

Supporting Information

Nickel-Catalyzed C(sp²)-C(sp³) Coupling via Photoactive Electron Donor-Acceptor Complex

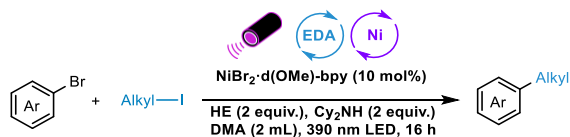
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1. General Information

Unless otherwise noted, all commercially available aryl bromides and alkyl iodides were purchased from Sigma-Aldrich and used as provided without further purification. Solvents for chromatography were HPLC grade. Anhydrous and degassed DMA used in reactions was purchased from Sigma-Aldrich in Sure/Seal™ bottle ($\geq 99\%$). All Analytical thin-layer chromatography (TLC) was performed on Merck silica gel aluminium plates with F-254 indicator, visualized by irradiation with UV light. Column chromatography was performed on silica gel (particle size 0.043–0.063 mm) by using Interchim PuriFlash®430 automatic purification system. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ were recorded on Bruker DRX-500 and AMX-400 instruments in CDCl_3 and are reported relative to the solvent residual peaks. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), bs (broad singlet), d (doublet), t (triplet), m (multiplet); coupling constants (J) are in Hertz (Hz). Mass spectra (EI-MS, 70 eV) were conducted on an Agilent 7890 gas chromatograph equipped with 5975C EI-MSD Triple-Axis Detector using DB5MS and HP5MS columns. HRMS analysis was performed using a Thermo LTQ Velos Orbitrap mass spectrometer (Thermo Scientific, Pittsburgh, PA, USA) equipped with an ESI source.

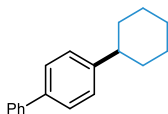
2. General Procedure for the Photoinduced $\text{C}(\text{sp}^2)\text{-C}(\text{sp}^3)$ Coupling of Aryl Bromides and Alkyl Iodides



A dry 5 mL vial equipped with a stirring bar was charged with an aryl bromide (0.2 mmol, 1 equiv.), $\text{NiBr}_2\cdot\text{d}(\text{OMe})\text{-bpy}$ (0.02 mmol) and HE (0.4 mmol, 2 equiv.) in glovebox. Anhydrous and degassed DMA (2 mL), Cy_2NH (2 equiv.) and alkyl iodide (0.40 mmol) were added subsequently via syringe. The reaction mixture was stirred for 16 h under the irradiation of 390 nm purple LED with fan cooling. After the reaction is completed, the mixture was transferred to a 100 mL round bottom flask via syringe. The solution was diluted with H_2O (30 mL), extract by ethyl acetate (3×20 mL), and the combined organic layers were concentrated with a rotary evaporator. The product was purified by flash column chromatography on silica gel using hexane/EtOAc as eluent.

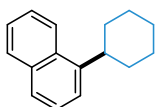
3. Spectroscopic Data of the Products

4-cyclohexyl-1,1'-biphenyl (3a)



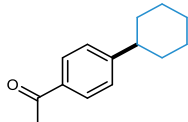
Yield: 80% (37.8 mg), white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.13 (s, 4H), 2.53 – 2.43 (m, 1H), 2.34 (s, 3H), 1.85 (t, $J = 9.4$ Hz, 4H), 1.76 (d, $J = 15.7$ Hz, 1H), 1.50 – 1.32 (m, 4H), 1.28 (d, $J = 2.0$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 145.2, 135.2, 129.0, 126.7, 44.2, 34.6, 27.0, 26.2, 21.0. Data in accordance with the literature¹.

1-cyclohexylnaphthalene (3b)



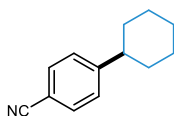
Yield: 63% (26.5 mg), colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.03 (d, $J = 8.4$ Hz, 1H), 7.76 (d, $J = 7.4$ Hz, 1H), 7.60 (d, $J = 7.9$ Hz, 1H), 7.45 – 7.26 (m, 4H), 3.35 – 3.13 (m, 1H), 2.07 – 1.71 (m, 5H), 1.55 – 1.39 (m, 4H), 1.32 – 1.19 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 143.9, 134.0, 131.4, 129.0, 126.3, 125.7, 125.6, 125.3, 123.3, 122.3, 39.3, 34.3, 27.3, 26.6. Data in accordance with the literature¹.

1-(4-cyclohexylphenyl) ethan-1-one (3c)



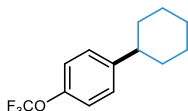
Yield: 80% (32.3 mg), colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.81 (d, $J = 8.4$ Hz, 2H), 7.22 (d, $J = 8.3$ Hz, 2H), 2.50 (s, 4H), 1.88 – 1.72 (m, 4H), 1.69 (d, $J = 13.9$ Hz, 1H), 1.42 – 1.27 (m, 4H), 1.24 – 1.11 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 197.9, 153.8, 135.0, 128.6, 127.1, 44.7, 34.1, 26.7, 26.6, 26.0. Data in accordance with the literature¹.

4-cyclohexylbenzotrile (3d)



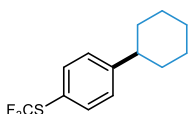
Yield: 64% (23.7 mg), colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.50 (d, $J = 8.2$ Hz, 2H), 7.23 (d, $J = 8.2$ Hz, 2H), 2.79 – 2.24 (m, 1H), 1.85 – 1.73 (m, 4H), 1.69 (d, $J = 8.5$ Hz, 1H), 1.31 (q, $J = 10.9, 10.5$ Hz, 4H), 1.19 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.5, 132.2, 127.7, 119.3, 109.6, 44.8, 34.0, 26.6, 25.9. Data in accordance with the literature².

1-cyclohexyl-4-(trifluoromethoxy) benzene (3e)



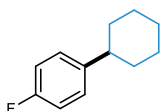
Yield:74% (36.1 mg), colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.13 (d, $J = 8.7$ Hz, 2H), 7.04 (d, $J = 8.3$ Hz, 2H), 2.50 – 2.36 (m, 1H), 1.84 – 1.72 (m, 4H), 1.68 (d, $J = 12.6$ Hz, 1H), 1.37 – 1.24 (m, 4H), 1.23 – 1.12 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 147.3, 147.0, 128.0, 120.9, 120.6 (q, $J = 256.3$ Hz), 44.0, 34.5, 26.8, 26.1. $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -57.9. Data in accordance with the literature¹.

(4-cyclohexylphenyl) (trifluoromethyl)sulfane (3f)



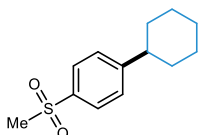
Yield:87% (45.3 mg), colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.48 (d, $J = 8.0$ Hz, 2H), 7.17 (d, $J = 8.0$ Hz, 2H), 2.55 – 2.37 (m, 1H), 1.85 – 1.72 (m, 4H), 1.68 (d, $J = 11.5$ Hz, 1H), 1.40 – 1.25 (m, 4H), 1.21 – 1.15 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 151.3, 136.5, 128.1, 129.75 (q, $J = 308.1$ Hz), 44.4, 34.2, 26.8, 26.1. $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -43.1. Data in accordance with the literature¹.

1-cyclohexyl-4-fluorobenzene (3g)



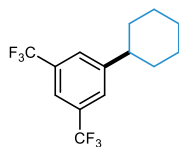
Yield:51% (18.2 mg), colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.11 – 7.03 (m, 2H), 6.94 – 6.83 (m, 2H), 2.47 – 2.33 (m, 1H), 1.83 – 1.72 (m, 4H), 1.67 (d, $J = 11.4$ Hz, 1H), 1.37 – 1.23 (m, 4H), 1.22 – 1.13 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 161.1 (d, $J = 242.9$ Hz), 143.8 (d, $J = 3.1$ Hz), 128.1 (d, $J = 7.7$ Hz), 114.9 (d, $J = 20.8$ Hz), 43.9, 34.7, 26.9, 26.1. $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -117.8. Data in accordance with the literature³.

1-cyclohexyl-4-(methylsulfonyl)benzene (3h)



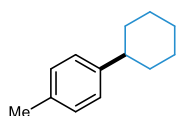
Yield:76% (36.2 mg), white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.78 (d, $J = 8.5$ Hz, 2H), 7.32 (d, $J = 8.5$ Hz, 2H), 2.97 (s, 3H), 2.57 – 2.48 (m, 1H), 1.86 – 1.75 (m, 4H), 1.70 (d, $J = 10.6$ Hz, 1H), 1.43 – 1.27 (m, 4H), 1.26 – 1.14 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 154.5, 137.9, 127.8, 127.5, 44.7, 44.6, 34.1, 26.6, 25.9. Data in accordance with the literature¹.

1-cyclohexyl-3,5-bis(trifluoromethyl)benzene (3i)



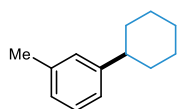
Yield:41% (24.3 mg), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.62 (s, 1H), 7.57 (s, 2H), 2.65 – 2.49 (m, 1H), 1.88 – 1.76 (m, 4H), 1.71 (d, J = 12.1 Hz, 1H), 1.44 – 1.27 (m, 4H), 1.25 – 1.16 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.30, 131.5 (q, J = 32.8 Hz), 127.1, 123.6 (d, J = 272.6 Hz), 120.1 – 119.8 (m), 44.4, 34.2, 26.6, 25.9. ^{19}F NMR (377 MHz, CDCl_3) δ -62.8. Data in accordance with the literature⁴.

1-cyclohexyl-4-methylbenzene (3j)



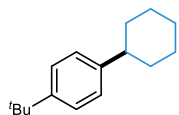
Yield:57% (19.9 mg), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.13 (s, 4H), 2.53 – 2.43 (m, 1H), 2.34 (s, 3H), 1.85 (t, J = 9.4 Hz, 4H), 1.76 (d, J = 15.7 Hz, 1H), 1.50 – 1.32 (m, 4H), 1.28 (d, J = 2.0 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.2, 135.2, 129.0, 126.7, 44.2, 34.6, 27.0, 26.2, 21.0. Data in accordance with the literature⁵.

1-cyclohexyl-3-methylbenzene (3k)



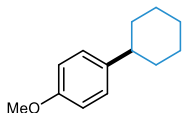
Yield:50% (17.4 mg), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.11 (t, J = 7.5 Hz, 1H), 6.93 (t, J = 7.6 Hz, 3H), 2.38 (td, J = 11.4, 3.5 Hz, 1H), 2.26 (s, 3H), 1.79 (t, J = 6.8 Hz, 4H), 1.67 (d, J = 13.8 Hz, 1H), 1.33 (q, J = 9.9, 9.0 Hz, 4H), 1.19 – 1.21 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 148.1, 137.8, 128.2, 127.7, 126.5, 123.8, 44.6, 34.5, 27.0, 26.2, 21.5. Data in accordance with the literature³.

1-(tert-butyl)-4-cyclohexylbenzene (3l)



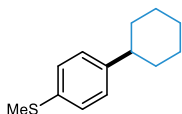
Yield:73% (31.6 mg), colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.23 (d, J = 8.3 Hz, 2H), 7.07 (d, J = 8.4 Hz, 2H), 2.39 (td, J = 11.4, 3.3 Hz, 1H), 1.78 (q, J = 7.3, 4.9 Hz, 4H), 1.66 (d, J = 12.4 Hz, 1H), 1.39 – 1.28 (m, 4H), 1.23 (s, 9H), 1.18 (d, J = 2.0 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 148.4, 145.1, 126.4, 125.1, 44.0, 34.5, 34.4, 31.5, 27.0, 26.2. Data in accordance with the literature¹.

1-cyclohexyl-4-methoxybenzene (3m)



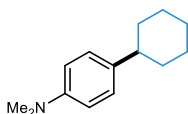
Yield: 88% (33.5 mg), white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.05 (d, $J = 8.6$ Hz, 2H), 6.76 (d, $J = 8.7$ Hz, 2H), 3.71 (s, 3H), 2.45 – 2.27 (m, 1H), 1.85 – 1.70 (m, 4H), 1.66 (d, $J = 12.5$ Hz, 1H), 1.39 – 1.22 (m, 4H), 1.22 – 1.07 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 157.7, 140.4, 127.7, 113.7, 55.3, 43.7, 34.8, 27.0, 26.2. Data in accordance with the literature¹.

(4-cyclohexylphenyl)(methyl)sulfane (3n)



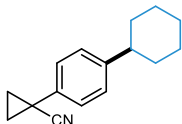
Yield: 61% (25.1 mg), white solid; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.13 (d, $J = 6.2$ Hz, 2H), 7.06 (d, $J = 8.3$ Hz, 2H), 2.39 (s, 4H), 1.83 – 1.71 (m, 4H), 1.67 (d, $J = 12.7$ Hz, 1H), 1.38 – 1.25 (m, 4H), 1.23 – 1.11 (m, 1H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 145.4, 135.1, 127.4, 127.2, 44.1, 34.5, 26.9, 26.2, 16.4. Data in accordance with the literature¹.

4-cyclohexyl-N, N-dimethylaniline (3o)



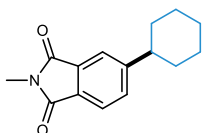
Yield: 75% (30.5 mg), colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.02 (d, $J = 8.4$ Hz, 2H), 6.64 (d, $J = 8.2$ Hz, 2H), 2.83 (s, 6H), 2.38 – 2.28 (m, 1H), 1.84 – 1.71 (m, 4H), 1.65 (d, $J = 13.1$ Hz, 1H), 1.37 – 1.23 (m, 4H), 1.22 – 1.14 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 149.0, 136.7, 127.4, 113.1, 43.5, 41.0, 34.8, 27.1, 26.3. Data in accordance with the literature⁶.

1-(4-cyclohexylphenyl) cyclopropane-1-carbonitrile (3p)



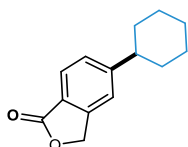
Yield: 52% (23.4 mg), colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.17 – 7.07 (m, 4H), 2.49 – 2.33 (m, 1H), 1.85 – 1.71 (m, 4H), 1.67 (d, $J = 15.1$ Hz, 1H), 1.60 (q, $J = 5.0$ Hz, 2H), 1.38 – 1.24 (m, 6H), 1.22 – 1.14 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 147.7, 133.3, 127.4, 125.8, 122.8, 44.1, 34.4, 26.8, 26.1, 17.9, 13.5. Data in accordance with the literature⁷.

5-cyclohexyl-2-methylisoindoline-1,3-dione (3q)



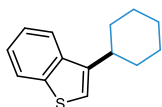
Yield:62% (30.1 mg), white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.66 (d, $J = 7.7$ Hz, 1H), 7.62 (d, $J = 1.5$ Hz, 1H), 7.44 (dd, $J = 7.6, 1.6$ Hz, 1H), 3.08 (s, 3H), 2.62 – 2.52 (m, 1H), 1.87 – 1.75 (m, 4H), 1.70 (d, $J = 14.2$ Hz, 1H), 1.45 – 1.27 (m, 4H), 1.26 – 1.15 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 168.9, 168.6, 132.7, 132.6, 129.9, 123.2, 121.6, 45.0, 34.2, 26.6, 25.9, 23.9. Data in accordance with the literature⁸.

5-cyclohexylisobenzofuran-1(3H)-one (3r)



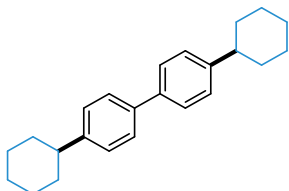
Yield:87% (37.6 mg), white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.75 (d, $J = 8.0$ Hz, 1H), 7.30 (d, $J = 8.0$ Hz, 1H), 7.24 (s, 1H), 5.21 (s, 2H), 2.64 – 2.49 (m, 1H), 1.88 – 1.75 (m, 4H), 1.71 (d, $J = 12.6$ Hz, 1H), 1.44 – 1.27 (m, 4H), 1.26 – 1.14 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 171.2, 155.3, 147.1, 128.3, 125.6, 123.5, 120.1, 69.6, 45.1, 34.3, 26.7, 26.0. Data in accordance with the literature¹.

3-cyclohexylbenzo[b]thiophene (3s)



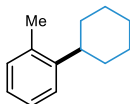
Yield:93% (40.2 mg), colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.77 (d, $J = 7.3$ Hz, 1H), 7.70 (d, $J = 7.1$ Hz, 1H), 7.31 – 7.20 (m, 2H), 6.98 (s, 1H), 2.93 – 2.73 (m, 1H), 2.01 (d, $J = 8.1$ Hz, 2H), 1.79 (d, $J = 8.4$ Hz, 2H), 1.73 (d, $J = 12.6$ Hz, 1H), 1.48 – 1.32 (m, 4H), 1.31 – 1.15 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 142.9, 140.6, 138.6, 124.1, 123.7, 123.0, 121.8, 119.2, 38.0, 33.6, 26.9, 26.4. Data in accordance with the literature⁹.

4,4'-dicyclohexyl-1,1'-biphenyl (3t)



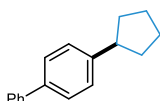
Yield:72% (45.8 mg), white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.42 (d, $J = 8.1$ Hz, 4H), 7.18 (d, $J = 8.1$ Hz, 4H), 2.45 (td, $J = 11.4, 5.1$ Hz, 2H), 1.89 – 1.73 (m, 9H), 1.68 (d, $J = 10.9$ Hz, 2H), 1.43 – 1.27 (m, 9H), 1.24 – 1.12 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 146.9, 138.7, 127.2, 126.9, 44.3, 34.5, 27.0, 26.2. Data in accordance with the literature¹.

1-cyclohexyl-2-methylbenzene (3u)



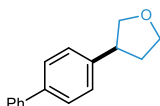
Yield:48% (16.7 mg), colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.26 (m, 1H), 7.20 (dd, $J = 17.3, 7.6$ Hz, 2H), 7.12 (t, $J = 7.3$ Hz, 1H), 2.80 – 2.68 (m, 1H), 2.37 (s, 3H), 1.87 (dd, $J = 19.6, 7.1$ Hz, 4H), 1.80 (m, 1H), 1.45 (t, $J = 9.7$ Hz, 4H), 1.37 – 1.29 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 146.4, 135.2, 131.7, 126.1, 125.5, 125.4, 40.1, 33.7, 27.2, 26.4, 19.4. Data in accordance with the literature¹.

4-cyclopentyl-1,1'-biphenyl (4a)



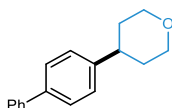
Yield:84% (37.3 mg), white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.49 (d, $J = 7.3$ Hz, 2H), 7.43 (d, $J = 8.2$ Hz, 2H), 7.33 (t, $J = 7.7$ Hz, 2H), 7.26 – 7.20 (m, 3H), 3.02 – 2.87 (m, 1H), 2.08 – 1.96 (m, 2H), 1.79 – 1.70 (m, 2H), 1.67 – 1.48 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 145.7, 141.2, 138.7, 128.8, 128.7, 127.6, 127.04, 126.98, 45.7, 34.7, 25.6. Data in accordance with the literature¹.

(S)-3-([1,1'-biphenyl]-4-yl)tetrahydrofuran (4b)



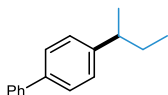
Yield:64% (28.7 mg), white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.50 (d, $J = 6.9$ Hz, 2H), 7.47 (d, $J = 8.3$ Hz, 2H), 7.35 (t, $J = 7.7$ Hz, 2H), 7.28 – 7.25 (m, 2H), 7.25 – 7.23 (m, 1H), 4.09 (t, $J = 8.0$ Hz, 1H), 4.02 (td, $J = 8.4, 4.5$ Hz, 1H), 3.86 (q, $J = 7.9$ Hz, 1H), 3.69 (t, $J = 8.0$ Hz, 1H), 3.37 (p, $J = 7.8$ Hz, 1H), 2.39 – 2.26 (m, 1H), 2.04 – 1.91 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 141.8, 140.9, 139.5, 128.8, 127.7, 127.3, 127.2, 127.0, 74.7, 68.6, 44.7, 34.7. Data in accordance with the literature¹.

4-([1,1'-biphenyl]-4-yl)tetrahydro-2H-pyran (4c)



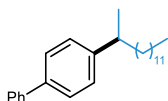
Yield:90% (42.9 mg), white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.50 (d, $J = 7.5$ Hz, 2H), 7.47 (d, $J = 8.2$ Hz, 2H), 7.35 (t, $J = 7.7$ Hz, 2H), 7.26 (d, $J = 7.4$ Hz, 1H), 7.22 (d, $J = 8.1$ Hz, 2H), 4.02 (dd, $J = 11.5, 2.4$ Hz, 2H), 3.54 – 3.39 (m, 2H), 2.78 – 2.66 (m, 1H), 1.85 – 1.75 (m, 2H), 1.75 – 1.67 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 145.0, 141.0, 139.3, 128.8, 127.3, 127.2, 127.1, 127.0, 68.4, 41.3, 34.0. Data in accordance with the literature¹⁰.

(S)-4-(sec-butyl)-1,1'-biphenyl (4d)



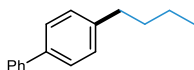
Yield:86% (36.1 mg), white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.51 (d, $J = 7.0$ Hz, 2H), 7.44 (d, $J = 8.2$ Hz, 2H), 7.34 (t, $J = 7.7$ Hz, 2H), 7.23 (t, $J = 7.3$ Hz, 1H), 7.17 (d, $J = 8.2$ Hz, 2H), 2.62 – 2.50 (m, 1H), 1.62 – 1.49 (m, 2H), 1.19 (d, $J = 7.0$ Hz, 3H), 0.78 (t, $J = 7.4$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 146.9, 141.2, 138.7, 128.8, 128.7, 127.5, 127.03, 126.97, 41.4, 31.2, 21.9, 12.3. Data in accordance with the literature¹¹.

(S)-4-(tetradecan-2-yl)-1,1'-biphenyl (4e)



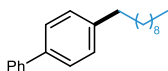
Yield:73% (51.1 mg), white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.50 (d, $J = 7.6$ Hz, 2H), 7.43 (d, $J = 8.0$ Hz, 2H), 7.33 (t, $J = 7.6$ Hz, 2H), 7.22 (t, $J = 7.4$ Hz, 1H), 7.16 (d, $J = 8.0$ Hz, 2H), 2.69 – 2.57 (m, 1H), 1.57 – 1.45 (m, 2H), 1.22 – 1.12 (m, 23H), 0.79 (t, $J = 6.7$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 147.2, 141.2, 138.7, 128.8, 128.7, 127.4, 127.04, 126.96, 39.7, 38.5, 32.0, 29.8, 29.74, 29.65, 29.4, 27.8, 22.8, 22.4, 14.2. Data in accordance with the literature¹.

4-butyl-1,1'-biphenyl (4f)



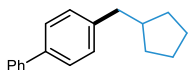
Yield:69% (29.0 mg), colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.50 (d, $J = 7.2$ Hz, 2H), 7.43 (d, $J = 6.3$ Hz, 2H), 7.34 (t, $J = 7.7$ Hz, 2H), 7.23 (t, $J = 7.4$ Hz, 1H), 7.17 (d, $J = 8.0$ Hz, 2H), 2.57 (t, $J = 7.8$ Hz, 2H), 1.56 (p, $J = 7.6$ Hz, 2H), 1.38 – 1.24 (m, 2H), 0.87 (t, $J = 7.3$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 142.1, 141.2, 138.6, 128.9, 128.8, 128.7, 127.03, 126.98, 35.3, 33.7, 22.5, 14.0. Data in accordance with the literature¹².

4-decyl-1,1'-biphenyl (4g)



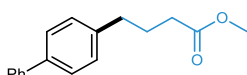
Yield:75% (44.1 mg), white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.50 (d, $J = 7.2$ Hz, 2H), 7.43 (d, $J = 8.1$ Hz, 2H), 7.33 (t, $J = 7.6$ Hz, 2H), 7.23 (t, $J = 7.3$ Hz, 1H), 7.17 (d, $J = 7.9$ Hz, 2H), 2.56 (t, $J = 7.8$ Hz, 2H), 1.63 – 1.51 (m, 2H), 1.30 – 1.16 (m, 14H), 0.80 (t, $J = 6.7$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 142.2, 141.2, 138.6, 128.9, 128.8, 128.7, 127.02, 126.98, 35.7, 32.0, 31.6, 29.69, 29.67, 29.6, 29.44, 29.40, 22.7, 14.2. Data in accordance with the literature¹³.

