

## Supporting Information

### Palladium-catalyzed synthesis of bis-substituted sulfoxonium ylides

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## General aspects

Otherwise noted, all reactions were carried out in flame-dried glassware under dry nitrogen atmosphere. THF was used after passage through Innovative Technology PureSolv MD system. Acetonitrile was purchased dry from Acros. Trimethylsulfoxonium iodide was purchased from FluoroChem. The aryl bromides were purchased from FluoroChem, Sigma Aldrich, Alfa Aesar, or TCI and were used as received. Pd(PPh<sub>3</sub>)<sub>4</sub> was purchased from Strem and stored in an argon filled glovebox at -30 °C. Pd<sub>2</sub>(dba)<sub>3</sub> was purchased from Sigma Aldrich and stored in an argon filled glovebox at room temperature. Flash chromatography: Merck silica gel 60 (230-400 mesh). NMR: <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>13</sup>C-HSQC and <sup>13</sup>C-HMBC spectra were recorded on a Bruker DRX 500 in CDCl<sub>3</sub>; <sup>19</sup>F{<sup>1</sup>H} spectra were recorded on a Bruker Avance 400 spectrometer; chemical shifts (δ) are given in ppm. The solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl<sub>3</sub>: δC = 77.0 ppm; residual CHCl<sub>3</sub> in CDCl<sub>3</sub>: δH = 7.26 ppm); apparent splitting patterns are designated using the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), quint. (quintuplet), sept. (septuplet), m (multiplet), br (broad), and the appropriate combinations. In <sup>13</sup>C NMR, most of the time, APT sequence was used to separate methylene groups and quaternary carbons (e, even) from methine and methyl groups (o, odd). If, due to relaxation issues, quaternary carbons could not be observed, an HMBC was carried out and the carbon was then noted (hmbc). IR: PerkinElmer Spectrum 100 FT-IR spectrometer, wavenumbers in cm<sup>-1</sup>. HRMS determined at the University of Liverpool on micromass LCT mass spectrometer (ES<sup>+</sup>) and Trio-1000 or Agilent QTOF 7200 mass spectrometers (CI). Melting points: Griffin melting point apparatus (not corrected). Elemental analyses: University of Liverpool. Compound 23 and estrone-OTf were prepared according to literature procedure<sup>i,ii</sup>.

## Synthesis of $\alpha$ -estersulfoxonium ylides

**2a:** Under  $N_2$ , trimethylsulfoxonium iodide (13.21g, 60 mmol, 3.0 equiv) was suspended in dry THF (120 mL) in a flame-dried round bottom flask that was protected from light with aluminium foil. Potassium *tert*-butoxide (6.73g, 60 mmol, 3.0 equiv) was added and the mixture was stirred at reflux for 2 hours. After cooling to 0 °C, methyl chloroformate (1.54 mL, 20 mmol, 1.0 equiv) in THF (40 mL) was added dropwise to the mixture via a dropping funnel. After stirring at room temperature for 1 hour, the mixture was filtered through a plug of celite (elution DCM). After evaporation of all volatiles, purification by flash chromatography (100% ethyl acetate) gave **2a** (2.63 g, 88%, white solid).

**m.p.:** 99-102 °C;  **$^1H$  NMR** (500 MHz,  $CDCl_3$ ):  $\delta$  3.93 (s, 1H), 3.58 (s, 3H), 3.35 (s, 6H);  **$^{13}C$  NMR** (125 MHz,  $CDCl_3$ ):  $\delta$  167.5 (hmbc), 55.2 (o), 49.8 (o), 41.8 (o, 2C); **IR** (neat):  $\nu$  = 3089 (w), 3012 (w), 2926 (w), 1623 (s), 1435 (m), 1344 (m), 1315 (m), 1174 (m), 1137 (s), 1030 (s), 998 (m), 967 (w), 916 (w), 870 (s), 764 (s), 702 (m), 689 (w)  $cm^{-1}$ ; **HRMS** (ESI) calcd for  $(C_5H_{10}O_3S + H)^+$ : 151.0423; found: 151.0427.

**3:** This compound was obtained (6.30 g, 77%, white solid) from ethyl chloroformate (4.8 mL, 50 mmol, 1.0 equiv), trimethylsulfoxonium iodide (33.02 g, 150 mmol, 3.0 equiv) and potassium *tert*-butoxide (16.83 g, 150 mmol, 3.0 equiv) following the general procedure described for the preparation of **2a** after purification by flash chromatography (100% ethyl acetate);

**m.p.:** 40-43 °C;  **$^1H$  NMR** (500 MHz,  $CDCl_3$ ):  $\delta$  4.08-3.93 (m, 2H), 3.93-3.77 (m, 1H), 3.31 (s, 6H), 1.15 (t,  $J$  = 6.4 Hz, 3H);  **$^{13}C$  NMR** (125 MHz,  $CDCl_3$ ):  $\delta$  167.3 (hmbc), 58.5 (o), 55.5 (hsqc), 42.1 (o, 2C), 14.7 (o); **IR** (neat):  $\nu$  = 3020 (w), 2977 (w), 2926 (w), 1618 (s), 1530 (w), 1485 (w), 1454 (w), 1374 (m), 1320 (s), 1300 (s), 1177 (m), 1130 (s), 1060 (w), 1026 (s), 994 (s), 950 (m), 877 (m), 861 (m), 761 (s), 722 (w), 686 (w)  $cm^{-1}$ ; **HRMS** (ESI) calcd for  $(C_6H_{12}O_3S + H)^+$ : 165.0580; found: 165.0584.

**20a:** This compound was obtained (569 mg, 34%, pale pink solid) from 4-nitrophenyl phenyl carbonate (2.00 g, 7.7 mmol, 1.0 equiv), trimethylsulfoxonium iodide (5.09 g, 23.2 mmol, 3.0 equiv) and potassium *tert*-butoxide (2.60 g, 23.2 mmol, 3.0 equiv) following the general procedure described for the preparation of **2a** after purification by flash chromatography (ethyl acetate/petroleum ether: 8/2) and recrystallisation (ethyl acetate/pentane);

**m.p.:** 107-109 °C;  **$^1H$  NMR** (500 MHz,  $CDCl_3$ ):  $\delta$  7.32 (t,  $J$  = 7.7 Hz, 2H), 7.14 (t,  $J$  = 7.1 Hz, 1H), 7.08 (d,  $J$  = 7.5 Hz, 2H), 4.18 (s, 1H), 3.32 (s, 6H);  **$^{13}C$  NMR** (125 MHz,  $CDCl_3$ ):  $\delta$  165.6 (e), 151.4 (e), 129.1 (o, 2C), 124.8 (o), 122.2 (o, 2C), 56.4 (o), 41.8 (o, 2C); **IR** (neat):  $\nu$  = 3121 (w), 3086 (w),

2449 (w), 2238 (w), 1947 (w), 1765 (s), 1751 (vs), 1656 (w), 1617 (m), 1595 (m), 1522 (vs), 1492 (m), 1460 (m), 1419 (w), 1345 (s), 1257 (vs), 1219 (vs), 1163 (m), 1106 (m), 1096 (m), 1045 (m), 1003 (m), 984 (m), 947 (m), 927 (m), 919 (m), 905 (m), 856 (s), 839 (m), 810 (m), 768 (m), 728 (m), 721 (m), 679 (m), 667 (m)  $\text{cm}^{-1}$ ; **HRMS** (ESI) calcd for  $(\text{C}_{10}\text{H}_{12}\text{O}_3\text{S} + \text{H})^+$ : 213.0588; found: 213.0580.

**21a**: This compound was obtained (1.13 g, 59%, yellow thick oil) from 4-nitrophenyl (2,2,3,3-tetramethyl-4,7,10-trioxa-3-siladodecan-12-yl) carbonate (2.15 g, 5 mmol, 1.0 equiv), trimethylsulfoxonium iodide (3.31 g, 15 mmol, 3.0 equiv) and potassium *tert*-butoxide (1.68 g, 15 mmol, 3.0 equiv) following the general procedure described for the preparation of **2a** after purification by flash chromatography (dichloromethane/methanol: 98/2 to 95/5);

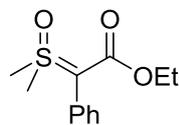
**<sup>1</sup>H NMR** (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.21-4.06 (m, 2H), 4.02-3.87 (m, 1H), 3.69 (t,  $J = 5.3$  Hz, 2H), 3.65-3.53 (m, 6H), 3.48 (t,  $J = 5.5$  Hz, 2H), 3.32 (s, 6H), 0.83 (s, 9H), 0.00 (s, 6H); **<sup>13</sup>C NMR** (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  72.6 (e), 70.7 (e), 70.4 (e), 69.7 (e), 62.7 (e), 61.8 (e), 55.9 (hmbc), 42.2 (o, 2C), 25.9 (o, 3C), 18.3 (e), -5.3 (o, 2C). The C=O from the ester was not observed, even by HMBC; **IR** (neat):  $\nu = 2928$  (m), 2857 (m), 1637 (s), 1462 (w), 1387 (m), 1330 (s), 1251 (m), 1180 (m), 1106 (s), 1029 (s), 940 (m), 835 (s), 777 (m), 759 (m), 723 (w)  $\text{cm}^{-1}$ ; **HRMS** (ESI) calcd for  $(\text{C}_{16}\text{H}_{34}\text{O}_6\text{SSi} + \text{H})^+$ : 383.1928; found: 383.1918.

**22a**: This compound was obtained (498 mg, 24%, yellow solid) from 4-nitrophenyl (2-(trimethylsilyl)ethyl) carbonate (2.50 g, 8.8 mmol, 1.0 equiv), trimethylsulfoxonium iodide (5.84 g, 24.5 mmol, 3.0 equiv), and potassium *tert*-butoxide (3.00 g, 24.5 mmol, 3.0 equiv) following the general procedure described for the preparation of **2a** after purification by flash chromatography (ethyl acetate/petroleum ether: 9/1);

**m.p.**: 94-96 °C; **<sup>1</sup>H NMR** (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.04 (t,  $J = 7.8$  Hz, 2H), 3.87 (s, 1H), 3.31 (s, 6H), 0.89 (t,  $J = 7.3$  Hz, 2H), -0.05 (s, 9H); **<sup>13</sup>C NMR** (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.5 (hmbc), 60.6 (e), 55.4 (hsqc), 42.2 (o, 2C), 17.7 (e), -1.5 (o, 3C); **IR** (neat):  $\nu = 3022$  (w), 2953 (w), 2895 (w), 1626 (s), 1520 (w), 1473 (w), 1411 (9w), 1382 (m), 1324 (vs), 1303 (m), 1248 (m), 1178 (m), 1127 (vs), 1045 (m), 1020 (vs), 995 (m), 969 (w), 945 (m), 855 (s), 830 (vs), 757 (s), 691 (s)  $\text{cm}^{-1}$ ; **Anal.** Calcd for  $\text{C}_9\text{H}_{20}\text{O}_3\text{SSi}$ : C 45.85, H 8.68, S 13.78; found: C 45.84, H 8.68, S 13.78.

## Synthesis of compounds 4–10, 12–22, and 24–26

**Compound 4.** Following **Method A**, in an argon filled glovebox, a J-Young Schlenck tube was charged



with Pd(PPh<sub>3</sub>)<sub>4</sub> (23 mg, 0.02 mmol, 0.1 equiv) and Cs<sub>2</sub>CO<sub>3</sub> (72 mg, 0.22 mmol, 1.1 equiv). The tube was then sealed and taken out of the glovebox. Under N<sub>2</sub>, the tube was then charged with **3** (82 mg, 0.50 mmol, 2.5 equiv). Three vacuum-nitrogen

cycles were performed and acetonitrile (1 mL) was then added to the reaction mixture. Bromobenzene (21 μL, 0.20 mmol, 1 equiv) was then added and the inner wall of the Schlenck tube was rinsed with acetonitrile (1 mL). The Schlenck tube was sealed, placed in a preheated oil bath set at 80 °C and stirred for 15 hours. The crude was then filtered over a plug of silica at room temperature using a DCM/MeOH (85/15) mixture to transfer all the material and for rinsing. After evaporation of all volatiles, purification by flash chromatography (hexane/ethyl acetate: 4/6 to 2/8) and recrystallization with the minimal amount of hot ethyl acetate/pentane gave **4** (35 mg, 73%, white solid).

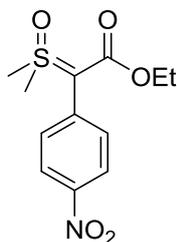
**m.p.:** 136-138 °C; **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.34-7.21 (m, 5H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.42 (s, 6H), 1.19 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 166.3 (e), 133.6 (o, 2C), 132.6 (e), 128.3 (o, 2C), 126.9 (o), 70.3 (e), 58.9 (e), 43.3 (o, 2C), 14.8 (o); **IR** (neat):  $\tilde{\nu}$  = 3019 (w), 2989 (w), 2918 (w), 1615 (s), 1592 (m), 1492 (w), 1483 (w), 1443 (w), 1392 (w), 1373 (m), 1337 (m), 1323 (m), 1206 (m), 1168 (s), 1116 (w), 1089 (m), 1071 (m), 1044 (s), 1021 (s), 1000 (m), 971 (w), 950 (w), 937 (m), 857 (w), 793 (m), 756 (m), 707 (s), 688 (m), 636 (m) cm<sup>-1</sup>; **HRMS** (ESI) calcd for (C<sub>12</sub>H<sub>16</sub>O<sub>3</sub>S + Na)<sup>+</sup>: 263.0712; found: 263.0710.

This compound can also be obtained using the same starting materials according to **Methods B** and **C** described below.

**Method B.** In an argon filled glovebox, a J-Young Schlenck tube was charged with P(*t*Bu<sub>3</sub>)<sub>2</sub> (8 mg, 0.04 mmol, 0.2 equiv), Pd<sub>2</sub>dba<sub>3</sub> (9 mg, 0.01 mmol, 0.05 equiv) and Cs<sub>2</sub>CO<sub>3</sub> (72 mg, 0.22 mmol, 1.1 equiv). The tube was then sealed and taken out of the glovebox. Under N<sub>2</sub>, acetonitrile (1 mL) was then added and the mixture was stirred at room temperature for 10 min. Then, bromobenzene (21 μL, 0.20 mmol, 1 equiv) was added followed by **3** (82 mg, 0.50 mmol, 2.5 equiv). The inner wall of the Schlenck tube was rinsed with acetonitrile (1 mL) and the tube was then sealed, placed in a preheated oil bath set at 80 °C and stirred for 15 hours. The purification method is identical to method A, except that recrystallization was not necessary. This method afforded **4** as white solid (38 mg, 80%).

**Method C.** This method is identical to **Method B**, except that P(*t*Bu<sub>3</sub>)<sub>2</sub> was replaced with XPhos (19 mg, 0.04 mmol, 0.2 equiv) and that all operations were performed out of the glove box under N<sub>2</sub> by using standard Schlenck technique. This method afforded **4** as white solid (44 mg, 92%).

**Compound 5.** Following **Method A**, in an argon filled glovebox, a J-Young Schlenk tube was charged



with Pd(PPh<sub>3</sub>)<sub>4</sub> (23 mg, 0.02 mmol, 0.1 equiv) and Cs<sub>2</sub>CO<sub>3</sub> (72 mg, 0.22 mmol, 1.1 equiv). The tube was then sealed and taken out of the glovebox. Under N<sub>2</sub>, the tube was then charged with **3** (82 mg, 0.50 mmol, 2.5 equiv) and bromo-4-nitrobenzene (40 mg, 0.2 mmol, 1.0 equiv). Three vacuum-nitrogen cycles were performed and acetonitrile was then added to the reaction mixture (2 mL). The Schlenk tube was

then sealed, placed in a preheated oil bath set at 80 °C and stirred for 15 hours. The crude was then filtered over a plug of silica at room temperature using a DCM/MeOH (85/15) mixture to transfer all the material and for rinsing. After evaporation of all volatiles, purification by flash chromatography (hexane/ethyl acetate: 4/6 to 2/8) and recrystallization with the minimal amount of hot ethyl acetate/pentane gave **5** (42 mg, 74%, yellowish green solid).

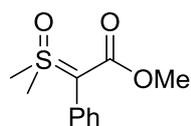
**m.p.:** 160-161 °C; **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 8.12 (dt, *J* = 9.0, 2.0 Hz, 2H), 7.47 (dt, *J* = 9.0, 2.1 Hz, 2H), 4.15 (q, *J* = 7.0 Hz, 2H), 3.54 (s, 6H), 1.25 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 165.3 (e), 144.9 (e), 140.2 (e), 131.6 (o, 2C), 123.0 (o, 2C), 68.5 (e), 59.4 (e), 44.2 (o, 2C), 14.6 (o); **IR** (neat): ν = 3031 (w), 3000 (w), 2924 (w), 1617 (s), 1586 (s), 1508 (s), 1492 (m), 1483 (m), 1396 (w), 1372 (m), 1336 (s), 1326 (s), 1215 (s), 1168 (s), 1106 (m), 1084 (s), 1039 (s), 1011 (m), 971 (w), 950 (w), 935 (m), 860 (m), 848 (m), 838 (m), 789 (w), 756 (m), 704 (s), 683 (m), 629 (w) cm<sup>-1</sup>; **HRMS** (ESI) calcd for (C<sub>12</sub>H<sub>15</sub>NO<sub>5</sub>S + Na)<sup>+</sup>: 308.0563; found: 308.0568.

This compound can also be obtained using the same starting materials according to **Methods B** and **C** described for compound **4**.

**Method B.** afforded **5** (54 mg, 95%) as a yellowish green solid.

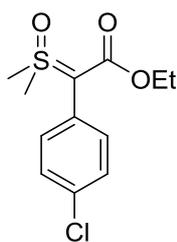
**Method C.** afforded **5** (51 mg, 89%) as a yellowish green solid.

**2:** This compound was obtained from **2a** (75 mg, 0.5 mmol, 2.5 equiv) and bromobenzene (21 μL, 0.2 mmol, 1.0 equiv) as a white solid following **Method B** after purification by flash chromatography (hexane/ethyl acetate: 35/65 to 2/8) (37 mg, 82%);



**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.36-7.25 (m, 5H), 3.61 (s, 3H), 3.42 (s, 6H), in agreement with previously reported data.<sup>iii</sup>

**6:** This compound was obtained from **3** (82 mg, 0.5 mmol, 2.5 equiv) and 1-bromo-4-chlorobenzene (38 mg, 0.2 mmol, 1.0 equiv) following:



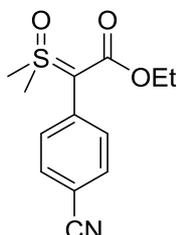
**Method A** for the preparation of **5** (45 mg, 81%, cream solid) after purification by flash chromatography (hexane/ethyl acetate: 4/6 to 2/8);

**Method B** (43 mg, 78%, cream solid) after purification by flash chromatography (hexane/ethyl acetate: 1/1 to 2/8);

**Method C** (52 mg, 95%, cream solid) after purification by flash chromatography (hexane/ethyl acetate: 1/1 to 2/8);

**m.p.:** 136-139 °C; **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.30-7.21 (m, 4H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.43 (s, 6H), 1.19 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 166.1 (hmbc), 134.6 (o, 2C), 132.6 (e), 131.0 (e), 128.4 (o, 2C), 68.6 (hmbc), 59.0 (e), 43.4 (o, 2C), 14.8 (o); **IR** (neat): ν = 3024 (w), 2995 (w), 2921 (w), 1613 (s), 1587 (m), 1494 (m), 1478 (m), 1456 (w), 1393 (w), 1373 (m), 1339 (m), 1326 (m), 1305 (w), 1208 (m), 1182 (m), 1166 (s), 1083 (s), 1060 (m), 1040 (s), 1012 (m), 970 (m), 952 (w), 934 (m), 839 (s), 815 (w), 785 (w), 755 (m), 720 (m), 687 (m) cm<sup>-1</sup>; **HRMS** (ESI) calcd for (C<sub>12</sub>H<sub>15</sub>ClO<sub>3</sub>S + Na)<sup>+</sup>: 297.0323; found: 297.0323.

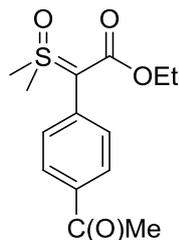
**7:** This compound was obtained from **3** (82 mg, 0.2 mmol, 2.5 equiv) and 4-bromobenzonitrile (36 mg, 0.2 mmol, 1.0 equiv) following:



**Method A** for the preparation of **5** (48 mg, 90%, white solid) after purification by flash chromatography (hexane/ethyl acetate: 1/1 to 2/8);

**m.p.:** 143-145 °C; **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.50 (s, 6H), 1.22 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 165.3 (e), 137.8 (e), 132.2 (o, 2C), 131.4 (o, 2C), 119.3 (e), 108.5 (e), 68.4 (o), 59.2 (e), 44.0 (o, 2C), 14.6 (o); **IR** (neat): ν = 3675 (w), 2980 (m), 2926 (m), 2219 (m), 1620 (s), 1595 (s), 1501 (m), 1483 (w), 1436 (w), 1395 (m), 1368 (s), 1338 (s), 1326 (m), 1303 (w), 1214 (s), 1181 (s), 1164 (s), 1110 (w), 1082 (s), 1040 (s), 968 (w), 632 (m), 842 (s), 795 (w), 755 (m), 725 (m), 688 (m) cm<sup>-1</sup>. **HRMS** (ESI) calcd for (C<sub>13</sub>H<sub>15</sub>NO<sub>3</sub>S + Na)<sup>+</sup>: 288.0665; found: 288.0670.

**8:** This compound was obtained from **3** (82 mg, 0.5 mmol, 2.5 equiv) and 4'-bromoacetophenone (40 mg, 0.2 mmol, 1.0 equiv) following:



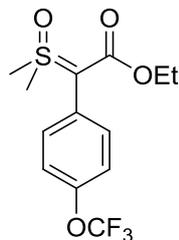
**Method A** for the preparation of **5** (44 mg, 77%, white solid) after purification by flash chromatography (hexane/ethyl acetate: 3/7 to 2/8) and recrystallisation (ethyl acetate/pentane);

**Method B** (48 mg, 85%, white solid) after purification by flash chromatography (hexane/ethyl acetate: 1/1 to 2/8);

**Method C** (49 mg, 86%, white solid) after purification by flash chromatography (hexane/ethyl acetate: 1/1 to 2/8);

**m.p.:** 98-102 °C; **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.88 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.49 (s, 6H), 2.58 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 197.7 (e), 165.7 (e), 138.2 (e), 134.5 (e), 132.2 (o, 2C), 128.1 (o, 2C), 69.4 (HMBC), 59.1 (e), 43.8 (e, 2C), 26.5 (e), 14.7 (e); **IR** (neat): ν = 2997 (w), 2920 (w), 1675 (m), 1615 (s), 1592 (s), 1556 (w), 1513 (w), 1479 (w), 1431 (w), 1395 (w), 1373 (m), 1338 (m), 1324 (m), 1264 (m), 1213 (s), 1169 (s), 1086 (s), 1075 (m), 1040 (s), 1022 (m), 962 (m), 934 (m), 853 (w), 834 (m), 789 (w), 756 (m), 735 (m), 715 (m), 686 (s), 634 (w) cm<sup>-1</sup>; **HRMS** (ESI) calcd for (C<sub>14</sub>H<sub>18</sub>O<sub>4</sub>S + Na)<sup>+</sup>: 305.0818; found: 305.0825.

**9:** This compound was obtained from **3** (82 mg, 0.5 mmol, 2.5 equiv) and 1-bromo-4-(trifluoromethoxy)benzene (30 μL, 0.2 mmol, 1.0 equiv) following:



**Method A** for the preparation of **4** (42 mg, 65%, white solid) after purification by flash chromatography (hexane/ethyl acetate: 1/1 to 2/8) and recrystallisation (ethyl acetate/pentane);

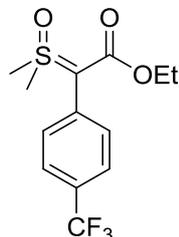
**Method B** (49 mg, 76%, white solid) after purification by flash chromatography (hexane/ethyl acetate: 35/65 to 25/75);

**Method C** (59 mg, 91% white solid) after purification by flash chromatography (hexane/ethyl acetate: 1/1 to 25/75);

**m.p.:** 135-136 °C; **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.34-7.29 (m, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 4.10 (q, *J* = 7.0 Hz, 2H), 3.42 (s, 6H), 1.19 (t, *J* = 7.2 Hz, 3H); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): 166.0 (e), 147.8 (e), 134.6 (o, 2C), 131.2 (e), 120.5 (e, q, *J* = 257.0 Hz), 120.5 (o, 2C), 68.4 (e), 59.0 (e), 43.5 (o, 2C), 14.7 (o); **<sup>19</sup>F** (376.5 MHz, CDCl<sub>3</sub>): δ -57.7; **IR** (neat): ν = 3031 (w), 3000 (w), 2925 (w), 1615 (s), 1598 (m), 1498 (m), 1483 (w), 1398 (w), 1374 (m), 1339 (w), 1327 (w), 1306 (w), 1255 (m), 1201 (s), 1174 (s), 1148 (s), 1086 (s), 1042 (s), 1016 (m), 973 (m), 938 (m), 920 (w), 958 (m), 836 (w), 813 (w), 777

(w), 757 (w), 735 (w) 691 (s), 642  $\text{cm}^{-1}$ ; **HRMS** (ESI) calcd for  $(\text{C}_{13}\text{H}_{15}\text{F}_3\text{O}_4\text{S} + \text{H})^+$ : 325.0716; found: 325.0722.

**10:** This compound was obtained from **3** (82 mg, 0.5 mmol, 2.5 equiv) and 4-bromobenzotrifluoride



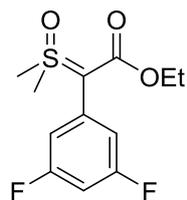
(28  $\mu\text{L}$ , 0.2 mmol, 1.0 equiv) following:

**Method A** for the preparation of **4** (49 mg, 79%, off-white solid) after purification by flash chromatography (hexane/ethyl acetate: 1/1 to 2/8) and recrystallisation (ethyl acetate/pentane);

**Method B** (61 mg, 98%, off-white solid) after purification by flash chromatography (hexane/ethyl acetate: 1/1 to 2/8);

**m.p.:** 124-126  $^{\circ}\text{C}$ ;  **$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.53 (d,  $J = 8.0$  Hz, 2H), 7.42 (d,  $J = 8.0$  Hz, 2H), 4.11 (q,  $J = 7.1$  Hz, 2H), 3.46 (s, 6H), 1.20 (t,  $J = 7.1$  Hz, 3H);  **$^{13}\text{C}$  NMR** (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  165.6 (e), 136.5 (e), 132.7 (o, 2C), 127.8 (e, q,  $J = 32.1$  Hz), 124.8 (o, q,  $J = 3.6$  Hz, 2C), 124.3 (e, q,  $J = 271.5$  Hz), 68.8 (e), 59.0 (e), 43.6 (o, 2C), 14.6 (o);  **$^{19}\text{F}$**  (376.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  -62.3; **IR** (neat):  $\nu = 2999$  (w), 2924 (w), 1621 (s), 1603 (s), 1515 (w), 1483 (w), 1375 (m), 1340 (m), 1320 (s), 1214 (m), 1192 (m), 1172 (s), 1118 (s), 1088 (s), 1065 (s), 1040 (s), 972 (m), 952 (m), 936 (m), 850 (m), 794 (w), 757 (m), 736 (m), 692 (m), 666 (m), 635 (w), 608 (m)  $\text{cm}^{-1}$ ; **HRMS** (ESI) calcd for  $(\text{C}_{13}\text{H}_{15}\text{F}_3\text{O}_3\text{S} + \text{H})^+$ : 309.0767; found: 309.0774.

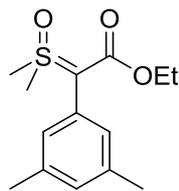
**12:** This compound was obtained from **3** (82 mg, 0.5 mmol, 2.5 equiv) and 1-bromo-3,5-difluorobenzene (23  $\mu\text{L}$ , 0.2 mmol, 1.0 equiv) following:



**Method A** for the preparation of **4** (53 mg, 96%, white solid) after purification by flash chromatography (hexane/ethyl acetate: 1/1 to 2/8);

**m.p.:** 97-99  $^{\circ}\text{C}$ ;  **$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.88-6.81 (m, 2H), 6.64 (td,  $J = 9.0$ , 2.2, 1H), 4.10 (q,  $J = 7.1$  Hz, 2H), 3.46 (s, 6H), 1.21 (t,  $J = 7.1$  Hz, 3H);  **$^{13}\text{C}$  NMR** (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  165.5 (e), 163.3 (e, d,  $J = 14.2$  Hz), 161.3 (e, d,  $J = 13.9$  Hz), 135.6 (e, t,  $J = 10.8$  Hz), 115.3 (o, d,  $J = 5.6$  Hz), 115.1 (o, d,  $J = 5.6$  Hz), 101.6 (o, t,  $J = 25.4$  Hz), 68.5 (hmbc), 59.1 (e), 43.6 (o, 2C), 14.6 (o);  **$^{19}\text{F}$**  (376.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  -111.4; **IR** (neat):  $\nu = 3071$  (w), 3019 (w), 2983 (w), 2934 (w), 1631 (s), 1615 (s), 1587 (s), 1472 (w), 1457 (w), 1426 (m), 1406 (m), 1372 (m), 1347 (w), 1330 (w), 1267 (s), 1215 (w), 1184 (s), 1153 (s), 1120 (s), 1093 (s), 1056 (m), 1024 (s), 981 (m), 930 (s), 859 (w), 829 (w), 759 (m), 727 (w), 694 (s), 678 (s)  $\text{cm}^{-1}$ . **HRMS** (ESI) calcd for  $(\text{C}_{12}\text{H}_{14}\text{F}_2\text{O}_3\text{S} + \text{H})^+$ : 277.0704; found: 277.0713.

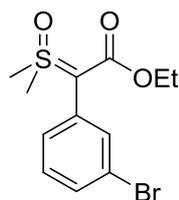
**13:** This compound was obtained from **3** (82 mg, 0.5 mmol, 2.5 equiv) and 1-bromo-3,5-dimethylbenzene (27  $\mu$ L, 0.2 mmol, 1.0 equiv) following:



**Method B** (41 mg, 76%, amorphous yellow solid) after purification by flash chromatography (hexane/ethyl acetate: 1/1 to 2/8);

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta$  6.92 (s, 2H), 6.88 (s, 1H), 4.11 (q,  $J$  = 7.0 Hz, 2H), 3.38 (s, 6H), 2.29 (s, 6H), 1.20 (t,  $J$  = 7.1 Hz, 3H); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta$  166.4 (e), 137.6 (e, 2C), 132.2 (e), 131.4 (o, 2C), 128.9 (o), 70.5 (e), 58.8 (e), 43.1 (o, 2C), 21.2 (o, 2C), 14.8 (o); **IR** (neat):  $\nu$  = 2980 (w), 2928 (w), 1736 (w), 1625 (m), 1608 (s), 1596 (s), 1516 (w), 1454 (w), 1420 (w), 1395 (w), 1367 (m), 1336 (w), 1266 (s), 1254 (s), 1184 (s), 1154 (s), 1090 (m), 1072 (m), 1020 (s), 947 (w), 932 (w), 848 (m), 822 (w), 796 (w), 757 (m), 726 (w), 701 (s) cm<sup>-1</sup>; **HRMS** (ESI) calcd for (C<sub>14</sub>H<sub>20</sub>O<sub>3</sub>S + H)<sup>+</sup>: 269.1216; found: 269.1206.

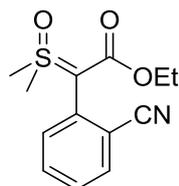
**14:** This compound was obtained from **3** (82 mg, 0.5 mmol, 2.5 equiv) and 1,3-dibromobenzene (24  $\mu$ L, 0.2 mmol, 1.0 equiv) following:



**Method A** for the preparation of **4** (38 mg, 60%, white solid) after purification by flash chromatography (hexane/ethyl acetate: 4/6 to 2/8) and recrystallisation with ethyl acetate/pentane;

**m.p.:** 42-45 °C; **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.48-7.45 (m, 1H), 7.37-7.32 (m, 1H), 7.23 (dt,  $J$  = 7.8, 1.3 Hz, 1H), 7.16 (t,  $J$  = 7.8 Hz, 1H), 4.10 (q,  $J$  = 7.1 Hz, 2H), 3.42 (s, 6H), 1.19 (t,  $J$  = 7.1 Hz, 1H); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): 165.9 (e), 136.1 (o), 134.7 (e), 131.8 (o), 129.6 (o), 129.5 (o), 121.9 (e), 69.0 (e), 59.0 (e), 43.5 (o, 2C), 14.7 (o); **IR** (neat):  $\nu$  = 3029 (w), 2998 (w), 2975 (w), 2924 (w), 2899 (w), 1614 (s), 1584 (m), 1554 (w), 1473 (m), 1404 (w), 1393 (w), 1367 (m), 1337 (m), 1322 (m), 1305 (w), 1293 (w), 1255 (w), 1205 (m), 1177 (s), 1160 (s), 1113 (w), 1095 (m), 1080 (m), 1070 (m), 1041 (s), 994 (w), 979 (w), 941 (m), 909 (w), 861 (w), 798 (m), 781 (m), 755 (m), 705 (s), 680 (m) cm<sup>-1</sup>; **HRMS** (ESI) calcd for (C<sub>12</sub>H<sub>15</sub>BrO<sub>3</sub>S + H)<sup>+</sup>: 318.9998; found: 319.0002.

**15:** This compound was obtained from **3** (82 mg, 0.5 mmol, 2.5 equiv) and 2-bromobenzonitrile (36 mg, 0.2 mmol, 1.0 equiv) following:

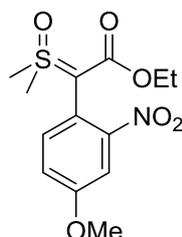


**Method A** for the preparation of **5** (46 mg, 87%, light yellow thick oil) after purification by flash chromatography (hexane/ethyl acetate: 4/6 to 2/8);

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.63 (dd,  $J$  = 7.7, 1.0 Hz, 1H), 7.51 (td,  $J$  = 7.7, 1.0 Hz, 1H), 7.43 (d,  $J$  = 7.5 Hz, 1H), 7.32 (td,  $J$  = 7.7, 0.7, 1H), 4.32-3.91 (m, 2H), 3.64 (s, 3H), 3.39 (s, 3H), 1.33-0.98 (m, 3H); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>):  $\delta$  165.7 (e), 136.1 (e), 135.7 (o), 132.7 (o), 132.3 (o), 127.4 (o),

119.4 (e), 117.9 (e), 65.2 (hmbc), 59.1 (e), 44.1 (o), 42.8 (o), 14.7 (o); **IR** (neat):  $\nu$  = 2981 (w), 2929 (w), 2223 (m), 1619 (s), 1590 (m), 1480 (m), 1444 (m), 1393 (w), 1368 (m), 1327 (m), 1229 (s), 1205 (s), 1185 (s), 1082 (m), 1021 (s), 979 (m), 939 (m), 857 (w), 759 (m), 733 (m), 687 (m), 645 (w)  $\text{cm}^{-1}$ ; **HRMS** (ESI) calcd for  $(\text{C}_{13}\text{H}_{15}\text{NO}_3\text{S} + \text{H})^+$ : 266.0845; found: 266.0844.

**16:** This compound was obtained from **3** (82 mg, 0.5 mmol, 2.5 equiv) and 5-bromo-2-nitroanisole (46 mg, 0.2 mmol, 1.0 equiv) following:

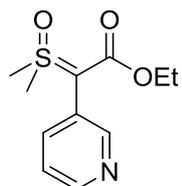


**Method A** for the preparation of **5** (37 mg, 59%, orange amorphous solid) after purification by flash chromatography (hexane/ethyl acetate: 35/65 to 2/8);

**Method B** (51 mg, 81%, orange amorphous solid) after purification by flash chromatography (hexane/ethyl acetate: 1/1 to 3/7);

**<sup>1</sup>H NMR** (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.34 (d,  $J$  = 8.5 Hz, 1H), 7.30 (d,  $J$  = 2.8 Hz, 1H), 7.04 (dd,  $J$  = 8.5, 2.8 Hz, 1H), 4.08-3.98 (m, 1H), 3.94-3.86 (m, 1H), 3.84 (s, 3H), 3.66 (s, 3H), 3.26 (s, 3H), 1.07 (t,  $J$  = 7.0 Hz, 3H); **<sup>13</sup>C NMR** (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  165.6 (e), 159.1 (e), 152.5 (e), 138.0 (o), 118.0 (o), 117.9 (e), 109.5 (o), 62.2 (e), 58.9 (e), 55.8 (o), 43.6 (o), 40.8 (o), 14.3 (o). **IR** (neat):  $\nu$  = 2983 (w), 1615 (s), 1561 (w), 1521 (s), 1409 (w), 1366 (s), 1332 (m), 1311 (m), 1291 (m), 1241 (s), 1229 (s), 1200 (s), 1146 (w), 1085 (m), 1020 (s), 976 (s), 943 (m), 858 (m), 804 (m), 759 (m), 729 (w), 688 (m), 670 (w), 642 (w)  $\text{cm}^{-1}$ ; **HRMS** (ESI) calcd for  $(\text{C}_{13}\text{H}_{17}\text{NO}_6\text{S} + \text{H})^+$ : 316.0849; found: 316.0851.

