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Supporting Information (SI)

The Catalyst-Free Chemoselective $\alpha\text{-Sulfenylation}/\beta\text{-Thiolation}$ for $\alpha,\beta\text{-Unsaturated Carbonyl Compounds}$

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1. Experimental Section

General Remarks

All reagents were of analytical grade and obtained from commercial suppliers; unless stated otherwise, all reagents were used without further purification. The solvents DMF, DMSO, THF and toluene were commercial anhydrous reagents and 1,4-dioxane was further disposed under sodium reflux. Chalcones were synthesized by standard method and were confirmed by GC-MS. The crude products were all recrystallized from 98% ethanol. The column chromatography was performed on Biotage Isolera Prime. The ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AM-400 spectrometer (400 MHz and 100 MHz, respectively) using TMS as internal standard. CDCl₃ was used as the NMR solvent for vatious products. Chemical shifts were recorded in parts per million (d) relative to CDCl₃ at 7.26 for ¹H NMR and 77.23 for ¹³C NMR. Gas chromatography-mass spectrometry (GC-MS) was performed on Agilent 7890A/5975C and Gas chromatograms were recorded on Agilent 7890A. Liquid chromatograms were recorded on Agilent 1260 Infinity.

2. Experimental Procedure

General procedure

General procedure A for optimization of α-Sulfenylation reaction condition: A mixture of the chalcone (104.1 mg, 0.5 mmol), N-(phenylthio)phthalimide, K₂CO₃ (6.9 mg, 0.05 mmol) and solvent was placed in a 10-mL reaction tube with a magnetic stirring bar. After being sealed with a cap, the reaction tube was purged with nitrogen for 10 min. The tube was then placed into an oil bath and the reaction was conducted at 70 °C for 2h. After the reaction was finished, dodecane (50.0 mg) was added into the mixture as an internal standard. The resulting suspension was diluted with water (2.0 mL) and extracted with ethyl acetate (6.5 mL). The upper clear mixture (0.5 mL) was collected for GC analysis.

General procedure B for α-Sulfenylation of α,β-unsaturated carbonyl compounds with N-(phenylthio)phthalimide: A mixture of the α,β-unsaturated ketone (0.5 mmol), N-(phenylthio)phthalimide (191.5 mg, 0.75 mmol), K_2CO_3 (6.9 mg, 0.05 mmol) and DMSO (1.5 mL) was placed in a 10-mL reaction tube with a magnetic stirring bar. After being sealed with a cap, the tube was heated at 70 °C for 3-6 hours. The resulting suspension was diluted with water (2.0 mL) and extracted with ethyl acetate (6.5 mL × 3). The combined organic layers were washed with brine and dried over MgSO₄, and the solvents were removed under vacuum. The resultant crude residue was purified by column chromatography to give the product 3 (eluent: EA: PE = 1:100~1:20). The products were further characterized by GC/MS, HRMS, 1 H NMR and 13 C NMR.

General procedure C for optimization of β-thiolation reaction condition: A mixture of the chalcone (104.1 mg, 0.5 mmol), diphenyldisulfide, bis(pinacolato)diboron (190.5 mg, 0.75 mmol), K_2CO_3 (6.9 mg, 0.05 mmol) and solvent was placed in a 10-mL reaction tube with a magnetic stirring bar. After being sealed with a cap, the reaction tube was purged with nitrogen for 10 min. The tube was then placed into an oil bath and the reaction was conducted at 70 °C for 2h. After the reaction was finished, biphenyl (15.0 mg) was added into the mixture as an internal standard. The resulting suspension was diluted with water (2.0 mL) and extracted with ethyl acetate (6.5 mL). The upper clear mixture (0.5 mL) was collected for LC analysis.

General procedure D for β-thiolation of α,β-unsaturated carbonyl compounds with diphenyldisulfide and bis(pinacolato)diboron: A mixture of the α ,β-unsaturated carbonyl compound (0.5 mmol), diphenyldisulfide (109.2 mg, 0.5 mmol), bis(pinacolato)diboron (190.5 mg, 0.75 mmol), K₂CO₃ (13.8 mg, 0.10 mmol) and n-BuOH (1.5 mL) was placed in a 10-mL reaction tube with a magnetic stirring bar. After being sealed with a cap, the reaction tube was purged with nitrogen for 10 min. The tube was then placed into an oil bath and the reaction was conducted at 80 °C for 2h. The resulting suspension was diluted with water (2.0 mL) and extracted with ethyl acetate (6.5 mL × 3). The combined organic layers were washed with brine and dried over MgSO₄, and the solvents were removed under vacuum. The resultant crude residue was purified by column chromatography to give the product 6 (eluent: EA: PE = 1:100~1:20). The products were further characterized by HRMS, ¹H NMR and ¹³C NMR.

General procedure E for β-thiolation of chalcone with 1,2-diaryldisulfides and bis(pinacolato)diboron: A mixture of the chalcone (104.1 mg, 0.5 mmol), 1,2-diaryldisulfide (0.5 mmol), bis(pinacolato)diboron (190.5 mg, 0.75 mmol), K_2CO_3 (13.8 mg, 0.10 mmol) and n-BuOH (1.5 mL) was placed in a 10-mL reaction tube with a magnetic stirring bar. After being sealed with a cap, the reaction was purged with nitrogen for 10 min. The tube was then placed into an oil bath and the reaction was conducted at 80 °C for 2h. The resulting suspension was diluted with water (2.0 mL) and extracted with ethyl acetate (6.5 mL × 3). The combined organic layers were washed with brine and dried over MgSO₄, and the solvents were removed under vacuum. The resultant crude residue was purified by column chromatography to give the product 6 (eluent: EA: PE = 1:100~1:20). The products were further characterized by HRMS, ¹H NMR and ¹³C NMR.

3. Characterization and NMR Spectra of the α-Sulfenylation Products:

3a 1,3-diphenyl-2-(phenylthio)prop-2-en-1-one.

Z/E = 80:20, major isomer: ${}^{1}H$ NMR (400 MHz, CDCl₃) δ 7.80 (d, J = 7.3 Hz, 2H), 7.73 (d, J = 7.2 Hz, 2H), 7.51-7.31 (m, 6H), 7.25-7.18 (m, 2H), 7.17-7.07 (m, 4H). ${}^{13}C$ NMR (101 MHz, CDCl₃) δ 194.40, 139.83, 137.40, 135.60, 134.66, 133.11, 132.49, 131.31(2C), 130.43(2C), 129.44, 129.39(2C), 128.96(2C), 128.49(2C), 128.12(2C), 127.39. MS (GC-MS) m/z: 316 (M+), 211, 178, 170, 134, 105, 77.

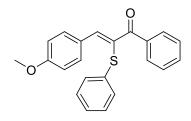
HRMS (EI) m/z calcd for $C_{21}H_{16}OS$ [M]+ 316.0922, found 316.0921.

3b 1-phenyl-2-(phenylthio)-3-(p-tolyl)prop-2-en-1-one.

Z/E = 83:17, major isomer: ${}^{1}H$ NMR (400 MHz, CDCl₃) δ 7.72 (d, J = 7.6 Hz, 4H), 7.48 (t, J = 7.3 Hz, 1H), 7.42-7.31 (m, 3H), 7.21 (dd, J = 16.3, 9.8 Hz, 4H), 7.16-7.07 (m, 3H), 2.39 (s, 3H). ${}^{13}C$ NMR (101 MHz, CDCl₃) δ 194.56, 140.94, 140.00, 137.62, 134.28, 133.53, 132.35, 131.85, 130.96 (2C), 130.59 (2C), 129.38 (2C), 129.24 (2C), 128.95 (2C), 128.10 (2C), 127.20, 21.54.

MS (GC-MS) m/z: 330 (M+), 315, 225, 210, 181, 165, 147, 105, 77. HRMS (EI) m/z calcd for $C_{22}H_{18}O_{2}S$ [M]+ 330.1078, found 330.1076.

3c 3-(4-methoxyphenyl)-1-phenyl-2-(phenylthio)prop-2-en-1-one.



Z/E = 86:14, major isomer: ${}^{1}H$ NMR (400 MHz, CDCl₃) δ 7.84 (d, J = 8.8 Hz, 2H), 7.71 (d, J = 7.8 Hz, 2H), 7.47 (dd, J = 14.4, 7.3 Hz, 2H), 7.42-7.31 (m, 2H), 7.26-7.07 (m, 5H), 6.94 (d, J = 8.7 Hz, 2H), 3.84 (s, 3H). ${}^{13}C$ NMR (101 MHz, CDCl₃) δ 194.72, 160.84, 142.08, 137.86, 133.93, 132.59 (2C), 132.20, 132.17, 130.39 (2C), 129.34 (2C), 128.95 (2C), 128.07 (2C), 127.24, 126.95, 113.97 (2C), 55.40.

MS (GC-MS) *m/z*: 346 (M+), 315, 237, 210, 197, 165, 149, 105, 77.

HRMS (EI) m/z calcd for $C_{22}H_{18}O_2S$ [M]+ 346.1028, found 346.1027.

3d 1-(4-methoxyphenyl)-3-phenyl-2-(phenylthio)prop-2-en-1-one.

Z/E = 95:5, major isomer: H NMR (400 MHz, CDCl₃) δ 7.78 (dd, J = 8.0, 6.2 Hz, 4H), 7.47-7.32 (m, 3H), 7.28-7.22 (m, 3H), 7.15-7.09 (m, 3H), 6.87-6.82 (m, 2H), 3.83 (s, 3H). H CNMR (101 MHz, CDCl₃) δ 192.91, 163.30, 138.16, 135.71, 134.83, 132.99, 131.93 (2C), 131.50 (2C), 130.27 (2C), 129.91, 129.16, 128.91 (2C), 128.46 (2C), 127.44, 113.45 (2C), 55.48.

MS (GC-MS) *m/z*: 346 (M+), 237, 211, 197, 135, 92, 77.

HRMS (EI) m/z calcd for $C_{22}H_{18}O_2S$ [M]+ 346.1028, found 346.1026.

3e -(4-bromophenyl)-1-phenyl-2-(phenylthio)prop-2-en-1-one.

Z/E = 70:30, major isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, J = 7.5 Hz, 2H), 7.58 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 7.40 (dd, J = 12.7, 7.2 Hz, 1H), 7.27 (t, J = 7.7 Hz, 2H), 7.21-7.15 (m, 3H), 7.13-7.08 (m, 1H), 7.07-7.00 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 194.16, 137.78, 137.14, 136.53, 133.54, 132.62, 131.79 (2C), 131.68 (2C), 131.52 (2C), 130.01, 129.34 (2C), 129.02 (2C), 128.15 (2C), 127.63, 123.56.

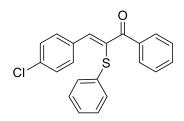
MS (GC-MS) *m/z*: C₂₁H₁₅⁷⁹BrOS 394 (M+), 315, 285, 245, 210, 165, 105, 77.

MS (GC-MS) *m/z*: C₂₁H₁₅⁸¹BrOS 352 (M+), 315, 287, 247, 210, 165, 105, 77.

HRMS (EI) m/z calcd for $C_{21}H_{15}^{79}$ BrOS [M]+ 394.0027, found 394.0025.

HRMS (EI) m/z calcd for $C_{21}H_{15}^{81}BrOS$ [M]+ 396.0007, found 396.0010.

3f 3-(4-chlorophenyl)-1-phenyl-2-(phenylthio)prop-2-en-1-one.



Z/E = 80:20, major isomer: ${}^{1}H$ NMR (400 MHz, CDCl₃) δ 7.72 (dd, J = 11.3, 8.2 Hz, 4H), 7.49 (dd, J = 13.2, 6.1 Hz, 1H), 7.44-7.31 (m, 4H), 7.28 (s, 1H), 7.19 (dd, J = 6.4, 3.0 Hz, 2H), 7.16-7.08 (m, 3H). ${}^{13}C$ NMR (101 MHz, CDCl₃) δ 194.19, 137.88, 137.17, 136.34, 135.21, 133.10, 132.93, 132.61, 131.61 (2C), 131.47 (2C), 129.35 (2C), 129.02 (2C), 128.73 (2C), 128.15 (2C), 127.60.

MS (GC-MS) *m/z*: C₂₁H₁₅³⁵ClOS 350 (M+), 315, 241, 210, 165, 105, 77.

MS (GC-MS) *m/z*: C₂₁H₁₅³⁷ClOS 352 (M+), 317, 243, 210, 165, 105, 77.

HRMS (EI) m/z calcd for $C_{21}H_{15}^{35}ClOS$ [M]+ 350.0532, found 350.0529.

HRMS (EI) m/z calcd for $C_{21}H_{15}^{37}ClOS$ [M]+ 352.0503, found 352.0505.

3g 1-(4-chlorophenyl)-3-phenyl-2-(phenylthio)prop-2-en-1-one.

Z/E = 90:10, major isomer: ${}^{1}H$ NMR (400 MHz, CDCl₃) δ 7.80 (d, J = 7.1 Hz, 2H), 7.65 (d, J = 8.5 Hz, 2H), 7.47-7.37 (m, 3H), 7.35 (s, 1H), 7.34-7.29 (m, 2H), 7.15 (ddd, J = 9.2, 7.0, 3.3 Hz, 5H). ${}^{13}C$ NMR (101 MHz, CDCl₃) δ 193.30, 139.51, 138.81, 135.68, 134.50, 132.82, 132.58, 131.41 (2C), 130.69 (2C), 130.45 (2C), 129.57, 129.04 (2C), 128.53 (2C), 128.41 (2C), 127.56.

MS (GC-MS) m/z: C₂₁H₁₅³⁵ClOS 350 (M+), 315, 241, 211, 178, 165, 139, 111.

MS (GC-MS) *m/z*: C₂₁H₁₅³⁷ClOS 352 (M+), 317, 243, 211, 178, 165, 141, 111.

HRMS (EI) m/z calcd for $C_{21}H_{15}^{35}ClOS$ [M]+ 350.0532, found 350.0529.

