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N-Butylpyrrolidone (NBP) as a Non-Toxic Substitute for NMP in Iron-Catalyzed C(sp^2)–C(sp^3) Cross-Coupling of Aryl Chlorides

Elwira Bisz,[*,‡] Martina Koston,[‡] and Michal Szostak[*,†]

[‡]*Department of Chemistry, Opole University, 48 Oleska Street, 45-052 Opole, Poland*
[†]*Department of Chemistry, Rutgers University, 73 Warren Street, Newark, NJ 07102, USA*

ebisz@uni.opole.pl; michal.szostak@rutgers.edu

Electronic Supplementary Information

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Corresponding Author:
Dr. E. Bisz
Department of Chemistry, Opole University
48 Oleska Street, 45-052 Opole, Poland
E-mail: ebisz@uni.opole.pl

Prof. Dr. M. Szostak
Department of Chemistry, Rutgers University
73 Warren Street, Newark, NJ 07102, United States
E-mail: michal.szostak@rutgers.edu

List of Known Compounds/General Methods

All compounds reported in the manuscript are commercially available or have been previously described in literature unless indicated otherwise. All experiments involving iron were performed using standard Schlenk techniques under argon or nitrogen atmosphere unless stated otherwise. All solvents were purchased at the highest commercial grade and used as received or after purification by distillation from sodium/benzophenone under nitrogen. All solvents were deoxygenated prior to use. All other chemicals were purchased at the highest commercial grade and used as received. Reaction glassware was oven-dried at 140 °C for at least 24 h or flame-dried prior to use, allowed to cool under vacuum and purged with argon (three cycles). All products were identified using ^{1}H NMR analysis and comparison with authentic samples. GC and/or GC/MS analysis was used for volatile products. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker spectrometers at 400 (^{1}H NMR) and 100 MHz (^{13}C NMR). All shifts are reported in parts per million (ppm) relative to residual $CHCl_3$ peak (7.27 and 77.2 ppm, ^{1}H NMR and ^{13}C NMR, respectively). All coupling constants (J) are reported in hertz (Hz). Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; brs, broad singlet. GC-MS chromatography was performed using Agilent HP5890/2 GC System using helium as the carrier gas at a flow rate of 1 mL/min and an initial oven temperature of 50 °C. The injector temperature was 250 °C. The detector temperature was 250 °C. For runs with the initial oven temperature of 50 °C, temperature was increased with a 10 °C/min ramp after 50 °C hold for 3 min to a final temperature of 250 °C, then hold at 250 °C for 15 min (splitless mode of injection, total run time of 35.0 min). High-resolution mass spectra (HRMS) were measured on a 7T Bruker Daltonics FT-MS instrument (for HRMS). Melting points were measured on Melt EMP (laboratory devices). All flash chromatography was performed using silica gel, 60 Å, 300 mesh. TLC analysis was carried out on aluminum plates coated with silica gel 60 F254, 0.2 mm thickness. The plates were visualized using a 254 nm ultraviolet lamp or iodine vapor. ^{1}H NMR and ^{13}C NMR data are given for all products in the Supplementary Information for characterization purposes. ^{1}H NMR, ^{13}C NMR and HRMS data are reported for all new compounds. All products have been previously reported, unless stated otherwise.

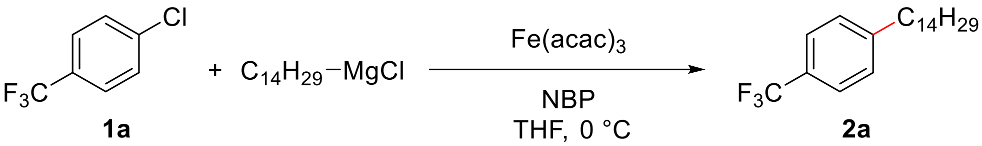
Experimental Procedures and Characterization Data

General Procedure for Iron-Catalyzed C(sp^2)–C(sp^3) Cross-Coupling. An oven-dried vial equipped with a stir bar was charged with an aryl chloride (neat, typically, 0.50 mmol, 1.0 equiv) and Fe(acac)$_3$ (typically, 5 mol%), placed under a positive pressure of argon and subjected to three evacuation/backfilling cycles under vacuum. Tetrahydrofuran (0.15 M) and NBP (neat, typically, 200-600 mol%) were sequentially added with vigorous stirring at room temperature, the reaction mixture was cooled to 0 °C, a solution of Grignard reagent (typically, 1.20 equiv) was added dropwise with vigorous stirring and the reaction mixture was stirred for the indicated time at 0 °C. After the indicated time, the reaction mixture was diluted with HCl (1.0 *N*, 1.0 mL) and Et$_2$O (1 x 30 mL), the organic layer was extracted with HCl (1.0 *N*, 2 x 10 mL), dried and concentrated. Note: for products containing basic nitrogen, NaOH (1.0 *N*) was used instead of HCl (1.0 *N*). A sample was analyzed by ^{1}H NMR (CDCl$_3$, 400 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples. Purification by chromatography on silica gel (EtOAc/hexanes) afforded the title product.

Representative Procedure for Iron-Catalyzed C(sp^2)–C(sp^3) Cross-Coupling at Low Catalyst and Ligand Loading. 1.0 g Scale. An oven-dried, two-necked flask (25 mL) equipped with a stir bar was charged with 2-chloro-6-methoxypyridine (1.00 g, 6.97 mmol, 1.0 equiv) and Fe(acac)$_3$ (2.46 mg, 6.97 µmol, 0.1 mol%). Tetrahydrofuran (4.08 mL, 0.63 M) and NBP (0.21 mL, 20 mol%) were sequentially added with vigorous stirring at room temperature, the reaction mixture was cooled to 0 °C, a solution of *n*-$C_{14}H_{29}MgCl$ (1.0 M in THF, 8.36 mL, 1.20 equiv) was added dropwise with vigorous stirring and the reaction mixture was stirred for 18 h at 0 °C. After the indicated time, the reaction mixture was diluted with NaOH (1.0 *N*, 3 mL) and Et$_2$O (1 x 50 mL), the organic layer was extracted with NaOH (1.0 *N*, 2 x 10 mL), dried and concentrated. A sample was analyzed by ^{1}H NMR (CDCl$_3$, 400 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples. Purification by chromatography on silica gel (EtOAc/hexanes) afforded the title product. Yield 85% (1.80 g). Colorless oil. Characterization data are included in the section below.

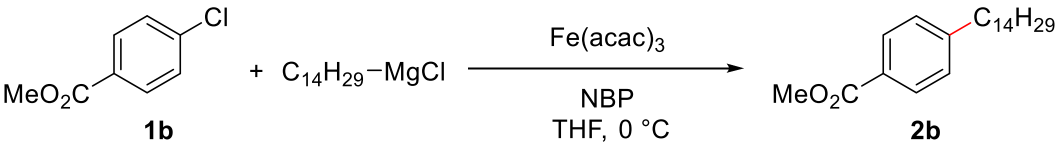
Iron-Catalyzed Cross-Coupling using N-Butylpyrrolidone

1-Tetradecyl-4-(trifluoromethyl)benzene (Table 2, 2a)



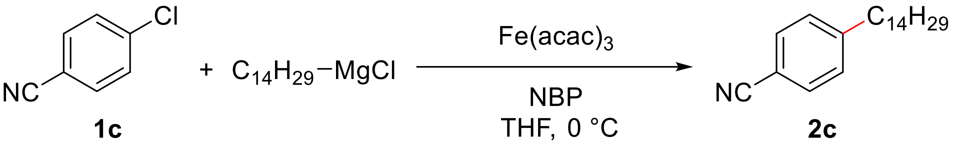
Prepared according to the general procedure using 1-chloro-4-(trifluoromethyl)benzene (0.50 mmol), Fe(acac)$_3$ (5 mol%), NBP (200 mol%), THF (0.15 M), and *n*-$C_{14}H_{29}MgCl$ (1.0 M in THF, 1.20 equiv). The reaction mixture was stirred for 10 min at 0 °C. Yield 98% (167.5 mg). Colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.51 (d, *J* = 8.0 Hz, 2 H), 7.27 (d, *J* = 8.0 Hz, 2 H), 2.64 (t, *J* = 7.8 Hz, 2 H), 1.66-1.56 (m, 2 H), 1.37-1.18 (m, 22 H), 0.88 (t, *J* = 6.8 Hz, 3 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 147.23, 128.86, 128.16 (q, J^F = 32.3 Hz), 125.33 (q, J^F = 3.7 Hz), 124.63 (q, J^F = 271.7 Hz), 36.01, 32.16, 31.44, 29.93, 29.89, 29.78, 29.68, 29.60, 29.45, 22.92, 14.32. Spectroscopic properties matched those described previously.[1,2]

Methyl 4-tetradecylbenzoate (Table 2, 2b)



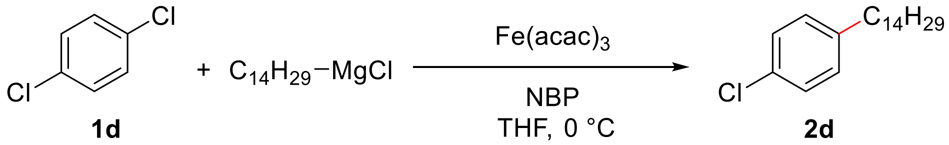
Prepared according to the general procedure using methyl 4-chlorobenzoate (0.50 mmol), Fe(acac)$_3$ (5 mol%), NBP (200 mol%), THF (0.15 M), and *n*-$C_{14}H_{29}MgCl$ (1.0 M in THF, 1.20 equiv). The reaction mixture was stirred for 10 min at 0 °C. Yield 98% (162.7 mg). White solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.95 (d, *J* = 8.4 Hz, 2 H), 7.24 (d, *J* = 8.5, 2 H), 3.90 (s, 3 H), 2.65 (t, *J* = 7.7 Hz, 2 H), 1.67-1.56 (m, 2 H), 1.35-1.20 (m, 22 H), 0.88 (t, *J* = 6.9 Hz, 3 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 167.39, 148.71, 129.78, 128.60, 127.74, 52.12, 36.19, 32.11, 31.33, 29.88, 29.84, 29.74, 29.64, 29.55, 29.44, 22.88, 14.31. Spectroscopic properties matched those described previously.[1,2]

4-Tetradecylbenzonitryle (Table 2, 2c)



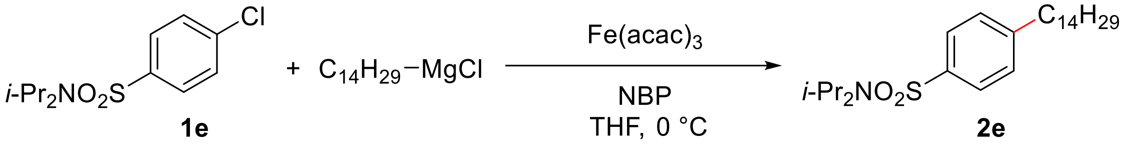
Prepared according to the general procedure using 4-chlorobenzonitrile (0.50 mmol), Fe(acac)$_3$ (5 mol%), NBP (600 mol%), THF (0.15 M), and *n*-$C_{14}H_{29}$MgCl (1.0 M in THF, 1.20 equiv). The reaction mixture was stirred for 10 min at 0 °C. Yield 84% (125.7 mg). White solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.56 (d, *J* = 8.3 Hz, 2 H), 7.27 (d, *J* = 8.4 Hz, 2 H), 2.65 (t, *J* = 7.7 Hz, 2 H), 1.67-1.53 (m, 2 H), 1.34-1.23 (m, 22 H), 0.88 (t, *J* = 6.9 Hz, 3 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 148.81, 132.28, 129.37, 119.41, 109.62, 36.30, 32.11, 31.17, 29.87, 29.84, 29.81, 29.71, 29.59, 29.55, 29.36, 22.88, 14.32. Spectroscopic properties matched those described previously.[1,2]

1-Chloro-4-tetradecylbenzene (Table 2, 2d)



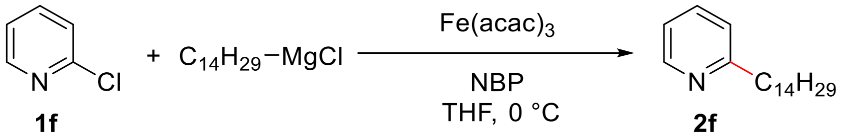
Prepared according to the general procedure using 1,4-dichlorobenzene (0.50 mmol), Fe(acac)$_3$ (5 mol%), NBP (300 mol%), THF (0.15 M), and *n*-$C_{14}H_{29}$MgCl (1.0 M in THF, 1.20 equiv). The reaction mixture was stirred for 60 min at 0 °C. Yield 64% (99.0 mg). White solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.22 (d, *J* = 8.4 Hz, 2 H), 7.09 (d, *J* = 8.4 Hz, 2 H), 2.56 (t, *J* = 7.7 Hz, 2 H), 1.62-1.52 (m, 2 H), 1.34-1.20 (m, 22 H), 0.88 (t, *J* = 6.8 Hz, 3 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 141.51, 131.39, 129.91, 128.46, 35.49, 32.13, 31.61, 29.90, 29.87, 29.78, 29.67, 29.58, 29.39, 22.90, 14.33. Spectroscopic properties matched those described previously.[3]

***N*,*N*-Diisopropyl-4-tetradecylbenzenesulfonamide (Table 2, 2e)**



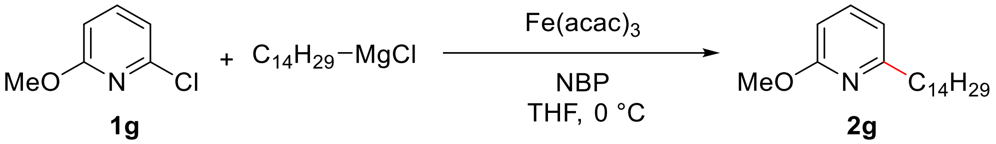
Prepared according to the general procedure using 4-chloro-*N*,*N*-diisopropylbenzenesulfonamide (0.50 mmol), $Fe(acac)_3$ (5 mol%), NBP (200 mol%), THF (0.15 M), and *n*-$C_{14}H_{29}MgCl$ (1.0 M in THF, 1.20 equiv). The reaction mixture was stirred for 10 min at 0 °C. Yield 98% (213.7 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.4 Hz, 2 H), 7.26 (d, *J* = 8.4 Hz, 2 H), 3.75-3.63 (m, 2 H), 2.65 (t, *J* = 7.7 Hz, 2 H), 1.66-1.55 (m, 2 H), 1.35-1.20 (m, 34 H), 0.88 (t, *J* = 6.8 Hz, 3 H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 147.54, 139.94, 128.85, 127.31, 48.65, 35.91, 32.08, 31.23, 29.85, 29.81, 29.78, 29.70, 29.58, 29.52, 29.34, 22.85, 22.08, 14.28. Spectroscopic properties matched those described previously.[1,2]

2-Tetradecylpyridine (Table 2, 2f)



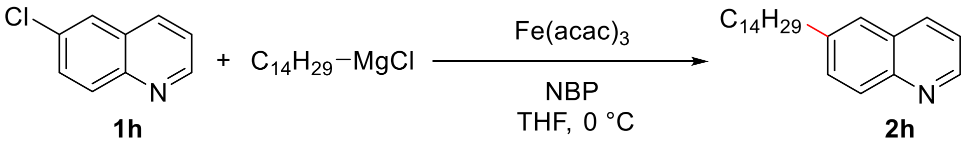
Prepared according to the general procedure using 2-chloropyridine (0.50 mmol), $Fe(acac)_3$ (5 mol%), NBP (600 mol%), THF (0.15 M), and *n*-$C_{14}H_{29}MgCl$ (1.0 M in THF, 2.0 equiv). The reaction mixture was stirred for 60 min at 0 °C. Yield 87% (119.8 mg). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.52 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1 H), 7.57 (td, *J* = 7.7, 1.9 Hz, 1 H), 7.13 (d, *J* = 7.8 Hz, 1 H), 7.08 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1 H), 2.78 (t, *J* = 7.7 Hz, 2 H), 1.77-1.66 (m, 2 H), 1.40-1.18 (m, 22 H), 0.88 (t, *J* = 6.9 Hz, 3 H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 162.70, 149.34, 136.31, 122.80, 120.95, 38.64, 32.08, 30.11, 29.84, 29.82, 29.73, 29.66, 29.58, 29.52, 22.85, 14.28. Spectroscopic properties matched those described previously.[1,2]

2-Methoxy-6-tetradecylpyridine (Table 2, 2g)



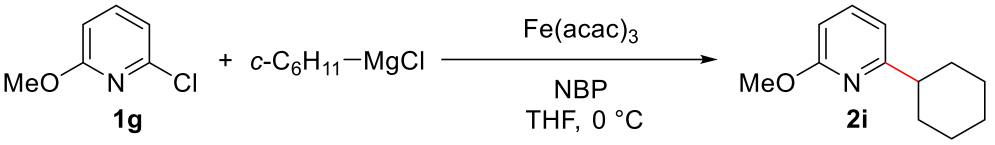
Prepared according to the general procedure using 2-chloro-6-methoxypyridine (0.50 mmol), Fe(acac)$_3$ (5 mol%), NBP (200 mol%), THF (0.15 M), and *n*-$C_{14}H_{29}$MgCl (1.0 M in THF, 1.2 equiv). The reaction mixture was stirred for 10 min at 0 °C. Yield 98% (149.8 mg). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.45 (dd, *J* = 8.2, 7.3 Hz, 1 H), 6.69 (d, *J* = 7.2 Hz, 1 H), 6.52 (d, *J* = 8.2 Hz, 1 H), 3.91 (s, 3 H), 2.67 (t, *J* = 7.7 Hz, 2 H), 1.76-1.65 (m, 2 H), 1.38-1.21 (m, 22 H), 0.88 (t, *J* = 6.9 Hz, 3 H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.79, 160.64, 138.76, 115.21, 107.24, 53.33, 38.12, 32.12, 29.88, 29.80, 29.74, 29.59, 29.56, 22.89, 14.32. Spectroscopic properties matched those described previously.[1,2]

6-Tetradecylquinoline (Table 2, 2h)



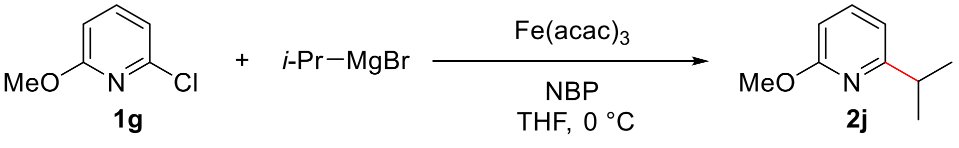
Prepared according to the general procedure using 6-chloroquinoline (0.50 mmol), Fe(acac)$_3$ (5 mol%), NBP (200 mol%), THF (0.15 M), and *n*-$C_{14}H_{29}$MgCl (1.0 M in THF, 1.2 equiv). The reaction mixture was stirred for 10 min at 0 °C. Yield 98% (159.4 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.85 (dd, *J* = 4.2, 1.7 Hz, 1 H), 8.08 (dd, *J* = 8.3, 1.0 Hz, 1 H), 8.02 (d, *J* = 9.2 Hz, 1 H), 7.59-7.54 (m, 2 H), 7.35 (dd, *J* = 8.3, 4.2 Hz, 1 H), 2.78 (t, *J* = 7.7 Hz, 2 H), 1.76-1.65 (m, 2 H), 1.39-1.21 (m, 22 H), 0.88 (t, *J* = 6.9 Hz, 3 H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.70, 147.24, 141.50, 135.67, 131.22, 129.32, 128.46, 126.14, 121.15, 36.08, 32.09, 31.43, 29.83, 29.75, 29.67, 29.53, 29.47, 22.86, 14.30. Spectroscopic properties matched those described previously.[1,2]

2-Cyclohexyl-6-methoxypyridine (Scheme 1, 2i)



Prepared according to the general procedure using 2-chloro-6-methoxypyridine (0.50 mmol), Fe(acac)$_3$ (5 mol%), NBP (200 mol%), THF (0.15 M), and c-C$_6$H$_{11}$MgCl (1.0 M in THF, 1.20 equiv). The reaction mixture was stirred for 1 h at 0 °C. Yield 95% (91.0 mg). Colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.47 (dd, *J* = 8.2, 7.3 Hz, 1 H), 6.70 (d, *J* = 7.3 Hz, 1 H), 6.52 (dd, *J* = 8.2, 0.6 Hz, 1 H), 3.92 (s, 3 H), 2.58 (tt, *J* = 11.7, 3.4 Hz, 1 H), 1.97-1.89 (m, 2 H), 1.88-1.78 (m, 2 H), 1.77-1.69 (m, 1 H), 1.58-1.47 (m, 2 H), 1.46-1.32 (m, 2 H), 1.33-1.23 (m, 1 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 164.74, 163.60, 138.87, 113.42, 107.28, 53.27, 46.16, 32.86, 26.72, 26.35. Spectroscopic properties matched those described previously.[4]

2-Isopropyl-6-methoxypyridine (Scheme 1, 2j)

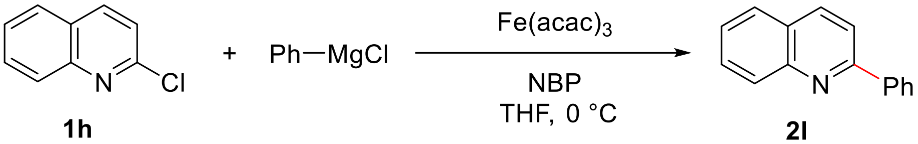


Prepared according to the general procedure using 2-chloro-6-methoxypyridine (0.50 mmol), Fe(acac)$_3$ (5 mol%), NBP (200 mol%), THF (0.15 M), and *i*-PrMgBr (1.0 M in THF, 2.0 equiv). The reaction mixture was stirred for 1 h at 0 °C. Yield 70% (53.2 mg). Colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.47 (dd, *J* = 8.2, 7.3 Hz, 1 H), 6.72 (d, *J* = 7.3 Hz, 1 H), 6.53 (dd, *J* = 8.2, 0.6 Hz, 1 H), 3.92 (s, 3 H), 2.99-2.88 (m, 1 H), 1.27 (d, *J* = 6.9 Hz, 6 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 165.46, 163.63, 138.91, 113.09, 107.35, 53.25, 36.06, 22.56. Note: isomerization to 2-methoxy-6-propylpyridine was not detected.[5] Selectivity (branched:linear) >20:1. Spectroscopic properties matched those described previously.[2]

2-Methoxy-6-phenethylpyridine (Scheme 1, 2k)

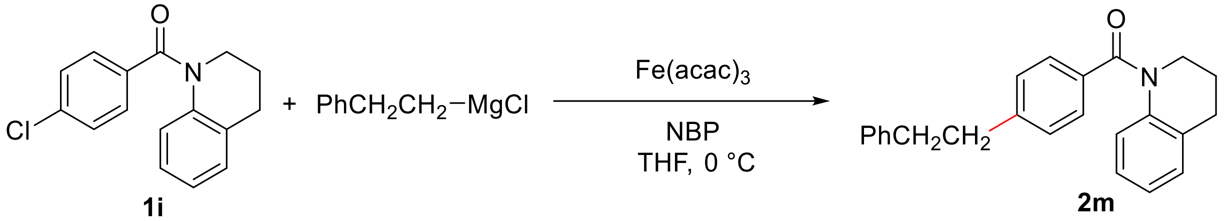
Prepared according to the general procedure using 2-chloro-6-methoxypyridine (0.50 mmol), Fe(acac)$_3$ (5 mol%), NBP (200 mol%), THF (0.15 M) and PhCH$_2$CH$_2$MgCl (1.0 M in THF, 2.0 equiv). The reaction mixture was stirred for 1 h at 0 °C. Yield 98% (104.9 mg). Colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.43 (dd, *J* = 8.2, 7.3 Hz, 1 H), 7.29-7.23 (m, 2 H), 7.22-7.15 (m, 3 H), 6.65 (d, *J* = 7.2 Hz, 1 H), 6.55 (d, *J* = 8.2 Hz, 1 H), 3.93 (s, 3 H), 3.09-3.03 (m, 2 H), 3.02-2.96 (m, 2 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 163.84, 159.21, 142.10, 138.85, 128.64, 128.45, 125.98, 115.47, 107.66, 53.39, 39.74, 35.58. Spectroscopic properties matched those described previously.[6]

