

Supporting Information

Rhodium-Catalyzed Rearrangement of S/Se-Ylides for the Synthesis of Substituted Vinylogous Carbonates

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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 metaland stored over molecular sieves 4Å under nitrogen atmosphere. All the diazo compoundswere synthesized from corresponding β -ketoesters and tosyl azideemploying literature procedure.¹ All the α -thioesters were achieved from thiol and bromoesters.² And α -selenoesters were synthesized from diphenylselenides and corresponding bromoesters.³

Column chromatography was performed using RankemSilica 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:

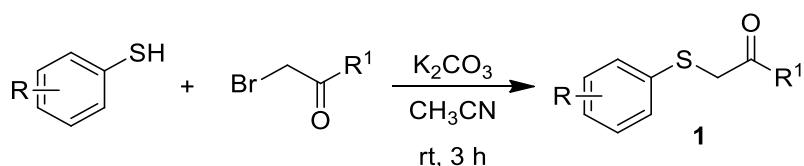
NMR data were recorded on 400 and 500 MHz spectrometers. ^{13}C and ^1H NMR spectra were referenced to signals of deuterio solvents and residual protiated solvents, respectively. Infrared spectra were recorded on a Thermo Nicolet iS10 FT spectrometer. HRMS were recorded by electron spry ionization (ESI)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

¹Y. Jiang, V. Z. Y. Khong, E. Lourdusamy and C.-M. Park, *Chem. Comm.* 2012, **48**, 3133-3135

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

³A. Bhalla, S. Sharma, K. K. Bhasin and S. S. Bari, *Synth. Commun.* 2007, **37**, 783-793

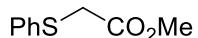
3. General procedure for synthesis of α -thiocarbonyl derivatives 1



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 at room temperature, 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.

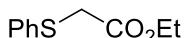
4. Properties of isolated α -thiocarbonyl derivatives 1

Thioester (1a): 347 mg; Yellow liquid; yield: 81%; $R_f = 0.63$ in 10:90 ethyl acetate/hexane;



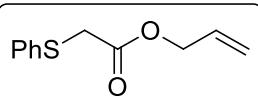
FTIR (Neat): 3272, 3109, 2928, 2856, 2356, 1712, 1642, 1550, 1396, 1270, 1225, 1079, 877 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.45-7.37 (m, 2H), 7.35-7.27 (m, 2H), 7.27-7.19 (m, 1H), 3.71 (s, 3H), 3.65 (s, 2H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 170.3, 135.0, 130.0, 129.2, 127.1, 52.6, 36.6; HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ calcd for $\text{C}_9\text{H}_{10}\text{O}_2\text{S}+\text{H}$ 183.0474; Found 183.0479

Thioester (1b): 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); $^{13}\text{C}\{\text{H}\}$ 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 (ESI) m/z: $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{12}\text{O}_2\text{S}+\text{H}$ 197.0631; Found 197.0632

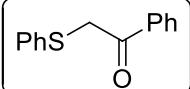
Thioester (1c): 330 mg; White solid; yield: 70%; $R_f = 0.63$ in 10:90 ethyl acetate/hexane;

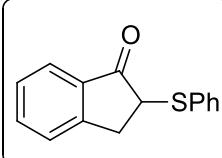


mp: 94-96 °C; FTIR (KBr): 3064, 2928, 2859, 1737, 1652, 1581, 1471, 1440, 1272, 1138, 991 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.43-7.39 (m, 2H), 7.32-7.27 (m, 2H), 7.25-7.20 (m, 1H), 5.85 (ddt, 1H, $J = 17.1, 10.1, 5.6$ Hz), 5.28 (dq, 1H, $J = 17.1, 1.4$ Hz), 5.22 (dt, 1H, $J = 10.4, 1.2$ 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,

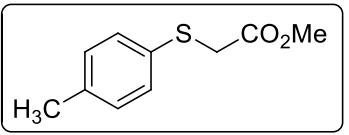
129.1, 127.1, 118.8, 66.2, 36.8; HRMS (ESI) m/z: [M+Na]⁺ calcd for C₁₁H₁₂O₂S+Na 231.0450; Found 231.0451

Thioketone (1d): 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, CDCl₃, 24 °C): δ 7.38-7.24 (m, 4H), 7.24-7.18 (m, 1H), 3.66 (s, 2H), 2.27 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C): δ 203.7, 134.7, 129.6, 129.2, 127.0, 44.7, 28.1; HRMS (ESI) m/z: [M+Na]⁺ calcd for C₉H₁₀OS+Na 189.0345; Found 189.0345

Thioketone (1e): 372 mg; Yellow solid; yield: 72%; R_f = 0.58 in 10:90 ethyl acetate/hexane;  mp: 93-95 °C; FTIR (KBr): 3213, 3175, 3060, 2987, 2306, 1690, 1591, 1439, 1266, 1170, 1093, 1025, 896 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 24 °C): δ 7.96-7.91 (m, 2H), 7.59-7.54 (m, 1H), 7.47-7.42 (m, 2H), 7.41-7.33 (m, 2H), 7.30-7.24 (m, 2H), 7.24-7.18 (m, 1H), 4.26 (s, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C): δ 194.1, 135.5, 134.8, 133.5, 130.6, 129.1, 128.7, 127.2, 41.3; HRMS (ESI) m/z: [M+K]⁺ calcd for C₁₄H₁₂OS+K 267.0240; Found 267.0245

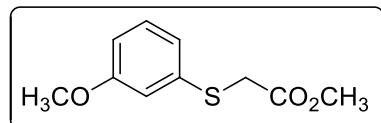
Thioketone (1f): 370 mg; White solid; yield: 68%; R_f = 0.63 in 10:90 ethyl acetate/hexane;  mp: 101-103 °C; FTIR (KBr): 3245, 3056, 2986, 2306, 1727, 1647, 1605, 1427, 1265, 1157, 1097, 898 cm⁻¹; ¹H NMR (500 MHz, CDCl₃, 24 °C): δ 7.77 (d, 1H, J = 7.2 Hz), 7.58 (t, 1H, J = 6.7 Hz), 7.51-7.44 (m, 2H), 7.41-7.32 (m, 2H), 7.30-7.20 (m, 3H), 4.07 (dd, 1H, J = 7.8, 3.6 Hz), 3.62 (dd, 1H, J = 7.2, 17.4 Hz), 3.12 (d, 1H, J = 17.4 Hz); ¹³C{¹H} NMR (125 MHz, CDCl₃, 24 °C): δ 202.3, 152.1, 135.3, 133.4, 132.3 (9), 132.3 (6), 129.0, 127.9, 127.7, 126.4, 124.6, 50.4, 34.9; HRMS (ESI) m/z: [M+H]⁺ calcd for C₁₅H₁₂OS+H 263.0501; Found 263.0526

2-(phenylthio)acetonitrile (1h): 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, CDCl₃, 24 °C): δ 7.65-7.49 (m, 2H), 7.46-7.31 (m, 3H), 3.56 (s, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C): δ 132.5, 132.2, 129.7, 129.1, 116.6, 21.5; HRMS (ESI) m/z: [M+K]⁺ calcd for C₈H₇NS+K 187.9931; Found 188.0137

Thioester (1i): 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, CDCl₃, 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); ¹³C{¹H} NMR 

(125 MHz, CDCl₃, 24 °C): δ 170.4, 137.5, 131.0, 129.9, 52.5, 37.3, 21.1; HRMS (ESI) m/z: [M+H]⁺ calcd for C₁₀H₁₂O₂S+H 197.0631; Found 197.0634

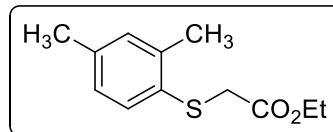
Thioester (1j): 356 mg; Colorless liquid; yield: 74%; R_f = 0.57 in 10:90 ethyl acetate/hexane;



FTIR (Neat): 3057, 2987, 2848, 2685, 2522, 2412, 2306, 2136, 1738, 1598, 1427, 1266, 1159, 1039, 985 cm⁻¹; ¹H NMR (500 MHz, CDCl₃, 24 °C): δ 7.21 (t, 1H, J = 7.9 Hz),

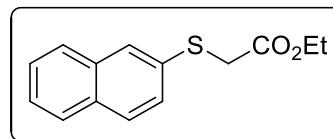
7.02-6.89 (m, 2H), 6.81-6.69 (m, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 3.66 (s, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C): δ 170.2, 160.0, 136.3, 130.0, 121.7, 114.9, 112.8, 55.4, 52.7, 36.3; HRMS (ESI) m/z: [M+Na]⁺ calcd for C₁₀H₁₂O₃S+Na 235.0399; Found 235.0393

Thioester (1k): 361 mg; Colorless liquid; yield: 71%; R_f = 0.67 in 10:90 ethyl acetate/hexane;



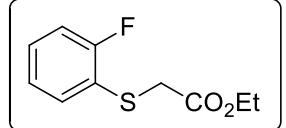
FTIR (Neat): 3227, 3056, 2981, 2871, 2346, 2333, 1733, 1651, 1606, 1448, 1271, 1133, 1028, 741 cm⁻¹; ¹H NMR (500 MHz, CDCl₃, 24 °C): δ 7.28 (d, 1H, J = 7.7 Hz), 7.01 (m, 1H), 6.96 (m, 1H), 4.13 (q, 2H, J = 7.1 Hz), 3.54 (s, 2H), 2.39 (s, 3H), 2.28 (s, 3H), 1.21 (t, 3H, J = 7.1 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃, 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 (ESI) m/z: [M+Na]⁺ calcd for C₁₂H₁₆O₂S+Na 247.0763; Found 247.0764

Thioester (1l): 429 mg; Yellow liquid; yield: 77%; R_f = 0.64 in 10:90 ethyl acetate/hexane;



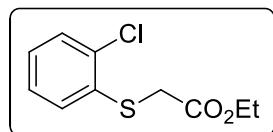
FTIR (Neat): 3273, 3166, 3057, 2978, 2929, 1733, 1656, 1623, 1588, 1454, 1397, 1388, 1376, 1275, 1134, 1027 cm⁻¹; ¹H NMR (500 MHz, CDCl₃, 24 °C): δ 7.84 (s, 1H), 7.82-7.70 (m, 3H), 7.51-7.39 (m, 3H), 4.16 (q, 2H, J = 7.1 Hz), 3.73 (s, 2H), 1.20 (t, 3H, J = 7.1 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C): 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 (ESI) m/z: [M+H]⁺ calcd for C₁₄H₁₄SO₂+H 247.0780; Found 247.0787

Thioester (1m): 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,



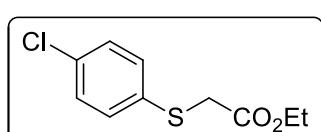
1432, 1272, 1143, 1028, 898 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 24 °C): δ 7.67-7.51 (m, 1H), 7.49-7.39 (m, 1H), 7.31-7.21 (m, 2H), 4.25 (q, 2H, J = 7.0 Hz), 4.12 (s, 2H), 1.29 (t, 3H, J = 7.0 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C): δ 168.0, 163.4, 152.1, 141.8, 124.3 (d, J = 30.4 Hz), 118.7, 110.1, 62.3, 34.3, 14.2; HRMS (ESI) m/z: [M+Na]⁺ calcd for C₁₀H₁₂FO₂S+Na: 237.0356; Found 237.0356

Thioester (1n): 402 mg; Colorless liquid; yield: 77%; $R_f = 0.63$ in 10:90 ethyl acetate/hexane;



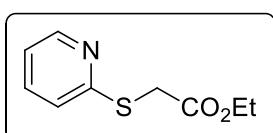
FTIR (Neat): 3057, 2986, 2306, 1734, 1609, 1579, 1444, 1271, 1134, 1030, 897 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.39-7.30 (m, 2H), 7.30-7.22 (m, 2H), 4.16 (q, 2H, $J = 7.1$ Hz), 3.60 (s, 2H), 1.22 (t, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 169.5, 133.5, 133.2, 131.5, 129.2, 61.7, 36.9, 14.1; HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{11}\text{ClO}_2\text{S}+\text{H}$ 231.0241; Found 231.0242

Thioester (1o): 417 mg; Light yellow liquid; yield: 80%; $R_f = 0.64$ in 10:90 ethyl



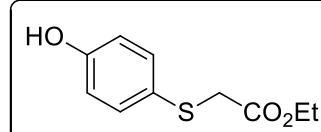
acetate/hexane; FTIR (KBr): 3127, 3055, 2981, 2934, 1733, 1625, 1588, 1457, 1283, 1155, 1019, 946 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.42-7.32 (m, 2H), 7.31-7.22 (m, 2H), 4.16 (q, 2H, $J = 7.1$ Hz), 3.60 (s, 2H), 1.22 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 169.5, 133.5, 133.2, 131.5, 129.2, 61.7, 36.9, 14.1; HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{10}\text{H}_{11}\text{ClO}_2\text{S}+\text{Na}$ 253.0060; Found 253.0062

Thioester (1p): 313 mg; Colorless semi solid; yield: 70%; $R_f = 0.41$ in 15:85 ethyl



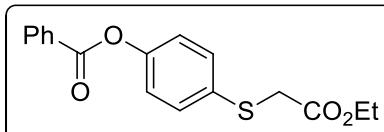
acetate/hexane; FTIR (KBr): 3297, 3254, 3056, 2984, 2684, 2527, 1455, 1416, 1274, 1144, 1030, 894, 754 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 8.39 (d, 1H, $J = 4.9$ Hz), 7.49 (td, 1H, $J = 1.8, 7.8$ Hz), 7.32 (d, 1H, $J = 8.1$ Hz), 7.02-6.95 (m, 1H), 4.2 (q, 2H, $J = 7.1$ Hz), 3.97 (s, 2H), 1.25 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 169.8, 157.0, 149.4, 136.1, 122.1, 119.8, 61.6, 32.4, 14.2; HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ calcd for $\text{C}_9\text{H}_{11}\text{NO}_2\text{S}+\text{H}$ 198.0583; Found 198.0584

Thioester (1q): 380 mg; Yellow semi solid; yield: 81%; $R_f = 0.38$ in 15:85 ethyl



acetate/hexane; FTIR (KBr): 3057, 2987, 2684, 2418, 2308, 1721, 1595, 1485, 1427, 1373, 1270, 1175, 1026, 888 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.41-7.29 (m, 2H), 6.80-6.64 (m, 2H), 4.15 (q, 2H, $J = 7.2$ Hz), 3.49 (s, 2H), 1.23 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 170.9, 156.4, 134.7, 124.2, 116.3, 61.8, 38.8, 14.1; HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{12}\text{O}_3\text{S}+\text{H}$ 213.0580; Found 213.0578

Thioester (1r): 564 mg; White semi solid; yield: 78%; $R_f = 0.56$ in 15:85 ethyl

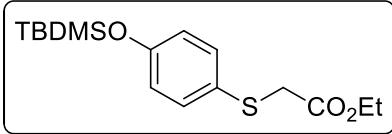


acetate/hexane; FTIR (KBr): 2971, 2952, 2926, 2858, 1738, 1678, 1648, 1630, 1590, 1545, 1457, 1396, 1264, 1201, 1170, 1069, 1085, 935 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 8.23-8.14 (m, 2H), 7.67-7.59 (m, 1H), 7.55-7.46 (m, 4H), 7.21-7.13 (m, 2H), 4.17 (q, 2H, $J = 7.0$ Hz), 3.63 (s, 2H), 1.24 (t, 3H, $J = 7.0$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 ,

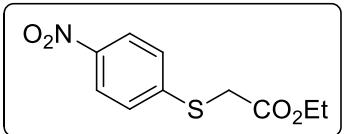
24 °C): δ 169.7, 165.0, 150.4, 133.8, 132.3, 132.0, 130.3, 129.4, 128.7, 122.5, 61.7, 37.4, 14.2; HRMS (ESI) m/z: [M+H]⁺ calcd. for C₁₇H₁₆O₄S+H 317.0842; Found 317.0842

Thioester (1s): 581 mg; Light green semi solid; yield: 70%; R_f = 0.41 in 15:85 ethyl acetate/hexane; FTIR (KBr): 3278, 3057, 2986, 2307, 1733, 1597, 1484, 1374, 1272, 1180, 1176, 1099, 1026, 857 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 24 °C): δ 7.75-7.61 (m, 2H), 7.37-7.22 (m, 4H), 6.98-6.84 (m, 2H), 4.15 (q, 2H, J = 7.1 Hz), 3.59 (s, 2H), 2.44 (s, 3H), 1.21 (t, 3H, J = 7.1 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C): δ 169.4, 148.5, 145.6, 134.3, 132.2, 131.0, 129.9, 128.5, 123.0, 61.7, 36.7, 21.7, 14.1; HRMS (ESI) m/z: [M+Na]⁺ calcd for C₁₇H₁₈O₅S₂+Na 389.0488; Found 389.0482

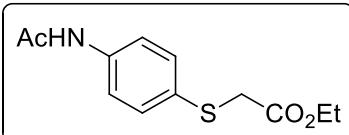
Thioester (1t): 518 mg; Colorless liquid; yield: 70%; R_f = 0.45 in 15:85 ethyl acetate/hexane;

 FTIR (Neat): 3056, 2948, 2863, 2307, 1731, 1591, 1487, 1419, 1266, 1156, 1027, 910 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 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); ¹³C{¹H} NMR (100 MHz, CDCl₃, 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 (ESI) m/z: [M+Na]⁺ calcd for C₁₆H₂₆O₃SSi+Na 349.1264; Found 349.1265

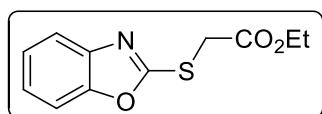
Thioester (1u): 333 mg; Yellow semisolid; yield: 61%; R_f = 0.39 in 15:85 ethyl acetate/hexane; mp: 131-132 °C; FTIR (KBr): 3061, 3002, 2951,

 2843, 1739, 1524, 1471, 1357, 1281, 1150, 1039, 855 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 24 °C): δ 8.14 (d, 2H, J = 8.7 Hz), 7.41 (d, 2H, J = 8.8 Hz), 4.22 (q, 2H, J = 7.1 Hz), 3.78 (s, 2H), 1.26 (t, 3H, J = 7.1 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C): δ 168.6, 145.6, 145.5, 126.8, 124.0, 62.1, 34.6, 14.1; HRMS (ESI) m/z: [M+H]⁺ calcd for C₁₀H₁₁NSO₄+Na 264.0301; Found 264.0307

Thioester (1v): 384 mg; White solid; yield: 67%; R_f = 0.40 in 15:85 ethyl acetate/hexane; mp:

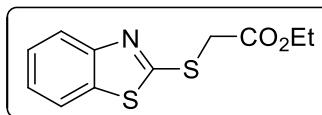
 144-145 °C; FTIR (KBr): 3041, 2948, 2860, 2307, 1736, 1591, 1487, 1409, 1266, 1156, 1027 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 24 °C): δ 7.75 (s, 1H), 7.46 (d, 2H, J = 8.4 Hz), 7.36 (d, 2H, J = 8.4 Hz), 8.4 (s, 2H), 3.70 (s, 3H), 3.59 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C): δ 170.4, 168.7, 137.6, 132.0, 129.5, 120.5, 52.6, 37.5, 24.6; HRMS (ESI) m/z: [M+Na]⁺ calcd for C₁₁H₁₃NO₃S+Na 262.0503; Found 262.0508

Thioester (1w): 376 mg; Colorless semi solid; Yield: 70%; $R_f = 0.40$ in 15:85 ethyl



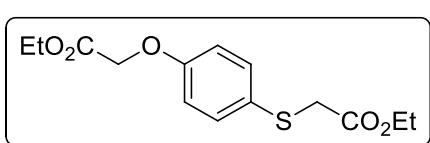
acetate/hexane; FTIR (Neat): 3268, 3200, 3056, 2986, 2854, 2383, 2311, 1739, 1654, 1591, 1500, 1428, 1265, 173, 1137, 1023, 937 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.62-7.64 (m, 1H), 7.47-7.41 (m, 1H), 7.30-7.23 (m, 2H), 4.27 (q, 2H, $J = 7.1$ Hz), 4.12 (s, 2H), 1.29 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 138.0, 163.3, 152.1, 141.8, 124.5, 124.2, 118.7, 110.1, 62.3, 34.3, 14.1; HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{11}\text{H}_{11}\text{NO}_3\text{S}+\text{H}$ 260.0352; Found 260.0353

Thioester (1x): 424 mg; Colorless semi solid; yield: 74%; $R_f = 0.46$ in 15:85 ethyl



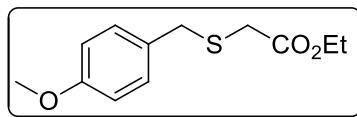
acetate/hexane; FTIR (Neat): 3062, 2982, 2932, 1736, 1460, 1427, 1387, 1376, 1297, 1269, 1173, 1167, 1002, 753 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.88-7.82 (m, 1H), 7.78-7.71 (m, 1H), 7.45-7.37 (m, 1H), 7.33-7.26 (m, 1H), 4.24 (q, 2H, $J = 7.1$ Hz), 4.16 (s, 2H), 1.28 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 168.4, 164.8, 153.0, 135.6, 126.2, 124.5, 121.8, 121.2, 62.1, 35.2, 14.2; HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{11}\text{H}_{11}\text{NO}_2\text{S}_2+\text{Na}$ 276.0123; Found 276.0126

Thioester (1y): 500 mg; Colorless liquid; yield: 74%; $R_f = 0.49$ in 15:85 ethyl acetate/hexane;



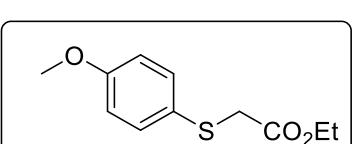
FTIR (Neat): 3219, 3149, 3092, 3057, 2986, 2937, 2869, 2306, 1736, 1679, 1647, 1635, 1533, 1425, 1352, 1225, 1100 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.46-7.37 (m, 2H), 6.92-6.76 (m, 2H), 4.60 (s, 2H), 4.26 (q, 2H, $J = 7.0$ Hz), 4.13 (q, 2H, $J = 7.0$ Hz), 3.54 (s, 2H), 1.29 (t, 3H, $J = 7.0$ Hz), 1.21 (t, 3H, $J = 7.0$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 169.9, 168.7, 157.8, 133.9, 126.5, 115.4, 65.5, 61.5, 61.4, 38.4, 14.2, 14.1; HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{14}\text{H}_{18}\text{O}_5\text{S}+\text{Na}$ 321.0767; Found 321.0778

Thioester (1z): 419 mg; Colorless liquid; yield: 77%; $R_f = 0.45$ in 15:85 ethyl acetate/hexane;



FTIR (Neat): 3157, 3056, 2987, 2843, 2306, 1731, 1645, 1608, 1552, 1507, 1428, 1265, 1171, 1134, 1030, 981 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.25 (d, 2H, $J = 8.4$ Hz), 6.85 (d, 2H, $J = 8.6$ Hz), 4.18 (q, 2H, $J = 7.0$ Hz), 3.79 (s, 3H), 3.79 (s, 2H), 3.05 (s, 2H), 1.29 (t, 3H, $J = 7.0$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 170.6, 158.9, 130.4, 129.2, 114.0, 61.4, 55.4, 35.8, 32.3, 14.3; HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{12}\text{H}_{16}\text{O}_3\text{S}+\text{Na}$ 263.0712; Found 263.0717

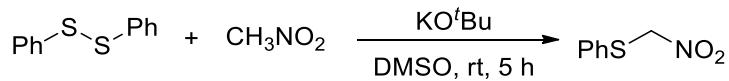
Thioester (1aa): 251 mg; Colorless liquid; yield: 77%; $R_f = 0.40$ in 15:85 ethyl



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

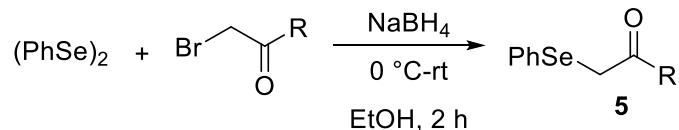
(d, 2H, $J = 8.9$ Hz), 7.84 (d, 2H, $J = 8.8$ Hz), 4.14 (q, 2H), 3.79 (s, 3H), 3.50 (s, 2H), 1.21 (t, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (125 MHz, CDCl_3 , 24 °C): δ 170.1, 159.8, 134.3, 125.1, 114.8, 61.5, 55.5, 38.8, 14.2

5. Synthesis of (nitromethyl)(phenyl)sulfide 1g



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 at room temperature 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 MgSO_4 , filtered, and concentrated to give a crude product, which was further purified by column chromatography with silica gel using ethylacetate/hexane as an eluent gave the product 55 mg in 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, CDCl_3 , 24 °C): δ 7.53-7.45 (m, 2H), 7.40-7.32 (m, 3H), 5.44 (s, 2H); $^{13}\text{C}\{\text{H}\}$ NMR (125 MHz, CDCl_3 , 24 °C): δ 132.2, 131.7, 129.7, 129.3, 79.5; HRMS (ESI) m/z: [M+Na]⁺ calcd for $\text{C}_7\text{H}_7\text{NO}_2\text{S}+\text{Na}$ 192.0090; Found 192.0096

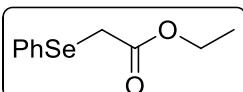
6. Synthesis of selenoester 5



In an oven dried 100 mL round bottom flask, diphenyldiselenide (1 g, 3.20 mmol, 1.0 equiv) was suspended in anhydrous EtOH (15 mL) and the mixture was cooled to 0 °C. NaBH_4 (0.36 g, 9.61 mmol, 3 equiv) was added portion-wise, which was accompanied by decolorization. After stirring the reaction mixture for 10 minutes at 0°C, a solution of ethyl bromoacetate (0.88 mL, 8.00 mmol, 2.5 equiv) in anhydrous EtOH (10mL) was added

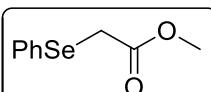
dropwise. The reaction mixture was allowed to stir for one hour and it was quenched by the addition of saturated aq. NH₄Cl. The mixture was diluted with Et₂O, the phases were separated and the aqueous phase was extracted ether. The combined organic layers were dried over Na₂SO₄ and the solvents were removed under reduced pressure. The excess of ethyl bromoacetate was removed in high vacuum to afford the selenoesters in good yields.

Selenoester (5a): 676 mg; Colorless liquid; Yield: 87%; R_f = 0.51 in 10:90 ethyl



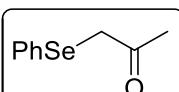
acetate/hexane; FTIR (Neat): 3058, 2982, 1730, 1579, 1474, 1442, 1409, 1367, 1264, 1102, 1031, 944 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 24 °C): δ 7.66-7.53 (m, 2H), 7.34-7.26 (m, 3H), 4.12 (q, 2H, J = 7.1 Hz), 3.50 (s, 2H), 1.19 (t, 3H, J = 7.2 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C): δ 171.0, 135.5, 129.3, 127.9, 61.4, 27.7, 14.1; HRMS (ESI) m/z: [M+Na]⁺ calcd for C₁₀H₁₂O₂Se+Na 266.9895; Found 266.9897

Selenoester (5b): 426 mg; Colorless liquid; Yield: 82%; R_f = 0.50 in 10:90 ethyl



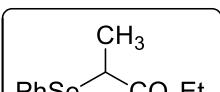
acetate/hexane; FTIR (Neat): 3051, 2991, 1728, 1562, 1454, 1410, 1367, 1269, 1104, 1038, 947 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 24 °C): δ 7.65-7.51 (m, 2H), 7.39-7.26 (m, 3H), 3.67 (s, 3H), 3.52 (s, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C): δ 171.4, 133.5, 129.3, 129.2, 128.0, 52.5, 27.4; HRMS (ESI) m/z: [M+H]⁺ calcd. for C₉H₁₀O₂Se+H 230.9919; Found 230.9922

Selenoketone (5c): 328 mg; Colorless liquid; Yield: 68%; R_f = 0.47 in 10:90 ethyl



acetate/hexane; FTIR (Neat): 3034, 2988, 1719, 1574, 1470, 1409, 1304, 1264, 1121, 1017, 949 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 24 °C): δ 7.64-7.43 (m, 2H), 7.41-7.26 (m, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C): δ 203.7, 133.4, 129.4, 128.7, 128.1, 36.9, 28.1; HRMS (ESI) m/z: [M+H]⁺ calcd. for C₉H₁₀OSe+H 214.9970; Found 214.9965

Selenoester (5f): 501 mg; Colorless liquid; Yield: 61%; R_f = 0.51 in 10:90 ethyl



acetate/hexane; FTIR (Neat): 3058, 2982, 1730, 1579, 1474, 1442, 1409, 1367, 1264, 1102, 1031, 944 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 24 °C): δ 7.60 (d, 2H, J = 6.6 Hz), 7.42-7.26 (m, 3H), 4.08 (q, 2H, J = 7.0 Hz), 3.76 (q, 1H, J = 7.1 Hz), 1.54 (d, 3H, J = 7.1 Hz), 1.16 (t, 3H, J = 7.1 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C): δ 173.5, 135.8, 129.0, 128.5, 127.9, 61.0, 37.4, 17.1, 14.1; HRMS (ESI) m/z: [M+H]⁺ calcd. for C₁₁H₁₄O₂Se+H 259.0232; Found 259.0232

7.Typical procedure for the synthesis of vinylogous carbonates 3

In an oven dried 10 mL reaction tube equipped with stir bar, α -thioester **1**(50 mg, 0.27 mmol, 1 equiv) and Rh₂(OAc)₄ (2.4 mg, 0.008 mmol, 2 mol%) were added under the nitrogen

atmosphere. Dry toluene (1.5 mL) was introduced followed by solution of diazo compound (64.2 mg, 0.41 mmol, 1.5 equiv) in 0.5 mL of dry toluene was introduced to the reaction mixture through syringe. Then, the reaction tube was sealed and stirred at 120 °C in preheated oilbath for 5 h. After the TLC analysis, the reaction mixture was cooled to room temperature and purified by column chromatography using mixture of hexane/ethyl acetate as an eluent to afford vinylogous carbonate **3** in high yield and purity.

8. Properties of isolated vinylogous carbonates 3

Vinylogous carbonate (3a): 70 mg; Colorless liquid; yield: 84%; $R_f = 0.60$ in 10:90 ethyl acetate/hexane; FTIR (Neat): 3101, 2956, 1620, 1595, 1472, 1439, 1331, 1163, 1088, 1040, 960, 835, 812, 787, 743, 691, 664, 566, 538, 502 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.60-7.45 (m, 2H), 7.43-7.31 (m, 3H), 5.60 (s, 1H), 5.00 (s, 1H), 4.20-4.06 (m, 2H), 3.69 (s, 3H), 2.37 (s, 3H), 1.26 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 169.3, 167.1, 166.4, 134.8, 129.6, 129.2, 95.1, 80.5, 59.9, 52.9, 18.8, 14.4; HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{18}\text{O}_5\text{S}+\text{H}$ 311.0948; Found 311.0950

Vinylogous carbonate (3b): 72 mg; Colorless liquid; yield: 83%; $R_f = 0.60$ in 10:90 ethyl acetate/hexane; FTIR (Neat): 3437, 3063, 2983, 1720, 1473, 1442, 1366, 1254, 1093, 1024, 751 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.61-7.40 (d, 2H, $J = 7.0$ Hz), 7.43-7.35 (m, 1H), 7.35-7.28 (m, 2H), 5.77 (s, 1H), 5.00 (s, 1H), 4.18-4.03 (m, 4H), 2.35 (s, 3H), 1.25 (t, 3H, $J = 7.1$ Hz), 1.19 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 169.3, 167.0, 166.9, 136.5, 129.5, 129.3, 126.1, 95.3, 73.9, 62.0, 59.8, 18.7, 14.4, 14.0; HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{16}\text{H}_{20}\text{O}_2\text{S}+\text{Na}$ 347.0924; Found 347.0929

Vinylogous carbonate (3c): 55 mg; Colorless liquid; Yield: 61%; $R_f = 0.62$ in 10:90 ethyl acetate/hexane; FTIR (Neat): 3061, 2982, 1754, 1713, 1632, 1442, 1398, 1343, 1266, 1142, 1054, 991, 937, 823 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.56-7.46 (m, 2H), 7.41-7.28 (m, 3H), 5.91 (m, 1H), 5.61 (s, 1H), 5.37-5.27 (m, 1H), 5.27-5.18 (m, 1H), 5.02 (s, 1H), 4.64-4.51 (m, 2H), 4.18-4.07 (m, 2H), 2.37 (s, 3H), 1.27-1.23 (m, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 169.3, 167.0, 165.6, 134.8, 131.1, 129.8, 129.5, 129.2, 119.4, 95.2, 80.5, 66.5, 59.8, 18.8, 14.4; HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{17}\text{H}_{20}\text{O}_5\text{S}+\text{Na}$ 359.0924; Found: 359.0933

Vinylogous carbonate (3d): 64 mg; Light yellow liquid; Yield: 80%; $R_f = 0.56$ in 10:90 ethyl acetate/hexane; FTIR (Neat): 3057, 2986, 2938, 2686, 2591, 2417, 2307, 2146, 1972, 1728, 1632, 1447, 1371, 1303, 1117, 1017, 938 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.52-7.41 (m, 2H), 7.40-7.30 (m, 3H), 5.51 (s, 1H), 5.04 (s, 1H), 4.13 (q, 2H, $J = 7.0$ Hz), 2.40 (s, 3H), 2.12 (s, 3H), 1.26 (t, 3H, $J = 7.0$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 198.8, 168.8, 167.04, 134.7, 129.6, 129.3, 129.2, 95.7, 85.6, 59.8, 26.1, 18.8, 14.4; HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{15}\text{H}_{18}\text{O}_4\text{S}+\text{Na}$ 317.0818; Found: 317.0821

Vinylogous carbonate (3e): 68 mg; Colorless liquid; Yield: 71%; $R_f = 0.59$ in 10:90 ethyl acetate/hexane; FTIR (Neat): 3064, 2980, 1702, 1629, 1474, 1444, 1397, 1343, 1249, 1139, 1055, 945, 819, 747 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 8.08-7.94 (m, 2H), 7.68-7.58 (m, 1H), 7.54-7.44 (m, 2H), 7.42-7.28 (m, 5H), 6.32 (s, 1H), 5.05 (s, 1H), 4.16-4.05 (m, 2H), 2.41 (s, 3H), 1.23 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 188.9, 169.6, 167.1, 134.4, 134.0, 133.7, 130.2, 129.5, 129.3, 129.1, 128.8, 95.4, 84.2, 59.8, 19.0, 14.4; HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{20}\text{O}_4\text{S}+\text{Na}$ 379.0952; Found: 379.0984

Vinylogous carbonate (3f): 60 mg; White solid; yield: 61%; $R_f = 0.63$ in 10:90 ethyl acetate/hexane; mp: 139-140 °C; FTIR (KBr): 3290, 2969, 1724, 1628, 1390, 1339, 1258, 1135, 1090, 1049, 914, 804 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.90-7.81 (m, 1H), 7.69-7.63 (m, 1H), 7.49-7.39 (m, 5H), 7.38-7.31 (m, 2H), 5.59 (s, 1H), 4.17 (q, 2H, $J = 7.1$ Hz), 3.72 and 3.65 (ABq, 2H, $J = 17.5$ Hz), 2.37 (s, 3H), 1.30 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 199.9, 167.4, 167.2, 146.7, 136.4, 135.8, 132.7, 130.0, 128.9, 128.7(9), 128.7(4), 126.3, 125.9, 99.0, 90.2, 59.9, 40.2, 19.2, 14.5; HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{20}\text{O}_4\text{S}+\text{H}$ 369.1155; Found 369.1154

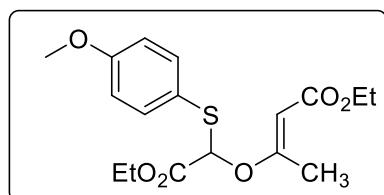
Vinylogous carbonate (3j): 70 mg; Colorless liquid; yield: 81%; $R_f = 0.63$ in 10:90 ethyl acetate/hexane; FTIR (Neat): 2980, 1910, 1713, 1633, 1490, 1438, 1398, 1339, 1247, 1141, 1051, 805 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.34 (m, 2H), 7.10-7.04 (m, 2H), 5.48 (s, 1H), 4.93 (s, 1H), 4.09-3.99 (m, 2H), 3.62 (s, 3H), 2.29 (s, 3H), 2.27 (s, 3H), 1.18 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 169.3, 167.0, 166.3, 140.0, 135.1, 130.0, 125.8, 95.0, 80.5, 59.7, 52.8, 21.3, 18.8, 14.3; HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{16}\text{H}_{20}\text{O}_5\text{S}+\text{Na}$ 347.0924; Found 347.0930

Vinylogous carbonate (3k): 92 mg; liquid; Colorless yield: 84%; $R_f = 0.32$ in 20:80 ethyl acetate/hexane; FTIR (Neat): 2925, 2860, 1712, 1631, 1493, 1135, 1055, 835, 748 cm⁻¹; ¹H NMR (500 MHz, CDCl₃, 24 °C): δ 7.43 (d, 2H, $J = 8.8$ Hz), 6.85 (d, 2H, $J = 8.8$ Hz), 5.48 (s, 1H), 5.01 (s, 1H), 4.21-4.08 (m, 4H), 3.80 (s, 3 H), 3.59 (s, 1H), 2.36 (s, 3 H), 1.25 (t, 3 H, $J = 7.1$ Hz), 1.22 (t, 3.5 H, $J = 7.1$ Hz); ¹³C{¹H} NMR (125 MHz, CDCl₃, 24 °C): δ 169.4, 167.2, 166.0, 161.1, 137.3, 127.3, 114.8, 95.1, 80.2, 62.2, 59.8, 55.5, 18.9, 14.4, 14.1

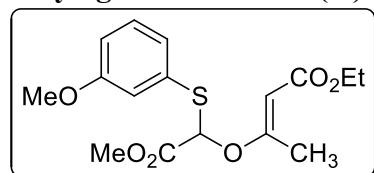
Vinylogous carbonate (3l): 65 mg; Light green liquid; yield: 71%; $R_f = 0.58$ in 10:90 ethyl acetate/hexane; FTIR (Neat): 2979, 2930, 2850, 1715, 1632, 1589, 1478, 1425, 1353, 1252, 1138, 1048, 856 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 24 °C): δ 7.25 (t, 1H, $J = 7.6$ Hz), 7.12-7.01 (m, 2H), 6.93-6.86 (m 1H), 5.16 (s, 1H), 5.00 (s, 1H), 4.20-4.04 (m, 2H), 3.80 (s, 3H), 3.72 (s, 3H), 2.38 (s, 3H), 1.25 (t, 3H, $J = 7.1$ Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C): δ 169.3, 167.0, 166.4, 159.8, 130.9, 130.0, 126.6, 119.5, 115.6, 95.1, 80.6, 59.8, 55.4, 53.0, 18.8, 14.4; HRMS (ESI) m/z: [M+H]⁺ calcd for C₁₆H₂₀O₆S+H 341.1053; Found 341.1055

Vinylogous carbonate (3m): 60 mg; Light yellow liquid; yield: 64%; $R_f = 0.60$ in 10:90 ethyl acetate/hexane; FTIR (Neat): 2982, 1753, 1714, 1631, 1445, 1396, 1341, 1265, 1139, 1051, 819 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 24 °C): δ 7.38 (d, 1H, $J = 7.8$ Hz), 7.07 (s, 1H), 6.97 (d, 1H, $J = 7.8$ Hz), 5.50 (s, 1H), 4.96 (s, 1H) 4.23-4.01 (m, 4H), 2.44 (s, 3H), 2.35 (s, 3H), 2.30 (s, 3H), 1.30 (m, 6H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C): δ 169.7, 167.1, 166.0, 142.4, 140.2, 136.4, 131.6, 127.5, 125.8, 94.7, 81.2, 62.2, 59.8, 21.2, 21.1, 18.8, 14.4, 14.0; HRMS (ESI) m/z: [M+Na]⁺ calcd for C₁₈H₂₄O₅S+Na 375.1237; Found 375.1246

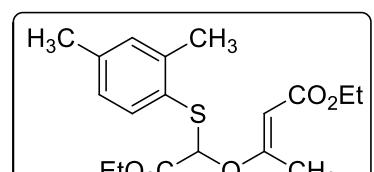
Vinylogous carbonate (3n): 78 mg; Colorless liquid; yield: 77%; $R_f = 0.61$ in 10:90 ethyl acetate/hexane; FTIR (Neat): 3056, 2985, 2306, 1751, 1713, 1632, 1425, 1397, 1341, 1266, 1140, 1054, 942 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 24 °C): δ 8.06-7.98 (m, 1H), 7.85-7.76 (m, 3H), 7.56 (dd, 1H, $J = 8.5$, 1.7 Hz), 7.53-7.47 (m, 2H), 5.65 (s, 1H), 5.04 (s, 1H), 4.17-4.07 (m, 4H), 2.40 (s, 3H), 1.23 (t, 3H, $J = 7.1$ Hz), 1.1 (t, 3H, $J = 7.1$ Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C): δ 169.4, 167.0, 165.9, 134.6, 133.4, 133.3, 131.0, 128.8, 127.9, 127.8, 127.2, 127.1, 126.8, 95.1, 80.7, 62.3, 59.8, 18.8, 14.3, 14.0; HRMS (ESI) m/z: [M+Na]⁺ calcd for C₂₀H₂₂O₅S+Na 397.1080; Found 397.1086



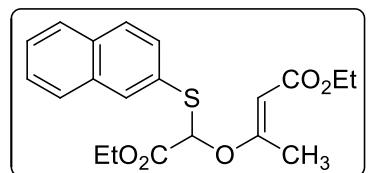
Vinylogous carbonate (3k): 92 mg; liquid; Colorless yield: 84%; $R_f = 0.32$ in 20:80 ethyl acetate/hexane; FTIR (Neat): 2925, 2860, 1712, 1631, 1493, 1135, 1055, 835, 748 cm⁻¹; ¹H NMR (500 MHz, CDCl₃, 24 °C): δ 7.43 (d, 2H, $J = 8.8$ Hz), 6.85 (d, 2H, $J = 8.8$ Hz), 5.48 (s, 1H), 5.01 (s, 1H), 4.21-4.08 (m, 4H), 3.80 (s, 3 H), 3.59 (s, 1H), 2.36 (s, 3 H), 1.25 (t, 3 H, $J = 7.1$ Hz), 1.22 (t, 3.5 H, $J = 7.1$ Hz); ¹³C{¹H} NMR (125 MHz, CDCl₃, 24 °C): δ 169.4, 167.2, 166.0, 161.1, 137.3, 127.3, 114.8, 95.1, 80.2, 62.2, 59.8, 55.5, 18.9, 14.4, 14.1



Vinylogous carbonate (3l): 65 mg; Light green liquid; yield: 71%; $R_f = 0.58$ in 10:90 ethyl acetate/hexane; FTIR (Neat): 2979, 2930, 2850, 1715, 1632, 1589, 1478, 1425, 1353, 1252, 1138, 1048, 856 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 24 °C): δ 7.25 (t, 1H, $J = 7.6$ Hz), 7.12-7.01 (m, 2H), 6.93-6.86 (m 1H), 5.16 (s, 1H), 5.00 (s, 1H), 4.20-4.04 (m, 2H), 3.80 (s, 3H), 3.72 (s, 3H), 2.38 (s, 3H), 1.25 (t, 3H, $J = 7.1$ Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C): δ 169.3, 167.0, 166.4, 159.8, 130.9, 130.0, 126.6, 119.5, 115.6, 95.1, 80.6, 59.8, 55.4, 53.0, 18.8, 14.4; HRMS (ESI) m/z: [M+H]⁺ calcd for C₁₆H₂₀O₆S+H 341.1053; Found 341.1055

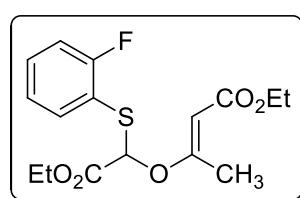


Vinylogous carbonate (3m): 60 mg; Light yellow liquid; yield: 64%; $R_f = 0.60$ in 10:90 ethyl acetate/hexane; FTIR (Neat): 2982, 1753, 1714, 1631, 1445, 1396, 1341, 1265, 1139, 1051, 819 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 24 °C): δ 7.38 (d, 1H, $J = 7.8$ Hz), 7.07 (s, 1H), 6.97 (d, 1H, $J = 7.8$ Hz), 5.50 (s, 1H), 4.96 (s, 1H) 4.23-4.01 (m, 4H), 2.44 (s, 3H), 2.35 (s, 3H), 2.30 (s, 3H), 1.30 (m, 6H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C): δ 169.7, 167.1, 166.0, 142.4, 140.2, 136.4, 131.6, 127.5, 125.8, 94.7, 81.2, 62.2, 59.8, 21.2, 21.1, 18.8, 14.4, 14.0; HRMS (ESI) m/z: [M+Na]⁺ calcd for C₁₈H₂₄O₅S+Na 375.1237; Found 375.1246

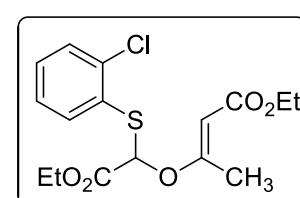


Vinylogous carbonate (3n): 78 mg; Colorless liquid; yield: 77%; $R_f = 0.61$ in 10:90 ethyl acetate/hexane; FTIR (Neat): 3056, 2985, 2306, 1751, 1713, 1632, 1425, 1397, 1341, 1266, 1140, 1054, 942 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 24 °C): δ 8.06-7.98 (m, 1H), 7.85-7.76 (m, 3H), 7.56 (dd, 1H, $J = 8.5$, 1.7 Hz), 7.53-7.47 (m, 2H), 5.65 (s, 1H), 5.04 (s, 1H), 4.17-4.07 (m, 4H), 2.40 (s, 3H), 1.23 (t, 3H, $J = 7.1$ Hz), 1.1 (t, 3H, $J = 7.1$ Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C): δ 169.4, 167.0, 165.9, 134.6, 133.4, 133.3, 131.0, 128.8, 127.9, 127.8, 127.2, 127.1, 126.8, 95.1, 80.7, 62.3, 59.8, 18.8, 14.3, 14.0; HRMS (ESI) m/z: [M+Na]⁺ calcd for C₂₀H₂₂O₅S+Na 397.1080; Found 397.1086

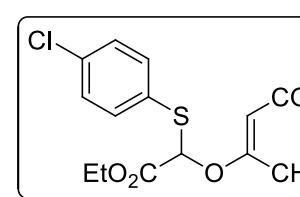
Vinylogous carbonate (3o): 74 mg; Colorless liquid; yield: 80%; $R_f = 0.60$ in 10:90 ethyl acetate/hexane; FTIR (Neat): 3061, 2983, 1713, 1632, 1473, 1444, 1395, 1340, 1264, 1140, 1060, 977 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.51 (td, 1H, $J = 7.9, 1.8$ Hz), 7.44-7.36 (m, 1H), 7.17-7.08 (m, 2H), 5.58 (s, 1H), 5.07 (s, 1H), 4.21-4.15 (m, 2H), 4.13 (q, 2H, $J = 7.1$ Hz), 2.35 (s, 3H), 1.26 (t, 3H, $J = 7.1$ Hz), 1.23 (t, 3H, $J = 7.2$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 169.2, 167.0, 165.6, 163.1 (d, $J = 249.4$ Hz), 137.8, 132.2 (d, $J = 8.1$ Hz), 124.6 (d, $J = 3.4$ Hz), 116.2 (d, $J = 22.9$ Hz), 95.1, 78.9, 62.3, 59.8, 18.6, 14.3, 13.9; HRMS (ESI) m/z: [M+H]⁺ calcd for $\text{C}_{16}\text{H}_{19}\text{FO}_2\text{S}+\text{H}$ 343.1010; Found 343.1010



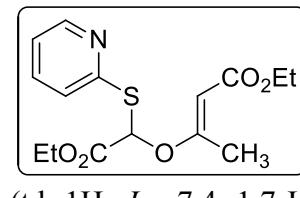
Vinylogous carbonate (3p): 80 mg; Green liquid; yield: 83%; $R_f = 0.61$ in 10:90 ethyl acetate/hexane; FTIR (Neat): 2932, 1714, 1631, 1417, 1262, 1139, 1048, 914 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 8.56-8.41 (m, 1H), 7.57 (td, 1H, $J = 1.8, 7.9$ Hz), 7.23 (dt, 1H, $J = 0.9, 7.1$ Hz), 7.15-7.04 (m, 1H), 6.79 (s, 1H), 5.24 (s, 1H), 4.35-4.24 (m, 2H), 4.11 (q, 2H, $J = 7.1$ Hz), 2.34 (s, 3H), 1.29 (t, 3H, $J = 7.1$ Hz), 1.24 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 169.7, 167.2, 149.7, 136.8, 122.9, 121.1, 95.0, 77.0, 62.4, 59.6, 18.6, 14.3, 13.9; HRMS (ESI) m/z: [M+H]⁺ calcd. for $\text{C}_{16}\text{H}_{19}\text{ClO}_5\text{S}+\text{H}$ 359.0714; Found 359.0719



Vinylogous carbonate (3q): 69 mg; Colorless liquid; yield: 71%; $R_f = 0.60$ in 10:90 ethyl acetate/hexane; FTIR (Neat): 3061, 2984, 2768, 1902, 1714, 1633, 1575, 1473, 1394, 1339, 1262, 1141, 1072, 824 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.49-7.40 (m, 2H), 7.35-7.28 (m, 2H), 5.55 (s, 1H), 5.01 (s, 1H), 4.20-4.09 (m, 4H), 2.37 (s, 3H), 1.29 (t, 3H, $J = 7.0$ Hz), 1.21 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 169.2, 167.0, 165.6, 136.1, 129.4, 128.1, 95.2, 80.0, 62.3, 59.9, 18.8, 14.4, 14.1; HRMS (ESI) m/z: [M+Na]⁺ calcd for $\text{C}_{16}\text{H}_{19}\text{ClO}_5\text{S}+\text{Na}$ 381.0534; Found: 381.0534



Vinylogous carbonate (3r): 65 mg; White semi solid; yield: 73%; $R_f = 0.50$ in 10:90 ethyl acetate/hexane; FTIR (KBr): 2983, 1752, 1714, 1632, 1452, 1397, 1241, 1138, 1053, 819 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.57 (dd, 1H, $J = 7.6, 1.7$ Hz), 7.45 (dd, 1H, $J = 7.8, 1.4$ Hz), 7.30 (td, 1H, $J = 7.4, 1.7$ Hz), 7.27-7.21 (m, 1H), 5.65 (s, 1H), 5.06 (s, 1H), 4.25-4.09 (m, 4H), 2.36 (s, 3H), 1.26 (t, 3H, $J = 7.1$ Hz), 1.23 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 169.4, 167.0, 165.6, 138.1, 136.1, 130.6, 130.2, 129.4, 127.4, 95.1, 79.4,



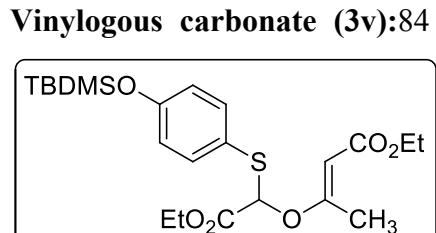
62.5, 59.8, 18.7, 14.4, 14.0; HRMS (ESI) m/z: [M+H]⁺ calcd. for C₁₅H₁₉NO₅S+H 326.1056; Found 326.1063.

Vinylogous carbonate (3s): 74 mg; Colorless liquid; yield: 81%; R_f = 0.51 in 20:80 ethyl acetate/hexane; FTIR (Neat): 3945, 3856, 3680, 3572, 3402, 3056, 2986, 2686, 2414, 2306, 1713, 1630, 1494, 1426, 1264, 1143, 1054, 895 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 24 °C): δ7.43-7.29 (m, 2H), 6.81-6.61 (m, 2H), 5.50 (s, 1H), 5.05 (s, 1H), 4.21 (m, 4H), 2.37 (s, 3H), 1.29-1.23 (m, 6H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C): δ169.4, 167.4, 166.5, 158.2, 137.5, 116.4, 95.2, 80.3, 62.4, 60.0, 18.8, 14.4, 14.1; HRMS (ESI) m/z: [M+Na]⁺ calcd for C₁₆H₂₀O₆S+Na 363.0873; Found 363.0868

Vinylogous carbonate (3t): 95 mg; Colorless liquid; yield: 79%; R_f = 0.53 in 20:80 ethyl acetate/hexane; FTIR (Neat): 3341, 3065, 2982, 2771, 2395, 2120, 2019, 1908, 1739, 1632, 1486, 1397, 1255, 1043, 874 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 24 °C): δ8.24-8.12 (m, 2H), 7.68-7.61 (m, 1H), 7.61-7.55 (m, 2H), 7.55-7.46 (m, 2H), 7.25-7.19 (m, 2H), 5.58 (s, 1H), 5.04 (s, 1H), 4.23-4.06 (m, 4H), 2.39 (s, 3H), 1.26 (t, 3H, J = 7.1 Hz), 1.22 (t, 3H, J = 7.0 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C): δ169.3, 167.0, 165.8, 164.7, 152.2, 136.2, 133.9, 130.2, 129.2, 128.7, 127.0, 122.6, 95.2, 80.5, 62.3, 59.8, 18.8, 14.4, 14.0; HRMS (ESI) m/z: [M+Na]⁺ calcd for C₂₃H₂₄O₇S+Na 467.1135; Found 467.1143

Vinylogous carbonate (3u): 94 mg; White semisolid; yield: 71%; R_f = 0.49 in 20:80 ethyl acetate/hexane; FTIR (Neat): 2982, 2932, 1751, 1714, 1632, 1484, 1377, 1242, 1180, 1141, 1093, 1053, 974, 941, 861 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 24 °C): δ7.73 (m, 2H), 7.48-7.38 (m, 2H), 7.35-7.28 (m, 2H), 7.01 (m, 2H), 5.54 (s, 1H), 4.99 (s, 1H), 4.12 (q, 4H, J = 6.9 Hz), 2.45 (s, 3H), 2.35 (s, 3H), 1.25 (t, 3H, J = 7.2 Hz), 1.18 (t, 3H, J = 7.0 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C): δ169.1, 166.9, 165.5, 150.6, 145.7, 136.0, 132.2, 129.9, 128.9, 128.6, 123.2, 95.3, 80.1, 62.4, 59.9, 21.8, 18.7, 14.4, 14.1; HRMS (ESI) m/z: [M+Na]⁺ calcd for C₂₃H₂₆O₈S₂+Na 517.0960; Found 517.0961

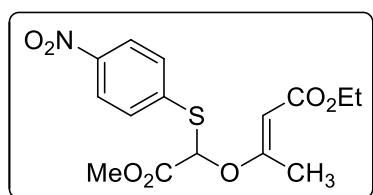
Vinylogous carbonate (3v): 84 mg; White liquid; yield: 68%; R_f = 0.49 in 20:80 ethyl acetate/hexane; FTIR (Neat): 3059, 2935, 2861, 1716, 1632, 1590, 1489, 1396, 1272, 1138, 1054, 908 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 24 °C): δ7.42-7.33 (m, 2H),



acetate/hexane; FTIR (Neat): 3059, 2935, 2861, 1716, 1632, 1590, 1489, 1396, 1272, 1138, 1054, 908 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 24 °C): δ7.42-7.33 (m, 2H),

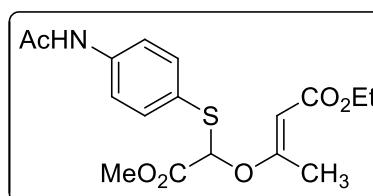
6.89-6.73 (m, 2H), 5.48 (s, 1H), 4.99 (s, 1H), 4.16-4.08 (m, 4H), 2.35 (s, 3H), 1.24 (t, 3H, J = 7.1 Hz), 1.20 (t, 3H, J = 7.0 Hz), 0.96 (s, 9H), 0.19 (s, 6H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 169.5, 167.1, 166.0, 157.4, 137.0, 120.8, 95.0, 80.9, 62.1, 59.7, 25.7, 18.8, 18.3, 14.4, 14.1, -4.3; HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{22}\text{H}_{34}\text{O}_6\text{SSi}+\text{Na}$ 477.1738; Found 477.1750

Vinylogous carbonate (3w): 64 mg; Yellow liquid; yield: 66%; R_f = 0.38 in 20:80 ethyl



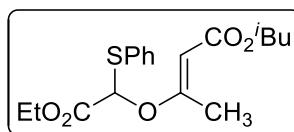
acetate/hexane; FTIR (Neat): 3341, 3065, 2982, 2771, 2395, 2120, 2019, 1908, 1739, 1632, 1486, 1397, 1255, 1043, 874 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 8.44 (d, 2H, J = 8.9 Hz), 8.13 (d, 2H, J = 8.9 Hz), 5.46 (s, 1H), 4.97 (s, 1H), 4.18-4.07 (m, 2H), 3.89 (s, 3H), 2.28 (s, 3H), 1.25 (t, 3H, J = 7.1 Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 168.7, 166.6, 165.7, 147.8, 139.3, 133.0, 126.8, 124.1, 124.0, 95.6, 78.9, 60.0, 53.3, 34.3, 18.6, 14.3; HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_7\text{S}+\text{H}$ 356.0798; Found 356.0799

Vinylogous carbonate (3x): 59 mg; White liquid; yield: 60%; R_f = 0.39 in 20:80 ethyl



acetate/hexane; FTIR (Neat): 3051, 2941, 2889, 1724, 1681, 1590, 1477, 1396, 1272, 1138, 1054, 918 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.71 (s, 1H), 7.62 (s, 0.4 H), 7.52 (d, 2H, J = 8.2 Hz), 7.48-7.40 (m, 2.8 H), 7.37 (d, 0.83 H, J = 8.3 Hz), 5.55 (s, 1H), 5.01 (s, 1H), 4.13 (q, 2H, J = 5.9 Hz), 3.70 (s, 4.2 H), 3.59 (s, 1H), 2.35 (s, 3.1 H), 2.16 (s, 4.2 H), 1.26 (t, 3.5 H, J = 6.9 Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 169.2, 168.7, 167.1, 166.4, 139.7, 136.3, 132.0, 123.6, 120.4, 120.0, 95.2, 80.3, 59.9, 52.9, 37.5, 24.7, 180.8, 14.4; HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{17}\text{H}_{21}\text{NO}_6\text{S}+\text{H}$ 368.1162; Found: 368.1166

Vinylogous carbonate (3y): 78 mg; Colorless liquid; yield: 82%; R_f = 0.50 in 20:80 ethyl



acetate/hexane; FTIR (Neat): 3290, 2969, 1724, 1628, 1390, 1339, 1258, 1135, 1090, 1049, 914 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.59-7.46 (m, 2H), 7.42-7.30 (m, 3H), 5.56 (s, 1H), 4.93 (s, 1H), 4.22-4.08 (m, 2H), 2.34 (s, 3H), 1.45 (s, 9H), 1.20 (t, 3H, J = 7.1 Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 168.3, 166.5, 166.0, 134.6, 130.2, 129.4, 129.2, 96.8, 80.6, 79.8, 62.2, 28.4, 18.6, 14.0; HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{18}\text{H}_{24}\text{O}_5\text{S}+\text{Na}$ 375.1237; Found 375.1246

Vinylogous carbonate(3z): 62 mg; Colorless liquid; yield: 78%; $R_f = 0.50$ in 20:80 ethyl acetate/hexane; FTIR (Neat): 3061, 2975, 1750, 1629, 1450, 1232, 1078, 1021, 857 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.59-7.46 (m, 2H), 7.42-7.31 (m, 3H), 5.60 (s, 1H), 5.41 (s, 1H), 4.16 (q, 2H, $J = 7.1$ Hz), 2.35 (s, 3H), 2.11 (s, 3H), 1.21 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 196.7, 169.0, 165.9, 134.6, 129.6, 129.2, 102.8, 80.8, 62.3, 32.2, 19.4, 14.1; HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{15}\text{H}_{18}\text{O}_4\text{S}+\text{Na}$ 317.0818; Found 317.0824

Vinylogous carbonate(3aa): 51 mg; Colorless liquid; yield: 71%; $R_f = 0.50$ in 20:80 ethyl acetate/hexane; FTIR (Neat): 3234, 2929, 1714, 1581, 1442, 1219, 1024, 966, 911, 797 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.54-7.44 (m, 2H), 7.43-7.31 (m, 3H), 5.53 (s, 1H), 5.45 (s, 1H), 2.37 (s, 3H), 2.13(4) (s, 3H), 2.13(2) (s, 3H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 199.1, 196.7, 168.3, 134.6, 129.6, 129.4, 103.4, 85.9, 32.2, 26.0, 19.3; HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{16}\text{O}_3\text{S}+\text{H}$ 265.0893; Found 265.0899

Vinylogous carbonate(3ab): 73 mg; Colorless liquid; yield: 72%; $R_f = 0.48$ in 20:80 ethyl acetate/hexane; FTIR (Neat): 3138, 2983, 2931, 1736, 1676, 1570, 1467, 1393, 1249, 1108, 1026, 884, 862 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.54-7.48 (m, 2H), 7.48-7.42 (m, 1H), 7.33-7.27 (m, 3H), 6.91 (d, 1H, $J = 3.4$ Hz), 6.51 (s, 1H), 6.44 (dd, 1H, $J = 1.7, 3.4$ Hz), 5.96 (s, 1H), 4.22-4.11 (m, 4H), 1.25 (t, 3H, $J = 7.1$ Hz), 1.18 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 166.8, 164.9, 154.7, 149.8, 144.9, 134.0, 131.3, 129.0, 128.8, 114.6, 112.3, 98.9, 86.8, 61.9, 60.3, 14.3, 14.0; HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{20}\text{O}_6\text{S}+\text{Na}$ 399.0873; Found 399.0879

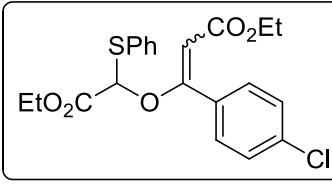
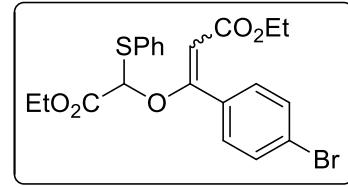
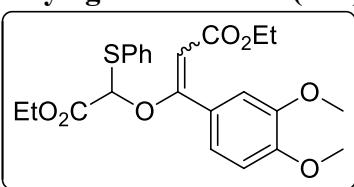
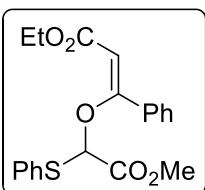
Vinylogous carbonate(3ac): 70 mg; Green liquid; yield: 71% (1:1 ratio); $R_f = 0.50$ in 20:80 ethyl acetate/hexane; FTIR (Neat): 2983, 1806, 1734, 1687, 1444, 1377, 1265, 1175, 1094, 1027, 846, 801 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.55-7.48 (m, 2H), 7.43-7.30 (m, 8H), 5.70 (s, 1H), 5.35 (s, 1H), 4.01 (m, 2H), 3.69 (s, 3H), 1.11 (t, 3H, $J = 7.0$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 167.6, 166.4, 166.0, 134.9, 133.4, 130.2, 129.7, 129.6, 129.3, 129.2, 127.9, 98.1, 81.6, 60.0, 53.0, 14.1; HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{20}\text{NO}_5\text{S}+\text{Na}$: 395.0924; Found: 395.0931

Vinylogous carbonate (3ac₁): Green liquid; yield: 71% (1:1 ratio); $R_f = 0.50$ in 20:80 ethyl acetate/hexane; FTIR (Neat): 3261, 1630, 1391, 1201, 1136, 1031, 1002, 941, 811 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.53-7.47 (m, 2H), 7.43-7.37 (m, 2H), 7.37 (m, 1H), 7.30-7.25 (m, 2H), 7.24-7.17 (m, 3H), 6.22 (s, 1H), 5.69 (s, 1H), 4.13-4.03 (m, 2H), 3.64 (s, 3H), 1.20 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 167.2, 164.9, 164.2, 134.8, 134.4, 130.9, 130.7, 129.0, 128.6, 127.8, 102.4, 86.0, 60.3, 52.8, 14.3; HRMS (ESI) m/z: [M+Na]⁺ calcd for $\text{C}_{20}\text{H}_{20}\text{NO}_5\text{S}+\text{Na}$ 395.0924; Found 395.0931

Vinylogous carbonate(3ad): 70 mg; Green liquid; yield: 72% (1:0.4 ratio); $R_f = 0.43$ in 20:80 ethyl acetate/hexane; FTIR (Neat): 3022, 2952, 1737, 1638, 1609, 1512, 1434, 1275, 1198, 1154, 1009, 917 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.51-7.48 (m, 2H), 7.41-7.12 (m, 6H), 7.01-6.88 (m, 1H), 6.87-6.77 (m, 1.5H), 6.32 (s, 1H), 5.78 (s, 1H), 4.30-4.09 (m, 6H), 3.91 (s, 3H), 3.89 (s, 1.3 H), 3.87 (s, 1.3 H), 3.81(s, 3H), 1.33-1.23 (m, 5H), 1.20 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 168.4, 166.9, 165.0, 164.4, 151.3, 149.1, 149.0, 148.8, 134.0, 131.2, 129.0, 128.8, 127.6, 121.8, 121.2, 111.0, 110.7, 100.4, 86.0, 61.9, 61.8, 60.2, 57.5, 56.0, 55.9, 14.4, 14.1(4), 14.1(1); HRMS (ESI) m/z: [M+Na]⁺ calcd for $\text{C}_{23}\text{H}_{26}\text{O}_7\text{S}+\text{Na}$ 469.1291; Found 469.1297

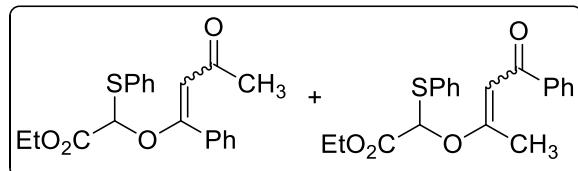
Vinylogous carbonate(3ae): 92 mg,Light green liquid; yield: 74% (1:0.3 ratio); $R_f = 0.43$ in 20:80 ethyl acetate/hexane;FTIR (Neat): 2926, 2855, 1807, 1739, 1692, 1610, 1576, 1512, 1444, 1371, 1275, 1178, 1094, 944 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): 7.73 (s, 1.1H), 7.59-7.43 (m, 4.5H), 7.38-7.16 (m, 5H), 6.80 (d, 0.3 H, $J = 8.7$ Hz), 6.40 (s, 1H), 5.77 (s, 1H), 4.25-4.10 (m, 4.3H), 3.80 (s, 0.3H), 1.28 (t, 3H, $J = 7.0$ Hz), 1.20 (t, 3H, $J = 7.0$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 166.6, 164.7, 162.4, 137.3, 135.5, 134.4 (9), 134.4 (5), 133.6, 130.9, 130.6, 130.0, 129.1 (8), 129.1 (2), 126.3, 122.7, 114.8, 102.5, 85.9, 62.1, 60.5, 14.3, 14.1; HRMS (ESI) m/z: [M+Na]⁺ calcd for $\text{C}_{21}\text{H}_{21}\text{BrO}_5\text{S}+\text{Na}$ 487.0185; Found 487.0188

Vinylogous carbonate(3af): 79 mg;Green liquid; yield: 70% (1:0.4 ratio); $R_f = 0.51$ in 20:80 ethyl acetate/hexane; FTIR (Neat): 3399, 3059, 2986, 2306, 1728, 1625, 1567, 1472, 1091, 1030, 897 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.59-7.44 (m, 4.5 H), 7.40-7.24 (m, 10.5 H), 6.40 (s, 0.44 H), 5.77 (s, 0.44 H), 5.69 (s, 1 H), 5.33 (s, 1H), 4.22-4.10 (m, 4.5 H), 4.02 (q, 2H, $J = 7.0$ Hz), 1.32-1.23 (m, 4H), 1.22-1.16 (m, 5H), 1.14 (t,



3H, $J = 7.0$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 166.6, 166.5, 165.8, 165.7, 164.7, 162.9, 136.8, 136.1, 134.0, 134.2, 133.6, 132.0, 130.7, 129.5, 129.1, 129.0, 128.9, 128.7, 128.0, 01.8, 97.7, 85.8, 81.5, 62.3, 62.0, 60.4, 60.1, 14.2, 14.1, 14.0; HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{21}\text{ClO}_5\text{S}+\text{H}$ 421.0871; Found 421.0869

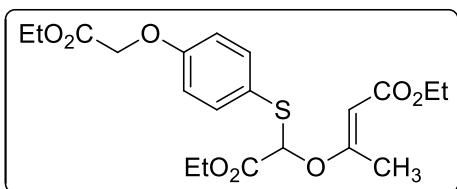
Vinylogous carbonate (3ag): 59 mg; Light yellow liquid; yield: 61% (1:0.7 ratio); $R_f = 0.50$



in 20:80 ethyl acetate/hexane; FTIR (Neat): 3056, 2896, 2784, 1984, 1821, 1776, 1680, 1589, 1411, 1278, 1173, 1005, 981 cm^{-1} ; ^1H

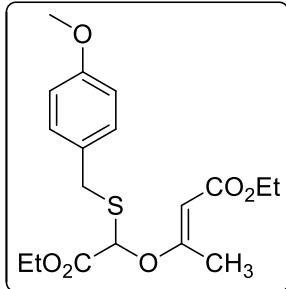
NMR (400 MHz, CDCl_3 , 24 °C): δ 8.01-7.89 (m, 3.7H), 7.62-7.49 (m, 5.2H), 7.49-7.40 (m, 4.4H), 7.40-7.31 (m, 4H), 7.31-7.24 (m, 5.7H), 7.23-7.15 (m, 3.2H), 5.60 (s, 1H), 5.40 (s, 1H), 5.12 (s, 2.4H), 4.42 (q, 1.5H, $J = 7.0$ Hz), 4.16 (q, 2.9H, $J = 7.0$ Hz), 2.35 (s, 3.2H), 2.11 (s, 3.1H), 1.52 (s, 2.2H), 1.20 (t, 5H, $J = 7.1$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 169.0, 165.9, 134.6, 133.6, 129.6, 129.3, 128.8, 128.7, 128.6, 128.3, 128.1, 102.8, 80.8, 67.1, 62.3, 48.5, 32.2, 29.8, 19.4, 14.1, 13.8; HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{20}\text{O}_4\text{S}+\text{Na}$ 379.0975; Found 379.0979

Vinylogous carbonate (3ah): 95 mg; Yellow liquid; yield: 83%; $R_f = 0.40$ in 20:80 ethyl



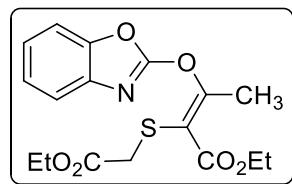
acetate/hexane; FTIR (Neat): 3056, 2986, 2306, 1752, 1631, 1492, 1424, 1265, 1203, 1141, 1053, 896 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.51-7.37 (m, 2H), 6.94-6.78 (m, 2H), 5.49 (s, 1H), 5.01 (s, 1H), 4.61 (s, 2H), 4.27 (q, 2H, $J = 7.1$ Hz), 4.18-4.08 (m, 4H), 2.36 (s, 3H), 1.29 (t, 3H, $J = 7.1$ Hz), 1.25 (t, 3H, $J = 7.1$ Hz), 1.21 (t, 3H, $J = 7.0$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 169.4, 168.5, 167.1, 165.9, 159.2, 137.1, 121.3, 115.4, 95.1, 80.6, 65.4, 62.1, 61.6, 59.8, 18.8, 14.4, 14.2, 14.1; HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{20}\text{H}_{26}\text{O}_8\text{S}+\text{Na}$ 449.1241; Found 449.1242

Vinylogous carbonate (3ai): 74 mg; Colorless liquid; yield: 75%; $R_f = 0.42$ in 20:80 ethyl

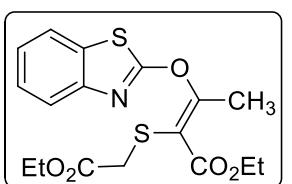


acetate/hexane; FTIR (Neat): 2983, 2839, 1714, 1630, 1513, 1463, 1367, 1249, 1139, 1046, 939, 837 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.25-7.17 (m, 2H), 6.87-6.80 (m, 2H), 5.30 (s, 1H), 4.93 (s, 1H), 4.30-4.17 (m, 2H), 4.1 (q, 2H, $J = 7.1$ Hz), 3.93, 3.85 (AB q, 2H, $J = 20.7$ Hz), 3.78 (s, 3H), 2.32 (s, 3H), 1.29 (t, 3H, $J = 7.2$ Hz), 1.25 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 169.5, 167.0, 166.5, 159.0, 130.2, 128.1, 114.0, 94.6, 76.8, 62.1, 59.6, 55.2, 33.6, 18.6, 14.3, 14.0; HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{18}\text{H}_{24}\text{O}_6\text{S}+\text{Na}$ 391.1186; Found: 391.1193.