4-(cyclopentylmethyl)-1,1'-biphenyl (4h)



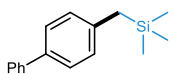
Yield:83% (39.2 mg), colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.51 (d, $J = 7.2$ Hz, 2H), 7.42 (d, $J = 6.1$ Hz, 2H), 7.34 (t, $J = 7.7$ Hz, 2H), 7.24 (t, $J = 7.4$ Hz, 1H), 7.16 (d, $J = 8.0$ Hz, 2H), 2.57 (d, $J = 7.4$ Hz, 2H), 2.11 – 1.97 (m, 1H), 1.71 – 1.61 (m, 2H), 1.61 – 1.52 (m, 2H), 1.49 – 1.41 (m, 2H), 1.19 – 1.11 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 141.6, 141.2, 138.5, 129.3, 128.7, 126.97, 126.92, 126.9, 42.0, 41.8, 32.6, 25.0. Data in accordance with the literature¹⁴.

methyl 4-([1,1'-biphenyl]-4-yl)butanoate (4i)



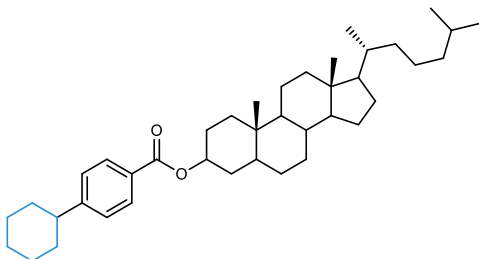
Yield:78% (39.6 mg), colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.49 (d, $J = 7.9$ Hz, 2H), 7.44 (d, $J = 8.3$ Hz, 2H), 7.34 (t, $J = 7.6$ Hz, 2H), 7.24 (t, $J = 7.3$ Hz, 1H), 7.17 (d, $J = 8.0$ Hz, 2H), 3.59 (s, 3H), 2.61 (t, $J = 7.6$ Hz, 2H), 2.28 (t, $J = 7.4$ Hz, 2H), 1.91 (p, $J = 7.5$ Hz, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 174.0, 141.1, 140.5, 139.0, 128.9, 128.7, 127.2, 127.1, 127.0, 51.6, 34.8, 33.4, 26.5. Data in accordance with the literature¹⁵.

([1,1'-biphenyl]-4-ylmethyl)trimethylsilane (4j)



Yield:68% (32.7 mg), white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.71 (d, $J = 7.0$ Hz, 2H), 7.59 (d, $J = 8.2$ Hz, 2H), 7.54 (t, $J = 7.7$ Hz, 2H), 7.42 (t, $J = 7.3$ Hz, 1H), 7.19 (d, $J = 8.2$ Hz, 2H), 2.25 (s, 2H), 0.15 (s, 9H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 141.3, 139.8, 136.8, 128.7, 128.5, 126.9, 126.8, 126.8, 26.8, -1.8. Data in accordance with the literature¹⁶.

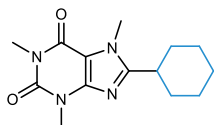
(10S,13R)-17-butyl-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-3-yl cyclohexylbenzoate (5a)



Yield:60% (62.2 mg), white solid; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.87 (d, $J = 8.3$ Hz, 2H), 7.17 (d, $J = 8.3$ Hz, 2H), 4.98 – 4.74 (m, 1H), 2.52 – 2.41 (m, 1H), 1.81 – 0.97 (m, 41H), 0.83 (d, $J = 6.4$ Hz, 3H), 0.80 (d, $J = 1.9$ Hz, 3H), 0.78 (d, $J = 2.3$ Hz, 6H), 0.58 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.2, 153.2, 129.7, 128.6, 126.8, 74.1, 56.5, 56.3, 54.3, 44.8, 44.7, 42.6, 40.0, 39.6, 36.9, 36.2, 35.9, 35.6, 34.2, 32.1, 28.7, 28.3, 28.1, 27.7, 26.8, 26.1, 24.3, 23.9, 22.9, 22.6, 21.3, 18.7, 12.3, 12.1. Data in accordance with the

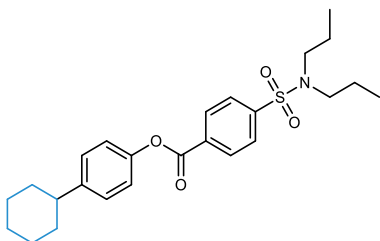
literature.¹

8-cyclohexyl-1,3,7-trimethyl-3,7-dihydro-1H-purine-2,6-dione (5b)



Yield:33% (18.2 mg), white solid; ¹H NMR (400 MHz, CDCl₃) δ 3.86 (s, 3H), 3.50 (s, 3H), 3.32 (s, 3H), 2.69 – 2.59 (m, 1H), 1.88 – 1.75 (m, 4H), 1.73 – 1.55 (m, 4H), 1.38 – 1.32 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 158.03, 155.51, 151.83, 148.14, 107.05, 35.83, 31.42, 30.96, 29.77, 27.85, 26.02, 25.58. Data in accordance with the literature¹⁷.

4-cyclohexylphenyl 4-(N,N-dipropylsulfamoyl)benzoate (5c)



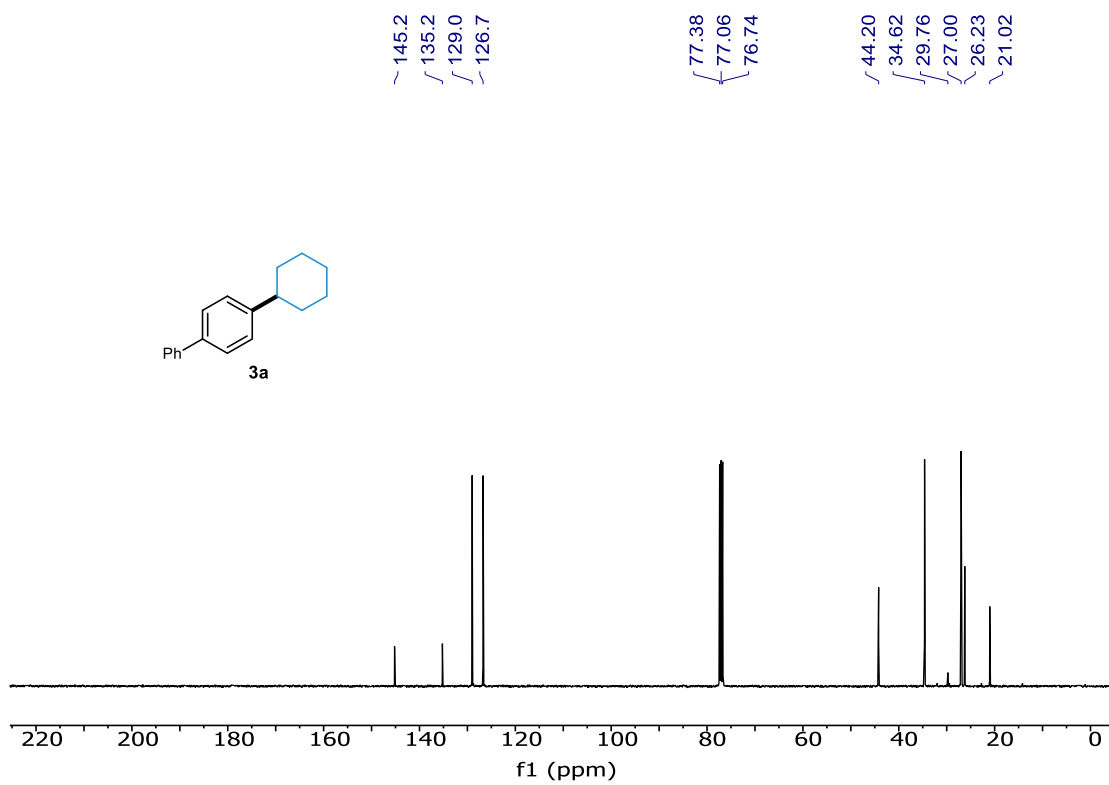
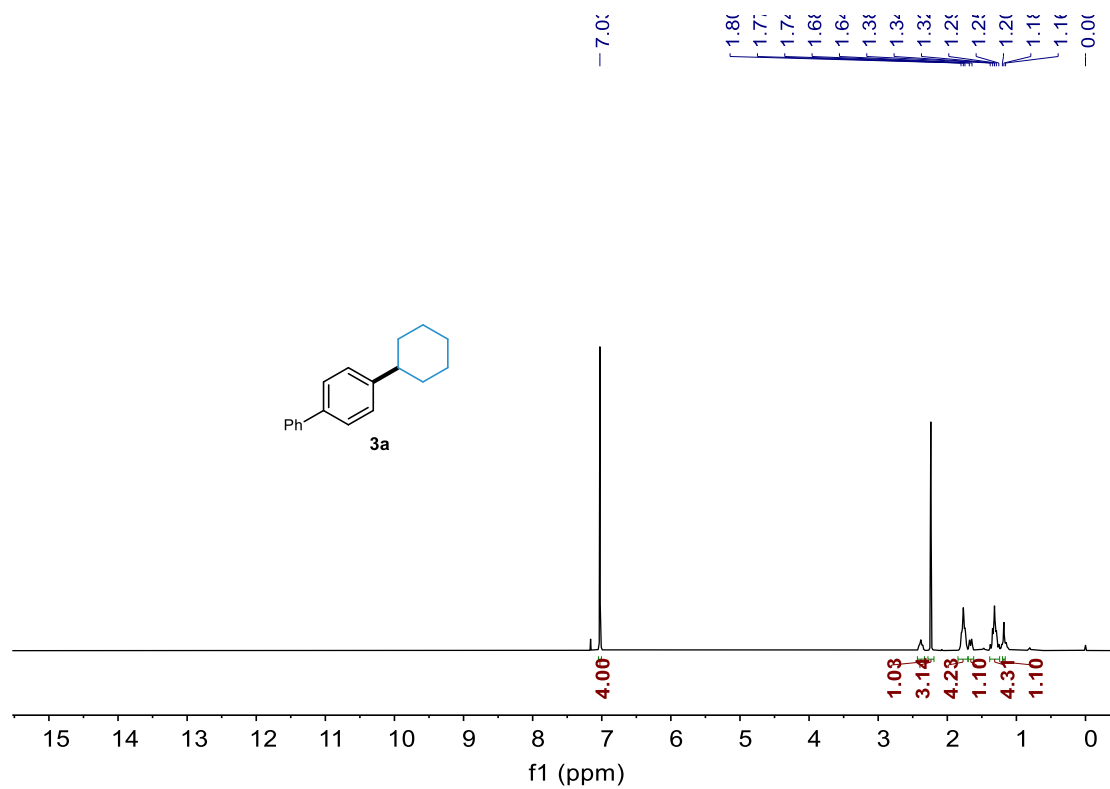
Yield:62% (55.0 mg), white solid; ¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 8.5 Hz, 2H), 7.87 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.05 (d, *J* = 8.6 Hz, 2H), 3.14 – 2.96 (m, 4H), 2.57 – 2.37 (m, 1H), 1.88 – 1.73 (m, 4H), 1.68 (d, *J* = 10.5 Hz, 1H), 1.52 – 1.44 (m, 4H), 1.42 – 1.26 (m, 4H), 1.21 – 1.16 (m, 1H), 0.81 (t, *J* = 7.4 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 164.1, 148.6, 146.1, 144.8, 133.1, 130.8, 127.9, 127.2, 121.1, 50.0, 44.1, 34.6, 26.9, 26.1, 22.0, 11.2. Data in accordance with the literature¹.

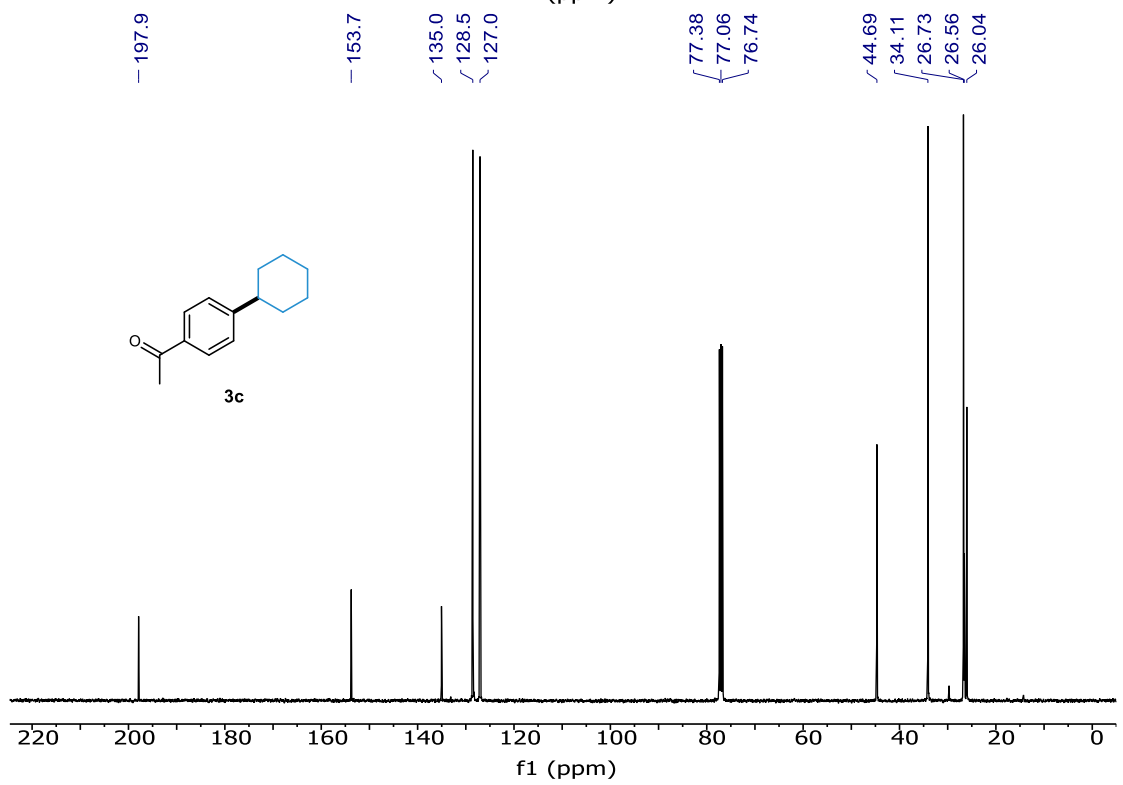
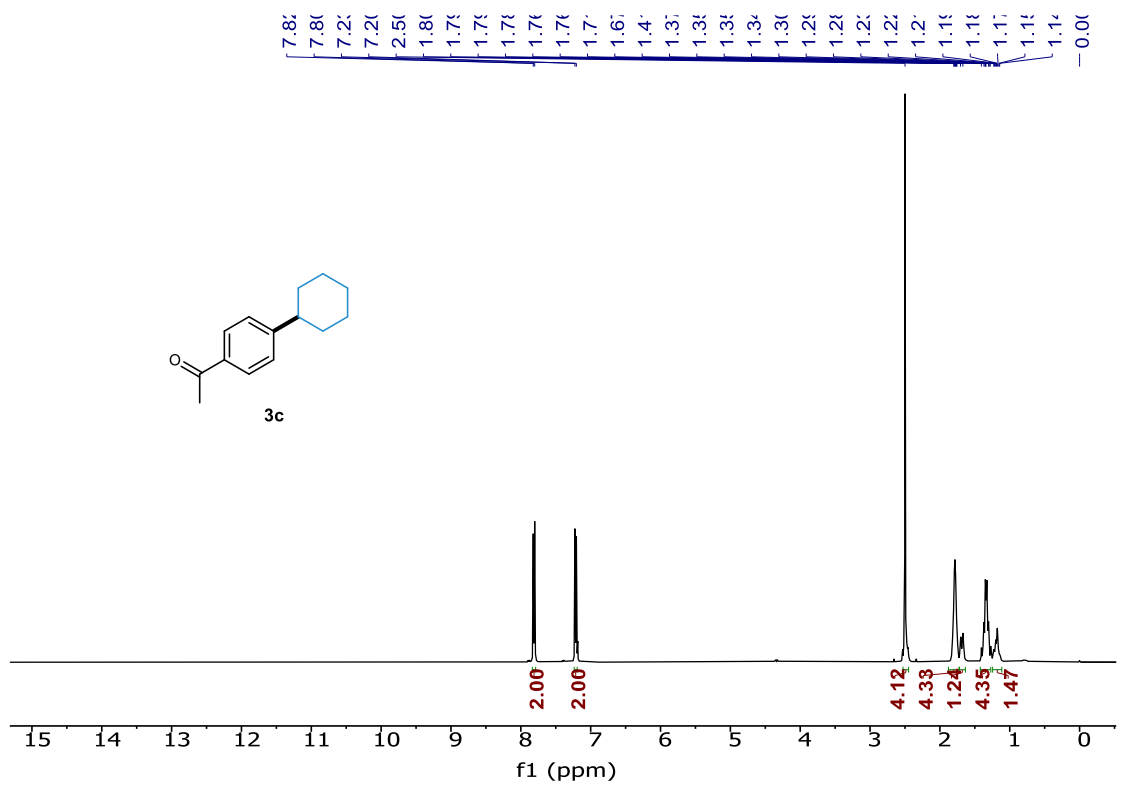
4. References

- [1] H. Yue, C. Zhu, L. Shen, Q. Geng, K. J. Hock, T. Yuan, L. Cavallo and M. Rueping, *Chem. Sci.*, 2019, **10**, 4430-4435.
- [2] T. Scherpf, H. Steinert, A. Großjohann, K. Dilchert, J. Tappen, I. Rodstein and V. H. Gessner, *Angew. Chem. Int. Ed.*, 2020, **59**, 20596-20603.
- [3] D. Liu, Y. Li, X. Qi, C. Liu, Y. Lan and A. Lei, *Org. Lett.*, 2015, **17**, 998-1001.
- [4] Q. H. Xu, L. P. Wei and B. Xiao, *Angew. Chem. Int. Ed.*, 2022, **61**, e202115592.
- [5] X. J. Wei, I. Abdiaj, C. Sambigiagio, C. Li, E. Zysman-Colman, J. Alcázar and T. Noël, *Angew. Chem. Int. Ed.*, 2019, **58**, 13030-13034.
- [6] W. M. Czaplik, M. Mayer and A. Jacobi von Wangelin, *Angew. Chem. Int. Ed.*, 2008, **48**, 607-610.

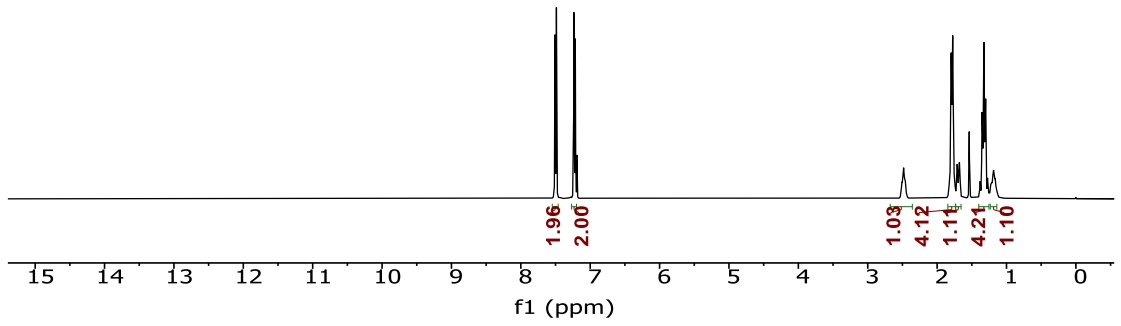
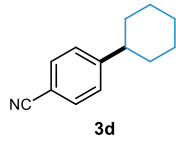
- [7] I. B. Perry, T. F. Brewer, P. J. Sarver, D. M. Schultz, D. A. DiRocco and D. W. C. MacMillan, *Nature*, 2018, **560**, 70-75.
- [8] Z. Jiao, L. H. Lim, H. Hirao and J. S. Zhou, *Angew. Chem. Int. Ed.*, 2018, **57**, 6294-6298.
- [9] X. Tian, J. Kaur, S. Yakubov and J. P. Barham, *ChemSusChem*, 2022, **15**, e202200906.
- [10] L. R. Mills, D. Gygi, J. R. Ludwig, E. M. Simmons, S. R. Wisniewski, J. Kim and P. J. Chirik, *ACS Cat.*, 2022, **12**, 1905-1918.
- [11] W. Liu, J. Li, P. Querard and C.-J. Li, *J. Am. Chem. Soc.*, 2019, **141**, 6755-6764.
- [12] Simon B. Blakey and David W. C. MacMillan, *J. Am. Chem. Soc.*, 2003, **125**, 6046-6047.
- [13] J. T. Guan, X. M. Song, Z. Y. Zhang, B. M. Wei and Z. Q. Dai, *Appl. Organomet. Chem.*, 2014, **29**, 87-89.
- [14] C. Zhu and J. Zhang, *Chem. Commun.*, 2019, **55**, 2793-2796.
- [15] K. Zheng, G. Xiao, T. Guo, Y. Ding, C. Wang, T.-P. Loh and X. Wu, *Org. Lett.*, 2020, **22**, 694-699.
- [16] M. Leiendecker, A. Chatupheeraphat and M. Rueping, *Org. Chem. Fron.*, 2015, **2**, 350-353.
- [17] M. Graužinytė, J. Forth, K. A. Rumble and P. S. Clegg, *Angew. Chem. Int. Ed.*, 2014, **54**, 1456-1460

5. Copies of Products ¹H NMR and ¹³C NMR:

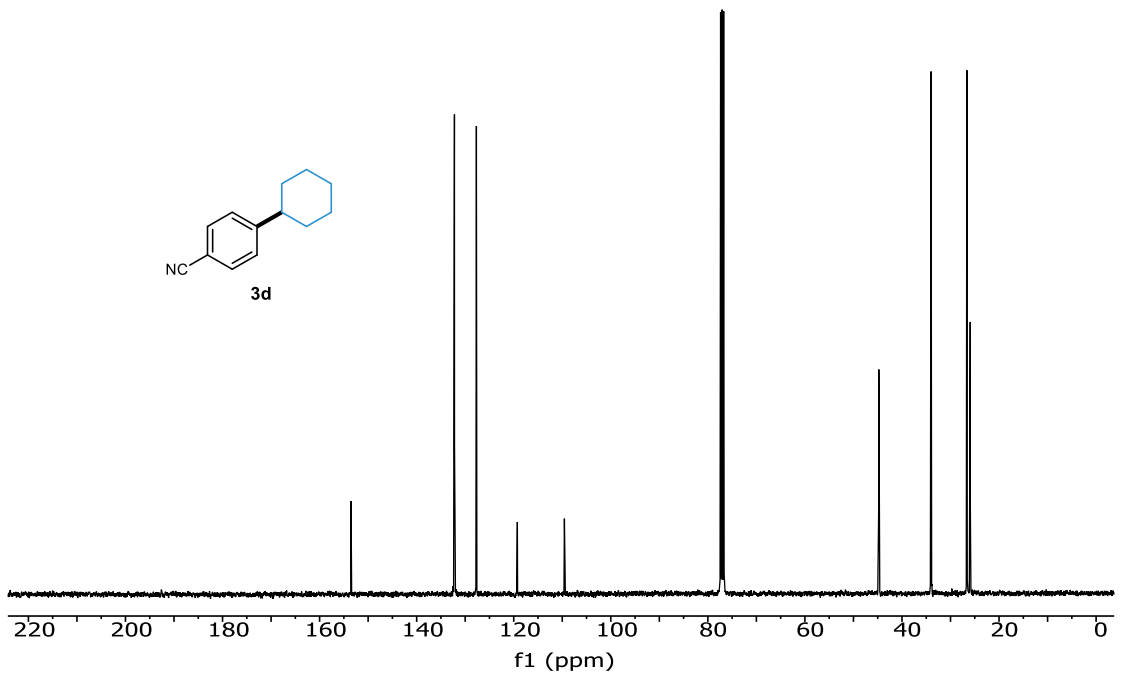
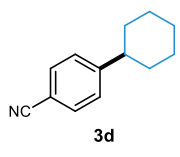