2-Phenylquinoline (Scheme 2, 2l)



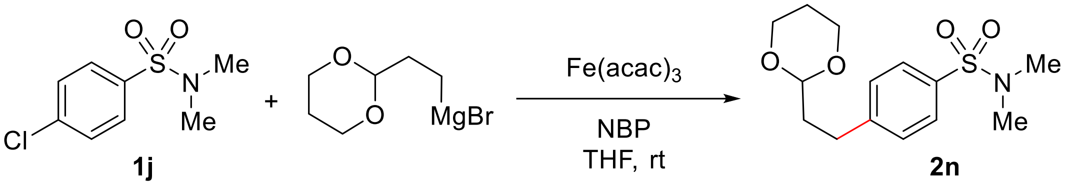
Prepared according to the general procedure using 2-chloroquinoline (0.50 mmol), Fe(acac)$_3$ (5 mol%), NBP (200 mol%), THF (0.15 M) and PhMgCl (1.0 M in 2-MeTHF, 2.0 equiv). The reaction mixture was stirred for 1 h at 0 °C. Yield 97% (99.7 mg). White solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.22-8.13 (m, 4 H), 7.86 (d, *J* = 8.6 Hz, 1 H), 7.81 (d, *J* = 9.3 Hz, 1 H), 7.75-7.68 (m, 1 H), 7.55-7.42 (m, 4 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 157.51, 148.44, 139.84, 136.92, 129.90, 129.81, 129.47, 129.00, 127.73, 127.62, 127.33, 126.43, 119.16. Spectroscopic properties matched those described previously.[7]

(3,4-Dihydroquinolin-1(2*H*)-yl)(4-phenethylphenyl)methanone (Scheme 3, 2m)



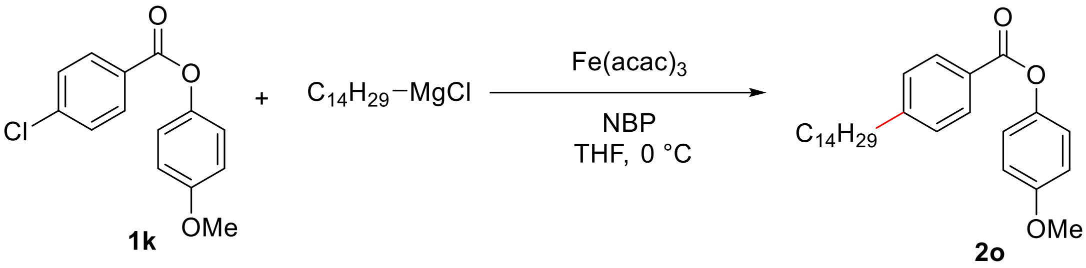
Prepared according to the general procedure using (4-chlorophenyl)(3,4-dihydroquinolin-1(2*H*)-yl)methanone (0.50 mmol), Fe(acac)$_3$ (5 mol%), NBP (200 mol%), THF (0.15 M) and PhCH$_2$CH$_2$MgCl (1.0 M in THF, 2.0 equiv). The reaction mixture was stirred for 1 h at 0 °C. Yield 65% (110.5 mg). Yellow solid. *New compound*. Mp = 115-117 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.29-7.21 (m, 4 H), 7.20-7.08 (m, 4 H), 7.06-6.95 (m, 3 H), 6.87 (t, *J* = 7.7 Hz, 1 H), 6.74-6.66 (m, 1 H), 3.90 (t, *J* = 6.5 Hz, 2 H), 2.91-2.85 (m, 4 H), 2.83 (t, *J* = 6.6 Hz, 2 H), 2.07-2.00 (m, 2H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 170.45, 144.16, 141.36, 139.61, 133.97, 131.71, 128.90, 128.61, 128.43, 128.33, 126.11, 125.80, 125.57, 124.56, 44.53, 37.84, 37.64, 27.10, 24.29. **HRMS** (ESI/ Q-TOF) *m/z*: [M + H]$^+$ calcd for $C_{24}H_{24}NO$ 342.1858 found 342.1856.

4-(2-(1,3-Dioxan-2-yl)ethyl)-*N*,*N*-dimethylbenzenesulfonamide (Scheme 3, 2n)



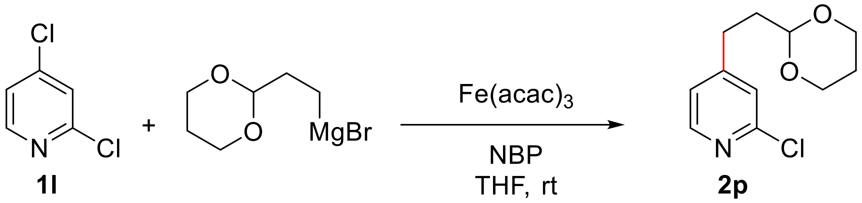
Prepared according to the general procedure using 4-chloro-*N*,*N*-dimethylbenzenesulfonamide (0.50 mmol), Fe(acac)$_3$ (5 mol%), NBP (600 mol%), THF (0.15 M), and (2-(1,3-dioxan-2-yl)ethyl)magnesium bromide (0.5 M in THF, 3.00 equiv). The reaction mixture was stirred overnight at 23 °C. Yield 98% (146.5 mg). White solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 4.52 (t, *J* = 5.1 Hz, 1H), 4.12 (dd, *J* = 10.7, 5.0 Hz, 2H), 3.80-3.72 (m, 2H), 2.84-2.78 (m, 2H), 2.70 (s, 6H), 2.15-2.02 (m, 1H), 1.96-1.89 (m, 2H), 1.40-1.33 (m, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 147.36, 132.86, 129.10, 127.96, 101.01, 66.93, 38.02, 36.17, 29.95, 25.80. Spectroscopic properties matched those described previously.[8]

4-Methoxyphenyl 4-tetradecylbenzoate (Scheme 3, 2o)



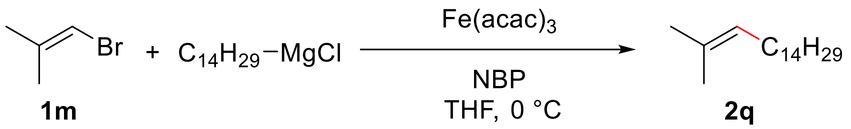
Prepared according to the general procedure using 4-methoxyphenyl 4-chlorobenzoate (0.50 mmol), Fe(acac)$_3$ (5 mol%), NBP (200 mol%), THF (0.15 M), and $C_{14}H_{29}MgCl$ (1.0 M in THF, 1.05 equiv). The reaction mixture was stirred for 180 min at 0 °C. Yield 77% (163.7 mg). White solid. **<u>^{1}H NMR (400 MHz, CDCl$_3$)</u>** δ 8.10 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 9.1 Hz, 2H), 6.93 (d, *J* = 9.1 Hz, 2H), 3.82 (s, 3H), 2.69 (t, *J* = 7.7 Hz, 2H), 1.69-1.60 (m, 2H), 1.35-1.24 (m, 22H), 0.88 (t, *J* = 6.8 Hz, 3H). **<u>^{13}C NMR (100 MHz, CDCl$_3$)</u>** δ 165.80, 157.39, 149.46, 144.64, 130.37, 128.79, 127.19, 122.67, 114.64, 55.77, 36.26, 32.11, 31.35, 29.84, 29.75, 29.65, 29.55, 29.44, 22.88, 14.32. Spectroscopic properties matched those described previously.[9]

4-(2-(1,3-Dioxan-2-yl)ethyl)-2-chloropyridine (Scheme 4, 2p)



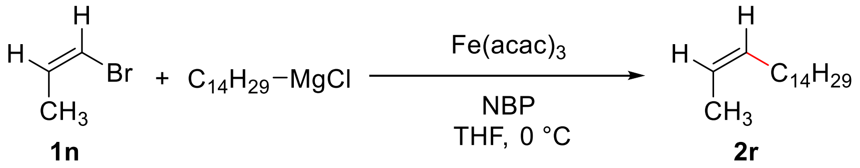
A previously published procedure was followed using NBP instead of NMP.[10] Prepared according to the general procedure using 2,4-dichloropyridine (0.50 mmol), Fe(acac)$_3$ (3.75 mol%), NBP (600 mol%), THF (0.15 M), and (2-(1,3-dioxan-2-yl)ethyl)magnesium bromide (0.5 M in THF, 2.00 equiv). The reaction mixture was stirred for 2 h at 23 °C. Yield 90% (102.5 mg). Colorless oil. **<u>^{1}H NMR (400 MHz, CDCl$_3$)</u>** δ 8.27 (dd, *J* = 5.1, 0.4 Hz, 1H), 7.18 (dd, *J* = 1.4, 0.6 Hz, 1H), 7.06 (dd, *J* = 5.1, 1.5 Hz, 1H), 4.51 (t, *J* = 5.0, 1H), 4.15-4.07 (m, 2H), 3.79-3.71 (m, 2H), 2.76-2.69 (m, 2H), 2.15-2.01 (m, 1H), 1.94-1.87 (m, 2H), 1.40-1.33 (m, 1H). **<u>^{13}C NMR (100 MHz, CDCl$_3$)</u>** δ 154.45, 151.72, 149.61, 124.36, 122.85, 100.74, 66.99, 35.24, 29.16, 25.82. Note: 4-/2-alkylation selectivity = 9.1:1.[10] Spectroscopic properties matched those described previously.[10]

2-Methylheptadec-2-ene (Scheme 5, 2q)



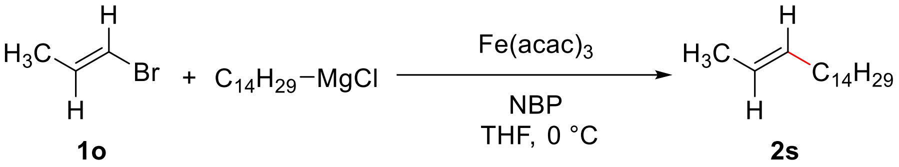
A previously published procedure was followed using NBP instead of NMP.[11] Prepared according to the general procedure using 1-bromo-2-methylprop-1-ene (0.50 mmol), Fe(acac)$_3$ (1 mol%), NBP (200 mol%), THF (0.50 M) and *n*-$C_{14}H_{29}$MgCl (1.0 M in THF, 1.1 equiv). The reaction mixture was stirred for 15 min at 0 °C. Yield 98% (123.5 mg). Colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 5.15-5.08 (m, 1 H), 2.00-1.91 (m, 2 H), 1.68 (brs, 3 H), 1.59 (brs, 3 H), 1.30-1.25 (m, 24 H), 0.88 (t, *J* = 6.9 Hz, 3 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 131.24, 125.19, 32.18, 30.16, 29.96, 29.87, 29.63, 28.29, 25.92, 22.94, 17.83, 14.33. Spectroscopic properties matched those described previously.[12]

(*Z*)-Heptadec-2-ene (Scheme 5, 2r)



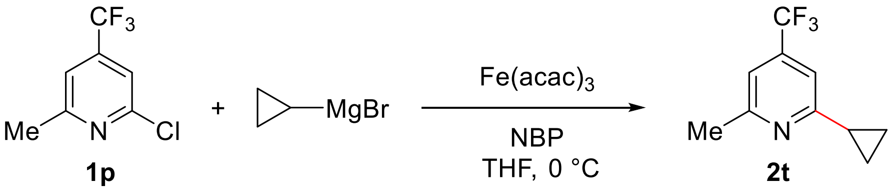
A previously published procedure was followed using NBP instead of NMP.[11] Prepared according to the general procedure using (*Z*)-1-bromoprop-1-ene (0.50 mmol), Fe(acac)$_3$ (1 mol%), NBP (200 mol%), THF (0.50 M) and *n*-$C_{14}H_{29}$MgCl (1.0 M in THF, 1.1 equiv). The reaction mixture was stirred for 15 min at 0 °C. Yield 96% (114.6 mg). Colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 5.49-5.32 (m, 2 H), 2.06-1.99 (m, 2 H), 1.62-1.56 (m, 3 H), 1.36-1.23 (m, 24 H), 0.88 (t, *J* = 6.9 Hz, 3 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 131.10, 123.76, 32.18, 29.95, 29.92, 29.83, 29.63, 29.56, 27.07, 22.94, 14.33, 12.93. Spectroscopic properties matched those described previously.[13]

(*E*)-Heptadec-2-ene (Scheme 5, 2s)



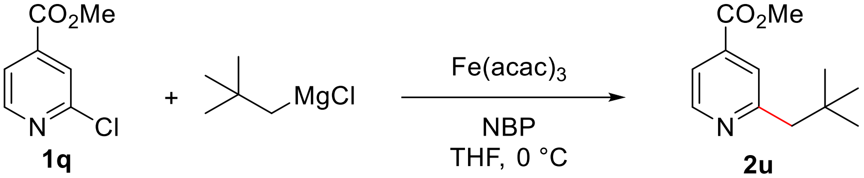
A previously published procedure was followed using NBP instead of NMP.[11] Prepared according to the general procedure using (*E*)-1-bromoprop-1-ene (0.50 mmol), Fe(acac)$_3$ (1 mol%), NBP (200 mol%), THF (0.50 M) and *n*-$C_{14}H_{29}$MgCl (1.0 M in THF, 1.1 equiv). The reaction mixture was stirred for 15 min at 0 °C. Yield 98% (116.7 mg). Colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 5.49-5.33 (m, 2 H), 1.99-1.92 (m, 2 H), 1.66-1.62 (m, 3 H), 1.34-1.23 (m, 24 H), 0.88 (t, *J* = 6.9 Hz, 3 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 131.90, 124.70, 32.85, 32.16, 29.94, 29.90, 29.86, 29.78, 29.61, 29.45, 22.92, 18.14, 14.33. Spectroscopic properties matched those described previously.[13]

2-Cyclopropyl-6-methyl-4-(trifluoromethyl)pyridine (Scheme 8, 2t)



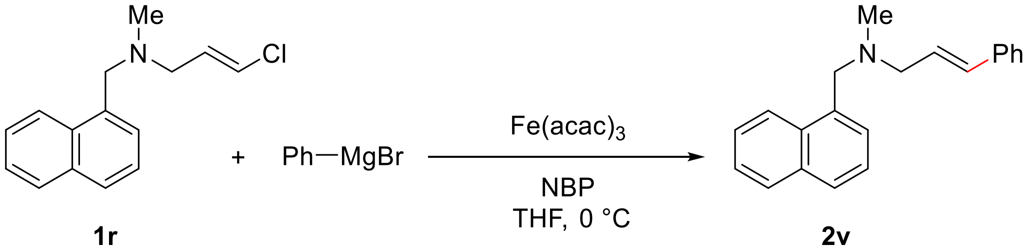
A previously published procedure was followed using NBP instead of NMP.[14] Prepared according to the general procedure using 2-chloro-6-methyl-4-(trifluoromethyl)pyridine (0.50 mmol), Fe(acac)$_3$ (5 mol%), NBP (200 mol%), THF (0.15 M), and cyclopropylmagnesium bromide (1.0 M in THF, 2.00 equiv). The reaction mixture was stirred for 1 h at 0 °C. Yield 81% (81.5 mg). Colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.09 (s, 2H), 2.54 (s, 3H), 2.11-2.03 (m, 1H), 1.06-0.99 (m, 4H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 164.07, 159.44, 138.49 (q, J^F = 33.2 Hz), 123.35 (q, J^F = 273.0 Hz), 115.46 (q, J^F = 3.4 Hz), 113.63 (q, J^F = 3.5 Hz), 24.80, 17.58, 10.38. Spectroscopic properties matched those described previously.[14]

Methyl 2-neopentylisonicotinate (Scheme 9, 2u)



A previously published procedure was followed using NBP instead of NMP.[15] Prepared according to the general procedure using methyl 2-chloroisonicotinate (0.50 mmol), Fe(acac)$_3$ (5 mol%), NBP (200 mol%), THF (0.22 M) and neopentylMgCl (1.0 M in THF, 2.5 equiv). The reaction mixture was stirred for 4 h at 0 °C. Yield 66% (68.5 mg). Colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.70 (d, *J* = 5.8 Hz, 1H), 7.69-7.66 (m, 2H), 3.96 (s, 3H), 2.77 (s, 2H), 0.97 (s, 9H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 166.22, 161.64, 149.79, 137.09, 123.87, 120.23, 52.80, 52.09, 32.34, 29.69. Spectroscopic properties matched those described previously.[15]

(*E*)-*N*-methyl-*N*-(naphthalen-1-ylmethyl)-3-phenylprop-2-en-1-amine (Scheme 10, 2v)

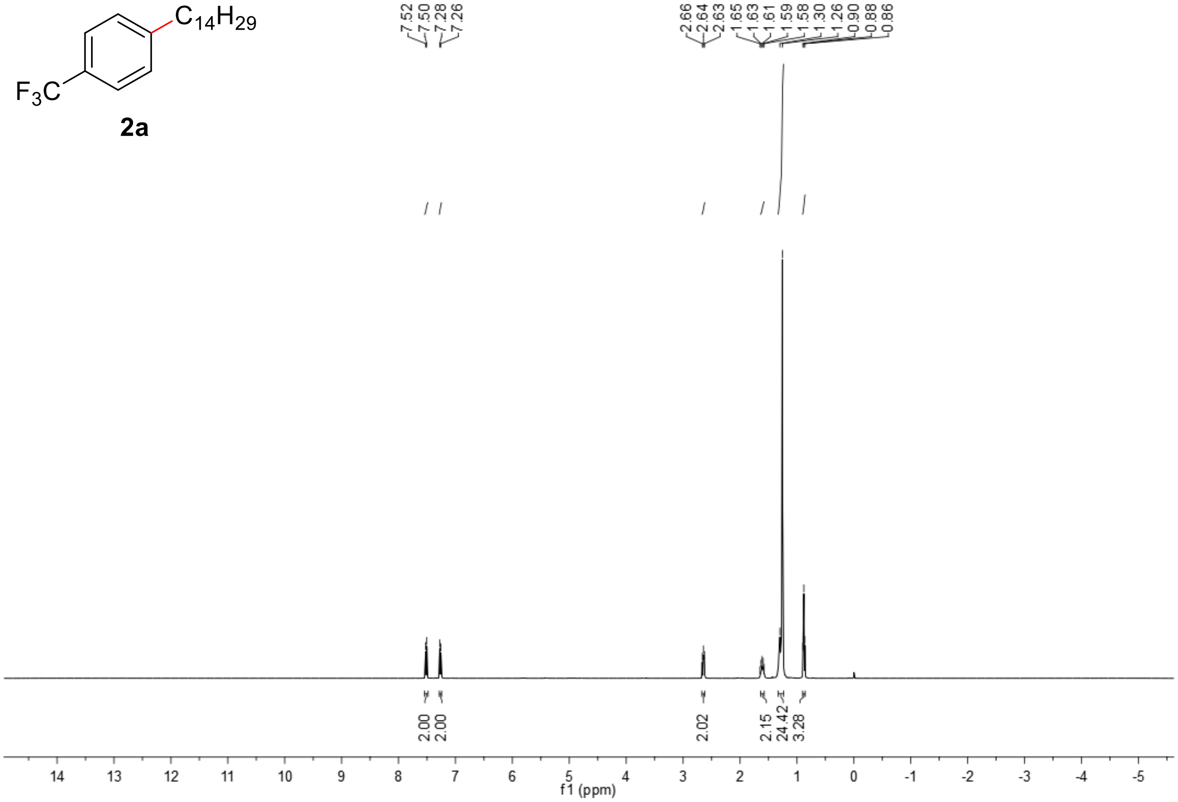


A previously published procedure was followed using NBP instead of NMP.[16] Prepared according to the general procedure using (*E*)-3-chloro-*N*-methyl-*N*-(naphthalen-1-ylmethyl)prop-2-en-1-amine (0.50 mmol), Fe(acac)$_3$ (1 mol%), NBP (80 mol%), THF (0.36 M) and PhMgBr (1.0 M in THF, 1.6 equiv). The reaction mixture was stirred for 1.5 h at 0 °C. Yield 98% (141.1 mg). Colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.29 (d, *J* = 8.4 Hz, 1 H), 7.83 (d, *J* = 8.0 Hz, 1 H), 7.76 (d, *J* = 8.0 Hz, 1 H), 7.54-7.35 (m, 6 H), 7.32-7.26 (m, 2 H), 7.23-7.17 (m, 1 H), 6.56 (d, *J* = 15.9 Hz, 1 H), 6.36 (dt, *J* = 15.9, 6.7 Hz, 1 H), 3.92 (s, 2 H), 3.26 (dd, *J* = 6.7, 1.2 Hz, 2 H), 2.26 (s, 3 H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 137.26, 135.02, 134.03, 132.81, 132.63, 128.70, 128.59, 128.09, 127.76, 127.61, 127.53, 126.46, 126.06, 125.74, 125.27, 124.78, 60.57, 60.27, 42.63.

Spectroscopic properties matched those described previously.[16] Note: isomerization of the olefin starting material (**1r**: *E*/*Z* >98:2) was not observed (**2v**: *E*/*Z* >98:2).

