SUPPORTING INFORMATION

Synthesis of Sulfones from Organozinc Reagents, DABSO, and Alkyl Halides

Benjamin N. Rocke*, Kevin B. Bahnck, Michael Herr, Sophie Lavergne, Vincent Mascitti, Christian Perreault, Jana Polivkova, and Andrei Shavnya

Pfizer Worldwide Medicinal Chemistry, Eastern Point Rd., Groton, CT 06340, USA

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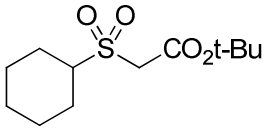
Experimental

General. Reactions were performed in oven- or heat gun-dried glassware under nitrogen. Solid reagents were added under air, and the reaction vessel's inert atmosphere was quickly re-established by repeatedly evacuating and back-filling the vessel with nitrogen. Prior to use, the nitrogen was passed through a tube packed with Drierite. Unless otherwise stated, products were estimated to be at least 95% pure. Analytical TLC was performed using EMD pre-coated silica gel 60 F_{254} glass plates (250 µm layer thickness). TLC spots were visualized under UV irradiation (λ = 254 nM) and/or with iodine, $KMnO_4$, or anisaldehyde stains.[1]

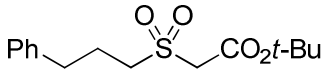
Materials. Commercial solvents (Acros AcroSeal and EMD Chemicals DriSolv products) and reagents were used without further purification. Commercial organozinc reagents were purchased from Aldrich or Reike Metals, Inc. DABSO ($DABCO{\cdot}SO_2$) was prepared according to precedent[2] or purchased from Aldrich; any coarse material was ground with a mortar and pestle. Zinc was purchased from Aldrich in either the <10 µm or <15 µm particle size. Benzyl bromide was eluted through a column of activity I basic alumina immediately prior to use. Commercial 2,5-diiodothiophene was purified by elution through a silica plug using heptane, after which it was isolated as a white, crystalline solid.

Instrumentation. Purifications were accomplished by medium performance liquid chromatography (MPLC) using Isco CombiFlash R_f (or similar) instruments and pre-packed Isco RediSep Gold (or similar) silica gel cartridges. Melting points were measured using a Büchi Melting Point B-545 apparatus and are reported without correction. Proton (^{1}H NMR) and carbon (^{13}C NMR) nuclear magnetic spectroscopy data were recorded on 400 or 500 MHz Varian or Bruker spectrometers. Chemical shifts are expressed in ppm (δ) downfield from tetramethylsilane and referenced to the deuterated solvent residual peak.[3] LCMS data were acquired on a Waters Acquity UPLC (or similar) instrument using a Waters Acquity HSS T3 column, water/MeCN gradient, and 0.1% (v/v) formic acid as a modifier. The column eluent was analyzed using a Waters SQ mass spectrometer with ESI and APCI methods scanning in both positive and negative ion modes from 100 to 2000 Da. GCMS data were acquired using a Hewlett Packard 6890 oven with an HP 6890 injector, HP-1 column (12 m×0.2 mm×0.33 µm), and helium carrier gas. The sample was analyzed on an HP 5973 mass selective detector scanning from 50 to 550 Da using EI. High resolution mass spectrometry (HRMS) was conducted on an Agilent 6220 TOF mass spectrometer in positive electrospray mode. Samples were separated by UPLC on an Agilent 1200 system prior to mass spectrometric analysis. The resulting spectra were automatically lockmass corrected, and the mass accuracy for all observed isotopes was calculated against the theoretical ion mass derived from the chemical formula using MassHunter software.

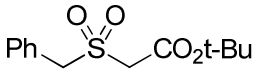
Typical procedure (using commercially available organozinc reagents). A dry, nitrogen-filled vial was charged with DABSO (66.1 mg, 0.55 eq.) and heated under dynamic vacuum in a 40 °C aluminum block for 20 min. After the nitrogen atmosphere was restored and the vial returned to r.t., a 0.50 M solution of an organozinc reagent in THF (1.00 mL) was added in one portion. The resulting mixture was vortexed for 2 min. to obtain a fine suspension and then stirred at r.t. for 15 min. DMSO (1.00 mL) and an alkylating agent were introduced to the reaction mixture, and the reaction mixture was placed in a 70 °C aluminum block for 1 h. The reaction mixture was then partitioned between MTBE (ca. 25 mL) and 1.0 M aq. HCl (ca. 25 mL). The MTBE layer was washed with brine, dried over sodium sulfate, and evaporated. Products were isolated from this crude material by MPLC (EtOAc/heptane gradient).



***tert*-Butyl 2-(cyclohexylsulfonyl)acetate** (**6a**). Compound **6a** (70.0 mg, 78%) was obtained as a clear, colorless oil according to the typical procedure using cyclohexylzinc(II) bromide solution (0.90 mL, 0.40 M in THF, 0.36 mmol), DABSO (53.2 mg, 0.221 mmol), *tert*-butyl bromoacetate (0.110 mL, 0.745 mmol), and DMSO (0.90 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 2 H), 3.26 (tt, *J*=12.2, 3.5 Hz, 1 H), 2.20–2.11 (m, 2 H), 1.96–1.86 (m, 2 H), 1.76–1.66 (m, 1 H), 1.64−1.43 (m, 11 H), 1.36−1.13 (m, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0 (1 C), 83.8 (1 C), 61.0 (1 C), 55.7 (1 C), 27.8 (3 C), 24.9 (1 C), 24.9 (2 C), 24.6 (2 C). HRMS (ESI) *m/z*: calc'd for $C_{12}H_{26}NO_4S$ [M+NH_4] 280.1577, found 280.1568.

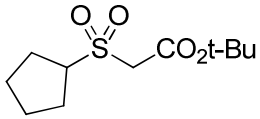


***tert*-Butyl 2-((3-phenylpropyl)sulfonyl)acetate** (**6b**). Compound **6b** (116 mg, 84%) was obtained as a clear, colorless oil according to the typical procedure using (3-phenylpropyl)zinc(II) bromide solution (0.93 mL, 0.5 M in THF, 0.46 mmol), DABSO (63.6 mg, 0.265 mmol), *tert*-butyl bromoacetate (0.16 mL, 1.1 mmol), and DMSO (0.93 mL). After introduction of *tert*-butyl bromoacetate, the reaction was heated in an aluminum block first at 70°C for 35 min. and then at 45 °C over 3 days. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.28 (m, 2H), 7.25−7.17 (m, 3H), 3.83 (s, 2H), 3.25−3.19 (m, 2H), 2.80 (t, *J*=7.43 Hz, 2H), 2.26−2.16 (m, 2H), 1.47 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0 (1 C), 139.7 (1 C), 128.7 (2 C), 128.4 (2 C), 126.5 (1 C), 84.1 (1 C), 58.7 (1 C), 52.7 (1 C), 34.2 (1 C), 27.8 (3 C), 23.4 (1 C). HRMS (ESI) *m/z*: calc'd for $C_{15}H_{26}NO_4S$ [M+NH_4] 316.1577, found 316.1567.

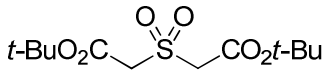


***tert*-Butyl 2-(benzylsulfonyl)acetate** (**6c**, method A). Compound **6c** (102 mg, 75%) was obtained as a clear, colorless oil that solidified upon standing according to the typical procedure using benzylzinc(II) bromide solution (1.0 mL, 0.5 M in THF, 0.5 mmol), DABSO (68.5 mg, 0.285 mmol), tert-butyl bromoacetate (0.17 mL, 1.2 mmol), and DMSO (1.0 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51−7.49 (m, 2 H), 7.42−7.37 (m, 3 H), 4.50 (s, 2 H), 3.68 (s, 2 H), 1.55 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (1 C), 130.9 (2 C), 129.2 (1 C), 129.1 (2 C), 127.9 (1 C), 84.2 (1 C), 59.3 (1 C), 55.7 (1 C), 27.9 (3 C). HRMS (ESI) *m/z*: calc'd for $C_{13}H_{22}NO_4S$ [M+NH_4] 288.1264, found 288.1276.

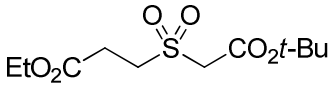
***tert*-Butyl 2-(benzylsulfonyl)acetate** (**6c**, method B). An oven-dried, nitrogen-filled vial was charged with benzylzinc(II) bromide solution (0.5 M in THF, 1.0 mL) and sparged with SO_2 (g) for 5 min. Addition of DMSO (1.0 mL) caused the previously white suspension to become clear and yellow. *tert*-Butyl bromoacetate (0.17 mL) was added in one portion, and the reaction mixture was placed in a 70 °C aluminum block for 1 h. After returning to r.t., the reaction mixture was partitioned between MTBE and 1.0 M aq. HCl. The aq. layer was extracted with MTBE, and the combined MTBE layers were washed with water, washed with brine, dried over sodium sulfate, and evaporated. Compound **6c** (84 mg, 62%) was obtained as a clear, colorless oil after MPLC purification (5−40% EtOAc/heptane gradient). Analytical data were consistent with that of the product obtained by method A.



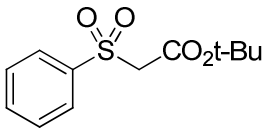
***tert*-Butyl 2-(cyclopentylsulfonyl)acetate** (**6d**). Compound **6d** (58.2 mg, 70%) was obtained as a clear, colorless oil that solidified upon standing according to the typical procedure using cyclopentylzinc(II) bromide solution (0.9 mL, 0.4 M in THF, 0.36 mmol), DABSO (50.1 mg, 0.208 mmol), *tert*-butyl bromoacetate (0.11 mL, 0.74 mmol), and DMSO (0.72 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 2 H), 3.81−3.74 (m, 1 H),2.12−1.98 (m, 4 H), 1.86−1.75 (m, 2 H), 1.71−1.60 (m, 2 H), 1.48 (s, 9 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1 (1 C), 83.8 (1 C), 61.4 (1 C), 57.6 (1 C), 27.8 (3 C), 26.7 (2 C), 26.0 (2 C). HRMS (ESI) *m/z*: calc'd for $C_{11}H_{24}NO_4S$ [M+NH_4] 266.1421, found 266.1423.