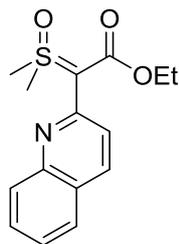
**17:** This compound was obtained from **3** (82 mg, 0.5 mmol, 2.5 equiv) and 3-bromopyridine (19  $\mu\text{L}$ , 0.2 mmol, 1.0 equiv) following:



**Method A** for the preparation of **4** (43 mg, 90%, off-white solid) after purification by flash chromatography (100% ethyl acetate to ethyl acetate/methanol: 9/1);

**m.p.:** 111-114  $^{\circ}\text{C}$ ; **<sup>1</sup>H NMR** (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.49 (d,  $J$  = 1.4 Hz, 1H), 8.38 (dd,  $J$  = 4.6, 1.0 Hz, 1H), 7.58 (td,  $J$  = 7.8, 1.9 Hz, 1H), 7.19 (dd,  $J$  = 7.8, 4.8 Hz, 1H), 4.06 (q,  $J$  = 7.1 Hz, 2H), 3.43 (s, 6H), 1.15 (t,  $J$  = 7.1 Hz, 3H); **<sup>13</sup>C NMR** (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  165.9 (e), 153.7 (o), 147.1 (o), 140.1 (o), 128.8 (e), 122.9 (o), 65.8 (e), 59.0 (e), 43.6 (o, 2C), 14.7 (o); **IR** (neat):  $\nu$  = 3021 (w), 2993 (w), 2920 (w), 1611 (s), 1580 (w), 1515 (w), 1475 (w), 1400 (w), 1369 (m), 1338 (m), 1322 (m), 1215 (m), 1169 (s), 1118 (w), 1088 (s), 1050 (s), 1031 (s), 1022 (s), 972 (m), 935 (m), 823 (w), 782 (w), 756 (m), 719 (s), 691 (m), 666 (w), 616 (w)  $\text{cm}^{-1}$ ; **HRMS** (ESI) calcd for  $(\text{C}_{11}\text{H}_{15}\text{NO}_3\text{S} + \text{H})^+$ : 242.0845; found: 242.0839.

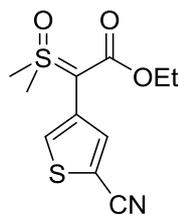
**18:** This compound was obtained from **3** (82 mg, 0.5 mmol, 2.5 equiv) and 2-bromoquinoline (42 mg, 0.2 mmol, 1.0 equiv) following:



**Method B** (55 mg, 95%, amorphous yellow solid) after purification by flash chromatography (hexane/ethyl acetate: 1/1 to 2/8);

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.95 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 8.6 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 4.22 (q, *J* = 7.0 Hz, 2H), 3.71 (s, 6H), 1.28 (t, *J* = 7.0 Hz, 3H); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 165.3 (e), 155.5 (e), 146.6 (e), 134.8 (o), 128.9 (o), 127.9 (o), 127.2 (o), 125.2 (e), 124.9 (o), 123.5 (o), 79.3 (e), 59.2 (e), 44.3 (o, 2C), 14.6 (o); **IR** (neat): ν = 2978 (w), 2931 (w), 2246 (w), 1634 (s), 1614 (s), 1594 (s), 1552 (m), 1497 (m), 1459 (m), 1389 (w), 1366 (m), 1342 (m), 1299 (s), 1259 (s), 1236 (s), 1174 (s), 1122 (w), 1075 (s), 1030 (s), 921 (w), 851 (w), 829 (m), 786 (w), 749 (s), 730 (s), 691 (m), 646 (w), 622 (w) cm<sup>-1</sup>; **HRMS** (ESI) calcd for (C<sub>15</sub>H<sub>17</sub>NO<sub>3</sub>S + H)<sup>+</sup>: 292.1002; found: 292.1010.

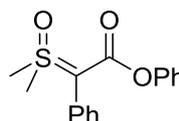
**19:** This compound was obtained from **3** (82 mg, 0.5 mmol, 2.5 equiv) and 4-bromothiophene-2-carbonitrile (38 mg, 0.2 mmol, 1.0 equiv) following:



**Method B** (36 mg, 67%, amorphous brown solid) after purification by flash chromatography (hexane/ethyl acetate: 4/6 to 2/8);

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.60 (s, 1H), 7.35 (s, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.46 (s, 6H), 1.23 (t, *J* = 7.2 Hz, 3H); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 165.3 (hmbc), 141.1 (o), 132.3 (e), 129.3 (o), 114.6 (e), 108.1 (e), 62.5 (hmbc), 59.3 (e), 43.6 (o, 2C) 14.7 (o); **IR** (neat): ν = 3085 (w), 3025 (w), 3012 (w), 2953 (w), 2930 (w), 2215 (m), 2735 (w), 1630 (s), 1520 (w), 1462 (w), 1420 (w), 1367 (m), 1344 (w), 1326 (w), 1309 (w), 1285 (s), 1192 (s), 1157 (s), 1129 (s), 1095 (m), 1073 (w), 1035 (s), 1020 (s), 987 (m), 879 (m), 852 (w), 829 (m), 799 (w), 757 (m), 730 (w), 690 (s) cm<sup>-1</sup>; **HRMS** (ESI) calcd for (C<sub>11</sub>H<sub>13</sub>NO<sub>3</sub>S<sub>2</sub> + H)<sup>+</sup>: 272.0410; found: 272.0413.

**20:** This compound was obtained from **20a** (106 mg, 0.5 mmol, 2.5 equiv) and bromobenzene (21 μL, 0.2 mmol, 1.0 equiv) following:

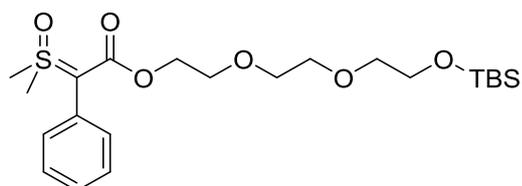


**Method B** (53 mg, 91%, white solid) after purification by flash chromatography (hexane/ethyl acetate: 1/1 to 100% ethyl acetate);

**m.p.:** 148-149 °C; **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.45 (d, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.34 – 7.27 (m, 3H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 2H), 3.43 (s, 6H); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 164.5 (e), 151.5 (e), 133.8 (o, 2C), 131.8 (e), 129.0 (o, 2C), 128.5 (o, 2C), 127.4 (o), 124.7 (o), 122.3 (o, 2C), 71.0 (e), 43.0 (o, 2C); **IR** (neat): ν = 3014 (w), 2937 (w), 1640 (s), 1593 (w),

1485 (m), 1455 (w), 1443 (w), 1416 (w), 1335 (m), 1304 (w), 1231 (m), 1189 (s), 1174 (s), 1161 (s), 1072 (w), 1041 (w), 1023 (m), 1006 (m), 991 (m), 924 (m), 915 (m), 796 (m), 762 (m), 752 (m), 737 (m), 702 (m), 693 (s), 655 (w)  $\text{cm}^{-1}$ ; **HRMS** (ESI) calcd for  $(\text{C}_{16}\text{H}_{16}\text{O}_3\text{S} + \text{H})^+$ : 289.0893; found: 289.0884.

**21:** This compound was obtained from **21a** (191 mg, 0.5 mmol, 2.5 equiv) and bromobenzene (21  $\mu\text{L}$ , 0.2 mmol, 1.0 equiv) following:

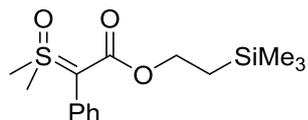


**Method B** ( $\text{PdP}(t\text{Bu}_3)_2$  (10 mol%) was used instead of  $\text{Pd}_2(\text{dba})_3$  and  $\text{PrBu}_3$ ) (80 mg, 87%, white amorphous solid) after purification by flash chromatography

(hexane/ethyl acetate: 3/7 to 2/8);

**$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.33-7.18 (m, 5H), 4.23-4.13 (m, 2H), 3.72 (t,  $J = 5.50$  Hz, 2H), 3.66-3.45 (m, 8H), 3.37 (s, 6H), 0.87 (s, 9H), 0.04 (s, 6H);  **$^{13}\text{C}$  NMR** (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  165.7 (e), 133.6 (o, 2C), 132.7 (e), 128.3 (o, 2C), 126.9 (o), 72.6 (e), 70.7 (e), 70.4 (hmbc), 70.5 (e), 69.5 (e), 62.7 (e), 62.3 (e), 43.4 (o, 2C), 26.0 (o, 3C), 18.4 (e), -5.23 (o, 2C); **IR** (neat):  $\nu = 3002$  (w), 2928 (m), 2855 (m), 1619 (s), 1593 (m), 1491 (w), 1471 (w), 1441 (w), 1406 (w), 1380 (m), 1338 (m), 1325 (m), 1248 (w), 1212 (m), 1168 (s), 1141 (m), 1091 (s), 1072 (m), 1062 (m), 1026 (w), 1003 (w), 970 (w), 938 (m), 912 (w), 831 (s), 813 (w), 776 (m), 756 (w), 706 (m), 690 (w), 661 (w)  $\text{cm}^{-1}$ ; **HRMS** (ESI) calcd for  $(\text{C}_{22}\text{H}_{38}\text{O}_6\text{SSi} + \text{H})^+$ : 459.2231; found: 459.2237.

**22:** This compound was obtained from **22a** (118 mg, 0.5 mmol, 2.5 equiv) and bromobenzene (21  $\mu\text{L}$ , 0.2 mmol, 1.0 equiv) following:

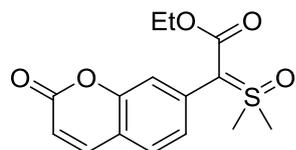


**Method B** (51 mg, 82%, grey solid) after purification by flash chromatography (hexane/ethyl acetate: 1/1 to 2/8);

**Method C** (58 mg, 94%, grey solid) after purification by flash chromatography (hexane/ethyl acetate: 1/1 to 2/8);

**m.p.:** 80-82  $^\circ\text{C}$ ;  **$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.34-7.20 (m, 5H), 4.14 (t,  $J = 8.4$  Hz, 2H), 3.40 (s, 6H), 0.92 (t,  $J = 8.4$  Hz, 2H), -0.06 (s, 9H);  **$^{13}\text{C}$  NMR** (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.6 (e), 133.8 (o, 2C), 132.6 (e), 128.3 (o, 2C), 127.0 (o), 70.4 (e), 61.0 (e), 43.2 (o, 2C), 17.7 (e), -1.52 (o, 3C); **IR** (neat):  $\nu = 3029$  (w), 3008 (w), 2949 (w), 2925 (w), 2895 (w), 1733 (w), 1611 (s), 1590 (m), 1490 (w), 1441 (w), 1388 (m), 1340 (m), 1326 (m), 1249 (m), 1211 (m), 1182 (s), 1167 (s), 1090 (m), 1061 (m), 1027 (m), 1005 (m), 977 (w), 954 (w), 934 (w), 914 (w), 852 (m), 832 (s), 793 (m), 756 (s), 706 (s), 689 (m), 641 (w), 604 (w)  $\text{cm}^{-1}$ . **HRMS** (ESI) calcd for  $(\text{C}_{15}\text{H}_{24}\text{O}_3\text{SSi} + \text{H})^+$ : 313.1288; found: 313.1298.

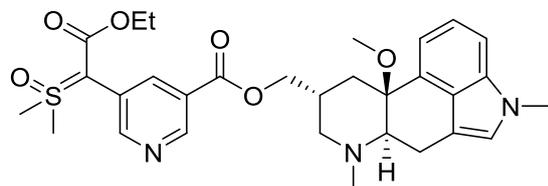
**24:** This compound was obtained from **3** (82 mg, 0.5 mmol, 2.5 equiv) and **23** (59 mg, 0.2 mmol, 1.0 equiv) following:



**Method B** (48 mg, 77%, yellowish solid) after purification by flash chromatography (hexane/ethyl acetate: 1/1 to 2/8);

**m.p.:** 144-147 °C; **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.64 (d, *J* = 9.4 Hz, 1H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.28 (s, 1H), 7.23 (d, *J* = 8.2 Hz, 1H), 6.31 (d, *J* = 9.5 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.50 (s, 6H), 1.20 (t, *J* = 7.0 Hz, 3H); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 165.5 (e), 161.1 (e), 153.7 (e), 143.3 (o), 137.2 (e), 128.4 (o), 126.8 (o), 119.8 (o), 116.5 (e), 115.4 (o), 69.0 (e), 59.2 (e), 43.9 (o, 2C), 14.7 (o); **IR** (neat): ν = 3049 (w), 3013 (w), 2975 (w), 2928 (w), 1718 (m), 1626 (m), 1598 (s), 1540 (w), 1500 (w), 1461 (w), 1444 (w), 1399 (m), 1367 (w), 1340 (w), 1315 (w), 1293 (m), 1278 (s), 1256 (s), 1227 (m), 1216 (m), 1185 (s), 1164 (m), 1138 (m), 1094 (w), 1066 (m), 1021 (s), 991 (m), 970 (m), 933 (s), 880 (m), 832 (s), 812 (w), 756 (s), 779 (w), 734 (w), 689 (m), 628 (w), 610 (m) cm<sup>-1</sup>; **HRMS** (ESI) calcd for (C<sub>15</sub>H<sub>16</sub>O<sub>5</sub>S + H)<sup>+</sup>: 309.0791; found: 309.0798.

**25:** This compound was obtained as a white solid from **3** (41 mg, 0.25 mmol, 2.5 equiv) and nicergoline (48 mg, 0.1 mmol, 1.0 equiv) following:

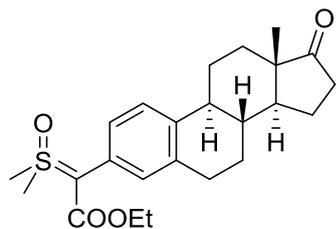


**Method C** (44 mg, 78%, white solid) after purification by flash chromatography (pure acetone to acetone/methanol: 85/15) followed by a second

column (DCM/methanol: 9/1);

**m.p.:** 78-80 °C; **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 9.01 (d, *J* = 2.0 Hz, 1H), 8.70 (d, *J* = 2.1 Hz, 1H), 8.21 (t, *J* = 2.1 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.20 (t, *J* = 7.0 Hz, 1H), 7.06 (d, *J* = 6.9 Hz, 1H), 6.80 (s, 1H), 4.38 (dd, *J* = 10.7, 5.0 Hz, 1H), 4.28 (dd, *J* = 10.9, 7.5 Hz, 1H), 4.11 (q, *J* = 7.0 Hz, 2H), 3.77 (s, 3H), 3.51 (s, 6H), 3.30-3.19 (m, 2H), 3.10-2.98 (m, 5H), 2.65 (br s, 1H), 2.56-2.34 (m, 4H), 2.23-2.06 (m, 1H), 1.40 (t, *J* = 13.4 Hz, 1H), 1.20 (t, *J* = 7.0 Hz, 3H); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 165.3, 165.1, 156.6, 147.2, 140.1, 134.8, 129.2, 128.4, 125.9, 125.0, 123.0, 121.1, 114.7, 109.7, 108.7, 73.2, 69.6, 67.5, 63.7, 60.1, 58.9, 49.2, 43.6, 43.4 (2C), 32.5, 31.0, 29.8, 21.9, 14.3; **IR** (neat): ν = 2932 (w), 2781 (w), 2200 (w), 1719 (s), 1615 (s), 1465 (m), 1420 (w), 1367 (m), 1306 (m), 1269 (s), 1221 (s), 1203 (s), 1165 (m), 1102 (w), 1070 (m), 1024 (s), 971 (w), 935 (w), 907 (s), 811 (w), 723 (s), 680 (w) cm<sup>-1</sup>; **HRMS** (ESI) calcd for (C<sub>30</sub>H<sub>37</sub>N<sub>3</sub>O<sub>6</sub>S + H)<sup>+</sup>: 568.2476; found: 568.2485.

**26:** This compound was obtained from **3** (82 mg, 0.5 mmol, 2.5 equiv) and estrone-OTf (81 mg, 0.2 mmol, 1.0 equiv) following:



**Method C** (63 mg, 76%, white solid) after purification by flash chromatography (hexane/ethyl acetate: 2/8);

**m.p.:** 42-45 °C; **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.22 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 7.9 Hz, 1H), 7.04 (s, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.42 (s, 3H), 3.40 (s, 3H), 2.92–2.86 (m, 2H), 2.50 (dd, *J* = 18.9, 9.0 Hz, 1H), 2.45–2.38 (m, 1H), 2.29 (td, *J* = 10.1, 3.7 Hz, 1H), 2.19–1.91 (m, 4H), 1.67–1.38 (m, 6H), 1.21 (t, *J* = 7.1 Hz, 3H), 0.91 (s, 3H); **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 220.9 (e), 166.4 (e), 138.4 (e), 136.3 (e), 134.0 (o), 131.0 (o), 129.7 (e), 125.3 (o), 69.6 (e), 58.8 (e), 50.6 (o), 48.0 (e), 44.4 (o), 43.4 (o), 43.4 (o), 38.1 (o), 35.9 (e), 31.6 (e), 29.3 (e), 26.6 (e), 25.6 (e), 21.6 (e), 14.9 (o), 13.9 (o); **IR** (neat): ν = 2928 (m), 1733 (s), 1625 (s), 1497 (w), 1453 (w), 1406 (w), 1367 (m), 1321 (m), 1228 (s), 1163 (s), 1082 (m), 1026 (s), 919 (w), 846 (w), 824 (w), 756 (w), 725 (s), 689 (m) cm<sup>-1</sup>; **HRMS** (ESI) calcd for (C<sub>24</sub>H<sub>32</sub>O<sub>4</sub>S + H)<sup>+</sup>: 417.2094; found: 417.2101.

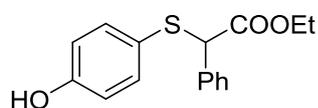
#### Gram-scale synthesis of compound 4

A heat gun dried 4 neck round bottomed flask under N<sub>2</sub> atmosphere was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (160 mg, 0.175 mmol, 0.025 equiv.), XPhos (334 mg, 0.7 mmol, 0.1 equiv) and Cs<sub>2</sub>CO<sub>3</sub> (2.509 g, 7.7 mmol, 1.1 equiv.). Three vacuum-nitrogen cycles were performed and acetonitrile (35 mL) was then added to the reaction mixture and the stirring was turned on. Bromobenzene (0.75 mL, 7.0 mmol, 1 equiv) was then added followed by **3** (2.874 g, 17.5 mmol, 2.5 equiv). Acetonitrile (35 mL) was added and the reaction mixture was heated to reflux using a heating block with a thin layer of oil for better contact. After 15 hours, the reaction mixture was allowed to cool down to room temperature and the crude was then filtered over a plug of silica at room temperature using a DCM/MeOH (85/15) mixture to transfer all the material and for rinsing. After evaporation of all volatiles, purification by flash chromatography (heptane/ethyl acetate: 4/6 to 3/7) gave **4** (1.166 g, 69%, white solid).

Compound **4** (1.403g, 83%, white solid) could also be obtained on the same scale using Pd<sub>2</sub>(dba)<sub>3</sub> (321 mg, 0.35 mmol, 0.05 equiv) and XPhos (667 mg, 1.4 mmol, 0.2 equiv).

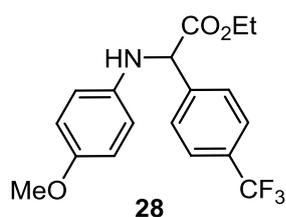
#### Synthesis of compound 27

Following the literature's procedure,<sup>iv</sup> under N<sub>2</sub>, **4** (48 mg, 0.2 mmol, 1.0 equiv) and 4-mercaptophenol (25 mg, 0.2 mmol, 1.0 equiv) were suspended in acetonitrile (0.2 mL). The reaction mixture was stirred for 24 hours at room temperature. The volatiles were removed under vacuum. Purification by flash chromatography (hexane/ethyl acetate: 9/1 to 8/2) afforded **27** as a white solid (46 g, 80%); **m.p.:** 54-



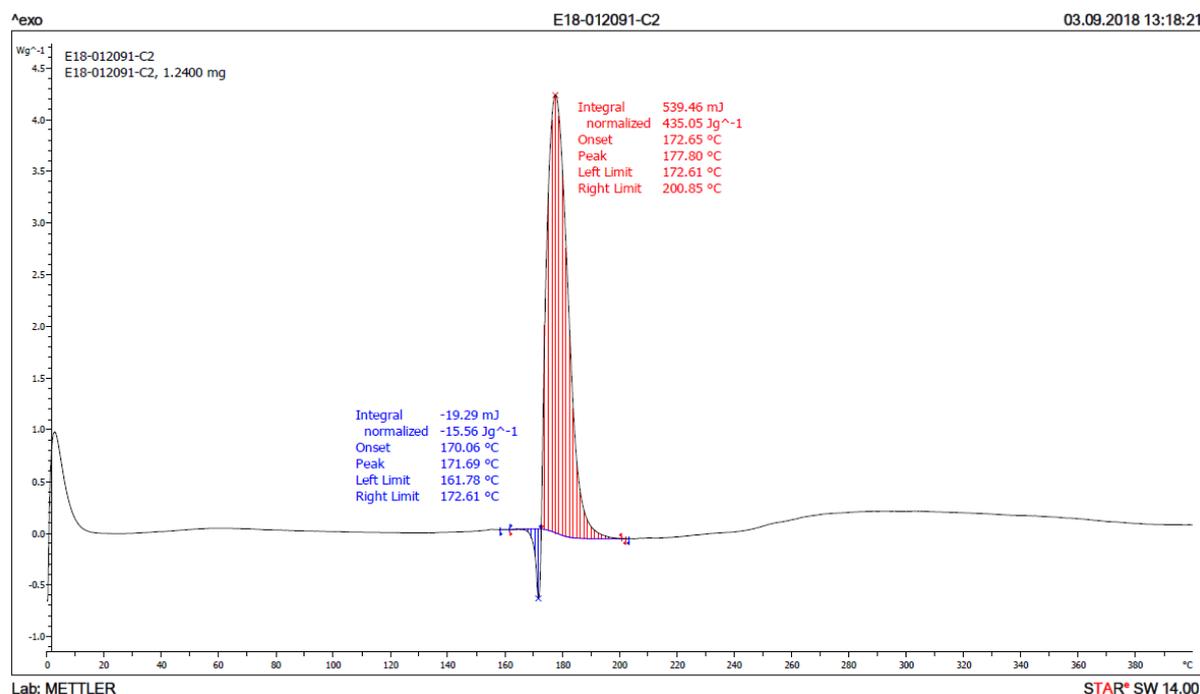
56 °C;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.44-7.39 (m, 2H), 7.34-7.25 (m, 5H), 6.71 (d,  $J = 8.6$  Hz, 2H), 5.84 (s, 1H), 4.78 (s, 1H), 4.19-4.07 (m, 2H), 1.19 (t,  $J = 7.0$  Hz, 3H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  171.2 (e), 156.6 (e), 136.4 (o, 2C), 135.6 (e), 128.6 (o, 4C), 128.3 (o), 123.5 (e), 116.1 (o, 2C), 61.9 (e), 57.5 (o), 14.0 (o); **IR** (neat):  $\nu = 3444$  (m), 3364 (br m), 2979 (w), 1710 (s), 1597 (m), 1579 (m), 1494 (m), 1465 (w), 1455 (w), 1427 (w), 1389 (w), 1368 (m), 1336 (m), 1304 (m), 1275 (s), 1210 (s), 1180 (s), 1152 (s), 1094 (m), 1076 (w), 1023 (s), 879 (w), 832 (s), 799 (w), 714 (m), 721 (m), 700 (m), 693 (m), 647 (w)  $\text{cm}^{-1}$ ; **HRMS** (ESI) calcd for  $(\text{C}_{16}\text{H}_{16}\text{O}_3\text{S} + \text{Na})^+$ : 311.0712; found: 311.0714.

### Synthesis of compound **28**



Following the literature's procedure,<sup>iii</sup> compound **10** (62 mg, 0.2 mmol, 1 equiv) and  $[\text{Ir}(\text{cod})\text{Cl}]_2$  (3.4 mg, 0.005 mmol, 0.025 equiv) were added to a dry Schlenk tube under nitrogen. After 3 vacuum/nitrogen cycles DCM (1 mL) was added followed by p-anisidine (37 mg, 0.3 mmol, 1.5 equiv). The mixture was stirred at room temperature for 4 hours before evaporation of the volatiles under vacuum. The residue thus obtained was purified by flash chromatography (heptane / ethyl acetate : 100/0 to 9/1) affording **28** (49 mg, 69%) as a light yellow oil.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ): 7.68–7.58 (m, 4H), 6.75–6.69 (m, 2H), 6.53–6.46 (m, 2H), 5.05 (d,  $J = 5.6$  Hz, 1H), 4.77 (d,  $J = 5.9$  Hz, 1H), 4.29–4.09 (m, 2H), 3.70 (s, 3H), 1.22 (t,  $J = 7.2$  Hz, 3H), in agreement with the literature.<sup>v</sup>

### DSC trace for compound **2**



<sup>i</sup> Woll M. G.; Qi H.; Turpoff A.; Zhang N.; Zhang X.; Chen G.; Li C.; Huang S.; Yang T.; Moon Y.-C.; Lee C.-S.; Choi S.; Almstead N. G.; Naryshkin N. A.; Dakka A.; Narasimhan J.; Gabbeta V.; Welch E.; Zhao X.; Risher N.; Sheedy J.; Weetall M.; Karp G. M. *J. Med. Chem.* **2016**, *59*, 6070–6085.

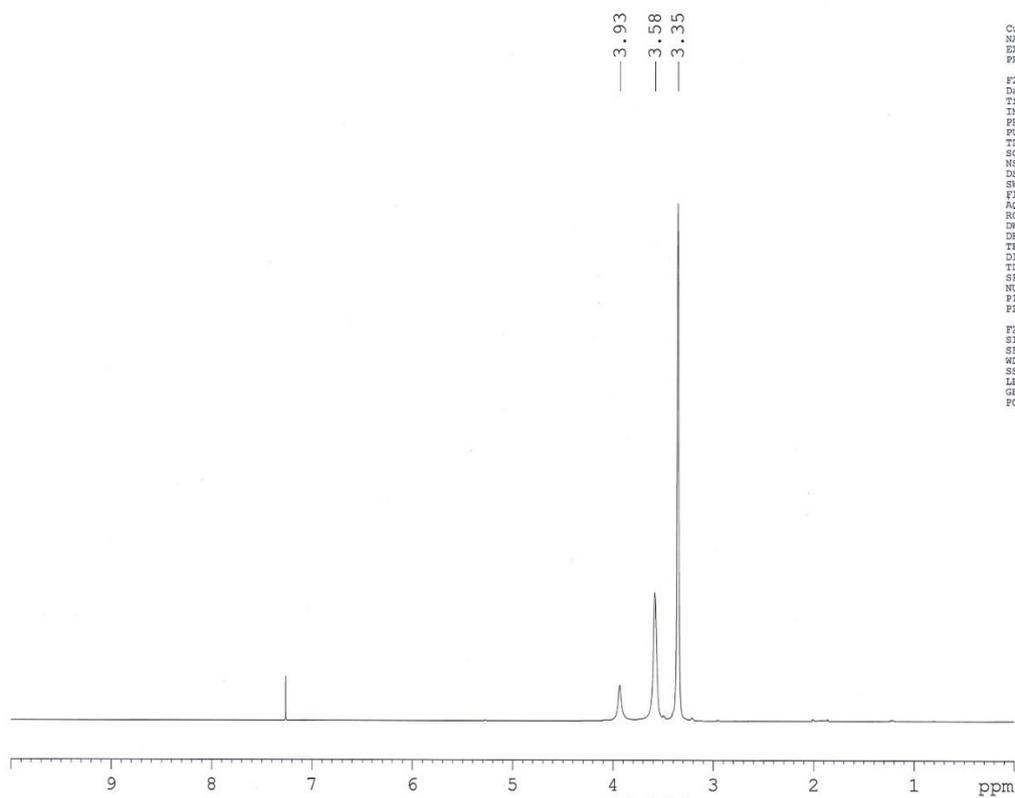
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<sup>ii</sup> Zhang Z.; Jiang X. *Org. Lett.* **2014**, *16*, 4400–4403.

<sup>iii</sup> Mangion I. K.; Nwamba I. K.; Shevlin M.; Huffman M. A. *Org. Lett.* **2009**, *11*, 3566–3569.

<sup>iv</sup> Dias R. M. P.; Burtoloso A. C. B. *Org. Lett.* **2016**, *18*, 3034–3037.

<sup>v</sup> Li, G.; Liang, Y.; Antilla, J. C. *J. Am. Chem. Soc.* **2008**, *129*, 5830–5831.