References

1. Fürstner, A.; Leitner, A. *Angew. Chem. Int. Ed.* **2002**, *41*, 609.
2. Fürstner, A.; Leitner, A.; Mendez, M.; Krause, H. *J. Am. Chem. Soc.* **2002**, *124*, 13856.
3. Scheiper, B.; Bonnekessel, M.; Krause, H.; Fürstner, A. *J. Org. Chem.* **2004**, *69*, 3949.
4. Xiao, B.; Liu, Z. J.; Liu, L.; Fu, Y. *J. Am. Chem. Soc.* **2013**, *135*, 616.
5. (a) Agrawal, T.; Cook, S. P. *Org. Lett.* **2013**, *15*, 96. (b) Perry, M. C.; Gillett, A. N.; Law, T. C. *Tetrahedron Lett.* **2012**, *53*, 4436.
6. Liu, Z.; Yao, Y.; Kogiso, M.; Zheng, B.; Deng, L.; Qiu, J. J.; Dong, S.; Lv, H.; Gallo, J. M.; Li, X.; Song, Y. *J. Med. Chem.* **2014**, *57*, 8307.
7. He, K.; Tan, F.; Zhou, C.; Zhou, G.; Yang X.; Li, Y. *Angew. Chem.* **2017**, *56*, 3080.
8. Bisz, E.; Szostak, M. *J. Org. Chem.* **2019**, *84*, 1640.
9. Bisz, E.; Szostak, M. *Molecules* **2020**, *25*, 230.
10. Malhotra, S.; Seng, P. S.; Koenig, S. G.; Deese, A. J.; Ford, K. A. *Org. Lett.* **2013**, *15*, 3698.
11. Cahiez, G.; Avedissian, H. *Synthesis* **1998**, *8*, 1199.
12. Cormier, R. A.; Hoban, J. *J. Chem. Educ*. **1984**, *61*, 927.
13. Notre, J.; Scott, E. L.; Franssen, M. C. R.; Sanders, J. P. M. *Tetrahedron Lett.* **2010**, *51*, 3712.
14. Risatti, C.; Natalie, Jr., K. J.; Shi, Z.; Conlon, D. A. *Org. Process Res. Dev.* **2013**, *17*, 257.
15. Andersen, S. M.; Bollmark, M.; Berg, R.; Fredriksson, C.; Karlsson, S.; Liljeholm, C.; Sorensen, H. *Org. Process Res. Dev.* **2014**, *18*, 952.
16. Shakhmaev, R. N.; Sunagatullina, A. Sh.; Zorin, V. V. *Russ. J. Org. Chem.* **2014**, *50*, 322.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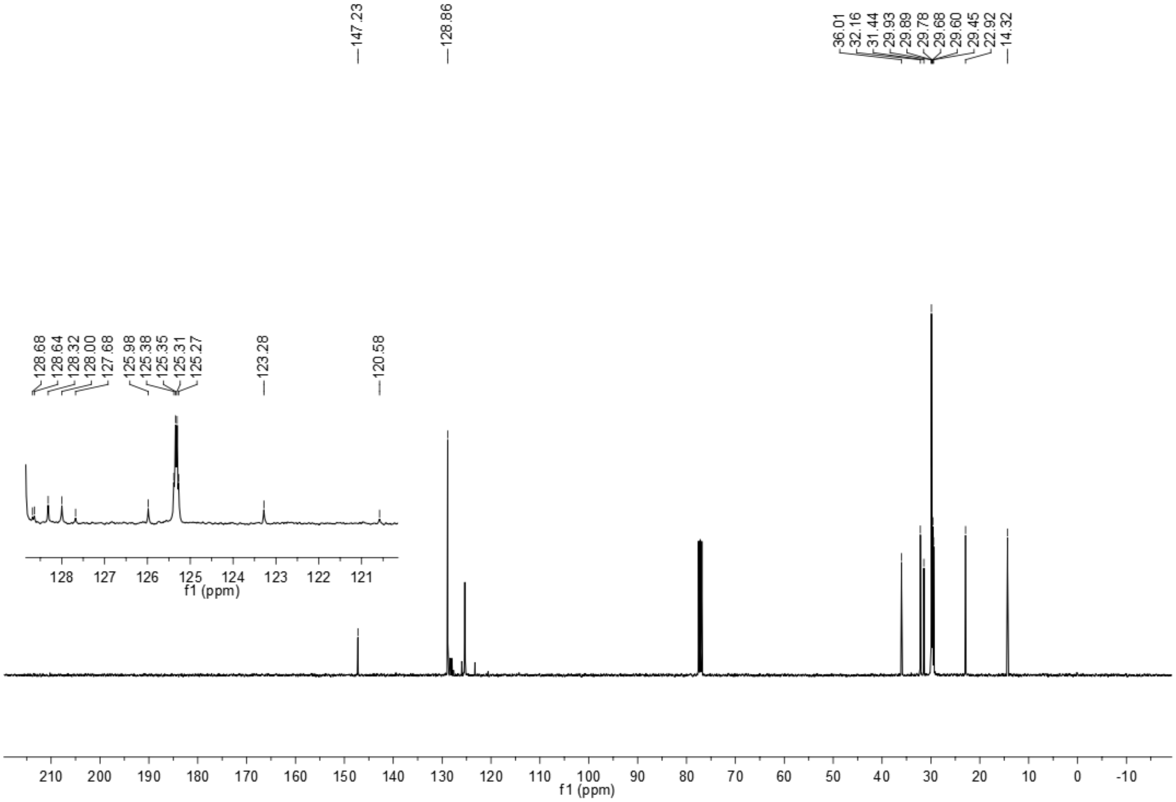
7.50
7.28
7.26
2.66
2.64
2.63
1.65
1.63
1.61
1.59
1.58
1.30
1.26
0.90
0.88
0.86
2.00
2.00
2.02
2.15
24.42
3.28
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
f1 (ppm)

2a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36.01
32.16
31.44
29.93
29.89
29.78
29.68
29.60
29.45
22.92
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128.68
128.64
128.32
128.00
127.68
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125.35
125.31
125.27
123.28
120.58
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f1 (ppm)
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200
190
180
170
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80
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40
30
20
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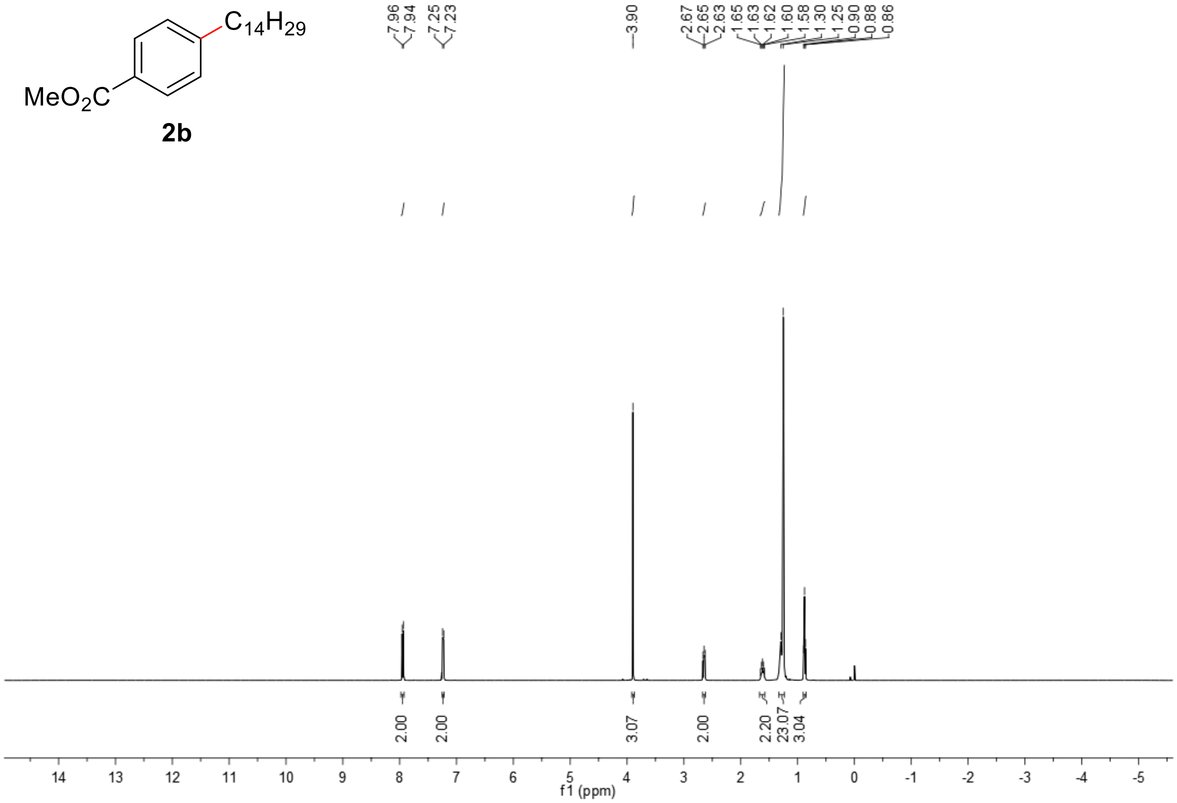
f1 (ppm)


$C_{14}H_{29}$
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7.94
7.25
7.23
3.90
2.67
2.65
2.63
1.65
1.63
1.62
1.60
1.58
1.30
1.25
0.90
0.88
0.86
2.00
2.00
3.07
2.00
2.20
23.07
3.04
14
13
12
11
10
9
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6
5
4
3
2
1
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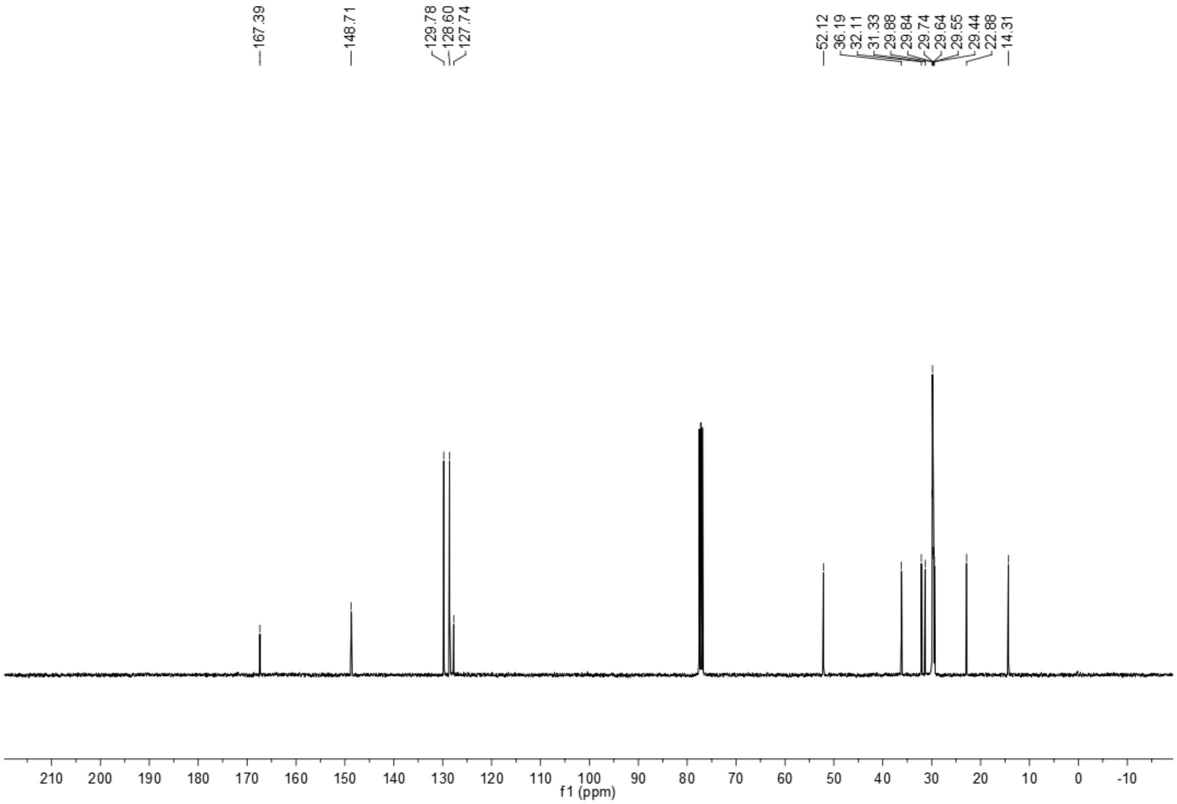
-2
-3
-4
-5
f1 (ppm)

2b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128.60
127.74
52.12
36.19
32.11
31.33
29.88
29.84
29.74
29.64
29.55
29.44
22.88
14.31
210
200
190
180
170
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120
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100
90
80
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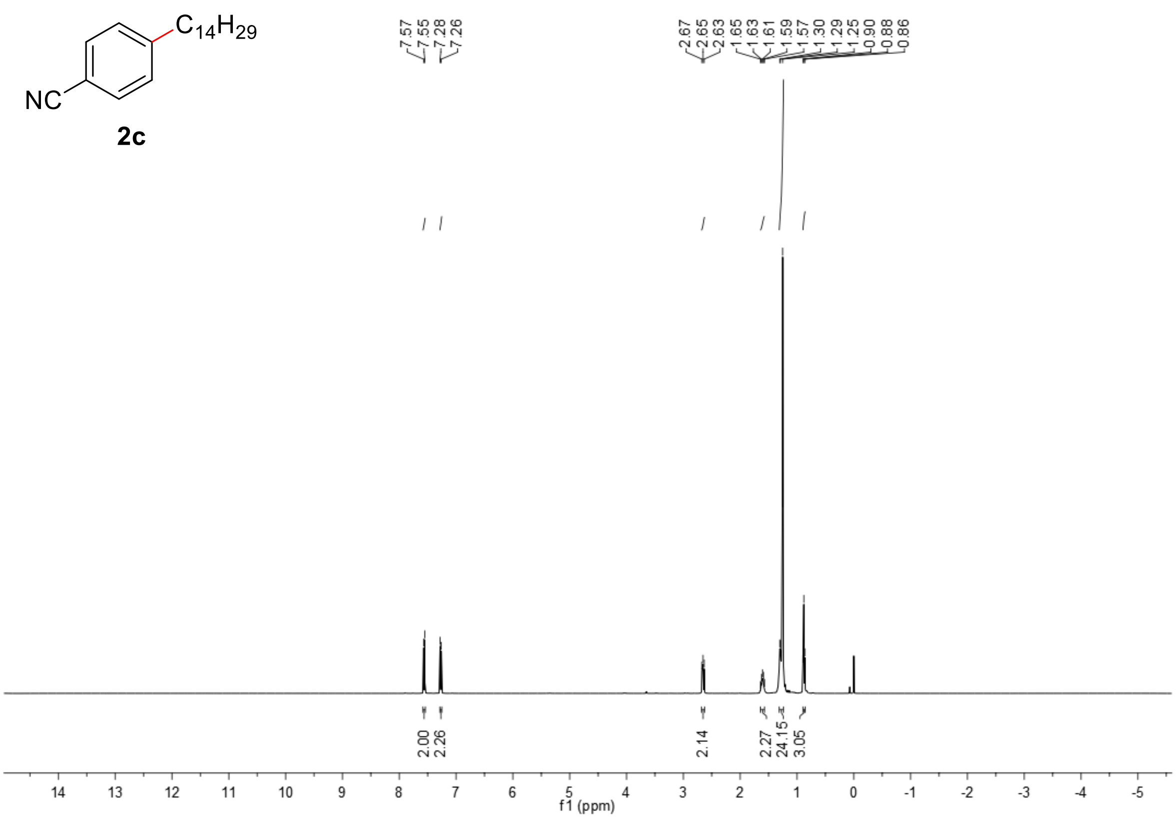
30
20
10
0
-10
f1 (ppm)


2c
C14H29
NC
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7.55
7.28
7.26
2.67
2.65
2.63
1.65
1.63
1.61
1.59
1.57
1.30
1.29
1.25
0.90
0.88
0.86
2.00
2.26
2.14
2.27
24.15
3.05
14
13
12
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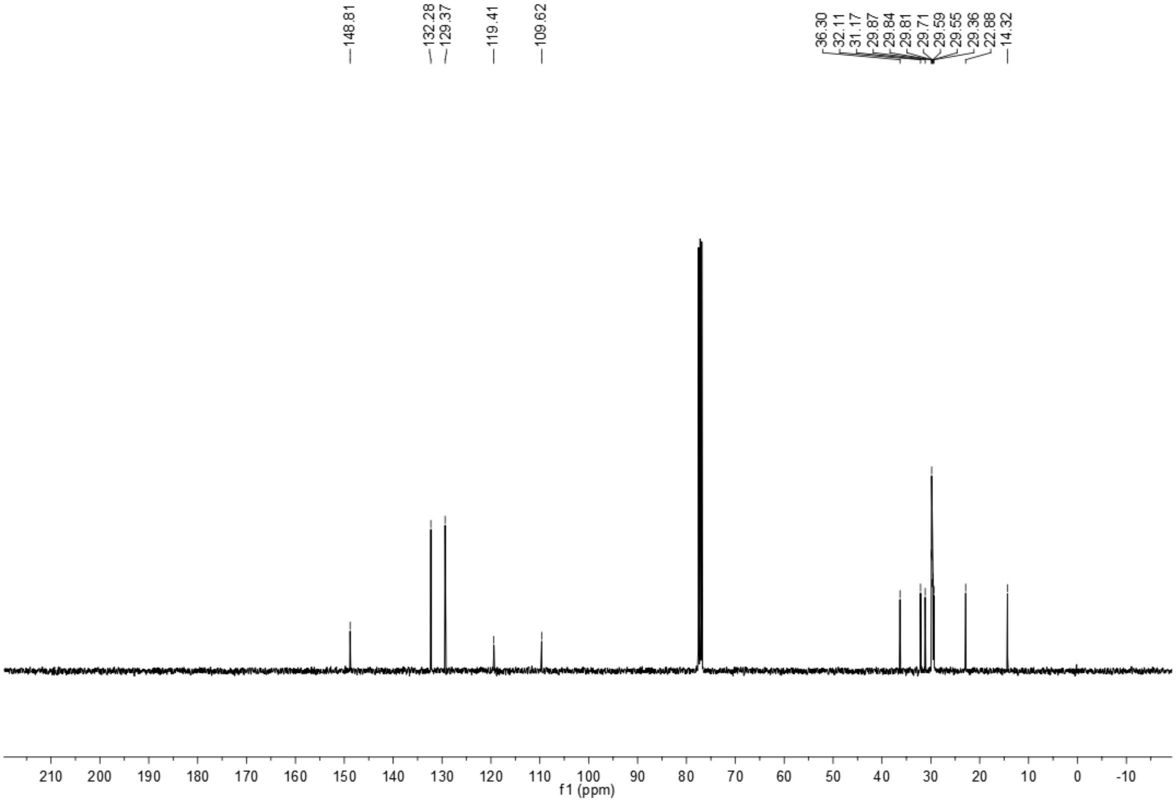
f1 (ppm)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29.59
29.55
29.36
22.88
14.32
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200
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180
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80
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30
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10
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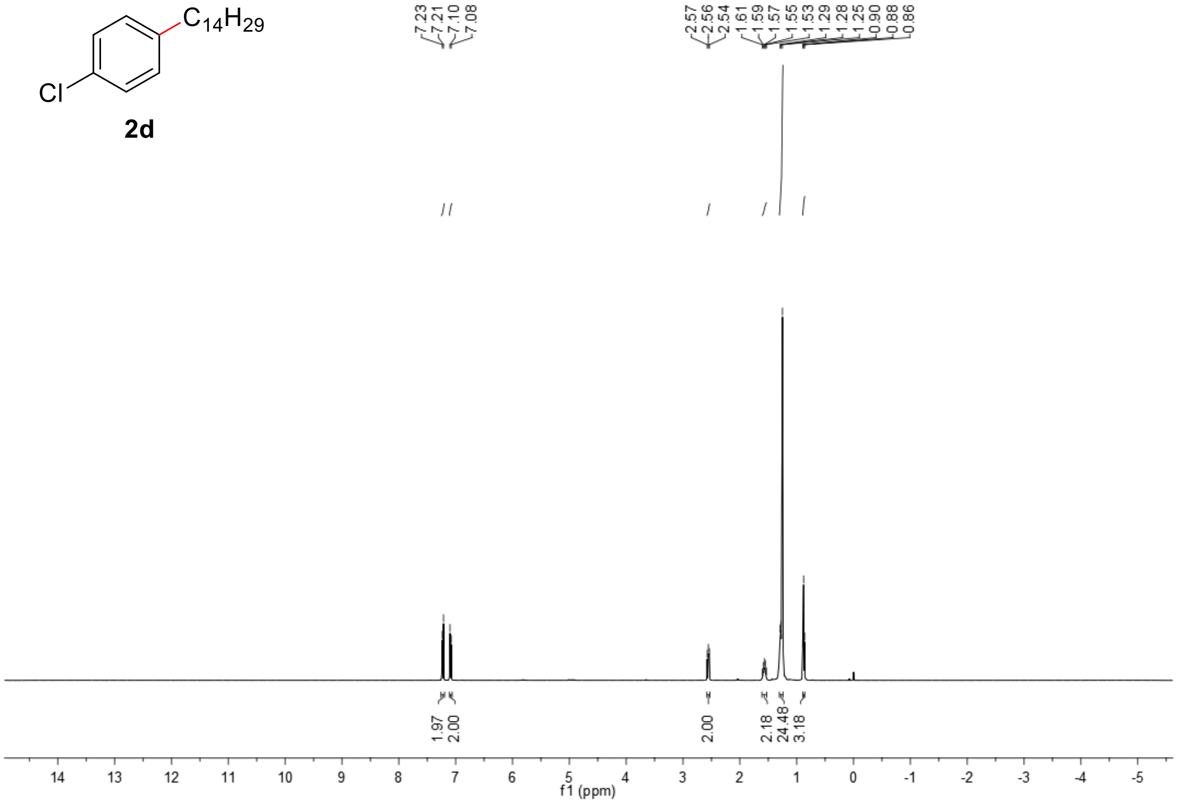
f1 (ppm)


C14H29
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7.10
7.08
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2.56
2.54
1.61
1.59
1.57
1.55
1.53
1.29
1.28
1.25
0.90
0.88
0.86
1.97
2.00
2.00
2.18
24.48
3.18
14
13
12
11
10
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-3
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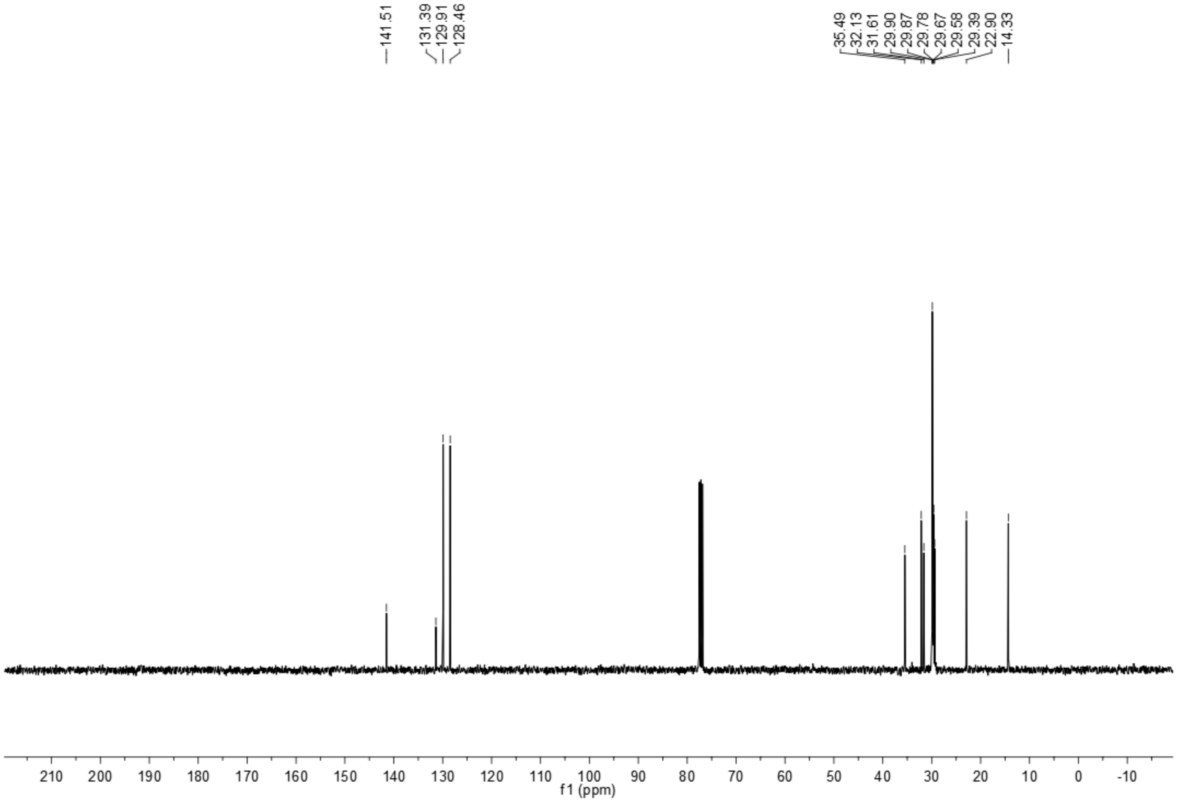
f1 (ppm)