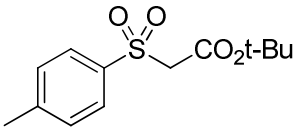
Di-*tert*-butyl 2,2'-sulfonyldiacetate (**6e**). Compound **6e** (87.4 mg, 63%) was obtained as a white solid, mp 53–55 °C, according to the typical procedure using (2-(*tert*-butoxy)-2-oxoethyl)zinc(II) chloride solution (0.94 mL, 0.5 M in diethyl ether, 0.47 mmol), DABSO (61.8 mg, 0.257 mmol), *tert*-butyl bromoacetate (184 mg, 0.941 mmol), and DMSO (0.94 mL). Due to the presence of a low-boiling solvent, the reaction mixture was stirred at r.t. for 16 h after addition of the alkylating agent. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.21 (s, 4 H), 1.51 (s, 18 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (2 C), 84.3 (2 C), 57.9 (2 C), 27.9 (6 C). HRMS (ESI) *m/z*: calc'd for $C_{12}H_{26}NO_6S$ [M+NH_4] 312.1475, found 312.1476.



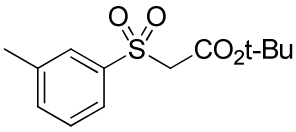
Ethyl 3-((2-(*tert*-butoxy)-2-oxoethyl)sulfonyl)propanoate (**6f**). Compound **6f** (46.0 mg, 34%) was obtained as a clear, colorless oil according to the typical procedure using (3-ethoxy-3-oxopropyl)zinc(II) bromide solution (0.95 mL, 0.5 M in THF, 0.48 mmol), DABSO (64 mg, 0.27 mmol), *tert*-butyl bromoacetate (0.14 mL, 0.95 mmol), and DMSO (0.95 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.19 (q, *J*=7.2 Hz, 2 H), 3.93 (s, 2 H), 3.64−3.57 (m, 2 H), 2.92−2.85 (m, 2 H), 1.51 (s, 9 H), 1.28 (t, *J*=7.2 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2 (1 C), 161.8 (1 C), 84.4 (1 C), 61.5 (1 C), 59.1 (1 C), 49.1 (1 C), 27.8 (3 C), 27.1 (s, 1 C), 14.1 (s, 1 C). HRMS (ESI) *m/z*: calc'd for $C_{11}H_{24}NO_6S$ [M+NH_4] 298.1319, found 298.1322.



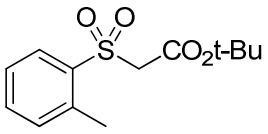
***tert*-Butyl 2-(phenylsulfonyl)acetate** (**6g**). Compound **6g** (57.8 mg, 44%) was obtained as a clear, colorless oil according to the typical procedure using phenylzinc(II) bromide solution (1.01 mL, 0.5 M in THF, 0.50 mmol), DABSO (66.4 mg, 0.276 mmol), *tert*-butyl bromoacetate (192 mg, 0.984 mmol), and DMSO (1.01 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J*=8.0 Hz, 2 H), 7.72−7.65 (m, 1 H), 7.62−7.55 (m, 2 H), 4.04 (s, 2 H), 1.36 (s, 9 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2 (1 C), 139.0 (1 C), 134.1 (1 C), 129.1 (2 C), 128.5 (2 C), 83.6 (1 C), 62.1 (1 C), 27.7 (3 C). HRMS (ESI) *m/z*: calc'd for $C_{12}H_{20}NO_4S$ [M+NH_4] 274.1108, found 274.1106.



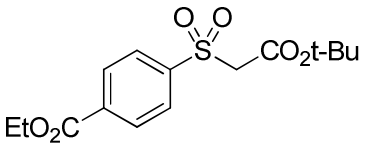
***tert*-Butyl 2-tosylacetate** (**6h**). Compound **6h** (48 mg, 36%) was obtained as a clear, colorless oil according to the typical procedure using *p*-tolylzinc(II) iodide solution (1.0 mL, 0.5 M in THF, 0.5 mmol), DABSO (68.5 mg, 0.285 mmol), *tert*-butyl bromoacetate (0.17 mL, 1.2 mmol), and DMSO (1.0 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84−7.81 (m, 2 H), 7.39−7.35 (m, 2 H), 4.01 (s, 2 H), 2.46 (s, 3 H), 1.38 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4 (1 C), 145.2 (1 C), 136.0 (1 C), 129.7 (2 C), 128.6 (2 C), 83.5 (1 C), 62.2 (1 C), 27.9 (3 C), 21.68 (1 C). HRMS (ESI) *m/z*: calc'd for $C_{13}H_{22}NO_4S$ [M+NH_4] 288.1264, found 288.1262.



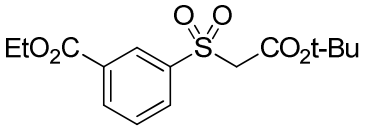
***tert*-Butyl 2-(*m*-tolylsulfonyl)acetate** (**6i**). Compound **6i** (46 mg, 34%) was obtained in ca. 91% purity[5] as a clear, colorless oil according to the typical procedure using *m*-tolylzinc(II) iodide solution (1.0 mL, 0.5 M in THF, 0.5 mmol), DABSO (66.1 mg, 0.275 mmol), *tert*-butyl bromoacetate (195 mg, 1.15 mmol), and DMSO (1.0 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77−7.71 (m, 2 H), 7.50−7.43 (m, 2 H), 4.02 (s, 2 H), 2.45 (s, 3 H), 1.36 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3 (1 C), 139.4 (1 C), 138.8 (1 C), 134.9 (1 C), 129.0 (1 C), 128.8 (1 C), 125.6 (1 C), 83.5 (1 C), 62.2 (1 C), 27.7 (3 C), 21.3 (1 C). HRMS (ESI) *m/z*: calc'd for $C_{13}H_{22}NO_4S$ [M+NH_4] 288.1264, found 288.1255.



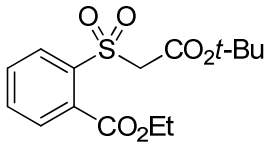
***tert*-Butyl 2-(*o*-tolylsulfonyl)acetate** (**6j**). Compound **6j** (59 mg, 44%) was obtained in ca. 81% purity[5] as a clear, colorless oil according to the typical procedure using *o*-tolylzinc(II) iodide solution (1.0 mL, 0.5 M in THF, 0.5 mmol), DABSO (66.1 mg, 0.275 mmol), *tert*-butyl bromoacetate (195 mg, 1.15 mmol), and DMSO (1.0 mL). An analytical sample obtained by complete removal of residual solvents under vacuum was used to obtain the spectra shown below. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J*=7.8, 1.6 Hz, 1 H), 7.56−7.52 (m, 1 H), 7.40−7.35 (m, 2 H), 4.08 (s, 2 H), 2.72 (s, 3 H), 1.30 (s, 9 H). ^{13}C NMR (100 MHz, CDCl3) δ 161.1 (1 C), 138.2 (1 C), 137.1 (1 C), 134.1 (1 C), 132.7 (1 C), 130.7 (1 C), 126.5 (1 C), 83.6 (1 C), 61.6 (1 C), 27.6 (3 C), 27.0 (1 C). HRMS (ESI) *m/z*: calc'd for $C_{13}H_{22}NO_4S$ [M+NH_4] 288.1264, found 288.1261.



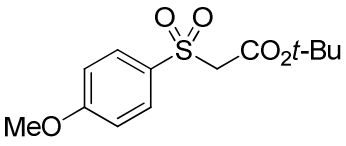
Ethyl 4-((2-(*tert*-butoxy)-2-oxoethyl)sulfonyl)benzoate (**6k**). Compound **6k** (59 mg, 65%) was obtained as a clear, colorless oil that solidified upon standing, mp 86–89 °C, according to the typical procedure using (4-(ethoxycarbonyl)phenyl)zinc(II) iodide solution (1.0 mL, 0.5 M in THF, 0.5 mmol), DABSO (66.1 mg, 0.275 mmol), *tert*-butyl bromoacetate (224 mg, 1.15 mmol), and DMSO (1.0 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25−8.23 (m, 2 H), 8.03−8.01 (m, 2 H), 4.43 (q, *J*=7.1 Hz, 2 H), 4.06 (s, 2 H), 1.42 (t, *J*=7.1 Hz, 3 H), 1.38 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9 (1 C), 161.0 (1 C), 142.5 (1 C), 135.5 (1 C), 131.2 (2 C), 128.6 (2 C), 84.0 (1 C), 61.9 (2 C), 61.8 (1 C), 27.7 (3 C), 14.2 (1 C). HRMS (ESI) *m/z*: calc'd for $C_{15}H_{24}NO_6S$ [M+NH_4] 346.1319, found 346.1318.



