

Supporting Information

Rhodium-Catalyzed Sommelet Hauser Type Rearrangement of α -Diazoimines: Synthesis of Functionalized Enamides

*Angula Chandra Shekar Reddy, Kuppan Ramachandran, Palagulla Maheswar Reddy and
Pazhamalai Anbarasan**

Department of Chemistry, Indian Institute of Technology Madras, Chennai-600036, India.

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1. General Comments:

All reactions were carried out under nitrogen atmosphere using oven dried reaction tubes. Dry toluenewas prepared by distilling over sodium metal and stored over molecular sieves 4Å under nitrogen atmosphere. All the *N*-sulfonyl 1,2,3-triazoles were synthesized from corresponding acetylene and tosyl azide employing literature procedure.¹ All the α -thioesters were achieved from thiol and bromoesters.²

Column chromatography was performed using Rankem Silica gel (100-200 mesh) and the solvent system used unless otherwise specified, was ethyl acetate-hexanes with various percentage of polarity depending on the nature of the substrate.

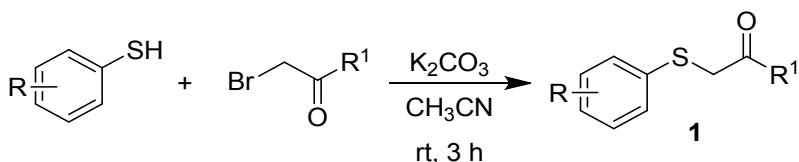
2. Analytical Methods:

NMR data were recorded on 400 and 500 MHz spectrometers. ¹³C and ¹H NMR spectra were referenced to signals of deutero solvents and residual protiated solvents, respectively. Infrared spectra were recorded on a Thermo Nicolet iS10 FT spectrometer. HRMS were recorded by electron spry ionization (ESI) method on a Q-TOF Micro with lock spray source. Melting points are corrected.

¹ J. Raushel, V. V. Fokin, *Org. Lett.* **2010**, *12*, 4952-4955.

² R. VenkatRagavan, V. Vijaykumar, N. K. Suchetha, *Eur. J. Med. Chem.* **2009**, *44*, 3852-3857

3. General procedure for synthesis of α -thiocarbonyl derivatives 1



To a solution of arylthiols (2.72 mmol, 1 equiv) in CH_3CN (6 mL), was added K_2CO_3 (564 mg, 4.09 mmol, 1.5 equiv) followed by solution of bromocarbonyl compound (4.09 mmol, 1.5 equiv) in CH_3CN (4 mL) was added drop wise over 3 min. After approximately 3 h analyzed by TLC, ethyl acetate was added to the crude products, washed with water, brine and then dried over Na_2SO_4 . The organic layer was filtered and evaporated under the reduced pressure. The obtained crude product was purified through column chromatography to afford the pure thiocarbonyl compounds in high yields.

4. Properties of isolated α -thiocarbonyl derivatives 1

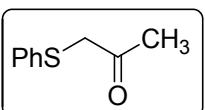
Thioester (2a): 395 mg; Light yellow liquid; Yield: 89%; $R_f = 0.63$ in 10:90 ethyl acetate/hexane; FTIR (Neat): 3213, 3149, 3142, 2922, 2337, 1635, 1544, 1507, 1421, 1401, 1336, 1260, 1195, 1098, 961 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.44-7.38 (m, 2H), 7.33-7.19 (m, 3H), 4.16 (q, 2H, $J = 7.1$ Hz), 3.63(s, 3H), 1.22 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 145.2, 136.2, 135.7, 134.5, 130.5, 129.9, 129.2, 128.6, 127.2, 122.0, 28.9; HRMS: calcd. for $\text{C}_{10}\text{H}_{12}\text{O}_2\text{S}+\text{H}$: 197.0631; found: 197.0632.

Thioester (2b): 347 mg; Yellow liquid; yield: 81%; $R_f = 0.63$ in 10:90 ethyl acetate/hexane; FTIR (Neat): 3272, 3109, 2928, 2856, 2356, 1712, 1642, 1550, 1396, 1270, 1225, 1079, 877 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.45-7.37 (m, 2H), 7.35-7.27 (m, 2H), 7.27-7.19 (m, 1H), 3.71 (s, 3H), 3.65 (s, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 170.3, 135.0, 130.0, 129.2, 127.1, 52.6, 36.6; HRMS: calcd. for $\text{C}_9\text{H}_{10}\text{O}_2\text{S}+\text{H}$: 183.0474; found: 183.0479.

Thioester (2c): 330 mg; White solid; yield: 70%; $R_f = 0.63$ in 10:90 ethyl acetate/hexane; mp: 94-96°C; FTIR (KBr): 3064, 2928, 2859, 1737, 1652, 1581, 1471, 1440, 1272, 1138, 991 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.43-7.39 (m, 2H), 7.32-7.27 (m, 2H), 7.25-7.20 (m, 1H), 5.85 (ddt, 1H, $J = 17.1, 10.1, 5.6$ Hz), 5.28 (dq, 1H, $J = 17.1, 1.4$ Hz), 5.22 (dt, 1H, $J = 10.4, 1.2$ Hz), 4.60 (dt, 1H, $J = 5.7, 1.3$

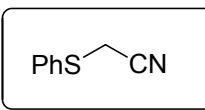
Hz), 3.66 (s, 2H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 169.5, 135.0, 131.7, 130.2, 129.1, 127.1, 118.8, 66.2, 36.8; HRMS: calcd. for $\text{C}_{11}\text{H}_{12}\text{O}_2\text{S}+\text{Na}$: 231.0450; found: 231.0451.

Thioketone (2d): 297 mg; Colourless liquid; yield: 79%; $R_f = 0.60$ in 10:90 ethyl



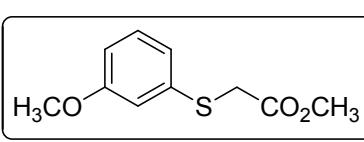
acetate/hexane; FTIR (Neat): 3061, 3004, 2925, 1714, 1638, 1583, 1477, 1430, 1404, 1359, 1278, 1230, 1151, 1088, 743 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.38-7.24 (m, 4H), 7.24-7.18 (m, 1H), 3.66 (s, 2H), 2.27 (s, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 203.7, 134.7, 129.6, 129.2, 127.0, 44.7, 28.1; HRMS: calcd. for $\text{C}_9\text{H}_{10}\text{OS}+\text{Na}$: 189.0345; found: 189.0345.

2-(phenylthio)acetonitrile (2g): 219 mg; Colorless liquid; yield: 65%; $R_f = 0.70$ in 10:90



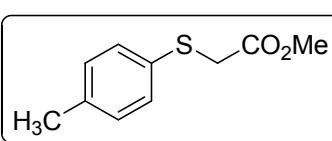
ethyl acetate/hexane; FTIR (Neat): 3405, 3390, 3376, 3362, 3344, 3298, 3289, 3362, 3298, 3171, 3057, 2927, 2856, 2307, 1739, 1586, 1472, 1431, 1266, 1195, 1034, 894 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.65-7.49 (m, 2H), 7.46-7.31 (m, 3H), 3.56 (s, 2H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 132.5, 132.2, 129.7, 129.1, 116.6, 21.5; HRMS: calcd. for $\text{C}_8\text{H}_7\text{NS}+\text{K}$: 187.9931; found: 188.0137.

Thioester (2h): 356 mg; Colorless liquid; yield: 74%; $R_f = 0.57$ in 10:90 ethyl



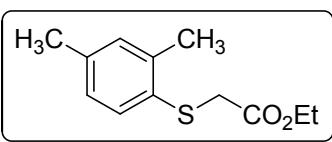
acetate/hexane; FTIR (Neat): 3057, 2987, 2848, 2685, 2522, 2412, 2306, 2136, 1738, 1598, 1427, 1266, 1159, 1039, 985 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3 , 24 °C): δ 7.21 (t, 1H, $J = 7.9$ Hz), 7.02-6.89 (m, 2H), 6.81-6.69 (m, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 3.66 (s, 2H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 170.2, 160.0, 136.3, 130.0, 121.7, 114.9, 112.8, 55.4, 52.7, 36.3; HRMS: calcd. for $\text{C}_{10}\text{H}_{12}\text{O}_3\text{S}+\text{Na}$: 235.0399; found: 235.0393.

Thioester (2i): 391 mg; Light green liquid; yield: 88%; $R_f = 0.64$ in 10:90 ethyl



acetate/hexane; FTIR (Neat): 3299, 3197, 3135, 3120, 3055, 2982, 2930, 2357, 1733, 1638, 1605, 1472, 1464, 1407, 1274, 1135, 1030, 810 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3 , 24 °C): δ 7.36-7.28 (m, 2H), 7.14-7.07 (m, 2H), 3.69 (s, 3H), 3.59 (s, 2H), 2.31 (s, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (125 MHz, CDCl_3 , 24 °C): δ 170.4, 137.5, 131.0, 129.9, 52.5, 37.3, 21.1; HRMS: calcd. for $\text{C}_{10}\text{H}_{12}\text{O}_2\text{S}+\text{H}$: 197.0631; found: 197.0634.

Thioester (2j): 361 mg; Colorless liquid; yield: 71%; $R_f = 0.67$ in 10:90 ethyl acetate/hexane;

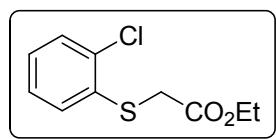


FTIR (Neat): 3227, 3056, 2981, 2871, 2346, 2333, 1733, 1651, 1606, 1448, 1271, 1133, 1028, 741 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3 , 24 °C): δ 7.28 (d, 1H, $J = 7.7$ Hz), 7.01 (m, 1H), 6.96 (m, 1H), 4.13 (q, 2H, $J = 7.1$ Hz), 3.54 (s, 2H), 2.39 (s, 3H), 2.28 (s, 3H), 1.21 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 169.9, 139.1, 137.4, 131.3, 131.2, 130.3,

127.4, 61.5, 36.7, 21.0, 20.4, 14.1; HRMS: calcd. for $C_{12}H_{16}O_2S+Na$: 247.0763; found: 247.0764.

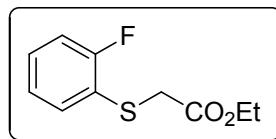
Thioester (2k): 356 mg; Colorless liquid; yield: 57%; $R_f = 0.40$ in 15:85 ethyl acetate/hexane; FTIR (Neat): 1739, 1494, 1285, 1247, 1030, 911, 762, 669 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3 , 24 °C): δ 7.42 (d, 2H, $J = 8.9$ Hz), 7.84 (d, 2H, $J = 8.8$ Hz), 4.14 (q, 2H), 3.79 (s, 3H), 3.50 (s, 2H), 1.21 (t, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (125 MHz, CDCl_3 , 24 °C): δ 170.1, 159.8, 134.3, 125.1, 114.8, 61.5, 55.5, 38.8, 14.2; HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ calcd for $C_{11}H_{14}O_3S+Na$ 249.2813; Found: 249.2818.

Thioester (2l): 402 mg; Colorless liquid; yield: 77%; $R_f = 0.63$ in 10:90 ethyl acetate/hexane;



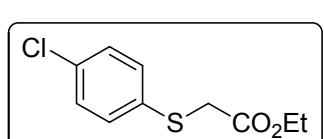
FTIR (Neat): 3057, 2986, 2306, 1734, 1609, 1579, 1444, 1271, 1134, 1030, 897 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.39-7.30 (m, 2H), 7.30-7.22 (m, 2H), 4.16 (q, 2H, $J = 7.1$ Hz), 3.60 (s, 2H), 1.22 (t, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 169.5, 133.5, 133.2, 131.5, 129.2, 61.7, 36.9, 14.1; HRMS: calcd. for $C_{10}H_{11}ClO_2S+H$: 231.0241; found: 231.0242.

Thioester (2m): 408 mg; Light green liquid; yield: 84%; $R_f = 0.62$ in 10:90 ethyl acetate/hexane; FTIR (Neat): 3058, 2987, 2306, 1733, 1580, 1465,



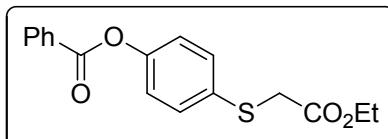
1432, 1272, 1143, 1028, 898 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.67-7.51 (m, 1H), 7.49-7.39 (m, 1H), 7.31-7.21 (m, 2H), 4.25 (q, 2H, $J = 7.0$ Hz), 4.12 (s, 2H), 1.29 (t, 3H, $J = 7.0$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 168.0, 163.4, 152.1, 141.8, 124.3 (d, $J = 30.4$ Hz), 118.7, 110.1, 62.3, 34.3, 14.2; HRMS: calcd. for $C_{10}H_{12}FO_2S+Na$: 237.0356; found: 237.0356.

Thioester (2n): 417 mg; Light yellow liquid; yield: 80%; $R_f = 0.64$ in 10:90 ethyl acetate/hexane; FTIR (KBr): 3127, 3055, 2981, 2934, 1733, 1625,



1588, 1457, 1283, 1155, 1019, 946 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.42-7.32 (m, 2H), 7.31-7.22 (m, 2H), 4.16 (q, 2H, $J = 7.1$ Hz), 3.60 (s, 2H), 1.22 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 169.5, 133.5, 133.2, 131.5, 129.2, 61.7, 36.9, 14.1; HRMS: calcd. for $C_{10}H_{11}ClO_2S+Na$: 253.0060; found: 253.0062.

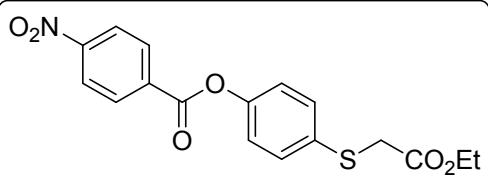
Thioester (2o): 564 mg; White semi solid; yield: 78%; $R_f = 0.56$ in 15:85 ethyl acetate/hexane; FTIR (KBr): 2971, 2952, 2926, 2858, 1738,



1678, 1648, 1630, 1590, 1545, 1457, 1396, 1264, 1201, 1170, 1069, 1085, 935 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 8.23-8.14 (m, 2H), 7.67-7.59 (m, 1H), 7.55-7.46 (m, 4H), 7.21-7.13 (m, 2H), 4.17 (q, 2H, $J = 7.1$ Hz), 3.60 (s, 2H), 1.22 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 170.1, 159.8, 134.3, 125.1, 114.8, 61.5, 55.5, 38.8, 14.2; HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ calcd for $C_{17}H_{18}O_2S+Na$ 300.1163; Found: 300.1163.

2H, $J = 7.0$ Hz), 3.63 (s, 2H), 1.24 (t, 3H, $J = 7.0$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 169.7, 165.0, 150.4, 133.8, 132.3, 132.0, 130.3, 129.4, 128.7, 122.5, 61.7, 37.4, 14.2; HRMS: calcd. for $\text{C}_{17}\text{H}_{16}\text{O}_4\text{S}+\text{H}$: 317.0842; found: 317.0842.

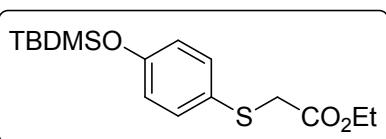
Thioester (2p): 420 mg; White semi solid; yield: 49%; $R_f = 0.56$ in 20:85 ethyl



acetate/hexane; FTIR (KBr): 3051, 2971, 2825, 1738, 1678, 1658, 1634, 1590, 1545, 1457, 1396, 1264, 1201, 1172, 1069, 1084 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 8.42-8.19 (m, 4H), 7.61-7.51

(m, 2H), 7.25-7.19 (m, 2H), 4.17 (q, 2H, $J = 7.0$ Hz), 3.63 (s, 2H), 1.23 (t, 3H, $J = 7.0$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 169.6, 163.2, 151.0, 149.6, 134.7, 133.1, 131.7, 131.4, 123.8, 122.1, 61.7, 37.1, 14.1; HRMS: calcd. for $\text{C}_{17}\text{H}_{16}\text{O}_4\text{S}+\text{H}$: 361.3691; found: 361.3697.

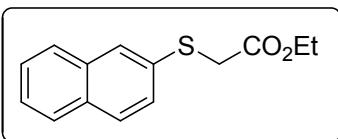
Thioester (2q): 518 mg; Colorless liquid; yield: 70%; $R_f = 0.45$ in 15:85 ethyl



acetate/hexane; FTIR (Neat): 3056, 2948, 2863, 2307, 1731, 1591, 1487, 1419, 1266, 1156, 1027, 910 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.21-7.10 (m, 2H), 6.68-6.49

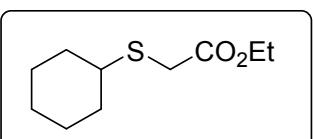
(m, 2H), 3.94 (q, 2H, $J = 7.0$ Hz), 3.33 (s, 2H), 1.02 (t, 3H, $J = 7.1$ Hz), 0.78 (s, 9H), 0.00 (s, 6H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 170.0, 155.9, 133.9, 125.9, 120.9, 61.4, 38.5, 25.7, 18.3, 14.2, -4.3; HRMS: calcd. for $\text{C}_{16}\text{H}_{26}\text{O}_3\text{SSi}+\text{Na}$: 349.1264; found: 349.1265.

Thioester (2r): 429 mg; liquid; yield: 77%; $R_f = 0.64$ in 10:90 ethyl acetate/hexane; FTIR



(Neat): 3273, 3166, 3057, 2978, 2929, 1733, 1656, 1623, 1588, 1454, 1397, 1388, 1376, 1275, 1134, 1027 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3 , 24 °C): δ 7.84 (s, 1H), 7.82-7.70 (m, 3H), 7.51-7.39 (m, 3H), 4.16 (q, 2H, $J = 7.1$ Hz), 3.73 (s, 2H), 1.20 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 169.8, 133.7, 132.5, 132.2, 128.7, 128.2, 127.8, 127.6, 127.3, 126.7, 126.1, 61.7, 36.7, 14.2; HRMS: calcd. for $\text{C}_{14}\text{H}_{14}\text{SO}_2+\text{H}$: 247.0780; found: 247.0787.

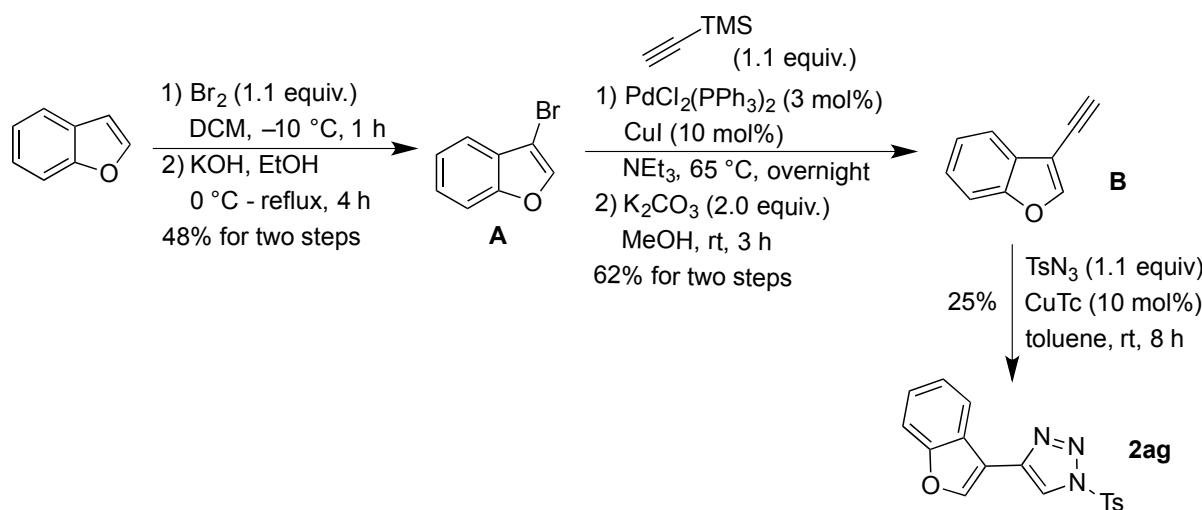
Thioester (2t): 1.68 g; liquid; yield: 89%; $R_f = 0.64$ in 5:95 ethyl acetate/hexane; FTIR



(Neat): 2981, 2927, 2854, 1731, 1450, 1365, 1268, 1133 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 4.17-4.12 (s, 2H), 3.22 (s, 2H), 2.77 (s, 1H), 1.96 (m, 2H), 1.75 (m, 2H), 1.59 (d, 1H, $J = 10$ Hz), 1.30-1.23 (m, 7H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 171.0, 61.3, 44.1, 33.2, 32.2, 26.0, 25.8, 14.2.; HRMS: calcd. for $\text{C}_{10}\text{H}_{18}\text{SO}_2+\text{Na}$: 225.0920; found: 225.0920.

Thioester (2u**):** 670 mg; liquid; yield: 87%; $R_f = 0.64$ in 5:95 ethyl acetate/hexane; FTIR (Neat): 2980, 2925, 28332, 1735, 1445, 1360, 1264, 1132 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 4.24-4.15 (m, 2H), 3.19 (s, 2H), 2.62 (t, 2H, $J = 8.4$ Hz), 1.59 (m, 2H), 1.38-1.25 (m, 17H), 0.90 (t, 3H, $J = 6.9$ Hz), 1.30-1.23 (m, 7H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 170.8, 61.4, 33.9, 32.8, 32.0, 29.7, 29.6, 29.4, 29.3, 29.1, 28.9, 22.8, 14.3.; HRMS: calcd. for $\text{C}_{14}\text{H}_{28}\text{SO}_2\text{Na}$: 283.1702; found: 283.1695.

5. Synthesis of 4-(Benzofuran-3-yl)-1-tosyl-1*H*-1,2,3-triazole (**2ag**):



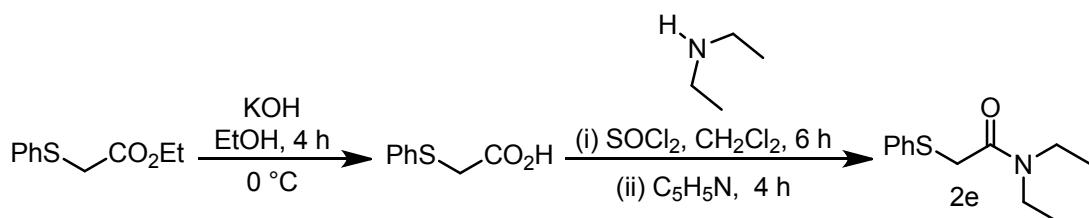
In a round bottom flask, benzofuran (1 g, 1.0 equiv.) was dissolved in 20 mL of DCM and cooled to $-10\text{ }^\circ\text{C}$. Bromine (0.6 mL, 1.1 equiv.) in DCM (3 mL) was slowly added at same temperature. The reaction mixture was stirred for 1 h at $-10\text{ }^\circ\text{C}$. Subsequently, aq. NaOH solution (1 mL, 1 M) was added and the reaction mixture was diluted with water (40 mL) followed by $\text{Na}_2\text{S}_2\text{O}_3$ solution (20 mL) was added. The resultant reaction mixture was extracted with DCM and the combined organic extract was dried over anhydrous Na_2SO_4 . The organic layer was filtered and concentrated under reduced pressure and the residue obtained was subjected for next step without any further purification. The dibromide obtained was dissolved in ethanol (20 mL) and saturated solution of KOH in ethanol (20mL) was added dropwise at $0\text{ }^\circ\text{C}$. Next, the reaction mixture was kept for refluxing for 4 h. After refluxing for 4 h, water was added (10 mL) and the reaction mixture containing EtOH was removed under reduced pressure. The aqueous residue was extracted with ethyl acetate and the organic extract was washed successively with water and brine followed by dried over anhydrous Na_2SO_4 . Upon filtration, this organic extract was concentrated under reduced

pressure and the residue was purified by silica gel flash column chromatography (petroleum ether: EtOAc, 20:1) and the product **A** was obtained in 56% yield as a dark yellow oil.

The 3-bromobenzofuran **A** was taken in round bottom flask along with trimethylsilylacetylene (1.1 equiv), PdCl₂(PPh₃)₂ (3 mol%), CuI (10 mol%) and Et₃N (10 mL). The reaction flask was sealed and kept for reflux overnight. The reaction mixture was cooled to room temperature and filtered through Celite. Evaporation solvent followed by column chromatography using ethylacetate : hexane (1:9) as an eluent afforded the timethylsilylalkyne in 72% yield. The isolated timethylsilylalkyne was treated with K₂CO₃ (2.0 equiv) in MeOH (8 mL) at room temperature for 3 hours. The reaction was monitored by TLC, after complete consumption of alkyne, the reaction mixture was diluted with water (10 mL) and extracted with DCM. Evaporation of solvent followed by column chromatography furnished the compound **B** in 85% yield.

The compound **B** (1.0 equiv) was taken in round bottom flask, followed by TsN₃ (1.1 equiv), CuTc (10 mol%) and toluene (4 mL) were added at room temperature and stirred for 8 hours. Evaporation of solvent followed by column purification using ethyl acetate : hexane (20:80) gave the compound **2ag** in 25% yield. FTIR (KBr): 2950, 2514, 1605, 1415, 123, 586cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 24 °C): δ 8.38 (s, 1H), 8.14 (s, 1H), 8.05 (d, 1H, J = 7.8 Hz); 7.90 (d, 1H, J = 7.1 Hz), 7.54 (d, 1H, J = 7.5 Hz), 7.40-7.28 (m, 6H), 2.44 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C): δ 155.6, 147.6, 143.3, 139.8, 133.1, 132.6, 128.9, 125.3, 123.6, 120.7, 118.9, 111.9, 111.4, 111.1, 104.8, 21.9.; HRMS: m/z: [M+H]⁺ Calcd. for C₁₇H₁₃N₃O₃S+Na: 362.0570; found: 362.0569.

6. Synthesis of *N,N*-diethyl-2-(phenylthio)acetamide:



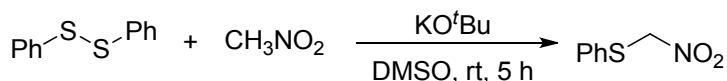
A solution of ethyl 2-(phenylthio)acetate (0.80 g, 4.0 mmol) in EtOH (10 mL) was added to an aqueous solution (10 mL) of potassium hydroxide (2.1 g, 38.0 mmol) at 0 °C. After being stirred for 4 h, by the TLC analysis, reaction mixture was evaporated and was acidified by 2 M HCl and extracted with EtOAc. The organic layer was washed with brine,

dried over anhydrous sodium sulfate, and concentrated in vacuum, purified through column chromatography to give 2-(phenylthio)acetic acid as a colorless liquid.

To a solution 2-(phenylthio)acetic acid (0.60 g, 3.57 mmol, 1 equiv) in dichloromethane, thionyl chloride (0.77 mL, 10.71 mmol, 3 equiv) was added and stirred at room temperature for 6 h. After consumption of acid (by TLC), excess thionyl chloride was then removed under reduced pressure to afford (phenylsulfanyl)acetyl chloride as a yellow liquid.

Pyridine (0.56 mL, 7.14 mmol, 2 equiv) was added to a stirred solution of diethylamine (0.74 mL, 7.14 mmol, 2 equiv) in dichloromethane at 0 °C and (phenylsulfonyl)acetyl chloride was also added drop wise to the reaction mixture at same temperature. By TLC analysis the reaction was quenched with water and extracted with dichloromethane, dried over Na₂SO₄ and concentrated in vacuum. Purified through column chromatography to afford corresponding amide as light yellow liquid; 210 mg; yield: 41%; FTIR (KBr): 3415, 2358, 2121, 1647, 1555, 1160, 670, 586 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 24 °C): δ 7.49-7.41 (m, 2H), 7.34-7.25 (m, 2H), 7.25-7.18 (m, 1H), 3.73 (s, 2H), 3.43-3.28 (m, 4H), 1.19 (t, 3H, *J* = 7.0 Hz), 1.10 (t, 3H, *J* = 7.0 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C): δ 167.6, 135.4, 130.5, 129.0, 127.0, 42.6, 40.5, 37.1, 14.4, 12.9; HRMS: m/z: [M+H]⁺ Calcd. for C₁₂H₁₇NOS: 224.1104; found: 224.1109.

7. Synthesis of (nitromethyl)(phenyl)sulfide 2f



In a 50 mL three-neck round-bottomed flask equipped with nitrogen inlet, 5 mL of dry and degassed dimethylsulfoxide and potassium *t*-butoxide (123 mg, 1.10 mmol) were added. The mixture was stirred till the complete dissolution of the base, the nitromethane (44 μL, 0.82 mmol) was added and stirred for 5 min. To the reaction mixture, diphenyldisulfide(92 mg, 0.42 mmol) was added as a suspension. The reaction mixture was stirred for 5 h and quenched with an excess of ammonium nitrate and 30 mL of water was added. Subsequently, the reaction mixture was acidified with dilute HCl to pH-4 and extracted with dichloromethane (3 × 10 mL). The organic layer obtained was washed with water (2 × 10 mL) to remove the traces of dimethylsulfoxide. Subsequently, it was dried with MgSO₄, filtered, and concentrated to give a crude product, which was further purified by column chromatography with silica gel using ethylacetate/hexaneas an eluent gave the product in 55

mg, 78% yield as yellow oil. R_f = 0.40 in 10:90 ethyl acetate/hexane; FTIR (KBr): 3061, 3002, 2951, 2843, 1739, 1524, 1471, 1357, 1281, 1150, 1039, 855 cm⁻¹; ¹H NMR (500 MHz, CDCl₃, 24 °C): δ 7.53-7.45 (m, 2H), 7.40-7.32 (m, 3H), 5.44 (s, 2H); ¹³C{¹H} NMR (125 MHz, CDCl₃, 24 °C): δ 132.2, 131.7, 129.7, 129.3, 79.5; HRMS: calcd. for C₇H₇NO₂S+Na: 192.0090; found: 192.0096.

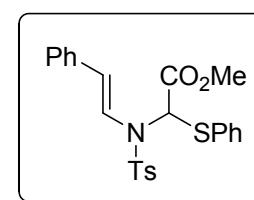
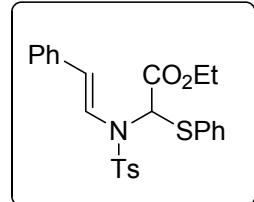
8. Typical procedure for the rhodium catalyzed rearrangement reaction

To a 10 mL reaction tube equipped with stir bar, *N*-sulfonyl-1,2,3-triazole **1** (0.20 mmol, 1 equiv), substituted arylsulfide **2** (0.40 mmol, 2 equiv) and Rh₂(Oct)₄ (0.004 mmol, 2 mol%) were introduced. Next, 1.5 mL of dry toluene was added under an argon atmosphere, and the reaction mixture was transferred to preheated oil-both at 120 °C and allowed to stir for 8 h. After completion of the reaction, monitored by TLC, the reaction mixture was cooled to room temperature and the solvent was evaporated under reduced pressure. The crude product that obtained was purified by column chromatography using hexane/ethyl acetate mixture as an eluent to afford enamide derivatives **3** in high yield and purity.

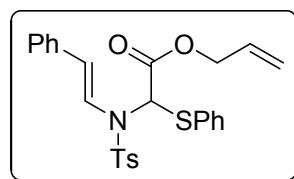
9. Properties of isolated enamides

Enamide (4a): 74 mg; Colorless liquid; yield: 80%; R_f = 0.55 in 20:80 ethyl acetate/hexane; FTIR (neat): 3196, 3068, 2985, 2928, 2810, 2206, 1953, 1886, 1795, 1737, 1599, 1489, 1341, 1266, 1156, 1092, 905 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.63-7.57 (m, 2H), 7.56-7.50 (m, 2H), 7.40-7.33 (m, 3H), 7.30 -7.25 (m, 4H), 7.23-7.16 (m, 3H), 6.94 (d, 1H, J = 14.6 Hz), 6.39-6.25 (m, 2H), 4.18-4.02 (m, 2H), 2.38 (s, 3H), 1.12 (t, 3H, J = 7.1 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 167.1, 144.2, 136.2, 136.0, 134.6, 133.3, 131.7, 129.6, 129.3, 129.1, 128.7, 127.8, 127.2, 126.0, 123.1, 119.4, 67.3, 62.7, 21.6, 14.0; HRMS: calcd. for C₂₅H₂₅NO₄S + Na: 490.1117; found: 490.1129.

Enamide (4b): 71 mg; Light green gummy liquid; yield: 79%; R_f = 0.55 in 20:80 ethyl acetate/hexane; FTIR (neat): 3056, 2986, 2357, 1686, 1427, 1265, 1171, 897, 740 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.60-7.55 (m, 2H), 7.54-7.48 (m, 2H), 7.38-7.33 (m, 3H), 7.31-7.26 (m, 4H), 7.24-7.18 (m, 3H), 6.94 (d, 1H, J = 14.7 Hz), 6.35 (s, 1H), 6.29 (s, 1H, J = 14.7 Hz), 3.65 (s, 3H), 2.39 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 167.6, 144.3, 135.9, 134.5, 133.3, 131.6, 129.6, 129.4, 129.2, 128.7, 127.8, 127.2, 126.0, 123.0, 119.4, 67.1, 53.4, 21.7; HRMS: calcd. for C₂₄H₂₃NO₄S + Na: 476.0961; found: 476.0966.

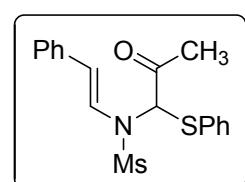


Enamide (4c): 62 mg; Colorless liquid; yield: 65%; $R_f = 0.52$ in 20:80 ethyl acetate/hexane;



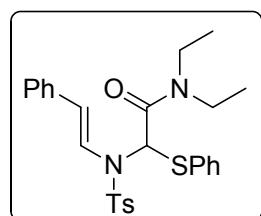
FTIR (neat): 3061, 2933, 2865, 2805, 1952, 1883, 1742, 1645, 1597, 1444, 1355, 1264, 1167, 1089, 1000, 937 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.63 (m, 2H), 7.56-7.50 (m, 2H) 7.40-7.33 (m, 3H), 7.31-7.25 (m, 4H), 7.23-7.18 (m, 3H), 6.94 (d, 1H, $J = 14.6$ Hz), 6.37 (s, 1H), 6.30 (d, 1H, $J = 14.6$ Hz), 5.72 (ddt, 1H, $J = 17.2, 10.5, 5.9$ Hz), 5.30-5.16 (m, 2H), 4.61-4.44 (m, 2H), 2.38 (s, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 166.8, 144.3, 135.9(8), 135.9(5), 134.6, 131.6, 130.9, 129.6, 129.4, 129.2, 128.7, 127.8, 127.2, 126.0, 122.9, 119.5, 119.4, 67.2, 67.1, 21.7; HRMS: calcd. for $\text{C}_{26}\text{H}_{25}\text{NO}_4\text{S}_2 + \text{Na}$: 502.1117; found: 502.1126

Enamide (4d): 40 mg; Light green gummy liquid; yield: 56%; $R_f = 0.49$ in 20:80 ethyl acetate/hexane;



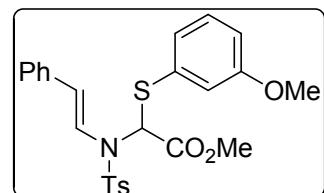
FTIR (neat): 3281, 3063, 2926, 2857, 2477, 2357, 1953, 1896, 1716, 1597, 1442, 1406, 1327, 1213, 1156, 976 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.61-7.55 (m, 2H), 7.38-7.34 (m, 3H), 7.33-7.31 (m, 4H), 7.25-7.19 (m, 1H), 6.97 (d, 1H, $J = 14.7$ Hz), 6.32 (d, 1H, $J = 14.7$ Hz), 6.28 (s, 1H), 2.70 (s, 3H), 2.39 (s, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 200.9, 135.4, 134.0, 132.1, 129.7, 129.1, 128.8, 127.5, 126.0, 122.8, 118.0, 75.1, 39.8, 27.0; HRMS: calcd. for $\text{C}_{18}\text{H}_{19}\text{NO}_3\text{S}_2 + \text{H}$: 362.0879; found: 362.0882.

Enamide (4e): 70 mg; White solid; yield: 71%; $R_f = 0.45$ in 20:80 ethyl acetate/hexane;



FTIR (KBr): 3183, 3057, 2984, 2935, 2411, 2363, 2306, 2127, 2056, 1933, 1890, 1800, 1732, 1653, 1435, 1350, 1266, 1163, 1039, 949 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.56-7.43 (m, 4H), 7.39-7.30 (m, 5H), 7.31-7.23 (m, 2H), 7.22-7.13 (m, 4H), 6.75 (d, 1H, $J = 14.3$ Hz), 6.46 (s, 1H), 3.71-3.41 (m, 2H), 3.44-3.16 (m, 2H), 2.35 (s, 3H), 1.36 (t, 3H, $J = 7.1$ Hz), 1.07 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 165.2, 144.0, 136.2, 135.9, 132.4, 129.5, 129.4, 128.6, 128.5, 127.7, 127.2, 126.3, 124.9, 124.3, 64.9, 42.7, 41.3, 21.6, 14.5, 12.8; HRMS: calcd. for $\text{C}_{27}\text{H}_{30}\text{N}_2\text{O}_3\text{S}_2 + \text{Na}$: 517.1590; found: 517.1595.

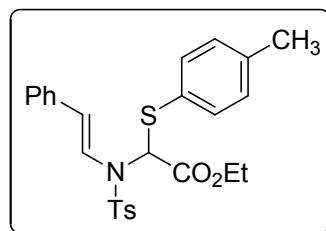
Enamide (4h): 78 mg; Colorless liquid; yield: 81%; $R_f = 0.49$ in 20:80 ethyl acetate/hexane;



FTIR (neat): 3061, 3018, 2938, 2852, 2357, 1746, 1645, 1589, 1470, 1449, 1351, 1247, 116, 1089, 1032, 940 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.63-7.54 (m, 2H), 7.31-7.26 (m, 4H), 7.24-7.15 (m, 4H), 7.09 (d, 1H, $J = 7.6$ Hz), 7.04 (s, 1H), 6.98-6.85 (m, 2H), 6.37 (s, 1H), 6.30 (d, 1H, $J = 14.6$ Hz), 3.78 (s, 3H), 3.67 (s, 3H), 2.39 (s, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 167.6, 160.0, 144.3, 136.0, 135.9, 132.9,

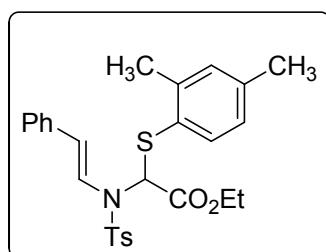
130.1, 129.6, 128.7, 127.8, 127.3, 126.1, 126.0, 123.1, 119.7, 118.7, 115.5, 67.1, 55.4, 53.4, 21.7; HRMS: calcd. for $C_{25}H_{25}NO_5S_2 + NH_4$: 501.1512; found: 501.1522.

Enamide (4i): 75 mg; Colorless liquid; yield: 72%; $R_f = 0.54$ in 20:80 ethyl acetate/hexane;



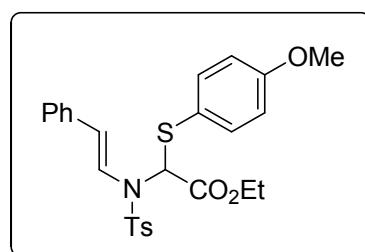
FTIR (neat): 3057, 3028, 2974, 2928, 2865, 2357, 1740, 1645, 1599, 1483, 1450, 1354, 1260, 1166, 1091, 936 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.62-7.53 (m, 2H), 7.44-7.40 (m, 1H), 7.34-7.25 (m, 5H), 7.24-7.13 (m, 5H), 7.01-6.90 (d, 1H, $J = 14.6$ Hz), 6.39-6.22 (m, 2H), 4.16-4.03 (m, 2H), 2.38 (s, 3H), 2.35 (s, 3H), 1.11 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 167.1, 144.2, 139.4, 136.1, 136.0, 134.9, 130.1, 129.5, 128.7, 127.7, 127.1, 125.9, 123.1, 118.8, 67.4, 62.7, 21., 21.4, 13.9; HRMS: calcd. for $C_{26}H_{27}NO_4S_2 + Na$: 504.1274; found: 504.1283.

Enamide (4j): 80 mg; Colorless liquid; yield: 81%; $R_f = 0.55$ in 20:80 ethyl acetate/hexane;



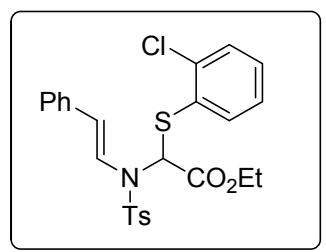
FTIR (neat): 3288, 2974, 2929, 2356, 1740, 1645, 1600, 1450, 1358, 1260, 1166, 1091, 937 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.60-7.49 (m, 2H), 7.46-7.37 (m, 1H), 7.34-7.26 (m, 4H), 7.23-7.16 (m, 3H), 7.06 (s, 1H), 7.02-6.87 (m, 2H), 6.36 (d, 1H, $J = 14.7$ Hz), 6.25 (s, 1H), 4.17-4.02 (m, 2H), 2.44 (s, 3H), 2.38 (s, 3H), 2.33 (s, 3H), 1.12 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 167.3, 144.1, 142.3, 139.7, 136.3, 136.2, 136.1, 131.6, 129.5, 128.7, 127.7 (6), 127.7 (2), 127.1, 127.0, 125.9, 123.2, 118.7, 66.5, 62.6, 21.6, 21.3, 20.9, 14.0; HRMS: calcd. for $C_{27}H_{29}NO_4S_2 + H$: 496.1611; found: 496.1615.

Enamide (4k): 56 mg; Colorless liquid; yield: 57%; $R_f = 0.48$ in 20:80 ethyl acetate/hexane;



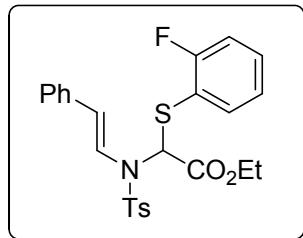
FTIR (neat): 3142, 3044, 2928, 2852, 2366, 2250, 1934, 1885, 1739, 1645, 1529, 1490, 1350, 1251, 1167, 1021, 937 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.64-7.58 (m, 2H), 7.48-7.44 (m, 2H), 7.31-7.26 (m, 4H), 7.25-7.19 (m, 3H), 6.96 (d, 1H, $J = 14.7$ Hz), 6.88-6.84 (m, 2H), 6.31 (d, 1H, $J = 14.7$ Hz), 6.22 (s, 1H), 4.16-4.03 (m, 2H), 3.81 (s, 3H), 2.39 (s, 3H), 1.11 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 167.1, 160.8, 144.2, 137.2, 136.2, 136.1, 129.6, 128.7, 127.8, 127.1, 125.9, 123.1, 121.7, 118.5, 114.8, 67.7, 62.7, 55.4, 21.7, 14.0; HRMS: calcd. for $C_{26}H_{27}NO_5S_2 + H$: 498.1403; found: 498.1417.

Enamide (4l): 74 mg; Colorless liquid; yield: 74%; $R_f = 0.53$ in 20:80 ethyl acetate/hexane; FTIR (neat): 3059, 2974, 2928, 2859,



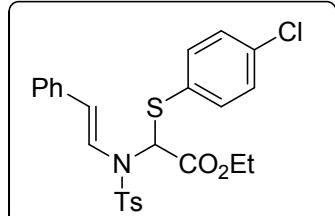
2357, 1904, 1740, 1645, 1599, 1471, 1359, 1262, 1167, 1092, 936 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.66-7.55 (m, 3H), 7.51-7.42 (m, 1H), 7.36-7.17 (m, 9H), 6.91 (1H, d, J = 14.7 Hz), 6.54 (s, 1H), 6.31 (1H, d, J = 14.7 Hz), 4.18-4.04 (m, 2H), 2.38 (s, 3H), 1.10 (t, 3H, J = 7.1 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 166.8, 144.3, 139.0, 137.0, 136.0, 130.7, 130.2, 130.0, 129.6, 128.7, 127.8, 127.5, 127.2, 126.0, 122.9, 119.0, 65.4, 62.9, 21.6, 14.0; HRMS: calcd. for C₂₅H₂₄ClNO₄S₂ + H: 502.0908; found: 502.0919.

Enamide (4m): 82 mg; Colorless liquid; yield: 84%; R_f = 0.53 in 20:80 ethyl acetate/hexane;



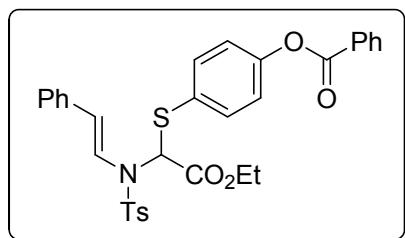
FTIR (neat): 3063, 2996, 2858, 2357, 1922, 1740, 1646, 1597, 1468, 1360, 1262, 1167, 1017, 936 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.69-7.56 (m, 2H), 7.50 (t, 1H, J = 7.4 Hz), 7.45-7.34 (m, 1H), 7.34-7.08 (m, 10H), 6.89 (d, 1H, J = 14.7 Hz), 6.48 (s, 1H), 6.30 (d, 1H, J = 14.7 Hz), 4.17-4.03 (m, 2H), 2.39 (s, 3H), 1.09 (t, 3H, J = 7.1 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 166.8, 144.3, 137.6, 136.1 (J = 8.0 Hz), 131.9 (J = 8.2 Hz), 129.6, 128.7, 127.8, 127.2, 126.0, 124.8 (J = 3.7 Hz), 122.7, 119.0, 116.3, 116.1, 65.6, 62.9, 21.6, 14.0; HRMS: calcd. for C₂₅H₂₄FNO₄S₂ + Na: 508.1023; found: 501.1033.

Enamide (4n): 80 mg; Colorless liquid; yield: 80%; R_f = 0.52 in 20:80 ethyl acetate/hexane;



FTIR (neat): 3061, 2982, 2860, 1740, 1646, 1599, 1448, 1408, 1348, 1264, 1164, 1021, 968 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.60-7.55 (m, 2H), 7.50-7.40 (m, 2H), 7.35-7.26 (m, 6H), 7.26-7.18 (m, 3H), 6.94 (d, 1H, J = 14.7 Hz), 6.31 (s, 1H), 6.28 (d, 1H, J = 14.7 Hz), 4.20-4.00 (m, 2H), 2.40 (s, 3H), 1.11 (t, 3H, J = 7.0 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 166.9, 144.4, 136.2, 136.0, 135.9, 135.7, 129.9, 129.7, 129.5, 128.8, 127.7, 127.2, 125.9, 122.8, 118.9, 67.2, 62.9, 21.7, 14.0; HRMS: calcd. for C₂₅H₂₄ClNO₄S₂ + K: 540.0467; found: 540.0457.

Enamide (4o): 78 mg; White semi solid; yield: 67%; R_f = 0.46 in 20:80 ethyl acetate/hexane;

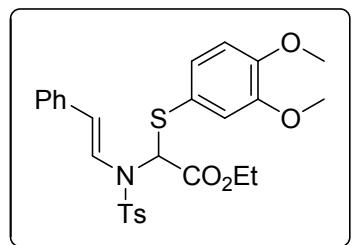


FTIR (neat): 3062, 2977, 2932, 2356, 1740, 1645, 1596, 1487, 1452, 1357, 1260, 1200, 1168, 1063, 937 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.23-8.15 (m, 2H), 7.66-7.57 (m, 5H), 7.54-7.49 (m, 2H), 7.32-7.27 (m, 4H), 7.27-7.22 (m, 4H), 7.22-7.20 (m, 1H), 6.97 (d, 1H, J = 14.7 Hz), 6.33 (s, 1H), 6.31 (d, 1H, J = 14.7 Hz), 4.19-4.06 (m, 2H), 2.39 (s, 3H), 1.13 (t, 3H, J = 7.1 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 167.0, 164.9, 151.9, 144.3, 136.2, 133.8, 130.3, 129.7,

129.4, 128.9, 128.8, 128.7, 127.8, 127.2, 126.0, 123.1, 122.7, 119.0, 67.4, 62.8, 21.7, 14.0; HRMS: calcd. for $C_{32}H_{29}NO_6S_2 + Na$: 610.1329; found: 610.1341.

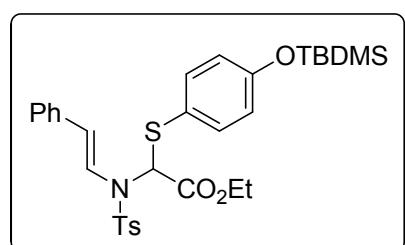
Enamide (4p): 78 mg; Colorless semi solid; yield: 62%; $R_f = 0.42$ in 20:80 ethyl acetate/hexane; FTIR (neat): 3295, 3166, 3056, 2982, 2926, 2856, 2358, 1797, 1644, 1599, 1437, 1347, 1267, 1201, 1167, 1060, 1201, 1167, 1060, 899 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.40-8.35 (m, 4H), 7.69-7.60 (m, 4H), 7.34-7.28 (m, 4H), 7.28-7.24 (m, 5H), 6.96 (d, 1H, $J = 14.7 \text{ Hz}$), 6.30 (s, 1H), 6.28 (d, 1H, $J = 14.7 \text{ Hz}$), 4.19-4.05 (m, 2H), 2.40 (s, 3H), 1.11 (t, 3H, $J = 7.0 \text{ Hz}$); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 166.9, 163.0, 151.4, 151.0, 144.4, 136.5, 136.0, 135.9, 134.8, 131.4, 129.7, 129.4, 128.8, 128.2, 127.8, 127.2, 125.9, 123.9, 122.8, 122.4, 118.6, 67.3, 62.9, 21.7, 14.0; HRMS: calcd. for $C_{32}H_{28}N_2O_8S_2 + Na$: 655.1179; found: 655.1182.

Enamide (4q): 71 mg; White semi solid; yield: 68%; $R_f = 0.45$ in 20:80 ethyl acetate/hexane;



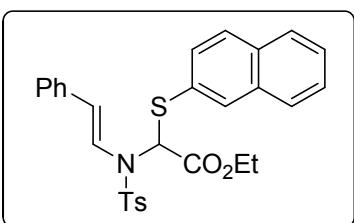
FTIR (neat): 3061, 2948, 2848, 2578, 2328, 1974, 1740, 1644, 1587, 1502, 1453, 1353, 1336, 1252, 1167, 1022, 937 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.63-7.58 (m, 2H), 7.33-7.27 (m, 4H), 7.24-7.19 (m, 3H), 7.13 (dd, 1H, $J = 8.3, 2.0 \text{ Hz}$), 7.05 (d, 1H, $J = 2.0 \text{ Hz}$), 6.97 (d, 1H, $J = 14.7 \text{ Hz}$), 6.82 (d, 1H, $J = 8.3 \text{ Hz}$), 6.31 (d, 1H, $J = 14.7 \text{ Hz}$), 6.29 (s, 1H), 4.16-4.03 (m, 2H), 3.89 (s, 3H), 3.84 (s, 3H), 2.39 (s, 3H), 1.12 (t, 3H, $J = 7.1 \text{ Hz}$); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 167.1, 150.3, 149.1, 144.2, 136.2, 136.1, 129.6, 128.8, 128.4, 127.7, 127.1, 125.9, 123.2, 122.0, 118.6, 118.0, 111.4, 67.7, 62.7, 56.0 (4), 56.0 (1), 21.7, 14.0; HRMS: calcd. for $C_{27}H_{29}NO_6S_2 + H$: 528.1509; found: 528.1522.

