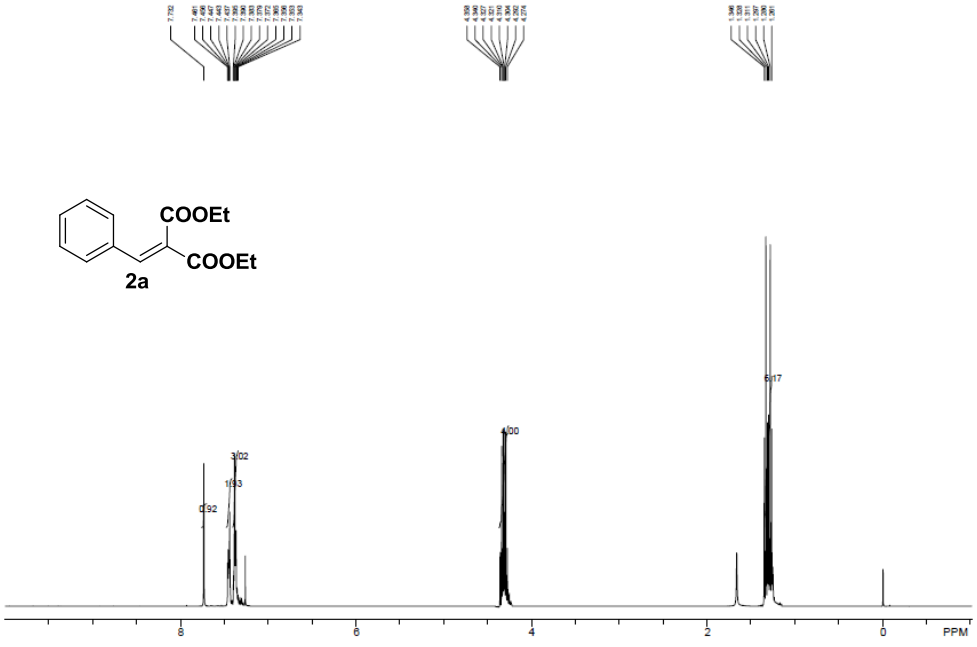
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.765	279572.594	8771245.000	51.1178
2		21.898	239405.281	8387649.500	48.8822
Total			518977.875	17158894.500	100.0000

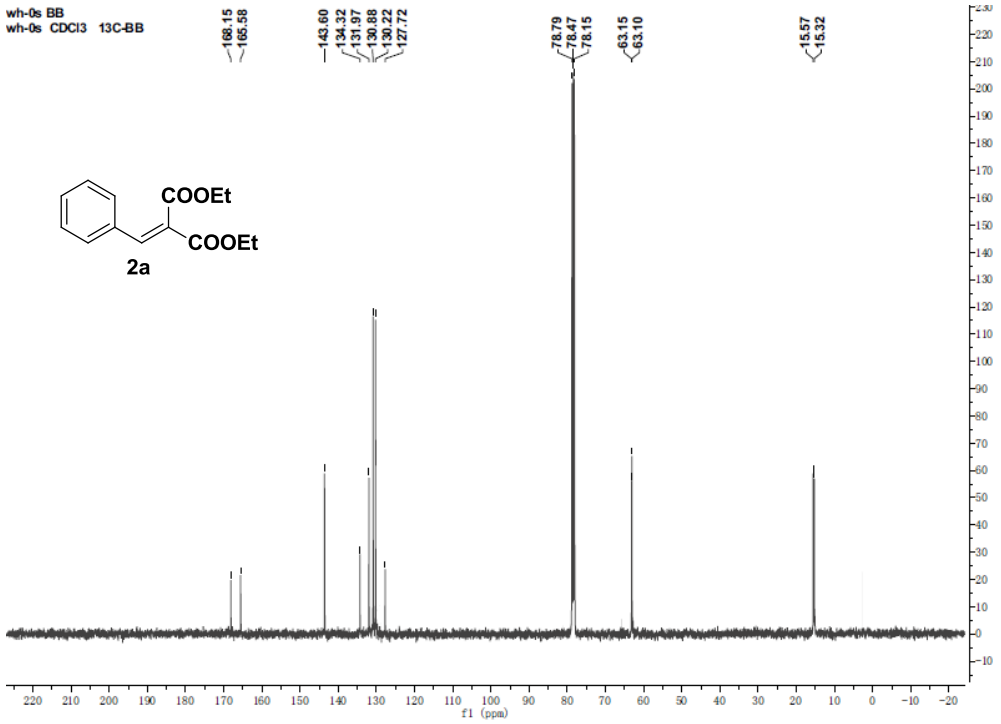


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.635	163748.797	5334541.500	96.9507
2		22.933	5498.404	167783.797	3.0493
Total			169247.201	5502325.297	100.0000

3. ^{1}H and ^{13}C NMR spectra for all compounds

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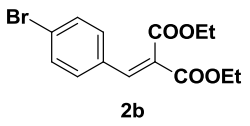
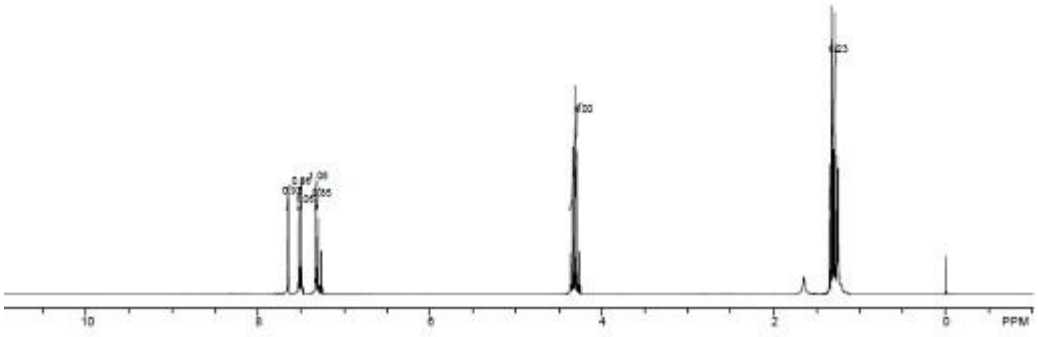
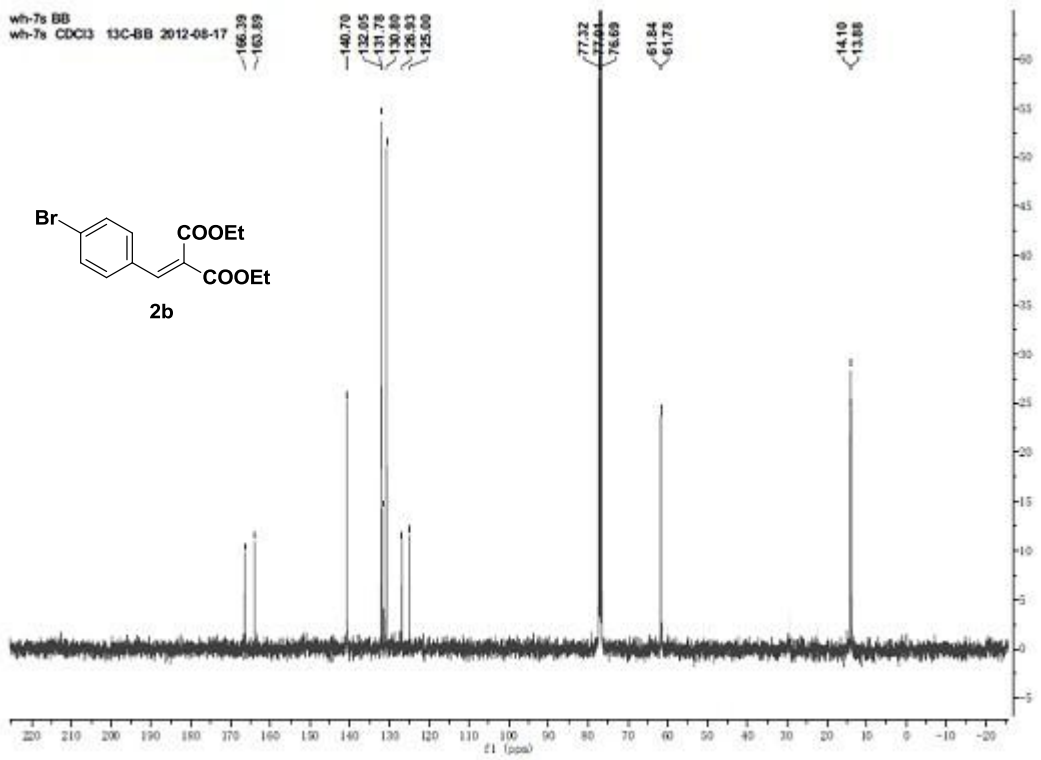
wh-0s CDCl3 13C-BB
168.15
165.58
143.60
134.32
131.97
130.88
130.22
127.72
78.79
78.47
78.15
63.15
63.10
15.57
15.32
COOEt
COOEt
2a
f1 (ppm)


Br
COOEt
COOEt
2b


PPM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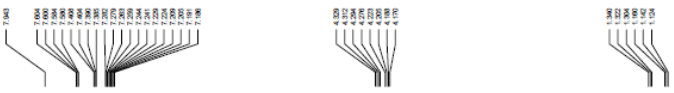
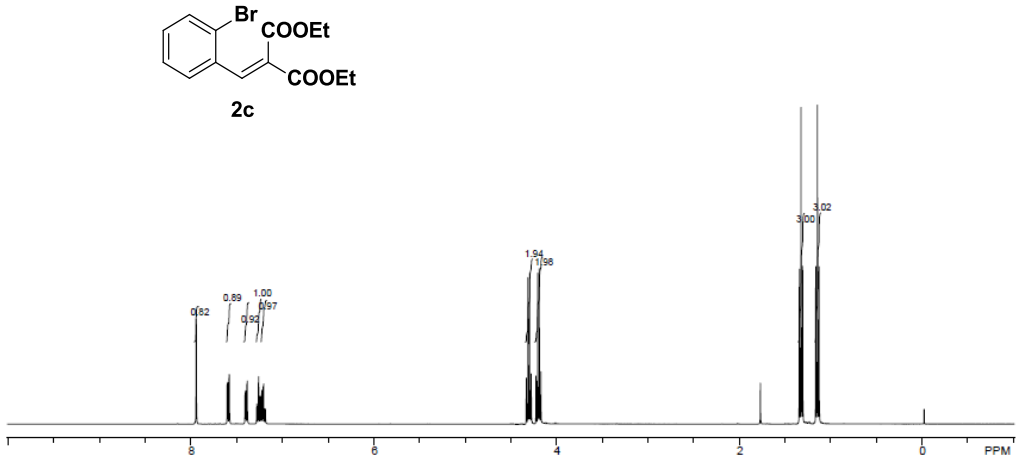
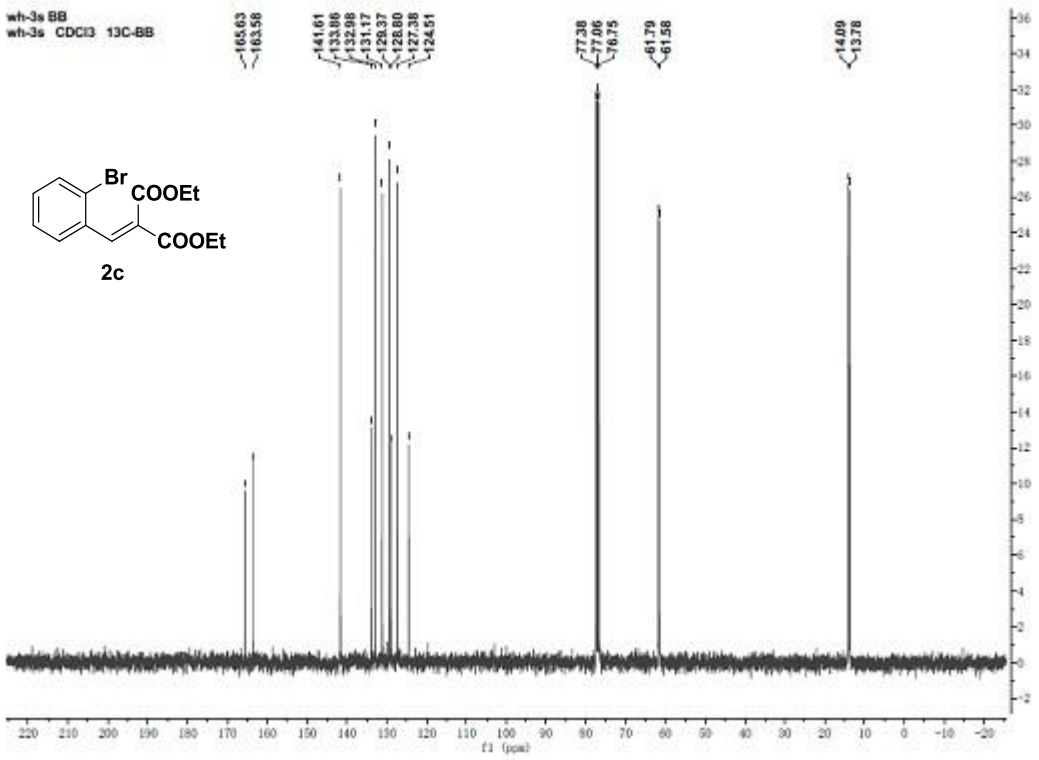
wh-7s CDCl3 13C-BB 2012-08-17
166.39
163.89
140.70
132.05
131.78
130.89
126.93
125.00
77.32
77.01
76.69
61.84
61.78
14.10
13.88
Br
COOEt
COOEt
2b
f1 (ppm)




Br
COOEt
COOEt
2c
0.82
0.89
0.92
1.00
0.97
1.94
1.98
3.00
3.02
PPM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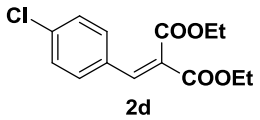
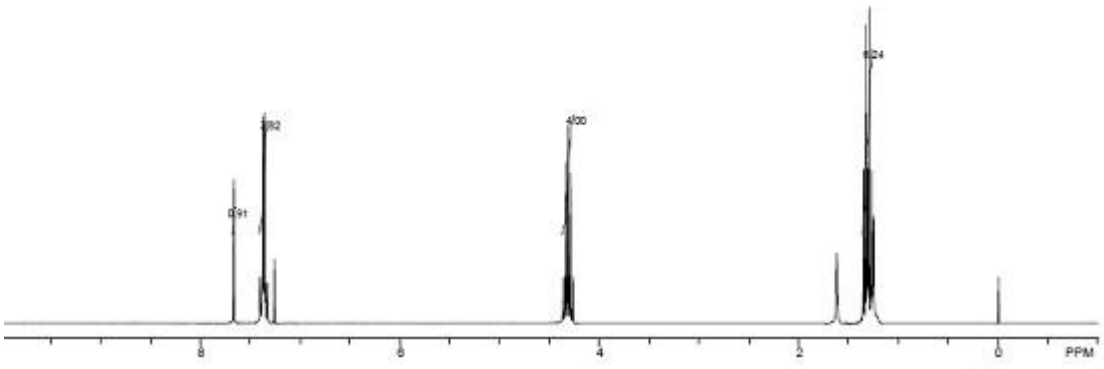
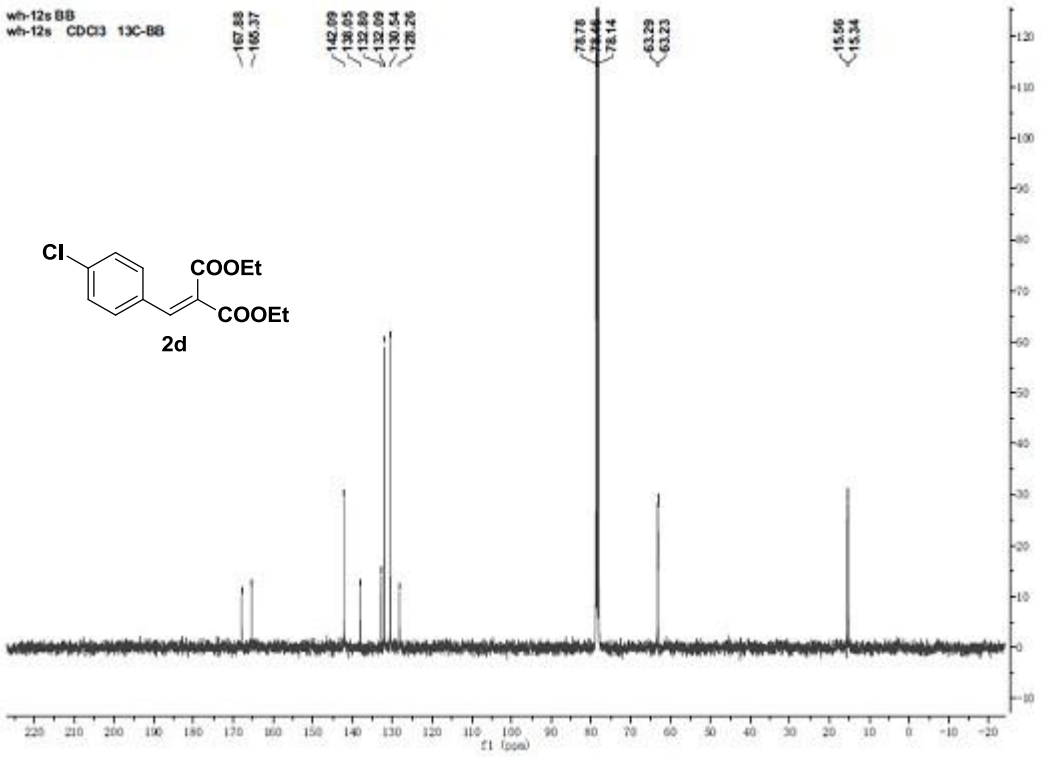
wh-3s CDCl3 13C-BB
165.63
163.58
141.61
133.86
132.98
131.17
129.37
128.80
127.38
124.51
77.38
77.06
76.75
61.79
61.58
14.09
13.78
Br
COOEt
COOEt
2c
f1 (ppm)


Cl
COOEt
COOEt
2d


1.24
4.00
2.02
0.91
PPM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wh-12s CDCl3 13C-BB
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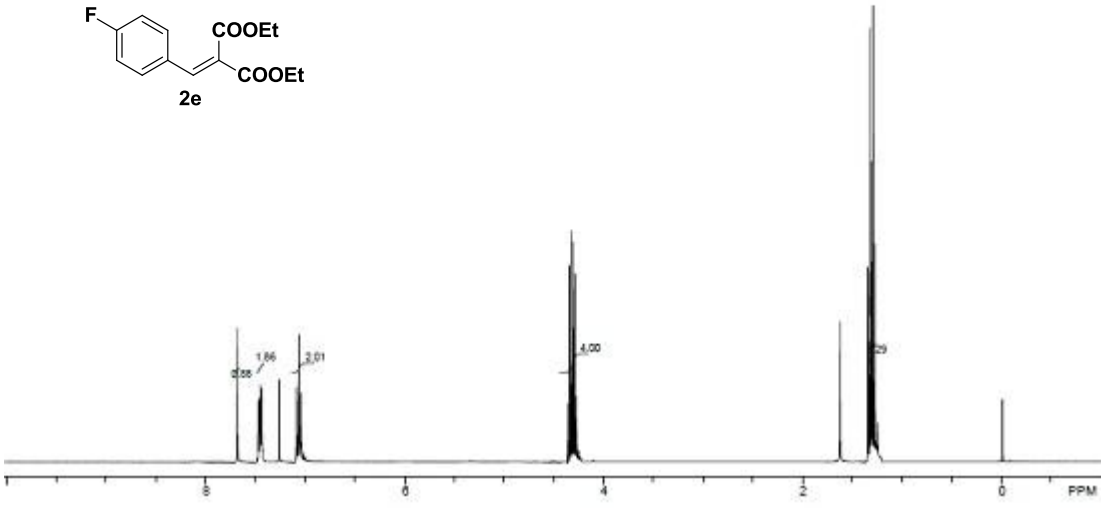
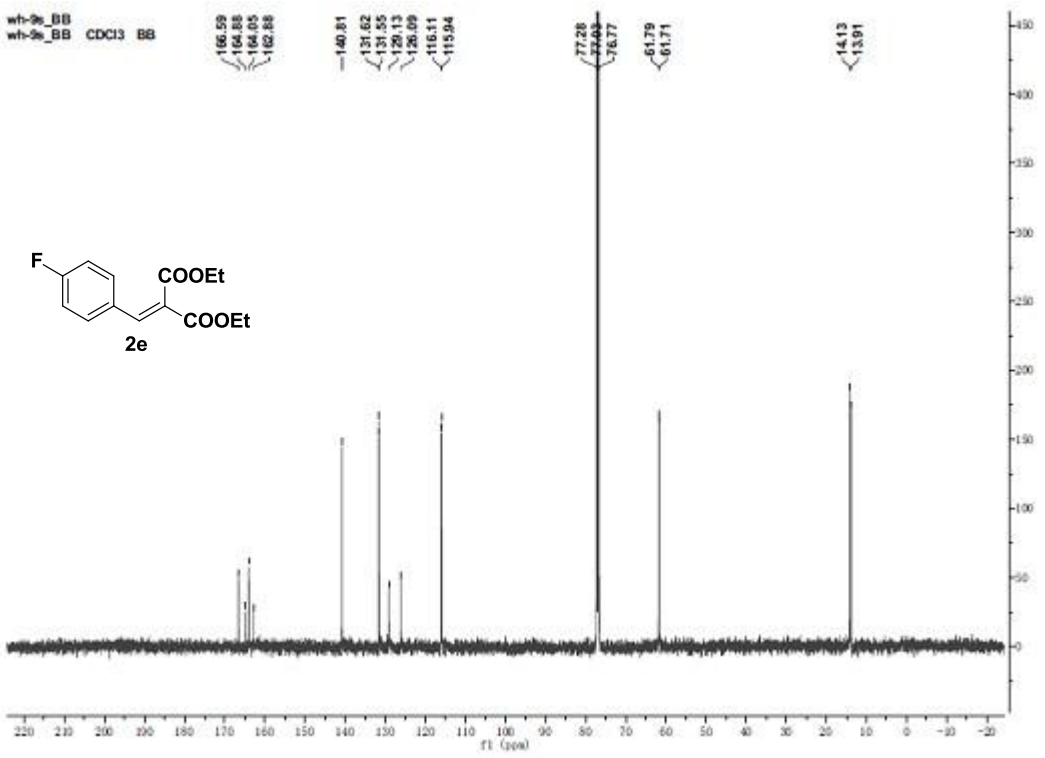
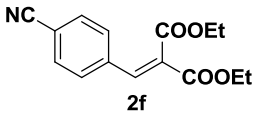
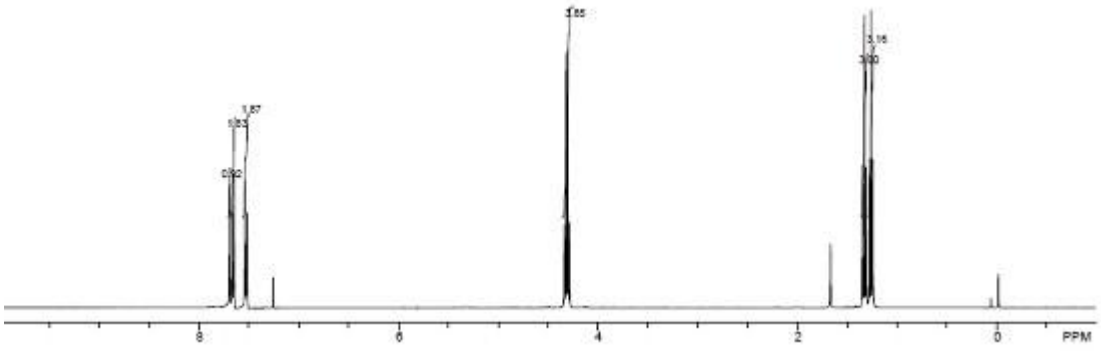
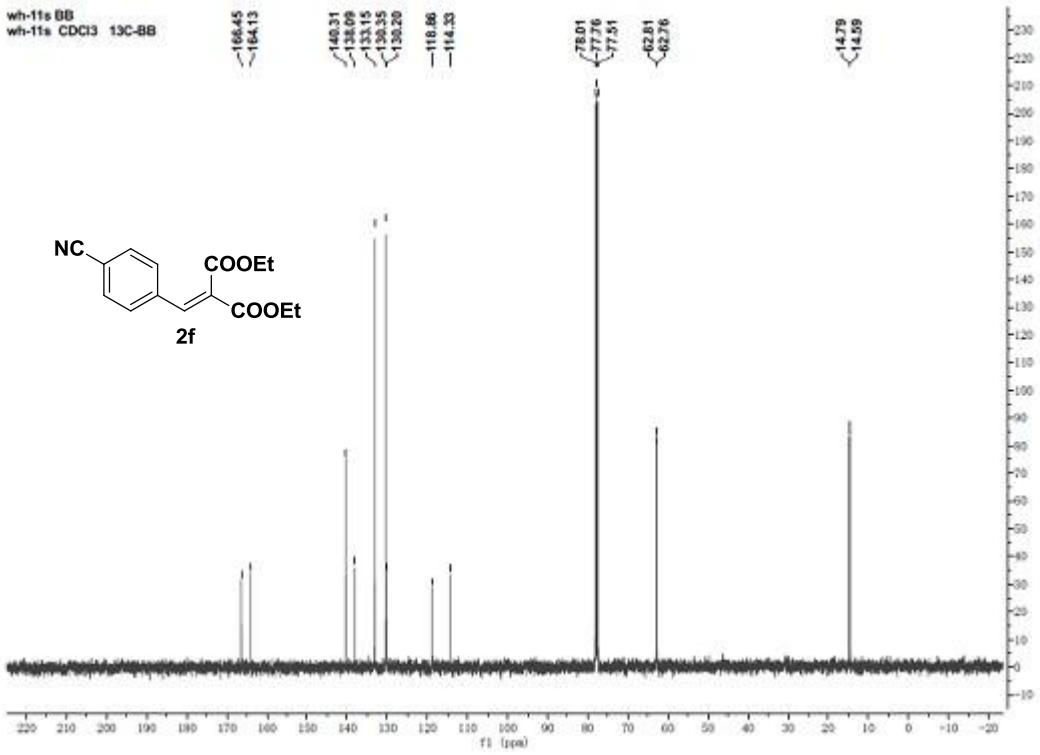
165.37
142.09
138.05
132.80
132.09
130.54
128.26
78.78
78.46
78.14
63.29
63.23
15.56
15.34
Cl
COOEt
COOEt
2d
f1 (ppm)