Ethyl 3-((2-(*tert*-butoxy)-2-oxoethyl)sulfonyl)benzoate (**6l**). Compound **6l** (132 mg, 80%) was obtained as a clear, colorless oil that solidified upon standing, mp 80–81 °C, according to the typical procedure using (3-(ethoxycarbonyl)phenyl)zinc(II) iodide solution (1.0 mL, 0.5 M in THF, 0.5 mmol), DABSO (66.1 mg, 0.275 mmol), tert-butyl bromoacetate (195 mg, 1.15 mmol), and DMSO (1.0 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (t, *J*=1.6 Hz, 1 H), 8.36 (dt, *J*=7.8, 1.4 Hz, 1 H), 8.15−8.12 (m, 1 H), 7.68 (t, *J*=7.6 Hz, 1 H), 4.43 (q, *J*=7.0 Hz, 2 H), 4.07 (s, 2 H), 1.42 (t, *J*=7.2 Hz, 3H), 1.38 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7 (1 C), 161.1 (1 C), 139.5 (1 C), 135.0 (1 C), 132.5 (1 C), 131.8 (1 C), 129.7 (1 C), 129.4 (1 C), 84.0 (1 C), 62.1 (1 C), 61.8 (1 C), 27.7 (3 C), 14.3 (1 C). HRMS (ESI) *m/z*: calc'd for $C_{15}H_{24}NO_6S$ [M+NH_4] 346.1319, found 346.1320.

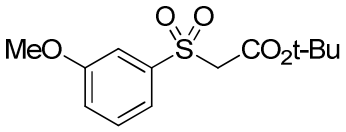


Ethyl 2-((2-(*tert*-butoxy)-2-oxoethyl)sulfonyl)benzoate (**6m**). Compound **6m** (72.8 mg, 85%) was obtained in ca. 92% purity[5] as a clear, colorless oil according to the typical procedure using (2-(ethoxycarbonyl)phenyl)zinc(II) bromide solution (0.97 mL, 0.27 M in THF,[4] 0.26 mmol), DABSO (63.6 mg, 0.265 mmol), *tert*-butyl bromoacetate (209 mg, 1.07 mmol), and DMSO (0.97 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J*=7.6 Hz, 1 H), 7.78−7.74 (m, 1 H), 7.73−7.63 (m, 2 H), 4.55 (s, 2 H), 4.44 (q, *J*=7.2 Hz, 2 H), 1.42 (t, *J*=7.2 Hz, 3 H), 1.39 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8 (s, 1 C), 161.7 (s, 1 C), 137.9 (s, 1 C), 133.7 (s, 1 C), 133.3 (s, 1 C), 131.7 (s, 1 C), 130.8 (s, 1 C), 129.9 (s, 1 C), 83.4 (s, 1 C), 62.5 (s, 1 C), 62.4 (s, 1 C), 27.7 (s, 3 C), 14.0 (s, 1 C). HRMS (ESI) *m/z*: calc'd for $C_{15}H_{24}NO_6S$ [M+NH_4] 346.1319, found 346.1318.

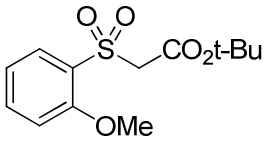


***tert*-Butyl 2-((4-methoxyphenyl)sulfonyl)acetate** (**6n**). Compound **6n** (52.5 mg, 38%) was obtained as a clear, colorless oil according to the typical procedure using (4-methoxyphenyl)zinc(II) bromide solution (0.96 mL, 0.5 M

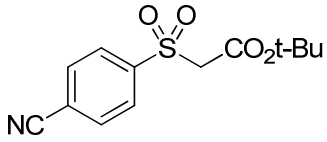
in THF, 0.48 mmol), DABSO (64 mg, 0.27 mmol), *tert*-butyl bromoacetate (164 mg, 0.841 mmol), and DMSO (0.96 mL). After introduction of the *tert*-butyl bromoacetate, heating was conducted for only 15 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90−7.84 (m, 2 H), 7.06−6.99 (m, 2 H), 4.00 (s, 2 H), 3.89 (s, 3 H), 1.39 (s, 9 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1 (1 C), 161.6 (1 C), 130.8 (2 C), 130.5 (s, 1 C), 114.3 (2 C), 83.5 (s, 1 C), 62.4 (s, 1 C), 55.7 (s, 1 C), 27.7 (s, 3 C). HRMS (ESI) *m/z*: calc'd for $C_{13}H_{22}NO_5S$ [M+NH_4] 304.1213, found 304.1215.



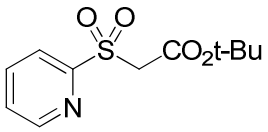
***tert*-Butyl 2-((3-methoxyphenyl)sulfonyl)acetate** (**6o**). Compound **6o** (48 mg, 34%) was obtained in ca. 82% purity[5] as a clear, colorless oil that solidified upon standing, mp 114–115 °C, according to the typical procedure using (3-methoxyphenyl)zinc(II) iodide solution (1.0 mL, 0.5 M in THF, 0.5 mmol), DABSO (66.1 mg, 0.275 mmol), *tert*-butyl bromoacetate (195 mg, 1.15 mmol), and DMSO (1.0 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.43 (m, 3 H), 7.21−7.18 (m, 1 H), 4.03 (s, 2 H), 3.88 (s, 3 H), 1.38 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2 (1 C), 160.0 (1 C), 140.1 (1 C), 130.2 (1 C), 120.67 (1 C), 120.65 (1 C), 113.0 (1 C), 83.7 (1 C), 62.1 (1 C), 55.8 (1 C), 27.7 (3 C). HRMS (ESI) *m/z*: calc'd for $C_{13}H_{19}O_5S$ [M+H] 287.0948, found 287.0947.



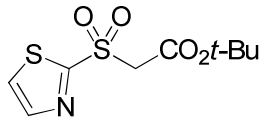
***tert*-Butyl 2-((2-methoxyphenyl)sulfonyl)acetate** (**6p**). Compound **6p** (55 mg, 38%) was obtained as a clear, colorless oil that solidified upon standing, mp 83–85 °C, according to the typical procedure using (2-methoxyphenyl)zinc(II) iodide solution (1.0 mL, 0.5 M in THF, 0.5 mmol), DABSO (66.1 mg, 0.275 mmol), *tert*-butyl bromoacetate (195 mg, 1.15 mmol), and DMSO (1.0 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, *J*=7.8, 1.6 Hz, 1 H), 7.60−7.64 (m, 1 H), 7.14−7.10 (m, 1 H), 7.06 (d, *J*=8.2 Hz, 1 H), 4.30 (s, 3 H), 4.01 (s, 2 H), 1.25 (s, 9 H). ^{13}C NMR (100 MHz, CDCl3) δ 161.5 (1 C), 157.3 (1 C), 135.8 (1 C), 103.7 (1 C), 126.9 (1 C), 120.7 (1 C), 112.2 (1 C), 83.1 (1 C), 60.3 (1 C), 56.4 (1 C), 27.5 (3 C). HRMS (ESI) *m/z*: calc'd for $C_{13}H_{22}NO_5S$ [M+NH_4] 304.1213, found 304.1210.



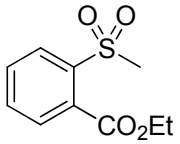
***tert*-Butyl 2-((4-cyanophenyl)sulfonyl)acetate** (**6q**). Compound **6q** (90 mg, 64%) was obtained as a clear, colorless oil that solidified upon standing, mp 98–100 °C, according to the typical procedure using (4-cyanophenyl)zinc(II) iodide solution (1.0 mL, 0.5 M in THF, 0.5 mmol), DABSO (68.5 mg, 0.285 mmol), *tert*-butyl bromoacetate (0.17 mL, 1.2 mmol), and DMSO (1.0 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09−8.07 (m, 2 H), 7.89−7.88 (m, 2 H), 4.07 (s, 2 H), 1.40 (s, 9 H). ^{13}C NMR (100 MHz, CDCl3) δ 160.9 (1 C), 142.9 (1 C), 132.8 (2 C), 129.4 (2 C), 117.9 (1 C), 117.0 (1 C), 84.3 (1 C), 61.7 (1 C), 27.7 (3 C). HRMS (ESI) *m/z*: calc'd for $C_{13}H_{19}N_2O_4S$ [M+NH_4] 299.106, found 299.1059.



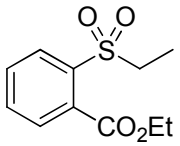
***tert*-Butyl 2-(pyridin-2-ylsulfonyl)acetate** (**6r**). Compound **6r** (82 mg, 64%) was obtained in ca. 93% purity[5] as a clear oil that solidified upon standing, mp 93–94 °C, according to the typical procedure using pyridin-2-ylzinc(II) bromide solution (1.0 mL, 0.5 M in THF, 0.5 mmol), DABSO (66.2 mg, 0.275 mmol), *tert*-butyl bromoacetate (195 mg, 1.15 mmol), and DMSO (1.0 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J*=4.7 Hz, 1 H), 8.1 (d, *J*=7.8 Hz, 1 H), 7.98 (t, *J*=7.6 Hz, 1 H), 7.57 (dd, *J*=6.8, 5.3 Hz, 1 H), 4.40 (s, 2 H), 1.30 (s, 9 H). ^{13}C NMR (100 MHz, CDCl3) δ 161.3 (1 C), 156.9 (1 C), 150.1 (1 C), 138.0 (1 C), 127.4 (1 C), 122.2 (1 C), 83.6 (1 C), 57.1 (1 C), 27.6 (3 C). HRMS (ESI) *m/z*: calc'd for $C_{11}H_{19}N_2O_4S$ [M+H] 258.0795, found 258.0789.



***tert*-Butyl 2-(thiazol-2-ylsulfonyl)acetate (6s)**. Compound **6s** (58 mg, 58%) was obtained as a clear, colorless oil according to the typical procedure using 2-thiazolylzinc(II) bromide solution (1 mL, 0.38 M in THF), DABSO (66.3 mg, 0.276 mmol), *tert*-butyl bromoacetate (195 mg, 1 mmol), and DMSO (1 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J*=3.1 Hz, 1 H), 7.80 (d, *J*=3.1 Hz, 1 H), 4.40 (s, 2 H), 1.40 (s, 9 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7 (1 C), 160.5 (1 C), 145.1 (1 C), 126.5 (1 C), 84.2 (1 C), 60.1 (1 C), 27.68 (3 C). HRMS (ESI) *m/z*: calc'd for $C_9H_{14}NO_4S_2$ [M+H] 264.0359, found 264.0348.

