Cyclic Ureas (DMI, DMPU) as Efficient, Sustainable Ligands in Iron-Catalyzed C(sp^2)–C(sp^3) Coupling of Aryl Chlorides and Tosylates

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Electronic Supplementary Information

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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 aqueous potassium permanganate solutions. ^{1}H NMR and ^{13}C NMR data are given for all products in the ESI 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.

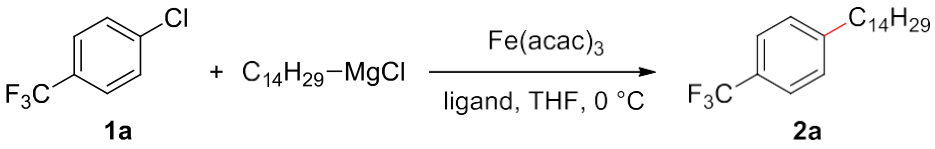
Experimental Procedures and Characterization Data

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 or an aryl tosylate substrate (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 ligand (neat, typically, 20-600 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_2O (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*). The sample was analyzed by ^1H 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. 3.0 g Scale. An oven-dried, two-necked flask (250 mL) equipped with a stir bar was charged with 4-chlorobenzonitrile (3.00 g, 21.81 mmol, 1.0 equiv) and $Fe(acac)_3$ (385.1 mg, 1.09 mmol, 5 mol%). Tetrahydrofuran (43.6 mL, 0.35 M) and DMI (14.15 ml, 600 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, 26.17 mL, 1.20 equiv) was added dropwise with vigorous stirring and the reaction mixture was stirred for 10 min at 0 °C. After the indicated time, the reaction mixture was diluted with HCl (1.0 *N*, 10 mL) and Et_2O (1 x 100 mL), the organic layer was extracted with HCl (1.0 *N*, 2 x 30 mL), dried and concentrated. The sample was analyzed by ^1H NMR ($CDCl_3$, 400 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples. Purification by recrystallization from toluene afforded the title product. Yield 91% (5.93 g). White solid. Characterization data are included in the section below.

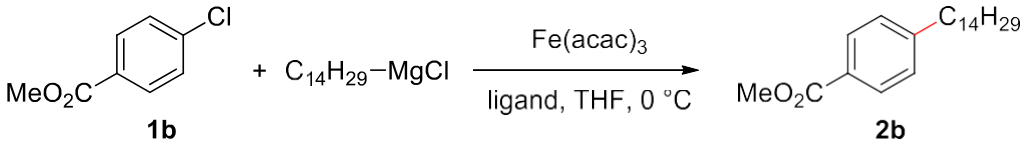
Iron-Catalyzed Cross-Coupling with Sustainable Ligands (Table 3)

1-Tetradecyl-4-(trifluoromethyl)benzene (Table 3, 2a)



Prepared according to the general procedure using 1-chloro-4-(trifluoromethyl)benzene (0.50 mmol), $Fe(acac)_3$ (5 mol%), DMPU (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 90% (153.9 mg). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 2.64 (t, *J* = 7.8 Hz, 2H), 1.66-1.56 (m, 2H), 1.37-1.18 (m, 22H), 0.88 (t, *J* = 6.8 Hz, 3H). **^{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. The run with DMI (200 mol%) afforded **2a** in 96% yield. Spectroscopic properties matched those described previously.[1,2]

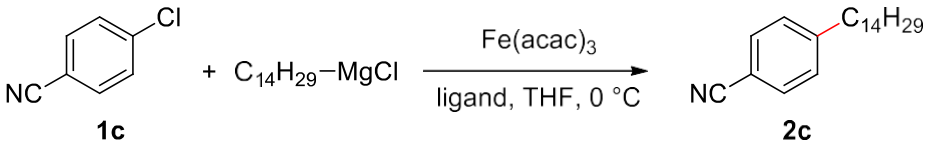
Methyl 4-tetradecylbenzoate (Table 3, 2b)



Prepared according to the general procedure using methyl 4-chlorobenzoate (0.50 mmol), $Fe(acac)_3$ (5 mol%), DMPU (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 95% (158.4 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.5, 2H), 3.90 (s, 3H), 2.65 (t, *J* = 7.7 Hz, 2H), 1.67-1.56 (m, 2H), 1.35-1.20 (m, 22H), 0.88 (t, *J* = 6.9 Hz, 3H). **^{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. The run with DMI (200 mol%) afforded **2b** in 93% yield. Spectroscopic properties matched those described previously.[1,2]

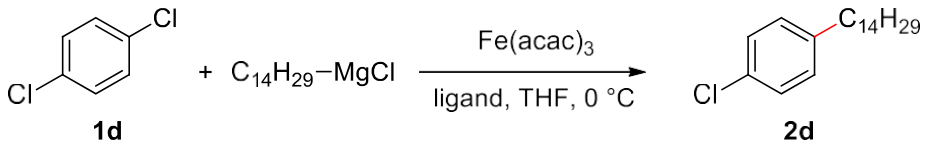
4-Tetradecylbenzonitryle (Table 3, 2c)



1c **2c**

Prepared according to the general procedure using 4-chlorobenzonitrile (0.50 mmol), $Fe(acac)_3$ (5 mol%), DMPU (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 92% (137.5 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 2.65 (t, *J* = 7.7 Hz, 2H), 1.67-1.53 (m, 2H), 1.34-1.23 (m, 22H), 0.88 (t, *J* = 6.9 Hz, 3H). **^{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. The run with DMI (600 mol%) afforded **2c** in 89% yield. Spectroscopic properties matched those described previously.[1,2]

1-Chloro-4-tetradecylbenzene (Table 3, 2d)

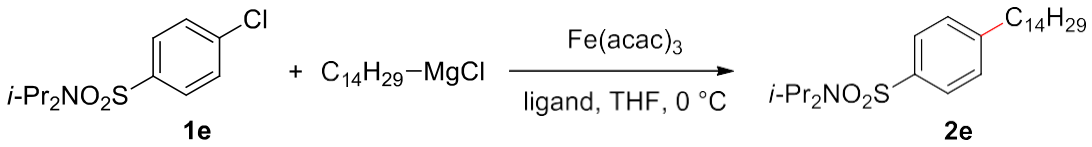


1d **2d**

Prepared according to the general procedure using 1,4-dichlorobenzene (0.50 mmol), $Fe(acac)_3$ (5 mol%), DMPU (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 60 min at 0 °C. Yield 67% (102.9 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.22 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 2.56 (t, *J* = 7.7 Hz, 2H), 1.62-1.52 (m, 2H), 1.34-1.20 (m, 22H), 0.88 (t, *J* = 6.8 Hz, 3H). **^{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,

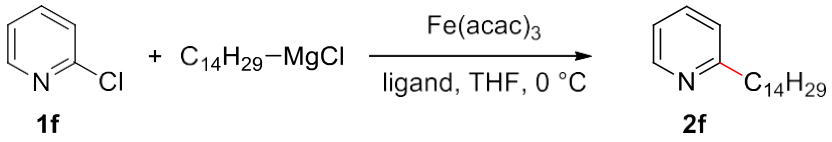
29.39, 22.90, 14.33. The run with DMI (600 mol%) afforded **2d** in 64% yield. Spectroscopic properties matched those described previously.[3]

N,*N*-Diisopropyl-4-tetradecylbenzenesulfonamide (Table 3, 2e)



Prepared according to the general procedure using 4-chloro-*N*,*N*-diisopropylbenzenesulfonamide (0.50 mmol), $Fe(acac)_3$ (5 mol%), DMPU (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 96% (209.4 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 3.75-3.63 (m, 2H), 2.65 (t, *J* = 7.7 Hz, 2H), 1.66-1.55 (m, 2H), 1.35-1.20 (m, 34H), 0.88 (t, *J* = 6.8 Hz, 3H). **^{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. The run with DMI (200 mol%) afforded **2e** in 94% yield. Spectroscopic properties matched those described previously.[1,2]

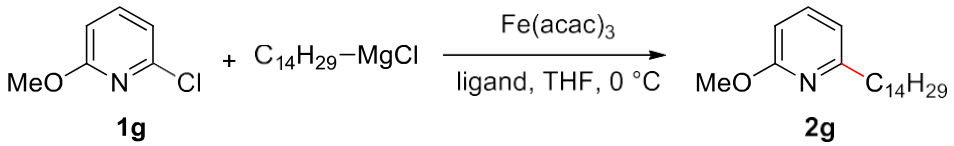
2-Tetradecylpyridine (Table 3, 2f)



Prepared according to the general procedure using 2-chloropyridine (0.50 mmol), $Fe(acac)_3$ (5 mol%), DMPU (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 93% (128.4 mg). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.52 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.57 (td, *J* = 7.7, 1.9 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.08 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H), 2.78 (t, *J* = 7.7 Hz, 2H), 1.77-1.66 (m, 2H), 1.40-1.18 (m, 22H), 0.88 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 162.70, 149.34,

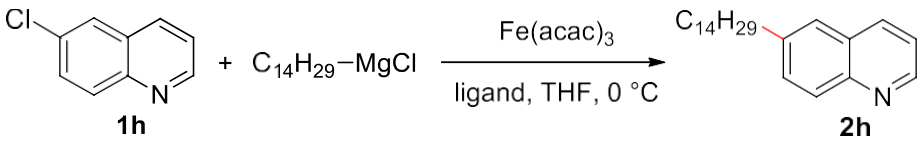
136.31, 122.80, 120.95, 38.64, 32.08, 30.11, 29.84, 29.82, 29.73, 29.66, 29.58, 29.52, 22.85, 14.28. The run with DMI (600 mol%) afforded **2f** in 88% yield. Spectroscopic properties matched those described previously.[1,2]