Enamide (4r): 88 mg; Colorless liquid; yield: 74%; $R_f = 0.48$ in 20:80 ethyl acetate/hexane;



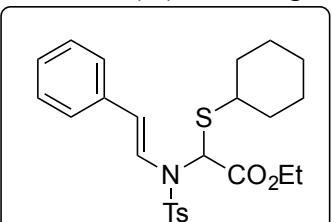
FTIR (neat): 3172, 3071, 2950, 2796, 2305, 1893, 1856, 1776, 1592, 1489, 1361, 1265, 1168, 1091, 910 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.42-7.38 (m, 2H), 7.22-7.17 (m, 2H), 7.10-7.06 (m, 4H), 7.03-7.00 (m, 2H), 6.75 (d, 1H, $J = 14.7 \text{ Hz}$), 6.61-6.56 (m, 2H), 6.11 (d, 1H, $J = 14.7 \text{ Hz}$), 6.01 (s, 1H), 3.94-3.82 (m, 2H), 2.18 (s, 3H), 0.90 (t, 3H, $J = 7.0 \text{ Hz}$), 0.77 (s, 9H), 0.01 (s, 6H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 167.2, 157.2, 144.2, 137.0, 136.3, 136.1, 129.6, 128.7, 127.8, 127.1, 125.9, 123.2, 122.7, 121.1, 118.7, 67.6, 62.6, 25.7, 21.6, 18.3, 14.0, -4.3; HRMS: calcd. for $C_{31}H_{39}NO_5S_2Si + Na$: 620.1931; found: 620.1946.

Enamide (4s): 65 mg; White gummy liquid; yield: 63%; $R_f = 0.53$ in 20:80 ethyl acetate/hexane; FTIR (neat): 3295, 3056, 2969, 2927, 2859,



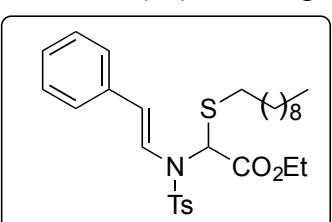
2356, 1920, 1740, 1644, 1596, 1492, 1450, 1355, 1262, 1167, 1090, 938 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.97-7.91 (m, 1H), 7.85-7.80 (m, 2H), 7.75-7.72 (m, 1H), 7.60 (dd, 1H, $J = 1.7, 8.5$ Hz), 7.53-7.49 (m, 2H), 7.48-7.44 (m, 2H), 7.32-7.27 (m, 4H), 7.24-7.19 (m, 1H), 7.05-6.94 (m, 3H), 6.46(s, 1H), 6.35(d, 1H, $J = 14.7$ Hz), 4.19-4.09 (m, 2H), 2.30 (s, 3H), 1.16 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 167.2, 144.1, 136.0, 135.9, 134.3, 133.6, 133.2, 130.8, 129.5, 129.1, 128.9, 128.7, 127.9, 127.8, 127.6, 127.2, 127.0, 126.7, 126.0, 123.1, 119.3, 67.4, 62.9, 21.6, 14.0; HRMS: calcd. for $\text{C}_{29}\text{H}_{27}\text{NO}_4\text{S}_2 + \text{NH}_4$: 535.1720; found: 535.1728.

Enamide (4t): 122 mg; Light green gummy liquid; yield: 76%; $R_f = 0.50$ in 20:80 ethyl acetate/hexane; FTIR (neat): 2923, 2854, 2358, 1739, 1643,



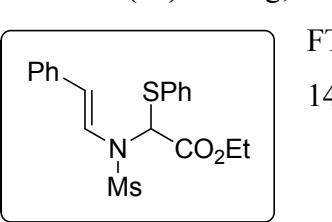
1450, 1357, 1257, 1222, 1160, 938 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 7.76 (d, 2H, $J = 7.8$ Hz), 7.29-7.25 (m, 7H), 6.35 (d, 1H, $J = 14.9$ Hz), 6.14 (s, 1H), 4.07-3.96 (m, 2H), 2.90 (t, 1H, $J = 9.5$ Hz), 2.41 (s, 3H), 2.16 (d, $J = 11.6$ Hz, 1H), 1.92 (d, 1H, $J = 8.3$ Hz), 1.81-1.72 (m, 3H), 1.49-1.20 (m, 8H), 1.08 (t, 3H, $J = 7.2$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 167.7, 144.3, 136.2, 129.7, 128.7, 127.7, 127.1, 126.0, 123.1, 119.7, 62.4, 62.1, 44.2, 33.8, 32.9, 26.1, 25.8, 25.8, 21.7, 13.9.; HRMS: calcd. for $\text{C}_{25}\text{H}_{31}\text{NO}_4\text{S}_2 + \text{Na}$: 496.1587; found: 496.1583.

Enamide (4u): 122 mg; Light green gummy liquid; yield: 81%; $R_f = 0.50$ in 20:80 ethyl acetate/hexane; FTIR (neat): 2920, 2851, 2357, 1732, 1634,



1452, 1358, 1241, 1214, 938 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ 7.76 (d, 2H, $J = 7.8$ Hz), 7.29-7.25 (m, 7H), 6.35 (d, 1H, $J = 14.9$ Hz), 6.14 (s, 1H), 4.07-3.96 (m, 2H), 2.90 (t, 1H, $J = 9.5$ Hz), 2.41 (s, 3H), 2.16 (d, $J = 11.6$ Hz, 1H), 1.92 (d, 1H, $J = 8.3$ Hz), 1.81-1.72 (m, 3H), 1.49-1.20 (m, 8H), 1.08 (t, 3H, $J = 7.2$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 167.7, 144.3, 136.2, 129.7, 128.7, 127.7, 127.1, 126.0, 123.1, 119.7, 62.4, 62.1, 44.2, 33.8, 32.9, 26.1, 25.8, 25.8, 21.7, 13.9; HRMS: calcd. for $\text{C}_{25}\text{H}_{31}\text{NO}_4\text{S}_2 + \text{Na}$: 496.1587; found: 496.1583.

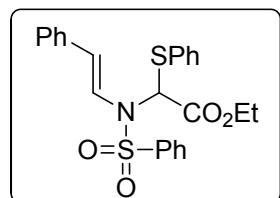
Enamide (4v): 57 mg; Colorless liquid; yield: 73%; $R_f = 0.51$ in 20:80 ethyl acetate/hexane;



FTIR (neat): 3193, 3061, 2982, 2933, 2860, 1740, 1646, 1599, 1448, 1408, 1348, 1264, 1164, 1021, 968 cm^{-1} ; ^1H NMR (400 MHz,

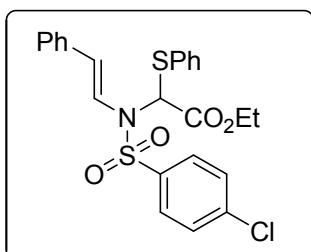
CDCl_3): δ 7.67-7.48 (m, 2H), 7.42-7.28 (m, 7H), 7.27-7.18 (m, 1H), 6.95 (d, 1H, J = 14.7 Hz), 6.38 (d, 1H, J = 14.8 Hz), 6.31 (s, 1H), 4.45-4.16 (m, 2H), 2.86 (s, 3H), 1.31 (t, 3H, J = 7.0 Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 167.3, 135.8, 134.8, 131.2, 129.4, 129.3, 128.8, 127.3, 125.9, 122.8, 118.2, 67.3, 63.2, 40.1, 14.2; HRMS: calcd. for $\text{C}_{19}\text{H}_{21}\text{NO}_4\text{S}_2^+$ Na: 414.0804; found: 414.0819.

Enamide (4w): 67 mg; Colorless liquid; yield: 75%; R_f = 0.53 in 20:80 ethyl acetate/hexane;



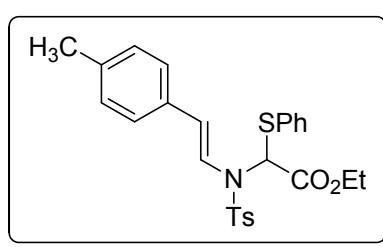
FTIR (neat): 3065, 2979, 2930, 2357, 1741, 1645, 1585, 1473, 1364, 1260, 1170, 1091, 1014, 937 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.75-7.67 (m, 2H), 7.57-7.51 (m, 3H), 7.45-7.41 (m, 2H), 7.38-7.33 (m, 3H), 7.32-7.26 (m, 4H), 7.23-7.19 (m, 1H), 6.95 (d, 1H, J = 14.7 Hz), 6.40-6.23 (m, 2H), 4.15-4.02 (m, 2H), 1.10 (t, 3H, J = 7.1 Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 167.0, 139.1, 135.9, 134.7, 133.3, 131.6, 129.4, 129.2, 129.0, 128.8, 127.7, 127.3, 126.0, 122.9, 119.8, 67.4, 62.8, 14.0; HRMS: calcd. for $\text{C}_{24}\text{H}_{23}\text{NO}_4\text{S}_2^+$ Na: 476.0961; found: 476.0966.

Enamide (4x): 68 mg; Colorless liquid; yield: 70%; R_f = 0.51 in 20:80 ethyl acetate/hexane;



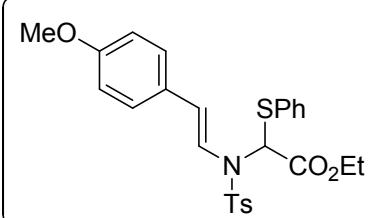
FTIR (neat): 3059, 2983, 2357, 1740, 1646, 1585, 1474, 1443, 1363, 1265, 1171, 1091, 937 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.75-7.67 (m, 2H), 7.57-7.51 (m, 3H), 7.45-7.41 (m, 2H), 7.38-7.33 (m, 3H), 7.32-7.26 (m, 4H), 7.23-7.19 (m, 1H), 6.95 (d, 1H, J = 14.7 Hz), 6.40-6.23 (m, 2H), 4.15-4.02 (m, 2H), 1.10 (t, 3H, J = 7.1 Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 167.0, 139.1, 135.9, 134.7, 133.3, 131.6, 129.4, 129.2, 129.0, 128.8, 127.7, 127.3, 126.0, 122.9, 119.8, 67.4, 62.8, 14.0; HRMS: calcd. for $\text{C}_{24}\text{H}_{22}\text{ClNO}_4\text{S}_2^+$ Na: 510.0571; found: 510.0575.

Enamide (4y): 71 mg; Colorless liquid; yield: 74%; R_f = 0.51 in 20:80 ethyl acetate/hexane;

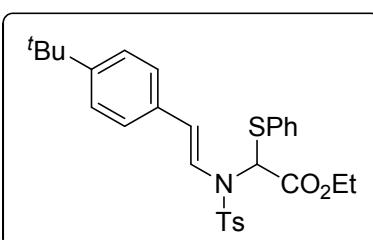


FTIR (neat): 3057, 3028, 2974, 2928, 2865, 2357, 1740, 1645, 1599, 1483, 1354, 1260, 1166, 1091, 936 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.62-7.56 (m, 2H), 7.55-7.51 (m, 2H), 7.37-7.33 (m, 3H), 7.22-7.16 (m, 4H), 7.13-7.07 (m, 2H), 6.87 (d, 1H, J = 14.6 Hz), 6.33 (s, 1H), 6.28 (d, 1H, J = 14.6 Hz), 4.18-4.04 (m, 2H), 2.38 (s, 3H), 2.32 (s, 3H), 1.11 (t, 3H, J = 7.1 Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 167.2, 144.2, 137.1, 136.1, 134.6, 133.0, 131.7, 129.6, 129.4, 129.3, 129.1, 127.8, 125.9, 122.1, 119.9, 67.3, 62.7, 21.6, 21.2, 14.0; HRMS: calcd. for $\text{C}_{26}\text{H}_{27}\text{NO}_4\text{S}_2^+$ Na: 504.1274; found: 504.1284.

Enamide (4z): 78 mg; Colorless gummy solid; yield: 79%; $R_f = 0.48$ in 20:80 ethyl acetate/hexane; FTIR (neat): 3061, 2948, 2848, 2573, 2328, 1974, 1740, 1644, 1587, 1502, 1453, 1353, 1336, 1252, 1167, 1092, 937 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.61-7.56 (m, 2H), 7.56-7.48 (m, 2H), 7.39-7.33 (m, 3H), 7.24-7.18 (m, 4H), 6.88-6.80 (m, 2H), 6.79-6.72 (m, 1H), 6.45-6.20 (m, 2H), 4.16-4.04 (m, 2H), 3.80 (s, 3H), 2.39 (s, 3H), 1.13 (t, 3H, $J = 7.1 \text{ Hz}$); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 167.2, 159.1, 144.1, 136.1, 134.5, 131.7, 129.6, 129.3, 129.0, 128.8, 128.4, 127.8, 127.6, 127.3, 121.0 (9), 121.0(5), 114.2, 67.4, 62.7, 55.4, 21.7, 14.0; HRMS: calcd. for $\text{C}_{26}\text{H}_{27}\text{NO}_5\text{S}_2 + \text{Na}$: 520.1223; found: 520.1229.

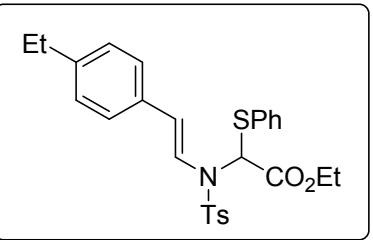


Enamide (4aa): 94 mg; Colorless gummy liquid; yield: 90%; $R_f = 0.51$ in 20:80 ethyl acetate/hexane; FTIR (neat): 3058, 2959, 2869, 2357, 1741, 1645, 1599, 1463, 1359, 1262, 1167, 1093, 935 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.64-7.56 (m, 2H), 7.56 (m, 2H), 7.37-7.30 (m, 5H), 7.25-7.17 (m, 4H), 6.90 (d, 1H, $J = 14.6 \text{ Hz}$), 6.34 (s, 1H), 6.29 (d, 1H, $J = 14.6 \text{ Hz}$), 4.17-4.03 (m, 2H), 2.38 (s, 3H), 1.31 (s, 9H), 1.11 (t, 3H, $J = 7.1 \text{ Hz}$); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 167.1, 150.3, 144.2, 136.1, 134.6, 133.1, 131.6, 129.6, 129.3, 129.1, 127.8, 125.7, 125.6, 122.3, 119.4, 67.3, 62.7, 34.6, 31.3, 21.6, 14.0; HRMS: calcd. for $\text{C}_{29}\text{H}_{33}\text{NO}_4\text{S}_2 + \text{Na}$: 546.1743; found: 546.1758.



Enamide (4ab): 45 mg; Colorless gummy liquid; yield: 80%; $R_f = 0.52$ in 20:80 ethyl acetate/hexane; FTIR (neat): 3262, 3053, 2968, 2927, 2863, 2357, 1740, 1645, 1598, 1451, 1357, 1259, 1168, 1091, 934 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.63-7.56 (m, 2H), 7.56-7.51 (m, 2H), 7.39-7.32 (m, 3H), 7.24-7.15 (m, 3H), 7.13-7.05 (m, 2H), 7.05-7.00 (m, 1H), 6.94 (d, 1H, $J = 14.6 \text{ Hz}$), 6.33 (s, 1H), 6.26 (d, 1H, $J = 14.6 \text{ Hz}$), 4.18-4.03 (m, 2H), 2.38 (s, 3H), 2.33 (s, 3H), 1.11 (t, 3H, $J = 7.1 \text{ Hz}$); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 167.1, 144.2, 138.3, 136.1, 135.8, 134.7, 131.6, 129.6, 129.3, 129.1, 128.6, 128.0, 127.7, 126.7, 123.1, 122.8, 119.2, 67.2, 62.8, 21.6, 21.5, 14.0; HRMS: calcd. for $\text{C}_{26}\text{H}_{27}\text{NO}_4\text{S}_2 + \text{Na}$: 504.1274; found: 504.1274.

Enamide (4ac): 87 mg; Colorless gummy liquid; yield: 88%; $R_f = 0.53$ in 20:80 ethyl acetate/hexane; FTIR (neat): 3057, 2971, 2933, 2872, 2356, 1740, 1646, 1600, 1442, 1355, 1265, 1168, 1091, 934 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.61-7.56 (m, 2H), 7.56-7.50

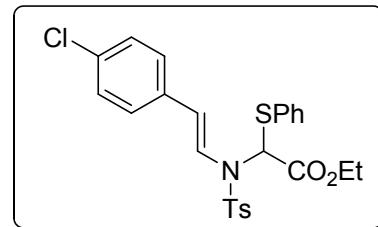


(m, 2H), 7.38-7.32 (m, 3H), 7.23-7.18 (m, 4H), 7.15-7.11 (m, 2H), 6.88 (d, 1H, $J = 14.6$ Hz), 6.34 (s, 1H), 6.29 (d, 1H, $J = 14.6$ Hz), 4.16-4.03 (m, 2H), 7.66 (q, 2H, $J = 7.6$ Hz), 2.38 (s, 3H), 1.22 (t, 3H, $J = 7.6$ Hz), 1.11 (t, 3H, $J = 7.2$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 167.1, 144.1, 143.5, 136.1, 134.6, 133.3, 131.7, 129.6, 129.3, 129.1, 128.2, 127.8, 126.0, 122.2, 119.8, 67.3, 62.7, 28.6, 21.6, 15.7, 14.0; HRMS: calcd. for $\text{C}_{27}\text{H}_{29}\text{NO}_4\text{S}_2 + \text{Na}^+$: 518.1430; found: 518.1437.

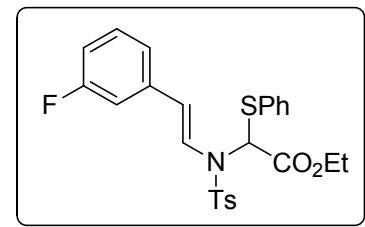
Enamide (4ad): 72 mg; Light green semi solid; yield: 71%; $R_f = 0.51$ in 20:80 ethyl acetate/hexane; FTIR (neat): 2925, 2857, 2357, 1892, 1740, 1645, 1609, 1447, 1351, 1257, 1166, 1092, 1020, 935 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): 7.64-7.59 (m, 2H), 7.58 (dd, 1H, $J = 7.5, 1.7$ Hz), 7.48 (dd, 1H, $J = 7.9, 1.3$ Hz), 7.34 (dd, 1H, $J = 7.6, 1.6$ Hz), 7.32-7.25 (m, 5H), 7.24-7.19 (m, 3H), 6.91 (d, 1H, $J = 14.7$ Hz), 6.54 (s, 1H), 6.30 (d, 1H, $J = 14.7$ Hz), 4.20-4.03 (m, 2H), 2.38 (s, 3H), 1.10 (s, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 166.8, 144.3, 139.0, 137.1, 136.0, 130.7, 130.2, 129.9, 129.6, 128.7, 127.8, 127.5, 127.2, 125.9, 122.8, 118.9, 65.4, 62.9, 21.6, 14.0; HRMS: calcd. for $\text{C}_{25}\text{H}_{24}\text{ClNO}_4\text{S}_2 + \text{NH}_4^+$: 519.1179; found: 519.1190.

Enamide (4ae): 76 mg; Colorless gummy liquid; yield: 79%; $R_f = 0.51$ in 20:80 ethyl acetate/hexane; FTIR (neat): 3581, 3466, 3304, 3064, 2929, 2860, 2357, 1741, 1645, 1597, 1477, 1445, 1358, 1259, 1166, 1090, 931 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.65-7.56 (m, 2H), 7.56-7.50 (m, 2H), 7.40-7.33 (m, 3H), 7.26-7.20 (m, 3H), 7.06-7.02 (m, 1H), 7.01-6.94 (m, 2H), 6.92-6.85 (m, 1H), 6.33 (s, 1H), 6.23 (s, 1H, $J = 14.6$ Hz), 4.18-4.05 (m, 2H), 2.39 (s, 3H), 1.12 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 167.0, 163.2 (d, $J = 246.4$ Hz), 144.4, 138.4 (d, $J = 8.0$ Hz), 135.8, 134.7, 131.4, 130.2 (d, $J = 8.4$ Hz), 129.7, 129.4, 129.3, 127.7, 124.2, 121.8, 116.7, 113.8 (d, $J = 21.2$ Hz), 112.3 (d, $J = 22.0$ Hz), 67.1, 62.8, 21.7, 14.0; HRMS: calcd. for $\text{C}_{25}\text{H}_{24}\text{FNO}_4\text{S}_2 + \text{NH}_4^+$: 503.1469; found: 503.1482.

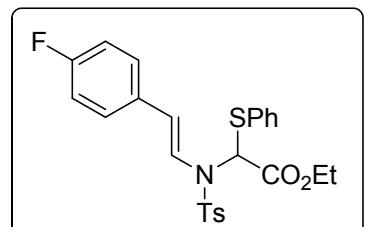
Enamide (4af): 68 mg; Light green gummy liquid; yield: 71%; $R_f = 0.50$ in 20:80 ethyl acetate/hexane; FTIR (neat): 3057, 2971, 2933, 2872, 2356, 1740, 1646, 1600, 1442, 1355, 1265, 1168, 1091, 934 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.52-7.39 (m, 4H), 7.37-7.24 (m, 3H), 7.19-7.11 (m, 4H), 6.95-6.87 (m, 2H), 6.78 (d, 1H, $J = 14.7$ Hz), 6.25 (m, 1H), 6.20 (d, 1H, $J = 14.7$ Hz), 4.09-3.97



^1H NMR (400 MHz, CDCl_3): 7.64-7.59 (m, 2H), 7.58 (dd, 1H, $J = 7.5, 1.7$ Hz), 7.48 (dd, 1H, $J = 7.9, 1.3$ Hz), 7.34 (dd, 1H, $J = 7.6, 1.6$ Hz), 7.32-7.25 (m, 5H), 7.24-7.19 (m, 3H), 6.91 (d, 1H, $J = 14.7$ Hz), 6.54 (s, 1H), 6.30 (d, 1H, $J = 14.7$ Hz), 4.20-4.03 (m, 2H), 2.38 (s, 3H), 1.10 (s, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 166.8, 144.3, 139.0, 137.1, 136.0, 130.7, 130.2, 129.9, 129.6, 128.7, 127.8, 127.5, 127.2, 125.9, 122.8, 118.9, 65.4, 62.9, 21.6, 14.0; HRMS: calcd. for $\text{C}_{25}\text{H}_{24}\text{ClNO}_4\text{S}_2 + \text{NH}_4^+$: 519.1179; found: 519.1190.



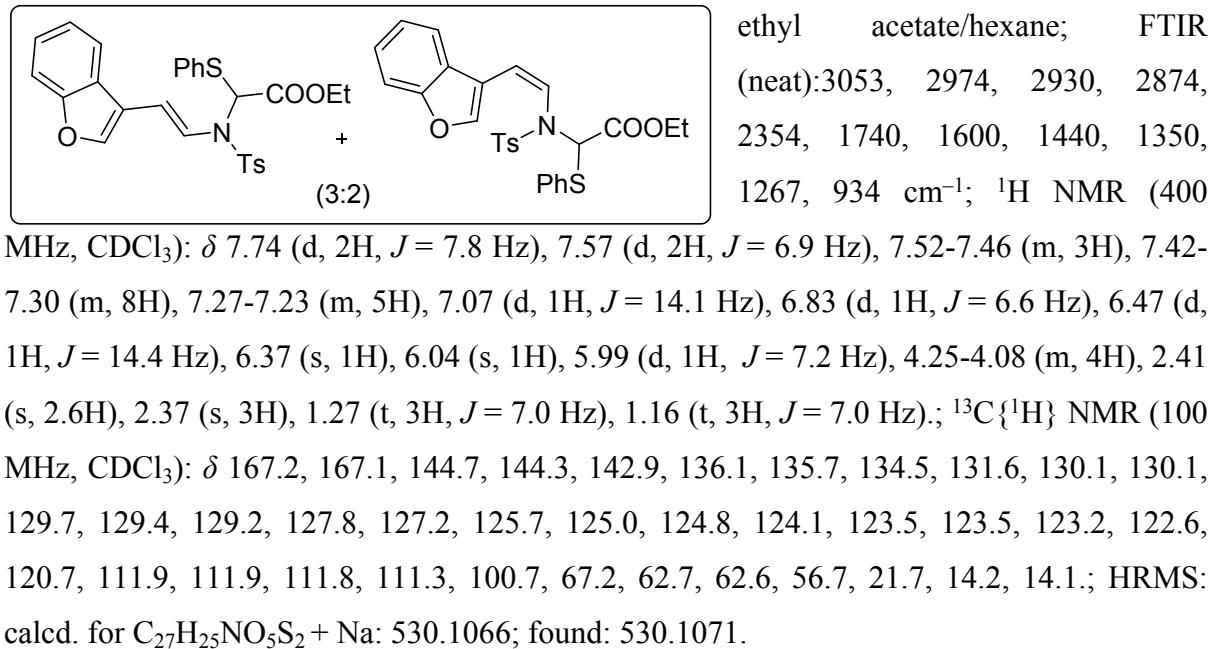
^1H NMR (400 MHz, CDCl_3): δ 7.65-7.56 (m, 2H), 7.56-7.50 (m, 2H), 7.40-7.33 (m, 3H), 7.26-7.20 (m, 3H), 7.06-7.02 (m, 1H), 7.01-6.94 (m, 2H), 6.92-6.85 (m, 1H), 6.33 (s, 1H), 6.23 (s, 1H, $J = 14.6$ Hz), 4.18-4.05 (m, 2H), 2.39 (s, 3H), 1.12 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 167.0, 163.2 (d, $J = 246.4$ Hz), 144.4, 138.4 (d, $J = 8.0$ Hz), 135.8, 134.7, 131.4, 130.2 (d, $J = 8.4$ Hz), 129.7, 129.4, 129.3, 127.7, 124.2, 121.8, 116.7, 113.8 (d, $J = 21.2$ Hz), 112.3 (d, $J = 22.0$ Hz), 67.1, 62.8, 21.7, 14.0; HRMS: calcd. for $\text{C}_{25}\text{H}_{24}\text{FNO}_4\text{S}_2 + \text{NH}_4^+$: 503.1469; found: 503.1482.



^1H NMR (400 MHz, CDCl_3): δ 7.52-7.39 (m, 4H), 7.37-7.24 (m, 3H), 7.19-7.11 (m, 4H), 6.95-6.87 (m, 2H), 6.78 (d, 1H, $J = 14.7$ Hz), 6.25 (m, 1H), 6.20 (d, 1H, $J = 14.7$ Hz), 4.09-3.97

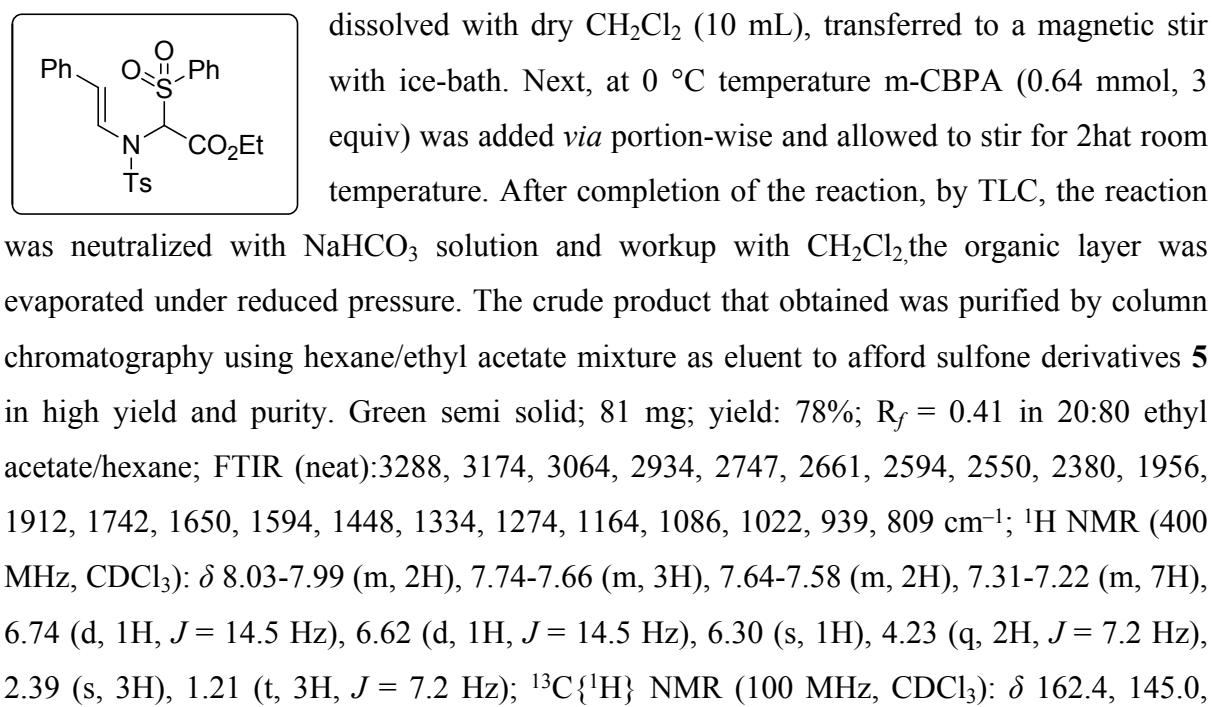
(m, 2H), 2.31 (s, 3H), 1.05 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 167.1, 162.1 (d, $J = 246.3$ Hz), 144.3, 135.9, 134.6, 132.0 (d, $J = 3.5$ Hz), 131.5, 129.6, 129.3, 129.2, 127.7, 127.4 (d, $J = 7.8$ Hz), 122.8, 118.4, 115.6 (d, $J = 21.6$ Hz), 67.2, 62.8, 21.7, 14.0; HRMS: calcd. for $\text{C}_{25}\text{H}_{24}\text{FNO}_4\text{S}_2 + \text{Na}$: 508.1023; found: 508.1017.

Enamide(4g): 16 mg; Light green gummy liquid; yield: 27% ($E/Z = 3/2$); $R_f = 0.50$ in 20:80



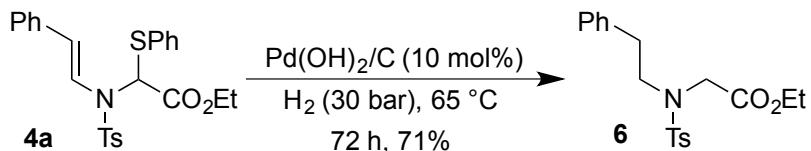
10. Synthesis of sulfone 5

To a 25 mL round bottom flask equipped with stir bar, enamide **3a** (0.21 mmol, 1 equiv) was



137.4, 135.4, 134.9, 134.8, 133.8, 129.8, 129.7, 129.2, 128.7, 128.2, 127.7, 126.3, 124.0, 122.6, 63.4, 21.7, 14.0; HRMS: calcd. for C₂₅H₂₅NO₆S₂ + Na: 522.1016; found: 522.1026.

11. Hydrogenation of enamide **4a**:



In a 250 mL autoclave Enamine **4a** was taken in 50 mg scale (1.0 equiv.) and 10% Pd-hydroxide on carbon (10 mol%) in MeOH was taken, followed by autoclave was closed tightly. Slowly hydrogen was purged three times. Finally 30 bar pressure was set inside the autoclave. The reaction was monitored for 72 h at 65 °C. After 72 h, the reaction mixture was filtered with celite three times using DCM solvent. The filtered solution was concentrated in high-vacuum pump, which was further purified by column chromatography with silica gel using ethylacetate/hexane as (5:95 ratio) an eluent gave the product **6** with 71% yield. FTIR (neat): 2992, 2931, 2887, 2350, 1741, 1633, 1432, 1351, 1260, 930 cm⁻¹; ¹H NMR (500 MHz, CDCl₃, 24 °C): δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.30-7.28 (m, 4H), 7.24 (d, *J* = 7.3 Hz, 1H), 7.17 (d, *J* = 7.3 Hz, 1H), 4.11-4.07 (m, 2H), 4.00 (s, 2H), 4.32 (s, 2H), 3.49 (d, *J* = 9.1 Hz, 2H) 2.90 (t, *J* = 9.1 Hz, 2H), 2.44 (s, 3H), 1.20 (t, *J* = 7.7 Hz, 3H); ¹³C{¹H} NMR (125 MHz, CDCl₃, 24 °C): δ 169.1, 143.5, 138.4, 136.9, 129.7, 128.9, 128.7, 127.5, 126.7, 61.4, 50.2, 48.8, 35.3, 21.6, 14.1. HRMS: calcd. for C₁₉H₂₃NO₄+ Na: 384.1240; found: 384.1242.

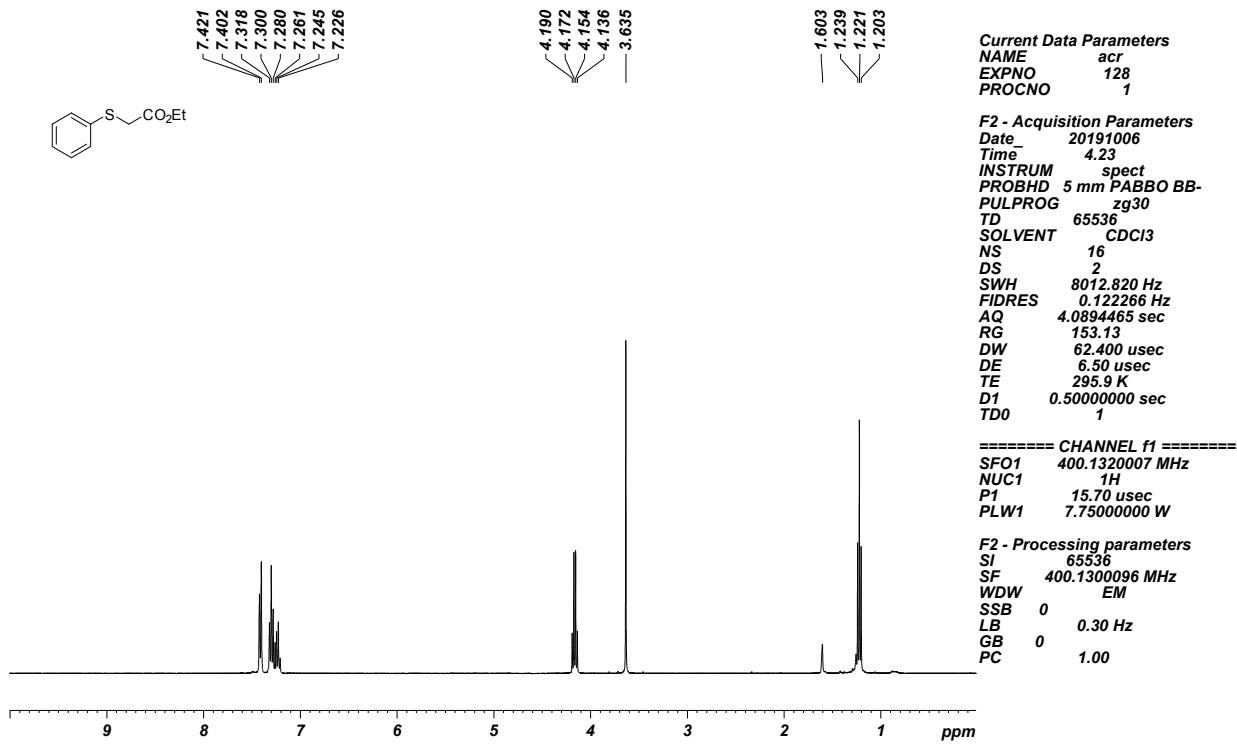
12. Crystallographic data and structure refinements summary for compound 4e

DATA	4e
Molecular Structure (ORTEP Structure)	
Formula	C ₂₇ H ₃₀ N ₂ O ₃ S ₂
Formula weight	494.65
Color	white
Temperature/K	293(2)
Radiation	Mo K α
Wavelength/ \AA	0.71073
Crystal system	Monoclinic
Space group	P21/c
<i>a</i> (\AA)	13.5570(9)
<i>b</i> (\AA)	15.9431(9)
<i>c</i> (\AA)	12.6454(8)
α ($^\circ$)	90
β ($^\circ$)	101.401(2)
γ ($^\circ$)	90
Volume (\AA^3)	2679.3(3)
<i>Z</i>	4
Density (g/ml)	1.226
μ (1/mm)	0.0077
<i>F</i> (000)	1048
θ (min, max)	2.217, 24.999
No. of unique reflns	4735
No. of parameters	500
<i>R</i> _obs, <i>wR</i> ₂ _obs	0.0605, 0.1537
$\Delta\rho_{\min}, \Delta\rho_{\max}$ (e \AA^{-3})	-0.220, 0.403
GooF	1.066

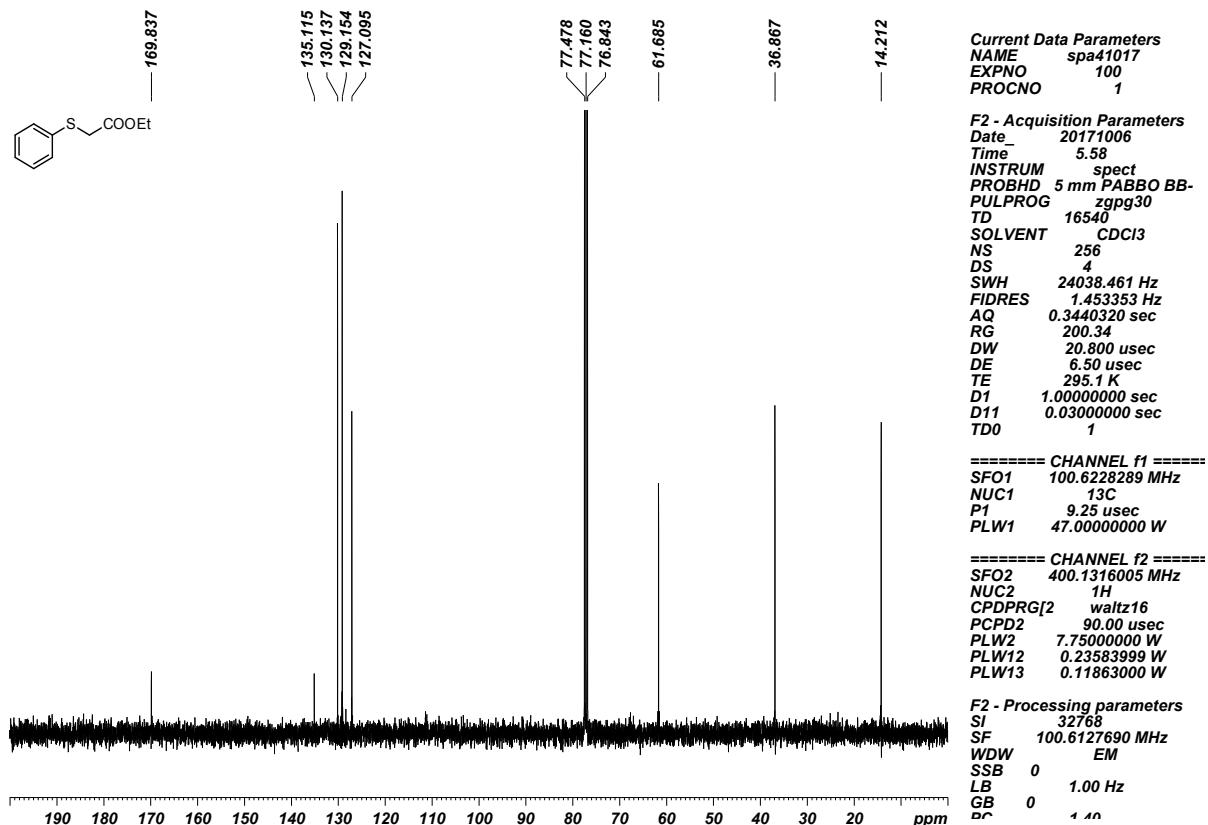
13. NMR spectra of isolated compounds

Thioester 4a

¹H NMR (400 MHz, CDCl₃, 24 °C)

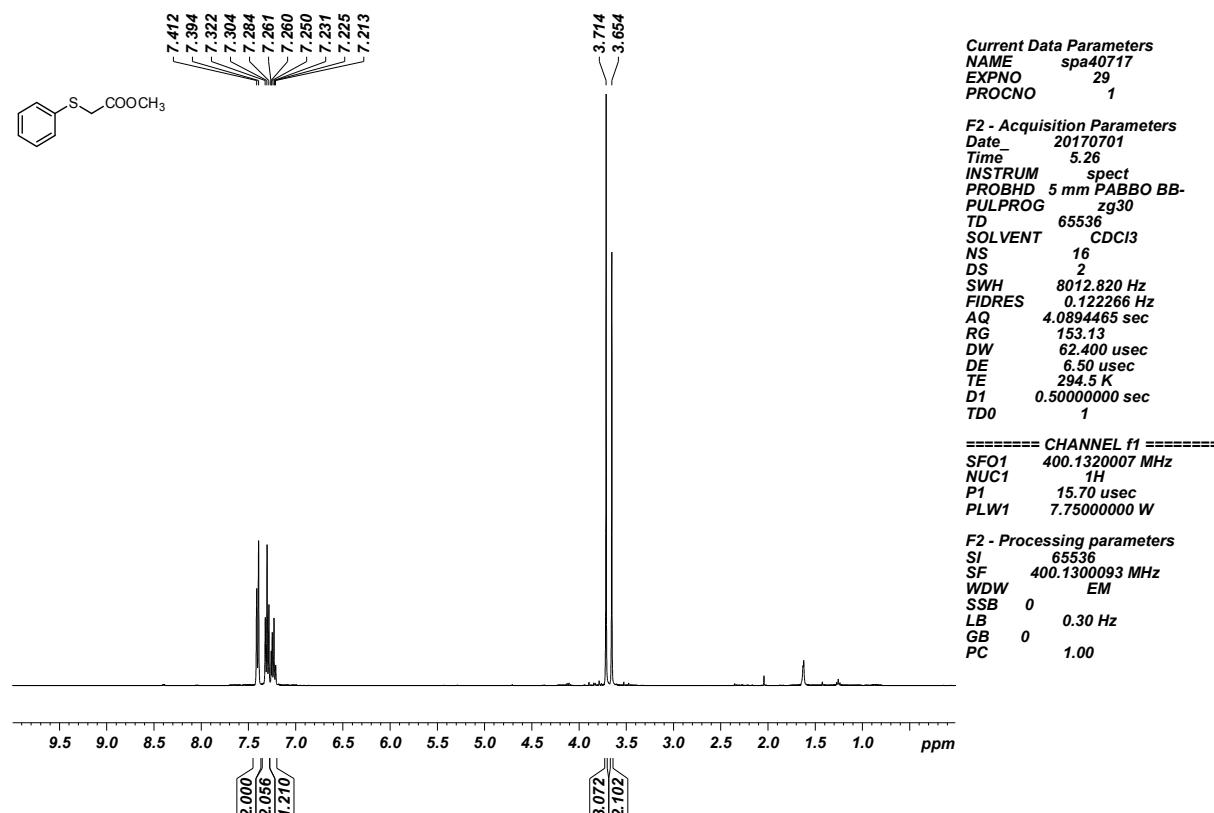


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

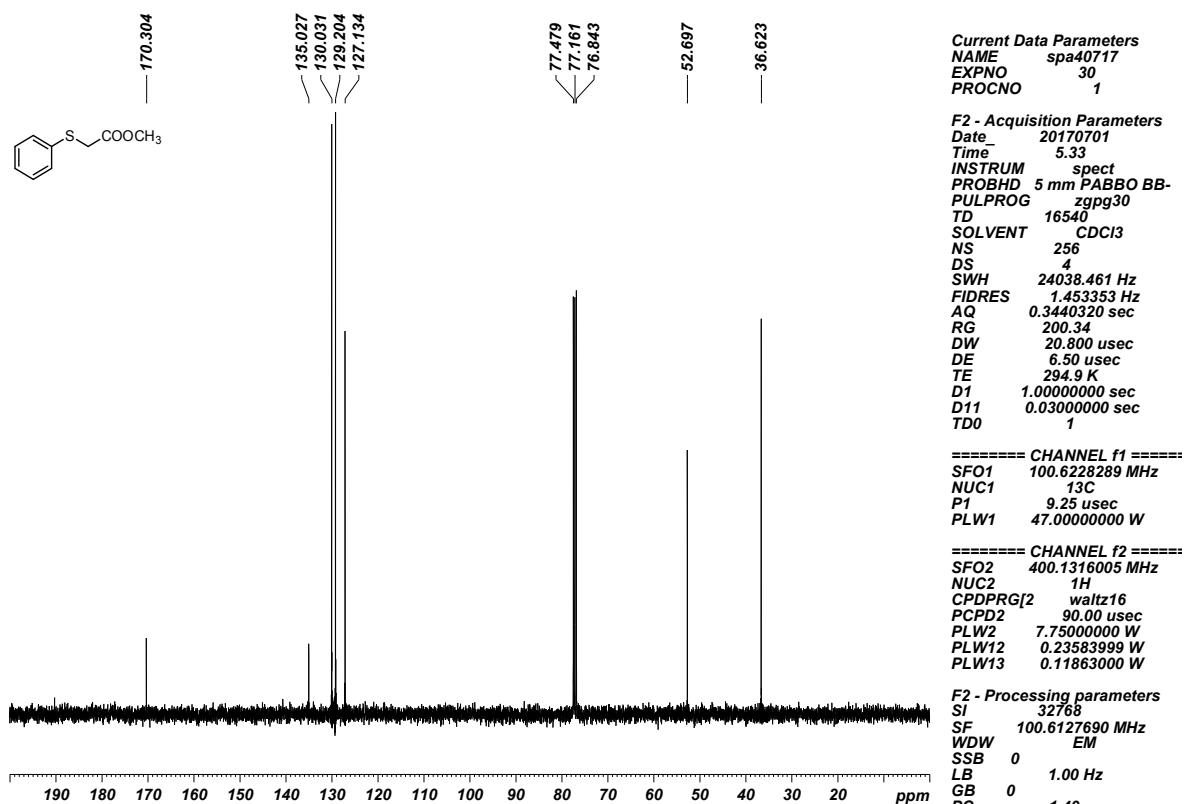


Thioester 1b

¹H NMR (400 MHz, CDCl₃, 24 °C)

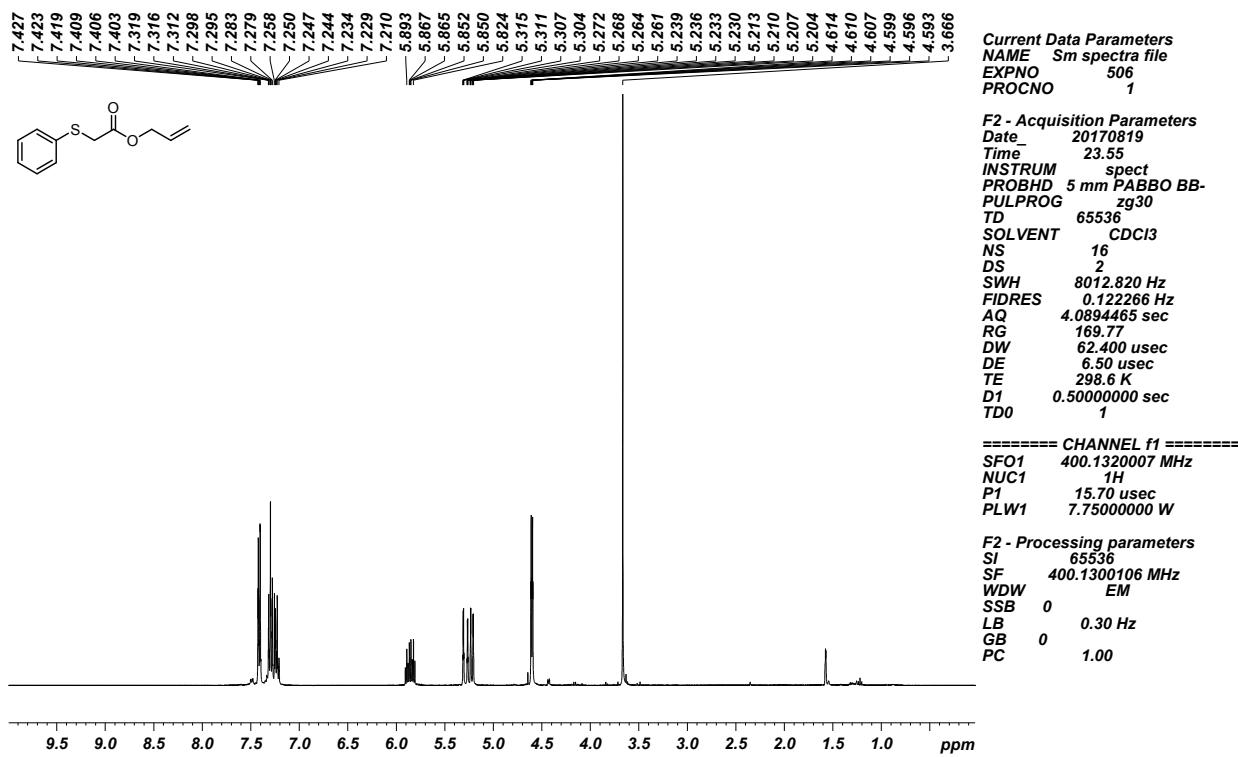


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

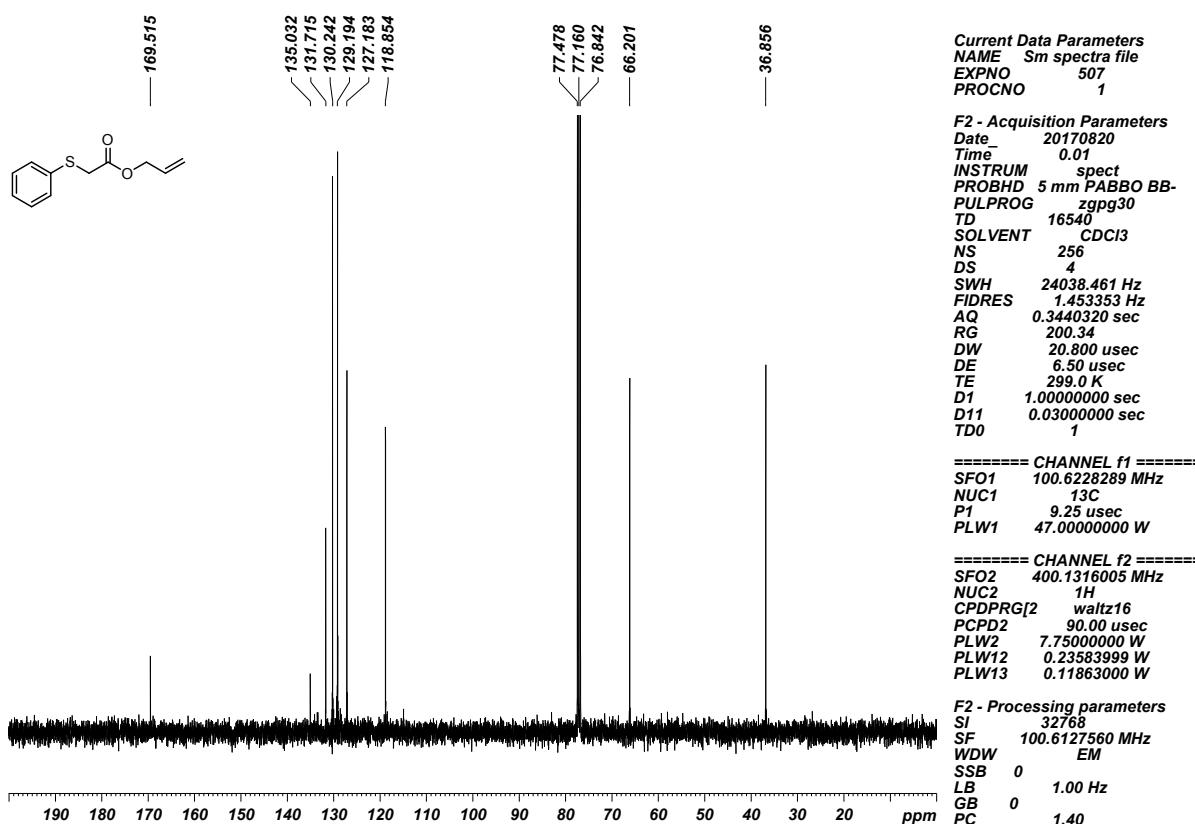


Thioester 1c

¹H NMR (400 MHz, CDCl₃, 24 °C)

