

Supporting Information

Stevens rearrangement of thioethers with arynes: a facile access to multi-substituted β -keto thioethers

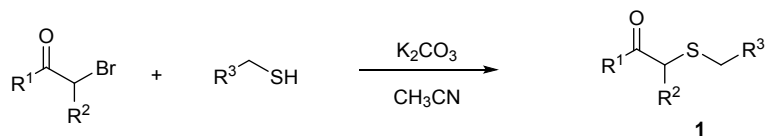
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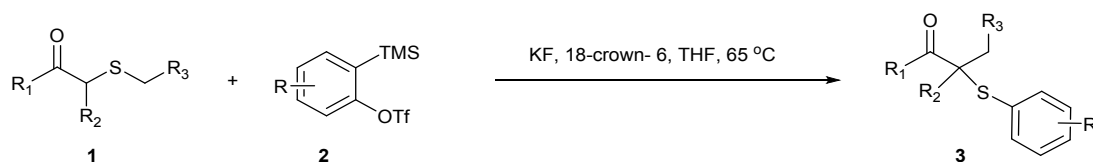
1. General Information

Unless otherwise noted, reactions were carried out in oven-dried glassware or sealed tube under atmosphere of nitrogen. Acetonitrile (CH_3CN) was distilled from calcium hydride. Tetrahydrofuran (THF) was dried and distilled from sodium. Reactions were monitored by analytical thin-layer chromatography (TLC) on Merck silica gel 60 F_{254} plates (0.25 mm), visualized by ultraviolet light (254 nm) or by staining with ceric ammonium molybdate. ^1H NMR spectra were obtained on an Agilent 400MR DD2 spectrometer at ambient temperature. Data were reported as follows: chemical shift on the δ scale using residual proton solvent as internal standard [δ 7.26 (CDCl_3); TMS: 0.00 ppm], multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets), integration, and coupling constant (J) in hertz (Hz). ^{13}C NMR spectra were obtained with proton decoupling on an Agilent 400MR DD2 (100 MHz) spectrometer and were reported in ppm with residual solvent for internal standard [δ 77.0 (CDCl_3)]. Melting point was determined by WRS-2A Digital Melting Point Apparatus. High resolution mass spectra were obtained on a Bruker SolariX 7.0T spectrometer. TMS = trimethylsilyl, Tf = trifluoromethanesulfonate, TBAF = tetrabutylammonium fluoride, TBAT = tetrabutylammonium difluorotriphenylsilicate.

2. General Procedures



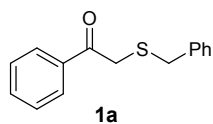
General procedure A¹: To a solution of 2-bromo-1-ethanone (5 mmol, 1 equiv) and thiol (6.0 mmol, 1.2 equiv) in CH₃CN (30 mL) at r.t., K₂CO₃ (6.0 mmol, 1.2 equiv) was added. The resulting reaction mixture was stirred for 3 h and water was then added to the mixture. The product was extracted with EtOAc (30 mL × 3), and the combined organic extracts were dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product **1**.¹



General Procedure B: To a solution of thioethers **1** (0.20 mmol, 1.0 equiv), KF (29.0 mg, 0.50 mmol, 2.5 equiv) and 18-crown-6 (66.0 mg, 0.25 mmol, 1.25 equiv) in anhydrous THF (3 mL) at r.t. was added β-trimethylsilyltriflate **2** (0.25 mmol, 1.25 equiv) dropwise, and the resulting reaction mixture was stirred for 4 h at 65 °C. Then the reaction mixture was concentrated and purified by column chromatograph (silica gel, petroleum ether:EtOAc) to yield multi-substituted β-keto thioethers **3**.

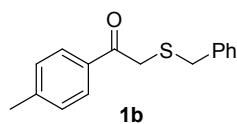
3. Characterization of Products

2-(Benzylthio)-1-phenylethan-1-one (**1a**):¹



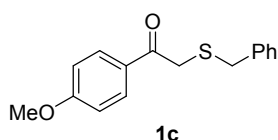
Prepared according to general procedure **A**, from 2-bromoacetophenone (2.0 g, 10.0 mmol, 1.0 equiv) and benzyl mercaptan (1.2 mL, 10.5 mmol, 1.05 equiv) to give **1a** (2.30 g, 95%) as white solid; R_f = 0.52 (silica gel, petroleum ether:EtOAc, 50:1); ^1H NMR (400 MHz, CDCl_3): δ 7.93 (d, J = 7.3 Hz, 2 H), 7.57 (t, J = 7.4 Hz, 1 H), 7.46 (t, J = 7.6 Hz, 2 H), 7.38 – 7.29 (m, 4 H), 7.28 – 7.25 (m, 1 H), 3.76 (s, 2 H), 3.67 (s, 2 H).

2-(Benzylthio)-1-(p-tolyl)ethan-1-one (**1b**):¹



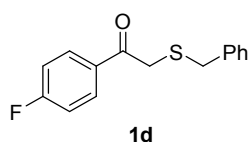
Prepared according to general procedure **A**, from 2-bromo-1-(4-methylphenyl)ethanone (1.06 g, 5.0 mmol, 1.0 equiv) and benzyl mercaptan (745 mg, 6.0 mmol, 1.2 equiv) to give **1b** (1.16 g, 91%) as white solid; R_f = 0.5 (silica gel, petroleum ether:EtOAc, 50:1); ^1H NMR (400 MHz, CDCl_3): δ 7.83 (d, J = 8.1 Hz, 2 H), 7.36 – 7.22 (m, 7 H), 3.75 (s, 2 H), 3.65 (s, 2 H), 2.41 (s, 3 H). ^{13}C NMR (100 MHz, CDCl_3): δ 194.1, 144.2, 137.3, 132.8, 129.3, 129.2, 128.8, 128.5, 127.2, 36.0, 35.8, 21.7.

2-(Benzylthio)-1-(4-methoxyphenyl)ethan-1-one (**1c**):¹



Prepared according to general procedure **A**, from 2-bromo-4'-methoxyacetophenone (1.14 g, 5.0 mmol, 1.0 equiv) and benzyl mercaptan (745 mg, 6.0 mmol, 1.2 equiv) to give **1c** (1.28 g, 94%) as white solid; R_f = 0.4 (silica gel, petroleum ether:EtOAc, 50:1); ^1H NMR (400 MHz, CDCl_3): δ 7.92 – 7.89 (m, 2 H), 7.36 – 7.22 (m, 5 H), 6.93 – 6.90 (m, 2 H), 3.87 (s, 3 H), 3.76 (s, 2 H), 3.63 (s, 2 H). ^{13}C NMR (100 MHz, CDCl_3): δ 193.2, 163.6, 137.4, 131.0, 129.2, 128.5, 128.4, 127.1, 113.8, 55.5, 36.1, 35.7.

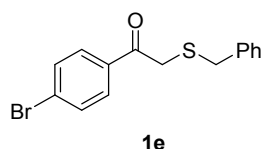
2-(Benzylthio)-1-(4-fluorophenyl)ethan-1-one (**1d**):



Prepared according to general procedure **A**, from 2-bromo-4'-fluoroacetophenone (1.08 g, 5.0 mmol, 1.0 equiv) and benzyl mercaptan

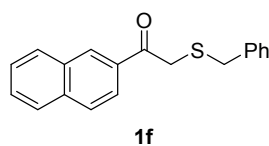
(745 mg, 6.0 mmol, 1.2 equiv) to give **1d** (1.16 g, 89%) as white solid; m.p. 58-60 °C; R_f = 0.4 (silica gel, petroleum ether:EtOAc, 50:1); ^1H NMR (400 MHz, CDCl_3): δ 7.96 – 7.93 (m, 2 H), 7.37 – 7.22 (m, 5 H), 7.12 (t, J = 8.6 Hz, 2 H), 3.75 (s, 2 H), 3.64 (s, 2 H). ^{13}C NMR (100 MHz, CDCl_3): δ 192.9, 165.1 (d, J = 254 Hz), 137.1, 131.7, 131.2 (d, J = 9.4 Hz), 129.2, 128.5, 127.3, 115.7 (d, J = 21.8 Hz), 36.1, 35.8. HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{13}\text{FNaOS}^+$ [$\text{M}+\text{Na}^+$]: 283.0563, found 283.0561.

2-(Benzylthio)-1-(4-bromophenyl)ethan-1-one (**1e**):²



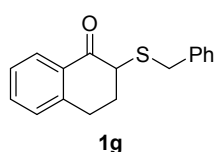
Prepared according to general procedure A, from 2,4'-dibromoacetophenone (1.39 g, 5.0 mmol, 1.0 equiv) and benzyl mercaptan (745 mg, 6.0 mmol, 1.2 equiv) to give **1e** (1.46 g, 91%) as white solid; R_f = 0.3 (silica gel, petroleum ether:EtOAc, 50:1); ^1H NMR (400 MHz, CDCl_3): δ 7.80 (d, J = 8.8 Hz, 2 H), 7.59 (d, J = 8.0 Hz, 2 H), 7.35 – 7.24 (m, 5 H), 3.74 (s, 2 H), 3.62 (s, 2 H). ^{13}C NMR (100 MHz, CDCl_3): δ 193.3, 137.1, 134.1, 131.9, 130.2, 129.2, 128.5, 128.5, 127.3, 36.1, 35.8.

2-(Benzylthio)-1-(naphthalen-2-yl)ethanone (**1f**):



Prepared according to general procedure A, from 2-bromo-2'-acetophenone (1.24 g, 5.0 mmol, 1.0 equiv) and benzyl mercaptan (745 mg, 6.0 mmol, 1.2 equiv) to give **1f** (1.39 g, 95%) as white solid; m.p. 63-65 °C; R_f = 0.5 (silica gel, petroleum ether:EtOAc, 50:1); ^1H NMR (400 MHz, CDCl_3): δ 8.42 (d, J = 1.8 Hz, 1 H), 8.04 – 7.82 (m, 4 H), 7.60 – 7.51 (m, 2 H), 7.42 – 7.21 (m, 5 H), 3.79 (s, 3 H). ^{13}C NMR (100 MHz, CDCl_3): δ 194.4, 137.3, 135.6, 132.7, 132.4, 130.5, 129.6, 129.3, 128.6, 128.5, 127.7, 127.2, 126.8, 124.2, 36.1, 35.9. HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{16}\text{NaOS}^+$ [$\text{M}+\text{Na}^+$]: 315.0814, found 315.0813.

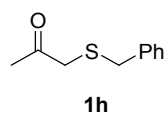
2-(Benzylthio)-3,4-dihydronaphthalen-1(2H)-one (**1g**):



Prepared according to general procedure A, from 2-bromo-1-tetralone (1.12 g, 5.0 mmol, 1.0 equiv) and benzyl mercaptan (745 mg, 6.0 mmol, 1.2 equiv) to give **1g** (1.00 g, 75%) as yellow solid; m.p. 57-58 °C; R_f = 0.5 (silica gel, petroleum ether:EtOAc, 20:1); ^1H NMR (400 MHz, CDCl_3): δ 8.12 (d, J = 7.9 Hz, 1 H), 7.47 (td, J

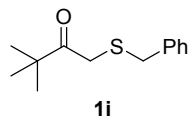
= 7.5, 1.4 Hz, 1 H), 7.41 (d, J = 7.2 Hz, 2 H), 7.37 – 7.18 (m, 6 H), 3.86 (d, J = 13.4 Hz, 1 H), 3.74 (d, J = 13.4 Hz, 1 H), 3.49 (t, J = 4.2 Hz, 1 H), 3.18 (ddd, J = 16.8, 11.8, 4.6 Hz, 1 H), 2.81 (dt, J = 17.1, 4.3 Hz, 1 H), 2.47 (ddt, J = 13.9, 11.9, 4.5 Hz, 1 H), 2.20 (dq, J = 13.9, 4.2 Hz, 1 H). ^{13}C NMR (100 MHz, CDCl_3): δ 192.8, 142.8, 137.6, 133.4, 130.8, 129.3, 128.6, 128.5, 128.2, 127.1, 126.8, 46.8, 34.7, 28.6, 26.0. HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{16}\text{NaOS}^+$ [$\text{M}+\text{Na}^+$]: 291.0814, found 291.0811.

1-(Benzylthio)propan-2-one (**1h**):³



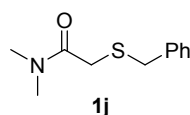
Prepared according to general procedure A, from 1-methylsulfonyloxypropan-2-one (1.2 g, 8.0 mmol, 1.0 equiv) and benzyl mercaptan (990 mg, 8.0 mmol, 1.0 equiv) to give **1h** (756 mg, 52%) as colorless oil; R_f = 0.5 (silica gel, petroleum ether:EtOAc, 10:1); ^1H NMR (400 MHz, CDCl_3): δ 7.34 – 7.21 (m, 5 H), 3.67 (s, 2 H), 3.10 (s, 2 H), 2.22 (s, 3 H). ^{13}C NMR (100 MHz, CDCl_3): δ 203.5, 137.1, 129.1, 128.4, 127.2, 40.7, 35.9, 27.9.

1-(Benzylthio)-3,3-dimethylbutan-2-one (**1i**):³



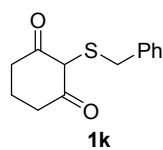
Prepared according to general procedure A, from 1-bromopinacolone (890 mg, 5.0 mmol, 1.0 equiv) and benzyl mercaptan (745 mg, 6.0 mmol, 1.2 equiv) to give **1i** (899 mg, 81%) as colorless oil; R_f = 0.48 (silica gel, petroleum ether:EtOAc, 10:1); ^1H NMR (400 MHz, CDCl_3): δ 7.37 – 7.21 (m, 5 H), 3.76 (s, 2 H), 3.26 (s, 2 H), 1.15 (s, 9 H). ^{13}C NMR (100 MHz, CDCl_3): δ 210.3, 137.4, 129.2, 128.4, 127.1, 44.1, 35.8, 34.6, 26.8.

2-(Benzylthio)-N,N-dimethylacetamide (**1j**):



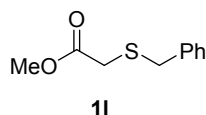
From ethyl 2-(benzylthio)acetate (210 mg, 1.0 mmol, 1.0 equiv) and 40% aqueous solution of dimethylamine (as solvent and reagent) to give **1j** (96 mg, 46%) as colorless oil; R_f = 0.4 (silica gel, petroleum ether:EtOAc, 1:1); ^1H NMR (400 MHz, CDCl_3): δ 7.38 – 7.33 (m, 2 H), 7.33 – 7.26 (m, 2 H), 7.26 – 7.17 (m, 1 H), 3.82 (s, 2 H), 3.17 (s, 2 H), 2.96 (s, 3 H), 2.93 (s, 3 H). ^{13}C NMR (100 MHz, CDCl_3): δ 168.9, 137.5, 129.0, 128.2, 126.9, 37.8, 36.0, 35.7, 32.2. MS calcd for $\text{C}_{11}\text{H}_{16}\text{NOS}^+$ [$\text{M}+\text{H}^+$]: 210, found 210.

2-(Benzylthio)cyclohexane-1,3-dione (**1k**):



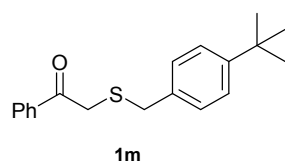
Prepared according to general procedure **A**, from 2-bromocyclohexane-1,3-dione (950 mg, 5.0 mmol, 1.0 equiv) and benzyl mercaptan (745 mg, 6.0 mmol, 1.2 equiv) to give **1k** (462 mg, 48%) as colorless oil; R_f = 0.4 (silica gel, petroleum ether:EtOAc, 1:2); ^1H NMR (400 MHz, CDCl_3): δ 7.56 (s, 1 H), 7.28 – 7.22 (m, 3 H), 7.13 – 7.11 (m, 2 H), 3.77 (s, 2 H), 2.43 (dt, J = 22.7, 6.5 Hz, 4 H), 1.91 (p, J = 6.4 Hz, 2 H). ^{13}C NMR (100 MHz, CDCl_3): δ 194.6, 179.4, 137.9, 128.8, 128.4, 127.3, 106.5, 37.7, 37.2, 28.0, 19.9. HRMS (ESI): calcd for $\text{C}_{13}\text{H}_{14}\text{NaO}_2\text{S}^+$ [$\text{M}+\text{Na}^+$]: 257.0607, found 257.0606.

methyl 2-(benzylthio)acetate (**1l**):



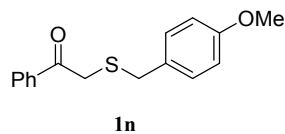
Prepared according to general procedure **A**, from methyl 2-bromoacetate (940 μL , 10.0 mmol, 1.0 equiv) and benzyl mercaptan (1.24 g, 10.0 mmol, 1.0 equiv) to give **1l** (1.7 g, 89%) as colorless oil; R_f = 0.6 (silica gel, petroleum ether:EtOAc, 10:1); ^1H NMR (400 MHz, CDCl_3): δ 7.35 – 7.30 (m, 4 H), 7.28 – 7.22 (m, 1 H), 3.82 (s, 2 H), 3.71 (s, 3 H), 3.08 (s, 2 H). ^{13}C NMR (100 MHz, CDCl_3): δ 170.8, 137.1, 129.1, 128.5, 127.3, 52.3, 36.4, 32.1.

2-((4-(Tert-butyl)benzyl)thio)-1-phenylethanone (**1m**):



Prepared according to general procedure **A**, from 2-bromoacetophenone (995 mg, 5.0 mmol, 1.0 equiv) and 4-(tert-Butyl)benzyl mercaptan (1.08 g, 6.0 mmol, 1.2 equiv) to give **1m** (1.28 g, 86%) as colorless oil; R_f = 0.5 (silica gel, petroleum ether:EtOAc, 50:1); ^1H NMR (400 MHz, CDCl_3): δ 7.93 (d, J = 7.3 Hz, 2 H), 7.60 – 7.53 (m, 1 H), 7.45 (t, J = 7.6 Hz, 2 H), 7.33 (d, J = 8.3 Hz, 2 H), 7.30 – 7.24 (m, 2 H), 3.74 (s, 2 H), 3.68 (s, 2 H), 1.31 (s, 9 H). ^{13}C NMR (100 MHz, CDCl_3): δ 194.5, 150.2, 135.5, 134.2, 133.3, 128.9, 128.7, 128.6, 125.4, 36.0, 35.7, 34.5, 31.3. HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{22}\text{NaOS}^+$ [$\text{M}+\text{Na}^+$]: 321.1284, found 321.1280.

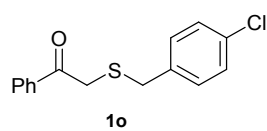
2-((4-Methoxybenzyl)thio)-1-phenylethan-1-one (**1n**):⁴



Prepared according to general procedure **A**, from 2-bromoacetophenone (995 mg, 5.0 mmol, 1.0 equiv) and 4-methoxybenzyl mercaptan (924 mg, 6.0 mmol, 1.2 equiv) to give **1n** (1.22 g, 90%) as white solid; R_f =

0.4 (silica gel, petroleum ether:EtOAc, 20:1); ^1H NMR (400 MHz, CDCl_3): δ 7.96–7.91 (m, 2 H), 7.60–7.54 (m, 1 H), 7.45 (t, J = 7.8 Hz, 2 H), 7.28–7.23 (m, 2 H), 6.86–6.81 (m, 2 H), 3.79 (s, 3 H), 3.72 (s, 2 H), 3.66 (s, 2 H). ^{13}C NMR (100 MHz, CDCl_3): δ 194.5, 158.8, 135.4, 133.3, 130.4, 129.2, 128.7, 128.6, 113.9, 55.2, 35.8, 35.5.

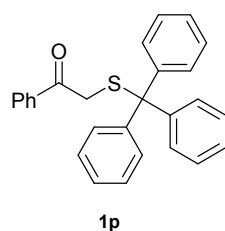
2-((4-Chlorobenzyl)thio)-1-phenylethan-1-one (**1o**):



Prepared according to general procedure **A**, from 2-bromoacetophenone (995 mg, 5.0 mmol, 1.0 equiv) and 4-chlorobenzyl mercaptan (948 mg, 6.0 mmol, 1.2 equiv) to give **1o** (1.27 g, 92%) as white solid; m.p. 91-92

$^{\circ}\text{C}$; R_f = 0.4 (silica gel, petroleum ether:EtOAc, 50:1); ^1H NMR (400 MHz, CDCl_3): δ 7.93 (dt, J = 8.3, 1.4 Hz, 2 H), 7.58 (td, J = 7.3, 1.5 Hz, 1 H), 7.46 (td, J = 7.7, 1.5 Hz, 2 H), 7.32–7.25 (m, 4 H), 3.72 (s, 2 H), 3.65 (s, 2 H). ^{13}C NMR (100 MHz, CDCl_3): δ 194.2, 135.8, 135.3, 133.4, 133.0, 130.6, 128.7, 128.6, 35.6, 35.3. HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{13}\text{ClNaOS}^+$ [$\text{M}+\text{Na}^+$]: 299.0268, found 299.0265.

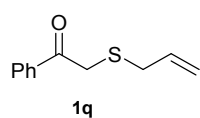
1-Phenyl-2-(tritylthio)ethan-1-one (**1p**):



Prepared according to general procedure **A**, from 2-bromoacetophenone (995 mg, 5.0 mmol, 1.0 equiv) and triphenylmethyl mercaptan (1.66 g, 6.0 mmol, 1.2 equiv) to give **1p** (1.83 g, 93%) as white solid; m.p. 110-112 $^{\circ}\text{C}$; R_f = 0.5

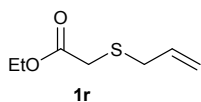
(silica gel, petroleum ether:EtOAc, 50:1); ^1H NMR (400 MHz, CDCl_3): δ 7.70–7.65 (m, 2 H), 7.55–7.45 (m, 7 H), 7.36 (t, J = 7.8 Hz, 2 H), 7.30 (dd, J = 8.5, 6.8 Hz, 6 H), 7.26–7.19 (m, 4 H), 3.56 (s, 2 H). ^{13}C NMR (100 MHz, CDCl_3): δ 195.1, 144.2, 135.7, 133.3, 129.5, 128.5, 128.1, 126.9, 67.2, 39.6. HRMS (ESI): calcd for $\text{C}_{27}\text{H}_{22}\text{NaOS}^+$ [$\text{M}+\text{Na}^+$]: 417.1284, found 417.1282.

2-(Allylthio)-1-phenylethanone (**1q**):⁵



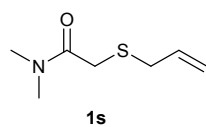
Prepared according to general procedure **A**, from 2-bromoacetophenone (995 mg, 5.0 mmol, 1.0 equiv) and allyl mercaptan (444 mg, 6.0 mmol, 1.2 equiv) to give **1q** (682 mg, 71%) as colorless oil; $R_f = 0.5$ (silica gel, petroleum ether:EtOAc, 50:1); ^1H NMR (400 MHz, CDCl_3): δ 8.00 – 7.95 (m, 2 H), 7.63 – 7.56 (m, 1 H), 7.47 (dd, $J = 8.4, 7.1$ Hz, 2 H), 5.78 (ddt, $J = 17.0, 9.8, 7.2$ Hz, 1 H), 5.23 – 5.14 (m, 2 H), 3.77 (s, 2 H), 3.19 (dt, $J = 7.2, 1.0$ Hz, 2 H). ^{13}C NMR (100 MHz, CDCl_3): δ 194.5, 135.5, 133.3, 132.9, 128.6, 118.5, 35.6, 34.7.

Ethyl 2-(allylthio)acetate (**1r**):



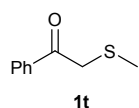
From ethyl 2-mercaptoacetate (0.6 mL, 5.0 mmol, 1.0 equiv) and allyl bromide (0.43 mL, 5.0 mmol, 1.0 equiv) to give **1r** (1.15 g, 95%) as colorless oil; $R_f = 0.68$ (silica gel, petroleum ether:EtOAc, 10:1); ^1H NMR (400 MHz, CDCl_3): δ 5.82 – 5.70 (m, 1 H), 5.19 – 5.12 (m, 2 H), 4.19 (q, $J = 7.1$, 2 H), 3.24 (d, $J = 7.1$, 2 H), 3.16 (s, 2 H), 1.29 (t, $J = 7.1$, 3 H). ^{13}C NMR (100 MHz, CDCl_3): δ 170.5, 132.9, 118.3, 61.2, 34.9, 31.7, 14.2. HRMS (ESI): calcd for $\text{C}_7\text{H}_{12}\text{NaO}_2\text{S}^+ [\text{M}+\text{Na}^+]$: 183.0450, found 183.0455.

2-(Allylthio)-N,N-dimethylacetamide (**1s**):



From **1q** (160 mg, 1.0 mmol, 1.0 equiv) and 40% aqueous solution of dimethylamine (as solvent and reagent) to give **1s** (64 mg, 40%) as colorless oil; $R_f = 0.38$ (silica gel, petroleum ether:EtOAc, 1:1); ^1H NMR (400 MHz, CDCl_3): δ 5.86 – 5.73 (m, 1 H), 5.26 – 5.11 (m, 2 H), 3.31 – 3.21 (m, 4 H), 3.07 (s, 3 H), 2.97 (s, 3 H). ^{13}C NMR (100 MHz, CDCl_3): δ 169.2, 133.1, 118.1, 37.8, 35.7, 34.6, 31.7. HRMS (ESI): calcd for $\text{C}_7\text{H}_{13}\text{NNaOS}^+ [\text{M}+\text{Na}^+]$: 182.0610, found 182.0610.

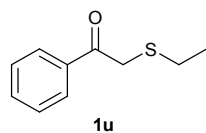
2-(Methylthio)-1-phenylethan-1-one (**1t**):⁶



From 2-bromoacetophenone (995 mg, 5.0 mmol, 1.0 equiv) and sodium thiomethoxide (1.2 equiv) to give **1t** (774 mg, 86%) as colorless oil; $R_f = 0.56$ (silica gel, petroleum ether:EtOAc, 10:1); ^1H NMR (400 MHz, CDCl_3): δ 7.98 (d, $J = 7.5$

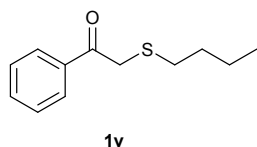
Hz, 2 H), 7.60 – 7.54 (m, 1 H), 7.50 – 7.43 (m, 2 H), 3.76 (s, 2 H), 2.13 (s, 3 H), ^{13}C NMR (100 MHz, CDCl_3): δ 193.9, 135.0, 133.2, 128.6, 128.5, 38.9, 15.8.

2-(Ethylthio)-1-phenylethan-1-one (**1u**):⁶



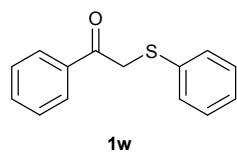
From 2-bromoacetophenone (995 mg, 5.0 mmol, 1.0 equiv) and ethanethiol (372 mg, 6.0 mmol, 1.2 equiv) to give **1u** (774 mg, 86%) as colorless oil; R_f = 0.4 (silica gel, petroleum ether:EtOAc, 50:1); ^1H NMR (400 MHz, CDCl_3): δ 7.98 (dt, J = 7.3, 1.4 Hz, 2 H), 7.60 – 7.55 (m, 1 H), 7.47 (dd, J = 8.4, 7.0 Hz, 2 H), 3.80 (s, 2 H), 2.59 (q, J = 7.4 Hz, 2 H), 1.27 (t, J = 7.4 Hz, 3 H). ^{13}C NMR (100 MHz, CDCl_3): δ 194.5, 135.2, 133.3, 128.7, 128.6, 36.7, 26.3, 14.1.

2-(Butylthio)-1-phenylethan-1-one (**1v**):⁶



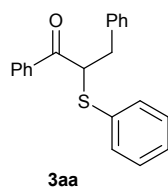
From 2-bromo-1-ethanone (995 mg, 5.0 mmol, 1.0 equiv) and butanethiol (540 mg, 6.0 mmol, 1.2 equiv) to give **1v** (874 mg, 84%) as colorless oil; R_f = 0.4 (silica gel, petroleum ether:EtOAc, 50:1); ^1H NMR (400 MHz, CDCl_3): δ 8.00 – 7.95 (m, 2 H), 7.60 – 7.55 (m, 1 H), 7.47 (td, J = 7.8, 7.4, 1.6 Hz, 2 H), 3.78 (s, 2 H), 2.57 (dd, J = 8.0, 6.8 Hz, 2 H), 1.64 – 1.54 (m, 2 H), 1.42 – 1.36 (m, J = 7.3 Hz, 2 H), 0.90 (t, J = 7.4 Hz, 3 H). ^{13}C NMR (100 MHz, CDCl_3) δ 194.5, 135.3, 133.2, 128.7, 128.6, 37.1, 32.0, 31.0, 21.8, 13.6.

1-Phenyl-2-(phenylthio)ethan-1-one (**1w**):⁵



Prepared according to general procedure A, from 2-bromo-1-ethanone (995 mg, 5.0 mmol, 1.0 equiv) and thiophenol (660 mg, 6.0 mmol, 1.2 equiv) to give **1w** (1.08 g, 95%) as colorless oil; R_f = 0.7 (silica gel, petroleum ether:EtOAc, 10:1); ^1H NMR (400 MHz, CDCl_3): δ 7.96 – 7.91 (m, 2 H), 7.57 (t, J = 7.4 Hz, 1 H), 7.46 (t, J = 7.7 Hz, 2 H), 7.39 (d, J = 7.3 Hz, 2 H), 7.30 – 7.18 (m, 3 H), 4.27 (s, 2 H).

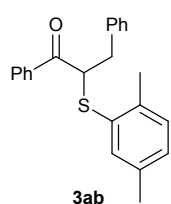
1,3-Diphenyl-2-(phenylthio)propan-1-one (**3aa**):⁷



Prepared according to general procedure B, from 2-(benzylthio)-1-phenylethan-1-

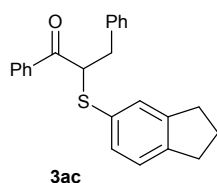
one **1a** (48 mg, 0.2 mmol, 1.0 equiv) and β -trimethylsilyltriflate **2a** (72 mg, 1.2 equiv) to give **3aa** (52 mg, 82%) as white solid; R_f = 0.68 (silica gel, petroleum ether:EtOAc, 10:1); ^1H NMR (400 MHz, CDCl_3): δ 7.83 (d, J = 7.6 Hz, 2 H), 7.51 (t, J = 7.2 Hz, 1 H), 7.39 (t, J = 7.6 Hz, 2 H), 7.32 – 7.15 (m, 10 H), 4.71 (dd, J = 8.4, 6.4 Hz, 1 H), 3.42 (dd, J = 14.0, 8.4 Hz, 1 H), 3.15 (dd, J = 14.0, 6.0 Hz, 1 H). ^{13}C NMR (100 MHz, CDCl_3): δ 195.2, 138.6, 136.2, 134.5, 133.0, 132.0, 129.3, 129.0, 128.7, 128.5, 128.5, 128.5, 126.6, 52.9, 37.3.