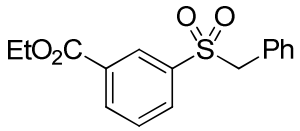


Ethyl 2-(methylsulfonyl)benzoate (**6t**). Compound **6t** (78.9 mg, 68%) was obtained as a clear, colorless oil according to the typical procedure using (2-(ethoxycarbonyl)phenyl)zinc(II) bromide solution (1.01 mL, 0.5 M in THF, 0.5 mmol), DABSO (67.0 mg, 0.279 mmol), MeI (150. mg, 1.06 mmol), and DMSO (1.01 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14−8.11 (m, 1 H), 7.72−7.63 (m, 3 H), 4.45 (q, *J*=7.2 Hz, 2 H), 3.35 (s, 3 H), 1.42 (t, *J*=7.2 Hz, 3 H). ^{13}C NMR (100 MHz, CDCl3) δ 167.1 (1 C), 139.0 (1 C), 133.47 (1 C), 133.45 (1 C), 131.1 (1 C), 129.8 (1 C), 129.6 (1 C), 62.5 (1 C), 45.0 (1 C), 14.0 (1 C). HRMS (ESI) *m/z*: calc'd for $C_{10}H_{16}NO_4S$ [M+NH_4] 246.0795, found 246.0797.

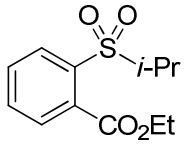


Ethyl 2-(ethylsulfonyl)benzoate (**6u**). Compound **6u** (172 mg, 71%) was obtained as thick clear oil according to the typical procedure using (2-(ethoxycarbonyl)phenyl)zinc(II) bromide solution (2.0 mL, 0.5 M in THF, 1 mmol), DABSO (133 mg, 0.552 mmol), ethyl iodide (0.170 mL, 2.1 mmol), and DMSO (2 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J*=7.80 Hz, 1 H), 7.70−7.66 (m, 2 H), 7.66−7.59 (m, 1 H), 4.42 (q, *J*=7.28 Hz, 2 H), 3.50 (q, *J*=7.41 Hz, 2 H), 1.39 (t, *J*=7.22 Hz, 3 H), 1.32 (t, *J*=7.41 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$-*d*) δ 167.20 (s, 1 C), 137.06 (s, 1 C),

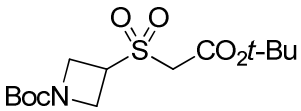
133.89 (s, 1 C), 133.48 (s, 1 C), 130.85 (s, 1 C), 130.77 (s, 1 C), 129.62 (s, 1 C), 62.42 (s, 1 C), 50.81 (s, 1 C), 50.81 (s, 1 C), 14.00 (s, 1 C). HRMS (ESI) *m/z*: calc'd for $C_{11}H_{14}O_4S$ [M+H] 243.0686, found 243.0693.



Ethyl 3-(benzylsulfonyl)benzoate (**6v**). Compound **6v** (137 mg, 89%) was obtained in ca. 93% purity as a white solid, mp 110–112 °C, according to the typical procedure using (3-(ethoxycarbonyl)phenyl)zinc(II) bromide solution (1.01 mL, 0.5 M in THF, 0.5 mmol), DABSO (67.2 mg, 0.280 mmol), benzyl bromide (178 mg, 1.04 mmol), and DMSO (1.01 mL). An analytical sample was obtain by repeated chromatography. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (t, *J*=1.8 Hz, 1 H), 8.27 (dt, *J*=7.8, 1.4 Hz, 1 H), 7.73 (ddd, *J*=7.8, 2.0, 1.2 Hz, 1 H), 7.51 (t, *J*=7.8 Hz, 1 H), 7.35−7.30 (m, 1 H), 7.29−7.24 (m, 2 H), 7.11−7.07 (m, 2 H), 4.39 (q, *J*=7.2 Hz, 2 H), 4.34 (s, 2 H), 1.39 (t, *J*=7.1 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8 (1 C), 138.4 (1 C), 134.6 (1 C), 132.6 (1 C), 131.6 (1 C), 130.8 (2 C), 129.6 (1 C), 129.0 (1 C), 128.9 (1 C), 128.7 (2 C), 127.8 (1 C), 62.9 (1 C), 61.7 (1 C), 14.3 (1 C). HRMS (ESI) *m/z*: calc'd for $C_{16}H_{20}NO_4S$ [M+NH_4] 322.1108, found 322.1095.



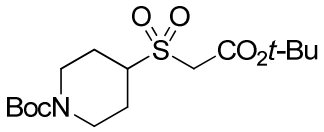
Ethyl 2-(isopropylsulfonyl)benzoate (**6w**). Compound **6w** (43.0 mg, 36%) was obtained as a clear, colorless oil in 92% purity[5] according to the typical procedure using (2-(ethoxycarbonyl)phenyl)zinc(II) bromide solution (0.94 mL, 0.5 M in THF, 0.47 mmol), DABSO (61.9 mg, 0.258 mmol), 2-iodopropane (167. mg, 0.982 mmol), and DMSO (0.94 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05−8.01 (m, 1 H), 7.69−7.66 (m, 2 H), 7.65−7.60 (m, 1 H), 4.43 (q, *J*=7.2 Hz, 2 H), 3.95 (spt, *J*=6.9 Hz, 1 H), 1.41 (t, *J*=7.1 Hz, 3 H), 1.35 (d, *J*=6.8 Hz, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3 (1 C), 136.3 (1 C), 134.2 (1 C), 133.2 (1 C), 131.5 (1 C), 130.4 (1 C), 129.6 (1 C), 62.4 (1 C), 55.3 (1 C), 15.2 (2 C), 14.0 (1 C). HRMS (ESI) *m/z*: calc'd for $C_{12}H_{20}NO_4S$ [M+NH_4] 274.1108, found 274.1107.



(1-(*tert*-Butoxycarbonyl)azetidin-3-yl)zinc(II) iodide (**5x**). An oven-dried, nitrogen-filled flask was charged with zinc dust (414 mg, 6.33 mmol) and DMAc (3.0 mL). This grey suspension was heated to 40 °C (internal reaction temperature), and a solution of 1,2-dibromoethane (90. µL, 1 mmol) and a solution of TMSCl (150 µL, 0.42 mmol) in DMAc (0.5 mL) was added dropwise. The internal reaction temperature rose to 55 °C, and heating was temporarily ended. After the reaction temperature stabilized at 40 °C, heating was continued for 30 min. *tert*-Butyl 3-iodoazetidine-1-carboxylate (896 mg, 3.16 mmol) was then added as a solution in DMAc (1.0 mL), and an exothermic reaction was again observed. After stirring at 40 °C for 30 min., heating was ended. Titration against iodine[4] showed this organozinc reagent to have a concentration of 0.5 M. This solution was used in the subsequent step within 1 h.

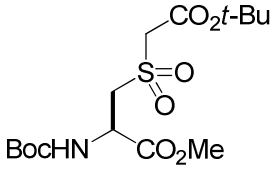
***tert*-Butyl 3-((2-(*tert*-butoxy)-2-oxoethyl)sulfonyl)azetidine-1-carboxylate** (**6x**). A heat gun-dried, nitrogen-filled vial was loaded with DABSO (48.5 mg, 0.202 mmol) and heated under dynamic vacuum in a 40 °C

aluminum block for 20 min. After the nitrogen atmosphere was restored and the vial returned to r.t., a portion of the organozinc reagent **5x** (0.7 mL, 0.35 mmol) was added in one portion. The resulting mixture was vortexed for 2 min. and then stirred at r.t. for 15 min. DMSO (0.9 mL) and *tert*-butyl bromoacetate (0.110 mL, 0.745 mmol) were added to the reaction mixture, and stirring was continued for 17 h at r.t. The reaction mixture was then partitioned between MTBE and 1.0 M aq. HCl. The MTBE layer was washed with brine, dried over sodium sulfate, and evaporated. The residue was purified by MPLC using an EtOAc/heptane gradient (0−50% EtOAc) to afford compound **6x** (81.2 mg, 81%) as a white solid, mp 115–116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.33−4.25 (m, 3 H), 4.23−4.14 (m, 2 H), 3.84 (s, 2 H), 1.49 (s, 9 H), 1.43 (s, 9 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6 (s, 1 C), 155.6 (s, 1 C), 84.6 (s, 1 C), 80.6 (s, 1 C), 58.0 (s, 1 C), 49.41 (s, 1 C), 49.35 (br. s, 2 C), 28.2 (s, 3 C), 27.8 (s, 3 C). HRMS (ESI) *m/z*: calc'd for $C_{14}H_{25}NNaO_6S$ [M+Na] 358.1295, found 358.1307.

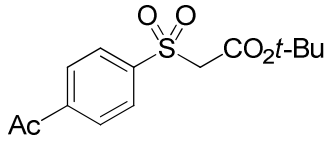


(1-(*tert*-butoxycarbonyl)piperidin-4-yl)zinc(II) iodide (**5y**). An oven-dried, nitrogen-filled flask was charged with zinc dust (422 mg, 6.45 mmol) and DMAc (4.0 mL). 1,2-Dibromoethane (90. µL, 1 mmol) was added, and the resulting grey suspension was heated to 56 °C (internal reaction temperature) for 5 min. After the reaction cooled to ca. 33 °C, TMSCl (170. µL, 1.34 mmol) was added; effervescence was observed, and the reaction temperature rose to 57 °C. The reaction temperature returned to 40 °C, and heat was applied to maintain this temperature for 15 min. *tert*-Butyl 4-iodopiperidine-1-carboxylate (1.02 g, 3.26 mmol) was then added as a solution in DMAc (0.50 mL), and an exothermic reaction was again observed. Heating was discontinued, and the reaction mixture was stirred at r.t. for 1 h. Titration against iodine[4] showed this organozinc reagent to have a concentration of 0.5 M. This solution was used in the subsequent step within 1 h.

