Supporting Information

Dual Nickel/Photoredox-Catalyzed Deaminative Cross-Coupling of Sterically Hindered Primary Amines

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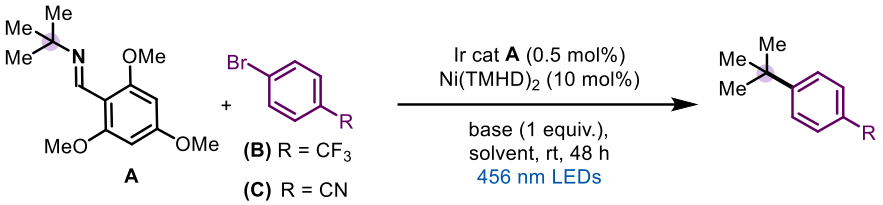
Contents

1. General Information

All reactions were carried out in anhydrous solvents and performed under ambient conditions unless otherwise noted. Commercial reagents and anhydrous solvents were purchased from Sigma-Aldrich and Fisher Scientific. All catalytic reactions were carried out under N_2 in 1dr vials with Teflon caps under irradiation from PR160-456nm Kessil 34W LED lamps. Thin layer chromatography was performed on SiliCycle® 250 µm, 60 Å plates. Visualization was accomplished with 254 nm UV light. Chromatographic purification was accomplished by flash chromatography on SiliCycle® Silica Flash® 40-63 µm, 60 Å or Teledyne ISCO CombiFlash®Rf+ LumenTM instrument CombiFlash pre-packed columns. Photocatalyst $[Ir(dF\text{-}CF_3\text{-}ppy)_2(dtbbpy)]PF_6$ A was synthesized according to the reported procedures.

^1H NMR spectra were recorded on Bruker 400 or 500 MHz spectrometers at ambient temperature. Chemical shift is reported in parts per million (ppm) from $CDCl_3$ (7.26 ppm) with multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet) and coupling constants (Hz). ^{13}C NMR was recorded on Bruker 500 or 400MHz spectrometers (126MHz) at ambient temperature. Chemical shifts are reported in ppm from $CDCl_3$ (77.16 ppm). Mass spectra (LRMS) were recorded on an Agilent 7890B GC System 5977B MSD GCMS with an EI ionization method. High resolution mass spectra (HRMS) were obtained from Columbia University Mass Spectrometry Facility on a JOEL JMSHZ110HF mass spectrometer using ESI+ /ASAP+ ionization model. Infrared spectra were recorded on a Perkin Elmer Spectrum Two FT-IR spectrometer. All cyclic voltammetry studies were performed on a CH Instruments Model 1232B potentiostat using an EDAQ 1-mm disk glassy carbon working electrode in conjunction with a Ag pseudo reference electrode and a platinum wire from VWR as a counter electrode. The silver pseudo reference electrode was submerged in anhydrous MeCN with 100 mM $TBAPF_6$ supporting electrolyte and was isolated from bulk solution with a glass frit. Ferrocene was added as a reference after each experiment. *In situ* LED-NMR experiments were performed with Goldstone Marketing LLC Mic-LED-420Z equipped with current controller BLCC-04, fiber coupling adapter FCA-SMA, and fiber patch cord (Extra Long) were purchased.

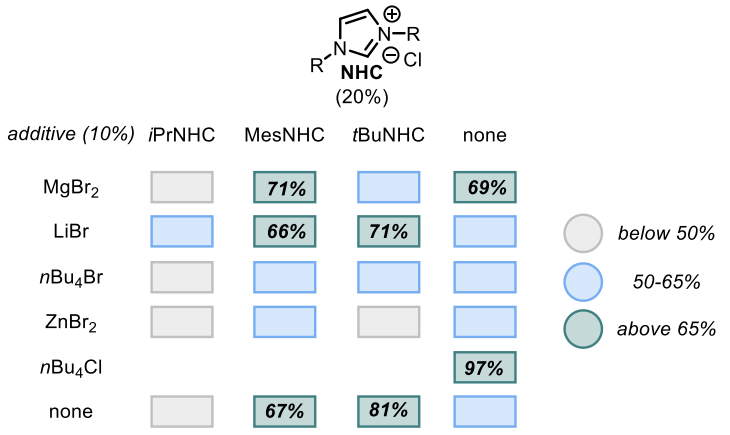
2. Extended Optimization –



entry	equiv **A**	halide (equiv.)	base	solvent	yield or pdt/IS
1	1	**B** (1.2)	none	DMSO (0.1M)	0.35*
2	1	**B** (1.2)	K_2HPO_4	DMSO (0.1M)	0.39*
3	1	**B** (1.2)	K_2HPO_4	DMA (0.1M)	0.12*
4	1	**B** (1.2)	K_2HPO_4	DMF (0.1M)	0.107*
5	1	**B** (1.2)	K_2HPO_4	NMP (0.1M)	0.0843*
6	1	**B** (1.2)	K_2HPO_4	ACN (0.1M)	0.1105*
7	1	**B** (1.2)	K_2HPO_4	$PhCF_3$ (0.1M)	0*
8	1	**C** (2)	K_2HPO_4	DMSO (0.1M)	25%
9	1	**C** (1.2)	K_2HPO_4	DMSO (0.1M)	31%
10	1	**C** (1.1)	K_2HPO_4	DMSO (0.1M)	39%
11	1.2	**C** (1)	K_2HPO_4	DMSO (0.1M)	39%
12	1.5	**C** (1)	K_2HPO_4	DMSO (0.1M)	48%
13	2	**C** (1)	K_2HPO_4	DMSO (0.1M)	58%
14	2	**C** (1)	Cs_2CO_3	DMSO (0.1M)	28%
15	2	**C** (1)	K_2CO_3	DMSO (0.1M)	14%
16	2	**C** (1)	$KHCO_3$	DMSO (0.1M)	27%
17	2	**C** (1)	KH_2PO_4	DMSO (0.1M)	45%

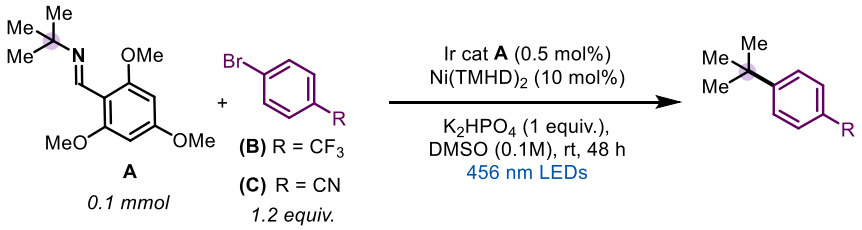
a) reactions were carried out on a 0.1 mmol scale according to General Procedure B. Yields or product ratios were determined by GCMS using mesitylene as an internal standard.

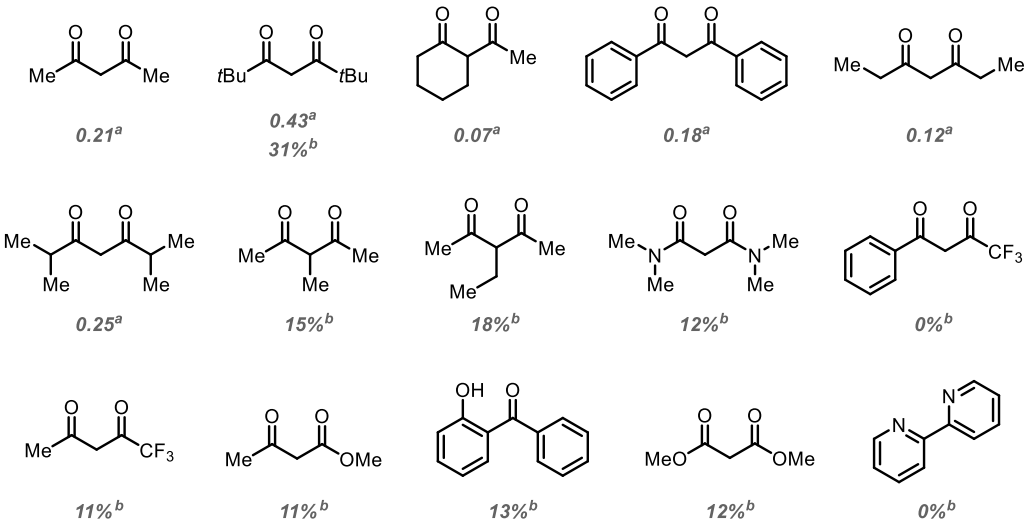
Additive Screening



all experiments were run on 0.1 mmol scale according to General Procedure B.

Ligand Screening



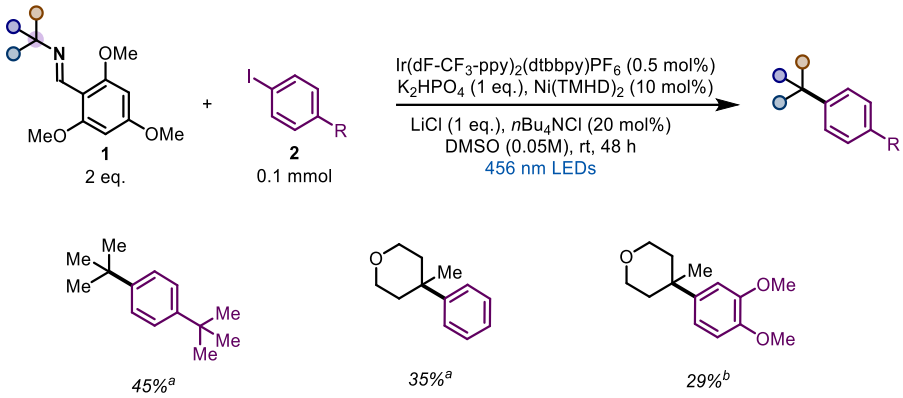


a) product/IS ratios were recorded by GCMS using mesitylene as an internal standard and using aryl halide **B** as the coupling partner. b) yields were recorded by GCMS using mesitylene as an internal standard using aryl halide **C** as the coupling partner.

Using Electron-rich Aryl Halides:

Electron-rich aryl bromides were not suitable coupling partners under these reaction conditions. Using them resulted in the majority of the starting material remaining. Below is a photo of the standard reaction conditions with 4-MeObromobenzene (left) and 4-MeOiodobenzene (right) as coupling partners. As evidenced, the nickel catalyst becomes deactivated, resulting in nickel black formation. We observe around 5% of the chlorinated arene and 10% of protodehalogenation when using electron-rich aryl iodides, indicating that oxidative addition can occur, but reductive elimination is also decelerated. This is consistent with outer-sphere reductive elimination via the polarity mismatch of the electron-rich, nucleophilic, tertiary alkyl radical and the electron-rich arene.

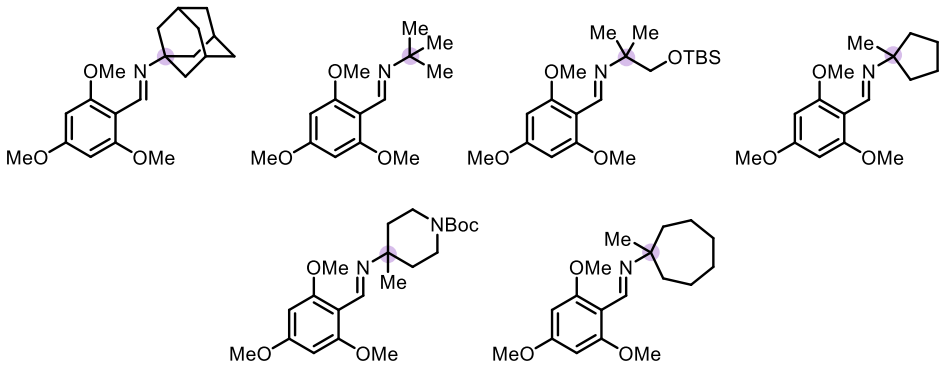
Additional electron-rich aryl iodides:



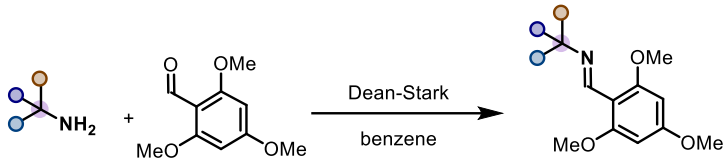
a. NMR yields with mesitylene as an internal standard. b. isolated yield.

3. Starting Material Synthesis –

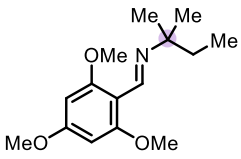
The following imines were synthesized according to a known literature procedure.[1]



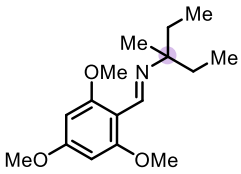
General Procedure A – *Synthesis of Imines*



Imines were synthesized according to a modified literature procedure.[1] A mixture of 2,4,6-trimethoxybenzaldehyde (1.0 equiv.) and primary amine (1.1 equiv. or 2.0 equiv. if volatile) in benzene (0.1M) was heated in a Dean-Stark apparatus to reflux overnight. The reaction was then cooled, dried with Na_2SO_4, filtered, and concentrated *in vacuo*. Volatile amines were pumped off and/or able to be washed away with hexanes, in which the imine would crash out (additional cooling sometimes required). Imines carried forward without further purification (95-100% purity).

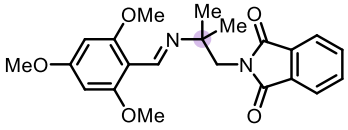


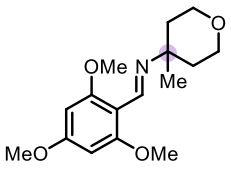
N-tert-pentyl-1-(2,4,6-trimethoxyphenyl)methanimine. Synthesized according to General Procedure A from commercially available *tert*-amyl amine (1.34 mL, 11.47 mmol) and 2,4,6-trimethoxybenzaldehyde (1.125g, 5.74 mmol). Light yellow solid (1.47g, 96%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.28 (s, 1H), 6.11 (s, 2H), 3.81 (s, 3H), 3.79 (s, 6H), 1.63 (q, *J* = 7.5 Hz, 2H), 1.23 (s, 6H), 0.87 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.87, 160.22, 151.10, 90.98, 60.42, 56.08, 55.45, 36.14, 26.86, 8.63. **IR** ($CDCl_3$): 2963.76, 1677.11, 1638.72, 1580.12, 1456.18, 1332.51, 1227.12, 1155.25, 1036.27, 952.91, 812.14 cm^{-1}. **HRMS-ESI** (positive) M = $C_{15}H_{23}NO_3$: calculated (M+H)+ m/z 267.1756; found (M+H)+ m/z 266.1767.



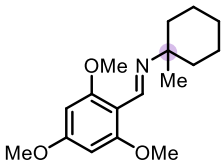
N-(3-methylpentan-3-yl)-1-(2,4,6-trimethoxyphenyl)methanimine. Synthesized according to General Procedure A from 3-methylpentan-3-aminium chloride (0.500g, 3.63 mmol), prepared according to a literature procedure,[2] 2,4,6-trimethoxybenzaldehyde (0.475 g, 2.42 mmol), and crushed potassium hydroxide (0.203 g, 3.63 mmol). Light yellow solid (0.501g, 74%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.20 (s, 1H), 6.12 (s, 2H), 3.82 (s, 3H), 3.79 (s, 6H), 1.61 (m, 4H), 1.16 (s, 3H), 0.85 (t, *J* = 7.5 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.22, 164.13, 159.94, 151.55, 90.80, 62.86, 55.96, 55.34, 33.97, 20.79, 8.11. **IR** ($CDCl_3$): 2964.59, 2936.73, 1678.88, 1639.46, 1604.78, 1456.68, 1413.46, 1332.24, 1206.21, 1154.74, 1127.75, 953.06, 811.26 cm^{-1}. **HRMS-ESI** (positive) M = $C_{15}H_{26}NO_3$: calculated (M+H)+ m/z 281.1952; found (M+H)+ m/z 281.1956.

2-(2-methyl-2-((2,4,6-trimethoxybenzylidene)amino)propyl)isoindoline-1,3-dione. Prepared according to General Procedure A from 2-(2-amino-2-methylpropyl)isoindoline-1,3-dione (0.255g, 1.17 mmol), prepared according to a literature procedure,[3] and 2,4,6-trimethoxybenzaldehyde (0.218g, 1.115 mmol). Tan solid (0.282g, 64%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.89 – 7.81 (m, 2H), 7.74 – 7.67 (m, 2H), 6.08 (s, 2H), 3.88 (d, *J* = 6.1 Hz, 2H), 3.81 (s, 3H), 3.75 (s, 6H), 1.33 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.80, 162.33, 160.64, 153.26, 133.87, 132.46, 123.27, 108.31, 90.85, 62.23, 56.01, 55.44, 48.86, 26.27. **IR** ($CDCl_3$): 2969.07, 1774.62, 1713.33, 1603.12, 1465.05, 1393.83, 1333.73, 1227.25, 1206.83, 1156.29, 1126.37, 1035.72, 911.74, 726.91 cm^{-1}. **HRMS-ESI** (positive) M = $C_{22}H_{24}N_2O_2$: calculated (M+H)+ m/z 398.1796; found (M+H)+ m/z 398.1800.

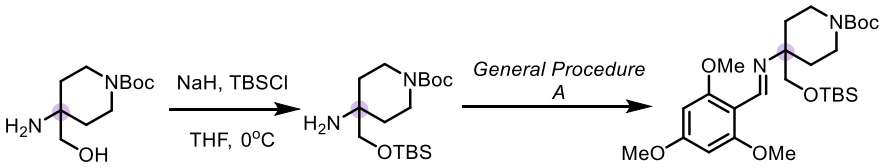




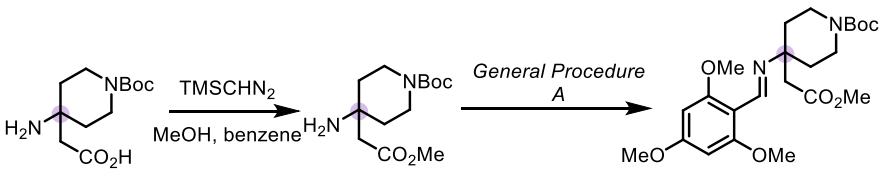
N-(4-methyltetrahydro-2H-pyran-4-yl)-1-(2,4,6-trimethoxyphenyl)methanimine. Synthesized according to General Procedure A from commercially available 4-methyltetrahydro-2H-pyran-4-aminium chloride (0.500 g, 3.3 mmol), 2,4,6-trimethoxybenzaldehyde (0.431 g, 2.2 mmol), and crushed potassium hydroxide (0.185 g, 3.3 mmol). White solid (0.652 g, 99%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.49 (s, 1H), 6.14 (s, 2H), 3.92 – 3.85 (m, 2H), 3.84 (s, 3H), 3.83 (s, 6H), 3.75 (m, 2H), 1.95 – 1.83 (m, 2H), 1.78 (m, 2H), 1.27 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.18, 160.31, 153.01, 108.54, 90.82, 64.46, 55.98, 55.34, 40.67, 39.27, 27.55. **IR** ($CDCl_3$): 2937.63, 2863.53, 1604.04, 1581.82, 1455.95, 1414.44, 1332.97, 1206.00, 1155.53, 1126.27, 1033.27, 907.78, 812.25, 728.93 cm^{-1}. **HRMS-ESI** (positive) M = $C_{16}H_{23}NO_4$: calculated (M+H)+ m/z 295.1738; found (M+H)+ m/z 295.1732.



N-(1-methylcyclohexyl)-1-(2,4,6-trimethoxyphenyl)methanimine. Prepared according to General Procedure A from 1-methylcyclohexan-1-aminium chloride (600 mg, 4.0 mmol), crush potassium hydroxide (224 mg, 4.0 mmol), and 2,4,6-trimethoxybenzaldehyde (524 mg, 2.67 mmol). Light yellow solid (724 mg, 93%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.40 (s, 1H), 6.11 (s, 2H), 3.82 (s, 3H), 3.80 (s, 6H), 1.82 (s, 2H), 1.68 – 1.53 (m, 4H), 1.50 – 1.46 (m, 4H), 1.18 (s, 3H). ^{13}C NMR (101 MHz, C_6D_6) δ 161.90, 160.26, 151.91, 109.34, 91.06, 59.33, 56.10, 55.40, 38.77, 27.74, 26.36, 22.63, 21.91. **IR** ($CDCl_3$): 2927.49, 2852.68, 1604.20, 1582.11, 1454.64, 1413.34, 1332.31, 1205.91, 1154.80, 1126.42, 1038.60, 811.96 cm^{-1}. **HRMS-ESI** (positive) M = $C_{17}H_{25}NO_3$: calculated (M+H)+ m/z 292.1913; found (M+H)+ m/z 292.1938.



***tert*-butyl 4-(((tert-butyldimethylsilyl)oxy)methyl)-4-((2,4,6-trimethoxybenzylidene)amino)piperidine-1-carboxylate.** In a flamed-dried schlenk flask under N_2 was added dry THF (10 mL) and NaH (76.0, 1.901 mmol). The solution was cooled to 0°C and *tert*-butyl 4-amino-4-(hydroxymethyl)piperidine-1-carboxylate (438 mg, 1.901 mmol), synthesized by a literature procedure,[4] in dry THF (5 mL) was added dropwise. The solution stirred for one hour at rt. The solution was cooled again to 0°C and a solution of TBSCl (287 mg, 1.901 mmol) in THF (3 mL) was added dropwise and the solution was allowed to stir for 3 hours at rt. Methanol (~10 mL) was added slowly, then extracted (3x) with hexanes and water, washed with brine, dried with $MgSO_4$ and concentrated to afford TBS protected alcohol. The imine was synthesized according to General Procedure A from the amine (200 mg, 0.580 mmol) and 2,4,6-trimethoxybenzaldehyde (0.109g, 0.527 mmol). Clear oil (0.234g, 85%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.46 (s, 1H), 6.11 (s, 2H), 3.83 (s, 3H), 3.79 (s, 6H), 3.50 (s, 2H), 3.11 (m, 2H), 1.91 (m, 2H), 1.72 – 1.69 (m, 2H), 1.46 (s, 9H), 1.32 – 1.24 (m, 2H), 0.88 (s, 9H), 0.02 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.25, 160.42, 155.92, 155.26, 108.70, 90.76, 79.20, 69.12, 61.62, 55.98, 55.47, 34.81, 31.74, 28.66, 26.01, 22.80, 18.44, 14.28, -5.40. **IR** ($CDCl_3$): 2928.72, 2855.40, 1689.17, 1603.87, 1462.28, 1415.79, 1364.46, 1277.06, 1247.80, 1128.15, 1156.59, 1090.01, 837.49, 776.36 cm^{-1}. **HRMS-ESI** (positive) M = $C_{26}H_{47}N_2O_6Si$: calculated (M+H)+ m/z 523.3203; found (M+H)+ m/z 523.3217.

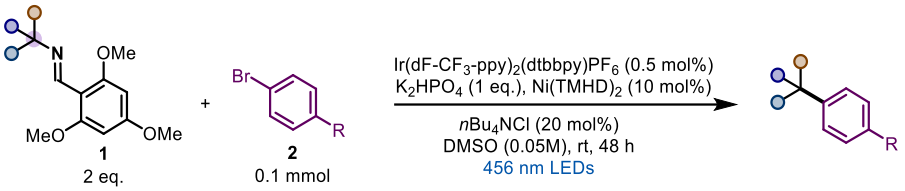


***tert*-butyl 4 (2-methoxy-2-oxoethyl)-4-((2,4,6-trimethoxybenzylidene)amino)piperidine-1-carboxylate.** To a 50 mL round bottom flask was added 2-(4-amino-1-(tert-butoxycarbonyl)piperidin-4-yl)acetic acid (450 mg, 1.742 mmol). The flask was evacuated and backfilled with nitrogen (3x), and dry MeOH (7 mL) and benzene (7 mL) was added. The solution was cooled to 0°C and TMS diazomethane (2M in hexanes) was added dropwise (1.742 mL, 3.484 mmol). The solution was allowed to stir overnight at rt, then concentrated. The residue was redissolved in EtOAc and 1N NaOH was added. The organic layer was washed with 1N NaOH, water, brine, and dried with $MgSO_4$ then concentrated to yield the methyl ester (0.317 g, 67%). The imine was synthesized according to General Procedure A from the amine (340 mg, 1.248 mmol) and 2,4,6-trimethoxybenzaldehyde (223 mg, 1.135 mmol). Clear oil (0.540g, 99%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 6.10 (s, 2H), 3.81 (s, 3H), 3.78 (s, 6H), 3.74 (m, 2H), 3.61 (s, 3H), 3.20 (m, 2H), 2.58 (s, 2H), 2.02 (m, 2H), 1.83 (m, 2H), 1.45 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.30, 164.23, 162.57, 160.49, 155.19, 108.23, 90.89, 79.31, 59.44, 56.07 (d, *J* = 5.9 Hz), 55.45, 51.41, 49.23, 47.37, 45.27, 37.68, 28.57. **IR** ($CDCl_3$): 2939.66, 1731.57, 1682.86, 1601.92, 1454.45, 1414.70, 1228.68, 1152.70, 1022.56, 973.45, 814.40 cm^{-1}. **HRMS-ESI** (positive) M = $C_{23}H_{34}N_2O_7$: calculated (M+H)+ m/z 451.2444; found (M+H)+ m/z 451.2448.

N-((1r,3R,5S,7r)-3,5-dimethyladamantan-1-yl)-1-(2,4,6-trimethoxyphenyl)methanimine. Prepared according to General Procedure A from Memantine (0.518g, 2.89 mmol), obtained through a basic wash of commercially available Memantine hydrochloride, and 2,4,6-trimethoxybenzaldehyde (0.540g, 2.75 mmol). White solid (0.960g, 98%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 6.11 (s, 2H), 3.82 (s, 3H), 3.79 (s, 6H), 2.22 (p, *J* = 3.1 Hz, 1H), 1.71 – 1.66 (m, 2H), 1.50 – 1.31 (m, 8H), 1.20 – 1.17 (m, 2H), 0.89 (s, 6H). **^{13}C NMR** (126 MHz, CDCl3) δ 161.94, 160.41, 150.54, 109.15, 91.09, 60.06, 56.22, 55.45, 51.10, 49.43, 43.15, 41.80, 32.64, 30.64, 30.58. **IR** ($CDCl_3$): 2941.61, 2900.74, 1603.93, 1454.47, 1412.65, 1330.95, 1227.91, 1206.31, 1155.86, 1128.06, 910.34, 812.82, 730.16 cm^{-1}. **HRMS-ESI** (positive) M = $C_{22}H_{31}NO_3$: calculated (M+H)+ m/z 359.2415; found (M+H)+ m/z 359.2417.

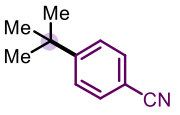
4. Product Synthesis and Characterization –

General Procedure B - *Deaminative arylation*



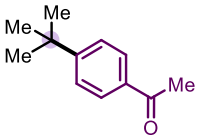
To a 1-dram vial equipped with a stir bar was added aryl bromide (0.1 mmol, 1 equiv), imine (0.2 mmol, 2 equiv), [Ir(dF-CF_3-ppy)$_2$dtbbpy]PF_6 (0.5 mol%), and *n*Bu_4NCl (5.54 mg, 20 mol%). The vial was then taken to a dry-glovebox and $Ni(TMHD)_2$ (4.25 mg, 10 mol%) and K_2HPO_4 (17.4 mg, 0.1 mmol, 1 equiv) were added (base can be added outside of the glovebox with the same result). DMSO (0.05 M) was added under an atmosphere of nitrogen. The vials were sealed with Teflon tape and illuminated with a Blue LED (Kessil, 34 W, 456 nm) for 48 h (a fan was set up to maintain room temperature). The reactions were then exposed to air and quenched with water, extracted with EtOAc (2x), washed with brine, and concentrated *in vacuo*. The crude mixture was then subjected to flash silica gel chromatography.

Note: if humidity levels are high, *n*Bu_4NCl should be stored in a dry atmosphere (in a desiccator or glovebox) to maintain yields.



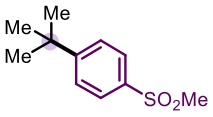
4-(*tert*-butyl)benzonitrile. Prepared according to General Procedure B from *N*-*tert*-butyl-1-(2,4,6-trimethoxyphenyl)methanimine (50.2 mg, 0.2 mmol) and 4-bromobenzonitrile (18.2 mg, 0.1 mmol). Colorless oil (14.9 mg, 94%). **1.0 mmol scale**: Prepared according to General Procedure B from *N*-*tert*-butyl-1-(2,4,6-trimethoxyphenyl)methanimine (502 mg, 2.0 mmol) and 4-bromobenzonitrile (182.0 mg, 1.0 mmol) and set up in a 50 mL schlenk tube, then irradiated with two 456-nm Kessil lamps. Yield (128.2 mg, 80%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 2H), 7.51 – 7.46 (m, 2H), 1.34 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.86, 132.14, 126.32, 119.19, 109.70, 35.44, 31.12.

Spectroscopic data matches with previously reported data.[5]



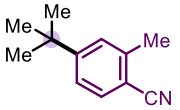
1-(4-(*tert*-butyl)phenyl)ethan-1-one. Prepared according to General Procedure B from *N*-*tert*-butyl-1-(2,4,6-trimethoxyphenyl)methanimine (50.2 mg, 0.2 mmol) and 1-(4-bromophenyl)ethan-1-one (19.9 mg, 0.1 mmol). Colorless oil (15.8 mg, 90%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 2.59 (s, 3H), 1.34 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.03, 156.98, 134.77, 128.44, 125.65, 35.26, 31.24, 26.71.

Spectroscopic data matches with previously reported data.[5]

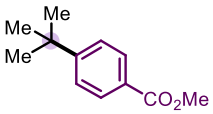


1-(*tert*-butyl)-4-(methylsulfonyl)benzene. Prepared according to General Procedure B from *N*-tert-butyl-1-(2,4,6-trimethoxyphenyl)methanimine (50.2 mg, 0.2 mmol) and 1-bromo-4-(methylsulfonyl)benzene (23.5 mg, 0.1 mmol). White solid (18.1 mg, 86%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 2H), 3.04 (s, 3H), 1.35 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.77, 137.74, 127.37, 126.49, 44.72, 35.40, 31.20.

Spectroscopic data matches with previously reported data.[5,6]

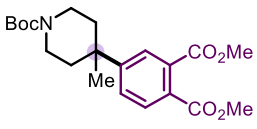


4-(*tert*-butyl)-2-methylbenzonitrile. Prepared according to General Procedure B from *N*-*tert*-butyl-1-(2,4,6-trimethoxyphenyl)methanimine (50.2 mg, 0.2 mmol) and 4-bromo-2-methylbenzonitrile (19.6 mg, 0.1 mmol). Colorless oil (15.1 mg, 87%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.1 Hz, 1H), 7.31 (d, *J* = 0.7 Hz, 1H), 7.29 – 7.27 (m, 1H), 2.54 (s, 3H), 1.31 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.47, 141.58, 132.30, 127.29, 123.43, 118.51, 109.72, 35.11, 30.97, 20.73. **IR** ($CDCl_3$): 2964.47, 2870.72, 2221.80, 1723.01, 1607.89, 1461.78, 1397.14, 1364.82, 1266.90, 1206.63, 1131.48, 904.46, 830.26, 730.36, 649.75, 617.72, 511.70, 443.48 cm^{-1}. **HRMS-ESI** (positive) M = $C_{12}H_{15}N$: calculated (M+H)+ m/z 174.1283; found (M+H)+ m/z 174.1289.



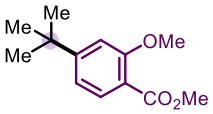
methyl 4-(*tert*-butyl)benzoate. Prepared according to General Procedure B from *N*-*tert*-butyl-1-(2,4,6-trimethoxyphenyl)methanimine (50.2 mg, 0.2 mmol) and methyl 4-bromobenzoate (21.5 mg, 0.1 mmol). Colorless oil (13.6 mg, 71%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.8 Hz, 2H), 7.45 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H), 1.34 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.31, 156.70, 129.59, 127.54, 125.49, 52.10, 35.23, 31.27.

Spectroscopic data matches with previously reported data.[6]



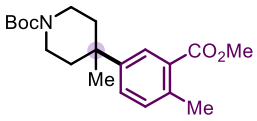
dimethyl 4-(1-(*tert*-butoxycarbonyl)-4-methylpiperidin-4-yl)phthalate. Prepared according to General Procedure B from *tert*-butyl-4-methyl-4-((2,4,6-trimethoxybenzylidene)amino)piperidine-1-carboxylate (78.4 mg, 0.2 mmol) and dimethyl 4-bromophthalate (27.3 mg, 0.1 mmol). Light yellow oil (13.3 mg, 60%). **R_f :** 0.3 in 30% EtOAc/hexanes. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 2.1 Hz, 1H), 7.49 (dd, *J* = 8.3, 2.1 Hz, 1H), 3.91 (s, 3H), 3.89 (s, 3H), 3.44 (tdd, *J* = 11.7, 9.4, 3.9 Hz, 4H), 2.18 – 1.93 (m, 2H), 1.76 – 1.63 (m, 2H), 1.44 (s, 9H), 1.27 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.49, 167.70, 154.86, 152.35, 132.62, 129.37, 129.16, 128.39, 126.25, 79.51, 52.68, 52.57, 36.90, 36.54, 28.44, 28.33. **IR** ($CDCl_3$): 2952.41, 1727.26, 1687.95, 1605.90, 1430.55, 1365.56, 1278.19, 1249.91, 1213.69, 1166.53, 1128.96, 1091.68, 1066.99, 966.12, 906.27, 861.92, 790.35, 772.02, 729.68,

647.96 cm^{-1}. **HRMS-ESI** (positive) M = $C_{21}H_{29}NO_6$: calculated (M+H)+ m/z 393.2132; found (M+H)+ m/z, 393.2374.

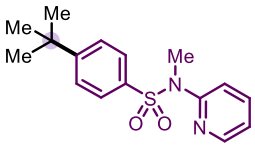


methyl 4-(*tert*-butyl)-2-methoxybenzoate. Prepared according to General Procedure B from *N*-tert-butyl-1-(2,4,6-trimethoxyphenyl)methanimine (50.2 mg, 0.2 mmol) and methyl 4-bromo-2-methoxybenzoate (24.5 mg, 0.1 mmol). Colorless oil (17.8 mg, 80%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 1H), 7.03 – 6.96 (m, 2H), 3.92 (s, 3H), 3.87 (s, 3H), 1.33 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.74, 159.33, 157.87, 131.67, 117.56, 117.21, 109.52, 56.12, 51.99, 35.43, 31.23.

Spectroscopic data matches with previously reported data.[6]

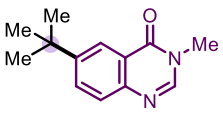


***tert*-butyl 4-(3-(methoxycarbonyl)-4-methylphenyl)-4-methylpiperidine-1-carboxylate.** Prepared according to General Procedure B from *tert*-butyl-4-methyl-4-((2,4,6-trimethoxybenzylidene)amino)piperidine-1-carboxylate (78.4 mg, 0.2 mmol) and methyl 5-bromo-2-methylbenzoate (22.9 mg, 0.1 mmol). Colorless oil (12.7 mg, 37%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 2.3 Hz, 1H), 7.36 (dd, *J* = 8.0, 2.3 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 3.89 (s, 3H), 3.48 (ddd, *J* = 13.7, 7.8, 3.6 Hz, 2H), 3.37 (ddd, *J* = 13.7, 7.7, 3.7 Hz, 2H), 2.56 (s, 3H), 2.05 (ddd, *J* = 11.6, 8.0, 3.8 Hz, 2H), 1.68 (ddd, *J* = 13.8, 7.7, 3.8 Hz, 2H), 1.45 (s, 9H), 1.25 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.42, 155.12, 145.87, 137.77, 132.08, 129.79, 129.60, 128.05, 79.50, 51.96 (d, *J* = 4.0 Hz), 36.85, 36.33, 32.06, 29.04, 28.61, 21.34. **IR** ($CDCl_3$): 2929.98, 1722.63, 1693.21, 1423.92, 1365.27, 1250.06, 1168.41, 1078.26, 967.69, 864.18, 830.38, 781.95 cm^{-1}. **HRMS-ESI** (positive) M = $C_{20}H_{29}NO_4$: calculated (M+Na)+ m/z 371.2027; found (M+H)+ m/z 371.2030.

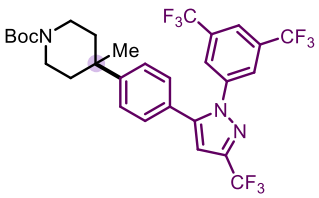


4-(*tert*-butyl)-*N*-methyl-N-(pyridin-2-yl)benzenesulfonamide.

Prepared according to General Procedure B from *N-tert*-butyl-1-(2,4,6-trimethoxyphenyl)methanimine (50.2 mg, 0.2 mmol) and 4-bromo-*N*-methyl-*N*-(pyridin-2-yl)benzenesulfonamide (32.7 mg, 0.1 mmol). Colorless oil (24.7 mg, 81%). **R_f:** 0.6 in 30% EtOAc/hexanes. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.32 – 8.27 (m, 1H), 7.75 – 7.66 (m, 2H), 7.50 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.11 (dd, *J* = 2.3, 1.2 Hz, 1H), 3.28 (s, 3H), 1.30 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.83, 153.95, 147.98, 137.68, 134.43, 127.51, 126.05, 121.10, 120.85, 35.58, 35.27, 31.18. **IR** ($CDCl_3$): 2962.94, 1588.87, 1467.43, 1434.86, 1351.87, 1268.50, 1179.80, 1159.53, 1112.37, 1085.14, 1068.29, 891.22, 873.98, 837.18, 785.97, 757.68, 711.66, 629.83, 585.56, 547.67 cm^{-1}. **HRMS-ASAP** (positive) M = $C_{16}H_{20}N_2O_2S$: calculated (M+H)+ m/z 306.1354; found (M+H)+ m/z 306.1353.

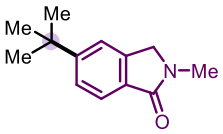


6-(*tert*-butyl)-3-methylquinazolin-4(3H)-one. Prepared according to General Procedure B from *N-tert*-butyl-1-(2,4,6-trimethoxyphenyl)methanimine (50.2 mg, 0.2 mmol) and 6-bromo-3-methylquinazolin-4(3*H*)-one (23.9 mg, 0.1 mmol). Colorless oil (12.8 mg, 58%). **R_f:** 0.1 in 30% EtOAc/hexanes. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 2.3 Hz, 1H), 8.01 (s, 1H), 7.81 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.65 (d, *J* = 8.6 Hz, 1H), 3.59 (s, 3H), 1.39 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.01, 150.98, 146.35 (d, *J* = 5.5 Hz), 132.34, 127.27, 122.43, 121.55, 35.22, 34.20, 31.43. **IR** ($CDCl_3$): 2960.31, 1870.07, 1671.22, 1607.34, 1491.96, 1466.00, 1364.38, 1337.63, 1357.29, 1211.59, 1131.39, 1058.17, 839.47, 795.09, 779.86, 615.11, 546.48 cm^{-1}. **HRMS-ASAP** (positive) M = $C_{13}H_{16}N_2O$: calculated (M+H)+ m/z 218.1372; found (M+H)+ m/z 218.1375.

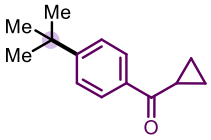


***tert*-butyl 4-(4-(1-(3,5-bis(trifluoromethyl)phenyl)-3-(trifluoromethyl)-1H-pyrazol-5-yl)phenyl)-4-methylpiperidine-1-carboxylate.** Prepared according to General Procedure B from 1-(3,5-bis(trifluoromethyl)phenyl)-5-(4-bromophenyl)-3-(trifluoromethyl)-1*H*-pyrazole (50.3 mg, 0.1 mmol) and *tert*-butyl-4-methyl-4-((2,4,6-trimethoxybenzylidene)amino)piperidine-1-carboxylate (78.4 mg, 0.2 mmol). Clear oil (31.0 mg, 50%). **R_f:** 0.2 in 10% EtOAc/hexanes. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.74 (s, 2H), 7.38

(d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.80 (s, 1H), 3.55 – 3.46 (m, 2H), 3.37 – 3.29 (m, 2H), 2.03 (m, 2H), 1.70 (m, 2H), 1.46 (s, 9H), 1.25 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.11, 150.71, 145.23, 140.31, 132.67 (q, *J* = 34.3 Hz), 129.32, 126.85, 126.01, 124.95, 123.73, 121.56, 106.78, 79.63, 36.88, 29.11, 28.58. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -61.65, -62.31. **IR** ($CDCl_3$): 2934.19, 1690.68, 1470.17, 1396.48, 1279.88, 1235.53, 1168.61, 1139.33, 972.47, 897.19, 814.06, 706.75, 681.15 cm^{-1}. **HRMS-ESI** (positive) M = $C_{29}H_{28}F_9N_3O_2$: calculated (M+Na)+ m/z 644.1935; found (M+H)+ m/z, 644.1922.