2-Methoxy-6-tetradecylpyridine (Table 3, 2g)



Prepared according to the general procedure using 2-chloro-6-methoxypyridine (0.50 mmol), $Fe(acac)_3$ (5 mol%), DMPU (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 94% (144.0 mg). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.45 (dd, *J* = 8.2, 7.3 Hz, 1H), 6.69 (d, *J* = 7.2 Hz, 1H), 6.52 (d, *J* = 8.2 Hz, 1H), 3.91 (s, 3H), 2.67 (t, *J* = 7.7 Hz, 2H), 1.76-1.65 (m, 2H), 1.38-1.21 (m, 22H), 0.88 (t, *J* = 6.9 Hz, 3H). **^{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. The run with DMI (200 mol%) afforded **2g** in 88% yield. Spectroscopic properties matched those described previously.[1,2]

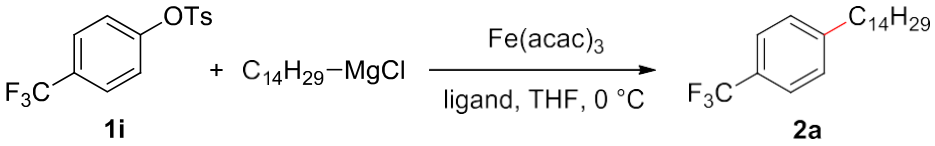
6-Tetradecylquinoline (Table 3, 2h)



Prepared according to the general procedure using 6-chloroquinoline (0.50 mmol), $Fe(acac)_3$ (5 mol%), DMPU (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 96% (155.7 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.85 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.08 (dd, *J* = 8.3, 1.0 Hz, 1H), 8.02 (d, *J* = 9.2 Hz, 1H), 7.59-7.54 (m, 2H), 7.35 (dd, *J* = 8.3, 4.2 Hz, 1H), 2.78 (t, *J* = 7.7 Hz, 2H), 1.76-1.65 (m, 2H), 1.39-1.21 (m, 22H), 0.88 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 149.70,

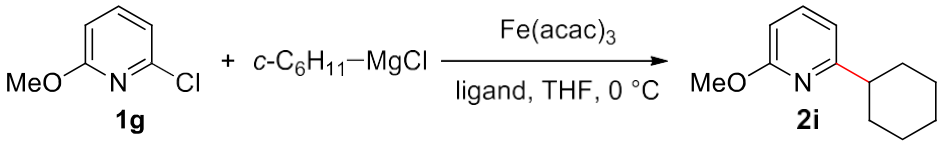
147.24, 141.50, 135.67, 131.22, 129.32, 128.46, 126.14, 121.15, 36.08, 32.09, 31.43, 29.83, 29.75, 29.67, 29.53, 29.47, 22.86, 14.30. The run with DMI (200 mol%) afforded **2g** in 98% yield. Spectroscopic properties matched those described previously.[1,2]

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



Prepared according to the general procedure using 4-(trifluoromethyl)phenyl 4-methylbenzenesulfonate (0.50 mmol), $Fe(acac)_3$ (5 mol%), DMPU (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 60 min at 0 °C. Yield 92% (157.0 mg). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 2.64 (t, *J* = 7.8 Hz, 2H), 1.66-1.56 (m, 2H), 1.37-1.18 (m, 22H), 0.88 (t, *J* = 6.8 Hz, 3H). **^{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. The run with DMI (600 mol%) afforded **2a** in 94% yield. Spectroscopic properties matched those described previously.[1,2]

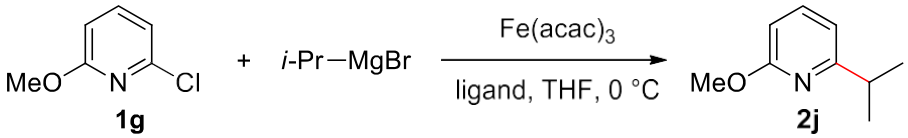
2-Cyclohexyl-6-methoxypyridine (Scheme 3, 2i)



Prepared according to the general procedure using 2-chloro-6-methoxypyridine (0.50 mmol), $Fe(acac)_3$ (5 mol%), DMI (200 mol%), THF (0.15 M), and *c*-$C_6H_{11}MgCl$ (1.0 M in THF, 1.20 equiv). The reaction mixture was stirred for 10 min at 0 °C. Yield 94% (89.7 mg). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 (dd, *J* = 8.2, 7.3 Hz, 1H), 6.70 (d, *J* = 7.3 Hz, 1H), 6.52 (dd, *J* = 8.2, 0.6 Hz, 1H), 3.92 (s, 3H), 2.58 (tt, *J* = 11.7, 3.4 Hz, 1H), 1.97-1.89 (m, 2H), 1.88-1.78

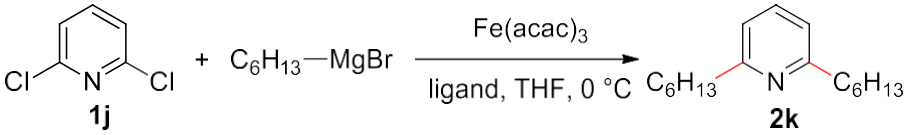
(m, 2H), 1.77-1.69 (m, 1H), 1.52 (ddd, *J* = 24.1, 12.2, 2.7 Hz, 2H), 1.46-1.32 (m, 2H), 1.33-1.23 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.74, 163.60, 138.87, 113.42, 107.28, 53.27, 46.16, 32.86, 26.72, 26.35. Spectroscopic properties matched those described previously.[4]

2-Isopropyl-6-methoxypyridine (Scheme 3, 2j)



Prepared according to the general procedure using 2-chloro-6-methoxypyridine (0.50 mmol), $Fe(acac)_3$ (5 mol%), DMI (600 mol%), THF (0.15 M), and *i*-PrMgBr (1.0 M in THF, 1.20 equiv). The reaction mixture was stirred for 60 min at 0 °C. Yield 67% (50.4 mg). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 (dd, *J* = 8.2, 7.3 Hz, 1H), 6.72 (d, *J* = 7.3 Hz, 1H), 6.53 (dd, *J* = 8.2, 0.6 Hz, 1H), 3.92 (s, 3H), 2.94 (m, 1H), 1.27 (d, *J* = 6.9 Hz, 6H). **^{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 2-methoxy-6-propylpyridine was not detected.[5] Selectivity (branched:linear) >20:1. Spectroscopic properties matched those described previously.[2]

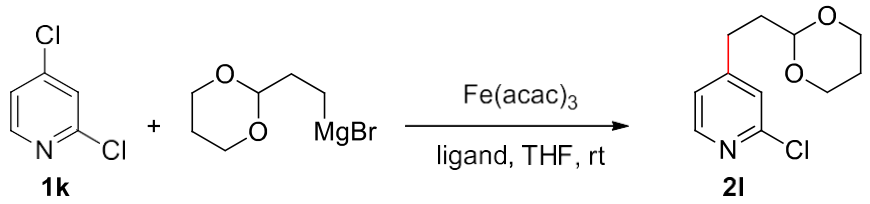
2,6-Dihexylpyridine (Scheme 5, 2k)



Prepared according to the general procedure using 2,6-dichloropyridine (0.50 mmol), $Fe(acac)_3$ (10 mol%), DMI (1200 mol%), THF (0.15 M), and *n*-C_6H_{13}MgBr (2.0 M in Et_2O, 4.80 equiv). The reaction mixture was stirred for 60 min at 0 °C. Yield 85% (105.1 mg). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 (t, *J* = 7.7, 1H), 6.93 (d, *J* = 7.7 Hz, 2H), 2.75 (t, *J* = 7.8 Hz, 4H), 1.74-1.63 (m, 4H), 1.40-1.24 (m, 12H), 0.87 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (100 MHz,**

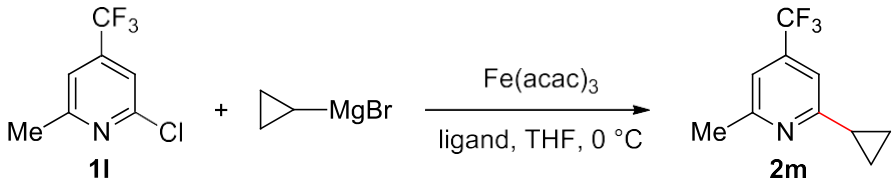
CDCl$_3$) δ 161.92, 136.34, 119.58, 38.65, 31.78, 30.24, 29.15, 22.61, 14.10. Spectroscopic properties matched those described previously.[2]

4-(2-(1,3-Dioxan-2-yl)ethyl)-2-chloropyridine (Scheme 6, 2l)



A previously published procedure was followed using DMI instead of NMP.[6] Prepared according to the general procedure using 2,4-dichloropyridine (0.50 mmol), Fe(acac)$_3$ (3.75 mol%), DMI (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 71% (80.8 mg). Colorless oil. **^{1}H NMR (400 MHz, CDCl$_3$)** 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). **^{13}C NMR (100 MHz, CDCl$_3$)** 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 = 5.1:1.[6] Spectroscopic properties matched those described previously.[6]