HRMS (EI) m/z calcd for $C_{21}H_{15}^{37}ClOS$ [M]+ 352.0503, found 352.0502.

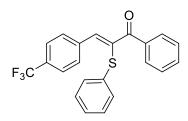
3h 1-(4-fluorophenyl)-3-phenyl-2-(phenylthio)prop-2-en-1-one.

Z/E = 77:23, major isomer: 1 H NMR (400 MHz, CDCl₃) δ 7.80 (d, J = 7.5 Hz, 2H), 7.75 (dd, J = 8.6, 5.5 Hz, 2H), 7.47-7.36 (m, 3H), 7.34 (s, 1H), 7.16 (ddd, J = 17.1, 7.0, 3.3 Hz, 5H), 7.01 (q, J = 8.5 Hz, 2H). 13 C NMR (101 MHz, CDCl₃) δ 192.98, 165.31 (d, $J_{CF} = 254.2$ Hz, 1C), 139.01, 135.33, 134.58, 133.56 (d, $J_{CF} = 3.0$ Hz, 1C), 131.90 (d, $J_{CF} = 9.3$ Hz, 2C), 131.48 (2C), 130.38 (2C), 129.45, 128.99 (2C), 128.60, 128.51 (2C), 127.55, 115.23 (d, $J_{CF} = 21.9$ Hz, 2C).

MS (GC-MS) *m/z*: 334 (M+), 241, 225, 211, 178, 123, 95.

HRMS (EI) m/z calcd for $C_{21}H_{15}FOS$ [M]+ 334.0828, found 334.0827.

3i 1-phenyl-2-(phenylthio)-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-one.



Z/E = 80:20, major isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, J = 8.1 Hz, 2H), 7.70 (dd, J = 15.8, 7.9 Hz, 4H), 7.51 (dd, J = 13.2, 6.2 Hz, 1H), 7.36 (t, J = 7.7 Hz, 2H), 7.26 (d, J = 8.6 Hz, 2H), 7.23-7.05 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 193.88, 138.15 (d, $J_{CF} = 1.0$ Hz, 1C), 136.86, 135.78, 133.56, 132.83, 132.08 (2C), 131.88, 131.11 (dd, $J_{CF} = 65.7$ Hz, 1C), 130.29 (2C), 129.34 (2C), 129.04 (2C), 128.79, 128.19 (2C), 125.36 (dd, $J_{CF} = 4.4$ Hz, 2C), 123.91 (q, $J_{CF} = 264.6$ Hz, 1C).

MS (GC-MS) *m/z*: 384(M+), 291, 275, 211, 178, 145.

HRMS (EI) *m/z* calcd for C₂₂H₁₅F₃OS [M]+ 384.0796, found 384.0797.

3j 3-(benzo[d][1,3]dioxol-5-yl)-1-phenyl-2-(phenylthio)prop-2-en-1-one.

Z/E = 85:15, major isomer: ${}^{1}H$ NMR (400 MHz, CDCl₃) δ 7.75-7.66 (m, 2H), 7.60 (d, J = 1.7 Hz, 1H), 7.50-7.45 (m, 1H), 7.41-7.32 (m, 3H), 7.26-7.18 (m, 3H), 7.17-7.07 (m, 3H), 6.85 (d, J = 8.1 Hz, 1H), 6.00 (s, 2H). ${}^{13}C$ NMR (101 MHz, CDCl₃) δ 194.62, 148.93, 147.82, 141.49, 137.68, 133.60, 132.83, 132.27, 130.59 (2C), 129.33 (2C), 128.98 (2C), 128.75, 128.09 (2C), 127.10, 126.69, 109.90, 108.36, 101.58.

MS (GC-MS) *m/z*: 360(M+), 251, 225, 197, 105, 77.

HRMS (EI) m/z calcd for $C_{22}H_{16}O_3S$ [M]+ 360.0820, found 360.0821.

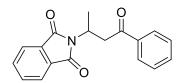
3k 3-(furan-2-yl)-1-phenyl-2-(phenylthio)prop-2-en-1-one.

Z/E = 85:15, major isomer: ${}^{1}H$ NMR (400 MHz, CDCl₃) δ 7.75-7.65 (m, 2H), 7.55 (d, J = 1.5 Hz, 1H), 7.48 (dt, J = 11.4, 6.6 Hz, 1H), 7.38-7.30 (m, 3H), 7.27-7.21 (m, 3H), 7.16-7.10 (m, 3H), 6.55 (dd, J = 3.5, 1.7 Hz, 1H). ${}^{13}C$ NMR (101 MHz, CDCl₃) δ 193.69, 150.61, 144.58, 137.59, 132.52, 132.33, 131.87, 130.79 (2C), 129.27 (2C), 129.02 (2C), 128.23, 128.17 (2C), 122.30, 116.13, 112.78.

MS (GC-MS) *m/z*: 306(M+), 197, 173, 129, 105, 77.

HRMS (EI) m/z calcd for $C_{19}H_{14}O_2S$ [M]+ 306.0715, found 306.0712.

3m' 2-(4-oxo-4-phenylbutan-2-yl)isoindoline-1,3-dione.



 1 H NMR (400 MHz, CDCl₃) δ 8.00-7.90 (m, 2H), 7.87-7.75 (m, 2H), 7.74-7.63 (m, 2H), 7.58-7.50 (m, 1H), 7.49-7.37 (m, 2H), 5.15-4.97 (m, 1H), 3.90 (dd, J = 17.7, 7.9 Hz, 1H), 3.51 (dd, J = 17.7, 6.2 Hz, 1H), 1.55 (d, J = 6.9 Hz, 3H). 13 C NMR (101 MHz, CDCl₃) δ 197.35, 168.28 (2C), 136.61, 133.86 (2C), 133.29, 131.99 (2C), 128.63 (2C), 128.06 (2C), 123.16 (2C), 42.92, 41.88, 19.03.

MS (GC-MS) *m/z*: 293(M+), 278, 188, 174, 146, 130, 105, 77.

HRMS (EI) m/z calcd for 293.1052, found 293.1053.

4. Characterization and NMR Spectra of the β-Thiolation Products:

6a 1,3-diphenyl-3-(phenylthio)propan-1-one.

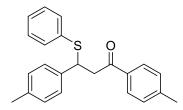
 1 H NMR (400 MHz, CDCl₃) δ 7.91-7.81 (m, 2H), 7.55-7.48 (m, 1H), 7.43-7.37 (m, 2H), 7.37-7.28 (m, 4H), 7.27-7.14 (m, 6H), 4.96 (dd, J = 8.1, 6.0 Hz, 1H), 3.65 (dd, J = 17.2, 8.1 Hz, 1H), 3.57 (dd, J = 17.2, 6.0 Hz, 1H). 13 C NMR (101 MHz, CDCl₃) δ 197.01, 141.26, 136.79, 134.32, 133.28, 132.79 (2C), 128.89 (2C), 128.65 (2C), 128.49 (2C), 128.10 (2C), 127.85 (2C), 127.56, 127.41, 48.29, 44.76.

HRMS (EI) m/z calcd for $C_{21}H_{18}OS$ [M]+ 318.1078, found 318.1088.

6b 1-phenyl-3-(phenylthio)-3-(p-tolyl)propan-1-one.

¹H NMR (400 MHz, CDCl₃) δ 7.91-7.79 (m, 2H), 7.51 (ddd, J = 6.8, 4.0, 1.2 Hz, 1H), 7.40 (dd, J = 10.5, 4.7 Hz, 2H), 7.37-7.29 (m, 2H), 7.27-7.18 (m, 5H), 7.05 (d, J = 8.0 Hz, 2H), 4.94 (dd, J = 8.0, 6.1 Hz, 1H), 3.64 (dd, J = 17.1, 8.3 Hz, 1H), 3.54 (dd, J = 17.2, 5.9 Hz, 1H), 2.27 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 197.15, 138.16, 137.05, 136.82, 134.60, 133.24, 132.58 (2C), 129.22 (2C), 128.90 (2C), 128.63 (2C), 128.11 (2C), 127.70 (2C), 127.44, 47.97, 44.86, 21.13. HRMS (EI) m/z calcd for C₂₂H₂₀OS [M]+ 332.1235, found 332.1236.

6c 3-(phenylthio)-1,3-di-p-tolylpropan-1-one.



¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, J = 8.2 Hz, 2H), 7.33 (dd, J = 7.5, 1.6 Hz, 2H), 7.25-7.16 (m, 7H), 7.04 (d, J = 7.9 Hz, 2H), 4.94 (dd, J = 8.1, 6.0 Hz, 1H), 3.61 (dd, J = 17.0, 8.3 Hz, 1H), 3.51 (dd, J = 17.0, 5.9 Hz, 1H), 2.36 (s, 3H), 2.26 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 196.74, 144.06, 138.28, 136.98, 134.71, 134.42, 132.55 (2C), 129.32 (2C), 129.21 (2C), 128.88 (2C), 128.26 (2C), 127.72 (2C), 127.39, 48.05, 44.72, 21.66, 21.14. HRMS (EI) m/z calcd for C₂₃H₂₂OS [M]+ 346.1391, found 346.1394.

6d 3-(4-methoxyphenyl)-1-phenyl-3-(phenylthio)propan-1-one.

 1 H NMR (400 MHz, CDCl₃) δ 7.86 (dd, J = 5.2, 3.3 Hz, 2H), 7.56-7.49 (m, 1H), 7.41 (dd, J = 10.5, 4.7 Hz, 2H), 7.36-7.29 (m, 2H), 7.28-7.19 (m, 5H), 6.84-6.72 (m, 2H), 4.93 (dd, J = 8.5, 5.7 Hz, 1H), 3.74 (s, 3H), 3.63 (dd, J = 17.1, 8.5 Hz, 1H), 3.53 (dd, J = 17.1, 5.7 Hz, 1H). 13 C NMR (101 MHz, CDCl₃) δ 197.19, 158.79, 136.81, 134.49, 133.23, 133.16, 132.70 (2C), 128.90 (2C), 128.87 (2C), 128.62 (2C), 128.08 (2C), 127.46, 113.87 (2C), 55.22, 47.71, 44.89. HRMS (EI) m/z calcd for $C_{22}H_{20}O_2S$ [M]+ 348.1184, found 348.1188.

6e 1-(4-methoxyphenyl)-3-phenyl-3-(phenylthio)propan-1-one.

¹H NMR (400 MHz, CDCl₃) δ 7.86 (dd, J = 8.9, 2.7 Hz, 2H), 7.37-7.28 (m, 4H), 7.27-7.14 (m, 6H), 6.88 (dd, J = 8.9, 2.7 Hz, 2H), 4.95 (dd, J = 9.5, 4.6 Hz, 1H), 3.81 (s, 3H), 3.60 (ddd, J = 16.9, 8.1, 2.9 Hz, 1H), 3.52 (ddd, J = 16.9, 6.0, 3.0 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 195.48, 163.64, 141.37, 134.41, 132.69 (2C), 130.40 (2C), 129.92, 128.83 (2C), 128.44 (2C), 127.83 (2C), 127.46, 127.32, 113.78 (2C), 55.48, 48.42, 44.32. HRMS (EI) m/z calcd for C₂₂H₂₀O₂S [M]+ 348.1184, found 348.1186.

6f 3-(3,5-dimethoxyphenyl)-1-phenyl-3-(phenylthio)propan-1-one.

¹H NMR (400 MHz, CDCl₃) δ 7.99-7.81 (m, 2H), 7.56-7.49 (m, 1H), 7.41 (t, J = 7.6 Hz, 2H), 7.38-7.30 (m, 2H), 7.26-7.17 (m, 3H), 6.49 (d, J = 2.2 Hz, 2H), 6.29 (t, J = 2.2 Hz, 1H), 4.89 (dd, J = 7.7, 6.3 Hz, 1H), 3.71 (s, 6H), 3.62 (dd, J = 17.2, 7.8 Hz, 1H), 3.53 (dd, J = 17.2, 6.2 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 196.96, 160.72 (2C), 143.65, 136.79, 134.38, 133.28, 132.72 (2C), 128.89 (2C), 128.64 (2C), 128.10 (2C), 127.55, 105.89 (2C), 99.51, 55.31 (2C), 48.47, 44.67. HRMS (EI) m/z calcd for $C_{23}H_{22}O_3S$ [M]+ 378.1290, found 378.1291.

6g 3-(4-bromophenyl)-1-phenyl-3-(phenylthio)propan-1-one.

 1 H NMR (400 MHz, CDCl₃) δ 7.93-7.80 (m, 2H), 7.55-7.50 (m, 1H), 7.41 (dd, J = 10.6, 4.8 Hz, 2H), 7.37-7.33 (m, 2H), 7.33-7.27 (m, 2H), 7.27-7.15 (m, 5H), 4.89 (dd, J = 7.8, 6.3 Hz, 1H), 3.65-3.51 (m, 2H). 13 C NMR (101 MHz, CDCl₃) δ 196.62, 140.47, 136.61, 133.76, 133.41, 133.00 (2C), 131.55 (2C), 129.55 (2C), 128.98 (2C), 128.69 (2C), 128.06 (2C), 127.84, 121.15, 47.77, 44.51.

HRMS (EI) m/z calcd for $C_{21}H_{17}^{79}$ BrOS [M]+ 396.0183, found 396.0187.

HRMS (EI) m/z calcd for $C_{21}H_{17}^{81}$ BrOS [M]+ 398.0163, found 398.0163.

6h 3-(4-chlorophenyl)-1-phenyl-3-(phenylthio)propan-1-one.

 1 H NMR (400 MHz, CDCl₃) δ 7.90-7.80 (m, 2H), 7.53-7.48 (m, 1H), 7.38 (dd, J = 10.6, 4.7 Hz, 2H), 7.33-7.28 (m, 2H), 7.27-7.13 (m, 7H), 4.91 (dd, J = 7.9, 6.3 Hz, 1H), 3.64-3.51 (m, 2H). 13 C NMR (101 MHz, CDCl₃) δ 196.67, 139.97, 136.63, 133.82, 133.43, 133.02 (3C), 129.24 (2C), 129.01 (2C), 128.71 (2C), 128.62 (2C), 128.08 (2C), 127.85, 47.73, 44.57.