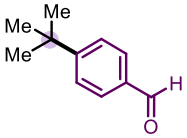


5-(*tert*-butyl)-2-methylisoindolin-1-one. Prepared according to General Procedure B from *N-tert*-butyl-1-(2,4,6-trimethoxyphenyl)methanimine (50.2 mg, 0.2 mmol) and 5-bromo-2-methylisoindolin-1-one (22.6 mg, 0.1 mmol). Light yellow oil (15.2 mg, 75%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 1H), 7.52 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.50 – 7.44 (d, *J* = 1.7 Hz, 1H), 4.37 (s, 2H), 3.21 (s, 3H), 1.38 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.91, 155.15, 141.26, 130.48, 125.56, 123.28, 119.52, 52.25, 35.40, 31.56, 29.61. **IR** ($CDCl_3$)**:** 2961.76, 1681.83, 1602.47, 1460.55, 1424.49, 1399.04, 1364.77, 1275.87, 1212.46, 1159.69, 1126.22, 908.81, 840.68, 776.93, 730.97, 698.88. **LRMS** (EI) [$C_{13}H_{17}NO$]: m/z calculated 203.13; found 203.1.

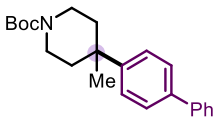


(4-(*tert*-butyl)phenyl)(cyclopropyl)methanone. Prepared according to General Procedure B from *N-tert*-butyl-1-(2,4,6-trimethoxyphenyl)methanimine (50.2 mg, 0.2 mmol) and (4-bromophenyl)(cyclopropyl)methanone (22.5 mg, 0.1 mmol). Clear oil (18.6 mg, 92%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.7 Hz, 2H), 7.50 (d, *J* = 8.7 Hz, 2H), 2.67 (m, 1H), 1.35 (s, 9H), 1.28 – 1.20 (m, 2H), 1.02 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 200.34, 156.54, 135.55, 128.13, 125.58, 35.21, 31.26, 17.10, 11.51.

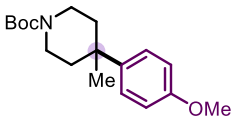
Spectroscopic data matches with previously reported data.[7]



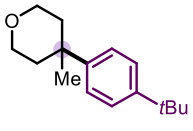
4-(*tert*-butyl)benzaldehyde. Prepared according to General Procedure B from *N-tert*-butyl-1-(2,4,6-trimethoxyphenyl)methanimine (50.2 mg, 0.2 mmol) and 4-bromobenzaldehyde (18.5 mg, 0.1 mmol). Colorless oil (9.6 mg, 59%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.82 (d, *J* = 8.9 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 1.36 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 192.21, 158.61, 134.24, 129.85, 126.15, 35.51, 31.23. Spectroscopic data matches with previously reported data.[5]



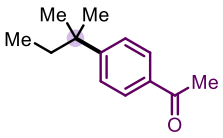
***tert*-butyl 4-([1,1'-biphenyl]-4-yl)-4-methylpiperidine-1-carboxylate**. Prepared according to General Procedure B from *tert*-butyl-4-methyl-4-((2,4,6-trimethoxybenzylidene)amino)piperidine-1-carboxylate (78.4 mg, 0.2 mmol), 4-iodo-1,1'-biphenyl (28.0 mg, 0.1 mmol), and LiCl (4.4 mg, 0.1 mmol). Clear oil (16.4 mg, 47%). **R_f:** 0.3 in 10% EtOAc/hexanes. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 – 7.56 (m, 4H), 7.49 – 7.40 (m, 4H), 7.39 – 7.32 (m, 1H), 3.54 (m, 2H), 3.48 – 3.42 (m, 2H), 2.13 (m, 2H), 1.73 (m, 2H), 1.48 (s, 9H), 1.32 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.02, 147.22, 140.78, 138.74, 128.75, 127.18, 127.15, 127.01, 126.18, 79.32, 36.73, 36.34, 29.10, 28.49. **IR** ($CDCl_3$): 2929.70, 1690.73, 1484.97, 1422.61, 1365.06, 1248.77, 1169.65, 1124.38, 1099.73, 908.39, 865.91, 836.33, 766.42, 733.14, 698.06 cm^{-1}. **HRMS-ESI** (positive) M = $C_{23}H_{29}NO_2$: calculated (M+Na)+ m/z 375.2129; found (M+H)+ m/z 375.2143.



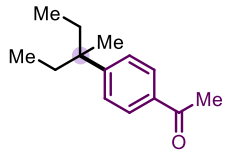
***tert*-butyl 4-(4-methoxyphenyl)-4-methylpiperidine-1-carboxylate**. Prepared according to General Procedure B from *tert*-butyl-4-methyl-4-((2,4,6-trimethoxybenzylidene)amino)piperidine-1-carboxylate (78.4 mg, 0.2 mmol), 1-iodo-4-methoxybenzene (23.4 mg, 0.1 mmol), and LiCl (4.4 mg, 0.1 mmol). Clear oil (11.6 mg, 38%). **R_f:** 0.2 in 10% EtOAc/hexanes. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.23 (m, 2H), 6.88 (m, 2H), 3.80 (s, 3H), 3.47 (m, 2H), 3.36 (m, 2H), 2.02 (m, 2H), 1.65 (m, 2H), 1.45 (s, 9H), 1.23 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.55, 155.02, 140.14, 126.73, 113.79, 79.26, 55.24, 36.91, 35.82, 29.27, 28.48. **IR** ($CDCl_3$): 2933.36, 1689.88, 1609.62, 1513.69, 1423.45, 1365.42, 1278.33, 1249.10, 1170.08, 1124.01, 1036.70, 908.99, 829.05, 732.09. **HRMS-ESI** (positive) M = $C_{18}H_{27}NO_3$: calculated (M+Na)+ m/z 328.1889; found (M+Na)+ m/z 328.1902.



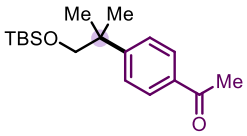
4-(4-(*tert*-butyl)phenyl)-4-methyltetrahydro-2*H*-pyran. Prepared according to General Procedure B from *N*-(4-methyltetrahydro-2*H*-pyran-4-yl)-1-(2,4,6-trimethoxyphenyl)methanimine (58.7 mg, 0.2 mmol) and 1-(tert-butyl)-4-iodobenzene (26.0 mg, 0.1 mmol) and LiCl (4.4 mg, 0.1 mmol). Clear oil (7.6 mg, 33%). **R_f:** 0.2 in 5% EtOAc/hexanes. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 3.79 – 3.74 (m, 2H), 3.72 – 3.66 (m, 2H), 2.10 (m, 2H), 1.77 – 1.69 (m, 2H), 1.32 (s, 9H), 1.29 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.35, 145.79, 128.68, 125.12 (d, *J* = 9.1 Hz), 64.40, 37.58, 35.08, 34.18, 32.90, 31.29 (d, *J* = 5.0 Hz). **IR** ($CDCl_3$): 2957.25, 2854.27, 1391.01, 1269.75, 1109.33, 1018.16, 828.14, 575.25 cm^{-1}. **LRMS** (EI) [$C_{16}H_{24}O$] m/z calculated 232.18; found 232.1.



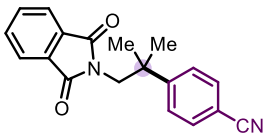
1-(4-(*tert*-pentyl)phenyl)ethan-1-one. Prepared according to General Procedure B from *N*-*tert*-pentyl-1-(2,4,6-trimethoxyphenyl)methanimine (53 mg, 0.2 mmol) and 1-(4-bromophenyl)ethan-1-one (19.9 mg, 0.1 mmol). Colorless oil (16.0 mg, 84%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.7 Hz, 2H), 7.42 (d, *J* = 8.7 Hz, 2H), 2.59 (s, 6H), 1.68 (q, *J* = 7.5 Hz, 2H), 0.68 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.05, 155.51, 134.72, 128.46, 126.33, 38.56, 36.83, 28.41, 26.68, 9.19. **IR** ($CDCl_3$) 2965.35, 2877.05, 1682.72, 1605.75, 1459.87, 1406.00, 1357.15, 1269.88, 1192.78, 1116.94, 1013.58, 957.10, 838.16, 628.60, 600.02, 556.88 cm^{-1}. **LRMS** (EI) [$C_{13}H_{18}O$] m/z calculated 190.14; found 190.1.



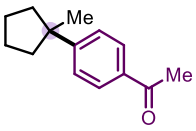
1-(4-(3-methylpentan-3-yl)phenyl)ethan-1-one. Prepared according to General Procedure B from *N*-(3-methylpentan-3-yl)-1-(2,4,6-trimethoxyphenyl)methanimine (55.8 mg, 0.2 mmol) and 1-(4-bromophenyl)ethan-1-one (19.9 mg, 0.1 mmol). Colorless oil (13.5 mg, 65%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 2.59 (s, 3H), 1.82 – 1.69 (m, 2H), 1.66 – 1.58 (m, 2H), 1.27 (s, 3H), 0.66 (t, *J* = 10 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.02, 153.81, 134.46, 128.10, 126.86, 55.34, 41.87, 35.18, 26.55, 22.60, 8.62. **IR** ($CDCl_3$): 2966.18, 2929.31, 1682.66, 1605.37, 1460.12, 1407.94, 1357.71, 1269.77, 1153.13, 956.52, 908.02, 825.51, 732.16, 600.94 cm^{-1}. **HRMS-ASAP** (positive) M = $C_{14}H_{20}O$: calculated (M+H)+ m/z 206.1626; found (M+H)+ m/z 206.1629.



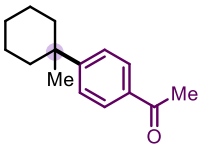
1-(4-(1-((*tert*-butyldimethylsilyl)oxy)-2-methylpropan-2-yl)phenyl)ethan-1-one. Prepared according to General Procedure B from *N*-(1-((*tert*-butyldimethylsilyl)oxy)-2-methylpropan-2-yl)-1-(2,4,6-trimethoxyphenyl)methanimine (76.2 mg, 0.2 mmol) and 1-(4-bromophenyl)ethan-1-one (19.9 mg, 0.1 mmol). Colorless oil (15.1 mg, 49%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 3.56 (s, 2H), 2.59 (s, 3H), 1.32 (s, 6H), 0.83 (s, 9H), -0.07 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.17, 153.78, 134.93, 128.12, 126.78, 72.61, 40.62, 26.73, 25.95, 25.36, 18.37, -5.49. **IR** ($CDCl_3$): 2929.68, 2856.4, 1684.30, 1806.32, 1359.65, 1270.48, 1092.35, 905.65, 837.08, 776.48, 731.30, 649.61 cm^{-1}. **HRMS-ASAP** (positive) M = $C_{18}H_{30}O_2Si$: calculated (M+H)+ m/z 308.2119; found (M+H)+ m/z 308.2123.



4-(1-(1,3-dioxoisoindolin-2-yl)-2-methylpropan-2-yl)benzonitrile. Prepared according to General Procedure B from 2-(2-methyl-2-((2,4,6-trimethoxybenzylidene)amino)propyl)isoindoline-1,3-dione (79.2 mg, 0.2 mmol) and 4-bromobenzonitrile (18.2 mg, 0.1 mmol). White solid (21.4 mg, 70%). **R_f:** 0.5 in 30% EtOAc/hexanes. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (dq, *J* = 5.0, 3.0 Hz, 1H), 7.72 (tt, *J* = 5.1, 2.5 Hz, 1H), 7.61 (dt, *J* = 5.0, 3.0 Hz, 1H), 7.58 – 7.52 (m, 1H), 3.81 (s, 0H), 1.43 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.65, 152.15, 134.27, 132.15, 127.32, 123.54, 119.09, 110.55, 49.38, 40.99, 26.82. **IR** ($CDCl_3$): 2973.15, 2228.18, 1775.54, 1714.61, 16.07.60, 1504.69, 1468.17, 1426.34, 1400.77, 1384.98, 1346.28, 1203.14, 1069.64, 1014.89, 910.46, 840.12, 727.69, 649.21, 569.43, 531.49 cm^{-1}. **HRMS-ASAP** (positive) M = $C_{19}H_{16}N_2O_2$: calculated (M+H)+ m/z 306.1322; found (M+H)+ m/z 306.1323.

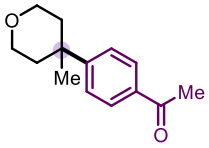


1-(4-(1-methylcyclopentyl)phenyl)ethan-1-one. Prepared according to General Procedure B from *N*-(1-methylcyclopentyl)-1-(2,4,6-trimethoxyphenyl)methanimine (55.4 mg, 0.2 mmol) and 1-(4-bromophenyl)ethan-1-one (19.9 mg, 0.1 mmol). Colorless oil (14.3 mg, 71%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 2.58 (s, 3H), 1.96 – 1.67 (m, 8H), 1.26 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.04, 157.37, 134.72, 128.45, 126.42, 47.65, 39.68, 29.39, 26.69, 23.82. **IR** ($CDCl_3$): 2957.48, 2871.01, 1681.90, 1604.85, 1564.01, 1405.92, 1358.02, 1271.04, 1190.16, 1086.59, 1014.49, 956.88, 904.67, 835.21, 727.86, 649.72, 599.76 cm^{-1}. **HRMS-ESI** (positive) M = $C_{14}H_{18}O$: calculated (M+H)+ m/z 204.1470; found (M+H)+ m/z, 204.1478.

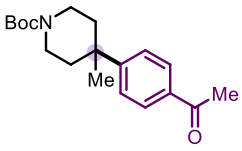


1-(4-(1-methylcyclohexyl)phenyl)ethan-1-one. Prepared according to General Procedure B from *N*-(1-methylcyclohexyl)-1-(2,4,6-trimethoxyphenyl)methanimine (58.2 mg, 0.2 mmol) and 1-(4-bromophenyl)ethan-1-one (19.9 mg, 0.1 mmol). Colorless oil (16.1 mg, 77%). **R_f :** 0.4 (10% EtOAc/hexanes). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 2.59 (s, 3H), 2.03 (dd, *J* = 9.0, 4.9 Hz, 2H), 1.64 – 1.52 (m, 4H), 1.43 (d, *J* = 5.1 Hz, 4H), 1.19 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.04, 155.99, 134.62, 128.57, 126.32, 38.65, 37.87, 26.68, 26.39, 22.75.

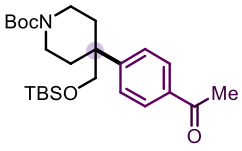
Spectroscopic data matches with previously reported data.[8]



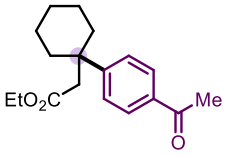
1-(4-(4-methyltetrahydro-2H-pyran-4-yl)phenyl)ethan-1-one. Prepared according to General Procedure B from *N*-(4-methyltetrahydro-2H-pyran-4-yl)-1-(2,4,6-trimethoxyphenyl)methanimine (58.6 mg, 0.2 mmol) and 1-(4-bromophenyl)ethan-1-one (19.9 mg, 0.1 mmol). Clear, colorless oil (12.9 mg, 59%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 3.77 (dd, *J* = 8.0, 3.3 Hz, 2H), 3.68 (dd, *J* = 6.8, 3.5 Hz, 2H), 2.60 (s, 4H), 2.12 (d, *J* = 3.7 Hz, 1H), 1.80 (d, *J* = 4.2 Hz, 0H), 1.31 (s, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.88, 154.78, 135.11, 128.78, 126.00, 64.49, 37.57, 36.30, 28.98, 26.70.
Spectroscopic data matches with previously reported data.[8]



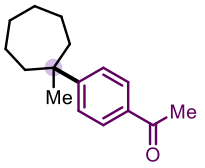
***tert*-butyl 4-(4-acetylphenyl)-4-methylpiperidine-1-carboxylate**. Prepared according to General Procedure B from *tert*-butyl-4-methyl-4-((2,4,6-trimethoxybenzylidene)amino)piperidine-1-carboxylate (78.4 mg, 0.2 mmol) and 1-(4-bromophenyl)ethan-1-one (19.9 mg, 0.1 mmol). Clear, colorless oil (22.9 mg, 72%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 3.48 (dd, *J* = 7.9, 3.7 Hz, 2H), 3.42 – 3.34 (m, 2H), 2.59 (s, 3H), 2.07 (s, 2H), 1.71 (s, 2H), 1.45 (s, 9H), 1.27 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.88, 155.06, 154.04, 135.13, 128.79, 126.12, 79.60, 37.09, 28.81, 28.59, 26.71.
Spectroscopic data matches with previously reported data.[8]



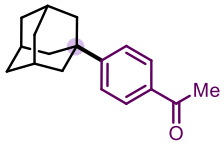
***tert*-butyl 4-(4-acetylphenyl)-4-(((*tert*-butyldimethylsilyl)oxy)methyl)piperidine-1-carboxylate.** Prepared according to General Procedure B from *tert*-butyl-4-(((*tert*-butyldimethylsilyl)oxy)methyl)-4-((2,4,6-trimethoxybenzylidene)amino)piperidine-1-carboxylate (104.4 mg, 0.2 mmol) and 1-(4-bromophenyl)ethan-1-one (19.9 mg, 0.1 mmol). Clear, colorless oil (21.9 mg, 49%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95 – 7.90 (m, 2H), 7.45 – 7.40 (m, 2H), 3.77 (m, 2H), 3.49 (s, 2H), 2.97 (m, 2H), 2.60 (s, 3H), 2.15 (m, 2H), 1.83 (m, 2H), 1.44 (s, 9H), 0.79 (s, 9H), -0.17 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.03, 155.16, 149.11, 135.29, 128.41, 127.77, 79.55, 71.89, 43.28, 31.50, 28.60, 26.73, 22.13, 18.32, -5.64. **IR** ($CDCl_3$): 2952.88, 2929.44, 1695.71, 1605.76, 1419.53, 1363.54, 1269.73, 1248.73, 1168.99, 1099.14, 1011.52, 837.84, 775.95, 596.45 cm^{-1}. **HRMS-ESI** (positive) M = $C_{25}H_{41}NO_4Si$: calculated (M+Na)+ m/z 470.4703; found (M+H)+ m/z, 470.2722.



ethyl 2-(1-(4-cyanophenyl)cyclohexyl)acetate. Prepared according to General Procedure B from ethyl (2-(1-((2,4,6-trimethoxybenzylidene)amino)cyclohexyl)acetate (72.6 mg, 0.2 mmol) and 1-(4-bromophenyl)ethan-1-one (19.9 mg, 0.1 mmol). Light yellow solid (11.2 mg, 41%). **R_f:** 0.2 in 10% EtOAc/hexanes. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 2H), 3.86 (q, *J* = 7.1 Hz, 2H), 2.59 (s, 3H), 2.54 (s, 2H), 2.26 – 2.17 (m, 2H), 1.86 – 1.76 (m, 2H), 1.64 – 1.57 (m, 2H), 1.49 – 1.35 (m, 4H), 0.99 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.01, 171.12, 135.02, 128.44, 127.18, 124.28, 60.06, 41.29, 36.25, 26.70, 26.22, 22.42, 14.15. **IR** ($CDCl_3$): 2931.75, 1729.34, 1681.89, 1605.48, 1454.17, 1271.21, 1150.00, 1032.68, 903.47, 725.15, 649.72 cm^{-1}. **HRMS-ASAP** (positive) M = $C_{18}H_{24}O_3$: calculated (M+H)+ m/z 290.1838; found (M+H)+ m/z 290.1831.

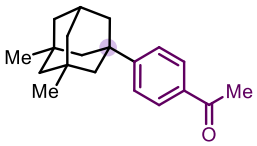


1-(4-(1-methylcycloheptyl)phenyl)ethan-1-one. Prepared according to General Procedure B from *N*-(1-methylcycloheptyl)-1-(2,4,6-trimethoxyphenyl)methanimine (71 mg, 0.2 mmol) and 1-(4-bromophenyl)ethan-1-one (19.9 mg, 0.1 mmol). Colorless oil (10.8 mg, 47%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 2.59 (s, 3H), 2.08 (d, *J* = 8.6 Hz, 1H), 1.71 (s, 1H), 1.51 (s, 10H), 1.23 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.05, 157.20, 134.55, 128.45, 126.38, 41.92, 40.80, 32.38, 30.02, 26.69, 23.82. **R_f:** 0.5 in 5% EtOAc/hexanes.
Spectroscopic data matches with previously reported data.[8]

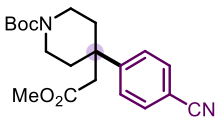


1-(4-((*3r*,*5r*,*7r*)-adamantan-1-yl)phenyl)ethan-1-one. Prepared according to General Procedure B from *N*-((*3r*,*5r*,*7r*)-adamantan-1-yl)-1-(2,4,6-trimethoxyphenyl)methanimine (69 mg, 0.2 mmol), 1-(4-bromophenyl)ethan-1-one (19.9 mg, 0.1 mmol), and $NiCl_2$dtbbpy$(H_2O)_4$ (4.7 mg, 0.01 mmol). White solid (17.6 mg, 69%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 2.59 (s, 4H), 2.12 (s, 3H), 1.93 (s, 6H), 1.85 – 1.72 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.10, 157.08, 134.79, 128.47, 125.27, 43.02, 36.84, 36.80, 28.94, 26.71.

Spectroscopic data matches with previously reported data.[5]

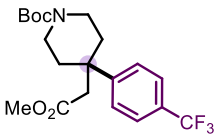


1-(4-((1r,3R,5S,7r)-3,5-dimethyladamantan-1-yl)phenyl)ethan-1-one. Prepared according to General Procedure B from N-((1r,3R,5S,7r)-3,5-dimethyladamantan-1-yl)-1-(2,4,6-trimethoxyphenyl)methanimine (71.4 mg, 0.2 mmol) and 1-(4-bromophenyl)ethan-1-one (19.9 mg, 0.1 mmol). Colorless oil (12.7 mg, 45%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 – 7.87 (m, 2H), 7.48 – 7.42 (m, 2H), 2.58 (s, 3H), 2.20 (hept, *J* = 3.3 Hz, 1H), 1.77 – 1.73 (m, 2H), 1.60 – 1.50 (m, 4H), 1.42 (q, *J* = 3.3 Hz, 4H), 1.28 – 1.16 (m, 2H), 0.89 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.98, 156.36, 134.70, 128.32, 125.26, 50.76, 49.24, 42.87, 41.47, 38.58, 31.52, 30.69, 29.89, 26.58. **IR** ($CDCl_3$): 2899.59, 2841.60, 1682.31, 1604.53, 1453.74, 1405.69, 1356.68, 1270.23, 1014.26, 903.86, 727.35, 649.62, 597.69. **HRMS-ASAP** (positive) M = $C_{20}H_{26}O$: calculated (M+H)+ m/z 284.2096; found (M+H)+ m/z 284.2097.

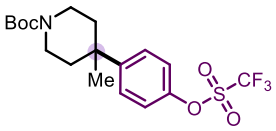


***tert*-butyl 4-(4-cyanophenyl)-4-(2-methoxy-2-oxoethyl)piperidine-1-carboxylate.** Prepared according to General Procedure B from *tert*-butyl 4 (2-methoxy-2-oxoethyl)-4-((2,4,6-trimethoxybenzylidene)amino)piperidine-1-carboxylate (90.1 mg, 0.2 mmol) and 4-bromobenzonitrile (18.2 mg, 0.1 mmol). Clear oil (20.2 mg, 56%). **R_f:** 0.2 in 30% EtOAc/hexanes. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.7 Hz, 2H), 7.43 (d, *J* = 8.7 Hz, 2H), 3.62 (m, 2H), 3.43 (s, 3H), 3.26 – 3.17 (m, 2H), 2.62 (s, 2H), 2.22 (m, 2H), 1.94 (m, 2H), 1.44 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.76, 154.92, 149.51, 132.44, 127.66, 118.82, 110.70, 79.92, 55.95, 51.54, 46.09, 39.77, 35.05, 28.55. **IR** ($CDCl_3$): 2973. 94, 2227.72, 1734.98, 1688.54, 1606.89, 1423.76, 1247.00, 1162.70,

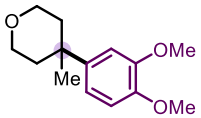
838.73 cm^{-1}. **HRMS-ESI** (positive) M = $C_{20}H_{26}N_2O_4$: calculated (M+Na)+ m/z 381.1790; found (M+Na)+ m/z 381.1800.



***tert*-butyl 4-(2-methoxy-2-oxoethyl)-4-(4-(trifluoromethyl)phenyl)piperidine-1-carboxylate.** Prepared accoridng to General Procedure B from *tert*-butyl 4 (2-methoxy-2-oxoethyl)-4-((2,4,6-trimethoxybenzylidene)amino)piperidine-1-carboxylate (90.1 mg, 0.2 mmol) and 1-bromo-4-(trifluoromethyl)benzene (22.5 mg, 0.1 mmol). Clear oil (26.0 mg, 65%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 3.70 – 3.60 (m, 2H), 3.42 (s, 3H), 3.20 (ddt, *J* = 13.8, 9.4, 4.8 Hz, 2H), 2.61 (s, 2H), 2.33 – 2.21 (m, 2H), 1.94 (ddd, *J* = 13.8, 9.4, 3.7 Hz, 2H), 1.44 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.94, 154.99, 147.84, 129.14, 128.82, 127.19, 125.60 (q, *J* = 3.7 Hz), 122.90, 79.78, 51.45, 46.63, 39.59, 35.17, 28.57. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.53. **IR** ($CDCl_3$): 2952, 1742, 1690, 1422, 1328.9, 1265.6, 1168.8, 1120.4, 1016.1, 800.2 cm^{-1}. **LRMS** (EI) [$C_{20}H_{26}F_3NO_4$]: m/z calculated 401.18, found 344.1 (loss of Boc *t*Bu).



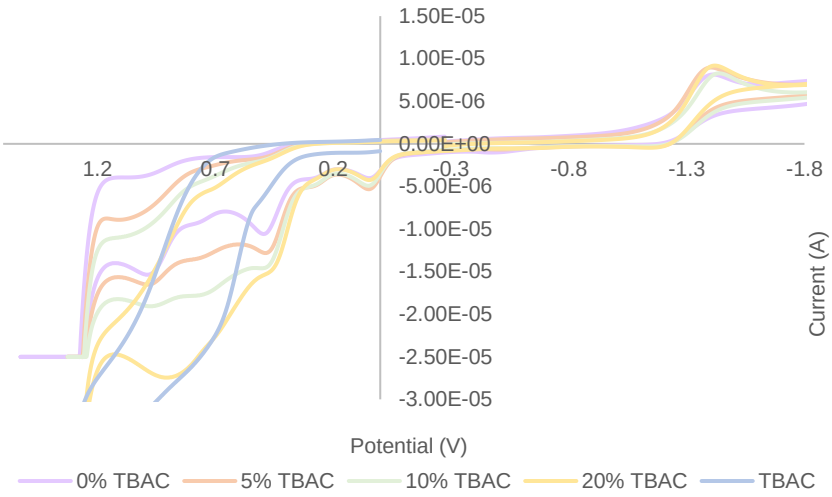
***tert*-butyl 4-methyl-4-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)piperidine-1-carboxylate.** Prepared according to Genral Procedure B from *tert*-butyl-4-methyl-4-((2,4,6-trimethoxybenzylidene)amino)piperidine-1-carboxylate (78.4 mg, 0.2 mmol) and 4-iodophenyl trifluoromethanesulfonate (35.2 mg, 0.1 mmol). Clear oil (28.9 mg, 68%). **R_f:** 0.5 in 30% EtOAc/hexanes. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 9.0 Hz, 2H), 7.23 (d, *J* = 8.9 Hz, 2H), 3.44 (dd, *J* = 7.2, 4.5 Hz, 4H), 2.00 (dt, *J* = 12.7, 6.0 Hz, 2H), 1.70 (dt, *J* = 13.2, 5.3 Hz, 2H), 1.45 (s, 9H), 1.27 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.03, 149.24, 147.77, 127.73, 121.36, 117.66 (d, *J* = 69.7 Hz), 79.67, 40.45, 36.89, 36.63, 28.60, 28.46. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -72.89. **IR** ($CDCl_3$): 2973.61, 2932.69, 1691.18, 1503.58, 1422.90, 1249.80, 1211.81, 1141.50, 890.51, 839.54 cm^{-1}. **HRMS-ESI** (positive) M = $C_{18}H_{24}F_3NO_5S$: calculated (M+Na)+ m/z 446.1225; found (M+H)+ m/z 446.1237.



4-(3,4-dimethoxyphenyl)-4-methyltetrahydro-2*H*-pyran. Prepared according to General Procedure B from *N*-(4-methyltetrahydro-2H-pyran-4-yl)-1-(2,4,6-trimethoxyphenyl)methanimine (58.7 mg, 0.2 mmol) and 4-iodo-1,2-dimethoxybenzene (26.4 mg, 0.1 mmol) and LiCl (4.4 mg, 0.1 mmol). Off-white solid (6.8 mg, 29%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.85 (m, 3H), 3.89 (s, 3H), 3.88 (s, 3H), 3.75 (m, 2H), 3.71 (m, 2H), 2.08 (m, 2H), 1.78 – 1.69 (m, 2H), 1.29 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.95, 147.25, 141.88, 117.77, 111.16, 109.53, 68.21, 64.62, 56.10, 56.00, 38.02, 35.48, 33.14, 29.85. **IR** ($CDCl_3$): 2922.93, 2849.83, 1589.78, 1462.53, 1260.02, 1244.75, 1147.80, 1029.12, 849.86, 806.15, 766.17 cm^{-1}. **LRMS** (EI) [$C_{14}H_{20}O_3$] m/z calculated 236.14; found 236.1.

5. Electrochemical Data –

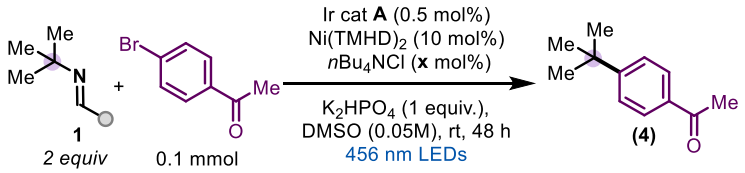
Samples were prepared with 0.2 mmol of $Ni(TMHD)_2$ in 2 mL of 0.1 M tetra-*N*-butylammonium hexafluorophosphate in dry, degassed acetonitrile. 100 μL of DMSO was used to solubilize the nickel catalyst. Measurements were taken using a glassy carbon working electrode, silver pseudo reference electrode and platinum counter electrode. Ferrocene was added as a reference after each experiment, and the graphs were normalized accordingly. The scan rate was set at 100 mV/s. TBAC solutions in MeCN were added to achieve 5%, 10%, 20% loading relative to the nickel catalyst. The last scan is TBAC alone.



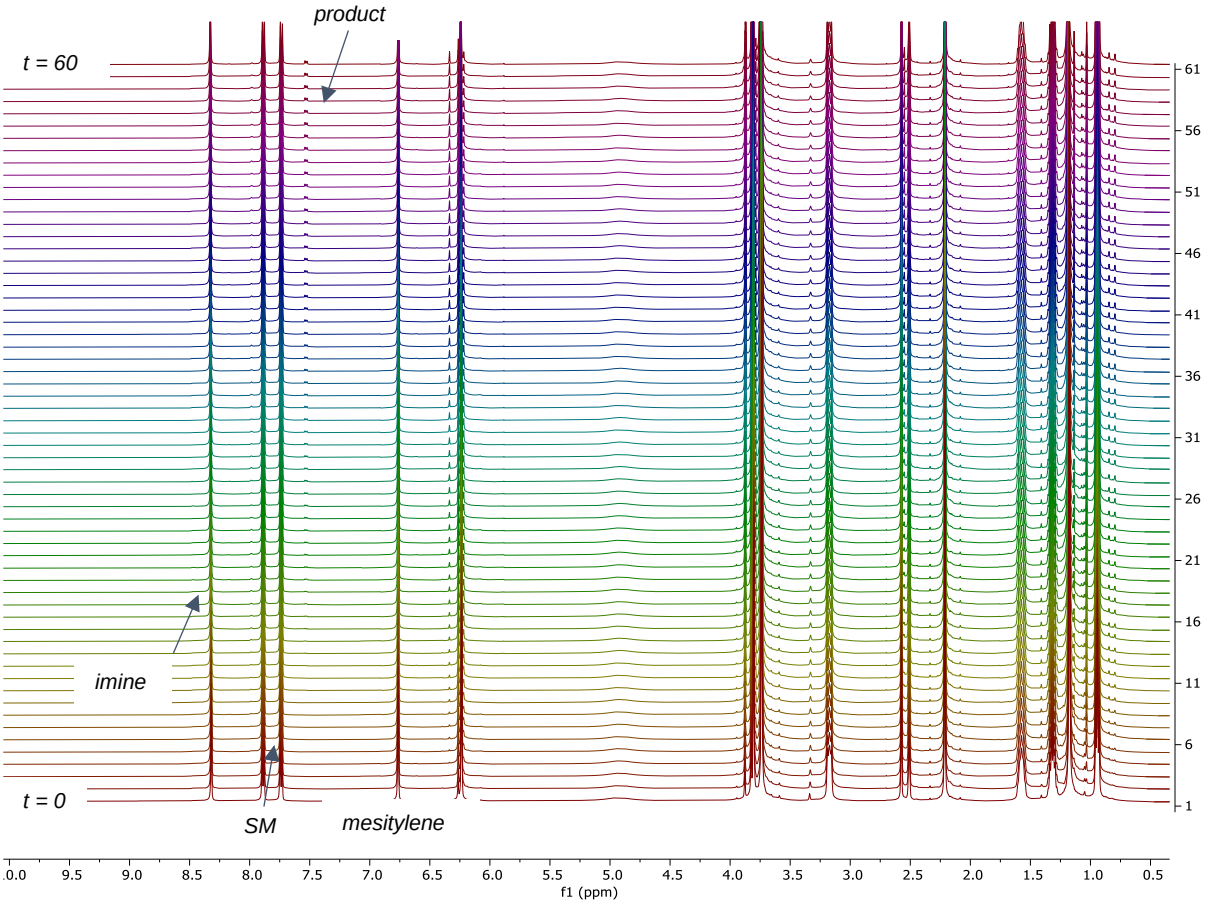
6. Kinetics Data

All LED-NMR experiments were run on a Bruker 500 MHz instrument equipped with the IDX probe using LED (λ = 420 nm).[9,10] The reaction was set up according to General Procedure B. *N-tert*-butyl-1-(2,4,6-trimethoxyphenyl)methanimine (0.1 mmol, 25.1 mg) was weighed outside the glove box and placed in a 1dr vial equipped with stir bar. The vial was brought into an N_2-filled glovebox. To this flask was added $Ni(TMHD)_2$ (4.25 mg, 0.01 mmol) and 0.1 mL of a stock solution of catalyst, $[Ir(dF\text{-}CF_3\text{-}ppy)_2(dtbbpy)]PF6$ (0.0005 mmol, 0.5 mg), 1-(4-bromophenyl)ethan-1-one (19.9 mg, 0.1 mmol) and $n Bu_4NCl$, followed by diluting the mixture up to a final volume of 2.0 mL DMSO-d_6. A 400 μl aliquot from this solution was transferred into a 5 mm thin wall NMR tube followed by the placement of the coaxial insert. The cap was then placed over the NMR tube and was sealed using Parafilm®. The sample was then wrapped in aluminum foil and brought out of the glovebox. Prior to the sample being placed inside the LED NMR setup the aluminum foil was removed. Mesitylene was used as the internal standard. For one-hour initial rate reactions, the reactions were run in duplicate and shown is the average yield of two experiments.