2-((2,5-Dimethylphenyl)thio)-1,3-diphenylpropan-1-one (**3ab**):



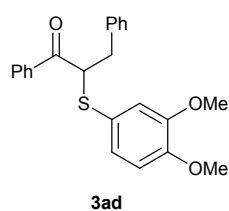
Prepared according to general procedure **B**, from 2-(benzylthio)-1-phenylethan-1-one **1a** (48 mg, 0.2 mmol, 1.0 equiv) and β -trimethylsilyltriflate **2b** (78 mg, 1.2 equiv) to give **3ab** (47 mg, 69%) as yellow oil; R_f = 0.65 (silica gel, petroleum ether:EtOAc, 10:1); ^1H NMR (400 MHz, CDCl_3): δ 7.70 (d, J = 7.2 Hz, 2 H), 7.47 (t, J = 7.2 Hz, 1 H), 7.31 (t, J = 7.6 Hz, 2 H), 7.26 – 7.15 (m, 5 H), 7.02 (d, J = 8.0 Hz, 1 H), 6.98 – 6.94 (m, 2 H), 4.66 (dd, J = 8.8, 6.0 Hz, 1 H), 3.48 (dd, J = 14.0, 8.8 Hz, 1 H), 3.18 (dd, J = 14.0, 6.0 Hz, 1 H), 2.18 (s, 3 H), 2.17 (s, 3 H). ^{13}C NMR (100 MHz, CDCl_3): δ 196.1, 138.7, 138.2, 136.4, 136.0, 135.0, 132.9, 132.0, 130.2, 129.3, 128.5, 128.4, 128.3, 126.6, 53.2, 37.6, 20.7, 20.3. HRMS (ESI): calcd for $\text{C}_{23}\text{H}_{22}\text{NaOS}^+$ [$\text{M}+\text{Na}^+$]: 369.1284, found 369.1281.

2-((2,3-Dihydro-1H-inden-5-yl)thio)-1,3-diphenylpropan-1-one (**3ac**):



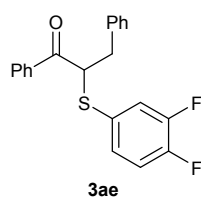
Prepared according to general procedure **B**, from 2-(benzylthio)-1-phenylethan-1-one **1a** (48 mg, 0.2 mmol, 1.0 equiv) and β -trimethylsilyltriflate **2c** (81 mg, 1.2 equiv) to give **3ac** (51 mg, 71%) as yellow oil; R_f = 0.61 (silica gel, petroleum ether:EtOAc, 10:1); ^1H NMR (400 MHz, CDCl_3): δ 7.84 (d, J = 7.6 Hz, 2 H), 7.51 (t, J = 7.6 Hz, 1 H), 7.38 (t, J = 8.0 Hz, 2 H), 7.25 – 7.15 (m, 5 H), 7.11 (d, J = 8.4 Hz, 2 H), 7.06 (d, J = 8.0 Hz, 1 H), 4.64 (dd, J = 8.4, 6.0 Hz, 1 H), 3.39 (dd, J = 14.0, 8.0 Hz, 1 H), 3.19 (dd, J = 14.0, 6.0 Hz, 1 H), 2.87 (t, J = 7.6 Hz, 2 H), 2.83 (dd, J = 9.2, 6.8 Hz, 2 H), 2.10 – 2.02 (m, 2 H). ^{13}C NMR (100 MHz, CDCl_3): δ 195.2, 145.6, 145.2, 138.9, 136.3, 133.0, 132.9, 131.2, 129.3, 128.6, 128.5, 128.4, 128.4, 126.4, 124.8, 53.1, 37.2, 32.6, 32.6, 25.4. HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{22}\text{NaOS}^+$ [$\text{M}+\text{Na}^+$]: 381.1284, found 381.1280.

2-((3,4-Dimethoxyphenyl)thio)-1,3-diphenylpropan-1-one (3ad):



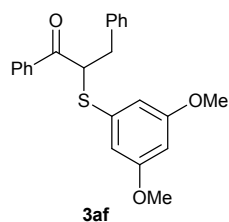
Prepared according to general procedure **B**, from 2-(benzylthio)-1-phenylethan-1-one **1a** (48 mg, 0.2 mmol, 1.0 equiv) and β -trimethylsilyltriflate **2d** (86 mg, 1.2 equiv) to give **3ad** (47 mg, 63%) as colorless oil; R_f = 0.65 (silica gel, petroleum ether:EtOAc, 10:1); ^1H NMR (400 MHz, CDCl_3): δ 7.84 (d, J = 7.2 Hz, 2 H), 7.53 (t, J = 7.6 Hz, 1 H), 7.40 (t, J = 7.6 Hz, 2 H), 7.28 – 7.16 (m, 4 H), 6.88 (dd, J = 8.2, 2.0 Hz, 1 H), 6.75 (d, J = 8.4 Hz, 1 H), 6.65 (d, J = 2.0 Hz, 1 H), 4.60 (dd, J = 7.6, 6.8 Hz, 1 H), 3.87 (s, 3 H), 3.72 (s, 3 H), 3.36 (dd, J = 14.0, 8.0 Hz, 1 H), 3.13 (dd, J = 14.0, 6.8 Hz, 1 H). ^{13}C NMR (100 MHz, CDCl_3): δ 195.1, 150.0, 148.6, 138.8, 136.2, 133.0, 129.4, 128.7, 128.5, 128.4, 126.5, 122.2, 118.2, 111.1, 55.8, 55.8, 53.3, 36.9. HRMS (ESI): calcd for $\text{C}_{23}\text{H}_{22}\text{NaO}_3\text{S}^+$ [$\text{M}+\text{Na}^+$]: 401.1182, found 401.1179.

2-((3,4-Difluorophenyl)thio)-1,3-diphenylpropan-1-one (3ae):



Prepared according to general procedure **B**, from 2-(benzylthio)-1-phenylethan-1-one **1a** (48 mg, 0.2 mmol, 1.0 equiv) and β -trimethylsilyltriflate **2e** (80 mg, 1.2 equiv) to give **3ae** (55 mg, 78%) as colorless oil; R_f = 0.72 (silica gel, petroleum ether:EtOAc, 10:1); ^1H NMR (400 MHz, CDCl_3): δ 7.83 (d, J = 7.6 Hz, 2 H), 7.55 (t, J = 7.2 Hz, 1 H), 7.42 (t, J = 7.6 Hz, 2 H), 7.30 – 7.18 (m, 5 H), 7.08 – 6.97 (m, 3 H), 4.66 (dd, J = 8.0, 6.8 Hz, 1 H), 3.36 (dd, J = 14.0, 8.0 Hz, 1 H), 3.11 (dd, J = 14.0, 6.4 Hz, 1 H). ^{13}C NMR (100 MHz, CDCl_3): δ 194.8, 138.2, 135.9, 133.3, 131.7 (dd, J = 6.3, 3.7 Hz), 129.3, 128.6, 128.5, 128.4, 126.8, 124.0 (dd, J = 16.0, 2.5 Hz), 117.6 (dd, J = 16.8, 1.6 Hz), 52.8, 37.0. HRMS (ESI): calcd for $\text{C}_{21}\text{H}_{16}\text{F}_2\text{NaOS}^+$ [$\text{M}+\text{Na}^+$]: 377.0782, found 377.0781.

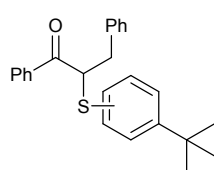
2-((3,5-Dimethoxyphenyl)thio)-1,3-diphenylpropan-1-one (3af):



Prepared according to general procedure **B**, from 2-(benzylthio)-1-phenylethan-1-one **1a** (48 mg, 0.2 mmol, 1.0 equiv) and β -trimethylsilyltriflate **2f** (86 mg, 1.2 equiv) to give **3af** (50 mg, 67%) as colorless oil; R_f = 0.65 (silica gel, petroleum ether:EtOAc, 10:1); ^1H NMR

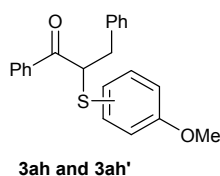
(400 MHz, CDCl₃): δ 7.81 (d, J = 7.2 Hz, 2 H), 7.51 (t, J = 7.6 Hz, 1 H), 7.38 (t, J = 7.6 Hz, 2 H), 7.27 – 7.16 (m, 5 H), 6.39 – 6.36 (m, 3 H), 4.72 (dd, J = 7.9, 6.7 Hz, 1 H), 3.68 (s, 6 H), 3.45 (dd, J = 14.0, 8.0 Hz, 1 H), 3.17 (dd, J = 14.0, 6.6 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ 195.6, 160.6, 138.6, 136.2, 134.4, 133.0, 129.4, 128.5, 128.4, 126.6, 111.0, 101.2, 55.4, 55.4, 53.3, 37.5. HRMS (ESI): calcd for C₂₃H₂₂NaO₃S⁺ [M+Na⁺]: 401.1182, found 401.1179.

2-((4-(tert-Butyl)phenyl)thio)-1,3-diphenylpropan-1-one (3ag) and 2-((3-(tert-butyl)phenyl)thio)-1,3-diphenylpropan-1-one (3ag'):



Prepared according to general procedure **B**, from 2-(benzylthio)-1-phenylethan-1-one **1a** (48 mg, 0.2 mmol, 1.0 equiv) and β -trimethylsilyltriflate **2g** (85 mg, 1.2 equiv) to give **3ag** and **3ag'** (ratio = 5:3, 54 mg, 73%) as colorless oil; R_f = 0.73 (silica gel, petroleum ether:EtOAc, 10:1); ¹H NMR (400 MHz, CDCl₃): δ 7.83 – 7.80 (m, 2 H), 7.51 (t, J = 7.4 Hz, 1 H), 7.37 (t, J = 7.8 Hz, 2 H), 7.34 – 7.09 (m, 9 H), 4.71 – 4.65 (m, 1 H), 3.44 – 3.36 (m, 1 H), 3.18 – 3.11 (m, 1 H), 1.30 (s, 3.3 H), 1.24 (s, 5.7 H). ¹³C NMR (100 MHz, CDCl₃): δ 195.3, 152.0, 138.7, 136.2, 134.5, 133.0, 131.9, 131.5, 129.3, 128.7, 128.5, 128.4, 126.5, 126.0, 125.8, 53.0, 37.1, 34.7, 31.1 (3 C). HRMS (ESI): calcd for C₂₅H₂₆NaOS⁺ [M+Na⁺]: 397.1597, found 397.1596.

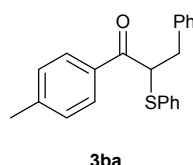
2-((4-Methoxyphenyl)thio)-1,3-diphenylpropan-1-one (3ah) and 2-((3-methoxyphenyl)thio)-1,3-diphenylpropan-1-one (3ah'):



Prepared according to general procedure **B**, from 2-(benzylthio)-1-phenylethan-1-one **1a** (48 mg, 0.2 mmol, 1.0 equiv) and β -trimethylsilyltriflate **2h** (78 mg, 1.2 equiv) to give **3ah** and **3ah'** (ratio = 4:3, 41 mg, 60%) as colorless oil; R_f = 0.58 (silica gel, petroleum ether:EtOAc, 10:1); ¹H NMR (400 MHz, CDCl₃): δ 7.86 (d, J = 7.6 Hz, 2 H), 7.82 (d, J = 7.6 Hz, 2.6 H), 7.54 – 7.48 (m, 2.4 H), 7.42 – 7.32 (m, 4.8 H), 7.27 – 7.15 (m, 15.6 H), 6.88 – 6.76 (m, 5.6 H), 4.71 (dd, J = 7.9, 6.6 Hz, 1 H), 4.58 (dd, J = 8.4, 6.0 Hz, 1.4 H), 3.79 (s, 4.3 H), 3.70 (s, 2.9 H), 3.43 (dd, J = 14.0, 8.2 Hz, 1 H), 3.33 (dd, J = 14.0, 8.4 Hz, 1.4 H), 3.16 (dd, J = 14.0, 6.4 Hz, 1 H), 3.09 (dd, J = 14.0, 6.0 Hz, 1.4 H). ¹³C NMR (100 MHz, CDCl₃): δ 195.4, 194.8, 160.6, 159.6, 138.8, 138.6, 137.4, 136.2, 136.0, 133.3, 133.0, 132.9, 129.7, 129.3, 129.2, 128.5, 128.4, 128.4, 126.6, 126.5, 126.2,

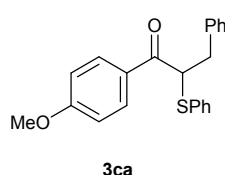
121.5, 118.9, 114.8, 114.4, 55.2, 53.0, 52.8, 37.3, 36.8. HRMS (ESI): calcd for $C_{22}H_{20}NaO_2S^+$ $[M+Na^+]$: 371.1076, found 371.1076.

3-Phenyl-2-(phenylthio)-1-(p-tolyl)propan-1-one (3ba):



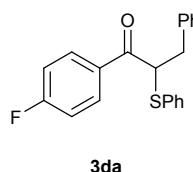
Prepared according to general procedure **B**, from 2-(benzylthio)-1-(p-tolyl)ethan-1-one **1b** (51 mg, 0.2 mmol, 1.0 equiv) and β -trimethylsilyltriflate **2a** (72 mg, 1.2 equiv) to give **3ba** (48 mg, 73%) as colorless oil; R_f = 0.48 (silica gel, petroleum ether:EtOAc, 10:1); 1H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.0 Hz, 2 H), 7.31 – 7.15 (m, 12 H), 4.68 (dd, J = 8.0, 6.4 Hz, 1 H), 3.39 (dd, J = 14.0, 8.4 Hz, 1 H), 3.12 (dd, J = 14.0, 6.1 Hz, 1 H), 2.38 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.1, 150.0, 148.6, 138.8, 136.2, 133.0, 129.4, 128.7, 128.5, 128.5, 128.4, 126.5, 122.2, 118.2, 111.1, 55.8, 55.8, 53.3, 36.9. HRMS (ESI): calcd for $C_{22}H_{20}NaOS^+$ $[M+Na^+]$: 355.1127, found 355.1126.

1-(4-Methoxyphenyl)-3-phenyl-2-(phenylthio)propan-1-one (3ca):



Prepared according to general procedure **B**, from 2-(benzylthio)-1-(4-methoxyphenyl)ethan-1-one **1c** (54 mg, 0.2 mmol, 1.0 equiv) and β -trimethylsilyltriflate **2a** (72 mg, 1.2 equiv) to give **3ca** (45 mg, 65%) as colorless oil; R_f = 0.45 (silica gel, petroleum ether:EtOAc, 10:1); 1H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 8.8 Hz, 2 H), 7.30 – 7.14 (m, 10 H), 6.85 (d, J = 8.8 Hz, 2 H), 4.67 (dd, J = 8.2, 6.4 Hz, 1 H), 3.83 (s, 3 H), 3.40 (dd, J = 14.0, 6.1 Hz, 1 H), 3.12 (dd, J = 14.0, 6.1 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.0, 163.5, 138.8, 134.2, 132.5, 130.8, 129.3, 129.0, 128.9, 128.5, 128.4, 126.5, 113.7, 55.4, 52.7, 37.5. HRMS (ESI): calcd for $C_{22}H_{20}NaO_2S^+$ $[M+Na^+]$: 371.1076, found 371.1073.

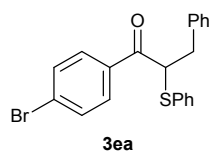
1-(4-Fluorophenyl)-3-phenyl-2-(phenylthio)propan-1-one (3da):



Prepared according to general procedure **B**, from 2-(benzylthio)-1-(4-fluorophenyl)ethan-1-one **1d** (52 mg, 0.2 mmol, 1.0 equiv) and β -trimethylsilyltriflate **2a** (72 mg, 1.2 equiv) to give **3da** (51 mg, 76%); R_f = 0.54 (silica gel, petroleum ether:EtOAc, 10:1) as colorless oil; 1H NMR (400 MHz,

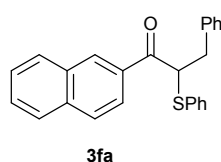
CDCl₃): δ 7.85 – 7.80 (m, 2 H), 7.33 – 7.15 (m, 10 H), 7.03 (t, J = 8.6 Hz, 2 H), 4.64 (dd, J = 8.5, 6.1 Hz, 1 H), 3.40 (dd, J = 14.0, 8.5 Hz, 1 H), 3.14 (dd, J = 14.0, 6.1 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ 193.8, 165.6 (d, J = 53.7 Hz), 138.5, 134.5, 132.5 (d, J = 13.0 Hz), 131.9, 131.1 (d, J = 92.4 Hz), 129.3, 129.0, 128.8, 128.5, 126.6, 115.6 (d, J = 21.8 Hz), 53.0, 37.3. HRMS (ESI): calcd for C₂₁H₁₇FNaOS⁺ [M+Na⁺]: 359.0876, found 359.0874.

1-(4-Bromophenyl)-3-phenyl-2-(phenylthio)propan-1-one (3ea):



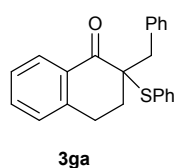
Prepared according to general procedure **B**, from 2-(benzylthio)-1-(4-bromophenyl)ethan-1-one **1e** (64 mg, 0.2 mmol, 1.0 equiv) and β -trimethylsilyltriflate **2a** (72 mg, 1.2 equiv) to give **3ea** (57 mg, 72%) as colorless oil; R_f = 0.49 (silica gel, petroleum ether:EtOAc, 10:1); ¹H NMR (400 MHz, CDCl₃): δ 7.67 (d, J = 8.5 Hz, 2 H), 7.50 (d, J = 8.4 Hz, 2 H), 7.33 – 7.16 (m, 10 H), 4.61 (dd, J = 8.4, 6.1 Hz, 1 H), 3.39 (dd, J = 14.0, 8.8 Hz, 1 H), 3.14 (dd, J = 14.0, 6.1 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ 194.2, 138.5, 134.9, 134.6, 131.8, 131.7, 130.0, 129.3, 129.1, 128.9, 128.5, 128.2, 126.7, 53.0, 37.2. HRMS (ESI): calcd for C₂₁H₁₇BrNaOS⁺ [M+Na⁺]: 419.0076, found 419.0072.

1-(Naphthalen-2-yl)-3-phenyl-2-(phenylthio)propan-1-one (3fa):



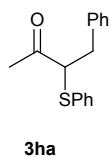
Prepared according to general procedure **B**, from 2-(benzylthio)-1-(naphthalen-2-yl)ethan-1-one **1f** (58 mg, 0.2 mmol, 1.0 equiv) and β -trimethylsilyltriflate **2a** (72 mg, 1.2 equiv) to give **3fa** (51 mg, 70%) as yellow oil; R_f = 0.52 (silica gel, petroleum ether:EtOAc, 10:1); ¹H NMR (400 MHz, CDCl₃): δ 8.22 (s, 1 H), 7.95 (dd, J = 8.7, 1.6 Hz, 1 H), 7.84 (d, J = 8.5 Hz, 2 H), 7.78 (d, J = 8.1 Hz, 1 H), 7.57 (ddd, J = 8.2, 6.9, 1.3 Hz, 1 H), 7.50 (ddd, J = 8.1, 6.8, 1.3 Hz, 1 H), 7.33 – 7.23 (m, 9 H), 7.21 – 7.16 (m, 1 H), 4.83 (dd, J = 8.2, 6.3 Hz, 1 H), 3.47 (dd, J = 14.0, 8.2 Hz, 1 H), 3.21 (dd, J = 14.0, 6.3 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ 195.1, 138.7, 135.5, 134.6, 133.3, 132.3, 132.2, 130.1, 129.6, 129.4, 129.0, 128.8, 128.5, 128.3, 127.7, 126.6, 126.6, 124.3, 53.3, 37.3. HRMS (ESI): calcd for C₂₅H₂₀NaOS⁺ [M+Na⁺]: 391.1127, found 391.1127.

2-Benzyl-2-(phenylthio)-3,4-dihydronaphthalen-1(2H)-one (**3ga**):



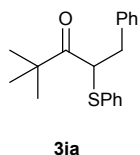
Prepared according to general procedure **B**, from 2-(benzylthio)-3,4-dihydronaphthalen-1(2H)-one **1g** (53 mg, 0.2 mmol, 1.0 equiv) and β -trimethylsilyltriflate **2a** (72 mg, 1.2 equiv) to give **3ga** (42 mg, 61%) as colorless oil; R_f = 0.57 (silica gel, petroleum ether:EtOAc, 10:1); ^1H NMR (400 MHz, CDCl_3): δ 8.11 (d, J = 7.8 Hz, 1 H), 7.46 – 7.38 (m, 4 H), 7.36 – 7.29 (m, 3 H), 7.20 – 7.10 (m, 6 H), 3.62 (d, J = 13.6 Hz, 1 H), 3.47 (ddd, J = 17.5, 12.7, 5.0 Hz, 1 H), 2.92 (d, J = 13.6 Hz, 1 H), 2.80 (ddd, J = 17.3, 5.1, 2.4 Hz, 1 H), 2.28 (td, J = 13.5, 13.1, 5.0 Hz, 1 H), 2.16 (ddd, J = 14.4, 5.1, 2.4 Hz, 1 H). ^{13}C NMR (100 MHz, CDCl_3): δ 191.1, 142.3, 137.5, 137.1, 133.0, 131.7, 131.0, 129.7, 129.3, 128.8, 128.5, 128.4, 128.0, 126.7, 126.5, 58.9, 42.6, 31.9, 25.5. HRMS (ESI): calcd for $\text{C}_{23}\text{H}_{20}\text{NaOS}^+$ [$\text{M}+\text{Na}^+$]: 367.1127, found 367.1125.

4-Phenyl-3-(phenylthio)butan-2-one (**3ha**):⁸



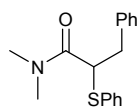
Prepared according to general procedure **B**, from 1-(benzylthio)propan-2-one **1h** (36 mg, 0.2 mmol, 1.0 equiv) and β -trimethylsilyltriflate **2a** (72 mg, 1.2 equiv) to give **3ha** (31 mg, 62%) as colorless oil; R_f = 0.46 (silica gel, petroleum ether:EtOAc, 10:1); ^1H NMR (400 MHz, CDCl_3): δ 7.37 – 7.16 (m, 10 H), 3.90 (dd, J = 8.3, 6.8 Hz, 1 H), 3.17 (dd, J = 14.2, 8.4 Hz, 1 H), 3.00 (dd, J = 14.2, 6.8 Hz, 1 H), 2.20 (s, 3H).

4,4-Dimethyl-1-phenyl-2-(phenylthio)pentan-3-one (**3ia**):



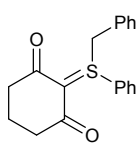
Prepared according to general procedure **B**, from 1-(benzylthio)-3,3-dimethylbutan-2-one **1i** (44 mg, 0.2 mmol, 1.0 equiv) and β -trimethylsilyltriflate **2a** (72 mg, 1.2 equiv) to give **3ia** (35 mg, 59%) as colorless oil; R_f = 0.56 (silica gel, petroleum ether:EtOAc, 10:1); ^1H NMR (400 MHz, CDCl_3): δ 7.42 – 7.38 (m, 2 H), 7.35 – 7.31 (m, 3 H), 7.25 – 7.14 (m, 3 H), 7.09 (d, J = 7.4 Hz, 2 H), 4.19 (dd, J = 10.2, 4.8 Hz, 1 H), 3.21 (dd, J = 13.3, 10.1 Hz, 1 H), 3.00 (dd, J = 13.3, 4.8 Hz, 1 H), 0.93 (s, 9 H). ^{13}C NMR (100 MHz, CDCl_3): δ 210.3, 138.6, 133.8, 132.9, 129.5, 129.0, 128.4, 128.4, 126.6, 51.9, 44.1, 39.1, 26.3. HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{22}\text{NaOS}^+$ [$\text{M}+\text{Na}^+$]: 321.1284, found 321.1280.

***N,N*-dimethyl-3-phenyl-2-(phenylthio)propanamide (3ja):**



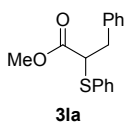
Prepared according to general procedure **B**, from 2-(benzylthio)-*N,N*-dimethylacetamide **1j** (42 mg, 0.2 mmol, 1.0 equiv) and β -trimethylsilyltriflate **2a** (72 mg, 1.2 equiv) to give **3ja** (32 mg, 57%) as colorless oil; R_f = 0.69 (silica gel, petroleum ether:EtOAc, 1:1); ^1H NMR (400 MHz, CDCl_3): δ 7.48 – 7.44 (m, 2 H), 7.33 – 7.15 (m, 8 H), 4.13 (dd, J = 9.6, 5.2 Hz, 1 H), 3.37 (dd, J = 13.5, 9.5 Hz, 1 H), 3.02 (dd, J = 13.5, 5.1 Hz, 1 H), 2.86 (s, 2 H), 2.68 (s, 3 H). ^{13}C NMR (100 MHz, CDCl_3): δ 170.3, 138.8, 133.5, 133.3, 129.1, 129.0, 128.4, 128.2, 126.6, 49.5, 39.0, 37.2, 36.0. HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{19}\text{NNaOS}^+$ [$\text{M}+\text{Na}^+$]: 308.1080, found 308.1078.

2-(Benzyl(phenyl)- λ^4 -sulfanylidene)cyclohexane-1,3-dione (3ka):



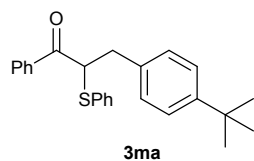
Prepared according to general procedure **B**, from 2-(benzylthio)cyclohexane-1,3-dione **1k** (46 mg, 0.2 mmol, 1.0 equiv) and β -trimethylsilyltriflate **2a** (72 mg, 1.2 equiv) to give **3ka** (42 mg, 68%) as colorless oil; R_f = 0.32 (silica gel, pure EtOAc); ^1H NMR (400 MHz, CDCl_3): δ 7.78 – 7.75 (m, 2 H), 7.52 – 7.47 (m, 1 H), 7.45 – 7.40 (m, 2 H), 7.33 – 7.26 (m, 5 H), 5.30 (d, J = 12.1 Hz, 1 H), 5.10 (d, J = 12.1 Hz, 1 H), 2.45 – 2.41 (m, 4 H), 1.92 – 1.85 (m, 2 H). ^{13}C NMR (100 MHz, CDCl_3): δ 193.5, 132.0, 130.5, 130.0, 129.7, 129.2, 129.0, 87.5, 77.2, 46.9, 38.2, 20.4. HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{18}\text{NaO}_2\text{S}^+$ [$\text{M}+\text{Na}^+$]: 333.0920, found 333.0920.

methyl 3-phenyl-2-(phenylthio)propanoate (3la):



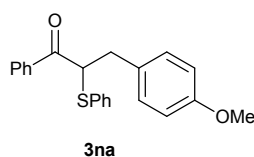
Prepared according to general procedure **B**, from methyl 2-(benzylthio)acetate **1l** (39 mg, 0.2 mmol, 1.0 equiv) and β -trimethylsilyltriflate **2a** (72 mg, 1.2 equiv) to give **3la** (28 mg, 53%) as colorless oil; R_f = 0.46 (silica gel, petroleum ether:EtOAc, 10:1); ^1H NMR (400 MHz, CDCl_3): δ 7.46 – 7.16 (m, 10 H), 3.90 (dd, J = 9.2, 6.3 Hz, 1 H), 3.58 (s, 3 H), 3.20 (dd, J = 13.9, 9.2 Hz, 1 H), 3.06 (dd, J = 13.9, 6.3 Hz, 1 H). ^{13}C NMR (100 MHz, CDCl_3): δ 172.1, 137.7, 133.1, 132.7, 129.0, 128.9, 128.5, 128.2, 126.9, 52.2, 52.1, 38.0. HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{16}\text{NaO}_2\text{S}^+$ [$\text{M}+\text{Na}^+$]: 295.0763, found 295.0762.

3-(4-(Tert-butyl)phenyl)-1-phenyl-2-(phenylthio)propan-1-one (3ma):



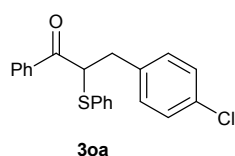
Prepared according to general procedure **B**, from 2-((4-(tert-butyl)benzyl)thio)-1-phenylethan-1-one **1m** (59 mg, 0.2 mmol, 1.0 equiv) and β -trimethylsilyltriflate **2a** (72 mg, 1.2 equiv) to give **3ma** (50 mg, 67%) as colorless oil; R_f = 0.62 (silica gel, petroleum ether:EtOAc, 10:1); ^1H NMR (400 MHz, CDCl_3): δ 7.85 – 7.81 (m, 2 H), 7.54 – 7.46 (m, 1 H), 7.41 – 7.35 (m, 2 H), 7.31 – 7.23 (m, 7 H), 7.17 – 7.13 (m, 2 H), 4.69 (dd, J = 8.3, 6.2 Hz, 1 H), 3.38 (dd, J = 14.1, 8.3 Hz, 1 H), 3.12 (dd, J = 14.1, 6.2 Hz, 1 H), 1.27 (s, 9 H). ^{13}C NMR (100 MHz, CDCl_3): δ 195.3, 149.4, 136.2, 135.6, 134.4, 132.9, 132.2, 128.9, 128.6, 128.5, 128.5, 125.4, 53.1, 36.8, 34.4, 31.3. HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{26}\text{NaOS}^+$ [$\text{M}+\text{Na}^+$]: 397.1597, found 397.1594.

3-(4-Methoxyphenyl)-1-phenyl-2-(phenylthio)propan-1-one (3na):



Prepared according to general procedure **B**, from 3-(4-methoxyphenyl)-1-phenyl-2-(phenylthio)propan-1-one **1n** (54 mg, 0.2 mmol, 1.0 equiv) and β -trimethylsilyltriflate **2a** (72 mg, 1.2 equiv) to give **3na** (28 mg, 41%) as colorless oil; R_f = 0.52 (silica gel, petroleum ether:EtOAc, 10:1); ^1H NMR (400 MHz, CDCl_3): δ 7.85 – 7.80 (m, 2 H), 7.54 – 7.48 (m, 1 H), 7.39 (t, J = 7.7 Hz, 2 H), 7.33 – 7.22 (m, 5 H), 7.16 – 7.11 (m, 2 H), 6.81 – 6.75 (m, 2 H), 4.66 (dd, J = 8.6, 6.0 Hz, 1 H), 3.75 (s, 3 H), 3.34 (dd, J = 14.1, 8.6 Hz, 1 H), 3.08 (dd, J = 14.1, 6.0 Hz, 1 H). ^{13}C NMR (100 MHz, CDCl_3): δ 195.3, 158.2, 136.2, 134.5, 133.0, 132.0, 130.6, 130.3, 129.0, 128.7, 128.5, 113.8, 55.2, 53.0, 36.4. HRMS (ESI): calcd for $\text{C}_{22}\text{H}_{20}\text{NaO}_2\text{S}^+$ [$\text{M}+\text{Na}^+$]: 371.1076, found 371.1077.

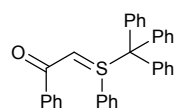
3-(4-Chlorophenyl)-1-phenyl-2-(phenylthio)propan-1-one (3oa):



Prepared according to general procedure **B**, from 2-((4-chlorobenzyl)thio)-1-phenylethan-1-one **1o** (55 mg, 0.2 mmol, 1.0 equiv) and β -trimethylsilyltriflate **1a** (72 mg, 1.2 equiv) to give **3oa** (50 mg, 71%) as colorless oil; R_f = 0.54 (silica gel, petroleum ether:EtOAc, 10:1); ^1H NMR (400 MHz, CDCl_3): δ 7.83 (d, J = 7.6 Hz, 2 H), 7.53 (t, J = 7.4 Hz, 1 H), 7.39 (t, J = 7.7 Hz, 2 H), 7.35 – 7.24 (m, 5 H), 7.21 (d, J = 8.4 Hz, 2 H), 7.15 (d, J = 8.4 Hz, 2 H), 4.65 (dd, J = 8.6, 6.0 Hz, 1 H), 3.36 (dd, J =

14.1, 8.6 Hz, 1 H), 3.10 (dd, $J = 14.1, 6.0$ Hz, 1 H). ^{13}C NMR (100 MHz, CDCl_3): δ 194.9, 137.1, 136.0, 134.7, 133.1, 132.4, 131.6, 130.7, 129.0, 128.9, 128.6, 128.6, 128.5, 52.6, 36.6. HRMS (ESI): calcd for $\text{C}_{21}\text{H}_{17}\text{ClNaOS}^+$ [$\text{M}+\text{Na}^+$]: 375.0581, found 375.0577.