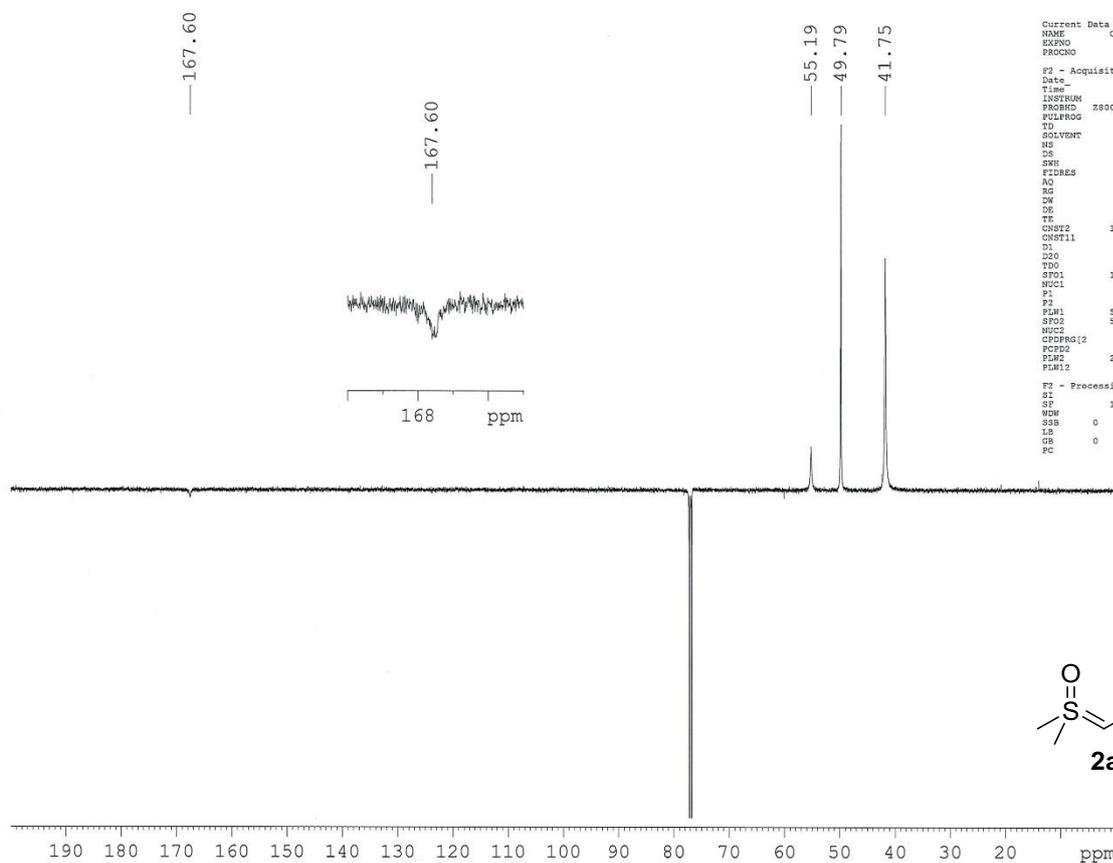
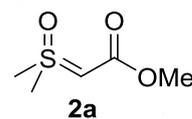
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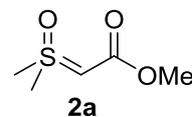
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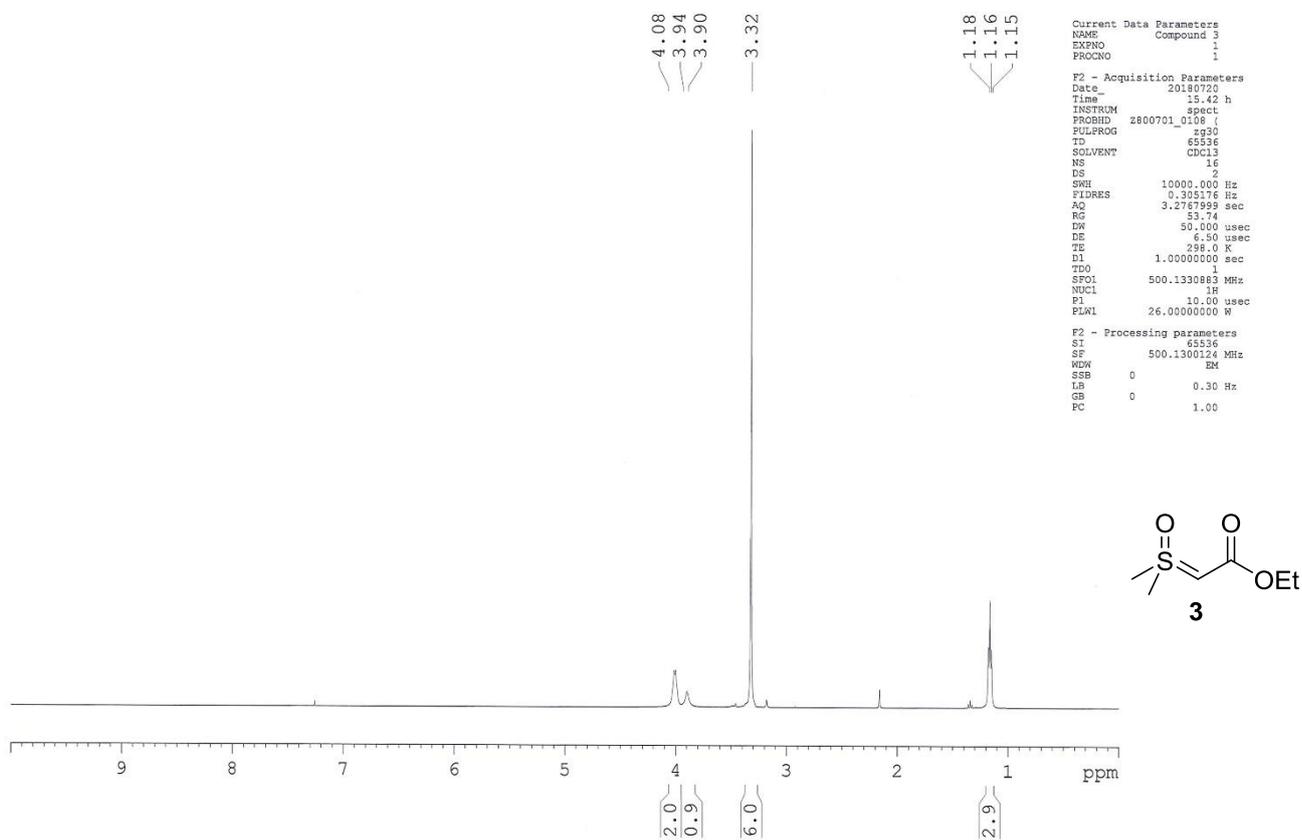
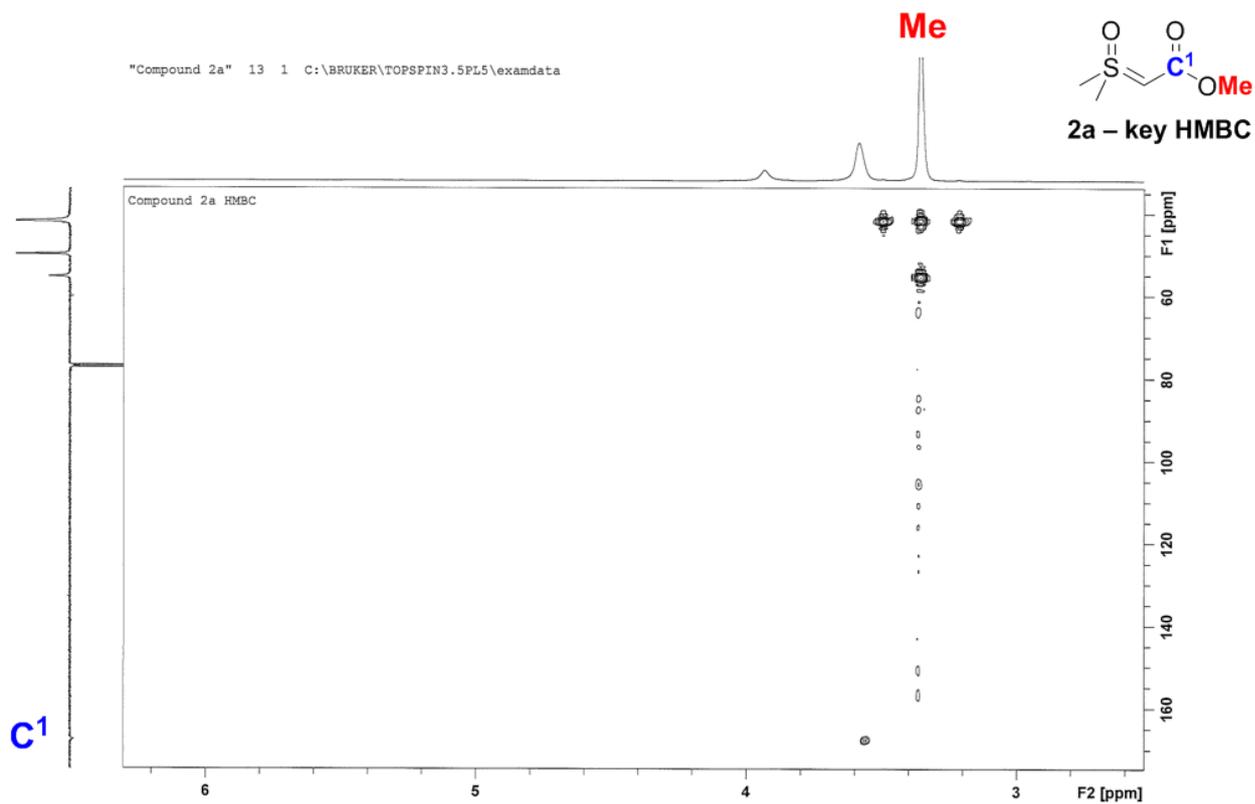
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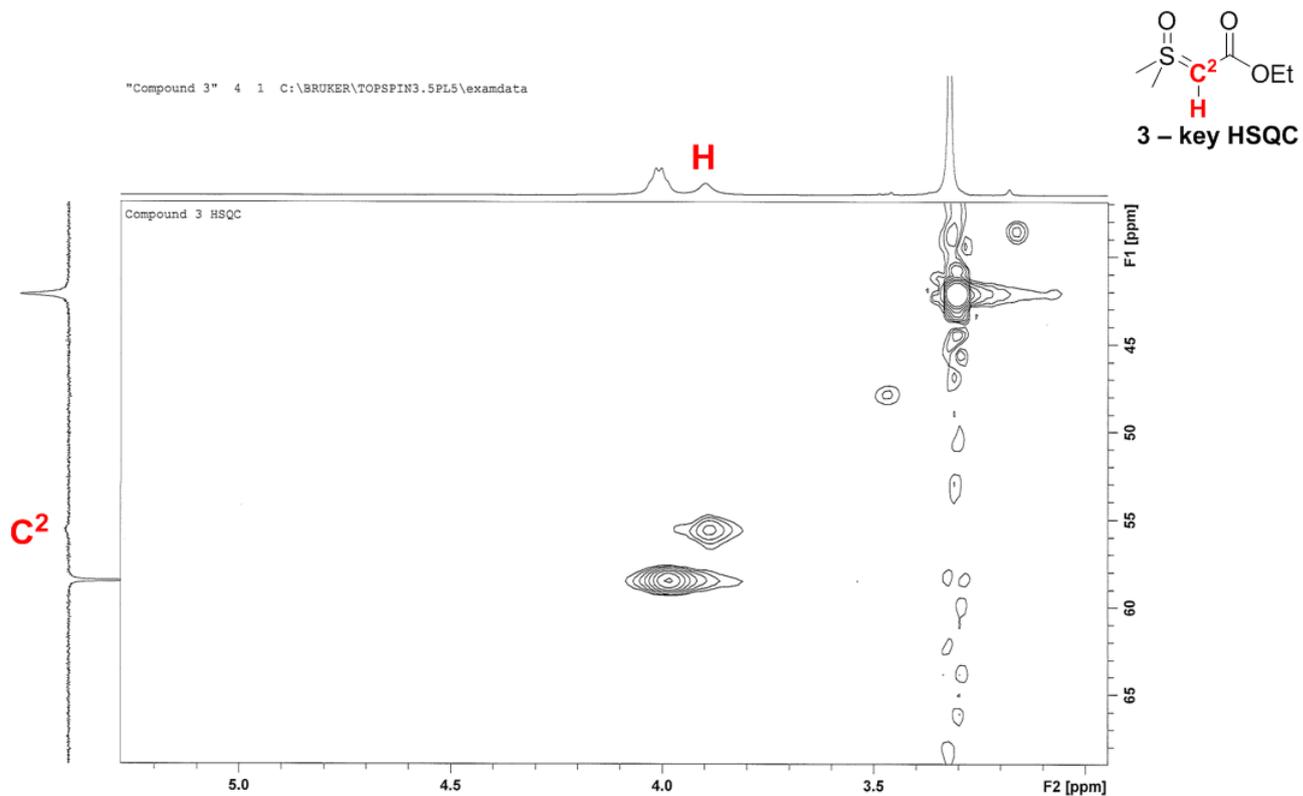
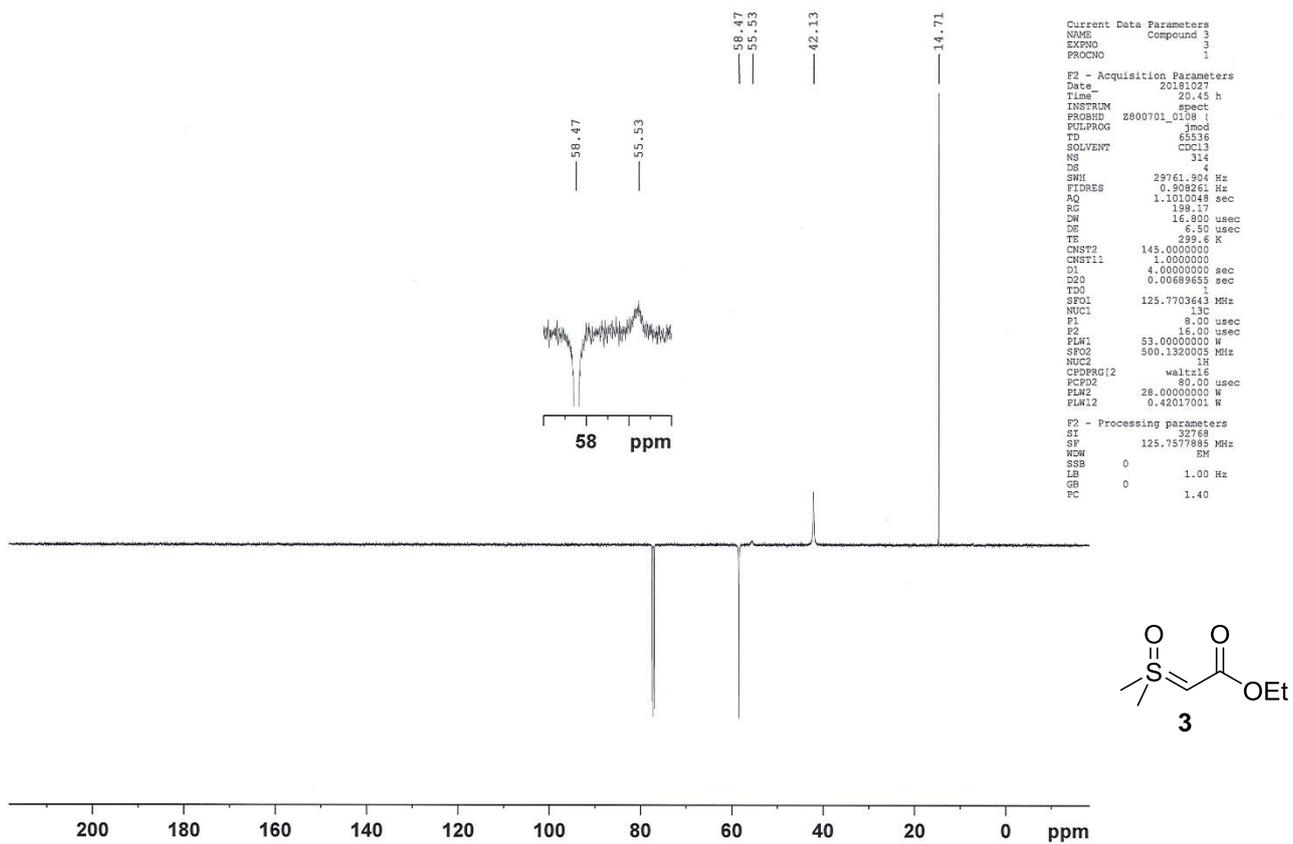
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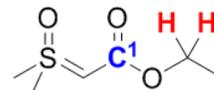
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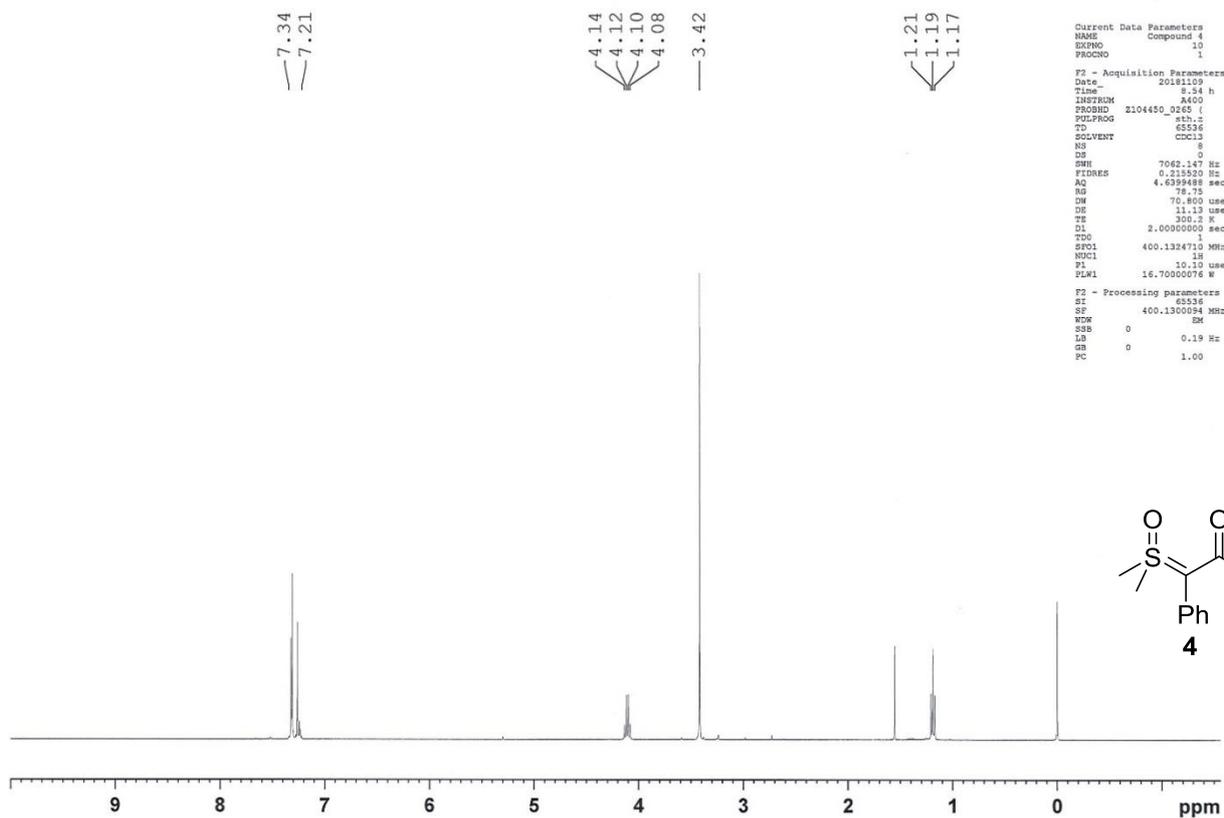
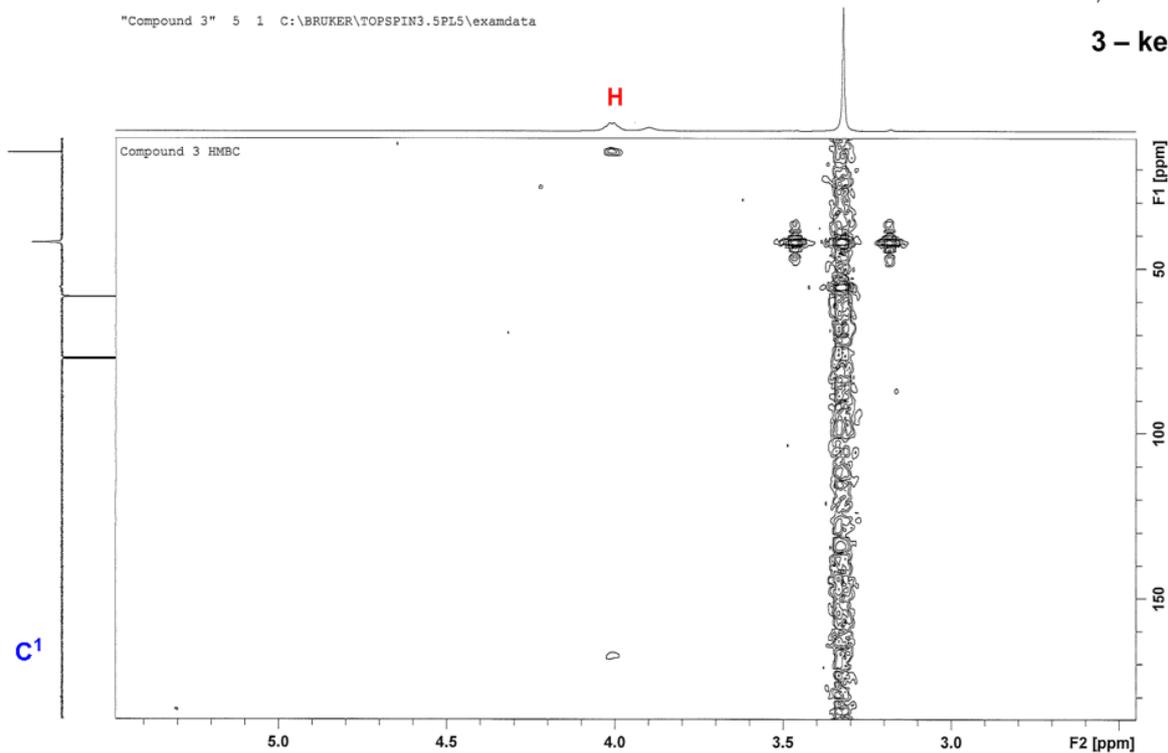


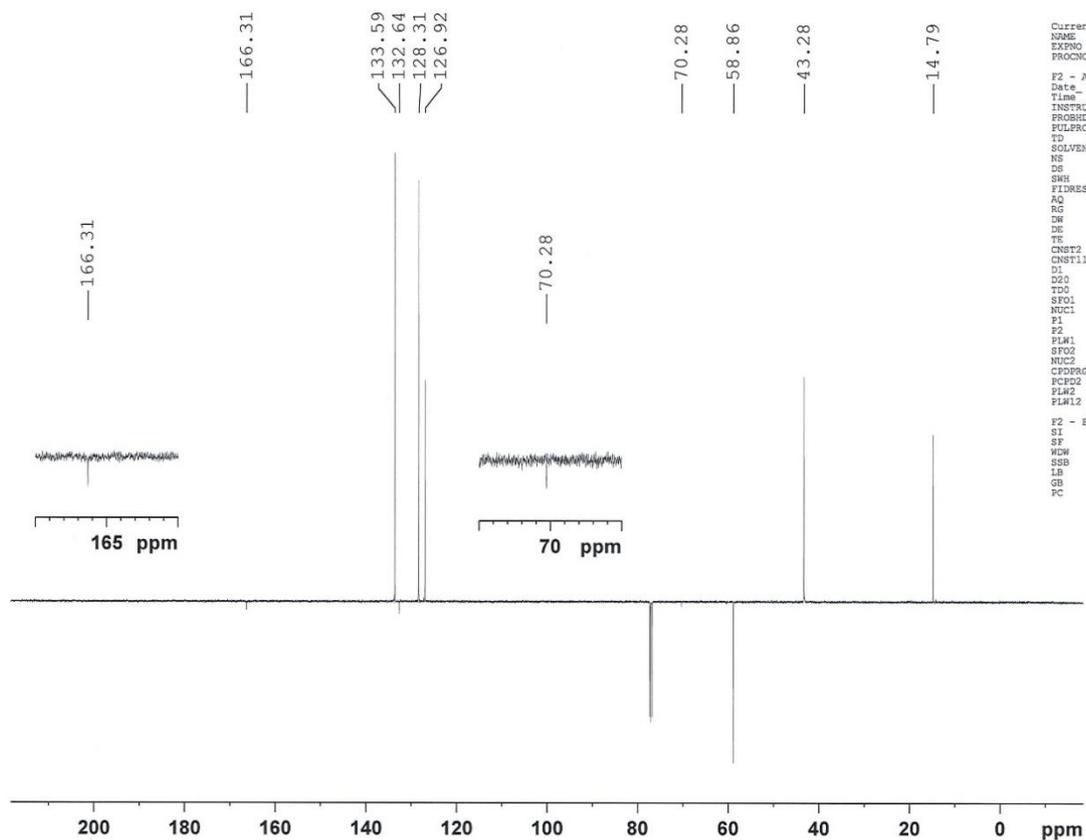






3 – key HMBC



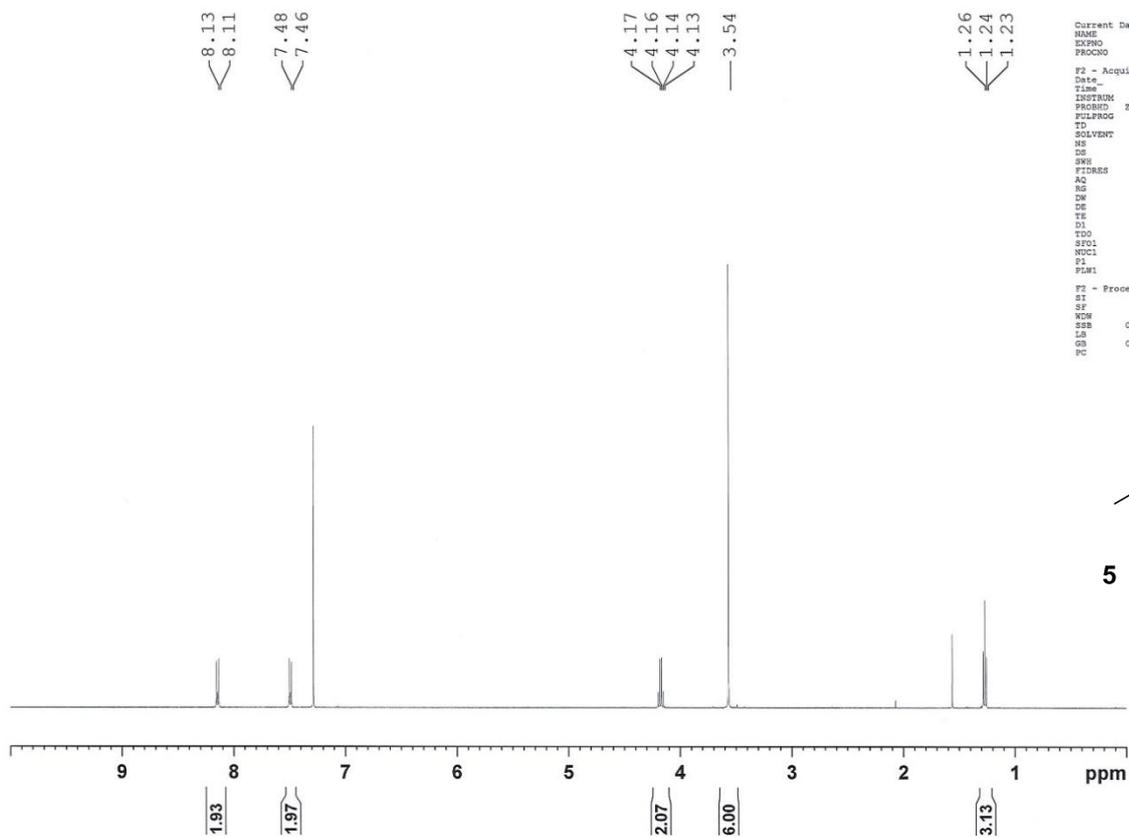
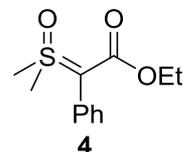


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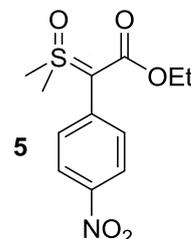


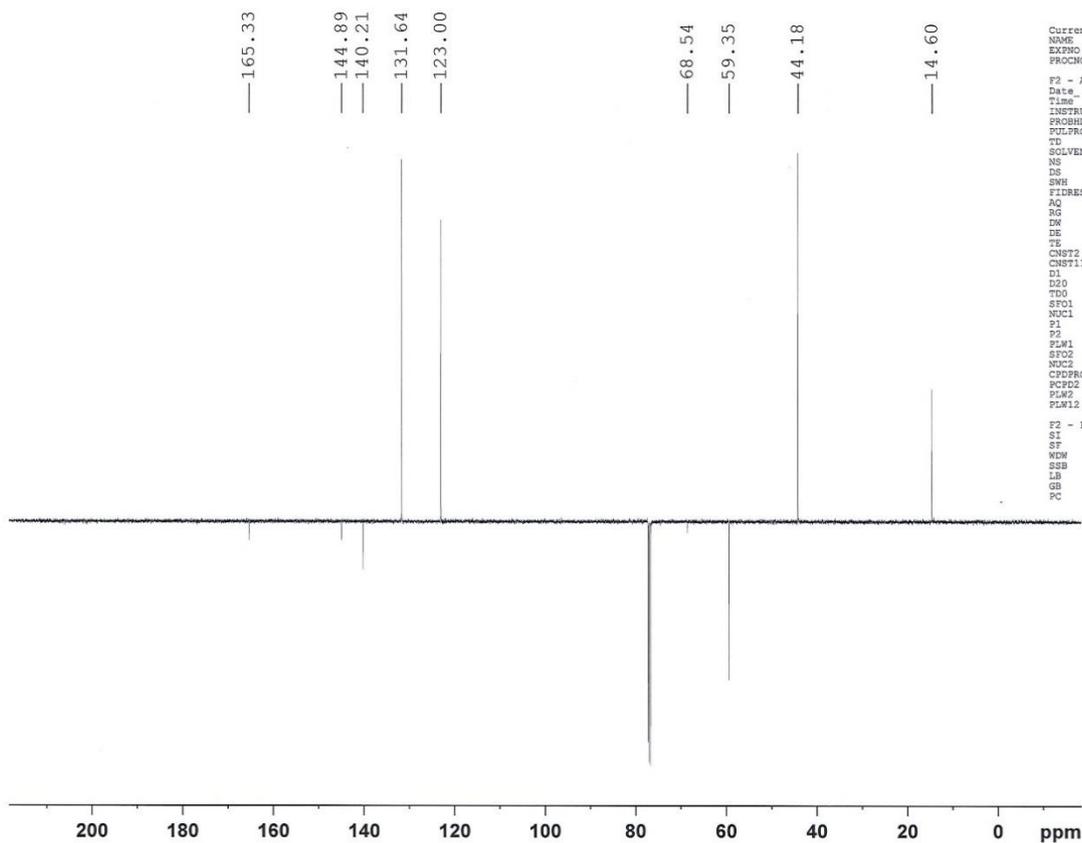
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LB         0.30 Hz
GB         0
PC         1.00
  
```



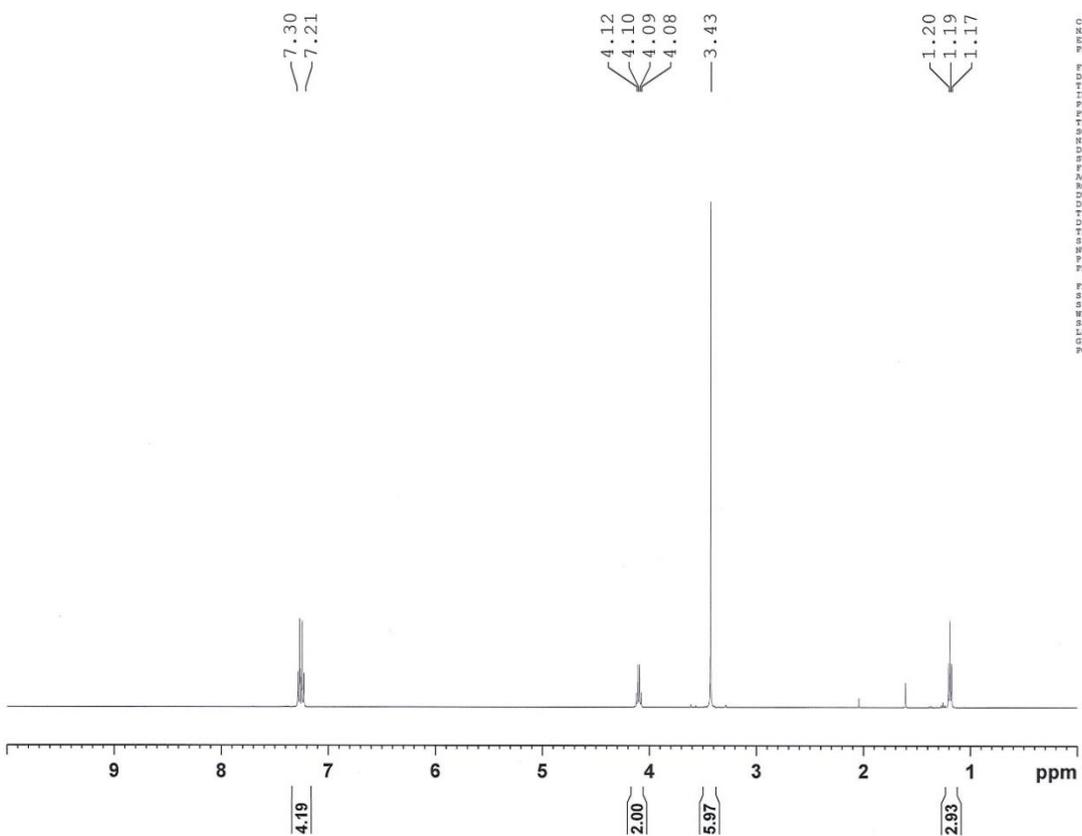
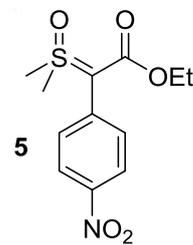


```

Current Data Parameters
NAME      Compound 5
EXPNO    12
PROCNO   1

F2 - Acquisition Parameters
Date_    20180604
Time     16.26 h
INSTRUM  spect
PROBHD   Z800701_0108 (
PULPROG  jmod
TD        65536
SOLVENT  CDCl3
NS        1024
DS        4
SWH       29761.904 Hz
FIDRES    0.908261 Hz
AQ        1.1010048 sec
RG        198.17
DW        16.800 usec
DE        6.50 usec
TE        298.0 K
CNST2    145.0000000
CNST1    1.0000000
D1        4.0000000 sec
D2        0.00669655 sec
TDO       1
SFO1     125.7703443 MHz
NUC1      13C
P1        8.00 usec
P2        16.00 usec
PLM1     53.0000000 W
SFO2     500.1320005 MHz
NUC2      1H
CPDPRG2  waltz16
PCPD2    80.00 usec
PLM2     28.0000000 W
PLM12    0.42017001 W

F2 - Processing parameters
SI        32768
SF        125.7577926 MHz
WDW       EM
SSB       0
LB        1.00 Hz
GB        0
PC        1.40
  
```

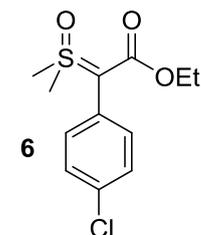


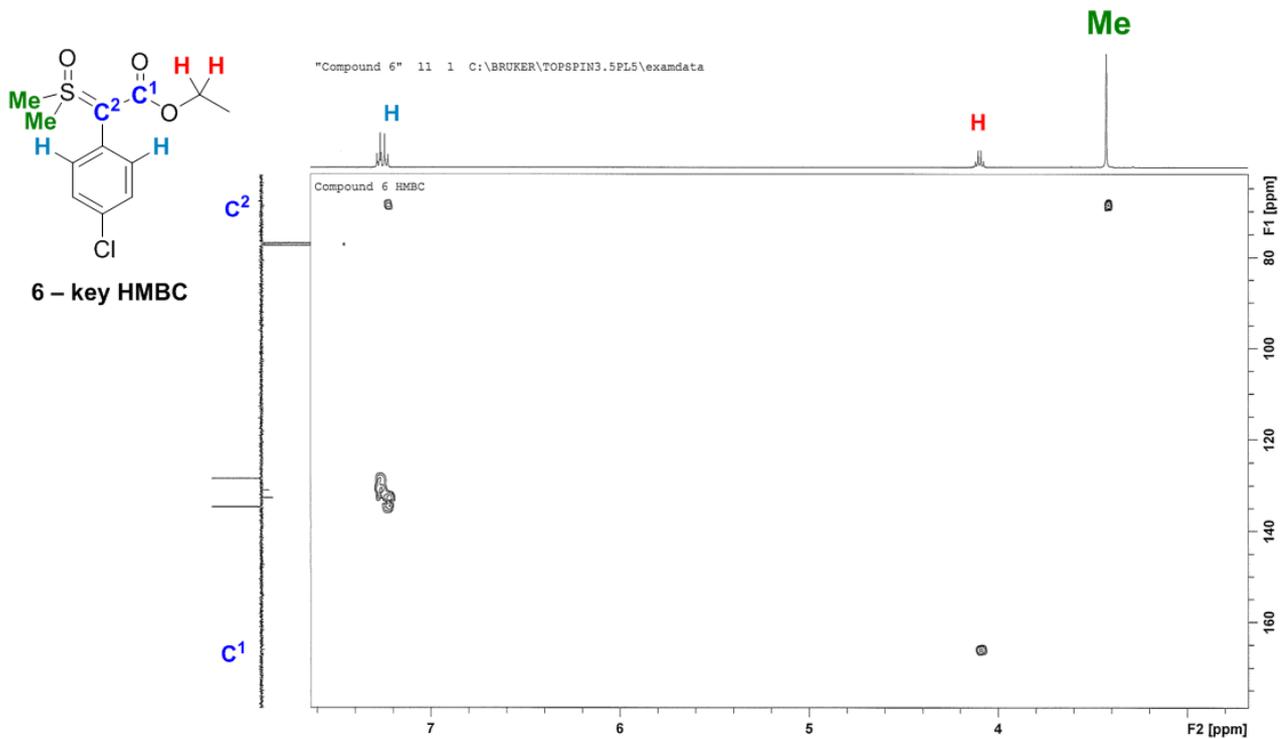
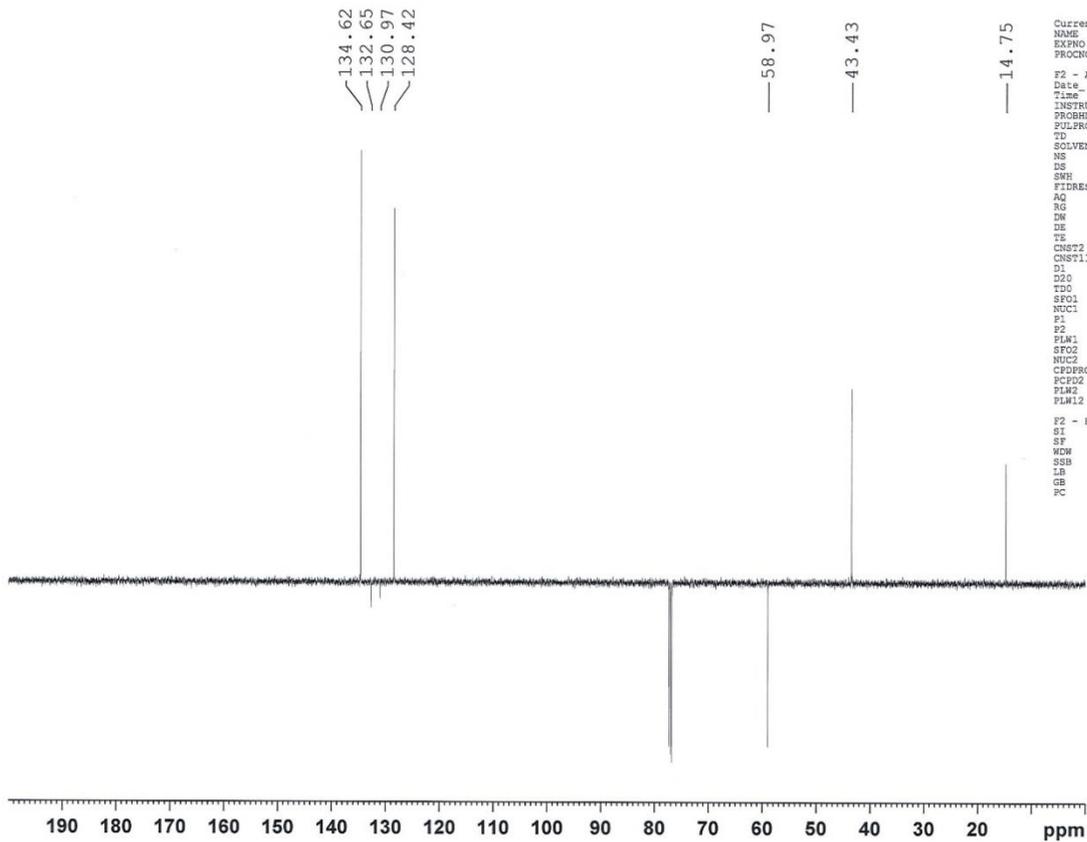
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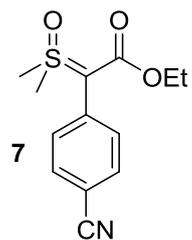
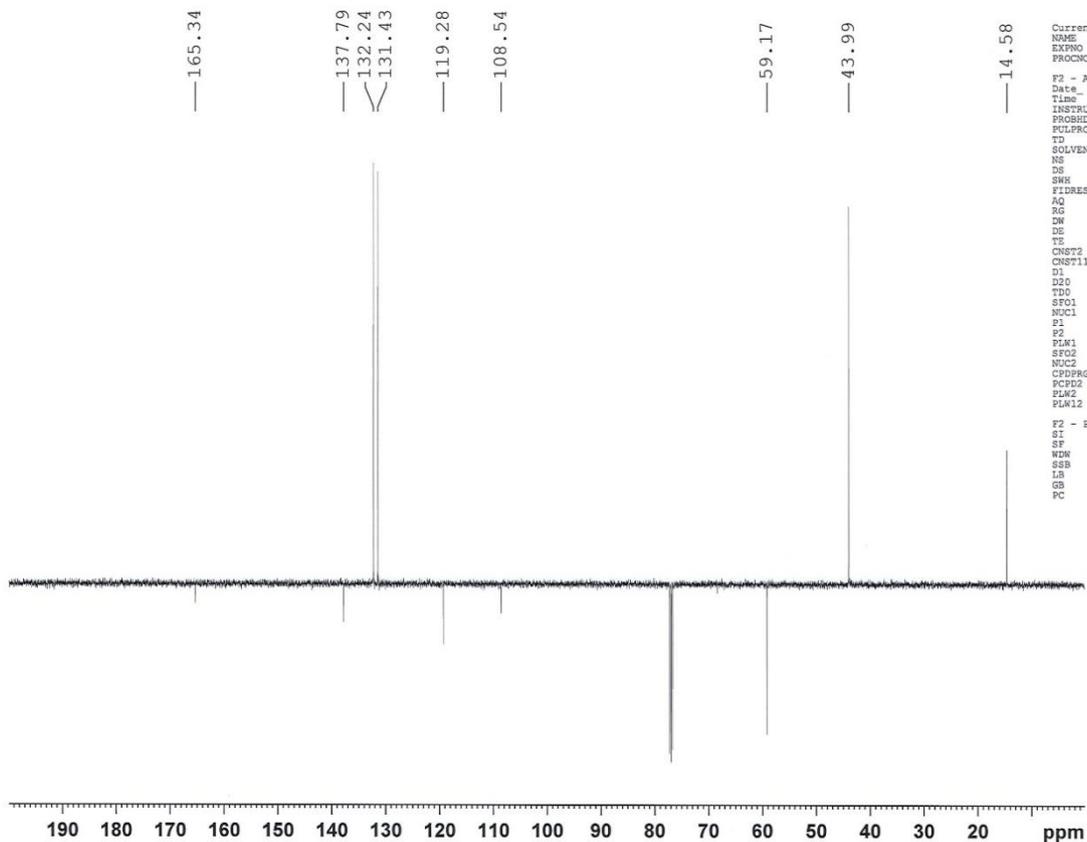
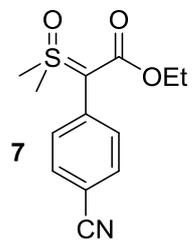
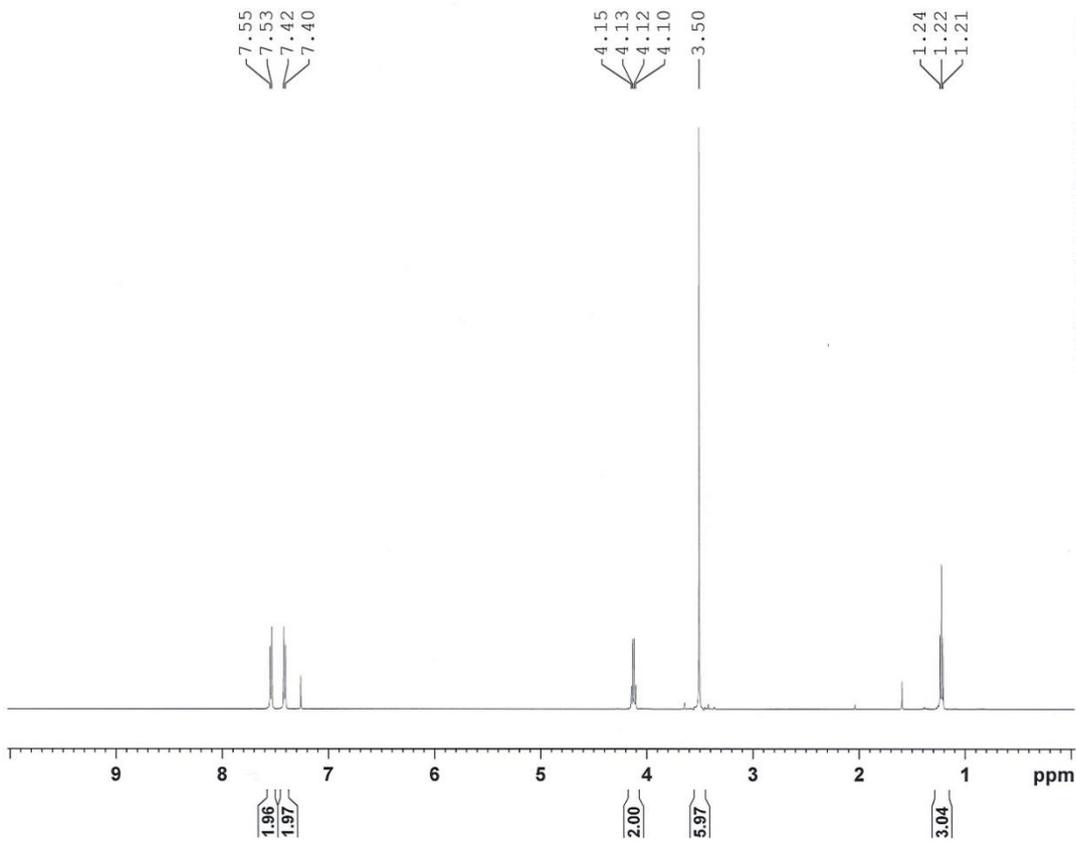
Current Data Parameters
NAME      Compound 6
EXPNO    1
PROCNO   1

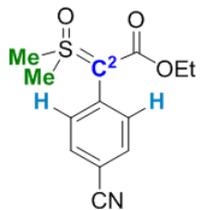
F2 - Acquisition Parameters
Date_    20180604
Time     14.47 h
INSTRUM  spect
PROBHD   Z800701_0108 (
PULPROG  zg30
TD        65536
SOLVENT  CDCl3
NS        16
DS        2
SWH       10000.000 Hz
FIDRES    0.305176 Hz
AQ        3.278788 sec
RG        198.17
DW        50.000 usec
DE        6.50 usec
TE        300.2 K
D1        1.0000000 sec
TDO       1
SFO1     500.1330883 MHz
NUC1      1H
P1        10.00 usec
P2        26.0000000 W

F2 - Processing parameters
SI        65536
SF        500.1300133 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB        0
PC        1.00
  