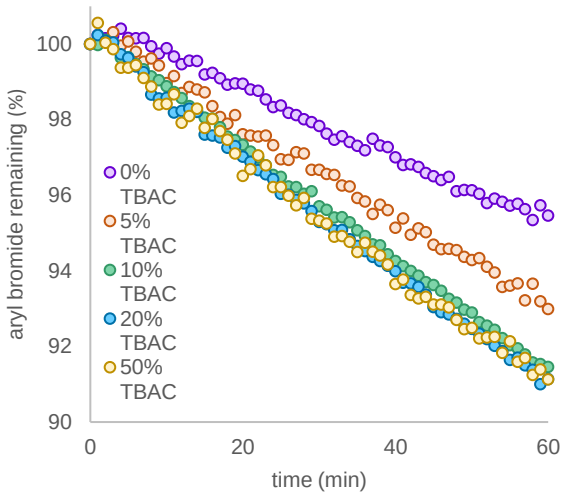
LED-NMR model reaction:

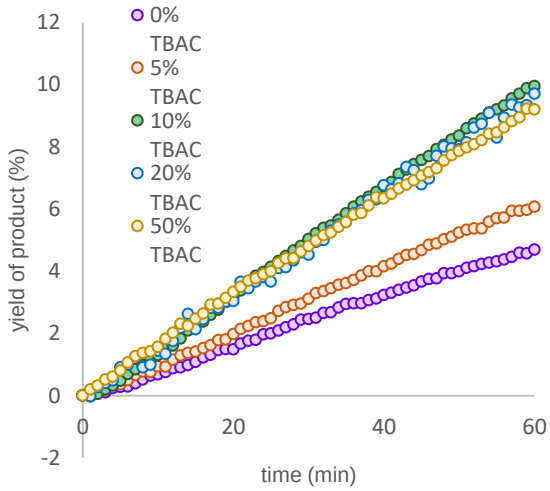


Model NMR Spectrum:



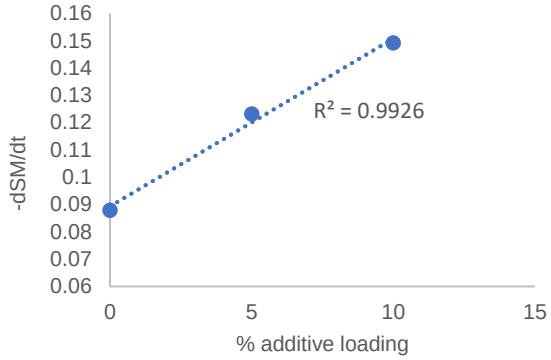
	TBAC equivalents									
	aryl halide					product				
time (min)	0%	5%	10%	20%	50%	0%	5%	10%	20%	50%
0	100	100	100	100	100	0	0	0	0	0
1	100.2367	100.0659	99.97301	100.2328	100.5595	0.0306	0.02355	-0.03375	-0.01575	0.1911
2	100.1507	100.3144	100.1052	100.0788	100.031	0.0615	0.2238	0.0477	0.26445	0.31815
3	100.2188	99.95595	99.89958	100.0365	99.86543	0.101775	0.1815	0.194175	0.402	0.515025
4	100.4044	100.0675	99.63817	99.72802	99.36857	0.236175	0.384	0.321975	0.4791	0.6045
5	100.1563	99.79112	99.65146	99.63372	99.36815	0.274275	0.357075	0.471525	0.9048	0.8055
6	100.1507	99.5356	99.46651	99.4014	99.4366	0.2919	0.491175	0.6927	0.98265	1.062675
7	100.1572	99.61594	99.32662	99.25353	99.10414	0.39165	0.6576	0.842475	1.25895	1.26915
8	99.94212	99.43143	99.14478	98.65598	98.86927	0.510375	0.766125	0.981225	0.90075	1.3725
9	99.74566	98.9679	99.04302	98.56063	98.39662	0.63825	0.751725	1.128825	0.9912	1.417425
10	99.88874	99.14855	98.87991	98.57258	98.41627	0.6771	0.93345	1.2975	1.4409	1.5627
11	99.66493	98.70127	98.73188	98.18214	98.66501	0.7506	0.924	1.4892	1.332	1.8228
12	99.4629	98.86748	98.56518	98.22876	97.91519	0.871875	1.153425	1.607475	1.7532	2.01105
13	99.55448	98.79413	98.35699	98.28405	98.09067	0.904425	1.281975	1.827825	2.1714	2.3016
14	99.54954	98.72163	98.21164	98.2004	98.28727	0.9765	1.368975	2.086875	2.62275	2.245275
15	99.19304	98.35569	98.04925	97.60101	97.78274	1.078575	1.404075	2.258175	2.12865	2.47005
16	99.23948	98.06326	98.02812	97.57501	98.01601	1.225125	1.51785	2.380275	2.4495	2.6292
17	99.08962	97.88868	97.79714	97.52432	97.6957	1.30965	1.614375	2.594325	2.8224	2.922225
18	98.92615	98.11762	97.55118	97.25798	97.46666	1.45995	1.7832	2.7585	2.8161	2.9556
19	98.95445	97.60756	97.45466	97.2937	97.10474	1.488075	1.80225	3.0006	3.00975	3.139275
20	98.9443	97.57681	97.32911	97.01633	96.50775	1.4826	1.977225	3.176925	3.03675	3.3282
21	98.79899	97.55467	97.15248	96.88002	96.69087	1.66755	2.1369	3.3723	3.6474	3.492375
22	98.76446	97.57296	96.99001	96.65807	97.05061	1.75875	2.22885	3.573375	3.4464	3.688725
23	98.53323	97.32476	96.78877	96.55524	96.79158	1.791825	2.35305	3.8415	3.66495	3.76395
24	98.32579	96.95148	96.53688	96.42522	96.21129	1.962	2.385	3.9657	3.8043	3.898125
25	98.37248	96.92975	96.48098	96.03649	96.21522	1.990725	2.48025	4.13235	3.6654	3.9912
26	98.17497	97.1329	96.23401	96.00615	95.98107	2.090175	2.71515	4.3212	4.09635	4.262325
27	98.12124	97.10273	96.21508	95.87719	95.73142	2.188125	2.838375	4.4832	4.12305	4.39935
28	98.01137	96.67122	96.03221	95.77987	95.92712	2.279625	2.910975	4.65615	4.3404	4.410075
29	97.93442	96.669	96.10258	95.57513	95.37761	2.435175	2.94645	4.801125	4.59225	4.62495
30	97.82887	96.56249	95.70764	95.29028	95.3275	2.455425	3.101625	5.02935	4.52835	4.803525
31	97.62645	96.53375	95.61322	95.23315	95.25202	2.50365	3.287325	5.211075	4.93965	4.9818
32	97.4631	96.25156	95.41171	95.06846	94.89781	2.6493	3.3483	5.390325	4.99485	5.153775
33	97.56322	96.23345	95.41878	95.07857	94.91415	2.67735	3.448575	5.455875	5.29635	5.235525
34	97.40773	95.92157	95.28422	94.8364	94.764	2.83095	3.558825	5.645475	5.4909	5.421675
35	97.30317	95.83135	95.06635	94.65661	94.49018	2.94495	3.6108	5.851875	5.57115	5.57085
36	97.18867	95.49981	94.92019	94.52003	94.7424	2.958075	3.7101	6.06945	5.84835	5.811975
37	97.48814	95.74633	94.6933	94.37045	94.50515	2.96415	3.858	6.2319	5.94975	5.8584
38	97.31481	95.60496	94.6759	94.25974	94.40519	3.064725	3.992025	6.3867	6.28485	6.105
39	97.26985	95.13553	94.43679	94.12841	94.16218	3.115725	3.988125	6.541125	6.3078	6.36585
40	97.00227	95.38213	94.26076	93.98473	93.64764	3.2247	4.1499	6.730275	6.75405	6.3366
41	96.80092	94.95542	94.11962	93.67769	93.76203	3.301725	4.2363	6.85605	6.62115	6.48105
42	96.81837	95.1233	93.99841	93.66403	93.35835	3.396825	4.394475	7.11375	6.8157	6.654375
43	96.74965	95.02017	93.86859	93.57223	93.26831	3.46725	4.51185	7.25685	7.34415	6.7782
44	96.58473	94.68814	93.7016	93.37169	93.30797	3.5379	4.54665	7.434375	7.2363	6.9129
45	96.49939	94.56687	93.61977	93.04022	93.10448	3.65625	4.663875	7.56855	6.78855	7.06305
46	96.40016	94.57558	93.47063	92.90061	93.10167	3.745275	4.839225	7.696125	6.9723	7.176075
47	96.48482	94.54324	93.25959	92.8402	93.0265	3.76455	4.88325	7.9197	7.7067	7.296675
48	96.10174	94.36389	93.15682	92.72095	92.69843	3.929925	5.02065	8.05755	8.00115	7.54425
49	96.13607	94.28403	92.96658	92.59619	92.45106	3.93345	5.099025	8.22915	7.94265	7.72365
50	96.12807	94.33012	92.89621	92.46224	92.48823	3.990825	5.23365	8.35515	7.90845	7.855125
51	96.03729	94.1028	92.64172	92.33314	92.21161	4.099275	5.32215	8.5887	8.13015	7.968675
52	95.7916	93.95128	92.55059	92.19314	92.23088	4.154325	5.36625	8.7405	8.60445	8.0739
53	95.90507	93.56819	92.43486	92.01204	92.25082	4.225275	5.3724	8.899125	8.73135	8.209125
54	95.82023	93.60465	92.21351	91.86902	91.82538	4.271925	5.581875	9.0864	9.0783	8.4138
55	95.72333	93.66789	92.02913	91.63762	92.12961	4.3047	5.6949	9.192975	8.28645	8.4498
56	95.77134	93.21966	91.94415	91.70105	91.58645	4.37535	5.714775	9.315525	8.92905	8.6214
57	95.63258	93.65824	91.78303	91.49631	91.6932	4.4574	5.93835	9.54345	9.34575	8.816325
58	95.34397	93.18864	91.57474	91.3814	91.24509	4.5912	5.93415	9.7014	9.25635	8.935425
59	95.73188	92.98591	91.53228	90.99568	91.38339	4.563825	5.962725	9.876975	9.3309	9.219675
60	95.45633	92.7281	91.45116	91.13266	91.12235	4.6848	6.0681	9.94275	9.6957	9.194025





The slopes of the starting material consumption are shown below.

additive loading(%)	*slope (-)*	*accel.*
0	0.0878	1
5	0.1231	1.40205
10	0.1492	1.699317
20	0.1544	1.758542
50	0.153	1.742597

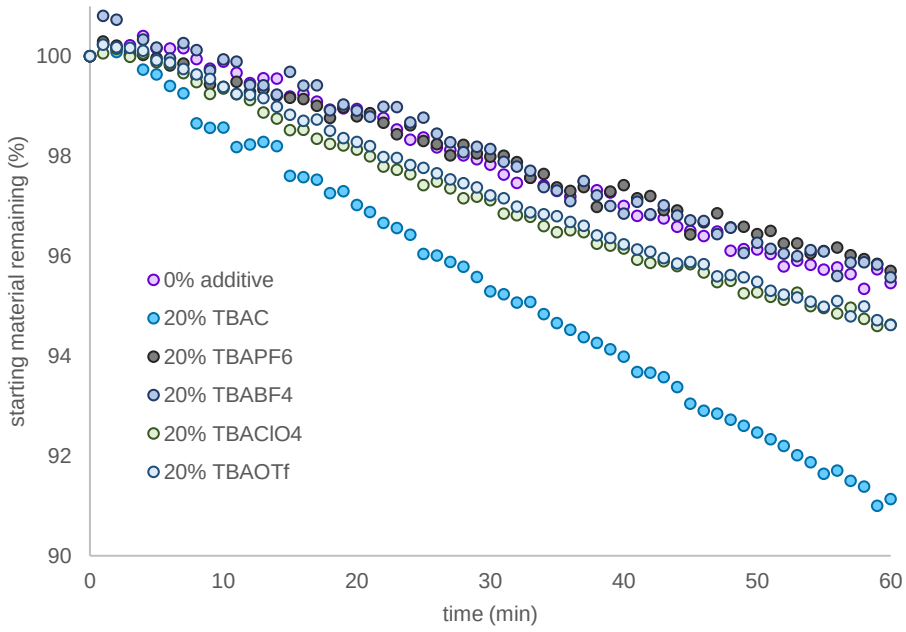


Using other anions –

Kinetic experiments were taken of other additives in the form of TBAX, where X = PF_6, BF_4, ClO_4, and OTf and set up according to the procedure mentioned above.

		Starting material remaining		
time	TBAPF6	TBABF4	TBAClO4	TBAOTf
0	100	100	100	100
1	100.2929	100.8079	100.0538	100.2285
2	100.2096	100.7288	100.1487	100.1799
3	100.0142	100.0992	99.98321	100.1645
4	100.0237	100.3339	100.0544	100.1104
5	99.95692	100.169	99.87384	99.91405
6	99.81006	99.95678	99.83858	99.86863
7	99.85246	100.2636	99.65901	99.74153
8	99.59248	100.1203	99.48249	99.6324
9	99.43391	99.71328	99.24256	99.54077
10	99.38185	99.93415	99.35125	99.38338
11	99.48852	99.88838	99.23408	99.24382
12	99.28196	99.42027	99.11793	99.22505
13	99.33792	99.41618	98.86816	99.15613
14	99.20937	99.22679	98.74625	98.98723
15	99.16308	99.68708	98.51683	98.82654
16	99.14239	99.40665	98.52344	98.70305
17	99.00536	99.41465	98.34625	98.72892

18	98.76132	98.91761	98.24281	98.5064
19	98.97178	99.03417	98.20924	98.36021
20	98.79676	98.90672	98.12463	98.28215
21	98.85561	98.78472	97.99457	98.19636
22	98.66296	98.98823	97.78652	97.97746
23	98.43435	98.97819	97.72463	97.96422
24	98.61157	98.67531	97.63188	97.82102
25	98.30258	98.76855	97.41738	97.75999
26	98.23848	98.45104	97.48877	97.65212
27	98.0114	98.2722	97.35379	97.534
28	98.22338	98.07805	97.1554	97.45783
29	98.04871	98.18746	97.18745	97.3722
30	97.98375	98.14032	97.11437	97.21245
31	98.00631	97.88372	96.84561	97.15568
32	97.87606	97.79065	96.81357	96.98662
33	97.56402	97.70778	96.7822	96.87213
34	97.63881	97.3758	96.59771	96.83097
35	97.3695	97.30977	96.47427	96.79391
36	97.30302	97.09605	96.51106	96.67689
37	97.37544	97.49848	96.47647	96.60624
38	96.98199	97.21448	96.24604	96.41321
39	97.28589	96.99787	96.20382	96.35912
40	97.41817	96.84524	96.14667	96.22854
41	97.15599	97.08159	95.92488	96.12824
42	97.19584	96.83571	95.86299	96.08346
43	96.91449	97.01557	95.89351	95.95304
44	96.91229	96.80712	95.79279	95.84738
45	96.43116	96.71507	95.83586	95.88207
46	96.67215	96.69703	95.6702	95.8346
47	96.85107	96.43396	95.47554	95.59079
48	96.57023	96.56175	95.50047	95.61603
49	96.58702	96.05655	95.24985	95.56982
50	96.43913	96.26261	95.27359	95.48308
51	96.50002	96.14282	95.18084	95.30504
52	96.24919	96.04532	95.12387	95.22272
53	96.25242	95.99206	95.26223	95.17115
54	96.05094	96.11474	94.99517	95.08394
55	96.09928	96.09143	94.95651	94.97938
56	96.16898	95.59456	94.8468	95.09718
57	96.01109	95.8692	94.9621	94.78966
58	95.93596	95.87107	94.73879	94.98663
59	95.84337	95.82751	94.59907	94.71018
60	95.70261	95.57125	94.62348	94.6195



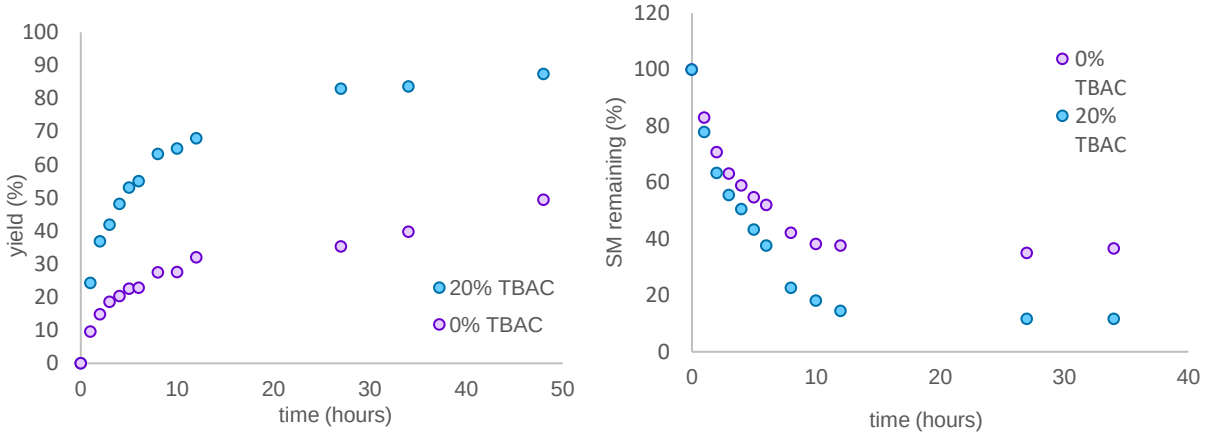
Although none of these additives show as significant of a rate enhancement as TBACl, $TBAClO_4$ and TBAOTf do show a slight rate enhancement. Below are the slopes and the relative rate increase compared to no additive loading.

anion	*slope (-)*	*accel.*
0%	0.0878	1
PF6	0.0762	0.867882
BF4	0.0867	0.987472
ClO4	0.0968	1.102506
OTf	0.0976	1.111617
Cl-	0.1544	1.758542

To obtain data for the full 48-hour experiment, the same model reaction was set up according to General Procedure B in DMSO-d_6 with mesitylene (0.1 mmol) as an internal standard. 20 μL aliquots were taken at the specified times and further diluted, then analyzed by ^{1}HNMR.

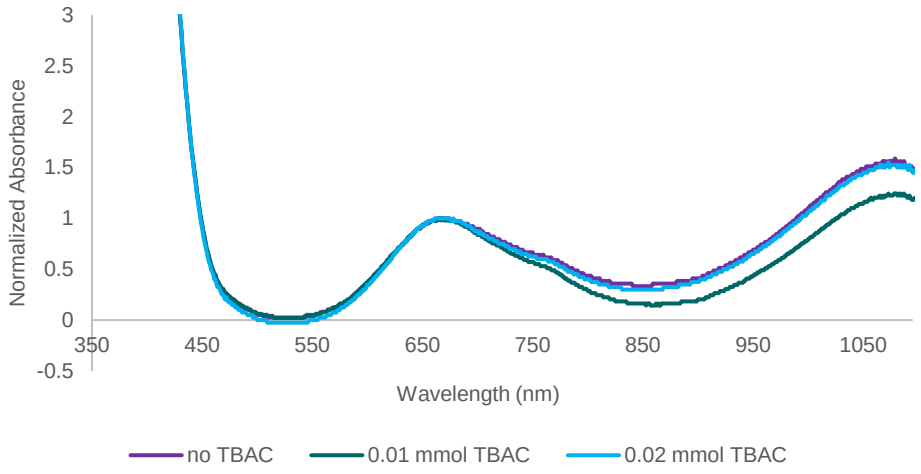
time (hours)	*product/IS*		*yield of product(%)*		*SM/IS*		*SM remaining*	
	0% TBAC	*20% TBAC*	*0% TBAC*	*20% TBAC*	*0% TBAC*	*20% TBAC*	*0% TBAC*	*20% TBAC*
0	0	0	0	0	0.1	0.1	100	100
1	0.009536	0.02423775	9.53571429	24.23775216	0.082944	0.077875	82.94379	77.875
2	0.014763	0.0368572	14.7630332	36.8572028	0.070795	0.063428	70.79545	63.4276
3	0.01861	0.04186166	18.6102418	41.86166008	0.063142	0.055597	63.14189	55.59684
4	0.020288	0.04811182	20.2876526	48.11181507	0.058958	0.050605	58.95773	50.60469
5	0.022488	0.05309659	22.4879679	53.09659091	0.054756	0.043327	54.75586	43.32682
6	0.022812	0.0549984	22.8124535	54.99839798	0.052035	0.037681	52.03466	37.68145
8	0.027429	0.06326657	27.4293056	63.26657264	0.042221	0.022704	42.22139	22.7044

10	0.027528	0.0648414	27.527907	64.84140297	0.038195	0.018087	38.19482	18.0871
12	0.031997	0.06791217	31.9968406	67.91216518	0.037681	0.014511	37.68145	14.51087
27	0.035332	0.08295873	35.3321759	82.95873181	0.035044	0.011635	35.04375	11.63453
34	0.039766	0.08357317	39.7659574	83.57317073	0.036567	0.011681	36.56739	11.68125
48	0.049444	0.0873577	49.4444444	87.35769598				

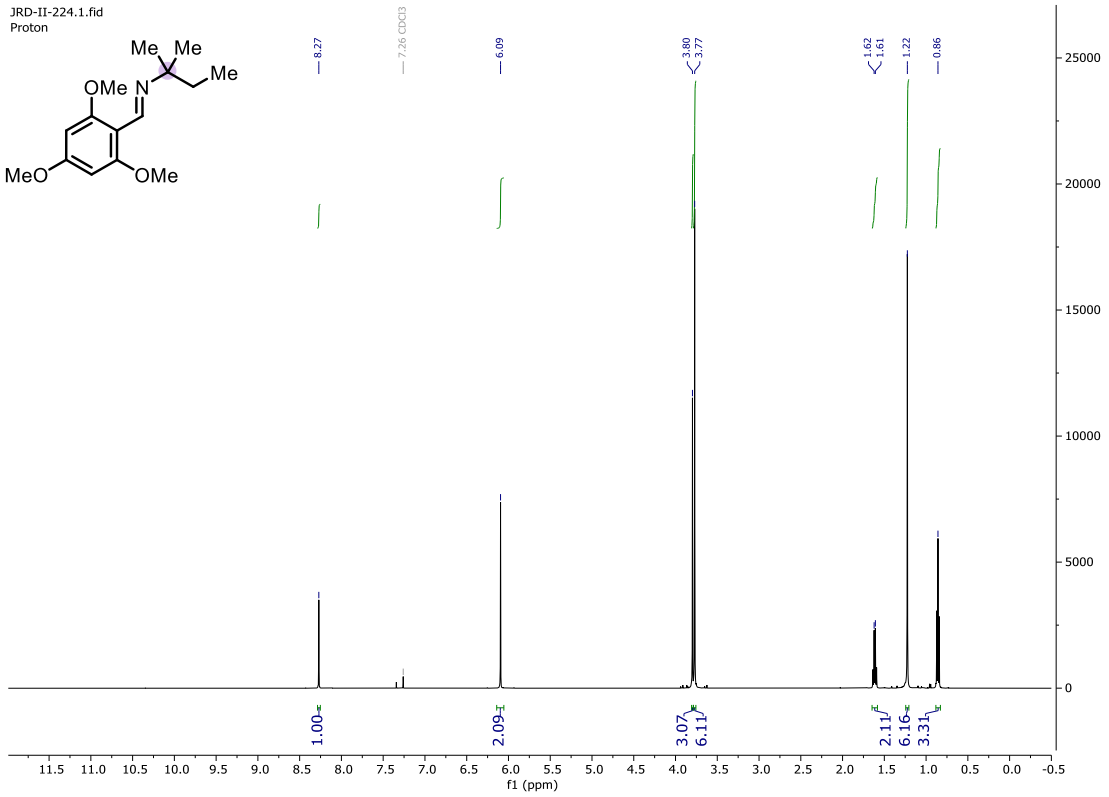


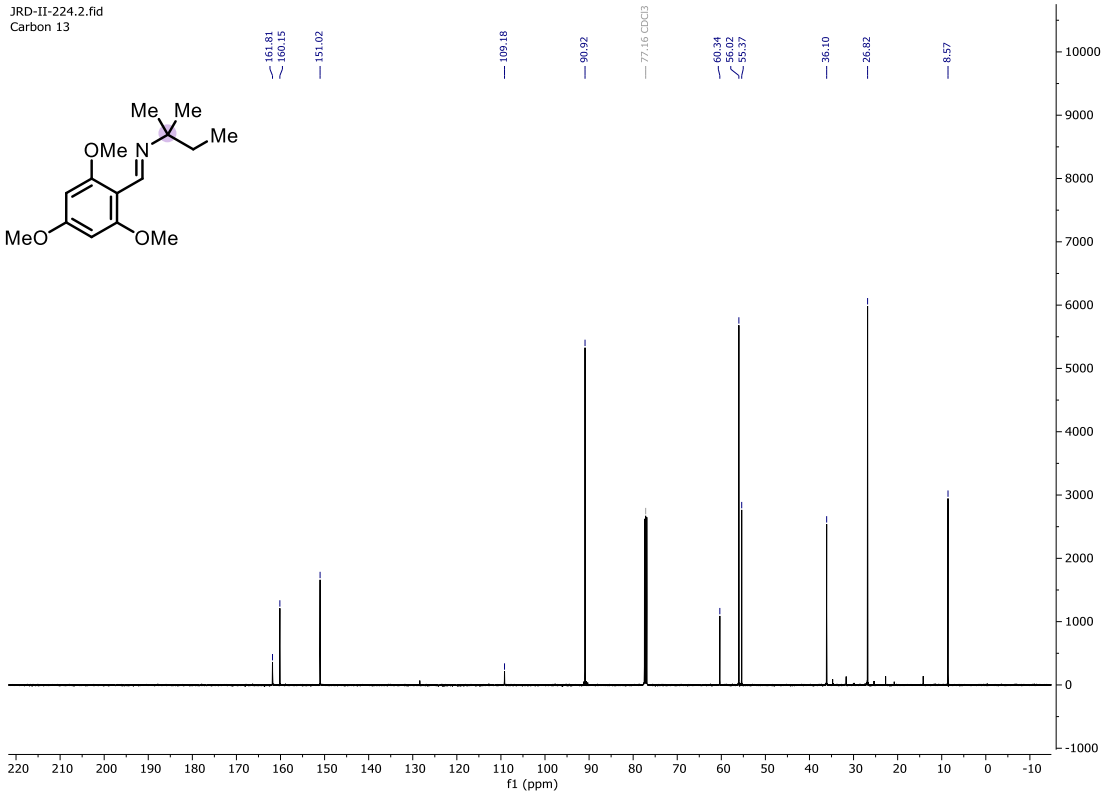
7. UV-Vis Data

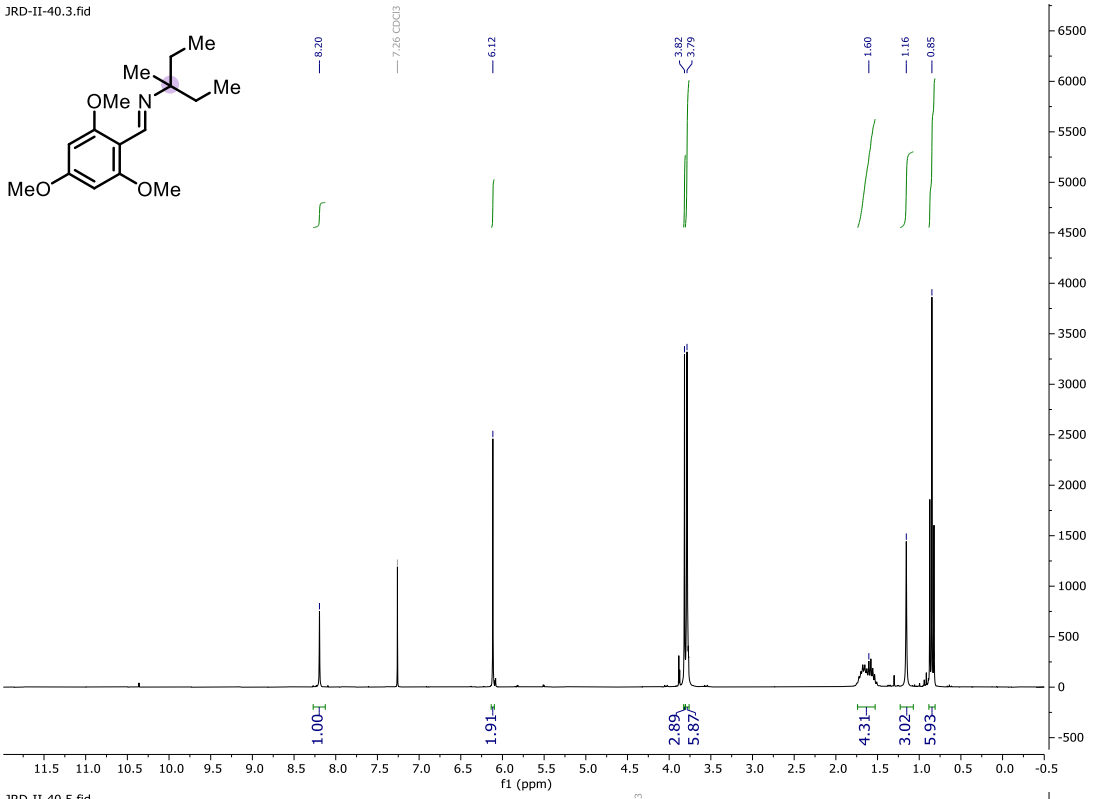
Samples were taken using 0.02 mmol of $Ni(TMHD)_2$ and 0, 0.01, and 0.02 mmol of nBu$_4$NCl in 2 mL of DMSO. The window of excitation was 350-1100 nm.

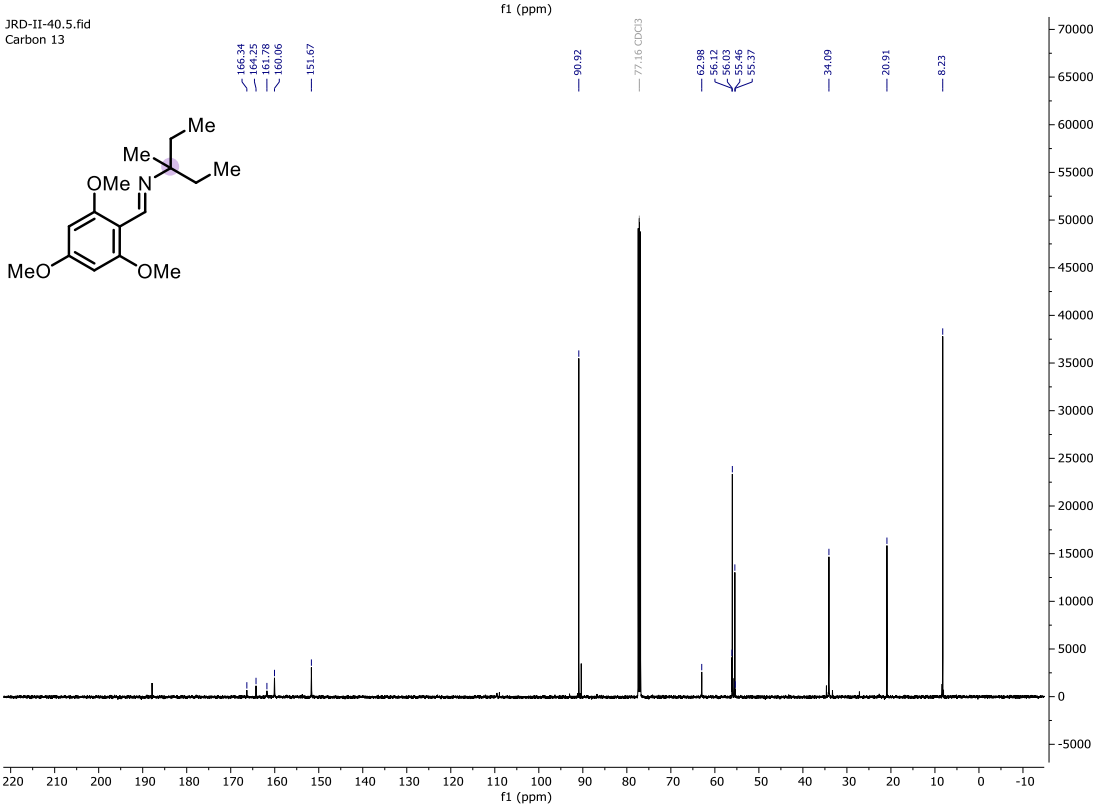


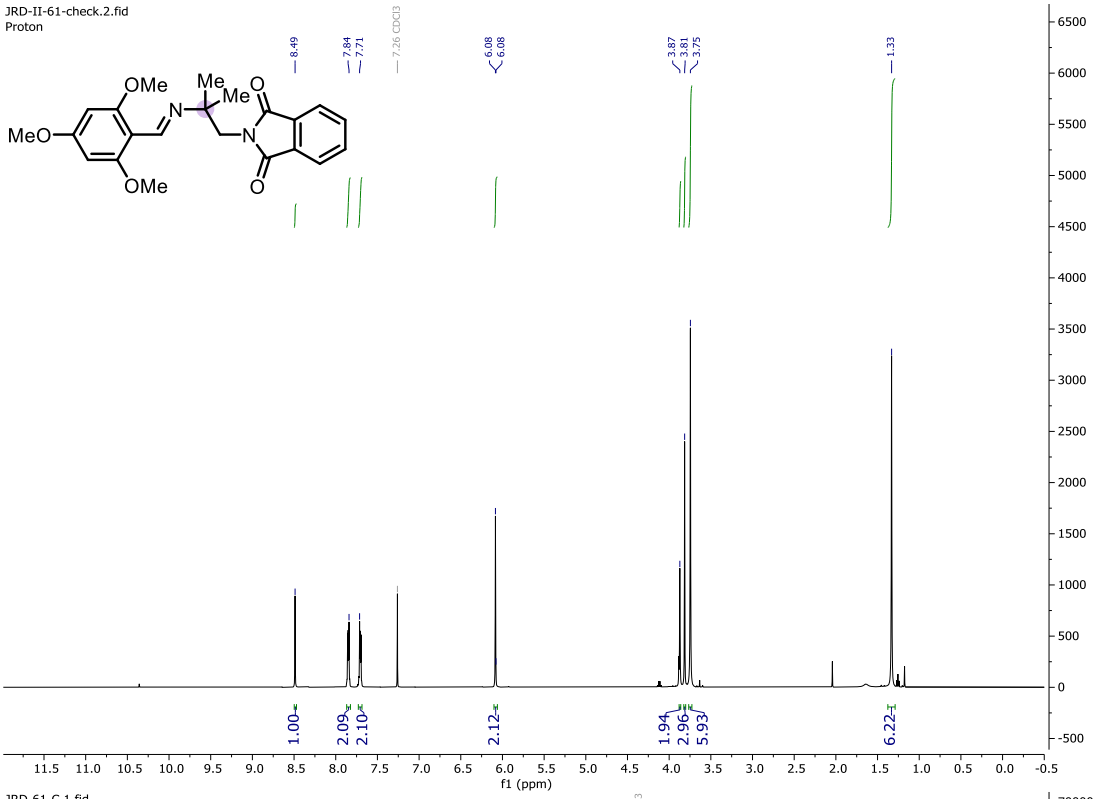
8. Spectra

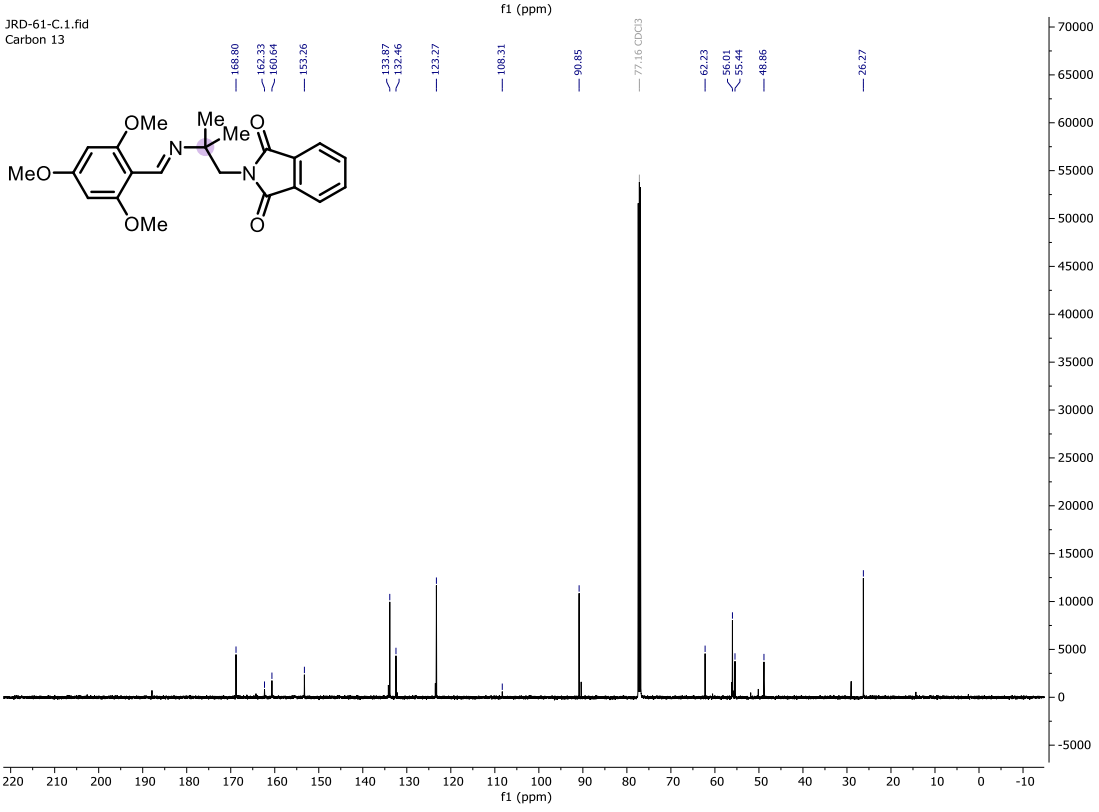

JRD-II-224.1.fid
Proton
Me Me
Me
OMe N
MeO
OMe
8.27
7.26 CDCl3
6.09
3.80
3.77
1.62
1.61
1.22
0.86
1.00
2.09
3.07
6.11
2.11
6.16
3.31
f1 (ppm)

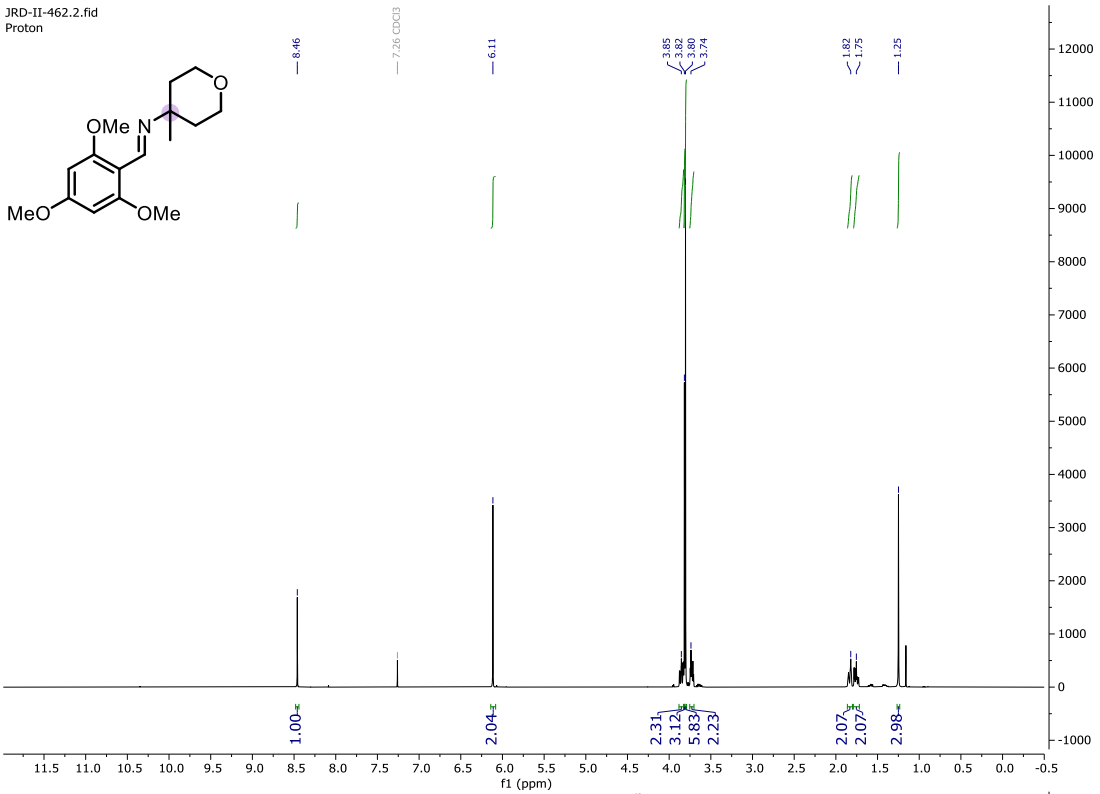

JRD-II-224.2.fid
Carbon 13
Me Me
Me
OMe N
MeO
OMe
161.81
160.15
151.02
109.18
90.92
77.16 CDCl3
60.34
56.02
55.37
36.10
26.82
8.57
f1 (ppm)

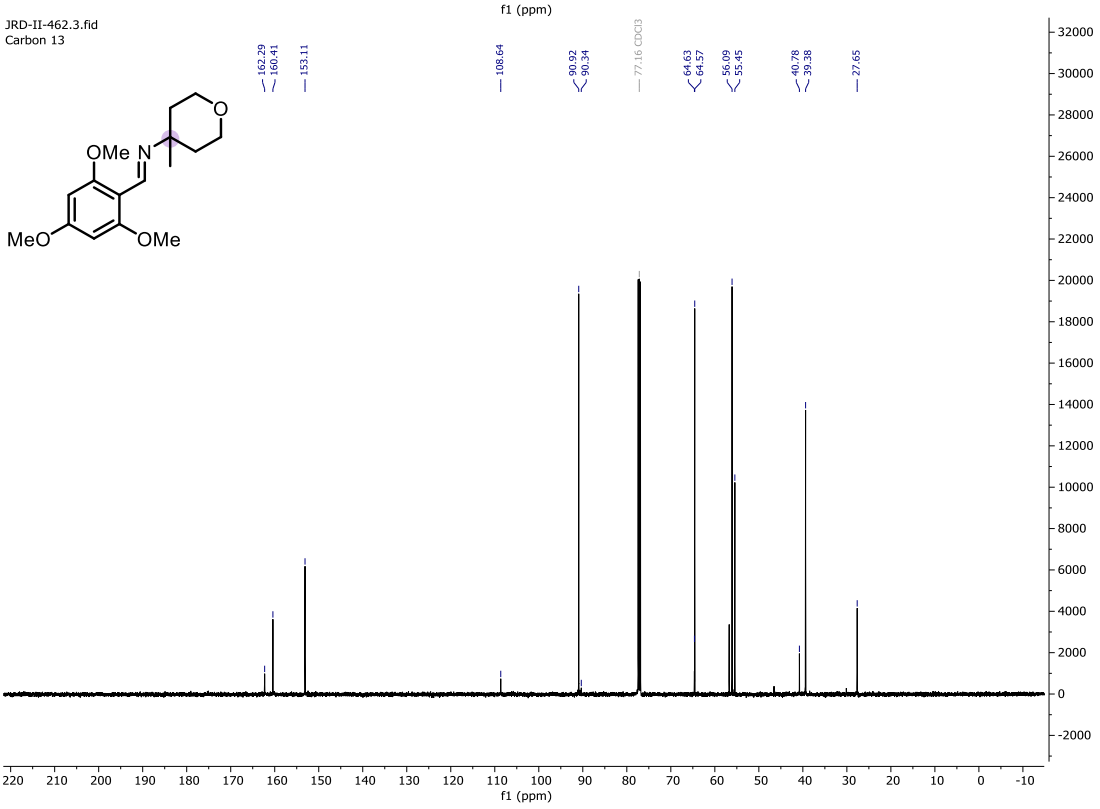

JRD-II-40.3.fid
Me
Me
Me
OMe
N
MeO
OMe
8.20
7.26 CDCl3
6.12
3.82
3.79
1.60
1.16
0.85
1.00
1.91
2.89
5.87
4.31
3.02
5.93
f1 (ppm)