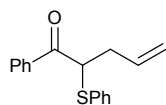
1,3,3,3-Tetraphenyl-2-(phenylthio)propan-1-one (3pa):



3pa

Prepared according to general procedure **B**, from 1-phenyl-2-(tritylthio)ethan-1-one **1p** (79 mg, 0.2 mmol, 1.0 equiv) and β -trimethylsilyltriflate **2a** (72 mg, 1.2 equiv) to give **3pa** (58 mg, 62%) as colorless oil; $R_f = 0.55$ (silica gel, petroleum ether:EtOAc, 10:1); ^1H NMR (400 MHz, CDCl_3): δ 7.47 – 7.23 (m, 18 H), 7.14 – 7.08 (m, 3 H), 7.01 (d, $J = 4.3$ Hz, 4 H), 5.86 (s, 1 H). ^{13}C NMR (100 MHz, CDCl_3): δ 196.0, 138.6, 134.9, 133.5, 132.1, 130.6, 129.6, 128.8, 128.3, 128.2, 128.1, 128.0, 127.6, 126.7, 63.6, 61.5. HRMS (ESI): calcd for $\text{C}_{33}\text{H}_{26}\text{NaOS}^+$ [$\text{M}+\text{Na}^+$]: 493.1597, found 493.1594.

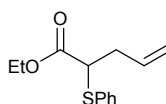
1-Phenyl-2-(phenylthio)pent-4-en-1-one (3qa):⁹



3qa

Prepared according to general procedure **B**, from 2-(allylthio)-1-phenylethan-1-one **1q** (38 mg, 0.2 mmol, 1.0 equiv) and β -trimethylsilyltriflate **2a** (72 mg, 1.2 equiv) to give **3qa** (46 mg, 86%) as colorless oil; $R_f = 0.58$ (silica gel, petroleum ether:EtOAc, 10:1); ^1H NMR (400 MHz, CDCl_3): δ 7.94 – 7.89 (m, 2 H), 7.55 (t, $J = 7.4$ Hz, 1 H), 7.44 (t, $J = 7.7$ Hz, 2 H), 7.37 – 7.24 (m, 5 H), 5.88 (ddt, $J = 17.1, 10.3, 6.8$ Hz, 1 H), 5.15 – 5.05 (m, 2 H), 4.50 (t, $J = 7.3$ Hz, 1 H), 2.76 (dt, $J = 14.7, 7.3$ Hz, 1 H), 2.59 (dt, $J = 14.3, 6.9$ Hz, 1 H). ^{13}C NMR (100 MHz, CDCl_3): δ 195.2, 136.1, 134.8, 133.1, 131.5, 128.9, 128.8, 128.6, 128.6, 117.7, 50.8, 35.1.

Ethyl 2-(phenylthio)pent-4-enoate (3ra):¹⁰

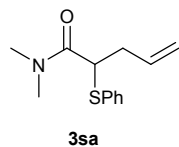


3ra

Prepared according to general procedure **B**, from ethyl 2-(allylthio)acetate **1r** (32 mg, 0.2 mmol, 1.0 equiv) and β -trimethylsilyltriflate **2a** (72 mg, 1.2 equiv) to give **3ra** (29 mg, 62%) as colorless oil; $R_f = 0.63$ (silica gel, petroleum ether:EtOAc, 10:1); ^1H NMR (400 MHz, CDCl_3): δ 7.49 – 7.44 (m, 2 H), 7.34 – 7.27 (m, 3 H), 5.81 (ddt, $J = 17.1, 10.2, 6.9$ Hz, 1 H), 5.17 – 5.06 (m, 2 H), 4.11 (qd, $J = 7.1, 1.8$ Hz, 2 H), 3.70 (dd, $J = 8.7, 6.4$ Hz, 1

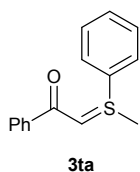
H), 2.67 – 2.58 (m, 1 H), 2.57 – 2.45 (m, 1 H), 1.17 (t, $J = 7.1$ Hz, 3 H). ^{13}C NMR (100 MHz, CDCl_3): δ 171.6, 133.8, 133.1, 133.0, 128.9, 128.0, 118.0, 61.1, 50.2, 35.8, 14.1.

N,N-dimethyl-2-(phenylthio)pent-4-enamide (3sa):



Prepared according to general procedure **B**, from 2-(allylthio)-N,N-dimethylacetamide **1s** (31 mg, 0.2 mmol, 1.0 equiv) and β -trimethylsilyltriflate **2a** (72 mg, 1.2 equiv) to give **3sa** (25 mg, 53%) as colorless oil; $R_f = 0.68$ (silica gel, petroleum ether:EtOAc, 1:1); ^1H NMR (400 MHz, CDCl_3): δ 7.50 – 7.44 (m, 2 H), 7.34 – 7.27 (m, 3 H), 5.81 (ddt, $J = 17.0, 10.1, 6.9$ Hz, 1 H), 5.14 – 5.02 (m, 2 H), 3.90 (dd, $J = 8.7, 5.9$ Hz, 1 H), 2.94 (s, 6 H), 2.76 (dt, $J = 14.8, 7.7$ Hz, 1 H), 2.47 (dt, $J = 13.8, 6.6$ Hz, 1 H). ^{13}C NMR (100 MHz, CDCl_3): δ 170.2, 135.1, 134.0, 132.6, 128.9, 128.3, 117.5, 47.2, 37.4, 36.5, 36.0. HRMS (ESI): calcd for $\text{C}_{13}\text{H}_{17}\text{NNaOS}^+ [\text{M}+\text{Na}^+]$: 258.0923, found 258.0924.

(Z)-2-(methyl(phenyl)- λ^4 -sulfanylidene)-1-phenylethan-1-one (3ta)¹¹:

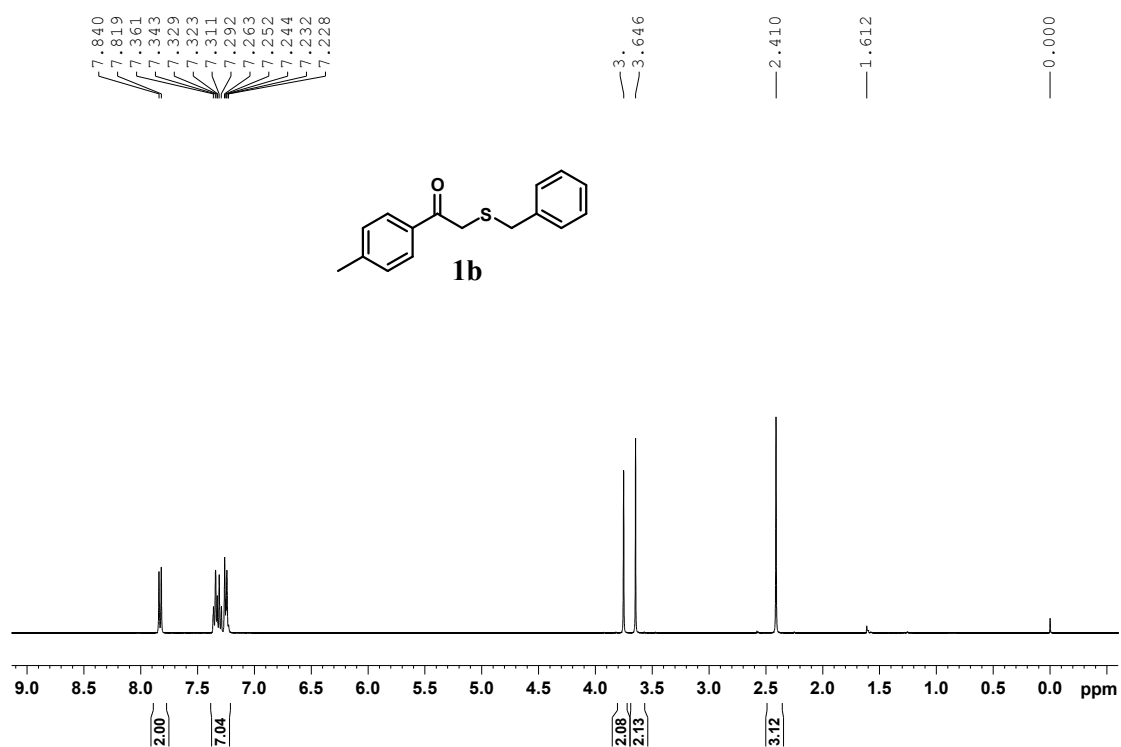
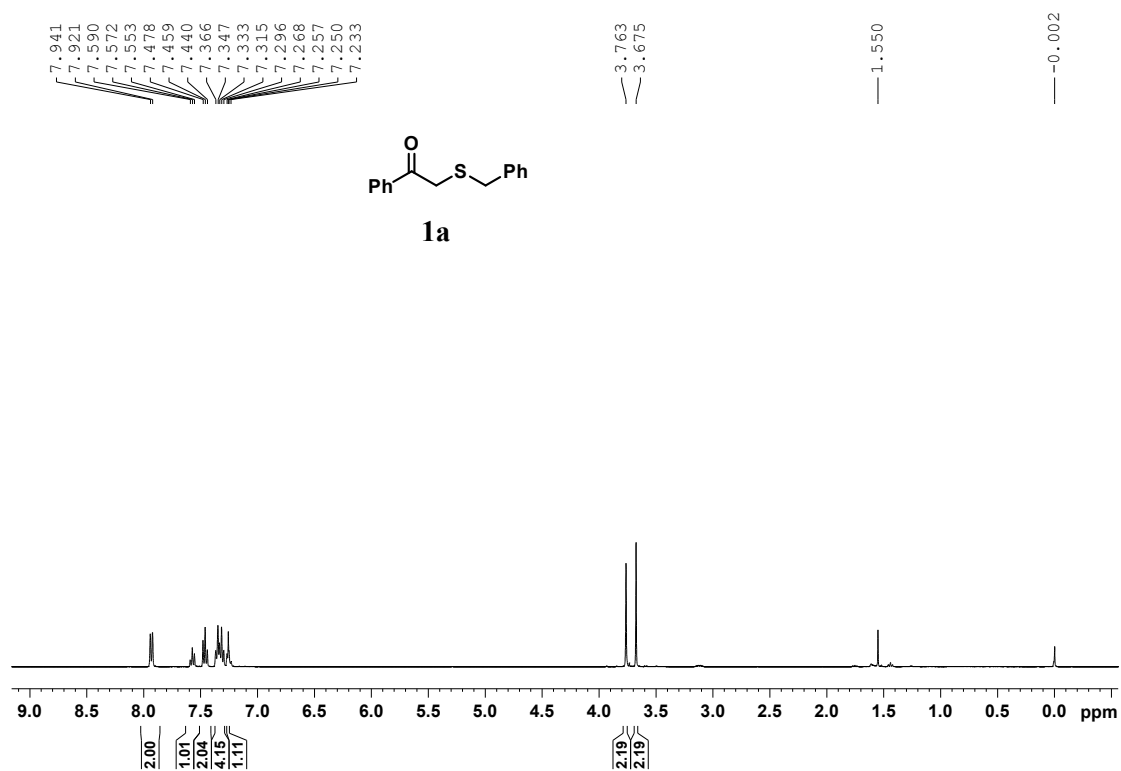


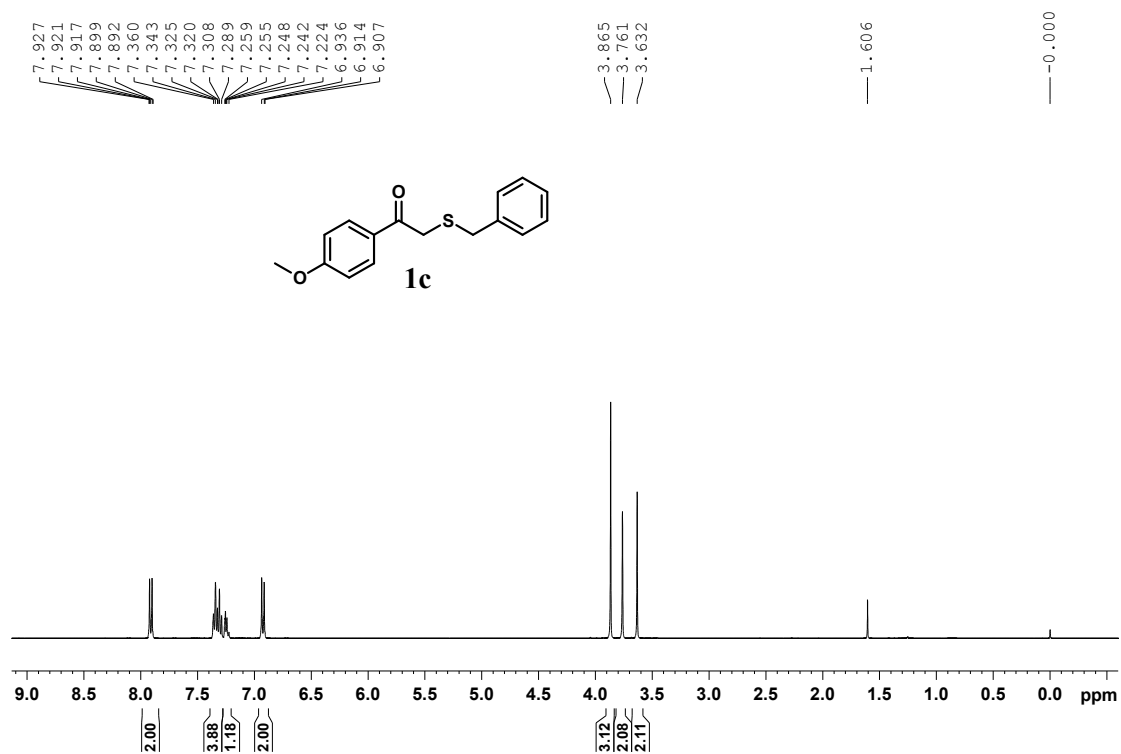
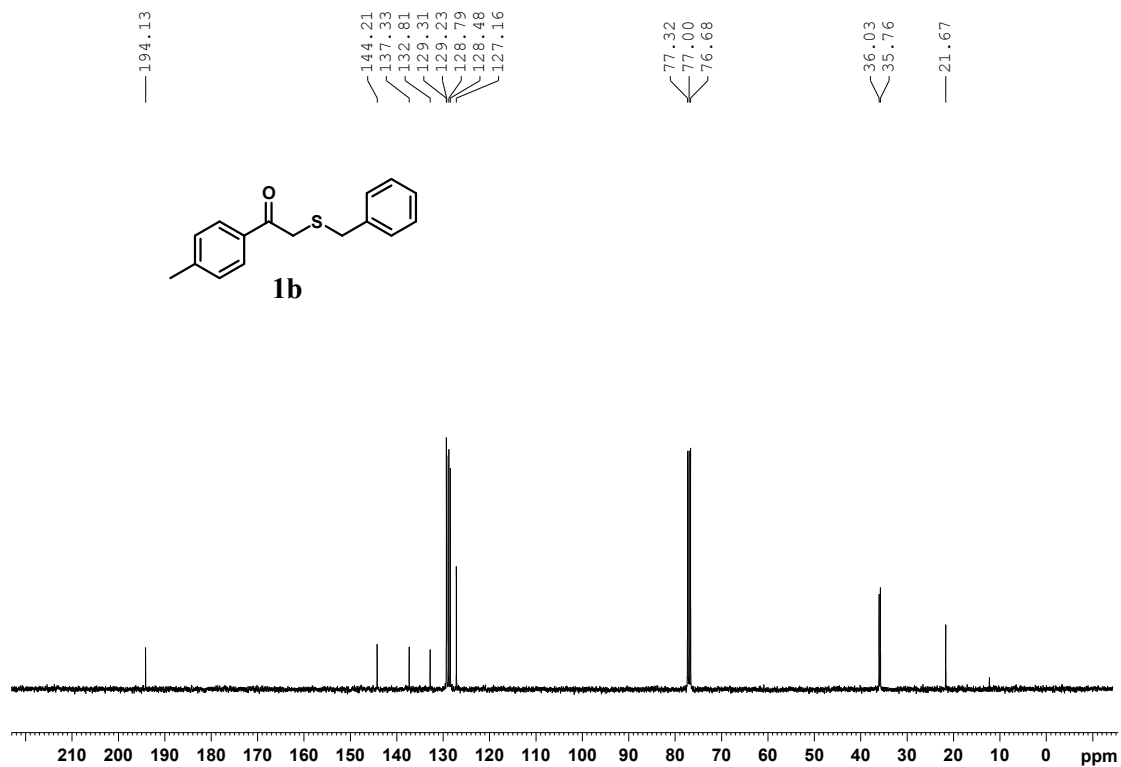
Prepared according to general procedure **B**, from 2-(methylthio)-1-phenylethan-1-one **1t** (33 mg, 0.2 mmol, 1.0 equiv) and β -trimethylsilyltriflate **2a** (72 mg, 1.2 equiv) to give **3ta** (25 mg, 82%) as colorless oil; $R_f = 0.25$ (EtOAc); ^1H NMR (400 MHz, CDCl_3): δ 7.88 – 7.83 (m, 2 H), 7.78 – 7.72 (m, 3 H), 7.51 – 7.46 (m, 3 H), 7.39 – 7.33 (m, 3 H), 4.58 (s, 1 H), 3.20 (s, 3 H).

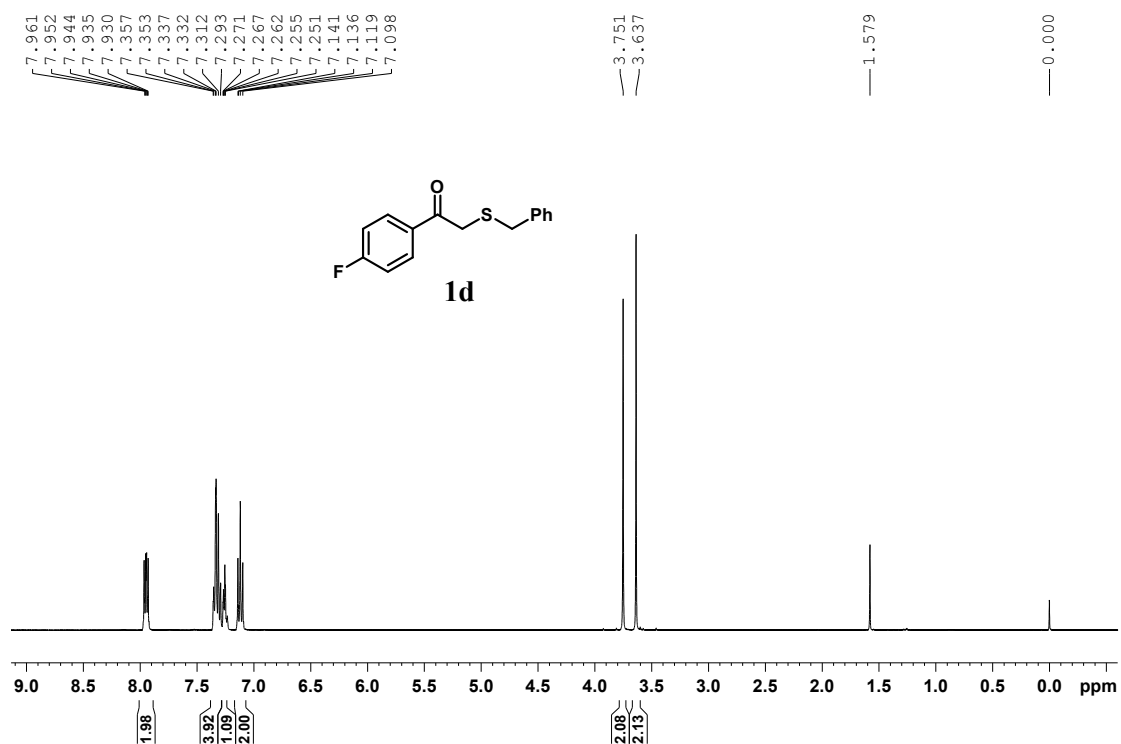
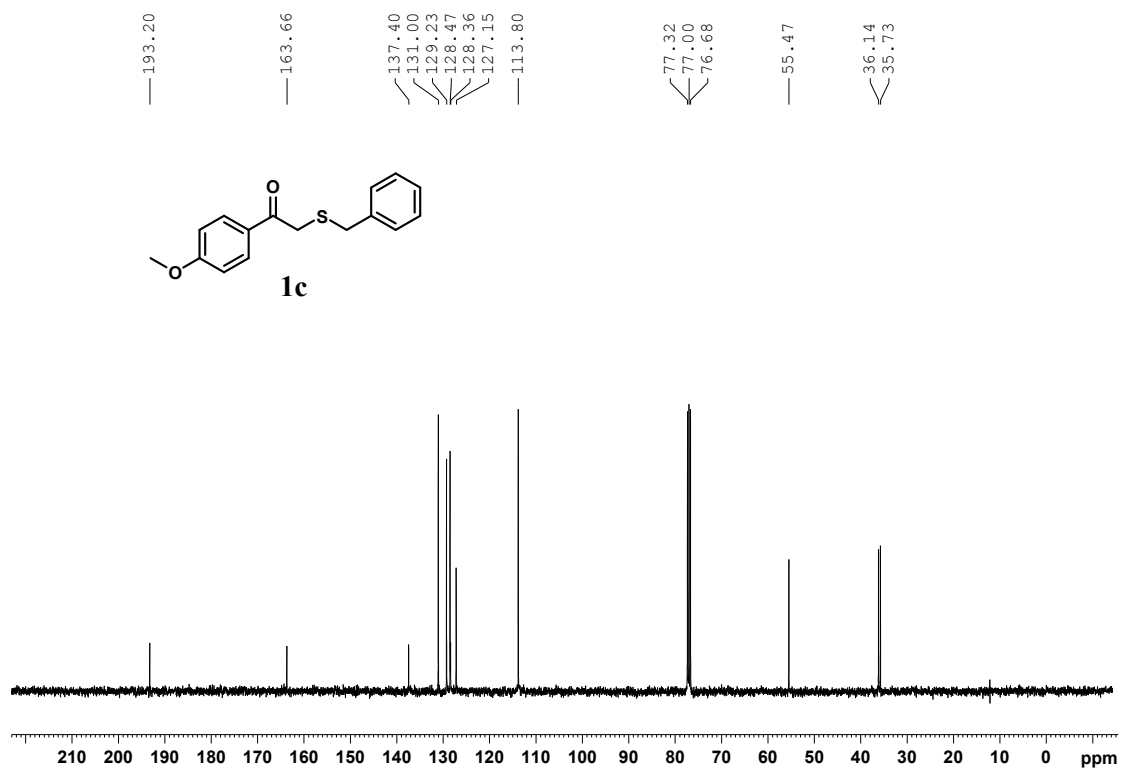
4. References

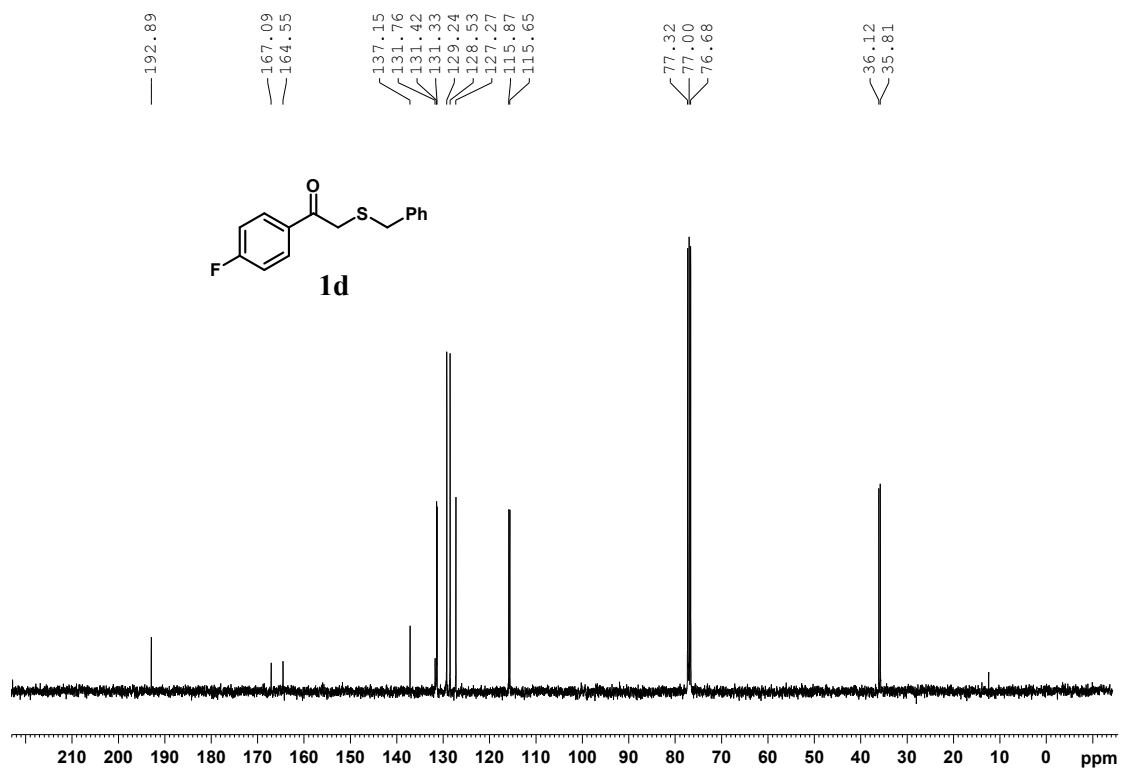
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5. NMR Spectra

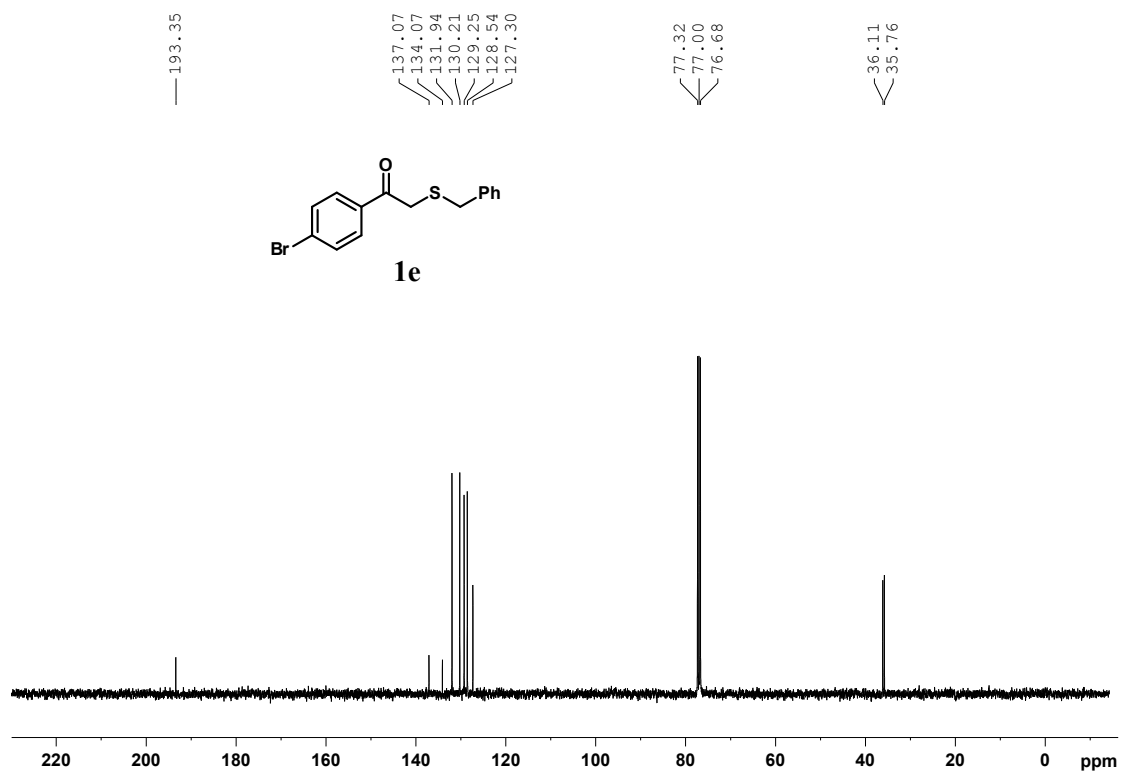
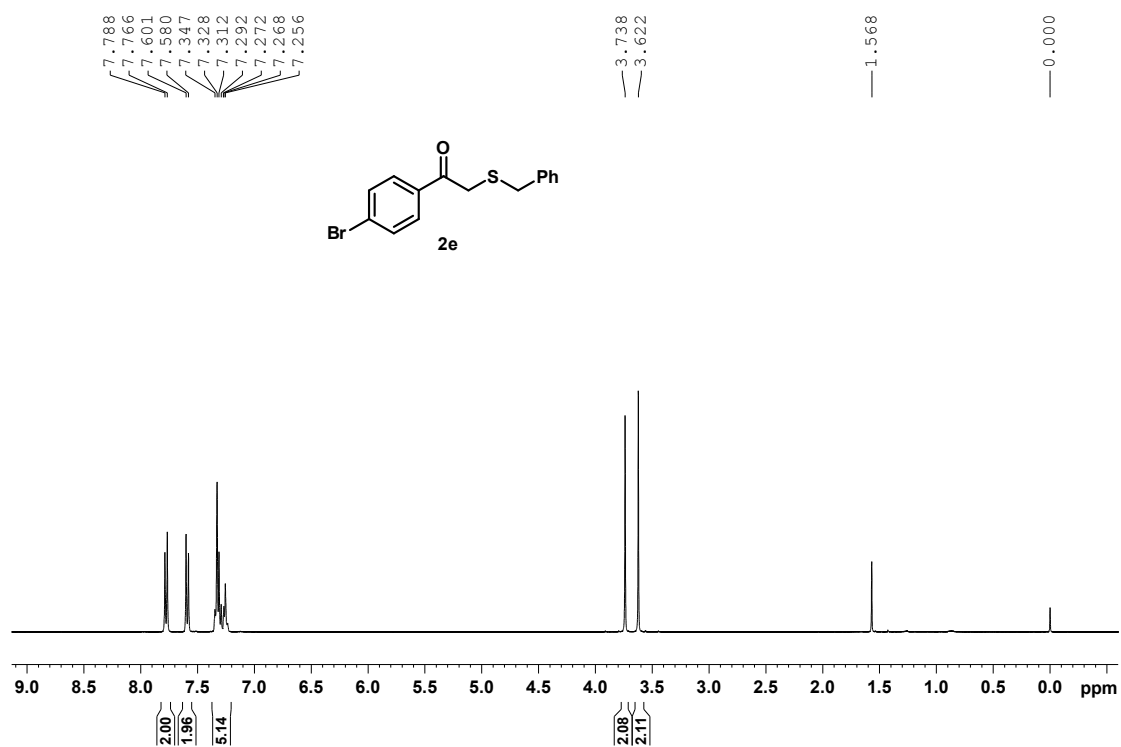


