

Photocatalytic C-C bond thio(seleno)esterification of 1,2-diketone-derived pro-aromatic intermediates

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1 General Information

Analytic Methods:

All ^1H , ^{13}C and ^{19}F NMR spectra were recorded on a Bruker Advance III 500 MHz NMR spectrometer at room temperature unless otherwise noted. The chemical shift (δ) values are quoted in ppm downfield of tetramethylsilane. The residual solvent signals were used as the references for ^1H and ^{13}C NMR spectra (CDCl_3 : $\delta_{\text{H}} = 7.26$ ppm, $\delta_{\text{C}} = 77.16$ ppm; $\text{DMSO}-d_6$: $\delta_{\text{H}} = 2.50$ ppm, $\delta_{\text{C}} = 39.52$ ppm). ^{19}F NMR spectra are not calibrated by an internal reference. Coupling constants (J) are quoted in Hz. The following abbreviations are used for signal multiplicity: bs = broad signal, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, tt = triplet of triplets, m = multiplet. High resolution mass spectra (HRMS) were recorded on Thermo Scientific™ Q Exactive™ Hybrid Quadrupole-Orbitrap Mass Spectrometer. The ATR IR Spectra of solid and liquid compounds were recorded on a Shimadzu IR Prestige-21 FTIR spectrometer. The wave numbers are expressed in $[\text{cm}^{-1}]$. Melting points of solid compounds were measured using one end closed glass capillaries in Stuart Melting Point SMP50 apparatus. Fluorolog Horiba Jobin Yvon Spectrofluorimeter, which has a photomultiplier detector, double monochromator, and xenon light source, was used for the fluorescence quenching studies.

Reagents and Methods: All the chemicals were purchased from Sigma-Aldrich, TCI chemicals, Alfa Aesar, Spectrochem, Avra, SRL and BLD Pharma and used without any further purification unless otherwise mentioned. Technical grade solvents: ethyl acetate, petroleum ether (40-60), hexane, acetone, dichloromethane were purchased from Merck and Avra and used after distillation. Tetrahydrofuran (THF), Diethylether (Et_2O) and Toluene were purchased from Spectrochem and dried over KOH pellets or CaH_2 and distilled over Sodium wire/benzophenone. Dichloromethane (DCM) and Acetone were purchased from Merck, dried and distilled over CaH_2 . The following dry solvents: DCM, THF, Et_2O and toluene were stored over molecular sieves with septa under nitrogen atmosphere and withdrawn using a syringe under positive nitrogen pressure. Anhydrous 1,4-Dioxane, and DMF were purchased from Sigma Aldrich and Acros Organics. The deuterated solvents, CDCl_3 (99.8%) and Dimethylsulfoxide - d_6 (99.5%) were purchased from Sigma-Aldrich, Leonid Chemicals and Cambridge Isotope Laboratories. Silica Gel Aluminium TLC plates were purchased from Merck. TLC was visualized using shortwave UV-254 nm or the stain made out of potassium permanganate followed by heating as the developer. Silica gel 230-400 mesh, purchased from Merck, was used for the column chromatography. The thermal reactions were conducted in a pre-heated oil bath. The blue LEDs ($\lambda_{\text{max}} = 456$ nm) were purchased from M/s Kessil. The reaction vessels were placed 10 cm away from the light sources and an electrical fan was used for cooling.

Note: No attempts were made to optimize yields for the synthesis of substrates.

1. Substrate Synthesis

1.1 Synthesis of dihydroquinazolinones & benzothiazolines from 1,2-diketones

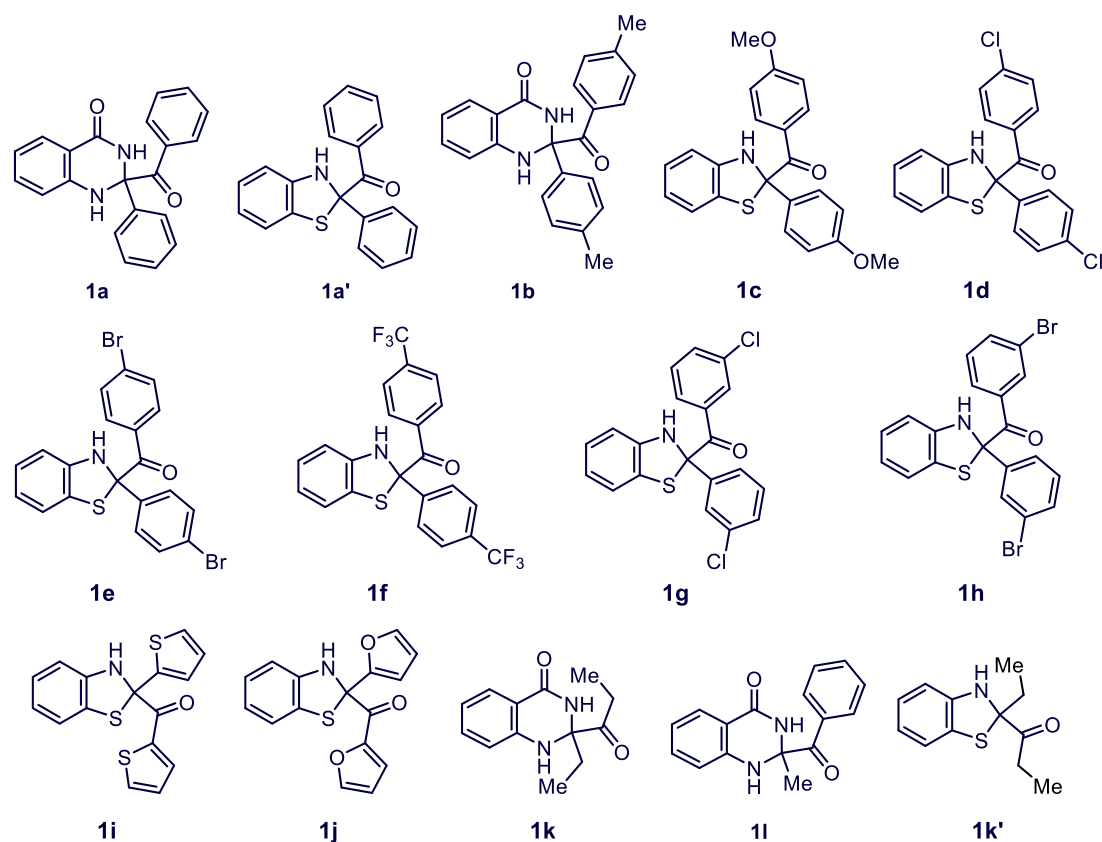
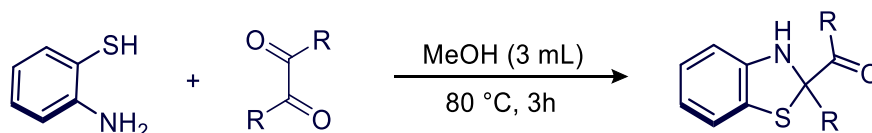


Figure S1: List of dihydroquinazolinones and benzothiazolines.

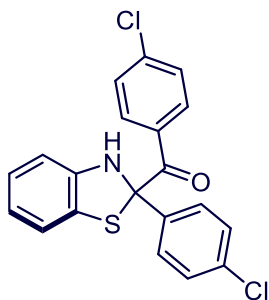
Dihydroquinazolinones **1a**,¹ **1b**, **1k**² & **1l**² were prepared following the reported literature. Benzothiazolines **1a'**, **1c**, **1e**, **1i-1j**, and **1k'** were prepared following the reported literature.³

General procedure for the synthesis of benzothiazolines (GP1):



Following a modified procedure reported by Zhu and co-workers,² in a sealed-tube equipped with a Teflon-coated stirring bar, 2-aminobenzenethiol (2.4 mmol, 1.2 equiv.) and 1,2-diketone (2.0 mmol, 1.0 equiv.) were taken followed by addition of MeOH (3 mL). The reaction mixture was heated at 80 °C for 3 h. After the completion as monitored by TLC, the reaction was quenched by adding brine solution and extracted with ethyl acetate (3×5 mL). The collected organic phase was washed with water and brine and dried over Na₂SO₄ and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography using silica gel (eluent: PE/EA = 10:1) to obtain pure benzothiazolines.

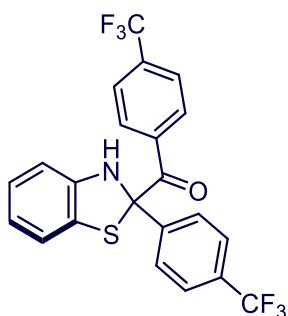
(4-Chlorophenyl)(2-(4-chlorophenyl)-2,3-dihydrobenzo[d]thiazol-2-yl)methanone (**1d'**)



Following **GP 1**, 2-aminobenzenethiol (250 mg, 2.4 mmol, 1.2 equiv.) and 1,2-bis(4-chlorophenyl)ethane-1,2-dione (**S4**, 558 mg, 2 mmol, 1 equiv.) afforded the compound **1d'** as a yellow liquid (625 mg, 1.62 mmol, 81%).

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.65 (d, *J* = 8.3 Hz, 2H), 7.56 (t, *J* = 8.2 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 7.5 Hz, 2H), 6.79 (d, *J* = 8.2 Hz, 2H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 193.2, 144.7, 140.1, 139.4, 135.1, 131.8, 131.1, 129.6, 128.9, 128.4, 126.6, 125.6, 121.7, 121.4, 112.3, 83.5; **HRMS (ESI-TOF)**: *m/z* calc. for (C₂₀H₁₃Cl₂NOS) [M+H]⁺: 386.0173; found: 386.0176; **IR (ATR) (ν cm⁻¹)**: 2981, 2946, 2890, 1753, 1606, 1516, 1470, 1349, 1271, 1207, 1164, 1076, 998, 872, 753.

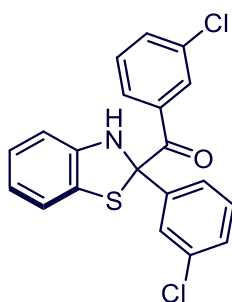
(4-(Trifluoromethyl)phenyl)(2-(4-(trifluoromethyl)phenyl)-2,3-dihydrobenzo[*d*]thiazol-2-yl)methanone (1f')



Following **GP 1**, 2-aminobenzenethiol (250 mg, 2.4 mmol, 1.2 equiv.) and 1,2-bis(4-(trifluoromethyl)phenyl)ethane-1,2-dione (**S6**, 692 mg, 2 mmol, 1 equiv.) afforded the compound **1f'** as an orange yellow solid (670 mg, 1.48 mmol, 74%).

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.80 (d, *J* = 8.0 Hz, 2H), 7.77 (t, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 7.9 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.11-7.09 (m, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 7.9 Hz, 2H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 193.0, 144.6, 144.3, 135.7, 134.8 (q, *J* = 33.1), 131.4 (q, *J* = 32.9 Hz), 130.6, 128.0, 127.5, 126.8, 126.6 (q, *J* = 7.3, 3.6 Hz), 125.7 (q, *J* = 3.6 Hz), 125.3, 123.8 (q, *J* = 272.7 Hz), 123.5 (q, *J* = 273.2 Hz), 122.1, 121.6, 83.8; **¹⁹F NMR (471 MHz, CDCl₃)** δ (ppm) = -62.76, -63.37; **HRMS (ESI-TOF)**: *m/z* calc. for (C₂₂H₁₄F₆NOS) [M+H]⁺: 454.0700; found: 454.0679; **IR (ATR) (ν cm⁻¹)**: 3382, 3019, 2970, 1802, 1694, 1516, 1477, 1334, 1178, 1139, 1075, 869, 752.

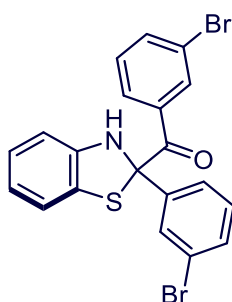
(3-Chlorophenyl)(2-(3-chlorophenyl)-2,3-dihydrobenzo[d]thiazol-2-yl)methanone (**1g'**)



Following **GP 1**, 2-aminobenzenethiol (250 mg, 2.4 mmol, 1.2 equiv.) and 1,2-bis(3-chlorophenyl)ethane-1,2-dione (**S7**, 558 mg, 2 mmol, 1 equiv.) afforded the compound **1g'** as yellow solid (602 mg, 1.56 mmol, 78%).

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.81 (s, 1H), 7.72 (s, 1H), 7.47-7.42 (m, 4H), 7.32 (d, *J* = 7.2 Hz, 1H), 7.25 (d, *J* = 10.5 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.81 (dd, *J* = 17.9, 7.9 Hz, 2H), 5.64 (s, 1H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 192.9, 144.7, 142.6, 135.6, 135.1, 134.5, 133.5, 130.7, 130.3, 129.7, 129.4, 128.4, 127.3, 126.6, 125.4, 125.0, 121.8, 121.5, 112.3, 83.7; **HRMS (ESI-TOF)**: *m/z* calc. for (C₂₀H₁₄Cl₂NOS) [M+H]⁺: 386.0173; found: 386.0182; **IR (ATR) (ν cm⁻¹)**: 3365, 3328, 3290, 3018, 2954, 2622, 2418, 2154, 1692, 1479, 1265, 799, 744, 661, 539, 515.

(3-Bromophenyl)(2-(3-bromophenyl)-2,3-dihydrobenzo[d]thiazol-2-yl)methanone (**1h'**)



Following **GP 1**, 2-aminobenzenethiol (250 mg, 2.4 mmol, 1.2 equiv.) and 1,2-bis(3-bromophenyl)ethane-1,2-dione (**S8**, 736 mg, 2 mmol, 1 equiv.) afforded the compound **1h'** as yellow solid (732 mg, 1.54 mmol, 77%).

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.91 (s, 1H), 7.80 (s, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.39 (dd, *J* = 15.7, 7.8 Hz, 3H), 7.16 (t, *J* = 7.7 Hz, 1H), 7.10 (t, *J* = 7.9 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.72 (dd, *J* = 19.0, 7.7 Hz, 2H), 5.57 (s, 1H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 192.8, 144.6, 142.8, 136.3, 134.6, 133.2, 132.3, 130.9, 130.1, 129.9, 128.8, 126.6, 125.5, 125.3, 123.7, 123.1, 121.8, 121.5, 112.3, 83.6; **HRMS (ESI-TOF)**: *m/z* calc. for (C₂₀H₁₄Br₂NOS) [M+H]⁺: 475.9143; found: 475.9171; **IR (ATR) (ν cm⁻¹)**: 3352, 3330, 3077, 2939, 2620, 1958, 1881, 1691, 1593, 1573, 1476, 1234, 1080, 746, 703.

1.2 Synthesis of disulfides and diselenides:

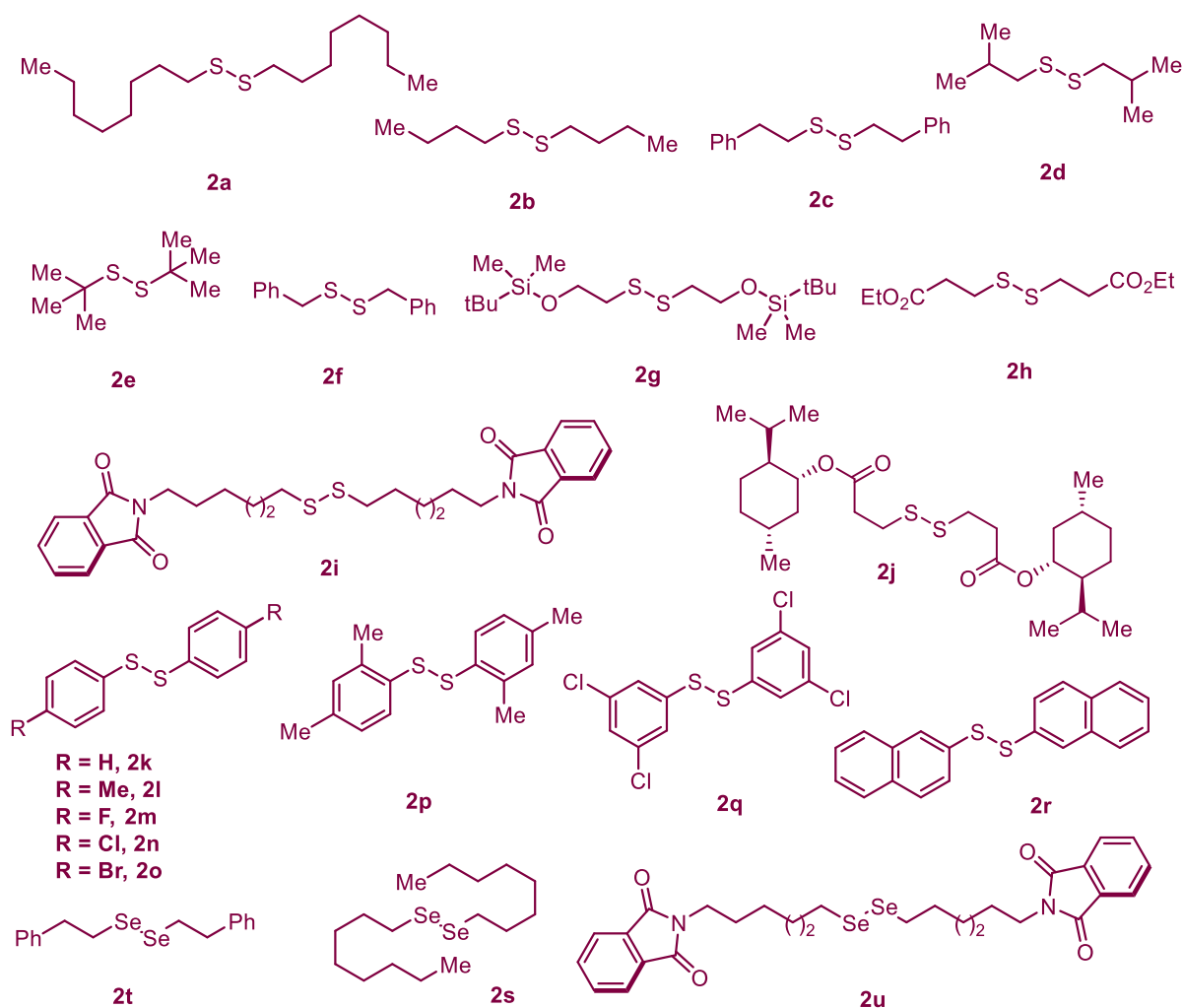
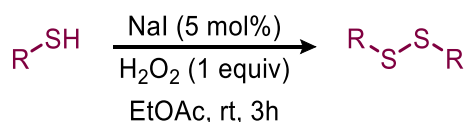


Figure S2: List of disulfides and diselenides.

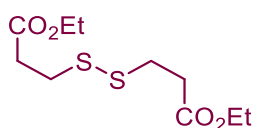
The disulfides **2a-2f** were prepared following the reported literature.⁴ The disulfides **2k-2r** were prepared following the reported literature.⁵ The diselenides **2p-2r** were prepared following the reported literature.⁶

General procedure for the synthesis of disulfides from aliphatic thiols (GP2)



Following a reported protocol by Mastalerz,¹ aliphatic thiol (1 equiv.) was taken to a round bottom flask containing a magnetic stirring bar. To reaction mixture NaI (5 mol%), H₂O₂ (1 equiv.) and ethyl acetate (1 M) was added in room temperature and stirred for 3 h in air atmosphere. The mixture was washed with water and extracted using ethyl acetate. The collected organic layer was dried over Na₂SO₄ and concentrated under reduced pressure to afford pure disulfide product.

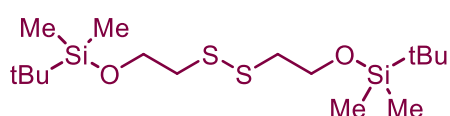
Diethyl 3,3'-disulfanediyldipropionate (2a)



Following **GP 2**, 2-((*tert*-butyldimethylsilyl)oxy)ethane-1-thiol (961 mg, 5 mmol, 1 equiv.) afforded the compound **2a** as a colorless oil (957 mg, 2.5 mmol, quantitative yield).

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 4.14 (q, *J* = 6.7 Hz, 4H), 2.91 (t, *J* = 6.8 Hz, 4H), 2.71 (t, *J* = 6.8 Hz, 4H), 1.25 (t, *J* = 6.8 Hz, 6H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 171.8, 60.9, 34.2, 33.3, 14.3; **HRMS (ESI-TOF)**: *m/z* calc. for (C₁₀H₁₈O₄S₂Na) [M+Na]⁺: 289.0544; found: 289.0534; **IR (ATR) (ν cm⁻¹)**: 2997, 2946, 1737, 1378, 1351, 1242, 1182, 1142, 1038, 932, 952, 787, 568.

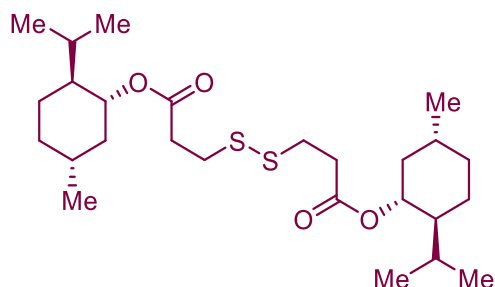
2,2,3,3,12,12,13,13-Octamethyl-4,11-dioxa-7,8-dithia-3,12-disilatetradecane (2g)



Following **GP 2**, 2-((*tert*-butyldimethylsilyl)oxy)ethane-1-thiol (961 mg, 5 mmol, 1 equiv.) afforded the compound **2g** as a colorless oil (957 mg, 2.5 mmol, quantitative yield).

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 3.85 (t, *J* = 6.8 Hz, 4H), 2.81 (t, *J* = 6.8 Hz, 4H), 0.89 (s, 18H), 0.07 (s, 12H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 62.1, 41.6, 26.0, 18.5, -5.1; **HRMS (ESI-TOF)**: *m/z* calc. for (C₁₆H₃₈O₂S₂Si₂Na) [M+Na]⁺: 405.1750; found: 405.1749; **IR (ATR) (ν cm⁻¹)**: 2969, 2946, 2901, 2872, 1475, 1260, 1094, 944, 837, 777, 670, 599.

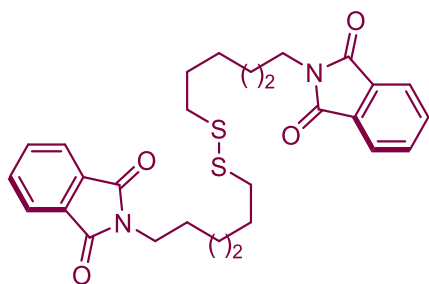
Bis((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl) 3,3'-disulfanediyldipropionate (2i)



Following **GP 2**, (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl-3-mercaptopropanoate (1.22 g, 5 mmol, 1 equiv.) afforded the compound **2i** as a colorless oil (1.22 g, 2.5 mmol, quantitative yield).

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 4.70 (td, *J* = 10.8, 4.1 Hz, 2H), 2.92 (t, *J* = 7.1 Hz, 4H), 2.70 (t, *J* = 7.1 Hz, 4H), 1.98 (d, *J* = 11.7 Hz, 2H), 1.89-1.85 (m, 4H), 1.67 (d, *J* = 11.3 Hz, 4H), 1.48-1.47 (m, 2H), 1.37 (t, *J* = 11.4, 2H), 1.08-0.93 (m, 6H), 0.89 (t, *J* = 5.5 Hz, 6H), 0.75 (d, *J* = 6.9 Hz, 6H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 171.4, 74.9, 47.1, 41.0, 34.6, 34.4, 33.5, 31.5, 26.4, 23.5, 22.1, 20.9, 16.4; **HRMS (ESI-TOF)**: *m/z* calc. for (C₂₆H₄₆O₄S₂Na) [M+Na]⁺: 509.2735; found: 509.2721; **IR (ATR) (ν cm⁻¹)**: 2968, 2938, 2883, 2738, 1730, 1662, 1532, 1350, 1217, 1150, 969, 886, 564.

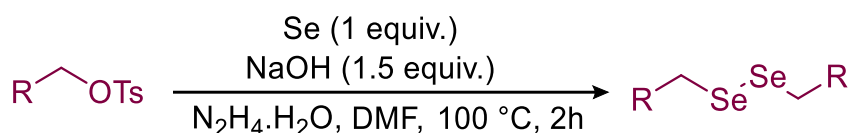
2,2'-(Disulfanediy)bis(pentane-5,1-diyl)bis(isoindoline-1,3-dione) (2j)



Following **GP 2**, 2-(5-mercaptopentyl)isoindoline-1,3-dione (1.25 g, 5 mmol, 1 equiv.) afforded the compound **2j** as a colorless oil (1.25 g, 2.5 mmol, quantitative yield).

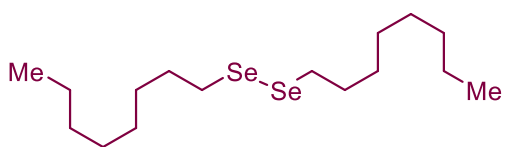
¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.80-7.75 (m, 4H), 7.69-7.66 (m, 4H), 3.60 (t, *J* = 7.1 Hz, 4H), 2.58 (t, *J* = 7.2 Hz, 4H), 1.64-1.56 (m, 8H), 1.39-1.26 (m, 8H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 168.3, 133.8, 132.1, 123.1, 38.8, 37.8, 29.0, 28.4, 28.0, 26.4; **HRMS (ESI-TOF)**: *m/z* calc. for (C₂₈H₃₂N₂O₄S₂Na) [M+H]⁺: 547.1701; found: 547.1721; **IR (ATR) (ν cm⁻¹)**: 3073, 2948, 2871, 2707, 1747, 1401, 1370, 1049, 740, 624, 532.

General procedure for the synthesis of diselenides from alkyl tosylates (GP4)



In a round bottom flask equipped with a Teflon-coated stirring bar, selenium (10 mmol), NaOH (15 mmol) in DMF (10.0 mL) and aq. N₂H₄ (0.3 mL) were taken under argon atmosphere. The mixture was heated at 100 °C for 15 min. After cooling to room temperature, tosylates (10 mmol) were added dropwise to the solution. The resulting solution was heated at 100 °C for 2 h and the reaction was monitored by checking TLC. After the completion of the reaction, it was quenched by adding water and extracted with ethyl acetate (3×20 mL). The combined organic phase was washed with water followed by brine solution, dried over Na₂SO₄, and concentrated under reduced pressure to afford the product that was used directly.

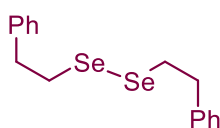
1,2-Dioctylidiselane (2s)



Following **GP 3**, octyl 4-methylbenzenesulfonate (1.42 g, 5 mmol, 1 equiv.) and selenium powder (395 mg, 5 mmol, 1 equiv.) afforded the compound **2s** as a yellow liquid (931 mg, 2.43 mmol, 97%).

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 2.81 (t, *J* = 7.4 Hz, 4H), 1.75-1.69 (m, 4H), 1.38 (m, 4H), 1.28 (m, 16H), 0.88 (t, *J* = 6.2 Hz, 6H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 32.0, 31.1, 30.4, 29.7, 29.3, 29.2, 22.8, 14.2; **HRMS (ESI-TOF)**: *m/z* calc. for (C₁₆H₃₅Se₂) [M+H]⁺: 387.1072; found: 387.1085; **IR (ATR) (ν cm⁻¹)**: 3097, 3074, 3040, 2939, 1509, 1501, 1458, 1254, 1186, 749, 600, 541, 539, 515.

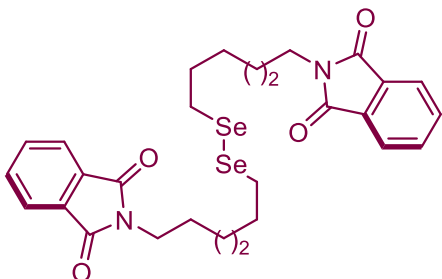
1,2-Diphenethylidiselane (2t)



Following **GP 3**, phenethyl 4-methylbenzenesulfonate (1.38 g, 5 mmol, 1 equiv.) and selenium powder (395 mg, 5 mmol, 1 equiv.) afforded the compound **2t** as a yellow liquid (874 mg, 2.38 mmol, 95%).

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.26 (t, *J* = 7.1 Hz, 4H), 7.17 (t, *J* = 10.2 Hz, 6H), 3.11 (t, *J* = 7.6 Hz, 4H), 3.01 (t, *J* = 7.6 Hz, 4H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 140.9, 128.6, 128.6, 126.5, 37.6, 30.8; **HRMS (ESI-TOF)**: *m/z* calc. for (C₁₆H₁₉Se₂) [M+H]⁺: 370.9820; found: 370.9833; **IR (ATR) (ν cm⁻¹)**: 2970, 2936, 2866, 2776, 2448, 2177, 1801, 1749, 1680, 1468, 1261, 1184, 724, 518.

2,2'-(Diselanediy)bis(pentane-5,1-diyl))bis(isoindoline-1,3-dione) (2u)



Following **GP 3**, 5-(1,3-dioxoisoindolin-2-yl)pentyl 4-methylbenzenesulfonate (1.94 g, 5 mmol, 1 equiv.) and selenium powder (395 mg, 5 mmol, 1 equiv.) afforded the compound **2u** as a yellow liquid (1.34 mg, 2.27 mmol, 91%).

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.74 (m, 4H), 7.63 (m, 4H), 2.80-2.77 (m, 4H), 1.64-1.60 (m, 8H), 1.38-1.28 (m, 8H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 168.3, 133.8, 132.0, 123.0, 37.8, 30.7, 29.8, 28.9, 28.4, 26.2; **HRMS (ESI-TOF)**: *m/z* calc. for (C₂₈H₃₃N₂O₄Se₂) [M+H]⁺: 621.0776; found: 621.0797; **IR (ATR) (ν cm⁻¹)**: 3379, 3351, 2948, 2872, 1718, 1506, 1467, 1397, 1262, 1099, 1068, 755, 724, 664, 625, 536, 516.

2. Optimization Studies

Optimization for the thioester synthesis from dihydroquinazolinone and disulfide.

In an oven-dried Schlenk tube containing a stirring bar, 4CzIPN (0.8 mg, 1 mol%), dihydroquinazolinone **1a** (33 mg, 0.1 mmol, 1 equiv.) and disulfide **2a** (67 mg, 0.25 mmol, 2.5 equiv.) was dissolved in DMF (1 mL, 0.1 M) under argon atmosphere. The reaction mixture was stirred at room temperature under light irradiation from blue LEDs for 12 h. Once the reaction was completed, the reaction mixture was extracted with ethyl acetate (3×5 mL) and the combined organic layers washed with brine three times. The organic phase was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography through silica gel (eluent: PE/EA = 98:2) to obtain the thioester **3aa**.

Table S1: Photocatalyzed thioesterification of dihydroquinazolinone with disulfide

| Entry | Variation from standard conditions | Yield(%) of 3aa ^b |
|-------|---|-------------------------------------|
| 1 | None | 96 |
| 2 | RB, instead of 4CzIPN | 57 |
| 3 | Eosin Y, instead of 4CzIPN | 81 |
| 4 | DMSO, instead of DMF | 71 |
| 5 | 1,2-DME instead of DMF | 54 |
| 6 | CH ₂ Cl ₂ , instead of DMF | 59 |
| 7 | 2a (2.0 equiv.), instead of 2a (2.5 equiv.) | 83 |
| 8 | 2a (1.5 equiv.), instead of 2a (2.5 equiv.) | 67 |
| 9 | 4CzIPN (2 mol%), instead of 4CzIPN (1 mol%) | 78 |
| 10 | Purple LEDs instead of Blue LEDs | 83 |
| 11 | w/o 4CzIPN | 0 |
| 12 | w/o light | 0 |

4CzIPN
Eosin Y: X = Br, Z = H
RB: X = I, Z = Cl

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.25 mmol), 4CzIPN (1 mol%), DMF (1 mL) at rt for 12 h, blue LEDs. ^bIsolated yield of **3aa**. DMF = *N,N*-dimethylformamide; DMSO = dimethylsulfoxide; 1,2-DME = 1,2-

dimethoxyethane. 4CzIPN = 2,4,5,6-Tetrakis(9H-carbazol-9-yl)isophthalonitrile; RB = Rose Bengal.

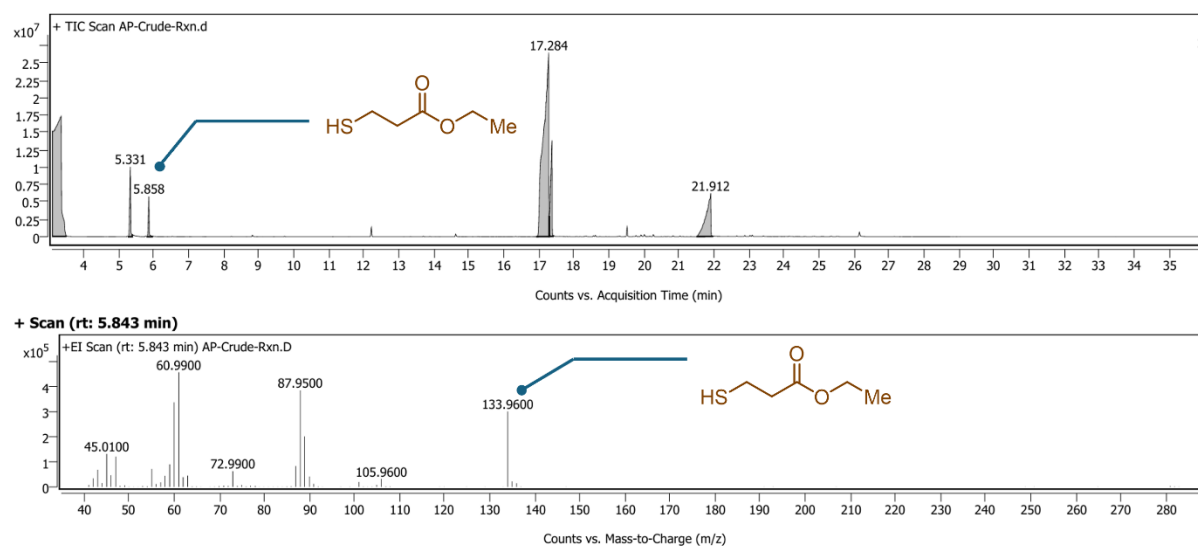


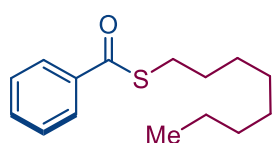
Figure S3: Detection of ethyl 3-mercaptopropanoate from crude reaction mixture by GC-MS analysis.

3. Synthesis and Characterization of Products

General procedure for thio(seleno)esterification from dihydroquinazolinones/benzothiazolines and disulfides/diselenides (GP5)

In an oven-dried Schlenk tube containing a stirring bar, 4CzIPN (1.6 mg, 1 mol%), dihydroquinazolinones/benzothiazolines **1** (0.2 mmol, 1 equiv.) and disulfide/diselenide **2** (0.5 mmol, 2.5 equiv.) was dissolved in DMF (2 mL, 0.1 M) under argon atmosphere. The reaction mixture was stirred at room temperature under light irradiation from blue LEDs for 12 h. Once the reaction was completed, the reaction mixture was extracted with ethyl acetate (3×10 mL). The combined organic layers were washed with brine three times, dried over Na₂SO₄ and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography through silica gel (eluent: petroleum ether /ethyl acetate) to obtain the thioester/selenoester **3**.

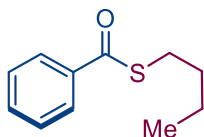
S-Octyl benzothioate (3aa)



Following **GP 5**, 2-benzoyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (**1a**, 66 mg, 0.2 mmol, 1 equiv.) and 1,2-dioctyldisulfane (**2a**, 145 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3aa** as a colorless oil (46 mg, 0.184 mmol, 92%). (eluent: petroleum ether /ethyl acetate = 200:1)

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.97 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 3.07 (t, *J* = 7.3 Hz, 2H), 1.70-1.64 (m, 2H), 1.44-1.40 (m, 2H), 1.32-1.26 (m, 8H), 0.88 (t, *J* = 6.3 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ (ppm) = 192.3, 137.5, 133.3, 128.7, 127.3, 32.0, 29.7, 29.3, 29.3, 29.2, 29.1, 22.8, 14.2. The spectroscopic data obtained were in agreement with the reported data for the compound **3aa**.⁷

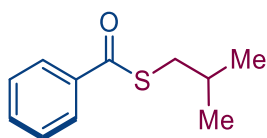
S-Butyl benzothioate (3ab)



Following **GP 5**, 2-benzoyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (**1a**, 66 mg, 0.2 mmol, 1 equiv.) and 1,2-dibutyl disulfane (**2b**, 89 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3ab** as a colorless oil (34 mg, 0.174 mmol, 87%). (eluent: petroleum ether /ethyl acetate = 200:1)

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.97 (d, *J* = 7.3 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 3.08 (t, *J* = 7.3 Hz, 2H), 1.69-1.63 (m, 2H), 1.50-1.42 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 192.3, 137.4, 133.3, 128.7, 127.3, 31.8, 28.9, 22.2, 13.8. The spectroscopic data obtained were in agreement with the reported data for the compound **3ab**.⁸

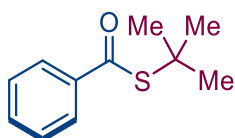
S-Isobutyl benzothioate (**3ac**)



Following **GP 5**, 2-benzoyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (**1a**, 66 mg, 0.2 mmol, 1 equiv.) and 1,2-diisobutyl disulfane (**2c**, 89 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3ac** as a colorless oil (35 mg, 0.182 mmol, 91%). (eluent: petroleum ether /ethyl acetate = 200:1)

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.99 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 3.00 (d, *J* = 6.7 Hz, 2H), 1.96-1.88 (m, 1H), 1.03 (t, *J* = 6.7 Hz, 6H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 192.2, 137.5, 133.3, 128.7, 127.4, 37.5, 29.0, 22.0. The spectroscopic data obtained were in agreement with the reported data for the compound **3ac**.⁹

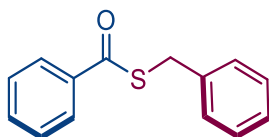
1,2-Di-tert-butyl disulfane (**3ad**)



Following **GP 5**, 2-benzoyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (**1a**, 66 mg, 0.2 mmol, 1 equiv.) and 1,2-di-tert-butyl disulfane (**2d**, 89 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3ad** as a colorless oil (33 mg, 0.168 mmol, 84%). (eluent: petroleum ether /ethyl acetate = 200:1)

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.92 (d, *J* = 7.7 Hz, 2H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 1.58 (s, 9H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 193.0, 138.4, 133.0, 128.6, 127.1, 48.3, 30.1. The spectroscopic data obtained were in agreement with the reported data for the compound **3ad**.¹⁰

S-Octyl benzothioate (**3ae**)

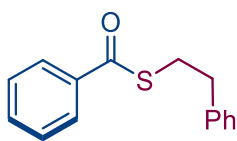


Following **GP 5**, 2-benzoyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (**1a**, 66 mg, 0.2 mmol, 1 equiv.) and 1,2-dibenzyl disulfane (**2e**, 123 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3ae** as a colorless oil (31 mg, 0.134 mmol, 67%). (eluent: petroleum ether /ethyl acetate = 200:1)

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.96 (d, *J* = 7.4 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.1 Hz, 2H), 7.43 (d, *J* = 7.5 Hz, 2H), 4.32 (s, 2H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 191.5, 137.6, 136.9, 133.6, 129.1, 128.8, 128.8, 127.5, 127.4,

33.5. The spectroscopic data obtained were in agreement with the reported data for the compound **3ae**.⁹

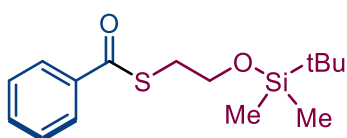
S-Phenethyl benzothioate (**3af**)



Following **GP 5**, 2-benzoyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (**1a**, 66 mg, 0.2 mmol, 1 equiv.) and 1,2-diphenylethyl disulfane (**2f**, 137 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3af** as a colorless oil (45 mg, 0.184 mmol, 92%). (eluent: petroleum ether /ethyl acetate = 200:1)

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.94 (d, *J* = 7.3 Hz, 2H), 7.53 (t, *J* = 7.0 Hz, 1H), 7.42 (t, *J* = 7.3 Hz, 2H), 7.31-7.20 (m, 5H), 3.29 (t, *J* = 7.4 Hz, 2H), 2.95 (t, *J* = 7.4 Hz, 2H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 191.9, 140.2, 137.3, 133.5, 128.8, 128.7, 128.7, 127.3, 126.7, 36.0, 30.6. The spectroscopic data obtained were in agreement with the reported data for the compound **3af**.⁹

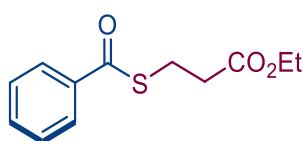
S-Octyl benzothioate (**3ag**)



Following **GP 5**, 2-benzoyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (**1a**, 66 mg, 0.2 mmol, 1 equiv.) and 2,2,3,3,12,12,13,13-octamethyl-4,11-dioxo-7,8-dithia-3,12-disilatetradecane (**2g**, 191 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3ag** as a colorless oil (50 mg, 0.168 mmol, 84%). (eluent: petroleum ether /ethyl acetate = 99:1)

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.97 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 3.82 (t, *J* = 6.4 Hz, 2H), 3.23 (t, *J* = 6.4 Hz, 2H), 0.90 (s, 9H), 0.08 (s, 6H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 192.0, 137.3, 133.5, 128.7, 127.4, 62.2, 31.9, 26.0, -5.1; **HRMS (ESI-TOF)**: *m/z* calc. for (C₁₅H₂₅O₂SSi) [M+H]⁺: 297.1345; found: 297.1335; **IR (ATR) (ν cm⁻¹)**: 3051, 2967, 2945, 2873, 2002, 1747, 1677, 1475, 1214, 11106, 919, 843, 781, 693, 602, 547, 516.

S-Octyl benzothioate (**3ah**)



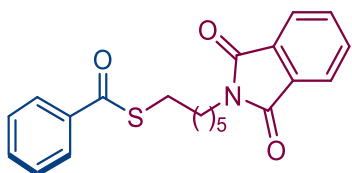
Following **GP 5**, 2-benzoyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (**1a**, 66 mg, 0.2 mmol, 1 equiv.) and diethyl 3,3'-disulfanediyldipropionate (**2h**, 133 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3ah** as a colorless oil (45 mg, 0.190 mmol, 95%). (eluent: petroleum ether /ethyl acetate = 98:2)

Following **GP 5**, phenyl(2-phenyl-2,3-dihydrobenzo[*d*]thiazol-2-yl)methanone (**1a'**, 64 mg, 0.2 mmol, 1 equiv.) and diethyl 3,3'-disulfanediyldipropionate (**2h**, 133 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3ah** as a colorless oil (42 mg, 0.170 mmol, 85%). (eluent: petroleum ether /ethyl acetate = 98:2)

Following **GP 5**, 2-benzoyl-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (**1l**, 54 mg, 0.2 mmol, 1 equiv.) and diethyl 3,3'-disulfanediyldipropionate (**2h**, 133 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3ah** as a colorless oil (44 mg, 0.186 mmol, 93%). (eluent: petroleum ether /ethyl acetate = 98:2)

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.95 (d, *J* = 7.4 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.32 (t, *J* = 7.0 Hz, 2H), 2.72 (t, *J* = 7.0 Hz, 2H), 1.28-1.25 (m, 3H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 191.7, 171.9, 137.0, 133.6, 128.8, 127.4, 60.9, 34.7, 24.2, 14.3; **HRMS (ESI-TOF)**: *m/z* calc. for (C₁₂H₁₄O₃SNa) [M+Na]⁺: 261.0561; found: 261.0552; **IR (ATR) (ν cm⁻¹)**: 2969, 2940, 1741, 1671, 1590, 1456, 1424, 1380, 1352, 1305, 1251, 1211, 1182, 1026, 914, 778, 693, 662.

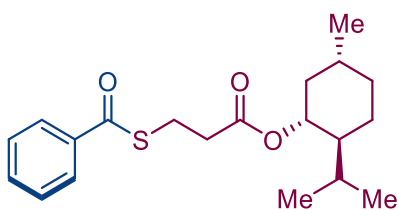
S-(6-(1,3-Dioxoisindolin-2-yl)hexyl) benzothioate (3ai)



Following **GP 5**, 2-benzoyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (**1a**, 66 mg, 0.2 mmol, 1 equiv.) and 2,2'-(disulfaneylbis(hexane-6,1-diyl))bis(isoindoline-1,3-dione) (**2i**, 262 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3ai** as a white solid (67 mg, 0.182 mmol, 91%). (eluent: petroleum ether /ethyl acetate = 95:5)

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.93 (d, *J* = 7.6 Hz, 2H), 7.82-7.81 (m, 2H), 7.69-7.67 (m, 2H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 3.67 (t, *J* = 7.1 Hz, 2H), 3.04 (t, *J* = 7.2 Hz, 2H), 1.71-1.63 (m, 4H), 1.49-1.43 (m, 2H), 1.40-1.36 (m, 2H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 192.1, 168.5, 137.3, 133.9, 133.3, 132.2, 128.6, 127.3, 123.2, 38.0, 29.5, 29.0, 28.6, 28.5, 26.5; **HRMS (ESI-TOF)**: *m/z* calc. for (C₂₁H₂₁NO₃SNa) [M+Na]⁺: 390.1140; found: 390.1146; **IR (ATR) (ν cm⁻¹)**: 3073, 2950, 2673, 1780, 1719, 1669, 1448, 1404, 1213, 1182, 1053, 918, 724, 695, 652, 605, 538.

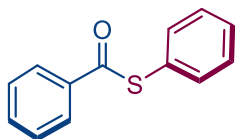
(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 3-(benzoylthio)propanoate (3aj)



Following **GP 5**, 2-benzoyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (**1a**, 66 mg, 0.2 mmol, 1 equiv.) and (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 3-(((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl)oxy)-3-oxopropyl)disulfaneyl)propanoate (**2j**, 243 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3aj** as a colorless liquid (62 mg, 0.178 mmol, 89%). (eluent: petroleum ether /ethyl acetate = 97:3)

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.95 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 4.72 (td, *J* = 10.9, 4.1 Hz, 1H), 3.32 (t, *J* = 6.9 Hz, 2H), 2.71 (t, *J* = 6.9 Hz, 2H), 1.99 (d, *J* = 11.9 Hz, 1H), 1.87-1.85 (m, 1H), 1.68-1.65 (m, 3H), 1.48-1.47 (m, 1H), 1.36 (t, *J* = 11.6 Hz, 1H), 1.08-0.94 (m, 2H), 0.89 (d, *J* = 6.4 Hz, 3H), 0.86 (d, *J* = 7.0 Hz, 3H), 0.75 (d, *J* = 6.9 Hz, 3H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 191.7, 171.4, 137.1, 133.6, 128.8, 127.4, 74.9, 47.1, 41.0, 34.9, 34.4, 31.5, 26.4, 24.4, 23.6, 22.1, 20.9, 16.5; **HRMS (ESI-TOF)**: *m/z* calc. for (C₂₀H₂₈O₃SNa) [M+Na]⁺: 371.1657; found: 371.1643; **IR (ATR) (ν cm⁻¹)**: 2968, 1739, 1675, 1458, 1375, 1253, 1212, 1182, 918, 806, 693, 652.