2-Cyclopropyl-6-methyl-4-(trifluoromethyl)pyridine (Scheme 7, 2m)



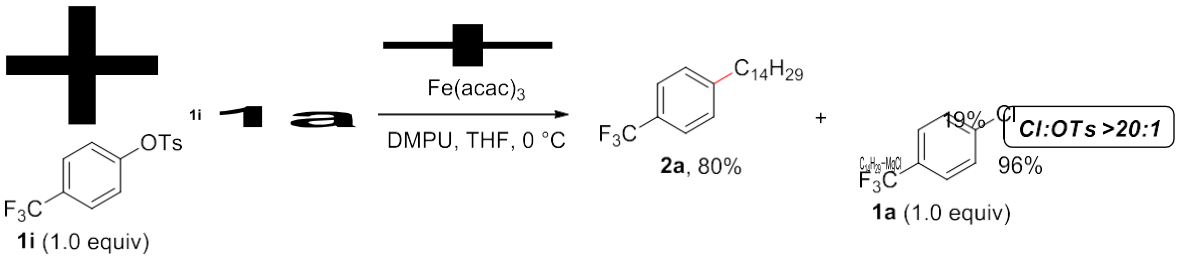
A previously published procedure was followed using DMI instead of NMP.[7] Prepared according to the general procedure using 2-chloro-6-methyl-4-(trifluoromethyl)pyridine (0.50 mmol), Fe(acac)$_3$ (5 mol%), DMI (200 mol%), THF (0.15 M), and cyclopropylmagnesium bromide (1.0 M in THF, 2.00 equiv). The reaction mixture was stirred for 1 h at 0 °C. Yield 80% (80.2 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.[7]

Determination of Relative Reactivity of Cl vs. OTs

General Procedure. According to the general procedure, an oven-dried vial equipped with a stir bar was charged with 1-chloro-4-(trifluoromethyl)benzene (**1a**, 0.50 mmol, 1.0 equiv), 4-(trifluoromethyl)phenyl 4-methylbenzenesulfonate (**1i**, 0.50 mmol, 1.0 equiv) and $Fe(acac)_3$ (5 mol%), placed under a positive pressure of argon and subjected to three evacuation/backfilling cycles under vacuum. Tetrahydrofuran (0.15 M) and DMPU (neat, 200 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, 0.80 equiv) was added dropwise with vigorous stirring and the reaction mixture was stirred for 10 min at 0 °C. Following the standard work-up, the sample was analyzed by ^1H NMR ($CDCl_3$, 400 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples. The observed selectivity indicates that synthetically useful levels of chemoselectivity in the cross-coupling of aryl chlorides and tosylates under these conditions can be obtained. Further studies on the chemoselectivity in iron-catalyzed cross-couplings are underway in our laboratories.

Scheme ESI-1. Competition Experiment in the Fe-Catalyzed C(sp^3)–C(sp^2) Cross-Coupling of Aryl Chlorides and Tosylates.[a]



[a]Conditions: **1a** (0.50 mmol), **1i** (0.50 mmol), $C_{14}H_{29}MgCl$ (0.80 equiv), $Fe(acac)_3$ (5 mol%), DMPU (200 mol%), THF (0.15 M), 0 °C, 10 min. All reactions carried out using standard Schlenk techniques. Reaction selectivity determined by ^1H NMR and/or GC-MS.