```

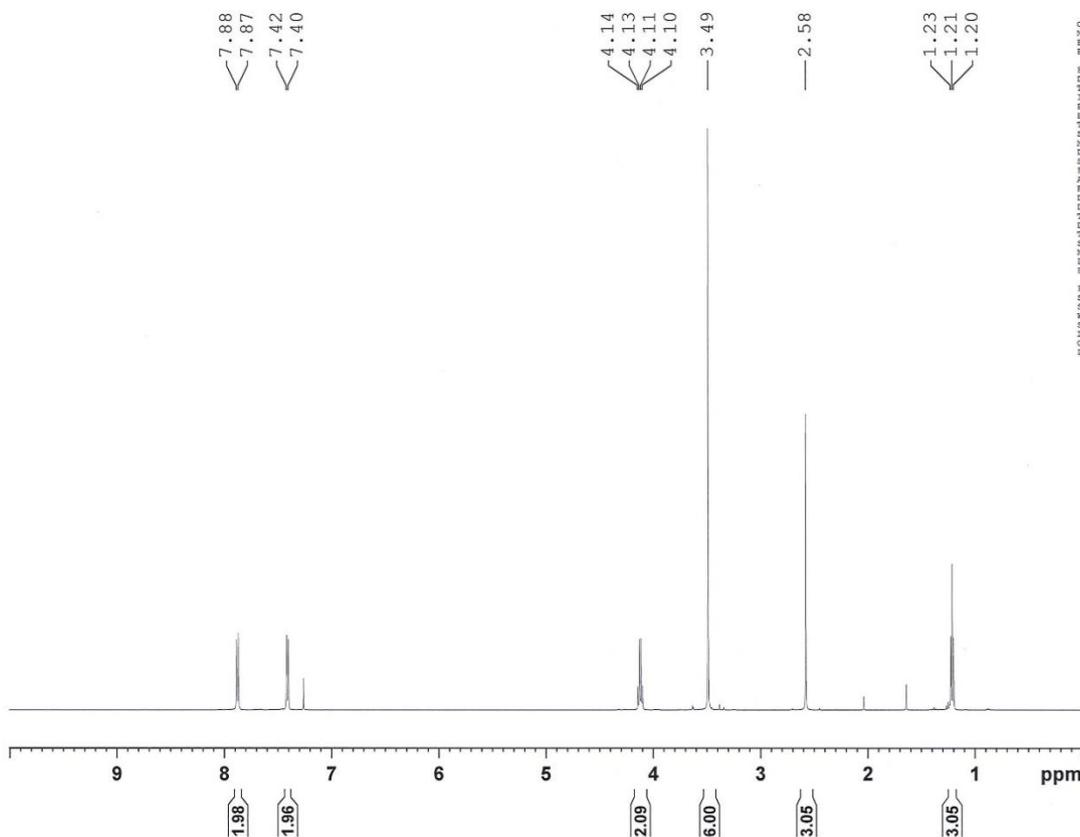
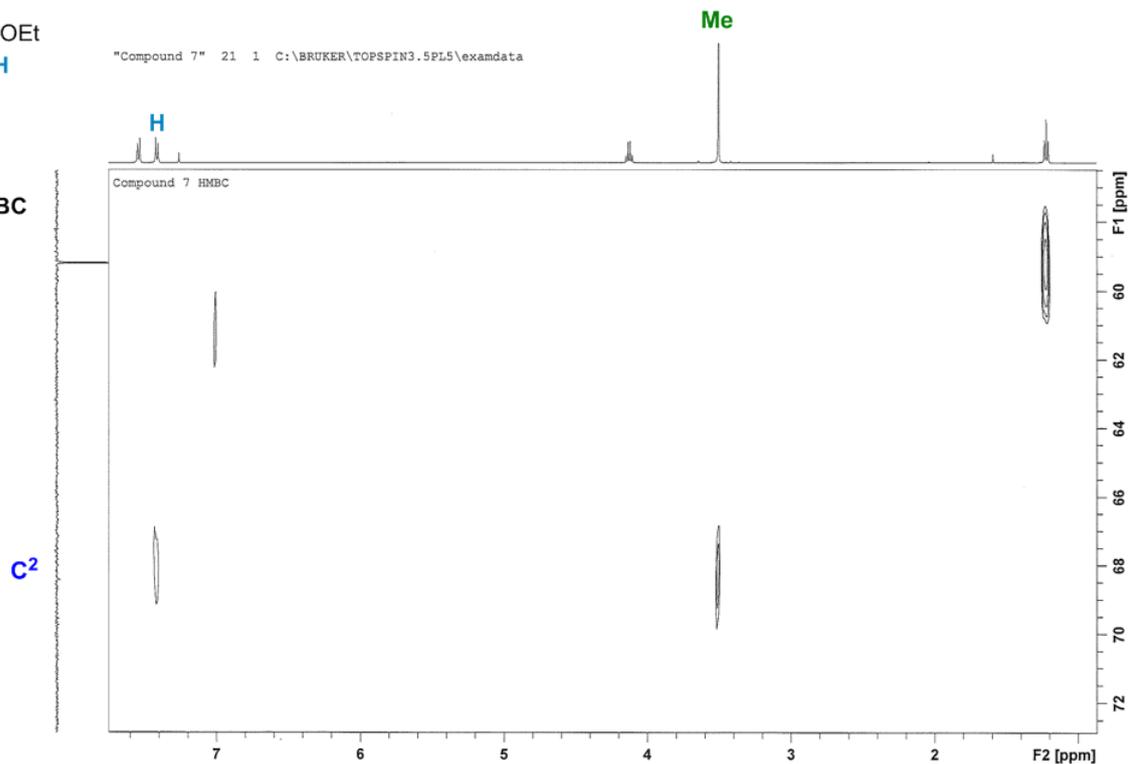




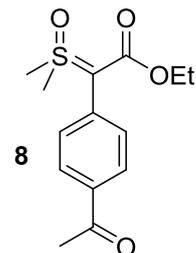


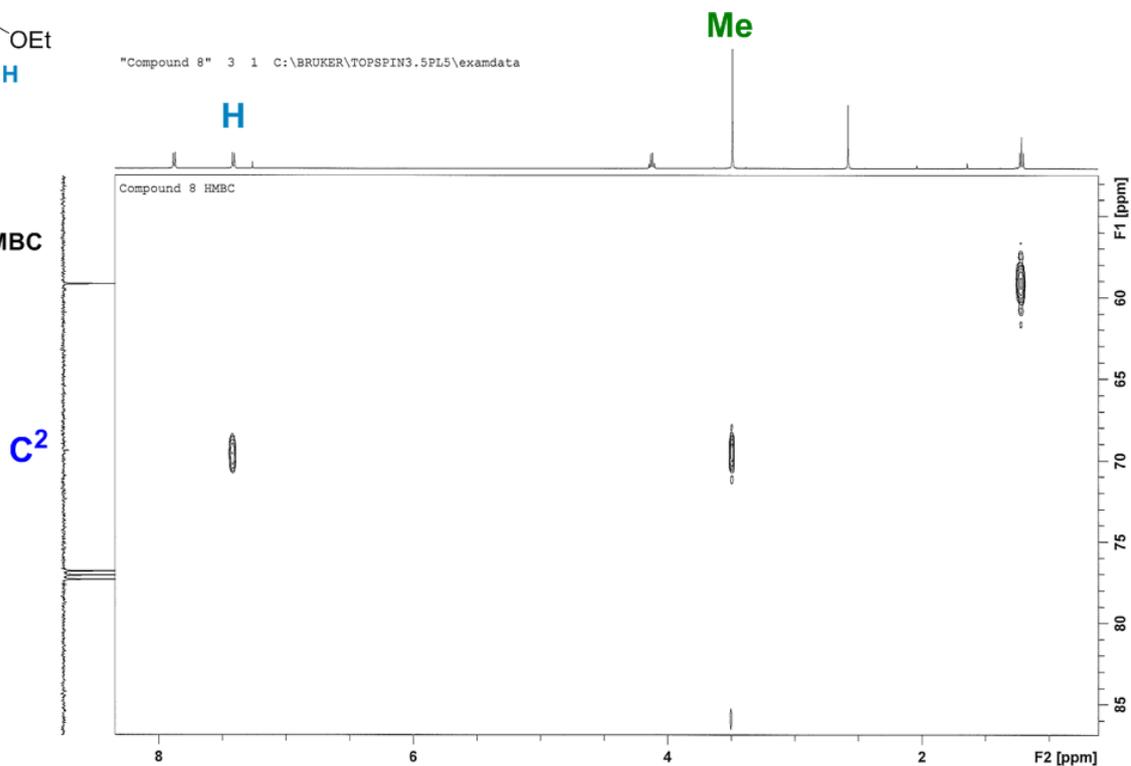
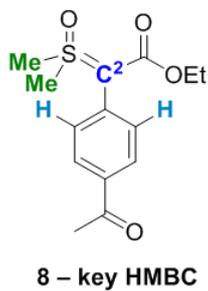
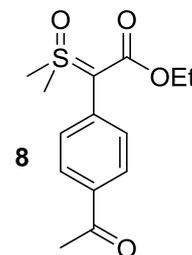
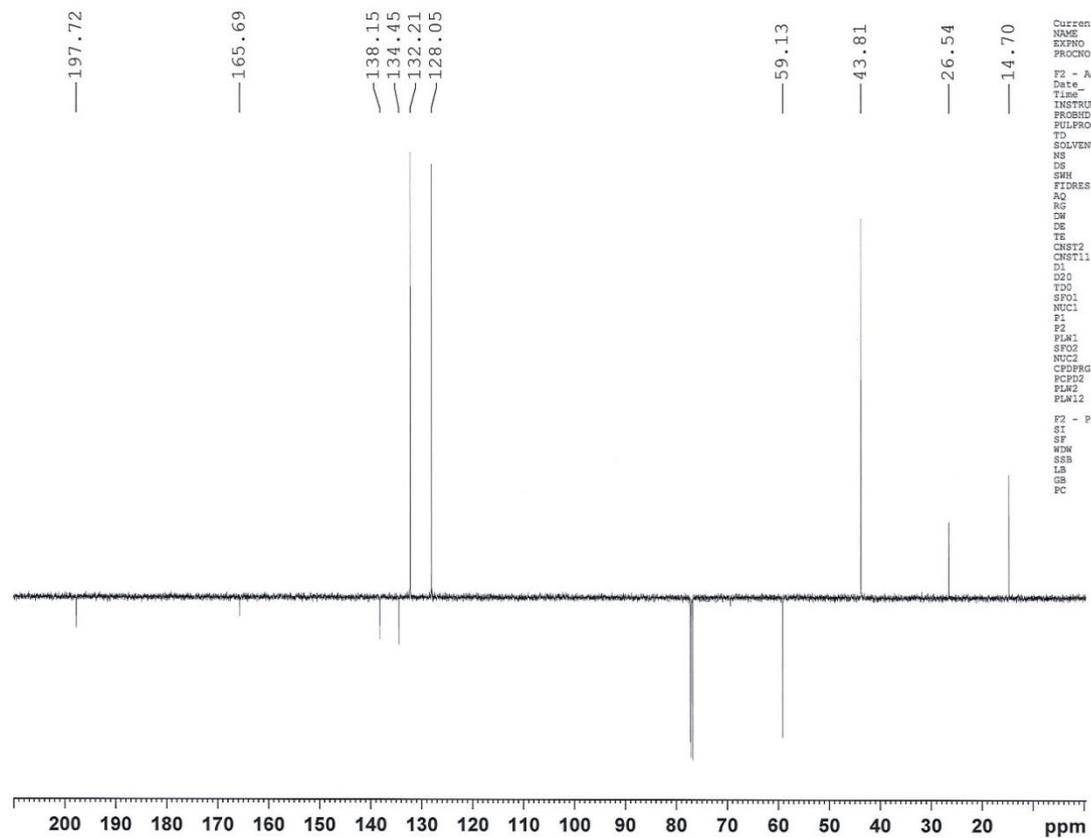


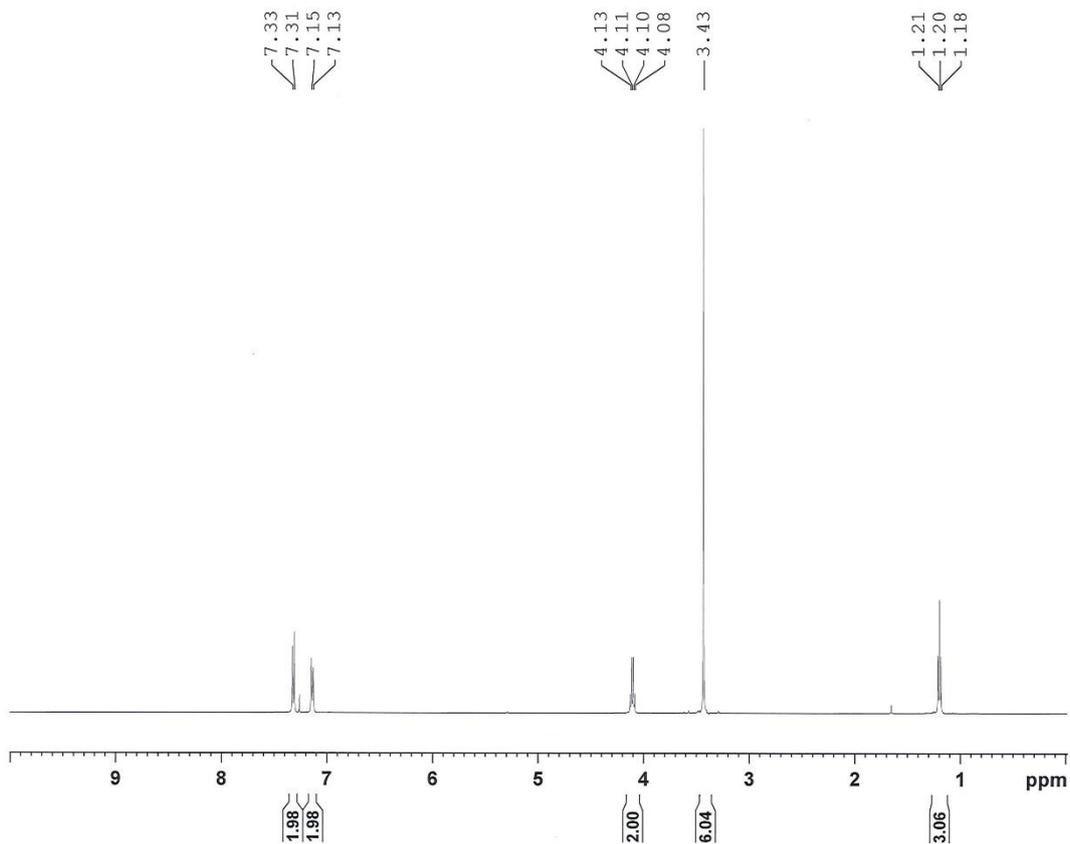
7 - key HMBC



Current Data Parameters  
 NAME Compound 8  
 EXPNO 1  
 PROCNO 1  
 F2 - Acquisition Parameters  
 Date\_ 20180601  
 Time 11:37 h  
 INSTRUM spect  
 PROBHD zgpg30  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 2  
 DS 2  
 SWH 10000.000 Hz  
 FIDRES 0.200176 Hz  
 AQ 3.2767999 sec  
 RG 198.17  
 DW 50.000 usec  
 DE 6.50 usec  
 TE 298.0 K  
 D1 1.0000000 sec  
 CTD  
 SFO1 500.1330883 MHz  
 NUCL1 13  
 P1 10.00 usec  
 PLW1 26.00000000 W  
 F2 - Processing parameters  
 SI 65536  
 SF 500.1300128 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



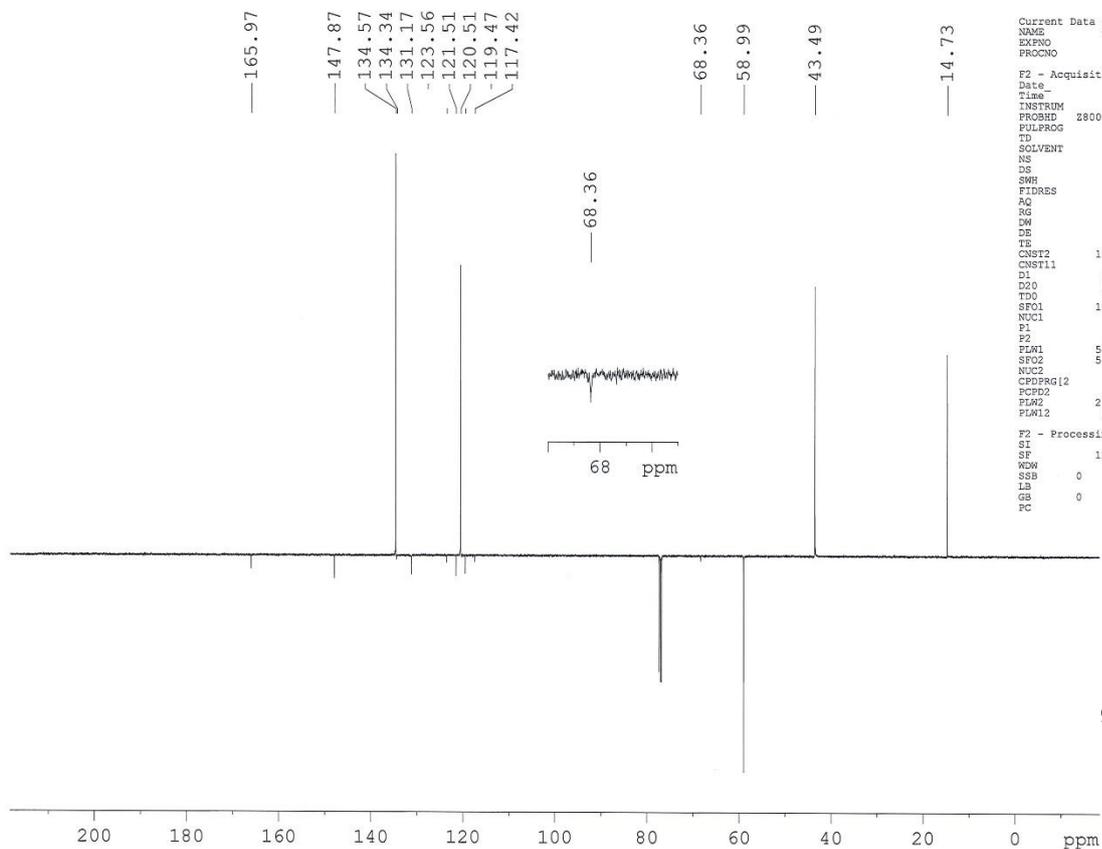
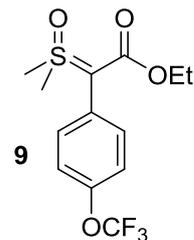




Current Data Parameters  
 NAME Compound 9  
 EXPNO 1  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20180703  
 Time 15.58 h  
 INSTRUM spect  
 PROBRD 2800701\_0108 ( FULPROG  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 2  
 SWH 10000.000 Hz  
 FIDRES 0.355176 Hz  
 AQ 3.2767999 sec  
 RG 198.17  
 DW 50.000 usec  
 DE 6.50 usec  
 TE 298.0 K  
 D1 1.0000000 sec  
 TDO 1  
 SFO1 500.1330083 MHz  
 NUC1 1H  
 P1 10.00 usec  
 PL1 26.0000000 W

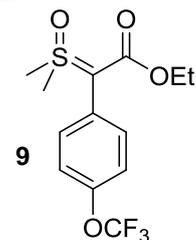
F2 - Processing parameters  
 SI 65536  
 SF 500.1300123 MHz  
 WDM EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00

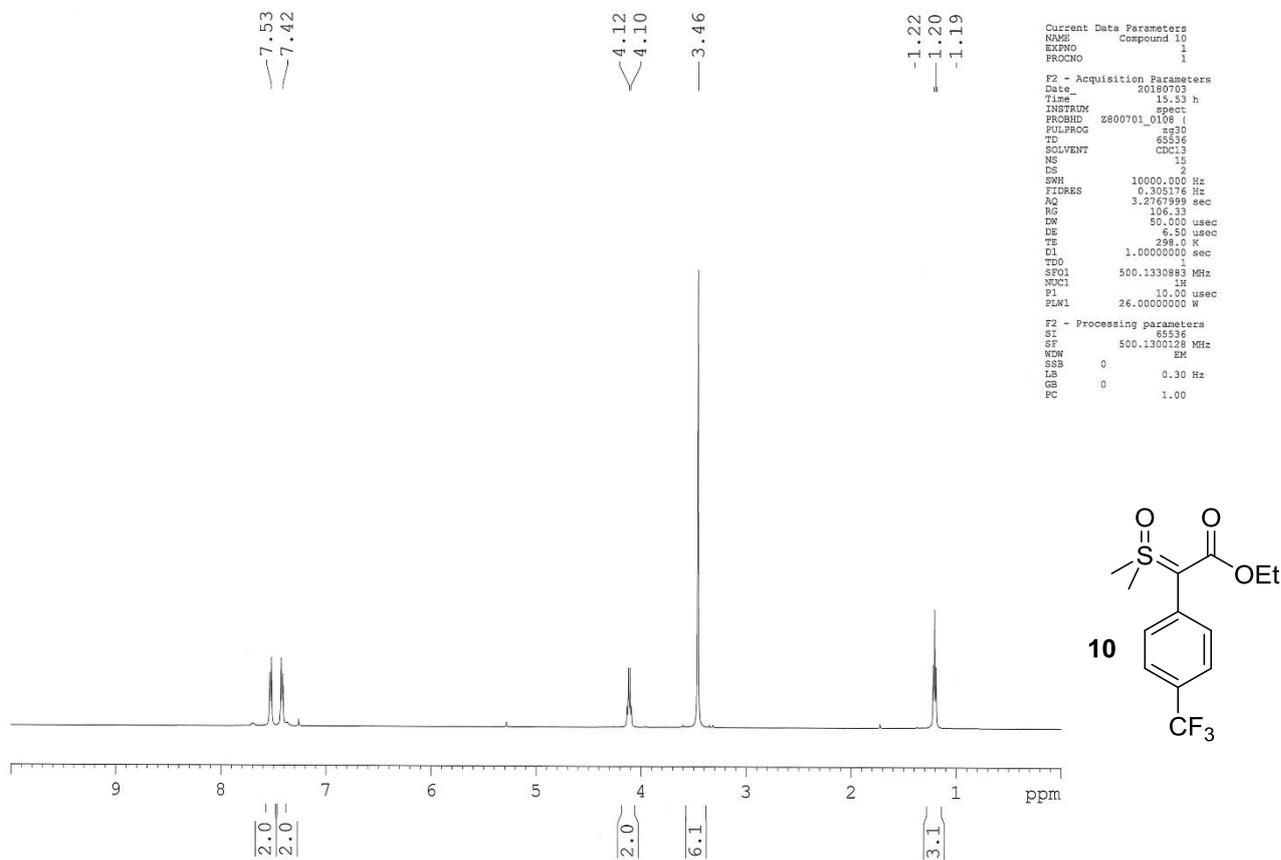
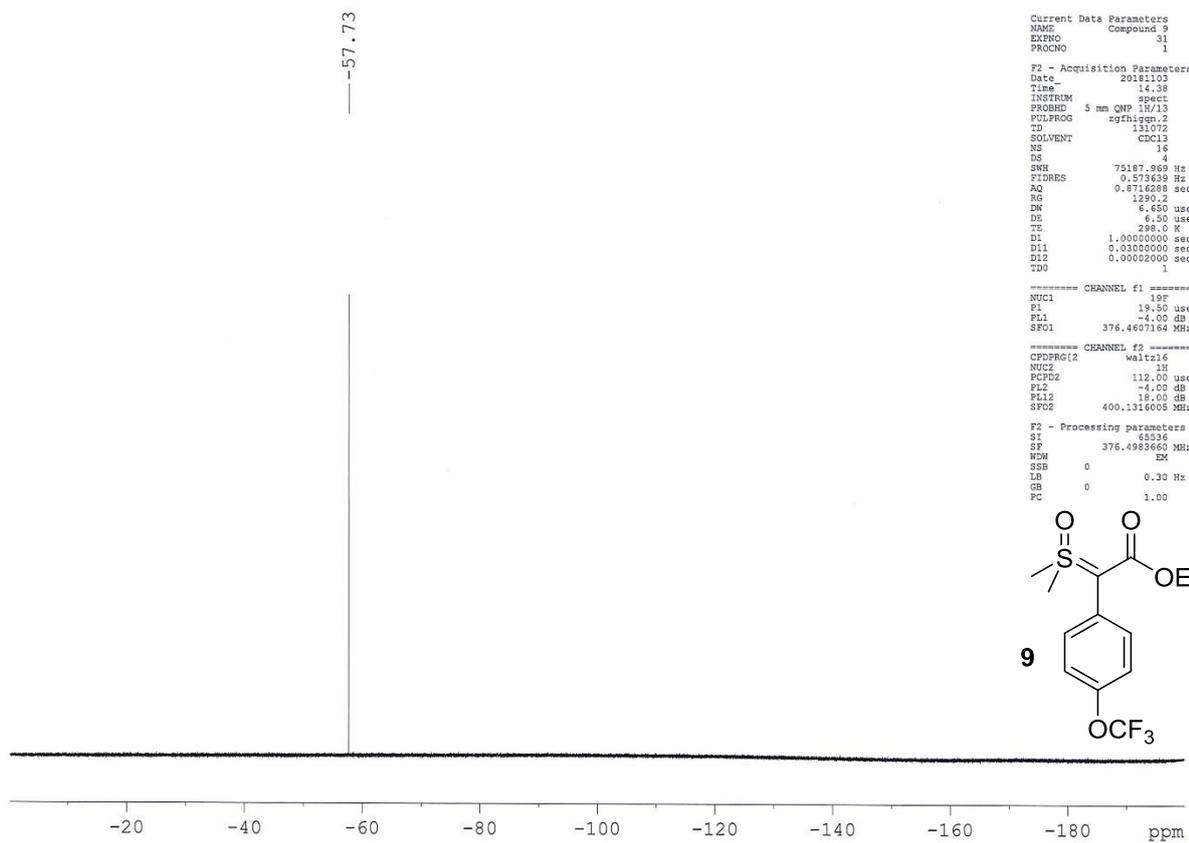


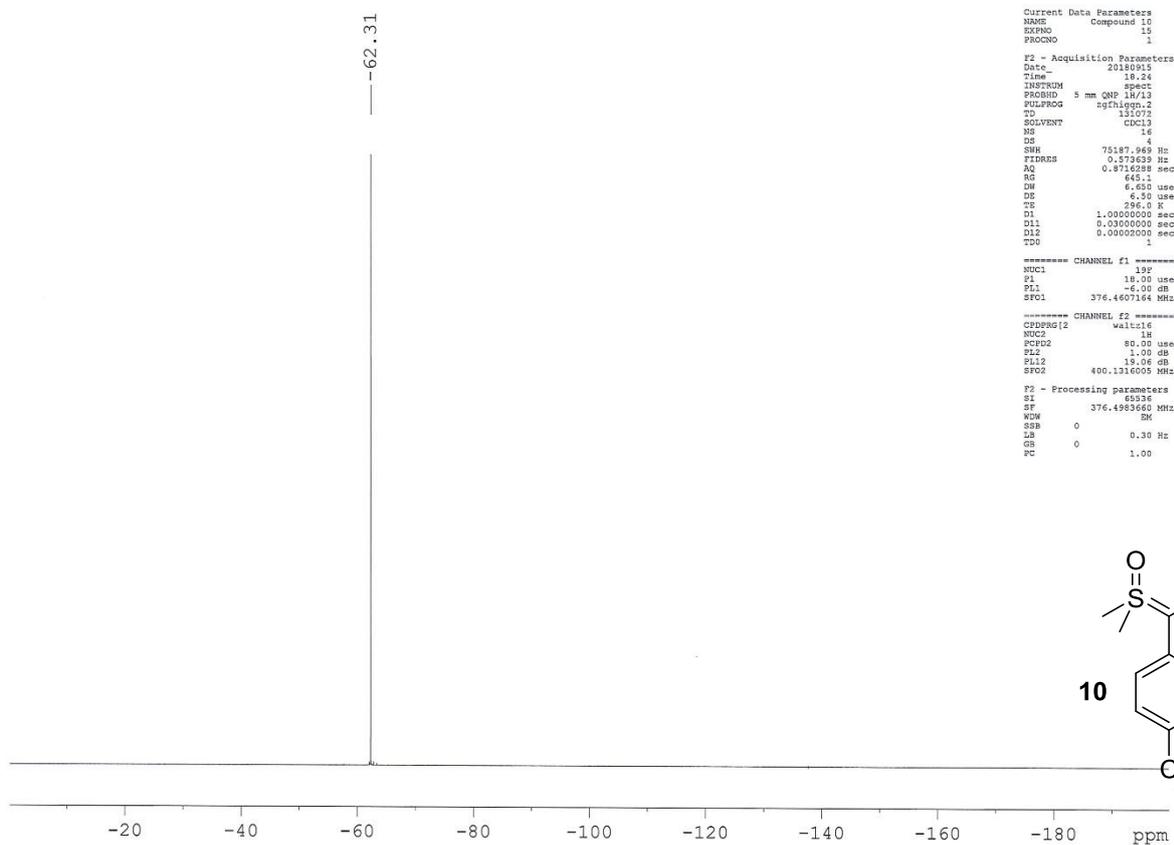
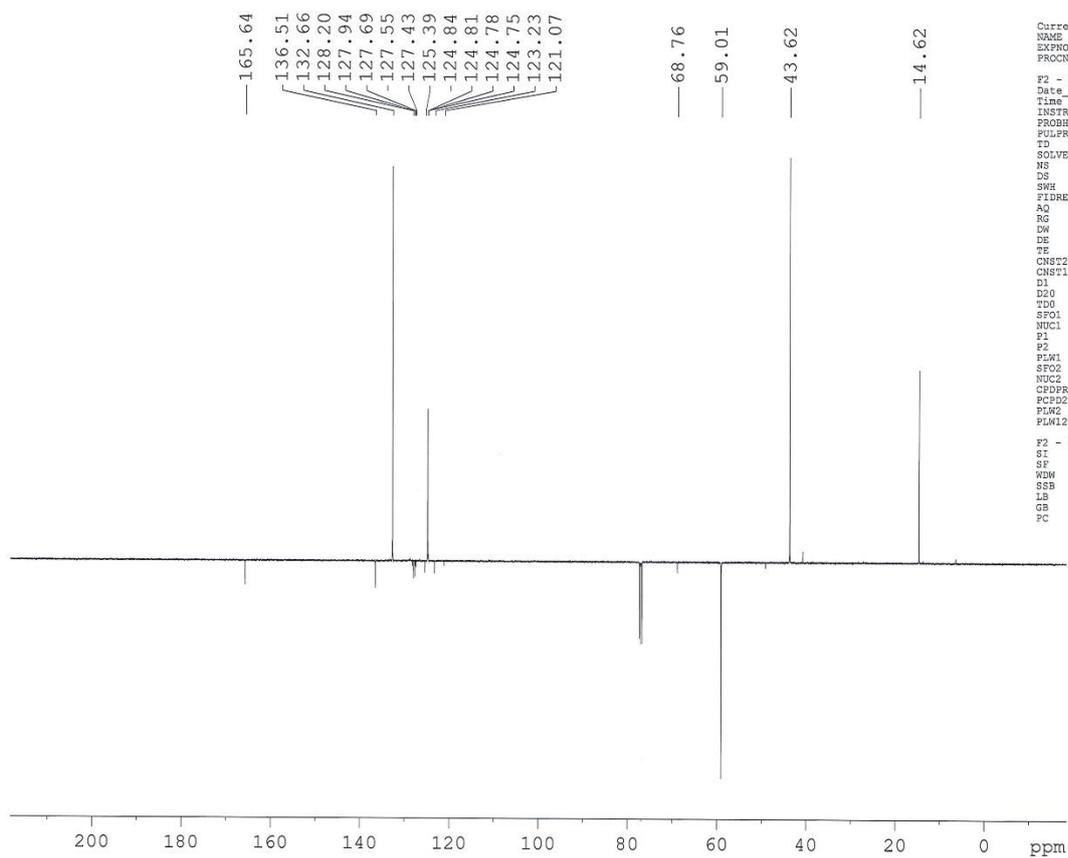
Current Data Parameters  
 NAME Compound 9  
 EXPNO 11  
 PROCNO 1