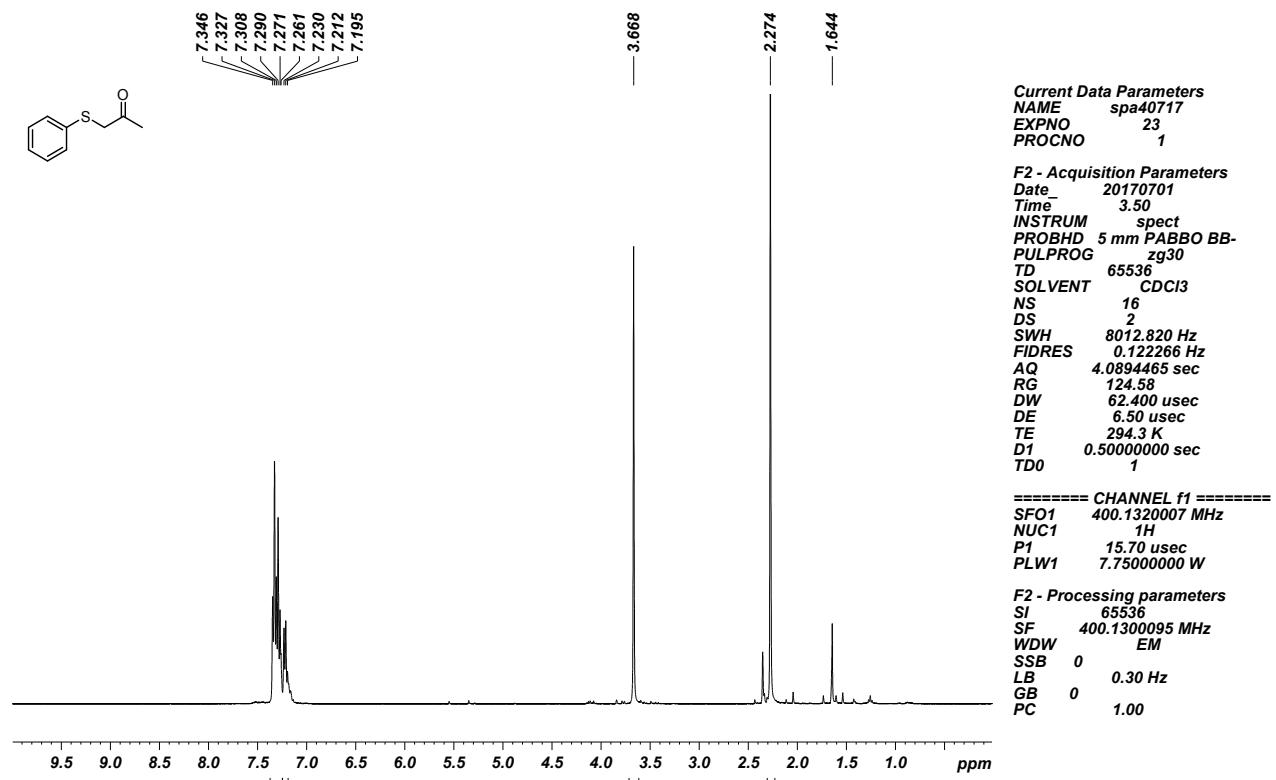


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

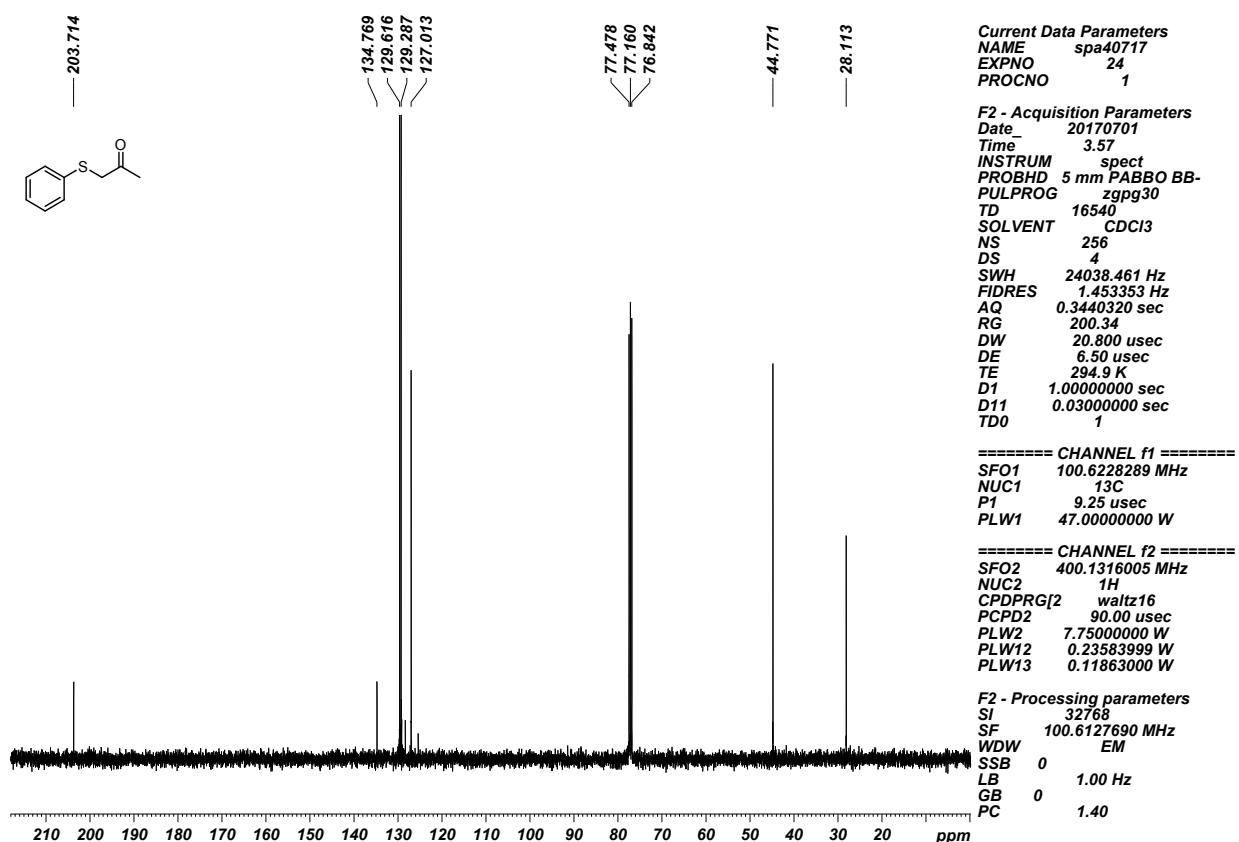


Thioketone 1d

¹H NMR (400 MHz, CDCl₃, 24 °C)

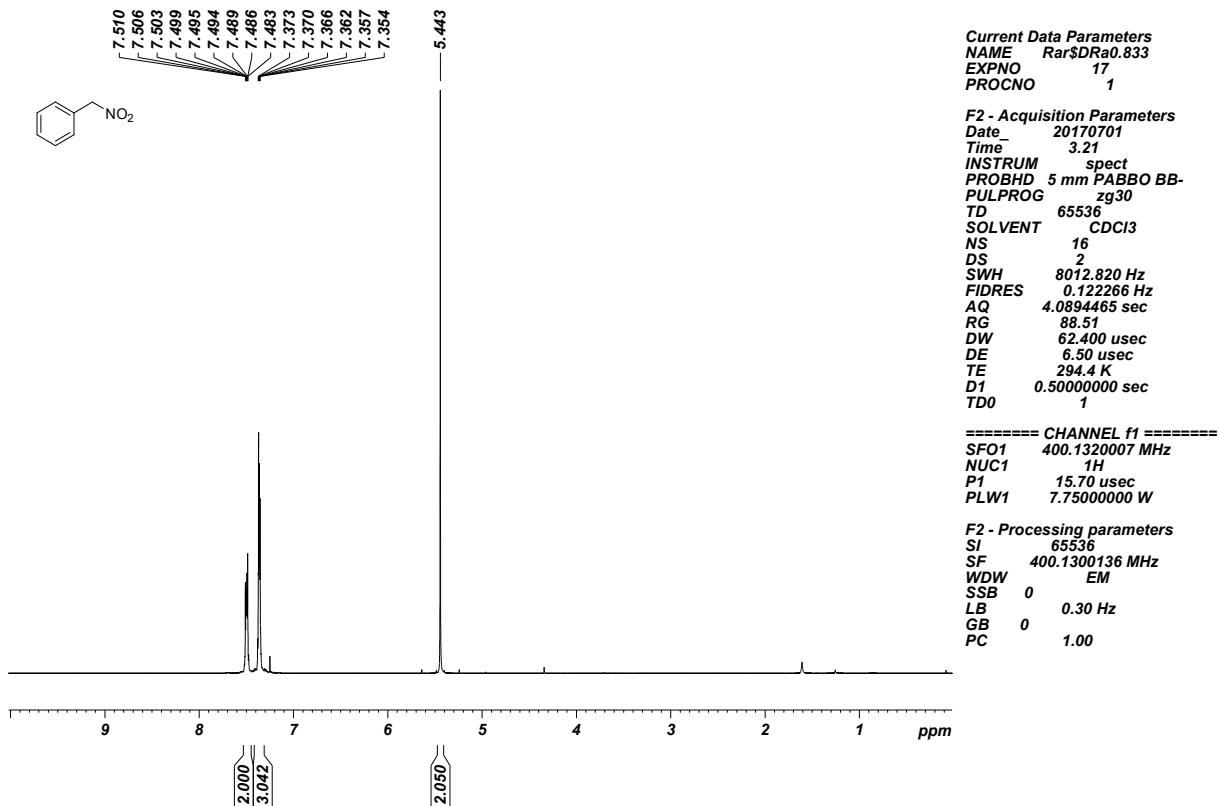


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

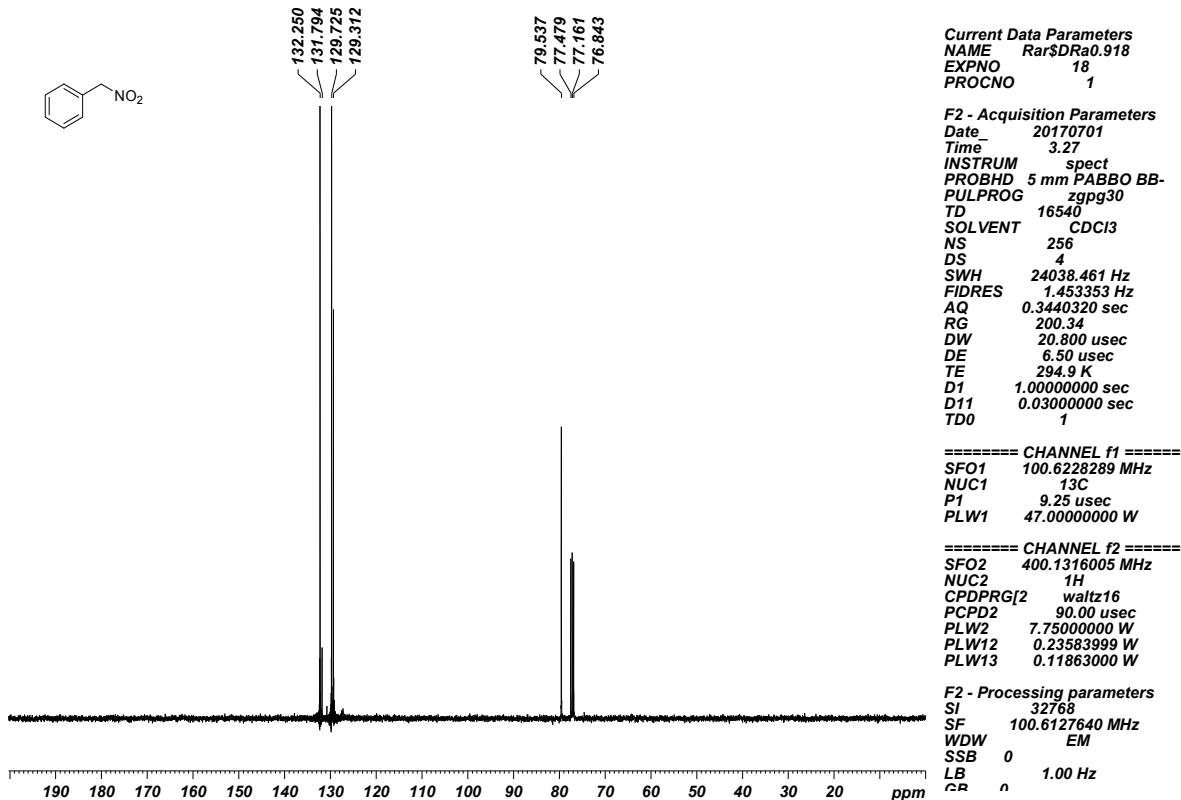


(Nitromethyl)benzene 1f

¹H NMR (400 MHz, CDCl₃, 24 °C)

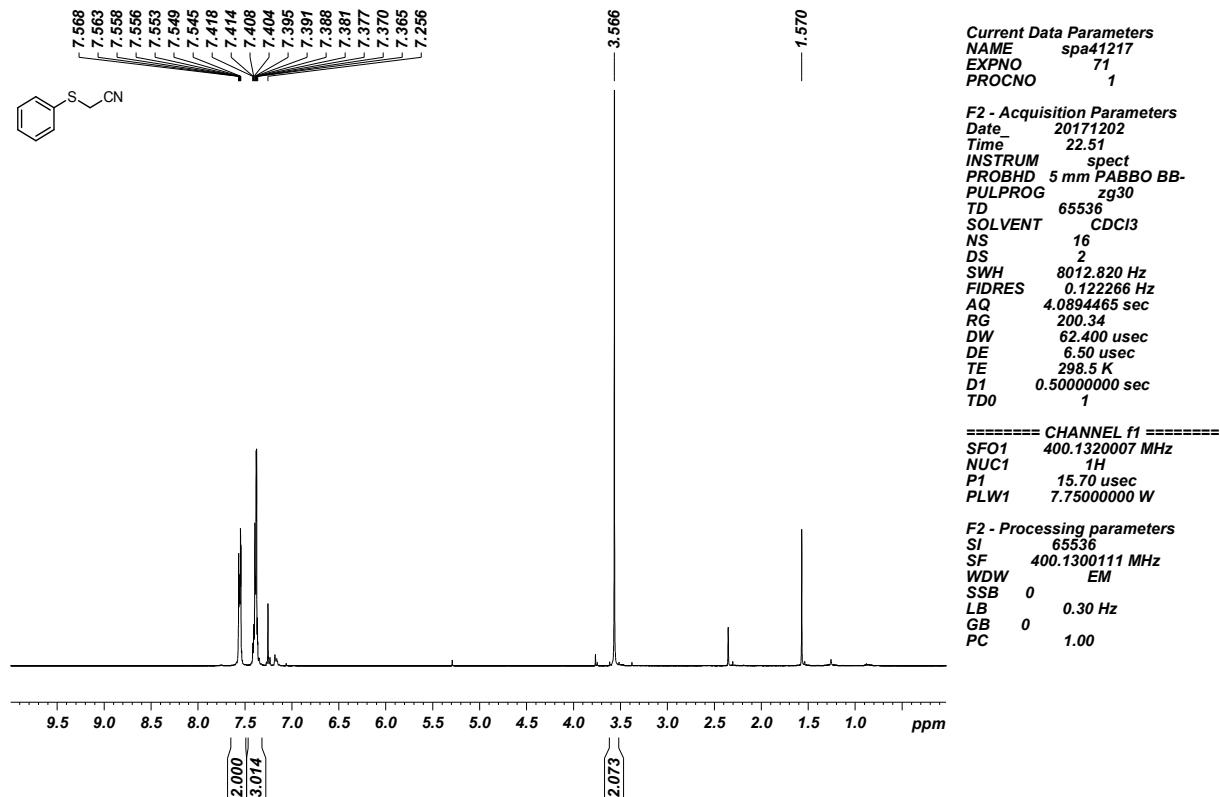


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

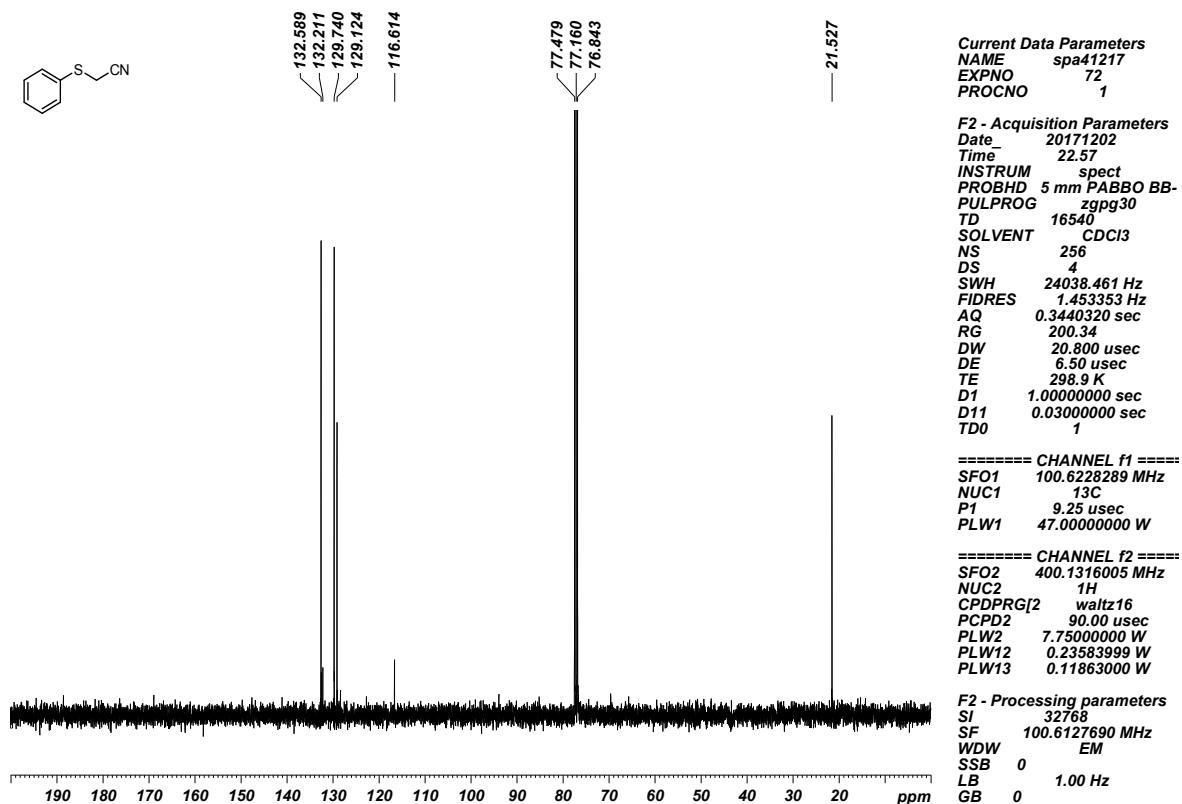


2-(Phenylthio)acetonitrile 1g

¹H NMR (400 MHz, CDCl₃, 24 °C)

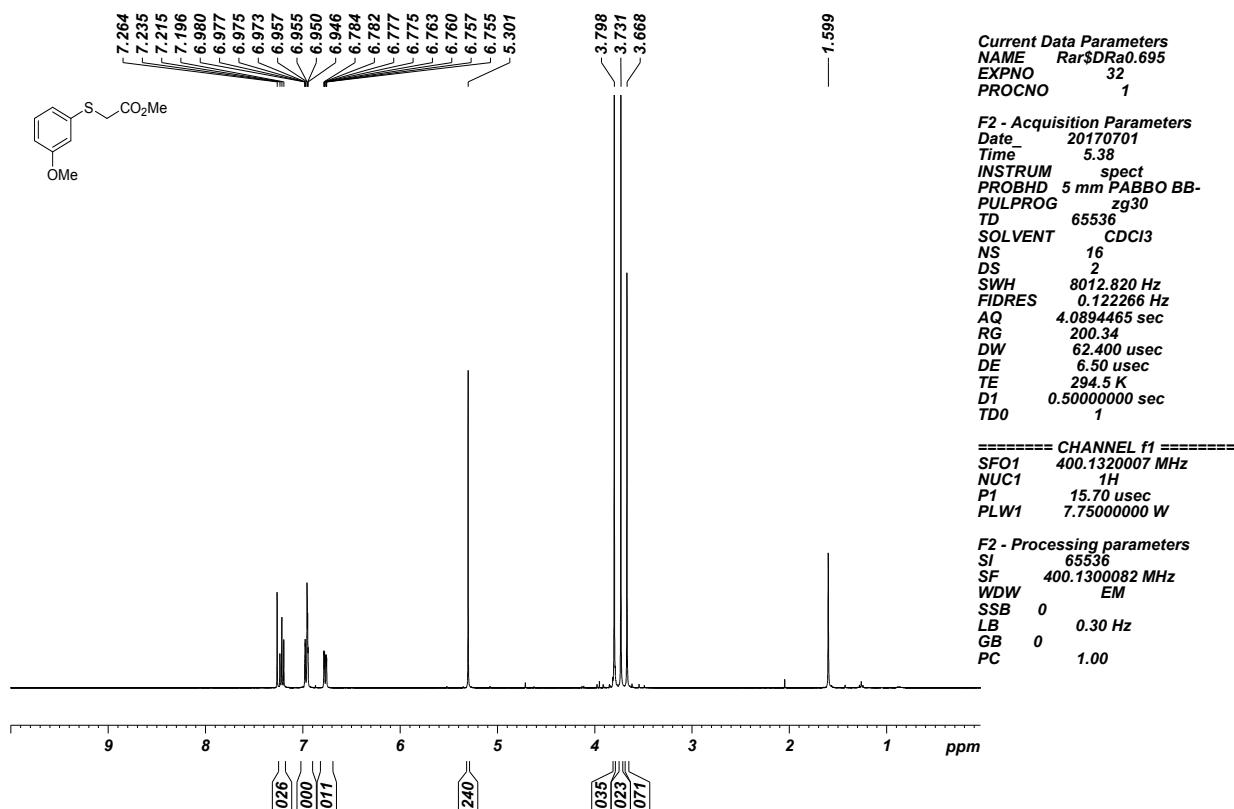


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

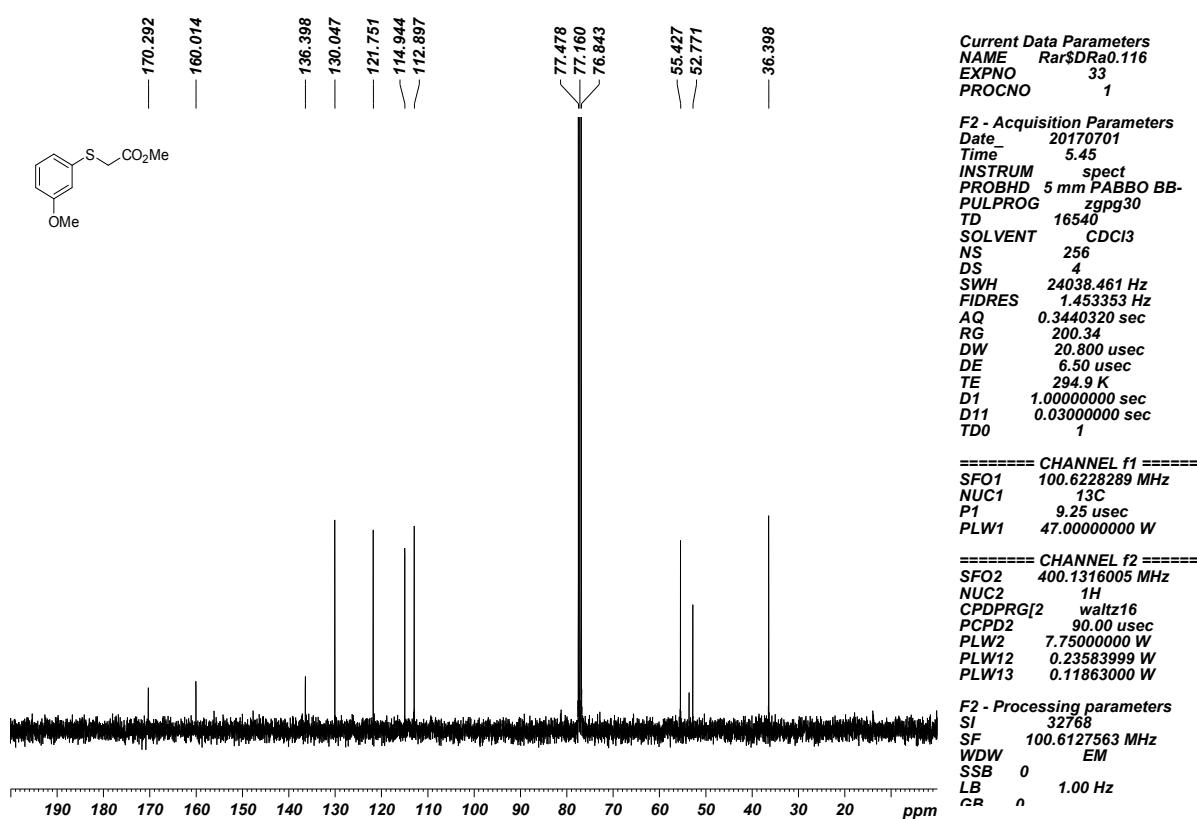


Thioester 1h

¹H NMR (400 MHz, CDCl₃, 24 °C)

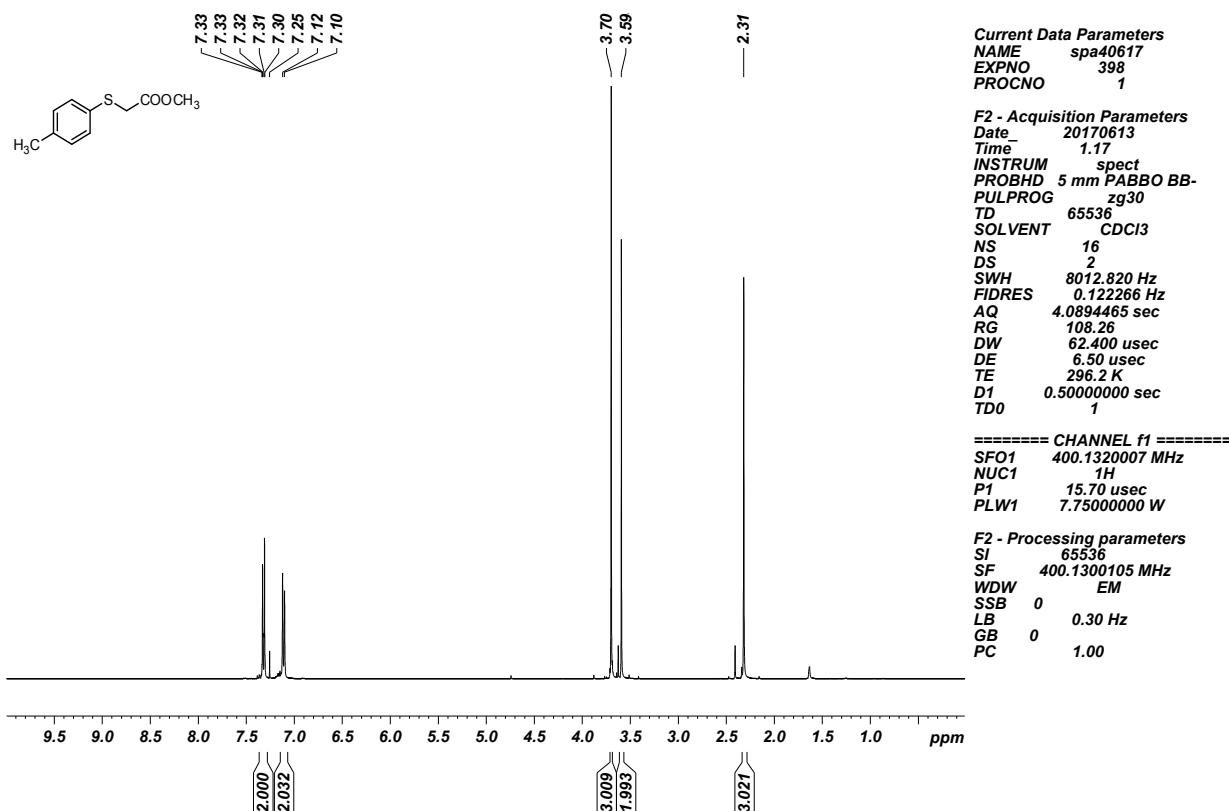


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

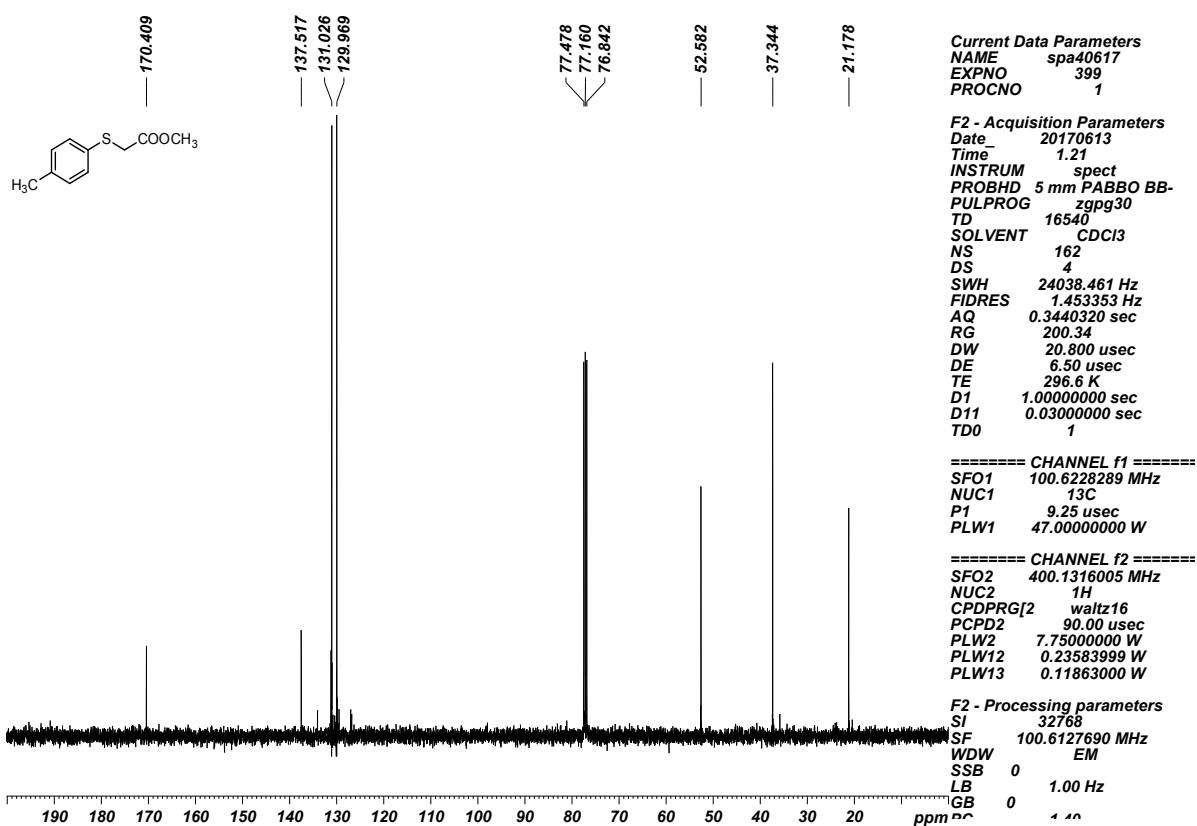


Thioester 1i

¹H NMR (400 MHz, CDCl₃, 24 °C)

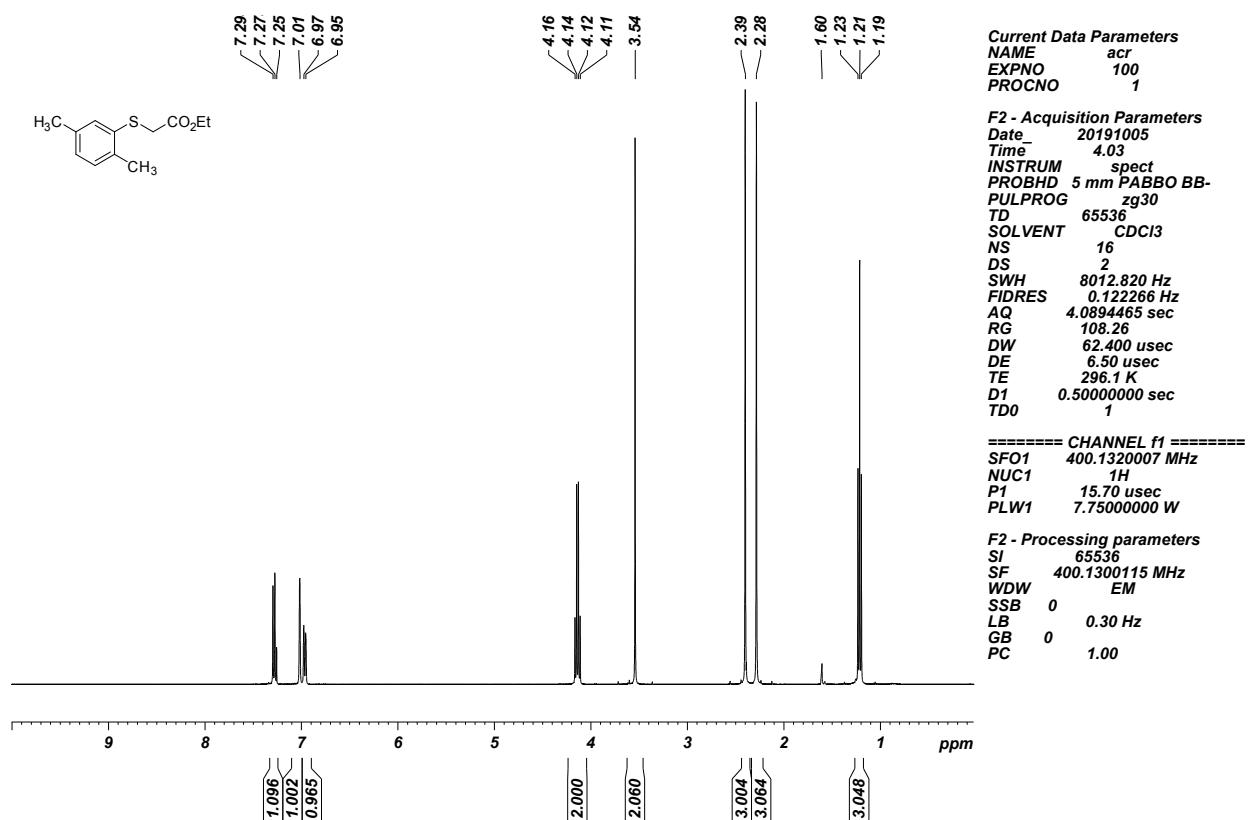


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

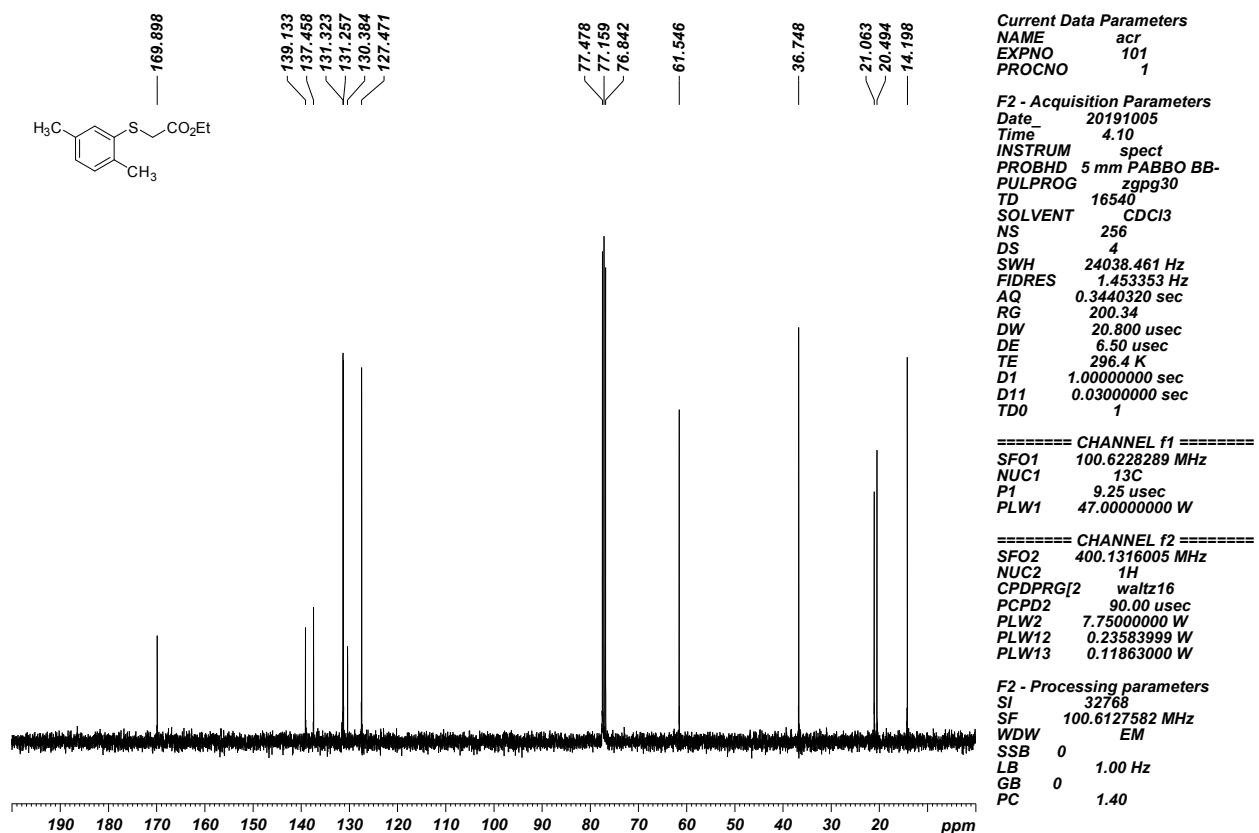


Thioester 1j

¹H NMR (400 MHz, CDCl₃, 24 °C)

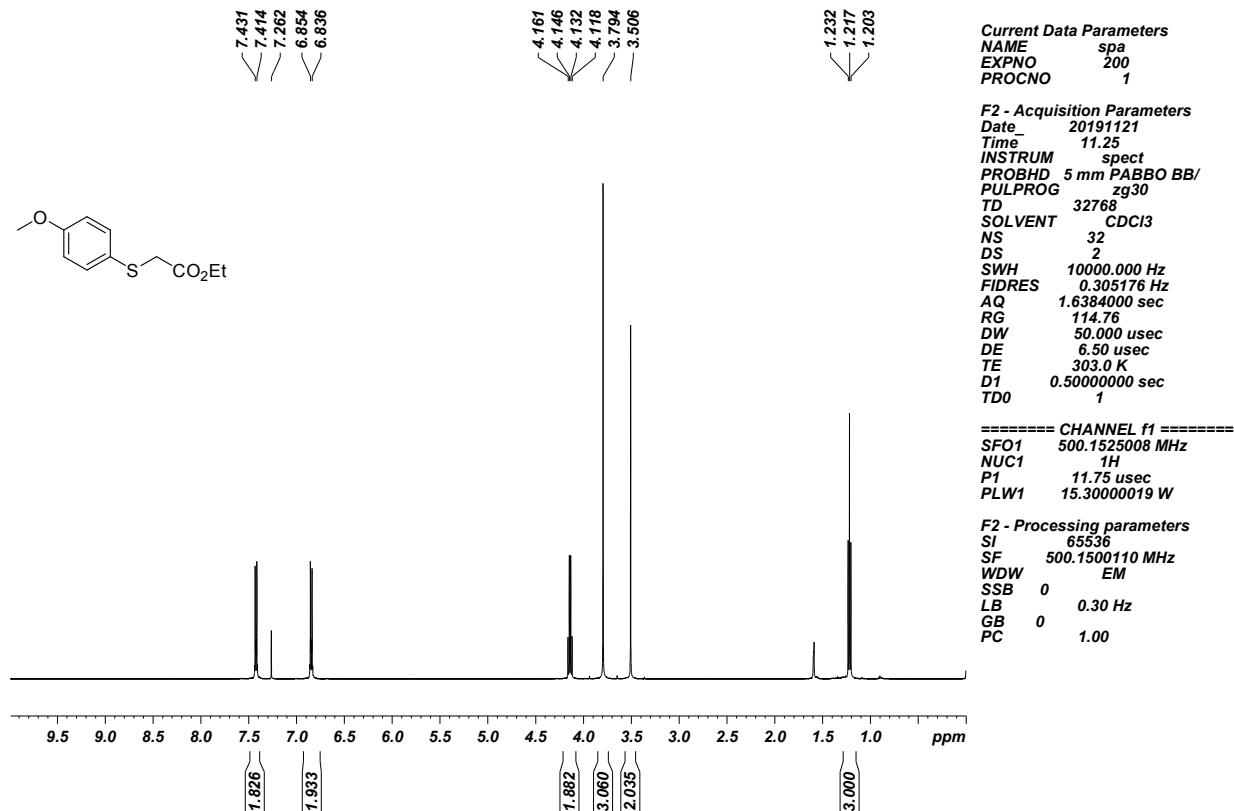


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

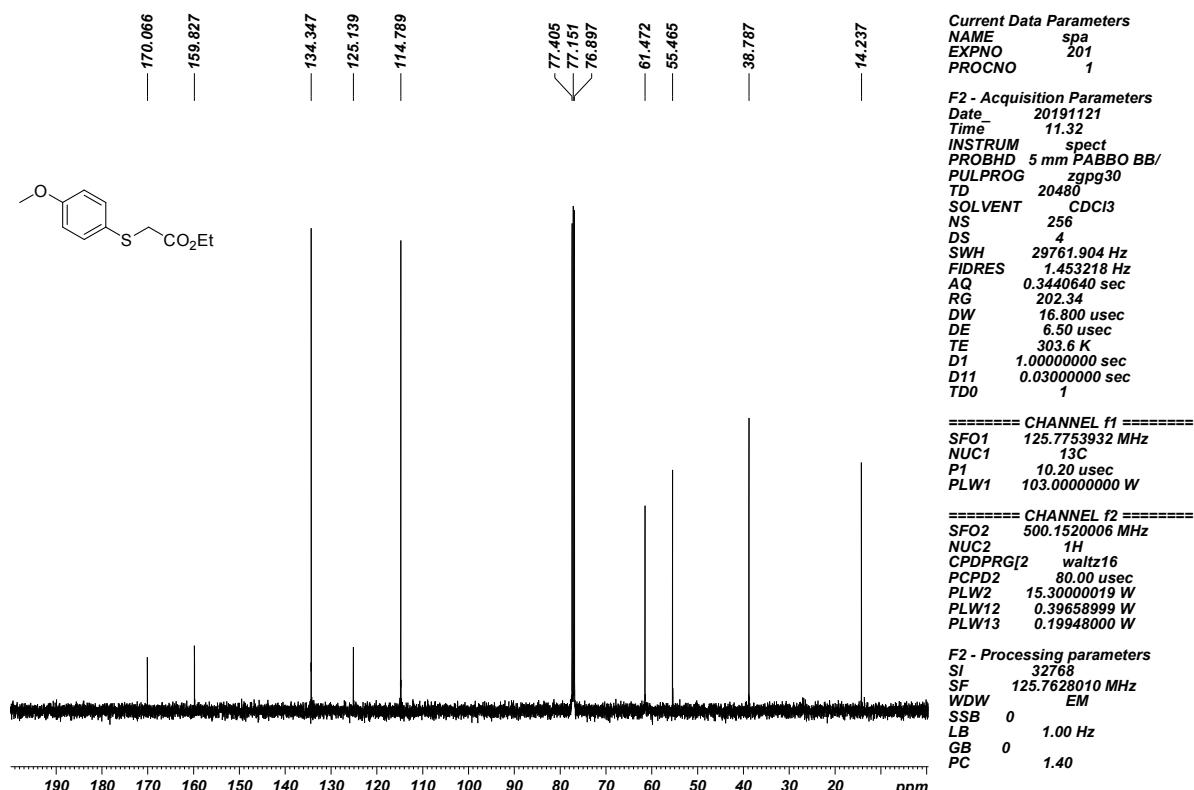


Thioester 1k

¹H NMR (500 MHz, CDCl₃, 24 °C)

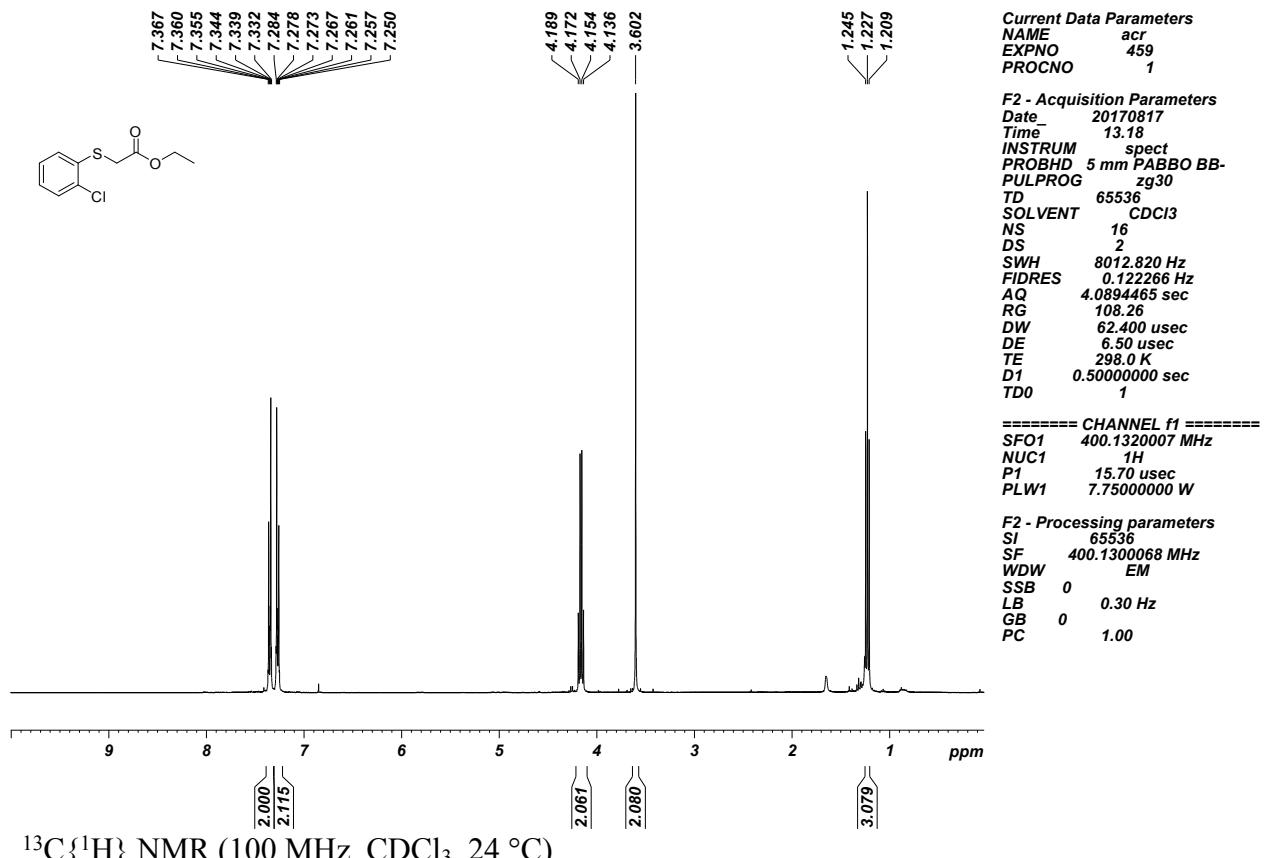


¹³C{¹H} NMR (125 MHz, CDCl₃, 24 °C)

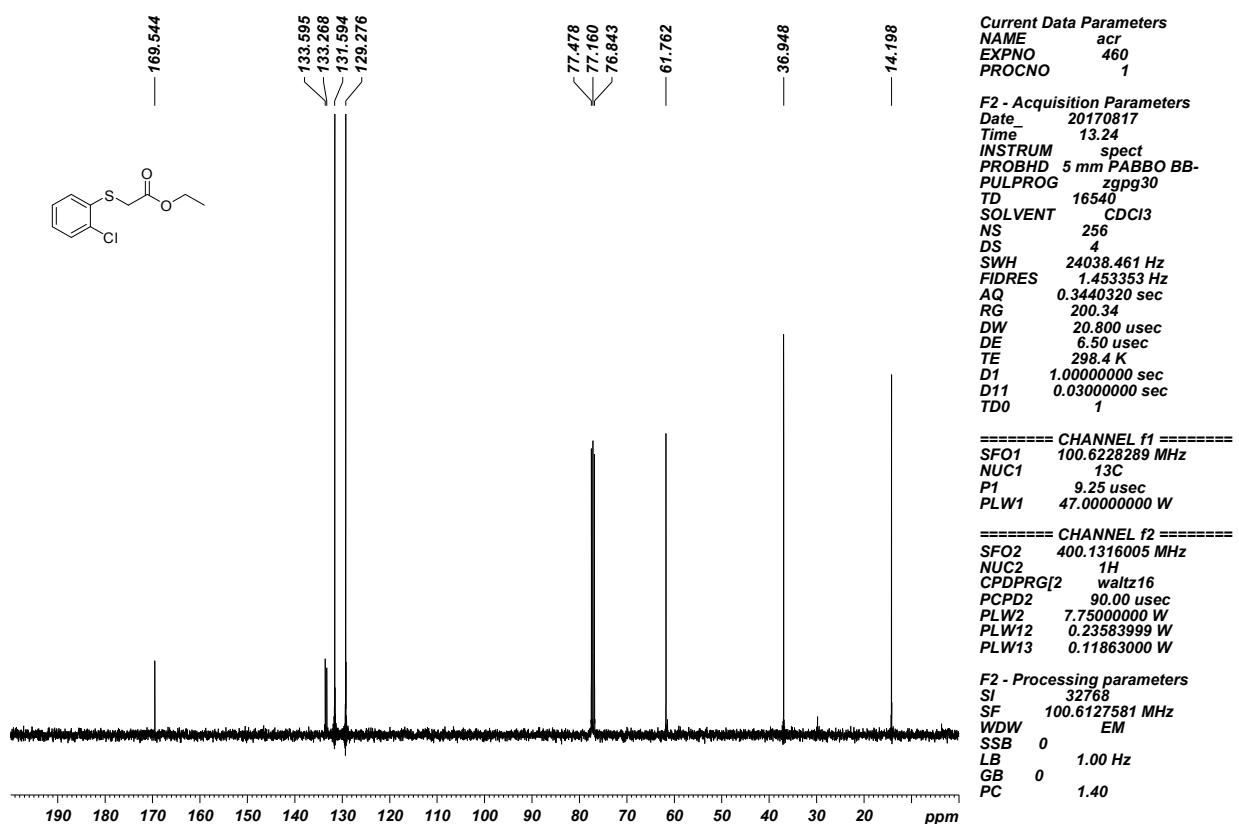


Thioester 11

¹H NMR (400 MHz, CDCl₃, 24 °C)