2d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32.13
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29.90
29.87
29.78
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22.90
14.33
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200
190
180
170
160
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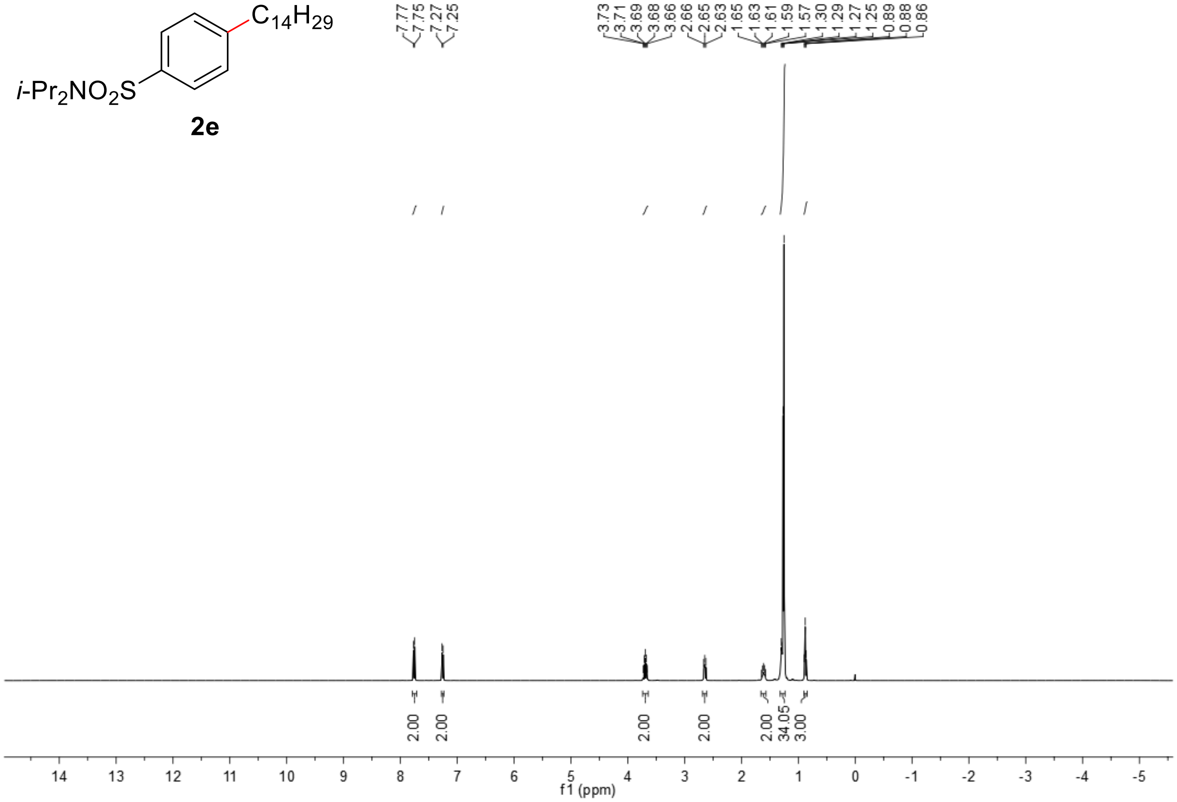
0
-10
f1 (ppm)


C14H29
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2.66
2.65
2.63
1.65
1.63
1.61
1.59
1.57
1.30
1.29
1.27
1.25
0.89
0.88
0.86
2.00
2.00
2.00
2.00
2.00
34.05
3.00
14
13
12
11
10
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4
3
2
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-3
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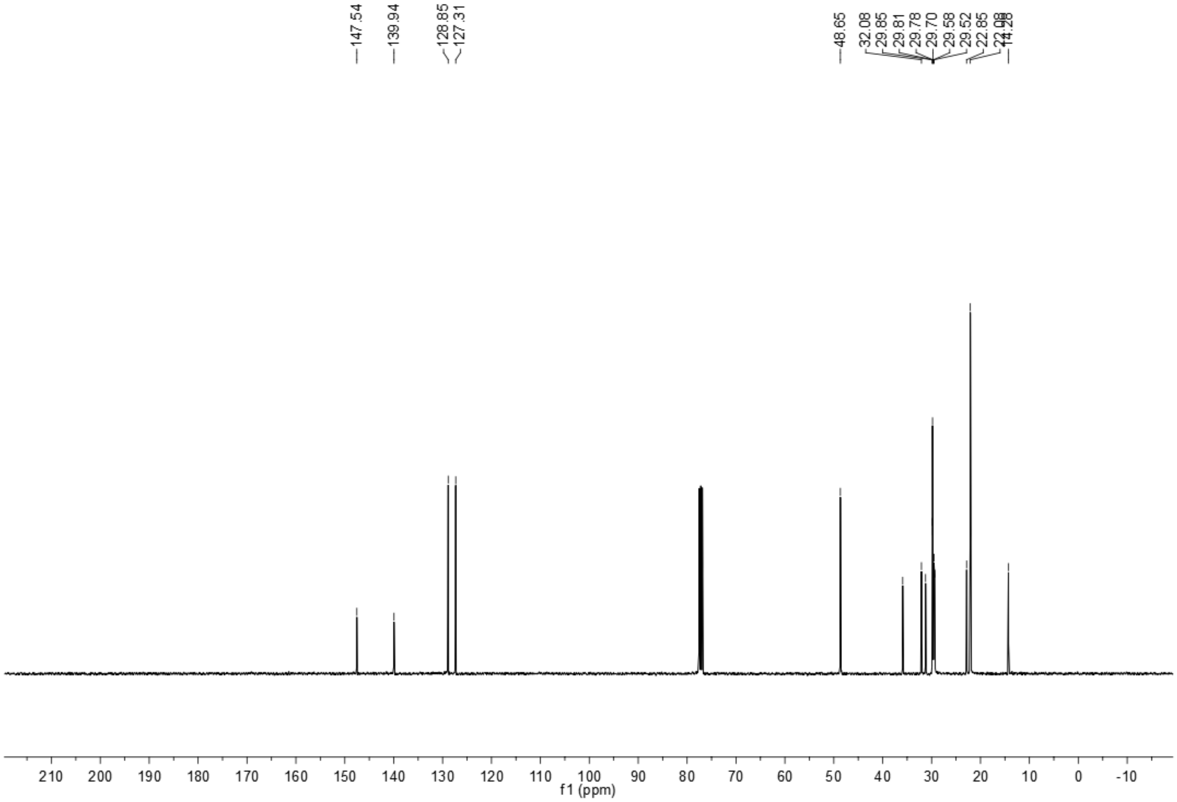
-5
f1 (ppm)

2e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200
190
180
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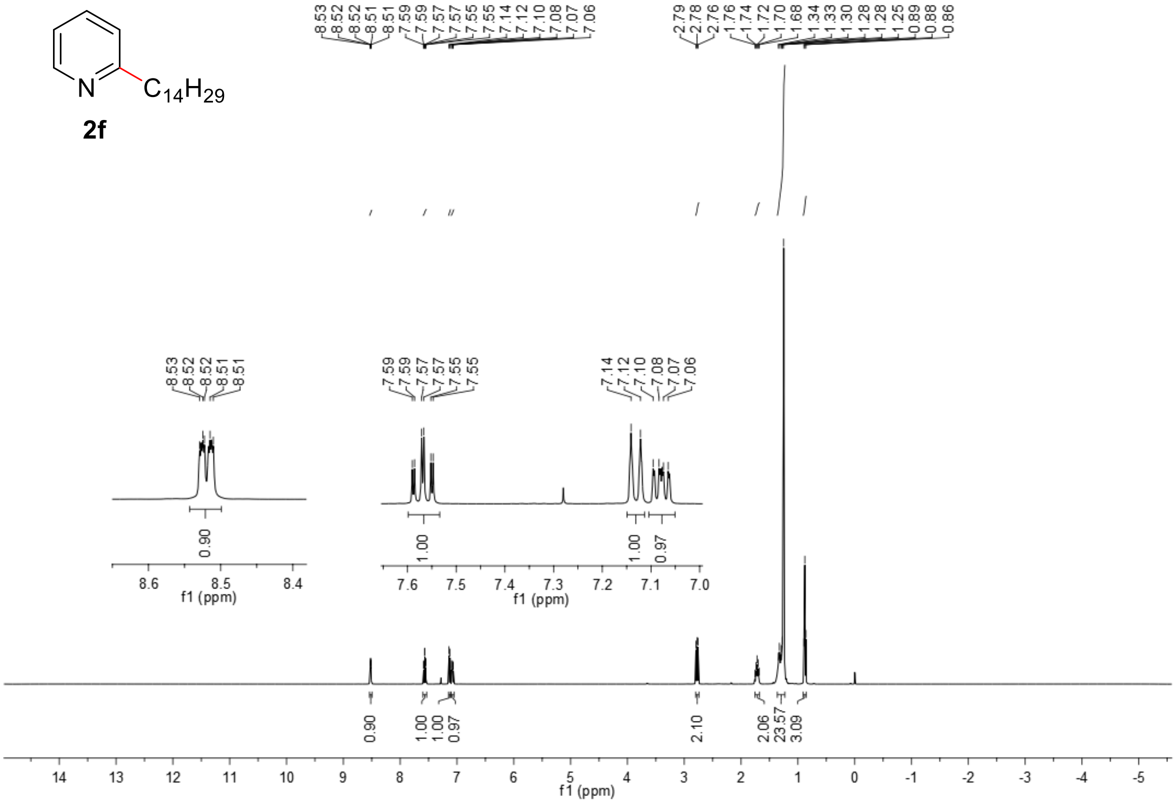
f1 (ppm)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1.70
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1.33
1.30
1.28
1.28
1.25
0.89
0.88
0.86
0.90
1.00
1.00
0.97
2.10
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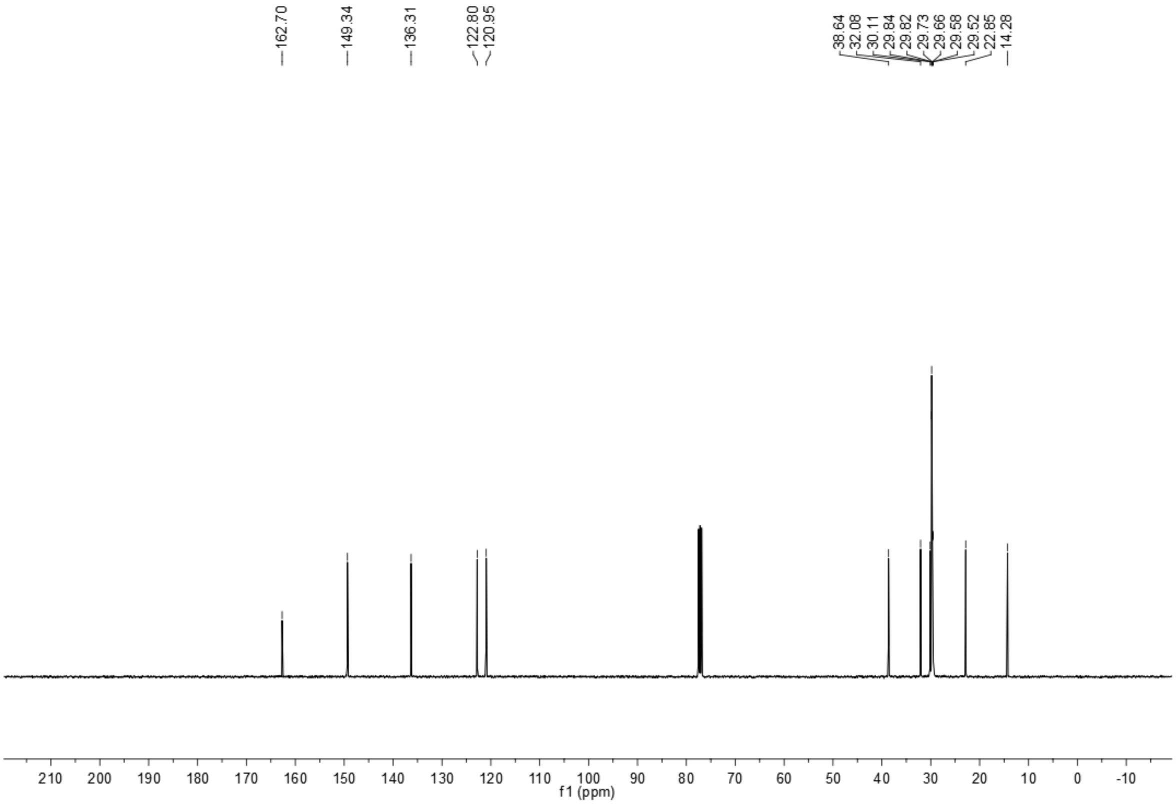
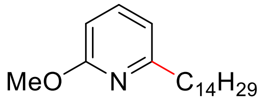
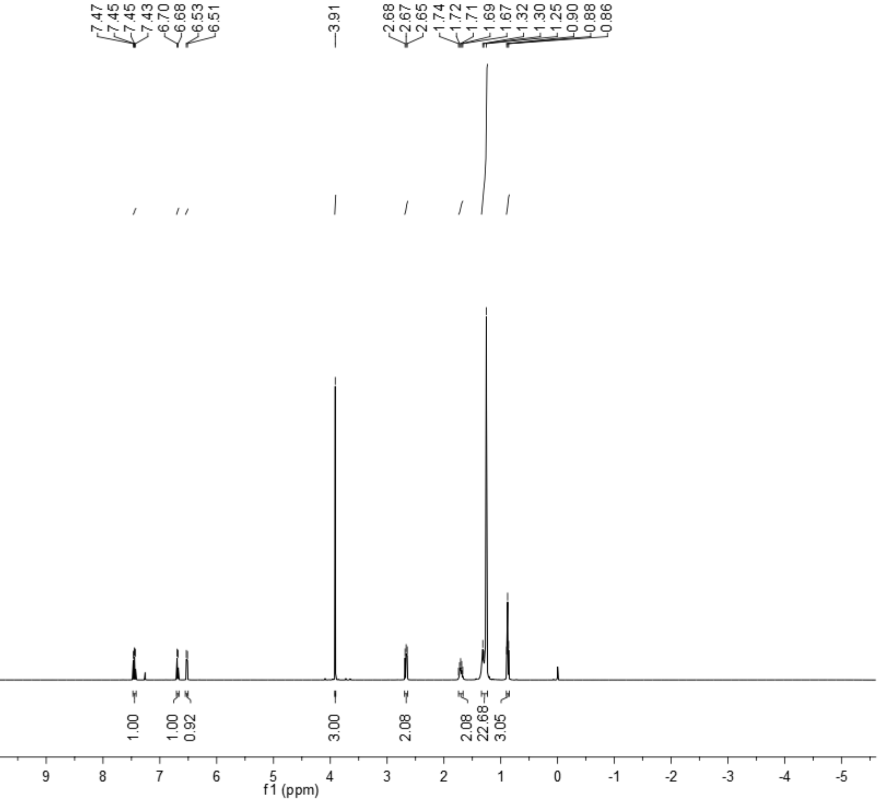
23.57
3.09
f1 (ppm)

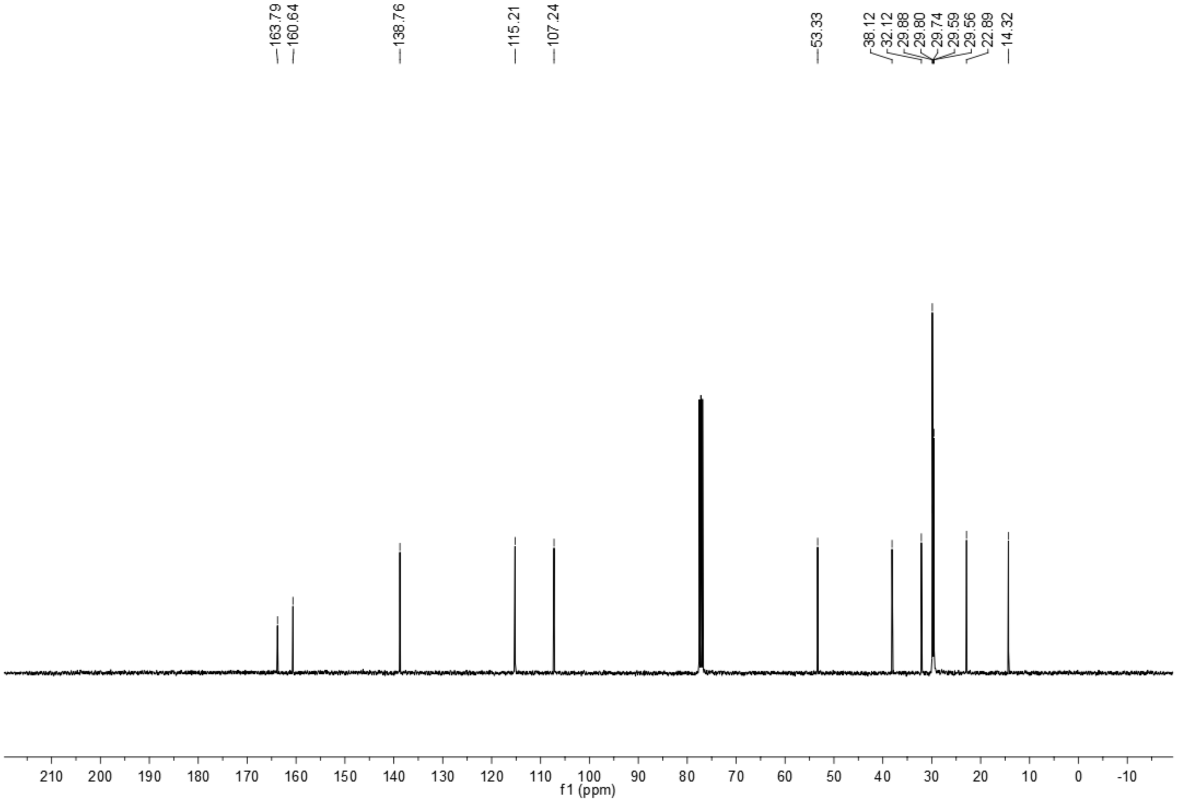
2f

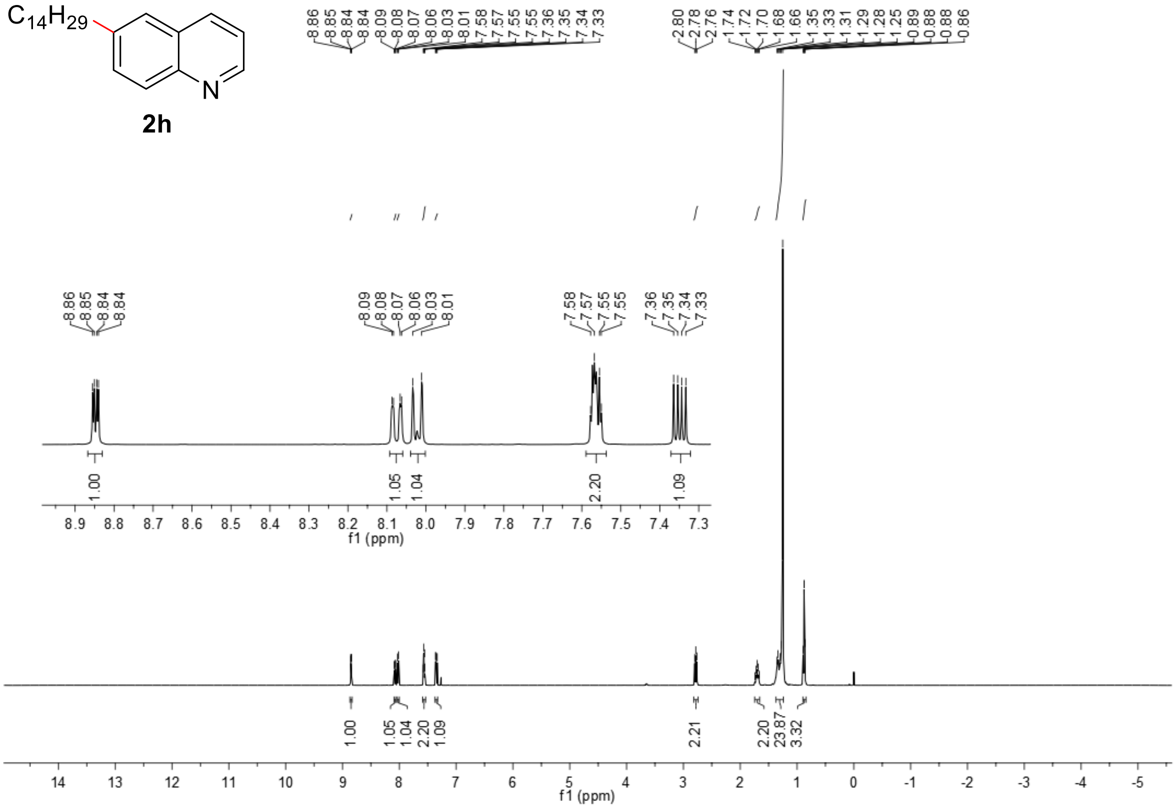

162.70
149.34
136.31
122.80
120.95
38.64
32.08
30.11
29.84
29.82
29.73
29.66
29.58
29.52
22.85
14.28
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


MeO
N
C14H29

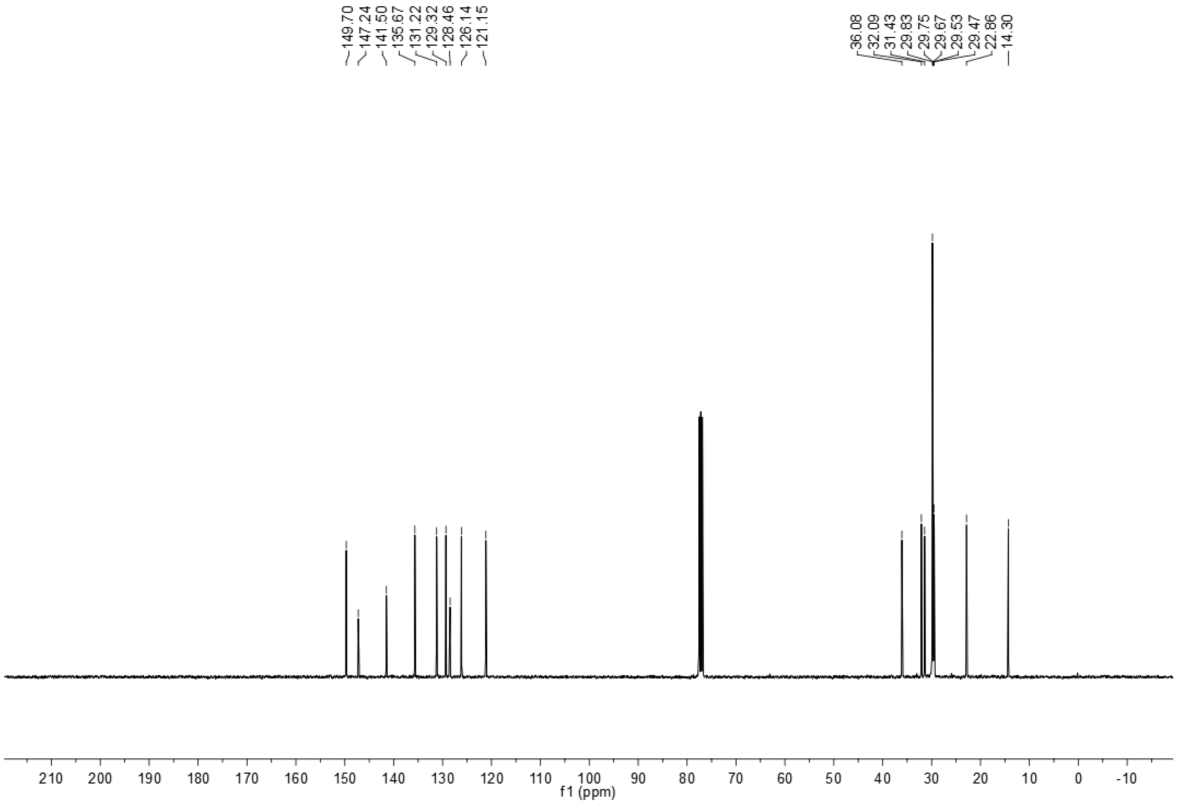
2g

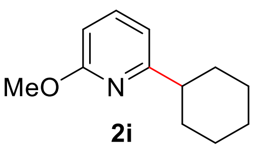

7.47
7.45
7.45
7.43
6.70
6.68
6.53
6.51
3.91
2.68
2.67
2.65
1.74
1.72
1.71
1.69
1.67
1.32
1.30
1.25
0.90
0.88
0.86
1.00
1.00
0.92
3.00
2.08
2.08
22.68
3.05
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
f1 (ppm)