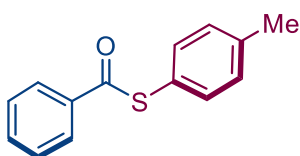
S-Phenyl benzothioate (3ak)



Following **GP 5**, 2-benzoyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (**1a**, 66 mg, 0.2 mmol, 1 equiv.) and 1,2-diphenyldisulfane (**2k**, 109 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3ak** as a colorless liquid (40 mg, 0.186 mmol, 93%). (eluent: petroleum ether /ethyl acetate = 200:1)

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 8.03 (d, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.52-7.46 (m, 7H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 190.3, 136.8, 135.3, 133.8, 129.7, 129.4, 128.9, 127.6, 127.5. The spectroscopic data obtained were in agreement with the reported data for the compound **3ak**.¹⁰

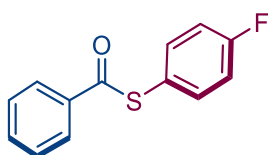
S-(*p*-Tolyl) benzothioate (**3al**)



Following **GP 5**, 2-benzoyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (**1a**, 66 mg, 0.2 mmol, 1 equiv.) and 1,2-di-*p*-tolylidysulfane (**2l**, 123 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3al** as a colourless liquid (44 mg, 0.192 mmol, 96%). (eluent: petroleum ether /ethyl acetate = 200:1)

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 8.02 (d, *J* = 7.7 Hz, 2H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 7.7 Hz, 2H), 2.40 (s, 3H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 190.7, 140.0, 136.9, 135.2, 133.7, 130.3, 128.9, 127.6, 123.9, 21.5. The spectroscopic data obtained were in agreement with the reported data for the compound **3al**.¹⁰

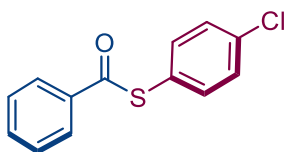
S-(4-fluorophenyl) benzothioate (**3am**)



Following **GP 5**, 2-benzoyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (**1a**, 66 mg, 0.2 mmol, 1 equiv.) and 1,2-bis(4-fluorophenyl)disulfane (**2m**, 127 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3am** as a colourless liquid (37 mg, 0.158 mmol, 79%). (eluent: petroleum ether /ethyl acetate = 200:1)

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 8.02 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.51-7.48 (m, 4H), 7.16 (t, *J* = 8.5 Hz, 2H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 190.3, 164.8 (d, *J* = 250.1 Hz), 137.3 (d, *J* = 8.6 Hz), 136.6, 133.9, 129.0, 127.6, 122.8 (d, *J* = 3.4 Hz), 116.8 (d, *J* = 22.8 Hz); **¹⁹F NMR (471 MHz, CDCl₃)** δ (ppm) = -111.06. The spectroscopic data obtained were in agreement with the reported data for the compound **3am**.¹⁰

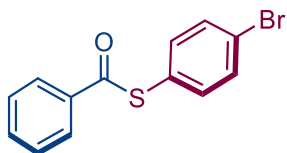
S-(4-Chlorophenyl) benzothioate (**3an**)



Following **GP 5**, 2-benzoyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (**1a**, 66 mg, 0.2 mmol, 1 equiv.) and 1,2-bis(4-chlorophenyl)disulfane (**2n**, 144 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3an** as a colorless liquid (41 mg, 0.166 mmol, 83%). (eluent: petroleum ether /ethyl acetate = 200:1)

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm) = 7.99 (d, J = 7.4 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.46 (d, J = 7.6 Hz, 2H), 7.43-7.41 (m, 4H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ (ppm) = 189.7, 136.5, 136.4, 136.1, 134.0, 129.6, 128.9, 127.6, 126.0. The spectroscopic data obtained were in agreement with the reported data for the compound **3an**.¹⁰

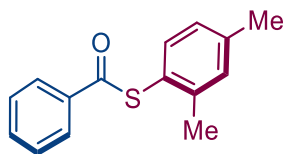
S-(4-bromophenyl) benzothioate (**3ao**)



Following **GP 5**, 2-benzoyl-2-phenyl-2,3-dihydroquinazolin-4(1H)-one (**1a**, 66 mg, 0.2 mmol, 1 equiv.) and 1,2-bis(4-bromophenyl)disulfane (**2o**, 188 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3ao** as a colourless liquid (51 mg, 0.172 mmol, 86%). (eluent: petroleum ether /ethyl acetate = 200:1)

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm) = 7.92 (d, J = 7.8 Hz, 2H), 7.51-7.46 (m, 3H), 7.37 (t, J = 7.5 Hz, 2H), 7.27 (d, J = 7.9 Hz, 2H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ (ppm) = 189.2, 136.5, 136.3, 133.9, 132.4, 128.8, 127.5, 126.5, 124.2. The spectroscopic data obtained were in agreement with the reported data for the compound **3ao**.¹⁰

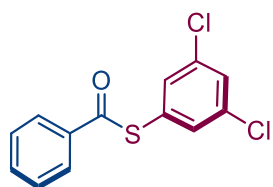
S-(2,4-Dimethylphenyl) benzothioate (**3ap**)



Following **GP 5**, 2-benzoyl-2-phenyl-2,3-dihydroquinazolin-4(1H)-one (**1a**, 66 mg, 0.2 mmol, 1 equiv.) and 1,2-bis(2,4-dimethylphenyl)disulfane (**2p**, 127 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3ap** as a colourless liquid (42 mg, 0.158 mmol, 87%). (eluent: petroleum ether /ethyl acetate = 200:1)

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm) = 8.01 (d, J = 7.4 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.32 (d, J = 7.8 Hz, 1H), 7.14 (s, 1H), 7.03 (d, J = 7.7 Hz, 1H), 2.32 (s, 6H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ (ppm) = 190.1, 142.4, 140.5, 136.9, 136.3, 133.6, 131.8, 128.8, 127.6, 127.6, 123.4, 21.4, 20.8; **HRMS (ESI-TOF)**: m/z calc. for ($\text{C}_{15}\text{H}_{15}\text{OS}$) [$\text{M}+\text{H}$] $^+$: 243.0844; found: 243.0849; **IR (ATR)** (ν cm^{-1}): 2935, 1681, 1454, 1208, 1180, 890, 815, 774, 685, 645, 621.

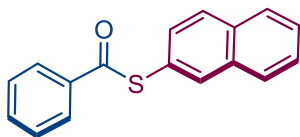
S-(3,5-Dichlorophenyl) benzothioate (**3aq**)



Following **GP 5**, 2-benzoyl-2-phenyl-2,3-dihydroquinazolin-4(1H)-one (**1a**, 66 mg, 0.2 mmol, 1 equiv.) and 1,2-bis(3,5-dichlorophenyl)disulfane (**2q**, 178 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3aq** as a white solid (42 mg, 0.148 mmol, 74%). (eluent: petroleum ether /ethyl acetate = 200:1)

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ (ppm) = 8.00 (d, J = 7.5 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.4 Hz, 2H), 7.44 (s, 1H), 7.43 (s, 2H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ (ppm) = 188.7, 136.2, 135.4, 134.3, 133.2, 130.6, 129.9, 129.1, 127.7; **HRMS (ESI-TOF)**: m/z calc. for ($\text{C}_{13}\text{H}_9\text{Cl}_2\text{OS}$) [$\text{M}+\text{H}$] $^+$: 284.9723; found: 284.9707; **IR (ATR)** (ν cm^{-1}): 2967, 2934, 1693, 1546, 1454, 1413, 1181, 1103, 902, 859, 804, 686.

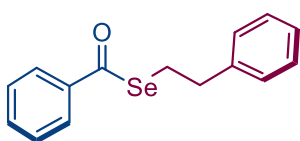
S-(4-Fluorophenyl) benzothioate (**3ar**)



Following **GP 5**, 2-benzoyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (**1a**, 66 mg, 0.2 mmol, 1 equiv.) and 1,2-di(naphthalen-2-yl)disulfane (**2r**, 159 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3ar** as a white solid (41 mg, 0.154 mmol, 77%). (eluent: petroleum ether /ethyl acetate = 200:1)

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 8.09-8.07 (m, 3H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.88 (dd, *J* = 14.0, 7.7 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.58-7.50 (m, 5H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 190.5, 136.8, 135.1, 133.8, 133.8, 133.6, 131.5, 129.0, 128.9, 128.1, 128.0, 127.7, 127.3, 126.7, 124.8. The spectroscopic data obtained were in agreement with the reported data for the compound **3ar**.¹⁰

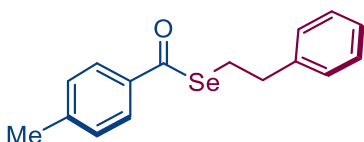
Se-Phenethyl benzoselenoate (**3as**)



Following **GP 5**, 2-benzoyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (**1a**, 66 mg, 0.2 mmol, 1 equiv.) and 1,2-diphenethyl)diselane (**2s**, 184 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3as** as an orange yellow liquid (42 mg, 0.144 mmol, 72%). (eluent: petroleum ether /ethyl acetate = 200:1)

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.83 (d, *J* = 7.5 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 2H), 7.26-7.15 (m, 5H), 3.26 (t, *J* = 7.7 Hz, 2H), 2.99 (t, *J* = 7.7 Hz, 2H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 194.9, 141.2, 139.3, 133.7, 128.9, 128.7, 128.7, 127.3, 126.6, 37.0, 26.8; **HRMS (ESI-TOF)**: *m/z* calc. for (C₁₅H₁₄OSe) [M]⁺: 290.0210; found: 290.0219; **IR (ATR) (ν cm⁻¹)**: 2939, 1681, 1456, 1267, 1208, 1099, 1024, 899, 802, 701, 679, 627.

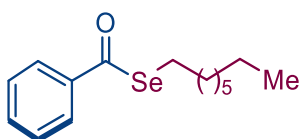
Se-Phenethyl 4-methylbenzoselenoate (**3bs**)



Following **GP 5**, 2-(4-methylbenzoyl)-2-(*p*-tolyl)-2,3-dihydroquinazolin-4(1*H*)-one (**1b**, 72 mg, 0.2 mmol, 1 equiv.) and 1,2-diphenethyl)diselane (**2s**, 184 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3bs** as an orange yellow liquid (45 mg, 0.148 mmol, 74%). (eluent: petroleum ether /ethyl acetate = 200:1)

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.73 (d, *J* = 7.8 Hz, 2H), 7.26-7.19 (m, 4H), 7.17-7.14 (m, 3H), 3.24 (t, *J* = 7.7 Hz, 2H), 2.98 (t, *J* = 7.6 Hz, 2H), 2.32 (s, 3H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 194.2, 144.6, 141.2, 136.7, 129.5, 128.6, 128.5, 127.3, 126.5, 36.9, 26.5, 21.7; **HRMS (ESI-TOF)**: *m/z* calc. for (C₁₆H₁₆OSeNa) [M+Na]⁺: 327.0265; found: 327.0279; **IR (ATR) (ν cm⁻¹)**: 3043, 2938, 1689, 1668, 1612, 1503, 1459, 1208, 1177, 809, 822, 702, 621.

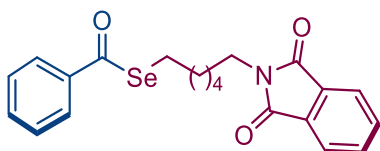
Se-Octyl benzoselenoate (**3at**)



Following **GP 5**, 2-benzoyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (**1a**, 66 mg, 0.2 mmol, 1 equiv.) and 1,2-dioctyl)diselane (**2t**, 192 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3at** as an orange yellow liquid (37 mg, 0.124 mmol, 62%). (eluent: petroleum ether /ethyl acetate = 200:1)

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.92 (t, *J* = 11.2 Hz, 2H), 7.58 (d, *J* = 7.1 Hz, 1H), 7.45 (d, *J* = 7.4 Hz, 2H), 3.10 (dd, *J* = 14.9, 7.7 Hz, 2H), 1.80-1.72 (m, 2H), 1.46-1.29 (m, 10H), 0.92-0.87 (m, 3H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 195.3, 139.4, 133.6, 128.9, 127.3, 32.0, 30.6, 30.2, 29.3, 29.3, 26.0, 22.8, 14.2; **HRMS (ESI-TOF):** *m/z* calc. for (C₁₅H₂₃OSe) [M+H]⁺: 299.0915; found: 299.0912; **IR (ATR) (ν cm⁻¹):** 2940, 2869, 2828, 2629, 2536, 2416, 2394, 2283, 2247, 1923, 1683, 1590, 1459, 1208, 1180, 892, 771, 680, 629, 604, 544, 515.

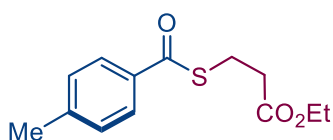
Se-Octyl benzoselenoate (3au)



Following **GP 5**, 2-benzoyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (**1a**, 66 mg, 0.2 mmol, 1 equiv.) and 2,2'-(diselanediy)bis(hexane-6,1-diyl)bis(isoindoline-1,3-dione) (**2u**, 192 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3au** as an orange yellow liquid (43 mg, 0.104 mmol, 52%). (eluent: petroleum ether /ethyl acetate = 95:5)

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.88 (d, *J* = 7.5 Hz, 2H), 7.85-7.82 (m, 2H), 7.71-7.69 (m, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 3.68 (t, *J* = 7.2 Hz, 2H), 3.07 (t, *J* = 7.2 Hz, 2H), 1.78-1.72 (m, 2H), 1.72-1.66 (m, 2H), 1.50-1.44 (m, 2H), 1.42-1.36 (m, 2H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 195.1, 168.6, 139.4, 134.0, 133.6, 132.3, 128.9, 127.3, 123.3, 38.1, 30.5, 29.7, 28.6, 26.5, 25.7; **HRMS (ESI-TOF):** *m/z* calc. for (C₂₁H₂₁NO₃Se) [M+Na]⁺: 416.0766; found: 416.0774; **IR (ATR) (ν cm⁻¹):** 3072, 3047, 2952, 2672, 1780, 1721, 1679, 1404, 1344, 1208, 1180, 1050, 892, 693, 680, 630, 537, 514.

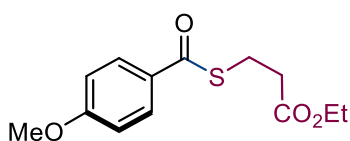
Ethyl 3-((4-methylbenzoyl)thio)propanoate (3bh)



Following **GP 5**, 2-(4-methylbenzoyl)-2-(*p*-tolyl)-2,3-dihydroquinazolin-4(1*H*)-one (**1b**, 72 mg, 0.2 mmol, 1 equiv.) and diethyl 3,3'-disulfanediyldipropionate (**2h**, 133 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3bh** as a colorless liquid (50 mg, 0.186 mmol, 93%). (eluent: petroleum ether /ethyl acetate = 97:3)

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.85 (d, *J* = 7.9 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.30 (t, *J* = 7.0 Hz, 2H), 2.72 (t, *J* = 7.0 Hz, 2H), 2.40 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 191.3, 171.9, 144.5, 134.5, 129.4, 127.5, 60.9, 34.7, 24.1, 21.8, 14.4; **HRMS (ESI-TOF):** *m/z* calc. for (C₁₃H₁₃F₃O₃SNa) [M+Na]⁺: 329.0435; found: 329.0449; **IR (ATR) (ν cm⁻¹):** 2969, 2942, 1745, 1669, 1616, 1214, 1182, 919, 828, 796, 651.

Ethyl 3-((4-methoxybenzoyl)thio)propanoate (3c'h)

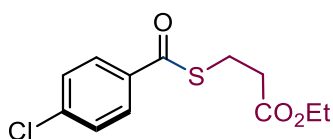


Following **GP 5**, (4-methoxyphenyl)(2-(4-methoxyphenyl)-2,3-dihydrobenzo[*d*]thiazol-2-yl)methanone (**1c'**, 76 mg, 0.2 mmol, 1 equiv.) and diethyl 3,3'-disulfanediyldipropionate (**2h**, 133 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3c'h** as a colorless liquid

(50 mg, 0.186 mmol, 93%). (eluent: petroleum ether /ethyl acetate = 97:3)

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.92 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 4.16 (q, *J* = 7.0 Hz, 2H), 3.85 (s, 3H), 3.29 (t, *J* = 6.9 Hz, 2H), 2.70 (t, *J* = 6.9 Hz, 2H), 1.26 (t, *J* = 7.0 Hz, 3H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 190.0, 171.9, 163.9, 129.7, 129.4, 113.8, 60.8, 55.5, 34.7, 23.9, 14.2; **HRMS (ESI-TOF)**: *m/z* calc. for (C₁₃H₁₆O₄SNa) [M+Na]⁺: 291.0667; found: 291.0662; **IR (ATR) (ν cm⁻¹)**: 2992, 2954, 2854, 1740, 1663, 1608, 1516, 1470, 1264, 1221, 1169, 1032, 916, 843, 649, 625.

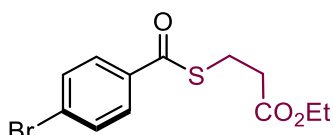
Ethyl 3-((4-chlorobenzoyl)thio)propanoate (3d'h)



Following **GP 5**, (4-chlorophenyl)(2-(4-chlorophenyl)-2,3-dihydrobenzo[*d*]thiazol-2-yl)methanone (**1d'**, 78 mg, 0.2 mmol, 1 equiv.) and diethyl 3,3'-disulfanediyldipropionate (**2h**, 133 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3d'h** as a colorless liquid (50 mg, 0.182 mmol, 91%). (eluent: petroleum ether /ethyl acetate = 97:3)

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.82 (d, *J* = 8.3 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.25 (t, *J* = 6.9 Hz, 2H), 2.65 (t, *J* = 6.9 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 3H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 190.5, 171.8, 140.0, 135.3, 129.1, 128.7, 61.0, 34.5, 24.3, 14.3; **HRMS (ESI-TOF)**: *m/z* calc. for (C₁₂H₁₃ClO₃SNa) [M+Na]⁺: 295.0172; found: 295.0177; **IR (ATR) (ν cm⁻¹)**: 2968, 2939, 1743, 1675, 1596, 1491, 1380, 1252, 1210, 1178, 1097, 1021, 919, 842, 740, 647.

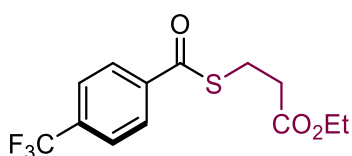
Ethyl 3-((4-bromobenzoyl)thio)propanoate (3e'h)



Following **GP 5**, (4-bromophenyl)(2-(4-bromophenyl)-2,3-dihydrobenzo[*d*]thiazol-2-yl)methanone (**1e'**, 96 mg, 0.2 mmol, 1 equiv.) and diethyl 3,3'-disulfanediyldipropionate (**2h**, 133 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3e'h** as a colorless liquid (55 mg, 0.174 mmol, 87%). (eluent: petroleum ether /ethyl acetate = 97:3)

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.81 (d, *J* = 7.8 Hz, 2H), 7.58 (d, *J* = 7.7 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.31 (t, *J* = 6.9 Hz, 2H), 2.71 (t, *J* = 6.9 Hz, 2H), 1.26 (t, *J* = 7.0 Hz, 3H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 190.7, 171.7, 135.7, 132.1, 128.8, 128.7, 61.0, 34.5, 24.3, 14.3; **HRMS (ESI-TOF)**: *m/z* calc. for (C₁₂H₁₃BrO₃SNa) [M+Na]⁺: 340.9646; found: 340.9627; **IR (ATR) (ν cm⁻¹)**: 2990, 2943, 2883, 1742, 1672, 1592, 1489, 1379, 1211, 1178, 1074, 1018, 917, 838, 724, 647.

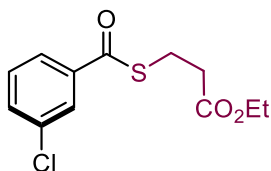
Ethyl 3-((4-(trifluoromethyl)benzoyl)thio)propanoate (3f'h)



Following **GP 5**, (4-bromophenyl)(2-(4-bromophenyl)-2,3-dihydrobenzo[*d*]thiazol-2-yl)methanone (**1f'**, 91 mg, 0.2 mmol, 1 equiv.) and diethyl 3,3'-disulfanediyldipropionate (**2h**, 133 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3f'h** as a colorless liquid (53 mg, 0.174 mmol, 87%). (eluent: petroleum ether /ethyl acetate = 97:3)

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 8.05 (d, *J* = 7.9 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.35 (t, *J* = 6.9 Hz, 2H), 2.74 (t, *J* = 6.8 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 190.9, 171.7, 139.8, 135.1 (q, *J* = 32.7 Hz), 127.7, 125.9 (q, *J* = 3.6 Hz), 123.7 (q, *J* = 273.0 Hz), 61.1, 34.4, 24.5, 14.3; **HRMS (ESI-TOF)**: *m/z* calc. for (C₁₃H₁₃F₃O₃SNa) [M+Na]⁺: 329.0435; found: 329.0449; **IR (ATR) (ν cm⁻¹)**: 2967, 2943, 1745, 1675, 1417, 1331, 1215, 1180, 1139, 1072, 924, 856, 780, 656.

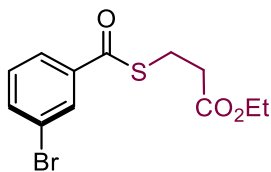
Ethyl 3-((3-chlorobenzoyl)thio)propanoate (3g'h)



Following **GP 5**, (3-chlorophenyl)(2-(3-chlorophenyl)-2,3-dihydrobenzo[*d*]thiazol-2-yl)methanone (**1g'**, 77 mg, 0.2 mmol, 1 equiv.) and diethyl 3,3'-disulfanediyldipropionate (**2h**, 133 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3g'h** as a colorless liquid (48 mg, 0.174 mmol, 89%). (eluent: petroleum ether /ethyl acetate = 97:3)

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.92 (s, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.32 (t, *J* = 6.9 Hz, 2H), 2.72 (t, *J* = 6.9 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 190.6, 171.8, 138.5, 135.1, 133.5, 130.1, 127.4, 125.5, 61.0, 34.5, 24.4, 14.3; **HRMS (ESI-TOF)**: *m/z* calc. for (C₁₂H₁₃ClO₃S) [M]⁺: 272.0274; found: 272.0280; **IR (ATR) (ν cm⁻¹)**: 3085, 2998, 2943, 2284, 1743, 1670, 1476, 1426, 1353, 1202, 964, 800, 776, 742, 698, 543.

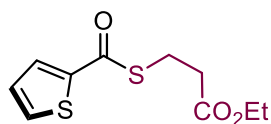
Ethyl 3-((3-bromobenzoyl)thio)propanoate (3h'h)



Following **GP 5**, (3-bromophenyl)(2-(3-bromophenyl)-2,3-dihydrobenzo[*d*]thiazol-2-yl)methanone (**1h'**, 95 mg, 0.2 mmol, 1 equiv.) and diethyl 3,3'-disulfanediyldipropionate (**2h**, 133 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3h'h** as a colorless liquid (56 mg, 0.176 mmol, 88%). (eluent: petroleum ether /ethyl acetate = 97:3)

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 8.07 (s, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 4.17 (q, *J* = 7.0 Hz, 2H), 3.32 (t, *J* = 6.8 Hz, 2H), 2.71 (t, *J* = 6.8 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 190.4, 171.7, 138.6, 136.4, 130.3, 130.3, 125.9, 123.0, 61.0, 34.5, 24.4, 14.3; **HRMS (ESI-TOF)**: *m/z* calc. for (C₁₂H₁₃BrO₃SNa) [M+Na]⁺: 338.9666; found: 338.9670; **IR (ATR) (ν cm⁻¹)**: 3084, 3060, 2940, 2124, 1743, 1665, 1573, 1473, 1380, 1353, 1200, 1103, 1075, 1025, 931, 798, 723, 697.

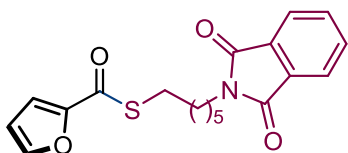
Ethyl 3-((4-methoxybenzoyl)thio)propanoate (3i'h)



Following **GP 5**, thiophen-2-yl(2-(thiophen-2-yl)-2,3-dihydrobenzo[*d*]thiazol-2-yl)methanone (**1i'**, 66 mg, 0.2 mmol, 1 equiv.) and diethyl 3,3'-disulfanediyldipropionate (**2h**, 133 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3i'h** as a colorless liquid (43 mg, 0.174 mmol, 87%). (eluent: petroleum ether /ethyl acetate = 97:3)

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.75 (d, *J* = 2.7 Hz, 1H), 7.59 (d, *J* = 4.7 Hz, 2H), 7.07 (t, *J* = 4.1 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.28 (t, *J* = 6.9 Hz, 2H), 2.70 (t, *J* = 6.9 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 183.6, 171.7, 141.9, 132.9, 131.3, 128.0, 60.8, 34.6, 24.2, 14.2; **HRMS (ESI-TOF)**: *m/z* calc. for (C₁₀H₁₂O₃S₂Na) [M+Na]⁺: 267.0125; found: 267.0134; **IR (ATR) (ν cm⁻¹)**: 3120, 2994, 1738, 1659, 1521, 1417, 1379, 1236, 1055, 900, 851, 722, 685, 623, 545.

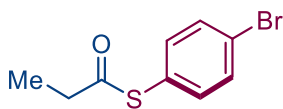
S-(6-(1,3-Dioxoisindolin-2-yl)hexyl) furan-2-carbothioate (3j'j)



Following **GP 5**, furan-2-yl(2-(furan-2-yl)-2,3-dihydrobenzo[*d*]thiazol-2-yl)methanone (**1j'**, 60 mg, 0.2 mmol, 1 equiv.) and 2,2'-(disulfaneylbis(hexane-6,1-diyl))bis(isoindoline-1,3-dione) (**2j**, 262 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3j'j** as a white solid (64 mg, 0.178 mmol, 89%). (eluent: petroleum ether /ethyl acetate = 90:10)

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.83-7.82 (m, 2H), 7.70-7.68 (m, 2H), 7.55 (bs, 1H), 7.15 (bs, 1H), 6.51 (bs, 1H), 3.67 (t, *J* = 7.2 Hz, 2H), 3.02 (t, *J* = 7.2 Hz, 2H), 1.69-1.62 (m, 4H), 1.48-1.43 (m, 2H), 1.40-1.34 (m, 2H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 180.7, 168.6, 151.1, 146.1, 134.0, 132.3, 123.3, 115.4, 112.3, 38.0, 29.6, 28.6, 28.5, 28.1, 26.5; **HRMS (ESI-TOF)**: *m/z* calc. for (C₁₉H₁₉NO₄SNa) [M+Na]⁺: 380.0933; found: 380.0948; **IR (ATR) (ν cm⁻¹)**: 3147, 2977, 2945, 2872, 2007, 1852, 1722, 1652, 1622, 1470, 1404, 1370, 1257, 1197, 1054, 1023, 963, 858, 778, 724, 556, 525.

S-(4-Bromophenyl) propanethioate (3ko)

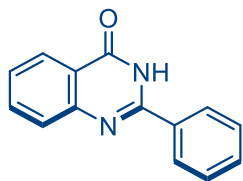


Following **GP 5**, 2-ethyl-2-propionyl-2,3-dihydroquinazolin-4(1H)-one (**1k**, 47 mg, 0.2 mmol, 1 equiv.) and 1,2-bis(4-bromophenyl)disulfane (**2o**, 188 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3ko** as a colorless liquid (37 mg, 0.152 mmol, 76%). (eluent: petroleum ether /ethyl acetate = 300:1)

Following **GP 5**, 1-(2-ethyl-2,3-dihydrobenzo[*d*]thiazol-2-yl)propan-1-one (**1k'**, 44 mg, 0.2 mmol, 1 equiv.) and 1,2-bis(4-bromophenyl)disulfane (**2o**, 188 mg, 0.5 mmol, 2.5 equiv.) afforded the compound **3ko** as a colorless liquid (36 mg, 0.146 mmol, 73%). (eluent: petroleum ether /ethyl acetate = 300:1)

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.52 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 2.67 (q, *J* = 7.5 Hz, 2H), 1.21 (t, *J* = 7.5 Hz, 3H); **¹³C NMR (126 MHz, CDCl₃)** δ (ppm) = 197.6, 136.1, 132.5, 127.0, 124.1, 37.3, 9.7; **HRMS (ESI-TOF)**: *m/z* calc. for (C₉H₉BrOSNa) [M+Na]⁺: 266.9455; found: 266.9443; **IR (ATR) (ν cm⁻¹)**: 2970, 2935, 1718, 1478, 1391, 1091, 1013, 928, 917, 736, 709, 602, 541, 520.

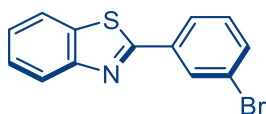
2-Phenylquinazolin-4(3*H*)-one (10a)



Following **GP 5**, 2-benzoyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (**1a**, 66 mg, 0.2 mmol, 1 equiv.) afforded 2-phenylquinazolin-4(3*H*)-one **10a** as a white solid (43 mg, 0.192 mmol, 96%). (eluent: petroleum ether /ethyl acetate = 90:10)

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 11.68 (s, 1H), 8.34-8.33 (m, 1H), 8.27-8.25 (m, 2H), 7.85-7.79 (m, 2H), 7.60-7.59 (m, 3H), 7.53-7.50 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ (ppm) = 164.0, 151.9, 149.7, 135.1, 133.0, 131.8, 129.2, 128.2, 127.6, 127.0, 126.5, 121.0. The spectroscopic data obtained were in agreement with the reported data for the compound ¹³

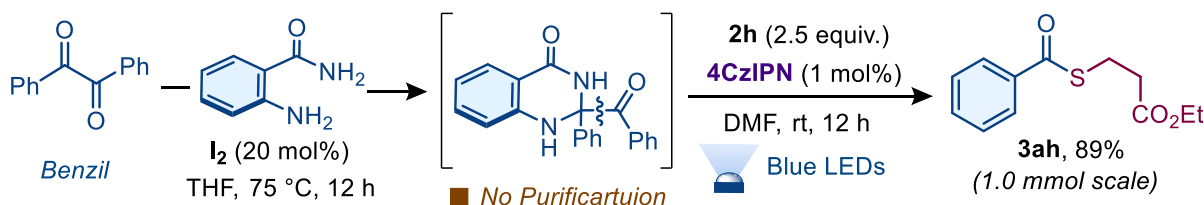
2-(3-Bromophenyl)benzo[d]thiazole (10h)



Following **GP 5**, thiophen-2-yl(2-(thiophen-2-yl)-2,3-dihydrobenzo[d]thiazol-2-yl)methanone (**1h'**, 66 mg, 0.2 mmol, 1 equiv.) afforded the compound 2-(3-bromophenyl)benzo[d]thiazole **10h** as a white solid (53 mg, 0.184 mmol, 92%). (eluent: petroleum ether /ethyl acetate = 99:1)

¹H NMR (500 MHz, CDCl₃) δ (ppm) = 8.27 (s, 1H), 8.08 (d, *J* = 8.1 Hz, 1H), 7.97 (d, *J* = 7.7 Hz, 1H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ (ppm) = 166.2, 154.1, 135.6, 135.2, 133.9, 130.6, 130.4, 126.7, 126.3, 125.7, 123.6, 123.3, 121.8; HRMS (ESI-TOF): *m/z* calc. for (C₁₃H₉BrNS) [M+H]⁺: 291.9619; found: 291.9618; IR (ATR) (ν cm⁻¹): 2204, 2105, 1505, 1203, 1105, 1007, 903, 801, 705.

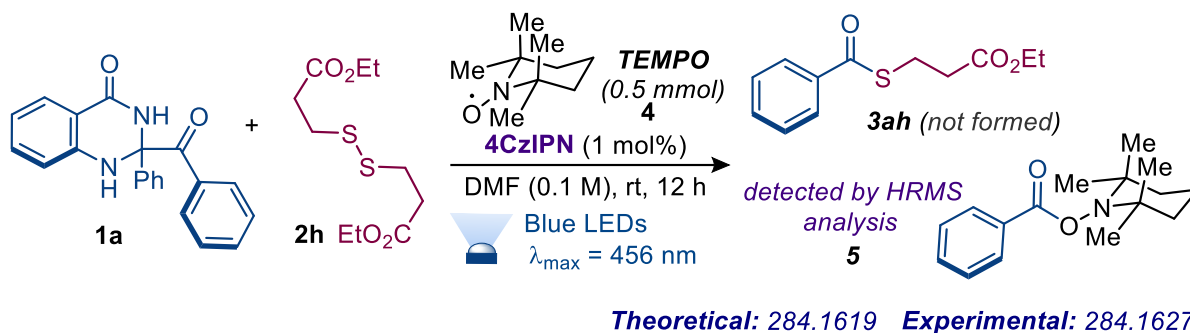
4. Scaled up one pot synthesis of thioester:



In an oven-dried Schlenk tube containing a stirring bar, 4CzIPN (8 mg, 1 mol%), dihydroquinazolinone **1a** (synthesized in situ from benzil and anthranilamide, and directly used) (330 mg, 1 mmol, 1 equiv.) and disulfide **2h** (665 mg, 2.5 mmol, 2.5 equiv.) were dissolved in DMF (10 mL) under argon atmosphere. The reaction mixture was stirred at room temperature under light irradiation from blue LEDs for 12 h. Once the reaction was completed, the reaction mixture was extracted with ethyl acetate (3×20 mL) and the combined organic layers were washed with brine three times. The organic phase was dried over Na₂SO₄ and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography through silica gel (eluent: petroleum ether /ethyl acetate = 98:2) to obtain the desired product **3ah**.

5. Mechanistic Studies

5.1 Radical Trapping Experiment with TEMPO:



An oven-dried Schlenk tube containing a stirring bar was charged with 4CzIPN (0.8 mg, 1 mol%), 2-benzoyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (**1a**, 33 mg, 0.1 mmol, 1 equiv.) and TEMPO (**4**, 78 mg, 0.5 mmol, 5 equiv.) under argon atmosphere and closed with a rubber septum. Subsequently, anhydrous DMF (1 mL) was added to the Schlenk tube followed by the addition of diethyl 3,3'-disulfanediyldipropionate (**2h**, 67 mg, 0.25 mmol, 2.5 equiv.). The reaction mixture was stirred for 12 h under light irradiation from blue LEDs at room temperature. The crude reaction mixture was diluted with methanol and analyzed by high resolution mass spectrometry. In HRMS analysis, the formation of 2,2,6,6-tetramethylpiperidin-1-yl benzoate (**5**) was detected (Figure S4).

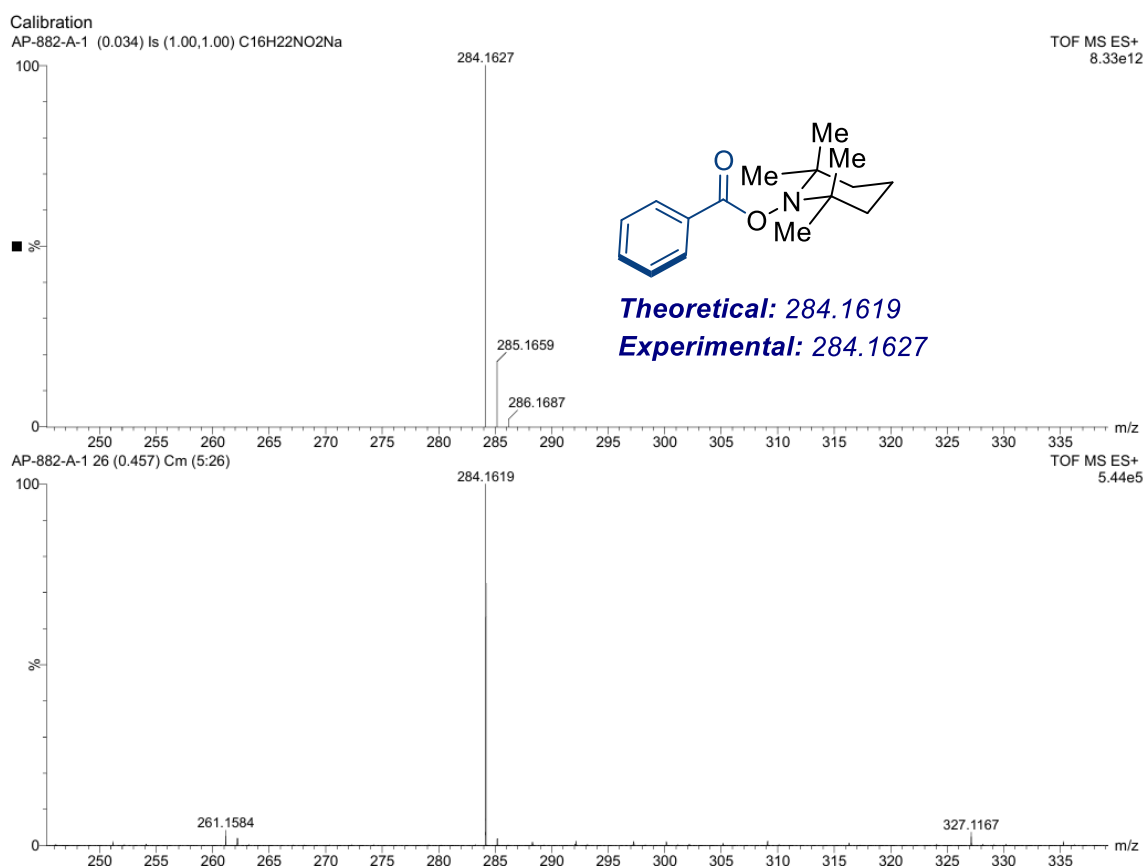
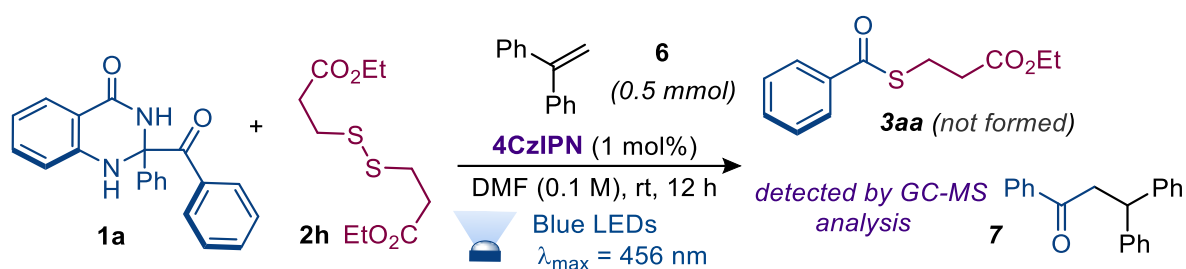


Figure S4: Detection of 2,2,6,6-tetramethylpiperidin-1-yl benzoate (**5**) in the crude reaction mixture of radical trapping experiment using TEMPO by HRMS analysis.

5.2 Radical Trapping Experiment with 1,1-diphenylethene:



An oven-dried Schlenk tube containing a stirring bar was charged with 4CzIPN (0.8 mg, 1 mol%) and 2-benzoyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (**1a**, 33 mg, 0.1 mmol, 1 equiv.) under argon atmosphere and closed with a rubber septum. Subsequently, anhydrous DMF (1 mL) was added to the Schlenk tube followed by the addition of diethyl 3,3'-disulfanediyldipropionate (**2h**, 67 mg, 0.25 mmol, 2.5 equiv.) and 1,1-diphenylethene (**6**, 90 mg, 0.5 mmol, 5 equiv.). The reaction mixture was stirred for 12 h under light irradiation from blue LEDs at room temperature. The crude reaction mixture was diluted with ethyl acetate and analyzed by gas chromatography mass spectrometry. In GC-MS analysis, the formation of 1,3,3-triphenylpropan-1-one (**7**) was detected (Figure S5).

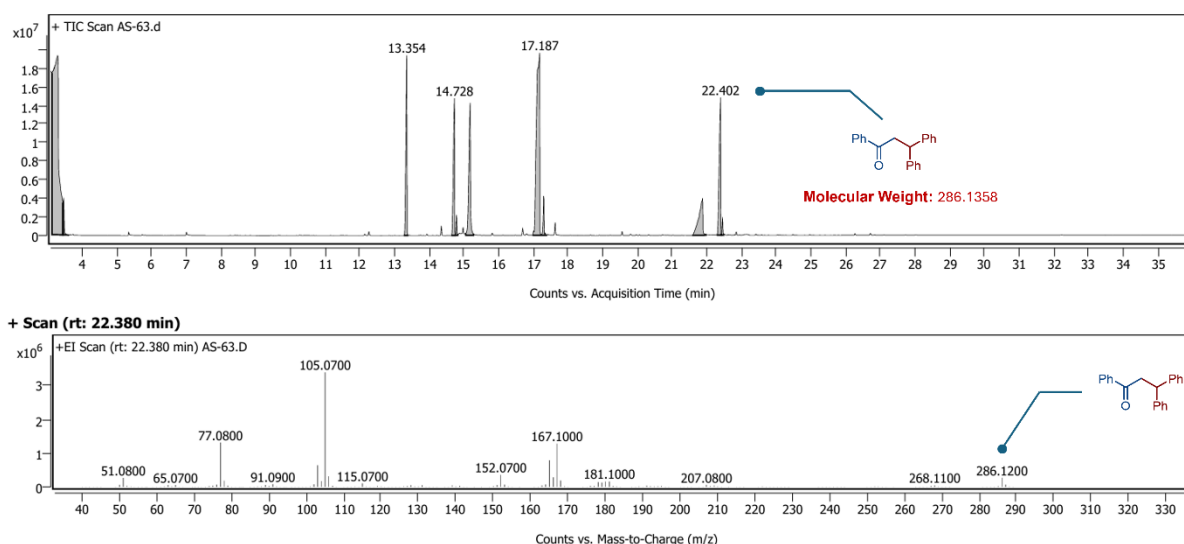
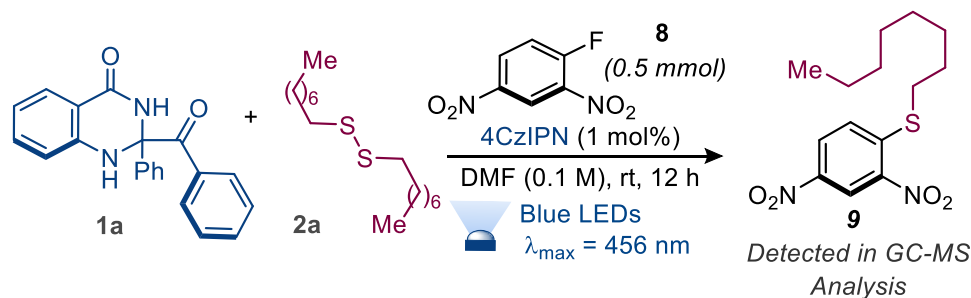


Figure S5: Detection of 1,3,3-triphenylpropan-1-one (**7**) in the crude reaction mixture of radical trapping experiment using 1,1-diphenylethene by GC-MS analysis.

5.3 Thiol trapping experiment with Sanger's reagent:



An oven-dried Schlenk tube containing a stirring bar was charged with 4CzIPN (0.8 mg, 0.001 mmol, 0.001 equiv.) and 2-benzoyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (**1a**, 33 mg, 0.1 mmol, 1 equiv.)

under argon atmosphere and closed with a rubber septum. Subsequently 1 mL anhydrous DMF was added to the Schlenk tube followed by the addition of 1,2-dioctylsulfane (**2a**, 73 mg, 0.25 mmol, 2.5 equiv.) and 1-fluoro-2,4-dinitrobenzene (**8**, 93 mg, 0.5 mmol, 5 equiv.). After that the Schlenk tube was stirred for 12 h under light irradiation from blue LEDs at room temperature. The crude reaction mixture was extracted with ethyl acetate and the combined organic layer washed with brine three times. The organic part was dried over Na₂SO₄, and solvent was removed under reduced pressure. The crude reaction mixture was analyzed by GC-MS analysis and the formation of (2,4-dinitrophenyl)(octyl)sulfane (**9**) was detected (Figure S6).

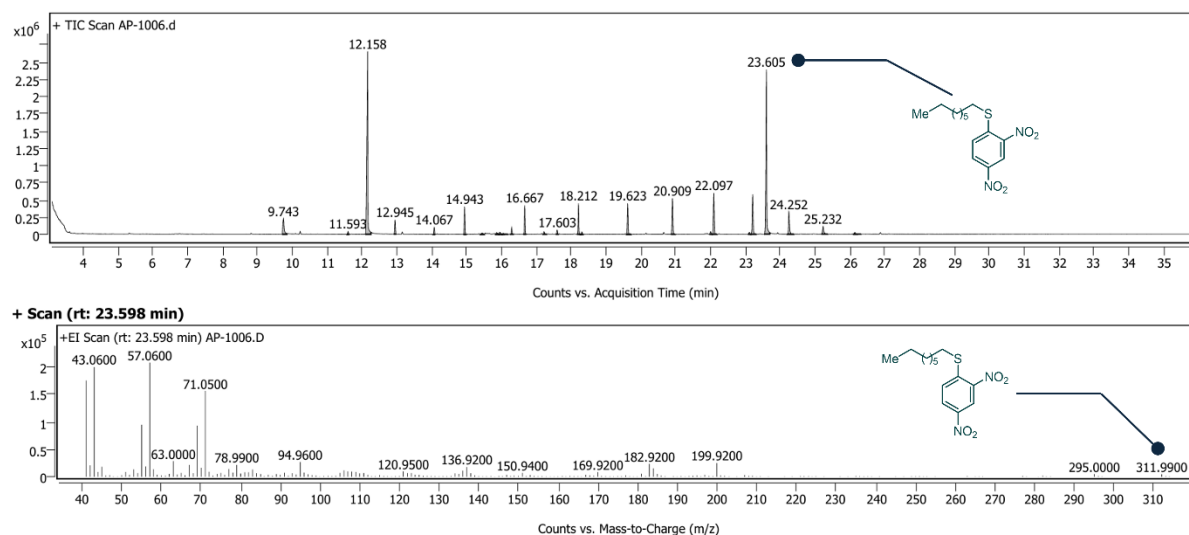


Figure S6: Detection of (2,4-dinitrophenyl)(octyl)sulfane (**6**) in the crude reaction mixture by GC-MS analysis.

5.4 Luminescence quenching studies:

Luminescence Quenching Study of 4CzIPN:

A 10 ml stock solution of 4CzIPN (0.7 mM) in anhydrous degassed DMF was prepared. 30 μ L 4CzIPN stock solution was transferred into a 4 mL quartz cuvette (path length: $l = 1.0$ cm) under an atmosphere of nitrogen and volume was made up to 3 mL by adding DMF, where an emission at maximum at 556 nm was observed upon irradiation at 500 nm. Separate solutions of quenchers phenyl(2-phenyl-2,3-dihydrobenzo[*d*]thiazol-2-yl)methanone (**1a'**, 150 mM), 2-benzoyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (**1a**, 150 mM) and diethyl 3,3'-disulfaneyldipropionate (**2h**, 150 mM) were prepared in anhydrous degassed DMF under nitrogen environment. The aliquots of the quencher **1a** solution in variable amounts were added to the quartz cuvette (path length: $l = 1.0$ cm) containing 30 μ L 4CzIPN (0.7 mM) solution under an atmosphere of nitrogen and volume was made up to 3 mL by adding DMF each time. The emission spectra were recorded (Figure S7). This measurement was repeated for the quencher **1a'** and **2h** (Figure S8-S9). The Stern-Volmer plot is also depicted in Figure S10.