HRMS (EI) m/z calcd for $C_{21}H_{17}^{35}ClOS$ [M]+ 352.0689, found 352.0687.

HRMS (EI) m/z calcd for $C_{21}H_{17}^{35}ClOS$ [M]+ 354.0659, found 354.0663.

6i 1-(4-chlorophenyl)-3-phenyl-3-(phenylthio)propan-1-one.

¹H NMR (400 MHz, CDCl₃) δ 7.83-7.75 (m, 2H), 7.40-7.35 (m, 2H), 7.31 (d, J = 7.3 Hz, 4H), 7.27-7.14 (m, 6H), 4.92 (t, J = 7.0 Hz, 1H), 3.56 (qd, J = 17.1, 7.0 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 195.85, 141.06, 139.75, 135.09, 134.15, 132.83 (2C), 129.50 (2C), 128.95 (2C), 128.90 (2C), 128.52 (2C), 127.79 (2C), 127.64, 127.48, 48.33, 44.72.

HRMS (EI) m/z calcd for $C_{21}H_{17}^{35}ClOS$ [M]+ 352.0689, found 352.0686.

HRMS (EI) m/z calcd for $C_{21}H_{17}^{35}ClOS$ [M]+ 354.0659, found 354.0660.

6j 1-(4-fluorophenyl)-3-phenyl-3-(phenylthio)propan-1-one

¹H NMR (400 MHz, CDCl₃) δ 7.96-7.82 (m, 2H), 7.37-7.28 (m, 4H), 7.28-7.15 (m, 6H), 7.13-7.03 (m, 2H), 4.93 (dd, J = 8.0, 6.2 Hz, 1H), 3.57 (qd, J = 17.1, 7.1 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 195.46, 165.83 (d, $J_{CF} = 255.1$ Hz, 1C), 141.15, 134.22, 133.23 (d, $J_{CF} = 3.0$ Hz, 1C), 132.80 (2C), 130.76 (d, $J_{CF} = 9.4$ Hz, 2C), 128.91 (2C), 128.52 (2C), 127.82 (2C), 127.62, 127.47, 115.75 (d, $J_{CF} = 21.9$ Hz, 2C), 48.34, 44.67.

HRMS (EI) *m/z* calcd for C₂₁H₁₇FOS [M]+ 336.0984, found 336.0982.

6k 1-phenyl-3-(phenylthio)-3-(4-(trifluoromethyl)phenyl)propan-1-one.

¹H NMR (400 MHz, CDCl₃) δ 7.87 (dd, J = 5.2, 3.4 Hz, 2H), 7.57-7.52 (m, 1H), 7.49 (d, J = 8.3 Hz, 2H), 7.46-7.37 (m, 4H), 7.35-7.27 (m, 2H), 7.26-7.19 (m, 3H), 5.04-4.88 (m, 1H), 3.66 (dd, J = 15.2, 5.6 Hz, 1H), 3.61 (dd, J = 15.2, 4.1 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 196.46, 145.62 (d, J_{CF} = 0.5 Hz, 1C), 136.53, 133.50 (2C), 133.15 (2C), 129.46 (dd, J_{CF} = 64.8, 32.4 Hz, 1C), 129.05 (2C), 128.74 (2C), 128.24 (2C), 128.07 (2C), 128.03, 125.42 (dd, J_{CF} = 7.4, 3.6 Hz, 2C), 124.12 (q, J_{CF} = 272.0 Hz, 1C), 47.97, 44.39.

HRMS (EI) m/z calcd for $C_{22}H_{17}F_3OS$ [M]+ 386.0952, found 386.0951.

6l 3-phenyl-3-(phenylthio)-1-(4-(trifluoromethyl)phenyl)propan-1-one.

¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, J = 8.1 Hz, 2H), 7.67 (d, J = 8.2 Hz, 2H), 7.38-7.28 (m, 4H), 7.28-7.14 (m, 6H), 4.92 (dd, J = 7.9, 6.3 Hz, 1H), 3.62 (qd, J = 17.2, 7.1 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 196.18, 140.92, 139.41, 134.52 (dd, J_{CF} = 65.5, 32.8 Hz, 1C), 134.03, 132.91 (2C), 128.94 (2C), 128.57 (2C), 128.41 (2C), 127.78 (2C), 127.74, 127.56, 125.71 (q, J_{CF} = 3.7 Hz, 2C), 123.56 (dd, J_{CF} = 545.4, 272.6 Hz, 1C), 48.30, 45.10. HRMS (EI) m/z calcd for C₂₂H₁₇F₃OS [M]+ 386.0952, found 386.0953.

TIKING (E1) m/2 calculot C_{22} 11[/1/305 [W]+ 360.0932, Touliu 360.0933

6m 4-(3-oxo-3-phenyl-1-(phenylthio)propyl)benzonitrile.

 1 H NMR (400 MHz, CDCl₃) δ 7.93-7.83 (m, 2H), 7.58-7.53 (m, 1H), 7.53-7.48 (m, 2H), 7.43 (dd, J = 10.6, 4.8 Hz, 2H), 7.41-7.35 (m, 2H), 7.31-7.26 (m, 2H), 7.26-7.19 (m, 3H), 4.92 (t, J = 7.1 Hz, 1H), 3.64 (d, J = 7.1 Hz, 2H). 13 C NMR (101 MHz, CDCl₃) δ 196.21, 147.06, 136.35, 133.64, 133.42 (2C), 132.96, 132.21 (2C), 129.10 (2C), 128.79 (2C), 128.66 (2C), 128.27, 128.06 (2C), 118.73, 111.02, 48.16, 44.04.

HRMS (EI) m/z calcd for $C_{22}H_{17}NOS$ [M]+ 343.1034 found 343,1033.

6n 3-(benzo[d][1,3]dioxol-5-yl)-1-phenyl-3-(phenylthio)propan-1-one.

 $^1\mathrm{H}$ NMR (400 MHz, CDCl₃) δ 7.84 (dd, J=5.2, 3.3 Hz, 2H), 7.53-7.47 (m, 1H), 7.41-7.36 (m, 2H), 7.36-7.30 (m, 2H), 7.26-7.17 (m, 3H), 6.89 (d, J=1.8 Hz, 1H), 6.75 (dd, J=8.0, 1.8 Hz, 1H), 6.63 (d, J=8.0 Hz, 1H), 5.84 (dd, J=3.0, 1.4 Hz, 2H), 4.90 (dd, J=8.4, 5.8 Hz, 1H), 3.59 (dd, J=17.1, 8.4 Hz, 1H), 3.50 (dd, J=17.1, 5.8 Hz, 1H). $^{13}\mathrm{C}$ NMR (101 MHz, CDCl₃) δ 197.00, 147.76, 146.82, 136.75, 135.05, 134.39 133.31, 132.66 (2C), 128.94 (2C), 128.66 (2C), 128.10 (2C), 127.56, 121.32, 108.14, 108.04, 101.07, 48.21, 44.96.

HRMS (EI) m/z calcd for $C_{22}H_{18}O_3S$ [M]+ 362.0977, found 362.0974.

60 3-(furan-2-yl)-1-phenyl-3-(phenylthio)propan-1-one.

¹H NMR (400 MHz, CDCl₃) δ 7.92 (dt, J = 8.5, 1.6 Hz, 2H), 7.58-7.52 (m, 1H), 7.47-7.41 (m, 2H), 7.38-7.30 (m, 3H), 7.28-7.22 (m, 3H), 6.21 (dd, J = 3.2, 1.9 Hz, 1H), 6.01 (d, J = 3.2 Hz, 1H), 4.98 (dd, J = 7.8, 6.3 Hz, 1H), 3.69 (dd, J = 17.3, 7.9 Hz, 1H), 3.53 (dd, J = 17.3, 6.3 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 196.54, 153.34, 141.94, 136.62, 133.80 (2C), 133.38, 133.31, 128.87 (2C), 128.69 (2C), 128.15 (2C), 128.06, 110.34, 107.40, 42.09 (2C), 41.67 (2C). HRMS (EI) m/z calcd for C₁₁₆H₁₆O₂S [M]+ 308.0871, found 308.0872.

6p 4-phenyl-4-(phenylthio)butan-2-one.

 1 H NMR (400 MHz, CDCl₃) δ 7.32-7.14 (m, 10H), 4.70 (dd, J = 7.7, 6.8 Hz, 1H), 3.10-2.97 (m, 2H), 2.03 (s, 3H). 13 C NMR (101 MHz, CDCl₃) δ 205.52, 141.08, 134.09, 132.91 (2C), 128.87 (2C), 128.52 (2C), 127.74 (2C), 127.64, 127.46, 49.53, 48.08, 30.70.

HRMS (EI) m/z calcd for $C_{116}H_{16}OS$ [M]+ 256.0922, found 256.0926.

6q 1-phenyl-3-(phenylthio)butan-1-one.

 1 H NMR (400 MHz, CDCl₃) δ 7.89 (dt, J = 8.5, 1.6 Hz, 2H), 7.58-7.52 (m, 1H), 7.48-7.39 (m, 4H), 7.34-7.21 (m, 3H), 3.90 (dqd, J = 9.0, 6.7, 4.6 Hz, 1H), 3.30 (dd, J = 16.9, 4.6 Hz, 1H), 3.10 (dd, J = 16.9, 9.0 Hz, 1H), 1.37 (d, J = 6.7 Hz, 3H). 13 C NMR (101 MHz, CDCl₃) δ 198.07, 136.87, 134.43, 133.27, 132.36 (2C), 129.00 (2C), 128.66 (2C), 128.09 (2C), 127.25, 45.50, 38.80, 21.04.

HRMS (EI) m/z calcd for C₁₁₆H₁₆OS [M]+ 256.0922, found 256.0923.

6r benzyl 3-(phenylthio)propanoate.

 1 H NMR (400 MHz, CDCl₃) δ 7.41-7.30 (m, 7H), 7.30-7.25 (m, 2H), 7.24-7.16 (m, 1H), 5.12 (s, 2H), 3.18 (t, J = 7.4 Hz, 2H), 2.67 (t, J = 7.4 Hz, 2H). 13 C NMR (101 MHz, CDCl₃) δ 171.58, 135.72, 135.15, 130.25 (2C), 129.04 (2C), 128.59 (2C), 128.33, 128.28 (2C), 126.64, 66.58, 34.48, 29.12.

HRMS (EI) m/z calcd for $C_{16}H_{16}O_2S$ [M]+ 272.0871, found 272.0873.

6u 1,3-diphenyl-3-(p-tolylthio)propan-1-one.

¹H NMR (400 MHz, CDCl₃) δ 7.92-7.81 (m, 2H), 7.54-7.48 (m, 1H), 7.39 (dd, J = 10.6, 4.7 Hz, 2H), 7.35-7.28 (m, 2H), 7.26-7.19 (m, 4H), 7.19-7.13 (m, 1H), 7.02 (d, J = 7.9 Hz, 2H), 4.88 (dd, J = 8.1, 6.1 Hz, 1H), 3.63 (dd, J = 17.1, 8.1 Hz, 1H), 3.55 (dd, J = 17.1, 6.1 Hz, 1H), 2.27 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 197.11, 141.45, 137.86, 136.88, 133.52 (2C), 133.24, 130.54, 129.71 (2C), 128.64 (2C), 128.47 (2C), 128.12 (2C), 127.90 (2C), 127.35, 48.76, 44.70, 21.18. HRMS (EI) m/z calcd for C₂₂H₂₀OS [M]+ 332.1235, found 332.1236.

6v 3-((4-methoxyphenyl)thio)-1,3-diphenylpropan-1-one.

 1 H NMR (400 MHz, CDCl₃) δ 7.92-7.82 (m, 2H), 7.55-7.48 (m, 1H), 7.40 (t, J = 7.7 Hz, 2H), 7.28-7.20 (m, 6H), 7.20-7.12 (m, 1H), 6.78-6.69 (m, 2H), 4.99-4.59 (m, 1H), 3.73 (s, 3H), 3.65-3.52 (m, 2H). 13 C NMR (101 MHz, CDCl₃) δ 197.14, 159.89, 141.45, 136.84, 136.28 (2C), 133.25, 128.65 (2C), 128.41 (2C), 128.10 (2C), 127.89 (2C), 127.29, 124.26, 114.42 (2C), 55.30, 49.44, 44.31.

HRMS (EI) m/z calcd for $C_{22}H_{20}O_2S$ [M]+ 348.1184, found 348.1185.

6w 3-((4-chlorophenyl)thio)-1,3-diphenylpropan-1-one.

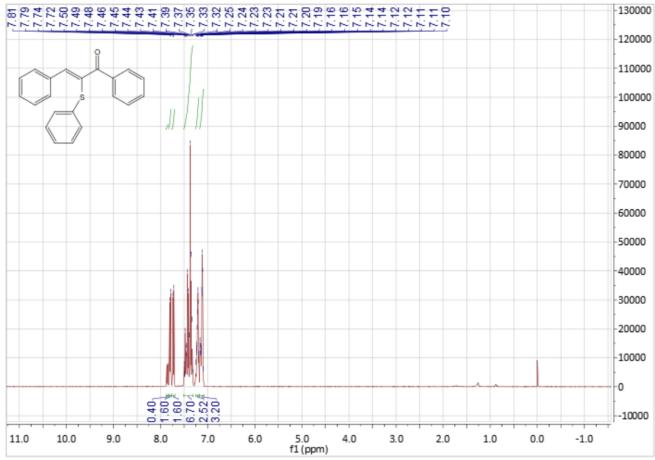
 1 H NMR (400 MHz, CDCl₃) δ 7.93-7.81 (m, 2H), 7.56-7.49 (m, 1H), 7.41 (dd, J = 10.6, 4.7 Hz, 2H), 7.31 (dd, J = 5.3, 3.4 Hz, 2H), 7.27-7.12 (m, 7H), 4.91 (t, J = 7.0 Hz, 1H), 3.66-3.51 (m, 2H). 13 C NMR (101 MHz, CDCl₃) δ 196.73, 141.07, 136.72, 134.26 (2C), 133.83, 133.36, 132.71, 129.00 (2C), 128.68 (2C), 128.55 (2C), 128.09 (2C), 127.82 (2C), 127.53, 48.57, 44.58.