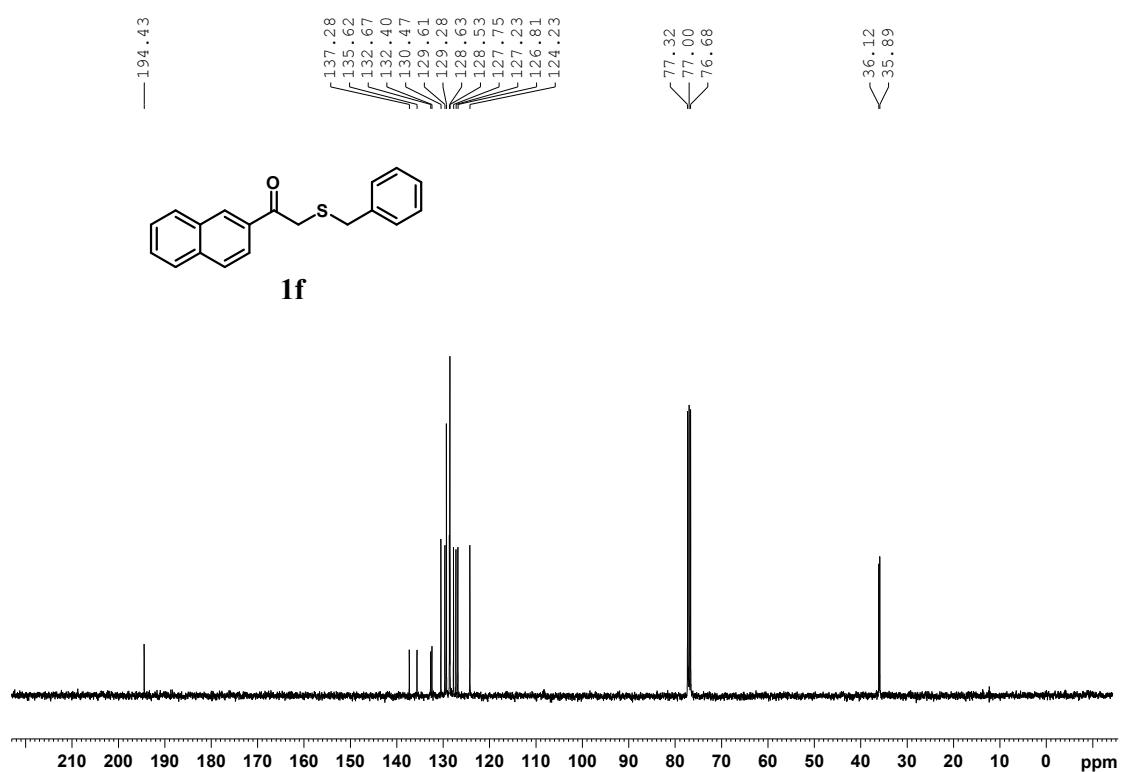
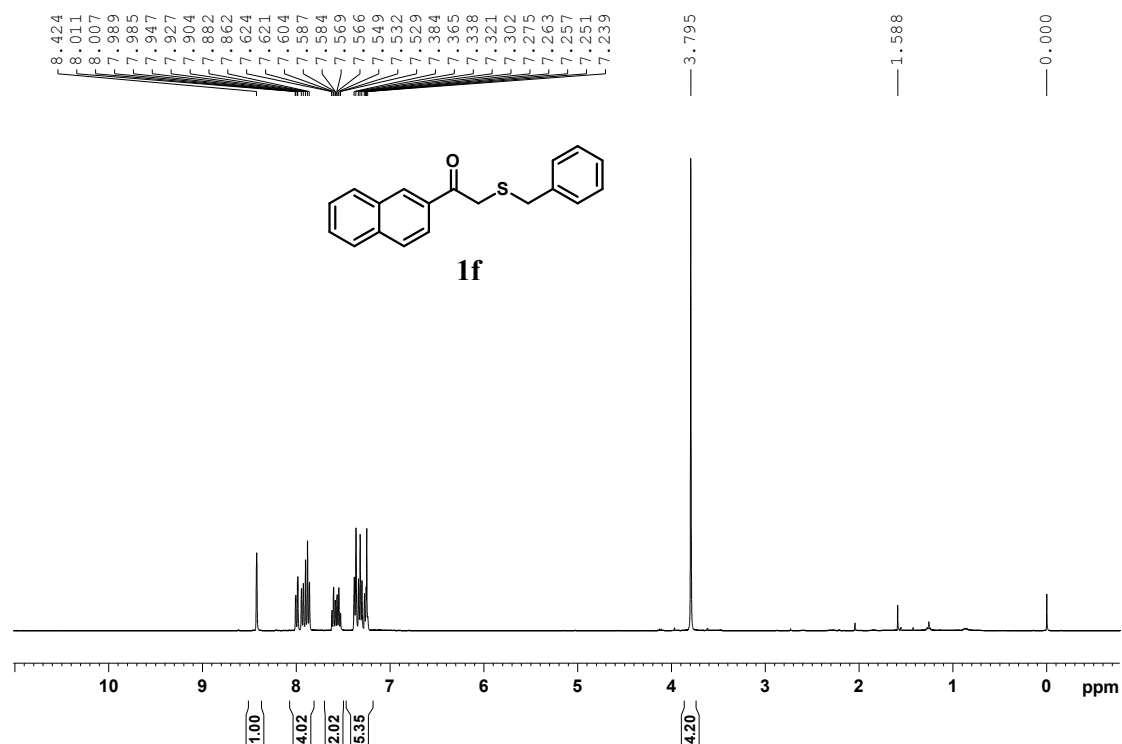


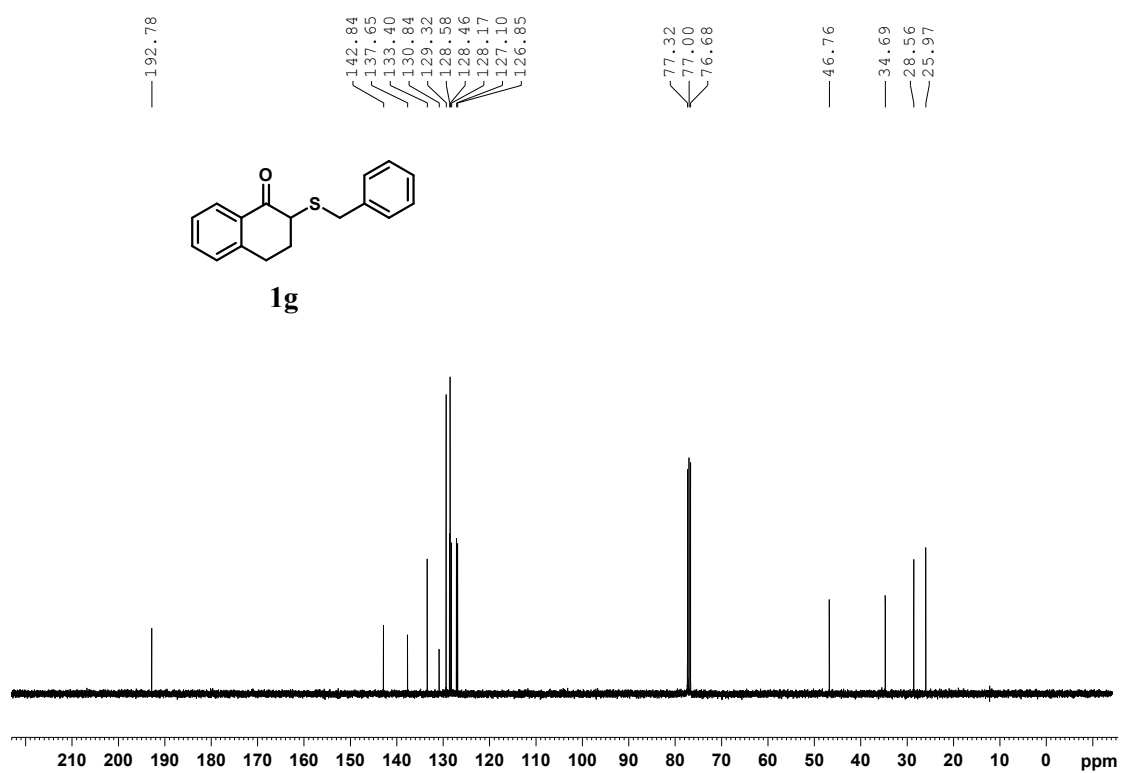
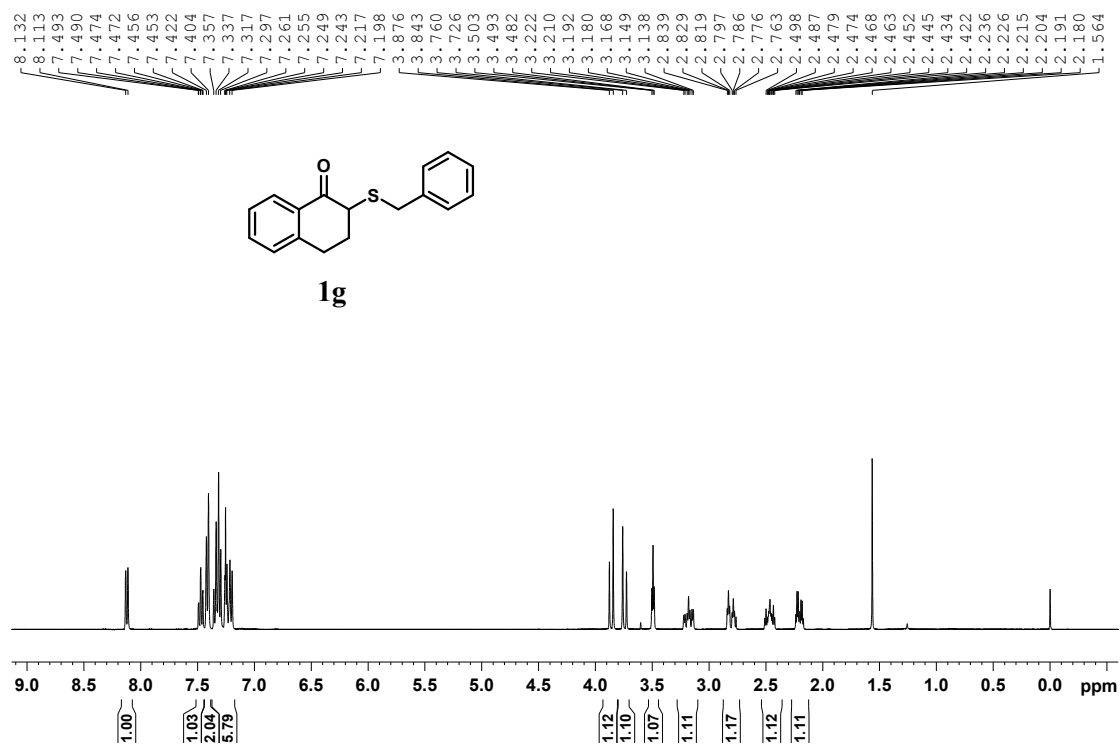


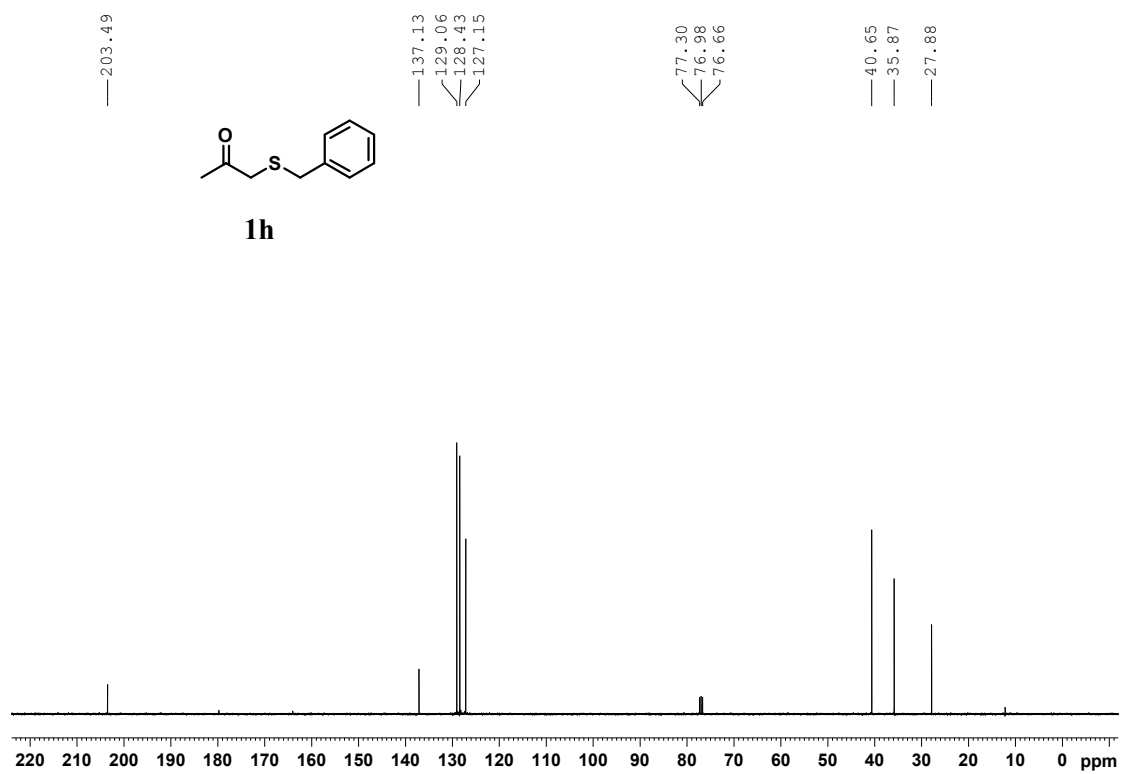
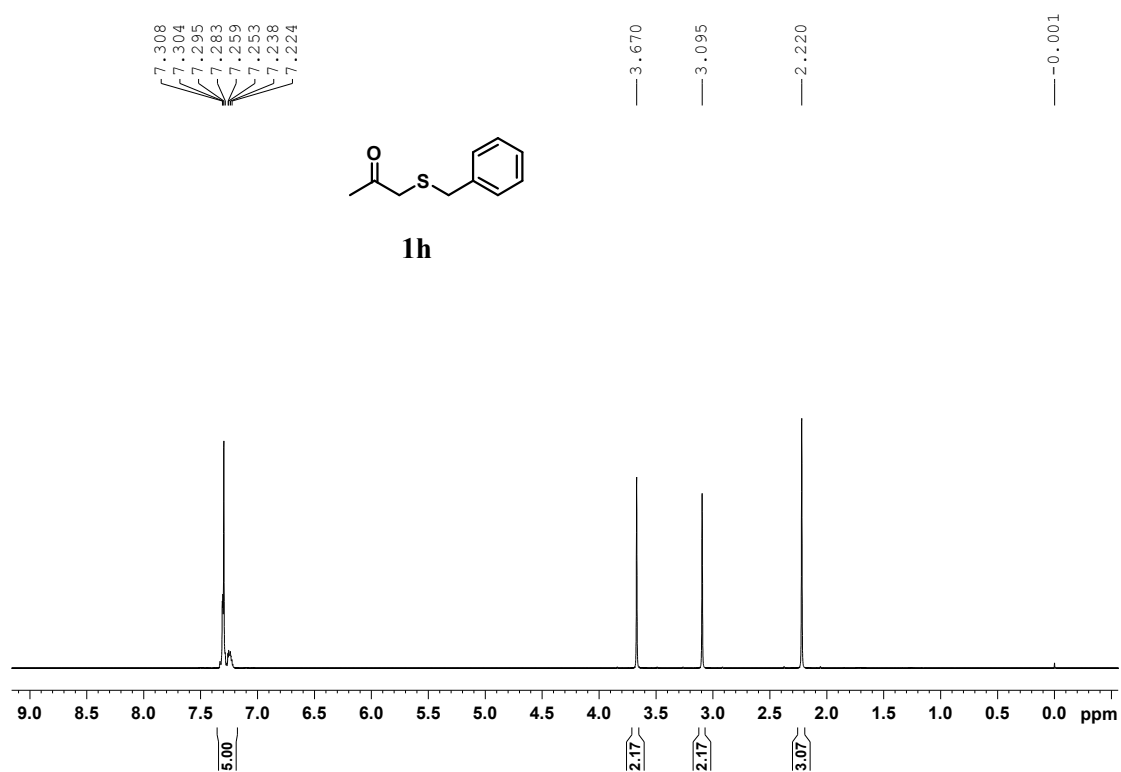


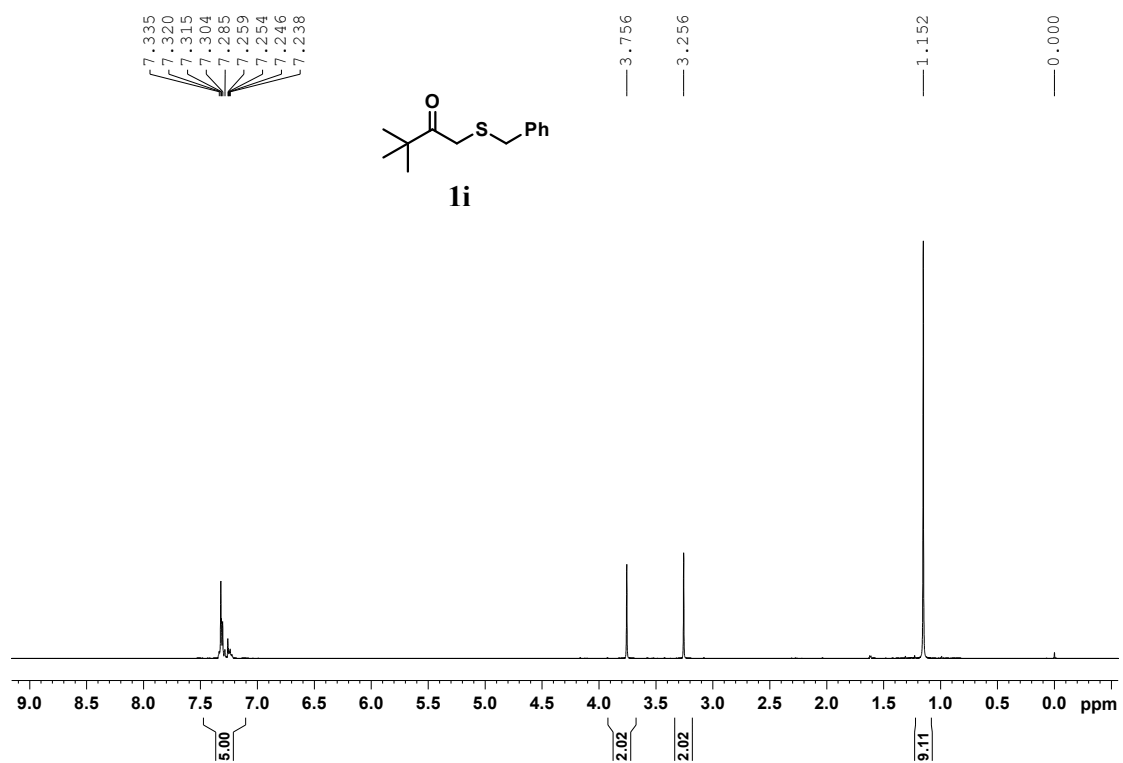
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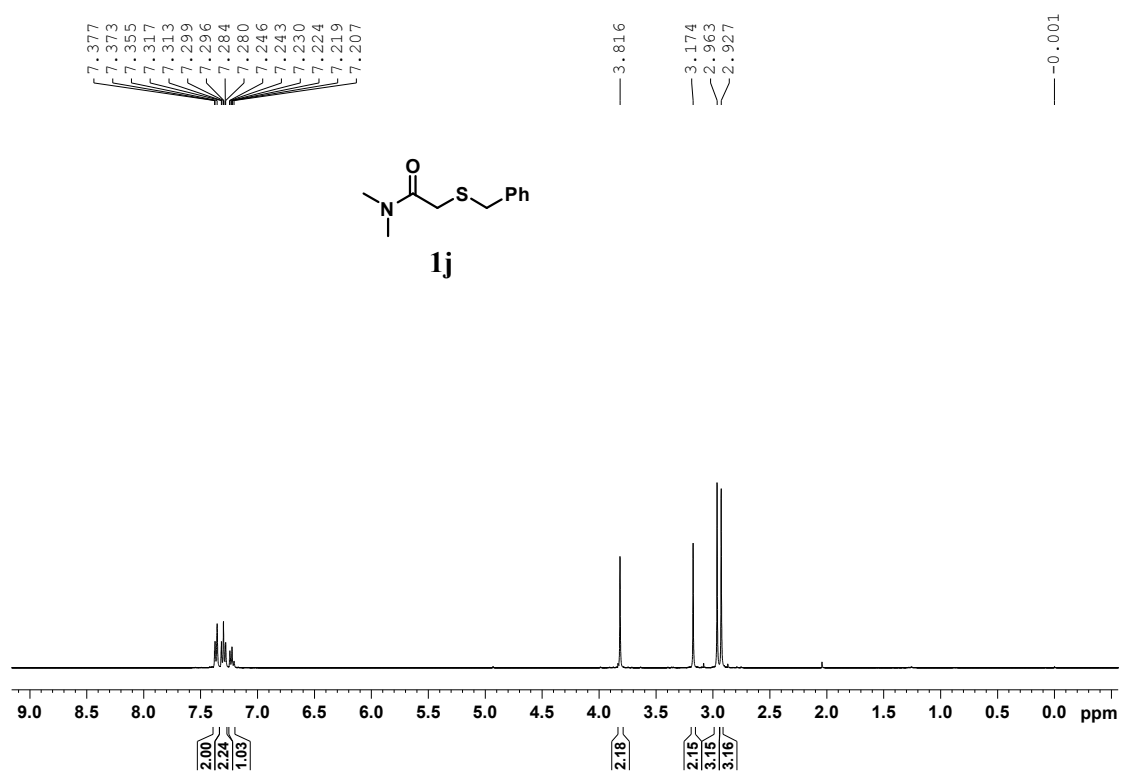
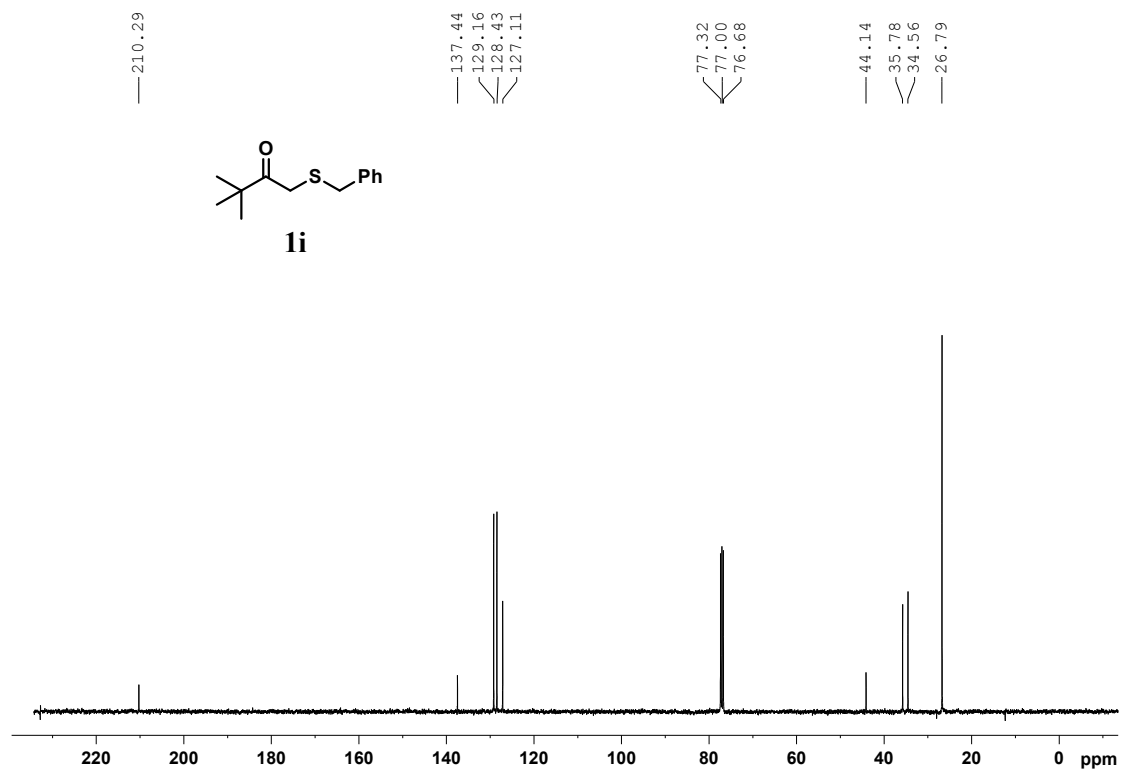


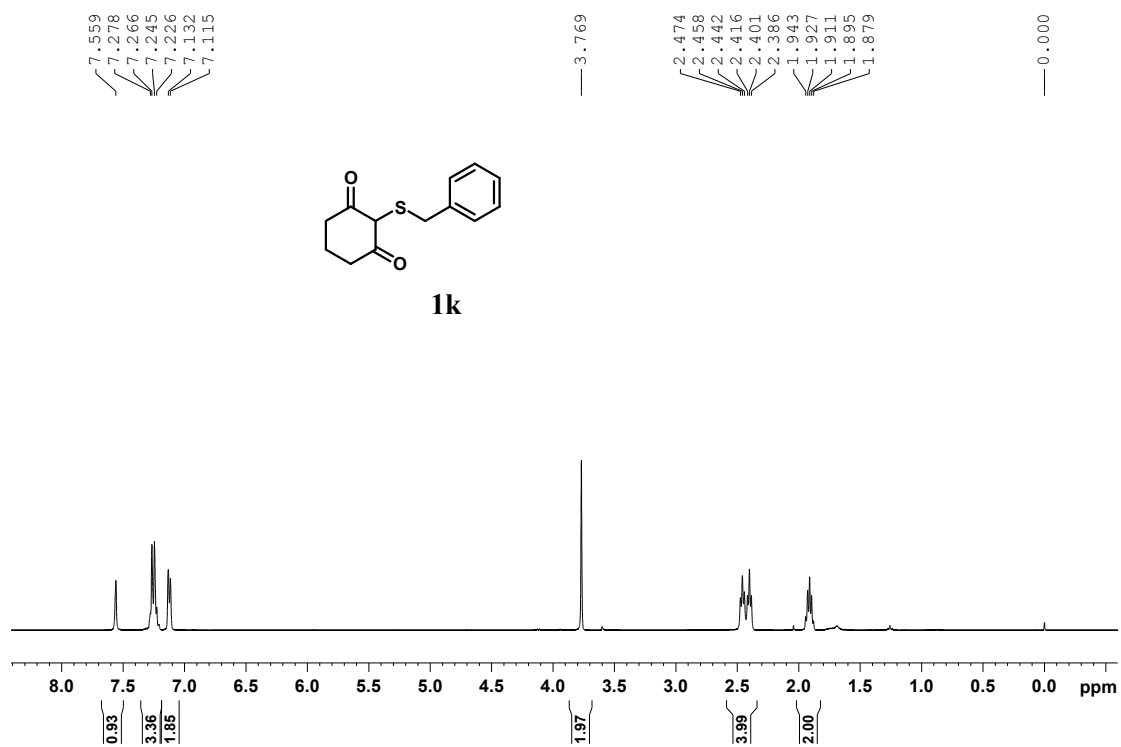
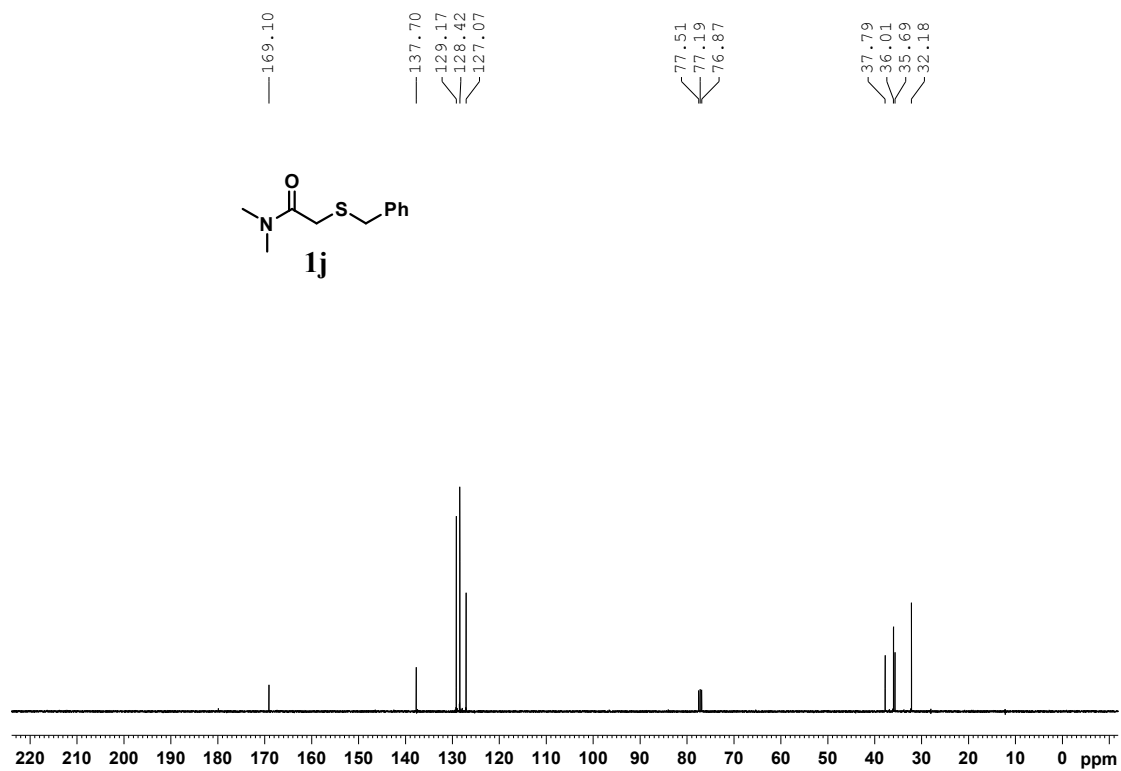