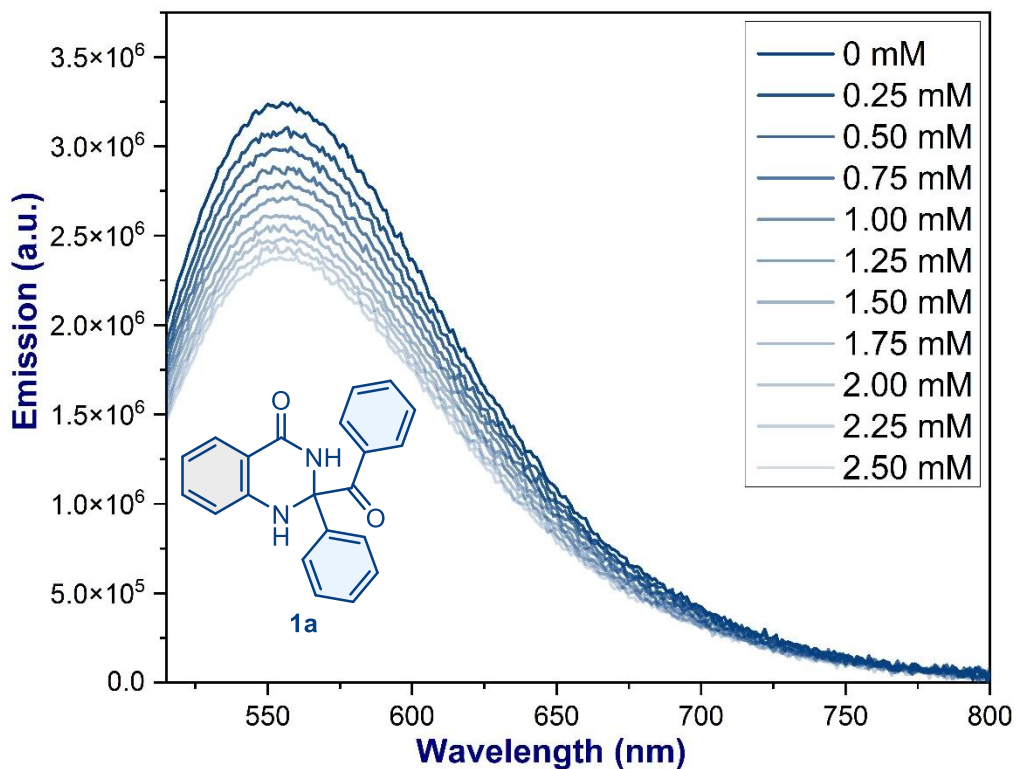


Figure S7: Emission spectra of a solution of 4CzIPN in DMF containing varying amounts of 2-benzoyl-2-phenyl-2,3-dihydroquinazolin-4(1H)-one (**1a**).

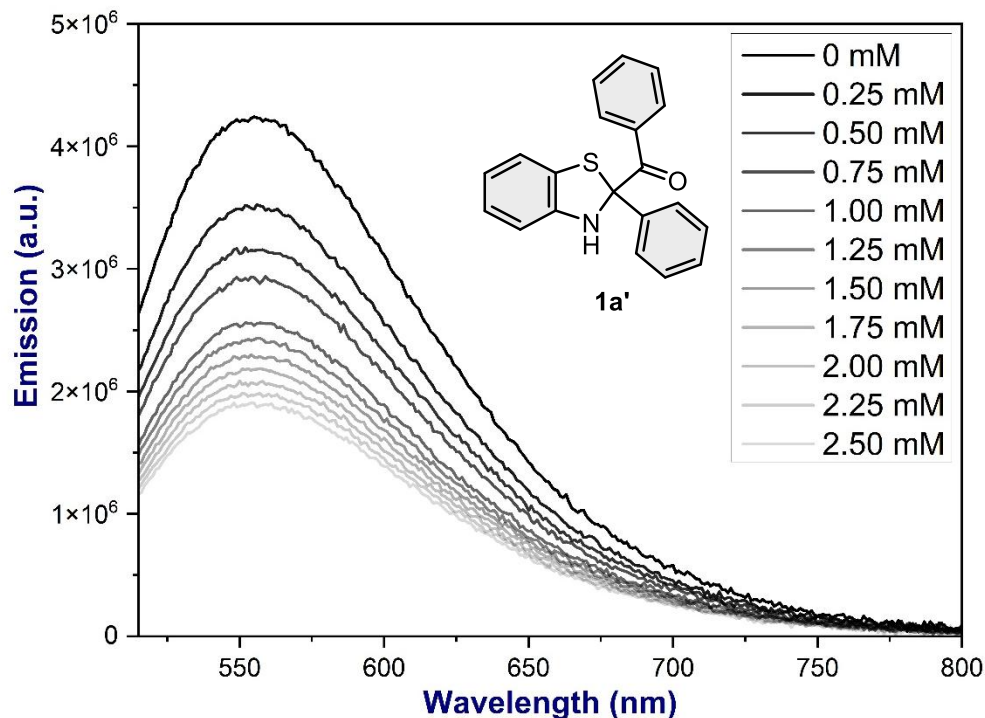


Figure S8: Emission spectra of a solution of 4CzIPN in DMF containing varying amounts of phenyl(2-phenyl-2,3-dihydrobenzo[d]thiazol-2-yl)methanone (**1a'**).

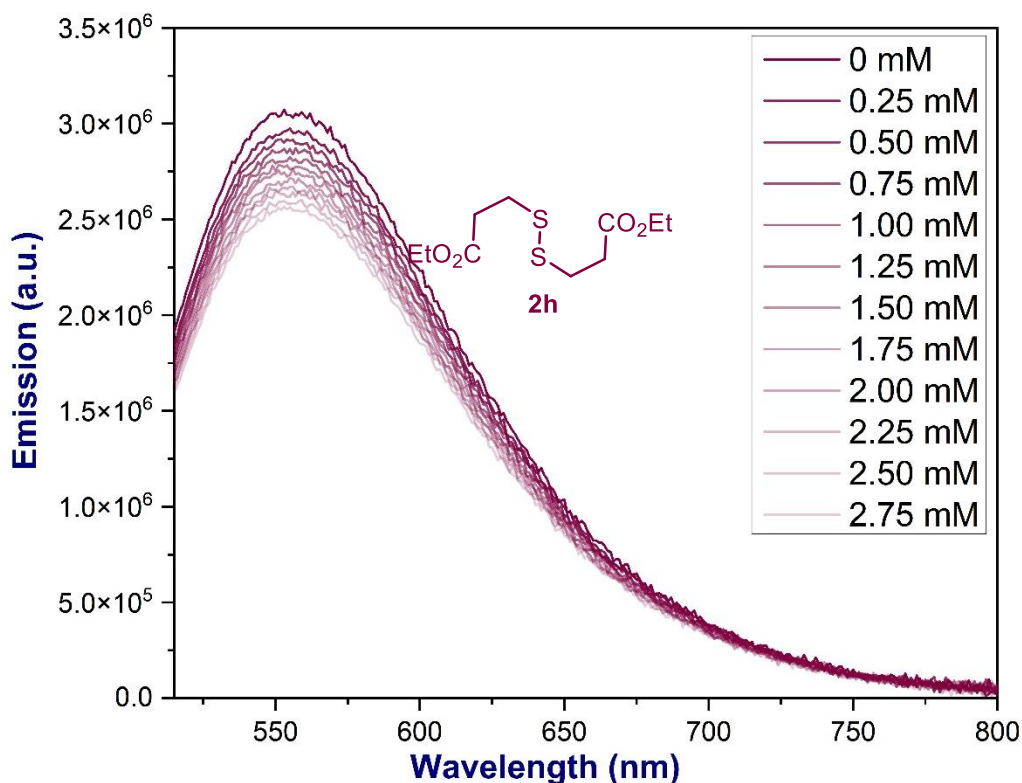


Figure S9: Emission spectra of a solution of 4CzIPN in DMF containing varying amounts of diethyl 3,3'-disulfanediyldipropionate (**2h**).

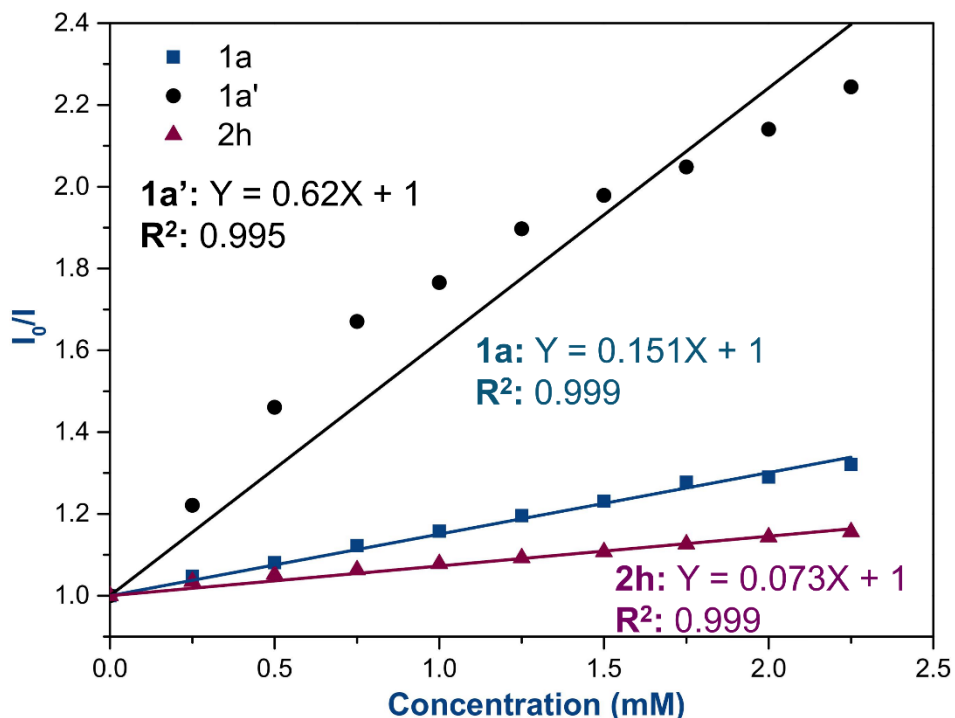


Figure S10: Stern Volmer Plots against X = phenyl(2-phenyl-2,3-dihydrobenzo[d]thiazol-2-yl)methanone (**1a'**), 2-benzoyl-2-phenyl-2,3-dihydroquinazolin-4(1H)-one (**1a**) and diethyl 3,3'-disulfanediyldipropionate (**2h**). Stern-Volmer constant, K_{SV} (**1a'**) = 0.62, K_{SV} (**1a**) = 0.151 and K_{SV} (**2h**) = 0.073.

5.5 On-Off experiment:

In an oven-dried Schlenk tube containing a stirring bar, 4CzIPN (1.6 mg, 1 mol%), 2-benzoyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (**1a**, 66 mg, 0.2 mmol, 1 equiv.) and 1,2-di-*p*-tolylidysulfane (**2I**, 123 mg, 0.5 mmol, 2.5 equiv.) were dissolved in DMF (2 mL, 0.1 M) under argon atmosphere and after 1 h time interval a small aliquot was taken and was extracted with EtOAc, followed by washing with brine solution. The organic layer was concentrated under reduced pressure and the yield of **3aI** formation was determined by ¹H NMR analysis using 1,1-dibromomethane as the internal standard.

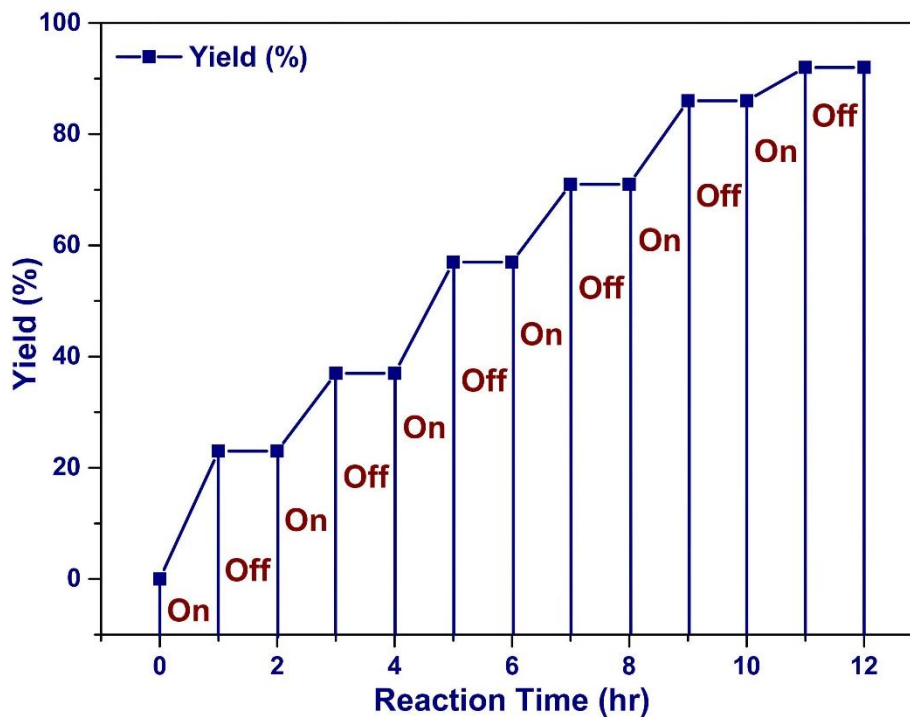


Figure S11: Light ON-OFF experiment.

5.6 Mechanistic Proposal for Benzothiazolines:

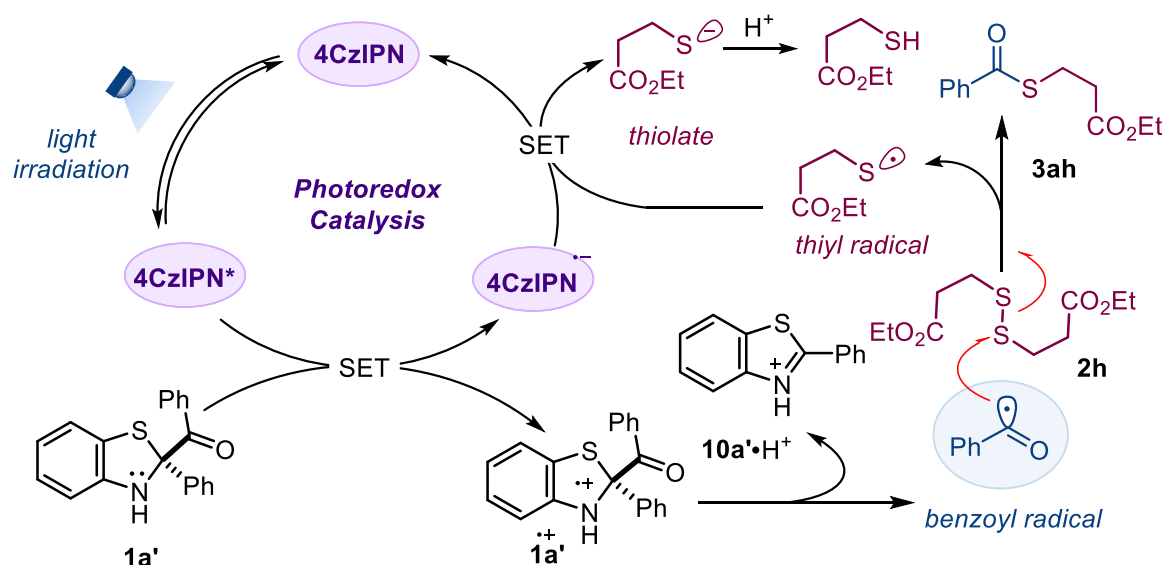


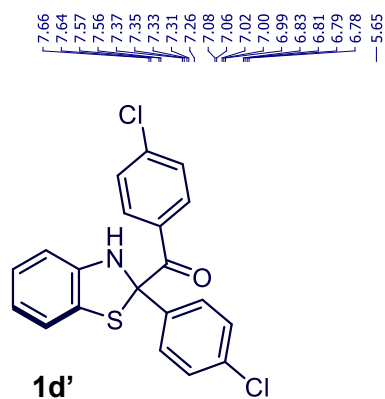
Figure S12: Mechanistic proposal involving benzothiazoline.

6 References:

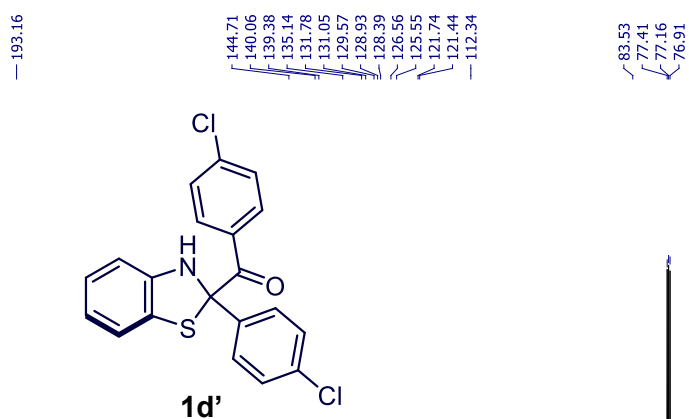
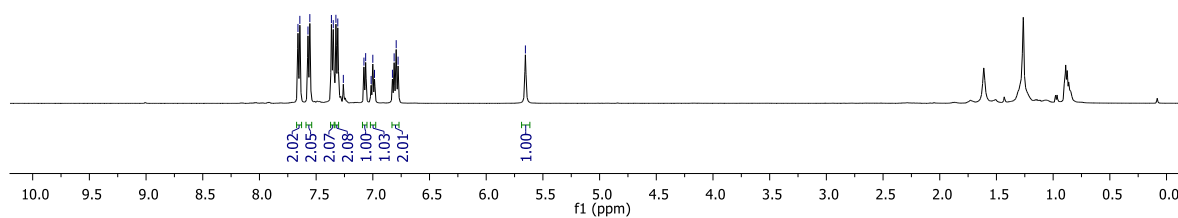
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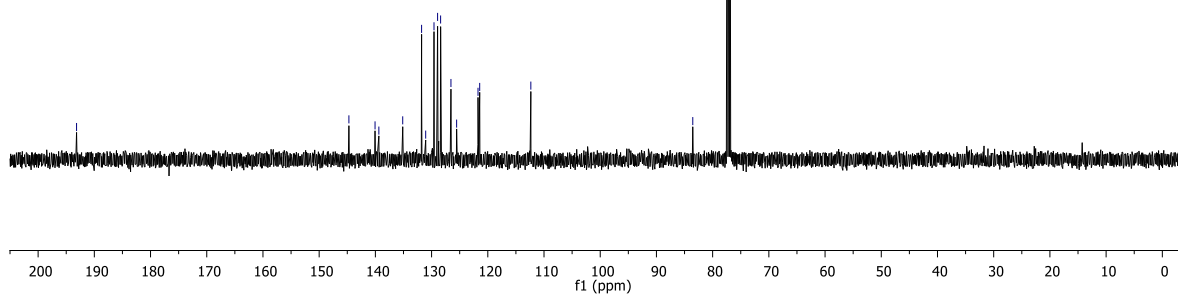
7 NMR Data

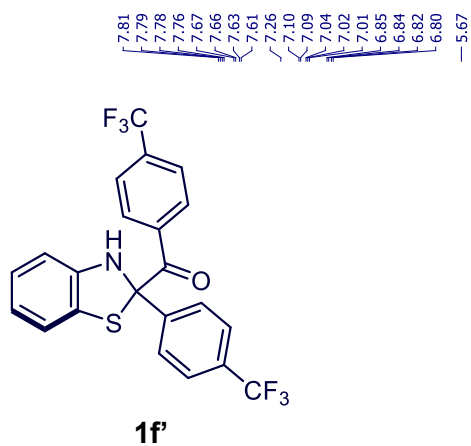


¹H NMR (500 MHz, CDCl₃)

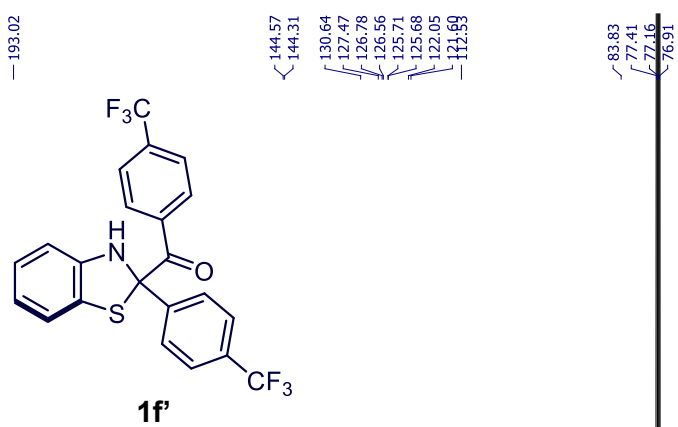
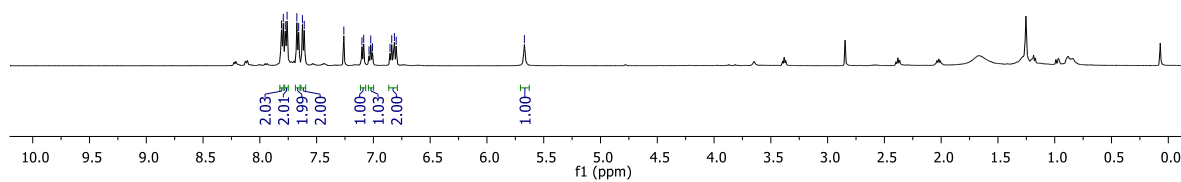


¹³C NMR (126 MHz, CDCl₃)

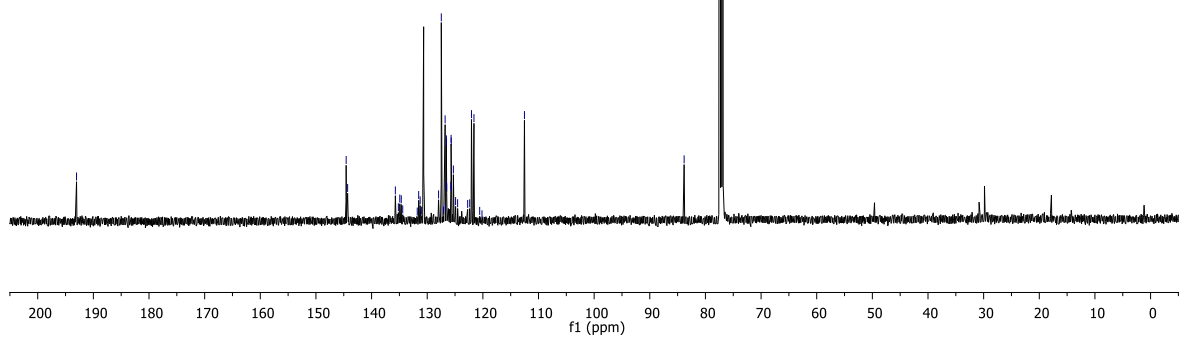


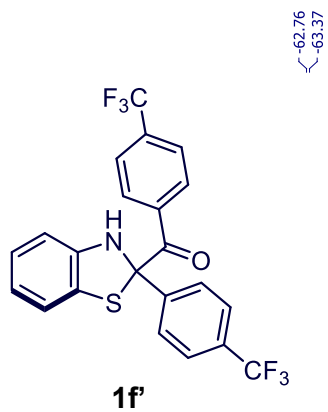


¹H NMR (500 MHz, CDCl₃)

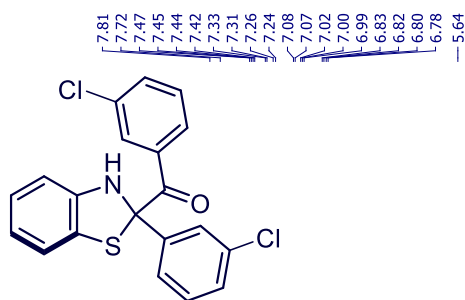
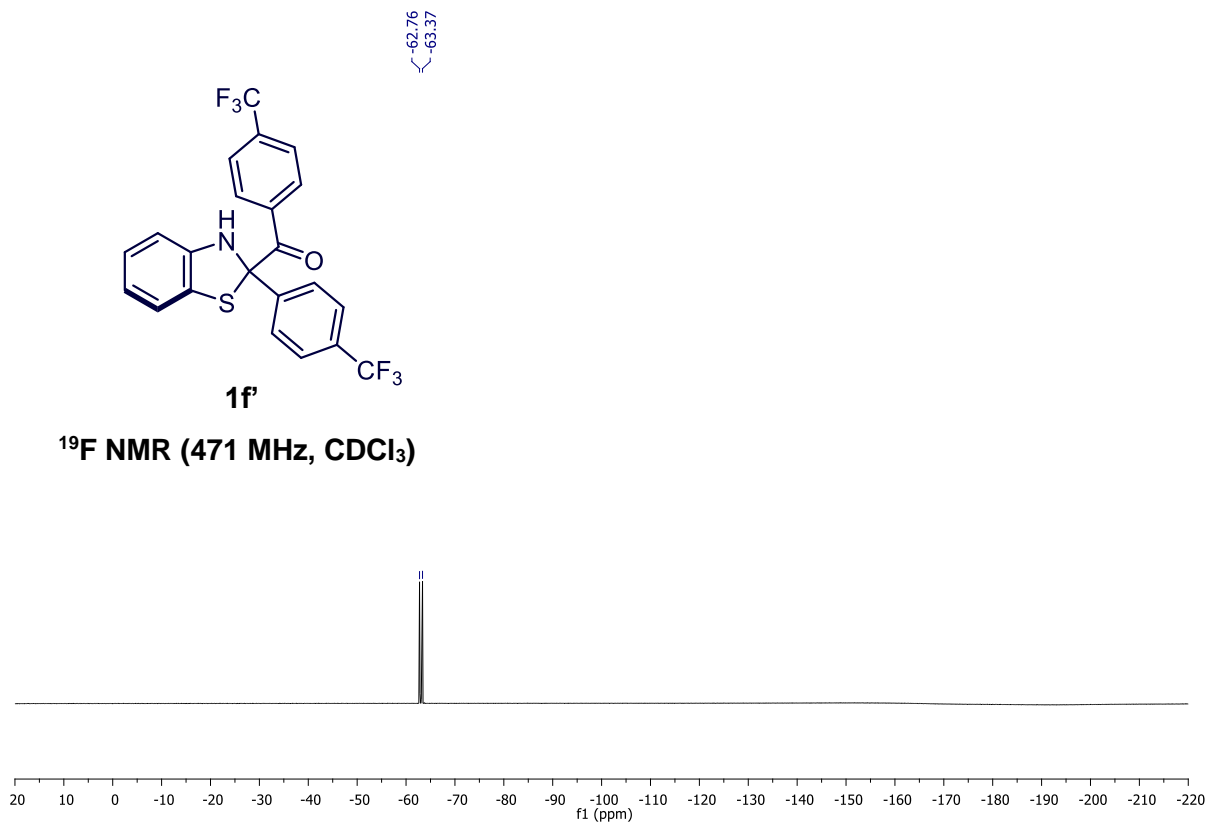


¹³C NMR (126 MHz, CDCl₃)

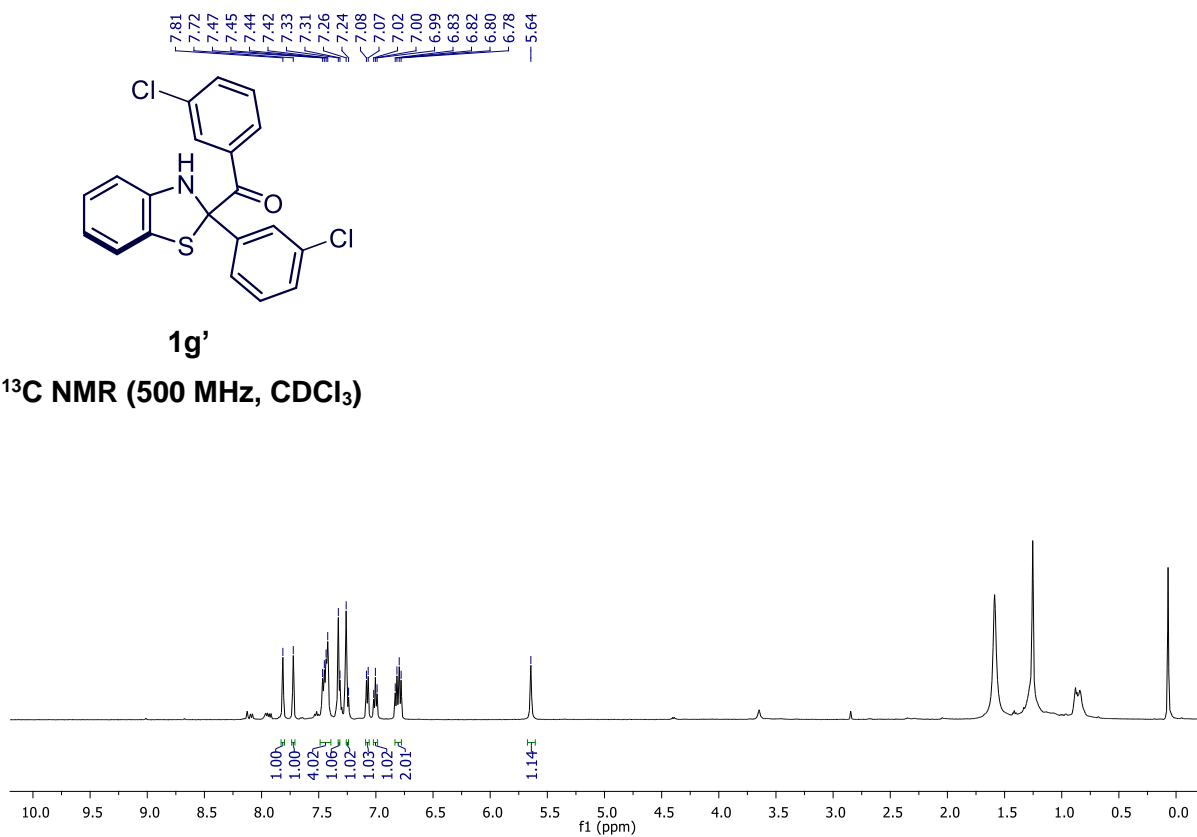


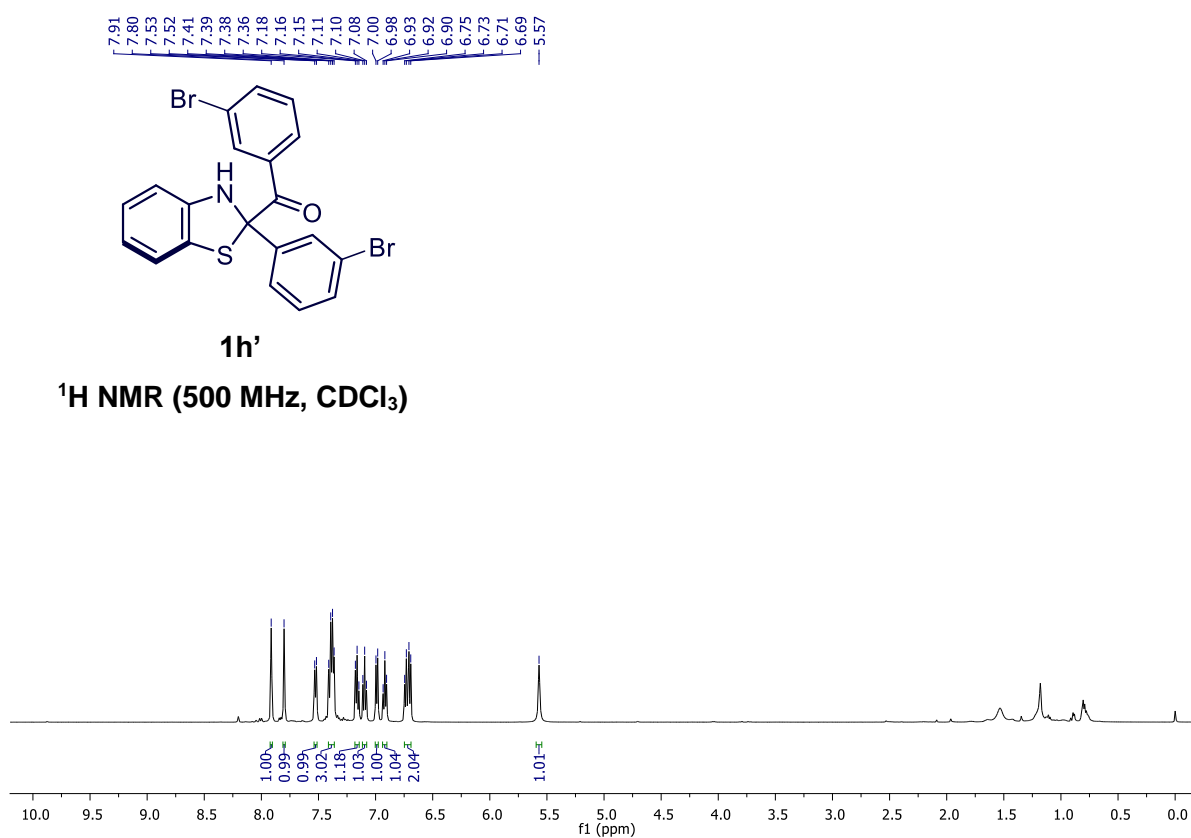
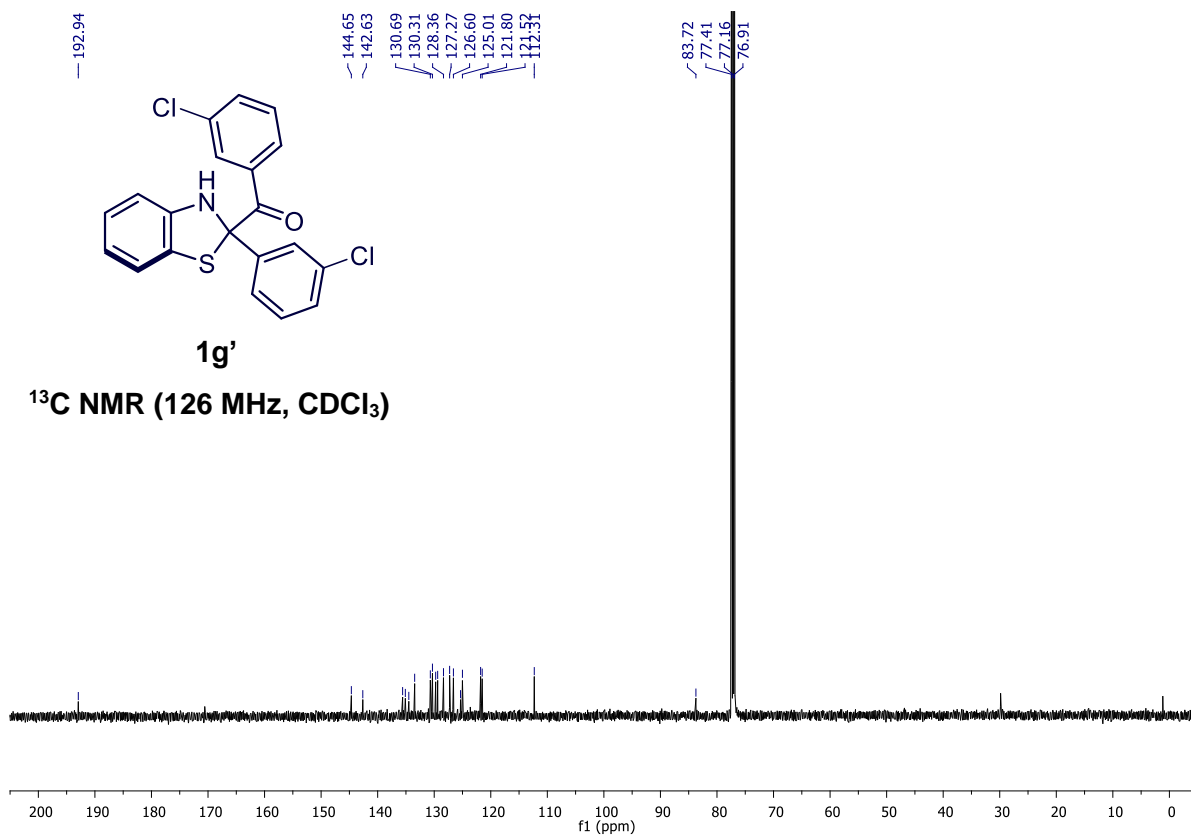


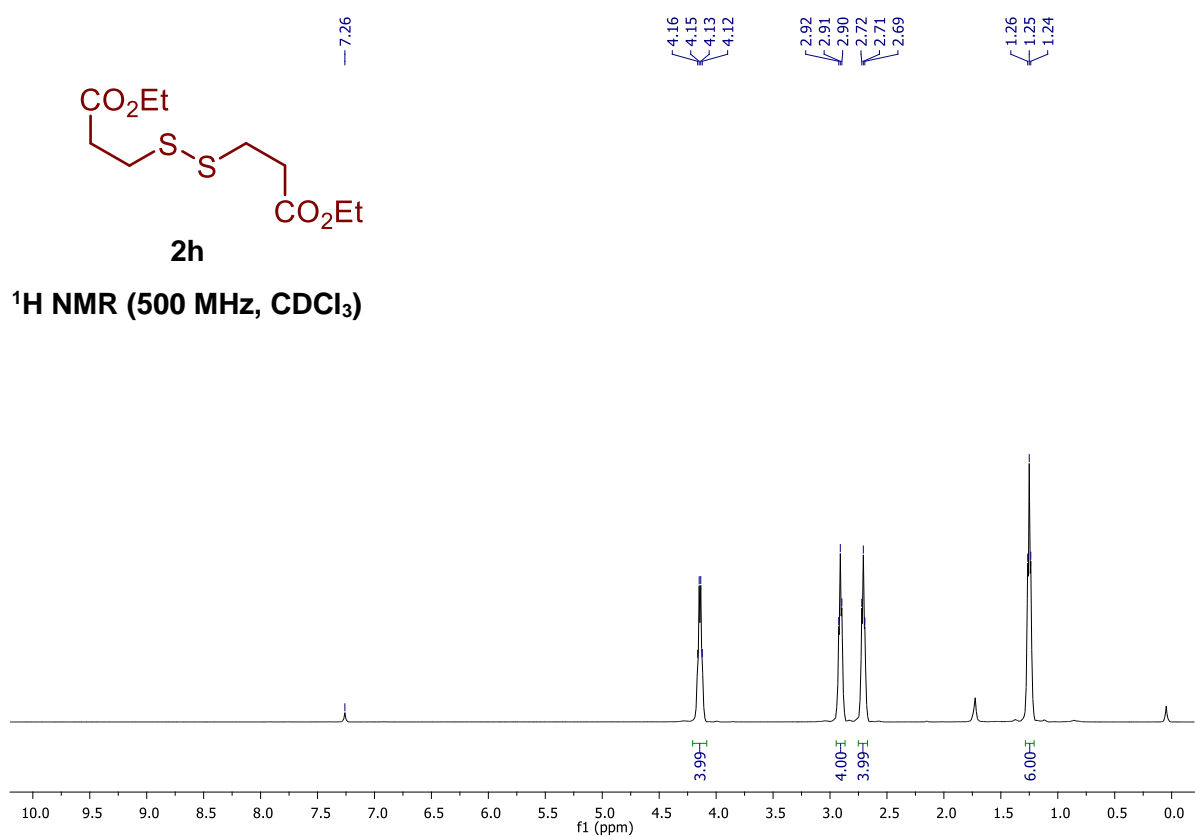
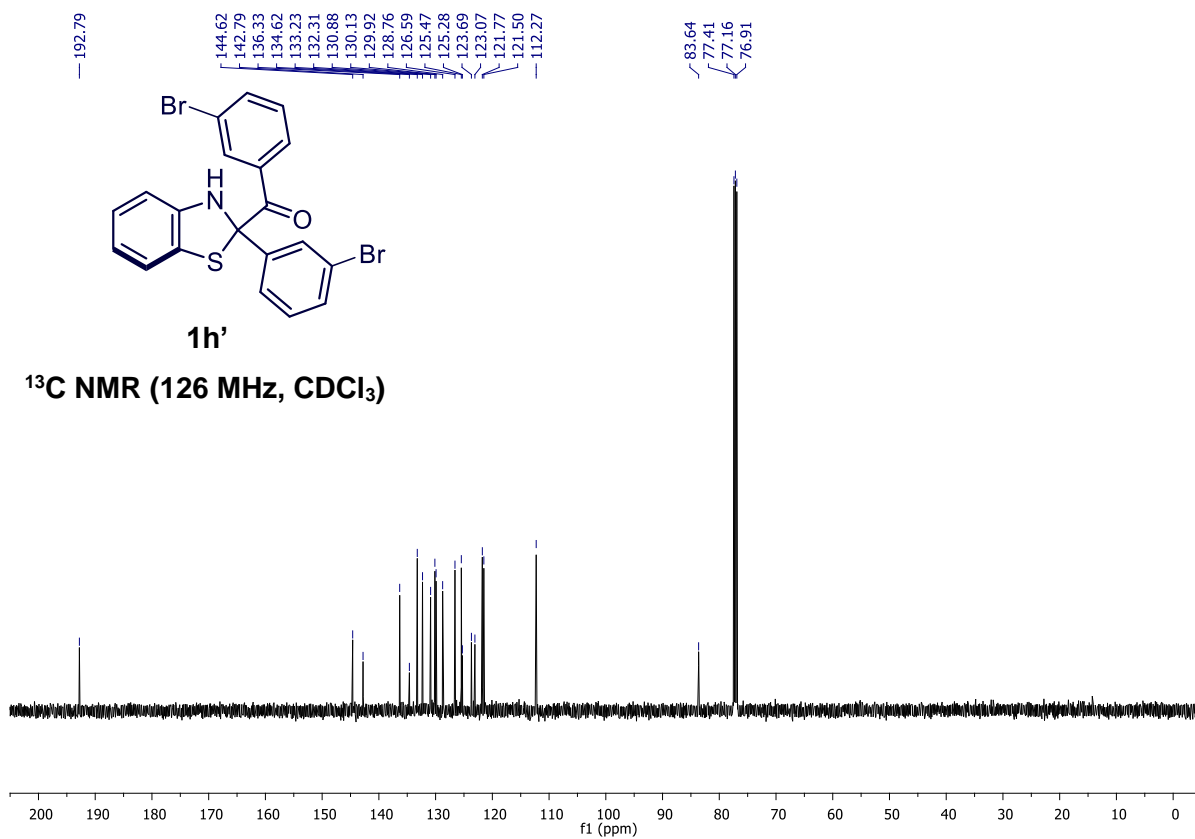
¹⁹F NMR (471 MHz, CDCl₃)

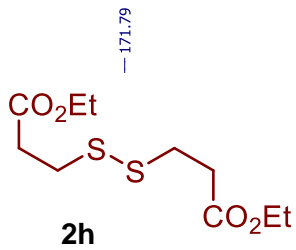


¹³C NMR (500 MHz, CDCl₃)

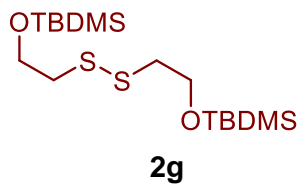
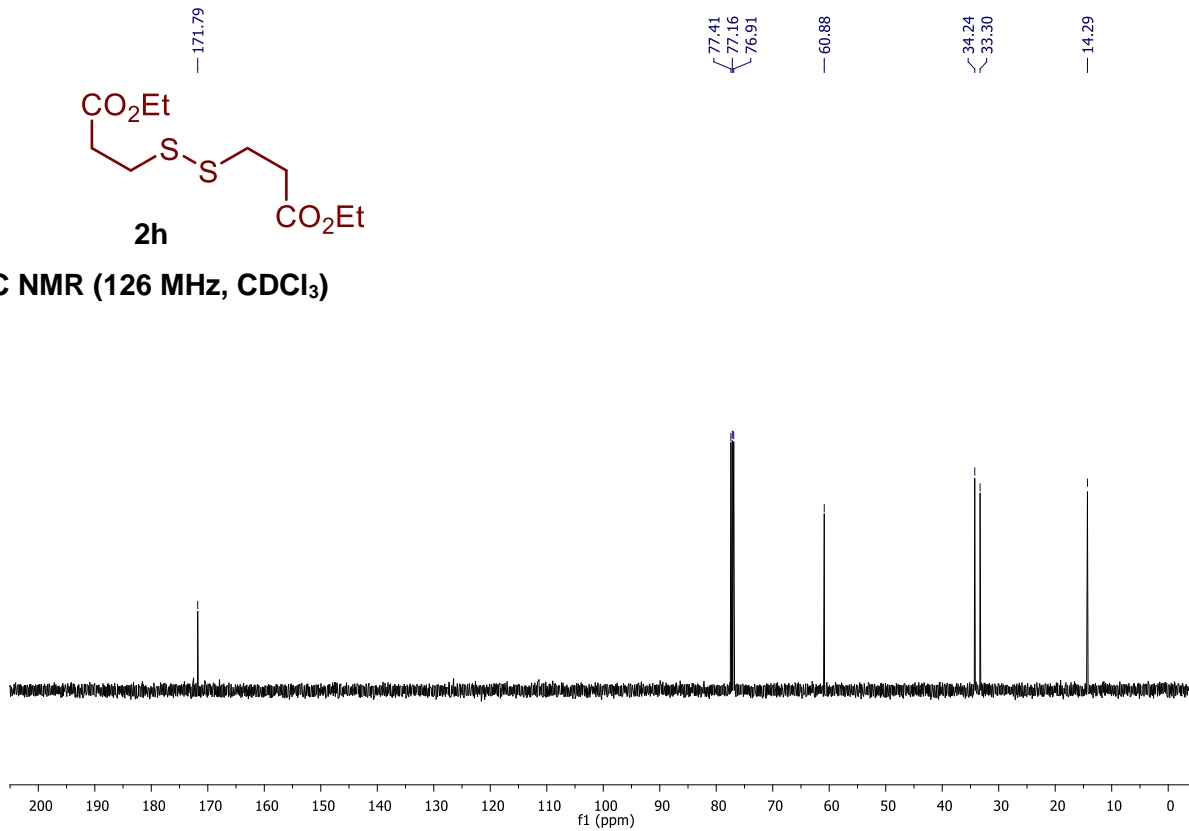




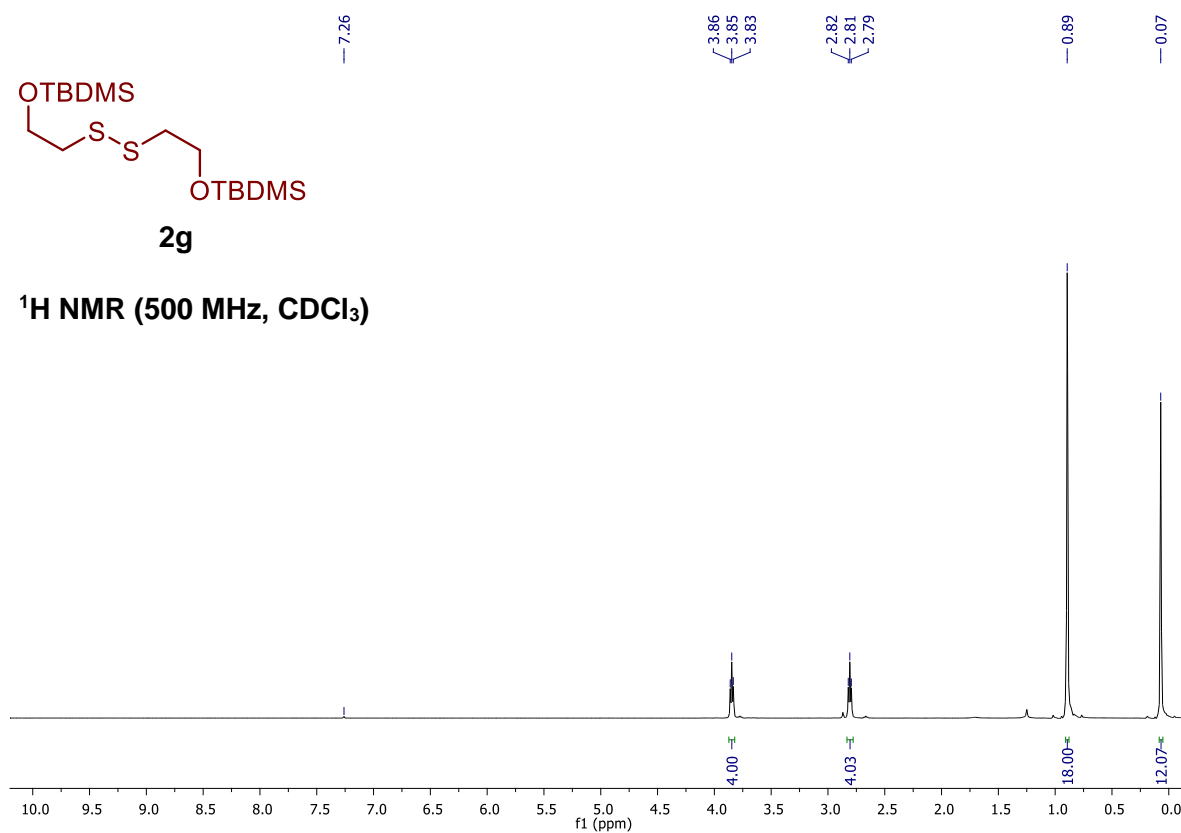


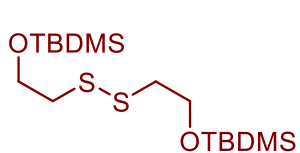


^{13}C NMR (126 MHz, CDCl_3)