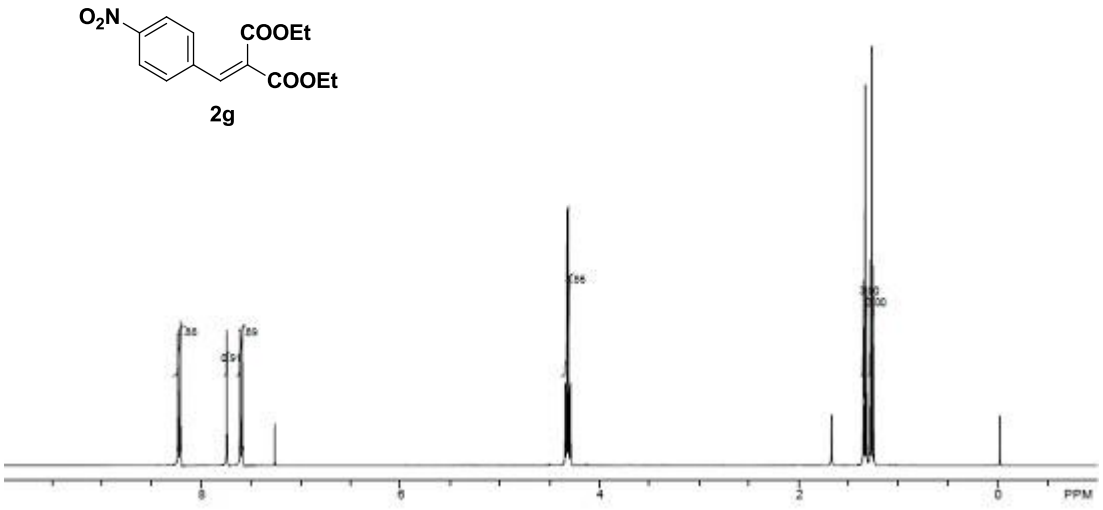

F
COOEt
COOEt
2e
0.88
1.86
2.01
4.00
2.29
PPM

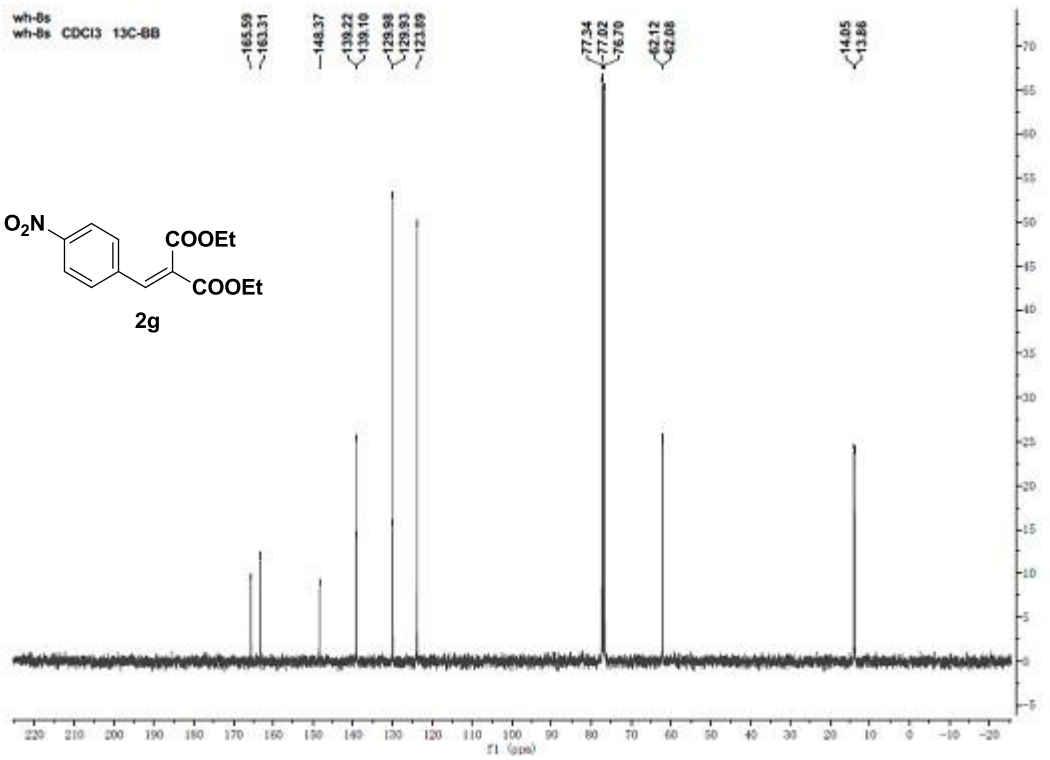

wh-9s_BB
wh-9s_BB CDCl3 BB
166.59
164.88
164.05
162.88
140.81
131.62
131.55
129.13
126.09
116.11
115.94
77.28
77.03
76.77
61.79
61.71
14.13
13.91
F
COOEt
COOEt
2e
f1 (ppm)


NC
COOEt
COOEt
2f


3.65
3.15
3.00
1.87
1.83
0.92
8
6
4
2
0
PPM


wh-11s BB
wh-11s CDCl3 13C-BB
166.45
164.13
140.31
138.09
133.15
130.35
130.20
118.86
114.33
78.01
77.76
77.51
62.81
62.76
14.79
14.59
NC
COOEt
COOEt
2f
f1 (ppm)


O2N
COOEt
COOEt
2g
PPM


wh-8s
wh-8s CDCl3 13C-BB
165.59
163.31
148.37
139.22
139.10
129.98
129.93
123.89
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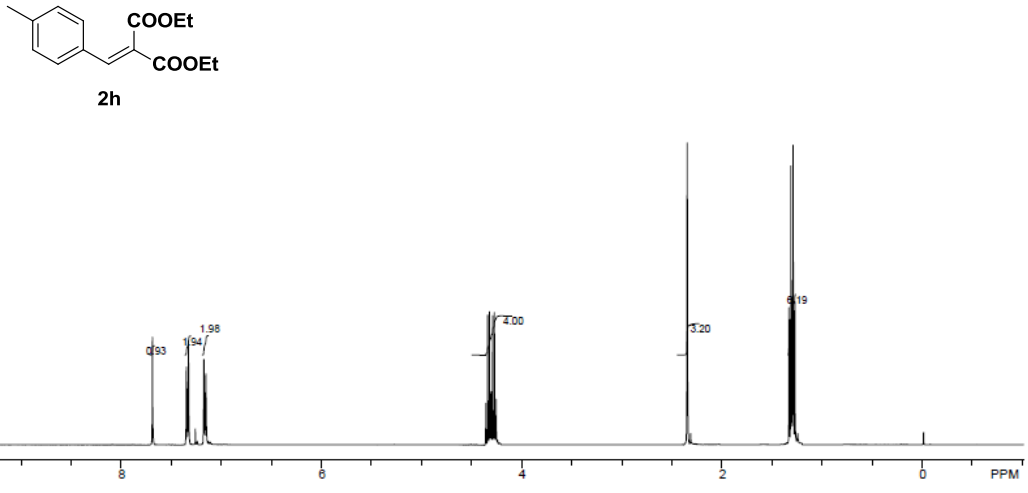
77.02
76.70
62.12
42.08
14.05
13.86
O2N
COOEt
COOEt
2g


COOEt
COOEt
2h
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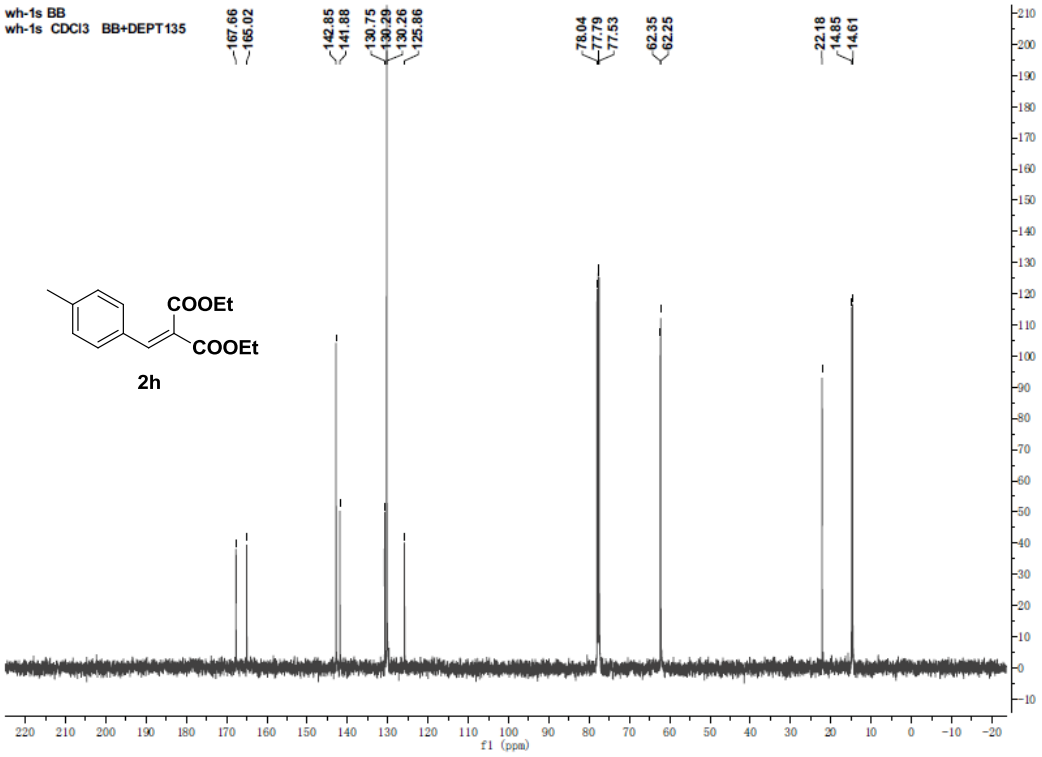
1.94
1.98
4.00
3.20
6.19
PPM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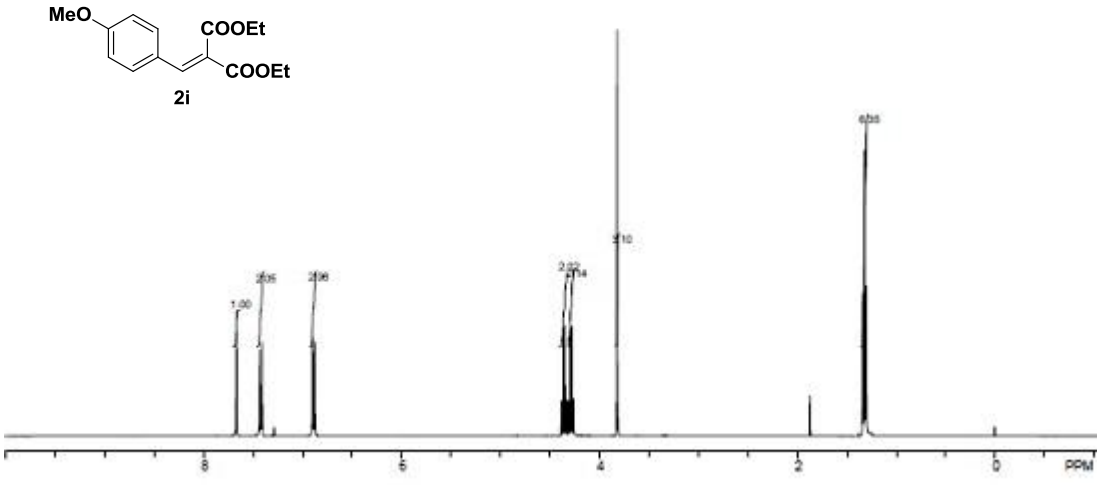
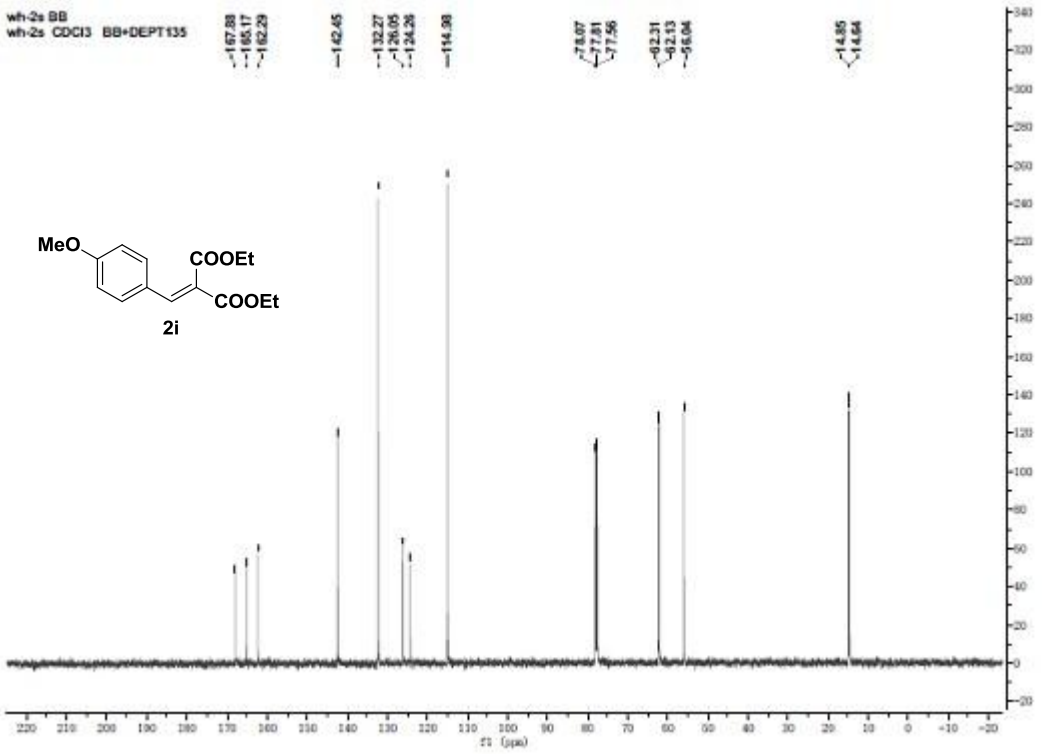
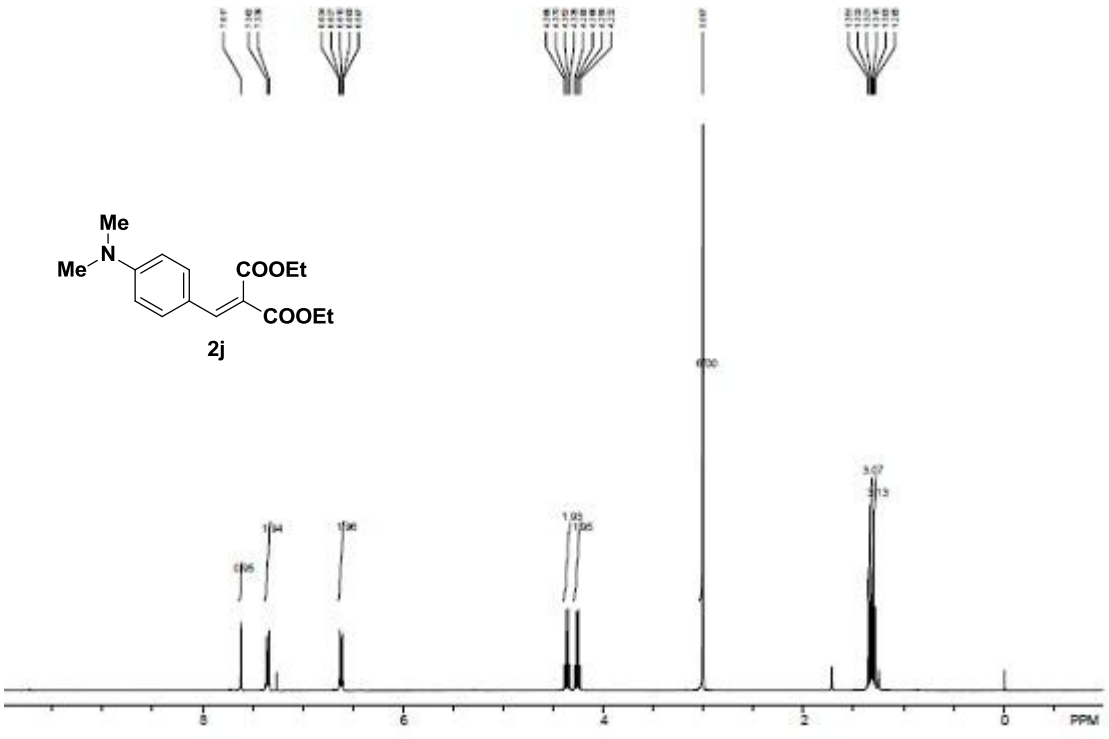
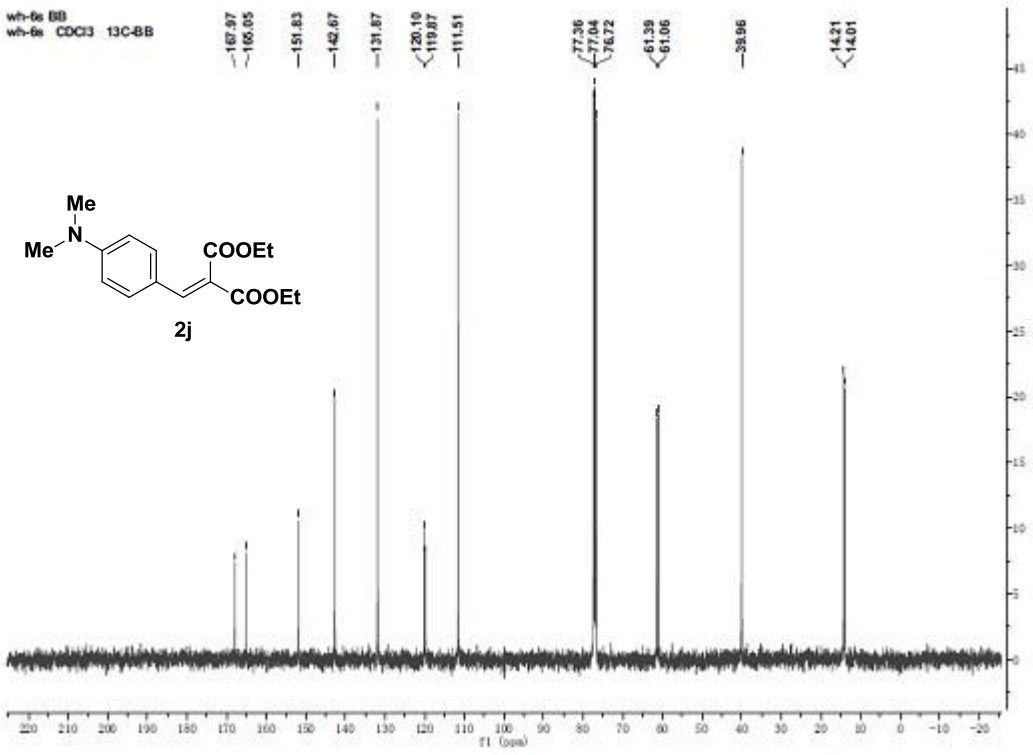
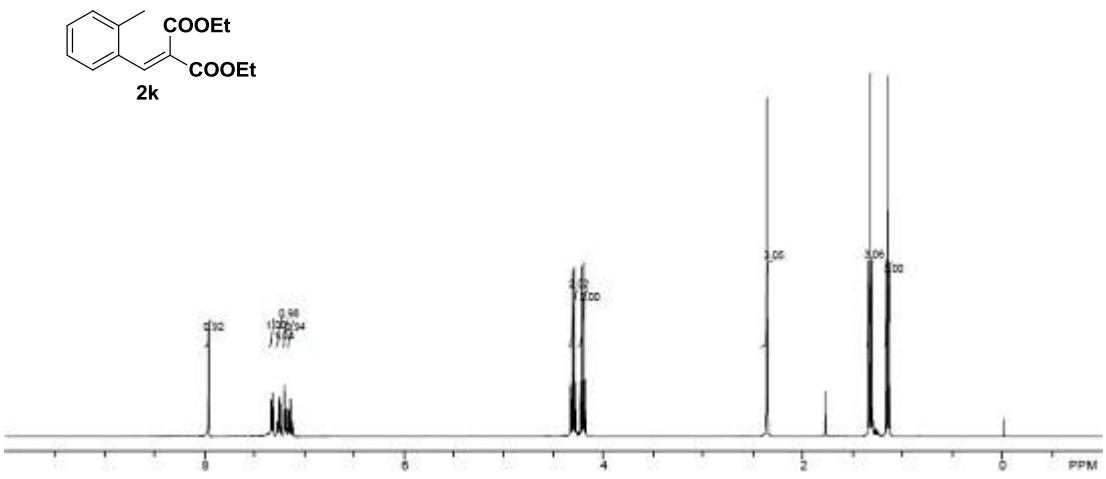
wh-1s CDCl3 BB+DEPT135
167.66
165.02
142.85
141.88
130.75
130.29
130.26
125.86
78.04
77.79
77.53
62.35
62.25
22.18
14.85
14.61
COOEt
COOEt
2h
f1 (ppm)

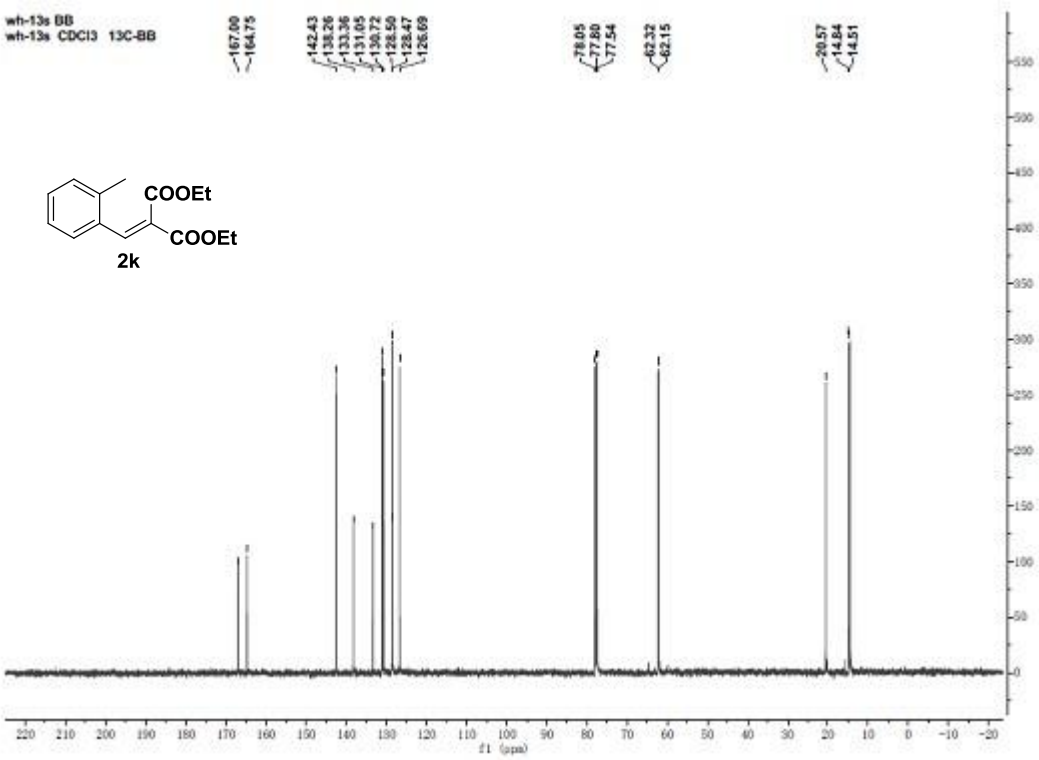

MeO
COOEt
COOEt
2i
ppm

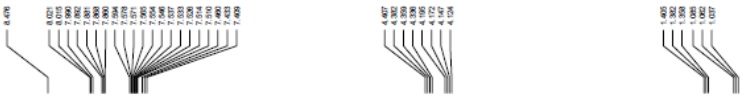

wh-2s BB
wh-2s CDCl3 BB+DEPT135
MeO
COOEt
COOEt
2i

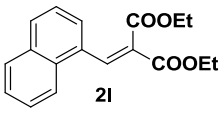

Me
N
Me
COOEt
COOEt
2j
PPM

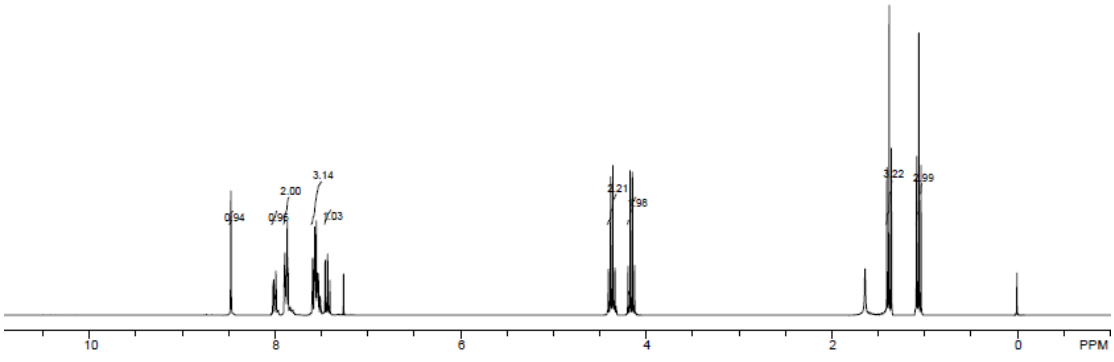

wh-6s BB
wh-6s CDCl3 13C-BB
167.97
165.05
151.83
142.67
131.87
120.10
119.87
111.51
77.36
77.04
76.72
61.39
61.06
38.96
14.21
14.01
Me
N
Me
COOEt
COOEt
2j

