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Supporting Information

Site-Selective, Remote sp^3 C–H Carboxylation Enabled by the Merger of Photoredox and Nickel Catalysis

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Supporting Information

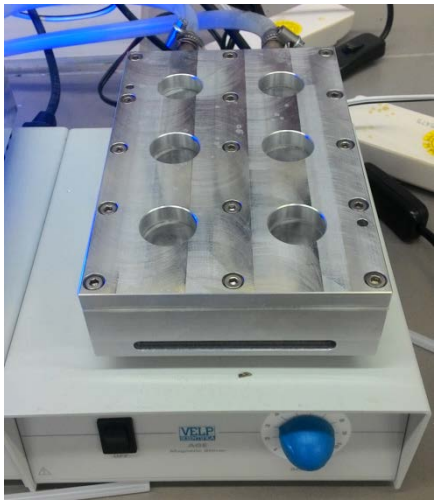
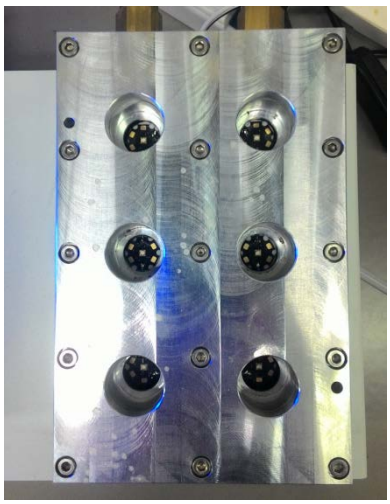
1 General Information

Analytic Methods: All NMR spectra were recorded at 294 K using Bruker 300, Bruker 400, and Bruker 500 MHz and DEU 400 NMR tubes from Deutero GmbH. The following deuterated solvent, purchased from Deutero GmbH or Sigma-Aldrich (minimal deuteration in brackets), were used: $CDCl_3$ (99.8%), acetone-d_6 (99.8%), DMSO-d_6 (99.8%), D_2O (99.9%). All chemical shifts (δ) are reported in parts per million (ppm) down field of tetramethylsilane (TMS). The coupling constant (*J*) is reported in Hertz (Hz). For ^{1}H and ^{13}C spectra, the residual solvent peak was used as internal reference ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; Acetone-d_6: δ_H = 2.05 ppm, δ_C = 29.84 ppm; DMSO-d_6: δ_H = 2.50 ppm, δ_C = 39.52 ppm; D_2O: δ_H = 4.79 ppm), while for ^{19}F spectra the absolute referencing to the ^{1}H spectrum was used, as suggested by the IUPAC. The following abbreviations are used for signal multiplicity: bs = broad signal, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of tripets, dq = doublet of quartets, tt = triplet of triplets, m = multiplet. Melting points were measured using open glass capillaries in a Büchi B540 apparatus. Infrared spectra (FT-IR) measurements were carried out on a Bruker Optics FT-IR Alpha spectrometer equipped with a DTGS detector, KBr beamsplitter at 4 cm^{-1} resolution using a one bounce ATR accessory with diamond windows (ICIQ) or on an Agilent Cary-630 benchtop spectrometer (Universität Regensburg). Mass spectra were recorded on a Waters LCT Premier spectrometer or in a MicroTOF Focus, Bruker Daltonics spectrometer at ICIQ and Jeol AccuTOF GCX, Agilent Q-TOF 6540 UHD, Finnigan MAT SSQ 710 A and ThermoQuest Finnigan TSQ 7000 at the Faculty of Chemistry and Pharmacy, Universität Regensburg. Elemental analysis measurements were obtained from the central analytic elemental analysis facilities (Vario MICRO Cube from Elementar Analysensysteme GmbH) of the Faculty of Chemistry and Pharmacy, Universität Regensburg. UV-VIS measurements were performed with an Agilent Cary 100 spectrometer using Hellma Analytics QS-High Precision Cell (Quartz glass, light-path: 10 mm). GC-FID measurements were performed using a Supelco 44176-01-C. equipped with a Nukol capillary column (44176-01-C, 15 m × 320 µm × 0.25 µm film) using helium as carrier gas (1 $ml \cdot min^{-1}$ flow. The data acquisition and evaluation were carried out using Agilent ChemStation Rev.B.02.01-SR2 [260]. Parameters: split ratio: 20:1, injection volume: 0.2 µl, inlet temperature: 280°C. Temperature ramp: hold 80°C for 1 minutes, gradient 15 $°C \cdot min^{-1}$ until 200 °C, hold for 3 minutes.

Reagents and methods: The chemicals were purchased from ACROS Organics, Sigma-Aldrich, Merck, TCI chemicals, ABCR, Alfa Aesar, Fluka and Fluorochem and used as received, unless otherwise stated. CO_2 was provided by Linde and dried by passing it through a Drierite® ($CaSO_4$) column. Reaction temperatures are referred to the temperature of the heating medium, unless otherwise stated. Technical grade solvents were purified as following: ethyl acetate, petroleum ether 40-60, dichloromethane, diethyl ether were purified by distillation. The following dry solvents were stored under molecular sieves with septa under nitrogen atmosphere and withdrawn using a syringe under positive nitrogen pressure: THF (from ACROS Organics), *N,N*-DMF (from ACROS Organics). Dry toluene (from Fischer scientific, analytical grade), diethyl ether (Aldrich) and MeCN (Carl ROTH) were prepared as following: 4 Å molecular sieves (20 % w/w) or 3 Å molecular sieves (for MeCN) were dried by heating at 250°C under approx. 10^{-2} mbar of pressure for at least one hour, then the analytical grade solvent was added and the flask was sealed under nitrogen atmosphere.

Flash chromatographic purifications were carried with the following stationary phases: MP alumina B – Super I (basic alumina) and MB alumina N – Super I (neutral alumina) from MP Biochemicals, Silica Gel 60M (Macherey-Nagel, 40-63 μm, 230-400 mesh) (using a Biotage® Isolera™ Spektra One automated system) or EM Science silica gel 60 (230-400 mesh). Reactions were monitored by TLC using Macherey-Nagel ALUGRAM® Xtra SIL G/UV254 aluminum plates, under UV visualization (254 or 366 nm), potassium permanganate or bromocresol green staining.

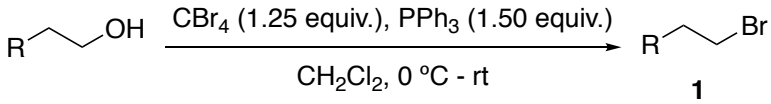
Benzylic photocarboxylation reactions were performed with 455 nm LEDs (OSRAM Oslon® SSL 80 royal- blue LEDs), which were installed at the bottom of a custom-made 6 vials holder (the distance between the flat-bottom of the vial and the light source was measured to be ~7 mm), equipped with a liquid cooling system (the thermostat was set @ 25°C) and a magnetic stirrer (~ 250 rpm). Primary carboxylation reactions were performed with 451 nm LEDs (OSRAM Oslon® SSL 80 royal- blue LEDs), which were installed at the bottom of a custom-made 8 flat-bottom Schlenk tubes holder (the distance between the flat-bottom Schlenk tube and the light source was measured to be ~7 mm), equipped with a liquid cooling system (the thermostat was set @ 10°C) and a magnetic stirrer (~ 500 rpm).


2 Synthesis of homobenzylic bromides

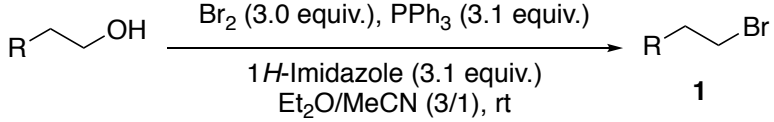
The homobenzylic bromide substrates **1b**,[1] **1c**,[2] **1d**,[3] **1e**,[4] **1f**,[5] **1i**,[6] **1j**,[7] **1l**,[8] **1m**,[9] **1n**[10] and **1o**[11] were synthesized according to the cited literature reports.

General procedure for the bromination of alcohols (GP1)



Following a procedure reported by Wills *et al.,*[12] in a round-bottom flask equipped with a teflon-coated stirring bar, the homobenzylic alcohol (1 equiv.) was dissolved in DCM (0.6 M) or DCM/MeCN (3/2, 0.6 M) or DCM/Et_2O (1/1, 0.6 M) and CBr_4 (1.25 equiv.) was added to the solution at 0 ºC. Then PPh_3 (1.5 equiv.) was added to the solution over 10 minutes. After stirring for 30 min at 0 ºC, the solution was warmed up to room temperature and continued stirring until disappearance of starting material (monitored by TLC). The reaction mixture was concentrated under reduced pressure and then the residue was stirred in diethyl ether for 10 min. The resulting precipitate was removed by filtration and the filtrate was concentrated under reduced pressure. The crude mixture was purified by flash column chromatography through silica (eluent = petroleum ether/ethyl acetate) to afford homobenzylic bromide (**1**).

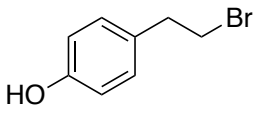
General procedure for the bromination of alcohols (GP2)



In a round-bottom flask equipped with a teflon-coated stirring bar, the homobenzylic alcohol (1.0 equiv.) was dissolved in dry Et_2O/MeCN (3/1, 0.1 M) under nitrogen atmosphere and then PPh_3 (3.1 equiv.) followed by 1*H*-imidazole (3.1 equiv.) was added to the solution. Then bromine (3.0 equiv.) was added to the reaction mixture dropwise over 10 minutes and then the resulting mixture was allowed to stir at rt until the disappearance of the starting material. The reaction mixture was filtered and rinsed with Et_2O. The organic layers were washed once with brine, dried over magnesium sulfate and the solvents were removed under reduced pressure. The crude mixture was purified by

flash column chromatography through silica (eluent = petroleum ether/ethyl acetate) to afford homobenzylic bromide (**1**).

4- (2- bromoethyl)phenol (1g)



1g

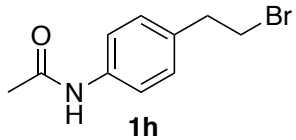
Following **GP1**, from 4-(2-hydroxyethyl)phenol (553 mg, 4.00 mmol), the homobenzyl bromide (**1g**) was obtained as white solid (588 mg, 2.92 mmol, 73% yield). [note: DCM/Et_2O (1/1, 0.6 M) was used as solvent for the reaction.]

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.13 – 7.04 (m, 2H), 6.84 – 6.73 (m, 2H), 4.75 (br, 1H), 3.52 (dd, *J* = 8.0, 7.3 Hz, 2H), 3.09 (t, *J* = 7.6 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 154.5, 131.4, 130.0, 115.6, 38.7, 33.6.

The experimental data are in agreement with the literature report.[13]

N- [4- (2- bromoethyl)phenyl]acetamide (1h)



1h

Following **GP1**, from *N*- [4- (2- hydroxyethyl)phenyl]acetamide (448 mg, 2.50 mmol), the homobenzyl bromide (**1h**) was obtained as white solid (551 mg, 2.28 mmol, 91% yield). *[note: DCM/MeCN (3/2, 0.6 M) was used as solvent for the reaction].* The product was purified by two times flash column chromatography (silica, CH_2Cl_2:MeOH = 100:0 to 95:5; silica, petroleum ether:ethyl acetate = 50:50).

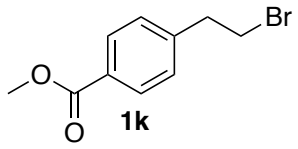
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.45 (d, *J* = 8.5 Hz, 2H), 7.24 (br, 1H), 7.16 (d, *J* = 8.4 Hz, 2H), 3.53 (t, *J* = 7.6 Hz, 2H), 3.12 (t, *J* = 7.6 Hz, 2H), 2.17 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 168.4, 136.8, 135.0, 129.4, 120.3, 38.9, 33.1, 24.7.

IR (ATR): ν = 3295, 2922, 2855, 1662, 1599, 1510, 1409, 1368, 1316, 1211, 1129, 1010, 962, 828, 719 cm^{-1}.

HRMS (ESI): m/z calc. for ($C_{10}H_{13}BrNO^+$) $[M+H]^+$: 242.0181; found: 242.0180.

Methyl 4- (2- bromoethyl)benzoate (1k)



1k

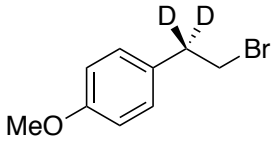
Following **GP2**, from methyl 4-(2-hydroxyethyl)benzoate (505 mg, 2.80 mmol), the homobenzyl bromide (**1k**) was obtained as light-orange colored oil (653 mg, 2.69 mmol, 96% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 8.08 – 7.90 (m, 2H), 7.31 – 7.24 (m, 2H), 3.90 (s, 3H), 3.57 (t, *J* = 7.4 Hz, 2H), 3.21 (t, *J* = 7.4 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 167.0, 144.1, 130.0, 128.9, 128.8, 52.2, 39.2, 32.3.

The experimental data are in agreement with the literature report.[14]

1- [2- Bromo(1,1)-*d_2*-ethyl]- 4- methoxybenzene (1e-d_2)



1e-d_2

Following **GP1**, from 2-(4-methoxyphenyl)ethan-2,2-*d_2*-1-ol (synthesized according to the literature report by Kang et al.)[15] (489 mg, 3.17 mmol), the homobenzyl bromide (**1e-d_2**) was obtained as light-orange oil (627 mg, 2.89 mmol, 91% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.17 – 7.09 (m, 2H), 6.90 – 6.82 (m, 2H), 3.80 (s, 3H), 3.51 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 158.7, 131.1, 129.8, 114.1, 55.4, 33.4.

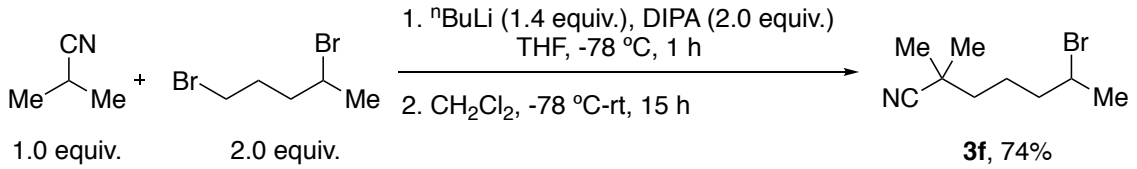
IR (ATR): ν = 2960, 2837, 1610, 1513, 1461, 1297, 1245, 1177, 1111, 1033, 954, 805, 745 cm^{-1}.

HRMS (ESI): m/z calc. for ($C_9H_9D_2{}^{79}OBr^+$) $[M]^+$: 216.0113; found: 216.0112; calc. for ($C_9H_9D_2O^{81}Br^+$) $[M]^+$: 218.0193; found: 218.0095.

3 Synthesis of secondary alkyl bromides

The secondary alkyl bromide substrates **3c**,[16] **3d**,[17] **3e**,[18] **3g**,[19] and **1j**[18] were synthesized according to the cited literature reports.

Synthesis of 6-Bromo-2,2-dimethylheptanenitrile (3f)



Diisopropylamine (2.02 g, 20 mmol) was dissolved in dry THF (35 mL) and cooled down to 0 ºC. n-BuLi (5.6 mL, 2.5M, 14 mmol) was added dropwise and the solution was cooled down to -78ºC. Isobutyronitrile (0.691g, 10.0 mmol) was added dropwise and stirred for 1 hour. This solution was then transferred dropwise to a solution of 1,4-dibromopentane (4.60g, 20 mmol) in THF (5 mL) at –78 ºC and stirred at –78 ºC for 2 h. Then, the reaction mixture was warmed up to rt and stirred overnight. The reaction was quenched with water and extracted with DCM. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography through silica gel (eluent: hexane/ethyl acetate = 9/1) to afford the pure product **3f** (1.62 g, 7.43 mmol, 74%) as a pale-yellow oil.

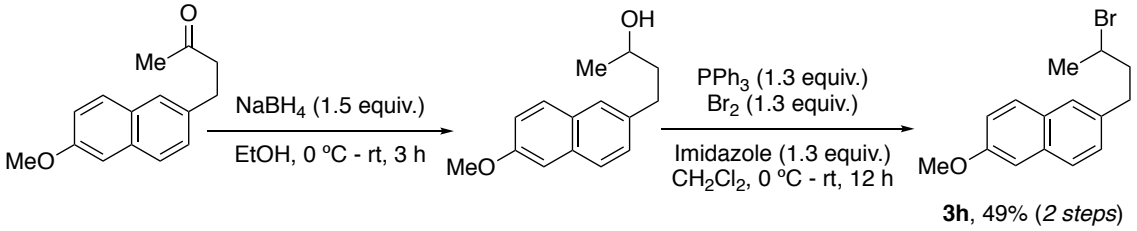
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 4.18 – 4.07 (m, 1H), 1.88 – 1.49 (m, 6H), 1.72 (d, *J* = 6.7 Hz, 3H), 1.35 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 125.1, 50.9, 40.9, 40.4, 32.4, 26.8, 26.7, 26.6, 23.7.

IR (ATR): ν = 2976, 2946, 2871, 2234, 1471, 1458, 1379, 1242, 1204, 1166 cm^{-1}.

HRMS (ESI): m/z calc. for ($C_9H_{17}BrN^+$) $[M+H]^+$: 218.0539; found: 218.0539.

Synthesis of 2-(3-bromobutyl)-6-methoxynaphthalene (3h)



3h, 49% (*2 steps*)

In an oven-dried Schlenk flash containing a magnetic stir bar under inert atmosphere, sodium borohydride (568 mg, 15.0 mmol, 1.5 equiv.) was added dropwise to the solution of Nabumetone (2.28 g, 10.0 mmol, 1.0 equiv.) in EtOH (28 mL) at 0 ºC. Once the addition is completed, the reaction mixture was allowed to warm up to rt and stirred for 3 h. The solvent was removed under the reduced pressure. The residue was dissolved in dichloromethane, washed with water, dried over $MgSO_4$ and concentrated under reduced pressure to get the pure alcohol (2.12 g, 9.18 mmol, 92%). The obtained alcohol was directly used in next step. In an oven-dried Schlenk flash containing a magnetic stir bar, triphenylphosphine (3.13 g, 11.94 mmol, 1.3 equiv.) was dissolved in dichloromethane (0.33M based on alcohol). After cooling the solution to 0 ºC, bromine (1.91 g, 11.94 mmol, 1.3 equiv.) was added dropwise and allowed to stir for 10 min to obtain a suspension. Then imidazole (813 mg, 11.94 mmol, 1.3 equiv.) followed by the alcohol substrate (2.12 g, 9.18 mmol, 1.0 equiv.) dissolved in dichloromethane (0.5M) was added to the suspension. The reaction mixture was allowed to warm up to rt and stirred overnight. The resulting reaction mixture was quenched with aq. 1M $NaHCO_3$ and extracted with dichloromethane (3 times). The combined organic phase was washed with brine solution, dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography through silica gel (eluent: hexane/ethyl acetate = 100/0-99/1) to afford the pure product **3h** (1.42 g, 4.86 mmol, 49%, two steps) as white solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.68 (d, *J* = 8.3 Hz, 2H), 7.58 (s, 1H), 7.31 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.16 – 7.12 (m, 1H), 7.12 (s, 1H), 4.16 – 4.05 (m, 1H), 3.92 (s, 3H), 3.05 – 2.83 (m, 2H), 2.28 – 2.06 (m, 2H), 1.75 (d, *J* = 6.7 Hz, 3H).

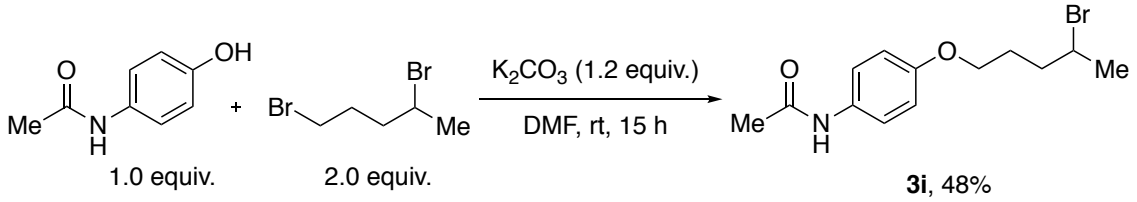
^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 157.4, 136.2, 133.2, 129.2, 129.1, 127.8, 127.1, 126.7, 119.0, 105.8, 55.4, 51.1, 42.8, 34.0, 26.7.

IR (ATR): ν = 2961, 2937, 2921, 1633, 1604, 1504, 1481, 1461, 1448, 1391, 1375, 1265, 1238, 1224, 1174, 1154, 1119, 1027, 848, 813, 614 cm^{-1}.

HRMS (ESI): m/z calc. for ($C_{15}H_{18}BrO^+$) $[M+H]^+$: 293.0536; found: 293.0540.

Melting Point: 58-60 ºC

Synthesis of *N*-(4-((4-bromopentyl)oxy)phenyl)acetamide (3i)



In a round-bottom flask containing a magnetic stir bar, paracetamol (756 mg, 5.0 mmol, 1.0 equiv.) and K_2CO_3 (830 mg, 6.0 mmol, 1.2 equiv.) in DMF (8.0 mL) was stirred at rt for 1 h. Then 1,4-dibromopentane (1.36 mL, 10 mmol, 2.0 equiv.) was added to the reaction mixture and stirred for overnight. The reaction mixture was diluted with water and extracted with dichloromethane. The combined organic layers were washed 2% NaOH aq. solution (2×20 mL) followed by water (2×20 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography through silica gel (eluent: hexane/ethyl acetate = 3/1) to afford the pure product **3i** (714 mg, 2.38 mmol, 48%) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.37 (d, *J* = 9.0 Hz, 2H),7.27 (bs, 1H), 6.83 (d, *J* = 9.0 Hz, 2H), 4.23 – 4.15 (m, 1H), 4.00 – 3.91 (m, 2H), 7.14 (s, 3H), 2.04 – 1.85 (m, 4H), 1.74 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 168.4, 155.9, 131.2, 122.1, 114.9, 67.5, 51.4, 37.8, 27.8, 26.7, 24.5.

IR (ATR): ν = 3296, 3258, 3198, 3140, 3095, 2954, 2901, 2855, 1660, 1604, 1548, 1506, 1474, 1411, 1233, 1214, 1173, 1031, 828, 754 cm^{-1}.

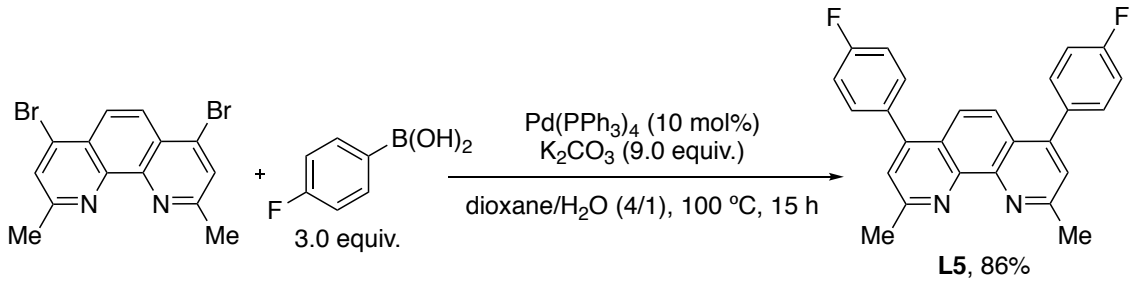
HRMS (ESI): m/z calc. for ($C_{13}H_{19}BrNO_2^+$) $[M+H]^+$: 300.0594; found: 300.0586.

Melting Point: 88-90 ºC

4 Synthesis of nitrogen-donor ligands

The ligand **L1** and **L7** were commercially available. The following ligands **L2**,[20] **L3**,[21][22] **L4**,[23] **L6**,[24] and **L9**[18] were synthesized according to the cited literature reports.

Synthesis of 4,7- bis(4- fluorophenyl)- 2,9- dimethyl- 1,10- phenanthroline (L5)



In a Schlenk tube equipped with a teflon-coated stirring bar, a suspension of 4,7-dibromo- 2,9- dimethyl- 1,10- phenanthroline (136 mg, 0.37 mmol, 1.0 equiv.), 4-fluorophenylboronic acid (156 mg, 1.1 mmol, 3.0 equiv.) and K_2CO_3 (462 mg, 3.34 mmol, 9.0 equiv.) in 1,4-dioxane:H_2O 4:1 (5 ml) was degassed by bubbling nitrogen for 5 min. Then $Pd(PPh_3)_4$ (46 mg, 37 µmol, 10 mol%) was added and the reaction mixture was stirred at 100°C for overnight under nitrogen atmosphere. The reaction was cooled down to room temperature. The reaction was purified by flash column chromatography through silica (eluent: petroleum ether:ethyl acetate 50:50 to 0:100) affording pure compound **L5** as a light-yellow solid (126 mg, 0.32 mmol, 86% yield).

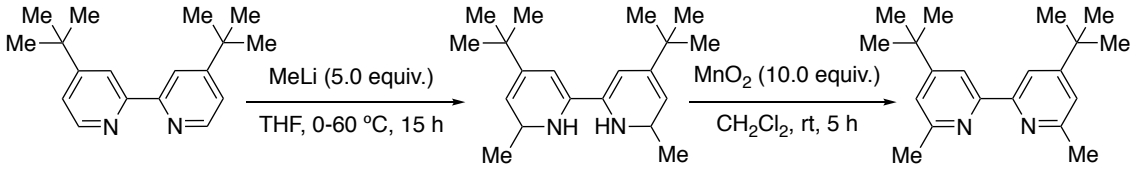
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.72 (s, 2H), 7.49 (m, 4H), 7.43 (s, 2H), 7.26 – 7.16 (m, 4H), 3.00 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 163.0 (d, $^1J(^{19}F\text{-}^{13}C)$ = 248.6 Hz), 159.0, 147.9, 145.6, 134.1 (d, $^4J(^{19}F\text{-}^{13}C)$ = 3.4 Hz), 131.5 (d, $^3J(^{19}F\text{-}^{13}C)$ = 8.1 Hz), 124.8, 124.3, 123.0, 115.8 (d, $^2J(^{19}F\text{-}^{13}C)$ = 21.5 Hz), 25.9.

^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = -113.23.

HRMS (ESI): m/z calc. for ($C_{26}H_{19}N_2F_2^+$) $[M+H]^+$: 397.1511; found: 397.1514.

Synthesis of 4,4'-di-*tert*-butyl-6,6'-dimethyl-2,2'-bipyridine (L8)



L8, 58% (2 steps)

To a solution of 4,4'-di-*tert*-butyl-2,2'-bipyridine (4.0 g, 15 mmol, 1.0 equiv.) in THF, MeLi (1.6 M) in diethyl ether (47 mL, 75 mmol, 5.0 equiv.) was dropwise added at 0 ºC. The resulting reaction mixture was heated at 60 ºC for overnight. The reaction mixture was cooled at rt and quenched with aq. NH_4Cl solution. The organic layers were extracted with DCM, washed with brine, dried with $MgSO_4$ and solvents were evaporated under reduced pressure. To the solution of compound in dichloromethane (0.3 M), activated MnO_2 (13.0 g, 150 mmol, 10.0 equiv.) was added and stirred at rt for 5 h. The reaction mixture was filtrated through celite and silica. The filtrate was concentrated and the crude was purified through silica gel (eluent: hexane/ethyl acetate = 4/1 – 1/1) to afford desired compound **L8** (2.58 g, 8.7 mmol, 58 %) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.13 (d, *J* = 1.5 Hz, 2H), 7.14 (d, *J* = 1.6 Hz, 2H), 2.63 (s, 6H), 1.37 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 161.0, 157.8, 156.6, 120.2, 115.7, 35.0, 30.8, 25.0.

IR (ATR): ν = 2959, 2905, 2870, 1591, 1557, 1477, 1390, 1360, 1290, 1222, 917, 862, 719, 619 cm^{-1}.

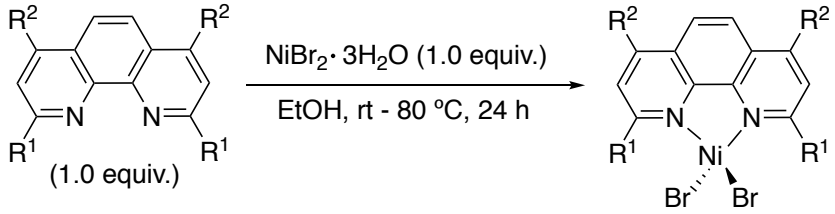
HRMS (ESI): m/z calc. for ($C_{20}H_{29}N_2^+$) $[M+H]^+$: 297.2325; found: 297.2325.

Melting Point: 190-192 ºC

5 Synthesis of (L)$NiBr_2$ complex

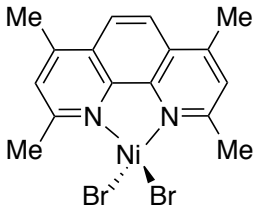
The following metal complexes (**L1**)$NiBr_2$,[25] (**L4**)$NiBr_2$[26] and (**L7**)$NiBr_2$[27] were synthesized according to the cited literature reports.

General procedure for the synthesis of L$NiBr_2$ complex (GP3)



Following a modified procedure reported by Budnikova *et al.,*[28] in a round-bottom flask equipped with a teflon-coated stirring bar, $NiBr_2 \cdot 3H_2O$ (1.0 equiv) was dissolved in absolute ethanol (0.17 M) under nitrogen atmosphere and then a solution of the ligand (1.0 equiv.) in absolute ethanol (0.17 M) was added dropwise over 10 minutes. The reaction mixture was stirred at rt – 80 ºC for 24 hours. The precipitate was filtered off, washed with absolute ethanol, diethyl ether and dried under high vacuum.

(2,4,7,9-tetramethyl-1,10-phenanthroline)nickel (II) dibromide [(L2)$NiBr_2$]

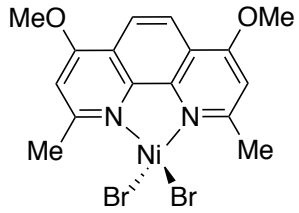


(**L2**)$NiBr_2$

Following **GP3**, pink-violet solid (49.5 mg, 20% yield) with **L2** was obtained.

HRMS (Q-TOF, ESI): m/z calc. for ($C_{16}H_{17}N_2Ni^+$) $[M-2Br+H]^+$: 295.0740; found: 295.0739. **Elemental Analysis:** Anal. calc. for $C_{16}H_{16}Br_2N_2Ni$: C, 42.25; H, 3.55; N, 6.16. Found: C, 41.86; H, 3.55; N, 5.89.

(4,7-dimethoxy-2,9-dimethyl-1,10-phenanthroline)nickel (II) dibromide [(L3)$NiBr_2$]

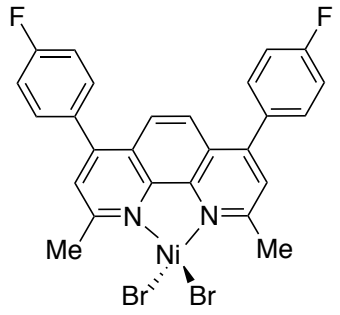


(**L3**)$NiBr_2$

Following **GP3**, pink-violet solid (203 mg, 75% yield) with **L3** was obtained.

HRMS (Q-TOF, ESI): m/z calc. for ($C_{16}H_{16}{}^{35}ClN_2NiO_2^+$) $[M\text{-}2Br+{}^{37}Cl]^+$: 361.0248; found: 361.0249; m/z calc. for ($C_{16}H_{16}{}^{37}ClN_2NiO_2^+$) $[M\text{-}2Br+{}^{37}Cl]^+$: 363.0213; found: 363.0213. **Elemental Analysis:** Anal. calc. for $C_{16}H_{16}Br_2N_2NiO_2$: C, 39.48; H, 3.31; N, 5.75. found: C, 39.61; H, 3.24; N, 5.59.

(4,7- bis(4- fluorophenyl)- 2,9- dimethyl- 1,10- phenanthroline)nickel (II) dibromide [(L5)$NiBr_2$]

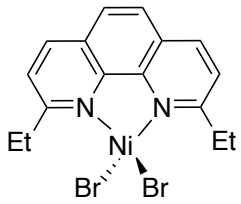


(**L5**)$NiBr_2$

Following **GP3**, blush pink solid (128 mg, 66% yield) with **L5** was obtained.

HRMS (Q-TOF, ESI): m/z calc. for ($C_{27}H_{19}F_2N_2O_2Ni^+$) $[M\text{-}2Br+HCO_2]^+$: 499.0763; found: 499.0765. **Elemental Analysis:** Anal. calc. for $C_{26}H_{18}F_2Br_2N_2Ni$: C, 50.78; H, 2.95; N, 4.56. Found: C, 50.72; H, 2.97; N, 4.48.

(2,9-diethyl-1,10-phenanthroline)nickel (II) dibromide [(L6)$NiBr_2$]



(**L6**)$NiBr_2$

Following **GP3**, violet solid (430 mg, 68% yield) with **L6** was obtained.

HRMS (Q-TOF, ESI): m/z calc. for ($C_{17}H_{17}N_2NiO_2^+$) $[M-2Br+HCO_2]^+$: 339.0638; found: 339.0639. **Elemental Analysis:** Anal. calc. for $C_{16}H_{16}Br_2N_2Ni$: C, 42.25; H, 3.55; N, 6.16. Found: C, 42.26; H, 3.61; N, 6.14.

6 Synthesis of additional reagents

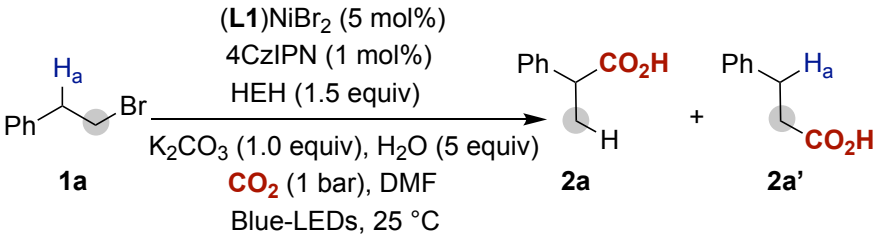
3,5- diethyl 2,6- dimethyl- 1,4- dihydropyridine- 3,5- dicarboxylate (Hantzsch ester, HEH) was synthesized according to the procedure reported by Christmann *et al.*[29]

2,4,5,6-Tetra(9*H*-carbazol-9-yl)isophthalonitrile (4CzIPN) was synthesized according to the procedure reported by Zhang *et al.*[30]

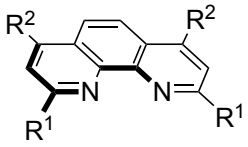
7 Optimizations of reaction conditions

7.1 General procedure for the photocarboxylation of 1a with CO_2

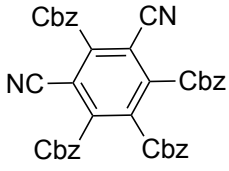
In an oven-dried flat-bottom vial equipped with a teflon-coated stirring bar, Hantzsch ester (1.0-2.0 equiv), 4-CzIPN (0.01 equiv), Ni-catalyst (0.05 equiv), base (1.0 equiv) and 4Å MS (50 mg) or additives were added and the vial was sealed with a PTFE septum. The vial was evacuated and back-filled under CO_2 flow at least three times. The solvent (2 ml) was added under CO_2 flow and then the system was degassed by applying vacuum for 3 min. Then the solution was saturated with CO_2 by bubbling the gas through the solvent for 3 min. Substrate **1a** (27.5 µl, 0.2 mmol, 1.0 equiv.) was added, then a CO_2 balloon was connected to the reaction vessel using a hypodermic needle and the reaction was irradiated under blue light (λ = 455 nm) for the indicated time. The reaction was quenched by the addition of HCl 2M (1 ml), then diluted with AcOEt (4 ml) and water (3 ml). The layers were separated, and the aqueous layer was extracted twice with AcOEt (4 ml each time). The combined organic layers were washed once again with water (2 ml), then with brine (2 ml) and the solvent removed under reduced pressure. The internal standard 1,3,5-trimethoxybenzene (approx. 15 mg) was added to the crude mixture and yield was determined by ^{1}H NMR analysis.



entry	deviation from standard conditions	yield (%)[a],[b]	2a:2a'
1	***none***	***66 (56)***	***90:10***
2	(**L2**)$NiBr_2$ instead of (**L1**)$NiBr_2$	36	70:30
3	(**L3**)$NiBr_2$ instead of (**L1**)$NiBr_2$	28	71:29
4	(**L4**)$NiBr_2$ instead of (**L1**)$NiBr_2$	30	62:38
5	(**L5**)$NiBr_2$ instead of (**L1**)$NiBr_2$	42	72:28
6	(**L6**)$NiBr_2$ instead of (**L1**)$NiBr_2$	55	85:15
7	$NiBr_2$·glyme/**L1** instead of (**L1**)$NiBr_2$	58	90:10
8	using HEH (1.0 equiv)	59	90:10
9	using HEH (2.0 equiv)	64	87:13
10[c]	using H_2O (10.0 equiv)	61	90:10
11	using 4Å MS instead of H_2O	50	85:15
12	using LiBr (1.0 equiv)	61	84:16
13	Cs_2CO_3 instead of K_2CO_3	35	42:58
14	no (**L1**)$NiBr_2$, no 4CzIPN or no light	0	—



R^1=Me; R^2=H (**L1**)
R^1=Me; R^2=Me (**L2**)
R^1=Me; R^2=OMe (**L3**)
R^1=Me; R^2=Ph (**L4**)
R^1=Me; R^2=4-F-C_6H_4 (**L5**)
R^1=Et; R^2=H (**L6**)



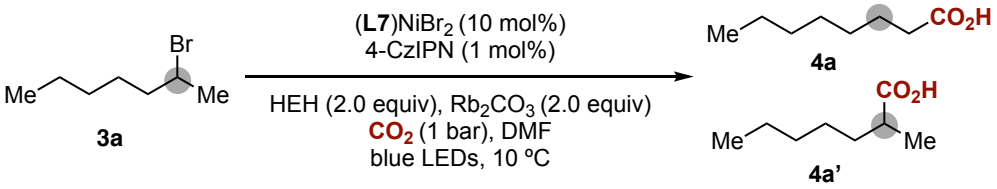
4CzIPN

Table S1: Optimization of the reaction conditions: **1a** (0.20 mmol), (**L1**)$NiBr_2$ (5 mol%), 4-CzIPN (1 mol%), HEH (1.5 equiv), K_2CO_3 (1.0 equiv), H_2O (5.0 equiv), CO_2 (1 bar), Blue-LEDs in DMF (0.1 M) at 25 ºC for 5 h. [a] Yields determined by NMR using 1,3,5-trimethoxybenzene as standard. [b] Isolated yield, average of two independent runs. [c] HEH (2.0 equiv) was used. DMF = dimethylformamide; Cz = carbazole; HEH = diethyl 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate.

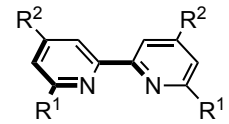
7.2 General procedure for the photocarboxylation of 3a with CO_2

An oven-dried Schlenk tube containing a magnetic stir bar was charged with $LNiBr_2$ (0.05-0.10 equiv.) or $NiBr_2$.glyme (0.10 equiv.) and ligand (**L**, 0.10 equiv), 4CzIPN (0.005-0.01 equiv.), Hantzsch ester (HEH, 2.00 equiv.) and the alkyl bromide (0.25 mmol, 1.00 equiv). The Schlenk tube was then taken inside a glovebox, where base (2.00 equiv.) was added. The tube was then taken out of the glovebox and connected to a vacuum line where it was evacuated and back-filled under CO_2 flow at least three times. Solvent (0.08M) was added under CO_2 flow. Once all the components were added, the Schlenk tube was closed at the atmospheric pressure of CO_2 (1 bar) and placed at a

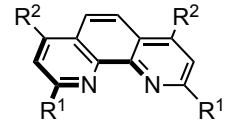
temperature-controlled photo-reactor maintained at 10 °C and stirred for 20 h in the presence of continuous light irradiation from blue LEDs (λ = 451 nm). The reaction mixture was quenched with 2M HCl aq. solution to release free acid by hydrolysis of carboxylate salt and diluted with ethyl acetate. The combined organic layers were extracted with ethyl acetate (at least three times), washed with water followed by brine solution. Anisole (27 µL) as internal standard was added to the solution and filtered through short pad of silica gel. The yield was determined by GC-FID analysis.



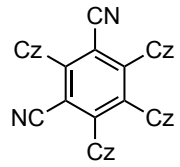
Entry	Deviation from standard conditions	Yield(%)[a],[b]	4a:4a'
1	***none***	***49 (48)***	***83:17***
2	$NiBr_2$.glyme (10%) & **L7**(10%)	38	85:15
3	$NiBr_2$.glyme (10%) & **L8**(10%)	15	83:17
4	$NiBr_2$.glyme (10%) & **L1**(10%)	26	89:11
5	$NiBr_2$.glyme (10%) & **L9**(10%)	24	74:26
6	***using TBAI (1.0 equiv.) as additive***	***44 (42)***	***99:1***
7	adding extra **L7**(10%)	38	83:17
8	(**L7**)$NiBr_2$ (5%) & 4-CzIPN (0.5%)	27	78:22
9	K_2CO_3 instead of Rb_2CO_3	34	82:18
10	no Rb_2CO_3	0	—
11	DMA instead of DMF	34	76:24
12	no (**L7**)$NiBr_2$, no 4-CzIPN, no light	0	—



R^1 = Me, R^2 = H (**L7**)
R^1 = Me, R^2 = ^{t}Bu (**L8**)



R^1 = Me, R^2 = H (**L1**)
R^1 = ^{n}Hex, R^2 = Ph (**L9**)



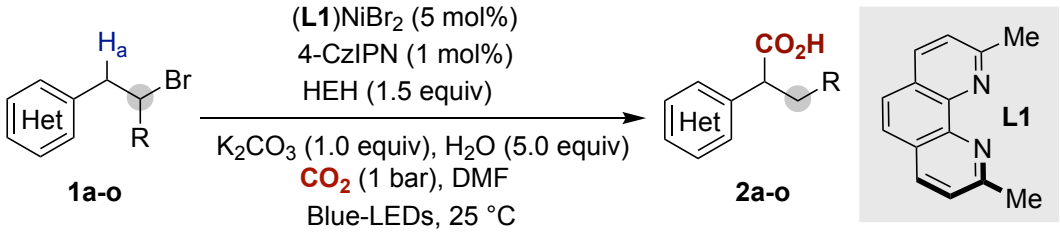
4-CzIPN

Table S2. Optimization of the reaction conditions. **3a** (0.25 mmol), (**L7**)$NiBr_2$ (10 mol%), 4-CzIPN (1 mol%), HEH (2.0 equiv), Rb_2CO_3 (2.0 equiv), CO_2 (1 bar), Blue-LEDs in DMF (0.08 M) at 10 °C for 20 h. [a] Yields determined by GC using anisole as standard. [b] Isolated yield, average of two independent runs.

8 Photocarboxylation of alkyl bromides with CO_2

8.1 Photocarboxylation reactions en route to aryl acetic acids

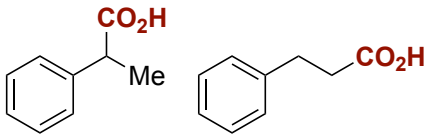
8.1.1 General procedure (GP4)



In an oven-dried flat-bottom vial equipped with a teflon-coated stirring bar, 4-CzIPN (0.01 equiv), (**L1**)$NiBr_2$ (0.05 equiv), K_2CO_3 (1.0 equiv) and Hantzsch ester (HEH, 1.5 equiv) were weighted and the vial was sealed with a PTFE septum. The vial was evacuated and back-filled under CO_2 flow at least three times. The solvent DMF (2 ml) was added under CO_2 flow and then the system was degassed by applying vacuum for 3 min. Then the solution was saturated with CO_2 by bubbling the gas through it for 3 min. Substrate **1a-o** (0.2 mmol, 1.0 equiv.) was added, then a CO_2 balloon was connected to the reaction vessel using a hypodermic needle and the reaction was irradiated under blue light (λ = 455 nm) for the indicated time. The reaction was quenched by the addition of HCl 2M (1 ml) and then diluted with ethyl acetate (4 ml) and water (3 ml). The layers were separated and the aqueous layer was extracted twice with ethyl acetate (4 ml each time). The combined organic layers were washed once again with water (2 ml) followed by brine (2 ml) and the solvent removed under reduced pressure. The residue was dissolved in diethyl ether (5 ml), which was extracted three times with aq. 1M NaOH (5 ml each time) and the combined water layers were washed twice with diethyl ether (5 ml each time), which was discarded. The water layer was acidified to pH = 2 with concentrated HCl, then extracted three times with ethyl acetate (10 ml each time). The combined organic layers were dried over sodium sulfate and the solvent was removed under reduced pressure affording a mixture of the branched and linear carboxylic acid (**2a-o**).

8.1.2 Characterization data

2-Phenylpropanoic acid (2a)/ 3-phenylpropanoic acid (2a')



2a **2a'**

Following **GP4**, an inseparable mixture (90:10) of **2a**/**2a'** from **1a** (0.2 mmol) was obtained as a colorless oil (17.0 mg, 0.11 mmol, 56% yield).

Following **GP5**, an inseparable mixture (23:77) of **2a**/**2a'** from **1a** (0.25 mmol) was obtained as a colorless oil (22.0 mg, 0.15 mmol, 59% yield).

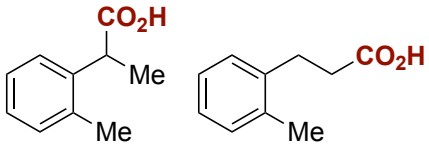
Branched acid 2a: **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) = 7.40-7.18 (s, 5H), 3.75 (q, *J* = 7.2 Hz, 1H), 1.52 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) = 180.9, 139.9, 128.8, 127.7, 127.5, 45.5, 18.2.

Linear acid 2a': **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) = 7.40-7.18 (s, 5H), 2.95 (t, *J* = 7.8 Hz, 2H), 2.68 (t, *J* = 7.8 Hz, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) = 179.3, 140.3, 128.7, 128.4, 126.5, 35.7, 30.7.

MS (ESI): m/z calc. for ($C_9H_{11}O_2^+$) $[M+H]^+$: 151.08; found: 151.08.

Spectroscopic data for **2a**/**2a'** match those previously reported in literature.[31]

2-(2-Methylphenyl)propanoic acid (2b) / 3-(2-methylphenyl)propanoic acid (2b')



2b **2b'**

Following **GP4**, an inseparable mixture (90:10) of **2b**/**2b'** from **1b** (0.2 mmol) was obtained as a light-yellow solid (17.0 mg, 0.10 mmol, 51% yield).

Branched acid 2b: **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.42 – 7.18 (m, 5H), 4.07 (q, *J* = 7.1 Hz, 1H), 2.47 (s, 3H), 1.58 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) = 180.5, 138.5, 136.0, 130.7, 127.3, 126.7, 126.6, 41.2, 19.8, 17.7.

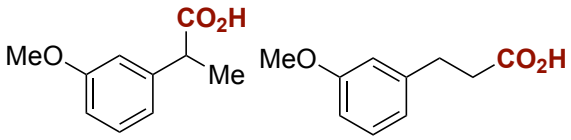
Linear acid 2b': **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.41 – 7.19 (m, 5H) [*overlapped with the major isomer*], 3.03 (dd, *J* = 8.9, 6.9 Hz, 2H), 2.72 (dd, *J* = 8.9, 7.1 Hz, 2H), 2.40

(s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.8, 138.4, 136.1, 130.5, 128.6, 126.7, 126.3, 34.4, 28.1, 19.4.

HRMS (ESI): m/z calc. for ($C_{10}H_{11}O_2^-$) $[M-H]^-$ 163.0765; found: 163.0767.

Spectroscopic data for **2b/2b'** match those previously reported in literature.[32],[33]

2-(3-Methoxyphenyl)propanoic acid (2c') / 3-(3-methoxyphenyl)propanoic acid (2c')



2c **2c'**

Following **GP4**, an inseparable mixture (85:15) of **2c**/**2c'** from **1c** (0.2 mmol) was obtained as a light-yellow gum (19.2 mg, 0.11 mmol, 52% yield).

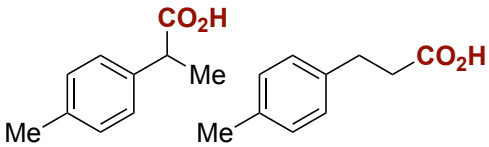
Branched acid 2c: **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) = 7.25 (t, *J* = 8.1 Hz, 1H), 6.94 – 6.89 (m, 1H), 6.88 (t, *J* = 2.1 Hz, 1H), 6.82 (ddd, *J* = 8.2, 2.6, 1.0 Hz, 1H), 3.81 (s, 3H), 3.72 (q, *J* = 7.2 Hz, 1H), 1.51 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) = 180.5, 159.9, 141.4, 129.8, 120.1, 113.6, 112.8, 55.4, 45.5, 18.2.

Linear acid 2c': **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) = 7.24 – 7.17 (m, 1H) [*overlapped with the major isomer*], 6.79 – 6.73 (m, 3H), 3.79 (s, 3H), 2.93 (t, *J* = 7.8 Hz, 2H), 2.72 – 2.61 (m, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) = 179.0, 159.8, 141.9, 129.7, 120.7, 114.2, 111.8, 55.3, 35.6, 30.7.

HRMS (ESI): m/z calc. for ($C_{13}H_{11}O_3^-$) $[M-H]^-$: 179.0714; found: 179.0718.

Spectroscopic data for **2c**/**2c'**match those previously reported in literature.[31]

2-(4-Methylphenyl)propanoic acid (2d)/ 3-(4-methylphenyl)propanoic acid (2d')



2d **2d'**

Following **GP4**, an inseparable mixture (93:7) of **2d**/**2d'** from **1d** (0.2 mmol) was obtained as an off-white solid (16.1 mg, 0.10 mmol, 48% yield).

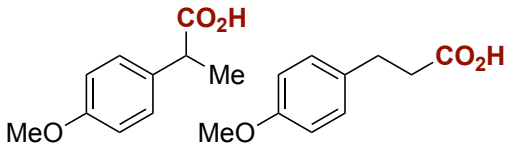
Branched acid 2d: **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) = 7.28 – 7.19 (m, 2H), 7.18 – 7.09 (m, 2H), 3.71 (q, *J* = 7.1 Hz, 1H), 2.34 (s, 3H), 1.50 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) = 180.7, 137.2, 137.0, 129.5, 127.6, 45.0, 21.2, 18.2.

Linear acid 2d': **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) = 7.29 – 7.18 (m, 2H) [overlaps with the major isomer], 7.18 – 7.08 (m, 2H) [overlaps with the major isomer], 2.91 (t, *J* = 7.7 Hz, 2H), 2.65 (t, *J* = 7.8 Hz, 2H), 2.33 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 136.0, 129.3, 128.3, 35.8, 30.3, 21.1. *[Note: Some signals are overlapped with the major isomer]*

HRMS (ESI): m/z calc. for ($C_{10}H_{11}O_2^-$) $[M-H]^-$: 163.0765; found: 163.0767.

Spectroscopic data for **2d/2d'** match those previously reported in literature.[31],[34]

2-(4-Methoxyphenyl)propanoic acid (2e) / 3-(4-methoxyphenyl)propanoic acid (2e')



2e **2e'**

Following **GP4**, an inseparable mixture (90:10) of **2e**/**2e'** from **1e** (0.2 mmol) was obtained as a light yellow solid (20.6 mg, 0.11 mmol, 57% yield).

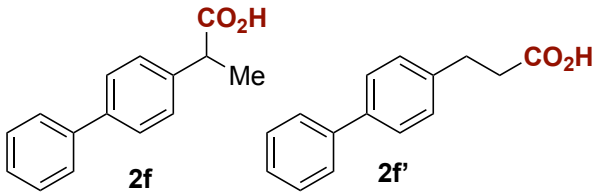
Branched acid 2e: **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) = 7.29 – 7.21 (m, 2H), 6.91 – 6.85 (m, 2H), 3.80 (s, 3H), 3.69 (q, *J* = 7.2 Hz, 2H), 1.49 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) = 181.1, 159.0, 132.0, 128.7, 114.2, 55.4, 44.6, 18.3.

Linear acid 2e': **^{1}H NMR (300 MHz, $CDCl_3$)** δ (ppm) = 7.16 – 7.08 (m, 2H), 6.85 – 6.80 (m, 2H), 3.79 (s, 3H), 2.89 (t, *J* = 7.7 Hz, 2H), 2.65 (t, *J* = 7.7 Hz, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) = 179.3, 158.21, 132.3, 129.4, 114.1, 36.0, 29.8. [*Note: One signal is overlapped with the other isomer.*]

MS (ESI): m/z calc. for ($C_{10}H_{13}O_3^+$) $[M+H]^+$: 181.09; found: 181.09.

Spectroscopic data for **2e**/**2e'** match those previously reported in literature.[31],[33]

2-{[1,1'-Biphenyl]-4-yl}propanoic acid (2f) / 3-{[1,1'-biphenyl]-4-yl}propanoic acid (2f')



2f **2f'**

Following **GP4**, an inseparable mixture (90:10) of **2f**/**2f'** from **1f** (0.2 mmol) was obtained as a white solid (20.5 mg, 0.09 mmol, 45% yield).

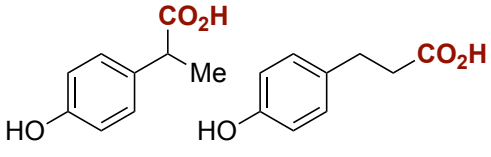
Branched acid 2f: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.62 – 7.54 (m, 4H), 7.49 – 7.32 (m, 5H), 3.81 (q, *J* = 7.2 Hz, 1H), 1.58 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) = 180.8, 140.8, 140.5, 138.9, 128. 9, 128.2, 127.6, 127.4, 127.2, 45.2, 18.3.

Linear acid 2f': ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.62 – 7.52 (m, 4H), 7.48 – 7.28 (m, 5H), 3.01 (t, *J* = 7.9 Hz, 2H), 2.73 (t, *J* = 7.9 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) = 179.2, 141.0, 139.5, 139.3, 128. 9, 128.8, 127.4, 127.3, 127.1, 35.6, 30.3.

MS (ESI): m/z: calc. for ($C_{15}H_{15}O_2^+$) $[M+H]^+$: 227.10; found: 227.10 (100%), 228.11 (16.2%), 229.11 (1.7%).

Spectroscopic data for **2f**/**2f'**match those previously reported in literature.[31],[35]

2-(4-Hydroxyphenyl)propanoic acid (2g) / 3-(4-hydroxyphenyl)propanoic acid (2g')



2g **2g'**

Following **GP4**, an inseparable mixture (85:15) of **2g**/**2g'** from **1g** (0.2 mmol) was obtained as a light crystalline solid (23.1 mg, 0.14 mmol, 70% yield).

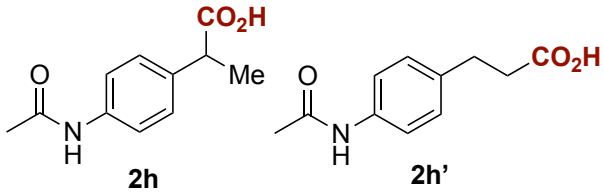
Branched acid 2g: ^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ (ppm) = 8.22 (br, 1H), 7.19 – 7.13 (m, 2H), 6.83 – 6.77 (m, 2H), 3.65 (q, *J* = 7.1 Hz, 1H), 1.39 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, Acetone-*d*$_6$)** δ (ppm) = 176.0, 157.2, 133.0, 129.3, 116.1, 44.9, 19.2.

Linear acid 2g': ^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ (ppm) = 8.08 (br, 1H), 7.07 (m, 2H), 6.76 – 6.73 (m, 2H), 2.81 (d, *J* = 7.5 Hz, 2H), 2.55 (d, *J* = 7.8 Hz, 2H). **^{13}C NMR (101 MHz, Acetone-*d*$_6$)** δ (ppm) = 174.1, 138.4, 132.6, 130.1, 115.4, 36.4, 30.8.

HRMS (ESI): m/z: calc. for ($C_9H_{10}O_3^-$) [M-H]$^-$: 165.0557; found: 165.0559.

Spectroscopic data for **2g**/**2g'** match those previously reported in literature.[31],[36]

2- (4- Acetamidophenyl)propanoic acid (2h) / 3- (4- acetamidophenyl)propanoic acid (2h')



Following **GP4**, an inseparable mixture (90:10) of **2h**/**2h'** from **1h** (0.2 mmol) was obtained as an off-white solid (27.0 mg, 0.13 mmol, 65% yield).

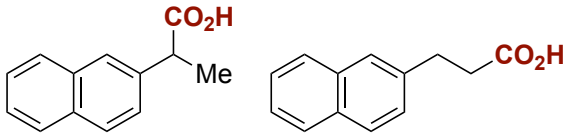
Branched acid 2h: ^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ (ppm) = 9.13 (br, 1H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 3.70 (q, *J* = 7.1 Hz, 1H), 2.06 (s, 3H), 1.41 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, Acetone-*d*$_6$)** δ (ppm) = 175.8, 139.4, 137.0, 128.6, 120.1, 45.3, 24.3, 19.2.

Linear acid 2h': ^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ (ppm) = 9.13 (br, 1H) *[overlapped with the major isomer],* 7.54 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 2.86 (t, *J* = 7.4 Hz, 2H), 2.58 (t, *J* = 8.0 Hz, 2H), 2.06 (s, 3H) [*overlapped with the major isomer].* **^{13}C NMR (101 MHz, Acetone-*d*$_6$)** δ (ppm) = 168.9, 139.3, 137.0 [*overlapped with the major isomer*], 129.4, 120.0, 36.1, 24.3, 20.6.

HRMS (ESI): m/z calc. for ($C_{11}H_{14}NO_3^+$) [M+H]$^+$ 208.0968 ; found: 208.0970.

IR (ATR): ν = 3321, 2926, 2859, 1692, 1644, 1595, 1536, 1454, 1405, 1316, 1256, 1211, 1182, 1118, 1074, 969, 839, 798, 745, 690 cm^{-1}.

2- (Naphthalen- 2- yl)propanoic acid (2i)/ 3- (naphthalen- 2- yl)propanoic acid (2i')



2g **2g'**

Following **GP4**, an inseparable mixture (93:7) of **2i**/**2i'** from **1i** (0.2 mmol) was obtained as a white solid (20.0 mg, 0.10 mmol, 49% yield).

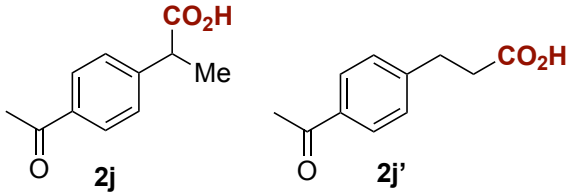
Branched acid 2i: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.86 – 7.78 (m, 3H), 7.77 (s, 1H), 7.53 – 7.40 (m, 3H), 3.92 (q, *J* = 7.1 Hz, 1H), 1.62 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) = 180.7, 137.3, 133.5, 132.8, 128.5, 128.0, 127.8, 126.5, 126.4, 126.1, 125.8, 45.6, 18.3.

Linear acid 2i': ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.89 – 7.70 (m, 4H), 7.47 (m, 3H), 3.12 (t, *J* = 7.8 Hz, 2H), 2.78 (t, *J* = 7.8 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) = 179.1, 137.7, 133.7, 132.3, 128.3, 127.7, 127.0, 126.6, 126.2, 125.6, 35.6, 30.8. [*Note: Some peaks are overlapped with the major isomer.*]

HRMS (ESI): m/z calc. for ($C_{13}H_{11}O_2^-$) [M-H]$^-$: 199.0765; found: 199.0766.

Spectroscopic data for **2i**/**2i'** match those previously reported in literature.[32]

2- (4- Acetylphenyl)propanoic acid (2j)/ 3- (4- acetylphenyl)propanoic acid (2j')



2j **2j'**

Following **GP4**, an inseparable mixture (85:15) of **2j**/**2j'** from **1j** (0.2 mmol) was obtained as a light-yellow gum (20.4 mg, 0.11 mmol, 53% yield).

Branched acid 2j: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.92 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 3.81 (q, *J* = 7.2 Hz, 1H), 2.59 (s, 3H), 1.54 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) = 198.0, 179.5, 145.2, 136.4, 128.9, 128.1, 45.5, 26.7, 18.1.

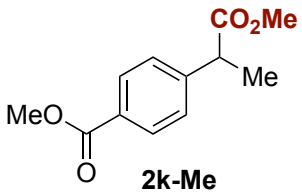
Linear acid 2j': ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.88 (dd, *J* = 8.1Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 3.00 (t, *J* = 7.6 Hz, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.58 (s, 3H). **^{13}C**

NMR (101 MHz, $CDCl_3$) δ (ppm) = 198.1, 178.3, 146.0, 135.6, 128.9, 128.7, 35.1, 30.6, 26.7.

MS (ESI): m/z calc. for ($C_{12}H_{11}O_2^+$) $[M+H]^+$: 193.08; found: 193.09 (100%), 194.09 (10.8%), 195.09 (1.1%).

Spectroscopic data for **2j**/**2j'** match those previously reported in literature.[31], [35]

Methyl 2- [4- (methoxycarbonyl)phenyl]propanoate (2k-Me)



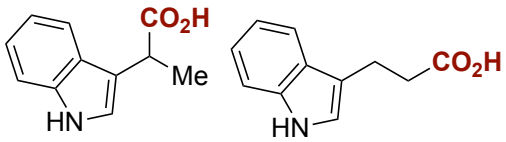
2k-Me

The product was obtained following **GP5**, then the crude carboxylic acid was converted into the corresponding methyl ester by treatment with a 2 M solution of $TMSCH_2N_2$ (in Et_2O) and purified by column chromatography, obtaining a colourless gum (21.0 mg, 0.09 mmol, 48% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 8.03 – 7.96 (m, 2H), 7.40 – 7.33 (m, 2H), 3.91 (s, 3H), 3.78 (q, *J* = 6.9 Hz, 1H), 3.67 (s, 3H), 1.52 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) = 174.3, 166.8, 145.6, 130.0, 129.1, 127.6, 52.2, 52.1, 45.5, 18.4.

Spectroscopic data for **2k-Me** match those previously reported in literature.[37]

2- (1*H*- Indol- 3- yl)propanoic acid (2m) / 3- (1H- indol- 3- yl)propanoic acid (2m')



2l **2l'**

Following **GP4**, an inseparable mixture (80:20) of **2l**/**2l'** from **1l** (0.2 mmol) was obtained as a light-orange gum (14.3 mg, 0.08 mmol, 38% yield).

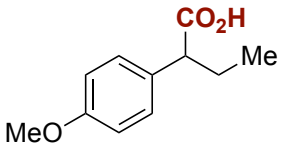
Branched acid 2l: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.09 (br, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.38 – 7.34 (m, 1H), 7.23-7.18 (m, 1H), 7.17 – 7.11 (m, 2H), 4.05 (q, *J* = 7.2 Hz, 1H), 1.63 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) = 180.8, 136.3, 126.5, 122.5, 121.9, 119.9, 119.4, 115.0, 111.4, 37.0, 17.6.

Linear acid 2l': ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.94 (s, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.22 – 7.17 (m, 1H), 7.17 – 7.10 (m, 2H), 3.10 (d, *J* = 7.7 Hz, 2H), 2.76 (t, *J* = 7.7 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) = 179.3, 136.4, 127.2, 122.2, 121.6, 119.5, 118.7, 114.7, 111.3, 34.7, 20.5. [*Note: Some peaks are overlapped with the major isomer.*]

HRMS (ESI): m/z: calc. for ($C_{11}H_{11}N_2O_2^+$) $[M+H]^+$: 190.0863; found: 190.0863.

Spectroscopic data for **2l**/ **2l'** match those previously reported in literature.[38],[39]

2- (4- Methoxyphenyl)butanoic acid (2m)



2m

Following **GP4**, an **2m** from **1m** (0.2 mmol) was obtained as a light tan solid (5.1 mg, 22% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.25 – 7.21 (m, 2H), 6.88 – 6.83 (m, 2H), 3.79 (s, 3H), 3.41 (t, *J* = 7.7 Hz, 1H), 2.14-2.00 (m, 1H), 1.85 – 1.70 (m, 1H), 0.90 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) =179.7, 159.1, 130.6, 129.2, 114.2, 55.4, 52.5, 26.5, 12.2.

Spectroscopic data for **2m** match those previously reported in literature.[40]

8.1.3 Scale up reaction for the photocarboxylation of 1a

In a 100 ml Schlenk flask equipped with a teflon-coated stirring bar, a rubber septum and a CO_2 inlet, Hantzsch ester (1.39 g, 5.5 mmol, 1.5 equiv.), 4-CzIPN (29 mg, 36 µmol, 0.01 equiv.), (**L1**)$NiBr_2$ (78 mg, 183 µmol, 0.05 equiv.) and K_2CO_3 (506 mg, 3.7 mmol, 1.0 equiv.) were added and then the system was purged-refilled three times with CO_2. DMF (36 ml) and water (330 µl) were added, then vacuum was applied under stirring for 3 min followed by CO_2 bubblimg for 5 min using a metal needle. Phenylethyl bromide **1a** (500 µl, 3.7 mmol, 1.0 equiv.) was added via a syringe, then the reaction was placed in a custom-made photoreactor and irradiated with 450 nm 12 LEDs array while CO_2 was constantly bubbled-through the solution. A cooling fan allowed to maintain the temperature of the reaction below 30°C. After 9 hours the bubbling was stopped and the CO_2 atmosphere was maintained for additional 15 h. After completion of the reaction, most of the solvent was removed under reduced pressure. The residue was partitioned between ethyl acetate (40 ml) and 2M HCl (20 ml), then the water layer was extracted twice more with ethyl acetate (40 ml each time). The combined organic layers were dried over magnesium sulfate, then the solvent was removed under reduced pressure. The residue was suspended in diethyl ether (40 ml), then extracted three times with 1M NaOH solution (40 ml each time) and the combined aqueous layers were washed twice with Et_2O (40 ml each time). The water layer was acidified up to pH = 2 by the careful addition of concentrated HCl and then it was extracted three times with ethyl acetate (75 ml each time). The combined organic layers were dried over magnesium sulfate, then the solvent was removed under reduced pressure to afford hydratropic acid **2a** as a light-yellow viscous oil (265 mg, 48% yield).

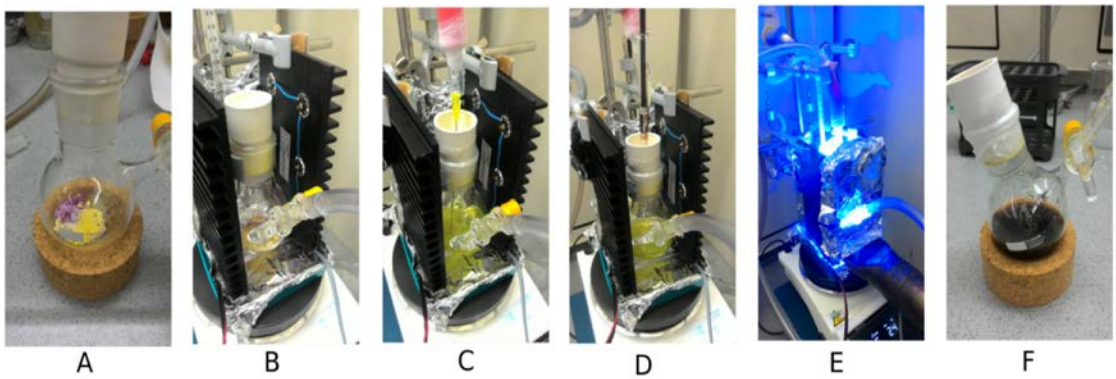
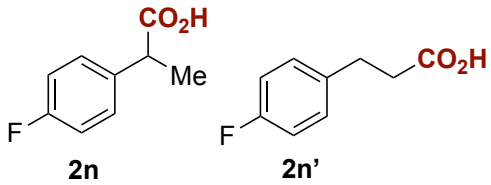


Figure S1: Experimental set-up for the millimolar scale carboxylation.

8.1.4 Additional examples

2- (4- fluorophenyl)propanoic acid (2n) / 3- (4- fluorophenyl)propanoic acid (2n')



2n **2n'**

Following **GP4**, an inseparable mixture (85:15) of **2n**/**2n'** from **1n** (0.2 mmol) was obtained as a light-yellow gum (13.1 mg, 0.08 mmol, 39% yield).

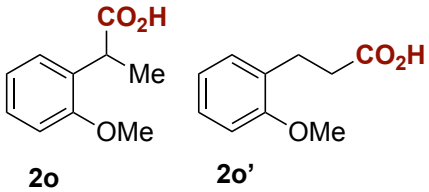
Branched acid 2n: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.29 (m, 2H), 7.06 – 6.99 (m, 2H), 3.73 (q, *J* = 7.2 Hz, 1H), 1.51 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) = 180.5, 162.3 (d, $^{1}J(^{19}F\text{-}^{13}C)$ = 245.8 Hz), 135.5 (d, $^{4}J(^{19}F\text{-}^{13}C)$ = 3.3 Hz), 129.3 (d, $^{3}J(^{19}F\text{-}^{13}C)$ = 8.2 Hz), 115.7 (d, $^{2}J(^{19}F\text{-}^{13}C)$ = 21.4 Hz), 44.7, 18.4. **^{19}F NMR (376 MHz, $CDCl_3$)** δ (ppm) = -115.3.

Linear acid 2n': ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.19 – 7.12 (m, 2H), 7.00 (m, 2H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.65 (t, *J* = 7.6Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ (ppm) = 178.9, 161.5 (d, $^{1}J(^{19}F\text{-}^{13}C)$ = 241.7 Hz), 135.9 (d, $^{4}J(^{19}F\text{-}^{13}C)$ = 3.1 Hz), 129.9 (d, $^{3}J(^{19}F\text{-}^{13}C)$ = 8.0 Hz), 115.4 *[overlapped multiplet with the other isomer]*, 35.8, 29.9. **^{19}F NMR (376 MHz, $CDCl_3$)** δ (ppm) = -116.9.

MS (ESI): m/z calc. for ($C_9H_{10}O_2F^+$) $[M+H]^+$ 169.06; found: 169.07 (100%), 170.07 (9.1), 171.07 (0.8).

Spectroscopic data for **2n**/**2n'** match those previously reported in literature.[31]

2- (2- Methoxyphenyl)propanoic acid (2o) / 3- (2- methoxyphenyl)propanoic acid (2o')



2o **2o'**

Following **GP4**, an inseparable mixture (90:10) of **2o**/**2o'** from **1o** (0.2 mmol) was obtained as a white solid (12.2 mg, 0.07 mmol, 34% yield).

Branch acid 2o: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.31 – 7.22 (m, 2H), 6.96 (td, *J* = 7.5, 1.1 Hz, 1H), 6.89 (dd, *J* = 8.6, 1.1 Hz, 1H), 4.09 (q, *J* = 7.2 Hz, 1H), 3.83 (s, 3H),

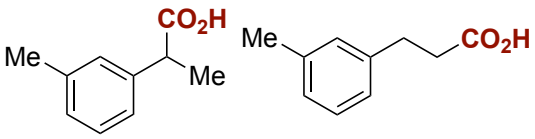
1.49 (d, J = 7.2 Hz, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) = 180.8, 156.8, 128.8, 128.5, 128.1, 120.9, 110.9, 55.6, 39.2, 17.0.

Linear acid 2o': ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.22 – 7.11 (m, 2H), 6.87 (m, 2H), 3.82 (s, 3H), 2.94 (t, J = 7.7 Hz, 2H), 2.71 – 2.62 (m, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) = δ 130.1, 128.6, 127.8, 120.5, 110.3, 55.3, 34.0, 26.0. *[Note: Some signals are below the detection limit or overlap with the major isomer.]*

HRMS (ESI): m/z calc. for ($C_{10}H_{11}O_3^-$) [M-H]$^-$: 179.0714; found: 179.0716.

Spectroscopic data for **2o**/**2o'** match those previously reported in literature.[41],[42]

2- (3- methylphenyl)propanoic acid / 3- (3- methylphenyl)propanoic acid (2c)



2o **2o'**

Following **GP4**, an inseparable mixture (90:10) of **2p**/**2p'** from **1p** (0.2 mmol) was obtained as a light-yellow gum (14.0 mg, 0.09 mmol, 43% yield).

Branch acid 2p: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.26 – 7.19 (m, 1H), 7.16 – 6.95 (m, 3H), 3.71 (q, J = 7.2 Hz, 1H), 2.35 (s, 3H), 1.50 (d, J = 7.2 Hz, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) = 180.7, 139.8, 138.5, 128.7, 128.4, 128.3, 124.7, 45.4, 21.6, 18.2.

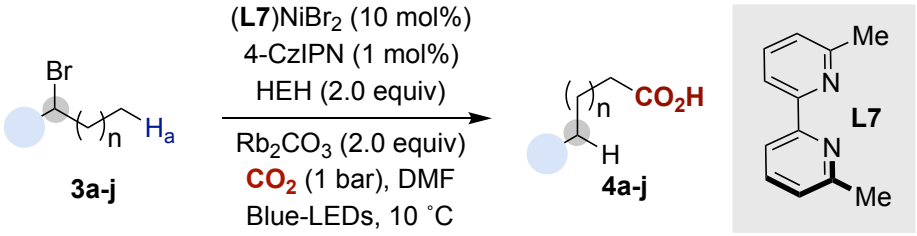
Linear acid 2p': ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.26 – 7.17 (m, 1H), 7.17 – 6.89 (m, 4H), 2.91 (t, J = 7.8 Hz, 1H), 2.67 (d, J = 7.8 Hz, 1H), 2.33 (s, 2H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ (ppm) = 179.1, 140.2, 138.3, 129.2, 128.6, 127.2, 125.4, 45.4, 35.7, 30.5. *[Note: Some signals are overlapped with the major isomer.]*

HRMS (ESI): m/z calc. for ($C_{10}H_{12}O_2Na^+$) [M+Na]$^+$: 187.0730 ; found: 187.0728.

Spectroscopic data for **2p**/**2p'** match those previously reported in literature.[41],[31]

8.2 Photocarboxylation reactions en route to primary carboxylic acids

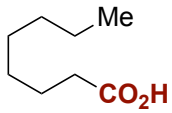
8.2.1 General procedure (GP5)



An oven-dried Schlenk tube containing a magnetic stir bar was charged with (**L7**)$NiBr_2$ (0.10 equiv.), 4-CzIPN (0.01 equiv.), Hantzsch ester (HEH, 2.00 equiv.), tetra-*n*-butylammonium iodide (TBAI, 1.00 equiv., if it is necessary) and the alkyl bromide (1.00 equiv., if it is solid). The Schlenk tube was then taken inside a glovebox, where Rb_2CO_3 (2.00 equiv) was added. The tube was then taken out of the glovebox and connected to a vacuum line where it was evacuated and back-filled under CO_2 flow at least three times. The alkyl bromide (1.0 equiv, if it is liquid) and DMF (0.08M) were added under CO_2 flow. Once all the components were added, the Schlenk tube was closed at the atmospheric pressure of CO_2 (1 bar) and placed at a temperature-controlled photo-reactor maintained at 10 ºC and stirred for 20 h in the presence of continuous light irradiation from blue LEDs (λ = 451 nm). The reaction mixture was quenched with 2 M HCl aq. solution to release free acid by hydrolysis of carboxylate salt and diluted with ethyl acetate. The combined organic layers were extracted with ethyl acetate (at least three times), washed with water followed by brine solution, dried over $MgSO_4$ and concentrated under reduced pressure. Then the crude mixture was dissolved in diethyl ether and the organic phase was three times extracted with aq. 1M NaOH solution. The combined aqueous phase was washed once again with diethyl ether and neutralized to pH = 2 using 2 M HCl aqueous solution. Finally, the acidic aqueous phase was three times extracted with ethyl acetate. The removal of solvent under reduced pressure delivered the pure carboxylic acid.

8.2.2 Characterization data

1-Octanoic acid (4a).



4a

Following **GP5** starting from 2-Bromoheptane (**3a**, 44.8 mg, 0.25 mmol) afforded the title compound **4a** as a colorless oil (17.30 mg, 0.12 mmol, 48 %) in 83:17 rr.

Following **GP5** starting from 2-Bromoheptane (**3a**, 44.8 mg, 0.25 mmol) in the presence of TBAI (92.6 mg, 0.25 mmol, 1.0 equiv.) as additive afforded the title compound **4a** as a colorless oil (17.30 mg, 0.12 mmol, 48 %) in 99:1 rr.