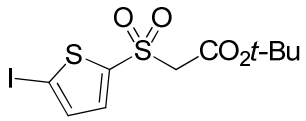
***tert*-Butyl 4-((2-(tert-butoxy)-2-oxoethyl)sulfonyl)piperidine-1-carboxylate** (**6y**). A heat gun-dried, nitrogen-filled vial was loaded with DABSO (48.5 mg, 0.202 mmol) and heated under dynamic vacuum in a 40 °C aluminum block for 20 min. After the nitrogen atmosphere was restored and the vial returned to r.t., a portion of the organozinc reagent **7y** (0.8 mL, 0.4 mmol) was added in one portion. The resulting mixture was vortexed for 2 min. and then stirred at r.t. for 15 min. DMSO (0.8 mL) and *tert*-butyl bromoacetate (0.120 mL, 0.813 mmol) were added to the reaction mixture, and stirring was continued for 17 h at r.t. The reaction mixture was then partitioned between MTBE and 1.0 M aq. HCl. The MTBE layer was washed with brine, dried over sodium sulfate, and evaporated. The residue was purified by MPLC using an EtOAc/heptane gradient (0−50% EtOAc) to afford compound **6y** (79.5 mg, 80.%) as a white solid, mp 109–110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.28 (br. s., 2 H), 3.85 (s, 2 H), 3.47 (tt, *J*=12.05, 3.56 Hz, 1 H), 2.75 (t, *J*=10.54 Hz, 2 H), 2.08 (d, *J*=12.49 Hz, 2 H), 1.77 (qd, *J*=12.42, 4.49 Hz, 2 H), 1.49 (s, 9 H), 1.44 (s, 9 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0 (s, 1 C), 154.2 (s, 1 C), 84.2 (s, 1 C), 80.1 (s, 1 C), 59.1 (s, 1 C), 55.8 (s, 1 C), 42.4 (br. s., 1 C), 28.3 (s, 3 C), 27.8 (s, 3 C), 24.2 (s, 1 C). HRMS (ESI) *m/z*: calc'd for $C_{16}H_{29}NNaO_6S$ [M+Na] 386.1608, found 386.1615.



(*R*)-Methyl 3-((2-(*tert*-butoxy)-2-oxoethyl)sulfonyl)-2-((*tert*-butoxycarbonyl)amino)propanoate (**6z**). Iodine (16.7 mg, 0.0658 mmol) was added to a stirred suspension of Zn (195.6 mg, 2.99 mmol) in DMF (416 mg). After the iodine color faded, a 41.2 wt. % solution of (*R*)-methyl 2-((*tert*-butoxycarbonyl)amino)-3-iodopropanoate in DMF (0.82 mL, 925 mg, 1.16 mmol) was added via syringe by weight difference. A second portion of iodine (16.8 mg) was then added, whereupon a mild exotherm was observed. After 15 min., stirring was ended, and the excess Zn was allowed to settle for 30 min. Meanwhile, a vial containing DABSO (154 mg, 0.640 mmol) was dried under high vacuum in a 40 °C aluminum block for 20 min. The organozinc solution was then transferred onto the DABSO, excluding the bulk of the excess Zn. The resulting mixture was vortexed and sonicated until the DABSO was finely suspended. After stirring for 10 min., *tert*-butyl bromoacetate (502 mg, 2.57 mmol) was added, and the resulting mixture was heated in a 70 °C aluminum block for 1 h. The reaction mixture was then partitioned between MTBE and 1.0 M aq. HCl. The MTBE layer was washed with brine, dried over sodium sulfate, and evaporated to afford a pale yellow oil. Repeated MPLC purification (0−90% EtOAc/heptane gradient followed by a 0−30% EtOAc/heptane gradient) afforded compound **6z** (343 mg, 78%) as a white solid, mp 62–63 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.55 (br. d, *J*=8.0 Hz, 1 H), 4.83−4.68 (m, 1 H), 3.97 (s, 2 H), 3.95−3.84 (m, 2 H), 3.81 (s, 3 H), 1.51 (s, 9 H), 1.45 (s, 9 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8 (s, 1 C), 161.8 (s, 1 C), 155.1 (s, 1 C), 84.5 (s, 1 C), 81.0 (s, 1 C), 60.3 (s, 1 C), 54.5 (s, 1 C), 53.2 (s, 1 C), 49.8 (s, 1 C), 28.2 (s, 3 C), 27.8 (s, 3 C). HRMS (ESI) *m/z*: calc'd for $C_{15}H_{31}N_2O_8S$ [M+NH_4] 399.1796, found 399.1789.



***tert*-Butyl 2-((4-acetylphenyl)sulfonyl)acetate** (**6aa**). Lithium chloride (131 mg, 3.1 mmol) was dried under dynamic vacuum at 175 °C for 10 min. Zn (354 mg, 5.4 mmol) was added, and the flask was again dried at 175 °C under vacuum for 15 min. The flask was filled with nitrogen and allowed to cool to ca. 21 °C. Anhydrous THF (4 ml) was then added, and the obtained suspension was stirred at r.t. 1,2-Dibromoethane (0.012 ml, 0.14 mmol) and TMSCl (0.037 ml, 0.29 mmol) were added successively, and the resulting mixture was stirred for 40 min. Next, 4-iodoacetophenone (700 mg, 2.8 mmol) was added, and stirring was continued for 4 h. GCMS analysis of the reaction mixture (quenched into EtOH) showed a ca. 3:1:1 mixture of acetophenone, 4-iodoacetophenone, and an acetophenone dimer. At this point, stirring was terminated, and, after allowing the unreacted zinc to settle, a portion of the clear, yellow supernatant (70% of its total volume) was withdrawn into a syringe and transferred into a new dried, nitrogen-filled flask. DABSO (342 mg, 1.4 mmol) was added, and the resulting suspension was stirred at r.t. for 18 h, by which time it was very thick. DMSO (3 ml) was added, and the resulting nearly clear, yellow solution was stirred for 30 min. *tert*-Butyl bromoacetate (1220 mg, 6.3 mmol) was finally added, and the reaction mixture was stirred at 65 °C for 1 h. Low-boiling components of the reaction mixture were removed by rotary evaporation, and the remaining solution was partitioned between EtOAc and water. The organic layer was washed with brine, dried over magnesium sulfate, and evaporated. MPLC purification the residue (10−60% EtOAc/heptane gradient) afforded compound **6aa** (120 mg, 20% yield based on the 70% portion transferred) as an off-white solid, mp 84.9–85.2 °C. ^{1}H NMR (400MHz, $CDCl_3$) δ 8.15−8.11 (m, 2H), 8.06−8.03 (m, 2H), 4.06 (s, 2H), 2.67 (s, 3H), 1.38 (s, 9H). ^{13}C NMR (101MHz, $CDCl_3$) δ 196.6 (1C), 161.0 (1C), 142.6 (1C), 141.1 (1C), 129.0 (2C), 128.8 (2C), 84.0 (1C), 61.8 (1 C), 27.7 (3C), 26.9 (1C). HRMS (ESI) *m/z*: calc'd for $C_{14}H_{22}NO_5S$ [M+NH_4] 316.1213, found 316.1212.



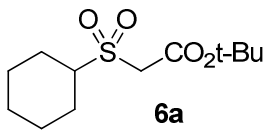
(5-Iodothiophen-2-yl)zinc(II) iodide (**5bb**). LiCl (122 mg, 2.88 mmol) was dried in a vial containing a PTFE/silicone septum under dynamic vacuum in a 180 °C aluminum block for 20 min. Zinc (265 mg, 4.05 mmol) was added, and heating under vacuum was resumed for a further 15 min. After the vial cooled to r.t., THF (1.4 mL) was added, and the resulting mixture was heated in a 55 °C aluminum block. 1,2-Dibromoethane (23.6 mg, 0.126 mmol) was added, followed after 2 min. by TMSCl (4.0 µL, 31 µmol); heating was continued for 10 min. The reaction mixture was cooled to ca. 21 °C, and a solution of 2,5-diiodothiophene (968 mg, 2.88 mmol) in THF (2.9 mL) was added, portionwise via syringe. Upon observation of a significant exotherm, the reaction mixture was briefly held in a r.t. water bath. Additional THF (0.60 mL) was used to complete the transfer. Within 10 min., the reaction mixture had returned to r.t. Titration against iodine[4] showed this organozinc reagent, which could be stored in a refrigerator for 3 days, to have a concentration of 0.556 M.

***tert*-Butyl 2-((5-iodothiophen-2-yl)sulfonyl)acetate** (**6bb**). Compound **6bb** (190. mg, 90.%) was obtained as a clear, colorless, viscous oil according to the typical procedure using (5-iodothiophen-2-yl)zinc(II) iodide solution (0.89 mL, 0.556 M in THF, 0.49 mmol), DABSO (71.6 mg, 0.298 mmol), *tert*-butyl bromoacetate (226 mg, 1.16 mmol), and DMSO (0.98 mL). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J*=3.9 Hz, 1 H), 7.33 (d, *J*=3.9 Hz, 1 H), 4.08 (s, 2 H), 1.44 (s, 9 H). ^{13}C NMR (101 MHz, CDCl3) δ 161.1 (s, 1 C), 144.7 (s, 1 C), 137.5 (s, 1 C), 136.1 (s, 1 C), 85.4 (s, 1 C), 84.1 (s, 1 C), 62.9 (s, 1 C), 27.8 (s, 3 C). HRMS (ESI) *m/z*: calc'd for $C_{10}H_{17}INO_4S_2$ [M+NH_4] 405.9638, found 405.9641.