References

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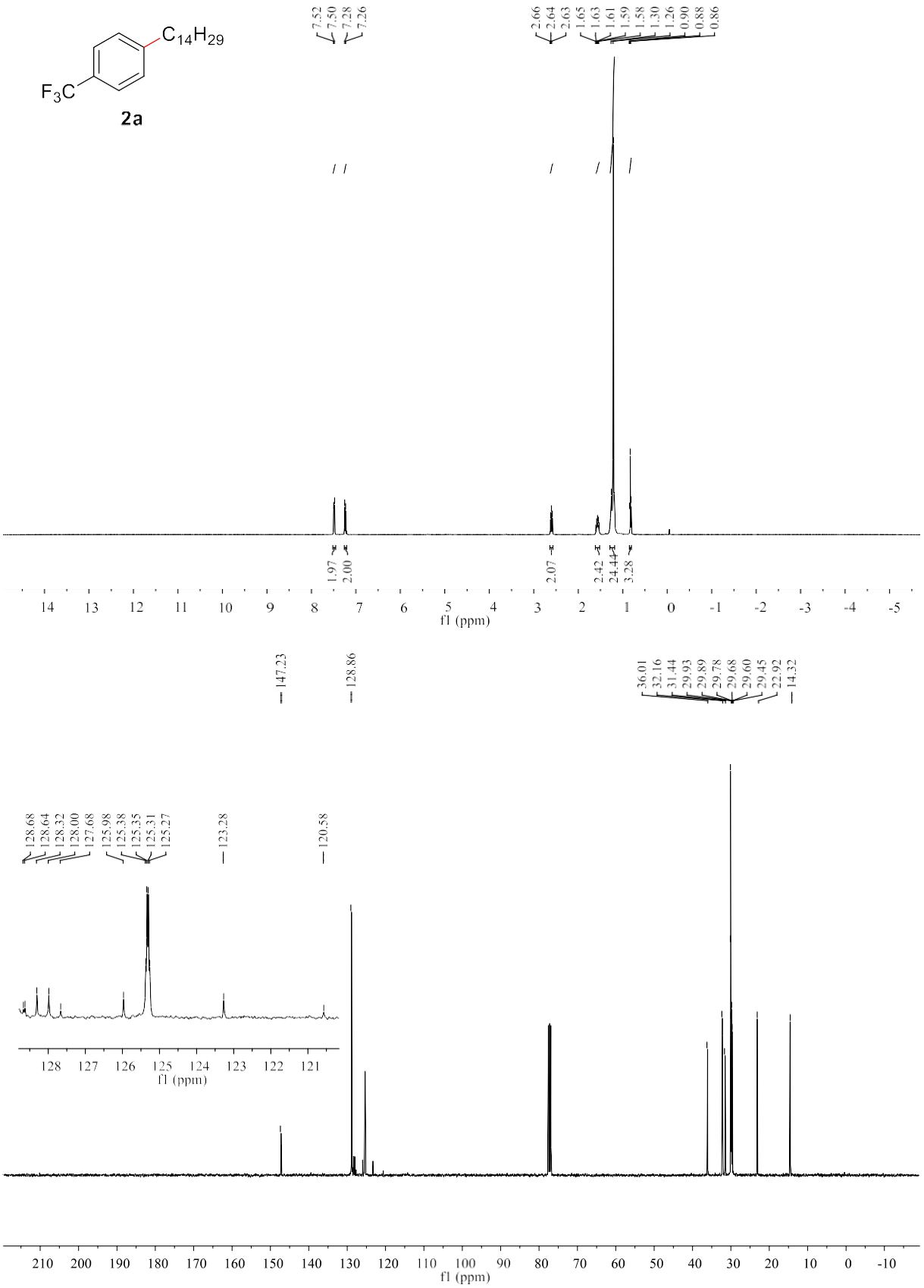
7. Risatti, C.; Natalie, Jr., K. J.; Shi, Z.; Conlon, D. A. *Org. Process Res. Dev.* **2013**, *17*, 257.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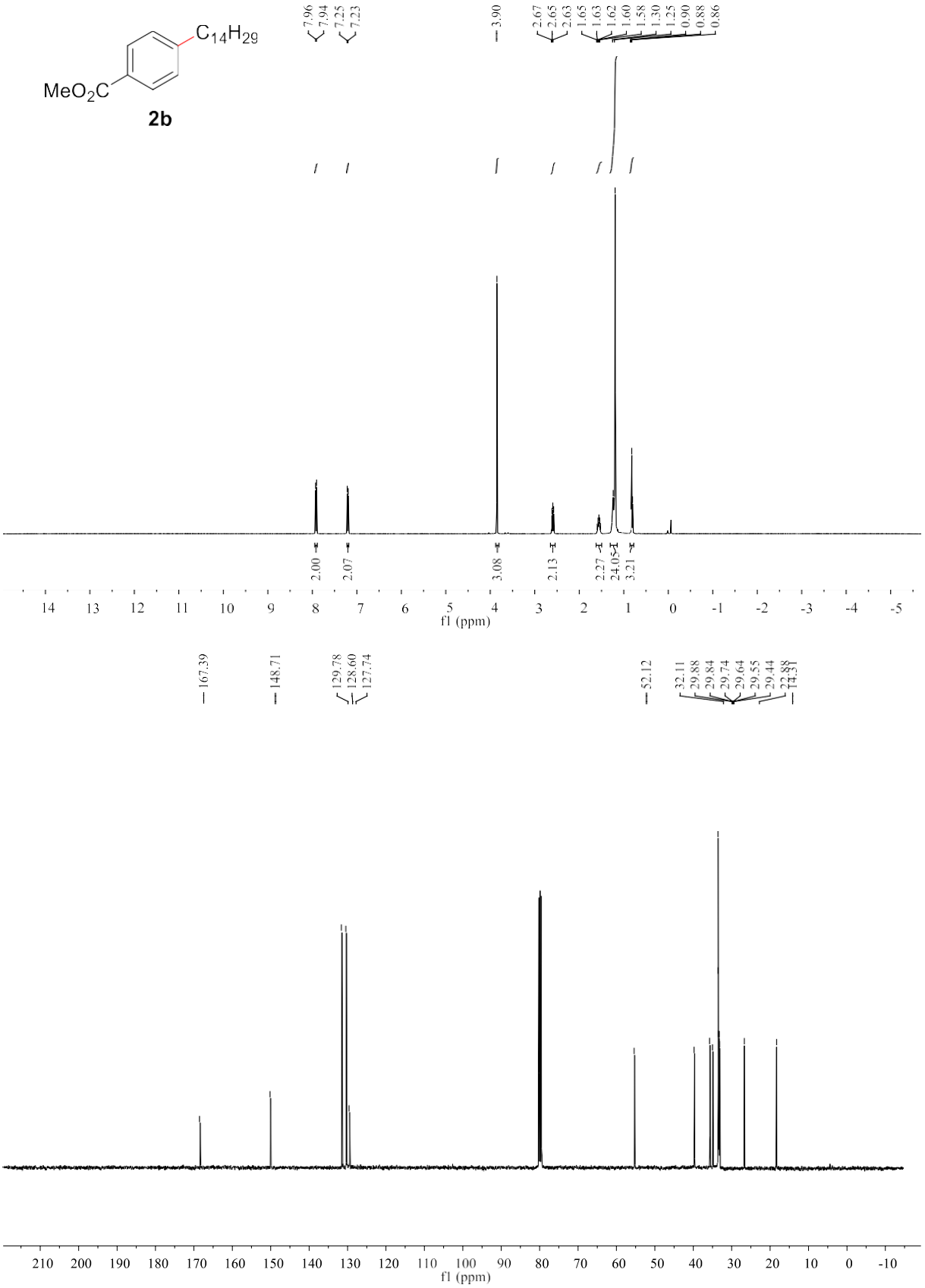
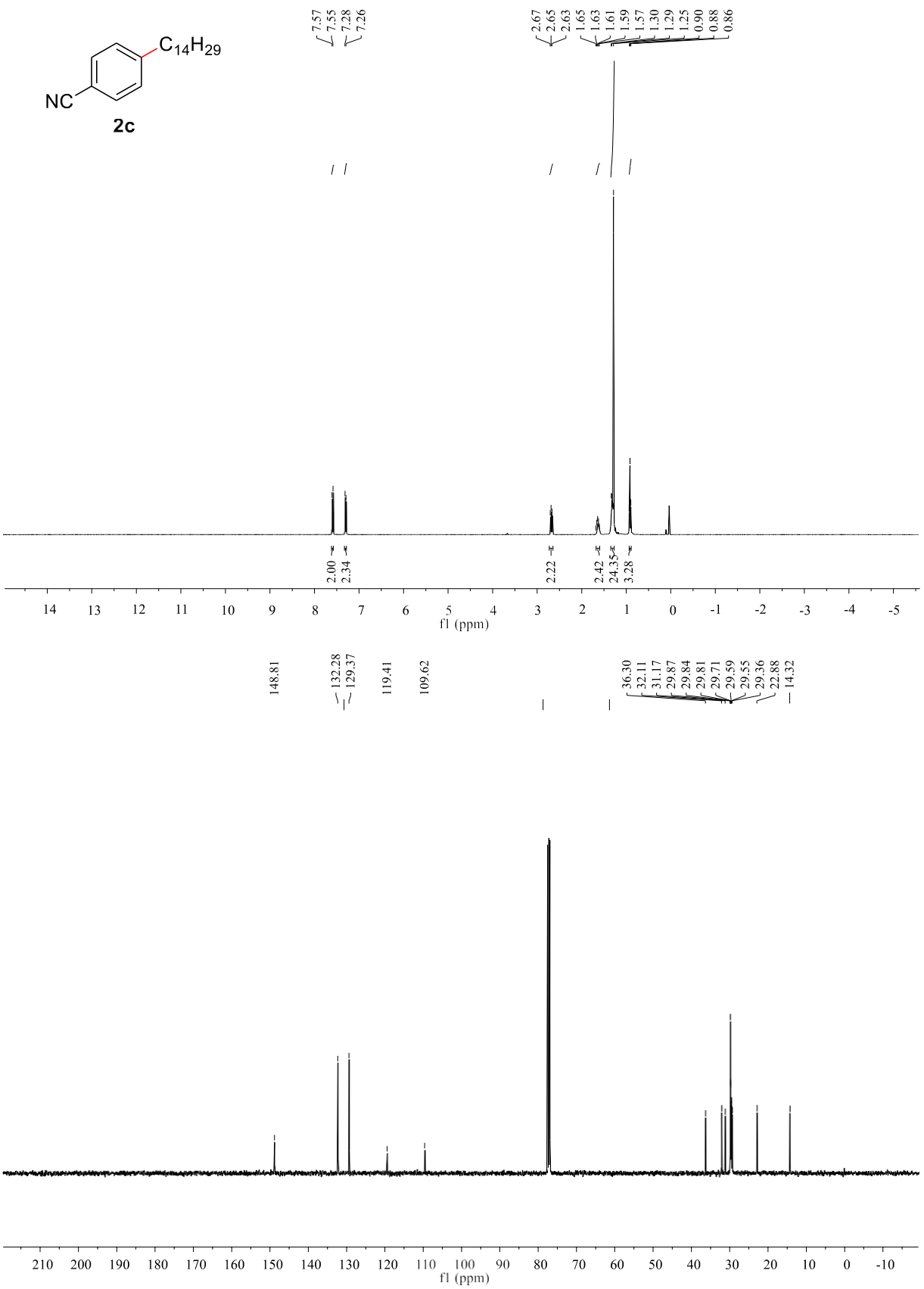
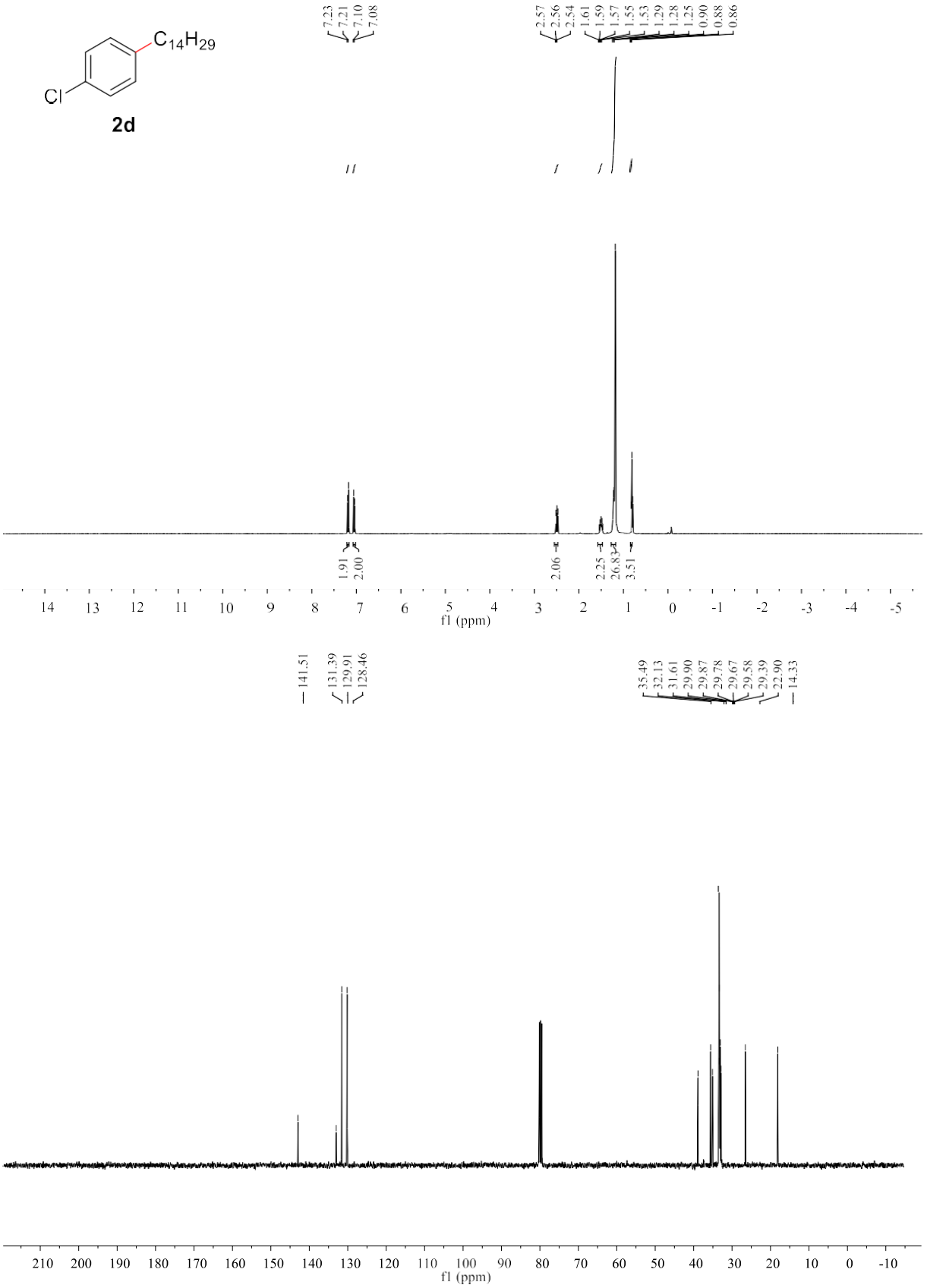
F3C
2a
7.52
7.50
7.28
7.26
2.66
2.64
2.63
1.65
1.63
1.61
1.59
1.58
1.30
1.26
0.90
0.88
0.86
1.97
2.00
2.07
2.42
24.44
3.28
f1 (ppm)
147.23
128.86
36.01
32.16
31.44
29.93
29.89
29.78
29.68
29.60
29.45
22.92
14.32
128.68
128.64
128.32
128.00
127.68
125.98
125.38
125.35
125.31
125.27
123.28
120.58
f1 (ppm)
f1 (ppm)