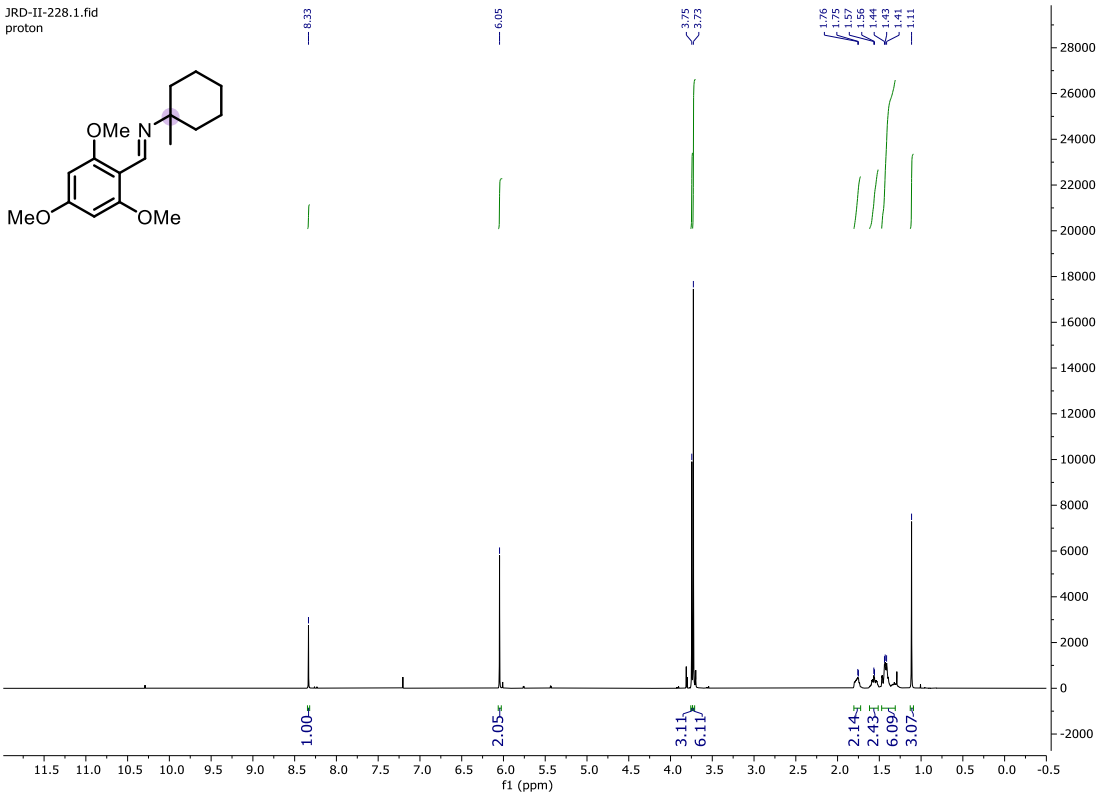

JRD-II-40.5.fid
Carbon 13
Me
Me
Me
OMe
N
MeO
OMe
166.34
164.25
161.78
160.06
151.67
90.92
77.16 CDCl3
62.98
56.12
56.03
55.46
55.37
34.09
20.91
8.23
f1 (ppm)

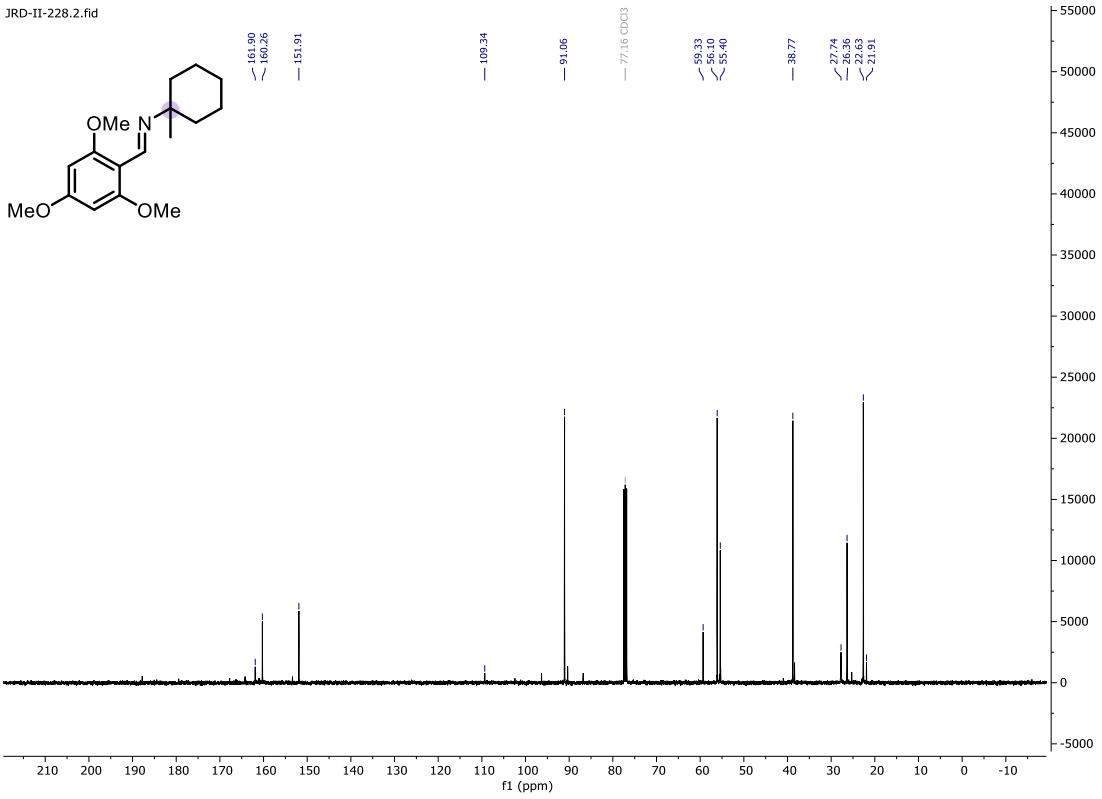

JRD-II-61-check.2.fid
Proton
8.49
7.84
7.71
7.26 CDCl3
6.08
6.08
3.87
3.81
3.75
1.33
OMe
Me
Me
O
N
MeO
N
OMe
O
O
1.00
2.09
2.10
2.12
1.94
2.96
5.93
6.22
f1 (ppm)

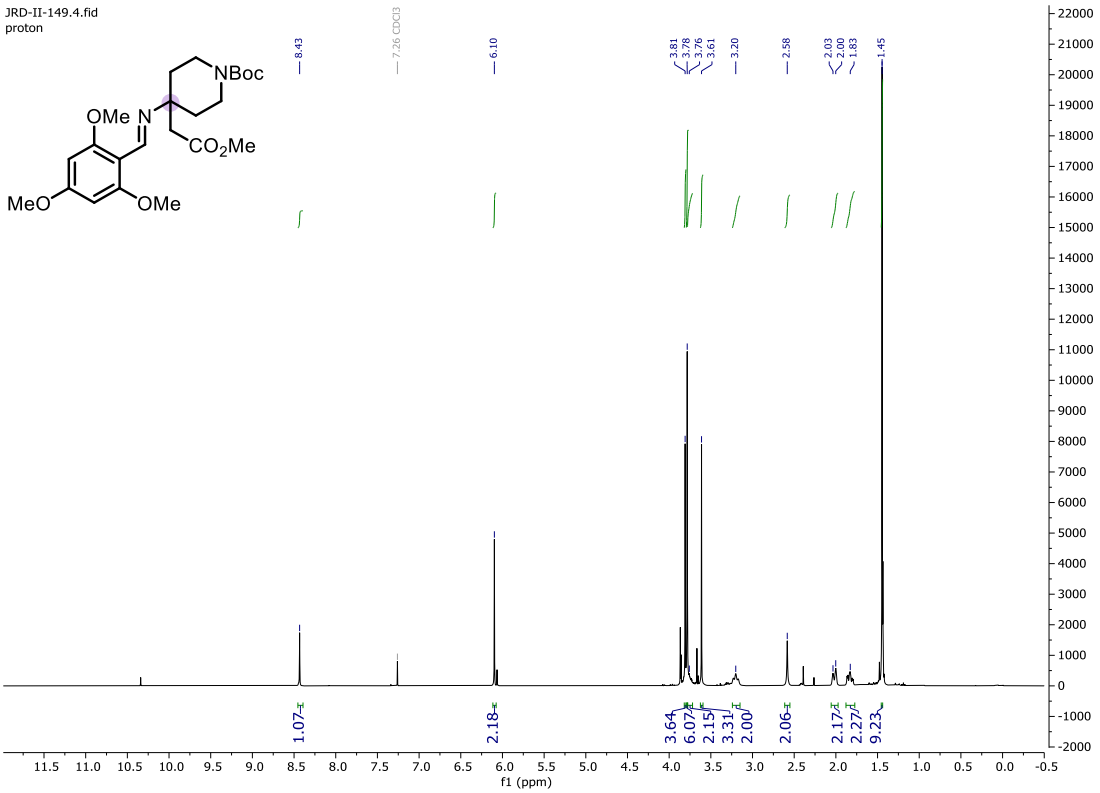

JRD-61-C.1.fid
Carbon 13
168.80
162.33
160.64
153.26
133.87
132.46
123.27
108.31
90.85
77.16 CDCl3
62.23
56.01
55.44
48.86
26.27
OMe
Me
Me
O
N
MeO
N
OMe
O
O
f1 (ppm)

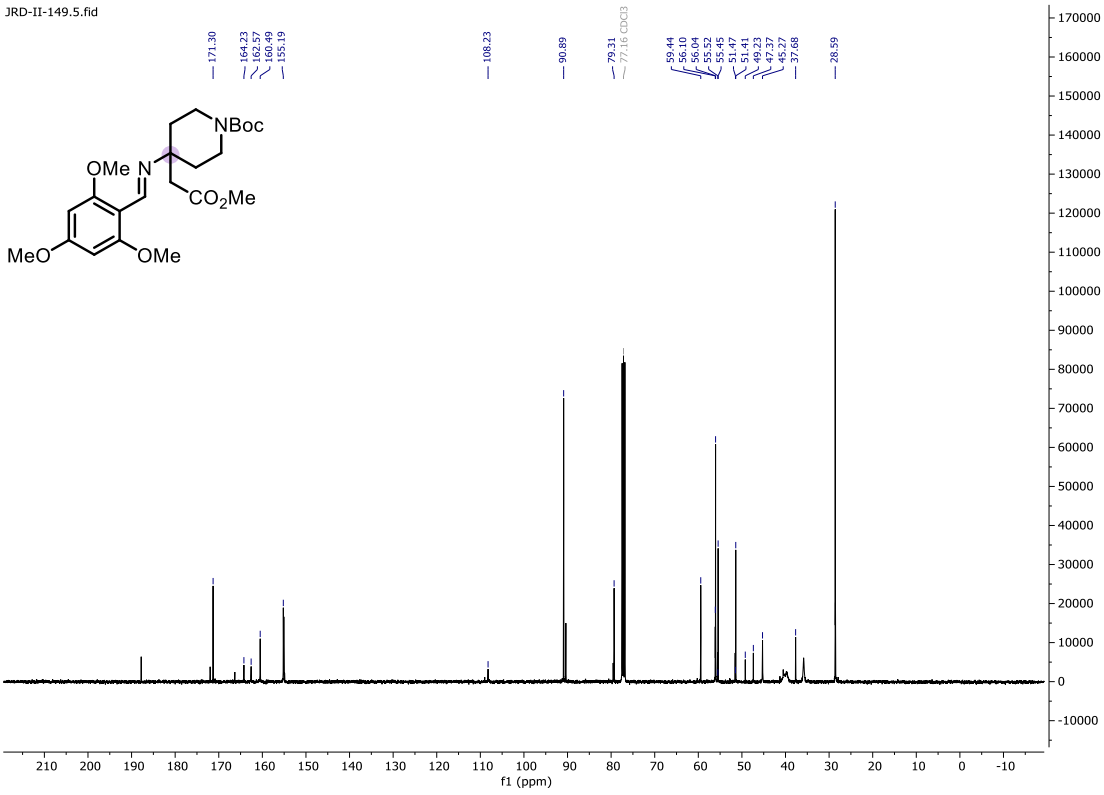

JRD-II-462.2.fid
Proton
OMe
N
O
MeO
OMe
8.46
7.26 CDCl3
6.11
3.85
3.82
3.80
3.74
1.82
1.75
1.25
1.00
2.04
2.31
3.12
5.83
2.23
2.07
2.07
2.98
f1 (ppm)

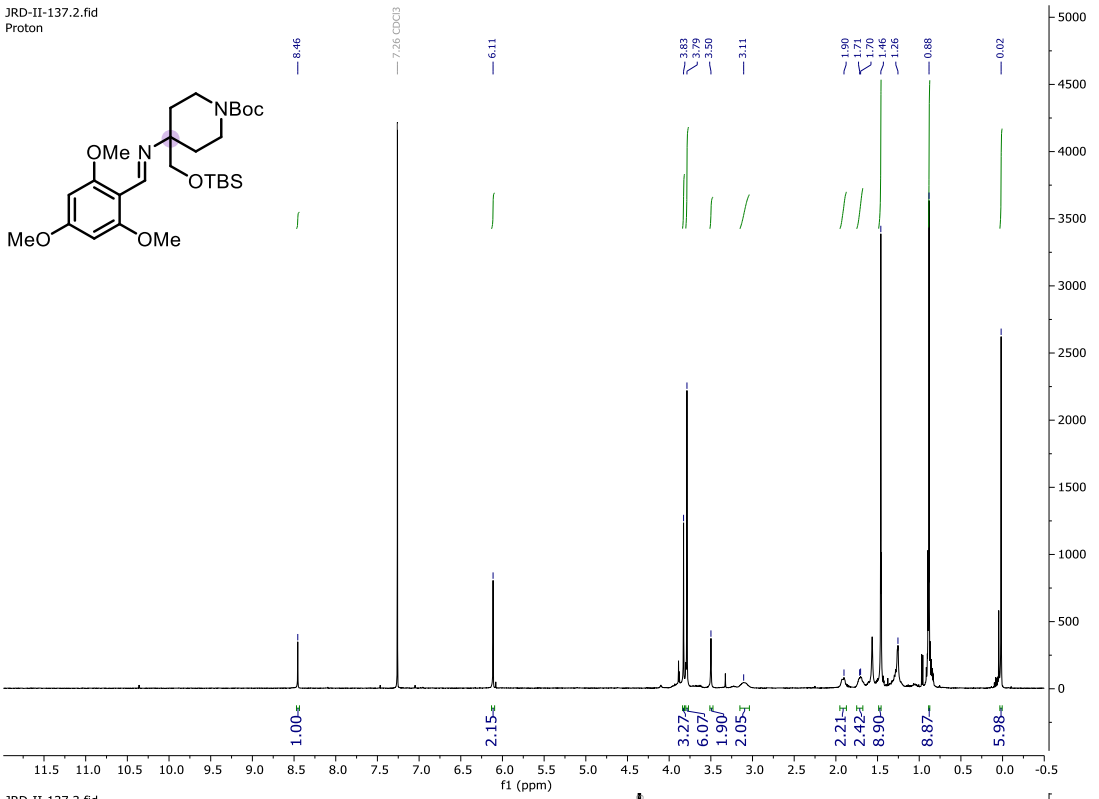

JRD-II-462.3.fid
Carbon 13
OMe
N
O
MeO
OMe
162.29
160.41
153.11
108.64
90.92
90.34
77.16 CDCl3
64.63
64.57
56.09
55.45
40.78
39.38
27.65
f1 (ppm)

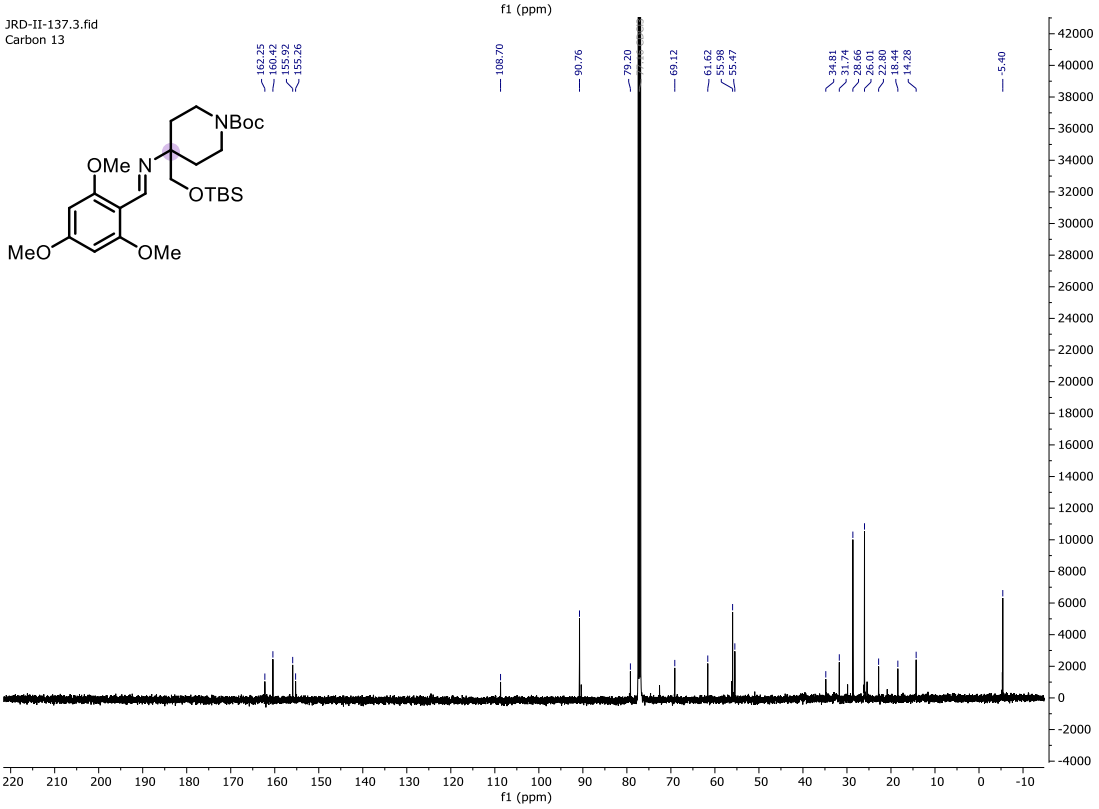

JRD-II-228.1.fid
proton
OMe
N
MeO
OMe
8.33
6.05
3.75
3.73
1.76
1.75
1.57
1.55
1.44
1.43
1.41
1.11
1.00
2.05
3.11
6.11
2.14
2.43
6.09
3.07
f1 (ppm)


JRD-II-228.2.fid
OMe
N
MeO
OMe
161.90
160.26
151.91
109.34
91.06
77.16 CDCl3
59.33
56.10
55.40
38.77
27.74
26.36
22.63
21.91
f1 (ppm)


JRD-II-149.4.fid
proton
NBoc
OMe
N
CO2Me
MeO
OMe
8.43
7.26 CDCl3
6.10
3.81
3.78
3.76
3.61
3.20
2.58
2.03
2.00
1.83
1.45
1.07
2.18
3.64
6.07
2.15
3.31
2.00
2.06
2.17
2.27
9.23
f1 (ppm)


JRD-II-149.5.fid
NBoc
OMe
N
CO2Me
MeO
OMe
171.30
164.23
162.57
160.49
155.19
108.23
90.89
79.31
77.16 CDCl3
59.44
56.10
56.04
55.52
55.45
51.47
51.41
49.23
47.37
45.27
37.68
28.59
f1 (ppm)


JRD-II-137.2.fid
Proton
NBoc
OMe
N
OTBS
MeO
OMe
8.46
7.26 CDCl3
6.11
3.83
3.79
3.50
3.11
1.90
1.71
1.70
1.46
1.26
0.88
0.02
1.00
2.15
3.27
6.07
1.90
2.05
2.21
2.42
8.90
8.87
5.98
f1 (ppm)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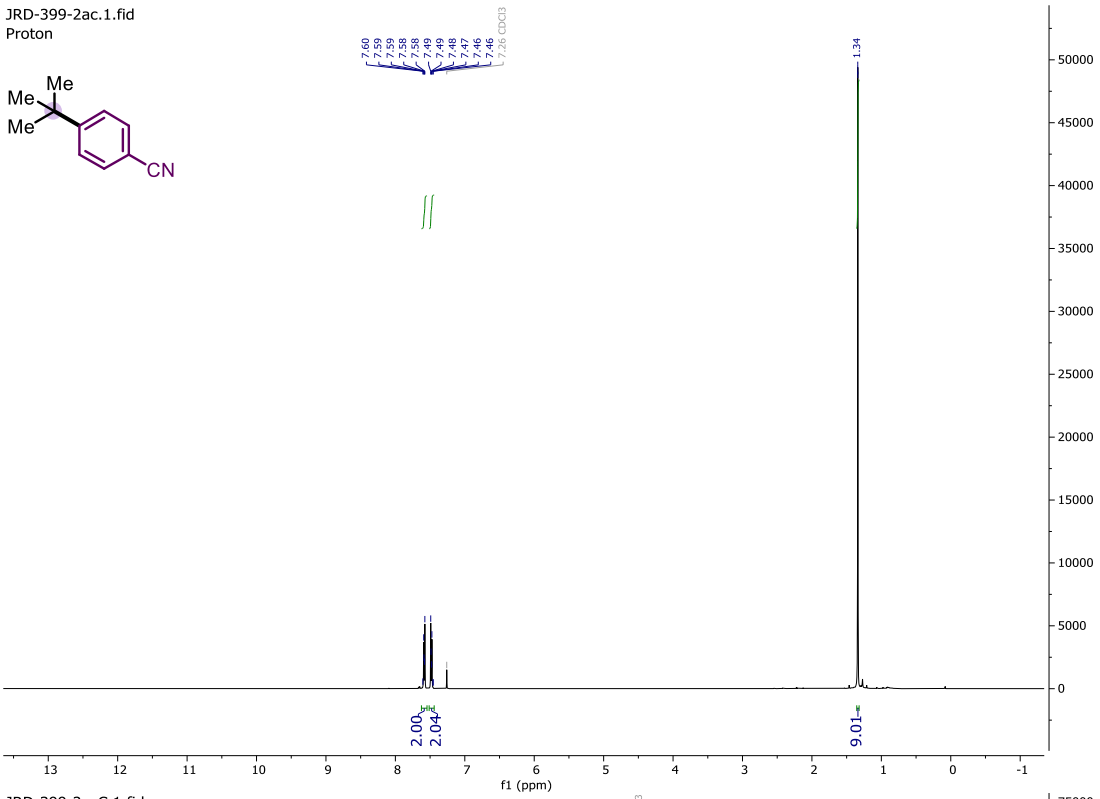
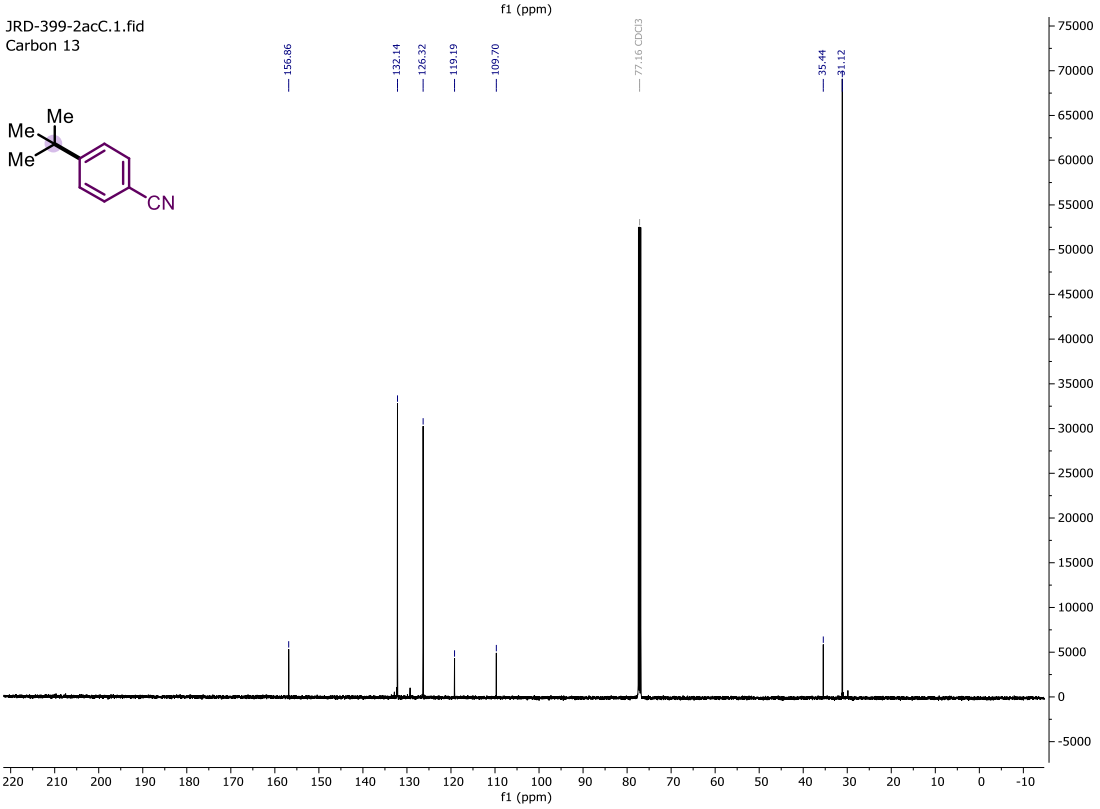
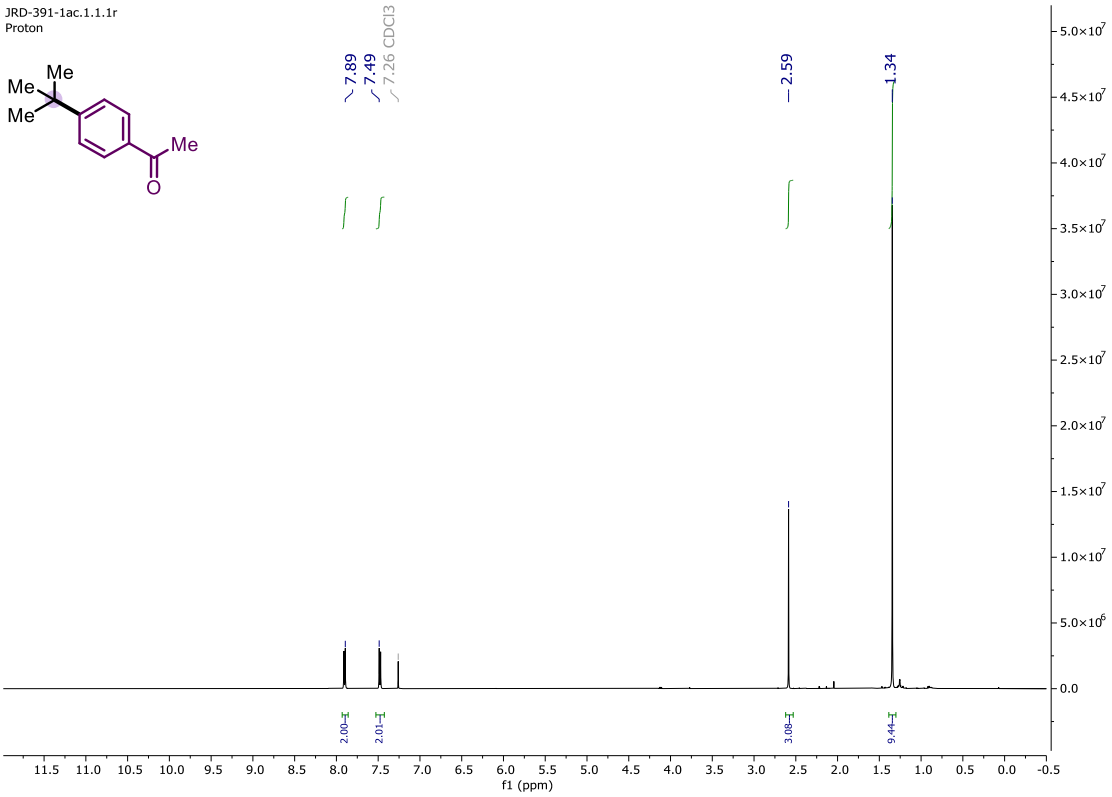
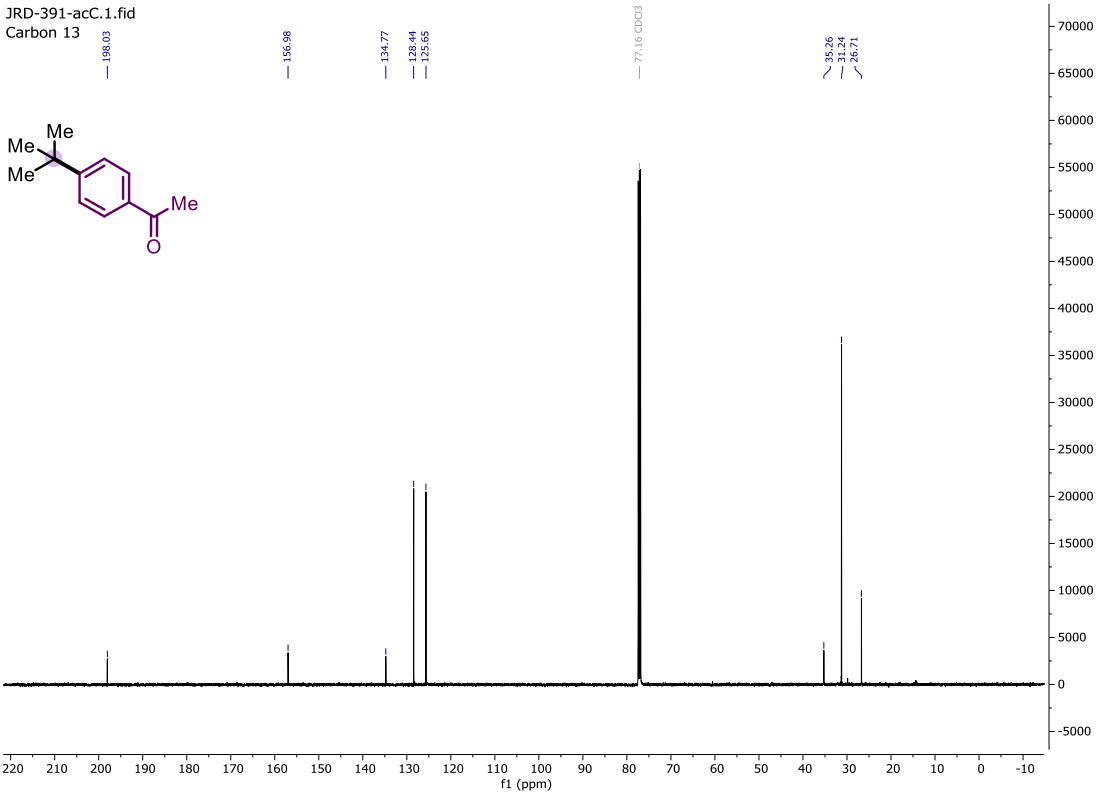
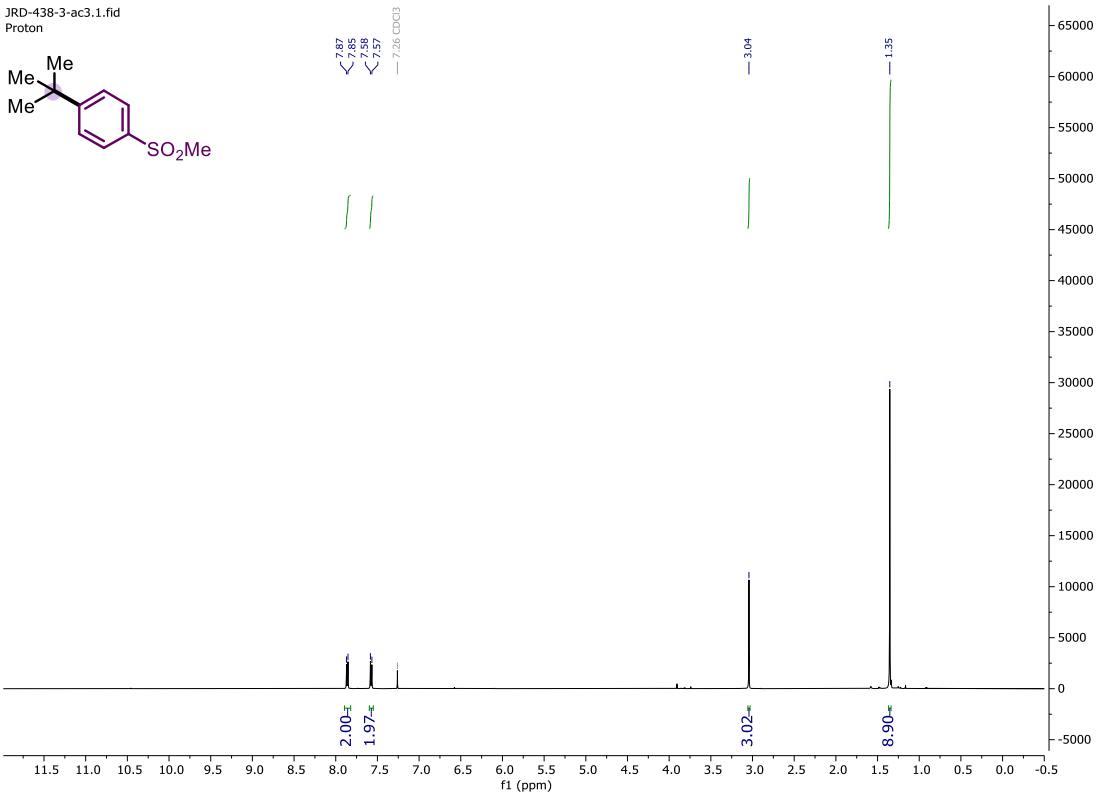
Carbon 13
NBoc
OMe
N
OTBS
MeO
OMe
162.25
160.42
155.92
155.26
108.70
90.76
79.20
69.12
61.62
55.98
55.47
34.81
31.74
28.66
26.01
22.80
18.44
14.28
-5.40
f1 (ppm)

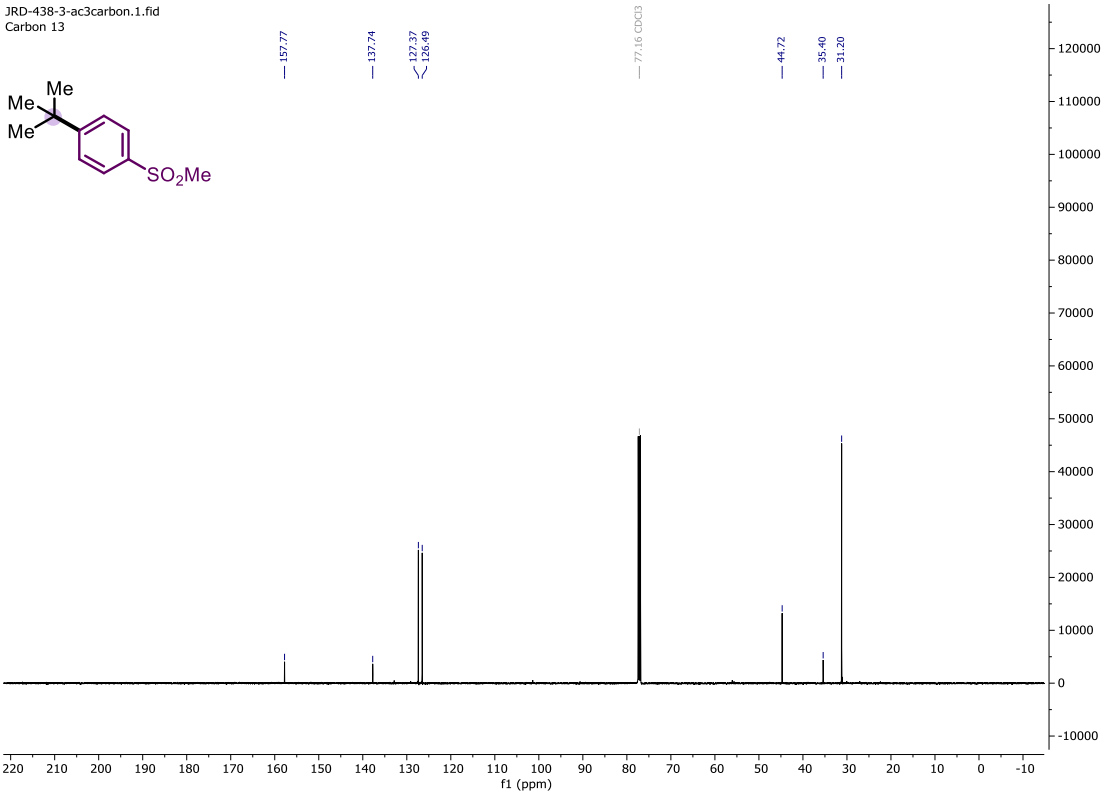

JRD-399-2ac.1.fid
Proton
Me
Me
CN
7.60
7.59
7.59
7.58
7.58
7.49
7.49
7.48
7.47
7.46
7.46
7.26 CDCl3
1.34
2.00
2.04
9.01
f1 (ppm)

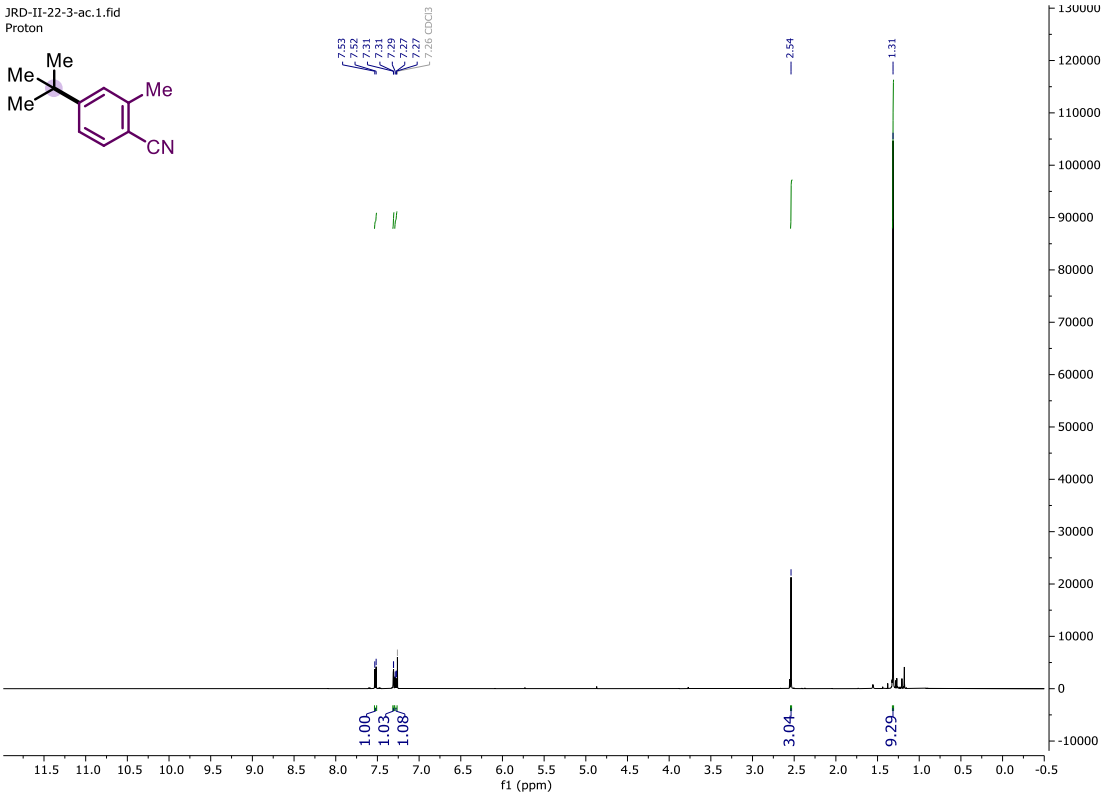

JRD-399-2acC.1.fid
Carbon 13
Me
Me
CN
156.86
132.14
126.32
119.19
109.70
77.16 CDCl3
35.44
31.12
f1 (ppm)