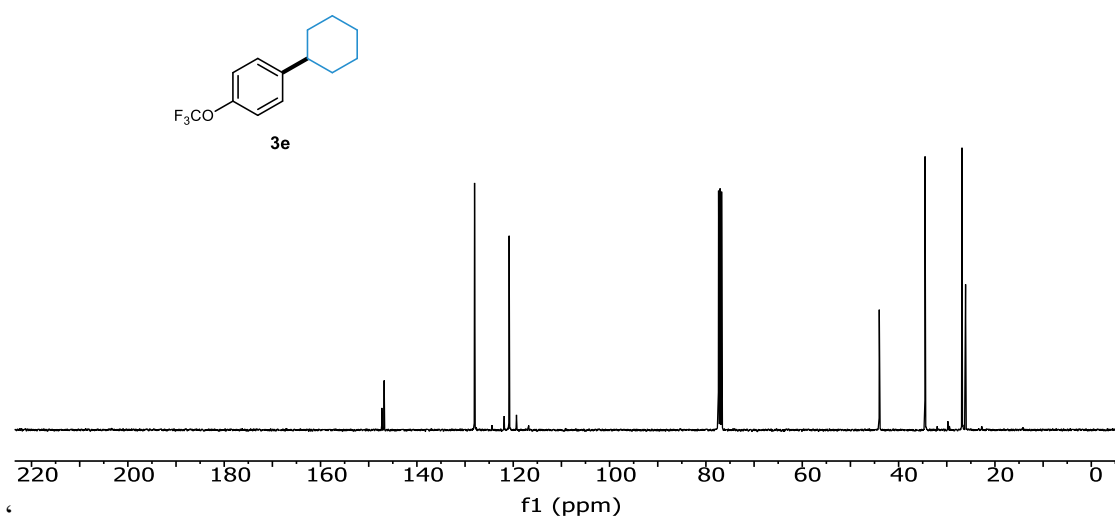
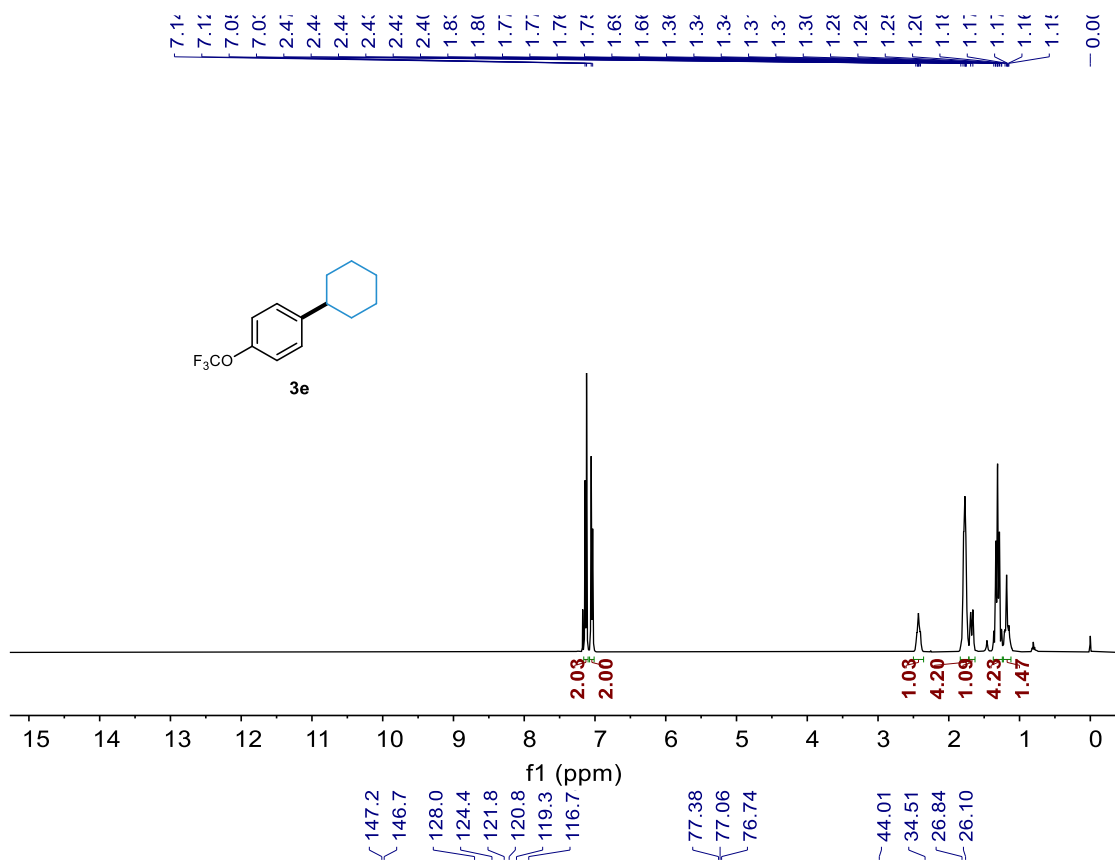


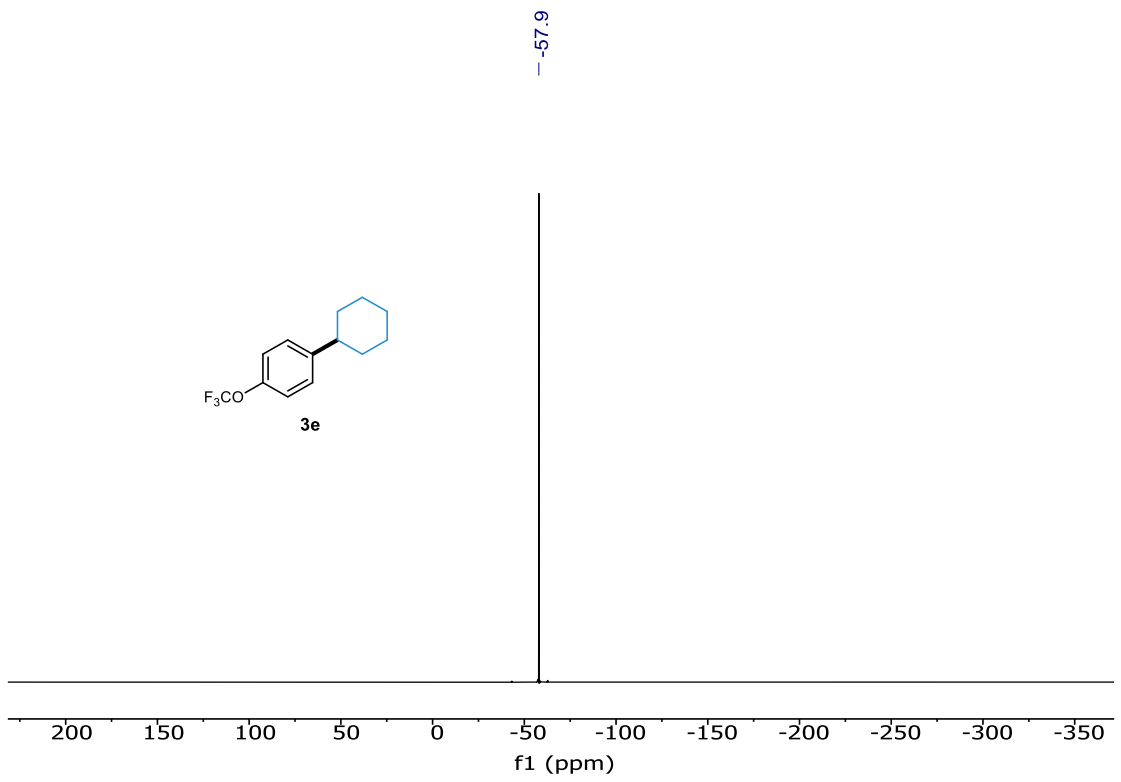
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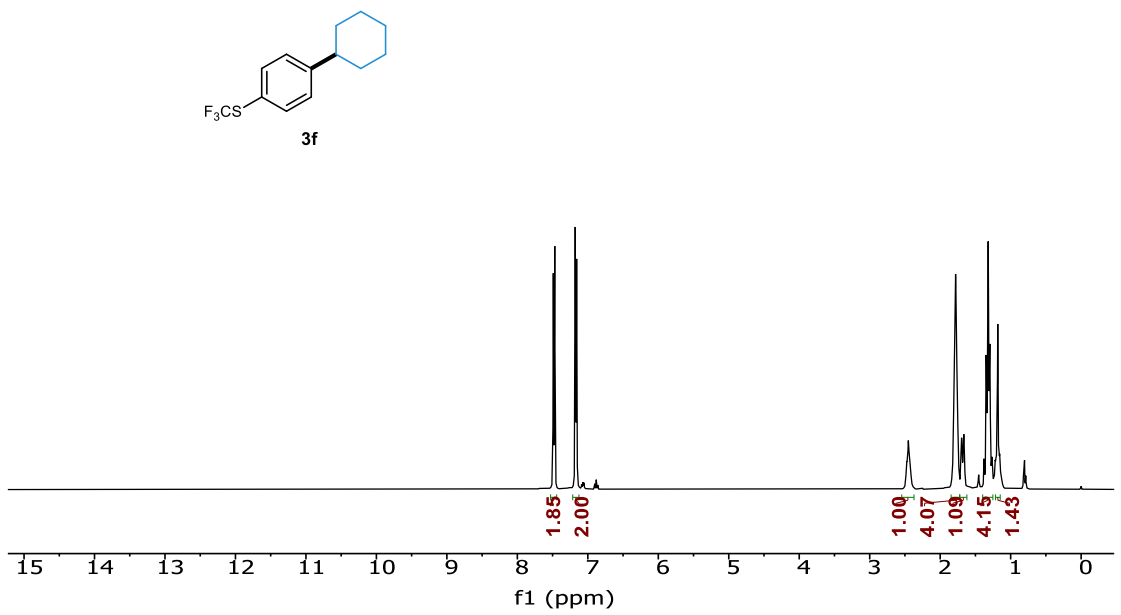
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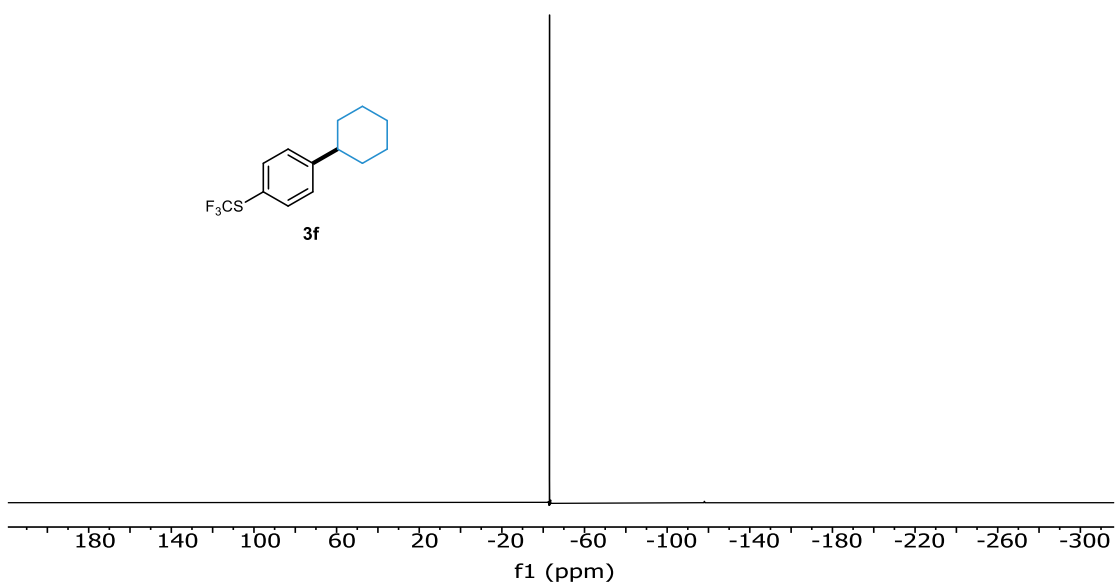
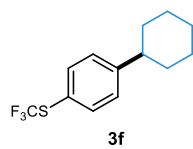
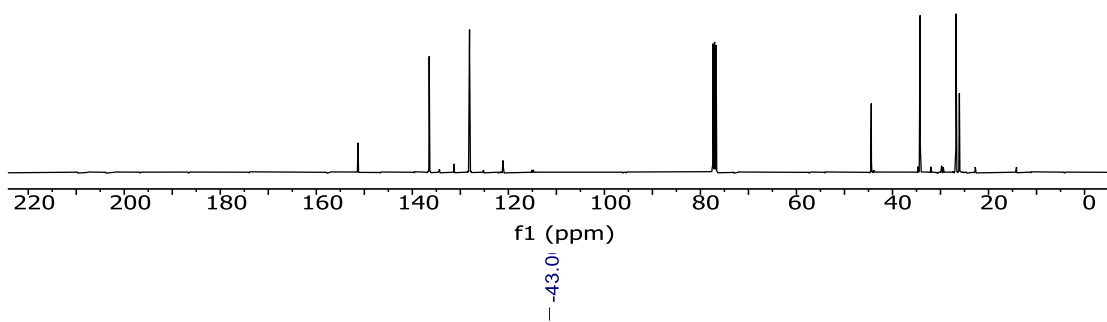
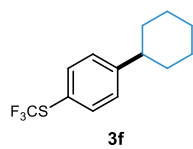




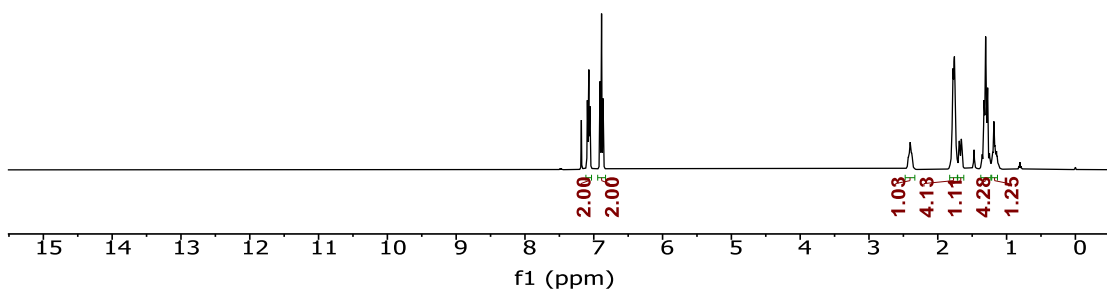
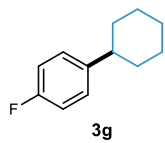
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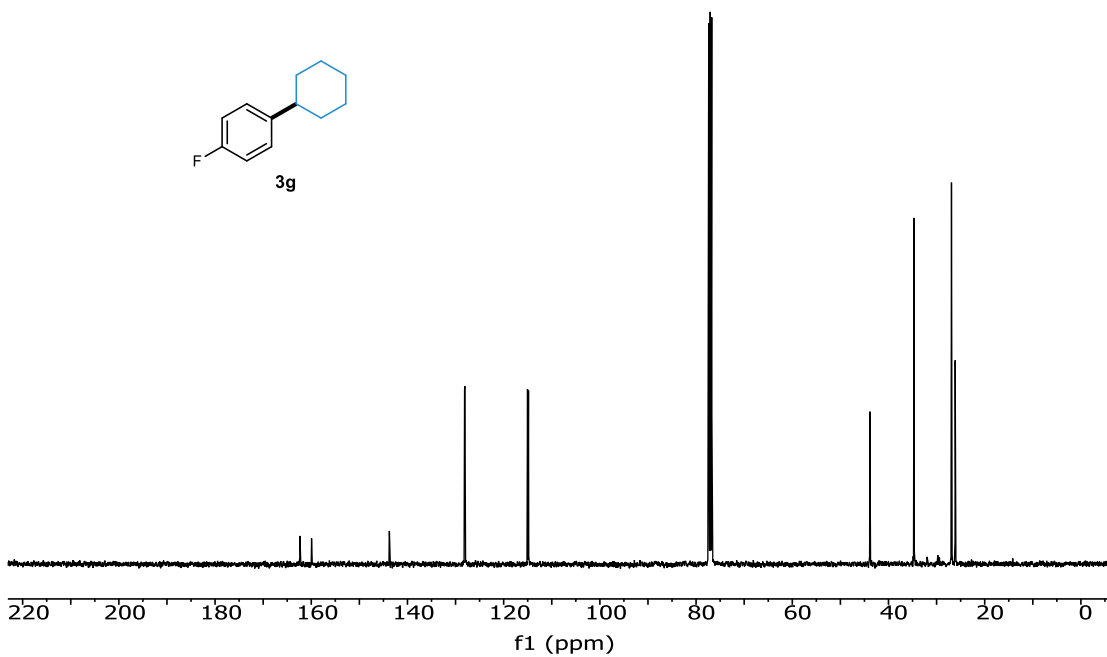
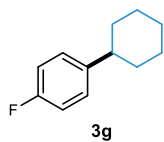
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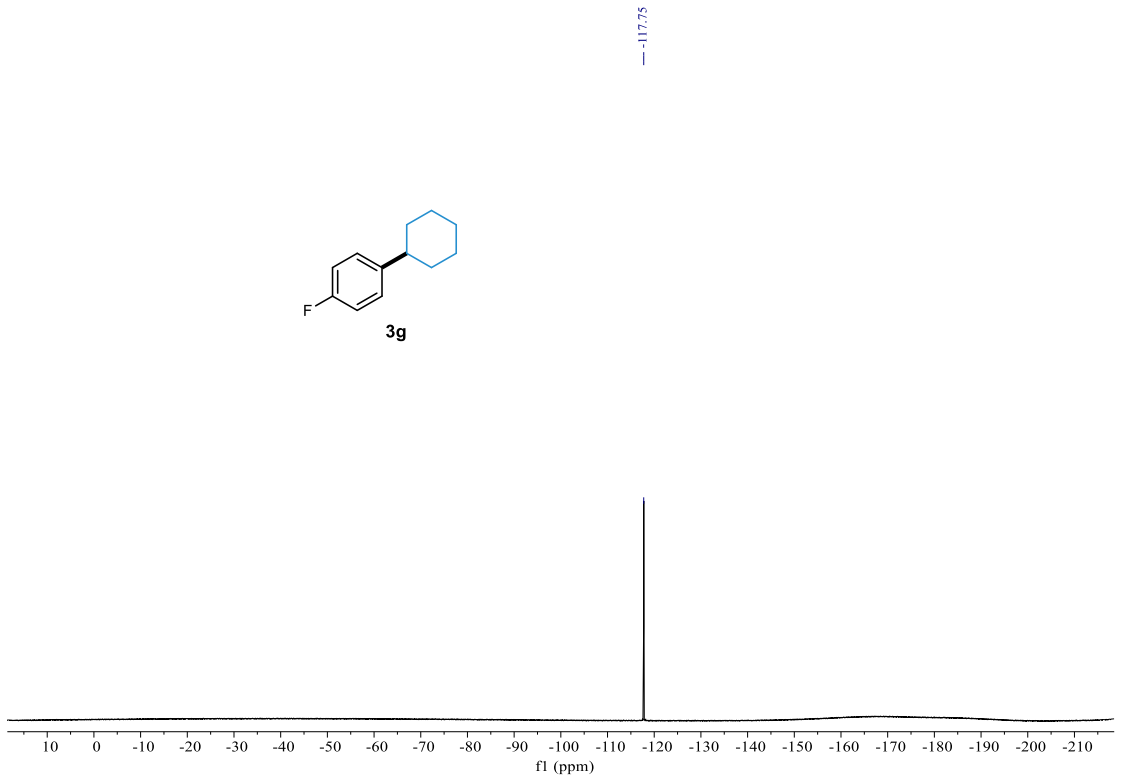
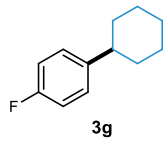


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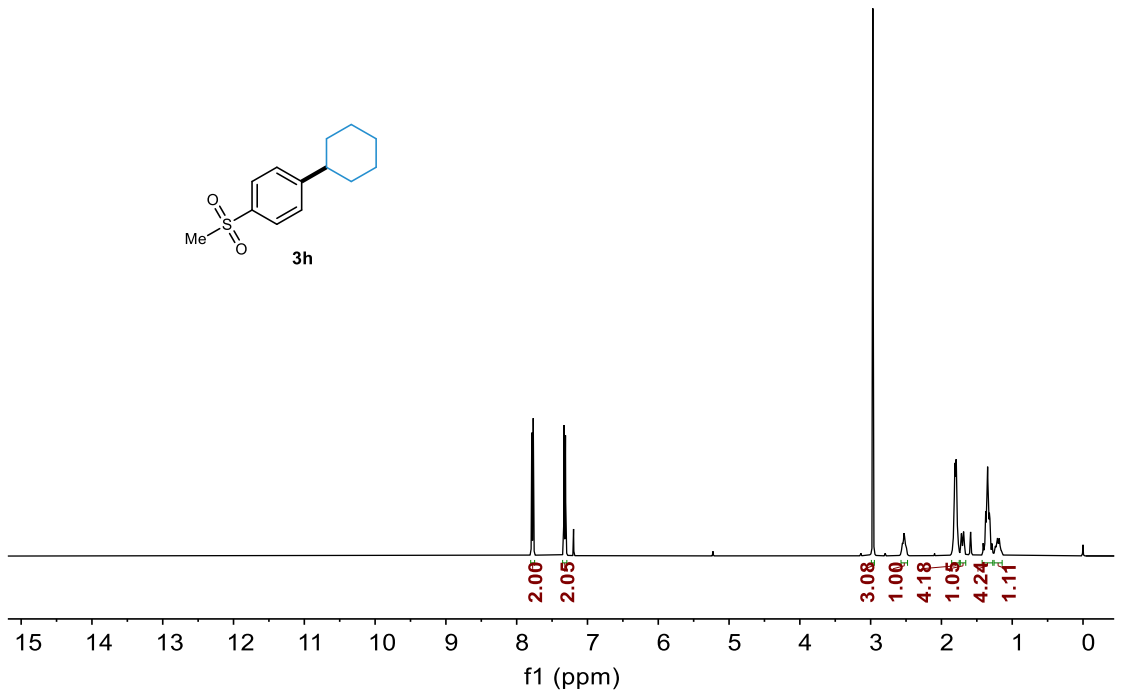
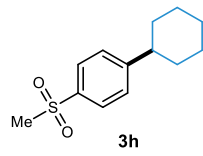


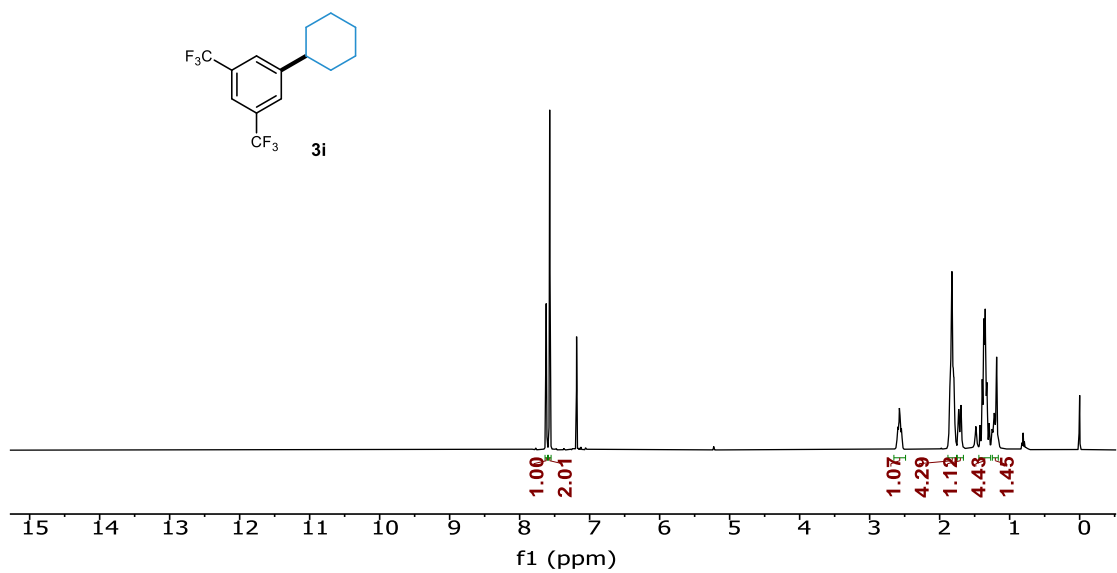
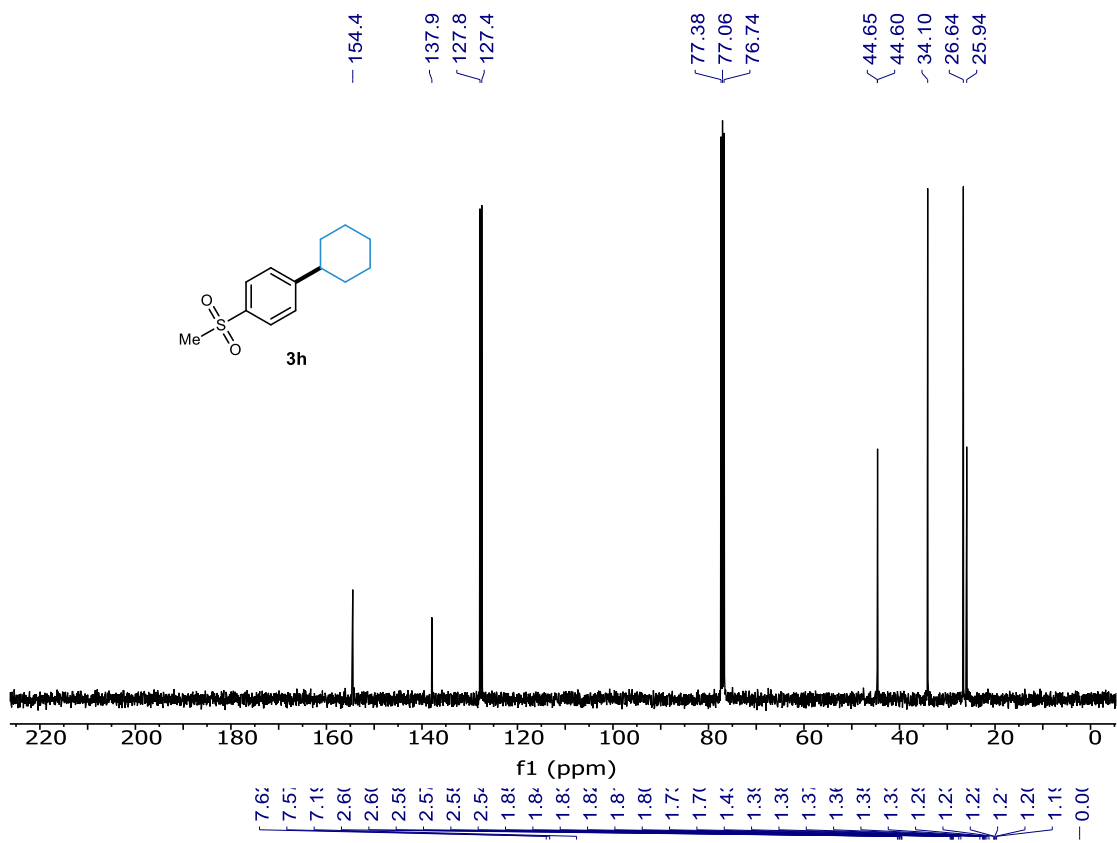
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159.9
143.7
143.7
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115.0
114.8
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77.06
76.74
43.88
34.69
26.90
26.13