163.79
160.64
138.76
115.21
107.24
53.33
38.12
32.12
29.88
29.80
29.74
29.59
29.56
22.89
14.32
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

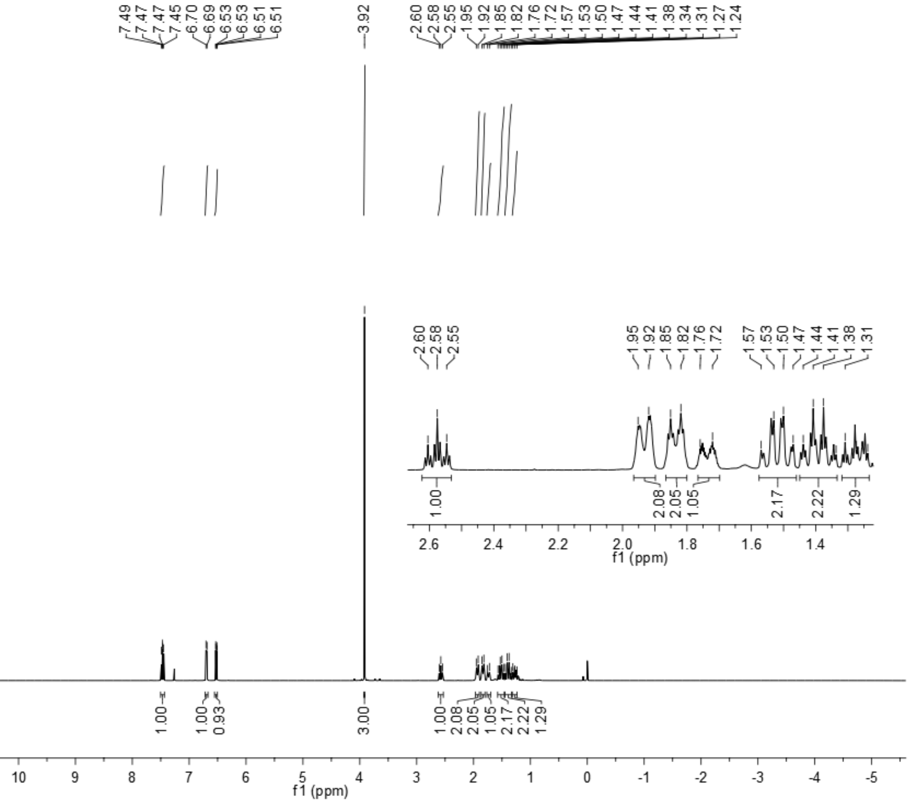

$C_{14}H_{29}$
N
8.86
8.85
8.84
8.84
8.09
8.08
8.07
8.06
8.03
8.01
7.58
7.57
7.55
7.55
7.36
7.35
7.34
7.33
2.80
2.78
2.76
1.74
1.72
1.70
1.68
1.66
1.35
1.33
1.31
1.29
1.28
1.25
0.89
0.88
0.88
0.86
1.00
1.05
1.04
2.20
1.09
8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3
f1 (ppm)
1.00
1.05
1.04
2.20
1.09
2.21
2.20
23.87
3.32
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5
f1 (ppm)

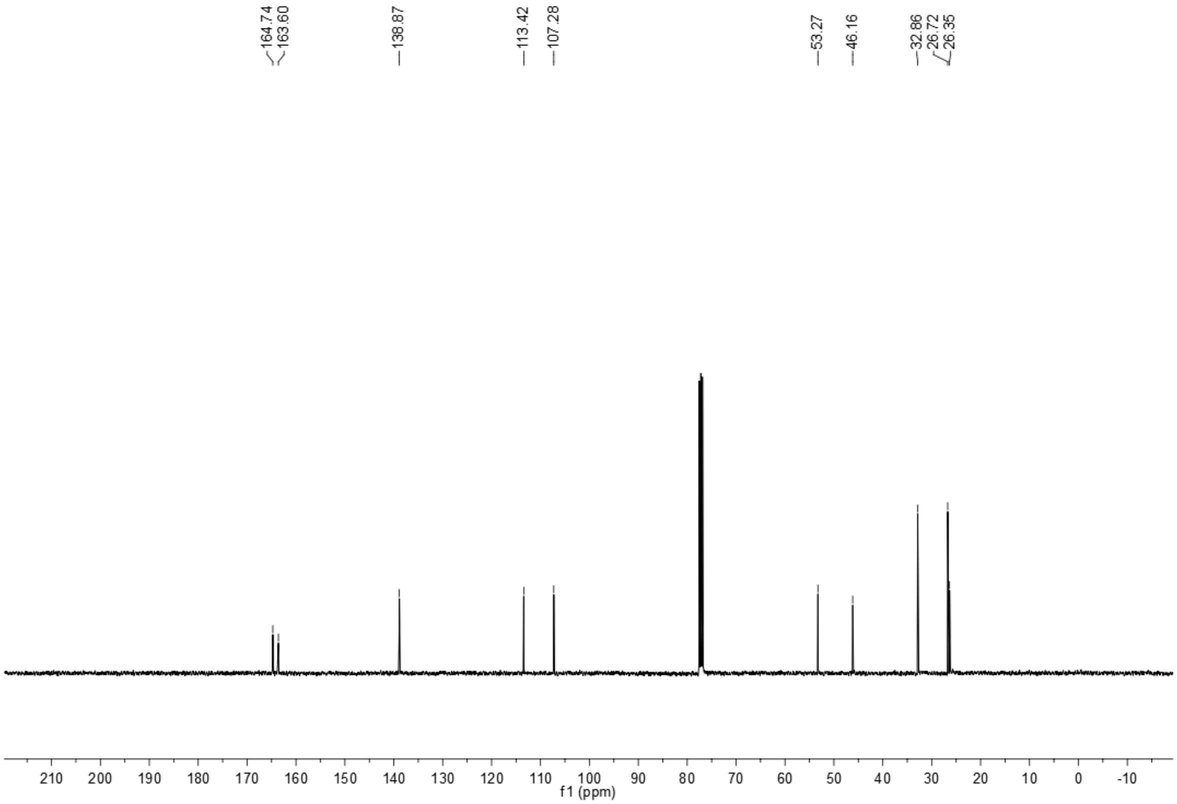
2h

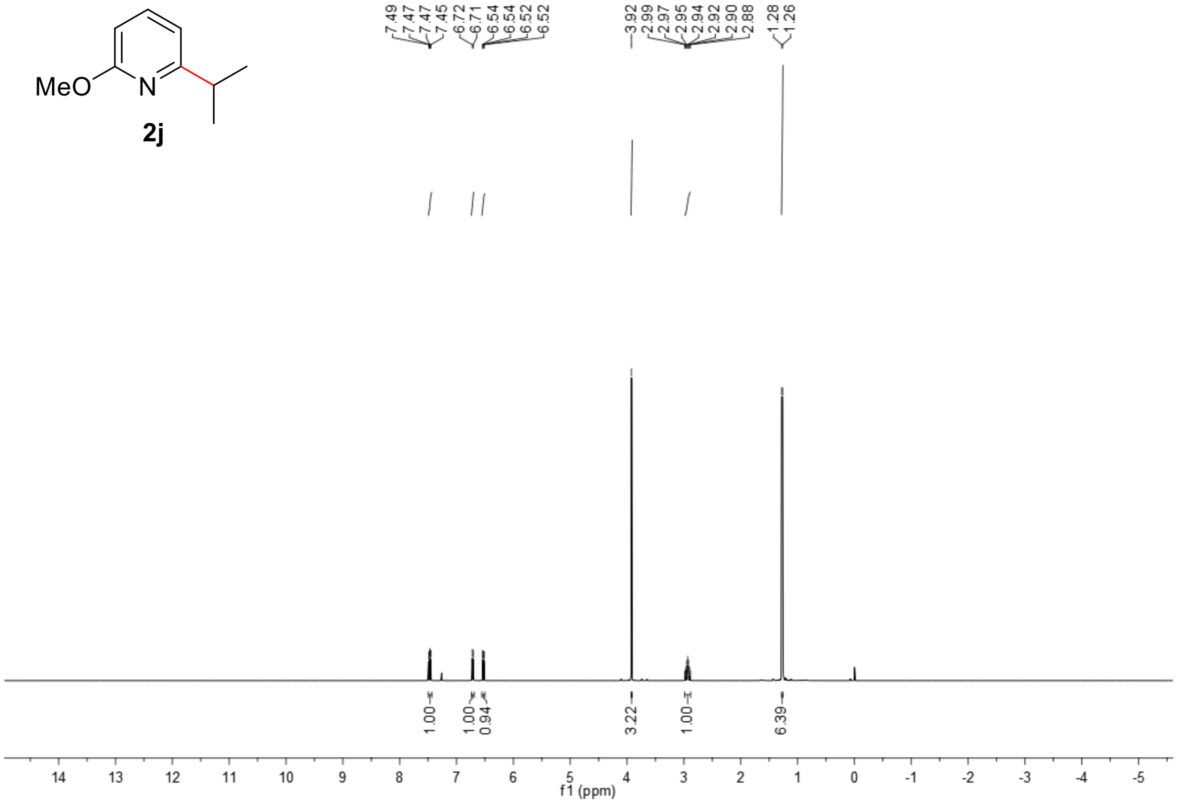

149.70
147.24
141.50
135.67
131.22
129.32
128.46
126.14
121.15
36.08
32.09
31.43
29.83
29.75
29.67
29.53
29.47
22.86
14.30
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


MeO
N

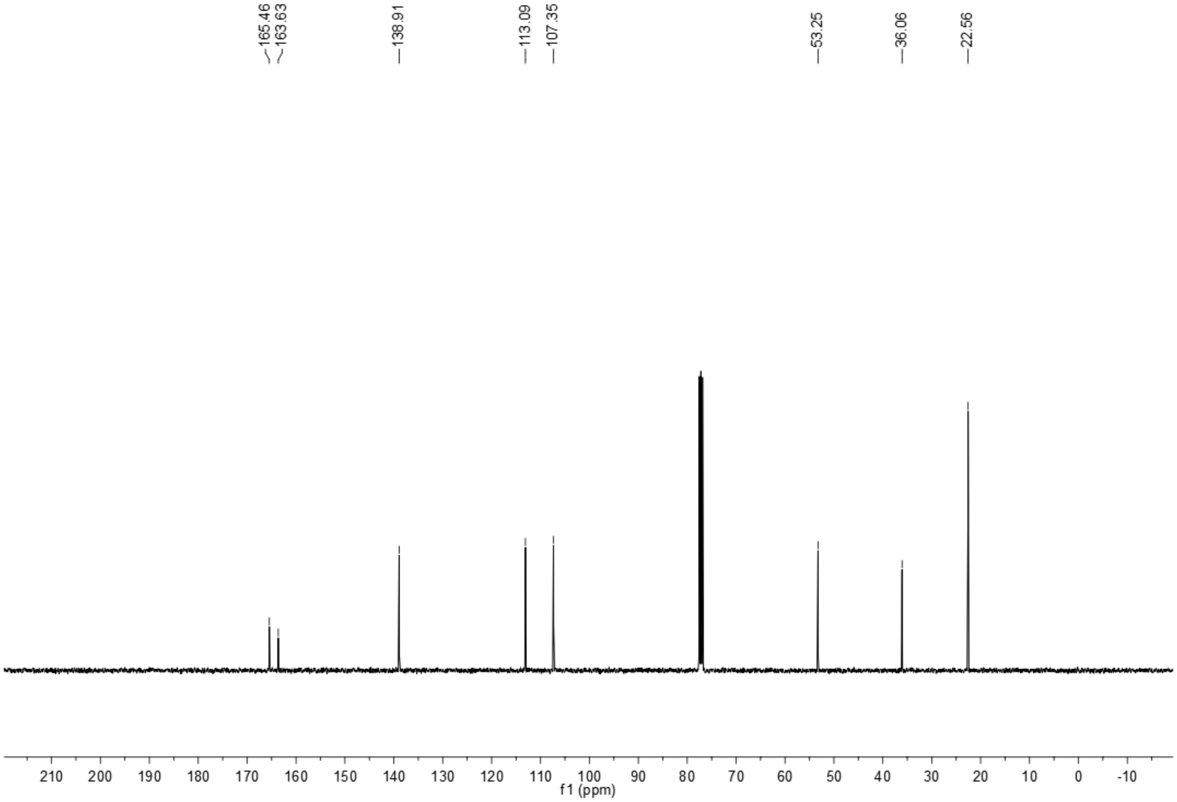
2i

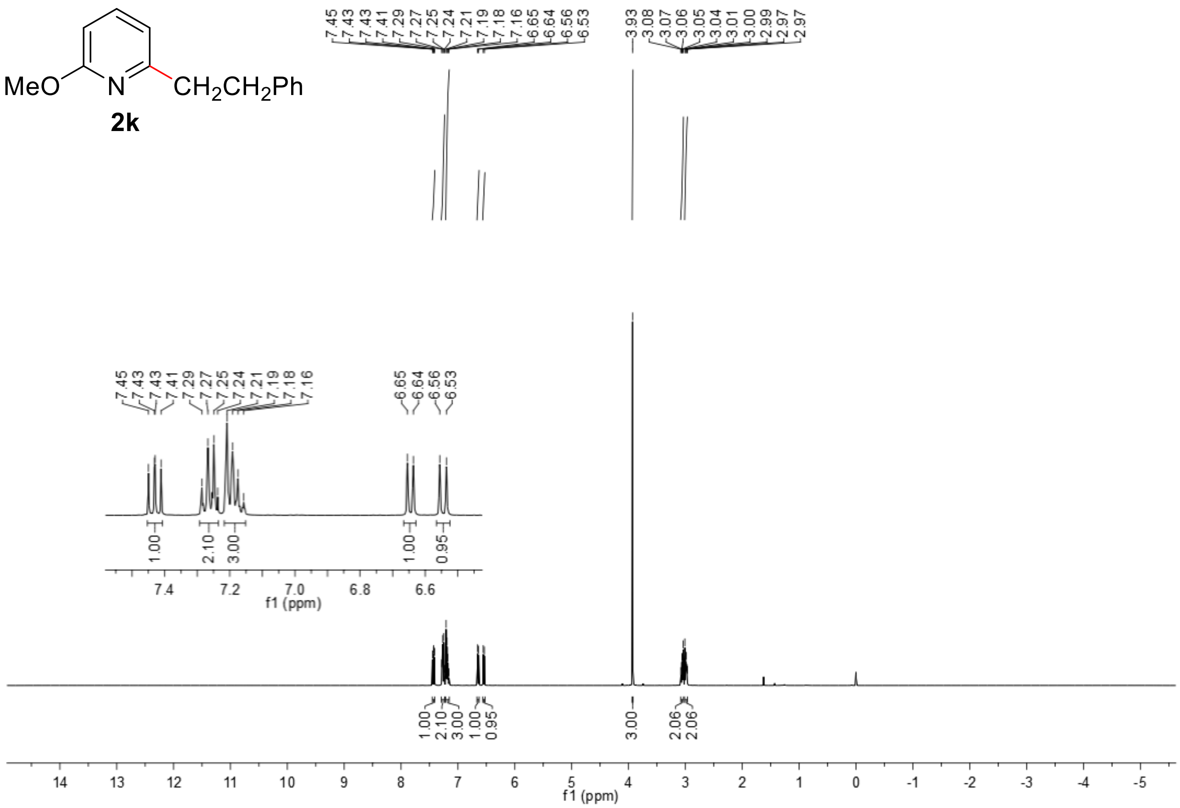

7.49
7.47
7.47
7.45
6.70
6.69
6.53
6.53
6.51
6.51
3.92
2.60
2.58
2.55
1.95
1.92
1.85
1.82
1.76
1.72
1.57
1.53
1.50
1.47
1.44
1.41
1.38
1.34
1.31
1.27
1.24
1.00
1.00
0.93
3.00
1.00
2.08
2.05
1.05
2.17
2.22
1.29
2.6
2.4
2.2
2.0
1.8
1.6
1.4
f1 (ppm)
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
f1 (ppm)


164.74
163.60
138.87
113.42
107.28
53.27
46.16
32.86
26.72
26.35
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

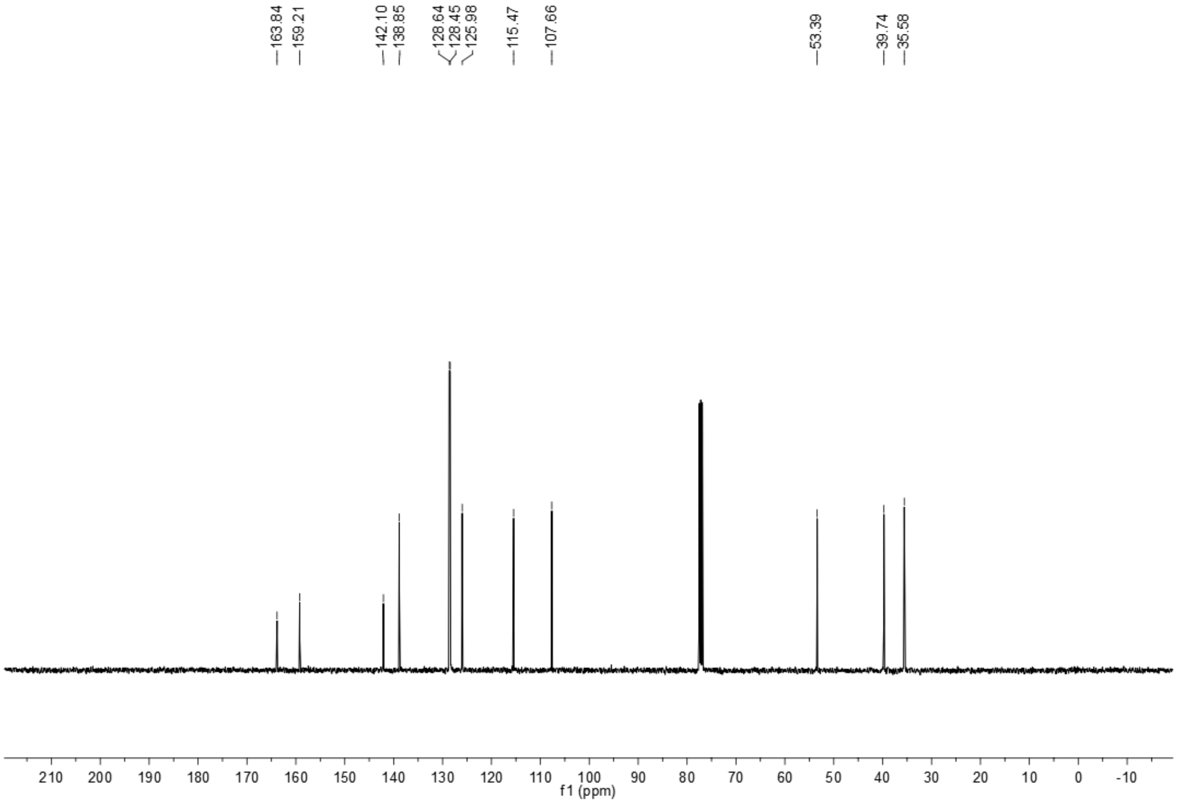

MeO
N
7.49
7.47
7.47
7.45
6.72
6.71
6.54
6.54
6.52
6.52
3.92
2.99
2.97
2.95
2.94
2.92
2.90
2.88
1.28
1.26
1.00
1.00
0.94
3.22
1.00
6.39
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
f1 (ppm)

2j

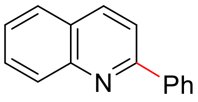

165.46
163.63
138.91
113.09
107.35
53.25
36.06
22.56
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


2k

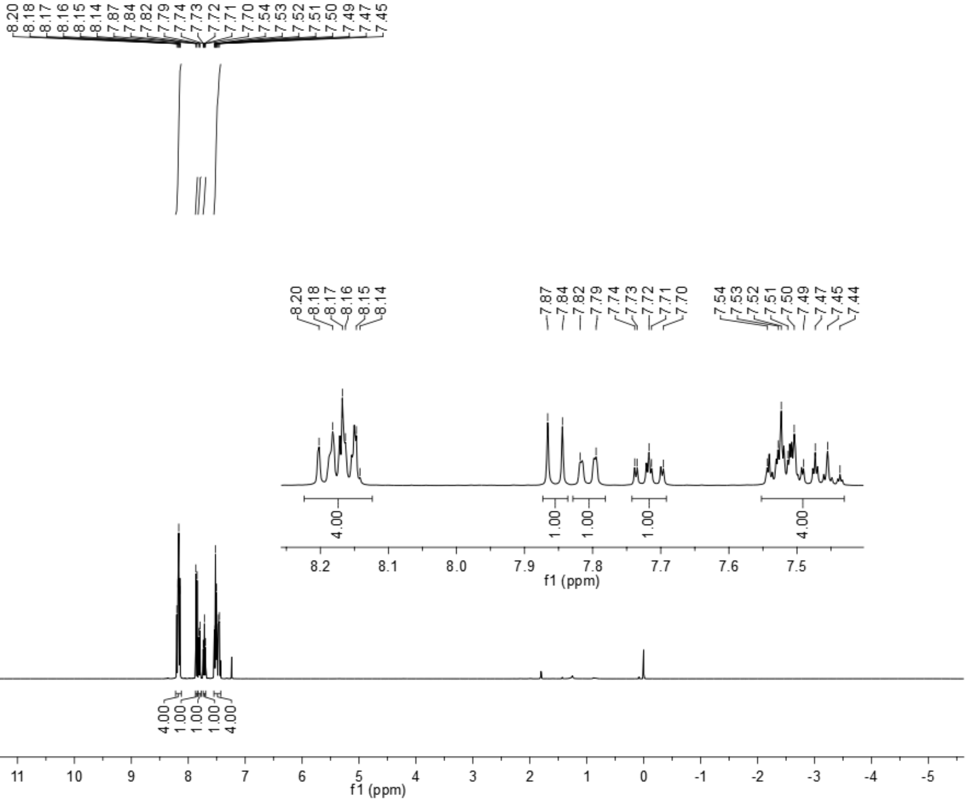
MeO
N
CH₂CH₂Ph
7.45
7.43
7.43
7.41
7.29
7.27
7.25
7.24
7.21
7.19
7.18
7.16
6.65
6.64
6.56
6.53
3.93
3.08
3.07
3.06
3.05
3.04
3.01
3.00
2.99
2.97
2.97
1.00
2.10
3.00
1.00
0.95
7.4
7.2
7.0
6.8
6.6
f1 (ppm)
1.00
2.10
3.00
1.00
0.95
3.00
2.06
2.06
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
f1 (ppm)