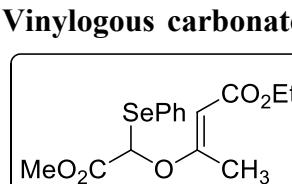
Vinylogous carbonate (4a): 76 mg; Colorless liquid; yield: 78%; $R_f = 0.45$ in 20:80 ethyl acetate/hexane; FTIR (Neat): 3265, 2987, 1767, 1593, 1480, 1395, 1254, 1142, 1028, 931 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.55 (m, 1H), 7.44 (m, 1H), 7.32-7.20 (m, 2H), 4.33 (q, 2H, $J = 7.1$ Hz), 4.11 (q, 2H, $J = 7.0$ Hz), 3.44 (s, 2H), 2.55 (s, 3H), 1.38 (t, 3H, $J = 7.1$ Hz), 1.22 (t, 3H, $J = 7.0$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 169.1, 164.8, 161.9, 159.9, 148.8, 140.6, 124.7, 123.7, 118.8, 116.9, 110.1, 62.1, 61.6, 35.4, 19.3, 14.2, 14.0; HRMS (ESI) m/z: $[\text{M}+\text{NH}_4]^+$ calcd. for $\text{C}_{17}\text{H}_{19}\text{NO}_6\text{S}+\text{NH}_4$ 383.1271; Found 383.1272



Vinylogous carbonate (4b): 75 mg; Yellow liquid; yield: 73%; $R_f = 0.46$ in 20:80 ethyl acetate/hexane; FTIR (Neat): 3408, 3056, 2987, 2306, 1724, 1620, 1529, 1441, 1266, 1217, 1056, 895 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.76-7.65 (m, 2H), 7.42 (m, 1H), 7.31-7.26 (m, 1H), 4.33 (q, 2H, $J = 7.1$ Hz), 4.10 (q, 2H, $J = 7.1$ Hz), 3.44 (s, 2H), 2.59 (s, 3H), 1.38 (t, 3H, $J = 7.1$ Hz), 1.21 (t, 3H, $J = 7.2$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 169.3, 168.8, 165.2, 164.0, 148.9, 132.8, 126.4, 124.4, 121.8, 121.5, 116.1, 62.0, 61.5, 35.6, 19.7, 14.3, 14.1; HRMS (ESI) m/z: $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{17}\text{H}_{19}\text{NO}_5\text{S}_2+\text{Na}$ 404.0597; Found 404.0606



Vinylogous carbonate (6a): 70 mg; Colorless liquid; yield: 72%; $R_f = 0.42$ in 20:80 ethyl acetate/hexane; FTIR (Neat): 2983, 2839, 1714, 1630, 1513, 1463, 1367, 1249, 1139, 1046, 939, 837 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.62 (d, 2H, $J = 7.0$ Hz), 7.43-7.35 (m, 1H), 7.35-7.28 (m, 2H), 5.77 (s, 1H), 5.00 (s, 1H), 4.18-4.03 (m, 4H), 2.35 (s, 3H), 1.25 (t, 3H, $J = 7.1$ Hz), 1.19 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 169.3, 167.0, 166.9, 136.5, 129.5, 129.3, 126.1, 95.3, 73.9, 62.0, 59.8, 18.7, 14.4, 14.0; HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{20}\text{O}_5\text{Se}+\text{H}$ 373.0549; Found 373.0547



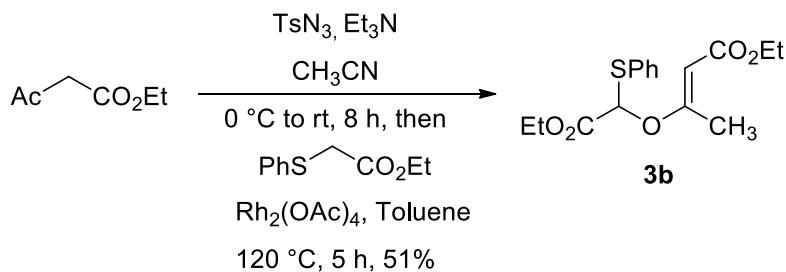
Vinylogous carbonate (6b): 67 mg; Colorless liquid; yield: 70%; $R_f = 0.42$ in 20:80 ethyl acetate/hexane; FTIR (Neat): 3056, 2986, 2306, 1752, 1631, 1492, 1424, 1360, 1258, 1139, 1046, 944 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.61 (d, 2H, $J = 7.2$ Hz), 7.40 (t, 1H, $J = 7.3$ Hz), 7.38-7.28 (m, 2H), 5.81 (s, 1H), 4.99 (s, 1H), 4.22-4.05 (m, 2H), 3.65 (s, 3H), 2.35 (s, 3H), 1.26 (s, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 169.2, 167.4, 167.0, 136.6, 129.6, 129.3, 125.9, 95.3, 73.7, 59.8, 52.7, 18.7, 14.4; HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{18}\text{O}_5\text{Se}+\text{H}$ 359.0392; Found 359.0393

Vinylogous carbonate (6c): 62 mg; Colorless liquid; yield: 68%; $R_f = 0.42$ in 20:80 ethyl acetate/hexane; FTIR (Neat): 2926, 2855, 1807, 1739, 1692, 1610, 1576, 1512, 1444, 1371, 1275, 1178, 1094, 914 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.57 (d, 2H, $J = 7.6$ Hz), 7.39 (t, 1H, $J = 7.6$ Hz), 7.36-7.29 (m, 2H), 5.75 (s, 1H), 5.07 (s, 1H), 4.14 (q, 2H, $J = 7.0$ Hz), 2.37 (s, 3H), 2.13 (s, 3H), 1.27 (s, 3H, $J = 7.0$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 198.9, 168.6, 167.0, 136.5, 129.5, 125.1, 95.9, 80.5, 59.9, 25.7, 18.7, 14.4; HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{18}\text{O}_4\text{Se} + \text{H}$ 343.0443; Found 343.0442

Vinylogous carbonate (6d): 70 mg; Colorless liquid; yield: 62%; $R_f = 0.39$ in 20:80 ethyl acetate/hexane; FTIR (Neat): 2983, 2847, 1721, 1670, 1545, 1463, 1367, 1249, 1144, 1046, 914, 887 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.62-7.57 (m, 2H), 7.48-7.43 (m, 1H), 7.36-7.30 (m, 1H), 7.30-7.21 (m, 3H), 6.91 (d, 1H, $J = 3.4$ Hz), 6.68 (s, 1H), 6.46 (q, 1H, $J = 1.7$ Hz), 5.98 (s, 1H), 4.17-4.09 (m, 4H), 1.25 (t, 3H, $J = 7.1$ Hz), 1.19 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 167.8, 164.9, 154.5, 149.6, 145.0, 136.0, 129.1, 128.9, 127.2, 114.6, 112.3, 99.2, 81.6, 67.2, 61.7, 60.9, 14.3, 14.0; HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{20}\text{O}_6\text{Se} + \text{H}$ 425.0498; Found 425.0503

Vinylogous carbonate (6e): 76 mg; Colorless liquid; yield: 65%; $R_f = 0.42$ in 20:80 ethyl acetate/hexane; FTIR (Neat): 3036, 2983, 2839, 1719, 1680, 1570, 1463, 1367, 1249, 1139, 1046, 939 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.65-7.52 (m, 4H), 7.45-7.29 (m, 4H), 7.27-7.20 (m, 2H), 6.43 (s, 1H), 5.80 (s, 1H), 4.22-4.10 (m, 4H), 1.29 (t, 3H, $J = 7.0$ Hz), 1.19 (t, 3H, $J = 7.0$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 167.8, 164.9, 164.1, 136.1, 134.6, 130.7, 129.1, 128.9, 128.7, 127.8, 127.0, 102.7, 80.4, 61.8, 60.4, 14.4, 14.0; HRMS (ESI) m/z: $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{22}\text{O}_5\text{Se} + \text{H}$ 435.0705; Found 435.0712

9. General procedure for one-pot transformations



In an oven dried 25 mL reaction tube, ethyl acetoacetate (0.1 mL, 0.76 mmol, 1 equiv) and tosyl azide (0.17 mL, 1.15 mmol, 1.5 equiv) were dissolved in CH₃CN (4 mL) and cooled to 0 °C. Next, triethylamine (0.16 mL, 1.15 mmol, 1.5 equiv) was introduced slowly drop-wise via syringe and the reaction mixture was allowed to stir at room temperature for 8 h. After TLC analysis, CH₃CN was removed under reduced pressure. To the reaction mixture, α-thioester (100 mg, 0.50 mmol, 0.66 equiv) and Rh₂(OAc)₄ (4.5 mg, 0.01 mmol, 2 mol%) were added followed by toluene (4 mL) was introduced. Reaction tube was sealed with septa, kept in pre-heated oil-both at 120 °C and stirred for 5 h. Next, reaction was cooled to room temperature and quenched with cold water and extracted with ethyl acetate. The obtained organic layer was concentrated in vacuum and purified through column chromatography using ethyl acetate and hexane as an eluent to give **3b** in 124 mg with 51% yield.

10. Synthesis of sulfone 7

To a 25 mL round bottom flask equipped with stir bar, vinylogous carbonate **3a** (70 mg, 0.21 mmol, 1 equiv) was dissolved in dry CH₂Cl₂ (10 mL). The reaction mixture was cooled to 0 °C with ice-bath followed by m-CBPA (0.64 mmol, 3 equiv) was added *via* portion-wise and allowed to stir for 2 h at room temperature. After completion of the reaction, monitored by TLC, the reaction was neutralized with saturated aq. NaHCO₃ and extracted with CH₂Cl₂. The organic layer was evaporated under reduced pressure and the crude product that obtained was purified by column chromatography using mixture of hexane/ethyl acetate as an eluent to afford sulfone derivative **7** in 57 mg with 76% yield as white semi solid. R_f = 0.43 in 20:80 ethyl acetate/hexane; FTIR (Neat): 3056, 1731, 144, 1265, 743, 689, 598, 527 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, 24 °C): δ 7.97-7.88 (m, 2H), 7.78-7.69 (m, 1H), 7.64-7.58 (m, 2H), 5.40 (s, 1H), 4.92 (s, 1H), 4.17-4.02 (m, 2H), 3.86 (s, 3H), 2.26 (s, 3H), 1.24 (t, 3H, J = 7.1 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C): δ 169.1, 166.3, 162.5, 135.2, 133.8, 130.0, 129.3, 95.6, 89.0, 60.2, 54.0, 18.2, 14.3; HRMS (ESI) m/z: [M+Na]⁺ calcd for C₁₅H₁₈N₂O₇S+Na 342.0773; Found 342.0781

11. Synthesis of furan derivative 8

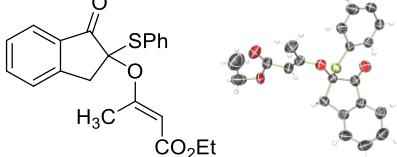
To a 10 mL oven dried reaction tube equipped with stir bar, vinylogous carbonate **3d** (0.20 mmol, 1 equiv) was dissolved in dry CH₂Cl₂ (2.5 mL) and cooled to 0 °C with ice-bath. TMSOTf (0.24 mmol, 1.2 equiv) was added *via* syringe and allowed to stir for 2 h at room temperature. After completion of the reaction, monitored by TLC, the reaction mixture was neutralized with NaHCO₃ and extracted with CH₂Cl₂. The organic layer was evaporated under

reduced pressure and the resultant crude product was purified by column chromatography using mixture of hexane/ethyl acetate as an eluent to afford furan derivative **8** in 24 mg with 45% yield as colorless liquid. $R_f = 0.43$ in 20:80 ethyl acetate/hexane; FTIR (Neat): 3267, 2930, 1716, 1580, 1417, 1203, 1023, 915, 844, 800 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , 24 °C): δ 7.24-7.16 (m, 2H), 7.13-7.03 (m, 3H), 4.11 (q, 2H, $J = 7.1$ Hz), 2.57 (s, 3H), 2.34 (s, 3H), 1.05 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C): δ 159.0, 138.4, 128.7, 126.1, 125.0, 60.1, 14.4, 13.9, 11.9; HRMS (ESI) m/z: [M+H]⁺ calcd. for $\text{C}_{15}\text{H}_{16}\text{O}_3\text{S}+\text{H}$ 277.0893; Found 277.0900.

12. Typical procedure for 1 mmol scale reaction

In an oven dried 50 mL schenk flask equipped with stir bar, α -thioester **1** (196 mg, 1 mmol, 1 equiv) and $\text{Rh}_2(\text{OAc})_4$ (8.8 mg, 0.028 mmol, 2 mol%) were added under the nitrogen atmosphere. Dry toluene (5 mL) was introduced followed by solution of diazo compound (234 mg, 1.5 mmol, 1.5 equiv) in 1 mL of dry toluene was introduced to the reaction mixture through syringe. Then, the reaction tube was sealed and stirred at 120 °C in oil bath for 5 h. After the TLC analysis, the reaction mixture was cooled to room temperature and purified by column chromatography using mixture of hexane/ethyl acetate as an eluent to afford vinylogous carbonate **3** in 248 mg with 76% yield.

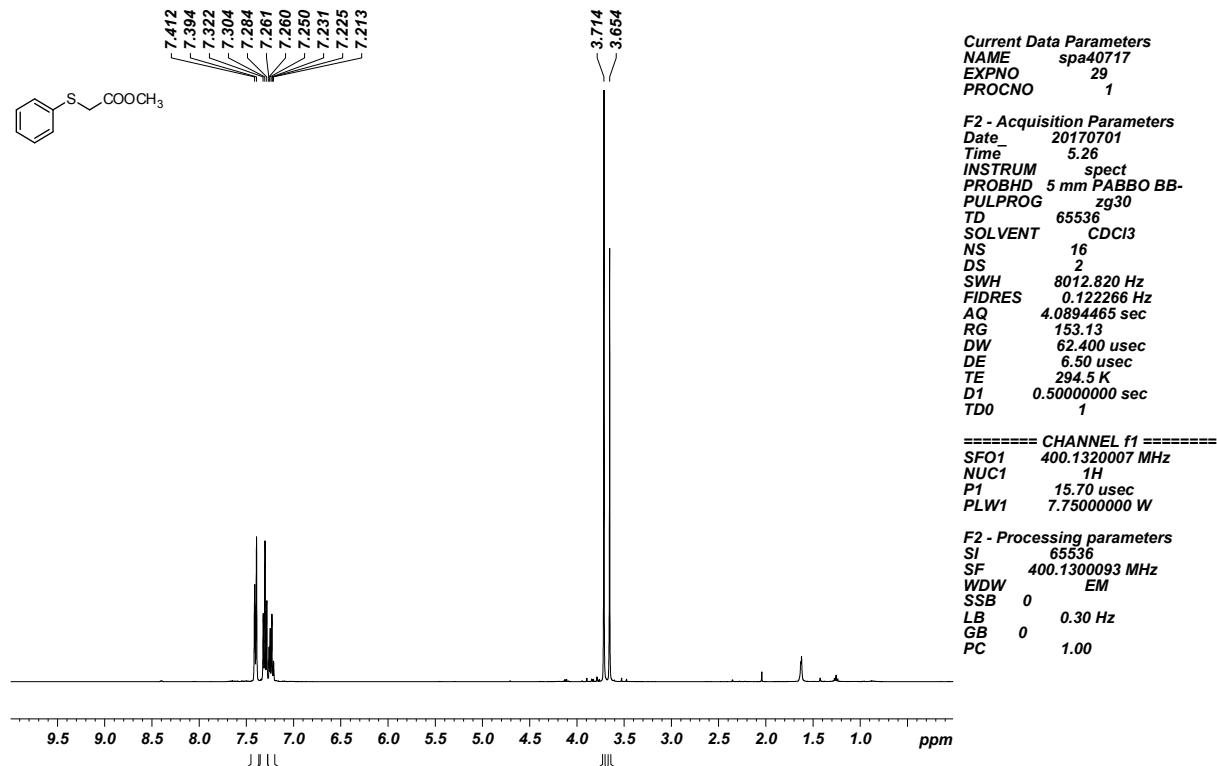
13. Crystallographic data and structure refinements summary for compound 3f.

DATA	3f
Molecular Structure (ORTEP Structure)	
Formula	C ₂₁ H ₂₀ O ₄ S
Formula weight	368.43
Color	Colorless
Temperature/K	293(2)
Radiation	Mo K α
Wavelength/ \AA	0.71073
Crystal system	Monoclinic
Space group	P21/n
<i>a</i> (\AA)	8.7374(6)
<i>b</i> (\AA)	21.3008(14)
<i>c</i> (\AA)	10.5344(7)
α ($^\circ$)	90
β ($^\circ$)	90.965(2)
γ ($^\circ$)	90
Volume (\AA^3)	1960.3(2)
<i>Z</i>	4
Density (g/ml)	1.248
μ (1/mm)	0.187
<i>F</i> (000)	776
θ (min, max)	0.72, 0.67
No. of unique reflns	3424
No. of parameters	340
<i>R</i> _obs, <i>wR</i> ₂ _obs	0.0673, 0.1329
$\Delta\rho_{\min}, \Delta\rho_{\max}$ (e \AA^{-3})	-0.215, 0.206
GooF	1.135

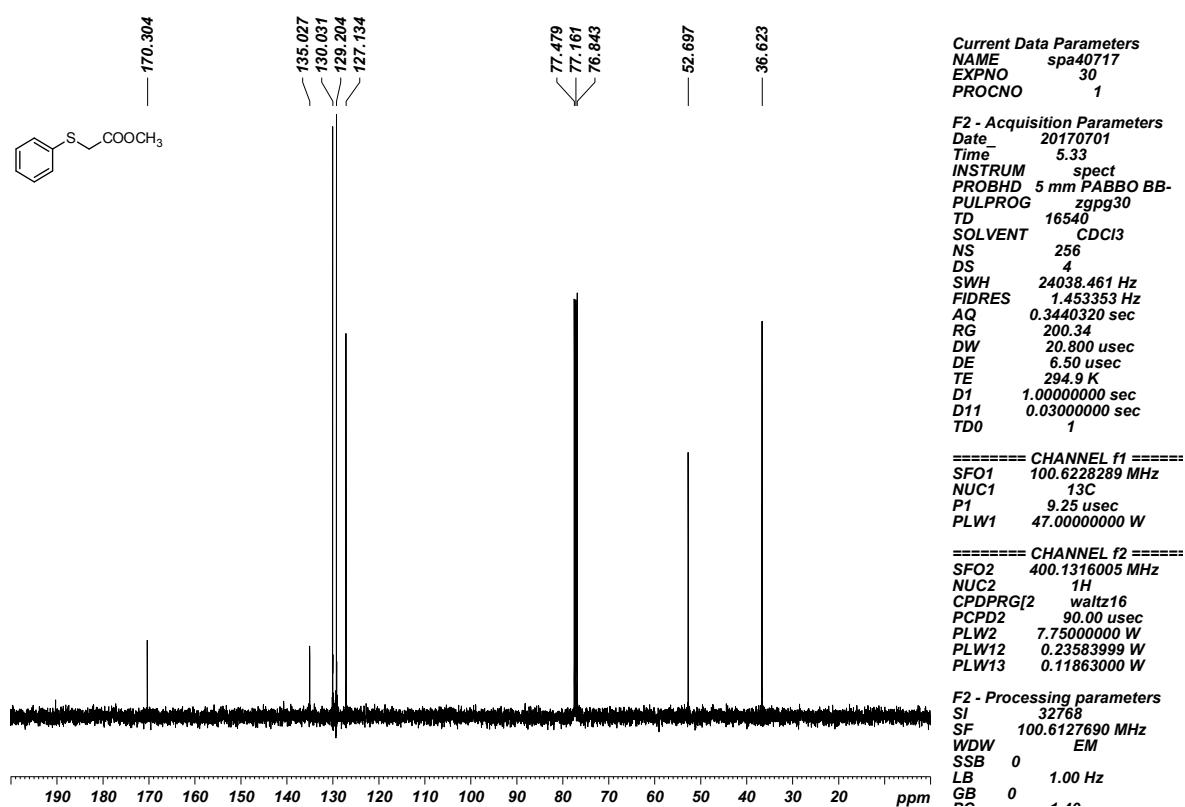
14. NMR spectra of isolated compounds

Thioester 1a

¹H NMR (400 MHz, CDCl₃, 24 °C)

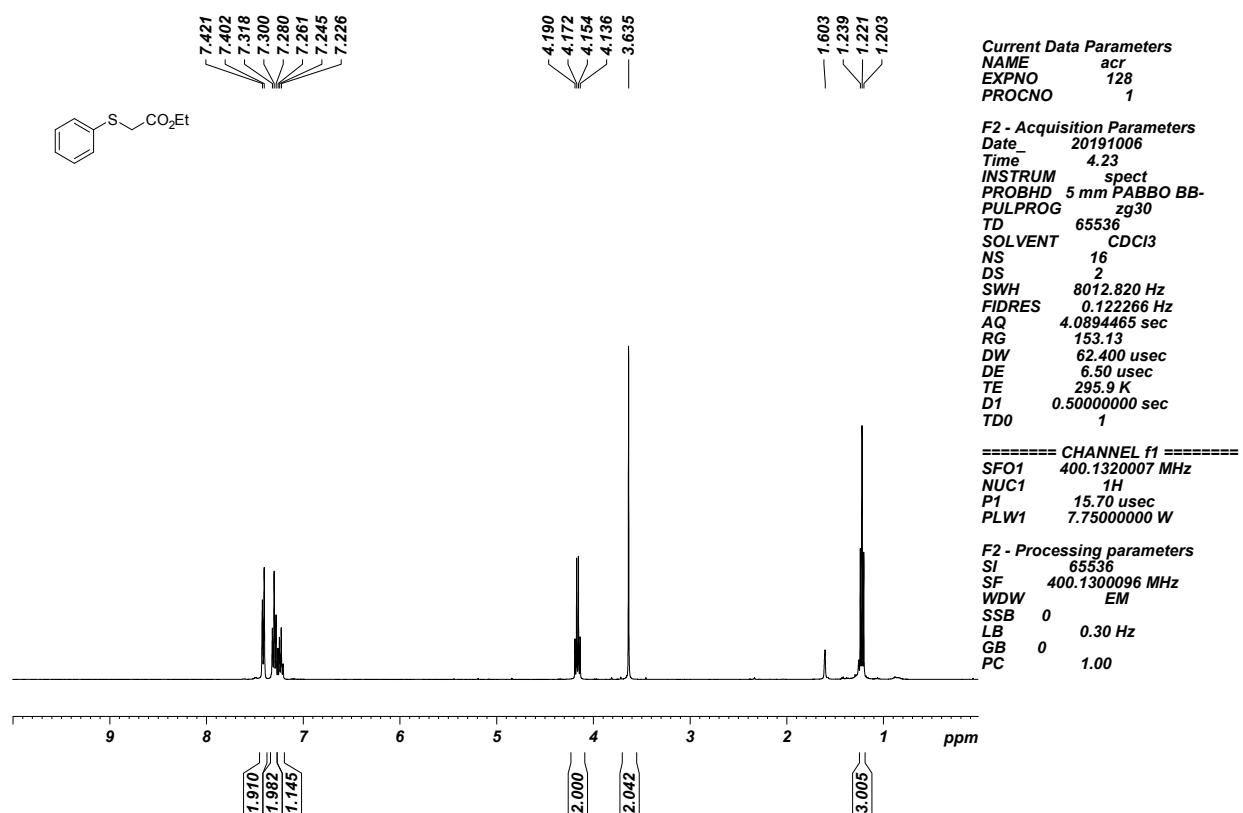


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

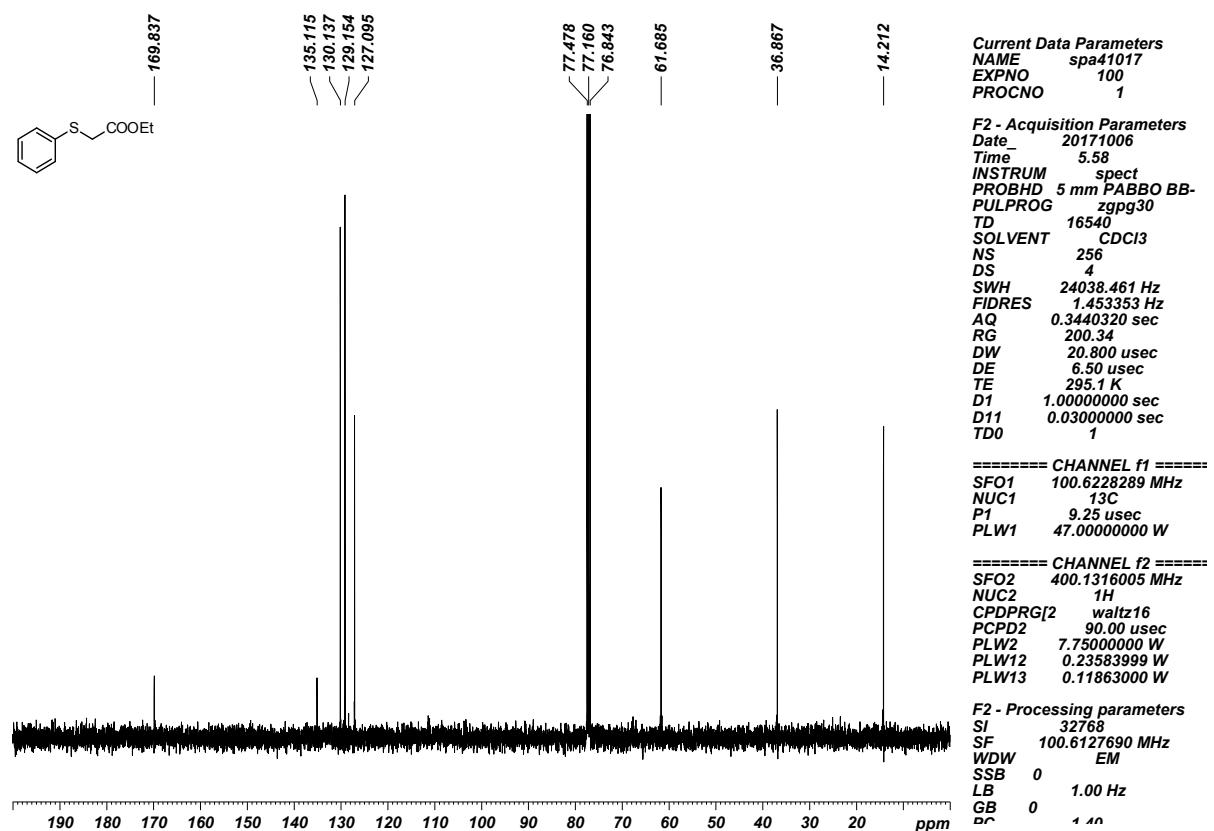


Thioester 1b

¹H NMR (400 MHz, CDCl₃, 24 °C)

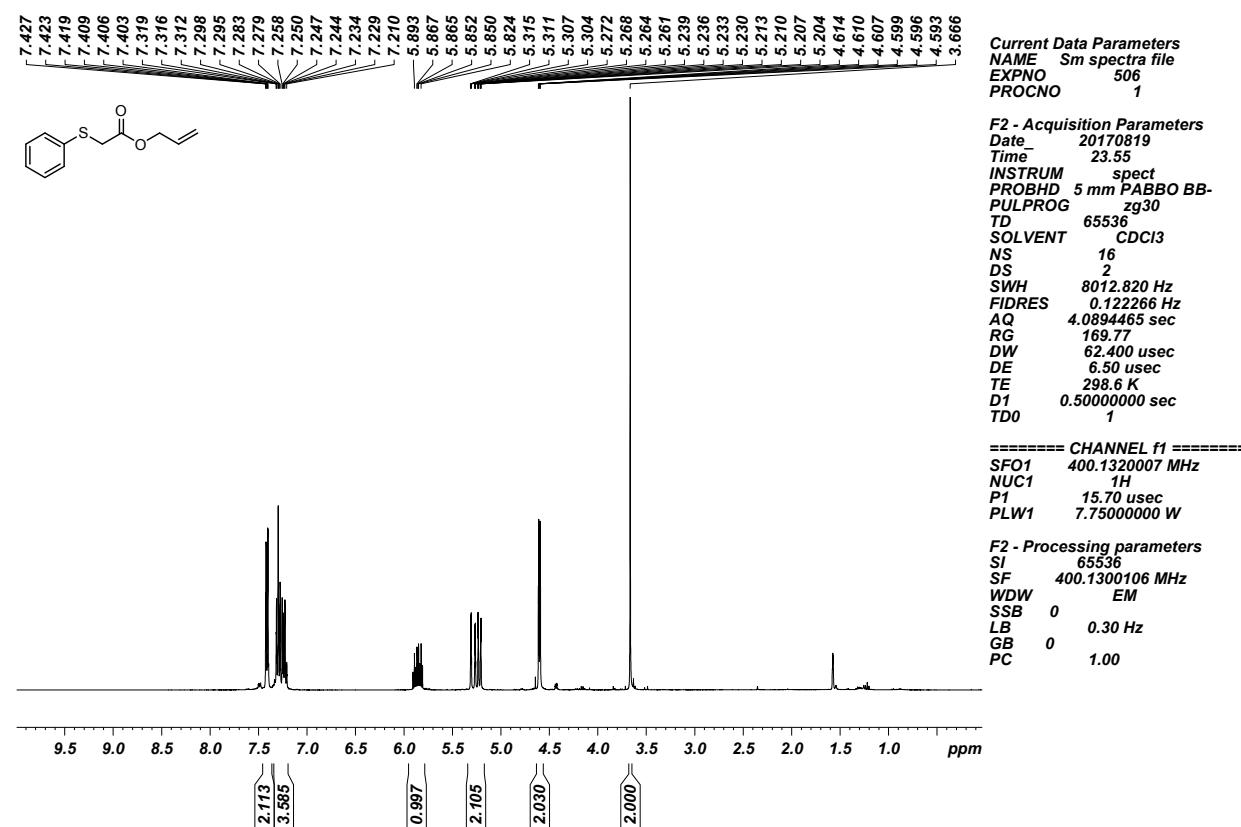


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

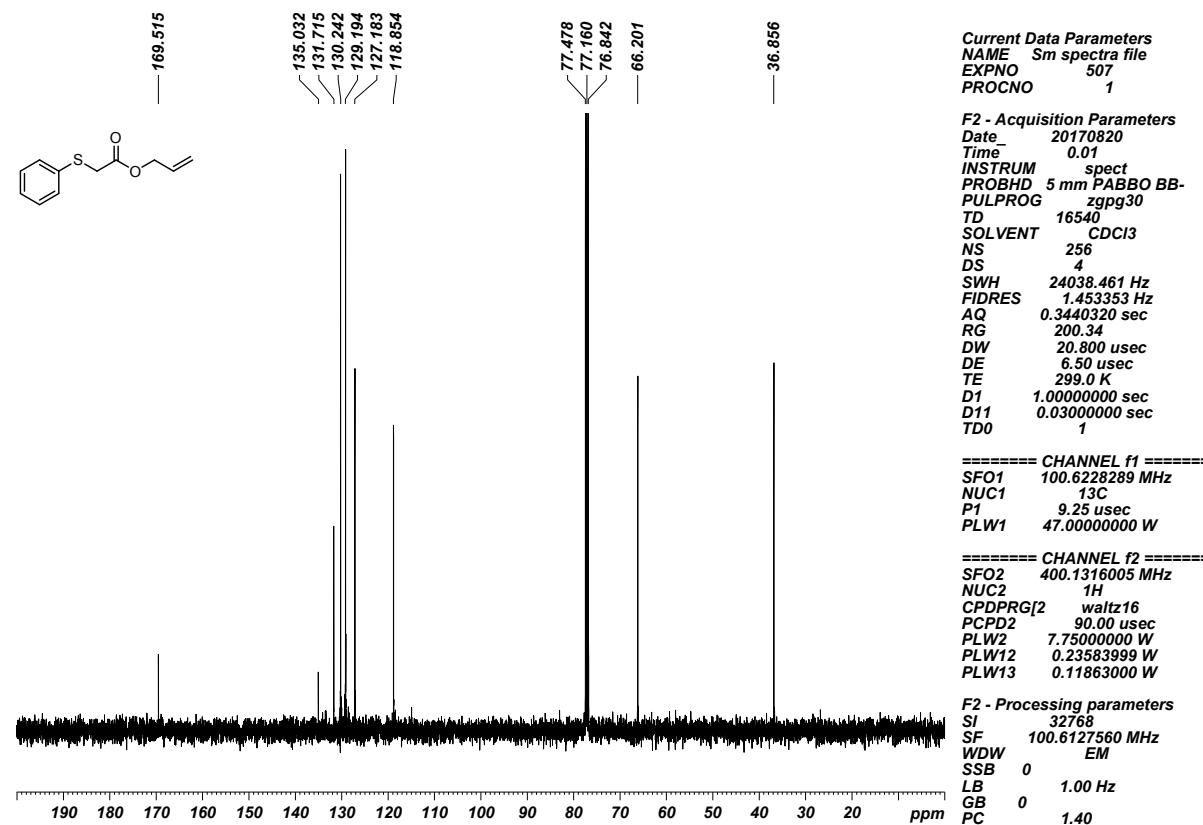


Thioester 1c

¹H NMR (400 MHz, CDCl₃, 24 °C)

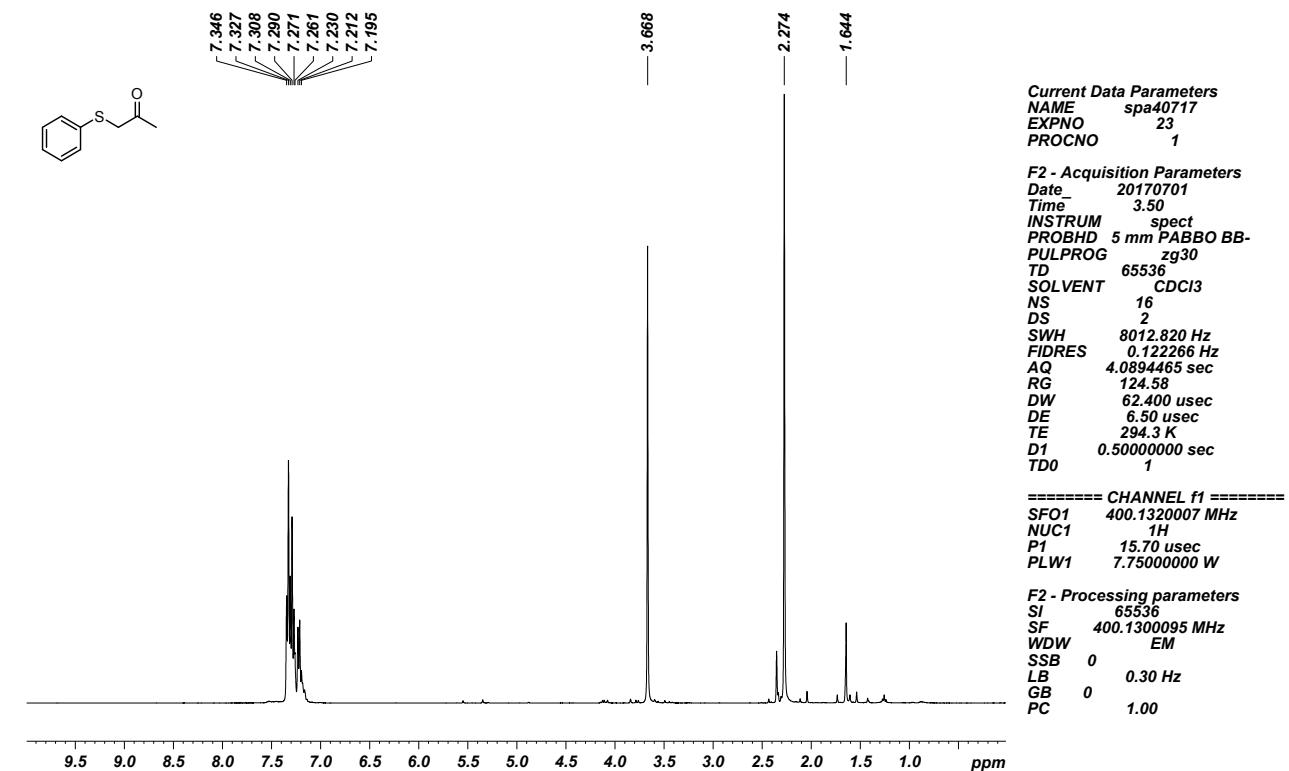


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

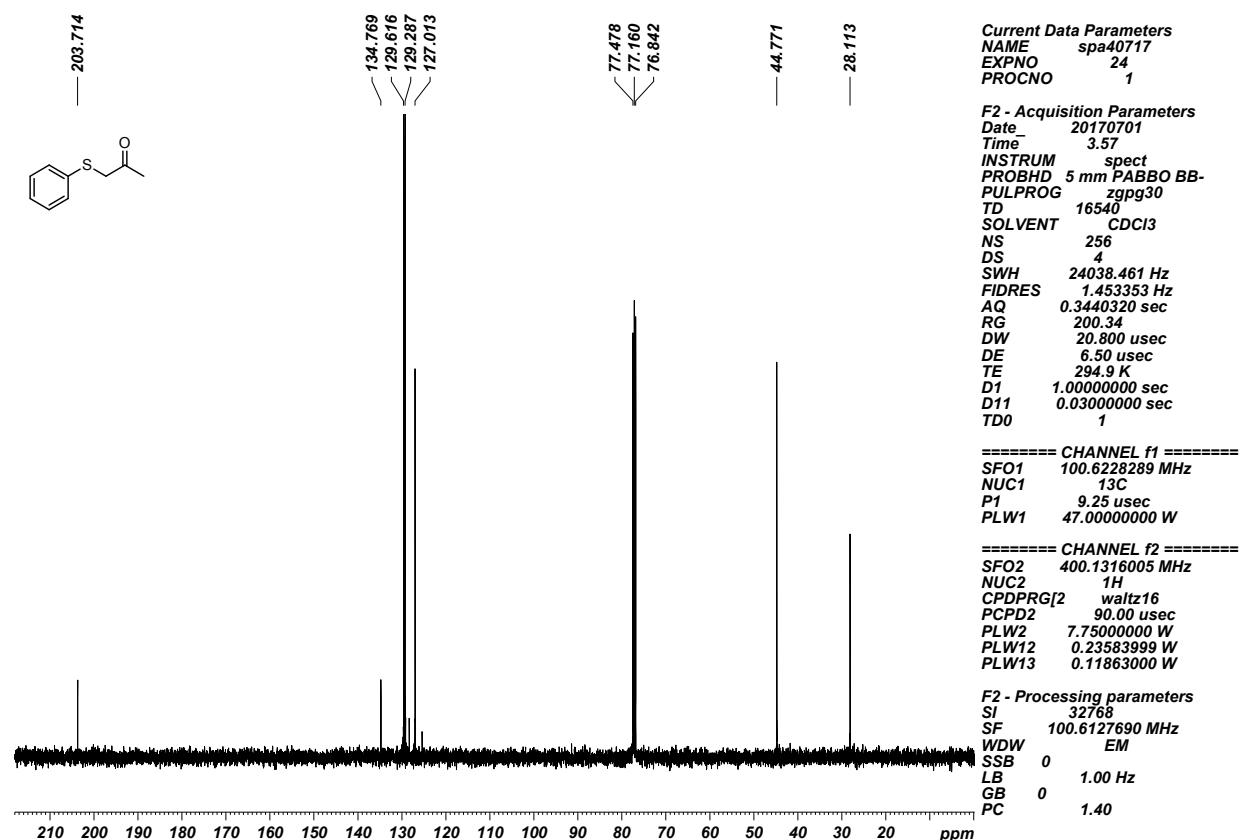


Thioketone 1d

¹H NMR (400 MHz, CDCl₃, 24 °C)

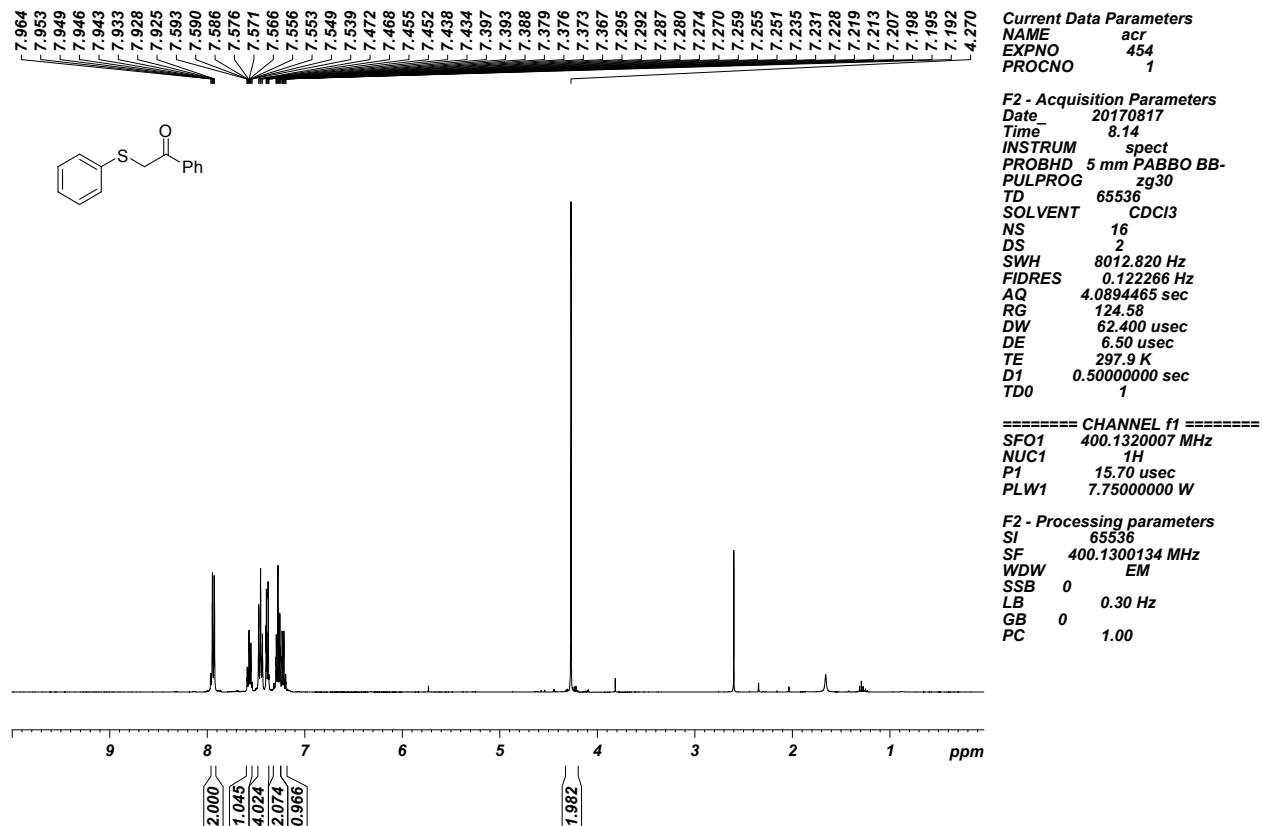


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

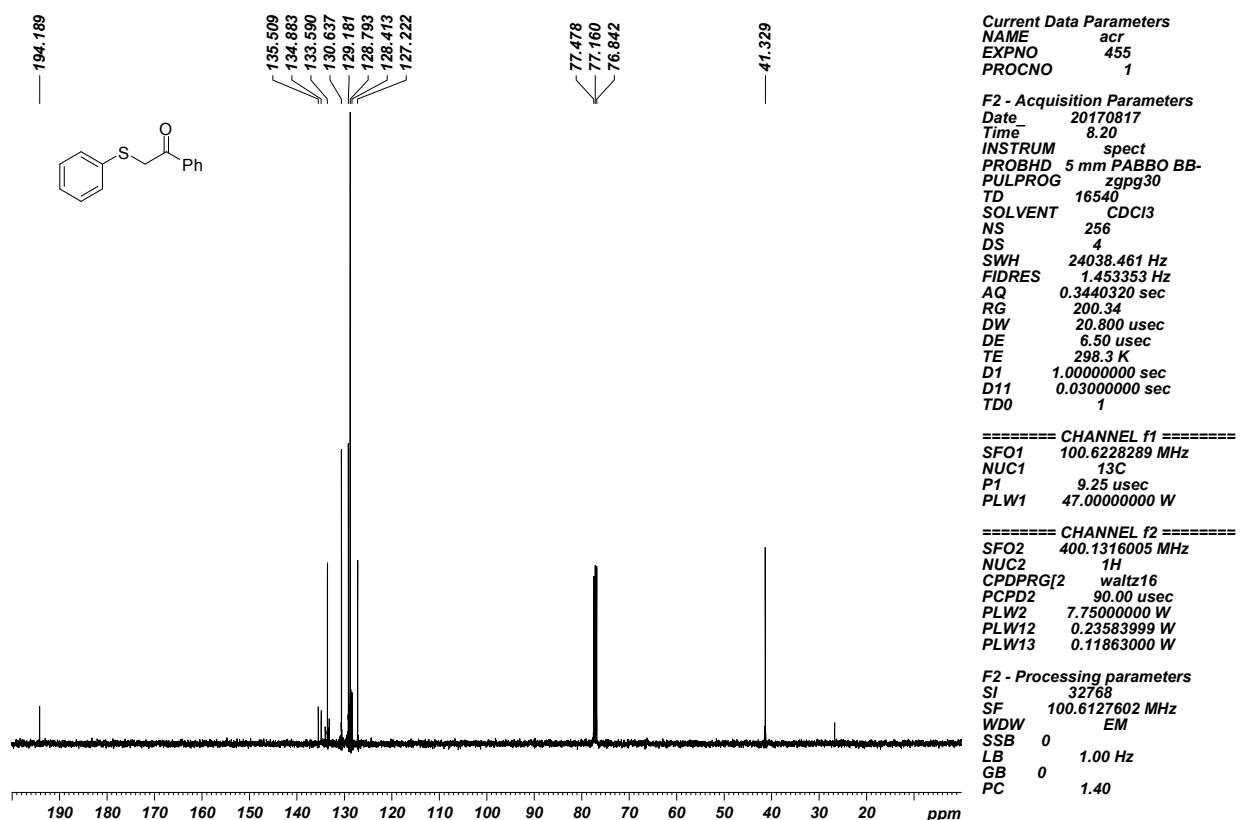


Thioketone 1e

¹H NMR (400 MHz, CDCl₃, 24 °C)

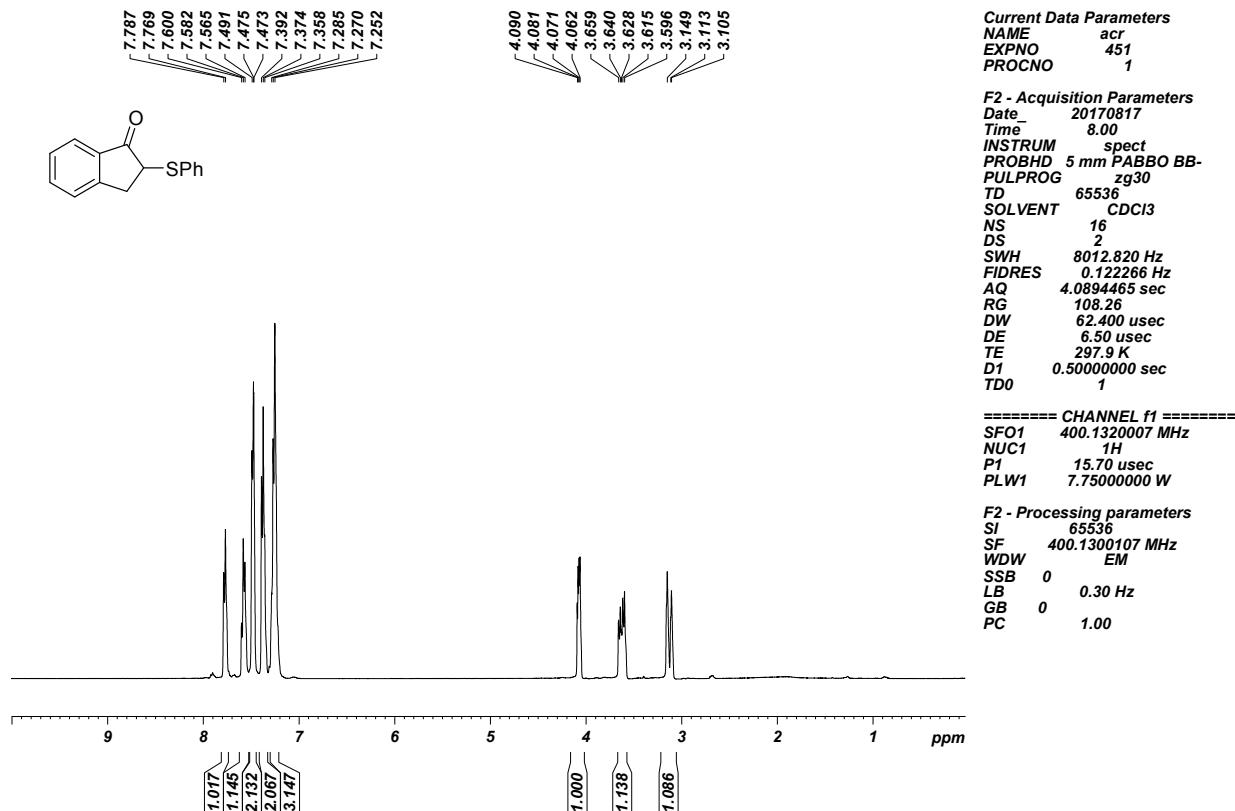


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

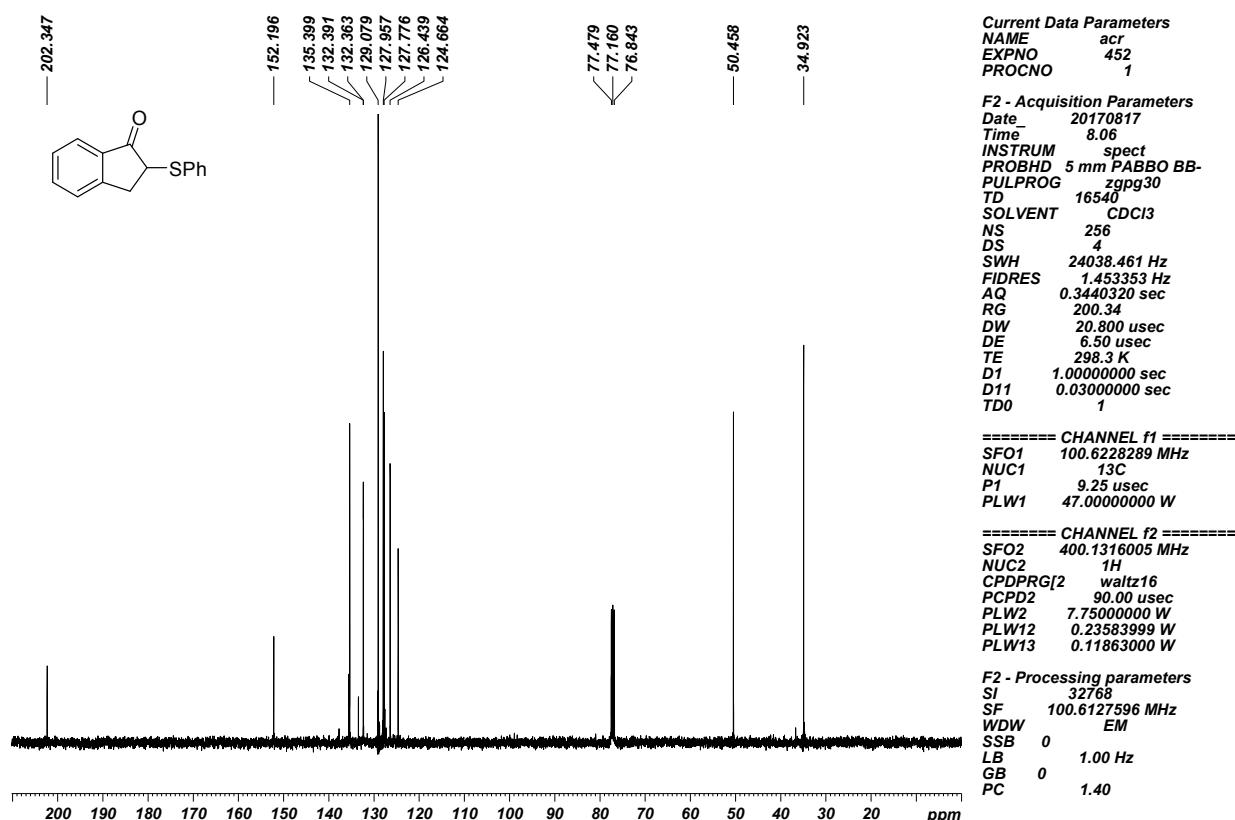


Thioketone 1f

¹H NMR (400 MHz, CDCl₃, 24 °C)

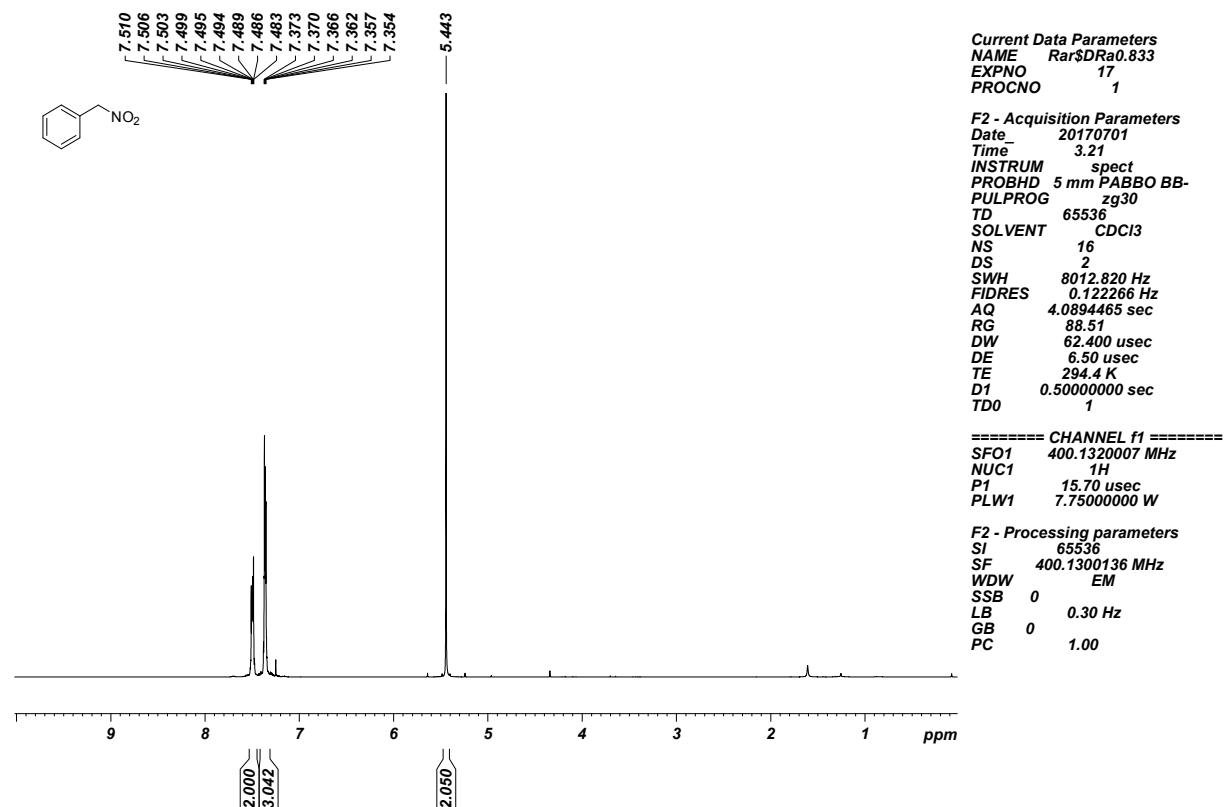


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

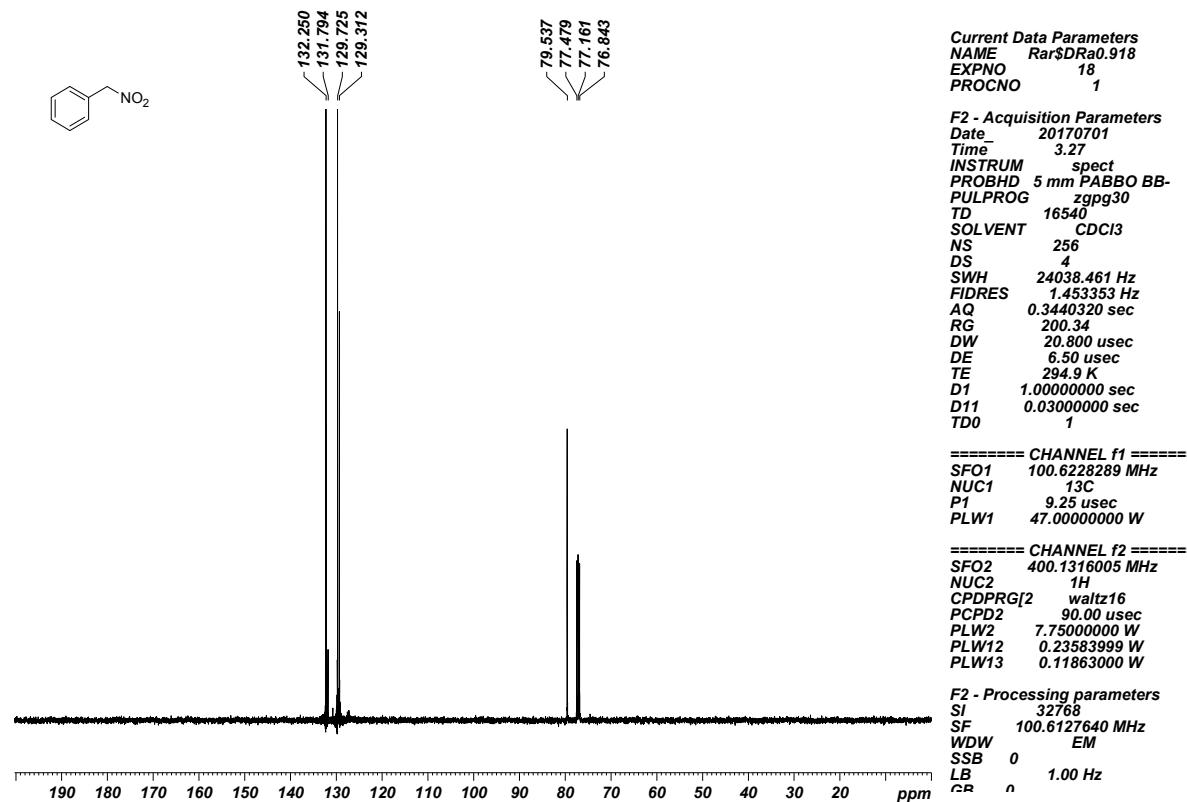


(Nitromethyl)benzene 1g

¹H NMR (400 MHz, CDCl₃, 24 °C)

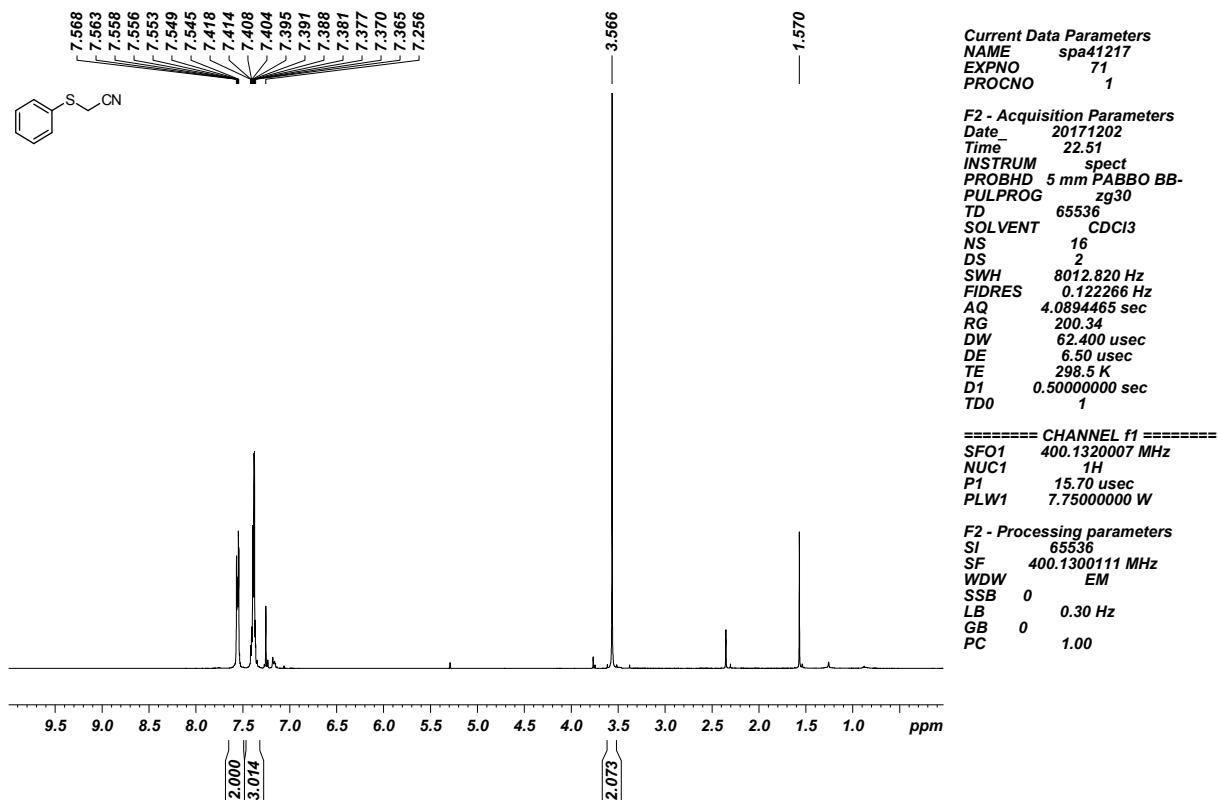


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

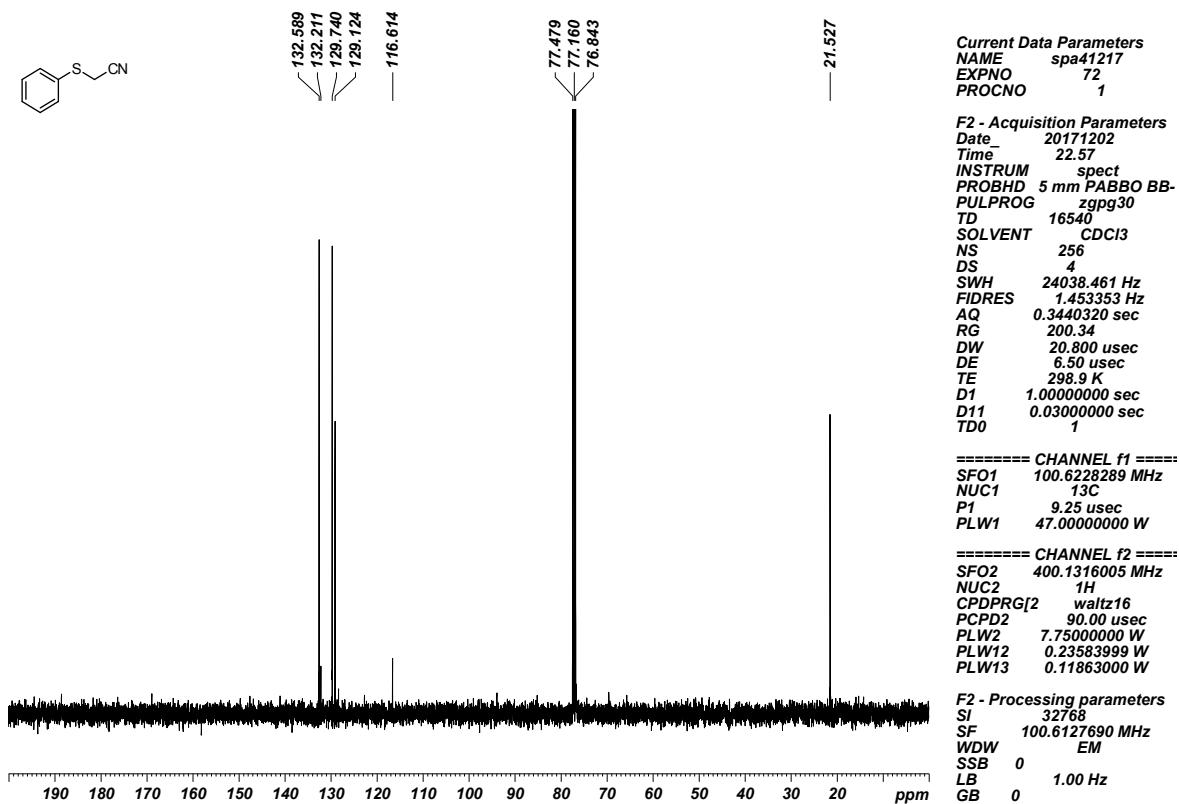


2-(Phenylthio)acetonitrile 1h

¹H NMR (400 MHz, CDCl₃, 24 °C)