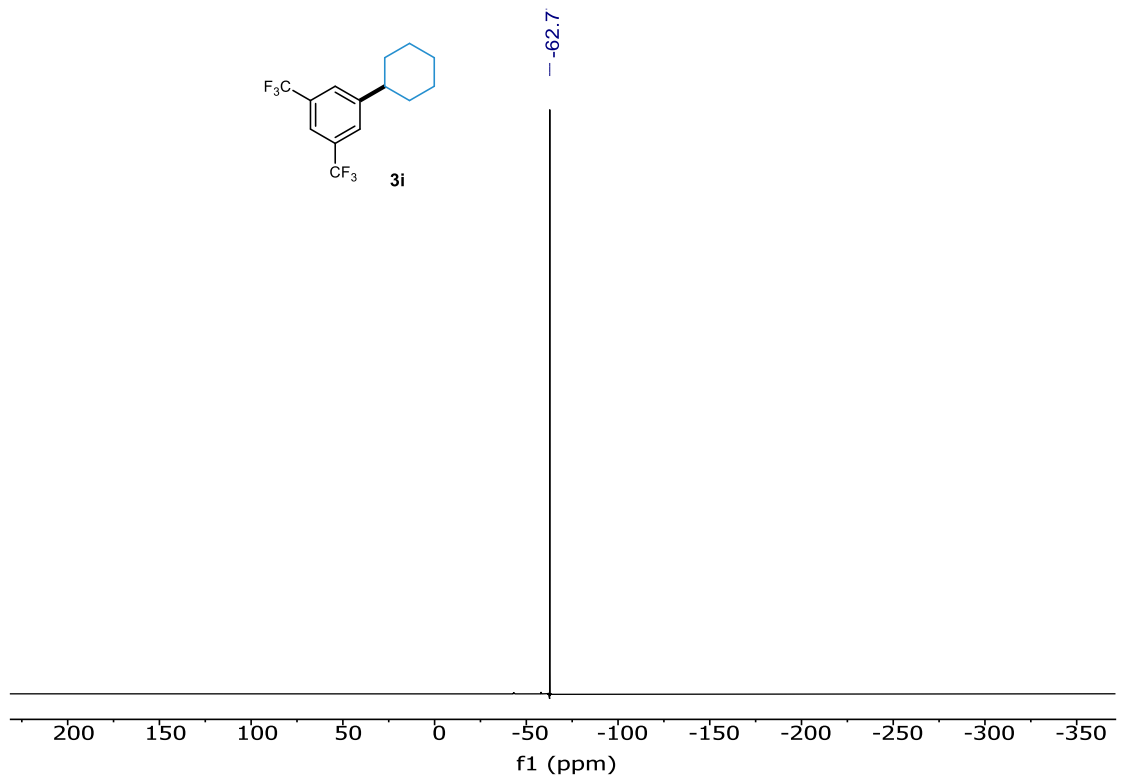
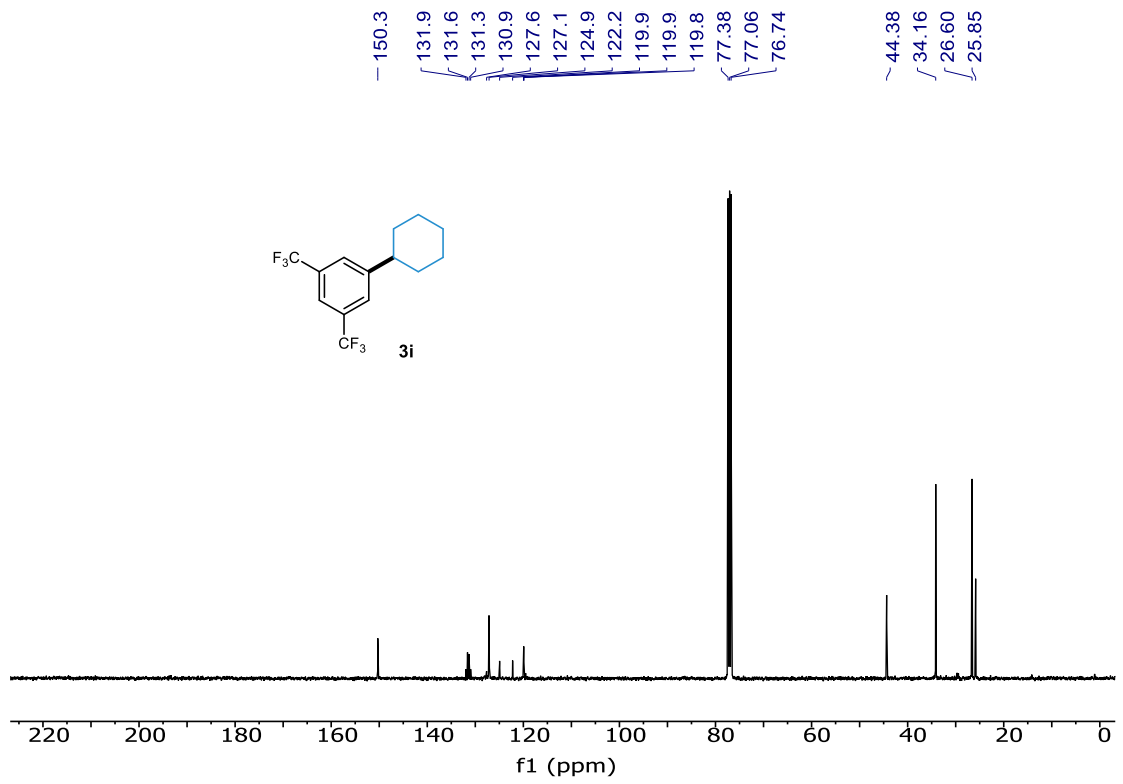


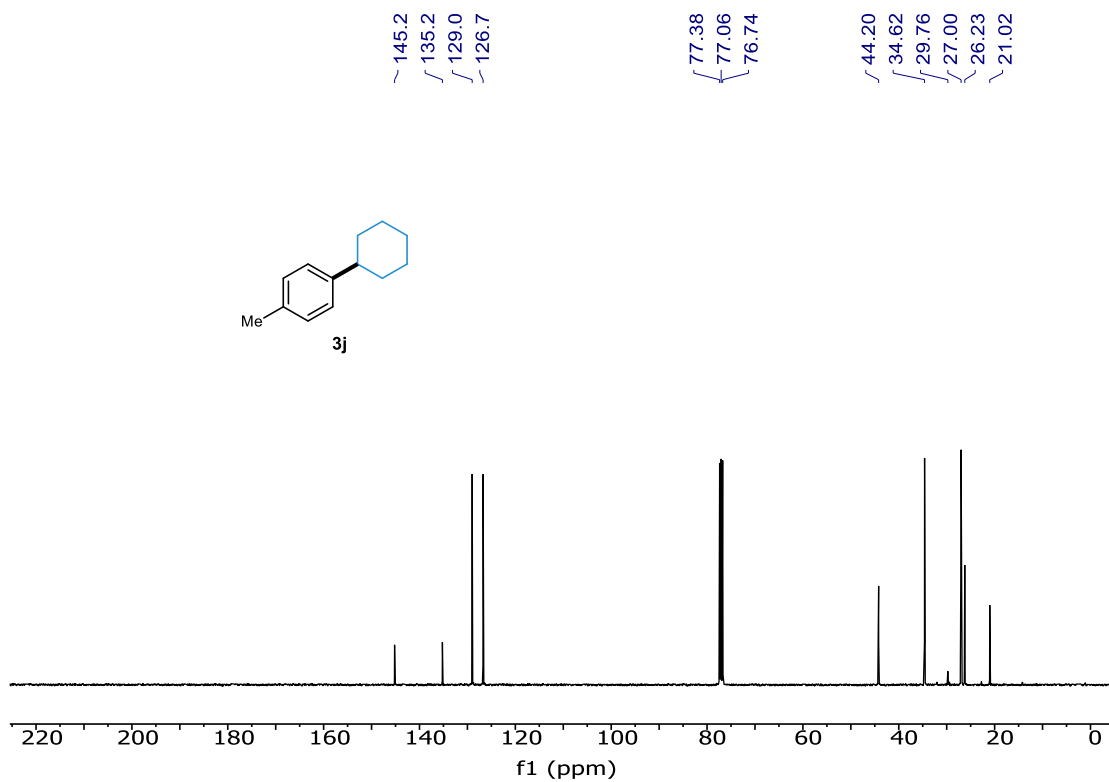
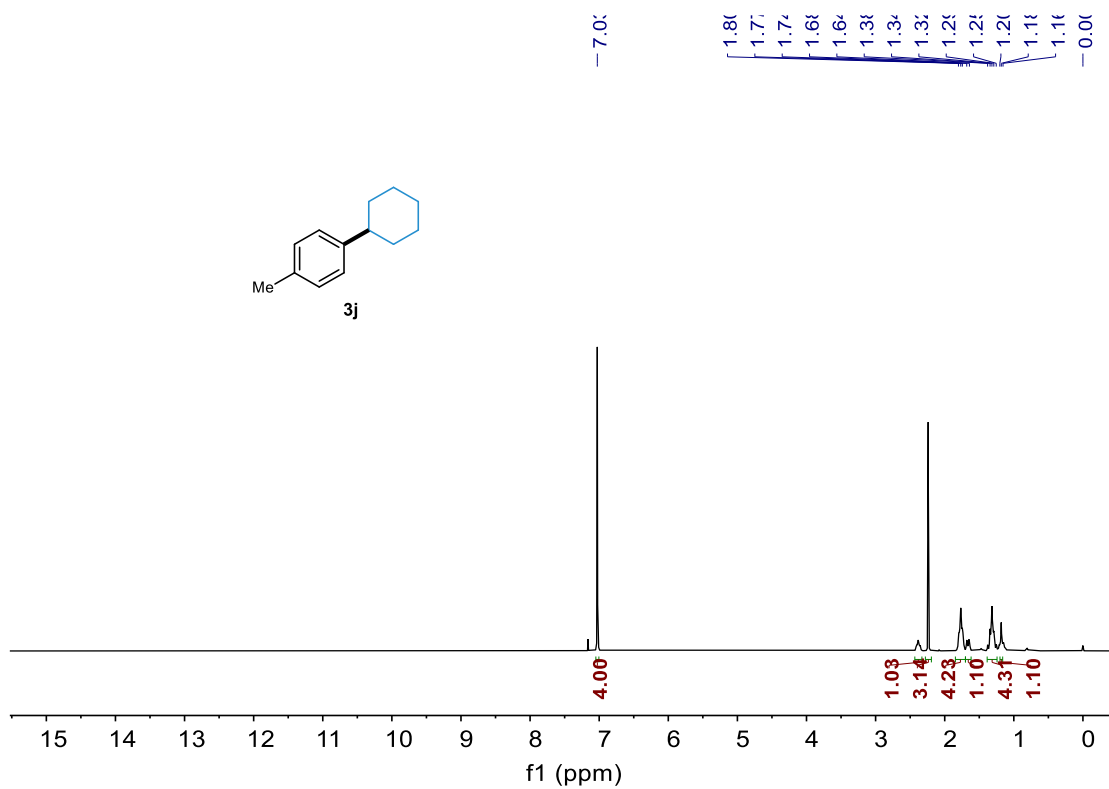


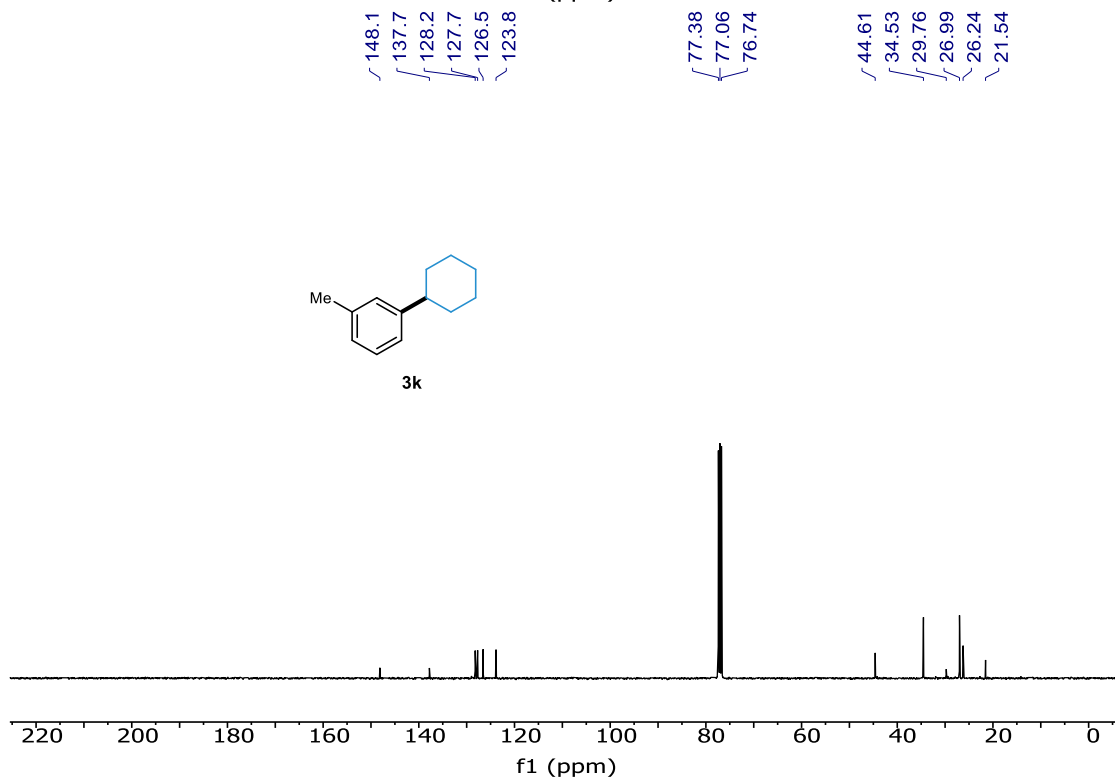
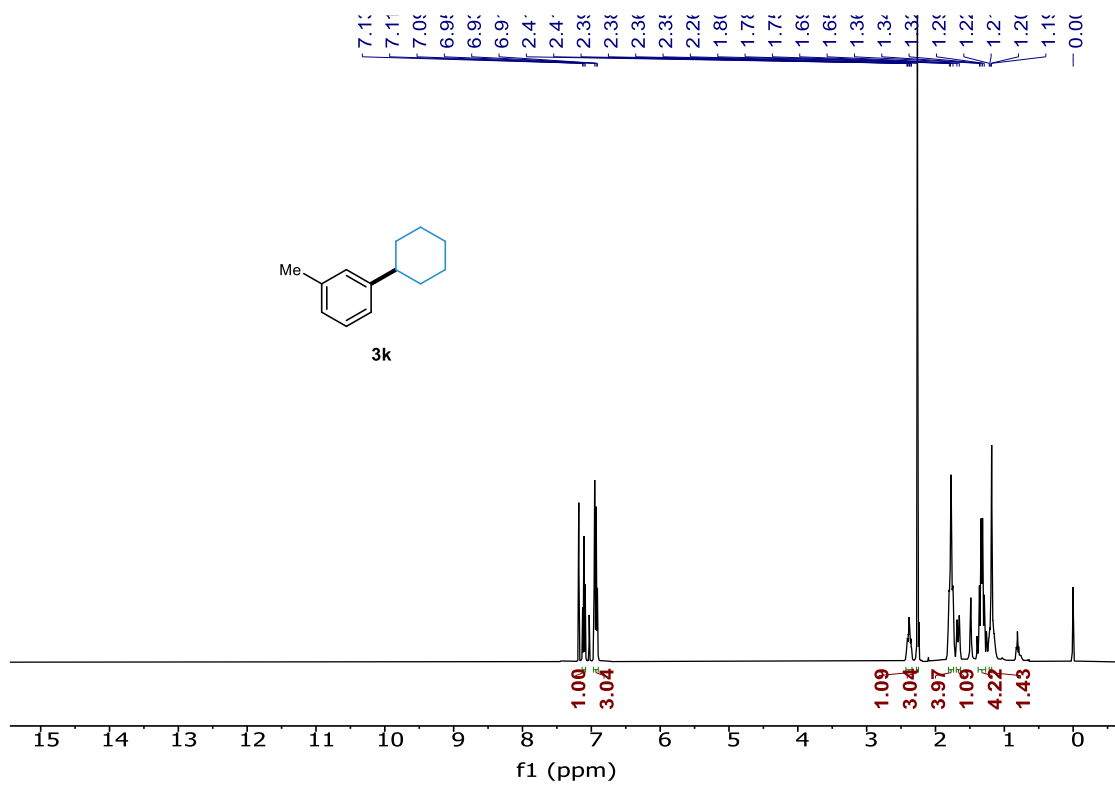
7.71
7.71
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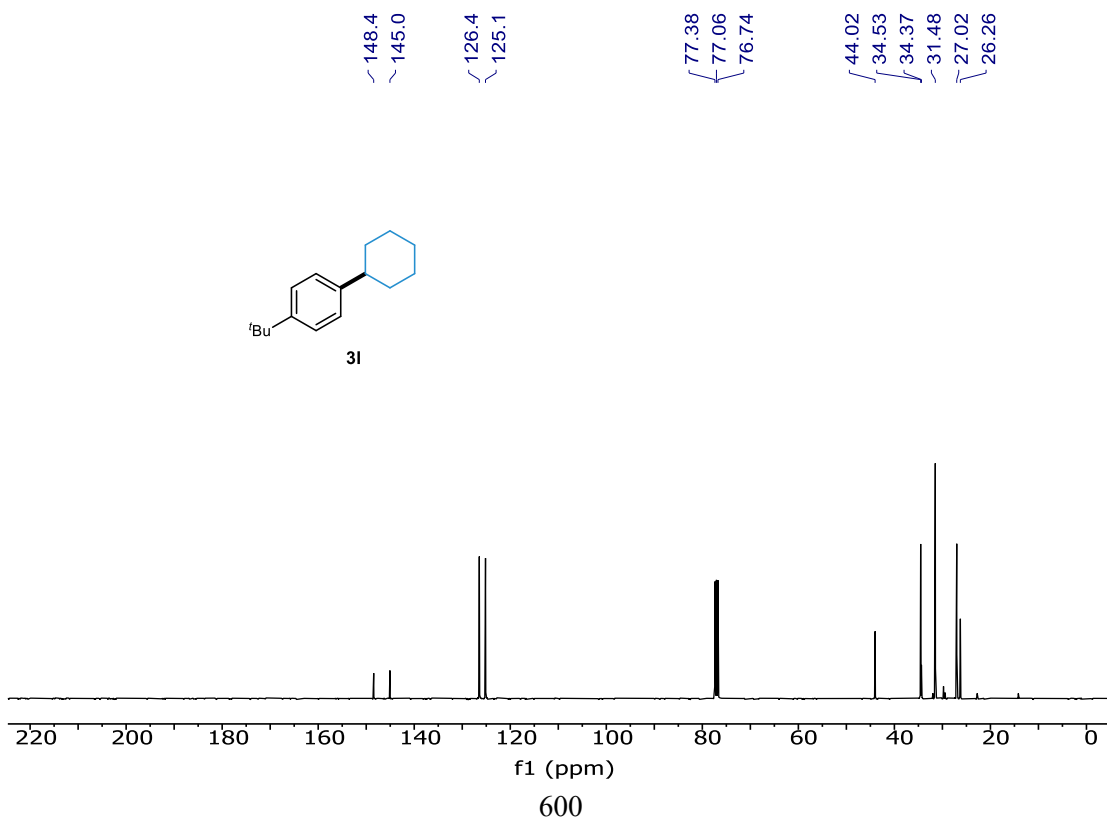
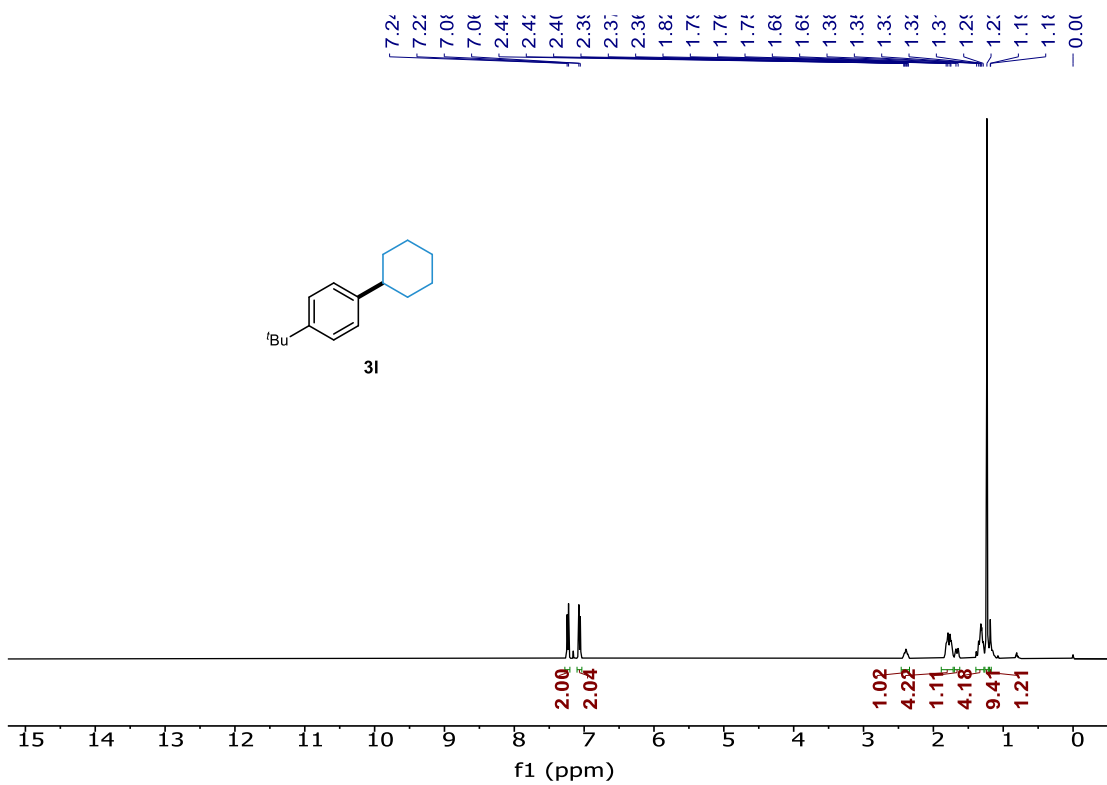