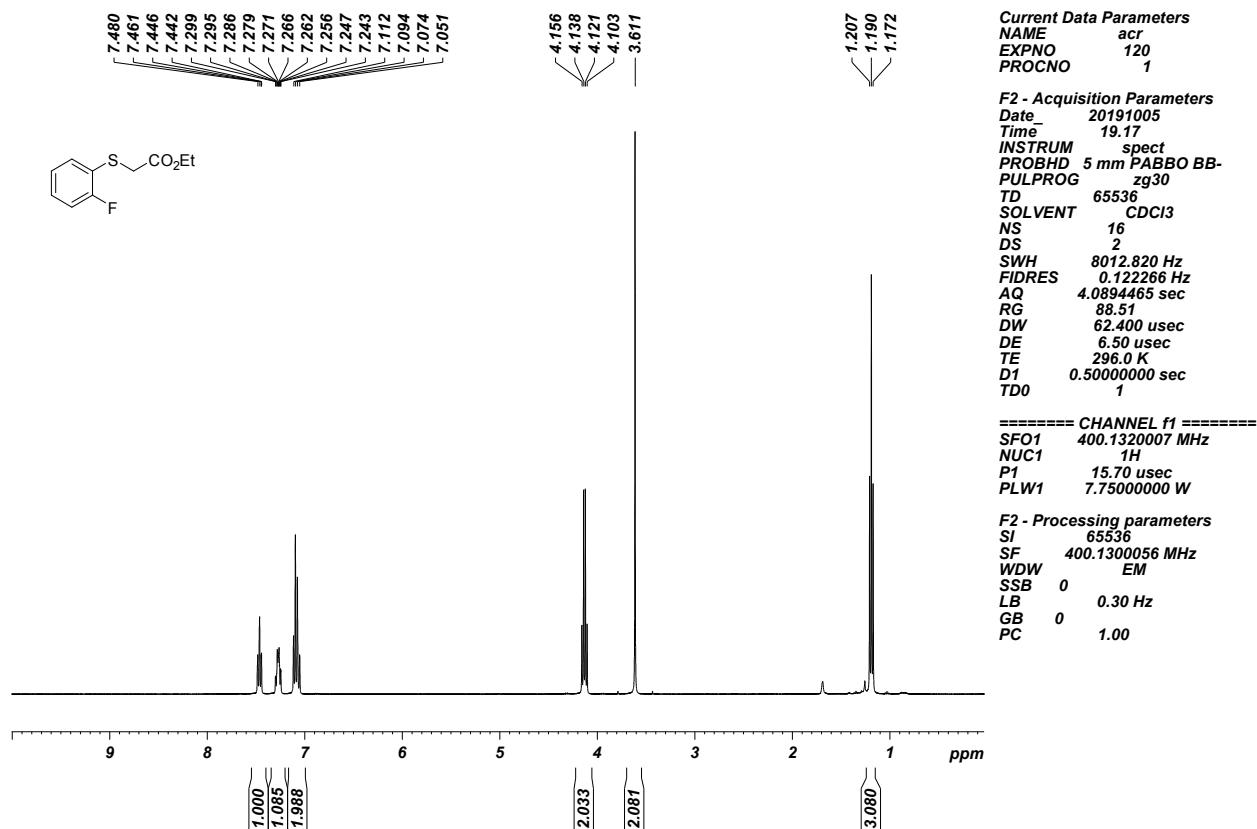


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

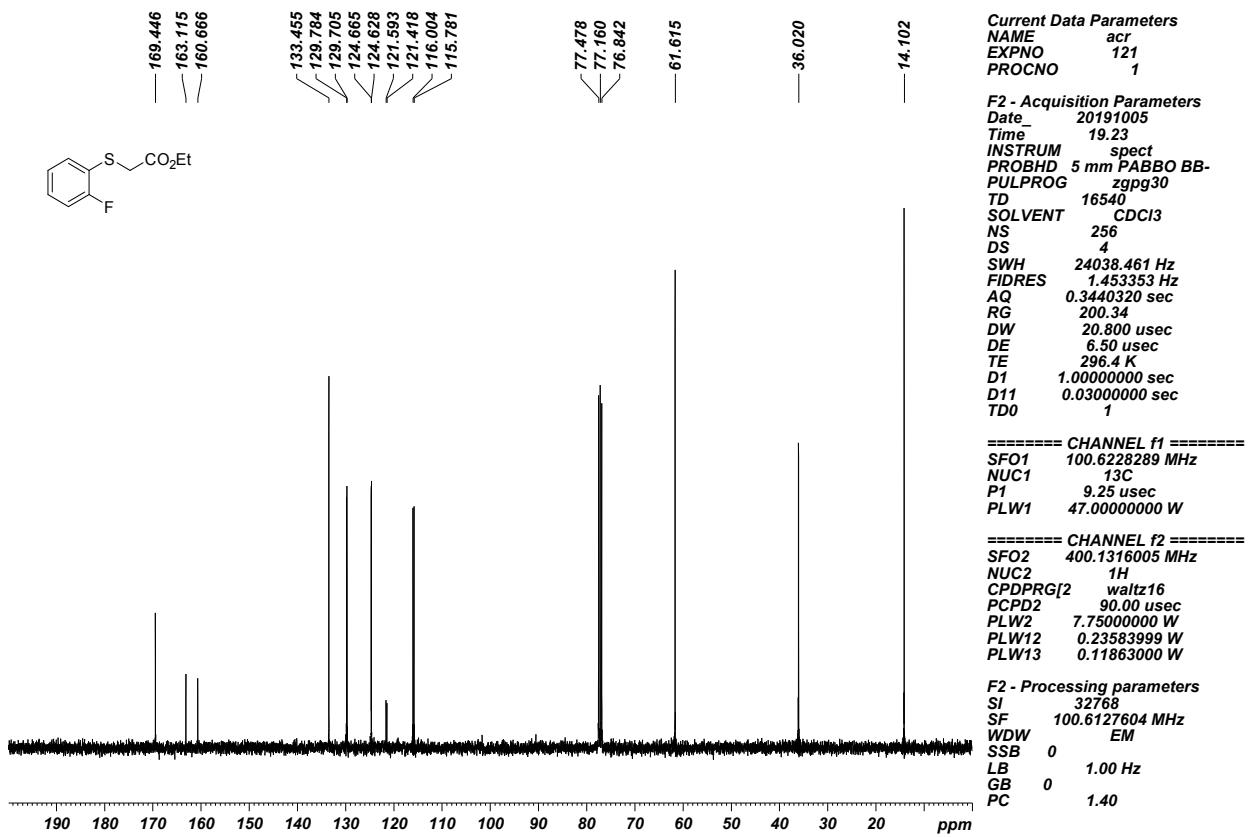


Thioester 1m

¹H NMR (400 MHz, CDCl₃, 24 °C)

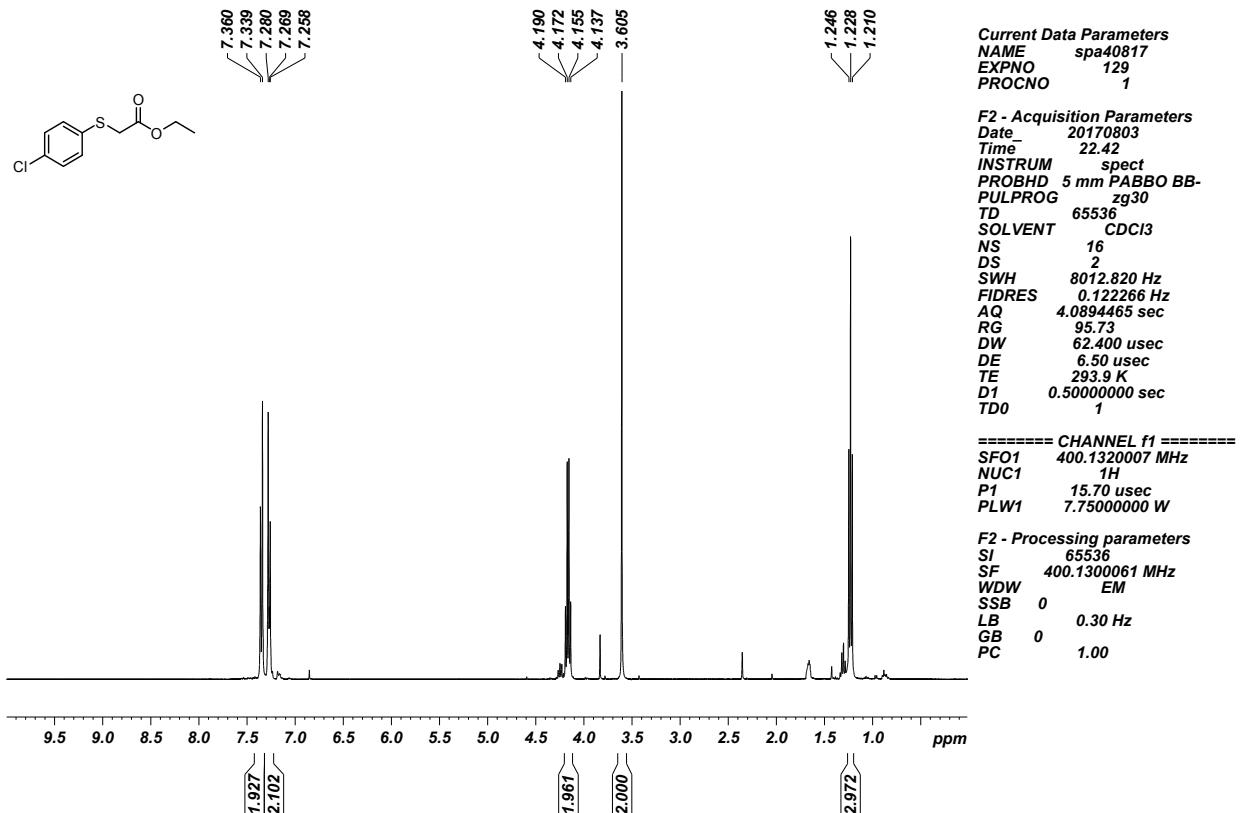


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

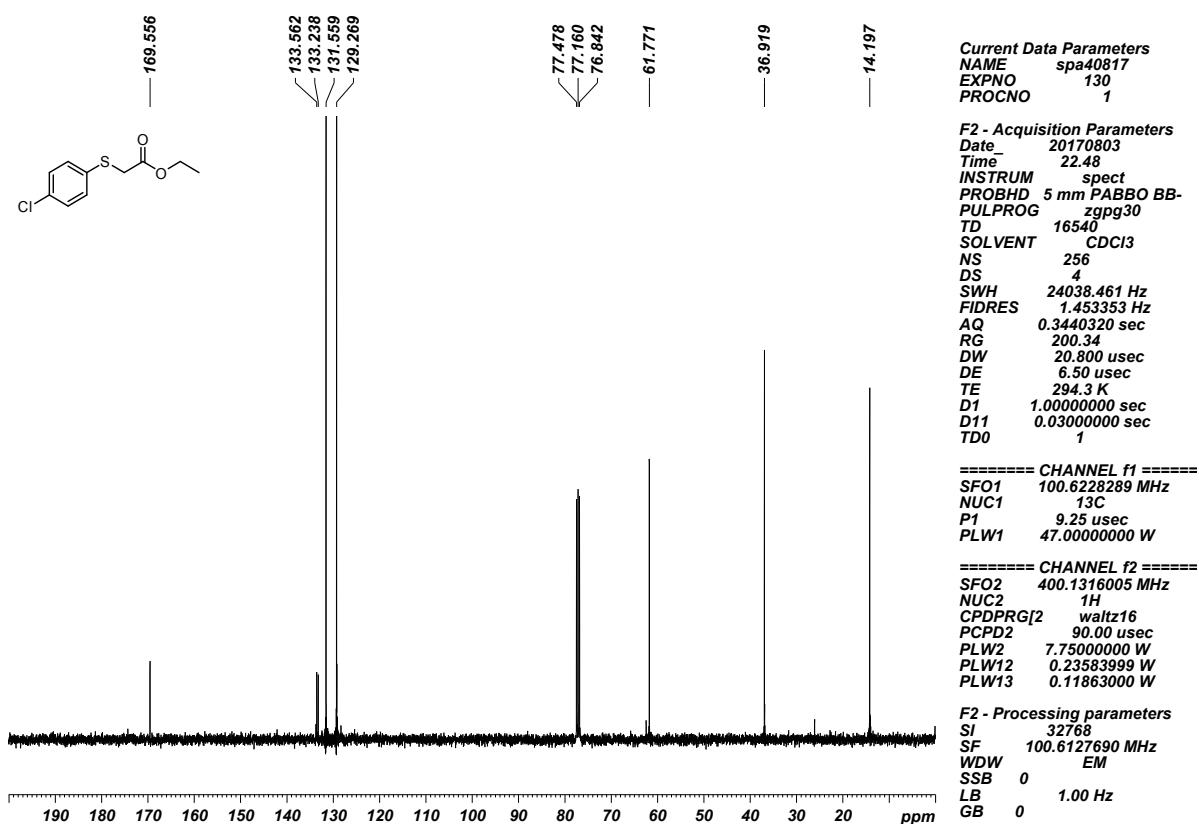


Thioester 1n

¹H NMR (400 MHz, CDCl₃, 24 °C)

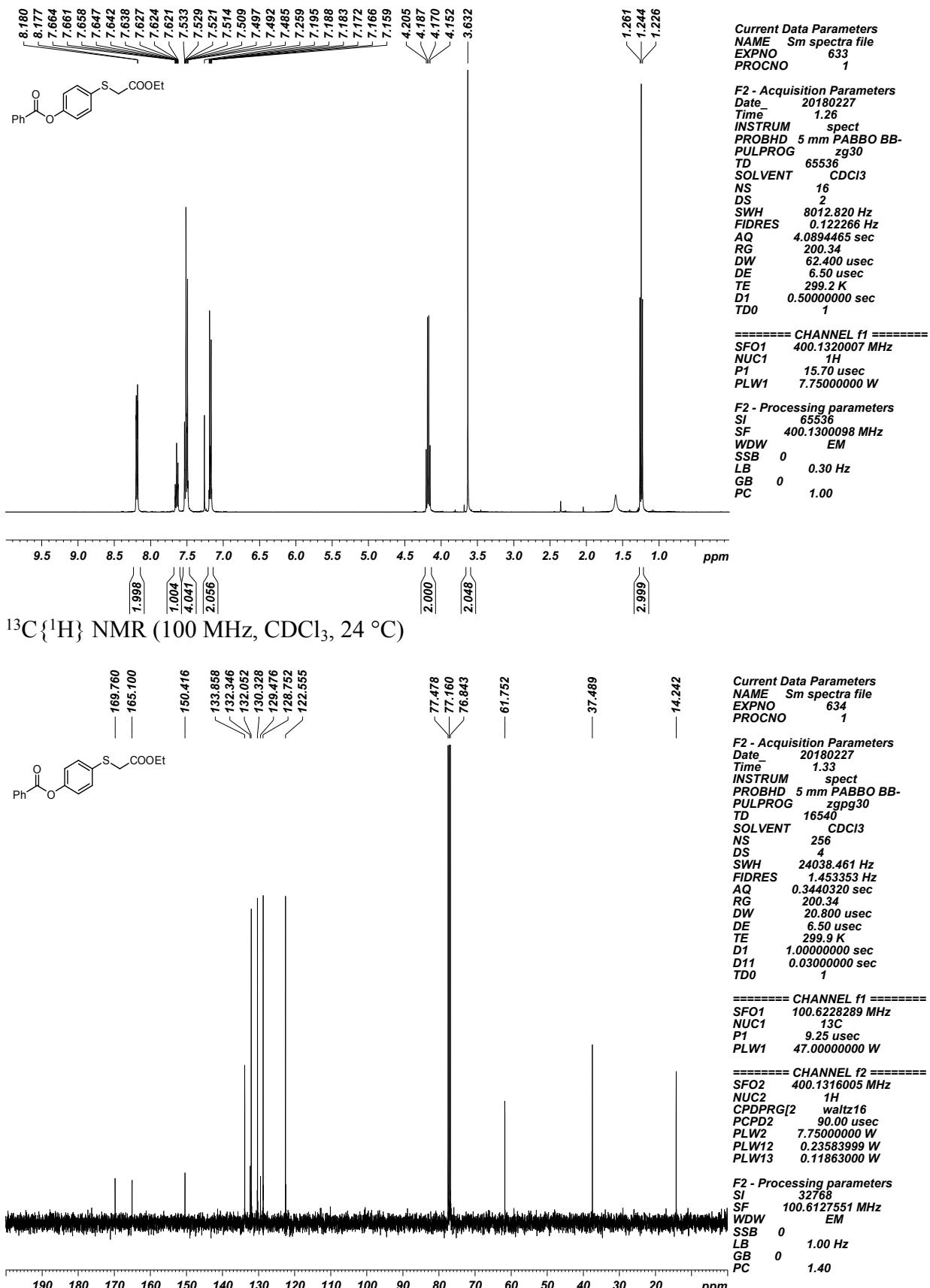


$^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C)



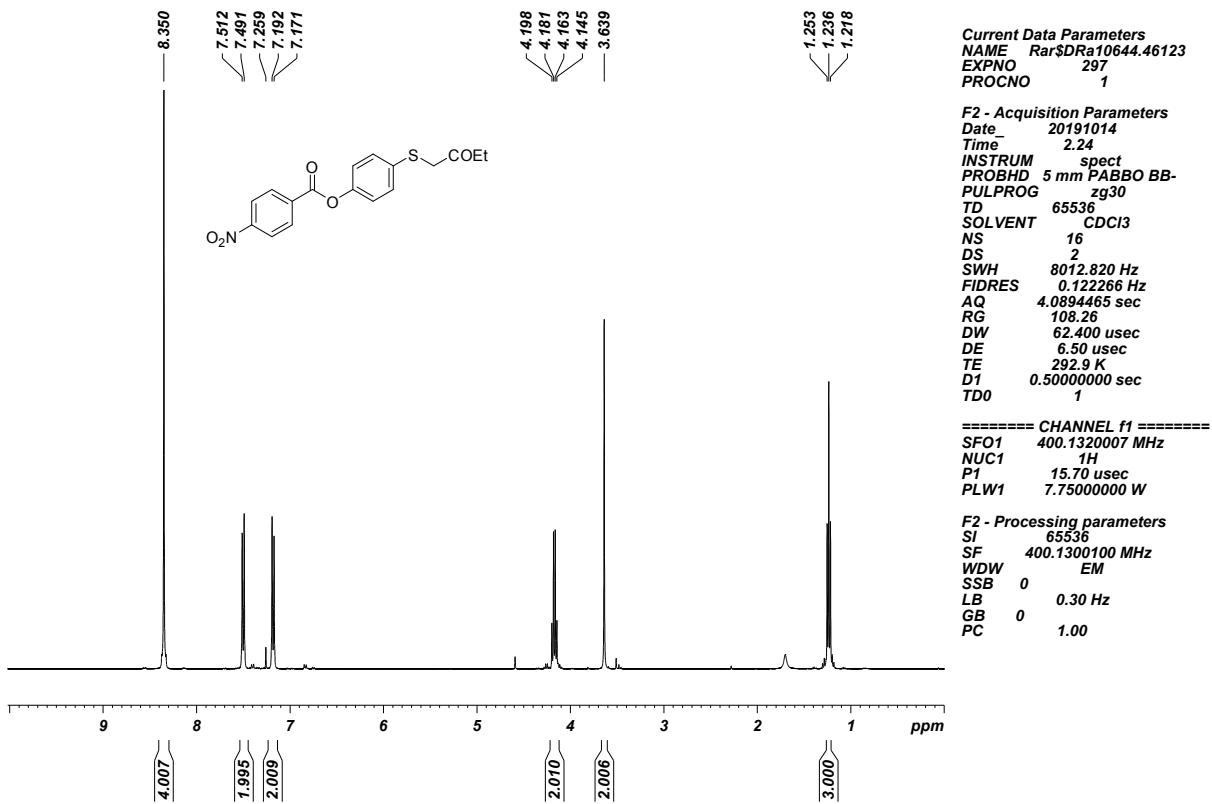
Thioester 1o

^1H NMR (400 MHz, CDCl_3 , 24 °C)

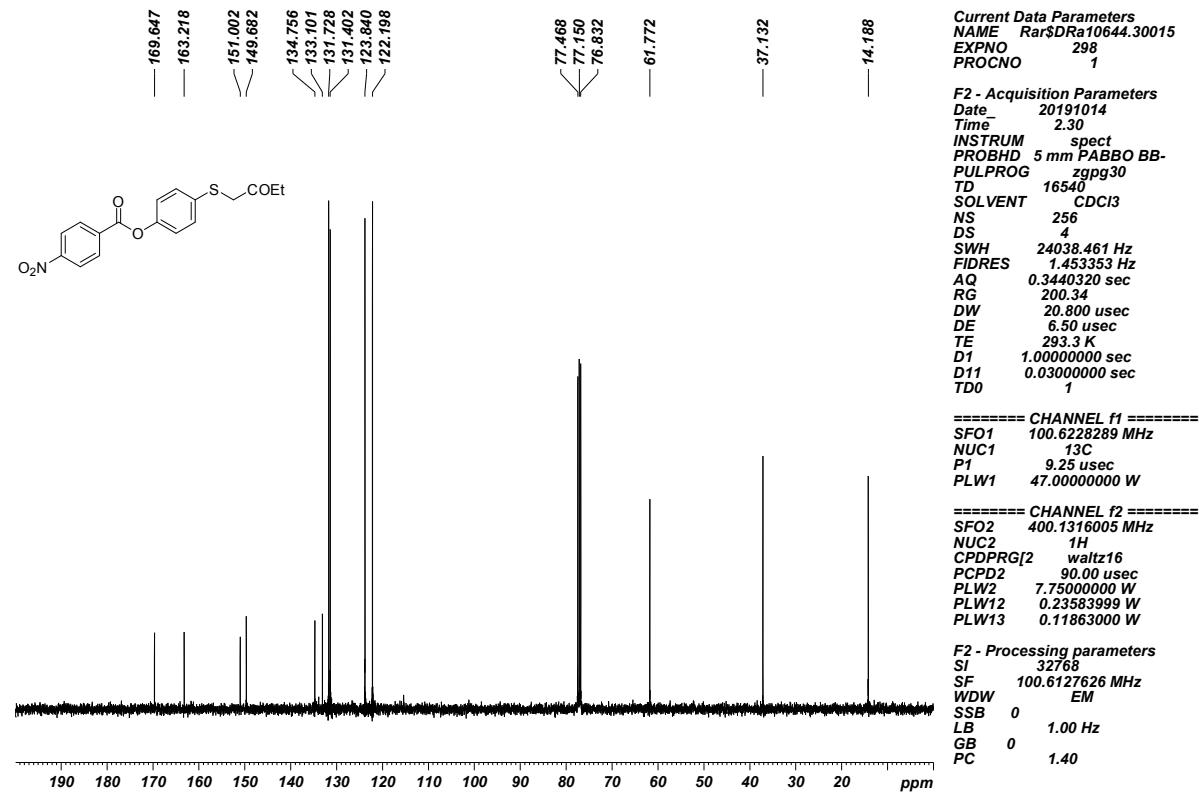


Thioester 1p

¹H NMR (400 MHz, CDCl₃, 24 °C)

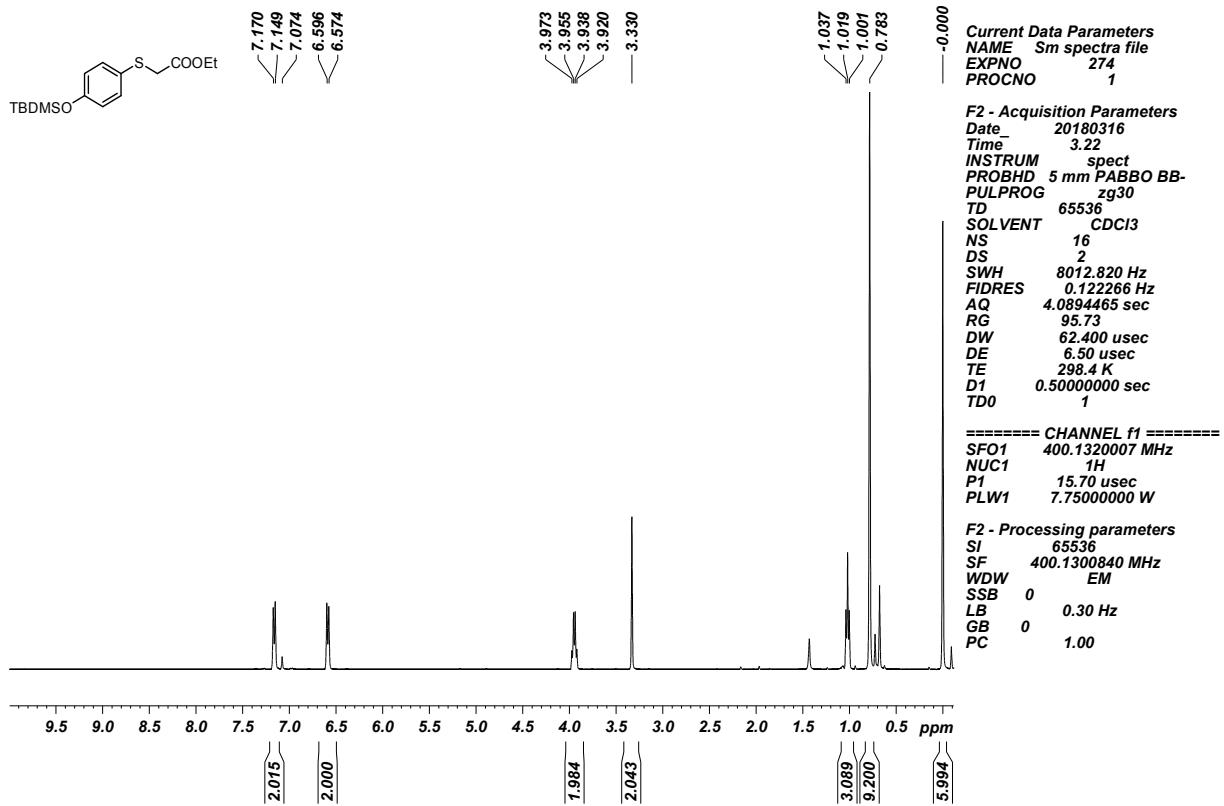


$^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C)

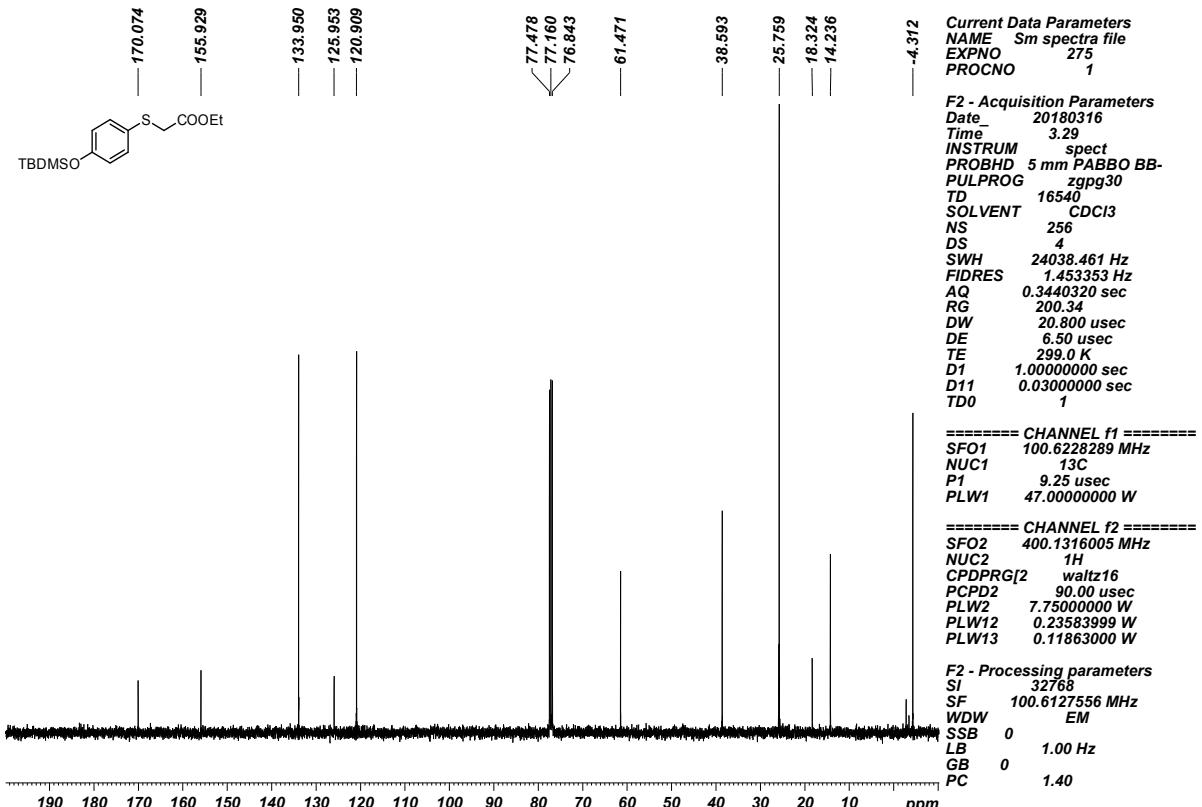


Thioester 1r

^1H NMR (400 MHz, CDCl_3 , 24 °C)

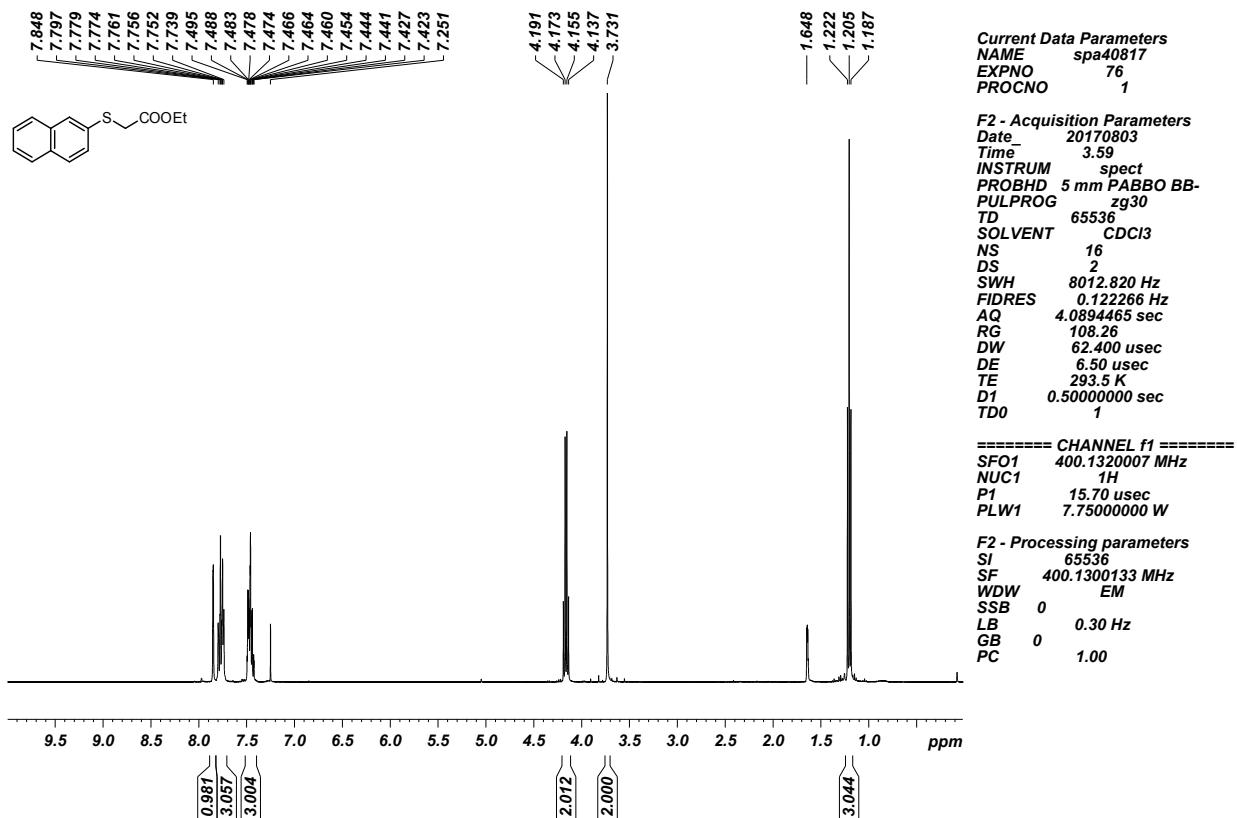


$^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C)

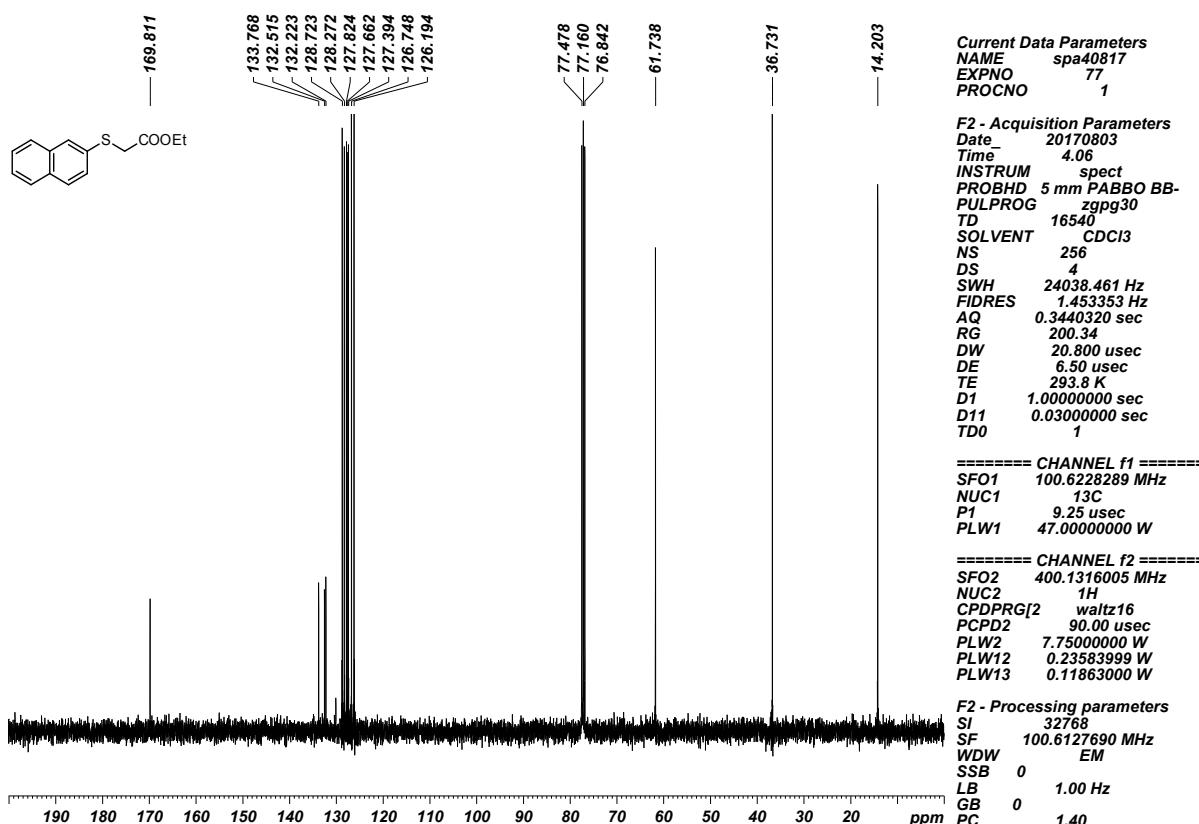


Thioester 1s

^1H NMR (400 MHz, CDCl_3 , 24 °C)

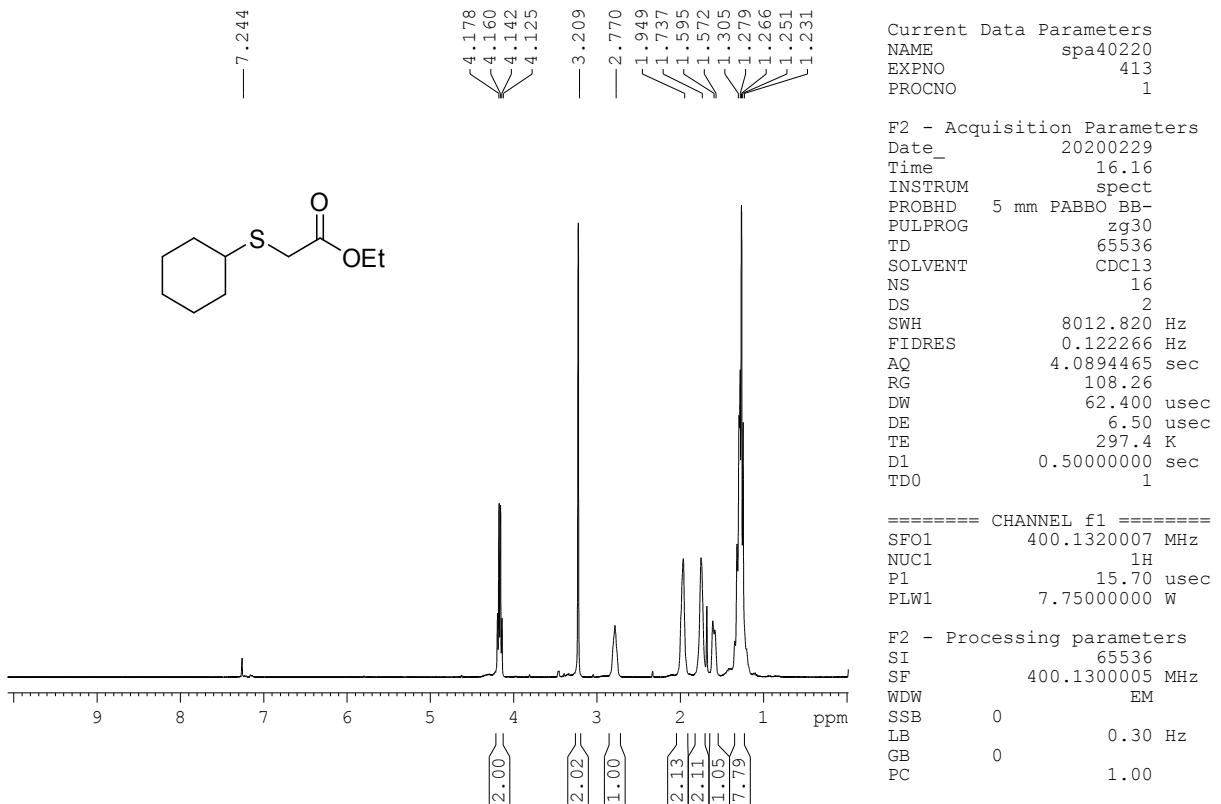


$^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C)

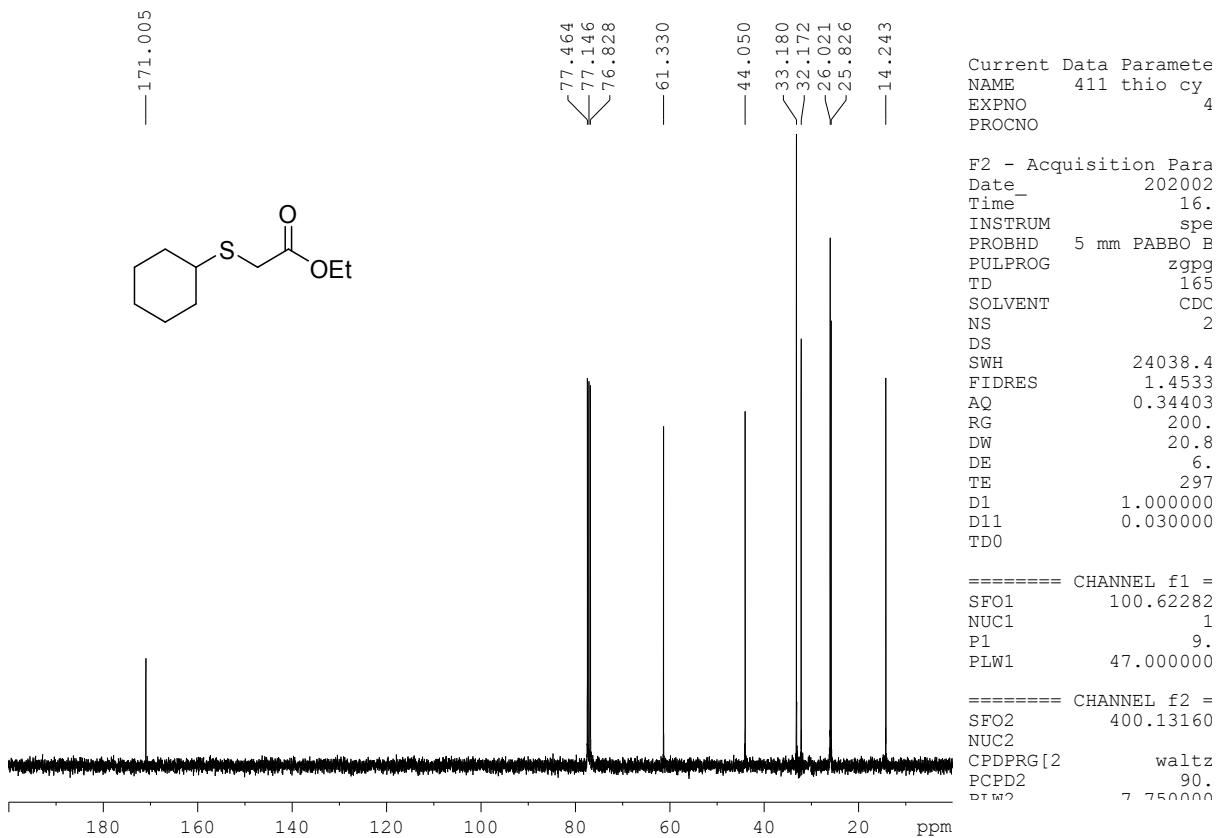


Thioester 2t

^1H NMR (400 MHz, CDCl_3 , 24 °C)

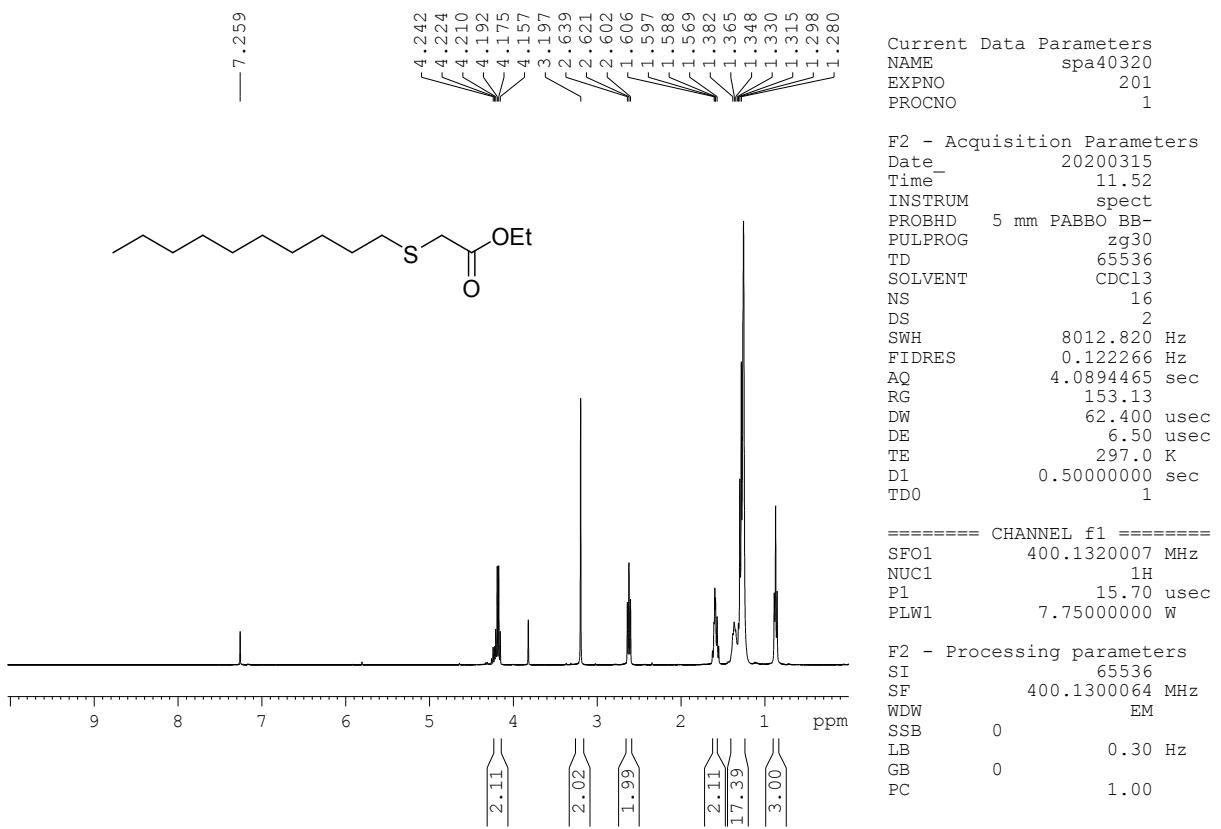


$^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C)

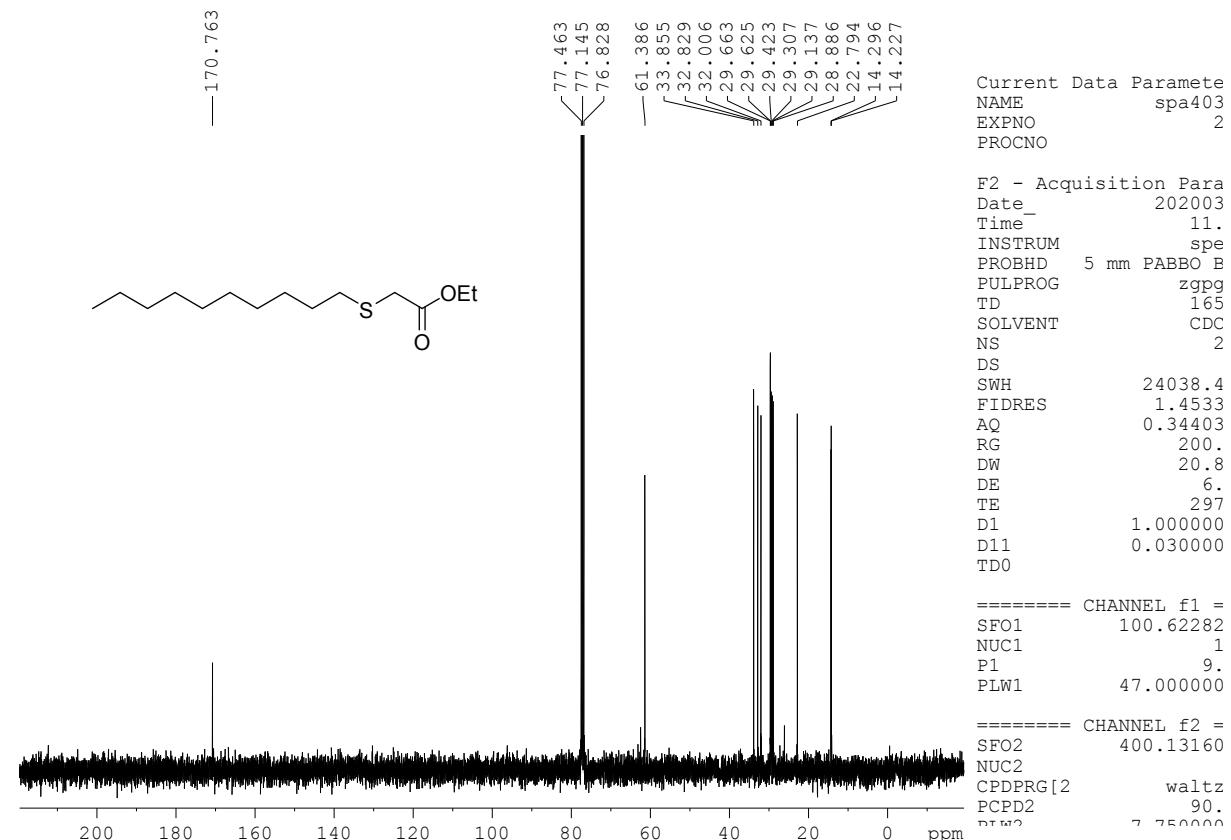


Thioester 2u

^1H NMR (400 MHz, CDCl_3 , 24 °C)

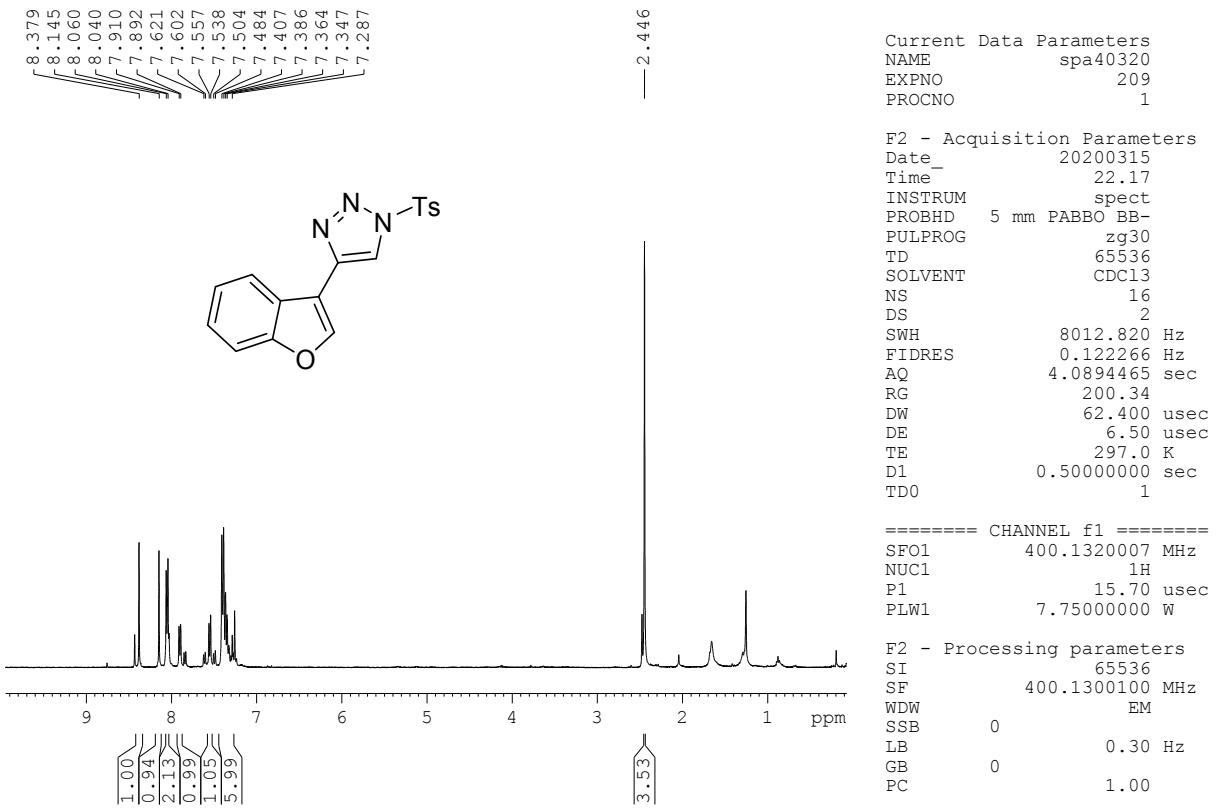


$^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C)