References and Notes

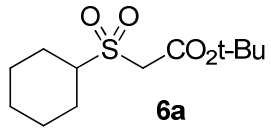
1. Touchstone, J. C.; Dobbins, M. F. Visualization Procedures. *Practice of Thin Layer Chromatography*; John Wiley & Sons: New York, 1978; pp. 161−223.
2. Nguyen, B.; Emmett, J. E.; Willis, C. M. *J. Am. Chem. Soc*. **2010**, *132*, 16372−16373.
3. Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.*, **1997**, *62*, 7512−7515.
4. Krasovskiy, A.; Knochel, P. *Synthesis*, **2006**, 890−891.
5. Purity estimates are primarily based on NMR area percent.

NMR data



6a

400 MHz, $CDCl_3$



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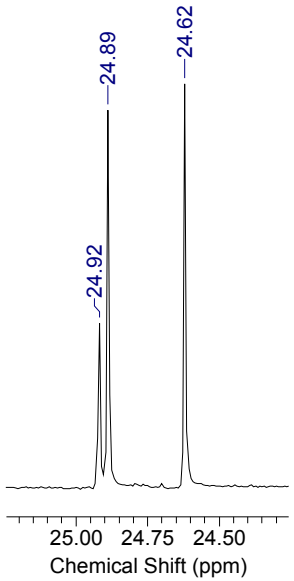

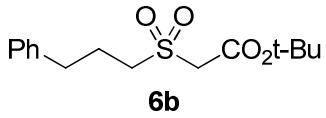

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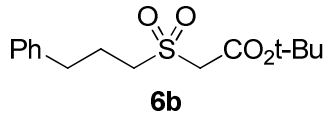

6b

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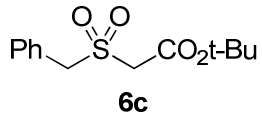

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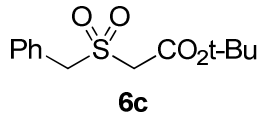

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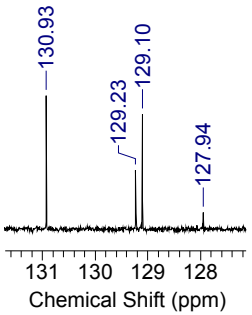

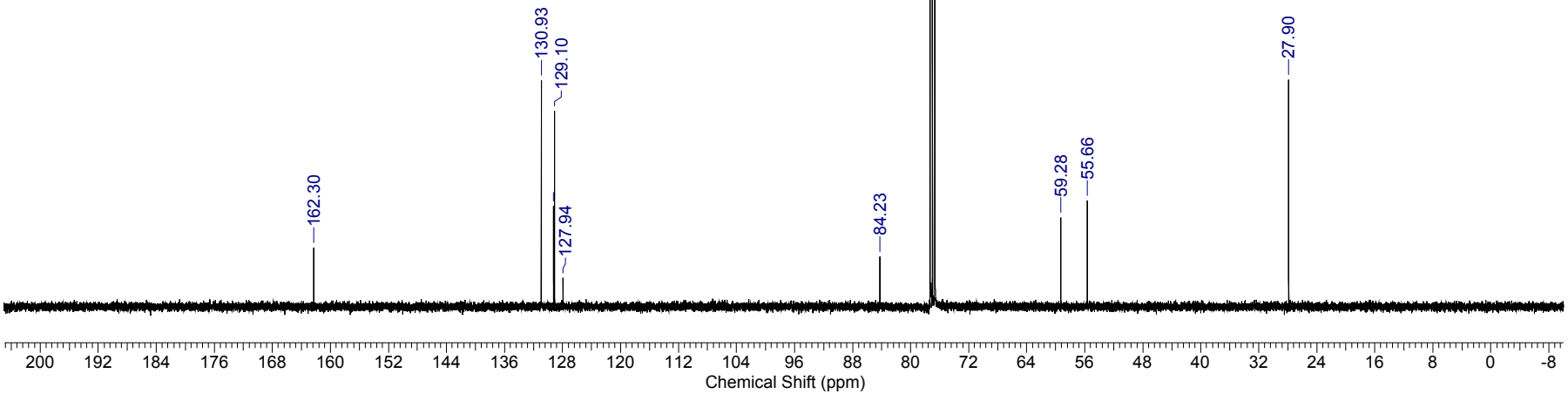

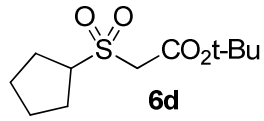

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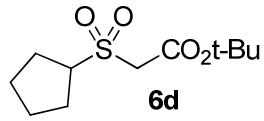

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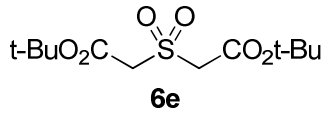

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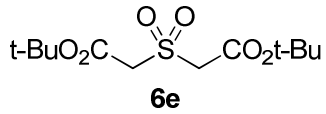

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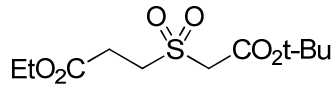

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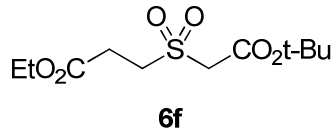

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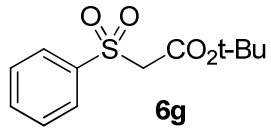

6g

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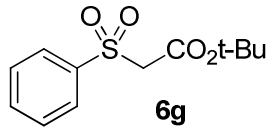

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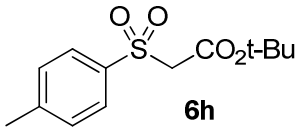

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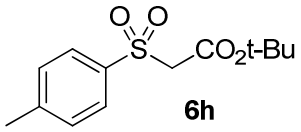

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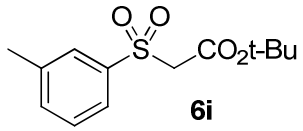

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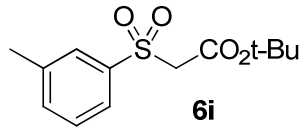

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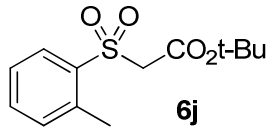

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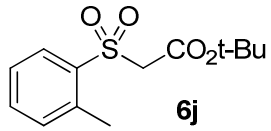

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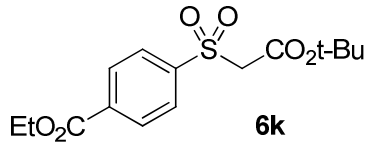

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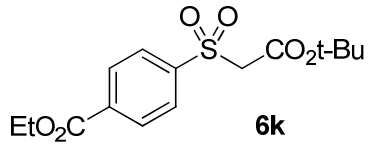

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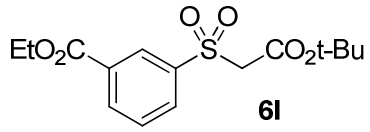

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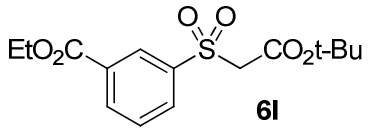

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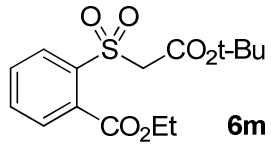

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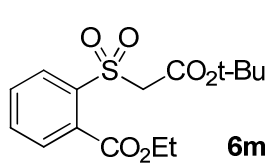

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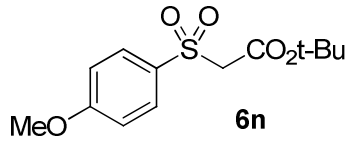

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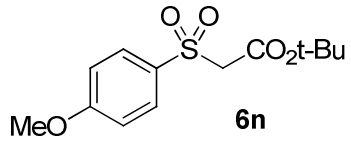

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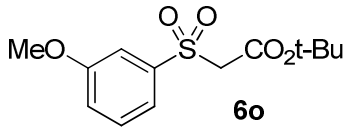

6o

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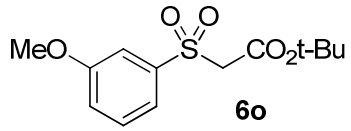

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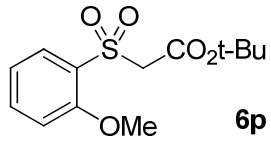

6p

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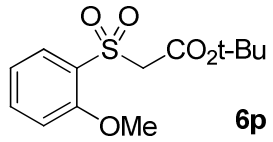

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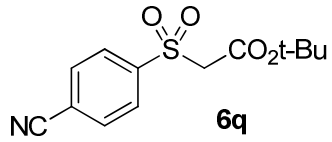

6q

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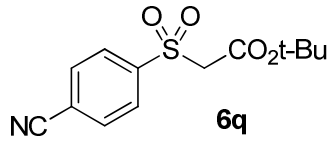

6q

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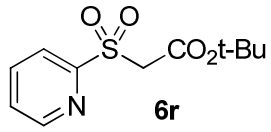
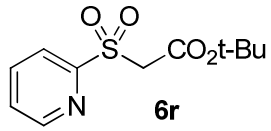