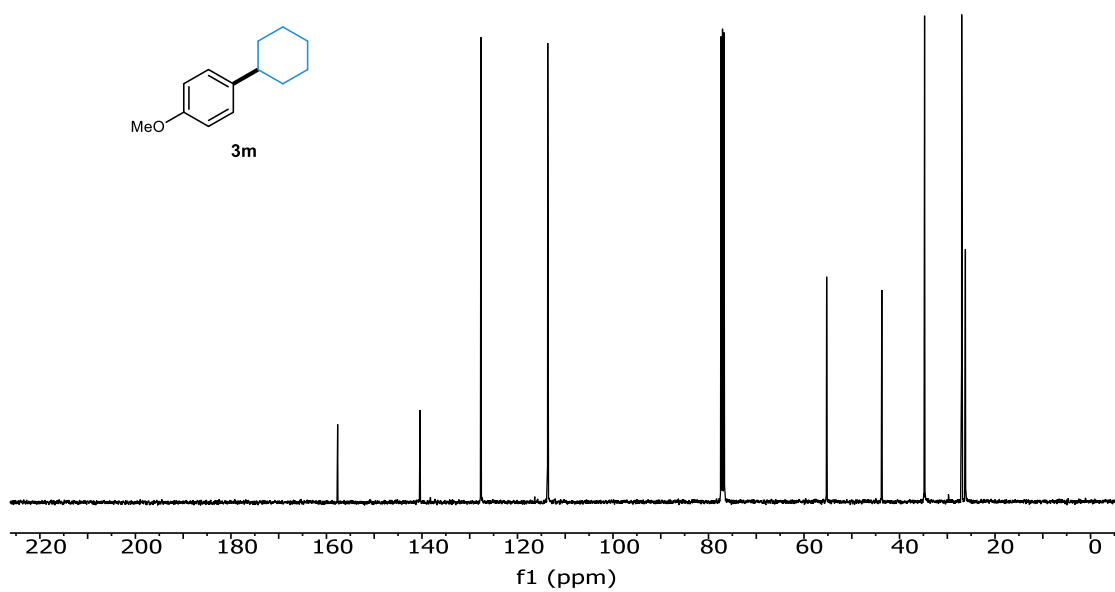
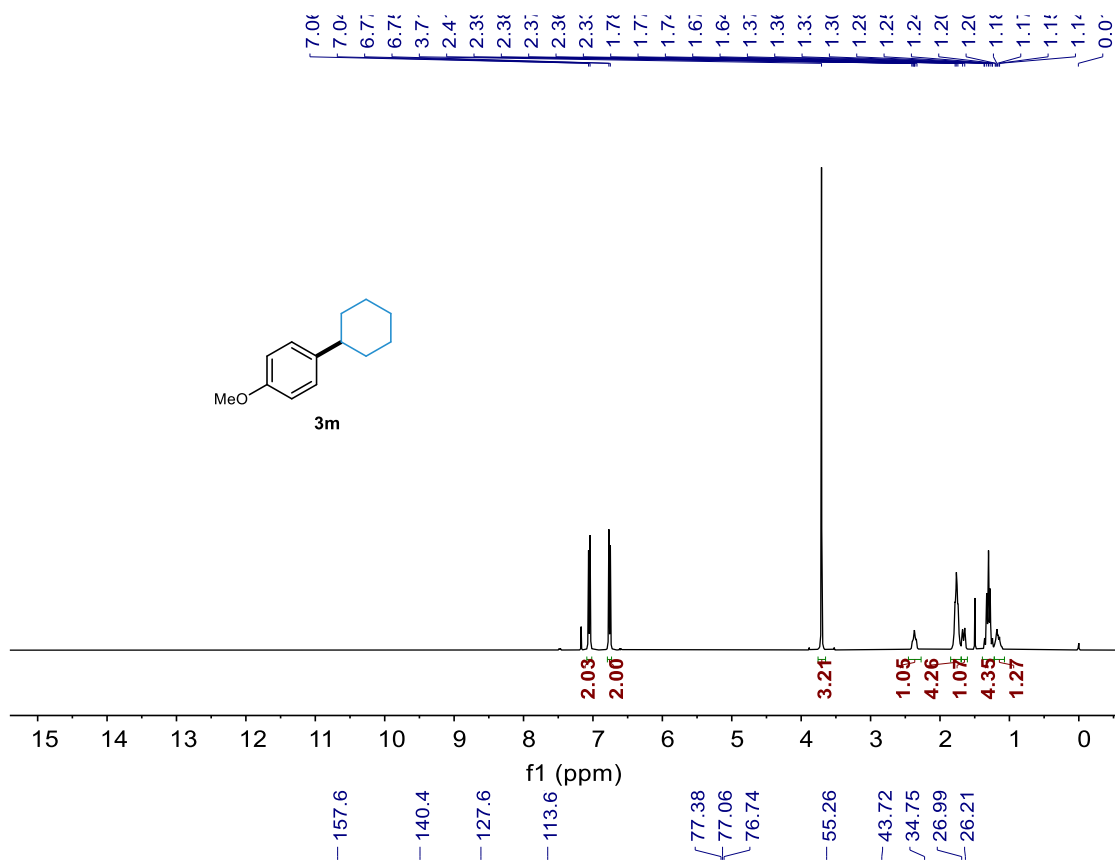


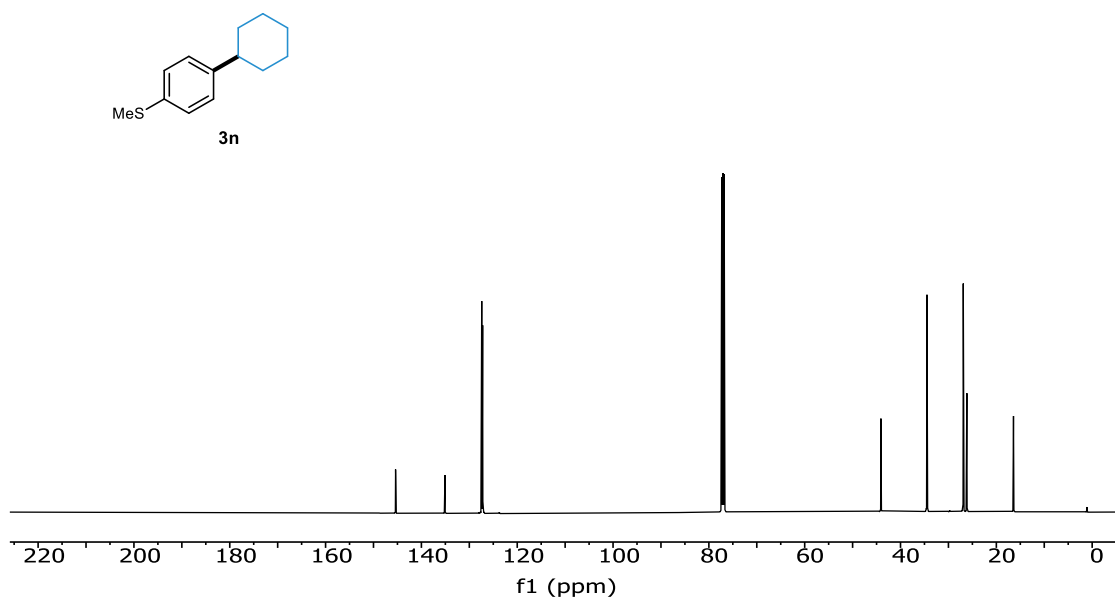
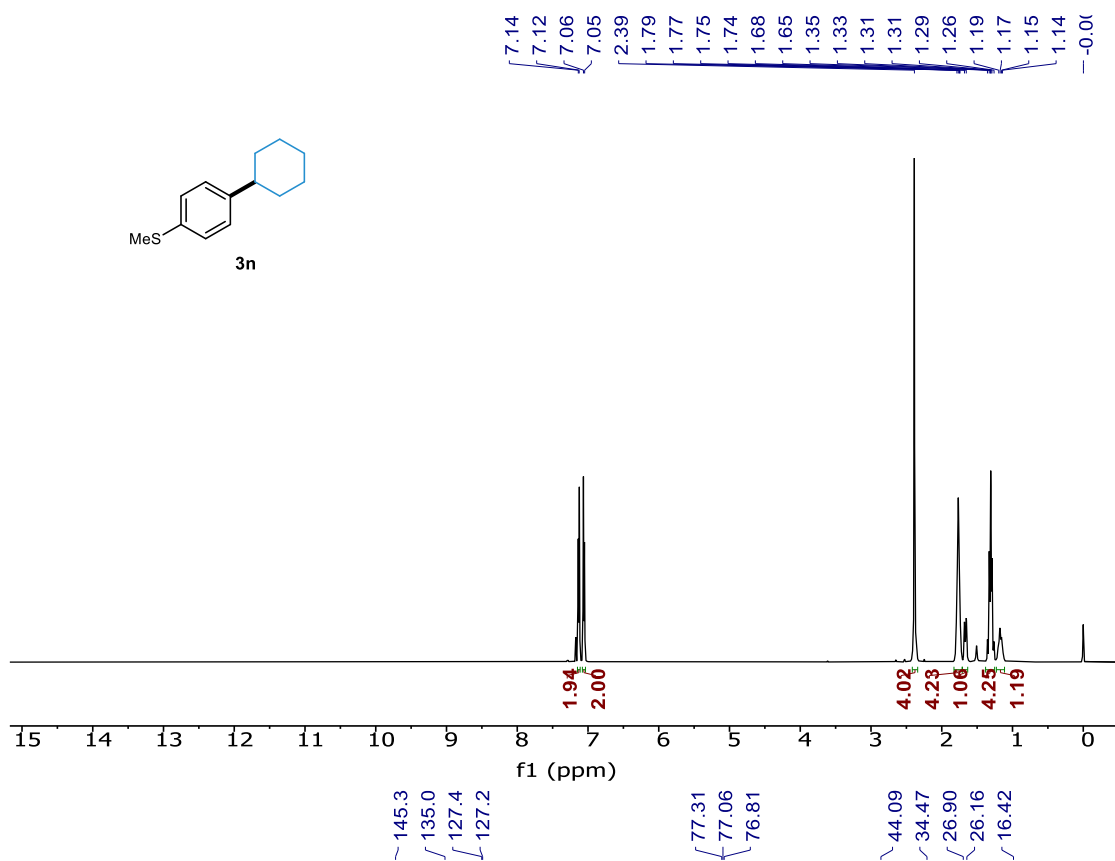


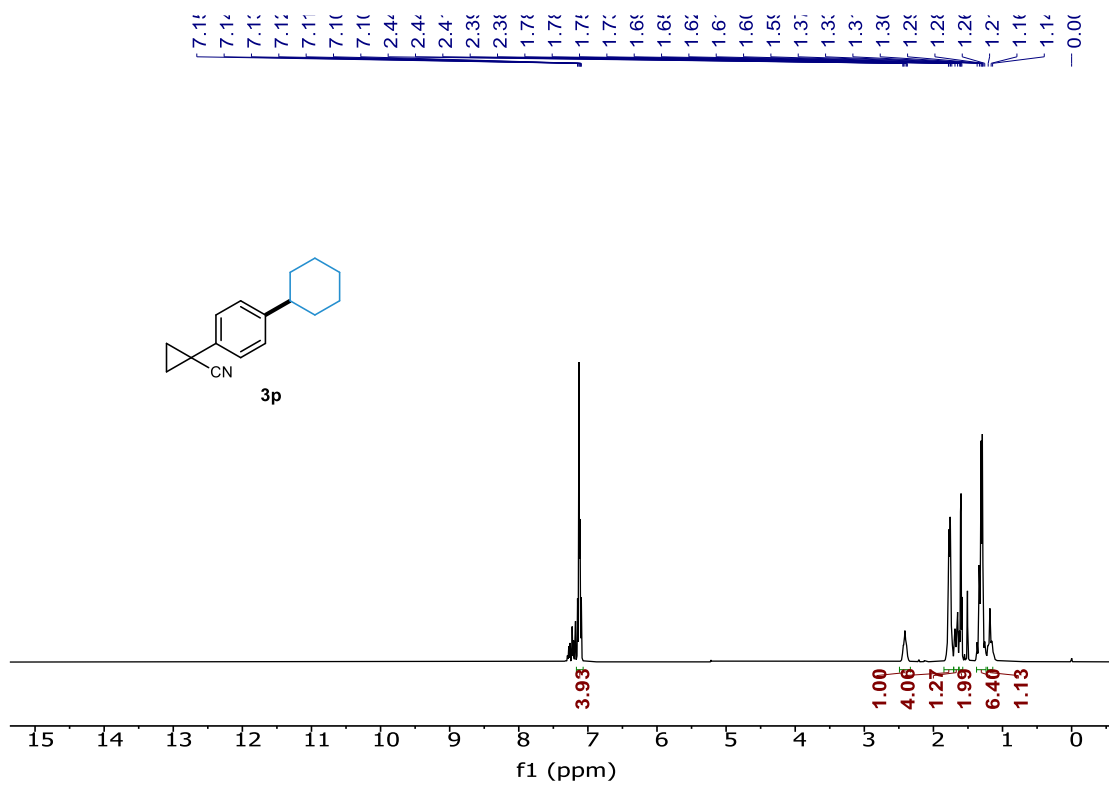




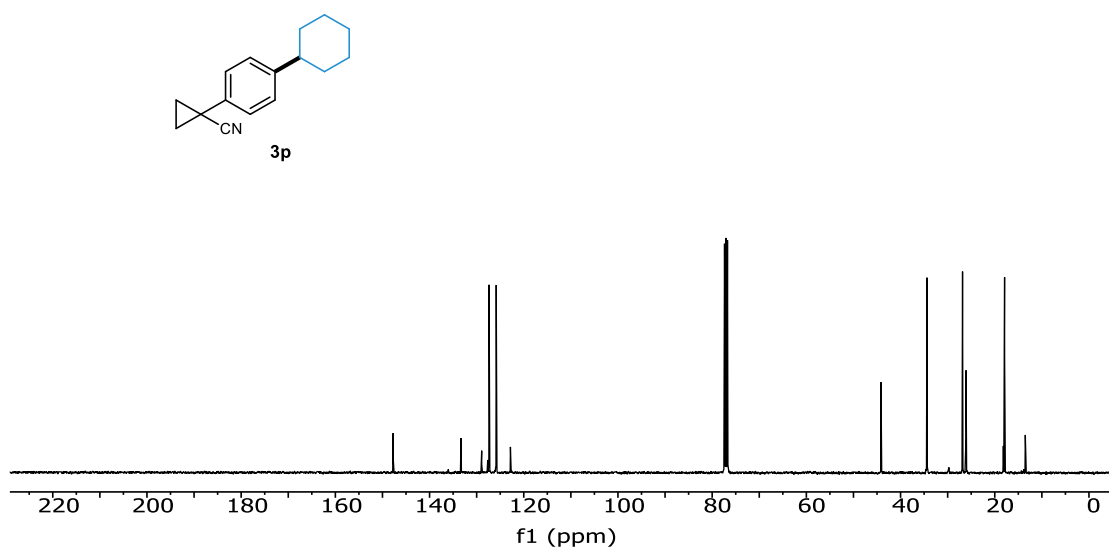


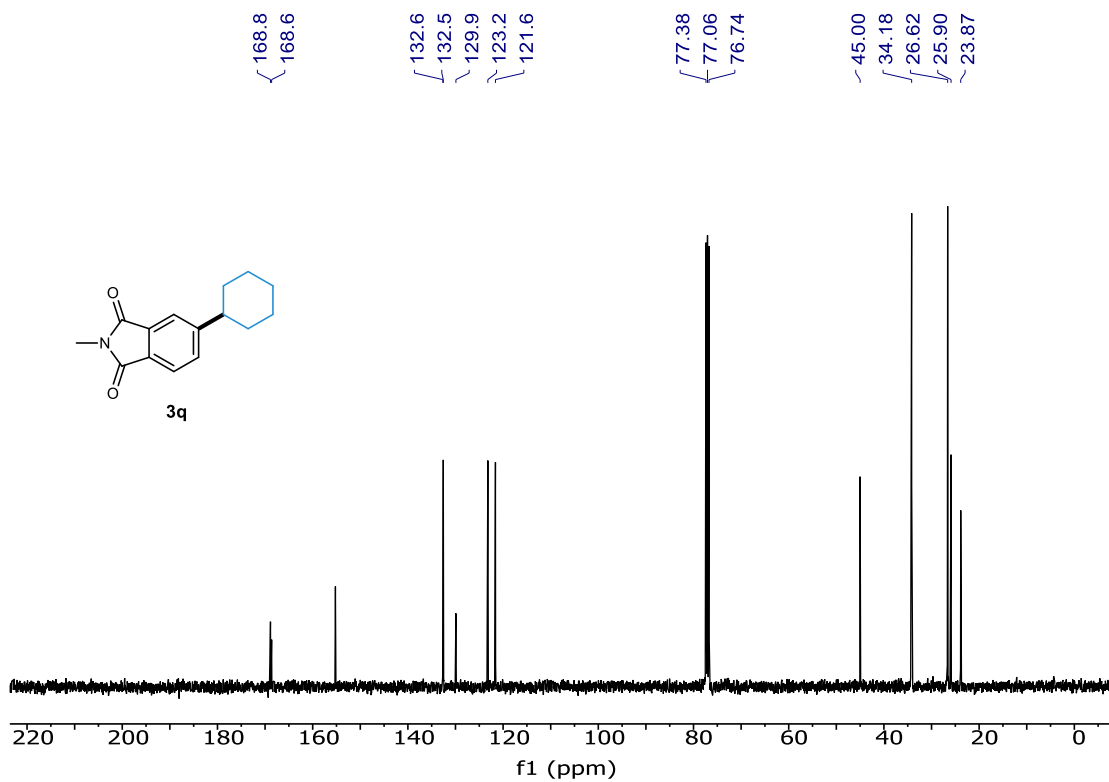
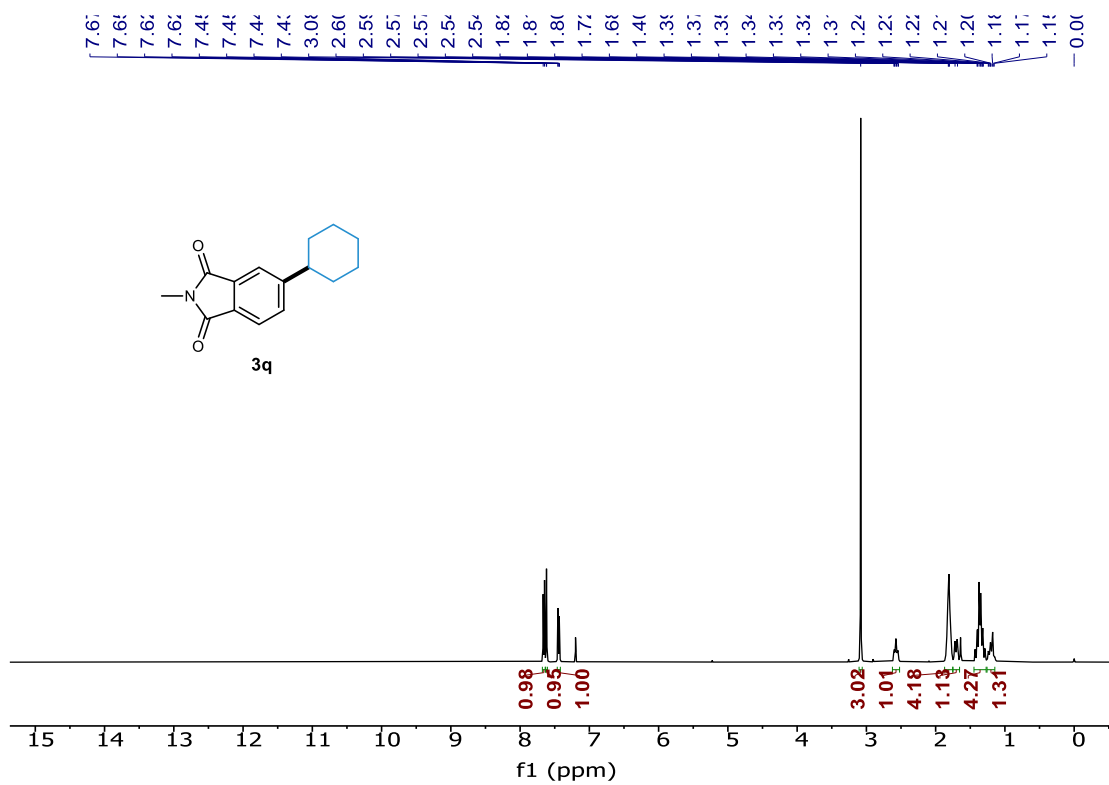


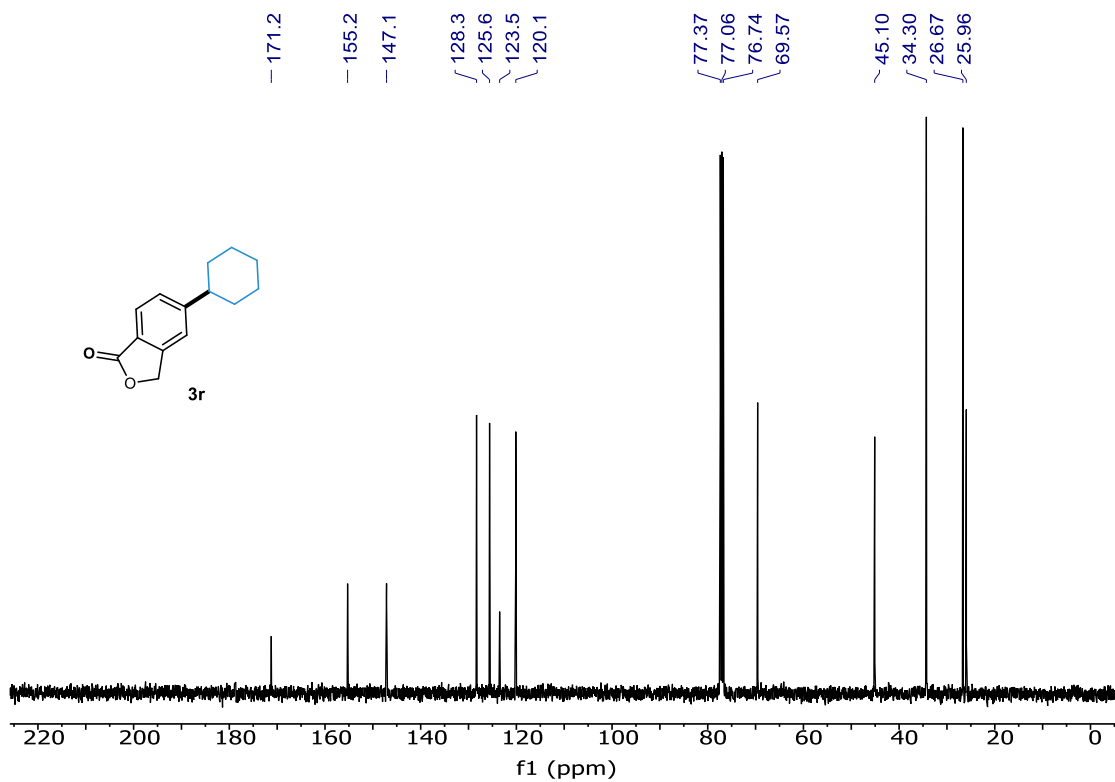
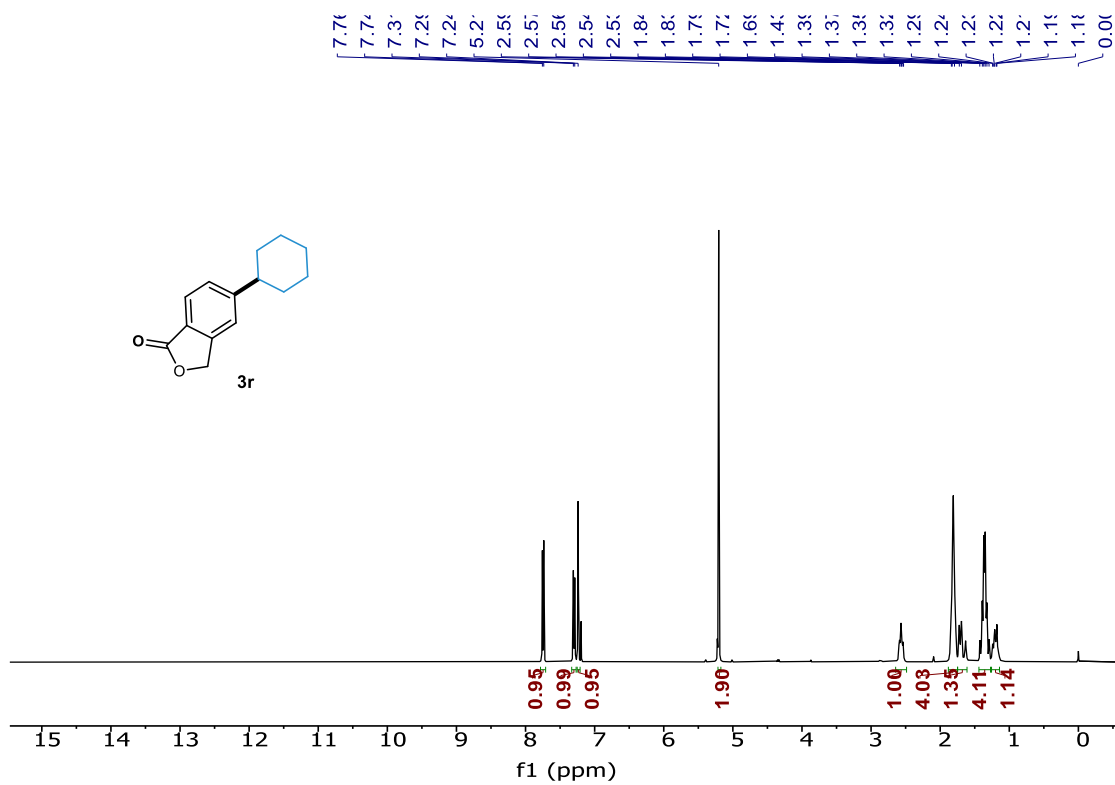