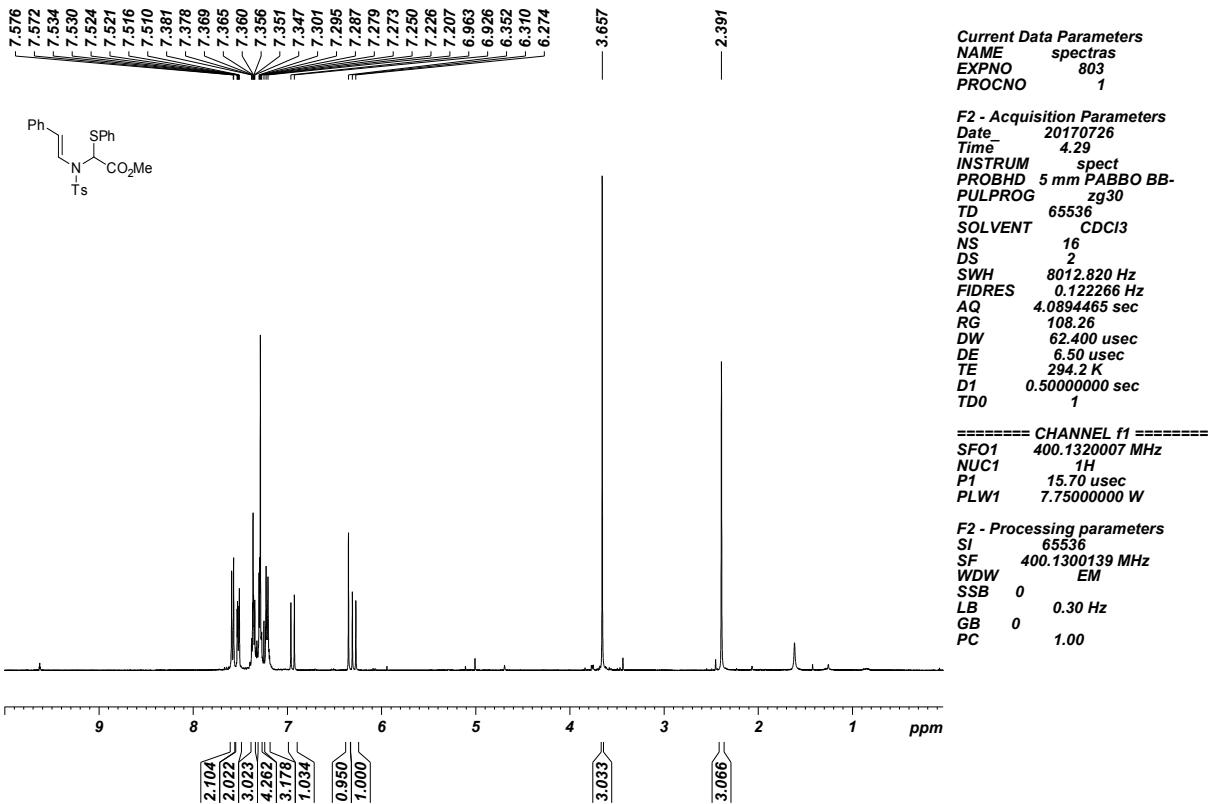
Thioester 2ag

^1H NMR (400 MHz, CDCl_3 , 24 °C)

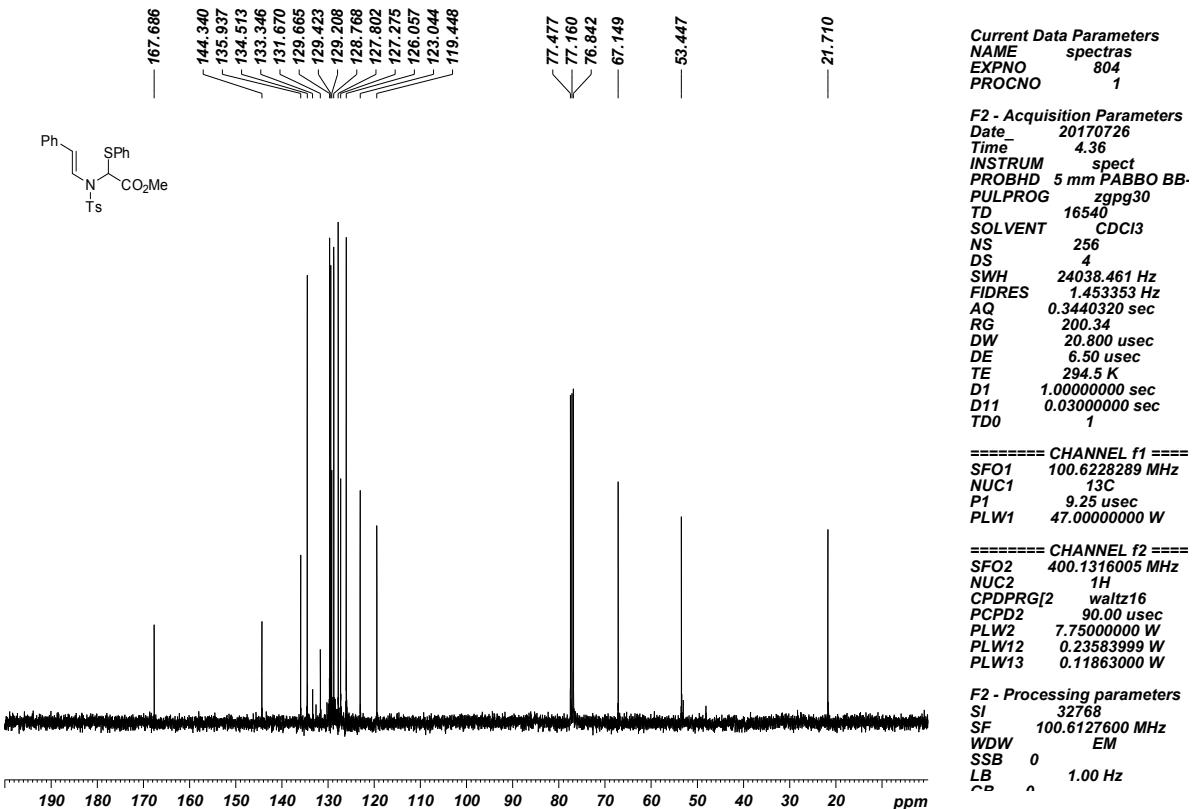


Enamide 4a

¹H NMR (400 MHz, CDCl₃, 24 °C)

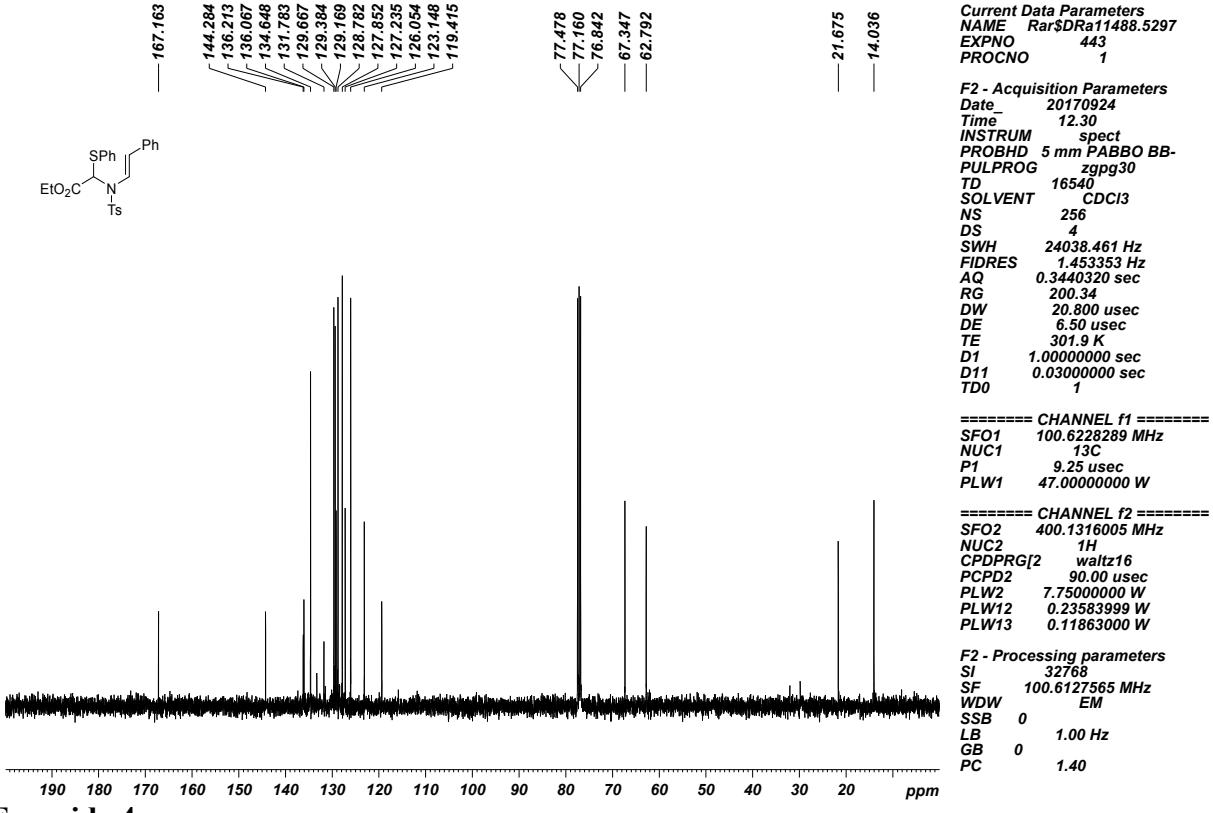
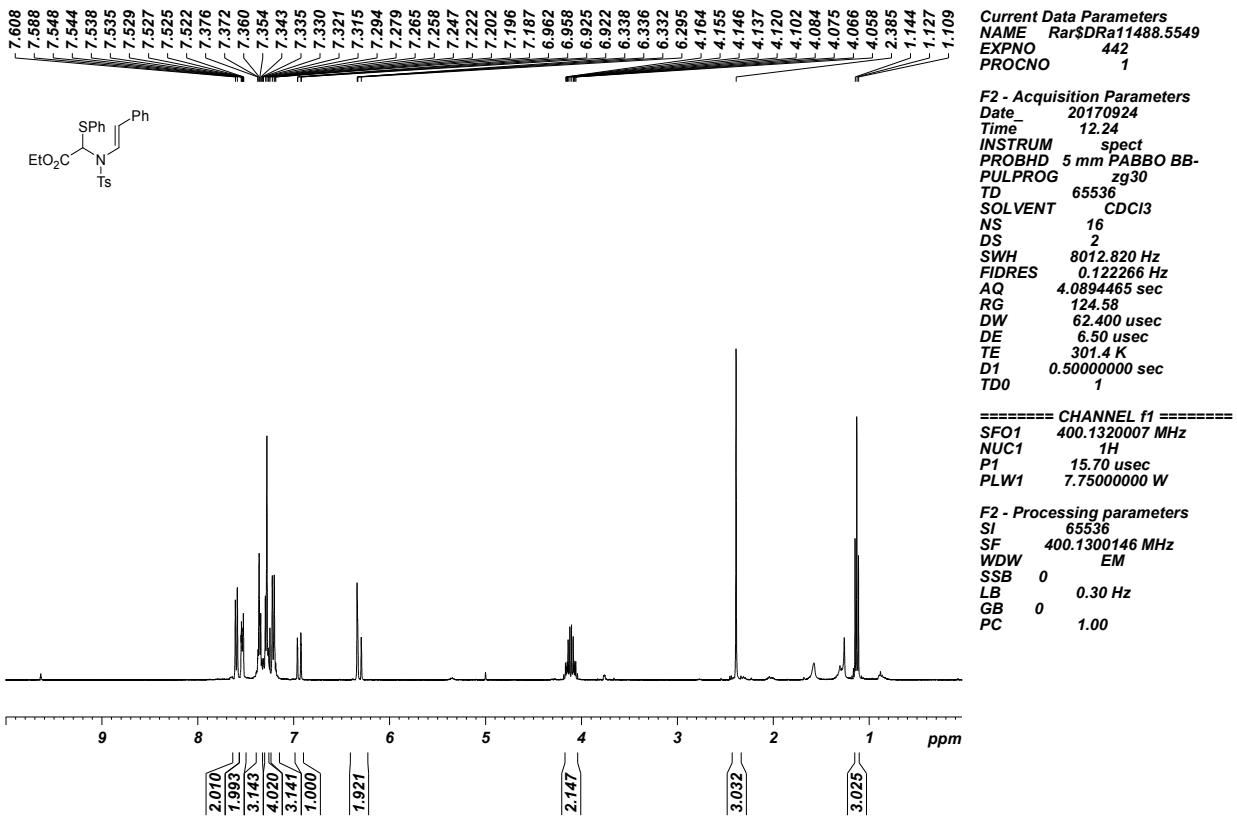


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)



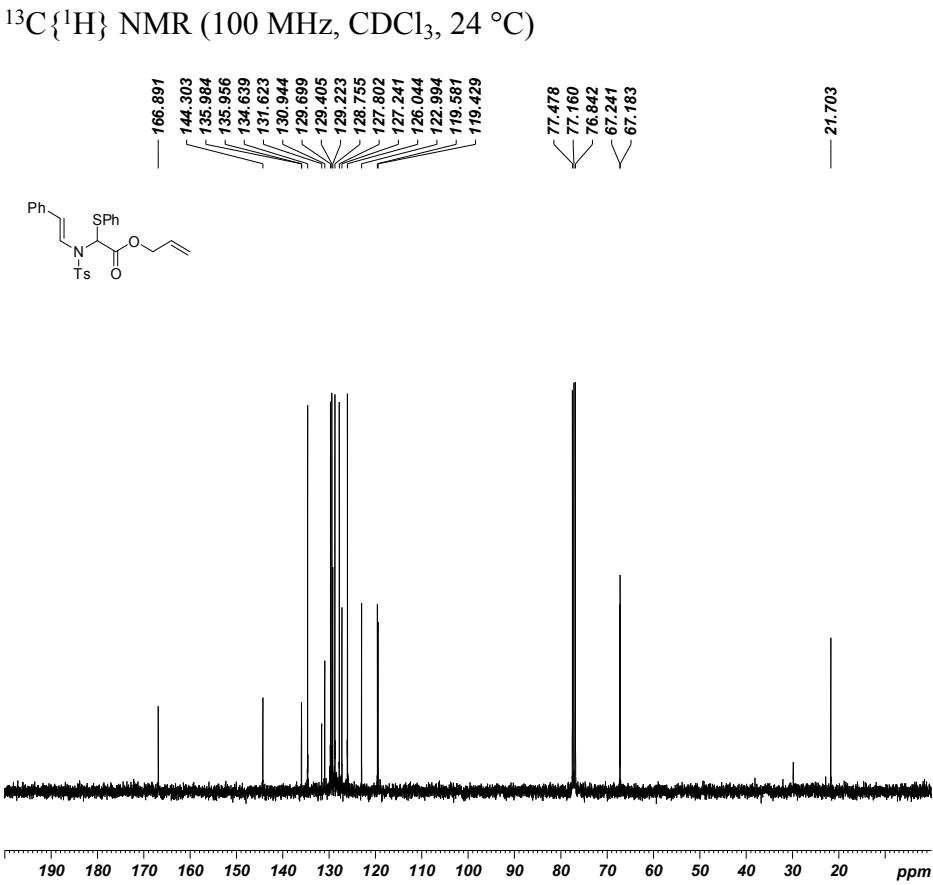
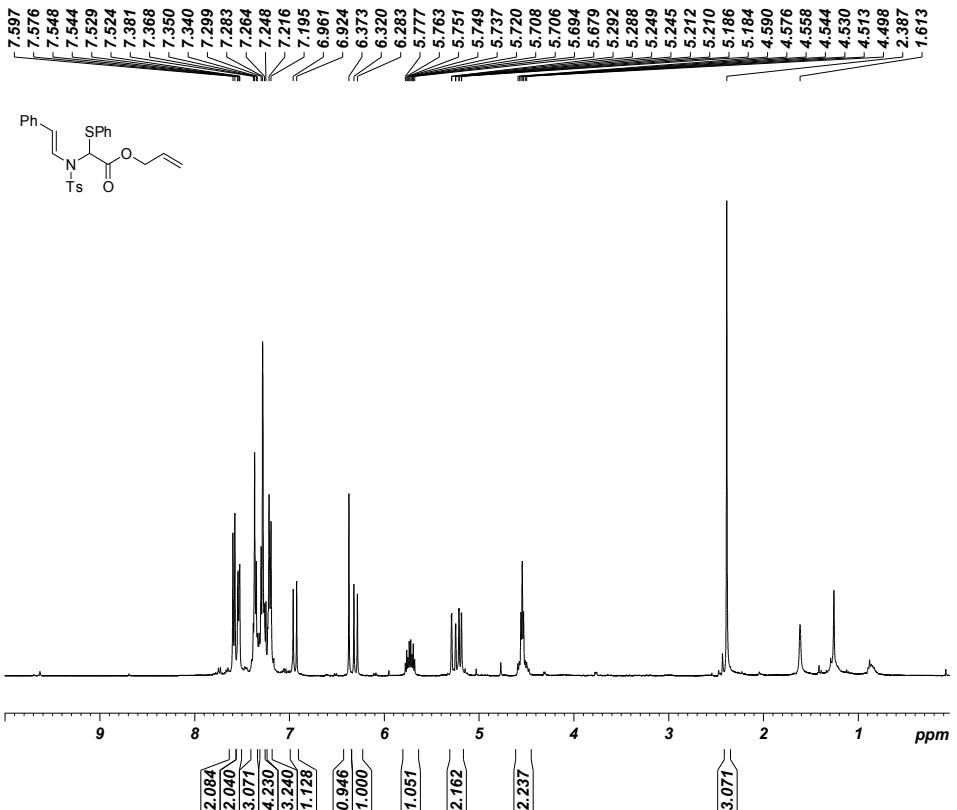
Enamide 4b

¹H NMR (400 MHz, CDCl₃, 24 °C)



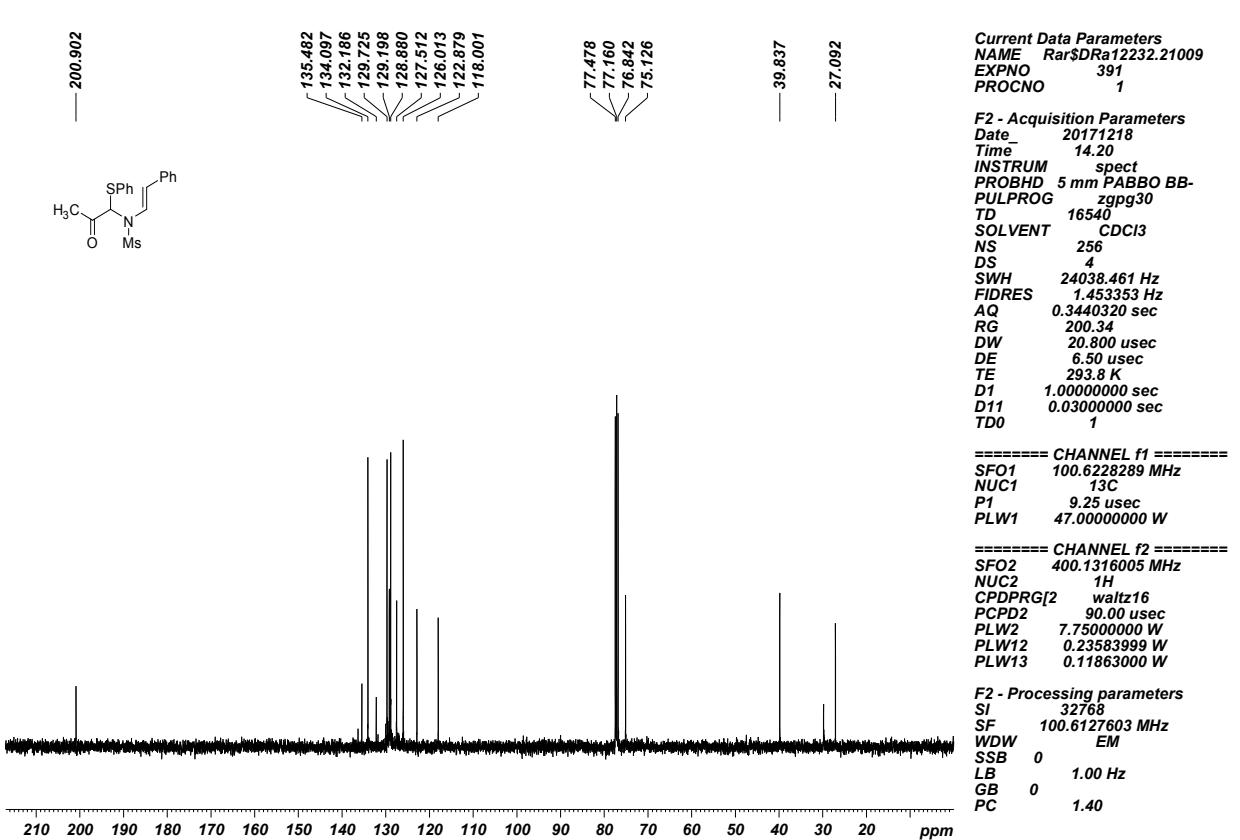
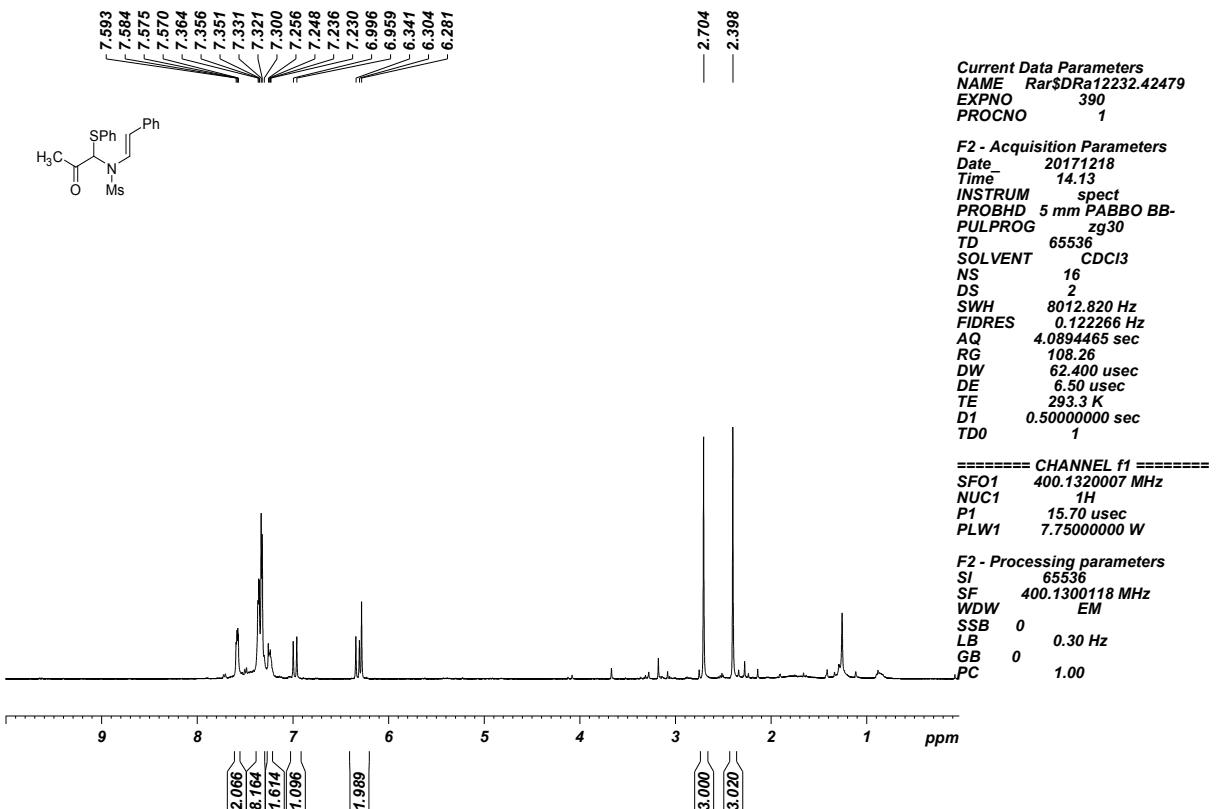
Enamide 4c

¹H NMR (400 MHz, CDCl₃, 24 °C)



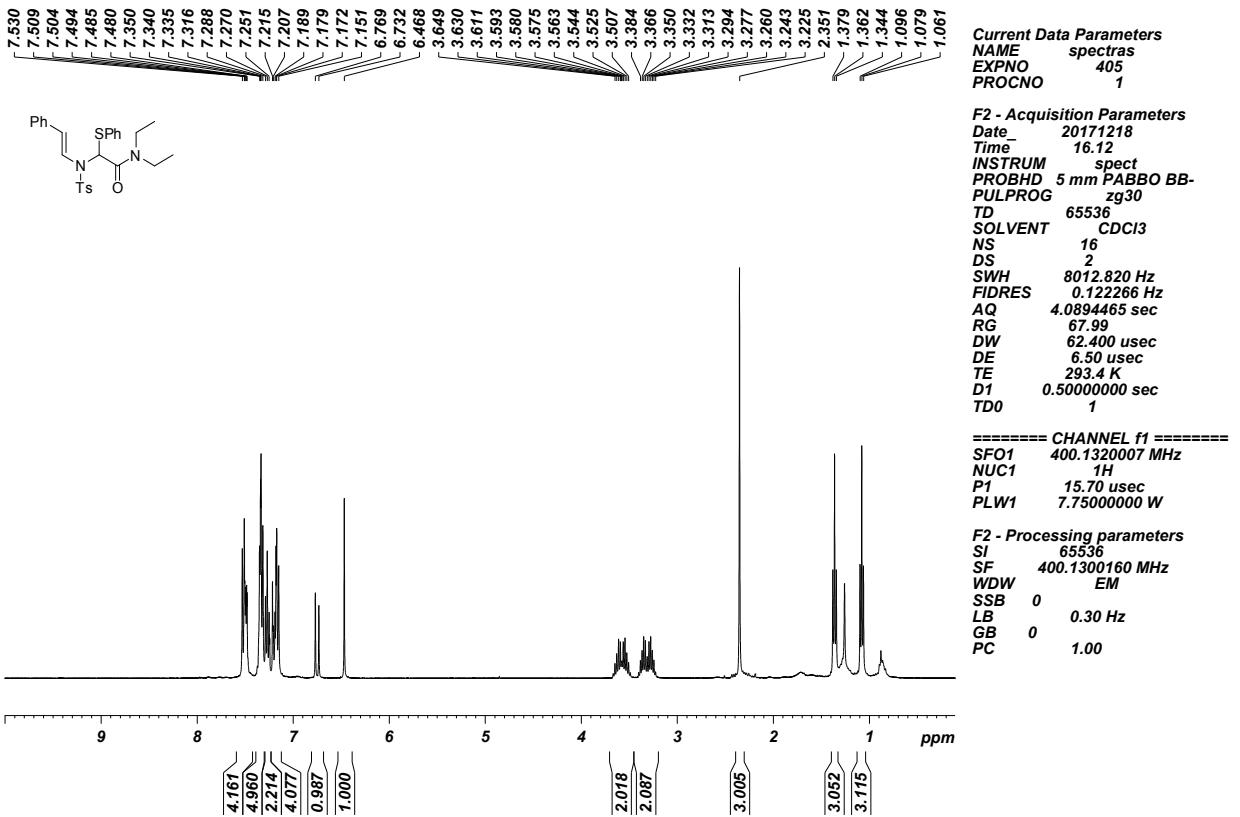
Enamide 4d

¹H NMR (400 MHz, CDCl₃, 24 °C)

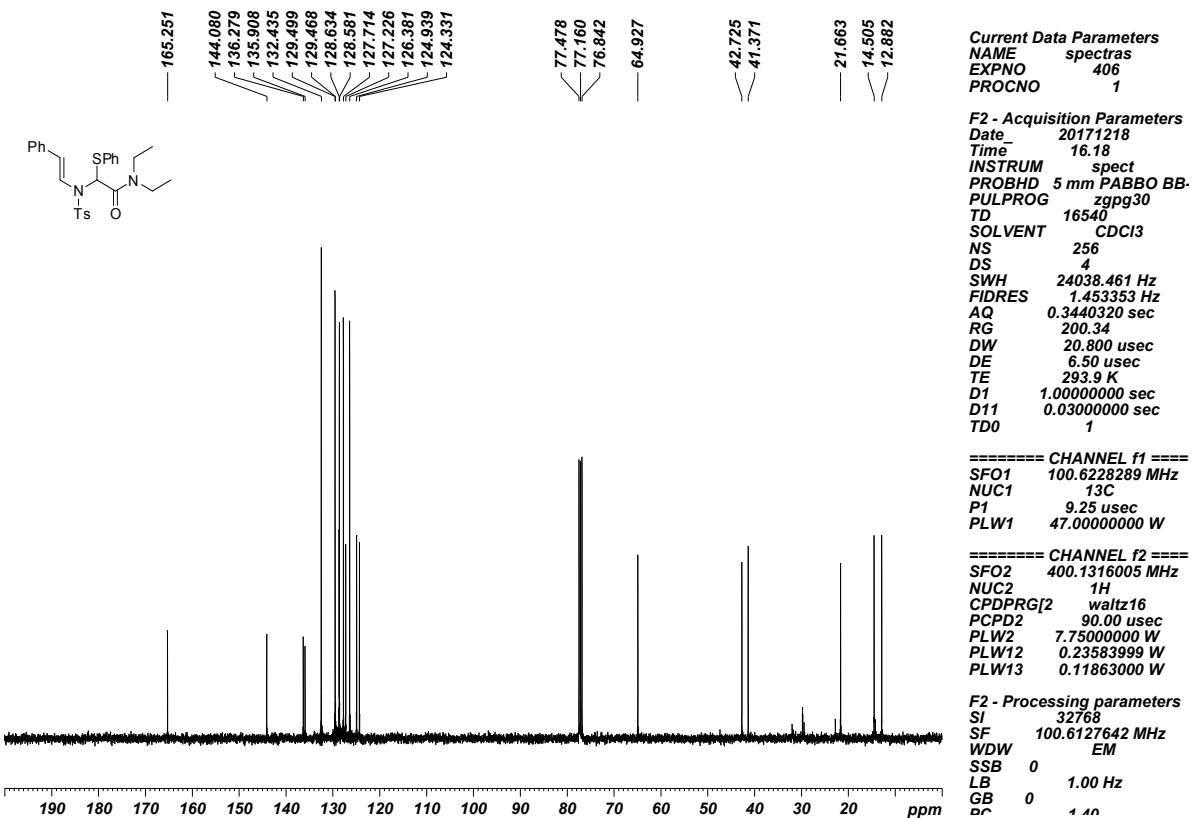


Enamide 4e

¹H NMR (400 MHz, CDCl₃, 24 °C)

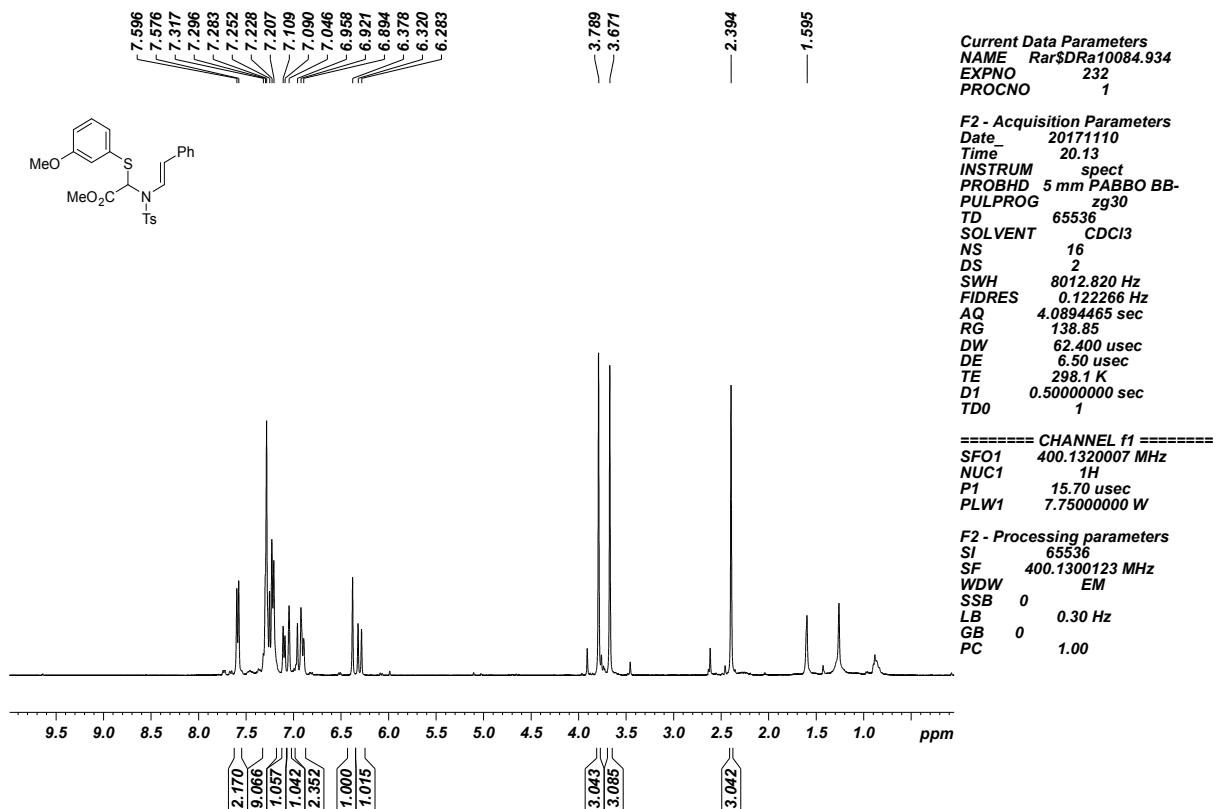


$^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C)

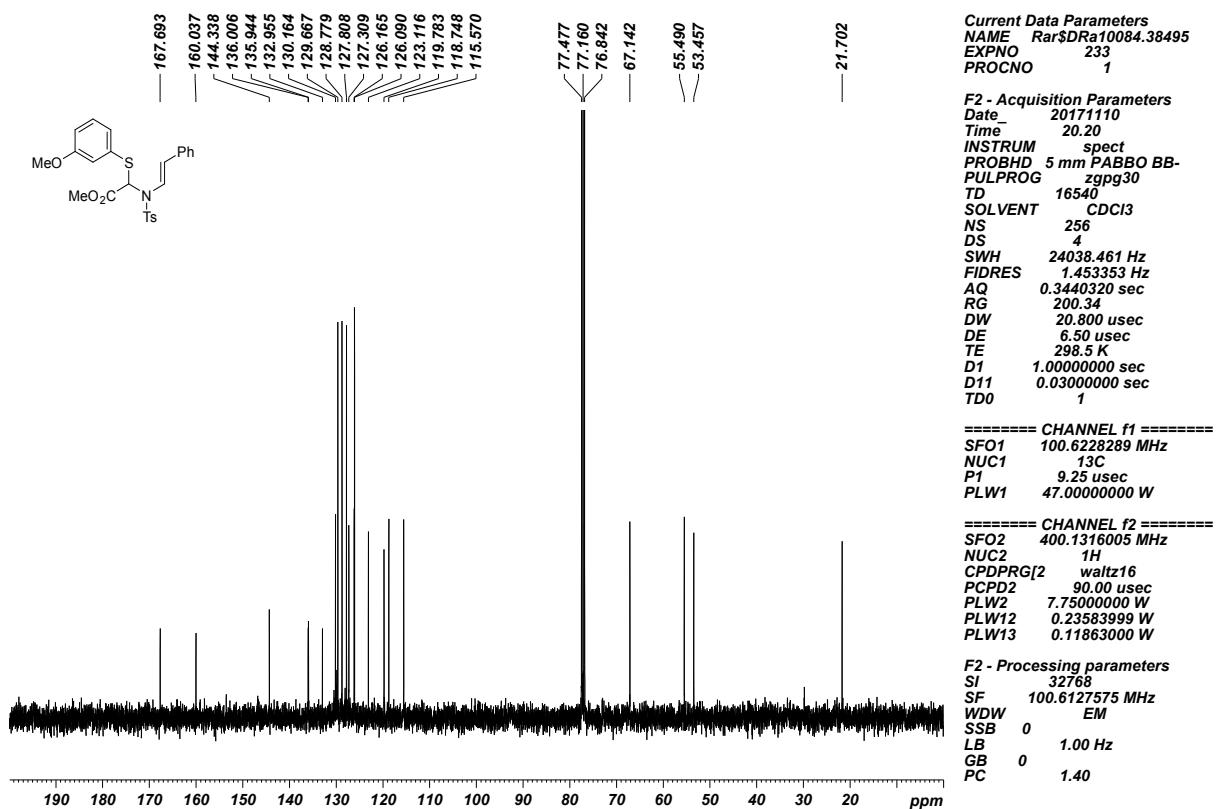


Enamide 4h

^1H NMR (400 MHz, CDCl_3 , 24 °C)

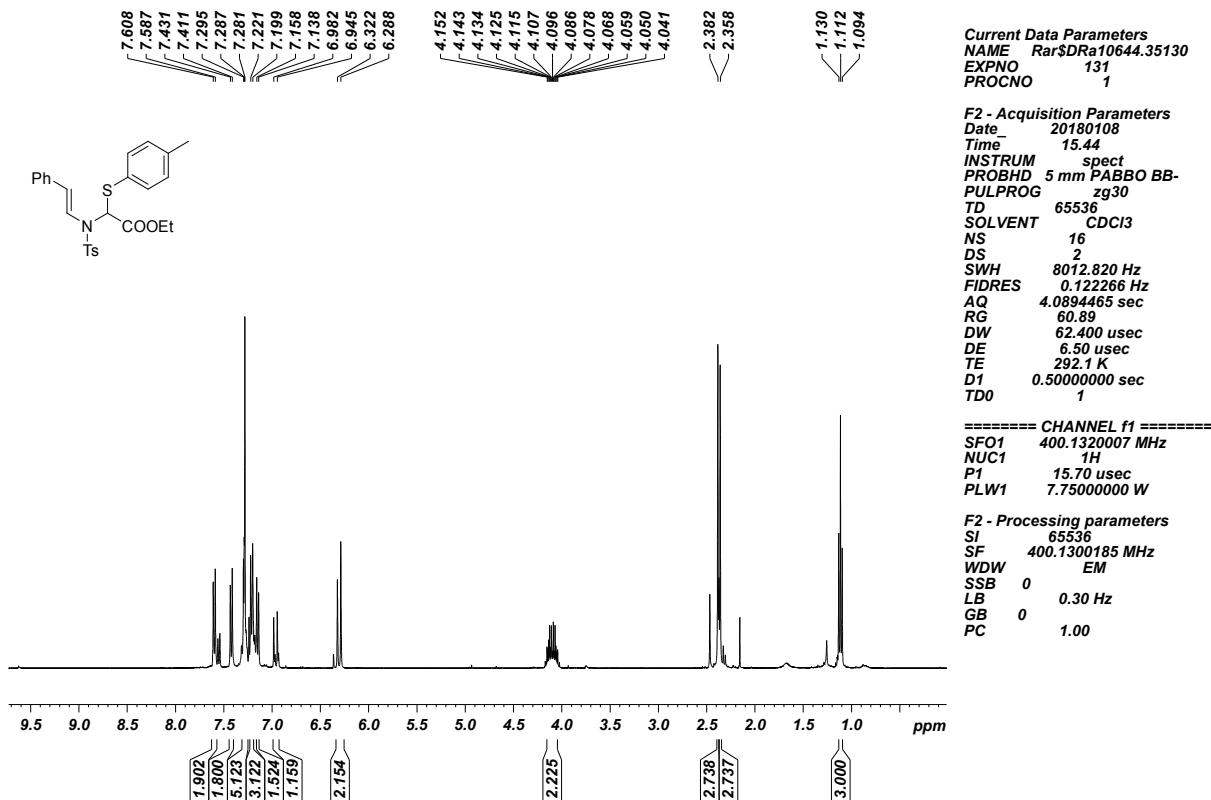


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

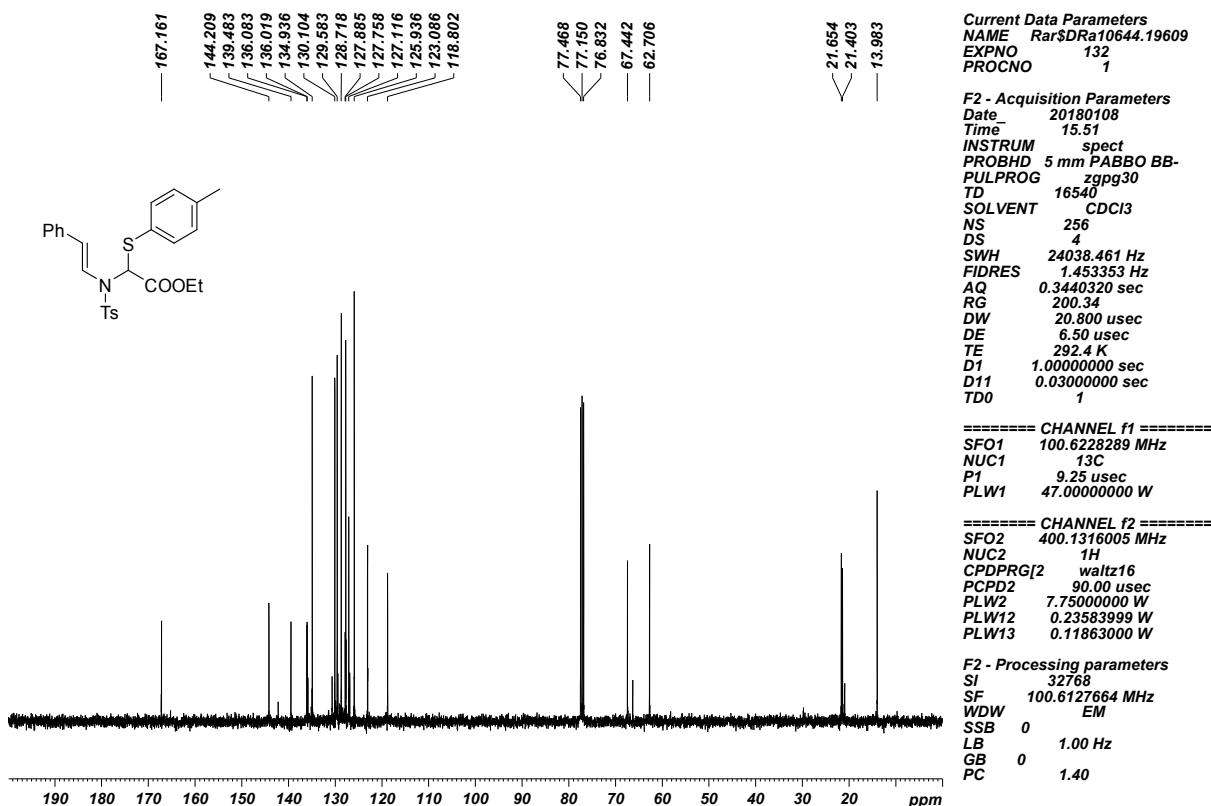


Enamide 4i

¹H NMR (400 MHz, CDCl₃, 24 °C)

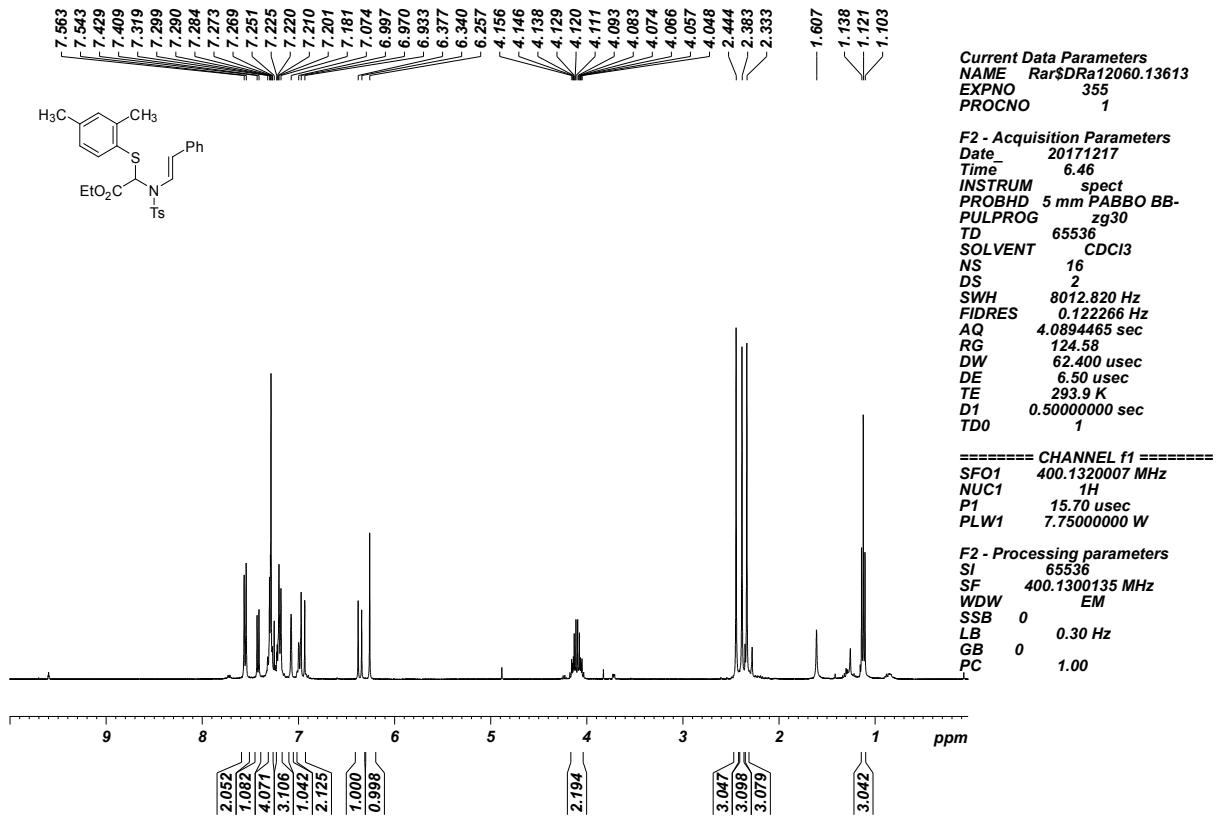


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

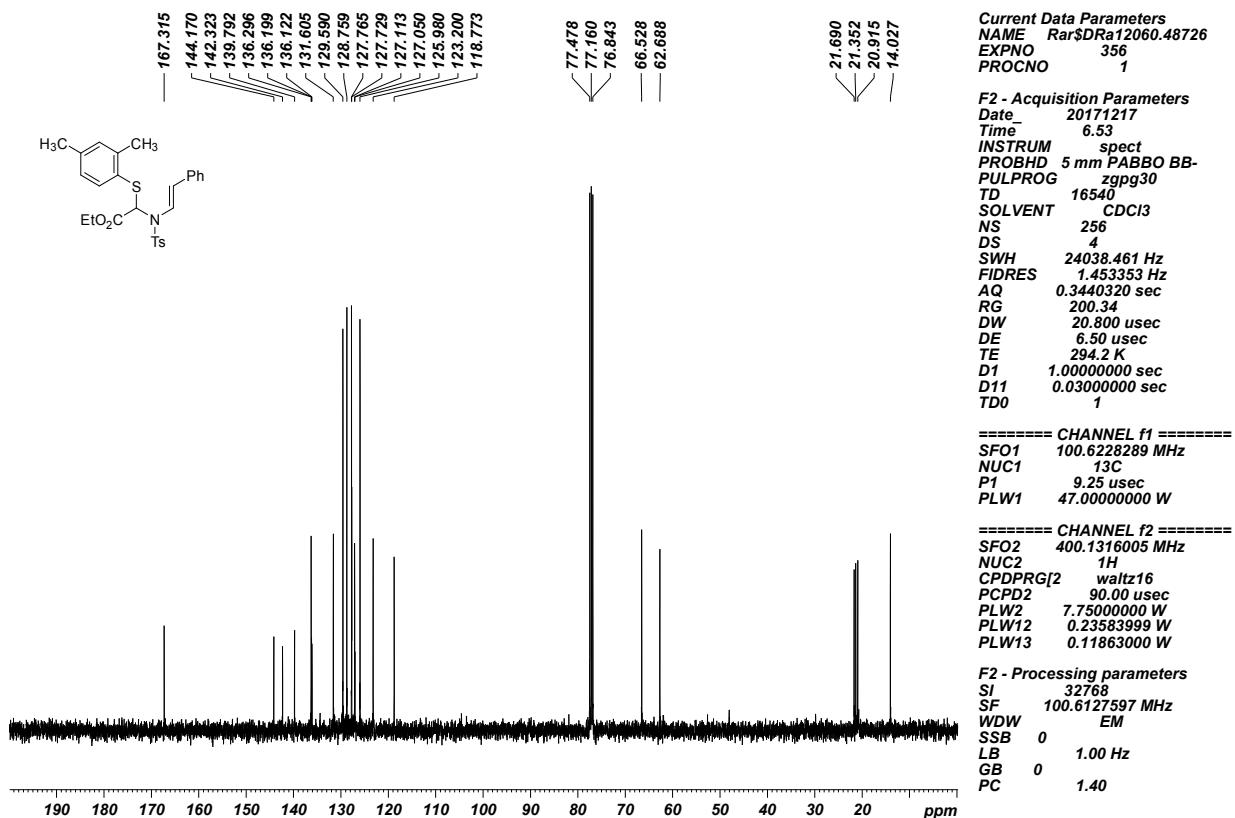


Enamide 4j

¹H NMR (400 MHz, CDCl₃, 24 °C)

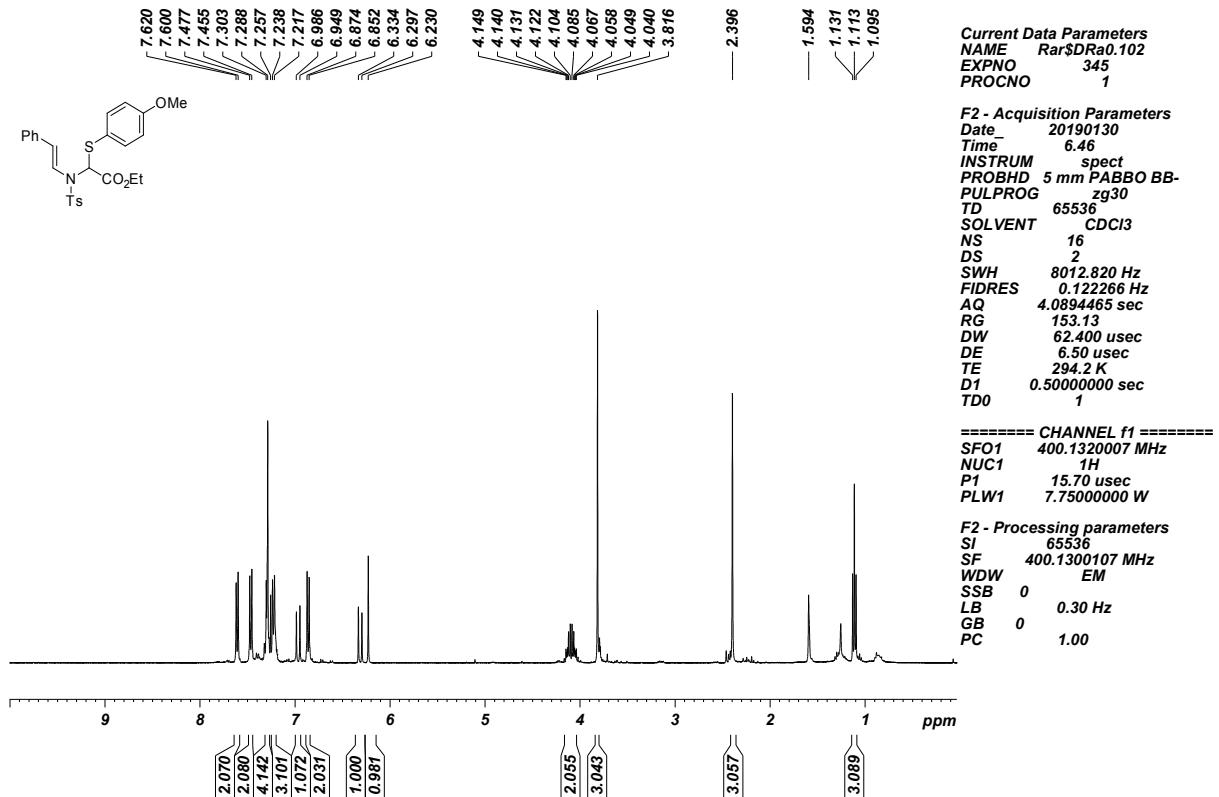


$^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C)