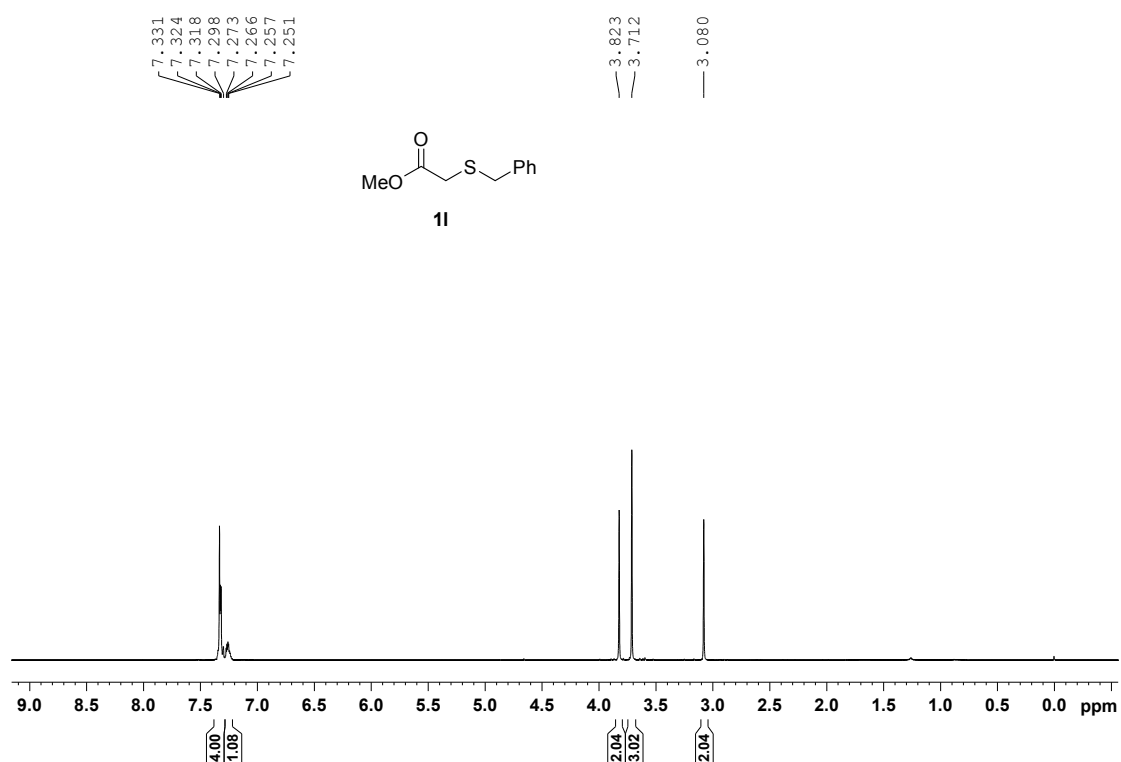
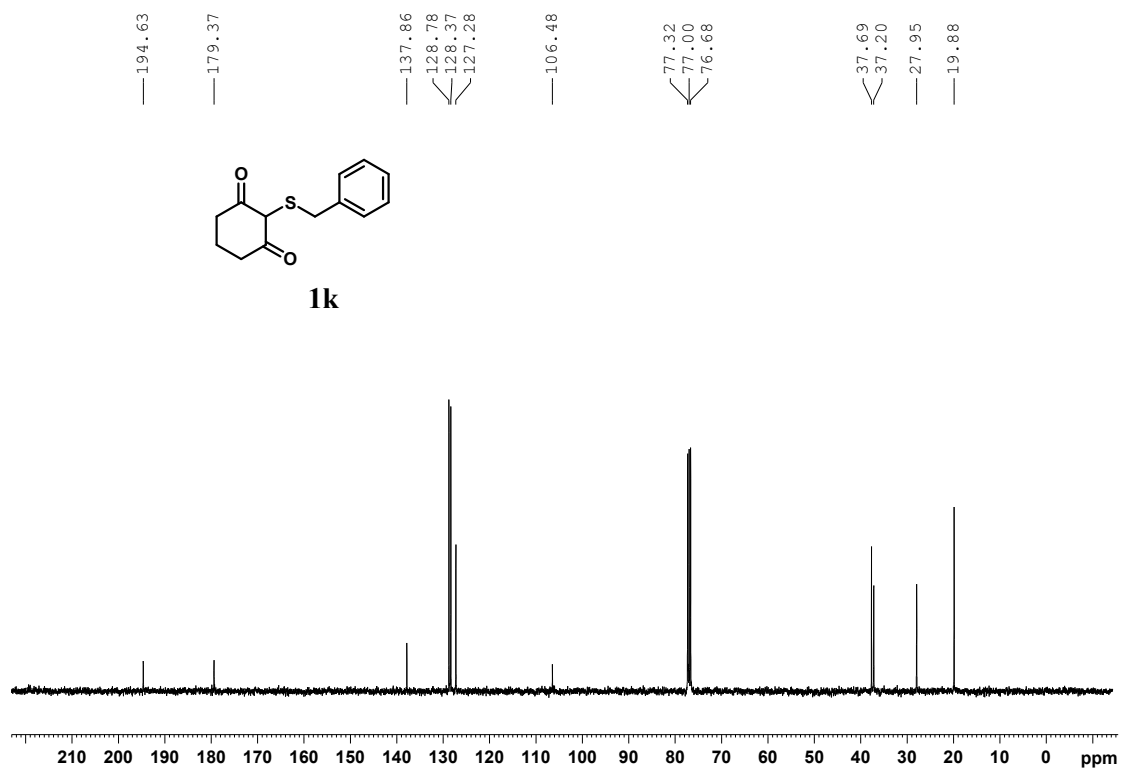


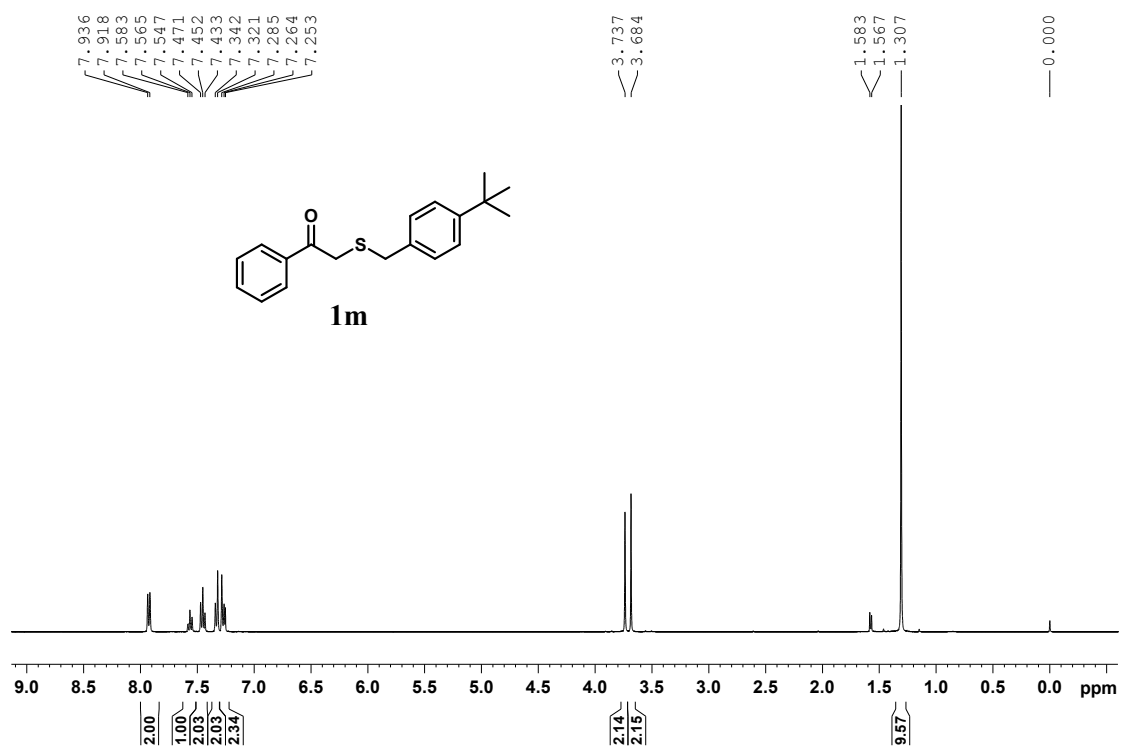
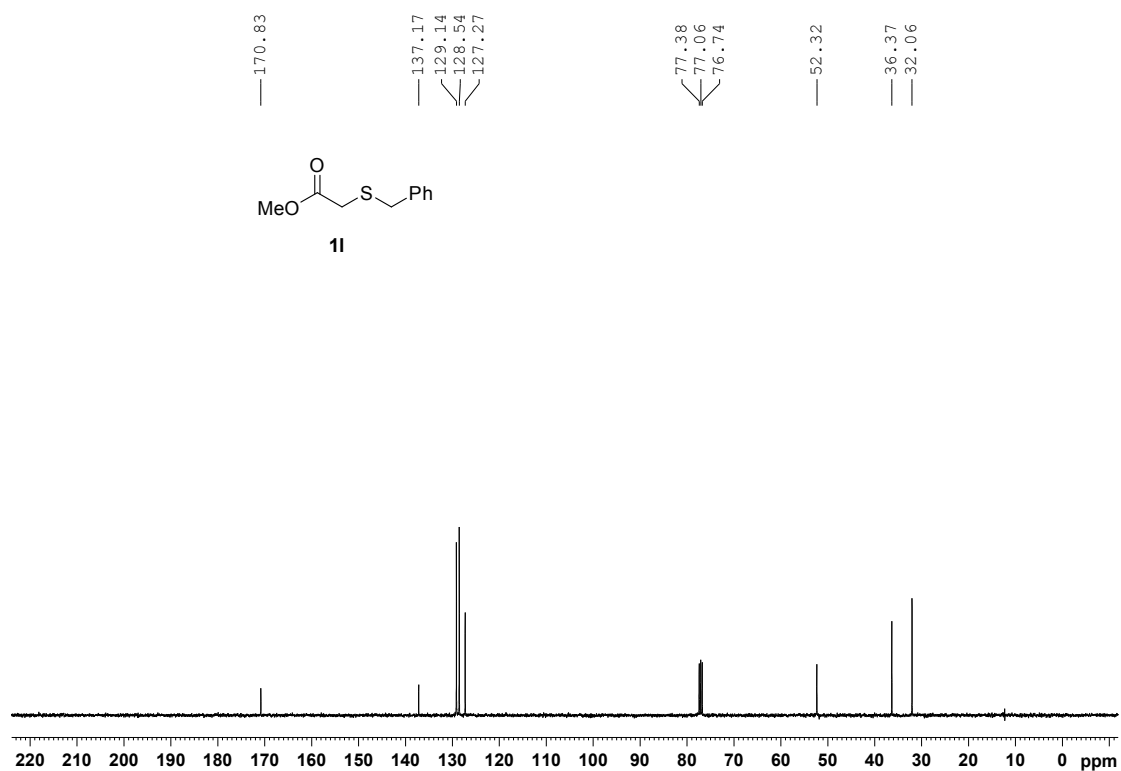


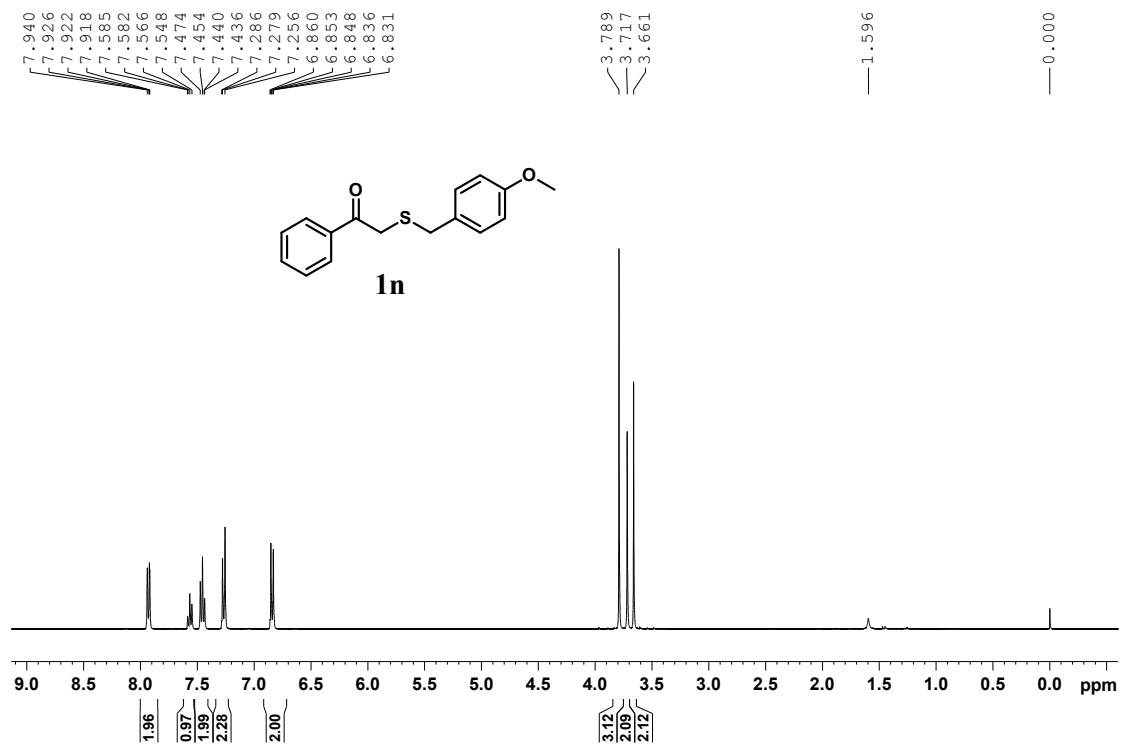
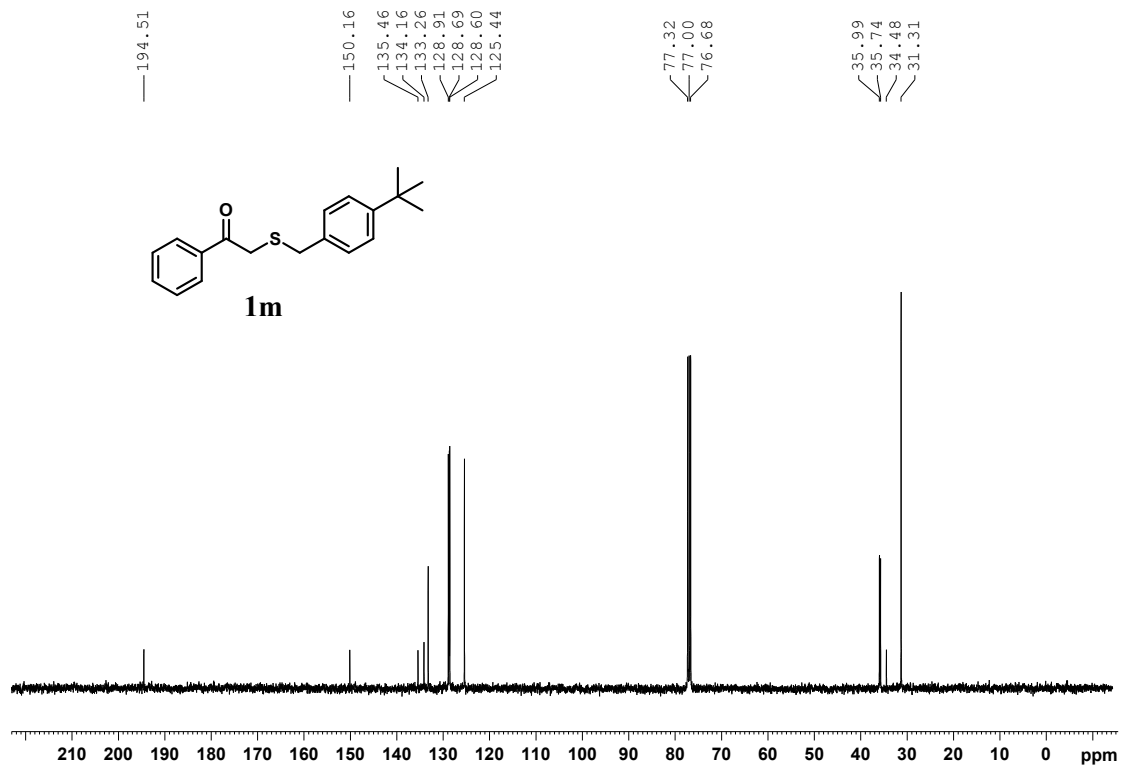


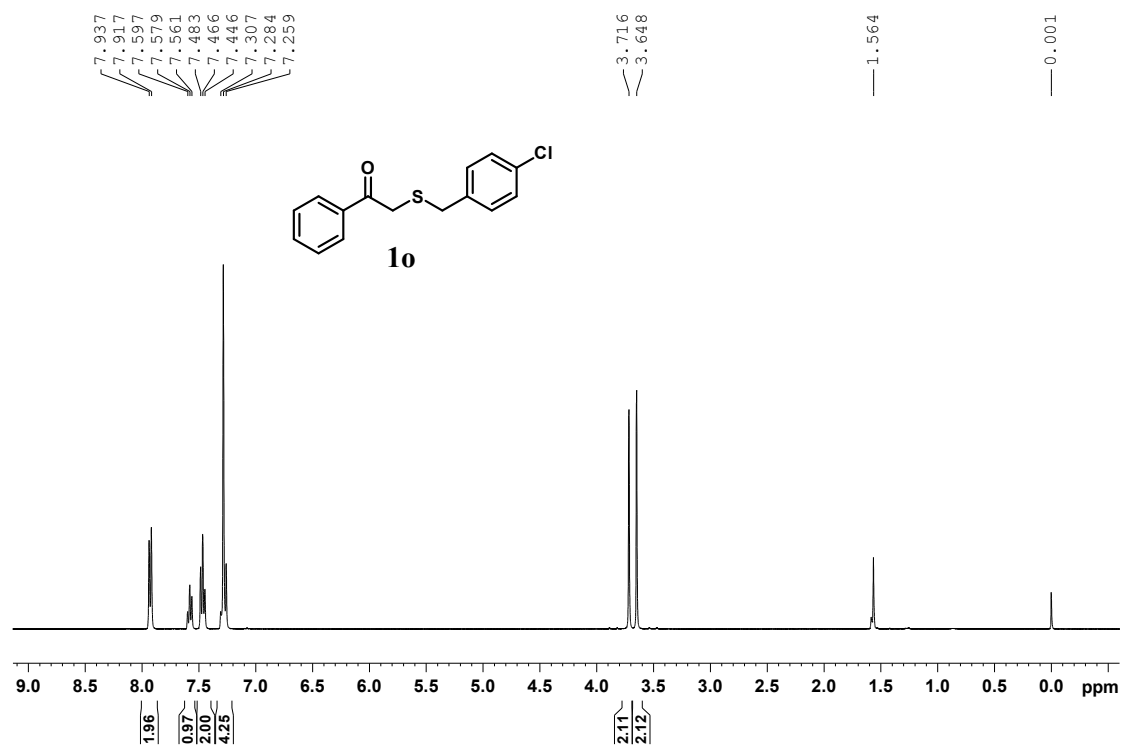
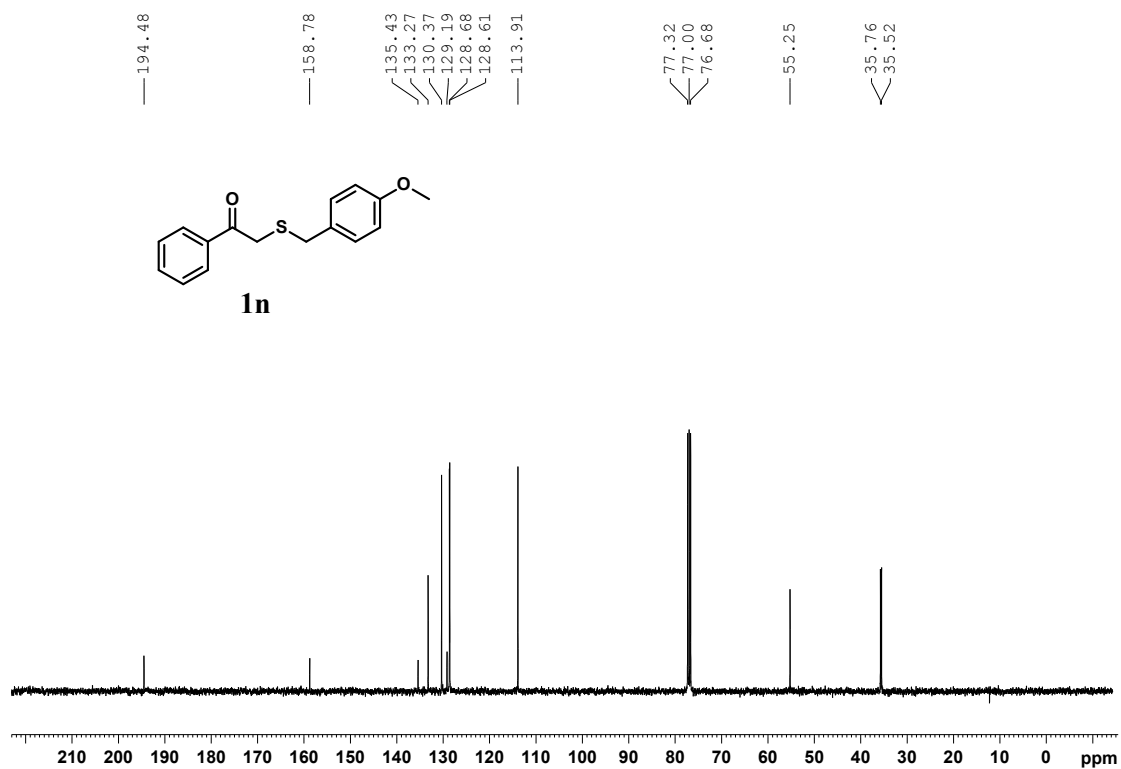


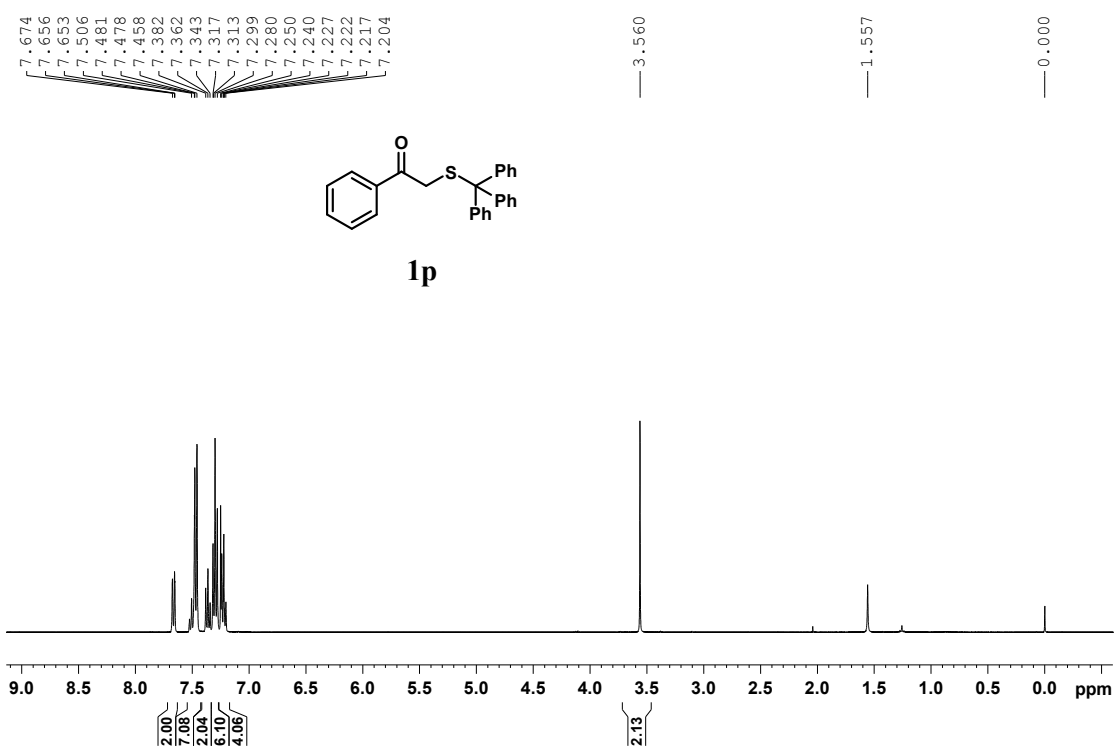
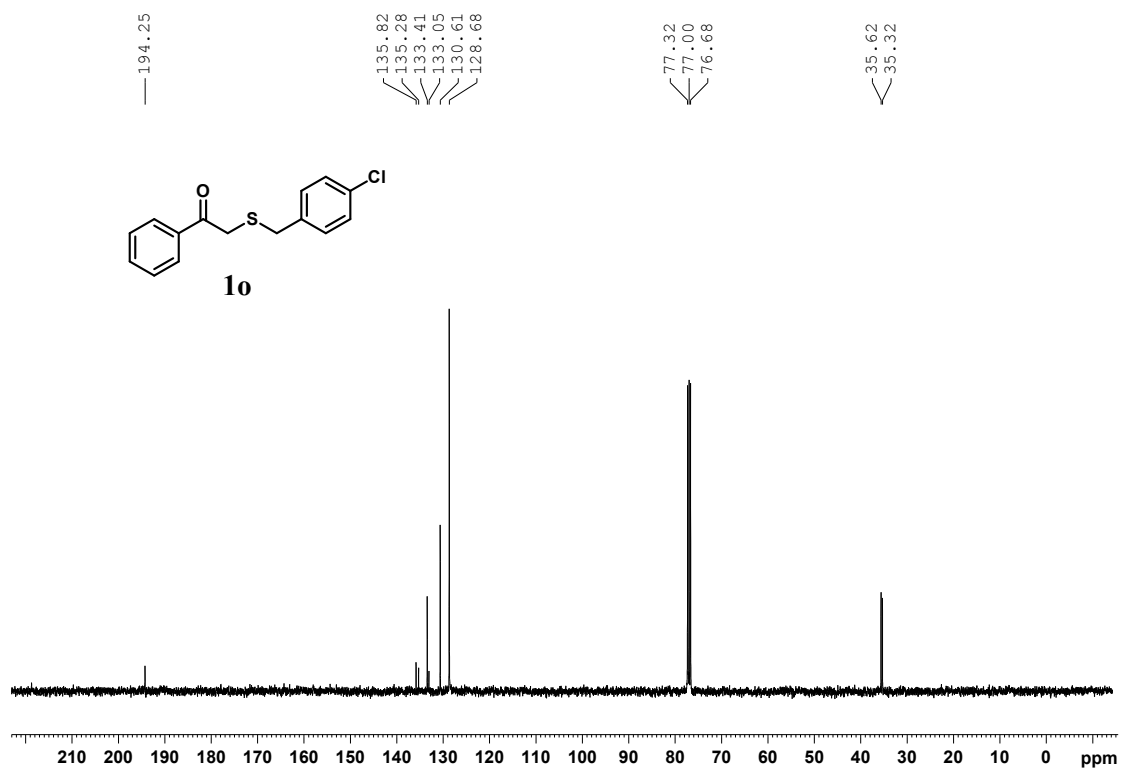


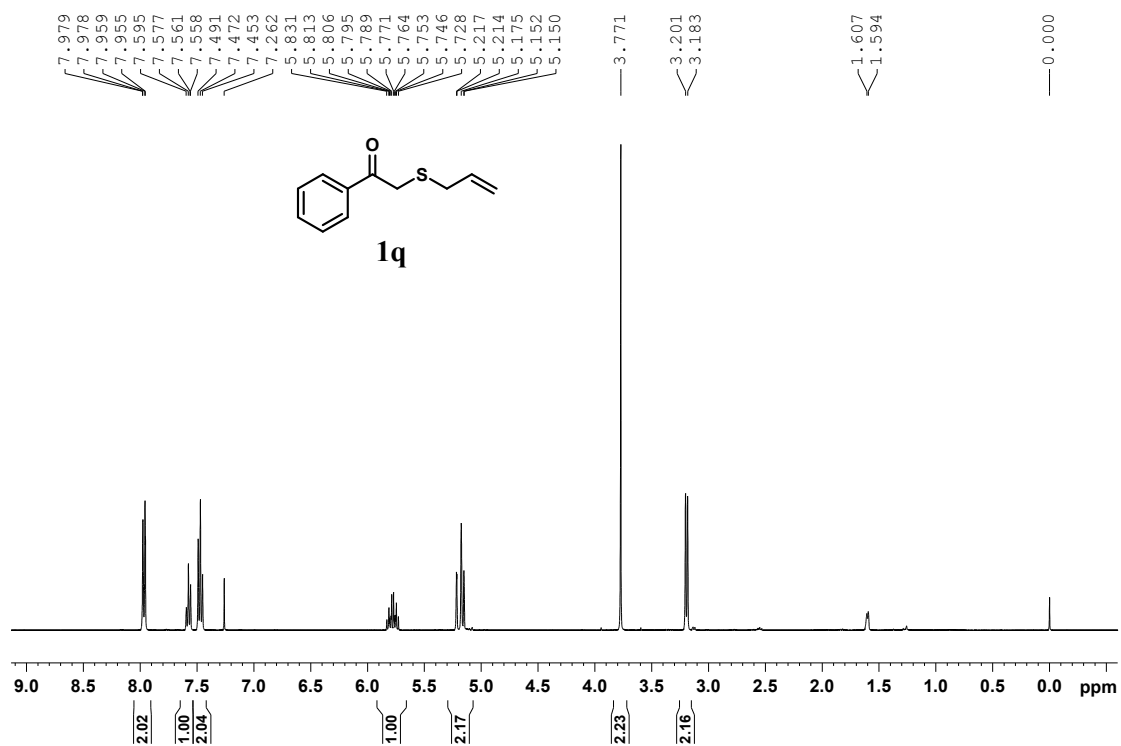
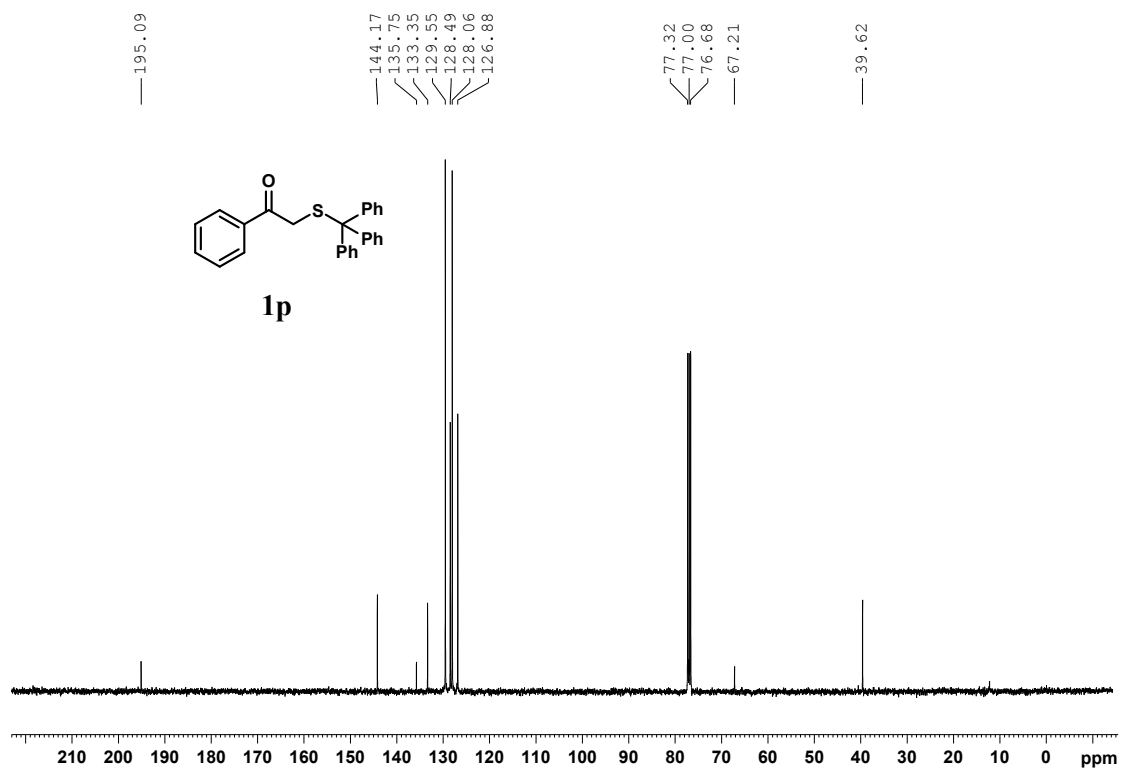