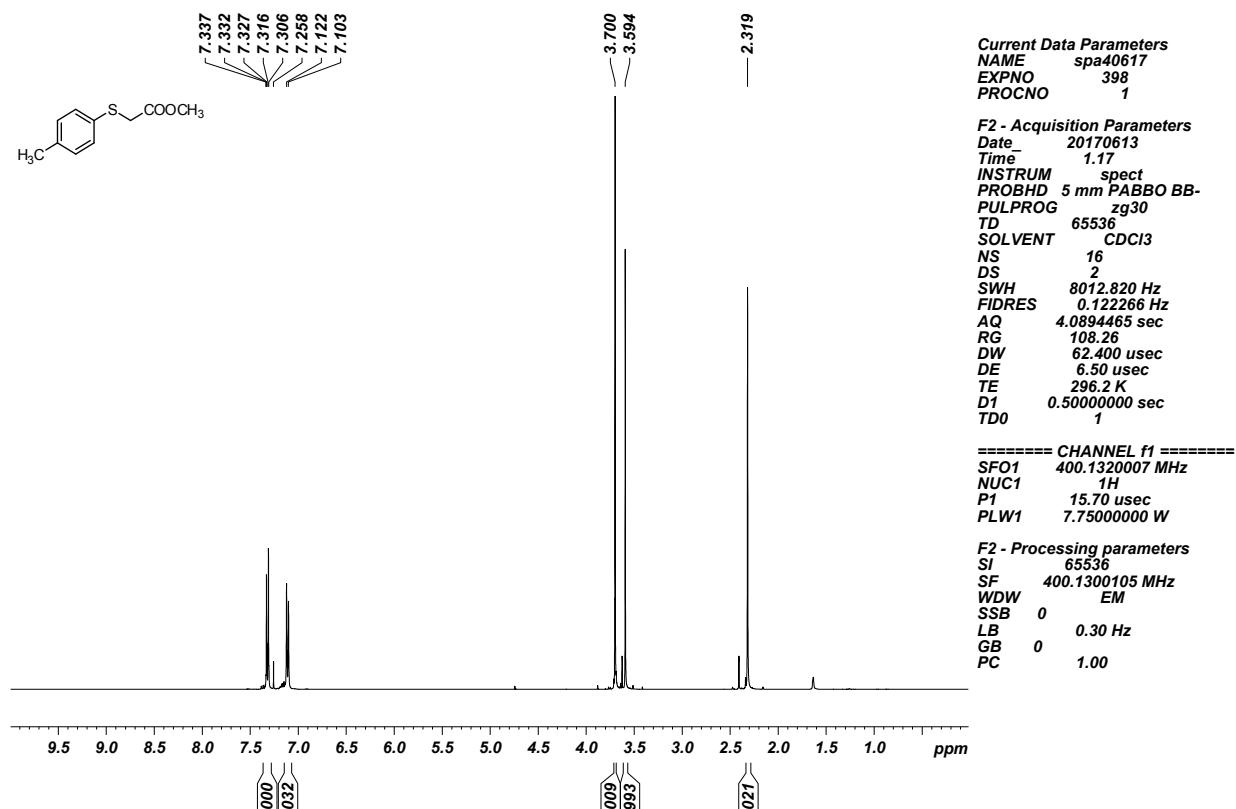


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

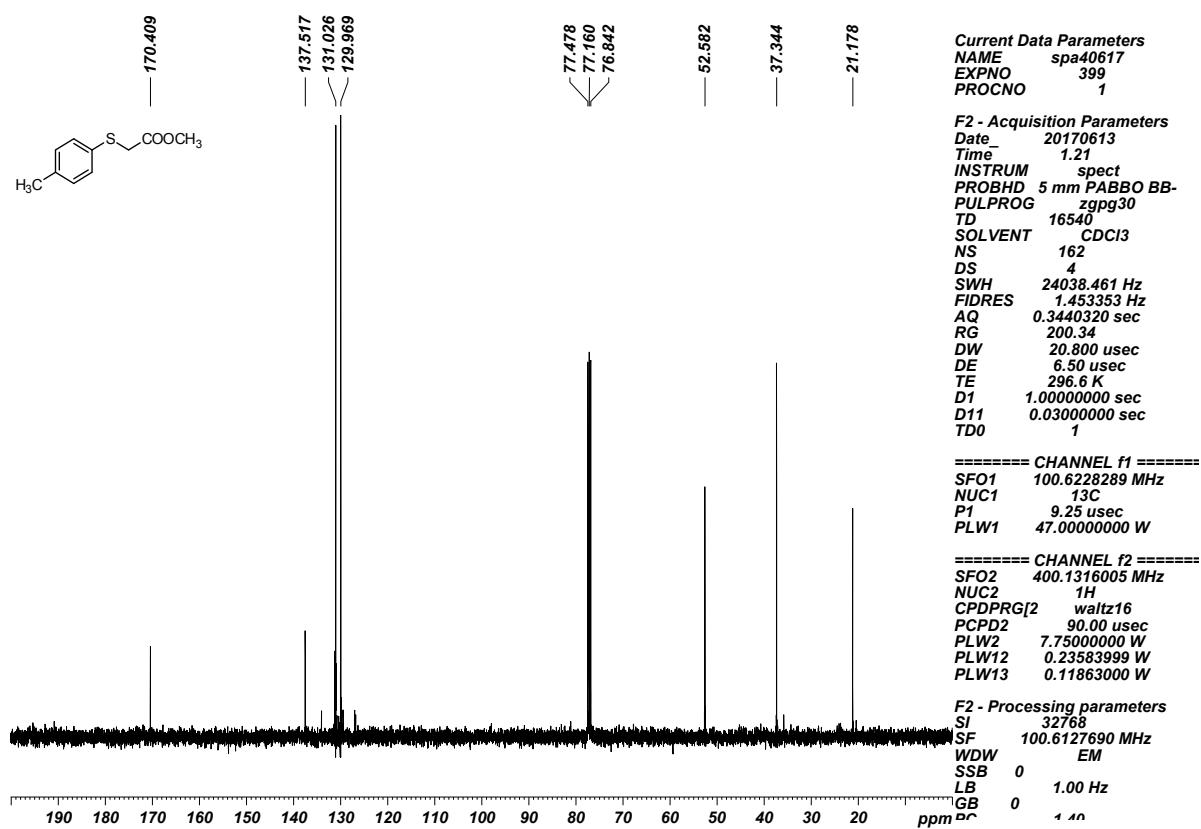


Thioester 1i

¹H NMR (400 MHz, CDCl₃, 24 °C)

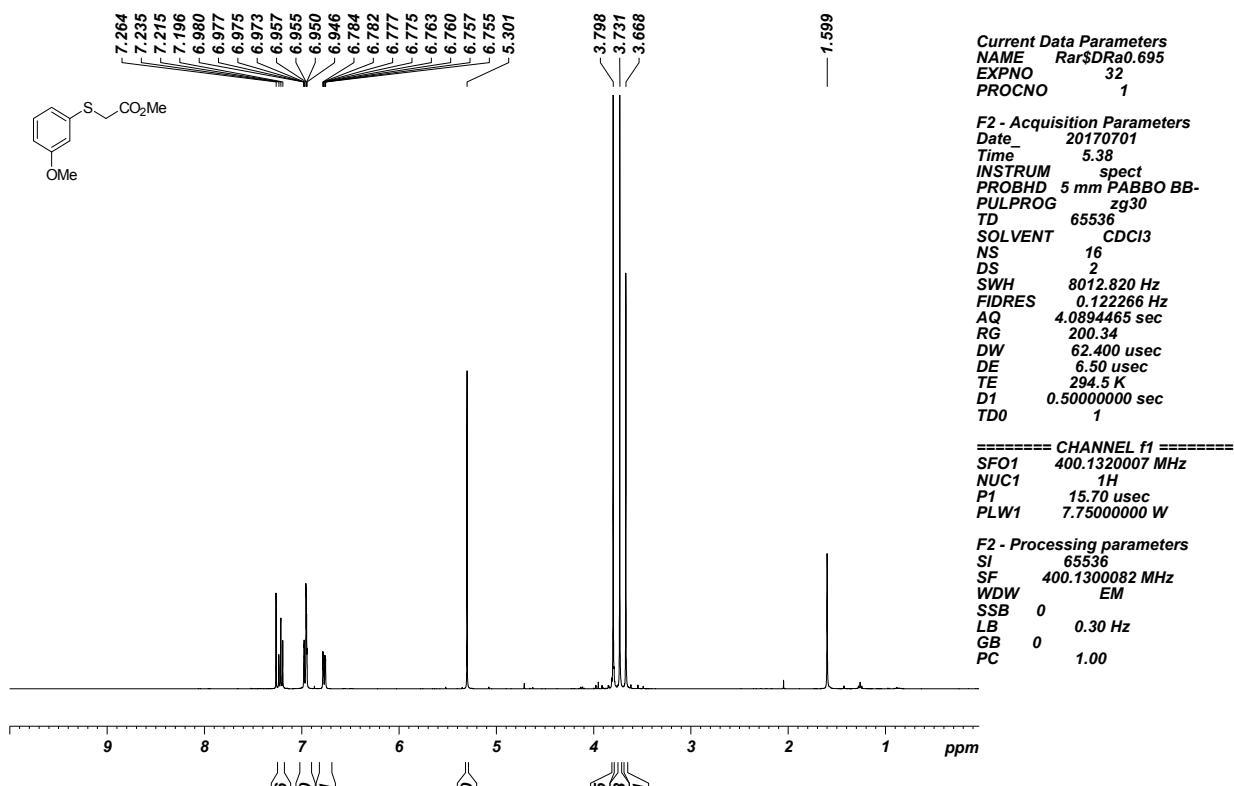


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

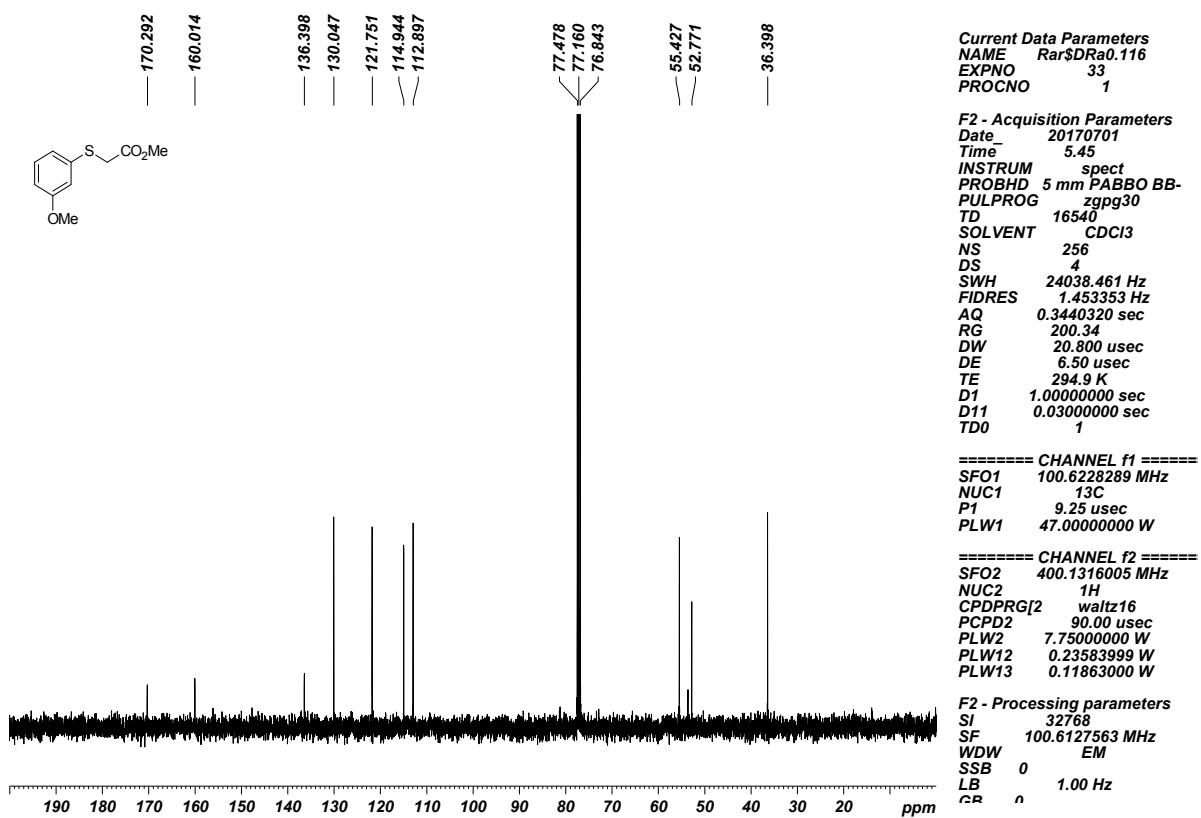


Thioester 1j

¹H NMR (400 MHz, CDCl₃, 24 °C)

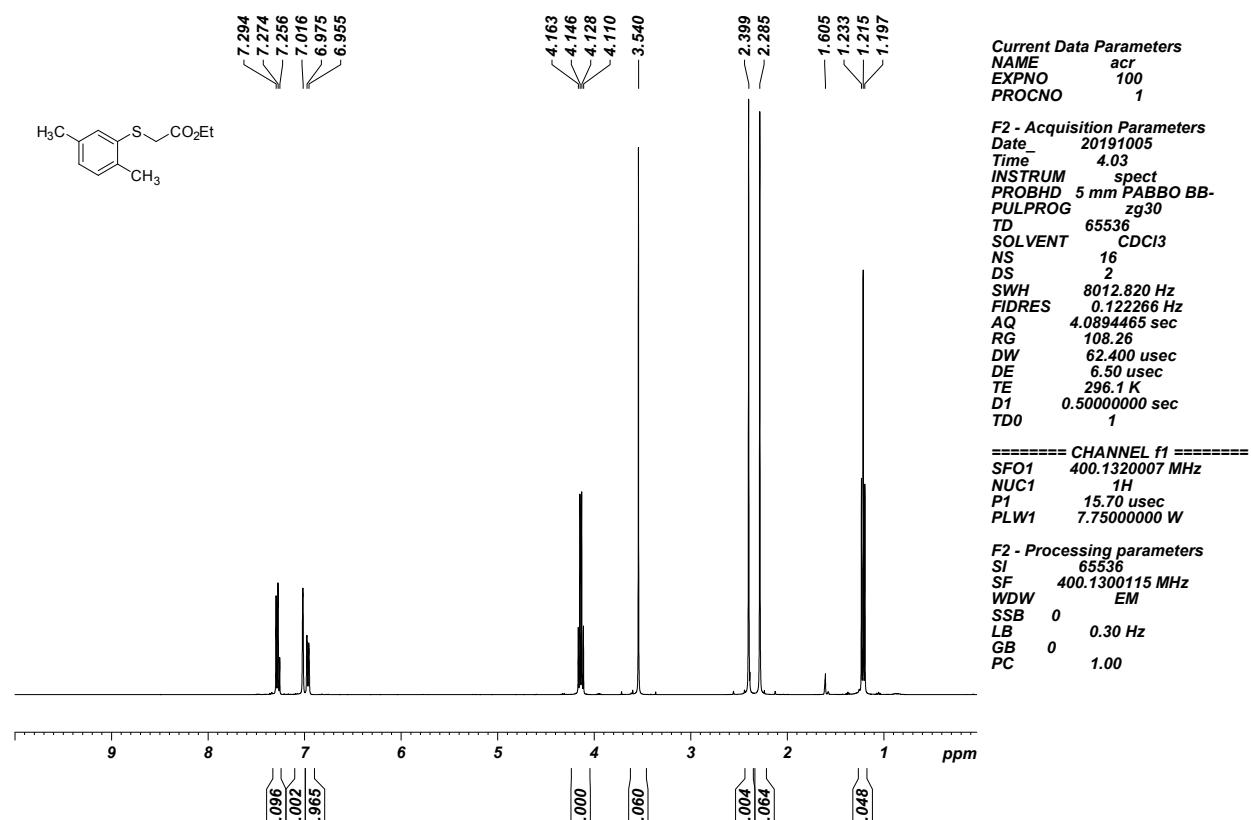


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

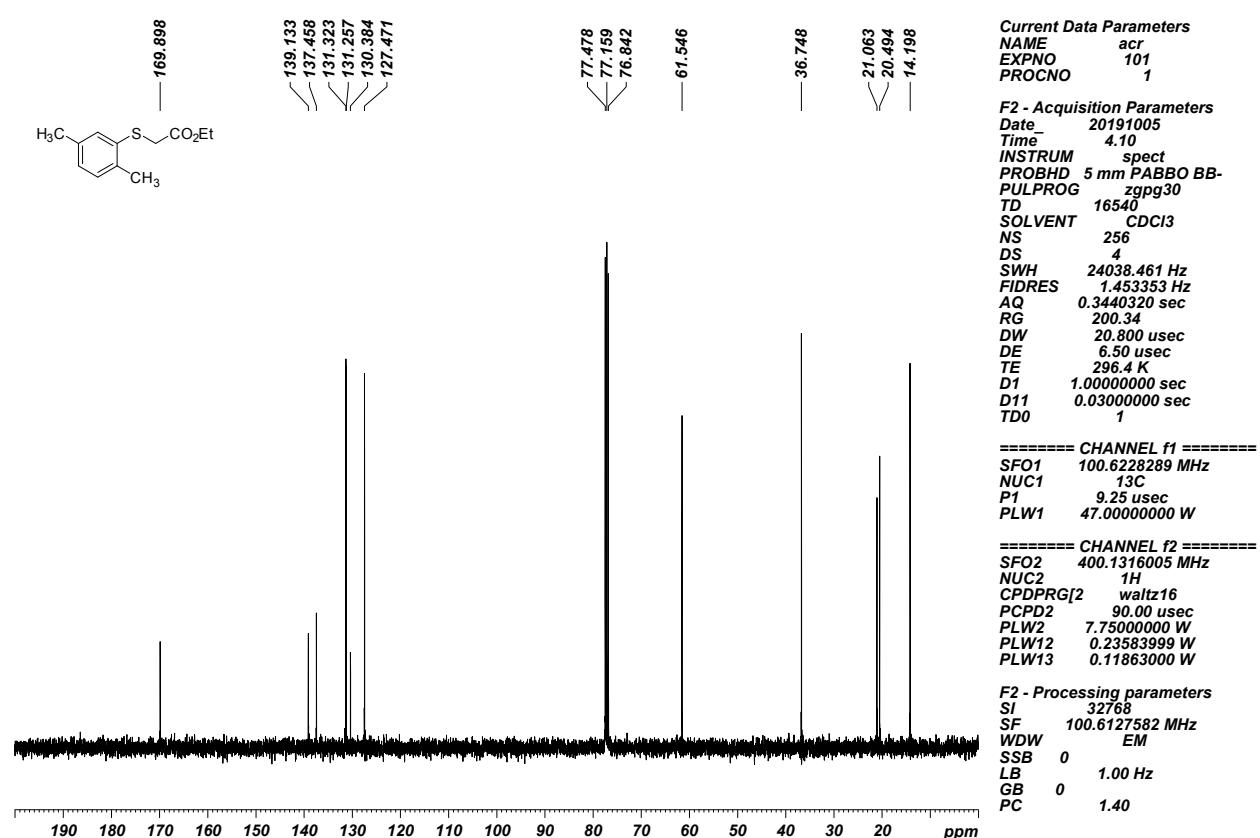


Thioester 1k

¹H NMR (400 MHz, CDCl₃, 24 °C)

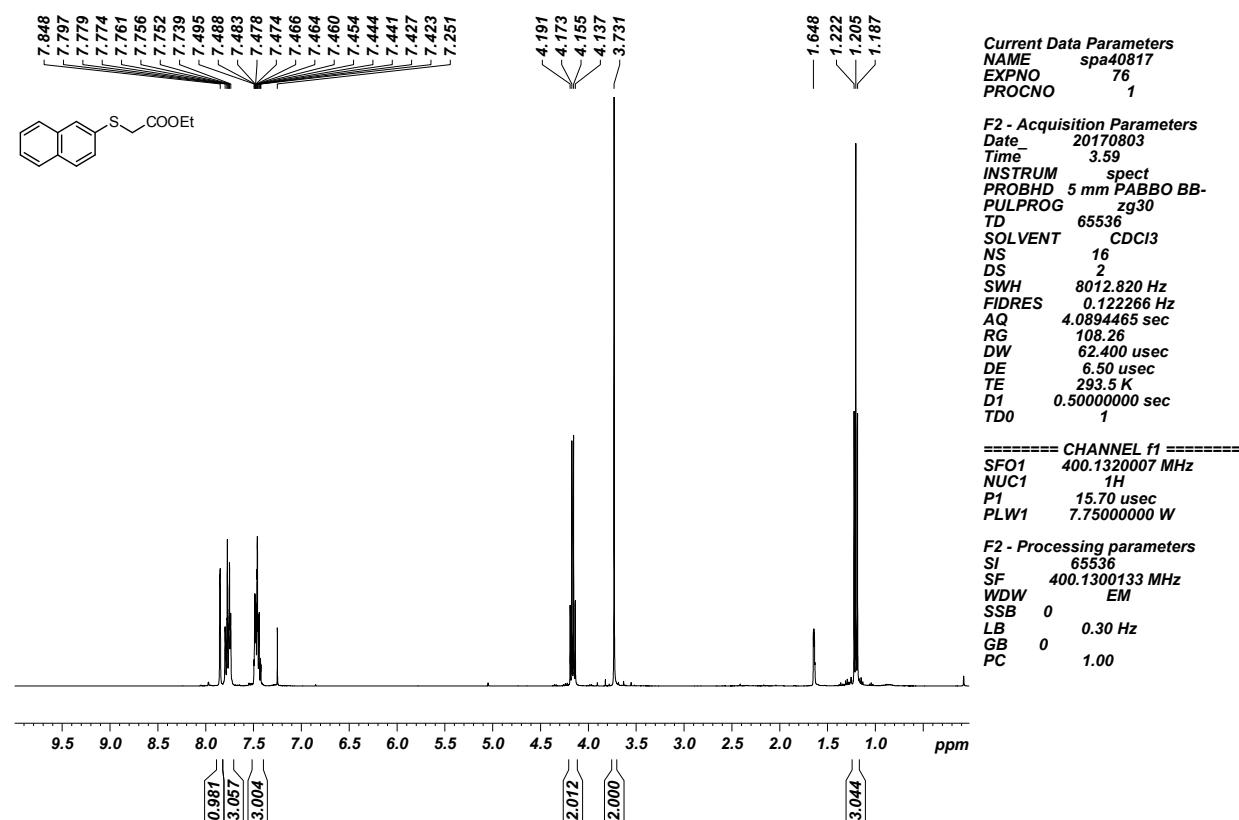


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

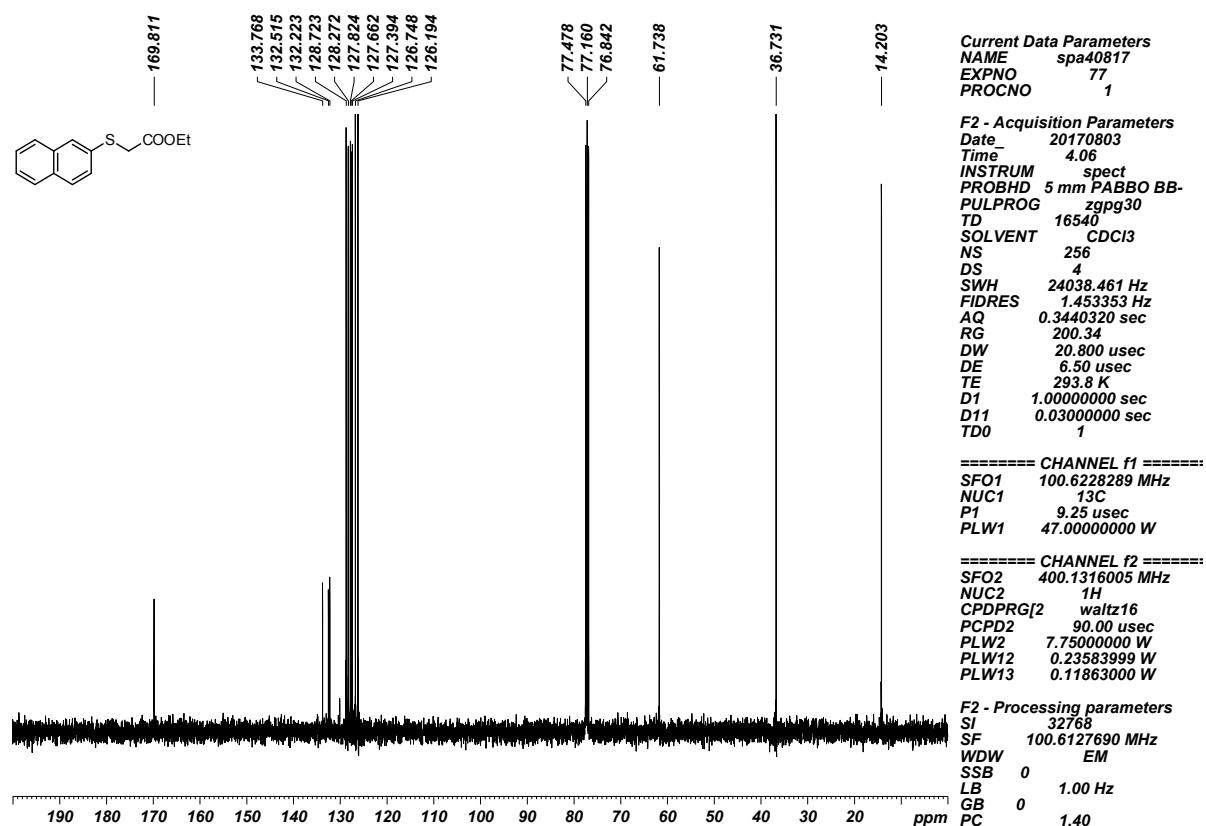


Thioester 11

¹H NMR (400 MHz, CDCl₃, 24 °C)

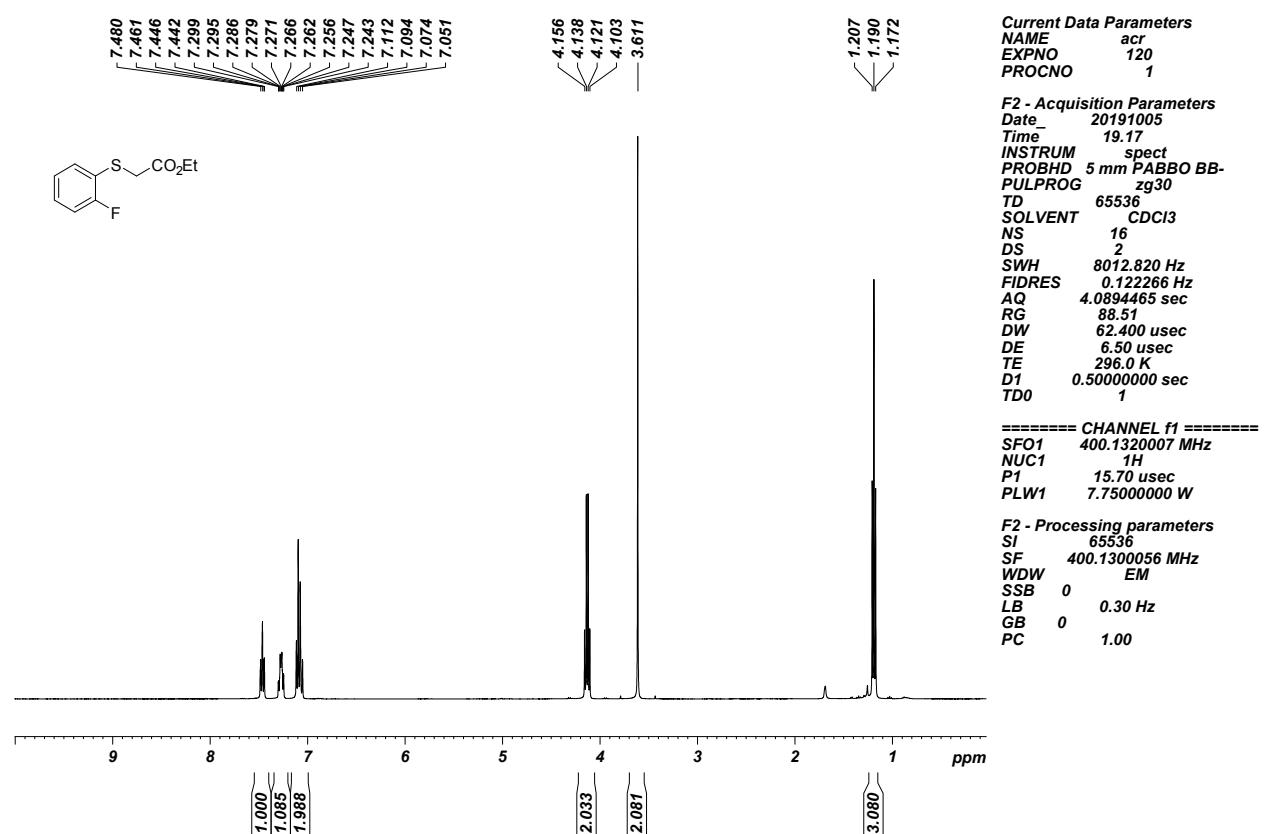


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

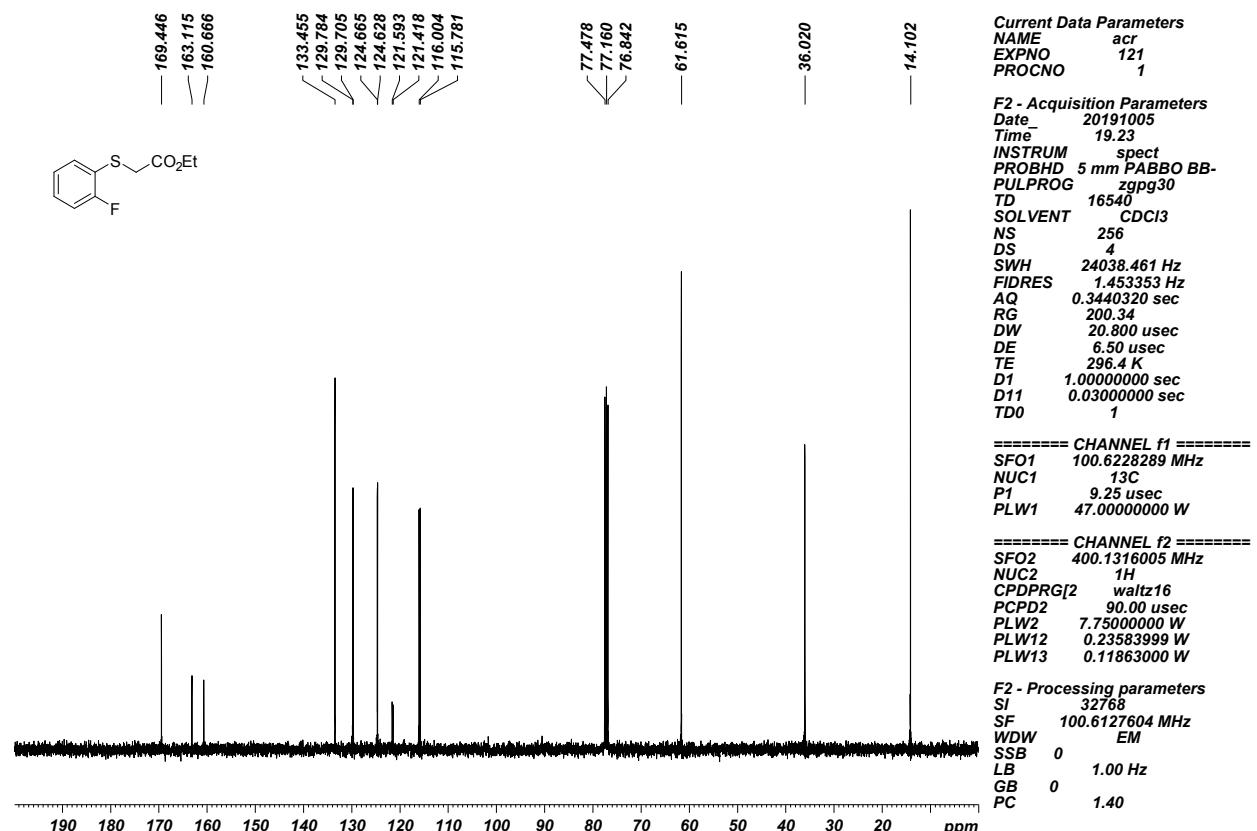


Thioester 1m

¹H NMR (400 MHz, CDCl₃, 24 °C)

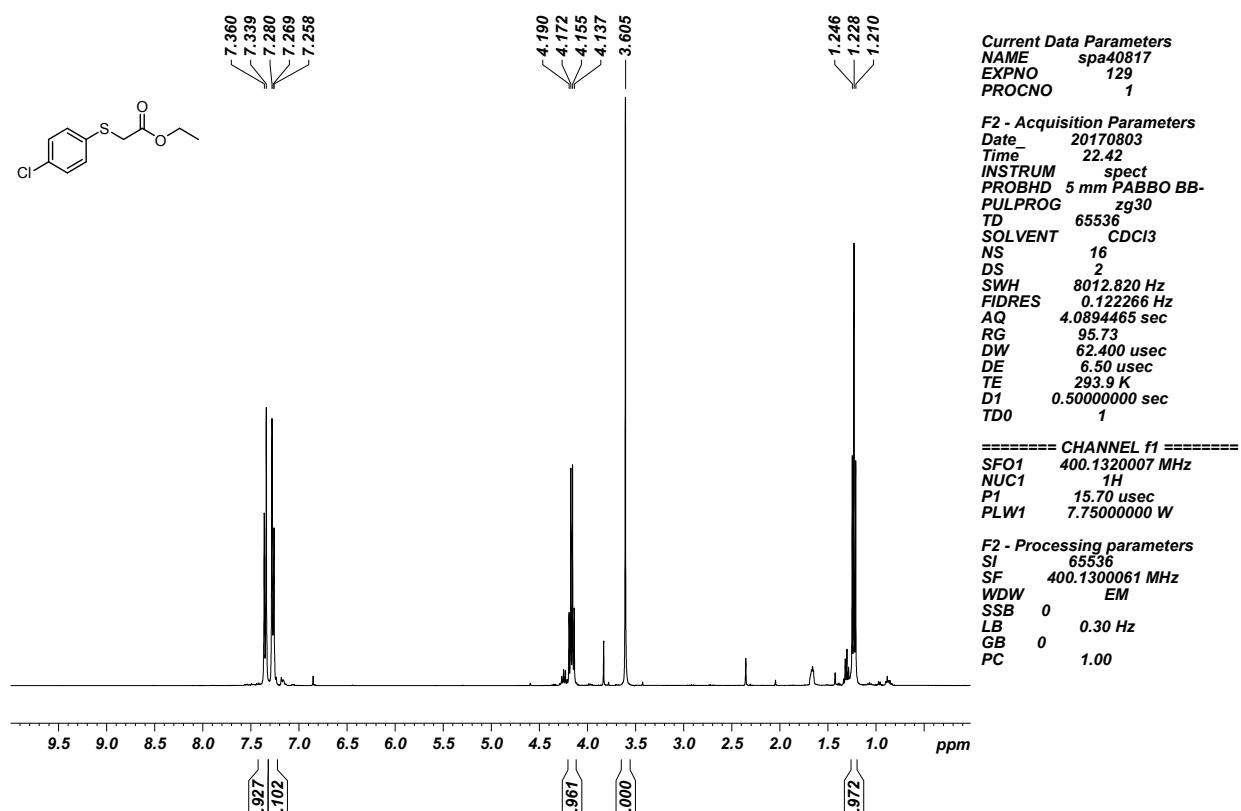


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

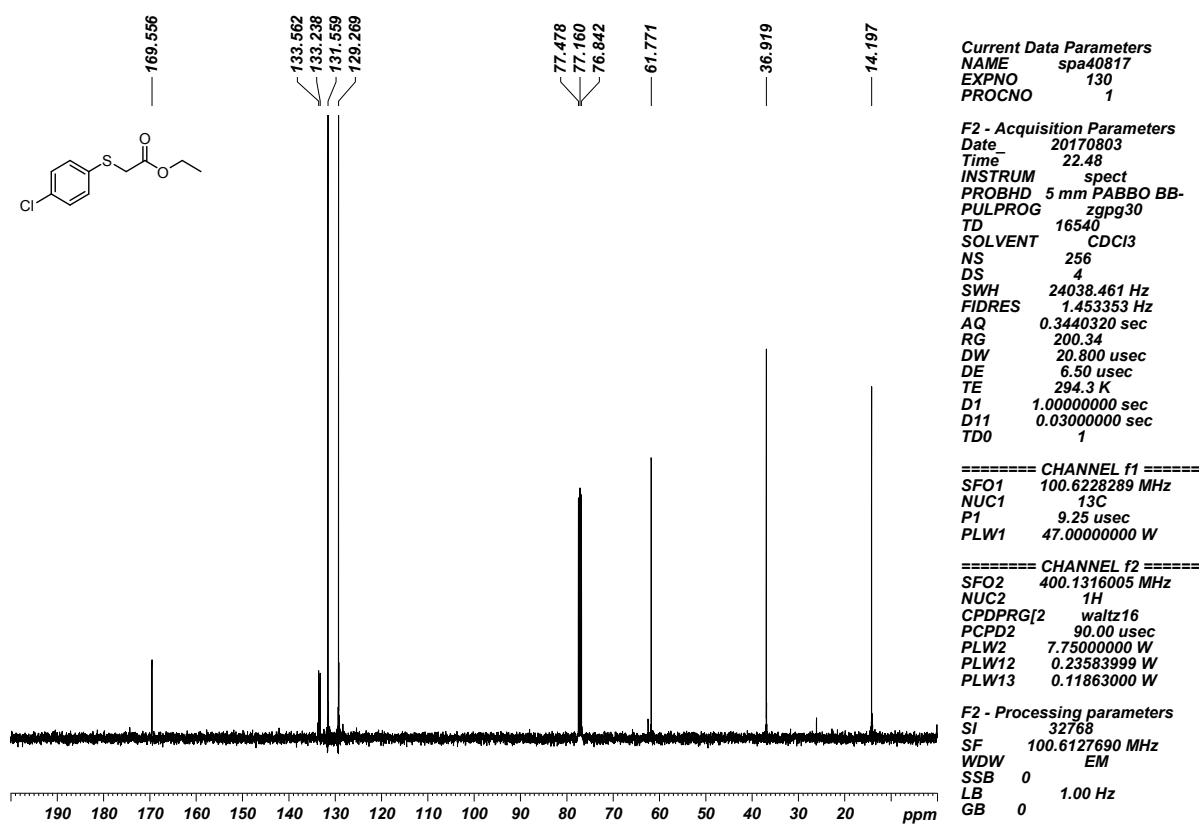


Thioester 1n

¹H NMR (400 MHz, CDCl₃, 24 °C)

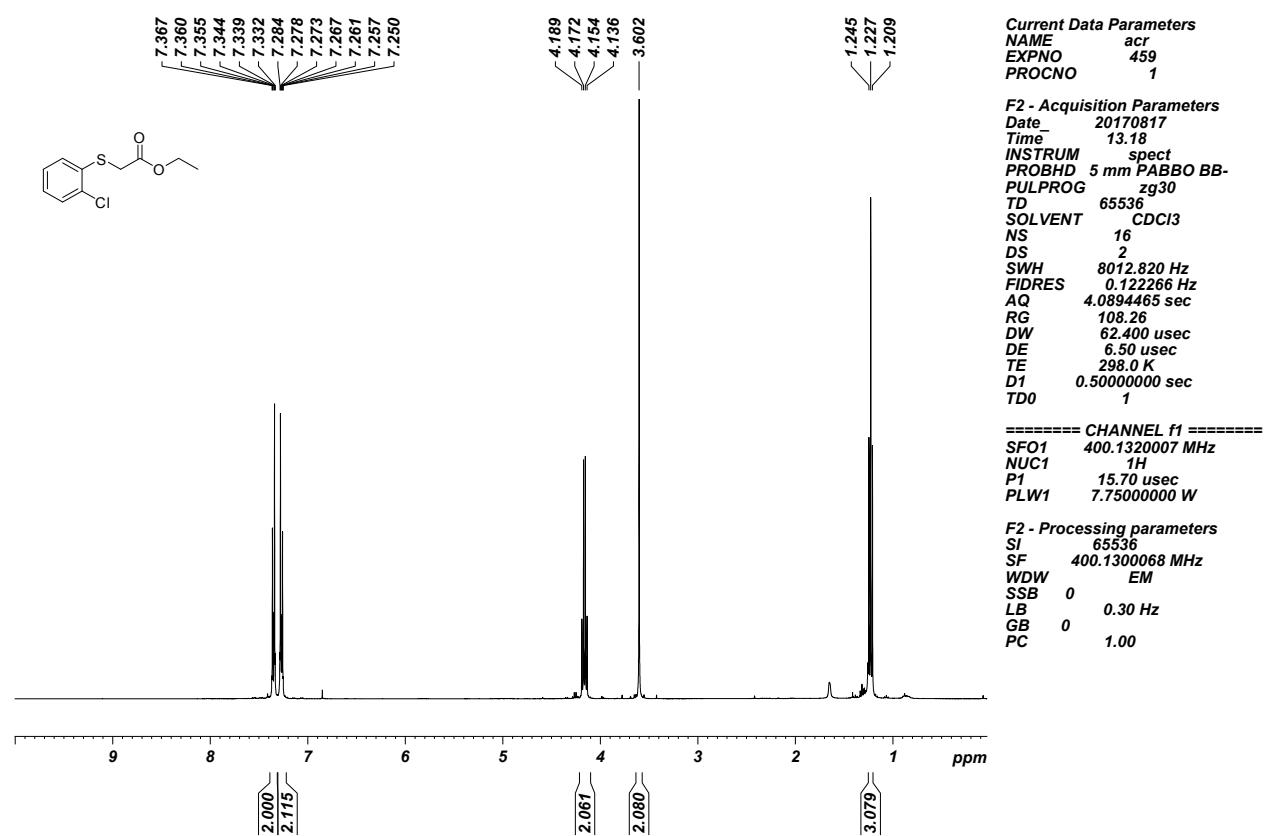


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

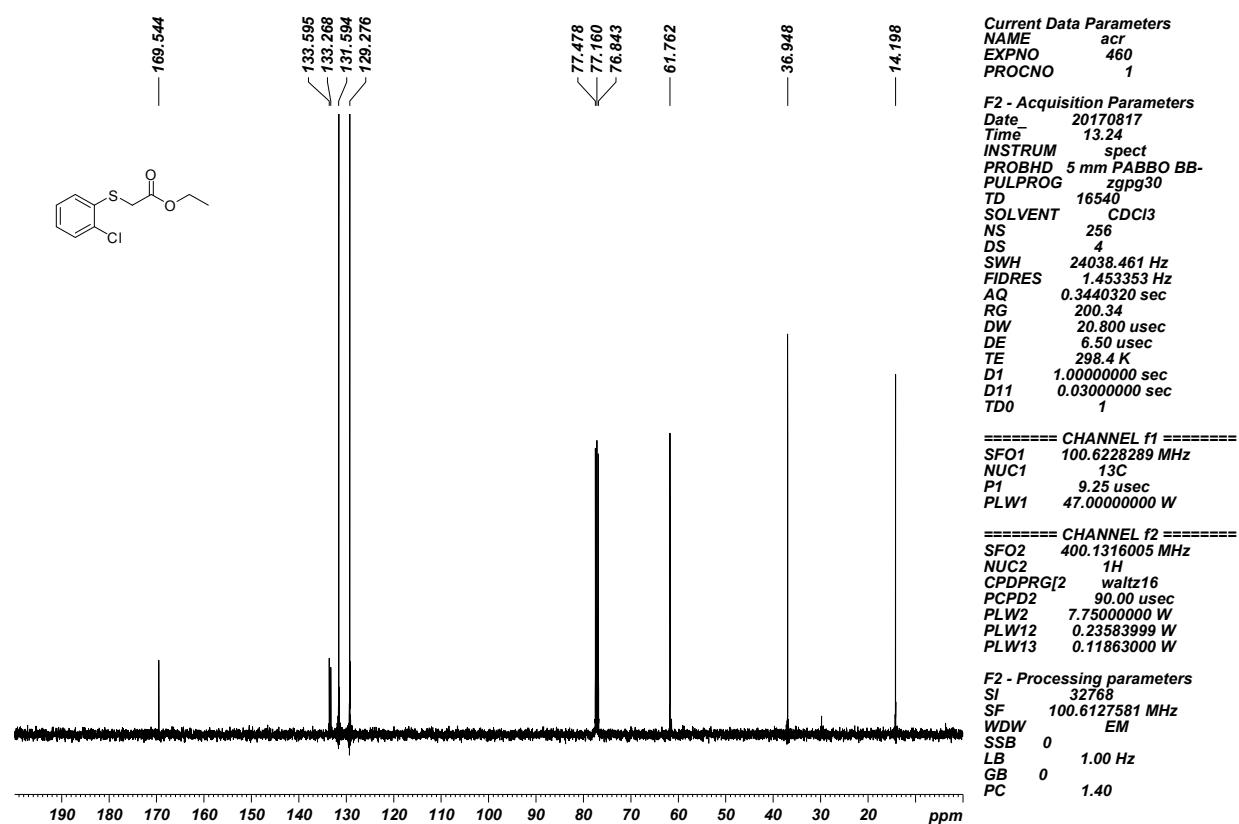


Thioester 1o

¹H NMR (400 MHz, CDCl₃, 24 °C)

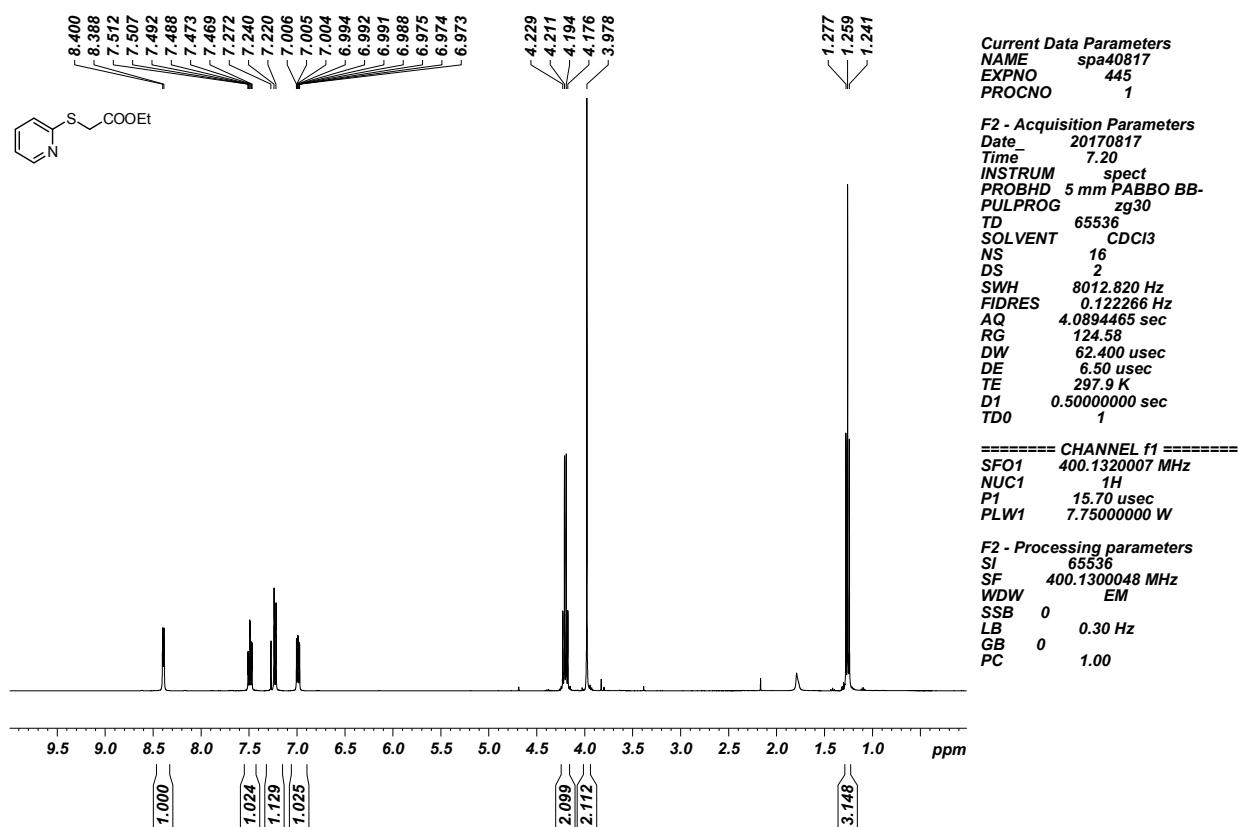


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

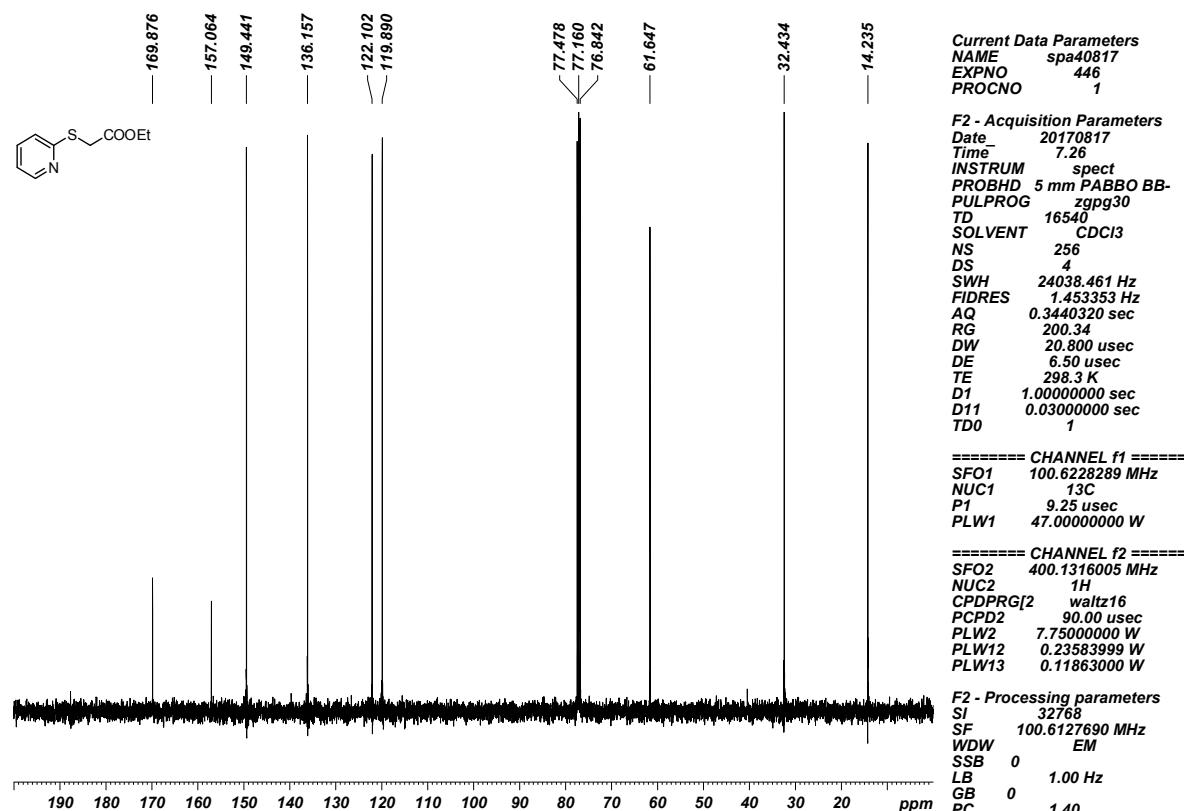


Thioester 1p

¹H NMR (400 MHz, CDCl₃, 24 °C)

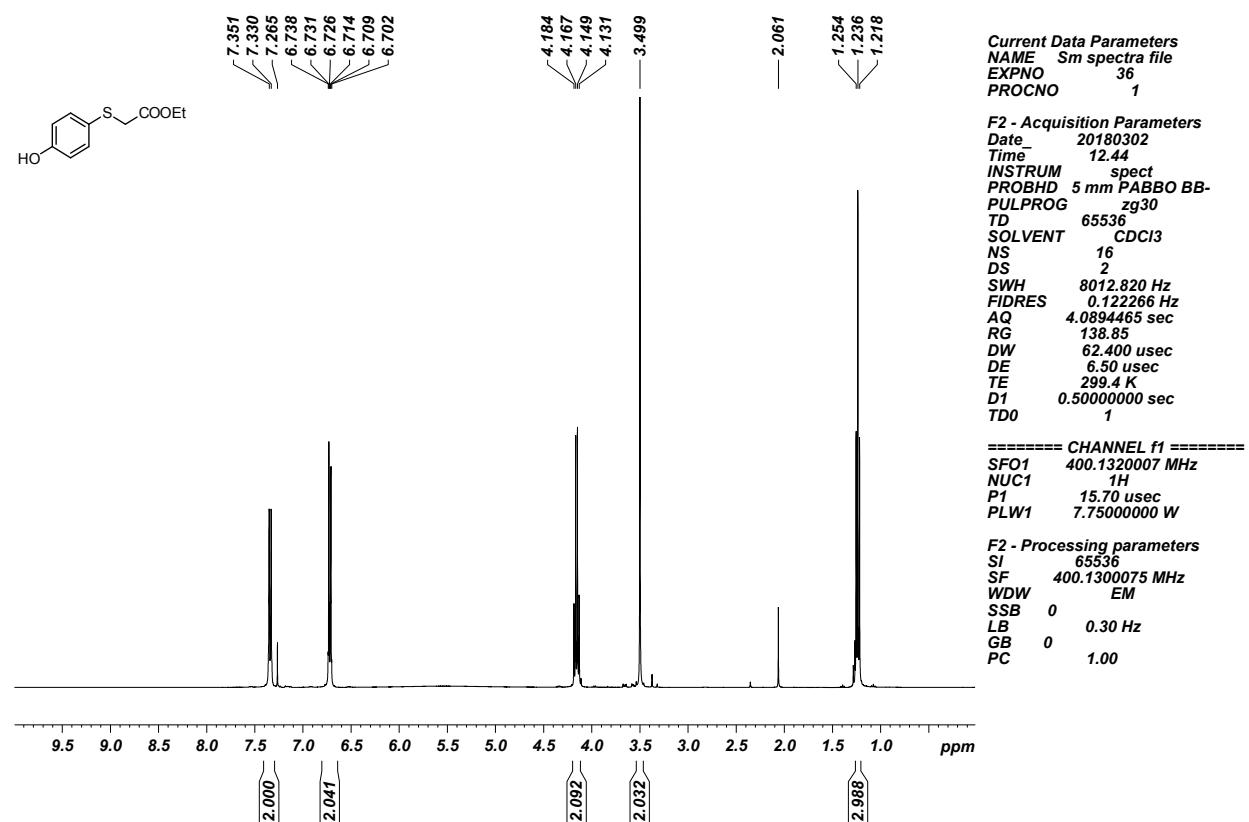


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

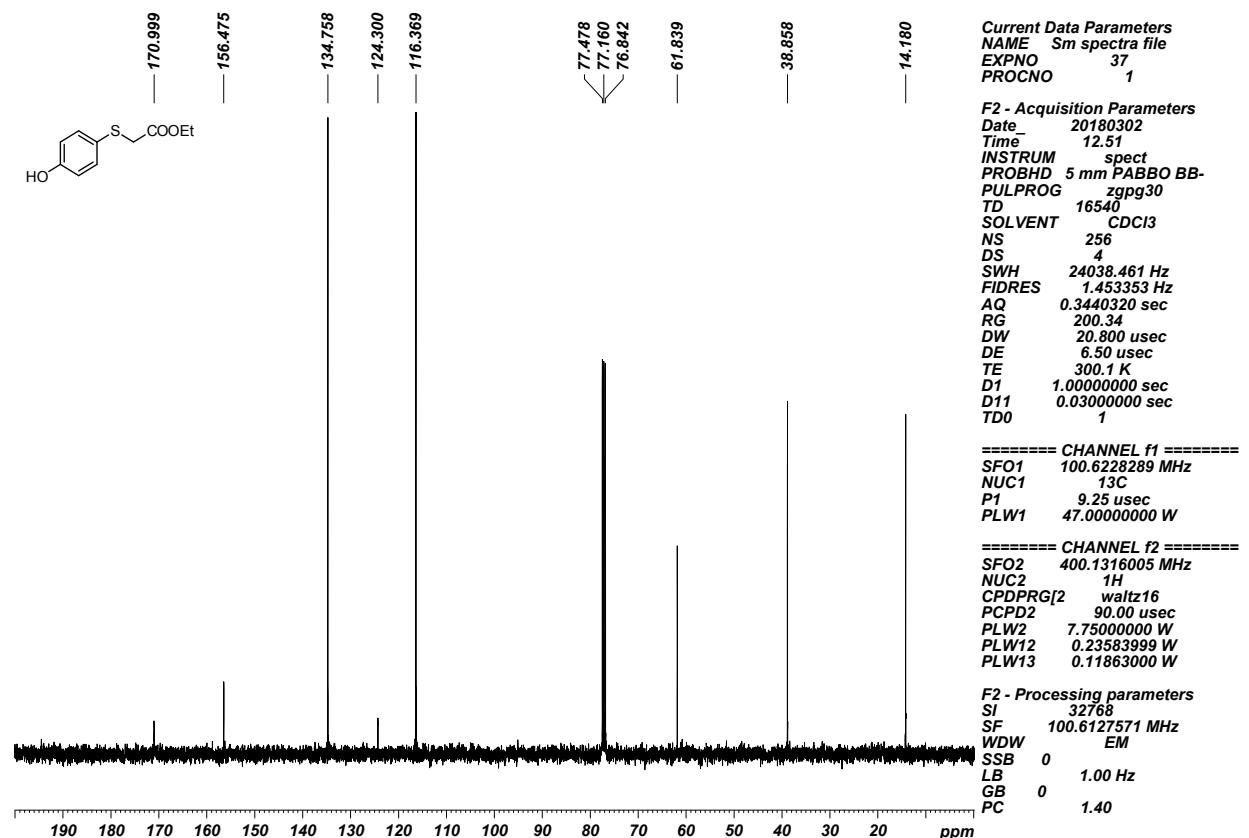


Thioester 1q

¹H NMR (400 MHz, CDCl₃, 24 °C)

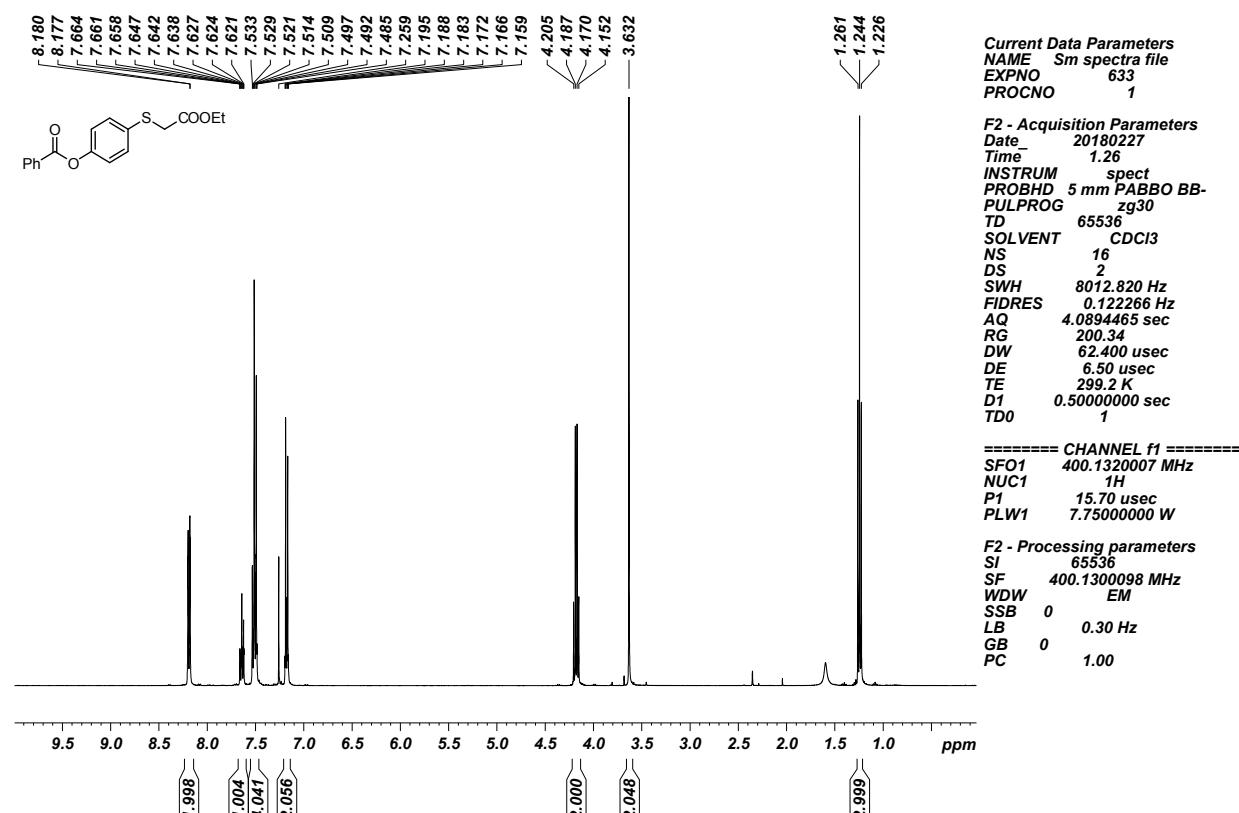


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

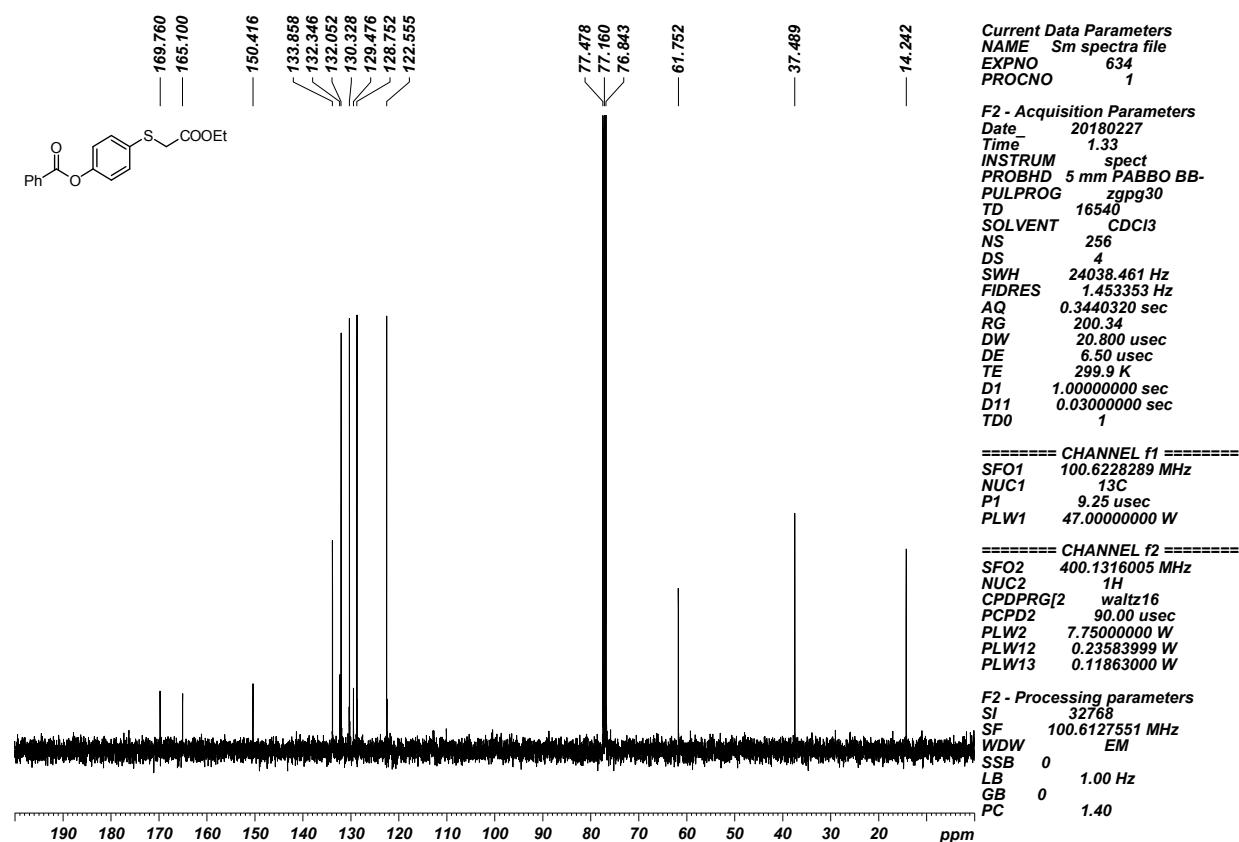


Thioester 1r

¹H NMR (400 MHz, CDCl₃, 24 °C)

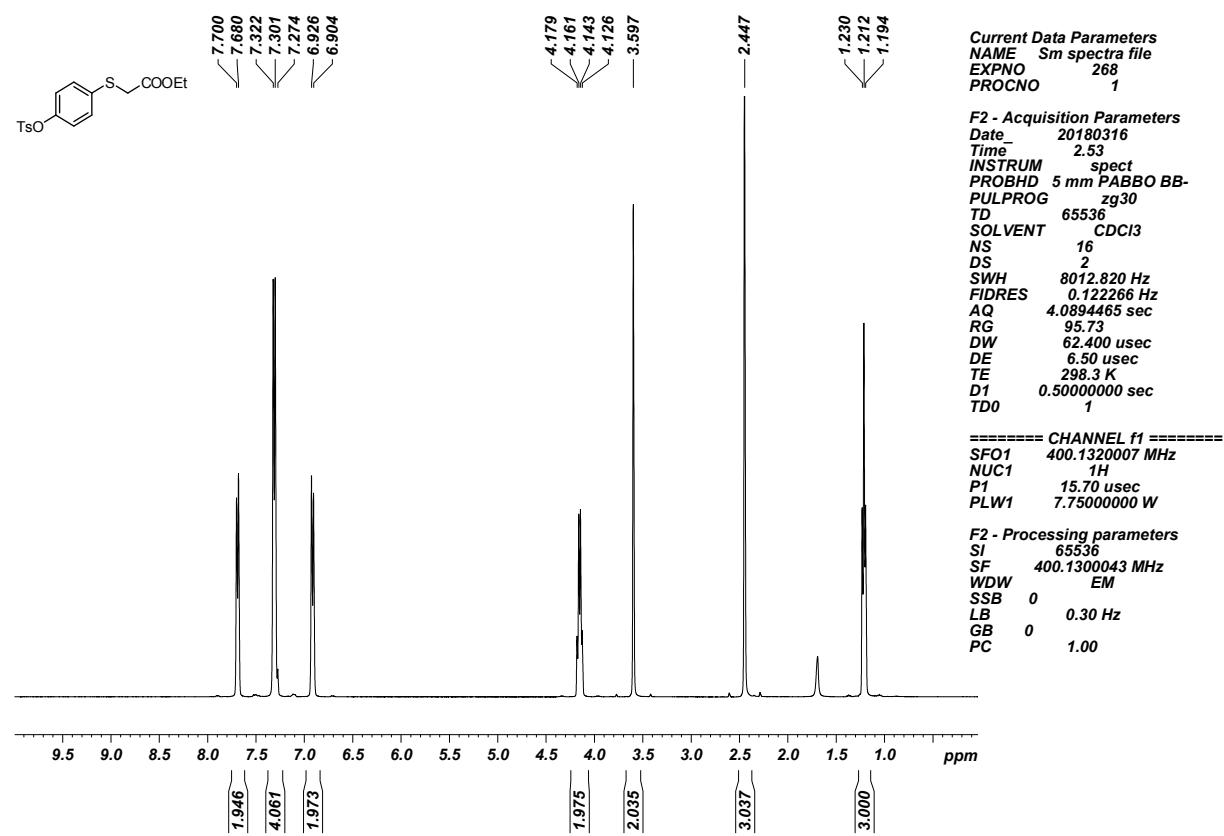


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

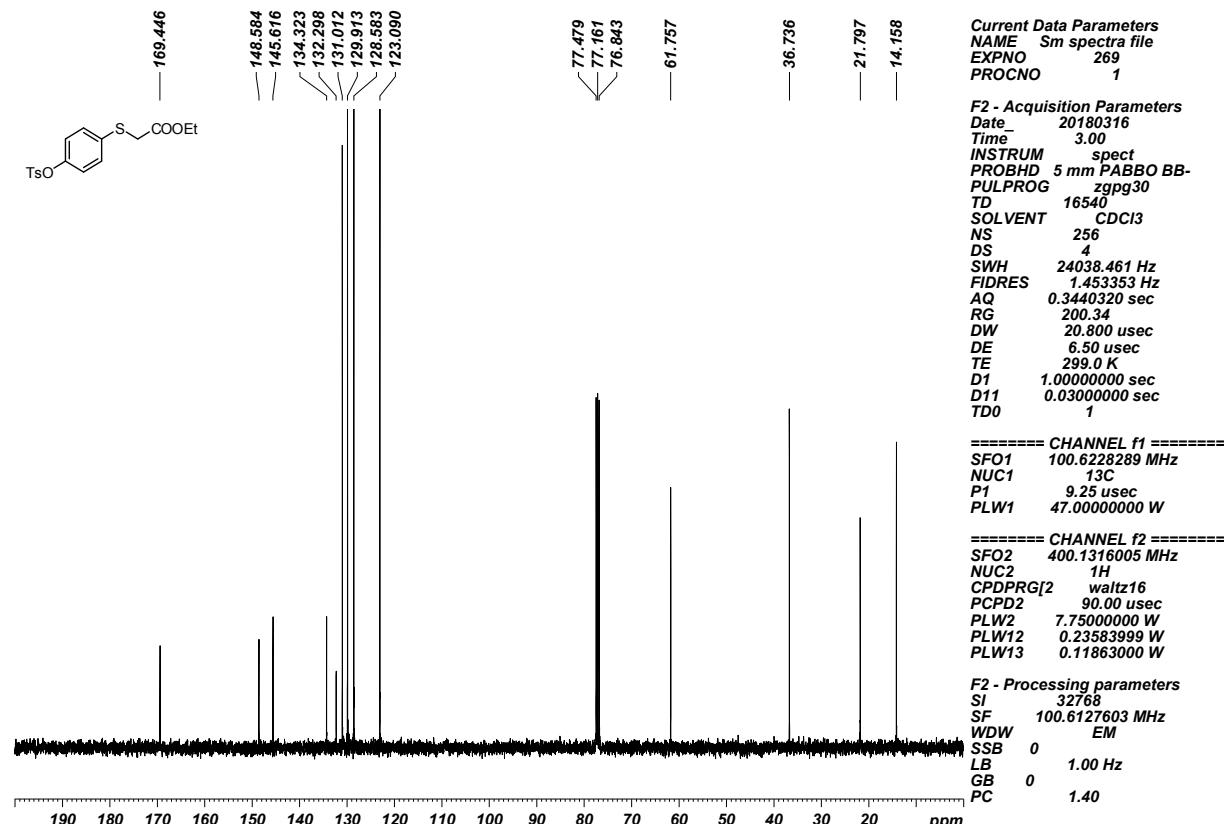


Thioester 1s

¹H NMR (400 MHz, CDCl₃, 24 °C)