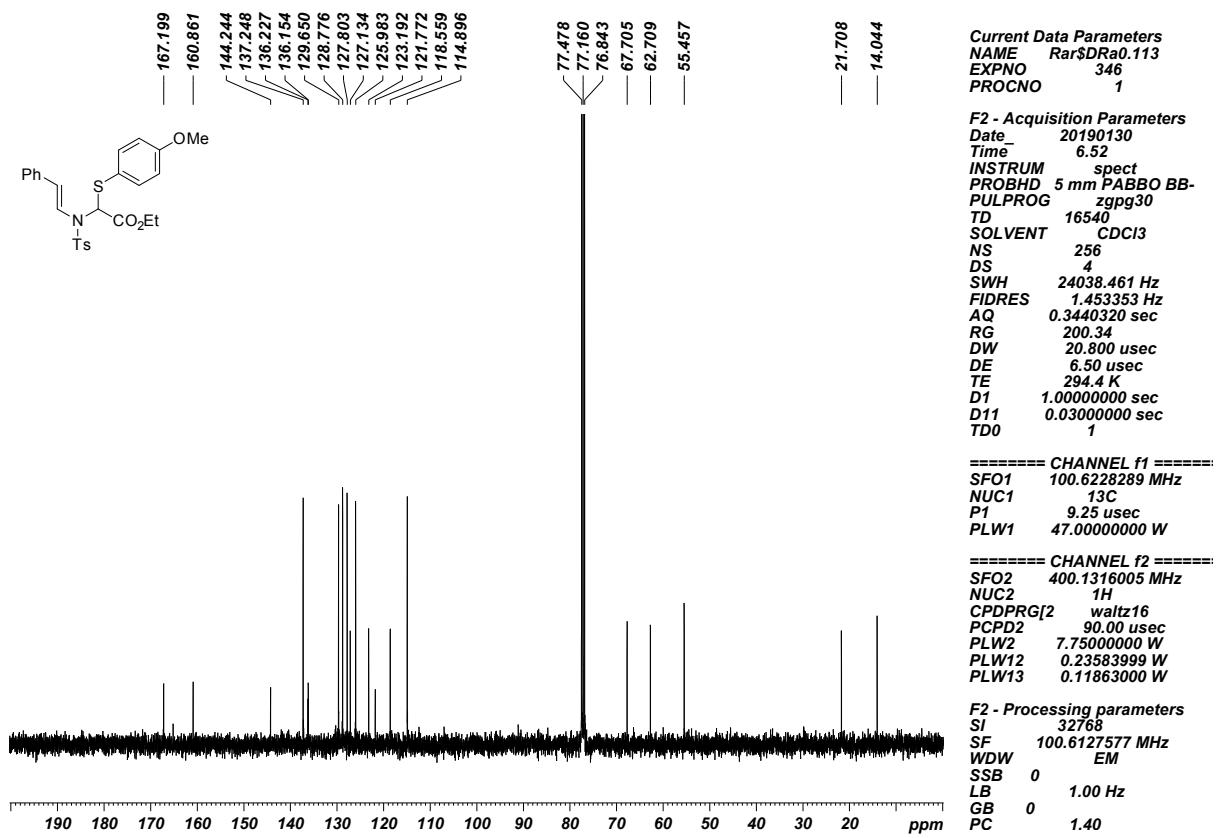


Enamide 4k

^1H NMR (400 MHz, CDCl_3 , 24 °C)

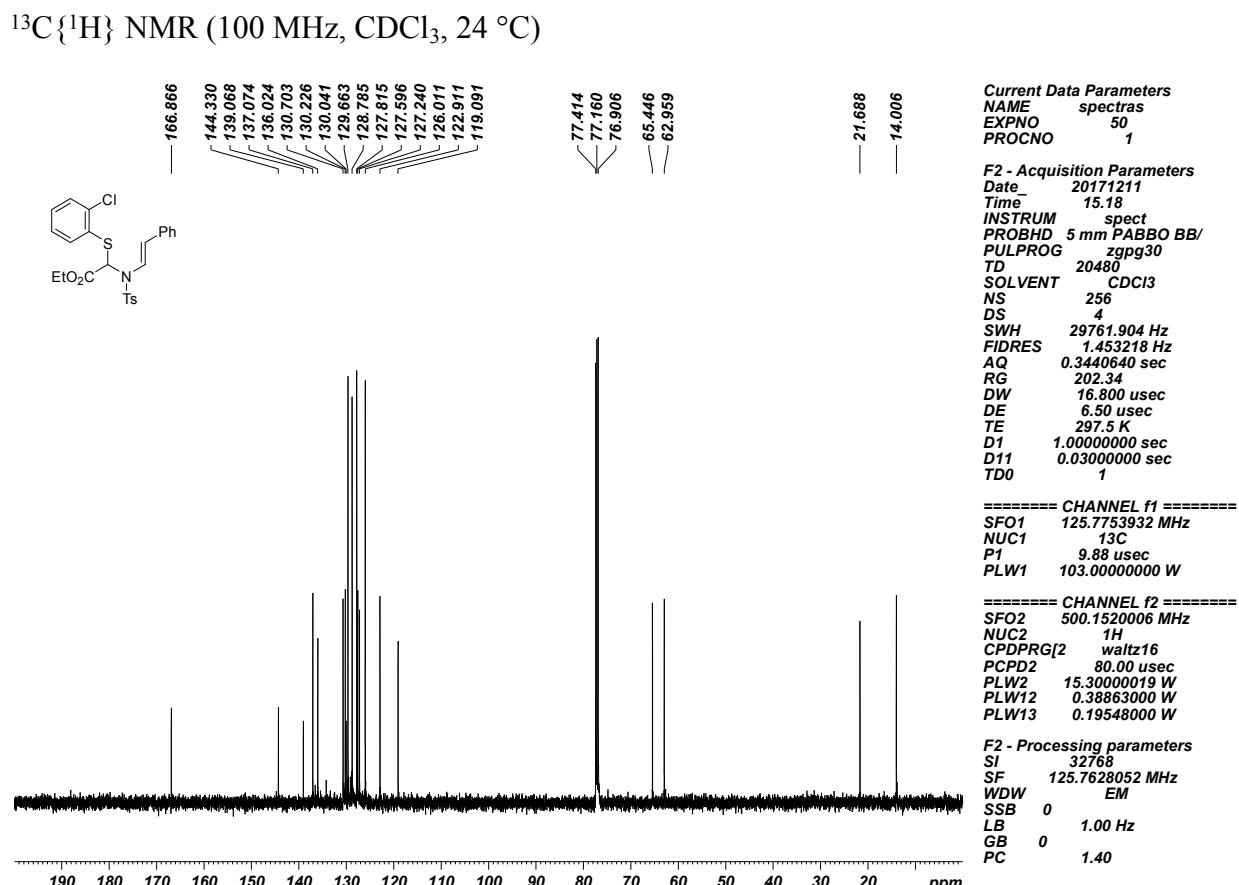
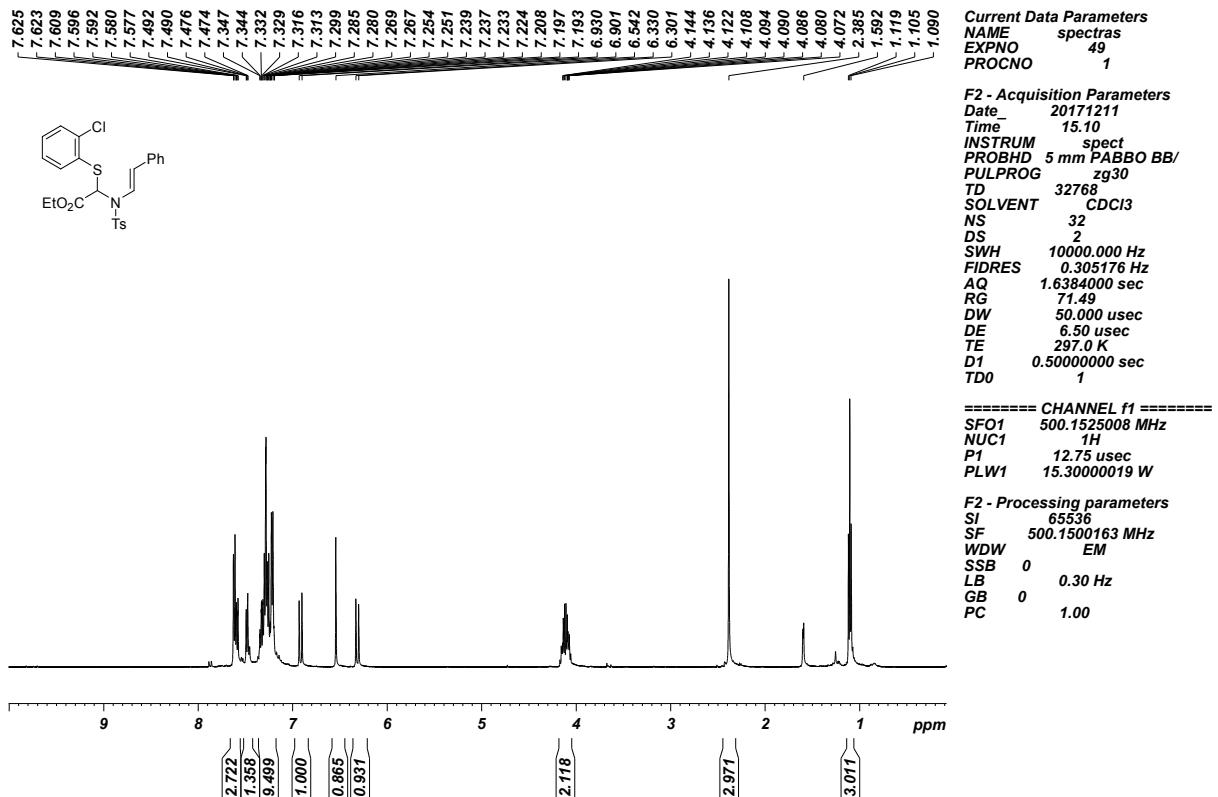


$^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C)



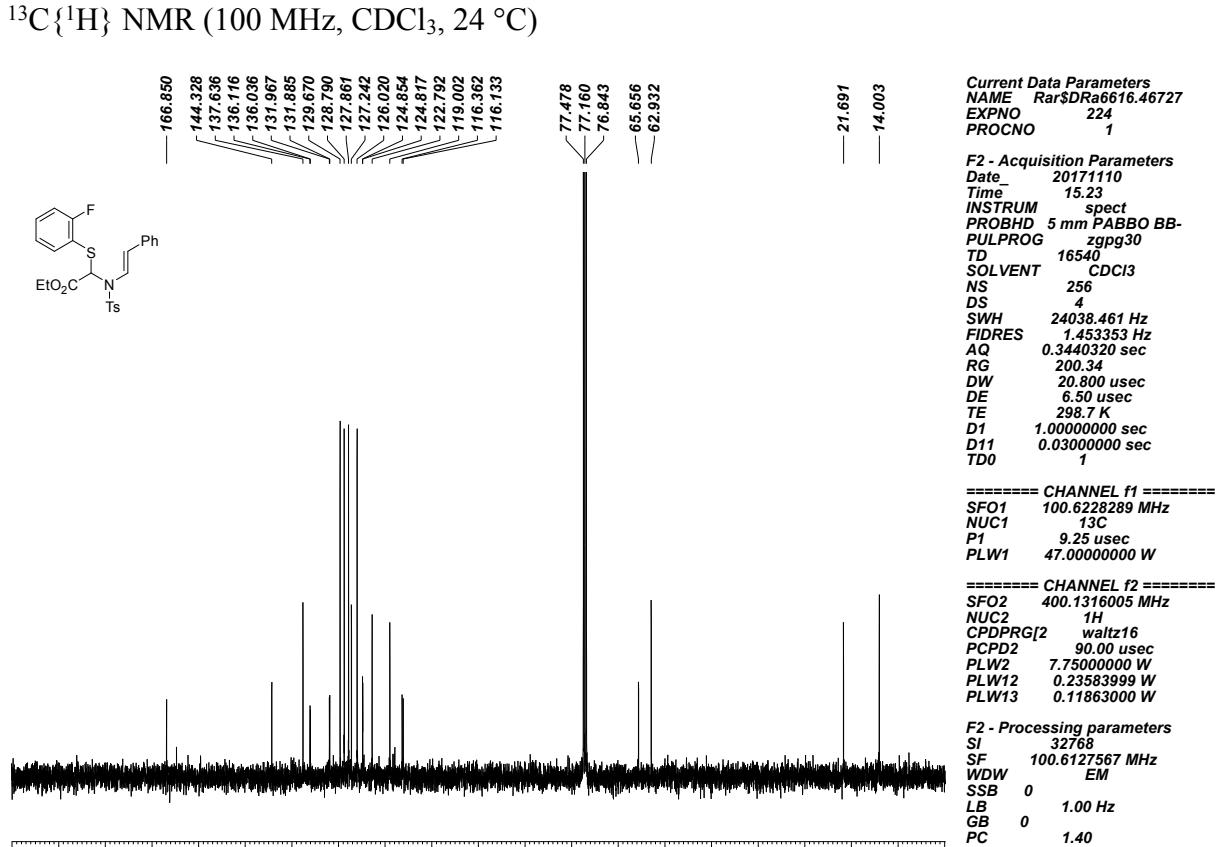
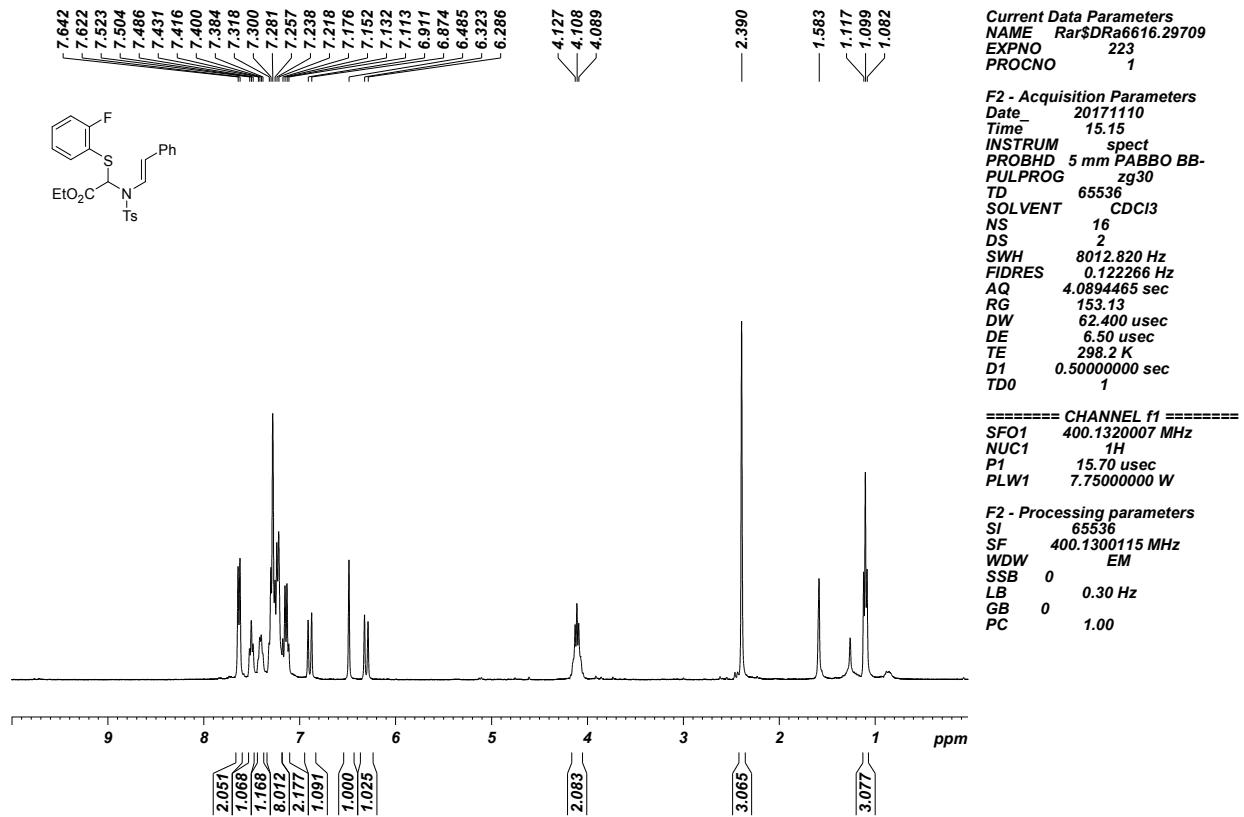
Enamide 4l

^1H NMR (400 MHz, CDCl_3 , 24 °C)



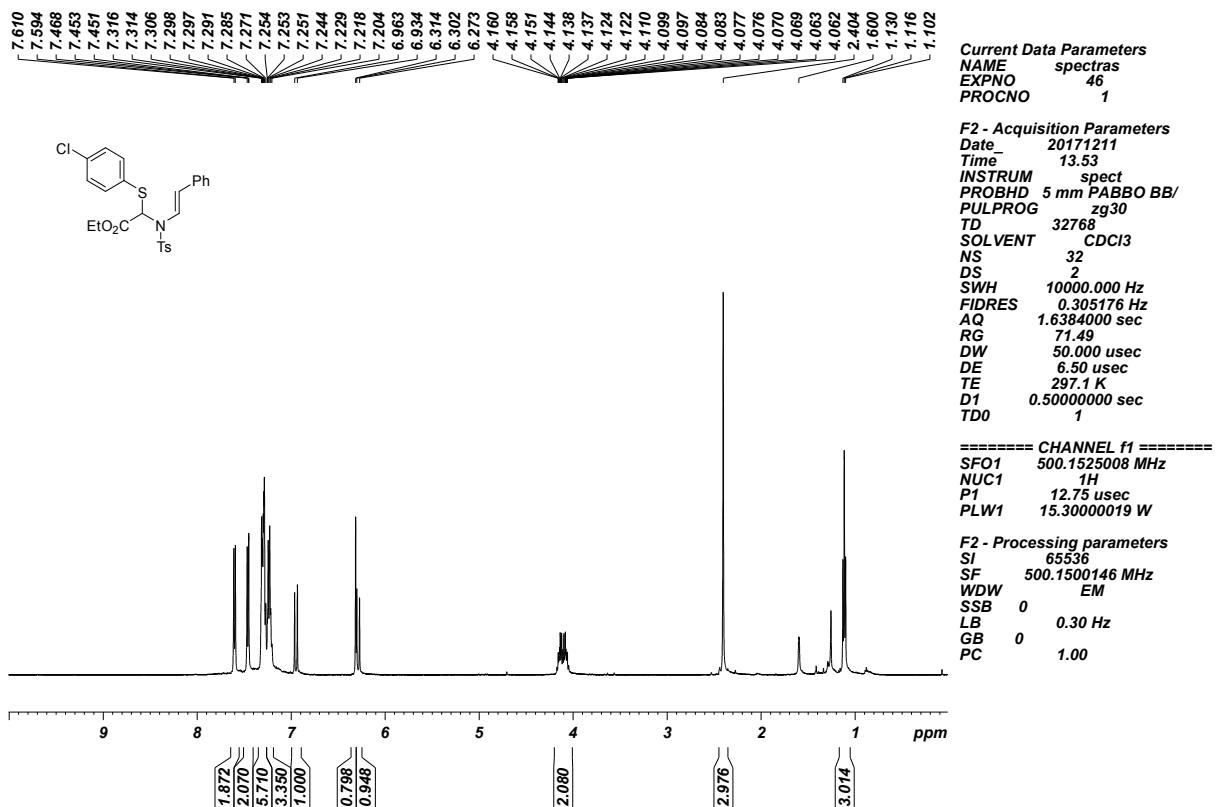
Enamide 4m

¹H NMR (400 MHz, CDCl₃, 24 °C)

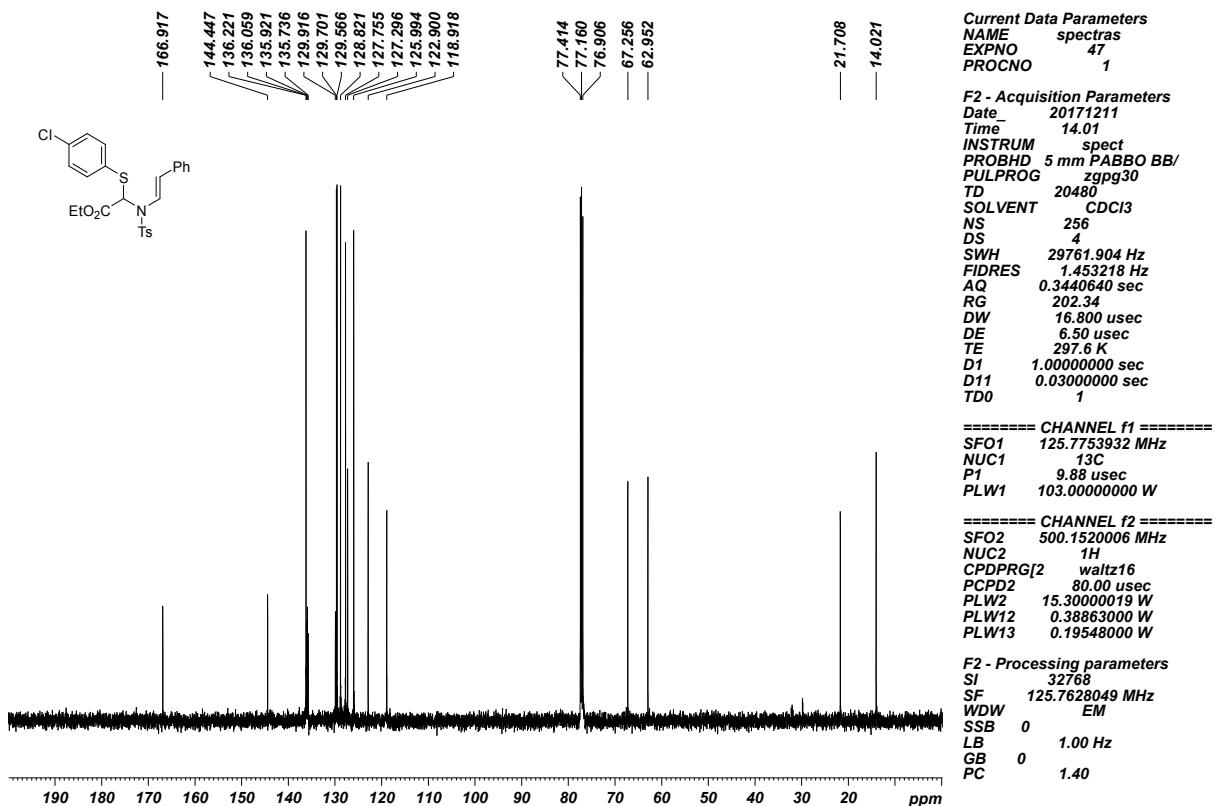


Enamide 4n

¹H NMR (400 MHz, CDCl₃, 24 °C)

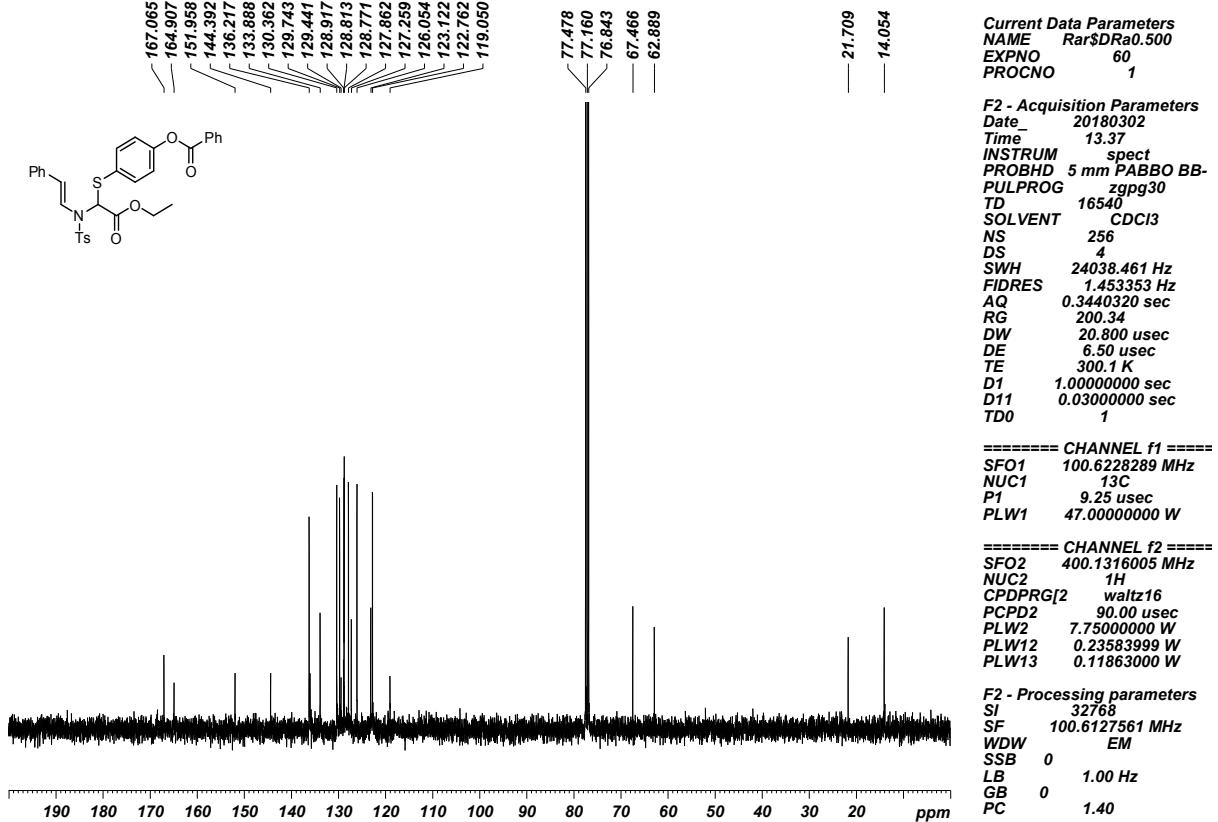
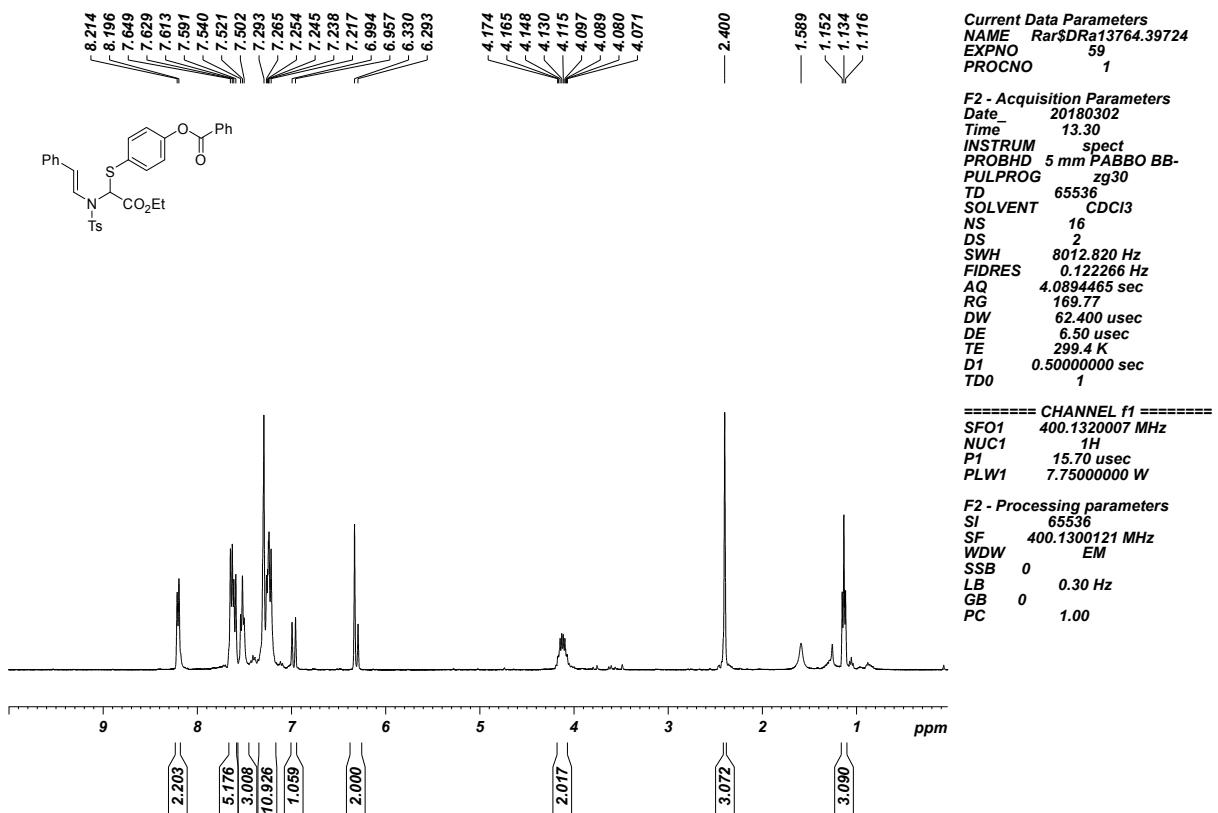


$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C)



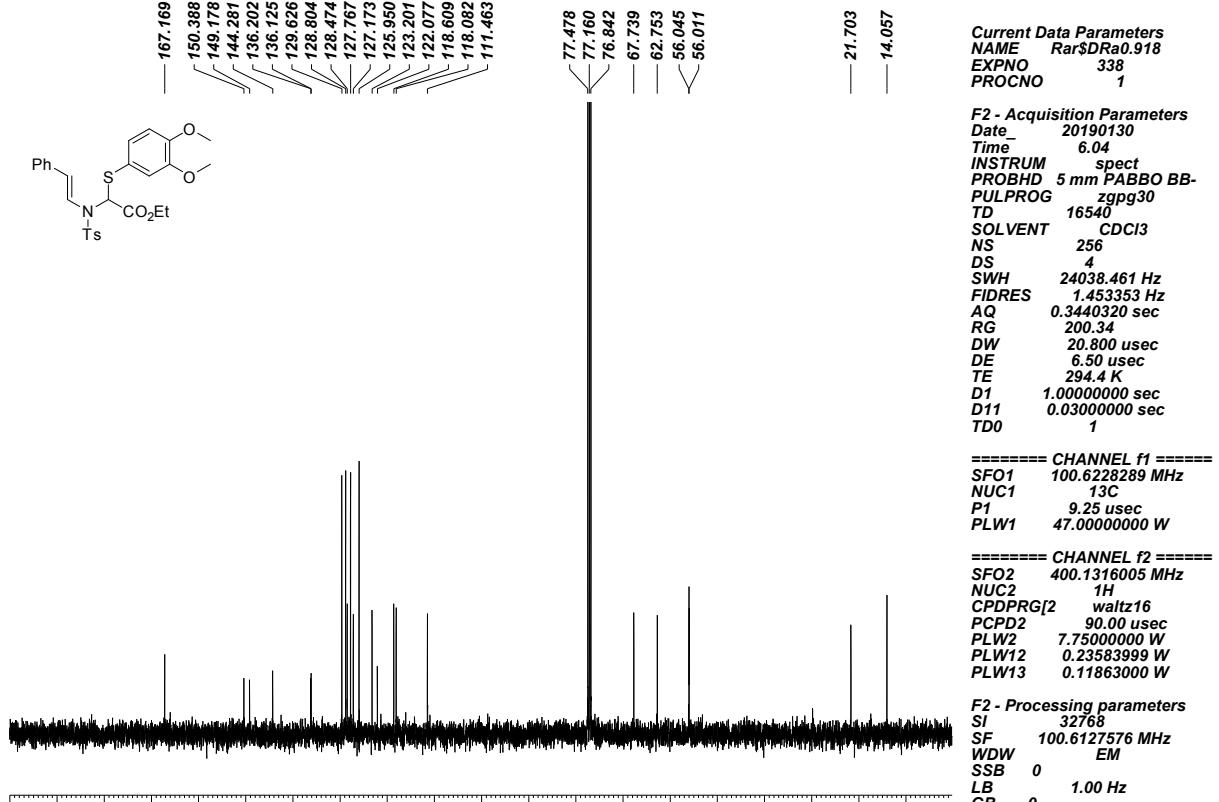
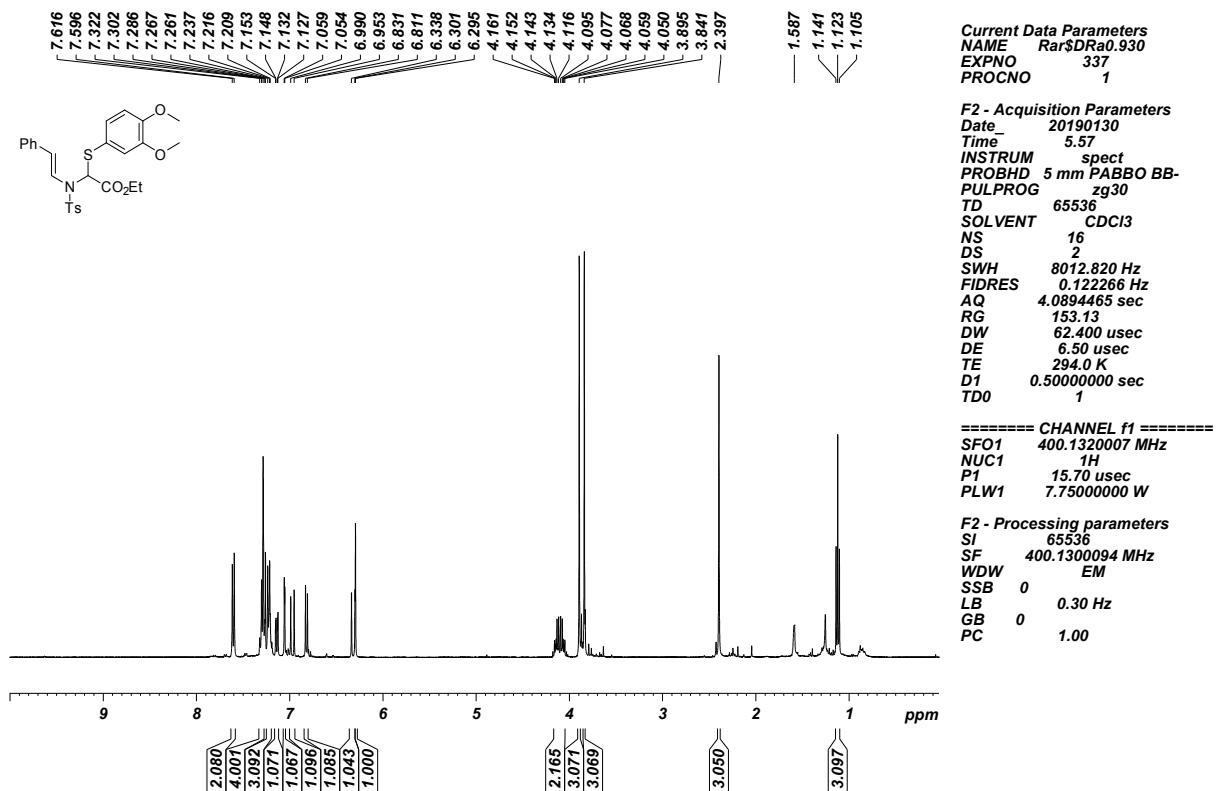
Enamide 4o

^1H NMR (400 MHz, CDCl_3 , 24 °C)



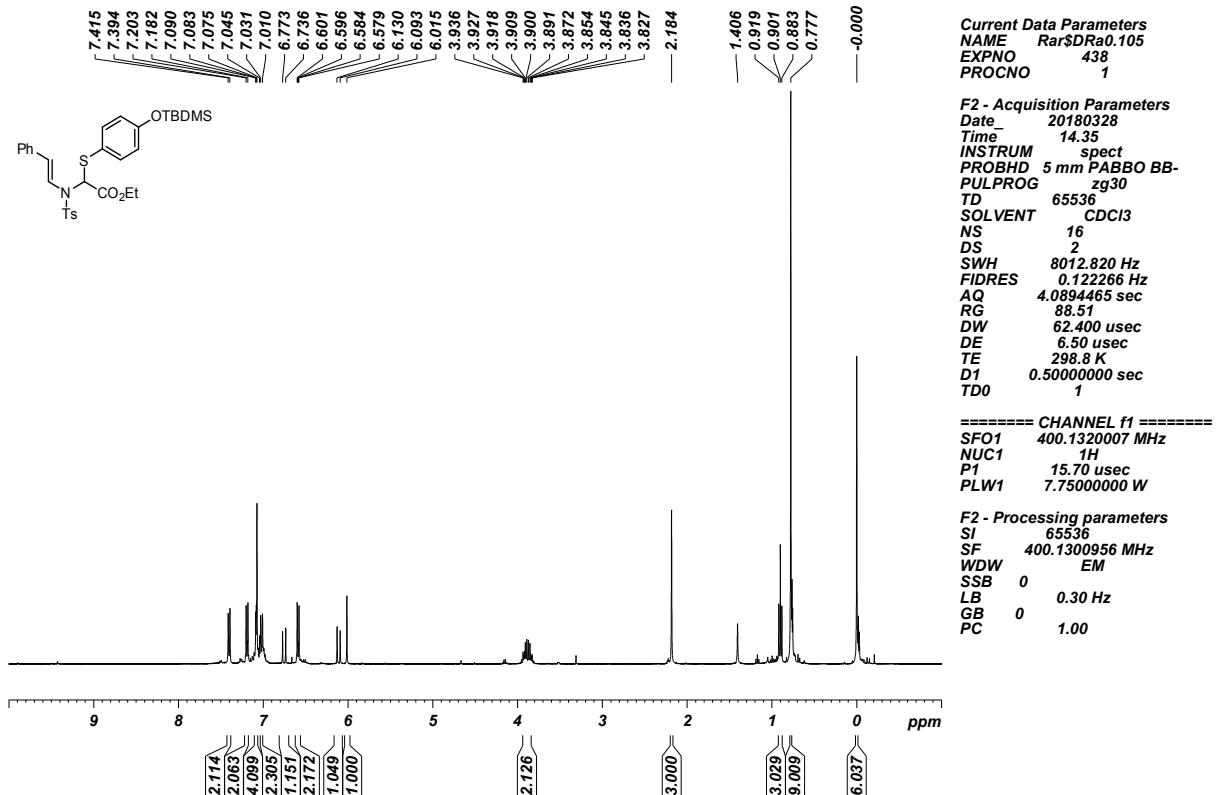
Enamide 4p

¹H NMR (400 MHz, CDCl₃, 24 °C)

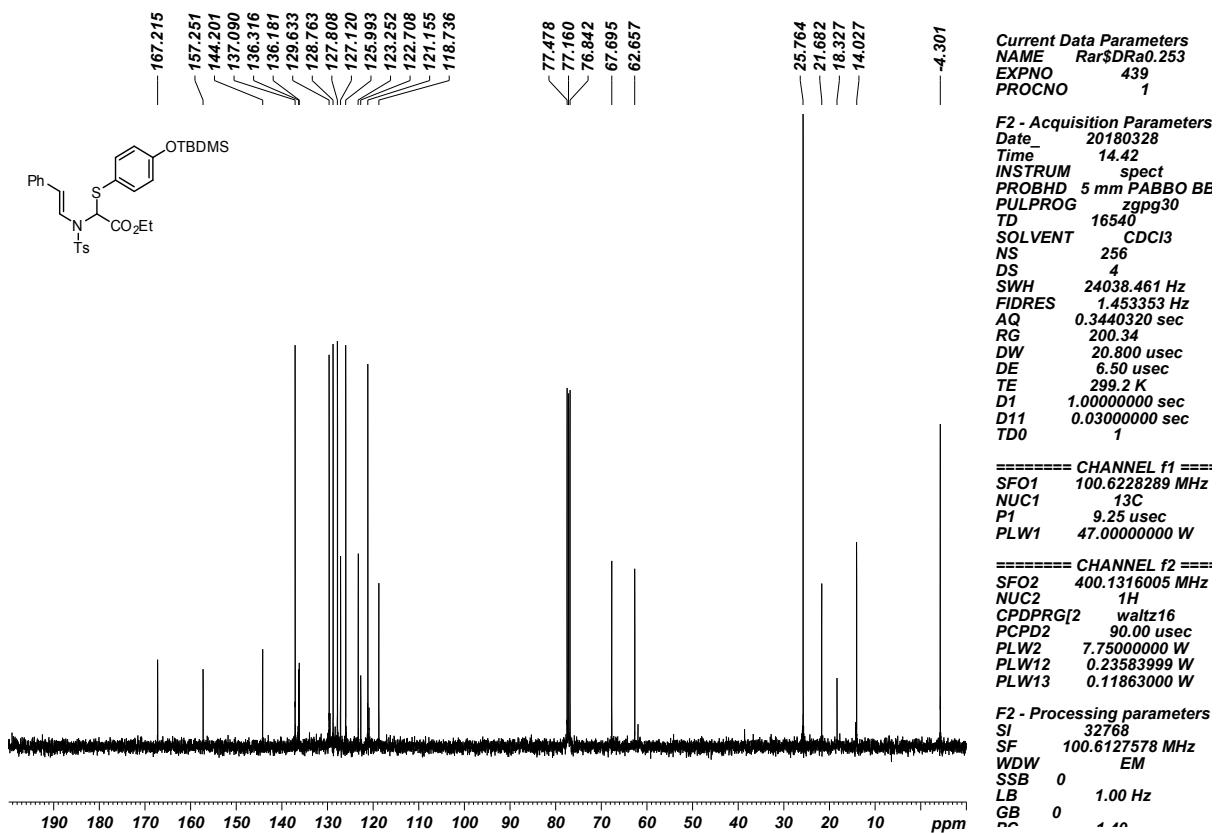


Enamide 4q

¹H NMR (400 MHz, CDCl₃, 24 °C)

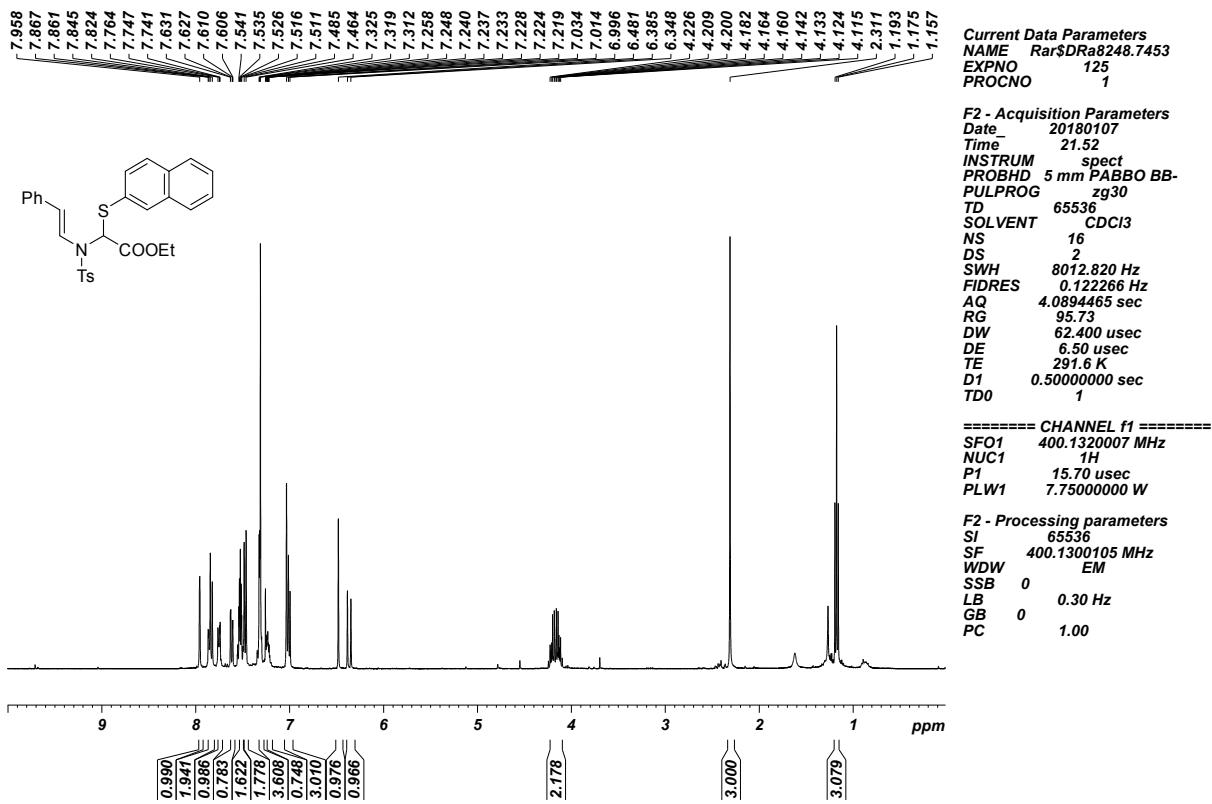


$^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C)

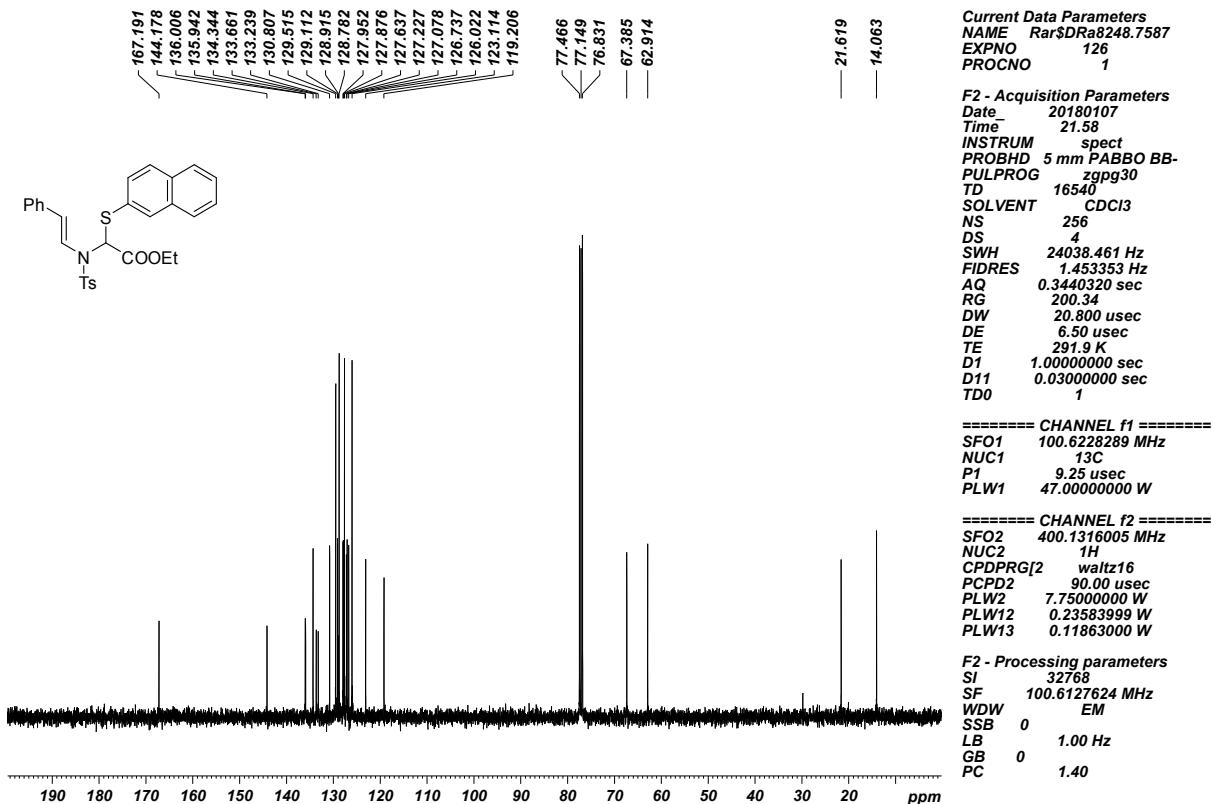


Enamide 4r

^1H NMR (400 MHz, CDCl_3 , 24 °C)