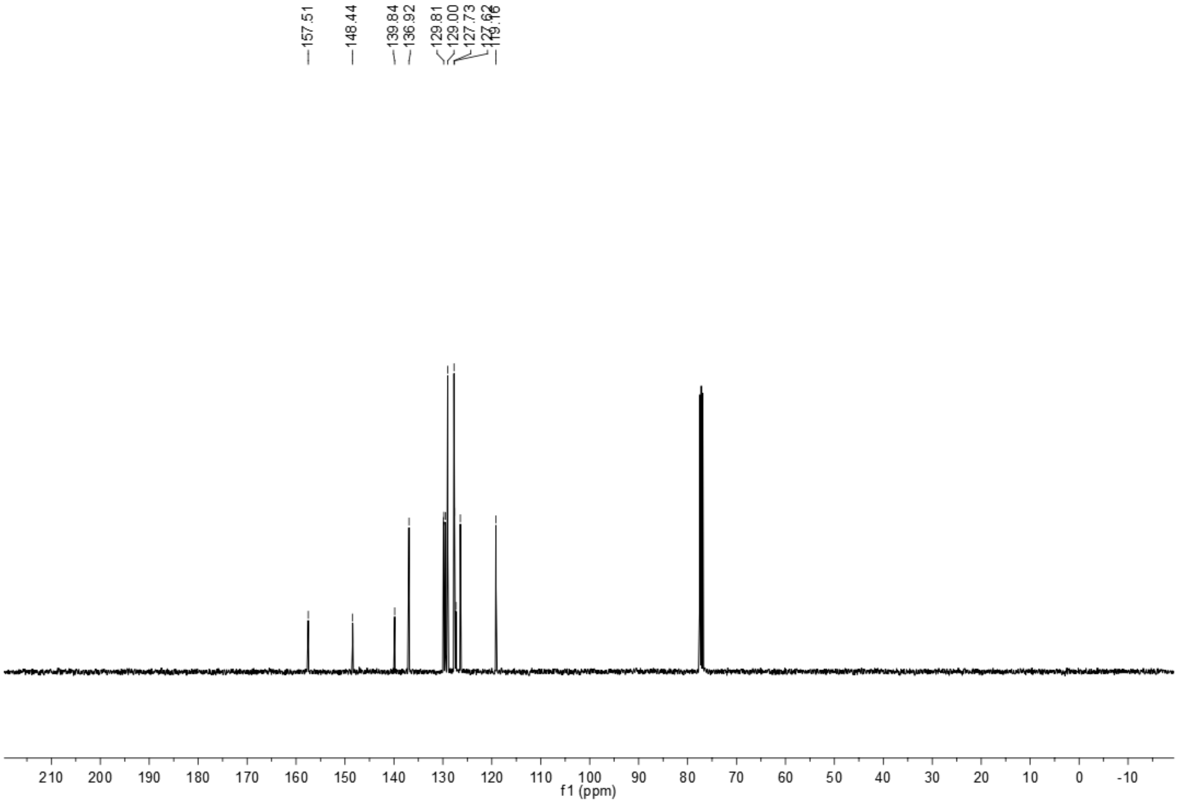


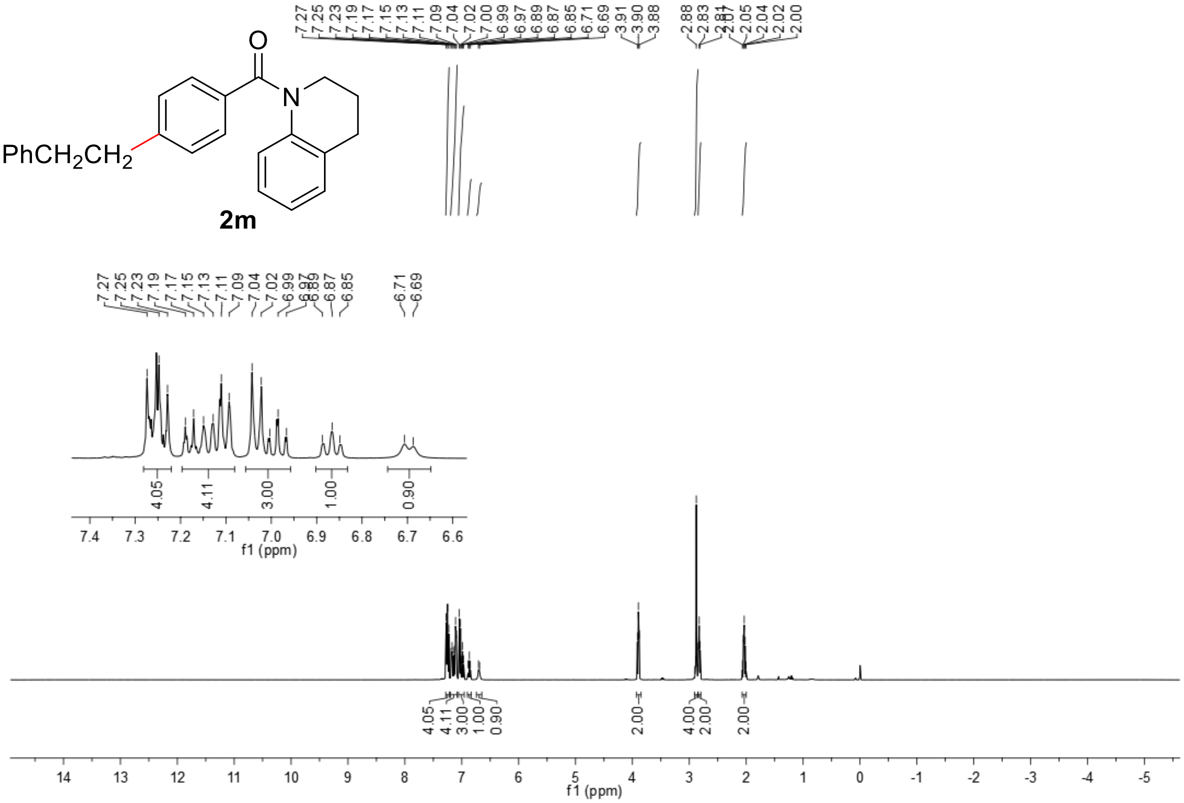
163.84
159.21
142.10
138.85
128.64
128.45
125.98
115.47
107.66
53.39
39.74
35.58
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


N
Ph

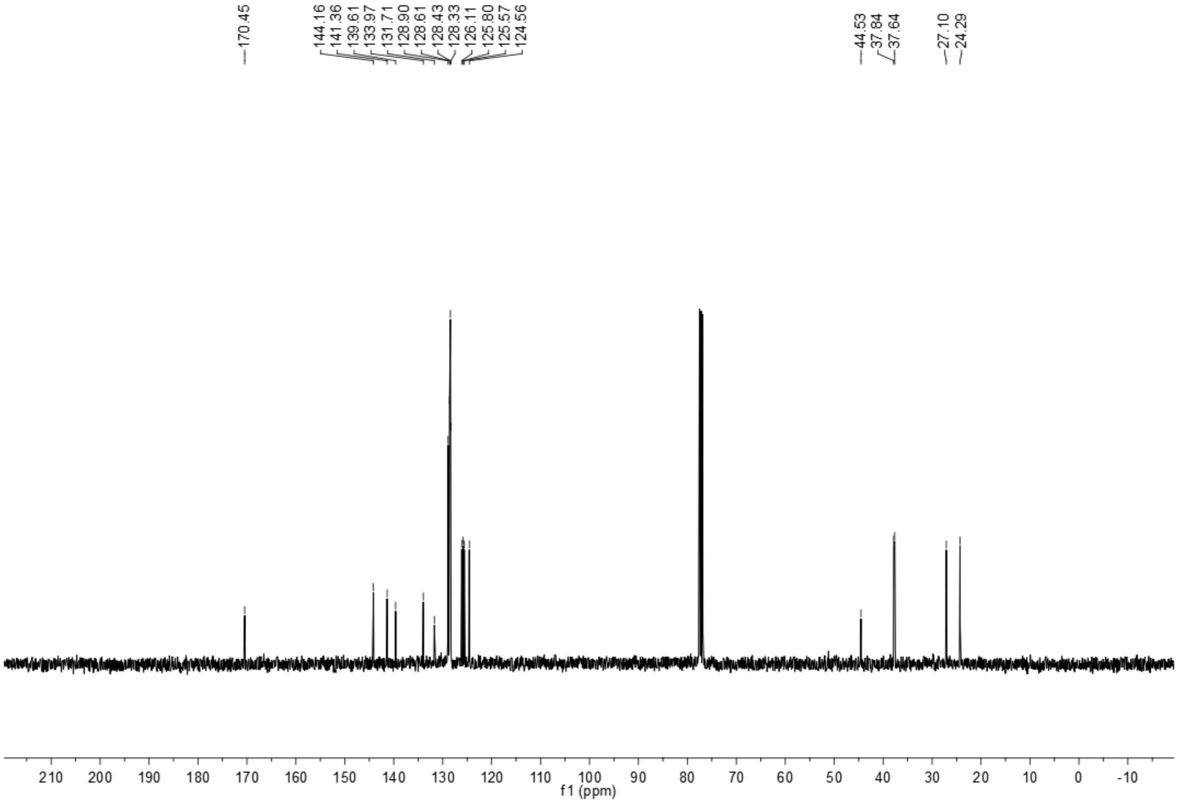
2l

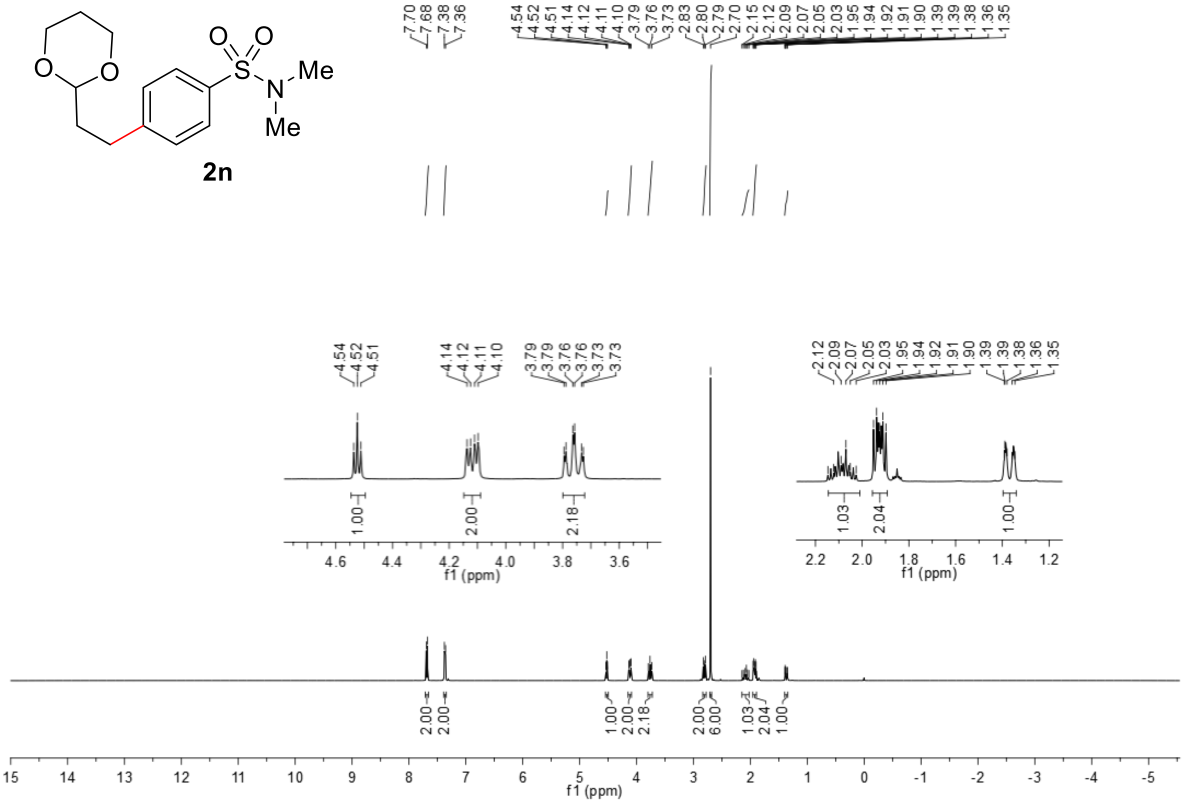

8.20
8.18
8.17
8.16
8.15
8.14
7.87
7.84
7.82
7.79
7.74
7.73
7.72
7.71
7.70
7.54
7.53
7.52
7.51
7.50
7.49
7.47
7.45
8.20
8.18
8.17
8.16
8.15
8.14
7.87
7.84
7.82
7.79
7.74
7.73
7.72
7.71
7.70
7.54
7.53
7.52
7.51
7.50
7.49
7.47
7.45
7.44
4.00
1.00
1.00
1.00
4.00
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
f1 (ppm)
4.00
1.00
1.00
1.00
4.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
f1 (ppm)


157.51
148.44
139.84
136.92
129.81
129.00
127.73
127.62
119.16
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


PhCH$_2$CH$_2$
O
N
7.27
7.25
7.23
7.19
7.17
7.15
7.13
7.11
7.09
7.04
7.02
7.00
6.99
6.97
6.89
6.87
6.85
6.71
6.69
3.91
3.90
3.88
2.88
2.83
2.81
2.07
2.05
2.04
2.02
2.00
4.05
4.11
3.00
1.00
0.90
7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6
f1 (ppm)
2.00
4.00
2.00
2.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5
f1 (ppm)

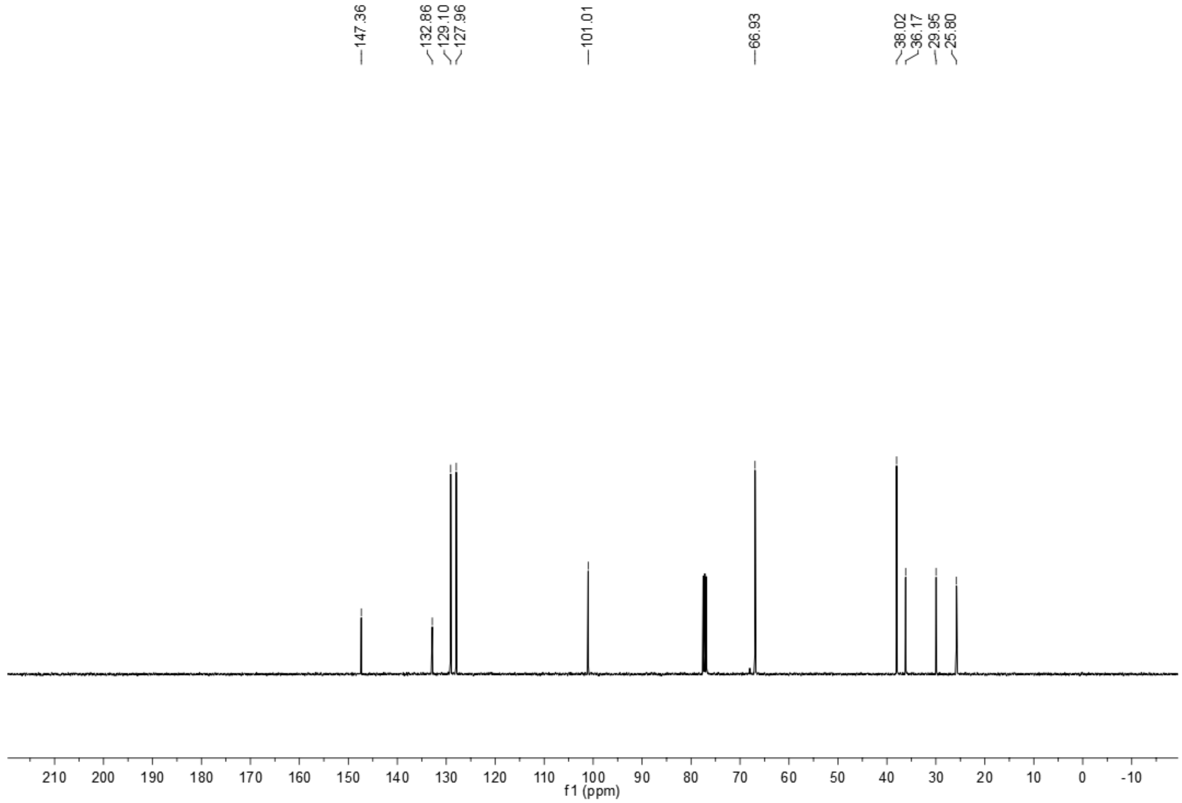
2m


170.45
144.16
141.36
139.61
133.97
131.71
128.90
128.61
128.43
128.33
126.11
125.80
125.57
124.56
44.53
37.84
37.64
27.10
24.29
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

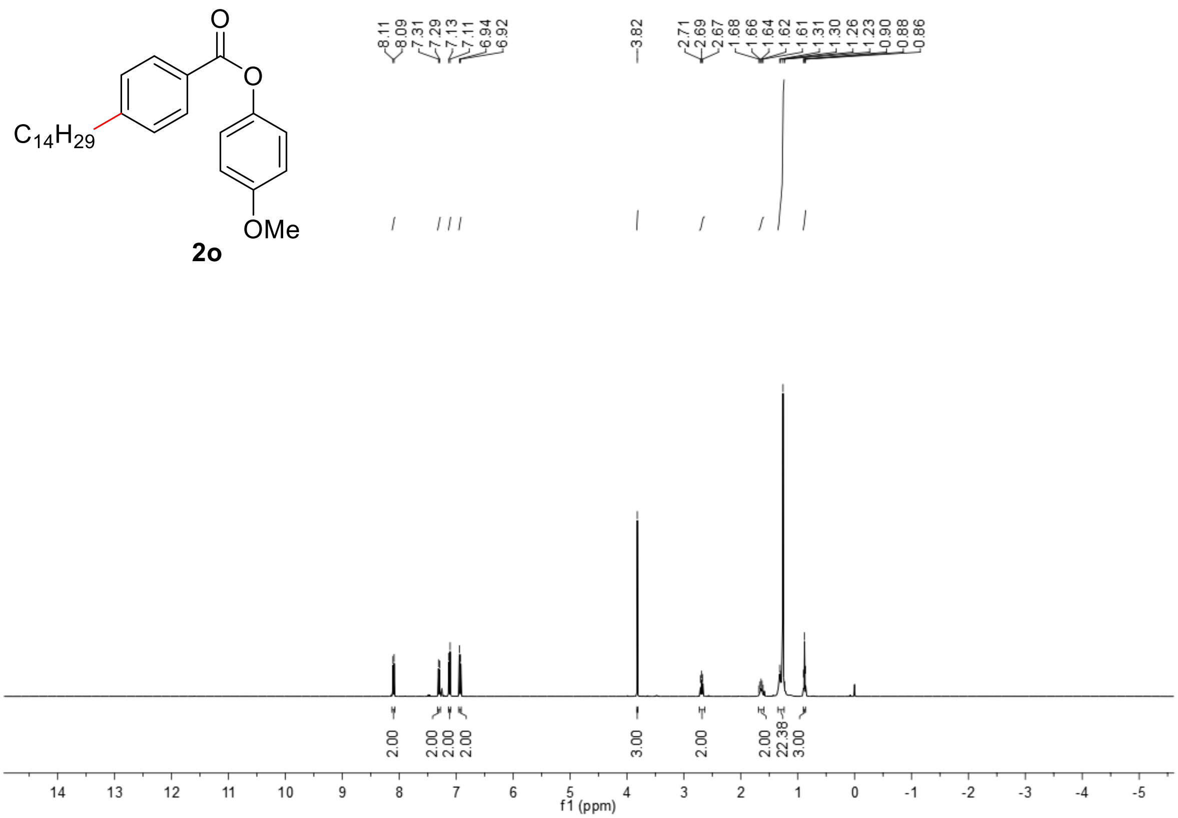


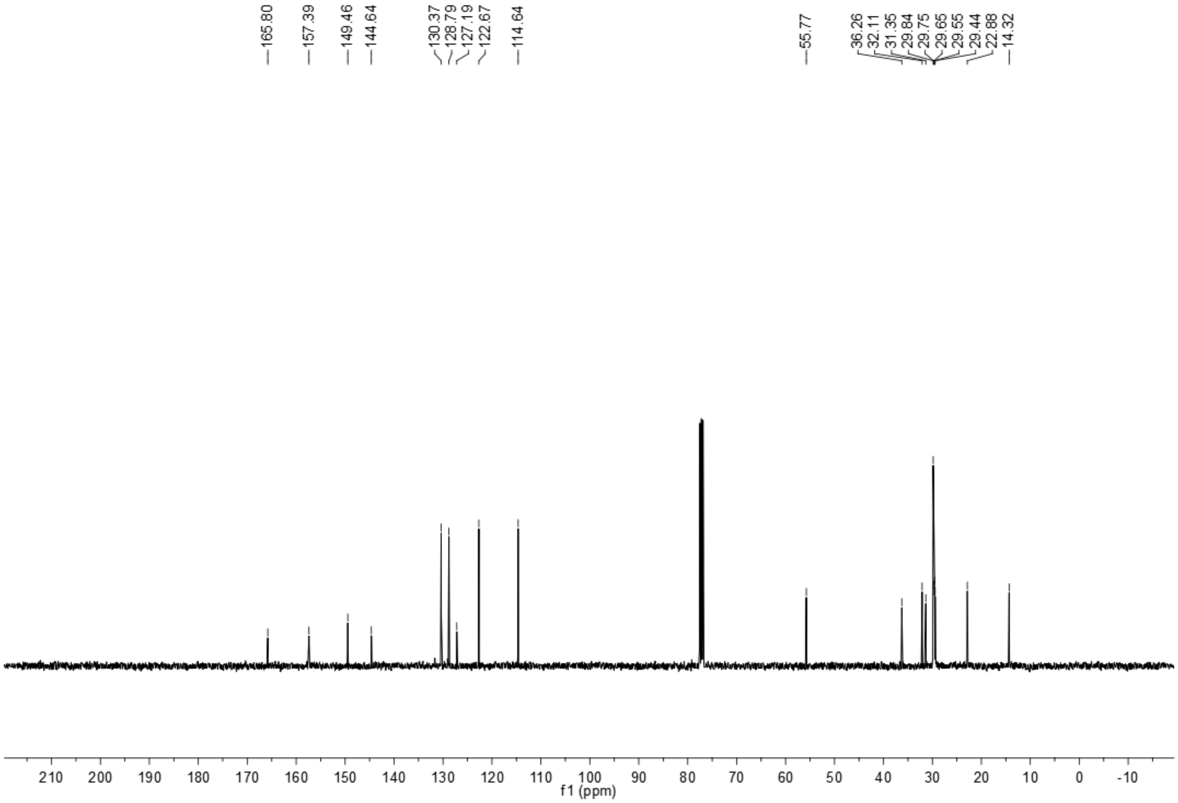
2n

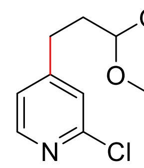
O
O
O
O
S
N
Me
Me
7.70 7.68 7.38 7.36 4.54 4.52 4.51 4.14 4.12 4.11 4.10 3.79 3.76 3.73 2.83 2.80 2.79 2.70 2.15 2.12 2.09 2.07 2.05 2.03 1.95 1.94 1.92 1.91 1.90 1.39 1.39 1.38 1.36 1.35
4.54 4.52 4.51 4.14 4.12 4.11 4.10 3.79 3.79 3.76 3.76 3.73 3.73
1.00 2.00 2.18
4.6 4.4 4.2 4.0 3.8 3.6
f1 (ppm)
2.12 2.09 2.07 2.05 2.03 1.95 1.94 1.92 1.91 1.90 1.39 1.39 1.38 1.36 1.35
1.03 2.04 1.00
2.2 2.0 1.8 1.6 1.4 1.2
f1 (ppm)
2.00 2.00 1.00 2.00 2.18 2.00 6.00 1.03 2.04 1.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5
f1 (ppm)