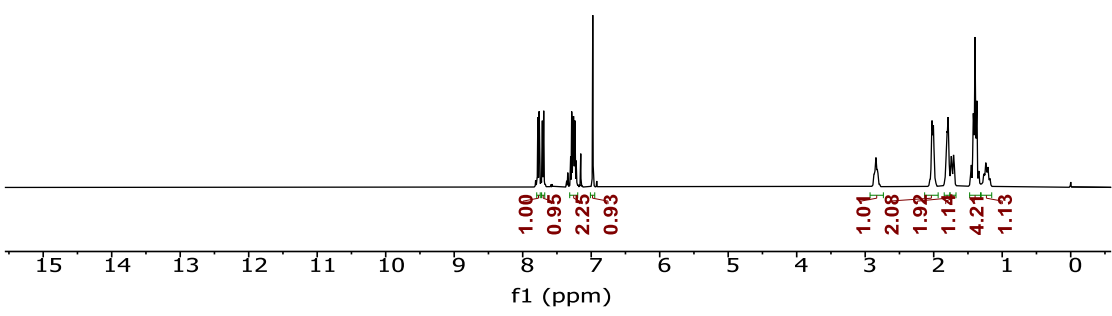
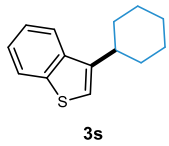
Chemical shift values (ppm): 147.7, 133.3, 127.3, 125.8, 122.8, 77.38, 77.06, 76.74, 44.15, 34.39, 26.84, 26.10, 17.92, 13.52



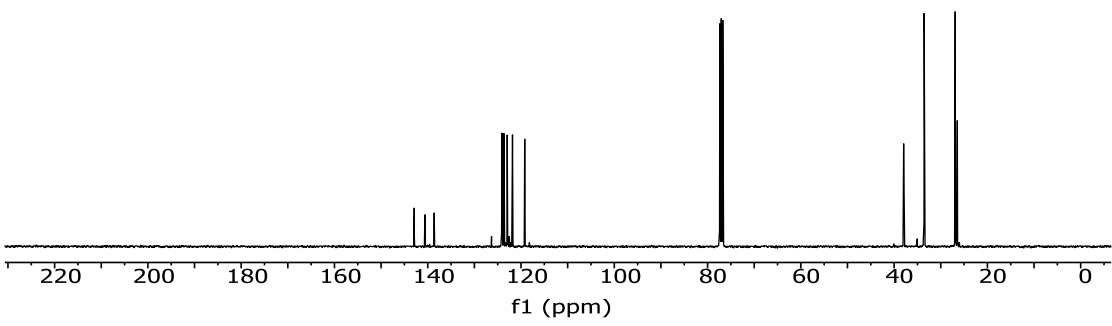
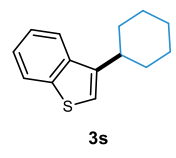


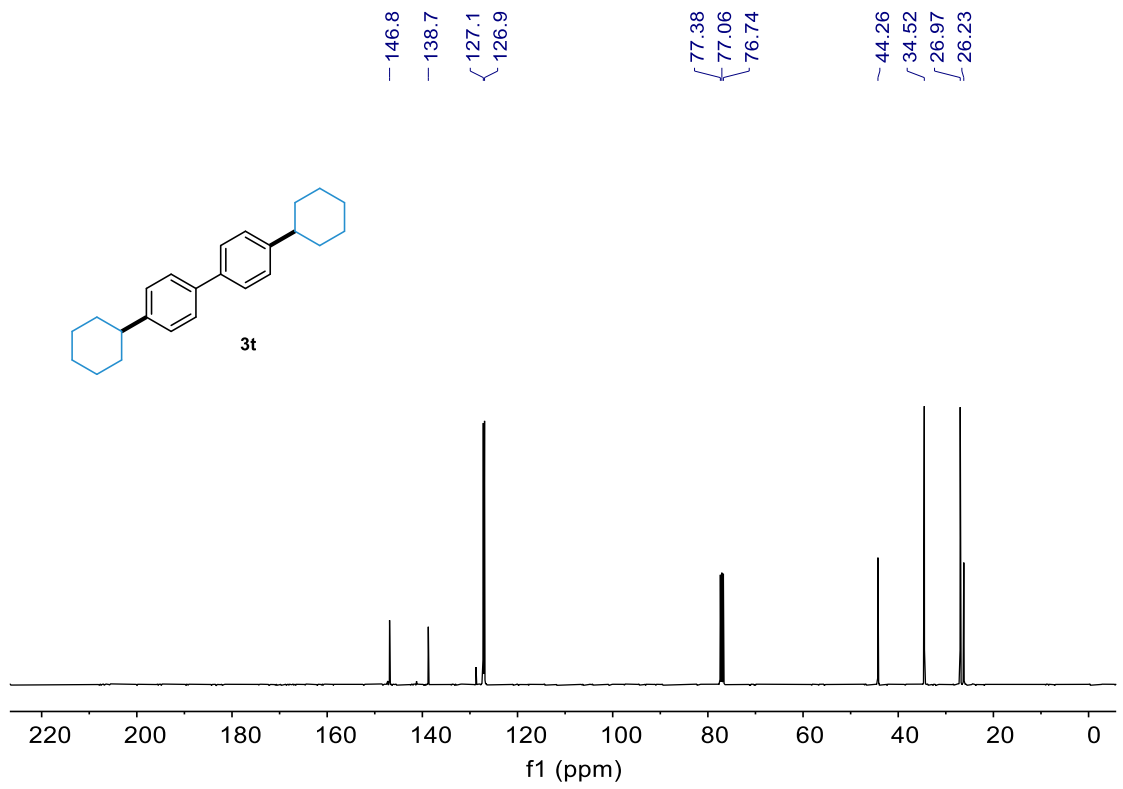
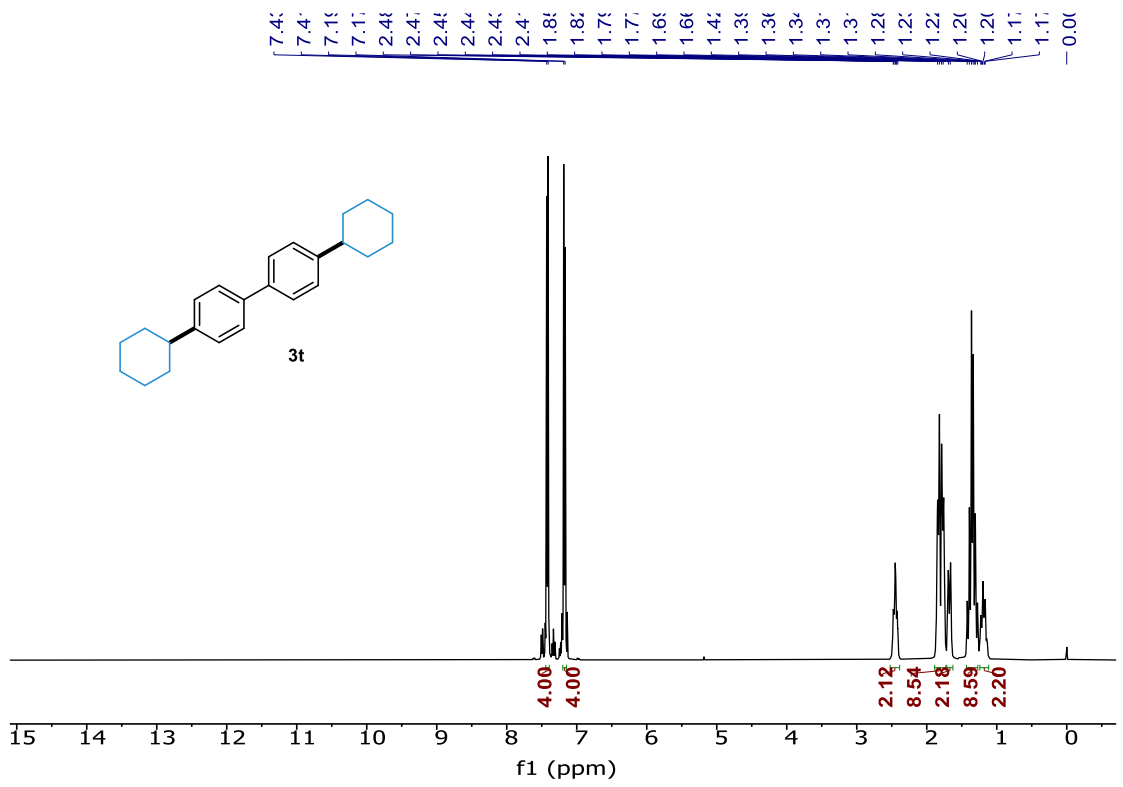


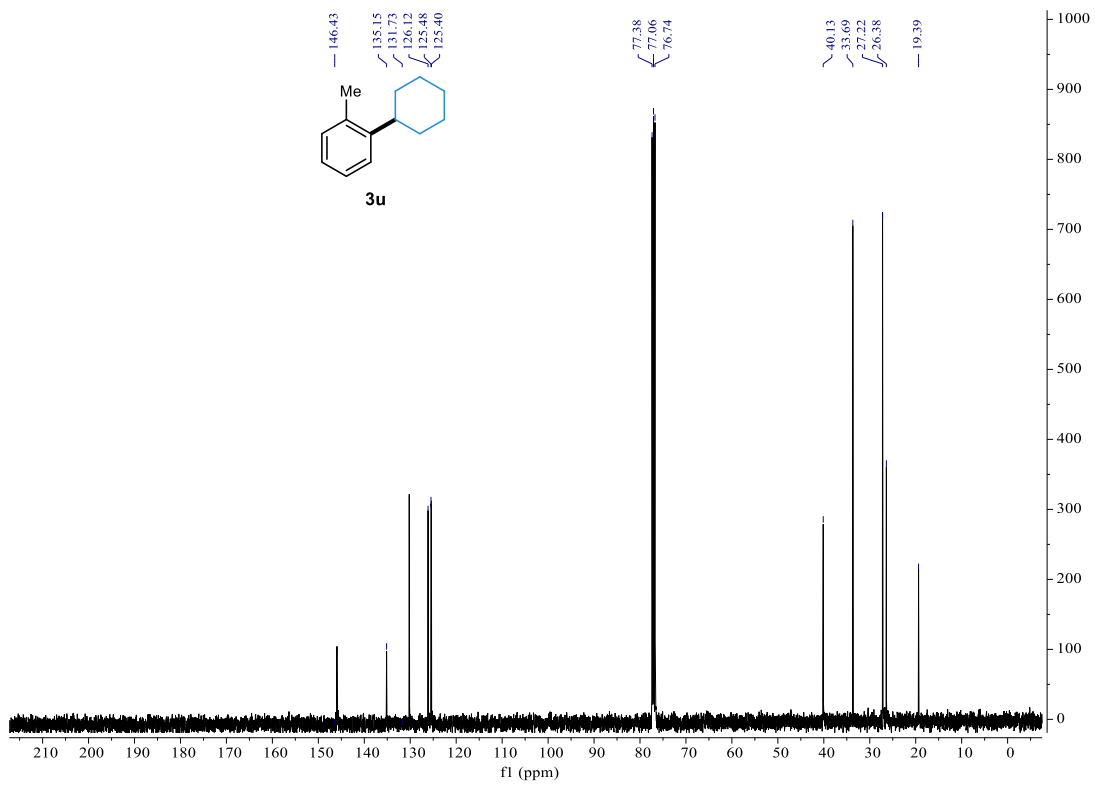
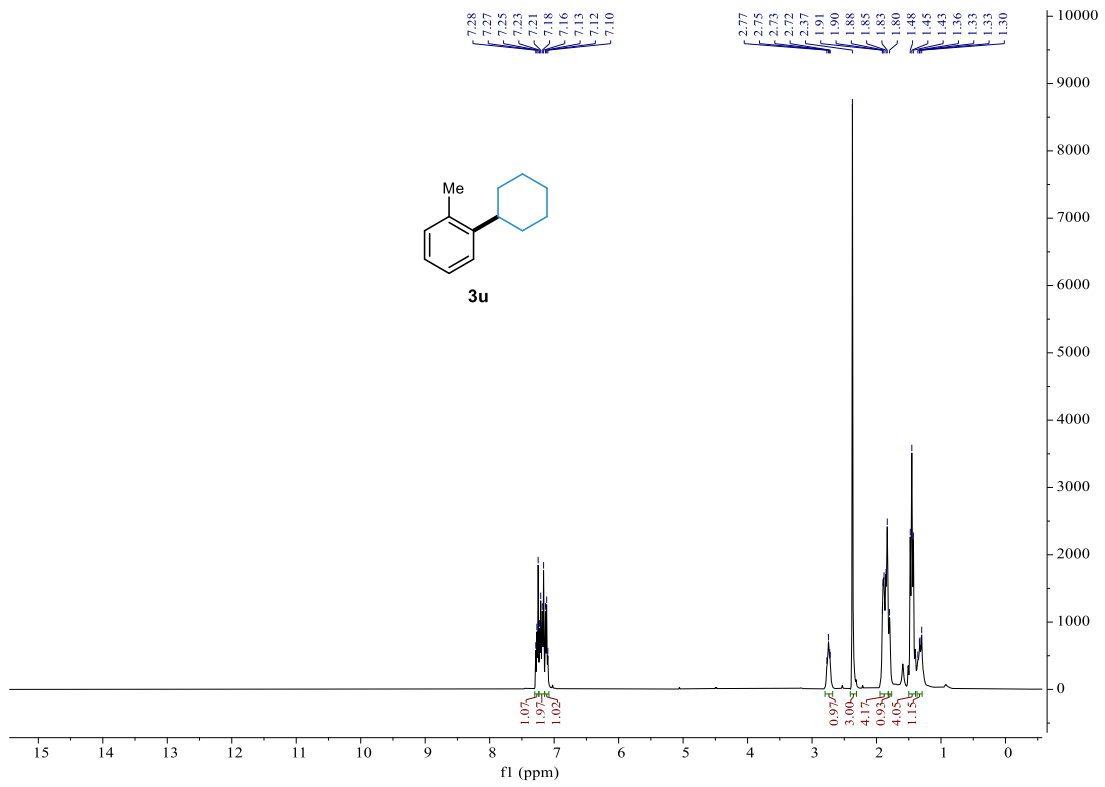
7.71 7.71 7.7 7.6 7.30 7.2 7.2 7.2 7.2 7.2 7.2 7.2 7.2 6.9 2.8 2.8 2.8 2.8 2.8 2.0 2.0 1.8 1.7 1.7 1.7 1.4 1.4 1.4 1.4 1.3 1.3 1.2 1.2 1.2 1.2 1.2 1.2 0.0

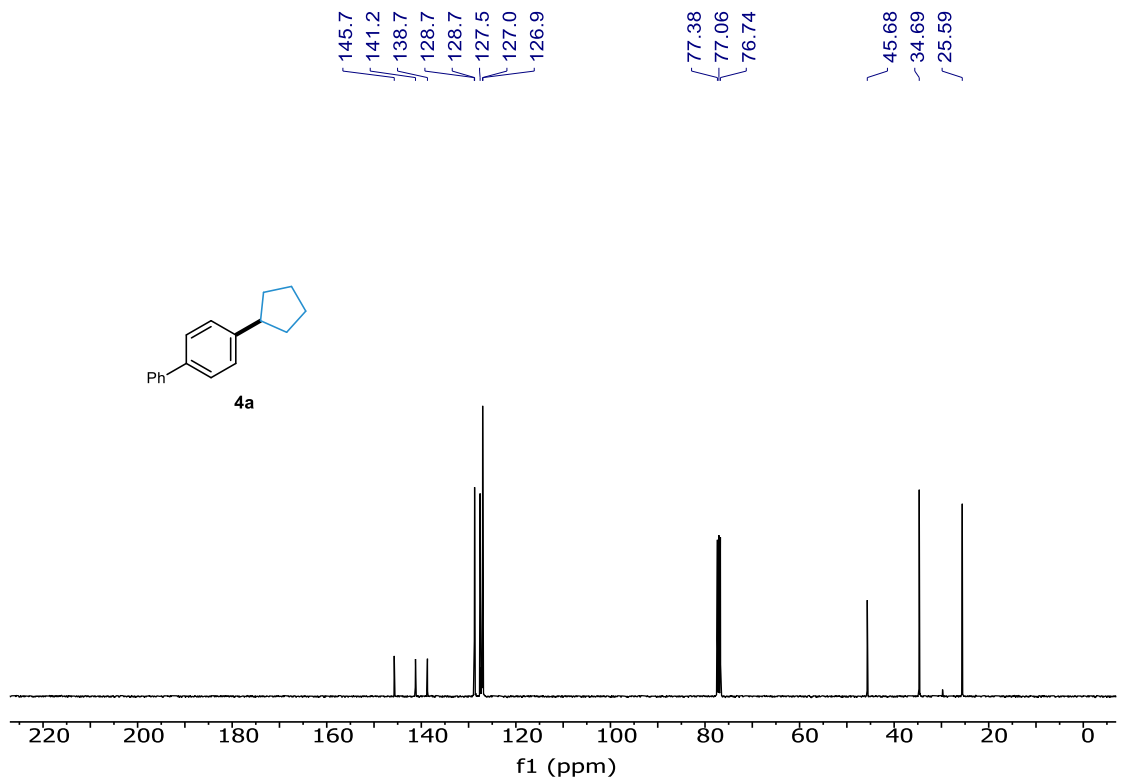
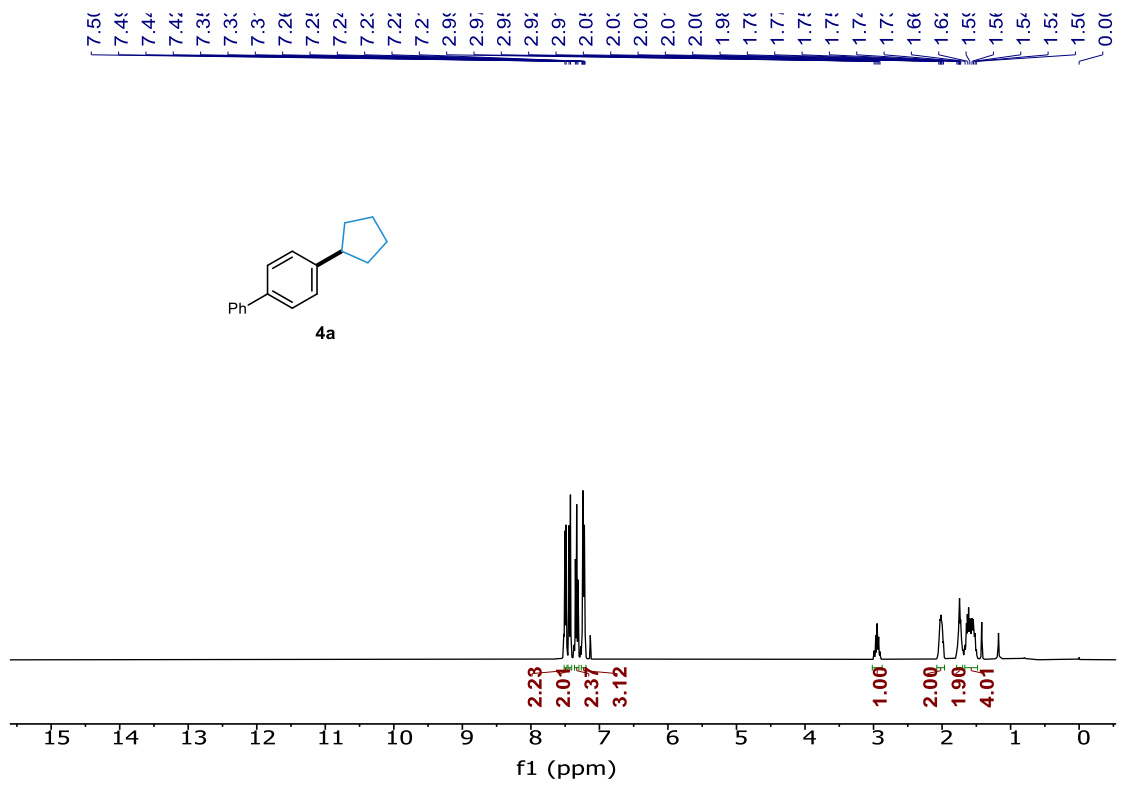


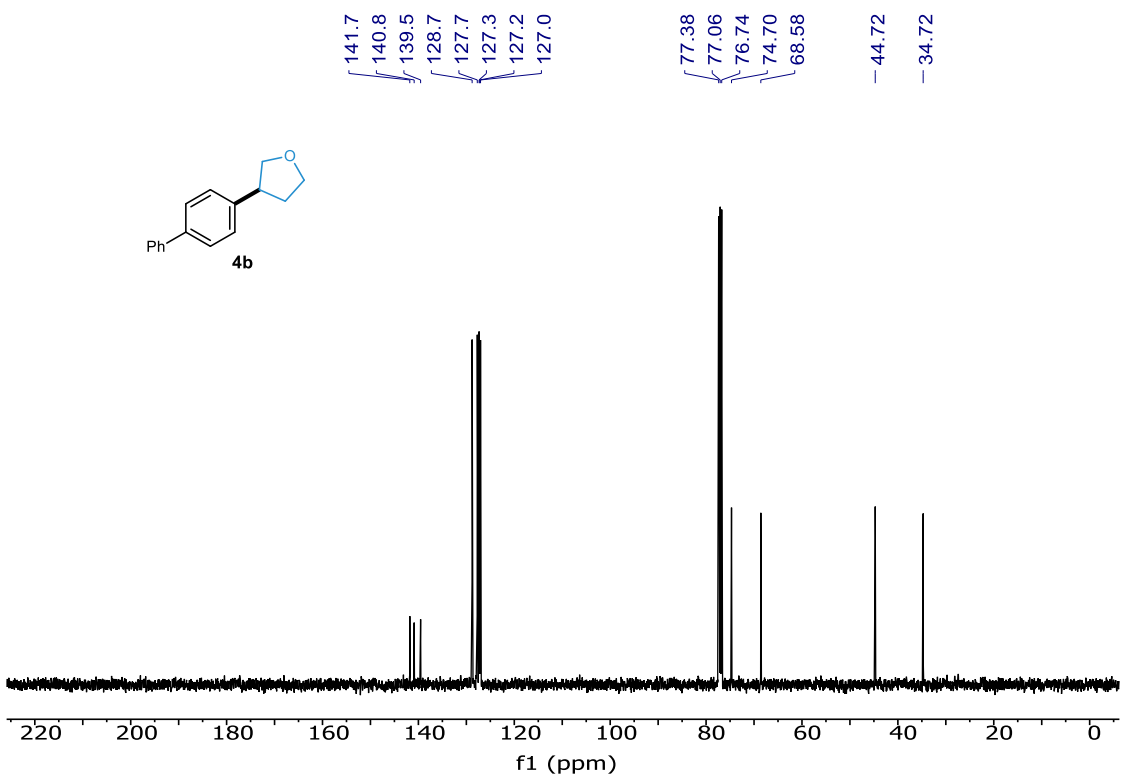
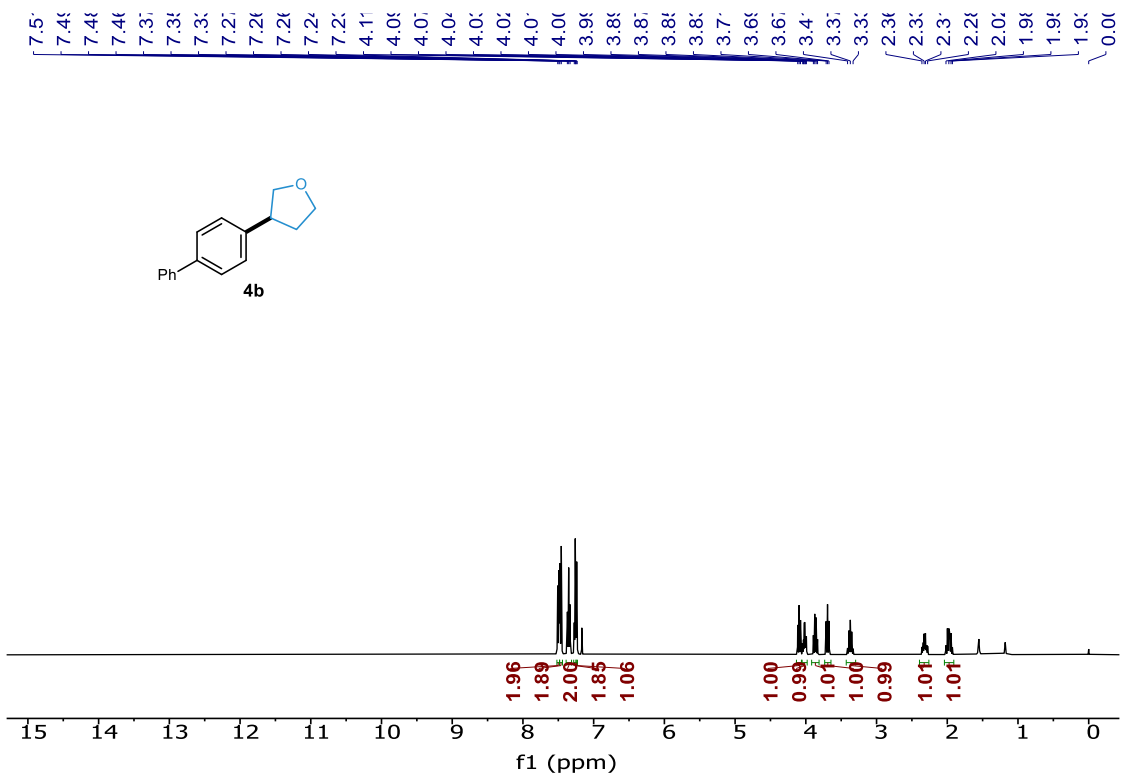
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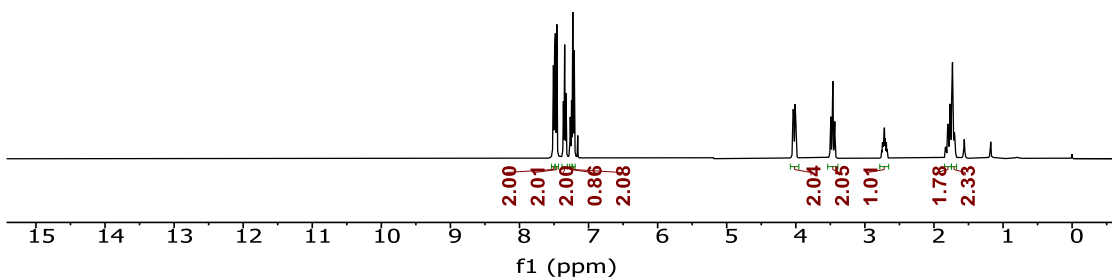
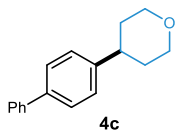