HRMS (EI) m/z calcd for $C_{21}H_{17}^{35}ClOS$ [M]+ 352.0689, found 352.0688. HRMS (EI) m/z calcd for $C_{21}H_{17}^{35}ClOS$ [M]+ 354.0659, found 354.0663.

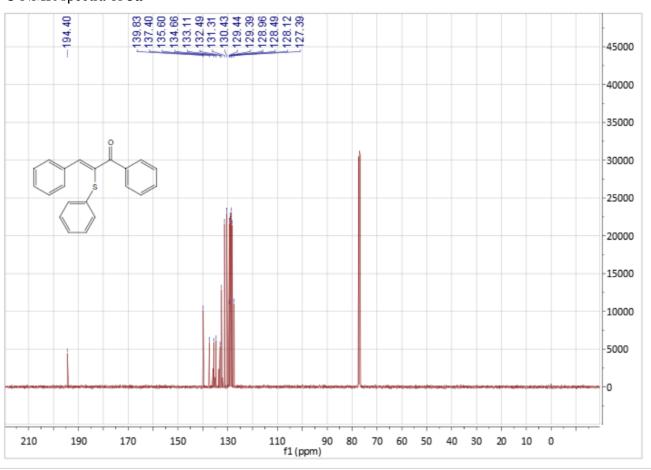
6x 3-((4-fluorophenyl)thio)-1,3-diphenylpropan-1-one.

¹H NMR (400 MHz, CDCl₃) δ 7.97-7.82 (m, 2H), 7.52 (dd, J = 10.5, 4.2 Hz, 1H), 7.42 (t, J = 7.7 Hz, 2H), 7.25 (tt, J = 12.2, 5.1 Hz, 6H), 7.20-7.12 (m, 1H), 7.00-6.77 (m, 2H), 4.84 (t, J = 7.1 Hz, 1H), 3.66-3.52 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 196.83, 162.74 (d, $J_{CF} = 248.2$ Hz, 1C), 141.18, 136.74, 135.98 (d, $J_{CF} = 8.3$ Hz, 2C), 133.35, 129.00 (d, $J_{CF} = 3.4$ Hz, 1C), 128.68 (2C), 128.48 (2C), 128.09 (2C), 127.83 (2C), 127.44, 115.93 (d, $J_{CF} = 21.8$ Hz, 2C), 49.16, 44.36. HRMS (EI) m/z calcd for C₂₁H₁₇FOS [M]+ 336.0984, found 336.0988.