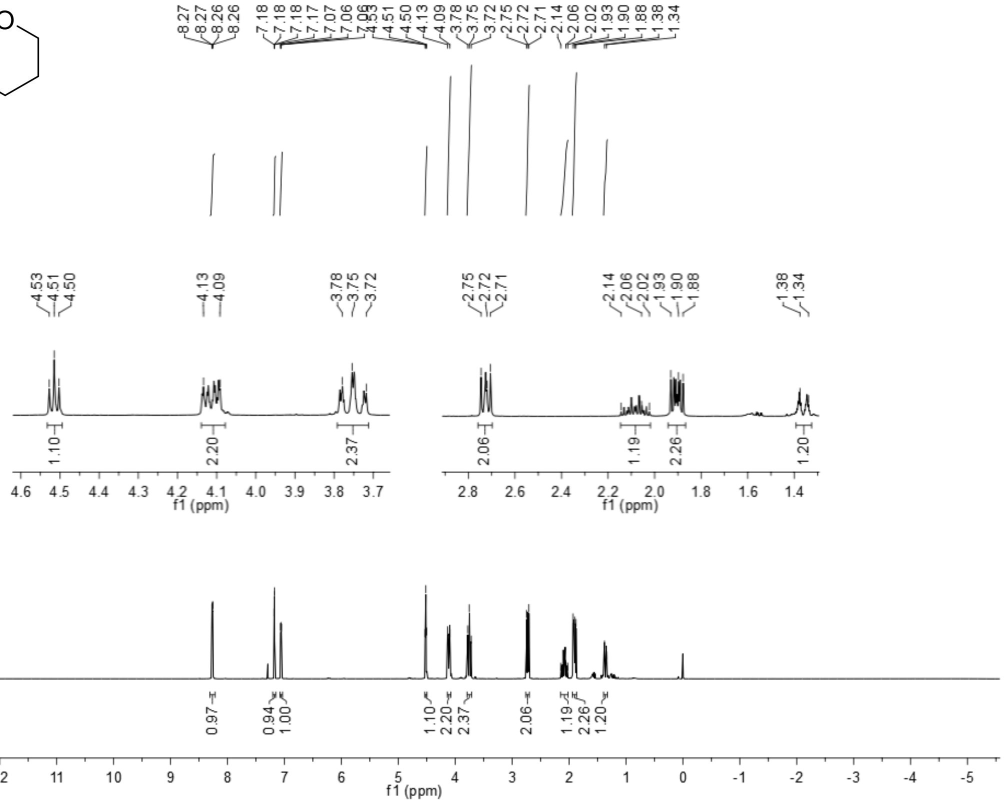
147.36
132.86 129.10 127.96
101.01
66.93
38.02 36.17 29.95 25.80
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


C14H29
O
O
OMe
2o
8.11
8.09
7.31
7.29
7.13
7.11
6.94
6.92
3.82
2.71
2.69
2.67
1.68
1.66
1.64
1.62
1.61
1.30
1.26
1.23
0.90
0.88
0.86
2.00
2.00
2.00
2.00
3.00
2.00
2.00
22.38
3.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
f1 (ppm)

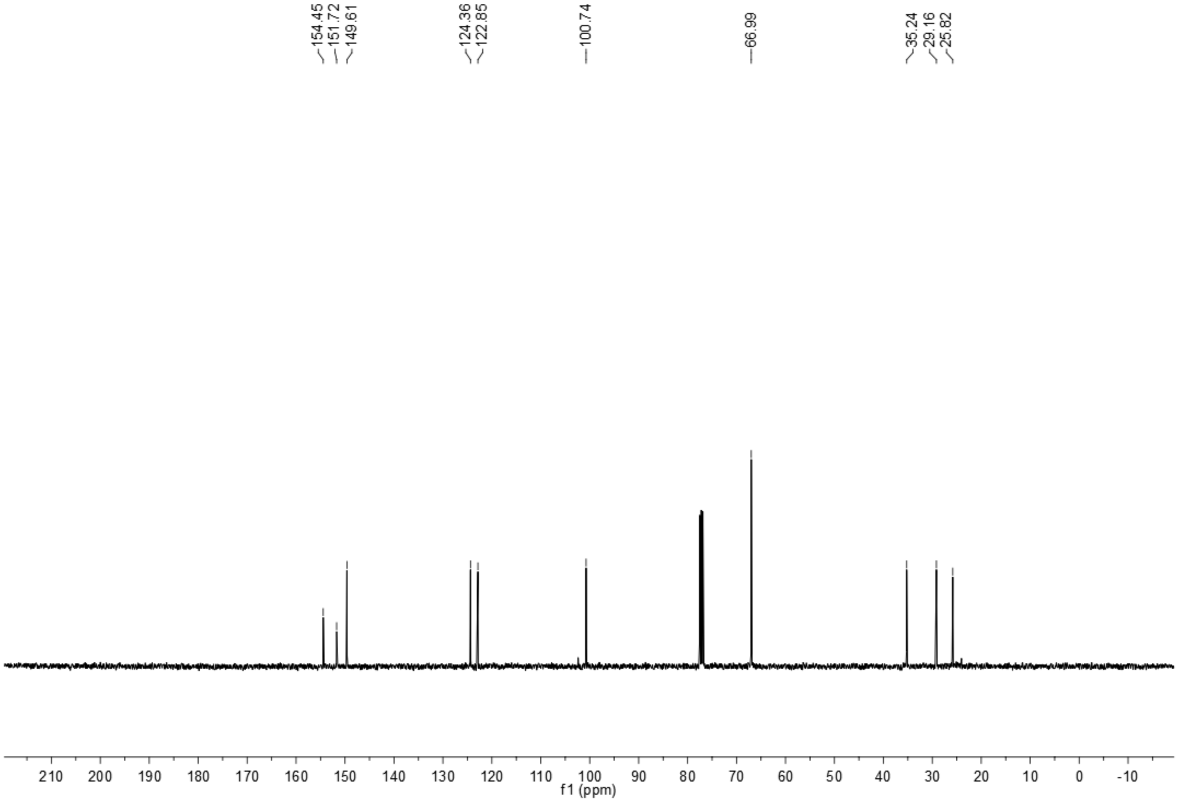

165.80
157.39
149.46
144.64
130.37
128.79
127.19
122.67
114.64
55.77
36.26
32.11
31.35
29.84
29.75
29.65
29.55
29.44
22.88
14.32
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

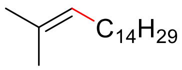

O
O
N
Cl

2p

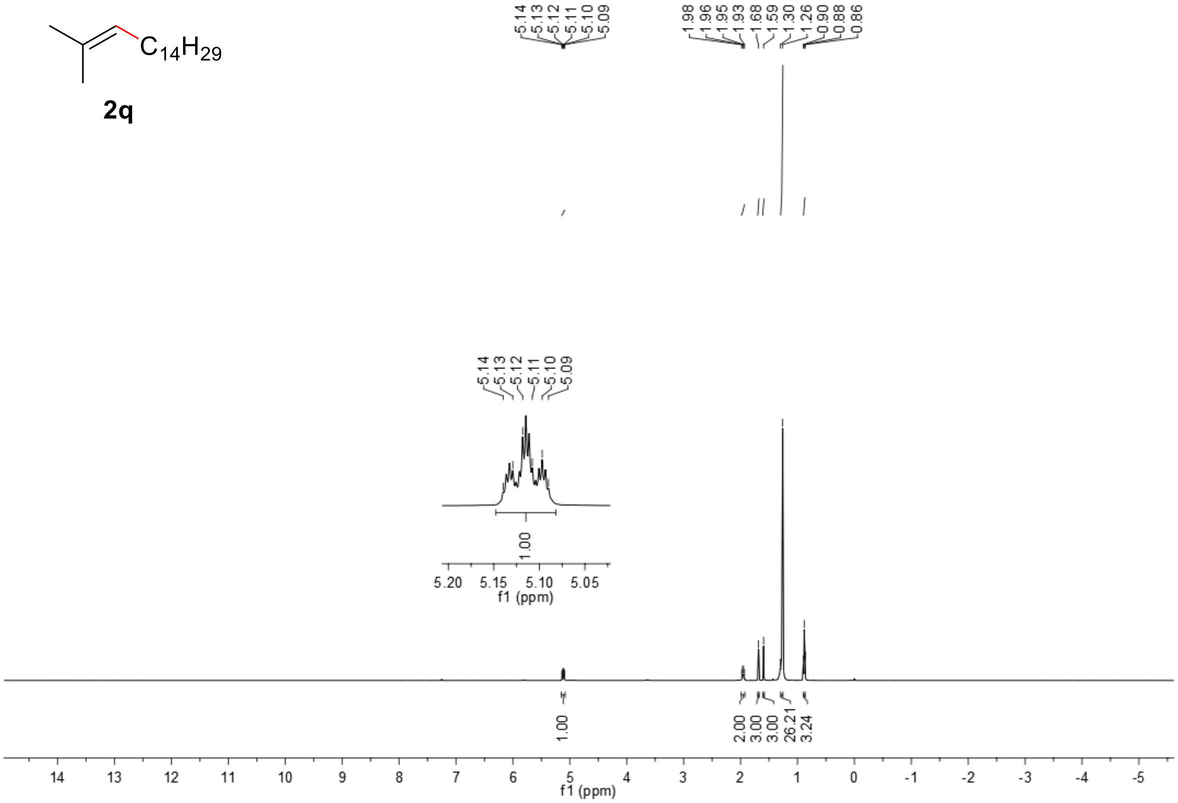

8.27
8.27
8.26
8.26
7.18
7.18
7.18
7.17
7.07
7.06
7.06
4.53
4.51
4.50
4.13
4.09
3.78
3.75
3.72
2.75
2.72
2.71
2.14
2.06
2.02
1.93
1.90
1.88
1.38
1.34
1.10
2.20
2.37
2.06
1.19
2.26
1.20
f1 (ppm)
0.97
0.94
1.00
f1 (ppm)

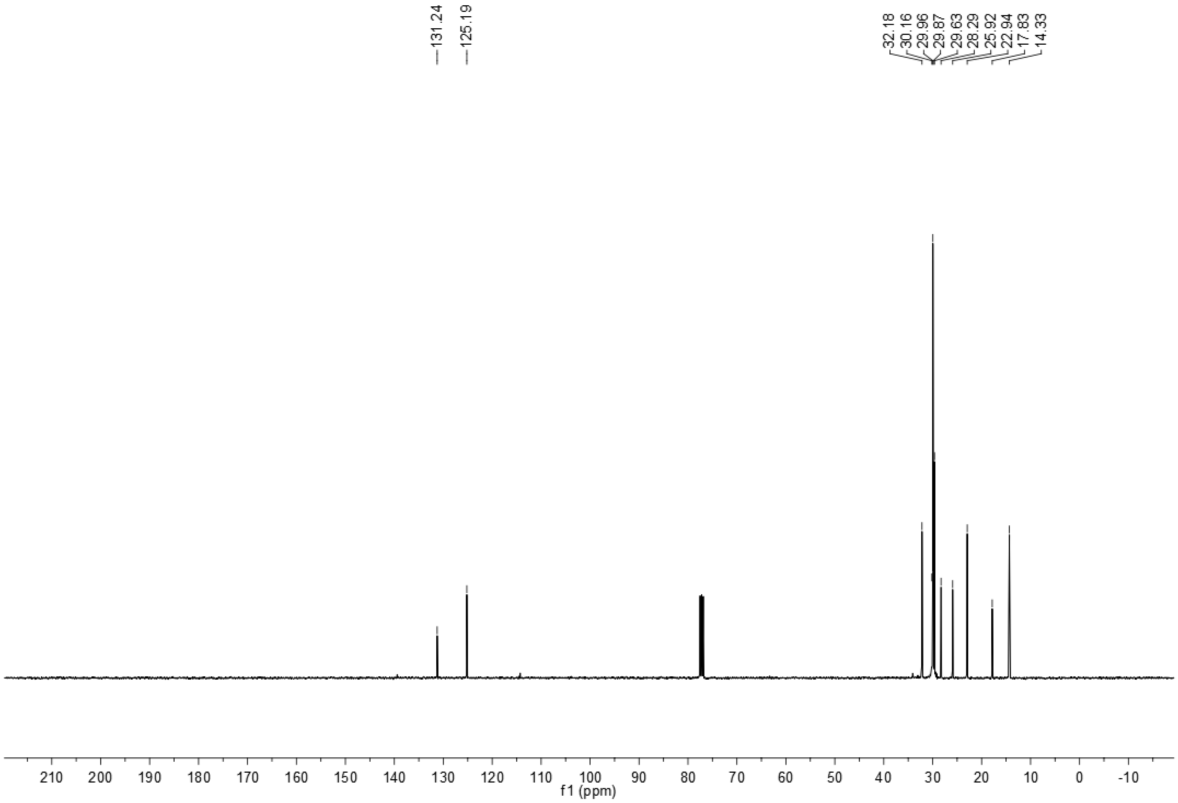
,

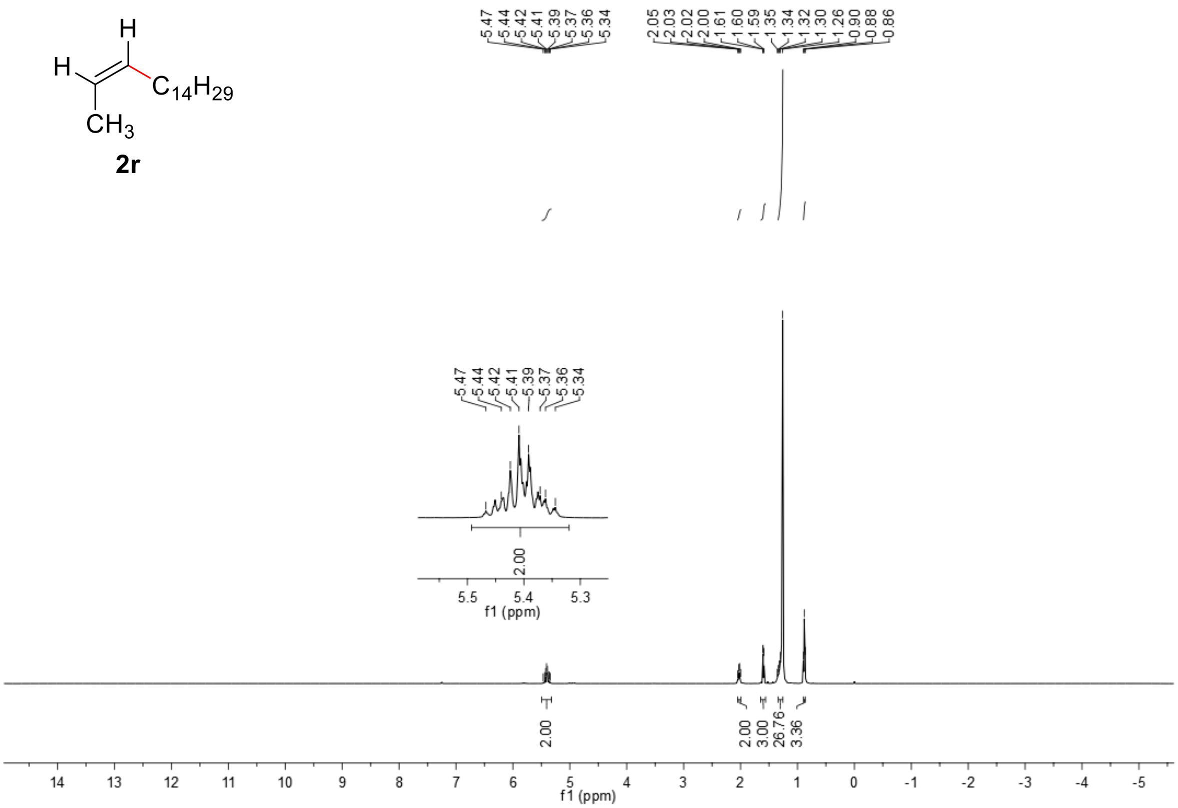

154.45
151.72
149.61
124.36
122.85
100.74
66.99
35.24
29.16
25.82
f1 (ppm)


C14H29

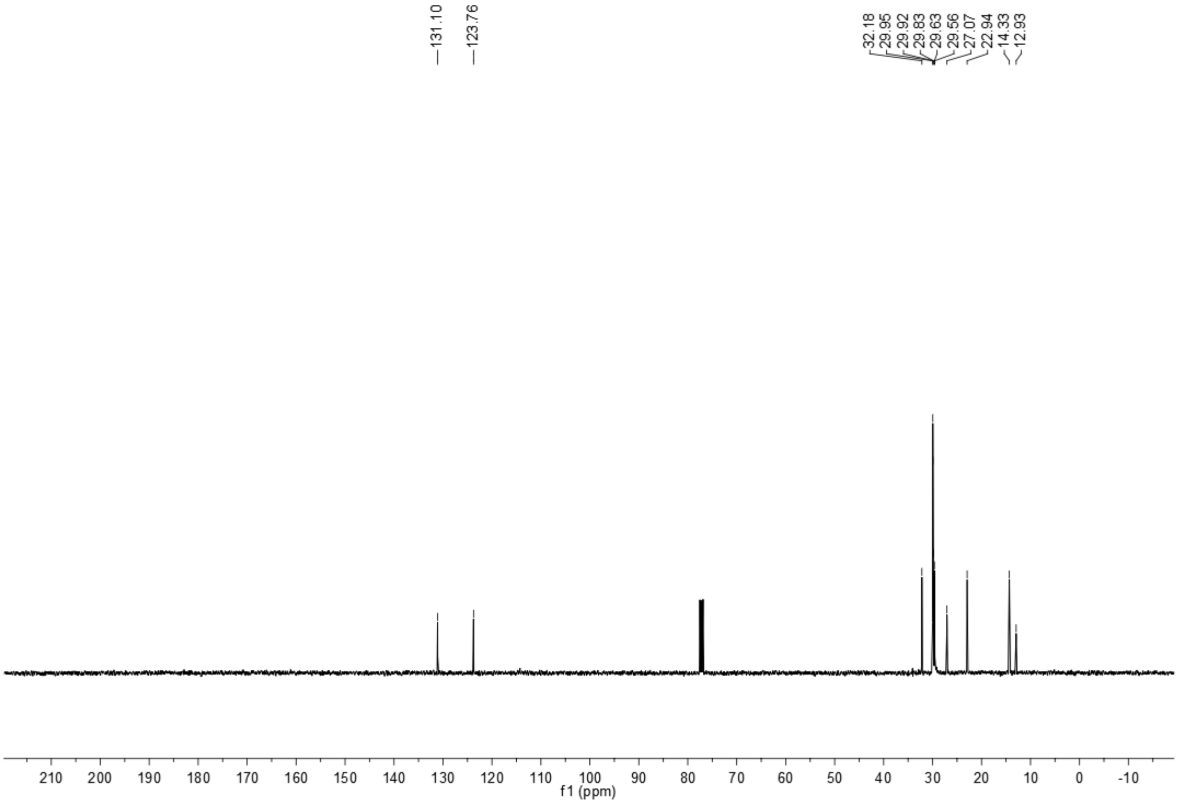
2q

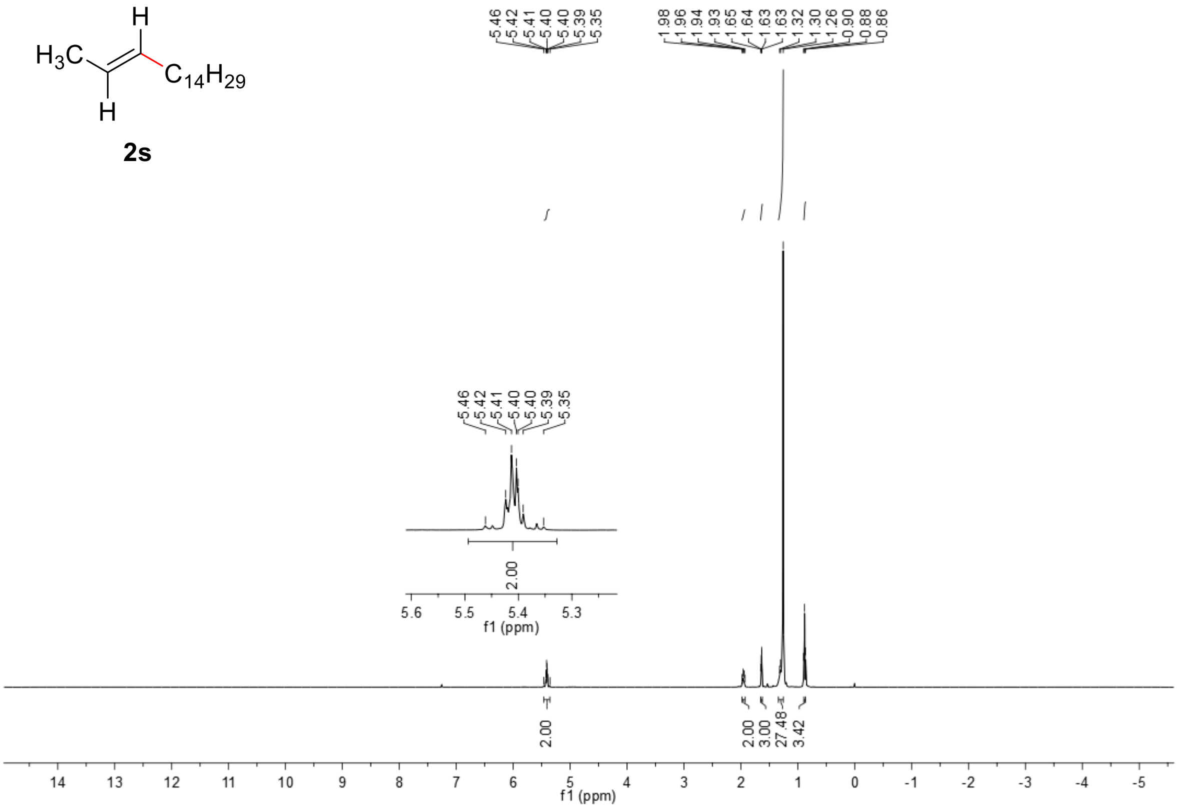

5.14
5.13
5.12
5.11
5.10
5.09
1.98
1.96
1.95
1.93
1.68
1.59
1.30
1.26
0.90
0.88
0.86
1.00
5.20 5.15 5.10 5.05
f1 (ppm)
1.00
2.00
3.00
3.00
26.21
3.24
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5
f1 (ppm)


131.24
125.19
32.18
30.16
29.96
29.87
29.63
28.29
25.92
22.94
17.83
14.33
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


H
H
$C_{14}H_{29}$
CH_3
5.47
5.44
5.42
5.41
5.39
5.37
5.36
5.34
2.05
2.03
2.02
2.00
1.61
1.60
1.59
1.35
1.34
1.32
1.30
1.26
0.90
0.88
0.86
2.00
5.5
5.4
5.3
f1 (ppm)
2.00
2.00
3.00
26.76
3.36
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
f1 (ppm)