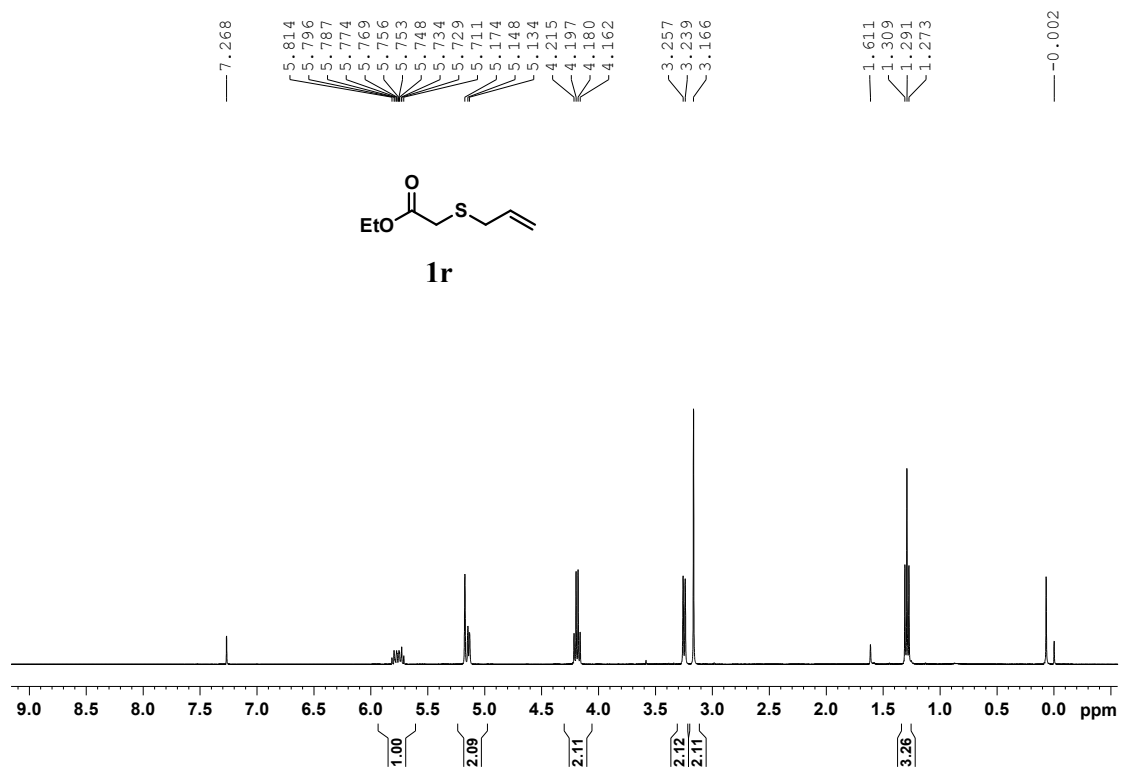
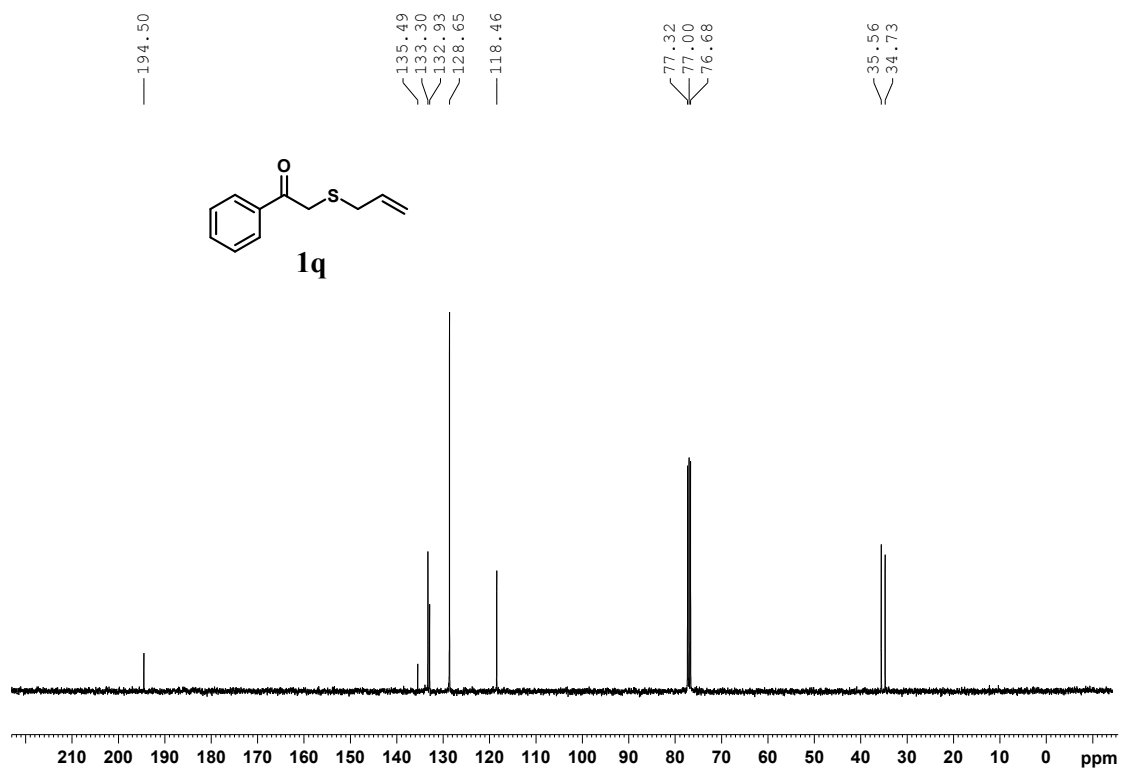


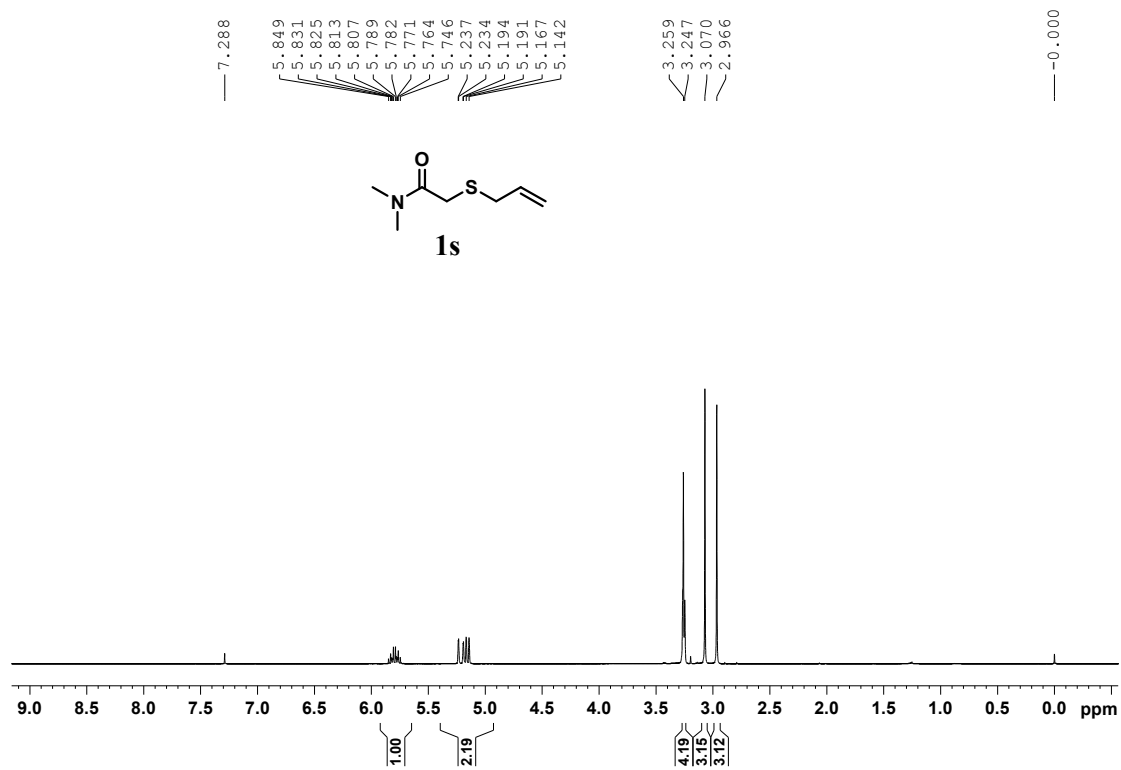
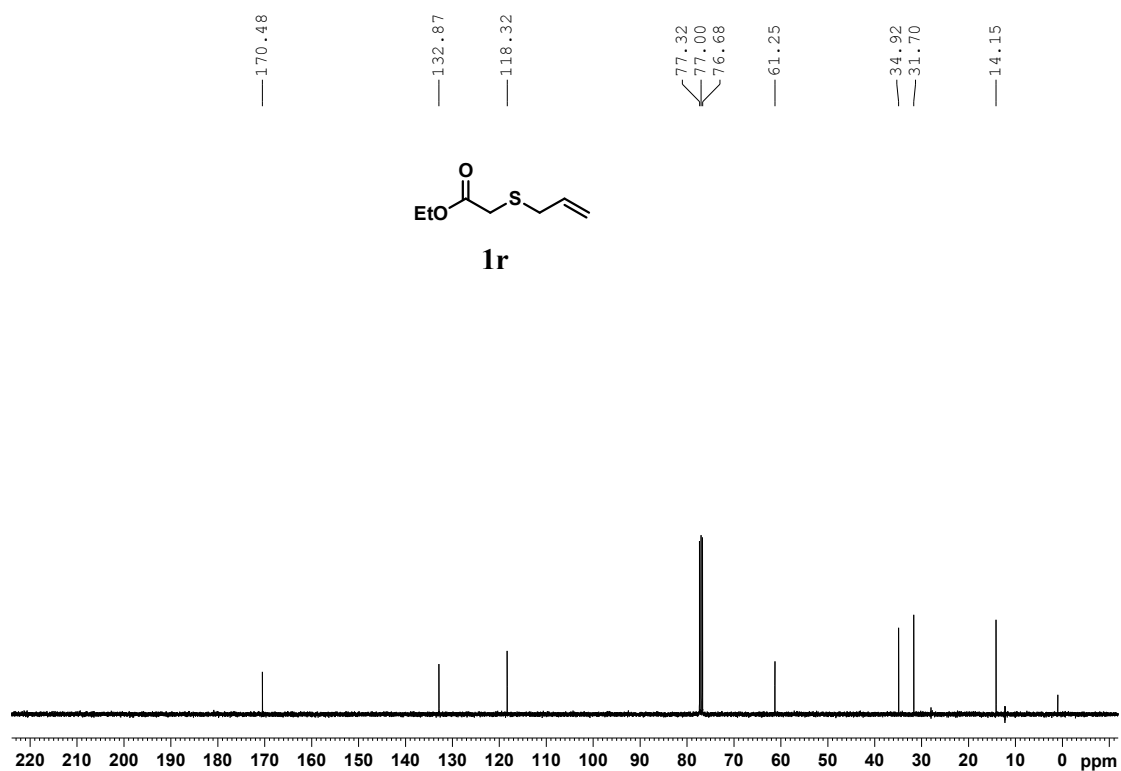


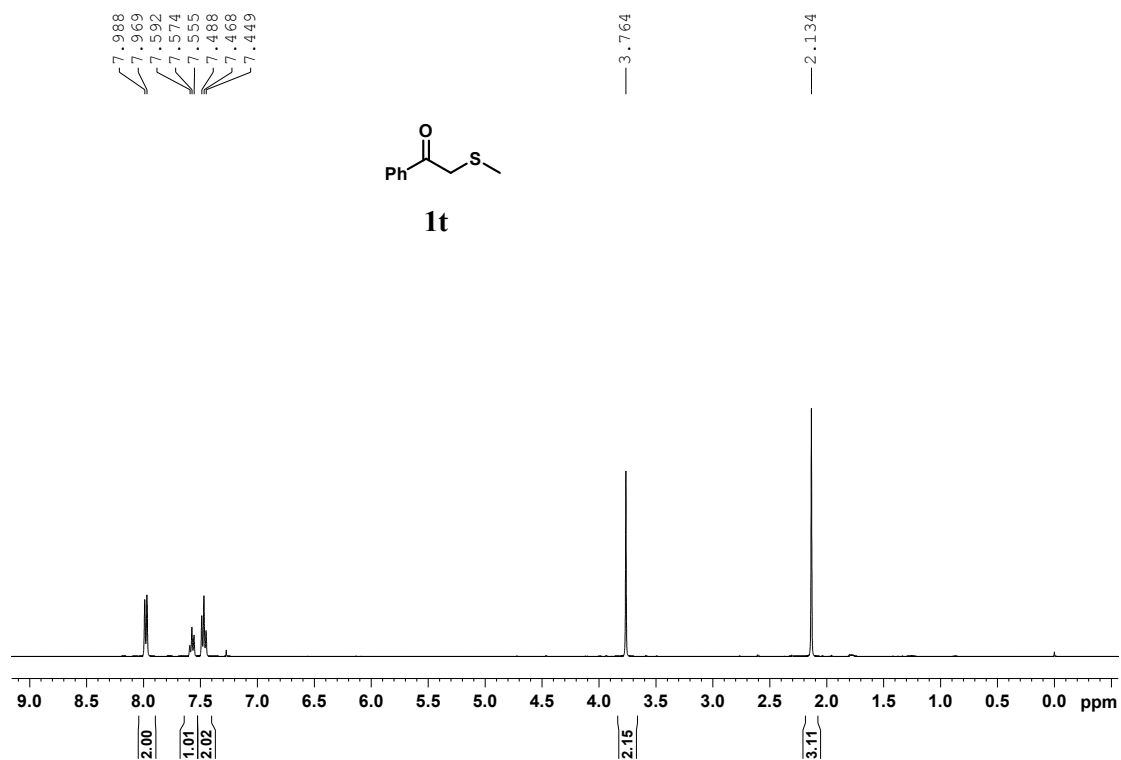
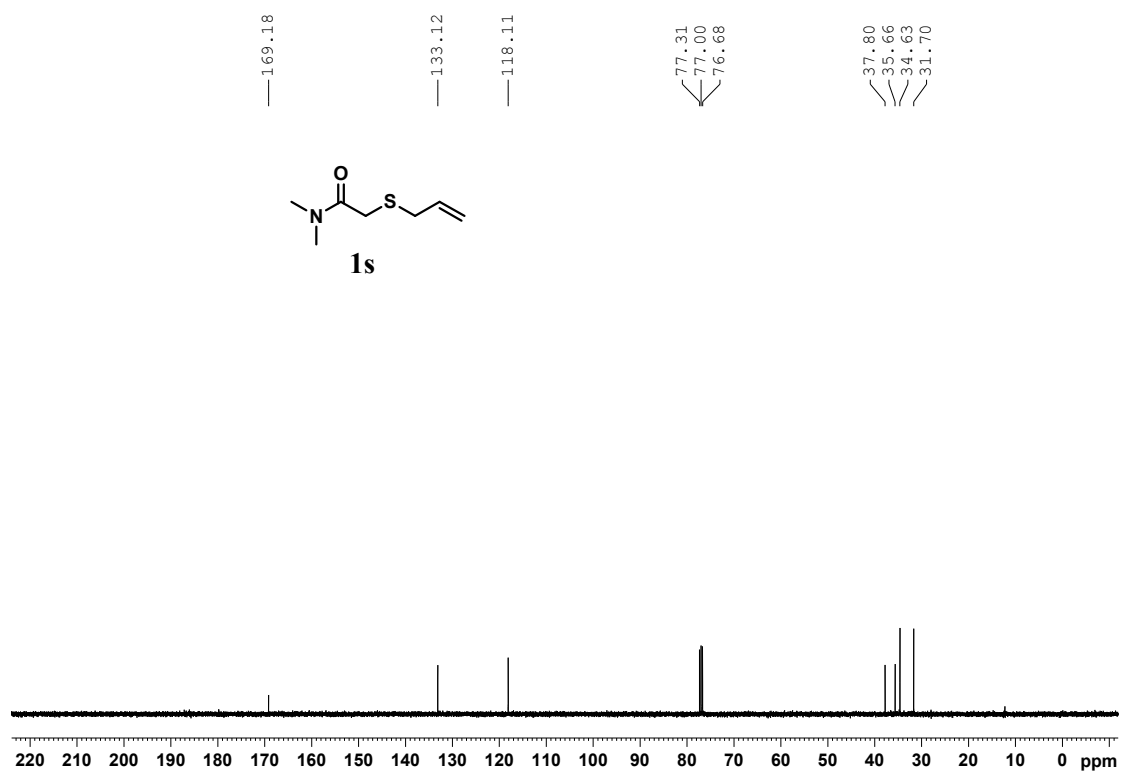


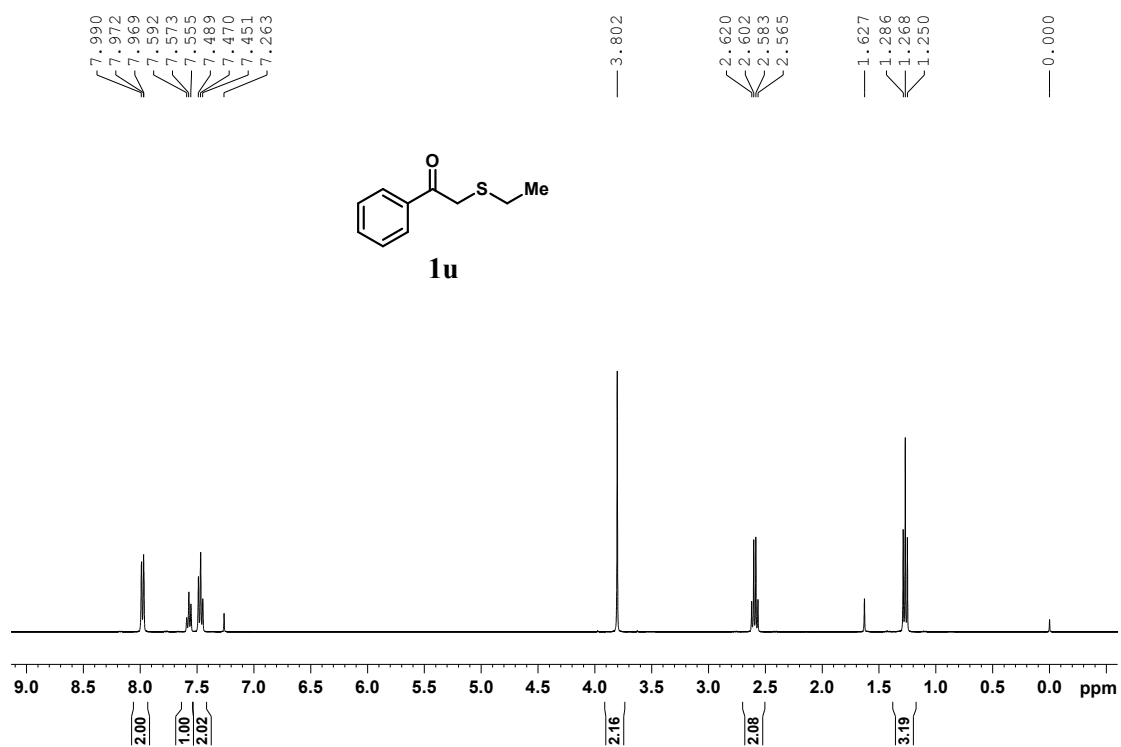
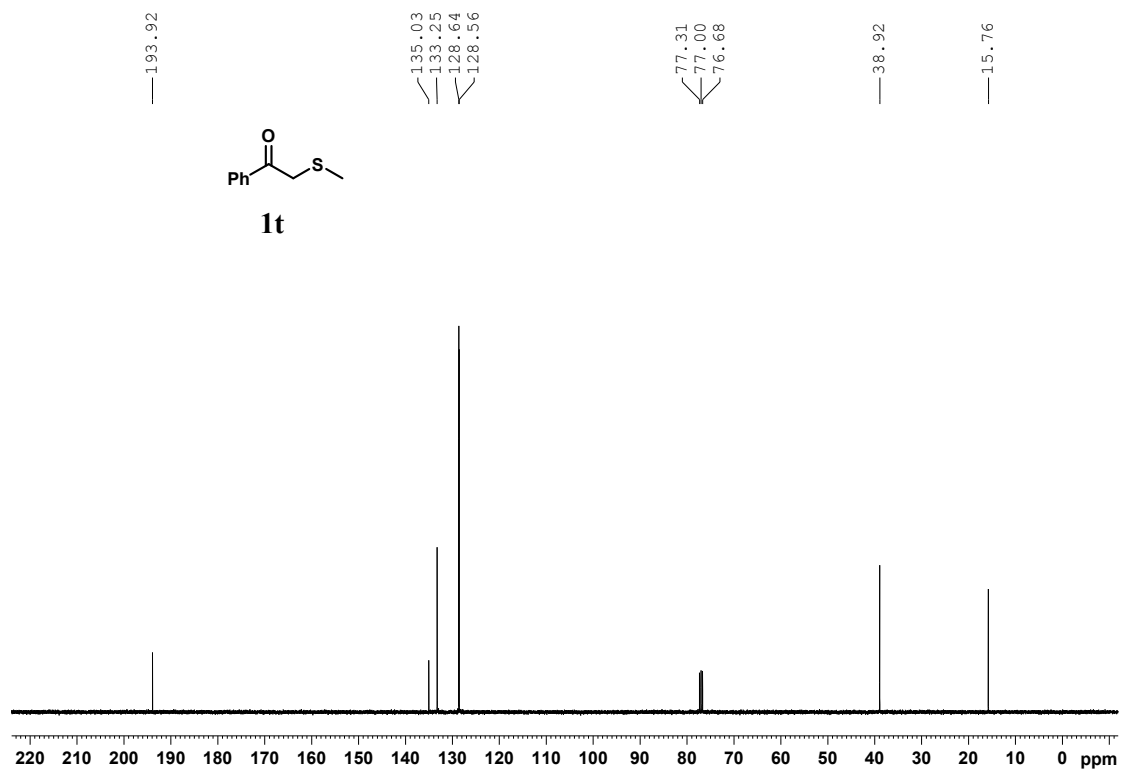


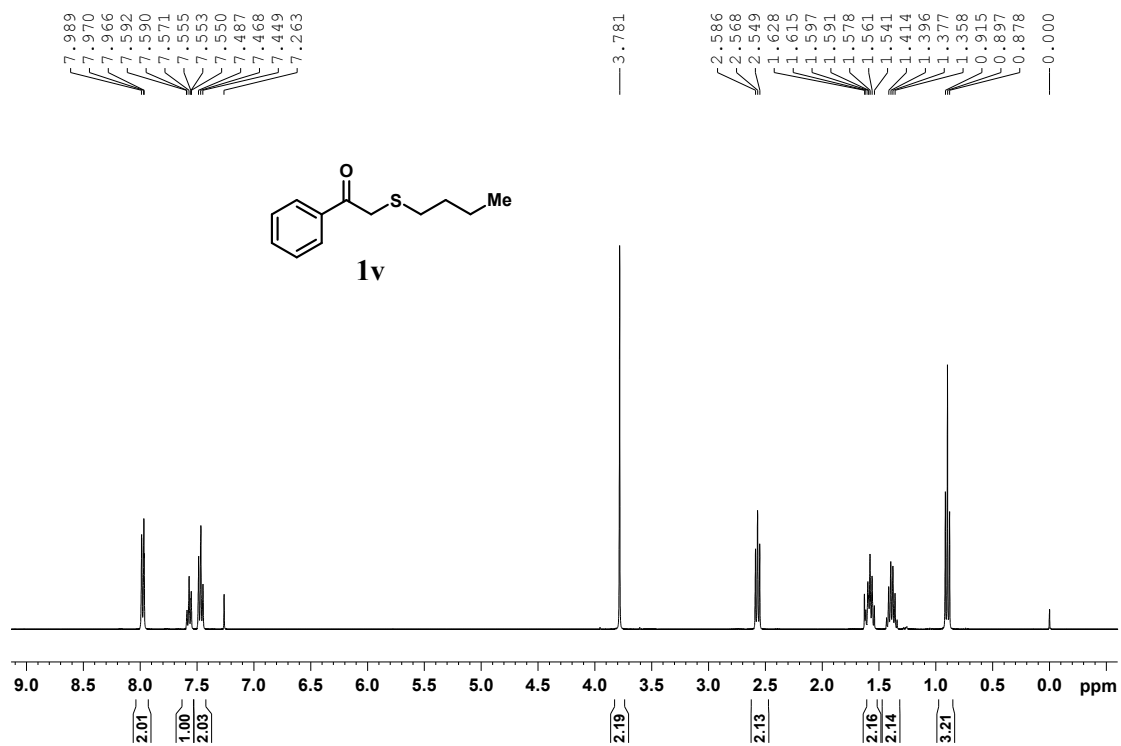
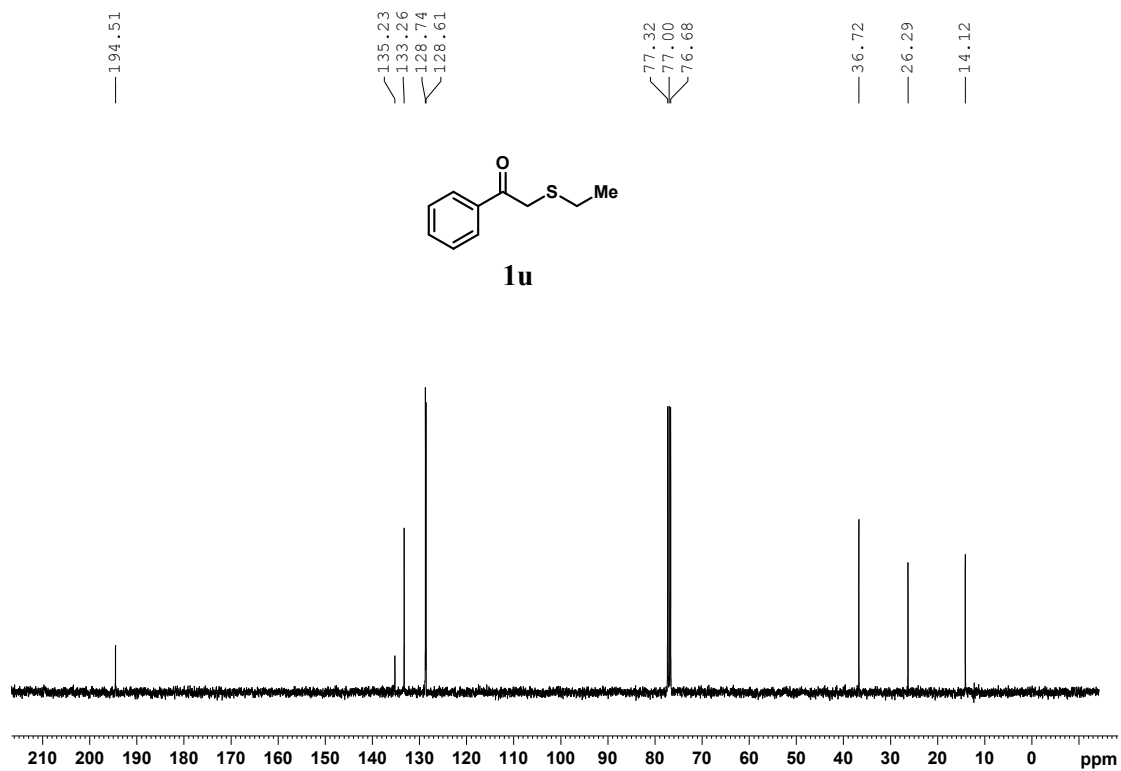


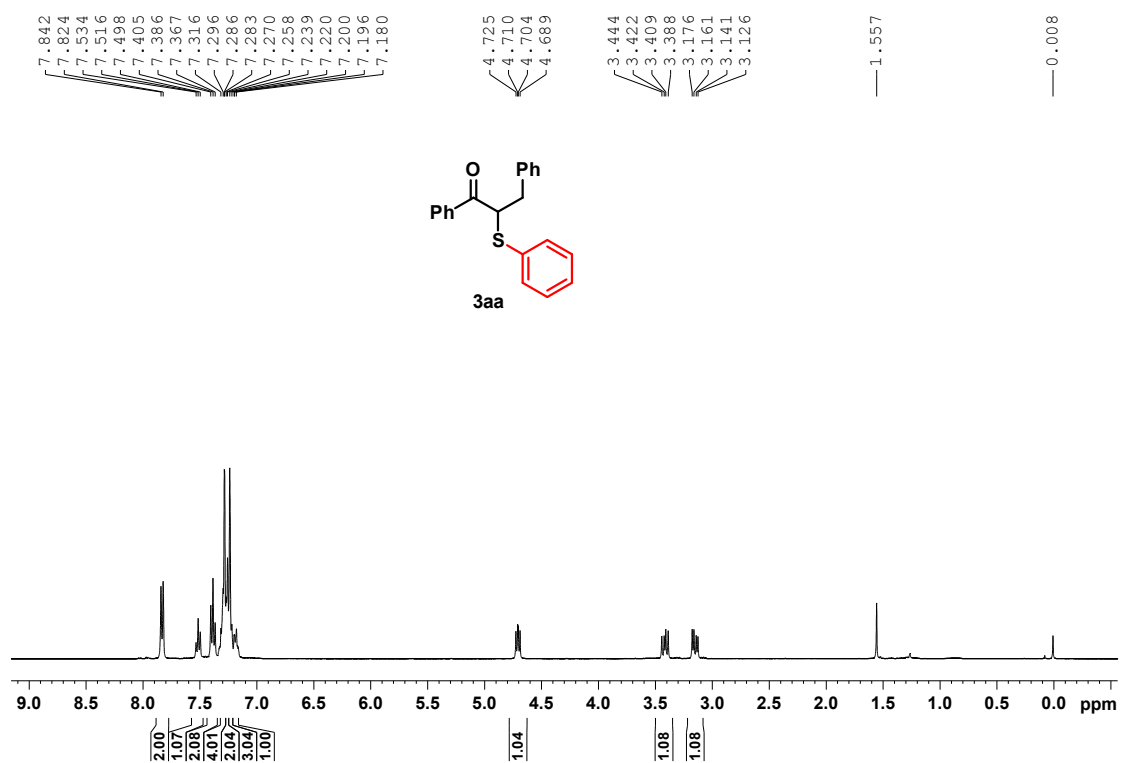
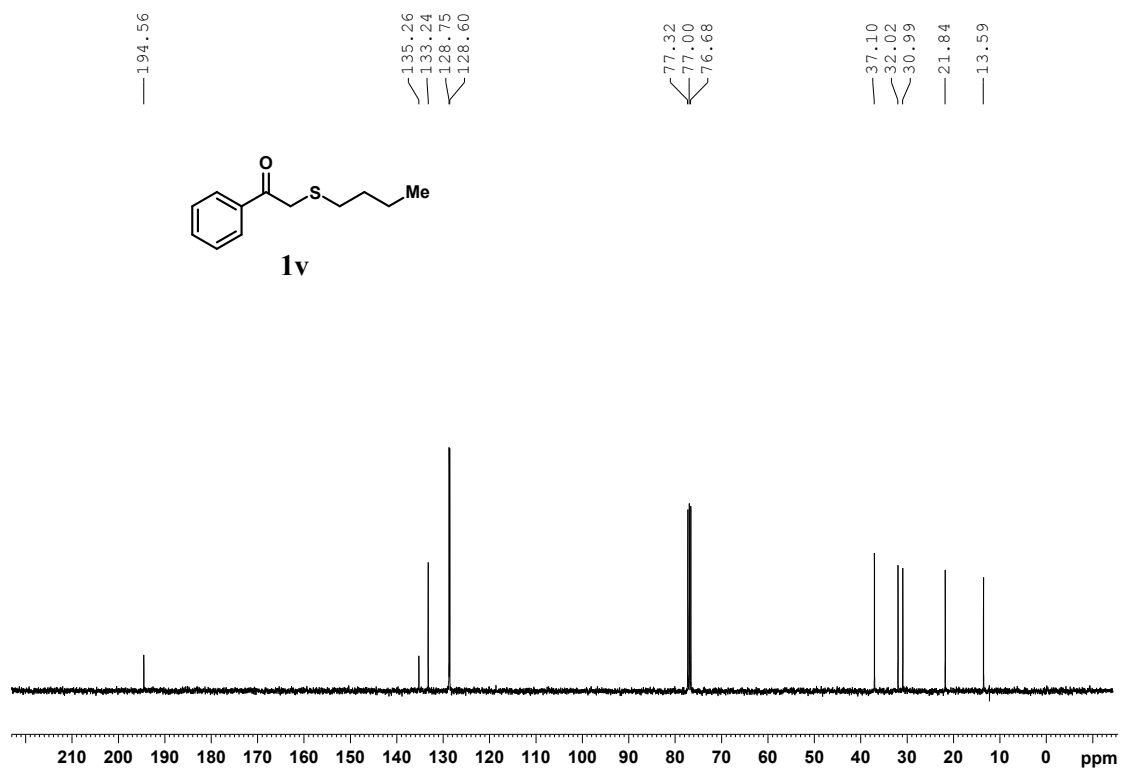