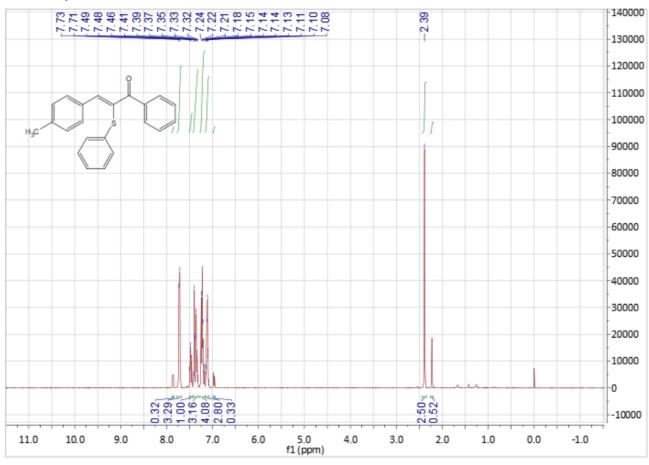
¹H NMR spectra of **3a**



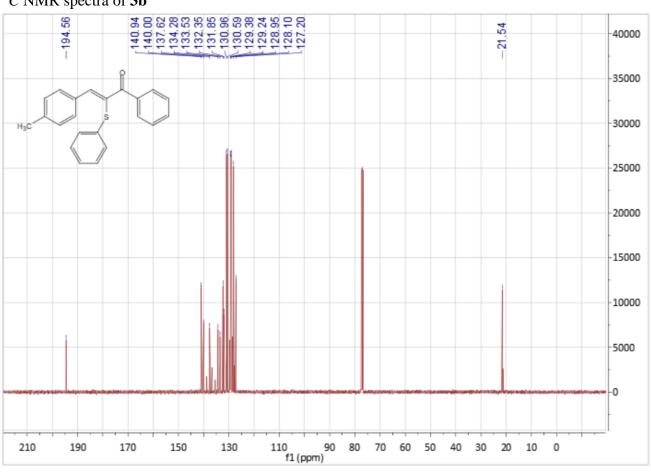
¹³C NMR spectra of 3a



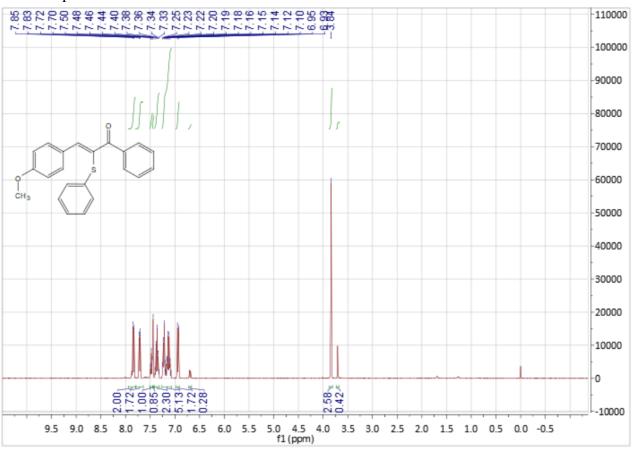
¹H NMR spectra of **3b**



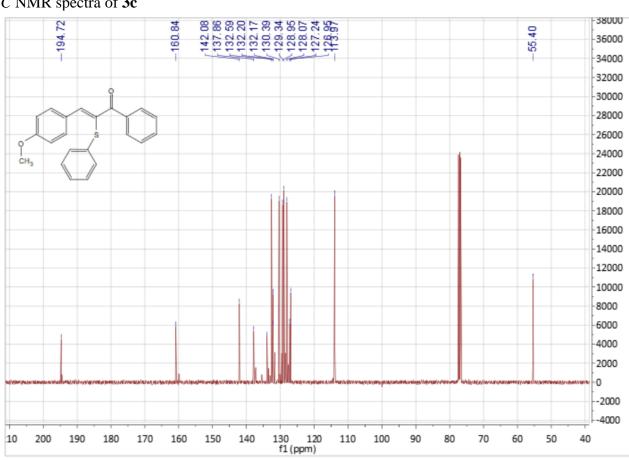
¹³C NMR spectra of **3b**



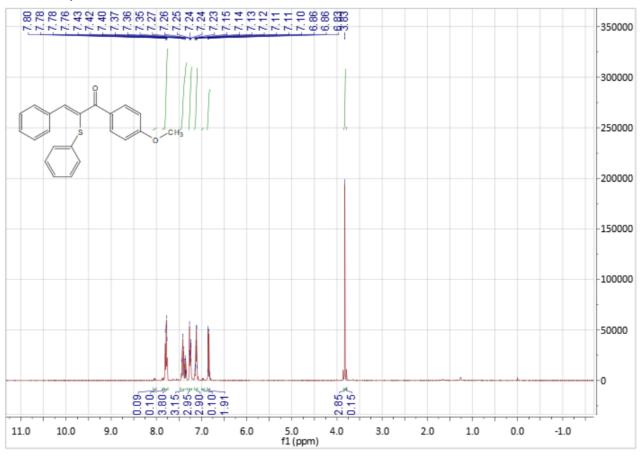
¹H NMR spectra of 3c



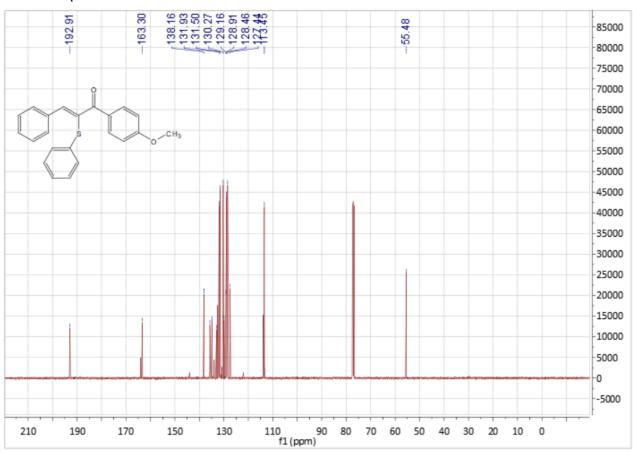
¹³C NMR spectra of 3c



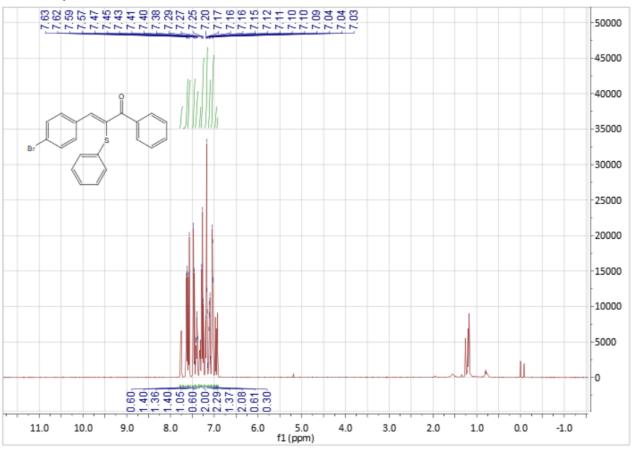
¹H NMR spectra of **3d**



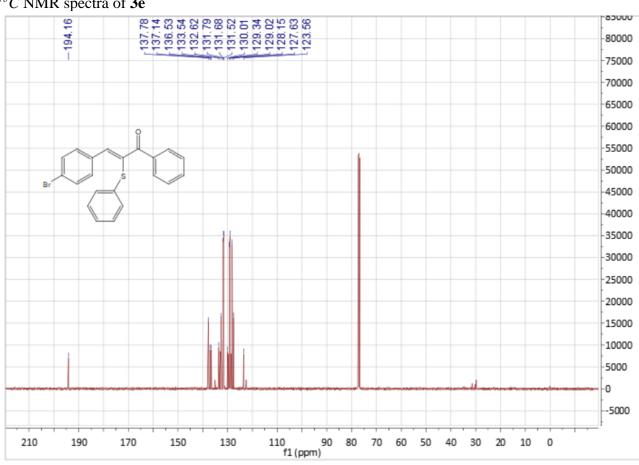
 ^{13}C NMR spectra of **3d**



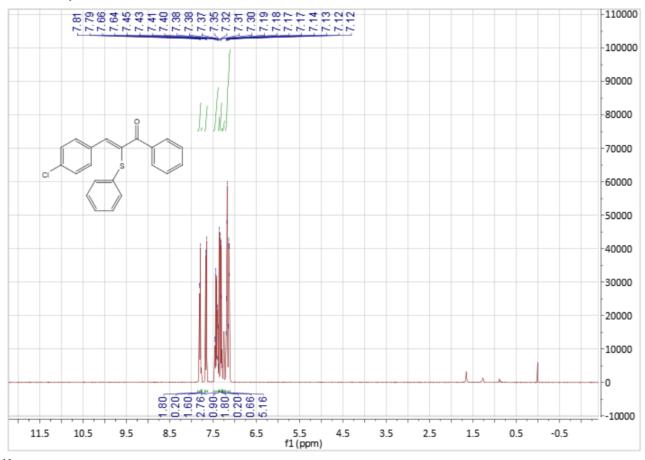
¹H NMR spectra of **3e**



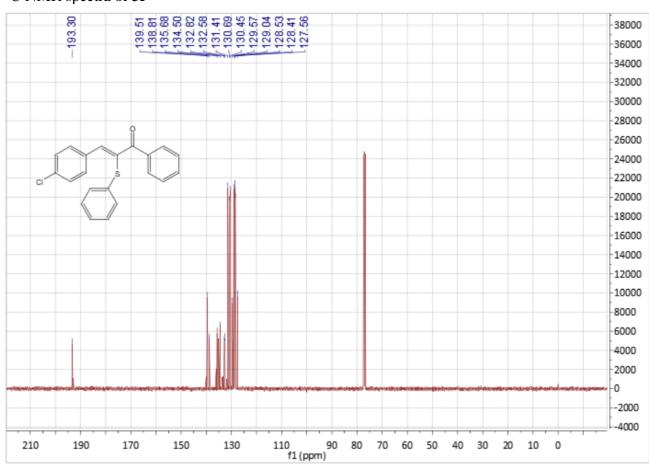
¹³C NMR spectra of **3e**



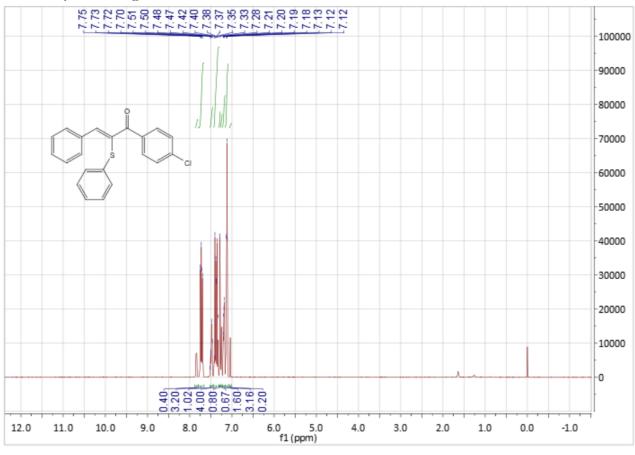
¹H NMR spectra of **3f**



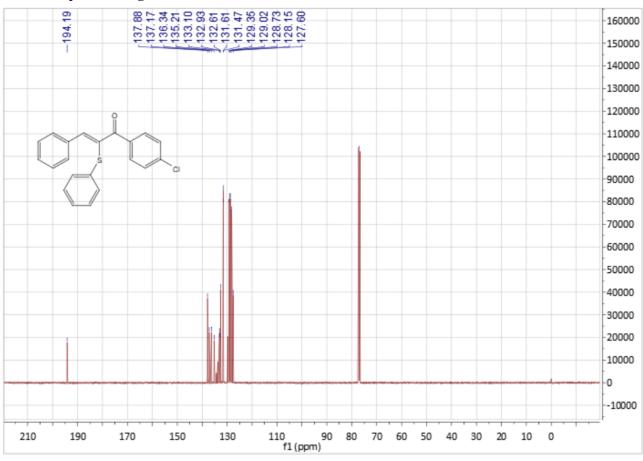
¹³C NMR spectra of **3f**



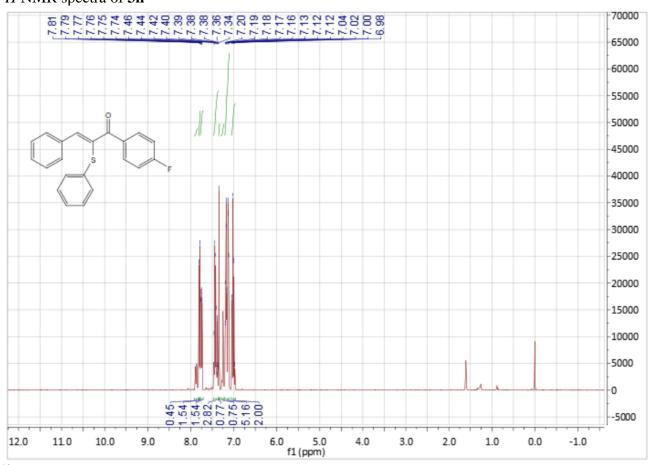
¹H NMR spectra of **3g**



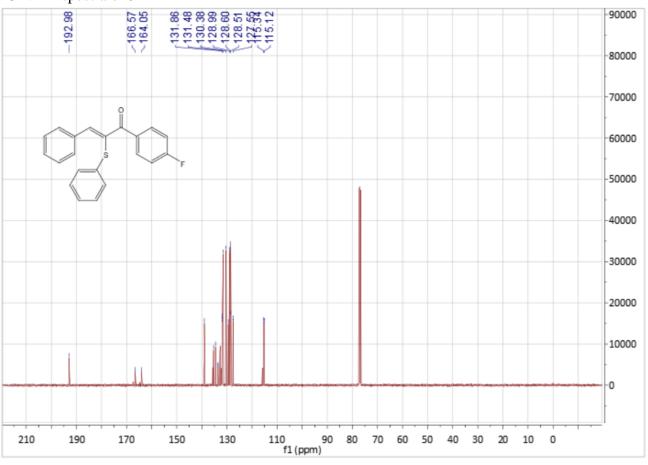
¹³C NMR spectra of **3g**



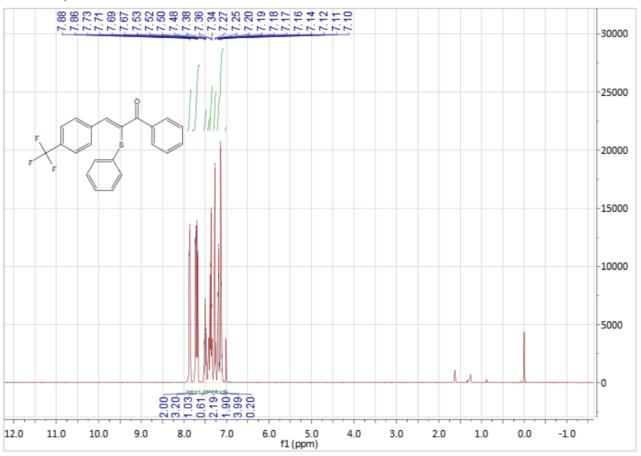
¹H NMR spectra of **3h**



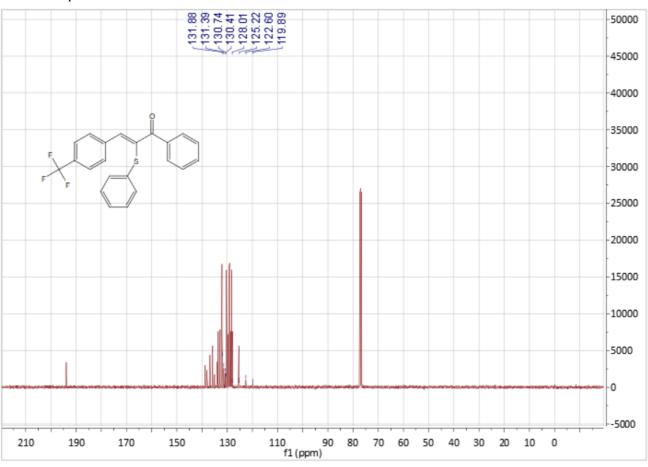
¹³C NMR spectra of **3h**



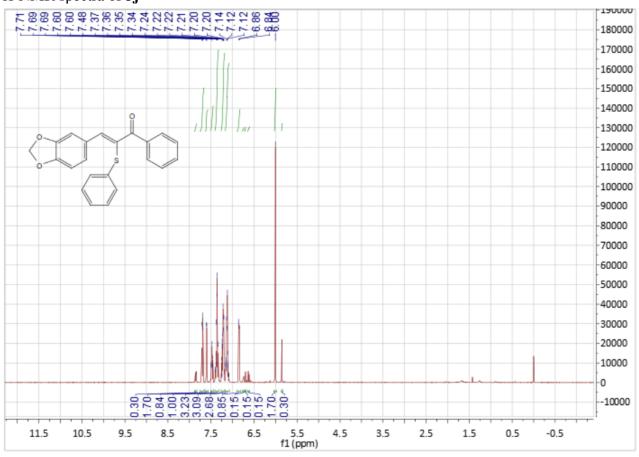
¹H NMR spectra of 3i



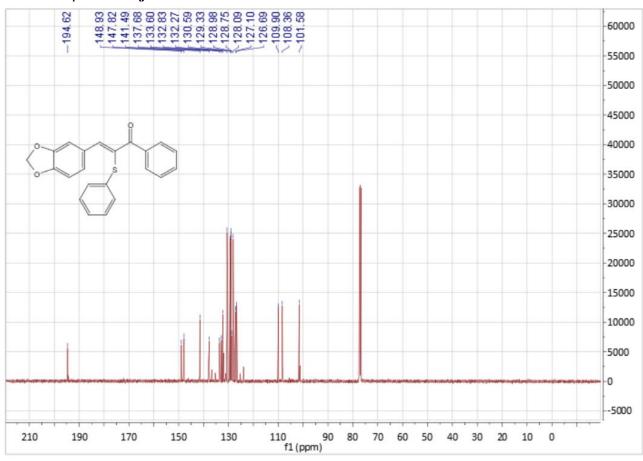
¹³C NMR spectra of 3i



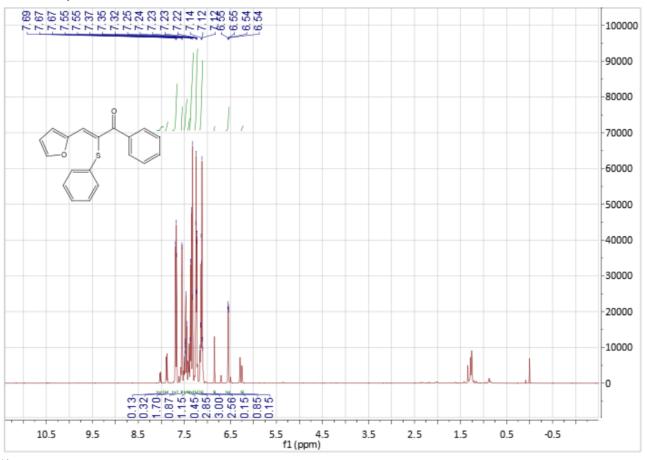
¹H NMR spectra of 3j



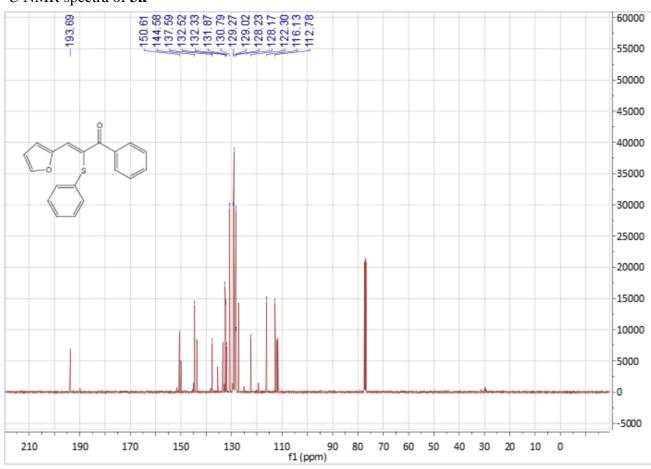
¹³C NMR spectra of **3j**



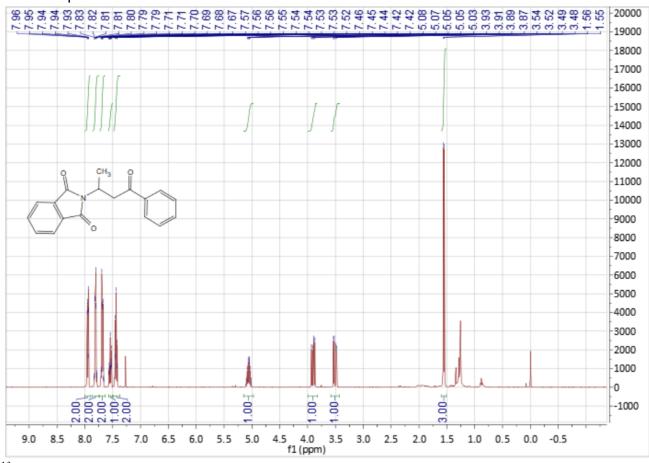
¹H NMR spectra of **3k**



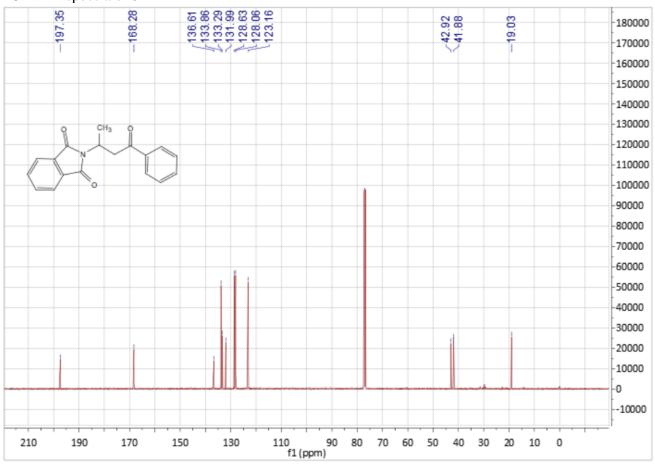
¹³C NMR spectra of **3k**



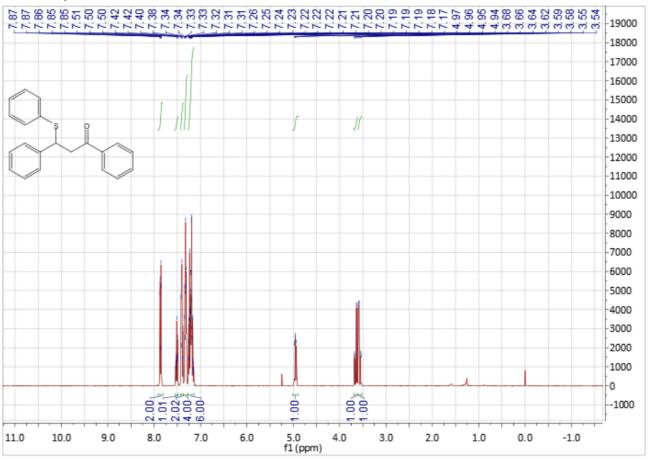
¹H NMR spectra of 3m'



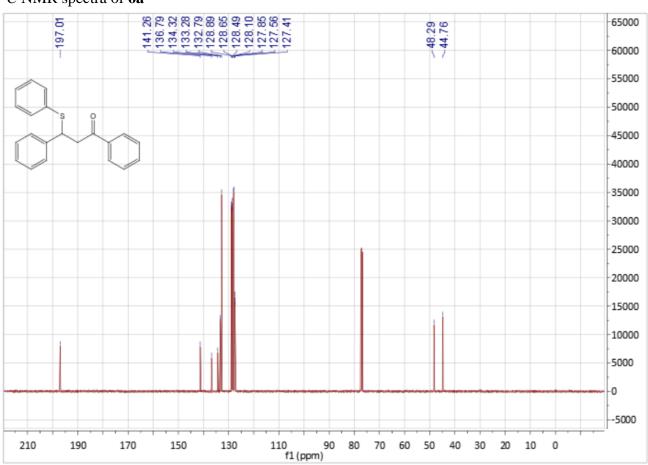
¹³C NMR spectra of 3m'