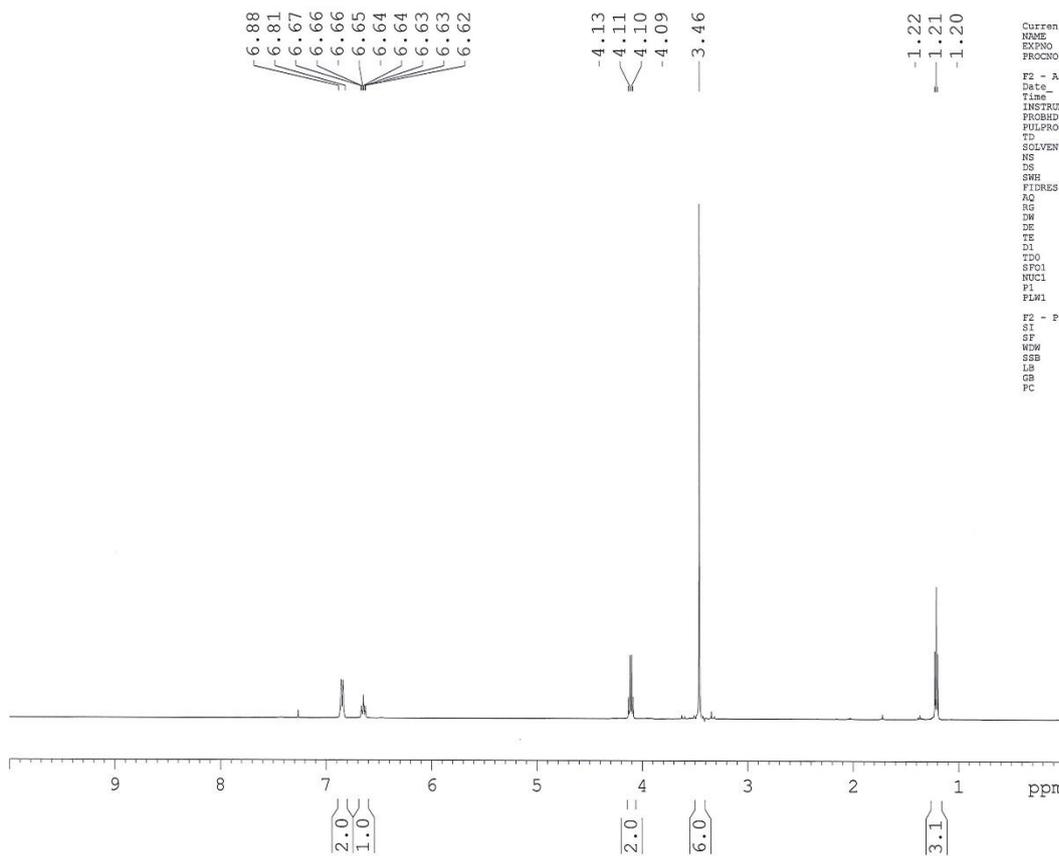
F2 - Acquisition Parameters  
 Date\_ 20180804  
 Time 14.41 h  
 INSTRUM spect  
 PROBRD 2800701\_0108 ( FULPROG  
 TD 65536  
 SOLVENT CDCl3  
 NS 915  
 DS 4  
 SWH 29761.904 Hz  
 FIDRES 0.308251 Hz  
 AQ 1.1010048 sec  
 RG 198.17  
 DW 16.800 usec  
 DE 6.50 usec  
 TE 298.0 K  
 CNST12 145.0000000  
 CNST11 1.0000000  
 D1 4.0000000 sec  
 D10 0.00689655 sec  
 TDO 1  
 SFO1 125.7703643 MHz  
 NUC1 13C  
 P1 8.00 usec  
 F2 16.00 usec  
 F2M1 53.0000000 W  
 SFO2 500.1320005 MHz  
 NUC2 1H  
 CPOPRG12 waltz16  
 PCPD2 80.00 usec  
 PLM2 28.0000000 W  
 PLM12 0.42017001 W

F2 - Processing parameters  
 SI 32768  
 SF 125.7577885 MHz  
 WDM EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40

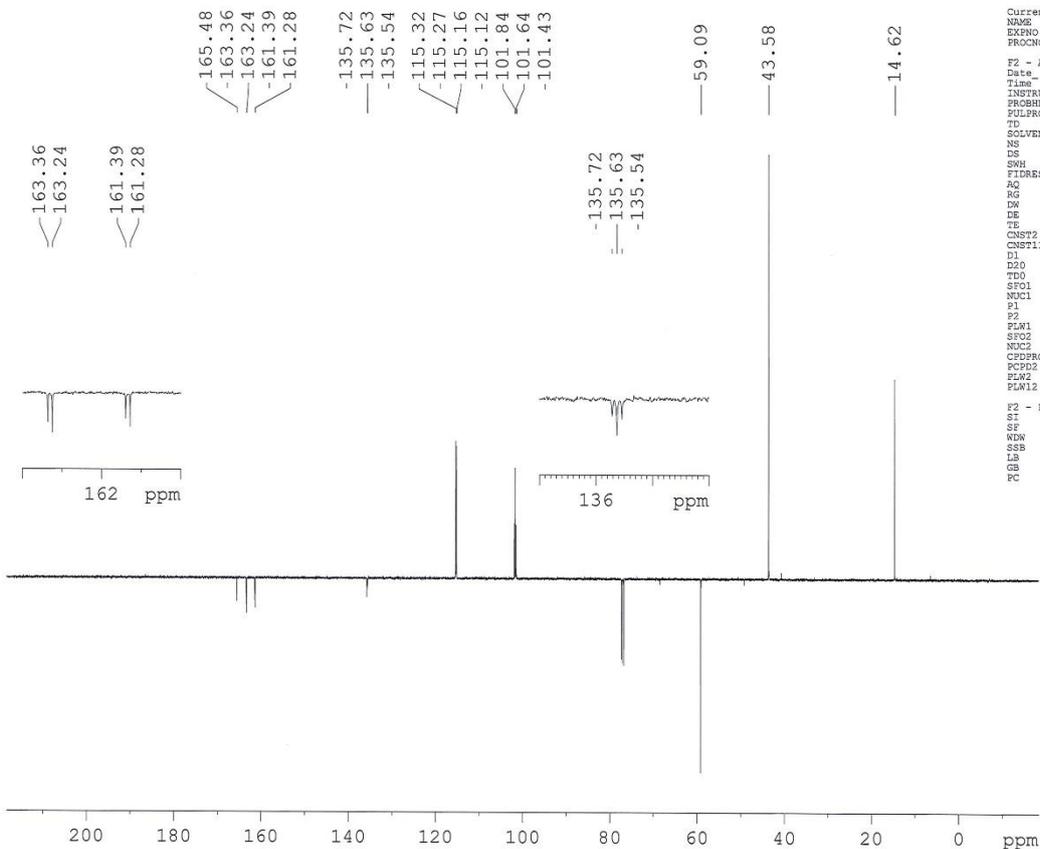
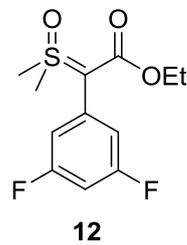




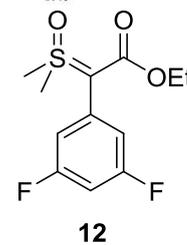


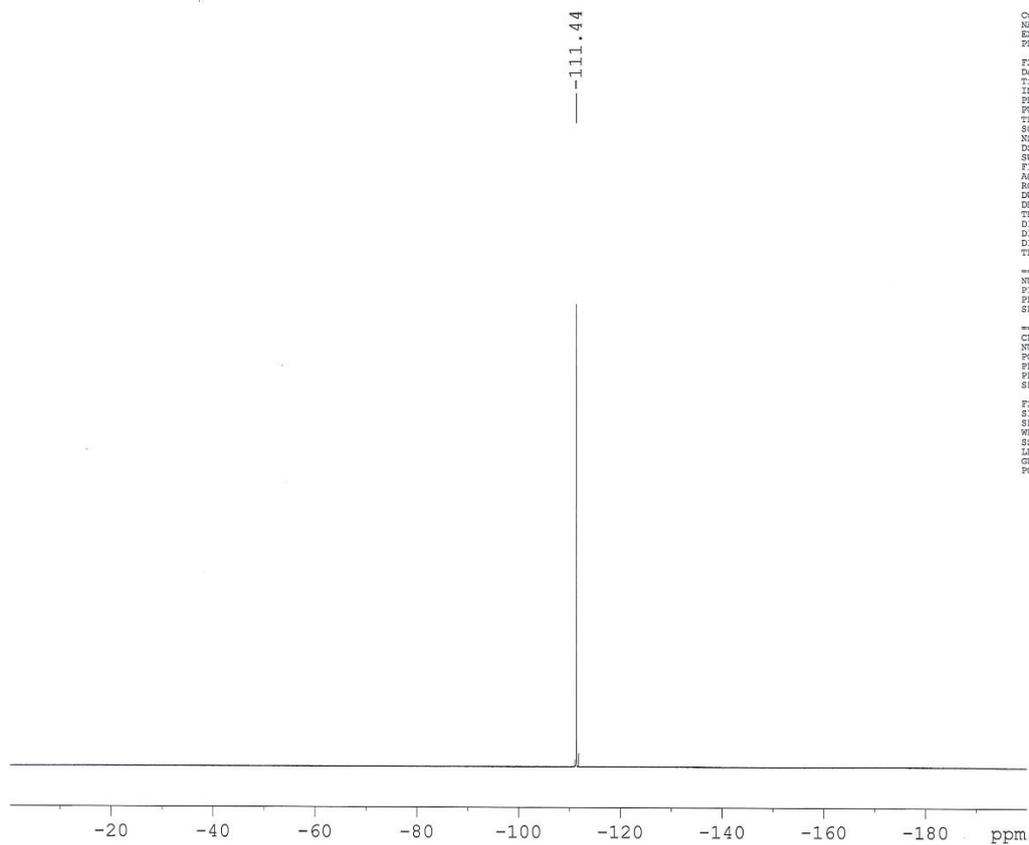


Current Data Parameters  
 Name Compound 12  
 EXPNO 1  
 PROCNO 1  
 F2 - Acquisition Parameters  
 Date\_ 20180503  
 Time\_ 16.27 h  
 INSTRUM spect  
 FREQHD 2800701\_0198  
 PULPROG zg30  
 TD 65536  
 SOLVENT ccd13  
 NS 16  
 DS 2  
 SWH 10000.000 Hz  
 FIDRES 0.305176 Hz  
 AQ 3.2767999 sec  
 RG 120.08  
 DW 50.000 usec  
 DE 1.50 usec  
 TE 298.0 K  
 D1 1.0000000 sec  
 TDO  
 SFO1 500.1330883 MHz  
 NUC1  
 P1 10.00 usec  
 PLW1 26.00000000 W  
 F2 - Processing parameters  
 SI 65536  
 SF 500.1320119 MHz  
 EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



Current Data Parameters  
 Name Compound 12  
 EXPNO 2  
 PROCNO 1  
 F2 - Acquisition Parameters  
 Date\_ 20180503  
 Time\_ 18.33 h  
 INSTRUM spect  
 FREQHD 2800701\_0198  
 PULPROG jmod  
 TD 65536  
 SOLVENT ccd13  
 NS 367  
 DS 4  
 SWH 29761.904 Hz  
 FIDRES 0.908261 Hz  
 AQ 1.1010048 sec  
 RG 198.17  
 DW 16.900 usec  
 DE 6.50 usec  
 TE 298.0 K  
 CNSTP2 145.0000000  
 CNP111 1.0000000  
 D1 4.0000000 sec  
 L20 0.0069965 sec  
 TDO  
 SFO1 125.7703643 MHz  
 NUC1 13C  
 P1 8.00 usec  
 P2 16.00 usec  
 PLW1 53.0000000 W  
 SFO2 500.1320005 MHz  
 NUC2 1H  
 PCPRG2 waltz16  
 PCP22 80.00 usec  
 PLW2 28.0000000 W  
 PLW12 0.42017001 W  
 F2 - Processing parameters  
 SI 32768  
 SF 125.7577957 MHz  
 EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40





```

Current Data Parameters
NAME      Compound 12
EXPNO    15
PROCNO   1

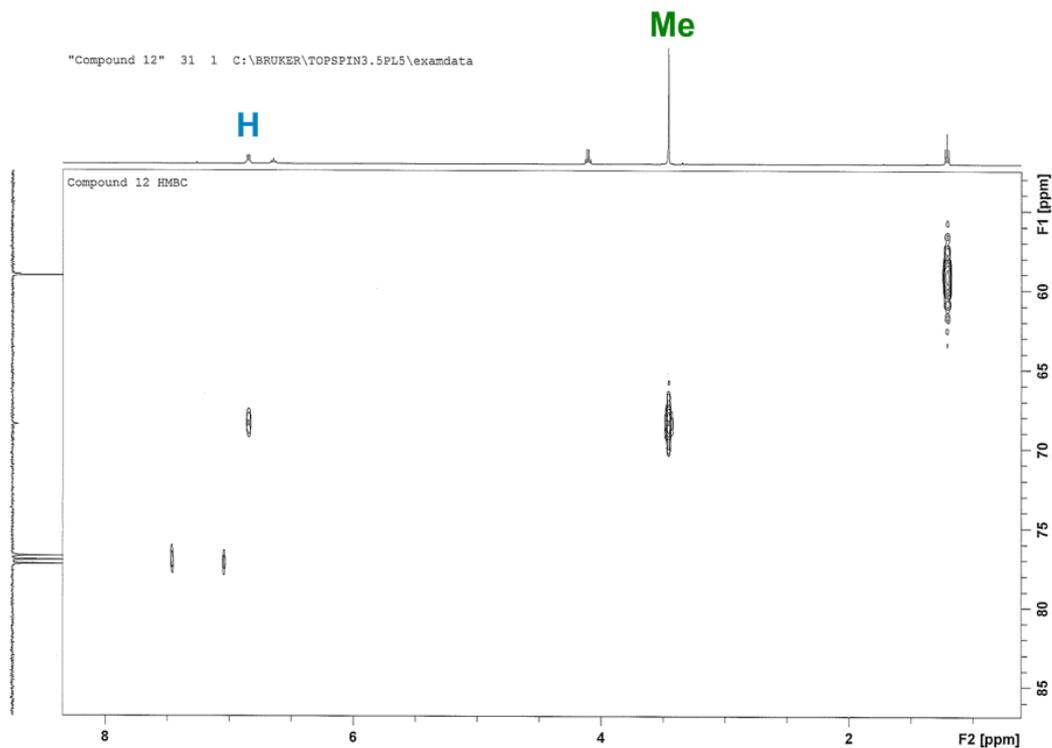
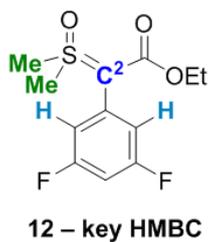
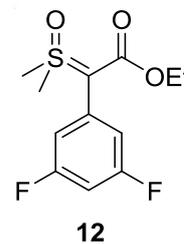
F2 - Acquisition Parameters
Date_    20180315
Time     17.17
INSTRUM spect
PROBHD   5 mm QNP 1H/13
PULPROG zgpg30m.2
TD       131072
SOLVENT  CDCl3
NS       16
DS       4
SWH      75187.969 Hz
FIDRES   0.573539 Hz
AQ       0.8716288 sec
RG       512.7
DN       6.690 usec
DE       6.50 usec
TE       373.2 K
D1       1.00000000 sec
D11      0.02000000 sec
D12      0.00002000 sec
TD0      1

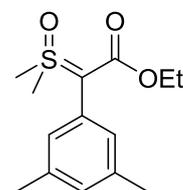
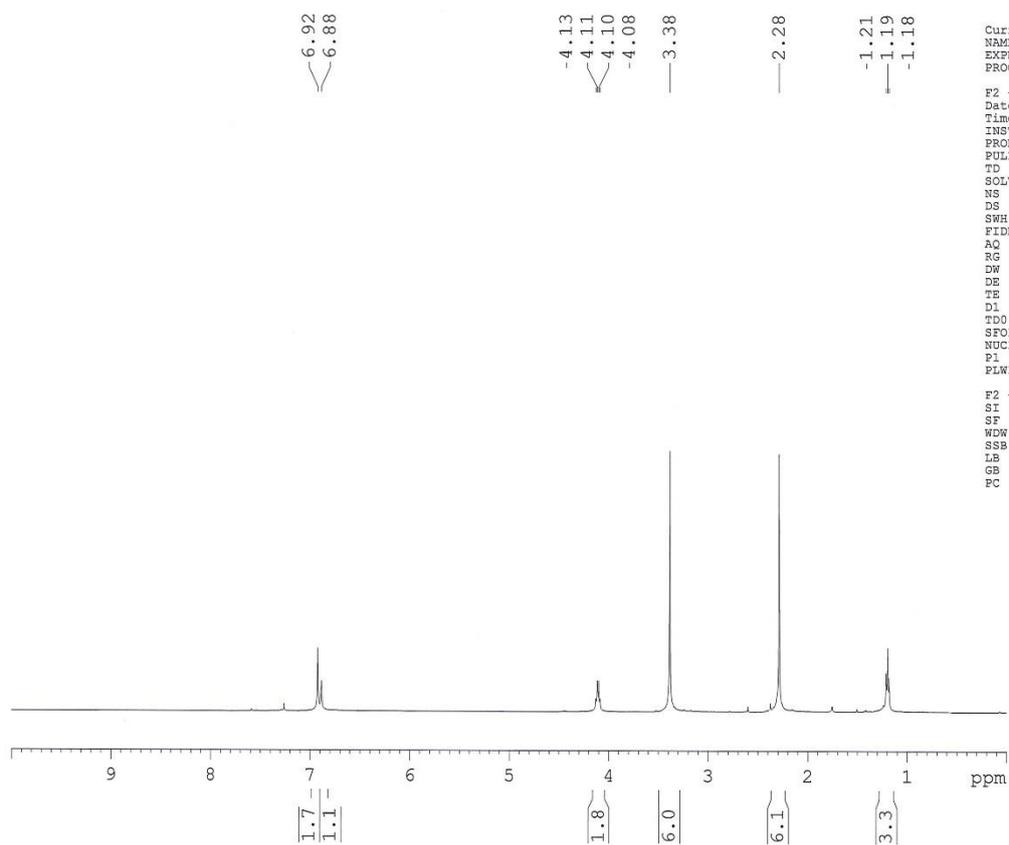
===== CHANNEL f1 =====
NUC1      13P
P1       18.00 usec
PL1      -6.00 dB
SFO1     376.4607164 MHz

===== CHANNEL f2 =====
CPDPRG2  waltz16
NUC2     1H
PCPD2    80.00 usec
PL2      1.00 dB
PL12     19.06 dB
SFO2     400.1316005 MHz

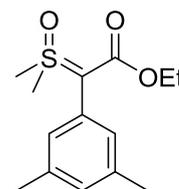
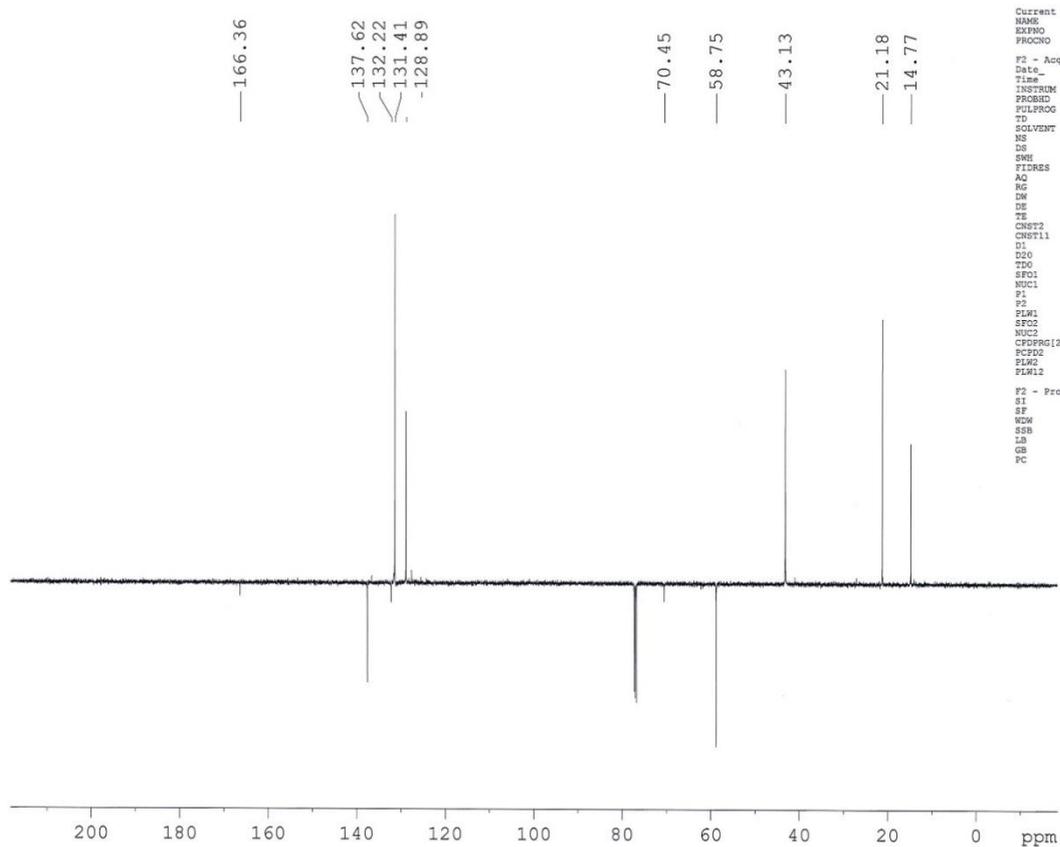
F2 - Processing parameters
SI       65536
SF       376.4583460 MHz
WDW      EM
SSB      0
LB       0.30 Hz
GB       0
PC       1.00

```

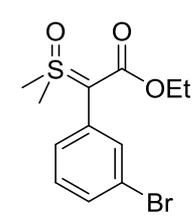
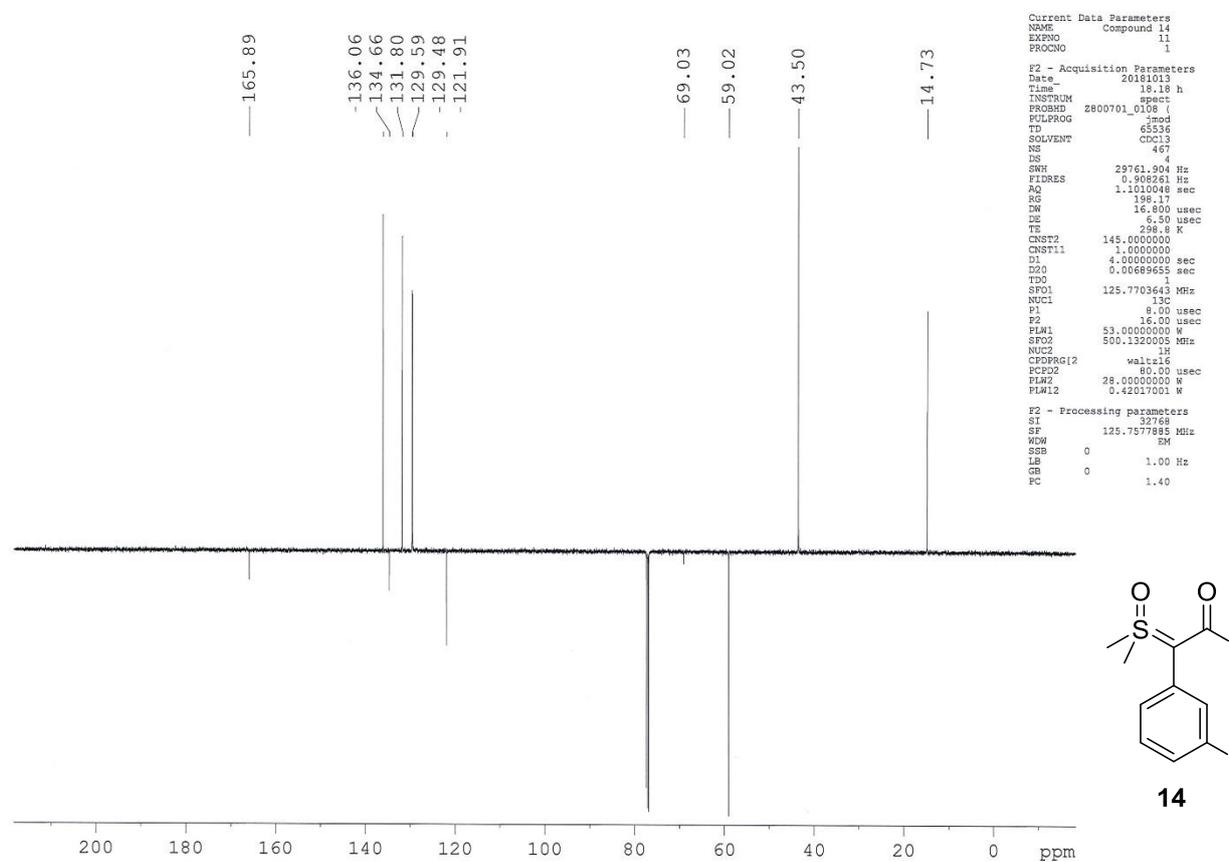
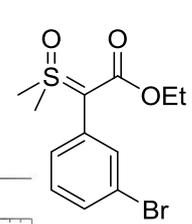
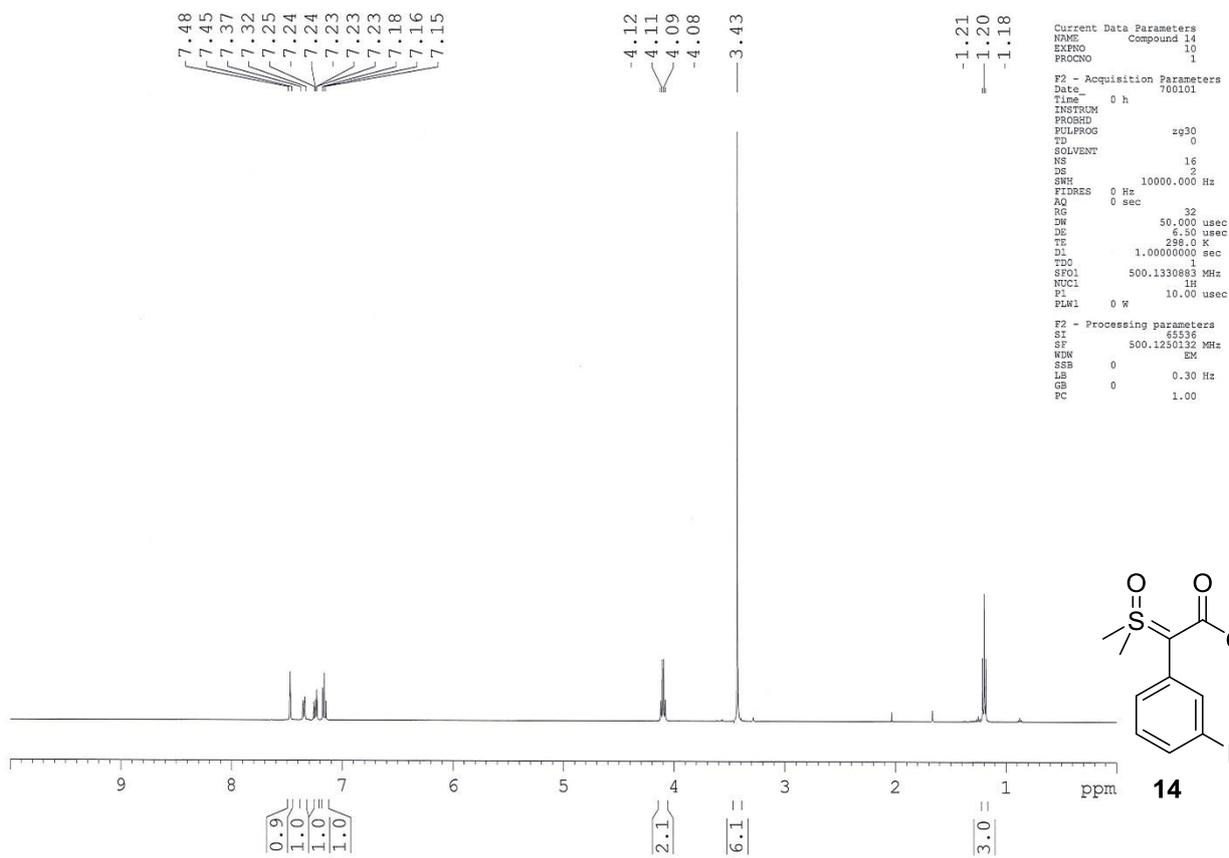


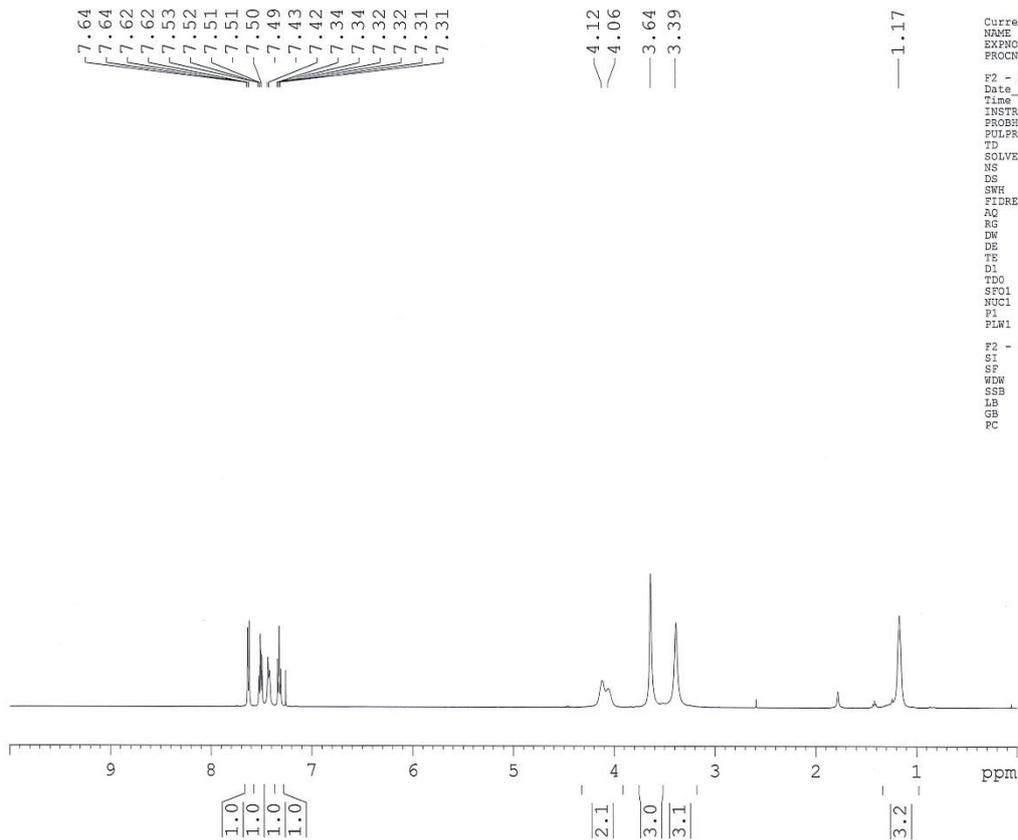


13



13

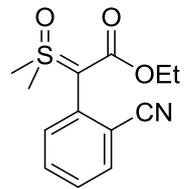




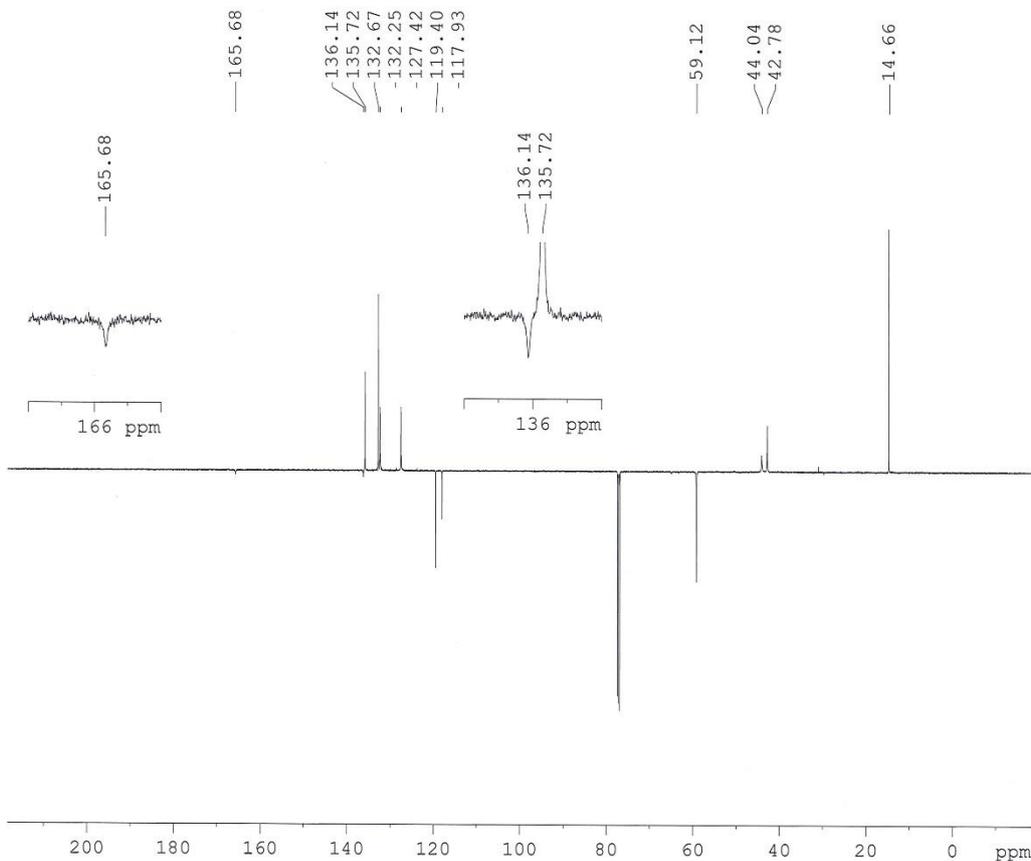
Current Data Parameters  
 NAME Compound 15  
 EXPNO 2  
 FRCNO 1

F2 - Acquisition Parameters  
 Date 20180622  
 Time 16.35 h  
 INSTRUM spect  
 FROTHD 2800701\_0108 ( )  
 FULPROG zg30  
 TD 65536  
 DI 16  
 SOLVENT CDCl3  
 NS 2  
 DS 2  
 SWH 10000.000 Hz  
 FIDRES 0.305176 Hz  
 AQ 3.2767999 sec  
 RG 120.08  
 DW 50.000 usec  
 DE 6.50 usec  
 TE 298.0 K  
 DI 1.0000000 sec  
 TDO 1  
 SF01 500.1330883 MHz  
 NUC1 1H  
 F1 10.00 usec  
 PLW1 26.0000000 W

F2 - Processing parameters  
 SI 65536  
 SF 500.1300123 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