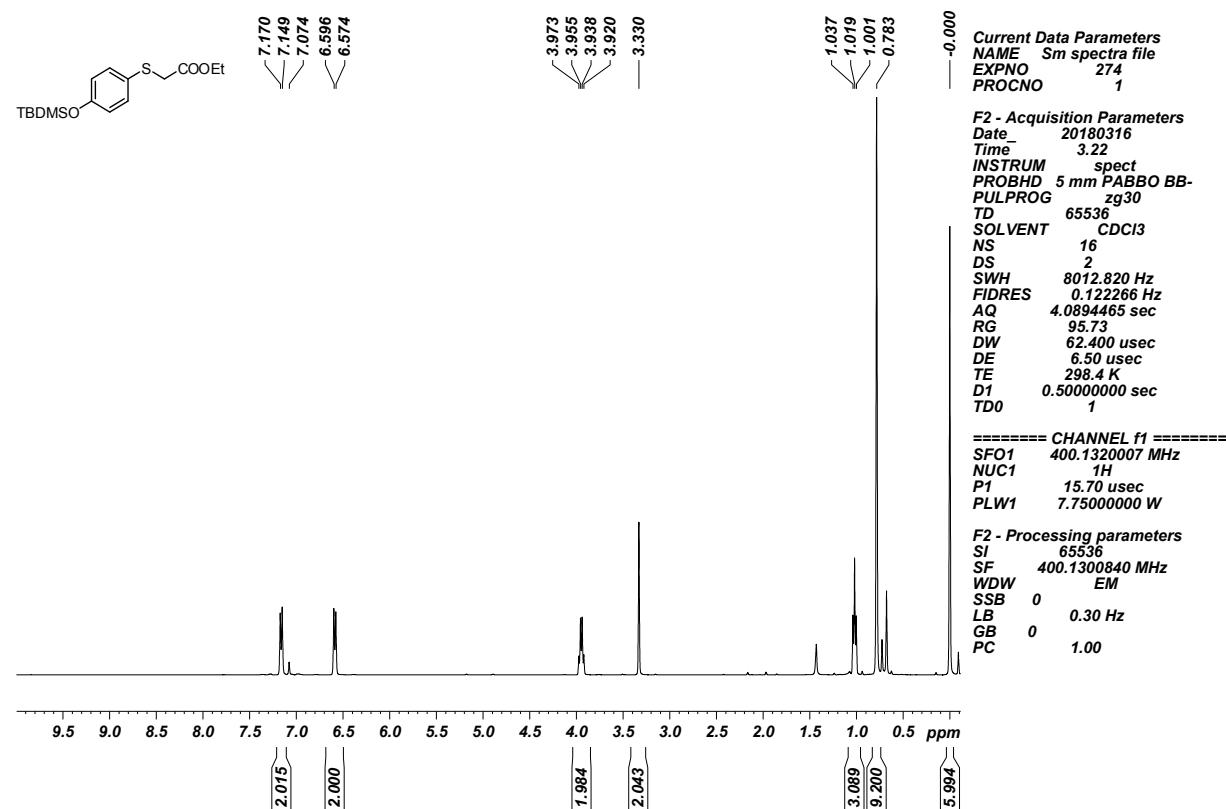


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

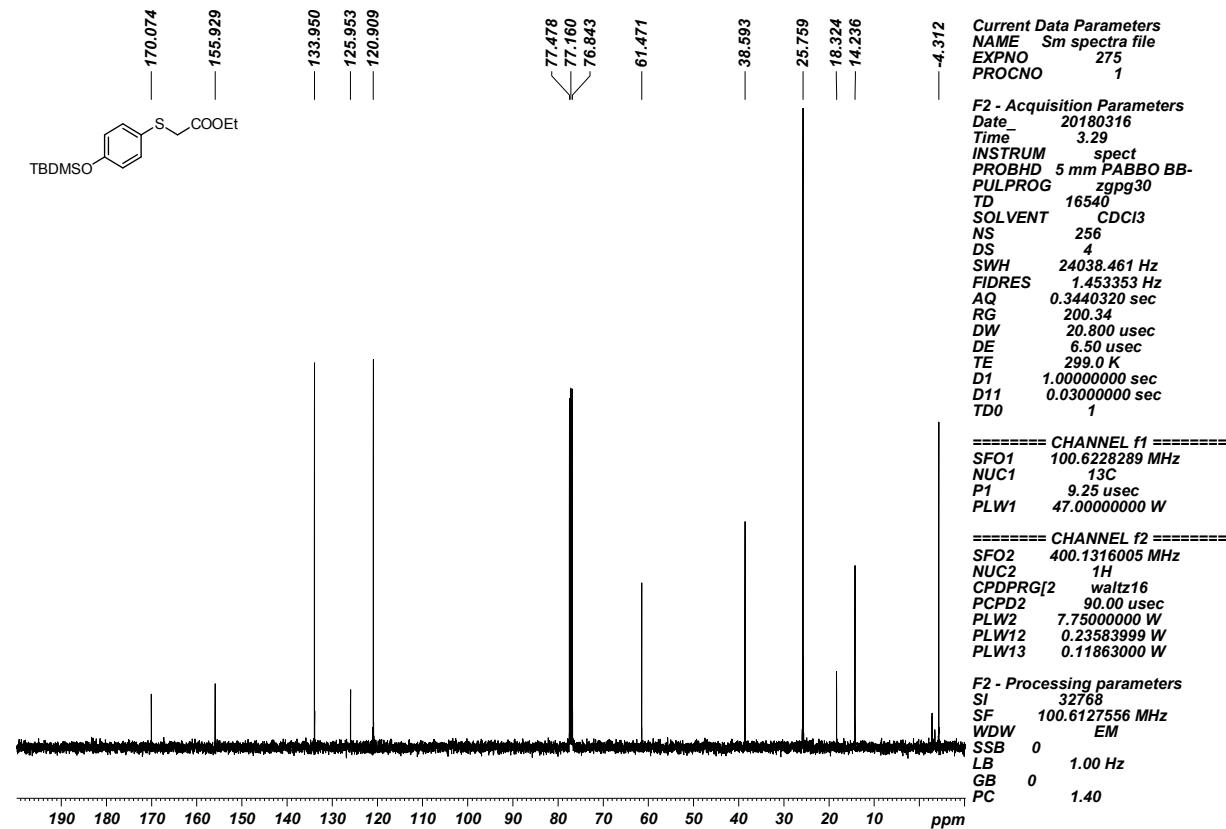


Thioester 1t

¹H NMR (400 MHz, CDCl₃, 24 °C)

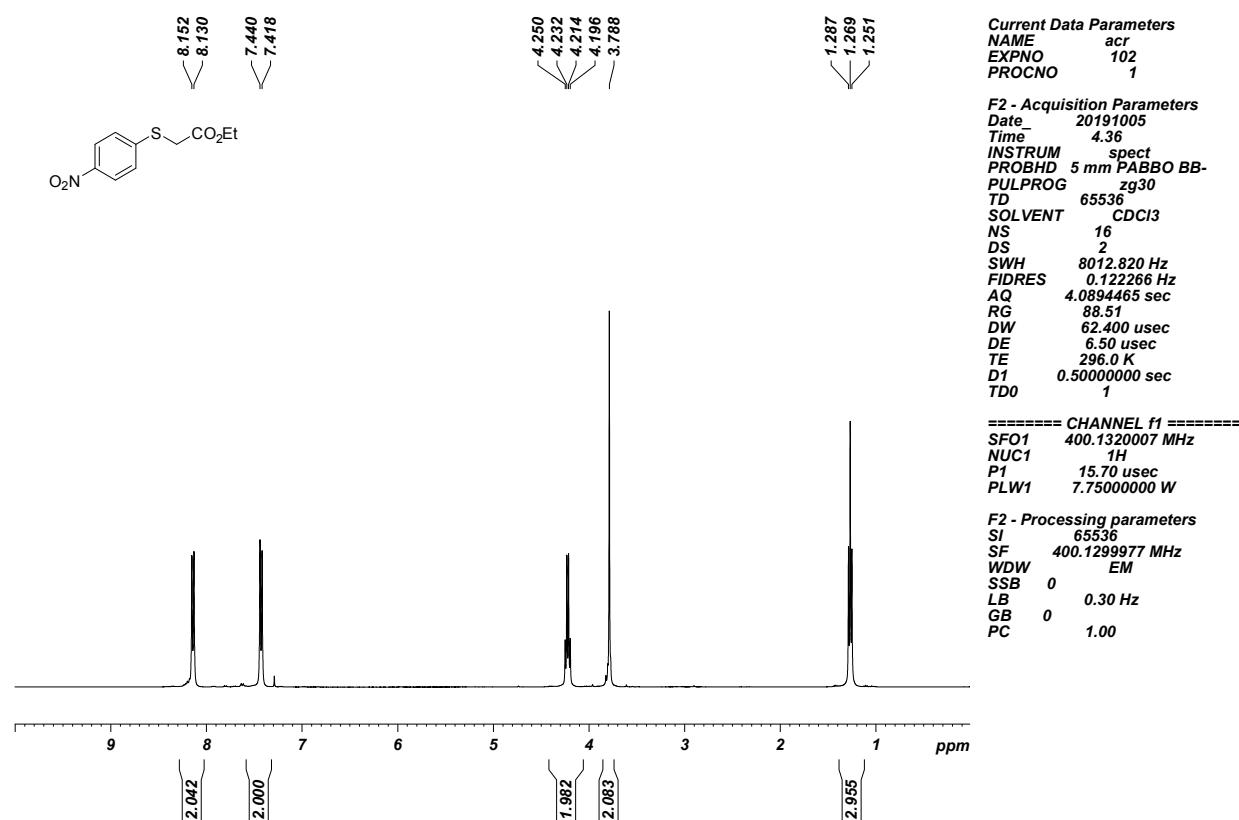


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

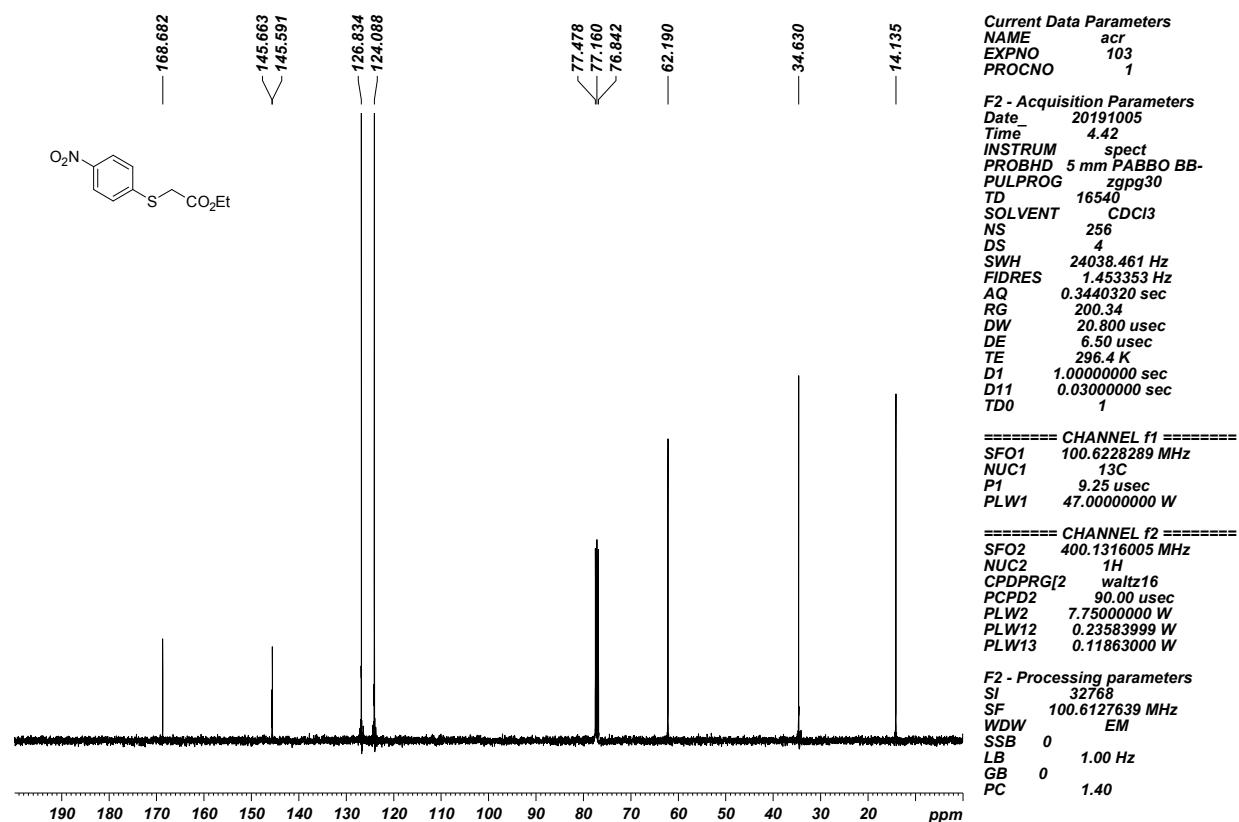


Thioester 1u

¹H NMR (400 MHz, CDCl₃, 24 °C)

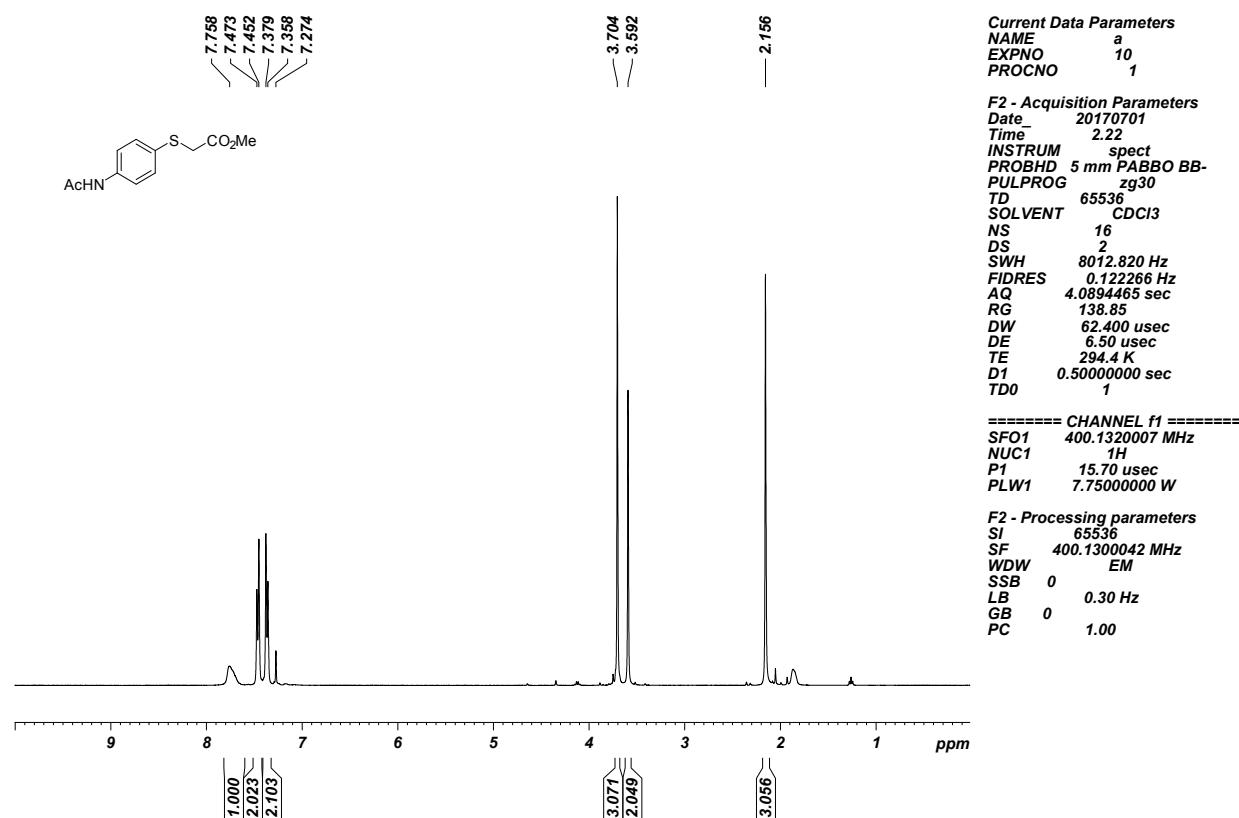


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

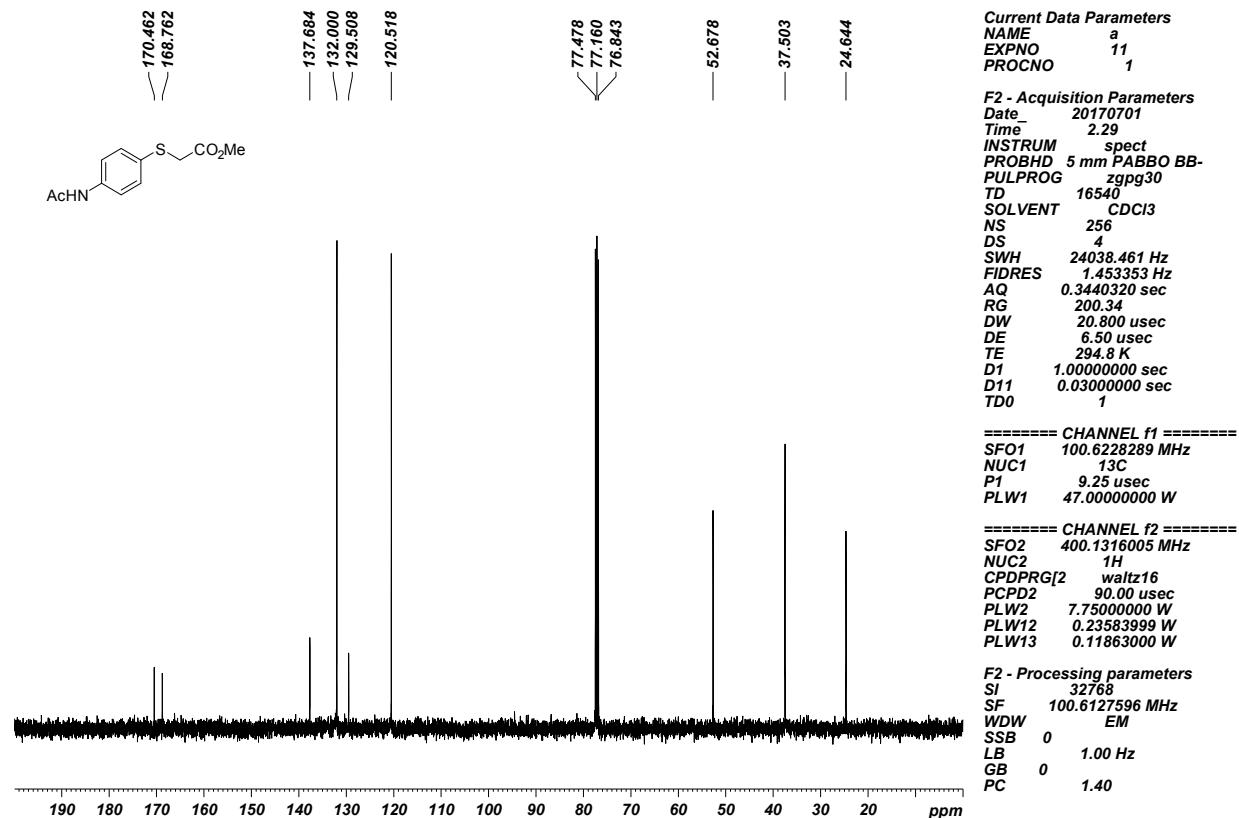


Thioester **1v**

¹H NMR (400 MHz, CDCl₃, 24 °C)

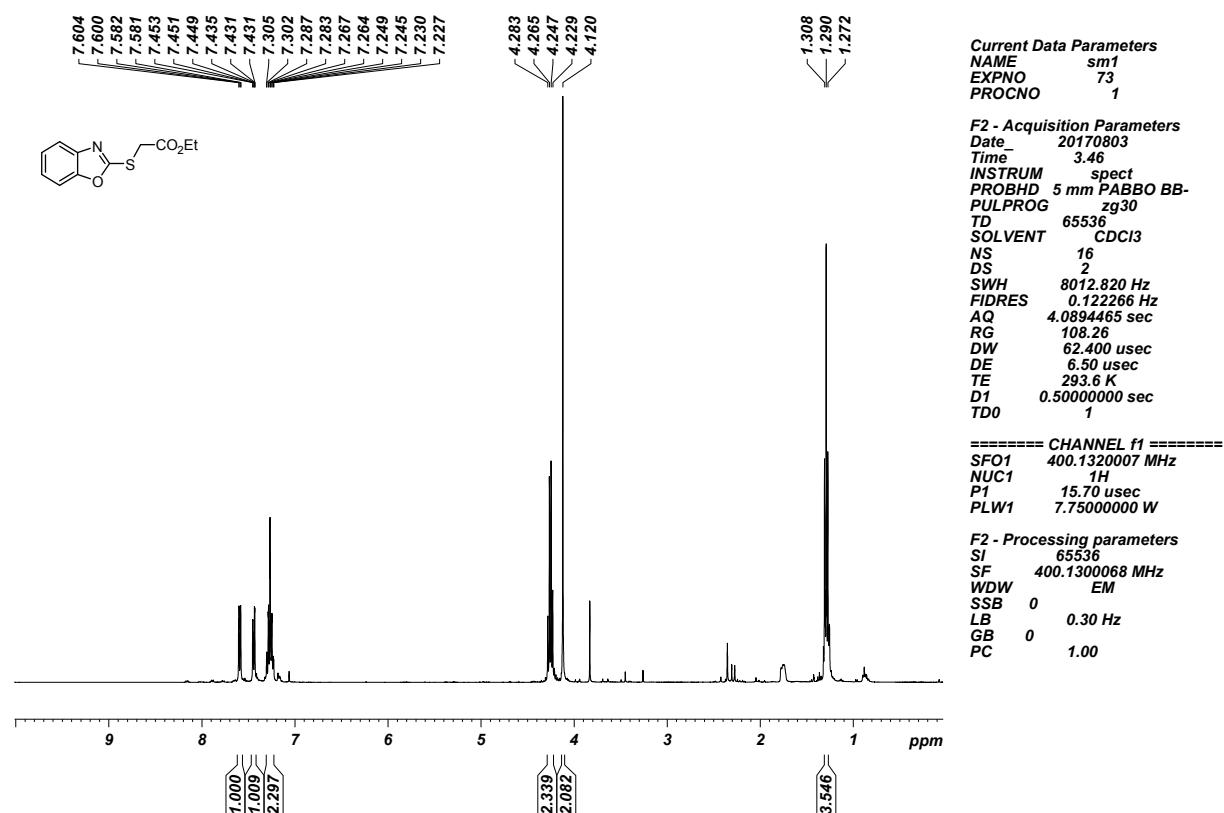


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

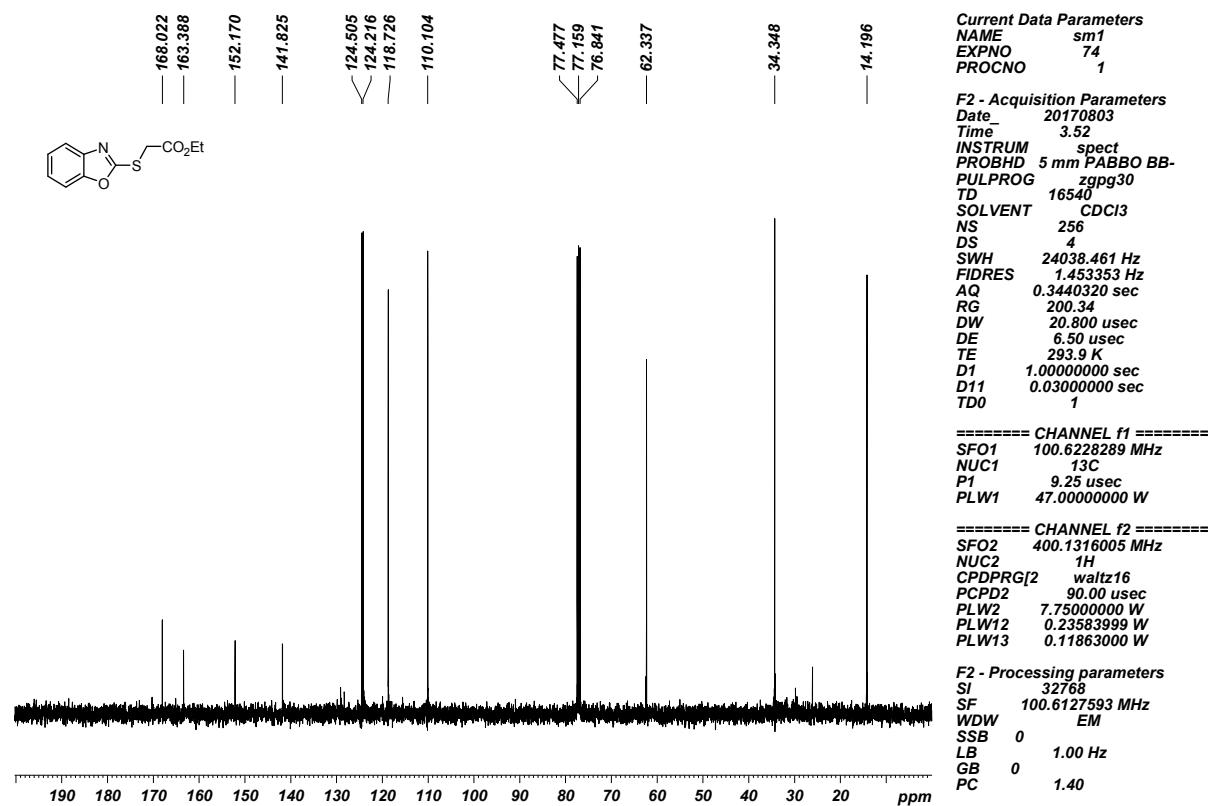


Thioester 1w

¹H NMR (400 MHz, CDCl₃, 24 °C)

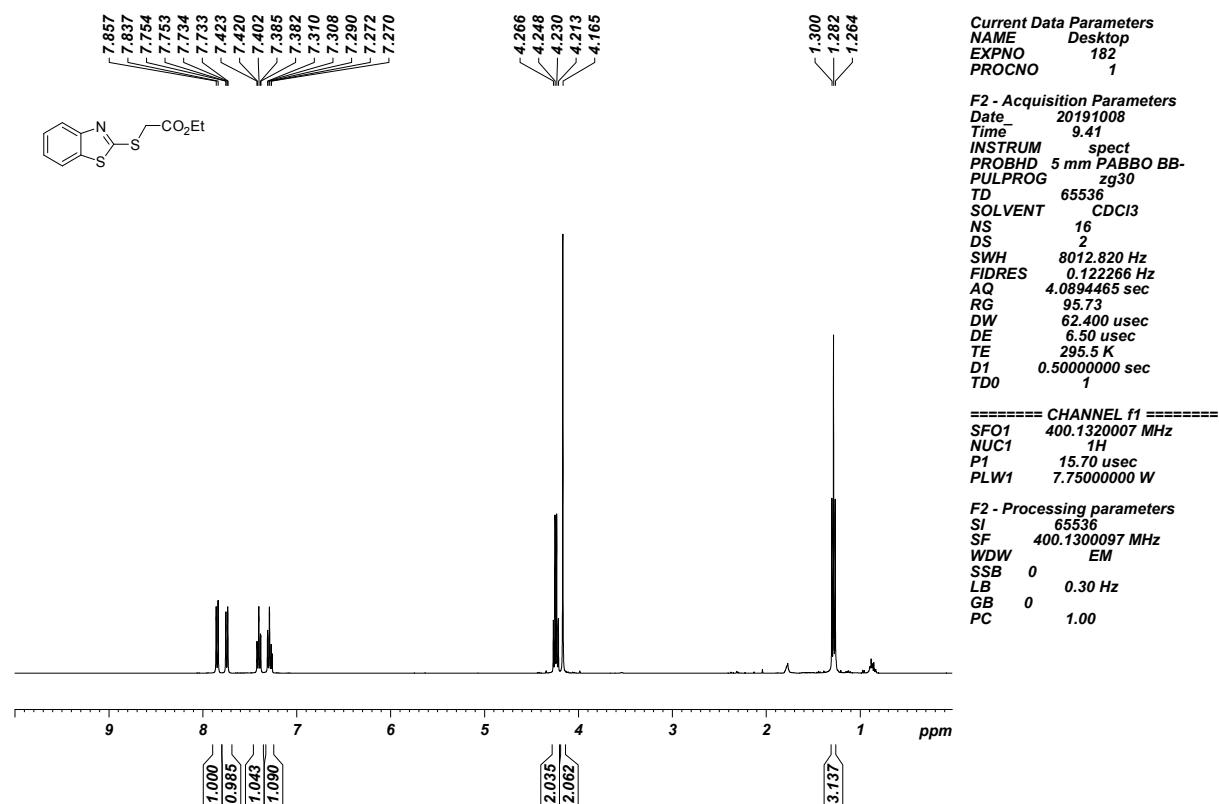


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

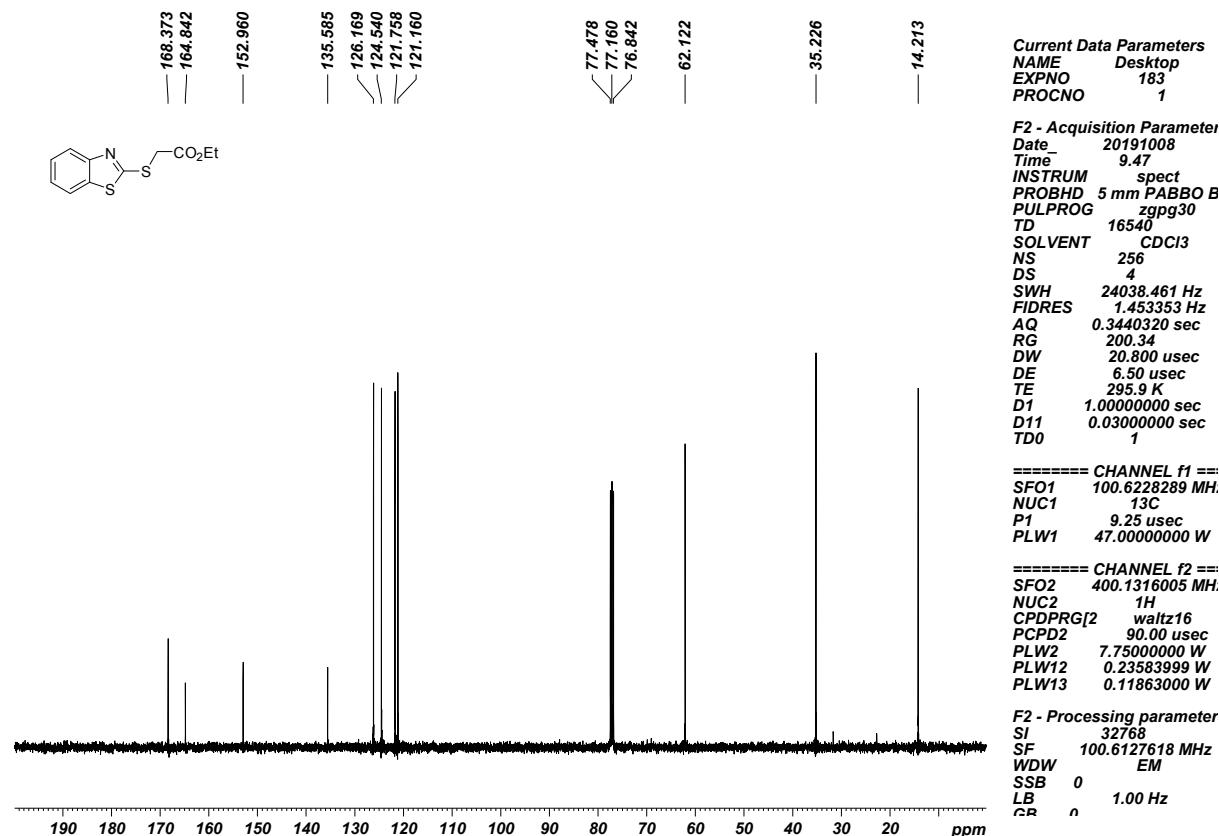


Thioester 1x

¹H NMR (400 MHz, CDCl₃, 24 °C)

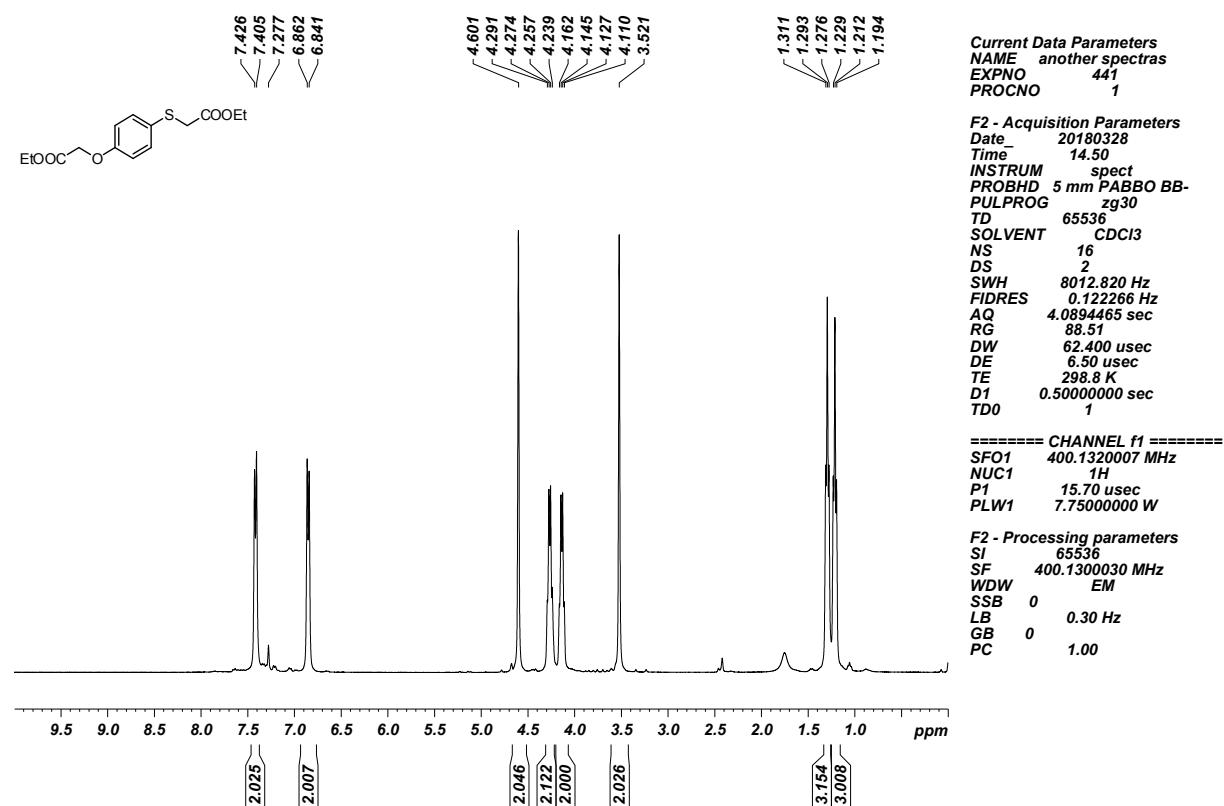


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

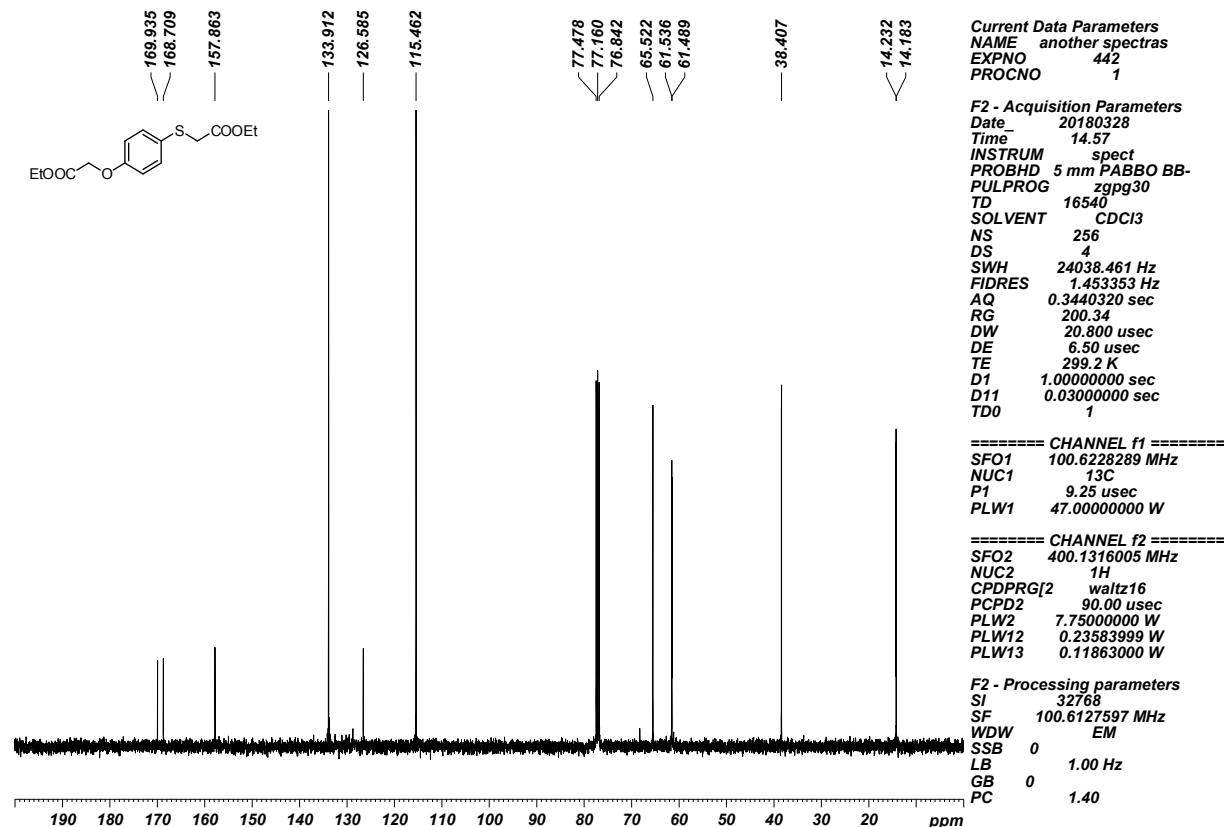


Thioester **1y**

¹H NMR (400 MHz, CDCl₃, 24 °C)

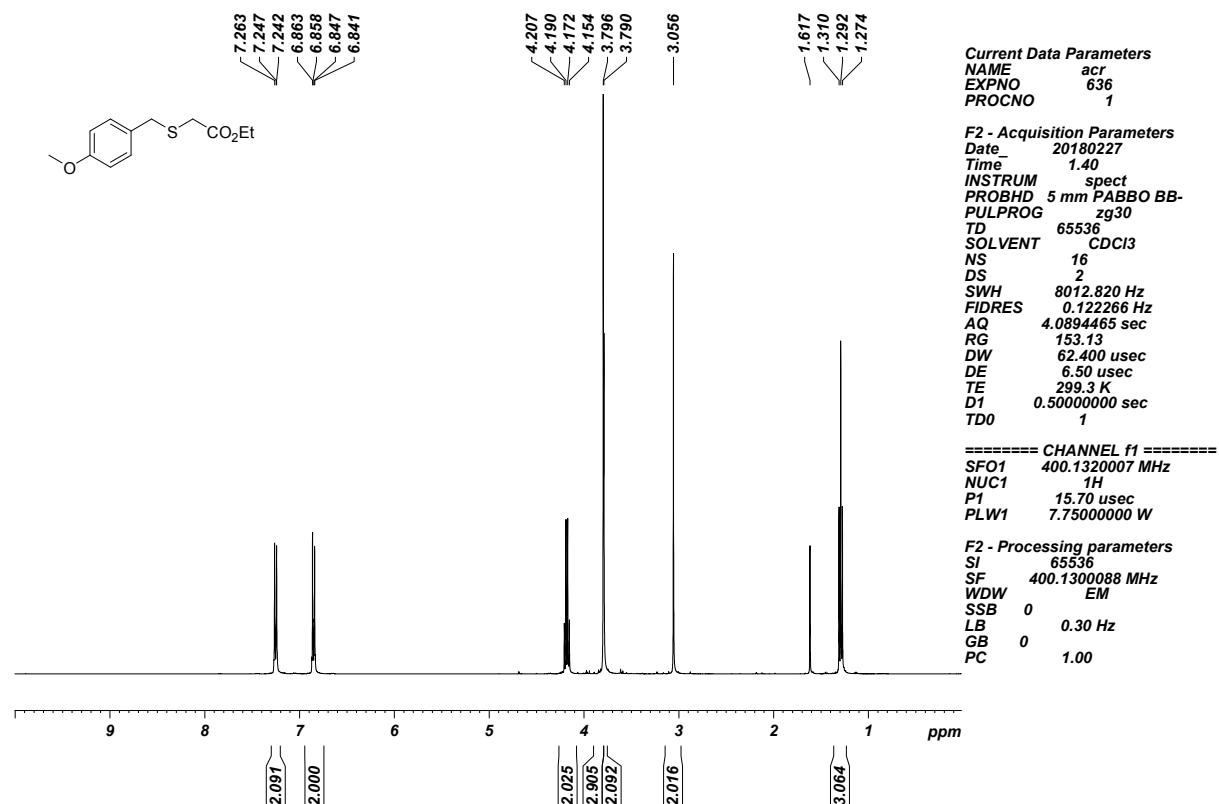


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

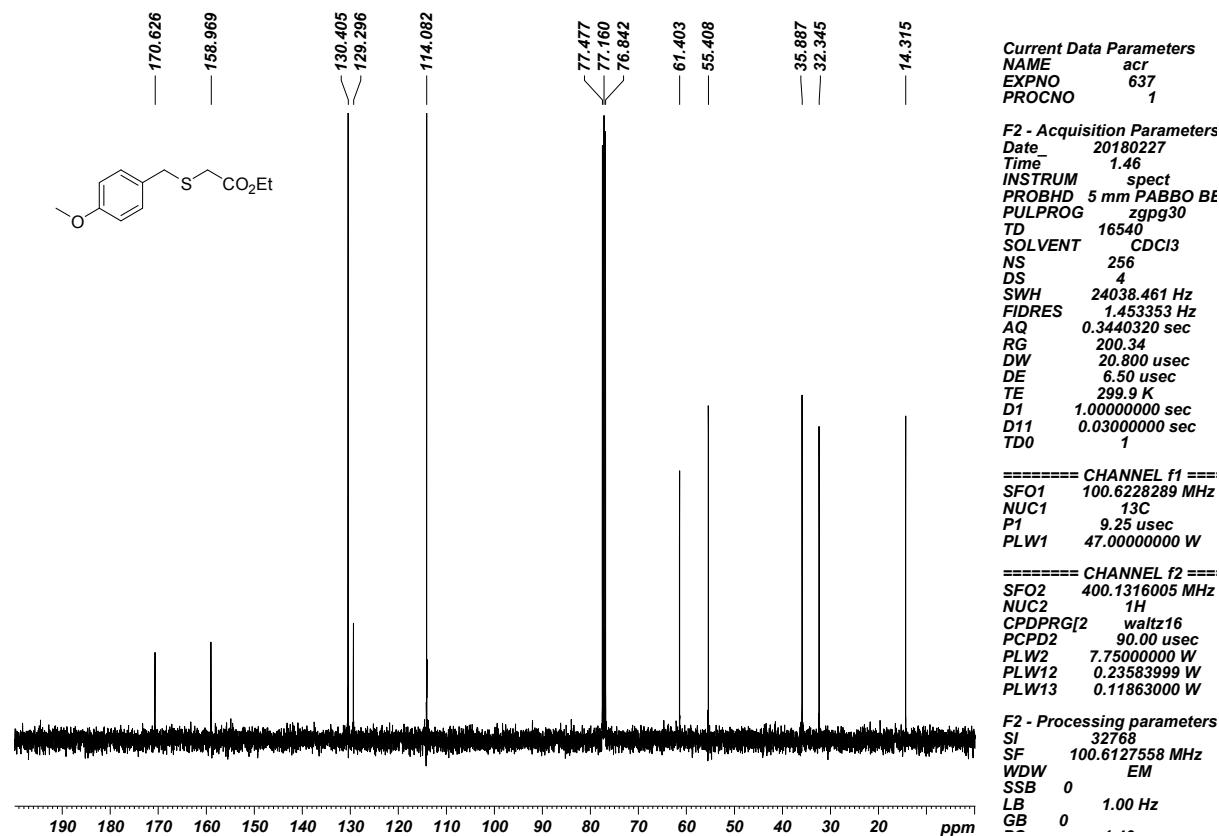


Thioester 1z

¹H NMR (400 MHz, CDCl₃, 24 °C)

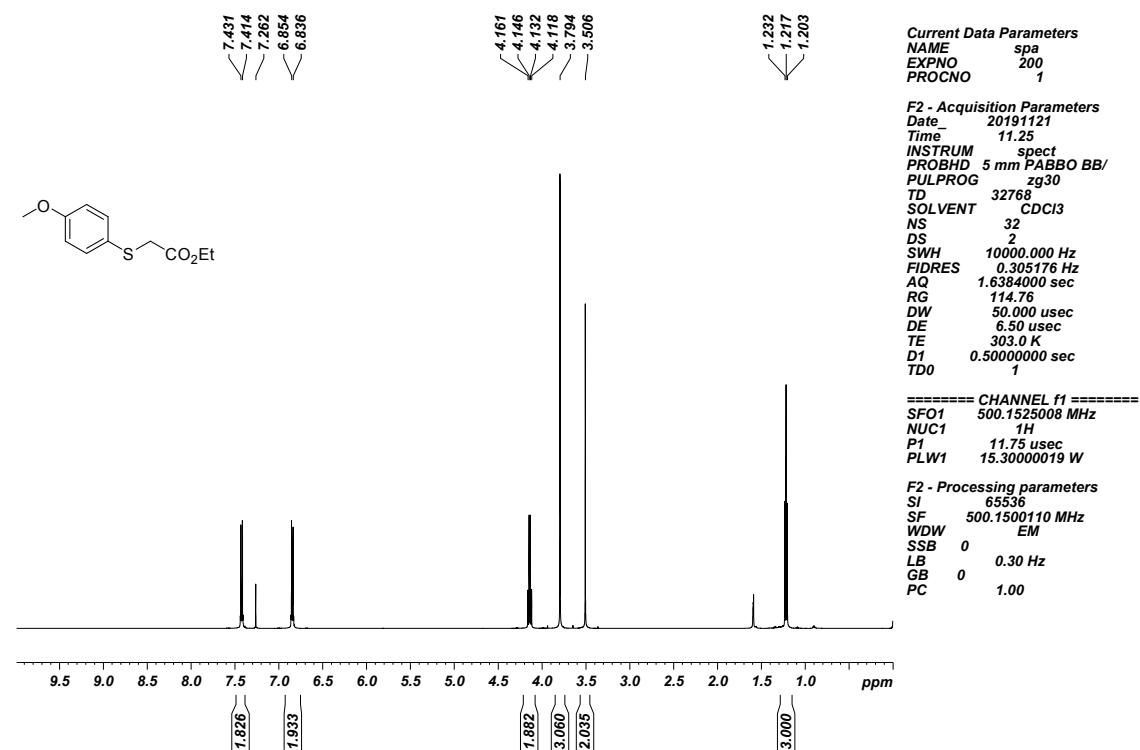


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

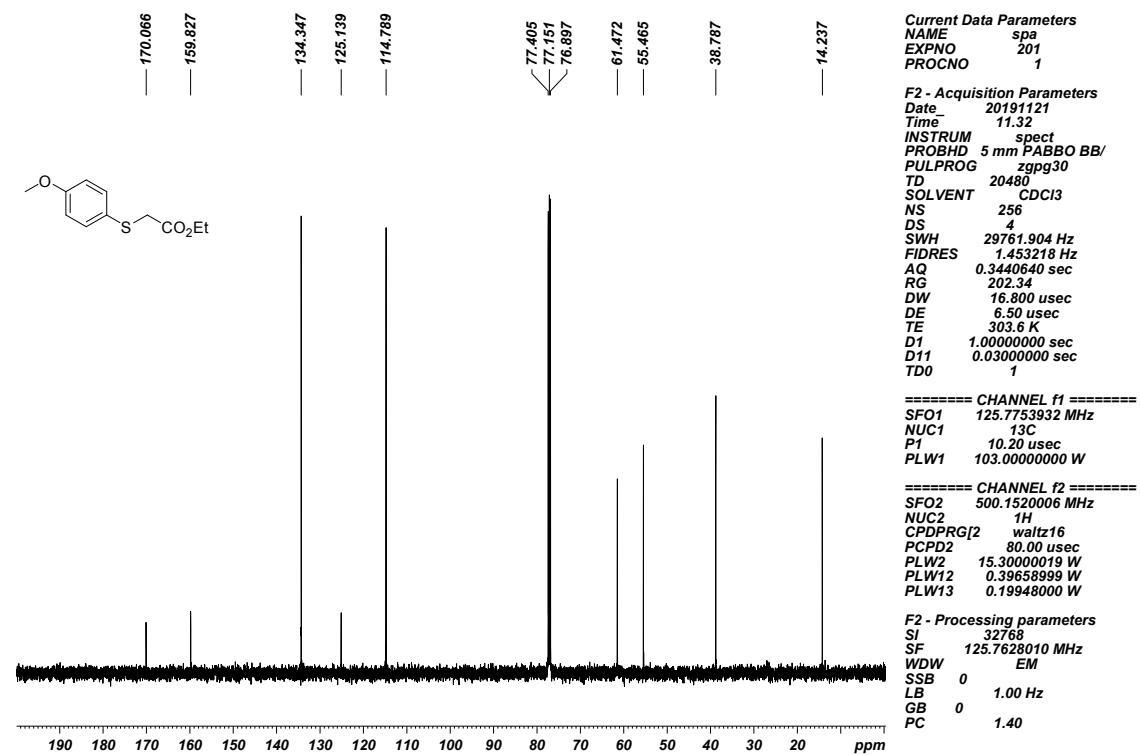


Thioester 1aa

¹H NMR (500 MHz, CDCl₃, 24 °C)

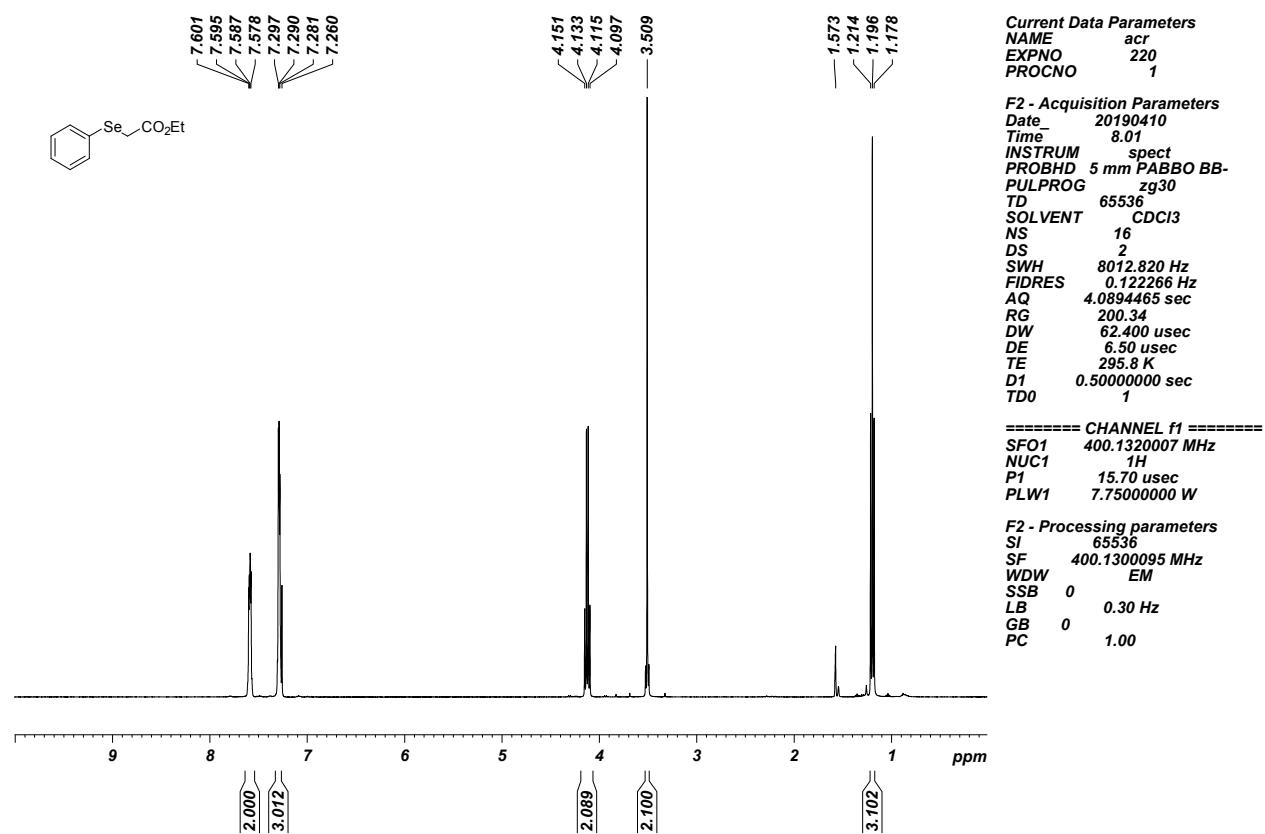


¹³C{¹H} NMR (125 MHz, CDCl₃, 24 °C)

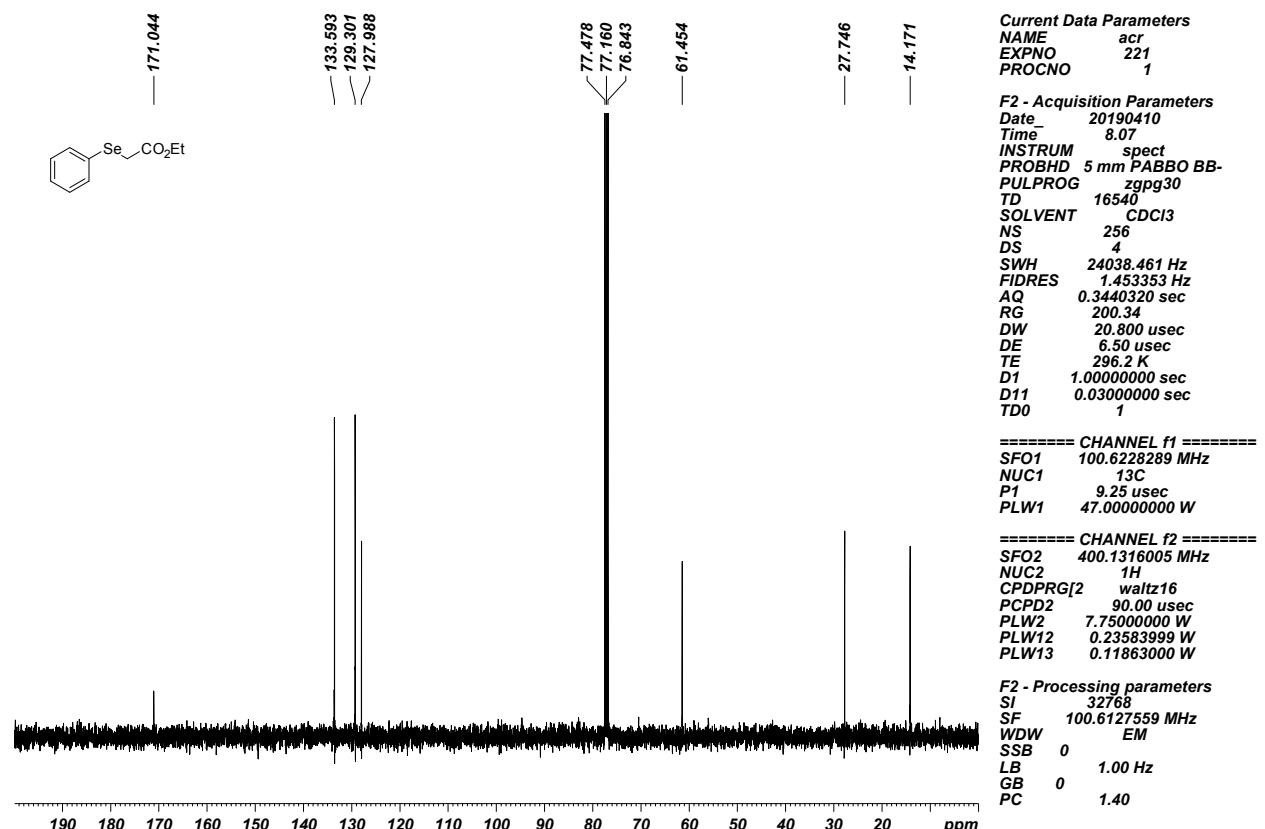


Selenoester 5a

¹H NMR (400 MHz, CDCl₃, 24 °C)

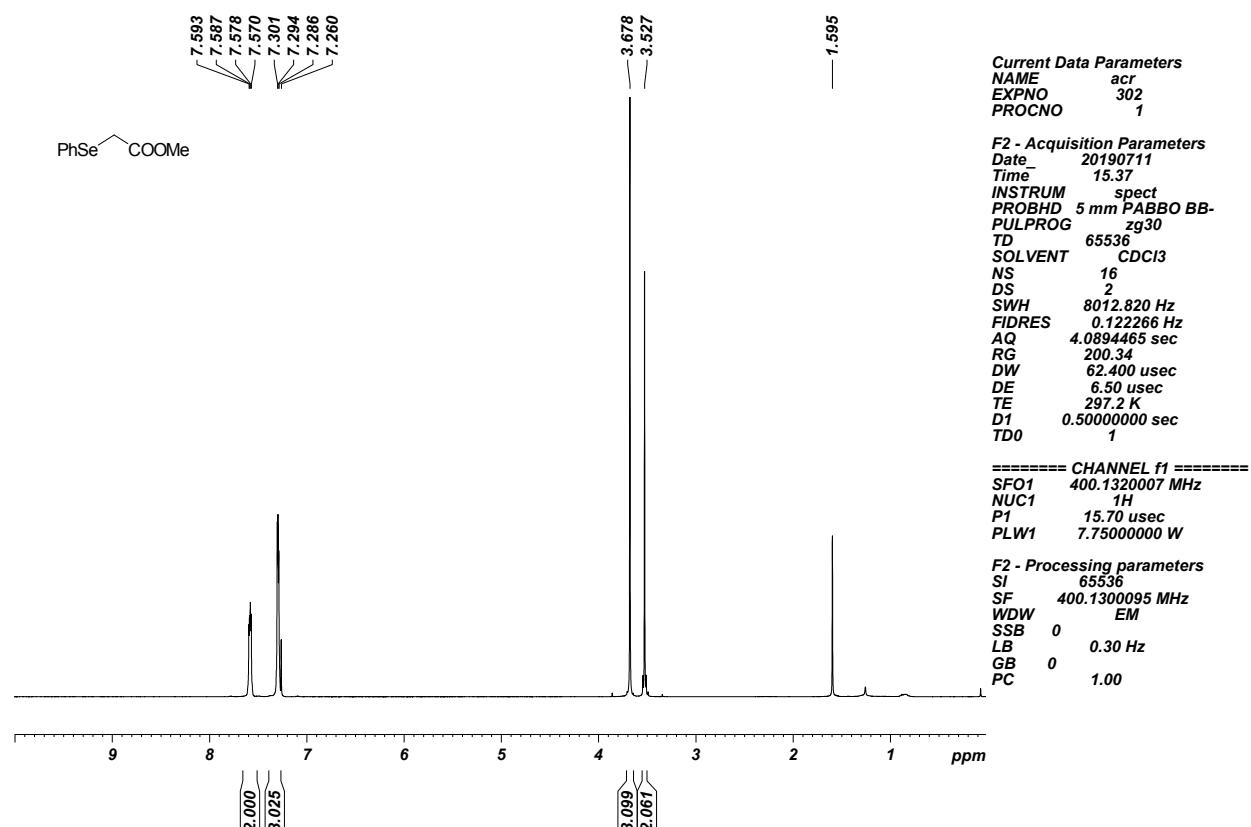


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

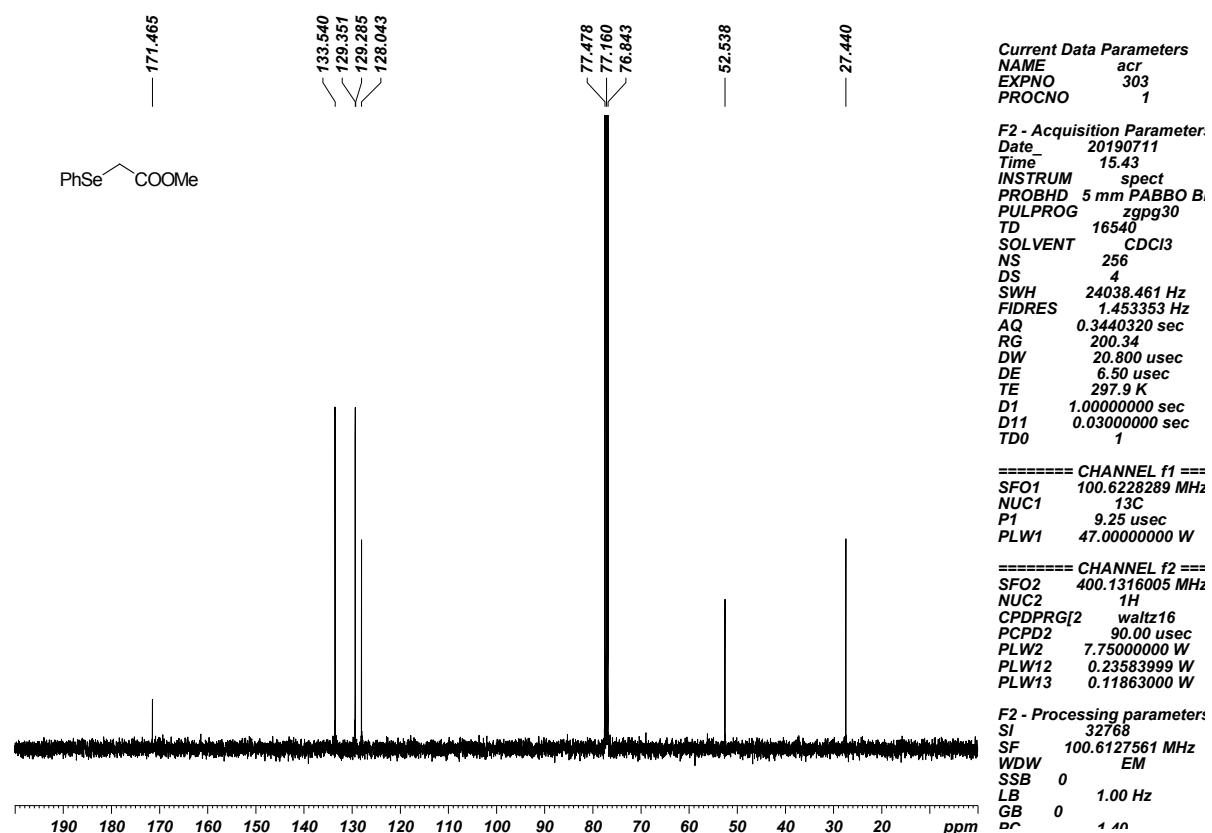


Selenoester 5b

¹H NMR (400 MHz, CDCl₃, 24 °C)