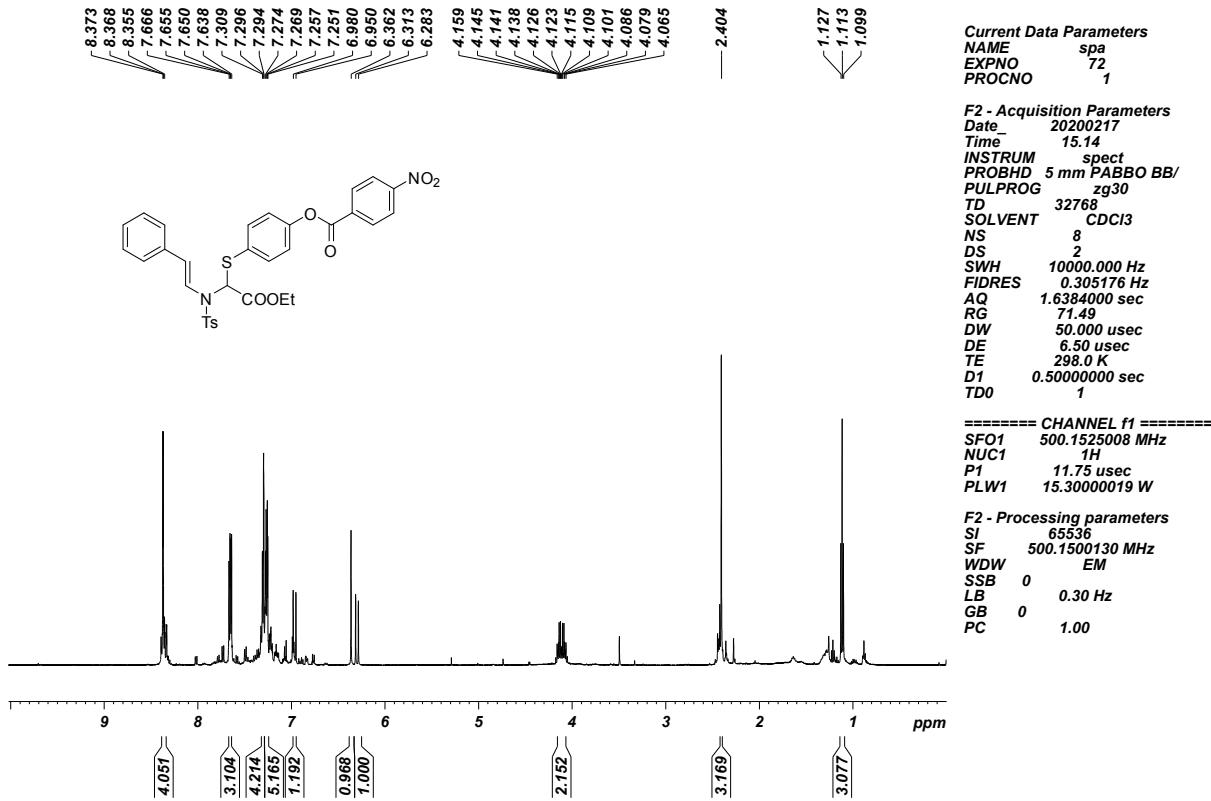


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

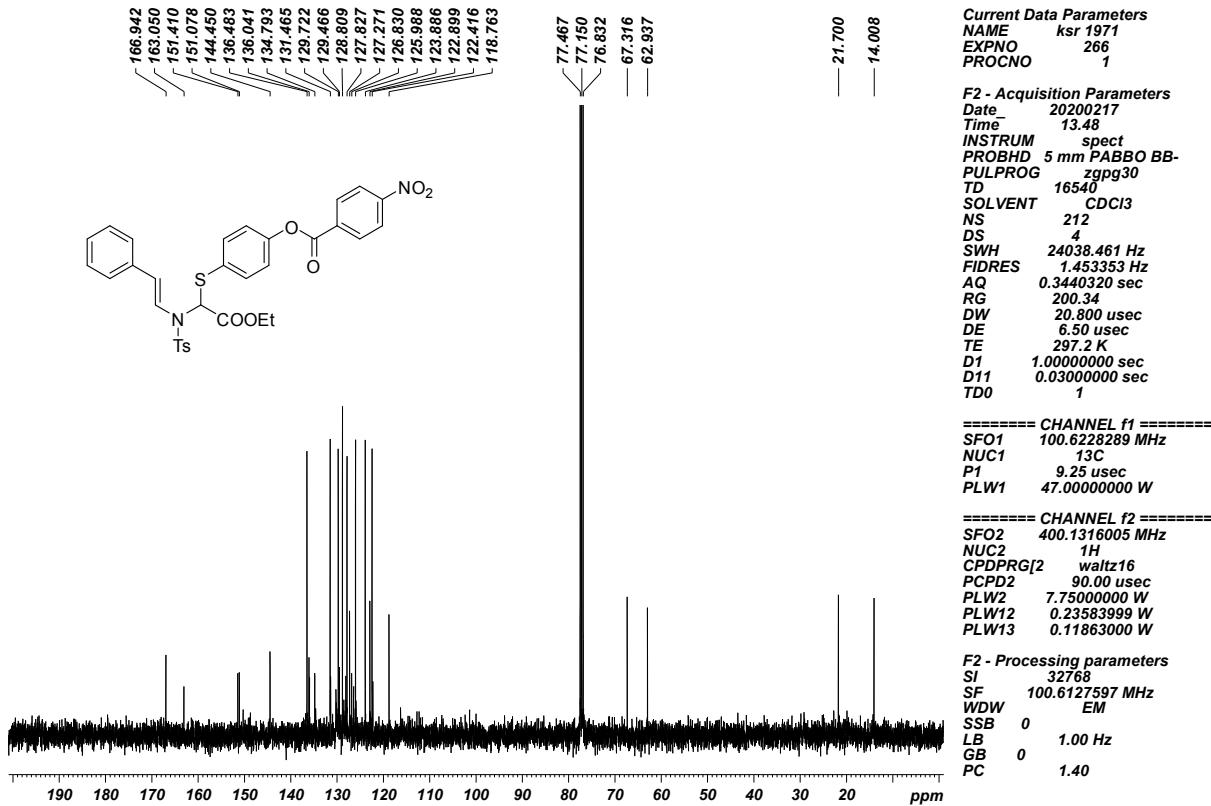


Enamide 4s

¹H NMR (400 MHz, CDCl₃, 24 °C)

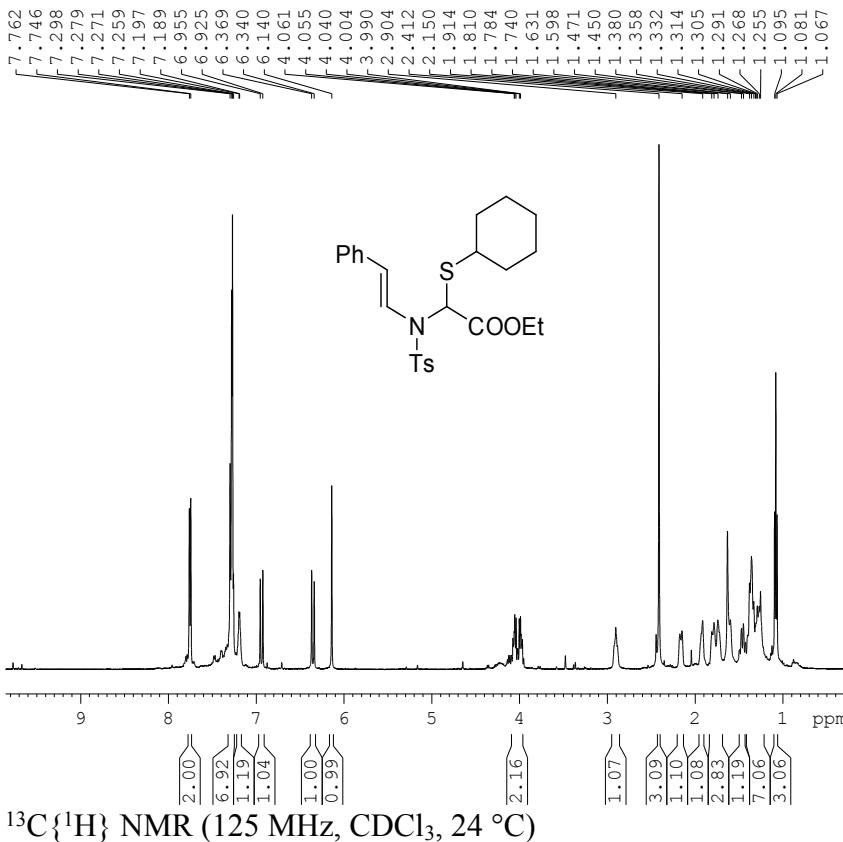


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)



Enamide 4t

¹H NMR (500 MHz, CDCl₃, 24 °C)

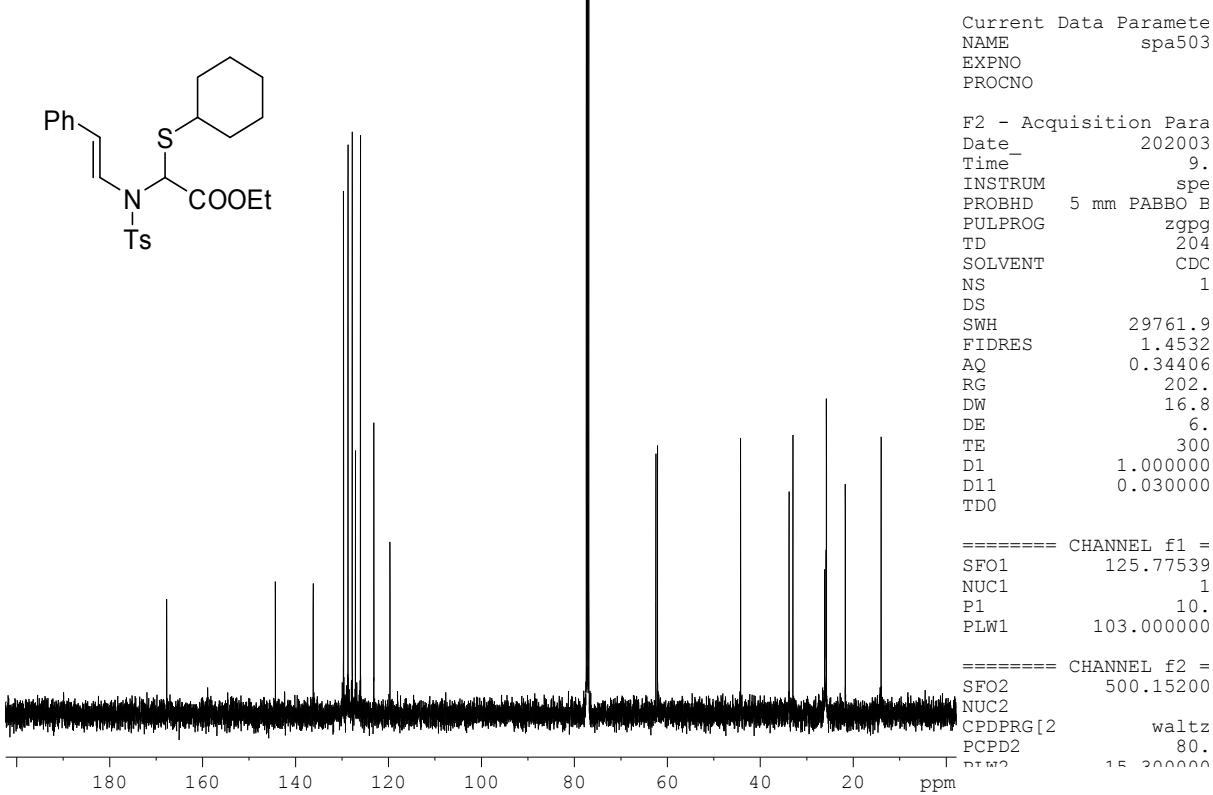


Current Data Parameters
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EXPNO 1
PROCNO 1

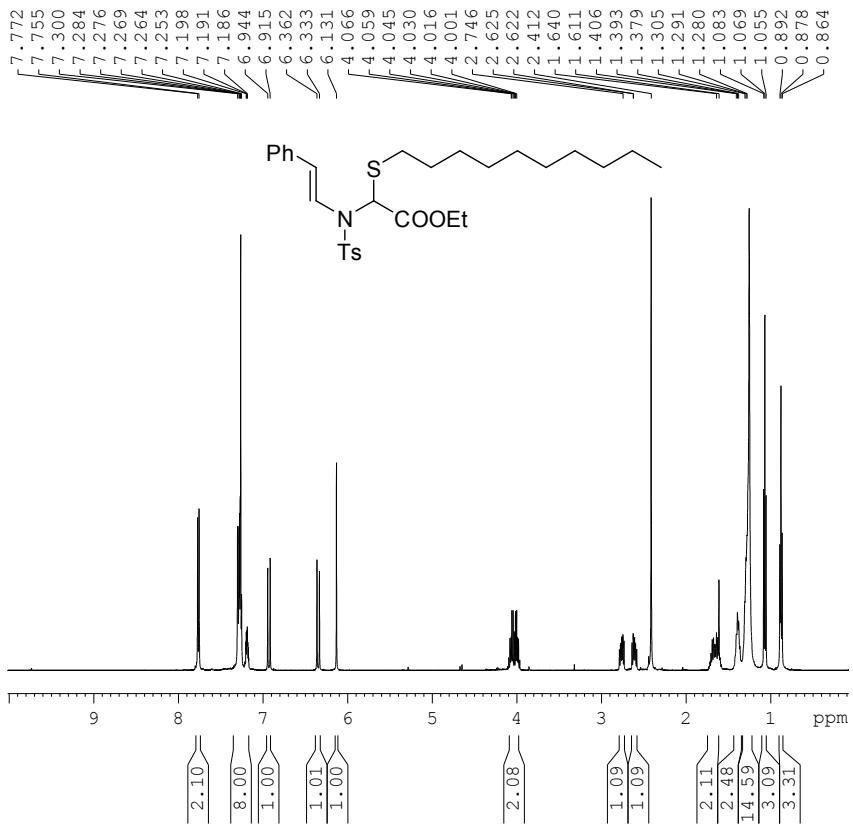
F2 - Acquisition Parameters
Date 20200302
Time 9.37
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT CDCl₃
NS 15
DS 2
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 1.6384000 sec
RG 64
DW 50.000 usec
DE 6.50 usec
TE 298.0 K
D1 0.5000000 sec
TDO 1

===== CHANNEL f1 =====
SFO1 500.1525008 MHz
NUC1 1H
P1 11.75 usec
PLW1 15.30000019 W

F2 - Processing parameters
SI 65536
SF 500.1500131 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Enamide 4u
¹H NMR (500 MHz, CDCl₃, 24 °C)



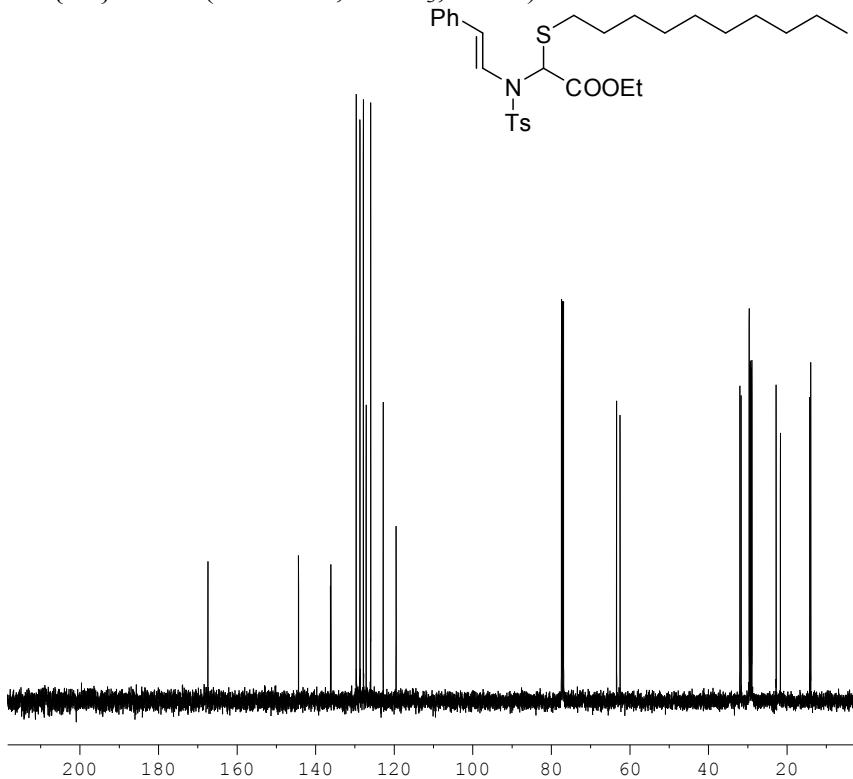
Current Data Parameters
NAME spa50320
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date 20200303
Time 15.03
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PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 1.6384000 sec
RG 31.24
DW 50.000 usec
DE 6.50 usec
TE 298.0 K
D1 0.5000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 500.1525008 MHz
NUC1 1H
P1 11.75 usec
PLW1 15.30000019 W

F2 - Processing parameters
SI 65536
SF 500.1500146 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

$^{13}\text{C}\{\text{H}\}$ NMR (125 MHz, CDCl_3 , 24 °C)



Current Data Parameters
NAME spa503
EXPNO
PROCNO

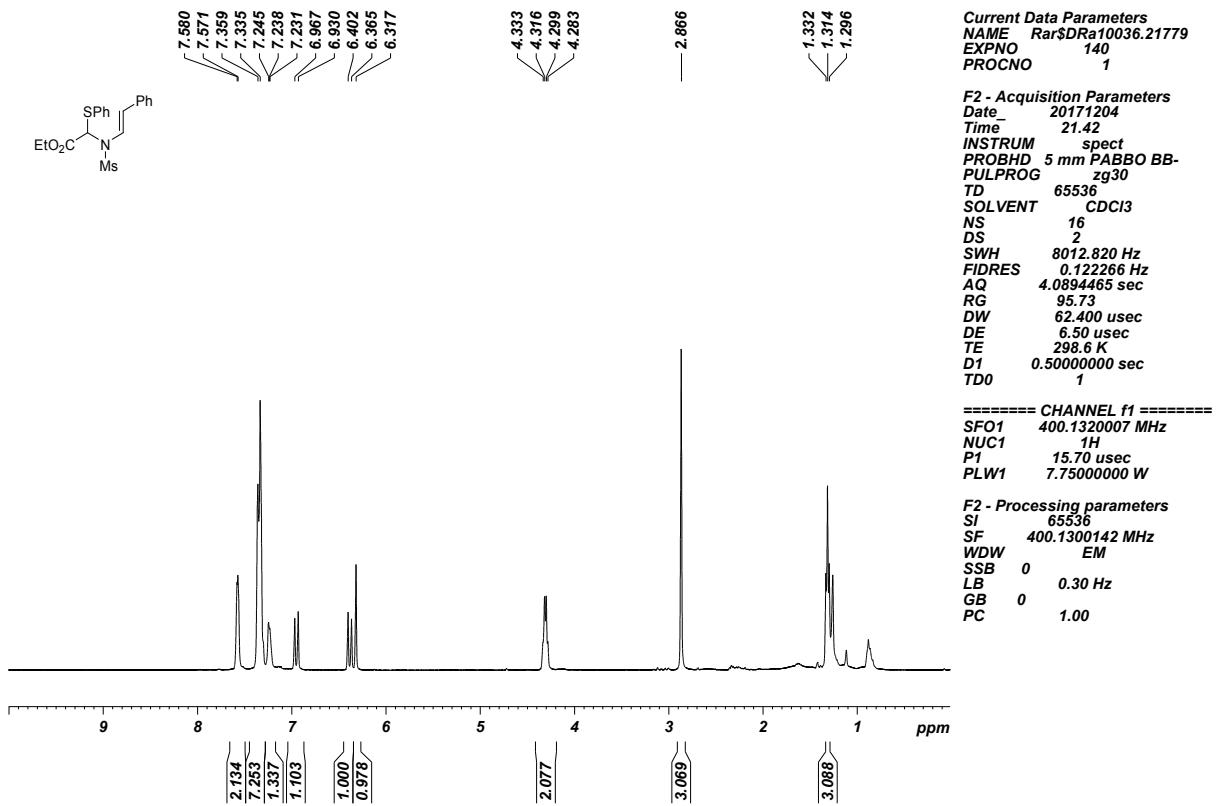
F2 - Acquisition Para
Date 202003
Time 15.
INSTRUM spe
PROBHD 5 mm PABBO B
PULPROG zgpg
TD 204
SOLVENT CDC
NS 2
DS
SWH 29761.9
FIDRES 1.4532
AQ 0.34406
RG 202.
DW 16.8
DE 6.
TE 300
D1 1.000000
D11 0.030000
TD0

===== CHANNEL f1 =
SFO1 125.77539
NUC1 1
P1 10.
PLW1 103.000000

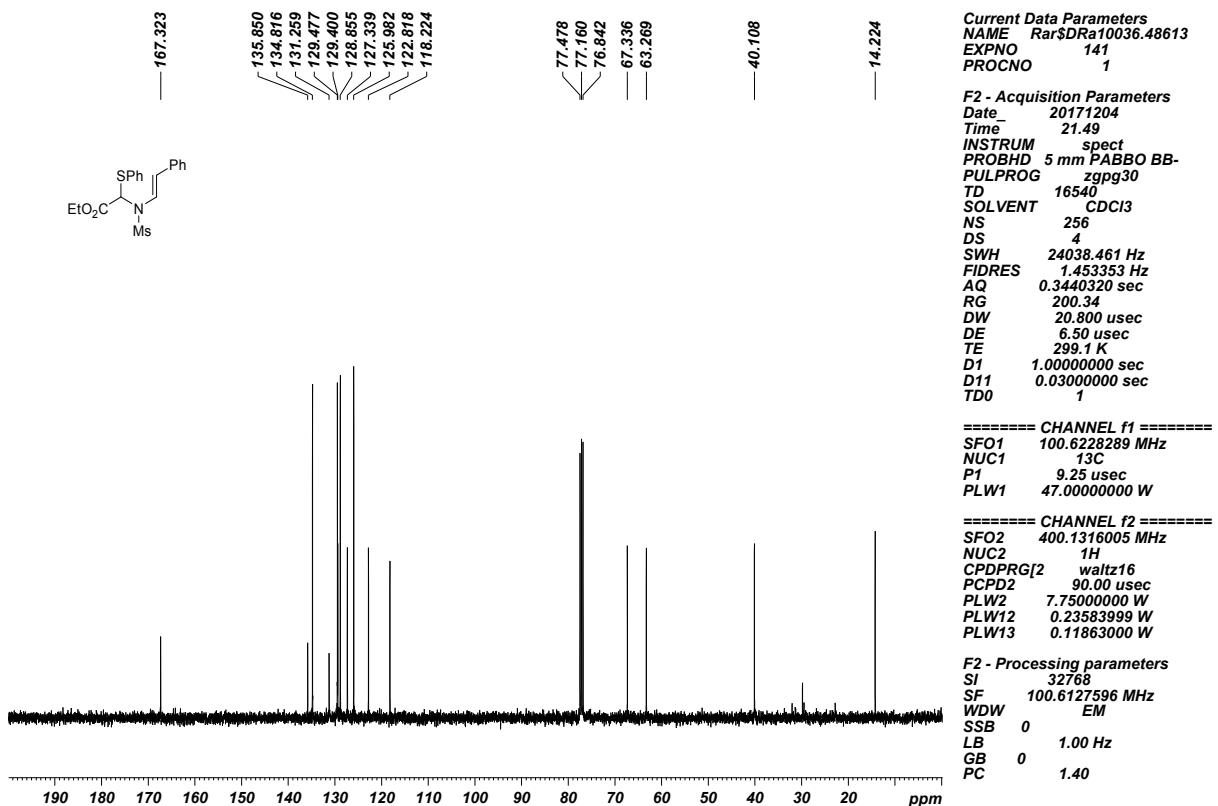
===== CHANNEL f2 =
SFO2 500.15200
NUC2
CPDPRG[2 waltz
PCPD2 80.
DW 15.200000

Enamide 4v

^1H NMR (400 MHz, CDCl_3 , 24 °C)

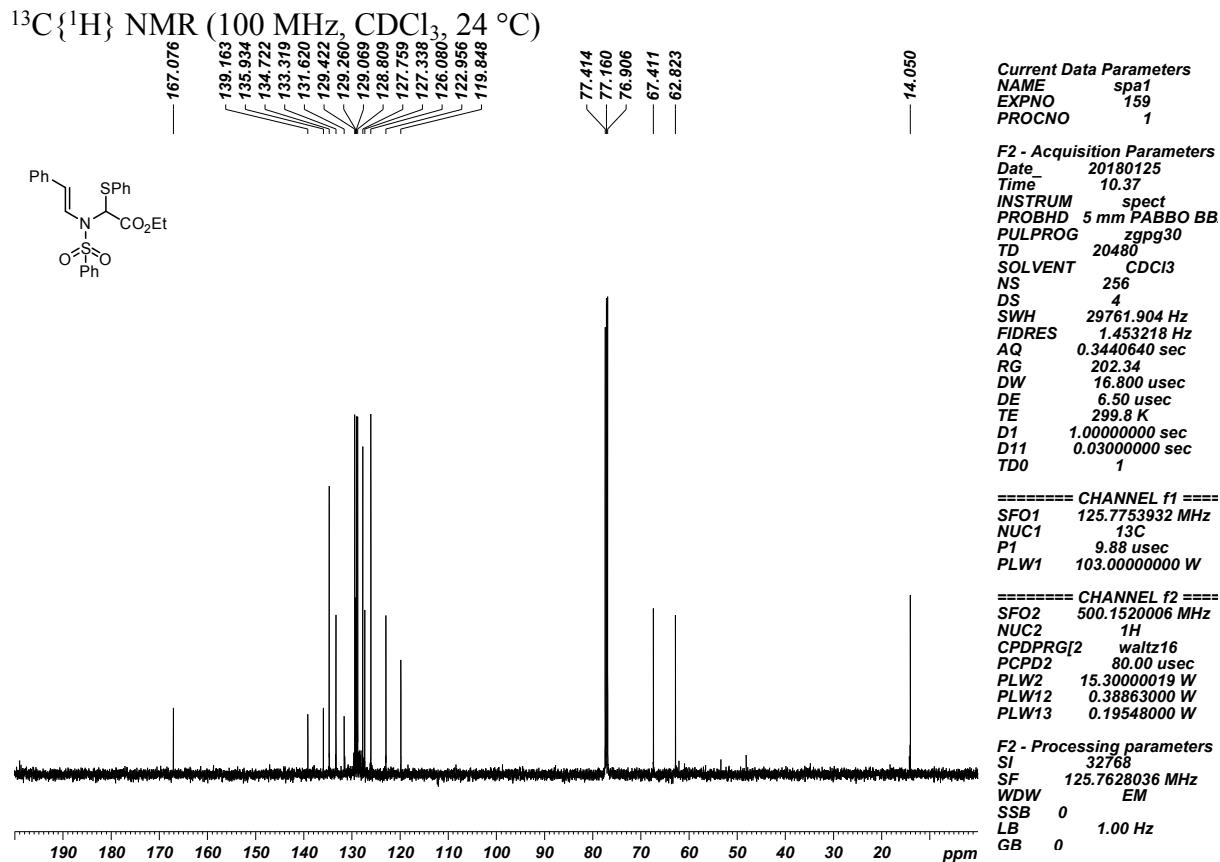
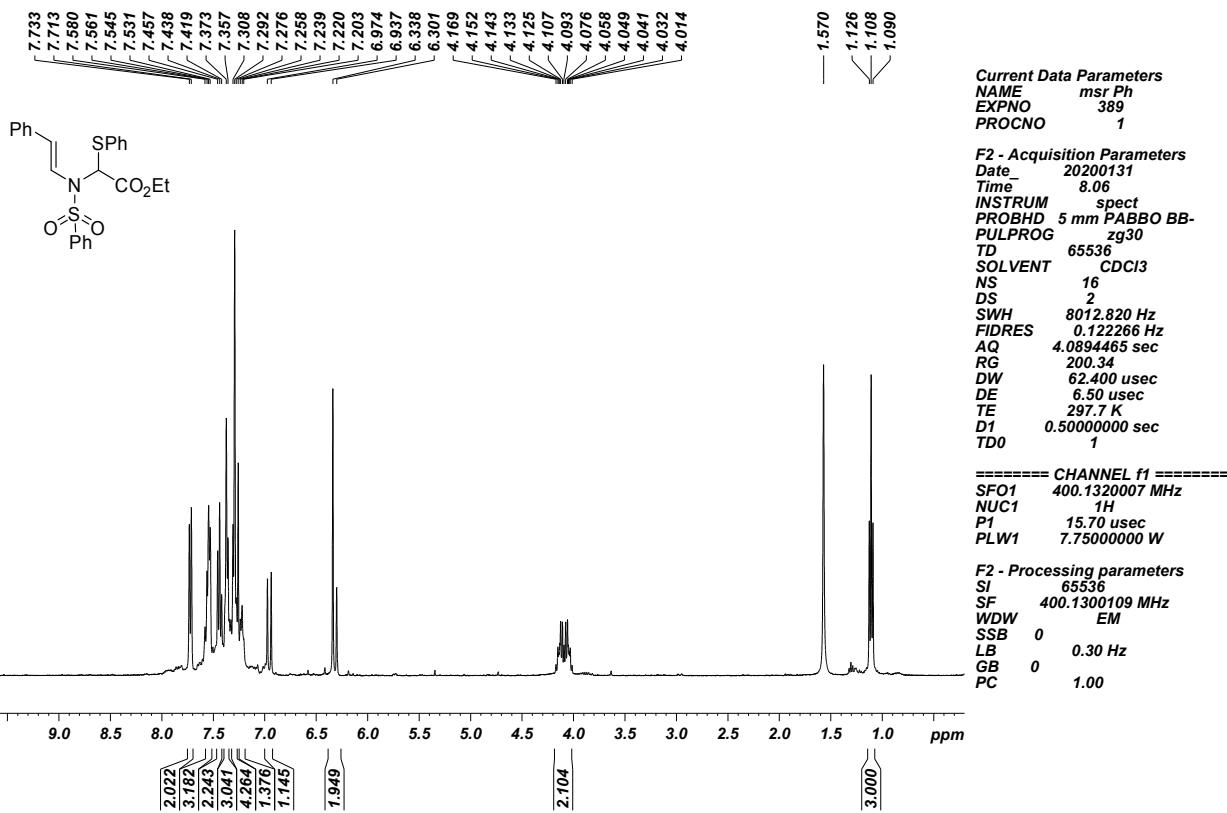


$^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C)



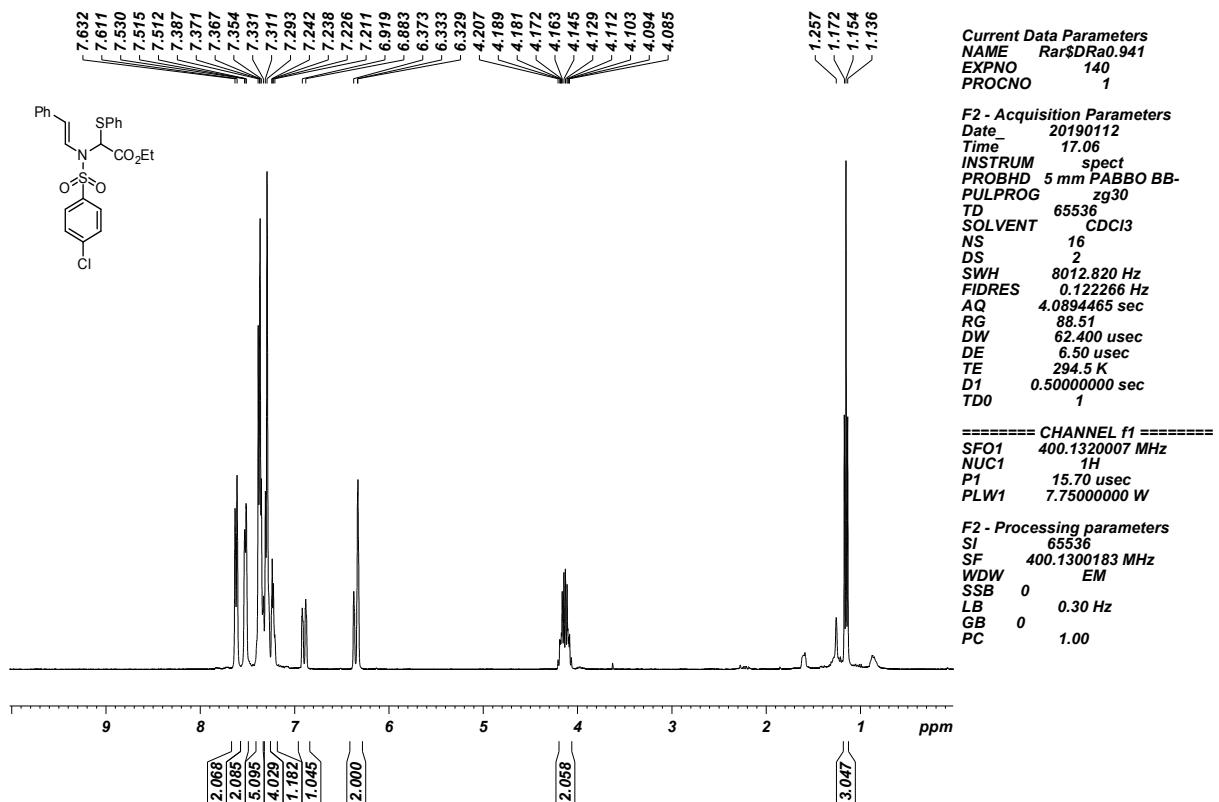
Enamide 4w

^1H NMR (400 MHz, CDCl_3 , 24 °C)

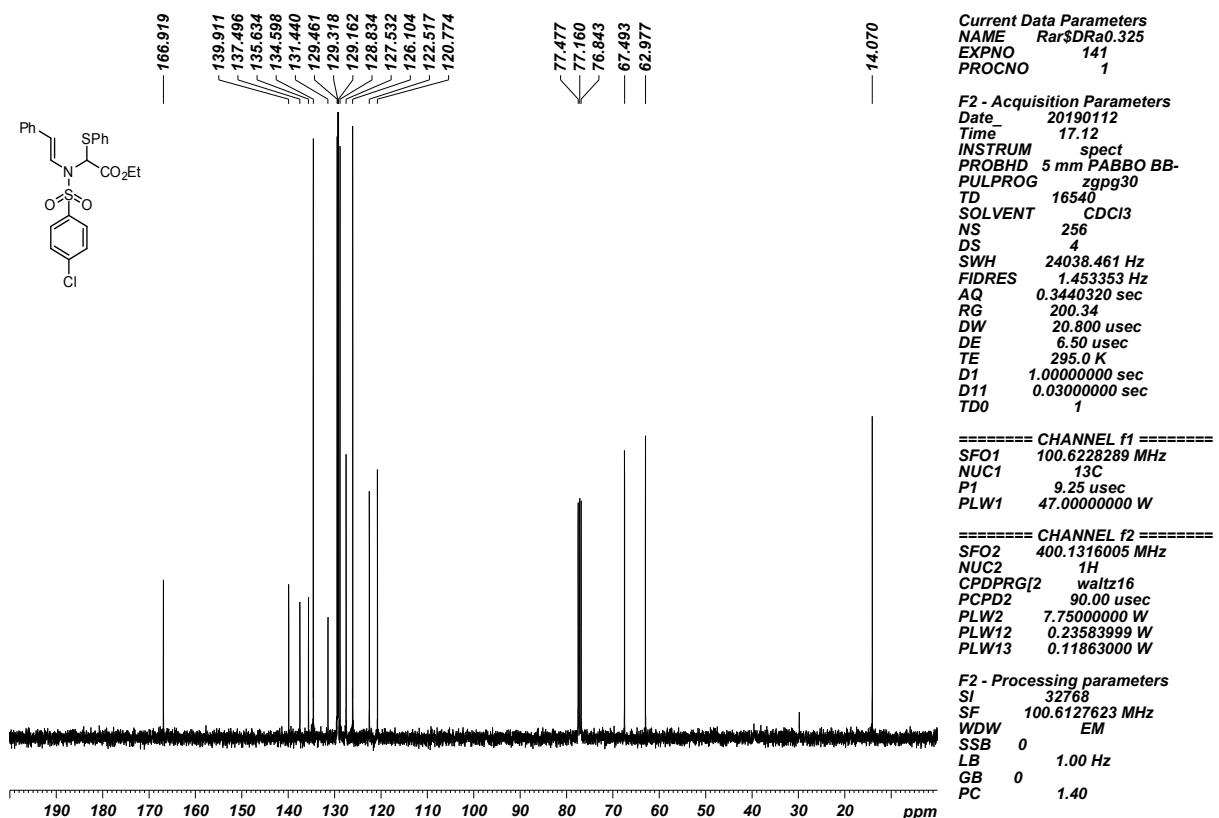


Enamide 4x

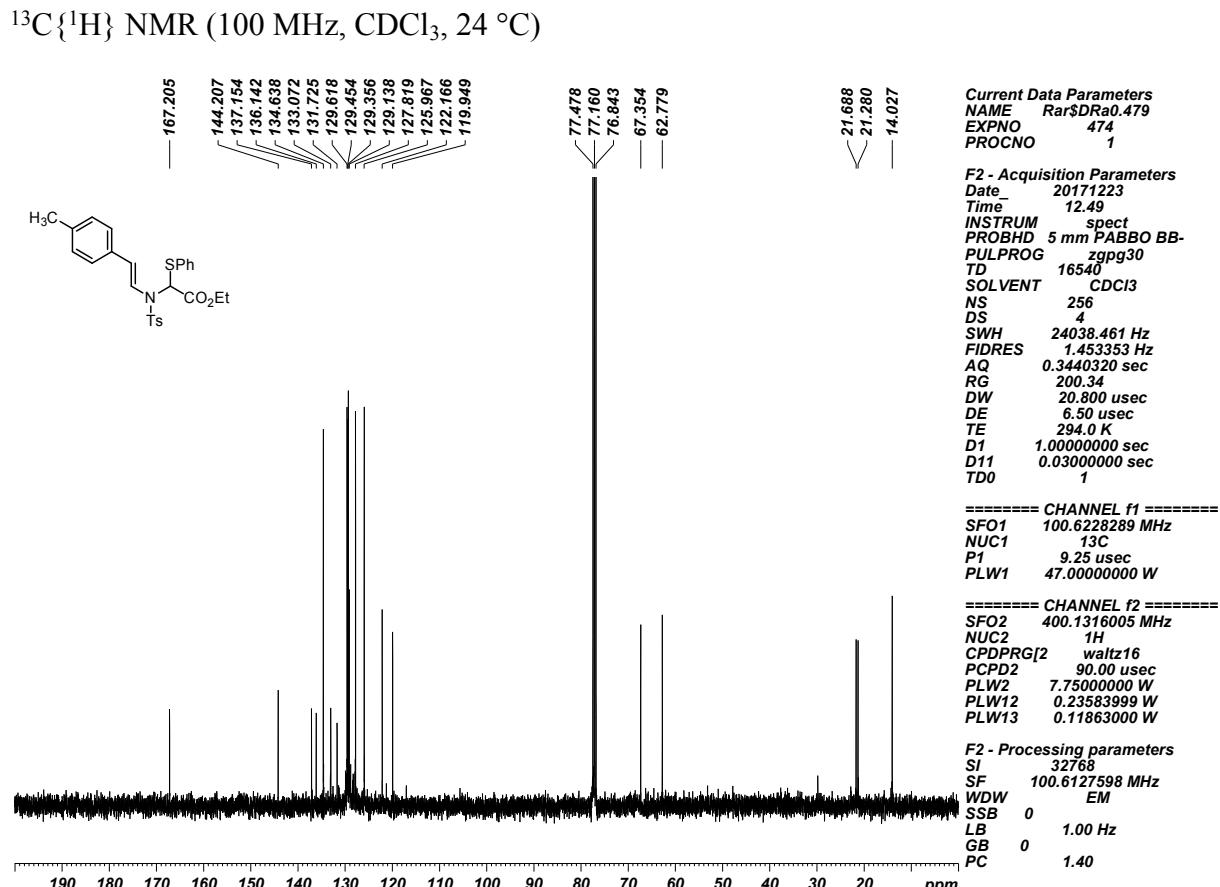
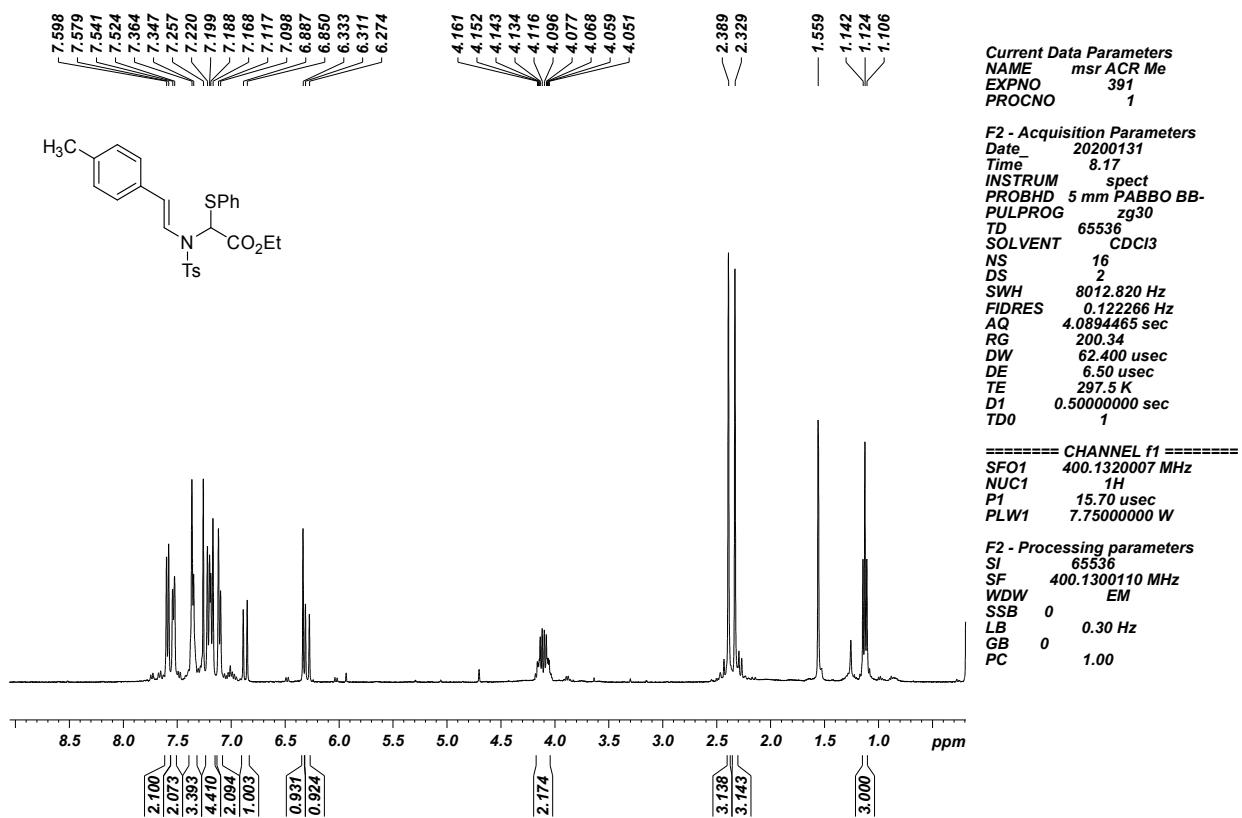
¹H NMR (400 MHz, CDCl₃, 24 °C)



$^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C)

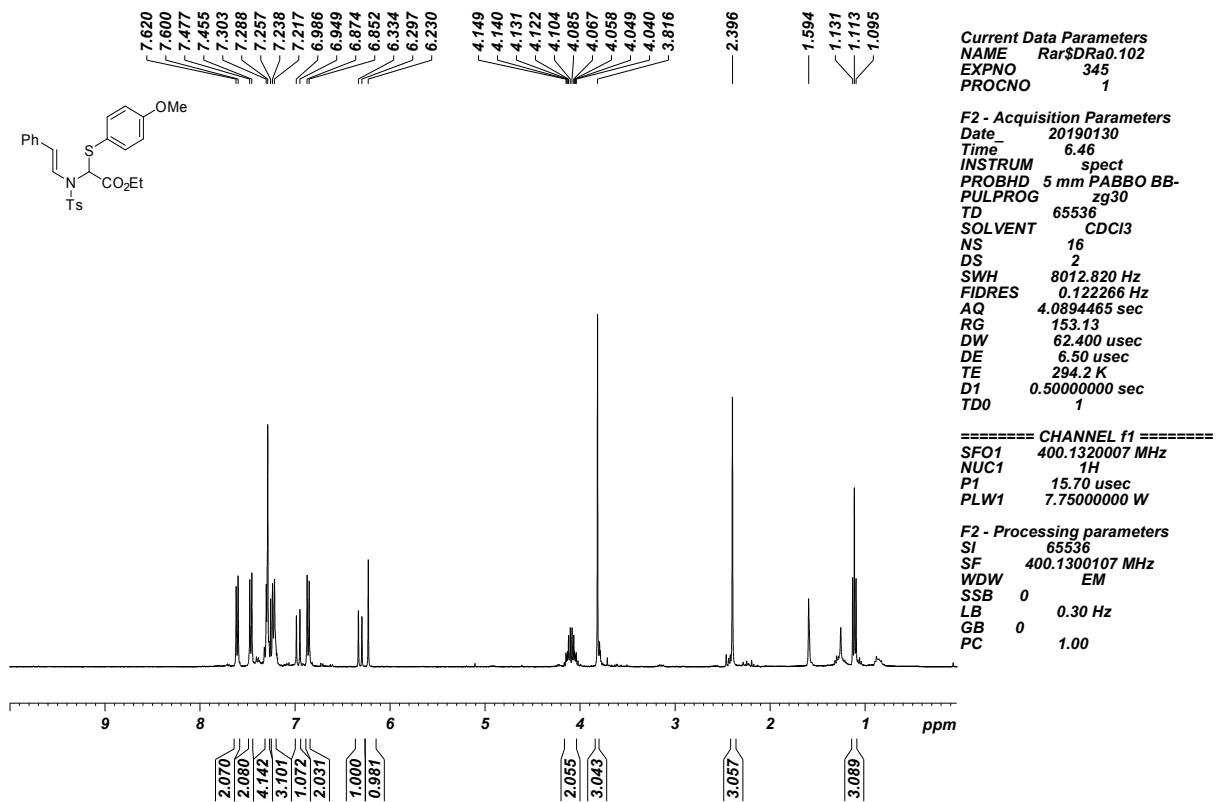


Enamide 4y
 ^1H NMR (400 MHz, CDCl_3 , 24 °C)

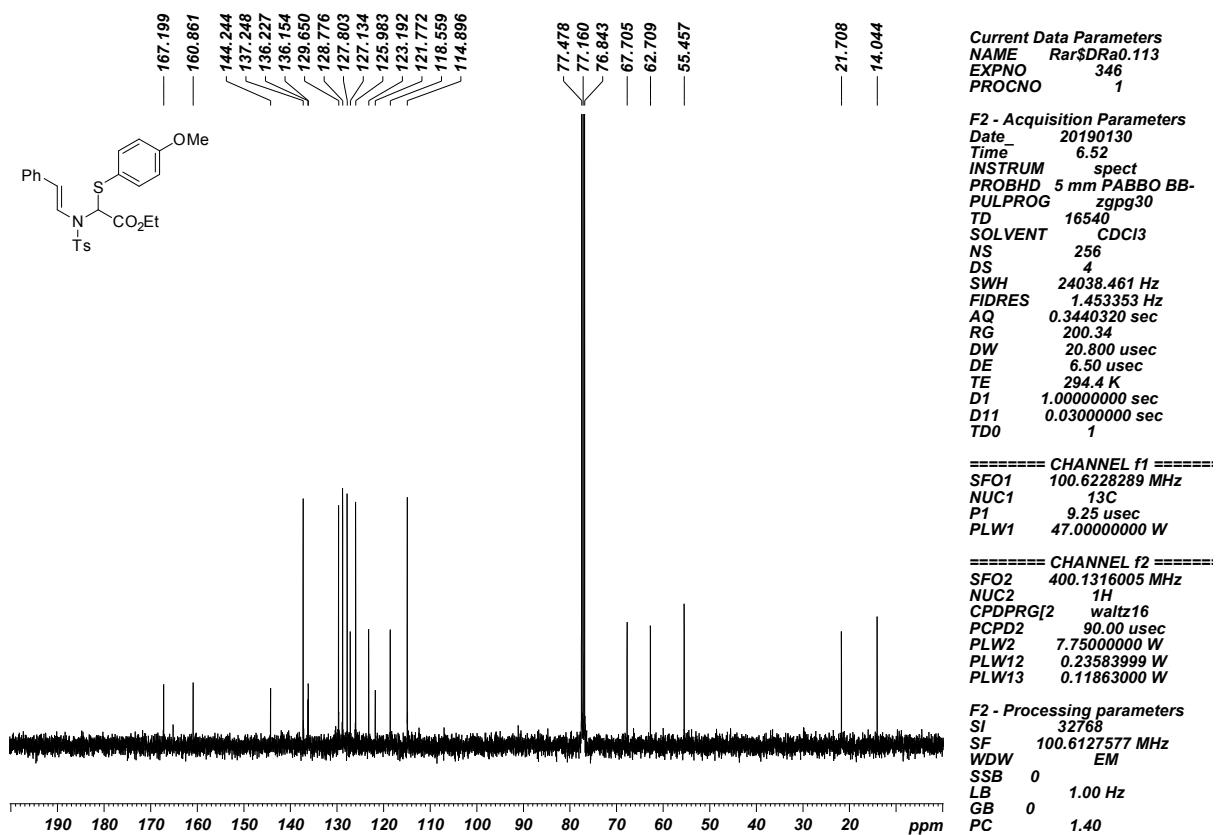


Enamide 4z

¹H NMR (400 MHz, CDCl₃, 24 °C)

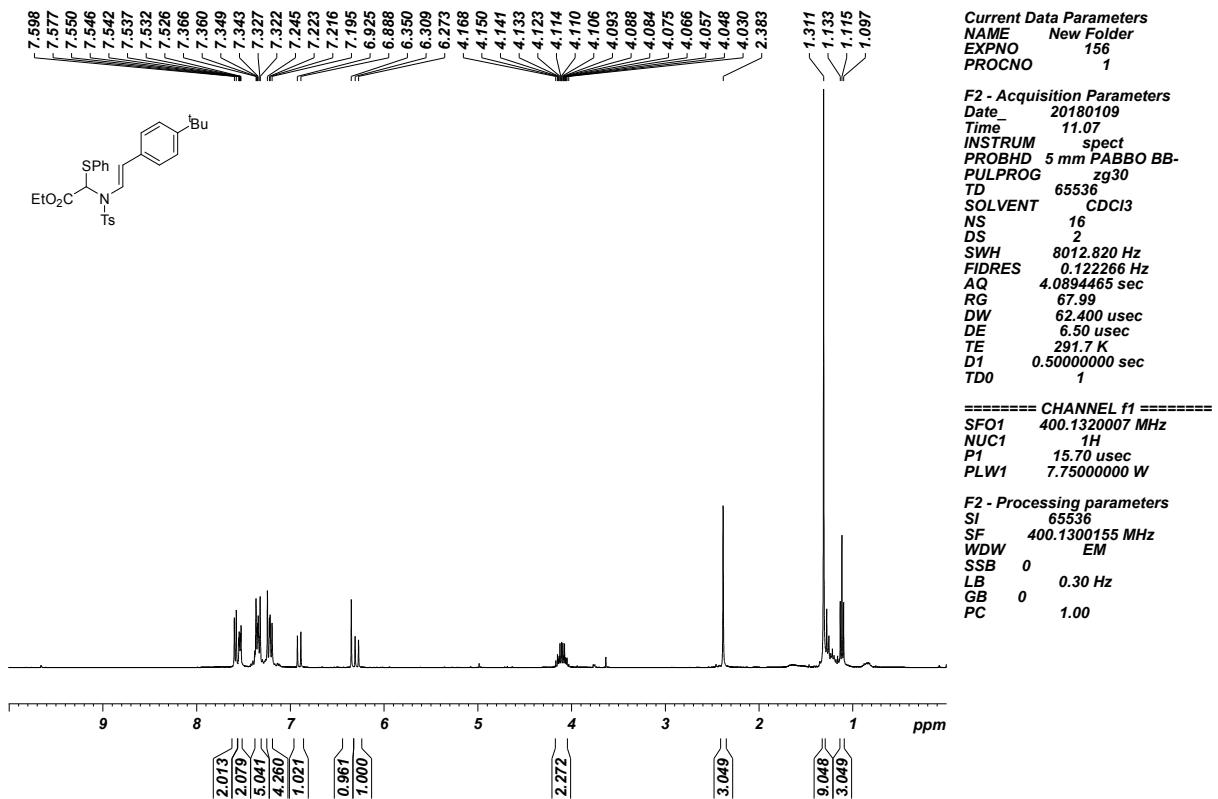


$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C)