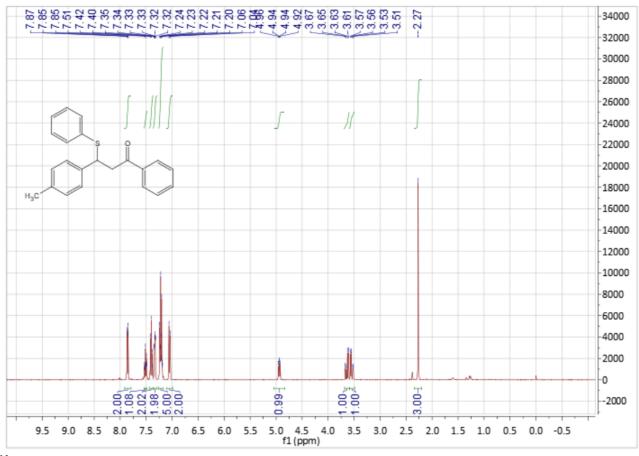
¹H NMR spectra of **6a**



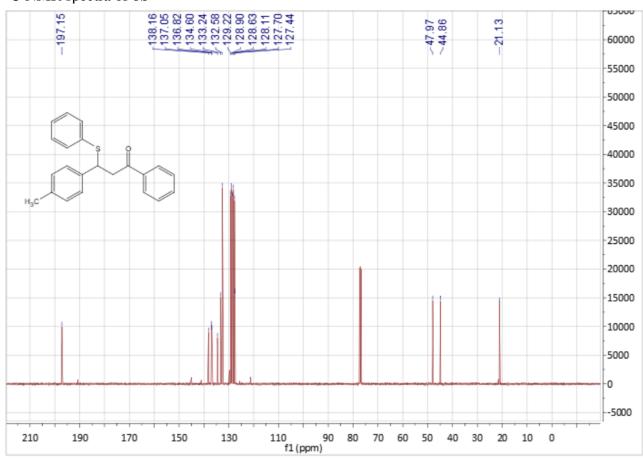
¹³C NMR spectra of **6a**



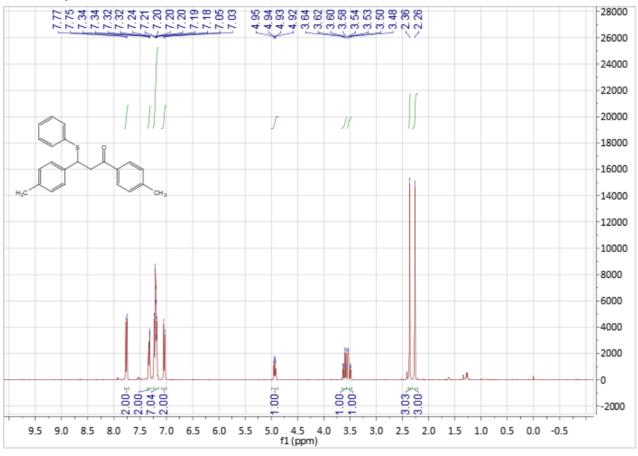
¹H NMR spectra of **6b**



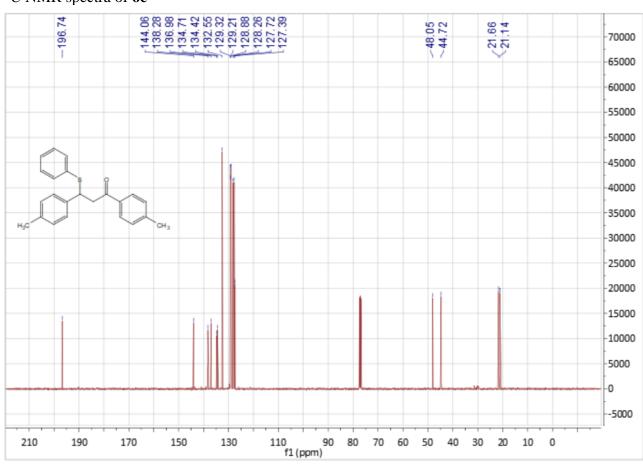
¹³C NMR spectra of **6b**



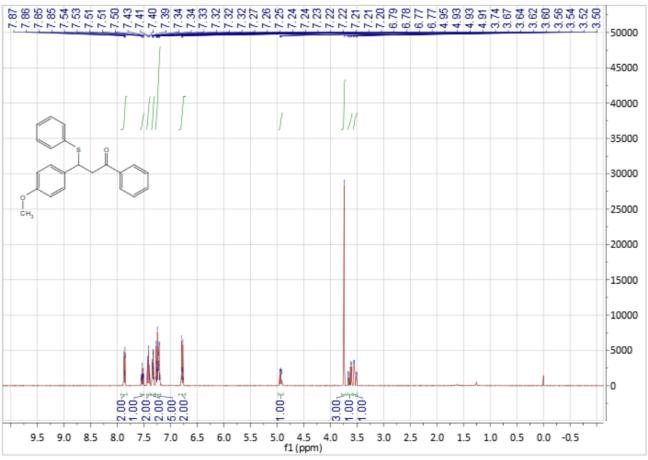
¹H NMR spectra of **6c**



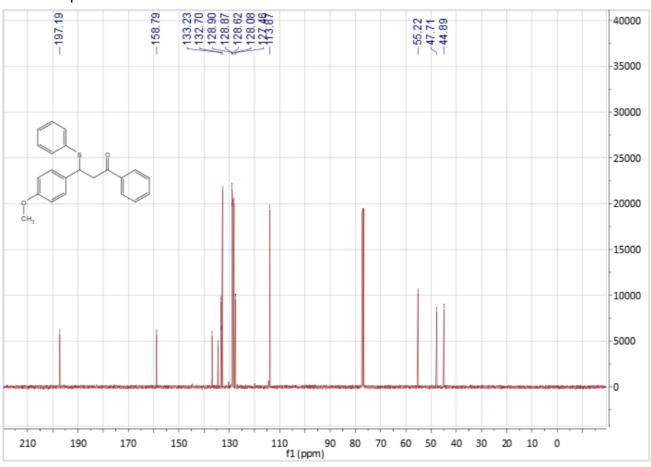
¹³C NMR spectra of **6c**



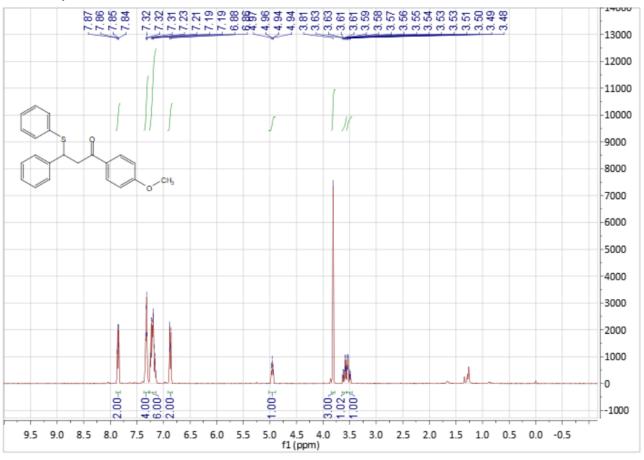
¹H NMR spectra of **6d**



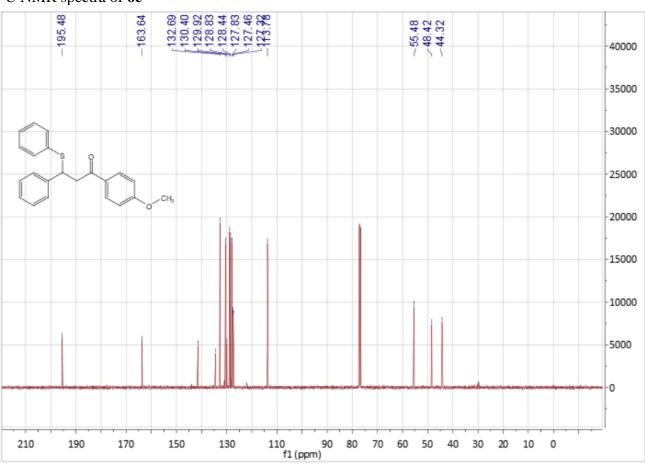
¹³C NMR spectra of **6d**



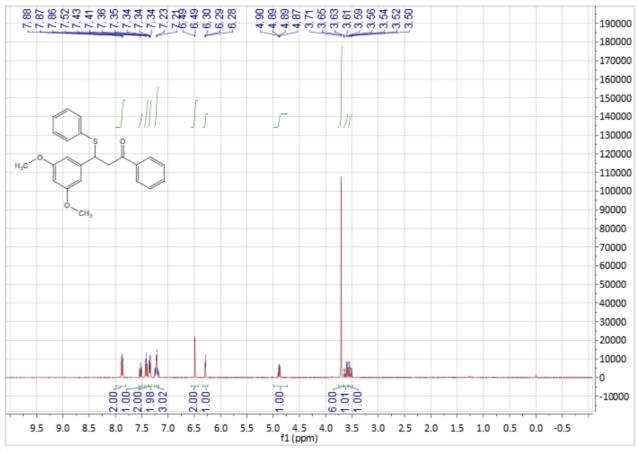
¹H NMR spectra of **6e**



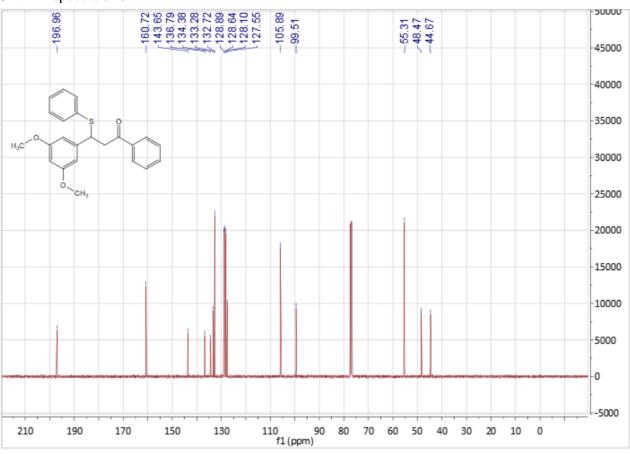
¹³C NMR spectra of **6e**



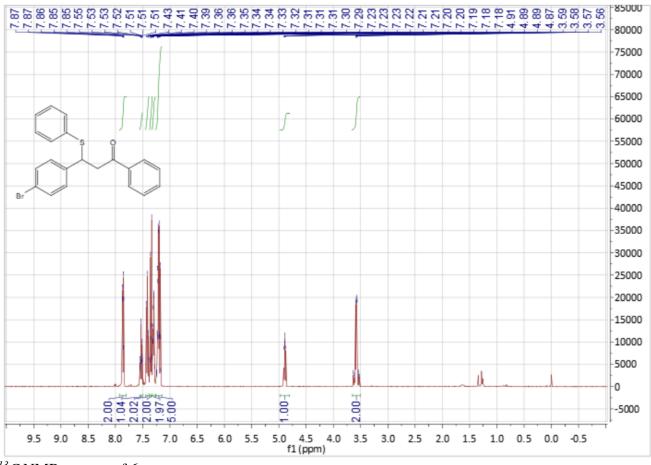
¹H NMR spectra of **6f**



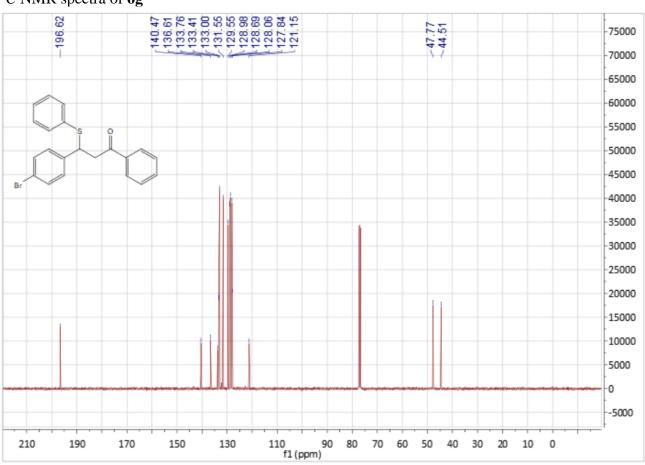
¹³C NMR spectra of **6f**



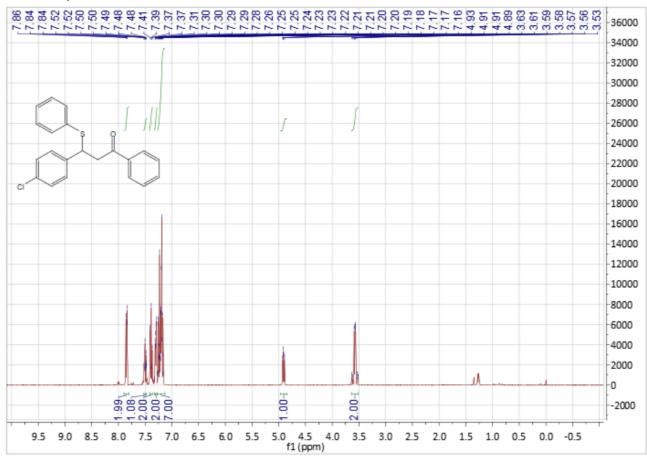
¹H NMR spectra of **6g**



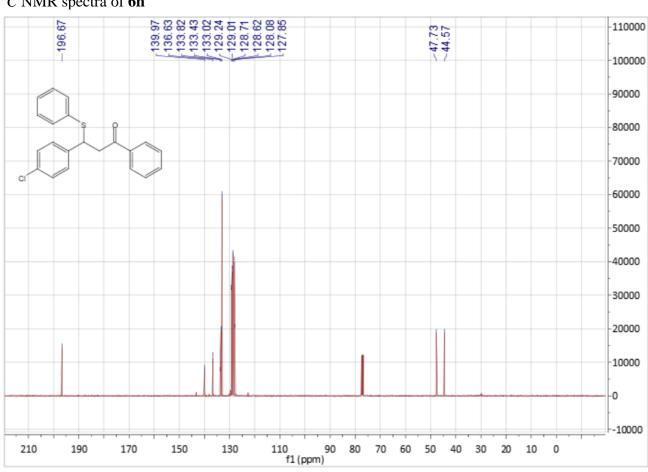
^{13}C NMR spectra of $\mathbf{6g}$