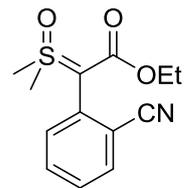
15



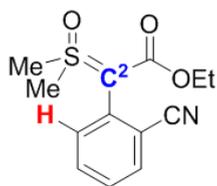
Current Data Parameters  
 NAME Compound 15  
 EXPNO 1  
 FRCNO 1

F2 - Acquisition Parameters  
 Date 20180622  
 Time 19.52 h  
 INSTRUM spect  
 FROTHD 2800701\_0108 ( )  
 FULPROG jmod  
 TD 65536  
 DI 16  
 SOLVENT CDCl3  
 NS 2048  
 DS 4  
 SWH 29761.204 Hz  
 FIDRES 0.908291 Hz  
 AQ 1.1010048 sec  
 RG 159.17  
 DW 16.800 usec  
 DE 6.50 usec  
 TE 298.2 K  
 CNST2 145.0000000  
 DI 1.0000000  
 TDO 5.0000000 sec  
 SF01 125.7703643 MHz  
 NUC1 13C  
 F1 8.00 usec  
 PLW1 53.0000000 W  
 SF02 500.1320005 MHz  
 NUC2 1H  
 F2 16.00 usec  
 PLW2 28.0000000 W  
 SF03 80.0000000 MHz  
 NUC3 13C  
 F3 0.42017001 W

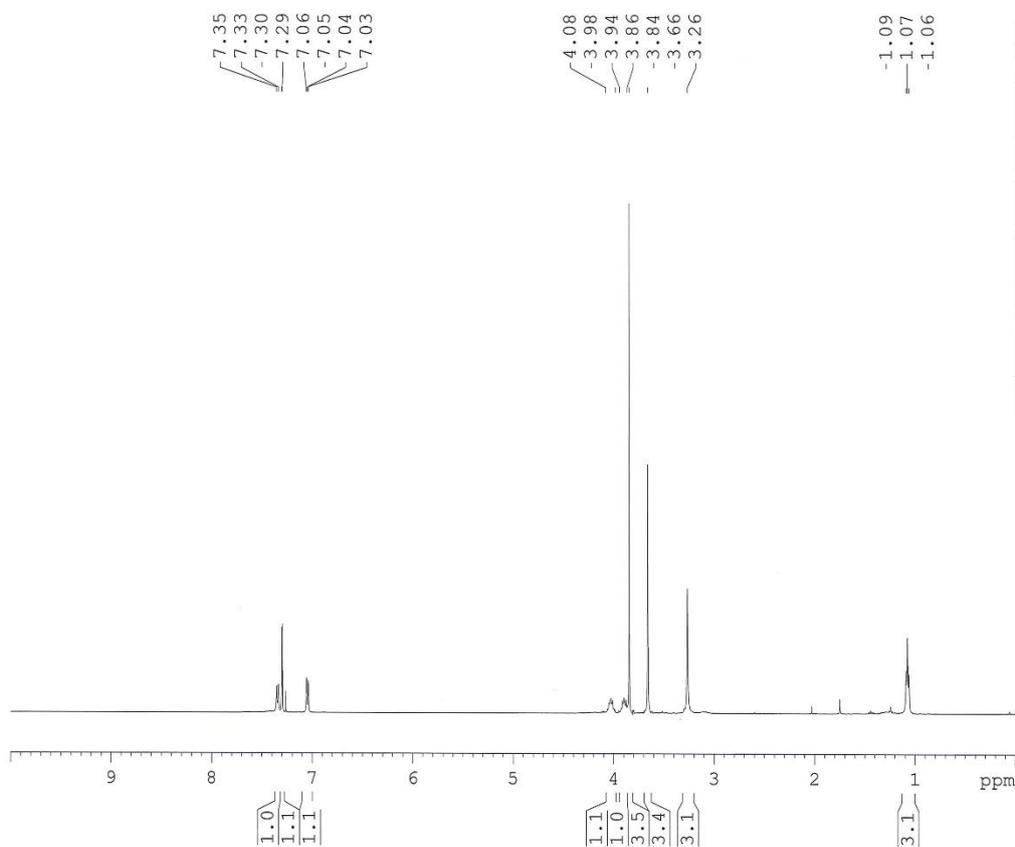
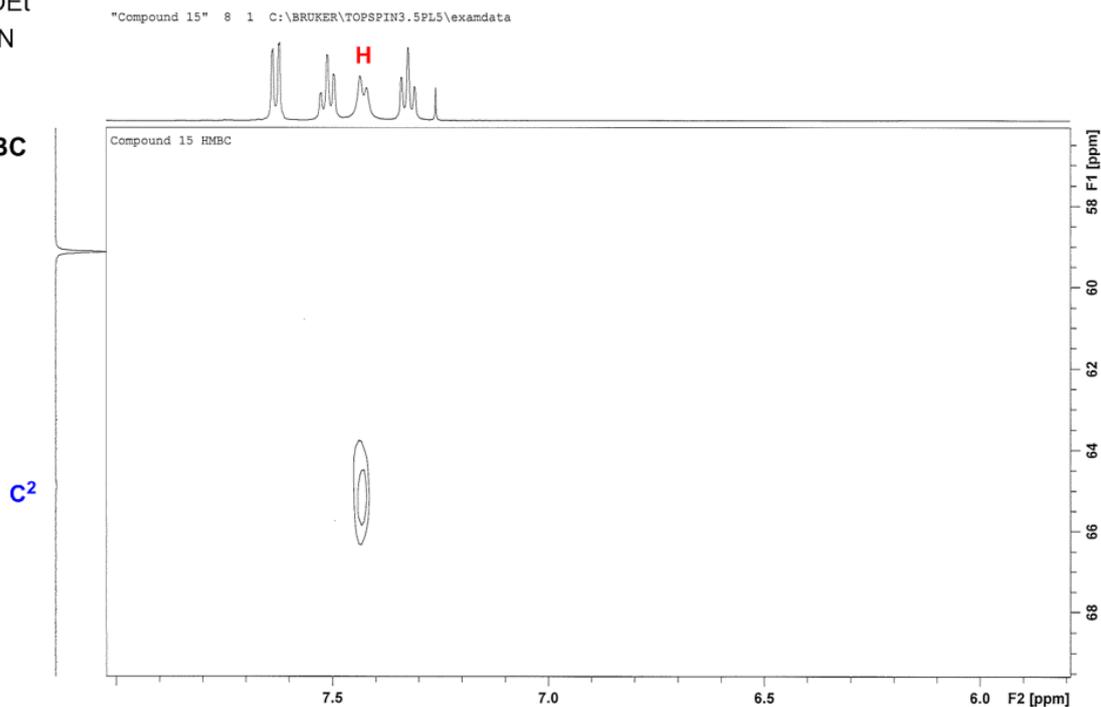
F2 - Processing parameters  
 SI 32768  
 SF 125.7577885 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40



15



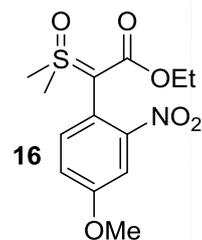
15 – key HMBC

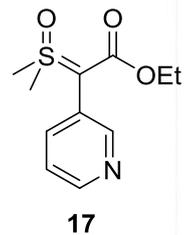
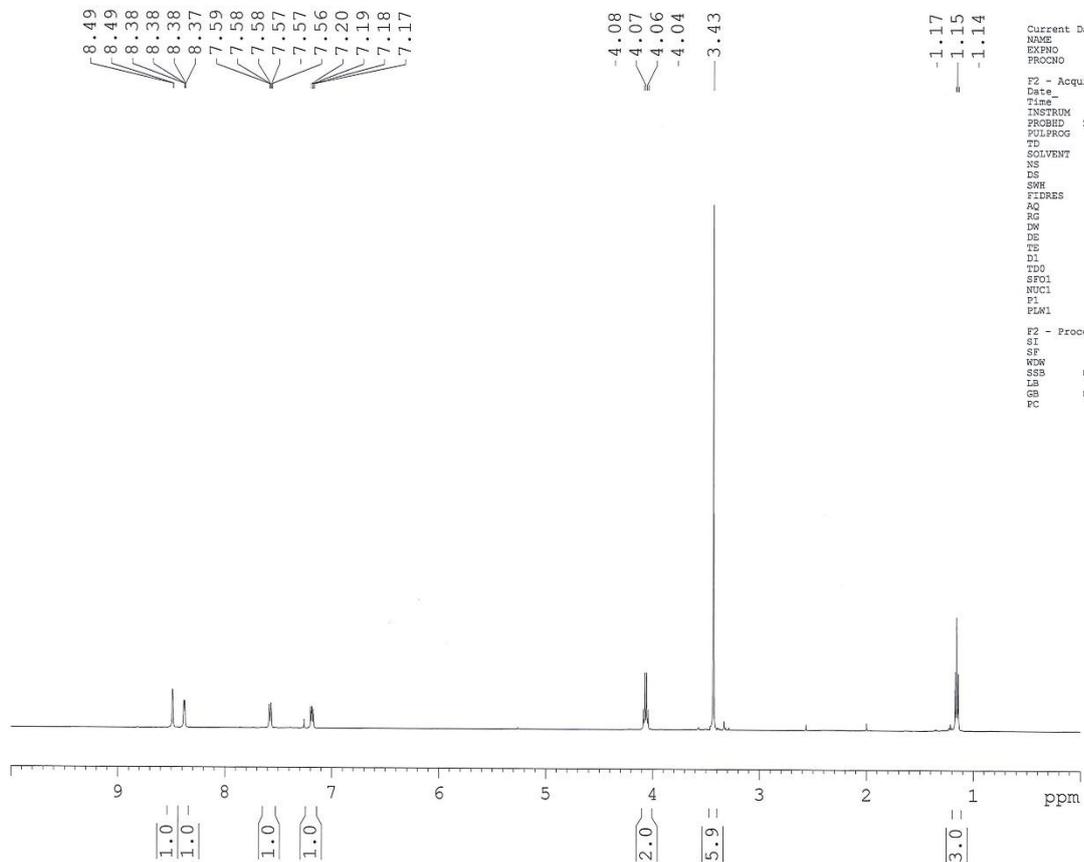
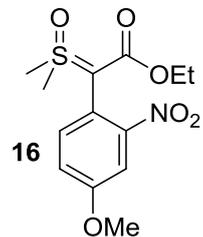
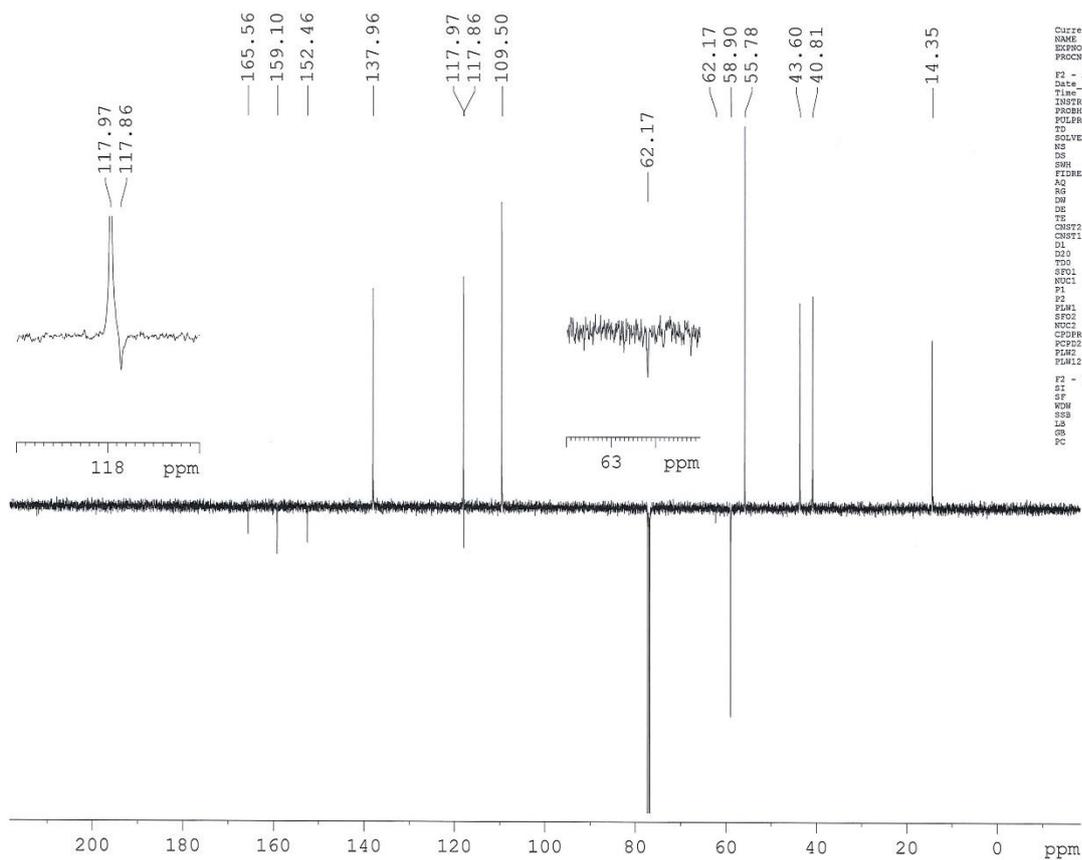


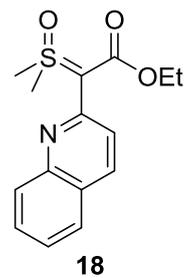
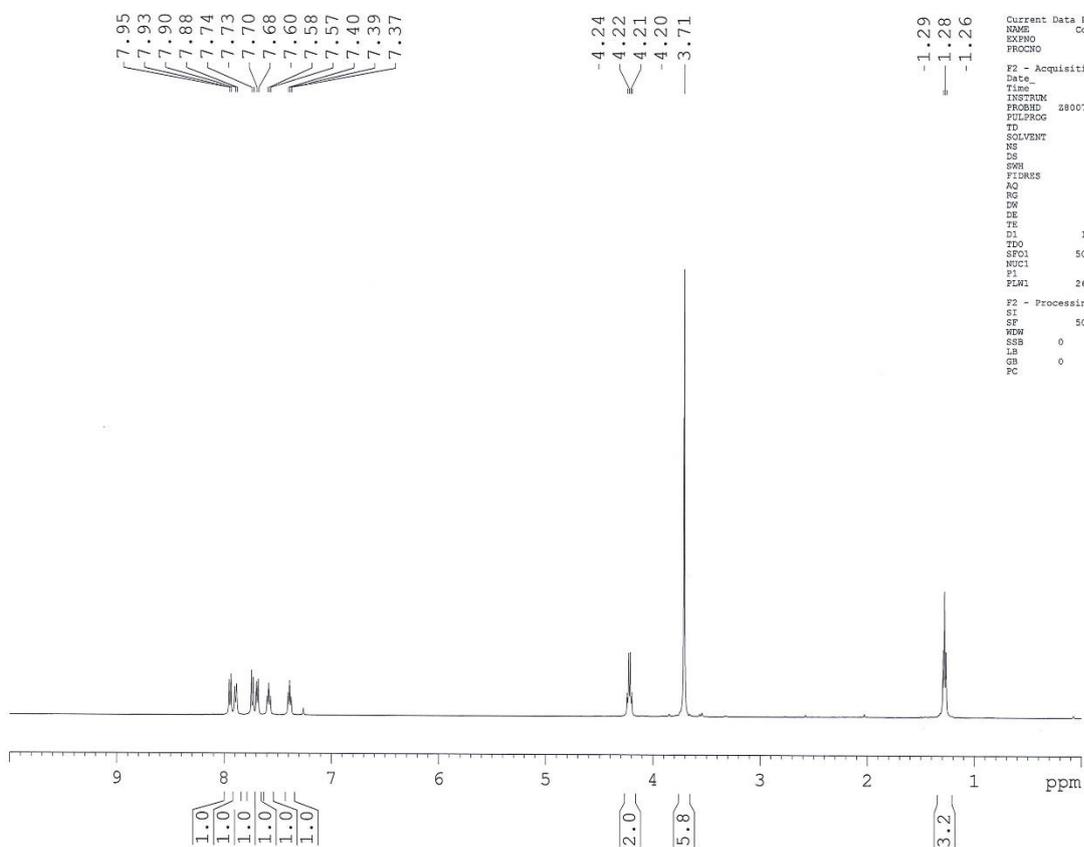
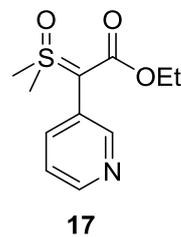
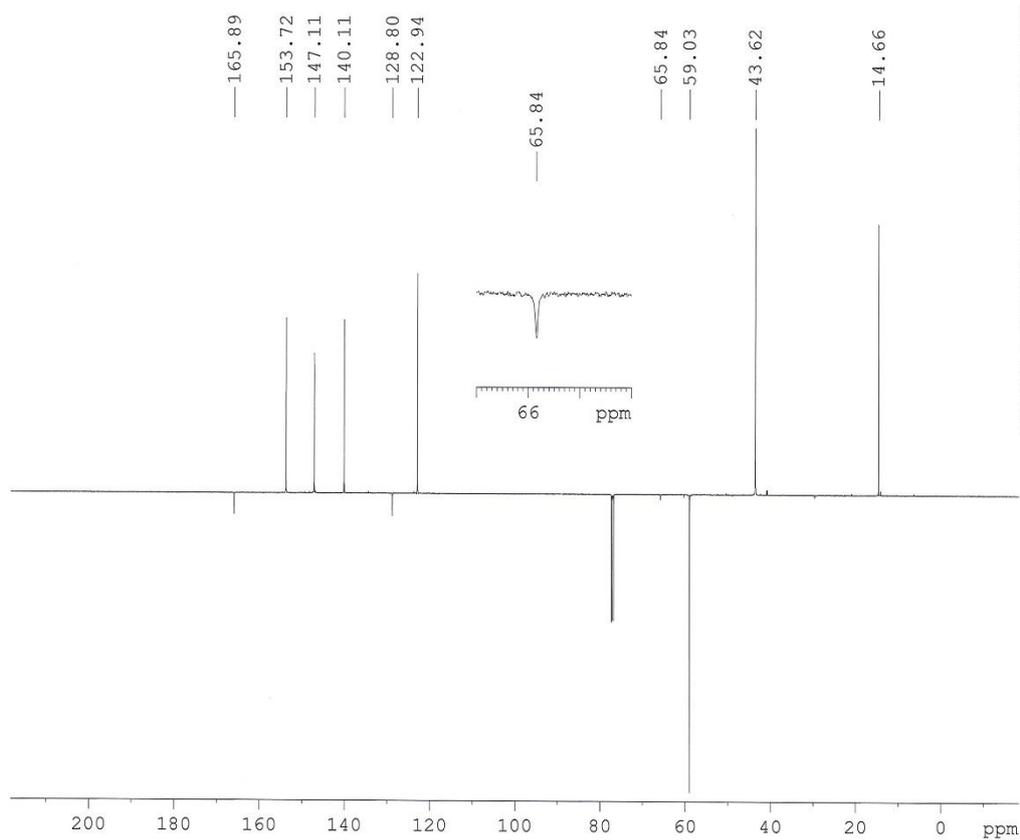
Current Data Parameters  
 NAME Compound 16  
 EXPNO 1  
 PROCNO 1

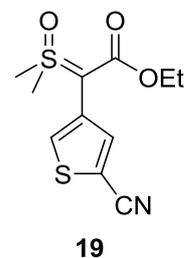
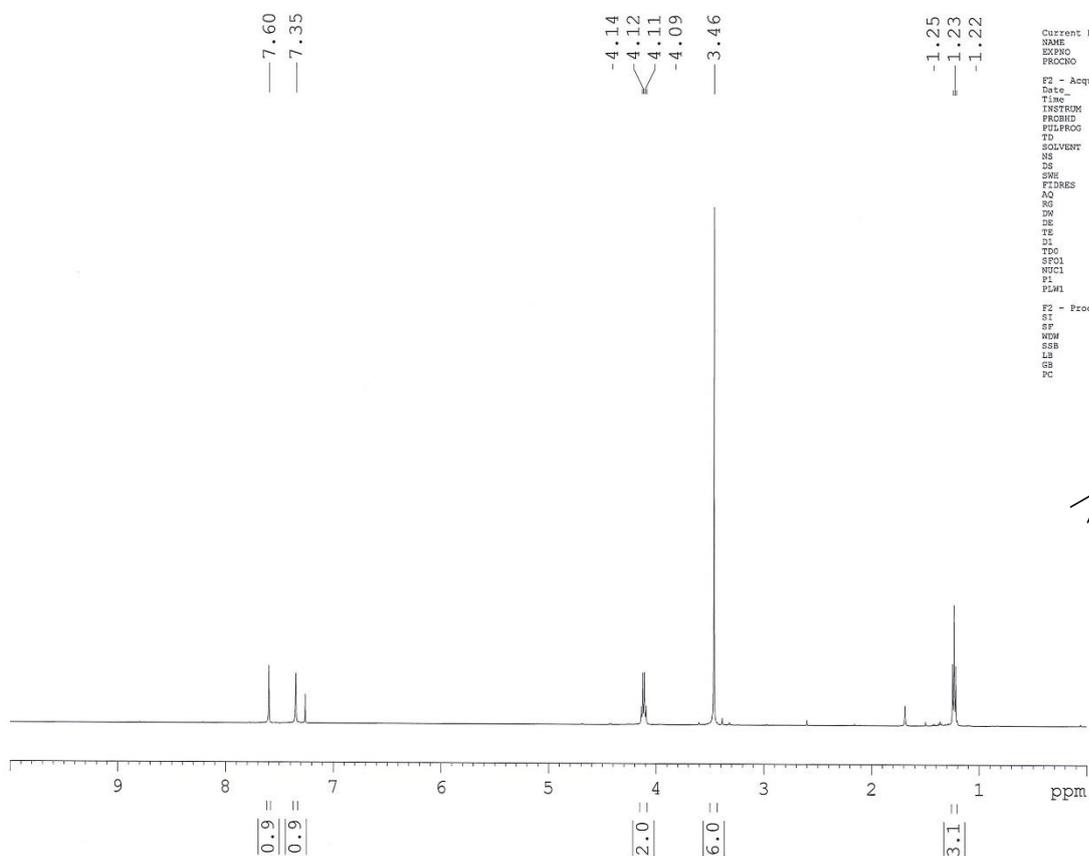
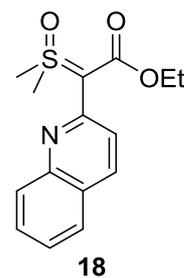
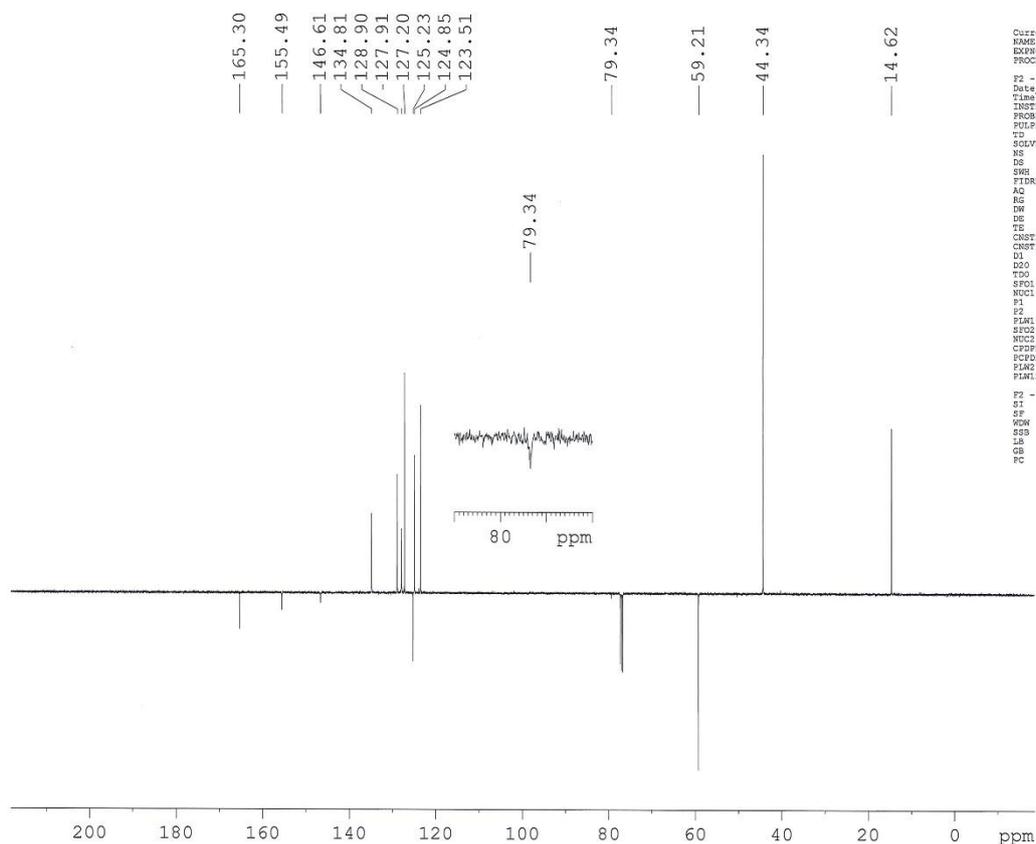
F2 - Acquisition Parameters  
 Date\_ 20180618  
 Time 12.18 h  
 INSTRUM spect  
 PROBHD Z800701\_0108 (1  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 2  
 SWH 10000.000 Hz  
 FIDRES 0.305176 Hz  
 AQ 3.2767899 sec  
 RG 120.08  
 DW 50.000 usec  
 DE 6.50 usec  
 TE 298.0 K  
 F1 1.0000000 sec  
 TDO  
 SFO1 500.1330883 MHz  
 NUC1 1H  
 P1 10.00 usec  
 PLW1 26.0000000 W

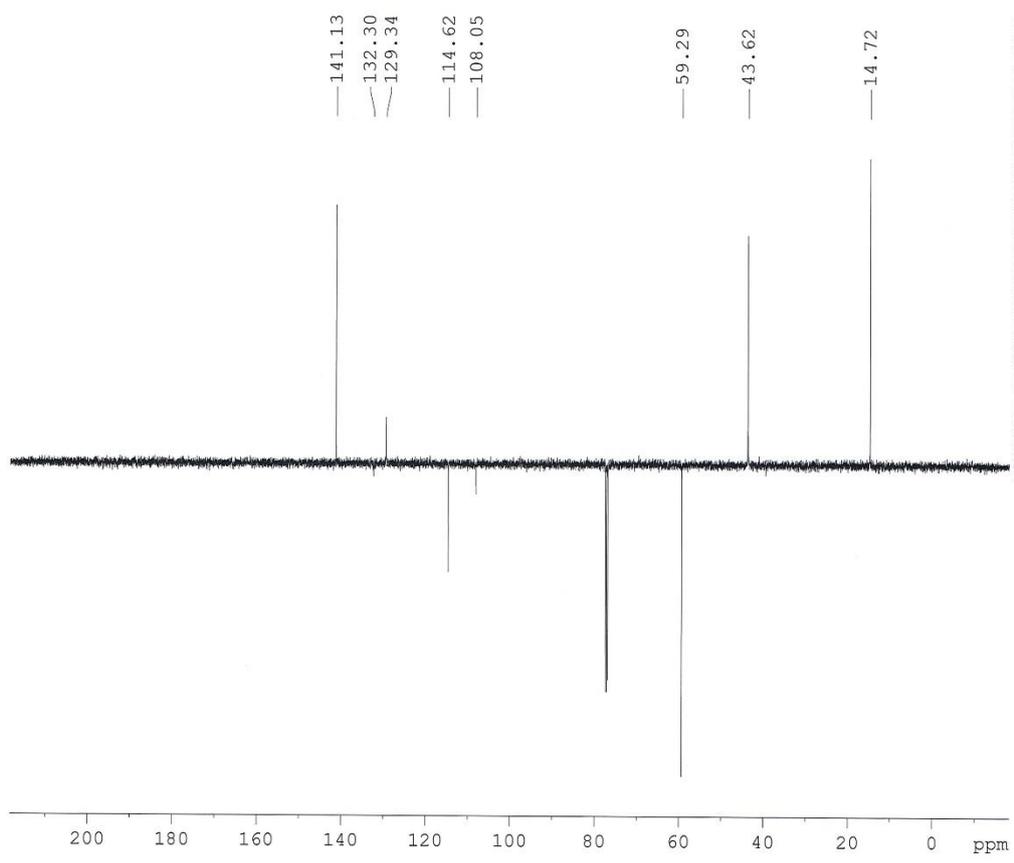
F2 - Processing parameters  
 SI 65536  
 SF 500.1300121 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00











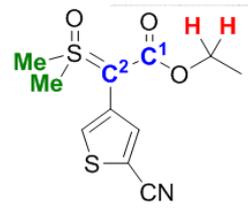
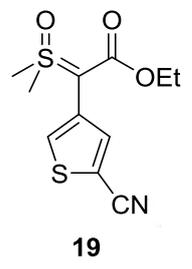
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Current Data Parameters
NAME      Compound 19
EXPNO    3
PROCNO   1

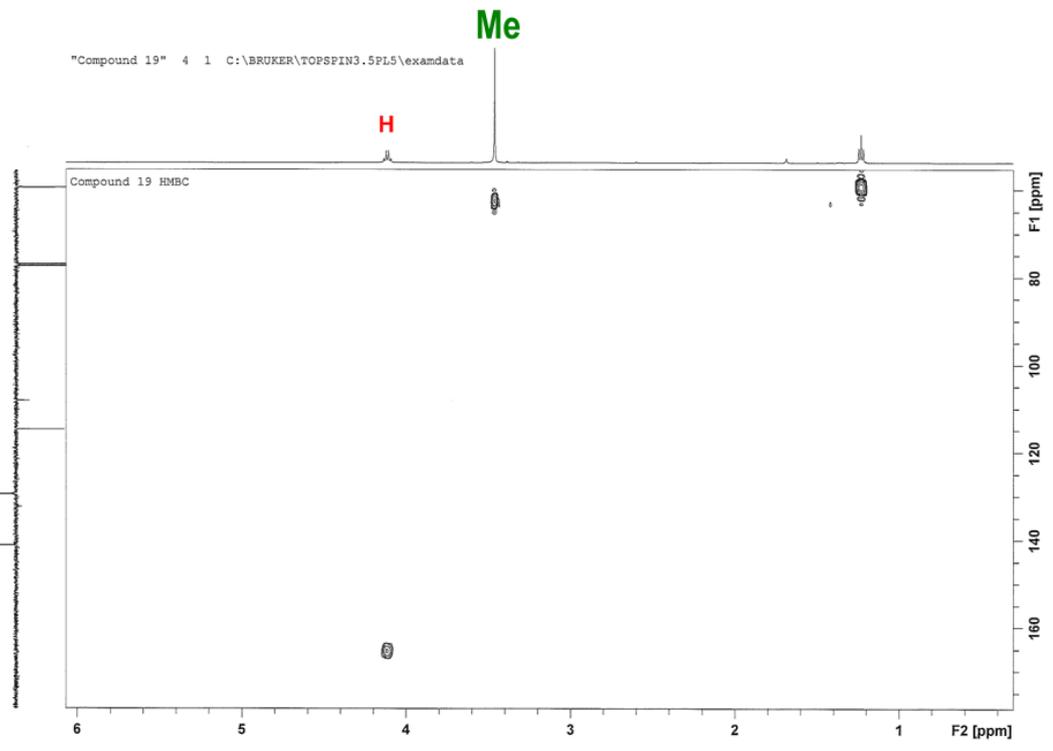
F2 - Acquisition Parameters
Date_    20180921
Time     2.54 h
INSTRUM  spect
PROBHD   zgpg30
PULPROG  zgpg30
TD        65536
SOLVENT  CDCl3
NS        5120
DS        4
SWH       29761.904 Hz
FIDRES    0.908263 Hz
AQ         1.1010048 sec
RG         399.17
DS         16.800 usec
DE         6.50 usec
TE         298.0 K
CNS22     145.0000000
CNST11    1.0000000
D1         4.0000000 sec
D2         0.00699655 sec
D30        0
TDO        0
SFO1       125.7703643 MHz
NUC1       13C
F1         8.00 usec
F2         16.00 usec
FLW1       53.0000000 W
SFO2       500.1320005 MHz
NUC2       1H
CPDPRG12  waltz16
PCPD2      80.00 usec
PLW2       28.0000000 W
PLW12      0.42017001 W

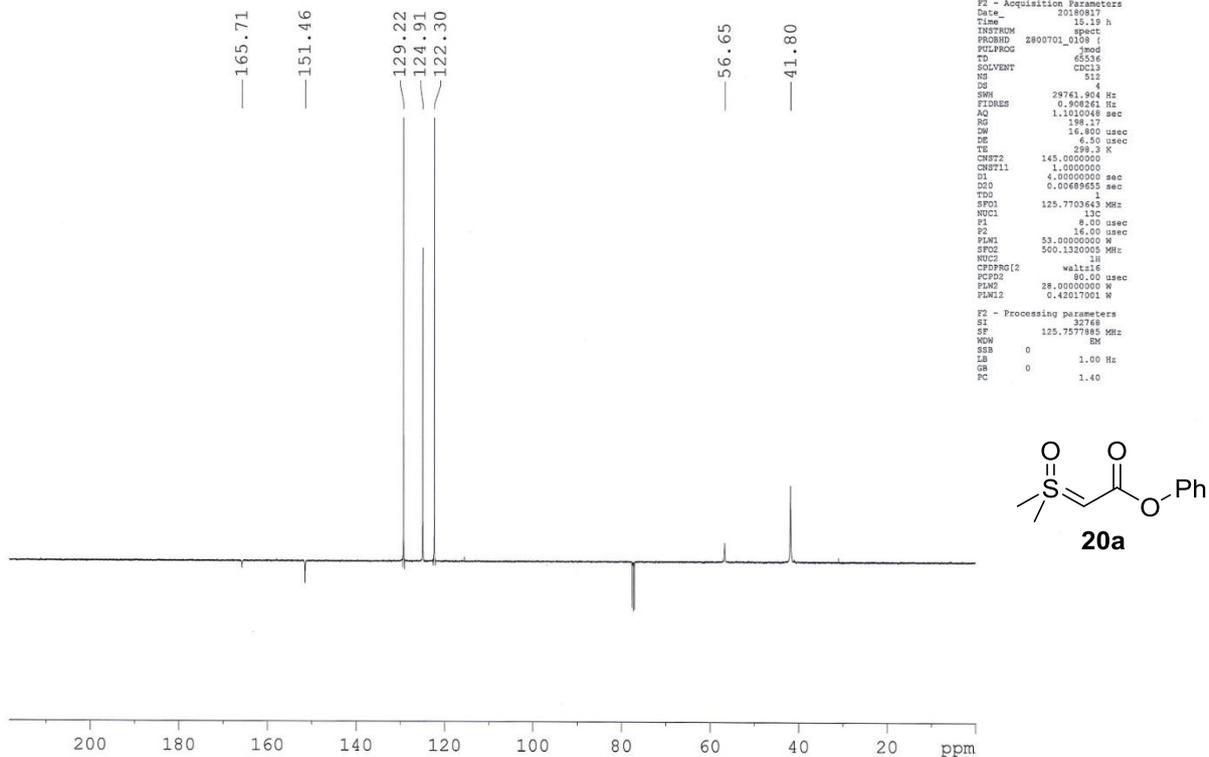
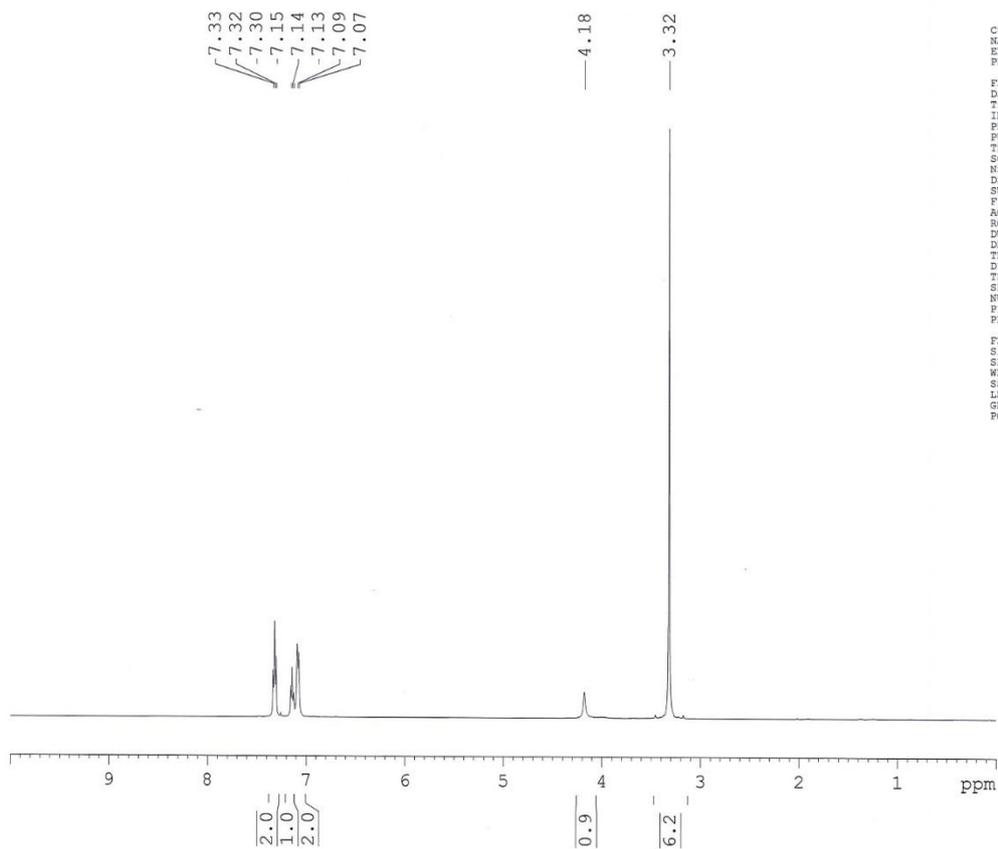
F2 - Processing parameters
SI         32768
SF         125.7577885 MHz
WDW        EM
SFB         0
LB          1.00 Hz
GB          0
PC          1.40