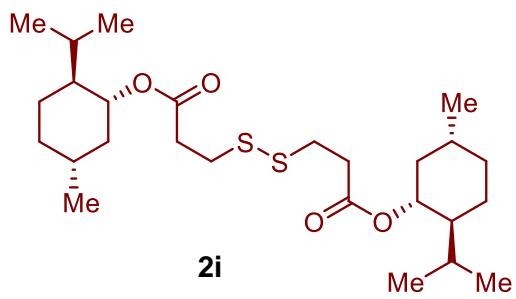
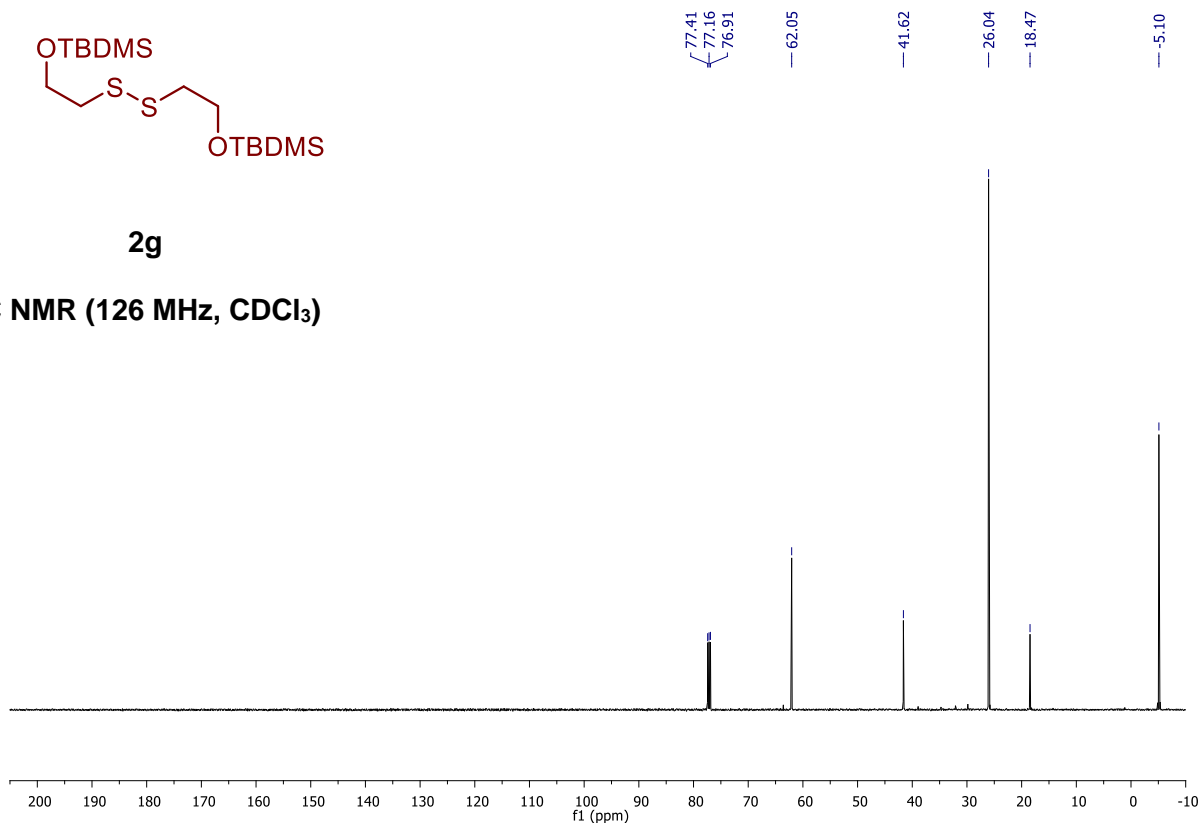
^1H NMR (500 MHz, CDCl_3)





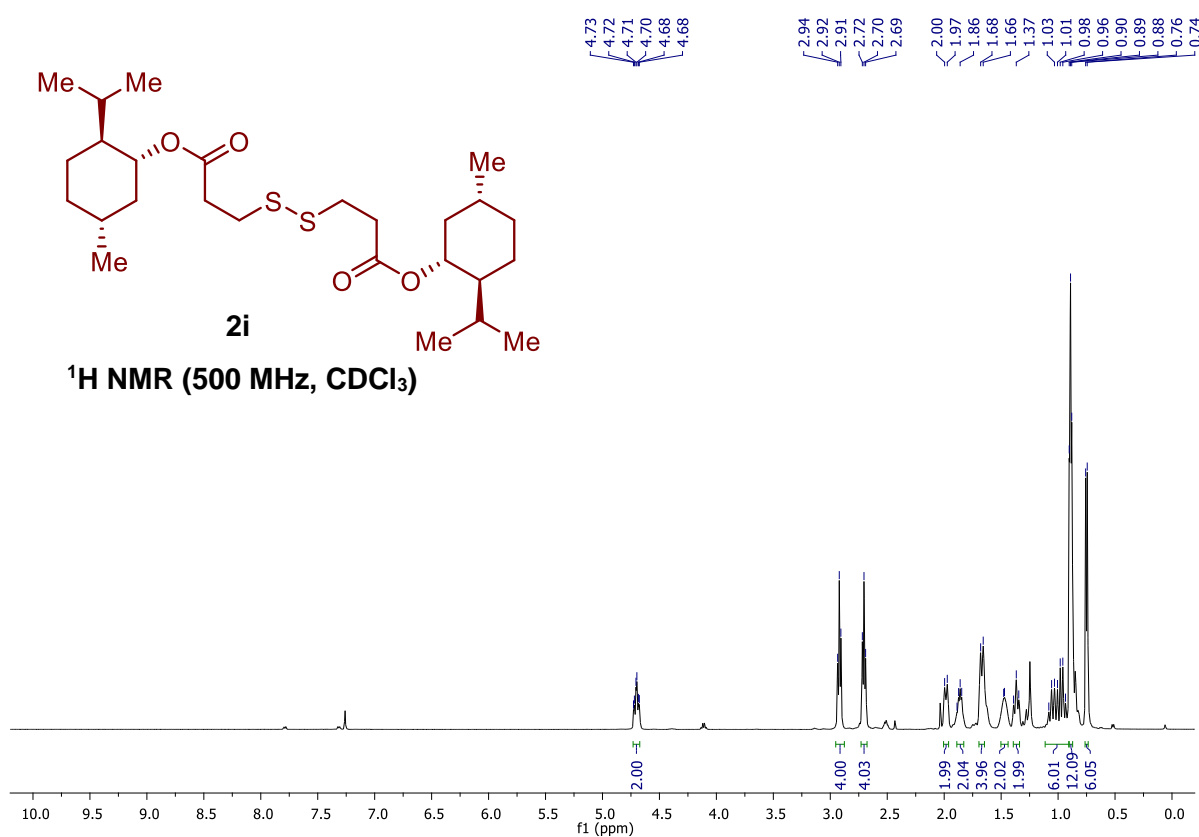
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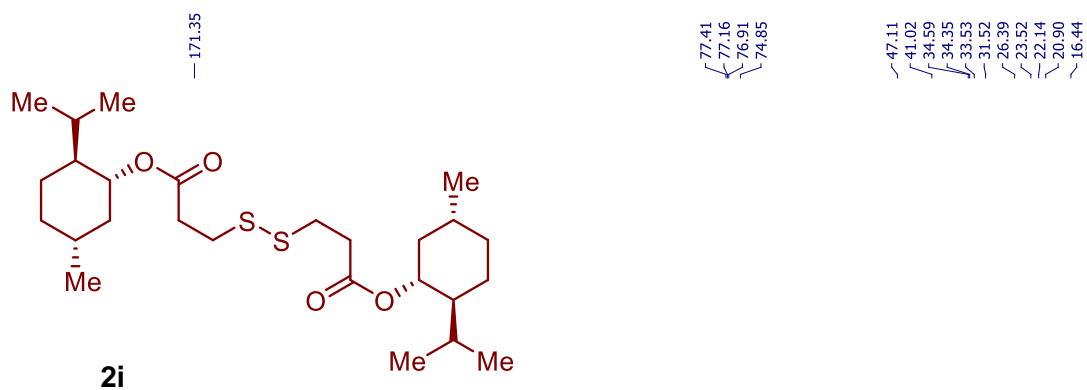
¹³C NMR (126 MHz, CDCl₃)



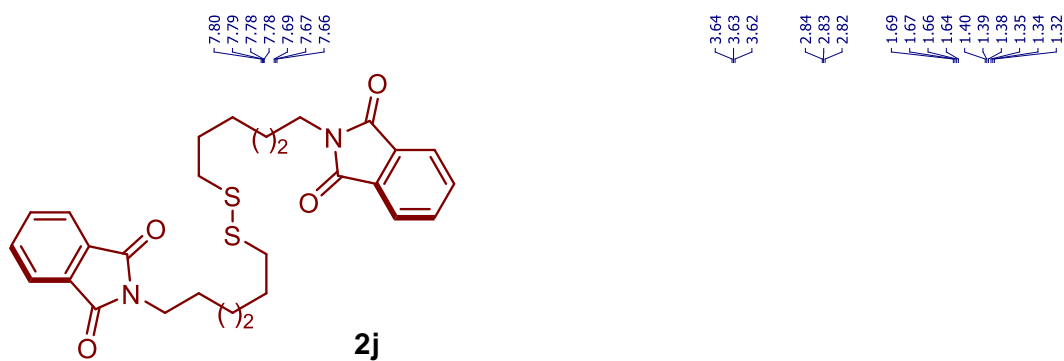
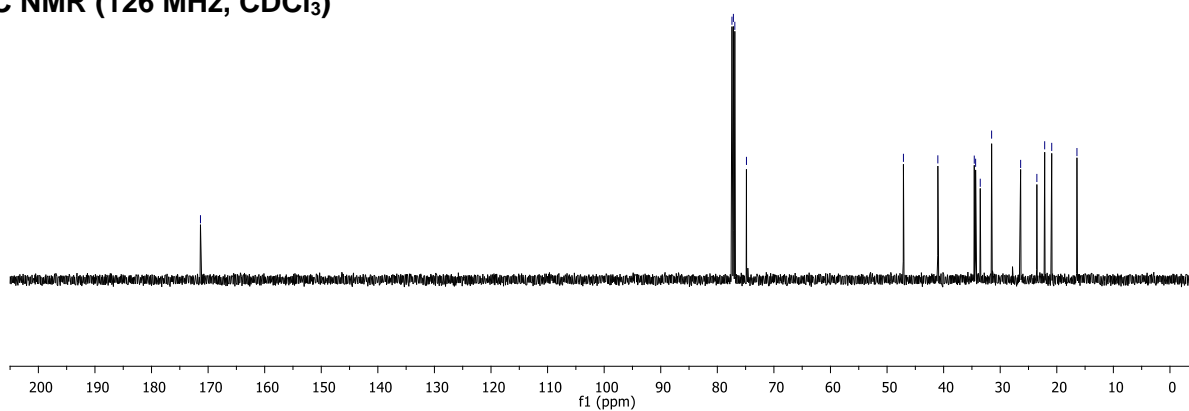
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¹H NMR (500 MHz, CDCl₃)

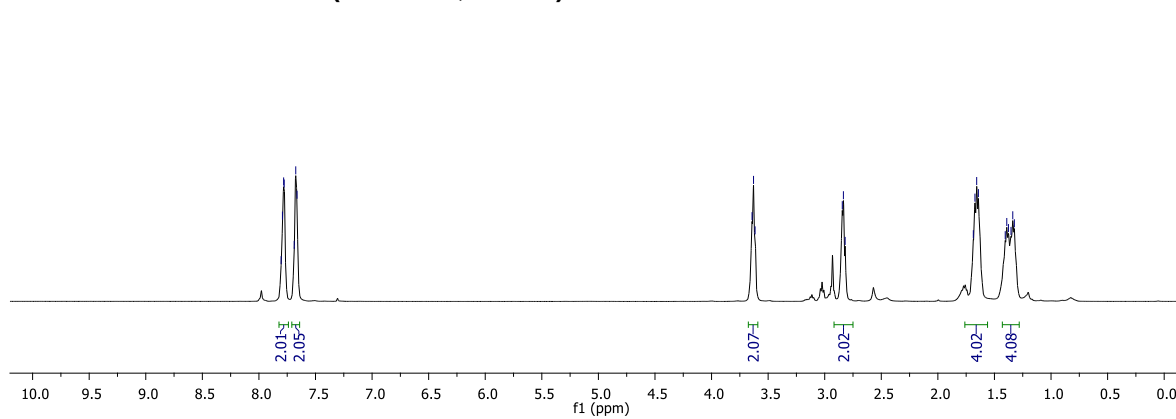


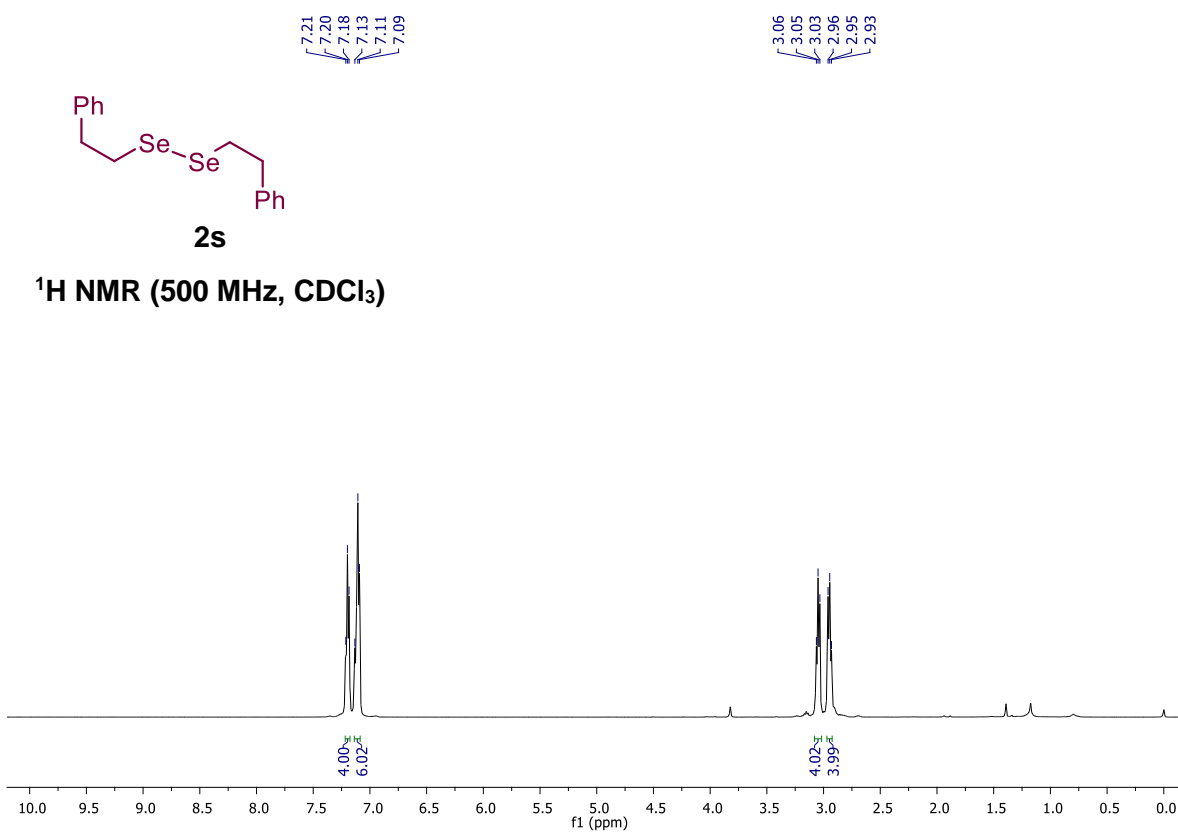
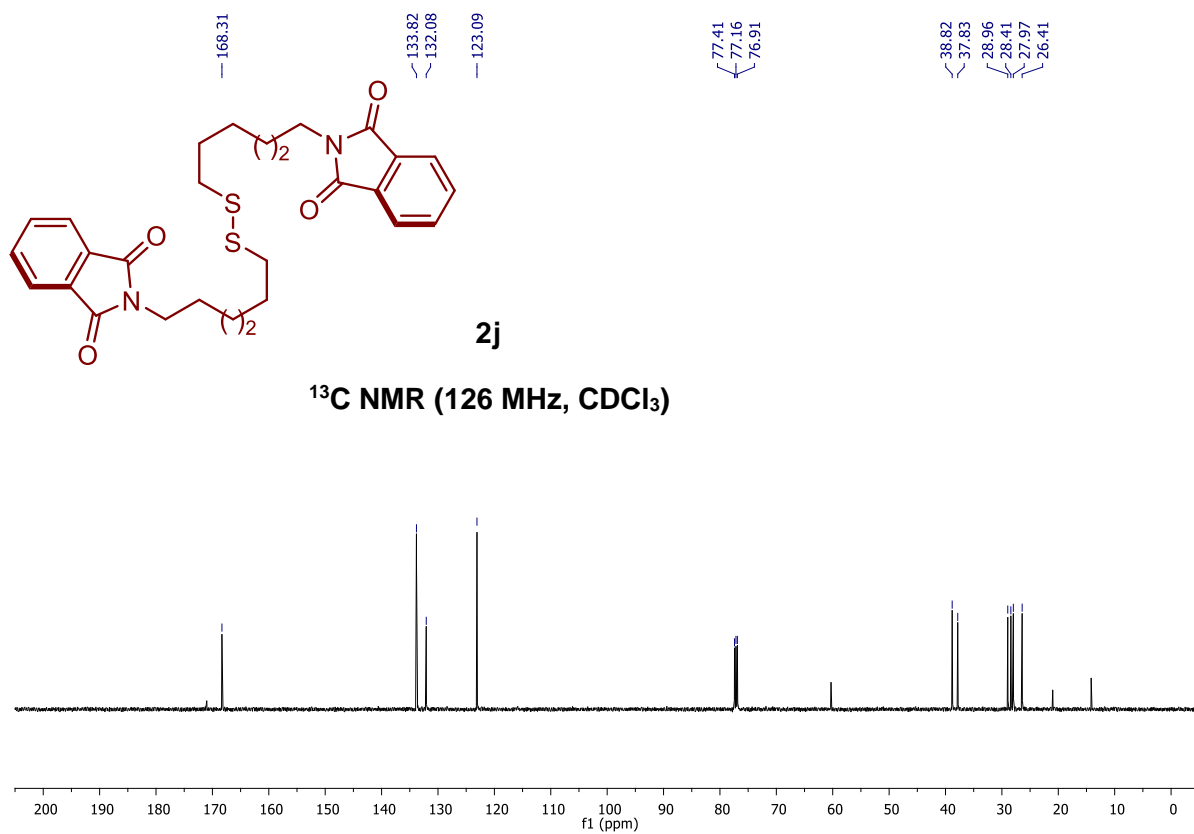


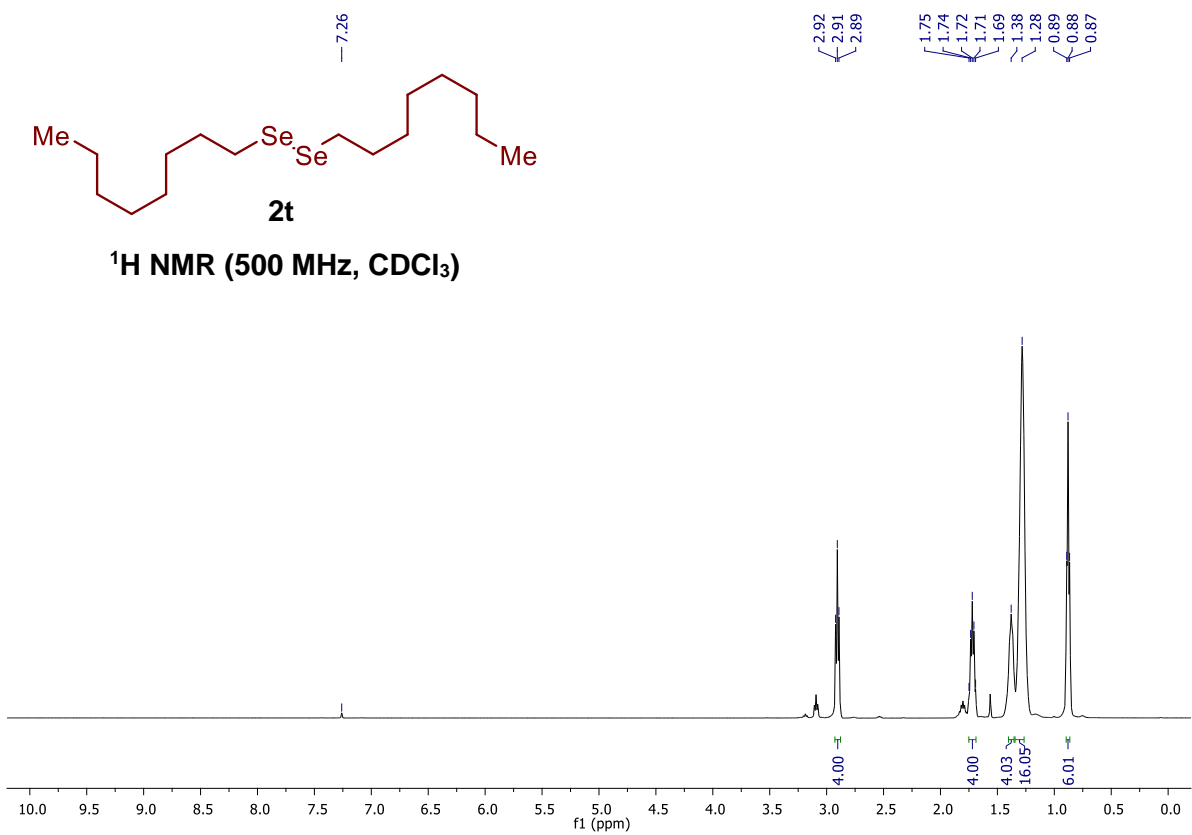
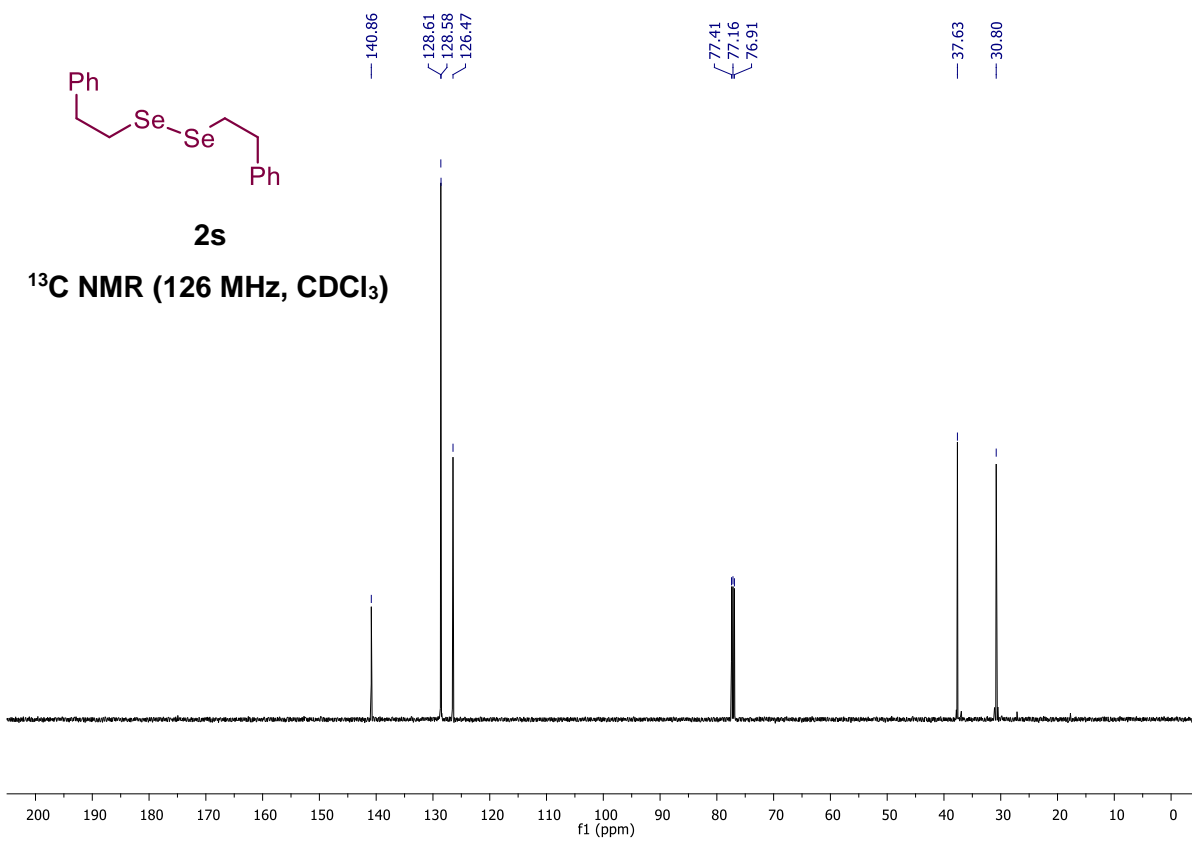
¹³C NMR (126 MHz, CDCl₃)

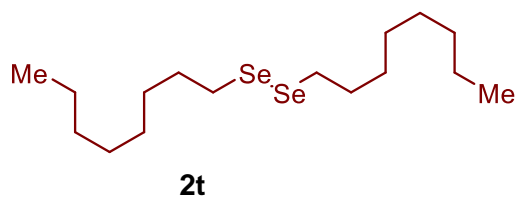


¹H NMR (500 MHz, CDCl₃)

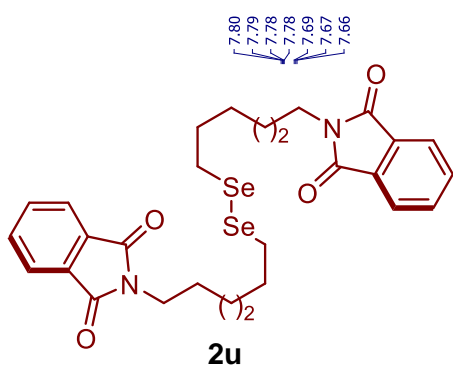
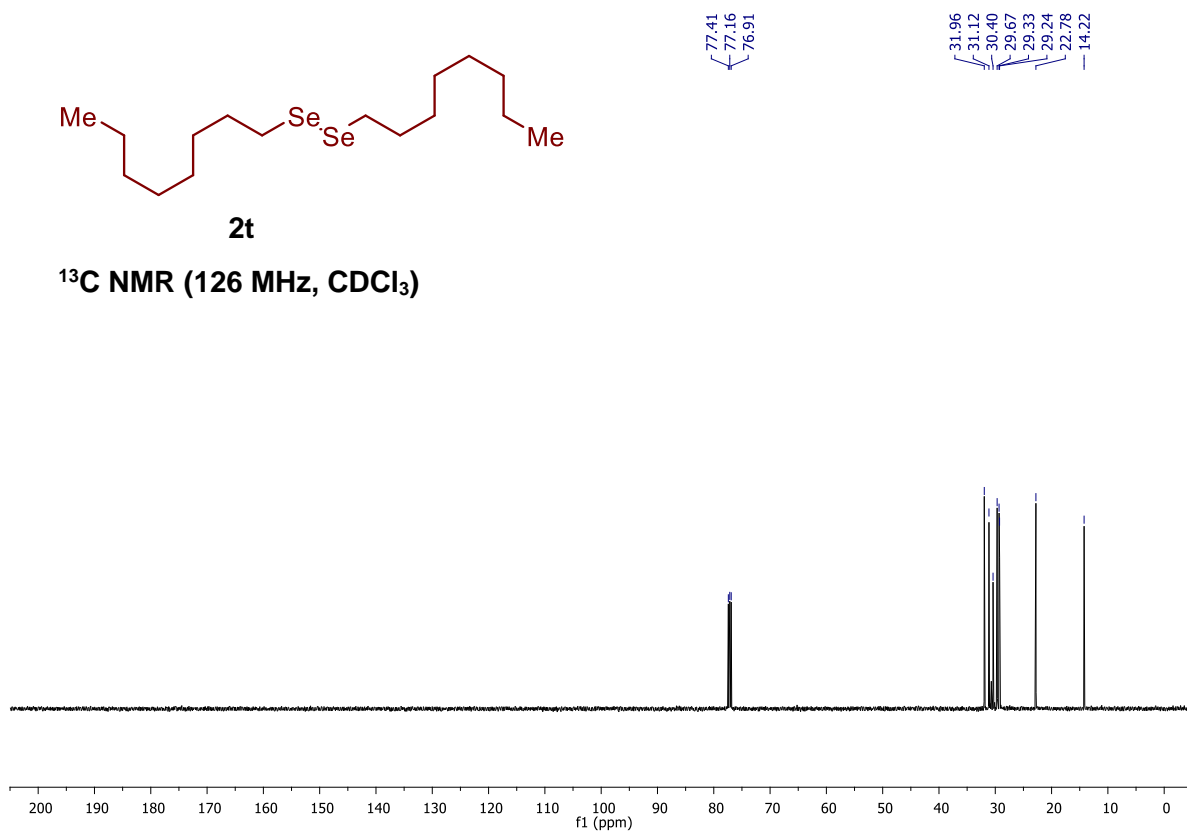




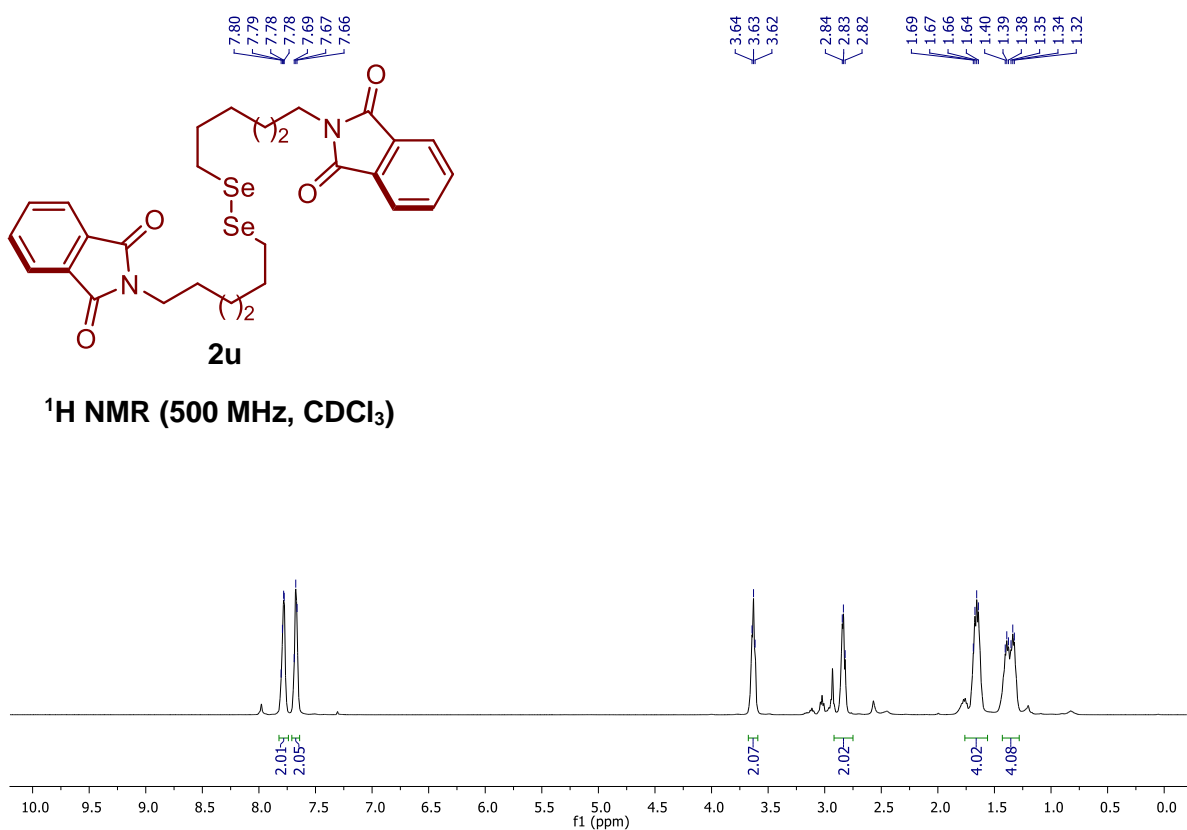


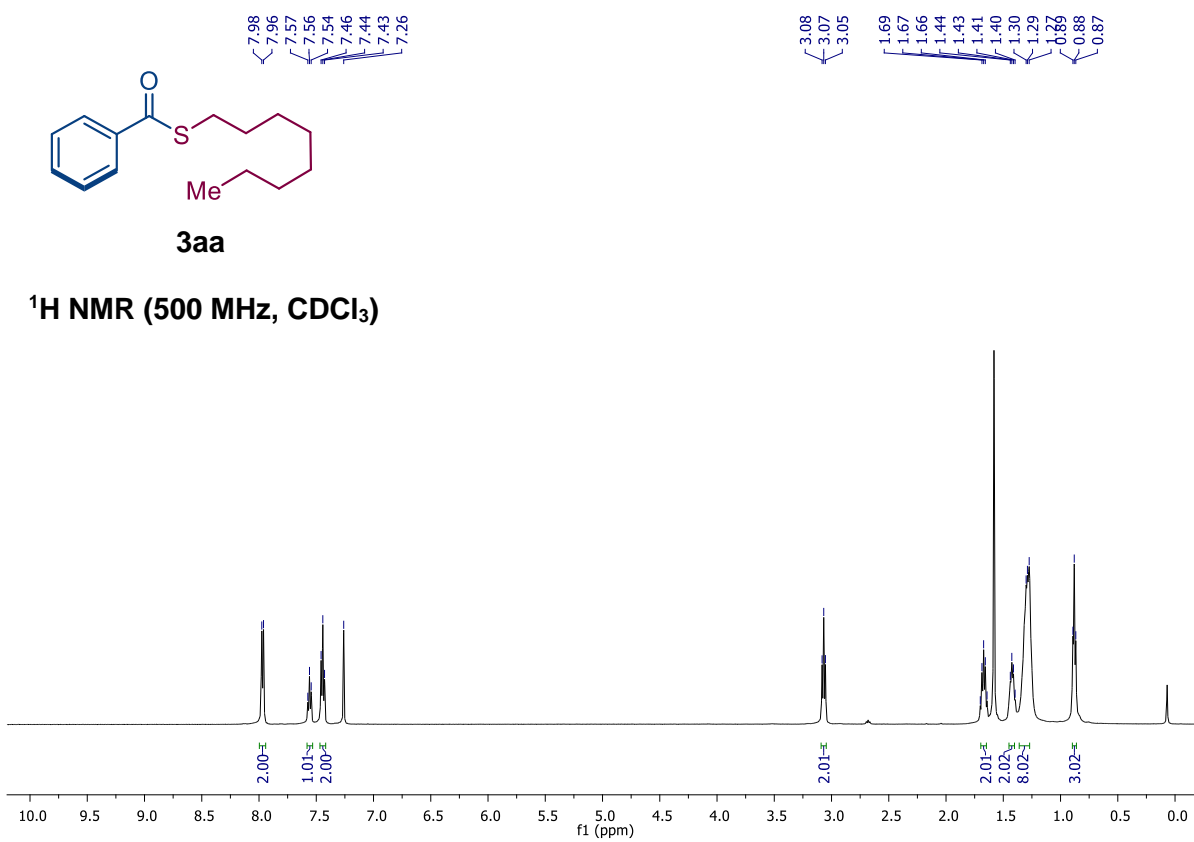
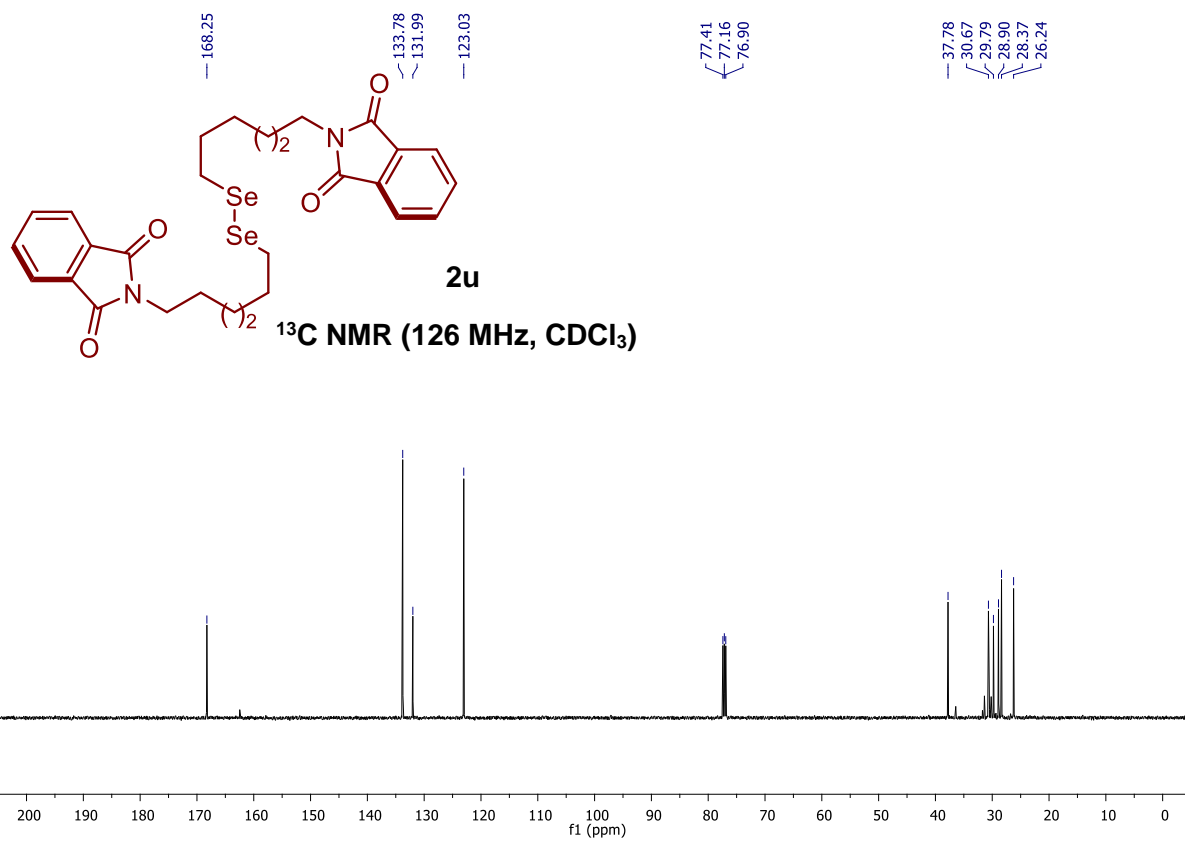


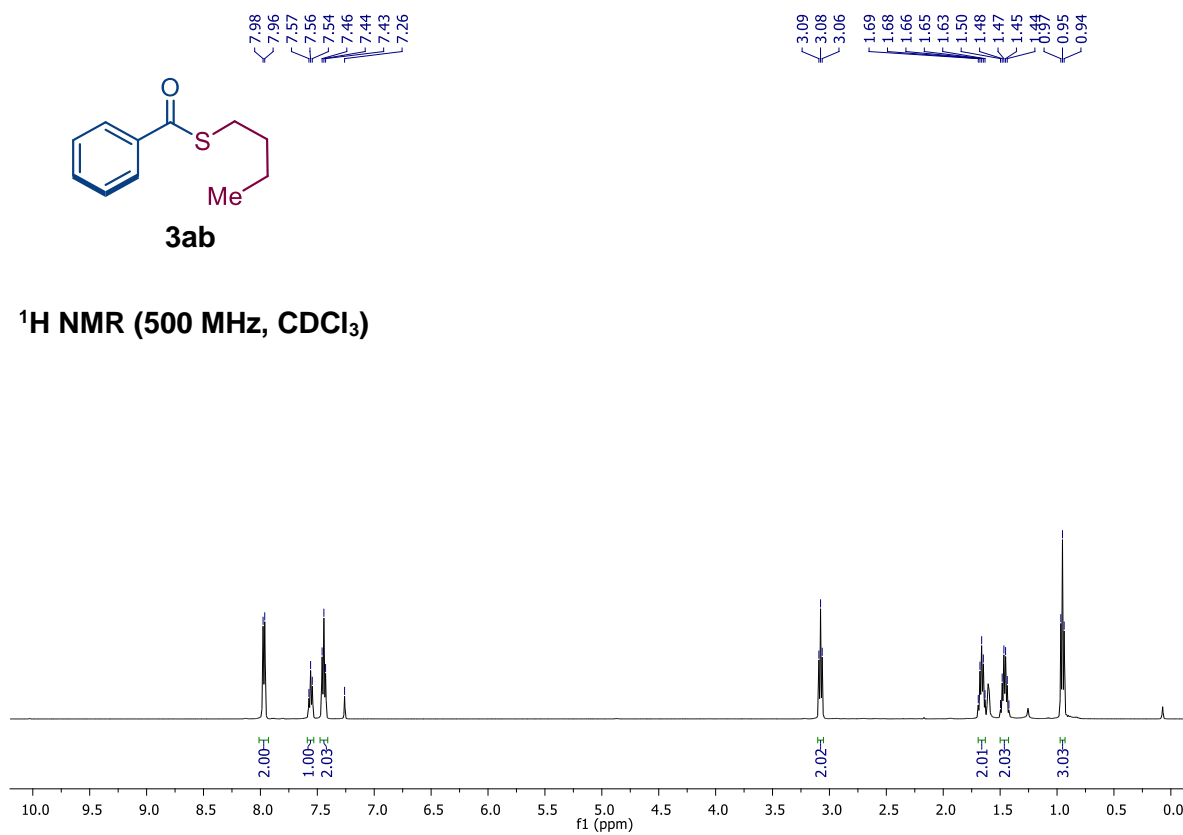
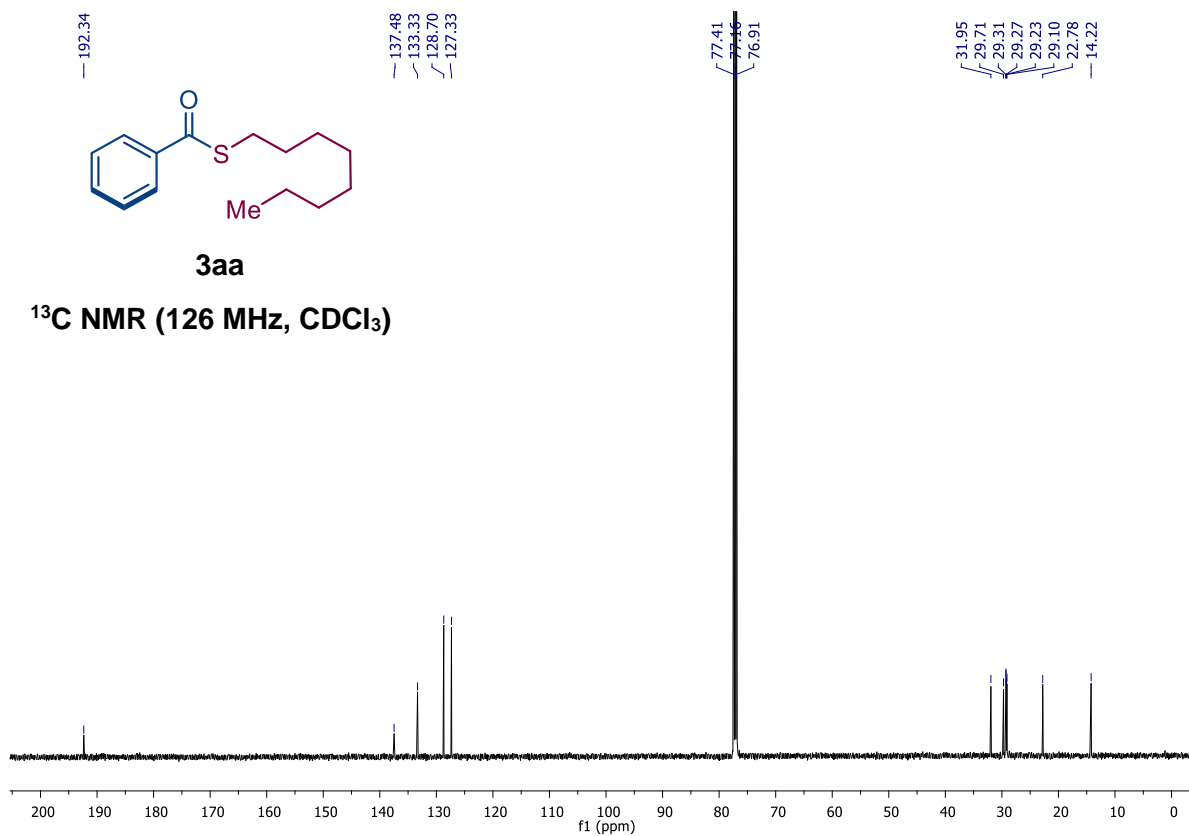
¹³C NMR (126 MHz, CDCl₃)



¹H NMR (500 MHz, CDCl₃)

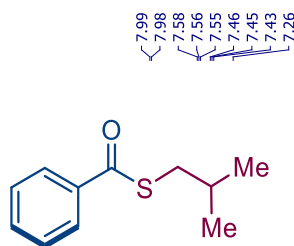
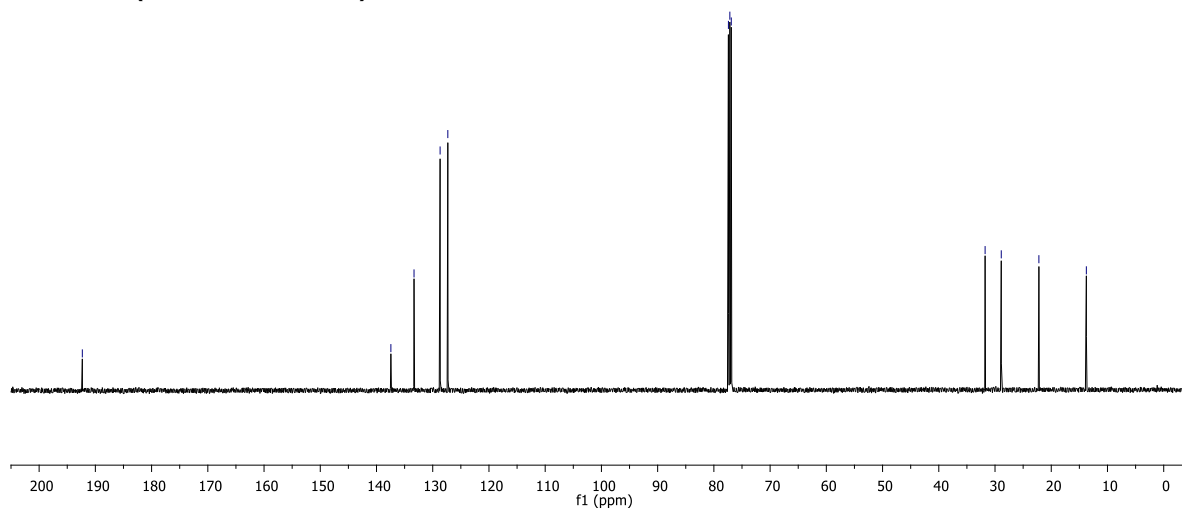