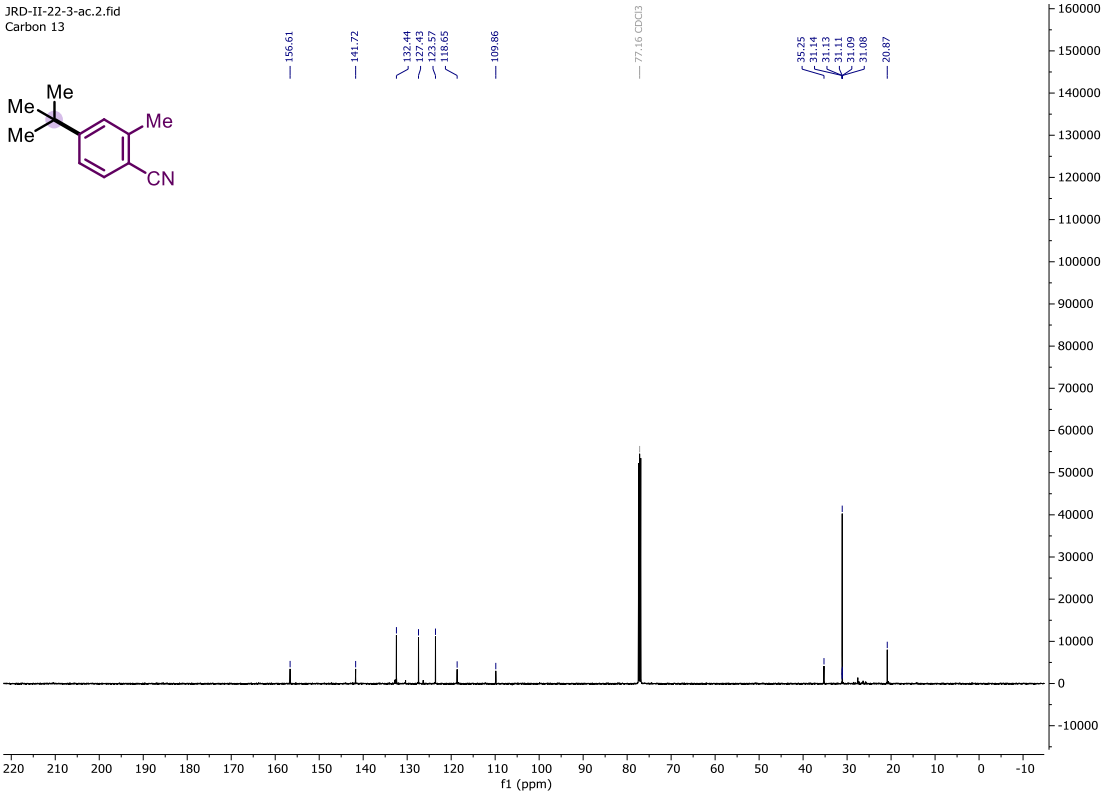

JRD-391-1ac.1.1.1r
Proton
Me
Me
Me
O
7.89
7.49
7.26 CDCl3
2.59
1.34
2.00
2.01
3.08
9.44
f1 (ppm)

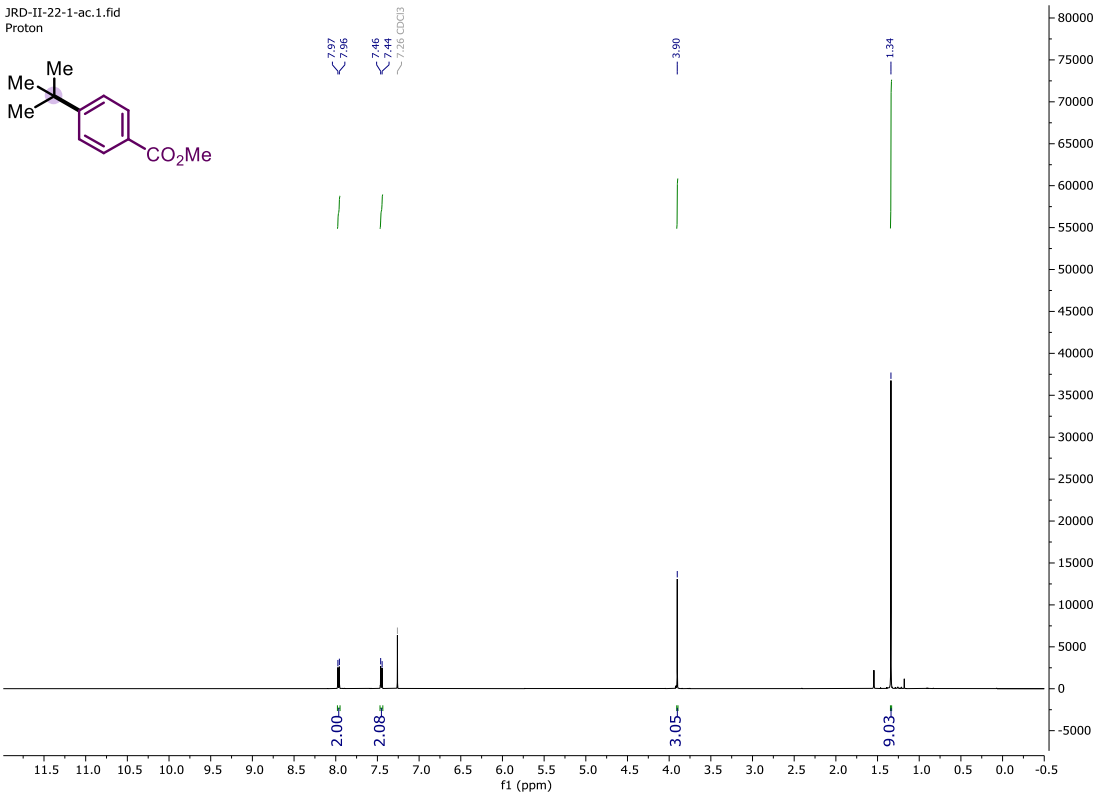

JRD-391-acC.1.fid
Carbon 13
198.03
156.98
134.77
128.44
125.65
77.16 CDCl3
35.26
31.24
26.71
Me
Me
Me
O
f1 (ppm)

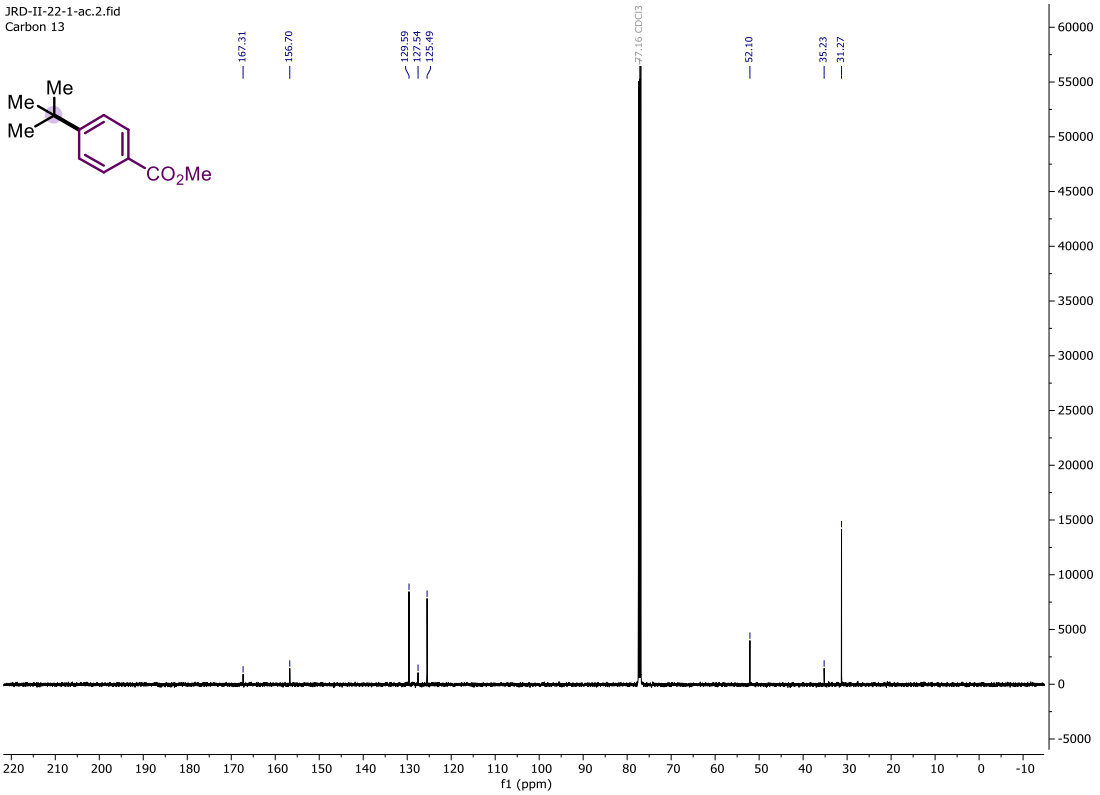

JRD-438-3-ac3.1.fid
Proton
Me
Me
SO2Me
7.87
7.85
7.58
7.57
7.26 CDCl3
3.04
1.35
2.00
1.97
3.02
8.90
f1 (ppm)

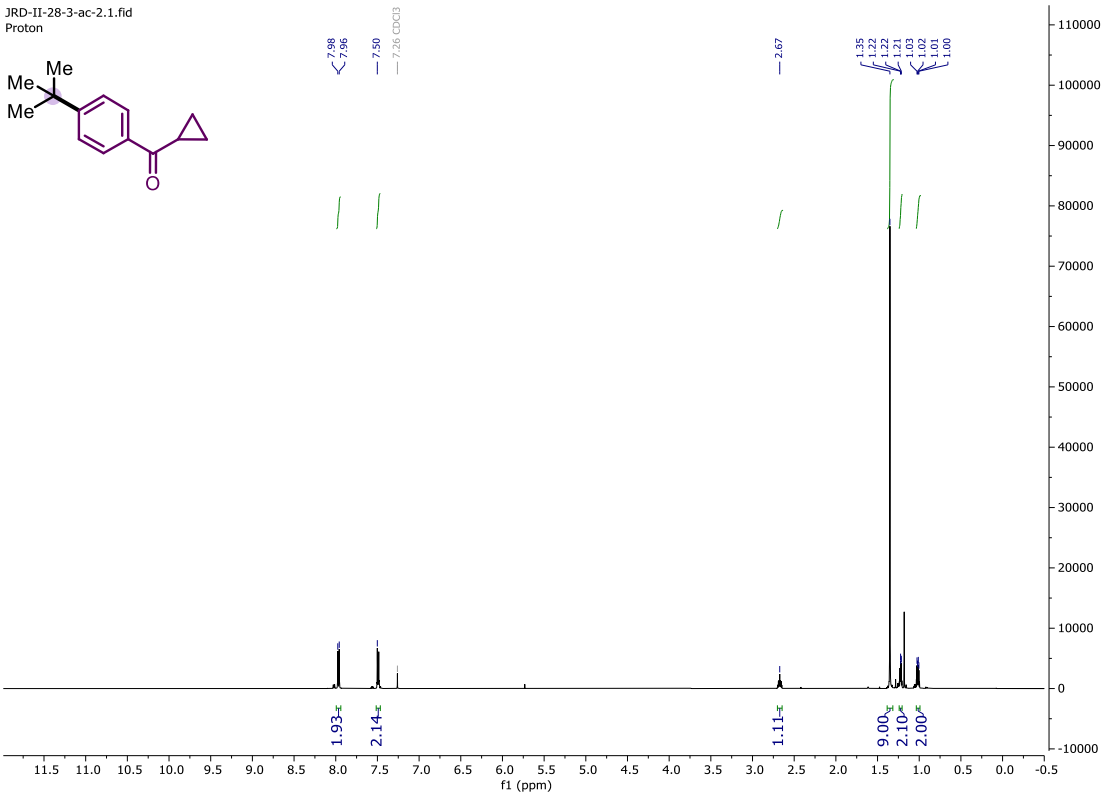

JRD-438-3-ac3carbon.1.fid
Carbon 13
Me
Me
SO2Me
157.77
137.74
127.37
126.49
77.16 CDCl3
44.72
35.40
31.20
f1 (ppm)

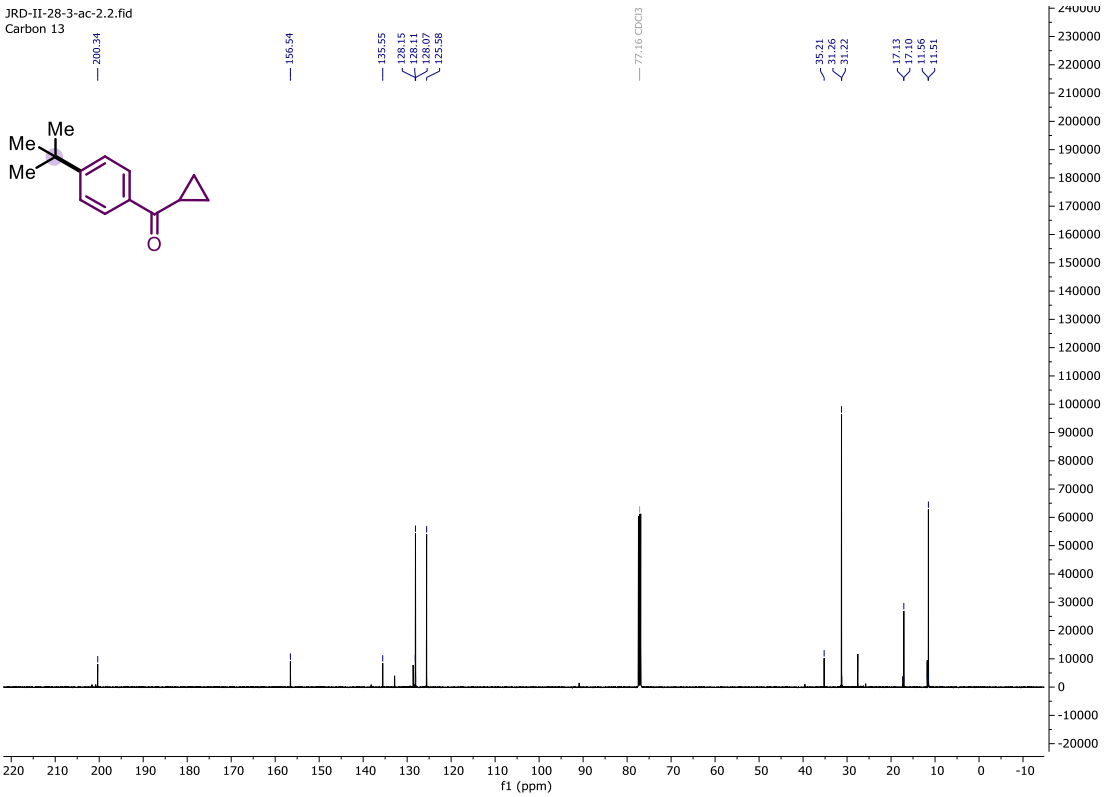

JRD-II-22-3-ac.1.fid
Proton
Me
Me
Me
CN
7.53
7.52
7.31
7.31
7.29
7.27
7.27
7.26 CDCl3
2.54
1.31
1.00
1.03
1.08
3.04
9.29
f1 (ppm)

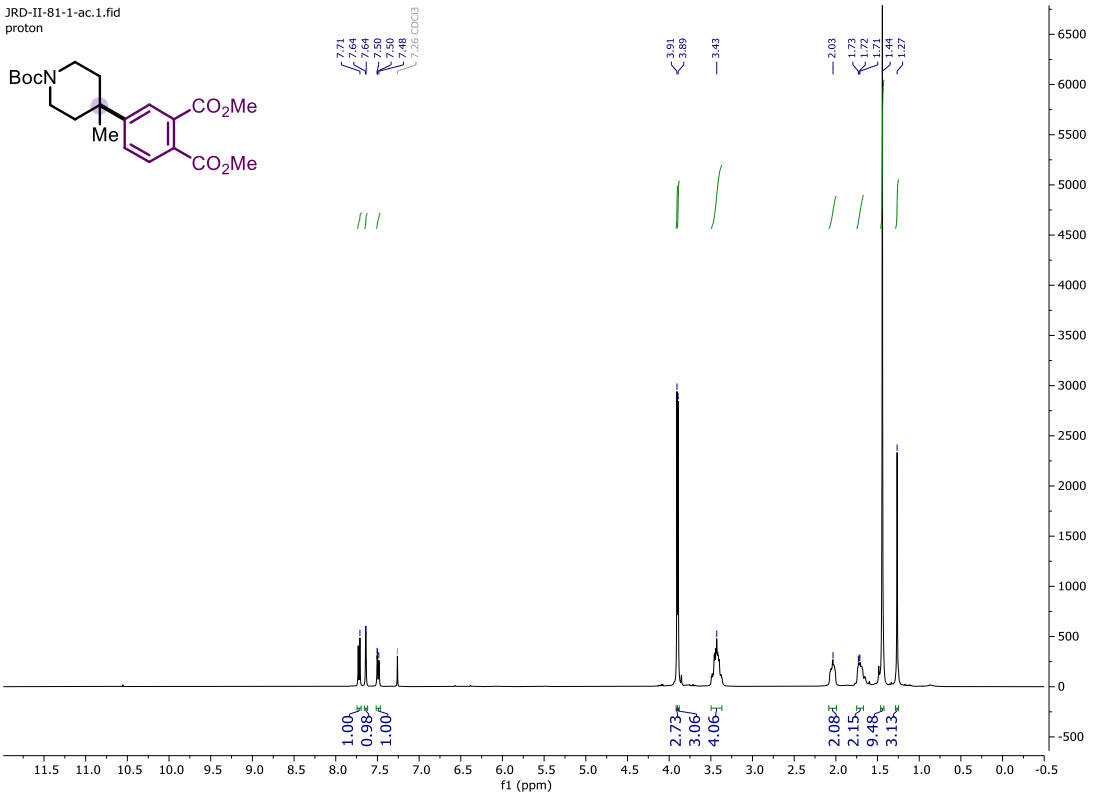

JRD-II-22-3-ac.2.fid
Carbon 13
Me
Me
Me
CN
156.61
141.72
132.44
127.43
123.57
118.65
109.86
77.16 CDCl3
35.25
31.14
31.13
31.11
31.09
31.08
20.87
f1 (ppm)

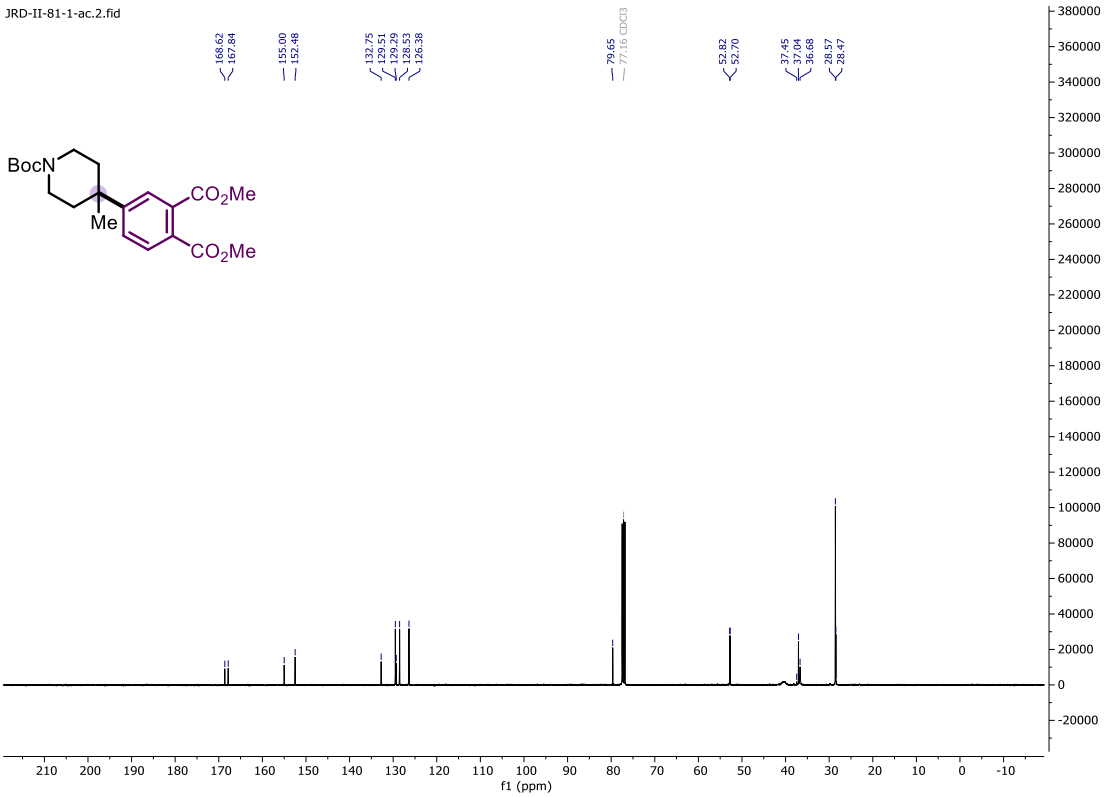

JRD-II-22-1-ac.1.fid
Proton
Me
Me
Me
CO2Me
7.97
7.96
7.46
7.44
7.26 CDCl3
3.90
1.34
2.00
2.08
3.05
9.03
f1 (ppm)

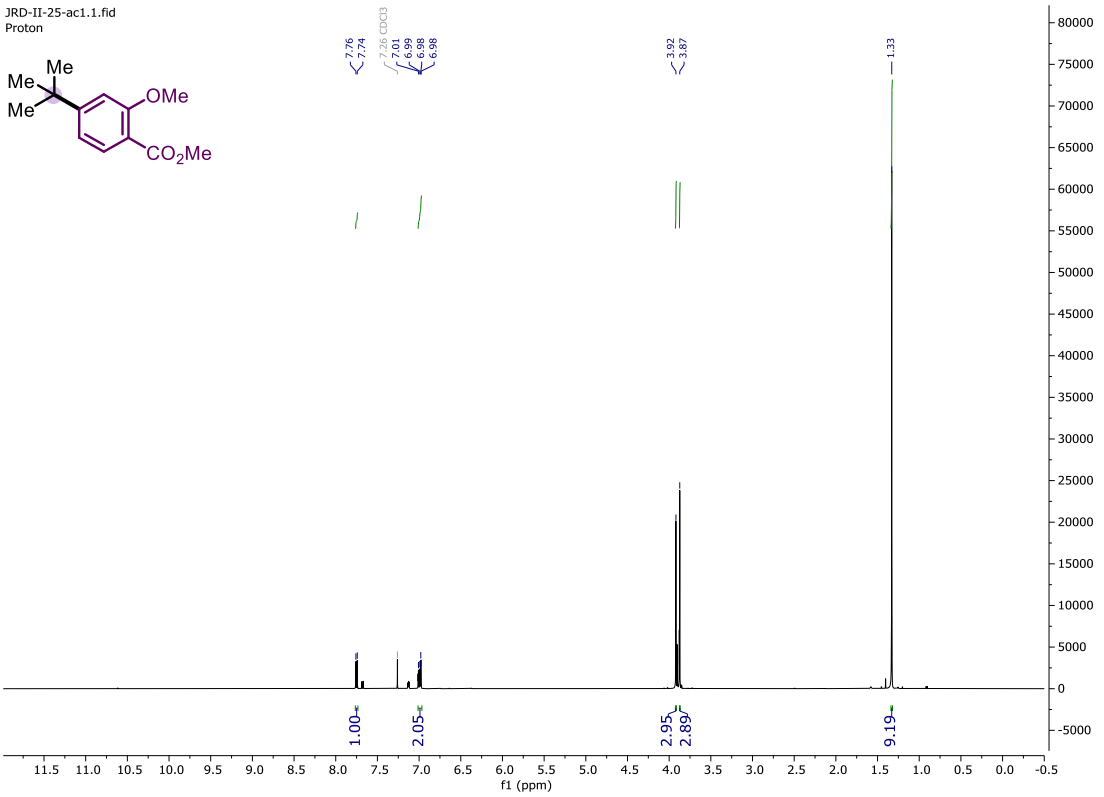

JRD-II-22-1-ac.2.fid
Carbon 13
Me
Me
Me
CO2Me
167.31
156.70
129.59
127.54
125.49
77.16 CDCl3
52.10
35.23
31.27
f1 (ppm)

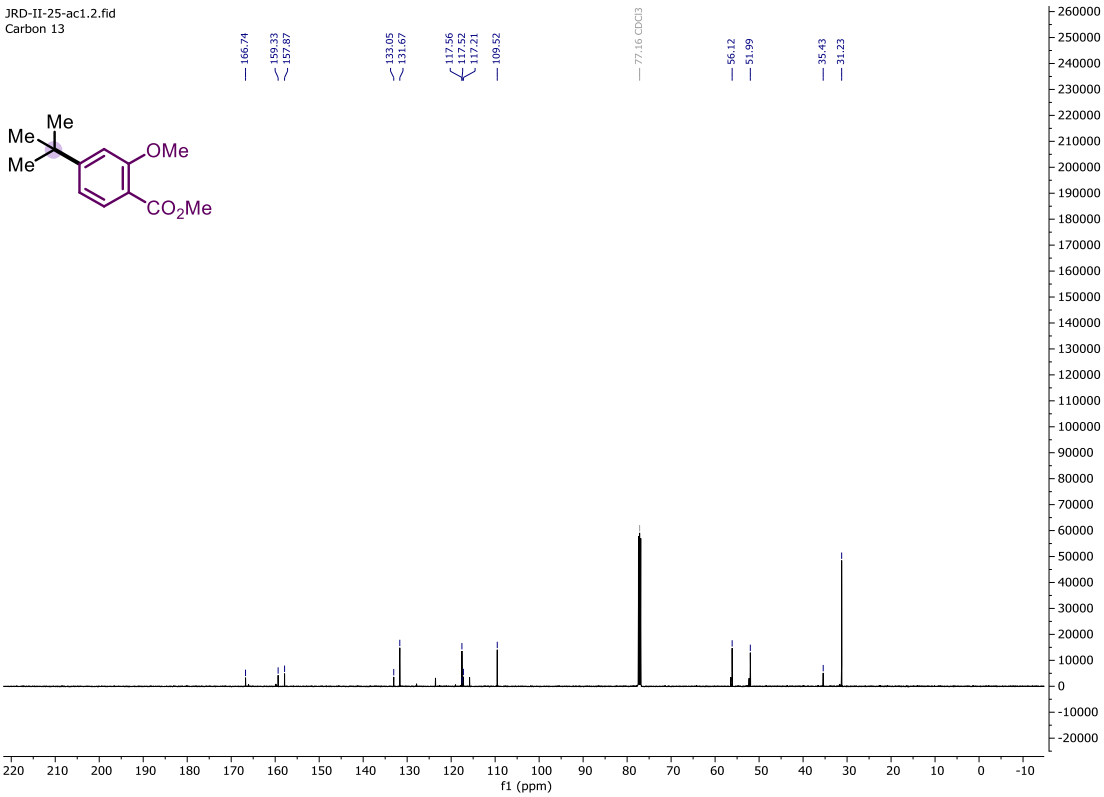

JRD-II-28-3-ac-2.1.fid
Proton
Me
Me
Me
O
7.98
7.96
7.50
7.26 CDCl3
2.67
1.35
1.22
1.22
1.21
1.03
1.02
1.01
1.00
1.93
2.14
1.11
9.00
2.10
2.00
f1 (ppm)

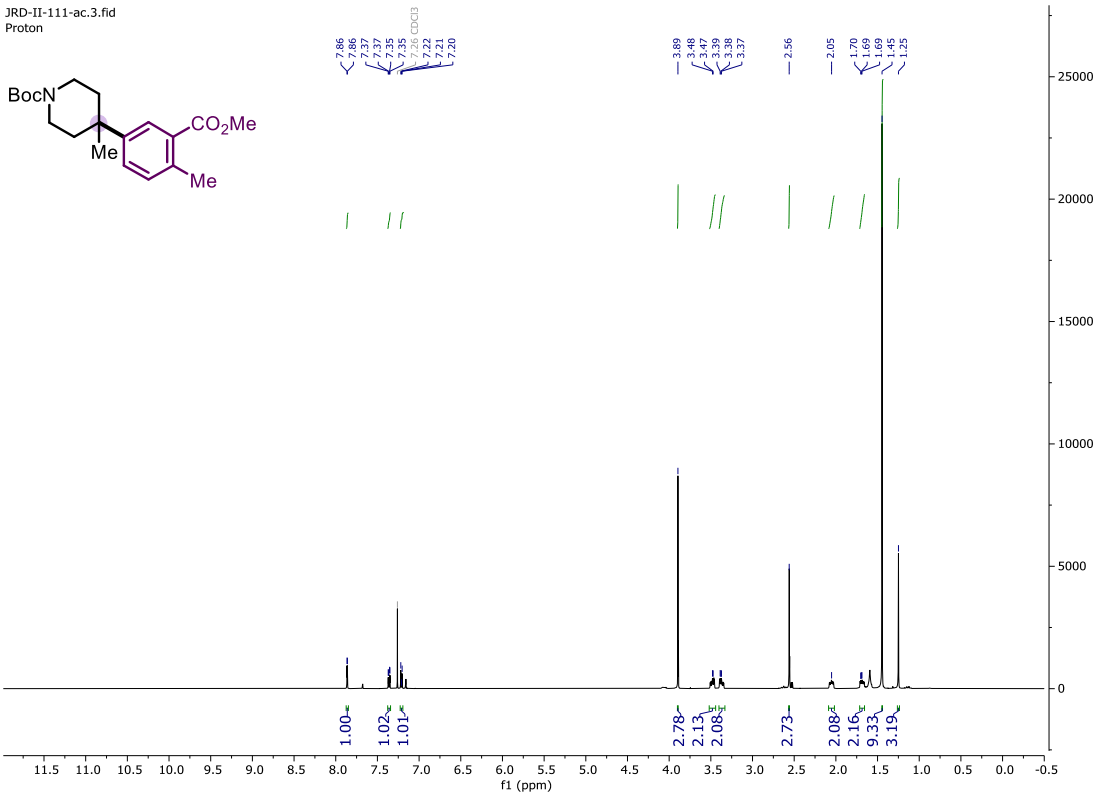

JRD-II-28-3-ac-2.2.fid
Carbon 13
Me
Me
Me
O
200.34
156.54
135.55
128.15
128.11
126.07
125.58
77.16 CDCl3
35.21
31.26
31.22
17.13
17.10
11.56
11.51
f1 (ppm)

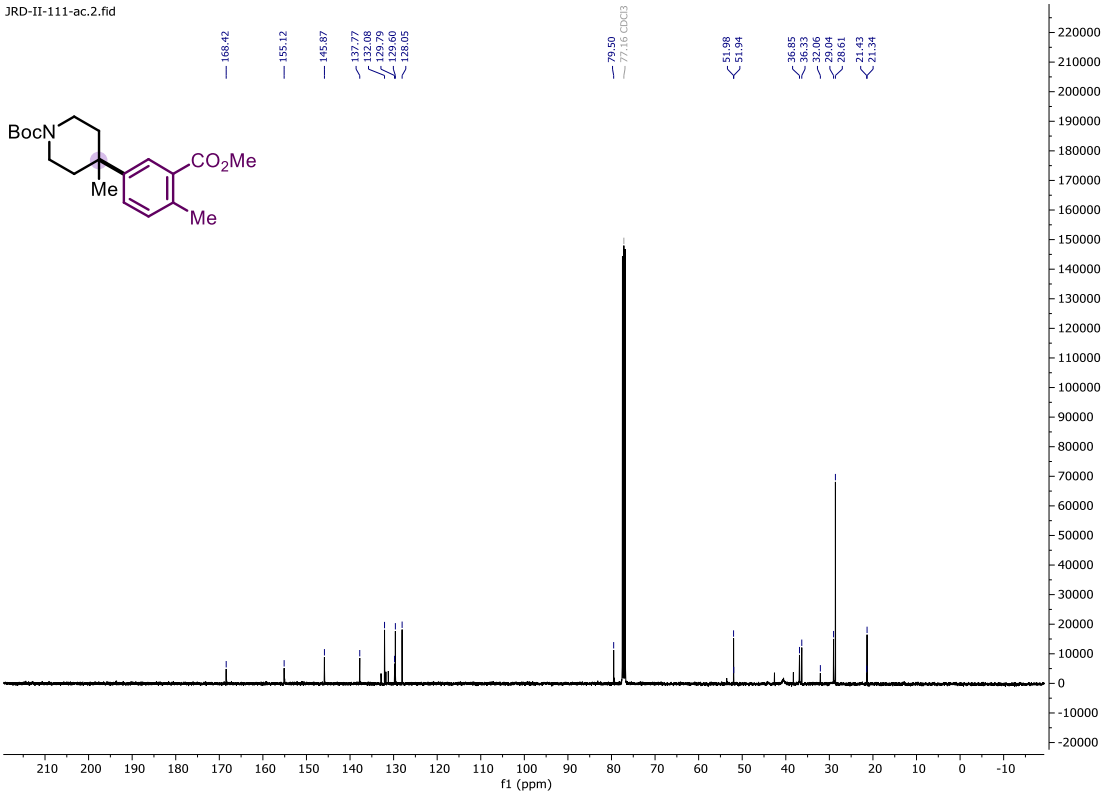

JRD-II-81-1-ac.1.fid
proton
BocN
Me
CO2Me
CO2Me
7.71
7.64
7.64
7.50
7.50
7.48
7.26 CDCl3
3.91
3.89
3.43
2.03
1.73
1.72
1.71
1.44
1.27
1.00
0.98
1.00
2.73
3.06
4.06
2.08
2.15
9.48
3.13
f1 (ppm)

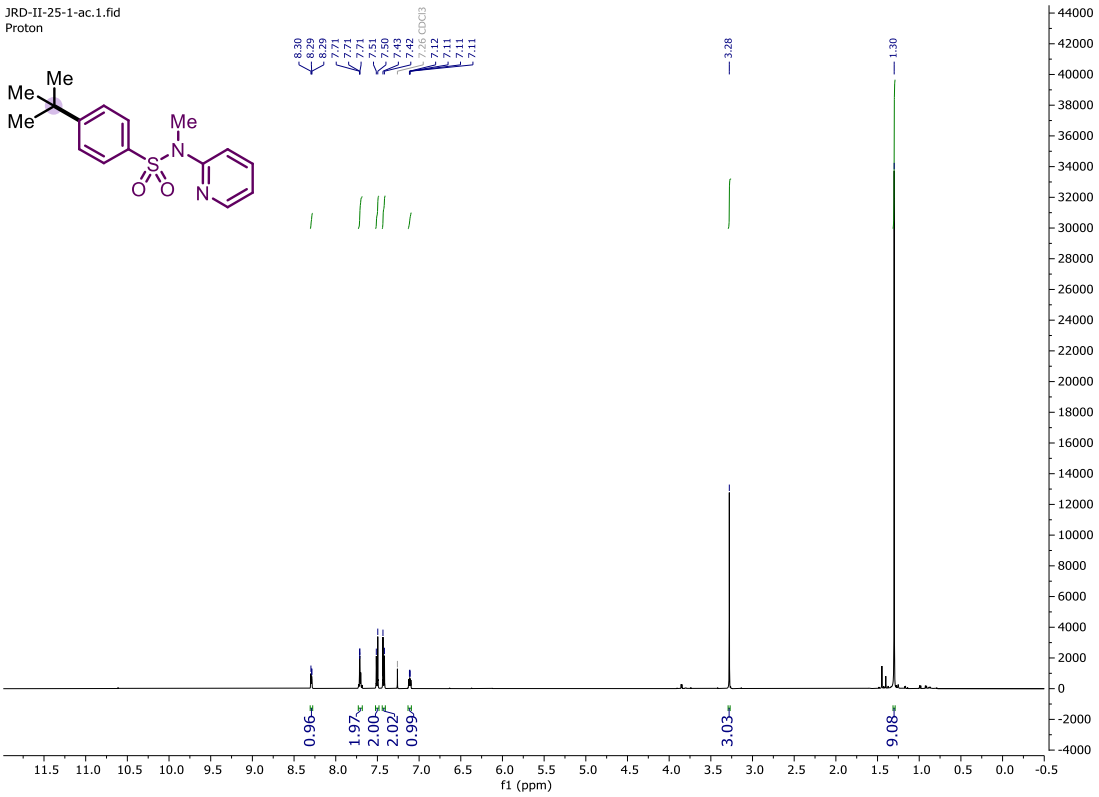

JRD-II-81-1-ac.2.fid
168.62
167.84
155.00
152.48
132.75
129.51
129.29
128.53
126.38
79.65
77.16 CDCl3
52.82
52.70
37.45
37.04
36.68
28.57
28.47
BocN
Me
CO2Me
CO2Me
f1 (ppm)

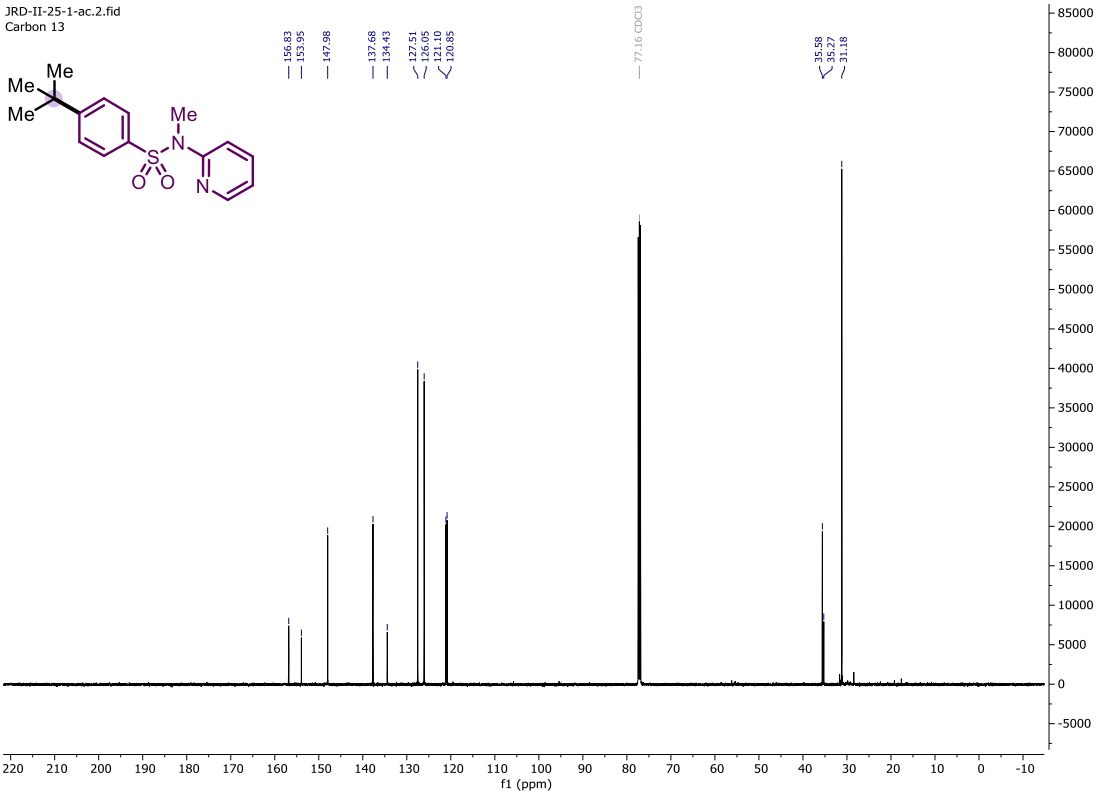

JRD-II-25-ac1.1.fid
Proton
Me
Me
OMe
CO2Me
7.76
7.74
7.26 CDCl3
7.01
6.99
6.98
6.98
3.92
3.87
1.33
1.00
2.05
2.95
2.89
9.19
f1 (ppm)

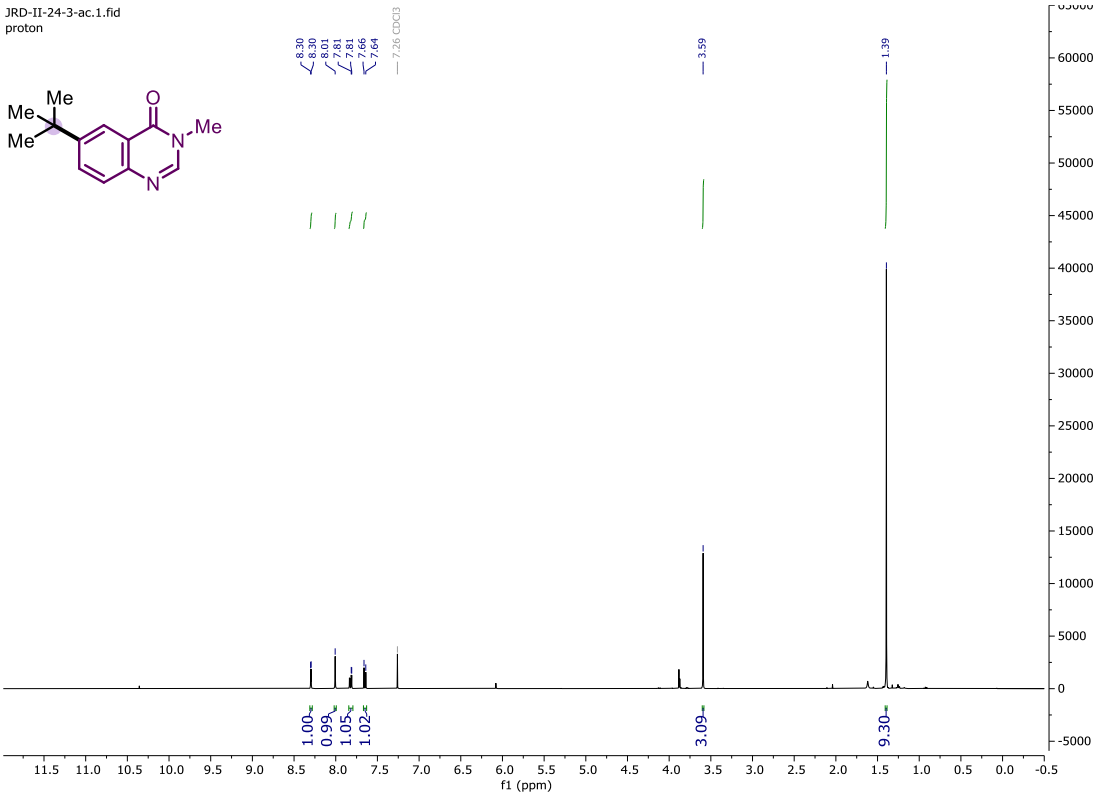

JRD-II-25-ac1.2.fid
Carbon 13
Me
Me
OMe
CO2Me
166.74
159.33
157.87
133.05
131.67
117.56
117.52
117.21
109.52
77.16 CDCl3
56.12
51.99
35.43
31.23
f1 (ppm)