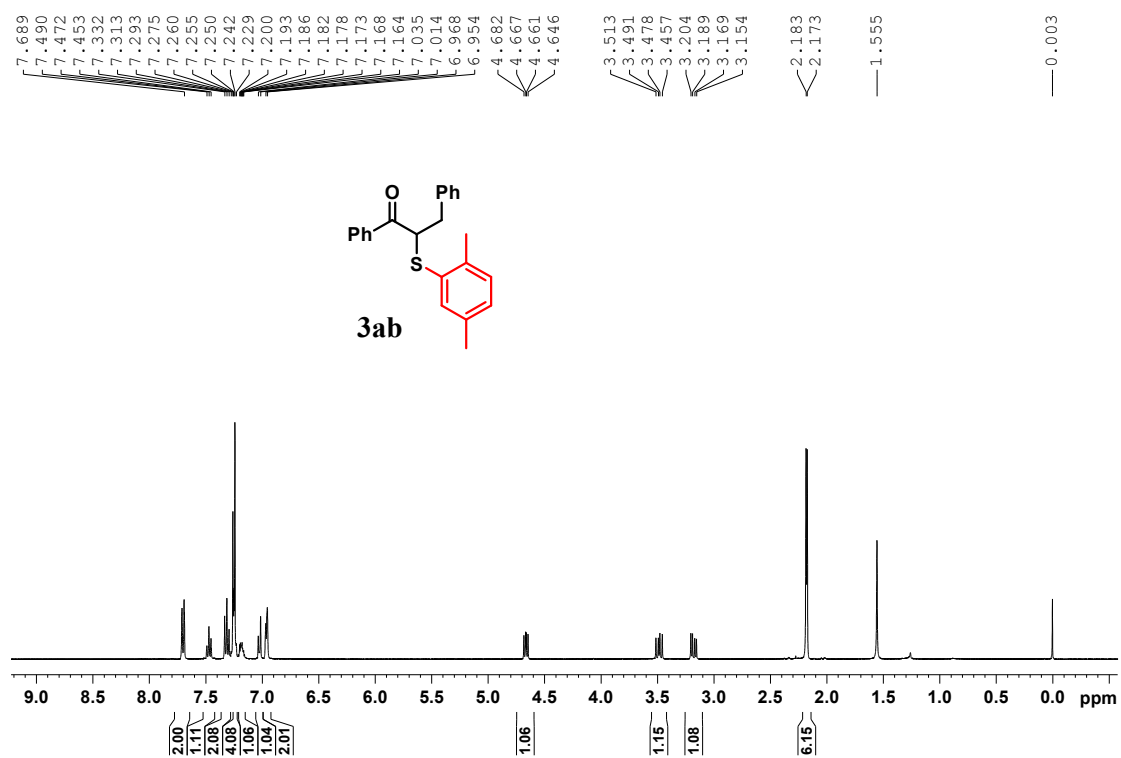
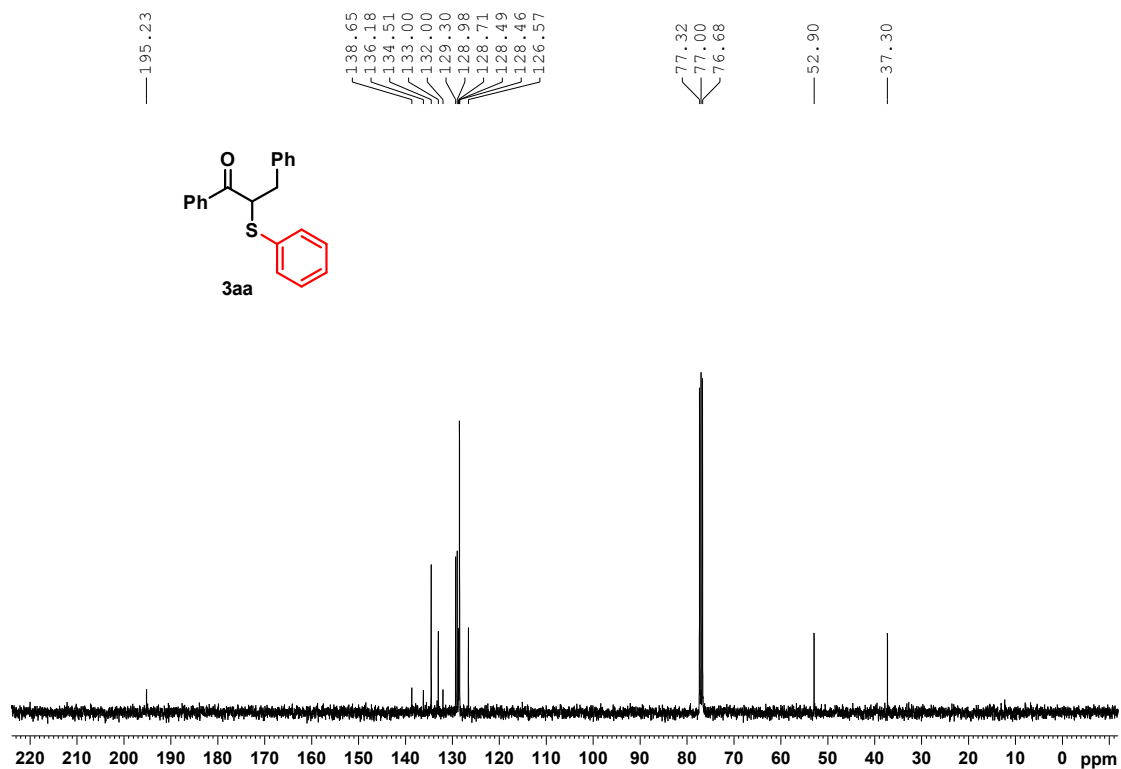


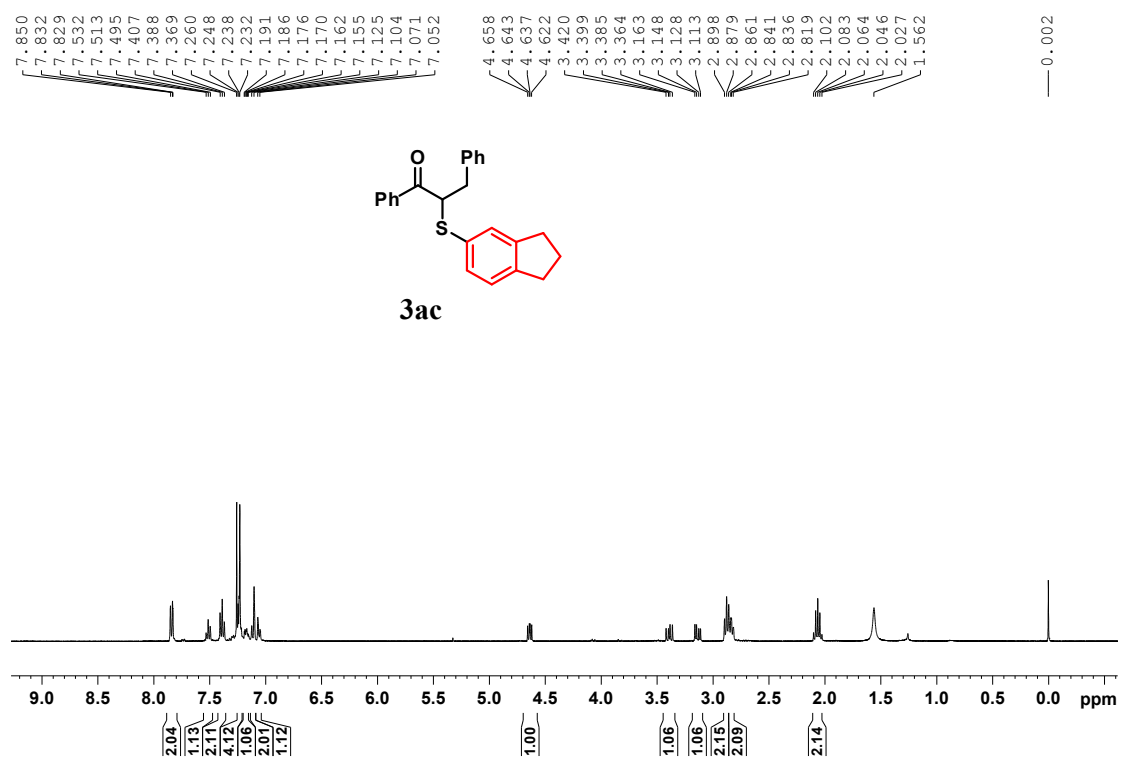
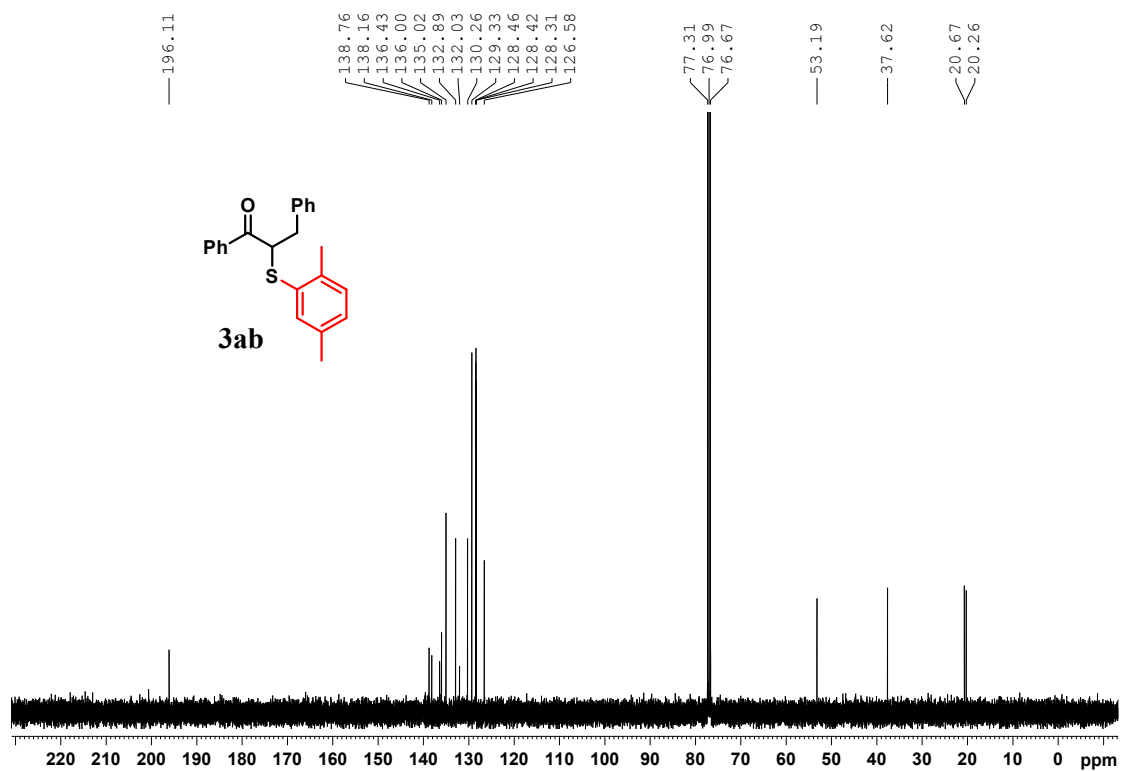


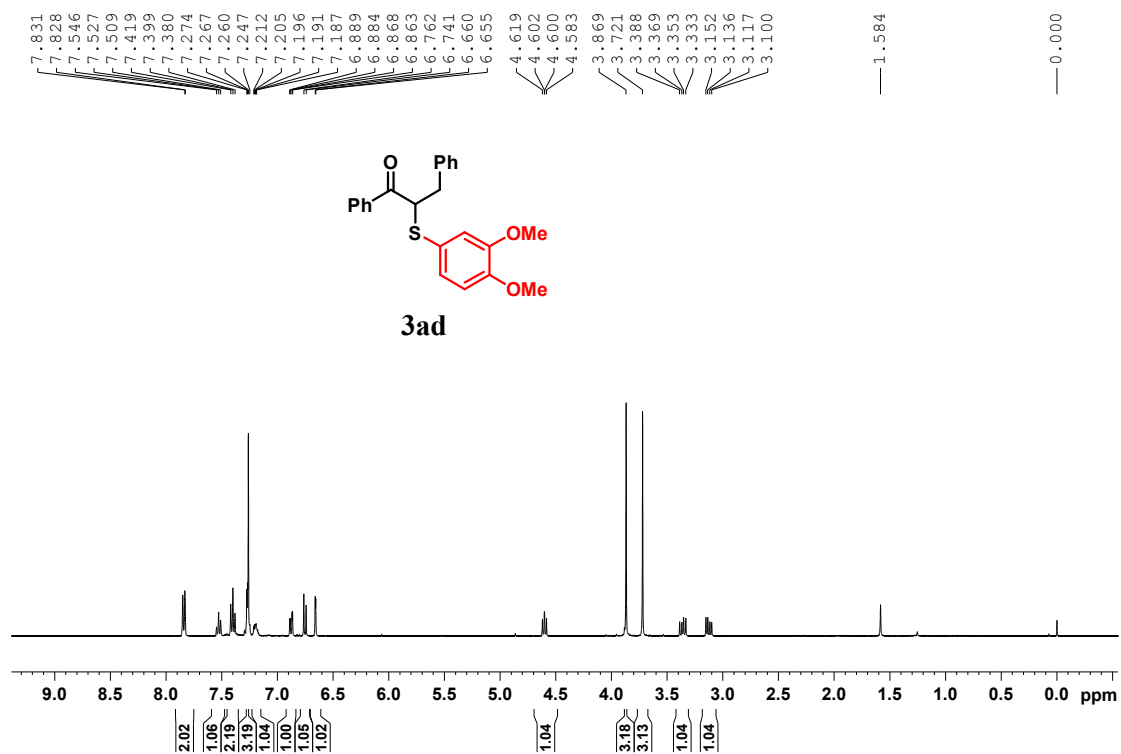
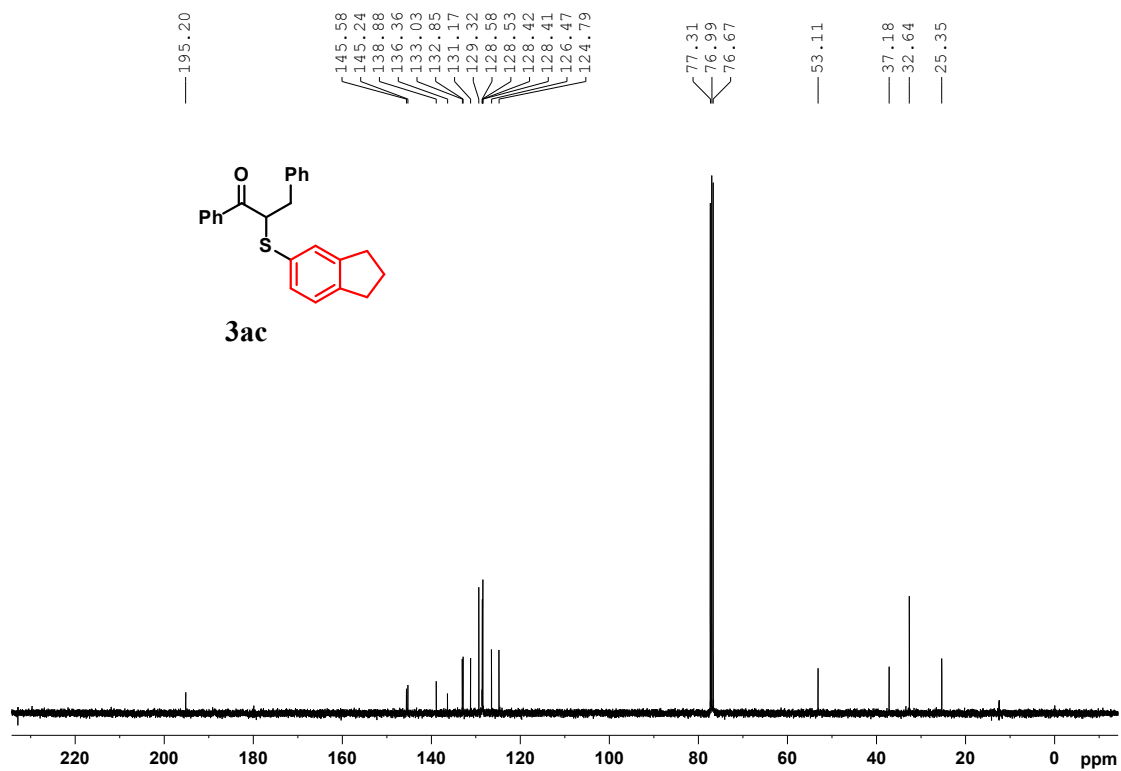


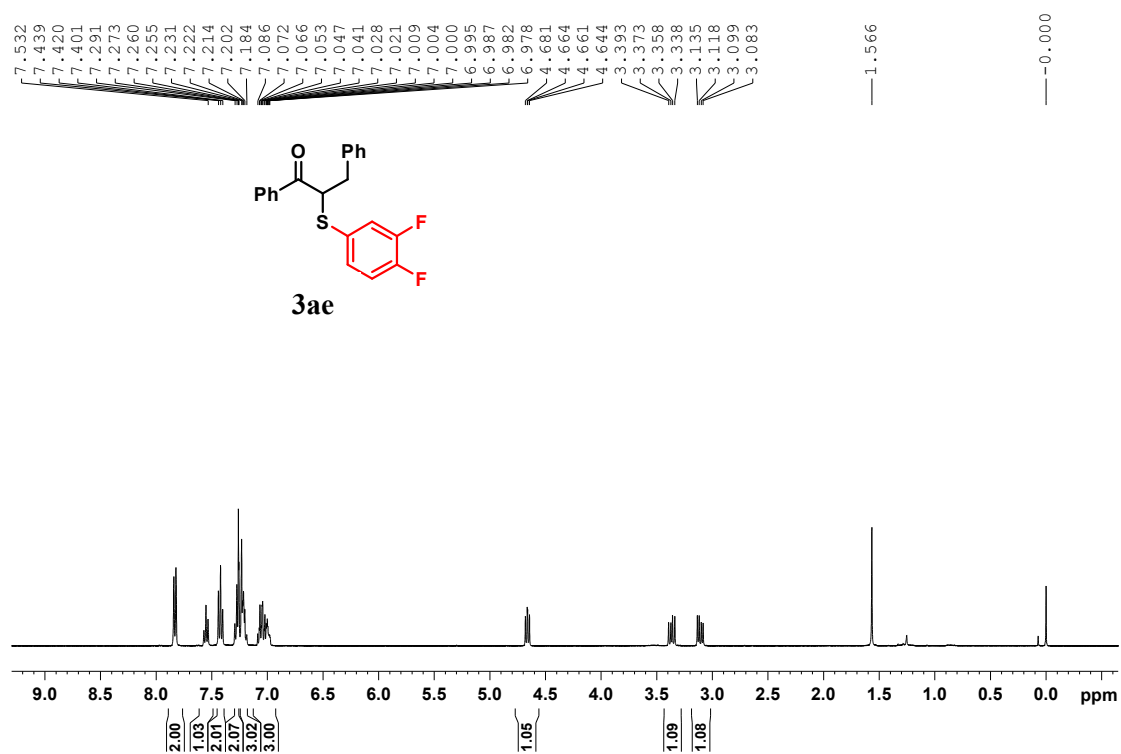
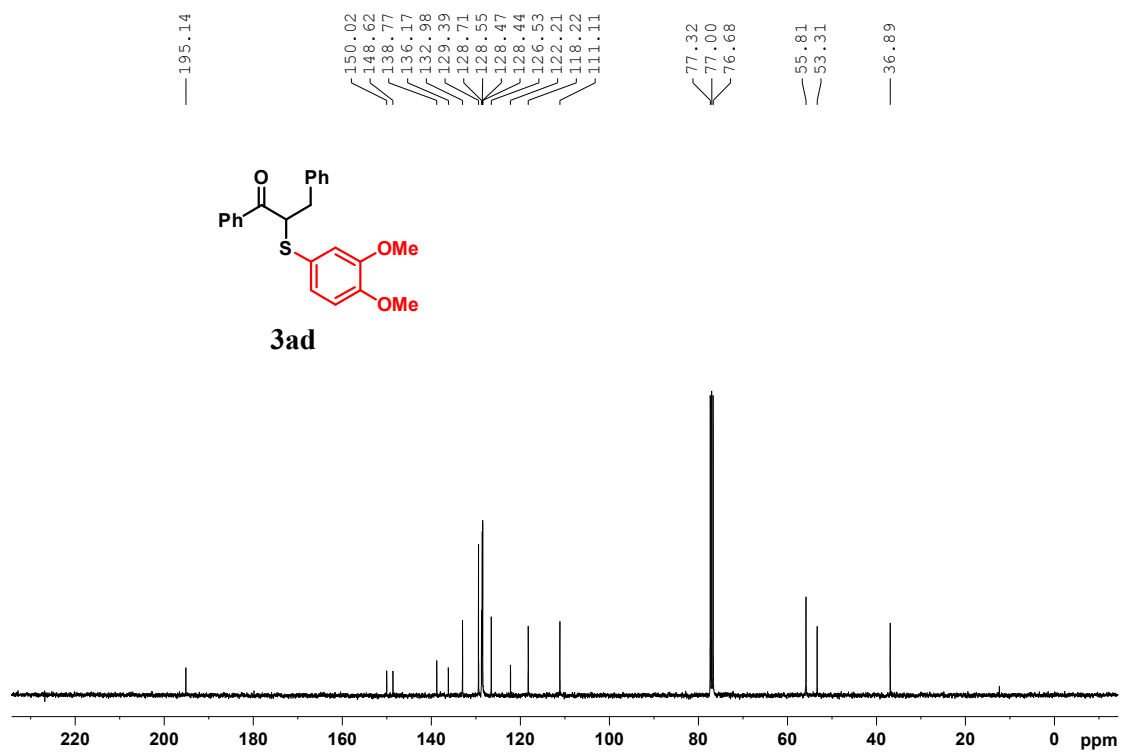


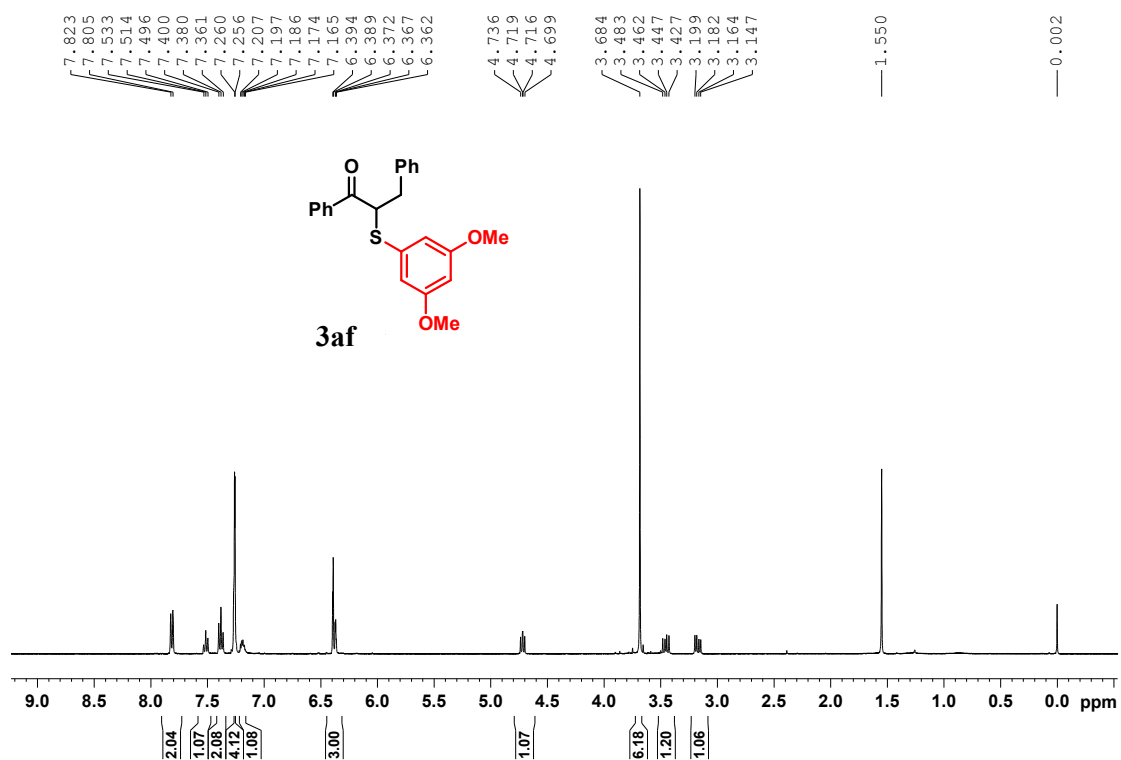
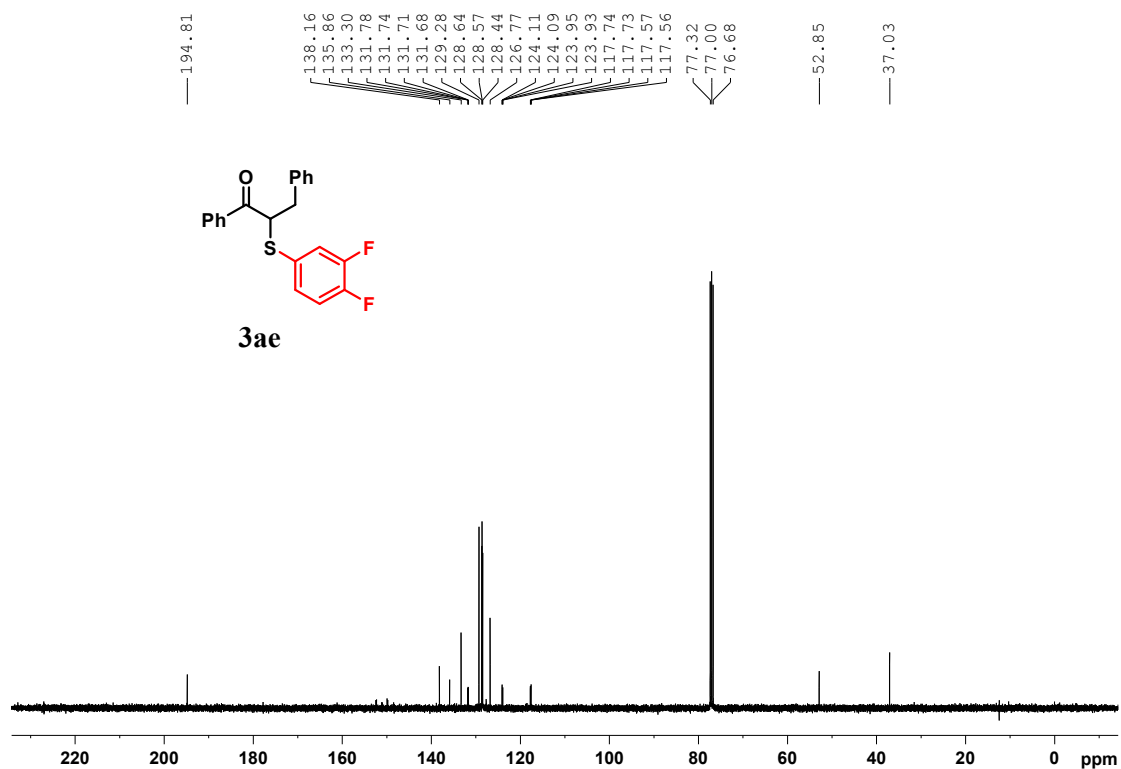