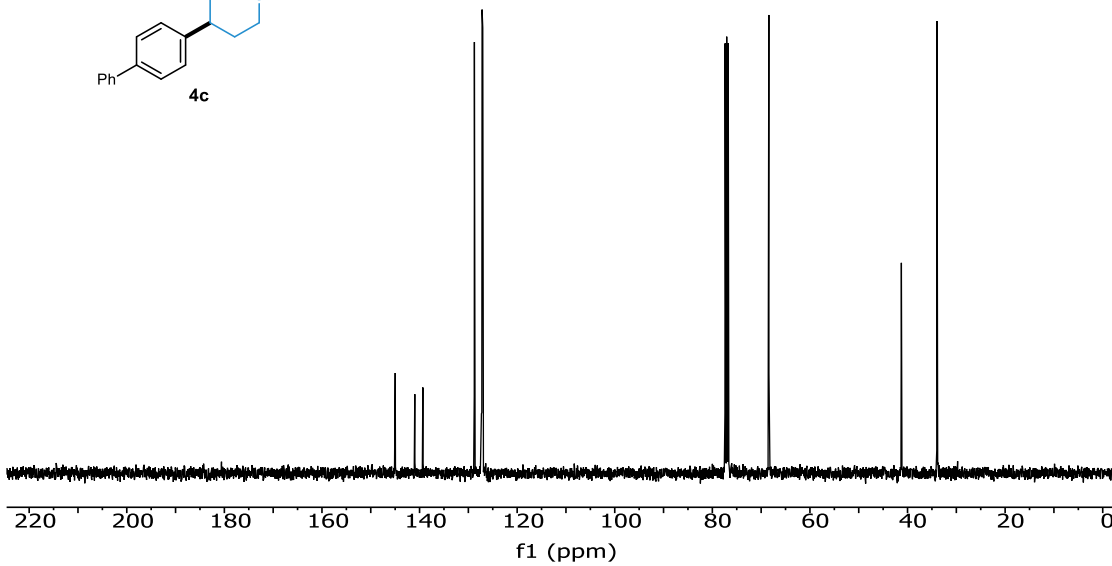
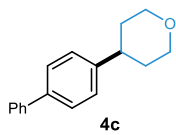


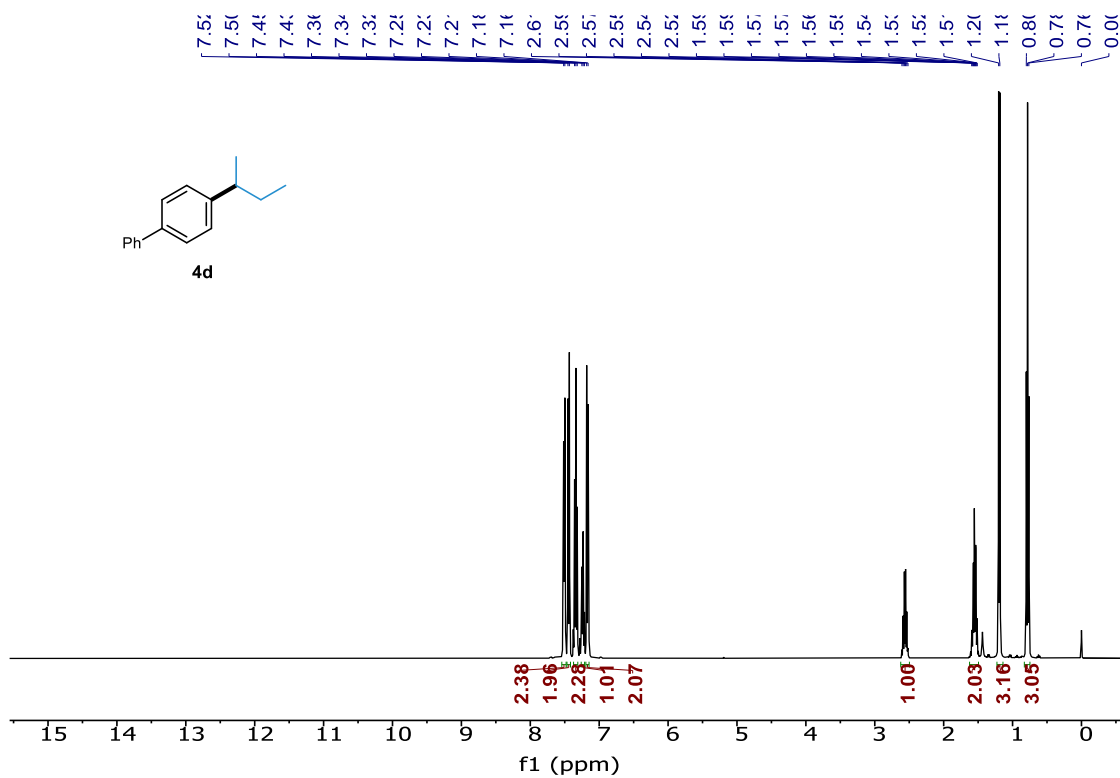


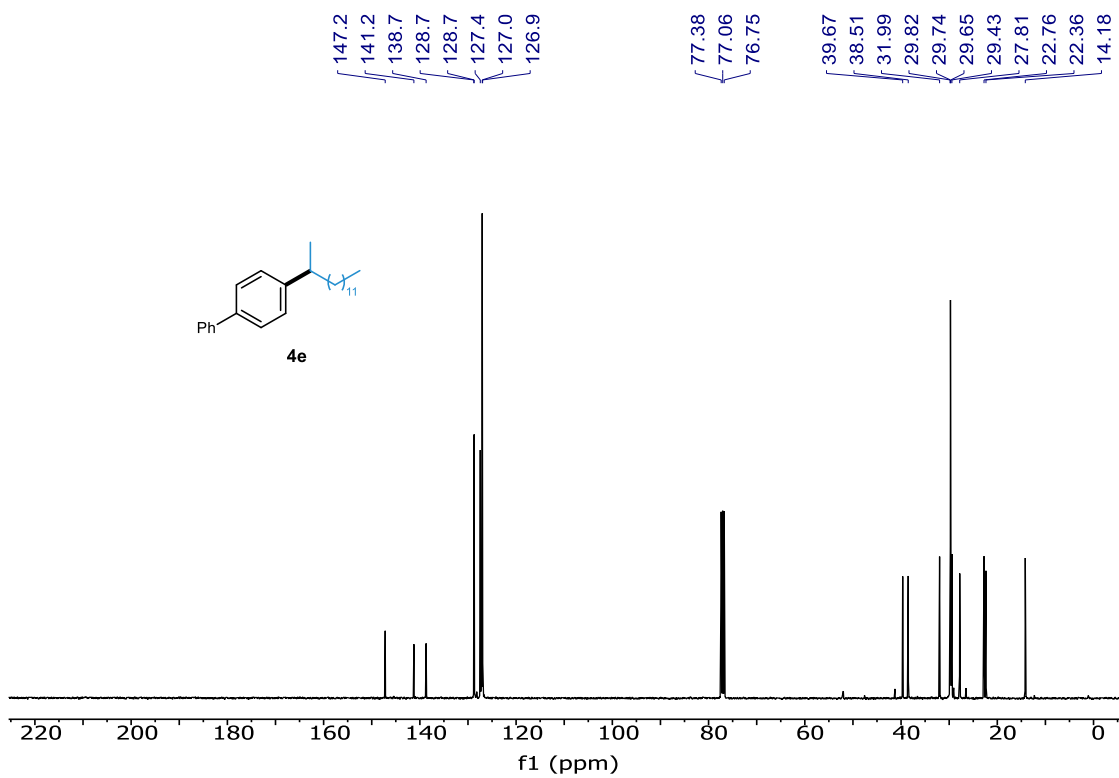
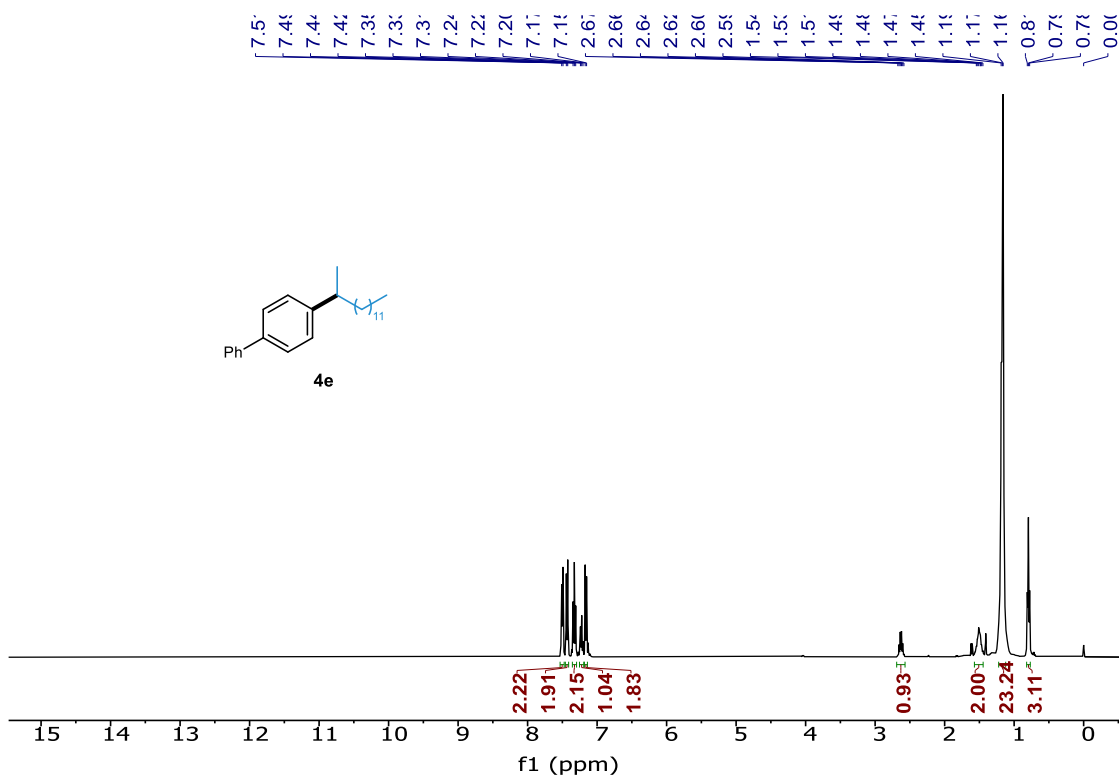
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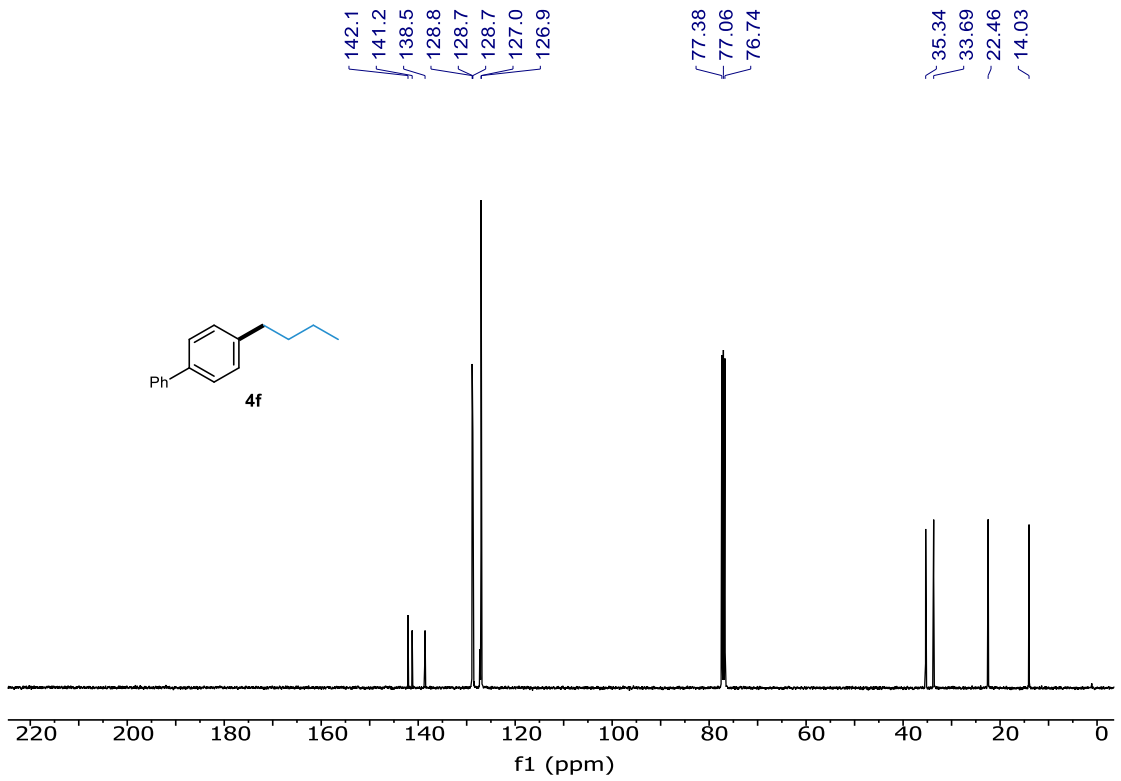
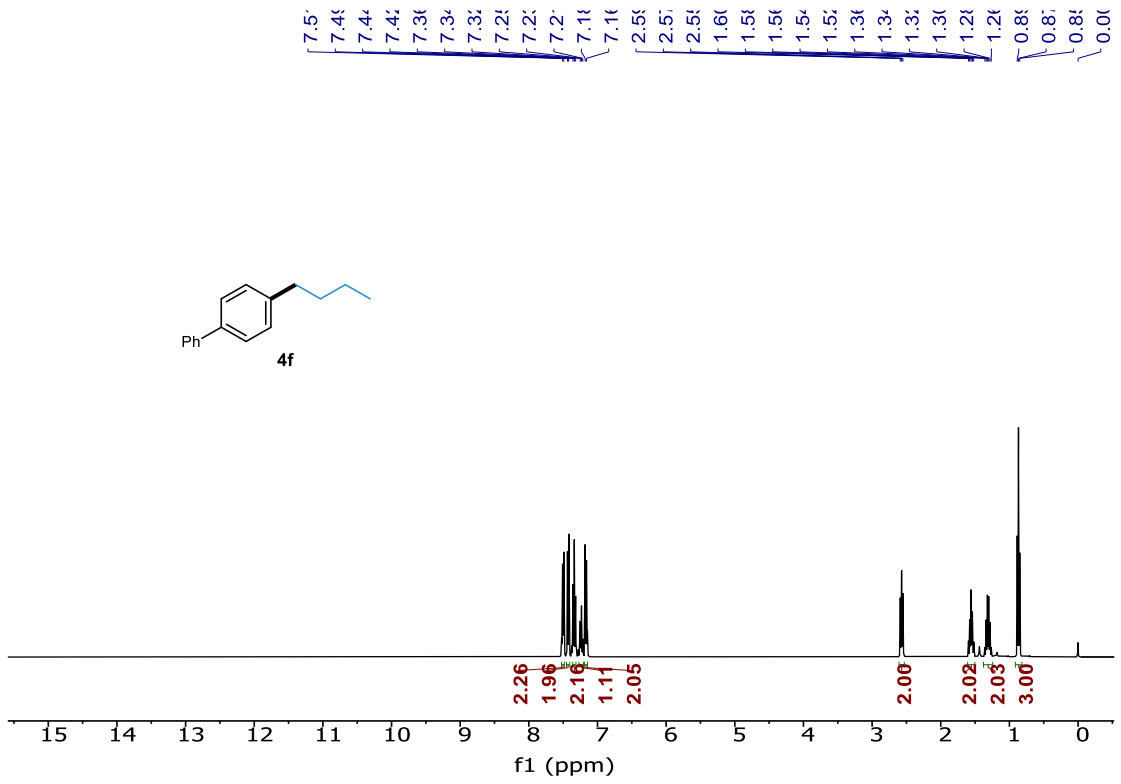
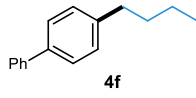


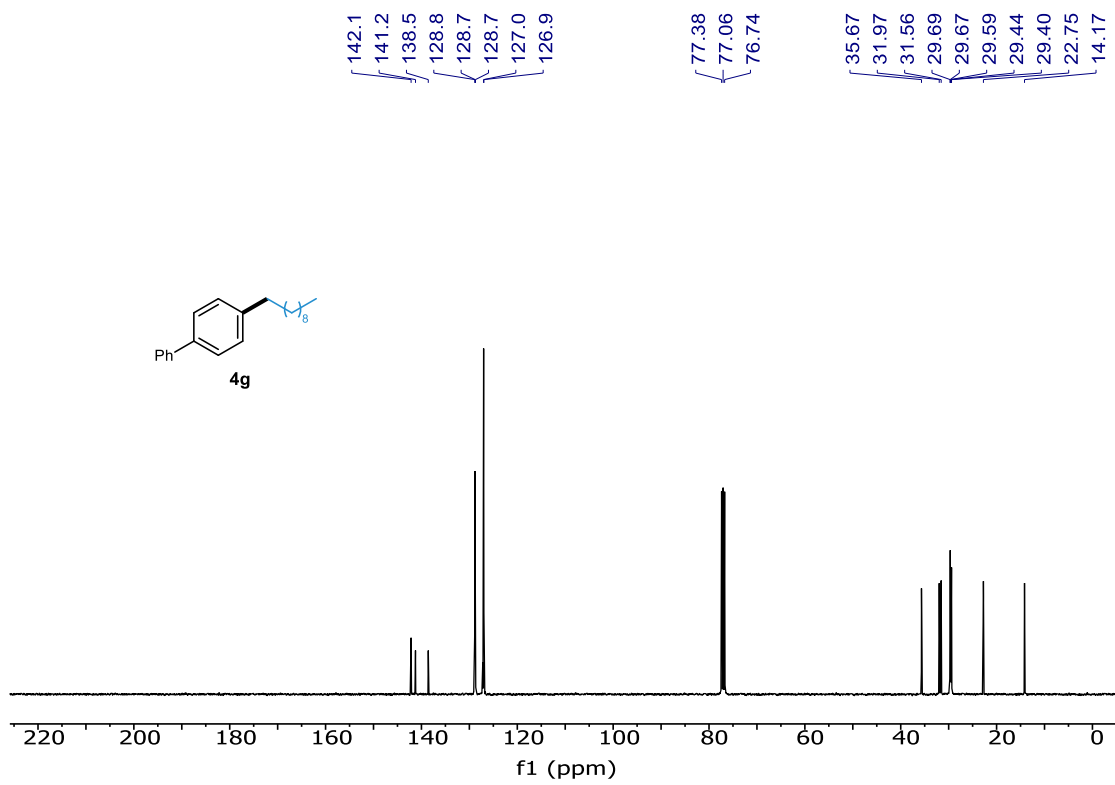
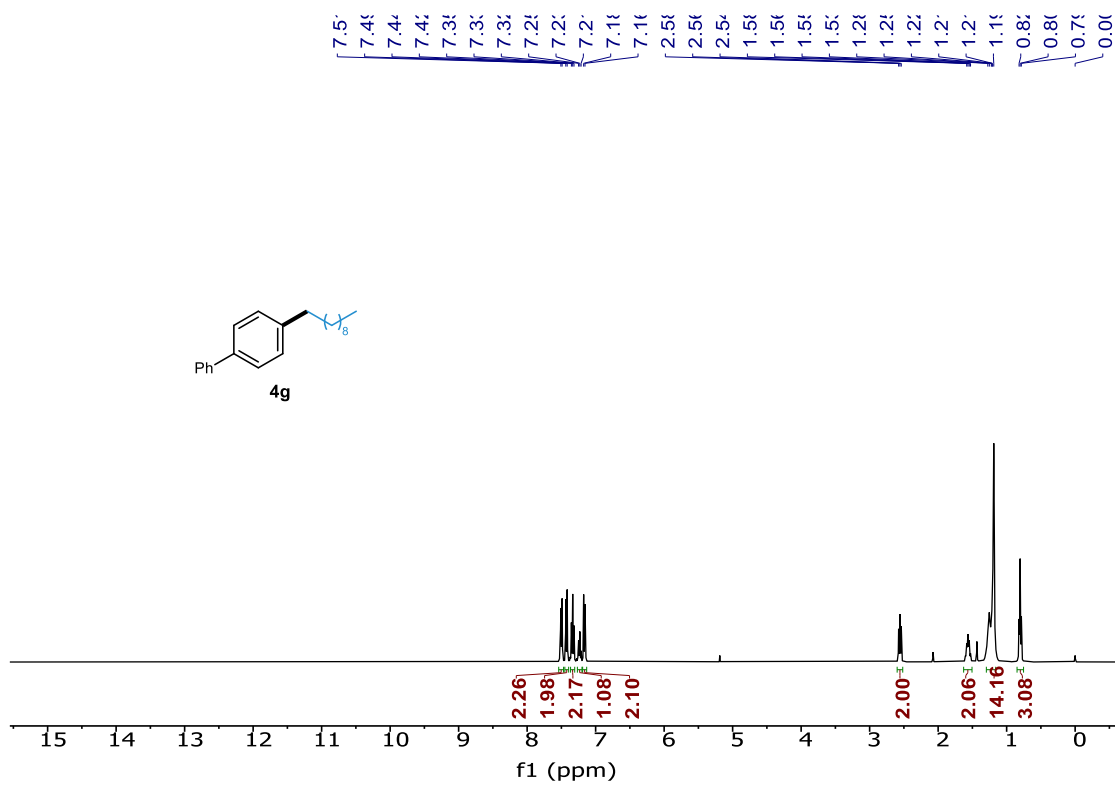
144.9
140.9
139.3
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127.0
77.38
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-33.96