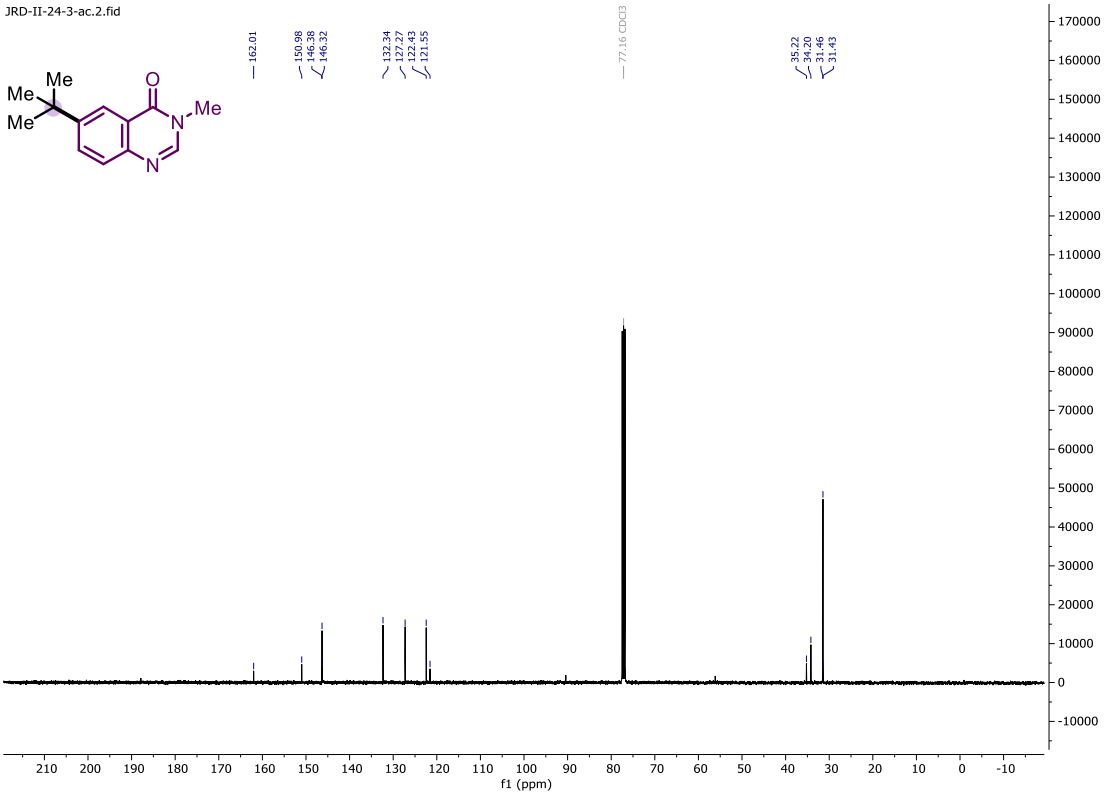

JRD-II-111-ac.3.fid
Proton
BocN
CO2Me
Me
Me
7.86
7.86
7.37
7.37
7.35
7.35
7.26 CDCl3
7.22
7.21
7.20
3.89
3.48
3.47
3.39
3.38
3.37
2.56
2.05
1.70
1.69
1.69
1.45
1.25
1.00
1.02
1.01
2.78
2.13
2.08
2.73
2.08
2.16
9.33
3.19
f1 (ppm)

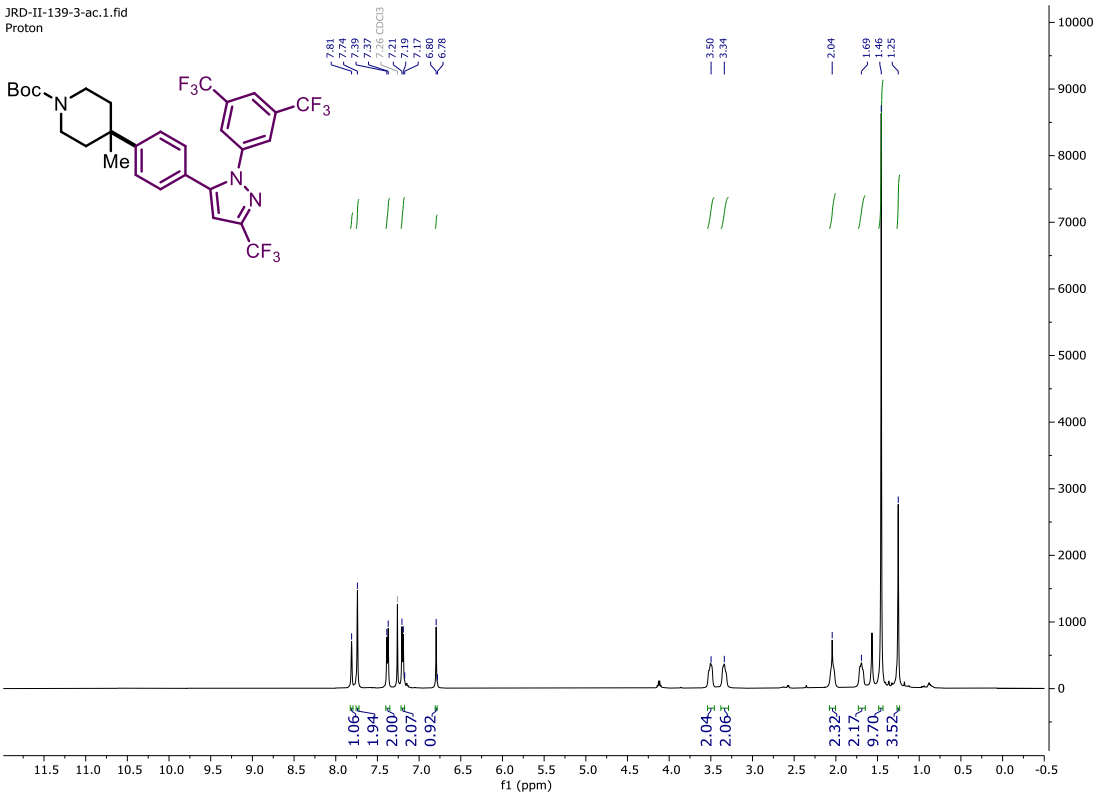

JRD-II-111-ac.2.fid
BocN
CO2Me
Me
Me
168.42
155.12
145.87
137.77
132.08
129.79
129.60
128.05
79.50
77.16 CDCl3
51.98
51.94
36.85
36.33
32.06
29.04
28.61
21.43
21.34
f1 (ppm)

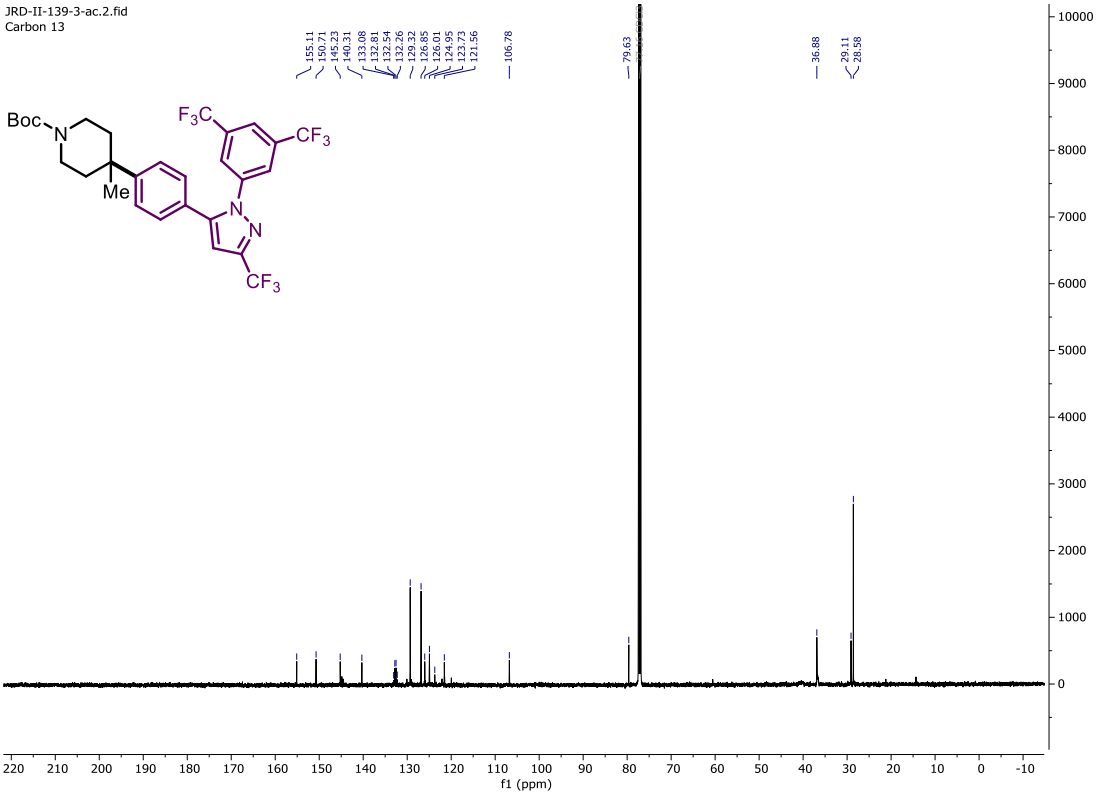

JRD-II-25-1-ac.1.fid
Proton
8.30
8.29
8.29
7.71
7.71
7.71
7.51
7.50
7.49
7.42
7.26 CDCl3
7.12
7.11
7.11
7.11
3.28
1.30
0.96
1.97
2.00
2.02
0.99
3.03
9.08
f1 (ppm)

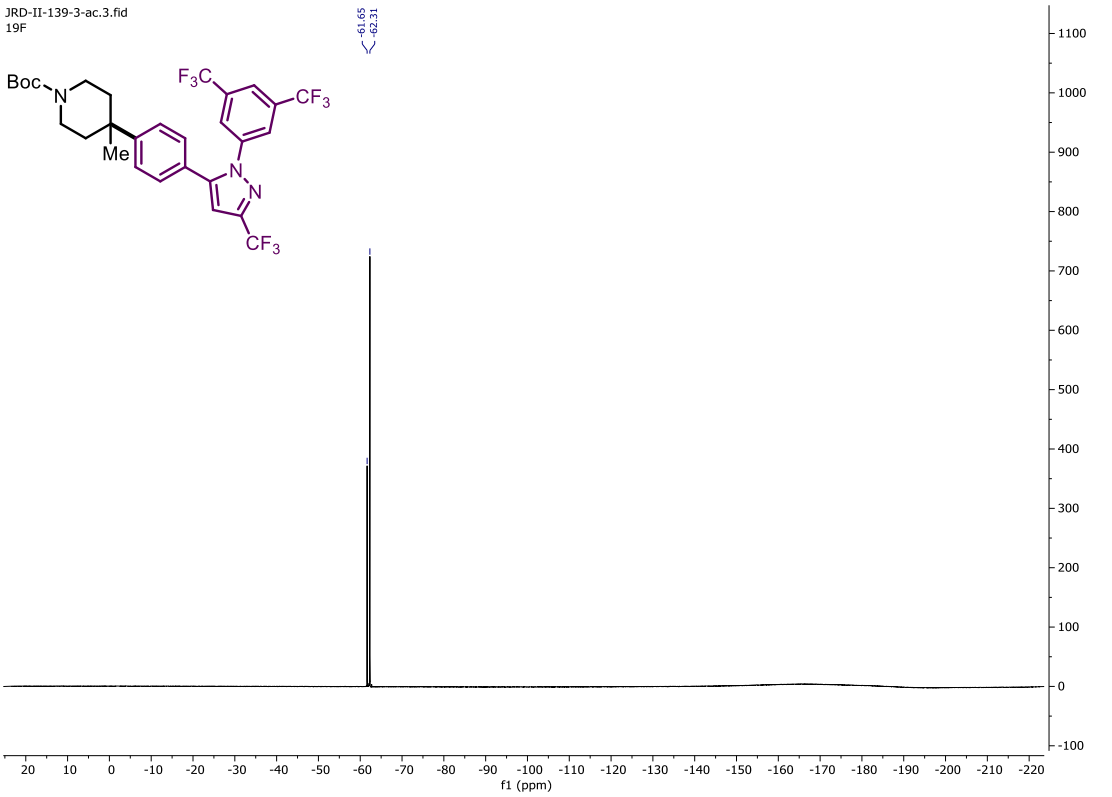

JRD-II-25-1-ac.2.fid
Carbon 13
156.83
155.95
147.98
137.68
134.43
127.51
126.05
121.10
120.85
77.16 CDCl3
35.58
35.27
31.18
f1 (ppm)

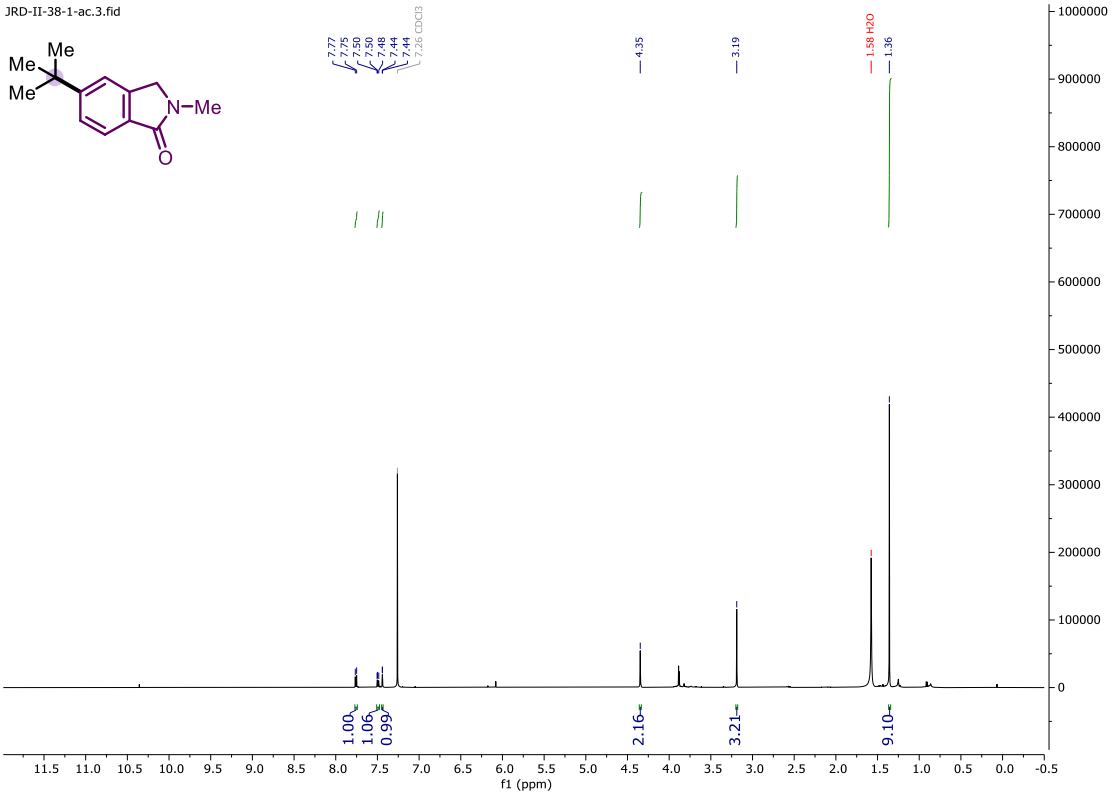

JRD-II-24-3-ac.1.fid
proton
8.30
8.30
8.01
7.81
7.81
7.66
7.64
7.26 CDCl3
3.59
1.39
1.00
0.99
1.05
1.02
3.09
9.30
f1 (ppm)

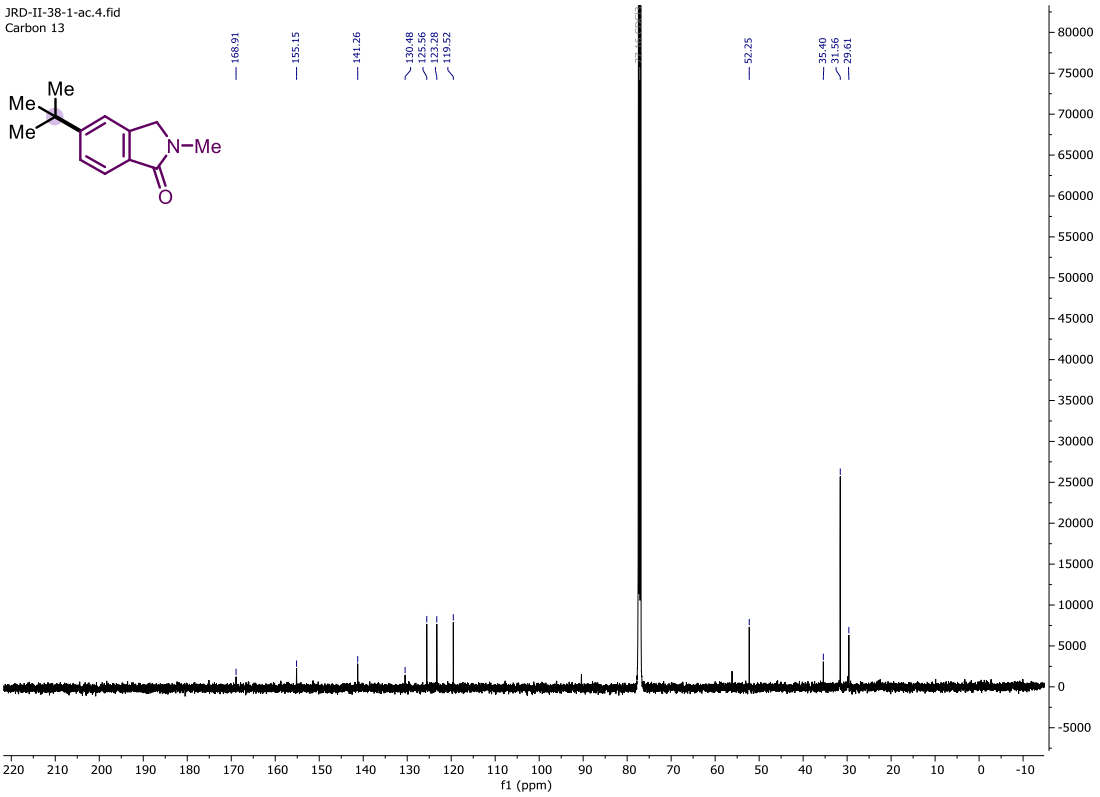

JRD-II-24-3-ac.2.fid
162.01
150.98
146.38
146.32
132.34
127.27
122.43
121.55
77.16 CDCl3
35.22
34.20
31.46
31.43
f1 (ppm)

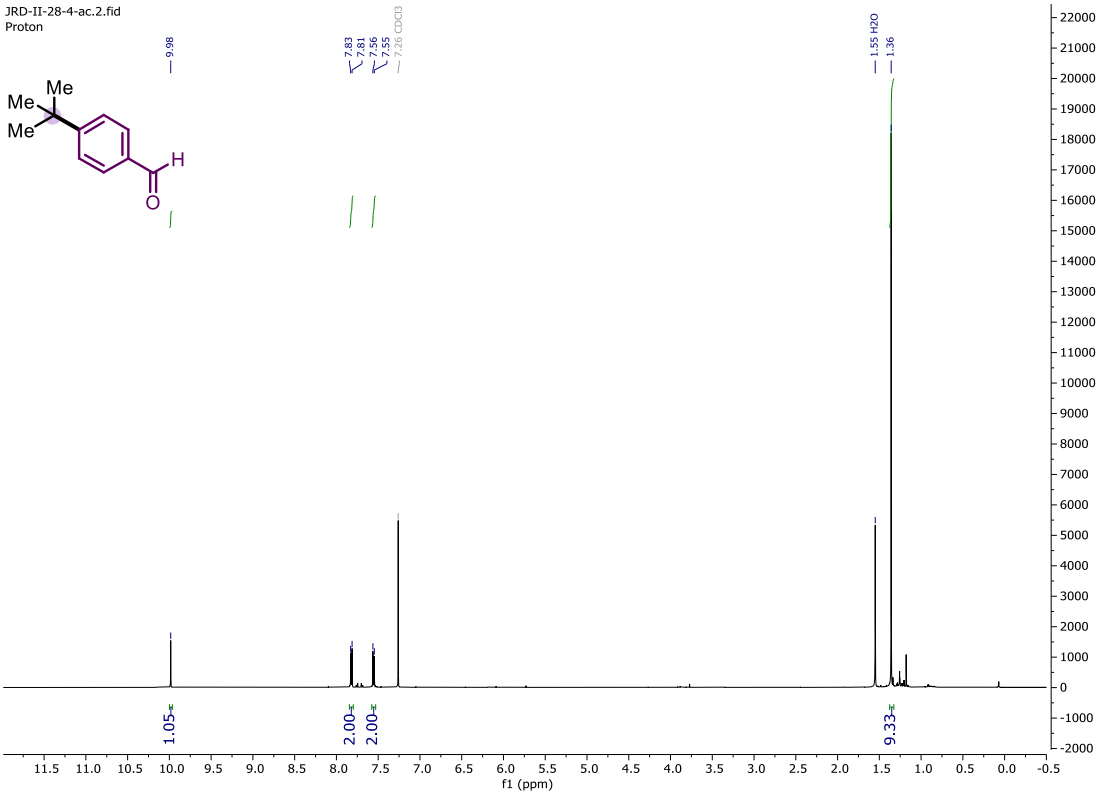

JRD-II-139-3-ac.1.fid
Proton
Boc
N
Me
F3C
CF3
N
N
CF3
7.81
7.74
7.39
7.37
7.26 CDCl3
7.21
7.19
7.17
6.80
6.78
3.50
3.34
2.04
1.69
1.46
1.25
1.06
1.94
2.00
2.07
0.92
2.04
2.06
2.32
2.17
9.70
3.52
f1 (ppm)

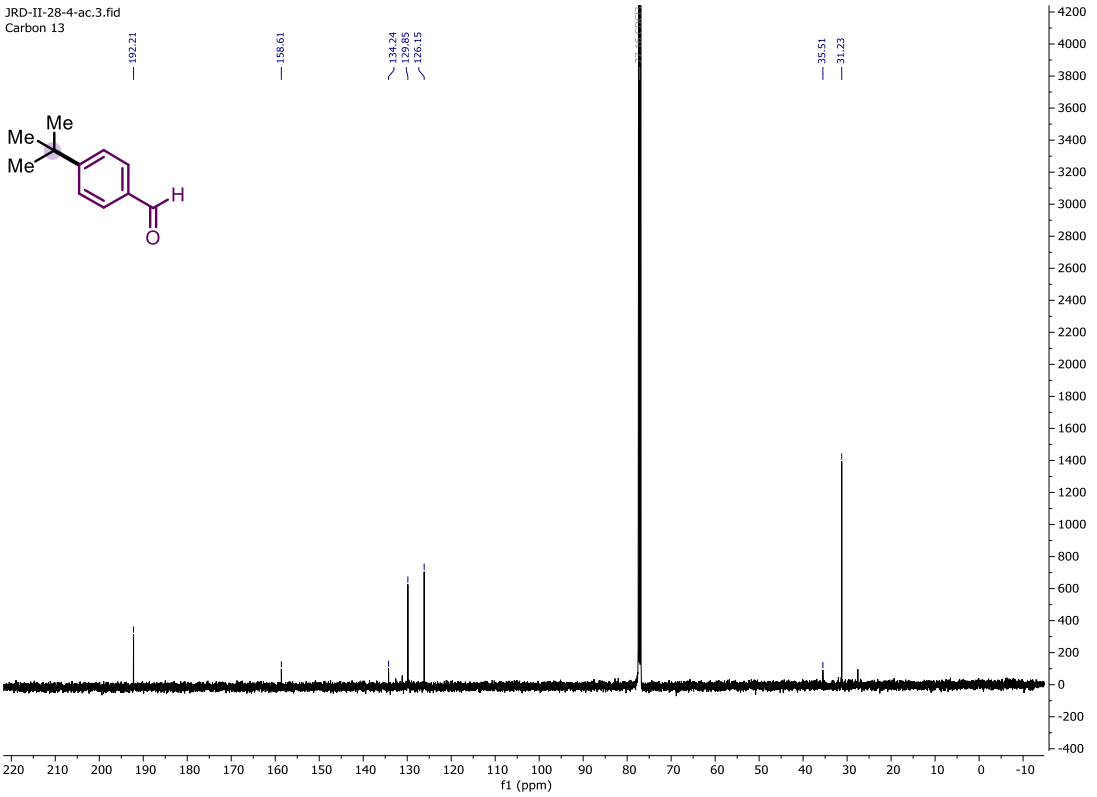

JRD-II-139-3-ac.2.fid
Carbon 13
Boc
N
Me
F3C
CF3
N
N
CF3
155.11
150.71
145.23
140.31
133.08
132.81
132.54
132.26
129.22
126.85
126.01
124.95
123.73
121.56
106.78
79.63
36.88
29.11
28.58
f1 (ppm)

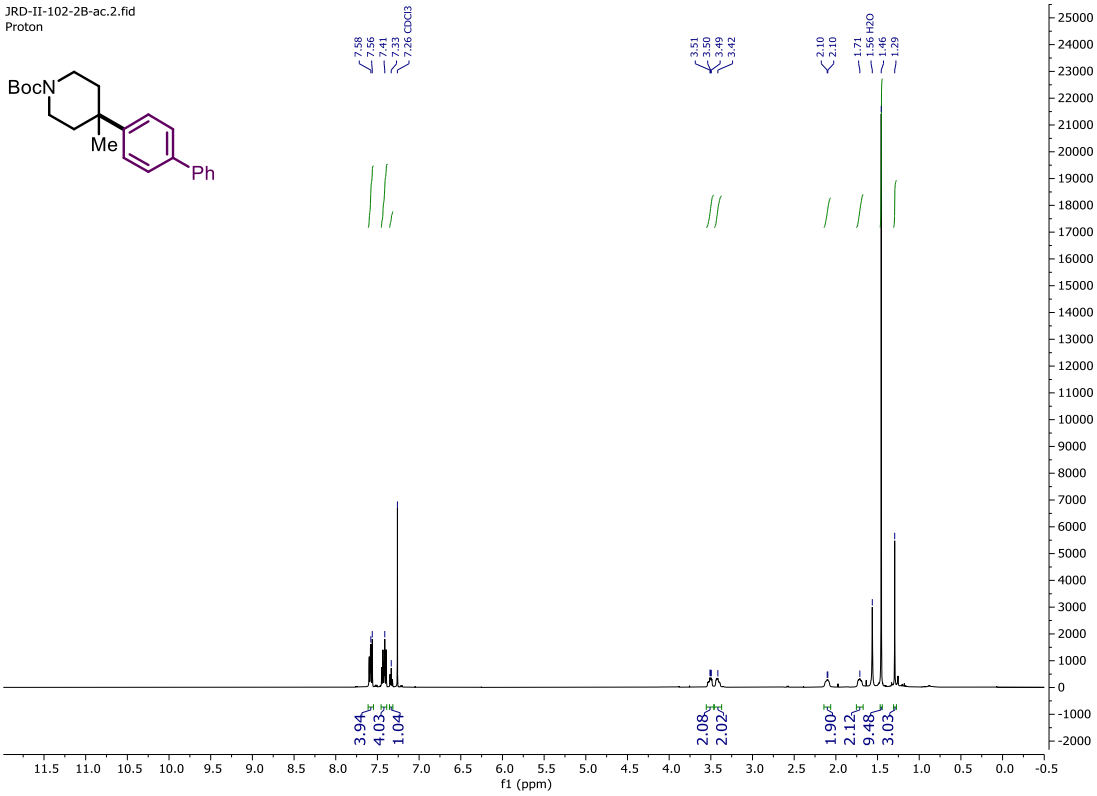

JRD-II-139-3-ac.3.fid
19F
-61.65
-62.31
Boc
N
Me
F3C
CF3
N
N
CF3
f1 (ppm)

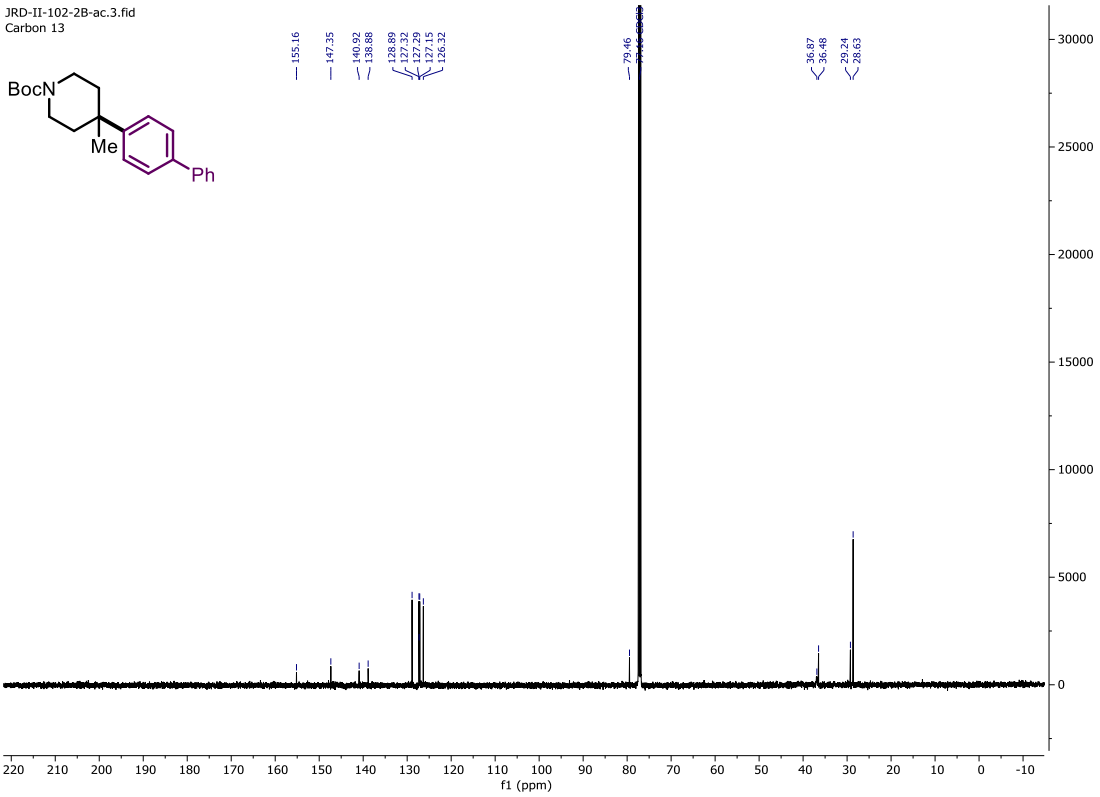

JRD-II-38-1-ac.3.fid
Me
Me
Me
N–Me
O
7.77
7.75
7.50
7.50
7.48
7.44
7.44
7.26 CDCl3
4.35
3.19
1.58 H2O
1.36
1.00
1.06
0.99
2.16
3.21
9.10
f1 (ppm)

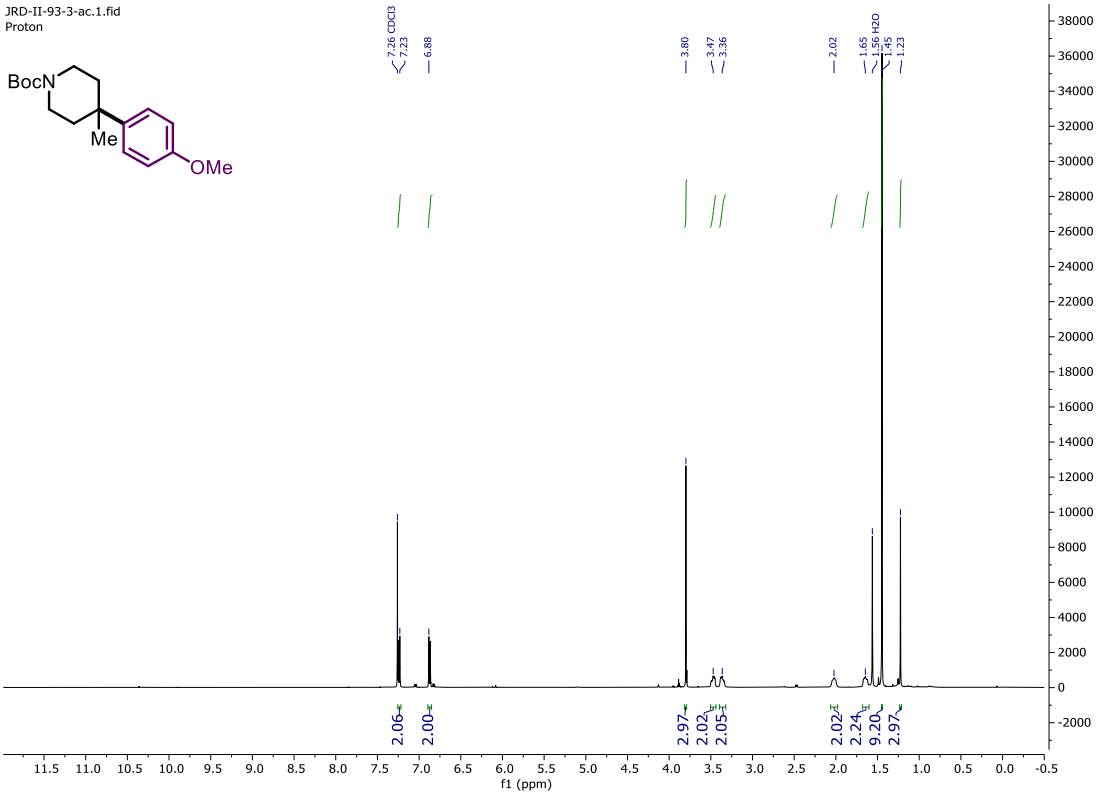

JRD-II-38-1-ac.4.fid
Carbon 13
Me
Me
Me
N–Me
O
168.91
155.15
141.26
130.48
125.56
123.28
119.52
52.25
35.40
31.56
29.61
f1 (ppm)

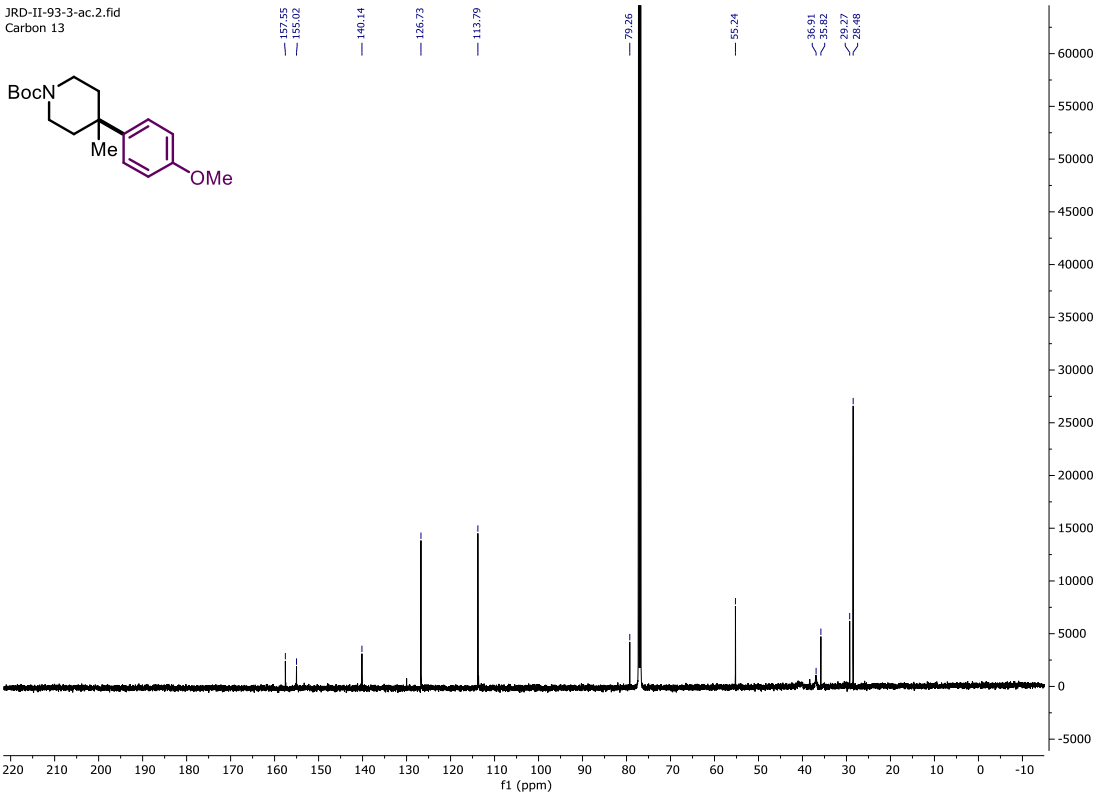

JRD-II-28-4-ac.2.fid
Proton
Me
Me
Me
H
O
9.98
7.83
7.81
7.56
7.55
7.26 CDCl3
1.55 H2O
1.36
1.05
2.00
2.00
9.33
f1 (ppm)

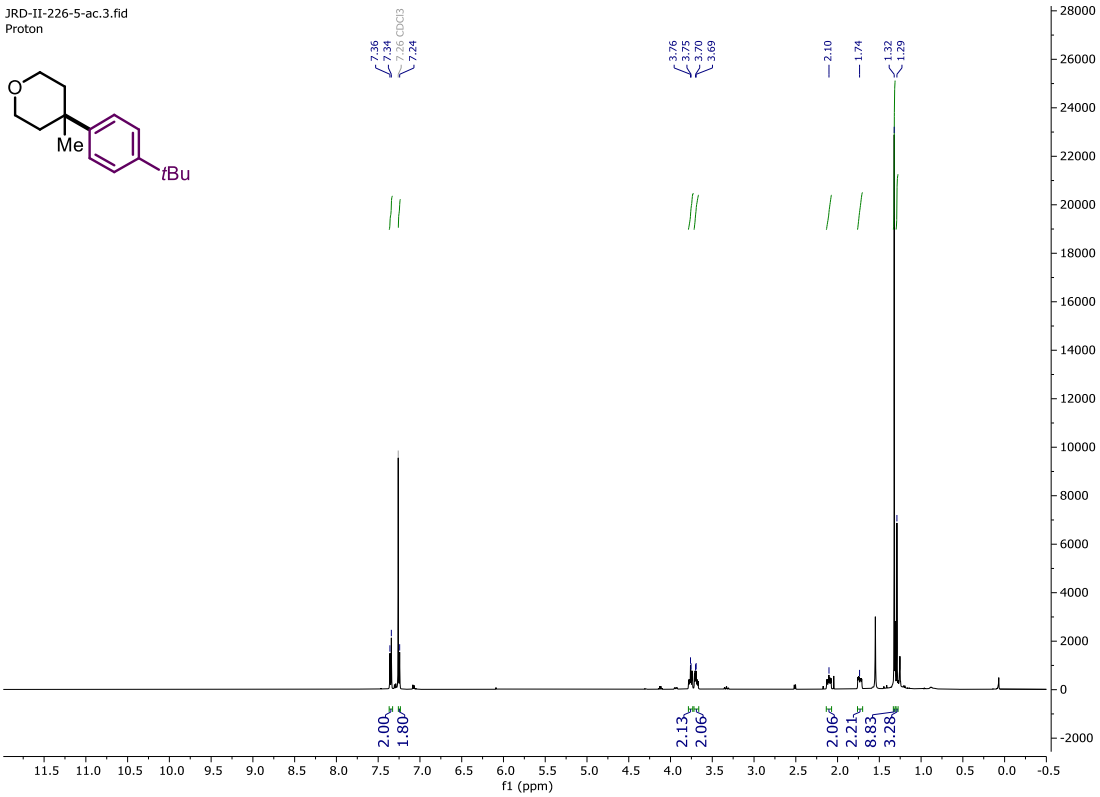

JRD-II-28-4-ac.3.fid
Carbon 13
192.21
158.61
134.24
129.85
126.15
35.51
31.23
Me
Me
Me
H
O
f1 (ppm)