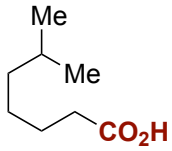
Following **GP5** starting from 3-Bromoheptane (**3a**, 44.8 mg, 0.25 mmol) in the presence of TBAI (92.6 mg, 0.25 mmol, 1.0 equiv.) as additive afforded the title compound **4a** as a colorless oil (15.3 mg, 0.106 mmol, 42 %) in 99:1 rr.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.35 (t, *J* = 7.5 Hz, 2H), 1.67 – 1.60 (m, 2H), 1.35 – 1.25 (m, 8H), 0.88 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 180.2, 34.3, 31.8, 29.2, 29.1, 24.9, 22.7, 14.2.

Spectroscopic data for **4a** match those previously reported in literature.[18]

6-Methylheptanoic acid (4b).



4b

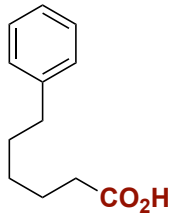
Following **GP5** starting from 2-Bromo-5-methylhexane (**3b**, 44.5 mg, 0.25 mmol) in the presence of TBAI (92.6 mg, 0.25 mmol, 1.0 equiv.) as additive afforded the title compound **4b** as a light-yellow oil (16.0 mg, 0.111 mmol, 44 %) in 99:1 rr.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.35 (t, *J* = 7.5 Hz, 2H), 1.62 (p, *J* = 7.5 Hz, 2H), 1.57 – 1.49 (m, 1H), 1.38 – 1.30 (m, 2H), 1.21 – 1.16 (m, 2H), 0.87 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 179.7, 38.7, 34.1, 28.0, 27.0, 25.1, 22.7.

Spectroscopic data for **4b** match those previously reported in literature.[43]

6-Phenylhexanoic acid (4c).



4c

Following **GP5** starting from (4-bromopentyl)benzene (**3c**, 56.8 mg, 0.25 mmol) afforded the title compound **4c** as a light-yellow oil (25.0 mg, 0.13 mmol, 52 %) in 99:1 rr.

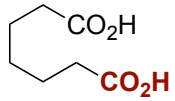
Following **GP4**, the title compound **4c** from (4-bromopentyl)benzene (**3c**, 56.8 mg, 0.25 mmol) was obtained as a light-yellow oil (3.0 mg, 0.02 mmol, 6%). No benzylic carboxylation product was detected.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.35 – 7.27 (m, 2H), 7.20 – 7.16 (m, 3H), 2.36 (t, *J* = 7.6 Hz, 2H), 2.36 (t, *J* = 7.5 Hz, 2H), 1.73 – 1.60 (m, 4H), 1.45 – 1.34 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 180.2, 142.6, 128.5, 128.4, 125.8, 35.8, 34.1, 31.2, 28.8, 24.7.

Spectroscopic data for **4c** match those previously reported in literature.[44]

Heptanedioic acid (4d).



4d

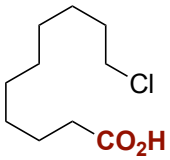
Following **GP5** starting from Methyl 5-bromohexanoate (**3d**, 52.3 mg, 0.25 mmol) afforded the title compound **4d** as a light-yellow viscous liquid (16.0 mg, 0.10 mmol, 40 %) in 99:1 rr upon hydrolysis of ester during work-up.

^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) = 12.00 (s, 2H), 2.19 (t, *J* = 7.3 Hz, 4H), 1.53 – 1.43 (m, 4H), 1.33 – 1.21 (m, 2H).

^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) = 174.4, 33.5, 28.1, 24.2.

Spectroscopic data for **4d** match those previously reported in literature.[45]

10-Chlorodecanoic acid (4e).



4e

Following **GP5** starting from 8-Bromo-1-chlorononane (**3e**, 60.4 mg, 0.25 mmol) afforded the title compound **4e** as a colorless oil (29.0 mg, 0.14 mmol, 56 %) in 80:20 rr.

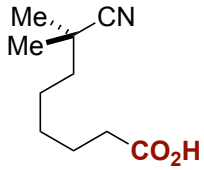
Following **GP-5** starting from 8-Bromo-1-chlorononane (**3e**, 60.4 mg, 0.25 mmol) in the presence of TBAI (92.6 mg, 0.25 mmol, 1.0 equiv.) as additive afforded the title compound **4e** as colorless oil (24.0 mg, 0.116 mmol, 46 %) in 99:1 rr.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 3.53 (t, *J* = 6.7 Hz, 2H), 3.53 (t, *J* = 6.7 Hz, 2H), 1.81 – 1.71 (m, 2H), 1.68 – 1.58 (m, 2H), 1.47 – 1.39 (m, 2H), 1.36 – 1.25 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 180.1, 45.3, 34.2, 32.8, 29.4, 29.3, 29.1, 28.9, 27.0, 24.8.

Spectroscopic data for **4e** match those previously reported in literature.[18]

7-Cyano-7-methyloctanoic acid (4f).



4f

Following **GP5** starting from 6-Bromo-2,2-dimethylheptanenitrile (**3f**, 54.5 mg, 0.25 mmol) afforded the title compound **4f** as a colorless oil (23.0 mg, 0.126 mmol, 50 %) in 99:1 rr.

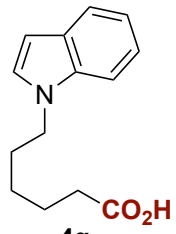
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 2.37 (t, *J* = 7.4 Hz, 2H), 1.67 (quin, *J* = 7.4 Hz, 2H), 1.54 – 1.46 (m, 4H), 1.43 – 1.36 (m, 2H), 1.33 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 180.0, 125.2, 40.9, 34.0, 32.5, 29.1, 26.8, 25.1, 24.5.

IR (ATR): ν = 2975, 2954, 2234, 1709, 1470, 1425, 1301, 1255, 1203, 945 cm^{-1}.

HRMS (ESI): m/z calc. for ($C_{10}H_{17}NO_2^-$) $[M-H]^-$: 182.1187; found: 182.1183.

6-(1*H*-Indol-1-yl)hexanoic acid (4g).



4g

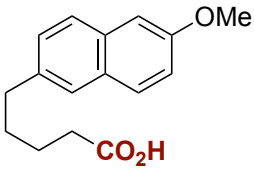
Following **GP5** starting from 1-(4-bromopentyl)-1*H*-indole (**3g**, 66.6 mg, 0.25 mmol) in the presence of TBAI (92.6 mg, 0.25 mmol, 1.0 equiv.) as additive afforded the title compound **4g** as light-yellow oil (27.0 mg, 0.117 mmol, 46 %) in 94:6 rr.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.66 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.35 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.23 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.15 – 7.08 (m, 2H), 6.51 (dd, *J* = 3.1, 0.9 Hz, 1H), 4.14 (t, *J* = 7.1 Hz, 2H), 2.35 (t, *J* = 7.4 Hz, 2H), 1.93 – 1.84 (m, 2H), 1.72 – 1.64 (m, 2H), 1.44 – 1.35 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 179.9, 136.0, 128.7, 127.9, 121.5, 121.1, 119.4, 109.4, 101.2, 46.2, 33.9, 30.0, 26.5, 24.4.

Spectroscopic data for **4g** match those previously reported in literature.[18]

5-(6-Methoxynaphthalen-2-yl)pentanoic acid (4h).



4h

Following **GP5** starting from 2-(3-bromobutyl)-6-methoxynaphthalene (**3h**, 73.3 mg, 0.25 mmol) in the presence of TBAI (92.6 mg, 0.25 mmol, 1.0 equiv.) afforded the title compound **4h** as a white solid (32.0 mg, 0.124 mmol, 50 %) in 99:1 rr.

Following **GP4**, the title compound **4h** from 2-(3-bromobutyl)-6-methoxynaphthalene (**3h**, 73.3 mg, 0.25 mmol) was obtained as a white solid (3.0 mg, 0.01 mmol, <5%). No benzylic carboxylation product was detected.

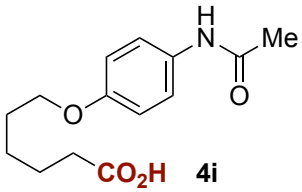
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.67 (d, *J* = 8.2 Hz, 2H), 7.54 (s, 1H), 7.29 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.15 – 7.11 (m, 1H), 7.11 (s, 1H), 3.91 (s, 3H), 2.77 (t, *J* = 7.0 Hz, 2H), 2.40 (t, *J* = 6.9 Hz, 2H), 1.76 – 1.70 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 179.8, 157.3, 137.3, 133.1, 129.2, 129.0, 127.9, 126.9, 126.4, 118.8, 105.8, 55.4, 35.6, 34.0, 30.9, 24.4.

Melting Point: 110-115 ºC

Spectroscopic data for **4h** match those previously reported in literature.[46]

6-(4-Acetamidophenoxy)hexanoic acid (4i).



4i

Following **GP5** starting from *N*-(4-((4-bromopentyl)oxy)phenyl)acetamide (**3i**, 75.0 mg, 0.25 mmol) afforded the title compound **4i** as a white solid (35.0 mg, 0.132 mmol, 53 %) in 99:1 rr.

^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) = 12.01 (s, 1H), 9.75 (s, 1H), 7.45 (d, *J* = 9.0 Hz, 2H), 6.84 (d, *J* = 9.0 Hz, 2H), 3.89 (t, *J* = 6.4 Hz, 2H), 2.22 (t, *J* = 7.2 Hz, 2H), 1.99 (s, 3H), 2.73 – 2.64 (m, 2H), 1.49 – 1.60 (m, 2H), 1.45 – 1.35 (m, 2H).

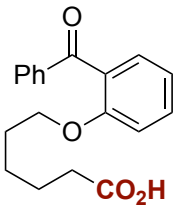
^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) = 174.5, 167.7, 154.4, 132.5, 120.5, 114.4, 67.4, 33.6, 28.5, 25.2, 24.3, 23.8.

IR (ATR): ν = 3305, 3046, 2950, 2872, 1690, 1660, 1600, 1532, 1512, 1474, 1410, 1301, 1243, 1203, 1110, 1045, 1025, 1010, 828 cm^{-1}.

HRMS (ESI): m/z calc. for ($C_{14}H_{18}NO_4^-$) $[M-H]^-$: 264.1241; found: 264.1251.

Melting Point: 116-118 ºC

6-(2-Benzoylphenoxy)hexanoic acid (4j).



4j

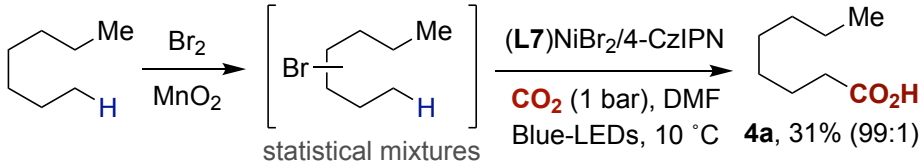
Following **GP5** starting from (2-((4-bromopentyl)oxy)phenyl)(phenyl)methanone (**3j**, 86.6 mg, 0.25 mmol) afforded the title compound **4j** as a colorless oil (40.0 mg, 0.128 mmol, 51 %) in 99:1 rr. Note: After acid-base extraction, the compound was further purified by flash column chromatography (eluent: hexane:ethyl acetate = 9:1 to 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.77 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.56 – 7.51 (m, 1H), 7.47 – 7.39 (m, 4H), 7.04 (td, *J* = 7.5, 0.9 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 3.87 (t, *J* = 6.1 Hz, 2H), 2.18 (t, *J* = 7.6 Hz, 2H), 1.48 – 1.41 (m, 4H), 1.07 – 1.00 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 197.1, 179.4, 157.0, 138.6, 132.8, 132.2, 129.9, 129.6, 129.2, 128.3, 120.8, 112.2, 67.9, 33.8, 28.7, 25.3, 24.3.

Spectroscopic data for **4j** match those previously reported in literature.[18]

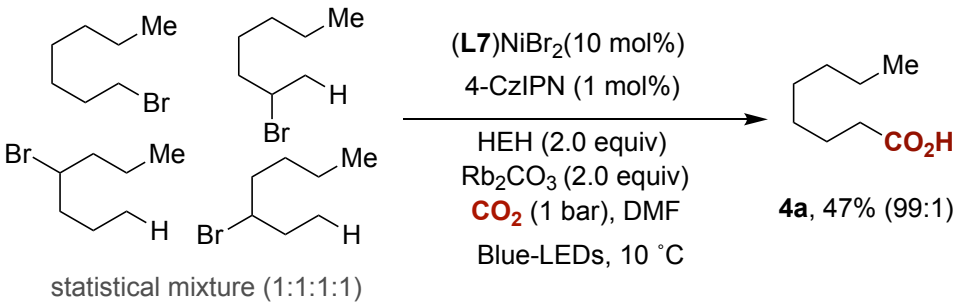
8.2.3 Regioconvergent photocarboxylation of n-heptane



Bromination step: According to the literature report,[18] n-heptane (1.25 mL), MnO_2 (44.0 mg, 0.50 mmol, 2.0 equiv) and Br_2 (13 µL, 0.25 mmol, 1.0 equiv) were added to a Schlenk tube and heated at 60 ºC for 4 h. The reaction was filtered through a plug of Celite, washing with *n*-pentane (5 mL). The filtrate was washed once with water (5 mL). The organic layer was then dried over anhydrous $MgSO_4$ and filtrate. Finally, the *n*-pentane was carefully evaporated in a rotatory evaporator. The crude mixture of isomeric bromoheptanes and the excess of n-heptane were directly used for the carboxylation step without any purification.

Carboxylation step. An oven-dried Schlenk tube containing a magnetic stir bar was charged with (**L7**)$NiBr_2$ (10.1 mg, 0.025 mmol, 0.1 equiv), 4-CzIPN (1.9 mg, 0.0025 mmol, 0.01 equiv), Hantzsch ester (HEH, 127 mg, 0.50 mmol, 2.00 equiv). The Schlenk tube was then taken inside a glovebox, where Rb_2CO_3 (115 mg, 0.50 mmol, 2.00 equiv) was added. The tube was then taken out of the glovebox and connected to a vacuum line where it was evacuated and back-filled under CO_2 flow at least three times. The crude statistical mixture of bromoheptanes and DMF (3 mL) were added under CO_2 flow. Once all the components were added, the Schlenk tube was closed at the atmospheric pressure of CO_2 (1 bar) and placed at a temperature-controlled photo-reactor maintained at 10 ºC and stirred for 20 h in the presence of continuous light irradiation from blue LEDs (λ = 451 nm). The reaction mixture was quenched with 2M HCl aq. solution to release free acid by hydrolysis of carboxylate salt and diluted with ethyl acetate. The combined organic layers were extracted with ethyl acetate (at least three times), washed with water followed by brine solution, dried over $MgSO_4$ and concentrated under reduced pressure. Then the crude mixture was dissolved in diethyl ether and the organic phase was three times extracted with aq. 1M NaOH solution. The combined aqueous phase was washed once again with diethyl ether and neutralized to pH = 2 using 2M HCl aqueous solution. Finally, the acidic aqueous phase was three times extracted with ethyl acetate. The removal of solvent under reduced pressure delivered the pure carboxylic acid (11 mg, 0.08 mmol, 31%).

8.2.4 Regioconvergent photocarboxylation of statistical mixture of bromoheptanes



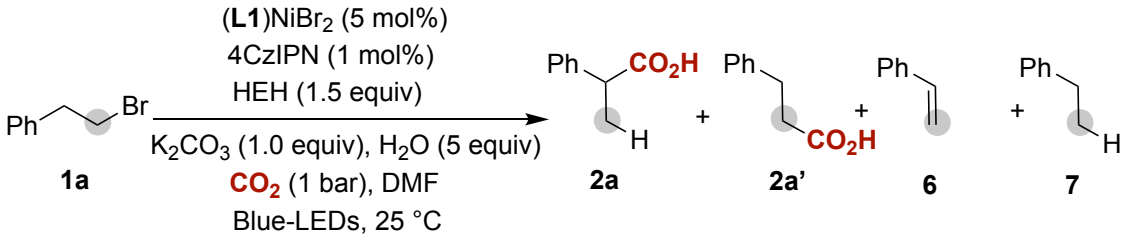
An oven-dried Schlenk tube containing a magnetic stir bar was charged with (**L7**)$NiBr_2$ (10.1 mg, 0.025 mmol, 0.1 equiv), 4-CzIPN (1.9 mg, 0.0025 mmol, 0.01 equiv), Hantzsch ester (HEH, 127 mg, 0.50 mmol, 2.00 equiv). The Schlenk tube was then taken inside a glovebox, where Rb_2CO_3 (115 mg, 0.50 mmol, 2.00 equiv) was added. The tube was then taken out of the glovebox and connected to a vacuum line where it was evacuated and back-filled under CO_2 flow at least three times. The 1:1:1:1 mixture of bromoheptanes (10 µL 1-bromoheptane, 10 µL 2-bromoheptane, 10 µL 3-bromoheptane and 10 µL 4-bromoheptane, 0.25 mmol, 1.0 equiv) and DMF (3 mL) were added under CO_2 flow. Once all the components were added, the Schlenk tube was closed at the atmospheric pressure of CO_2 (1 bar) and placed at a temperature-controlled photo-reactor maintained at 10 ºC and stirred for 20 h in the presence of continuous light irradiation from blue LEDs (λ = 451 nm). The reaction mixture was quenched with 2M HCl aq. solution to release free acid by hydrolysis of carboxylate salt and diluted with ethyl acetate. The combined organic layers were extracted with ethyl acetate (at least three times), washed with water followed by brine solution, dried over $MgSO_4$ and concentrated under reduced pressure. Then the crude mixture was dissolved in diethyl ether and the organic phase was three times extracted with aq. 1M NaOH solution. The combined aqueous phase was washed once again with diethyl ether and neutralized to pH = 2 using 2M HCl aqueous solution. Finally, the acidic aqueous phase was three times extracted with ethyl acetate. The removal of solvent under reduced pressure delivered the pure carboxylic acid (17 mg, 0.12 mmol, 47%).

9 Mechanistic Investigation

9.1 Photocarboxylation of homobenzylic bromides

9.1.1 Kinetic profile of the model reaction

In kinetic analysis, the consumption of homobenzylic bromide (**1a**) and the formation of the putative intermediate styrene **6** and the byproduct ethylbenzene **7** was detected at different time interval by GC-FID. The formation of acids **2a**/**2a'** at different time interval was followed by ^{1}H NMR using 1,3,5-trimethoxy benzene as internal reference.



The photocarboxylation of model substrate **1a** was conducted for 120 min following **GP4**. After appropriate time interval, an aliquot of the reaction solution was collected using a Hamilton syringe, which was previously purged three times under CO_2 atmosphere, and added to the stock solution of ethyl acetate containing 1,3,5-trimethoxybenzene as internal standard. The obtained solution was filtered through a Macherey-Nagel CHROMAFIL® O-20/15 MS PTFE filter and analyzed by GC-FID to calculate the amount of remaining starting material (**1a**), styrene-intermediate **6** and the byproduct ethylbenzene (**7**) at different time interval. To follow the acid formation, several reactions (one for each desired time) were set up according to the **GP4** and then the reaction was quenched with 2M HCl after the desired time and extracted three times with ethyl acetate. To the combined organic layer the internal standard 1,3,5-trimethoxybenzene was added, then an aliquot of the solution was dried under reduced pressure followed by high vacuum to remove most of the residual DMF. The crude mixture was analyzed by ^{1}H NMR to calculate the amount of acids **2a**/**2a'** formed.

In Figure S2, the kinetic plot reveals that the starting material (**1a**) was fully consumed within one hour and the desired product can be obtained. Interestingly, a small and almost constant amount of styrene **6** was detected during the reaction, but its amount decayed to zero when the reaction completed. This observation suggests that the styrene **6** could be potential intermediate in this process. However, the formation of byproduct ethylbenzene (**7**) continued over the time.

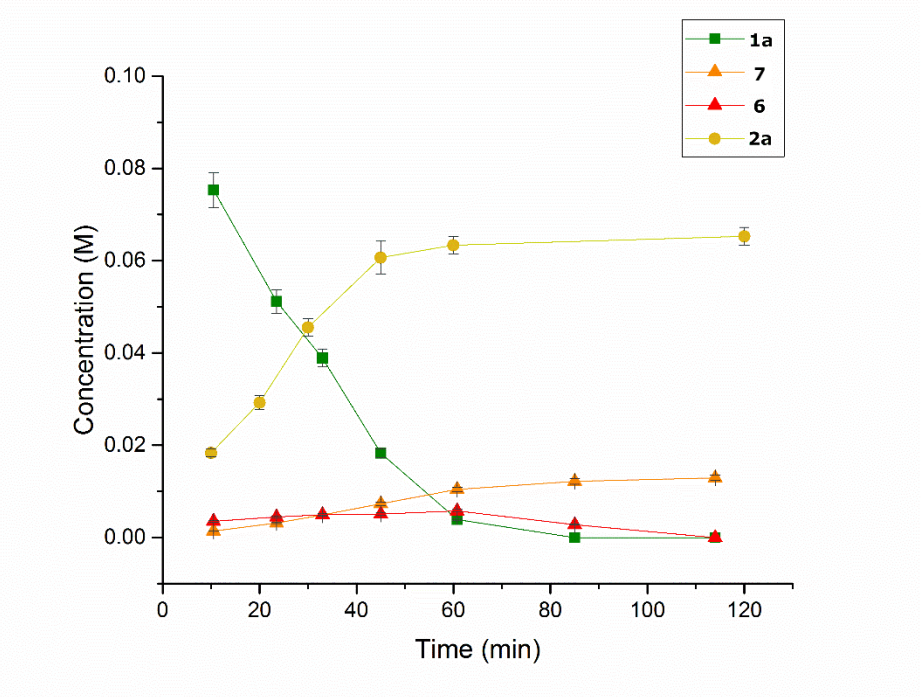


Figure S2: Kinetic profile of the photocarboxylation of substrate (**1a**) with CO_2.

9.1.2 Intermittent illumination experiment

In order to verify if the continuous illumination was required for the reaction, the intermittent illumination of the reaction was performed. The reaction was set-up according to **GP4** and the illumination was alternatively switched on or off (0-10 min: ON; 10-20 min: OFF; 20-35 min: ON; 35-60 min: OFF). The following sampling protocol was used: a 50 µl aliquot of the reaction solution was collected using a Hamilton syringe, which was previously purged three times under CO_2 atmosphere, then dissolved in an ethyl acetate stock solution containing internal standard. The obtained solution was filtered through a Macherey-Nagel CHROMAFIL® O-20/15 MS PTFE filter and analyzed using GC-FID.

In Figure S3, the plot demonstrates that the reaction can only proceed in the presence of LED illumination (white zones). No significant conversion was observed when the illumination was switched off (dark regions).

Table S3: Kinetic profile of the consumption of **1a** upon intermittent irradiation.							
Min.	5	10	15	20	25	35	50
[**1a**]/ M×10^{-2}	8.5	7.0	7.1	6.8	5.7	3.2	3.0

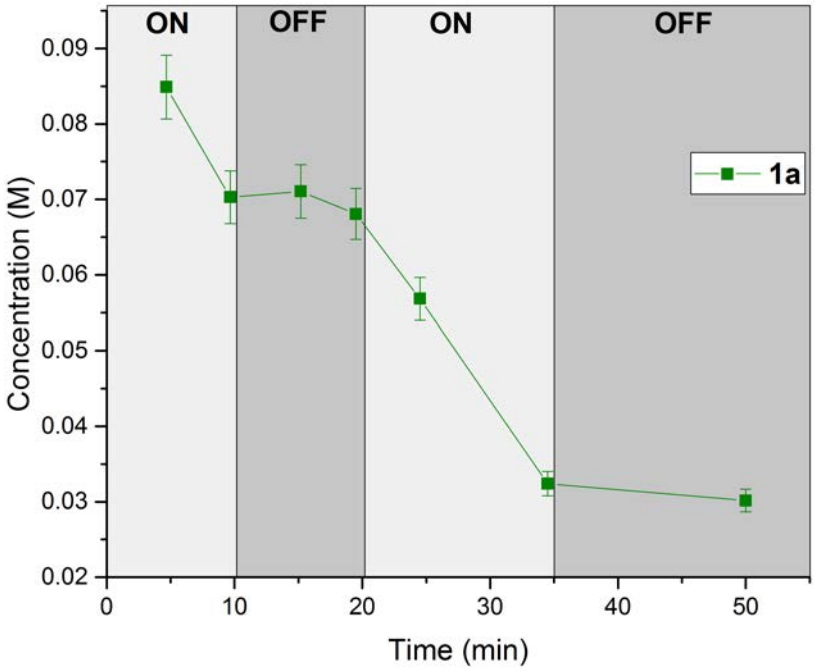
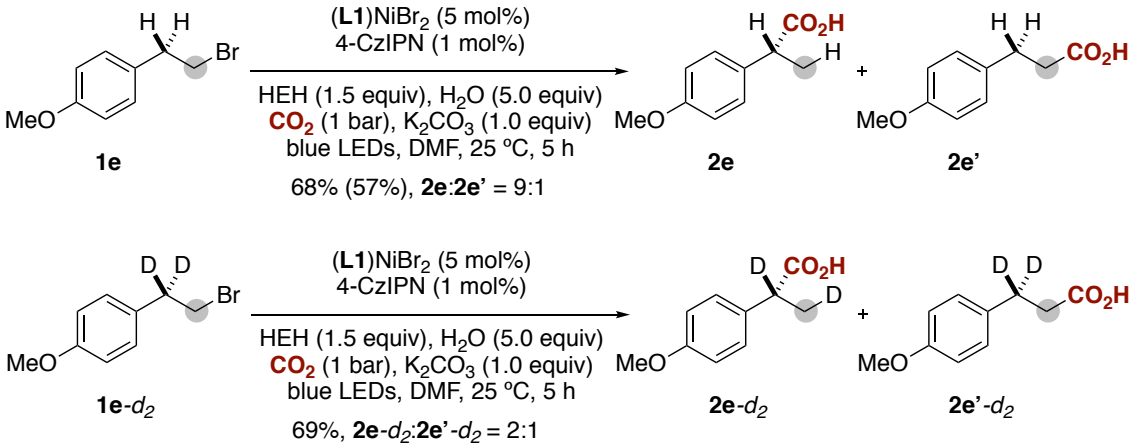


Figure S3: Kinetic profile of the photocarboxylation of substrate (**1a**) under intermittent illumination.

9.1.3 Deuterium labelling experiments

Photocarboxylation of (non)deuterated substrate 1e and 1e-*d*$_2$



Following **GP4**, the photocarboxylation of non-deuterated substrate **1e** and deuterated substrate **1e-*d*$_2$** were independently performed. Both the substrates **1e** and **1e-*d*$_2$** delivered corresponding acids **2e**/**2e'** and **2e-*d*$_2$**/**2e'-*d*$_2$** in 68% yields. However, the selectivity was different such as **2e**/**2e'** were obtained in 9:1 ratio, while **2e-*d*$_2$**/**2e'-*d*$_2$** were delivered in 2.1:1. As described by the LC-MS spectra (Figure S4), the acids **2e-*d*$_2$**/**2e'-*d*$_2$** contain almost all the deuterium within the molecules, thus dictating no H/D exchange with other reagents.

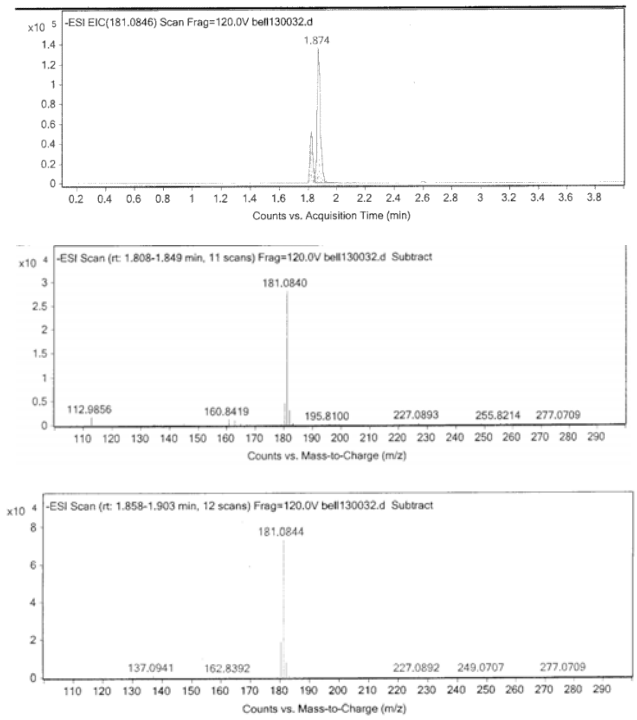
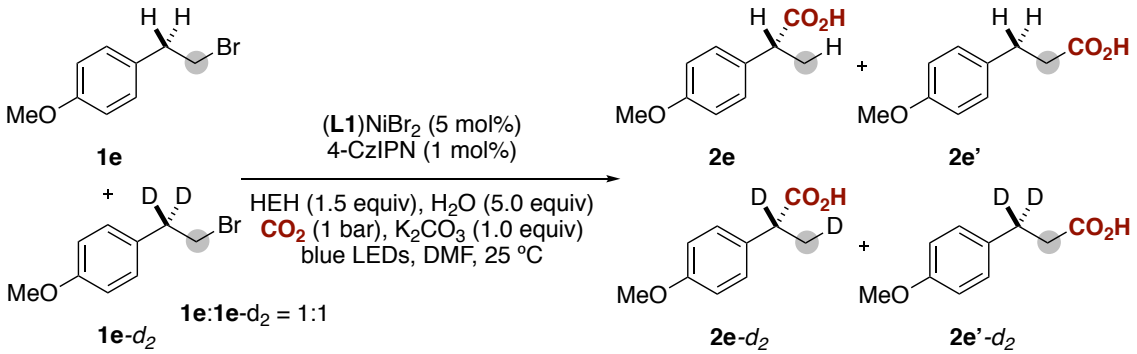


Figure S4: LC-MS spectra (negative mode) of **2e-*d*$_2$**/**2e'-*d*$_2$**.

Intermolecular competition experiment between 1e and 1e-*d*$_2$



To measure the kinetic isotope effect, the intermolecular competition experiment was performed with the equimolar mixture of **1e** and **1e-*d*$_2$** following the procedure **GP4**. The

sampling was performed after 10 and 20 min. After 10 min, 100 µl aliquot of the reaction mixture was collected using a Hamilton syringe, which was previously purged three times under CO_2 atmosphere and then dissolved in 1 mL ethyl acetate and the obtained solution was filtered through a Macherey-Nagel CHROMAFIL® O-20/15 MS PTFE filter and analyzed by high-resolution mass spectroscopy. The sampling procedure was repeated after 20 min. The isotopic pattern of the peak associated with the branched product **2e**/**2e-*d*$_2$** was analyzed by the comparison with the expected natural abundance pattern and the relative amounts of **2e** and **2e-*d*$_2$** were determined (Figure S5). The obtained kinetic isotope effect (KIE) value is as follow:

KIE (10 min): 1.00 KIE (20 min): 0.98 **KIE (average): 0.99±0.01**

In summary, by analyzing the initial rates of the reaction, no kinetic isotope effect was observed, therefore suggesting that the β-elimination step is not rate determining.

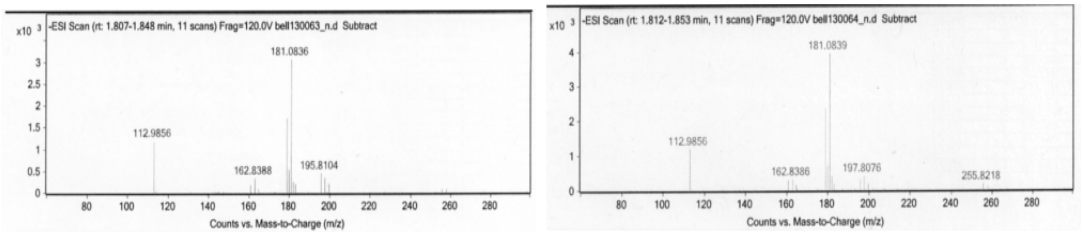
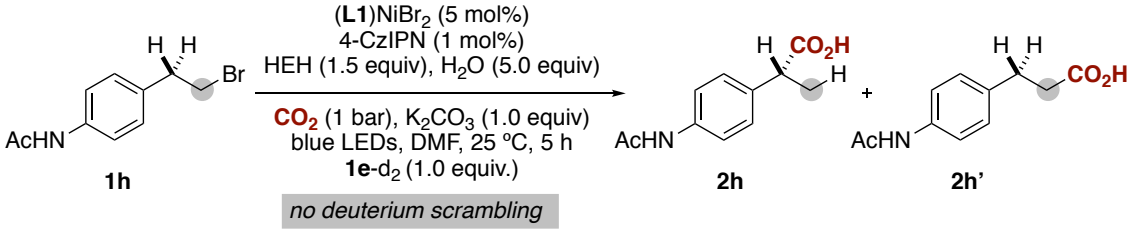


Figure S5: Isotope pattern of products **2e** and **2e-*d*$_2$** after 10 min and 20 min.

Scrambling between deuterated substrate (1e-*d*$_2$) & non-deuterated substrate (1h)



In order to assess the scrambling of hydrogen atoms during the reaction, the photocarboxylation of non-deuterated **1h** was performed in the presence of 1.0 equivalent of deuterium substrate **1e-*d*$_2$** following **GP4**. The analysis of the reaction mixture by mass spectroscopy revealed that no deuterium scrambling with **1h** occurred under the reaction conditions (for **2h**, M-H: 100%, M-H+1: 12.5, M-H+2: 1.3%). This result suggests that

the migratory insertion that follows the elimination step is fast and no H/D scrambling occurs.

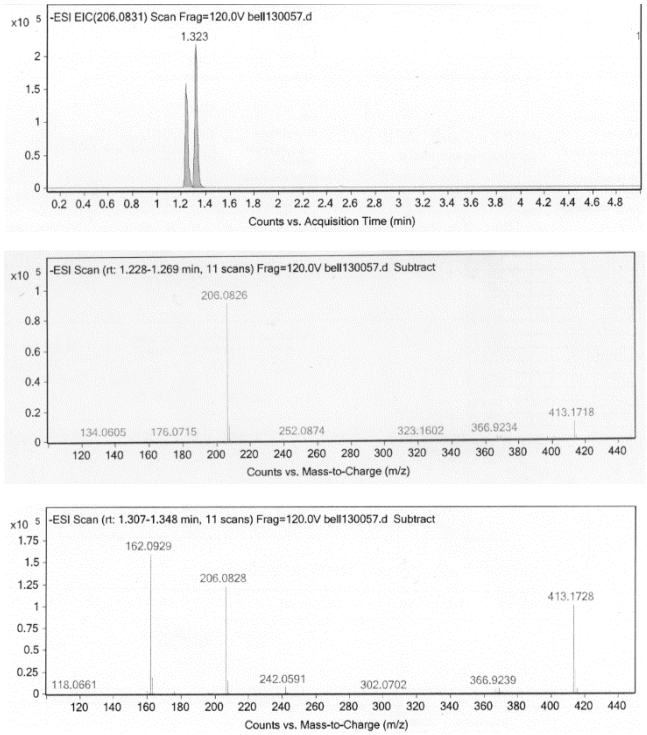
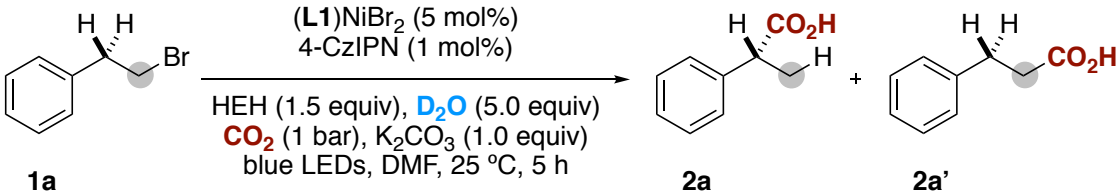


Figure S6: LC-MS spectra of the product **2h** and **2h'**.

Photocarboxylation of substrate 1a in the presence of D_2O instead of H_2O



In order to elucidate whether the additive H_2O is able to scramble protons with the putative intermediates of the catalytic cycle, we performed the photocarboxylation reaction of substrate **1a** in the presence of D_2O instead of H_2O, according to **GP4**. The ^1H NMR revealed no deuterium incorporation at α- or β-positions of the acid **2a**. Furthermore, the high-resolution mass analysis of so-formed acid **2a** indicated that if any incorporation of deuterium from D_2O occurs during the process, it is very little amount (~ 4%) (Table S4).

Table S4: Isotopic pattern of the product **2a**		
Ion	M+H (150)	M+H+1 (151)
counts	11697	1652
found abundance	100%	14.1%
expected abundance	100%	10.0%

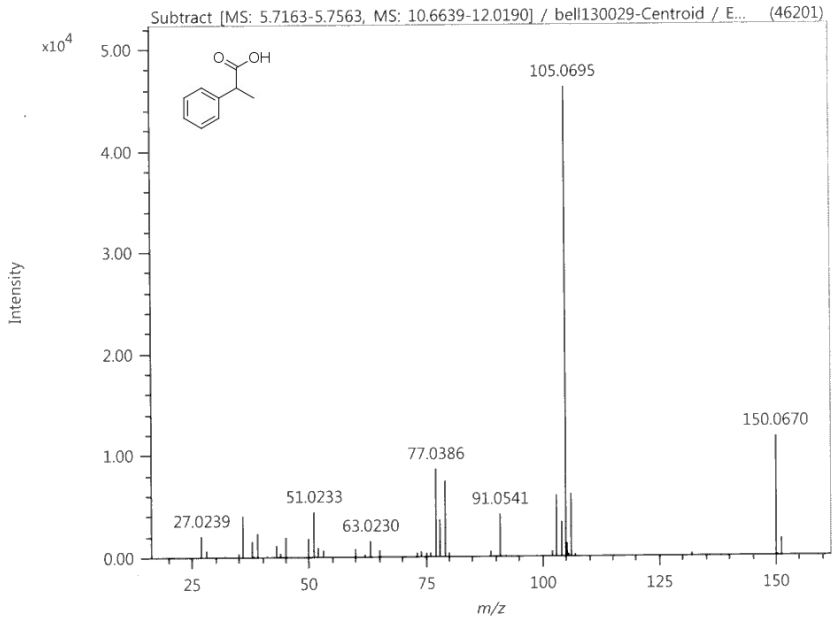
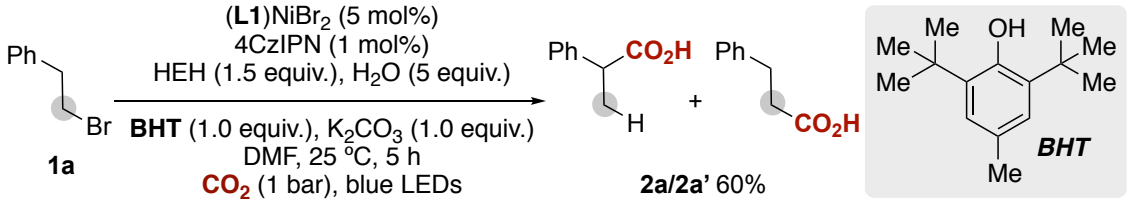


Figure S7: MS spectra of the product **2a** in the presence of D_2O.

9.1.4 Radical inhibition experiment



Following **GP4**, the photocarboxylation of substrate **1a** was performed in the presence of 1.0 equivalent of the radical scavenger BHT (dibutylhydroxytoluene). The product **2a**/**2a'** was obtained in 60% yield, thus suggesting no radical inhibition of the reaction.

9.1.5 Cyclic Voltammetric (CV) measurements of (L1)$NiBr_2$

The reduction potentials of (**L1**)$NiBr_2$ were measured using cyclic voltammetry in MeCN (analytical grade), using ferrocene ($E_{1/2}$ (Fe^+/Fe) = +0.380 V vs. SCE)[47] as internal reference. The measurement was carried out using a Metrohm Autolab PGSTAT302N device using a glassy carbon working electrode, a platinum wire counter-electrode and a silver wire as pseudo-reference electrode. Tetrabutylammonium tetrafluoroborate (0.1 M, Fluka) was used as supporting electrolyte. Prior to the measurement, the solvent was degassed by purging with argon. All the measurements were performed under argon atmosphere.

The combined UV-vis and cyclic voltammetry experiments was carried out using a Metrohm Autolab PGSTAT302N device and an Agilent 8453 spectrometer, using an OTTLE (Optically Transparent Thin-Layer Electrochemical) cell from Frantisek Hartl (path length: 0.02 cm)[48] equipped with two platinum minigrids as working electrode and counter-electrode. A silver wire was used as pseudo-reference electrode. Tetrabutylammonium tetrafluoroborate (0.1 M, Fluka) was used as supporting electrolyte. Prior to the measurement the solvent was degassed by purging argon. All the measurements were performed under argon atmosphere.

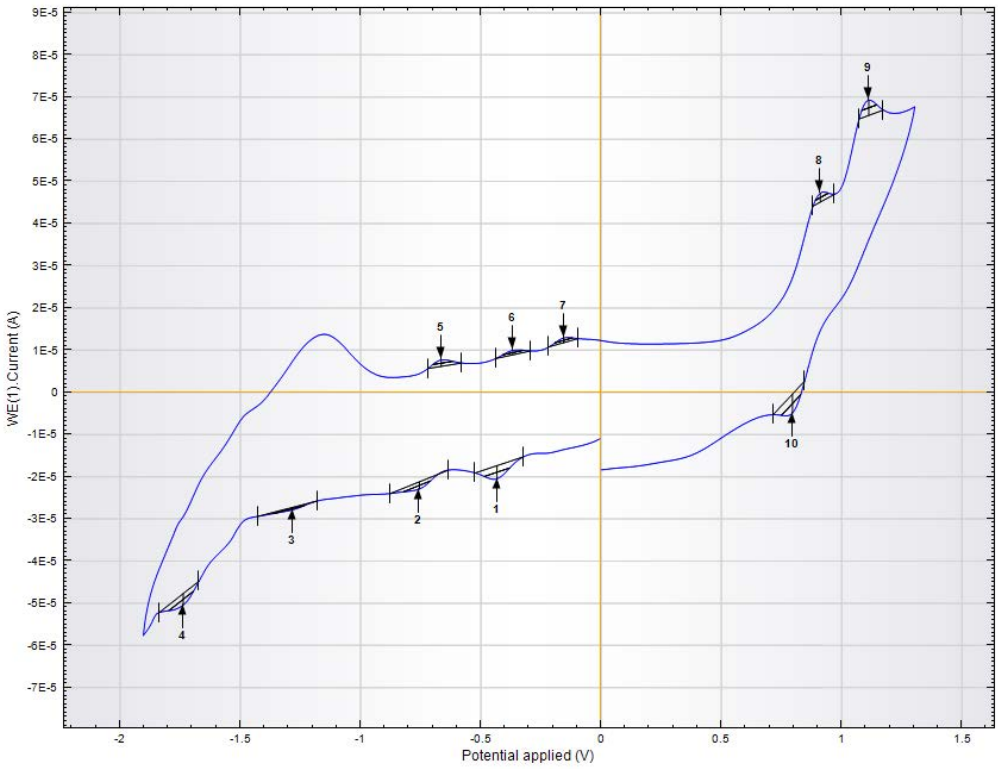


Figure S8: Cyclic Voltammetry of (**L1**)$NiBr_2$ in the presence of ferrocene (peak 8, 9). Silver wire was used as pseudo-reference electrode.

Index	Potential (V)	Index	Potential (V)
1	-0.43304	6	-0.36758
2	-0.75531	7	-0.1561
3	-1.284	8	0.91141
4	-1.7372	9	1.1128
5	-0.66467	10	0.79559

The following values were obtained from the cyclic voltammetry experiment:

$E_{1/2}$ (Ni^{2+}/Ni^{+})= -0.88 vs. SCE $E_{1/2}$ (Ni^{+}/Ni^{0})= -1.18 vs. SCE

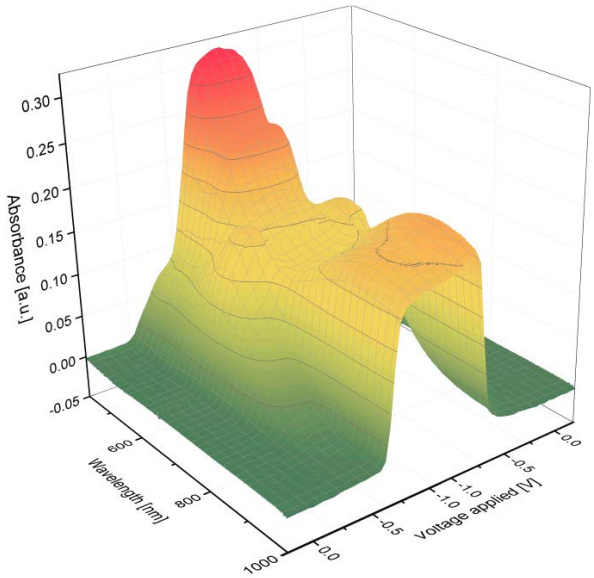


Figure S9: Combined cyclic voltammogram and UV-Vis spectra of (**L1**)$NiBr_2$.

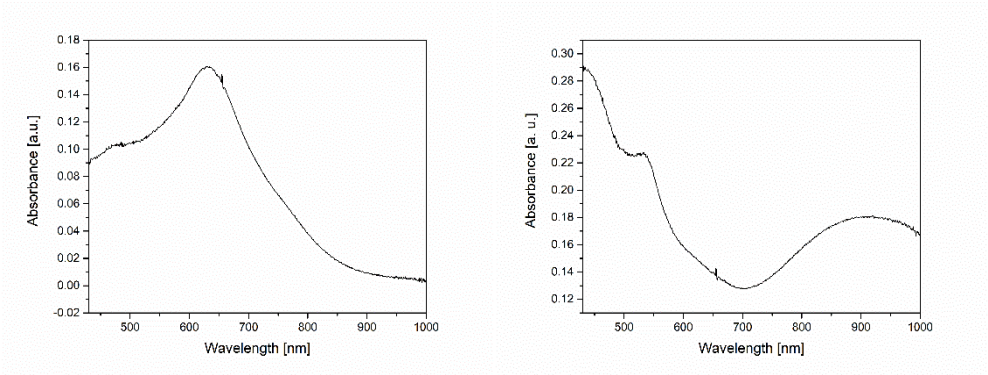


Figure S10: UV-Vis spectra of the Ni(I) species (λ_{max} = ~ 630 nm) (left) and Ni(0) species (λ_{max} = ~ 900 nm) (right) at variable potential applied. Silver wire was used as pseudo-reference electrode.

By combining cyclic voltammetry and UV-vis spectroscopy Figure S9, the UV-Vis spectra of the Ni(I) and Ni(0) species from the reduction of (**L1**)$NiBr_2$ precatalyst was obtained. As shown in Figure S10, the low-valent nickel species generated from the electrochemical reduction of (**L1**)$NiBr_2$ precatalyst show a very different UV-vis spectrum. The Ni(I) species is characterized by an intense absorption maximum at ~ 630 nm, while the corresponding Ni(0) species has an absorption peak centered at ~ 900 nm.

9.1.6 Time-resolved UV-Vis experiments

Experimental set-up: The UV-Vis measurement where performed using an Agilent 8453 spectrometer using a temperature-controlled (20.0 °C) fluorescence cuvette (1 cm optical pathway, both faces can transmit light) equipped with a bullet-shaped Teflon-coated stirring bar (length: 6 mm, ~ 250 rpm). A single blue LED OSRAM Oslon® SSL 80 royal- blue LEDs (λ_{max}= 455 nm (± 15 nm), 3.5 V, 700 mA), equipped with a metallic passive cooling element, was placed approx. 5 mm away from one transmitting side of the cuvette, at 90° from the measuring beam. Unless otherwise stated, the spectra were recorded every second.

Preparation of a stock-solution of (***L1***)*$NiBr_2$ and 4-CzIPN. (Solution A)*: In a vial equipped with a teflon-coated stirring bar, (**L1**)$NiBr_2$ ($5 \cdot 10^{-3}$ M) and 4-CzIPN (10^{-3} M) were added, then the corresponding amount of DMF (Fischer scientific, analytical grade) was added and the solution was stirred for 5 minutes.

Preparation of the solution of Hantzsch ester. (Solution B): In a vial equipped with a teflon-coated stirring bar, Hantzsch ester (approx. 500 mg) was added to DMF (approx.10 ml, Fischer scientific, analytical grade). The suspension was stirred for 30 minutes to obtain a saturated solution.

Preparation of the solution C for UV-Vis spectroscopy: In the fluorescence cuvette, solution A (300 µl) followed by solution B (100 µl) were added to DMF (2 ml). The mixture was degassed by bubbling argon using a needle for 100 seconds, then sealed using a PTFE stopper.

Preparation of the solution D for UV-Vis spectroscopy: In the fluorescence cuvette, solution A (300 µl), solution B (100 µl) and phenylethylbromide (**1a)** (30 µl) were sequentially added to DMF (2 ml). The mixture was degassed by bubbling argon using a needle for 100 seconds, then sealed using a PTFE stopper.

UV-Vis analysis upon illumination of solution C

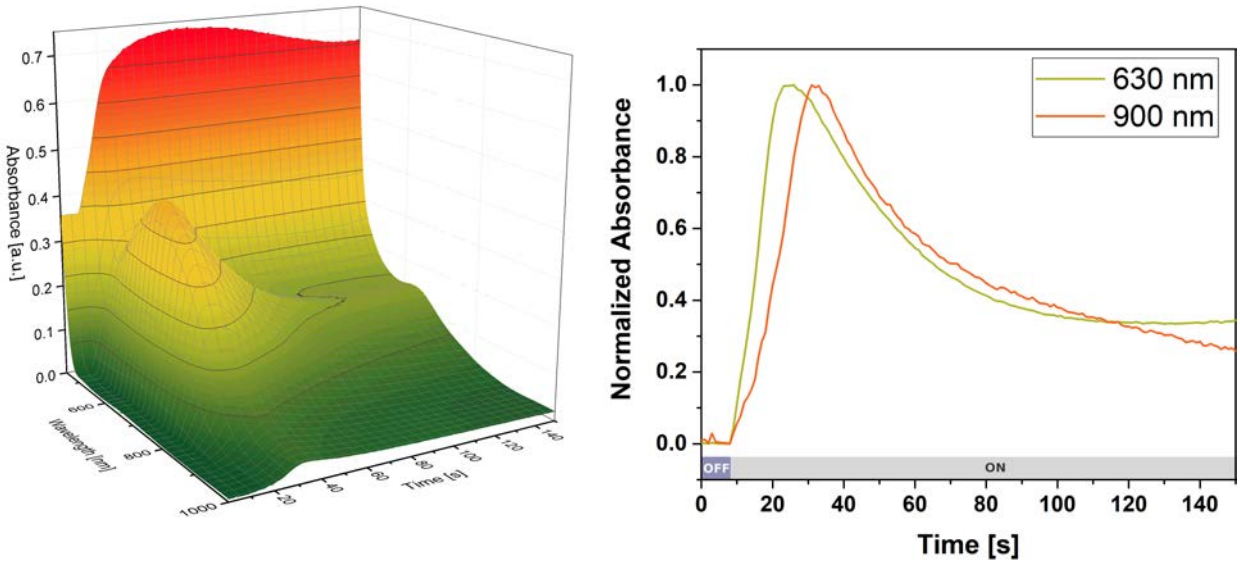


Figure S11: UV-Vis spectrum of solution C over time (left). Evolution of the absorption at 630 and 900 nm over time (normalized) (right).

Upon illuminating the solution, the fast formation of Ni(I) species (~ 630 nm) could be detected. The formation of Ni(0) species could also be seen at higher wavelengths (~ 900

nm). Despite the partial overlap with the Ni(I) absorption tail, it was possible to detect the presence of Ni(0) species by comparing the change of the intensity at 630 and 900 nm over time (Figure S11). Moreover, as exhibited in Figure S11, the build-up of Ni(0) species occurred later than the initial formation of Ni(I) species. After reaching a maximum, both species decrease, probably due to the competitive oxidative decomposition.

When the same experiment was repeated in the absence of either light, Hantzsch ester or 4-CzIPN, no reduction could be detected, thus confirming that all these components are necessary to form the catalytically competent species.

UV-Vis analysis upon illumination of solution D

Upon starting the illumination, the formation of the Ni(I) and Ni(0) species could be detected, while the intensity of the absorption maxima was strongly reduced (Figure S12). In addition, the kinetic profile appeared to be much slower than the case, where substrate **1a** is absent. This behavior is consistent with the fact that **1a** could react with the low-valent nickel species, as postulated by the proposed catalytic cycle.

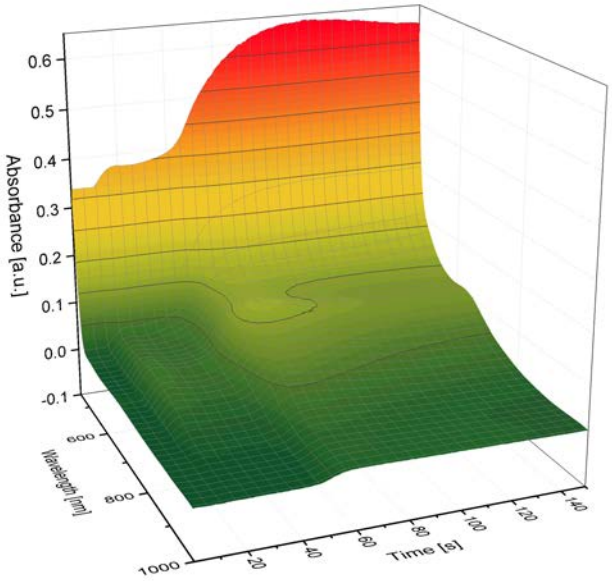


Figure S12: UV-Vis spectra of solution D over time.

UV-Vis analysis upon illumination of solution C, followed by the addition of **1a**.

During the first irradiation period, the UV-Vis pattern was consistent with the previous observation, while upon the addition of substrate **1a**, an extremely fast consumption of

both Ni(I) and Ni(0) species was observed. This behavior is consistent with the fact that substrate **1a** could react with the low-valent nickel species, as postulated by the proposed catalytic cycle (Figure S13).

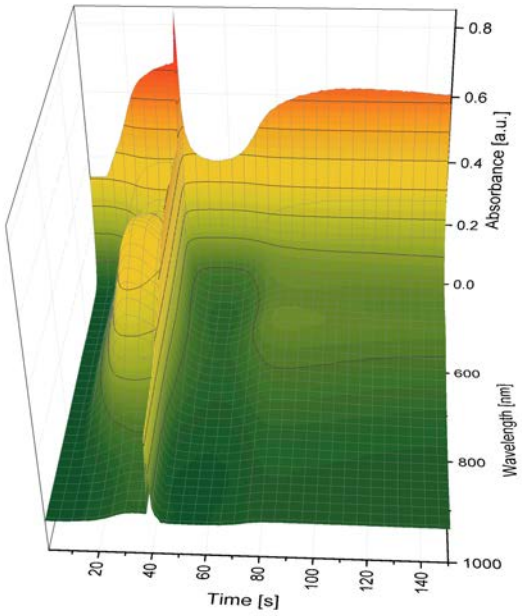
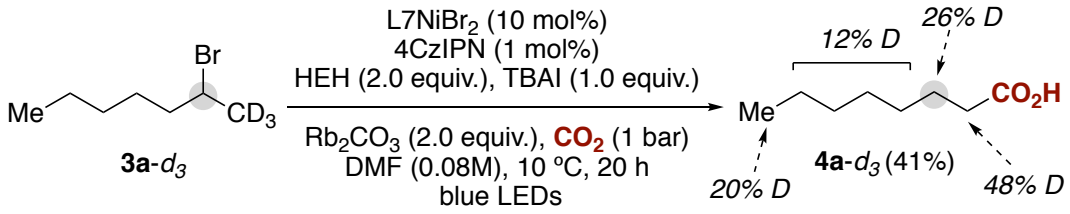


Figure S13: UV-Vis of solution C before and after the addition of substrate **1a**. The injection spike is clearly visible at t = ~ 40 s.

9.2 Photocarboxylation of unactivated secondary alkyl bromides

9.2.1 Deuterium labelling experiment



Following **GP5**, the photocarboxylation of deuterated 2-bromoheptane (**3a**-d_3, 0.25 mmol) was performed. The desired product **4a**-d_3 (15 mg, 0.102 mmol, 41%) was obtained as colorless oil. The ^{2}H NMR spectra revealed the scrambling of deuterium isotope throughout the hydrocarbon chain via β-hydride elimination/reinsertion.

^{2}H NMR (77 MHz, $CHCl_3$): δ (ppm) = 2.32 (s, 0.96D), 1.62 (s, 0.52D), 1.15 (s, 0.92D), 0.86 (s, 0.61D).

Spectroscopic data for **4a**-d_3 match those previously reported in literature.[18]

KIE determination:

Following GP5, the photocarboxylation of substrate **3a** and **3a**-d_3 were performed (a set of four reactions for each substrate). The reactions for both **3a** and **3a**-d_3 were stopped after 30 min, 60 min, 90 min and 120 min. The reactions were quenched with 2M HCl and diluted with ethyl acetate. The anisole (1.0 equiv.) as internal standard was added to the solution and filtered through short pad of silica gel. The yield was determined by GC-FID analysis. The obtained yields in the form of concentration were plotted against time (Figure S14).

The determined KIE = (K_H/K_D) = 1.12 ± 0.01

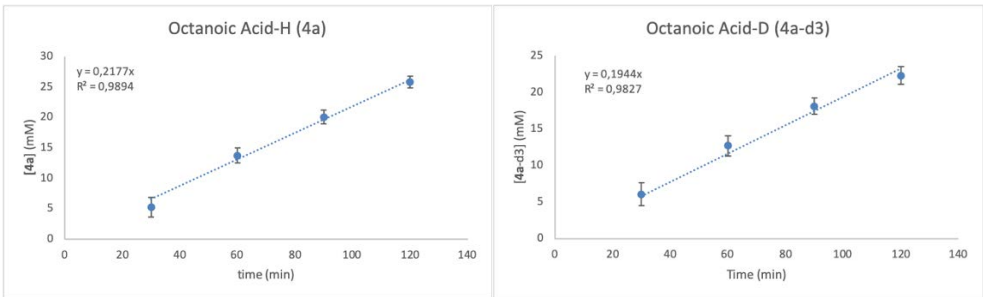
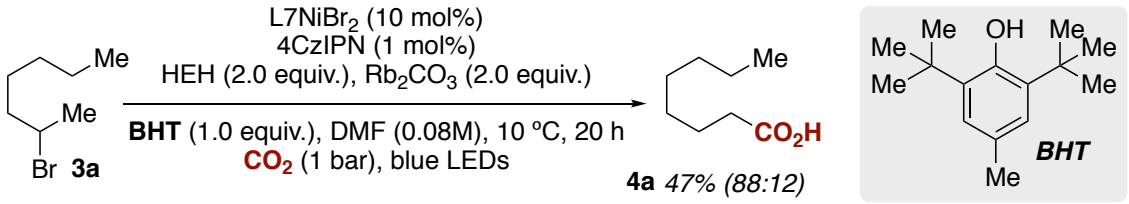


Figure S14: Determination of the initial rates of **4a** and **4a**-d_3 formation.

9.2.2 Radical inhibition experiment



Following the general procedure **GP5**, the photocarboxylation of substrate **3a** was performed in the presence of 1.0 equivalent of the radical scavenger BHT (dibutylhydroxytoluene). The product **4a** was obtained in 47% yield, thus suggesting no radical inhibition of the reaction.

9.2.3 Cyclic Voltammetric (CV) measurements of (L7)$NiBr_2$

The reduction potentials of (**L7**)$NiBr_2$ were measured using cyclic voltammetry in MeCN (analytical grade), using ferrocene ($E_{1/2}$ (Fe^+/Fe) = +0.380 V vs. SCE)[47] as internal reference. The measurement was carried out using a Metrohm Autolab PGSTAT302N device using a glassy carbon working electrode, a platinum wire counter-electrode and a silver wire as pseudo-reference electrode. Tetrabutylammonium tetrafluoroborate (0.1 M, Fluka) was used as supporting electrolyte. Prior the measurement the solvent was degassed by bubbling argon through a hypodermic needle. All the measurements were performed under argon atmosphere.

The combined UV-Vis and cyclic voltammetry experiments was carried out using a Metrohm Autolab PGSTAT302N device and an Agilent 8453 spectrometer, using an OTTLE (Optically Transparent Thin-Layer Electrochemical) cell from Frantisek Hartl (path length: 0.02 cm)[48] equipped with two platinum minigrids as working electrode and counter-electronde. A silver wire was used as pseudo-reference electrode. Tetrabutylammonium tetrafluoroborate (0.1 M, Fluka) was used as supporting electrolyte. Prior the measurement the solvent was degassed by bubbling argon through a hypodermic needle. All the measurements were performed under argon atmosphere.

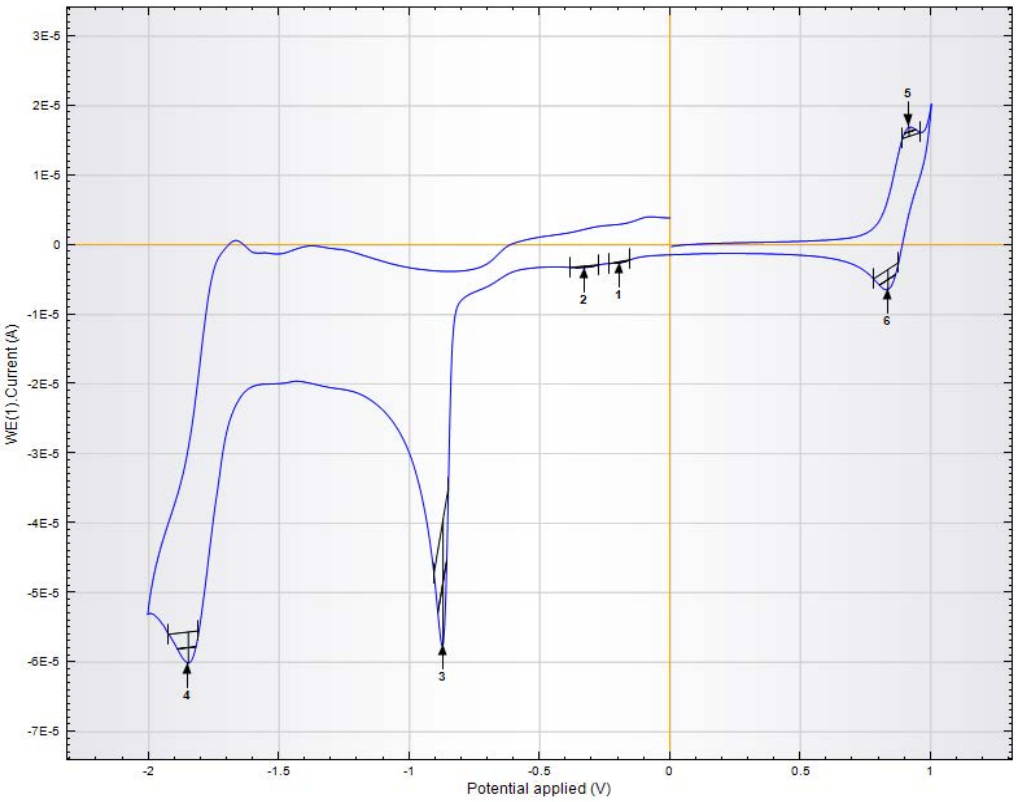


Figure S15: Cyclic Voltammetry of (**L7**)$NiBr_2$ in the presence of ferrocene (peak 5, 6). Silver wire was used as pseudo-reference electrode.

Index	Potential (V)
1	-0.19135
2	-0.3273
3	-0.87112
4	-1.848
5	+0.91644
6	+0.83588

The following values were obtained from the cyclic voltammetry experiment:

$E_{1/2}$ (Ni^{2+}/Ni^{+})= -0.78 vs SCE $E_{1/2}$ (Ni^{+}/Ni^{0})= -1.33 vs SCE

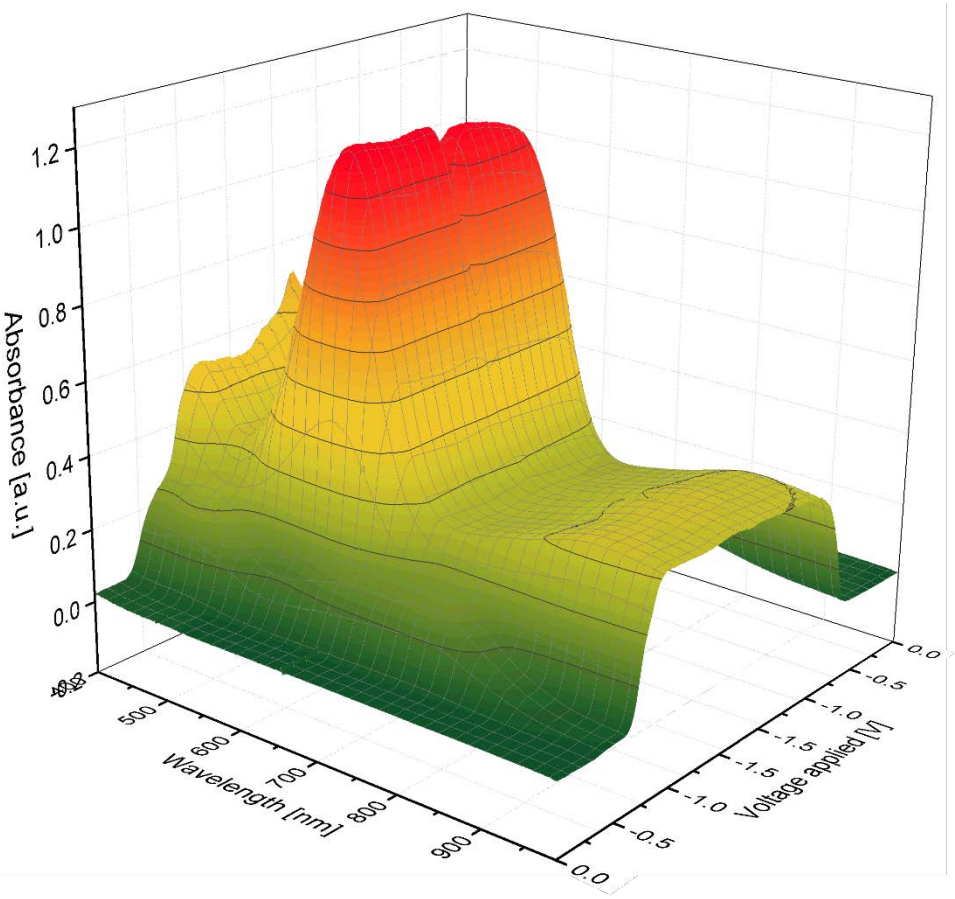


Figure S16: Combined cyclic voltammogram and UV-Vis spectra of (**L7**)$NiBr_2$. Silver wire was used as pseudo-reference electrode.

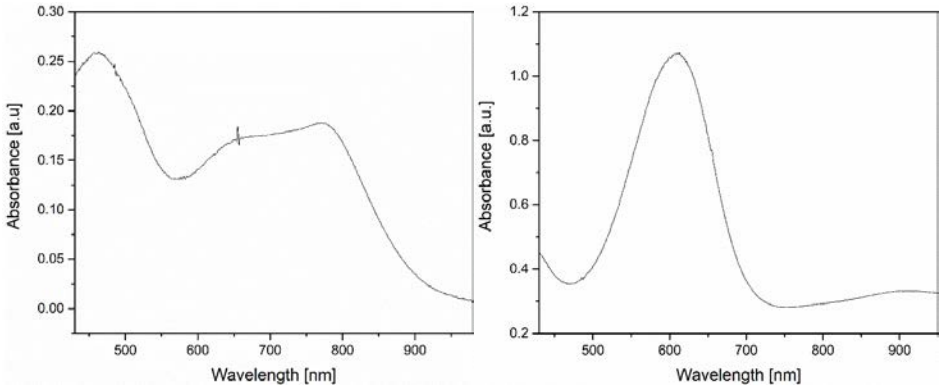


Figure S17: UV-Vis spectra of the Ni(I) species (λ_{max} = ~ 772 nm) (left) and Ni(0) species (λ_{max} = ~ 910 nm) (right) at variable potential applied. Silver wire was used as pseudo-reference electrode.

By combining cyclic voltammetry and UV-vis spectroscopy of Figure S16, the UV-Vis spectra of the Ni(I) and Ni(0) species from the reduction of (**L7**)$NiBr_2$ precatalyst was obtained. As shown in Figure S17, the low-valent nickel species generated from the electrochemical reduction of (**L7**)$NiBr_2$ precatalyst show a very different UV-vis

spectrum. The Ni(I) species is characterized by an intense absorption maximum at ~ 772 nm, while the corresponding Ni(0) species has an absorption peak centered at ~ 910 nm. The Ni(0) species has a more pronounced absorption around 600 nm, however in this region multiple species intensely absorbs under working conditions. Hence, we decided to follow the peak with maximum at 910 nm as a fingerprint for the formation of the low-valent Ni(0) species.

9.2.4 Time-resolved UV-Vis experiments

Experimental set-up: The UV-Vis measurement where performed using an Agilent 8453 spectrometer using a temperature-controlled (20.0 °C) fluorescence cuvette (1 cm optical pathway, both faces can transmit light) equipped with a bullet-shaped Teflon-coated stirring bar (length: 6 mm, ~ 250 rpm). A single blue LED OSRAM Oslon® SSL 80 royal- blue LEDs (λ_{max}= 455 nm (± 15 nm), 3.5 V, 700 mA), equipped with a metallic passive cooling element, was placed approx. 5 mm away from one transmitting side of the cuvette, at 90° from the measuring beam. Unless otherwise stated, the spectra were recorded every second.

*Preparation of a stock-solution of (**L7**)$NiBr_2$ and 4-CzIPN. (Solution A)*: In a vial equipped with a teflon-coated stirring bar, (**L7**)$NiBr_2$ ($5 \cdot 10^{-3}$ M) and 4-CzIPN (10^{-3} M) were added and then the corresponding amount of DMF was added and the solution was stirred for 5 min.

Preparation of the solution of Hantzsch ester. (Solution B): In a vial equipped with a teflon-coated stirring bar, Hantzsch ester (approx. 500 mg) was added to DMF (approx.10 mL). The suspension was stirred for 30 minutes to obtain a saturated solution.

Preparation of the solution C for UV-Vis spectroscopy: In the fluorescence cuvette, solution A (500 µl) followed by solution B (100 µl) were added to DMF (1 ml). The mixture was degassed by bubbling argon using a needle for 100 seconds, then sealed using a PTFE stopper.

Preparation of the solution D for UV-Vis spectroscopy: In the fluorescence cuvette, solution A (500 µl), solution B (100 µl) and phenylethylbromide (**1a)** (30 µl) were

sequentially added to DMF (1 ml). The mixture was degassed by bubbling argon using a needle for 100 seconds, then sealed using a PTFE stopper.

UV-Vis analysis upon illumination of solution C

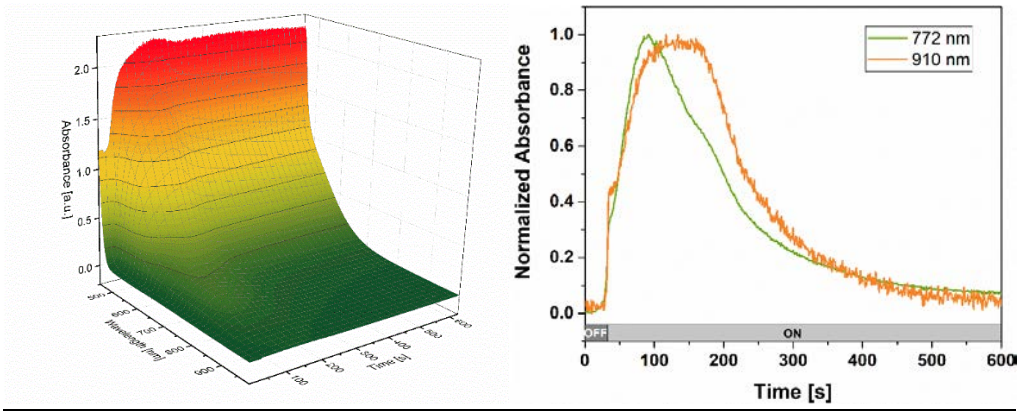


Figure S18: UV-Vis spectrum of solution C over time (left). Evolution of the absorption at 772 and 910 nm over time (normalized) (right).

Upon illuminating the solution, the fast formation of Ni(I) species (~ 772 nm) could be detected. The formation of Ni(0) species could also be seen at higher wavelengths (~ 910 nm). Despite the partial overlap with the Ni(I) absorption tail, it was possible to detect the presence of Ni(0) species by comparing the change of the intensity at 772 and 910 nm over time (Figure S18). Moreover, as shown in Figure S, the build-up of Ni(0) species occurred later than the initial formation of Ni(I) species. After reaching a maximum, both species decrease, probably due to the competitive oxidative decomposition.

When the same experiment was repeated in the absence of either light, Hantzsch ester or 4-CzIPN, no reduction could be detected, thus confirming that all these components are necessary to form the catalytically competent species.

UV-Vis analysis upon illumination of solution D

Upon starting the illumination, the formation of the Ni(I) and Ni(0) species could be detected and a negligible quenching of the intensity was observed (Figure S19). This behavior is consistent with the fact that **3a** most likely undergoes oxidative addition much slower than its counterpart **1a**, which benefits from the assistance of the aromatic ring.

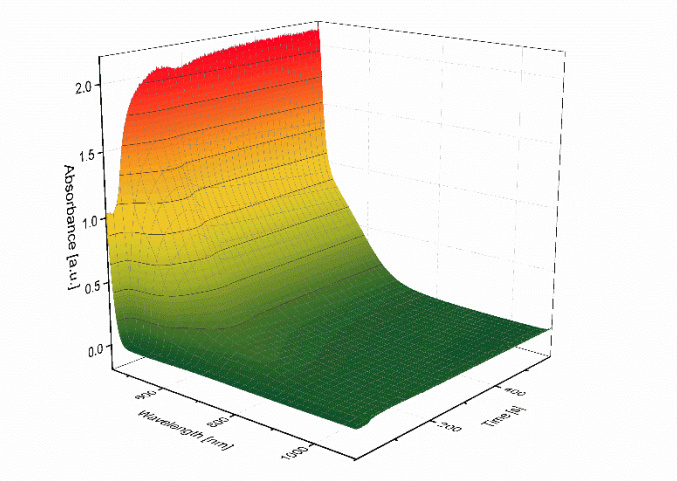


Figure S19: UV-vis spectra of solution D over time.

UV-Vis analysis upon illumination of solution C, followed by the addition of **3a**.

Both during the first irradiation period and after the addition of the alkyl bromide **3a**, the behavior of the system was consistent with the previous observations. This supports the fact that the oxidative addition of **3a** occurs at a relative low rate compared to the competitive oxidative pathways, therefore little quenching of the intensity could be observed. (Figure S20).

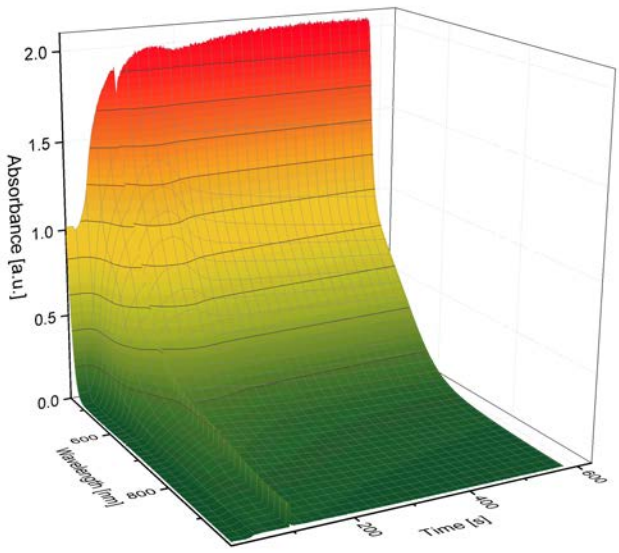
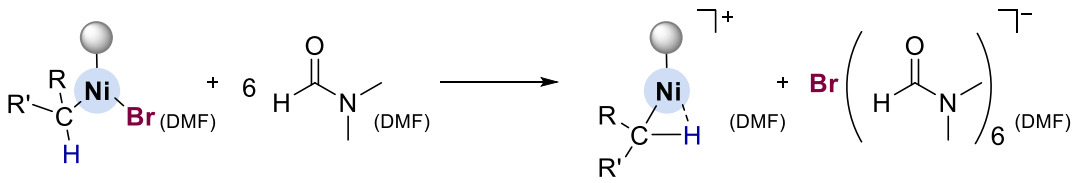


Figure S20 UV-vis of solution C before and after addition of **3a**. The injection spike is clearly visible at t = ~ 100 s.