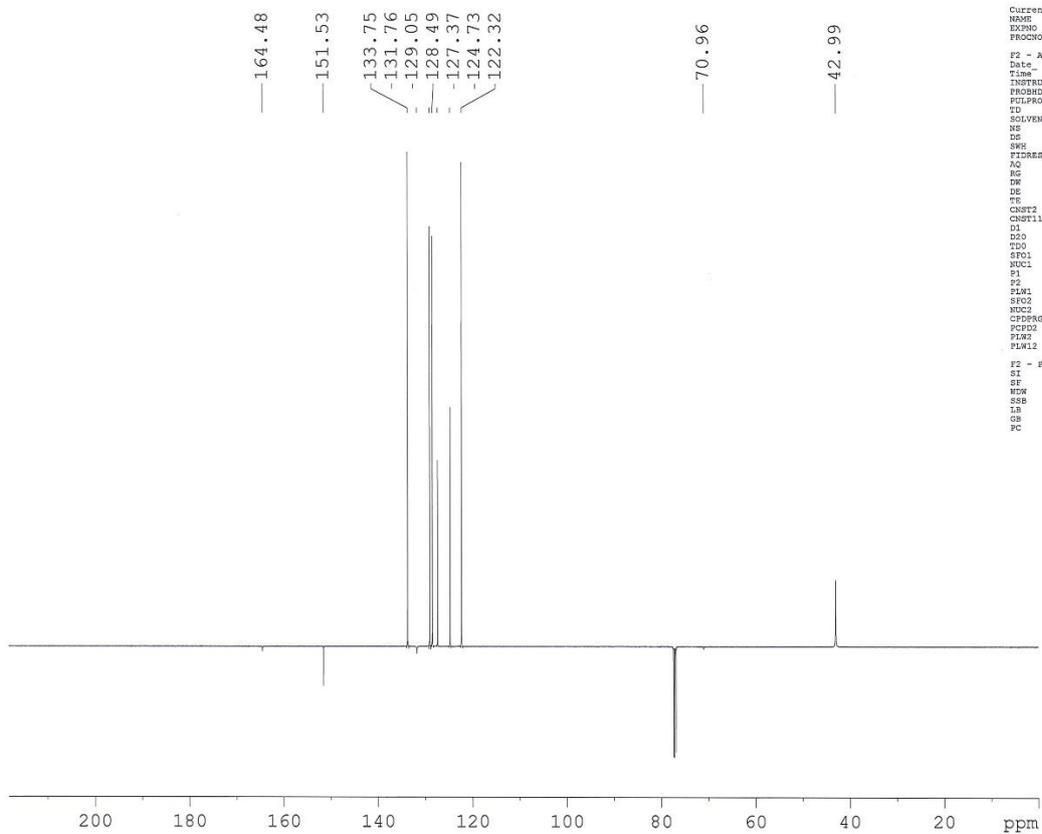
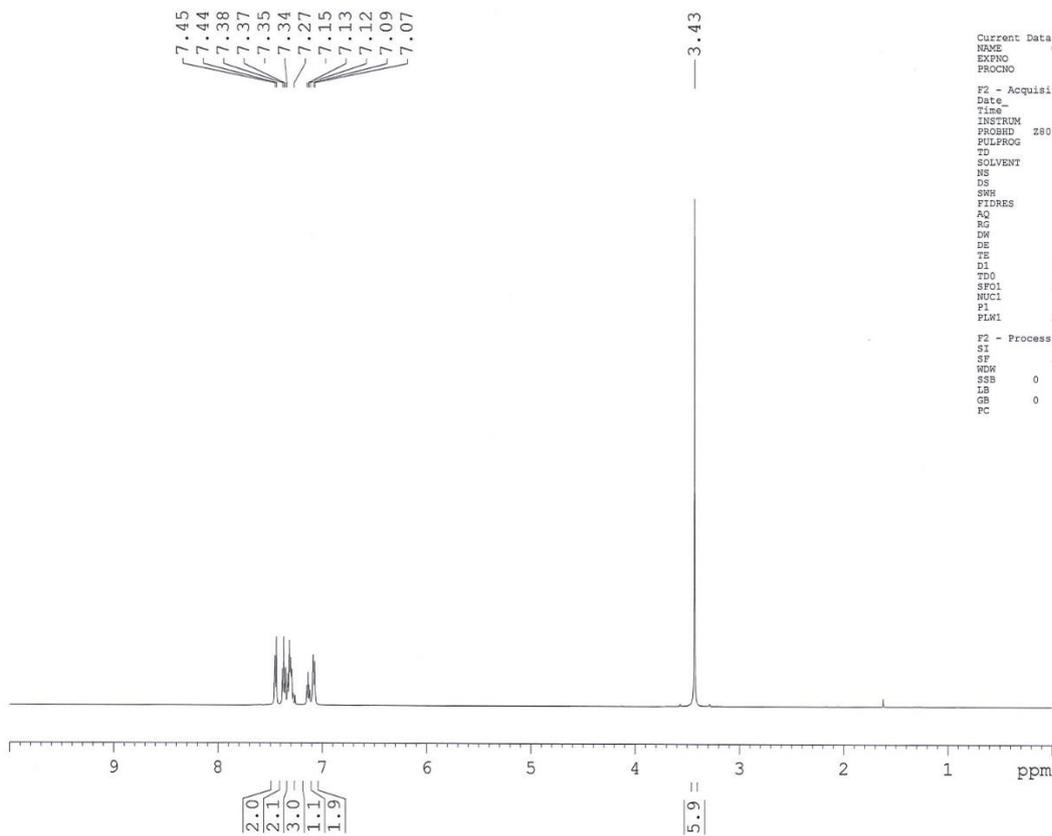
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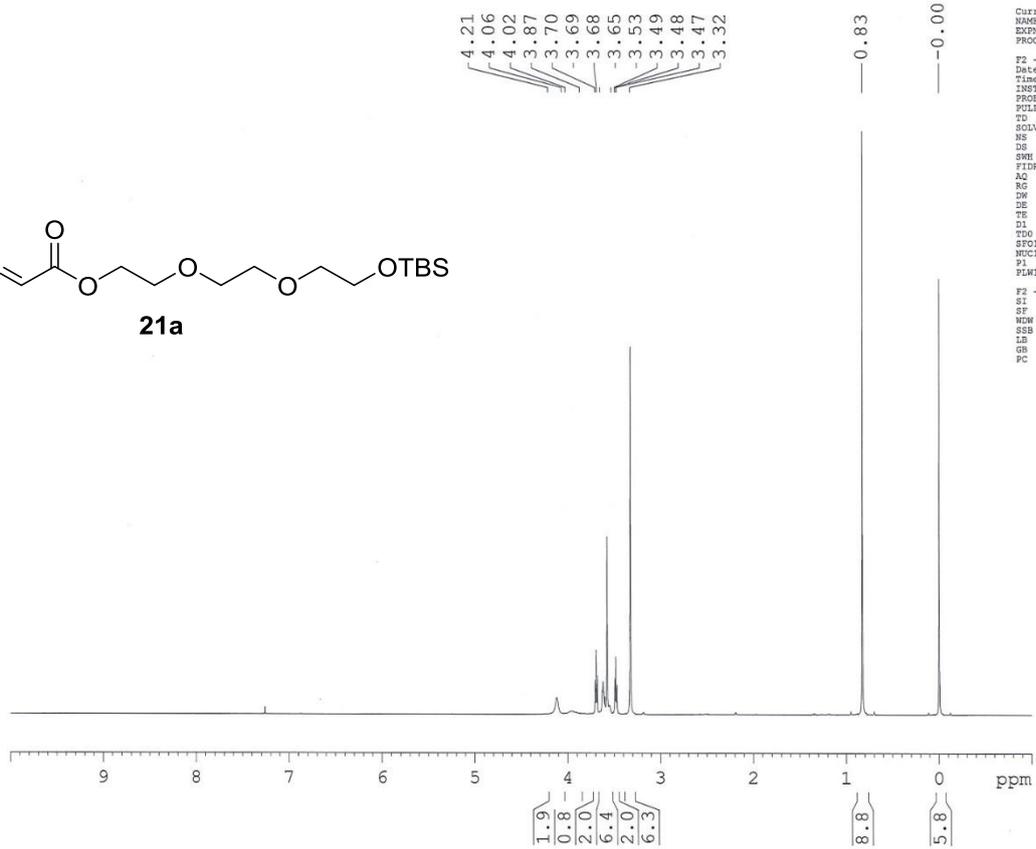
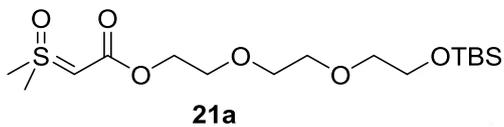


**19 - key HMBC**



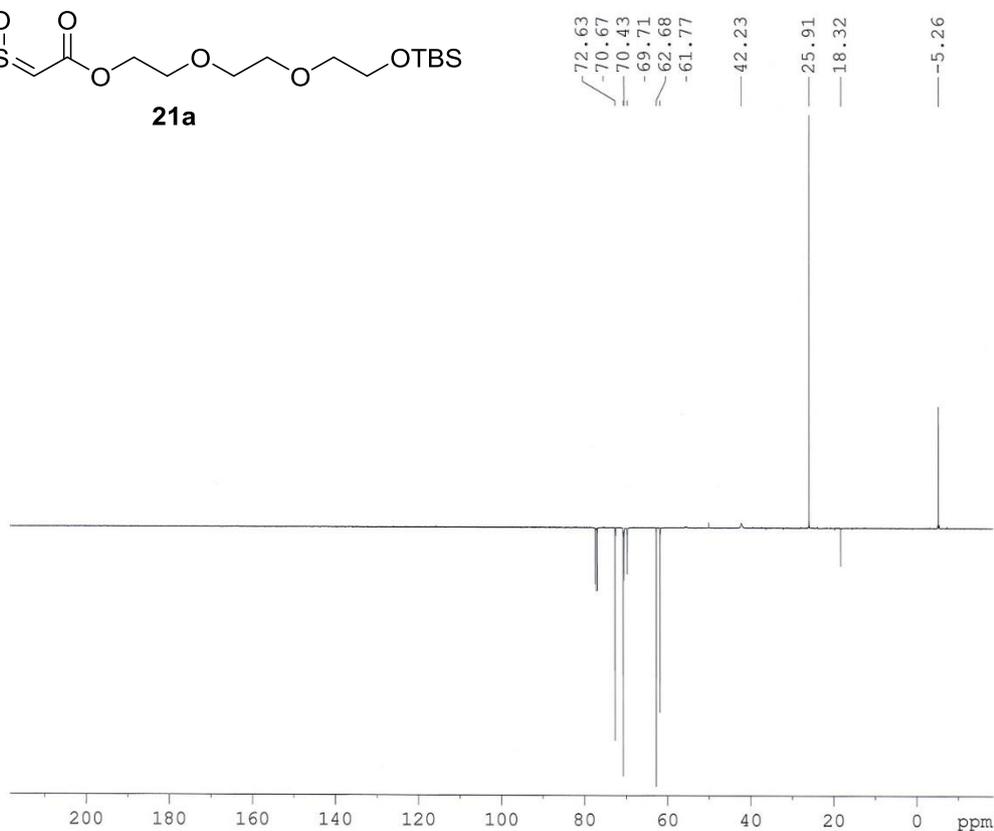
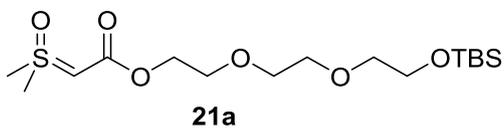






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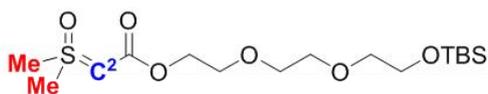
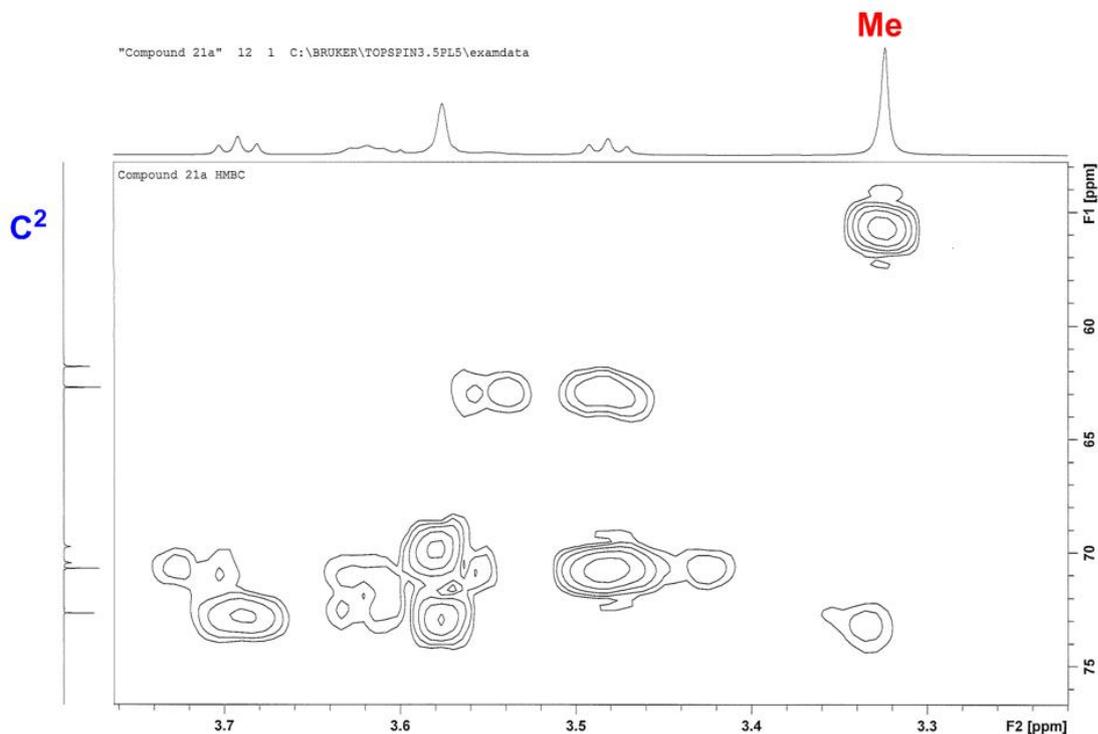
Current Data Parameters
NAME      Compound 21a
EXPNO    10
PROCNO   1
-----
F2 - Acquisition Parameters
Date_    20181020
Time     18.13 h
INSTRUM  spect
PROBHD   Z800701_0108 (
PULPROG  zg30
TD        65536
SOLVENT  CDCl3
NS        16
DS        2
SWH       10000.000 Hz
FIDRES    0.305176 Hz
AQ        3.2767999 sec
RG        30.81
DW        50.000 usec
DE        6.50 usec
TE        299.0 K
D1        1.00000000 sec
TDO       1
SFO1      500.1330883 MHz
NUC1      1H
P1        10.00 usec
PLM1      26.00000000 W
-----
F2 - Processing parameters
SI        65536
SF        500.1300122 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB        0
PC        1.00
  
```



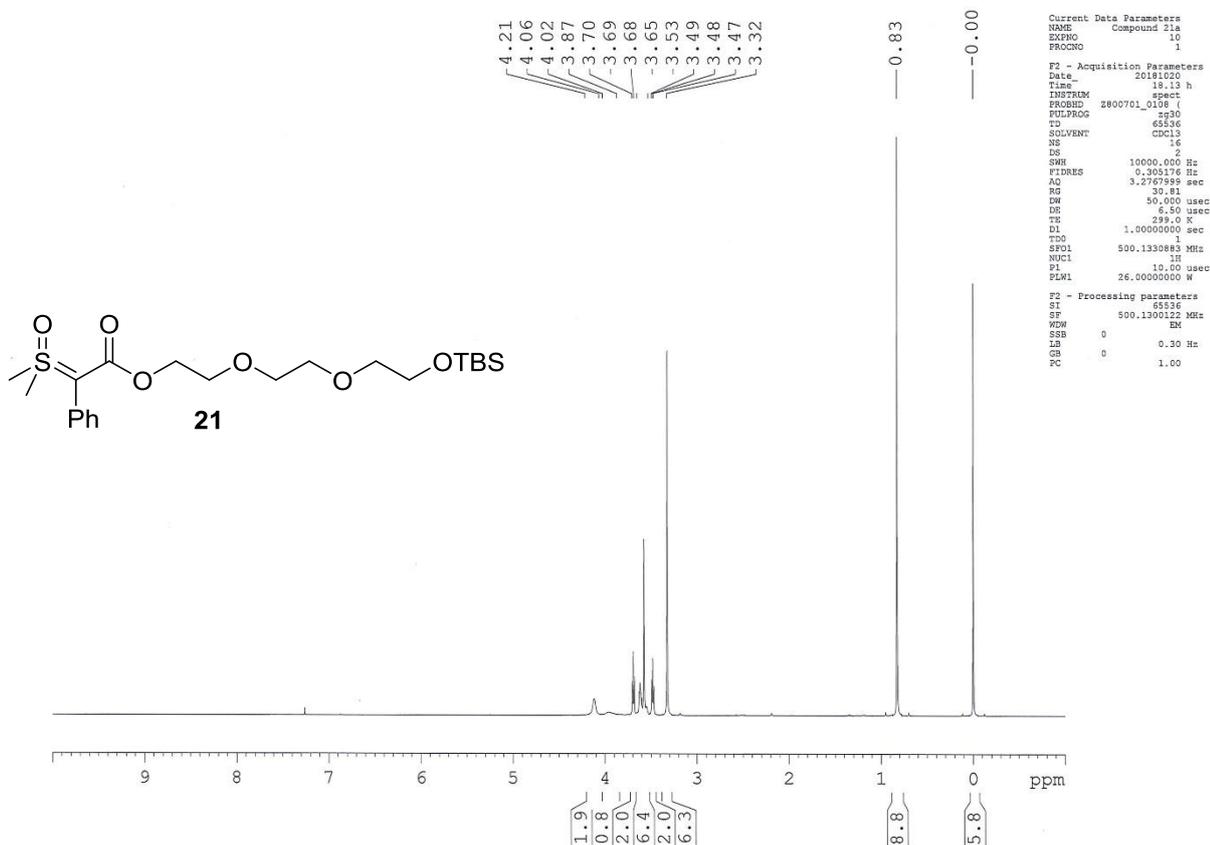
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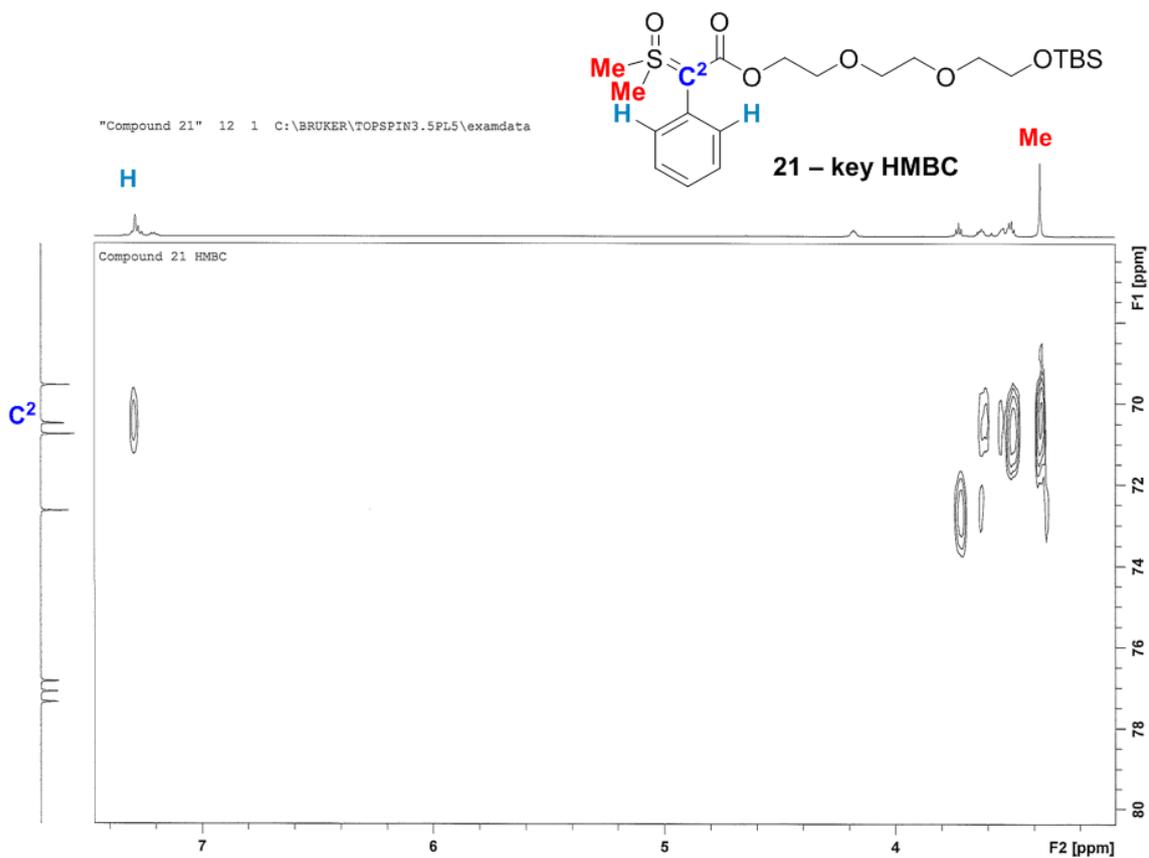
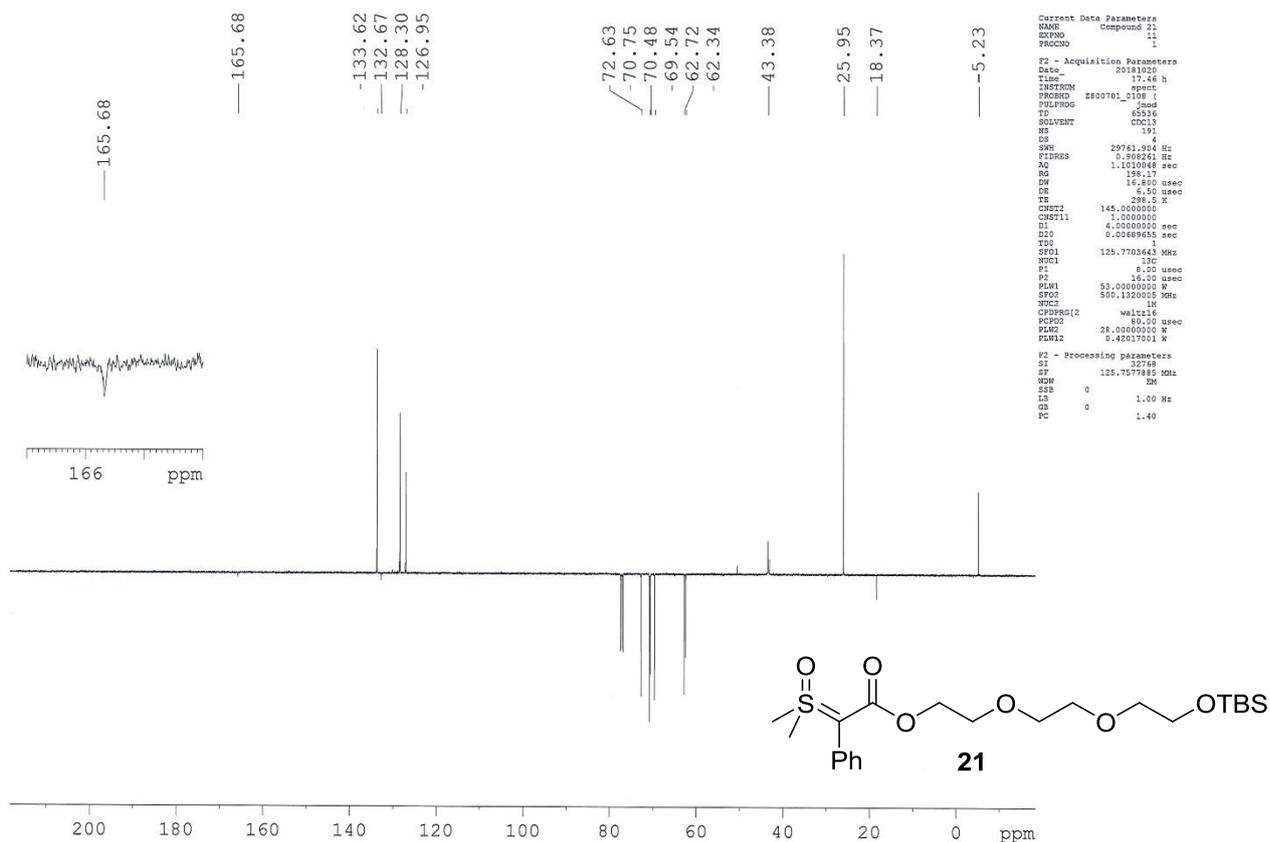
Current Data Parameters
NAME      Compound 21a
EXPNO    11
PROCNO   1
-----
F2 - Acquisition Parameters
Date_    20181020
Time     19.50 h
INSTRUM  spect
PROBHD   Z800701_0108 (
PULPROG  zgpg30
TD        65536
SOLVENT  CDCl3
NS        1101
DS        4
SWH       29761.904 Hz
FIDRES    0.908261 Hz
AQ        1.1010048 sec
RG        198.17
DW        16.900 usec
DE        6.50 usec
TE        299.0 K
-----
CNST2    145.0000000
CNST11   1.0000000
P1        4.0000000 sec
D20       0.00689605 sec
TDO       1
SFO1      125.7703643 MHz
NUC1      13C
P1        8.00 usec
P2        16.00 usec
PLM1      53.00000000 W
SFO2      500.1320005 MHz
NUC2      1H
CPDPRG2  waltz16
PCPD2     90.00 usec
PLM2      28.00000000 W
PLM12     0.42017001 W
-----
F2 - Processing parameters
SI        32768
SF        125.7577885 MHz
WDW       EM
SSB       0
LB        1.00 Hz
GB        0
PC        1.40
  
```

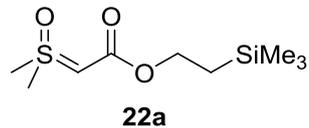
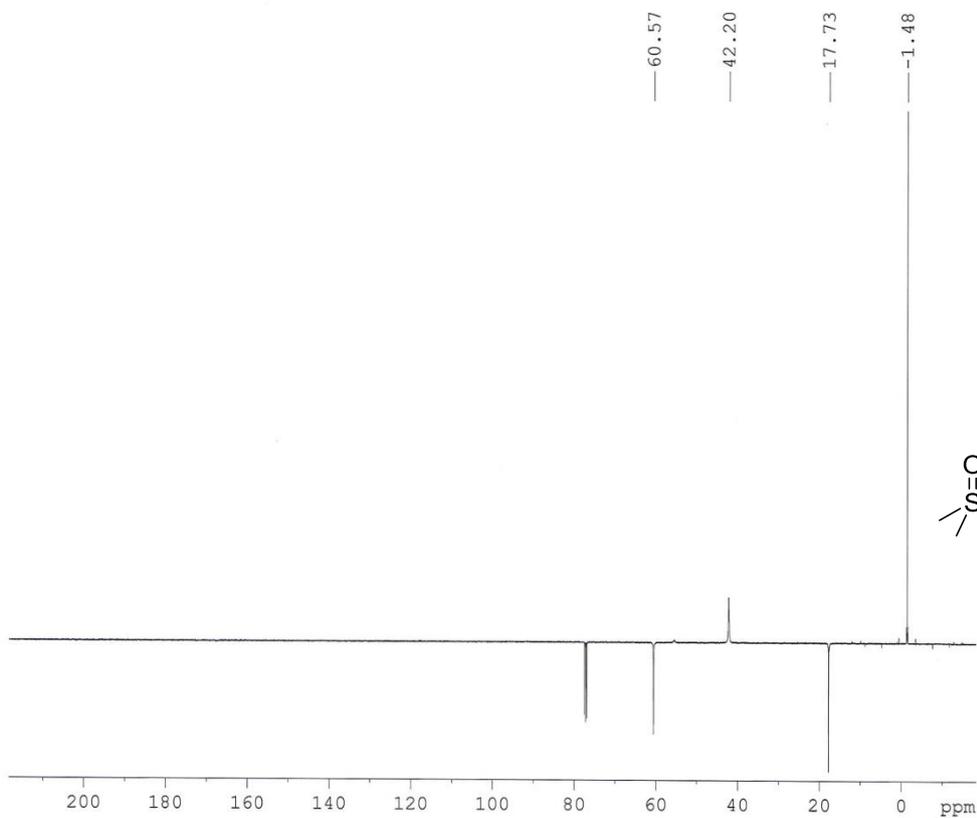
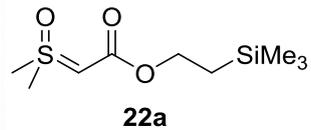
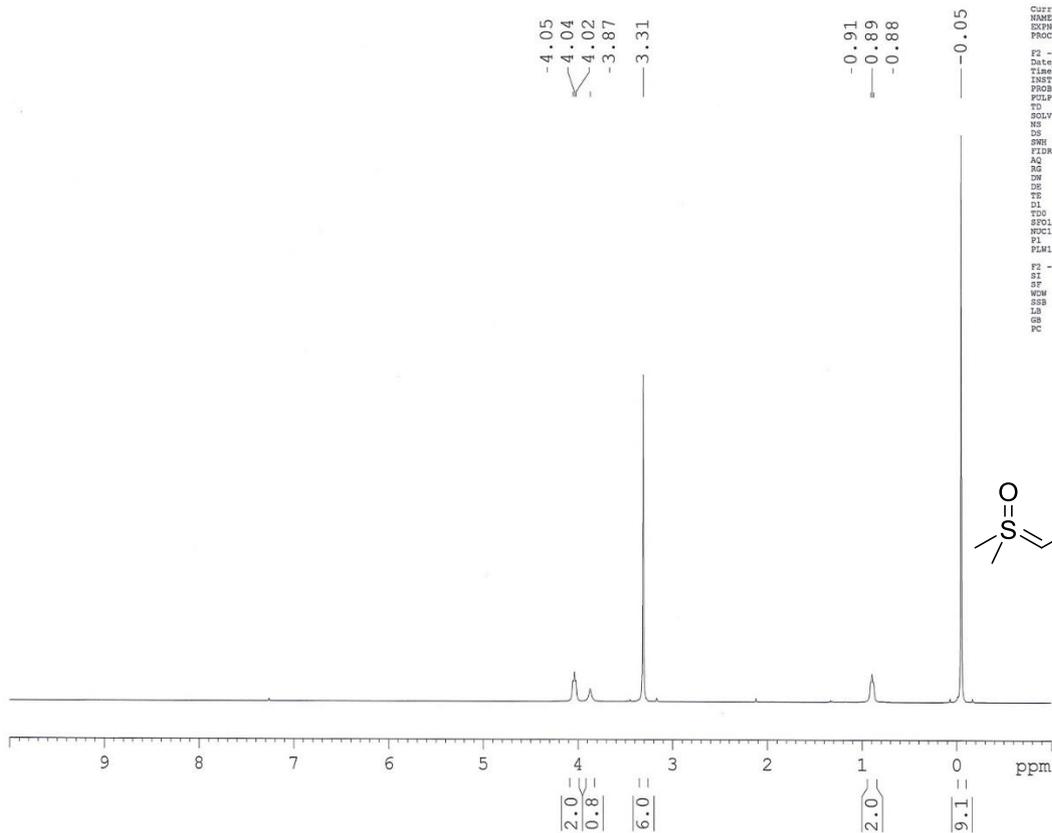
"Compound 21a" 12 1 C:\BRUKER\TOPSPIN3.5PL5\examdata

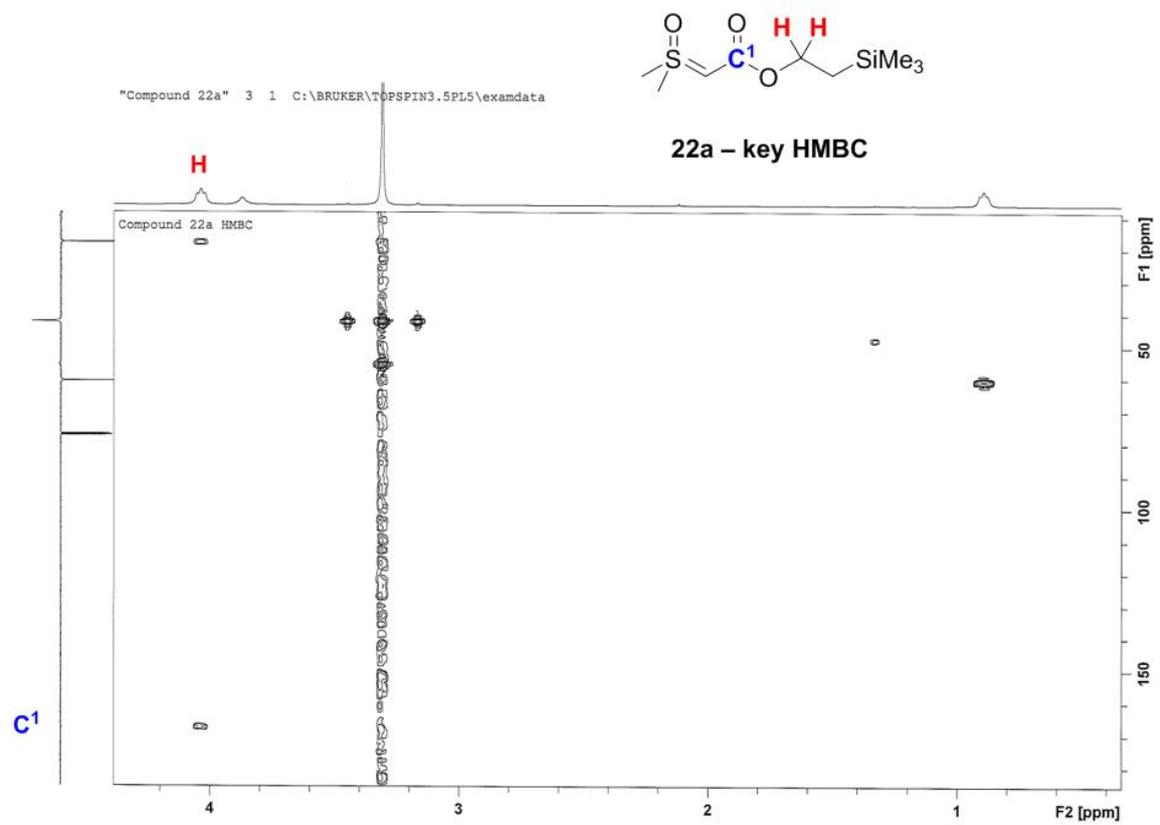
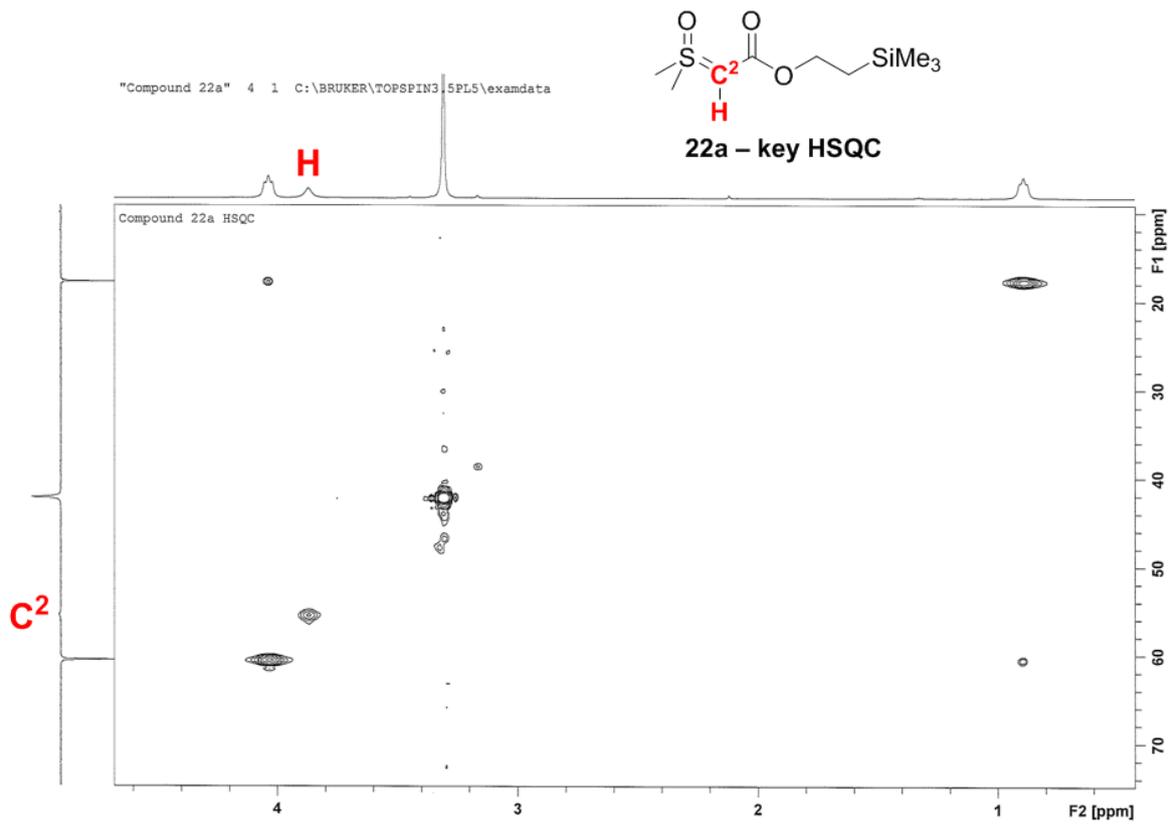