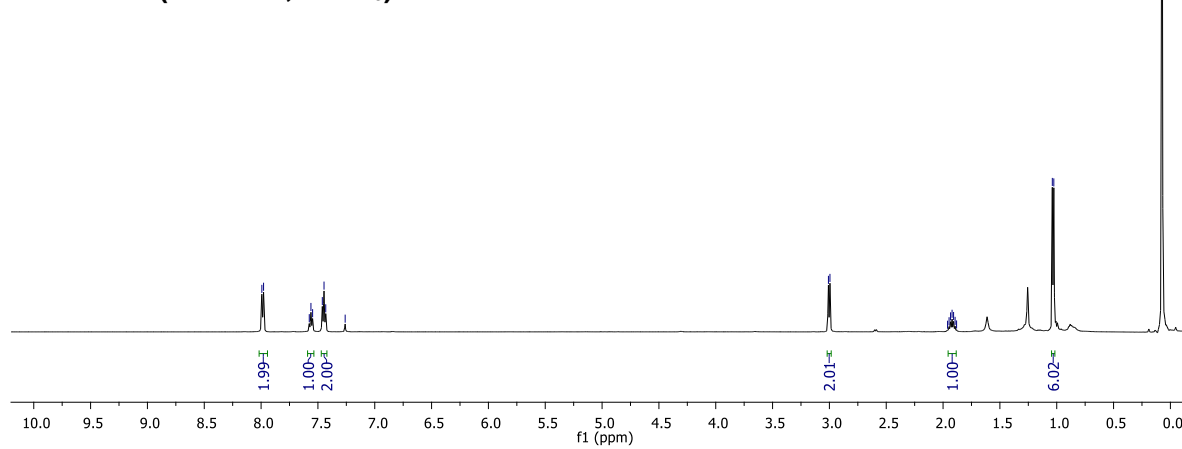


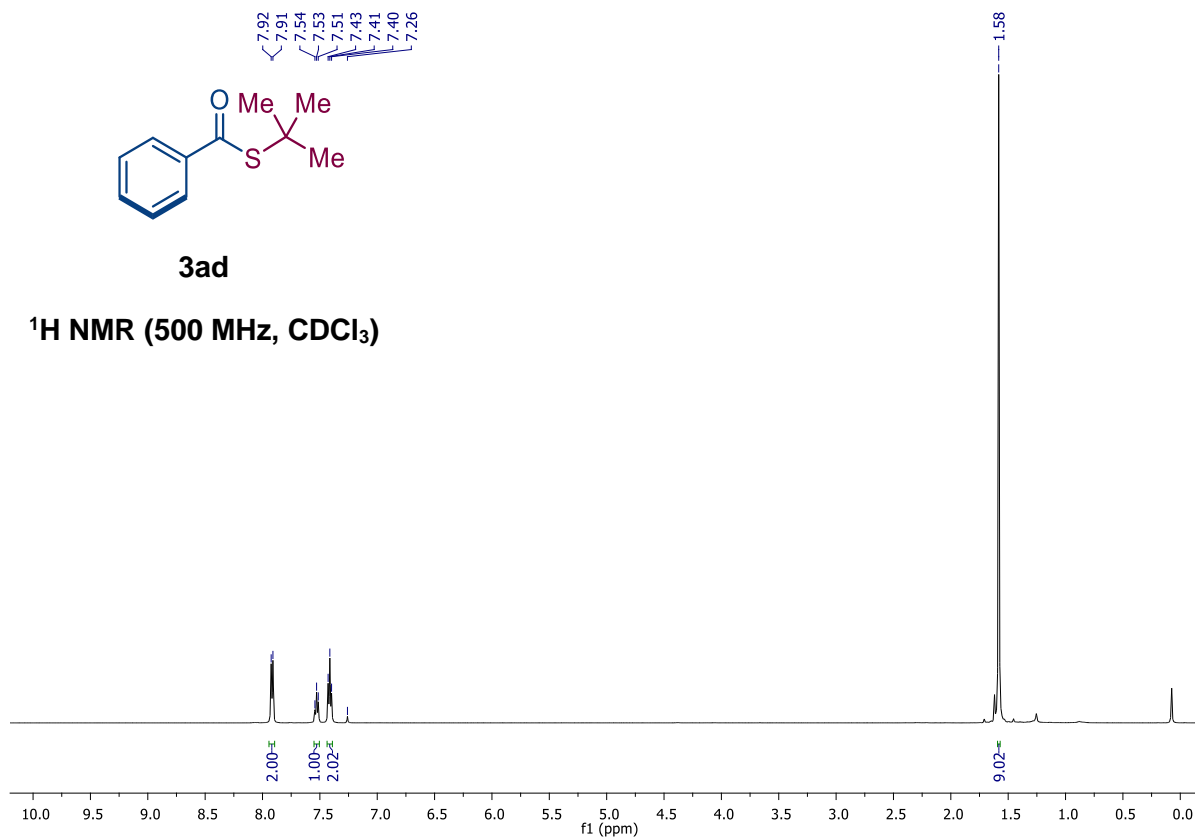
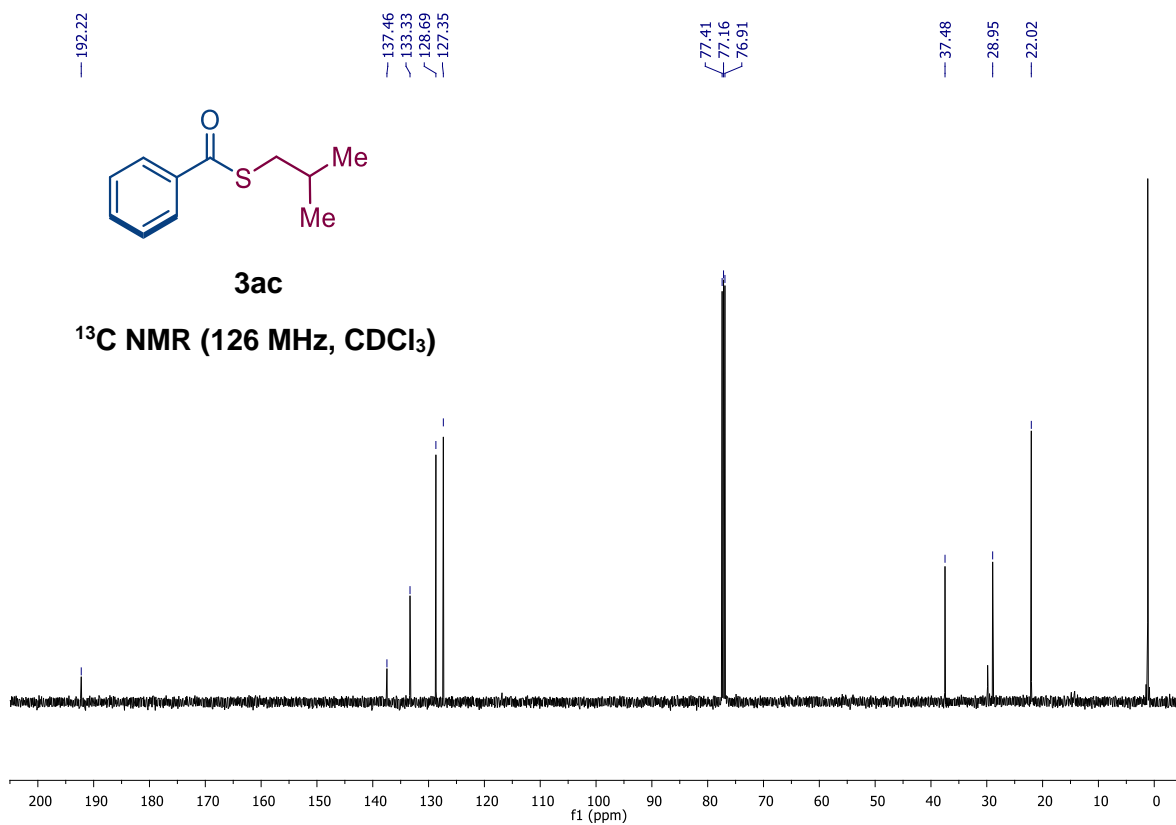


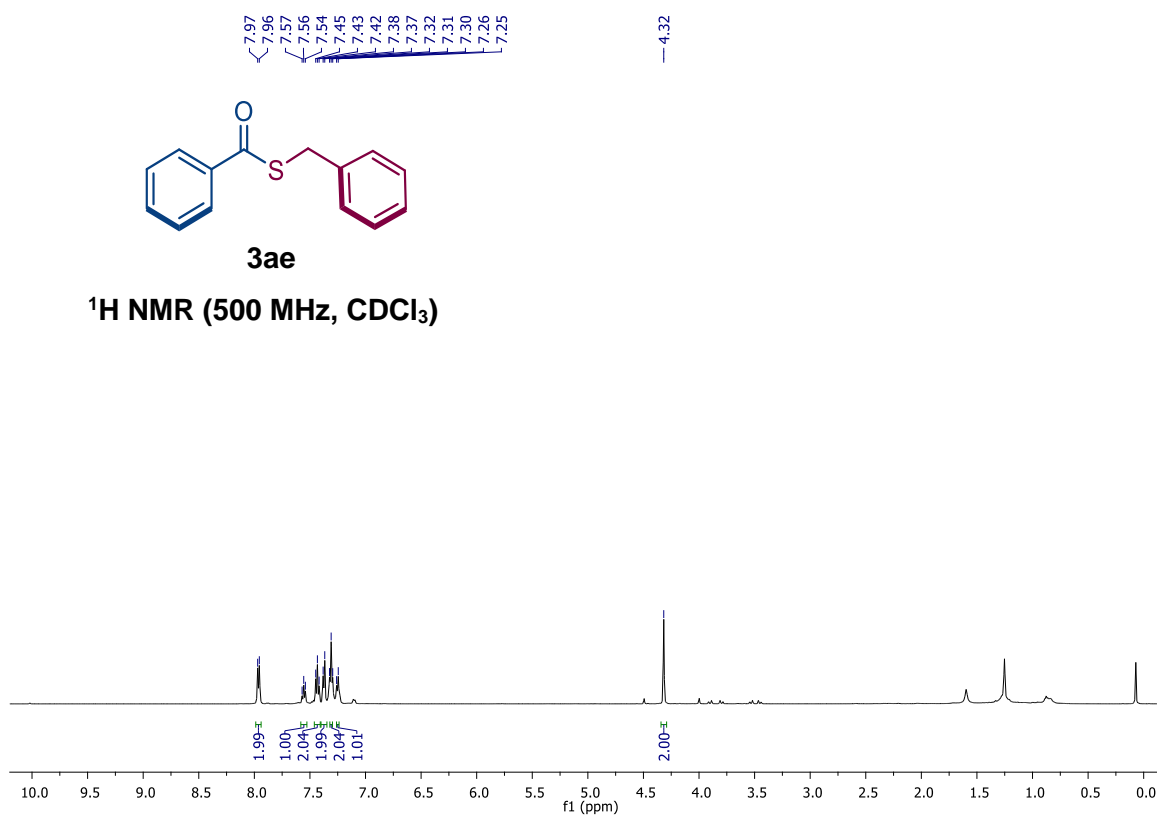
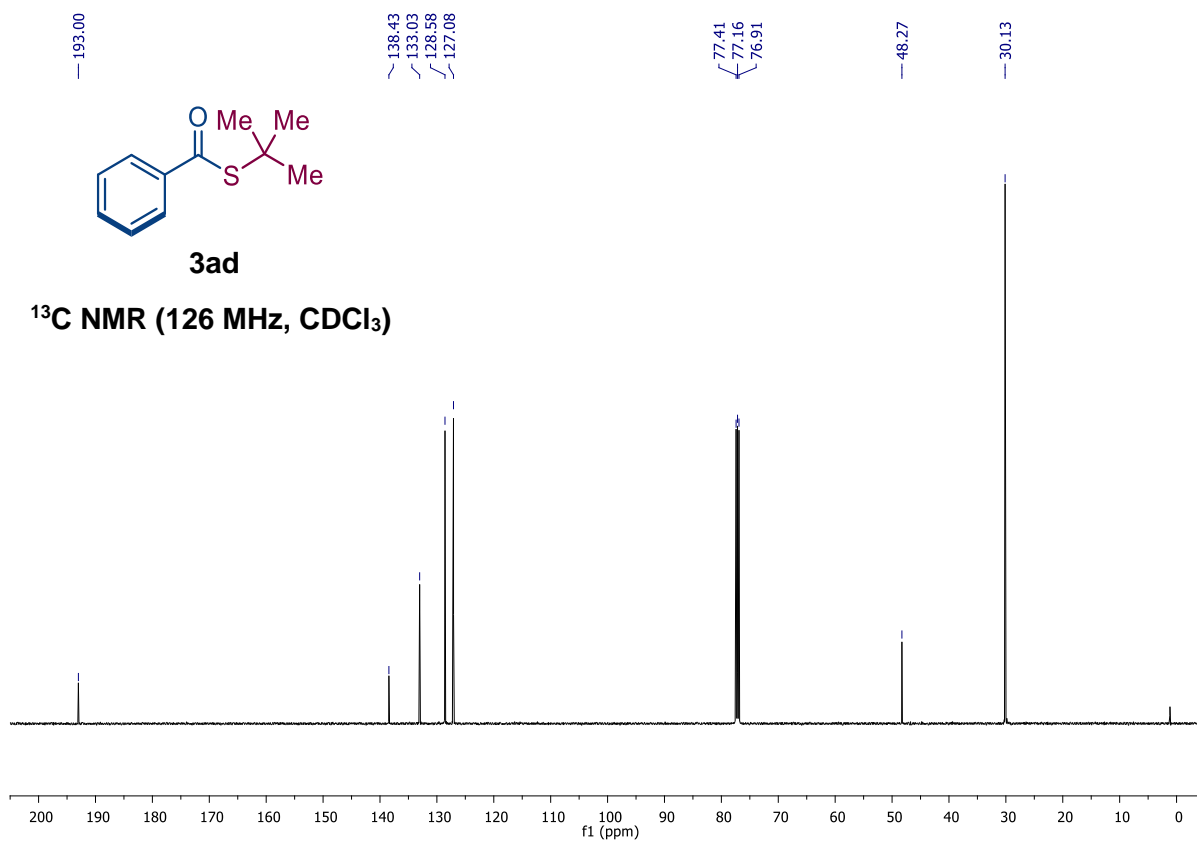
^{13}C NMR (126 MHz, CDCl_3)

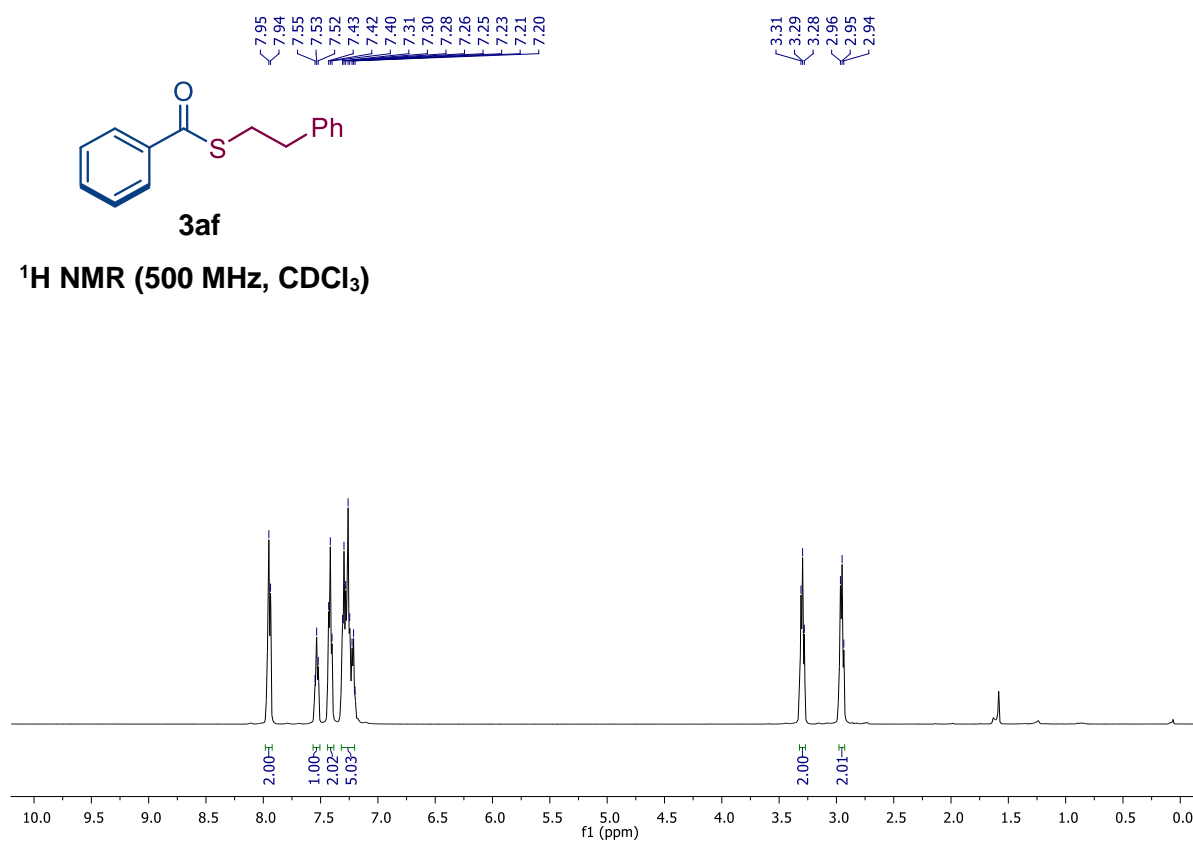
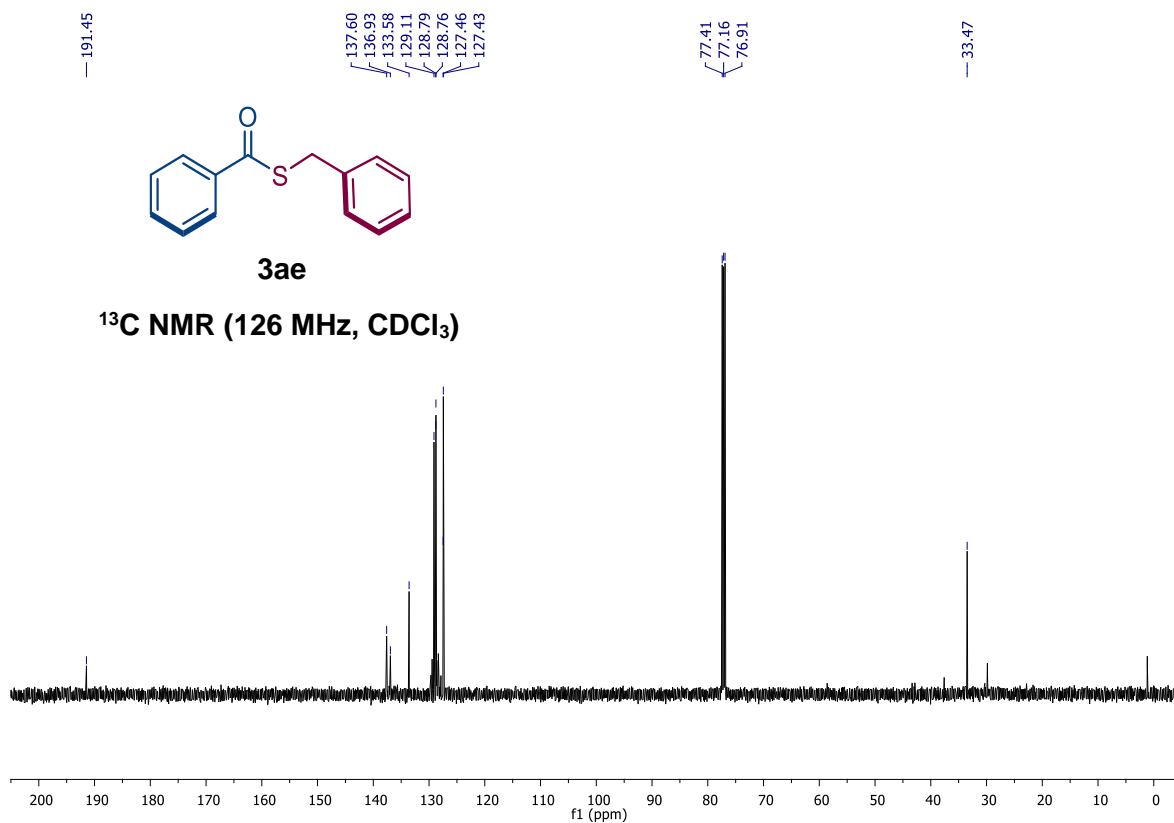


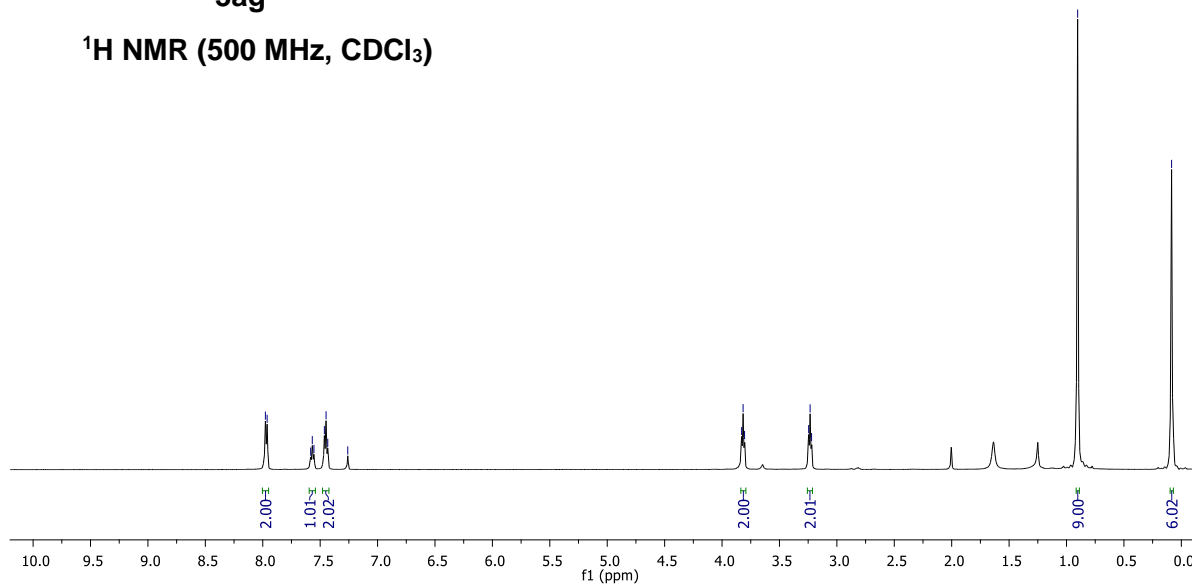
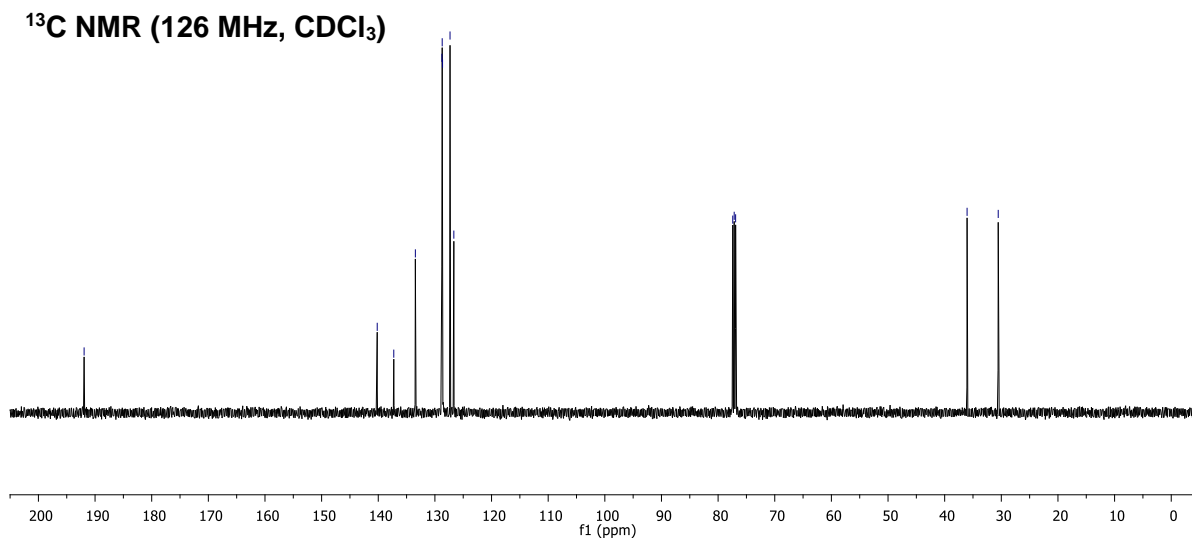
^1H NMR (500 MHz, CDCl_3)

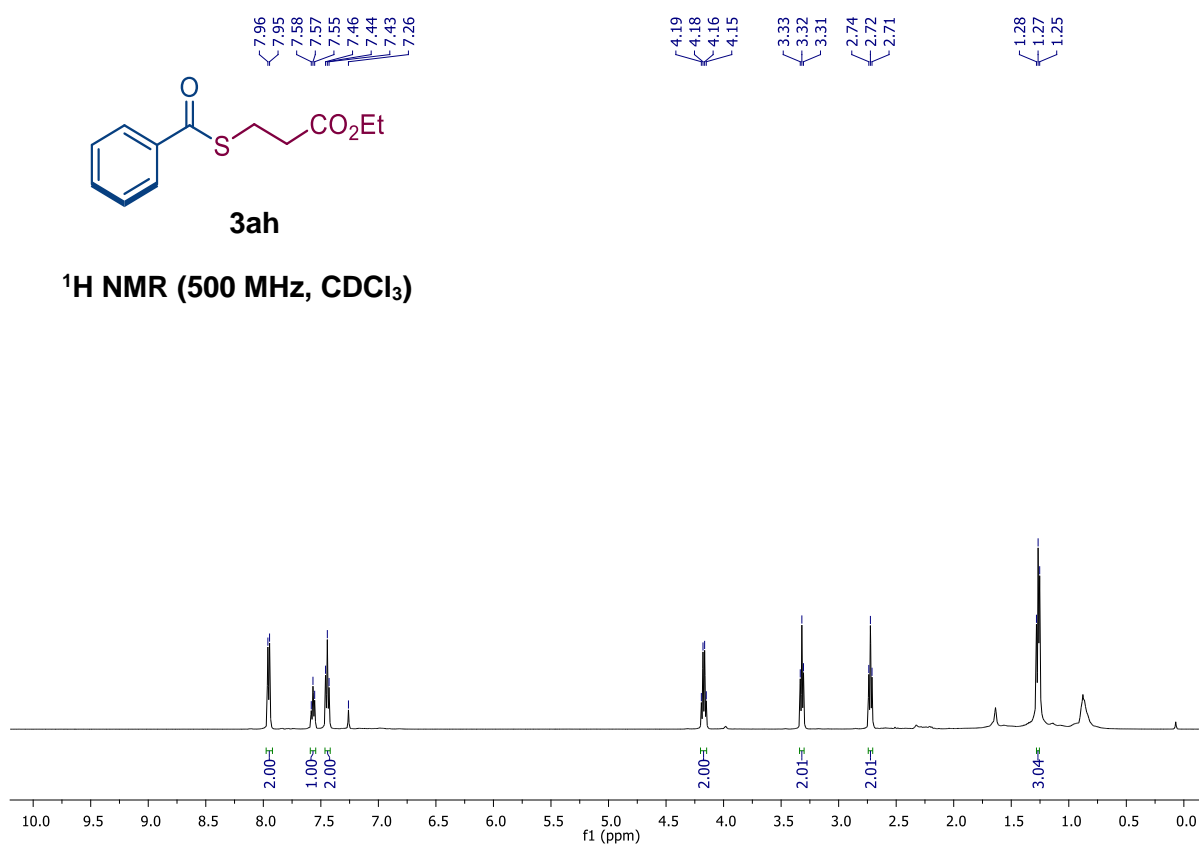
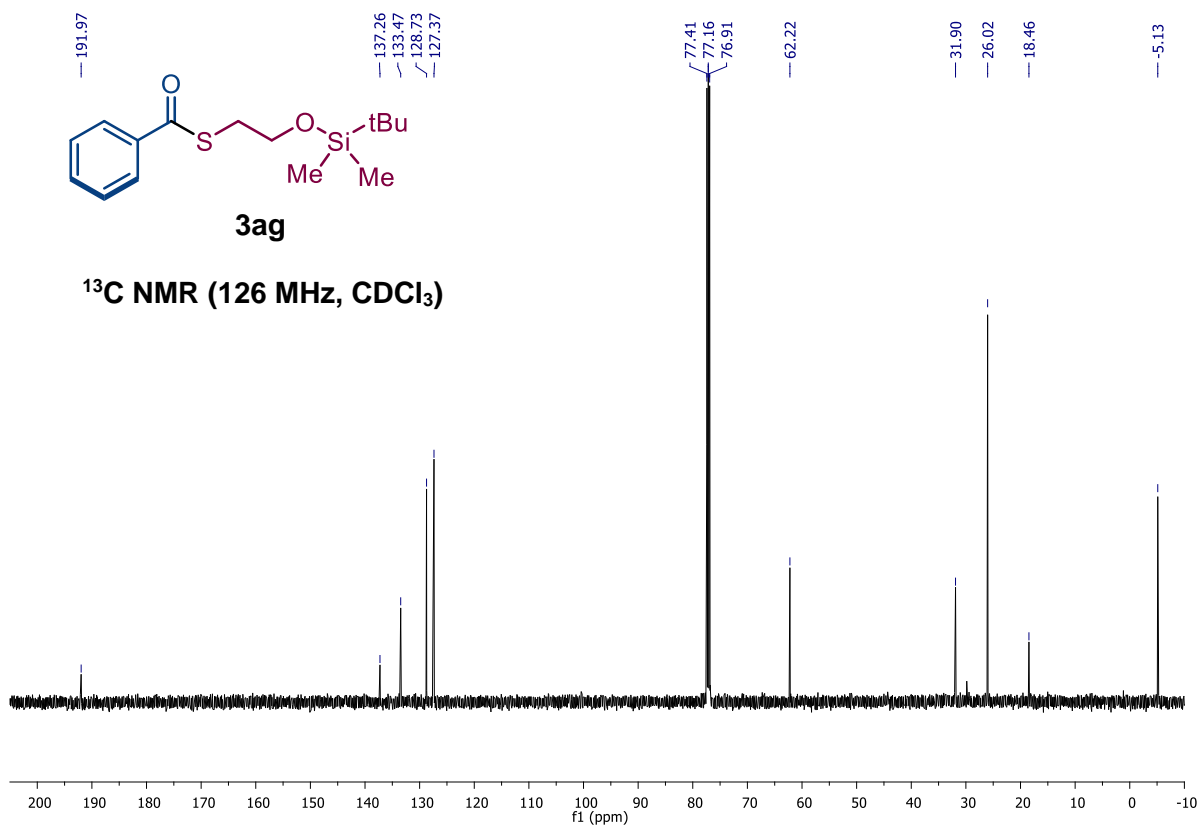


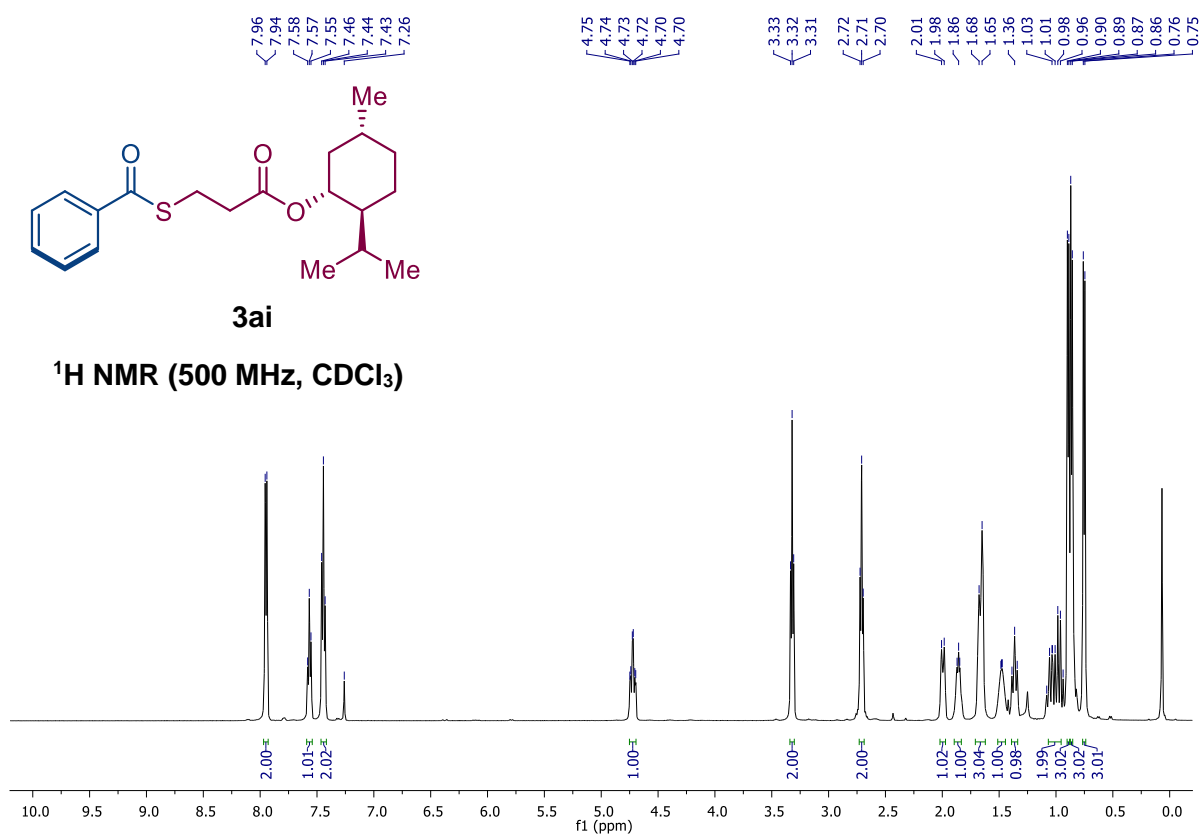
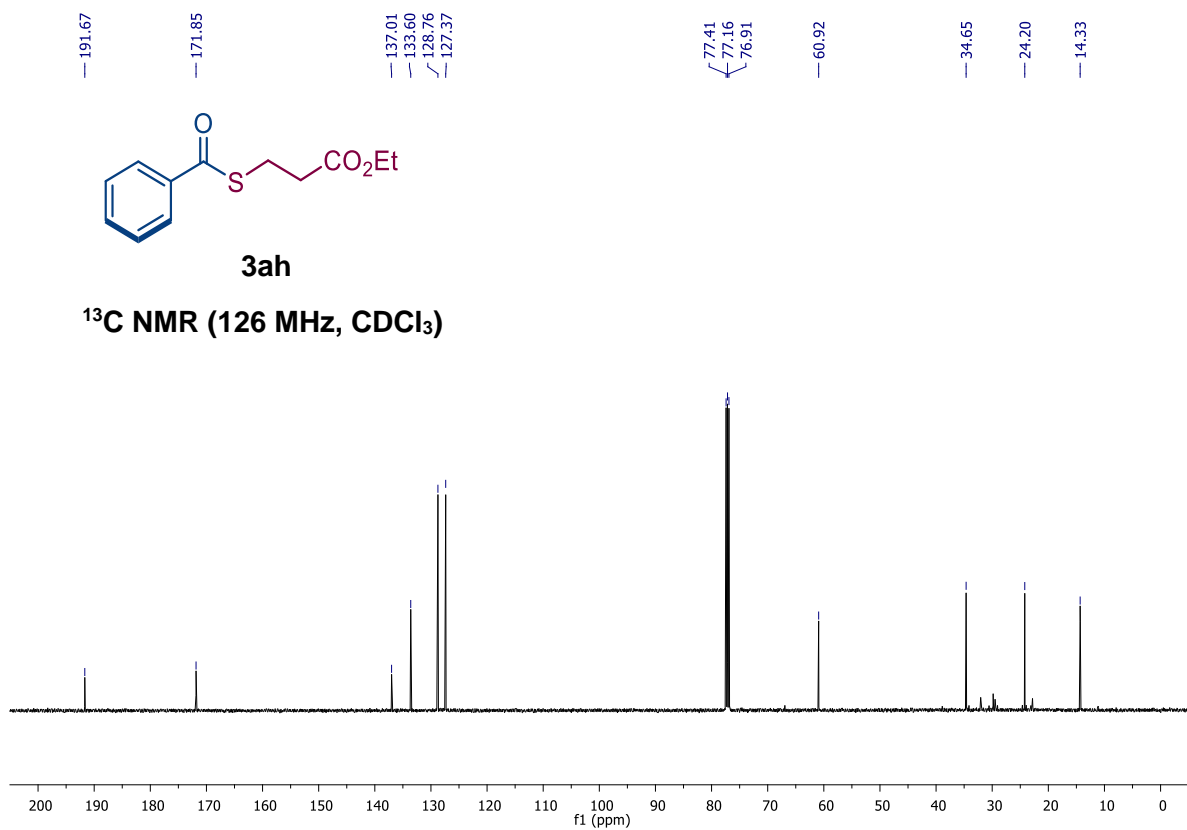


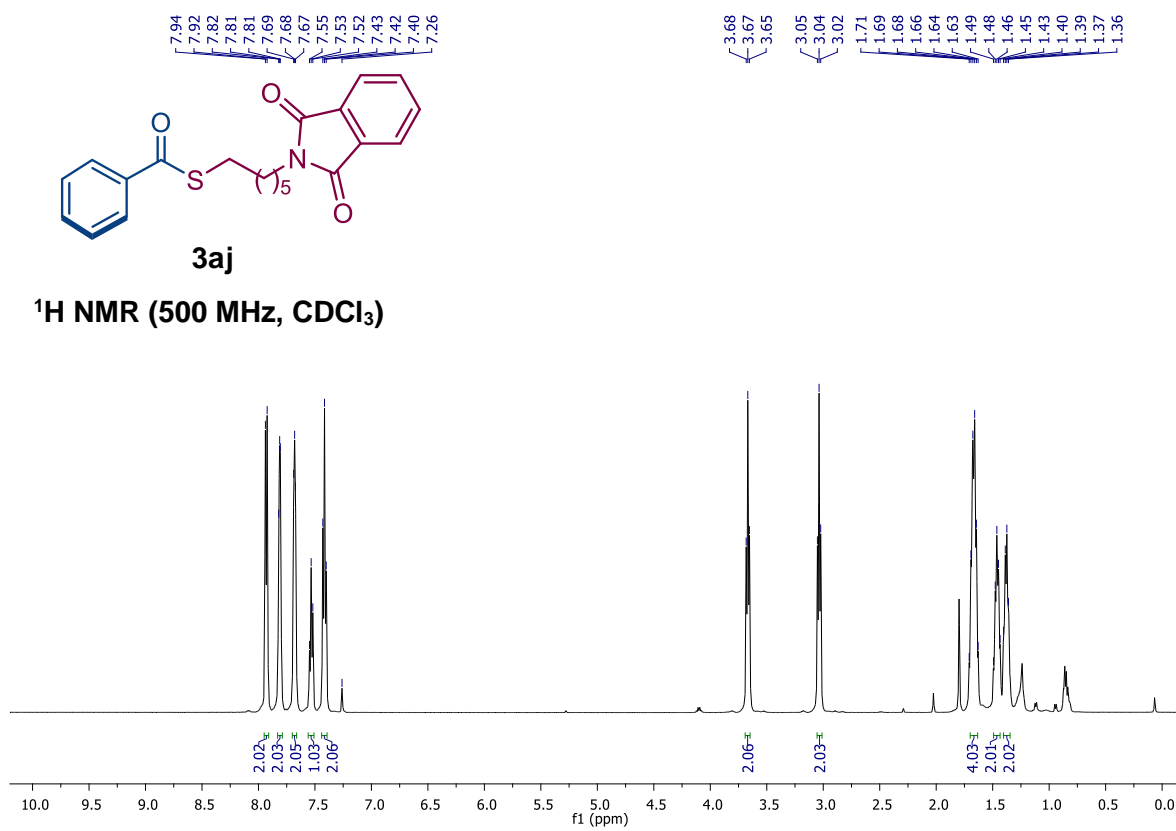
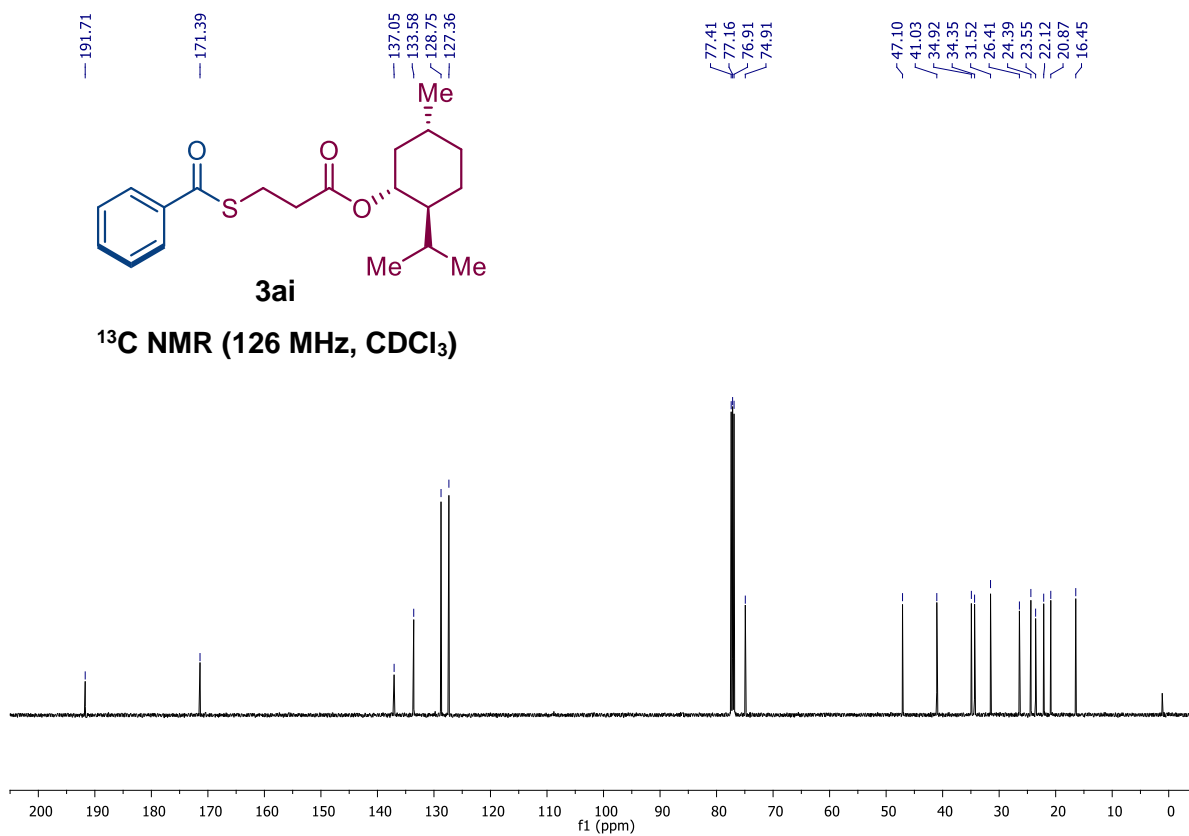