9.3 DFT calculations

Calculations were performed using Gaussian 09, Revision E.01[49] at the Universität Regensburg HPC-cluster "Athene". All the optimizations were performed using spin-unrestricted broken-symmetry DFT using UωB97X-D/6-31g(d) in the gas phase at 298 K.[50] The identity of the stationary points was confirmed by frequency analysis: intermediates had zero imaginary frequency, while transition states had one imaginary frequency. The intermediates and the corresponding transition states were verified by the animation of the imaginary frequency; the thermochemistry was calculated at the same level of theory, summing the contribution of CO_2 when not explicitly present as reactant or carboxy compound.

The solvent corrections were taken into account via incorporation of the electronic energy obtained in *N,N*-DMF at 298 K using the SMD solvation model,[51] using UωB97X-D/6-31g(d) and UωB97X-D/def2-TZVP (the energies in the potential energy diagram diagrams are reported according to the latter level of theory).[52,53] The bromide loss from the oxidative insertion product was estimated considering the following reaction (Scheme S1):

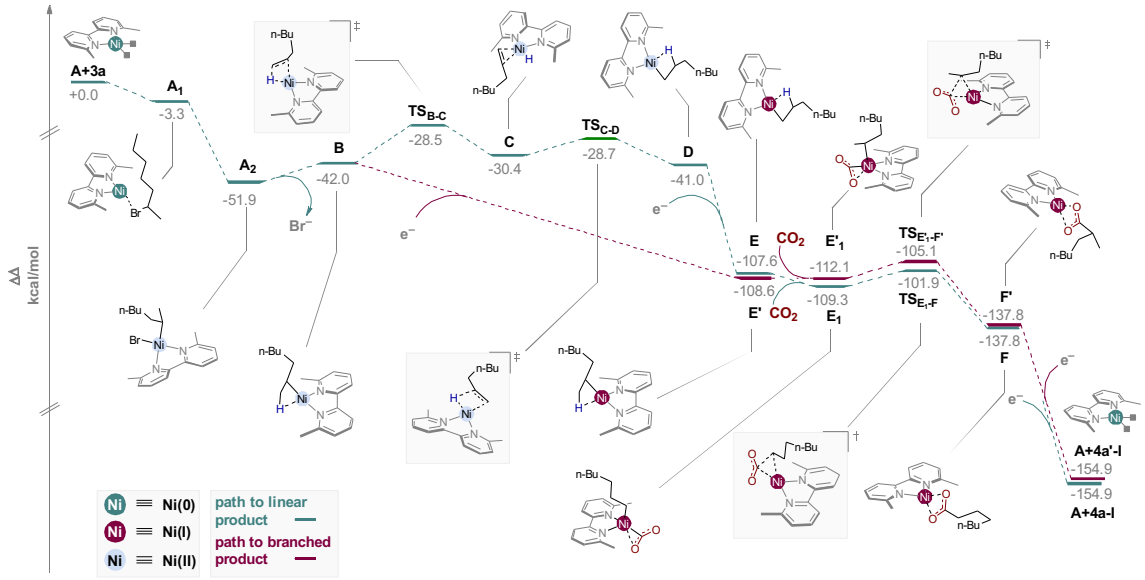


Scheme S1 *Reaction used for solvent correction purposes.*

To have a better precision in our analysis, all the molecules in this transformation were optimized in solvent at the SMD(DMF)-BS-UωB97X-D/6-31g(d).

All the distances and coordinates are given in Ångstrom (Å), energies are given in Hartree (1 Ha = 627.509474 kcal·mol^{-1}). Rendered structures were obtained using CYLview 1.0b[54] and ChemCraft 1.8.[55] The following color-code was used in visual representations: carbon = gray, nitrogen = blue, hydrogen = white, nickel = green, oxygen = red, bromide = dark red, potassium = purple.

9.3.1 Calculated intermediates and transition states for (L7)NiBr$_2$

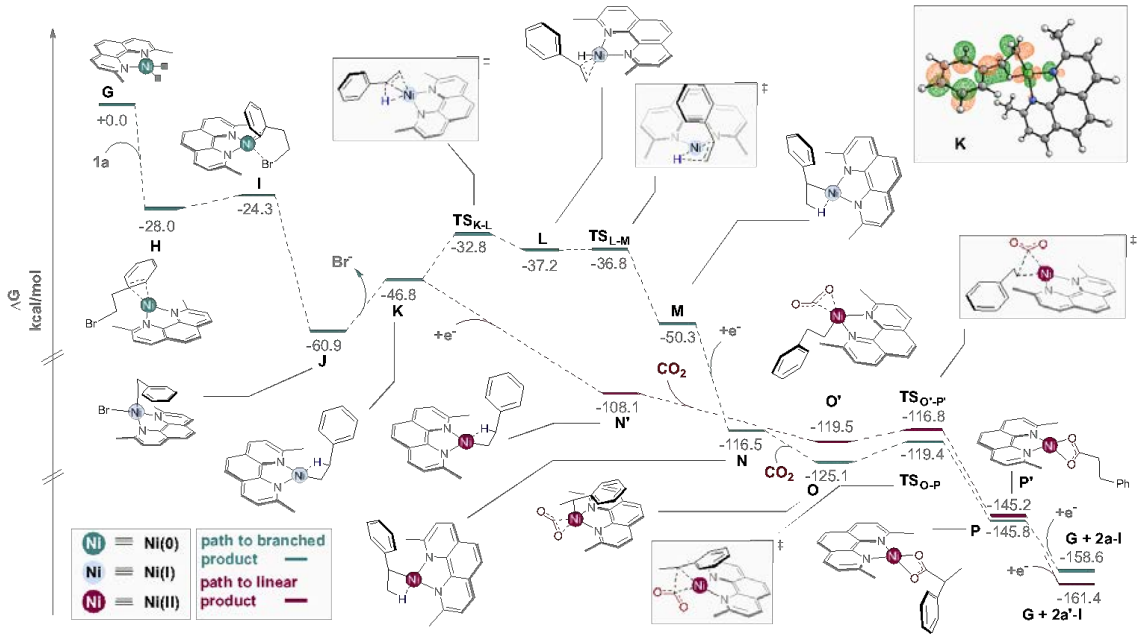


Scheme S2 *Proposed mechanism for the sp^3 C-H carboxylation of unactivated alkyl halides at the SMD(DMF)-BS-UwB97X-D/def2-TZVP//BS-UwB97X-D/6-31G(d) level of theory.*

The DFT-calculated catalytic cycle (Scheme S2) starts from the coordinatively unsaturated **Ni(0)/L7** species **A**, which is used together with the model substrate **3a** as the energetic reference. This species can coordinate the substrate **3a** *via* the initial interaction of the metal center with the bromine atom, to give the associated complex $\mathbf{A_1}$. The oxidative addition to form the Ni(II) complex $\mathbf{A_2}$ is thermodynamically favorable ($\Delta G_{A1\text{-}A2} \approx$ -52 kcal·mol^{-1}) and could be followed by bromide de-coordination towards **B**, stabilized by agostic interaction. The first isomerization step occurs *via* a β-hydride elimination ($\Delta G_{B\text{-}C}^{\ddagger} \approx 13.5$ kcal·mol^{-1}) and provides the alkenyl-Ni(II) complex **C**, which re-inserts through an almost barrierless process ($\Delta G_{C\text{-}D}^{\ddagger} \approx 2$ kcal·mol^{-1}). By comparing intermediates **B** and **D**, a slight destabilization of the terminal Ni(II) complex **D** compared to the branched Ni(II) homologue **B**, could be observed ($\Delta G_{B\text{-}D} \approx +1$ kcal·mol^{-1}). Indeed, such small energetic difference allegedly causes the system to be in equilibrium between complexes **B**, **C** and **D**. Interestingly, while the effect of TBAI could not be included explicitly on the calculation, its contribution to increase the selectivity of carboxylation reactions is known from previous literature (see Ref. 3c in the main text). In both cases, the SET from the reduced photocatalyst 4-CzIPN$^{\bullet-}$ likely forms the corresponding alkyl-

Ni(I) complex **E**. While the energetic barrier of the electron-transfer process cannot be computed, we can expect this process to be the product-determining step of the catalytic cycle (*see mechanistic evidences and explanation later in the paragraph*). The intermediate **E** coordinates CO_2 *via* an η^2(C-O) coordination followed by the migratory insertion step ($\mathbf{TS_{E1-F}}$). The carboxylate-Ni(I) complex **F** can liberate the conjugate base of product **4a** (**4a-I**) by a single-electron reduction sequence and forms the catalytically competent species **A**. The same considerations can be derived for the branched product obtained by direct reduction of intermediate **B** to **E'**, that ultimately leads to the byproduct **4a'-I**. It is interesting to notice that the highest barrier in the process is represented by $\mathbf{TS_{B-C}}$. The absence of a Kinetic Isotope Effect (*see the previous section on the Mechanistic Investigation*) advocates for a rate determining step which occurs after the chain-walking process. As already mentioned, the SET from the Ni(II) (**D/D'**) to the Ni(I) species **E/E'** is most likely dictating the observed selectivity.

9.3.2 Calculated intermediates and transition states for (L1)NiBr$_2$



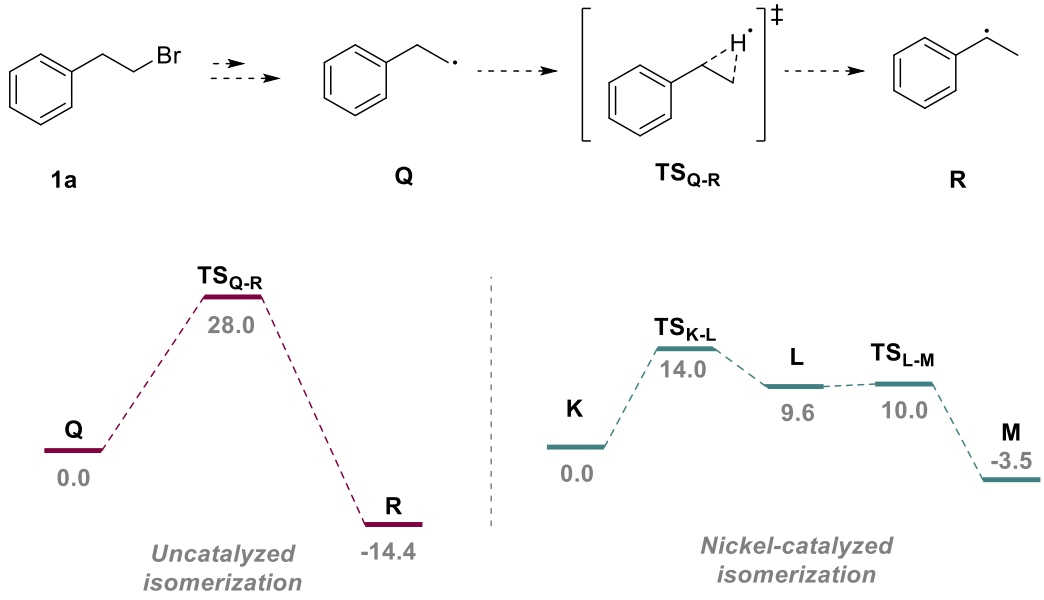
Scheme S3 *Proposed mechanism for the sp^3 C-H carboxylation of homobenzylic alkyl halides halides at the SMD(DMF)-BS-UwB97X-D/def2-TZVP//BS-UwB97X-D/6-31G(d) level of theory. In the box, the filled orbital that is involved in the agnostic interaction is reported.*

The DFT-calculated catalytic cycle (Scheme S3) starts from the coordinatively unsaturated Ni(0) species **G**, which is used as the energetic reference. This species can coordinate the substrate **1a** *via* the π-system, in particular *via* an η^2 interaction to give **H**. The subsequent interaction of the Ni-center with the bromide could be established at a small energetic expense (ΔG_{H-I} = 4.3 kcal·mol^{-1}), forming a distorted tetrahedral **I** complex, which undergoes oxidative addition to **J**. Notably, the intermediate **J** was found to be stabilized by an additional shifted face-to-face π-π interaction between the substrate and the neocuproine ligand. The aforementioned labile ligand could be extruded to give the distorted square-planar **K**, in which an agostic interaction could be observed (*see molecular orbitals in picture*). Notably, the interaction weakens the C-H bond, thus permitting the facile β-H elimination through **TS$_{K-L}$** ($\Delta G^{\ddagger} \approx 14$ kcal·mol^{-1}). The intermediate complex **L** could undergo a barrierless migratory insertion through **TS$_{L-M}$** to form **M**, which was also found to be stabilized by a β-agostic interaction. Both the branched **M** and linear **K** Ni(II) complexes can be reduced to give **N** and **N'**, respectively. They both retain the β-agostic interactions, but the former is approximately 8 kcal·mol^{-1} lower in energy. Both complexes can coordinate CO_2 in an η^2(C,O) fashion: in the case of **O** (branched complex) an additional shifted face-to-face π-π interaction was observed,

while absent in **O'**. The two Ni(I)-alkyl complexes undergo the migratory insertion ($\mathbf{TS_{O-P}}$, $\mathbf{TS_{O'-P'}}$), which was relatively low in activation barrier ($\Delta G^{\ddagger} \approx 3$ and 6 kcal·mol^{-1}, respectively) to yield the Ni(I)-carboxylate complexes **P** and **P'**. A second SET regenerates the catalytically-active Ni(0) complex **G** and liberates the product **2a-I** (and **2a-I** from **G'**). Another hint regarding the mechanism is represented by the different product distribution obtained with the deuterated compounds. In the case of the *d*-labelled reagent, $\mathbf{TS_{K-L}}$ would rise due to the presence of the heavier isotope. Even though this transformation does not become the rate-determining one, the diminished selectivity towards the benzylic product can be explained by considering that the equilibrium between **K** and **M** is influenced by the variation of the kinetic barriers. With the *d*-labelled compound, a greater amount of **K** will be present in solution, if compared to the corresponding protium-substituted reagent. Hence, the reduction from **K** to **N'** that forms ultimately **2a'-I** is more likely to occur with the deuterated **1a**.
In this case, the **K-M** equilibrium responsible for the selectivity of the reaction is pushed towards the population of **M** not only by kinetic effects but also by thermodynamics.

9.3.3 Uncatalyzed chain-walking of the homobenzylic radical

As the isomerization of the homobenzylic radical **Q**, which could be generated under light-irradiation, to the benzyl radical **R** could not be excluded *a priori*, we decided to evaluate the potential isomerization pathway towards the more stable **R** in the absence of nickel catalyst (Scheme S4).



Scheme S4 *Upper: plausible isomerization mechanism in the absence of nickel catalysis calculated at the at the SMD(DMF)-BS-UwB97X-D/def2-TZVP//BS-UwB97X-D/6-31G(d) level of theory; lower: comparison of the uncatalyzed and nickel-catalyzed energetic profile (left: compound **Q** was set as reference; right: intermediate **K** was set as reference).*

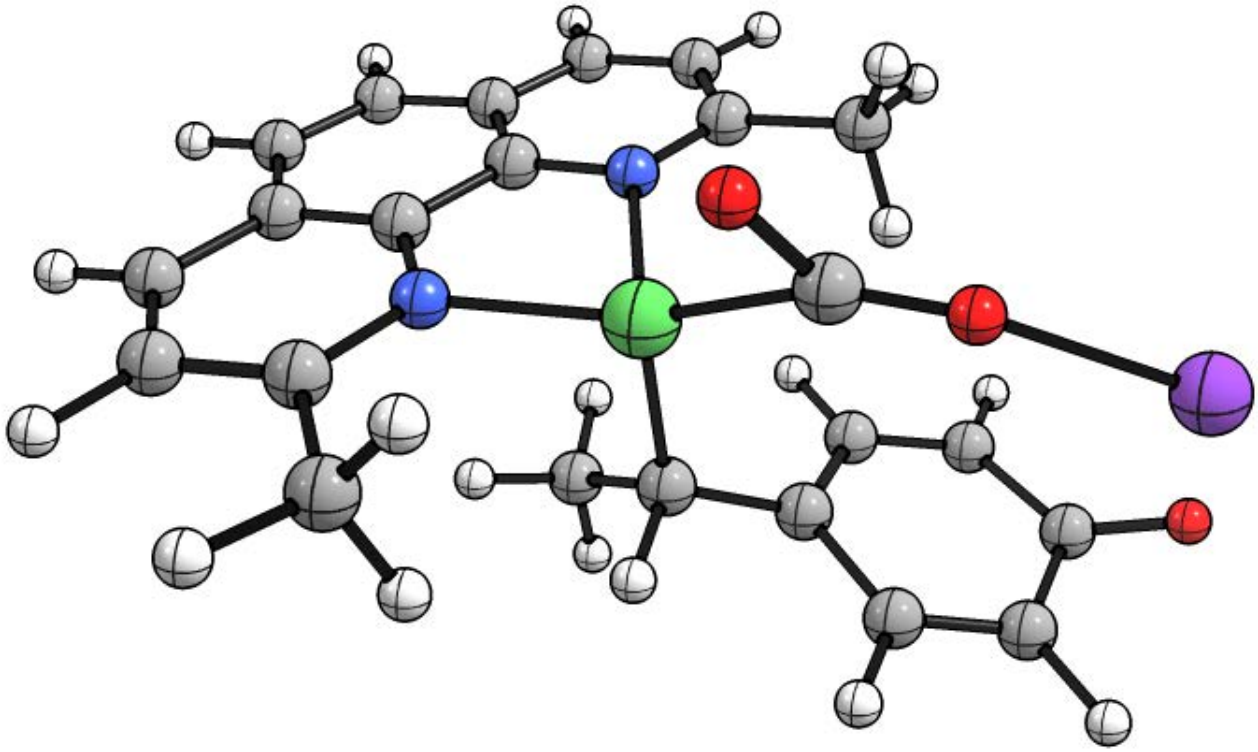
The calculated three-centered transition state $\mathbf{TS_{Q-R}}$ proved to be too high in energy to be overcome at ordinary temperatures ($\Delta G^{\ddagger}$ = 28.0 kcal·mol^{-1}), thus corroborating the hypothesis that the nickel catalyst is required to allow the chain-migration process to occur lower right). As already reported in(Scheme S4), the uncatalyzed energy barrier is replaced by two accessible transition states, which correspond to the β-H elimination ($\mathbf{TS_{K-L}}$) and the migratory insertion process ($\mathbf{TS_{L-M}}$).

9.3.4 Cartesian coordinates

2h+K^++CO_2

C	2.0186546191	-2.4530405195	-1.5452338193
C	2.9406646866	-1.4383192442	-1.4386727498
C	2.5102109263	-0.1328723315	-1.1301973309
C	1.1317152862	0.0485790695	-0.9414789975
C	0.6518057908	-2.1862127017	-1.3293504492
C	3.3908525494	0.9929066184	-0.9980399069
C	0.6091280621	1.3537962456	-0.6337096393
C	1.4946022167	2.4356024491	-0.5139530555
C	2.9028117925	2.2223311549	-0.6991366763
C	0.9262647087	3.6892917476	-0.2168062001
H	1.5654711765	4.5605793556	-0.1050683267
C	-0.4356714586	3.7953846372	-0.0823171034
C	-1.2604113274	2.6584307796	-0.2296143898
H	4.456443653	0.839290975	-1.1404680053
H	2.3301791208	-3.4631622604	-1.7875572765
H	3.9980325505	-1.6342063239	-1.5935885609
H	3.5708244077	3.072561563	-0.5978436208
H	-0.8961195421	4.7525392487	0.1360714188
N	-0.7340193834	1.4631536391	-0.4835050396
N	0.2390118644	-0.961613344	-1.0271489618
C	-2.7507816904	2.7717464167	-0.1267435835
H	-3.2119502971	2.5046154462	-1.0823569373
H	-3.1301878501	2.0837604904	0.636006014
H	-3.0467127901	3.7901997217	0.1366767363
C	-0.400547436	-3.2523355683	-1.4030926572
H	-0.7930137625	-3.4585157066	-0.4007603019
H	-1.2365391721	-2.9127846111	-2.0229430117
H	-0.0056462416	-4.1828020654	-1.8169877129
Ni	-1.6344364402	-0.4161818147	-0.4614545394
C	-0.182418112	-0.7050373516	2.034452063
H	0.6162726427	-1.2493921802	1.5167164491
H	-0.1653450343	-1.0166202725	3.0872338077
C	-1.5655209478	-0.9653790744	1.4234788742
H	-1.6895978765	-2.0599162413	1.3483812586
H	0.0865365581	0.3590348577	2.0192227332
C	-2.6768453851	-0.449947537	2.2813171463
C	-3.7855892434	-1.2458086164	2.5891840057
C	-2.7171047512	0.8709821535	2.7525101459
C	-4.9088944449	-0.741957728	3.2309725627
H	-3.7809791572	-2.2923961409	2.2815442703
C	-3.8399301468	1.4114479552	3.3659605848
H	-1.8523786402	1.5168965318	2.5905809924
C	-5.0429158927	0.6521293664	3.5442000341
H	-5.7594380962	-1.3894438135	3.4437167542
H	-3.8527313631	2.4553471628	3.6741370783
O	-4.5684941431	-0.0184362072	-0.529023223
C	-3.431213934	-0.2327504217	-0.9108359911
O	-2.8765644862	-0.4050048258	-2.0324671236
O	-6.1798620417	1.1893472709	3.7909621571
K	-6.3098688337	0.8401415949	1.1772845847

Energy = -3331.4570448
Zero-point correction = 0.385837 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.326653
Sum of electronic and zero-point Energies = -3331.071207
Sum of electronic and thermal Energies = -3331.043805
Sum of electronic and thermal Enthalpies = -3331.042861
Sum of electronic and thermal Free Energies = -3331.130392
G + ZVPE = -3330.744555
Energy (DMF-6-31G(d)) = -3331.5059117
Energy (DMF-def2-TZVP) = -3332.1924095



CO_2

O	-1.58621682	-2.1508762491	2.6113247187
C	-2.1509774894	-1.1374455653	2.5172885003
O	-2.7155314607	-0.1239134156	2.422909681

Energy = -188.520006
Zero-point correction = 0.010343 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = -0.005710
Sum of electronic and zero-point Energies = -188.509663
Sum of electronic and thermal Energies = -188.506689
Sum of electronic and thermal Enthalpies = -188.505745
Sum of electronic and thermal Free Energies = -188.525716
G + ZVPE = -188.515373

3a

C	-3.3529209603	0.2084108014	0.0488263175
H	-3.1015281159	0.916899738	0.8415089036
Br	-2.2064305891	0.7843700565	-1.459596376
C	-4.8067928062	0.3573291748	-0.3670118657
H	-5.4549502815	0.098045645	0.4789263172
H	-5.0307842982	1.3824014515	-0.6721729763
H	-5.0432623961	-0.311294105	-1.2004224204
C	-2.9879451605	-1.2104496651	0.4667688806
H	-3.7116830694	-1.5064029495	1.240928998
H	-3.1463723982	-1.8847304721	-0.384762664
C	-1.5719424634	-1.3766091798	1.0139536983
H	-0.8504316267	-1.072946047	0.2460984156
H	-1.4291802022	-0.6934518681	1.8633697276
C	-1.2750217802	-2.8082552599	1.4586528367
H	-2.0003547595	-3.113909408	2.2265454916
H	-1.4221576366	-3.489777073	0.6087802447
C	0.1424421941	-2.9820875937	2.0044333332
H	0.8641980584	-2.6732236317	1.236889141
H	0.2883080275	-2.3022373776	2.8544746692
C	0.439824339	-4.4158870883	2.4393907021
H	0.3269053537	-5.1118990086	1.6001784011
H	1.4614639631	-4.5143737137	2.8204847176
H	-0.2466653916	-4.7368904262	3.2314585065

Energy = -2847.4525701
Zero-point correction = 0.211350 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.173812
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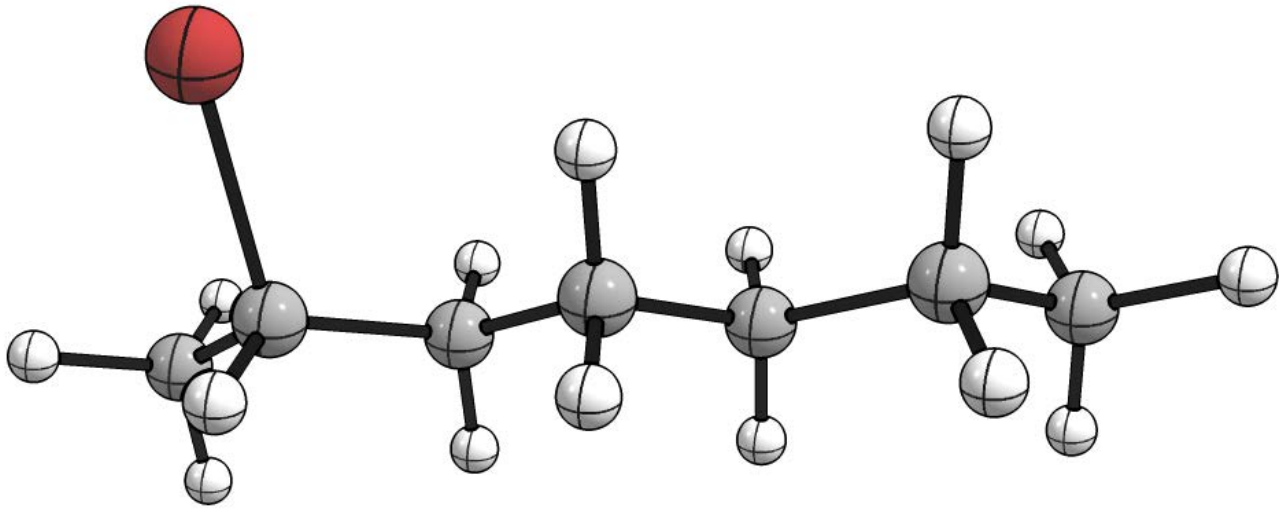
Sum of electronic and thermal Energies = -2847.230623
Sum of electronic and thermal Enthalpies = -2847.229679
Sum of electronic and thermal Free Energies = -2847.278758
G + ZVPE = -2847.067408
Energy (DMF-6-31G(d)) = -2847.4614837
Energy (DMF-def2-TZVP) = -2850.0430538



4a-I

O	-3.7032534258	-0.7288604786	0.8203694526
C	-3.2831455379	0.2920635228	0.2271139654
C	-1.018104015	-0.9684055361	0.0657253105
H	-1.4834861308	-1.5570509538	0.8631809601
H	-1.2424299201	-1.5013010427	-0.8707979022
C	-1.7191189904	0.3867934217	0.0622375398
H	-1.3383305612	0.98884149	0.9044656752
H	-1.5033390817	0.9613955752	-0.8468671554
C	0.5009479975	-0.9103502976	0.2561781885
H	0.716332541	-0.4199466514	1.2168984936
H	0.9116826275	-1.9306045408	0.3307036002
C	1.2340234189	-0.1733363141	-0.8682048118
H	0.9106353616	0.8756743187	-0.8843314432
H	0.9183509179	-0.601676006	-1.8299835157
C	2.7624701834	-0.2302144578	-0.7792030644
H	3.0905609996	-1.2808630977	-0.7823961006
H	3.1967409392	0.2288927434	-1.6799224414
C	3.3448130746	0.4679821658	0.4519106592
H	2.9874963904	-0.0298795634	1.3610341425
H	2.9599598233	1.4958260017	0.4948837239
C	4.8728356281	0.4906728952	0.4528320996
H	5.2579659006	1.0189445831	-0.4281106779
H	5.2705447174	0.990995981	1.3432924473
H	5.2806157051	-0.5274203332	0.4303449265
O	-3.9168955632	1.2684135744	-0.2278630723

Energy = -464.2475363
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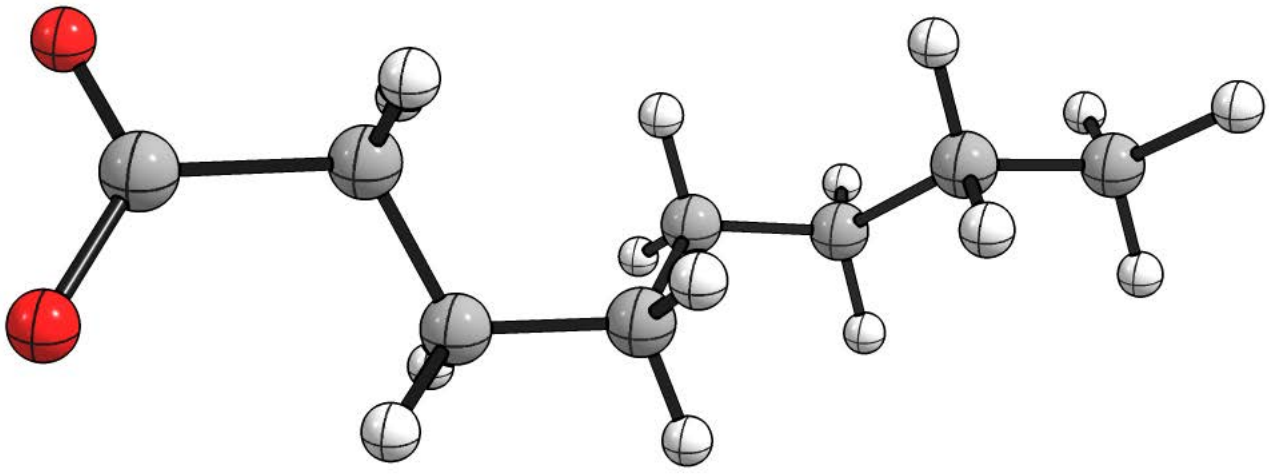
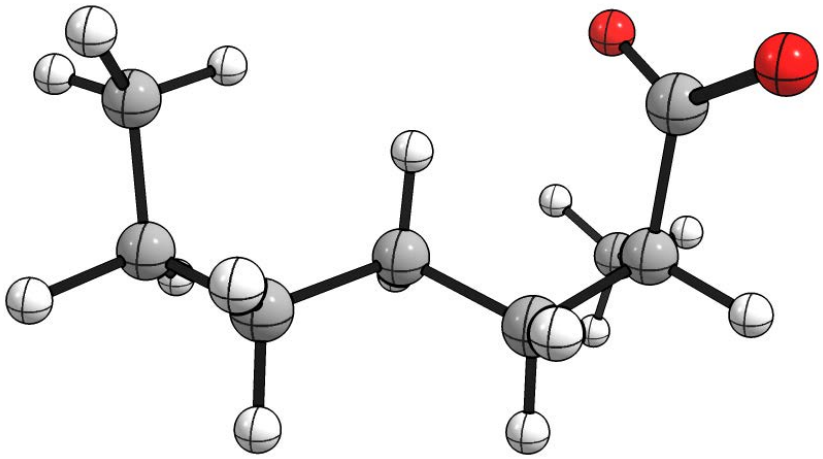
Thermal correction to Gibbs Free Energy = 0.182946
Sum of electronic and zero-point Energies = -464.024649
Sum of electronic and thermal Energies = -464.012792
Sum of electronic and thermal Enthalpies = -464.011848
Sum of electronic and thermal Free Energies = -464.064590
G + ZVPE = -463.841703
Energy (DMF-6-31G(d)) = -464.3391565
Energy (DMF-def2-TZVP) = -464.5317523



4a'-I

O	-2.2909724129	1.2236929224	-1.4159472606
C	-1.9562339884	0.7738027035	-0.2983173115
C	-0.3510628572	-1.0951701788	-0.8330857796
H	-0.2228600188	-2.1817421452	-0.9803204409
H	-0.3054472971	-0.6278606067	-1.8255206842
C	-1.743872243	-0.7873746037	-0.25565657
H	-2.478177355	-1.2258398226	-0.9440277007
C	0.8059046954	-0.5697954291	0.0224120079
H	0.5644966295	0.4554083554	0.3236909192
H	0.8755441046	-1.1546279995	0.9520002821
C	2.151398762	-0.6278547553	-0.701281922
H	2.1096843229	0.0210759645	-1.5883966477
H	2.3176384473	-1.6488285075	-1.0773330826
C	3.3497618879	-0.2188382195	0.1623902954
H	3.4078415188	-0.8871168963	1.0335504201
H	4.2780851594	-0.3726929231	-0.4062407642
C	3.2912970188	1.2319614669	0.6427477021
H	2.4259766786	1.4031815376	1.2896875199
H	3.2031699141	1.9191705136	-0.2071899052
C	-1.9364344496	-1.3705227368	1.1419632086
H	-1.6369797116	-2.4292128645	1.1985878315
H	-1.3551682097	-0.7865772768	1.8610836987
H	-2.986426766	-1.2969203281	1.4499213498
H	4.1939751025	1.5022091563	1.2041757523
O	-1.7087359324	1.3908976733	0.7669880814

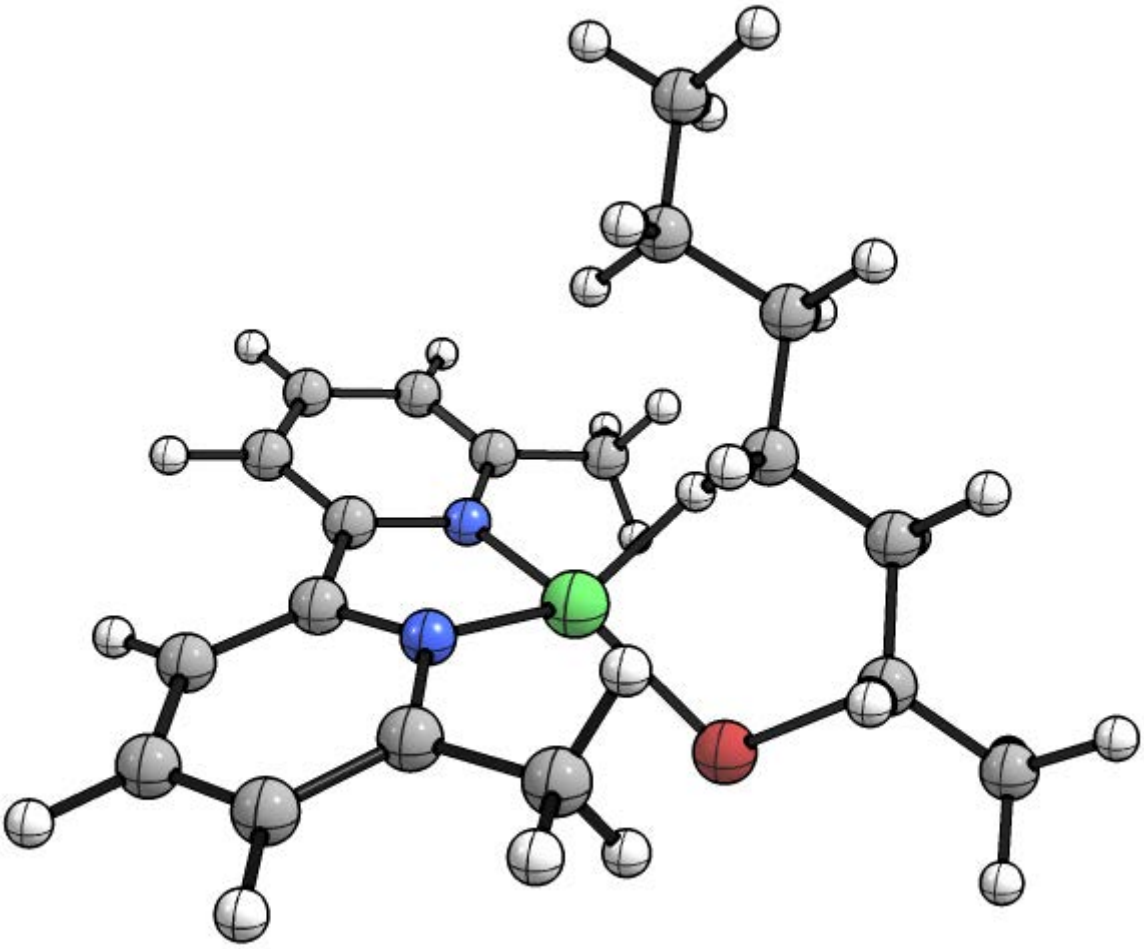
Energy = -464.2521106
Zero-point correction = 0.222698 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.183043
Sum of electronic and zero-point Energies = -464.029412
Sum of electronic and thermal Energies = -464.017474
Sum of electronic and thermal Enthalpies = -464.016530
Sum of electronic and thermal Free Energies = -464.069068
G + ZVPE = -463.846370
Energy (DMF-6-31G(d)) = -464.3400257
Energy (DMF-def2-TZVP) = -464.5309136



A_1

C	-1.9652111416	-3.7540185338	0.2528966002
C	-3.2285986829	-3.3944468948	-0.2352624317
C	-3.4651855735	-2.0674848286	-0.5232446924
C	-2.4473490434	-1.126870818	-0.3305569561
C	-0.987924216	-2.7925472375	0.4176608747
C	-2.5920363853	0.2831932401	-0.6244435992
C	-3.8144519733	0.9620534283	-0.6563410999
C	-3.8304017789	2.3221588562	-0.8801699674
H	-4.7643911794	2.8742091252	-0.899898074
C	-2.6071530099	2.9816428471	-1.0697944046
C	-1.4234507587	2.2731981094	-1.0365233053
H	-1.749553667	-4.783743809	0.5208436946
H	-3.9992104129	-4.1436843287	-0.3855144593
H	-2.5816827856	4.0488868441	-1.2666152259
N	-1.3971061298	0.9197249834	-0.8395876853
N	-1.2012226689	-1.4756545435	0.1290167133
C	-0.0996780533	2.9439717377	-1.2587389183
H	0.4425075016	3.0875490535	-0.3163710647
H	0.5344998911	2.3176433295	-1.898581514
H	-0.2247729736	3.9278458108	-1.7200206928
C	0.3669043698	-3.1456396294	0.9574373371
H	1.1169153474	-3.1736011349	0.1584745619
H	0.6828552024	-2.3820833112	1.6773079324
H	0.3576672286	-4.1202332235	1.4533579046
Ni	0.0689199361	-0.1534459751	-0.4401332428
C	3.259492863	-0.7572003942	0.3384121418
H	2.9172894837	-1.5423672305	1.0179011393
Br	2.0195841112	-0.9364126962	-1.2426763415
H	-4.7354711381	0.4204919144	-0.4675969165
H	-4.4197343399	-1.7503894341	-0.9302850267
C	4.6752965322	-1.0102788173	-0.1406820767
H	5.3679214523	-0.941368028	0.7065761365
H	4.7743828925	-2.0056777312	-0.582040193
H	4.973921641	-0.2681286364	-0.8876330777
C	3.0428892226	0.6164424755	0.9567744242
H	3.668384603	0.6500787964	1.8605977175
H	3.4254326132	1.3900544841	0.2776582048
C	1.5999505035	0.9280048651	1.3417255978
H	1.0084213239	1.0942453411	0.4120524316
H	1.1721426802	0.0740334731	1.878554755
C	1.4308855031	2.18134044	2.1926274631
H	2.0445292976	2.0997040075	3.1012304922
H	1.8124226712	3.0548208101	1.6432298087
C	-0.0291690612	2.4158553334	2.5851331145
H	-0.655151017	2.4335338105	1.6837875183
H	-0.3803076395	1.5585084539	3.1739880247
C	-0.2305857265	3.7063318349	3.3751749705
H	0.0693039867	4.5796088775	2.7841118914
H	-1.2794736659	3.8392750932	3.6584833443
H	0.3681221642	3.7061088598	4.2936671709

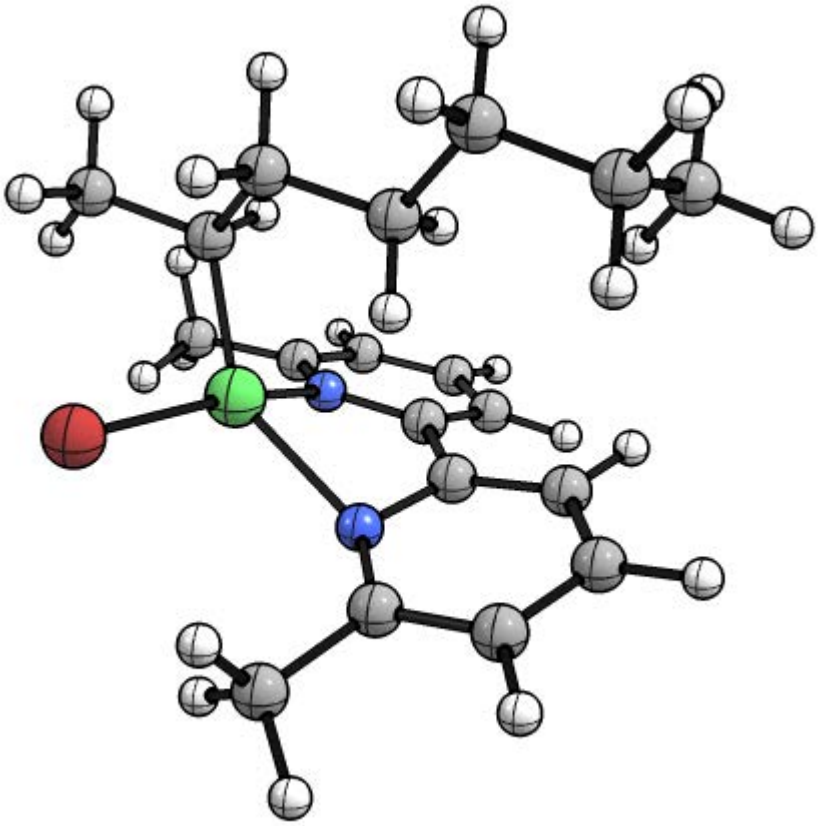
Energy = -4929.4246696
Zero-point correction = 0.429855 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.373937
Sum of electronic and zero-point Energies = -4928.994815
Sum of electronic and thermal Energies = -4928.969708
Sum of electronic and thermal Enthalpies = -4928.968764
Sum of electronic and thermal Free Energies = -4929.050733
G + ZVPE = -4928.620878
Energy (DMF-6-31G(d)) = -4929.4482558
Energy (DMF-def2-TZVP) = -4932.4472426



A_2

C	1.4434201384	-2.8471704339	-1.6003898063
C	2.5893600443	-2.289938585	-1.061876842
C	2.5956339553	-0.9300851628	-0.7737563098
C	1.425824229	-0.2135699389	-0.9695264737
C	0.3003522572	-2.0609944524	-1.7913222092
C	1.3391146972	1.2463492874	-0.7603667662
C	2.4321472887	2.0972860933	-0.842819469
C	2.2110397244	3.466175513	-0.7667748849
H	3.0417999794	4.1613724424	-0.8317684325
C	0.9098862503	3.9295458895	-0.6550172535
C	-0.1479542915	3.0244827558	-0.5662256173
H	1.4178121747	-3.8921666994	-1.8909741803
H	3.4749472284	-2.8938354409	-0.8918038518
H	0.6972296947	4.9930592972	-0.6398554571
N	0.0823150578	1.6986333209	-0.5762713863
N	0.2752637711	-0.7704232099	-1.412542267
C	-1.5649786455	3.5039218294	-0.4718129314
H	-2.2527491675	2.7558340471	-0.8715921106
H	-1.8434761921	3.6825541856	0.5713551075
H	-1.6854101559	4.4408829517	-1.0225253143
C	-0.9063410004	-2.6487131893	-2.4557872841
H	-1.5861119217	-3.0797489194	-1.7158822905
H	-1.4655603027	-1.876912295	-2.9856029099
H	-0.5985741734	-3.4291291151	-3.1584705643
Ni	-1.184837943	0.313044317	-0.2842028967
C	-1.1410128651	-0.1538461828	2.453978538
H	-1.8635954178	-0.9794027316	2.4488554572
H	-1.1566343136	0.2664416733	3.4742360471
C	-1.5983221525	0.9394187304	1.4757010684
H	-0.9374312383	1.8043707943	1.654600474
Br	-2.9546403733	-1.083576312	-0.3882469057
C	0.2521763713	-0.7226653427	2.1800567796
H	0.2155628845	-1.3371166333	1.270126797
H	0.9453929236	0.1064823192	1.9750667339
C	0.7982825523	-1.5936588167	3.3102275664
H	0.9036166101	-0.9927321582	4.2248836399
H	0.0588951312	-2.3732399164	3.5361408863
C	-3.0230804574	1.3762370129	1.8145109967
H	-3.6977256461	0.5178425654	1.8665242306
H	-3.0496920021	1.8890658785	2.7886533749
H	-3.4453420209	2.0572091098	1.0682896904
C	2.1381462638	-2.2587357236	2.9763958042
H	2.0298952403	-2.8216672214	2.0387611899
H	2.3819113621	-2.9950147747	3.7525303576
C	3.3005911497	-1.2738689395	2.8455654098
H	3.1096101003	-0.5295556792	2.0650256975
H	3.4607875067	-0.731722781	3.7848071361
H	4.2333129021	-1.7911313725	2.5938885906
H	3.428235189	1.7011418981	-1.0008373263
H	3.4823296528	-0.4495403446	-0.3771563126

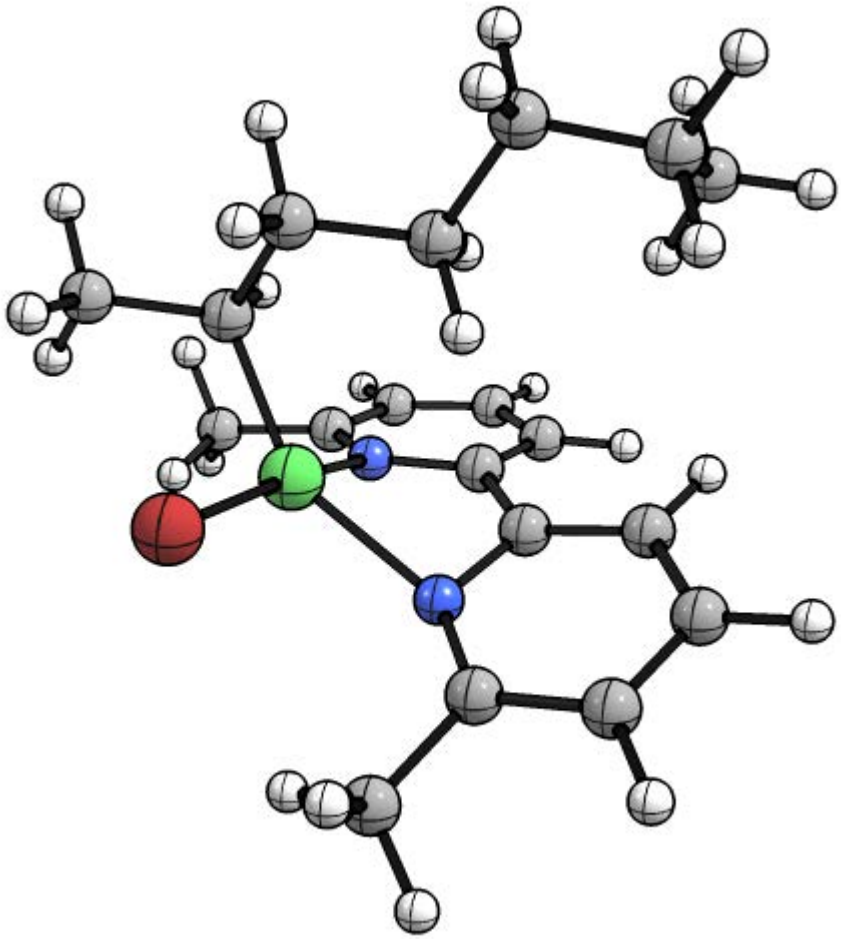
Energy = -4929.5169541
Zero-point correction = 0.431682 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.376510
Sum of electronic and zero-point Energies = -4929.085272
Sum of electronic and thermal Energies = -4929.060493
Sum of electronic and thermal Enthalpies = -4929.059549
Sum of electronic and thermal Free Energies = -4929.140444
G + ZVPE = -4928.708762
Energy (DMF-6-31G(d)) = -4929.5444921
Energy (DMF-def2-TZVP) = -4932.5290997



A_2-solv

C	1.2275689296	-2.9365456773	-2.0114418212
C	2.3881184725	-2.5320727325	-1.3740682994
C	2.4698190338	-1.2312835201	-0.8856953899
C	1.3487311924	-0.4240287347	-0.991205285
C	0.1340983322	-2.0672367713	-2.0884610506
C	1.3403148137	1.0133145067	-0.6411144003
C	2.4825726744	1.793055135	-0.5582793895
C	2.3300726086	3.167710896	-0.4069005468
H	3.2022845094	3.8101148145	-0.3420743063
C	1.0544689837	3.7076409049	-0.3906120559
C	-0.058172885	2.8663526929	-0.4507365607
H	1.1546600677	-3.9187624744	-2.467089273
H	3.2361311804	-3.2042227699	-1.290488612
H	0.9017999765	4.7801372896	-0.333838824
N	0.0988034855	1.5336986891	-0.5227193376
N	0.1740366498	-0.8546177137	-1.5127239141
C	-1.4461883241	3.4313865534	-0.4514701815
H	-2.1640085759	2.6874965313	-0.8026030745
H	-1.7407688578	3.7499392234	0.553953122
H	-1.4892165818	4.3086837083	-1.104048787
C	-1.0814576637	-2.463319018	-2.8712596559
H	-1.6718479216	-3.2110385918	-2.3355144688
H	-1.7198139174	-1.5997104646	-3.0610829204
H	-0.7653092267	-2.8960167213	-3.8267844171
Ni	-1.172988735	0.1490006052	-0.2632727011
C	-1.1497020482	-0.1118643049	2.5328642348
H	-1.793856642	-0.9993146417	2.5821485474
H	-1.2255569316	0.3841800759	3.5171736165
C	-1.6687820322	0.8516415838	1.4532359117
H	-1.0930983628	1.7802993352	1.5849705968
Br	-2.7194974819	-1.5322845964	-0.1576827356
C	0.2970214475	-0.5613656154	2.3219480444
H	0.3417088593	-1.223701835	1.445775487
H	0.9096691932	0.3172675948	2.0773724762
C	0.9175943307	-1.3028119212	3.5041810859
H	0.9738092789	-0.6328178904	4.3746872477
H	0.2571535236	-2.132767471	3.7922158644
C	-3.131433923	1.2085900999	1.7065436087
H	-3.768131023	0.3183781113	1.6900659985
H	-3.2568298443	1.6964275158	2.6878652133
H	-3.5251101813	1.8981456647	0.949854275
C	2.3127502937	-1.8586500903	3.1959286978
H	2.2394829424	-2.5564647958	2.3498745089
H	2.6638429234	-2.446559264	4.0537272124
C	3.3489452785	-0.7821536811	2.8726650523
H	3.0851156233	-0.219734463	1.9698946602
H	3.4373525549	-0.0630237729	3.6968158027
H	4.3380755856	-1.2245463562	2.707849421
H	3.4664366109	1.3478963052	-0.6454319362
H	3.3807538531	-0.8632524081	-0.4282372214

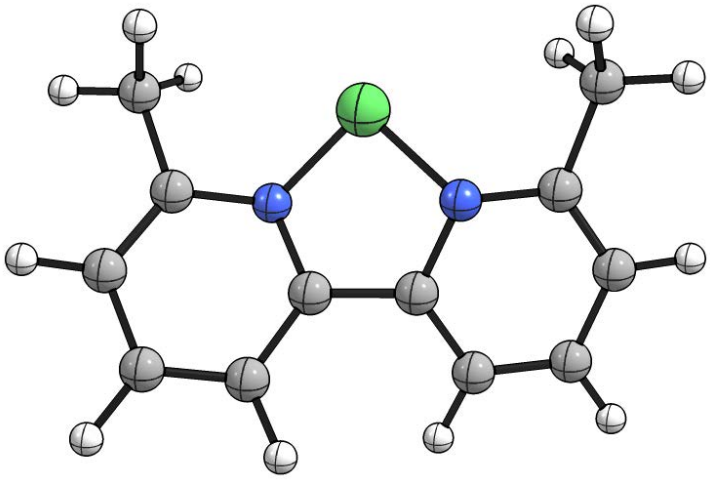
Energy = -4929.5449154
Zero-point correction = 0.430883 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.375407
Sum of electronic and zero-point Energies = -4929.114033
Sum of electronic and thermal Energies = -4929.089287
Sum of electronic and thermal Enthalpies = -4929.088343
Sum of electronic and thermal Free Energies = -4929.169508
G + ZVPE = -4928.738625



A

C	-2.2846115567	-3.4647544061	0.8185087792
C	-3.5470060438	-3.0382365352	0.3658192611
C	-3.6751413289	-1.7603071402	-0.1301031402
C	-2.5650385524	-0.9063536288	-0.1461662097
C	-1.21982615	-2.5937764832	0.8029563546
C	-2.5409485179	0.4092625491	-0.7367554944
C	-3.6624149295	1.2272663231	-0.9238310915
C	-3.5012392981	2.5098127772	-1.3977106941
H	-4.3571897042	3.1614433306	-1.538755911
C	-2.1989471196	2.9775811005	-1.654047816
C	-1.1216133377	2.1411147915	-1.4743422987
H	-2.145111313	-4.4719346707	1.197871821
H	-4.3931455854	-3.717282121	0.3764343899
H	-2.035630782	3.9895925323	-2.010349964
N	-1.2769775064	0.8326680626	-1.1061581068
N	-1.3591728816	-1.2900311262	0.4124034059
C	0.2972805471	2.5618349002	-1.7191562035
H	0.8544801112	2.6267794878	-0.7758305858
H	0.8002287167	1.814949374	-2.3474087977
H	0.3571589257	3.5389943572	-2.2060799225
C	0.1580034664	-2.9694546056	1.2619109034
H	0.8542453845	-3.0132437619	0.4146418177
H	0.5349285746	-2.2088805498	1.9583007447
H	0.174480609	-3.9457986179	1.7538421434
Ni	-0.0790839759	-0.2084452162	-0.2515099691
H	-4.6436113338	0.859424735	-0.6421009575
H	-4.6132694184	-1.4233494583	-0.5588224584

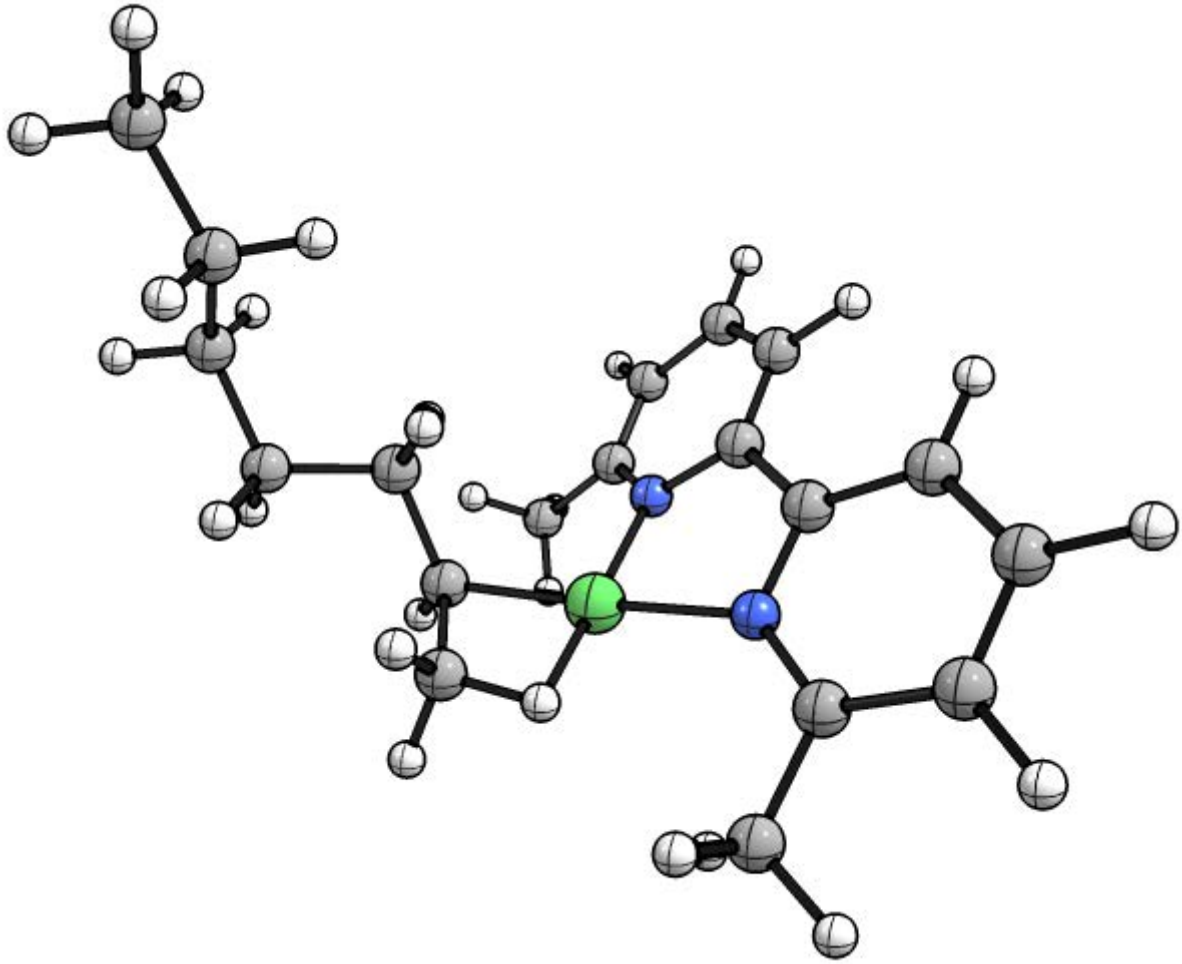
Energy = -2081.8984864
Zero-point correction = 0.215774 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.174630
Sum of electronic and zero-point Energies = -2081.682712
Sum of electronic and thermal Energies = -2081.669093
Sum of electronic and thermal Enthalpies = -2081.668149
Sum of electronic and thermal Free Energies = -2081.723857
G + ZVPE = -2081.508083
Energy (DMF-6-31G(d)) = -2081.924293
Energy (DMF-def2-TZVP) = -2082.3707816



B

C	-0.5471936055	3.448072554	-0.876877701
C	-1.3334447106	3.4465885018	0.263969046
C	-1.729995716	2.2338919402	0.8168587967
C	-1.3064819766	1.0601122564	0.2131500968
C	-0.1333740037	2.2367872012	-1.4307895367
C	-1.7658436169	-0.2921175727	0.6170148722
C	-2.6619372065	-0.5207245565	1.647560819
C	-3.1481928584	-1.8100296525	1.8344179014
H	-3.8454476021	-2.0213709025	2.6380009487
C	-2.7672351959	-2.8056172176	0.9524773707
C	-1.8479401107	-2.5285993189	-0.061256592
H	-0.2502958809	4.3788911483	-1.346720437
H	-1.6541821361	4.3814165891	0.7110912533
H	-3.1770634615	-3.8061492481	1.0331147635
N	-1.3140660558	-1.29785194	-0.1778632274
N	-0.4982620071	1.0688244454	-0.87308173
C	-1.4741891105	-3.5941746126	-1.0481671365
H	-1.2102056606	-3.1590982238	-2.0131857738
H	-0.6238923568	-4.183386131	-0.6911634627
H	-2.3141635231	-4.2785451656	-1.1897160262
C	0.7316692587	2.1938919539	-2.6568653672
H	1.7853632525	2.0582287474	-2.3847503877
H	0.4365887841	1.3726874544	-3.3162024483
H	0.6577331825	3.1276560031	-3.2180572768
Ni	0.2111093673	-0.7181330473	-1.1026474336
C	2.1919623776	-1.1045866506	-1.5694407552
H	1.5778436536	-0.1184493955	-1.7276989937
H	2.5664676257	-1.2841564259	-2.5781686839
C	1.3417124067	-2.1862968929	-1.0059183124
H	1.1663251832	-2.9990648141	-1.7136837595
C	1.6735622634	-2.6759335093	0.3908194258
H	1.8365377595	-1.8150036083	1.0529962302
H	0.8166388752	-3.2206995623	0.8107098832
C	2.904693983	-3.5905790616	0.4224993438
H	2.7576252893	-4.4012109821	-0.3032707372
H	3.7813704394	-3.0245629601	0.0779438239
C	3.1962067613	-4.1928789703	1.7995230101
H	4.0415196506	-4.885775483	1.7033711299
H	2.338701774	-4.8017323015	2.1199065428
C	3.5209796708	-3.1664086914	2.8872302444
H	4.3351671919	-2.5161865765	2.5387892903
H	2.6551110917	-2.5136477388	3.0591605614
C	3.9198035909	-3.8238148995	4.2074877075
H	4.1390926066	-3.0761901196	4.9758308169
H	3.1155083984	-4.4660702172	4.5836967266
H	4.8114433326	-4.4477166025	4.0822913198
H	2.9918635275	-0.7511574476	-0.913747746
H	-2.3672528437	2.2184311533	1.6919540485
H	-2.9925240586	0.2847352209	2.2907934914

Energy= -2357.5399768
Zero-point correction= 0.431349 (Hartree/Particle)
Thermal correction to Gibbs Free Energy= 0.379318
Sum of electronic and zero-point Energies= -2357.108628
Sum of electronic and thermal Energies= -2357.086120
Sum of electronic and thermal Enthalpies= -2357.085175
Sum of electronic and thermal Free Energies= -2357.160659
G + ZVPE = -2356.729310
Energy(DMF-631G(d))= -2357.6190886
Energy(DMF-def2-TZVP)= -2358.1329088

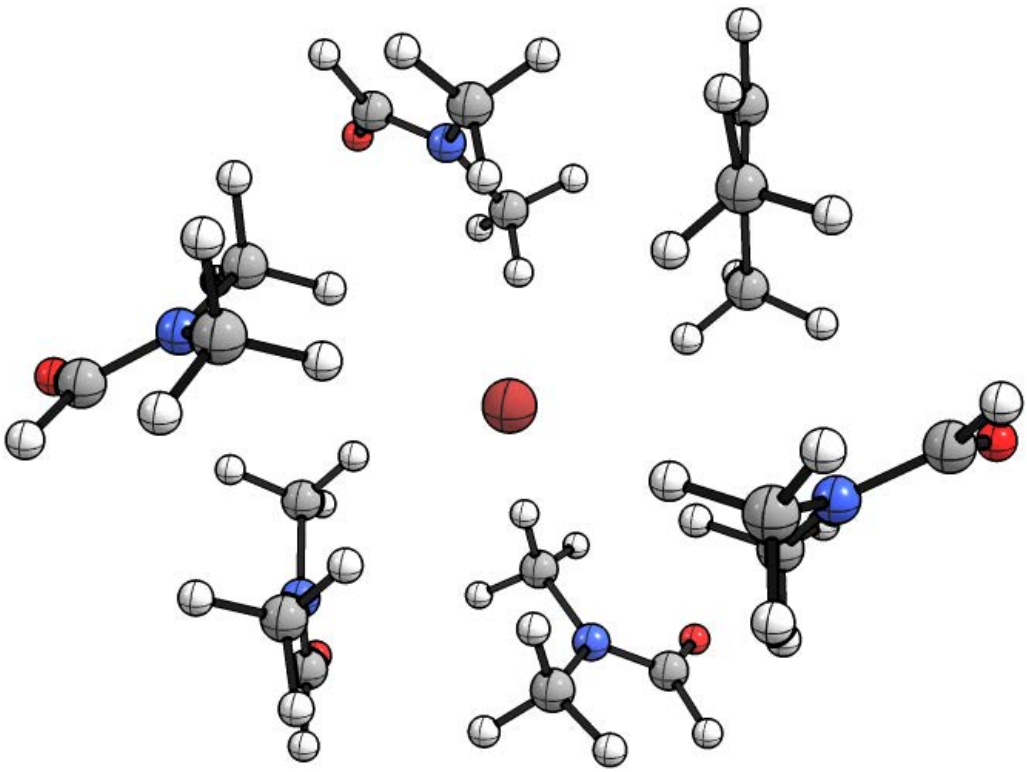


Bromide+DMF-solv

Br	0.001054	-0.000402	0.57972
C	-3.489325	-3.549625	-0.729789
O	-3.725784	-3.732522	-1.920501
H	-3.441402	-4.386565	-0.010104
N	-3.254971	-2.35976	-0.145371
C	-3.011824	-2.238307	1.279048
H	-2.856496	-3.228146	1.71672
H	-2.117255	-1.625643	1.435792
H	-3.864324	-1.763462	1.780845
C	-3.291013	-1.126429	-0.909444
H	-2.390587	-0.547087	-0.679481
H	-3.322655	-1.369657	-1.972292
H	-4.178835	-0.537296	-0.646077
C	4.900494	-0.913202	1.730605
O	5.732693	-1.043858	0.837702
H	5.129939	-0.371608	2.665697
N	3.637257	-1.379391	1.706184
C	2.738443	-1.228293	2.834847
H	3.162812	-0.527881	3.559479
H	1.776064	-0.844465	2.478078
H	2.57546	-2.194115	3.331417
C	3.144366	-2.151834	0.58239
H	3.025967	-3.206155	0.865234
H	2.172235	-1.753247	0.275969
H	3.857364	-2.081853	-0.239893
C	-4.899524	0.91332	1.736228
O	-5.733731	1.041365	0.84483
H	-5.126931	0.374796	2.673582
N	-3.636194	1.379017	1.707338
C	-2.734936	1.231342	2.834521
H	-3.157518	0.532599	3.561808
H	-1.773178	0.846937	2.476726
H	-2.571287	2.198509	3.328249
C	-3.145996	2.148286	0.580234
H	-2.174111	1.749625	0.273181
H	-3.860477	2.075333	-0.240503
H	-3.027822	3.203586	0.859499
C	1.68627	-4.347439	-1.576522
O	2.185379	-4.269716	-2.693926
H	2.100423	-5.014342	-0.798996
N	0.608093	-3.664721	-1.142711
C	0.080296	-3.832467	0.196957
H	0.76176	-4.443905	0.794646
H	-0.030242	-2.848354	0.666028
H	-0.898525	-4.326929	0.169247
C	-0.090809	-2.732679	-2.008349
H	-0.16588	-1.76509	-1.499566
H	0.472354	-2.626996	-2.936509
H	-1.098019	-3.103145	-2.237197
C	3.488182	3.553481	-0.727665
O	3.724599	3.737042	-1.918284
H	3.440234	4.390025	-0.007498
N	3.253927	2.363239	-0.143981
C	3.01139	2.240782	1.280466
H	2.857052	3.230383	1.719055
H	2.116412	1.628716	1.437123

H	3.863858	1.765016	1.781434
C	3.291229	1.130339	-0.908697
H	4.182157	0.544249	-0.649069
H	2.393569	0.54795	-0.675615
H	3.317998	1.373969	-1.971596
C	-1.687818	4.34369	-1.579822
O	-2.185892	4.264892	-2.697618
H	-2.103202	5.010713	-0.803046
N	-0.609327	3.662288	-1.14477
C	-0.082759	3.830935	0.195275
H	-0.764791	4.442649	0.792044
H	0.027749	2.84708	0.664926
H	0.895962	4.325597	0.167852
C	0.091847	2.731175	-2.009567
H	1.098829	3.103123	-2.237027
H	0.167774	1.763709	-1.500688
H	-0.469984	2.624688	-2.938432

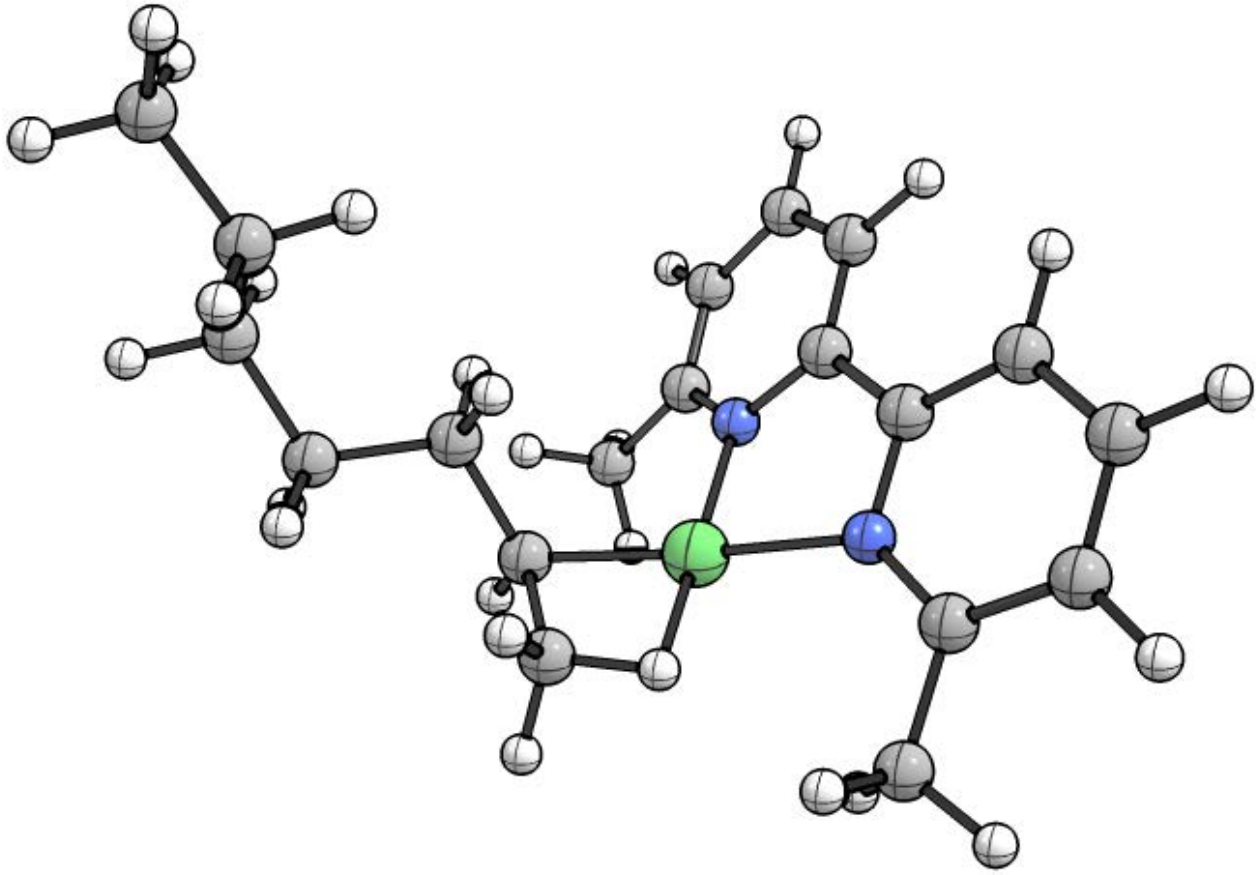
Energy = -4062.6172323
Zero-point correction = 0.637273 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.552462
Sum of electronic and zero-point Energies = -4061.979959
Sum of electronic and thermal Energies = -4061.935183
Sum of electronic and thermal Enthalpies = -4061.934238
Sum of electronic and thermal Free Energies = -4062.064770
G + ZVPE = -4061.427497



B-solv

C	-0.4890336803	3.4228318649	-0.8290327386
C	-1.243751414	3.4188214409	0.3330102064
C	-1.656638092	2.2072330802	0.8775197197
C	-1.2795200538	1.0358209771	0.2394148102
C	-0.1193064026	2.2116311591	-1.414640815
C	-1.7607670032	-0.3132096786	0.6253942093
C	-2.6656522188	-0.5413122186	1.6486900965
C	-3.1698335991	-1.8265583927	1.8146725607
H	-3.875838487	-2.0375848908	2.6108838046
C	-2.7966455392	-2.8176255308	0.9237676408
C	-1.8686448499	-2.5394088868	-0.0812715353
H	-0.1804920472	4.3534066424	-1.2925509169
H	-1.527908602	4.3530255148	0.8062351193
H	-3.2187037972	-3.8143991798	0.9889561853
N	-1.3201081001	-1.3143125189	-0.1812445749
N	-0.5005342041	1.0449564167	-0.8676039635
C	-1.4941717704	-3.5968608147	-1.0740157635
H	-1.2296617953	-3.1533289649	-2.0357888383
H	-0.6417001055	-4.1847349234	-0.7189202657
H	-2.3343360792	-4.2821547621	-1.2143070695
C	0.7143392341	2.1661165474	-2.6592787657
H	1.7705835401	2.0113386406	-2.4074947431
H	0.3961357051	1.3464964562	-3.3101080148
H	0.6371501099	3.1073218298	-3.208692397
Ni	0.1932793876	-0.7431873653	-1.1282146364
C	2.1756804503	-1.1172564253	-1.6019288446
H	1.5586758875	-0.142063001	-1.7752153097
H	2.5509275338	-1.3019670314	-2.6101217954
C	1.3339672853	-2.2035479792	-1.0317892647
H	1.1638458796	-3.0252166575	-1.7309827284
C	1.6683845942	-2.6781587298	0.369421059
H	1.809957417	-1.8055921567	1.020868821
H	0.8191999702	-3.2382338233	0.7852059071
C	2.9165910996	-3.5670016909	0.4203149385
H	2.7902060978	-4.3882495103	-0.2983535938
H	3.7853506308	-2.9863655738	0.0784986769
C	3.2093157341	-4.1558238628	1.8033333817
H	4.0711835652	-4.8327662393	1.7243056666
H	2.3583609424	-4.7763756654	2.1201199348
C	3.5008327935	-3.1157585164	2.8872163056
H	4.311365971	-2.456439672	2.5466816168
H	2.6223769506	-2.475552459	3.0363106792
C	3.8863001113	-3.7541523861	4.2199808608
H	4.0831792141	-2.9958140656	4.9862600754
H	3.0828852643	-4.4027697894	4.5902892039
H	4.7887908587	-4.3690542058	4.1172355617
H	2.9708964102	-0.7467423392	-0.9493927421
H	-2.2661215819	2.1904941112	1.7725480144
H	-2.9909756149	0.2623798958	2.297200201

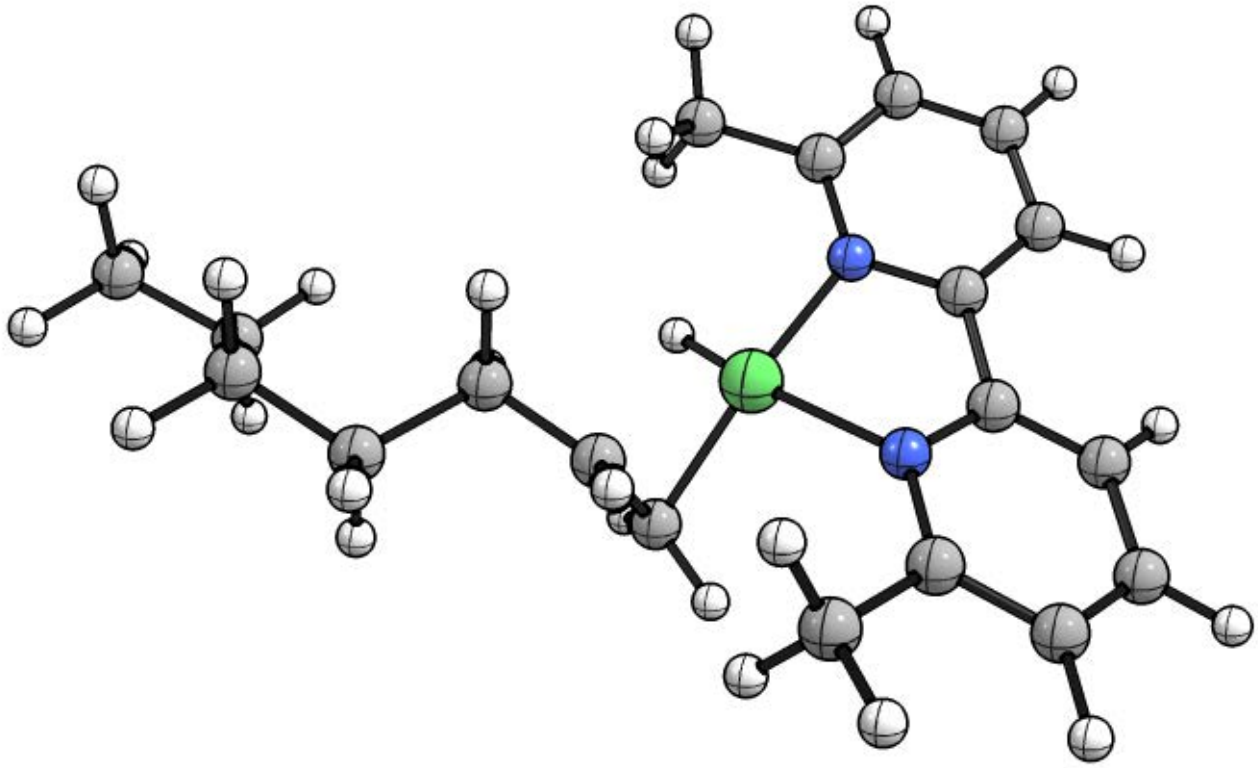
Energy = -2357.6192416
Zero-point correction = 0.430739 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.378950
Sum of electronic and zero-point Energies = -2357.188503
Sum of electronic and thermal Energies = -2357.166076
Sum of electronic and thermal Enthalpies = -2357.165132
Sum of electronic and thermal Free Energies = -2357.240292
G + ZVPE = -2356.809553