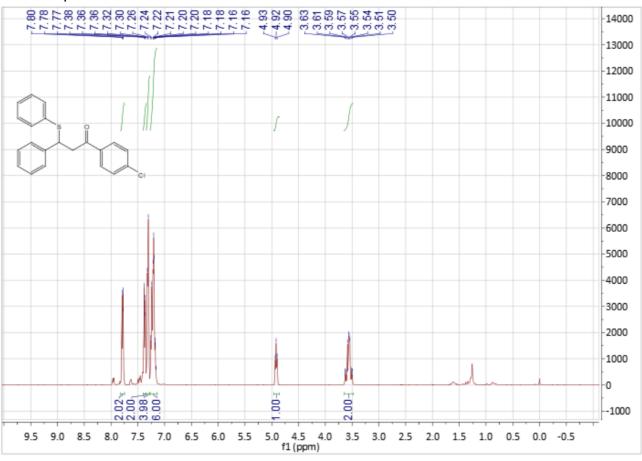
¹H NMR spectra of **6h**



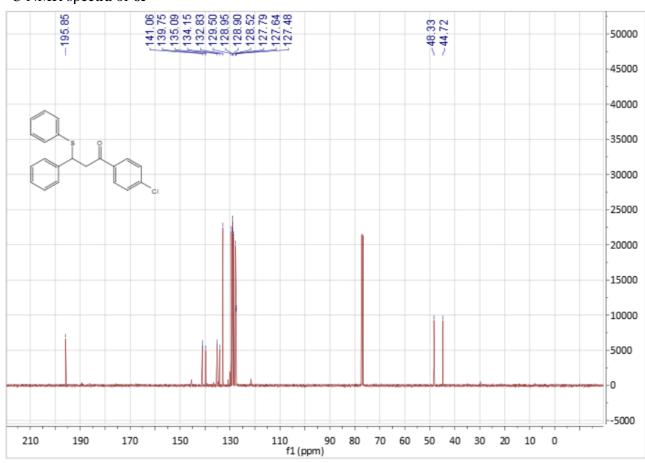
¹³C NMR spectra of **6h**



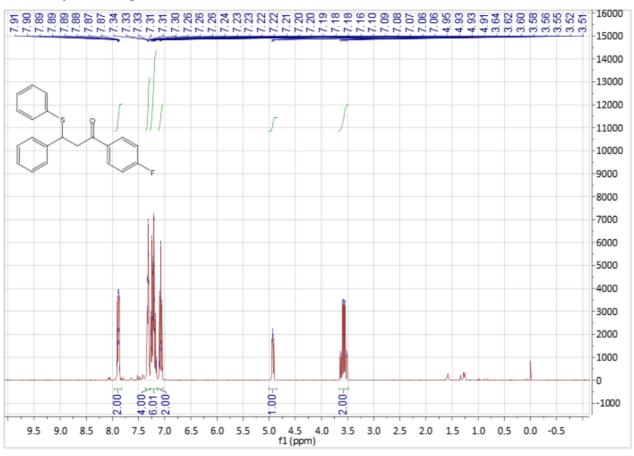
¹H NMR spectra of **6i**



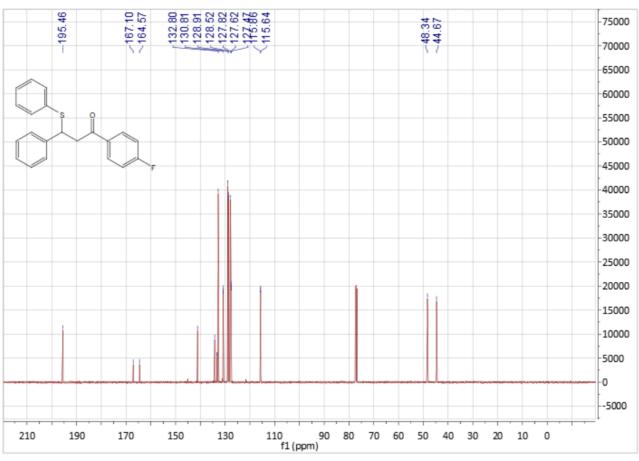
¹³C NMR spectra of **6i**



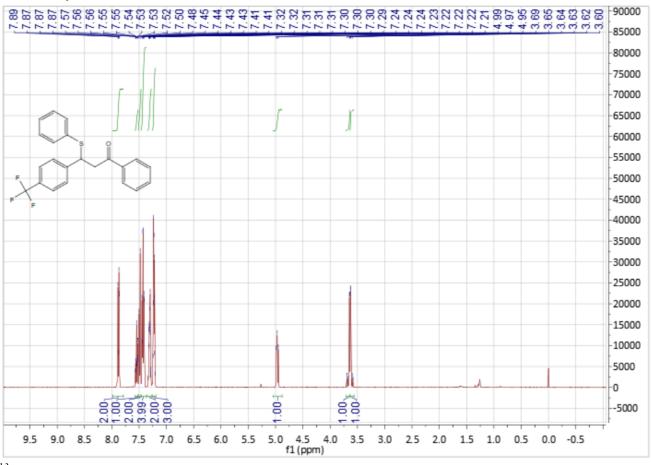
¹H NMR spectra of **6j**



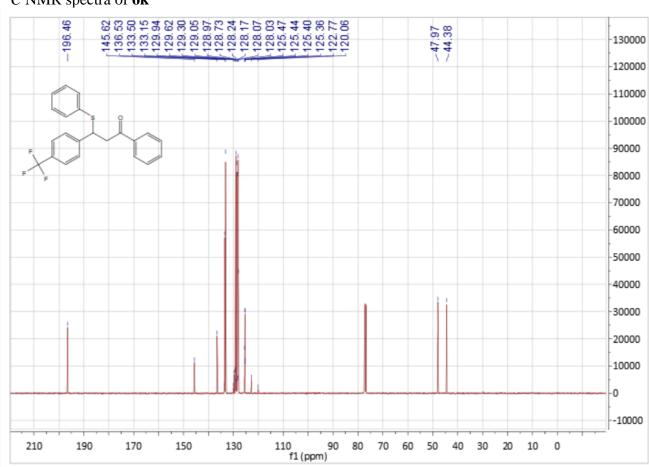
¹³C NMR spectra of **6j**



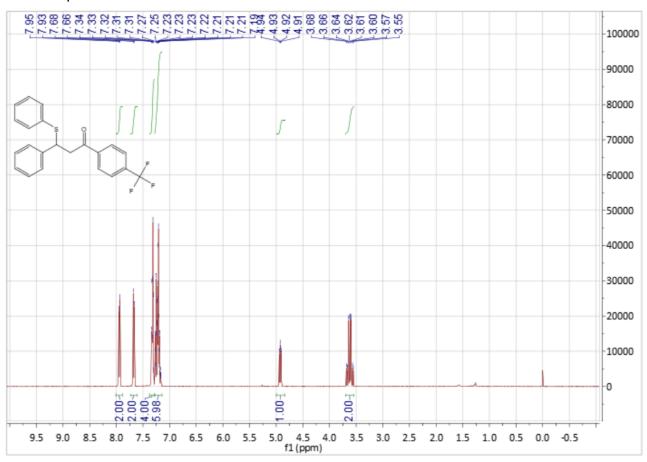
¹H NMR spectra of **6k**



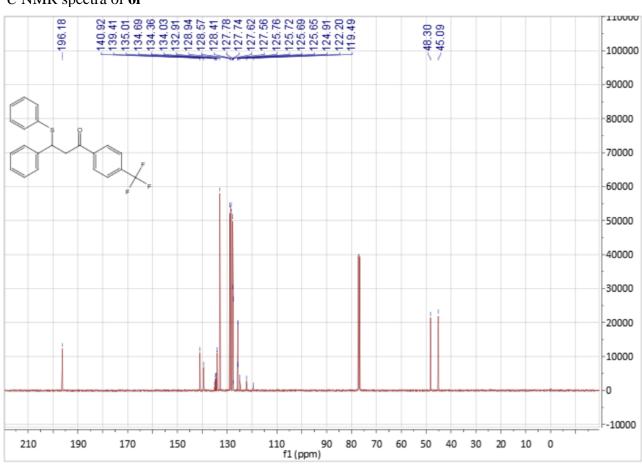
¹³C NMR spectra of **6k**



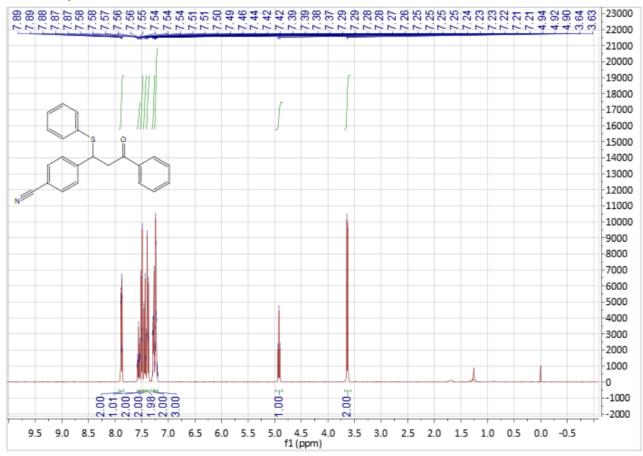
¹H NMR spectra of **61**



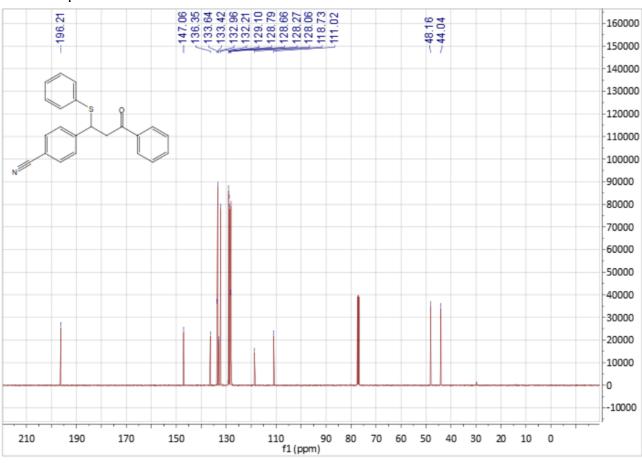
¹³C NMR spectra of **6l**



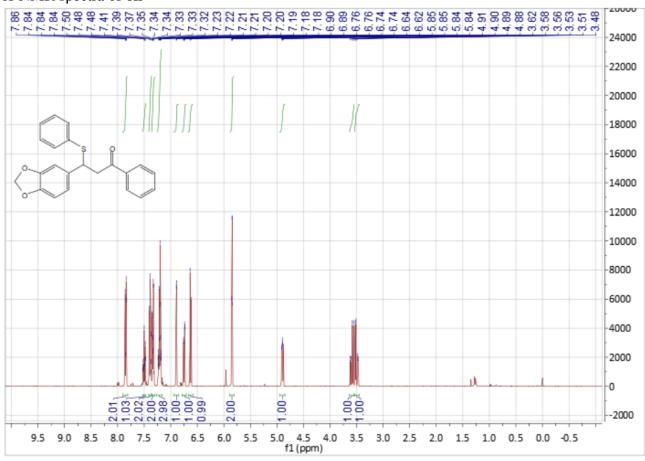
¹H NMR spectra of **6m**



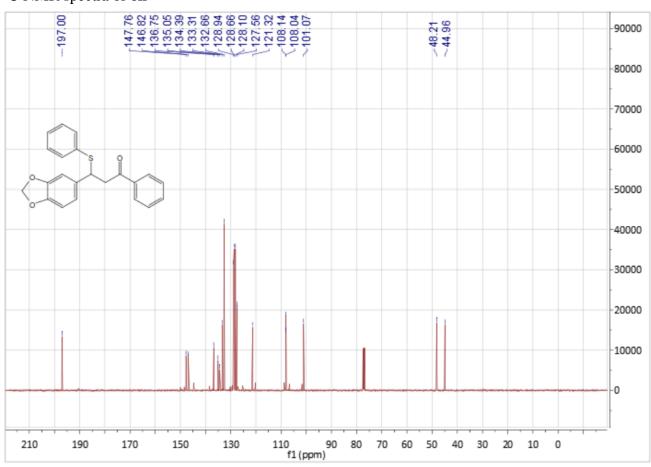
¹³C NMR spectra of **6m**



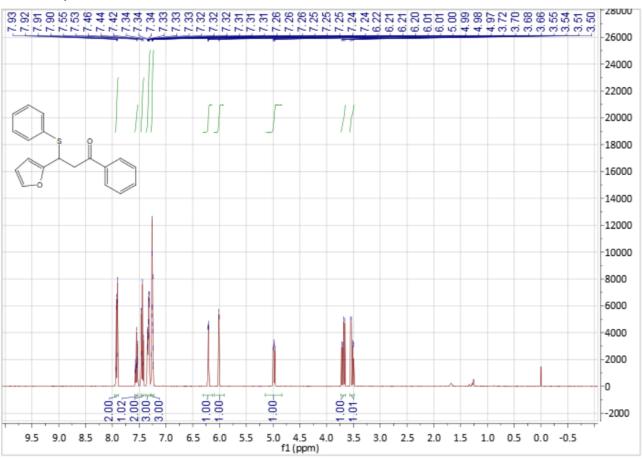
¹H NMR spectra of **6n**



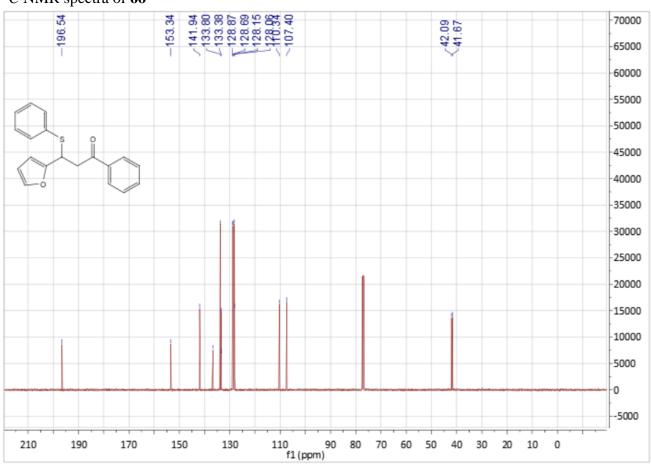
¹³C NMR spectra of **6n**