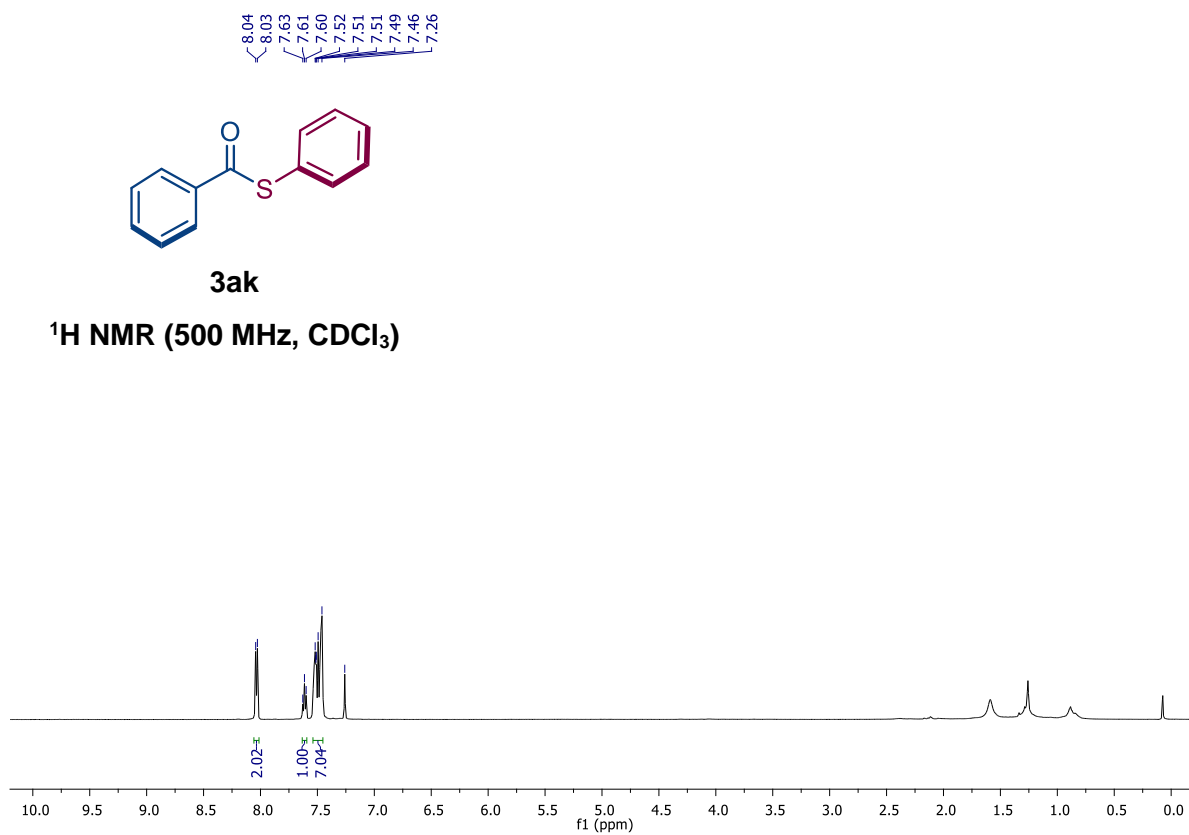
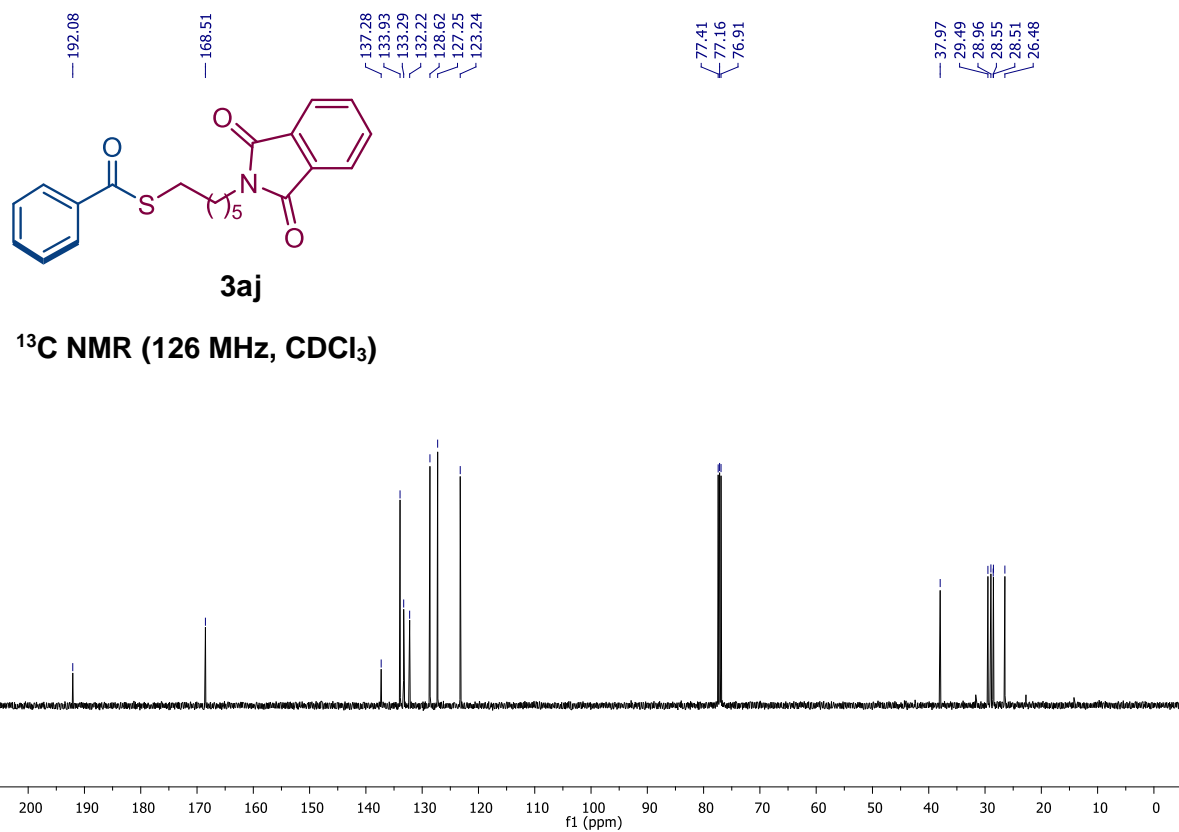


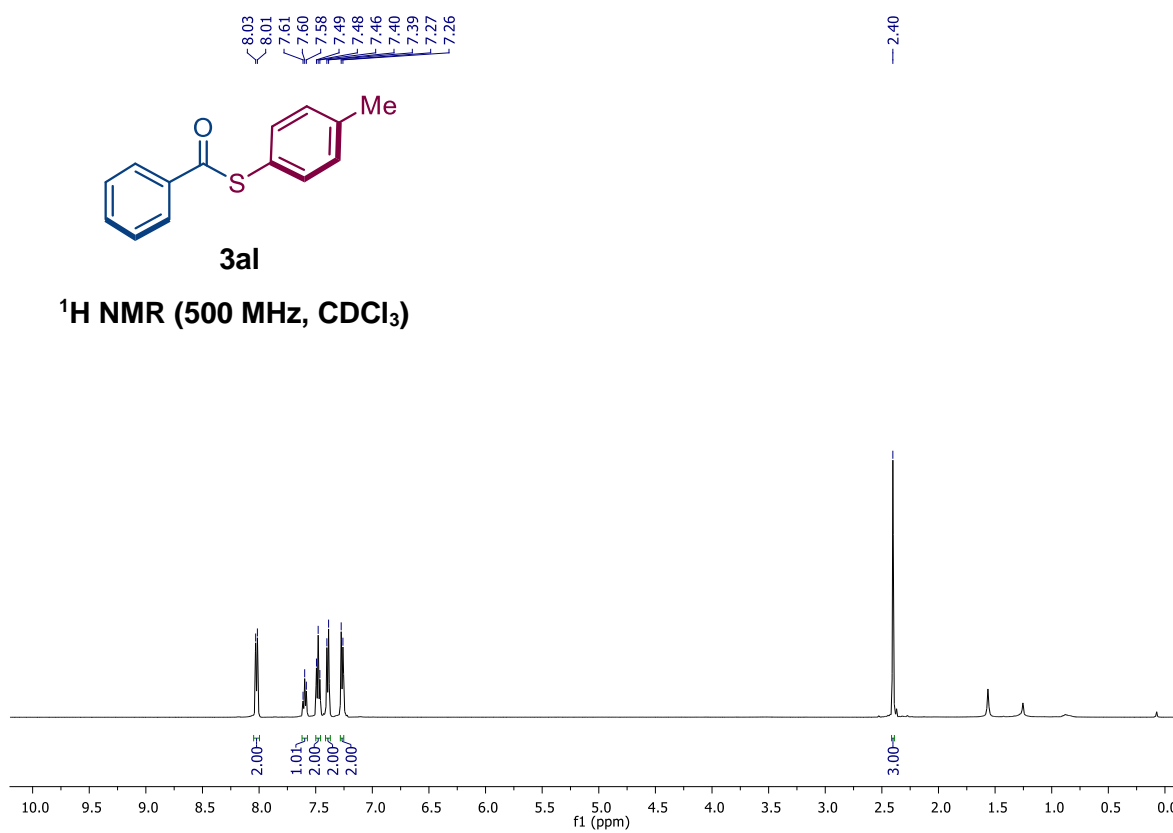
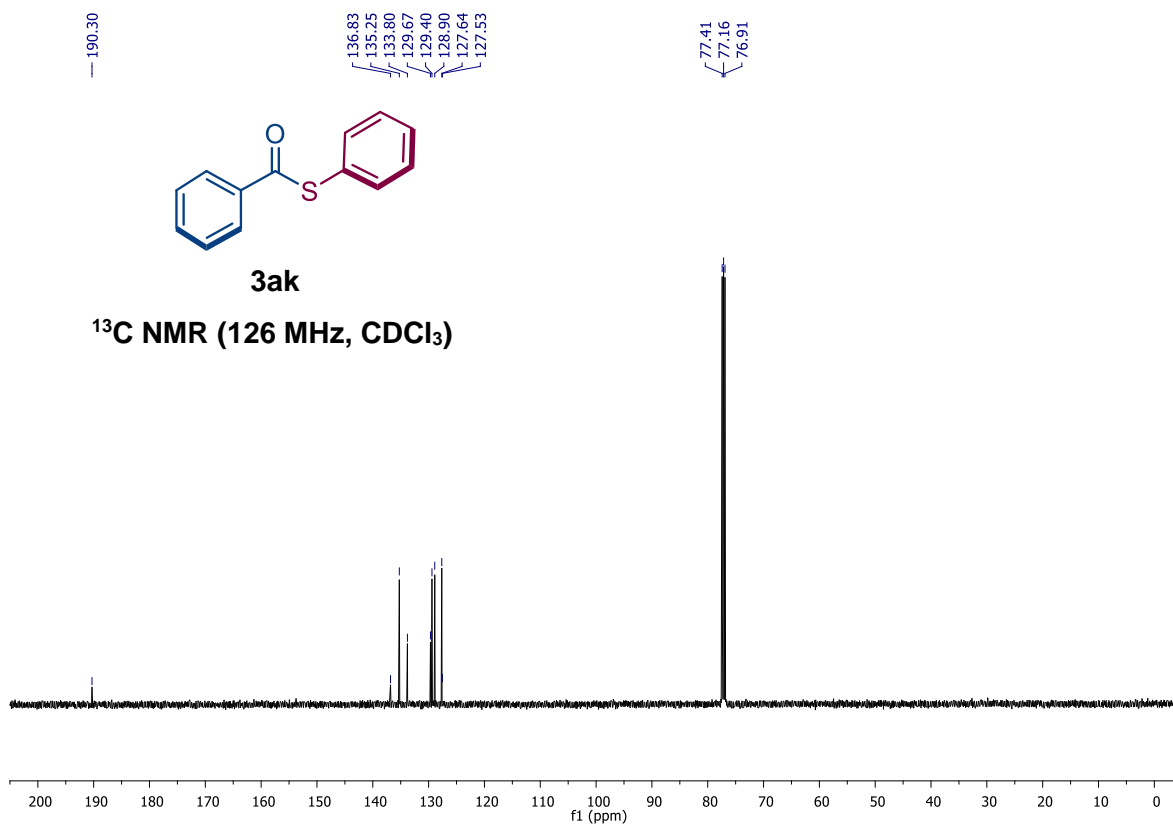


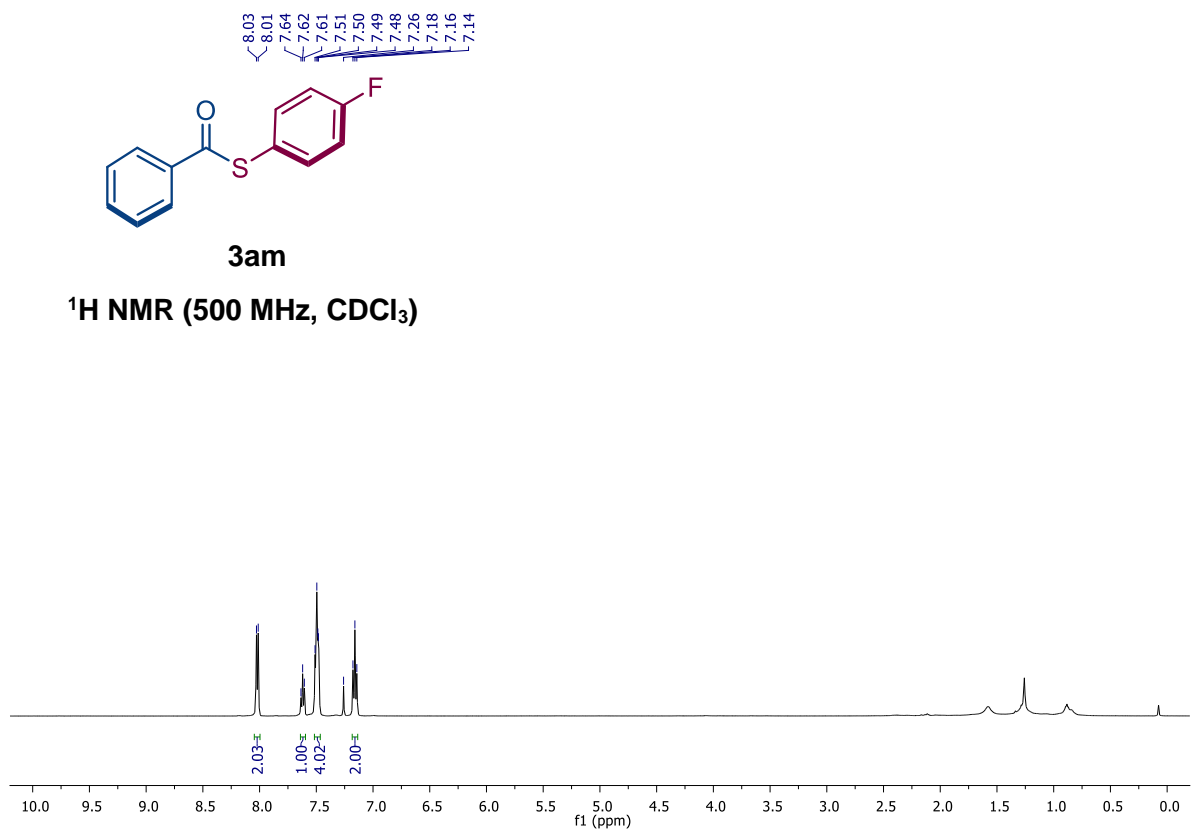
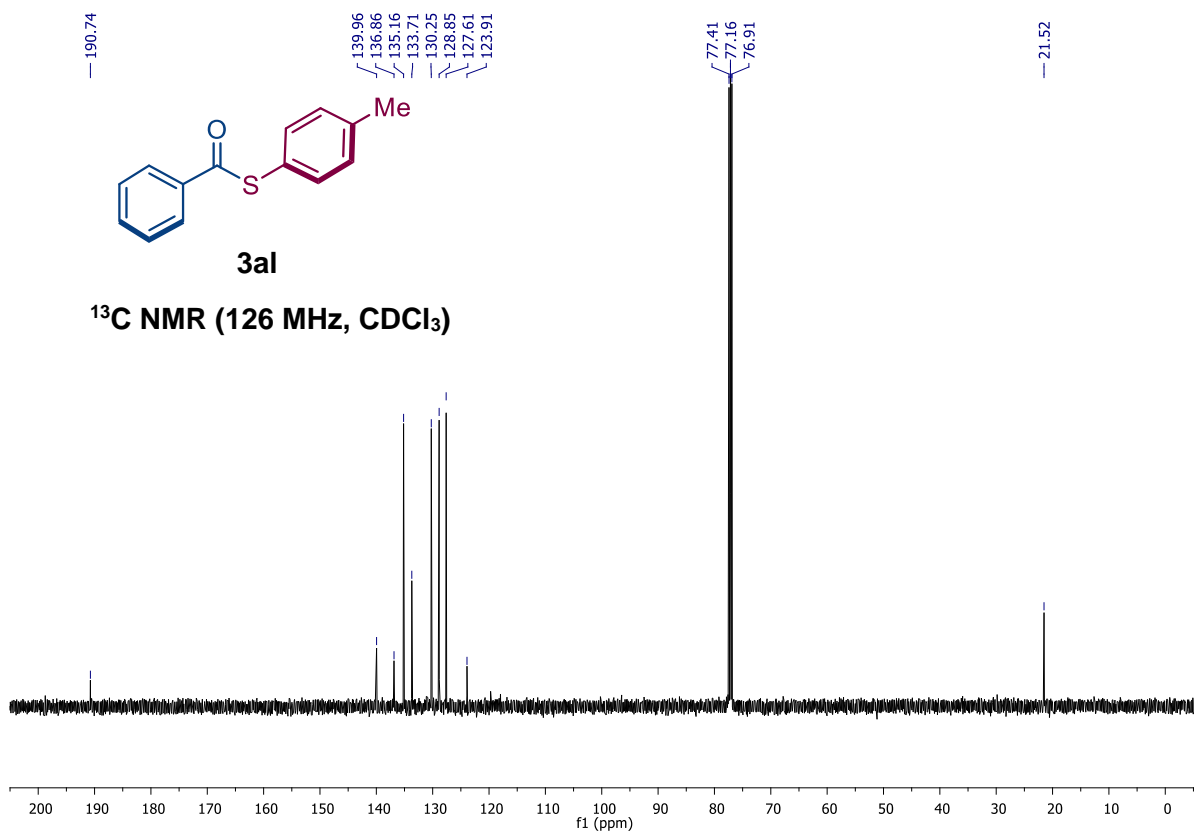


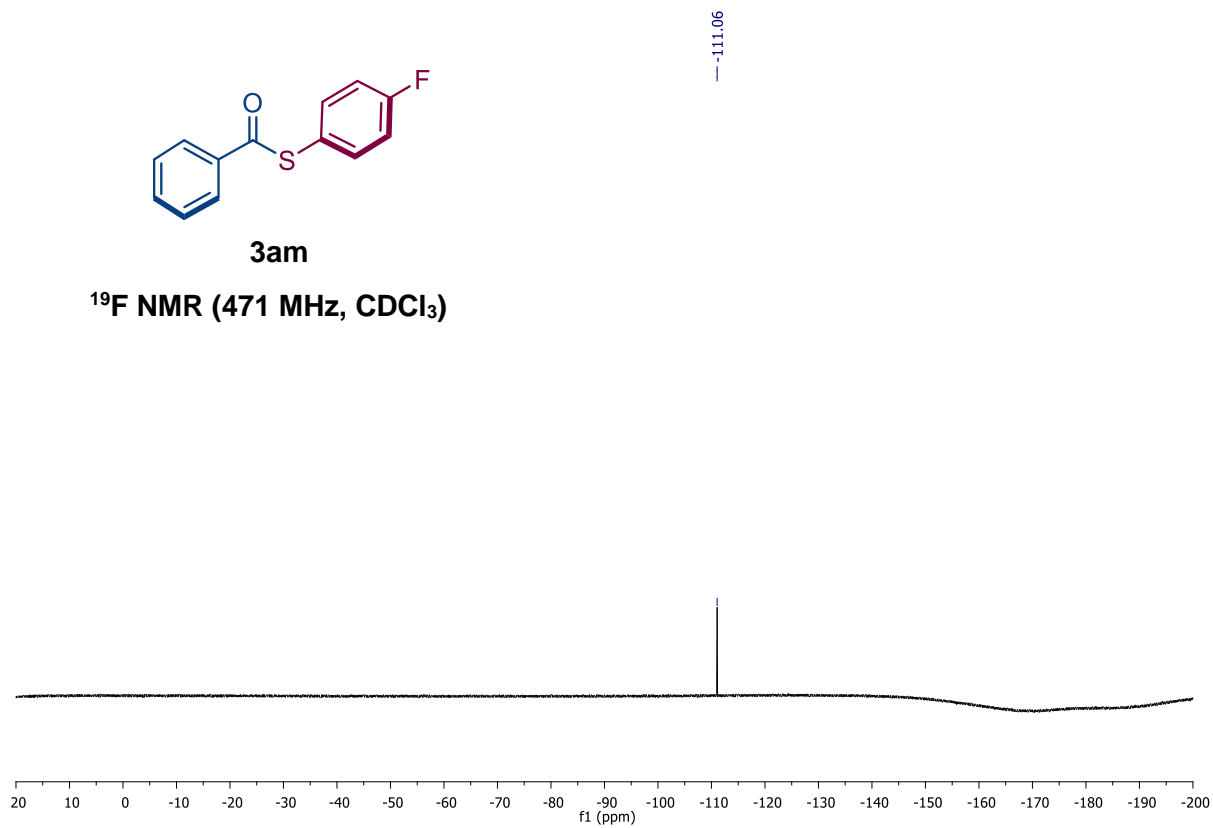
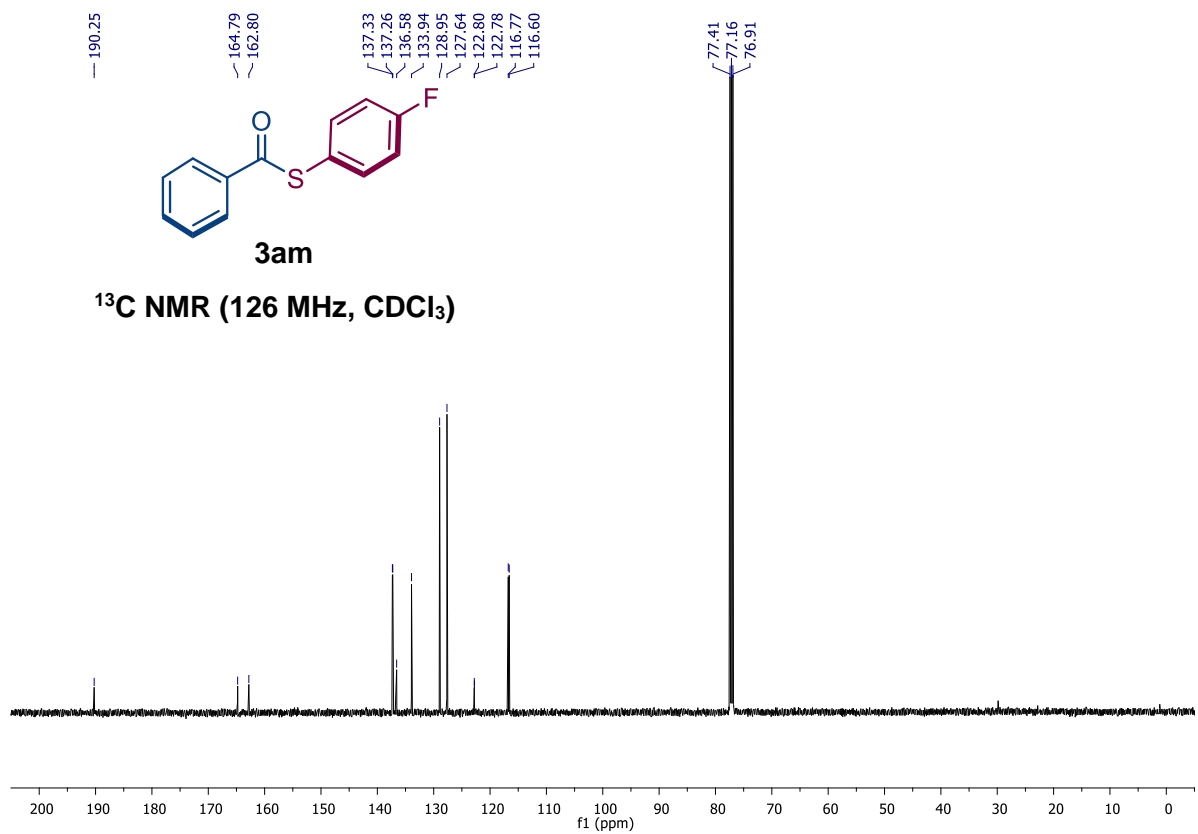


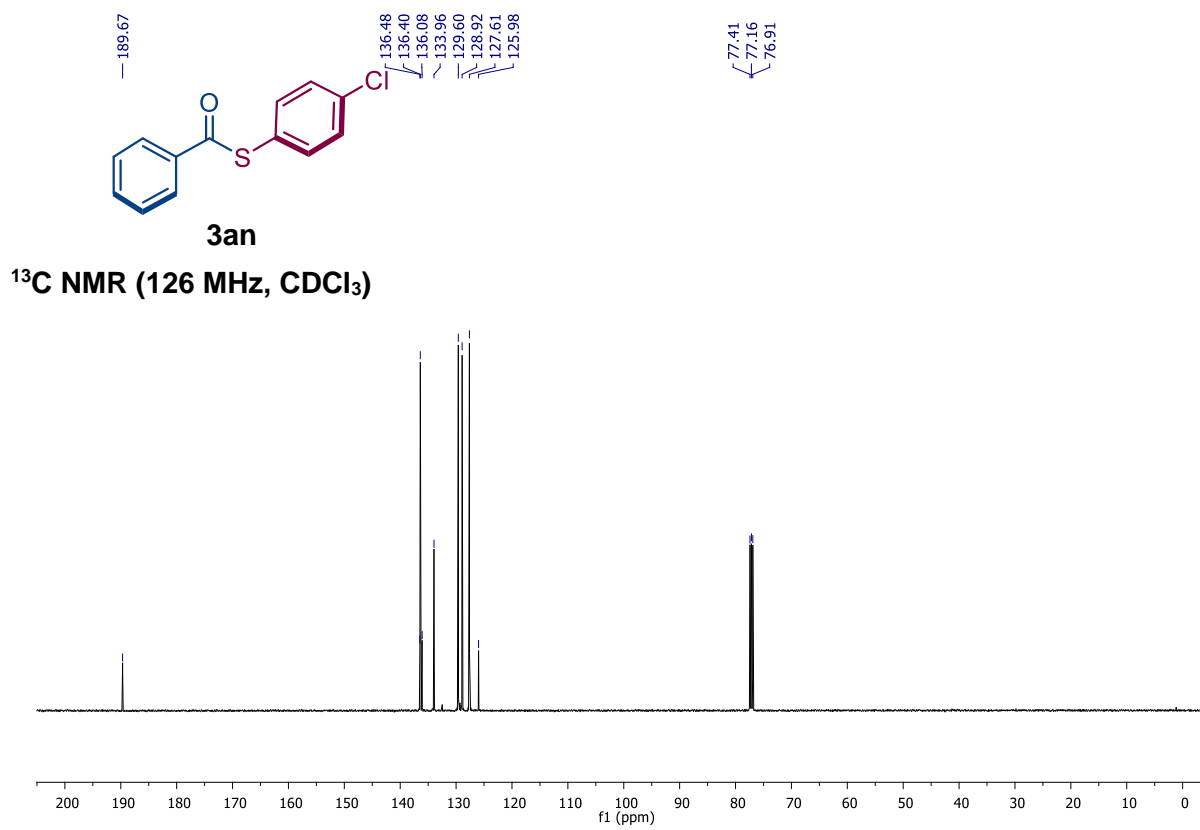
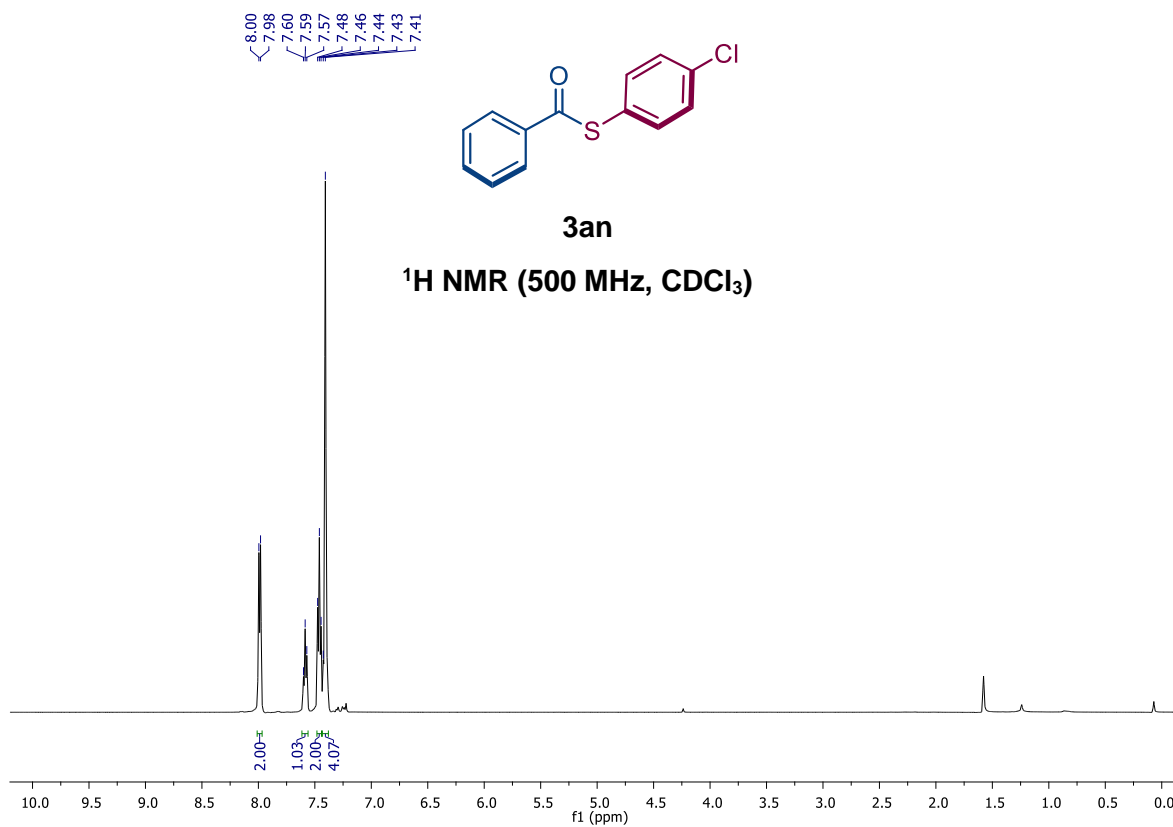


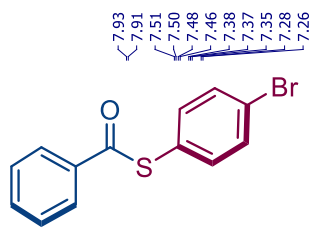






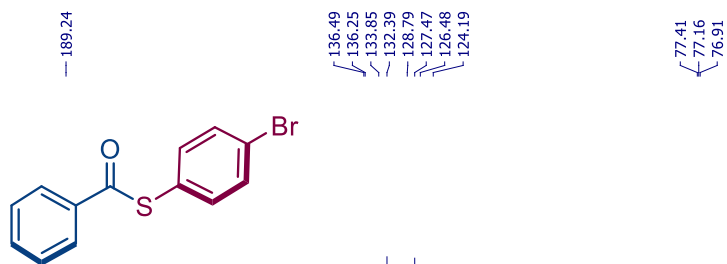
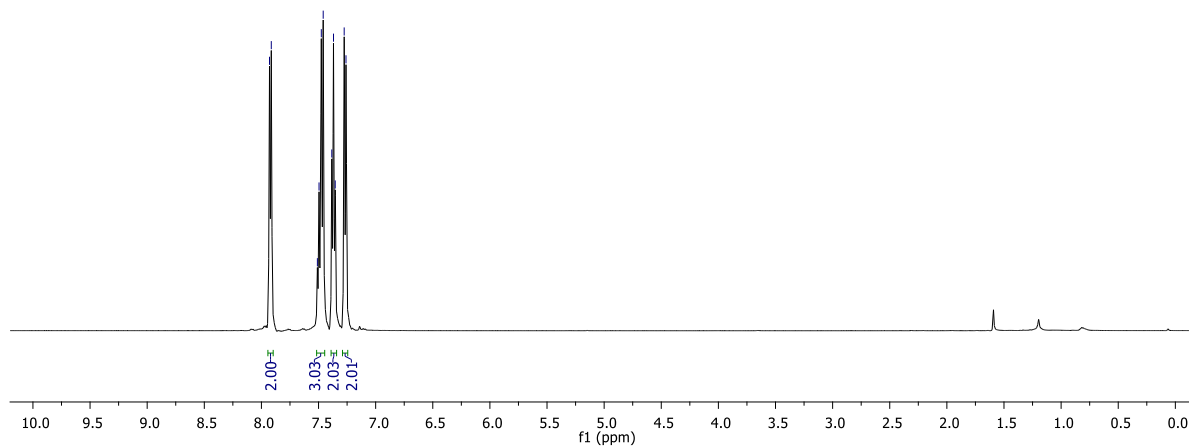






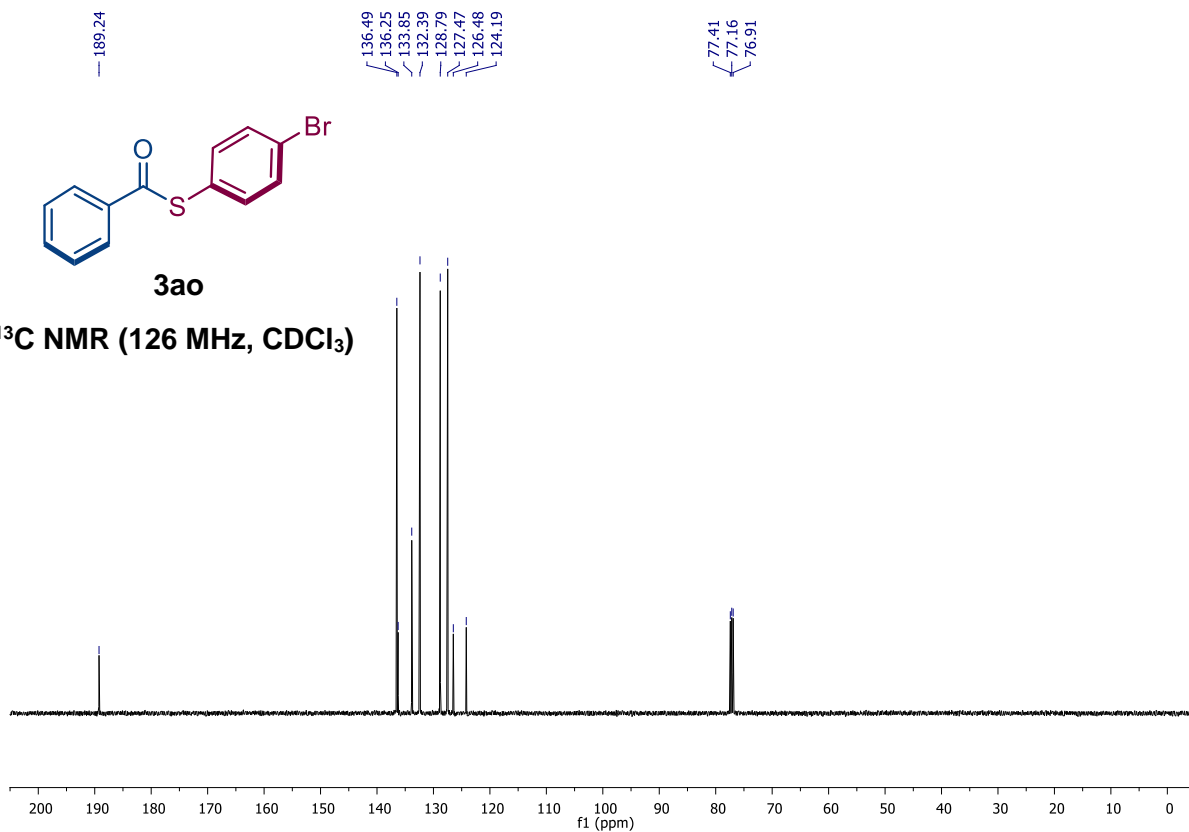
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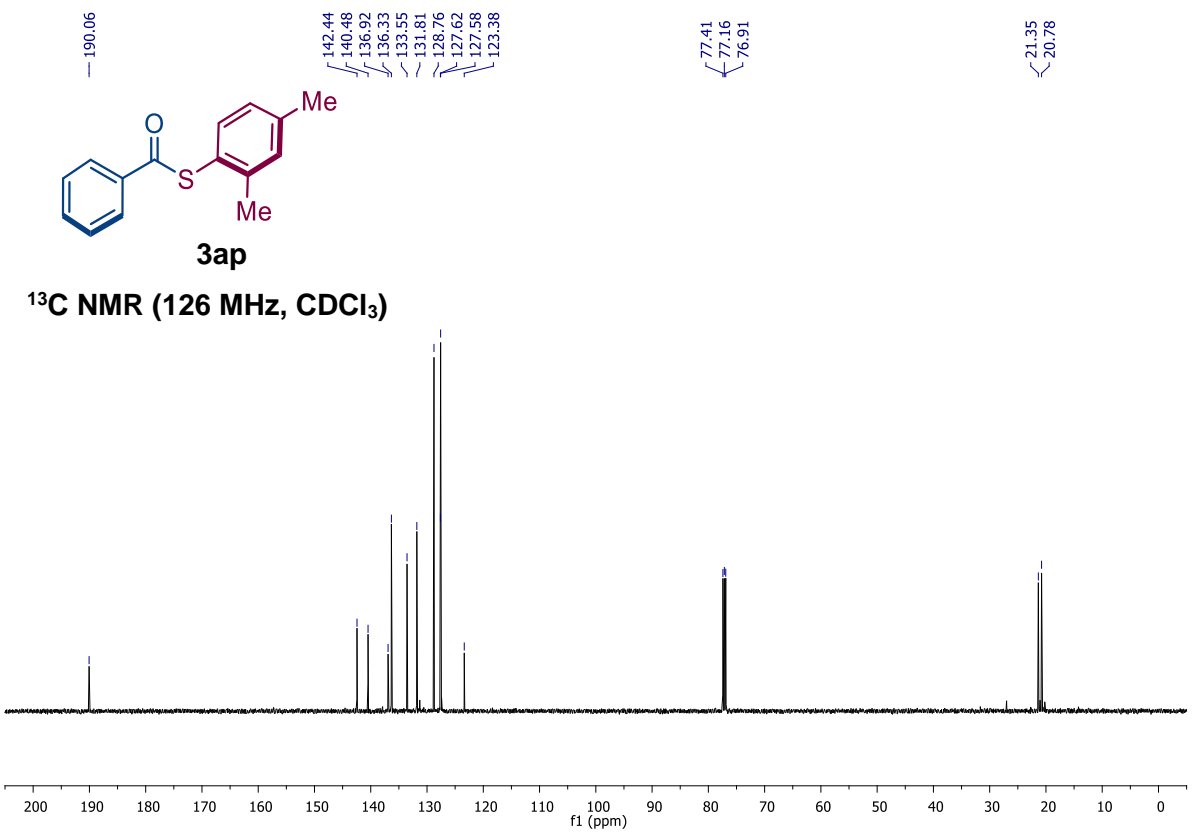
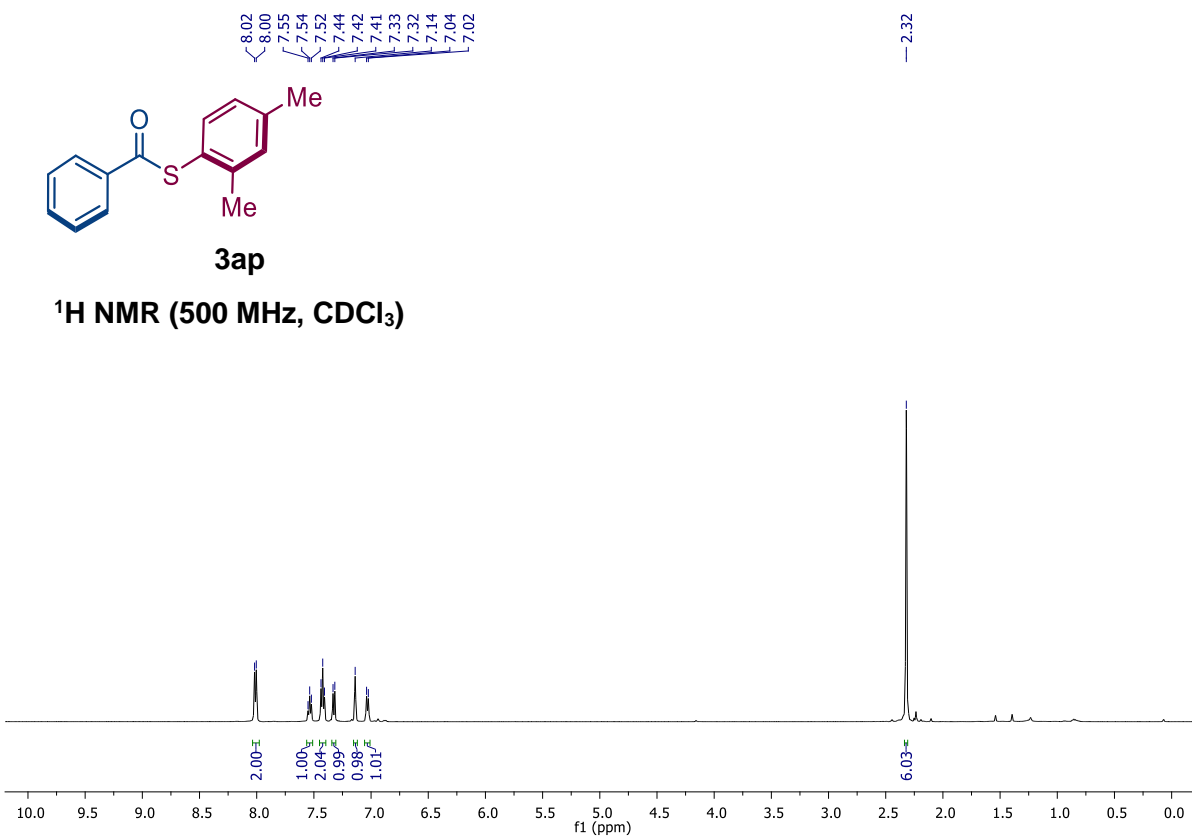
$^1\text{H NMR}$ (500 MHz, CDCl_3)

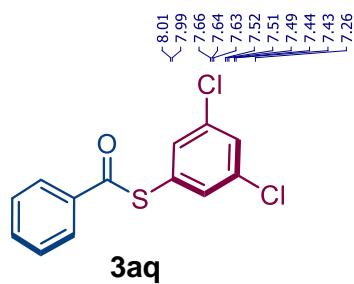


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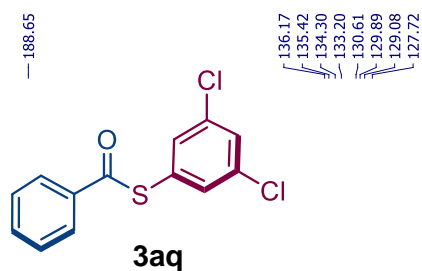
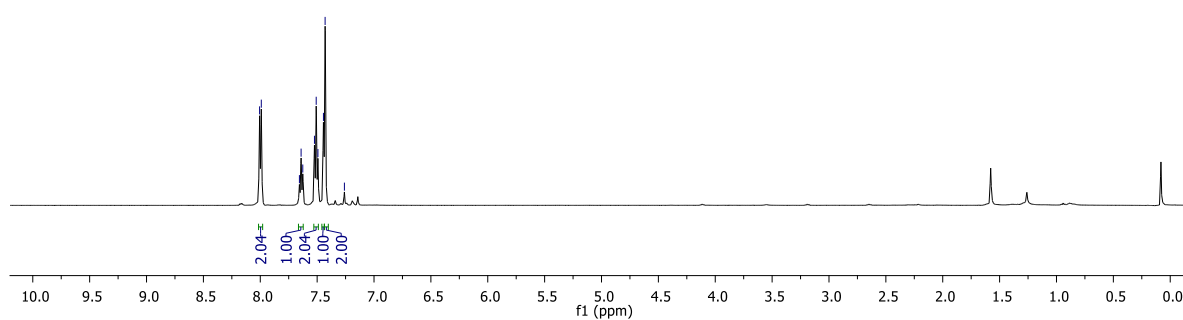
$^{13}\text{C NMR}$ (126 MHz, CDCl_3)



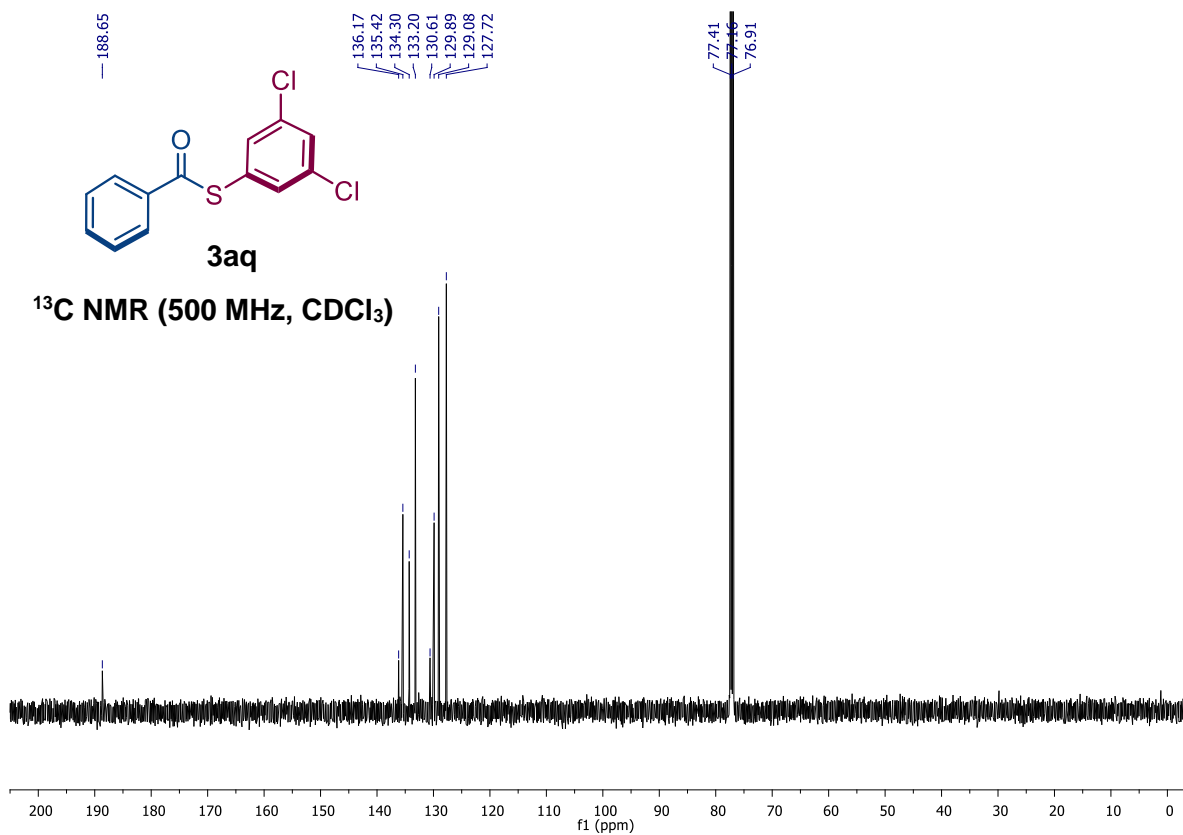


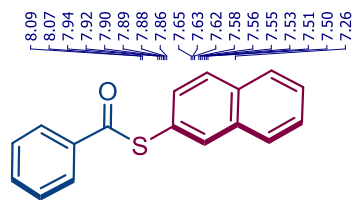


^1H NMR (500 MHz, CDCl_3)



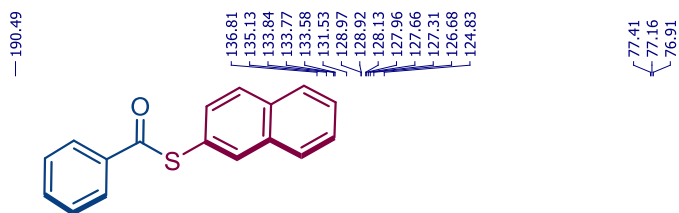
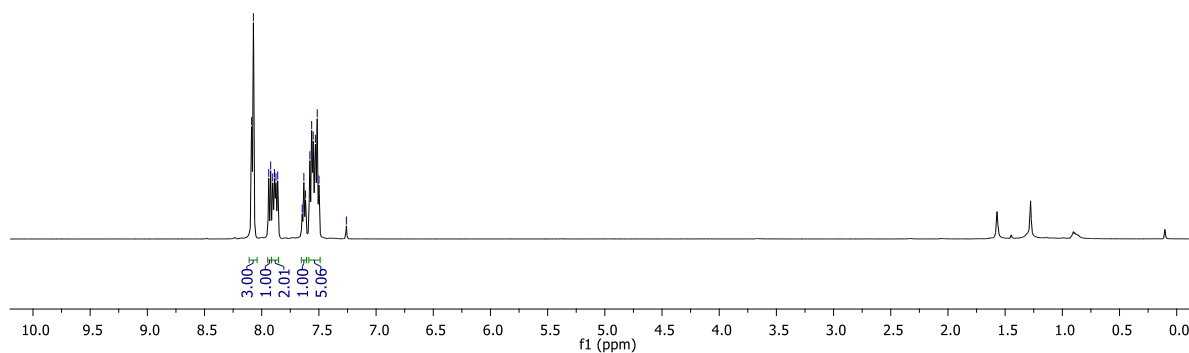
^{13}C NMR (500 MHz, CDCl_3)