C

C	1.0357998262	3.7044187471	0.1766948022
C	2.4008348888	3.4899122967	0.0793701758
C	2.879844791	2.1899268782	-0.0382344406
C	1.9655732807	1.1492343441	-0.0779147543
C	0.1559349984	2.6242415035	0.1144344546
C	2.3493117766	-0.2839391283	-0.0727581893
C	3.657950793	-0.7037509314	-0.2567549233
C	3.9570872567	-2.0489161783	-0.0856491104
H	4.9695956578	-2.4110896404	-0.2280273221
C	2.9484996018	-2.9093211859	0.311240684
C	1.6437003744	-2.4353540193	0.460297801
H	0.6390973778	4.7054195379	0.3009883034
H	3.0927442569	4.3243810783	0.1182039437
H	3.1594141208	-3.9531961802	0.5134980939
N	1.3384434933	-1.145277225	0.2122044445
N	0.6328541303	1.3721984291	-0.0312795505
C	0.5752496156	-3.3651979288	0.9602680959
H	-0.0158255001	-2.8827111927	1.7427059676
H	-0.0987735786	-3.6938708781	0.1638625898
H	1.0300483873	-4.2602882919	1.3890150046
C	-1.3259271657	2.8260384099	0.2114076121
H	-1.7813776495	2.7869306714	-0.7838692316
H	-1.7905195518	2.0454761404	0.8179338558
H	-1.5527362065	3.798688849	0.6531892661
Ni	-0.340040745	-0.2062717256	-0.4165861879
C	-1.8838887427	-1.4886374336	-0.2676266379
H	-1.266989619	0.6317749471	-1.0978099805
H	-1.6348707807	-2.1252179432	0.5789906063
C	-1.1987139335	-1.6710145044	-1.4516031243
H	-1.6100293495	-1.2872554106	-2.3820692484
H	-0.4626721816	-2.4633169772	-1.5654061783
C	-3.2239294581	-0.8180021878	-0.1525449407
H	-3.3987893869	-0.1796561512	-1.0235678042
H	-3.2463528822	-0.1698258879	0.7345550522
C	-4.3377806122	-1.870322239	-0.0291553853
H	-4.087649407	-2.5700628558	0.7788631323
H	-4.3688681055	-2.4589834362	-0.9551597386
C	-5.7161970745	-1.2623400575	0.2456670027
H	-6.4322552739	-2.0827047489	0.3806591139
H	-5.6898615459	-0.7197882483	1.2011816366
C	-6.2315482484	-0.3307552563	-0.8535543893
H	-5.5699727612	0.5403932407	-0.9479658082
H	-6.1940009329	-0.8545255614	-1.8183145232
C	-7.6562641538	0.151852362	-0.5870536187
H	-7.7171184528	0.6903312696	0.365383396
H	-8.0017487972	0.8263642796	-1.3761610796
H	-8.3539466055	-0.6911281352	-0.5374758864
H	3.9455729216	2.0033655803	-0.0694076618
H	4.435055643	-0.0010047244	-0.5297094396

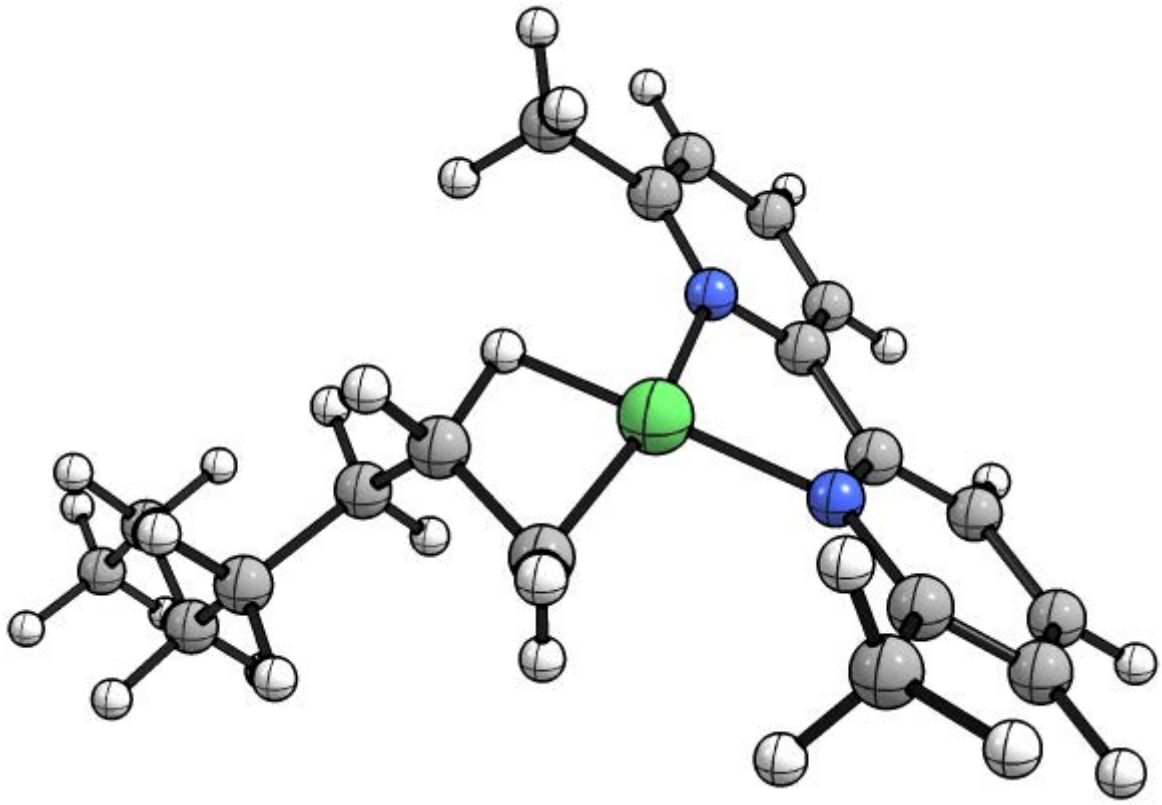
Energy = -2357.5150735
Zero-point correction = 0.429210 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.374261
Sum of electronic and zero-point Energies = -2357.085864
Sum of electronic and thermal Energies = -2357.063037
Sum of electronic and thermal Enthalpies = -2357.062093
Sum of electronic and thermal Free Energies = -2357.138957
G + ZVPE = -2356.709747
Energy (DMF-6-31G(d)) = -2357.5920888
Energy (DMF-def2-TZVP) = -2358.1055915



D

C	-0.6771054962	3.4760430947	-1.1450950298
C	-1.5406510822	3.5410570283	-0.0637378479
C	-1.9610467002	2.3631796781	0.543550411
C	-1.4807705412	1.157471859	0.0557778962
C	-0.2117450269	2.2369028779	-1.5835610181
C	-1.9350621131	-0.1713201285	0.5320362277
C	-2.9207147501	-0.3348345564	1.4905565349
C	-3.3722340592	-1.618551201	1.7733477754
H	-4.1404530985	-1.7779135502	2.5223427464
C	-2.8525130459	-2.6819882227	1.0582438883
C	-1.8480457193	-2.4689516189	0.1116830104
H	-0.3567563928	4.3764181761	-1.6569333959
H	-1.9011591064	4.4990321417	0.2954696973
H	-3.2170862899	-3.6898786951	1.2201314921
N	-1.3686004377	-1.2284765376	-0.1098614355
N	-0.5992333622	1.1039274357	-0.9694733169
C	-1.3104794658	-3.6233405597	-0.6778942227
H	-1.1096199632	-3.3305828238	-1.7097504068
H	-0.3791466426	-3.9936419899	-0.2399572202
H	-2.0308664545	-4.4442607566	-0.6796367056
C	0.7282726594	2.129289714	-2.7492782898
H	1.7653661638	2.0302846547	-2.406294739
H	0.4845910893	1.2625119333	-3.3697457095
H	0.6756525492	3.0238169084	-3.3732519889
Ni	0.1615420488	-0.6667110679	-1.0521351756
C	2.1856113405	-0.9744670379	-1.447466132
H	1.4922466028	-0.049754004	-1.6868140908
H	2.572775855	-1.1529410751	-2.4554627494
C	1.3488628639	-2.0909385888	-0.9491564054
H	1.572975036	-2.4256971449	0.0669495238
H	1.2383060501	-2.9286950501	-1.6363726794
C	3.2547696753	-0.4068604094	-0.515537646
H	3.5690360416	0.5823059573	-0.8687277782
H	2.821111978	-0.2640636881	0.4835852617
C	4.4648176595	-1.3386473418	-0.423860734
H	4.1167174609	-2.3445101451	-0.1570739803
H	4.9276001922	-1.4224725564	-1.4167234
C	5.5149112726	-0.883309339	0.5932114624
H	6.2998078128	-1.6479213373	0.6462186414
H	5.059412465	-0.8441329813	1.5928488064
C	6.1625509651	0.4672404149	0.2783341505
H	6.5755432582	0.4417684995	-0.7392513177
H	5.4016036271	1.2587886172	0.284599149
C	7.2653244199	0.8310866982	1.2709163354
H	7.7100398106	1.8019450408	1.0327002659
H	6.8718884058	0.8824873245	2.2924269068
H	8.0662735309	0.0837313539	1.2604883576
H	-2.655794617	2.3983638196	1.3729116247
H	-3.3476851598	0.5175039701	2.0031385699

Energy = -2357.5396839
Zero-point correction = 0.432276 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.379752
Sum of electronic and zero-point Energies = -2357.107408
Sum of electronic and thermal Energies = -2357.085128
Sum of electronic and thermal Enthalpies = -2357.084184
Sum of electronic and thermal Free Energies = -2357.159932
G + ZVPE = -2356.727656
Energy (DMF-6-31G(d)) = -2357.6185
Energy (DMF-def2-TZVP) = -2358.1326405

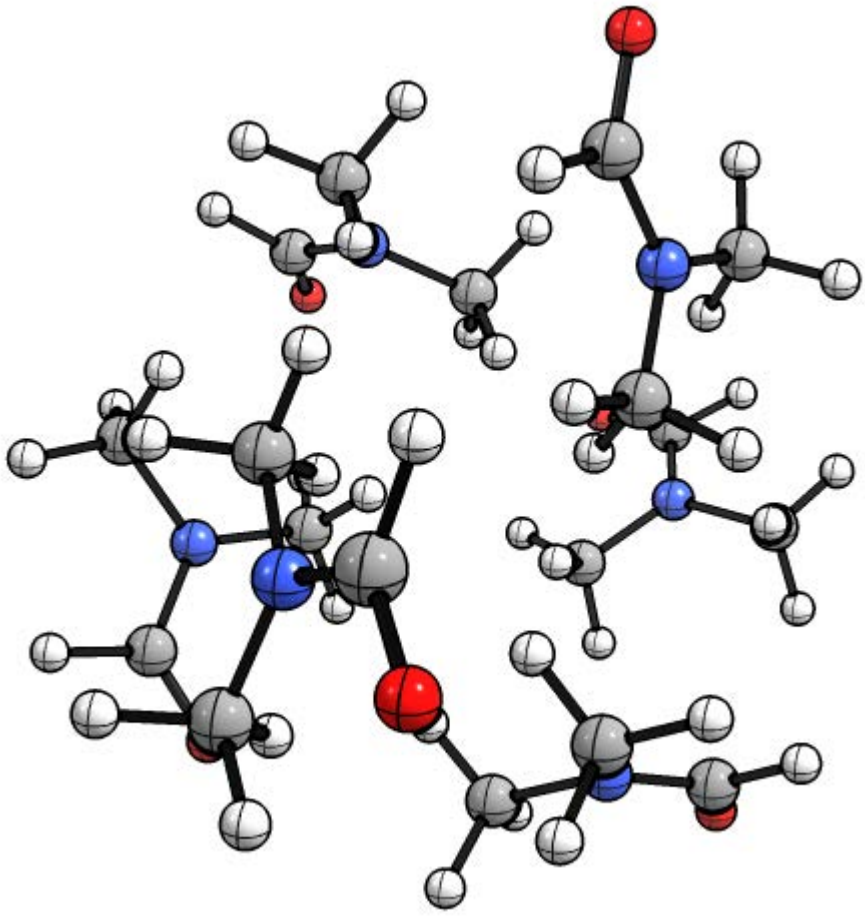


DMF-solv

C	2.89595	-3.141887	0.941283
O	3.376187	-2.829297	2.025198
H	2.677905	-4.192206	0.681185
N	2.572806	-2.289465	-0.053816
C	2.009532	-2.753378	-1.30343
H	1.877228	-3.837818	-1.27455
H	1.033304	-2.283713	-1.474409
H	2.665351	-2.496117	-2.142811
C	2.819132	-0.868458	0.067961
H	1.893836	-0.309731	-0.114391
H	3.183957	-0.646819	1.070149
H	3.566776	-0.547439	-0.667338
C	-3.411245	-0.778077	-2.576376
O	-4.442079	-0.156845	-2.803131
H	-2.632327	-0.918683	-3.346371
N	-3.084718	-1.362795	-1.402795
C	-1.823902	-2.047769	-1.213813
H	-1.278089	-2.092812	-2.159777
H	-1.20695	-1.522849	-0.473707
H	-1.995895	-3.070557	-0.85949
C	-3.977812	-1.300464	-0.264784
H	-4.269807	-2.312044	0.042289
H	-3.48902	-0.811246	0.584956
H	-4.867491	-0.737308	-0.547651
C	1.483635	-0.374315	-3.649706
O	2.498797	-0.709325	-4.247842
H	0.529939	-0.919262	-3.764902
N	1.381355	0.665165	-2.793081
C	0.124562	1.016594	-2.168006
H	-0.657833	0.32383	-2.486496
H	0.211652	0.974391	-1.075326
H	-0.173823	2.033189	-2.450569
C	2.513468	1.531089	-2.53765
H	2.668532	1.639617	-1.459467
H	3.401737	1.089481	-2.989894
H	2.343006	2.525364	-2.968362
C	-2.177469	-2.363857	2.580398
O	-2.665857	-1.339974	3.047388
H	-2.765793	-3.289668	2.459489
N	-0.900255	-2.508033	2.172844
C	-0.413618	-3.749346	1.608004
H	-1.221106	-4.48494	1.57388
H	-0.043867	-3.588516	0.588843
H	0.404378	-4.150415	2.216887
C	0.029214	-1.398766	2.245945
H	0.170769	-0.943593	1.25802
H	-0.364687	-0.646832	2.93085
H	1.000709	-1.752352	2.605518
C	-1.75225	3.816955	0.730598
O	-1.392045	4.364621	1.76741
H	-1.670781	4.315014	-0.250992
N	-2.272174	2.576046	0.633792
C	-2.743695	2.040352	-0.626235
H	-2.494004	2.722993	-1.442112
H	-2.274265	1.070452	-0.818856
H	-3.830113	1.895157	-0.606475

C	-2.485614	1.757364	1.808945
H	-3.557794	1.601284	1.97839
H	-2.015643	0.776852	1.684804
H	-2.054308	2.259003	2.675493
C	3.415998	2.415591	1.239548
O	3.889284	1.601425	2.024108
H	4.054944	3.057684	0.608536
N	2.100331	2.64012	1.031865
C	1.638939	3.707848	0.167396
H	2.488399	4.157822	-0.352298
H	0.937816	3.316635	-0.57828
H	1.124819	4.478499	0.752142
C	1.093426	1.924178	1.788708
H	0.534493	2.614481	2.430094
H	0.384192	1.444153	1.105671
H	1.584638	1.164992	2.397895

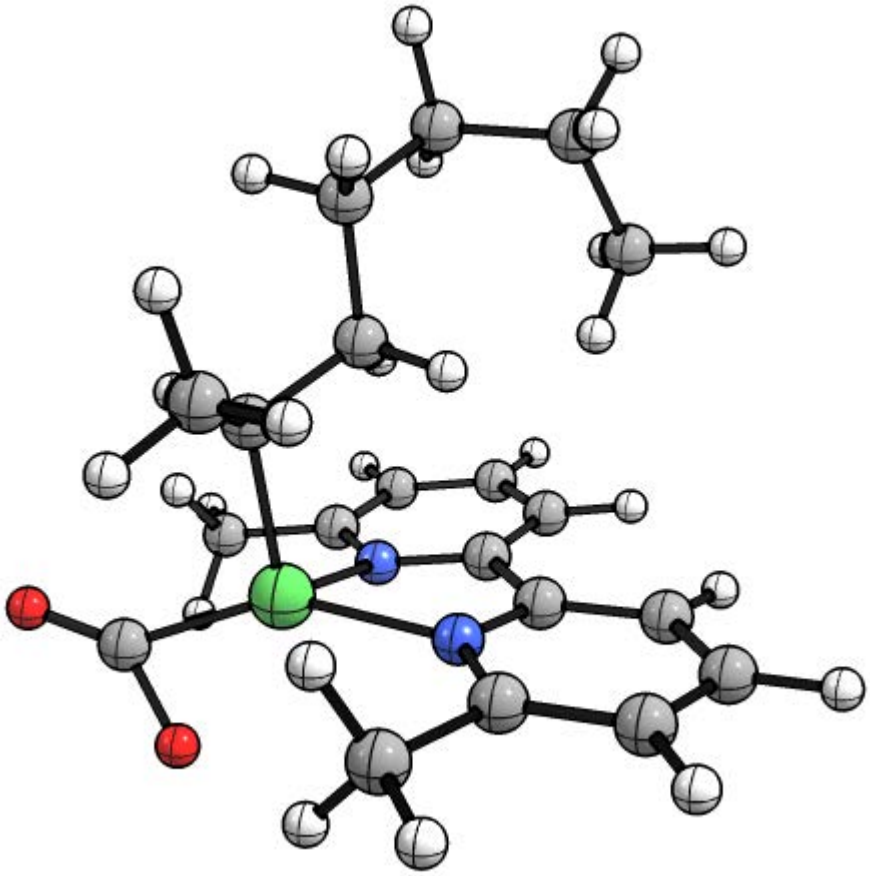
Energy = -1490.7033966
Zero-point correction = 0.634266 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.553409
Sum of electronic and zero-point Energies = -1490.069130
Sum of electronic and thermal Energies = -1490.026307
Sum of electronic and thermal Enthalpies = -1490.025363
Sum of electronic and thermal Free Energies = -1490.149987
G + ZVPE = -1489.515721



E'_1

C	0.6360870824	-3.7993062453	-0.7758533011
C	1.5926184711	-3.2333264909	-1.6070148554
C	1.5277328045	-1.8772239982	-1.8959221709
C	0.5090985725	-1.1220662498	-1.3216101737
C	-0.3614780472	-2.990937303	-0.2349211759
C	0.3235558324	0.3306028427	-1.5661463824
C	1.252421325	1.1021963923	-2.2560548718
C	1.0052984147	2.4581340223	-2.412104438
H	1.7175964753	3.088024483	-2.9354102228
C	-0.15834094	2.9960107594	-1.8848225335
C	-1.0508608366	2.1720978252	-1.1984757231
H	0.6504124312	-4.8593740031	-0.5474833071
H	2.3768971618	-3.8464906683	-2.0393792934
H	-0.3800166486	4.0524694162	-1.9882118263
N	-0.7992966064	0.8612522808	-1.0449031088
N	-0.3956754854	-1.6753545332	-0.4969225725
C	-2.308905696	2.7155453839	-0.5931168986
H	-3.1853452865	2.1988300799	-0.9949067362
H	-2.3187470402	2.5564559838	0.489140328
H	-2.410286387	3.7840526649	-0.7973936504
C	-1.4516920456	-3.531609327	0.6424830006
H	-1.3697895387	-3.1238918308	1.6553611981
H	-2.43090415	-3.2379280763	0.2514526296
H	-1.4049422926	-4.6212159035	0.7059250124
Ni	-1.6952893771	-0.3640872971	0.3577096495
C	0.6660997513	0.6691078432	1.7061324952
H	1.1941025025	-0.2076392538	1.3001322262
C	-0.7962147146	0.2996283308	1.967422565
H	0.7210749272	1.4464277734	0.9307786351
O	-4.113292657	0.8044461243	1.4844661365
C	-3.4437771186	0.08397109	0.7928187756
O	-3.5804536102	-0.839241707	-0.0627119371
H	-1.3154051519	1.2032093576	2.3173327273
H	2.2502408506	-1.4279439935	-2.5658065309
H	2.165733611	0.6671498014	-2.6420938667
C	1.4466007854	1.1851527339	2.9223534997
H	1.6411361681	0.3592960487	3.6196651847
H	0.8105054249	1.8988368161	3.4648871056
C	2.7761482234	1.8765733781	2.5943874607
H	2.582691687	2.746720177	1.9494661088
H	3.1834578644	2.2793471651	3.5305950606
C	3.8538053685	0.9961948392	1.9373623562
H	4.8394115995	1.4163837245	2.1741395712
H	3.8324217717	-0.0031182835	2.3933788285
C	3.7538717406	0.8662818255	0.4146877118
H	2.840119945	0.3515037577	0.1066969752
H	3.7489909068	1.8556286175	-0.0590501902
C	-0.908141299	-0.7534297624	3.0767123763
H	-0.3000427389	-1.6411185082	2.8449316109
H	-0.5523795228	-0.3812233559	4.0485008314
H	-1.9435169921	-1.0826912824	3.2257923659
H	4.6071663838	0.306811595	0.0138814905

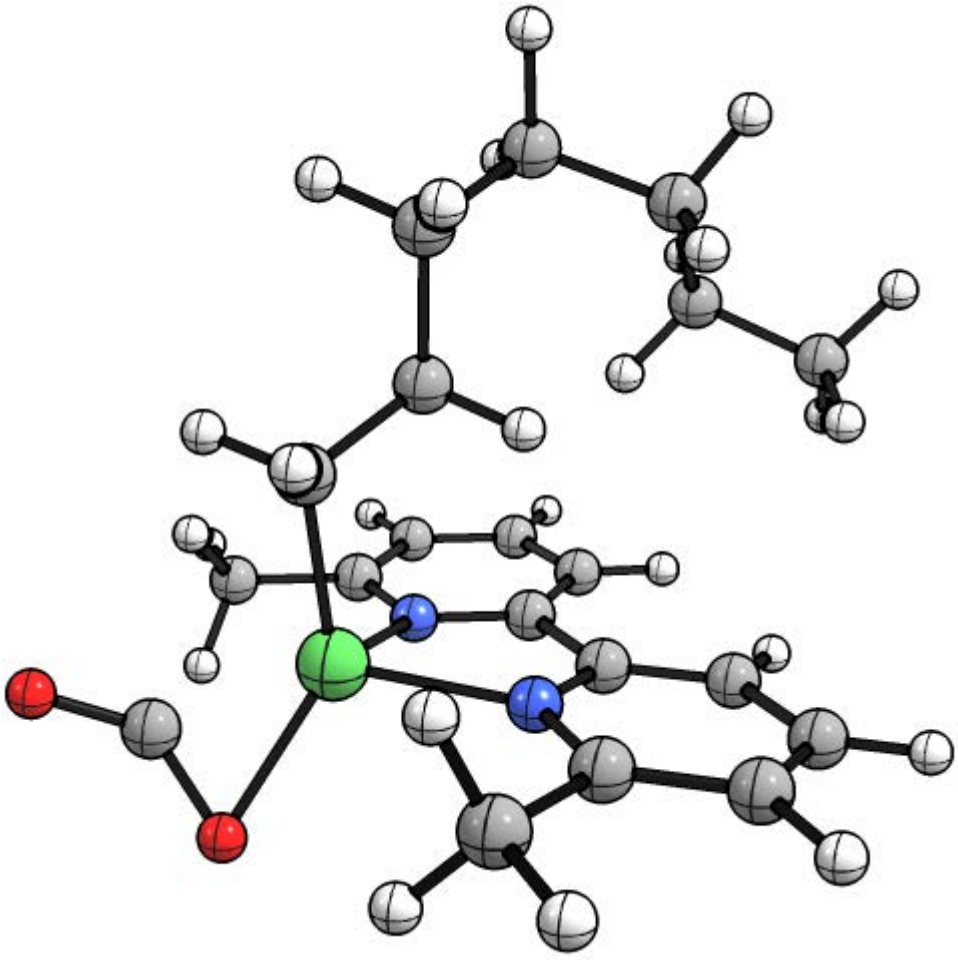
Energy = -2546.244042
Zero-point correction = 0.442527 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.384316
Sum of electronic and zero-point Energies = -2545.801515
Sum of electronic and thermal Energies = -2545.774994
Sum of electronic and thermal Enthalpies = -2545.774050
Sum of electronic and thermal Free Energies = -2545.859726
G + ZVPE = -2545.417199
Energy (DMF-6-31G(d)) = -2546.2762883
Energy (DMF-def2-TZVP) = -2546.8589755



E_1

C	1.8313027755	3.6228989731	1.2285994221
C	2.72649343	3.5534838931	0.1697046334
C	2.8774770855	2.3578685199	-0.5197589708
C	2.1149566724	1.2620747989	-0.1258057969
C	1.1017785638	2.4883837507	1.5762707655
C	2.1663924726	-0.0640568849	-0.7914640863
C	2.8757905593	-0.2856227114	-1.9670819189
C	2.838962294	-1.5492464337	-2.538153872
H	3.3781585677	-1.7512953184	-3.4580365747
C	2.0980857415	-2.5451720143	-1.9214707257
C	1.4002351176	-2.2605221396	-0.7472115734
H	1.6953630773	4.5432638333	1.7858409459
H	3.3067734426	4.4245433474	-0.1175101709
H	2.0449408374	-3.5418306358	-2.3453861429
N	1.4446151257	-1.0347392598	-0.1985520804
N	1.2517244121	1.3414888512	0.8987796621
C	0.5673047881	-3.3009652269	-0.0627766655
H	0.9503357291	-3.5055202241	0.9412946711
H	-0.4619348754	-2.9512489902	0.0582675306
H	0.5648597125	-4.2346608411	-0.6300026614
C	0.1091150012	2.4700131334	2.7004946824
H	-0.8999773852	2.3049637841	2.3061483539
H	0.33144281	1.6474976096	3.3882148014
H	0.1154582699	3.4102298788	3.256369404
Ni	0.161255953	-0.3376692956	1.2666495723
C	-1.1631470786	0.4320295042	-1.1997263362
H	-0.4575325415	1.2747672175	-1.1627039904
C	-1.4570429786	-0.0558168182	0.2171800924
H	-2.0655723141	0.70506016	0.7365030879
H	-0.6505698938	-0.361536166	-1.7656600974
O	-1.2040828956	-2.5049899339	2.6632564101
C	-0.3933048894	-1.6384305532	2.4763330001
O	0.6013795494	-1.0989255439	3.0425854474
H	-2.0887618163	-0.9522859137	0.1735743175
H	3.5767208399	2.2903397162	-1.3436434361
H	3.4277143819	0.5139792285	-2.4453720835
C	-2.3866597173	0.8779898456	-2.0031609834
H	-2.8585318029	1.7250006276	-1.4837414909
H	-3.1294991333	0.069262594	-2.0037091417
C	-2.0878170234	1.285567554	-3.4532058262
H	-1.7571471824	0.4018112174	-4.0178435139
H	-3.0264262658	1.6082551805	-3.9200242566
C	-1.0328822129	2.3988280449	-3.6005569306
H	-1.2949010247	3.0532281534	-4.4424753776
H	-1.0533303065	3.0382622379	-2.7057817696
C	0.3947907662	1.88772035	-3.8233047889
H	0.6443791536	1.137782823	-3.0651518327
H	0.4390634126	1.3680621046	-4.7899177646
C	1.4342586423	3.005842978	-3.7912981084
H	1.433179262	3.5080908226	-2.8164357386
H	2.4459998239	2.6221535955	-3.9713255182
H	1.227378527	3.7642667759	-4.5553486149

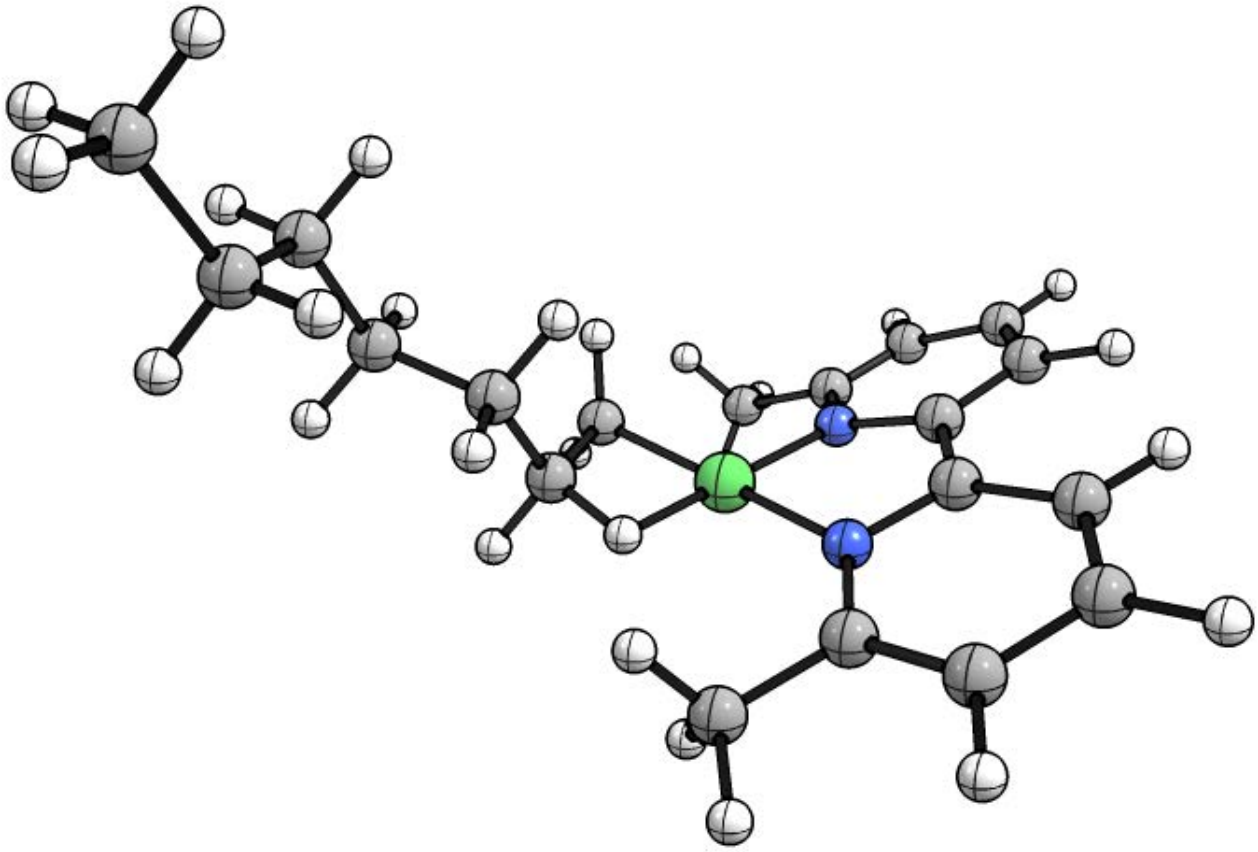
Energy = -2546.2466858
Zero-point correction = 0.442809 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.384209
Sum of electronic and zero-point Energies = -2545.803877
Sum of electronic and thermal Energies = -2545.777517
Sum of electronic and thermal Enthalpies = -2545.776573
Sum of electronic and thermal Free Energies = -2545.862476
G + ZVPE = -2545.419667
Energy (DMF-6-31G(d)) = -2546.2796777
Energy (DMF-def2-TZVP) = -2546.8634782



E

C	-0.7260357546	3.4811792354	-1.145998119
C	-1.7256918461	3.5348205572	-0.1464506347
C	-2.1528041282	2.3755269958	0.4370087414
C	-1.5826248679	1.1379696162	0.0464172888
C	-0.1734147868	2.2648419702	-1.4805072294
C	-2.0076942765	-0.133842514	0.5077314452
C	-3.0462133589	-0.3344646024	1.4497251494
C	-3.4806736494	-1.5993294788	1.7254896229
H	-4.277483872	-1.7662708531	2.4437711916
C	-2.8984599273	-2.6887869857	1.0393676827
C	-1.855944091	-2.4704798504	0.1649513159
H	-0.3908103165	4.3817015941	-1.6479252929
H	-2.1610014601	4.4872080125	0.1401711848
H	-3.264046998	-3.698030742	1.1906960526
N	-1.3646854726	-1.2239250267	-0.0725879906
N	-0.5589778566	1.1070799295	-0.8859043778
C	-1.2566286245	-3.6347530294	-0.5708819932
H	-1.0944567471	-3.3847567554	-1.6222435485
H	-0.2910482896	-3.9204348632	-0.1444340914
H	-1.9242128623	-4.4983458202	-0.5120740953
C	0.8968163122	2.1864366261	-2.5359862291
H	1.8804056075	1.9891383534	-2.0919726864
H	0.6812005823	1.3857878593	-3.2518580668
H	0.9675694449	3.127913554	-3.0859314271
Ni	0.1654960842	-0.6618314955	-0.9690690444
C	2.1748640789	-0.9600179288	-1.4422878027
H	1.4854293968	-0.0385418731	-1.6481815755
H	2.5427156963	-1.1311668493	-2.4600361972
C	1.3582314938	-2.0925675299	-0.9258971469
H	1.635857004	-2.4386510343	0.0738450534
H	1.2548242432	-2.9285024416	-1.6178167264
C	3.2746075858	-0.4086217436	-0.5371948421
H	3.5828286197	0.5849172719	-0.8862901678
H	2.8650901155	-0.2735261919	0.4727147527
C	4.4841141333	-1.3421045531	-0.4809623424
H	4.136543942	-2.3496544697	-0.2208225448
H	4.9284761801	-1.4165625083	-1.483819877
C	5.5569165504	-0.9071274264	0.5210705178
H	6.3392397119	-1.676938304	0.5577278388
H	5.1169801754	-0.8698194617	1.5278497771
C	6.2088063592	0.4414973451	0.2073982092
H	6.6097645663	0.4195442429	-0.8153445409
H	5.4508920751	1.2345558155	0.2250552148
C	7.3245452823	0.7962370112	1.1888361577
H	7.7743364211	1.7652706259	0.9497013586
H	6.9406635056	0.8476950359	2.2142316531
H	8.1202113771	0.0424375735	1.1701984614
H	-2.9358150136	2.397949713	1.186074797
H	-3.4978610352	0.519640184	1.9408604435

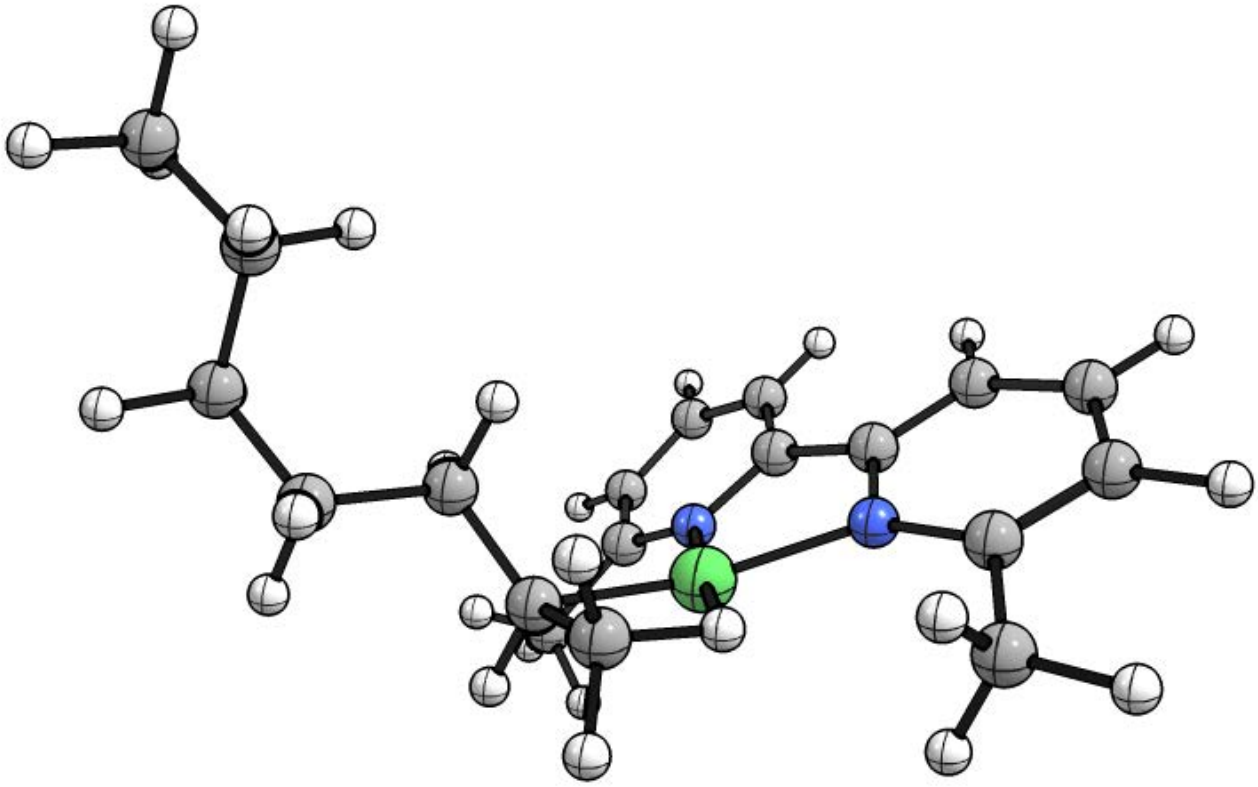
Energy = -2357.6921286
Zero-point correction = 0.429645 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.376739
Sum of electronic and zero-point Energies = -2357.262483
Sum of electronic and thermal Energies = -2357.240075
Sum of electronic and thermal Enthalpies = -2357.239130
Sum of electronic and thermal Free Energies = -2357.315390
G + ZVPE = -2356.885745
Energy (DMF-6-31G(d)) = -2357.7123047
Energy (DMF-def2-TZVP) = -2358.2331129



E'

C	4.1179444602	-1.5515376245	1.2149474898
C	4.2666204494	-0.3742327291	1.9848109987
C	3.4047026007	0.6686233758	1.789876773
C	2.3677783861	0.5549308392	0.8304294818
C	3.0810408079	-1.6374708758	0.3121796198
C	1.479382044	1.5995584806	0.4656592981
C	1.4701801013	2.8880519542	1.053625479
C	0.6915359078	3.8739264706	0.5173932903
H	0.6764616461	4.8664303534	0.9569197057
C	-0.0637778684	3.5964559672	-0.6456351638
C	-0.0790392332	2.3201698554	-1.1638046251
H	4.8063898753	-2.3813912056	1.327428133
H	5.0698078509	-0.2946303193	2.7109264985
H	-0.6243520516	4.3803382271	-1.1423683151
N	0.6185627592	1.3044468192	-0.5873360681
N	2.1939933367	-0.6276720148	0.1314734509
C	-0.8445272701	2.0400954038	-2.4274413004
H	-0.2834143202	1.3607426987	-3.0741505235
H	-1.8148521373	1.5794909858	-2.2230872992
H	-1.0248658955	2.9727160562	-2.9684367393
C	2.8898835792	-2.8822445111	-0.511863557
H	2.0274778081	-3.4622119135	-0.160831693
H	2.7225582624	-2.631504469	-1.5650101473
H	3.7679818447	-3.5294891588	-0.4484894352
Ni	0.5356085198	-0.5316310797	-0.8323936421
C	-0.6068283881	-2.2228026172	-1.2016691819
H	0.521559815	-2.154835512	-0.9251054968
H	-0.5697210615	-2.8171384303	-2.116968644
C	-1.2175440944	-0.8676399574	-1.3512163686
H	-1.5081695933	-0.6587075137	-2.3839170732
C	-2.3070269811	-0.5010610986	-0.359973106
H	-1.9761989836	-0.7633442269	0.6539232722
H	-2.4506063607	0.5882213299	-0.3494208371
C	-3.6478818286	-1.1822033592	-0.6583898961
H	-3.9092404396	-0.9945376274	-1.7089428123
H	-3.5265999432	-2.2713866157	-0.565013137
C	-4.8046879558	-0.7222996159	0.2326636764
H	-5.7280118992	-1.2145181084	-0.1026594837
H	-4.9643460357	0.3562878531	0.0902765432
C	-4.6083969022	-1.0055250756	1.7234197012
H	-4.3735967276	-2.0700675066	1.8618705655
H	-3.7414636251	-0.4476985271	2.0975868687
C	-5.8375414035	-0.6396298826	2.5540340619
H	-5.6740462183	-0.831429208	3.6195267803
H	-6.0838622796	0.4223376688	2.43903291
H	-6.7129666912	-1.2186154685	2.2377046129
H	-0.9968164931	-2.8234655387	-0.374400527
H	3.5250942315	1.5900222952	2.3480095842
H	2.0875173952	3.0867411572	1.9223692777

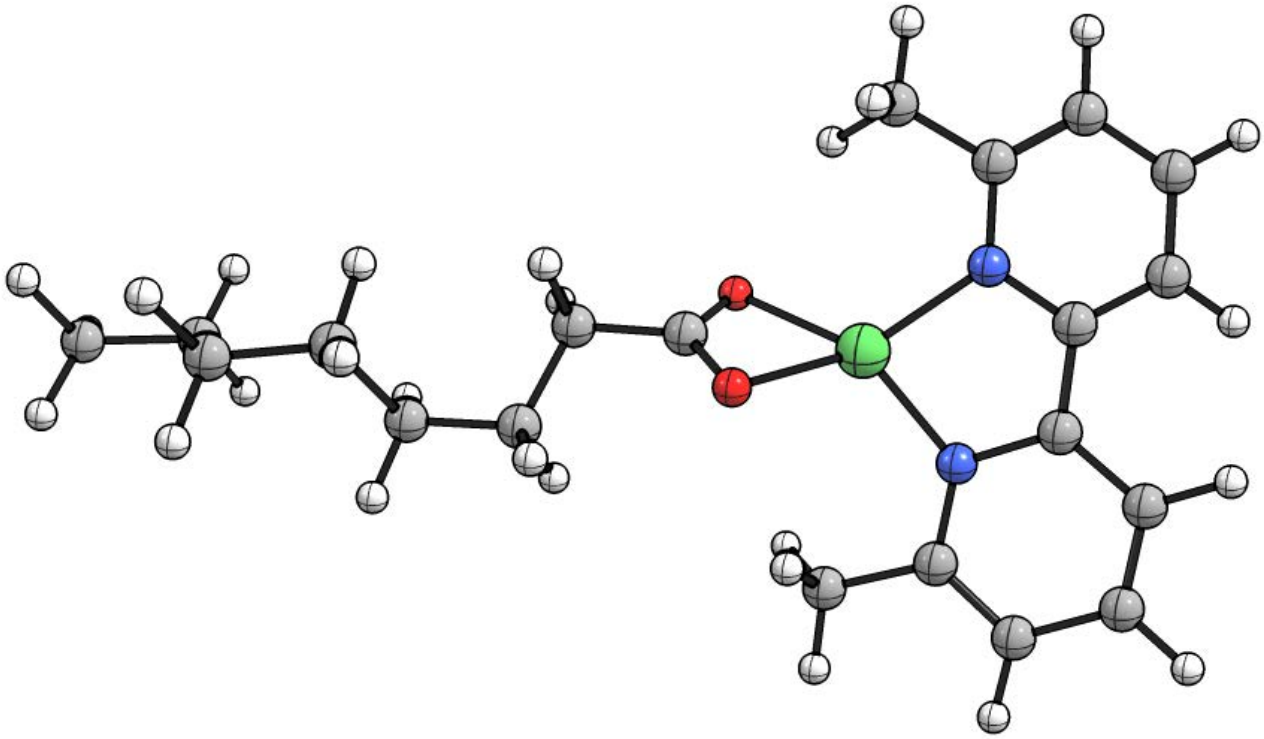
Energy = -2357.6918178
Zero-point correction = 0.428648 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.375042
Sum of electronic and zero-point Energies = -2357.263170
Sum of electronic and thermal Energies = -2357.240428
Sum of electronic and thermal Enthalpies = -2357.239483
Sum of electronic and thermal Free Energies = -2357.316776
G + ZVPE = -2356.888128
Energy (DMF-6-31G(d)) = -2357.7116596
Energy (DMF-def2-TZVP) = -2358.2320566



F

C	-3.9096852631	3.0560790657	0.425216062
C	-5.024491817	2.1858376571	0.4084172831
C	-4.8294183463	0.8428040804	0.2251539535
C	-3.5196641005	0.3415105251	0.050139986
C	-2.6486445486	2.5365997957	0.2583536939
C	-3.2008841391	-1.043258984	-0.1237943842
C	-4.1529535184	-2.0585706031	-0.3713177952
C	-3.7386520528	-3.354205719	-0.5298911421
H	-4.4604530886	-4.1409404514	-0.7260966915
C	-2.3607981801	-3.6610990266	-0.4480495458
C	-1.4597317565	-2.6490872919	-0.2183489463
H	-4.0403790487	4.123817375	0.5616759883
H	-6.0254910316	2.579950223	0.5529174025
H	-2.011652183	-4.681746099	-0.5573146099
N	-1.8612875184	-1.3604506509	-0.043348462
N	-2.4438260991	1.205866592	0.0550143393
C	0.0171587986	-2.8994277542	-0.11006983
H	0.5694309143	-2.322208362	-0.857967026
H	0.3851557842	-2.5845606288	0.8742633611
H	0.2477960474	-3.9596297281	-0.2386711876
C	-1.4191449512	3.3987496115	0.2518286845
H	-0.70120093	3.0652680673	1.0075179238
H	-0.9168255041	3.3367209332	-0.7214595027
H	-1.670286469	4.445104695	0.4408884499
Ni	-0.7407438534	0.2461981659	0.0393378917
O	1.0731145743	0.0507458421	-0.8412612131
O	0.7981936027	1.1054605878	1.0518143116
C	1.5738509082	0.6813098962	0.1415988282
C	3.8676929439	-0.3017854008	-0.2344715148
H	3.5644827918	-1.1698846048	0.3641308552
H	3.6049245281	-0.5338266132	-1.272520692
C	3.0583006447	0.9183692957	0.2157341375
H	3.3113583766	1.2146015119	1.238232161
H	3.2786062148	1.776021718	-0.4326225795
H	-5.6726339476	0.16177781	0.2412950551
H	-5.2033995762	-1.8060457047	-0.4596036695
C	5.3803640968	-0.1073566893	-0.1060148571
H	5.6338483709	0.0594745298	0.9492928686
H	5.87787404	-1.04267825	-0.3968450694
C	5.9356743402	1.0345433189	-0.9628511601
H	5.6020314057	2.0006433862	-0.5598488943
H	5.510233946	0.9586706314	-1.9730840543
C	7.463818298	1.0451118939	-1.066775174
H	7.8015505971	0.1115947955	-1.5394046542
H	7.7682185444	1.8576921856	-1.740280168
C	8.1840742905	1.2170441118	0.2723542552
H	7.9572214201	0.3666119142	0.927022368
H	7.7937080836	2.1095434463	0.7806330299
C	9.6985532757	1.3382947687	0.1118453992
H	9.9603228141	2.2082951403	-0.5014478286
H	10.197272521	1.4473033892	1.0804078641
H	10.1128119695	0.4505735511	-0.380344921

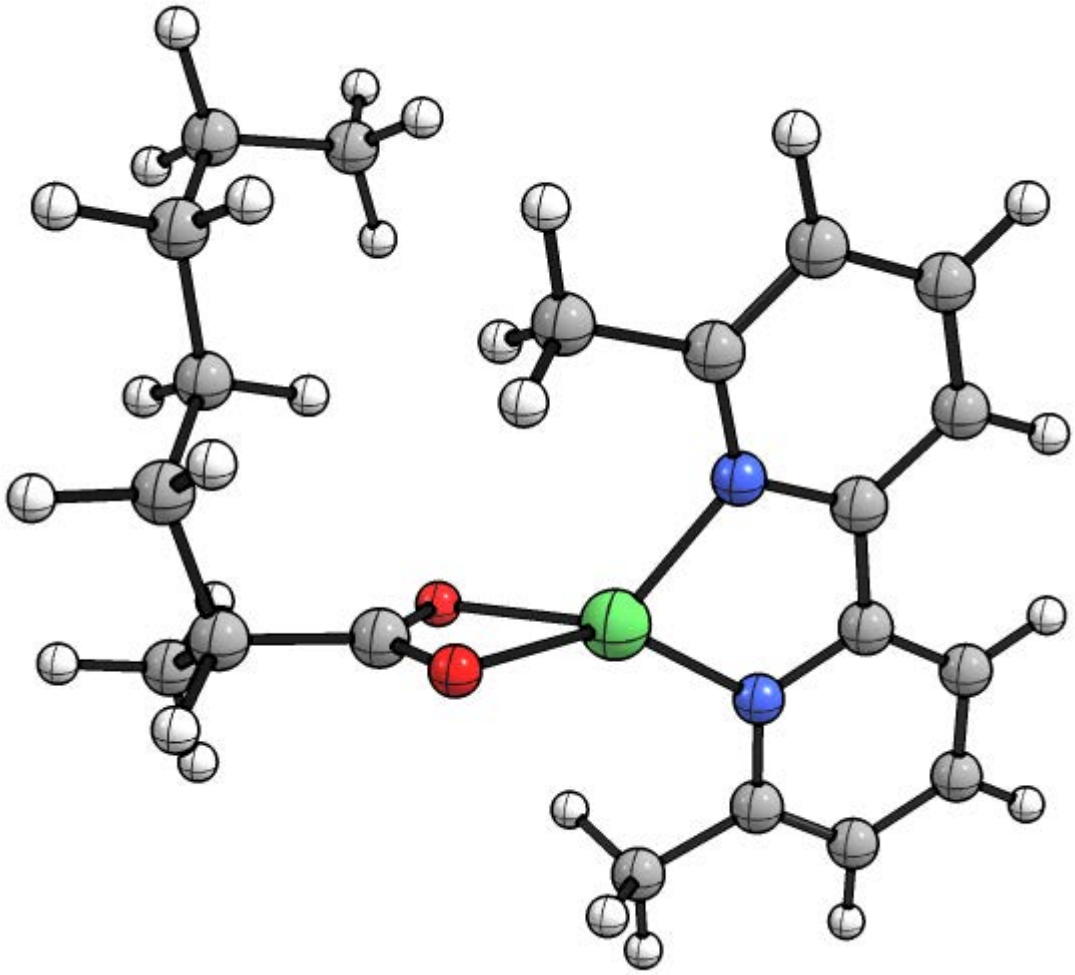
Energy = -2546.2769136
Zero-point correction = 0.443668 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.383887
Sum of electronic and zero-point Energies = -2545.833245
Sum of electronic and thermal Energies = -2545.806932
Sum of electronic and thermal Enthalpies = -2545.805988
Sum of electronic and thermal Free Energies = -2545.893027
G + ZVPE = -2545.449359
Energy (DMF-6-31G(d)) = -2546.3100179
Energy (DMF-def2-TZVP) = -2546.9050784



F'

C	-4.2433939309	2.8407678205	0.9677442215
C	-5.2347431844	1.9143888725	0.5676938649
C	-4.8515068981	0.690131736	0.0766879398
C	-3.4835941923	0.3770136937	-0.0193713533
C	-2.9189775517	2.5008547494	0.8599210811
C	-2.9394445174	-0.8608236392	-0.5115152687
C	-3.698295749	-1.9577804754	-0.9618742983
C	-3.0527520362	-3.0878040698	-1.4018731119
H	-3.6223974378	-3.9435686326	-1.7507547269
C	-1.6468775569	-3.1300672303	-1.3971239032
C	-0.9412455556	-2.0325449232	-0.9501026091
H	-4.5184703434	3.8153825023	1.3562681982
H	-6.286127755	2.1703328176	0.6480886053
H	-1.1144167312	-4.0100710781	-1.7400346423
N	-1.571420488	-0.9152696637	-0.5123369178
N	-2.5300013835	1.2849182997	0.3763758969
C	0.5585983522	-1.9930136639	-0.9270960872
H	0.9238367566	-1.1993366202	-1.588396871
H	0.9237838328	-1.7702734872	0.0805893192
H	0.9872079082	-2.941415738	-1.2598897418
C	-1.7907370816	3.4086915335	1.2531376459
H	-1.2047219385	2.9596889223	2.0652534934
H	-1.111624273	3.5604068304	0.4050306885
H	-2.1516270645	4.3837674767	1.5885849866
Ni	-0.7400622255	0.7176522999	0.1531255674
O	0.871946178	1.6482186238	-0.6577247149
O	0.9786096444	0.5175188802	1.2105622966
C	1.5571820448	1.2154910934	0.3214460263
C	3.7734853284	0.2250868589	-0.1767908092
H	4.8362793117	0.2942889865	0.0891404986
H	3.3855488511	-0.6696701225	0.3271627095
C	3.0472851429	1.4581035335	0.408302675
H	3.2841240643	1.4927844645	1.4772341215
H	-5.5978929374	-0.0305422322	-0.238625776
H	-4.7810360053	-1.9083763199	-0.9573265552
C	3.6358153442	0.0596918752	-1.6924860431
H	2.5933255915	0.2329687936	-1.9830625818
H	4.2236765079	0.8322515466	-2.2053343527
C	4.0973580456	-1.3179730056	-2.1690748454
H	3.4923975698	-2.0920517441	-1.674657916
H	5.1322686216	-1.4812570782	-1.838772906
C	4.0184241004	-1.5120020844	-3.6869105935
H	4.6111424627	-0.7306272675	-4.1812225503
H	4.4925490119	-2.4666667205	-3.9467574017
C	2.5923352558	-1.4976774235	-4.2390377684
H	2.099470967	-0.5345903604	-4.0693541364
H	1.9802630075	-2.2721066254	-3.7613385782
C	3.4594155566	2.7696554623	-0.2573191202
H	4.5481813558	2.8867874983	-0.2241844032
H	3.1346020748	2.80003662	-1.3001172669
H	3.0086090916	3.6259909555	0.253964831
H	2.5854827171	-1.6858497511	-5.3176464363

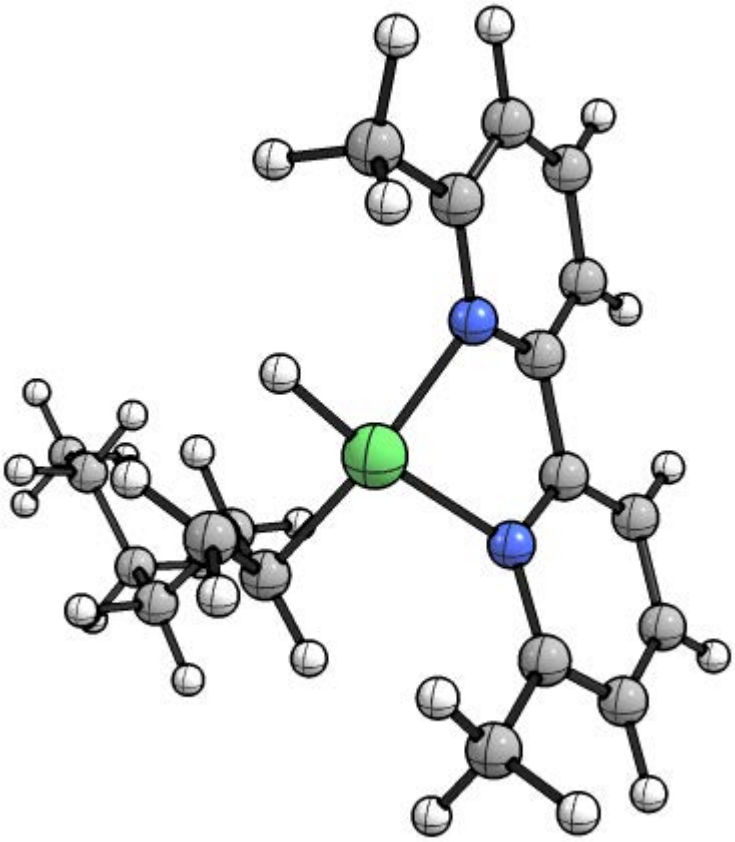
Energy = -2546.2970471
Zero-point correction = 0.444318 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.386390
Sum of electronic and zero-point Energies = -2545.852730
Sum of electronic and thermal Energies = -2545.826678
Sum of electronic and thermal Enthalpies = -2545.825734
Sum of electronic and thermal Free Energies = -2545.910657
G + ZVPE = -2545.466339
Energy (DMF-6-31G(d)) = -2546.3192526
Energy (DMF-def2-TZVP) = -2546.9081615



TS_{B-C}

C	2.417303	-3.388556	0.379678
C	2.606415	-2.931363	1.672388
C	2.350531	-1.595769	1.962475
C	1.885696	-0.775214	0.948657
C	1.920011	-2.527738	-0.600957
C	1.731104	0.692959	1.084308
C	2.123258	1.415544	2.198823
C	2.096764	2.805621	2.131182
H	2.395211	3.399668	2.988483
C	1.737994	3.416841	0.94258
C	1.338852	2.636637	-0.144546
H	2.644913	-4.415066	0.116212
H	2.971465	-3.599654	2.444973
H	1.772015	4.495709	0.836571
N	1.280483	1.298597	-0.040432
N	1.634457	-1.245549	-0.300545
C	1.02736	3.277085	-1.467016
H	0.113479	3.87876	-1.424938
H	1.843605	3.949316	-1.747794
H	0.925271	2.524829	-2.25075
C	1.706216	-3.014481	-2.003106
H	1.977821	-2.24569	-2.729659
H	2.305476	-3.907863	-2.192758
H	0.654129	-3.271616	-2.165659
Ni	0.444685	-0.039869	-1.179969
C	-1.072953	0.398266	-2.478141
H	-0.013913	-1.131548	-1.98509
H	-0.640106	0.99221	-3.281371
C	-1.275556	0.941737	-1.221635
H	-1.072721	1.997663	-1.072462
C	-2.198425	0.317521	-0.209253
H	-2.279356	-0.758343	-0.401948
H	-1.775422	0.432065	0.799006
C	-3.591477	0.965628	-0.245196
H	-3.482676	2.049424	-0.111238
H	-4.024865	0.815759	-1.242572
C	-4.545488	0.417722	0.819946
H	-5.481868	0.987132	0.769309
H	-4.125699	0.606622	1.818133
C	-4.864379	-1.072445	0.677016
H	-5.212291	-1.269956	-0.345995
H	-3.951576	-1.666728	0.814406
C	-5.918461	-1.544544	1.676866
H	-6.120138	-2.614018	1.56421
H	-5.589304	-1.371458	2.707675
H	-6.863308	-1.008884	1.534979
H	-1.664754	-0.446488	-2.816688
H	2.520985	-1.209442	2.959479
H	2.469272	0.919883	3.097024

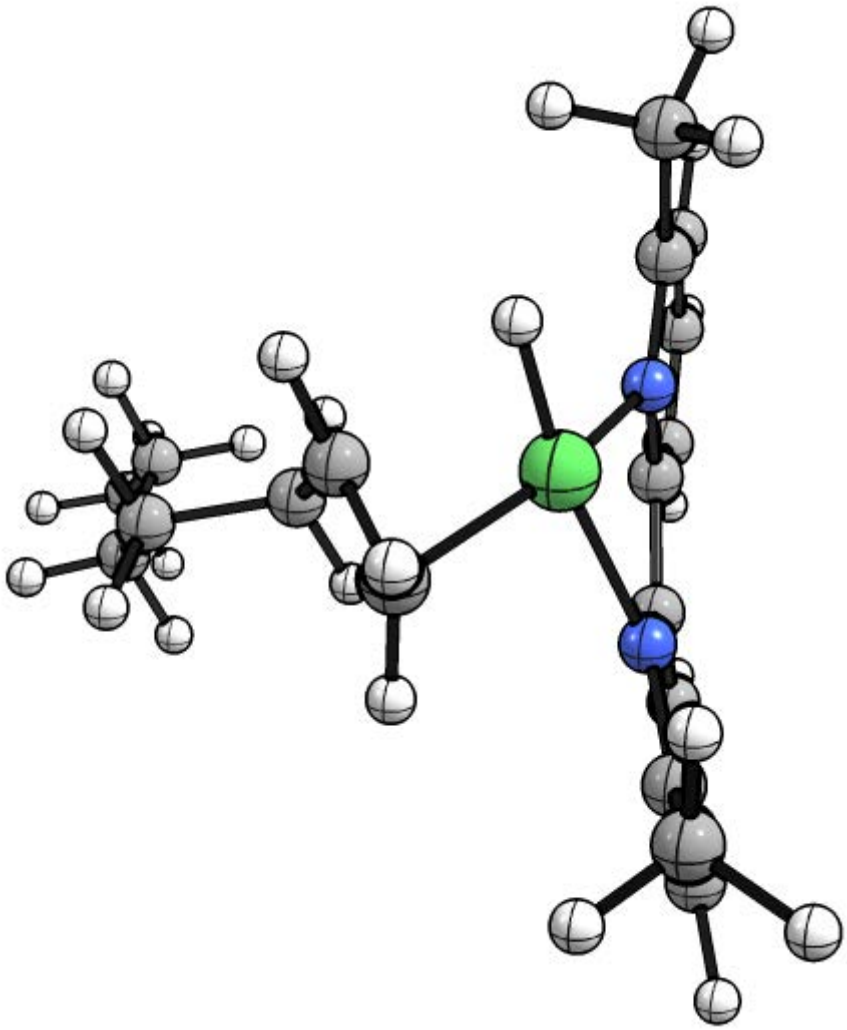
Energy = -2357.5119149
Zero-point correction = 0.427573 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.374261
Sum of electronic and zero-point Energies = -2357.084342
Sum of electronic and thermal Energies = -2357.061769
Sum of electronic and thermal Enthalpies = -2357.060825
Sum of electronic and thermal Free Energies = -2357.137654
G + ZVPE = -2356.710081
Energy (DMF-6-31G(d)) = -2357.5890983
Energy (DMF-def2-TZVP) = -2358.1060002



$TS_{C\text{-}D}$

C	-0.689966	3.825359	0.302263
C	-0.643763	3.491315	1.644667
C	-0.850363	2.168875	2.020008
C	-1.070671	1.22392	1.031347
C	-0.891527	2.832495	-0.658299
C	-1.445254	-0.183576	1.316032
C	-1.645651	-0.687817	2.590661
C	-2.159863	-1.974471	2.722494
H	-2.325635	-2.397843	3.707443
C	-2.50042	-2.686249	1.585566
C	-2.25773	-2.136208	0.32506
H	-0.567963	4.853859	-0.017489
H	-0.471662	4.253352	2.397311
H	-2.962105	-3.664898	1.657672
N	-1.682732	-0.927033	0.20846
N	-1.05236	1.547081	-0.287159
C	-2.682119	-2.866213	-0.916035
H	-2.621518	-2.21925	-1.791642
H	-2.066951	-3.754739	-1.090571
H	-3.716837	-3.203451	-0.804183
C	-0.937773	3.182133	-2.115734
H	-0.001102	2.903216	-2.610157
H	-1.751382	2.655339	-2.61978
H	-1.082576	4.256594	-2.246788
Ni	-0.803931	-0.056454	-1.314187
C	0.964234	-0.715361	-1.960219
H	-0.368055	0.721577	-2.421033
H	1.353579	-0.237685	-2.855726
C	-0.020715	-1.693819	-2.087936
H	-0.063992	-2.489038	-1.347744
H	-0.395435	-1.951268	-3.076231
C	1.873455	-0.626268	-0.761211
H	2.065678	0.426938	-0.524646
H	1.388435	-1.073868	0.117121
C	3.204646	-1.347791	-1.031119
H	2.989432	-2.378925	-1.335715
H	3.707934	-0.867451	-1.880327
C	4.139166	-1.359525	0.181839
H	5.018046	-1.966189	-0.069415
H	3.644172	-1.871816	1.019176
C	4.608944	0.023674	0.638273
H	5.05331	0.552636	-0.21548
H	3.749756	0.626045	0.963001
C	5.622854	-0.05388	1.778394
H	5.946095	0.943262	2.092351
H	5.195205	-0.559072	2.651839
H	6.513752	-0.613717	1.47398
H	-0.849479	1.894114	3.067136
H	-1.429905	-0.096896	3.471706

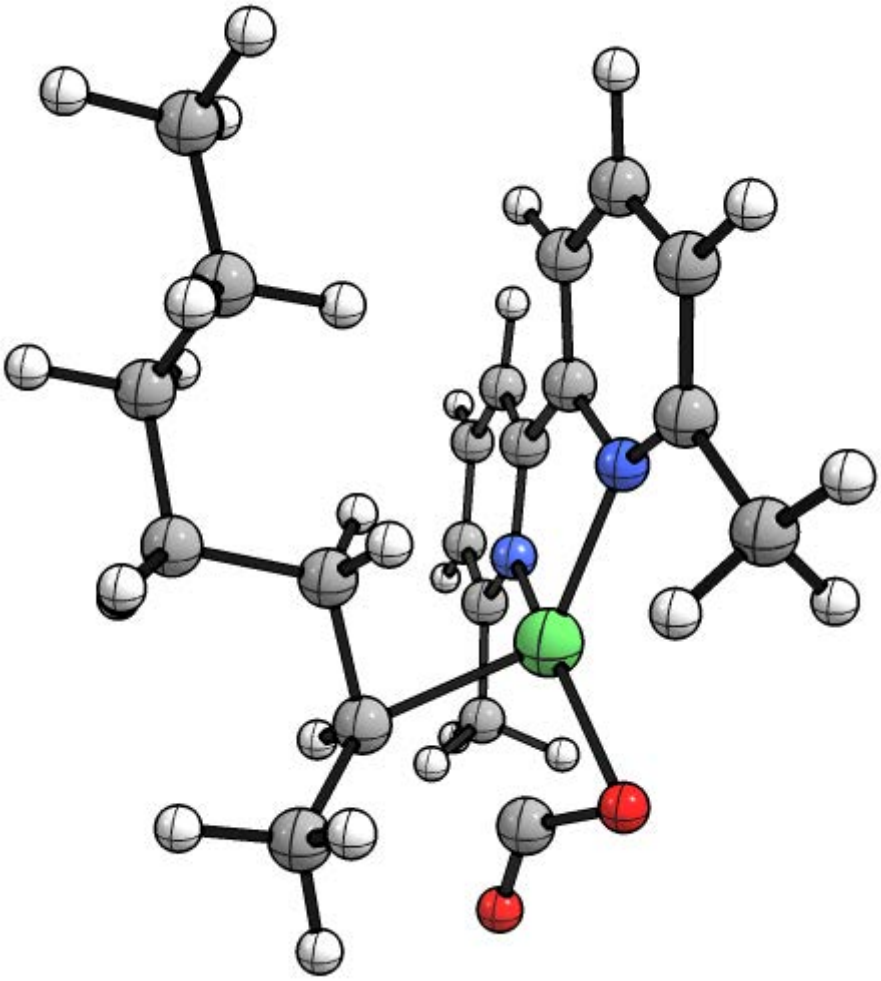
Energy = -2357.5131261
Zero-point correction = 0.427925 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.375291
Sum of electronic and zero-point Energies = -2357.085201
Sum of electronic and thermal Energies = -2357.062834
Sum of electronic and thermal Enthalpies = -2357.061890
Sum of electronic and thermal Free Energies = -2357.137835
G + ZVPE = -2356.709910
Energy (DMF-6-31G(d)) = -2357.5901986
Energy (DMF-def2-TZVP) = -2358.1042793



$TS_{E'1\text{-}F'1}$

C	3.1767261826	-0.4416226583	-1.704838406
C	3.7018604622	0.3892574423	-0.7260100657
C	2.846396958	1.212924451	-0.0054511069
C	1.4862041424	1.166292183	-0.2898603729
C	1.8003212893	-0.4519130154	-1.9338646218
C	0.4768156512	2.0054291165	0.4064198168
C	0.8173358295	3.1113862015	1.1753784051
C	-0.2005184761	3.8458669308	1.7686324502
H	0.032607495	4.7112593645	2.3808897868
C	-1.5162668811	3.4685689588	1.5524167229
C	-1.7980531528	2.3566606052	0.7563381695
H	3.819606234	-1.0910742297	-2.2888266129
H	4.7676977624	0.3940673187	-0.5212913605
H	-2.3351185188	4.0323261502	1.9854647568
N	-0.8046795919	1.6262127171	0.2164230326
N	0.9775206356	0.3385750845	-1.2225792414
C	-3.2061186569	1.9587801563	0.4406198211
H	-3.394655576	0.9023536834	0.6438383128
H	-3.9179423115	2.5691068302	1.0016434328
H	-3.4024043456	2.0910678715	-0.6285213923
C	1.1676441983	-1.3441942682	-2.9577018193
H	1.9253149414	-1.8448548574	-3.56535902
H	0.5347356043	-2.0965265346	-2.4764890921
H	0.502114669	-0.7686759028	-3.6063074249
Ni	-0.9766021983	-0.0599382037	-0.8528945255
C	-1.7297205203	-1.5355890604	0.504610516
H	-2.3705209767	-1.0356724095	1.2394436455
O	-3.7657185268	-0.8069175442	-0.9819580079
C	-2.5795069623	-0.9833673731	-1.1727236275
O	-1.8545807871	-1.268738323	-2.1760737357
C	-0.2741574456	-1.5538858822	1.0341635599
H	0.0609538799	-0.5386998684	1.2755006215
H	0.3939501967	-1.9325356083	0.2487467468
C	-0.0200282121	-2.3846523886	2.3027241386
H	-0.0388979257	-3.455851994	2.0690076763
H	-0.826608971	-2.2055706338	3.0260616614
C	1.3253820375	-2.0313010176	2.9470125187
H	1.3008566767	-0.9832464624	3.2815171413
H	1.4674689872	-2.6385655214	3.8512588626
C	2.5299382561	-2.2248392711	2.0218602077
H	2.5396156069	-3.2597051002	1.6534257125
H	2.424192592	-1.5848972052	1.1373841181
C	3.8570506794	-1.906269174	2.7068904824
H	3.8764943021	-0.8666135031	3.0559023084
H	4.0169049776	-2.5498122561	3.5795172481
H	1.852216765	3.4078127281	1.2962795239
H	3.2334744333	1.8556021655	0.7760786531
H	4.7046780892	-2.0473487606	2.0273184794
C	-2.2015502558	-2.9854964948	0.3377212174
H	-2.1326771934	-3.5345127723	1.2843572547
H	-3.239468103	-3.0346444442	0.0031250726
H	-1.5804994456	-3.5079609204	-0.3997595407

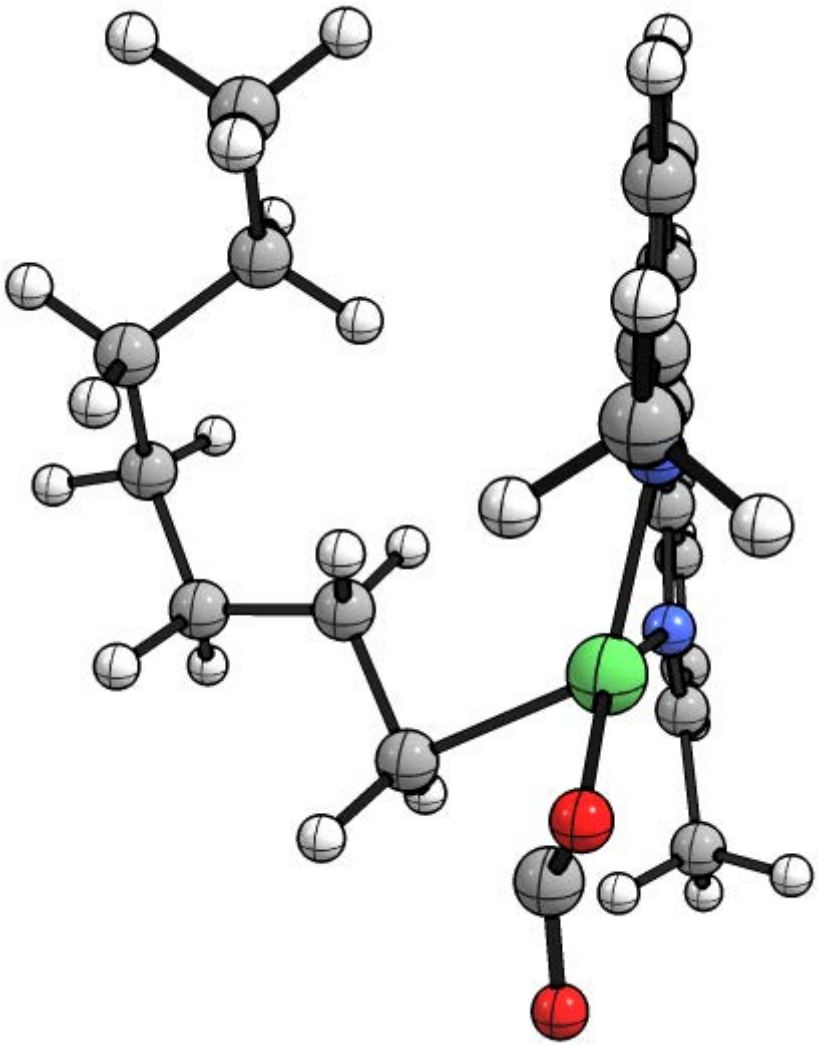
Energy = -2546.2203842
Zero-point correction = 0.442119 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.384237
Sum of electronic and zero-point Energies = -2545.778265
Sum of electronic and thermal Energies = -2545.752360
Sum of electronic and thermal Enthalpies = -2545.751416
Sum of electronic and thermal Free Energies = -2545.836147
G + ZVPE = -2545.394028
Energy (DMF-6-31G(d)) = -2546.2532798
Energy (DMF-def2-TZVP) = -2546.8465676



TS_{E1-F1}

C	-2.51596452	-1.1079570467	-2.1721151633
C	-2.4282410243	-2.284116711	-1.4422661104
C	-1.3026818022	-2.5164625632	-0.6639057375
C	-0.2968926364	-1.5558627926	-0.6442751094
C	-1.4802491953	-0.1774580088	-2.1033939967
C	0.9659706497	-1.7076756151	0.1260499433
C	1.2449379001	-2.813052935	0.921468091
C	2.4779186424	-2.8814573661	1.5555044274
H	2.7211142461	-3.726200574	2.1920523598
C	3.4007583533	-1.8680081052	1.3467831036
C	3.0657210306	-0.7828960869	0.5361841661
H	-3.3837680451	-0.8971569747	-2.7871345147
H	-3.2288711788	-3.0159348606	-1.4779506009
H	4.3837738204	-1.907722017	1.802851903
N	1.8466489118	-0.6968389884	-0.0286854137
N	-0.3925143398	-0.4106755306	-1.3475858391
C	4.0545641947	0.2957459675	0.2171488749
H	3.6754430476	1.2962242687	0.4430906913
H	4.9938531228	0.1351394337	0.751770915
H	4.2638017346	0.2924337376	-0.8581837226
C	-1.5236746736	1.1184483426	-2.8532032945
H	-2.4231101347	1.1850384034	-3.4701462969
H	-1.4956895055	1.9660960045	-2.1619595815
H	-0.6398352454	1.2244640049	-3.4880826389
Ni	1.0121436142	0.9277237646	-0.807998239
C	0.9798364028	2.1948108483	0.8382216768
H	1.7850488232	1.8831188678	1.5118202103
O	2.8686982274	3.1660100765	-0.6496444827
C	1.7892132024	2.6527781196	-0.8566321555
O	0.9374913881	2.6644296553	-1.7962480998
C	-0.3729343182	1.5988962498	1.2643896253
H	-0.2934172426	0.5118936716	1.4020359994
H	-1.1112886159	1.7575112665	0.466873098
C	-0.9234822153	2.2032036885	2.5591291269
H	-1.1212173812	3.2714209122	2.3935046303
H	-0.1494136594	2.1511232069	3.3361942438
C	-2.1988460837	1.5276290294	3.0779213789
H	-1.9655529199	0.4967779945	3.3816867725
H	-2.5093828009	2.047544463	3.9922267403
C	-3.3705806821	1.5053163919	2.0785736287
H	-4.3173920469	1.6297695184	2.6202063195
H	-3.2956134824	2.3717352363	1.4056913925
C	-3.4758722934	0.2235427483	1.2448574059
H	-2.5374017212	0.0402819513	0.7084296149
H	-3.6098419061	-0.6289629406	1.9246876833
C	-4.6309879378	0.2713936949	0.2475555466
H	-4.7327921843	-0.6736821779	-0.2959196529
H	-5.5820338229	0.4702304045	0.7554552476
H	-4.4761877318	1.0672011946	-0.4910457448
H	0.8937770987	3.2792555102	0.9602666174
H	0.519899978	-3.6067685465	1.0527020411
H	-1.2167974221	-3.4313752968	-0.0909429008