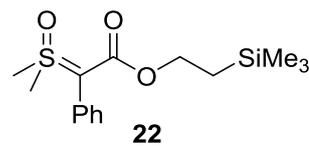
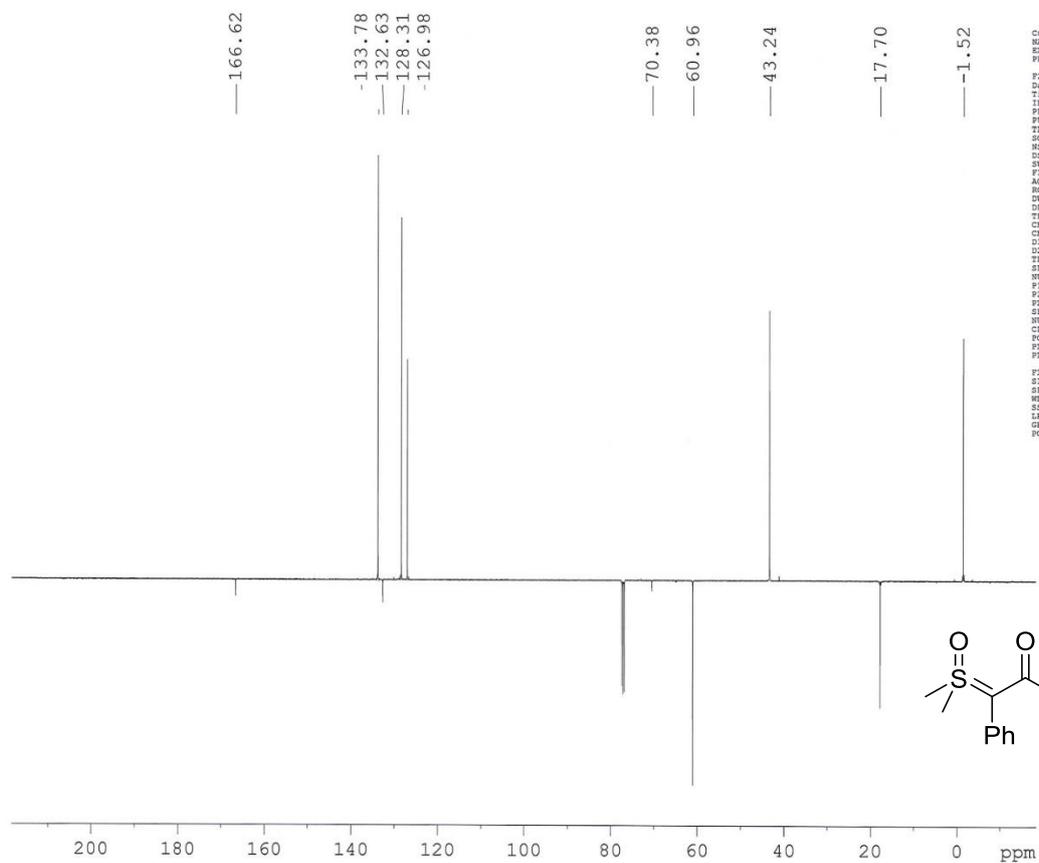
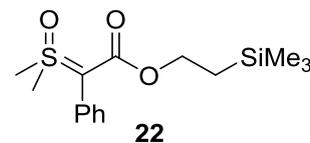
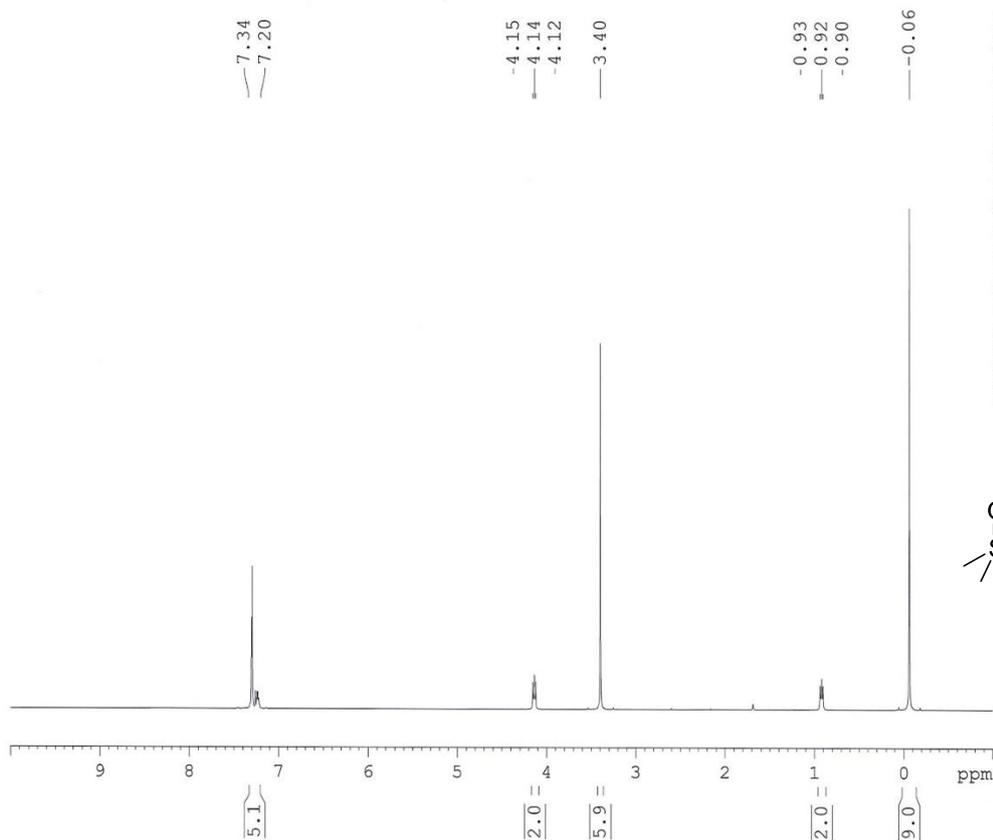
21a - key HMBC

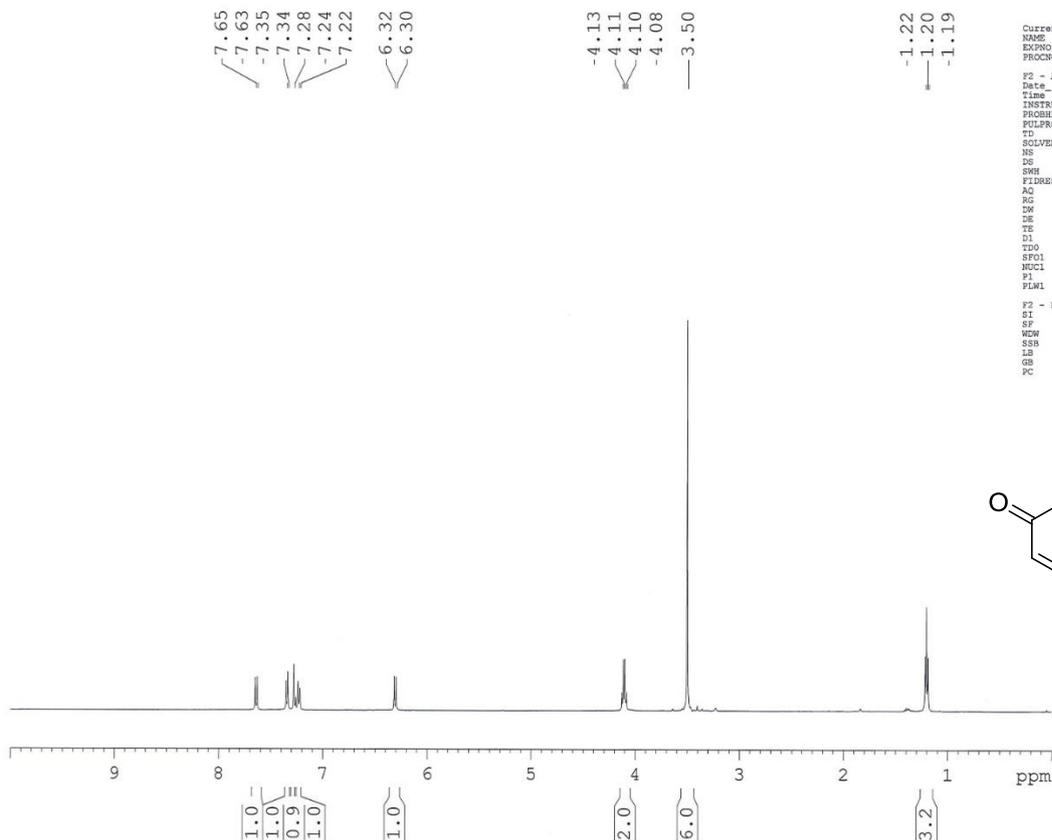




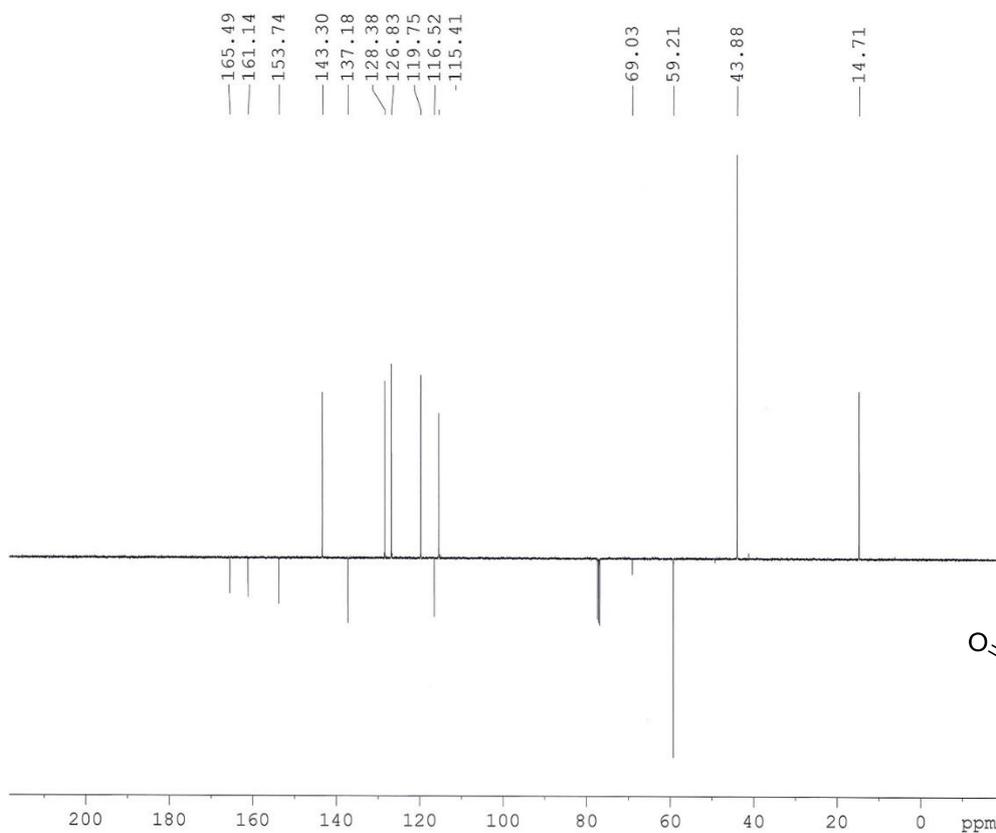
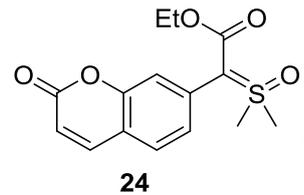




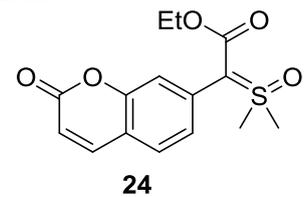




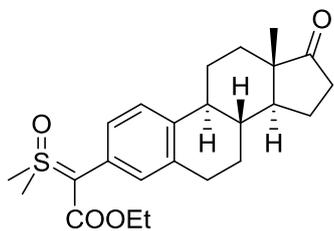
Current Data Parameters  
 NAME Compound 24  
 EXPNO 2  
 PROCNO 1  
 F2 - Acquisition Parameters  
 Date 20180919  
 Time 11:21 h  
 INSTRUM spect  
 PROBHD Z800701\_0108 ( )  
 PULPROG zg30  
 TD 65536  
 SCLVNT CDCl3  
 NS 6  
 DS 2  
 SWH 10000.000 Hz  
 FIDRES 0.308176 Hz  
 AQ 3.2767959 sec  
 RG 1024  
 DW 50.000 usec  
 DE 6.50 usec  
 TE 298.0 K  
 D1 1.00000000 sec  
 TRO 1  
 SFO1 500.1330883 MHz  
 NUC1 1H  
 P1 10.00 usec  
 PLW1 26.00000000 W  
 F2 - Processing parameters  
 SI 65536  
 SF 500.1300125 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



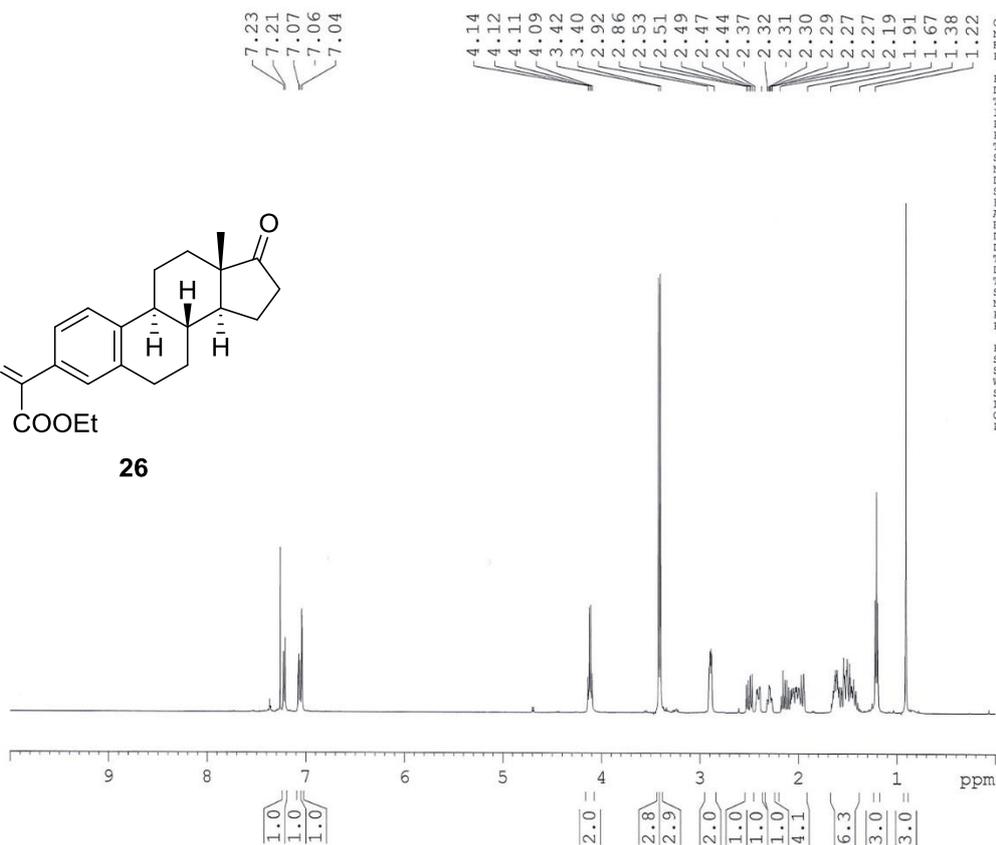
Current Data Parameters  
 NAME Compound 24  
 EXPNO 3  
 PROCNO 1  
 F2 - Acquisition Parameters  
 Date 20180919  
 Time 11:47 h  
 INSTRUM spect  
 PROBHD Z800701\_0108 ( )  
 PULPROG jmod  
 TD 65536  
 SCLVNT CDCl3  
 NS 4  
 DS 4  
 SWH 29761.904 Hz  
 FIDRES 0.908261 Hz  
 AQ 1.1010048 sec  
 RG 198.17  
 DW 16.800 usec  
 DE 6.50 usec  
 TE 298.0 K  
 CNST2 145.000000  
 CNST11 1.000000  
 D1 4.0000000 sec  
 D20 0.00689655 sec  
 TRO 1  
 SFO1 125.7703643 MHz  
 NUC1 13C  
 P1 8.00 usec  
 P2 16.00 usec  
 PLW1 53.0000000 W  
 SFO2 500.1320005 MHz  
 NUC2 1H  
 CPDPRG2 waltz16  
 PCPD2 80.00 usec  
 PLW2 28.0000000 W  
 PLW12 0.42017001 W  
 F2 - Processing parameters  
 SI 32768  
 SF 125.7577885 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40







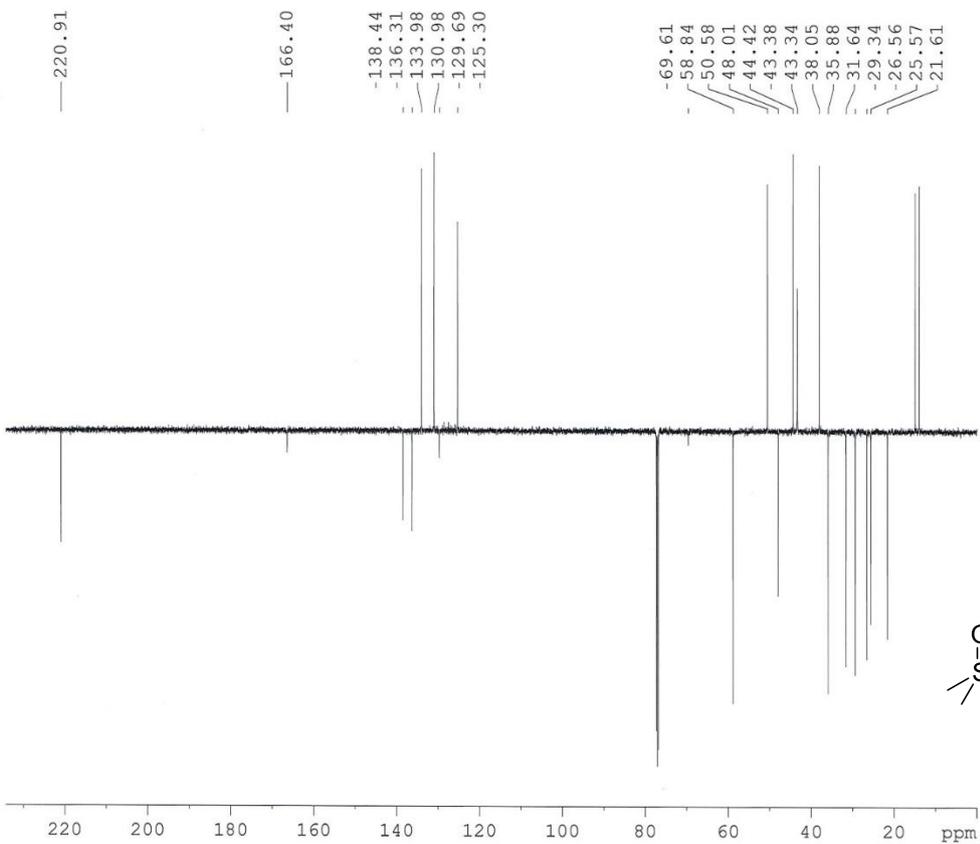
26



Current Data Parameters  
 NAME Compound 26  
 EXPNO 10  
 PROCNO 1

F2 - Acquisition Parameters  
 Date 20181027  
 Time 21.43 h  
 INSTRUM spect  
 PROBHD Z800701\_0108 ( )  
 PULPROG zg30  
 TD 65536  
 SOLVENT CDCl3  
 NS 16  
 DS 2  
 SWH 10000.000 Hz  
 FIDRES 0.305176 Hz  
 AQ 3.274799 sec  
 RG 155.66  
 DW 50.000 usec  
 DE 6.50 usec  
 TE 298.3 K  
 D1 1.00000000 sec  
 TDO 1  
 SFO1 500.1330883 MHz  
 NUC1 1H  
 P1 10.00 usec  
 PLW1 26.00000000 W

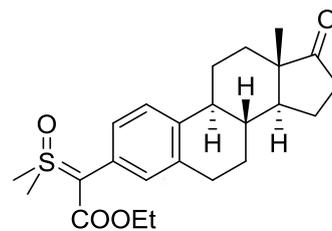
F2 - Processing parameters  
 SI 65536  
 SF 500.1300124 MHz  
 WDW EM  
 SSB 0  
 LB 0.30 Hz  
 GB 0  
 PC 1.00



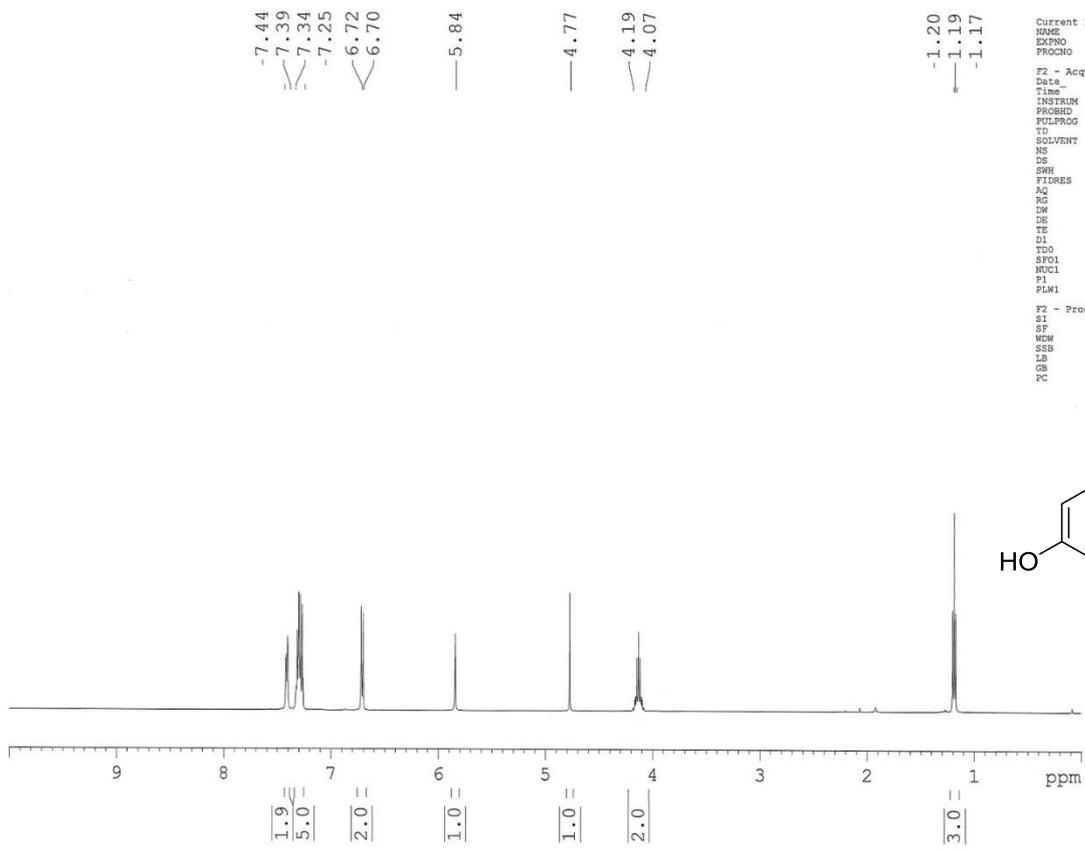
Current Data Parameters  
 NAME Compound 26  
 EXPNO 31  
 PROCNO 1

F2 - Acquisition Parameters  
 Date 20181103  
 Time 16.25 h  
 INSTRUM spect  
 PROBHD Z800701\_0108 ( )  
 PULPROG jmod  
 TD 65536  
 SOLVENT CDCl3  
 NS 963  
 DS 4  
 SWH 31250.000 Hz  
 FIDRES 0.933674 Hz  
 AQ 1.0485760 sec  
 RG 198.17  
 DW 16.000 usec  
 DE 6.50 usec  
 TE 298.0 K  
 CNST2 145.0000000  
 CNST11 1.0000000  
 D1 4.0000000 sec  
 D20 0.00689655 sec  
 TDO 1  
 SFO1 125.7716219 MHz  
 NUC1 13C  
 P1 6.00 usec  
 P2 16.00 usec  
 PLW1 53.00000000 W  
 SFO2 500.1320005 MHz  
 NUC2 1H  
 CPMRG[2] waltz16  
 PCPD2 80.00 usec  
 PLW2 28.00000000 W  
 PLW12 0.42017001 W

F2 - Processing parameters  
 SI 32768  
 SF 125.7577885 MHz  
 WDW EM  
 SSB 0  
 LB 1.00 Hz  
 GB 0  
 PC 1.40



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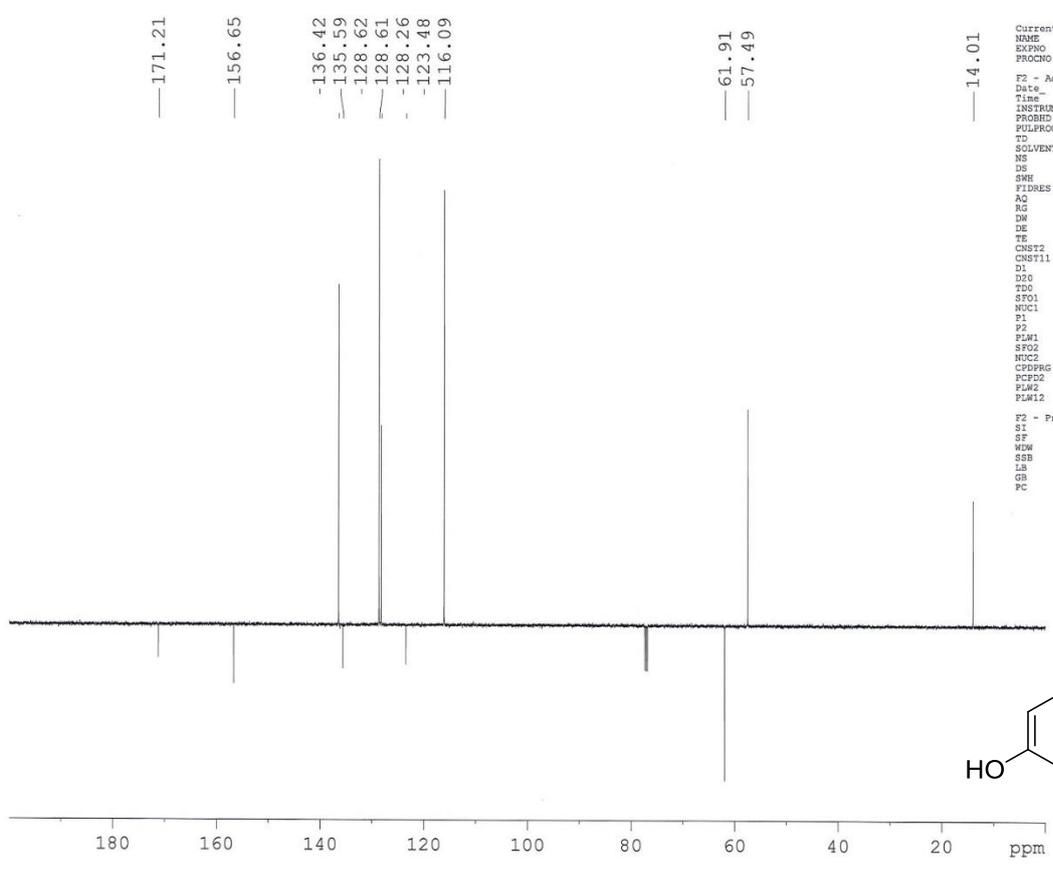
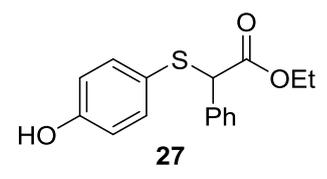


```

Current Data Parameters
NAME      Compound 27
EXPNO    2
PROCNO   1

F2 - Acquisition Parameters
Date_    20180918
Time     19.18 h
INSTRUM  spect
PROBHD   Z800701_019
PULPROG  zg30
TD       65536
SOLVENT  CDCl3
NS       4
DS       2
SWH      10000.000 Hz
FIDRES   0.305176 Hz
AQ       3.2767999 sec
RG       120.08
DW       50.000 usec
DE       6.50 usec
TE       298.0 K
D1       1.0000000 sec
TDO     500.133083 MHz
SFO1     500.133083 MHz
NUC1     1H
PI       10.00 usec
PLW1    26.0000000 W

F2 - Processing parameters
SI       65536
SF       500.1300127 MHz
WDW      EM
SSB      0
LB       0.30 Hz
GB       0
PC       1.00
  
```

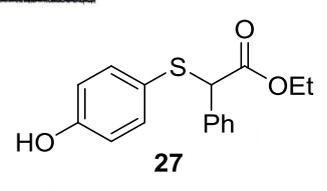


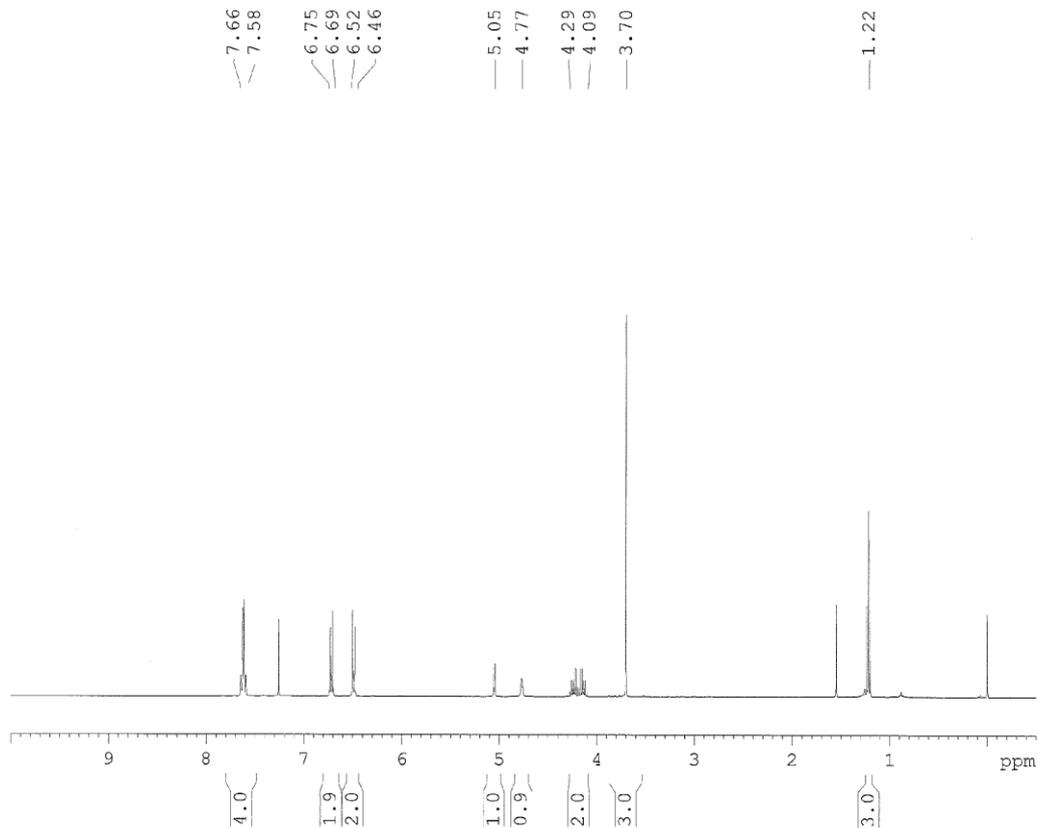
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Current Data Parameters
NAME      Compound 27
EXPNO    3
PROCNO   1

F2 - Acquisition Parameters
Date_    20180918
Time     19.30 h
INSTRUM  spect
PROBHD   Z800701_019
PULPROG  jmod
TD       65536
SOLVENT  CDCl3
NS       4
DS       169
SWH      29761.904 Hz
FIDRES   0.908261 Hz
AQ       1.1010048 sec
RG       198.17
DW       16.800 usec
DE       6.50 usec
TE       298.0 K
D1       145.000000 sec
CNST11   1.0000000
DI       2.0000000 sec
D20     0.0068965 sec
TDO     125.770364 MHz
SFO1    125.770364 MHz
NUC1     13C
PI       8.00 usec
PLW1    53.0000000 W
SFO2     500.1320005 MHz
NUC2     1H
CPDPRG2  waltz16
PCPD2    80.00 usec
PLW2    28.0000000 W
PLW12    0.42017001 W

F2 - Processing parameters
SI       65536
SF       125.7577885 MHz
WDW      EM
SSB      0
LB       1.00 Hz
GB       0
PC       1.40
  
```





```

Current Data Parameters
NAME      Compound 28
EXPNO    10
PROCNO   1

F2 - Acquisition Parameters
Date_    20181214
Time     14.06 h
INSTRUM  R400
PROBHD   2104450_0265 (
PULPROG  sth.z
TD       65536
SOLVENT  CDCl3
NS       8
DS       0
SWH      7062.147 Hz
FIDRES   0.215520 Hz
AQ       4.6398489 sec
RG       55.34
DW       70.800 usec
DE       11.13 usec
TE       300.0 K
D1       2.0000000 sec
TD0      1
SFO1     400.1324710 MHz
NUC1     1H
P1       10.10 usec
PLWL     16.70000076 W

F2 - Processing parameters
SI       65536
SF       400.1300109 MHz
WDW      EM
SSB      0
LB       0.19 Hz
GB       0
PC       1.00

```