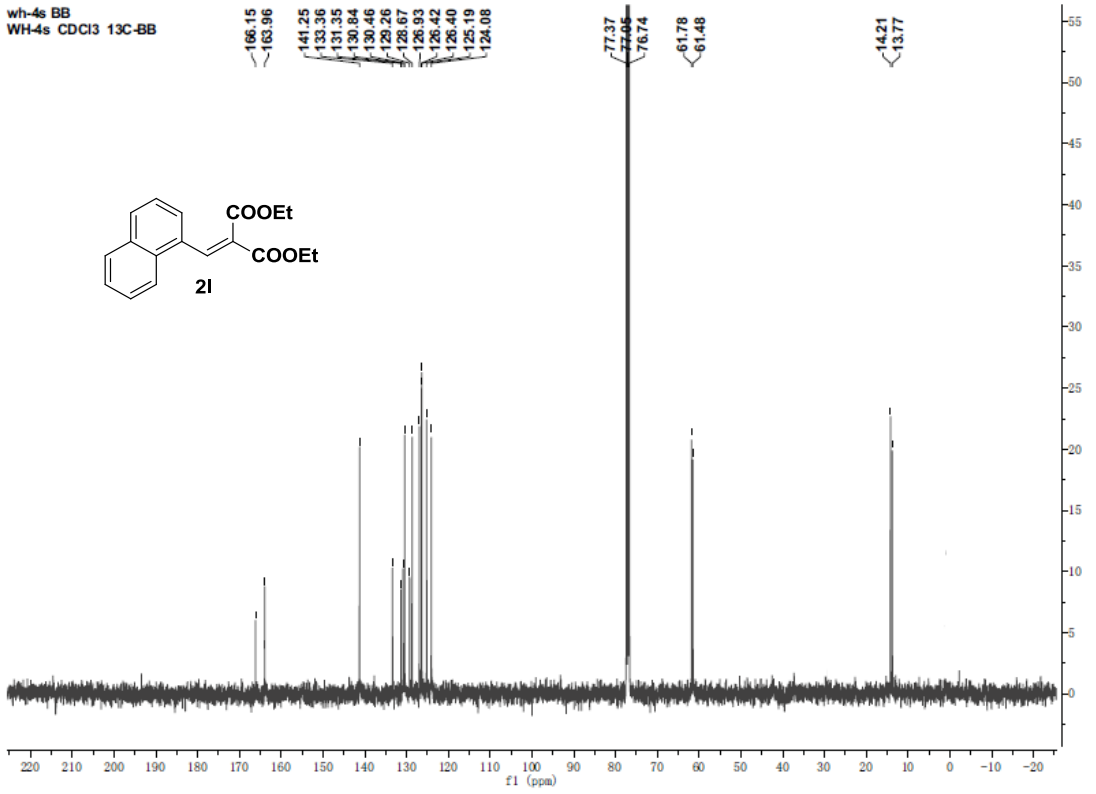

COOEt
COOEt
2k
PPM

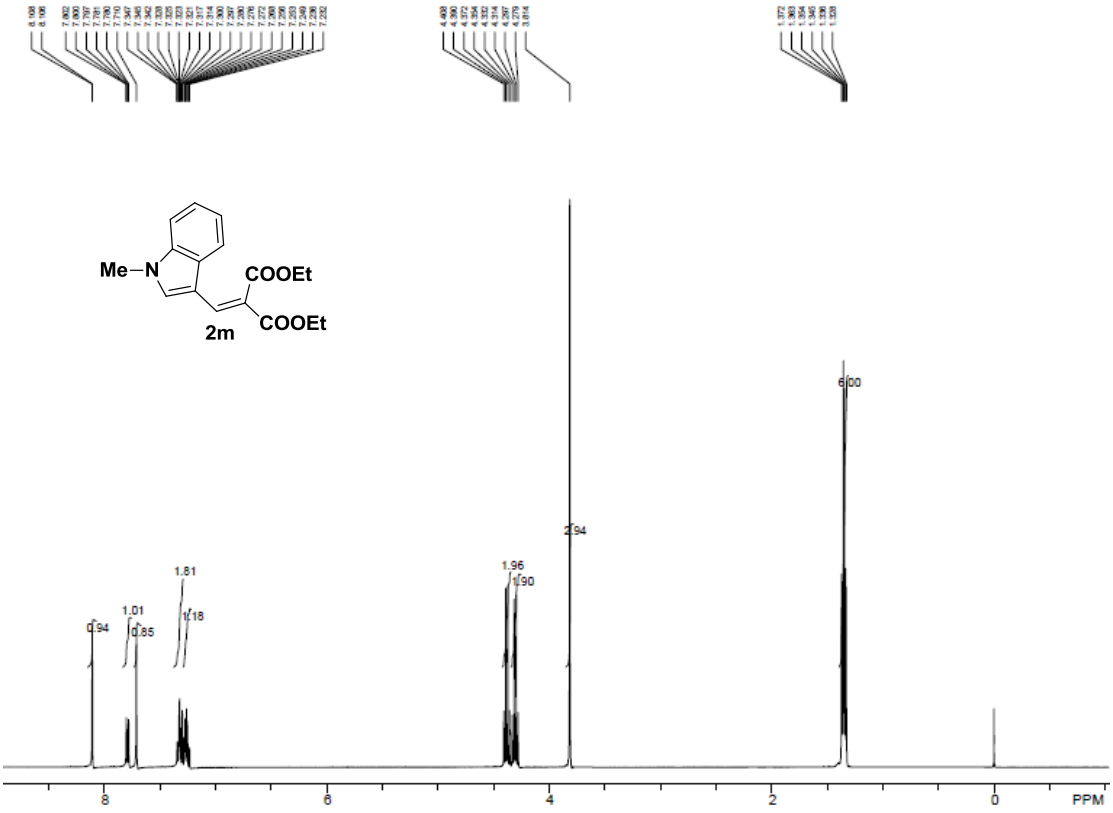

wh-13s BB
wh-13s CDCl3 13C-BB
167.00
164.75
142.43
138.26
133.36
131.05
130.72
128.59
128.47
126.69
78.05
77.80
77.54
62.32
62.15
20.57
14.84
14.51
COOEt
COOEt
2k
f1 (ppm)

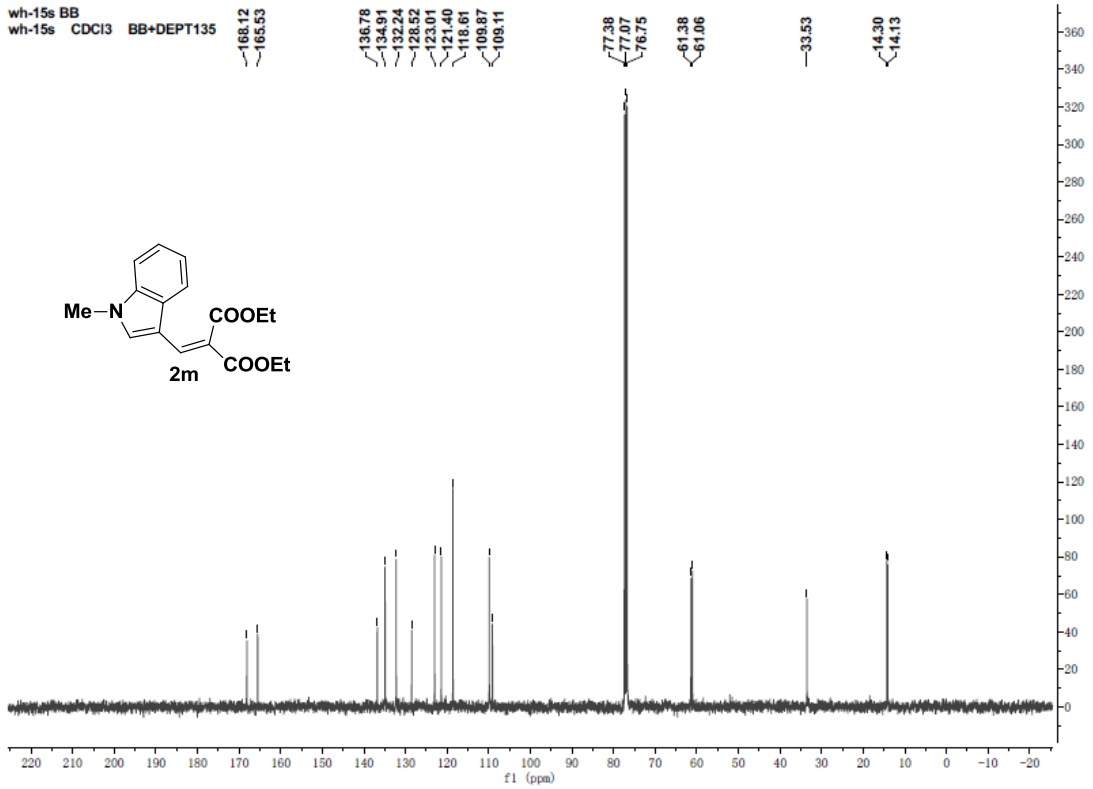


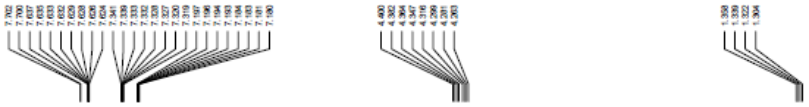

COOEt
COOEt
2l

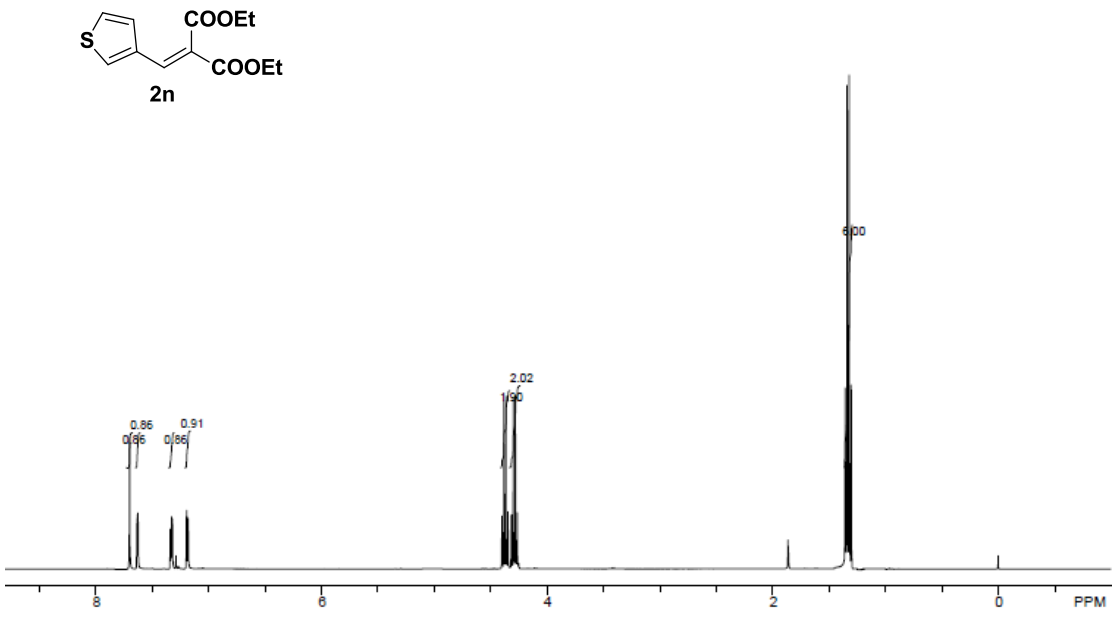

0.94
0.95
2.00
3.14
1.03
2.21
1.98
3.22
2.99
PPM

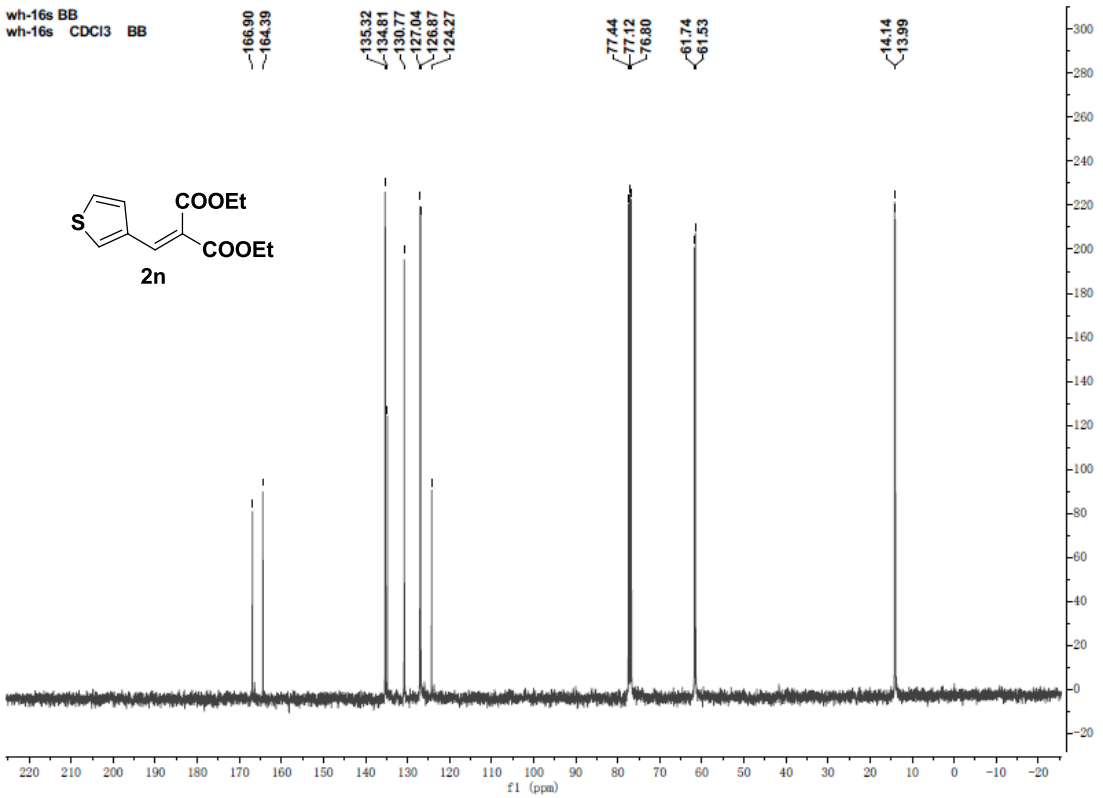

wh-4s BB
WH-4s CDCl3 13C-BB
166.15
163.96
141.25
133.36
131.35
130.84
130.46
129.26
128.67
126.93
126.42
126.40
125.19
124.08
77.37
77.05
76.74
61.78
61.48
14.21
13.77
COOEt
COOEt
2l
f1 (ppm)

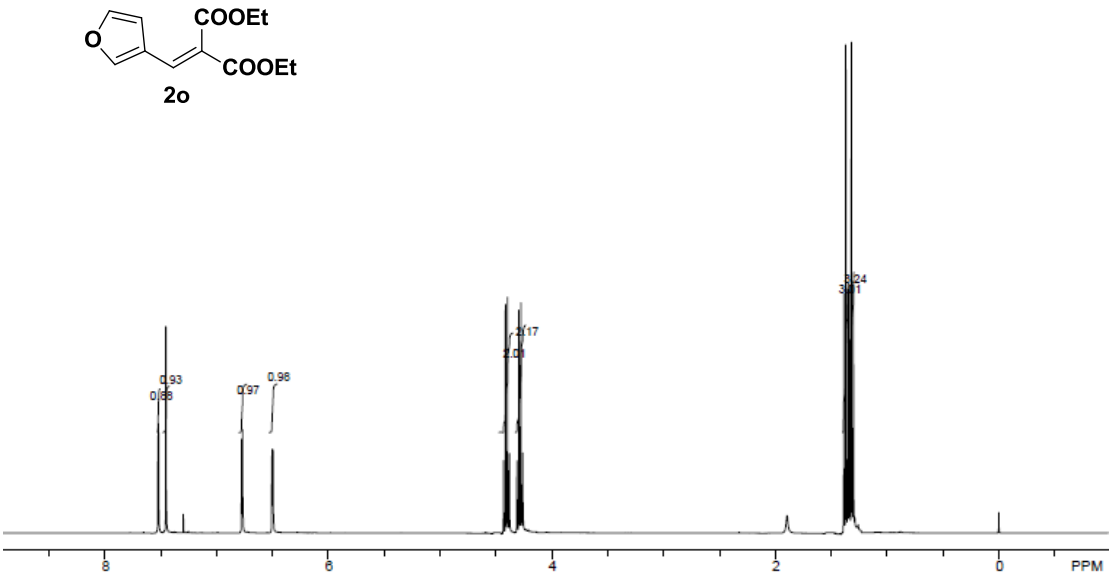

Me–N
COOEt
COOEt
2m
6.00
2.94
1.96
1.90
1.81
1.18
1.01
0.85
0.94
PPM

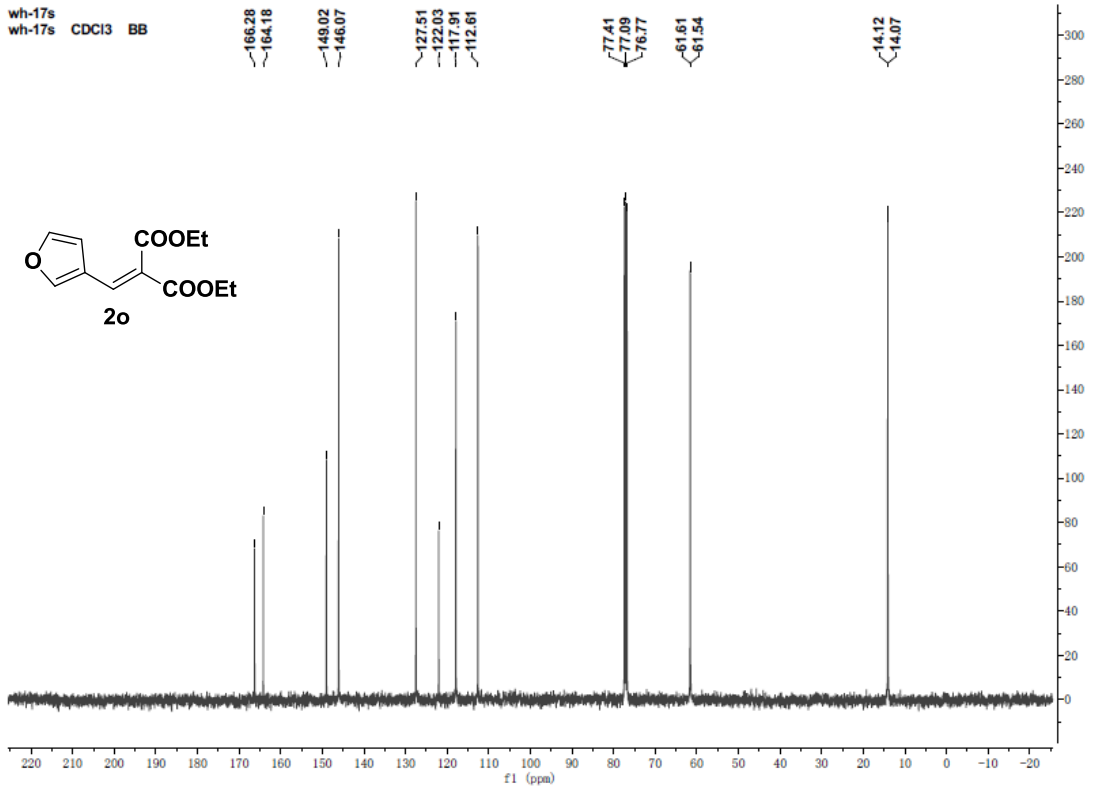

wh-15s BB
wh-15s CDCl3 BB+DEPT135
168.12
165.53
136.78
134.91
132.24
128.52
123.01
121.40
118.61
109.87
109.11
77.38
77.07
76.75
61.38
61.06
33.53
14.30
14.13
Me—N
COOEt
COOEt
2m
f1 (ppm)

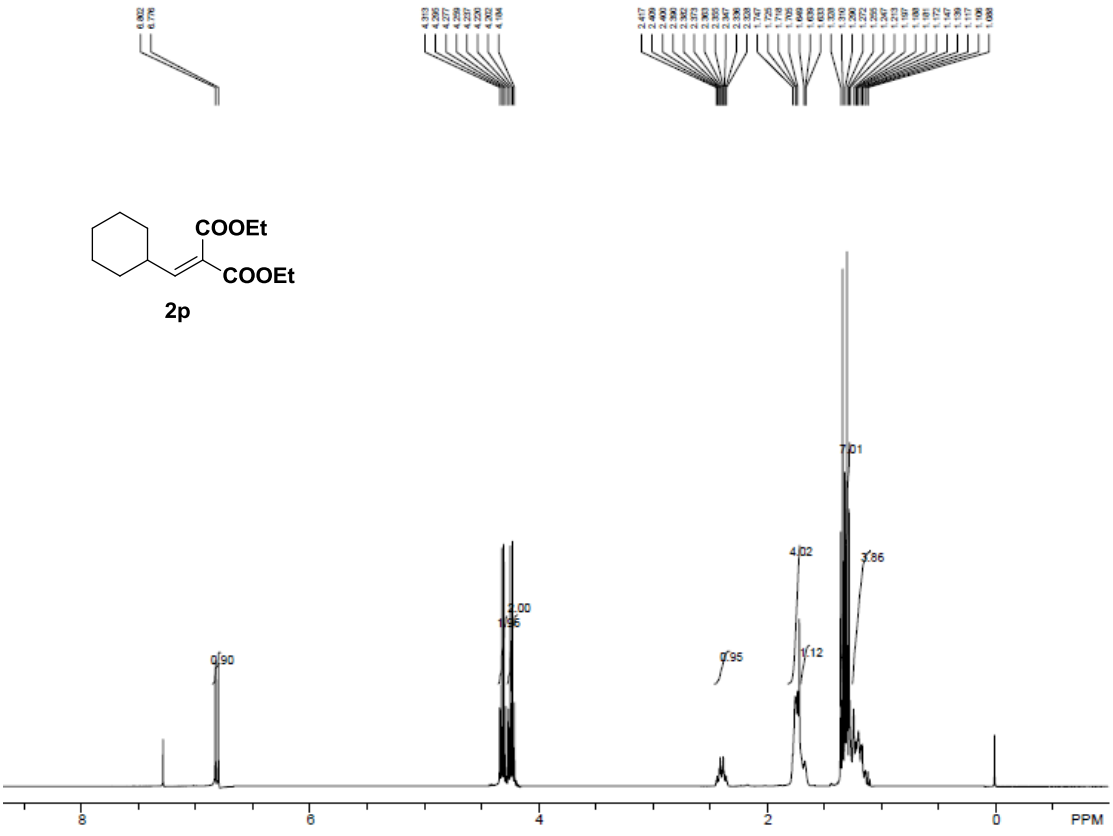


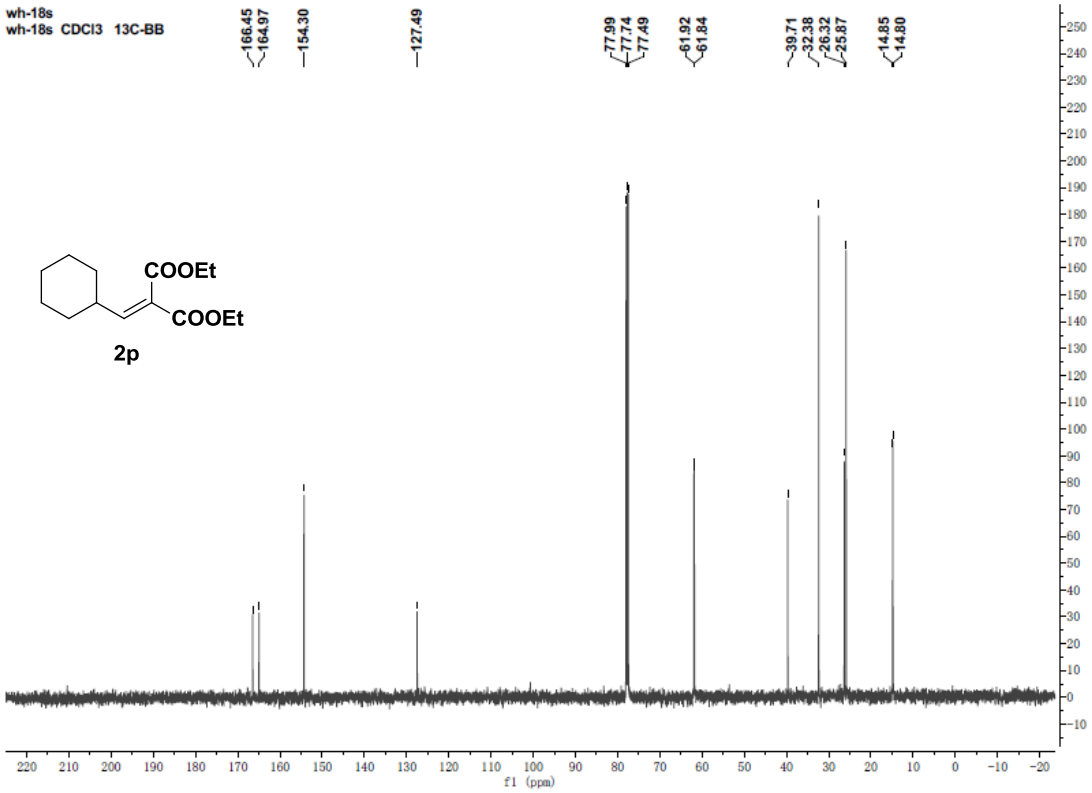

S
COOEt
COOEt
2n
6.00
2.02
1.90
0.86
0.91
PPM

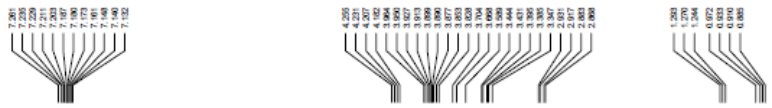

wh-16s BB
wh-16s CDCl3 BB
166.90
164.39
135.32
134.81
130.77
127.04
126.87
124.27
77.44
77.12
76.80
61.74
61.53
14.14
13.99
COOEt
COOEt
S
2n
f1 (ppm)