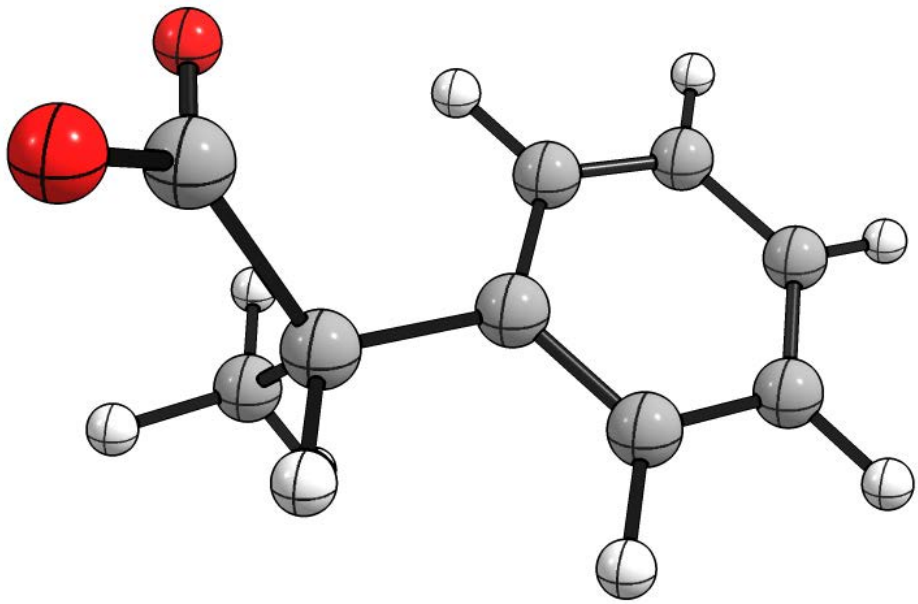
Energy = -2546.2253075
Zero-point correction = 0.442796 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.386354
Sum of electronic and zero-point Energies = -2545.782512
Sum of electronic and thermal Energies = -2545.756966
Sum of electronic and thermal Enthalpies = -2545.756022
Sum of electronic and thermal Free Energies = -2545.838953
G + ZVPE = -2545.396157
Energy (DMF-6-31G(d)) = -2546.2586083
Energy (DMF-def2-TZVP) = -2546.8545683



2a-I

C	1.4364786636	0.9047862123	-1.6719977541
H	1.4122445753	-0.0772657289	-2.1533358984
H	2.4512451404	1.3061052007	-1.7828011061
C	1.0888674312	0.7444844814	-0.1853874103
H	1.2193171221	1.7079215098	0.3207620096
H	0.7383915562	1.5774552556	-2.1899772131
C	-0.355843774	0.324095408	-0.0365061345
C	-1.3348448995	1.2405307146	0.360412653
C	-0.764655563	-0.9858944043	-0.3265892783
C	-2.6760523136	0.8752093021	0.4622387624
H	-1.0363886628	2.260934622	0.5939871659
C	-2.1016697663	-1.3534864103	-0.2253302495
H	0.0108729071	-1.699047425	-0.5925642613
C	-3.0680000076	-0.4265598803	0.1658540296
H	-3.4147598256	1.6100433746	0.7762585088
H	-2.3933499523	-2.3783703531	-0.4465439274
H	-4.1131253385	-0.7180386652	0.2453194873
O	2.1951270175	-1.3837124462	-0.1021807529
O	2.7002306108	0.1494037533	1.4874742912
C	2.1028354643	-0.2757101301	0.4817298719

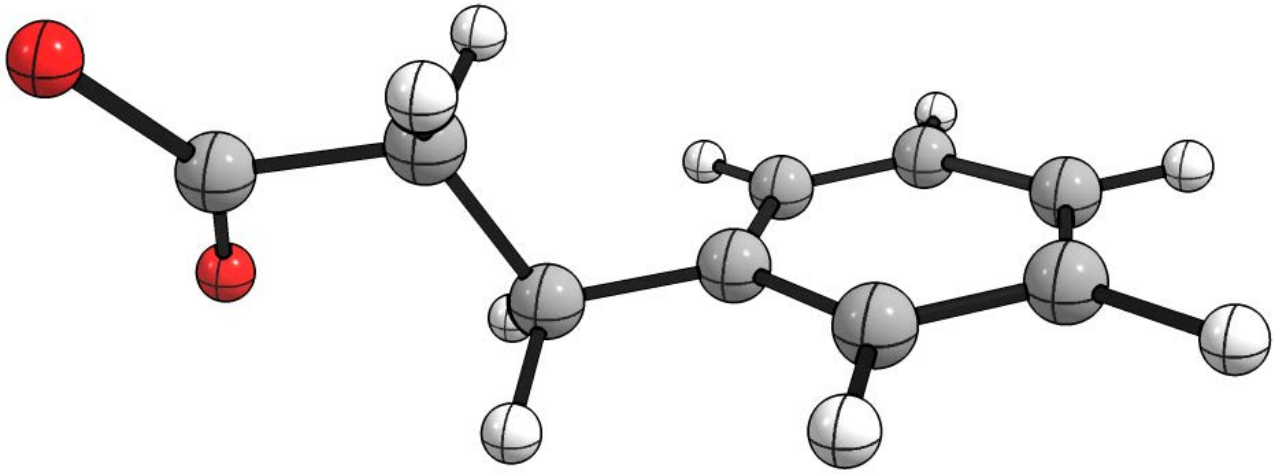
Energy = -498.7162539
Zero-point correction = 0.160952 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.125063
Sum of electronic and zero-point Energies = -498.555302
Sum of electronic and thermal Energies = -498.545709
Sum of electronic and thermal Enthalpies = -498.544764
Sum of electronic and thermal Free Energies = -498.591191
G + ZVPE = -498.430239
Energy (DMF-6-31G(d)) = -498.8053921
Energy (DMF-def2-TZVP) = -499.0052571



2a'-I

C	1.5399535675	-0.2147912467	-0.4906586583
H	1.4084339808	-1.1989375818	-0.9565706472
H	1.2579449152	0.5272826653	-1.2530401992
C	-0.8392139329	-0.0167775086	0.3790256496
C	-1.4517222428	1.1754769071	-0.0263649826
C	-1.6283036872	-1.1717503036	0.4045236708
C	-2.794143436	1.2143878735	-0.3888519036
H	-0.8546004799	2.0843138757	-0.0563156392
C	-2.9728305823	-1.1417041509	0.0437921214
H	-1.1716839078	-2.1098984719	0.7128045681
C	-3.5647905232	0.0537797394	-0.3550221846
H	-3.2433711972	2.1556874243	-0.697454783
H	-3.5606095576	-2.0565310297	0.0748650545
H	-4.6150292776	0.0822206505	-0.6346657006
C	3.0619201372	0.0033481036	-0.1497215253
O	3.8555778762	-0.5332716167	-0.9502130646
O	3.2904313973	0.7103234837	0.8592017974
C	0.6248592161	-0.0520767276	0.7284575664
H	0.9375731643	0.8683478582	1.2315742527
H	0.8188970947	-0.8682564005	1.4358147579

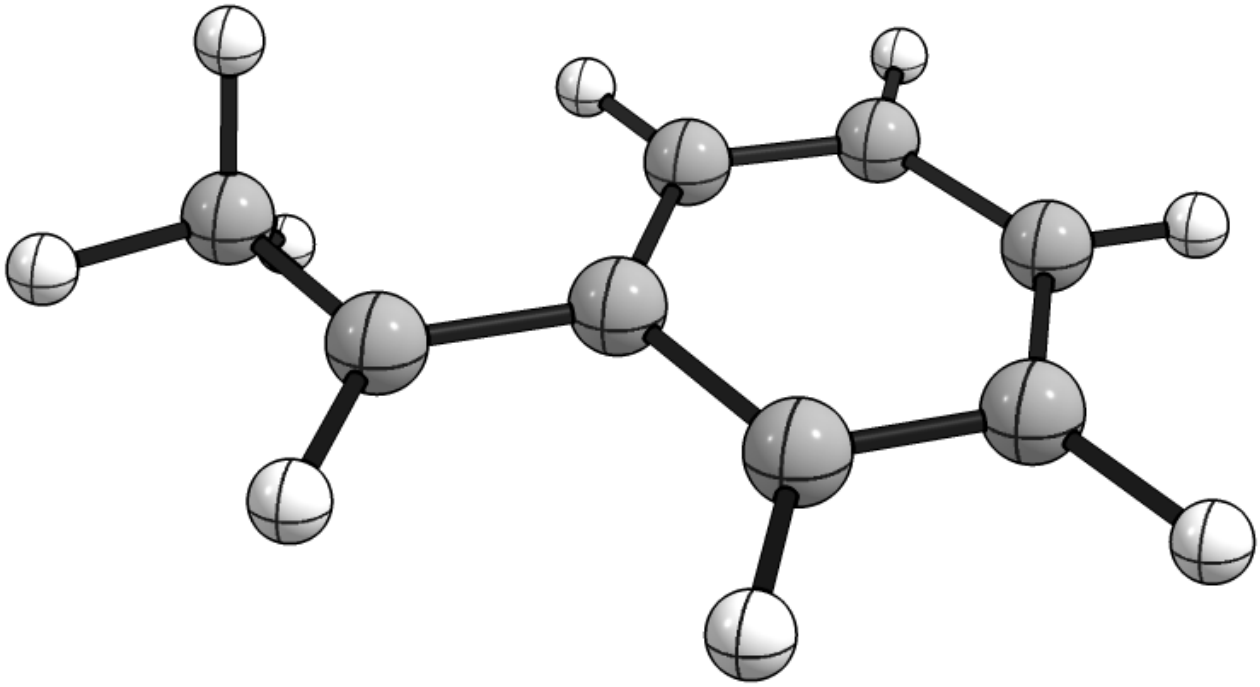
Energy = -498.711313
Zero-point correction = 0.160536 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.122257
Sum of electronic and zero-point Energies = -498.550777
Sum of electronic and thermal Energies = -498.541011
Sum of electronic and thermal Enthalpies = -498.540067
Sum of electronic and thermal Free Energies = -498.589056
G + ZVPE = -498.428520
Energy (DMF-6-31G(d)) = -498.8041843
Energy (DMF-def2-TZVP) = -310.1234282



R

C	-1.8291831498	-0.6522613455	0.0000016678
H	-2.0761788186	-1.7109729784	0.0000687265
C	-0.4583485448	-0.3003641698	0.0000141526
C	0.542625697	-1.3076100431	0.000002258
C	-0.0218934511	1.0503436109	0.0000123613
C	1.8871872214	-0.9840544234	-0.0000094151
H	0.2351665505	-2.350601197	0.0000043976
C	1.3273011556	1.3638921086	0.0000036206
H	-0.7575796858	1.8490751857	0.0000265735
C	2.291983555	0.3542851916	-0.0000085662
H	2.6318247726	-1.7748529491	-0.0000148331
H	1.6354449389	2.4057463994	0.0000109794
H	3.3481520417	0.6057290684	-0.0000195239
C	-2.9503852664	0.3356219115	-0.0000188011
H	-2.915935211	0.992451402	-0.8809888857
H	-3.9202451832	-0.1676997838	-0.0003715263
H	-2.9163726977	0.9920078351	0.8813004282

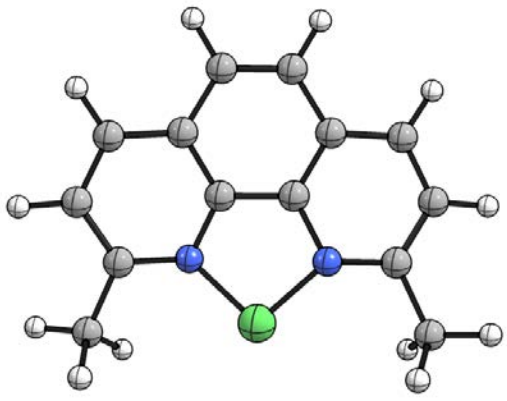
Energy = -310.1234282
Zero-point correction = 0.144522 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.112063
Sum of electronic and zero-point Energies = -309.978907
Sum of electronic and thermal Energies = -309.971523
Sum of electronic and thermal Enthalpies = -309.970579
Sum of electronic and thermal Free Energies = -310.011365
G + ZVPE = -309.866843
Energy (DMF-6-31G(d)) = -310.1322444
Energy (DMF-def2-TZVP) = -310.2400421



G

C	3.4245192833	0.5031566983	-0.111989117
C	2.8202726608	1.7536755552	-0.106164656
C	1.4252599626	1.8285945771	-0.0383329623
C	0.7092852178	0.6175360924	0.0255302665
C	2.6665751372	-0.6578281393	0.0341722201
C	0.6783199659	3.0585832279	-0.0371102573
C	-0.70877878	0.6179921792	-0.0213174613
C	-1.4238879113	1.8297003953	0.0399145802
C	-0.676066323	3.0591472159	0.0359780056
C	-2.8189481622	1.7559253047	0.1079629439
H	-3.4131000714	2.6635159345	0.1599890259
C	-3.4240751911	0.5058450303	0.1165890014
C	-2.6669712801	-0.6559965321	-0.0270418294
H	1.228383219	3.9950799536	-0.0715740854
H	4.5045620071	0.4165787238	-0.1759290506
H	3.4150633462	2.6607321912	-0.1601686998
H	-1.2254608824	3.9961101519	0.0683871337
H	-4.5041752511	0.4201709096	0.180783453
N	-1.3247911262	-0.6109221897	-0.1974938372
N	1.3244248057	-0.6114261479	0.2044154132
C	-3.2885585276	-2.0185860575	-0.0923464295
H	-2.8164218749	-2.5927095816	-0.9003741474
H	-3.1220919981	-2.5709326781	0.8401251496
H	-4.3672937435	-1.9689884974	-0.2649724188
C	3.2872212209	-2.0207010096	0.1025956794
H	2.8148373275	-2.5925889227	0.9120596785
H	3.1202219441	-2.5751388529	-0.8285386479
H	4.3660187502	-1.9714399581	0.2749252439
Ni	-0.0006012428	-1.8235231761	0.0045755533

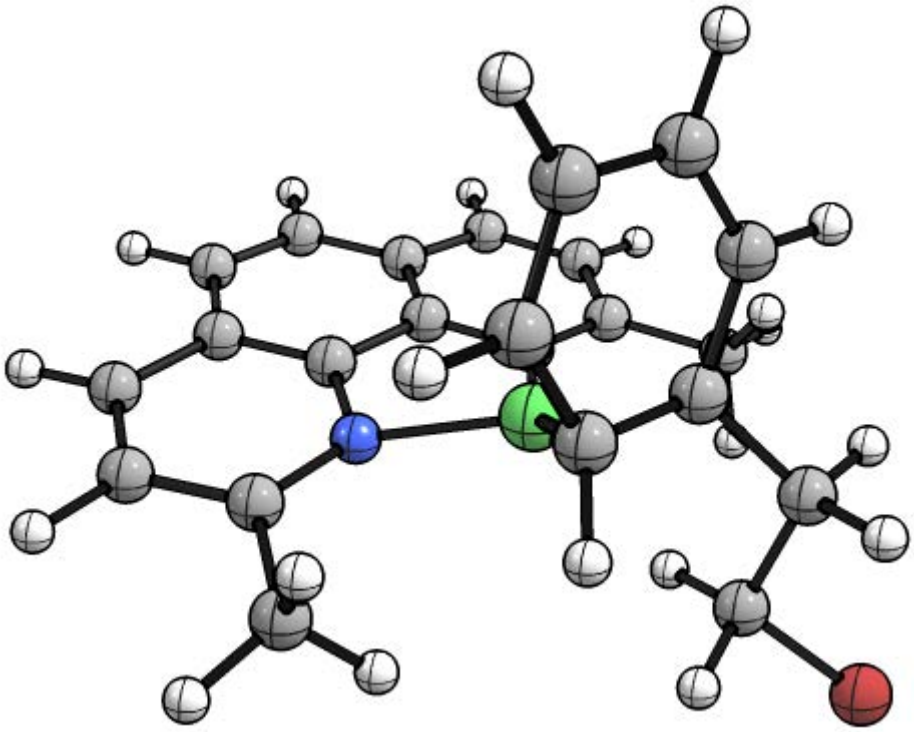
Energy = -2158.1022149
Zero-point correction = 0.228959 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.187862
Sum of electronic and zero-point Energies = -2157.873256
Sum of electronic and thermal Energies = -2157.859107
Sum of electronic and thermal Enthalpies = -2157.858163
Sum of electronic and thermal Free Energies = -2157.914352
G + ZVPE = -2157.685393
Energy (DMF-6-31G(d)) = -2158.1249582
Energy (DMF-def2-TZVP) = -2158.597988



H

C	-3.2942113154	-2.3191549367	-1.715383136
C	-4.2407214519	-1.3568942215	-1.4579911142
C	-3.8345653605	-0.133195538	-0.8946978457
C	-2.4712440648	0.0064818516	-0.5935030428
C	-1.9413394069	-2.1011475901	-1.3859917924
C	-4.7256695055	0.9619918137	-0.6371954798
C	-1.9729363981	1.2505046254	-0.0761203687
C	-2.8591094318	2.321444914	0.1186246865
C	-4.2568827514	2.1383067312	-0.1527328389
C	-2.3059164893	3.5349221582	0.5648133724
H	-2.9469443075	4.3950730032	0.7360981868
C	-0.9488555081	3.614545553	0.7590286841
C	-0.1233366893	2.4912923614	0.5477650925
H	-5.7827657192	0.831411252	-0.8497789135
H	-3.5738872699	-3.2601003462	-2.177400724
H	-5.2863968996	-1.5220383313	-1.7016158289
H	-4.9318420314	2.9695781692	0.0299081655
H	-0.4913885758	4.5429826421	1.0832283919
N	-0.6294407318	1.3157511381	0.1613775053
N	-1.5443621111	-0.9701127841	-0.7989460397
C	1.3521370349	2.5939657788	0.780618802
H	1.6355784768	1.9658362317	1.6285937134
H	1.9241821324	2.2542106318	-0.087495272
H	1.641824112	3.6249025564	0.997504494
C	-0.9088523835	-3.1457267837	-1.6843671761
H	0.02447297	-2.6773737855	-2.0046586085
H	-0.6883113205	-3.7325363963	-0.7878528132
H	-1.2579422746	-3.8274669721	-2.4646940522
Ni	0.0531497418	-0.4967672202	0.1647527176
C	2.8945399785	-0.4541627975	0.7418988686
H	3.2456060554	0.4858168499	1.1823870354
H	3.6482814414	-1.2113155447	0.994790143
C	1.5325011437	-0.821948812	1.322738431
C	0.8762549722	-2.0512211757	0.8320201233
C	1.3399921269	-0.5043433963	2.7263999213
C	0.088013209	-2.8188649759	1.7744895314
H	1.4036968076	-2.6482970696	0.0811859493
C	0.4981105254	-1.2059490052	3.5318305673
H	1.9083822239	0.325115423	3.1490307651
C	-0.147610123	-2.3903057493	3.0438853493
H	-0.3178836894	-3.7788334647	1.4565865456
H	0.3618673019	-0.912481068	4.5692707529
H	-0.7664237081	-2.9785484637	3.7161512337
C	2.8355438636	-0.2931887221	-0.7706454838
H	1.9844225228	0.3211487365	-1.0673075664
H	2.7867262713	-1.2464491119	-1.2972015878
Br	4.4254891619	0.6190076063	-1.4739924963

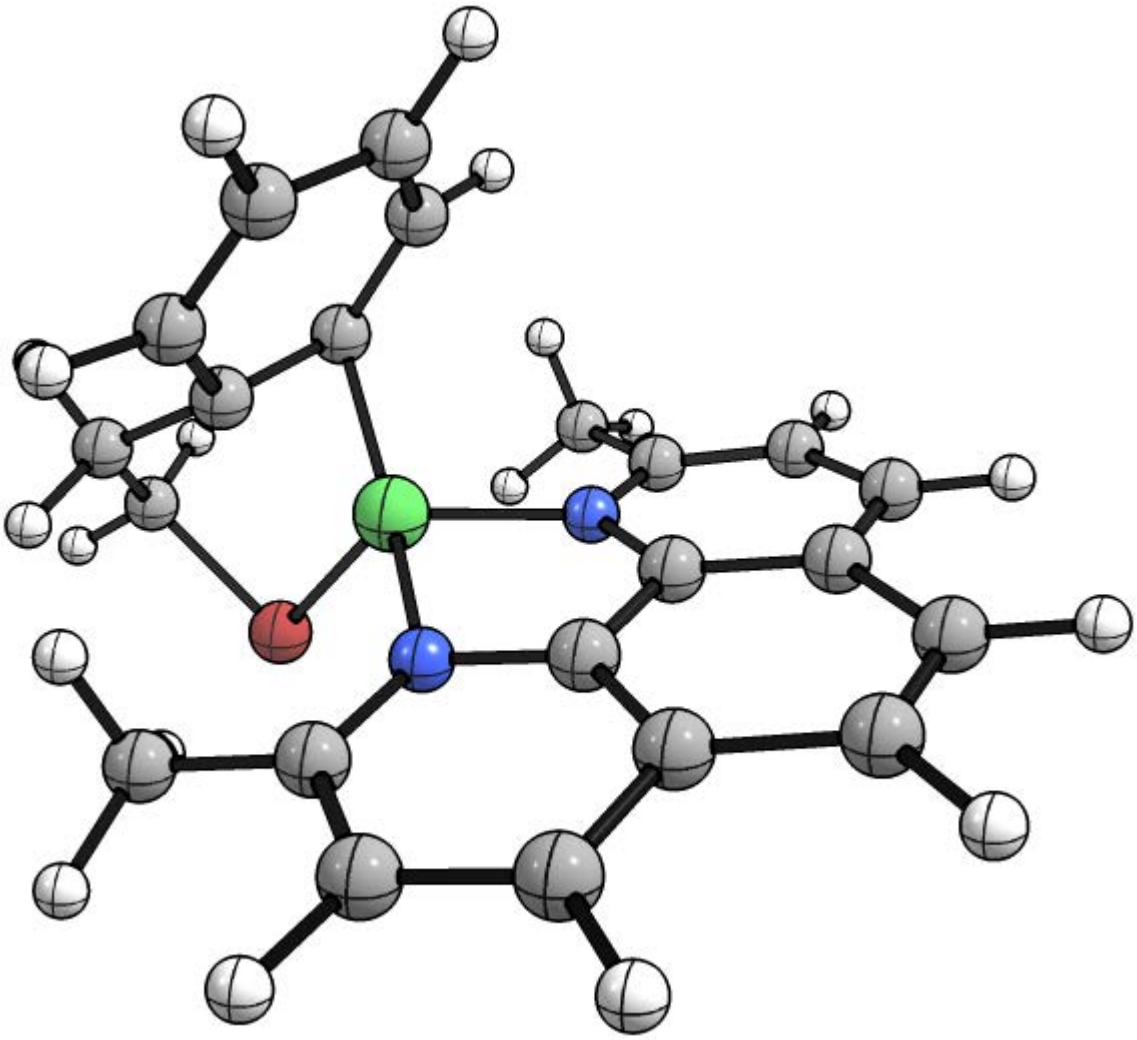
Energy = -5040.1176903
Zero-point correction = 0.382613 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.329928
Sum of electronic and zero-point Energies = -5039.735077
Sum of electronic and thermal Energies = -5039.712288
Sum of electronic and thermal Enthalpies = -5039.711344
Sum of electronic and thermal Free Energies = -5039.787762
G + ZVPE = -5039.405149
Energy (DMF-6-31G(d)) = -5040.2248353
Energy (DMF-def2-TZVP) = -5043.1860583



I

C	-2.3053297111	-3.2553918914	-0.3649698234
C	-3.4599525964	-2.5084379623	-0.2978043766
C	-3.3634824536	-1.1064685425	-0.283077168
C	-2.0719687429	-0.5556411438	-0.3072216386
C	-1.0462872771	-2.6284634125	-0.3891390928
C	-4.4956701197	-0.223334037	-0.2571398847
C	-1.8956884586	0.8646862641	-0.3414803509
C	-3.0195120238	1.7071505251	-0.3475135643
C	-4.3302069636	1.1224620822	-0.2869716466
C	-2.7815400489	3.0900837737	-0.4247732515
H	-3.61412237	3.787969778	-0.4267249423
C	-1.4831305771	3.536353773	-0.5180186419
C	-0.4096052246	2.6267939643	-0.5119871955
H	-5.4903321277	-0.6584701605	-0.2182889075
H	-2.3514167438	-4.3389919033	-0.4043006204
H	-4.4345846915	-2.9875980714	-0.2731041811
H	-5.1906371772	1.785762604	-0.2733069295
H	-1.2694287803	4.5967726481	-0.6049866434
N	-0.6069027094	1.3098739531	-0.3925656618
N	-0.9305897502	-1.2983972107	-0.3235987233
C	1.0030651728	3.1116022251	-0.6250976316
H	1.4536454316	3.1820880049	0.370661346
H	1.6007968125	2.4056992074	-1.2063537305
H	1.046728685	4.0988615521	-1.0933626434
C	0.2150161126	-3.4348119958	-0.4749838405
H	0.9562893842	-2.9141483648	-1.0868553407
H	0.652453405	-3.5696596521	0.5198783596
H	0.0207808074	-4.4229593456	-0.9017140793
Ni	0.5958567119	-0.1707207126	0.0359795499
C	3.3014454483	0.6980011585	0.798679382
H	3.3358987688	1.749978567	0.4888281841
H	4.0443698148	0.5885668249	1.6053247384
C	1.9118702372	0.3557181833	1.3247912311
C	1.5217110511	-1.0591164747	1.4436057546
C	1.4267277216	1.2474290475	2.3611437882
C	0.6665500456	-1.4336159208	2.5472793789
H	2.2280556832	-1.8337702536	1.1304559125
C	0.5484315753	0.8535136399	3.3233173901
H	1.8020137473	2.2717211956	2.373249373
C	0.1506781761	-0.5197498314	3.4156285229
H	0.4352368445	-2.4893487306	2.6869336152
H	0.189939934	1.5670537643	4.0605012475
H	-0.5148064199	-0.834257204	4.2149843363
C	3.81477145	-0.166857873	-0.335979775
H	3.9869176432	-1.1992976551	-0.0330057857
H	4.7165465698	0.2340826458	-0.7976442109
Br	2.4881930657	-0.2929041729	-1.794719177

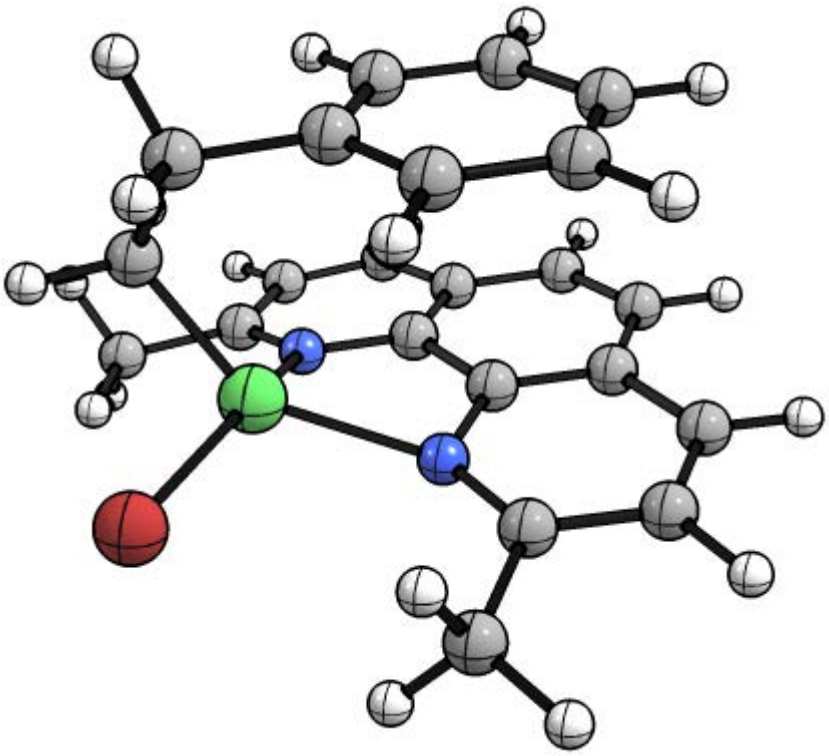
Energy = -5040.1317286
Zero-point correction = 0.382024 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.330510
Sum of electronic and zero-point Energies = -5039.749705
Sum of electronic and thermal Energies = -5039.727023
Sum of electronic and thermal Enthalpies = -5039.726079
Sum of electronic and thermal Free Energies = -5039.801219
G + ZVPE = -5039.419195
Energy (DMF-6-31G(d)) = -5040.159697
Energy (DMF-def2-TZVP) = -5043.1800923



J

C	0.7992856551	-3.1885124967	-1.4660263526
C	2.0969538871	-2.795018531	-1.2769455679
C	2.3625533628	-1.4372194218	-1.0247316668
C	1.2552941819	-0.5812011862	-0.9393199571
C	-0.261777924	-2.2544141587	-1.40073867
C	3.686078421	-0.9072608936	-0.8713116845
C	1.4810733901	0.8175088935	-0.7186343123
C	2.783707982	1.3299828564	-0.6669474524
C	3.8928084033	0.4232980838	-0.710976753
C	2.9121253732	2.7308372945	-0.5910058715
H	3.8988327365	3.1825216815	-0.5397502539
C	1.782670918	3.5095387287	-0.6251658319
C	0.5021482253	2.9164048769	-0.6449571865
H	4.5243380886	-1.596982138	-0.9104267174
H	0.5637863347	-4.2243061209	-1.6852941781
H	2.9137793748	-3.5090203996	-1.3358519926
H	4.898011706	0.8253701597	-0.6248888923
H	1.8537876357	4.5922640477	-0.621496877
N	0.3699508706	1.5912473176	-0.6235760407
N	-0.0384581533	-0.9700196383	-1.1185018682
C	-0.7231464106	3.7805534017	-0.7105625342
H	-1.6120102204	3.1770268059	-0.8975721087
H	-0.8708065795	4.3255891675	0.2270314346
H	-0.6081124614	4.5175157878	-1.5125110566
C	-1.6540869048	-2.7296271456	-1.6736439767
H	-2.2350600738	-2.7658112194	-0.7474182663
H	-2.1803169297	-2.0383593702	-2.3329437336
H	-1.6320198342	-3.7255754723	-2.1237992798
Ni	-1.1879963932	0.5669771727	-0.2660656564
C	-1.529961707	0.5895136499	2.4578225274
H	-2.4142601833	-0.0541397381	2.4356831288
H	-1.556226878	1.1350492924	3.4133917755
C	-0.2859963471	-0.2715082826	2.4215110118
C	0.9800757886	0.2959757143	2.6006576744
C	-0.3612308626	-1.6423831771	2.161544564
C	2.1332851305	-0.4784587853	2.5277473052
H	1.0596984691	1.3638353014	2.7934780062
C	0.7892726274	-2.4243027867	2.0914651077
H	-1.3368399241	-2.093214721	1.995679646
C	2.0412241186	-1.8454145547	2.2753111126
H	3.1065474345	-0.0146416781	2.6636967825
H	0.7054377334	-3.4882224018	1.8875542746
H	2.9406234709	-2.4520580254	2.2161539268
C	-1.5828060945	1.5872964859	1.2902158612
H	-0.8136370203	2.3521577189	1.4711374583
H	-2.5515777795	2.0983720927	1.2884597443
Br	-3.323080922	-0.1824244773	-0.4127935188

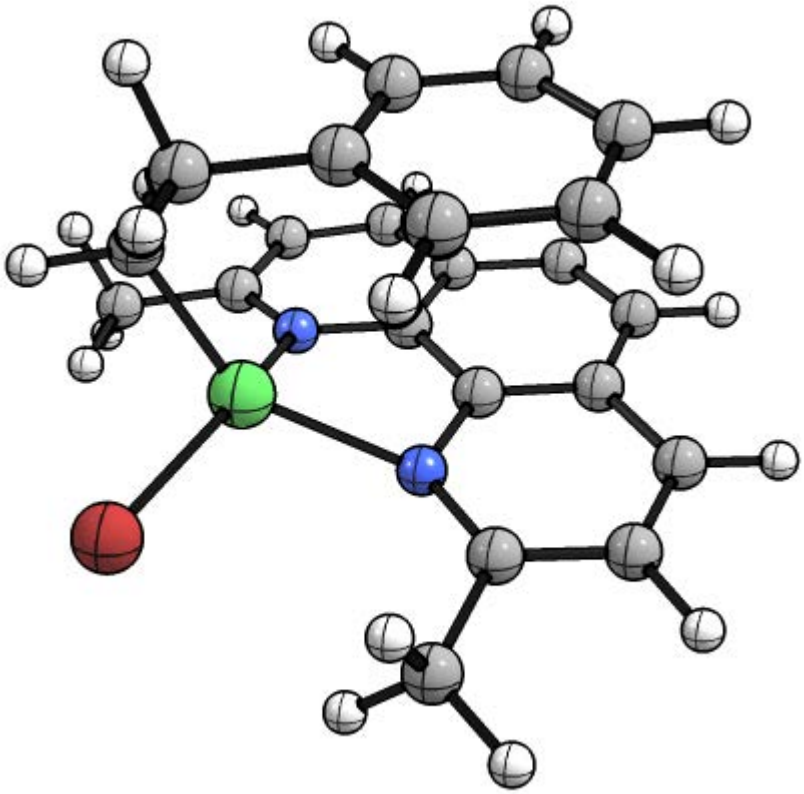
Energy = -5040.1937433
Zero-point correction = 0.383596 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.331549
Sum of electronic and zero-point Energies = -5039.810147
Sum of electronic and thermal Energies = -5039.787355
Sum of electronic and thermal Enthalpies = -5039.786411
Sum of electronic and thermal Free Energies = -5039.862194
G + ZVPE = -5039.478598
Energy (DMF-6-31G(d)) = -5040.2248353
Energy (DMF-def2-TZVP) = -5043.2410744



J-solv

C	0.8050432771	-3.1700697654	-1.5144951866
C	2.1016060726	-2.7632505757	-1.3439587138
C	2.3567761768	-1.4014786161	-1.0936590736
C	1.2432412326	-0.5549989025	-0.9876867788
C	-0.2633251233	-2.2466506616	-1.4277015016
C	3.6793611302	-0.8642801163	-0.9534039903
C	1.4604936973	0.8420955885	-0.7529109797
C	2.7597351733	1.3630680327	-0.7126868039
C	3.8766991336	0.4675960905	-0.7829968372
C	2.882152588	2.7649184472	-0.6150575457
H	3.8675847498	3.2192374419	-0.5722601089
C	1.7480491301	3.5363759971	-0.6160409219
C	0.4708772936	2.9344521222	-0.6220801952
H	4.5198185693	-1.5497646618	-1.0100743371
H	0.576752187	-4.2076685104	-1.7325669375
H	2.9255492646	-3.467318322	-1.4155253649
H	4.877847785	0.8807989908	-0.7056515512
H	1.8112353137	4.6192339399	-0.5942064198
N	0.3451905476	1.6080700932	-0.6252054646
N	-0.0522479314	-0.9601203981	-1.1413605149
C	-0.7532323076	3.7983971498	-0.6399691155
H	-1.6512929213	3.2041620935	-0.8145059343
H	-0.866187207	4.3373717742	0.3064395394
H	-0.6559098625	4.5459823735	-1.4344432327
C	-1.6534987825	-2.7441893686	-1.6723688334
H	-2.1947400581	-2.8433568661	-0.7263989881
H	-2.2197258783	-2.046738537	-2.2906670638
H	-1.6197539187	-3.7220628023	-2.1595174346
Ni	-1.1951345473	0.5521739957	-0.2463782172
C	-1.4931005836	0.51937312	2.4900848325
H	-2.3620007308	-0.1462150785	2.4546434859
H	-1.5365438009	1.0469066283	3.456044774
C	-0.2330210431	-0.3187437118	2.4505485971
C	1.0238346536	0.273024502	2.624497955
C	-0.2846404877	-1.6930964597	2.1986644556
C	2.1909441188	-0.4828630454	2.5536303481
H	1.0884751476	1.3430480466	2.811551466
C	0.8799274283	-2.4564363625	2.1290403472
H	-1.2510084186	-2.166646397	2.0400999745
C	2.1229327438	-1.8538249613	2.3070383097
H	3.1559231919	-0.0011893289	2.687413359
H	0.8141947089	-3.5225834649	1.9291233879
H	3.0328973417	-2.4442816859	2.2459788304
C	-1.5662182174	1.5378129893	1.3401276901
H	-0.8024563578	2.3060061477	1.5235517041
H	-2.5390326209	2.0446532417	1.3698551602
Br	-3.3622738578	-0.1747902062	-0.4163761699

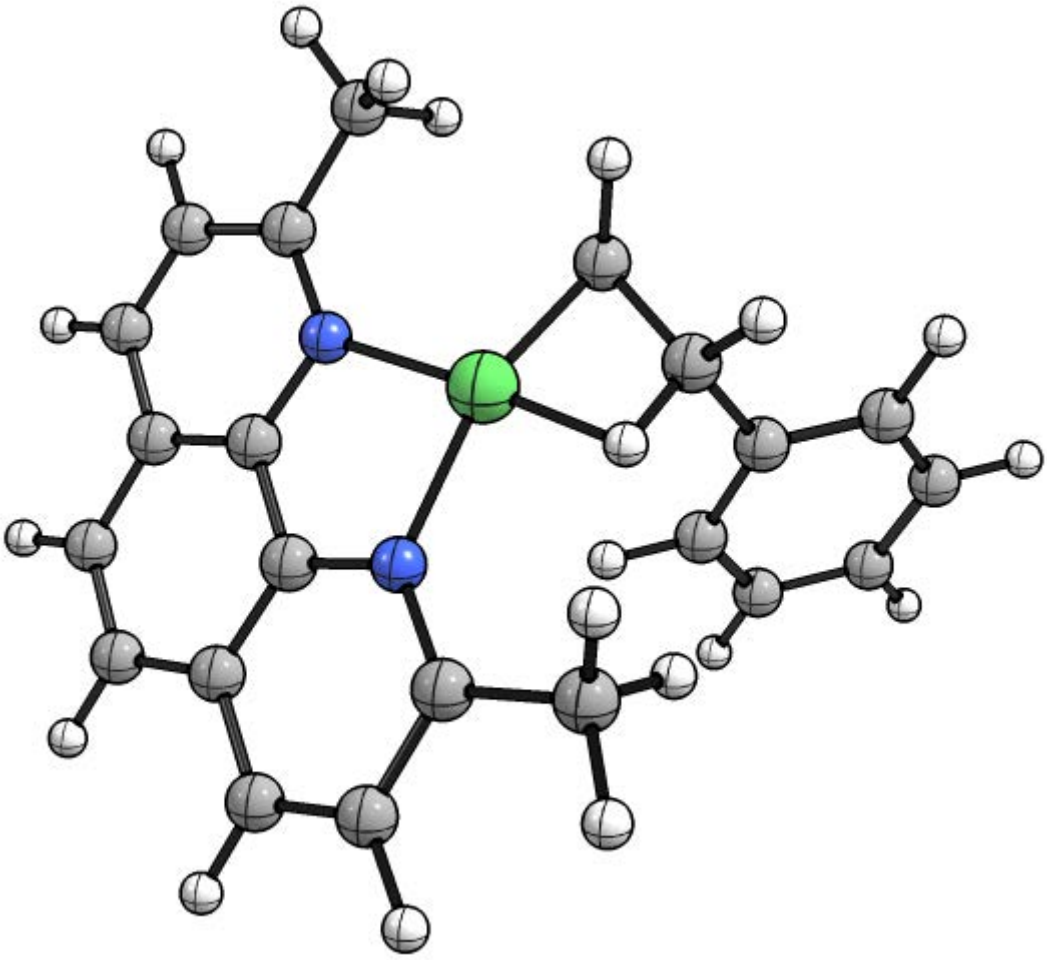
Energy = -5040.2254044
Zero-point correction = 0.383239 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.331744
Sum of electronic and zero-point Energies = -5039.842165
Sum of electronic and thermal Energies = -5039.819406
Sum of electronic and thermal Enthalpies = -5039.818462
Sum of electronic and thermal Free Energies = -5039.893660
G + ZVPE = -5039.510421



K

C	-0.6348218343	-3.4958106125	0.7803909066
C	-1.8070765708	-3.4689212717	0.067596042
C	-2.3679277341	-2.2279576372	-0.2980662717
C	-1.6610011977	-1.0809213274	0.083955612
C	0.017125055	-2.2960785664	1.1366138789
C	-3.6047686601	-2.088911907	-1.0094877172
C	-2.1818354831	0.2183730229	-0.2208097262
C	-3.4119502386	0.32781492	-0.8795884182
C	-4.1072019881	-0.8594492777	-1.2854882397
C	-3.9091490674	1.6303032256	-1.0871405143
H	-4.8566775155	1.7755981259	-1.5971373986
C	-3.1966583278	2.6996425467	-0.6120559217
C	-1.9583005313	2.5169449039	0.0434182885
H	-4.1362981302	-2.9860148102	-1.3103331308
H	-0.1949697491	-4.4388075574	1.0839868933
H	-2.3105376033	-4.3916816546	-0.2049108589
H	-5.0516180487	-0.7516545098	-1.809254643
H	-3.5732747103	3.7087708415	-0.7330551586
N	-1.4463091886	1.2927028248	0.2041323144
N	-0.4893665415	-1.1143858855	0.777377581
C	-1.2299030265	3.7167050494	0.5653594886
H	-0.8380456313	3.5318159144	1.5670545686
H	-0.3886115656	3.9721190861	-0.0856646237
H	-1.8996341256	4.5779705479	0.604666888
C	1.2987584694	-2.3360459662	1.9163154105
H	2.1485930206	-2.0737859957	1.2737617944
H	1.2690491221	-1.6375029567	2.7579210391
H	1.4800202481	-3.3361030418	2.3142644555
Ni	0.2381036258	0.6898678953	0.8327566268
C	2.2864146845	0.9987357677	1.0157849683
H	1.6268780944	0.0783711441	1.3361928303
H	2.788864216	1.1777124427	1.9703369315
C	3.211659528	0.4369794483	-0.0310689516
C	4.5509957238	0.8234689053	-0.0579169257
C	2.7389669487	-0.4557286217	-0.9935344902
C	5.4026704306	0.3292866623	-1.0402675
H	4.9278783248	1.5160250208	0.6899770116
C	3.5902425129	-0.9525417565	-1.9757303215
H	1.6959907387	-0.768734572	-0.9745666623
C	4.9247852575	-0.5599458575	-1.9999659603
H	6.4437272619	0.635826001	-1.0537615453
H	3.2124572521	-1.6477440227	-2.7189330351
H	5.5928996356	-0.9466138129	-2.762665843
C	1.3937188062	2.1265965158	0.6332033141
H	1.5079844801	2.4775358072	-0.3940630465
H	1.3696967433	2.947149443	1.3493269504

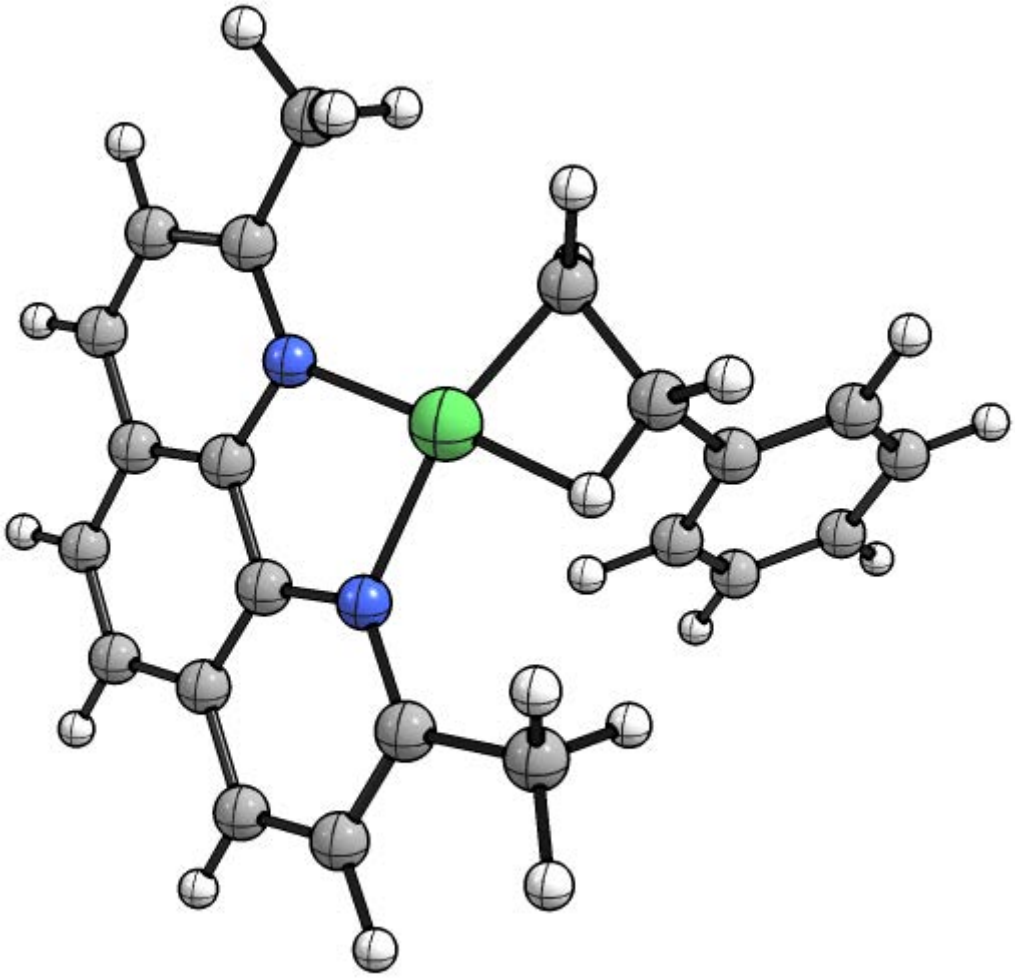
Energy = -2468.2098314
Zero-point correction = 0.383134 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.333690
Sum of electronic and zero-point Energies = -2467.826697
Sum of electronic and thermal Energies = -2467.806127
Sum of electronic and thermal Enthalpies = -2467.805183
Sum of electronic and thermal Free Energies = -2467.876141
G + ZVPE = -2467.493007
Energy (DMF-6-31G(d)) = -2468.2913585
Energy (DMF-def2-TZVP) = -2468.8364775



K-solv

C	-0.7023340673	-3.5119571828	0.8554782245
C	-1.8399438439	-3.4765718818	0.0881669806
C	-2.3670988223	-2.2305984642	-0.3116173815
C	-1.6625247649	-1.0910770214	0.0935748708
C	-0.0498337906	-2.3168682685	1.2280733906
C	-3.571176961	-2.0761031721	-1.0751067505
C	-2.1548048692	0.2136881461	-0.2299255598
C	-3.3565458761	0.340020009	-0.9350734406
C	-4.0471253022	-0.8396574463	-1.3719607281
C	-3.8322427922	1.6491998354	-1.1526200163
H	-4.7571237168	1.8060041372	-1.6995293381
C	-3.1304253251	2.707039247	-0.6365247295
C	-1.9219778778	2.5054675644	0.0677632503
H	-4.0986715789	-2.9691784992	-1.3955654998
H	-0.2881453414	-4.4563142305	1.1903723132
H	-2.3448822106	-4.3934231347	-0.2011550091
H	-4.9684210063	-0.7167586807	-1.9329238548
H	-3.4910539314	3.7220456201	-0.7597045304
N	-1.4265588196	1.2760054555	0.2334262064
N	-0.5232786018	-1.1343688976	0.8349300168
C	-1.2061154796	3.6885153765	0.6377034786
H	-0.8219141901	3.469741797	1.6359516512
H	-0.3607252536	3.9707884109	0.0020899417
H	-1.8851876192	4.5422016283	0.695227309
C	1.1948635863	-2.354532662	2.0601023213
H	2.0739889413	-2.14973915	1.4365761562
H	1.1559486357	-1.6026687837	2.8540011102
H	1.3265205526	-3.3390605619	2.5140390814
Ni	0.2410034166	0.651692906	0.8854746051
C	2.3021861918	0.935831506	1.0162872339
H	1.6610521682	0.0064774886	1.3156431111
H	2.8273856303	1.0927656303	1.9618307239
C	3.2133998844	0.4247645162	-0.0669562254
C	4.5078504416	0.9355354832	-0.1854912894
C	2.7765889011	-0.5373138011	-0.9790924661
C	5.3490826528	0.4938489404	-1.2028462198
H	4.855797534	1.682715333	0.5234887485
C	3.6177109639	-0.9826424614	-1.9963482146
H	1.7723078416	-0.9459713493	-0.8826992664
C	4.9062562125	-0.4671023473	-2.1112726756
H	6.3535193031	0.8993212186	-1.2856530071
H	3.265706794	-1.734671093	-2.6967410991
H	5.5651529654	-0.8137400448	-2.902101697
C	1.4046164388	2.0781911815	0.6775156107
H	1.4967179365	2.4581735913	-0.3424421798
H	1.4019950493	2.8812561117	1.4145608429

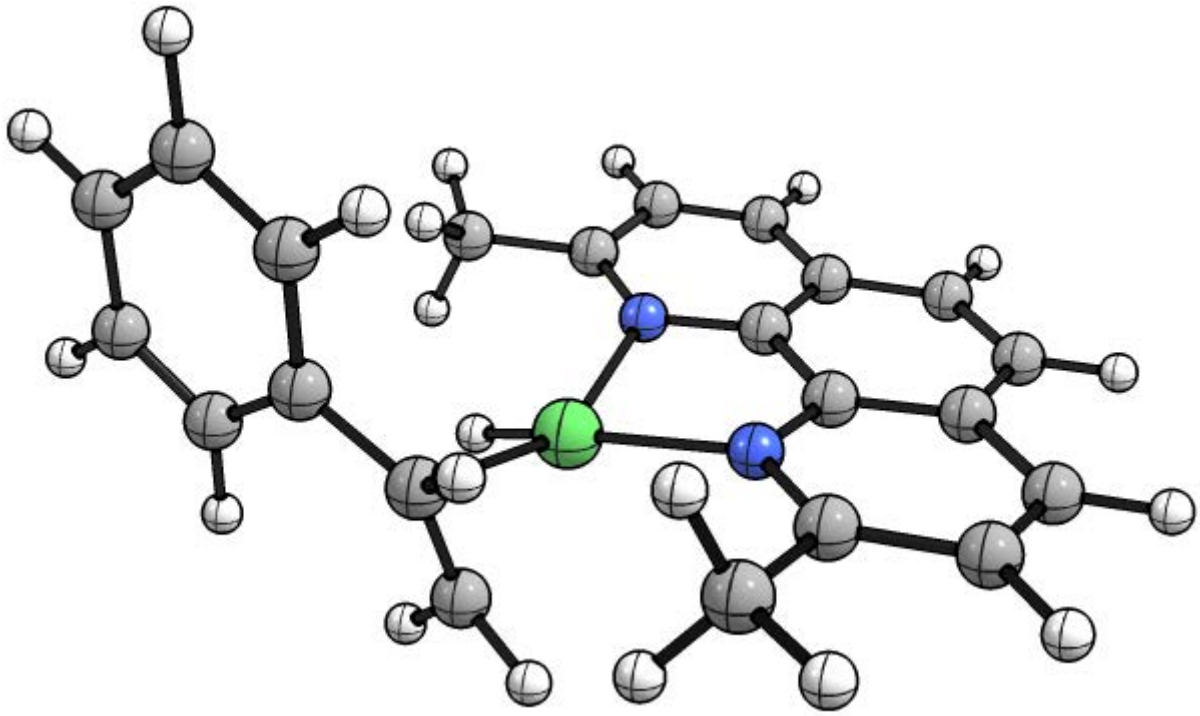
Energy = -2468.291745
Zero-point correction = 0.382563 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.333004
Sum of electronic and zero-point Energies = -2467.909182
Sum of electronic and thermal Energies = -2467.888559
Sum of electronic and thermal Enthalpies = -2467.887614
Sum of electronic and thermal Free Energies = -2467.958741
G + ZVPE = -2467.576178



L

C	-0.7814303482	3.6032544195	-0.0260708433
C	-2.1431053313	3.4395194081	-0.079201775
C	-2.6913261036	2.1396806392	-0.0671388159
C	-1.7857782518	1.076668526	0.0311888802
C	0.0717453374	2.4868264021	0.1021089673
C	-4.0934689029	1.8621004646	-0.1726456402
C	-2.2427532573	-0.2808681924	-0.0645919093
C	-3.617554788	-0.5188363964	-0.2075026445
C	-4.537447041	0.582119007	-0.2296132664
C	-4.0201354142	-1.8601288561	-0.3552788133
H	-5.0737061435	-2.1036926414	-0.45425164
C	-3.0634126603	-2.8392153162	-0.4080732708
C	-1.6931258579	-2.5190744929	-0.2875093219
H	-4.7895934509	2.6935960568	-0.2161470818
H	-0.3410645282	4.592704376	-0.0704787835
H	-2.8008383849	4.3005419085	-0.1532413687
H	-5.5976369358	0.3677939453	-0.3190651547
H	-3.3438490636	-3.8752152561	-0.5592515612
N	-1.2878984672	-1.2627344558	-0.0757253432
N	-0.4439901959	1.2562245866	0.1617835382
C	-0.6872317408	-3.6198045637	-0.4664031447
H	-0.063893034	-3.421099014	-1.3437148144
H	-0.0353797897	-3.7404637143	0.4005804951
H	-1.1913402428	-4.5734786484	-0.6309792934
C	1.5578667505	2.6623283726	0.1727581819
H	1.9003387568	2.5924940047	1.2109554343
H	2.0766297781	1.8852594553	-0.3950195105
H	1.8465694522	3.6411712418	-0.2164844587
Ni	0.4088784187	-0.3699338231	0.6230946429
C	1.8919620033	-1.6787492244	0.376397928
H	1.3003416195	0.4436858831	1.3760511985
H	1.5449189643	-2.3710986434	-0.3858619788
C	3.067190848	-0.8882835776	-0.0351992691
C	3.2486961699	-0.6377306262	-1.4007922492
C	3.9761518451	-0.3426865818	0.8799047391
C	4.3023961348	0.1551124911	-1.844385014
H	2.5564697952	-1.0678509308	-2.1214106585
C	5.0302159792	0.4432639473	0.437554747
H	3.8624970269	-0.539770569	1.9415252486
C	5.1933318798	0.699086755	-0.9245441176
H	4.4322465167	0.3391749243	-2.9059366934
H	5.7350450477	0.8517127969	1.1547101202
H	6.0212163032	1.3121968717	-1.2660497404
C	1.3655801944	-1.7911412194	1.6524380891
H	1.8696406418	-1.3681636482	2.5150600964
H	0.675807985	-2.5964306174	1.8895440762

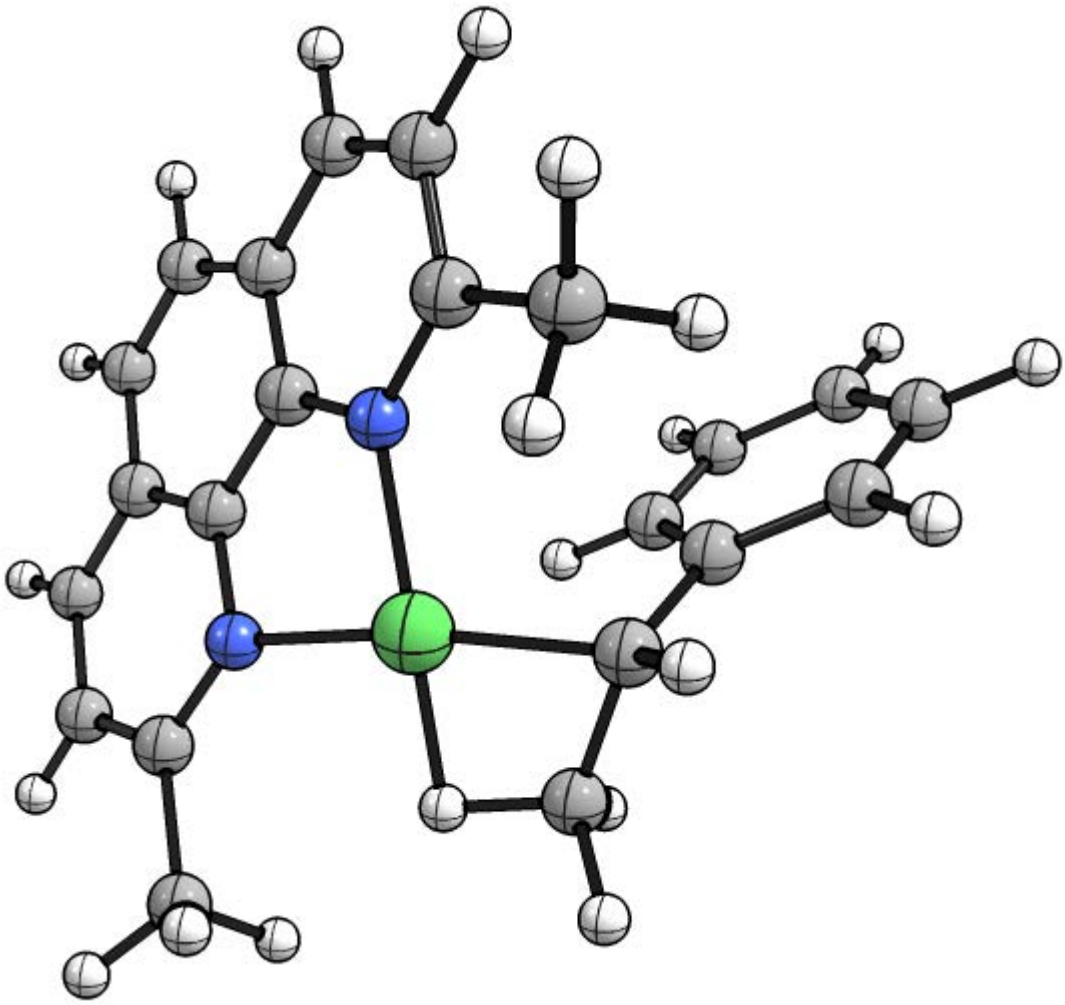
Energy = -2468.1874341
Zero-point correction = 0.380125 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.329938
Sum of electronic and zero-point Energies = -2467.807309
Sum of electronic and thermal Energies = -2467.786126
Sum of electronic and thermal Enthalpies = -2467.785181
Sum of electronic and thermal Free Energies = -2467.857496
G + ZVPE = -2467.477371
Energy (DMF-6-31G(d)) = -2468.2656356
Energy (DMF-def2-TZVP) = -2468.8109225



M

C	4.0371043281	-1.3105394305	0.7467403215
C	4.1606268036	0.0123564997	1.0931573333
C	3.1292514545	0.9168543102	0.7625735417
C	2.0114005484	0.3814326438	0.1121337475
C	2.8762479364	-1.7737657281	0.0911367991
C	3.1736815804	2.3246933371	1.032070889
C	0.9527049813	1.2414914146	-0.3236116135
C	1.0439903411	2.618374014	-0.1004272004
C	2.1705809739	3.1406922922	0.6180024394
C	0.0133339625	3.4170321443	-0.6410424711
H	0.020864233	4.4916719107	-0.4854225991
C	-0.964066961	2.8246277898	-1.3964539803
C	-0.9843315058	1.4245378117	-1.5925402087
H	4.0332737201	2.72797552	1.5577030231
H	4.8283417799	-2.0171153871	0.9705508529
H	5.0513694889	0.3700968266	1.6008918792
H	2.2154596304	4.2087035638	0.8061100513
H	-1.7408031739	3.4208053524	-1.862010187
N	-0.0687558317	0.6478963003	-1.0128737316
N	1.8796760272	-0.9384078461	-0.1978646771
C	-2.0326037531	0.8203297256	-2.4718141262
H	-1.6797212277	-0.1092426153	-2.9201988923
H	-2.9359124497	0.6081055609	-1.890482228
H	-2.3017777731	1.5184803819	-3.2680646537
C	2.7324297951	-3.2192069179	-0.285518598
H	2.1495080156	-3.7596105205	0.4704016236
H	2.2288686899	-3.3239434068	-1.2505248771
H	3.7082505491	-3.7045015879	-0.3537014715
Ni	0.0147168184	-1.2127541764	-0.6913539307
C	-1.0141018514	-2.8894259729	-0.0682981098
H	0.1391639891	-2.7503676694	-0.1981237066
H	-1.1711459251	-3.8036951889	-0.6423115968
C	-1.7791221762	-1.7111825167	-0.5718777505
H	-2.297367261	-1.9194415354	-1.5093927847
H	-1.1087142595	-3.0799224971	1.0023858257
C	-2.615768573	-0.9404811571	0.3879920393
C	-3.9652921498	-0.6986369437	0.1105888003
C	-2.0789730965	-0.4112033556	1.5697020316
C	-4.754049565	0.0490436356	0.9797775285
H	-4.4060641725	-1.1156244195	-0.7922301036
C	-2.8644665043	0.3322596783	2.4418627121
H	-1.0326691027	-0.5840950447	1.8176449858
C	-4.2052748976	0.5694732381	2.1477261913
H	-5.8010864692	0.2173769875	0.7479445489
H	-2.429209794	0.7307500415	3.3532153362
H	-4.8189507525	1.1517524059	2.8274119816

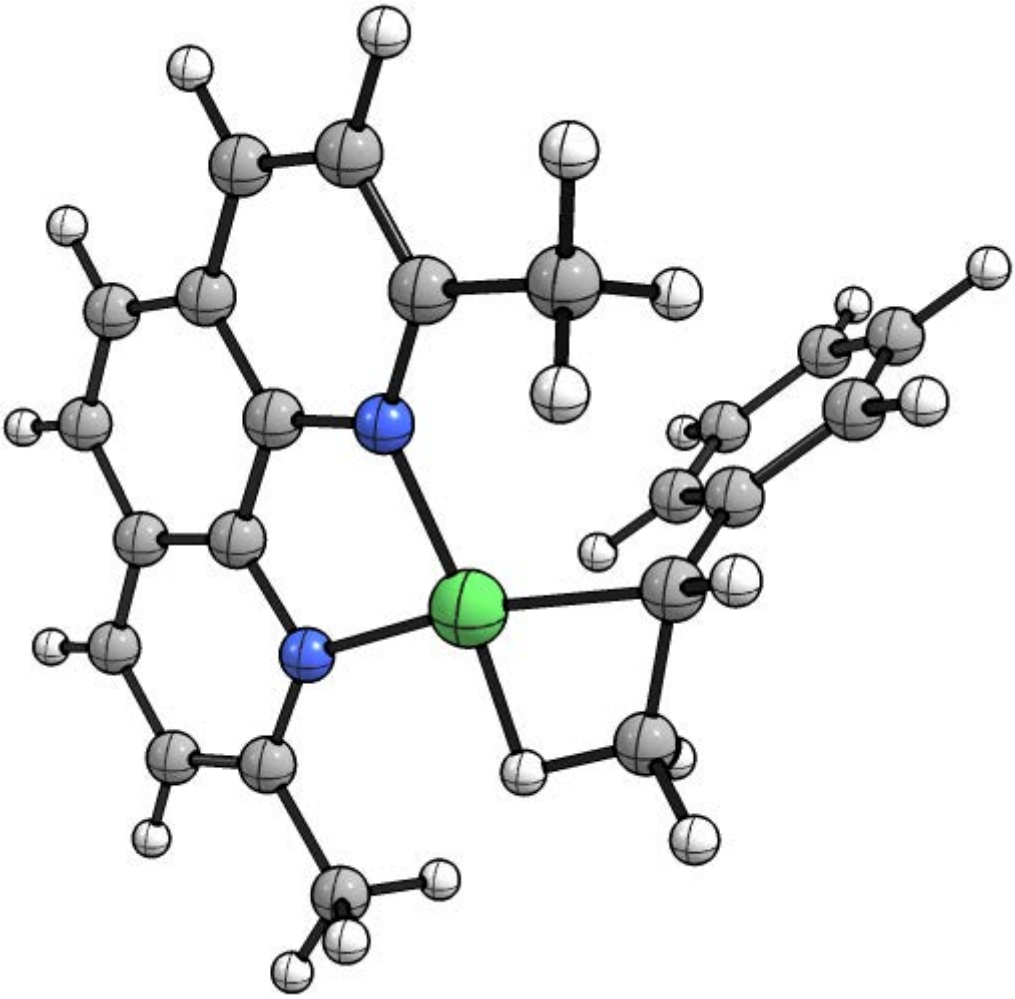
Energy = -2468.2137082
Zero-point correction = 0.382578 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.333061
Sum of electronic and zero-point Energies = -2467.831130
Sum of electronic and thermal Energies = -2467.810094
Sum of electronic and thermal Enthalpies = -2467.809150
Sum of electronic and thermal Free Energies = -2467.880647
G + ZVPE = -2467.498069
Energy (DMF-6-31G(d)) = -2468.2958451
Energy (DMF-def2-TZVP) = -2468.8408315



N

C	3.6278988742	-2.0957848236	0.6319414222
C	4.0934165038	-0.8457364335	1.0823534397
C	3.3246787197	0.2806851531	0.8481363845
C	2.0862017524	0.113768551	0.1704045498
C	2.4067488991	-2.2034934574	-0.0073537707
C	3.7009947041	1.6190779641	1.2353757348
C	1.2848243816	1.2115919181	-0.1435718199
C	1.6875183999	2.529489002	0.2072522352
C	2.9220948813	2.6839143047	0.9348731434
C	0.8879565302	3.5814035072	-0.2012957785
H	1.1576470378	4.6045798217	0.0454514977
C	-0.2485276273	3.3106348222	-0.973877372
C	-0.602702106	2.0052627542	-1.2883991165
H	4.638250362	1.7537333174	1.7687495515
H	4.2212392744	-2.9898607008	0.7889766639
H	5.0484571939	-0.7618324978	1.5927766927
H	3.2238583539	3.6876283757	1.2226932886
H	-0.8621919873	4.1217908375	-1.3492347942
N	0.1200868645	0.9466621532	-0.8547308638
N	1.6105658524	-1.1256263979	-0.2259812322
C	-1.8004288827	1.7587360794	-2.15669774
H	-1.5860215022	0.9873226747	-2.9007232977
H	-2.6527117146	1.4271452636	-1.5572796284
H	-2.0872141901	2.6774703815	-2.6745156042
C	1.9118411166	-3.5449795944	-0.4720534539
H	1.0294636488	-3.8627960703	0.0966773988
H	1.6379843281	-3.5149507722	-1.5334563404
H	2.6819081198	-4.3091911671	-0.3434464416
Ni	-0.1806958644	-0.8952394109	-0.8888315988
C	-1.4522369153	-2.516688417	-0.9472043165
H	-0.291710972	-2.5060920615	-1.0100814858
H	-1.6911852381	-3.1287867787	-1.8194014414
C	-2.039544362	-1.1402557453	-1.0016184658
H	-2.5504732226	-0.9488819987	-1.9458666026
H	-1.643773913	-3.0738496965	-0.0270744932
C	-2.8300259741	-0.6837153107	0.1726954649
C	-4.0967269517	-0.1122190503	0.0051805438
C	-2.3291946348	-0.785576621	1.4791093859
C	-4.833581899	0.3461911891	1.0934035329
H	-4.513974063	-0.0341455729	-0.9966420622
C	-3.065371288	-0.3380605157	2.5686218471
H	-1.3436325433	-1.2157325181	1.6456057764
C	-4.3213944486	0.2350685802	2.3818694422
H	-5.813430586	0.786894124	0.9324216612
H	-2.6505445381	-0.4279380482	3.5685558678
H	-4.8936667378	0.591063102	3.2332114023

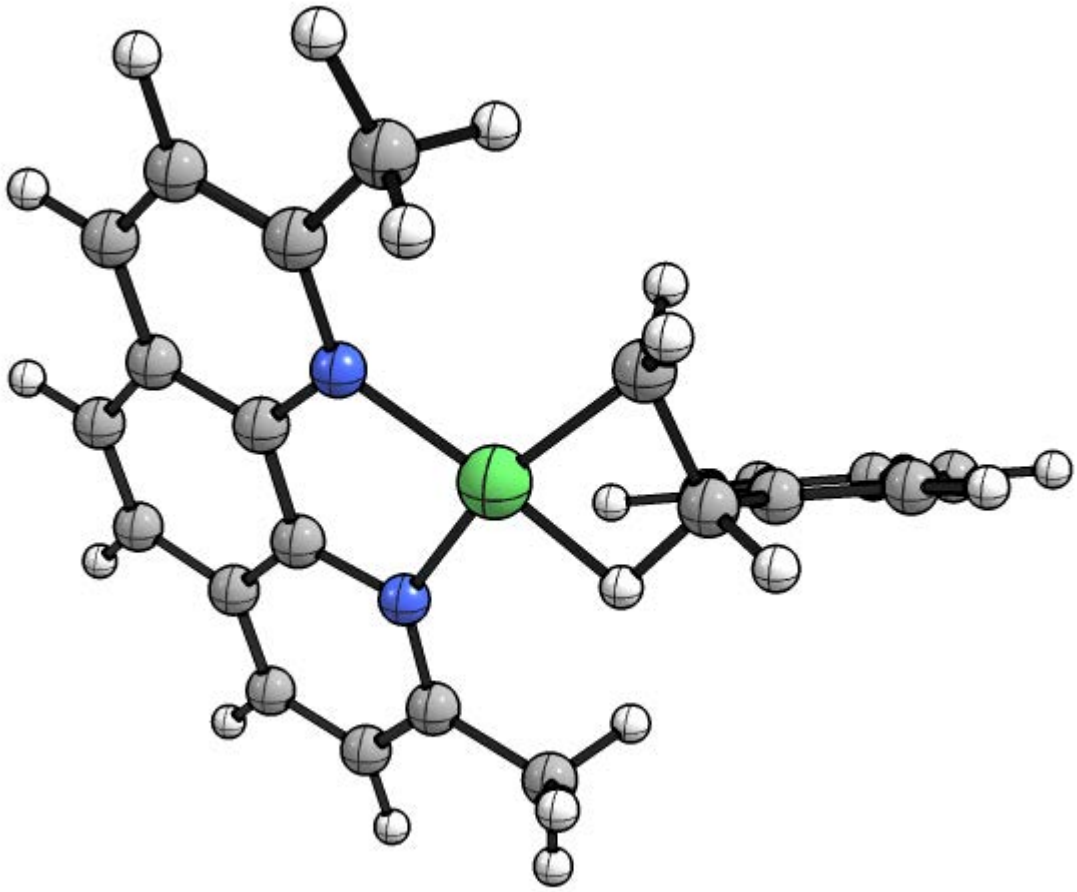
Energy = -2468.3614482
Zero-point correction = 0.379653 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.328588
Sum of electronic and zero-point Energies = -2467.981795
Sum of electronic and thermal Energies = -2467.960658
Sum of electronic and thermal Enthalpies = -2467.959714
Sum of electronic and thermal Free Energies = -2468.032860
G + ZVPE = -2467.653207
Energy (DMF-6-31G(d)) = -2468.3869781
Energy (DMF-def2-TZVP) = -2468.9389918



N'

C	-0.682414302	3.4989751292	-0.7409893506
C	-1.9116104694	3.4484260161	-0.0599934012
C	-2.4447728375	2.2180595204	0.277964842
C	-1.7049784167	1.0529988845	-0.0677463182
C	0.0006001773	2.3341179779	-1.0468742722
C	-3.7096361362	2.0361594588	0.9470867703
C	-2.19767082	-0.2222634903	0.2085364197
C	-3.4635193355	-0.3873676906	0.8364909563
C	-4.1910863866	0.8003514074	1.2119556216
C	-3.9304787349	-1.6736227356	1.0288957993
H	-4.8926197501	-1.8429974849	1.5040498941
C	-3.1565669153	-2.7520322069	0.5743252586
C	-1.9236564901	-2.5432772328	-0.0255424218
H	-4.2742470718	2.9217387398	1.2266919156
H	-0.2572738893	4.4521608785	-1.0347754714
H	-2.444965548	4.3627173994	0.1846491848
H	-5.1507095608	0.6755565623	1.7066379534
H	-3.5197921986	-3.7679067438	0.6814849028
N	-1.4096211634	-1.2986876232	-0.190714723
N	-0.47394899	1.1122777388	-0.6991406887
C	-1.1446331256	-3.7252863934	-0.5230679101
H	-0.8316882074	-3.5733690837	-1.5597601519
H	-0.2425602832	-3.8857928417	0.0731254062
H	-1.7548893844	-4.6303975363	-0.4714857219
C	1.3121042551	2.4025455705	-1.7794977703
H	2.1427813531	2.0714752693	-1.1447650336
H	1.2942229445	1.7705133521	-2.6753171489
H	1.5242157262	3.4270002924	-2.093930158
Ni	0.2421182123	-0.6699323293	-0.801399681
C	2.2900480523	-0.9253781749	-1.0548876556
H	1.6125896695	-0.0119458936	-1.329829866
H	2.7852513644	-1.0679989629	-2.01998992
C	3.2335814188	-0.3987742271	-0.0071210881
C	4.5775852858	-0.7722666341	-0.0148157008
C	2.7718816282	0.4502249962	1.000138754
C	5.4441650147	-0.3099036515	0.9700890611
H	4.9450085477	-1.432937632	-0.7961980013
C	3.6378385261	0.915566187	1.9848294124
H	1.7268426854	0.753527252	1.0051833686
C	4.9767117818	0.5367682345	1.9725055526
H	6.4885834972	-0.6073842289	0.9519649428
H	3.2647231007	1.5791300962	2.7592225822
H	5.655197975	0.9007790443	2.7381291659
C	1.4329398334	-2.0939268877	-0.6823715022
H	1.6078770448	-2.4759880221	0.3252077311
H	1.4285410743	-2.8954703302	-1.4215830555

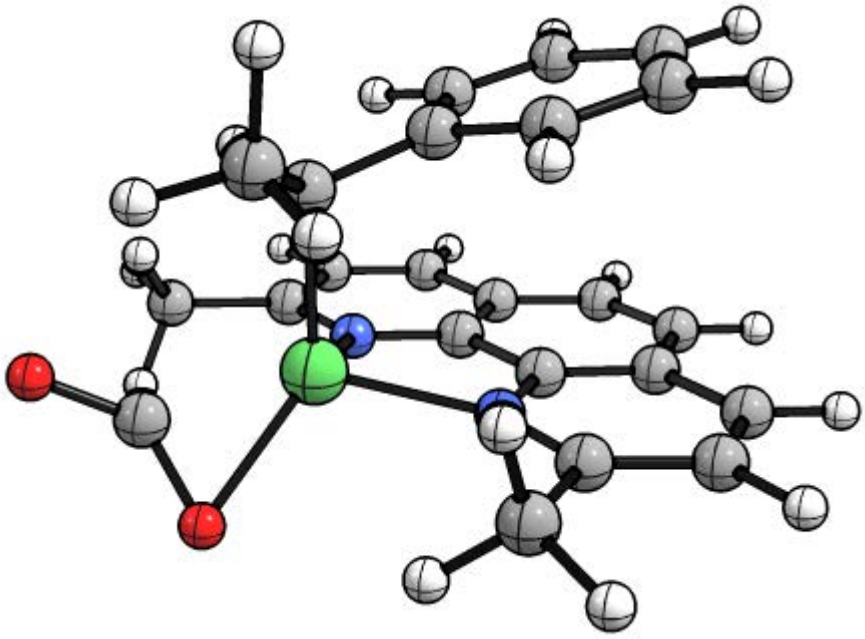
Energy = -2468.3596173
Zero-point correction = 0.379856 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.329639
Sum of electronic and zero-point Energies = -2467.979761
Sum of electronic and thermal Energies = -2467.958924
Sum of electronic and thermal Enthalpies = -2467.957980
Sum of electronic and thermal Free Energies = -2468.029978
G + ZVPE = -2467.650122
Energy (DMF-6-31G(d)) = -2468.3836449
Energy (DMF-def2-TZVP) = -2468.9346207