C14H29
MeO2C
2b
7.96
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
2.07
3.08
2.13
2.27
24.05
3.21
f1 (ppm)
167.39
148.71
129.78
128.60
127.74
52.12
32.11
29.88
29.84
29.74
29.64
29.55
29.44
22.88
14.31
f1 (ppm)


C14H29
NC
2c
7.57
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
2.34
2.22
2.42
24.35
3.28
f1 (ppm)
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
f1 (ppm)


C14H29
Cl
2d
7.23
7.21
7.10
7.08
2.57
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
1.91
2.00
2.06
2.25
26.83
3.51
f1 (ppm)
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131.39
129.91
128.46
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29.87
29.78
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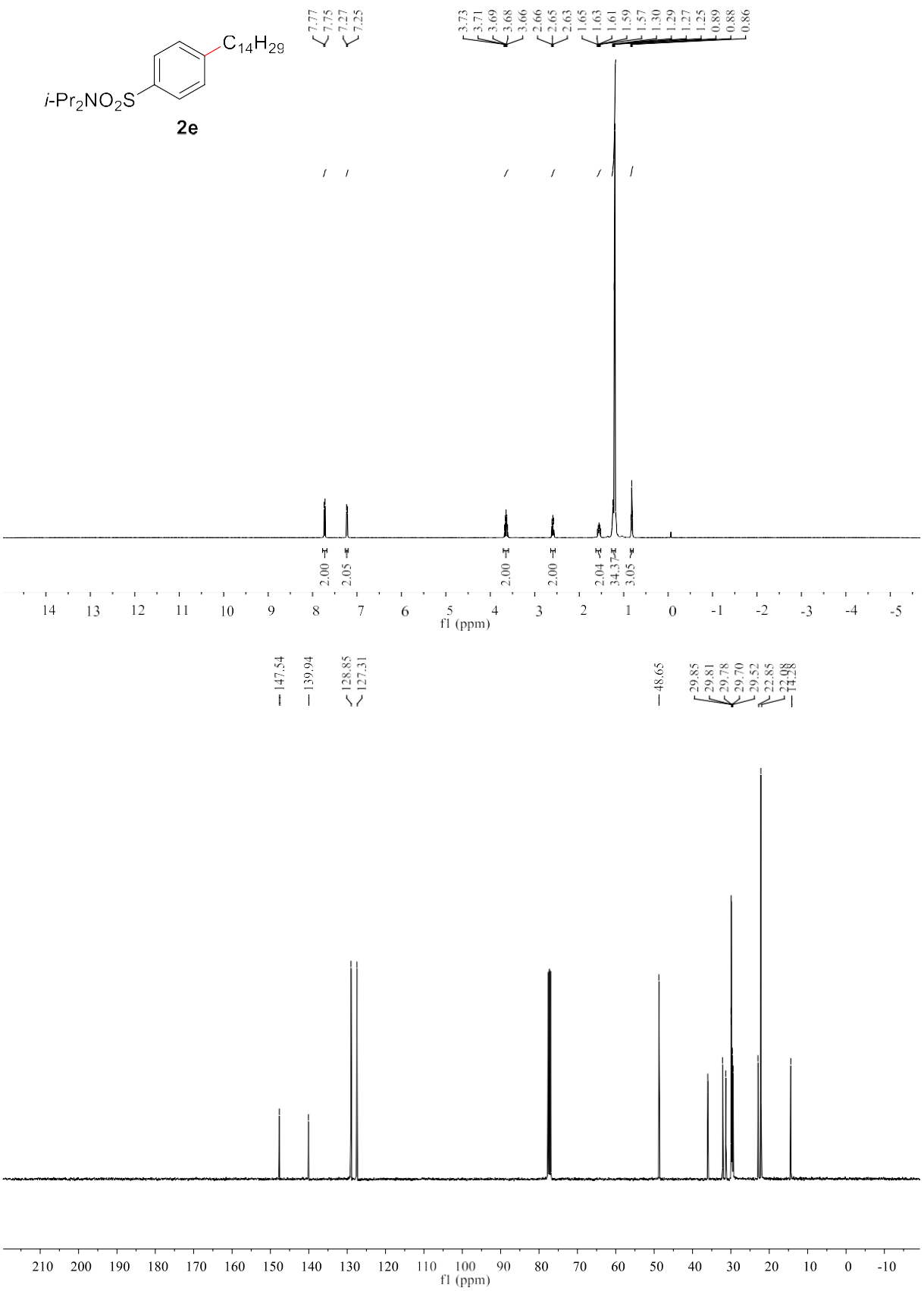
29.58
29.39
22.90
14.33
f1 (ppm)