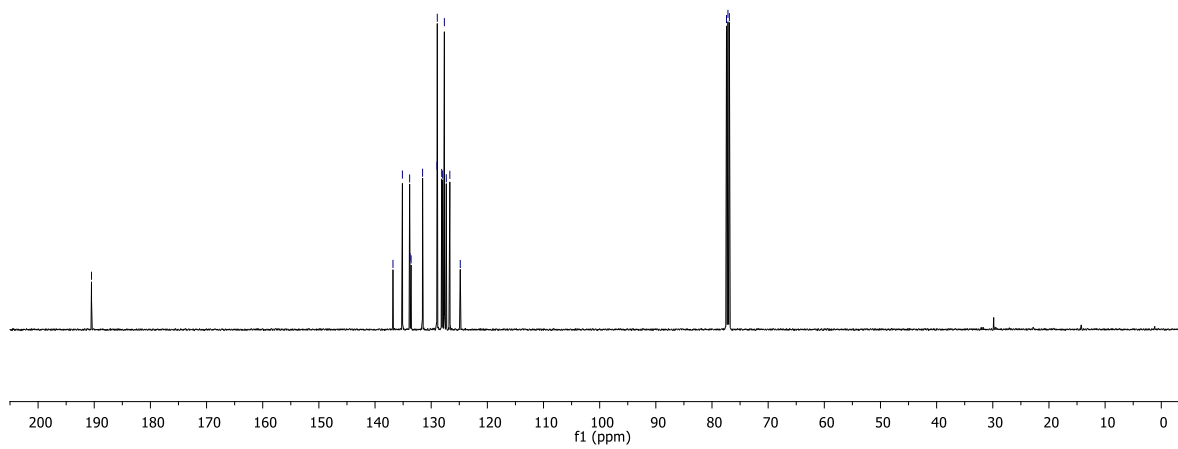
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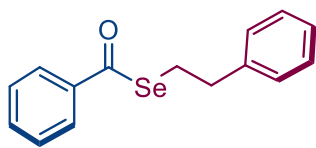
¹H NMR (500 MHz, CDCl₃)



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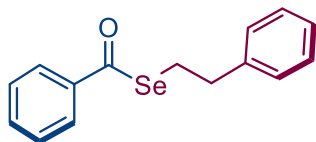
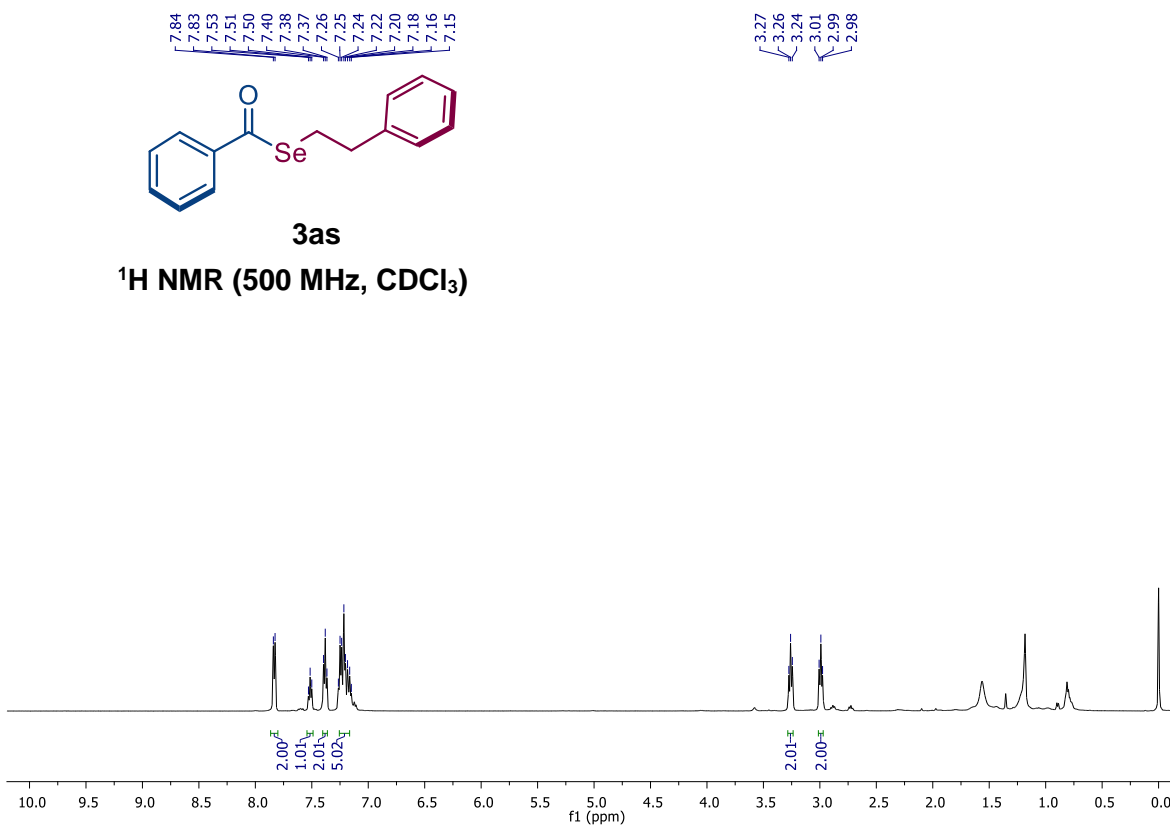
¹³C NMR (500 MHz, CDCl₃)





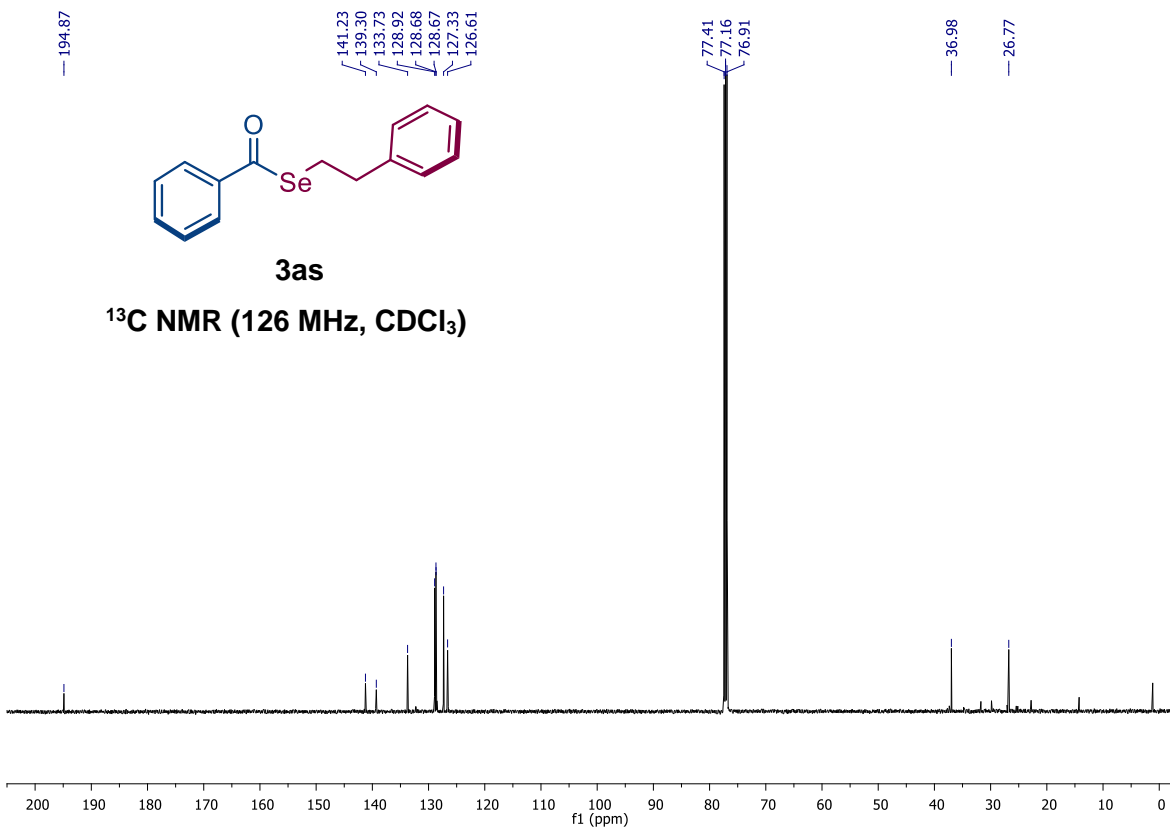
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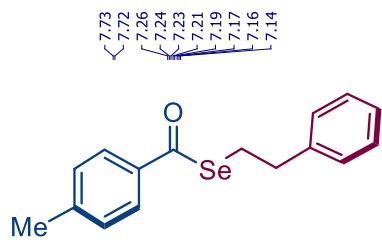
¹H NMR (500 MHz, CDCl₃)



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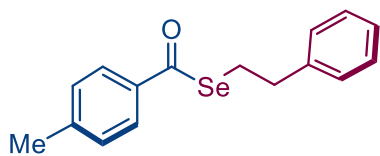
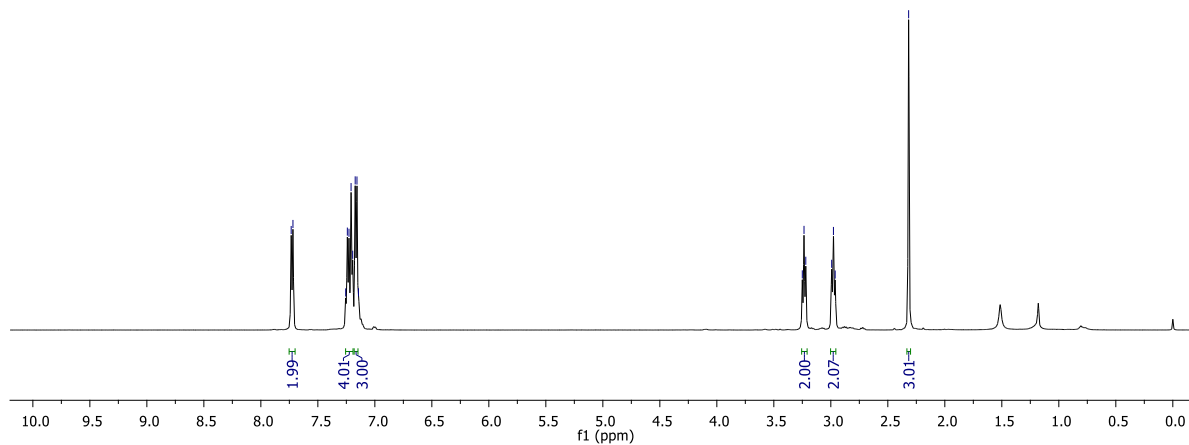
¹³C NMR (126 MHz, CDCl₃)





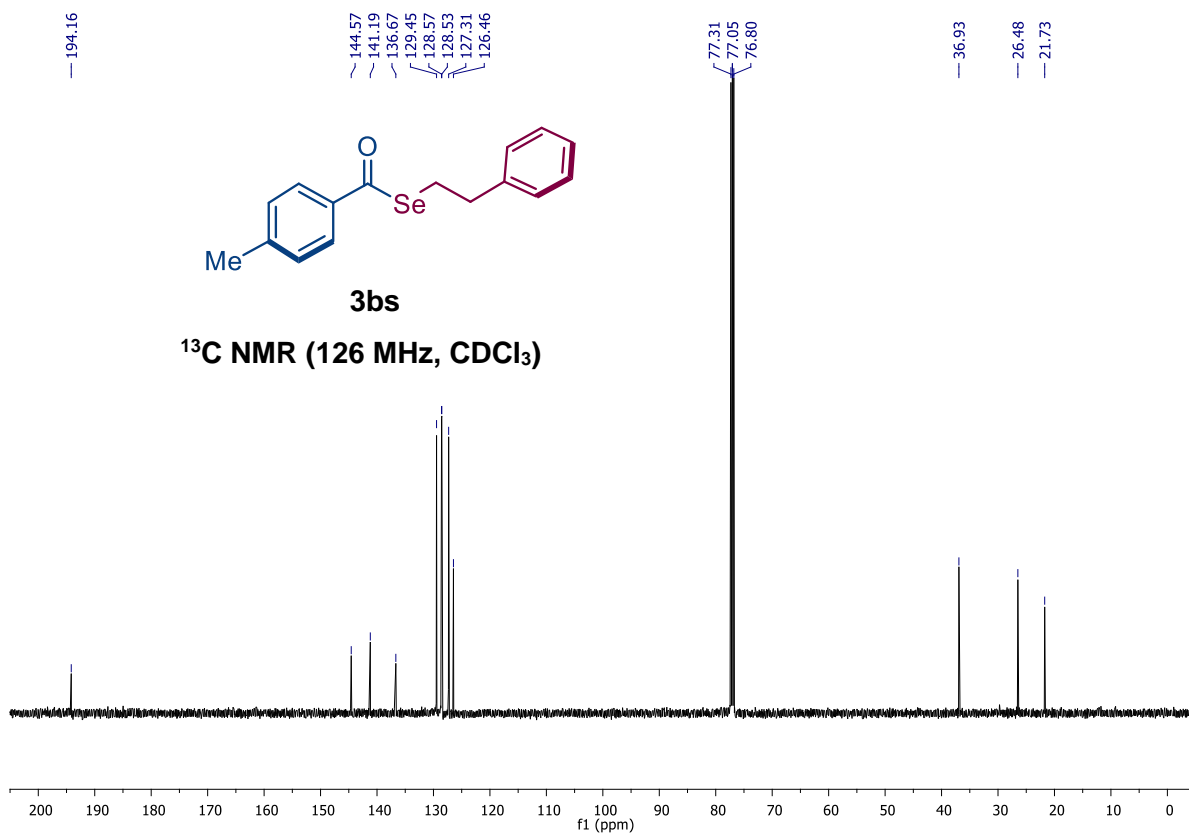
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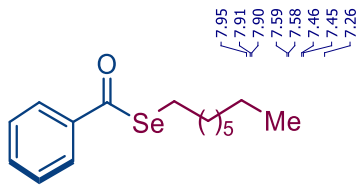
$^1\text{H NMR}$ (500 MHz, CDCl_3)



3bs

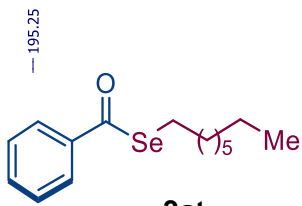
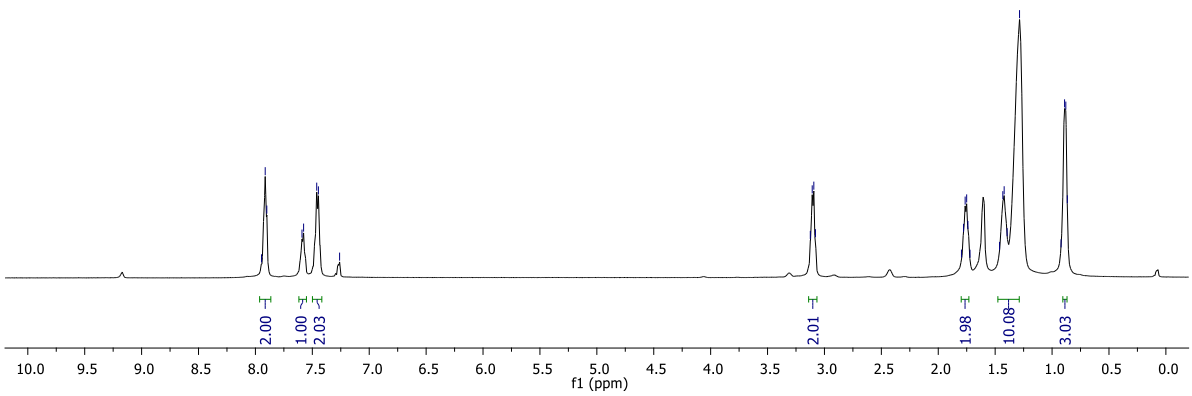
$^{13}\text{C NMR}$ (126 MHz, CDCl_3)





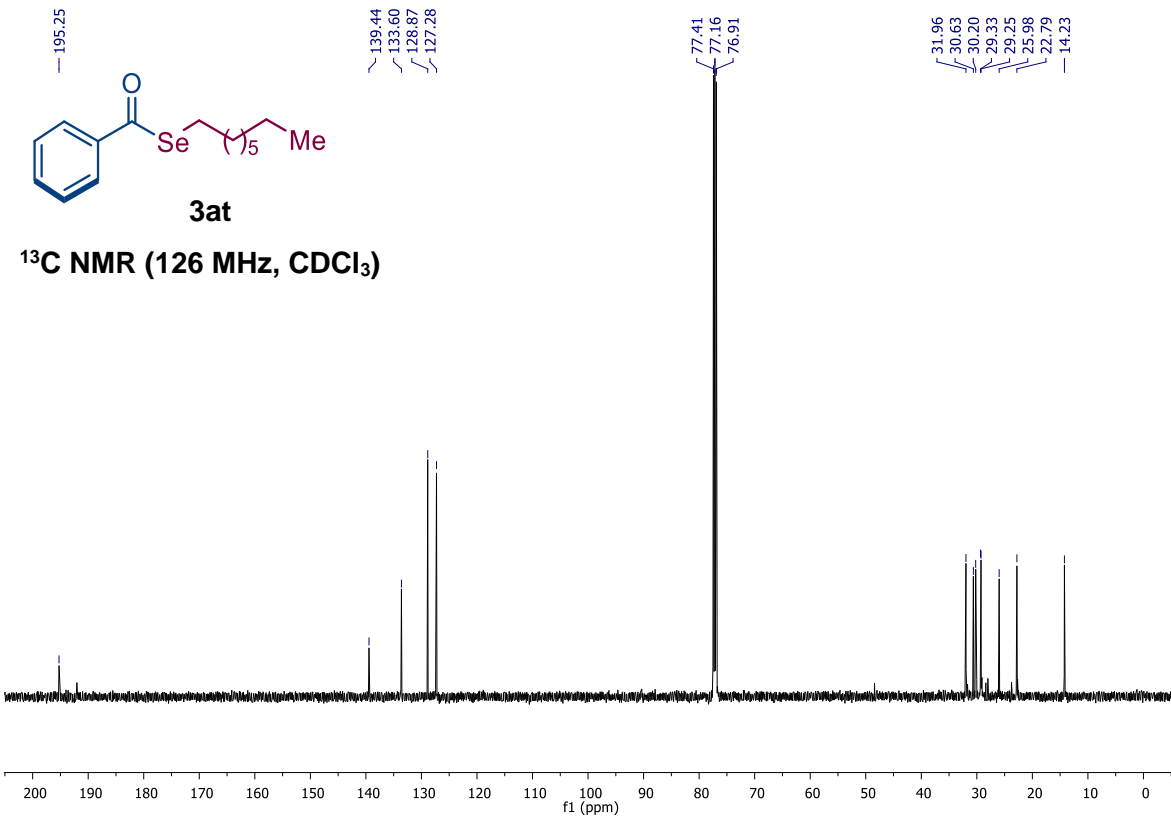
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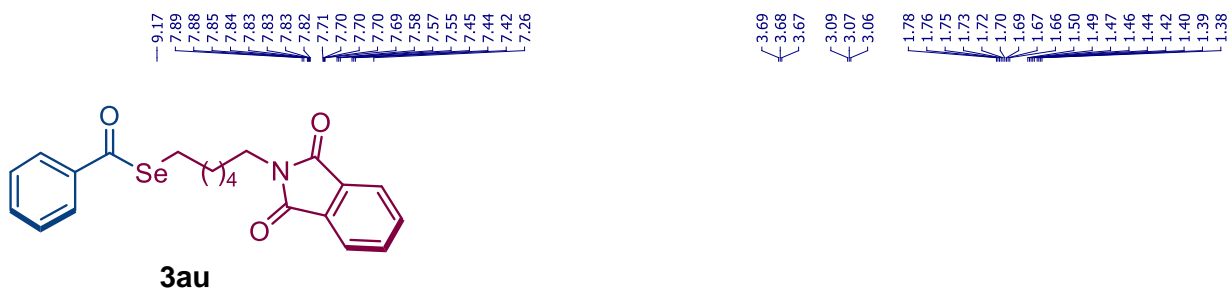
^1H NMR (500 MHz, CDCl_3)



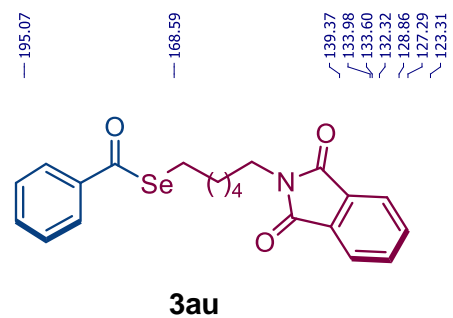
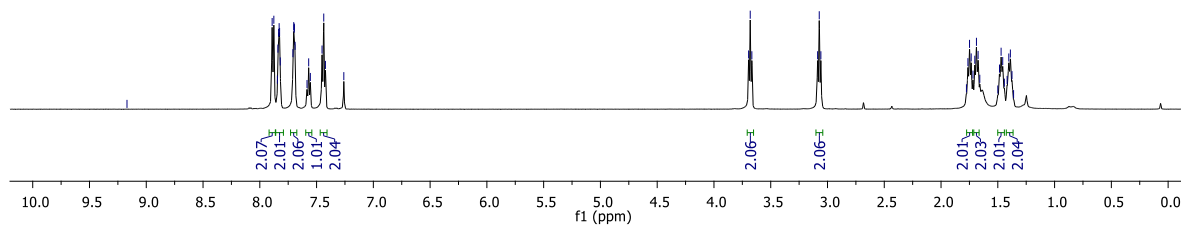
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^{13}C NMR (126 MHz, CDCl_3)

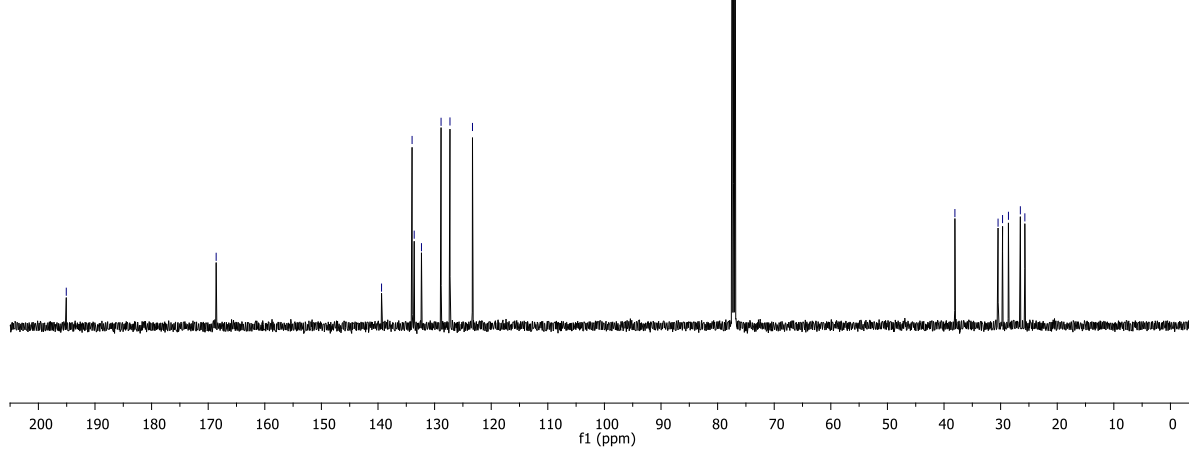


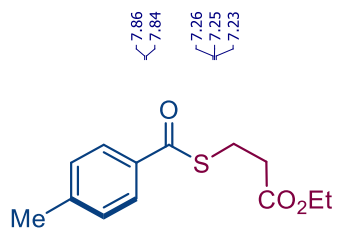


¹H NMR (500 MHz, CDCl₃)



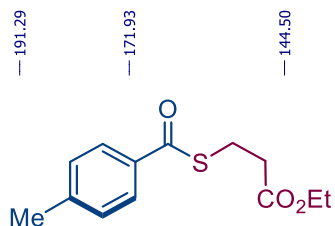
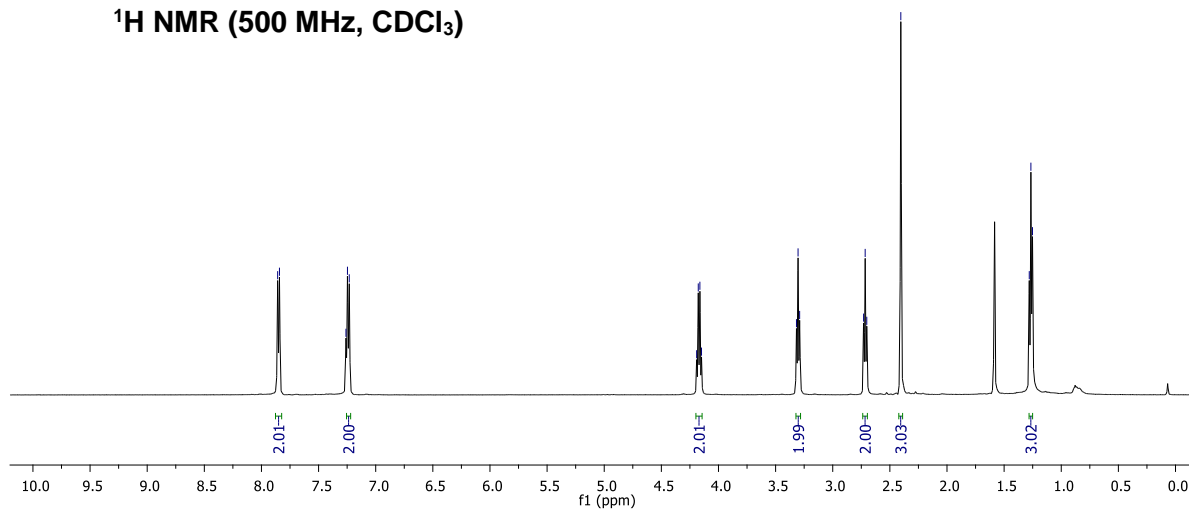
¹³C NMR (126 MHz, CDCl₃)





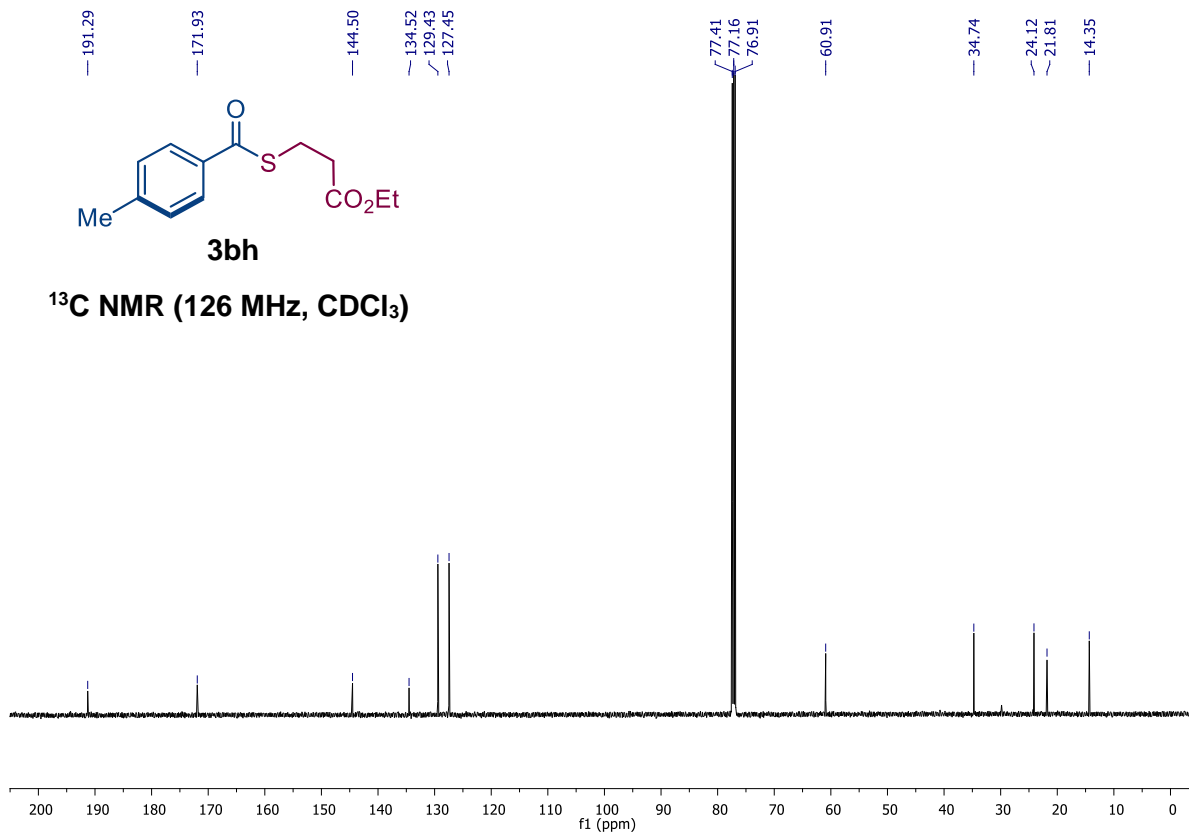
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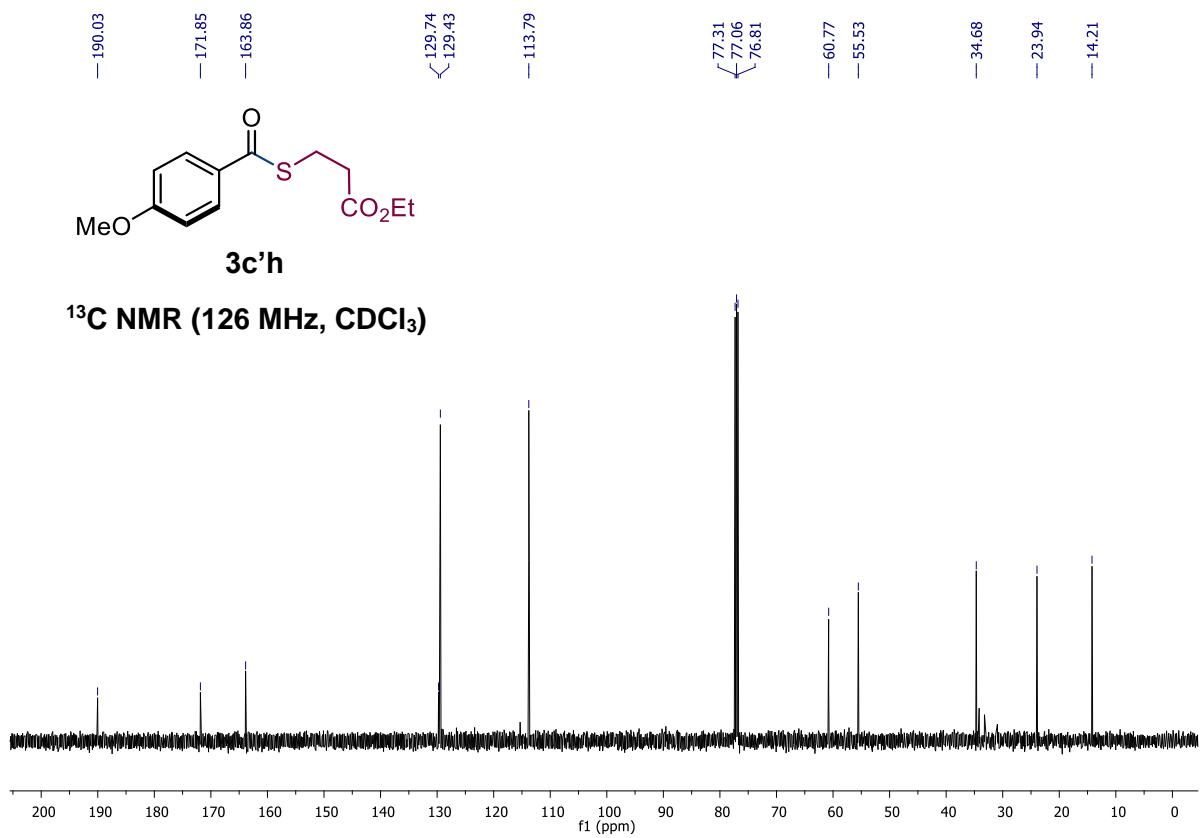
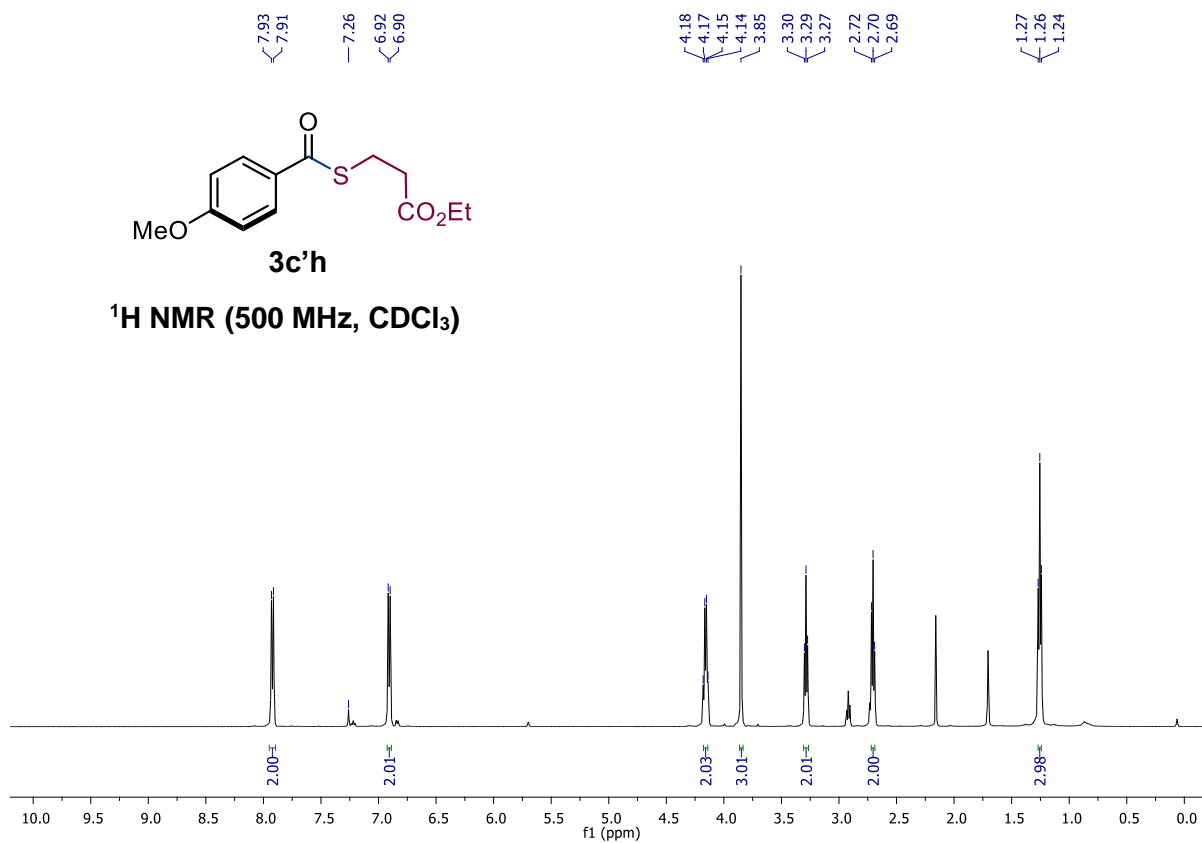
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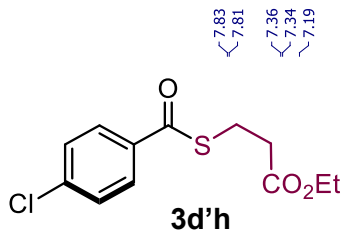


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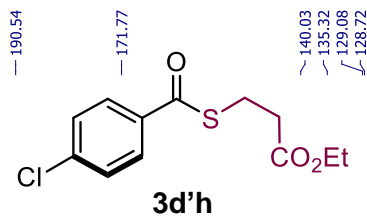
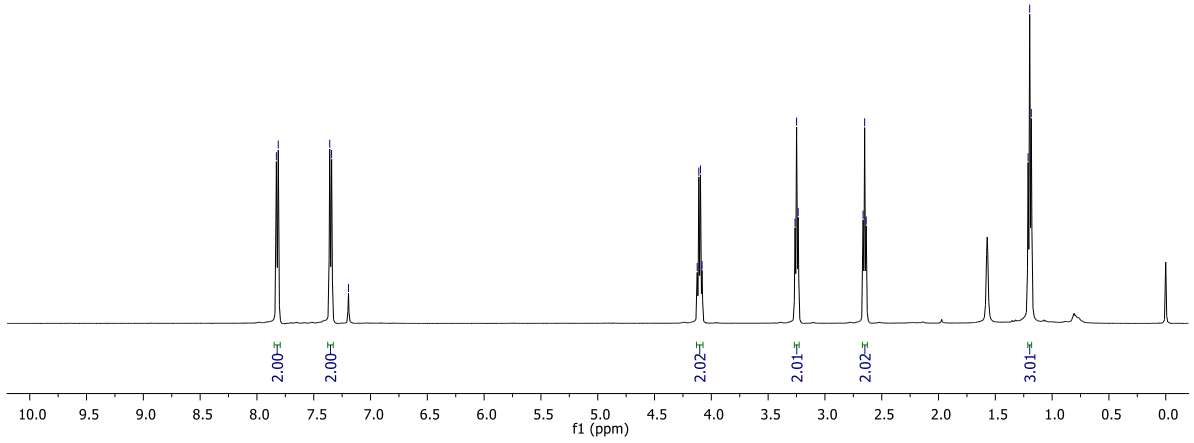
¹³C NMR (126 MHz, CDCl₃)



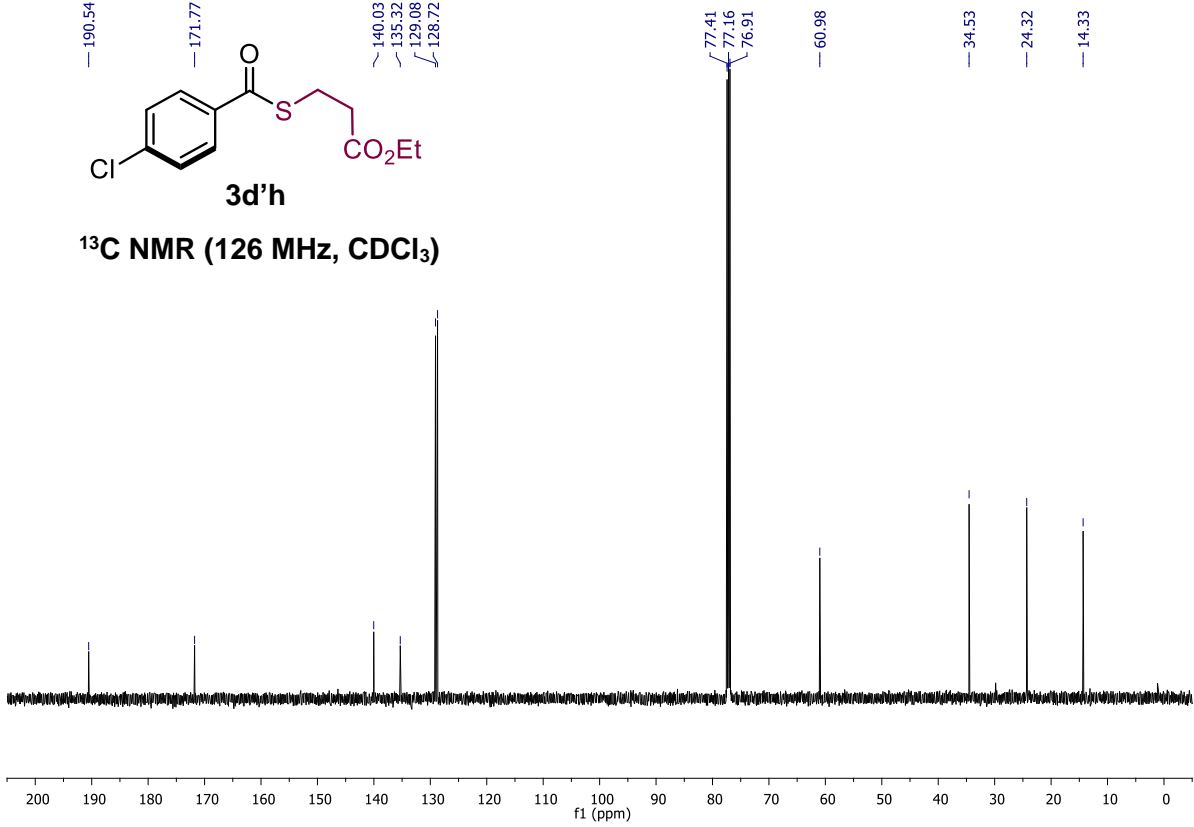


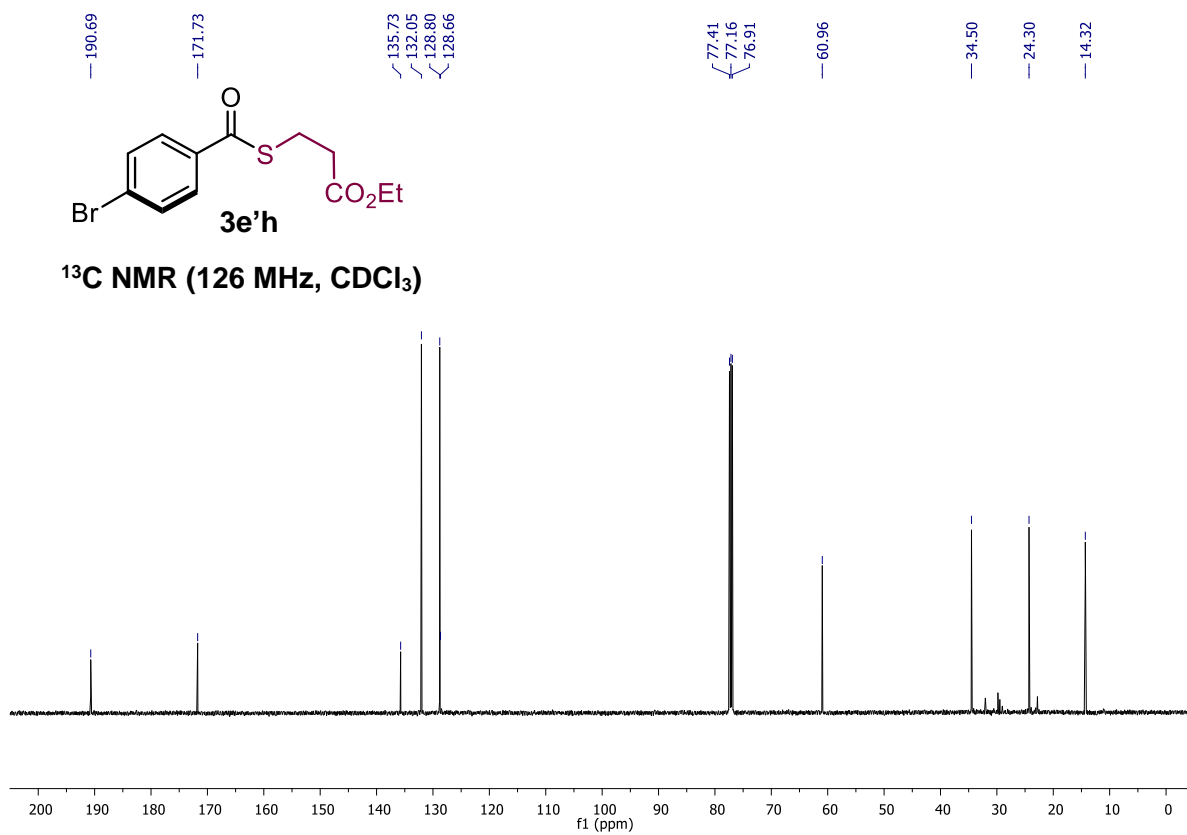
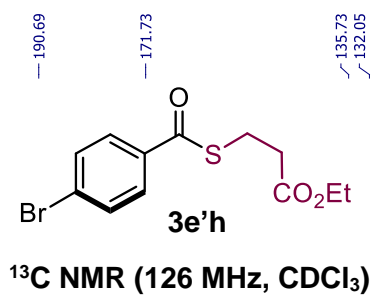
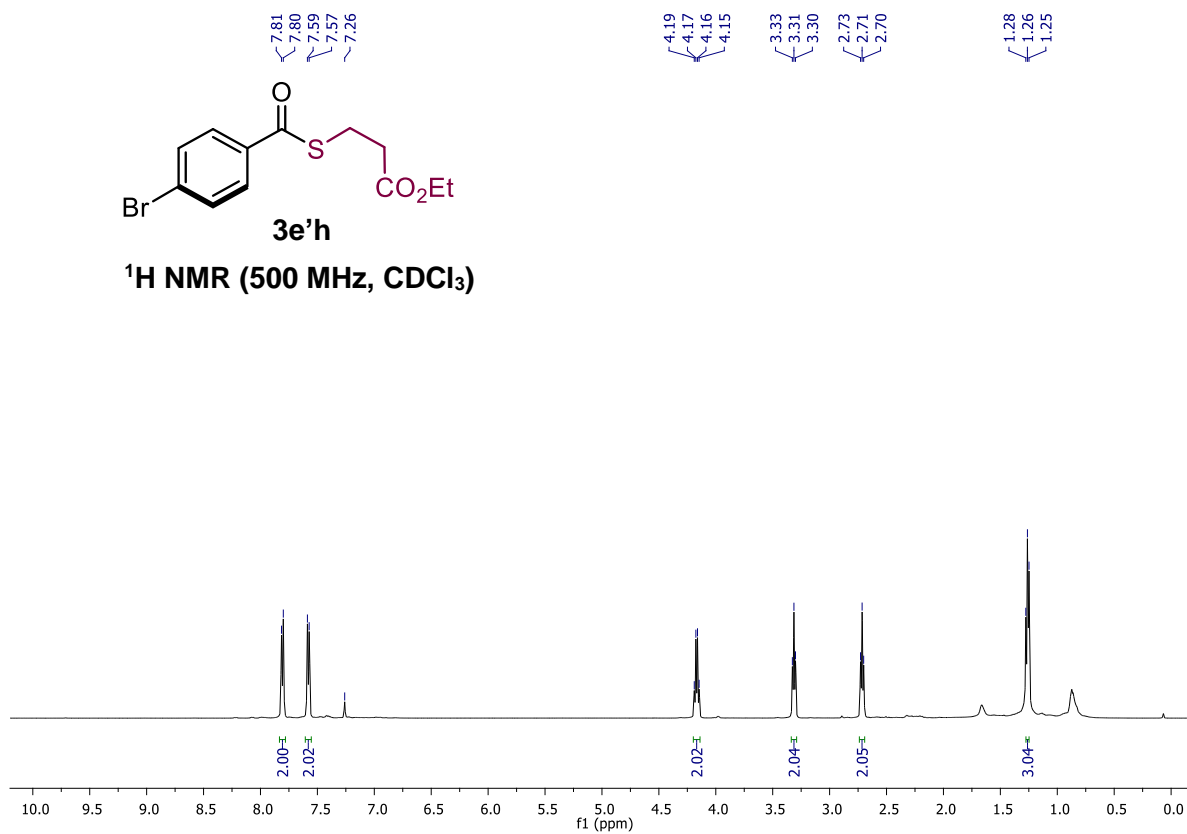
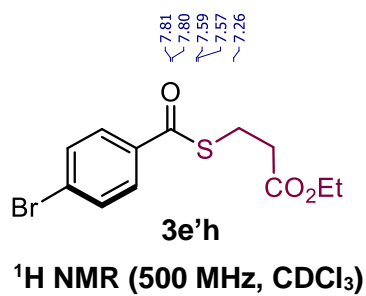