O

C	1.9194077633	-2.5726440966	-1.6855935125
C	2.8908752305	-1.6041810754	-1.6051906979
C	2.5302256114	-0.2801418903	-1.2906479609
C	1.1683941507	-0.0332575148	-1.065902114
C	0.5740220348	-2.2408742814	-1.4310078497
C	3.4684558974	0.8001922573	-1.18536389
C	0.723805268	1.2936954871	-0.7292028173
C	1.6646177905	2.3312668451	-0.6354923653
C	3.0521247231	2.0520756804	-0.8743838122
C	1.1762149506	3.5989403817	-0.2728993789
H	1.8627244386	4.4362369997	-0.1818372467
C	-0.1663525204	3.7607446742	-0.0287901618
C	-1.0475940855	2.6655854953	-0.1412063676
H	4.5206239525	0.5933585616	-1.356805669
H	2.1738605021	-3.5981030805	-1.9310019142
H	3.9341685817	-1.8485654716	-1.7843347569
H	3.7656670489	2.8667036962	-0.7914155358
H	-0.5653763746	4.7280409762	0.2563472836
N	-0.5992929453	1.461256127	-0.4886873558
N	0.2244137818	-0.9984139697	-1.1241757909
C	-2.5131788185	2.8228515006	0.128922612
H	-3.0946809584	2.6106917421	-0.7735692355
H	-2.846657601	2.1121164811	0.8901227012
H	-2.7444235542	3.8376365463	0.460689004
C	-0.5180048135	-3.268483254	-1.4531640338
H	-0.7560227618	-3.5759032922	-0.4279379948
H	-1.4276358214	-2.8516257071	-1.894849718
H	-0.2221387982	-4.159212223	-2.0127241211
Ni	-1.5625804388	-0.3594773572	-0.3570104277
C	-2.1639014875	-1.9242243872	2.0002162029
H	-3.2377201402	-1.7640807004	1.866665433
H	-1.9865049251	-2.1927135831	3.0519759131
C	-1.3909297089	-0.6656656952	1.5932431836
H	-1.8557824274	0.1949940177	2.0899639854
H	-1.8993914608	-2.8074187723	1.4026043901
C	0.0565011015	-0.6830884791	1.9436011367
C	0.7333051683	0.5074319084	2.2591108975
C	0.8345543899	-1.852536502	1.8942713644
C	2.1078429941	0.5411250245	2.4624067102
H	0.16109425	1.4312049047	2.3268040821
C	2.210352229	-1.8251356638	2.0959101698
H	0.3529989528	-2.8037843039	1.6825436526
C	2.8623625116	-0.6259120671	2.3712974129
H	2.5928753086	1.4868492059	2.6908106109
H	2.7770605955	-2.7512376474	2.0384617448
H	3.9370938627	-0.6027008148	2.5263689732
O	-4.3939993132	0.091163303	0.1345611904
C	-3.4104534609	-0.2032775106	-0.4895109666
O	-3.0611641493	-0.6016555099	-1.6353474645

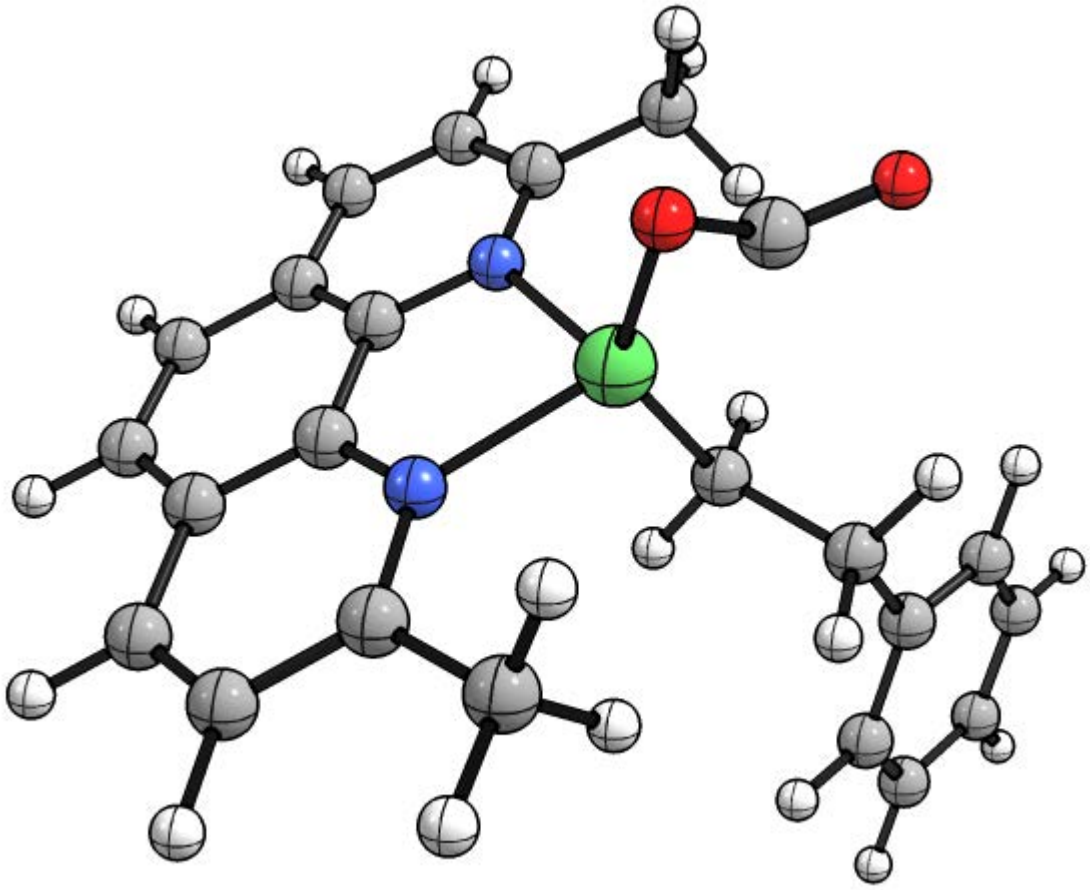
Energy = -2656.9292707
Zero-point correction = 0.393168 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.338668
Sum of electronic and zero-point Energies = -2656.536103
Sum of electronic and thermal Energies = -2656.511117
Sum of electronic and thermal Enthalpies = -2656.510173
Sum of electronic and thermal Free Energies = -2656.590603
G + ZVPE = -2656.197435
Energy (DMF-6-31G(d)) = -2656.9642374
Energy (DMF-def2-TZVP) = -2657.5788187



O'

C	2.1203106579	3.4500967662	0.7371486777
C	3.0568616052	3.172896382	-0.23093934
C	3.1537346054	1.8684022243	-0.7542623374
C	2.2664659579	0.9125874856	-0.2338103661
C	1.2613966217	2.4316463799	1.1975259328
C	4.089732716	1.4776128728	-1.7702651309
C	2.3048845831	-0.4440084996	-0.7144548602
C	3.2220700312	-0.7929570396	-1.717558774
C	4.1191591493	0.2029857683	-2.2332321158
C	3.1972476937	-2.1295658773	-2.1614731463
H	3.8863777942	-2.4543404144	-2.9360939098
C	2.2964424551	-3.006450745	-1.6098705982
C	1.4086376505	-2.5766233134	-0.5986045175
H	4.7729068795	2.2250763149	-2.1627864371
H	2.0301272302	4.4469881713	1.154817522
H	3.7234109523	3.9497688898	-0.5951676491
H	4.8259257208	-0.0878643932	-3.0048455917
H	2.254835643	-4.0386980617	-1.940048368
N	1.4278052587	-1.3194708252	-0.1655549805
N	1.3462556853	1.1986667277	0.7130101958
C	0.4281328468	-3.5241203866	0.0231324645
H	0.7088828782	-3.7416327885	1.0587058755
H	-0.5685864059	-3.0778245317	0.0598410743
H	0.386451633	-4.4657058148	-0.5292526904
C	0.2049892999	2.6728572104	2.2345494125
H	-0.7879970458	2.5788633894	1.7801222629
H	0.2759202648	1.9214639502	3.0276286232
H	0.2913419942	3.6672252711	2.6782761967
Ni	0.1409851287	-0.3928902893	1.1734033633
C	-2.7000199242	0.2249871537	0.6819376562
H	-2.9735225132	-0.5569021467	1.3990593631
C	-1.3820948414	-0.1569993264	-0.0099076702
H	-1.5624565584	-1.0700438994	-0.5955576898
H	-2.5721678901	1.149543726	1.2637121583
O	-1.3722646075	-2.4067898416	2.6287008438
C	-0.5272191402	-1.5741919574	2.4317085053
O	0.4324486838	-1.0046845662	3.0306574113
H	-1.1349433829	0.6234833924	-0.7493612886
C	-3.8292559404	0.4271465362	-0.300635734
C	-4.6599471462	-0.636277315	-0.6633410832
C	-4.0359208074	1.6639521015	-0.917046248
C	-5.6634820854	-0.4715232898	-1.6135005739
H	-4.5135447045	-1.6048562684	-0.1904069297
C	-5.0373701693	1.836570252	-1.8677406311
H	-3.3983032505	2.5032012669	-0.6448651626
C	-5.8562973266	0.7668785941	-2.2202514729
H	-6.3005285225	-1.3113141036	-1.8781513566
H	-5.1818691659	2.8084911235	-2.3321281287
H	-6.6404955626	0.898017115	-2.9604928898

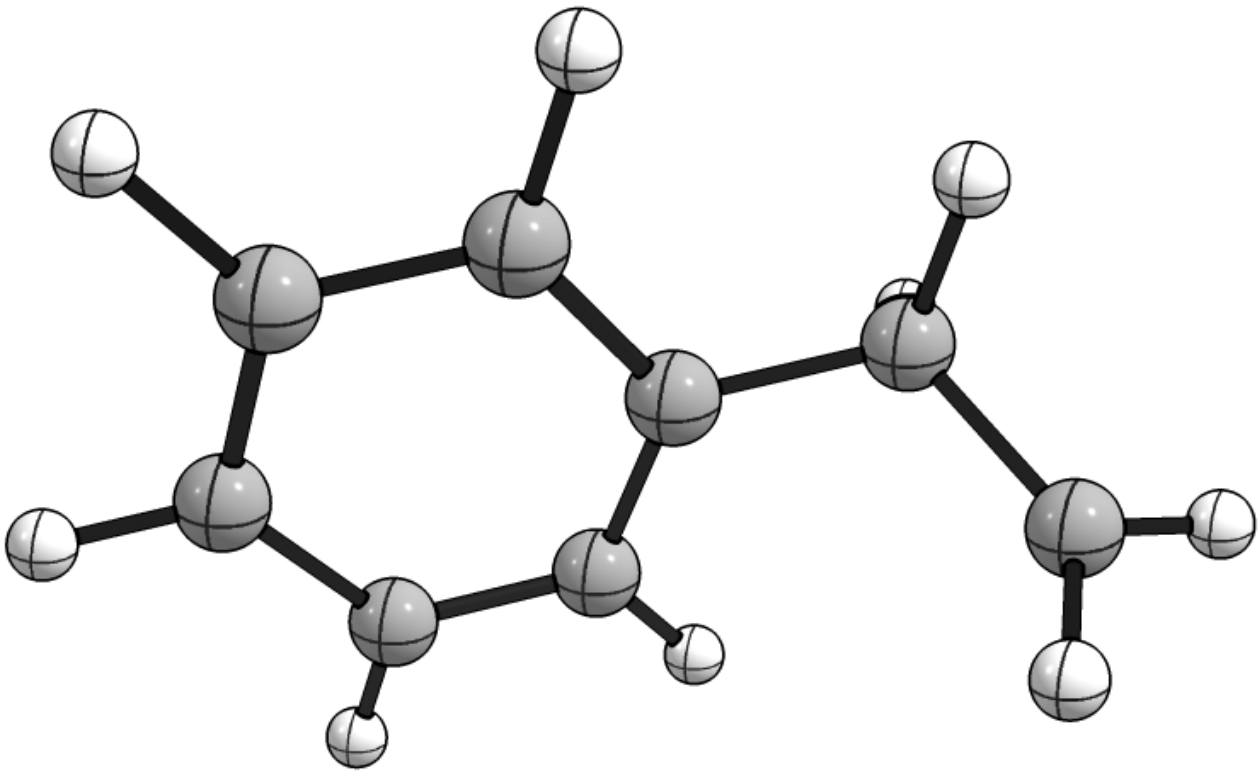
Energy = -2656.9102785
Zero-point correction = 0.393159 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.335455
Sum of electronic and zero-point Energies = -2656.517120
Sum of electronic and thermal Energies = -2656.492005
Sum of electronic and thermal Enthalpies = -2656.491061
Sum of electronic and thermal Free Energies = -2656.574823
G + ZVPE = -2656.181664
Energy (DMF-6-31G(d)) = -2656.9500187
Energy (DMF-def2-TZVP) = -2657.5667139



Q

C	0.4756933681	-0.220727989	0.1875657683
C	-0.4133042891	-1.2780167126	-0.0071674535
C	-0.033691395	1.0806695184	0.2202103012
C	-1.7775446884	-1.0458269617	-0.1636468209
H	-0.0330170347	-2.2964646646	-0.0405063742
C	-1.3948517217	1.3177298957	0.0641087541
H	0.6504841038	1.9132902102	0.36591528
C	-2.2730602997	0.2535709057	-0.1283820612
H	-2.4534940907	-1.8823241676	-0.316686781
H	-1.7725344386	2.3359414749	0.0928163187
H	-3.3360741963	0.4370912666	-0.2533490682
C	2.8254858877	0.3753591251	-0.5021499605
H	2.471955533	0.6974129886	-1.4764230125
H	3.8705861991	0.53247584	-0.2566234464
C	1.9591873159	-0.4668122495	0.3730165196
H	2.166159402	-1.536836301	0.1975951163
H	2.2284494333	-0.2962598692	1.4259316803

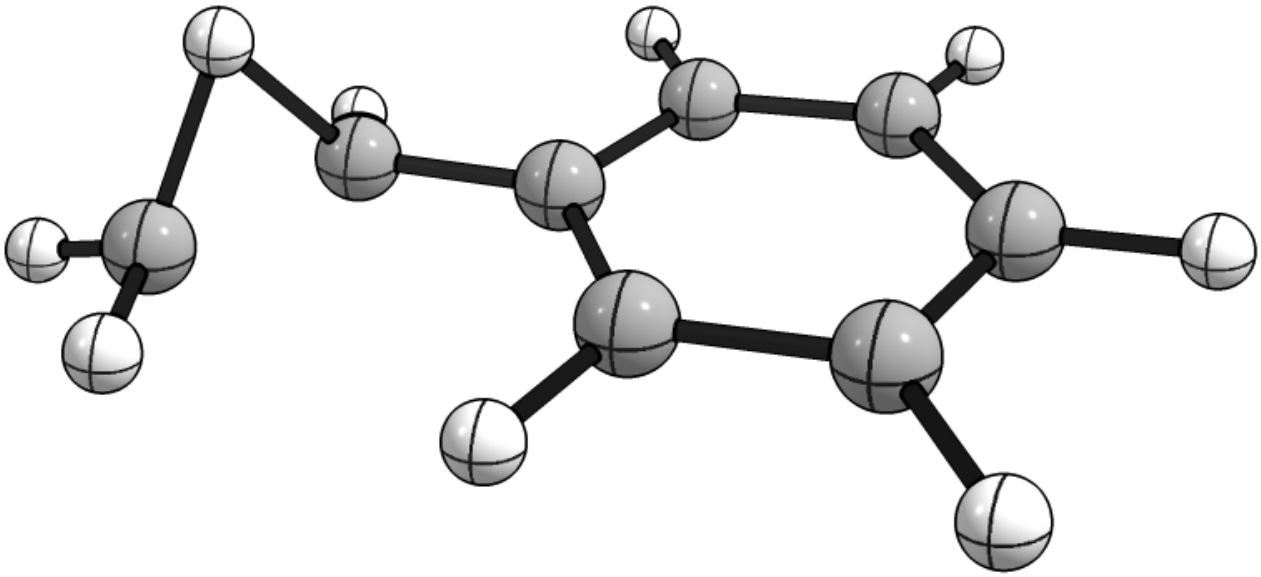
Energy = -310.0989848
Zero-point correction = 0.143646 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.111122
Sum of electronic and zero-point Energies = -309.955339
Sum of electronic and thermal Energies = -309.947832
Sum of electronic and thermal Enthalpies = -309.946888
Sum of electronic and thermal Free Energies = -309.987863
G + ZVPE = -309.844217
Energy (DMF-6-31G(d)) = -310.1068822
Energy (DMF-def2-TZVP) = -310.2152399



$TS_{Q\text{-}R}$

C	1.8762243842	0.5869378534	0.0196027758
H	2.510090842	0.3116713431	-1.033833155
H	2.1444852349	1.6051868454	0.2901919371
C	0.4580845345	0.2522278068	0.0255297816
C	-0.4943281911	1.2890439454	0.0078101874
C	-0.0144799208	-1.0716742944	0.0281376749
C	-1.8531212693	1.0154313774	-0.0085197306
H	-0.1515397941	2.3212656922	0.0091661731
C	-1.3779881776	-1.3414184817	0.0054476547
H	0.6875031188	-1.8991312061	0.0634990938
C	-2.3064598431	-0.3043993069	-0.0141831586
H	-2.5662049625	1.8349539543	-0.0170833873
H	-1.7178703483	-2.3734463063	0.0110634998
H	-3.370622557	-0.5189000824	-0.0297044862
C	2.9921330777	-0.3890067625	0.0183051107
H	2.8039233134	-1.4484106836	-0.0971905224
H	3.9798476028	-0.0560424101	0.3111090707

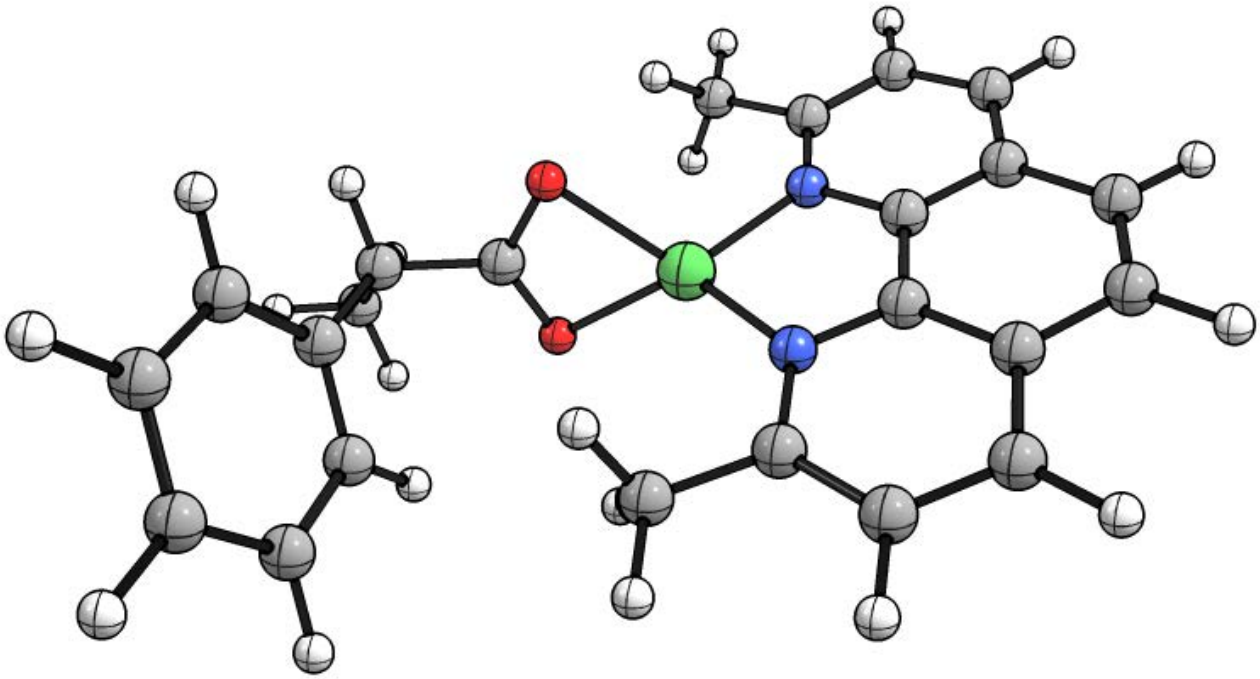
Energy = -310.040865
Zero-point correction = 0.140042 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.108180
Sum of electronic and zero-point Energies = -309.900823
Sum of electronic and thermal Energies = -309.893773
Sum of electronic and thermal Enthalpies = -309.892829
Sum of electronic and thermal Free Energies = -309.932685
G + ZVPE = -309.792643
Energy (DMF-6-31G(d)) = -310.0516539
Energy (DMF-def2-TZVP) = -310.1641138



P

C	2.1982763965	-3.0159595435	1.3690206632
C	3.4504513539	-2.4256680878	1.5888377618
C	3.663343324	-1.11646703	1.1511668226
C	2.5963392949	-0.4698011427	0.4969011042
C	1.1866174218	-2.3281635103	0.7210296151
C	4.8902940892	-0.3781994395	1.3226966128
C	2.7311021167	0.8573948305	0.0397466628
C	3.9369157653	1.5705628922	0.2178248724
C	5.0233111081	0.8979100358	0.8796625368
C	3.9736366909	2.8805060501	-0.2612242212
H	4.8761395695	3.4752379799	-0.1486223178
C	2.8495244847	3.4184702118	-0.8788862056
C	1.6898116292	2.6522523166	-1.021980642
H	5.7187356352	-0.8721708043	1.8232390298
H	2.0076226933	-4.0289854774	1.7082520971
H	4.239222607	-2.9719559286	2.0969509794
H	5.9564180541	1.4362802865	1.0206991382
H	2.8603454066	4.4363501336	-1.2531901116
N	1.6312277968	1.3917340733	-0.5719674603
N	1.3760775983	-1.0596948987	0.2625248951
C	0.4499876631	3.176651319	-1.6859458228
H	0.2524091667	2.6219992252	-2.6109482811
H	-0.4168999452	3.0367899361	-1.0320878004
H	0.5454141177	4.2358798345	-1.9356043299
C	-0.1772809287	-2.8983384195	0.475616674
H	-0.9403565993	-2.319802463	1.01143741
H	-0.4300787164	-2.8418784202	-0.5894693795
H	-0.249550928	-3.9387031176	0.801523307
Ni	0.1498856108	0.0987214641	-0.5897342461
O	-1.4140149787	-0.5235961201	-1.7405151344
O	-1.648582862	0.9168992572	-0.104504567
C	-2.166154533	0.1462370794	-0.9644744533
C	-3.670833047	-0.0363515626	-1.0179074245
H	-4.1082217979	0.8279696034	-0.5100806159
C	-4.1849913981	-0.1058137282	-2.45946244
H	-5.2662412119	-0.2721545306	-2.4637405622
H	-3.9744466042	0.8275968226	-2.9914966256
H	-3.7020974385	-0.9190441203	-3.0066731945
C	-4.0134834922	-1.2838563988	-0.2135544006
C	-4.769965714	-1.1866824592	0.9541188541
C	-3.5624117319	-2.5432259898	-0.620147966
C	-5.0762715979	-2.3218554173	1.7003079975
H	-5.1192529725	-0.212209343	1.2852291877
C	-3.8654370632	-3.6777526123	0.124634205
H	-2.9523450259	-2.6277698523	-1.5143632777
C	-4.6244133953	-3.5710721709	1.2878855553
H	-5.6665480081	-2.2267646643	2.6070492613
H	-3.5041485115	-4.648315023	-0.2030098392
H	-4.8594547726	-4.457317116	1.8699129757

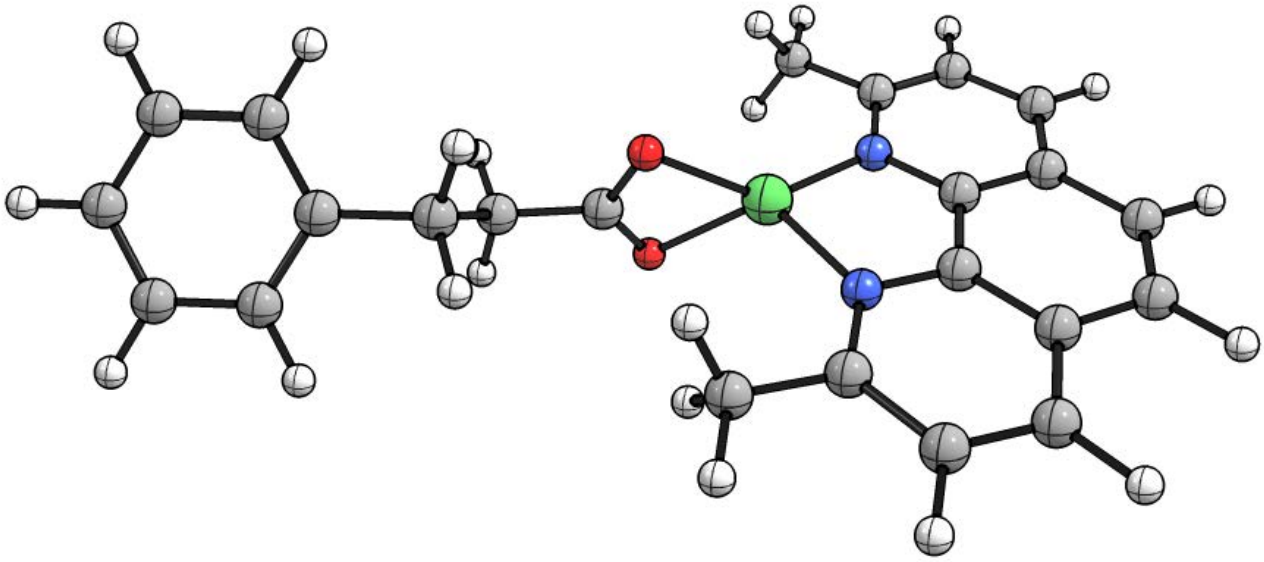
Energy = -2656.9584028
Zero-point correction = 0.394130 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.336197
Sum of electronic and zero-point Energies = -2656.564273
Sum of electronic and thermal Energies = -2656.539268
Sum of electronic and thermal Enthalpies = -2656.538324
Sum of electronic and thermal Free Energies = -2656.622206
G + ZVPE = -2656.228076
Energy (DMF-6-31G(d)) = -2656.9853242
Energy (DMF-def2-TZVP) = -2657.6103402



P'

C	1.8088282803	3.9460811149	0.0839298002
C	3.1645622876	3.5810273046	0.0897226618
C	3.4948446311	2.2229111098	0.0585776067
C	2.4361926919	1.2942650987	0.0227278059
C	0.8129942072	2.9900406931	0.0467531114
C	4.8403950361	1.7055326912	0.0626576657
C	2.6958181865	-0.0909844602	-0.0044155542
C	4.0204804358	-0.5838523587	0.0014086611
C	5.0935448461	0.3716461983	0.0347850501
C	4.1787148445	-1.9702329914	-0.0242038561
H	5.1763685206	-2.4014545895	-0.0222682821
C	3.0583734822	-2.7911151507	-0.0516118383
C	1.7755210843	-2.2325271512	-0.0544750898
H	5.6619012442	2.4162053177	0.0905076602
H	1.5268483195	4.9938832217	0.1084893832
H	3.9433622174	4.3365465032	0.1198449133
H	6.1162695917	0.0049093819	0.0384077243
H	3.1638442365	-3.8702841601	-0.070006326
N	1.5977995241	-0.90678364	-0.0329254262
N	1.1061893595	1.656557614	0.0149018975
C	0.5340744966	-3.0760222133	-0.0787871219
H	-0.0798235344	-2.8633912119	0.8031184213
H	-0.0684300582	-2.8339397236	-0.9608791312
H	0.7747415937	-4.141438071	-0.0958033525
C	-0.6502462225	3.3125205964	0.0343512188
H	-1.1192766914	2.9234274447	-0.8790636701
H	-1.1536150418	2.8377571479	0.8870541429
H	-0.8325402532	4.3886685204	0.0830427918
Ni	-0.0559665172	0.1761701088	-0.0380755564
O	-1.5923075708	-0.631641528	1.0207558461
O	-1.595121891	-0.5293234694	-1.1640829496
C	-2.1718482136	-0.861915158	-0.0850377221
C	-3.6495286834	-2.6550347004	0.9171393345
H	-2.9345522518	-3.4464457226	0.6618757337
H	-3.3592162046	-2.2700638554	1.8993292396
C	-3.5295584409	-1.5166505175	-0.1070723759
H	-3.7391994395	-1.8661210955	-1.1214472928
H	-4.2712301434	-0.7420846193	0.1269849175
C	-5.0494960282	-3.2175053469	0.9584352347
C	-5.4181678428	-4.2931452725	0.1483318968
C	-6.0217865652	-2.6354039293	1.7754824893
C	-6.7237479033	-4.7757960332	0.1521273195
H	-4.6718092589	-4.7587634122	-0.4916563234
C	-7.3284238769	-3.1127809763	1.7823261818
H	-5.747471935	-1.7986145211	2.4141708098
C	-7.6840432655	-4.1855254264	0.9688469964
H	-6.9916504807	-5.6155242851	-0.4826811289
H	-8.070005073	-2.6482568621	2.4259857096
H	-8.7033065499	-4.5600758247	0.9724137922

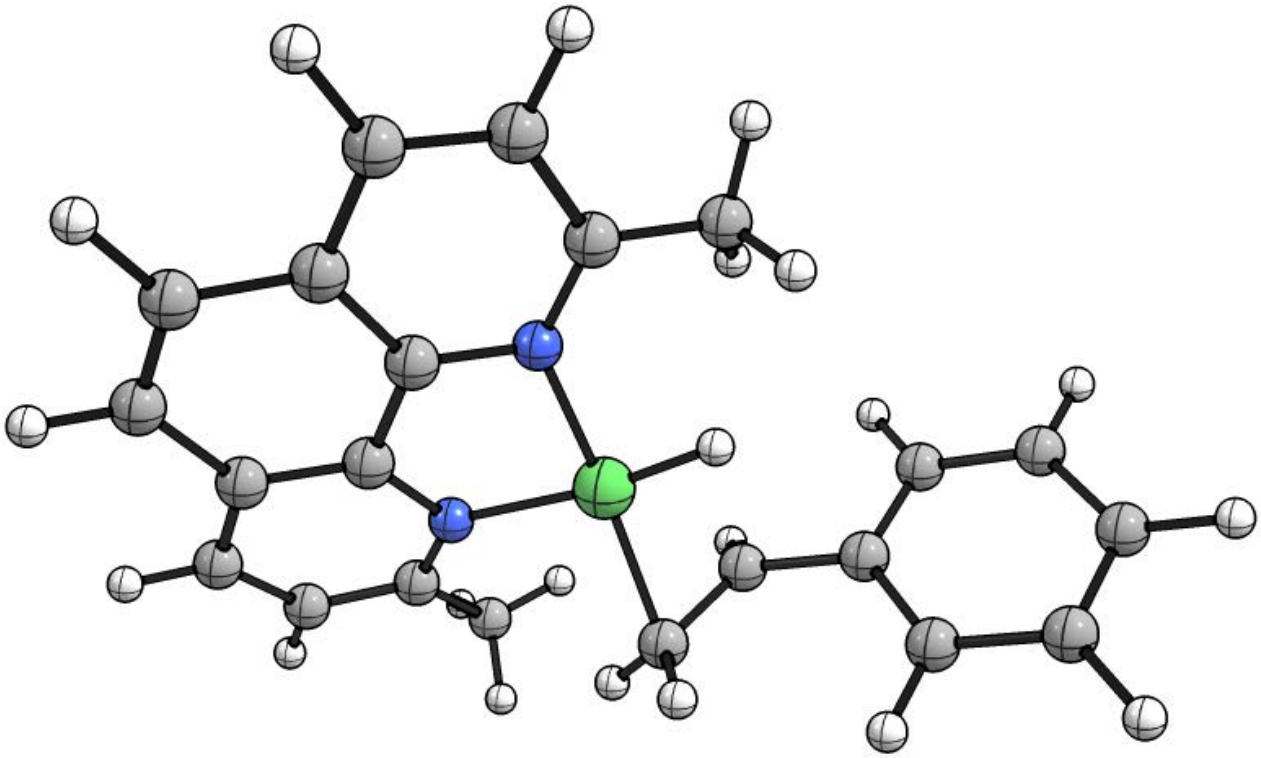
Energy = -2656.9564377
Zero-point correction = 0.394179 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.335320
Sum of electronic and zero-point Energies = -2656.562258
Sum of electronic and thermal Energies = -2656.537402
Sum of electronic and thermal Enthalpies = -2656.536457
Sum of electronic and thermal Free Energies = -2656.621118
G + ZVPE = -2656.226939
Energy (DMF-6-31G(d)) = -2656.9860386
Energy (DMF-def2-TZVP) = -2657.6086172



TS_{K-L}

C	-1.0345667375	3.5969509506	-0.2569352524
C	-2.3152732472	3.4124081674	0.2005122162
C	-2.8151239629	2.1018384203	0.3517648756
C	-1.931722389	1.058184038	0.0558954973
C	-0.2013167619	2.4928272399	-0.5419188168
C	-4.1572536905	1.7903885918	0.7513137302
C	-2.3851998877	-0.2987165162	0.1047983856
C	-3.7194781231	-0.574925806	0.4200949953
C	-4.5925819456	0.5045280019	0.7813946129
C	-4.1265240102	-1.922975783	0.3164207604
H	-5.1473916303	-2.2016706377	0.5600826234
C	-3.2357563742	-2.8562172614	-0.1470471552
C	-1.903793813	-2.4938189709	-0.4527450344
H	-4.8264068593	2.6056195362	1.0074665566
H	-0.6415547147	4.5958827837	-0.4078787633
H	-2.9512191174	4.2639282062	0.4237798124
H	-5.6168683468	0.274984162	1.057312208
H	-3.5390934504	-3.8870492248	-0.2948734286
N	-1.4749929641	-1.2474616448	-0.2638383617
N	-0.6468164348	1.2470483892	-0.3619400918
C	-0.9855615359	-3.5167712952	-1.0547604837
H	-0.1041190316	-3.0484787503	-1.495391105
H	-0.6693456306	-4.2619283873	-0.3169381825
H	-1.5136771992	-4.0558205798	-1.847045082
C	1.1906927257	2.7082271981	-1.0557011279
H	1.9236643007	2.6036865577	-0.2476199958
H	1.4379436484	1.9708897417	-1.8228036963
H	1.2953522192	3.7091126159	-1.4803560692
Ni	0.3023304748	-0.4023884857	-0.1776971547
C	2.1250231873	-1.3312542046	-0.2159361962
H	1.4835947819	0.382251916	-0.1667801321
H	2.0886047726	-1.7533229458	-1.2242952721
C	3.4354212163	-0.6820351783	0.0802165448
C	4.0995520172	0.0074391532	-0.9394576013
C	4.0343850081	-0.7751057122	1.3366466844
C	5.3289692219	0.6083598464	-0.705140484
H	3.6447468181	0.0745692196	-1.925682953
C	5.2668160782	-0.1724907336	1.5730377002
H	3.5549538968	-1.337884414	2.1316639115
C	5.9145812748	0.5220177749	0.5566081676
H	5.8347221897	1.1368017633	-1.5070999921
H	5.7272078275	-0.258717979	2.5520745658
H	6.8784099314	0.9851860318	0.7416139543
C	1.2422857414	-1.8616769482	0.7253425542
H	1.3840086532	-1.630516066	1.7803361881
H	0.7424353273	-2.800838967	0.5319769264

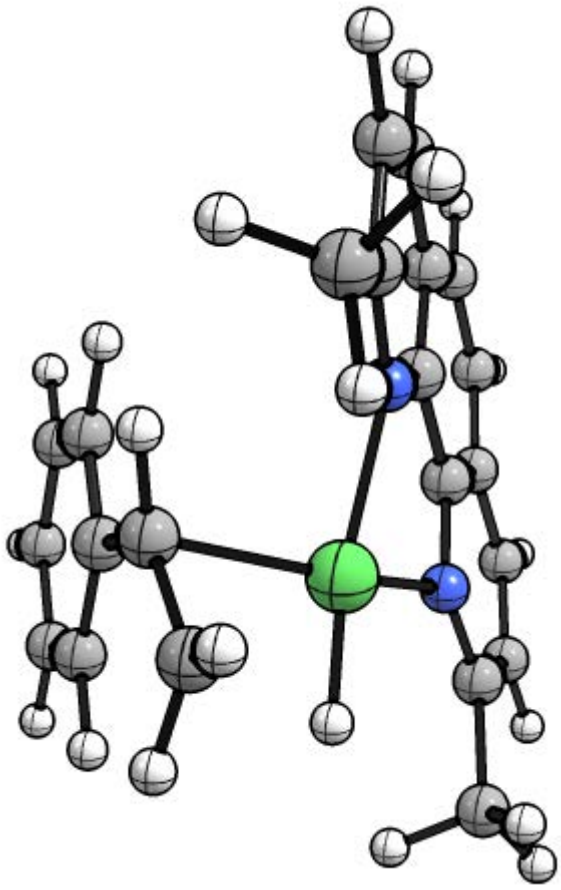
Energy = -2468.1750505
Zero-point correction = 0.378383 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.328397
Sum of electronic and zero-point Energies = -2467.796668
Sum of electronic and thermal Energies = -2467.775771
Sum of electronic and thermal Enthalpies = -2467.774827
Sum of electronic and thermal Free Energies = -2467.846653
G + ZVPE = -2467.468270
Energy (DMF-6-31G(d)) = -2468.2548099
Energy (DMF-def2-TZVP) = -2468.8041208



$TS_{L\text{-}M}$

C	0.849089041	3.60701425	-0.6978876394
C	1.8344191254	3.285859629	0.2004627477
C	2.1023613532	1.9287019355	0.4741454269
C	1.2996691093	0.9878778663	-0.179123916
C	0.0795408532	2.6005176435	-1.3238162591
C	3.147250904	1.4746134011	1.3463512282
C	1.5626897033	-0.4077669037	-0.0083693454
C	2.6337486387	-0.8293340462	0.7860996121
C	3.4052273438	0.1499566721	1.4951969975
C	2.8992979589	-2.2160886052	0.8024679204
H	3.710619141	-2.605384354	1.4103770878
C	2.1550524646	-3.0519447869	0.0088704334
C	1.0889487657	-2.5446063937	-0.7675786267
H	3.7436905258	2.2148505898	1.8702196252
H	0.6453672354	4.6430672029	-0.942963067
H	2.4194594182	4.0632543978	0.6828080363
H	4.2124583777	-0.1873096878	2.1375487113
H	2.3734464174	-4.113398177	-0.0385871383
N	0.7704440261	-1.2533579066	-0.7241920965
N	0.2948938977	1.3126071587	-1.0454599879
C	0.3269850918	-3.4582806081	-1.6818786303
H	-0.2687580296	-4.1875145304	-1.1221320979
H	-0.3278640472	-2.8903204041	-2.3442581562
H	1.0283149427	-4.0256242731	-2.3012740758
C	-0.9878050568	2.9811619165	-2.3043690058
H	-0.996687582	2.2971918335	-3.1555670667
H	-1.9733996822	2.9346596808	-1.828587238
H	-0.8323459324	3.9994749337	-2.6671901511
Ni	-0.8126338432	-0.2321377523	-1.2873311945
C	-2.0375321974	-1.5214926385	-0.4207500162
H	-1.8248403142	0.6141969621	-1.847258298
H	-1.5493367473	-2.4851431	-0.3210985954
C	-2.2354534853	-0.7960679295	0.846846732
C	-1.4776272929	-1.1837849258	1.961030911
C	-3.0901419303	0.3087412466	0.9635748315
C	-1.5692602163	-0.4892446968	3.1597268282
H	-0.8120753231	-2.0408263573	1.8812349939
C	-3.183296344	1.0012429246	2.164217274
H	-3.6971008647	0.6226853296	0.1197287316
C	-2.4224179474	0.6072211735	3.2628553009
H	-0.9816831009	-0.805733547	4.0156005613
H	-3.8593585775	1.8463405778	2.2459944201
H	-2.5021038487	1.1473974362	4.2007738486
C	-2.593016329	-1.1909808257	-1.6469916703
H	-3.4459303159	-0.5286947704	-1.7336803746
H	-2.4918668309	-1.8879553433	-2.4753385946

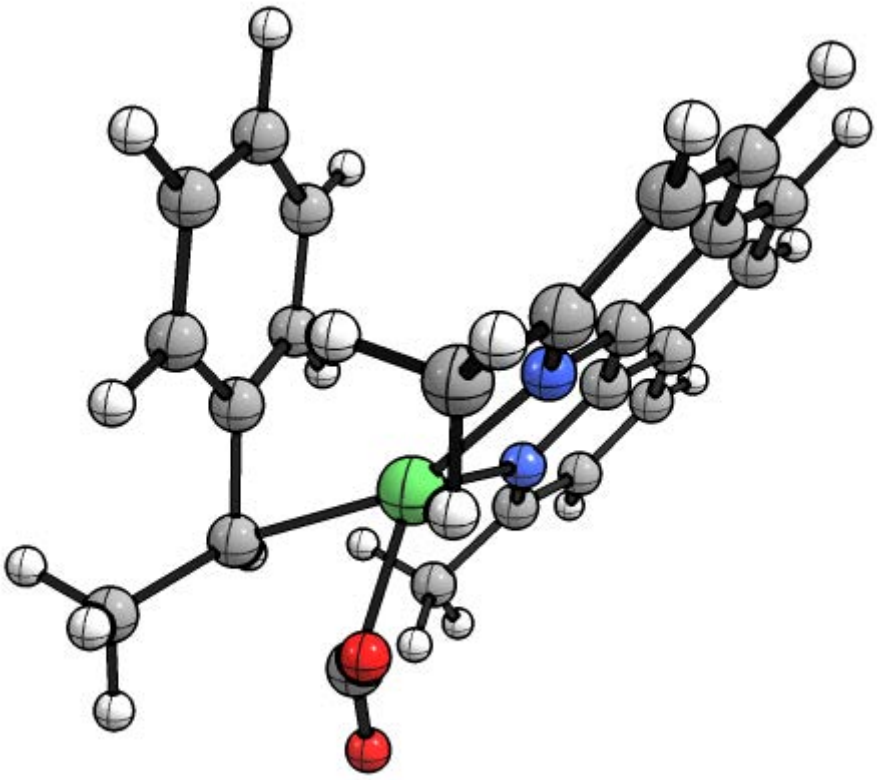
Energy = -2468.186101
Zero-point correction = 0.378508 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.328067
Sum of electronic and zero-point Energies = -2467.807593
Sum of electronic and thermal Energies = -2467.786731
Sum of electronic and thermal Enthalpies = -2467.785787
Sum of electronic and thermal Free Energies = -2467.858034
G + ZVPE = -2467.479526
Energy (DMF-6-31G(d)) = -2656.933771
Energy (DMF-def2-TZVP) = -2468.8138551



$TS_{O\text{-}P}$

C	1.6609430305	-3.2150720542	-1.1379925443
C	2.8779196336	-2.7053316833	-0.7645328203
C	2.9785493686	-1.3452880001	-0.4135347522
C	1.7955110113	-0.5888772879	-0.4437281405
C	0.5181994676	-2.3865838661	-1.1629928018
C	4.2160264397	-0.7175402332	-0.0540255216
C	1.8347750924	0.8123048802	-0.1102501931
C	3.0694486302	1.4041525827	0.2058080016
C	4.2603304044	0.6055446607	0.2354965925
C	3.0670778634	2.7857832298	0.4769537243
H	3.9980200403	3.2912981631	0.7184712622
C	1.8834979514	3.4733781873	0.4209009963
C	0.6764789764	2.8019054549	0.1209050253
H	5.1182922497	-1.3219352564	-0.032276682
H	1.5585187127	-4.2555777105	-1.4263741254
H	3.7648732566	-3.3329386097	-0.7496376461
H	5.1993247535	1.086907253	0.4929588811
H	1.8508777326	4.5401568728	0.6147090416
N	0.6574968713	1.4939988874	-0.1336014005
N	0.5951525041	-1.104265419	-0.809410646
C	-0.6120856667	3.5664180024	0.1284344667
H	-1.3083655388	3.1997574012	-0.6323391571
H	-1.0960847998	3.4662428148	1.1080636414
H	-0.4250785498	4.6311496612	-0.0349114659
C	-0.8079215996	-2.9263881754	-1.596677713
H	-1.4526233893	-3.0625002	-0.7221993263
H	-1.315058932	-2.2184082164	-2.2550018788
H	-0.6911754128	-3.8908305664	-2.0969714611
Ni	-0.9194338321	0.171797067	-0.4702601242
C	-4.190806018	0.5346456677	0.1947612512
H	-4.6341842861	1.3681857519	-0.3553414282
H	-4.7127791668	0.4300974955	1.1547058021
C	-2.7041070296	0.79062576	0.424168656
H	-2.5561991476	1.7951172453	0.8204049693
H	-4.3655823066	-0.3717106499	-0.3910731085
C	-2.0261910514	-0.2297691112	1.2754318407
C	-0.9569411718	0.1429524296	2.1249265913
C	-2.3819089241	-1.5977082221	1.2611819927
C	-0.2420538172	-0.8001926436	2.8535391537
H	-0.713297248	1.1968002668	2.2287300719
C	-1.6649232051	-2.5351046412	1.993962503
H	-3.2192924806	-1.9205406576	0.6513312954
C	-0.5790461702	-2.1494841815	2.7791269532
H	0.5775787089	-0.4765114798	3.4891504992
H	-1.957419774	-3.5811210906	1.9510342614
H	-0.0213148427	-2.8878755736	3.3470599998
O	-2.5371699775	2.0685579471	-1.9312709109
C	-2.3168117029	0.9381866976	-1.5467372754
O	-2.3077296462	-0.2155029154	-2.0315892939

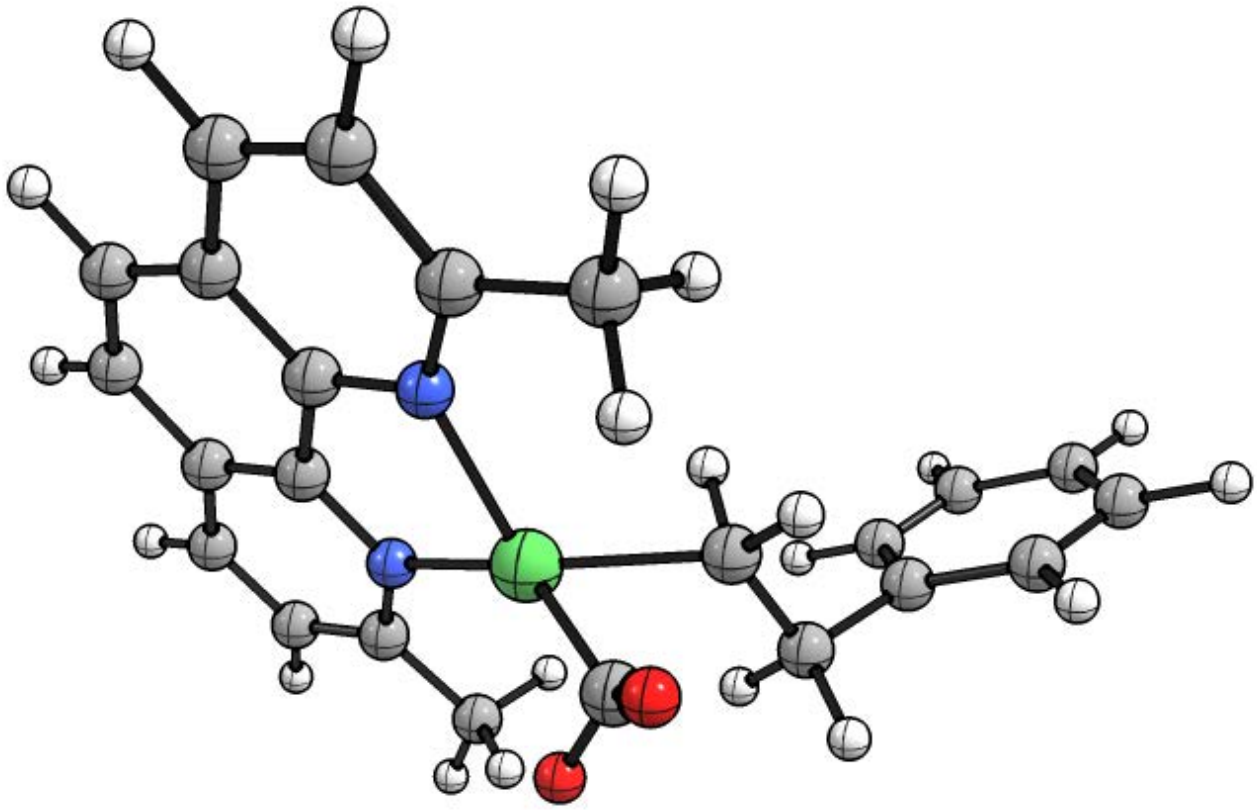
Energy = -2656.9127352
Zero-point correction = 0.392789 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.337531
Sum of electronic and zero-point Energies = -2656.519947
Sum of electronic and thermal Energies = -2656.495609
Sum of electronic and thermal Enthalpies = -2656.494665
Sum of electronic and thermal Free Energies = -2656.575204
G + ZVPE = -2656.182415
Energy (DMF-6-31G(d)) = -2656.9471299
Energy (DMF-def2-TZVP) = -2657.5681862



$TS_{O'-P'}$

C	-2.5622290531	-3.4288628851	-0.0495365983
C	-3.6883179254	-2.8237446036	-0.5526713325
C	-3.7139140629	-1.4234030758	-0.7126789414
C	-2.5591857391	-0.7248276119	-0.331107378
C	-1.4395335825	-2.652781476	0.3094764658
C	-4.8371107543	-0.6947500101	-1.2289279063
C	-2.5028613817	0.7074178246	-0.4672062198
C	-3.6175004256	1.392647307	-0.9720220819
C	-4.7892547034	0.6554888078	-1.3519850287
C	-3.5087593459	2.7943016494	-1.0697850682
H	-4.343006448	3.3767458517	-1.4508565936
C	-2.3446087149	3.4049723121	-0.6782325585
C	-1.2612948662	2.6412748351	-0.1862253725
H	-5.7274728394	-1.2458975081	-1.5170179425
H	-2.52037103	-4.5048330136	0.0801483656
H	-4.5584090467	-3.4132574333	-0.8285875147
H	-5.6418007956	1.204560423	-1.7409451416
H	-2.2349385059	4.4818408565	-0.7444677647
N	-1.3500278456	1.3156687611	-0.0811869309
N	-1.4565513765	-1.3298481385	0.1719425362
C	0.0213540009	3.3005356922	0.2137542689
H	0.3444885556	2.9650564029	1.2068307044
H	0.8121748984	3.0270099145	-0.4932763017
H	-0.0819393336	4.3882781508	0.2108172402
C	-0.1796023684	-3.2702351957	0.8347970971
H	-0.3390374673	-4.3069120379	1.1404694958
H	0.5894660769	-3.2593770826	0.0527122811
H	0.2024249823	-2.6855614058	1.6768155951
Ni	-0.0714158854	-0.0112401389	0.7540997212
C	2.9626040952	-0.4900366661	0.8023024573
H	3.3644663951	-0.3502458269	1.8118853576
C	1.8653894809	0.5468095202	0.5401586623
H	2.2465692389	1.5567540126	0.6946696969
H	2.5302724383	-1.497684432	0.7848295127
O	0.9971336202	1.6046415548	2.8585281306
C	0.8510266128	0.5408718714	2.293404454
O	0.6050197751	-0.6481579731	2.6205931927
H	1.5841824156	0.4907024451	-0.5308289135
C	4.0765109695	-0.3916909398	-0.2119987786
C	5.0780372632	0.5739744565	-0.0766226515
C	4.1052333907	-1.2201931697	-1.3359048679
C	6.0770280413	0.7088312463	-1.0350265501
H	5.0697360709	1.2267636456	0.7935294083
C	5.102222863	-1.0903315905	-2.2991631615
H	3.3350237795	-1.9800867093	-1.4544840981
C	6.0926536389	-0.1237485675	-2.1518693525
H	6.8481990987	1.46388355	-0.9090236146
H	5.1078420106	-1.74887555	-3.163609322
H	6.8732770712	-0.021871729	-2.9002397726

Energy = -2656.894582
Zero-point correction = 0.392162 (Hartree/Particle)
Thermal correction to Gibbs Free Energy = 0.335488
Sum of electronic and zero-point Energies = -2656.502420
Sum of electronic and thermal Energies = -2656.477882
Sum of electronic and thermal Enthalpies = -2656.476937
Sum of electronic and thermal Free Energies = -2656.559094
G + ZVPE = -2656.166932
Energy (DMF-6-31G(d)) = -2656.933771
Energy (DMF-def2-TZVP) = -2468.8138551



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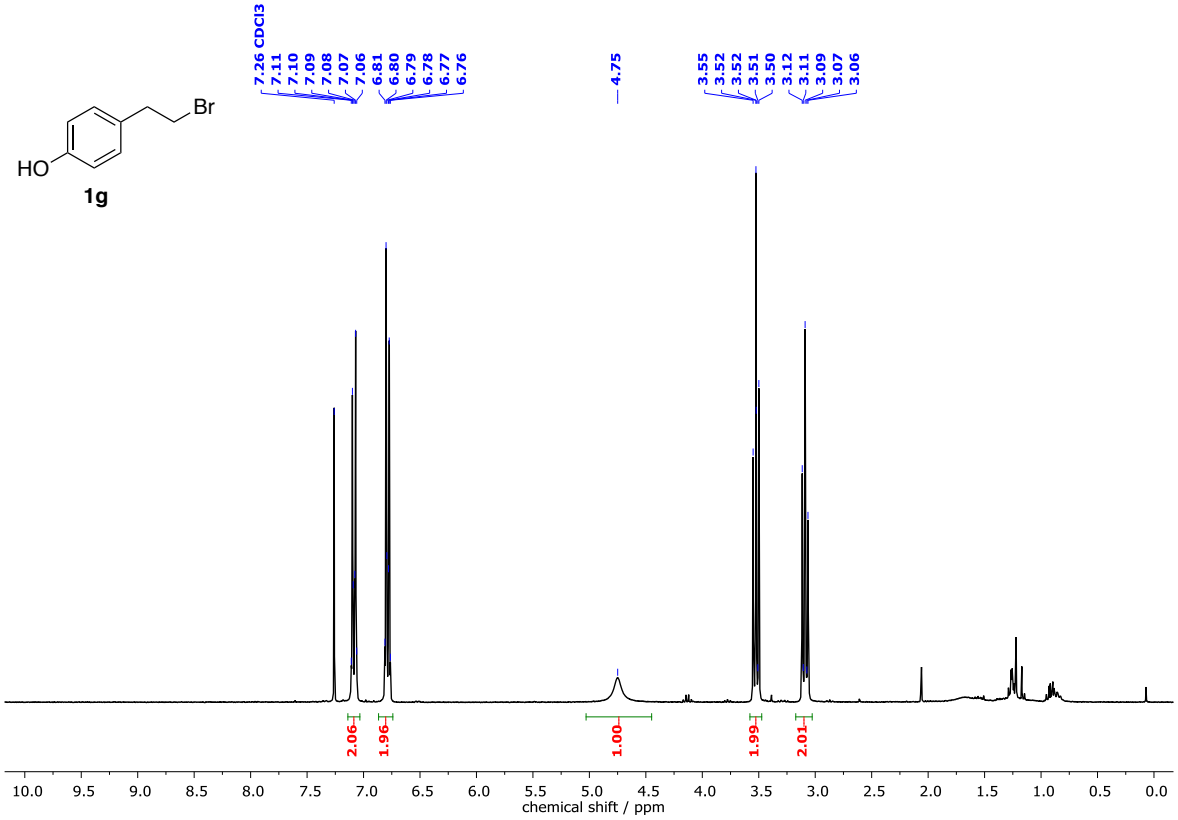
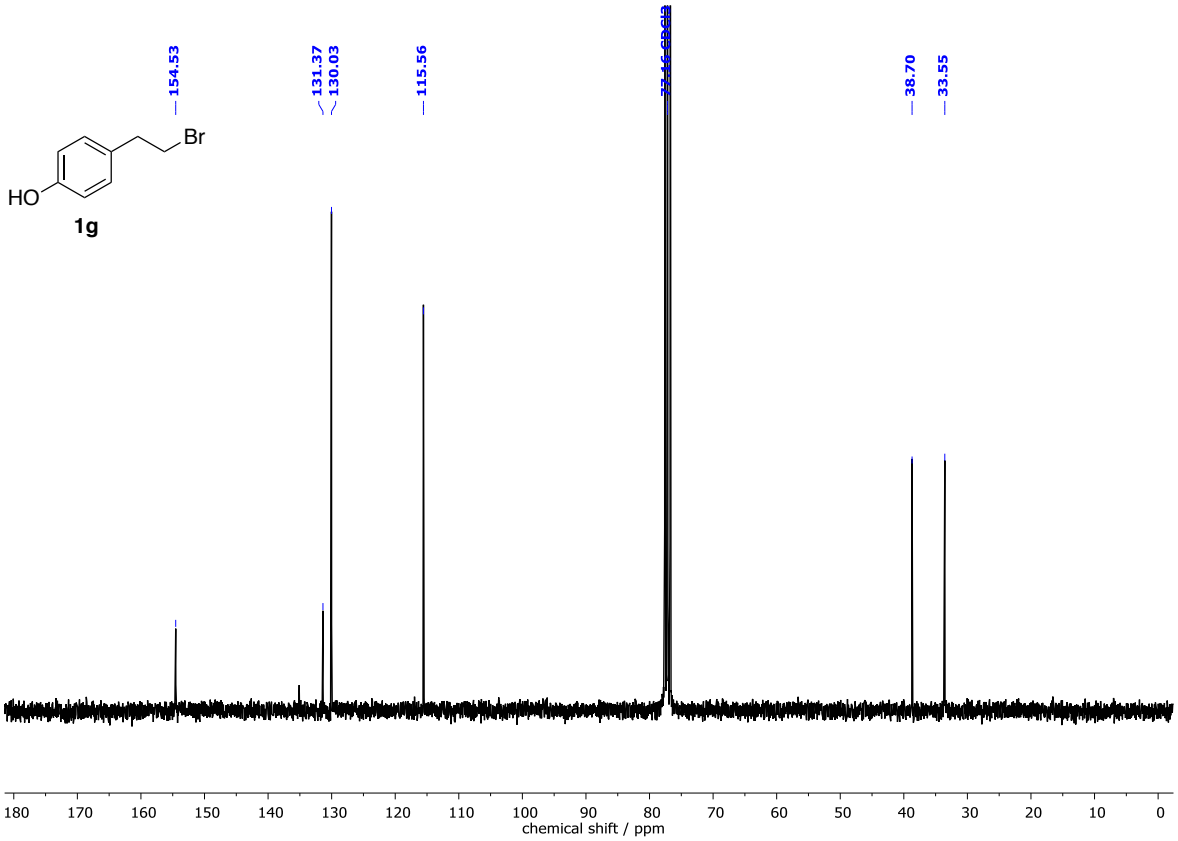
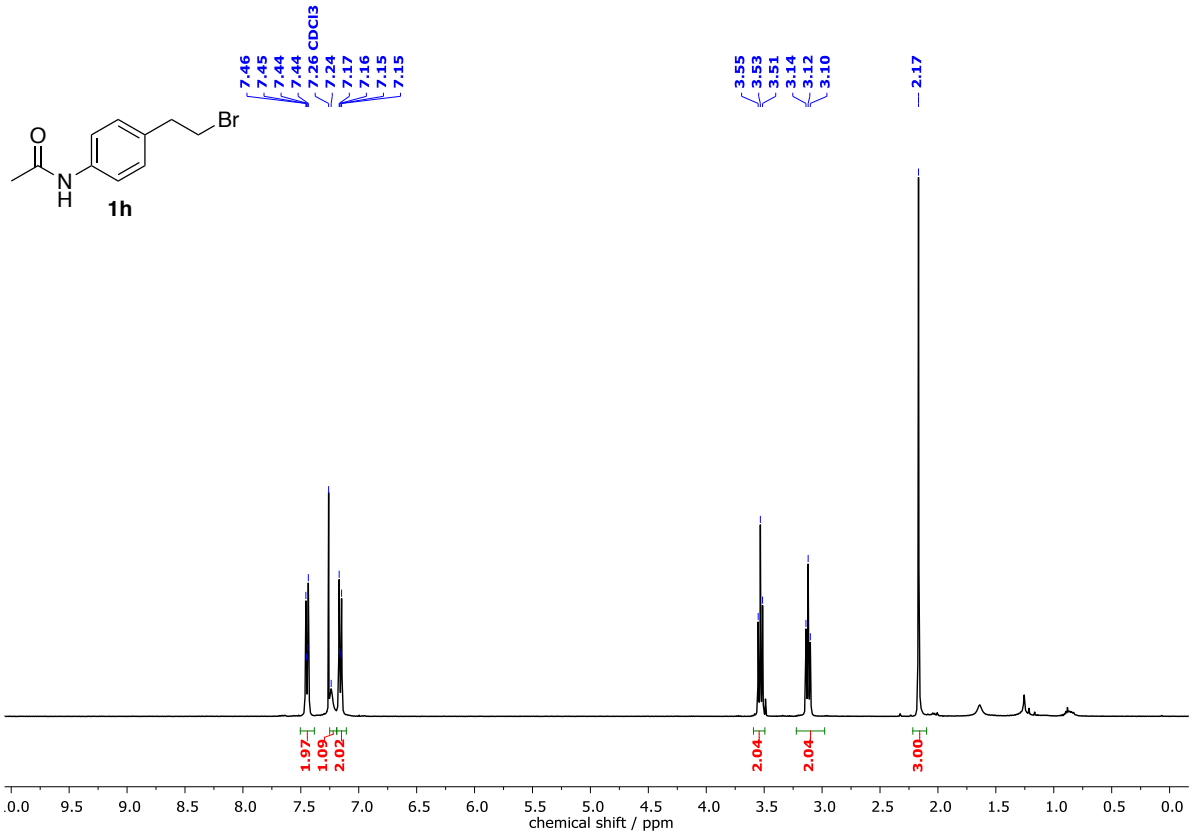
11 NMR Spectra



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7.44
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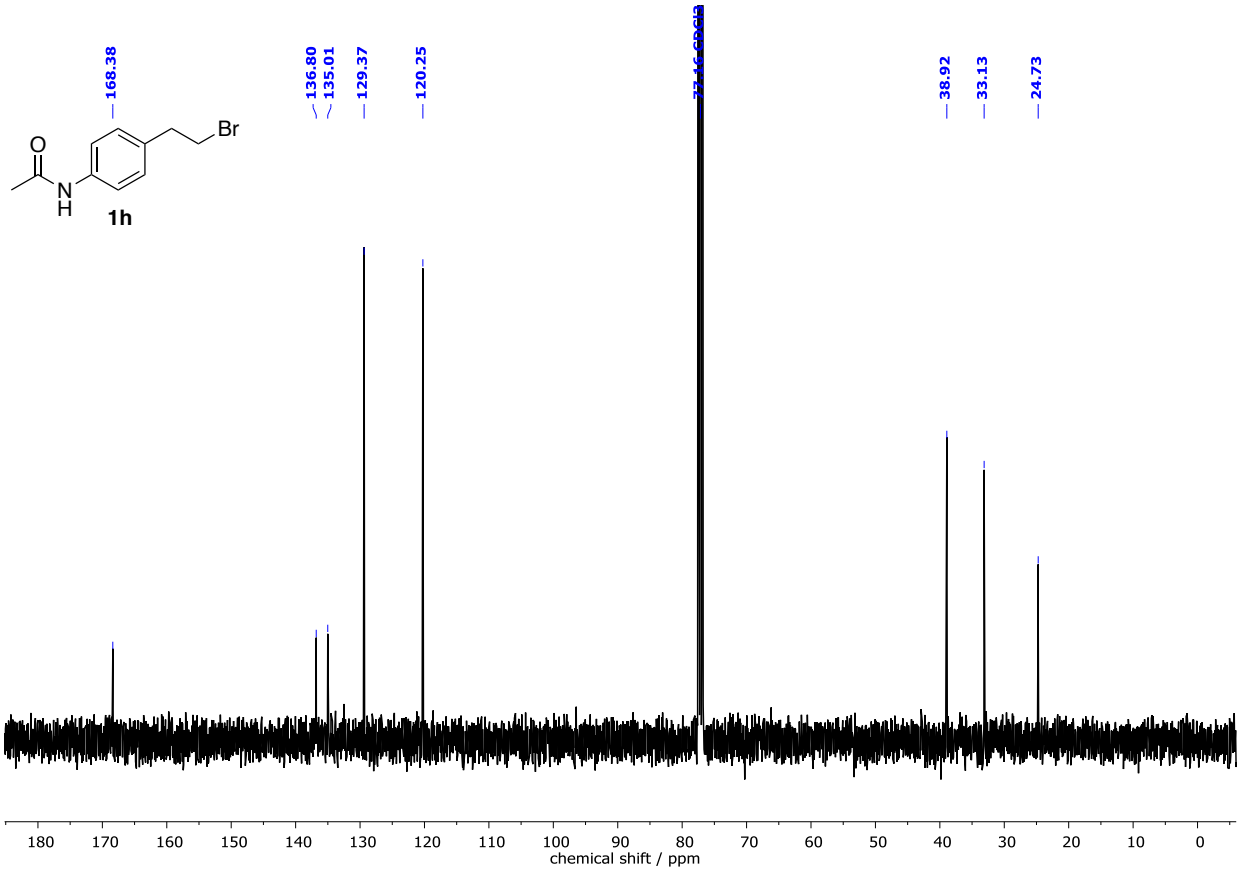
7.24
7.17
7.16
7.15
7.15
3.55
3.53
3.51
3.14
3.12
3.10
2.17
O
N
H
Br
1h
1.97
1.09
2.02
2.04
2.04
3.00
chemical shift / ppm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136.80
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Br
O
N
H
1h
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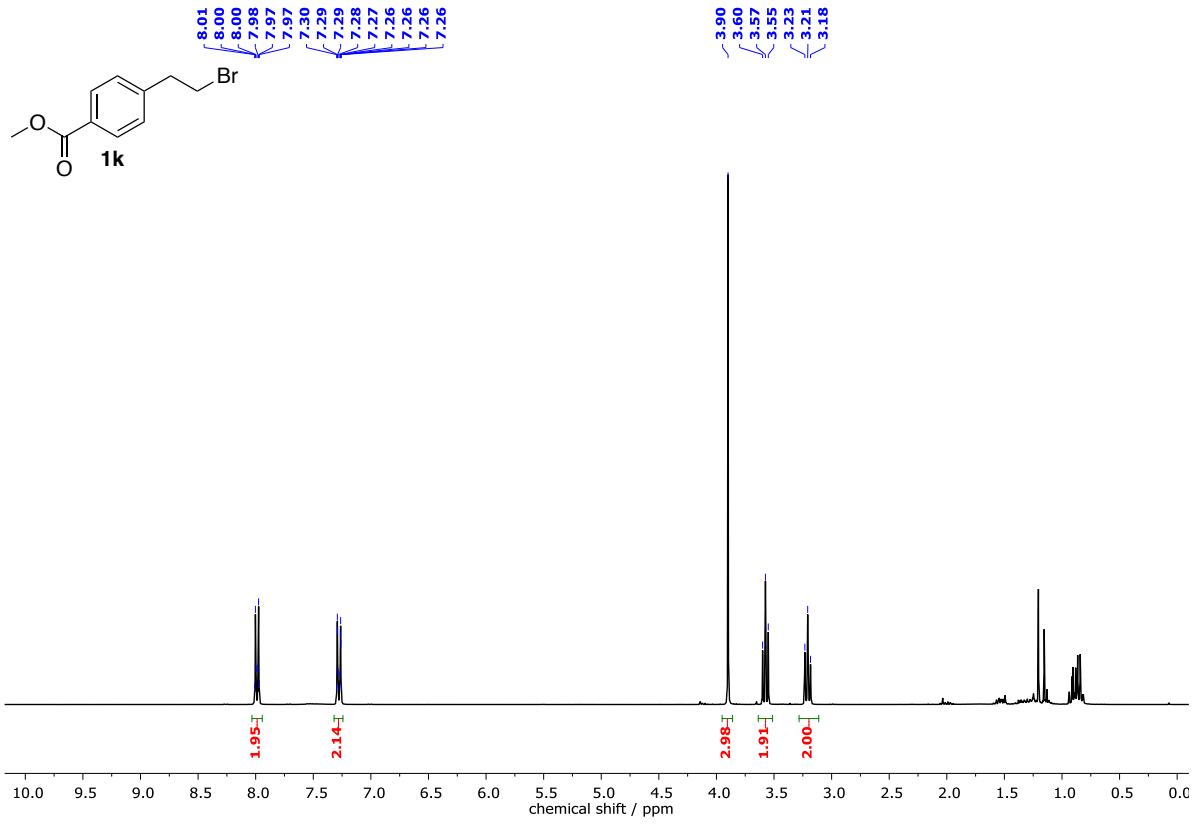
chemical shift / ppm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8.00
8.00
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7.97
7.97
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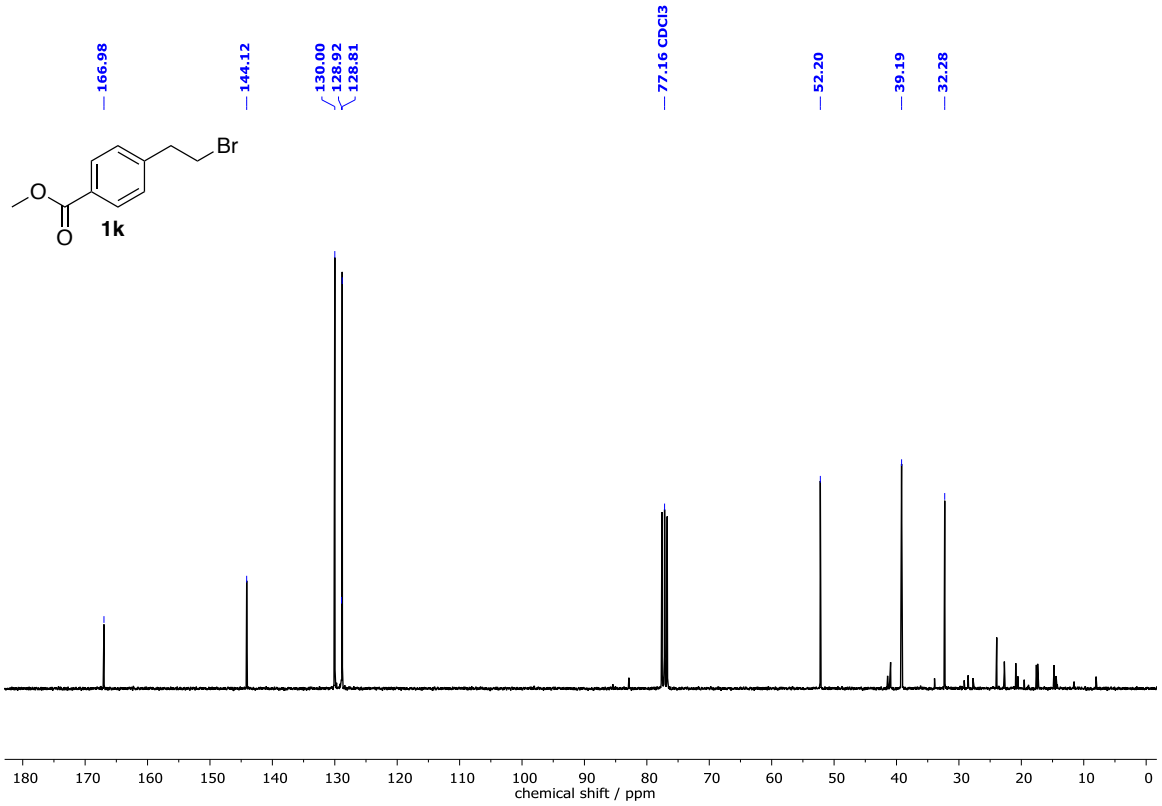
7.29
7.28
7.27
7.26
7.26
7.26
7.26
3.90
3.60
3.57
3.55
3.23
3.21
3.18
Br
O
O
1k
1.95
2.14
2.98
1.91
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
chemical shift / ppm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130.00
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128.81
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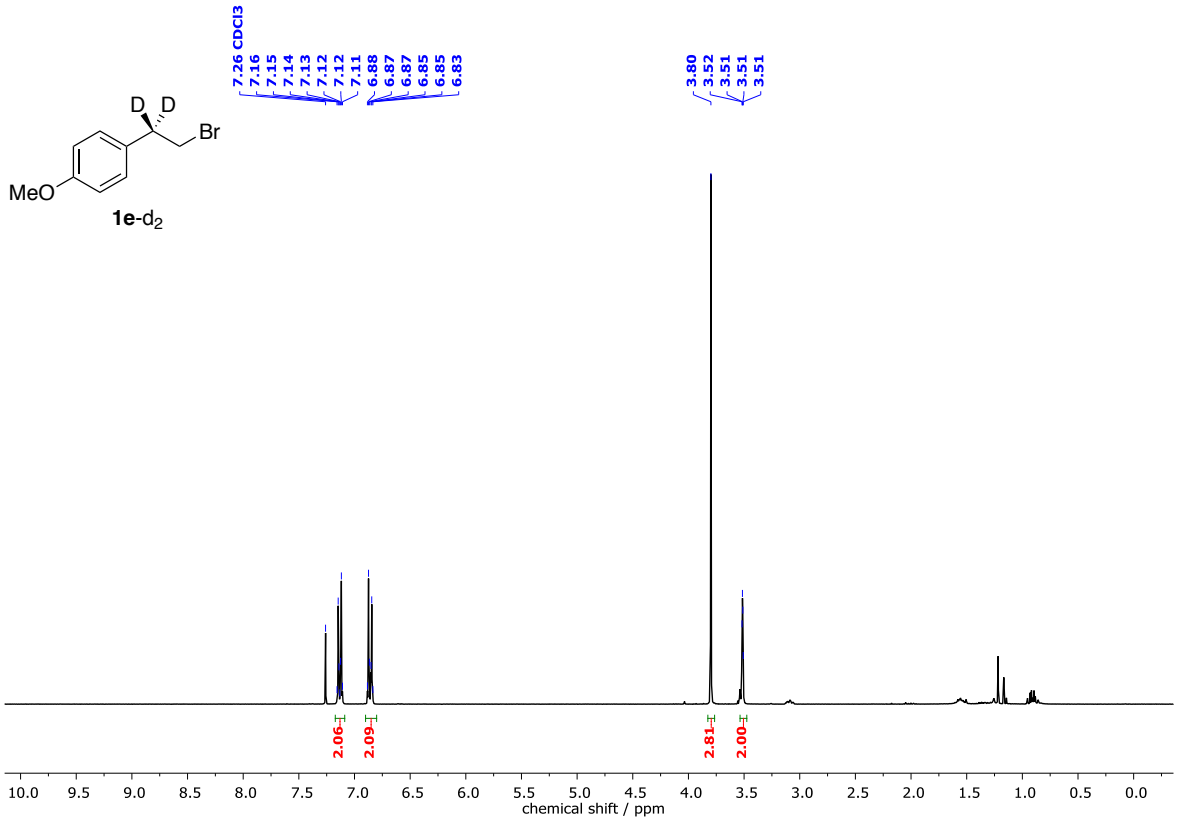
Br
O
O
1k
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift / ppm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7.16
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7.12
7.12
7.11
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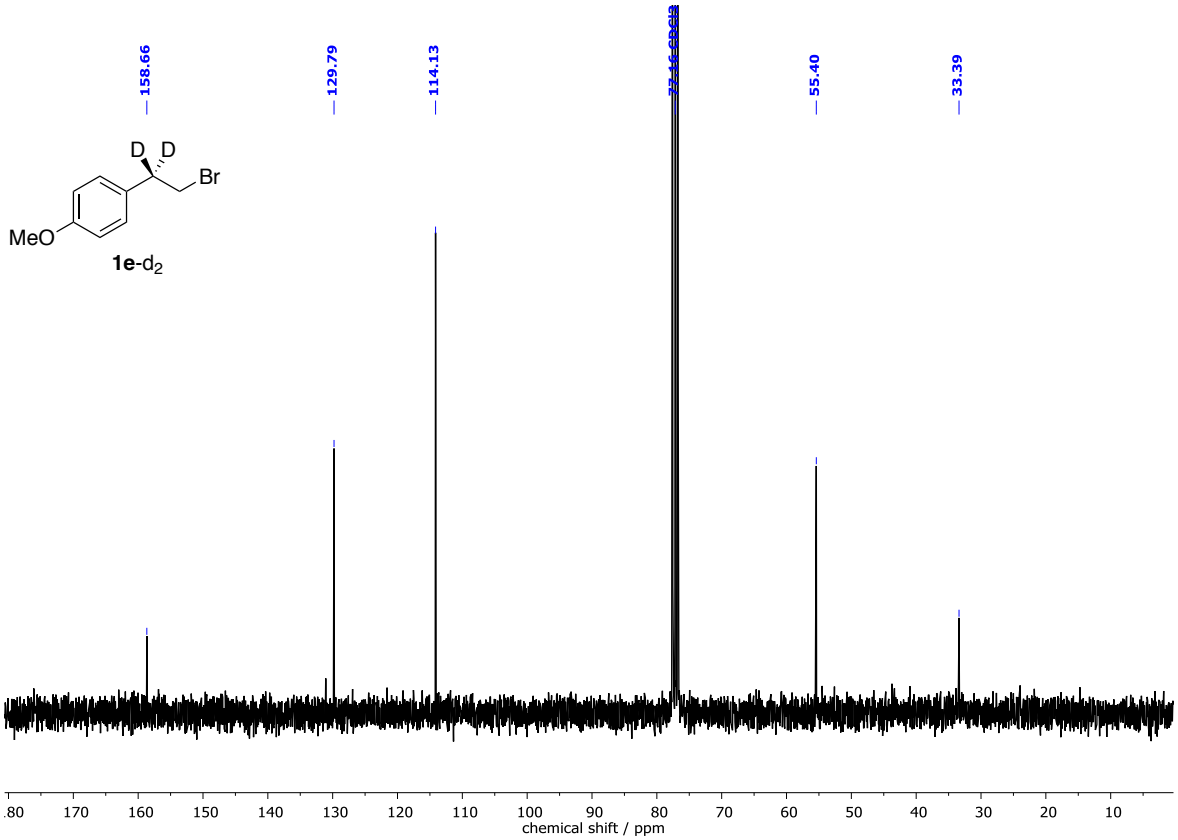
6.87
6.87
6.85
6.85
6.83
3.80
3.52
3.51
3.51
3.51
D
D
Br
MeO
1e-d2
2.06
2.09
2.81
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
chemical shift / ppm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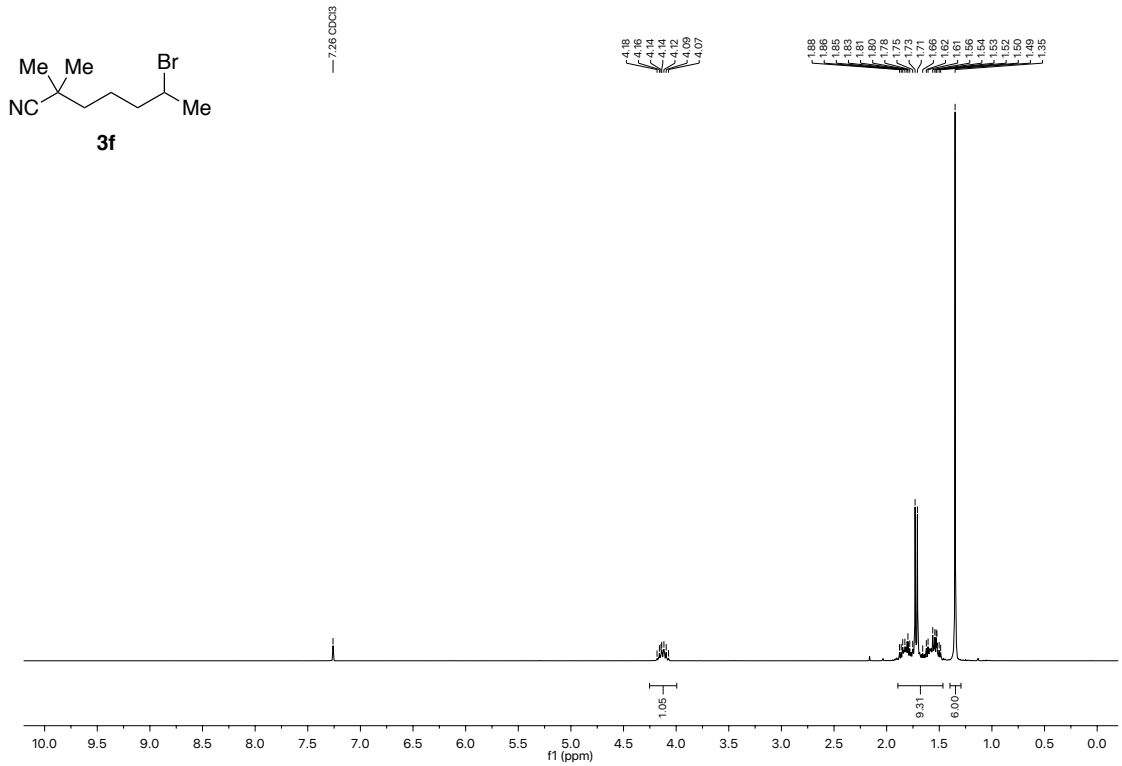
55.40
33.39
D D
Br
MeO
1e-d2
chemical shift / ppm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Br
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4.14
4.14
4.12
4.09
4.07
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1.86
1.85
1.83
1.81
1.80
1.78
1.75
1.73
1.71
1.66
1.62
1.61
1.56
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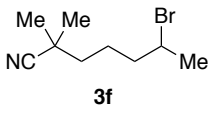
1.53
1.52
1.50
1.49
1.35
1.05
9.31
6.00
f1 (ppm)