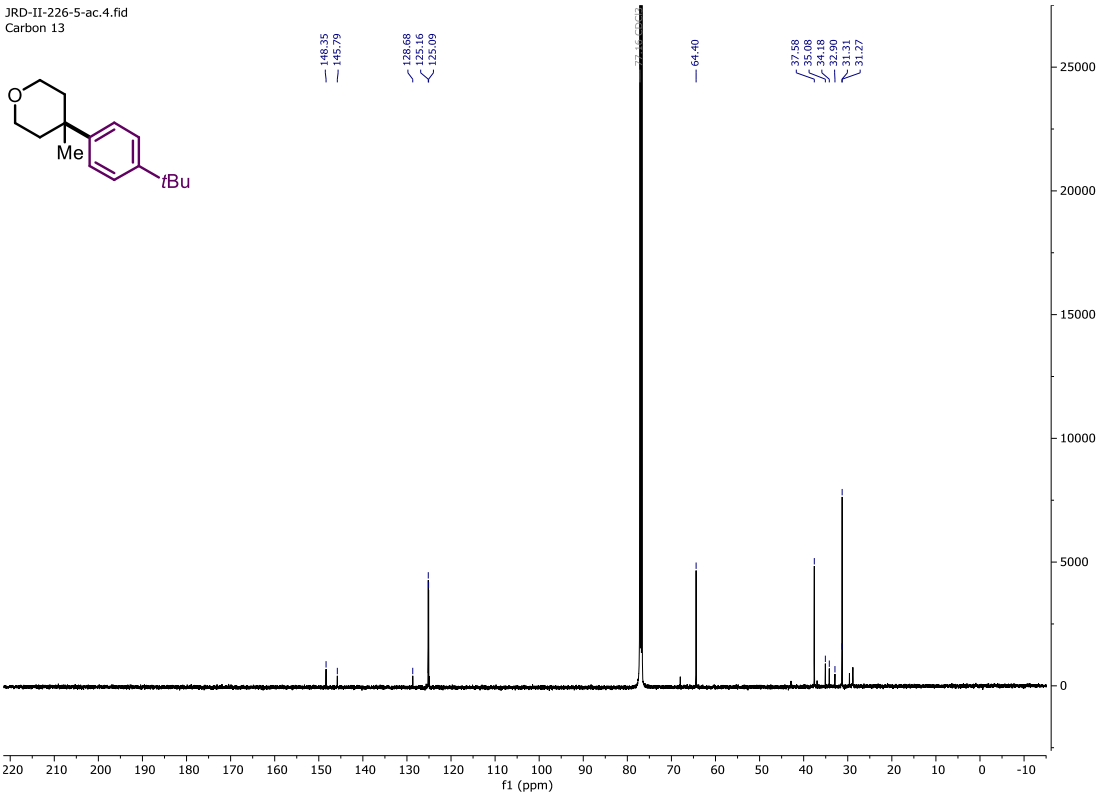

JRD-II-102-2B-ac.2.fid
Proton
7.58
7.56
7.41
7.33
7.26 CDCl3
3.51
3.50
3.49
3.42
2.10
2.10
1.71
1.56 H2O
1.46
1.29
BocN
Me
Ph
3.94
4.03
1.04
2.08
2.02
1.90
2.12
9.48
3.03
f1 (ppm)

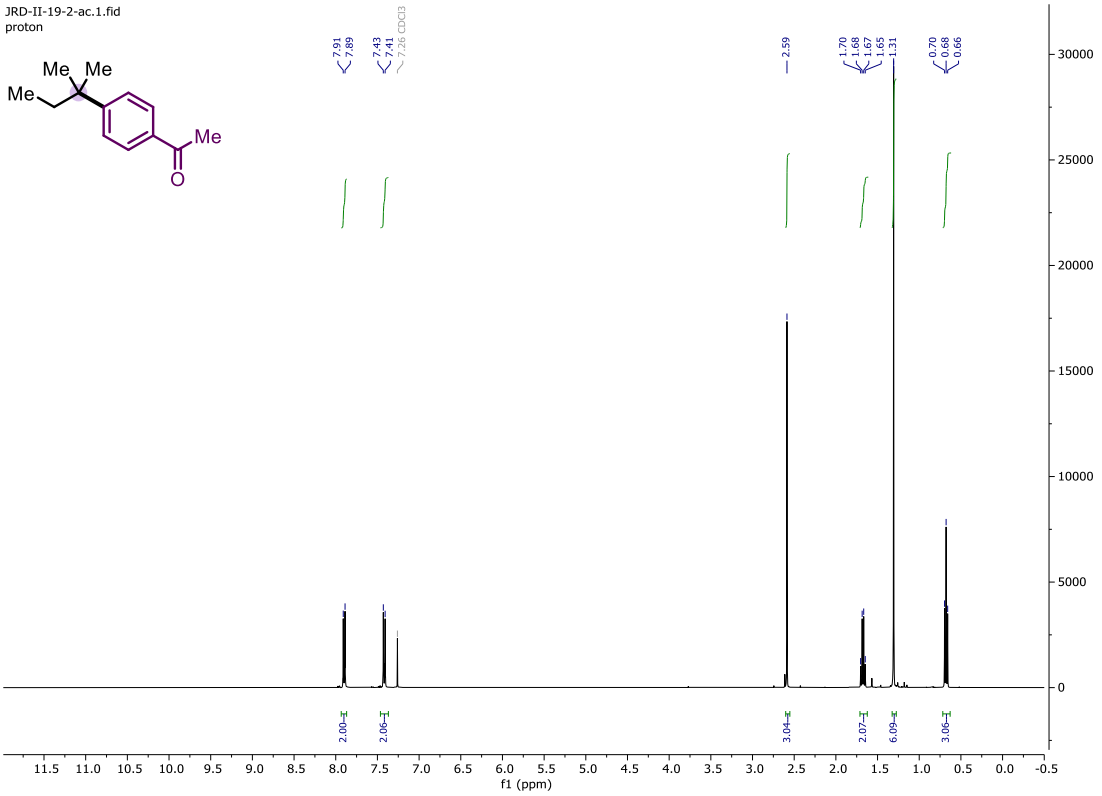

JRD-II-102-2B-ac.3.fid
Carbon 13
BocN
Me
Ph
155.16
147.35
140.92
138.88
128.89
127.32
127.29
127.15
126.32
79.46
36.87
36.48
29.24
28.63
f1 (ppm)

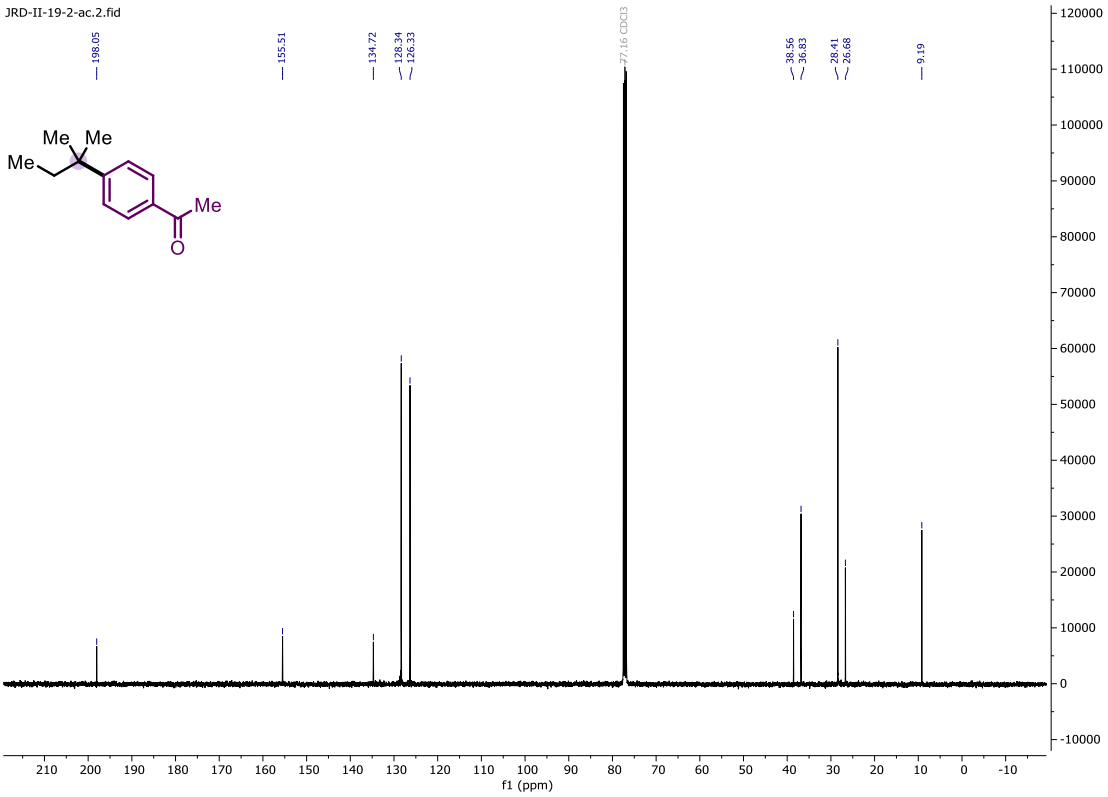

JRD-II-93-3-ac.1.fid
Proton
BocN
Me
OMe
7.26 CDCl3
7.23
6.88
3.80
3.47
3.36
2.02
1.65
1.56 H2O
1.45
1.23
2.06
2.00
2.97
2.02
2.05
2.02
2.24
9.20
2.97
f1 (ppm)

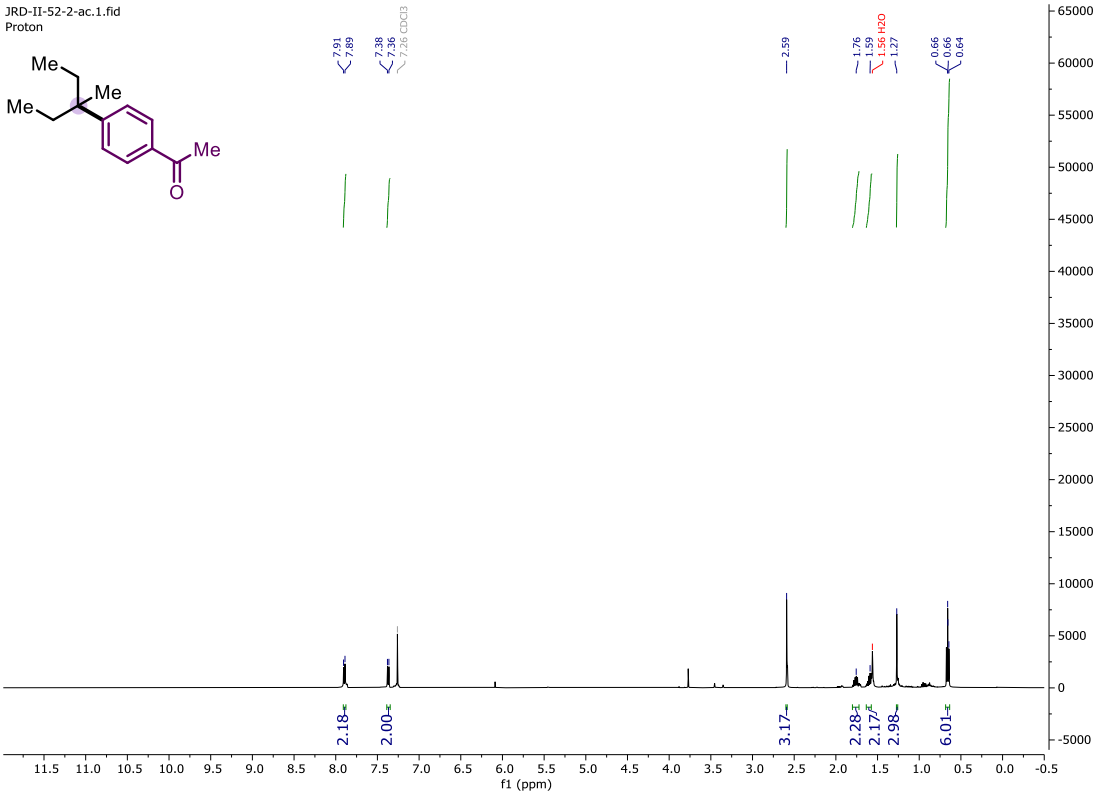

JRD-II-93-3-ac.2.fid
Carbon 13
BocN
Me
OMe
157.55
155.02
140.14
126.73
113.79
79.26
55.24
36.91
35.82
29.27
28.48
f1 (ppm)

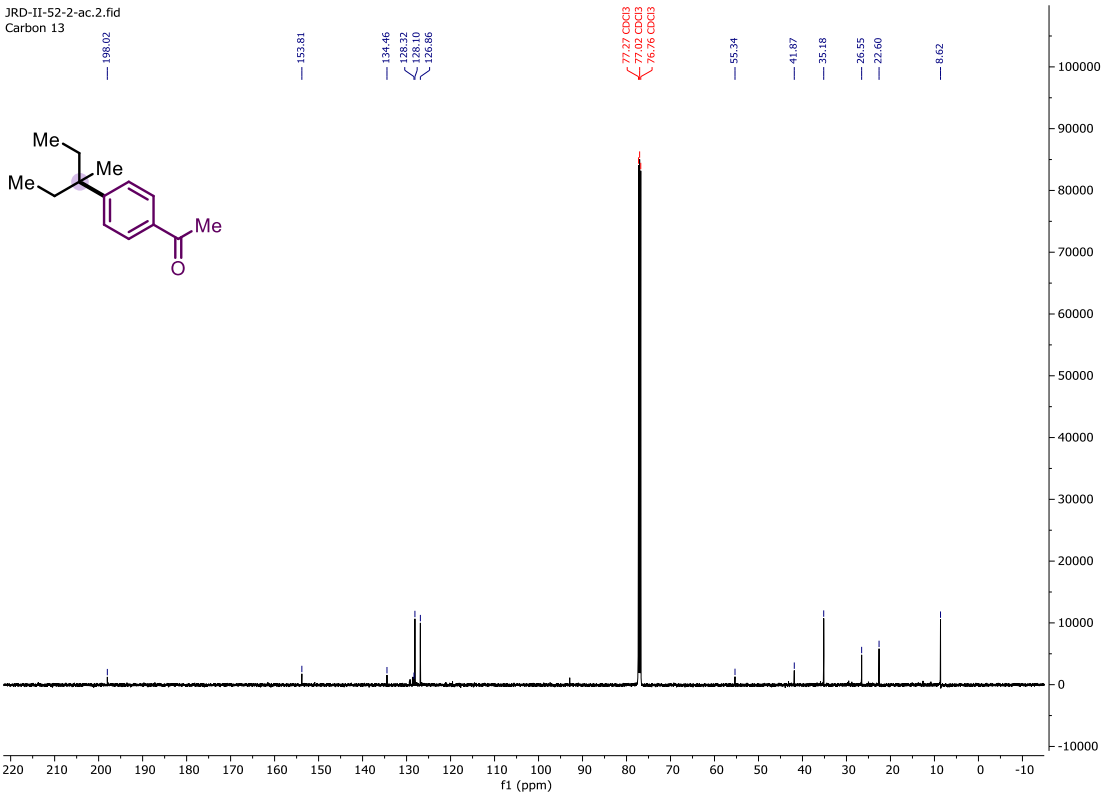

JRD-II-226-5-ac.3.fid
Proton
O
Me
tBu
7.36
7.34
7.26
CDCl3
7.24
3.76
3.75
3.70
3.69
2.10
1.74
1.32
1.29
2.00
1.80
2.13
2.06
2.06
2.21
8.83
3.28
f1 (ppm)

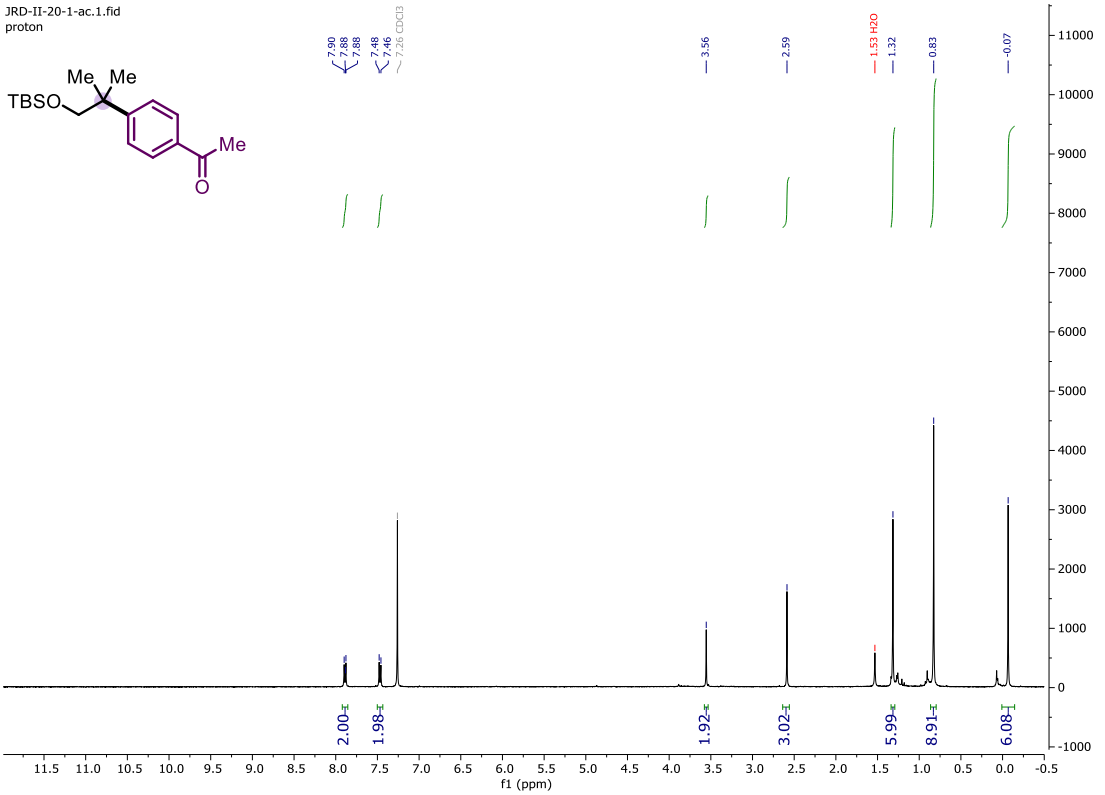

JRD-II-226-5-ac.4.fid
Carbon 13
148.35
145.79
128.68
125.16
125.09
64.40
37.58
35.08
34.18
32.90
31.31
31.27
Me
tBu
f1 (ppm)

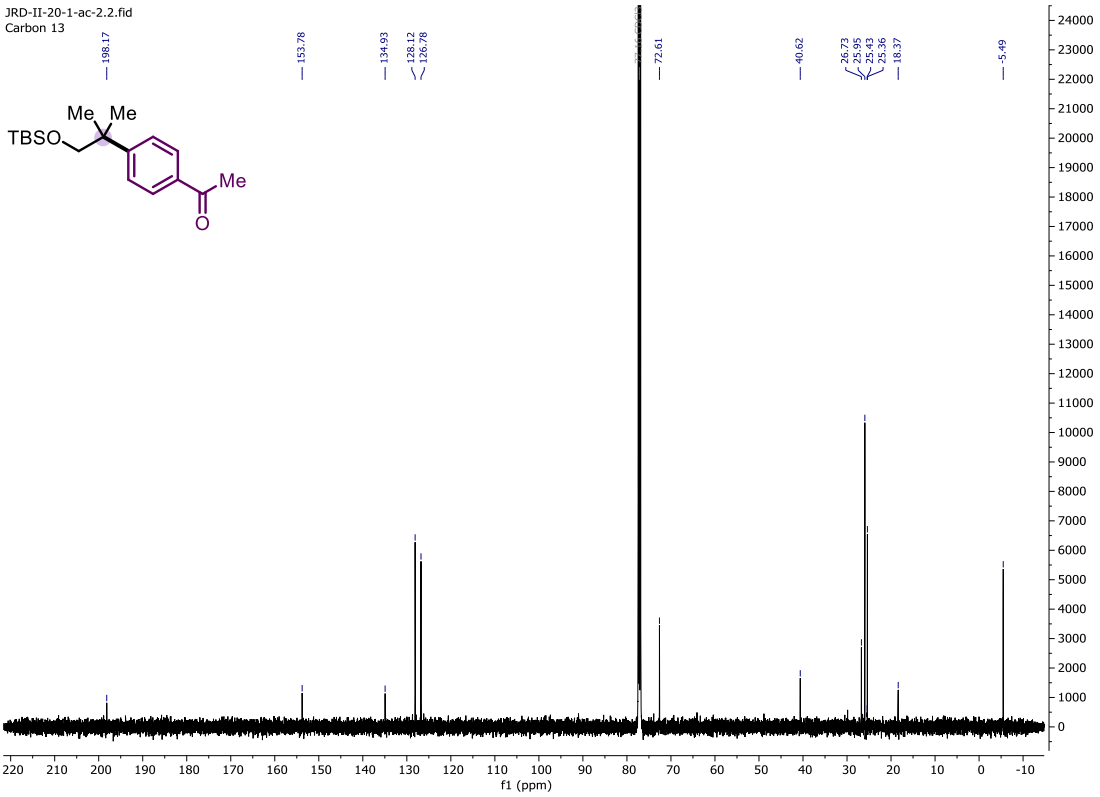

JRD-II-19-2-ac.1.fid
proton
7.91
7.89
7.43
7.41
7.26 CDCl3
2.59
1.70
1.68
1.67
1.65
1.31
0.70
0.68
0.66
Me
Me
Me
Me
O
2.00
2.06
3.04
2.07
6.09
3.06
f1 (ppm)

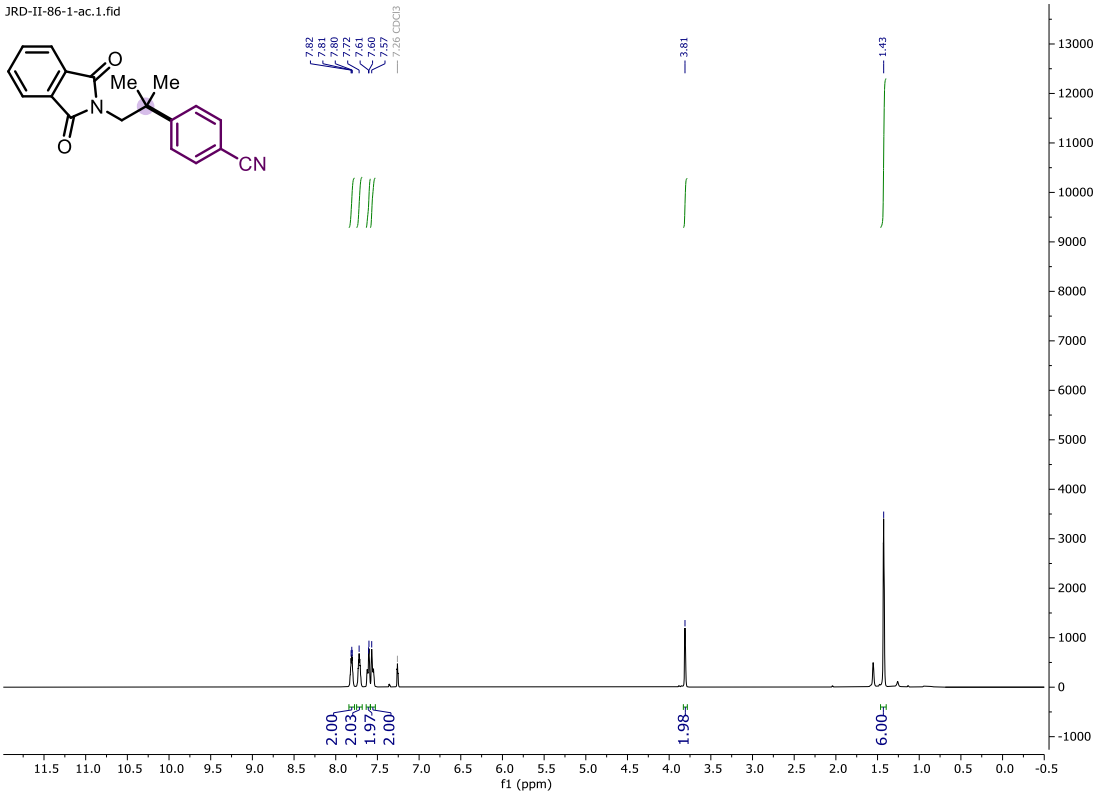

JRD-II-19-2-ac.2.fid
198.05
155.51
134.72
128.34
126.33
77.16 CDCl3
38.56
36.83
28.41
26.68
9.19
Me
Me
Me
Me
O
f1 (ppm)

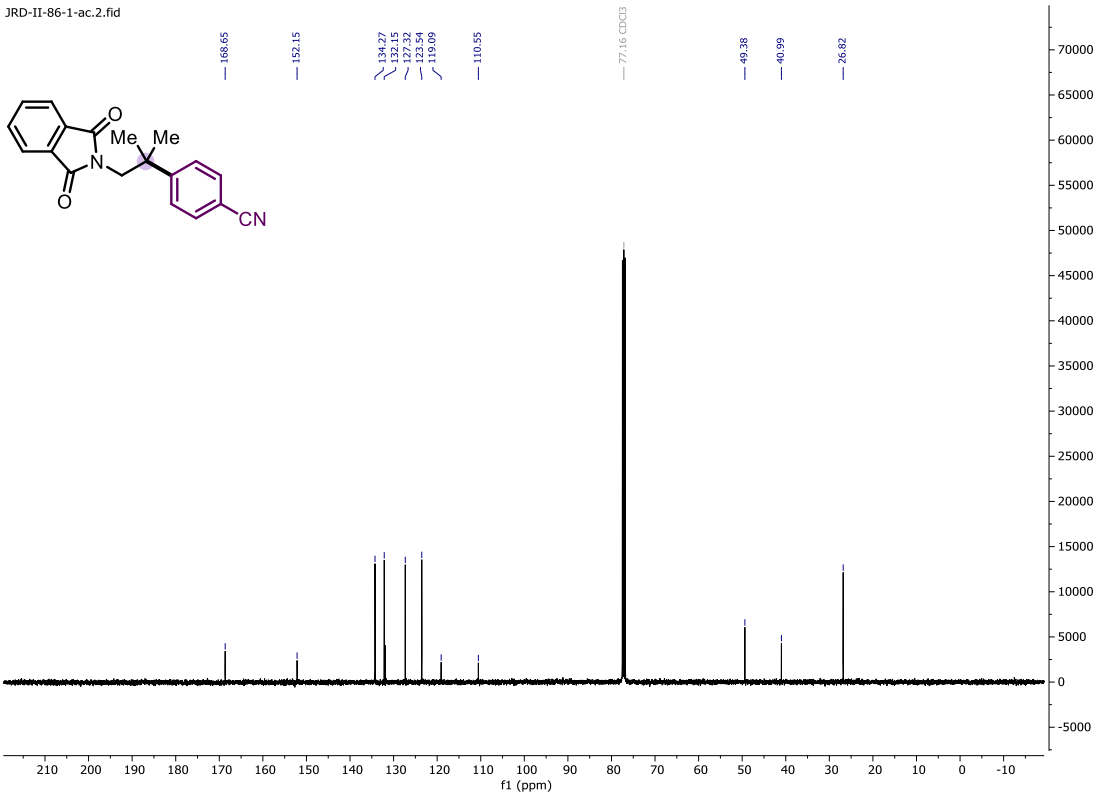

JRD-II-52-2-ac.1.fid
Proton
7.91
7.89
7.38
7.36
7.26 CDCl3
2.59
1.76
1.59
1.56 H2O
1.27
0.66
0.66
0.64
Me
Me
Me
Me
O
2.18
2.00
3.17
2.28
2.17
2.98
6.01
f1 (ppm)

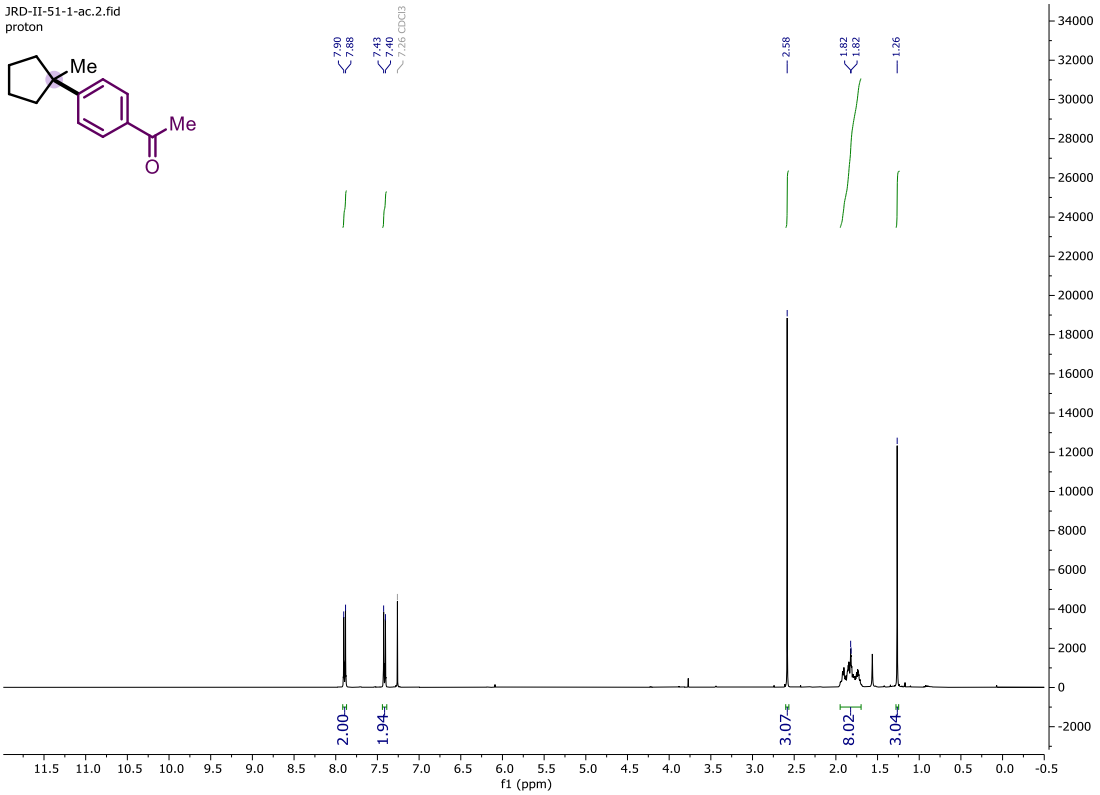

JRD-II-52-2-ac.2.fid
Carbon 13
198.02
153.81
134.46
128.32
128.10
126.86
77.27 CDCl3
77.02 CDCl3
76.76 CDCl3
55.34
41.87
35.18
26.55
22.60
8.62
Me
Me
Me
Me
O
f1 (ppm)

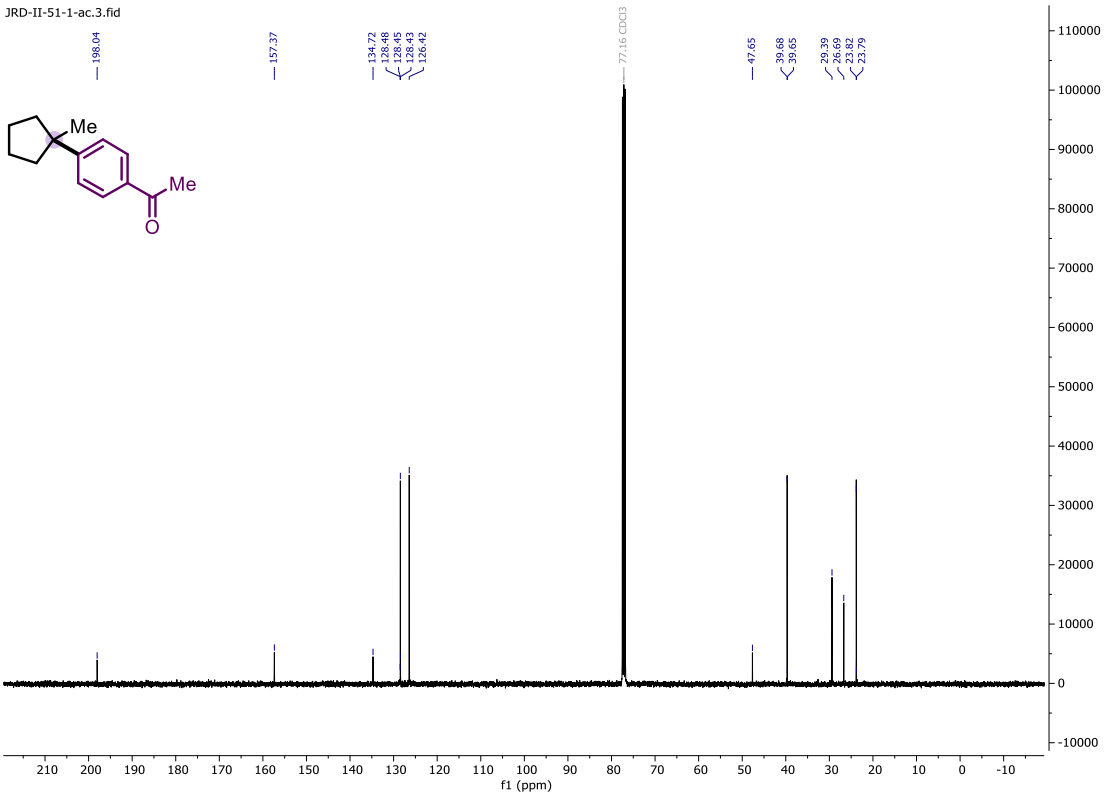

JRD-II-20-1-ac.1.fid
proton
7.90
7.88
7.88
7.48
7.46
7.26 CDCl3
3.56
2.59
1.53 H2O
1.32
0.83
-0.07
Me
Me
TBSO
Me
O
2.00
1.98
1.92
3.02
5.99
8.91
6.08
f1 (ppm)

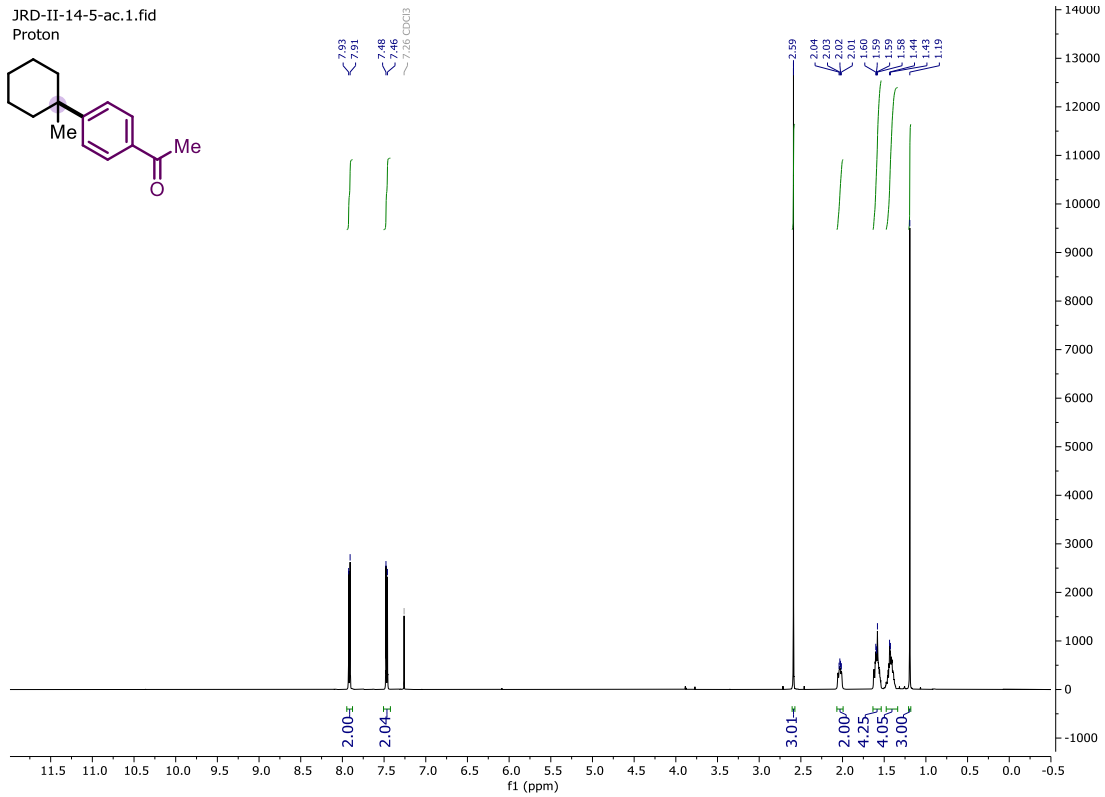

JRD-II-20-1-ac-2.2.fid
Carbon 13
198.17
153.78
134.93
128.12
126.78
72.61
40.62
26.73
25.95
25.43
25.36
18.37
-5.49
Me Me
TBSO
Me
O
f1 (ppm)

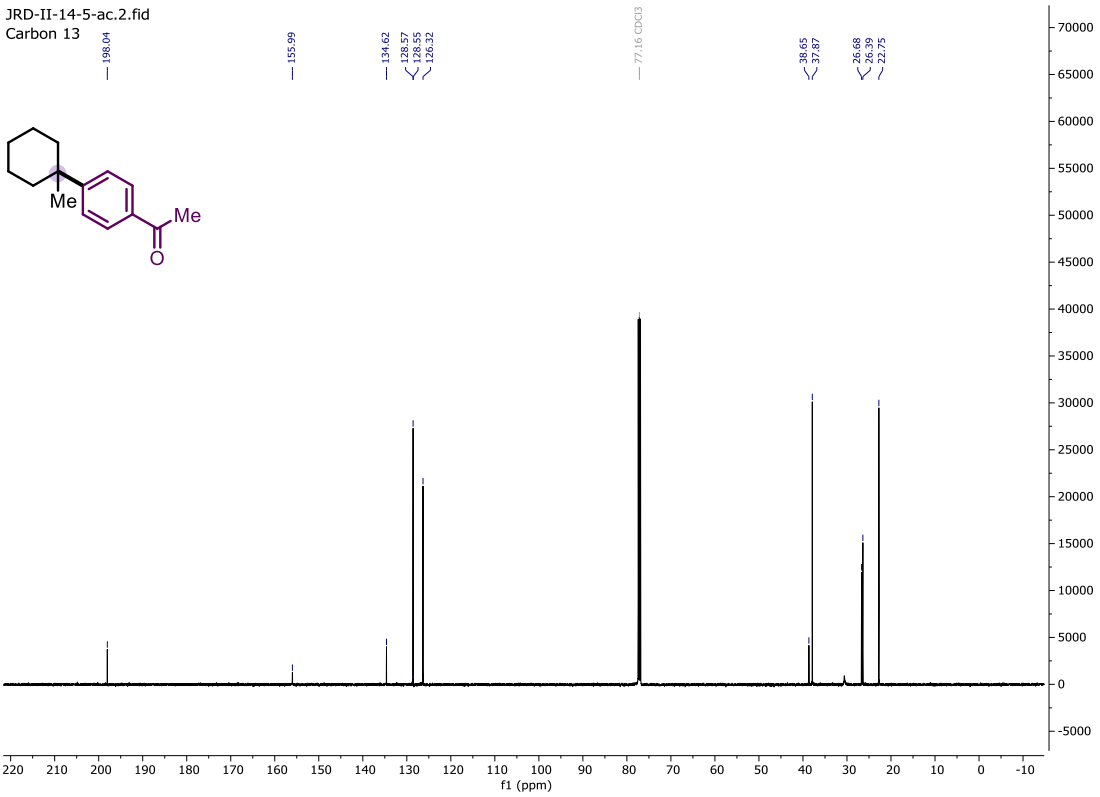

JRD-II-86-1-ac.1.fid
7.82
7.81
7.80
7.72
7.61
7.60
7.57
7.26 CDCl3
3.81
1.43
O
Me Me
N
O
CN
2.00
2.03
1.97
2.00
1.98
6.00
f1 (ppm)