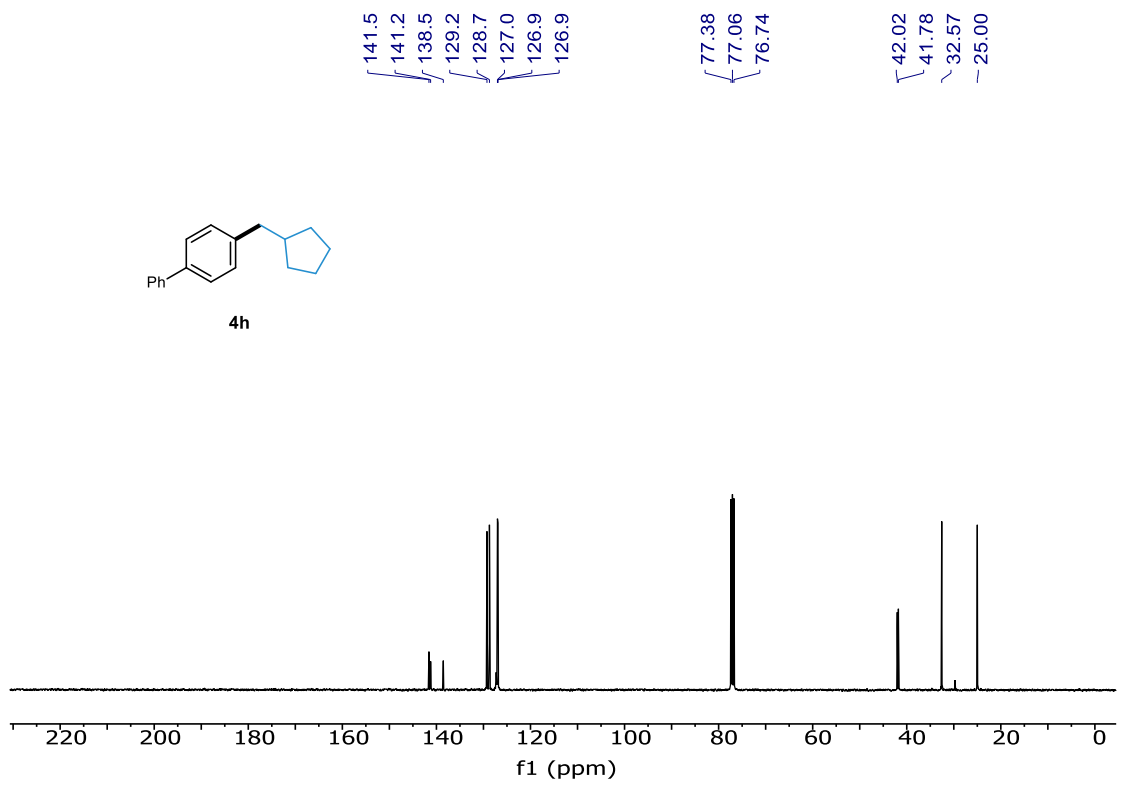
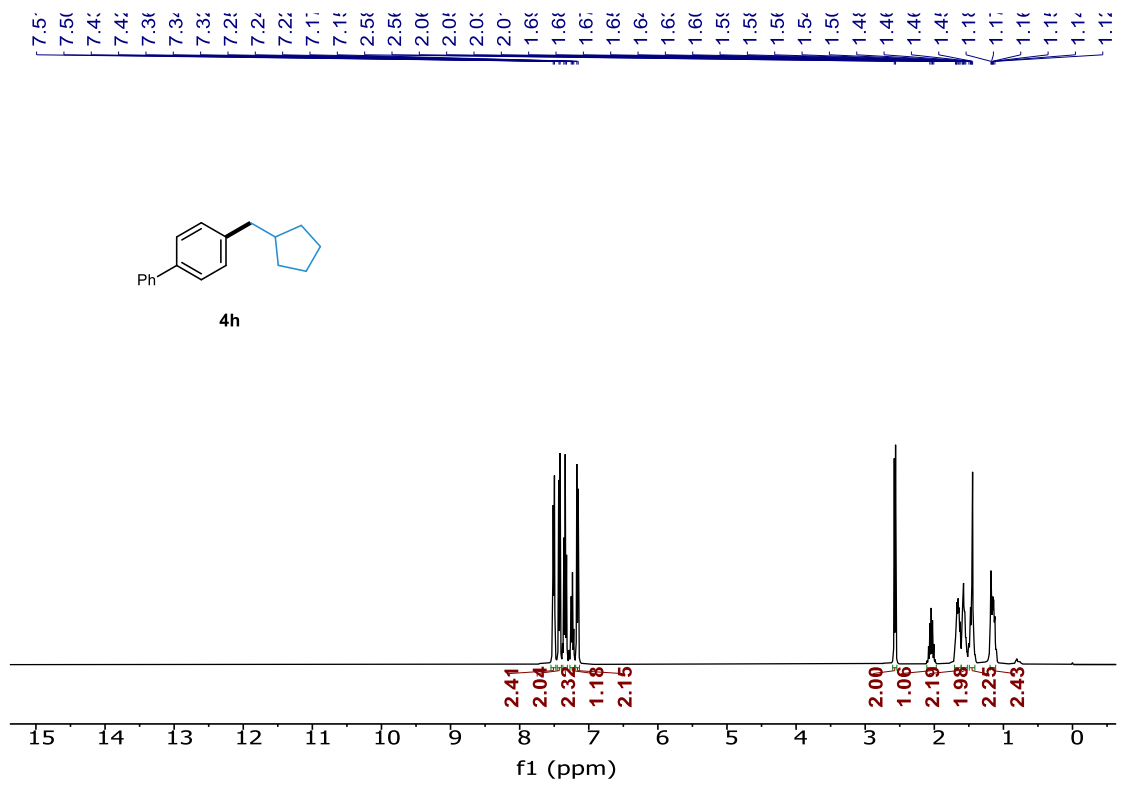


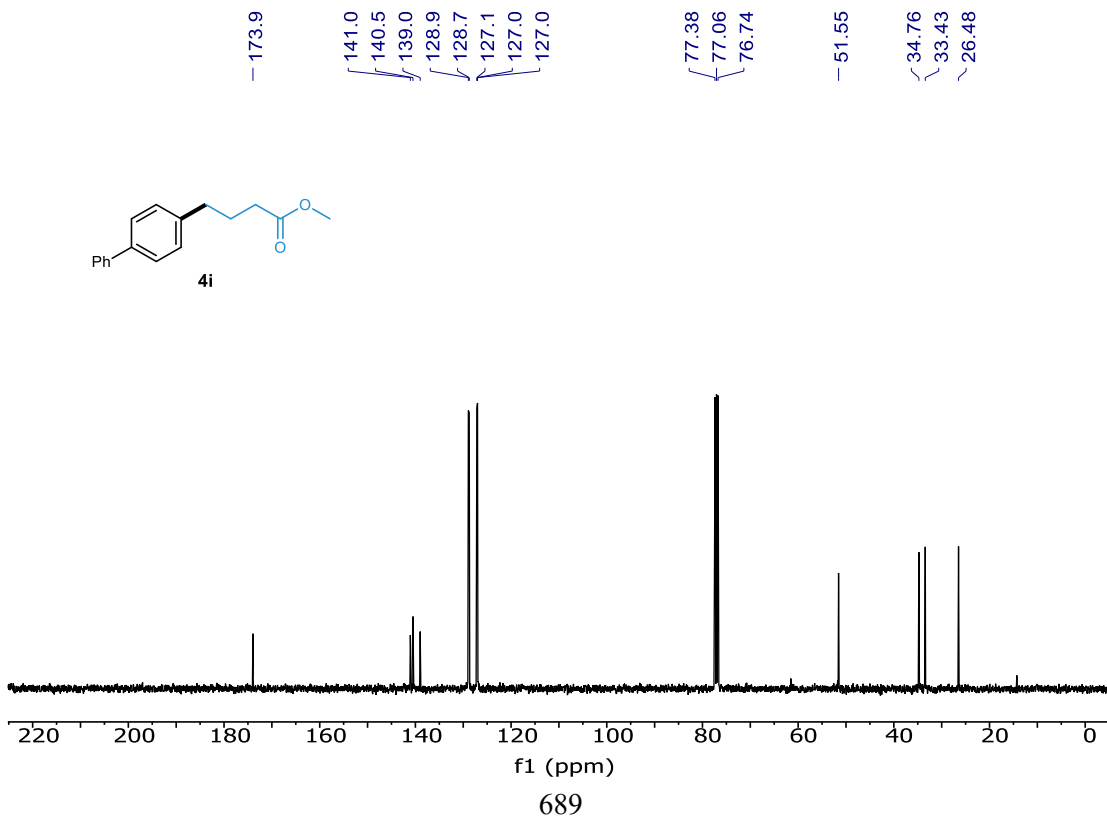
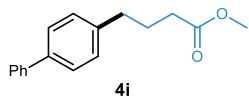
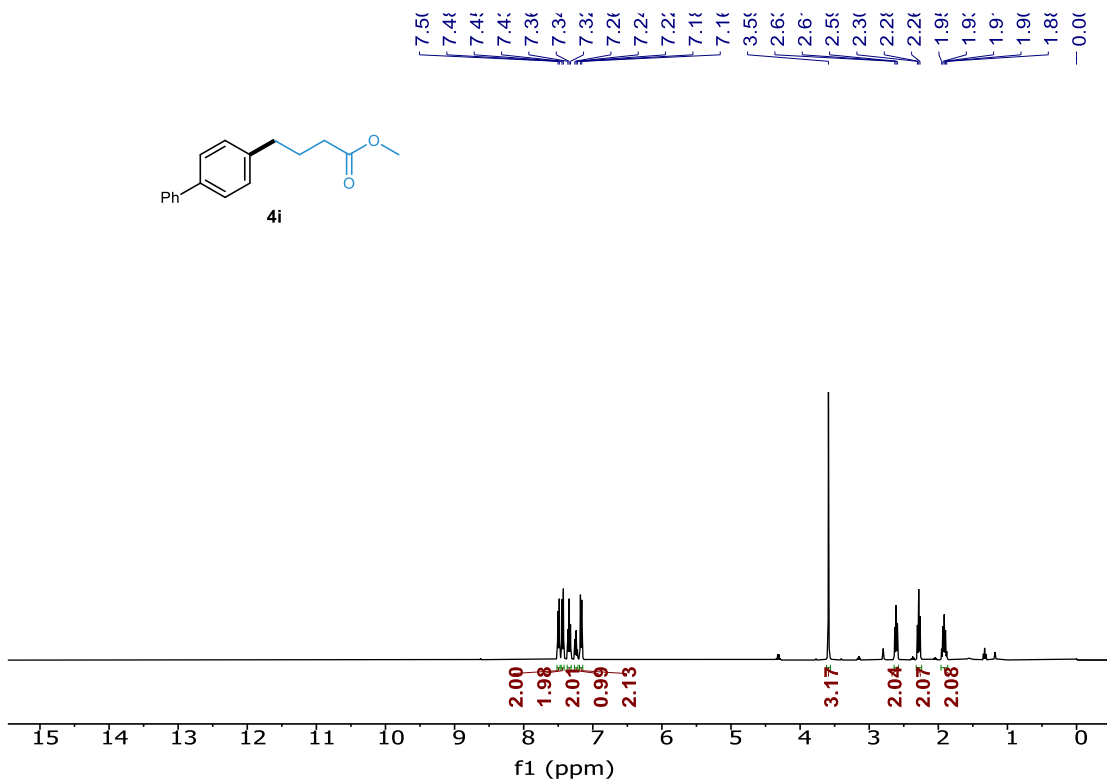
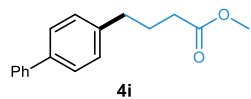


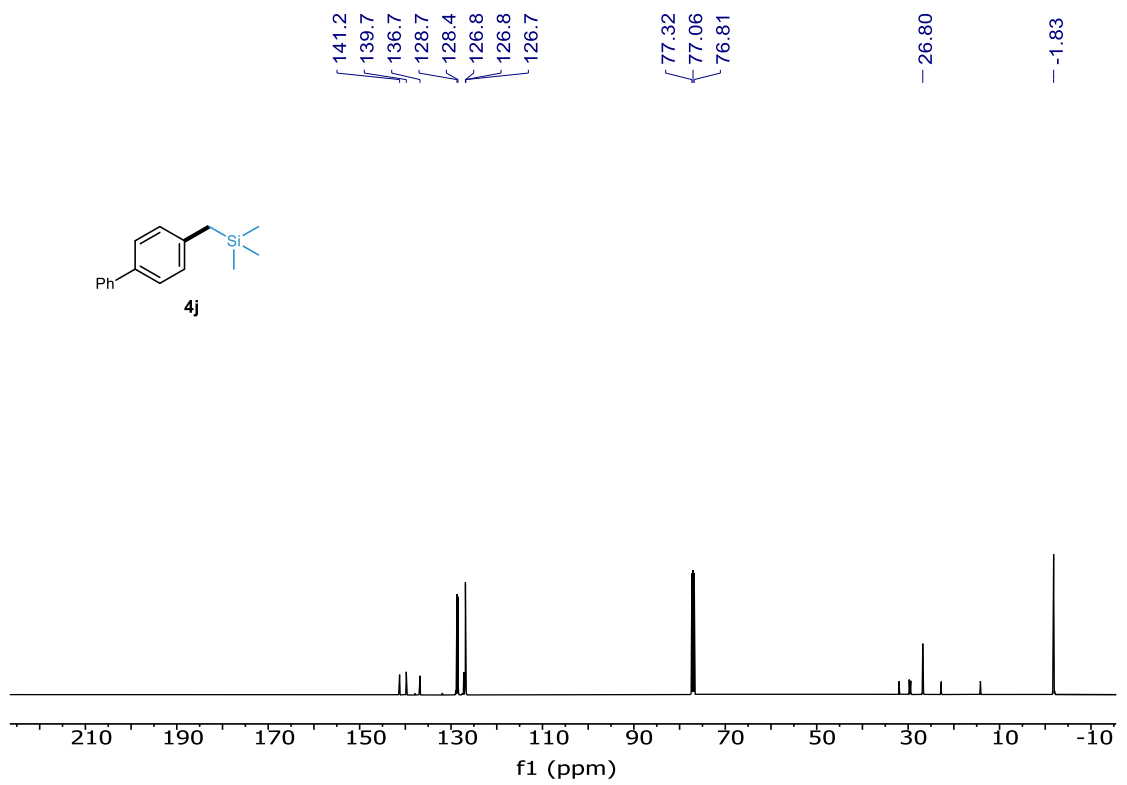
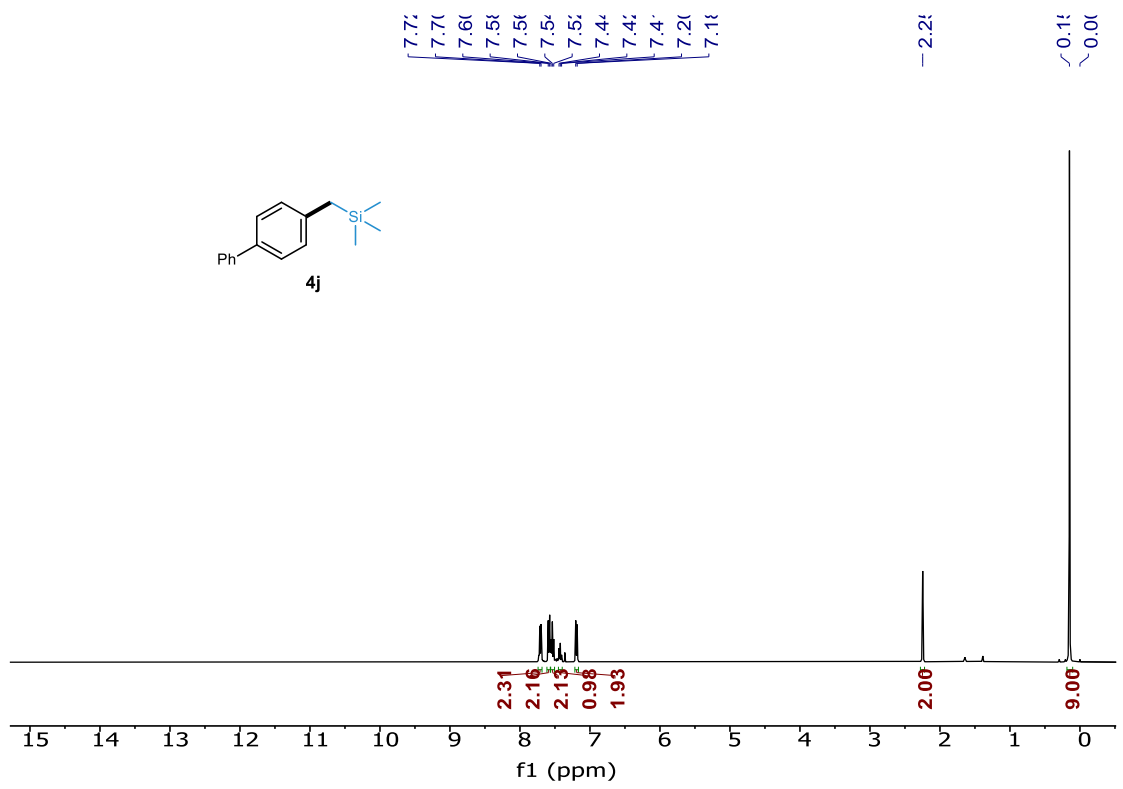


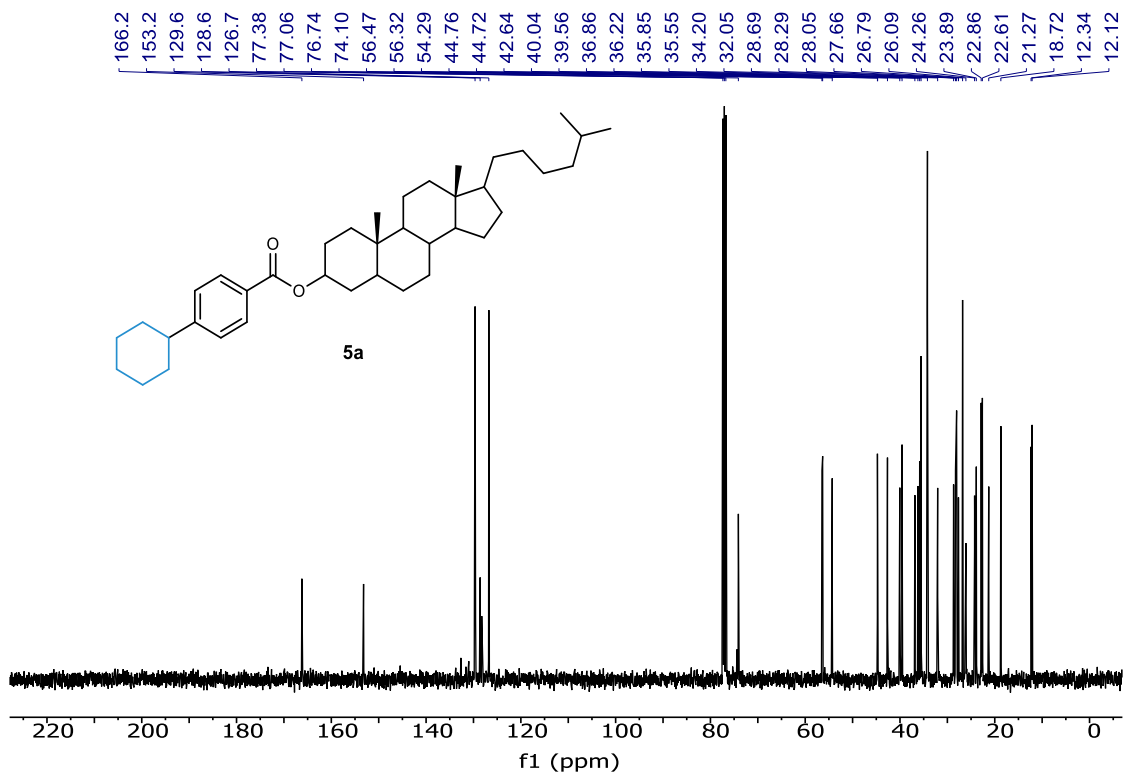
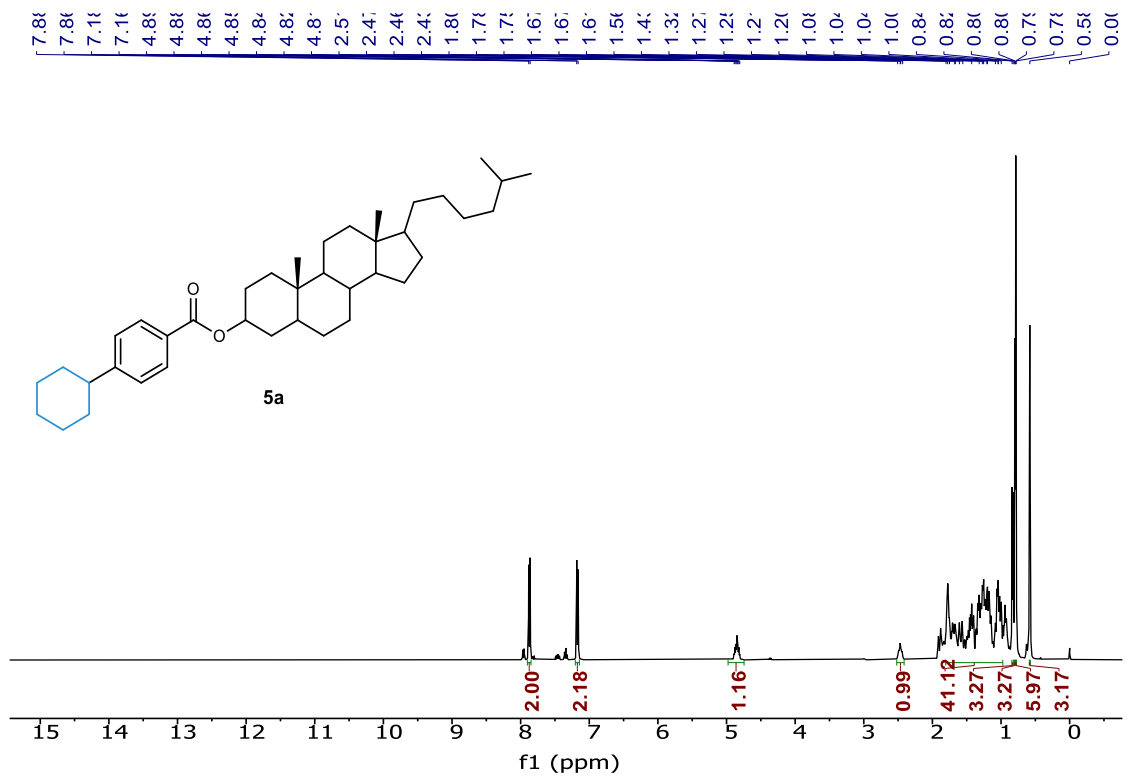


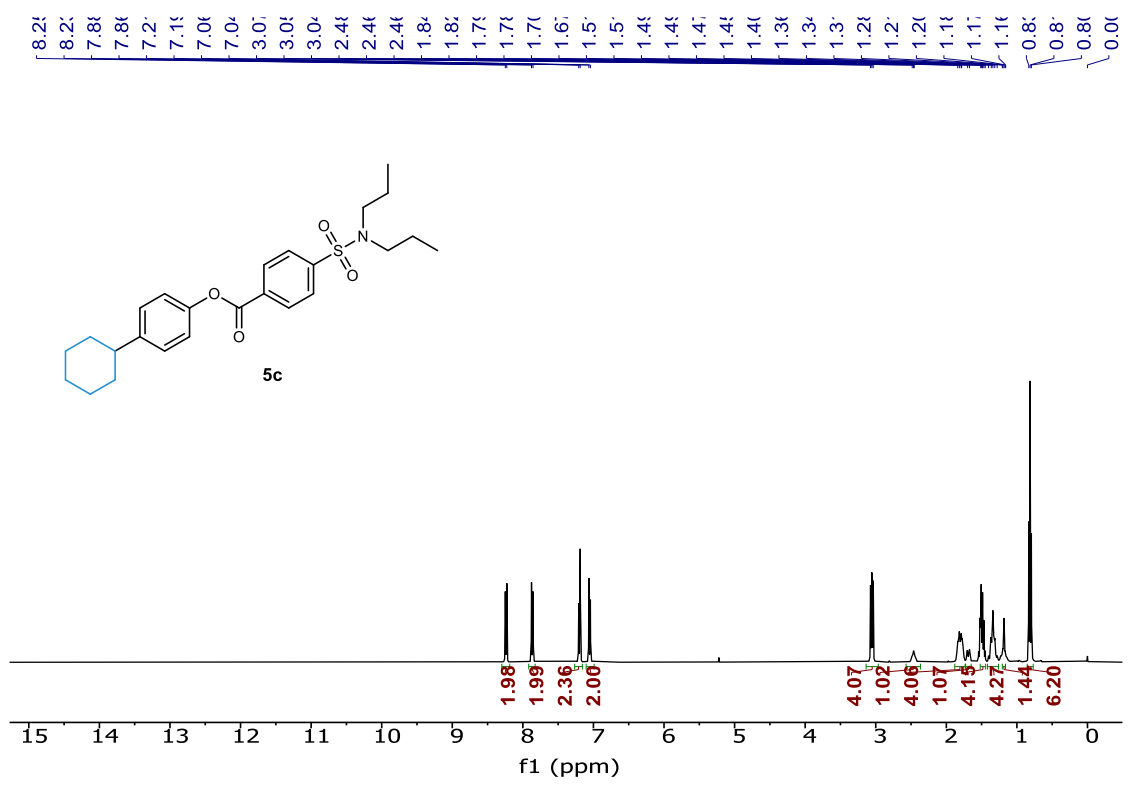












- 164.0
- 148.5
- 146.1
- 144.8
- 133.0
- 130.8
- 127.9
- 127.1
- 121.1
- 77.38
- 77.06
- 76.74
- 49.98
- 44.09
- 34.56
- 26.88
- 26.14
- 21.98
- 11.20