Me
Me
Br
NC
Me

3f

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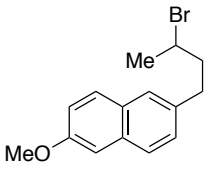
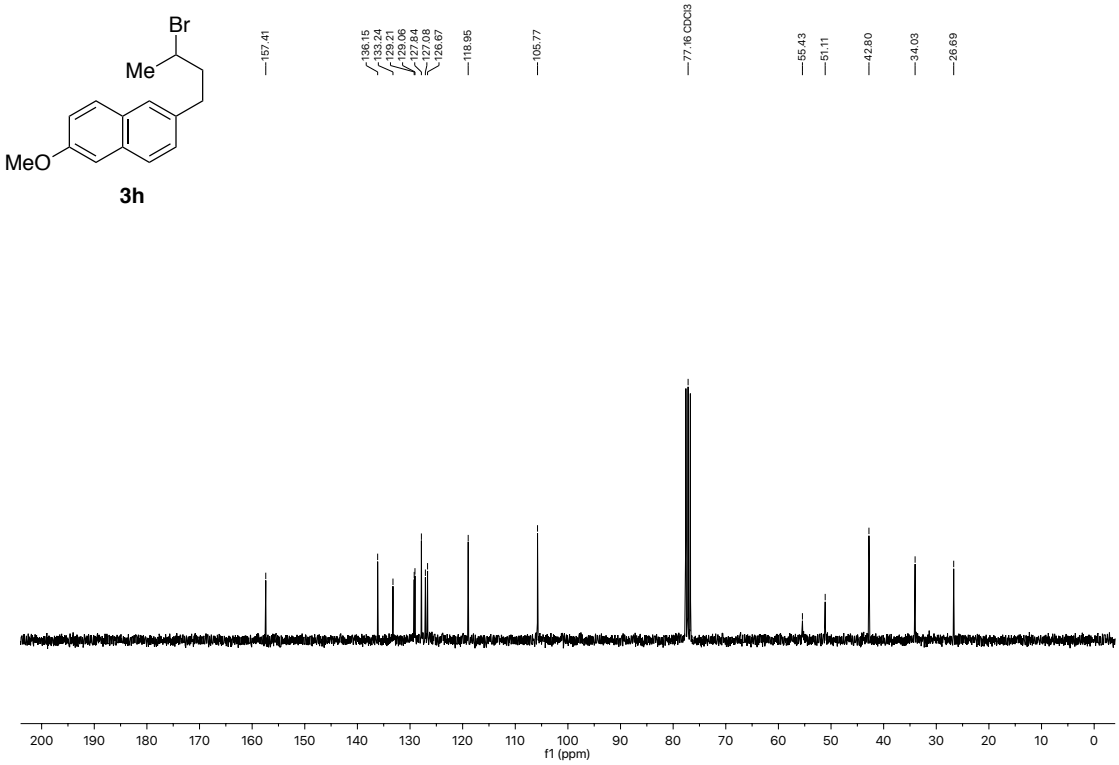
77.16 CDCl3
50.90
40.90
40.39
32.42
26.76
26.74
26.57
23.72
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Br
Me
MeO

3h

7.70
7.67
7.58
7.33
7.32
7.30
7.29
7.28 CDCl3
7.16
7.15
7.12
4.16
4.14
4.12
4.11
4.10
4.09
4.08
4.05
3.92
3.05
3.03
3.02
3.00
2.98
2.97
2.95
2.93
2.90
2.88
2.86
2.83
2.28
2.26
2.25
2.23
2.21
2.20
2.18
2.17
2.16
2.15
2.15
2.13
2.12
2.11
2.08
2.07
2.06
1.76
1.74
2.00
1.00
1.00
1.99
1.04
3.00
2.03
2.02
2.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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Me
MeO
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129.06
127.84
127.08
126.67
118.96
105.77
77.16 CDCl3
55.43
51.11
42.80
34.03
26.69
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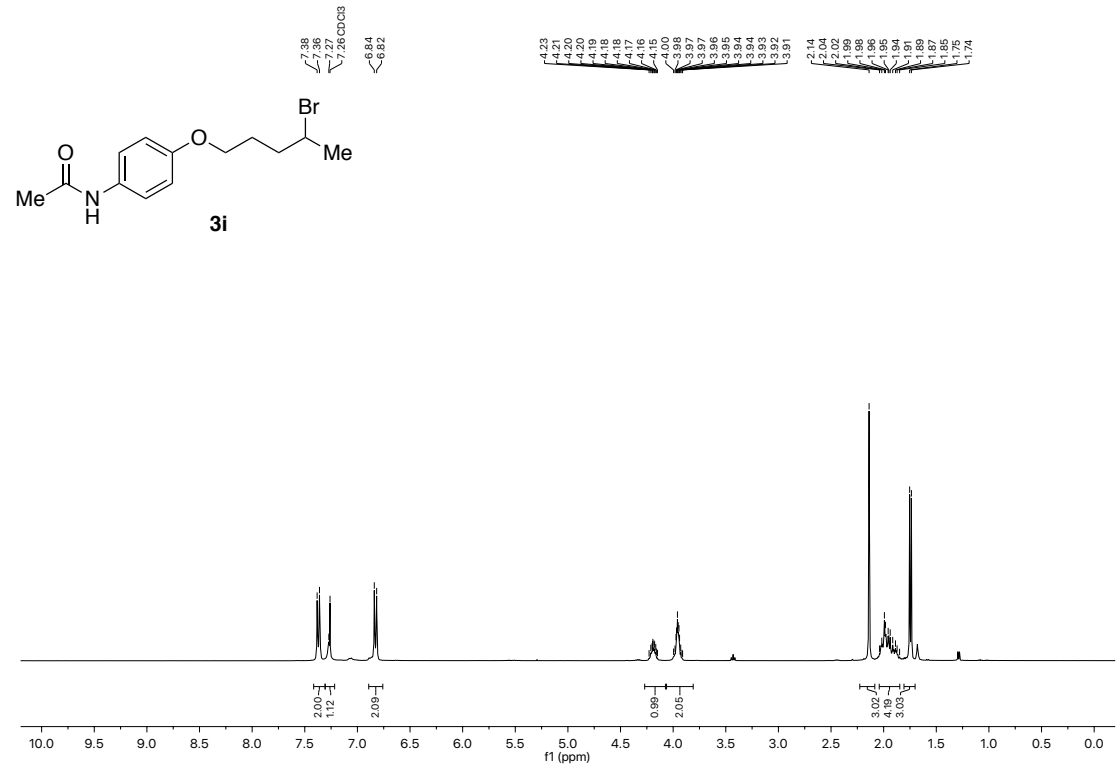
f1 (ppm)

3h


7.38
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7.26 CDCl3
6.84
6.82
4.23
4.21
4.20
4.20
4.19
4.18
4.18
4.17
4.16
4.15
4.00
3.98
3.97
3.97
3.96
3.95
3.94
3.94
3.93
3.92
3.91
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2.02
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1.98
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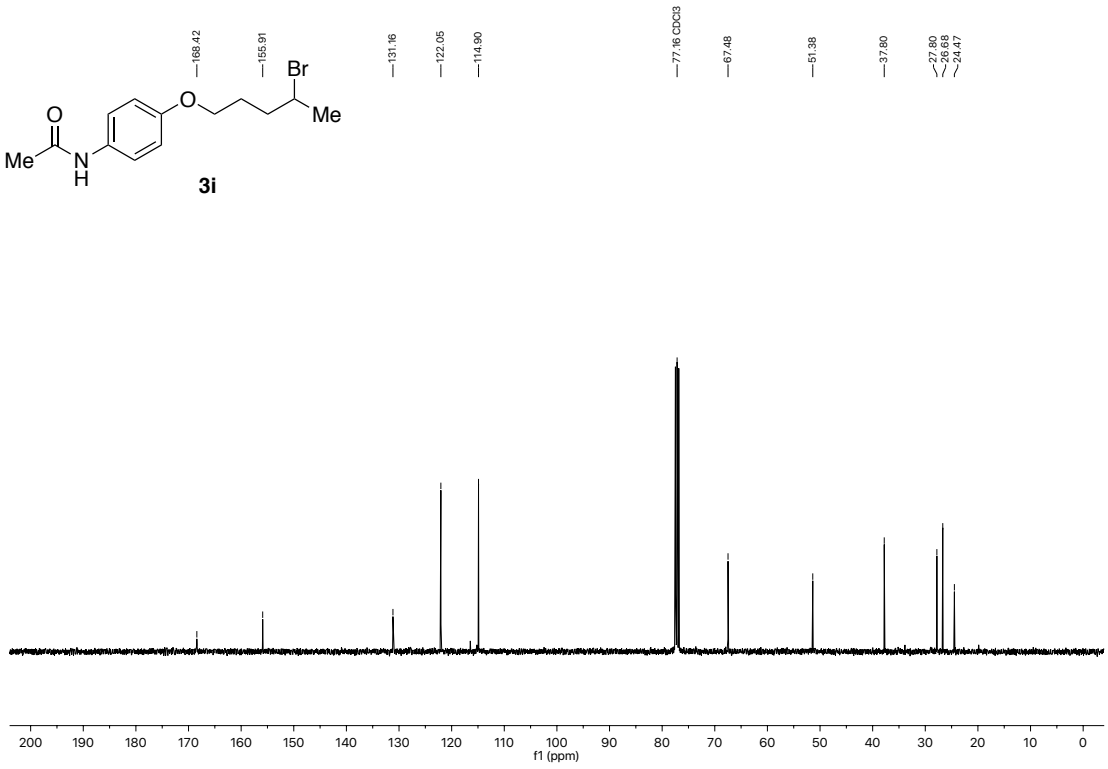
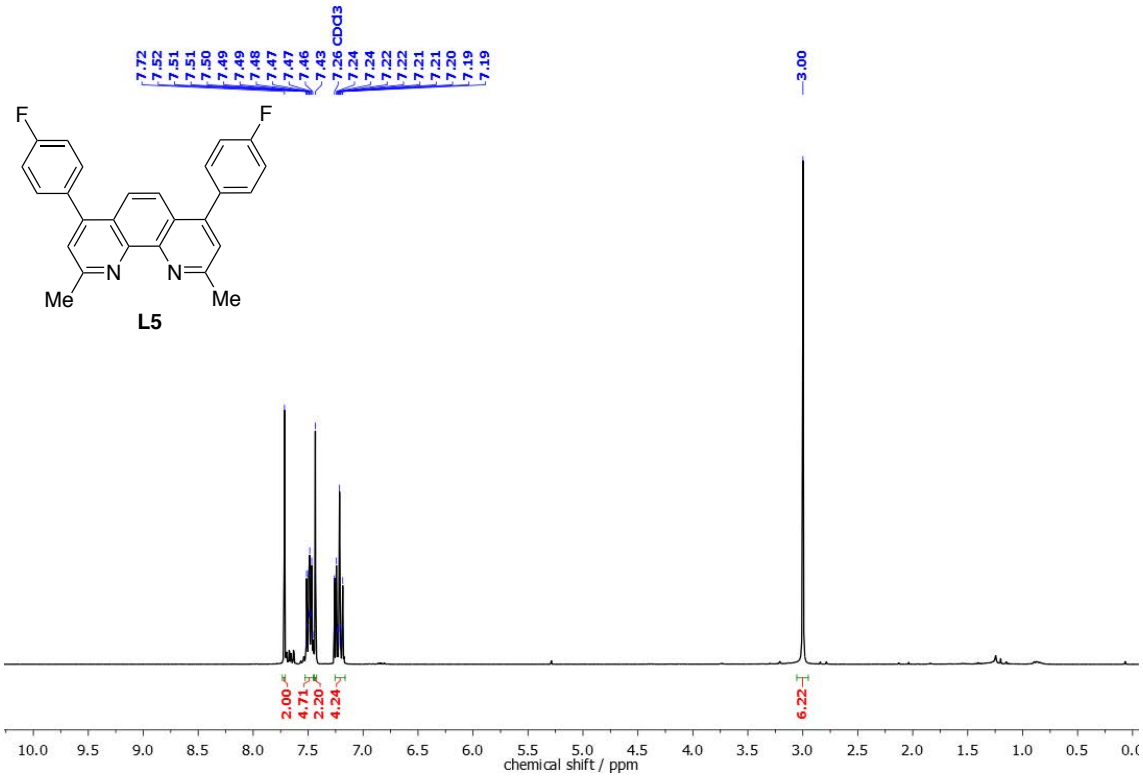
1.89
1.87
1.85
1.75
1.74
Br
O
Me
Me
N
H
2.00
1.12
2.09
0.99
2.05
3.02
4.19
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3i

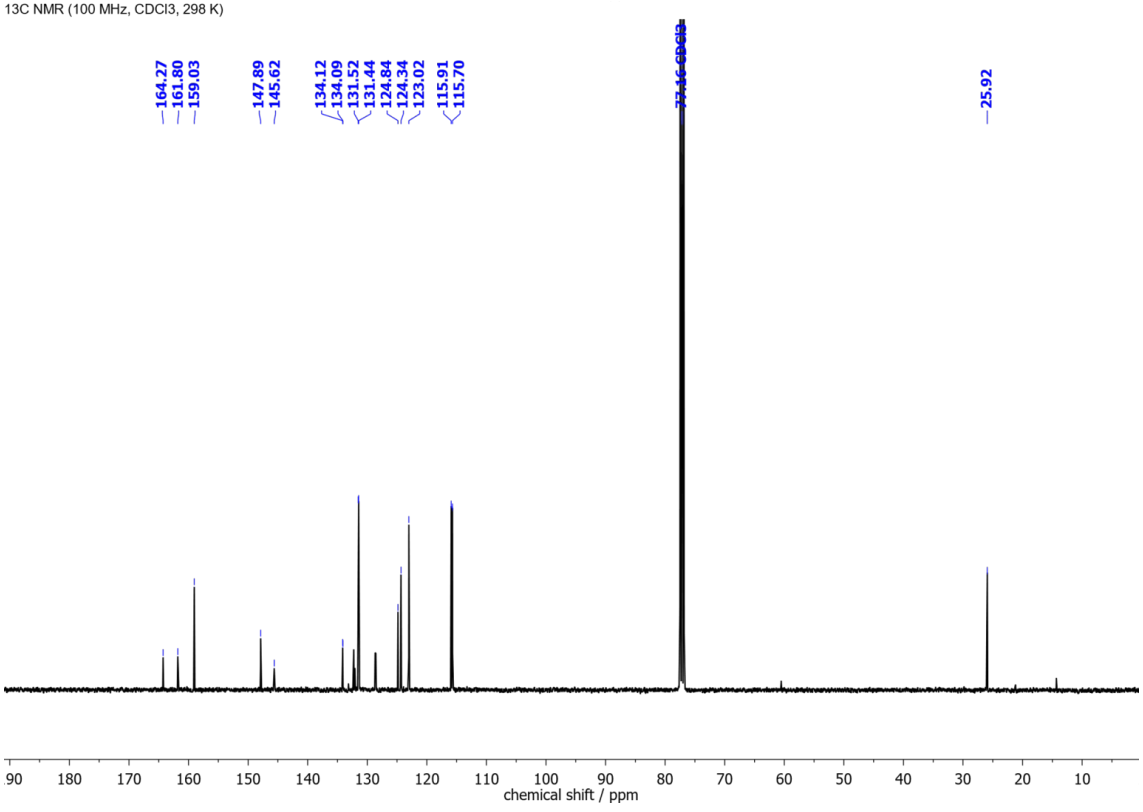

168.42
155.91
131.16
122.05
114.90
77.16 CDCl3
67.48
51.38
37.80
27.80
26.68
24.47
Br
Me
O
O
Me
N
H
3i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

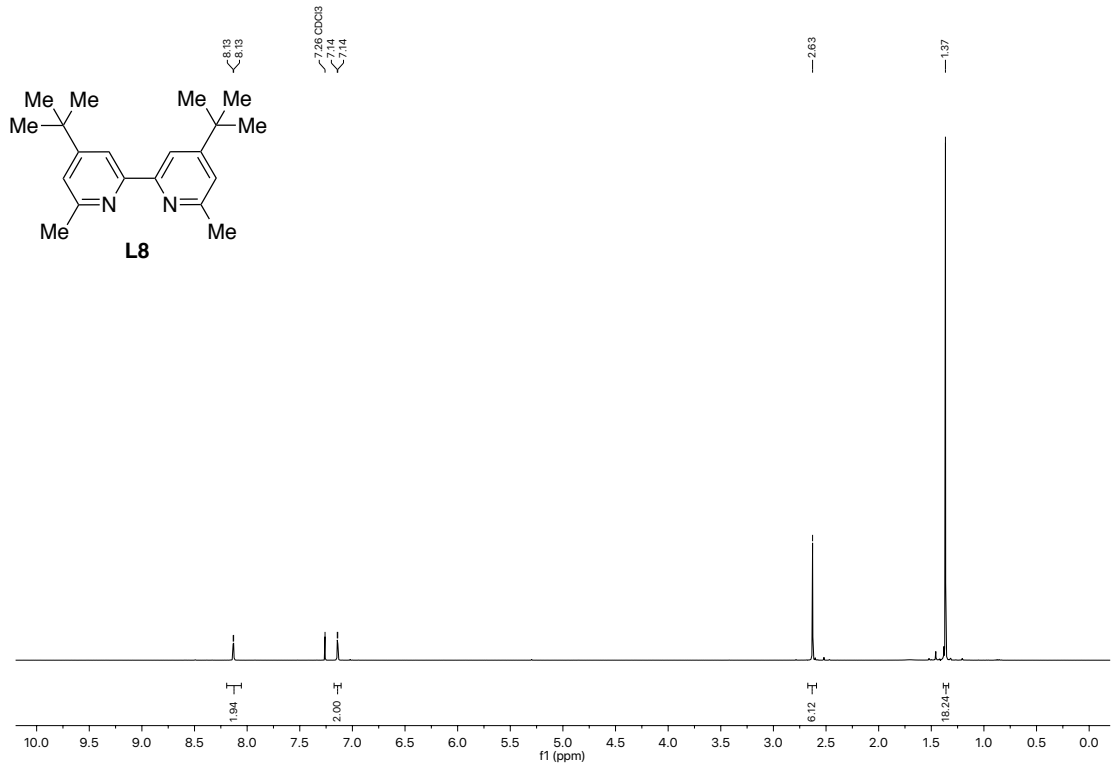
1H NMR (300 MHz, CDCl3, 294 K)

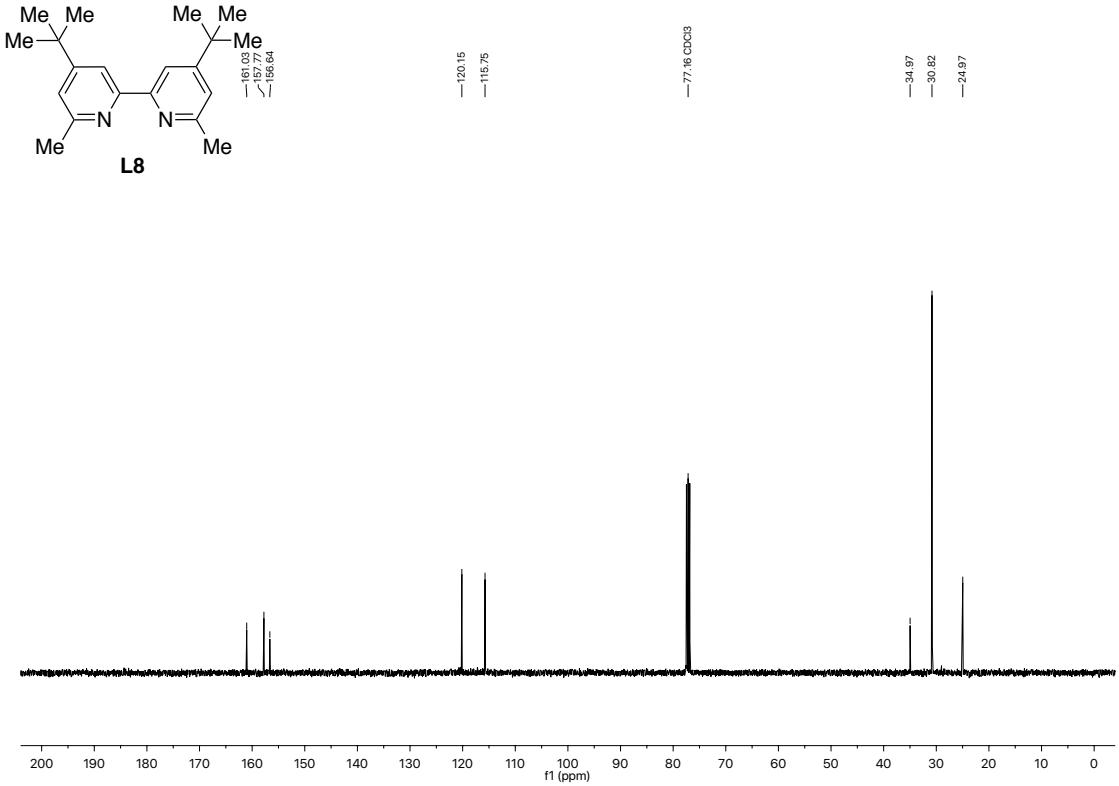


L5

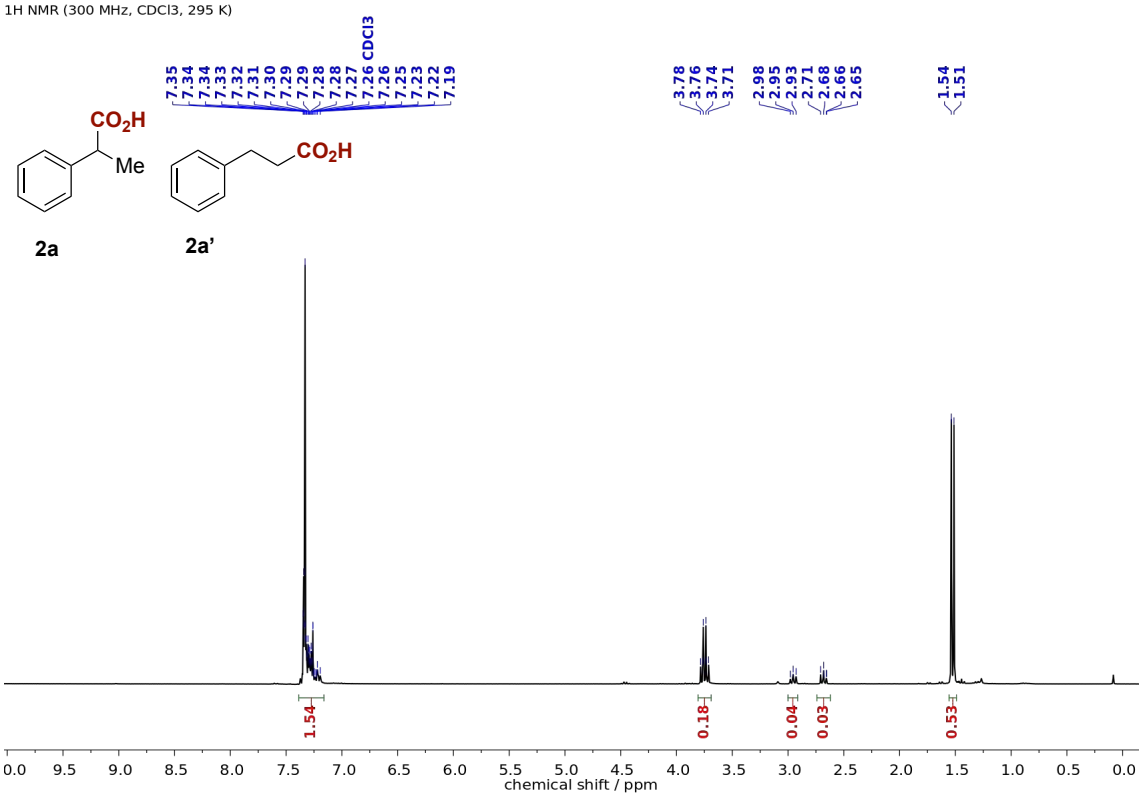
13C NMR (100 MHz, CDCl3, 298 K)



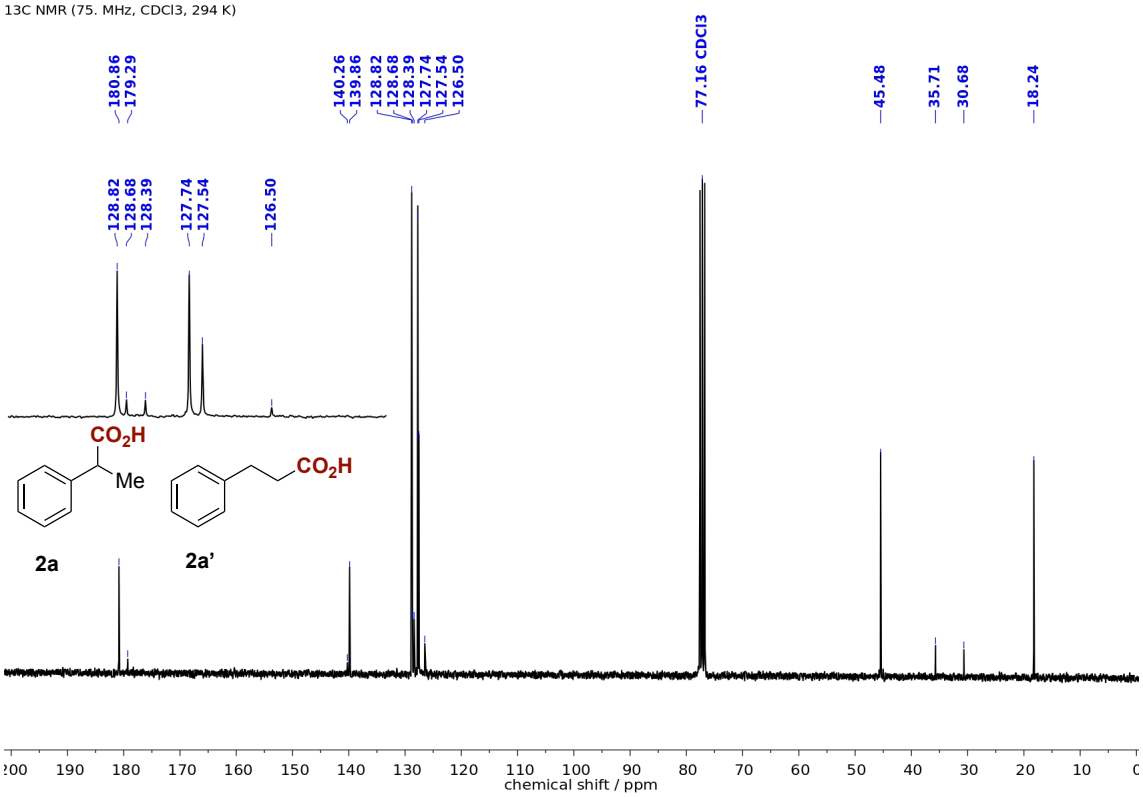

8.13
8.13
7.26 CDCl3
7.14
7.14
2.63
1.37
Me Me
Me
Me Me
Me
N
N
Me
Me
L8
1.94
2.00
6.12
18.24
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Me Me
Me
Me Me
Me
N
N
Me
Me
L8
161.03
157.77
156.64
120.15
115.75
77.16 CDCl3
34.97
30.82
24.97
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

1H NMR (300 MHz, CDCl3, 295 K)

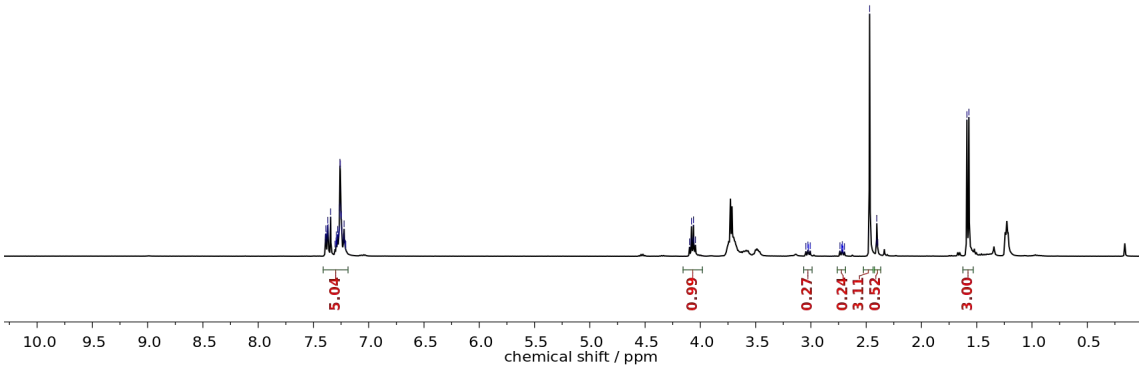


13C NMR (75. MHz, CDCl3, 294 K)

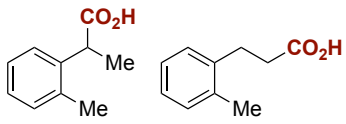


1H NMR (400 MHz, CDCl3, 298 K)

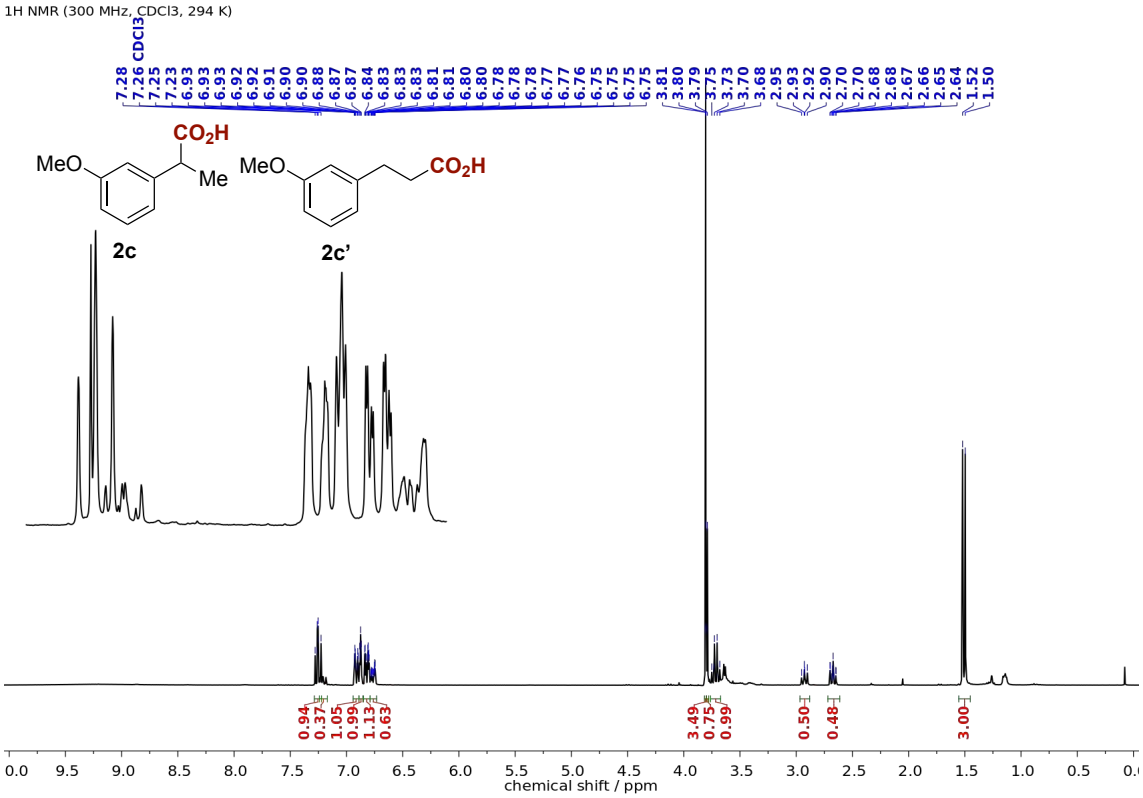
2b **2b'**

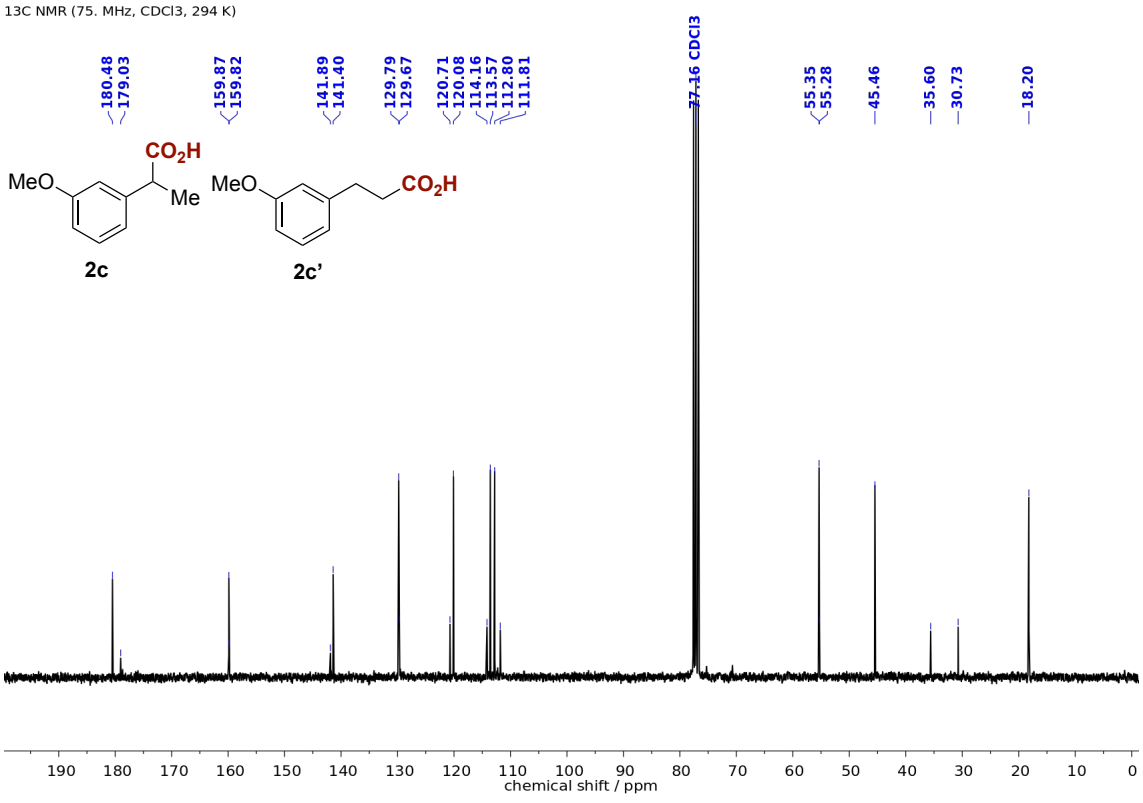


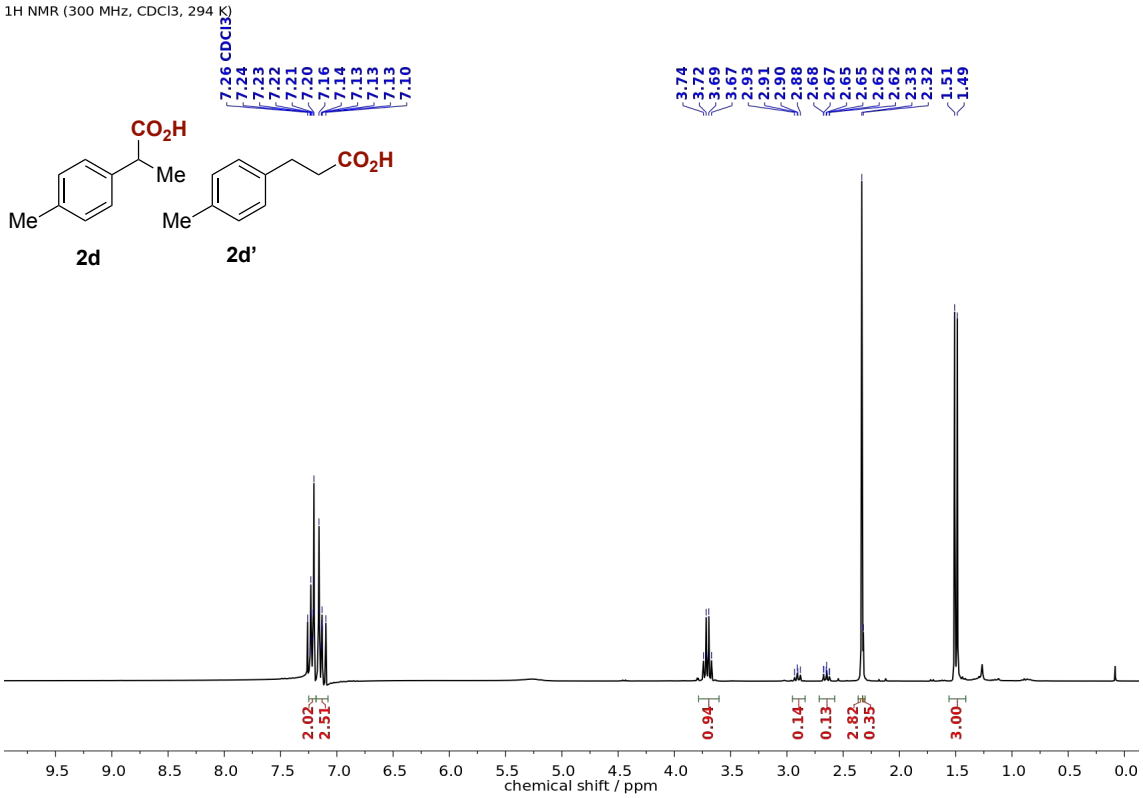
13C NMR (100 MHz, CDCl3, 298 K)

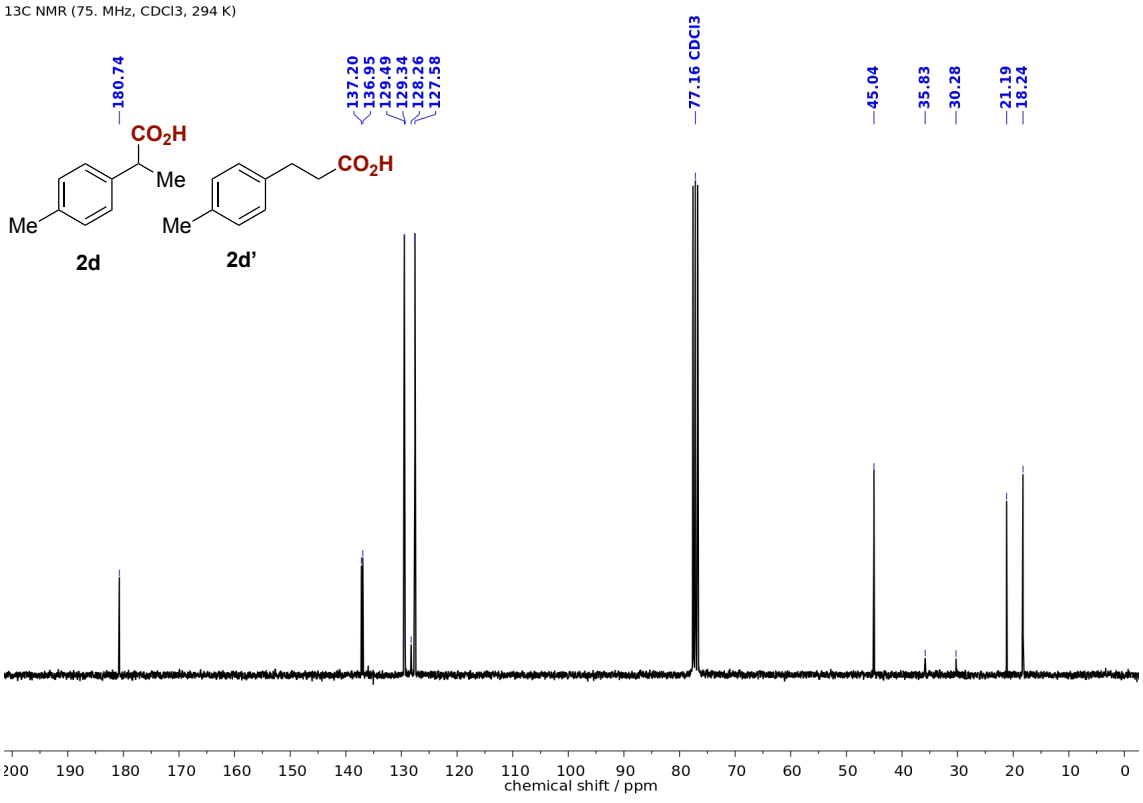


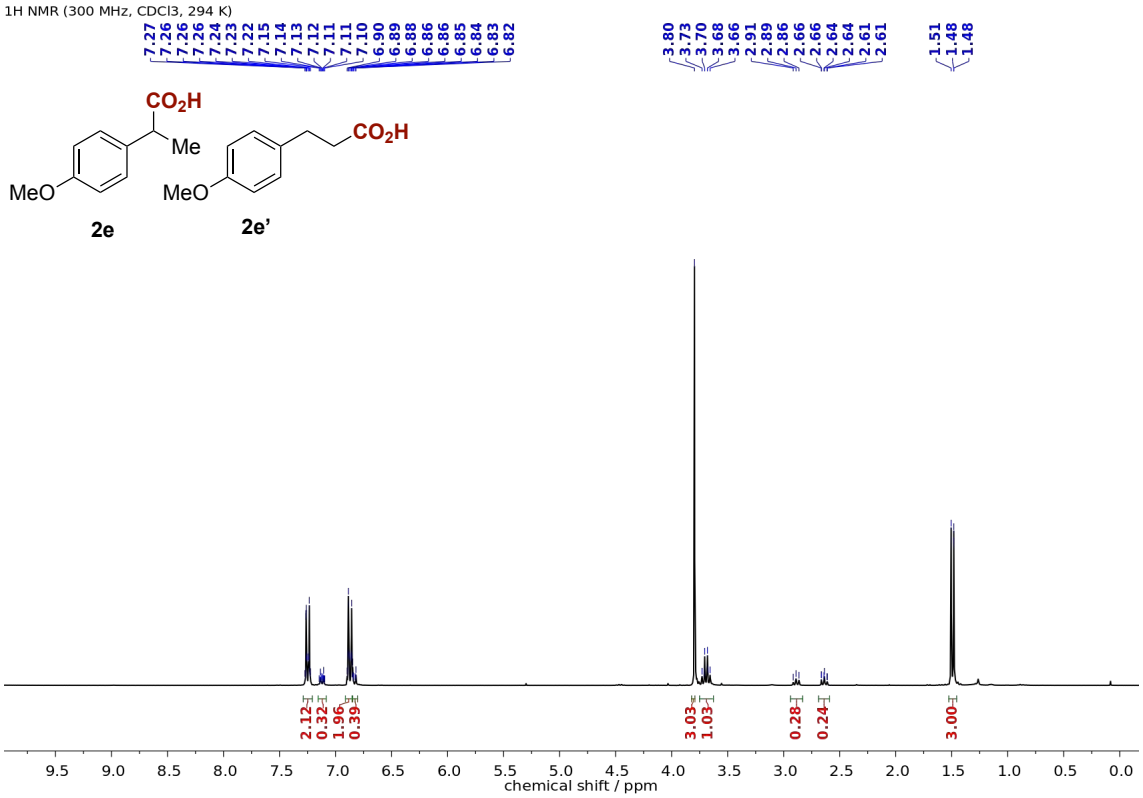
2b **2b'**

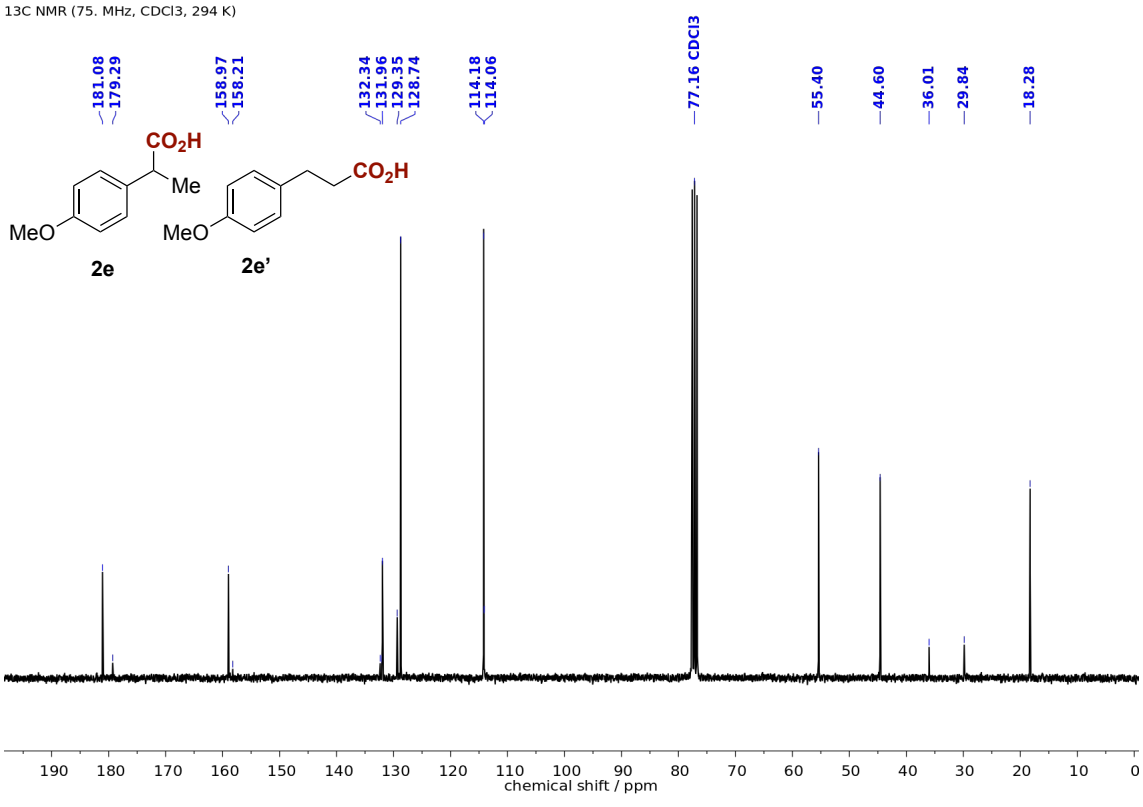

1H NMR (300 MHz, CDCl3, 294 K)
7.28 CDCl3
7.26
7.25
7.23
6.93
6.93
6.92
6.92
6.91
6.90
6.90
6.88
6.87
6.87
6.84
6.83
6.83
6.83
6.81
6.81
6.80
6.80
6.78
6.78
6.78
6.77
6.76
6.75
6.75
6.75
6.75
3.81
3.80
3.79
3.75
3.73
3.70
3.68
2.95
2.93
2.92
2.90
2.70
2.70
2.68
2.68
2.67
2.66
2.65
2.64
1.52
1.50
CO2H
MeO
Me
2c
MeO
CO2H
2c'
0.94
0.37
1.05
0.99
1.13
0.63
3.49
0.75
0.99
0.50
0.48
3.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
chemical shift / ppm

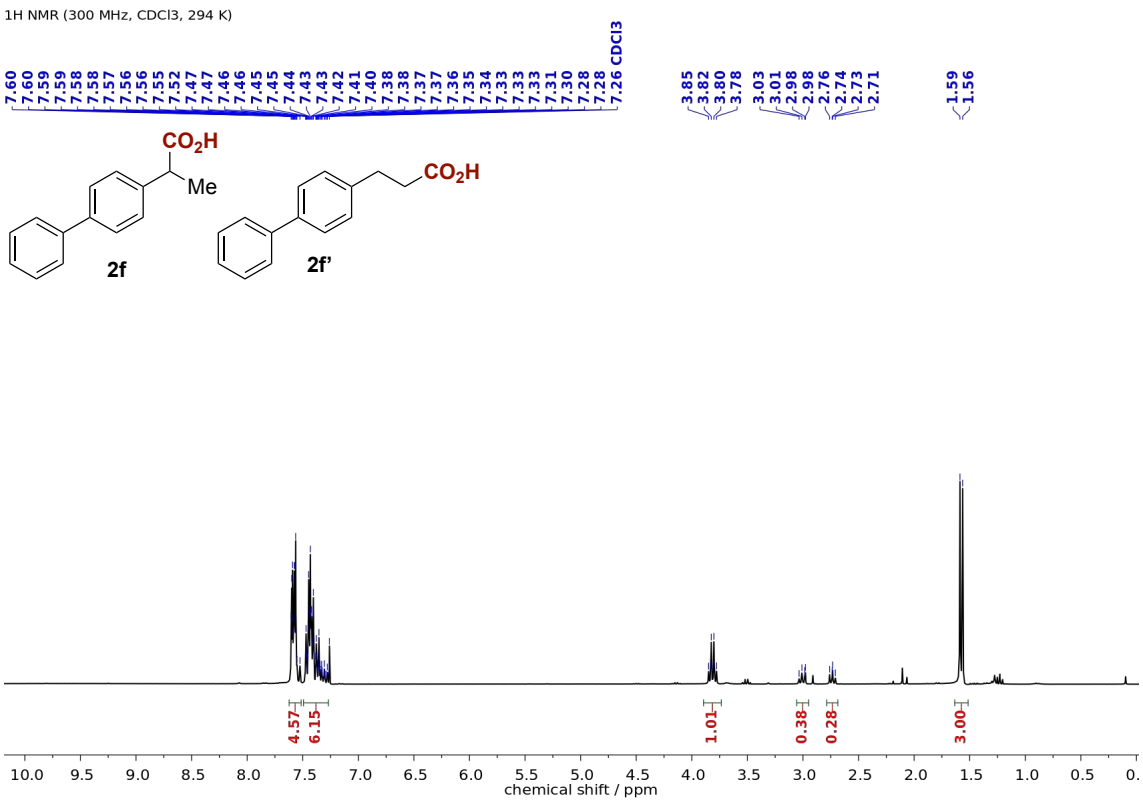

13C NMR (75. MHz, CDCl3, 294 K)
180.48
179.03
159.87
159.82
141.89
141.40
129.79
129.67
120.71
120.08
114.16
113.57
112.80
111.81
77.16 CDCl3
55.35
55.28
45.46
35.60
30.73
18.20
CO2H
MeO
Me
2c
MeO
CO2H
2c'
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift / ppm

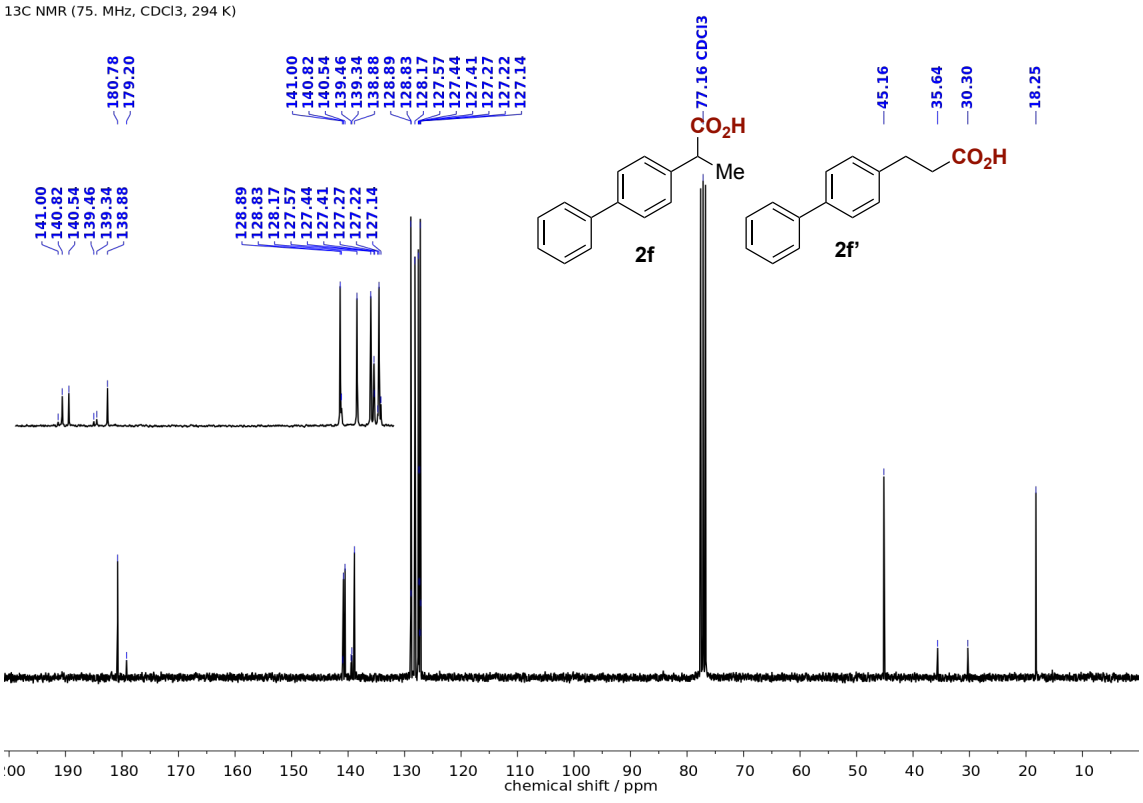

1H NMR (300 MHz, CDCl3, 294 K)
7.26 CDCl3
7.24
7.23
7.22
7.21
7.20
7.16
7.14
7.13
7.13
7.10
3.74
3.72
3.69
3.67
2.93
2.91
2.90
2.88
2.68
2.67
2.65
2.65
2.62
2.62
2.33
2.32
1.51
1.49
CO2H
Me
Me
2d
CO2H
Me
2d'
2.02
2.51
0.94
0.14
0.13
2.82
0.35
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
chemical shift / ppm

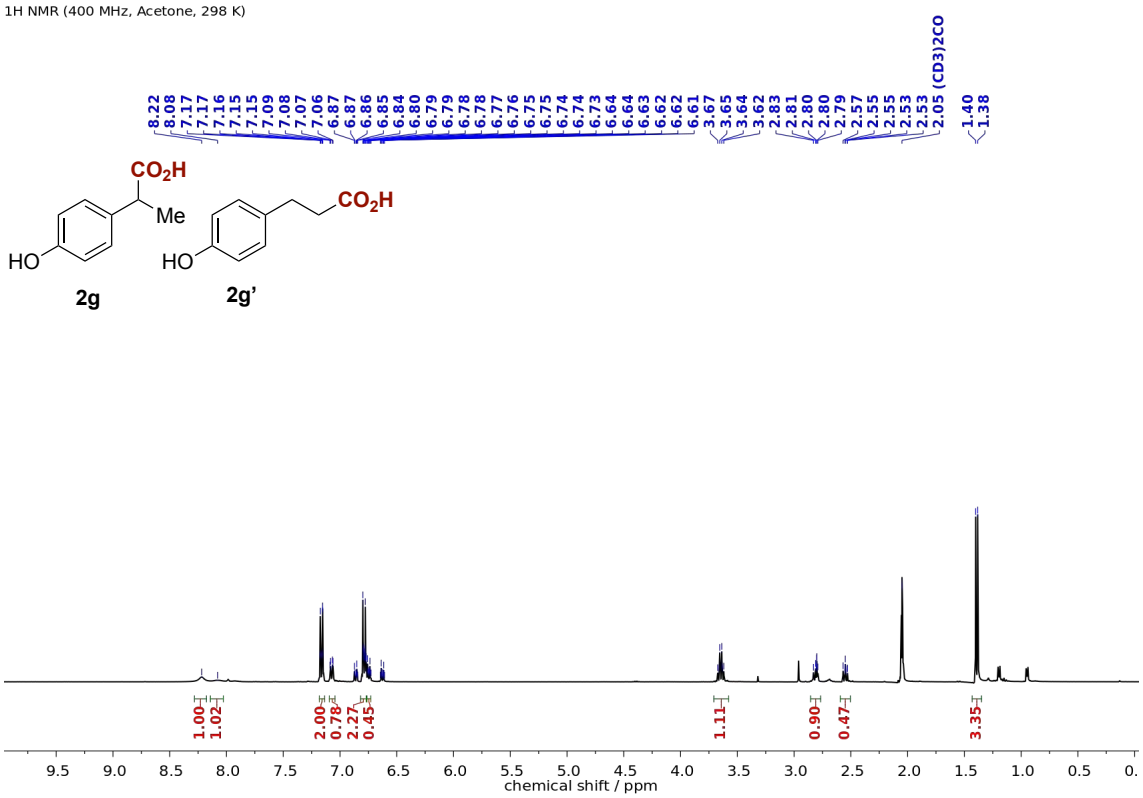

13C NMR (75. MHz, CDCl3, 294 K)
180.74
137.20
136.95
129.49
129.34
128.26
127.58
77.16 CDCl3
45.04
35.83
30.28
21.19
18.24
CO2H
Me
Me
2d
CO2H
Me
2d'
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift / ppm

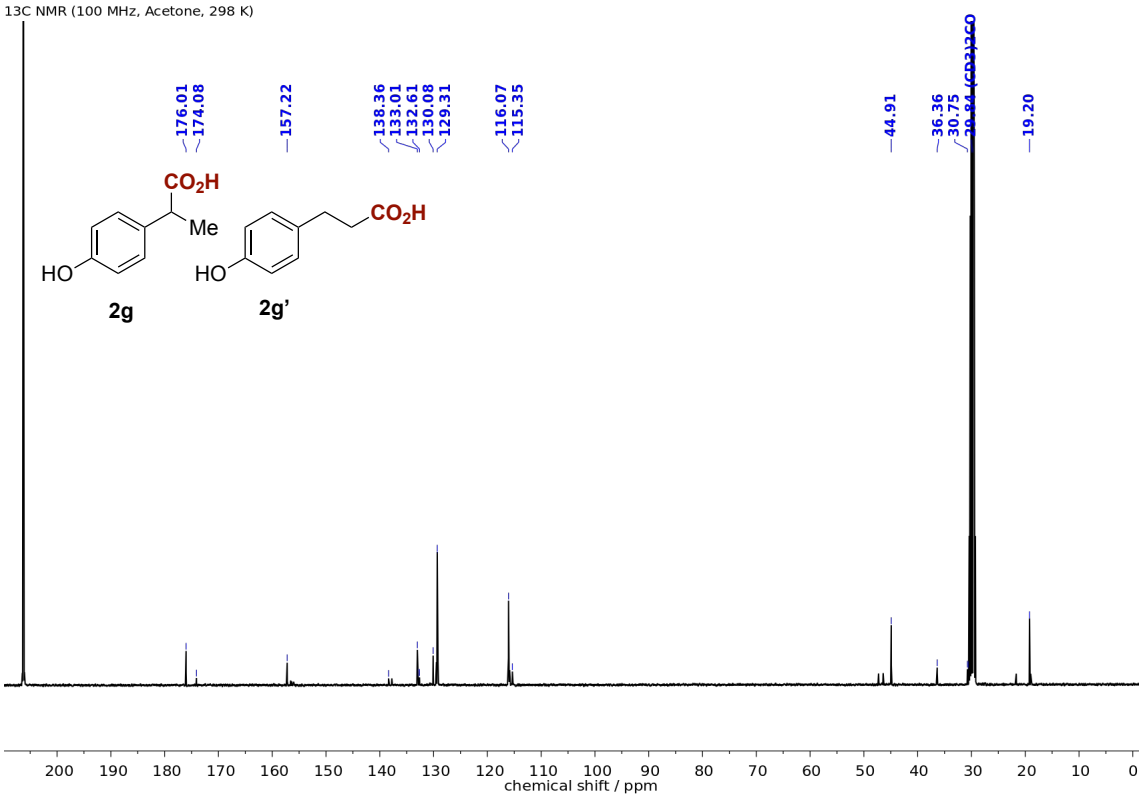

1H NMR (300 MHz, CDCl3, 294 K)
7.27 7.26 7.26 7.26 7.24 7.23 7.22 7.15 7.14 7.13 7.12 7.11 7.11 7.10 6.90 6.89 6.88 6.86 6.86 6.85 6.84 6.83 6.82
3.80 3.73 3.70 3.68 3.66 2.91 2.89 2.86 2.66 2.66 2.64 2.64 2.61 2.61
1.51 1.48 1.48
CO2H
Me
MeO
2e
CO2H
MeO
2e'
2.12 0.32 1.96 0.39
3.03 1.03
0.28 0.24
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
chemical shift / ppm

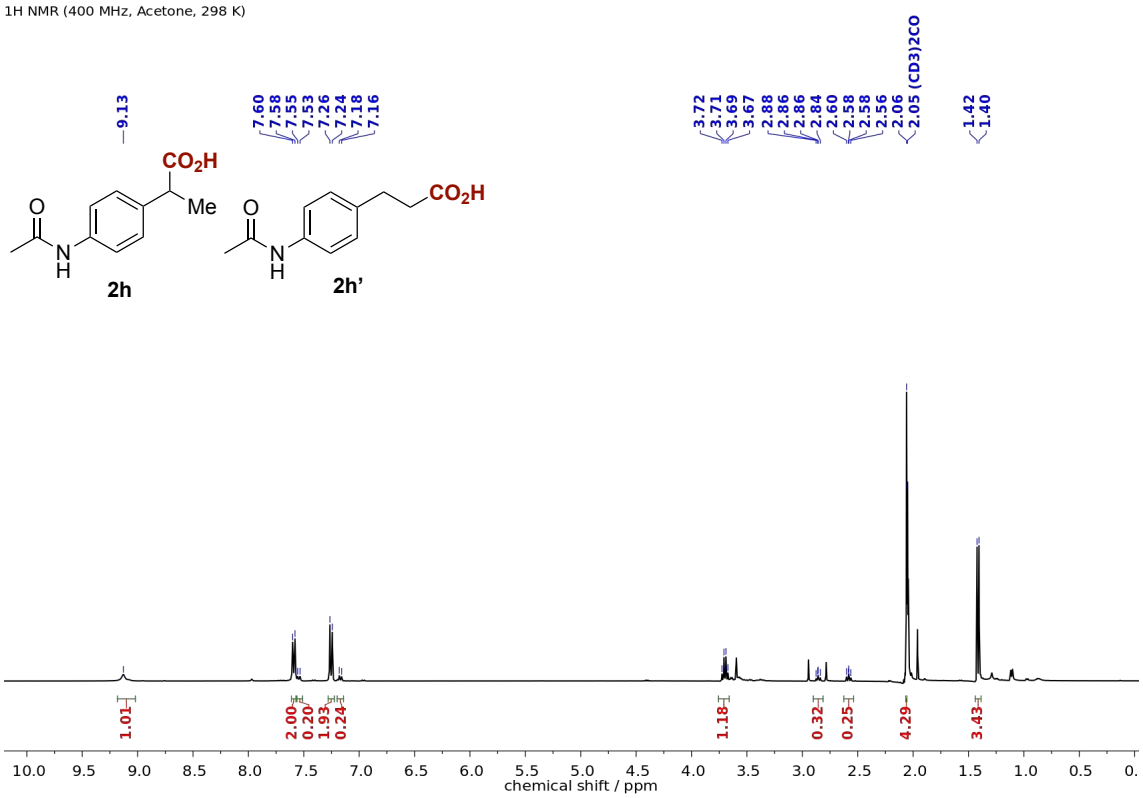

13C NMR (75. MHz, CDCl3, 294 K)
181.08 179.29
158.97 158.21
132.34 131.96 129.35 128.74
114.18 114.06
77.16 CDCl3
55.40
44.60
36.01
29.84
18.28
CO2H
Me
MeO
2e
CO2H
MeO
2e'
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift / ppm

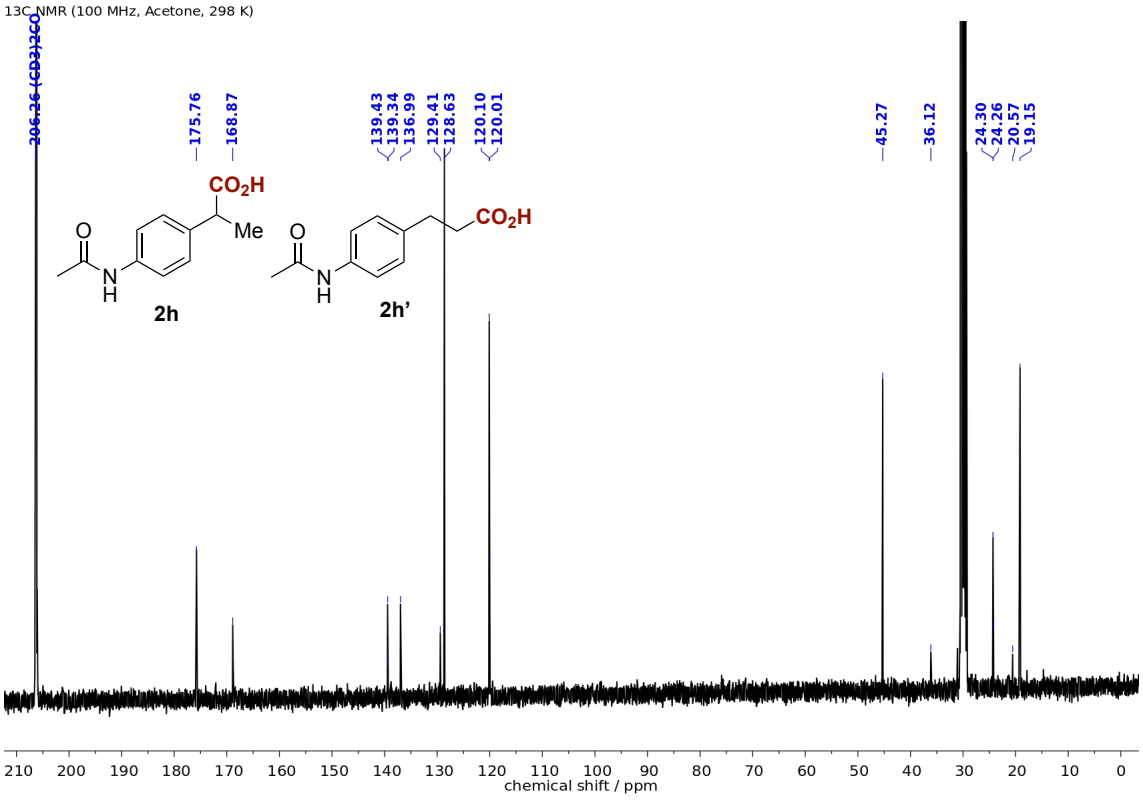

1H NMR (300 MHz, CDCl3, 294 K)
7.60 7.60 7.59 7.59 7.58 7.57 7.56 7.56 7.55 7.52 7.47 7.47 7.46 7.46 7.45 7.45 7.44 7.43 7.43 7.42 7.41 7.40 7.38 7.38 7.37 7.37 7.36 7.35 7.34 7.33 7.33 7.31 7.30 7.28 7.28 7.26 CDCl3
3.85 3.82 3.80 3.78 3.03 3.01 2.98 2.98 2.76 2.74 2.73 2.71
1.59 1.56
CO2H
Me
2f
CO2H
2f'
4.57 6.15 1.01 0.38 0.28 3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
chemical shift / ppm


13C NMR (75. MHz, CDCl3, 294 K)
180.78 179.20
141.00 140.82 140.54 139.46 139.34 138.88 128.89 128.83 128.17 127.57 127.44 127.41 127.27 127.22 127.14
77.16 CDCl3
45.16 35.64 30.30 18.25
CO2H
Me
2f
CO2H
2f'
:00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
chemical shift / ppm

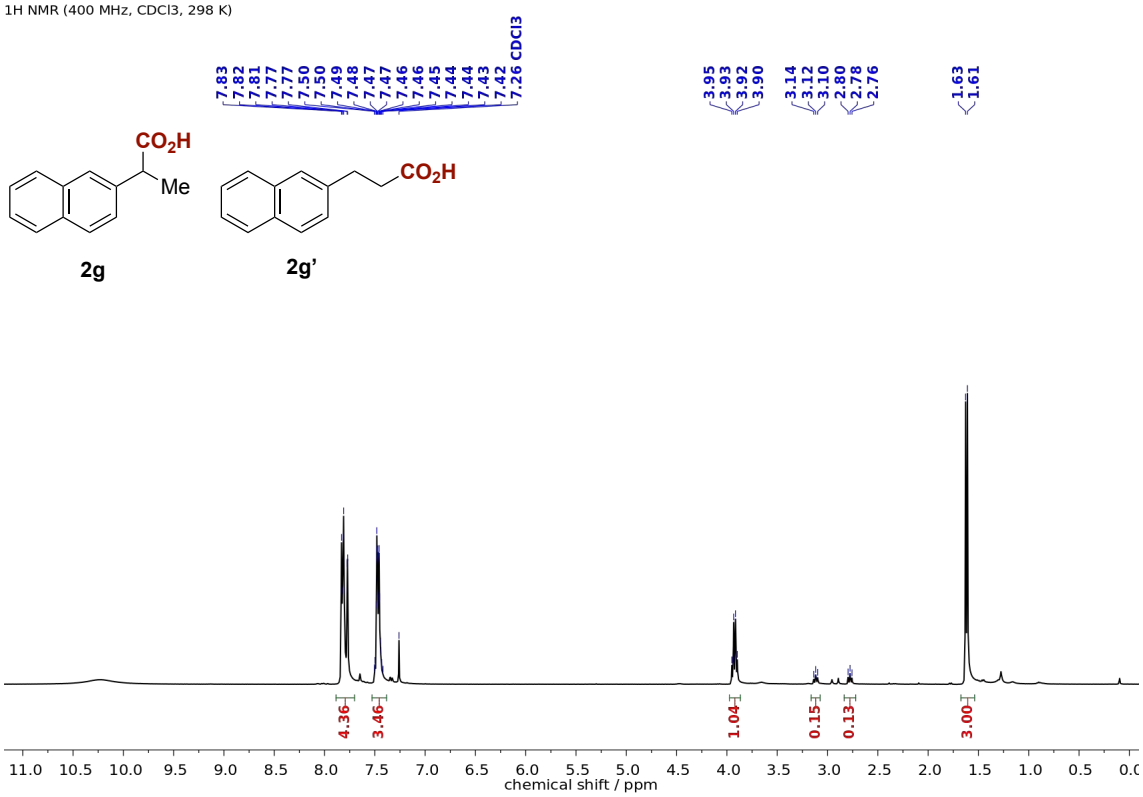

1H NMR (400 MHz, Acetone, 298 K)
8.22
8.08
7.17
7.17
7.16
7.15
7.15
7.09
7.08
7.07
7.06
6.87
6.87
6.86
6.85
6.84
6.80
6.79
6.79
6.78
6.78
6.77
6.76
6.75
6.75
6.74
6.74
6.73
6.64
6.64
6.63
6.62
6.62
6.61
3.67
3.65
3.64
3.62
2.83
2.81
2.80
2.80
2.79
2.57
2.55
2.55
2.53
2.05 (CD3)2CO
1.40
1.38
CO2H
Me
HO
2g
CO2H
HO
2g'
1.00
1.02
2.00
0.78
2.27
0.45
1.11
0.90
0.47
3.35
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
chemical shift / ppm