C14H29
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2e
7.77
7.75
7.27
7.25
3.73
3.71
3.69
3.68
3.66
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
2.05
2.00
2.00
2.04
34.37
3.05
f1 (ppm)
147.54
139.94
128.85
127.31
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29.85
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29.78
29.70
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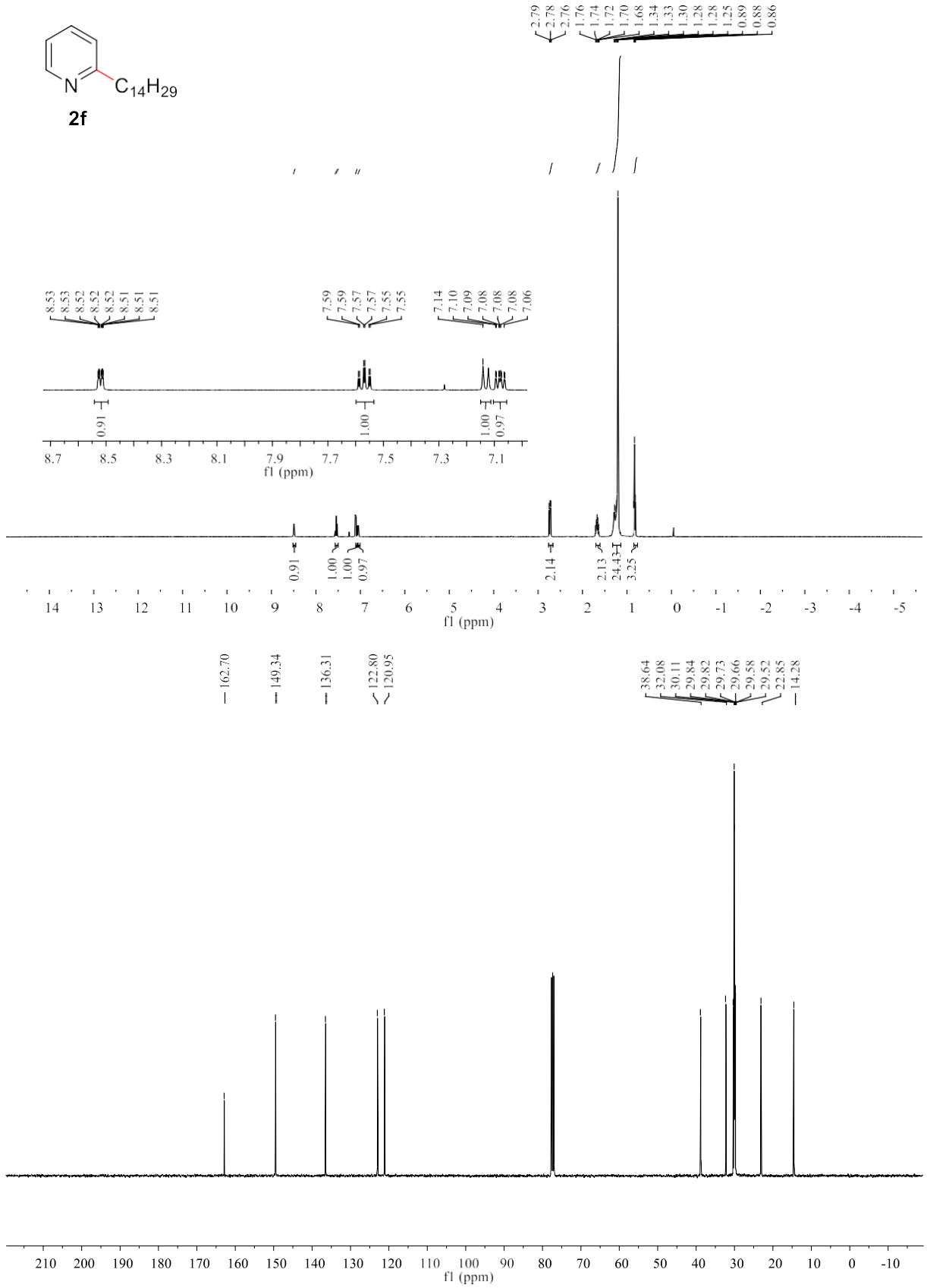
22.85
22.08
14.28
f1 (ppm)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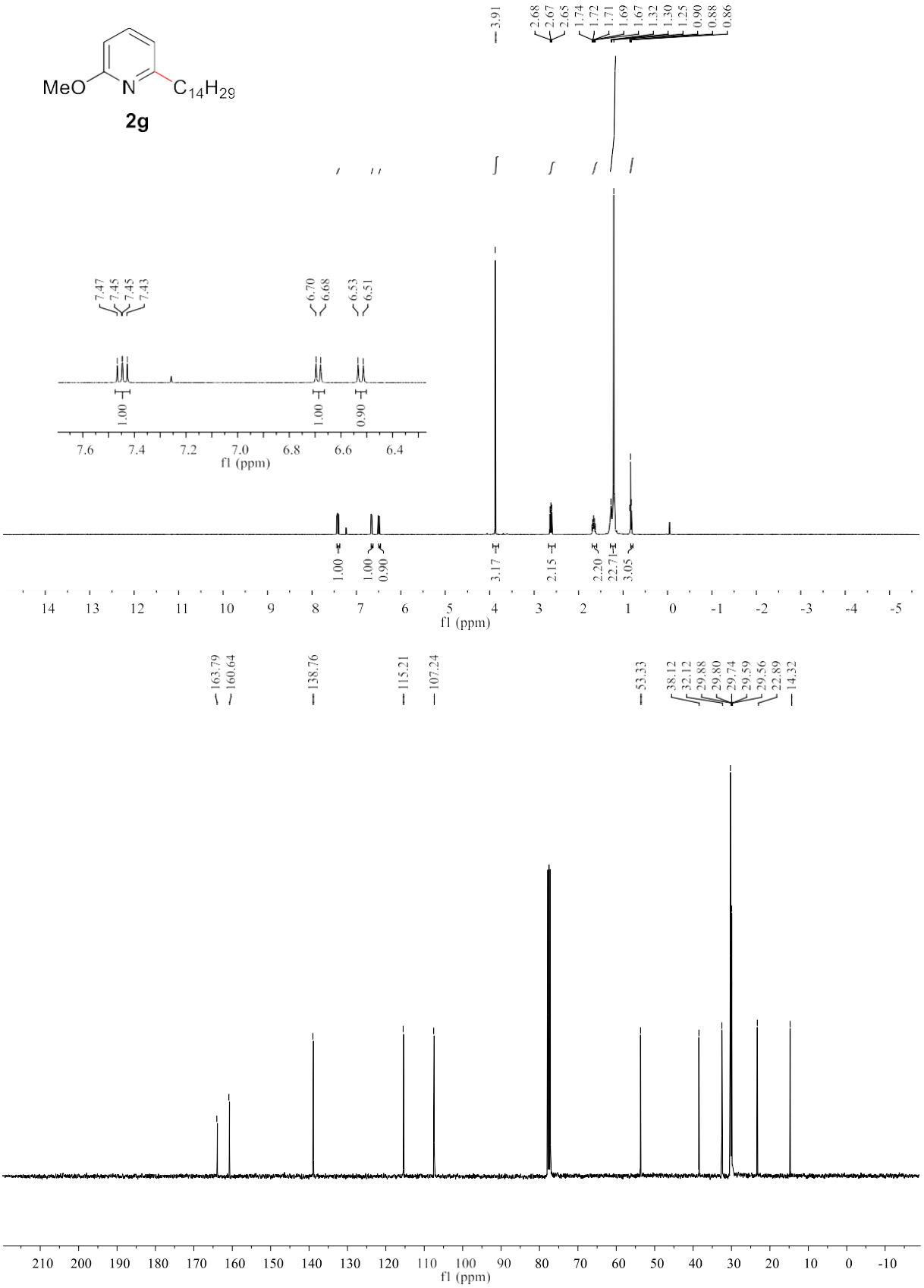
C14H29
2f
f1 (ppm)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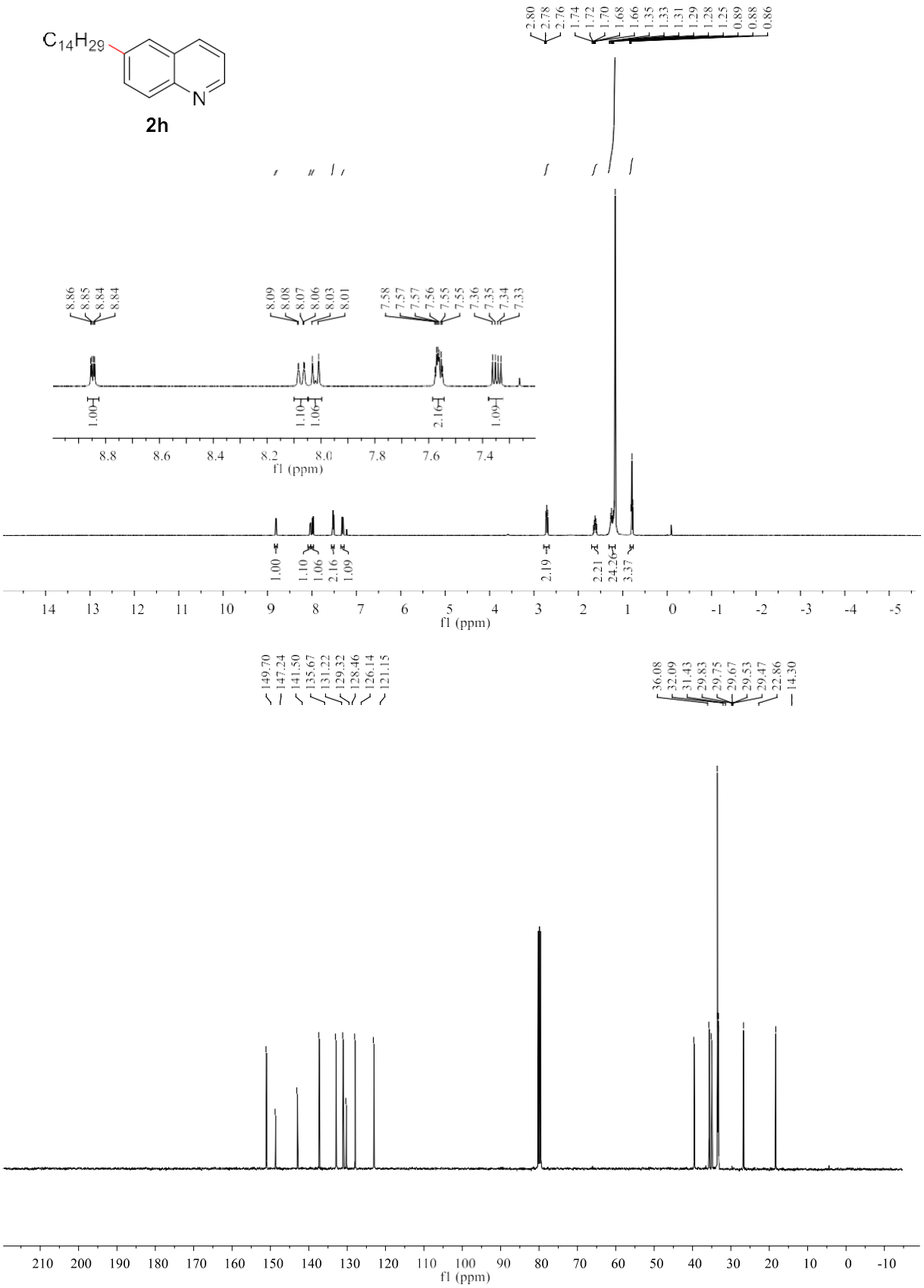
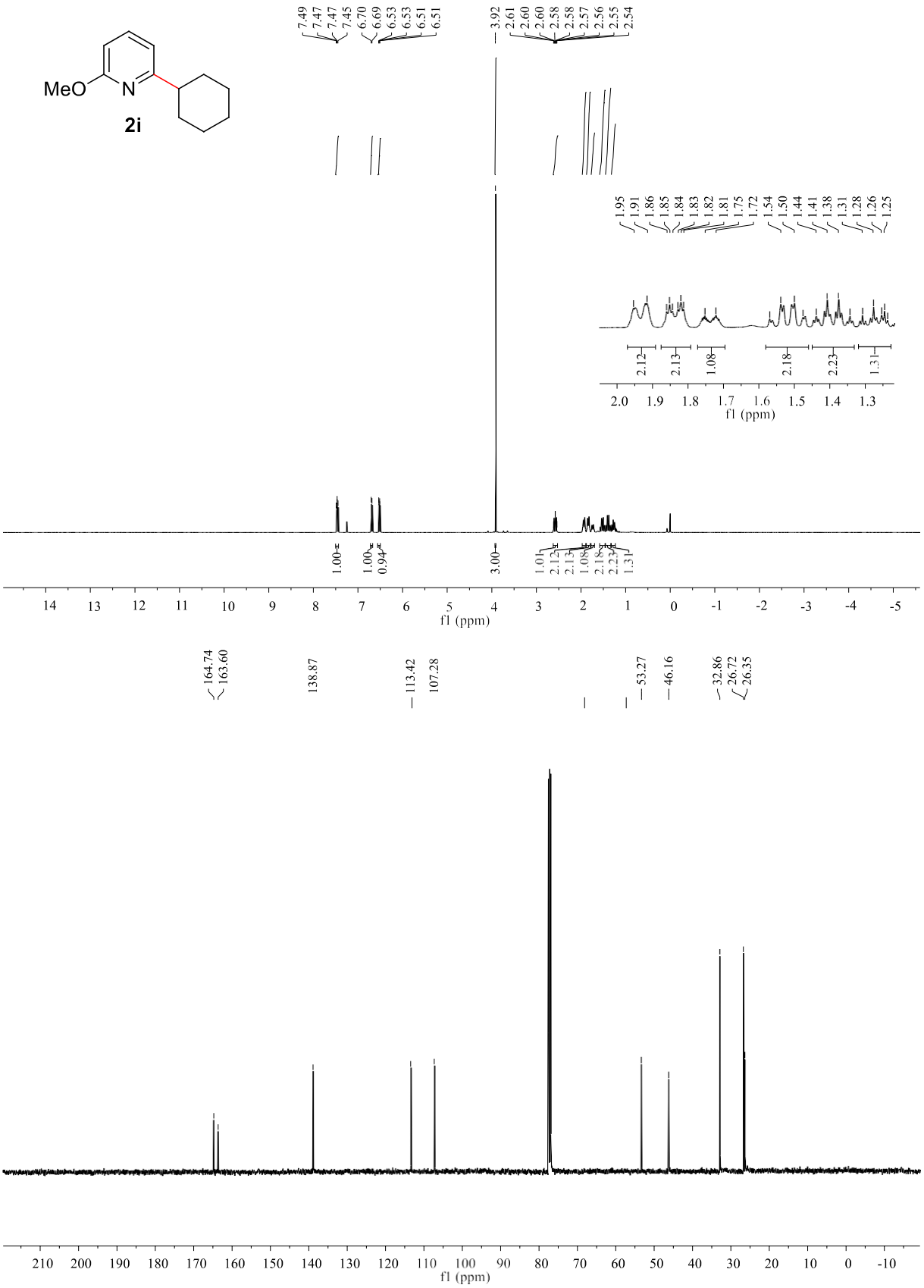
N
C14H29
2g
f1 (ppm)