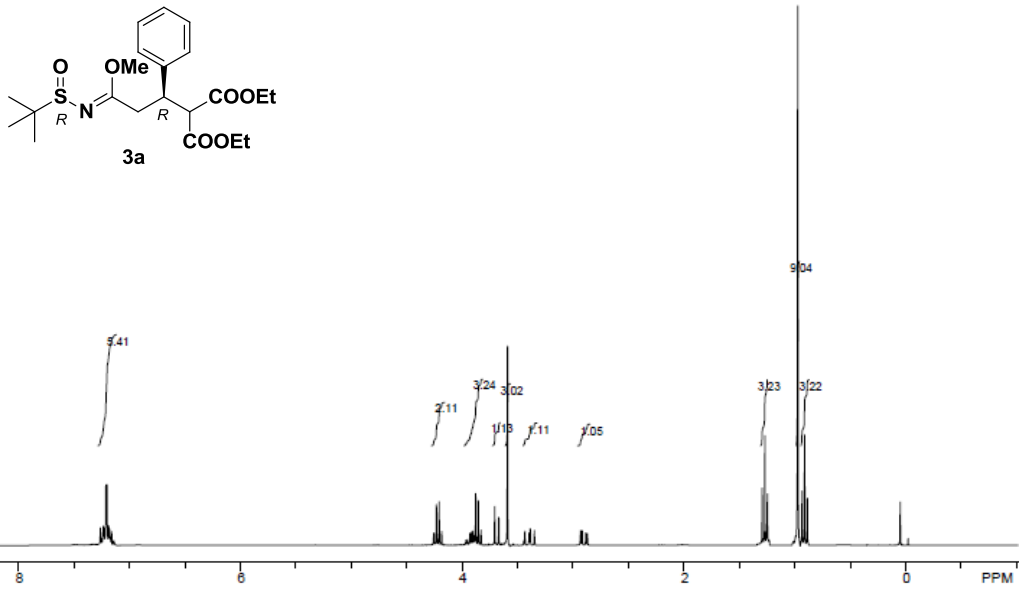

COOEt
COOEt
O
2o
0.93
0.88
0.97
0.98
2.17
2.00
3.24
3.01
PPM

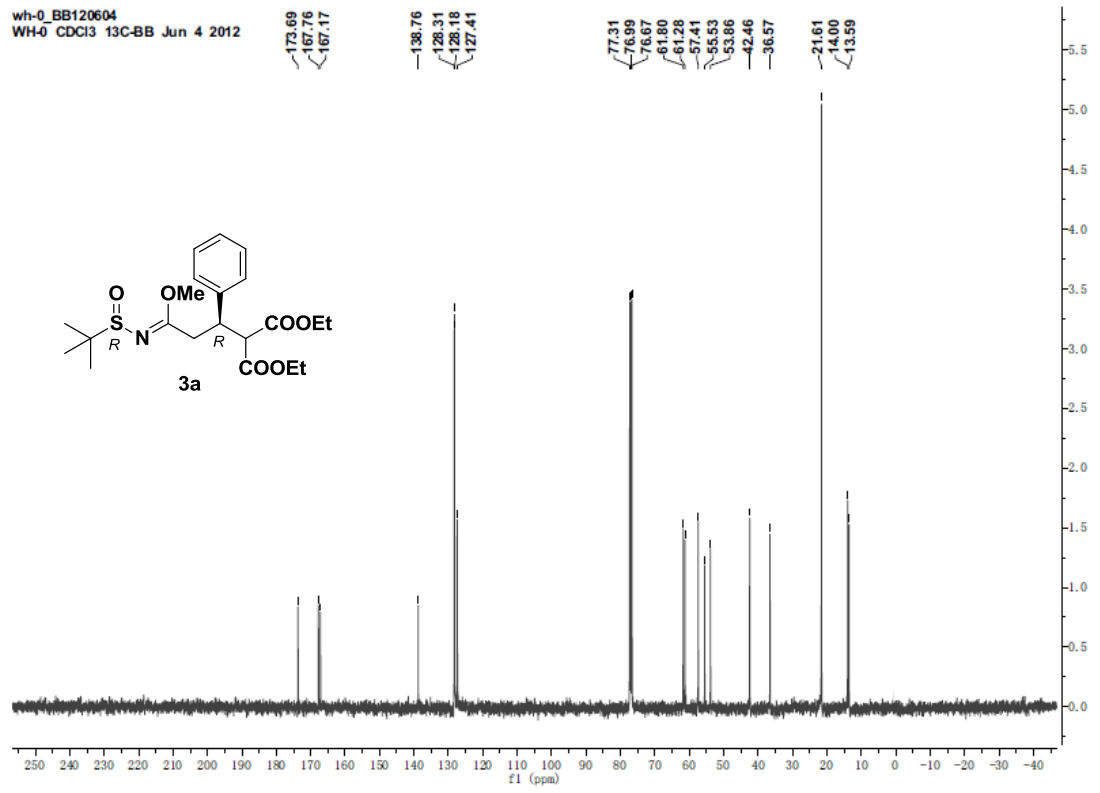

wh-17s
wh-17s CDCl3 BB
166.28
164.18
149.02
146.07
127.51
122.03
117.91
112.61
77.41
77.09
76.77
61.61
61.54
14.12
14.07
COOEt
COOEt
2o
f1 (ppm)

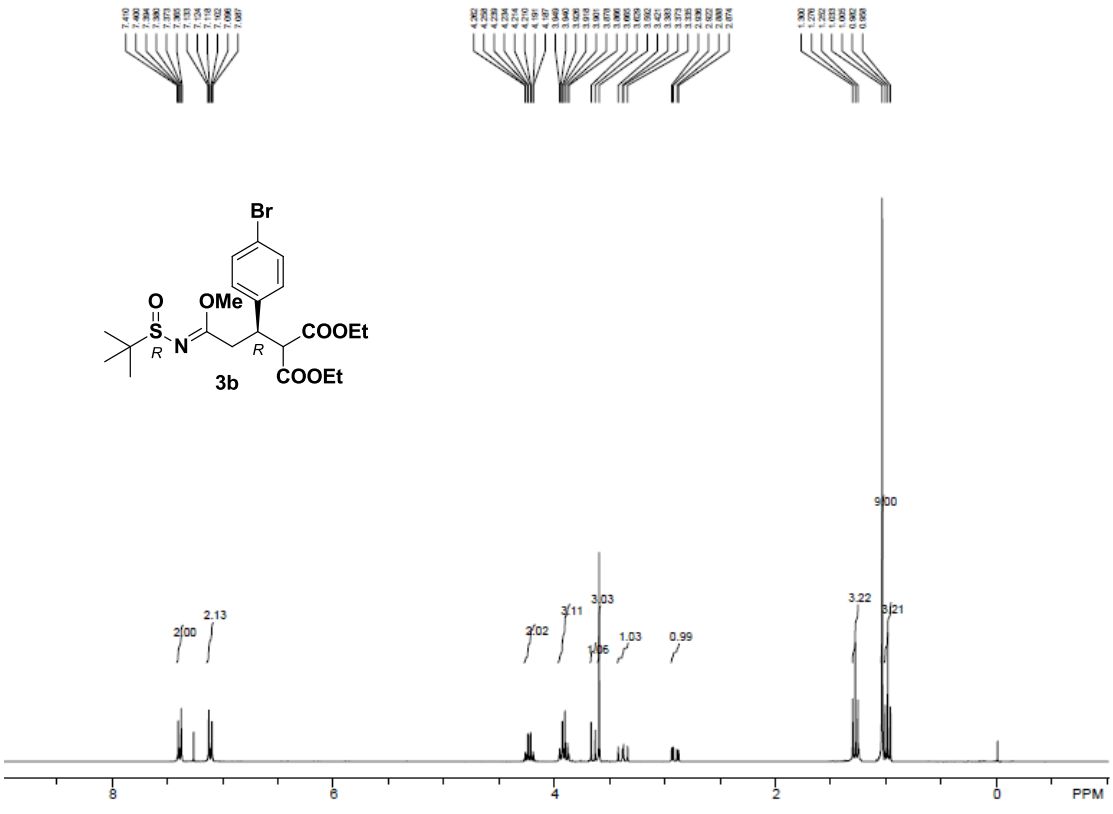

COOEt
COOEt
2p
0.90
2.00
0.95
4.02
1.12
7.01
3.86
PPM

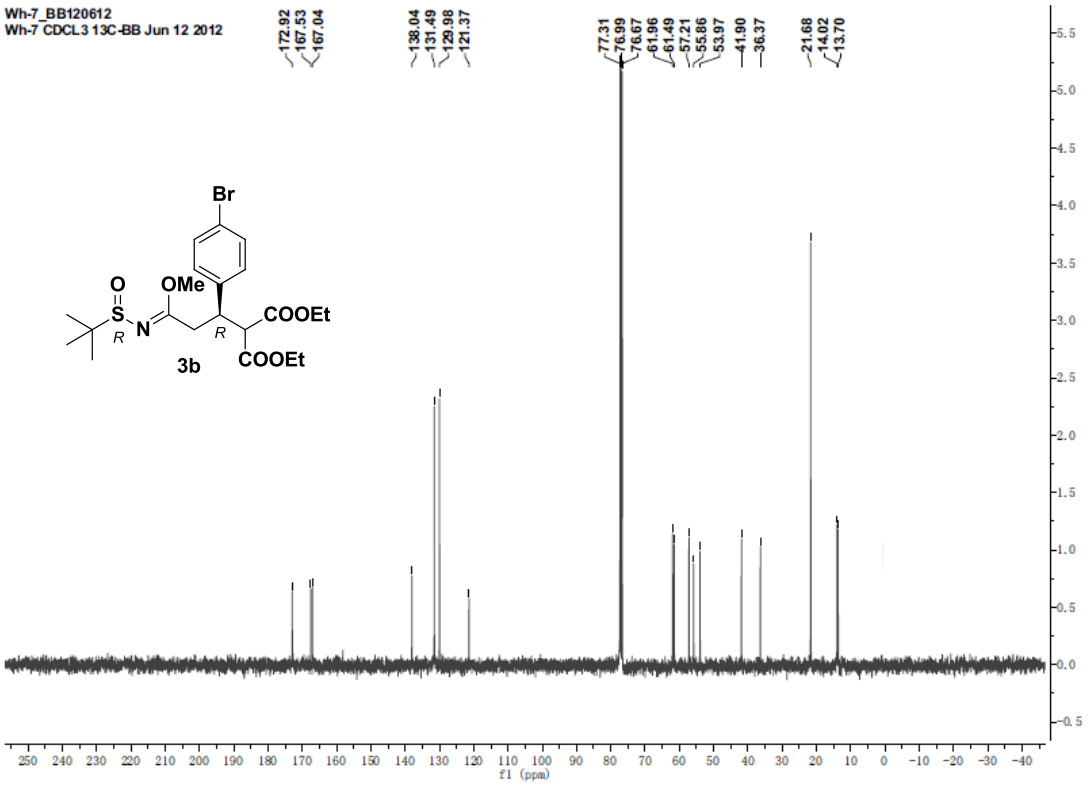

wh-18s
wh-18s CDCl3 13C-BB
166.45
164.97
154.30
127.49
77.99
77.74
77.49
61.92
61.84
39.71
32.38
26.32
25.87
14.85
14.80
COOEt
COOEt
2p
f1 (ppm)

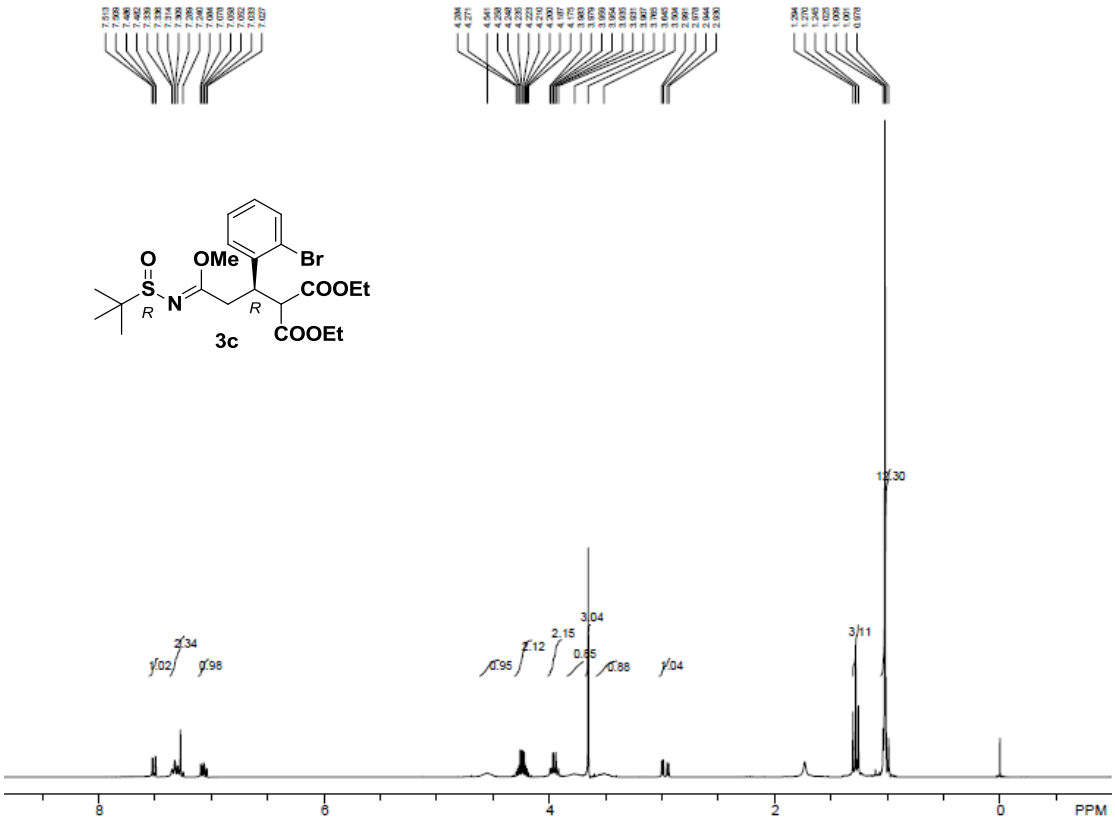


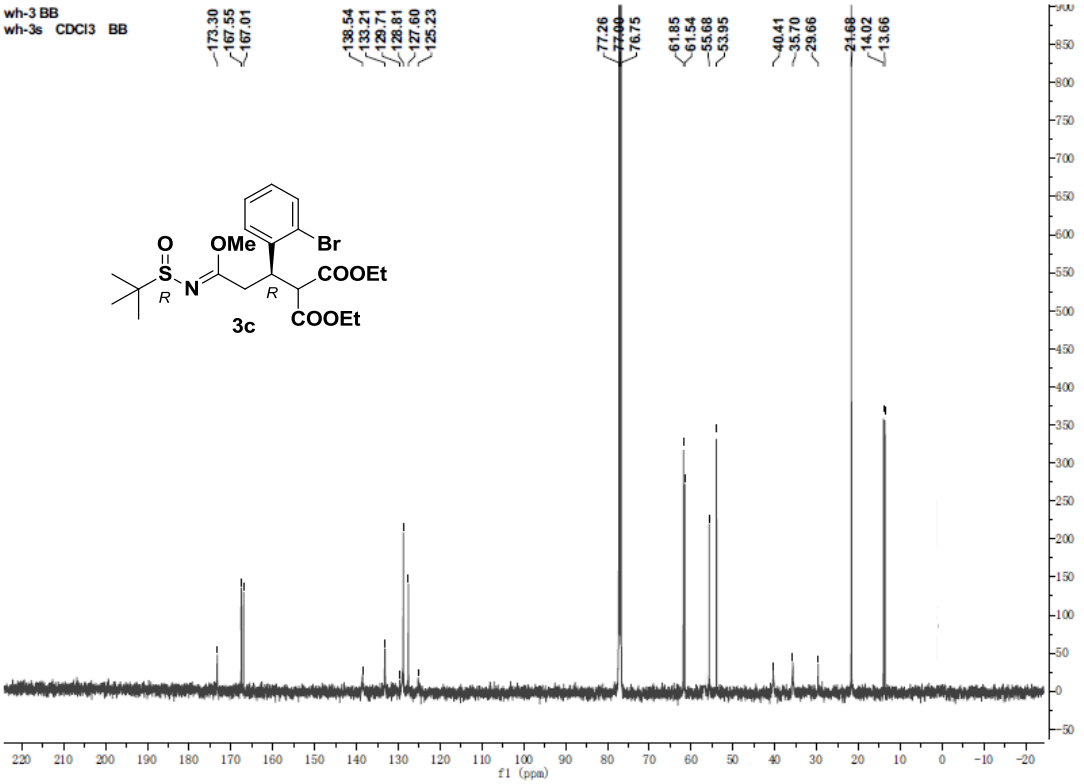

O
OMe
S
N
R
R
COOEt
COOEt
3a
9.04
5.41
3.24
3.02
3.23
3.22
2.11
1.13
1.11
1.05
PPM

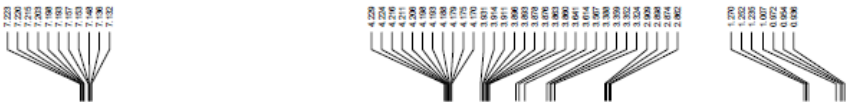

wh-0_BB120604
WH-0 CDCl3 13C-BB Jun 4 2012
173.69
167.76
167.17
138.76
128.31
128.18
127.41
77.31
76.99
76.67
61.80
61.28
57.41
55.53
53.86
42.46
36.57
21.61
14.00
13.59
O
S
N
R
OMe
R
COOEt
COOEt
3a
f1 (ppm)

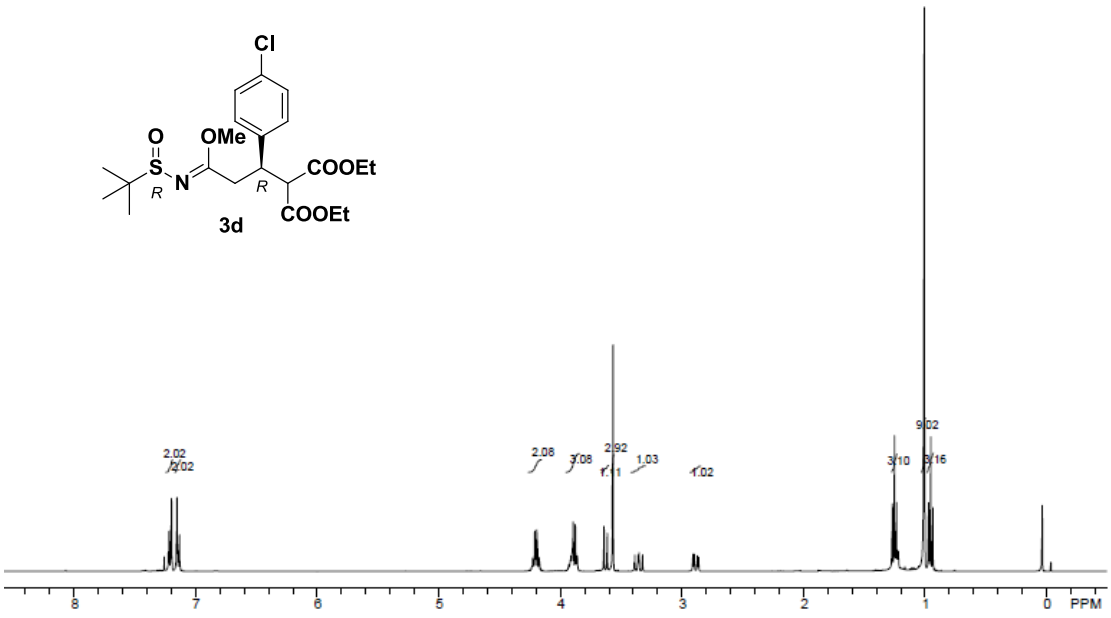

Br
O
S
N
R
OMe
R
COOEt
COOEt
3b
2.00
2.13
2.02
3.11
3.03
1.06
1.03
0.99
3.22
3.21
9.00
PPM

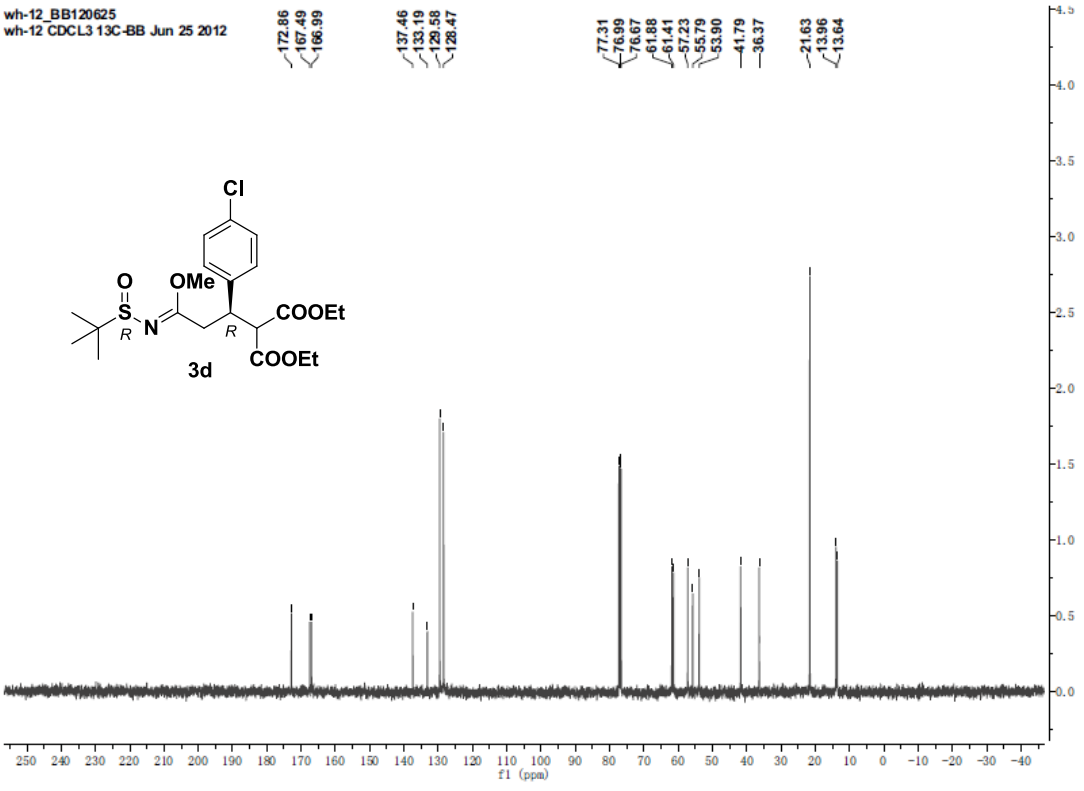

Wh-7_BB120612
Wh-7 CDCL3 13C-BB Jun 12 2012
172.92
167.53
167.04
138.04
131.49
129.98
121.37
77.31
76.99
76.67
61.96
61.49
57.21
55.86
53.97
41.90
36.37
21.68
14.02
13.70
Br
O
OMe
S
N
R
R
COOEt
COOEt
3b
f1 (ppm)

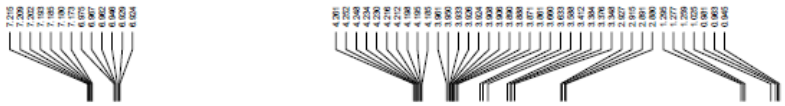

O
OMe
Br
S
N
R
R
COOEt
COOEt
3c
12.30
3.04
3.11
2.34
2.15
2.12
1.02
0.98
0.95
0.85
0.88
1.04
PPM

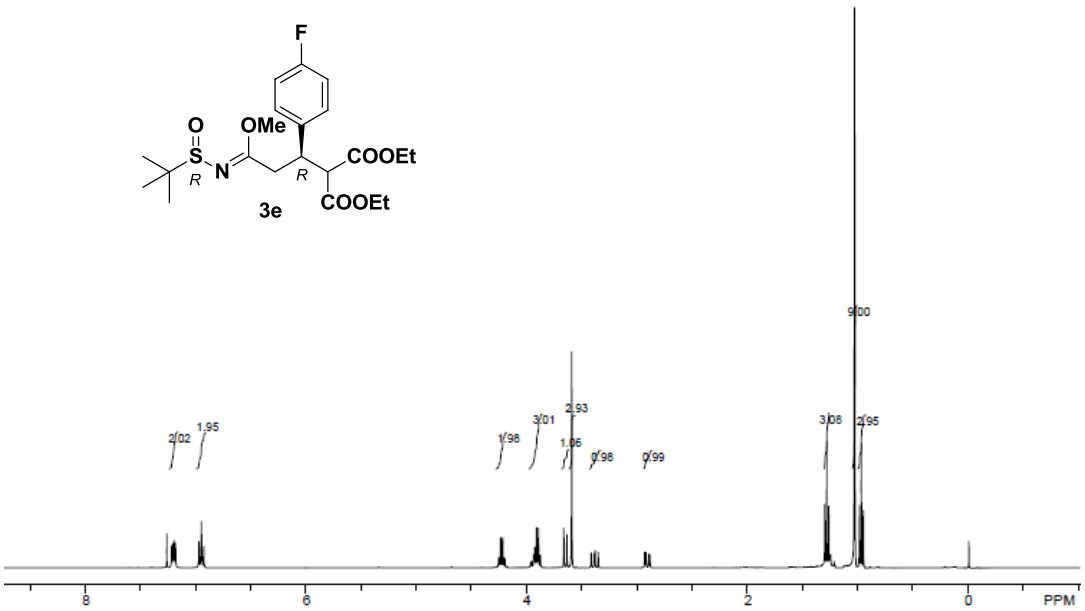

wh-3 BB
wh-3s CDCl3 BB
173.30
167.55
167.01
138.54
133.21
129.71
128.81
127.60
125.23
77.26
77.00
76.75
61.85
61.54
55.68
53.95
40.41
35.70
29.66
21.68
14.02
13.66
O
OMe
Br
S
N
R
R
COOEt
COOEt
3c
f1 (ppm)

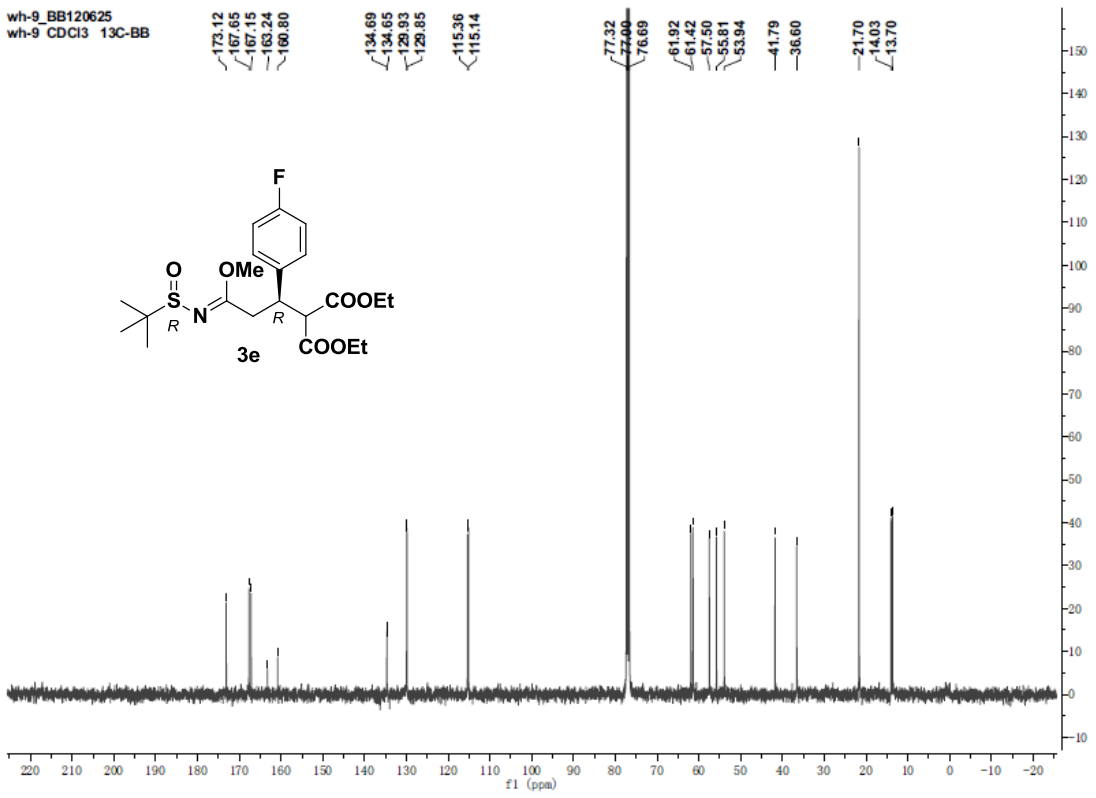


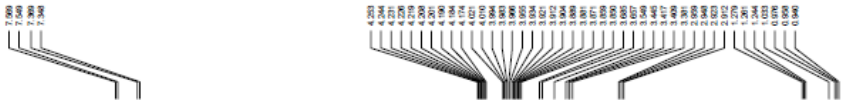

Cl
O
OMe
S
N
R
R
COOEt
COOEt
3d
2.02
2.08
3.08
2.92
1.11
1.03
1.02
3.10
9.02
3.16
PPM