13C NMR (100 MHz, Acetone, 298 K)
176.01
174.08
157.22
138.36
133.01
132.61
130.08
129.31
116.07
115.35
44.91
36.36
30.75
29.84 (CD3)2CO
19.20
CO2H
Me
HO
2g
CO2H
HO
2g'
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift / ppm

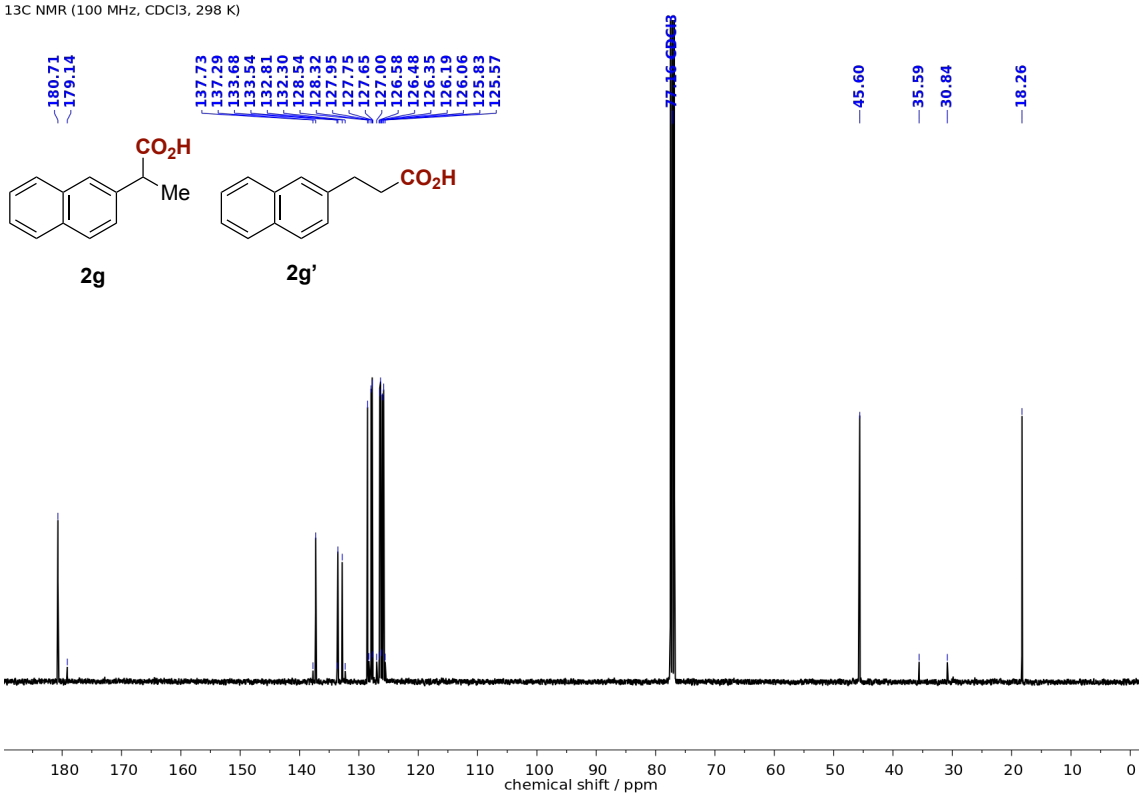

1H NMR (400 MHz, Acetone, 298 K)
9.13
7.60
7.58
7.55
7.53
7.26
7.24
7.18
7.16
3.72
3.71
3.69
3.67
2.88
2.86
2.86
2.84
2.60
2.58
2.58
2.56
2.06
2.05 (CD3)2CO
1.42
1.40
CO2H
Me
O
N
H
2h
CO2H
O
N
H
2h'
1.01
2.00
0.20
1.93
0.24
1.18
0.32
0.25
4.29
3.43
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
chemical shift / ppm

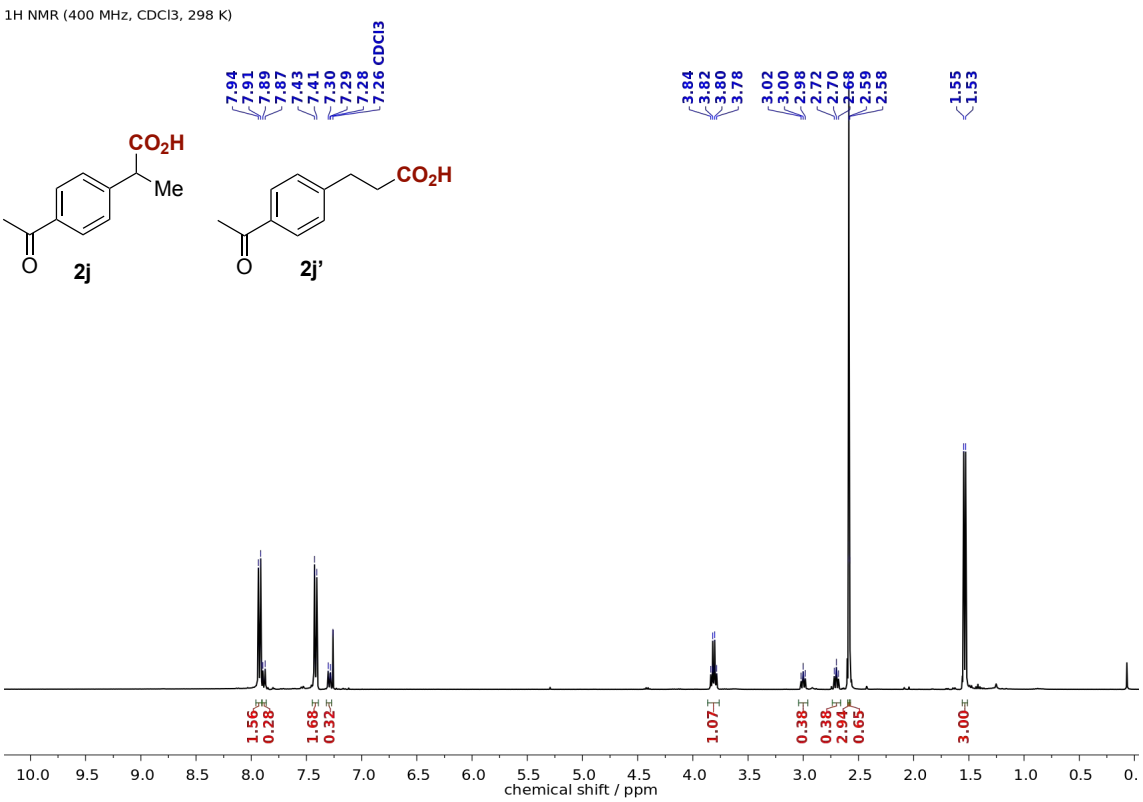

13C NMR (100 MHz, Acetone, 298 K)
206.26 (CD3)2CO
175.76
168.87
139.43
139.34
136.99
129.41
128.63
120.10
120.01
45.27
36.12
24.30
24.26
20.57
19.15
CO2H
Me
O
N
H
2h
CO2H
O
N
H
2h'
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift / ppm

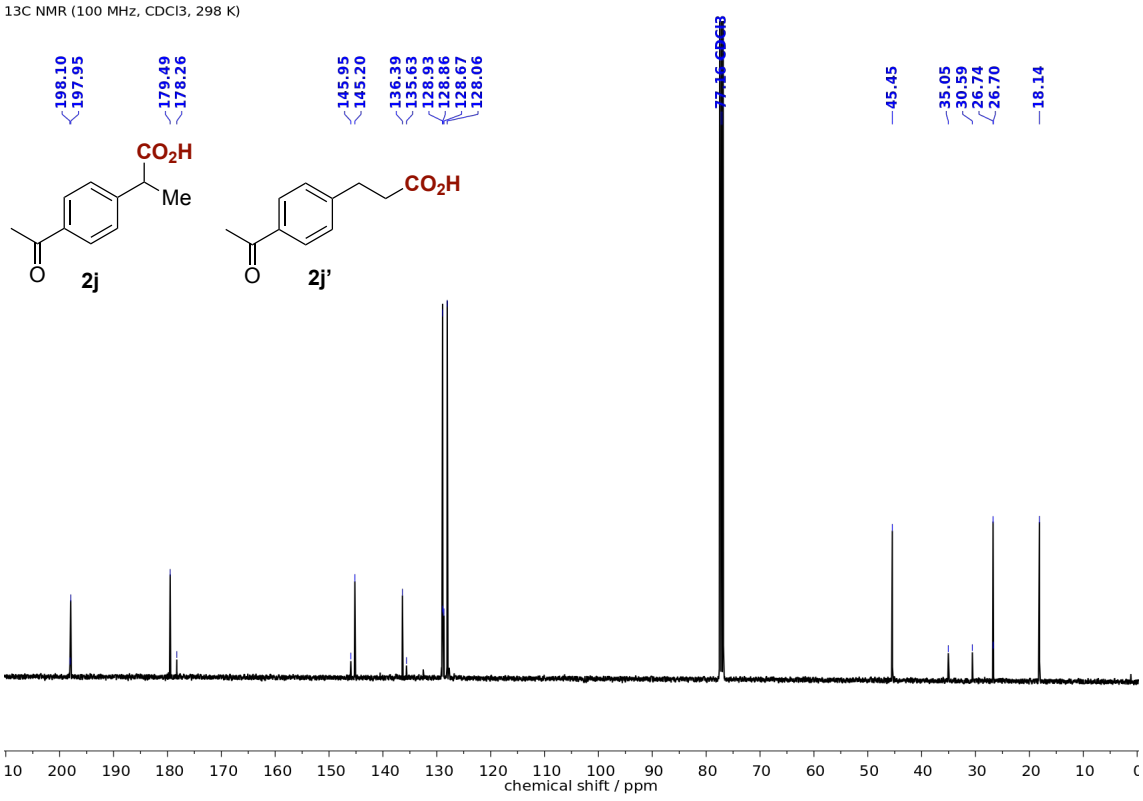
1H NMR (400 MHz, CDCl3, 298 K)

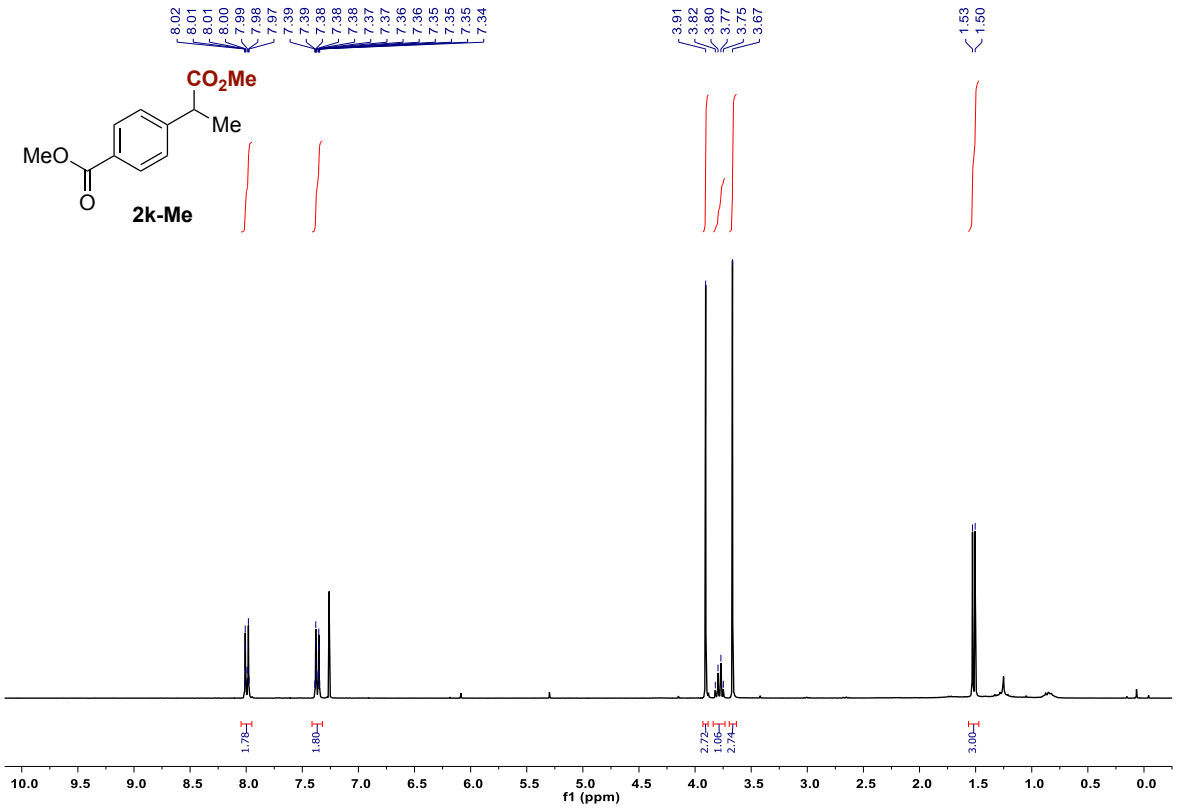


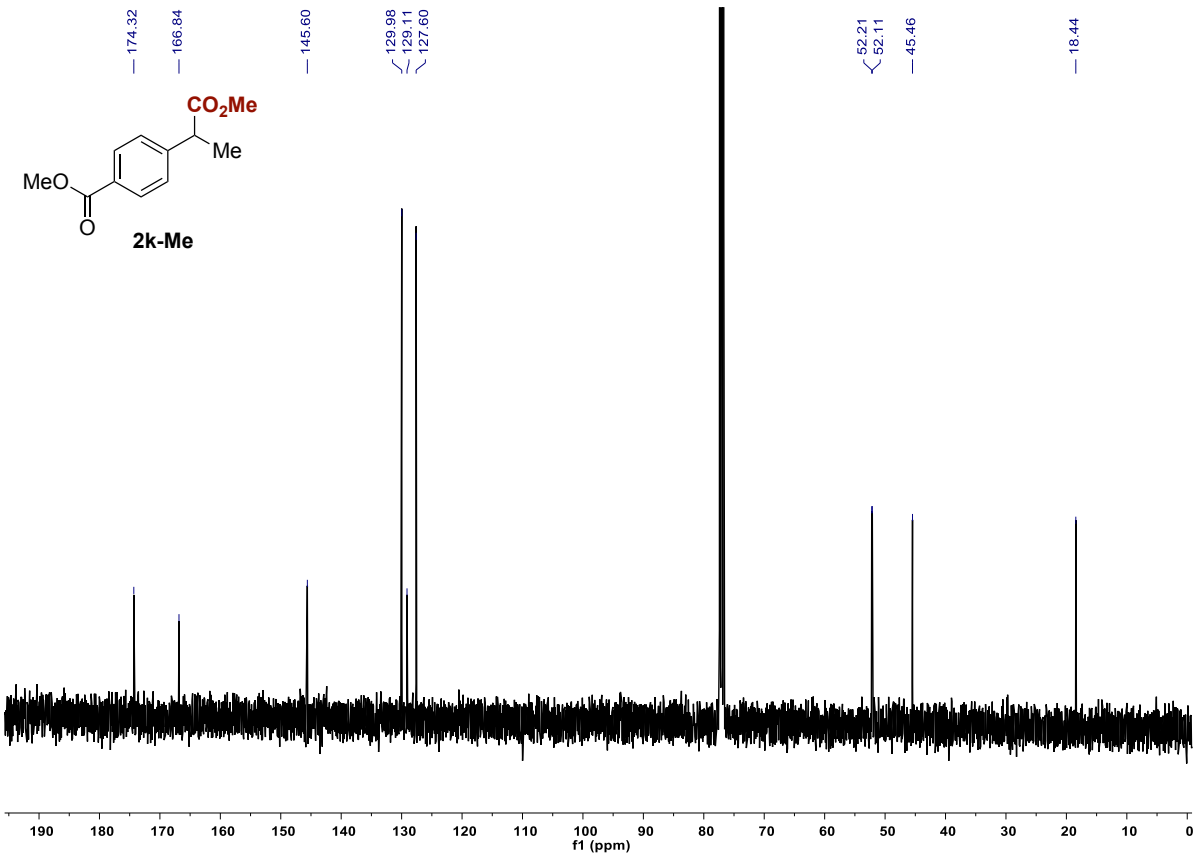
13C NMR (100 MHz, CDCl3, 298 K)



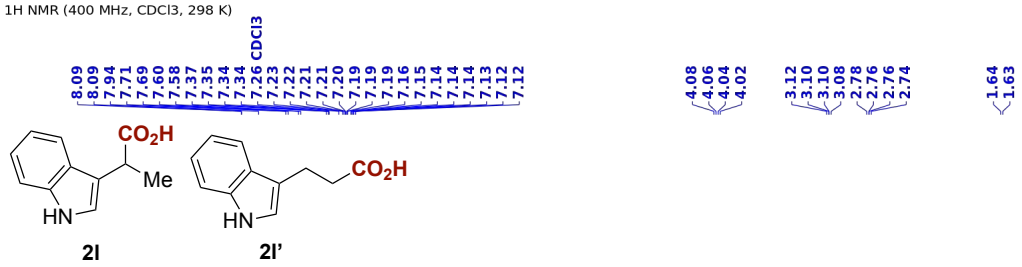

1H NMR (400 MHz, CDCl3, 298 K)
7.94
7.91
7.89
7.87
7.43
7.41
7.30
7.29
7.28
7.26 CDCl3
3.84
3.82
3.80
3.78
3.02
3.00
2.98
2.72
2.70
2.68
2.59
2.58
1.55
1.53
CO2H
Me
2j
CO2H
2j'
1.56
0.28
1.68
0.32
1.07
0.38
0.38
2.94
0.65
3.00
chemical shift / ppm

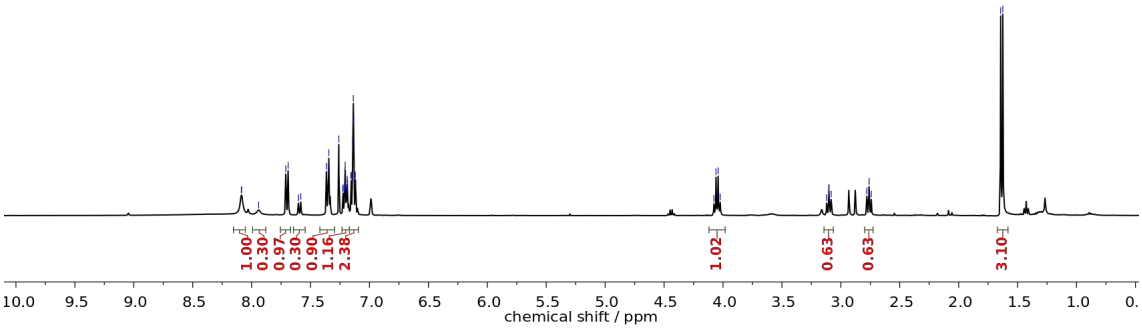

13C NMR (100 MHz, CDCl3, 298 K)
198.10
197.95
179.49
178.26
145.95
145.20
136.39
135.63
128.93
128.86
128.67
128.06
77.16 CDCl3
45.45
35.05
30.59
26.74
26.70
18.14
CO2H
Me
2j
CO2H
2j'
chemical shift / ppm


8.02
8.01
8.01
8.00
7.99
7.98
7.97
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.35
7.34
3.91
3.82
3.80
3.77
3.75
3.67
1.53
1.50
CO2Me
Me
MeO
O
2k-Me
1.78
1.80
2.72
1.06
2.74
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

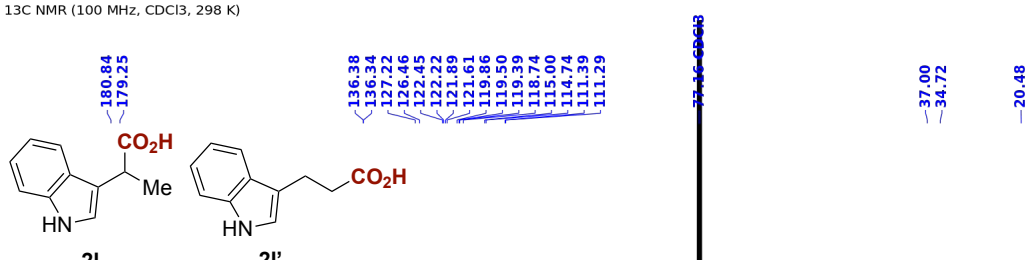

174.32
166.84
145.60
129.98
129.11
127.60
52.21
52.11
45.46
18.44
CO2Me
Me
MeO
O
2k-Me
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

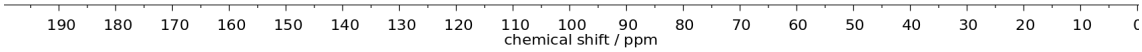
1H NMR (400 MHz, CDCl3, 298 K)



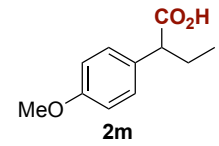


13C NMR (100 MHz, CDCl3, 298 K)



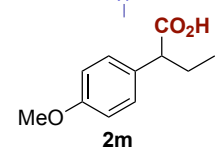


1H NMR (400 MHz, CDCl3, 298 K)

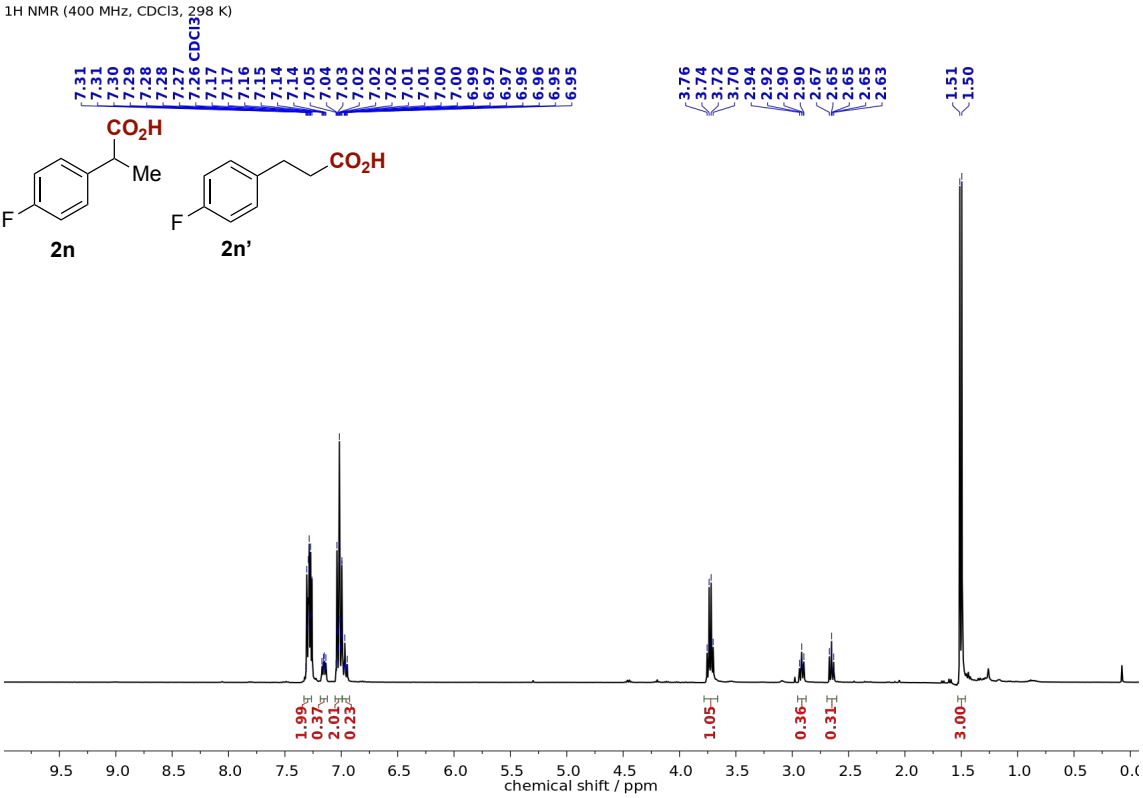


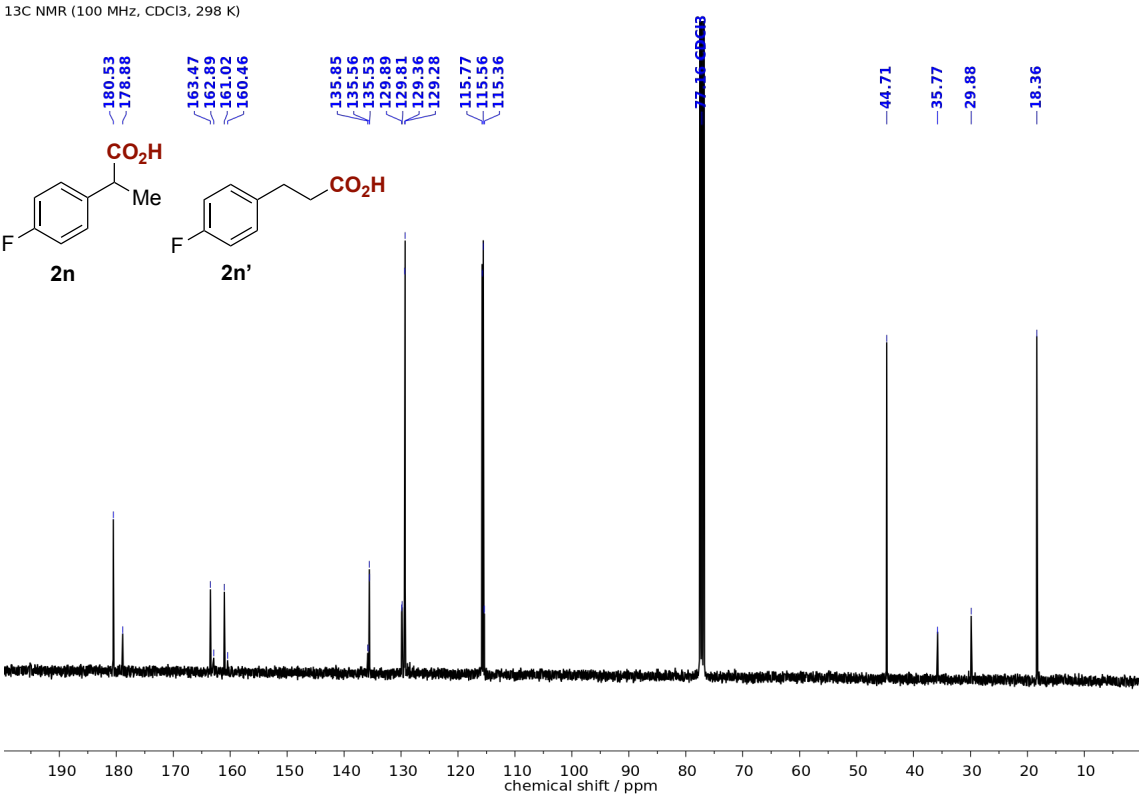
2m

13C NMR (100 MHz, CDCl3, 298 K)

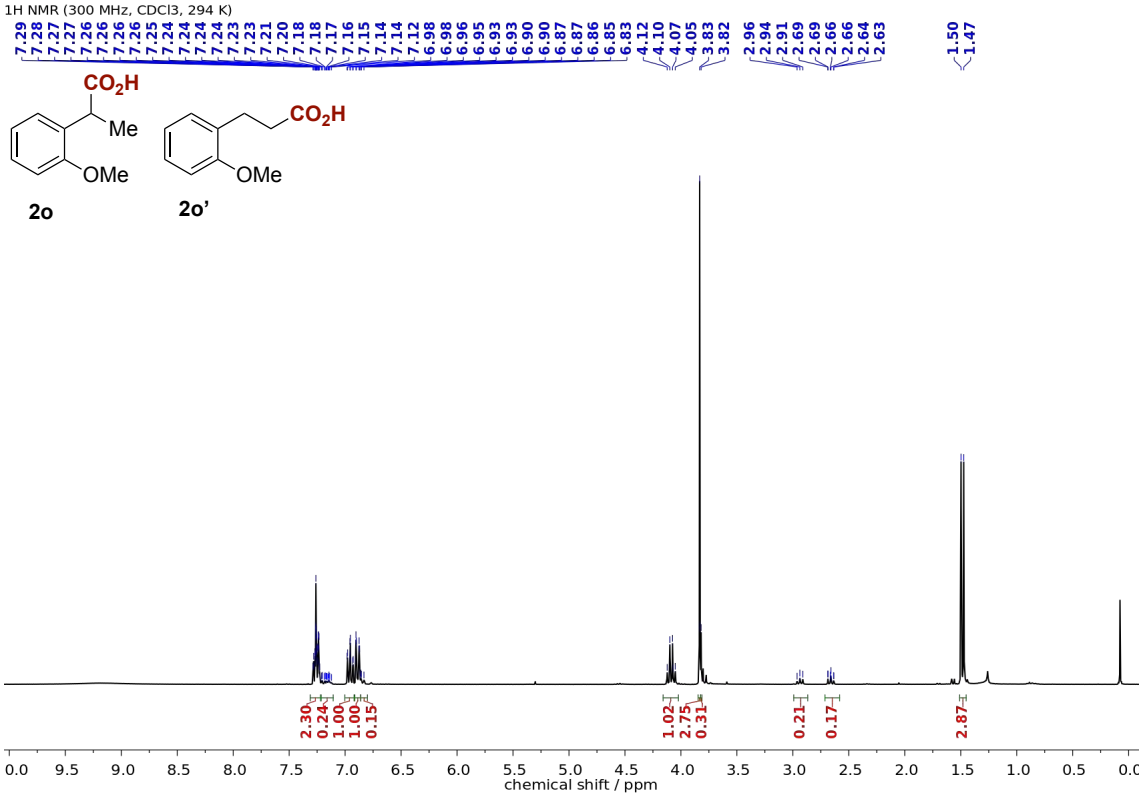


2m

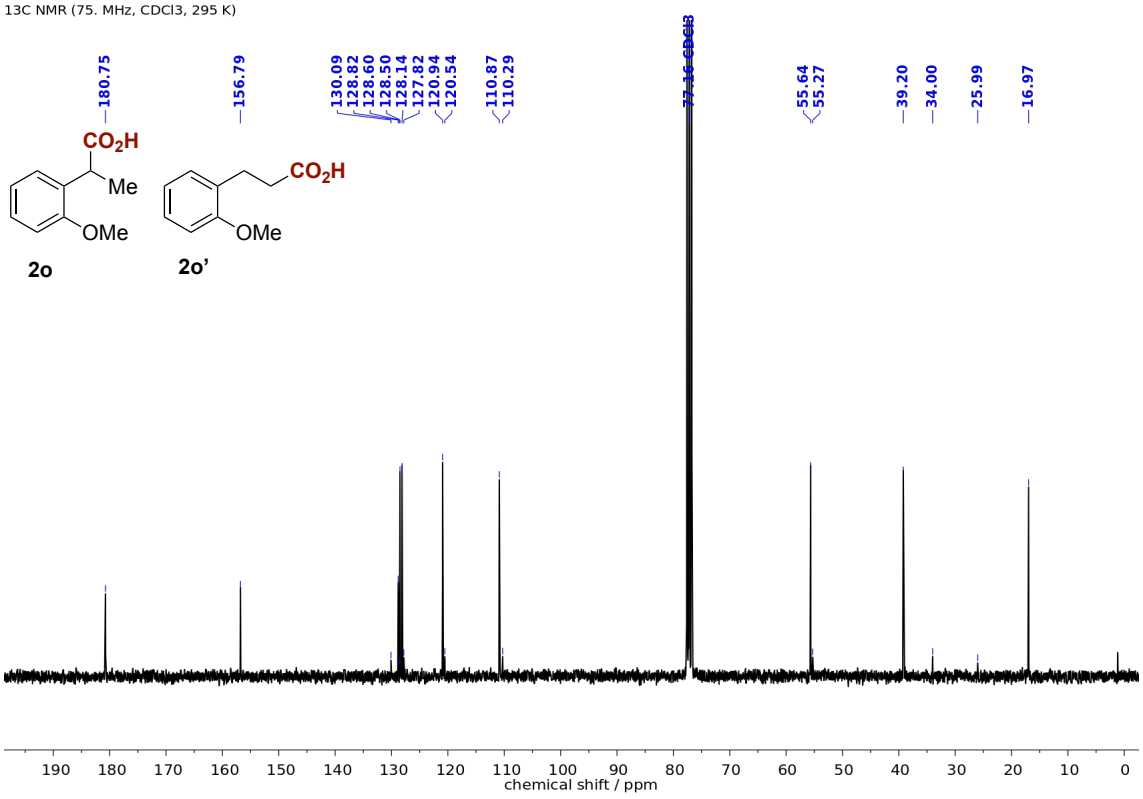

1H NMR (400 MHz, CDCl3, 298 K)
CDCl3
7.31 7.31 7.30 7.29 7.28 7.28 7.27 7.26 7.17 7.17 7.16 7.15 7.14 7.14 7.05 7.04 7.03 7.02 7.02 7.02 7.01 7.01 7.00 7.00 6.99 6.97 6.97 6.96 6.96 6.95 6.95
3.76 3.74 3.72 3.70 2.94 2.92 2.90 2.90 2.67 2.65 2.65 2.65 2.63
1.51 1.50
CO2H
Me
F
2n
CO2H
F
2n'
1.99 0.37 2.01 0.23 1.05 0.36 0.31 3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
chemical shift / ppm


13C NMR (100 MHz, CDCl3, 298 K)
180.53 178.88
163.47 162.89 161.02 160.46
135.85 135.56 135.53 129.89 129.81 129.36 129.28
115.77 115.56 115.36
77.16 CDCl3
44.71
35.77
29.88
18.36
CO2H
Me
F
2n
CO2H
F
2n'
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
chemical shift / ppm

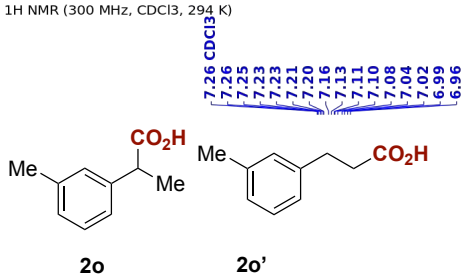
1H NMR (300 MHz, CDCl3, 294 K)



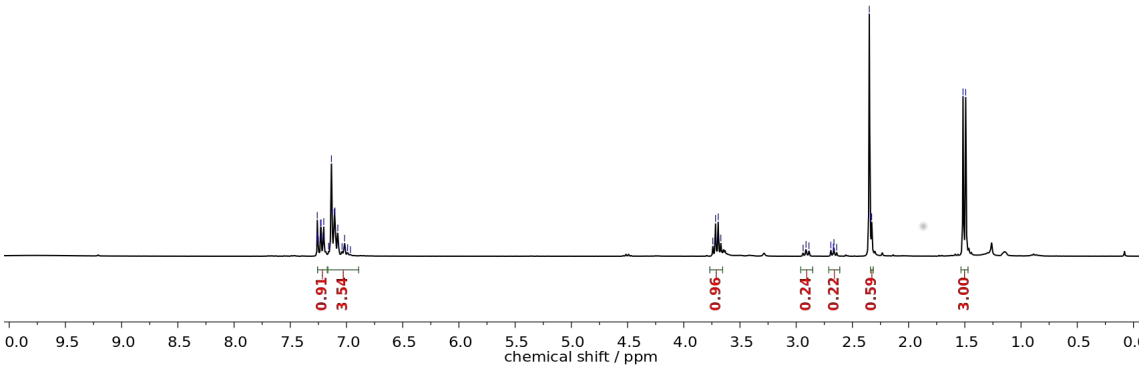
13C NMR (75. MHz, CDCl3, 295 K)



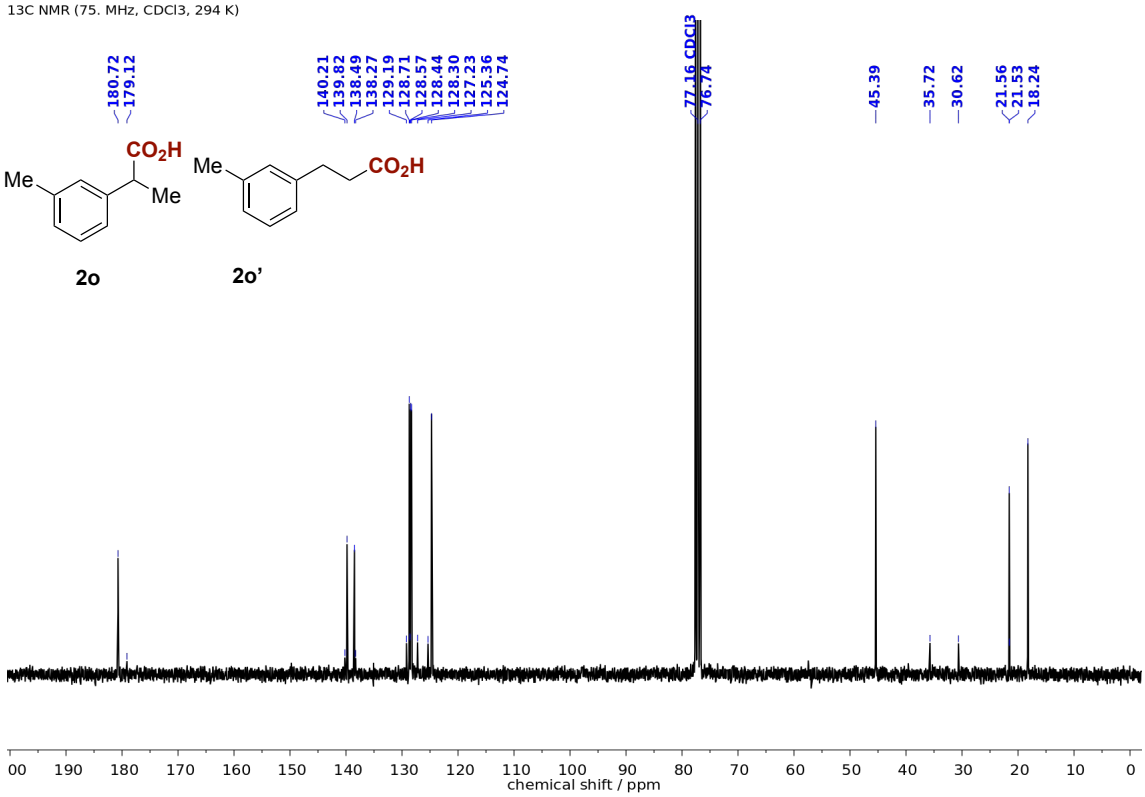
1H NMR (300 MHz, CDCl3, 294 K)



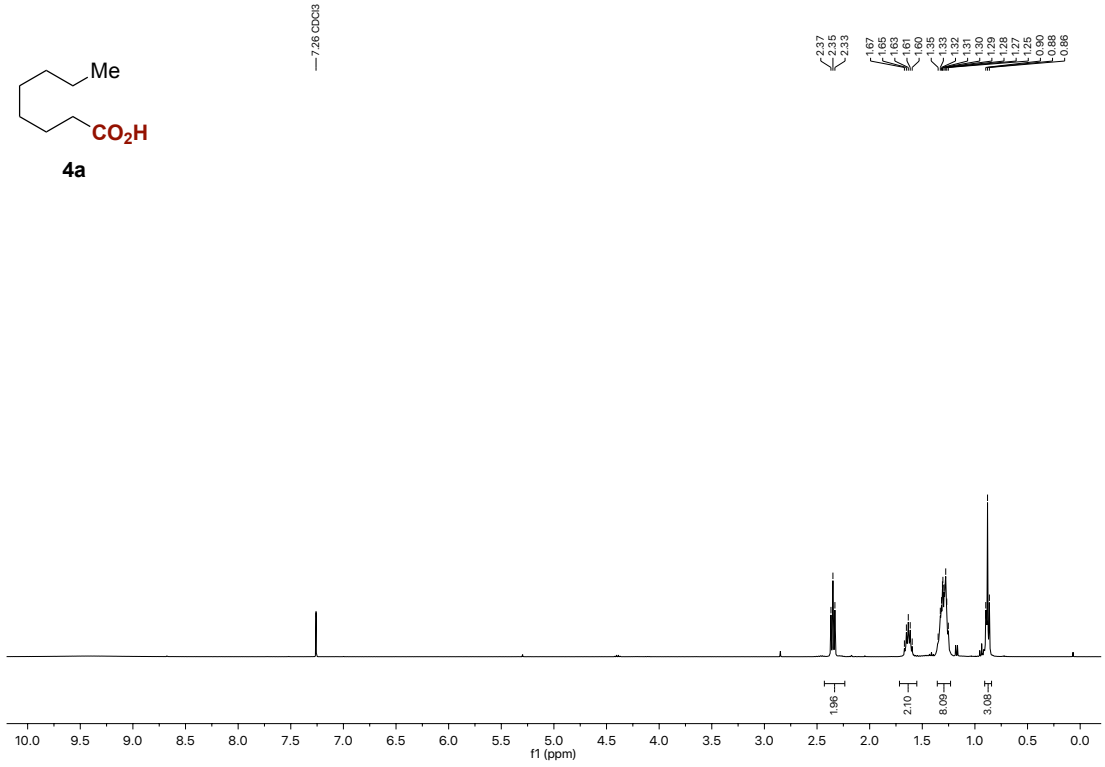
2o **2o'**

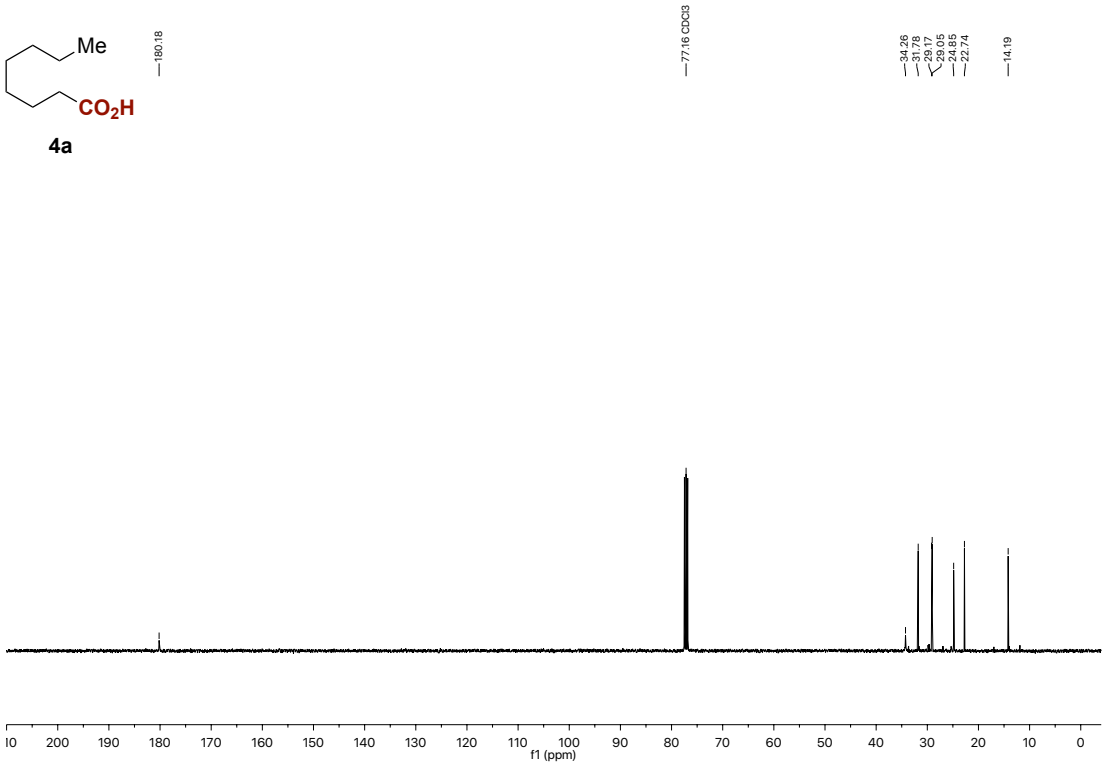


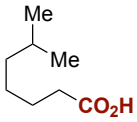
13C NMR (75. MHz, CDCl3, 294 K)



2o **2o'**

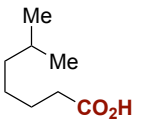

Me
CO2H
4a
7.26 CDCl3
2.37
2.35
2.33
1.67
1.65
1.63
1.61
1.60
1.35
1.33
1.32
1.31
1.30
1.29
1.28
1.27
1.25
0.90
0.88
0.86
1.96
2.10
8.09
3.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Me
CO2H
4a
180.18
77.16 CDCl3
34.26
31.78
29.17
29.05
24.85
22.74
14.19
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
Me
CO2H

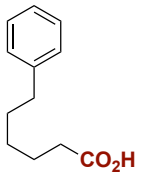
4b

7.26 CDCl3
2.37
2.35
2.34
1.66
1.64
1.62
1.60
1.58
1.57
1.55
1.53
1.52
1.50
1.49
1.38
1.36
1.35
1.34
1.33
1.32
1.30
1.21
1.20
1.19
1.17
1.16
0.88
0.86
2.00
1.96
1.01
2.17
2.11
6.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Me
Me
CO2H

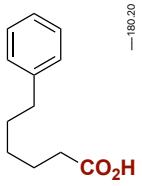
4b

179.66
77.16 CDCl3
38.67
34.13
27.95
26.99
25.06
22.71
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


CO2H

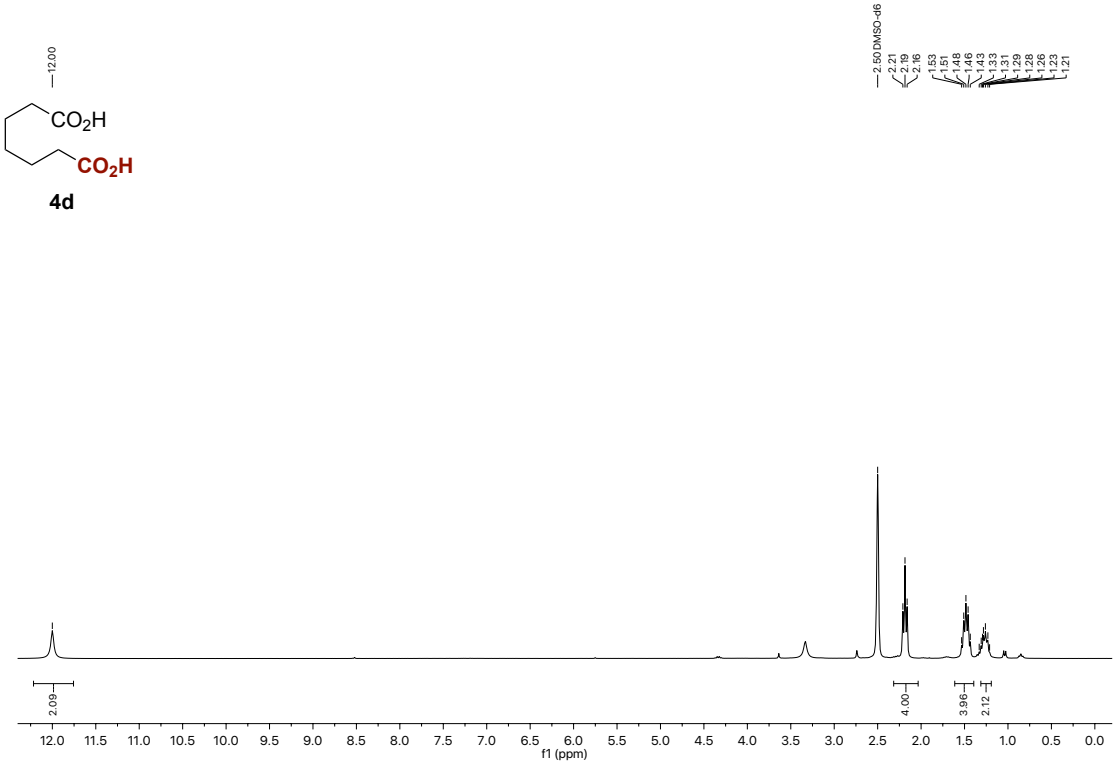
4c

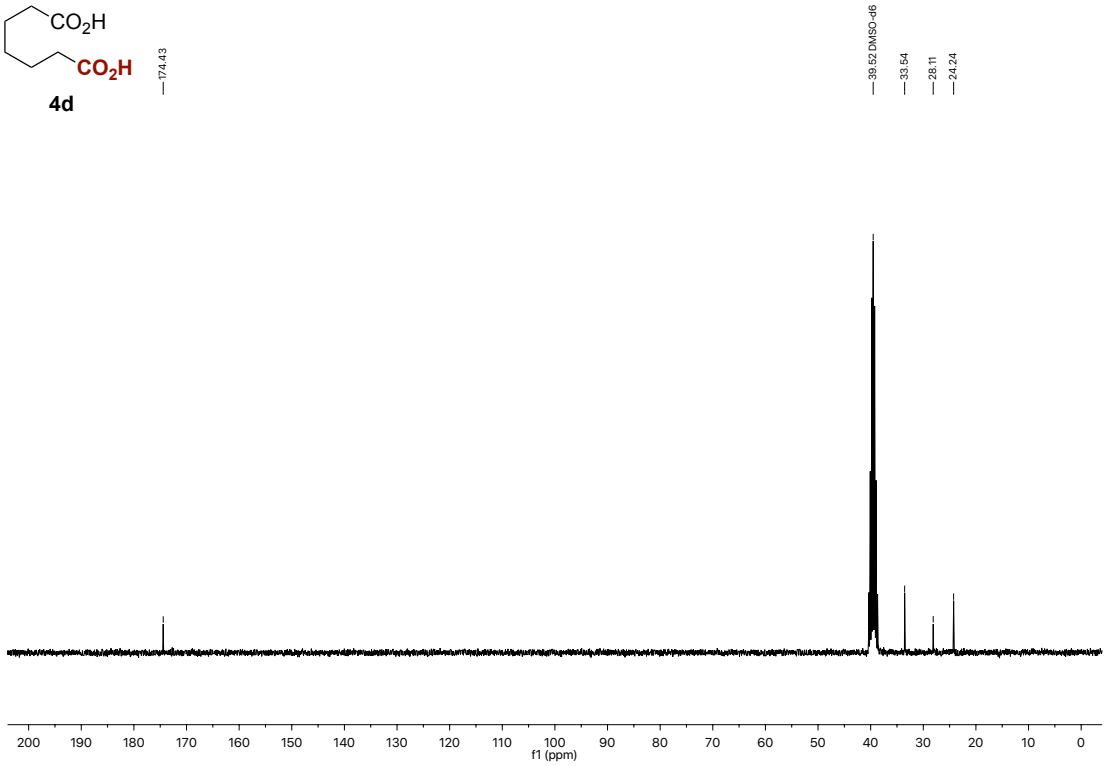
7.35
7.33
7.31
7.30
7.29
7.28
7.28
7.27
7.26 CDCl3
7.20
7.19
7.18
7.16
2.65
2.62
2.60
2.38
2.36
2.33
1.73
1.70
1.68
1.65
1.63
1.60
1.45
1.43
1.42
1.40
1.37
1.34
2.11
3.02
2.05
1.93
4.00
2.04
f1 (ppm)

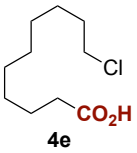

CO2H

4c

180.20
142.58
128.52
128.43
125.84
77.16 CDCl3
35.83
34.72
31.21
28.81
24.66
f1 (ppm)

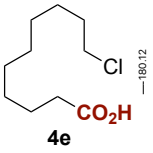

12.00
CO2H
CO2H
4d
2.50 DMSO-d6
2.21
2.19
2.16
1.53
1.51
1.48
1.46
1.43
1.33
1.31
1.29
1.28
1.26
1.23
1.21
2.09
4.00
3.96
2.12
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


CO2H
CO2H
4d
174.43
39.52 DMSO-d6
33.54
28.11
24.24
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Cl
CO2H

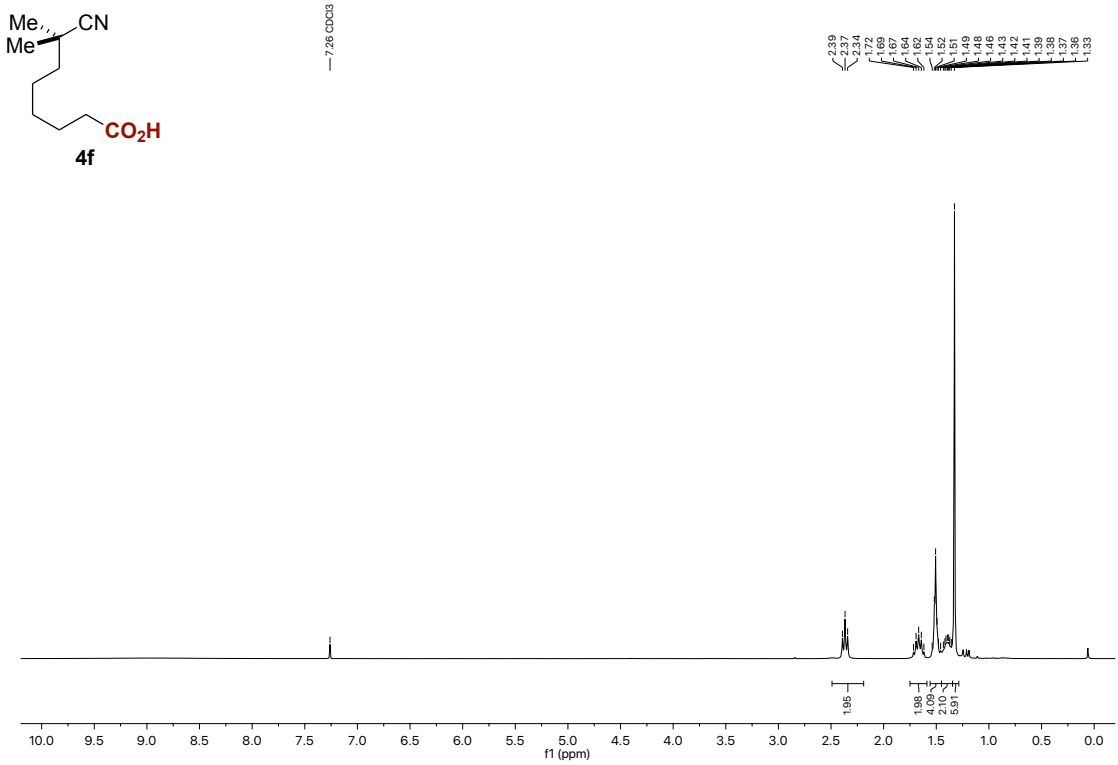
4e

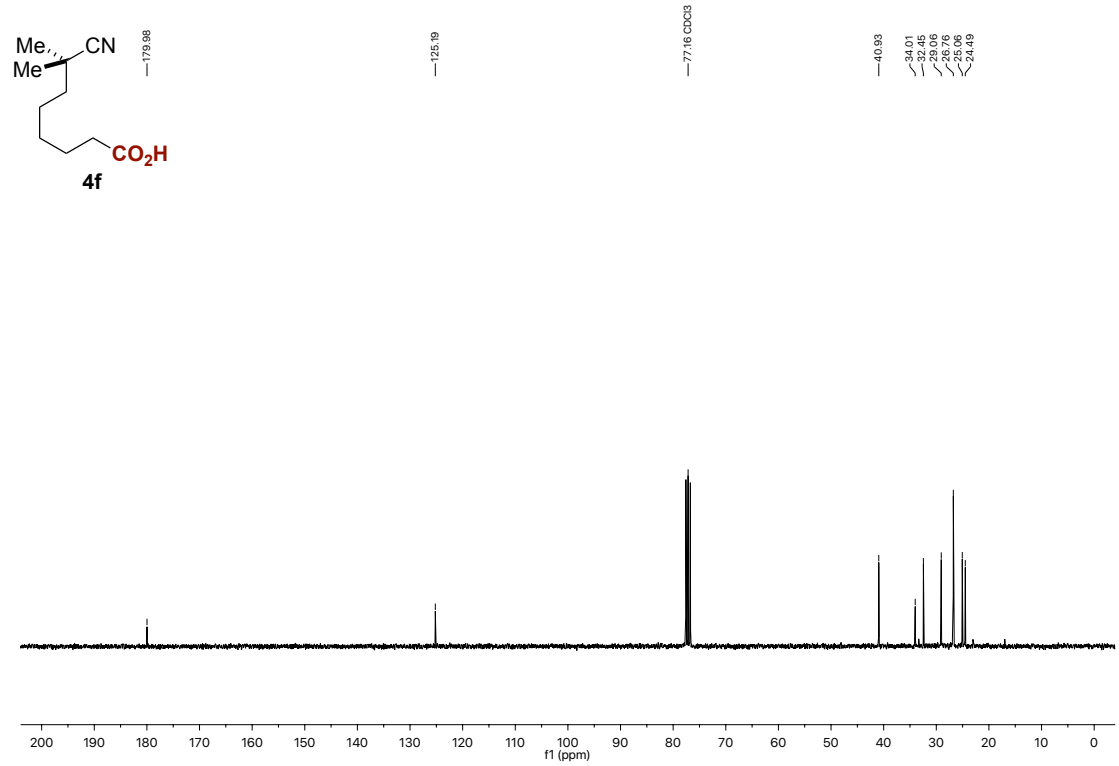
7.26 CDCl3
3.55
3.53
3.50
2.37
2.35
2.32
1.81
1.79
1.76
1.74
1.71
1.68
1.65
1.63
1.61
1.58
1.47
1.44
1.42
1.41
1.39
1.36
1.33
1.32
1.30
1.25
1.96
2.01
2.00
2.16
1.12
8.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

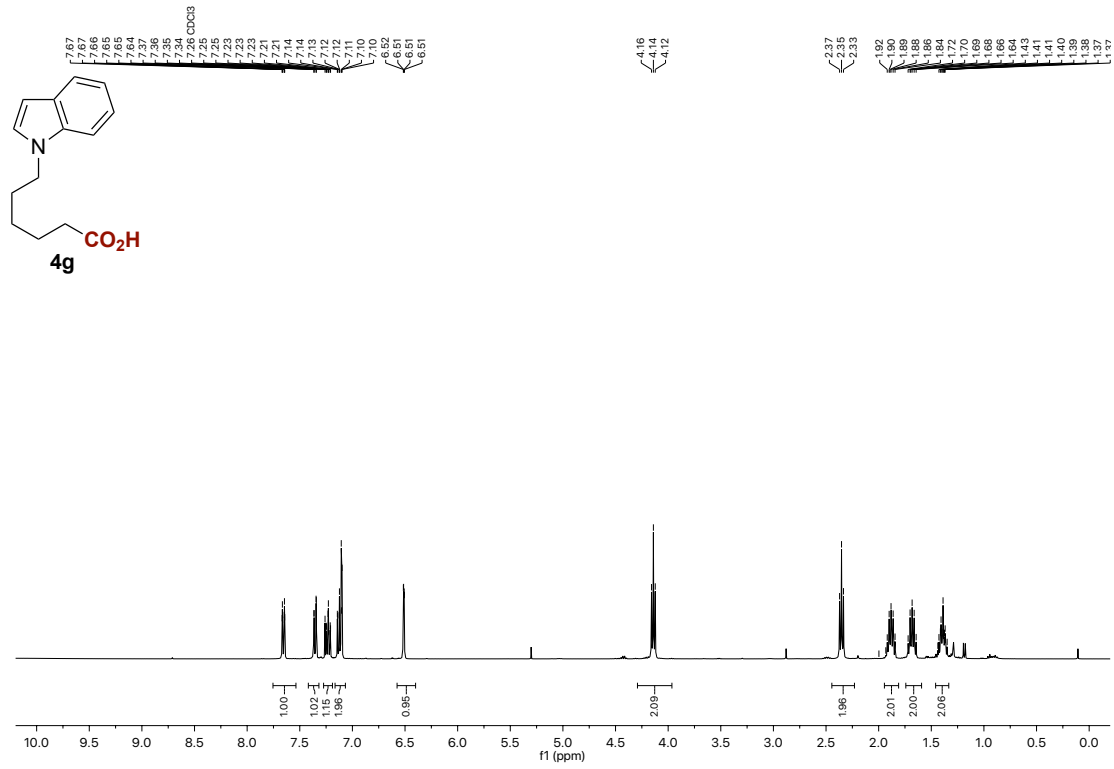

Cl
CO2H

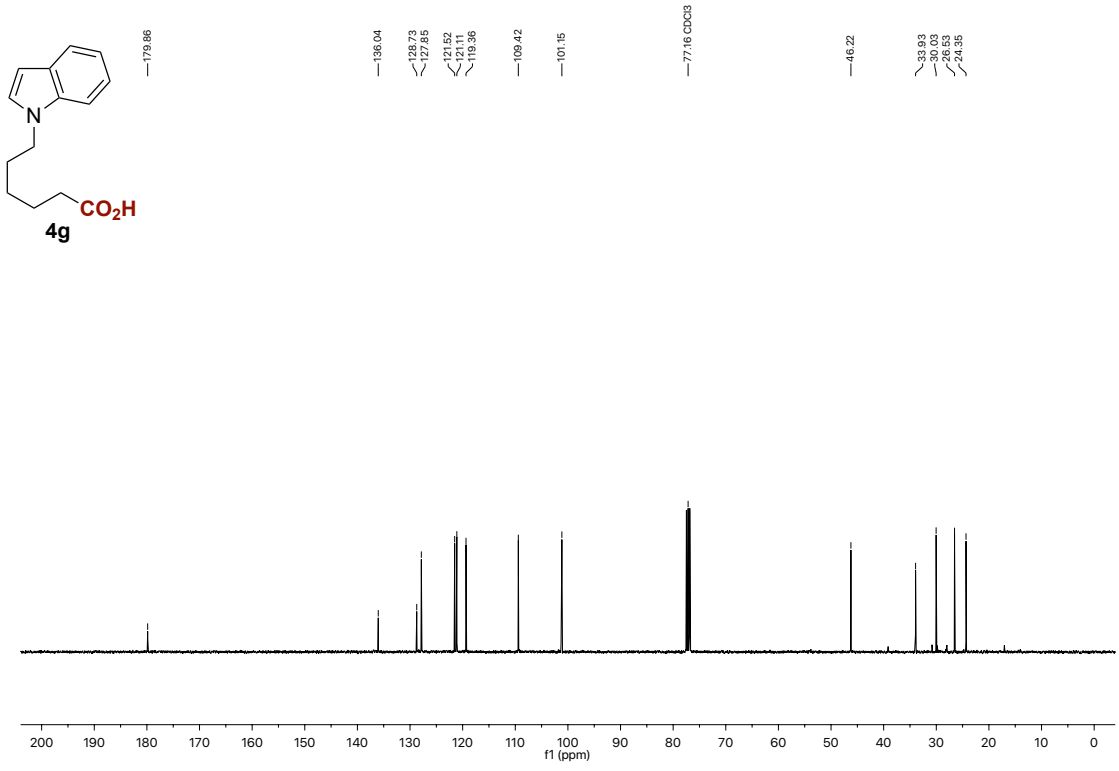
4e

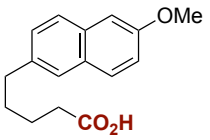
180.12
77.16 CDCl3
45.28
34.15
32.76
29.36
29.25
29.13
28.94
26.98
24.77
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
CN
Me
CO2H
4f
7.26 CDCl3
2.39
2.37
2.34
1.72
1.69
1.67
1.64
1.62
1.54
1.52
1.51
1.49
1.48
1.46
1.43
1.42
1.41
1.39
1.38
1.37
1.36
1.33
1.95
1.98
4.09
2.10
5.91
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Me
CN
Me
CO2H
4f
179.98
125.19
77.16 CDCl3
40.93
34.01
32.45
29.06
26.76
25.06
24.49
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

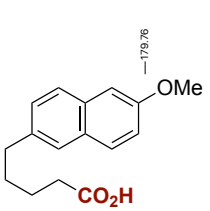

7.67
7.67
7.66
7.65
7.65
7.64
7.37
7.36
7.35
7.34
7.26 CDCl3
7.25
7.23
7.23
7.21
7.21
7.14
7.13
7.12
7.12
7.11
7.10
7.10
6.52
6.51
6.51
6.51
4.16
4.14
4.12
2.37
2.35
2.33
1.92
1.90
1.88
1.88
1.86
1.84
1.72
1.70
1.69
1.68
1.66
1.64
1.43
1.41
1.41
1.40
1.39
1.38
1.37
N
CO2H
4g
1.00
1.02
1.15
1.96
0.95
2.09
1.96
2.01
2.00
2.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


179.86
136.04
128.73
127.85
121.52
121.11
119.36
109.42
101.15
77.16 CDCl3
46.22
33.93
30.03
26.53
24.35
N
CO2H
4g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OMe
CO2H

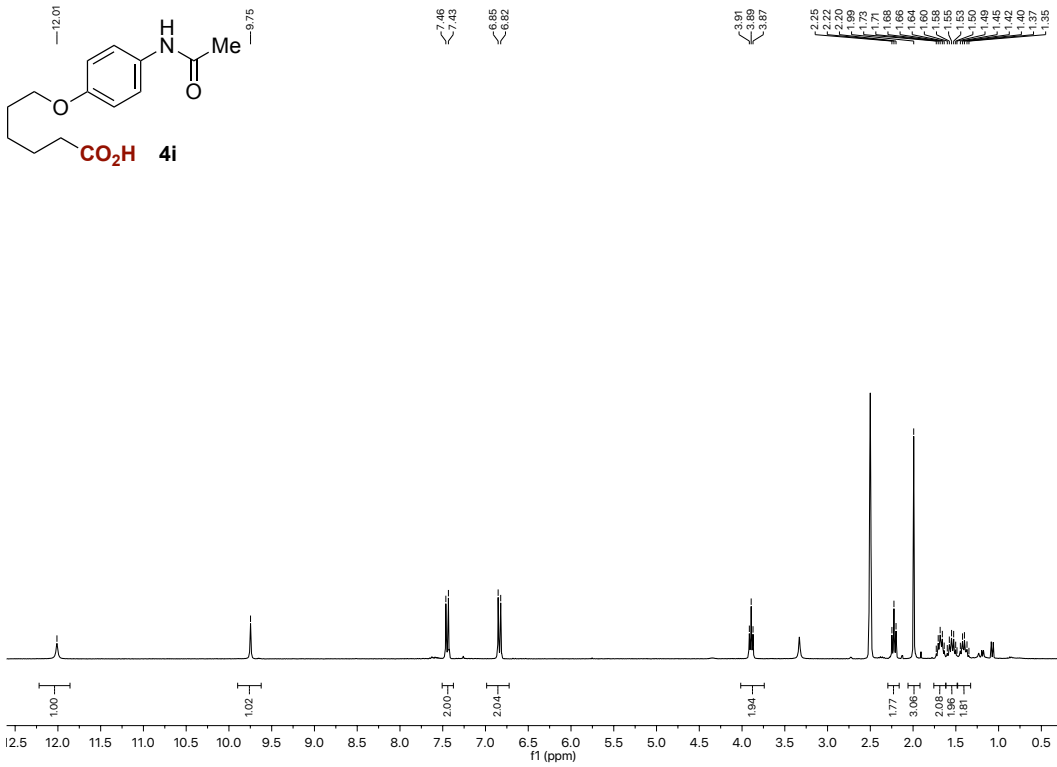
4h

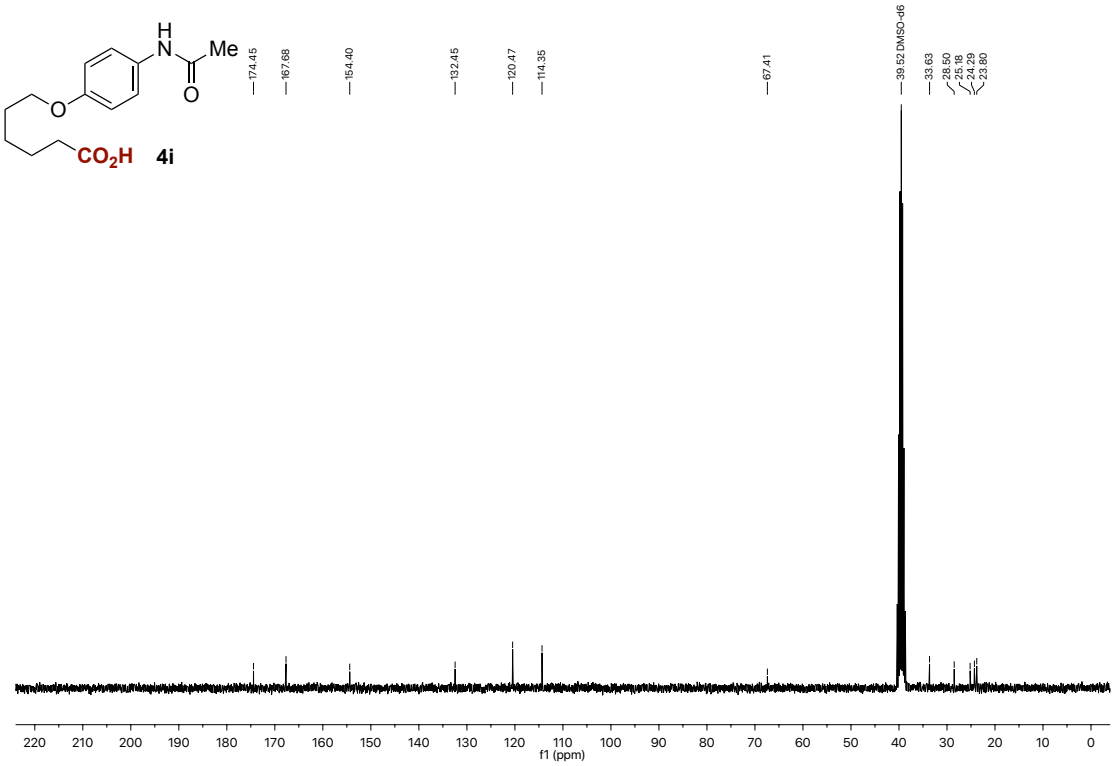
7.68
7.66
7.54
7.30
7.30
7.27
7.27
7.27
7.26 CDCl3
7.15
7.14
7.11
3.91
2.79
2.77
2.75
2.42
2.40
2.38
1.76
1.75
1.74
1.73
1.70
2.13
1.02
1.08
2.12
3.14
2.00
1.91
3.97
f1 (ppm)

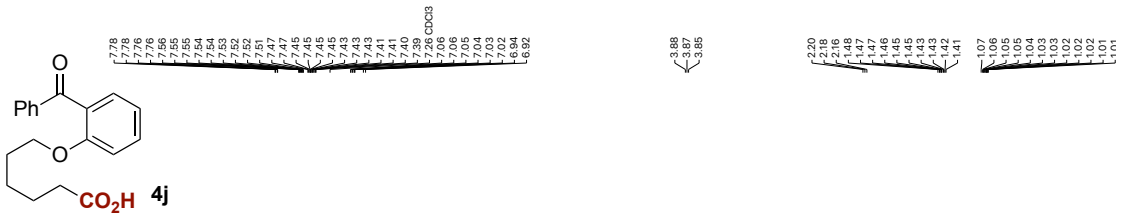

OMe
CO2H

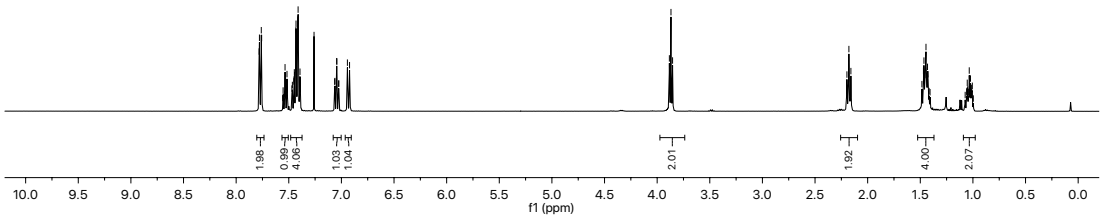
4h

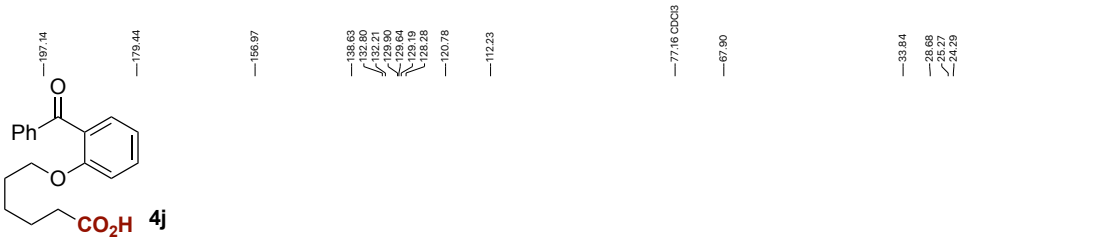
179.76
157.28
137.29
133.11
129.21
129.03
127.87
126.90
126.38
118.81
105.78
77.16 CDCl3
55.43
35.59
34.01
30.86
24.43
f1 (ppm)

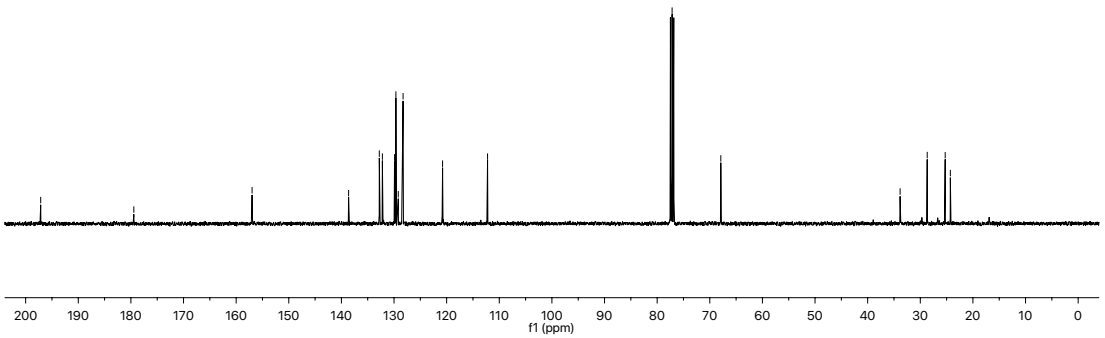

12.01
9.75
7.46
7.43
6.85
6.82
3.91
3.89
3.87
2.25
2.22
2.20
1.99
1.73
1.71
1.68
1.66
1.64
1.60
1.58
1.55
1.53
1.50
1.49
1.45
1.42
1.40
1.37
1.35
H
N
Me
O
O
CO2H
4i
1.00
1.02
2.00
2.04
1.94
1.77
3.06
2.08
1.96
1.81
f1 (ppm)


H
N
Me
O
O
CO2H
4i
174.45
167.68
154.40
132.45
120.47
114.35
67.41
39.52 DMSO-d6
33.63
28.50
25.18
24.29
23.80
f1 (ppm)


7.78
7.78
7.76
7.76
7.56
7.55
7.55
7.54
7.54
7.53
7.52
7.51
7.47
7.47
7.45
7.45
7.45
7.45
7.43
7.43
7.43
7.41
7.41
7.40
7.39
7.26 CDCl3
7.06
7.06
7.05
7.04
7.03
7.02
6.94
6.92
3.88
3.87
3.85
2.20
2.18
2.16
1.48
1.47
1.47
1.46
1.45
1.45
1.43
1.43
1.42
1.41
1.07
1.06
1.06
1.05
1.04
1.03
1.03
1.02
1.02
1.01
1.01
Ph
O
O
CO2H
4j


1.98
0.99
4.06
1.03
1.04
2.01
1.92
4.00
2.07
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


197.14
179.44
156.97
138.63
132.80
132.21
129.90
129.64
129.19
128.28
120.78
112.23
77.16 CDCl3
67.90
33.84
28.68
25.27
24.29
Ph
O
O
CO2H
4j


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{2}H NMR of **4a**-d_3