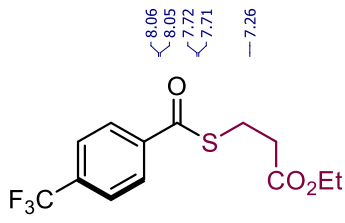
¹H NMR (500 MHz, CDCl₃)



¹³C NMR (126 MHz, CDCl₃)

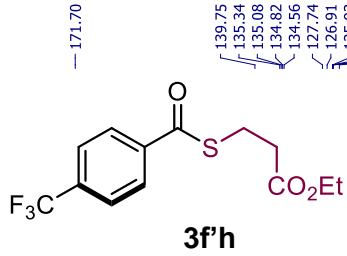
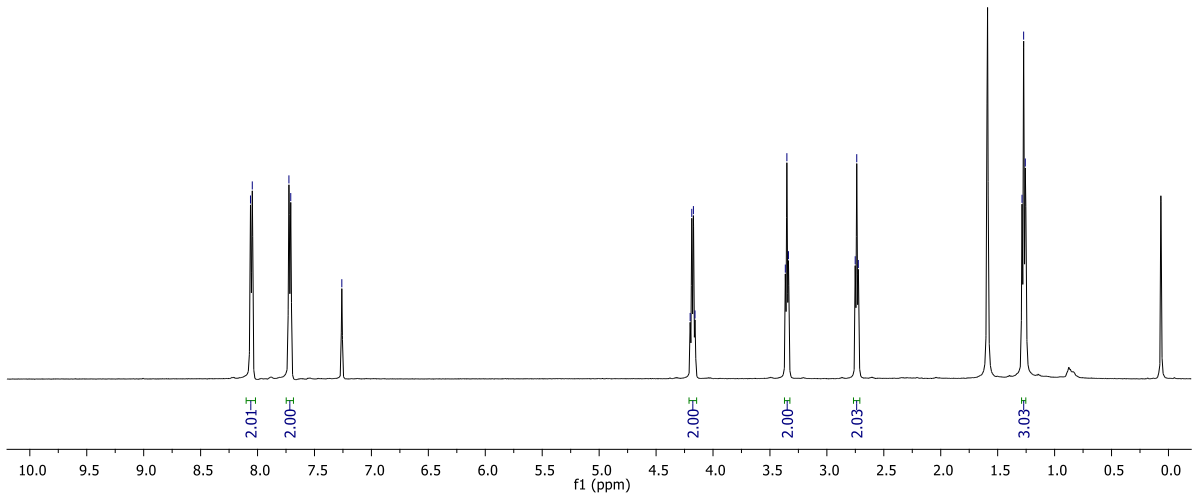






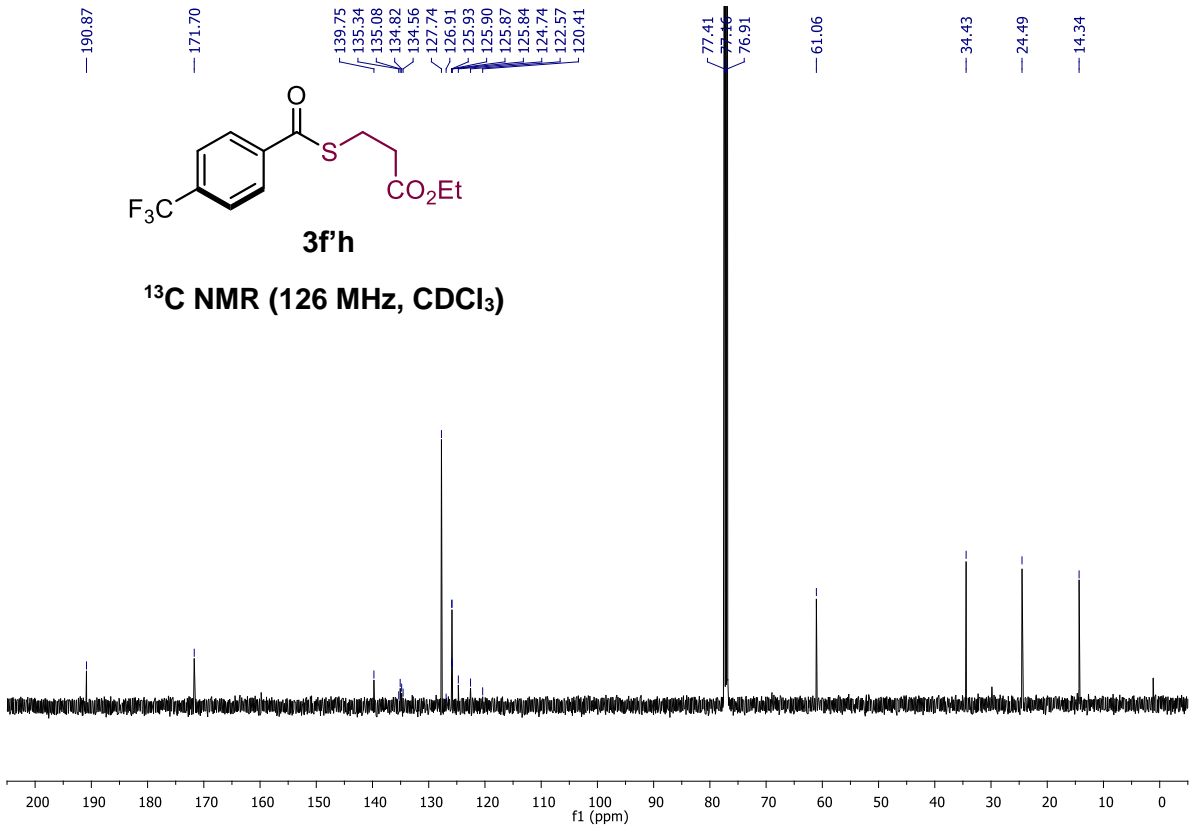
3f'h

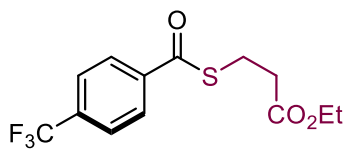
¹H NMR (500 MHz, CDCl₃)



3f'h

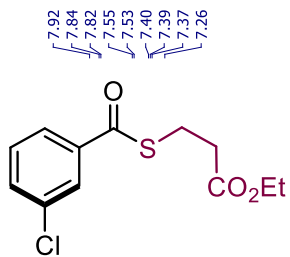
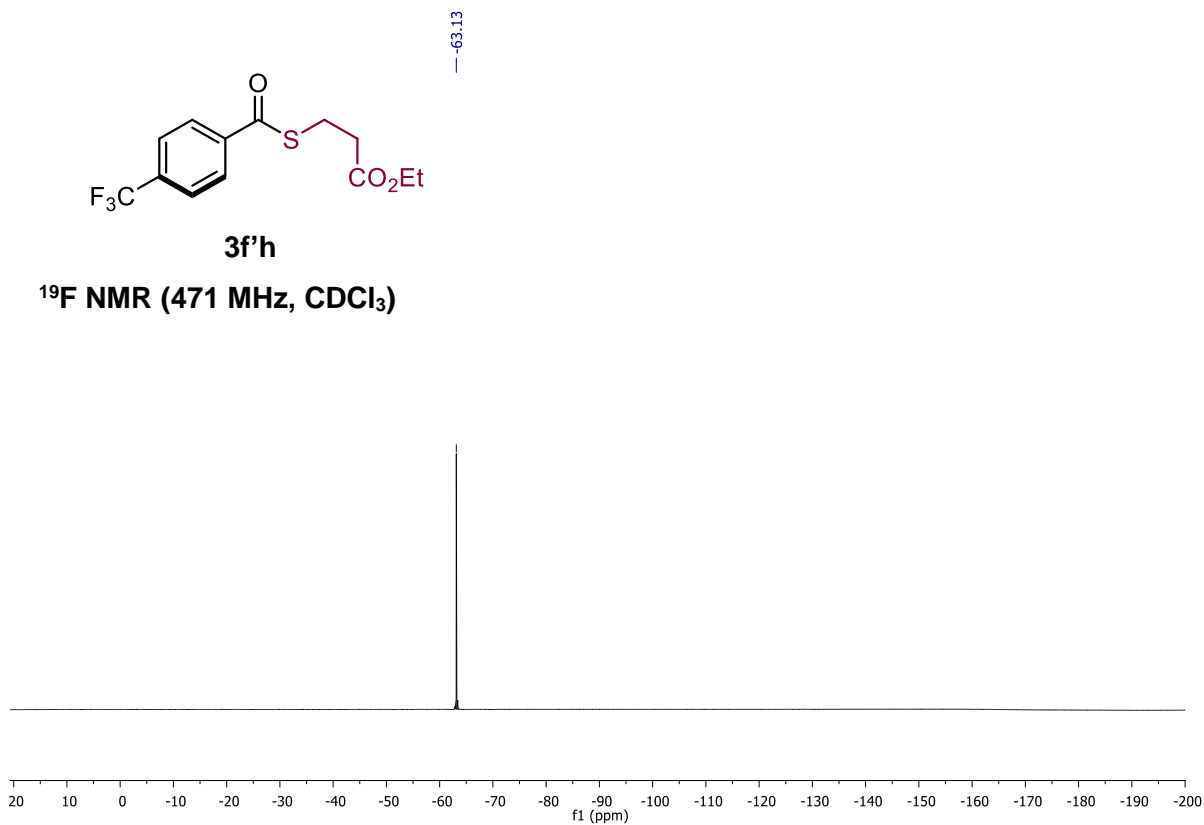
¹³C NMR (126 MHz, CDCl₃)





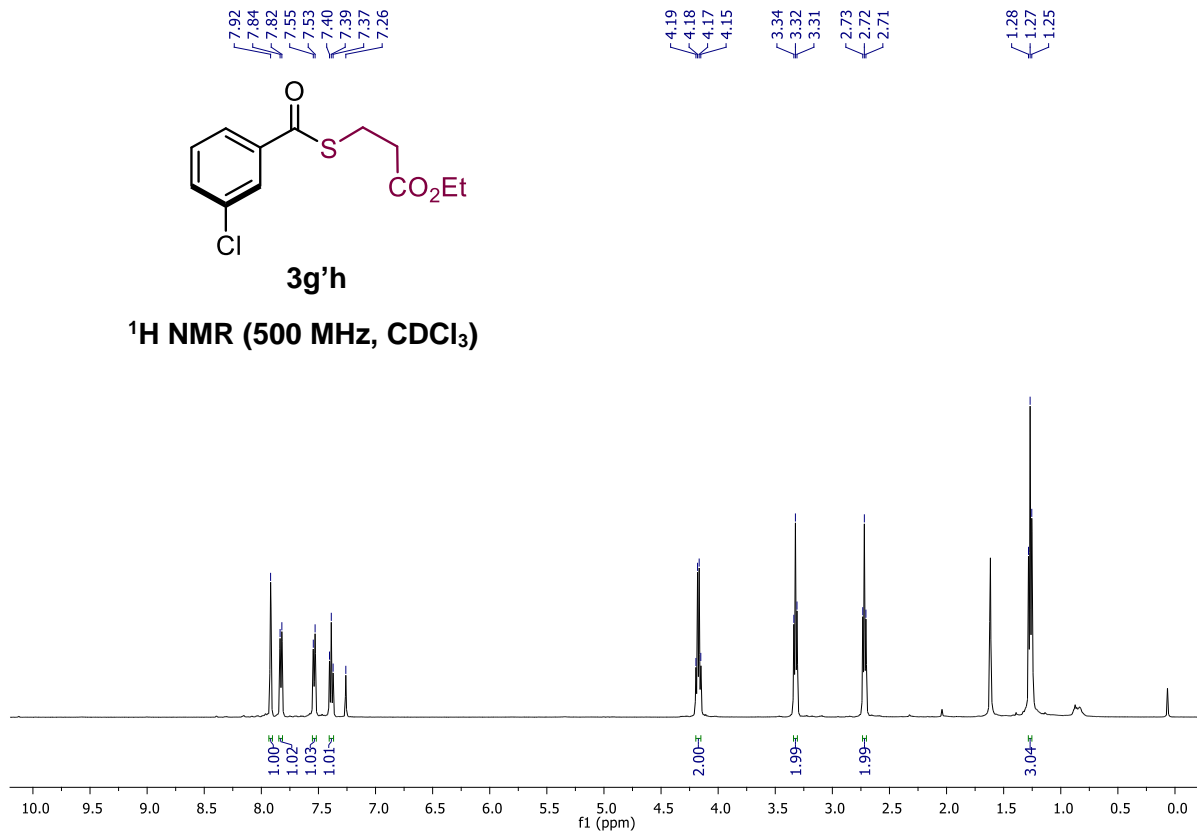
3f'h

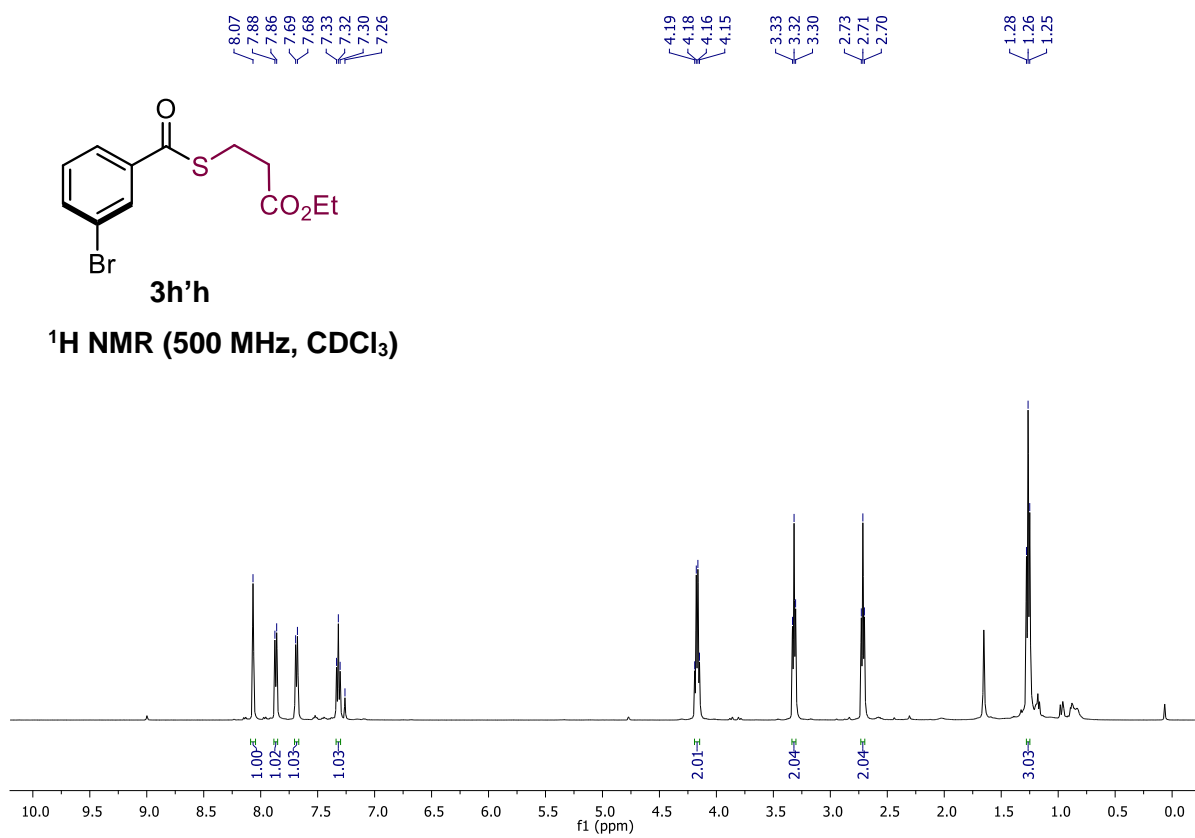
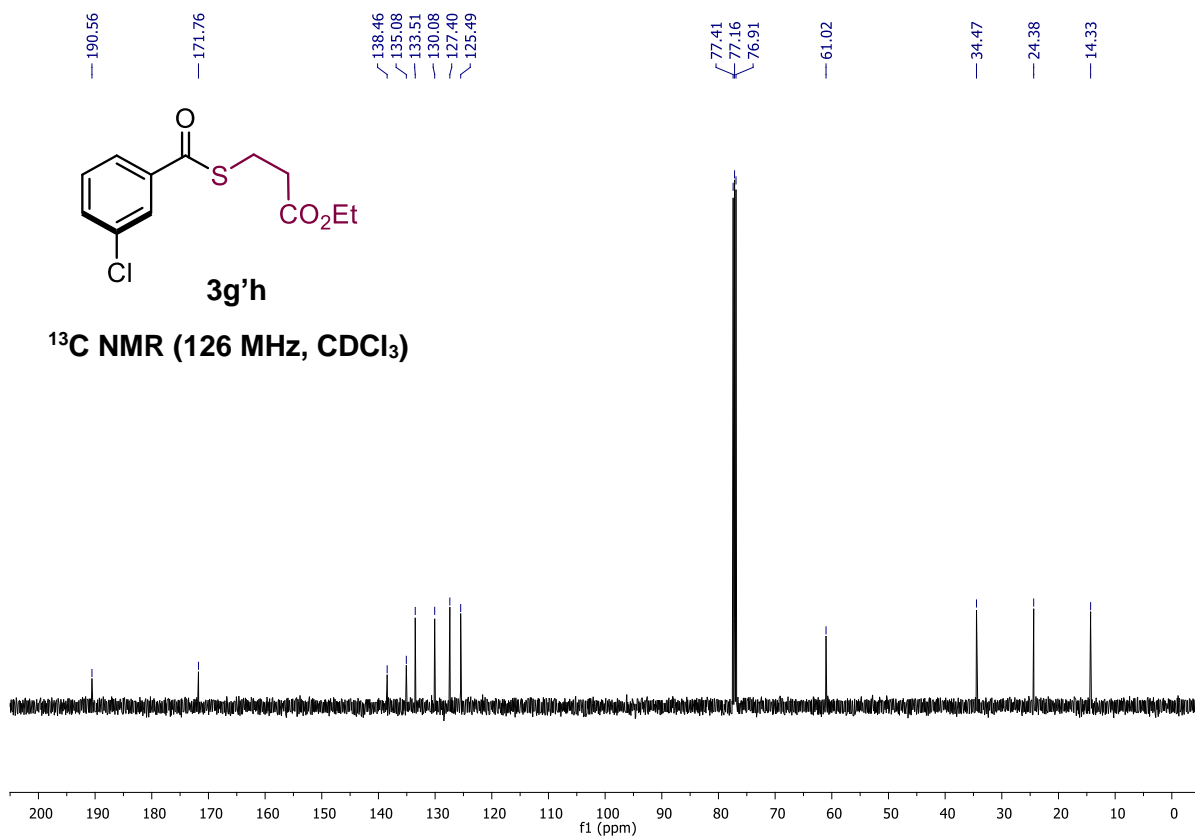
¹⁹F NMR (471 MHz, CDCl₃)

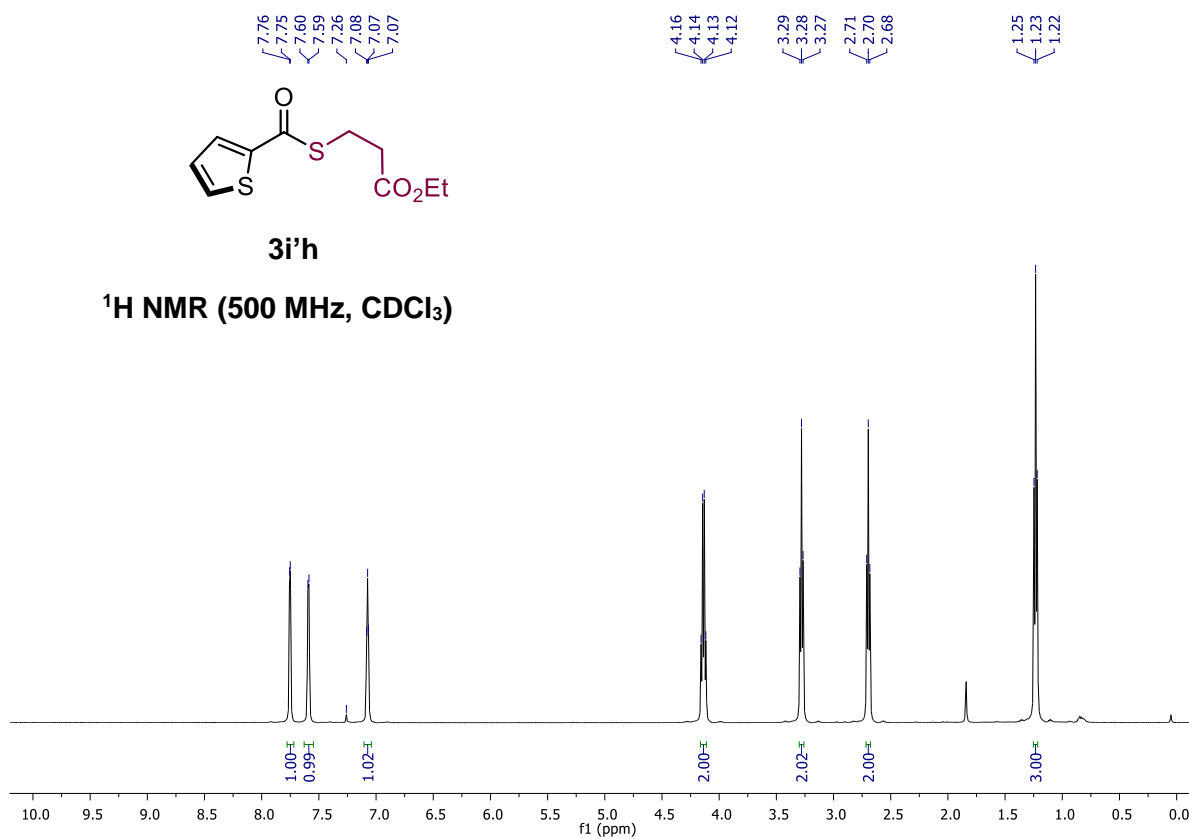
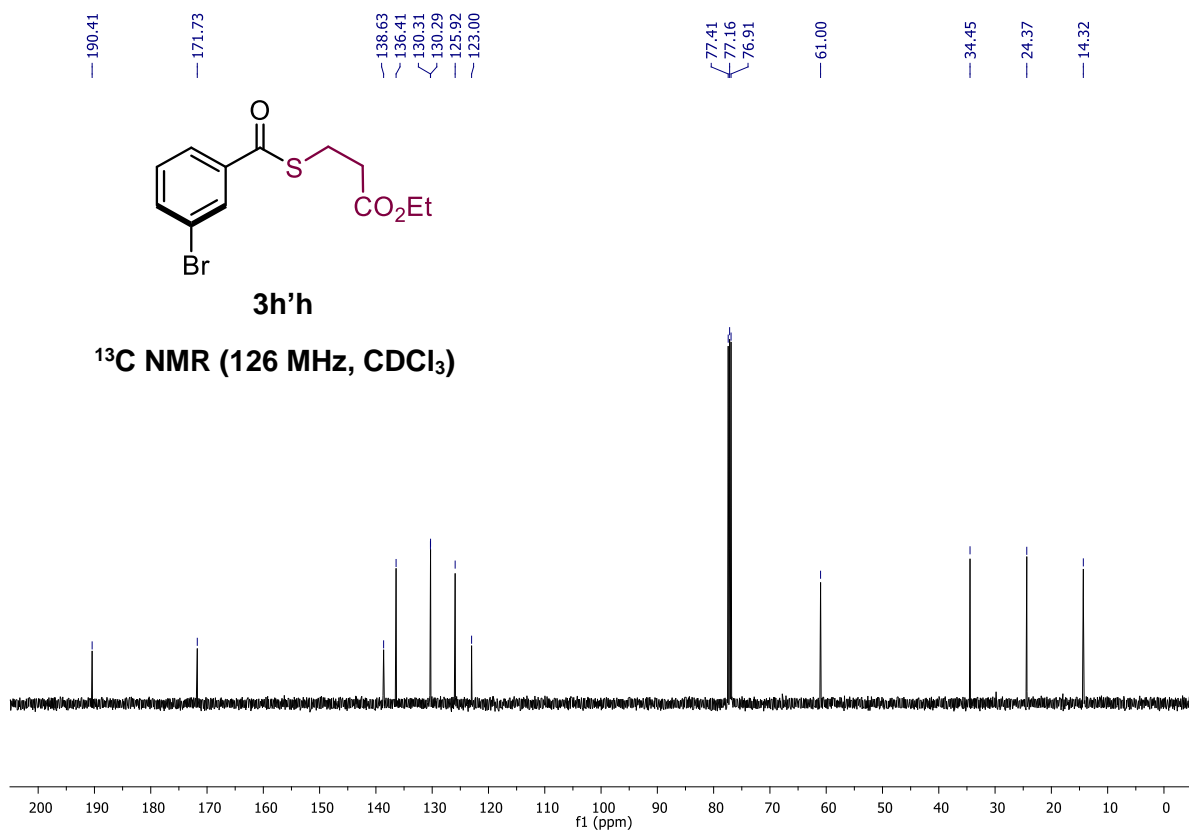


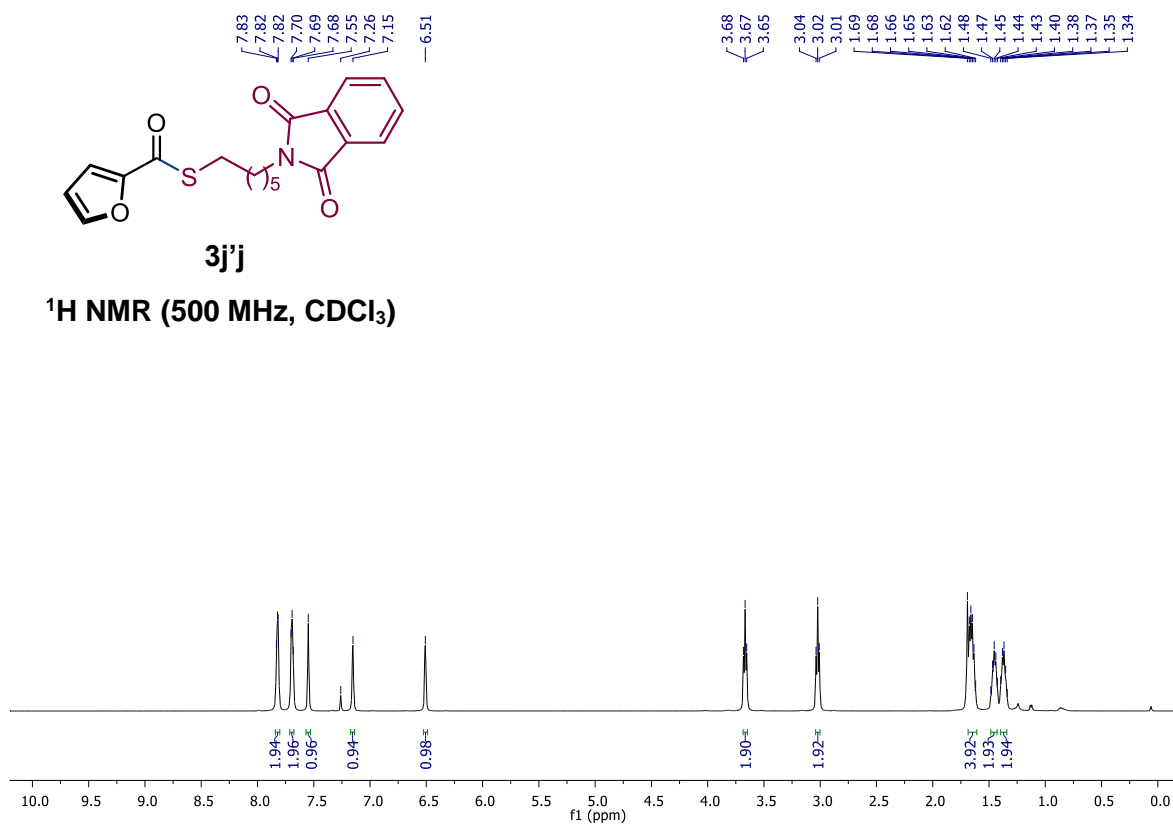
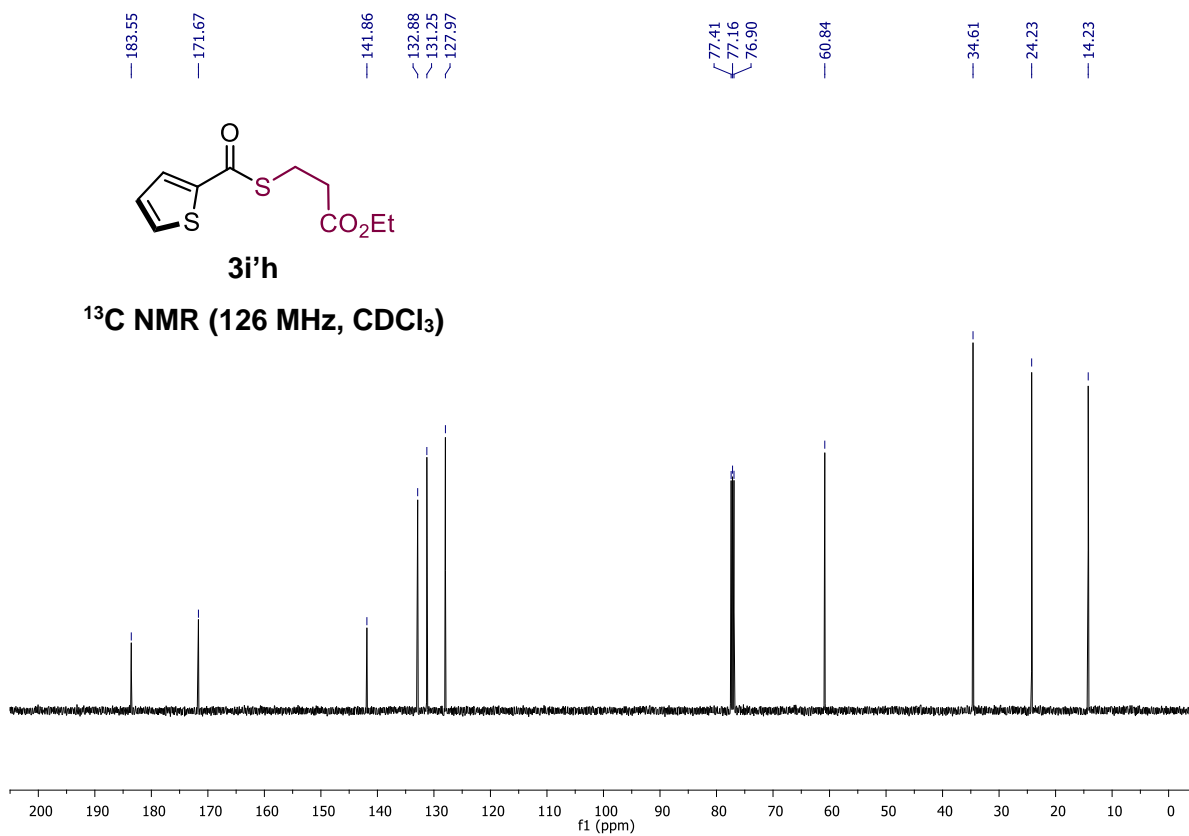
3g'h

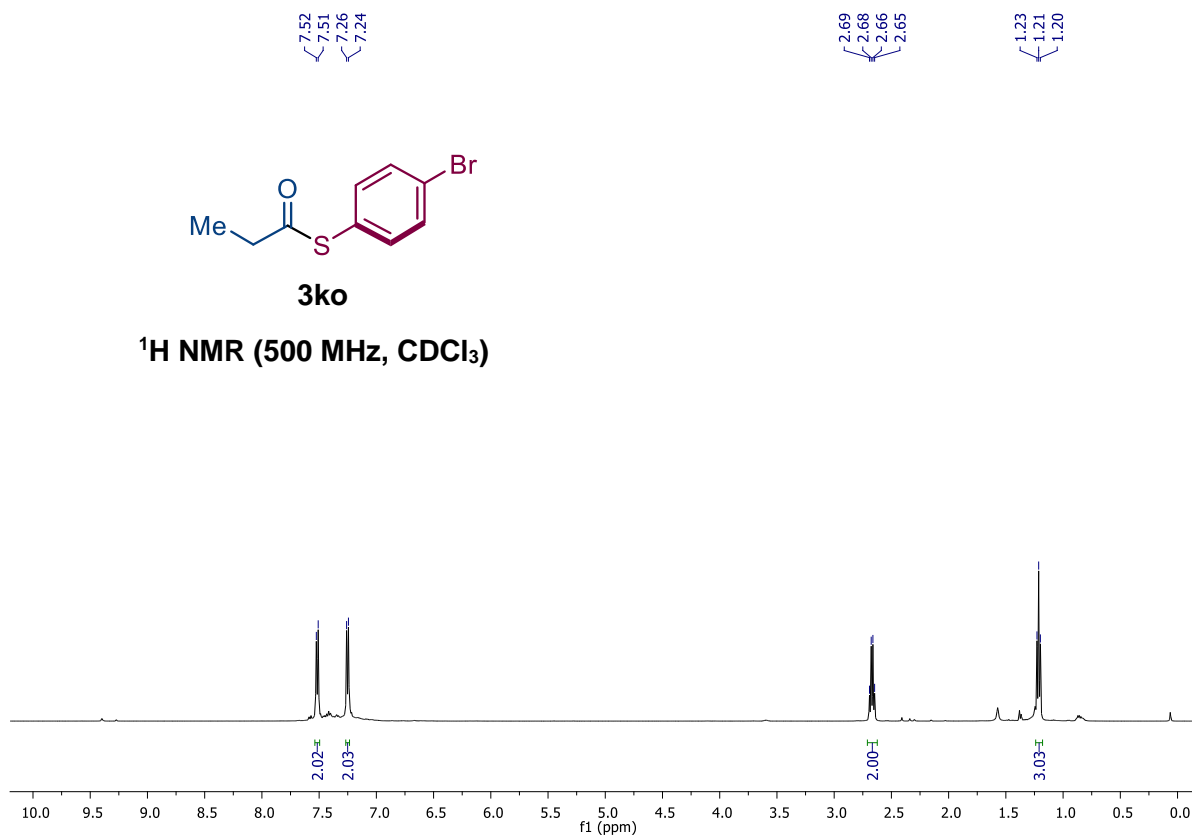
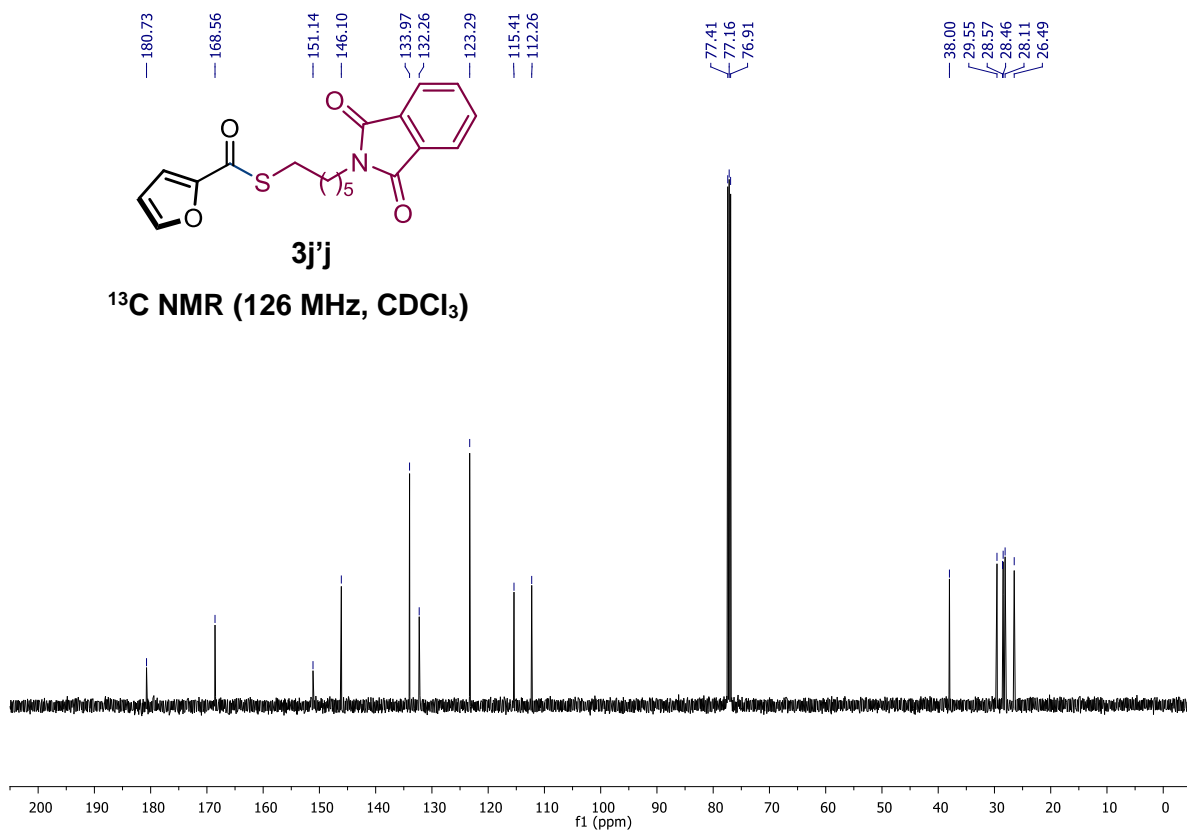
¹H NMR (500 MHz, CDCl₃)











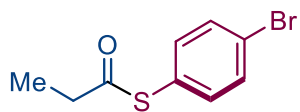
— 197.62

~ 136.07
~ 132.47
~ 127.04
~ 124.06

~ 77.41
~ 77.16
~ 76.91

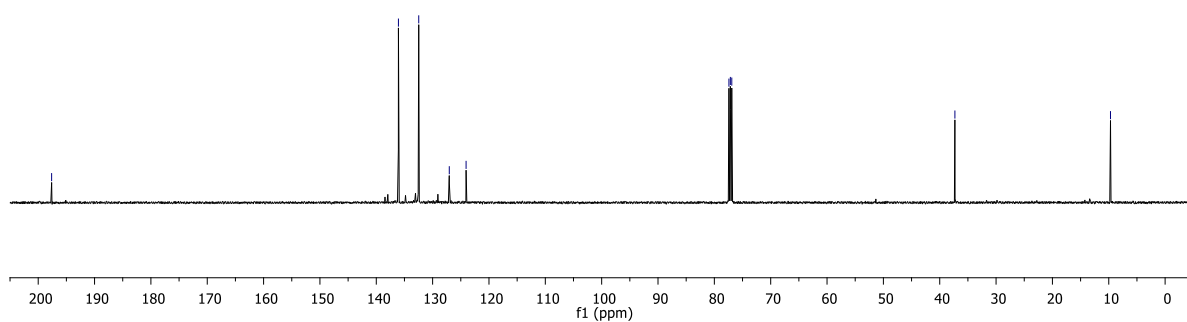
— 37.31

— 9.69



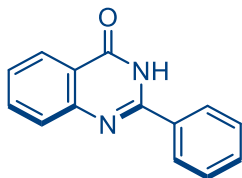
3ko

¹³C NMR (126 MHz, CDCl₃)



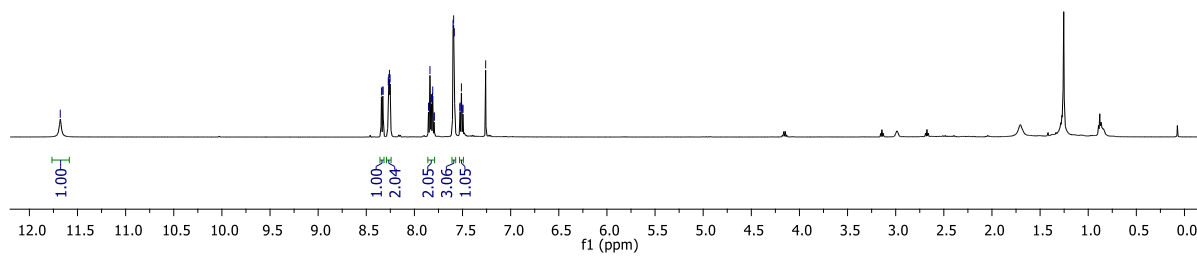
— 11.68

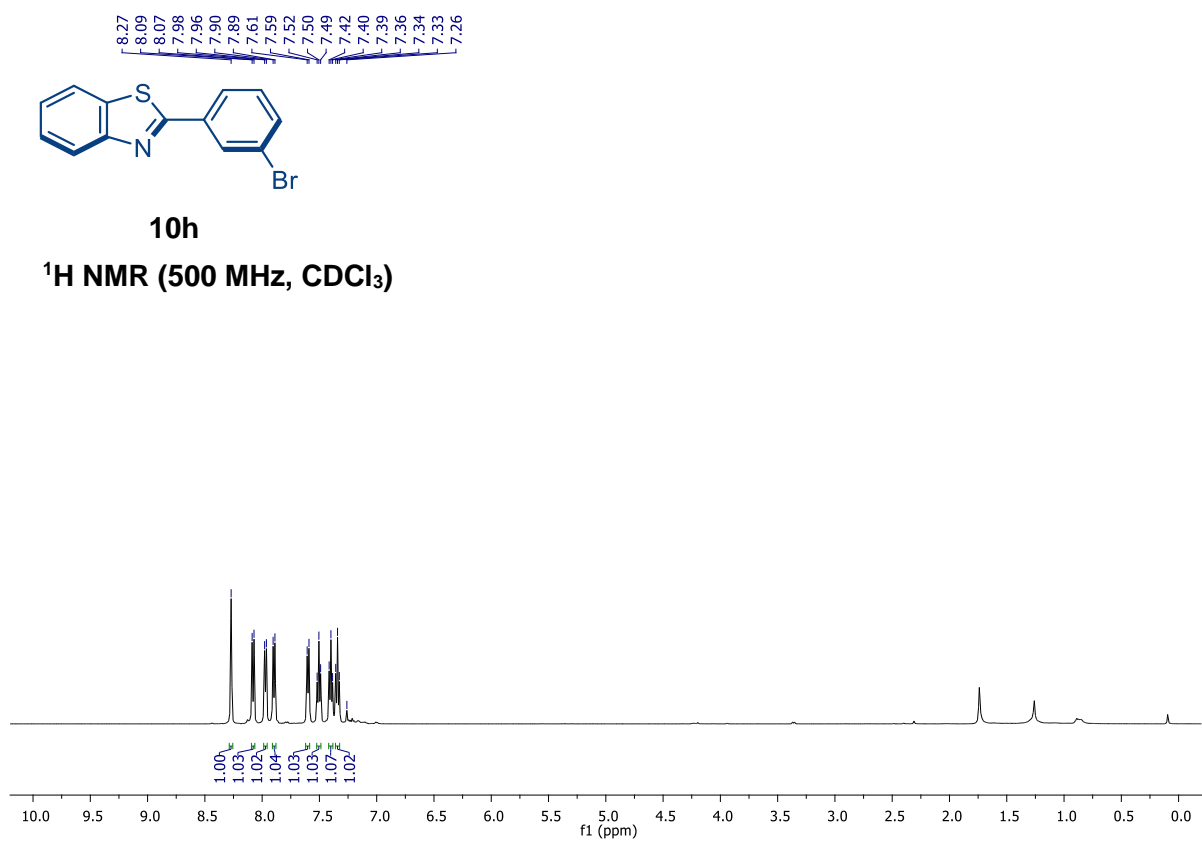
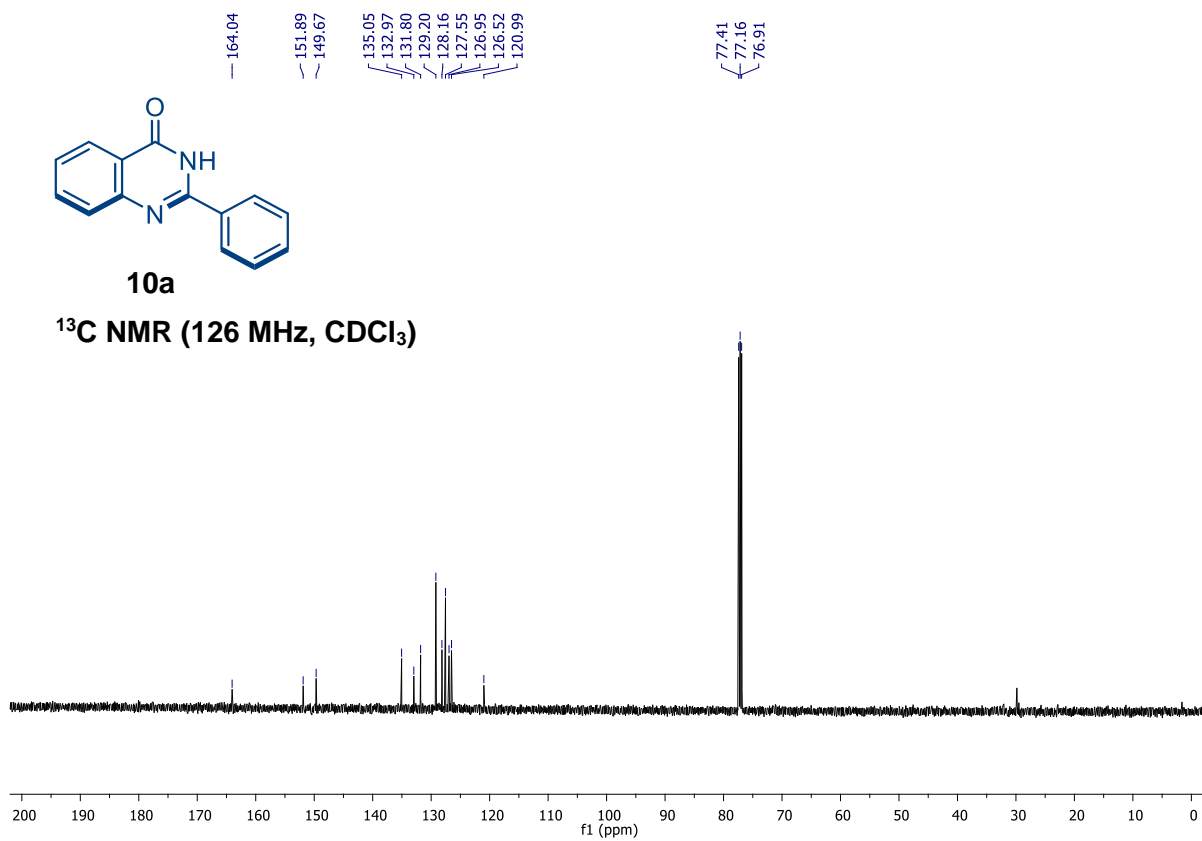
8.34
8.33
8.33
8.27
8.27
8.26
8.26
8.25
7.85
7.84
7.83
7.82
7.81
7.81
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7.59
7.53
7.53
7.51
7.50
7.50
7.26

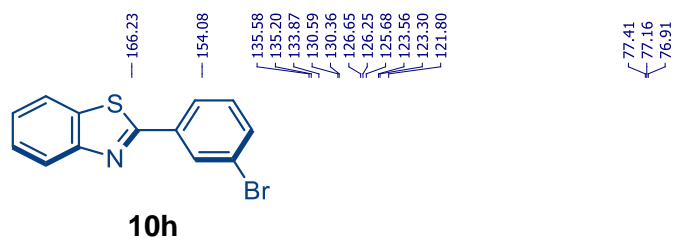


10a

¹H NMR (500 MHz, CDCl₃)







^{13}C NMR (126 MHz, CDCl_3)