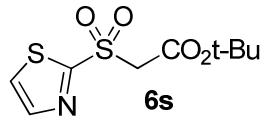
6r

400 MHz, $CDCl_3$



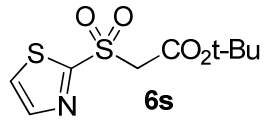
6r

101 MHz, $CDCl_3$



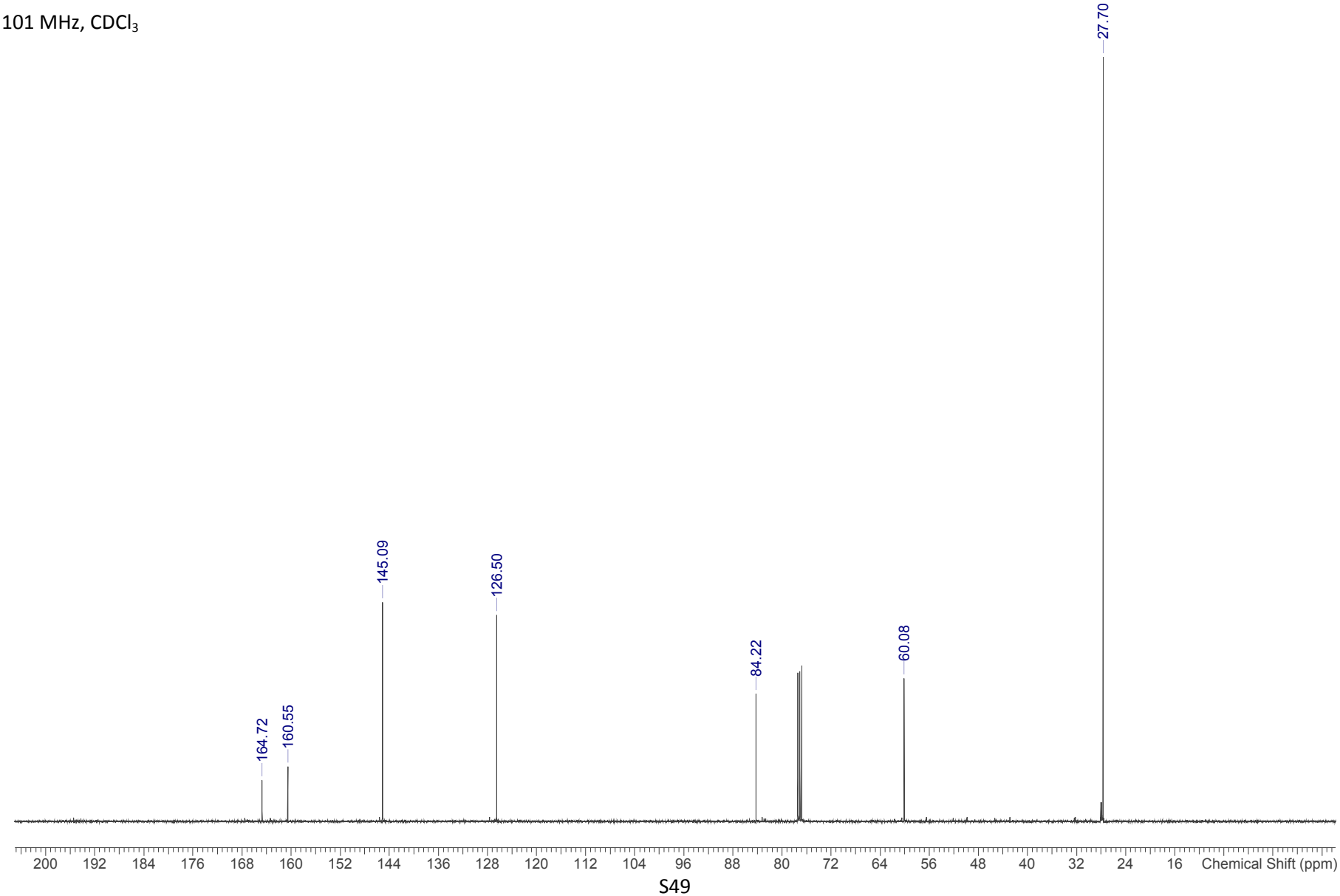
6s

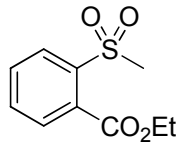
400 MHz, $CDCl_3$



6s

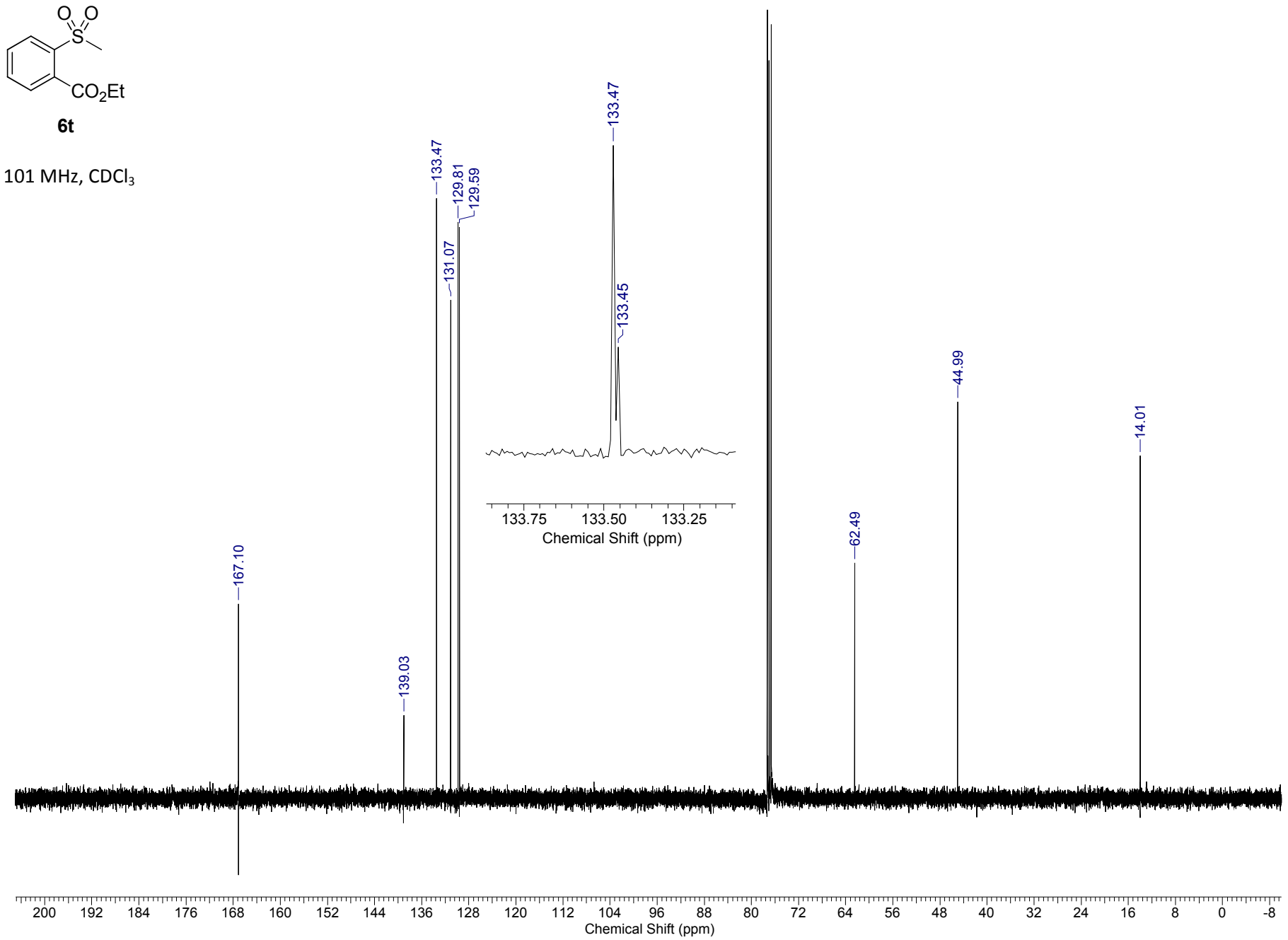
101 MHz, $CDCl_3$

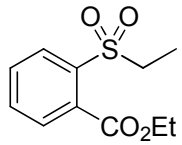




6t

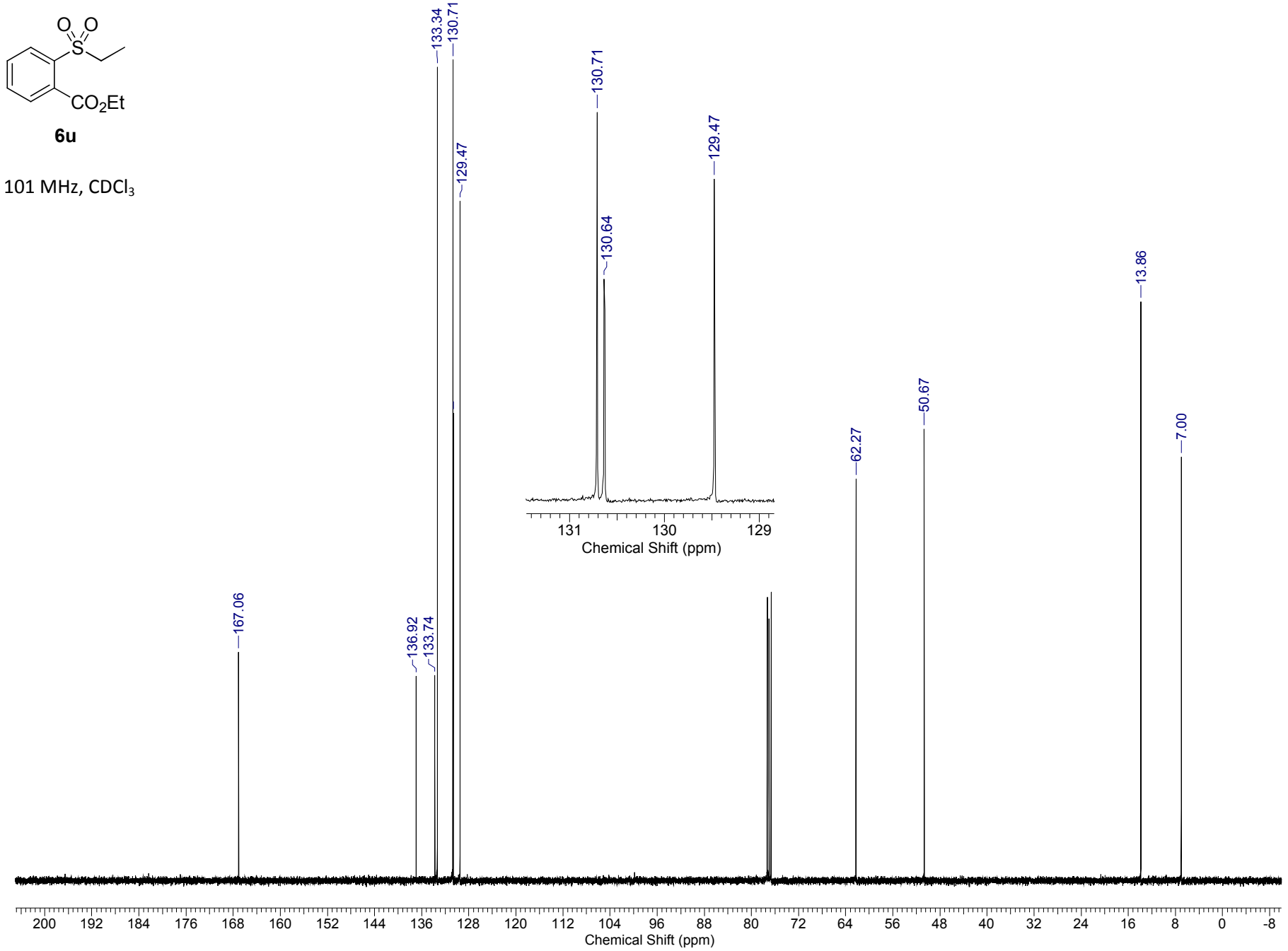
400 MHz, $CDCl_3$

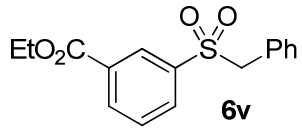

O O
S
CO2Et
6t
101 MHz, CDCl3
133.47
129.81
129.59
131.07
133.47
133.45
133.75
133.50
133.25
Chemical Shift (ppm)
167.10
139.03
62.49
44.99
14.01
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 -8
Chemical Shift (ppm)



6u

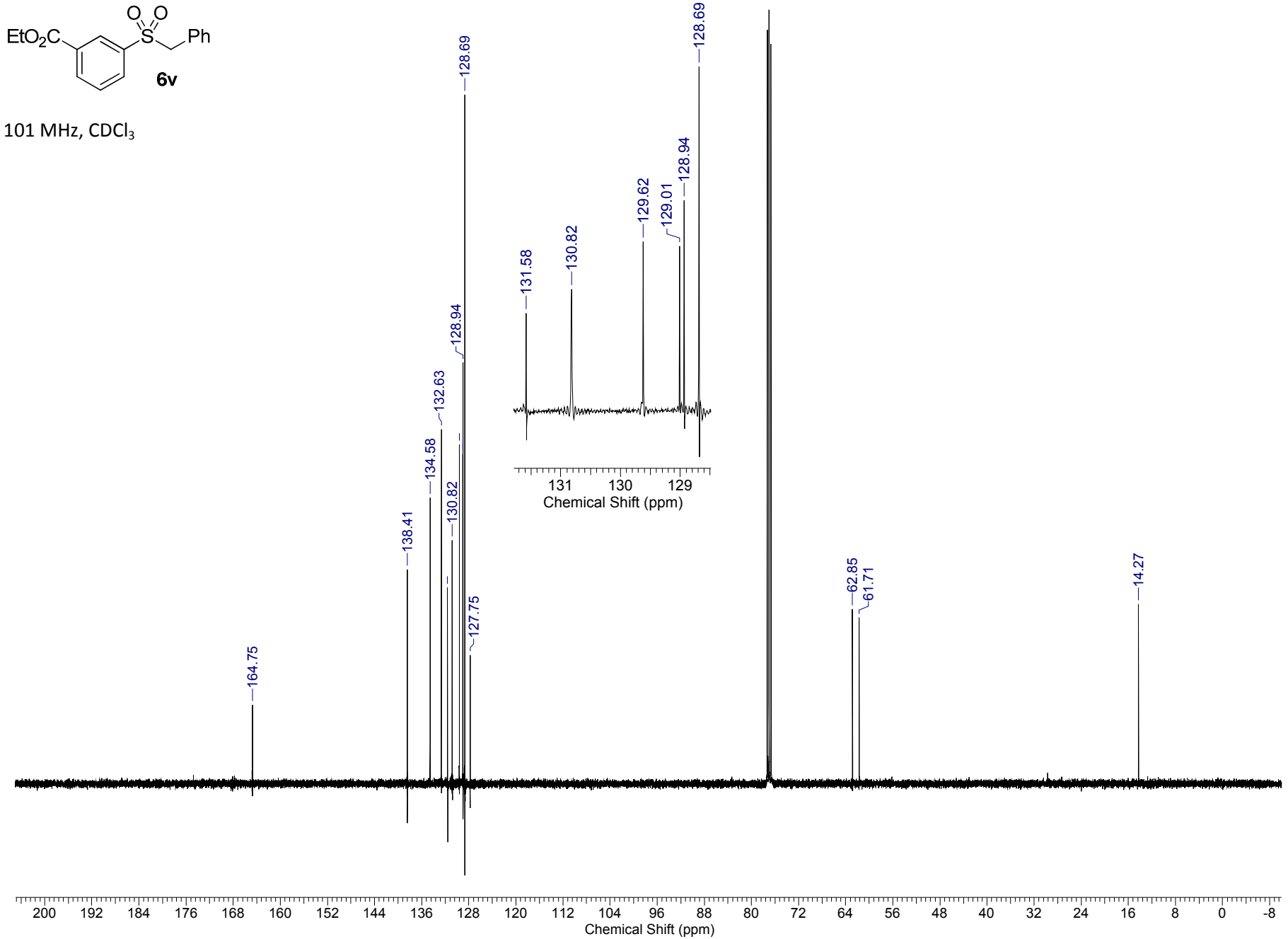
400 MHz, $CDCl_3$

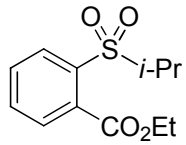

6u
101 MHz, CDCl3
133.34
130.71
129.47
130.71
130.64
129.47
13.86
50.67
62.27
7.00
167.06
136.92
133.74
131
130
129
Chemical Shift (ppm)
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
-8
Chemical Shift (ppm)



6v