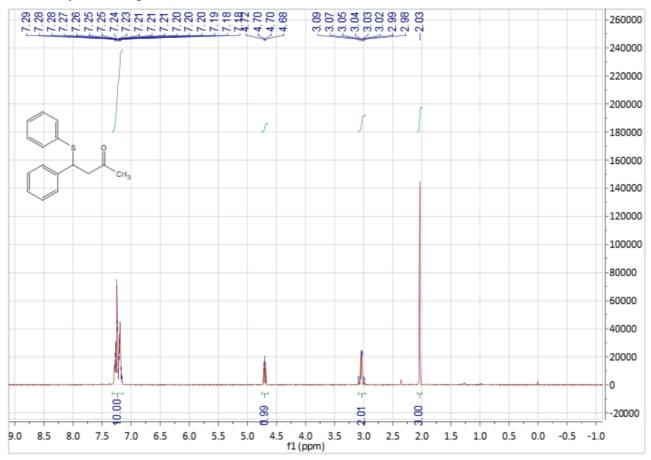
¹H NMR spectra of **60**



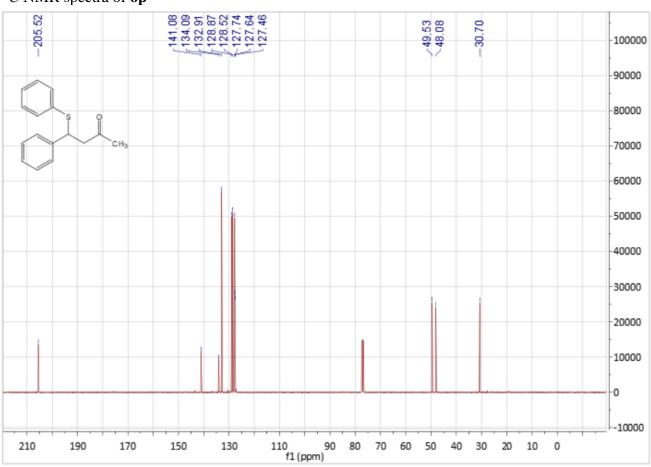
¹³C NMR spectra of **60**



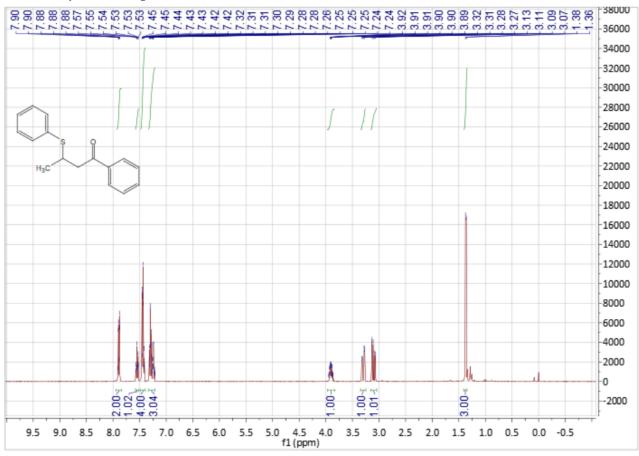
¹H NMR spectra of **6p**



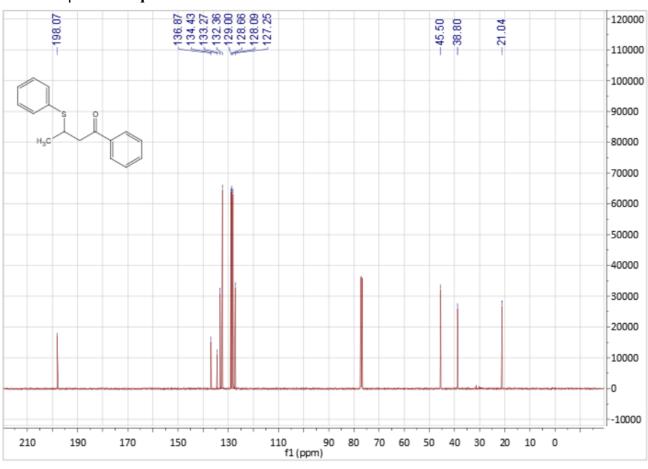
¹³C NMR spectra of **6p**



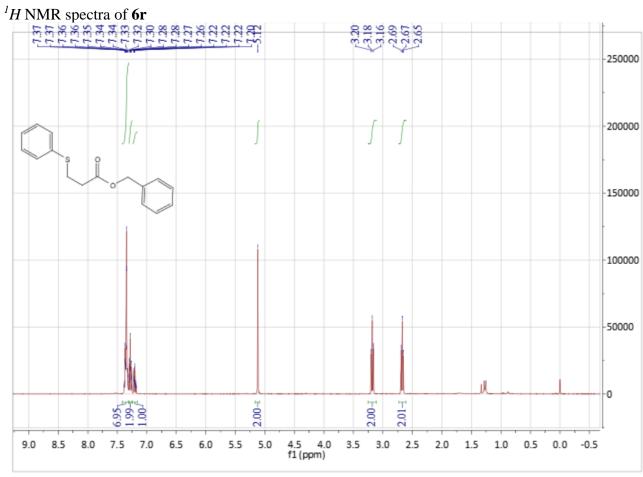
¹H NMR spectra of **6q**



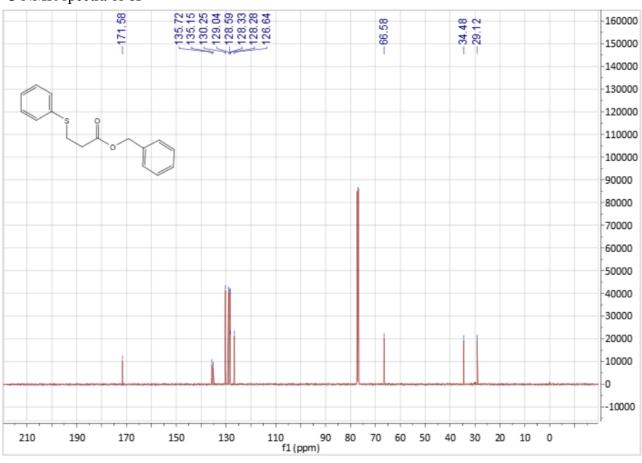
¹³C NMR spectra of **6q**



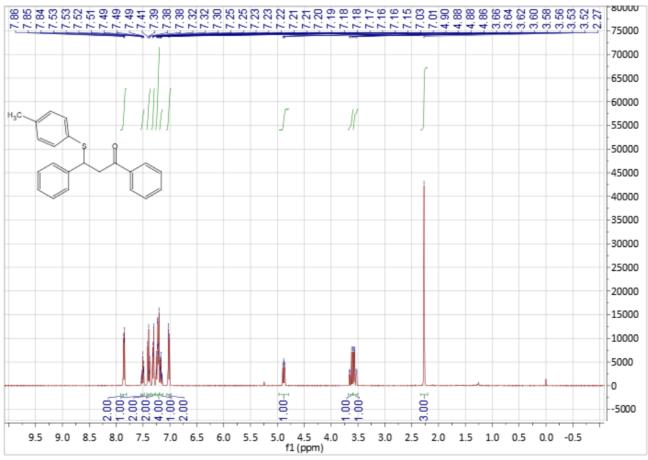




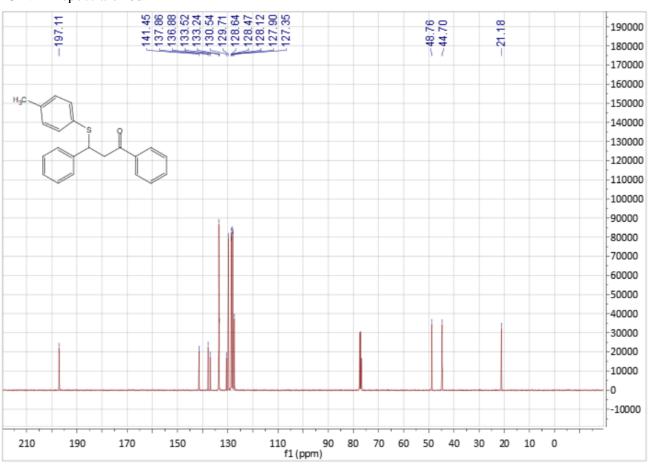
¹³C NMR spectra of **6r**



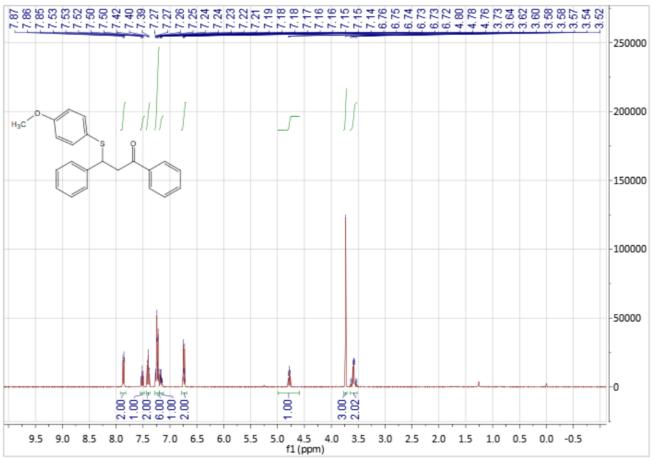
¹H NMR spectra of **6u**



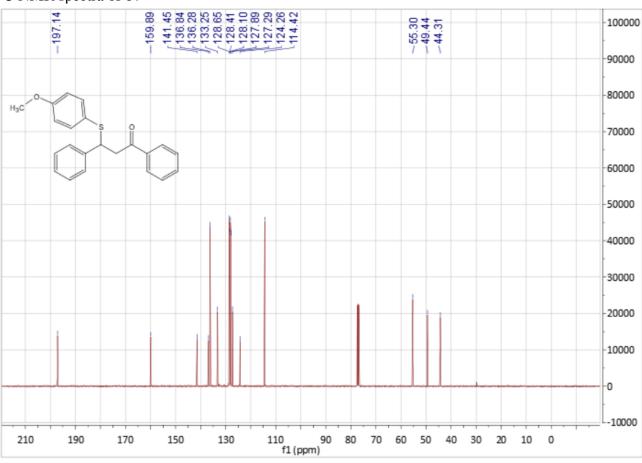
¹³C NMR spectra of **6u**



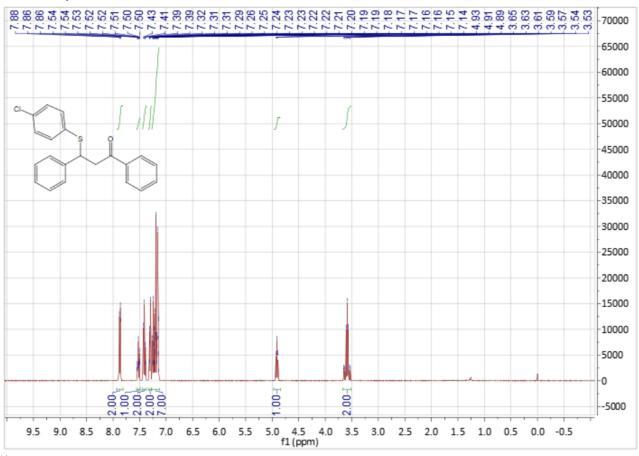
¹H NMR spectra of **6v**



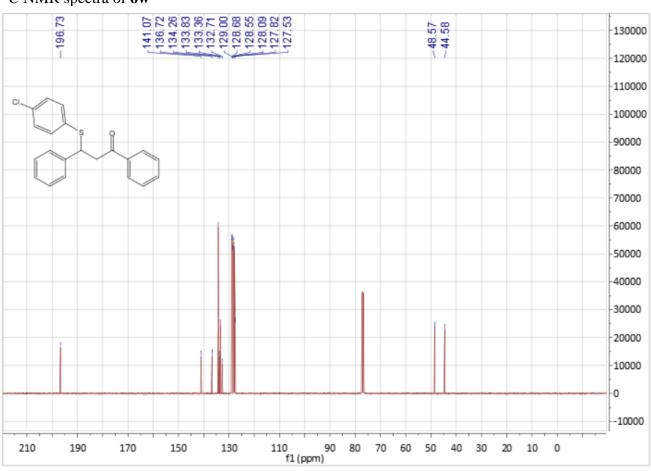
¹³C NMR spectra of **6v**



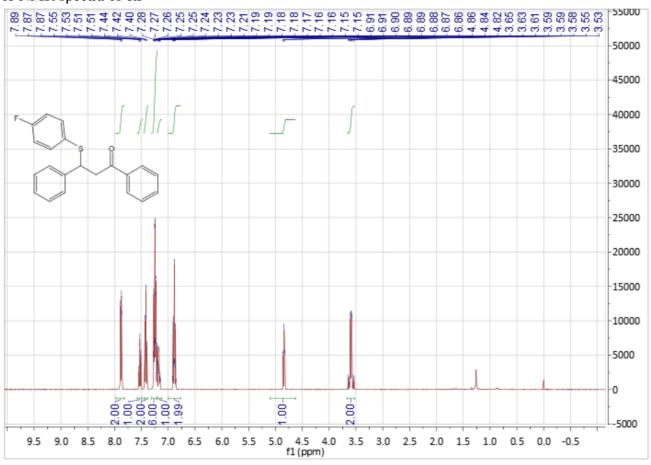
¹H NMR spectra of **6w**



¹³C NMR spectra of **6w**



¹H NMR spectra of **6x**



¹³C NMR spectra of **6x**