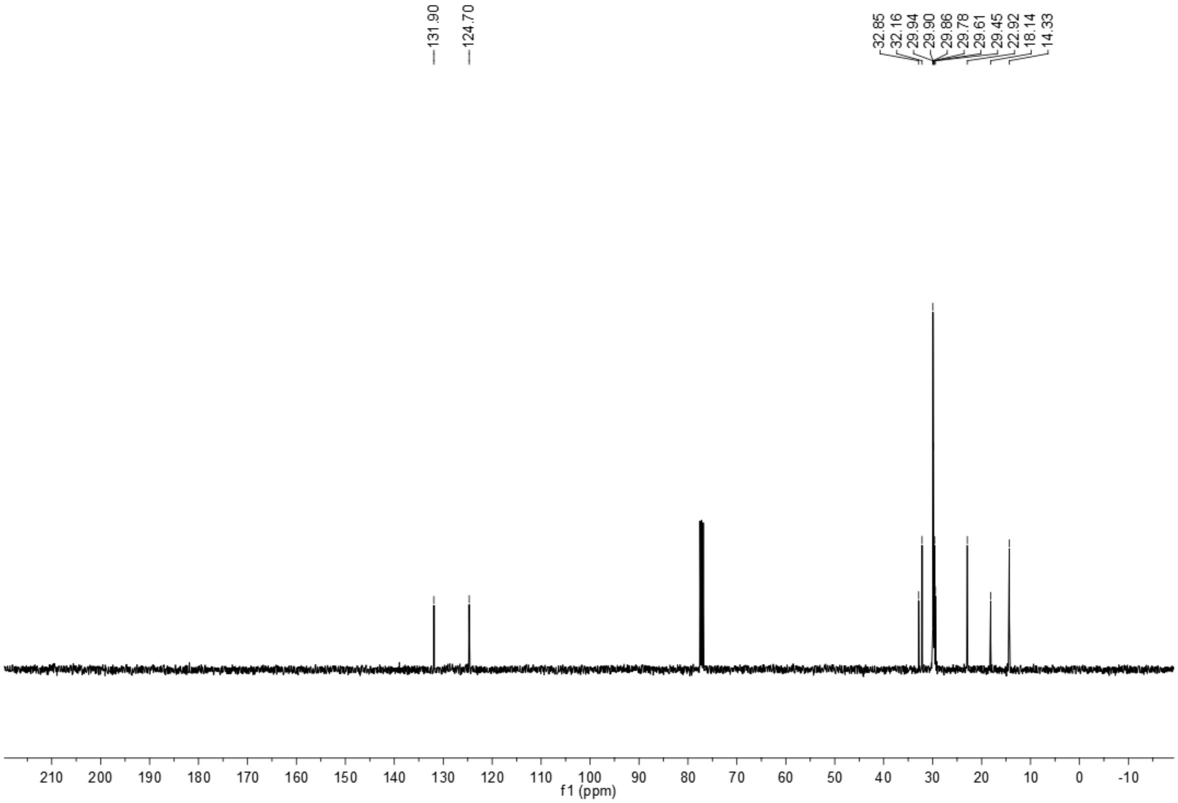
2r


131.10
123.76
32.18
29.95
29.92
29.83
29.63
29.56
27.07
22.94
14.33
12.93
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

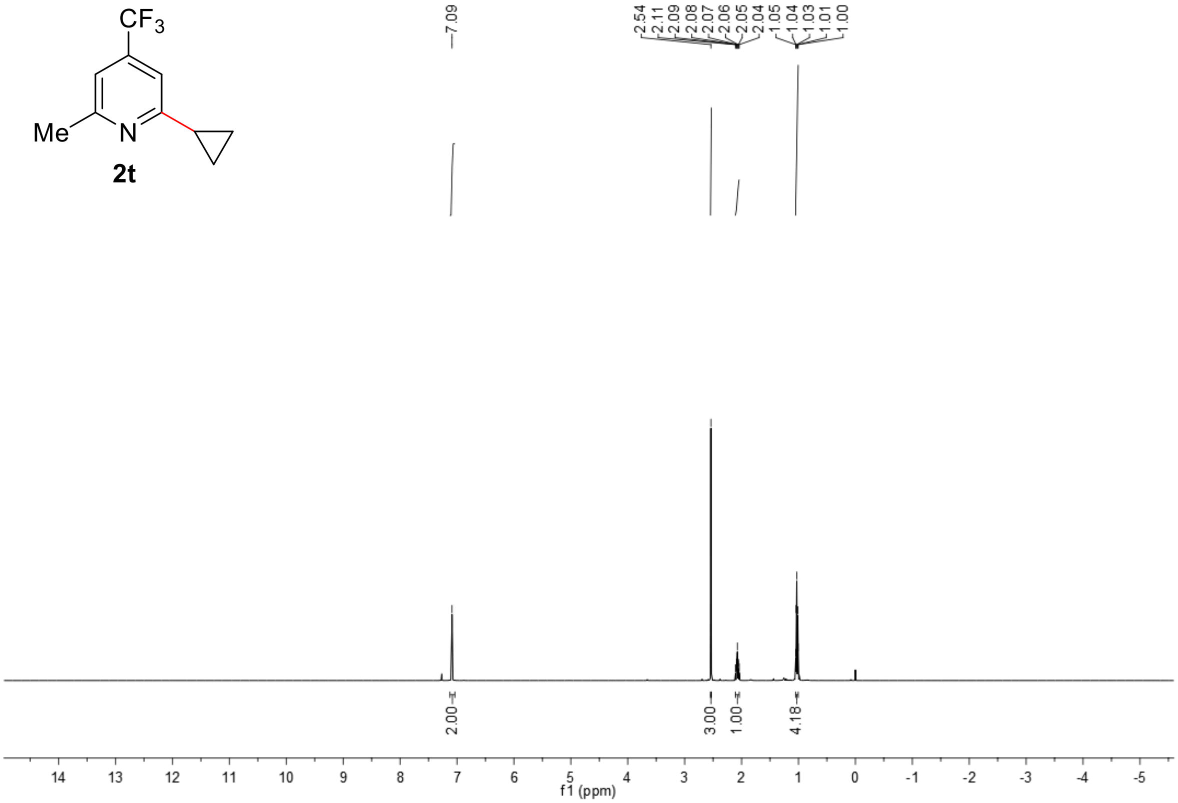


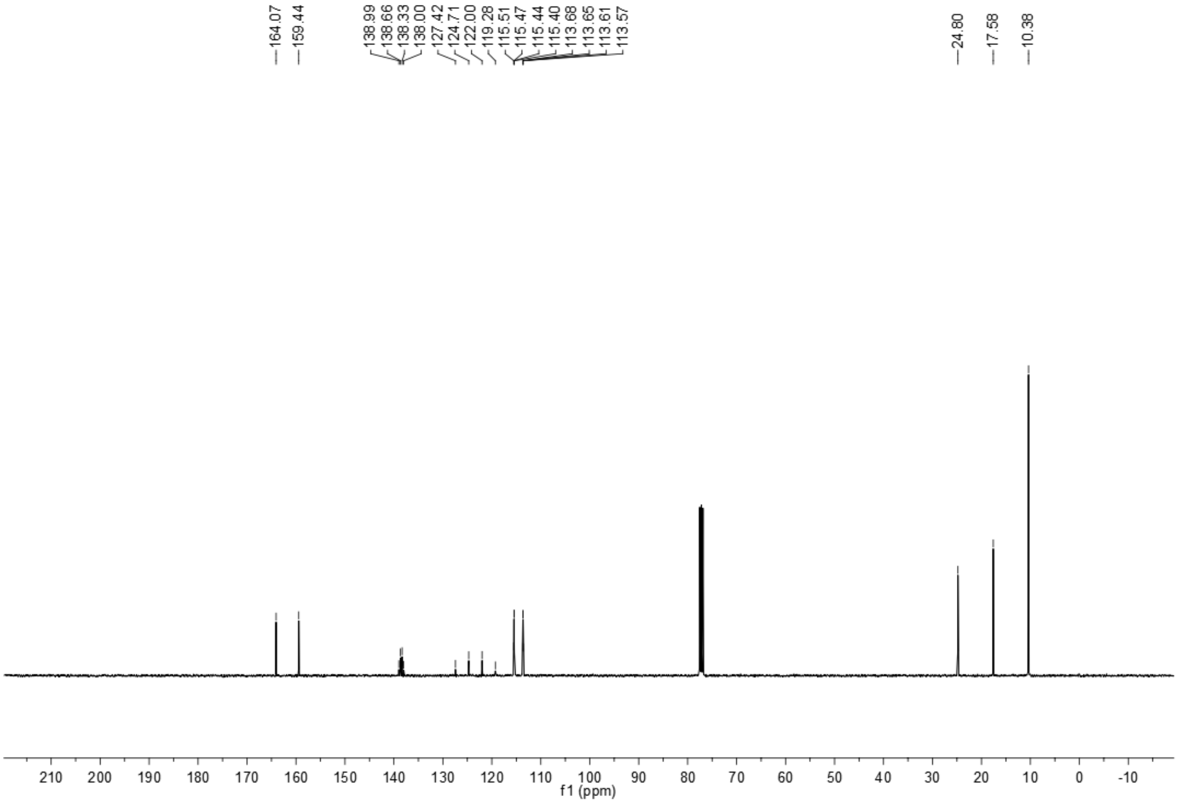
2s

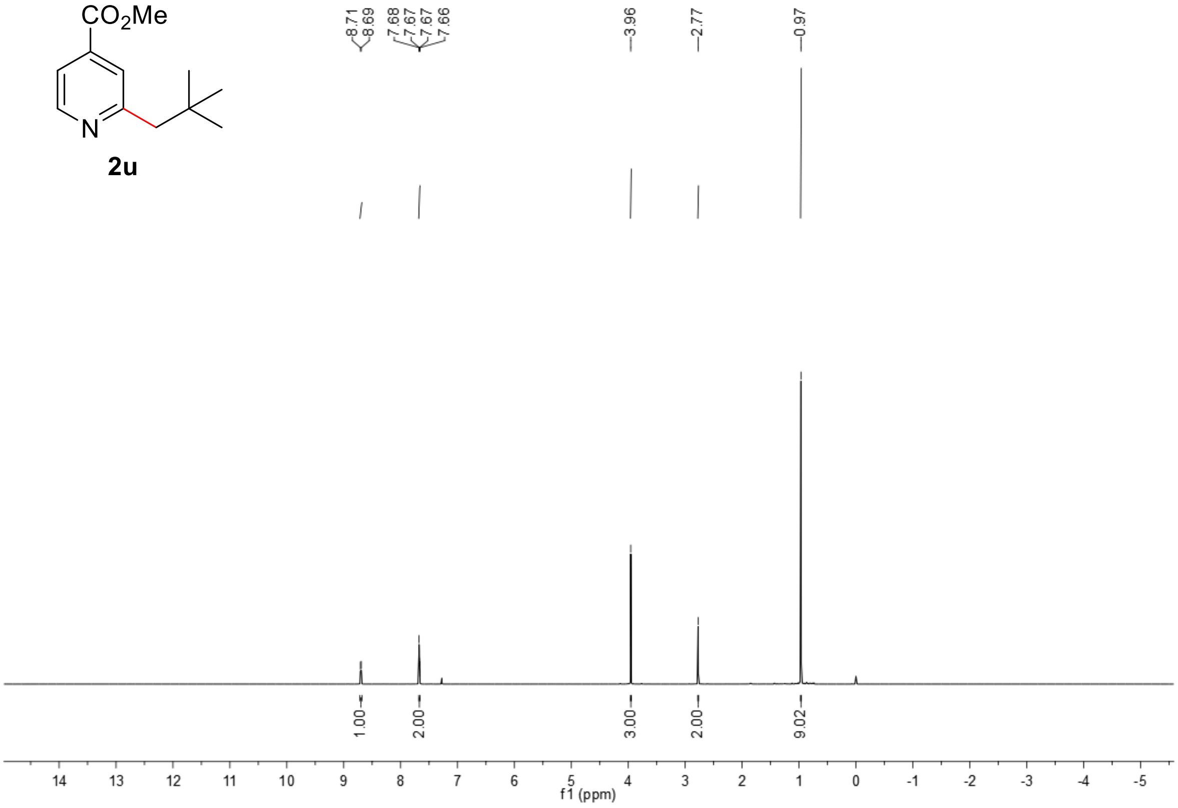
H
H$_3$C
C$_{14}$H$_{29}$
H
5.46
5.42
5.41
5.40
5.40
5.39
5.35
1.98
1.96
1.94
1.93
1.65
1.64
1.63
1.63
1.32
1.30
1.26
0.90
0.88
0.86
2.00
5.6
5.5
5.4
5.3
f1 (ppm)
2.00
2.00
3.00
27.48
3.42
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
f1 (ppm)



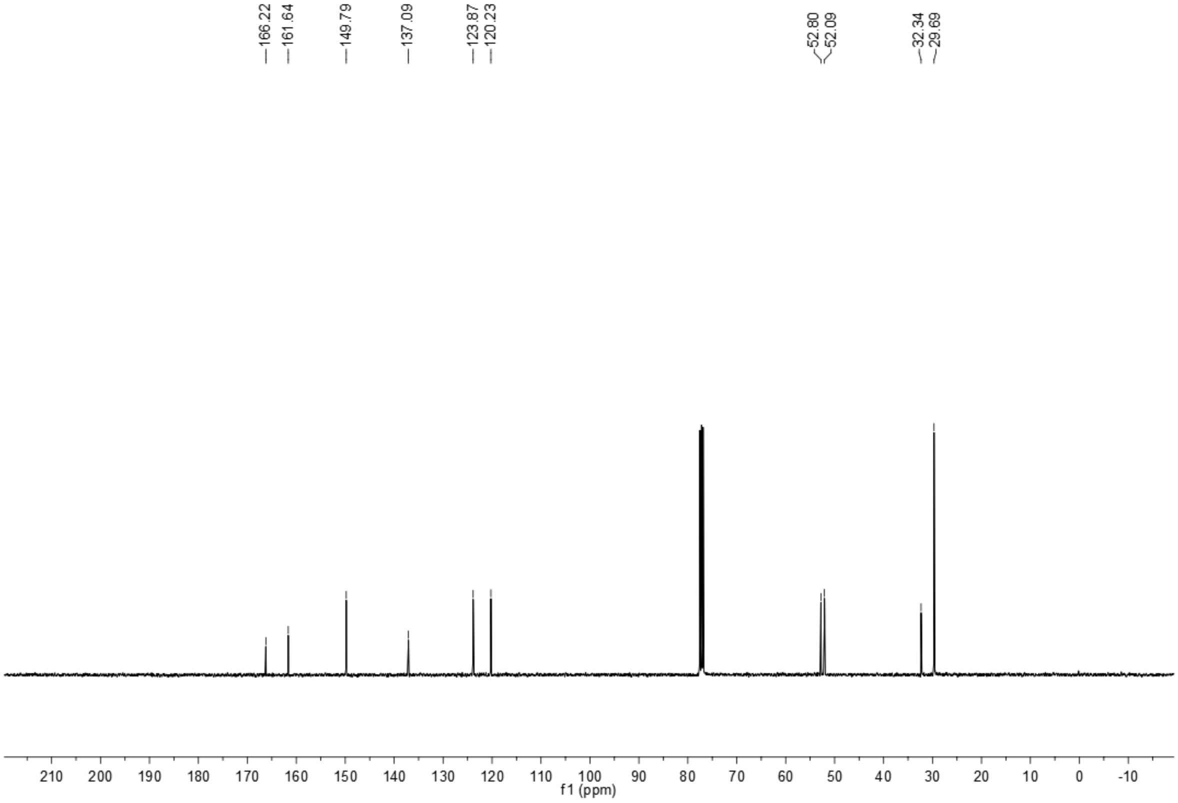
131.90
124.70
32.85
32.16
29.94
29.90
29.86
29.78
29.61
29.45
22.92
18.14
14.33
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

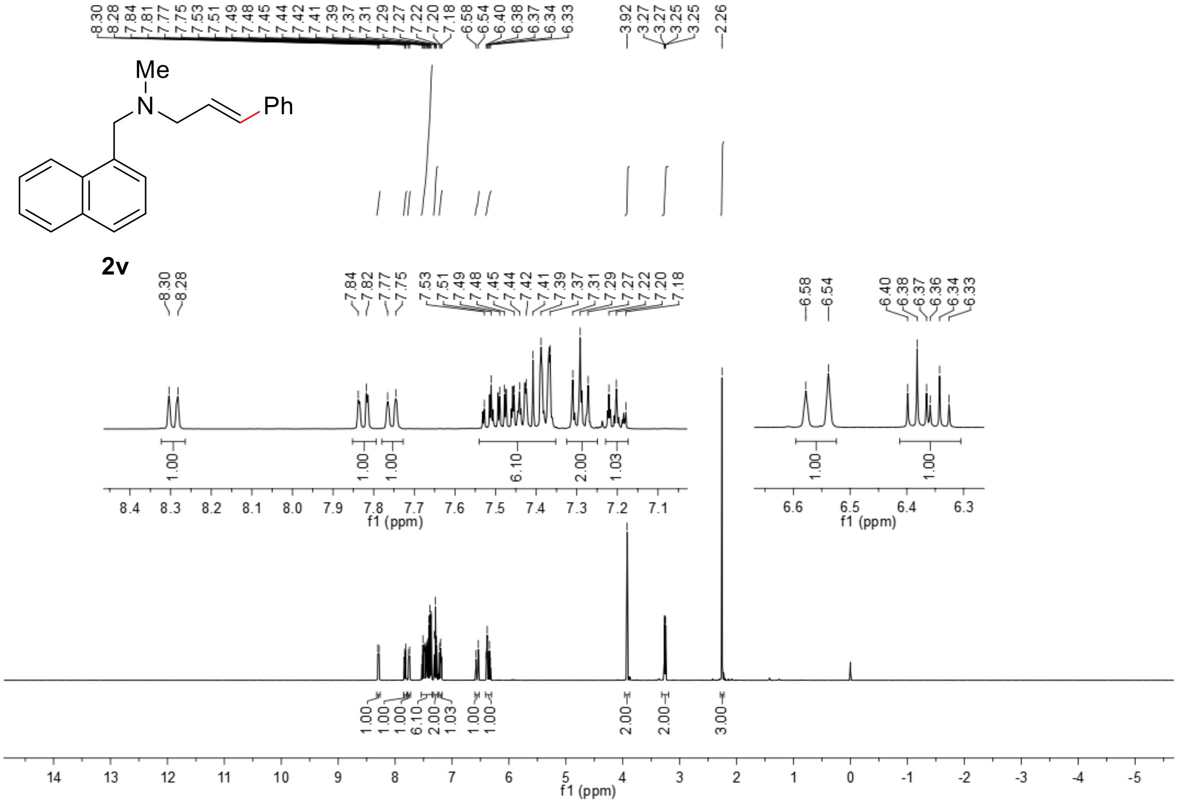

2t
CF3
Me
N
7.09
2.54
2.11
2.09
2.08
2.07
2.06
2.05
2.04
1.05
1.04
1.03
1.01
1.00
2.00
3.00
1.00
4.18
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
f1 (ppm)

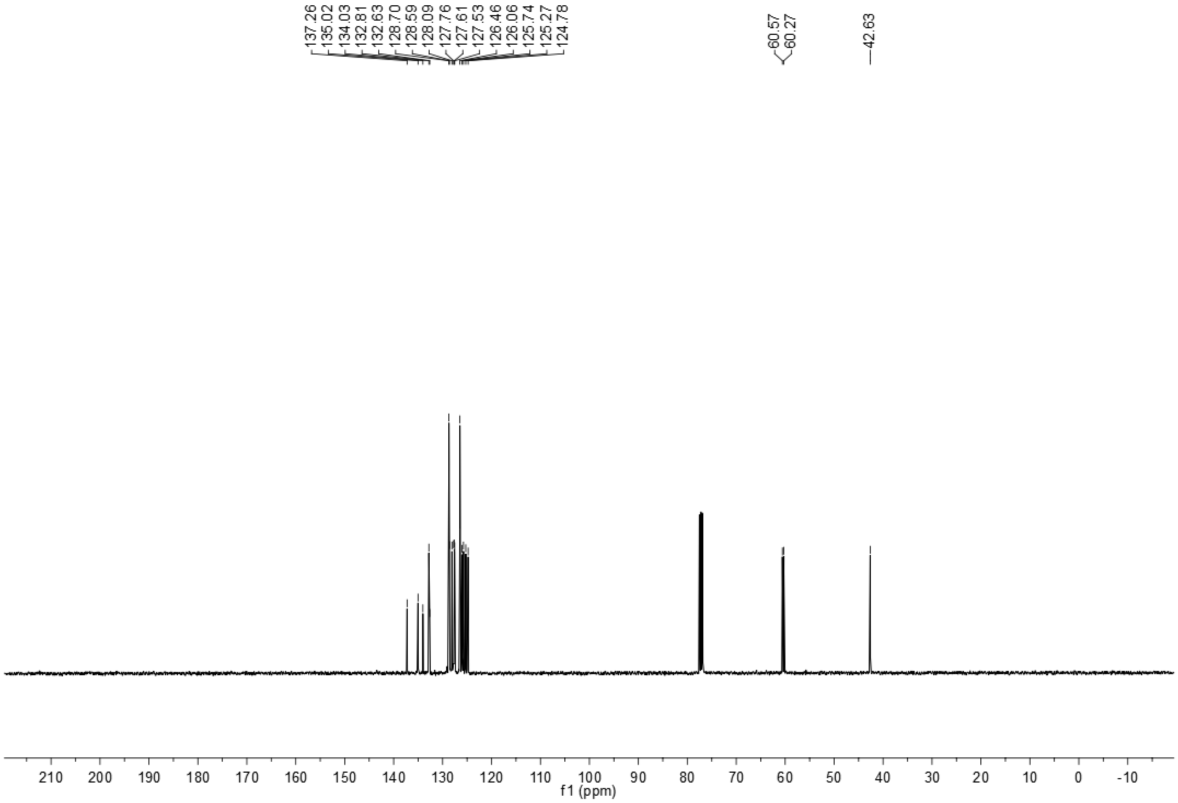

164.07
159.44
138.99
138.66
138.33
138.00
127.42
124.71
122.00
119.28
115.51
115.47
115.44
115.40
113.68
113.65
113.61
113.57
24.80
17.58
10.38
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CO2Me
N
8.71
8.69
7.68
7.67
7.67
7.66
3.96
2.77
0.97
1.00
2.00
3.00
2.00
9.02
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
f1 (ppm)

2u


166.22
161.64
149.79
137.09
123.87
120.23
52.80
52.09
32.34
29.69
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.30
8.28
7.84
7.81
7.77
7.75
7.53
7.51
7.49
7.48
7.45
7.44
7.42
7.41
7.39
7.37
7.31
7.29
7.27
7.22
7.20
7.18
6.58
6.54
6.40
6.38
6.37
6.34
6.33
3.92
3.27
3.27
3.25
3.25
2.26
Me
N
Ph
2v
1.00
1.00
1.00
6.10
2.00
1.03
1.00
1.00
2.00
2.00
3.00
f1 (ppm)


137.26
135.02
134.03
132.81
132.63
128.70
128.59
128.09
127.76
127.61
127.53
126.46
126.06
125.74
125.27
124.78
60.57
60.27
42.63
f1 (ppm)