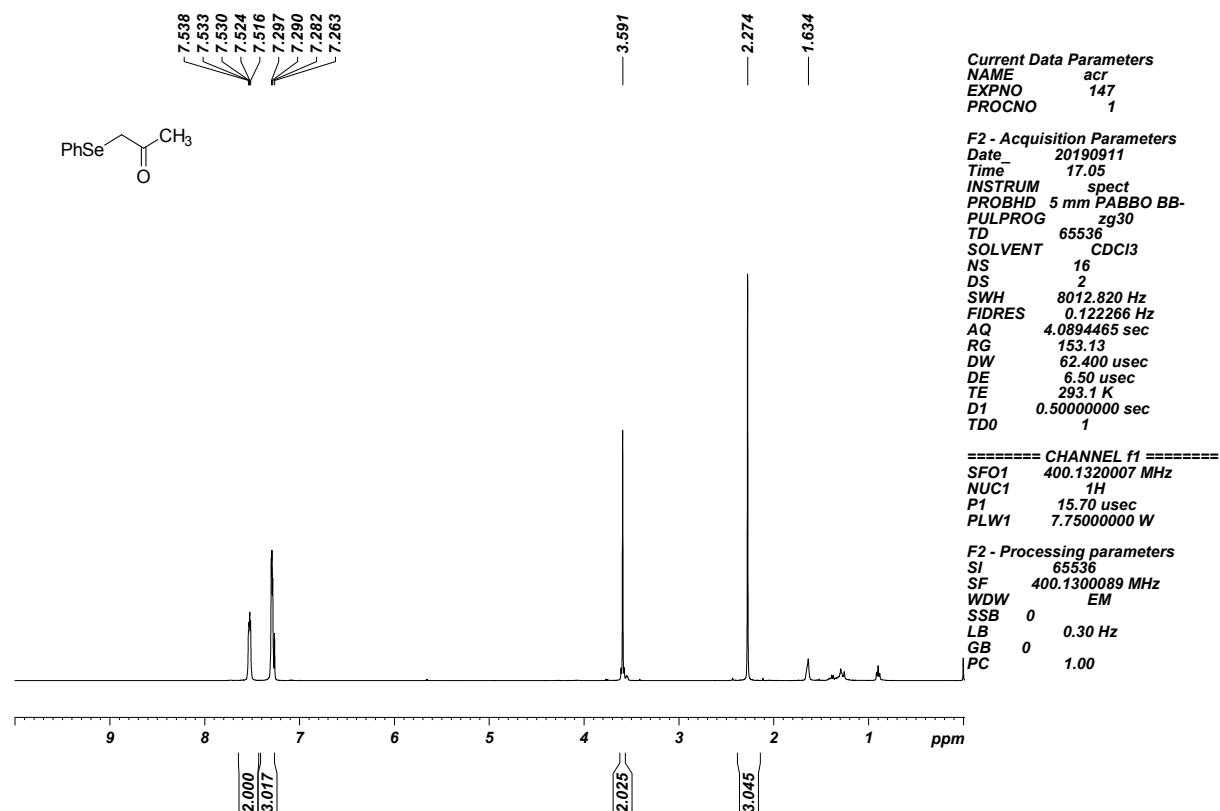


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

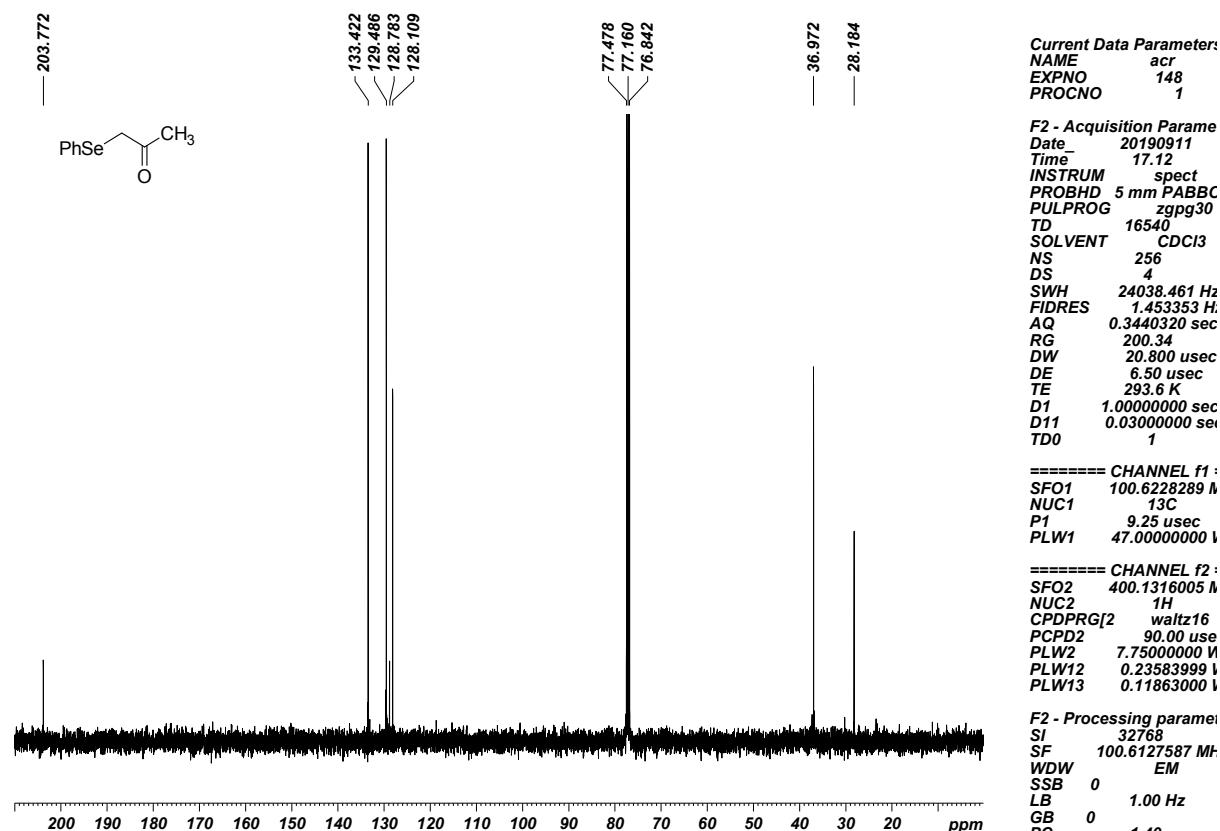


Selenoketone 5c

¹H NMR (400 MHz, CDCl₃, 24 °C)

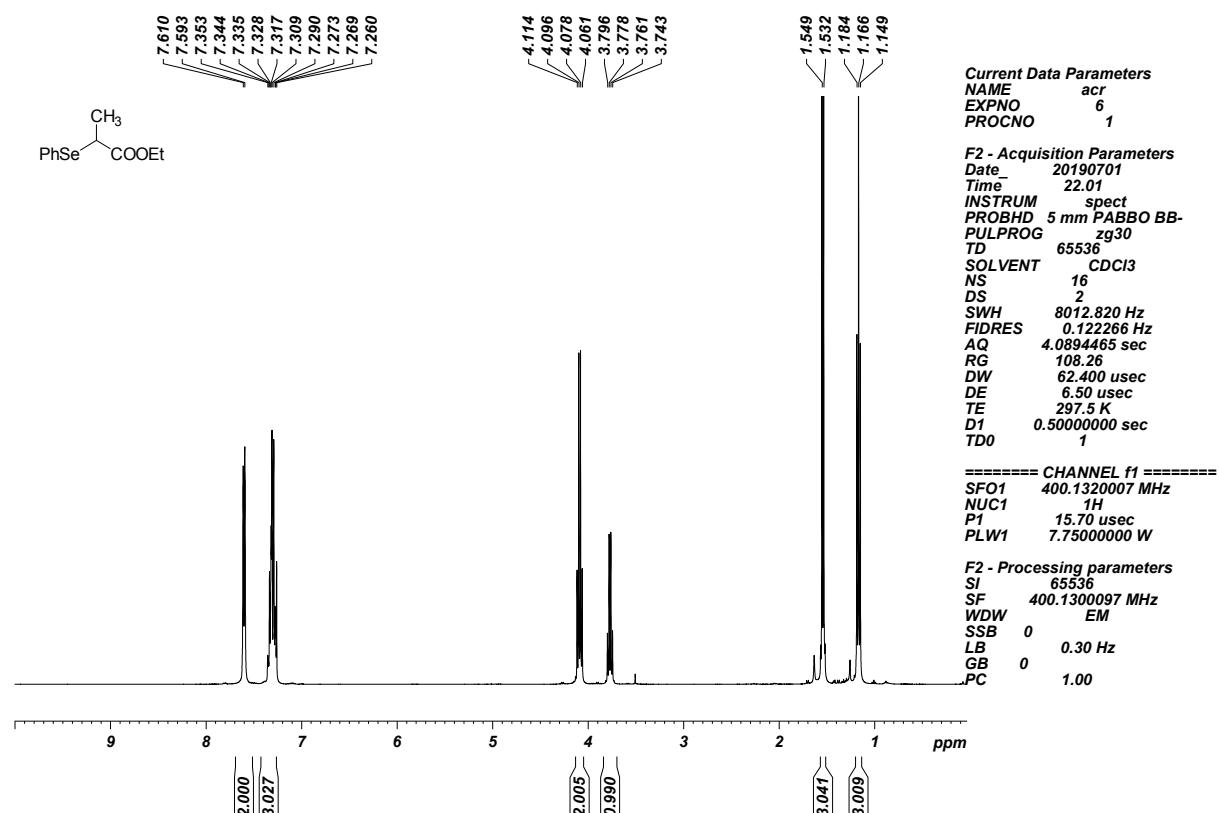


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

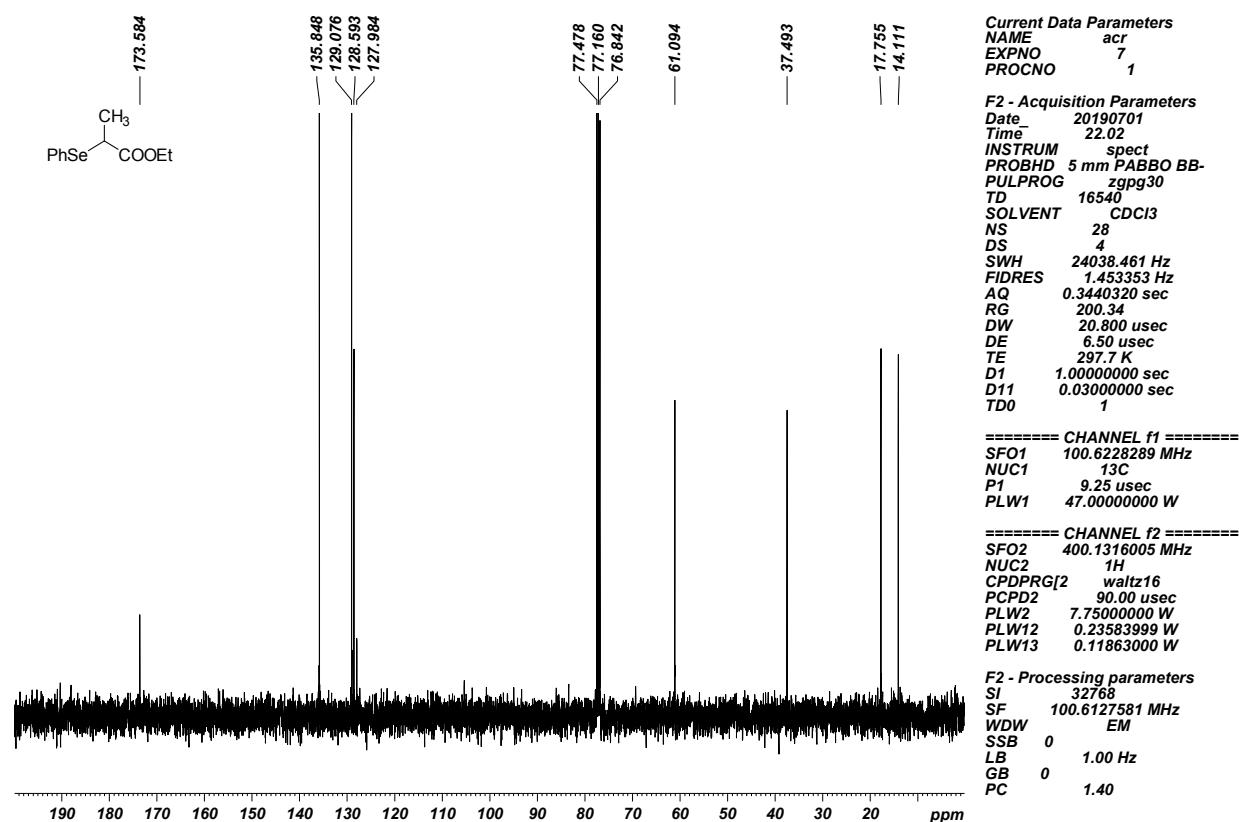


Selenoester 5f

¹H NMR (400 MHz, CDCl₃, 24 °C)

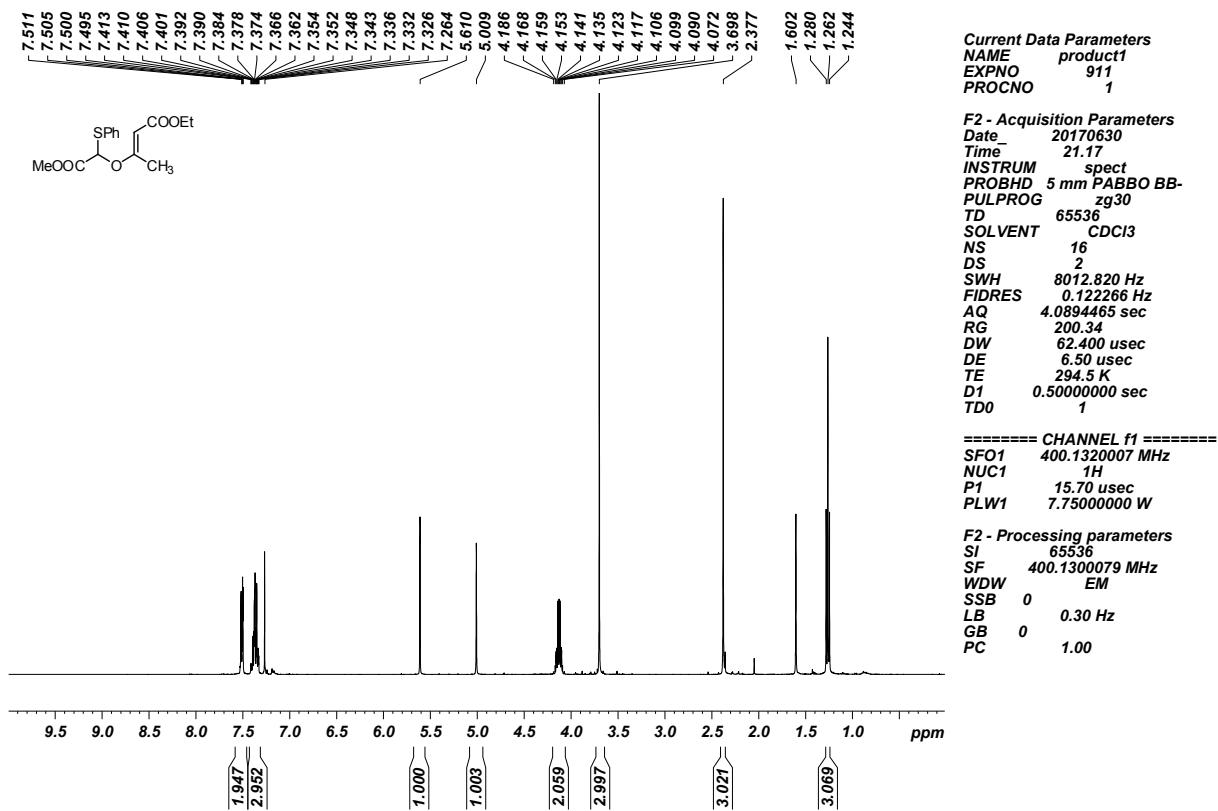


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

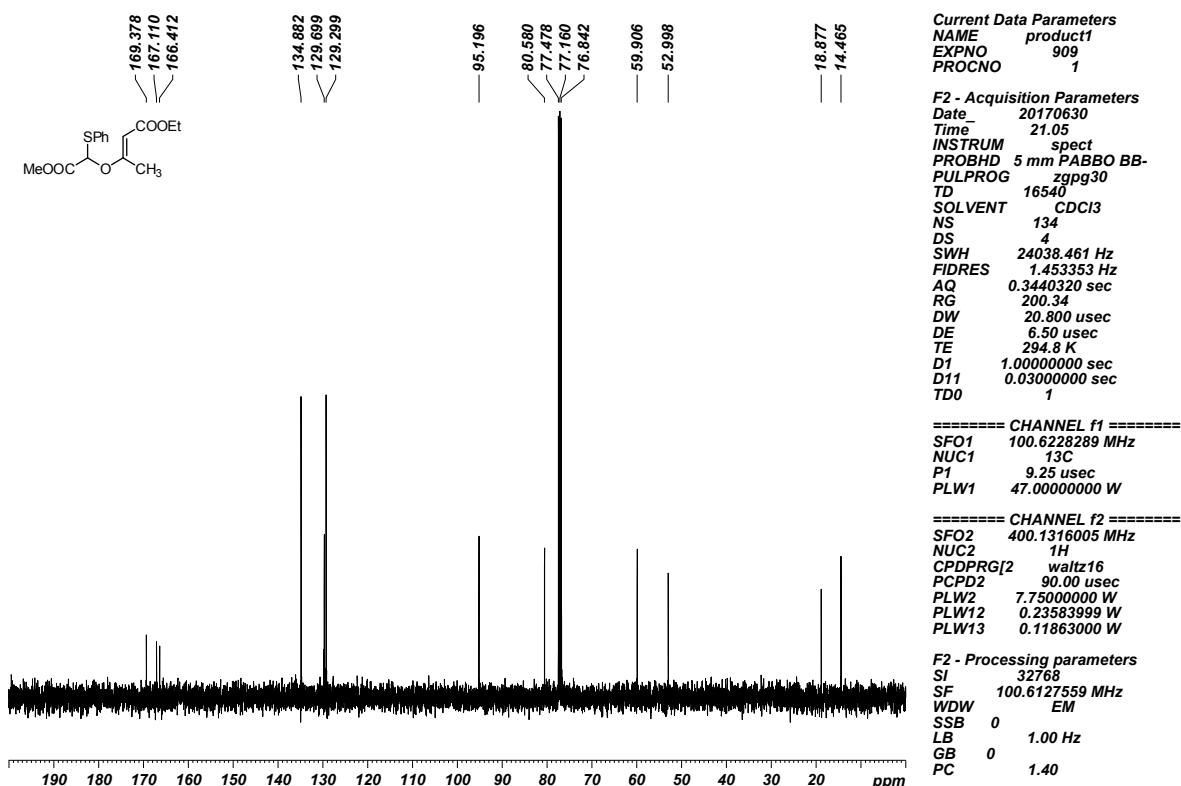


Vinylogous carbonate 3a

¹H NMR (400 MHz, CDCl₃, 24 °C)

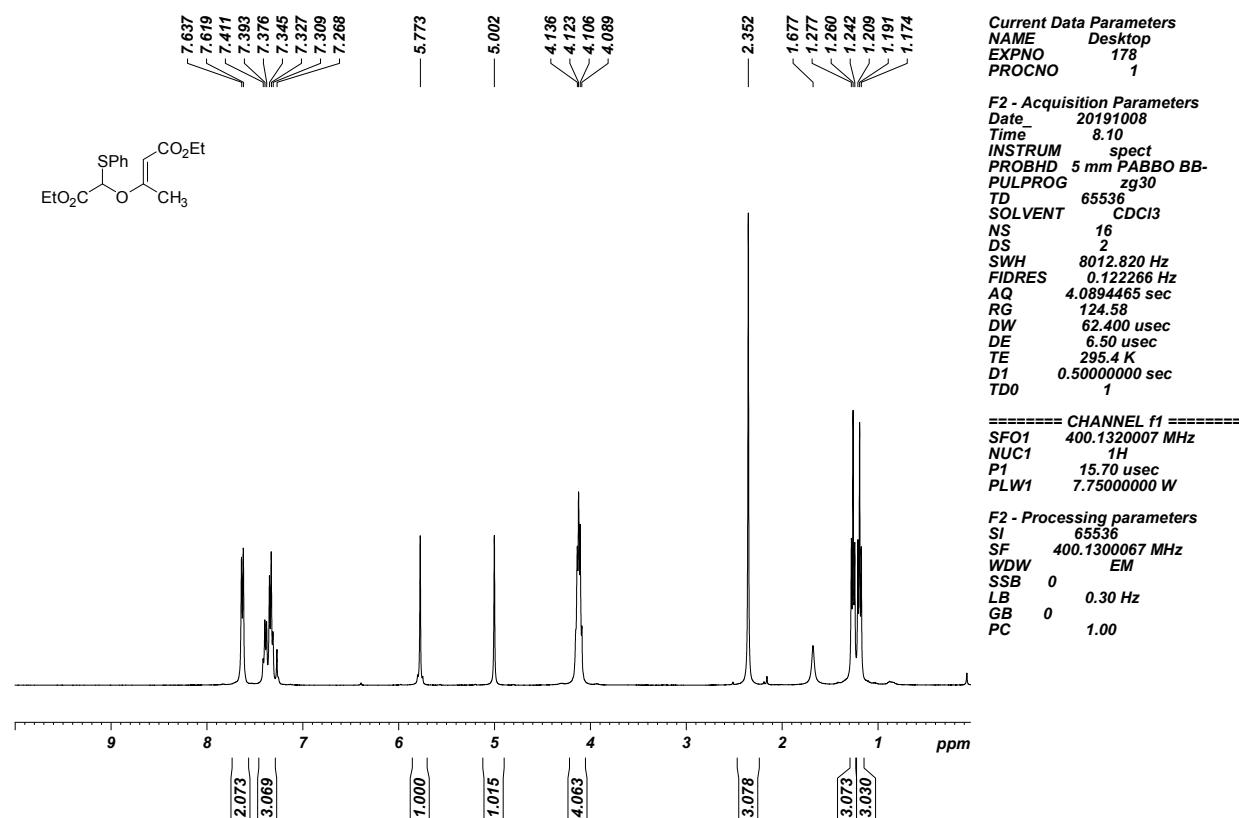


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

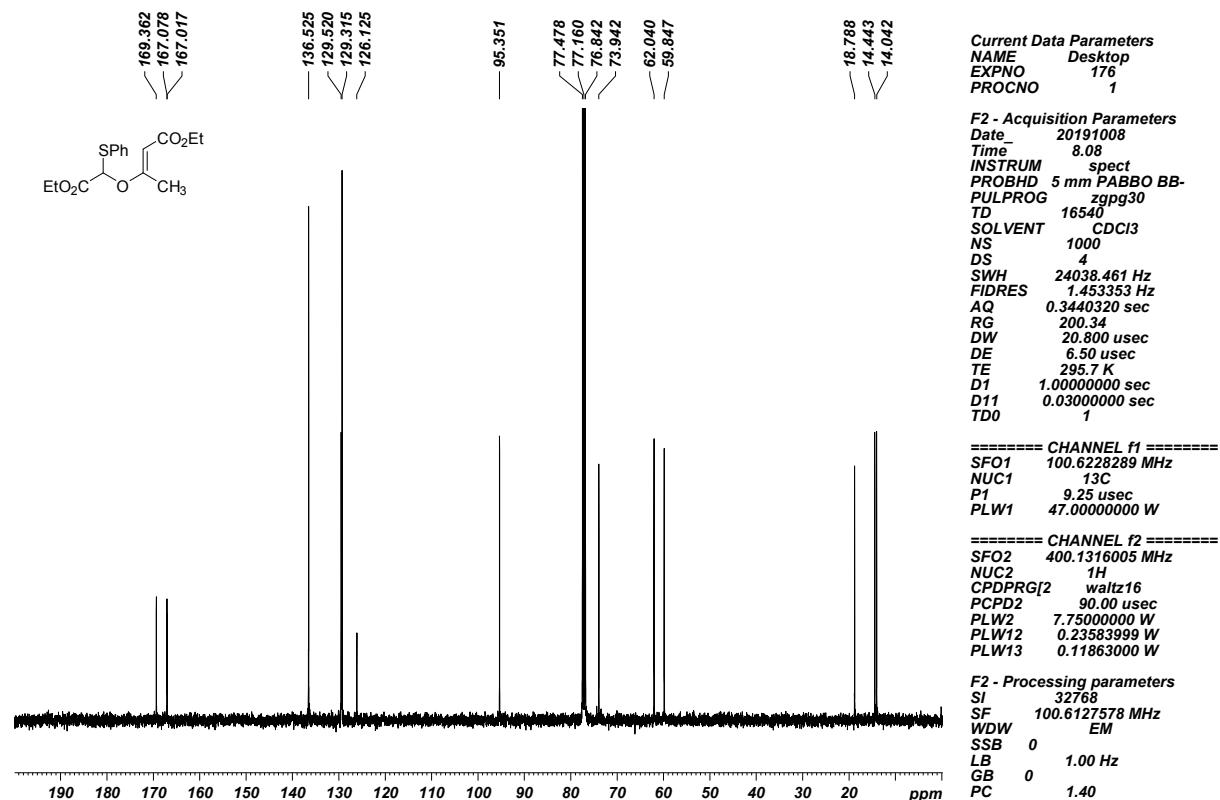


Vinylogous carbonate 3b

¹H NMR (400 MHz, CDCl₃, 24 °C)

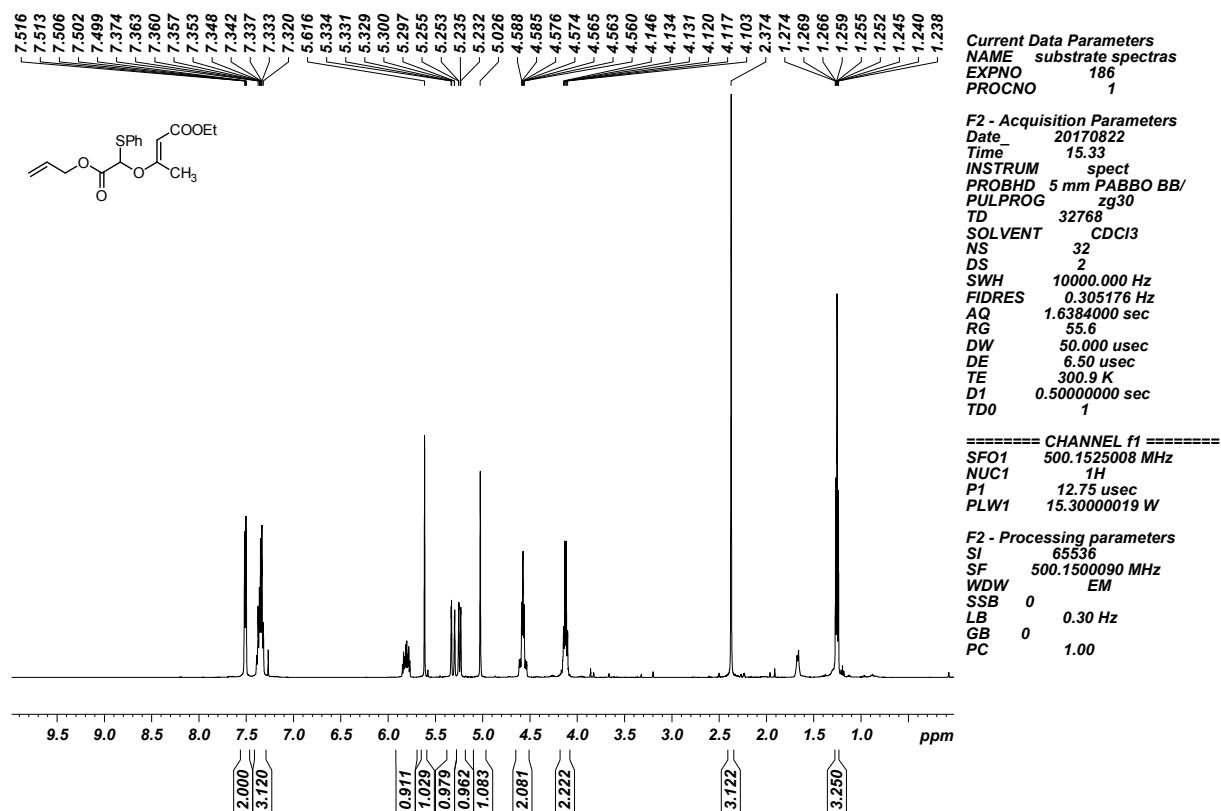


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

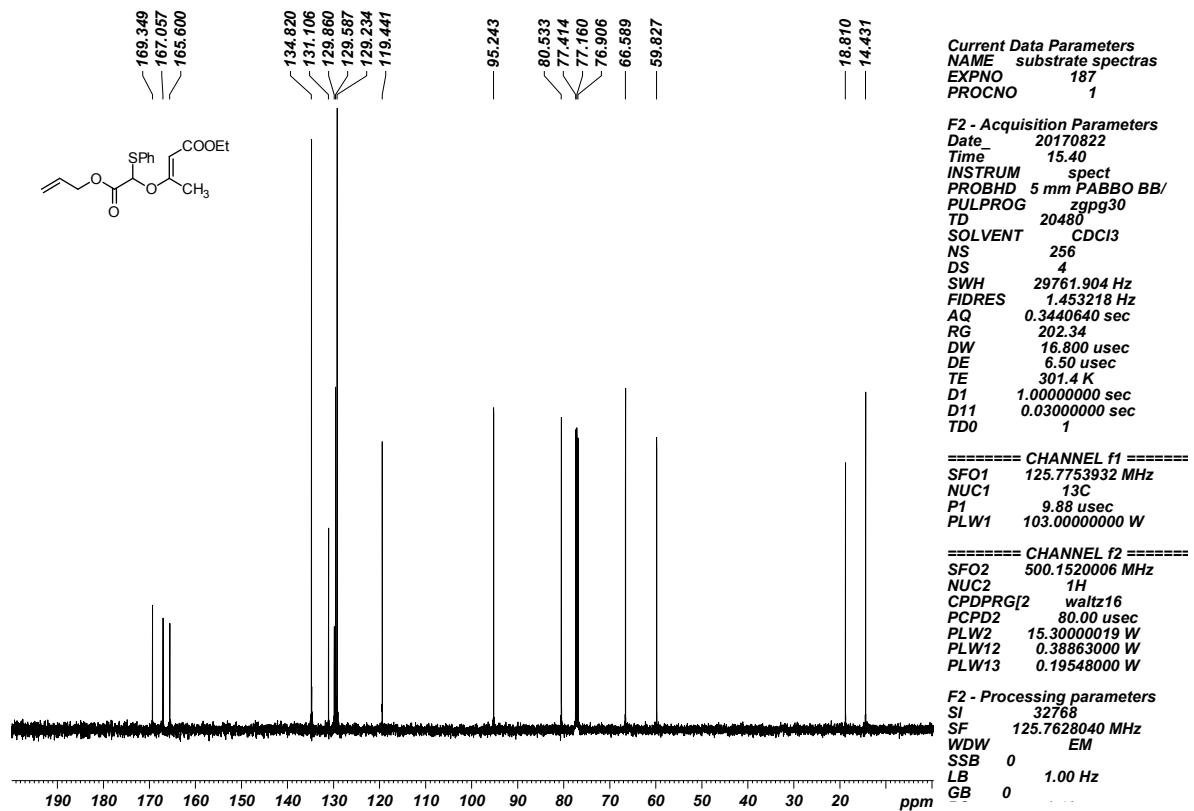


Vinylogous carbonate 3c

¹H NMR (400 MHz, CDCl₃, 24 °C)

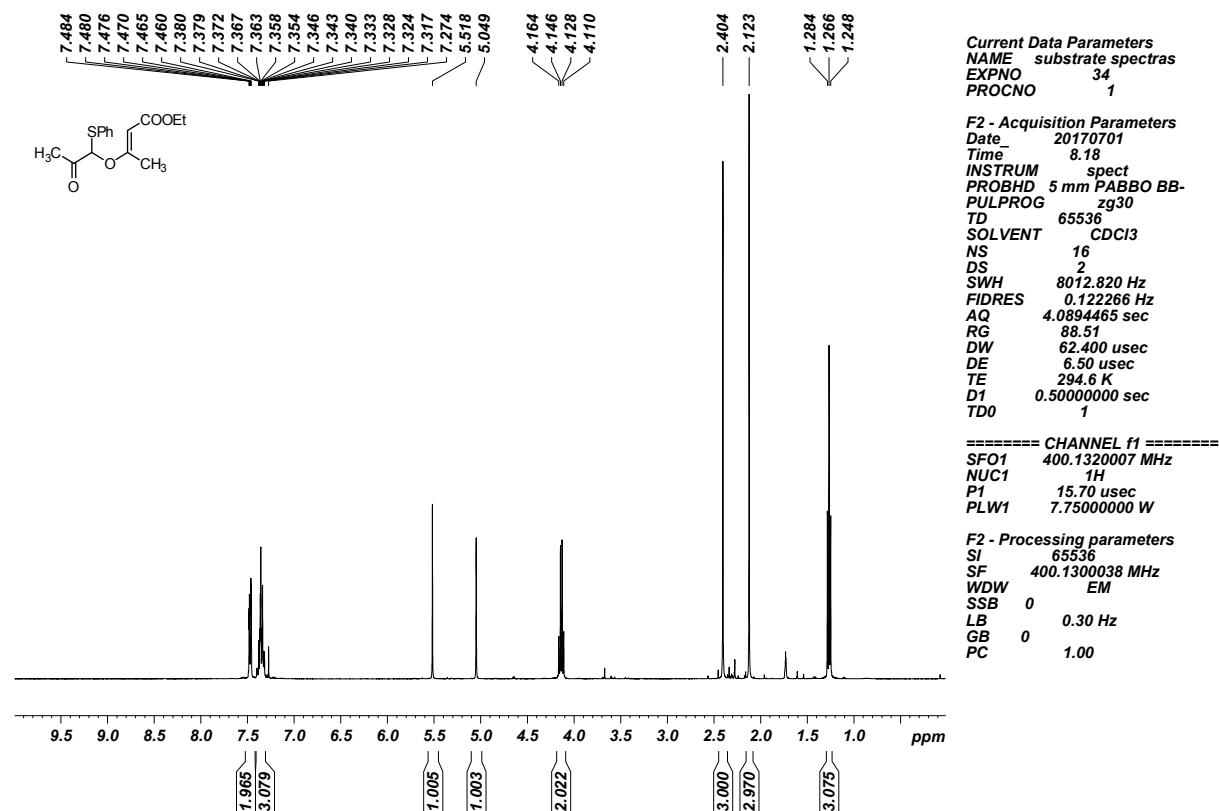


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

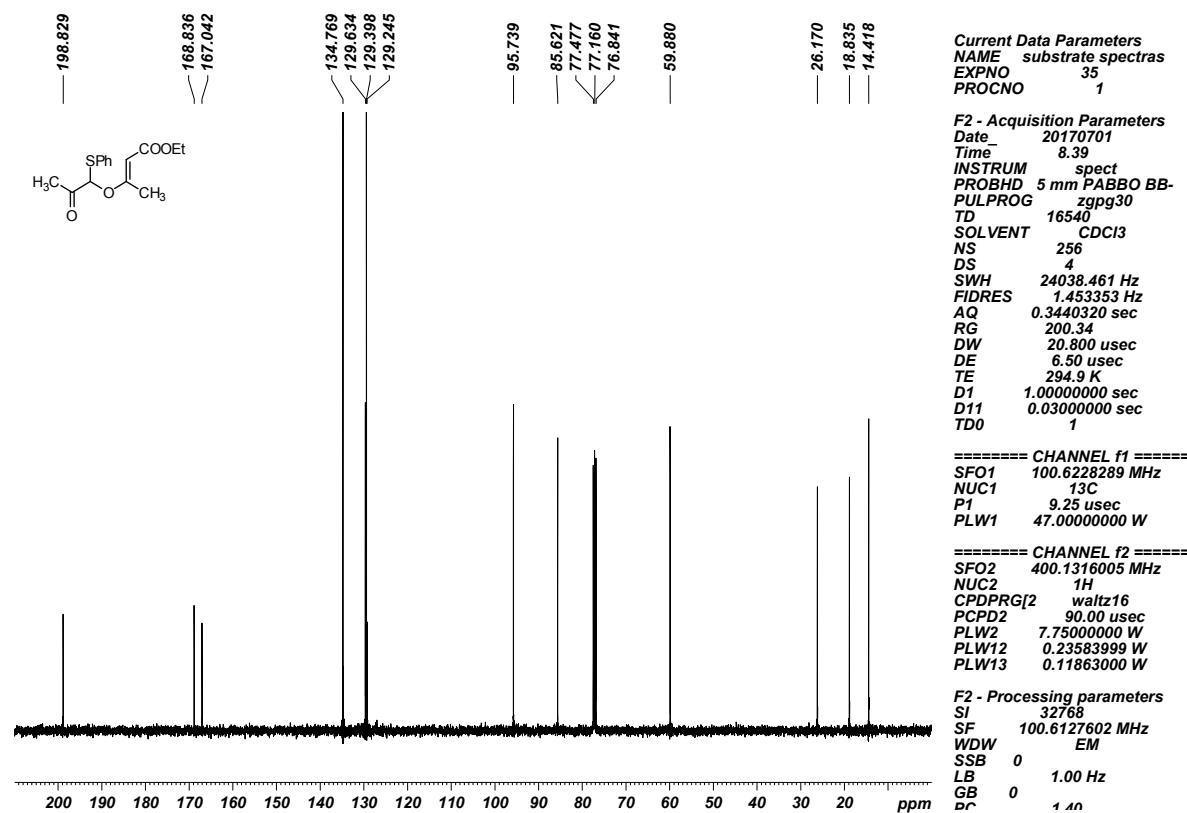


Vinylogous carbonate 3d

¹H NMR (400 MHz, CDCl₃, 24 °C)

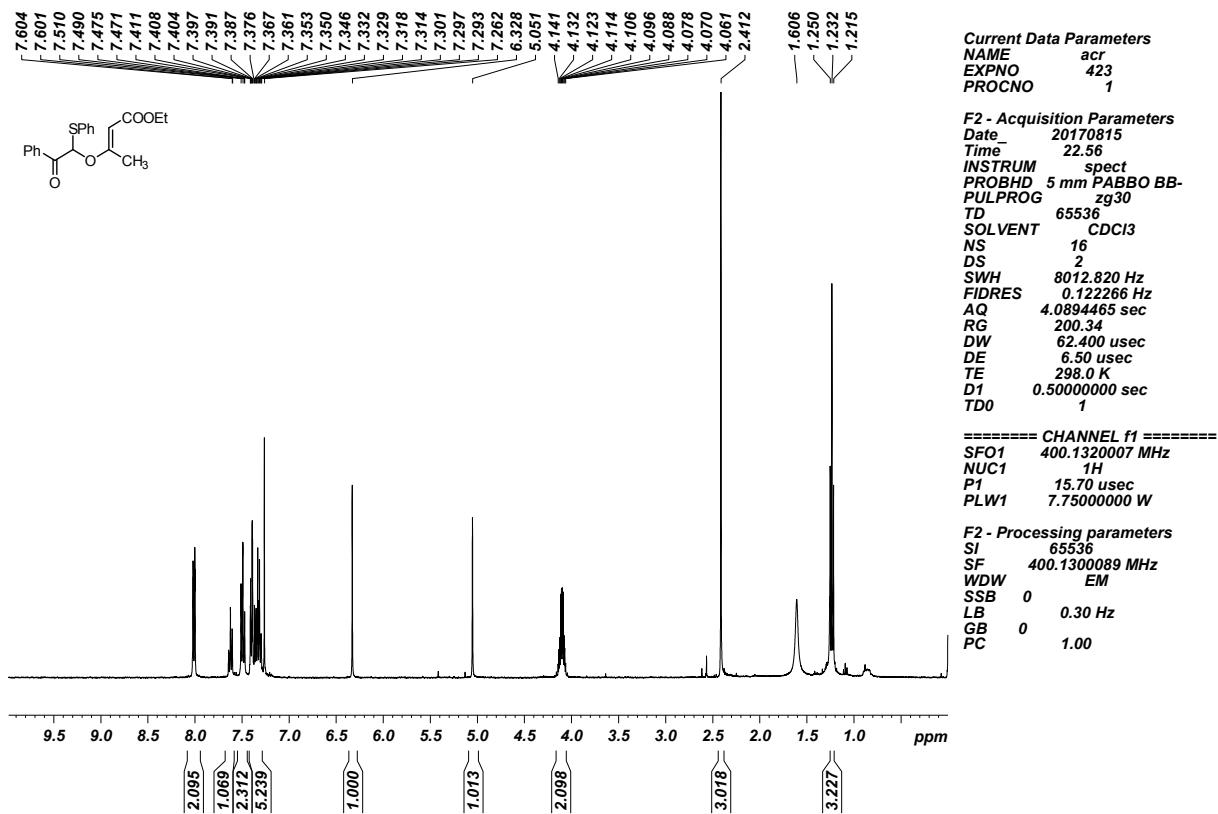


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

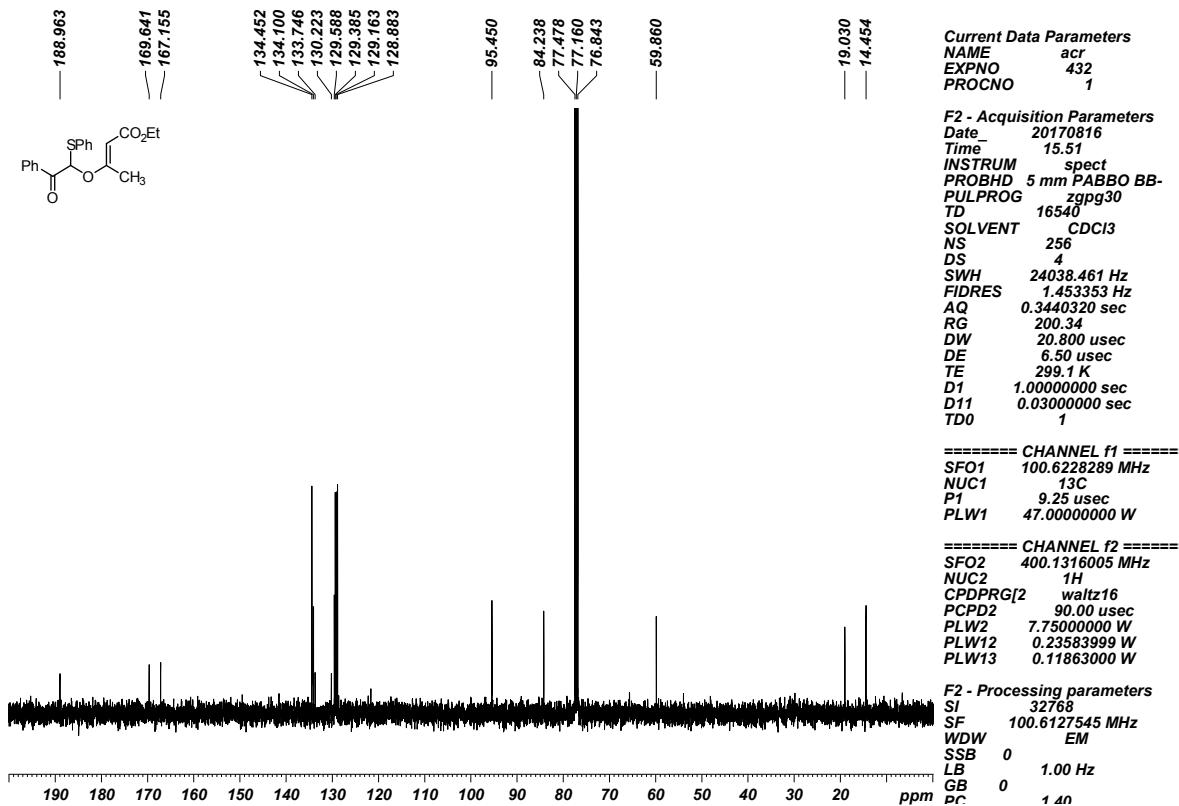


Vinylogous carbonate 3e

¹H NMR (400 MHz, CDCl₃, 24 °C)

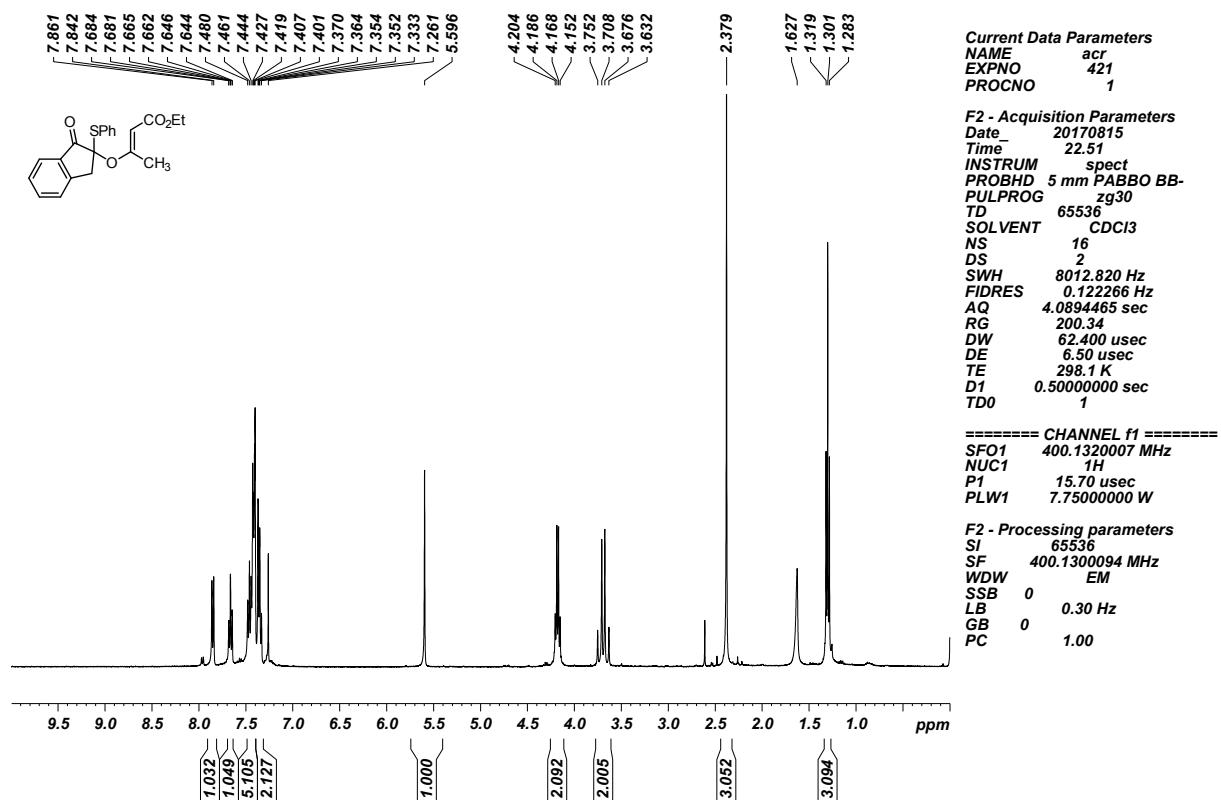


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

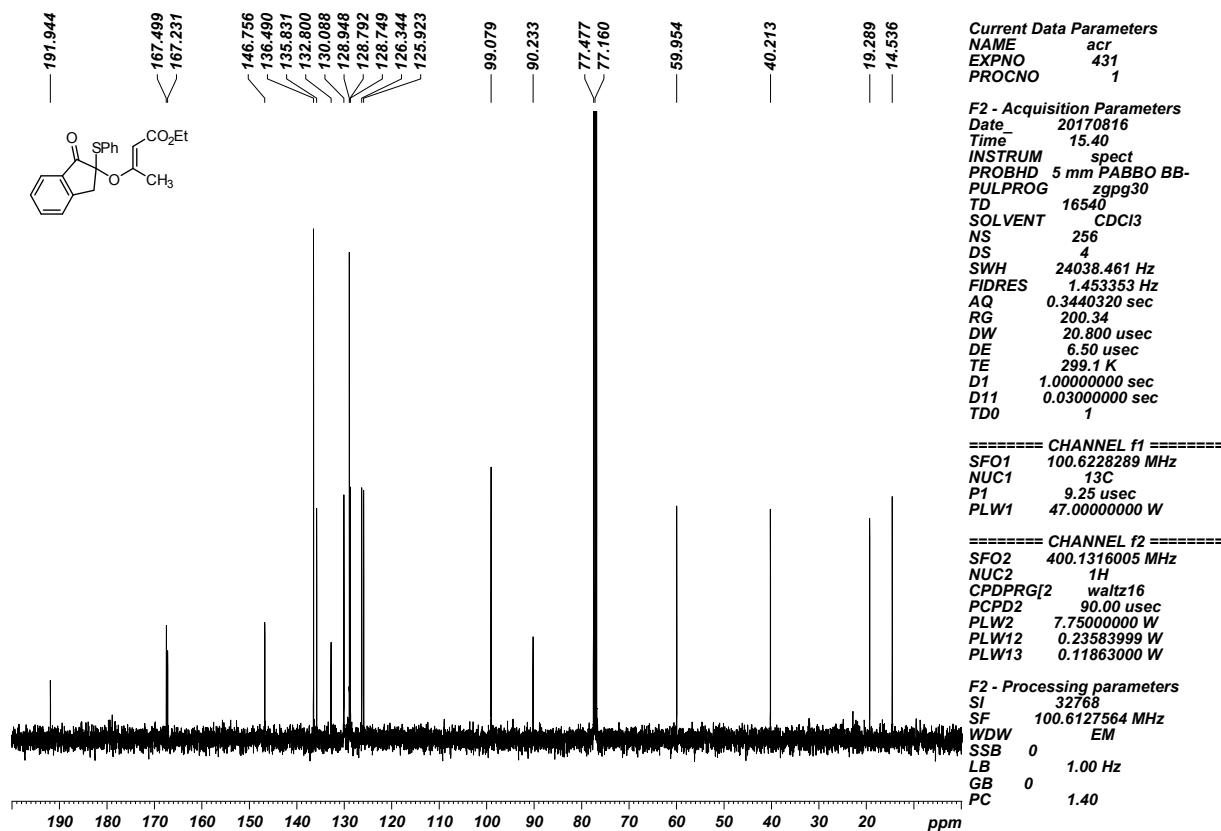


Vinylogous carbonate 3f

¹H NMR (400 MHz, CDCl₃, 24 °C)

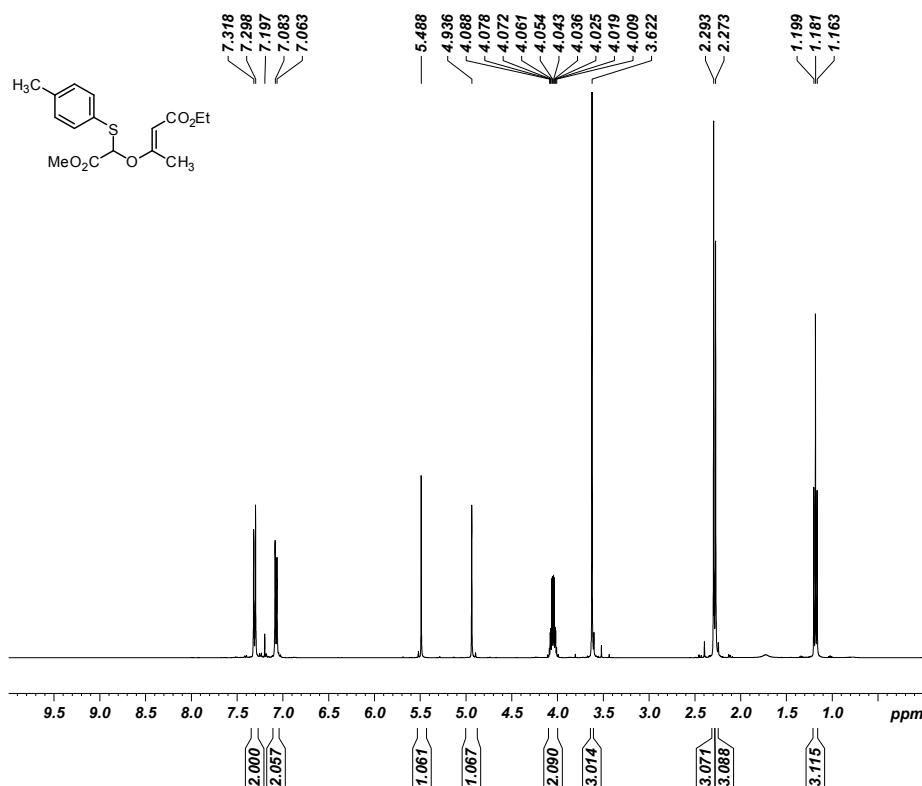


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)



Vinylogous carbonate 3j

¹H NMR (400 MHz, CDCl₃, 24 °C)



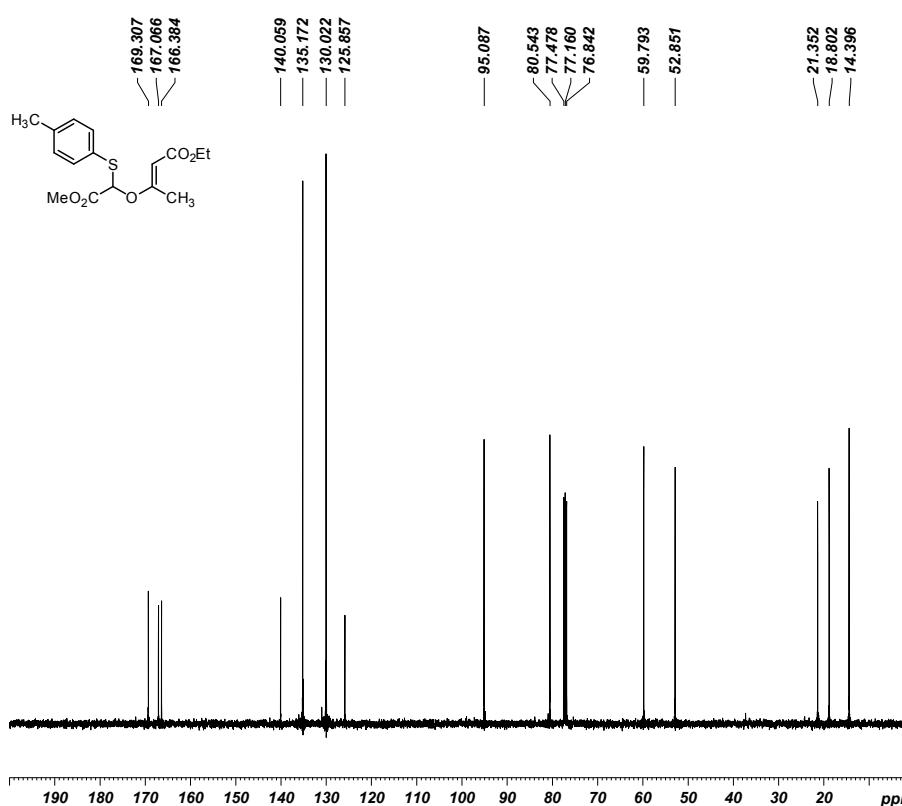
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 TD 65536
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 DS 2
 SWH 8012.820 Hz
 FIDRES 0.122266 Hz
 AQ 4.0894465 sec
 RG 60.89
 DW 62.400 usec
 DE 6.50 usec
 TE 294.5 K
 D1 0.50000000 sec
 TDO 1

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 NUC1 1H
 P1 15.70 usec
 PLW1 7.75000000 W

F2 - Processing parameters
 SI 65536
 SF 400.1300346 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)



Current Data Parameters
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 EXPNO 447
 PROCNO 1

F2 - Acquisition Parameters
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 Time 18.23
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 PULPROG zgpg30
 TD 16540
 SOLVENT CDCl₃
 NS 256
 DS 4
 SWH 24038.461 Hz
 FIDRES 1.453353 Hz
 AQ 0.3440320 sec
 RG 200.34
 DW 20.800 usec
 DE 6.50 usec
 TE 294.9 K
 D1 1.0000000 sec
 D11 0.03000000 sec
 TDO 1

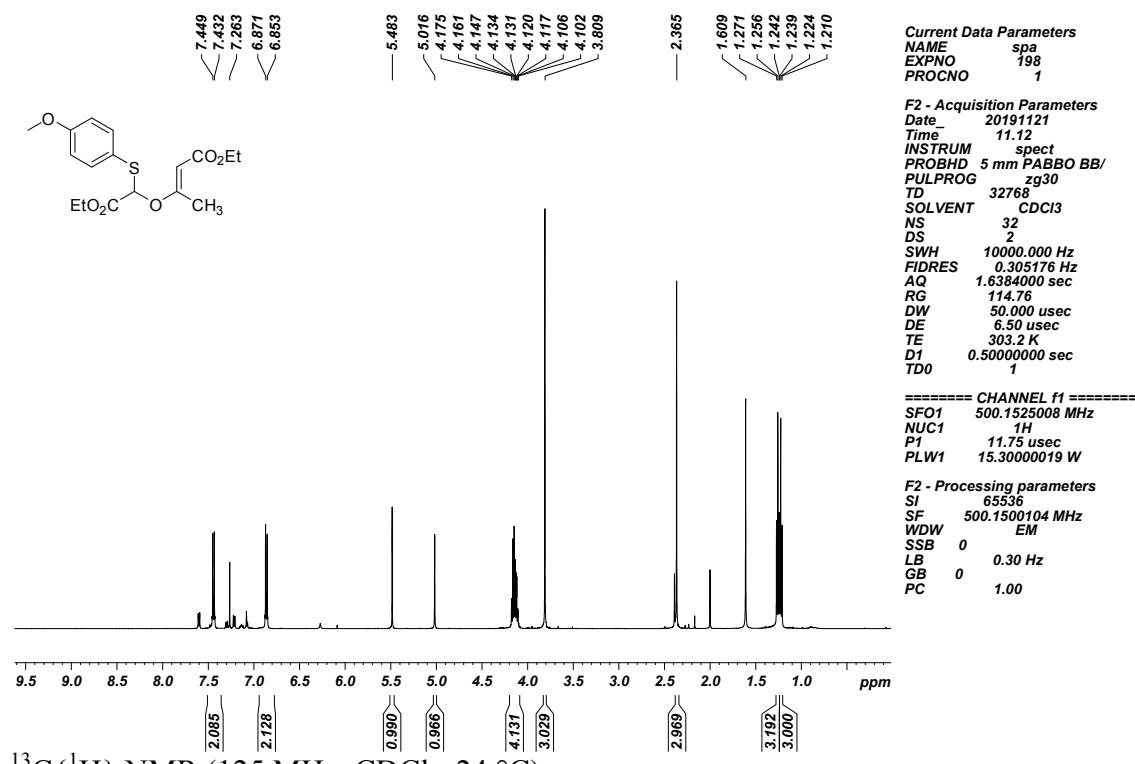
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 NUC1 13C
 P1 9.25 usec
 PLW1 47.00000000 W

===== CHANNEL f2 ======
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 NUC2 1H
 CPDPRG[2] waltz16
 PCPD2 90.00 usec
 PLW2 7.75000000 W
 PLW12 0.23583999 W
 PLW13 0.11863000 W

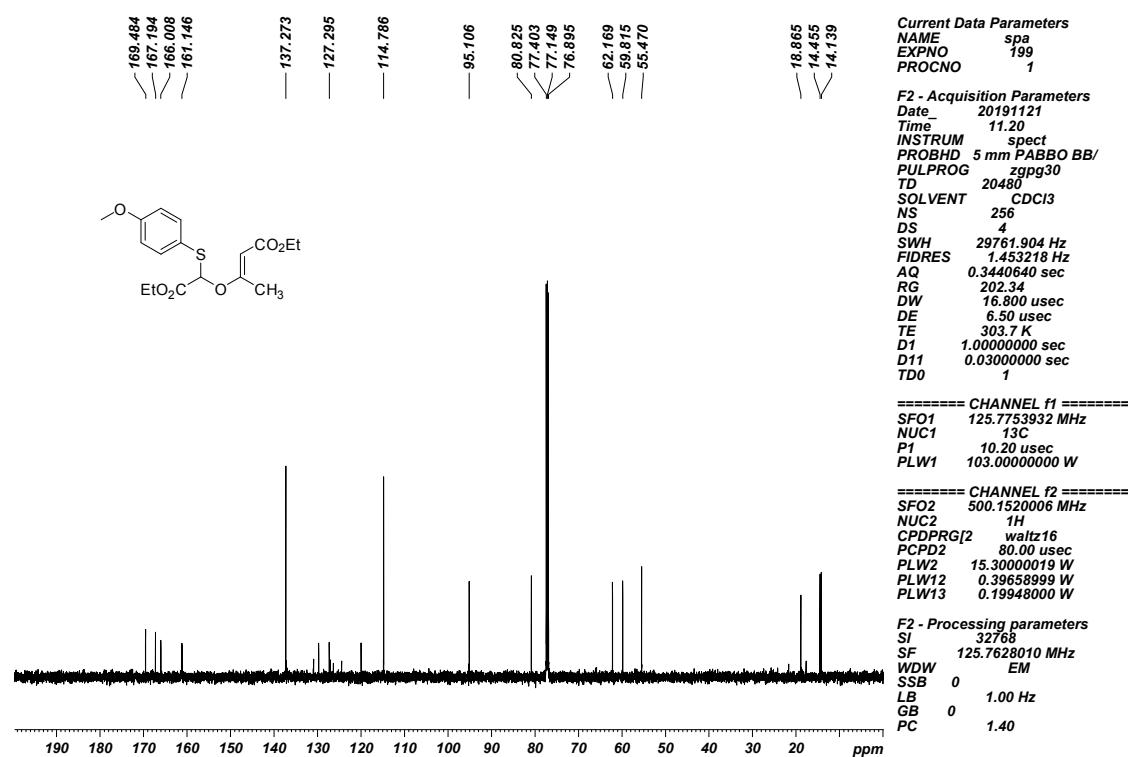
F2 - Processing parameters
 SI 32768
 SF 100.6127625 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

Vinylogous carbonate 3k

¹H NMR (500 MHz, CDCl₃, 24 °C)

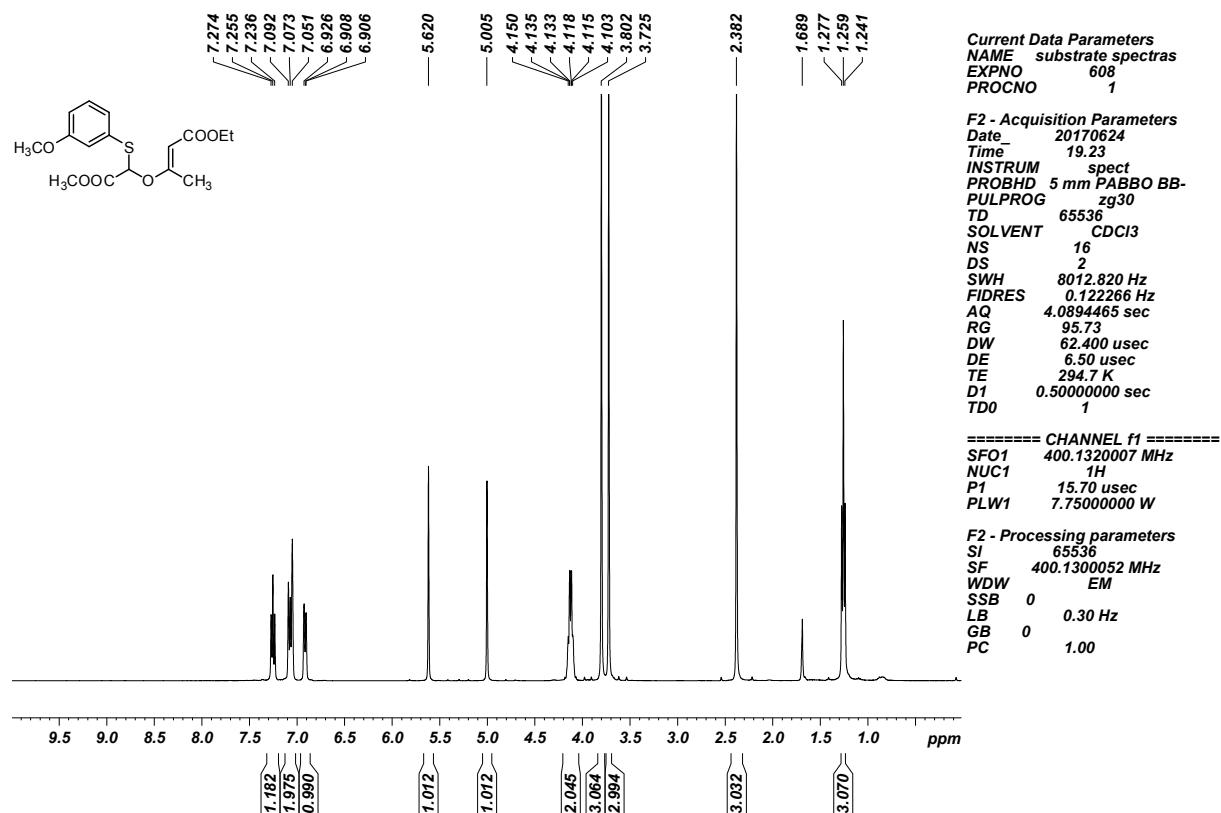


¹³C{¹H} NMR (125 MHz, CDCl₃, 24 °C)

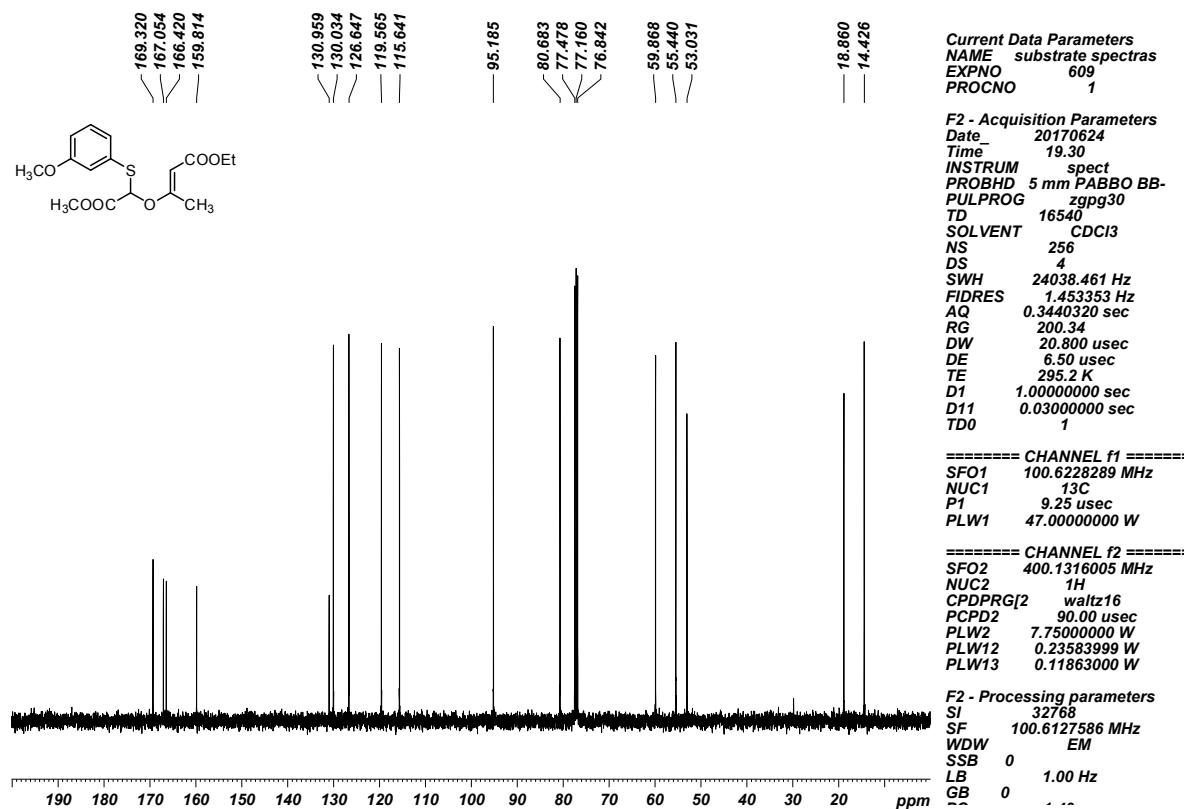


Vinylogous carbonate 3l

¹H NMR (400 MHz, CDCl₃, 24 °C)