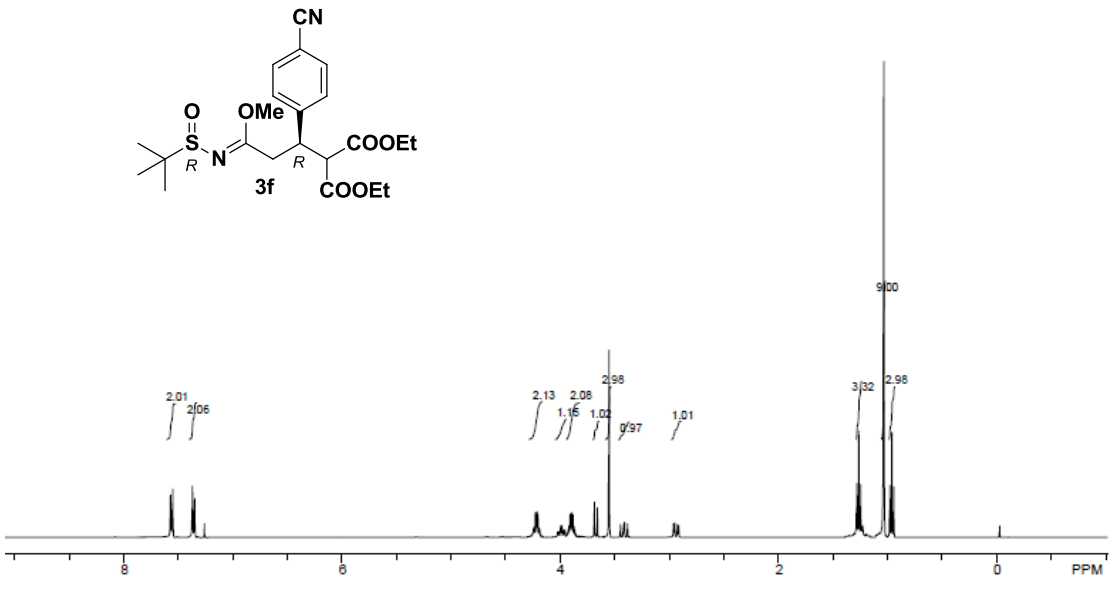

wh-12_BB120625
wh-12 CDCL3 13C-BB Jun 25 2012
172.86
167.49
166.99
137.46
133.19
129.58
128.47
77.31
76.99
76.67
61.88
61.41
57.23
55.79
53.90
41.79
36.37
21.63
13.96
13.64
Cl
O
S
N
R
OMe
R
COOEt
COOEt
3d
f1 (ppm)

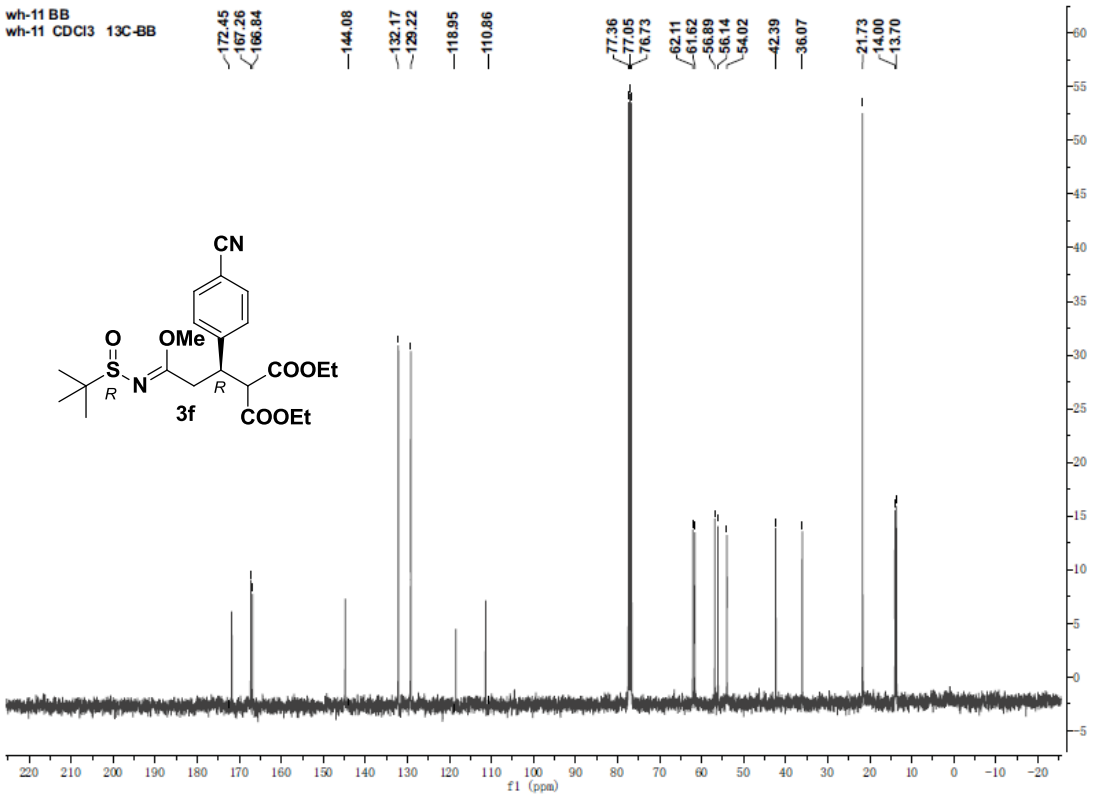


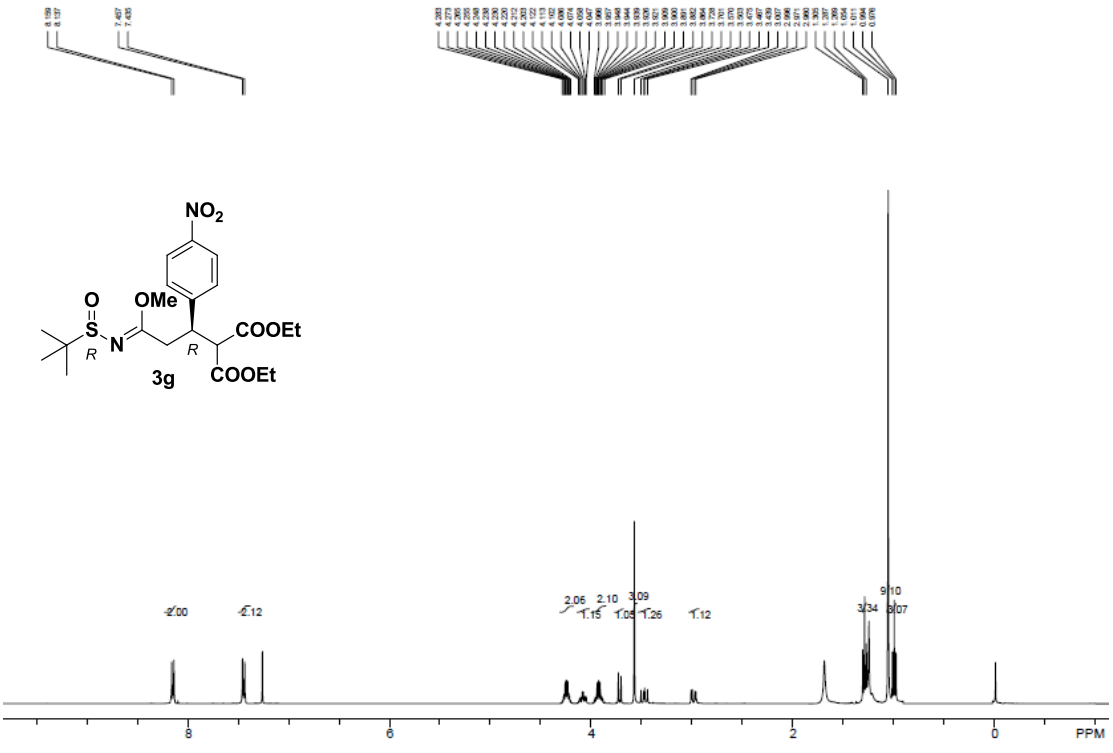

F
O
S
N
R
OMe
R
COOEt
COOEt
3e
9.00
3.08
2.95
2.93
3.01
2.02
1.95
1.98
1.06
0.98
0.99
PPM

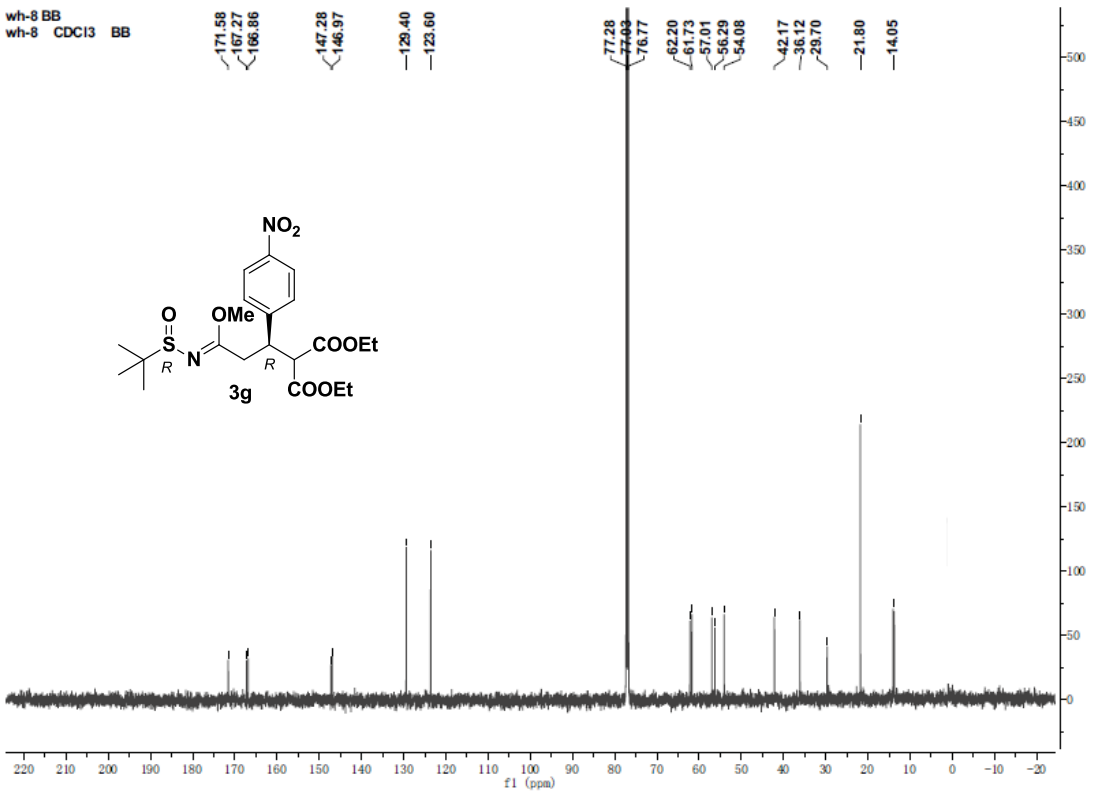

wh-9_BB120625
wh-9 CDCl3 13C-BB
173.12
167.65
167.15
163.24
160.80
134.69
134.65
129.93
129.85
115.36
115.14
77.32
77.00
76.69
61.92
61.42
57.50
55.81
53.94
41.79
36.60
21.70
14.03
13.70
F
O
S
N
R
OMe
R
COOEt
COOEt
3e
f1 (ppm)

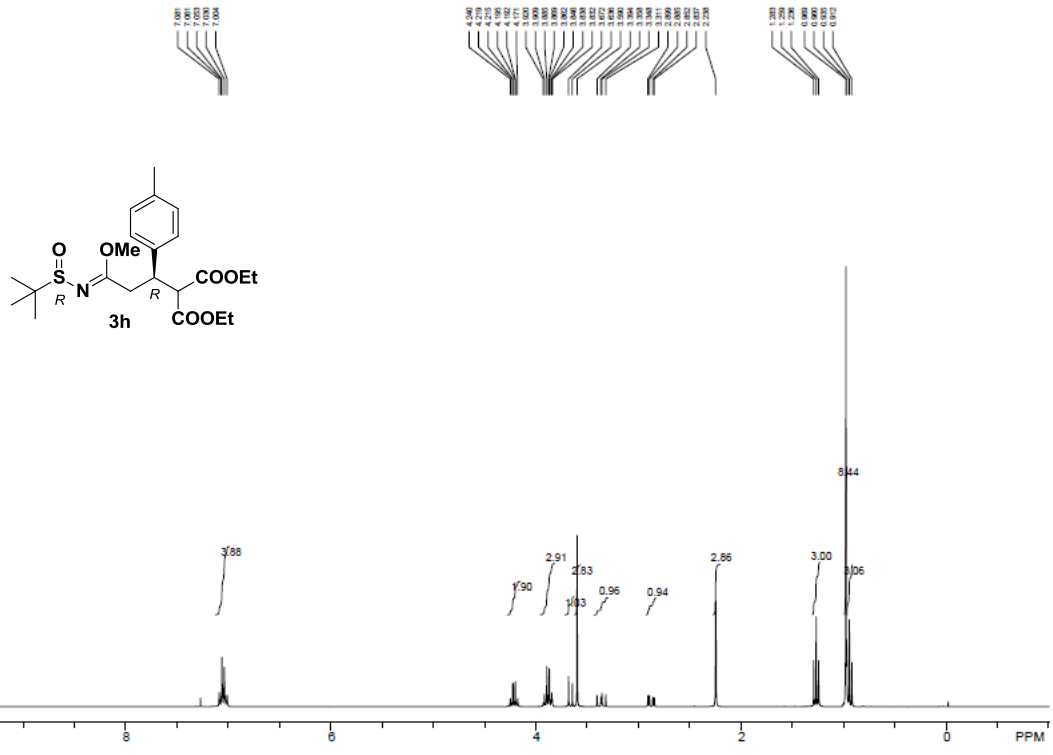


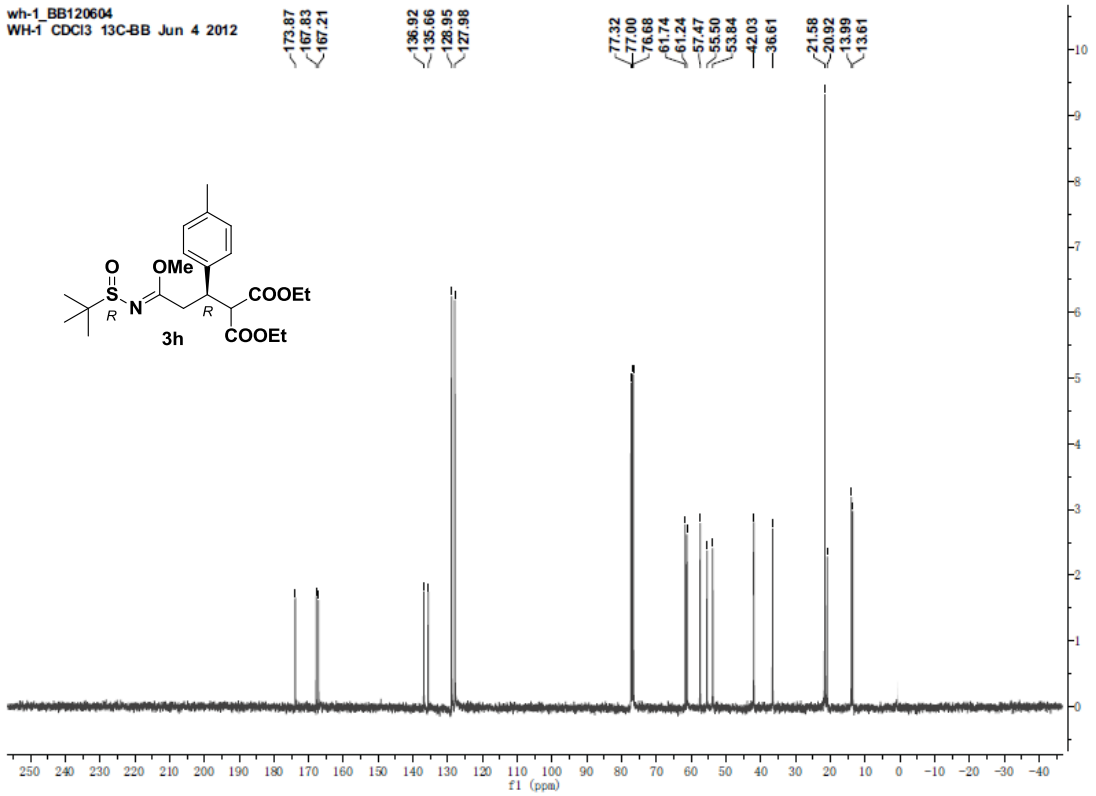

CN
O
S
N
R
OMe
R
COOEt
COOEt
3f
2.01
2.06
2.13
2.08
1.15
1.02
2.98
0.97
1.01
9.00
3.32
2.98
PPM


wh-11 BB
wh-11 CDCl3 13C-BB
172.45
167.26
166.84
144.08
132.17
129.22
118.95
110.86
77.36
77.05
76.73
62.11
61.62
56.89
56.14
54.02
42.39
36.07
21.73
14.00
13.70
CN
O
S
N
R
OMe
R
COOEt
COOEt
3f
f1 (ppm)


NO2
O
S
N
R
OMe
R
COOEt
COOEt
3g
PPM

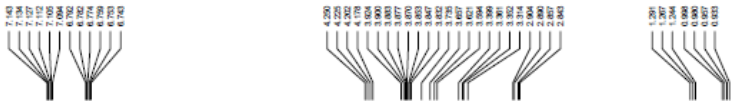

wh-8 BB
wh-8 CDCl3 BB
171.58
167.27
166.86
147.28
146.97
129.40
123.60
77.28
77.03
76.77
62.20
61.73
57.01
56.29
54.08
42.17
36.12
29.70
21.80
14.05
NO2
O
S
N
R
OMe
R
COOEt
COOEt
3g
f1 (ppm)

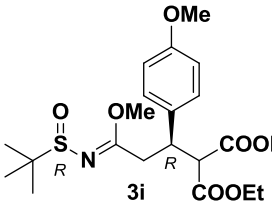

O
S
N
R
OMe
R
COOEt
COOEt
3h
3.88
2.91
2.83
1.90
1.93
0.96
0.94
2.86
3.00
8.44
8.06
PPM


wh-1_BB120604
WH-1 CDCl3 13C-BB Jun 4 2012
173.87
167.83
167.21
136.92
135.66
128.95
127.98
77.32
77.00
76.68
61.74
61.24
57.47
55.50
53.84
42.03
36.61
21.58
20.92
13.99
13.61
f1 (ppm)

O
S
N
R
OMe
R
COOEt
COOEt

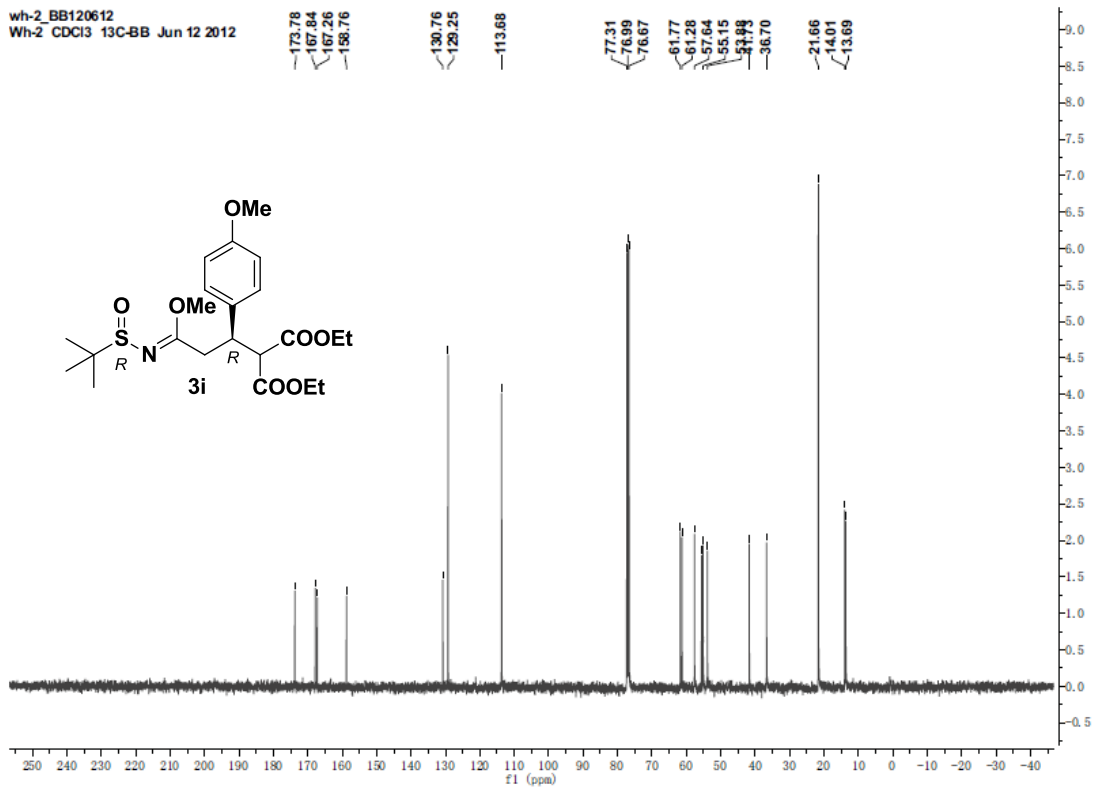
3h

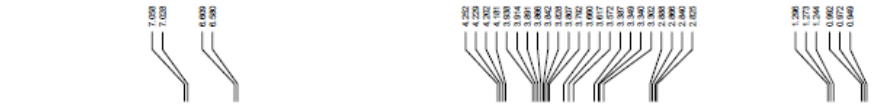


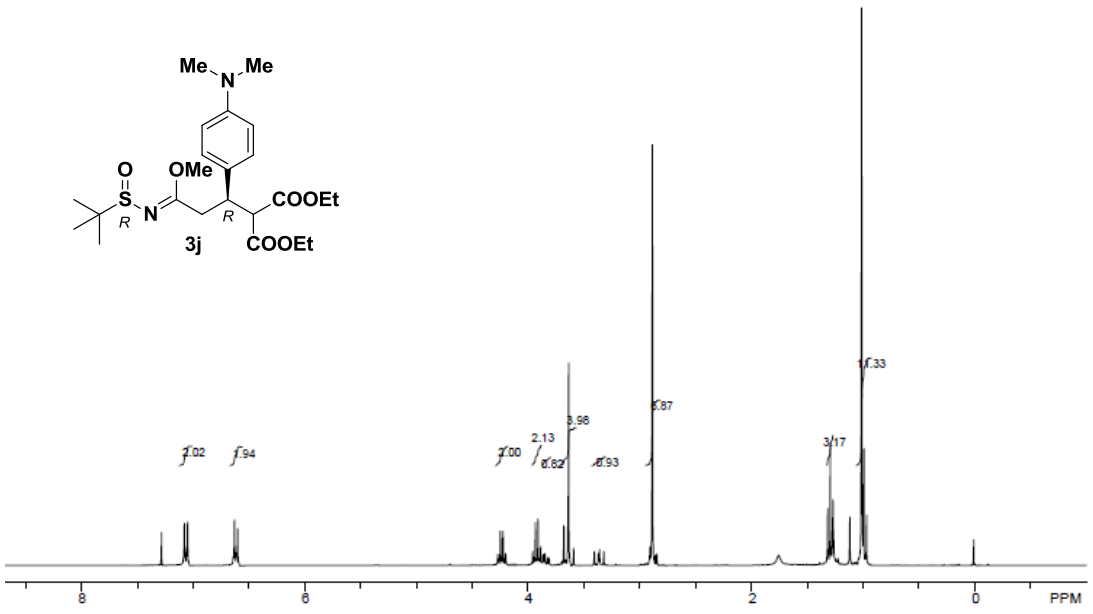

OMe
O
S
N
R
OMe
R
COOEt
COOEt

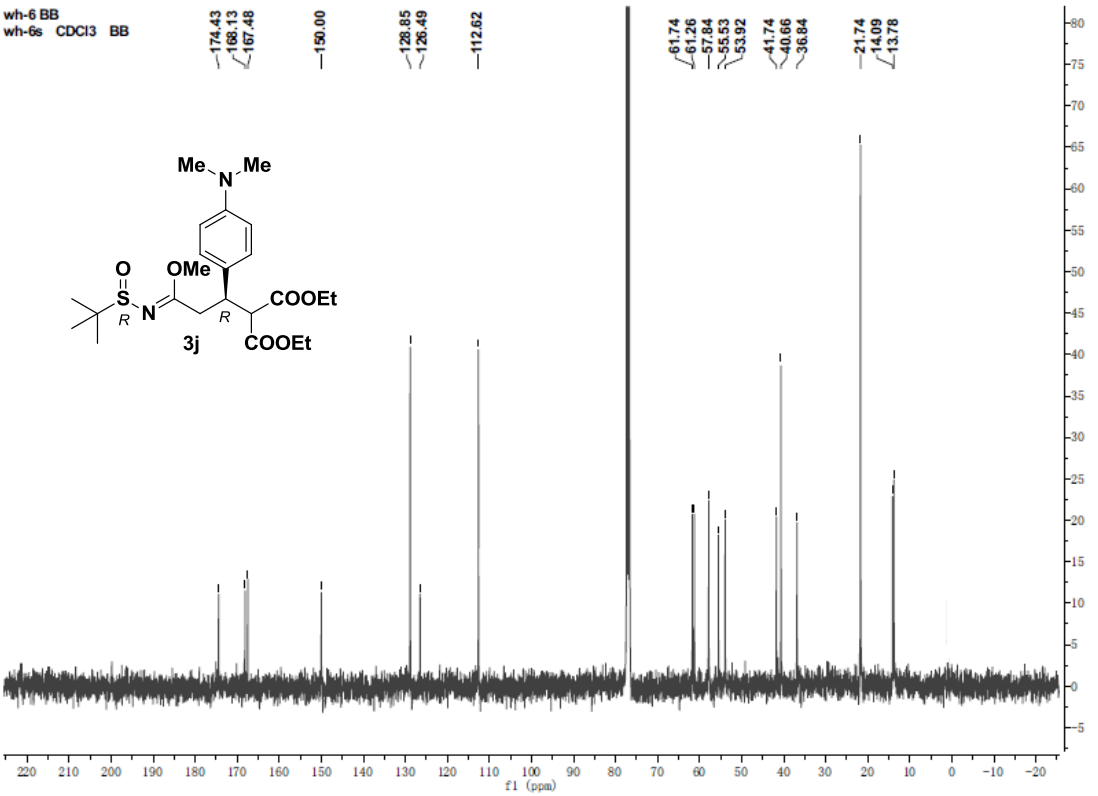
3i

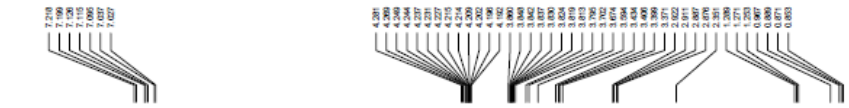
9.00
3.10
3.09
2.93
2.07
1.98
2.01
1.09
1.04
1.01
3.03
3.09
PPM