C14H29
N
2h
f1 (ppm)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6.69
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6.53
6.51
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1.28
1.26
1.25
2.12
2.13
1.08
2.18
2.23
1.31
f1 (ppm)
1.00
1.00
0.94
3.00
1.01
f1 (ppm)
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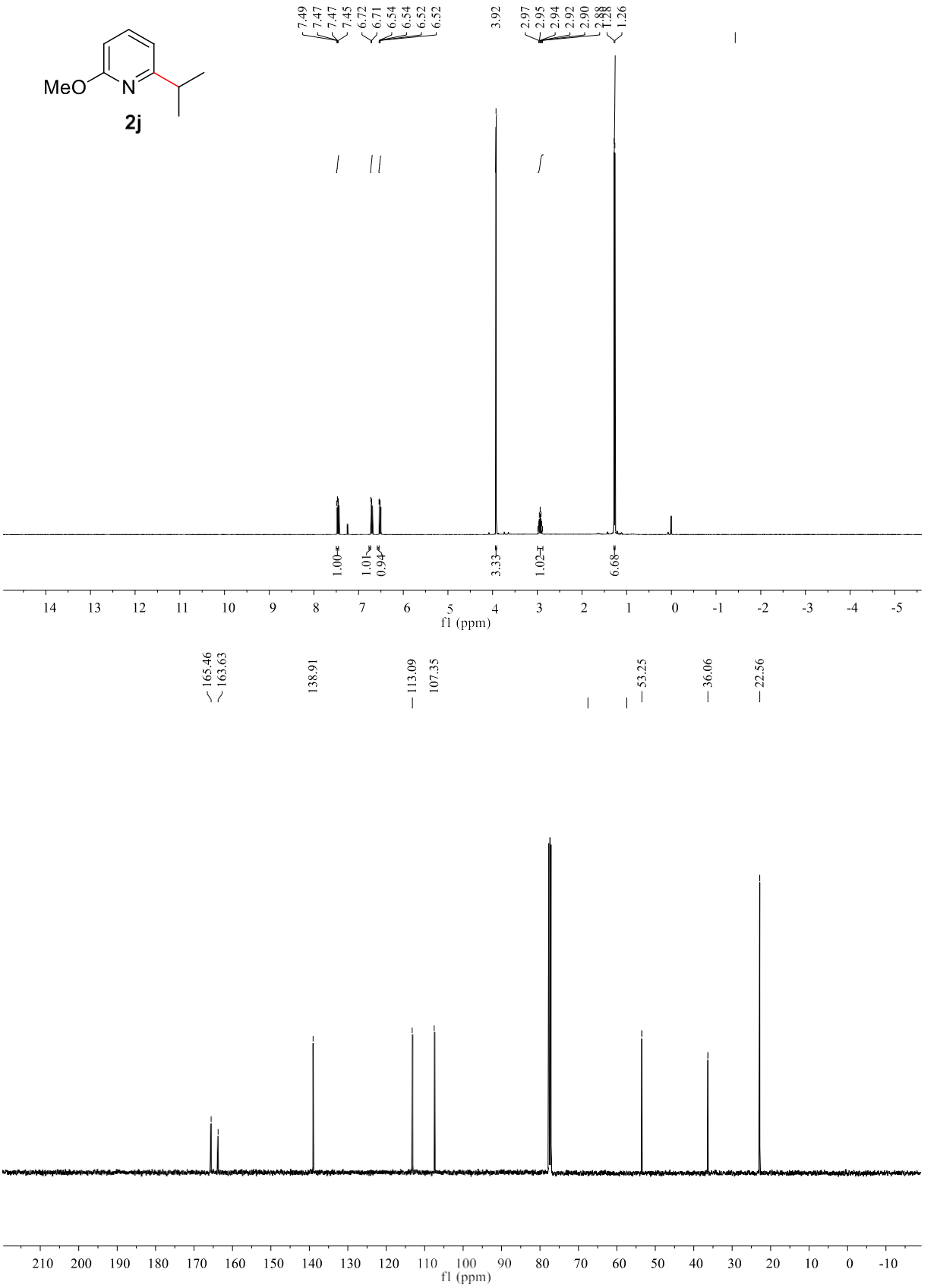
46.16
32.86
26.72
26.35
f1 (ppm)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3.92
2.97
2.95
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2.90
2.88
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1.01
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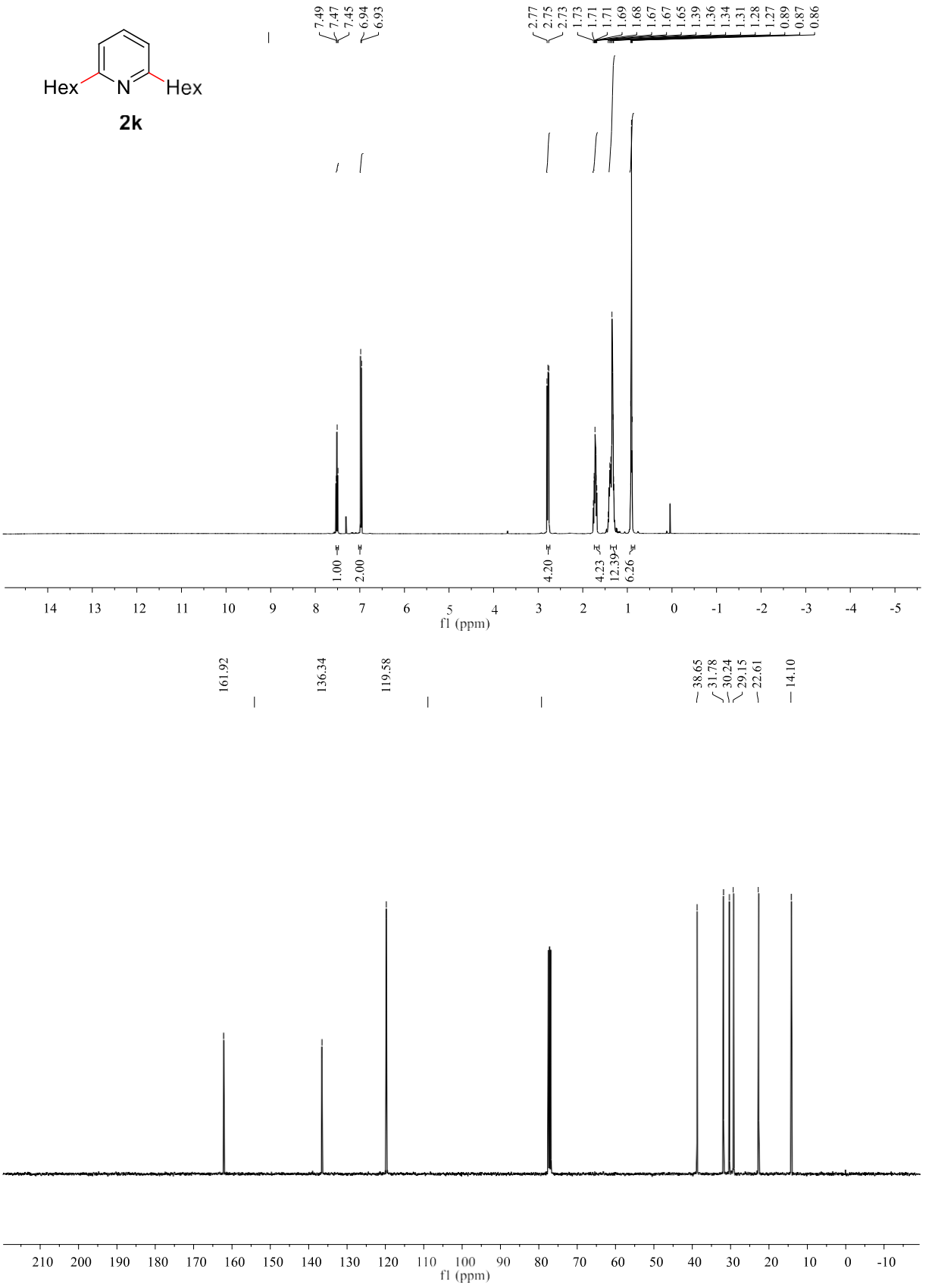