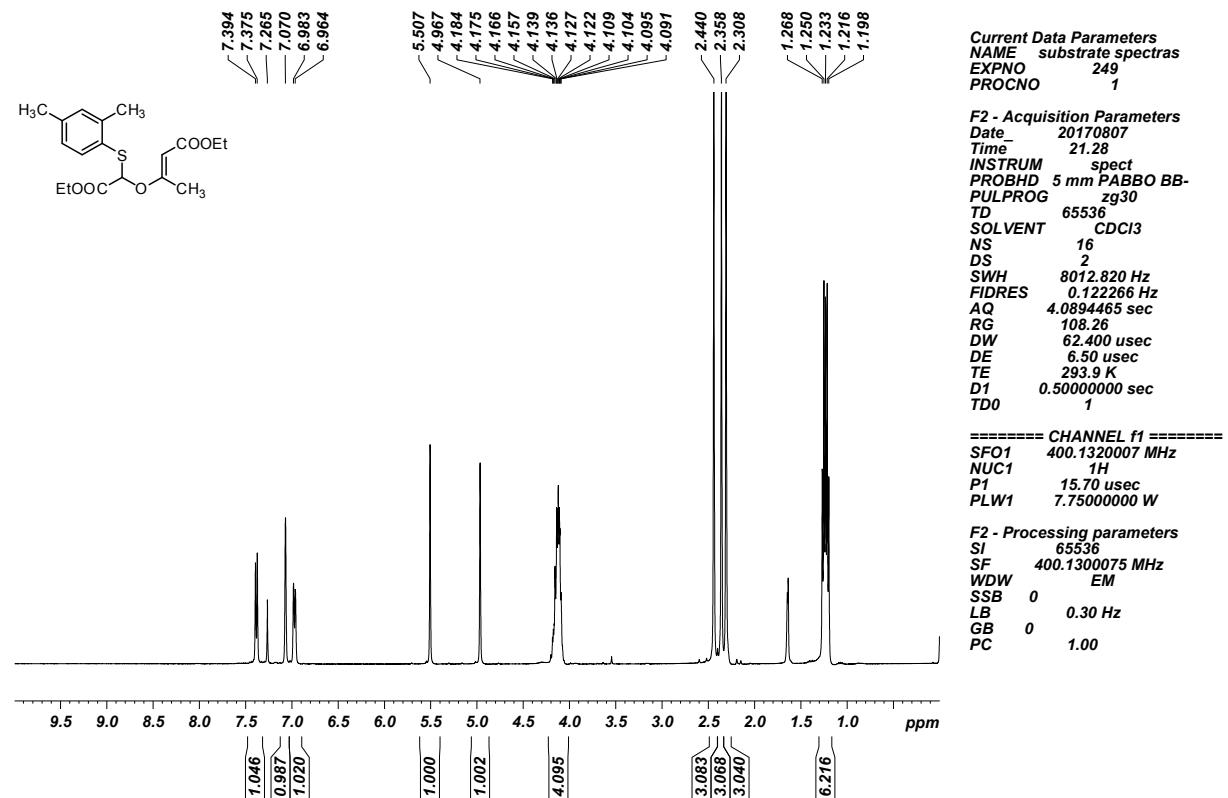


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

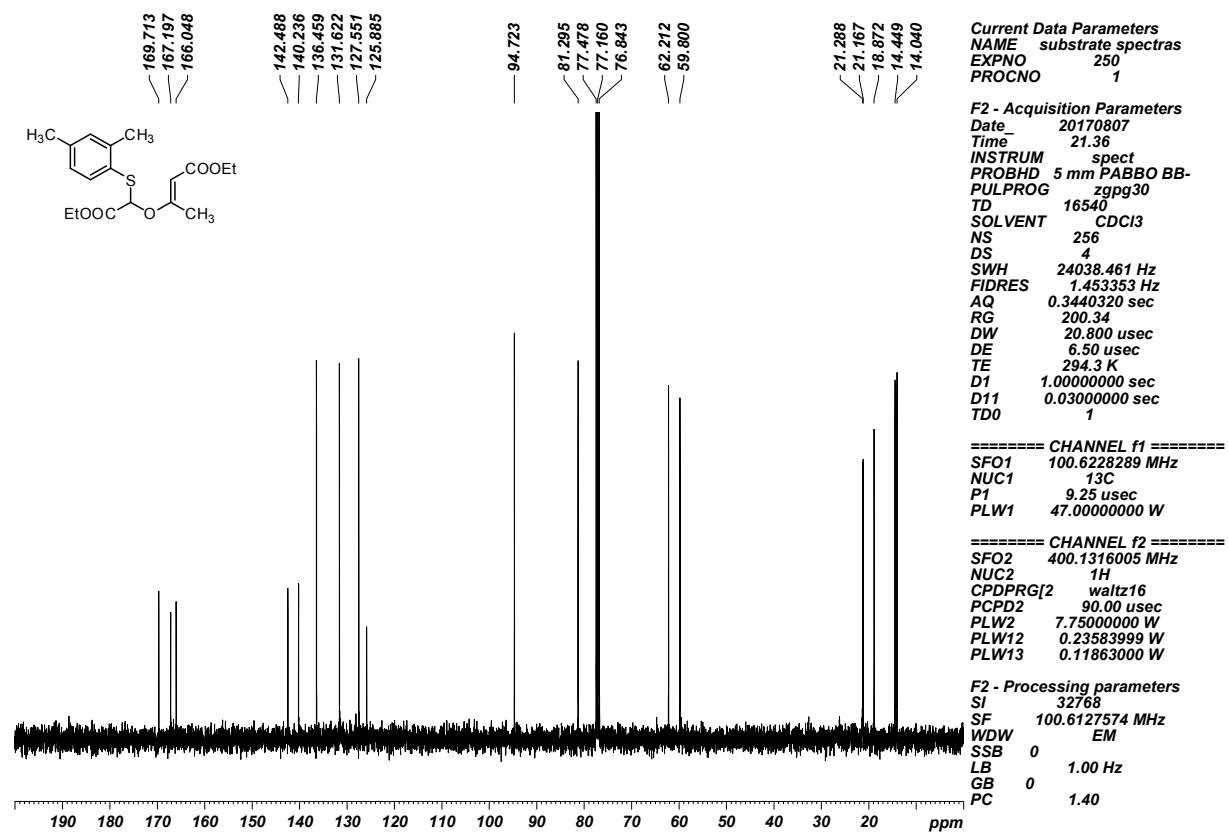


Vinylogous carbonate 3m

¹H NMR (400 MHz, CDCl₃, 24 °C)

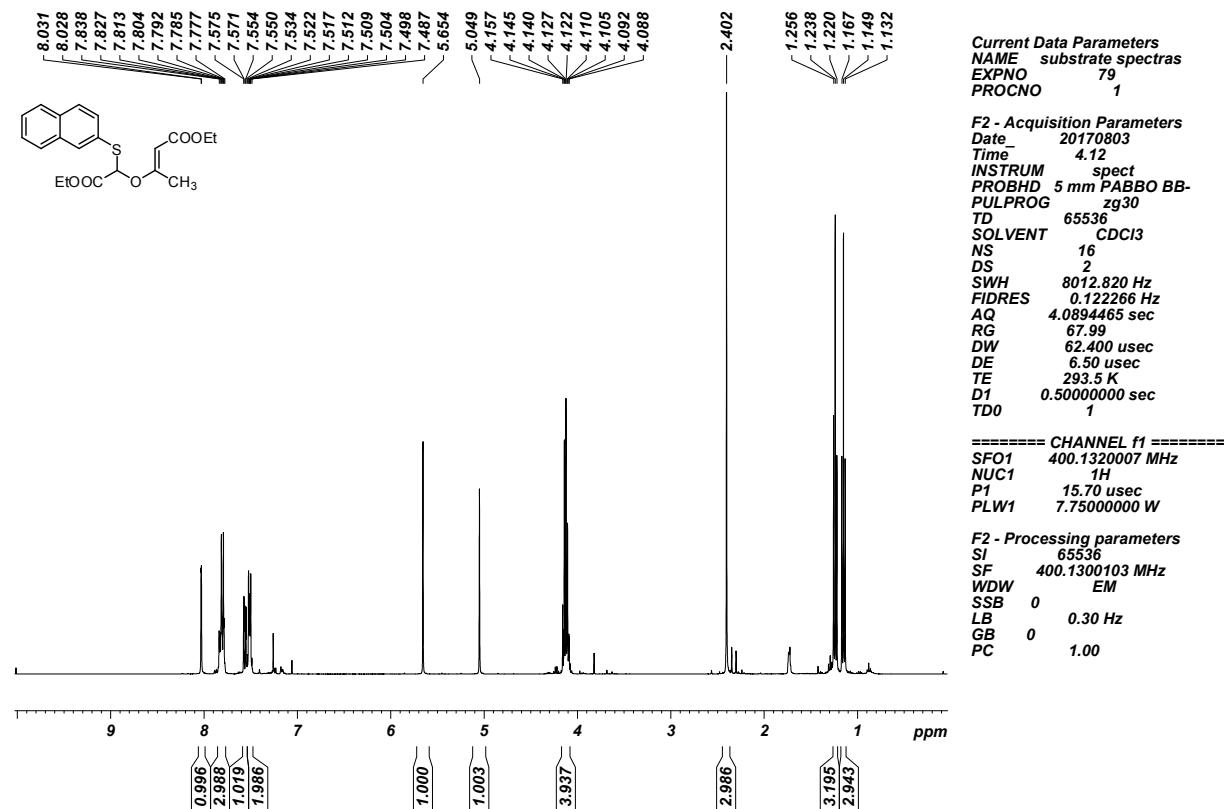


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

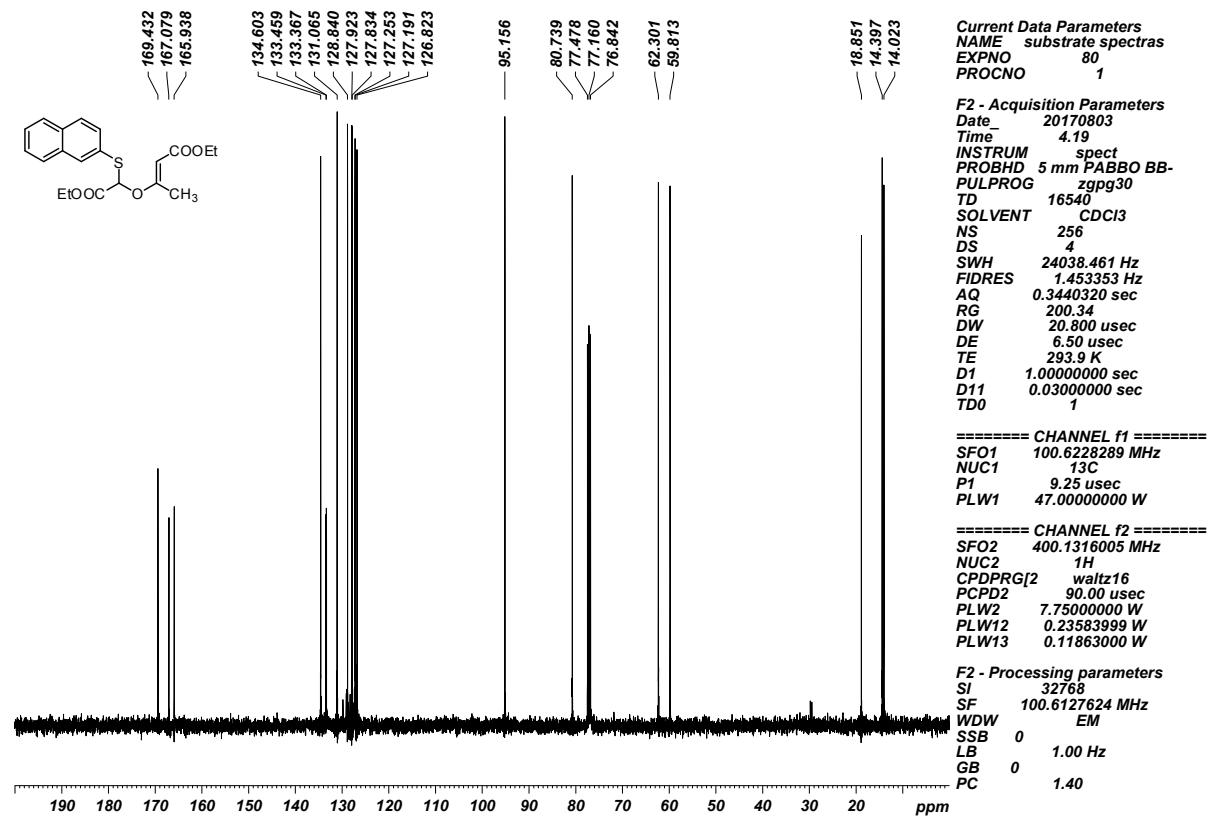


Vinylogous carbonate 3n

¹H NMR (400 MHz, CDCl₃, 24 °C)

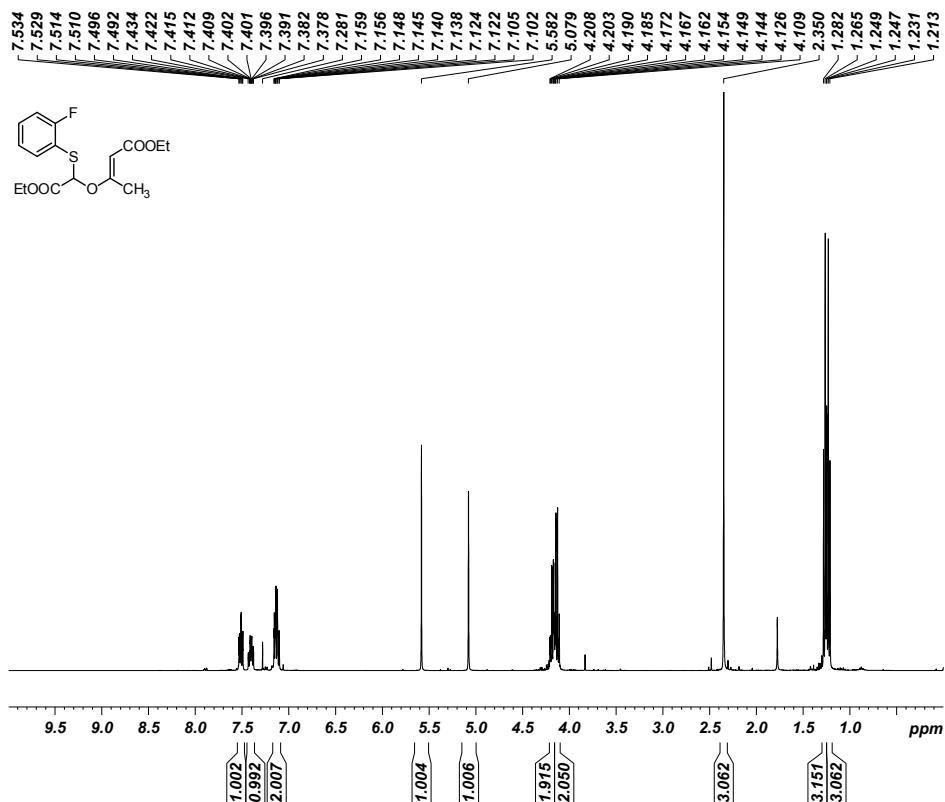


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)



Vinylogous carbonate 3o

¹H NMR (400 MHz, CDCl₃, 24 °C)



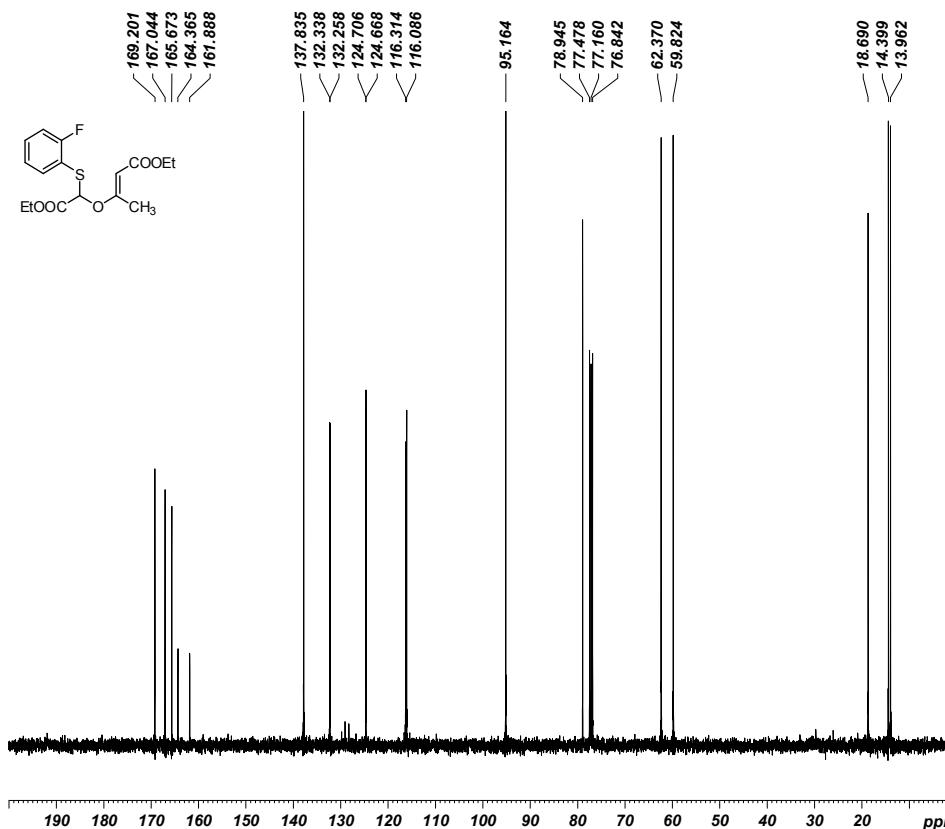
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SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 60.89
DW 62.400 usec
DE 6.50 usec
TE 293.5 K
D1 0.50000000 sec
T0D 1

===== CHANNEL f1 =====
SFO1 400.1320007 MHz
NUC1 1H
P1 15.70 usec
PLW1 7.7500000 W

F2 - Processing parameters
 SI 65536
 SF 400.1300010 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

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



Current Data Parameters
NAME substrate spectra
EXPNO 93
PROCNO 1

F2 - Acquisition Parameters
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 Time 6.15
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PULPROG zgpp30
TD 16540
SOLVENT CDCl3
NS 256
DS 4
SWH 24038.461 Hz
FIDRES 1.453353 Hz
AQ 0.3440320 sec
RG 200.34
DW 20.800 usec
DE 6.50 usec
TE 293.9 K
D1 1.0000000 sec
D11 0.03000000 sec
T0D 1

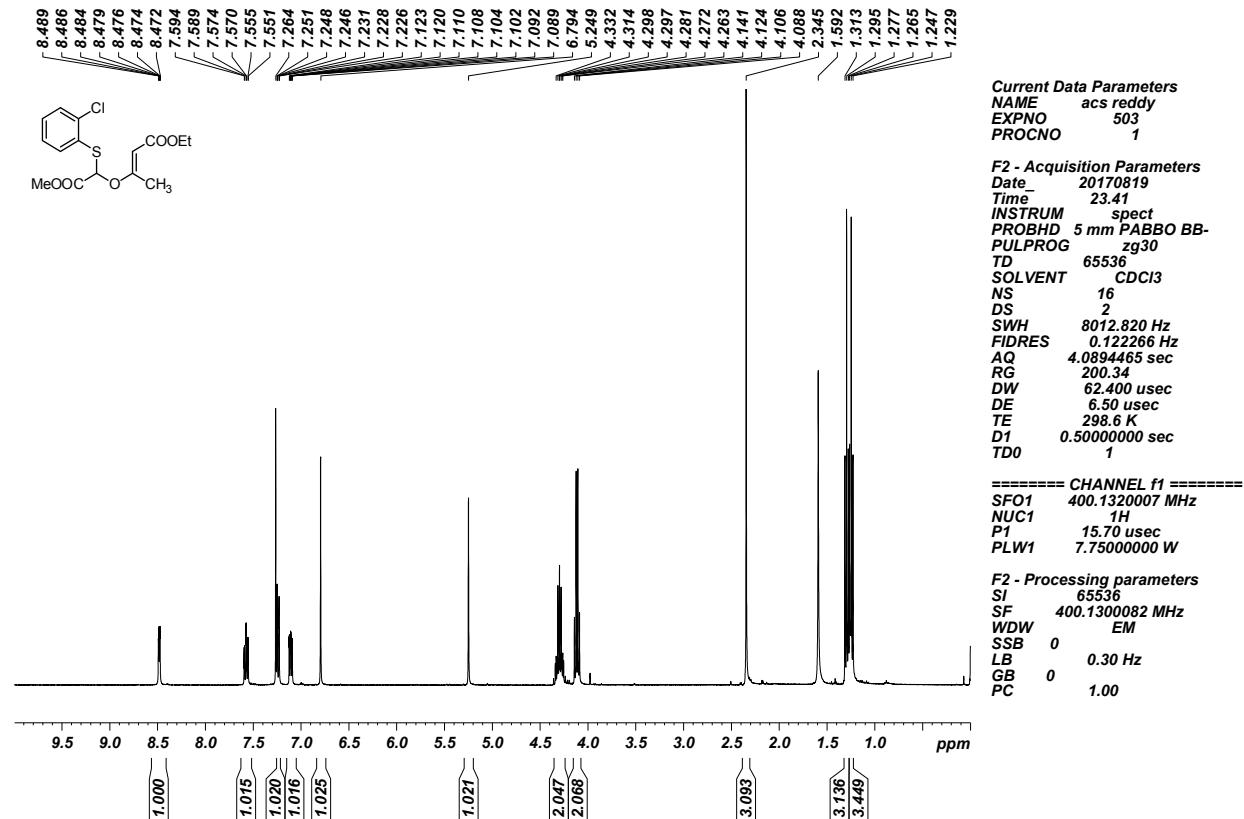
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NUC1 13C
P1 9.25 usec
PLW1 47.00000000 W

===== CHANNEL f2 =====
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NUC2 1H
CPDPRG[2] waltz16
PCPD2 90.00 usec
PLW2 7.7500000 W
PLW12 0.23583999 W
PLW13 0.11863000 W

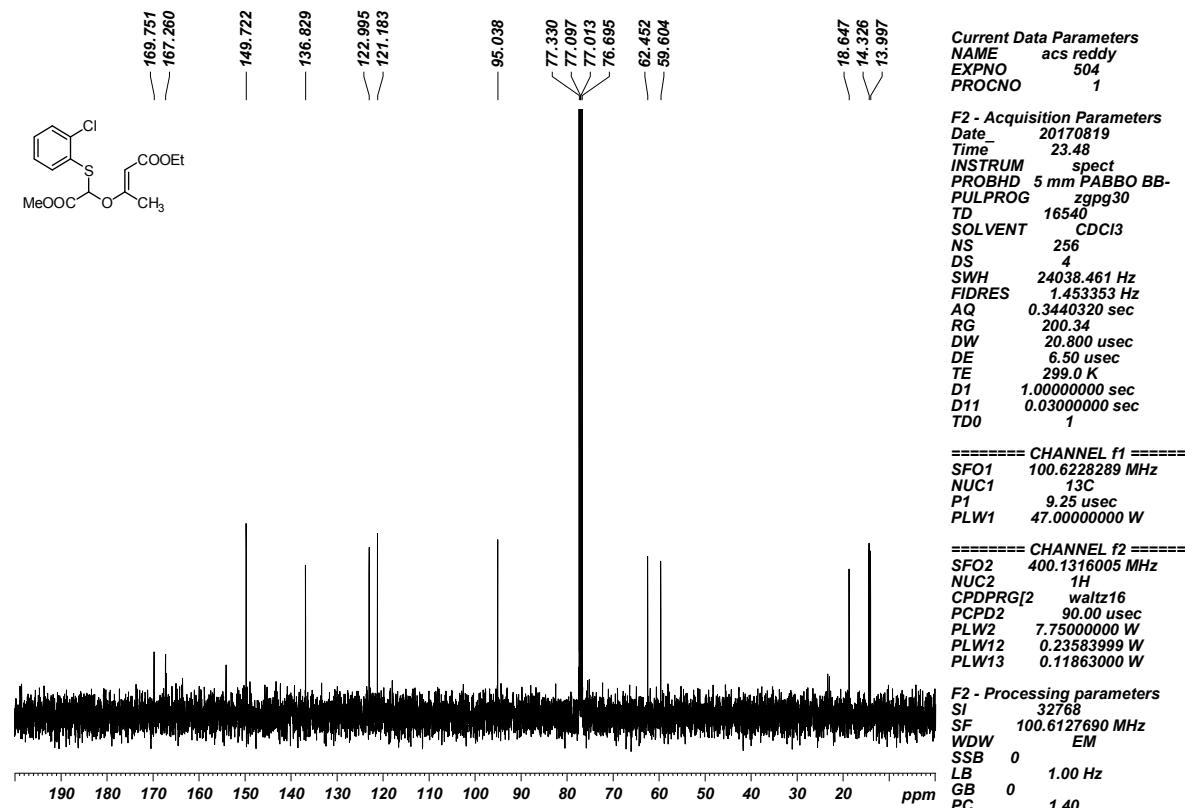
F2 - Processing parameters
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 SF 100.6127613 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

Vinylogous carbonate 3p

¹H NMR (400 MHz, CDCl₃, 24 °C)

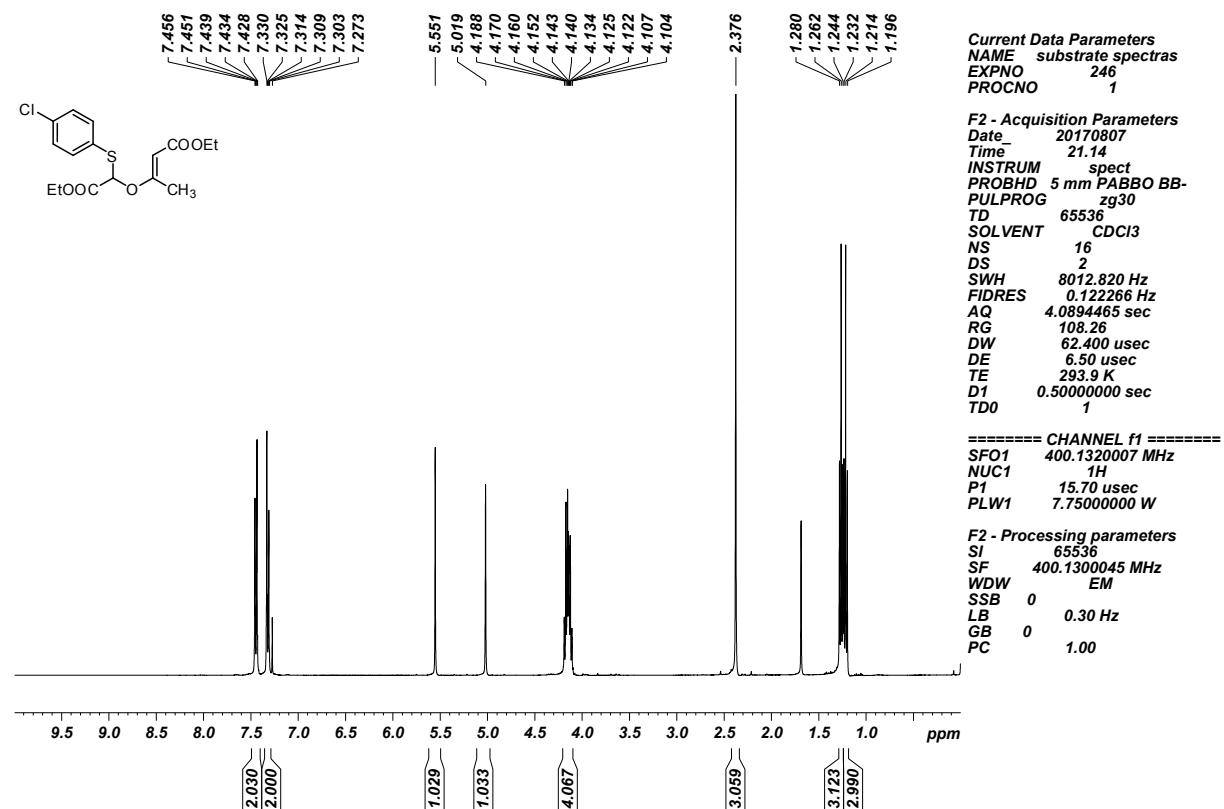


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

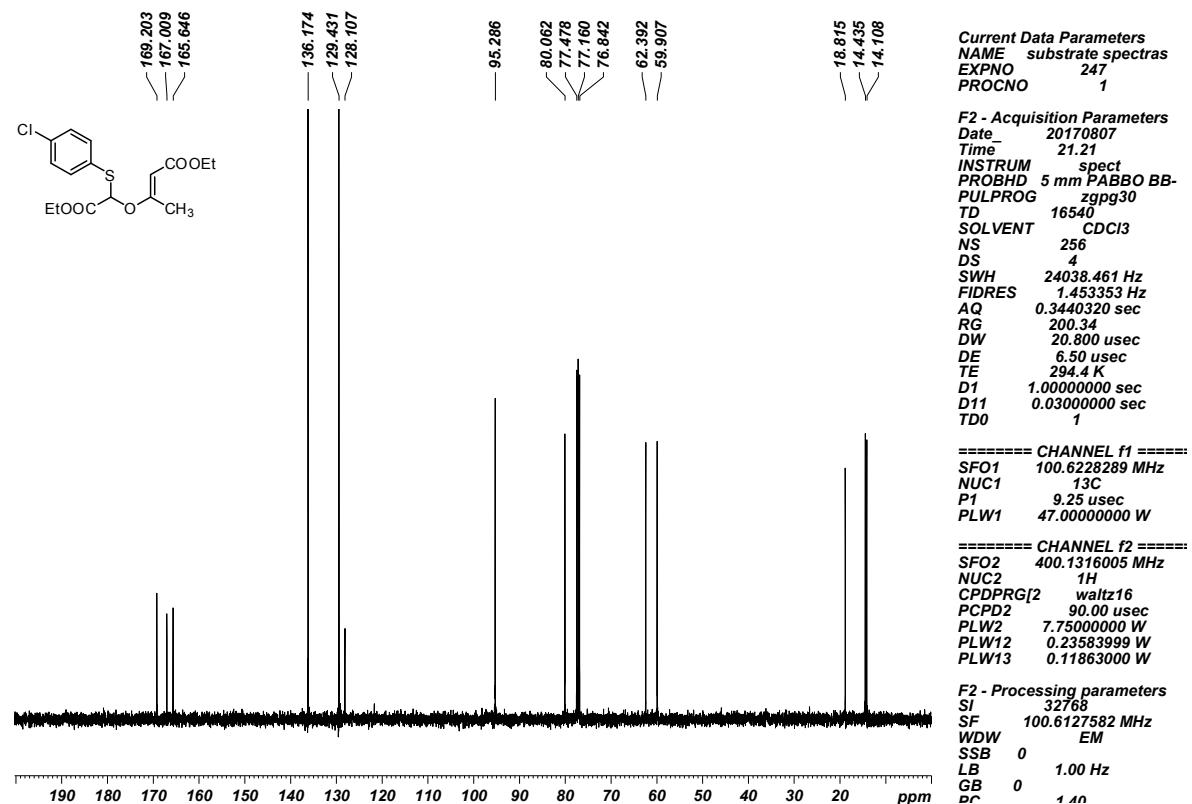


Vinylogous carbonate 3q

¹H NMR (400 MHz, CDCl₃, 24 °C)

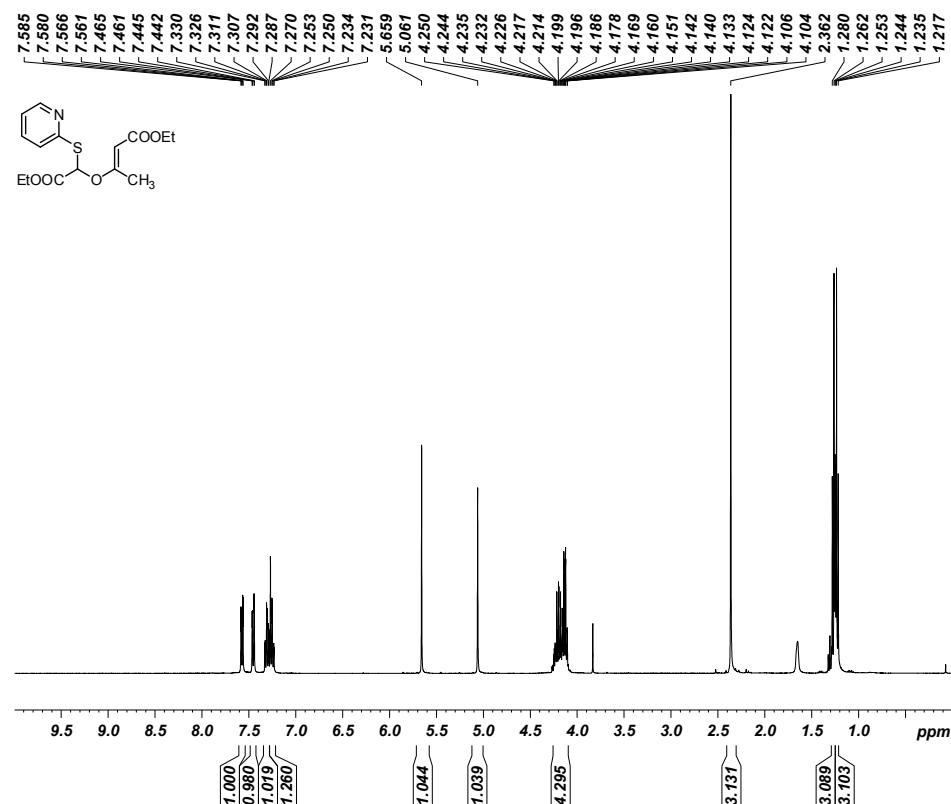


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)



Vinylogous carbonate 3r

¹H NMR (400 MHz, CDCl₃, 24 °C)

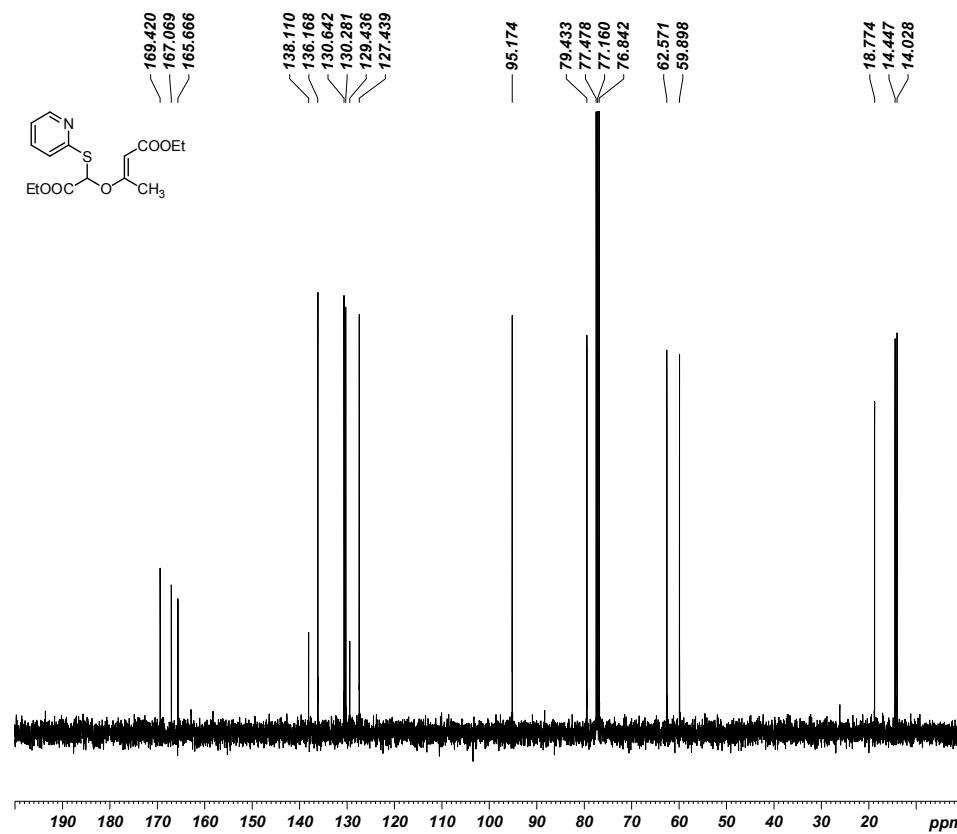


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SOLVENT CDCl₃
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SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 138.85
DW 62.400 usec
DE 6.50 usec
TE 294.3 K
D1 0.5000000 sec
TD0 1

===== CHANNEL f1 =====
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NUC1 1H
P1 15.70 usec
PLW1 7.75000000 W

F2 - Processing parameters
SI 65536
SF 400.1300057 MHz
WDW EM
SSB 0 0.30 Hz
LB 0 0.30 Hz
GB 0 1.00
PC 1.00

¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)



Current Data Parameters
NAME substrate spectra
EXPNO 285
PROCNO 1

F2 - Acquisition Parameters
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Time 22.58
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PULPROG zgpg30
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SOLVENT CDCl₃
NS 256
DS 4
SWH 24038.461 Hz
FIDRES 1.453353 Hz
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RG 200.34
DW 20.800 usec
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TD0 1

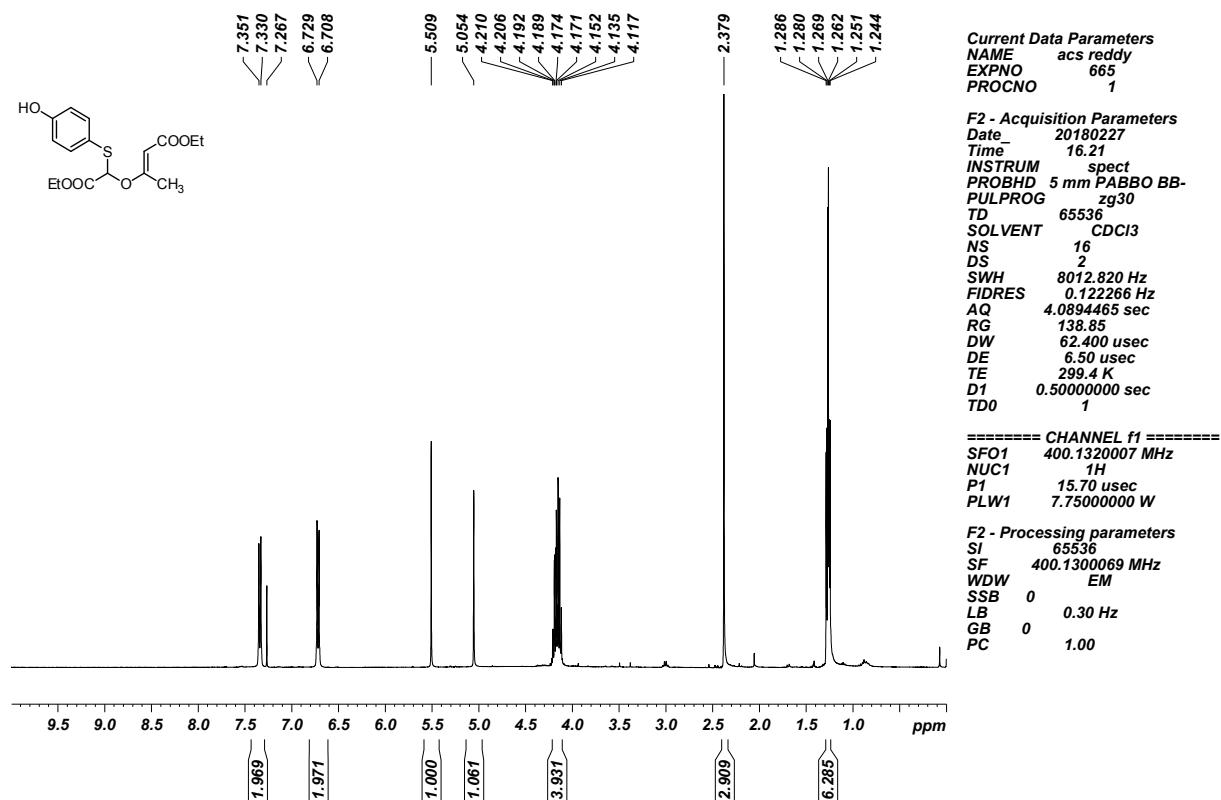
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PLW1 47.00000000 W

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NUC2 1H
CPDPRG[2] waltz16
PCPD2 90.00 usec
PLW2 7.75000000 W
PLW12 0.23583999 W
PLW13 0.11863000 W

F2 - Processing parameters
SI 32768
SF 100.6127572 MHz
WDW EM
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LB 0 1.00 Hz
GB 0 1.40
PC 1.40

Vinylogous carbonate 3s

¹H NMR (400 MHz, CDCl₃, 24 °C)

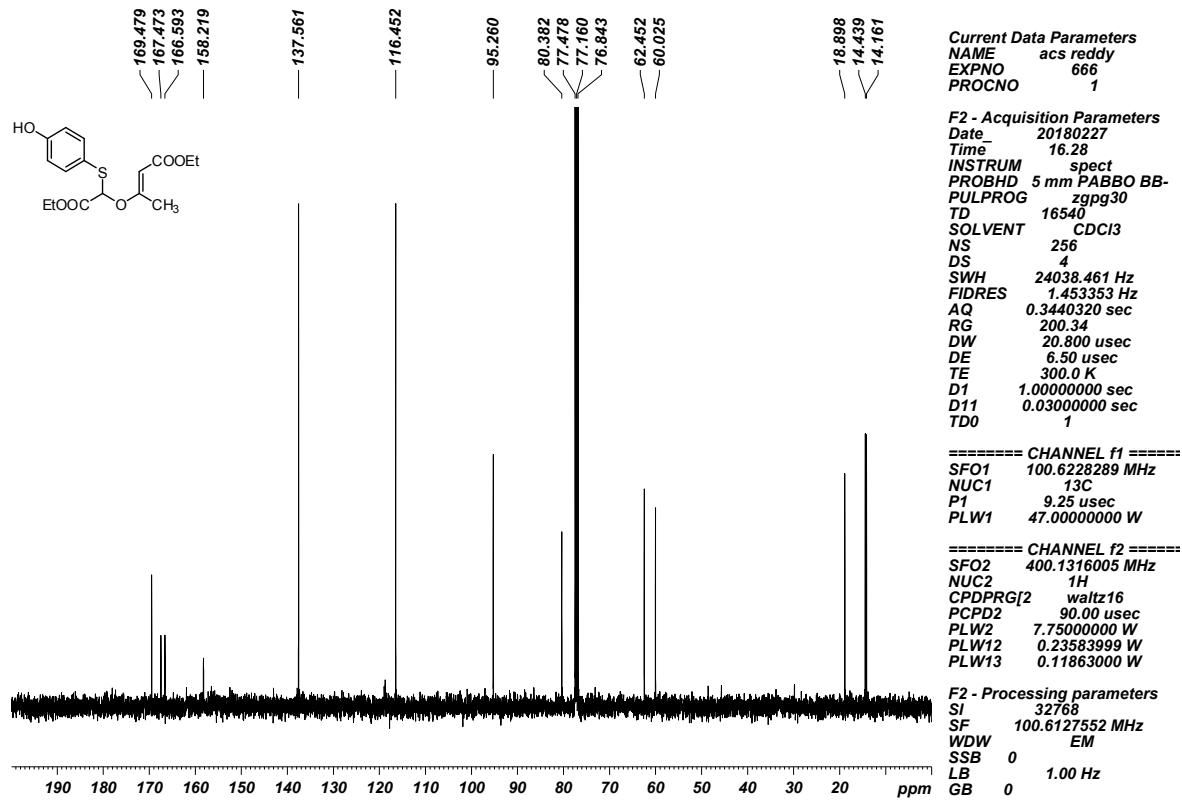


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TD 65536
SOLVENT CDCl₃
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FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 138.85
DW 62.400 usec
DE 6.50 usec
TE 299.4 K
D1 0.5000000 sec
TD0 1

===== CHANNEL f1 ======
SFO1 400.1320007 MHz
NUC1 1H
P1 15.70 usec
PLW1 7.75000000 W

F2 - Processing parameters
SI 65536
SF 400.1300069 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)



F2 - Acquisition Parameters
Date 20180227
Time 16.28
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 16540
SOLVENT CDCl₃
NS 256
DS 4
SWH 24038.461 Hz
FIDRES 1.453353 Hz
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DW 20.800 usec
DE 6.50 usec
TE 300.0 K
D1 1.0000000 sec
D11 0.03000000 sec
TD0 1

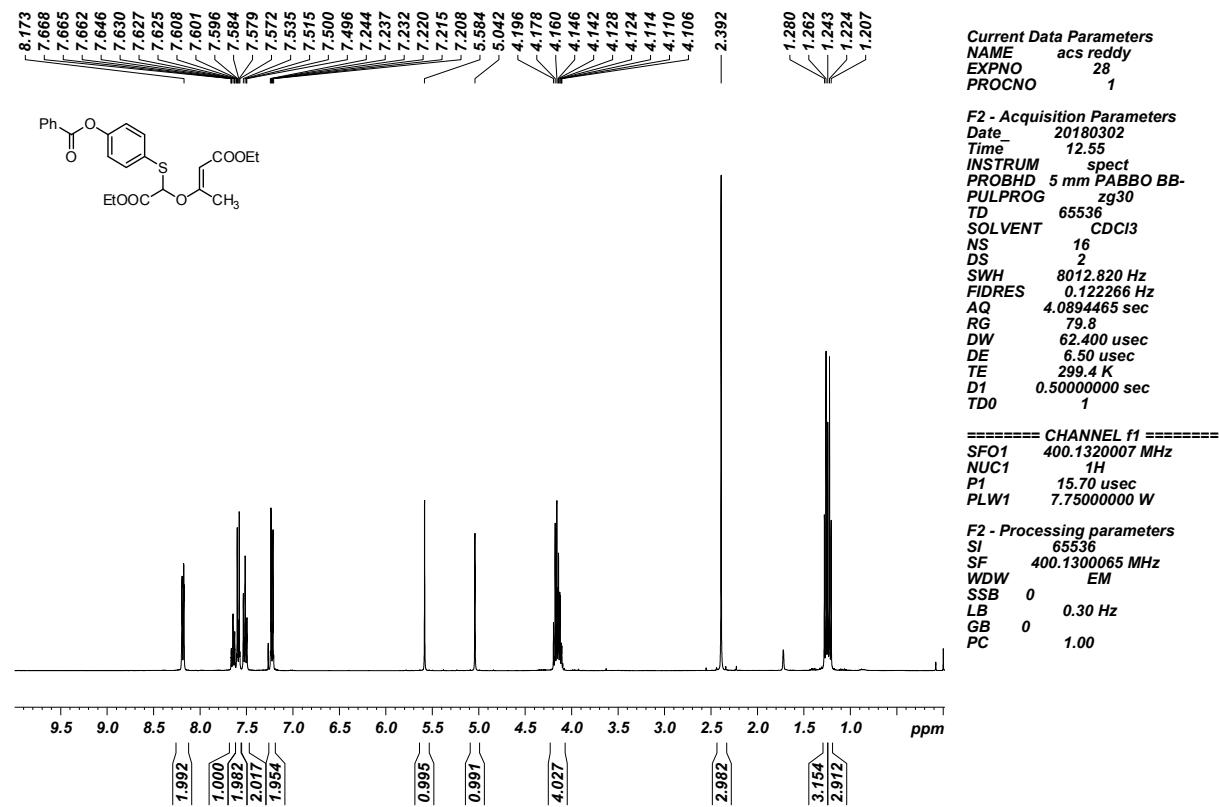
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NUC1 ¹³C
P1 9.25 usec
PLW1 47.00000000 W

===== CHANNEL f2 ======
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NUC2 1H
CPDPG[2] waltz16
PCPD2 90.00 usec
PLW2 7.75000000 W
PLW12 0.23583999 W
PLW13 0.11863000 W

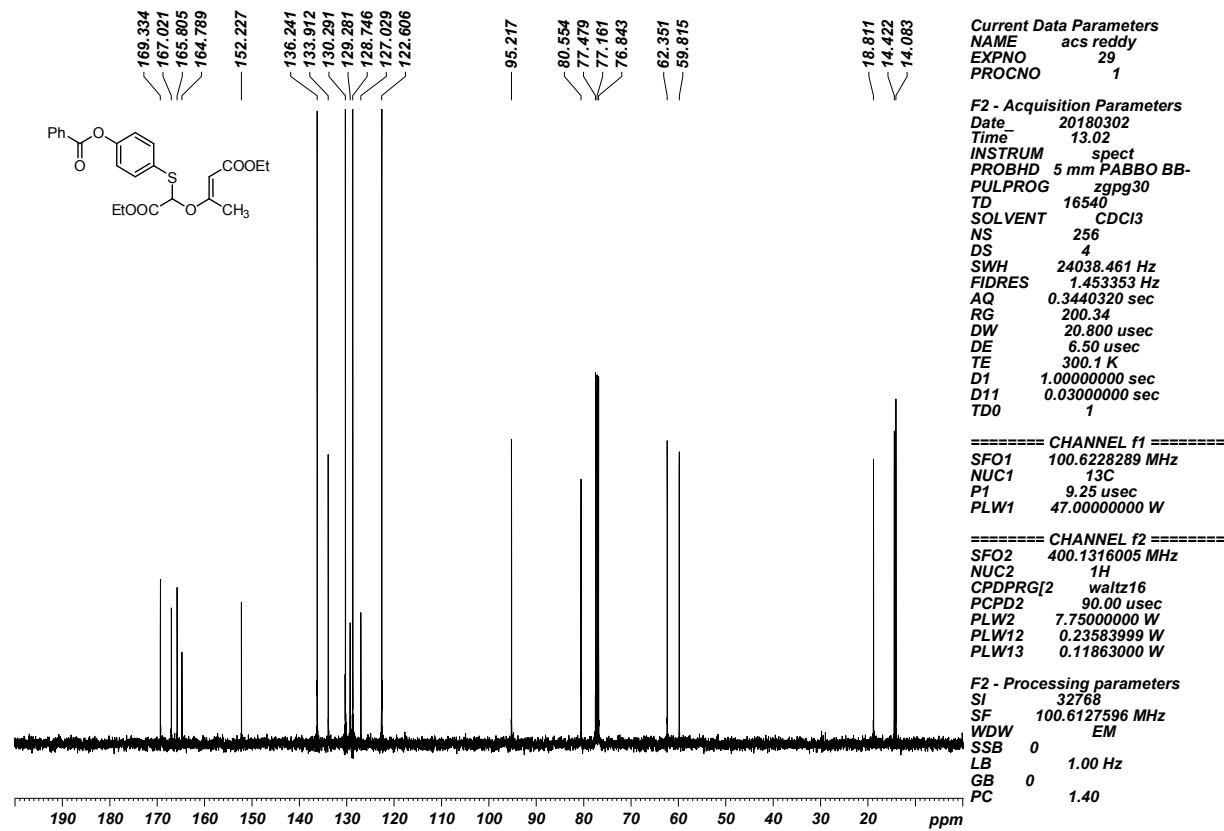
F2 - Processing parameters
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SSB 0
LB 1.00 Hz
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Vinylogous carbonate 3t

¹H NMR (400 MHz, CDCl₃, 24 °C)

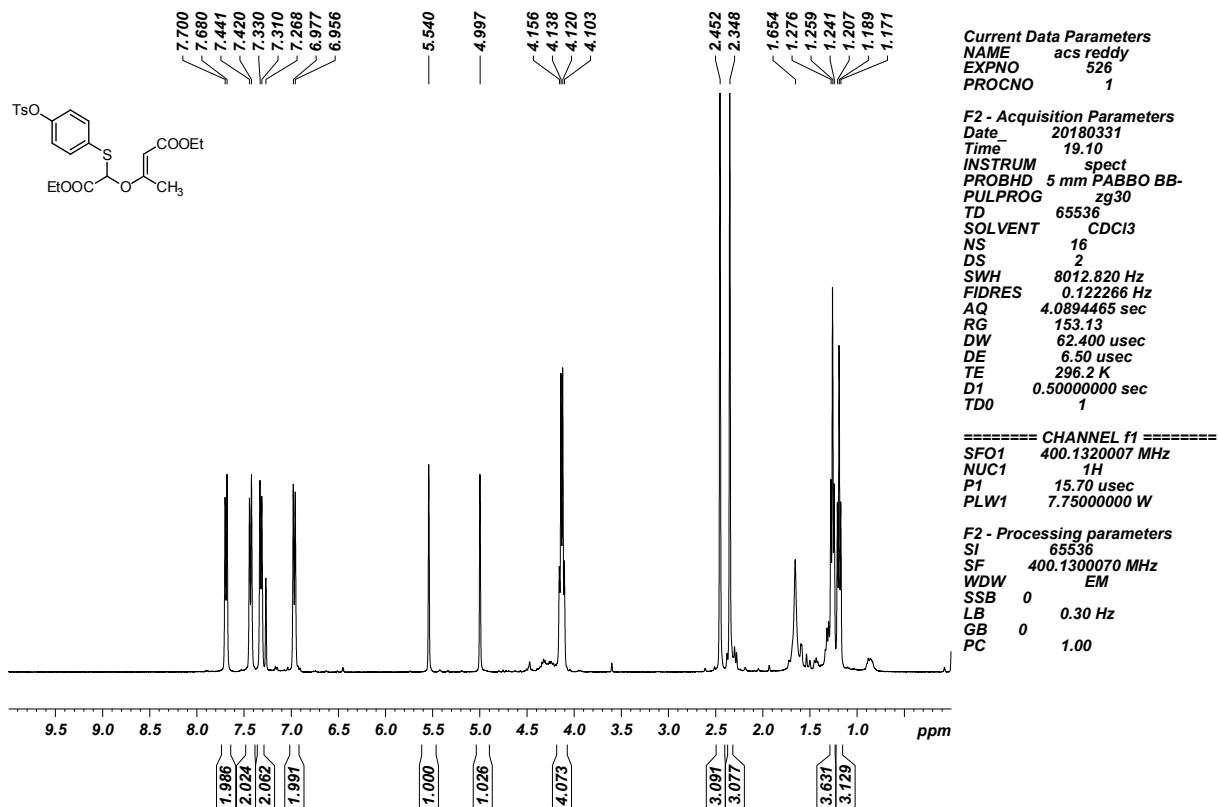


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

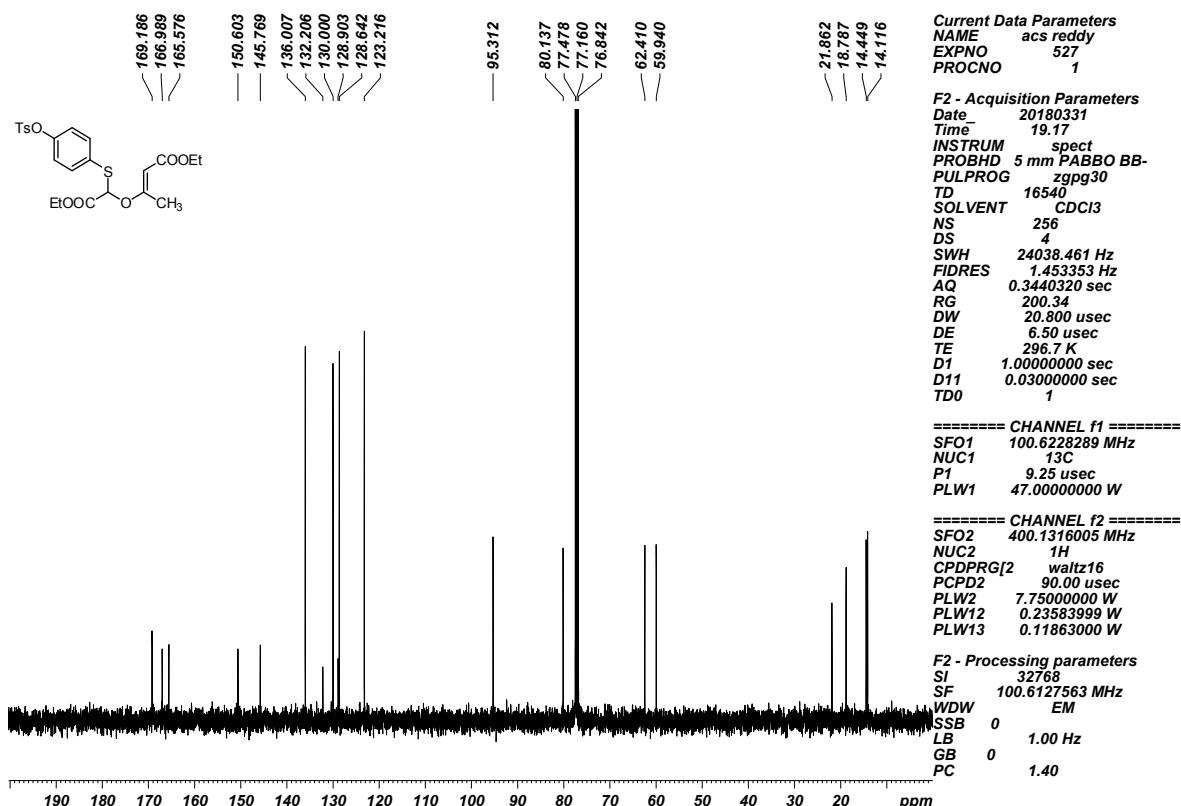


Vinylogous carbonate 3u

¹H NMR (400 MHz, CDCl₃, 24 °C)

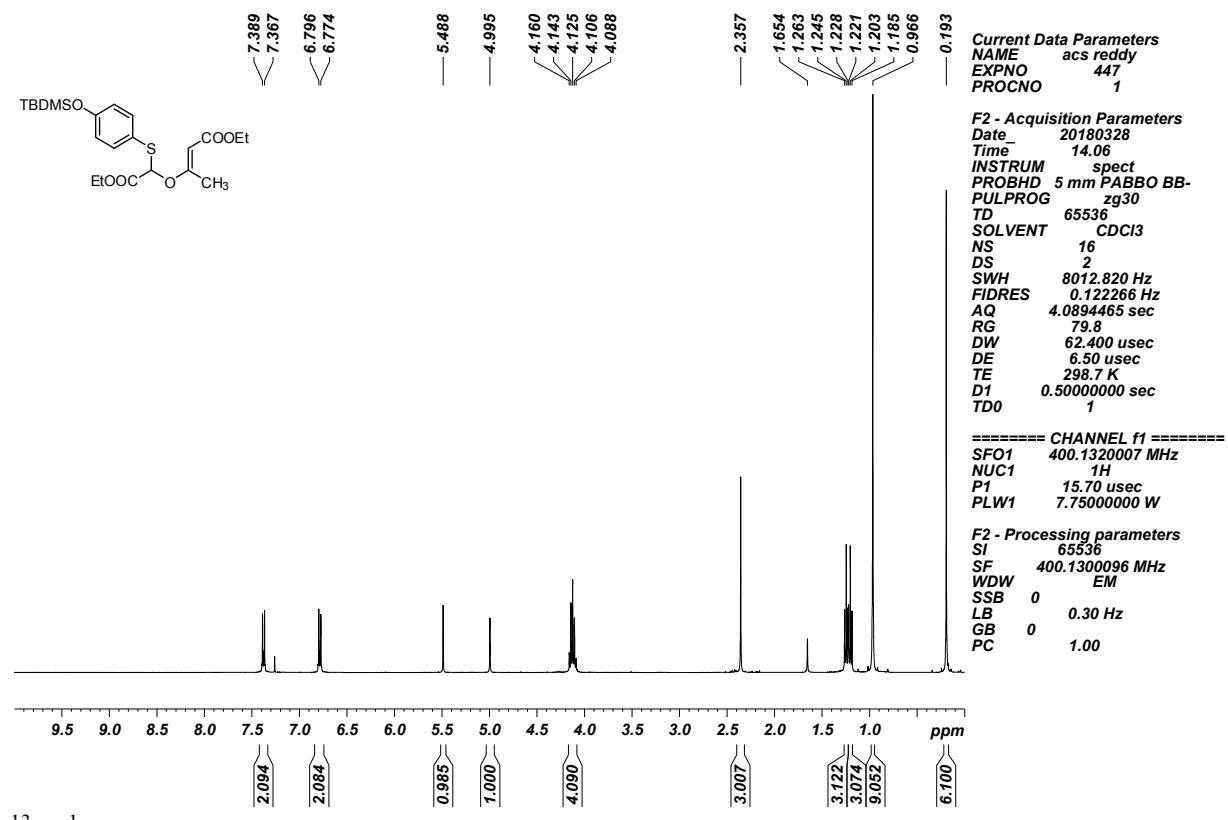


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

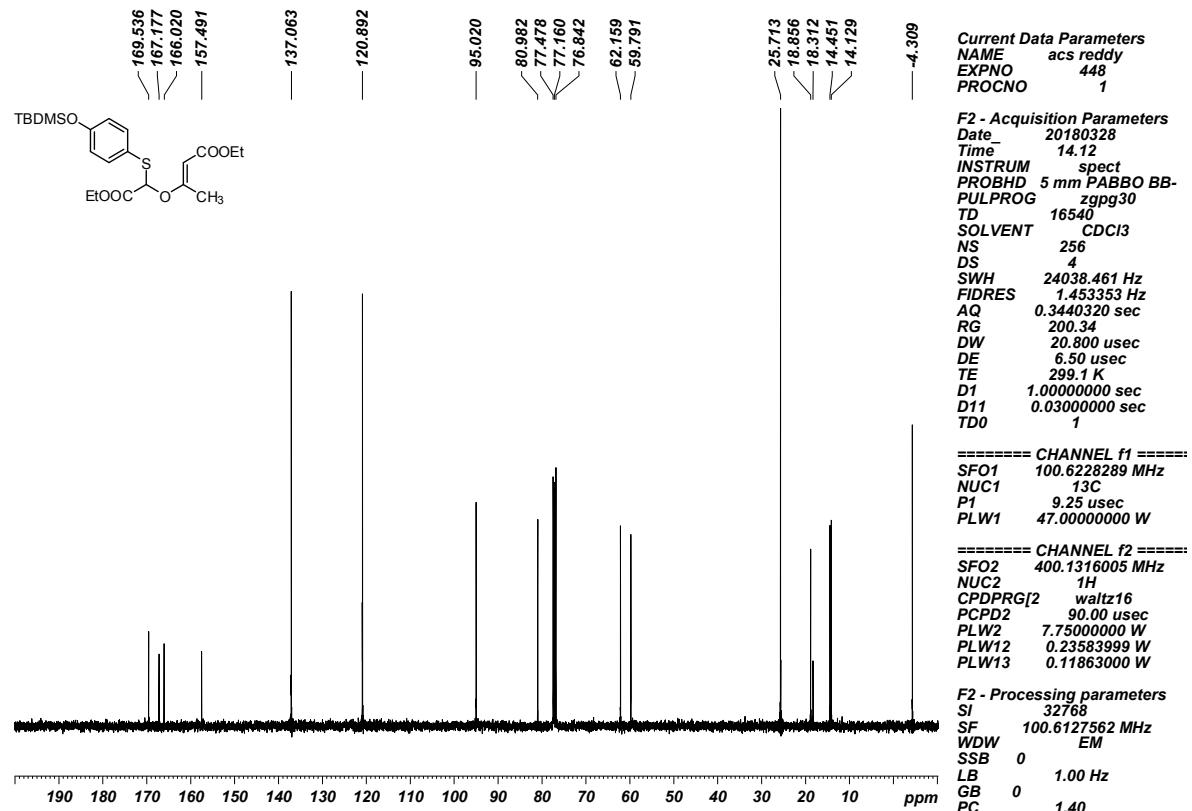


Vinylogous carbonate 3v

¹H NMR (400 MHz, CDCl₃, 24 °C)

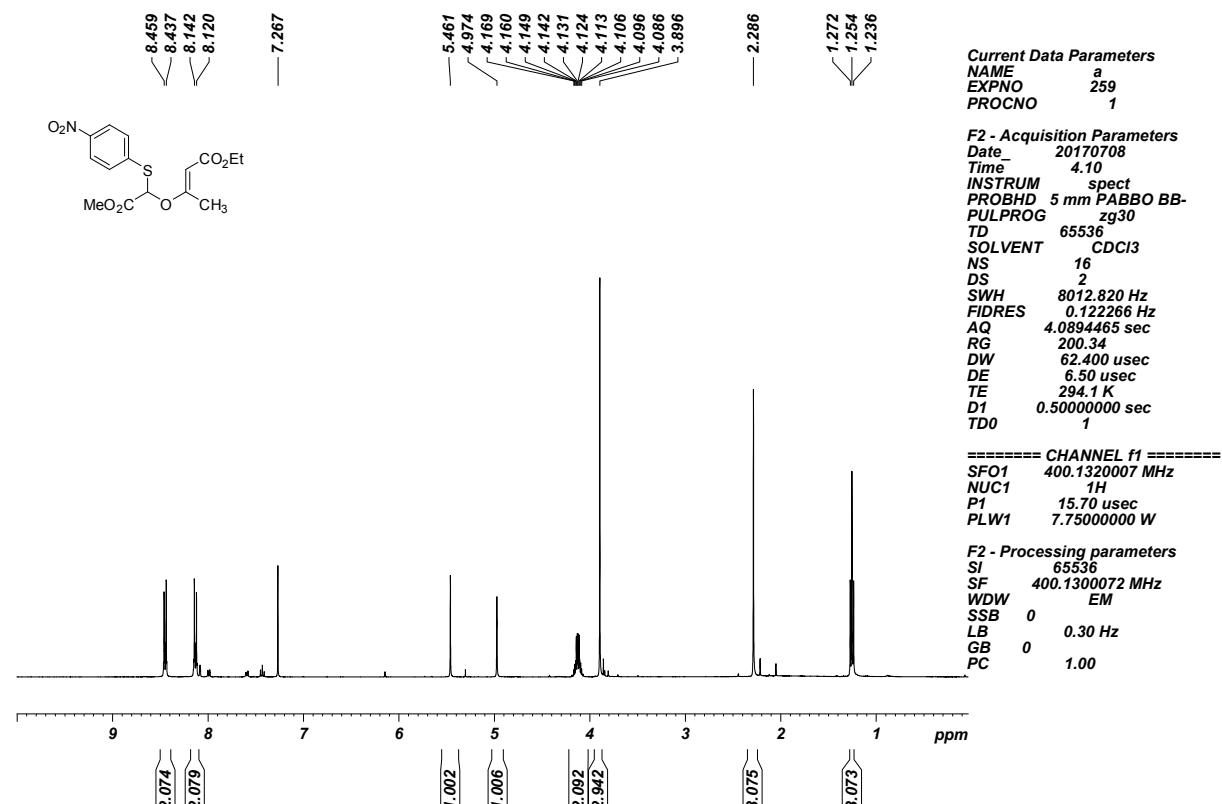


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

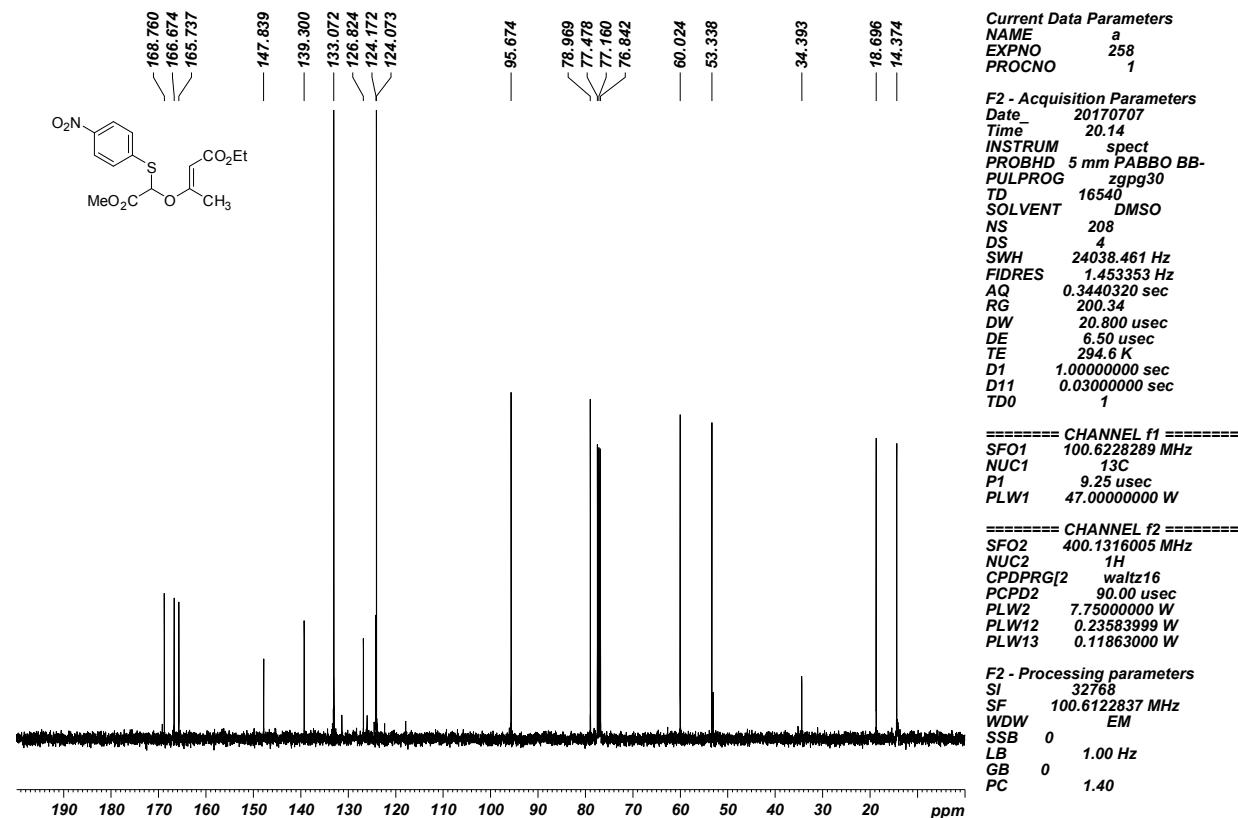


Vinylogous carbonate 3w

¹H NMR (400 MHz, CDCl₃, 24 °C)