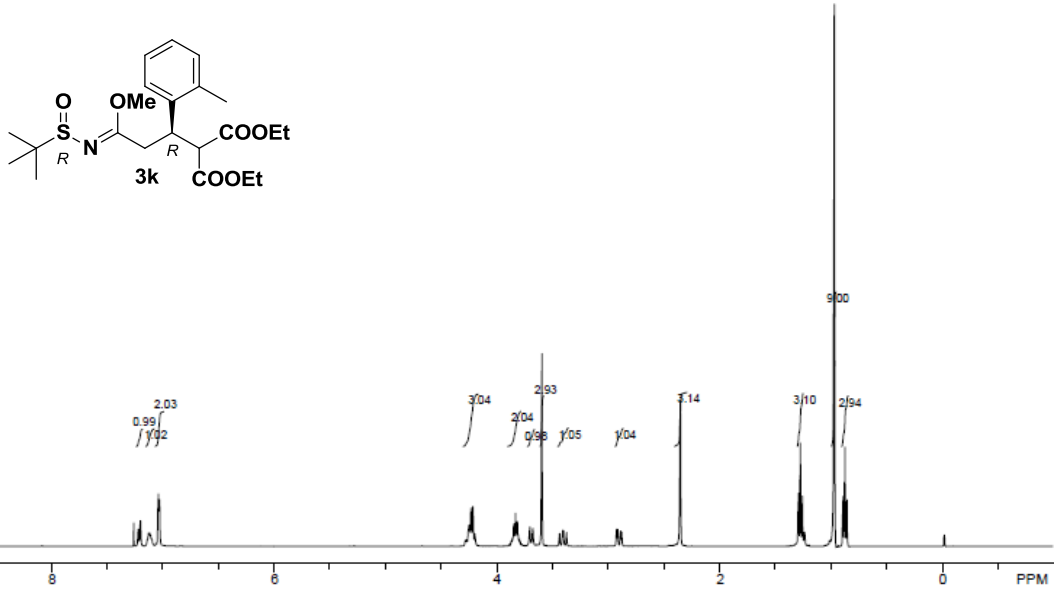

wh-2_BB120612
Wh-2 CDCl3 13C-BB Jun 12 2012
173.78
167.84
167.26
158.76
130.76
129.25
113.68
77.31
76.99
76.67
61.77
61.28
57.64
55.15
53.88
41.73
36.70
21.66
14.01
13.69
OMe
O
S
N
R
OMe
R
COOEt
COOEt
3i
f1 (ppm)

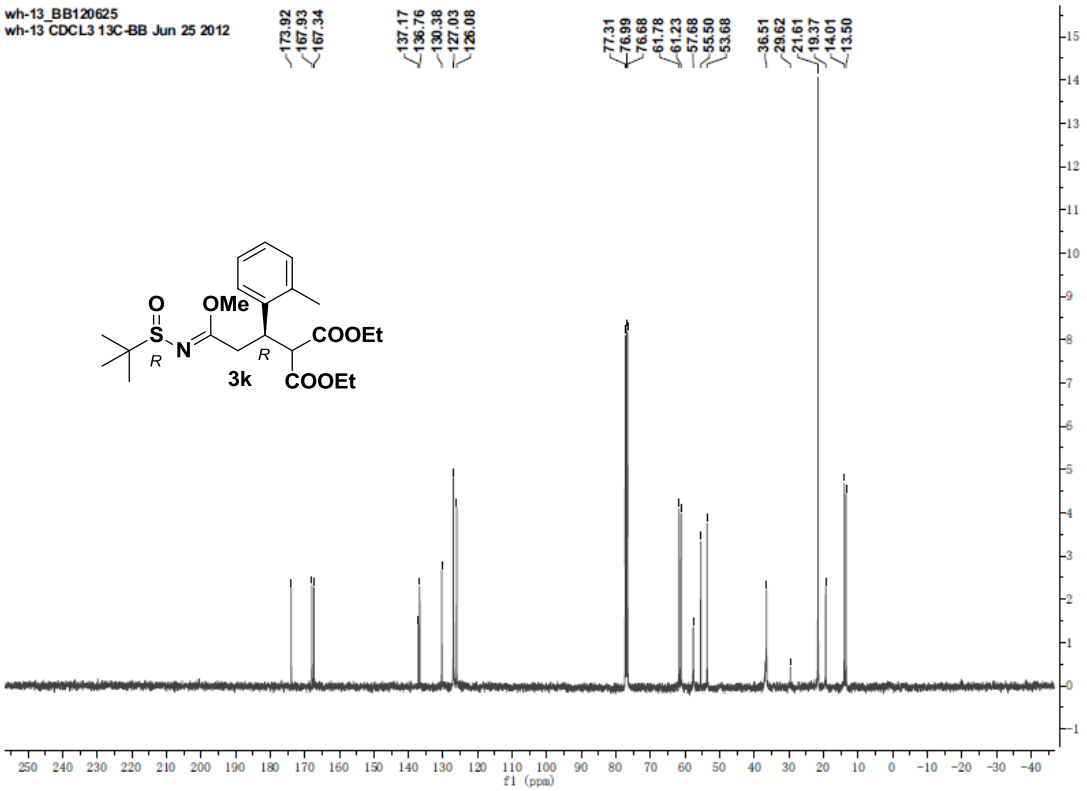


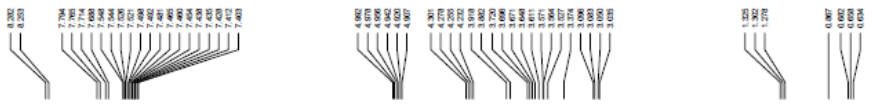

Me
N
Me
O
S
N
R
OMe
R
COOEt
COOEt
3j
1.02
0.94
3.00
2.13
0.82
3.98
0.93
6.87
3.17
11.33
PPM

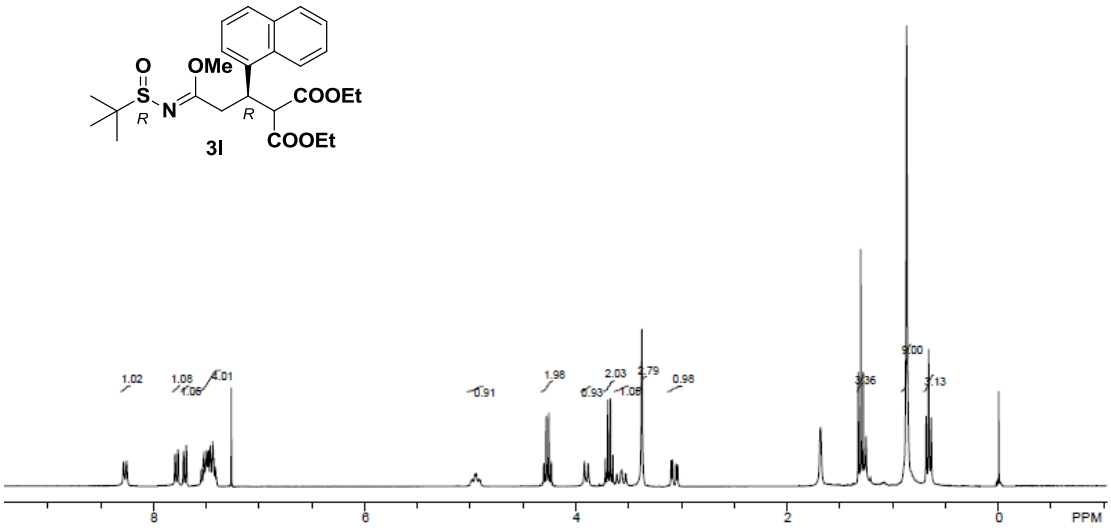

wh-6 BB
wh-6s CDCl3 BB
174.43
168.13
167.48
150.00
128.85
126.49
112.62
61.74
61.26
57.84
55.53
53.92
41.74
40.66
36.84
21.74
14.09
13.78
Me
N
Me
O
S
N
OMe
R
R
COOEt
COOEt
3j
f1 (ppm)

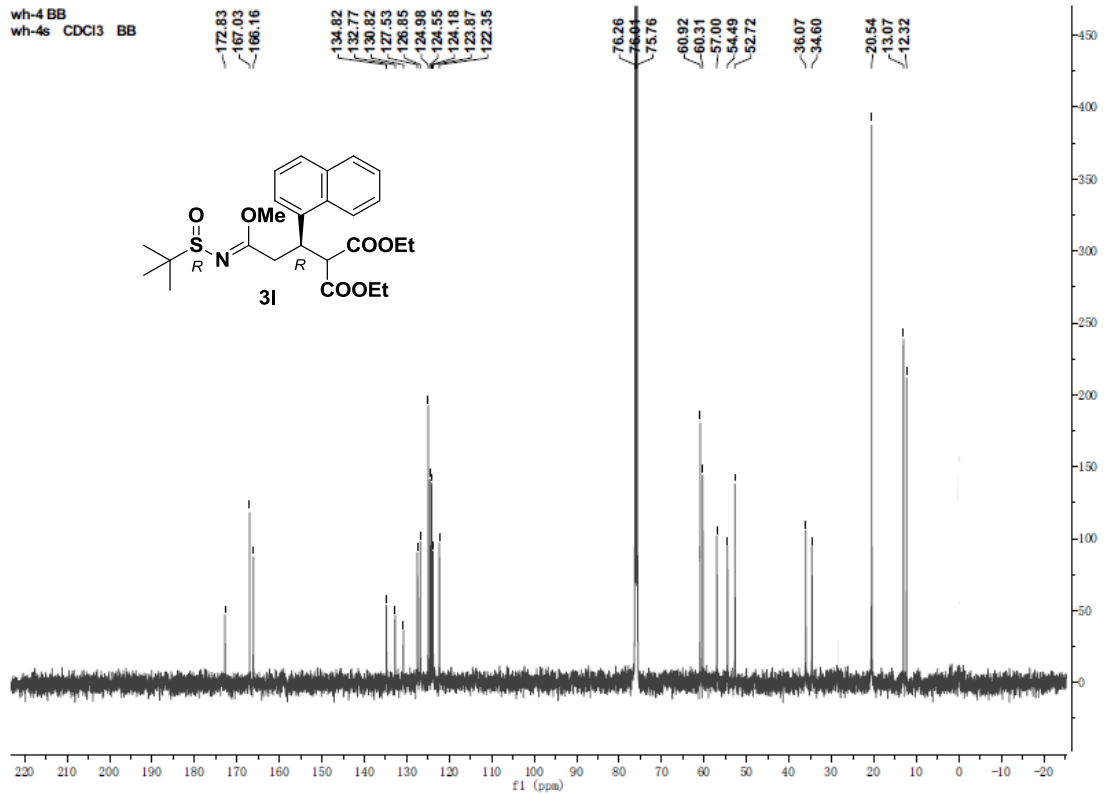


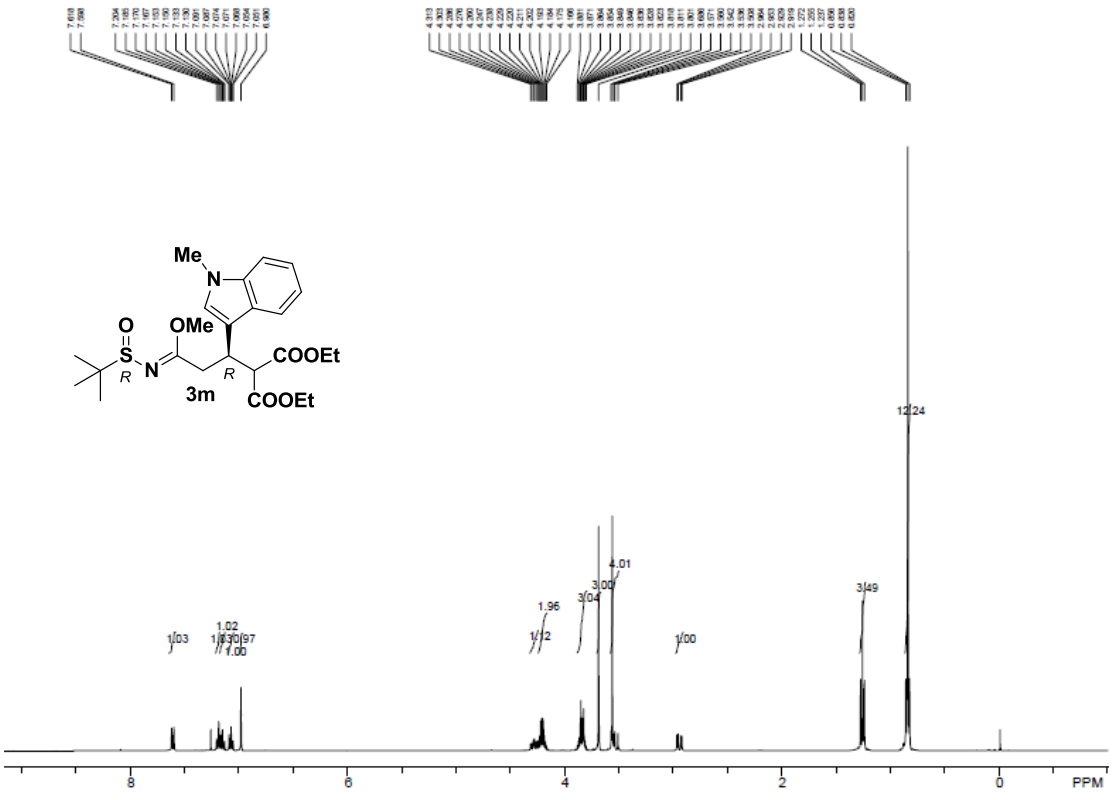

O
S
N
OMe
R
R
COOEt
COOEt
3k
9.00
3.14
3.10
2.94
2.93
3.04
2.04
2.03
0.99
PPM

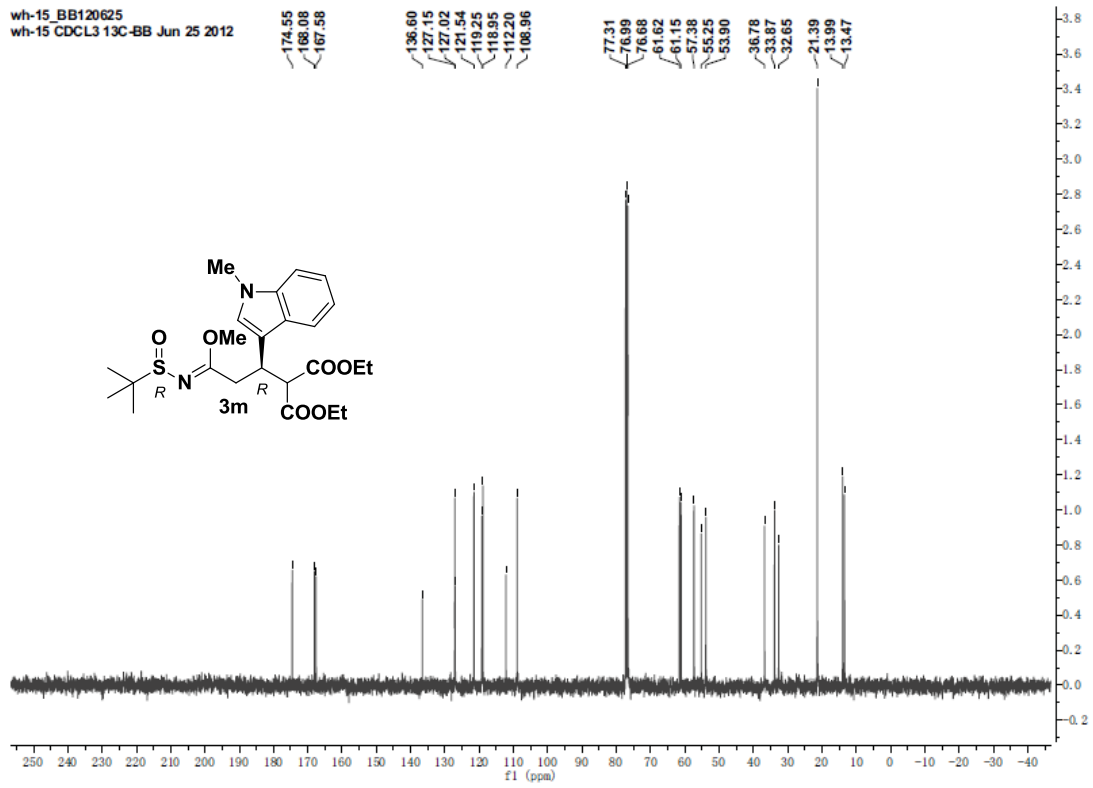

wh-13_BB120625
wh-13 CDCL3 13C-BB Jun 25 2012
173.92
167.93
167.34
137.17
136.76
130.38
127.03
126.08
77.31
76.99
76.68
61.78
61.23
57.68
55.50
53.68
36.51
29.62
21.61
19.37
14.01
13.50
O
S
N
R
OMe
R
COOEt
COOEt
3k
f1 (ppm)

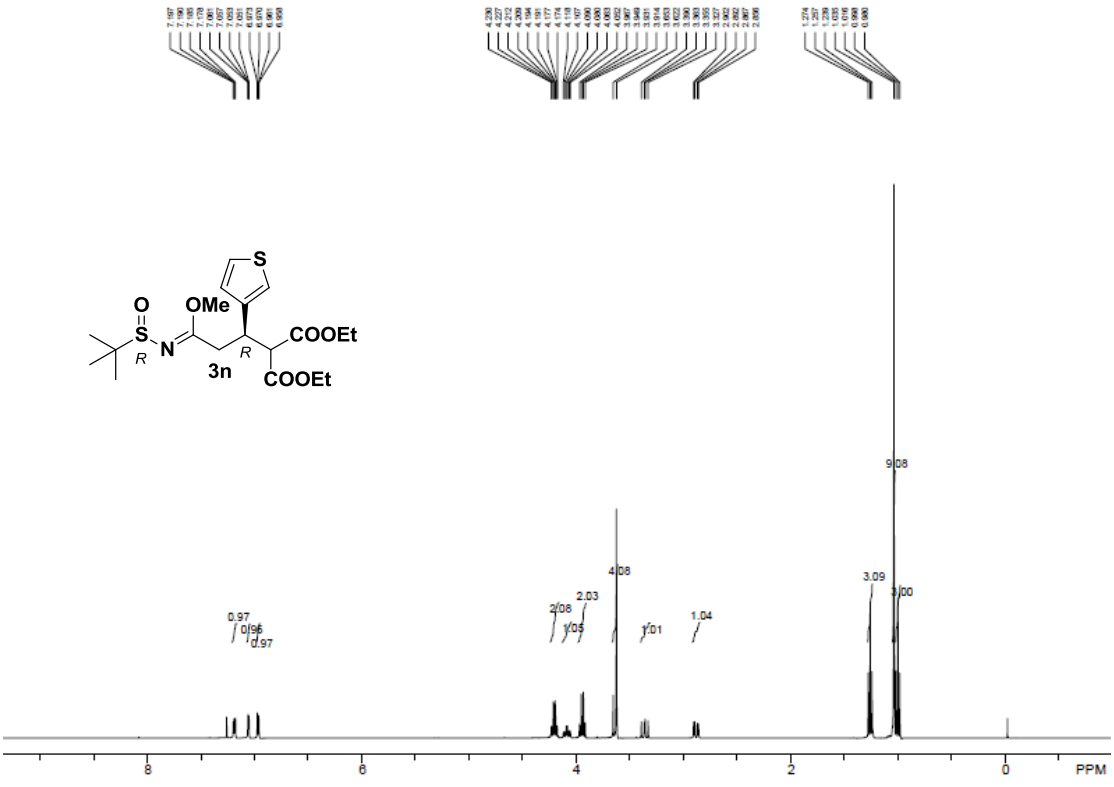


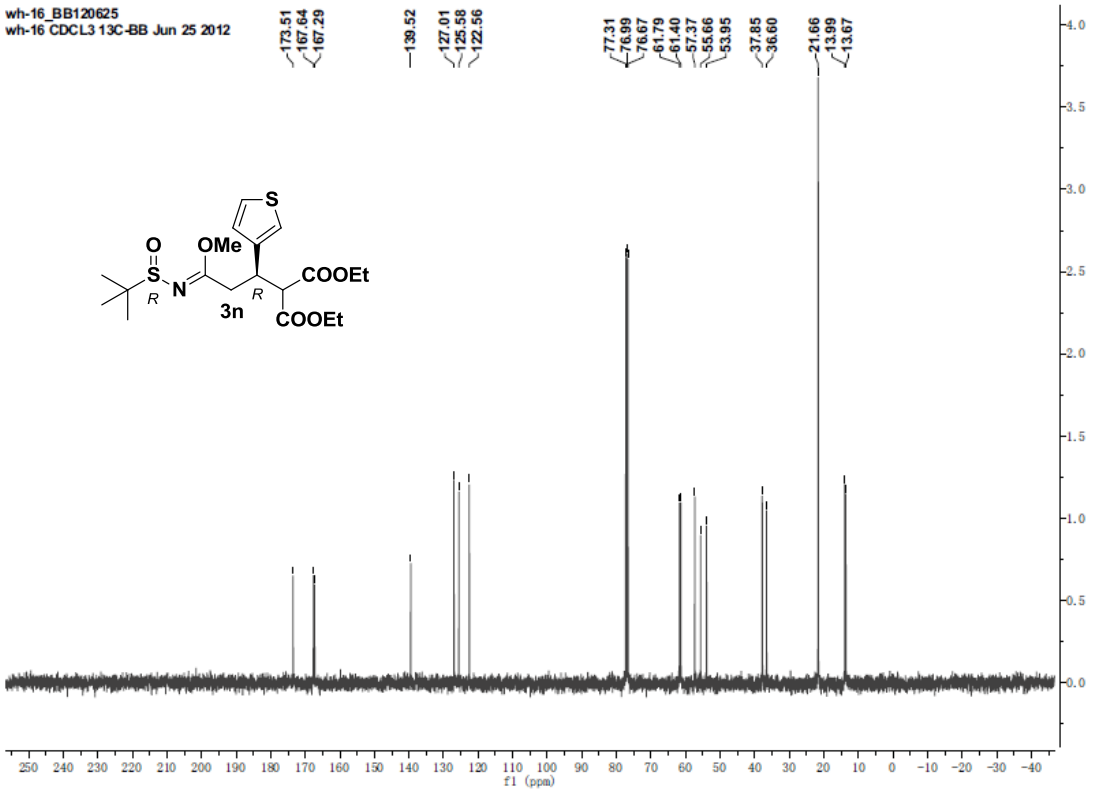

O
S
N
R
OMe
R
COOEt
COOEt
3l
1.02
1.08
1.08
4.01
0.91
1.98
0.93
2.03
1.08
2.79
0.98
3.06
9.00
3.13
PPM

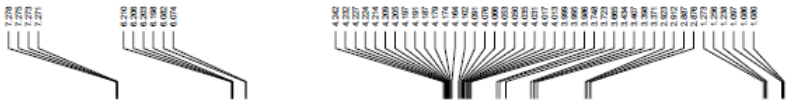

wh-4 BB
wh-4s CDCl3 BB
172.83
167.03
166.16
134.82
132.77
130.82
127.53
126.85
124.98
124.55
124.18
123.87
122.35
76.26
76.64
75.76
60.92
60.31
57.00
54.49
52.72
36.07
34.60
20.54
13.07
12.32
O
S
R
N
OMe
R
COOEt
COOEt
3l
f1 (ppm)

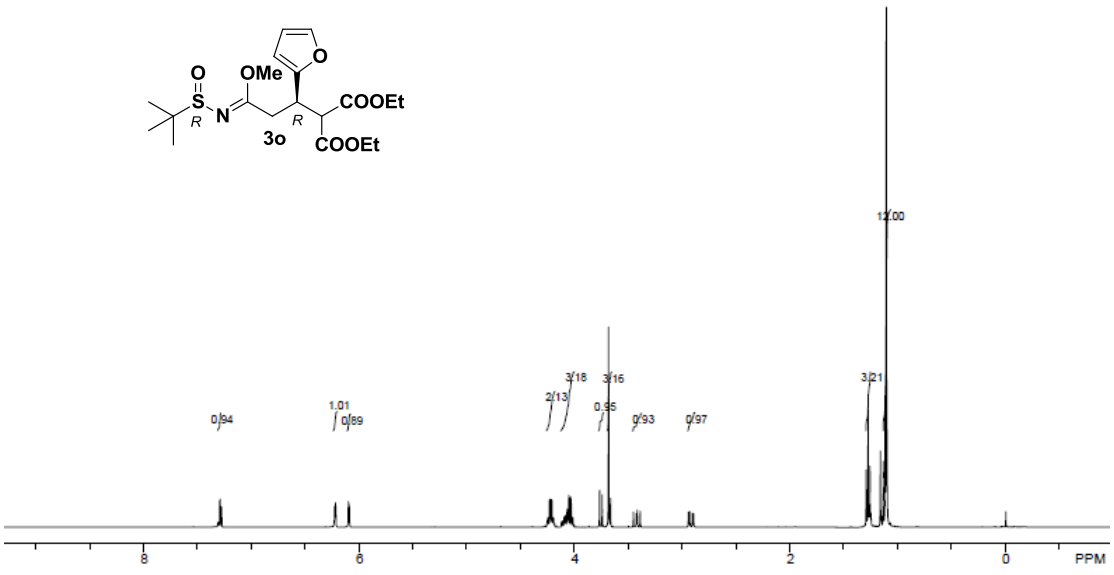

Me
N
O
S
R
N
OMe
R
COOEt
COOEt
3m
12.24
4.01
3.00
3.04
1.96
3.49
1.03
1.02
1.00
1.12
1.00
PPM