f1 (ppm)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1.71
1.69
1.68
1.67
1.67
1.65
1.39
1.36
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1.31
1.28
1.27
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0.86
1.00
2.00
4.20
4.23
12.39
6.26
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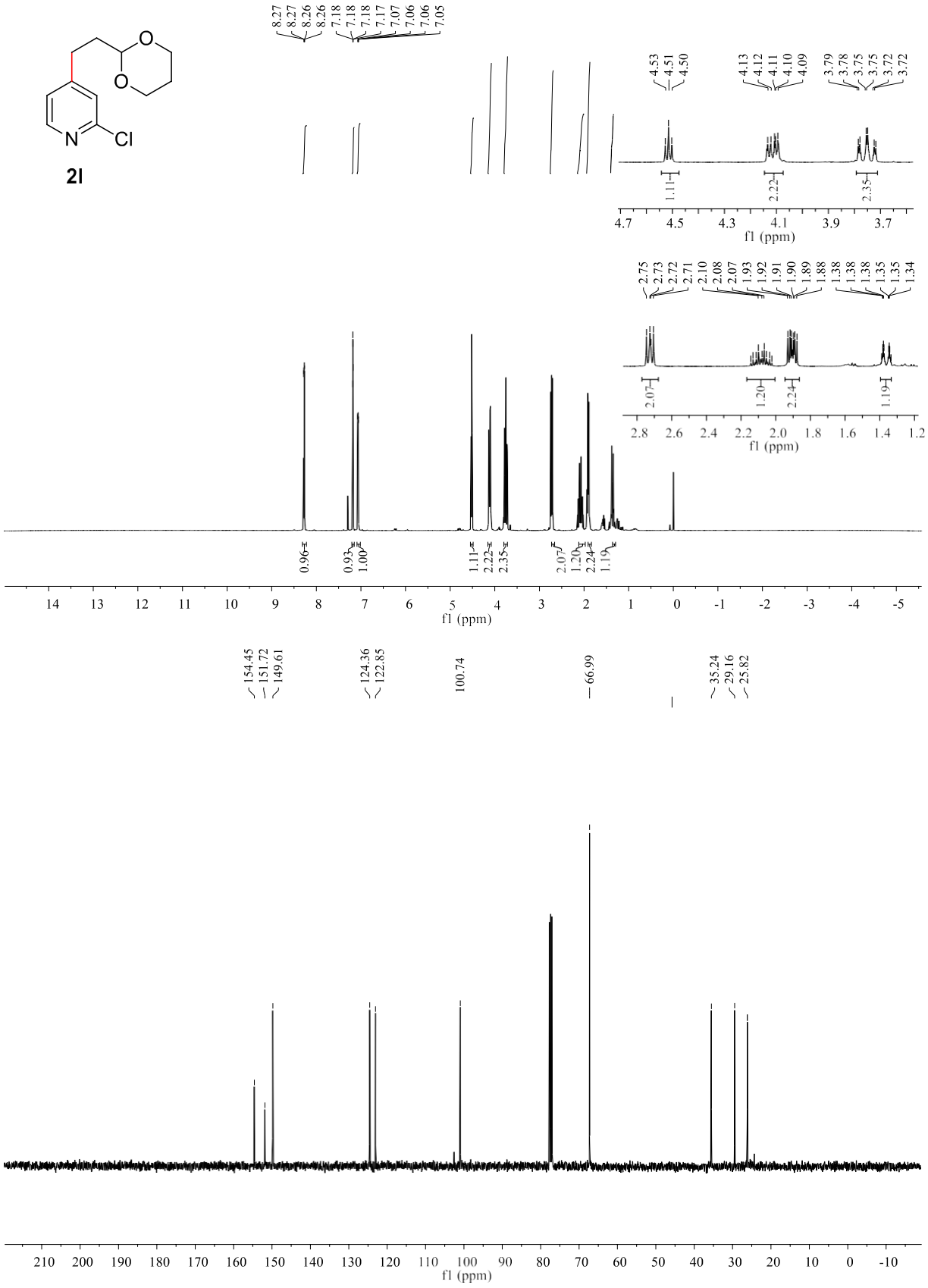
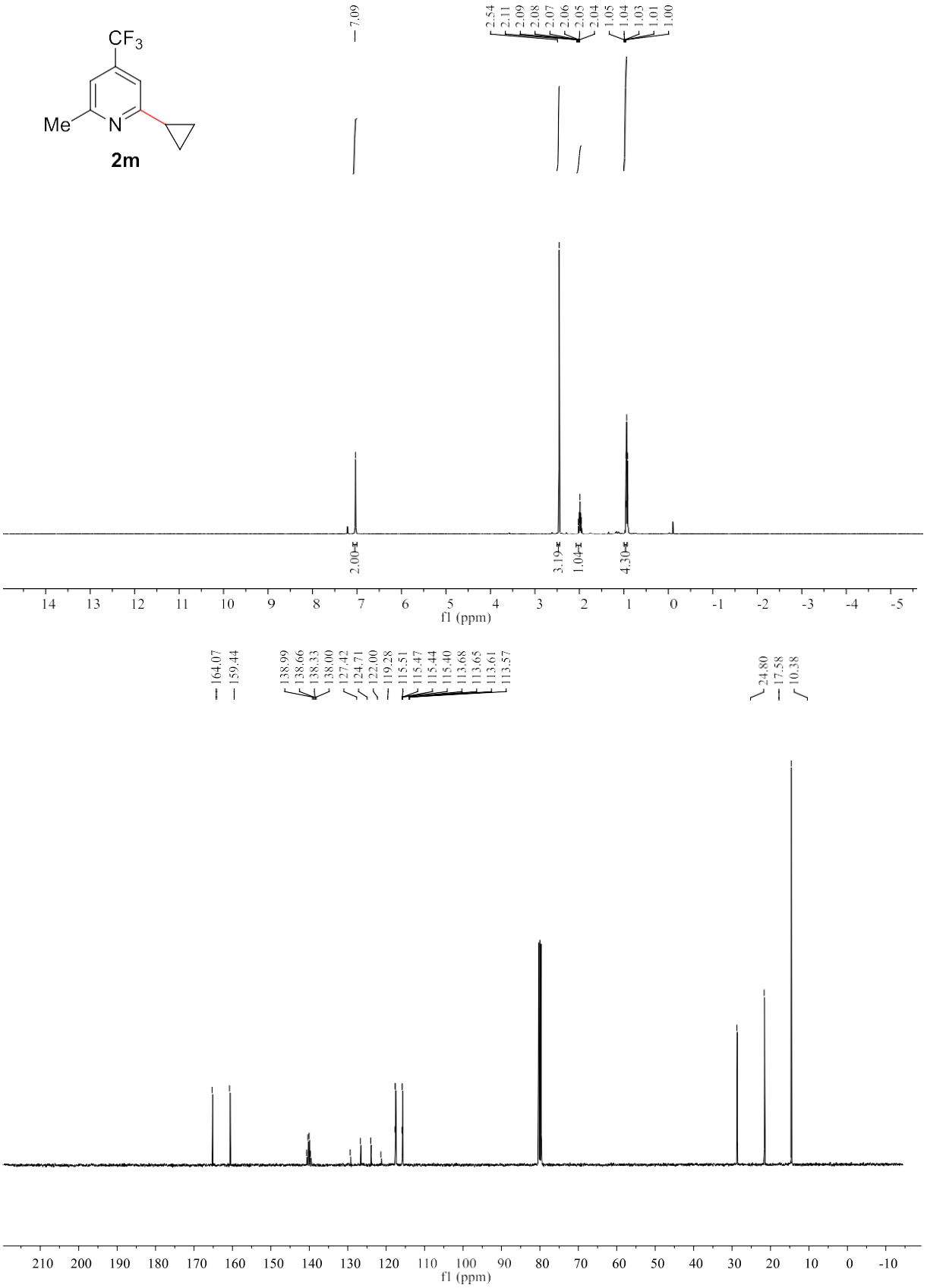
14.10
f1 (ppm)


2l
f1 (ppm)
f1 (ppm)
f1 (ppm)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138.66
138.33
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113.68
113.65
113.61
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24.80
17.58
10.38
f1 (ppm)