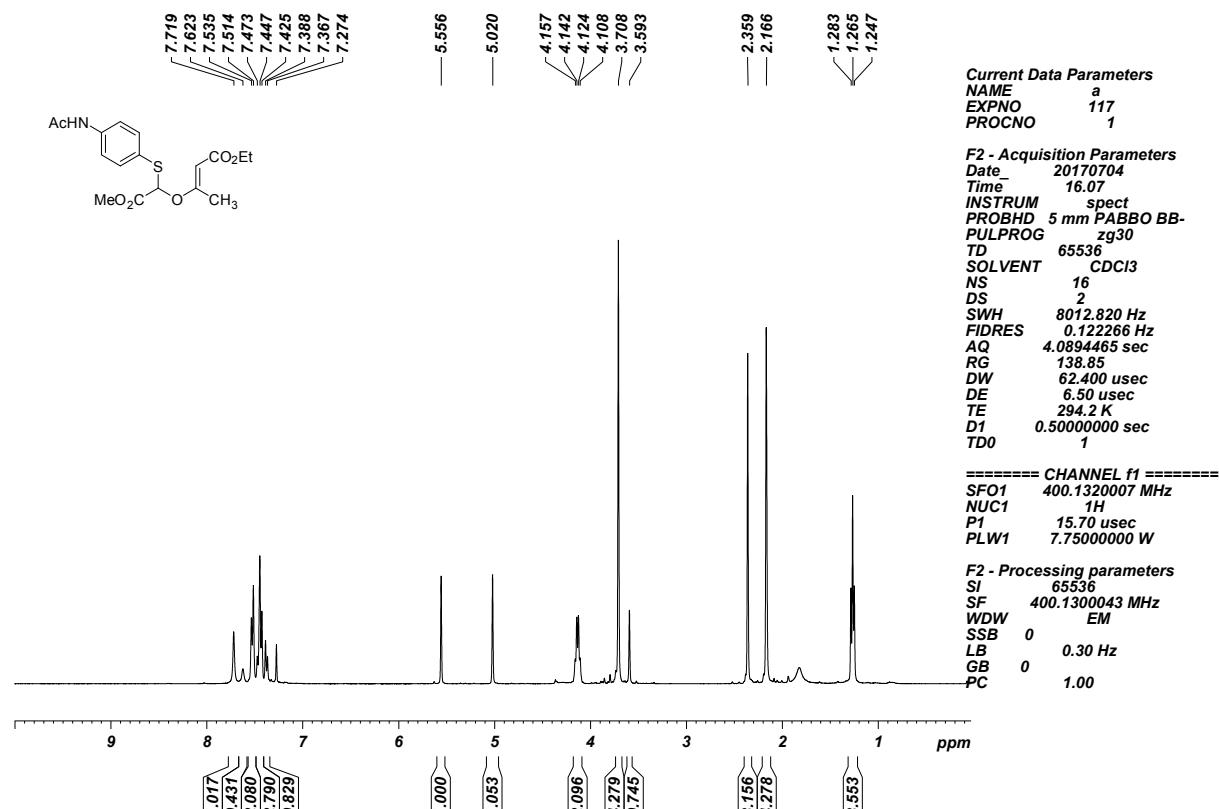


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

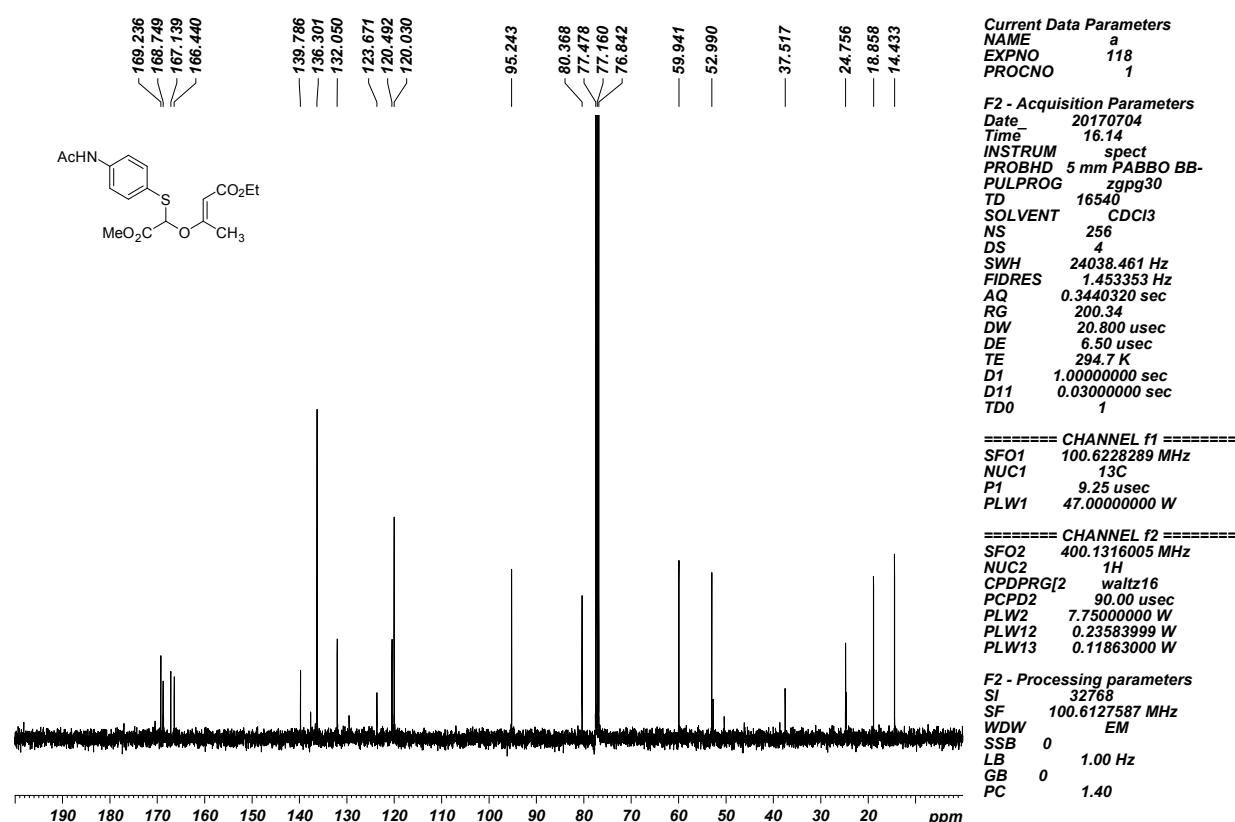


Vinylogous carbonate 3x

¹H NMR (400 MHz, CDCl₃, 24 °C)

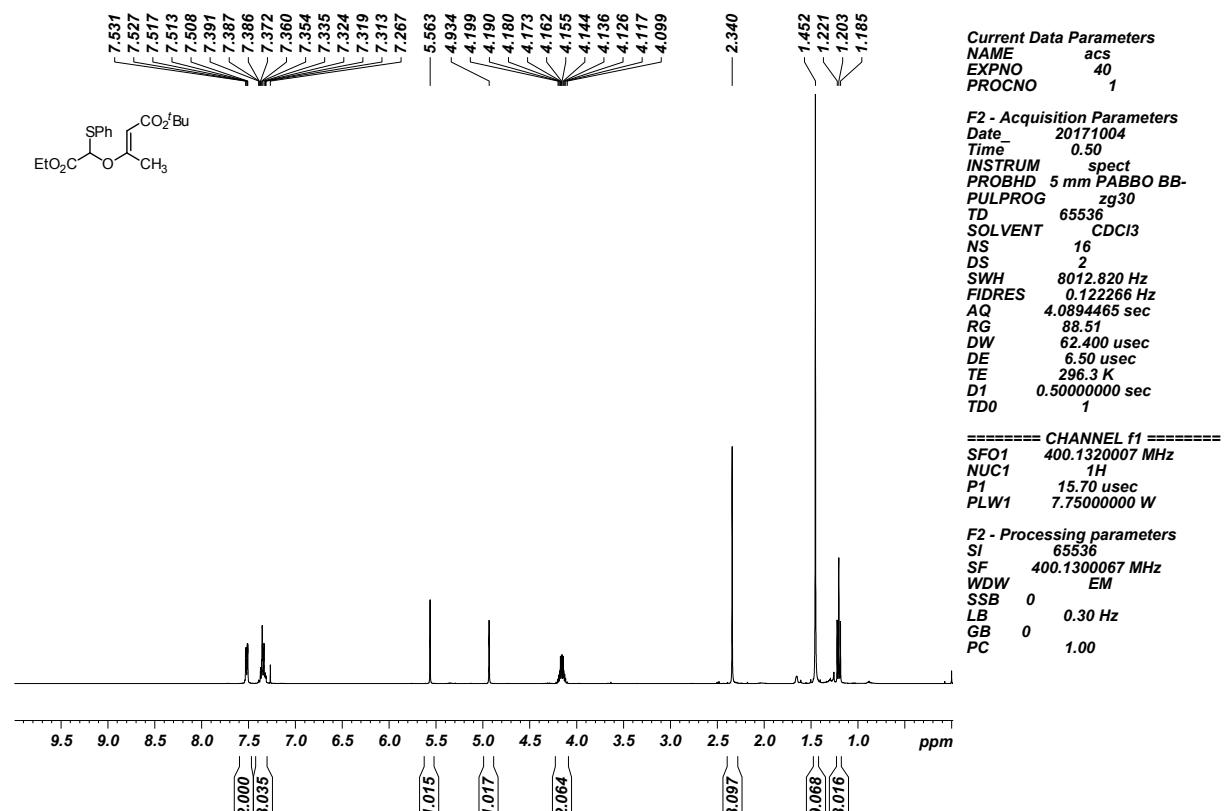


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

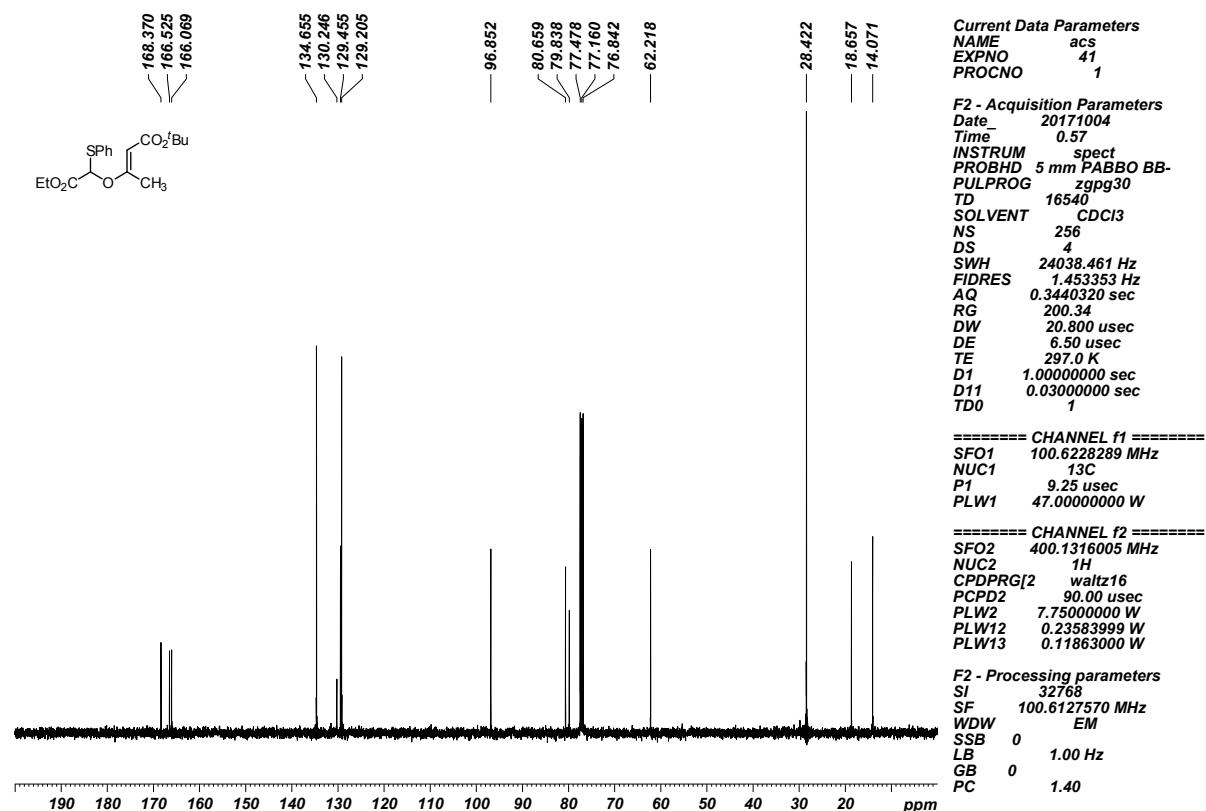


Vinylogous carbonate 3y

¹H NMR (400 MHz, CDCl₃, 24 °C)

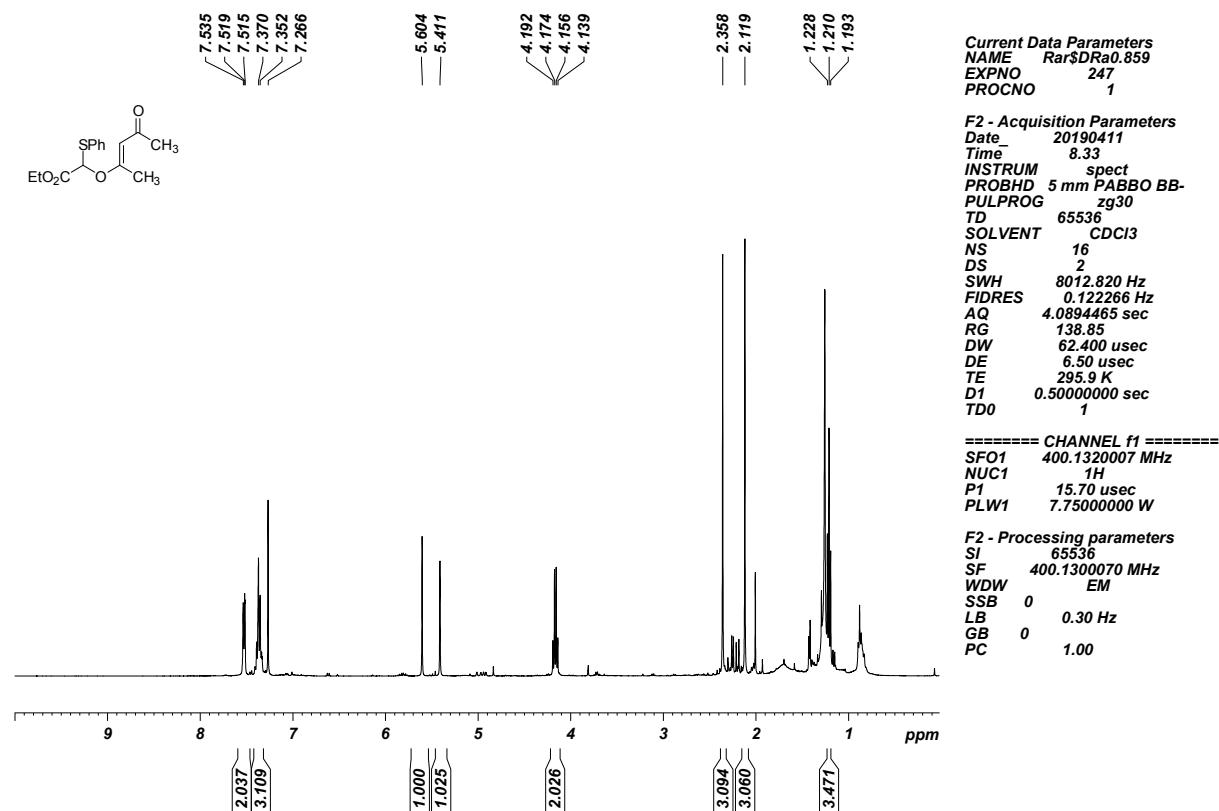


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

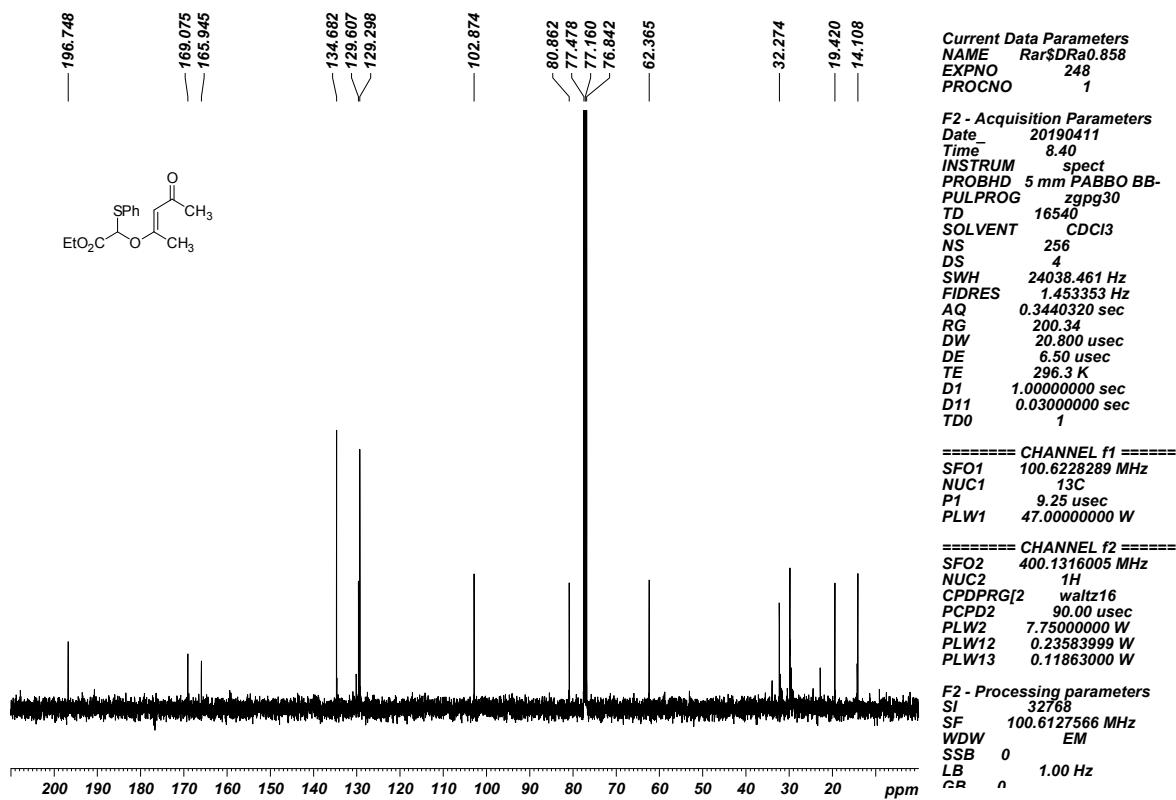


Vinylogous carbonate 3z

¹H NMR (400 MHz, CDCl₃, 24 °C)

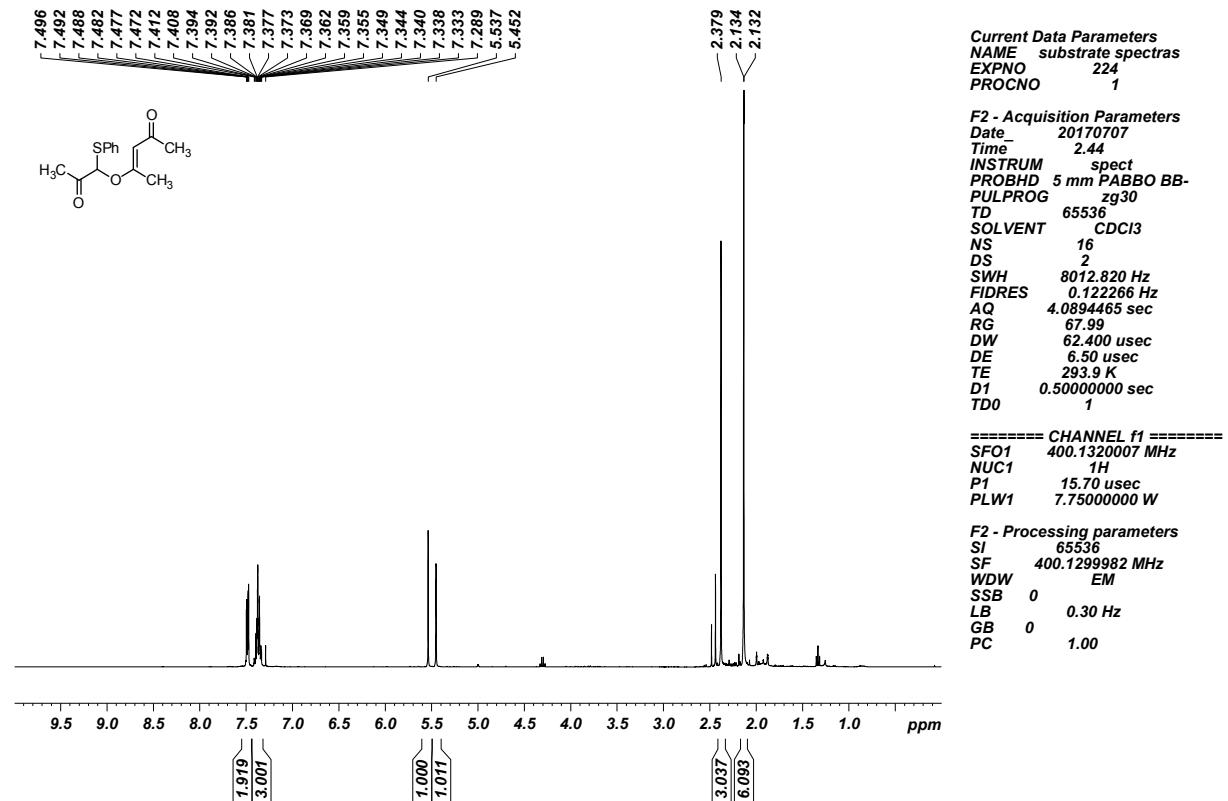


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

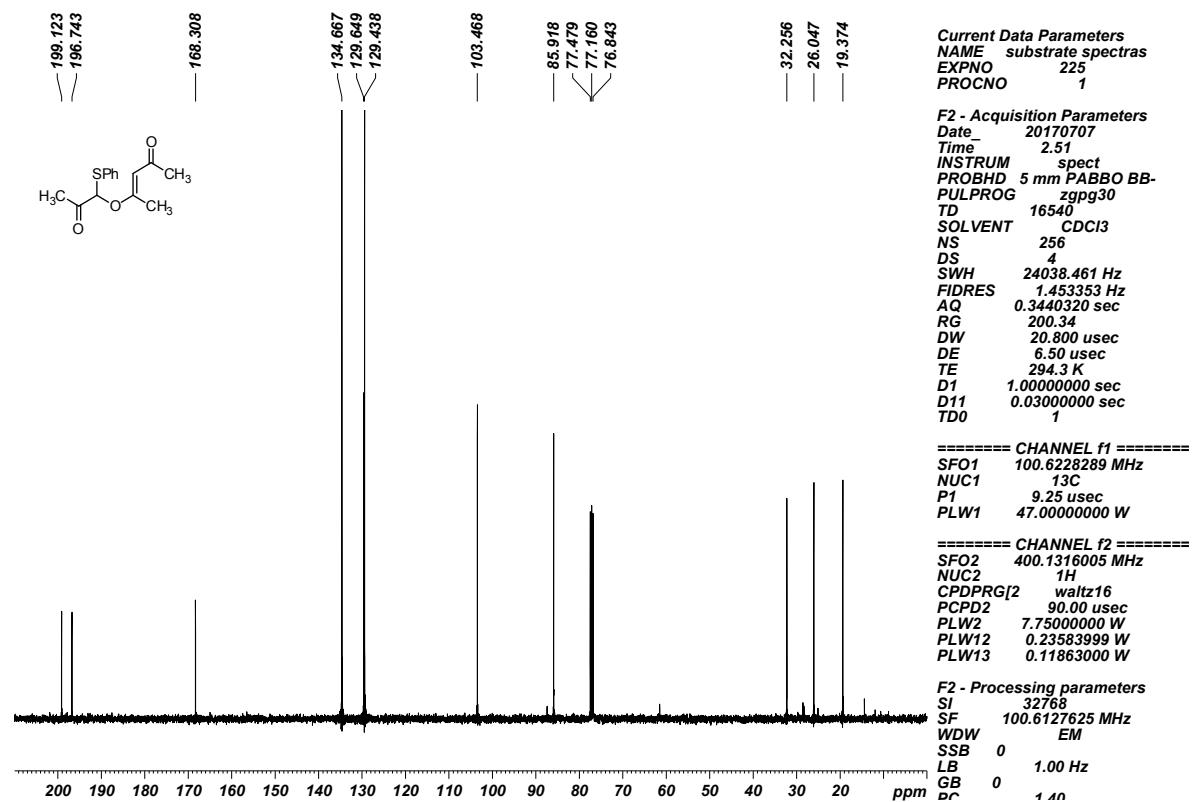


Vinylogous carbonate 3aa

¹H NMR (400 MHz, CDCl₃, 24 °C)

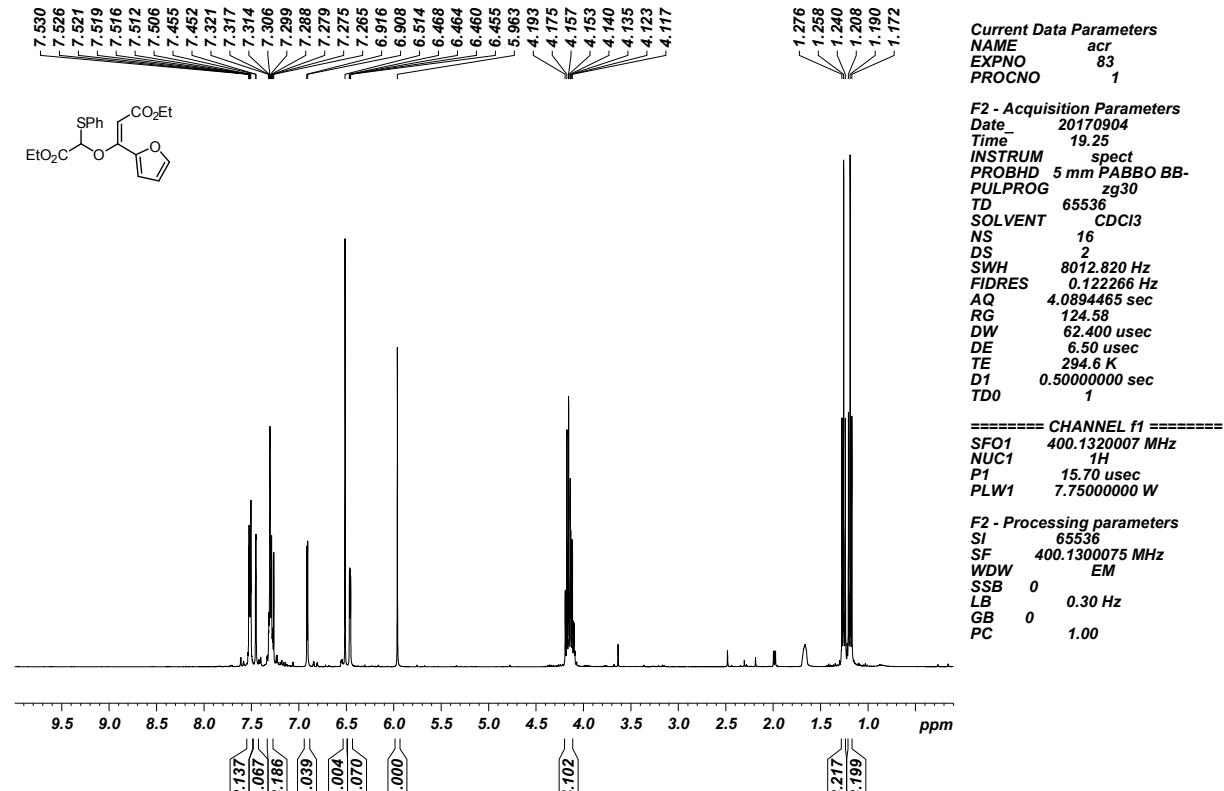


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

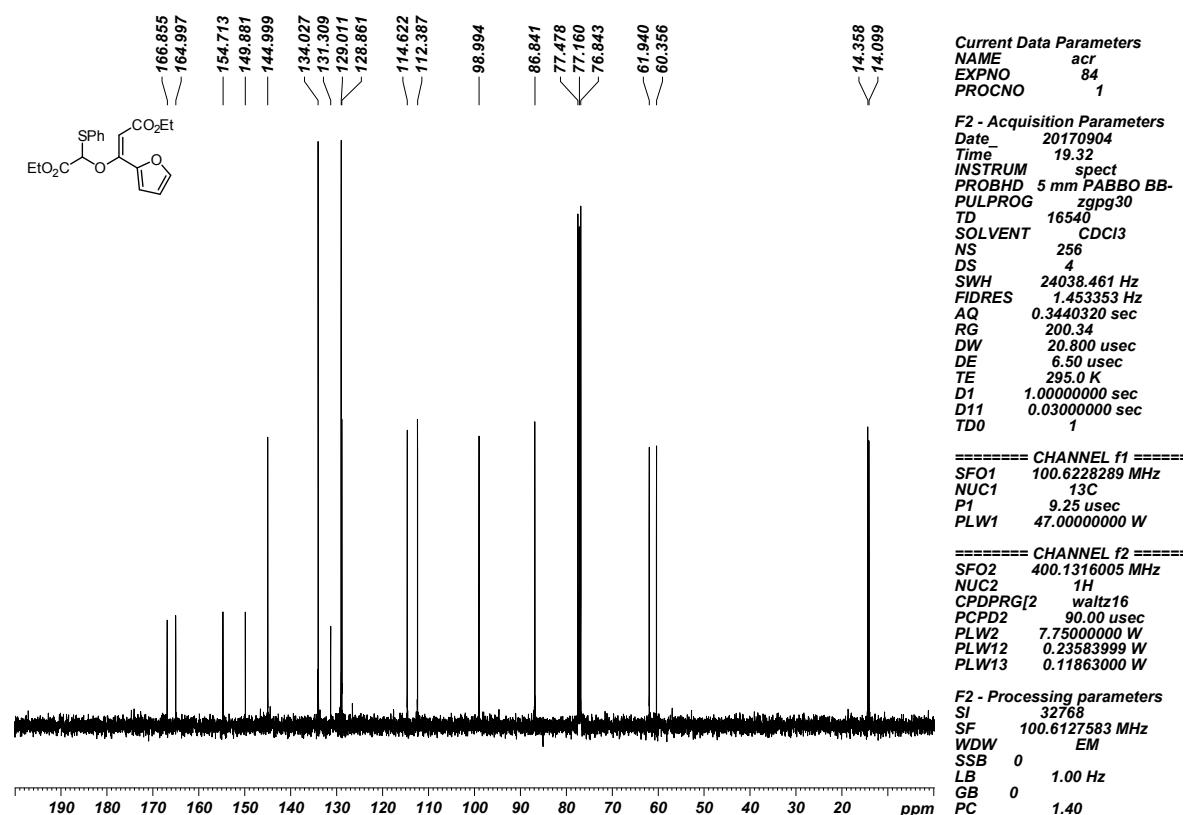


Vinylogous carbonate 3ab

¹H NMR (400 MHz, CDCl₃, 24 °C)

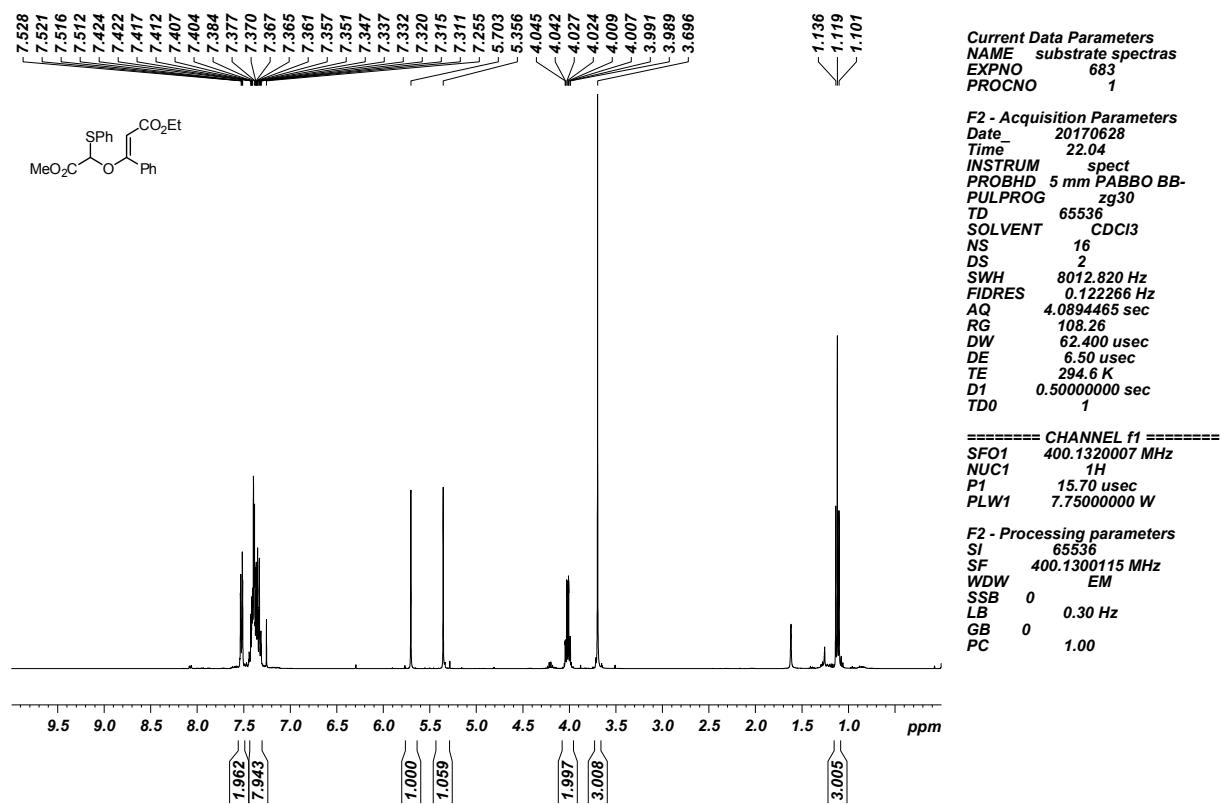


$^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , 24 °C)

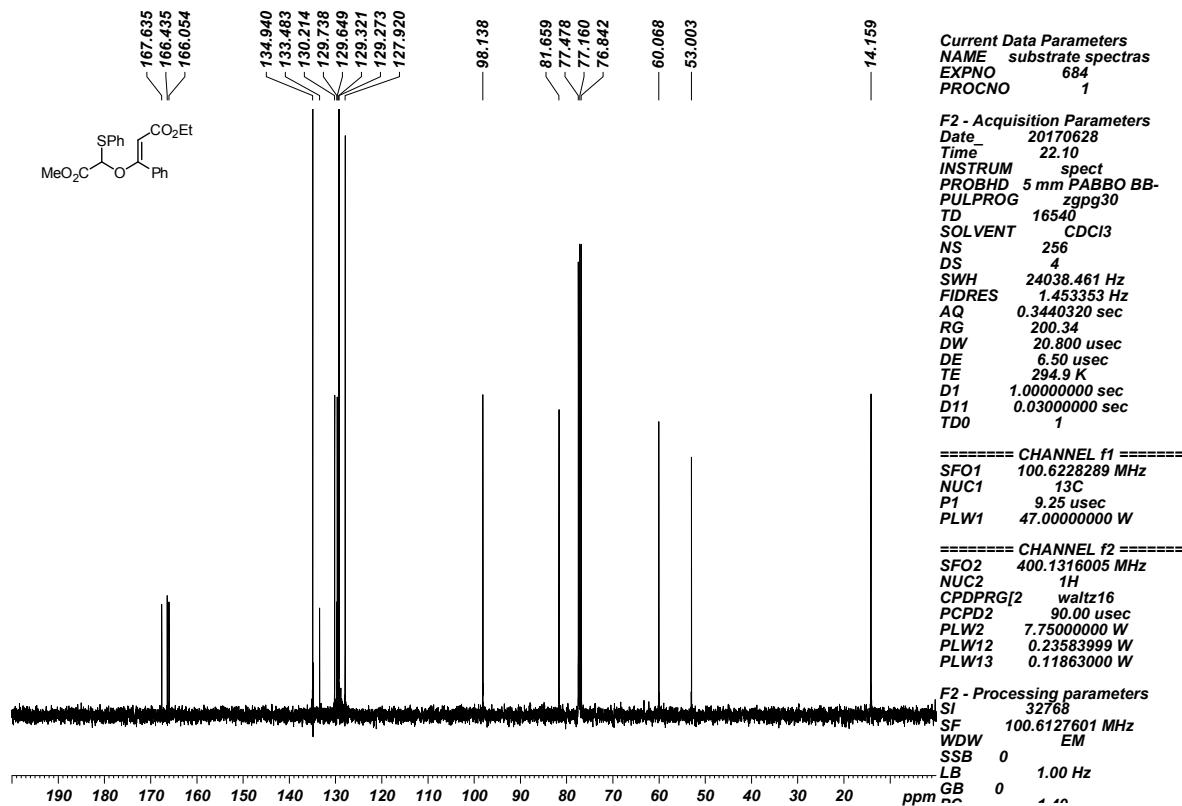


Vinylogous carbonate 3ac (E isomer)

¹H NMR (400 MHz, CDCl₃, 24 °C)

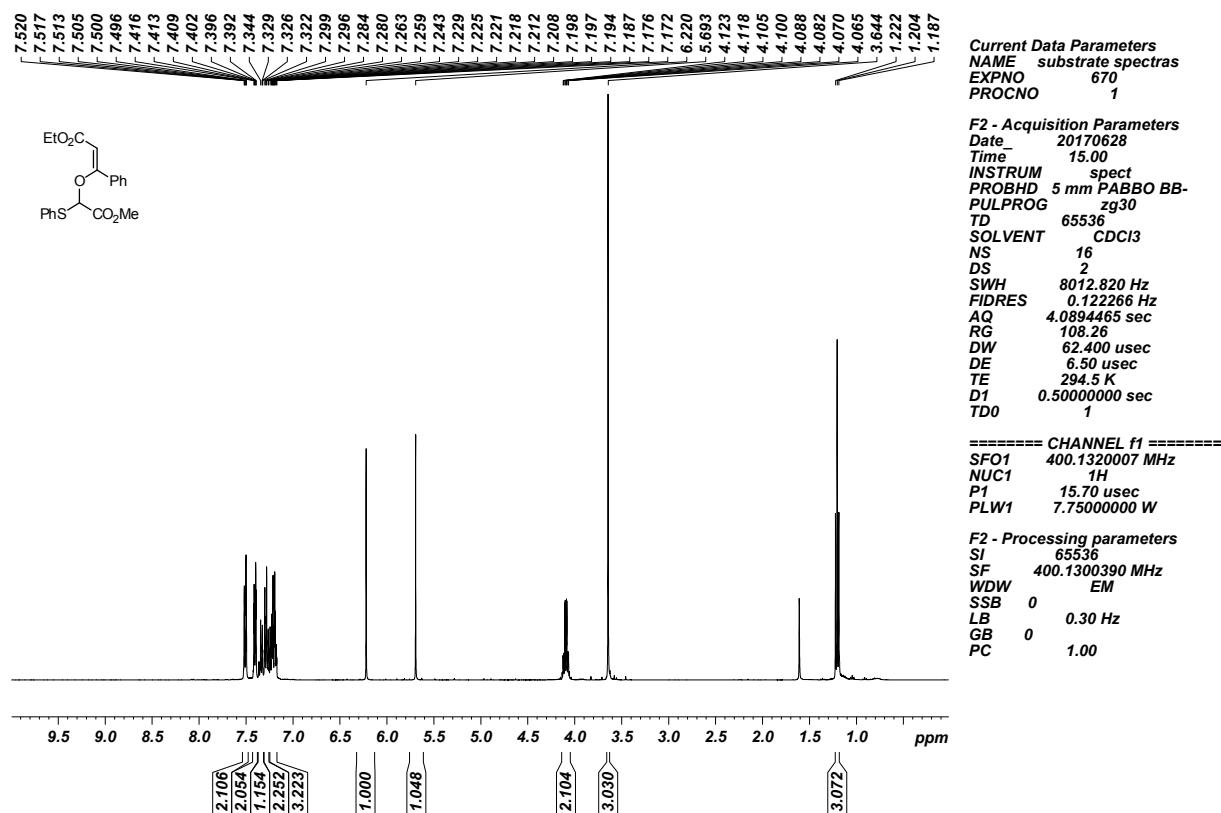


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)



Vinylogous carbonate 3ac (Z isomer)

¹H NMR (400 MHz, CDCl₃, 24 °C)

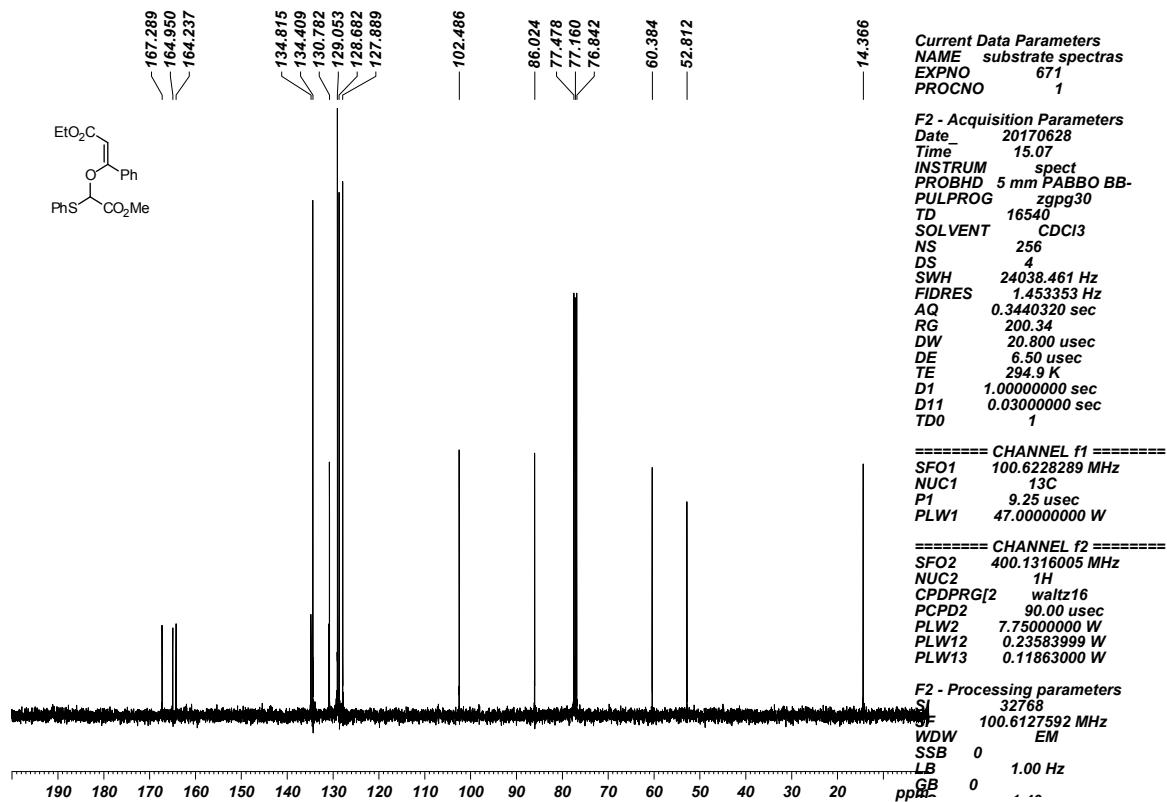


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TD 65536
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DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 108.26
DW 62.400 usec
DE 6.50 usec
TE 294.5 K
D1 0.50000000 sec
TD0 1

===== CHANNEL f1 ======
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NUC1 1H
P1 15.70 usec
PLW1 7.75000000 W

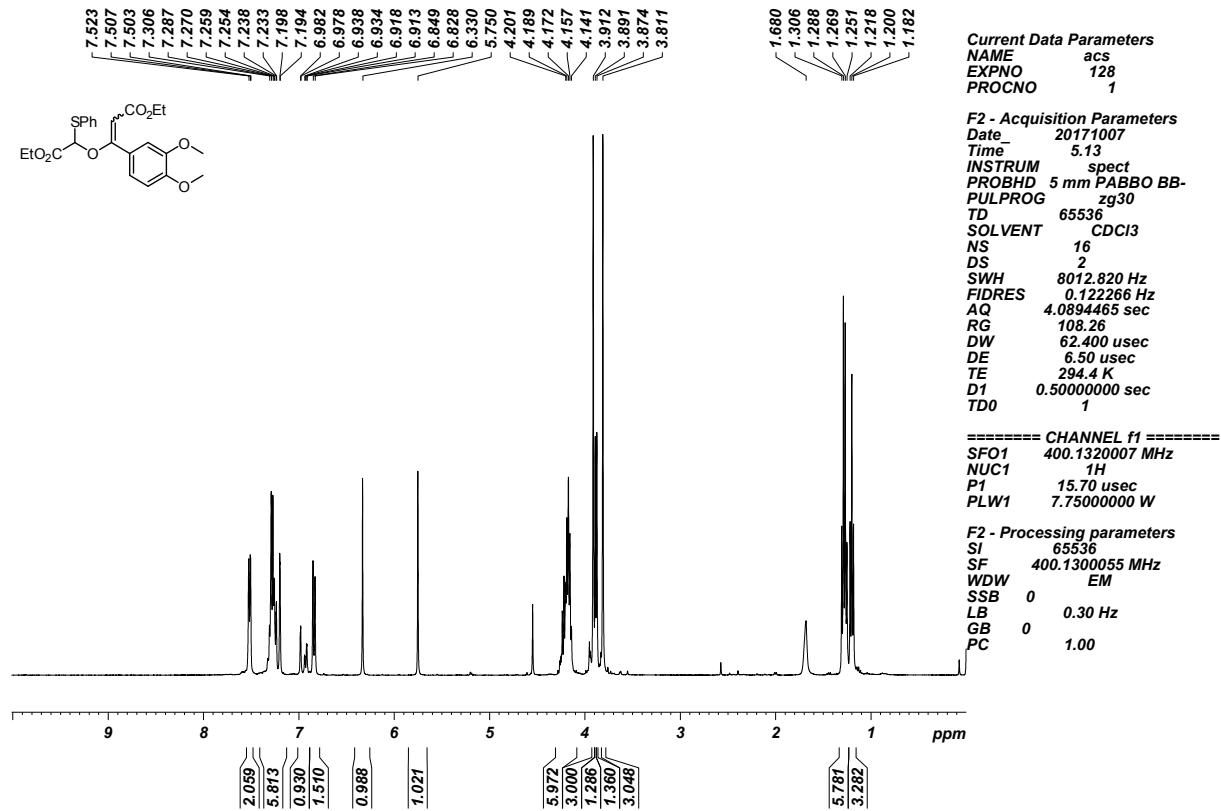
F2 - Processing parameters
SI 65536
SF 400.1300390 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0 1.00
PC

¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

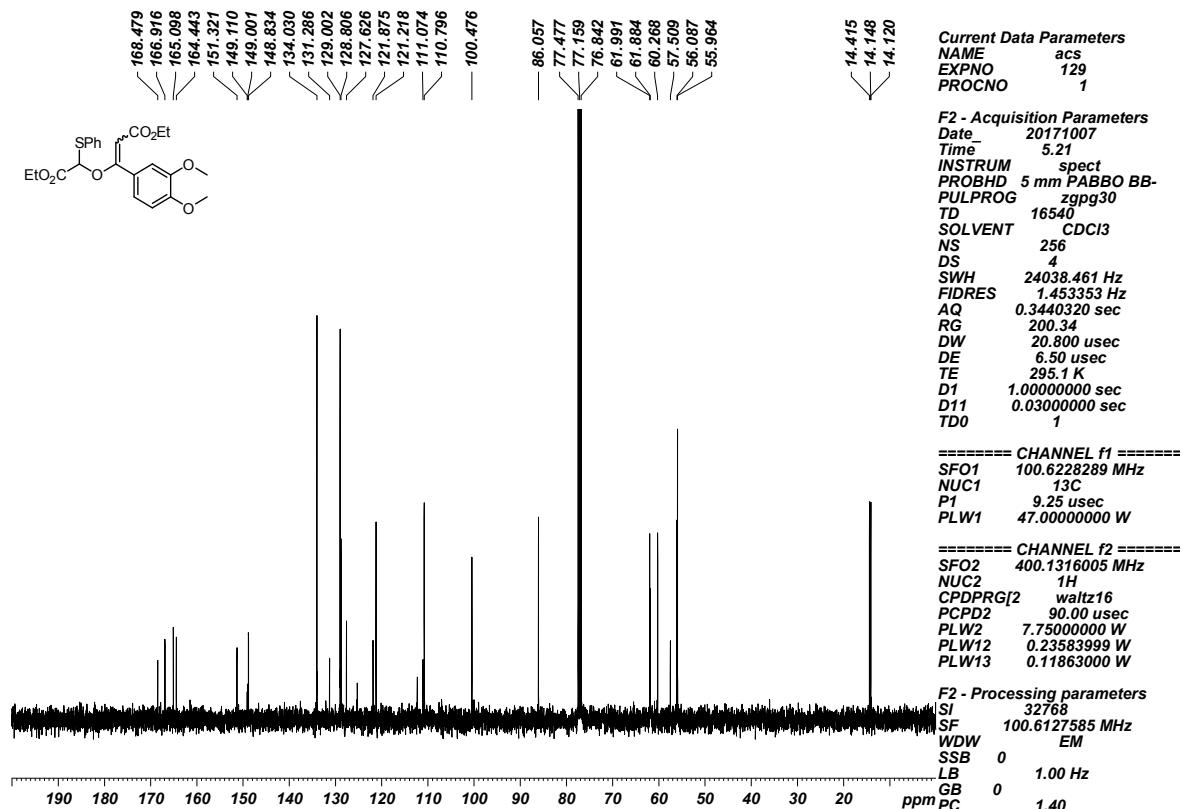


Vinylogous carbonate 3ad (E/Z isomeric mixture)

¹H NMR (400 MHz, CDCl₃, 24 °C)

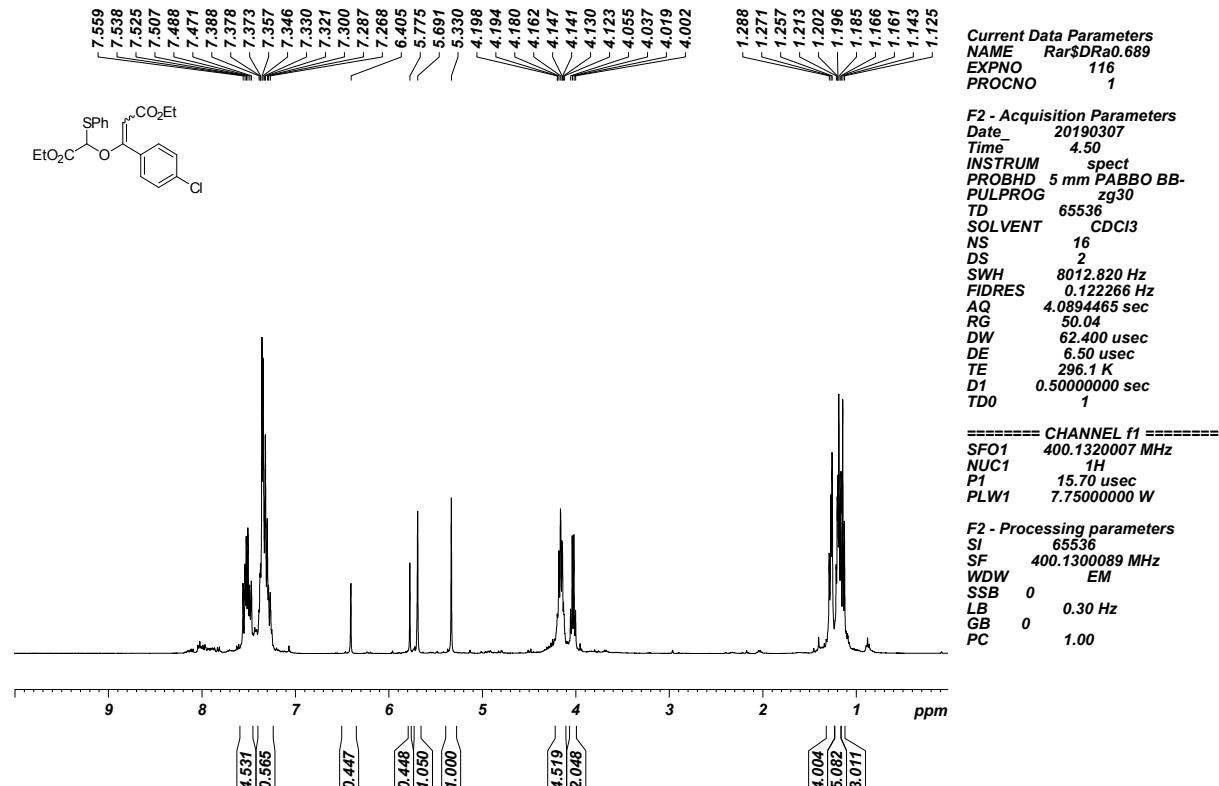


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

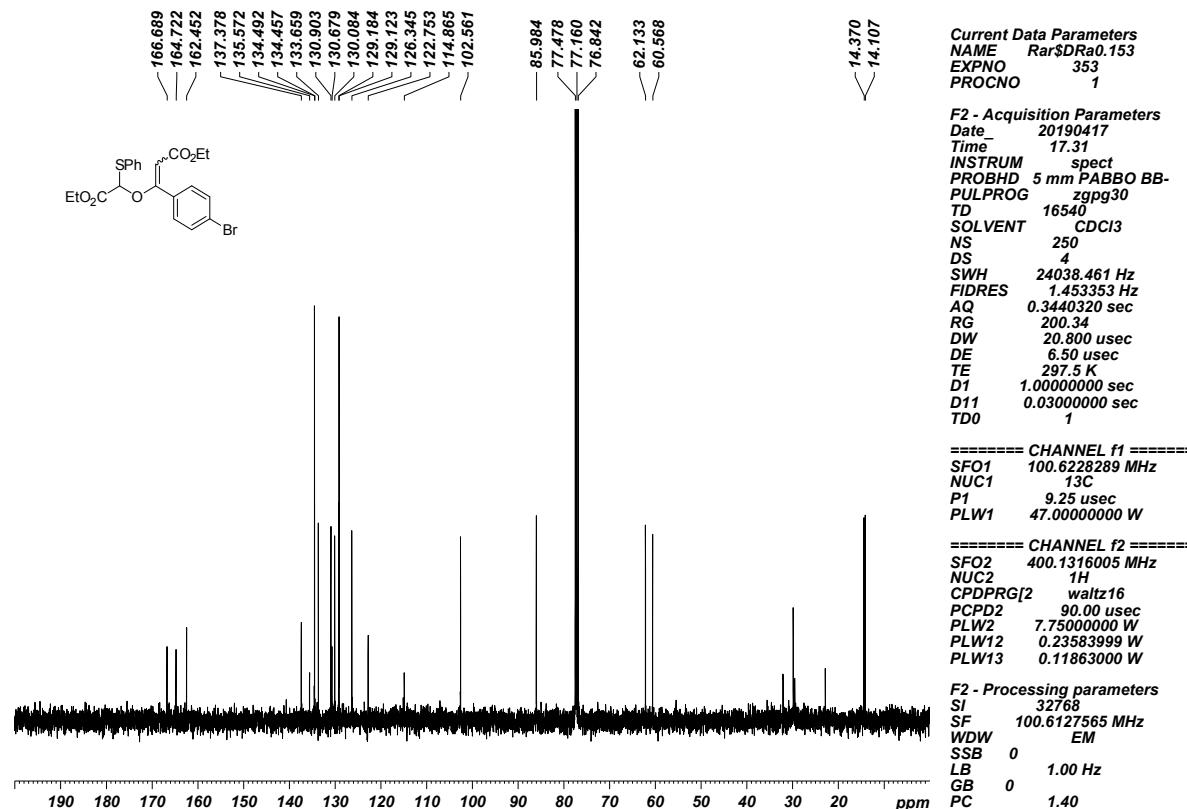


Vinylogous carbonate 3ae (E/Z isomeric mixture)

¹H NMR(400 MHz, CDCl₃, 24 °C)

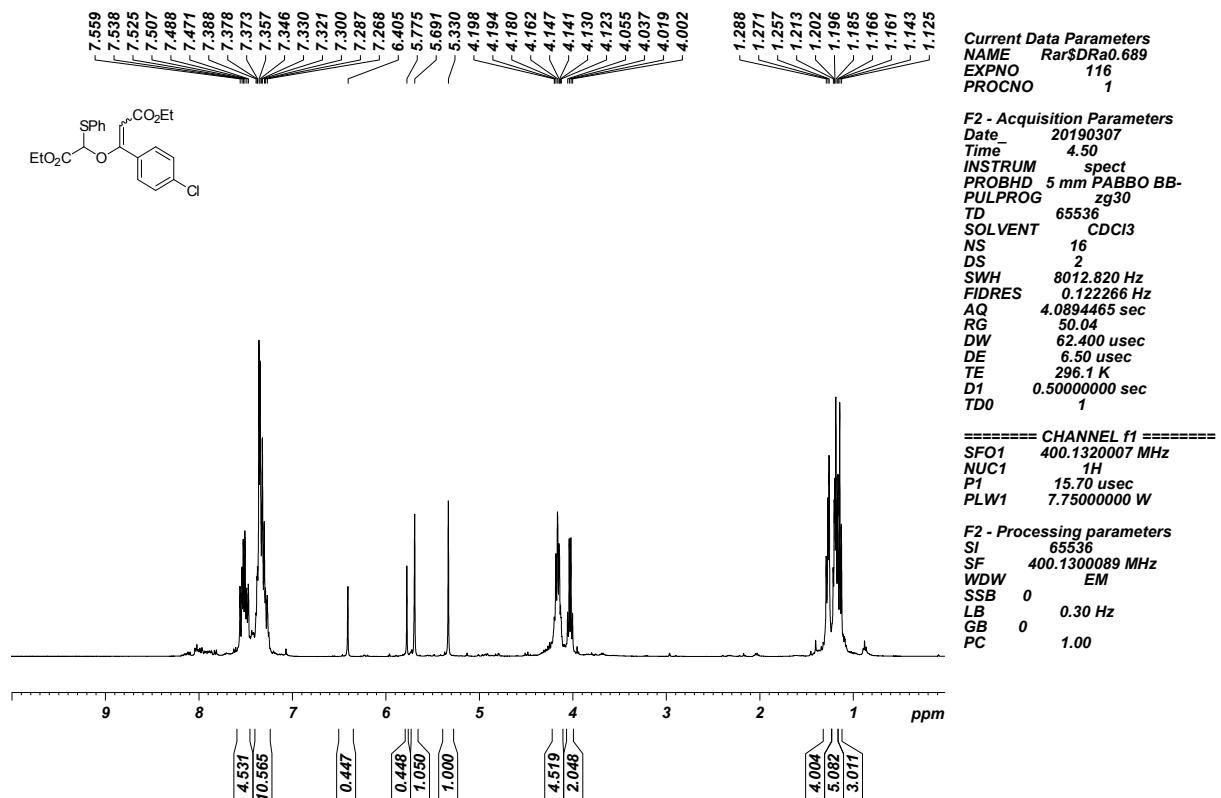


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

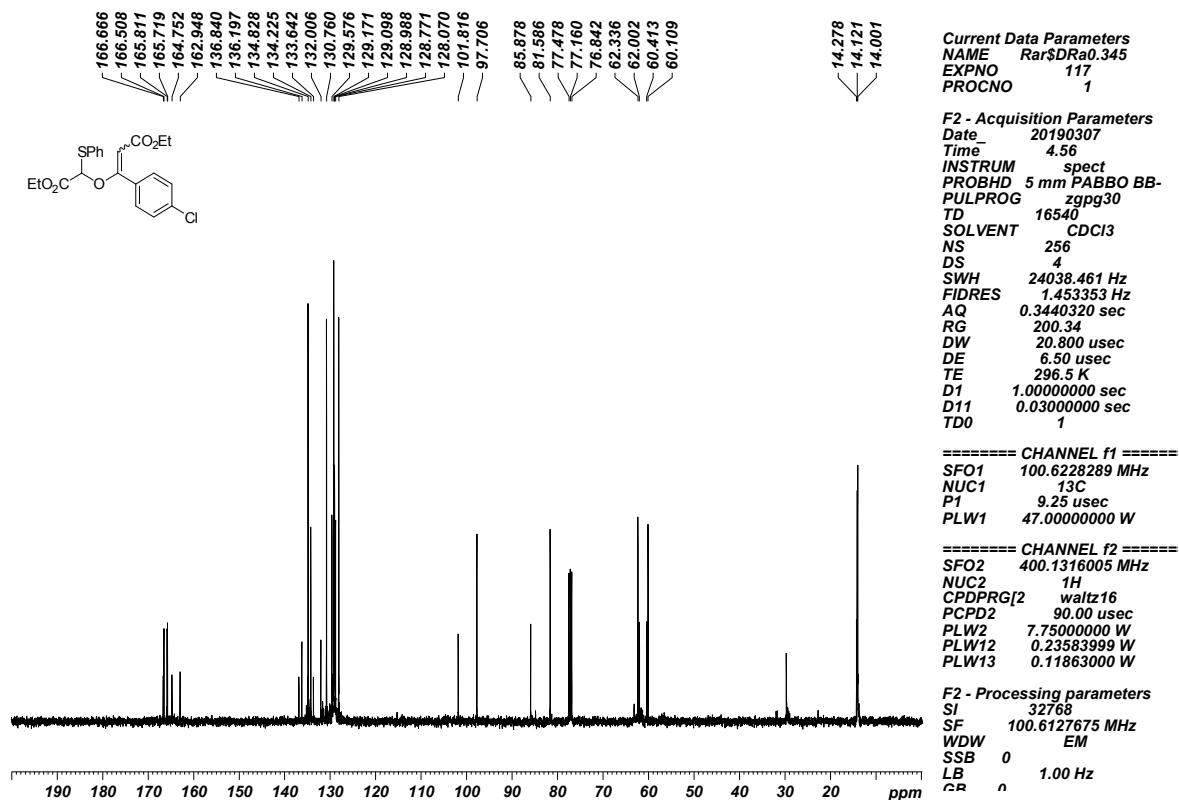


Vinylogous carbonate 3af (E/Z isomeric mixture)

¹H NMR (400 MHz, CDCl₃, 24 °C)

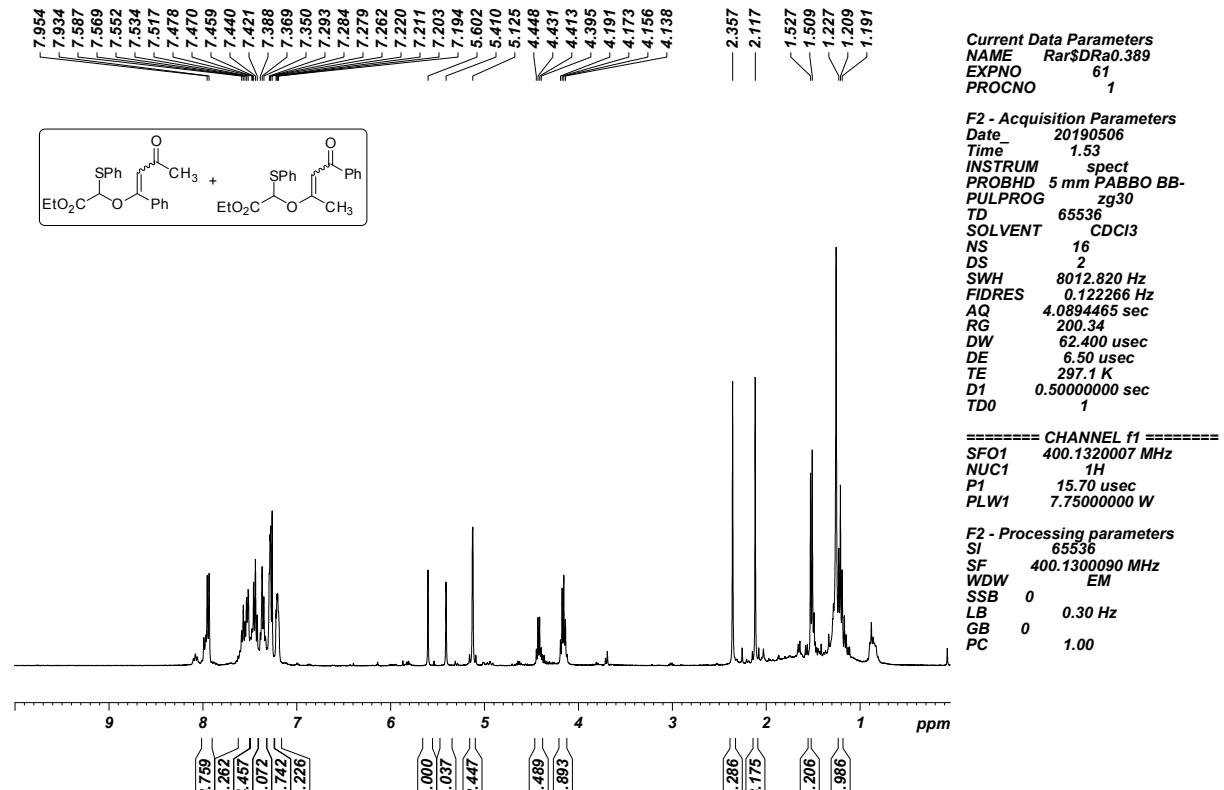


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

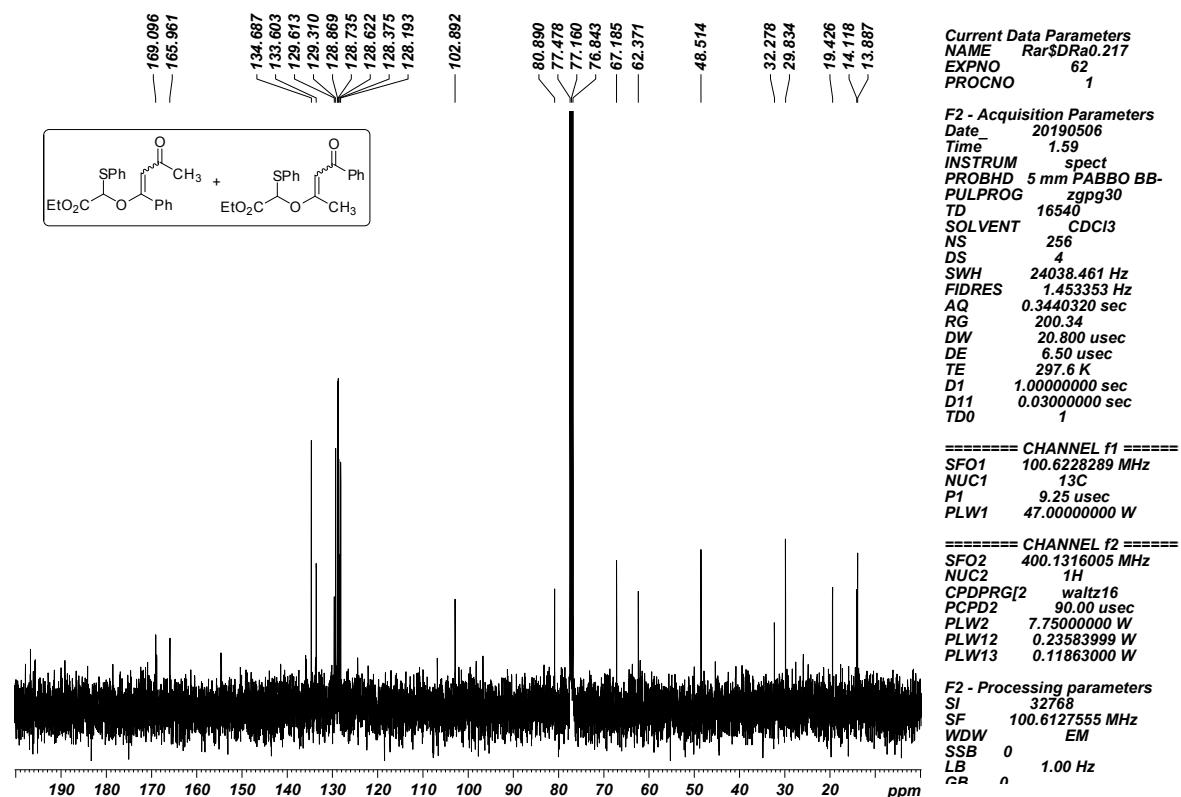


Vinylogous carbonate 3ag

¹H NMR (400 MHz, CDCl₃, 24 °C)