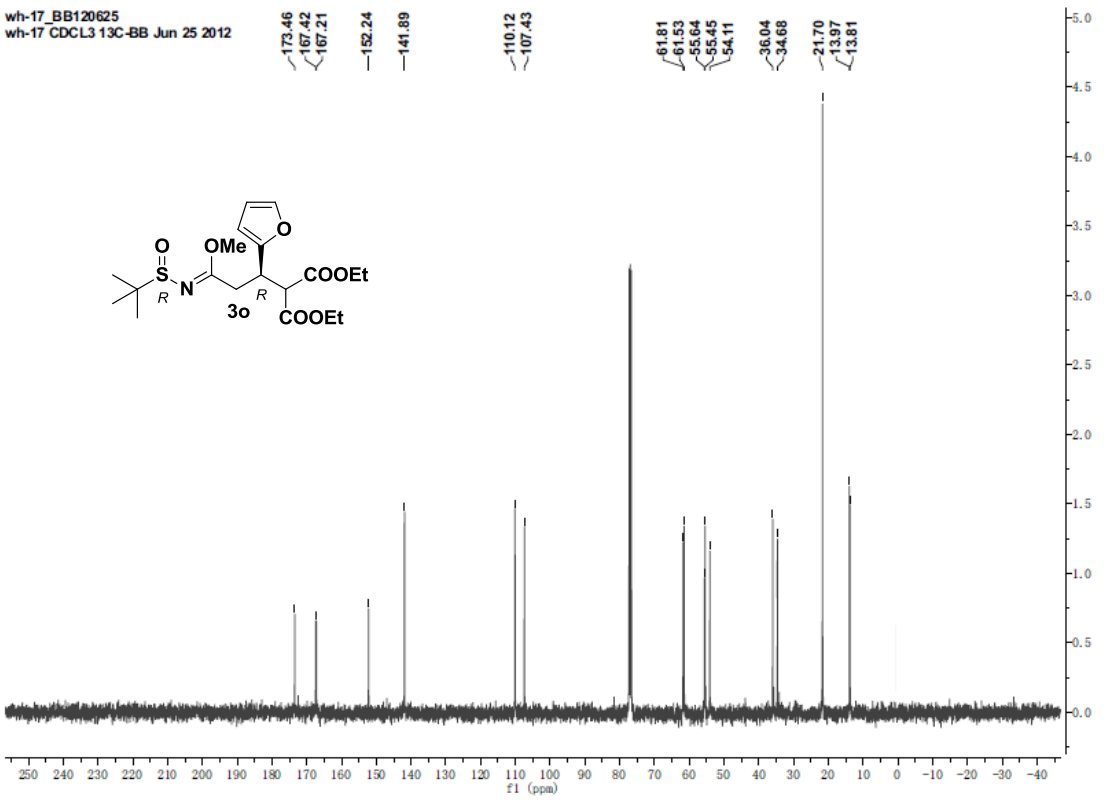

wh-15_BB120625
wh-15 CDCL3 13C-BB Jun 25 2012
174.55
168.08
167.58
136.60
127.15
127.02
121.54
119.25
118.95
112.20
108.96
77.31
76.99
76.68
61.62
61.15
57.38
55.25
53.90
36.78
33.87
32.65
21.39
13.99
13.47
Me
N
O
S
N
OMe
R
R
COOEt
COOEt
3m
f1 (ppm)

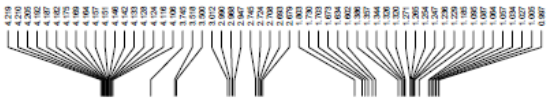

S
O
S
N
OMe
R
R
COOEt
COOEt
3n
9.08
4.08
3.09
3.00
2.03
2.08
1.04
0.97
PPM

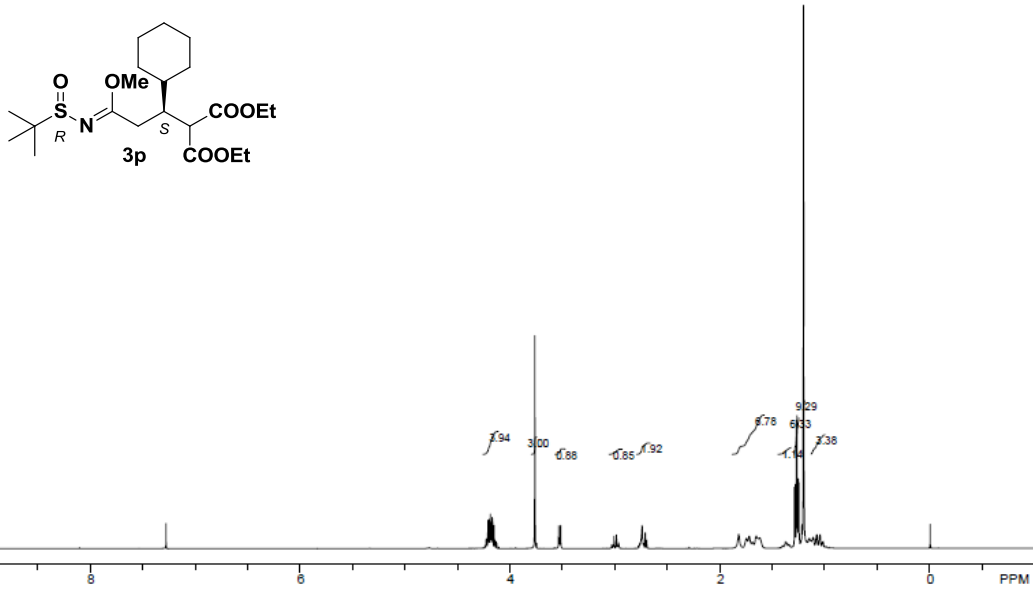

wh-16_BB120625
wh-16 CDCL3 13C-BB Jun 25 2012
173.51
167.64
167.29
139.52
127.01
125.58
122.56
77.31
76.99
76.67
61.79
61.40
57.37
55.66
53.95
37.85
36.60
21.66
13.99
13.67
S
O
OMe
S
N
R
R
COOEt
COOEt
3n
f1 (ppm)

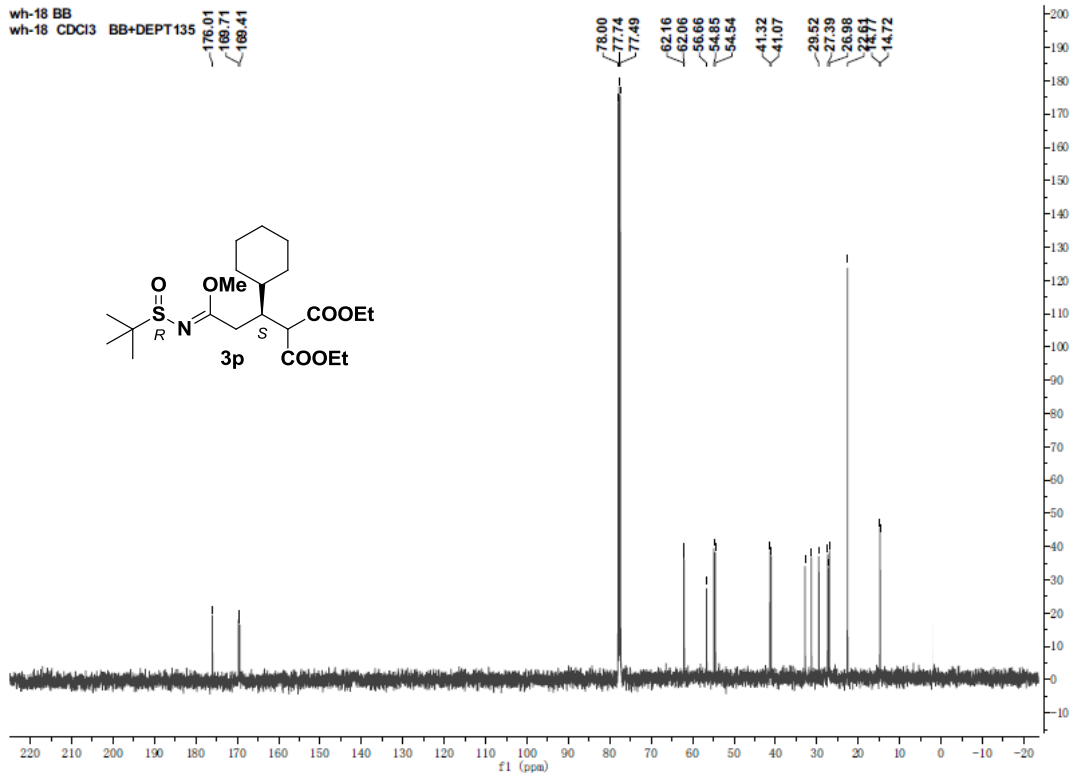


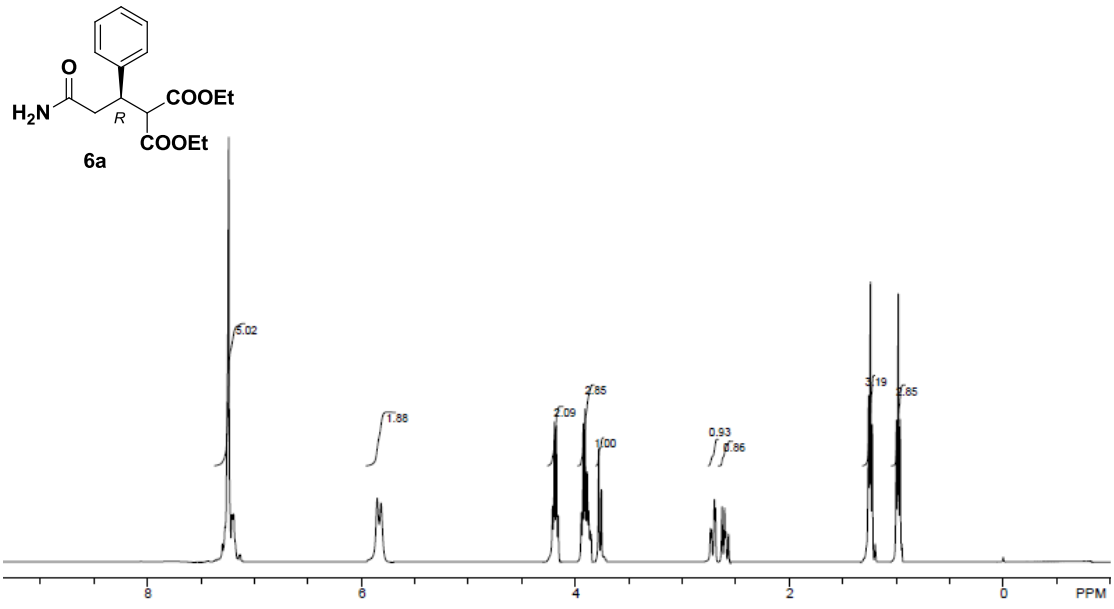

O
O
OMe
S
N
R
R
COOEt
COOEt
3o
12.00
3.21
3.18
3.16
2.13
1.01
0.94
0.89
0.95
0.93
0.97
PPM

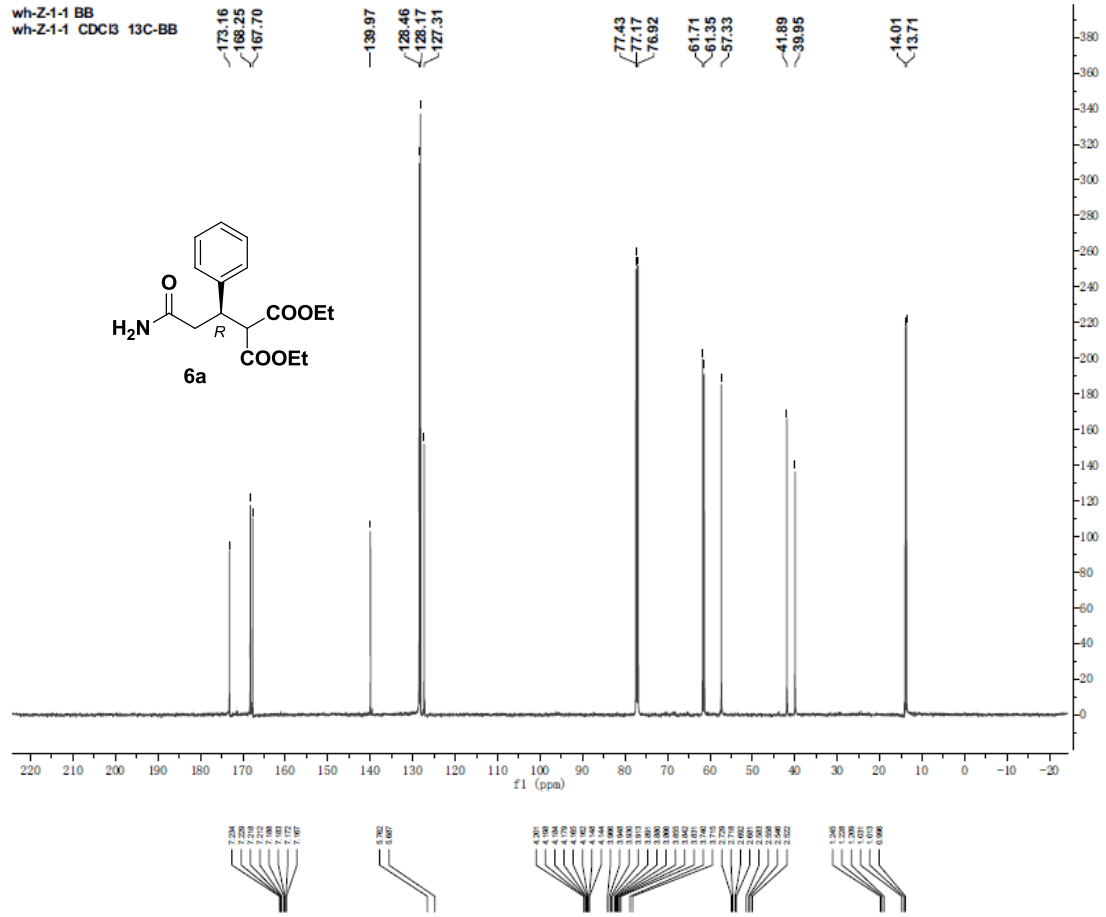

wh-17_BB120625
wh-17 CDCL3 13C-BB Jun 25 2012
173.46
167.42
167.21
152.24
141.89
110.12
107.43
61.81
61.53
55.64
55.45
54.11
36.04
34.68
21.70
13.97
13.81
O
OMe
O
S
N
R
R
COOEt
COOEt
3o
f1 (ppm)




O
OMe
S
N
R
S
COOEt
COOEt
3p
1.94
3.00
0.88
0.85
1.92
9.78
9.29
6.33
1.14
7.38
PPM

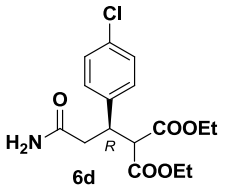

wh-18 BB
wh-18 CDCl3 BB+DEPT135
176.01
169.71
169.41
78.00
77.74
77.49
62.16
62.06
56.66
54.85
54.54
41.32
41.07
29.52
27.39
26.98
22.61
14.72
O
S
N
R
OMe
S
COOEt
COOEt
3p
f1 (ppm)


O
H2N
R
COOEt
COOEt
6a
5.02
1.88
2.09
2.85
1.00
0.93
0.86
3.19
1.85
PPM

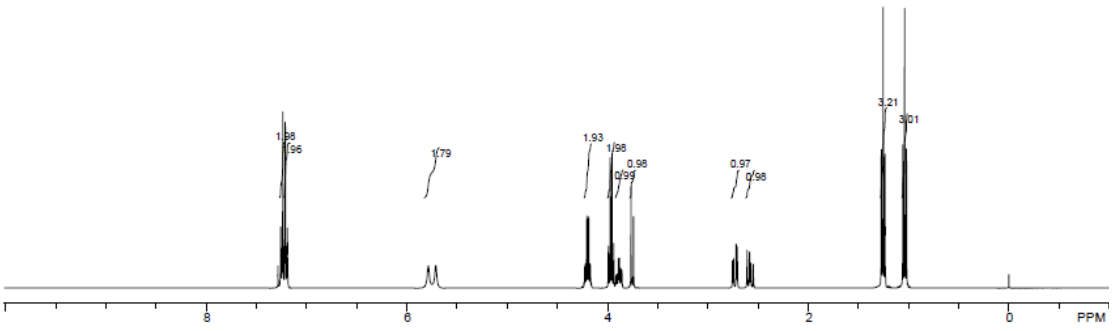

wh-Z-1-1 BB
wh-Z-1-1 CDCl3 13C-BB
173.16
168.25
167.70
139.97
128.46
128.17
127.31
77.43
77.17
76.92
61.71
61.35
57.33
41.89
39.95
14.01
13.71
f1 (ppm)

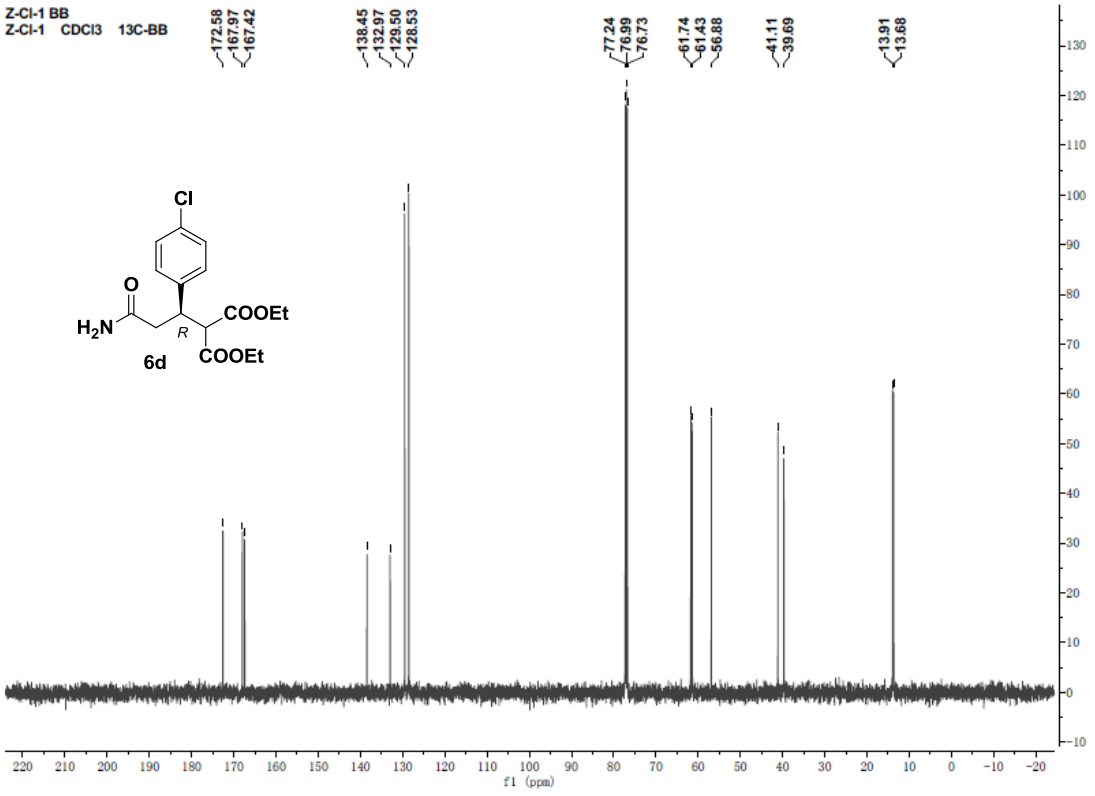
O
H2N
R
COOEt
COOEt

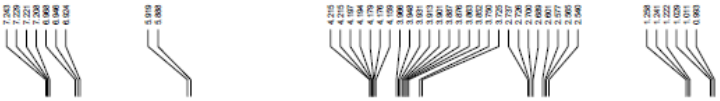
6a

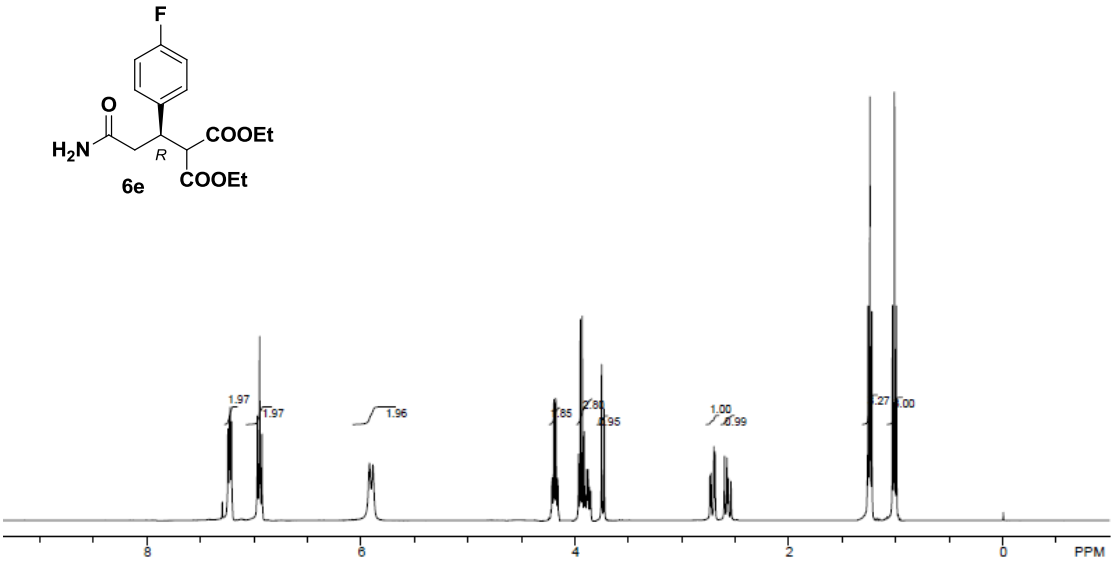

Cl
O
H2N
R
COOEt
COOEt

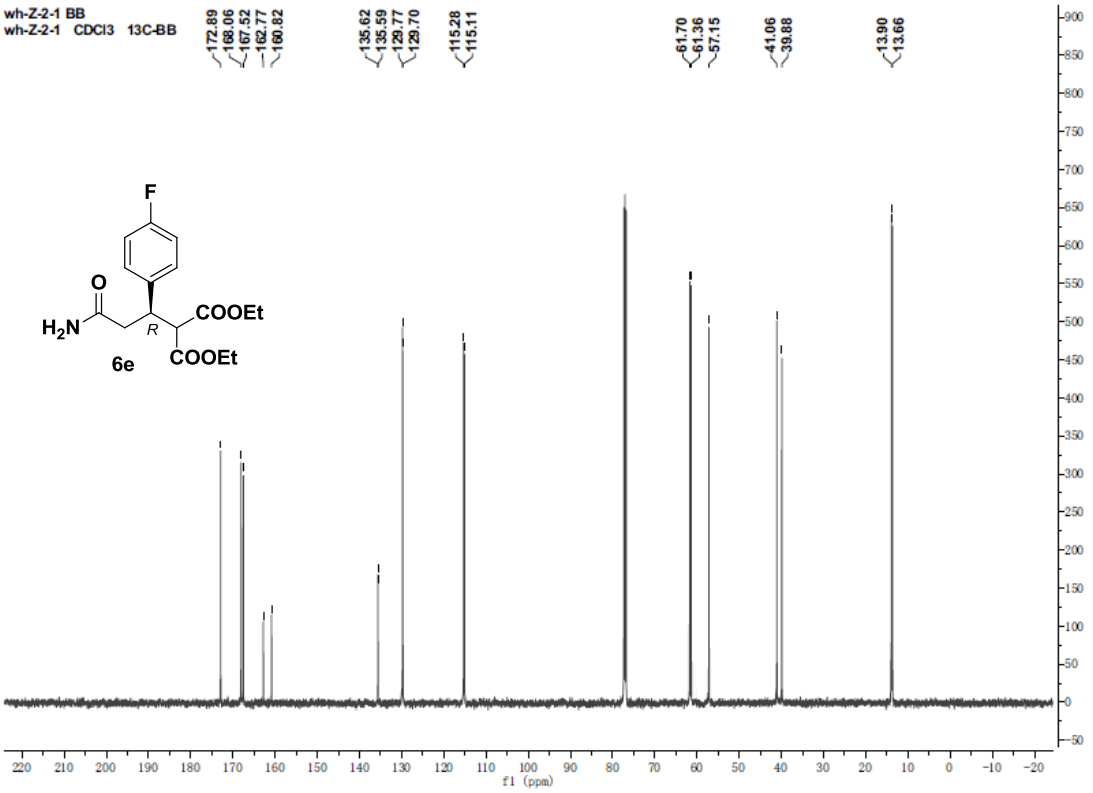
6d

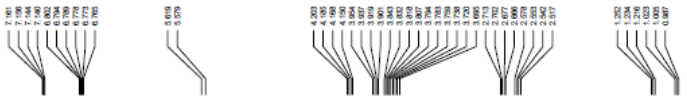

1.98
1.96
1.79
1.93
1.98
0.98
0.99
0.97
0.98
3.21
3.01
PPM

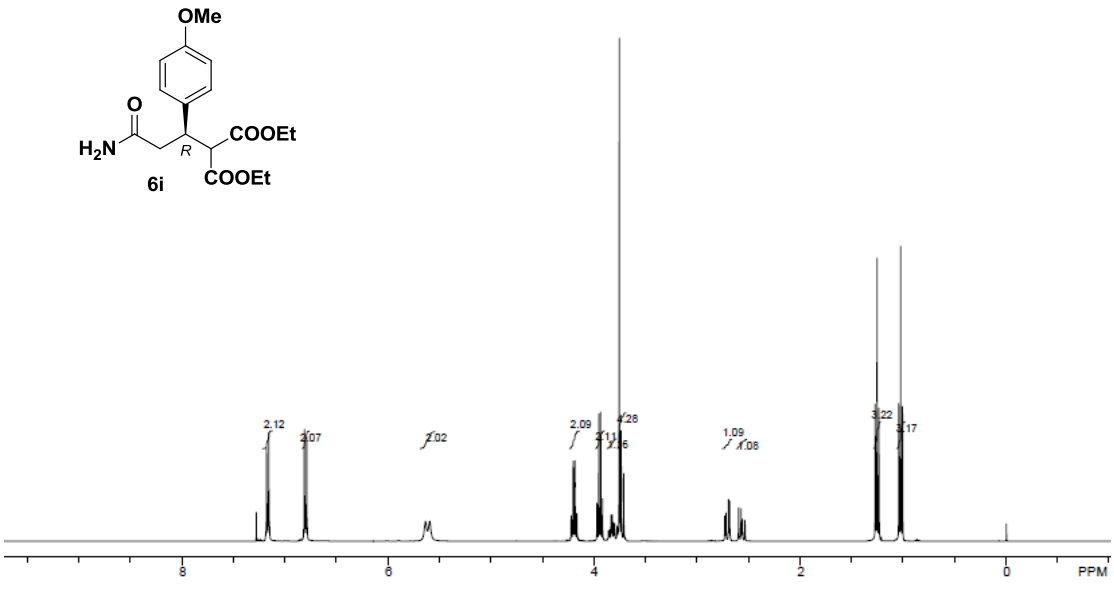

Z-Cl-1 BB
Z-Cl-1 CDCl3 13C-BB
172.58
167.97
167.42
138.45
132.97
129.50
128.53
77.24
76.99
76.73
61.74
61.43
56.88
41.11
39.69
13.91
13.68
Cl
O
H2N
R
COOEt
COOEt
6d
f1 (ppm)