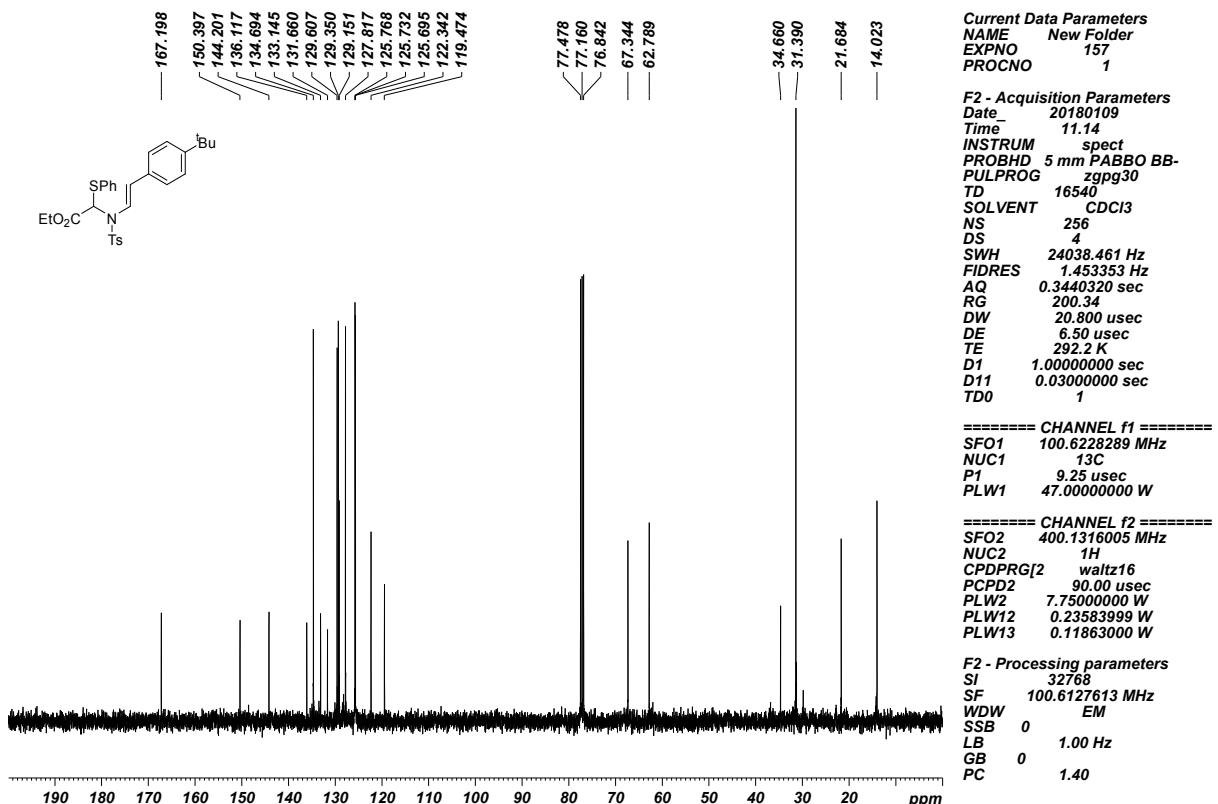


Enamide 4aa

^1H NMR (400 MHz, CDCl_3 , 24 °C)

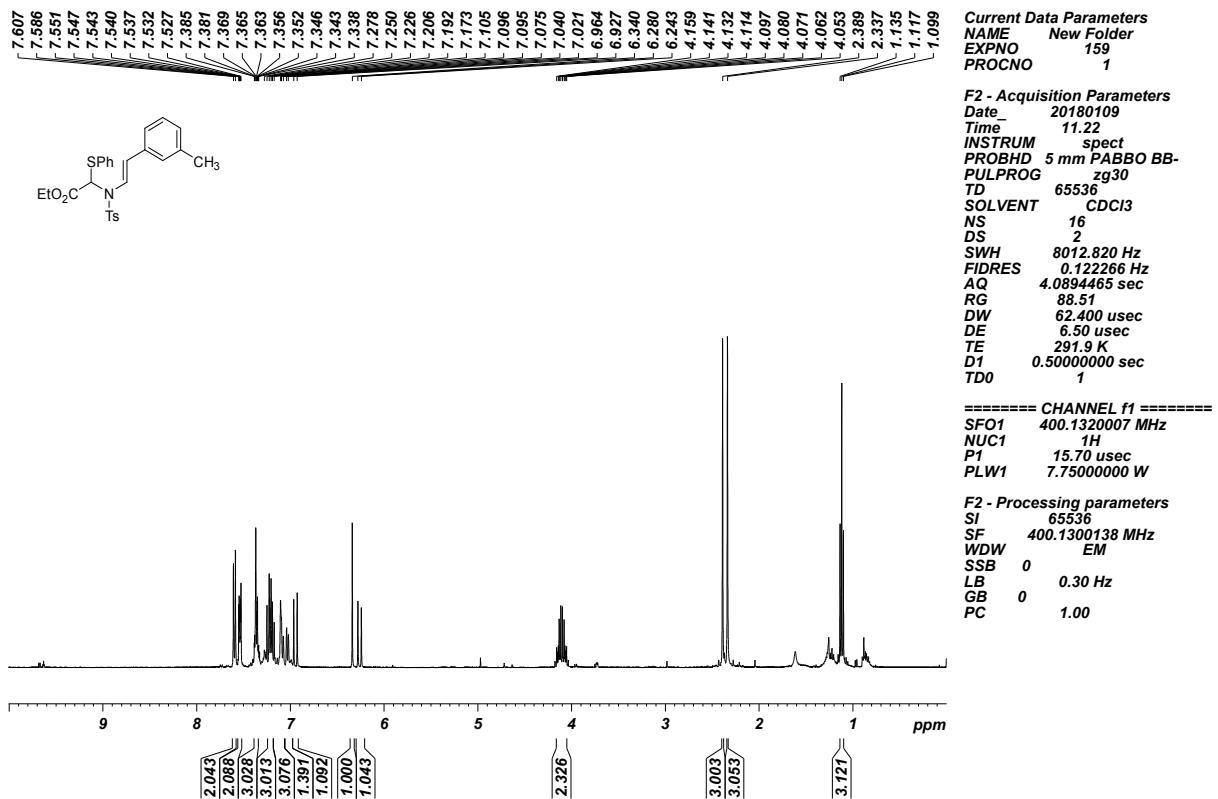


$^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C)

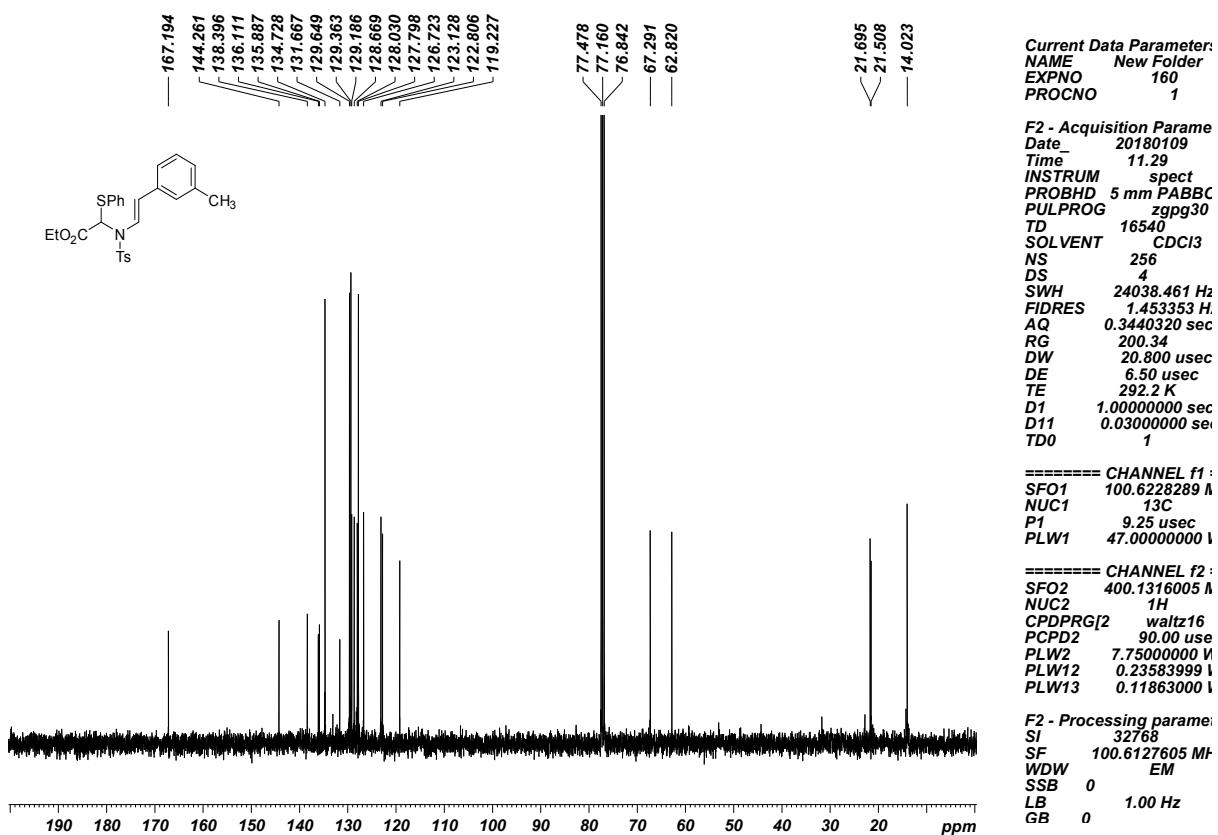


Enamide 4ab

^1H NMR (400 MHz, CDCl_3 , 24 °C)

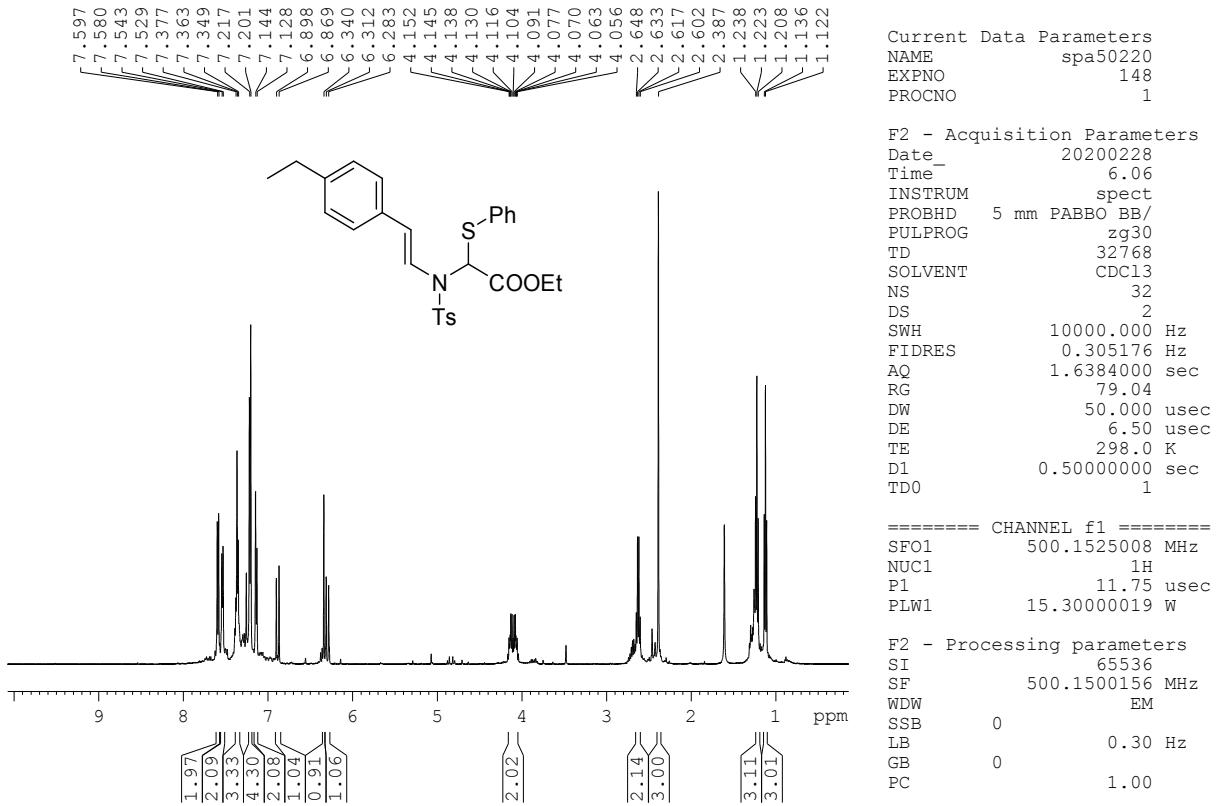


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

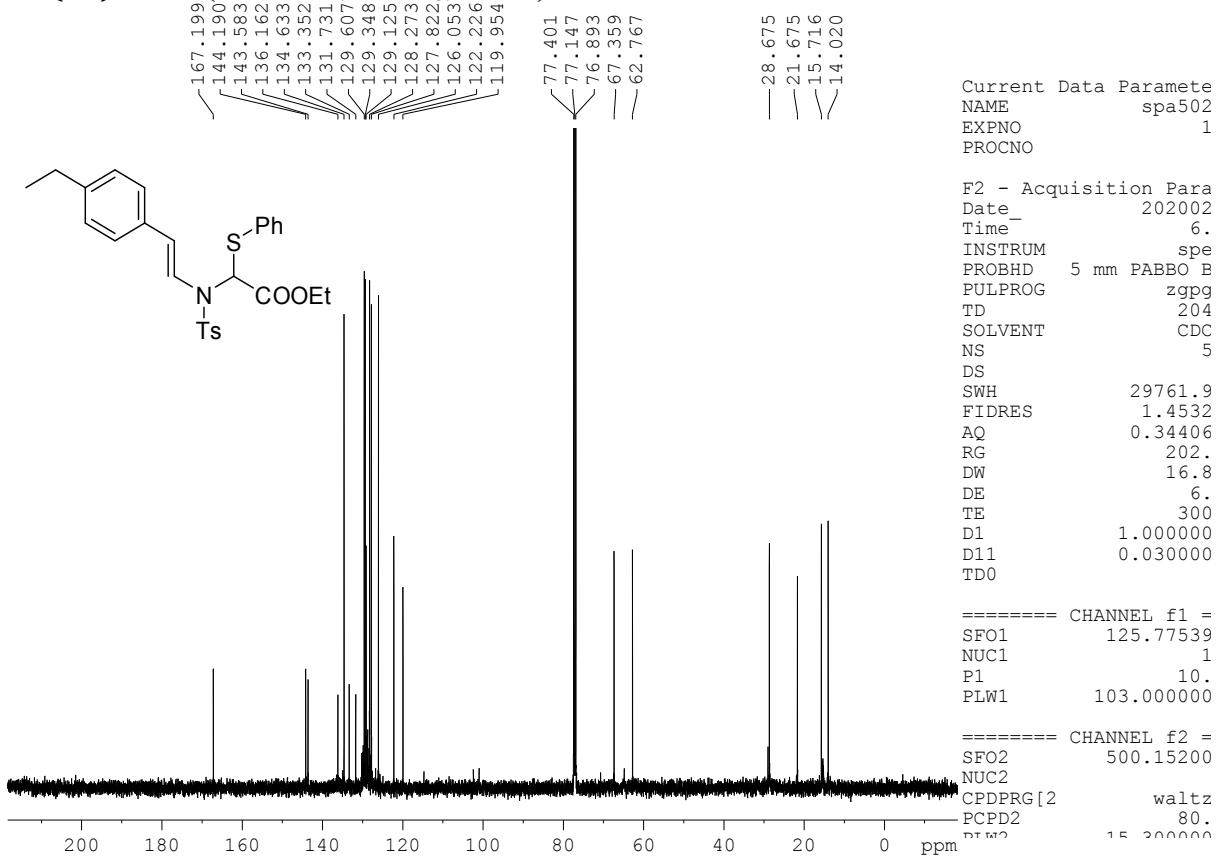


Enamide 4ac

¹H NMR (400 MHz, CDCl₃, 24 °C)

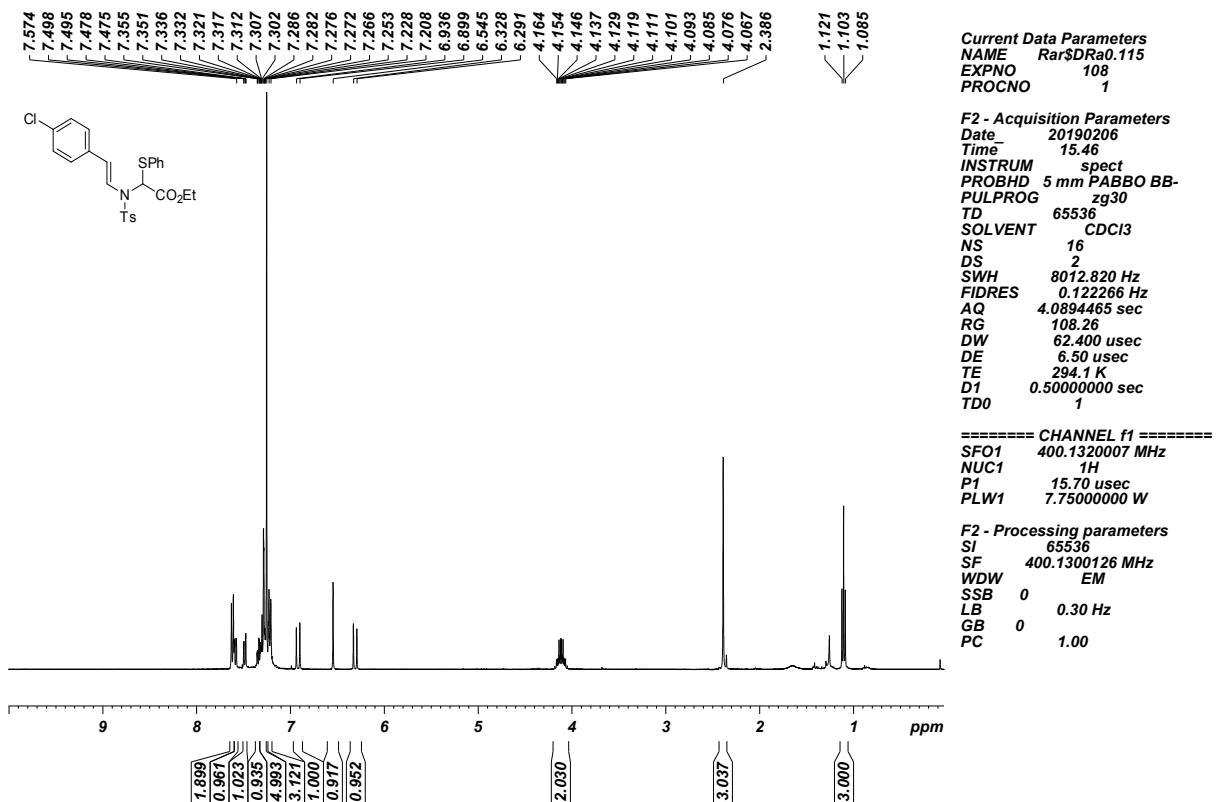


¹³C{¹H} NMR (125 MHz, CDCl₃, 24 °C)

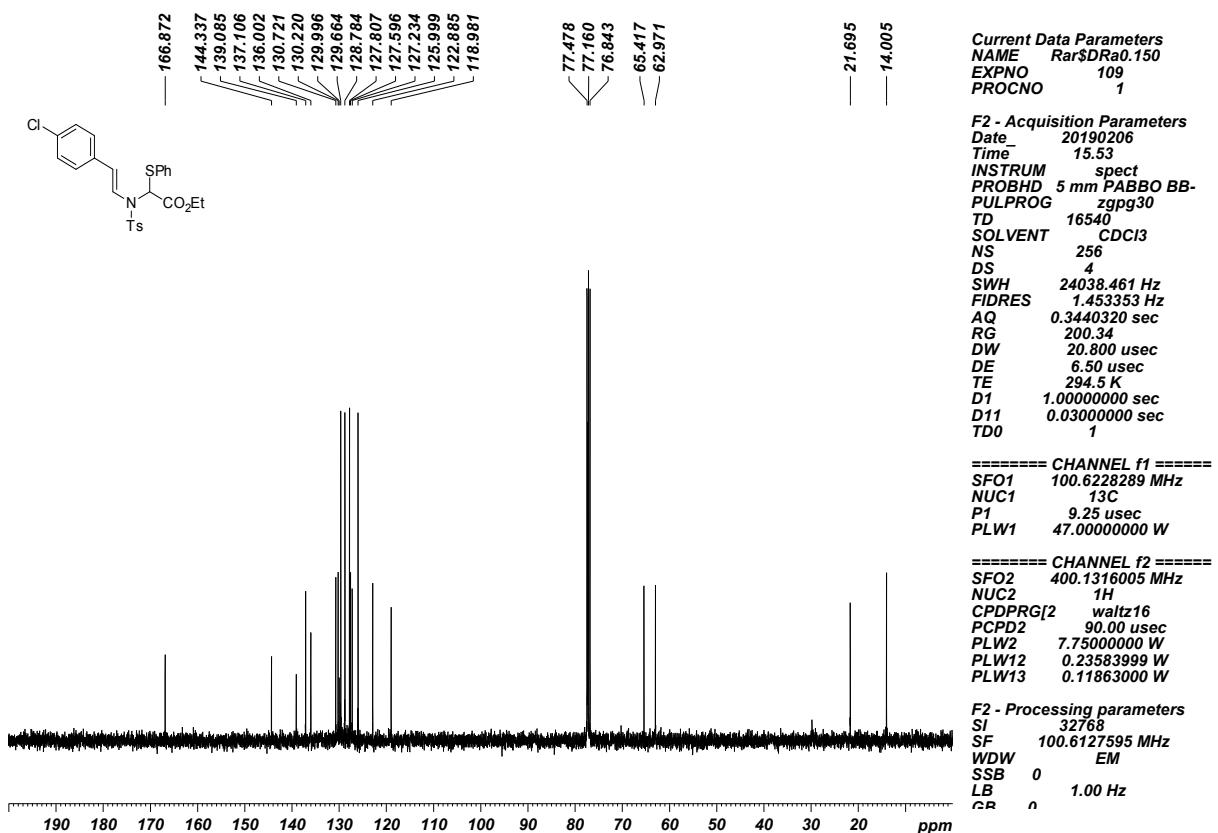


Enamide 4ad

¹H NMR (400 MHz, CDCl₃, 24 °C)

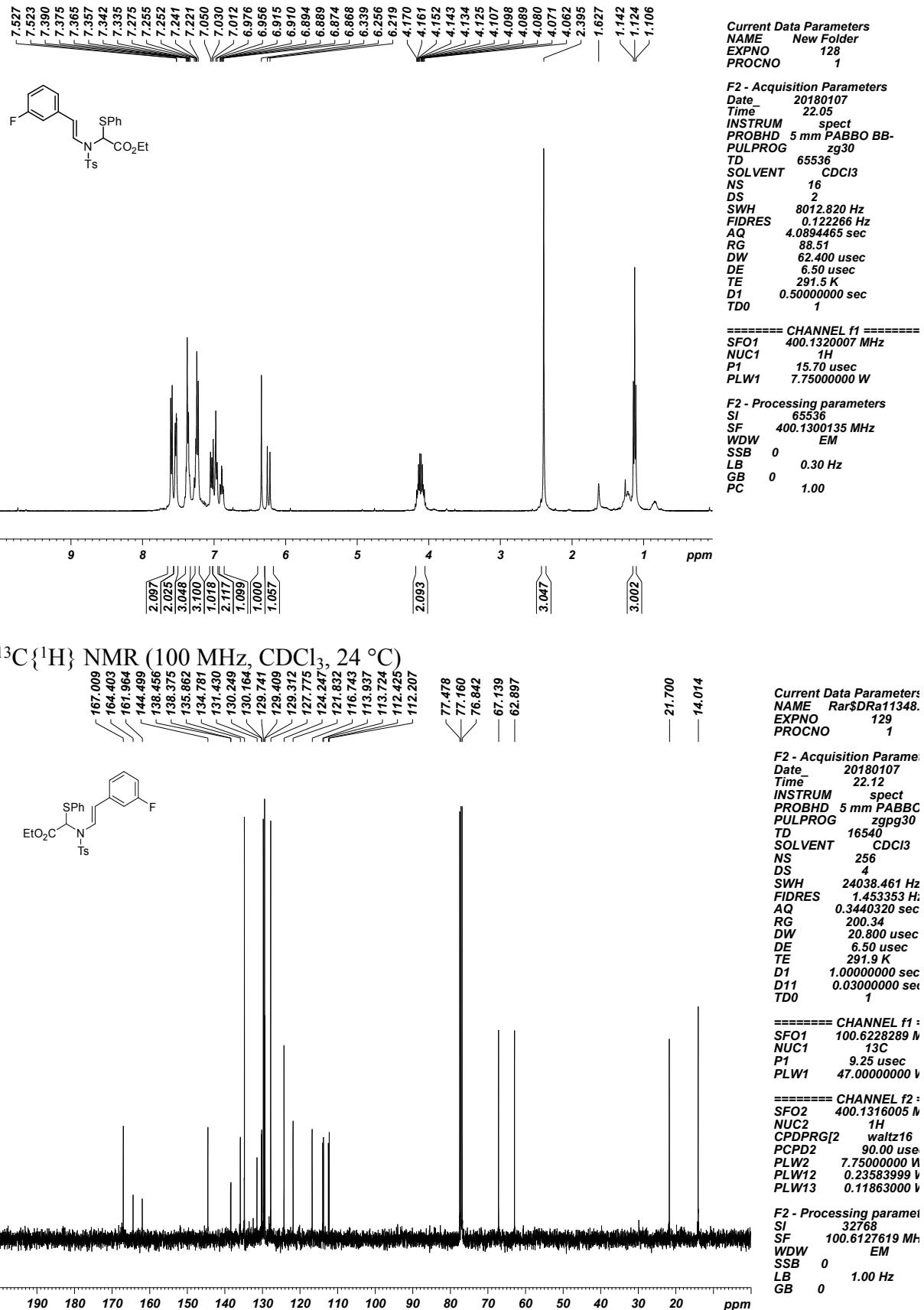


$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C)



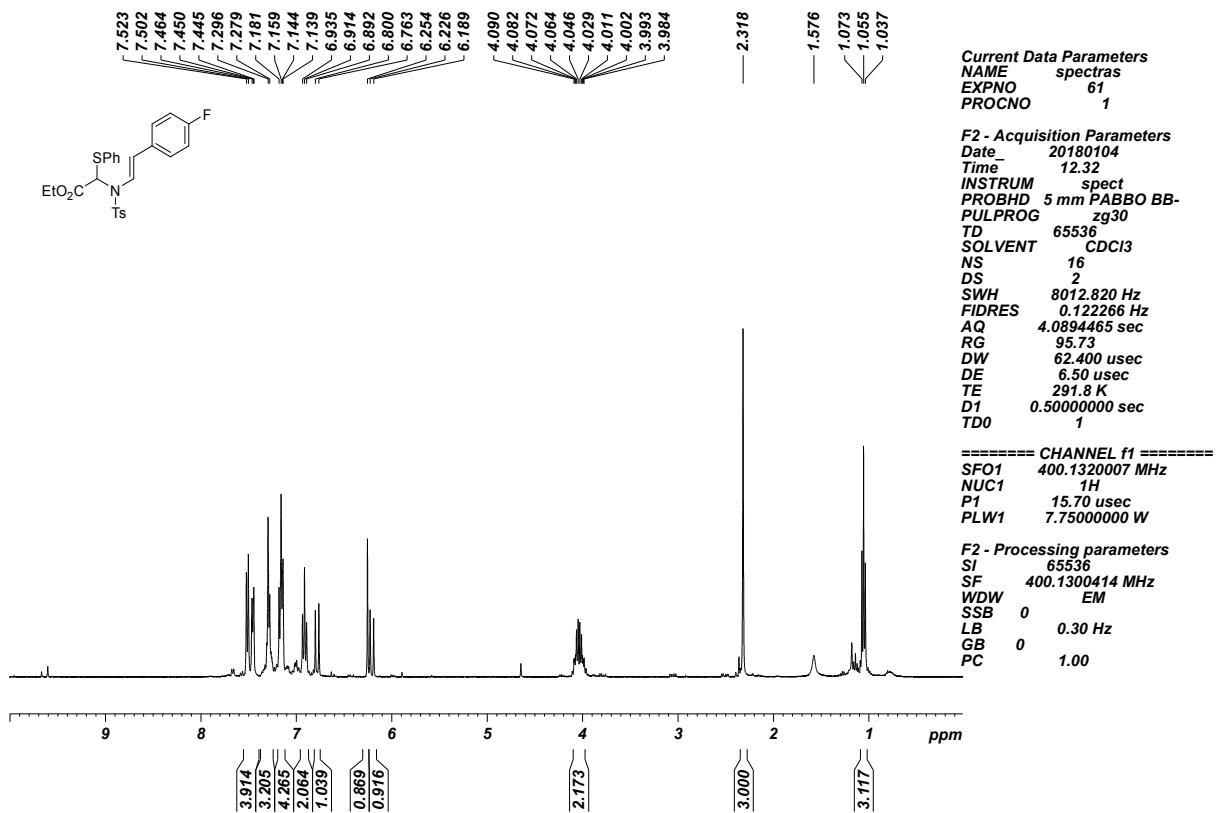
Enamide 4ae

^1H NMR (400 MHz, CDCl_3 , 24 °C)

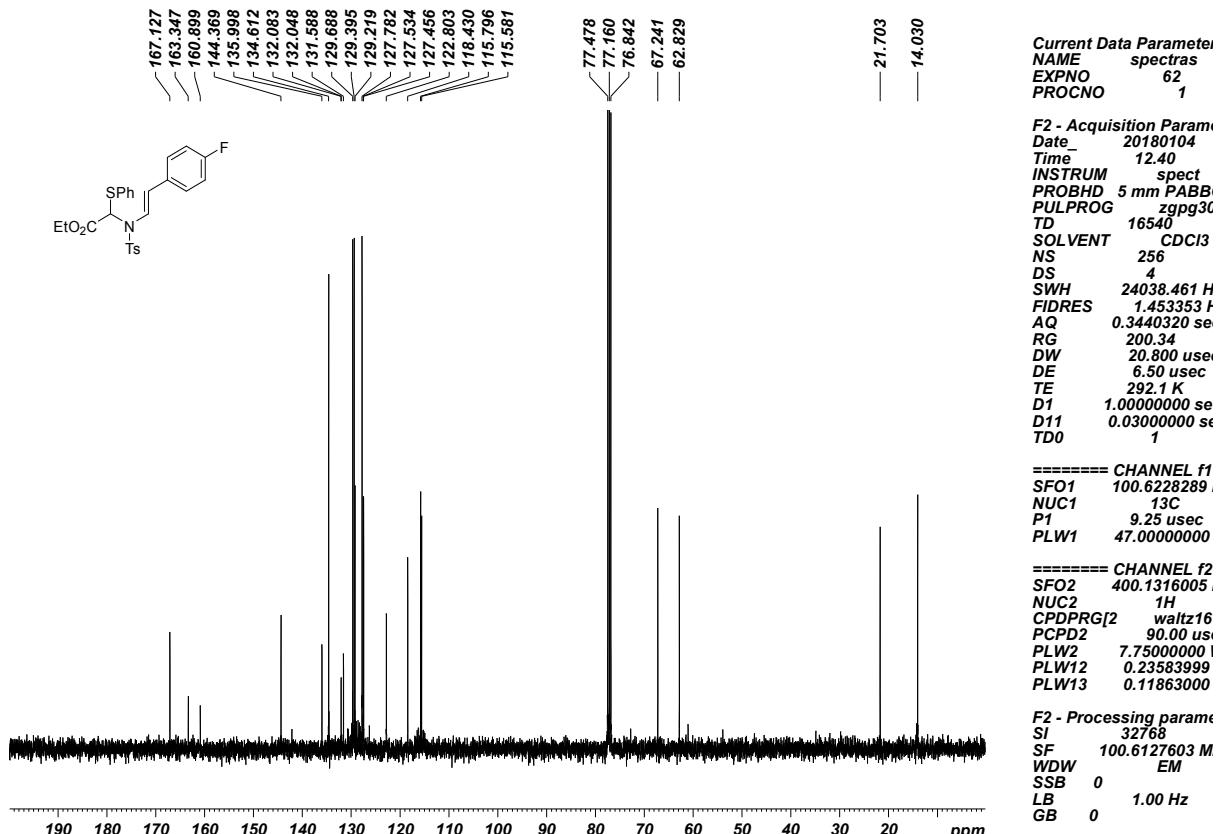


Enamide 4af

¹H NMR (400 MHz, CDCl₃, 24 °C)

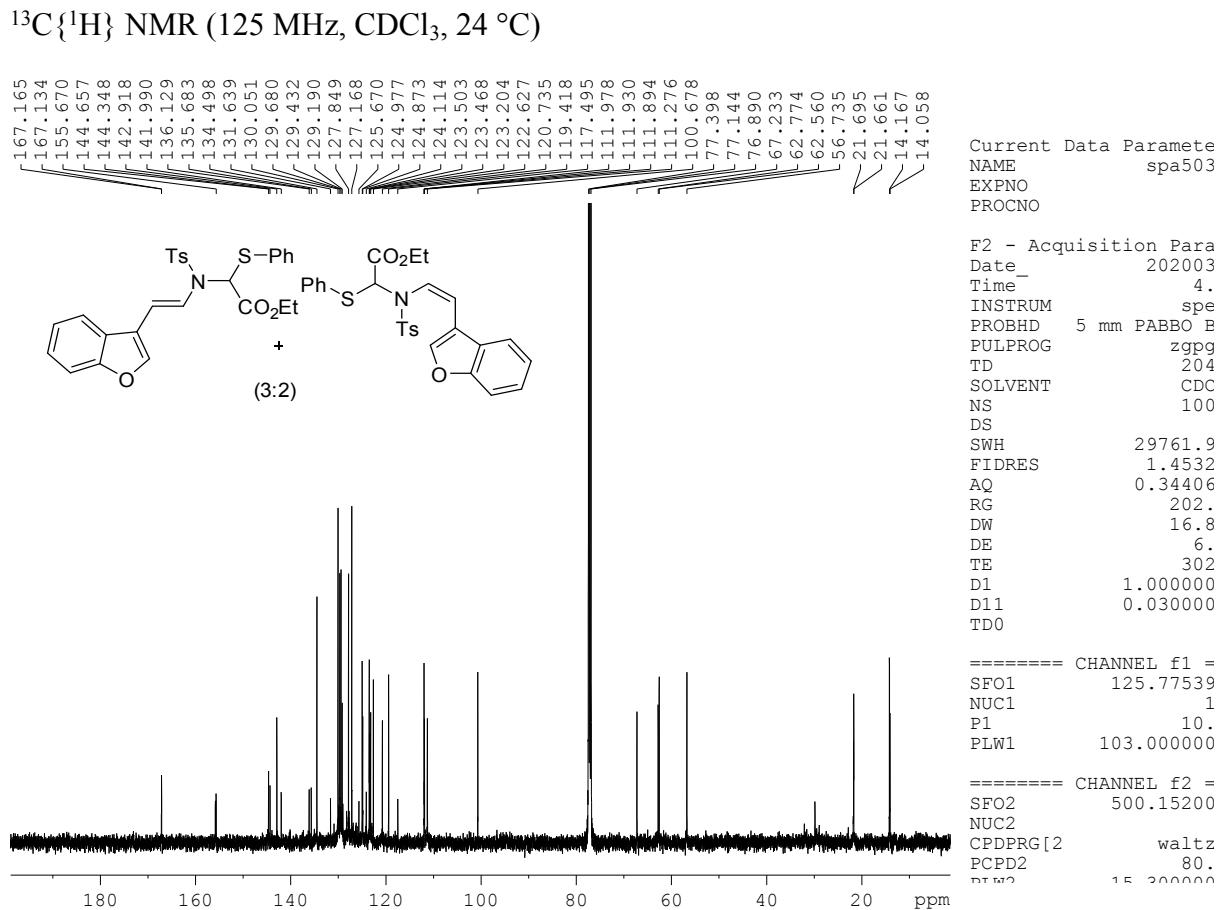
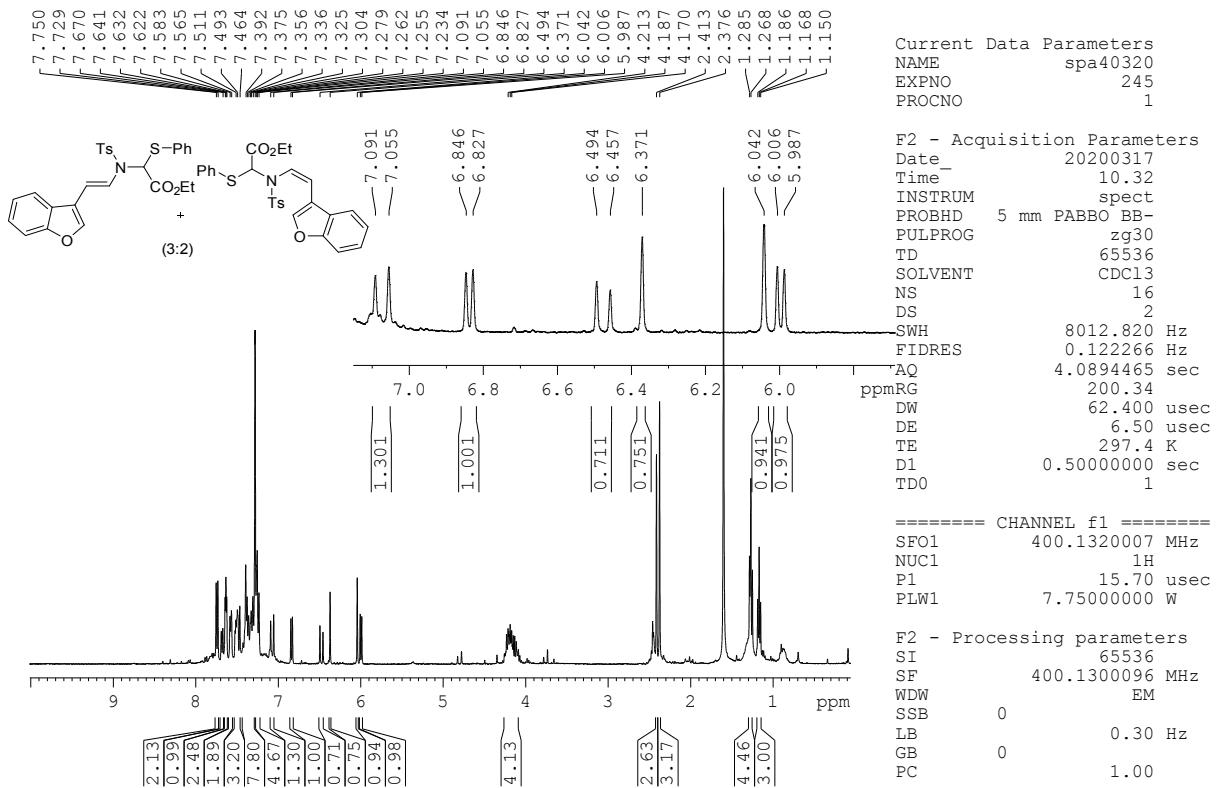


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)



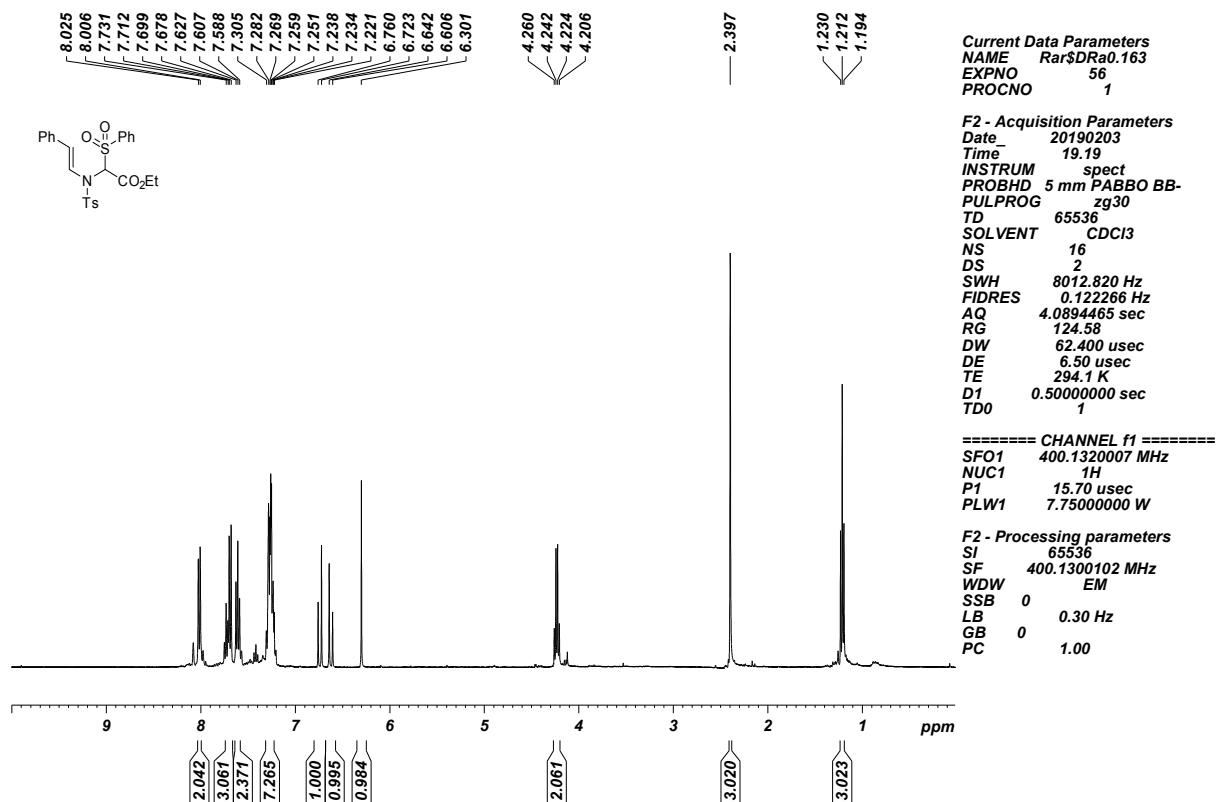
Enamide 4ag

¹H NMR (400 MHz, CDCl₃, 24 °C)

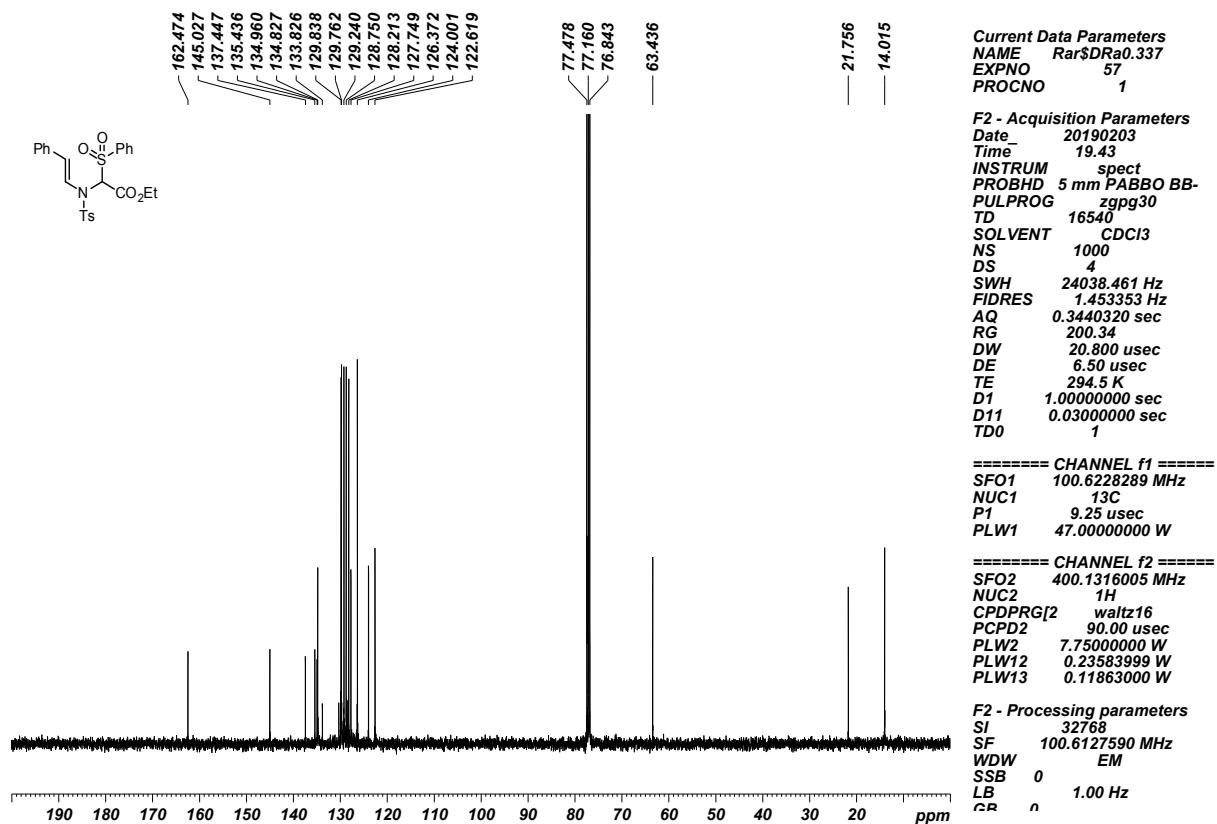


Sulfone 5

¹H NMR (400 MHz, CDCl₃, 24 °C)

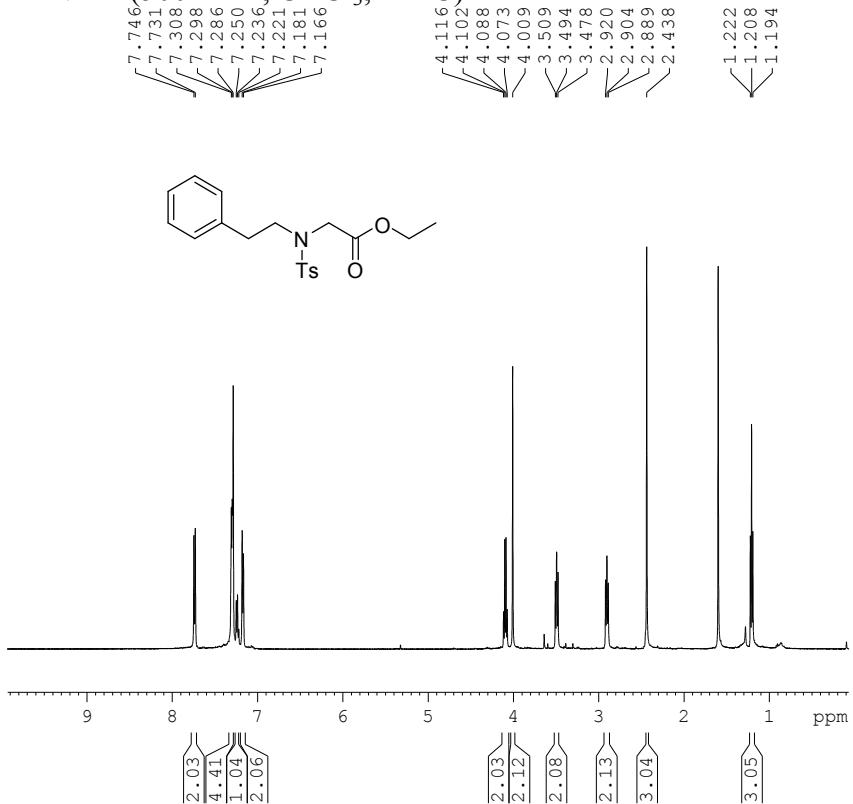


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)



Compound 6

¹H NMR (500 MHz, CDCl₃, 24 °C)



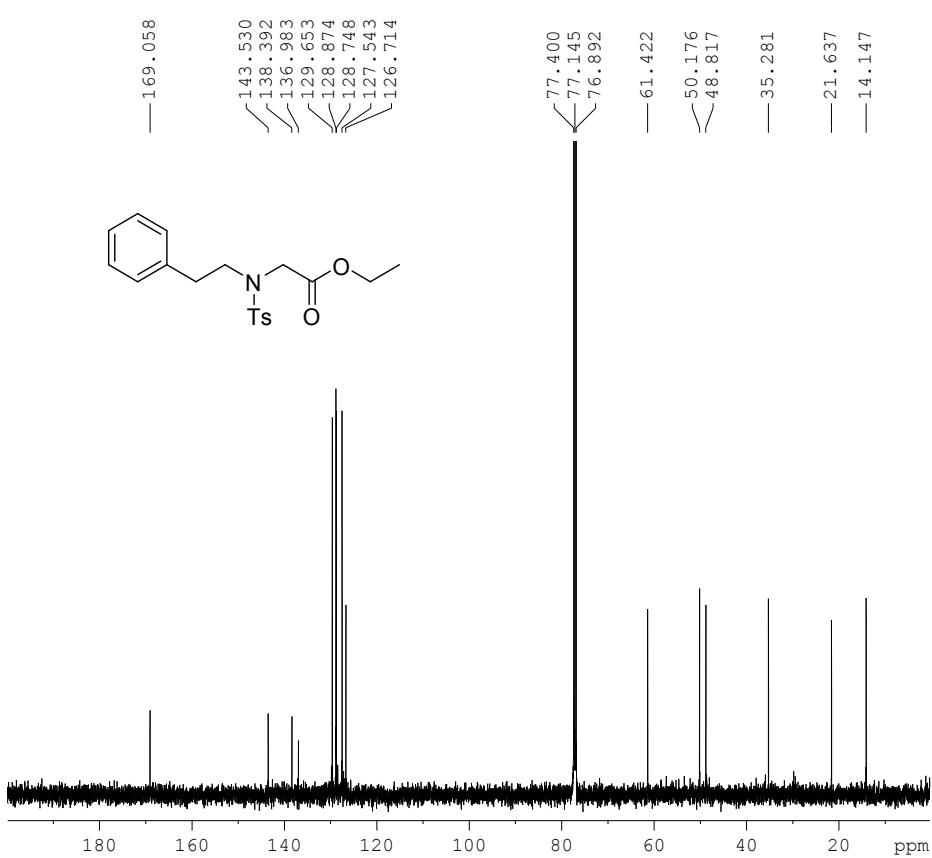
Current Data Parameters
NAME spa50320
EXPNO 23
PROCNO 1

F2 - Acquisition Parameters
Date_ 20200306
Time_ 10.22
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 1.6384000 sec
RG 138.53
DW 50.000 usec
DE 6.50 usec
TE 298.0 K
D1 0.5000000 sec
TDO 1

===== CHANNEL f1 =====
SFO1 500.1525008 MHz
NUC1 1H
P1 11.75 usec
PLW1 15.30000019 W

F2 - Processing parameters
SI 65536
SF 500.1500120 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

¹³C{¹H} NMR (125 MHz, CDCl₃, 24 °C)



Current Data Parameters
NAME spa503
EXPNO
PROCNO

F2 - Acquisition Para
Date_ 202003
Time_ 9.
INSTRUM spe
PROBHD 5 mm PABBO B
PULPROG zgpg
TD 204
SOLVENT CDC
NS 5
DS
SWH 29761.9
FIDRES 1.4532
AQ 0.34406
RG 202.
DW 16.8
DE 6.
TE 300
D1 1.000000
D11 0.030000
TDO 0

===== CHANNEL f1 =
SFO1 125.77539
NUC1 1
P1 10.
PLW1 103.000000

===== CHANNEL f2 =
SFO2 500.15200
NUC2
CPDPG[2 waltz
PCPD2 80.
DW 15.200000