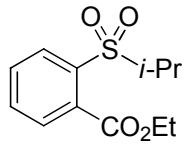
400 MHz, $CDCl_3$


EtO2C
O
O
S
Ph
6v
101 MHz, CDCl3
164.75
138.41
134.58
132.63
130.82
128.94
128.69
127.75
62.85
61.71
14.27
131.58
130.82
129.62
129.01
128.94
128.69
131
130
129
Chemical Shift (ppm)
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
-8
Chemical Shift (ppm)



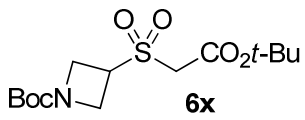
6w

400 MHz, $CDCl_3$



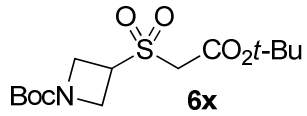
6w

101 MHz, $CDCl_3$



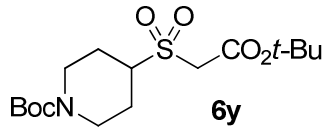
6x

400 MHz, $CDCl_3$



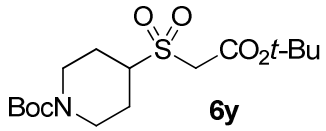
6x

101 MHz, $CDCl_3$



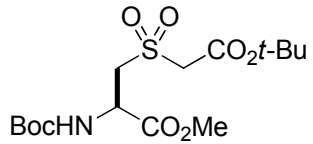
6y

400 MHz, $CDCl_3$



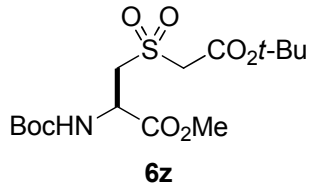
6y

101 MHz, $CDCl_3$



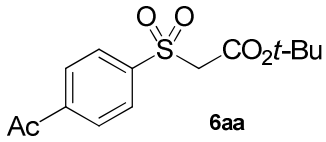
6z

400 MHz, $CDCl_3$



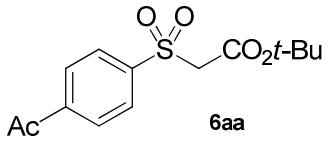
6z

101 MHz, $CDCl_3$



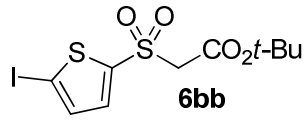
6aa

400 MHz, $CDCl_3$



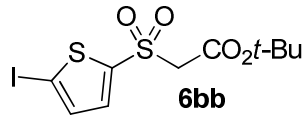
6aa

101 MHz, $CDCl_3$



6bb

400 MHz, $CDCl_3$



6bb

101 MHz, $CDCl_3$