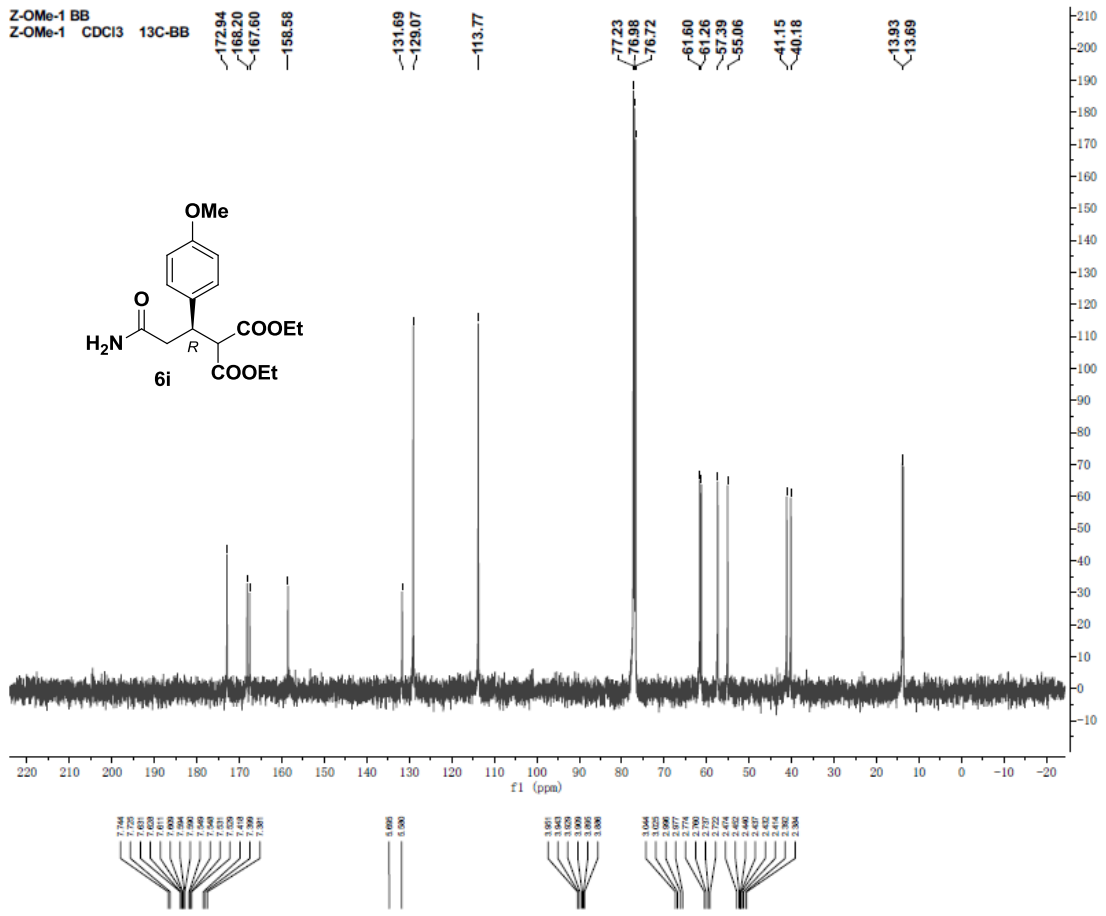


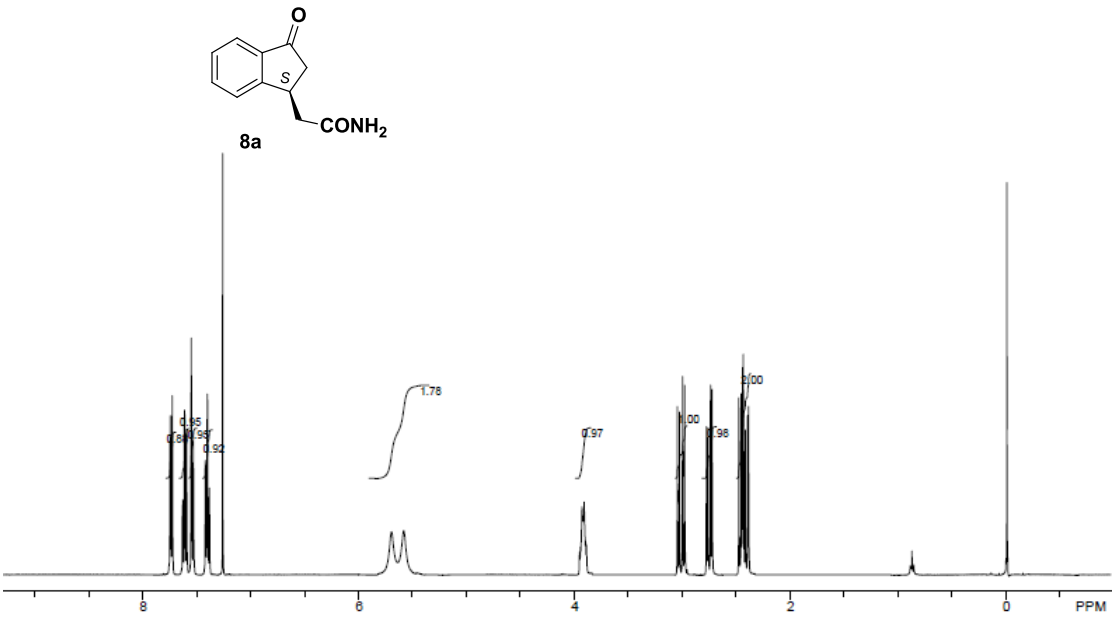

F
O
H2N
R
COOEt
COOEt
6e
1.97
1.97
1.96
1.85
2.80
3.95
1.00
0.99
2.27
3.00
PPM

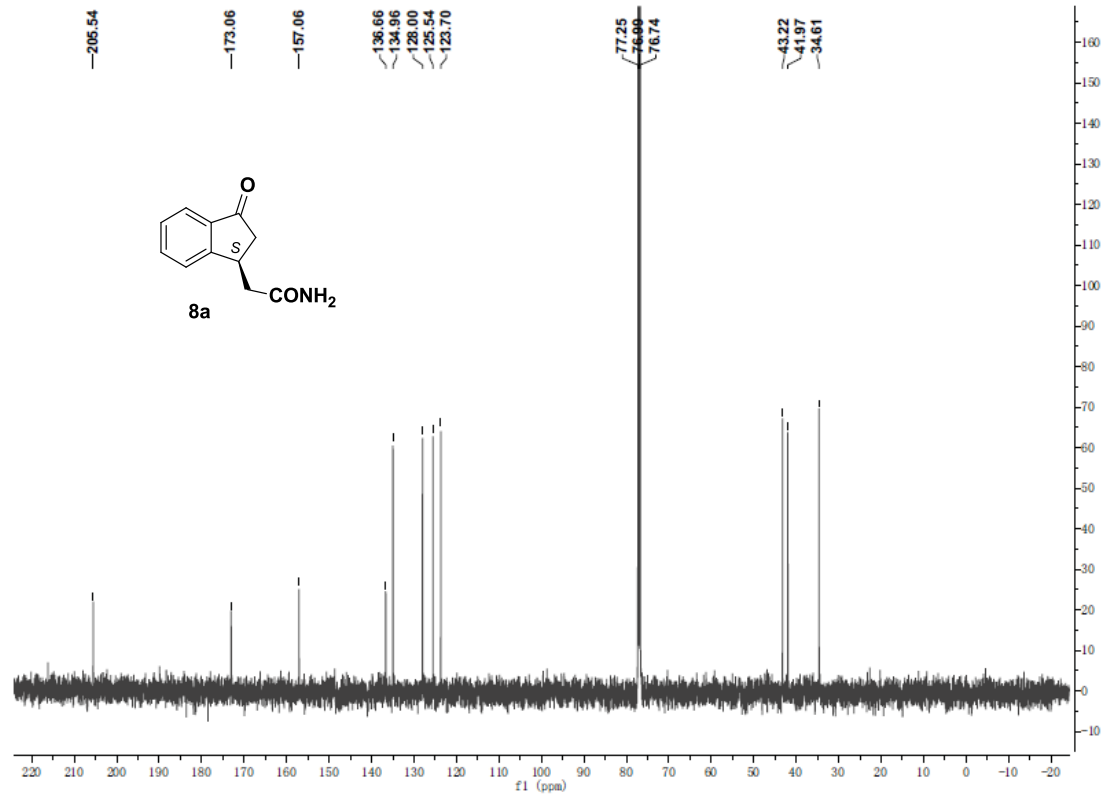

wh-Z-2-1 BB
wh-Z-2-1 CDCl3 13C-BB
172.89
168.06
167.52
162.77
160.82
135.62
135.59
129.77
129.70
115.28
115.11
61.70
61.36
57.15
41.06
39.88
13.90
13.66
F
O
H2N
R
COOEt
COOEt
6e
f1 (ppm)

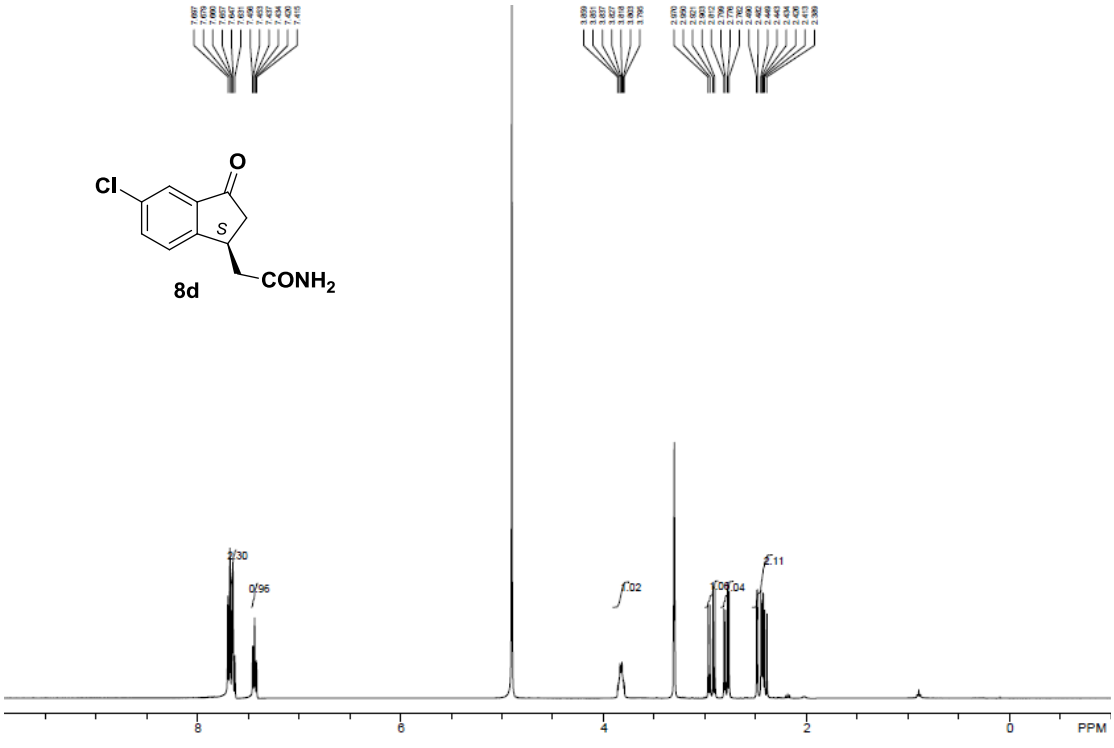


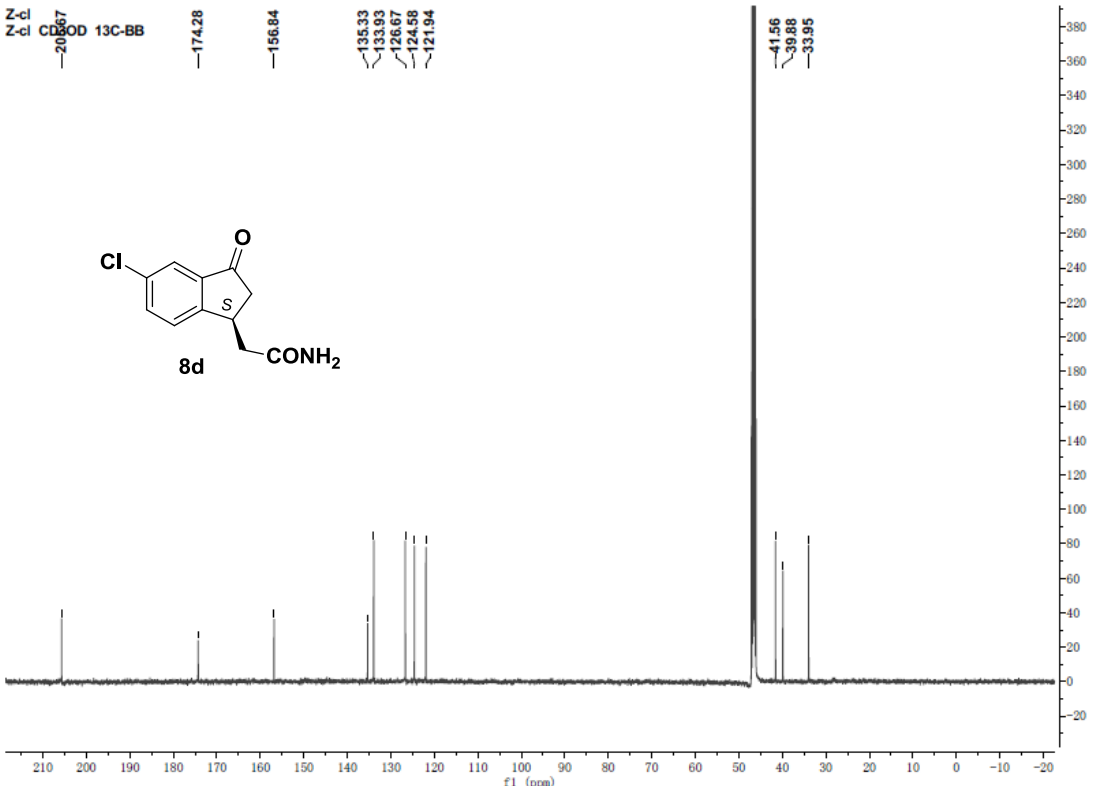

OMe
O
H2N
R
COOEt
COOEt
6i
2.12
2.07
2.02
2.09
2.11
2.28
1.09
1.08
3.22
3.17
PPM

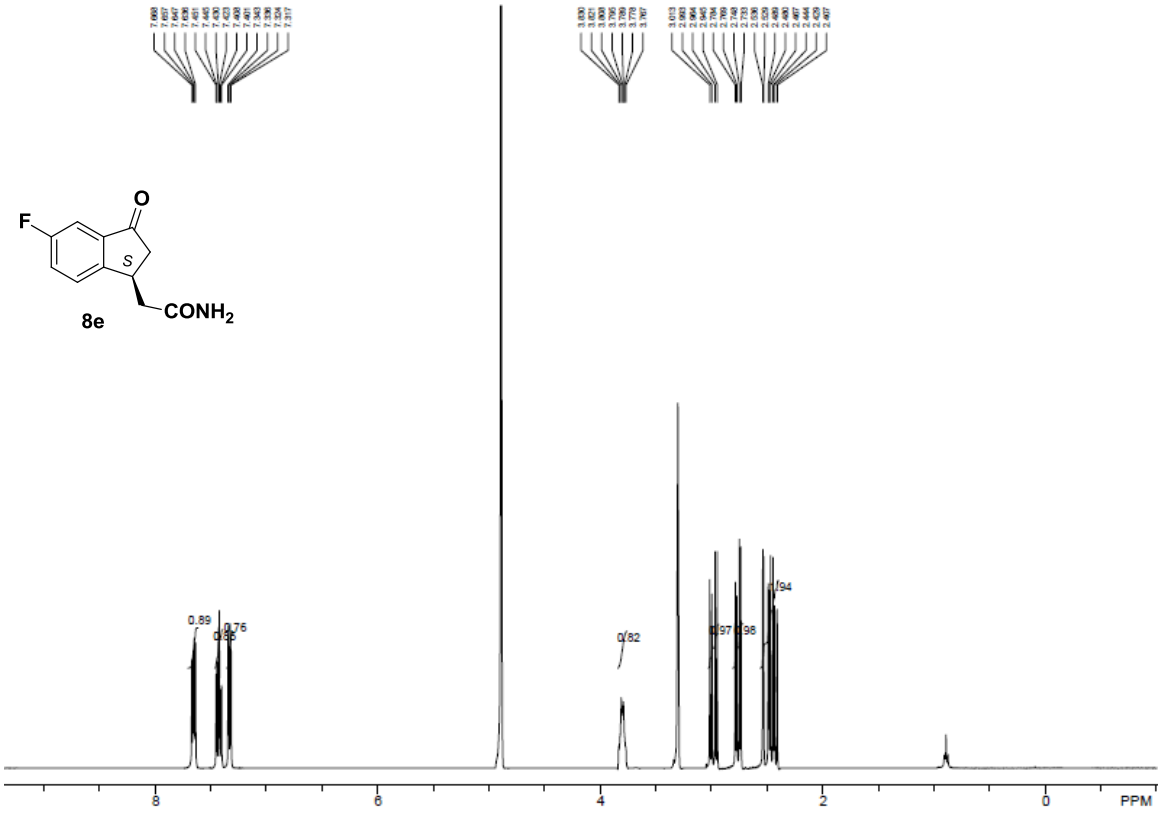

Z-OMe-1 BB
Z-OMe-1 CDCl3 13C-BB
172.94
168.20
167.60
158.58
131.69
129.07
113.77
77.23
76.98
76.72
61.60
61.26
57.39
55.06
41.15
40.18
13.93
13.69
OMe
O
H2N
R
COOEt
COOEt
6i
f1 (ppm)

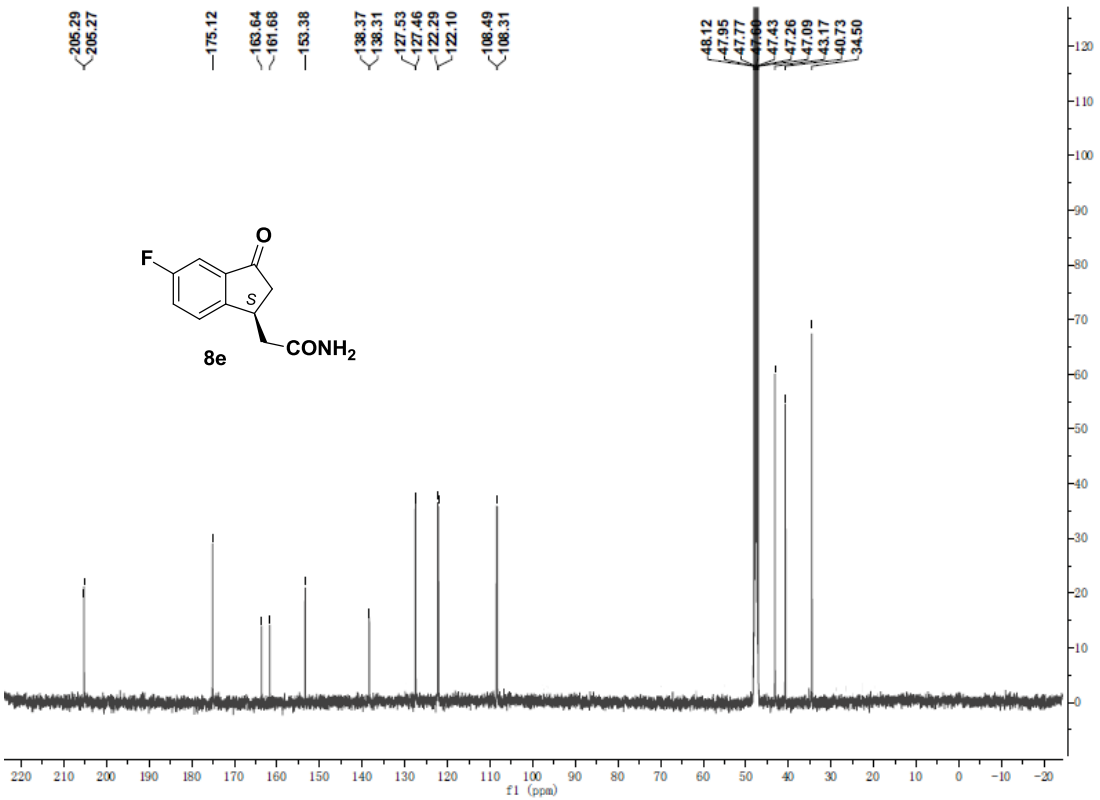

O
S
CONH2
8a
1.78
0.97
1.00
0.98
1.00
0.85
0.97
0.92
PPM

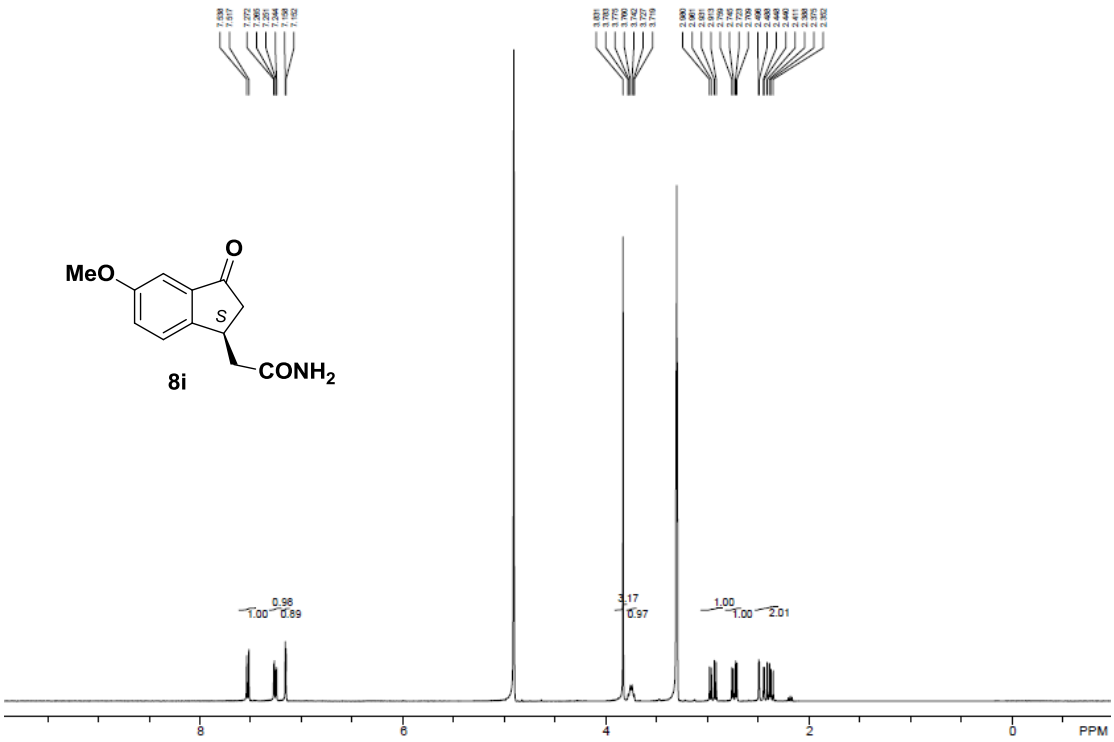

205.54
173.06
157.06
136.66
134.96
128.00
125.54
123.70
77.25
76.99
76.74
43.22
41.97
34.61
O
S
CONH2
8a
f1 (ppm)

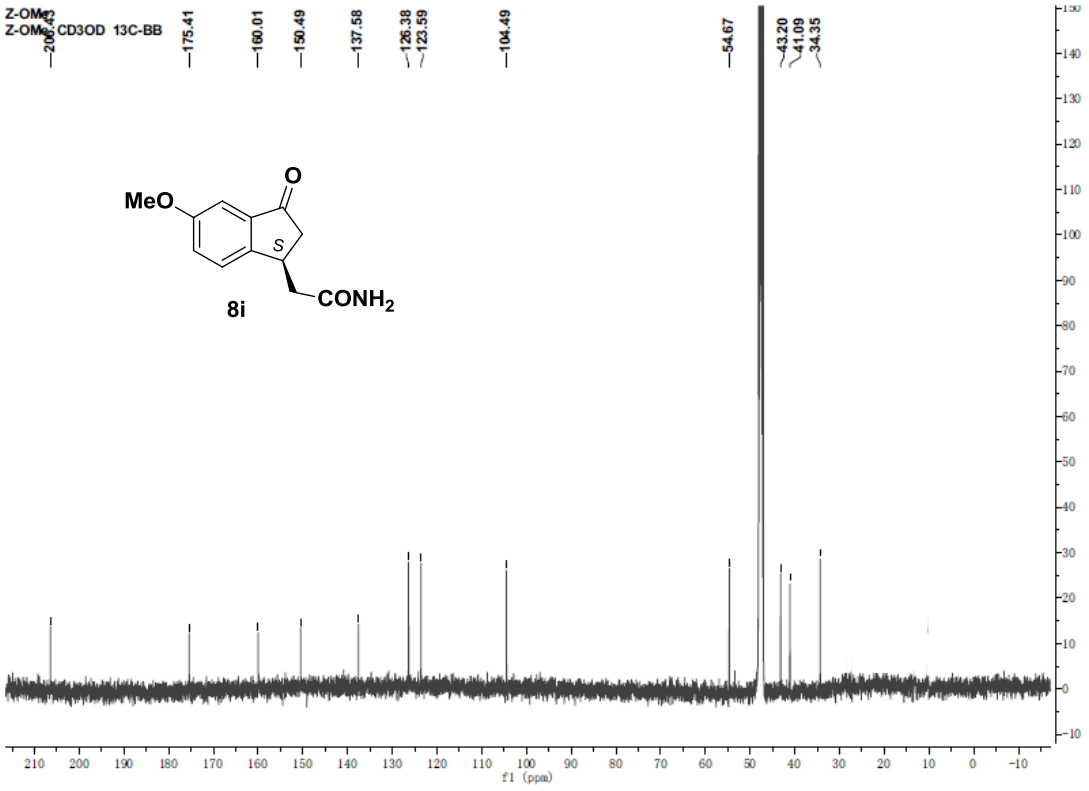

Cl
O
S
CONH2
8d
1.30
0.96
1.02
1.06
1.04
1.11
PPM


Z-cl
Z-cl CD3OD 13C-BB
49.07
174.28
156.84
135.33
133.93
126.67
124.58
121.94
41.56
39.88
33.95
Cl
O
S
CONH2
8d
f1 (ppm)


F
O
S
CONH2
8e
0.89
0.76
0.82
0.97
0.98
1.94
PPM


205.29
205.27
175.12
163.64
161.68
153.38
138.37
138.31
127.53
127.46
122.29
122.10
108.49
108.31
48.12
47.95
47.77
47.60
47.43
47.26
47.09
43.17
40.73
34.50
F
O
S
CONH2
8e
f1 (ppm)


MeO
O
S
CONH2
8i
0.96
1.00
0.89
3.17
0.97
1.00
1.00
2.01
PPM


Z-OMe3
Z-OMe3 CD3OD 13C-BB
206.43
175.41
160.01
150.49
137.58
126.38
123.59
104.49
54.67
43.20
41.09
34.35
MeO
O
S
CONH2
8i
f1 (ppm)