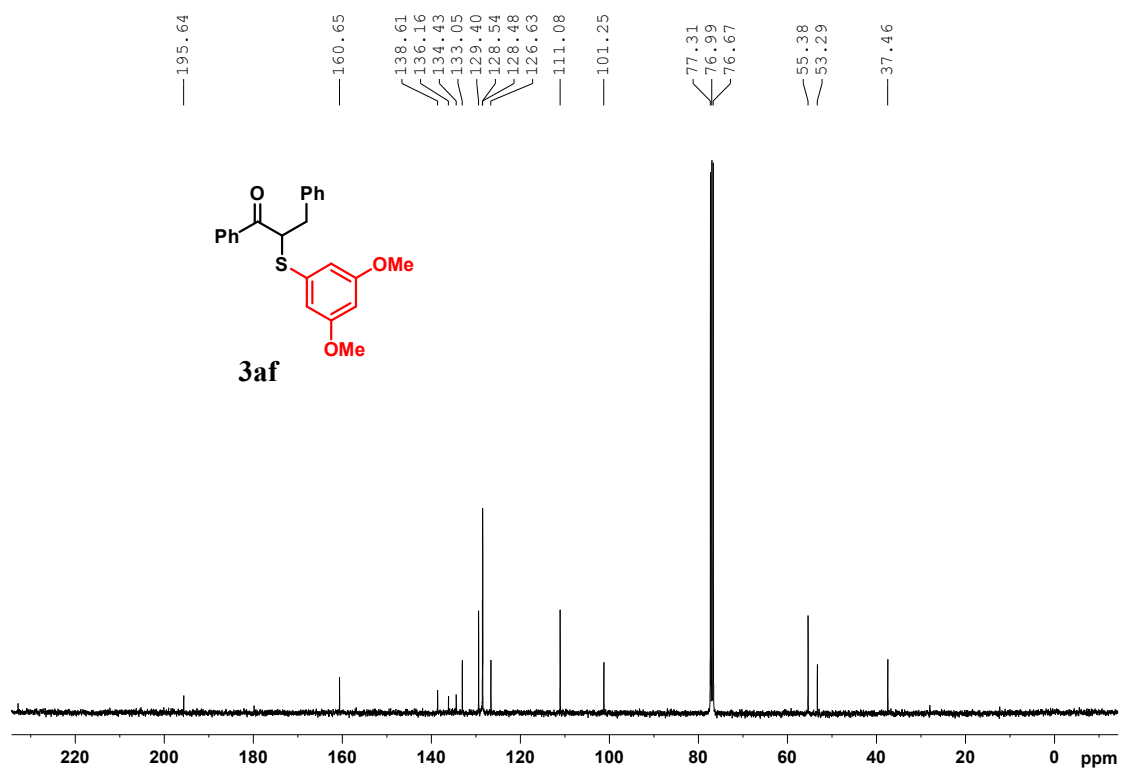






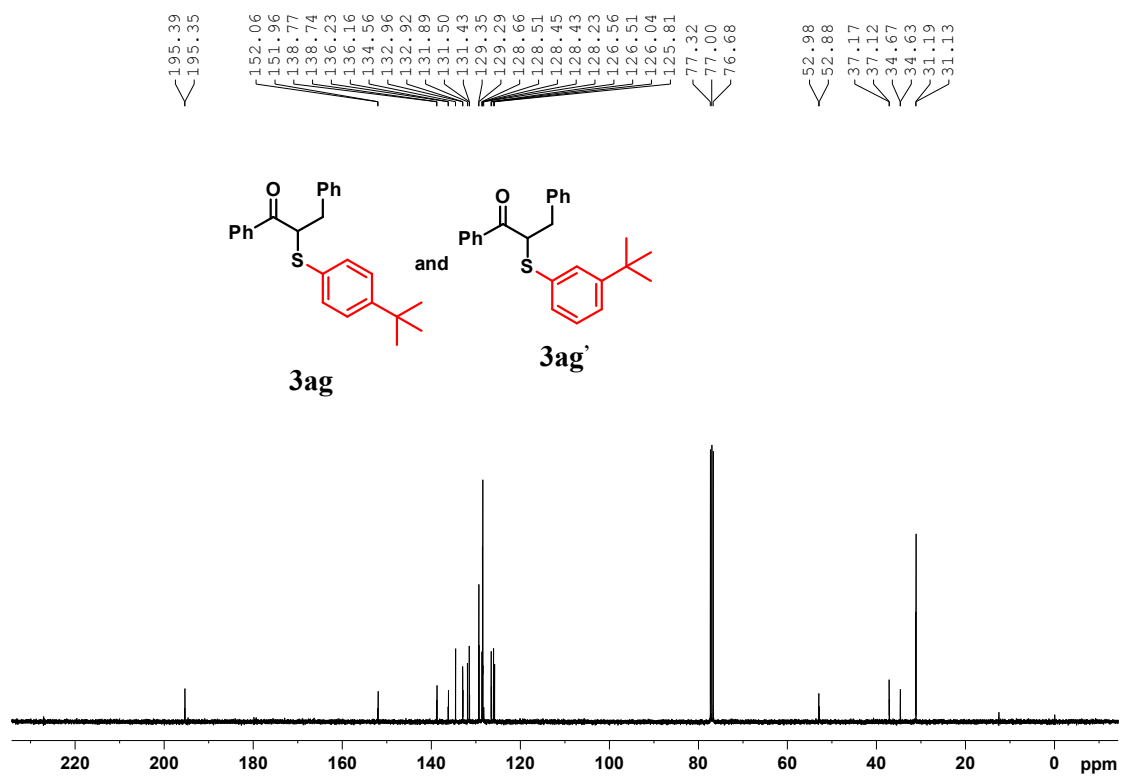
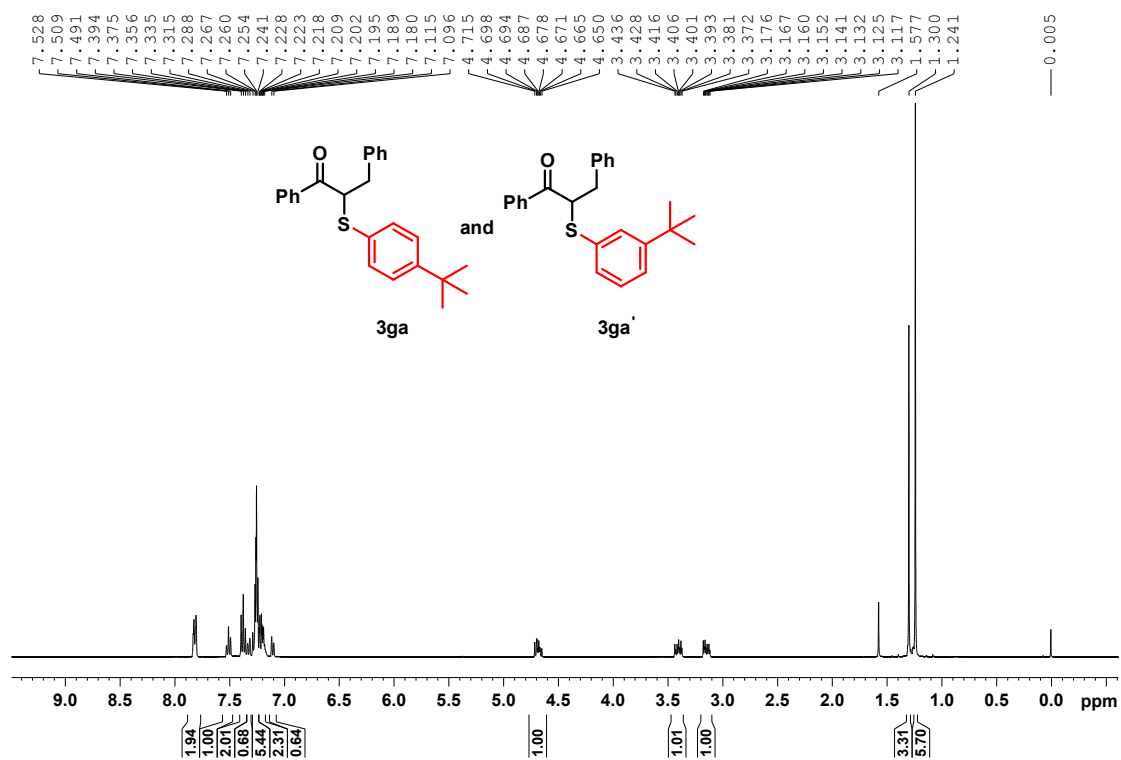


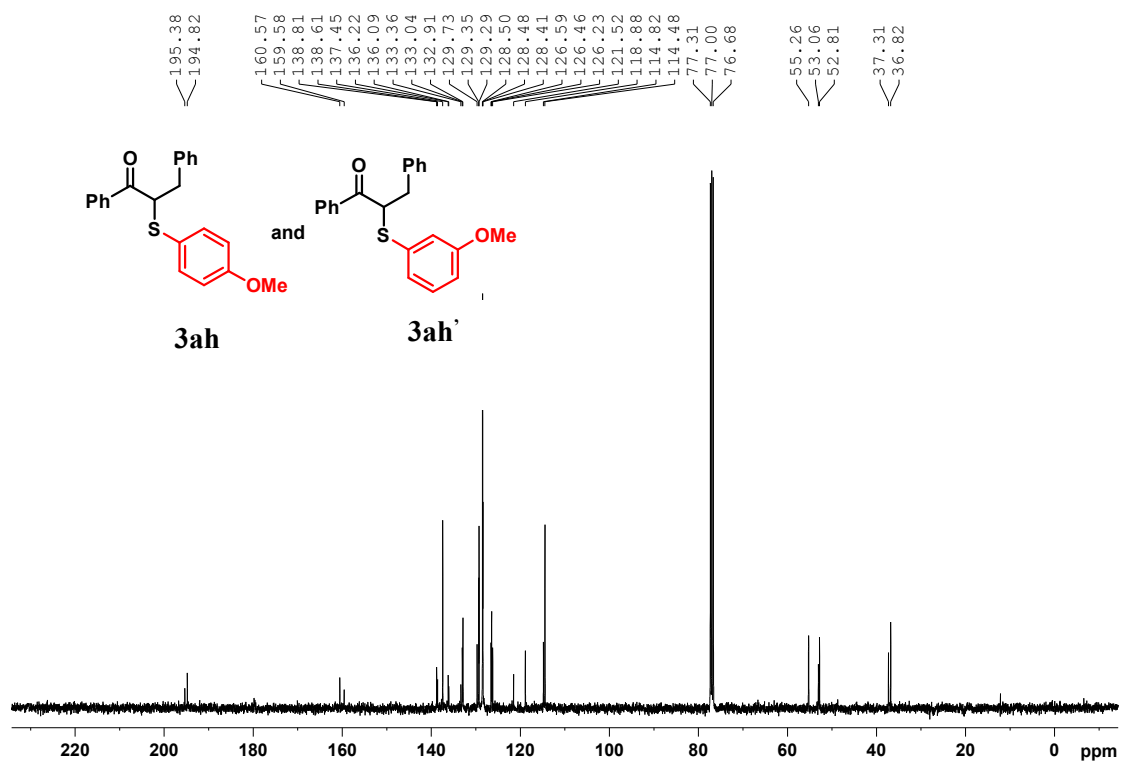
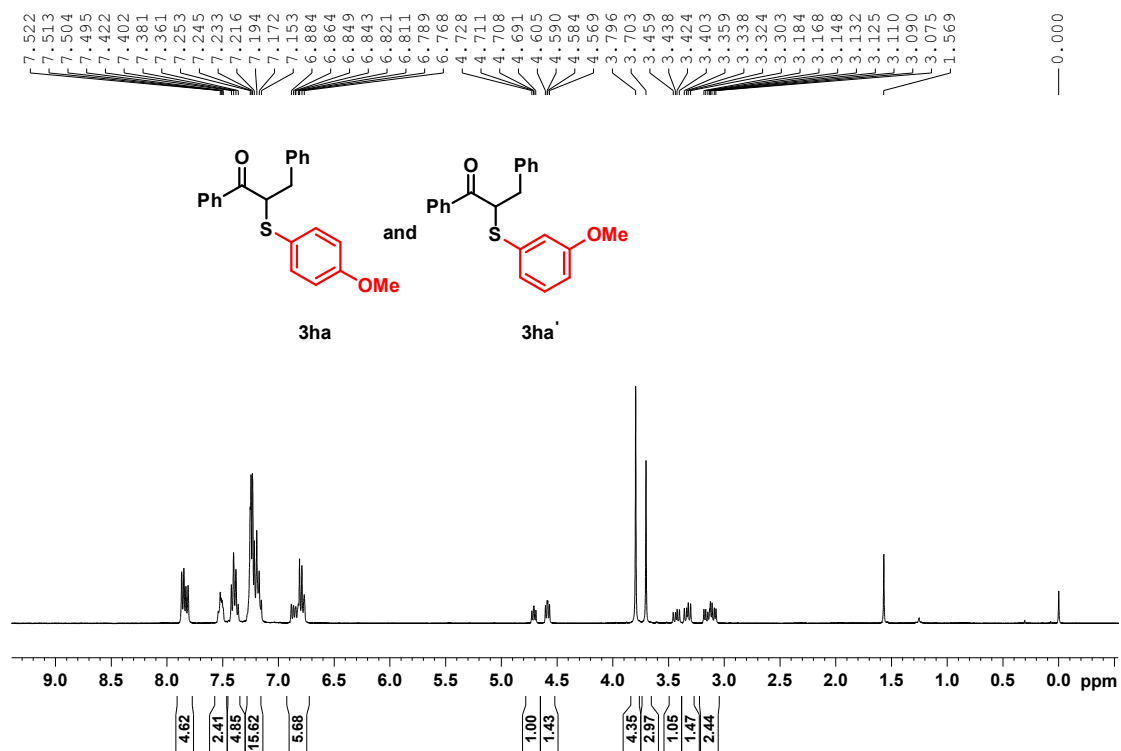


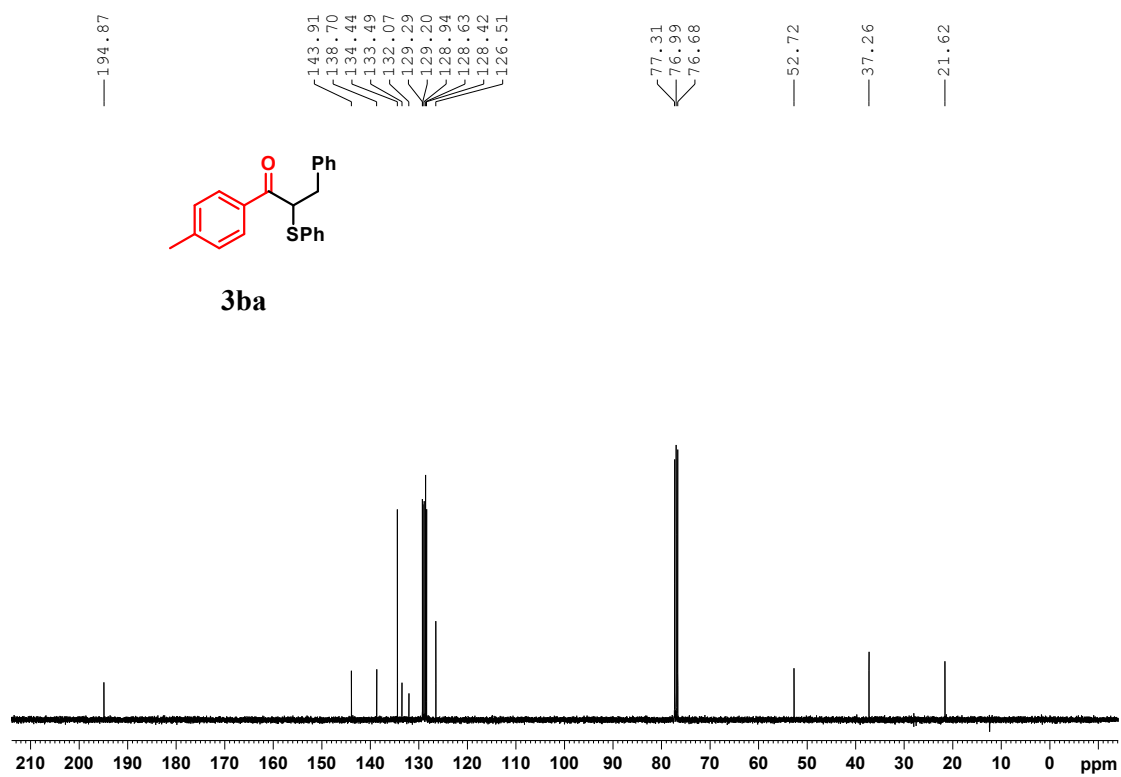
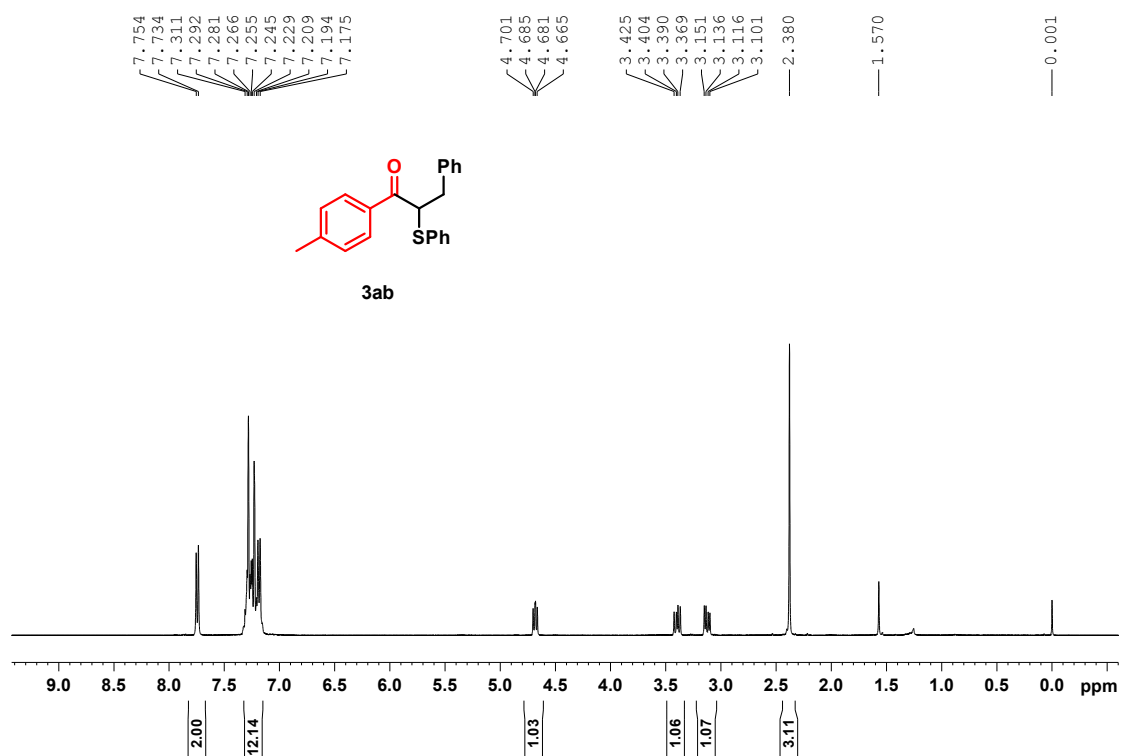


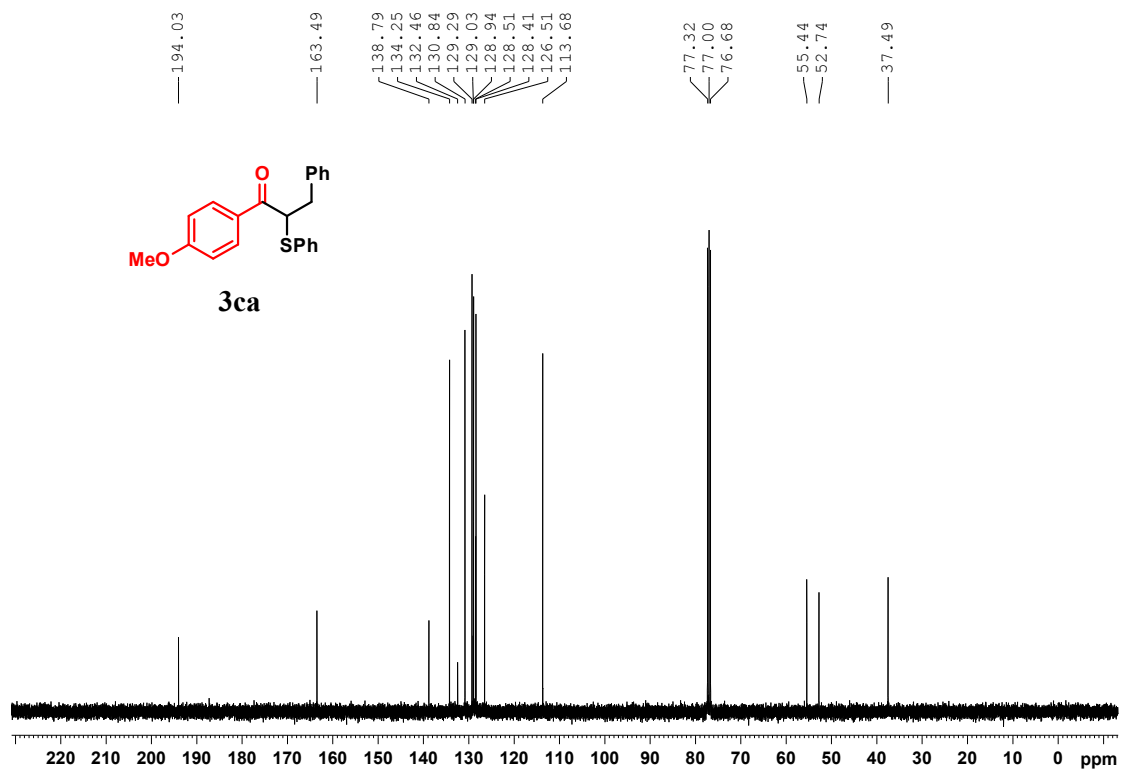
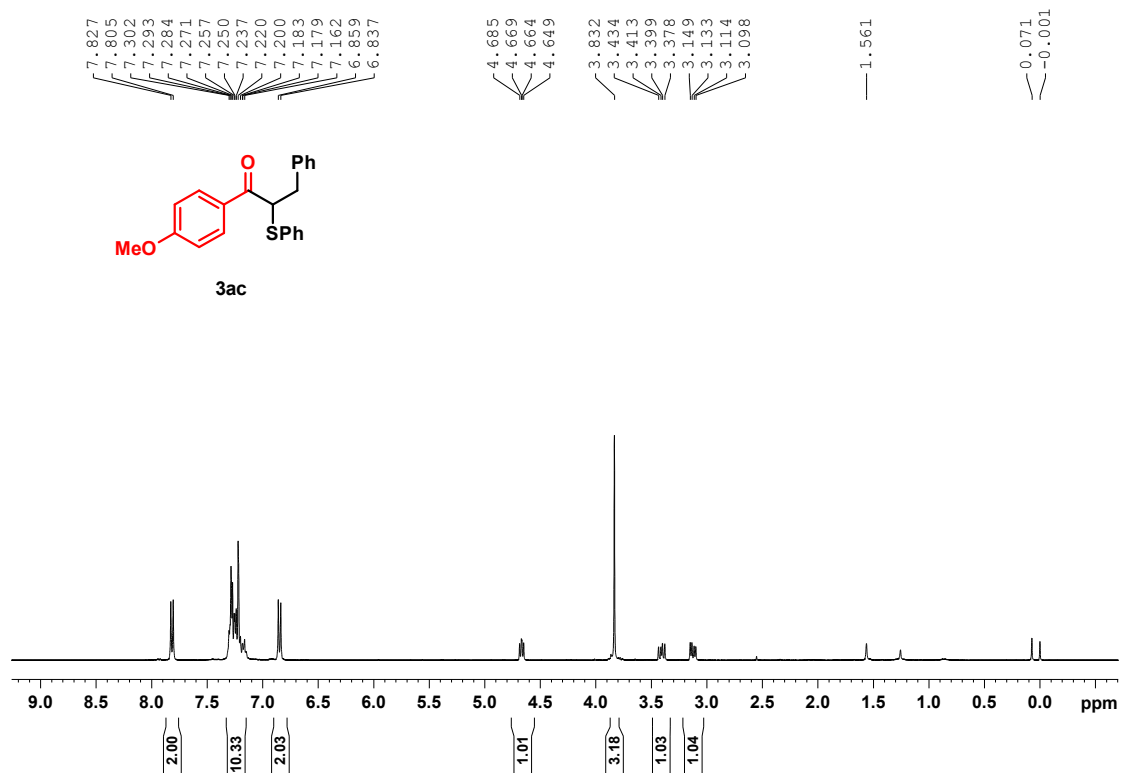
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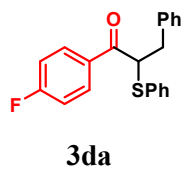
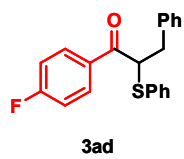
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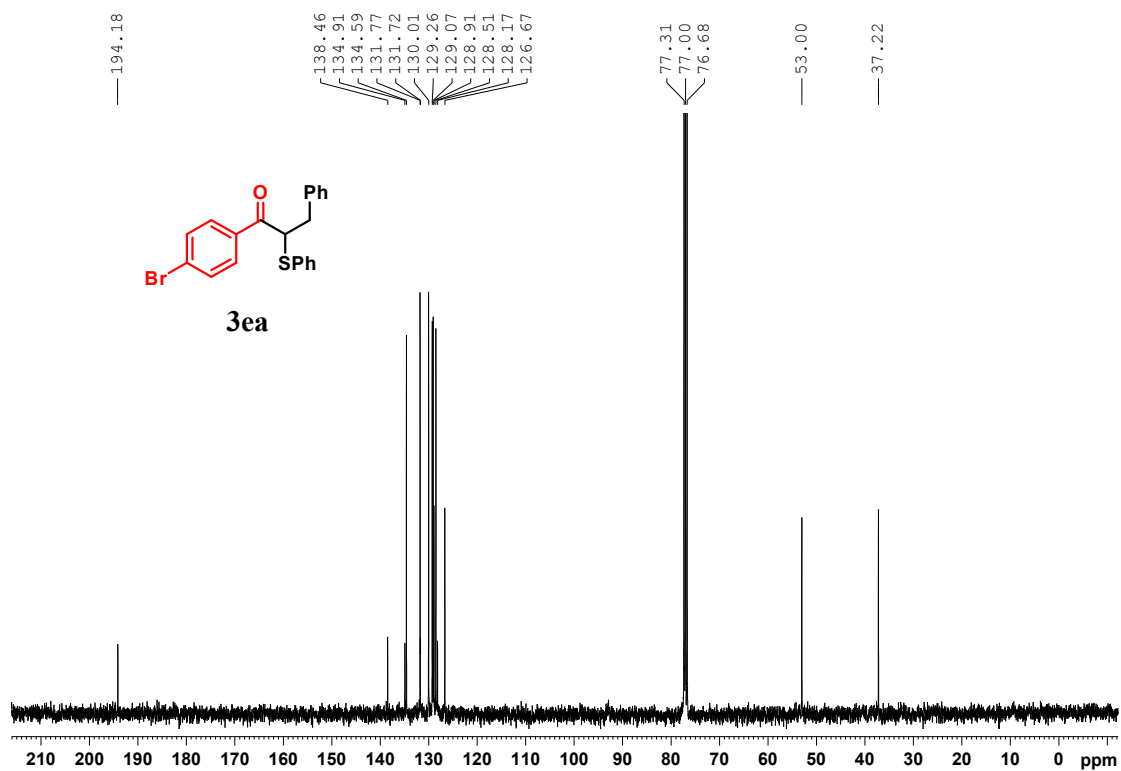
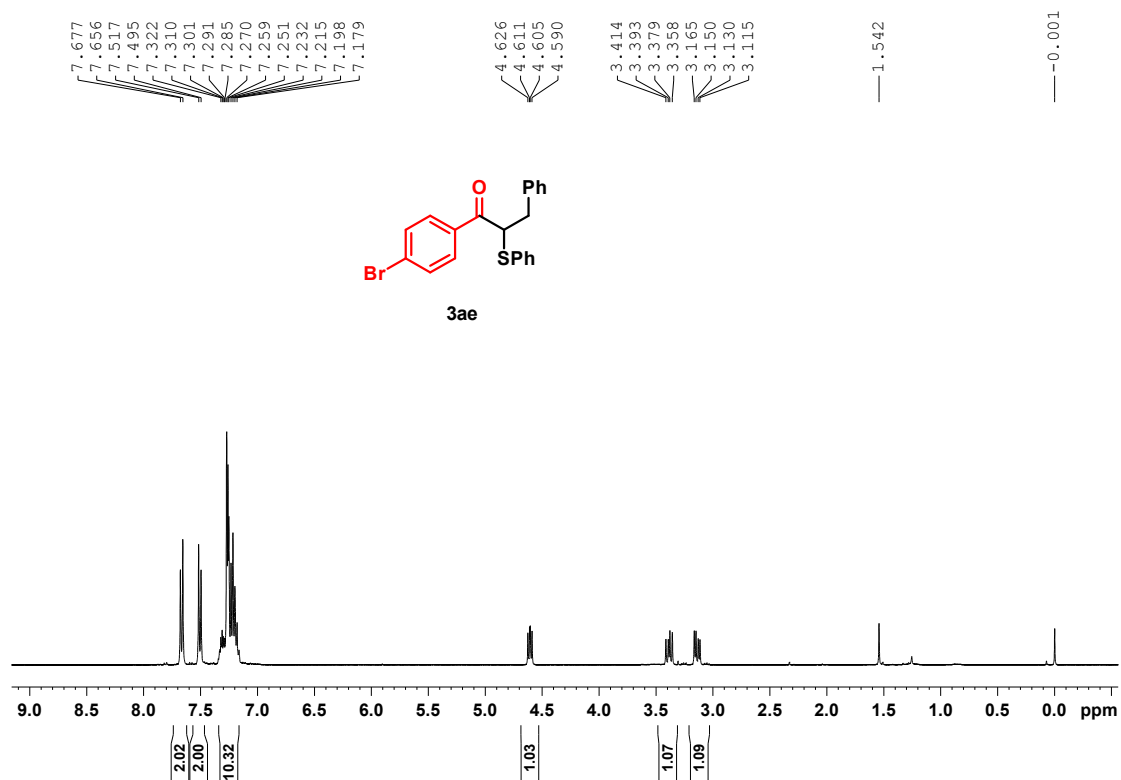


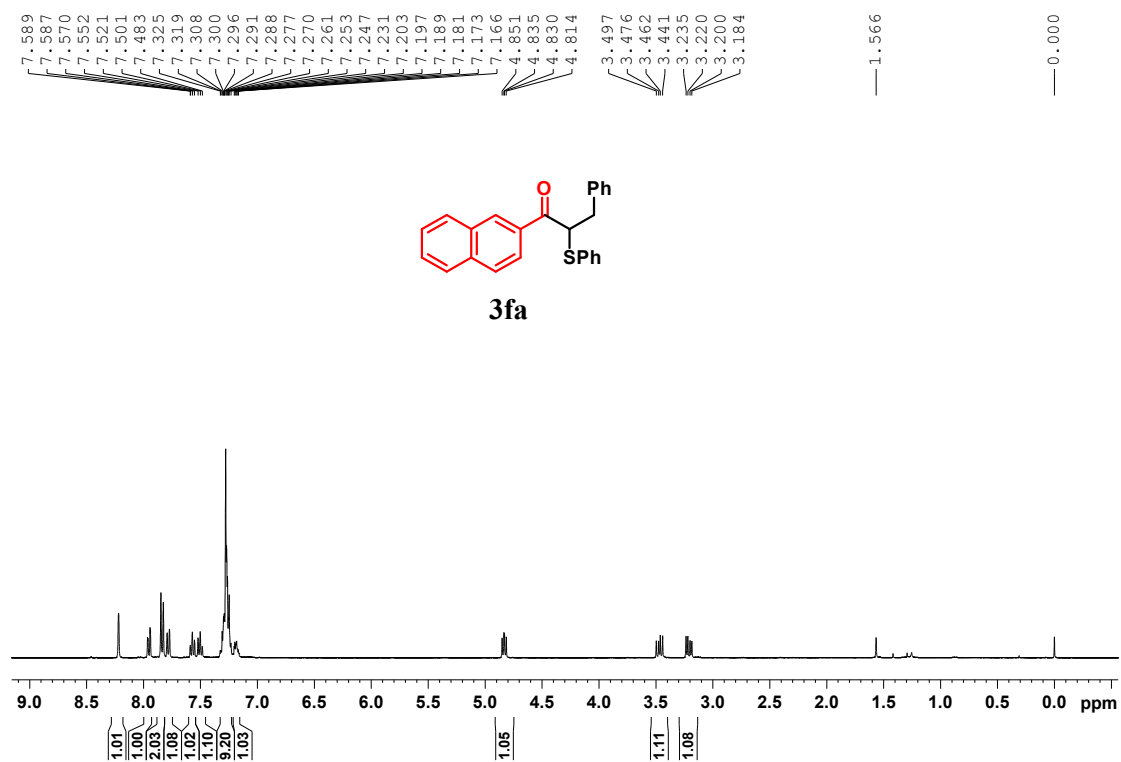












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