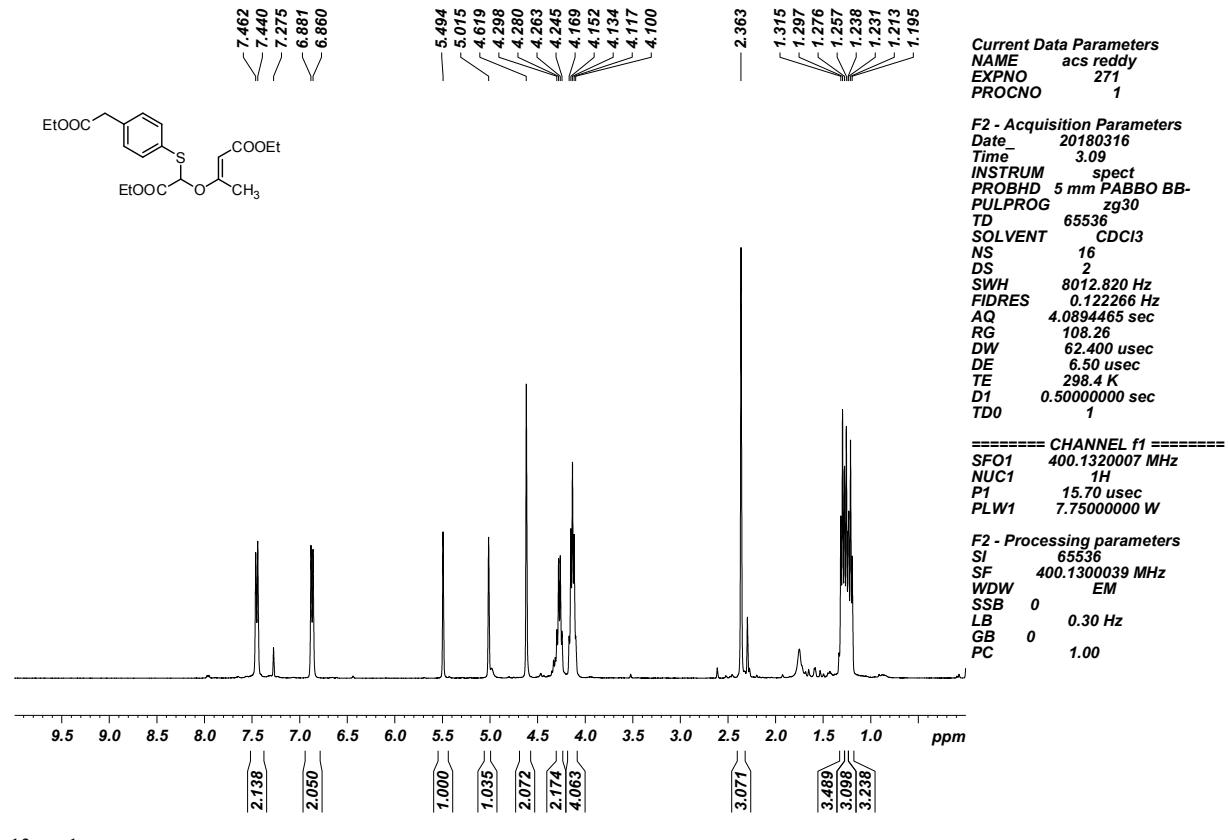


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

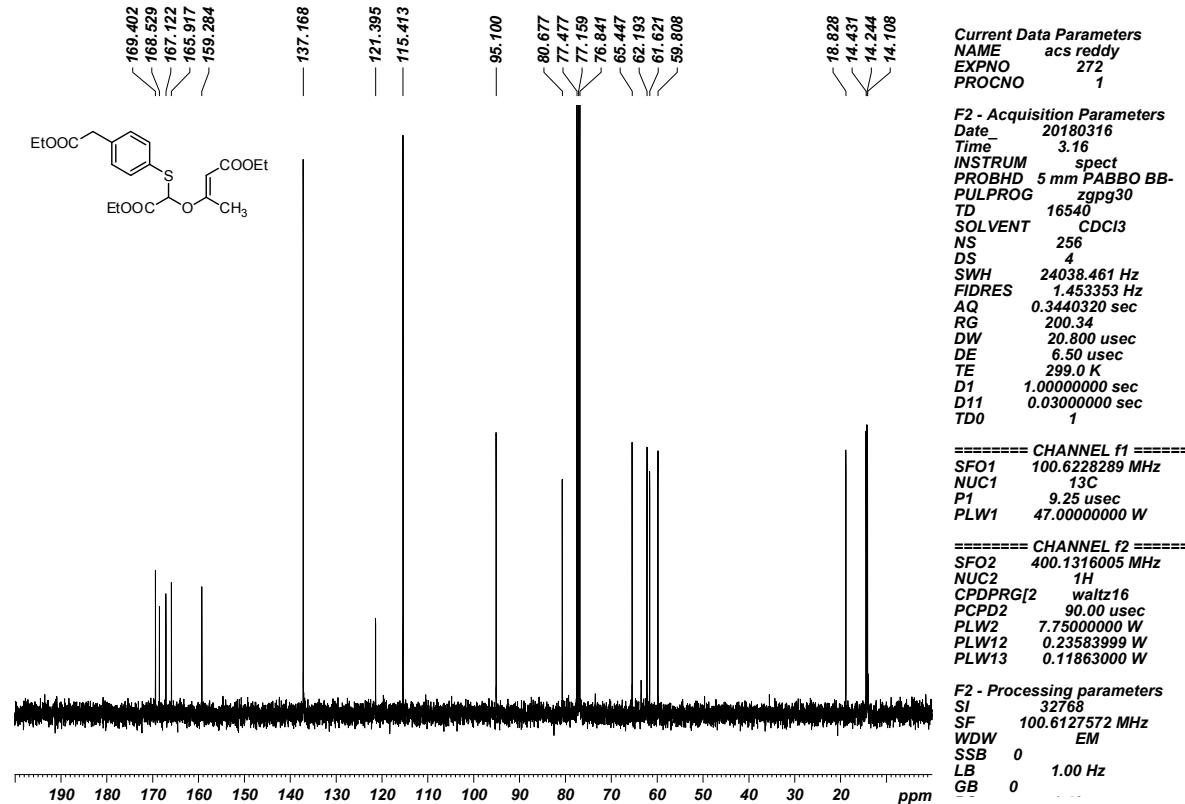


Vinylogous carbonate 3ah

¹H NMR (400 MHz, CDCl₃, 24 °C)

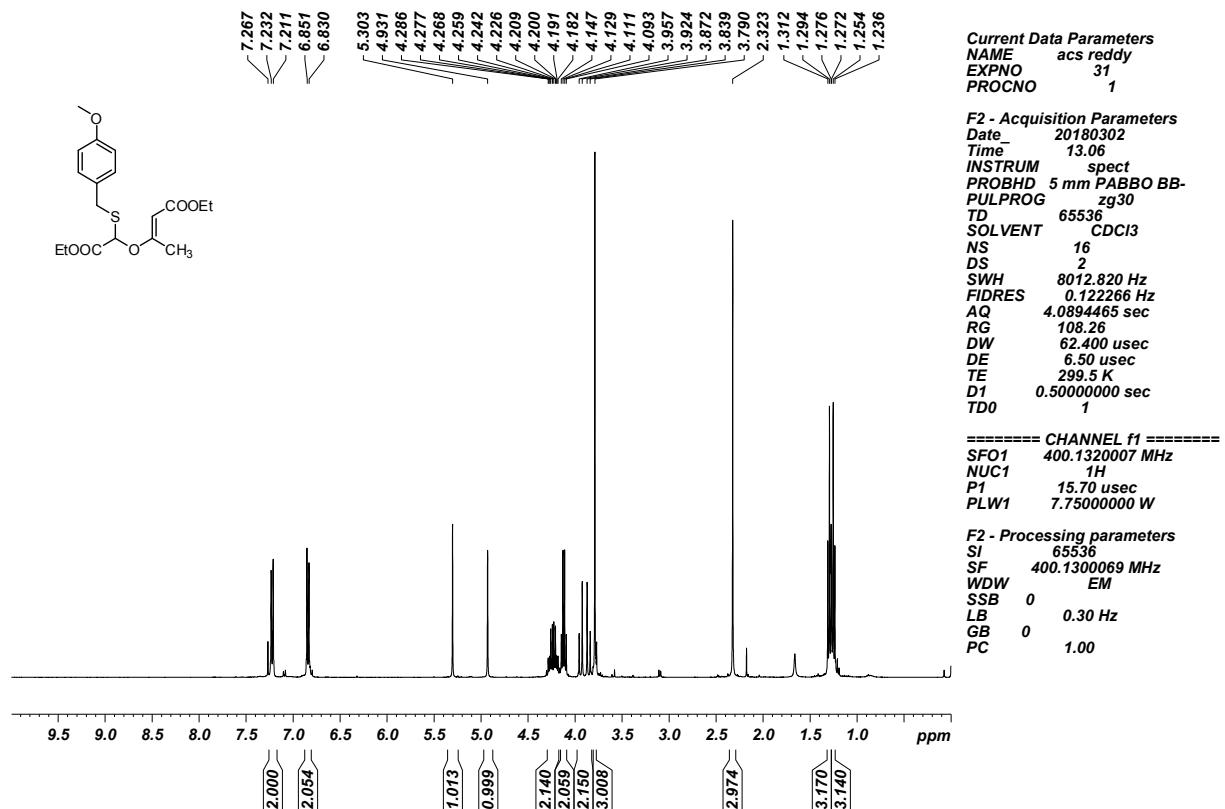


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

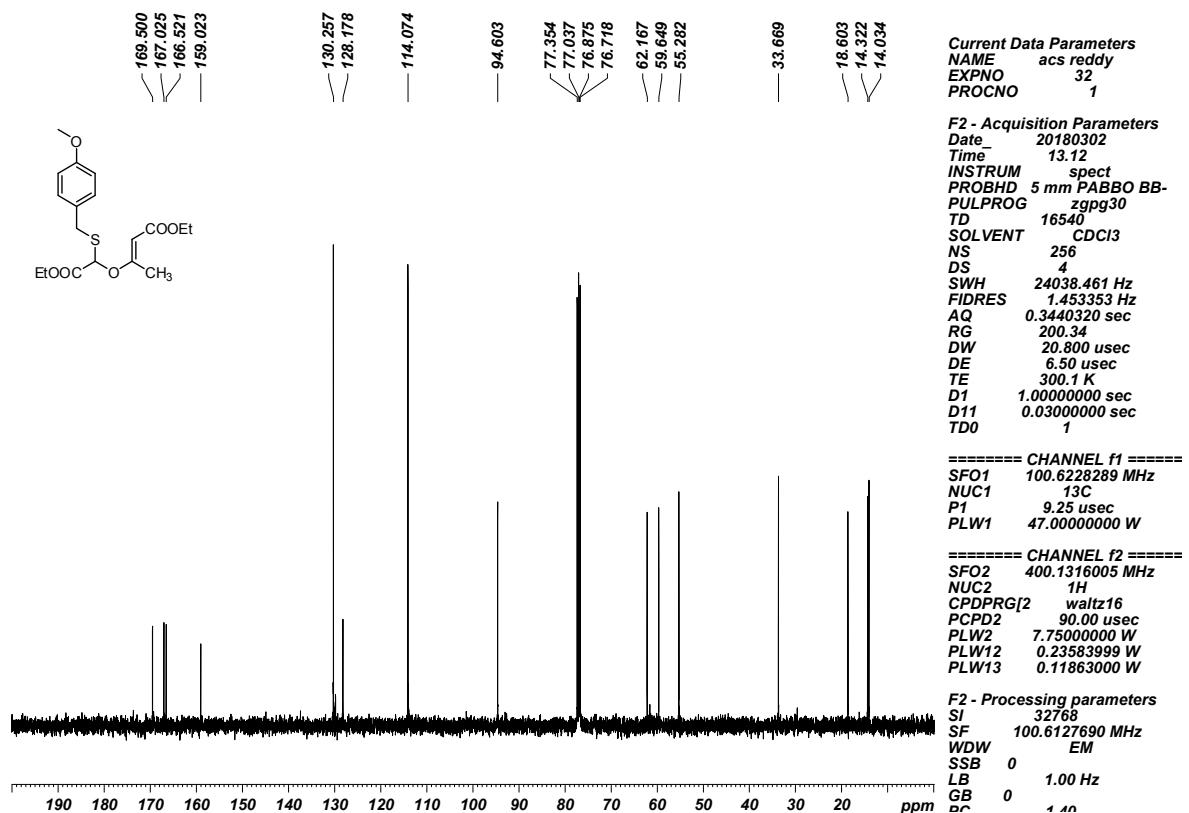


Vinylogous carbonate 3ai

¹H NMR (400 MHz, CDCl₃, 24 °C)

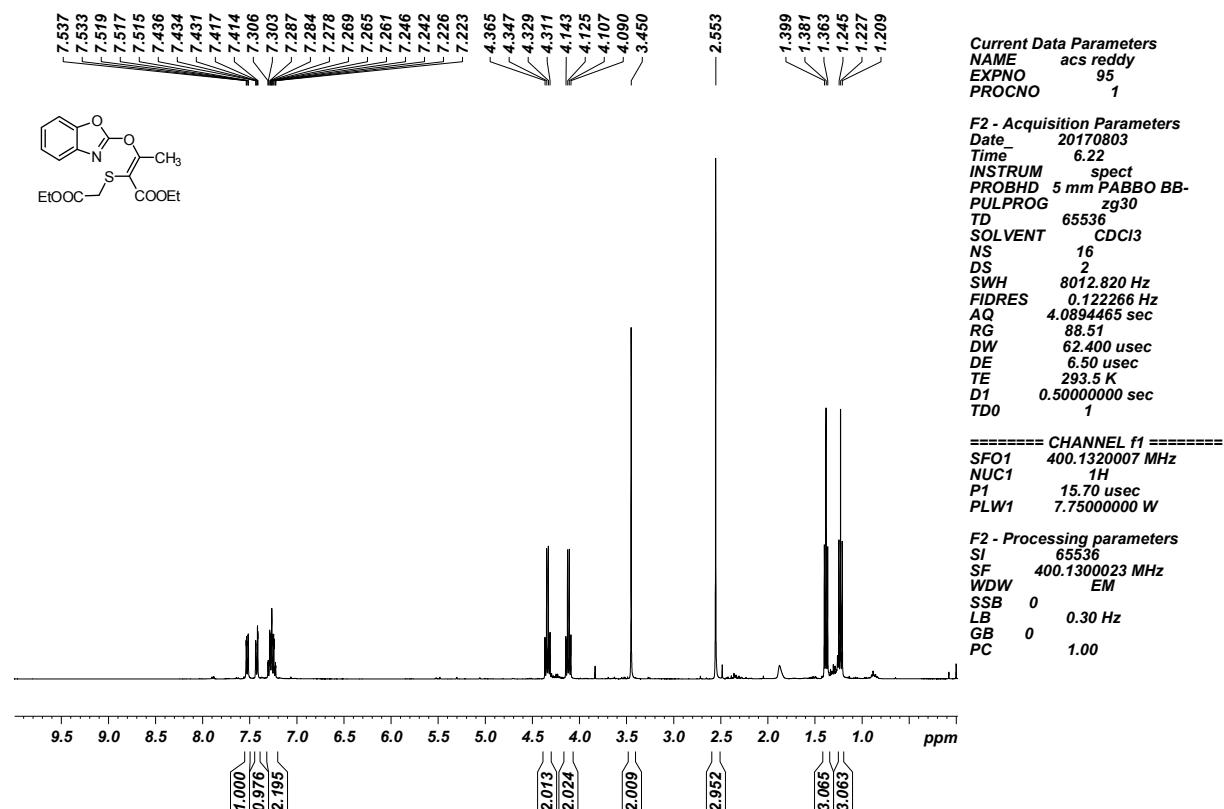


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

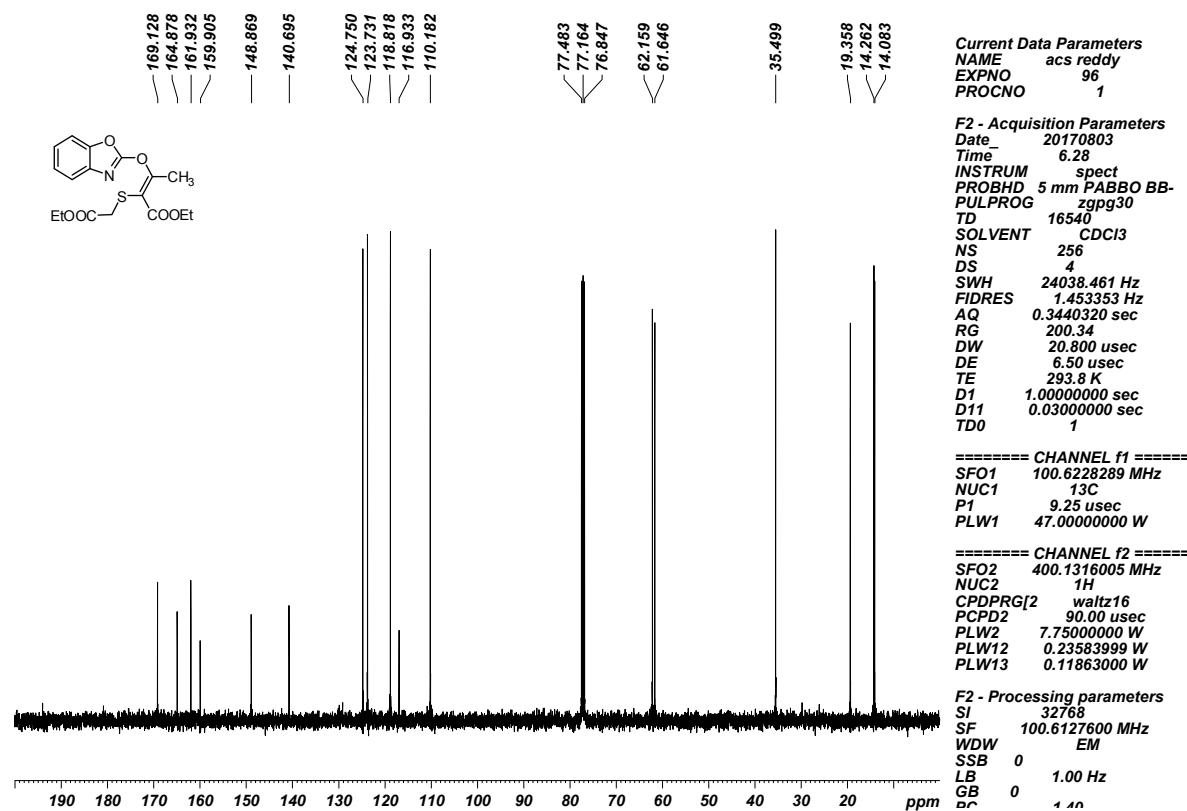


Vinylogous carbonate 4a

¹H NMR (400 MHz, CDCl₃, 24 °C)

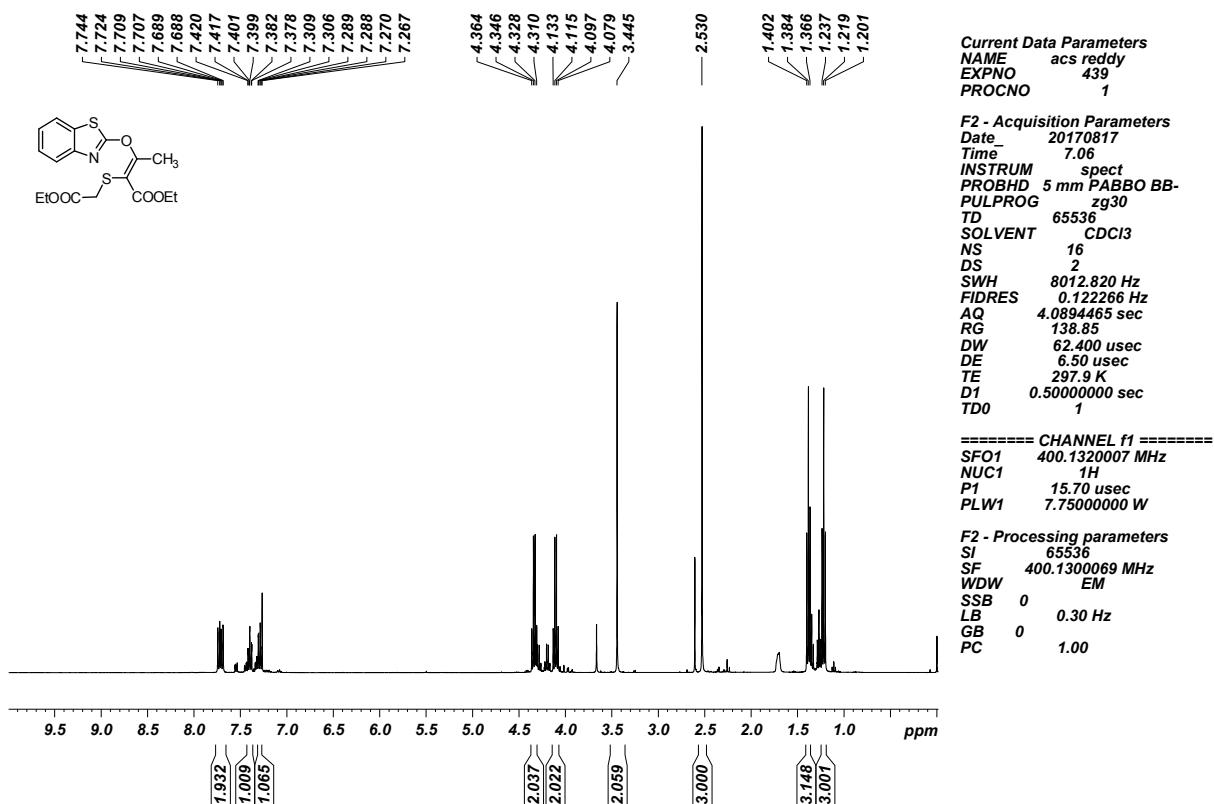


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

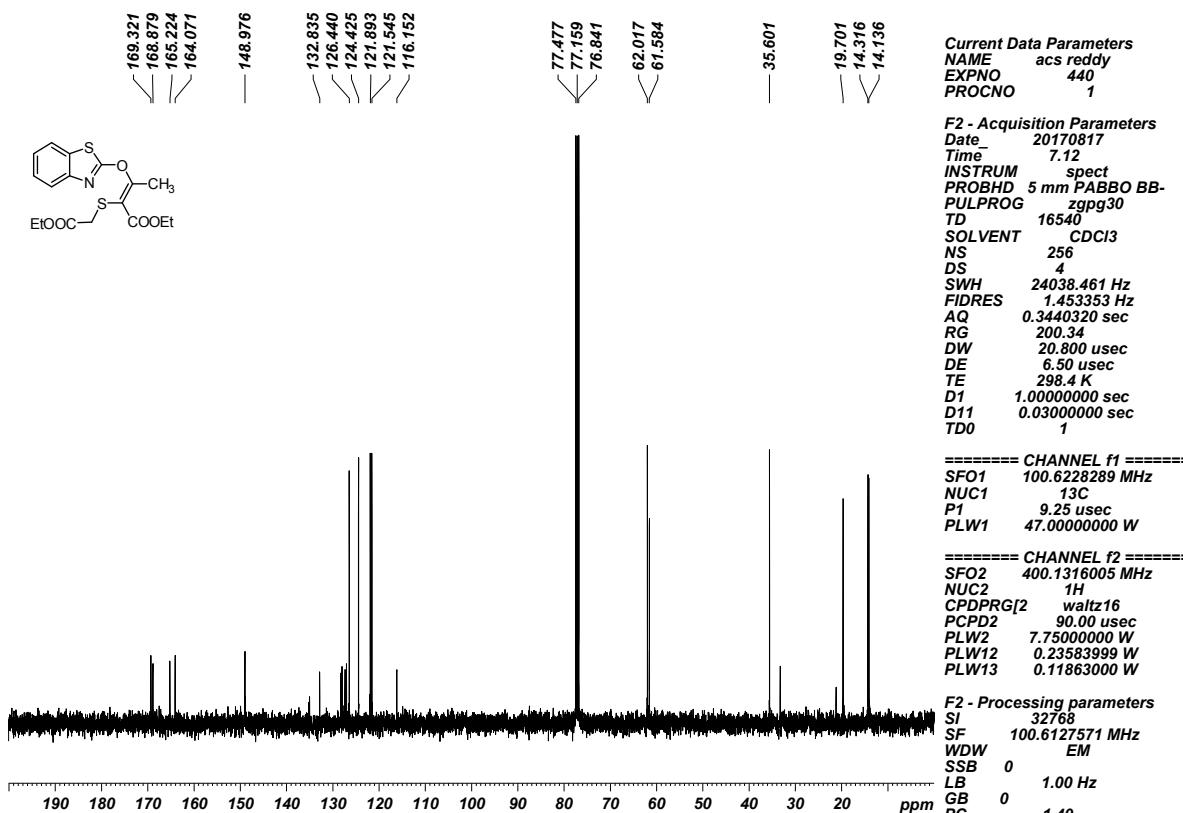


Vinylogous carbonate 4b

¹H NMR (400 MHz, CDCl₃, 24 °C)

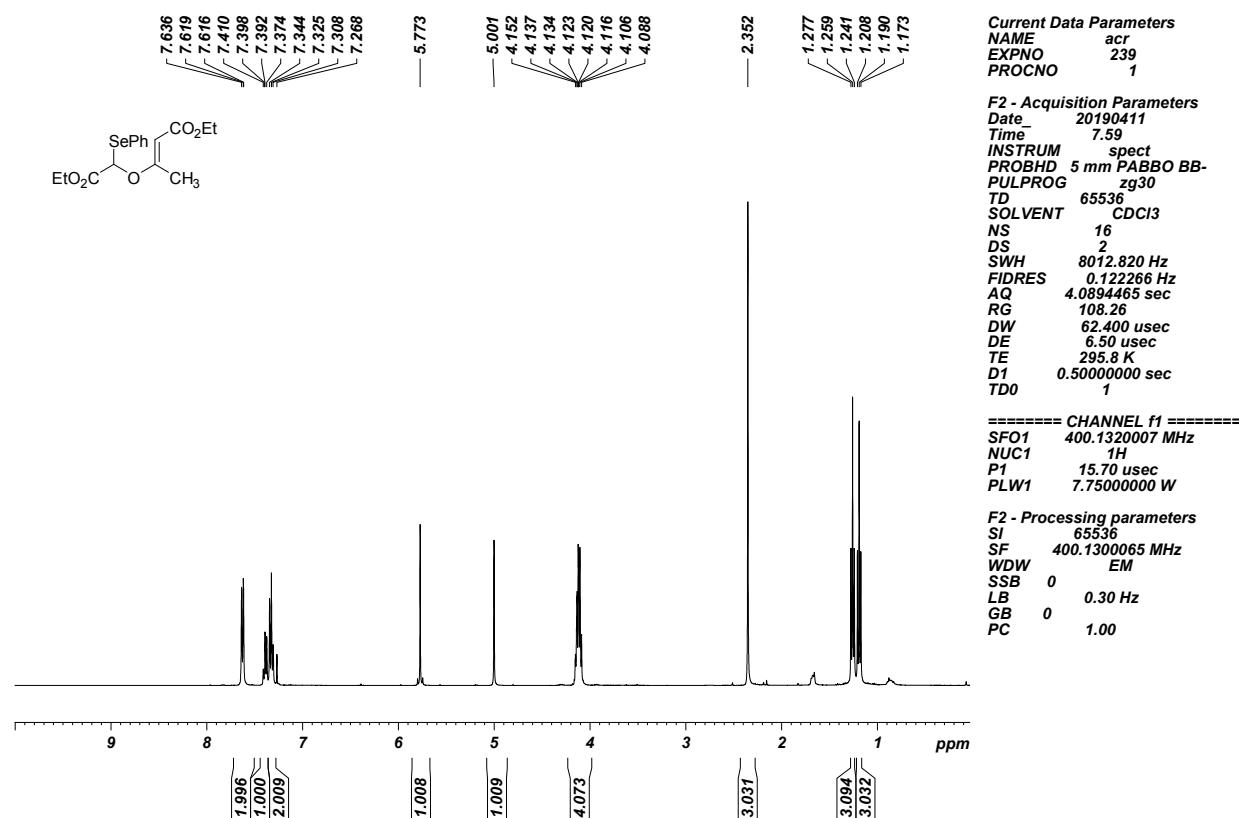


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

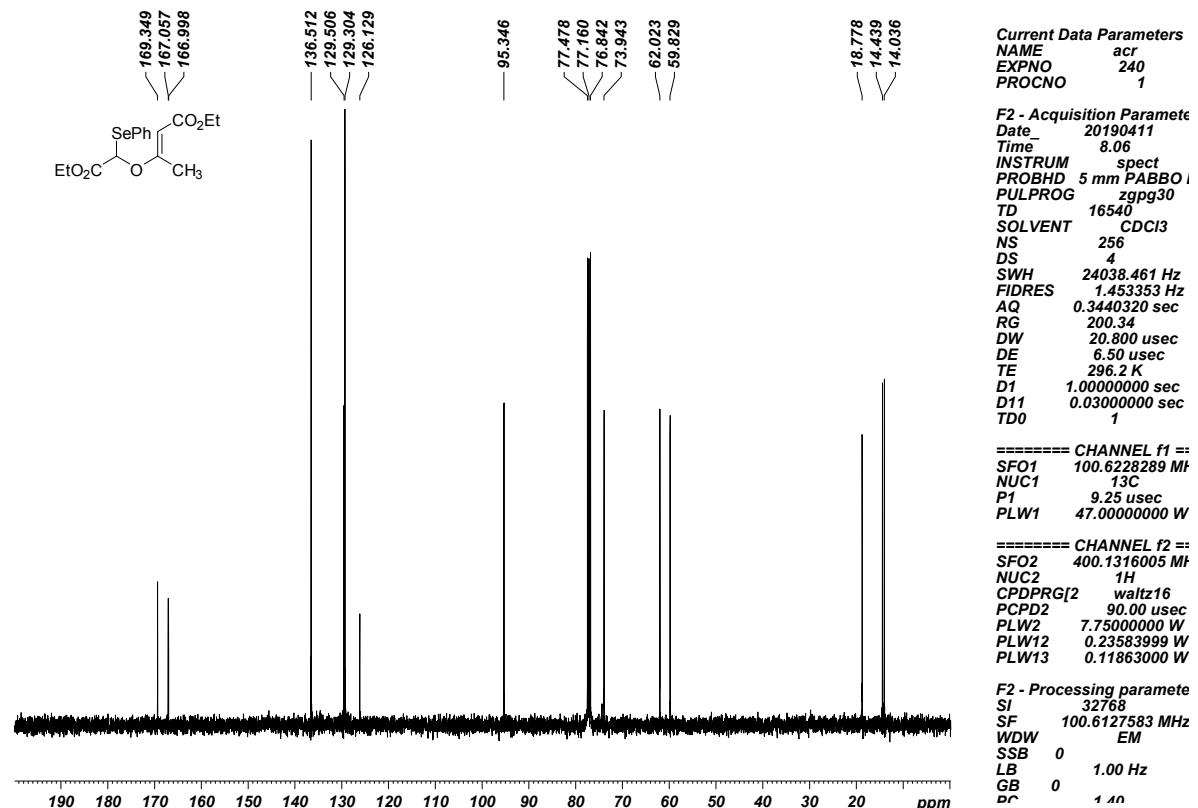


Vinylogous carbonate 6a

¹H NMR (400 MHz, CDCl₃, 24 °C)

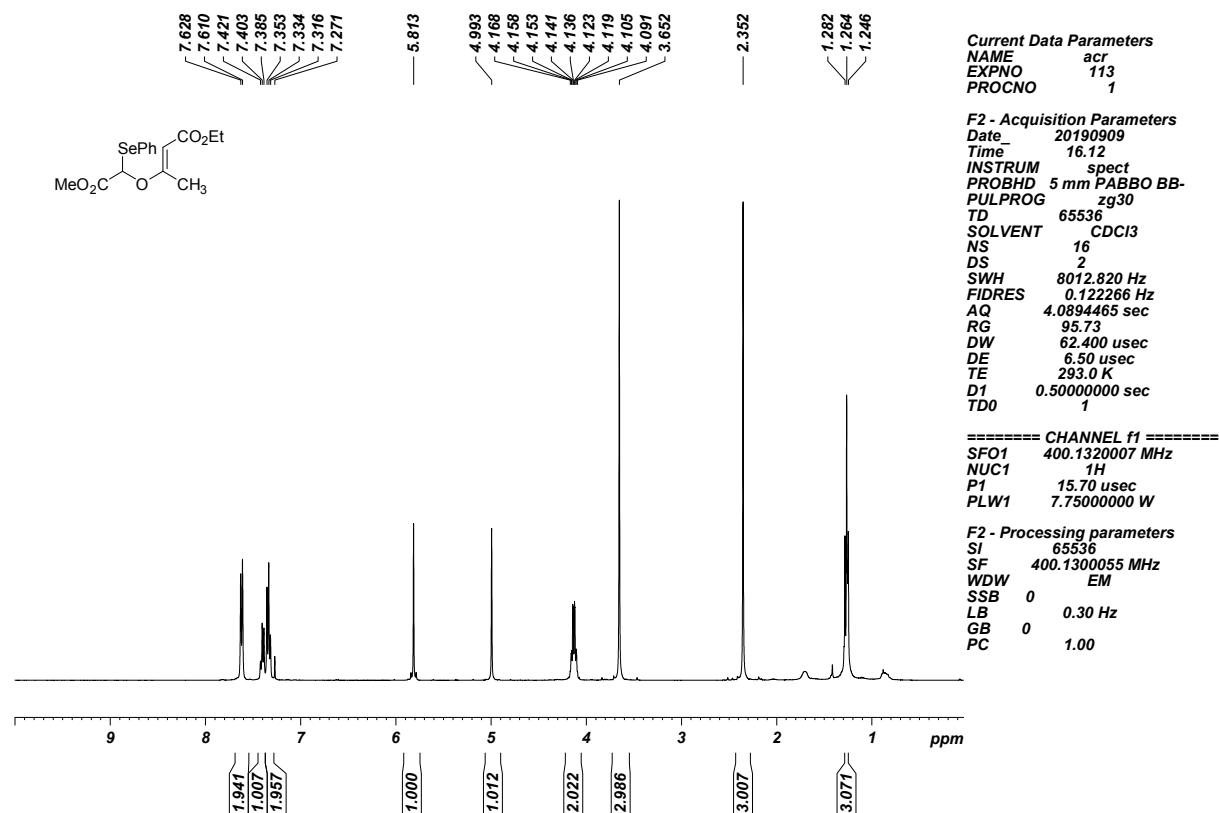


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

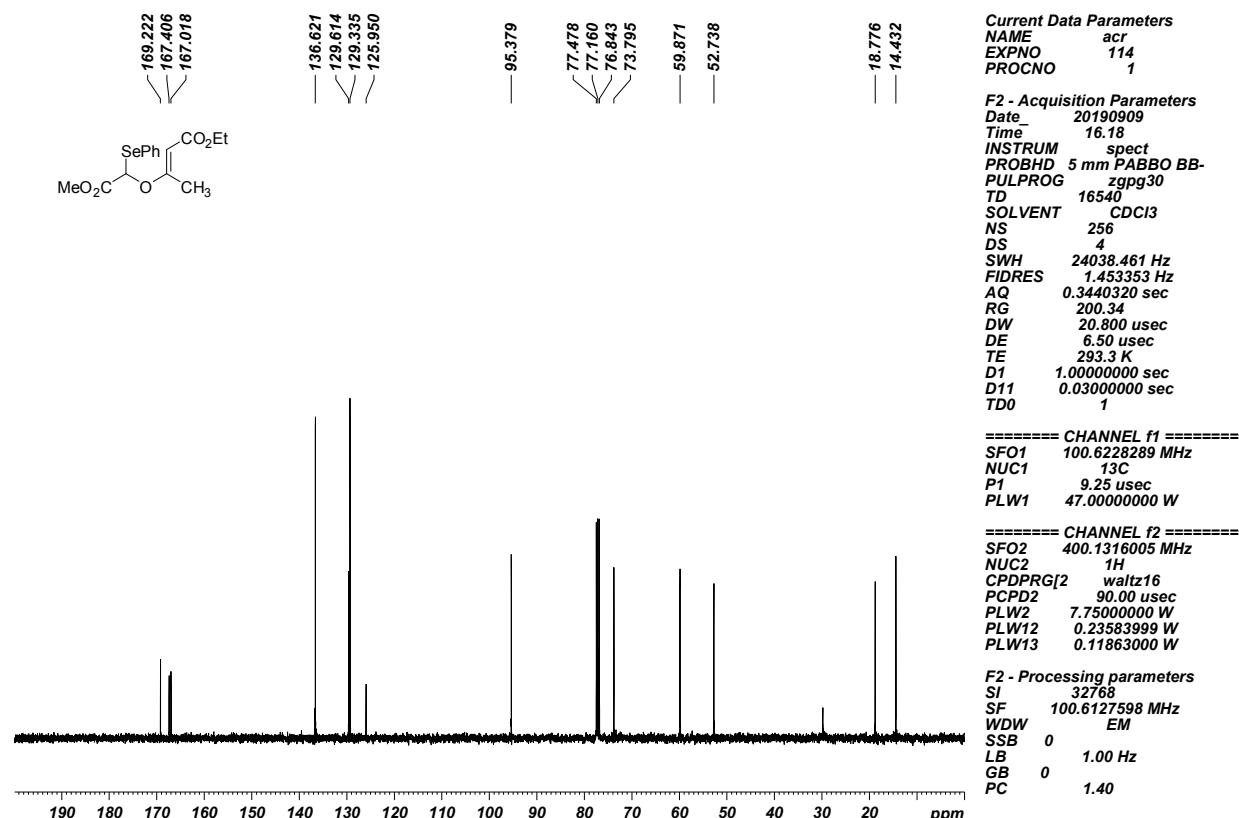


Vinylogous carbonate 6b

¹H NMR (400 MHz, CDCl₃, 24 °C)

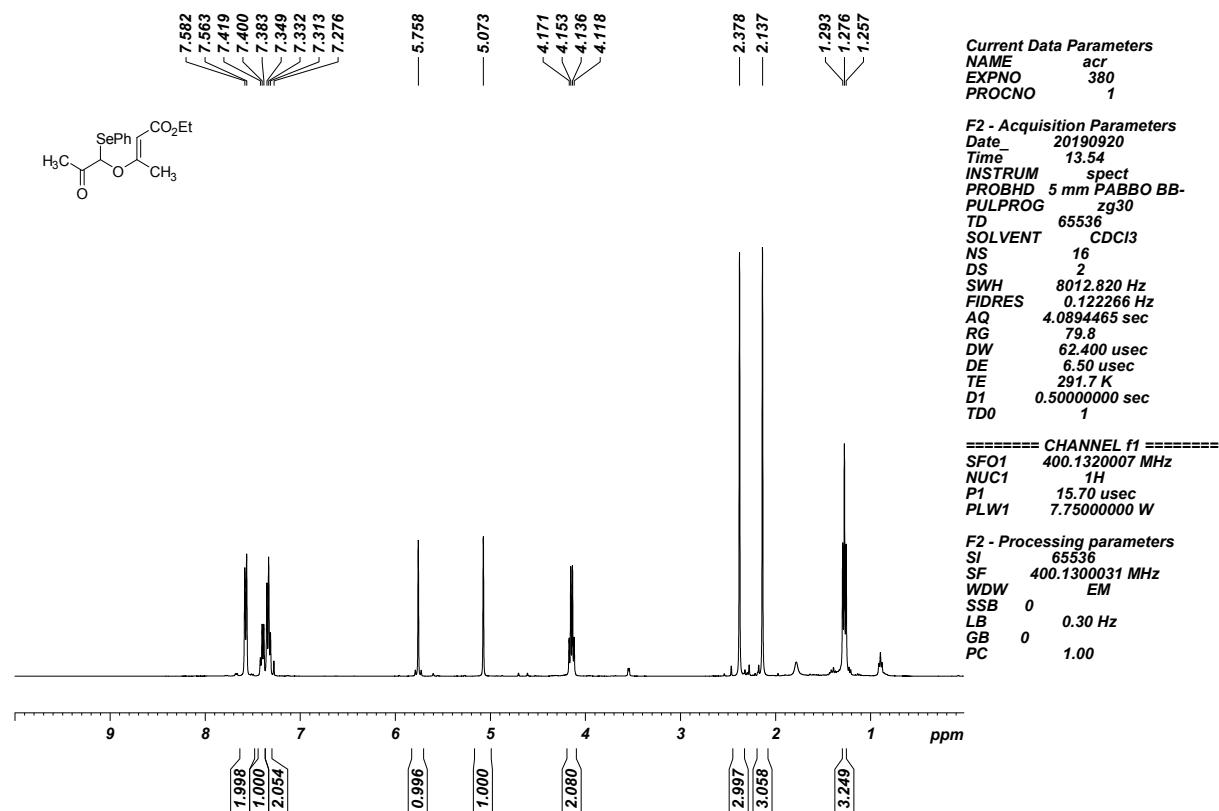


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

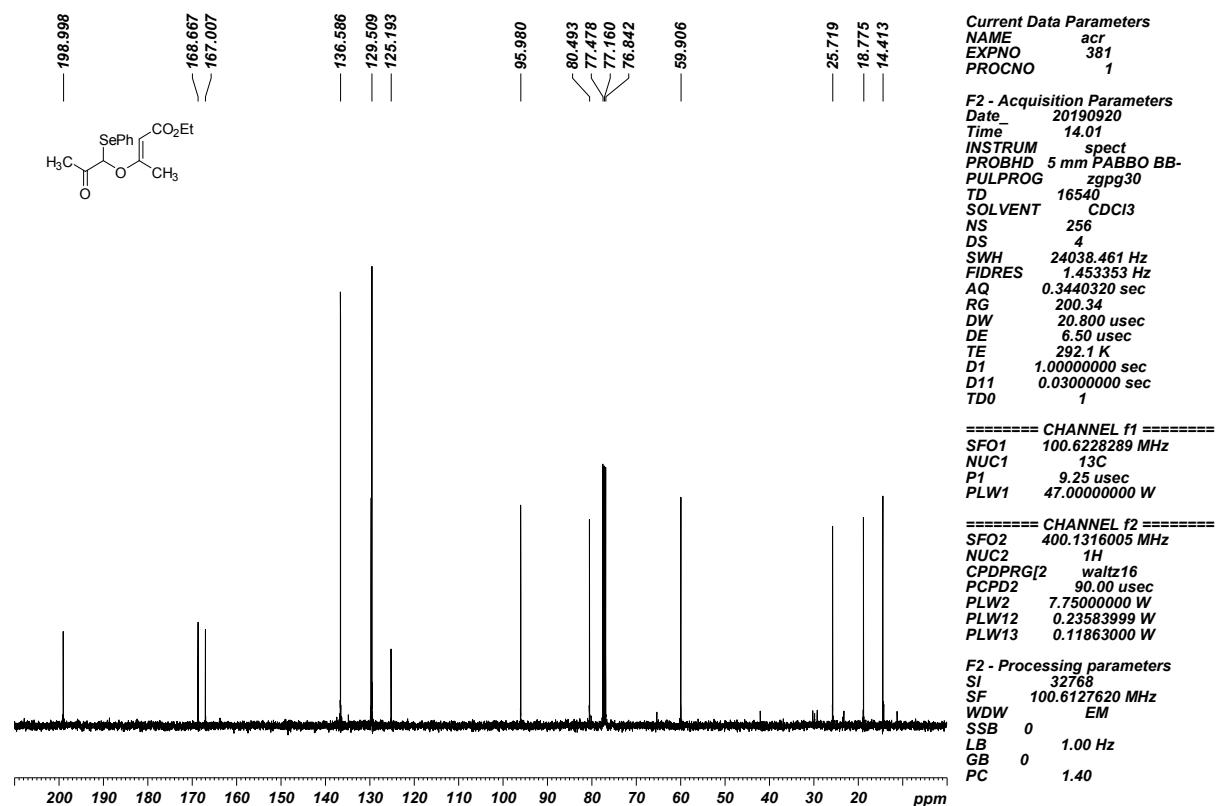


Vinylogous carbonate 6c

¹H NMR (400 MHz, CDCl₃, 24 °C)

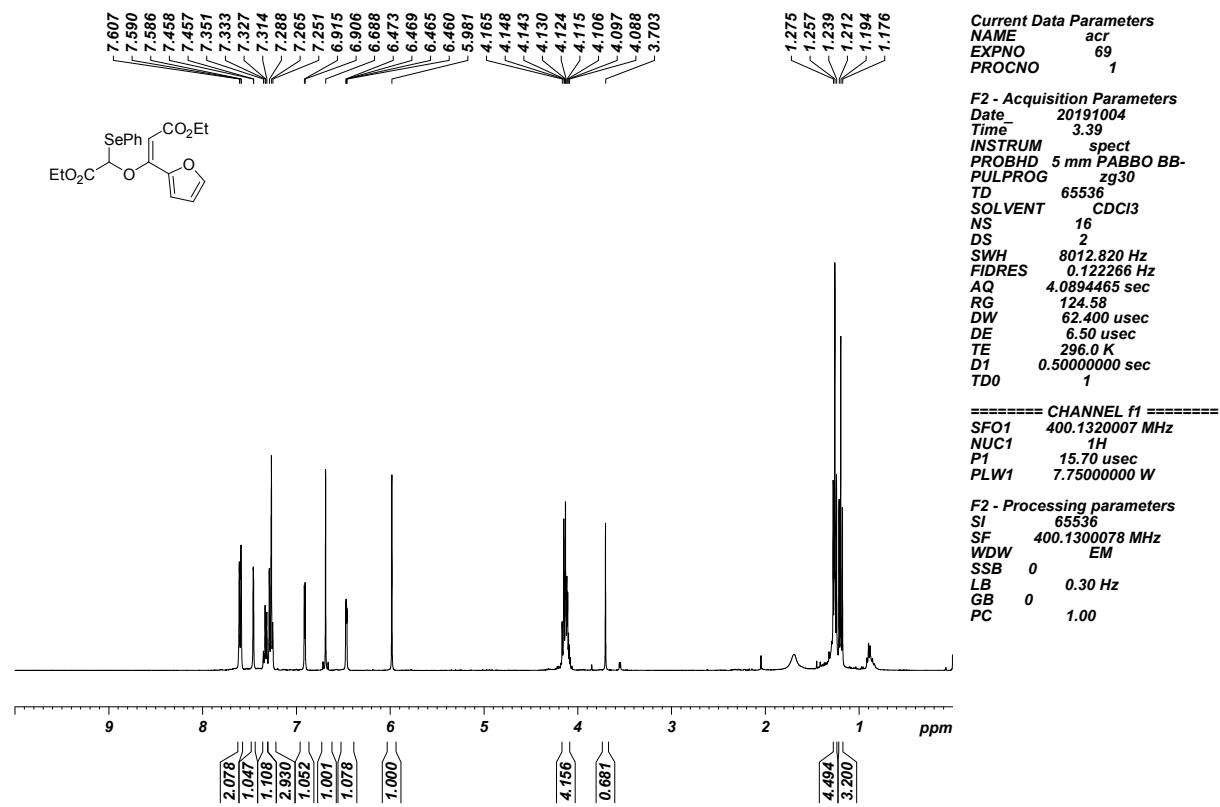


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

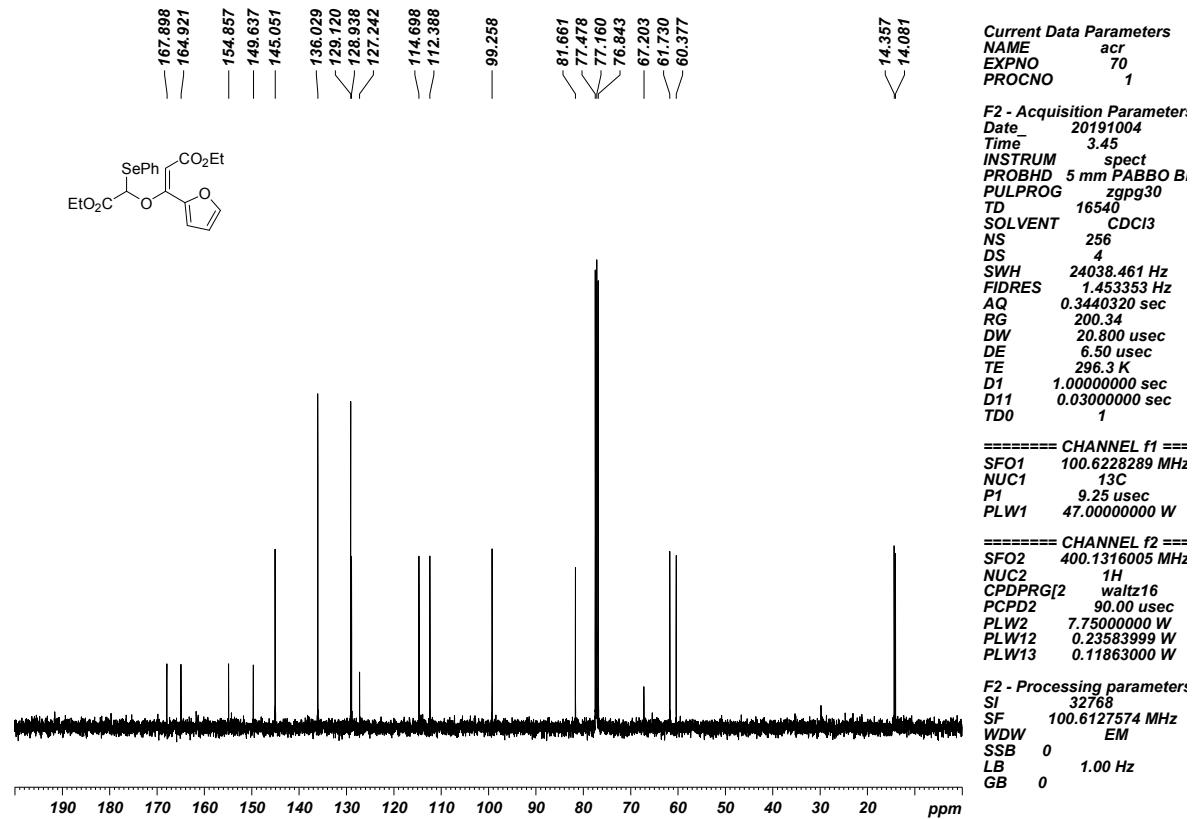


Vinylogous carbonate 6d

¹H NMR (400 MHz, CDCl₃, 24 °C)

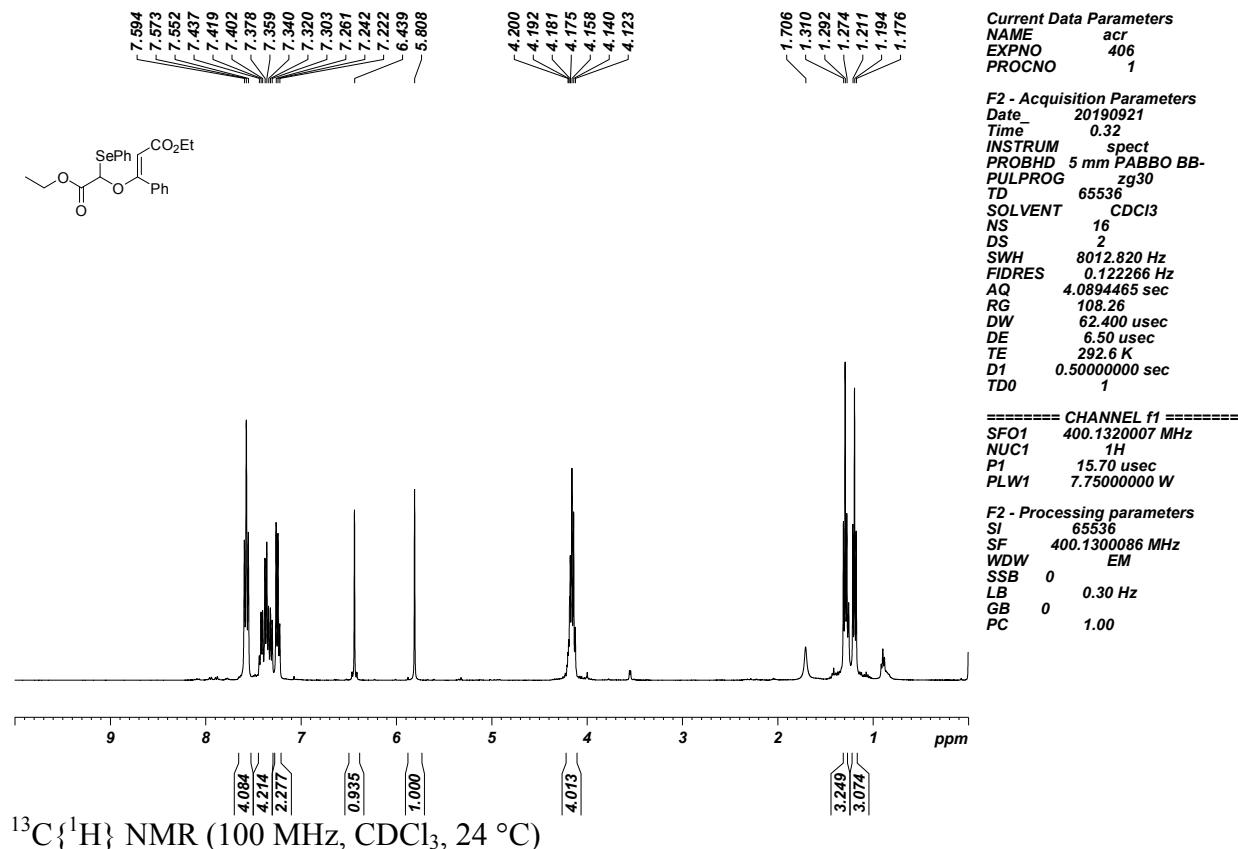


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

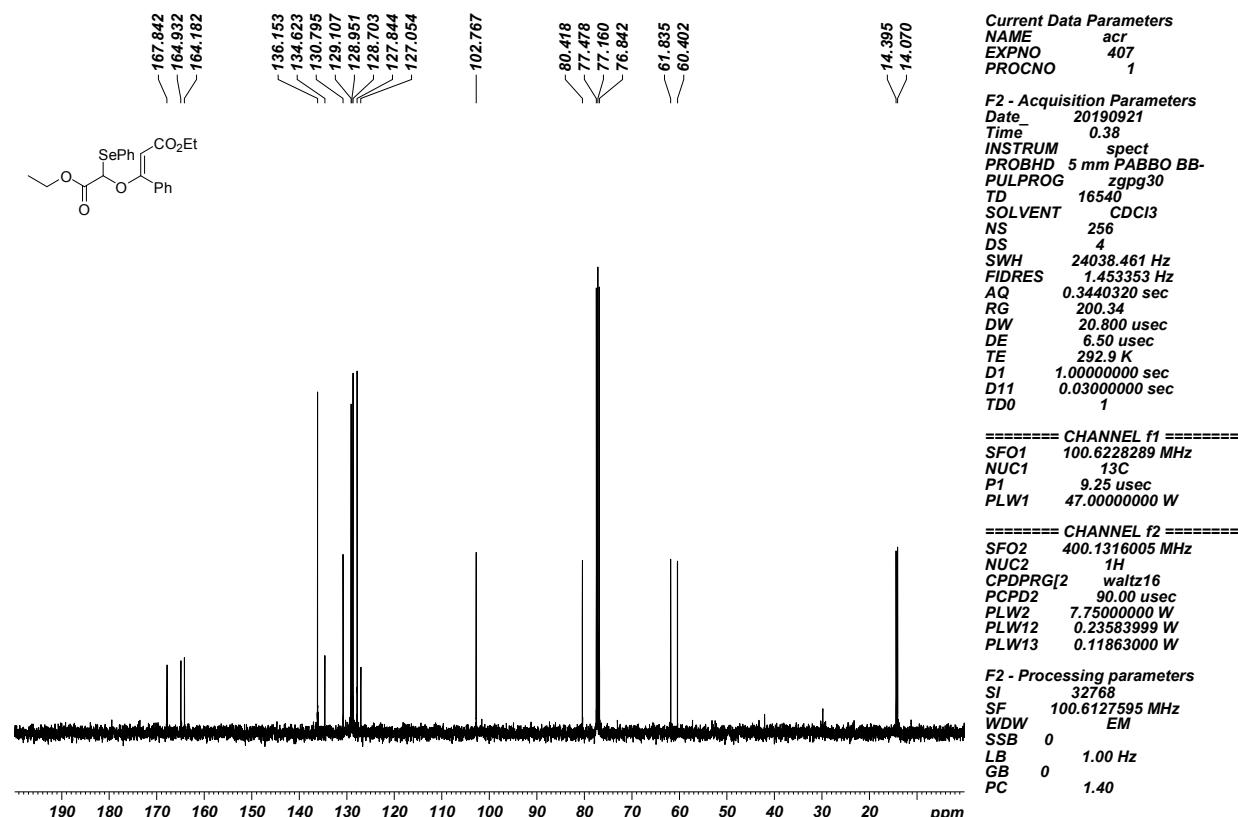


Vinylogous carbonate 6e

¹H NMR (400 MHz, CDCl₃, 24 °C)

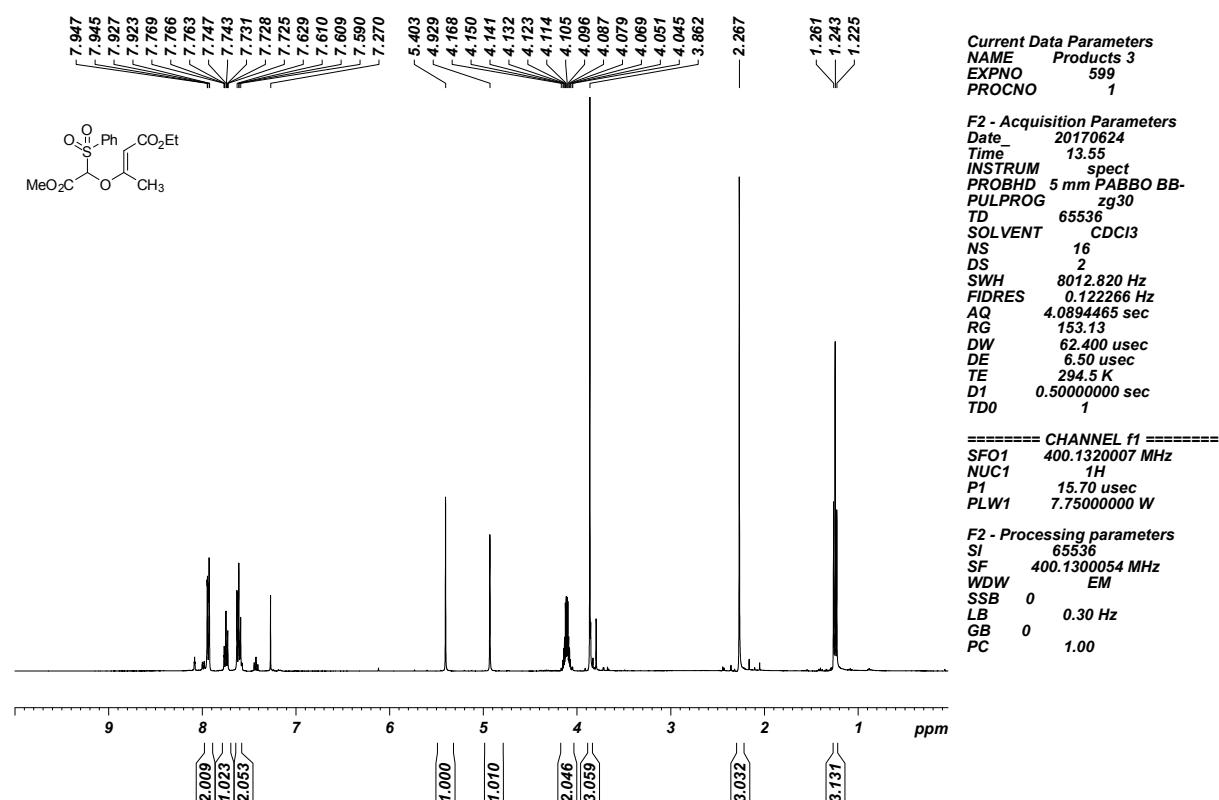


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

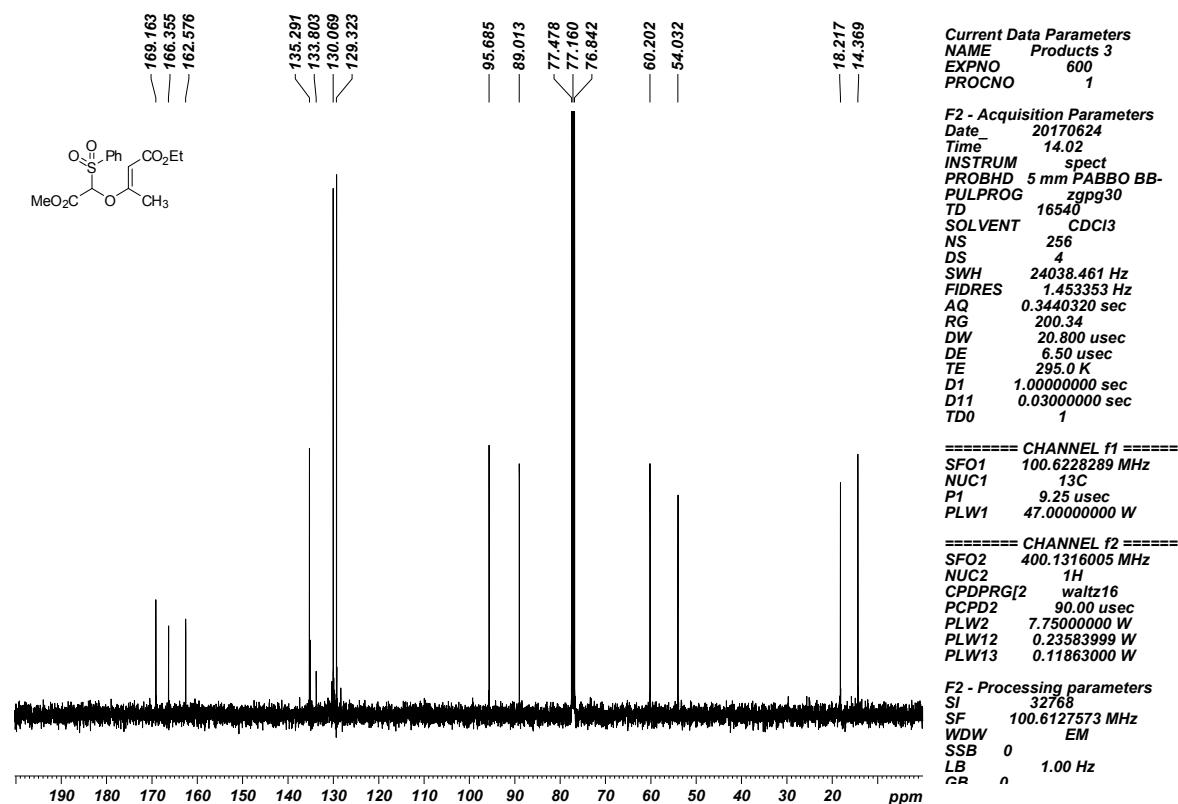


Sulfone 7

¹H NMR (400 MHz, CDCl₃, 24 °C)

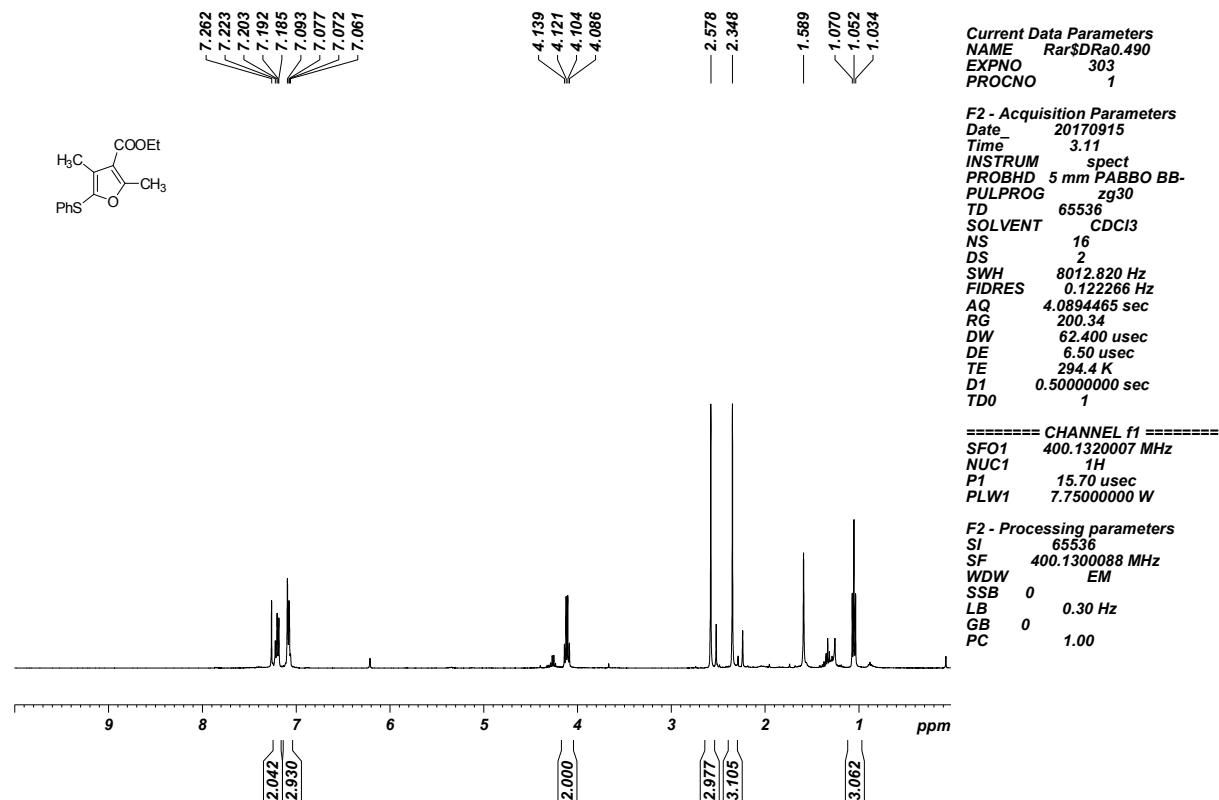


¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)

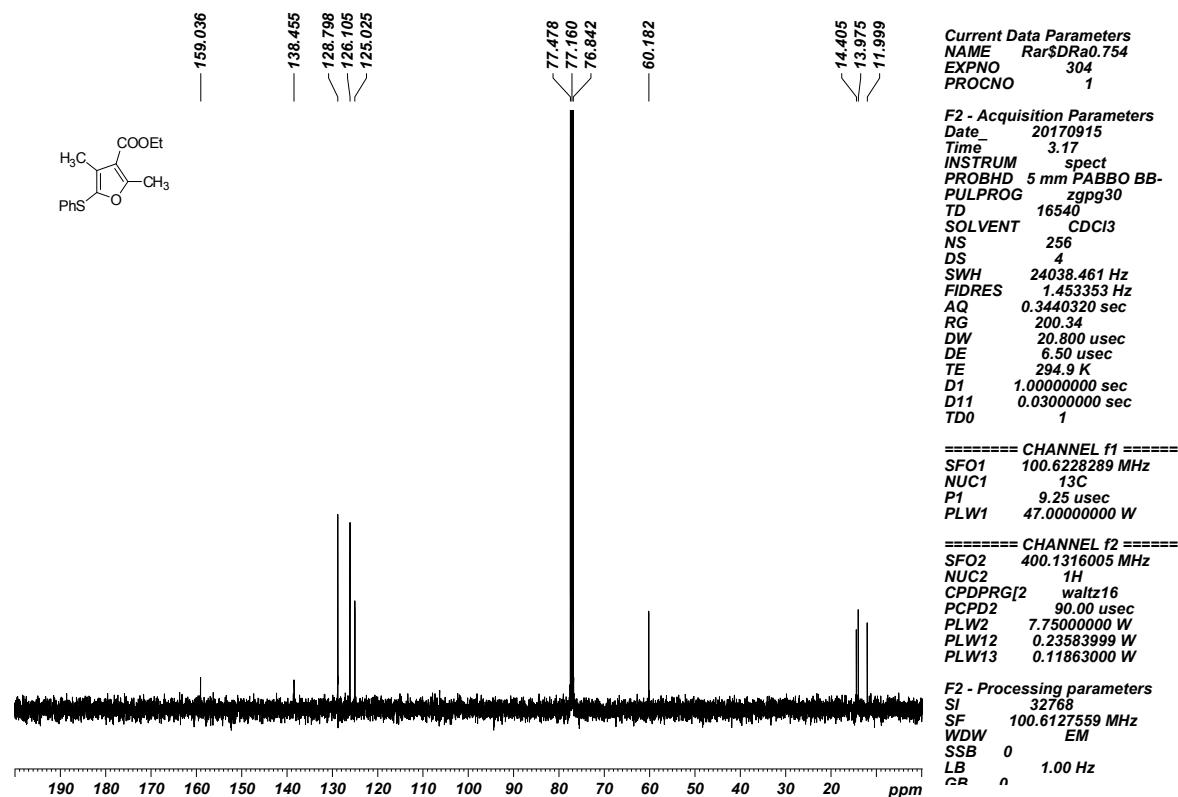


Furan8

¹H NMR (400 MHz, CDCl₃, 24 °C)



¹³C{¹H} NMR (100 MHz, CDCl₃, 24 °C)



NOE Experiment 3b