JRD-II-86-1-ac.2.fid
168.65
152.15
134.27
132.15
127.32
123.54
119.09
110.55
77.16 CDCl3
49.38
40.99
26.82
O
Me
Me
N
O
CN
f1 (ppm)


JRD-II-51-1-ac.2.fid
proton
7.90
7.88
7.43
7.40
7.26 CDCl3
2.58
1.82
1.82
1.26
Me
Me
O
2.00
1.94
3.07
8.02
3.04
f1 (ppm)


JRD-II-51-1-ac.3.fid
198.04
157.37
134.72
134.46
128.45
128.43
126.42
77.16 CDCl3
47.65
39.68
39.65
29.39
26.69
23.82
23.79
Me
Me
O
f1 (ppm)


JRD-II-14-5-ac.1.fid
Proton
7.93
7.91
7.48
7.46
7.26 CDCl3
2.59
2.04
2.03
2.02
2.01
1.60
1.59
1.59
1.58
1.44
1.43
1.19
Me
Me
O
2.00
2.04
3.01
2.00
4.25
4.05
3.00
f1 (ppm)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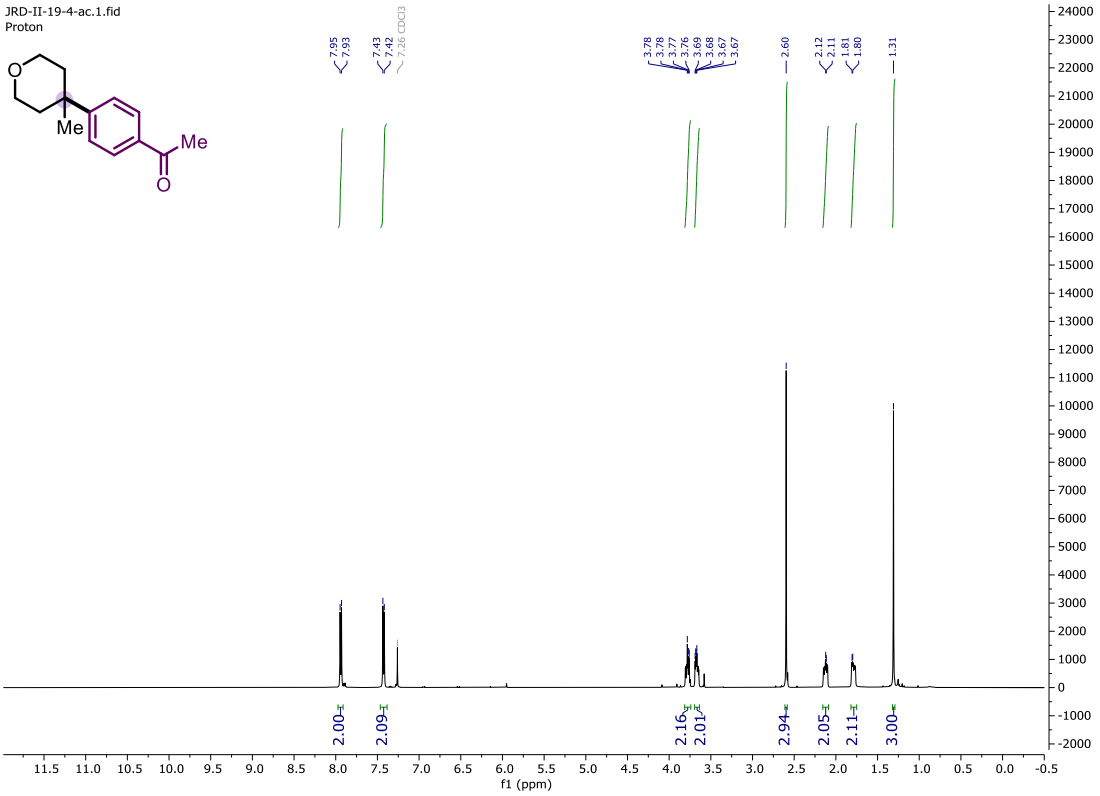
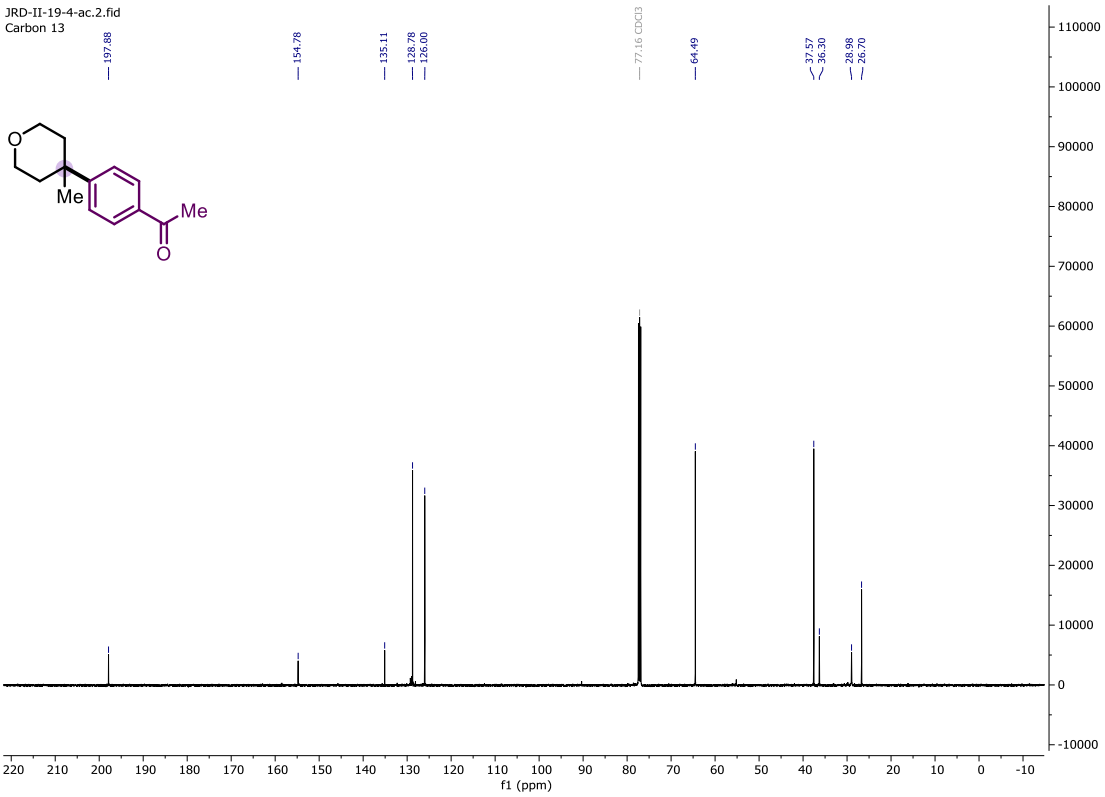
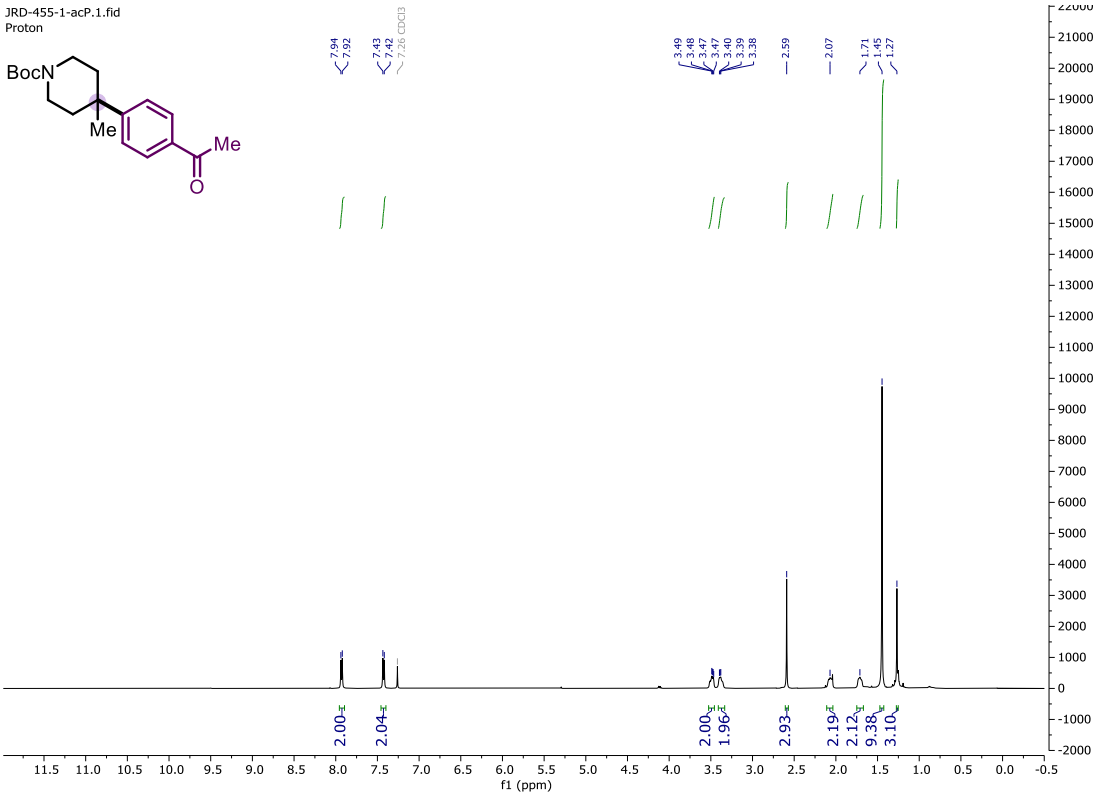
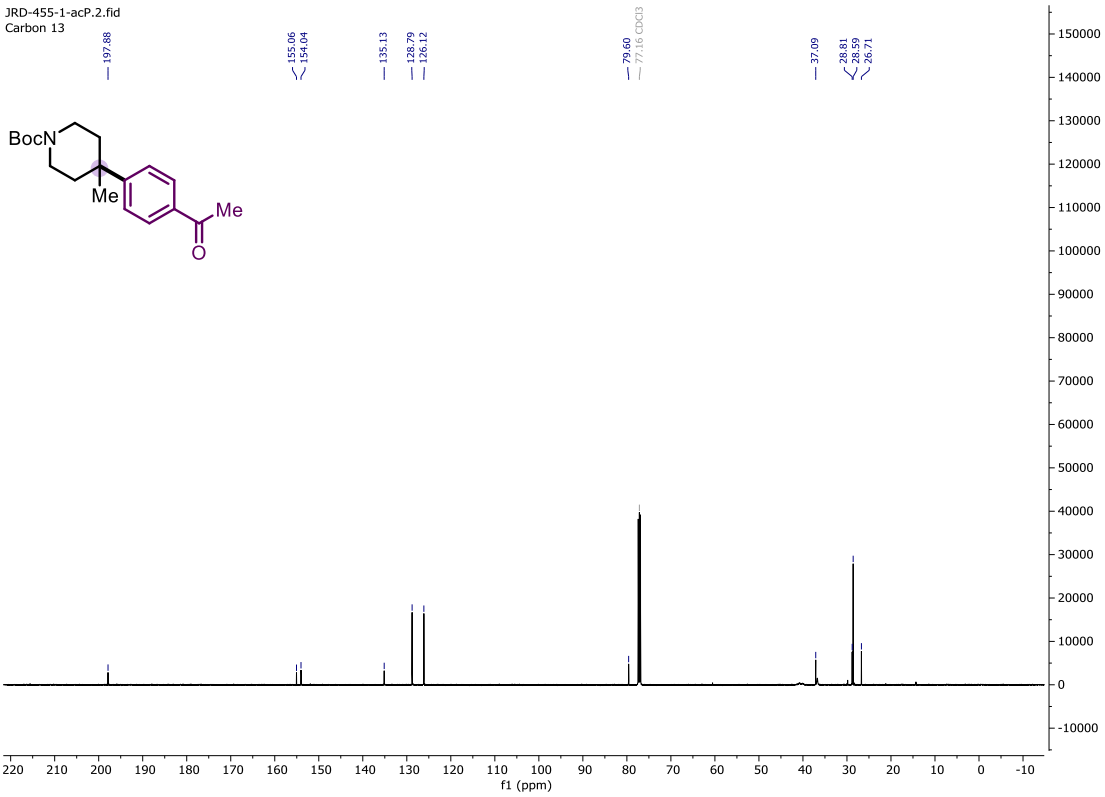
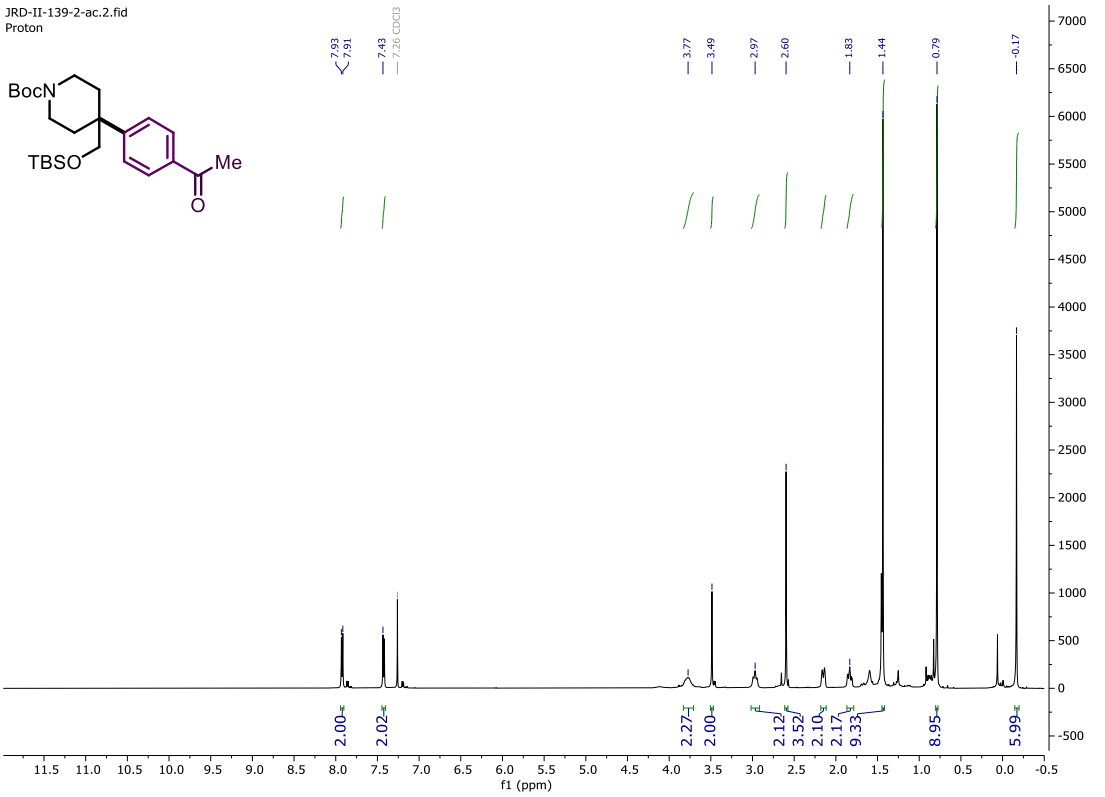
Carbon 13
198.04
155.99
134.62
128.57
128.55
126.32
77.16 CDCl3
38.65
37.87
26.68
26.39
22.75
Me
Me
O
f1 (ppm)

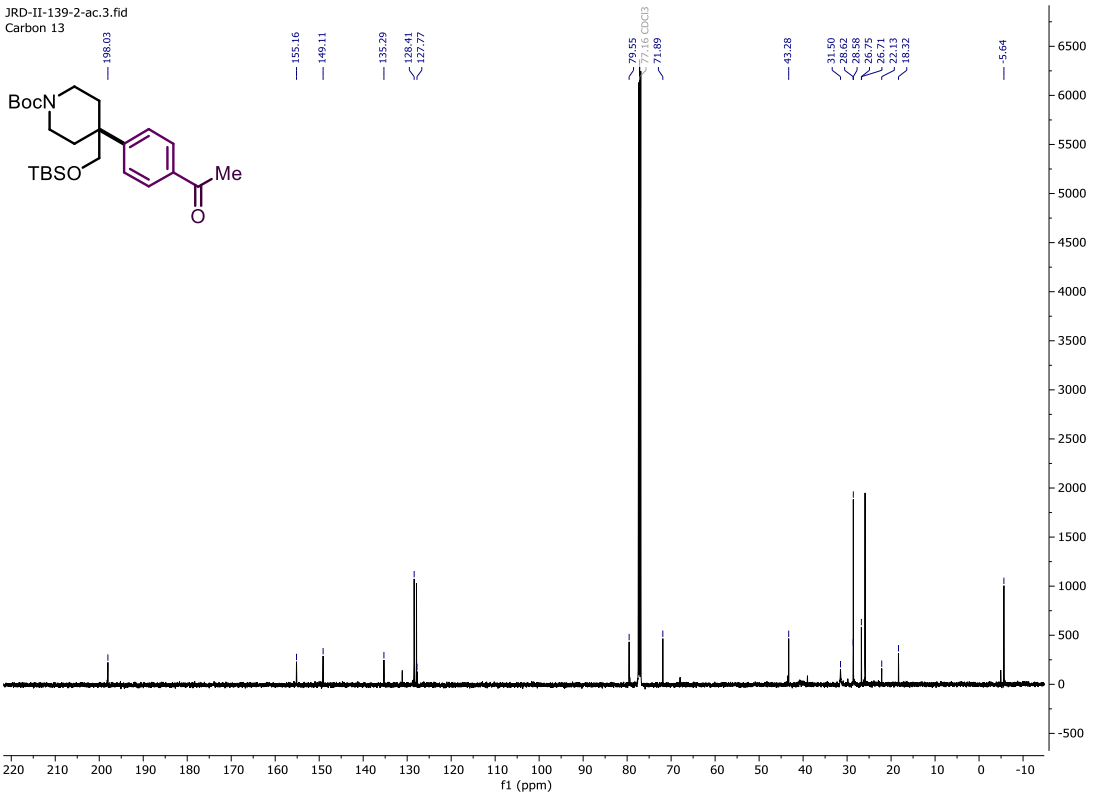

JRD-II-19-4-ac.1.fid
Proton
7.95
7.93
7.43
7.42
7.26 CDCl3
3.78
3.78
3.77
3.76
3.69
3.68
3.67
3.67
2.60
2.12
2.11
1.81
1.80
1.31
Me
Me
O
2.00
2.09
2.16
2.01
2.94
2.05
2.11
3.00
f1 (ppm)

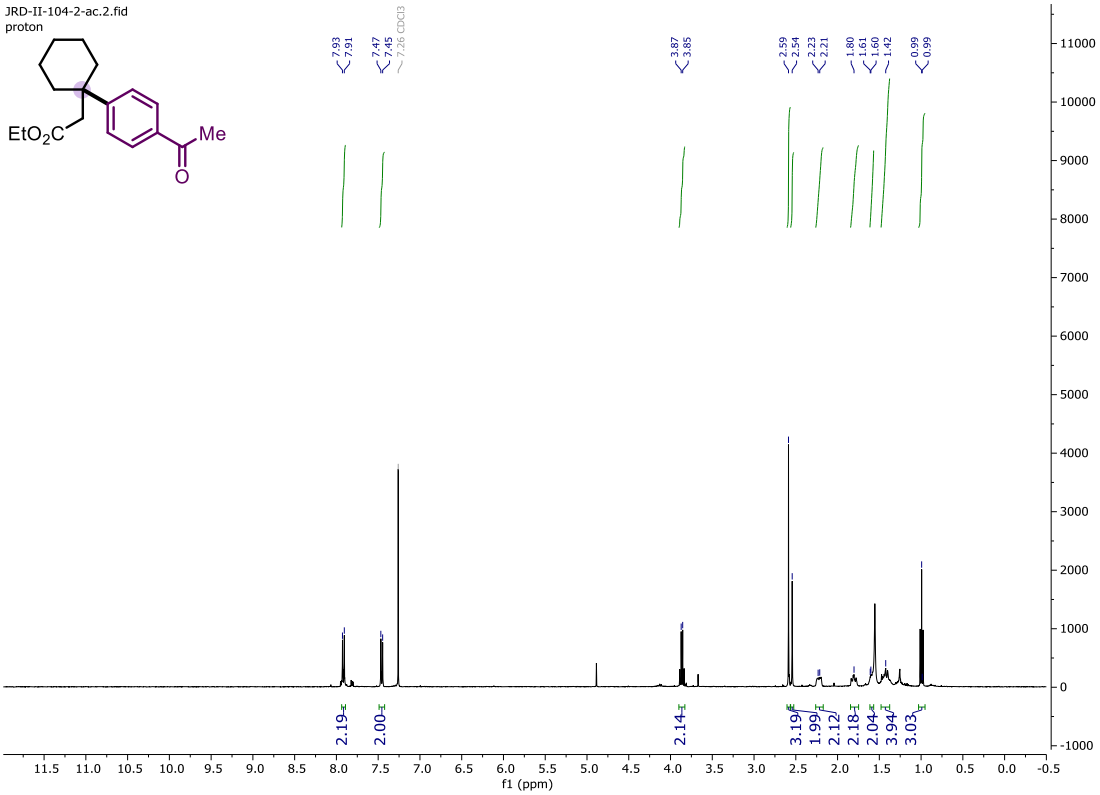

JRD-II-19-4-ac.2.fid
Carbon 13
197.88
154.78
135.11
128.78
126.00
77.16 CDCl3
64.49
37.57
36.30
28.98
26.70
Me
Me
O
f1 (ppm)

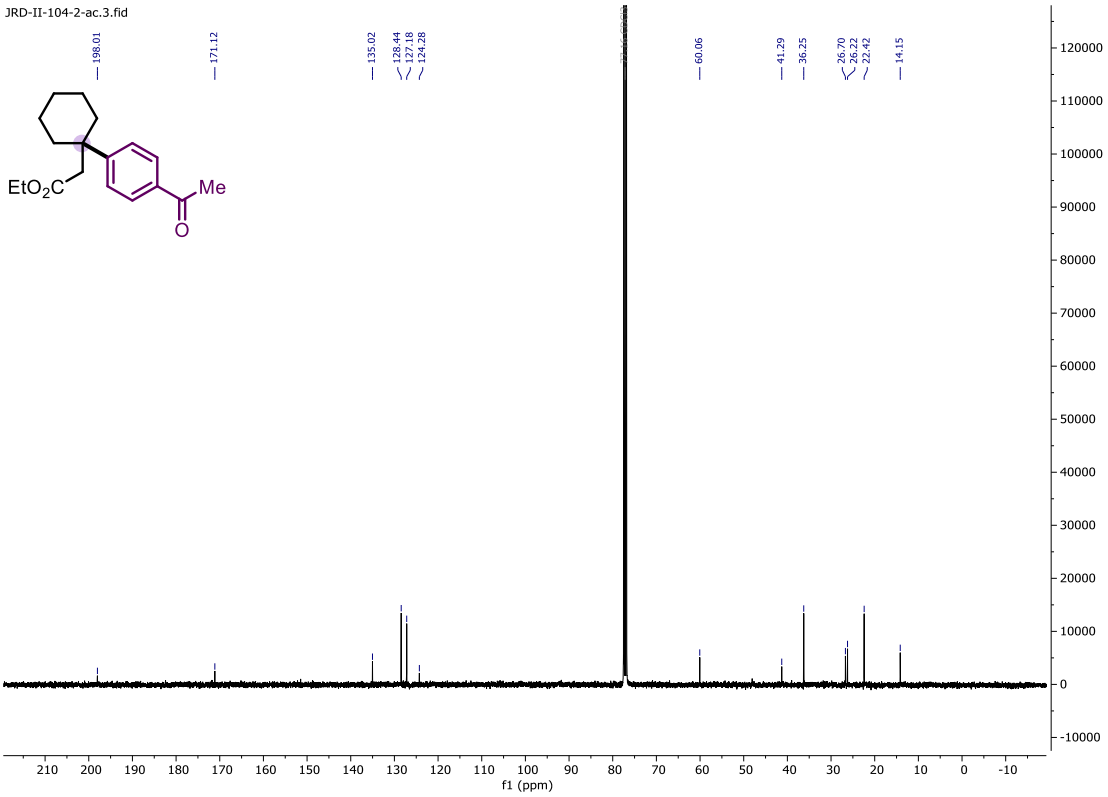

JRD-455-1-acP.1.fid
Proton
BocN
Me
Me
O
7.94
7.92
7.43
7.42
7.26 CDCl3
3.49
3.48
3.47
3.47
3.40
3.39
3.38
2.59
2.07
1.71
1.45
1.27
2.00
2.04
2.00
1.96
2.93
2.19
2.12
9.38
3.10
f1 (ppm)

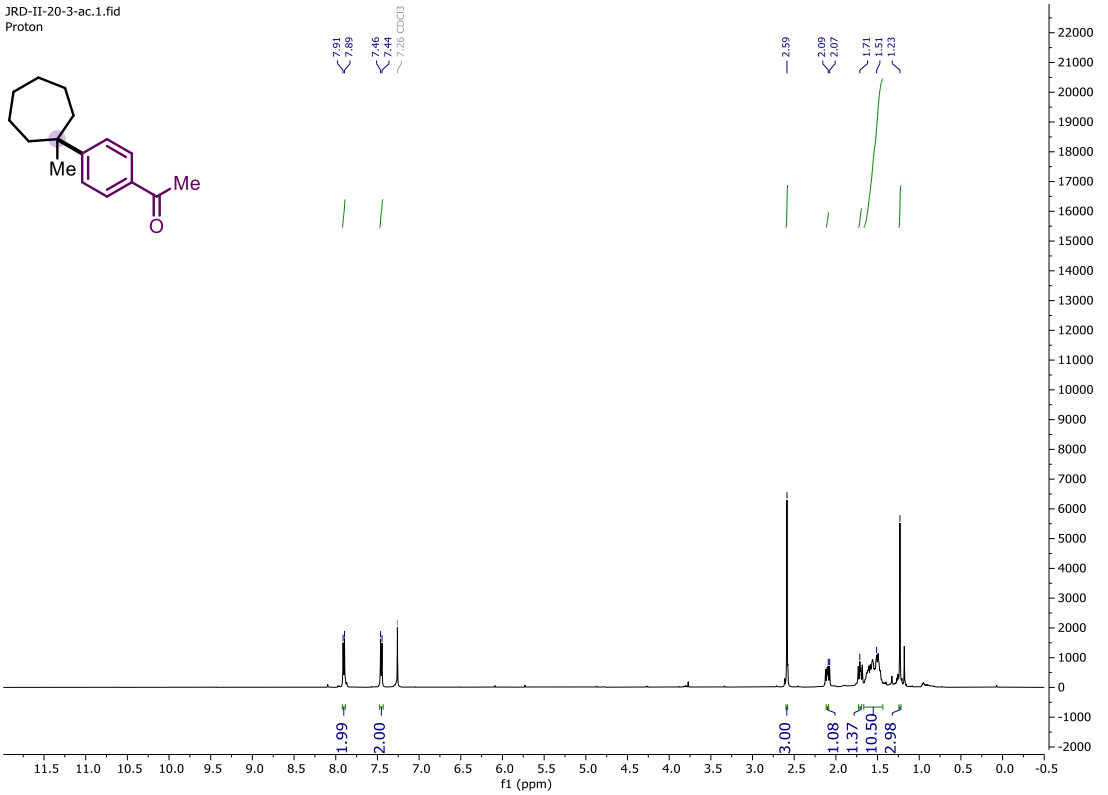

JRD-455-1-acP.2.fid
Carbon 13
197.88
155.06
154.04
135.13
128.79
126.12
79.60
77.16 CDCl3
37.09
28.81
28.59
26.71
BocN
Me
Me
O
f1 (ppm)

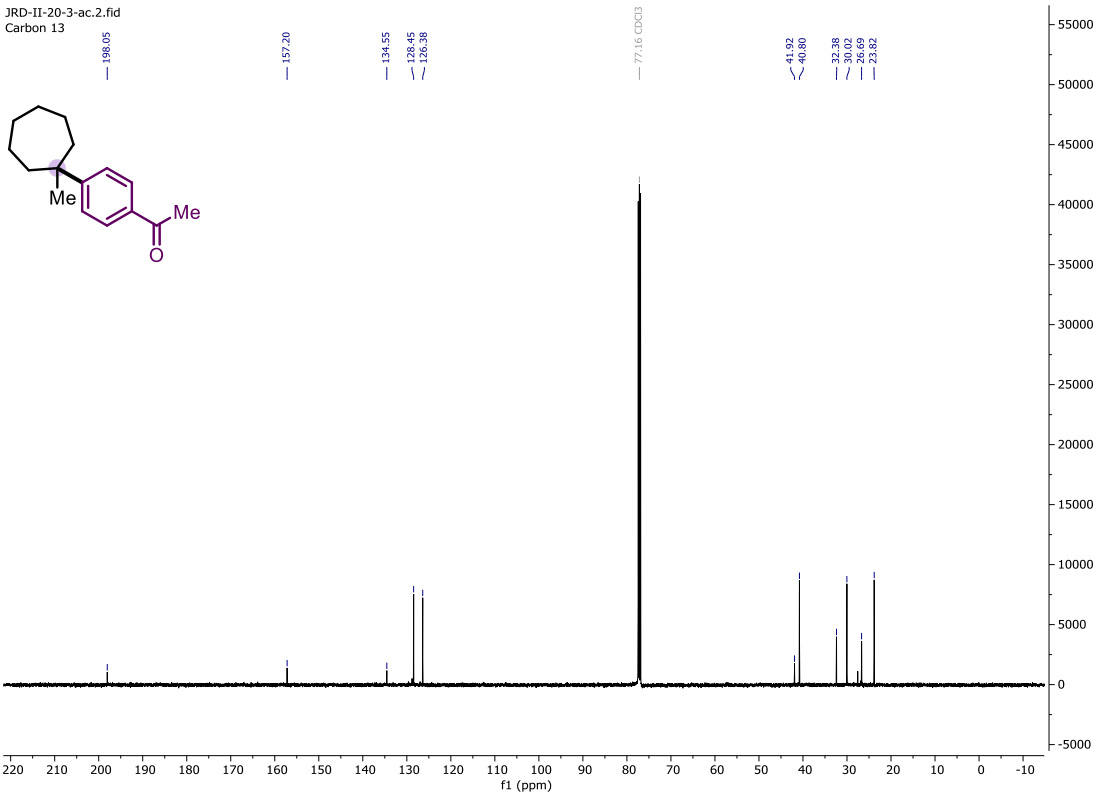

JRD-II-139-2-ac.2.fid
Proton
7.93
7.91
7.43
7.26 CDCl3
3.77
3.49
2.97
2.60
1.83
1.44
0.79
-0.17
BocN
TBSO
Me
O
2.00
2.02
2.27
2.00
2.12
3.52
2.10
2.17
9.33
8.95
5.99
f1 (ppm)

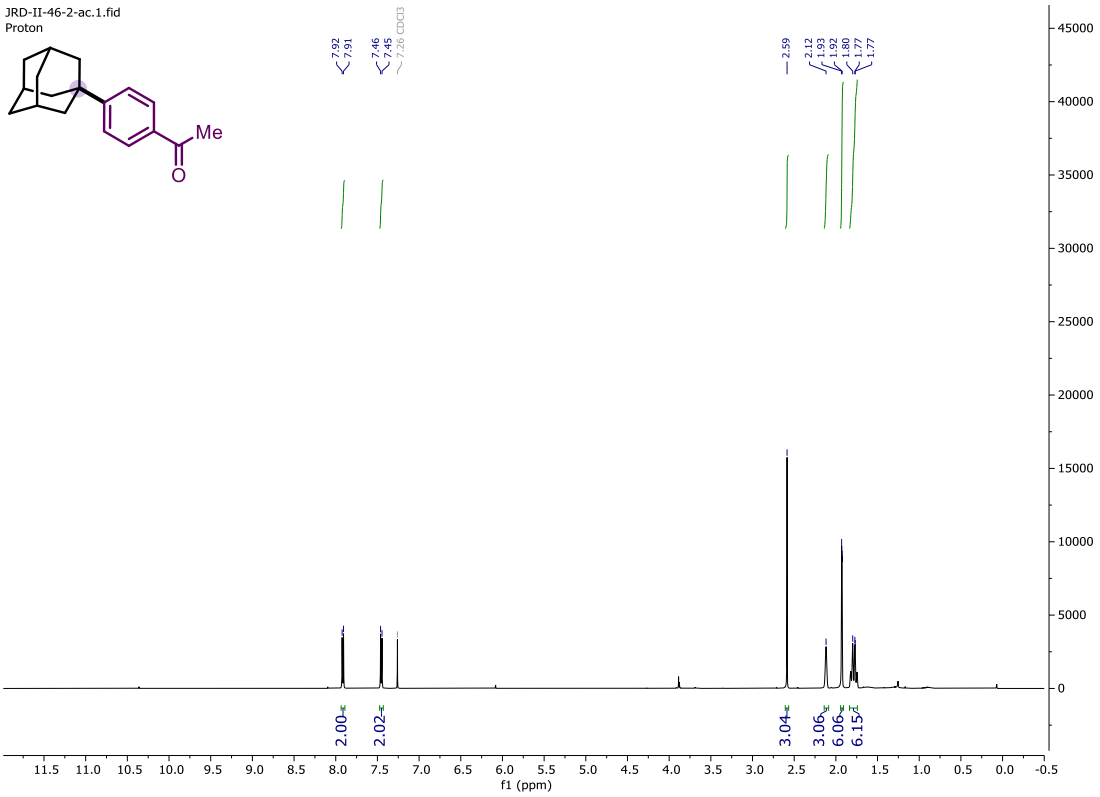

JRD-II-139-2-ac.3.fid
Carbon 13
BocN
TBSO
Me
O
198.03
155.16
149.11
135.29
128.41
127.77
79.55
77.16 CDCl3
71.89
43.28
31.50
28.62
28.58
26.75
26.71
22.13
18.32
-5.64
f1 (ppm)

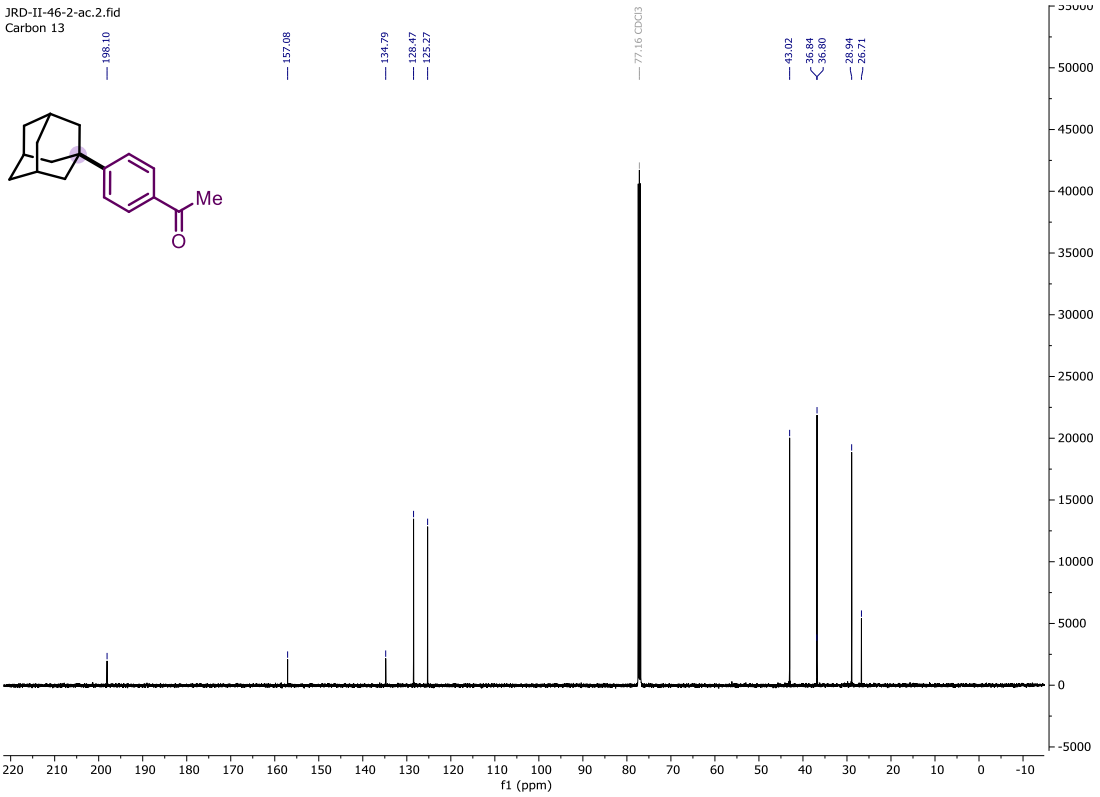

JRD-II-104-2-ac.2.fid
proton
EtO2C
Me
O
7.93
7.91
7.47
7.45
7.26 CDCl3
3.87
3.85
2.59
2.54
2.23
2.21
1.80
1.61
1.60
1.42
0.99
0.99
2.19
2.00
2.14
3.19
1.99
2.12
2.18
2.04
3.94
3.03
f1 (ppm)

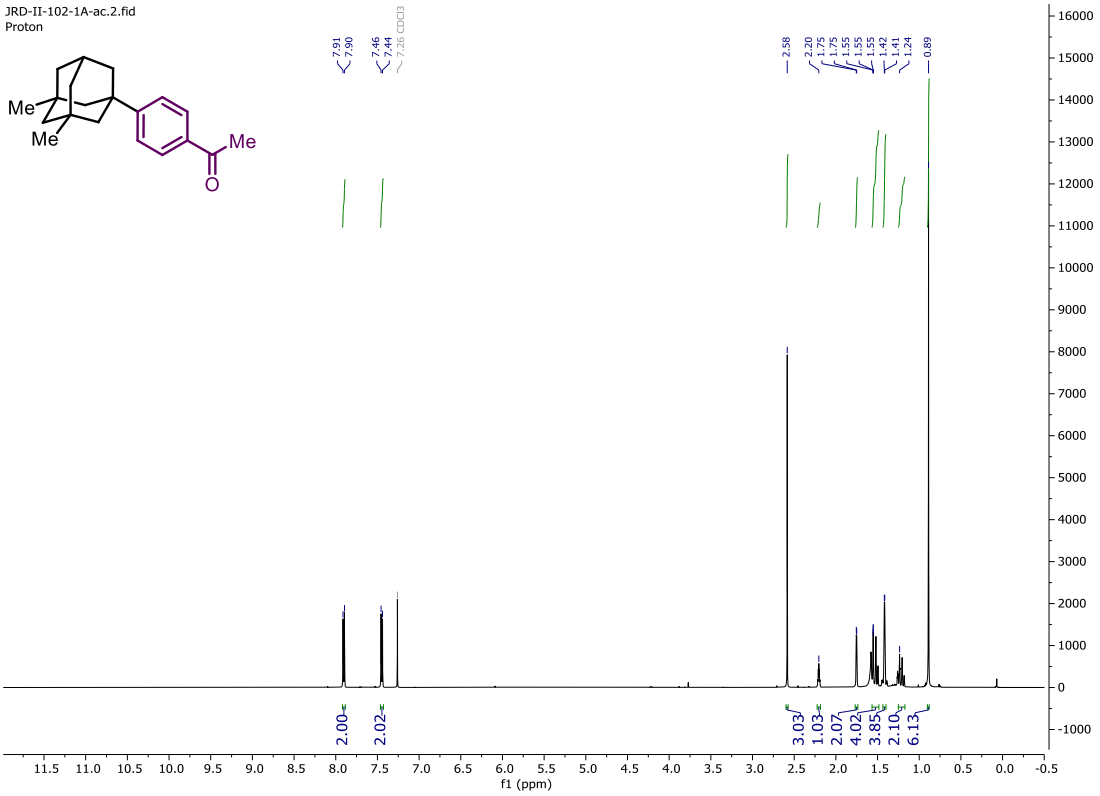

JRD-II-104-2-ac.3.fid
198.01
171.12
135.02
128.44
127.18
124.28
77.16
60.06
41.29
36.25
26.70
26.22
22.42
14.15
EtO2C
Me
O
f1 (ppm)

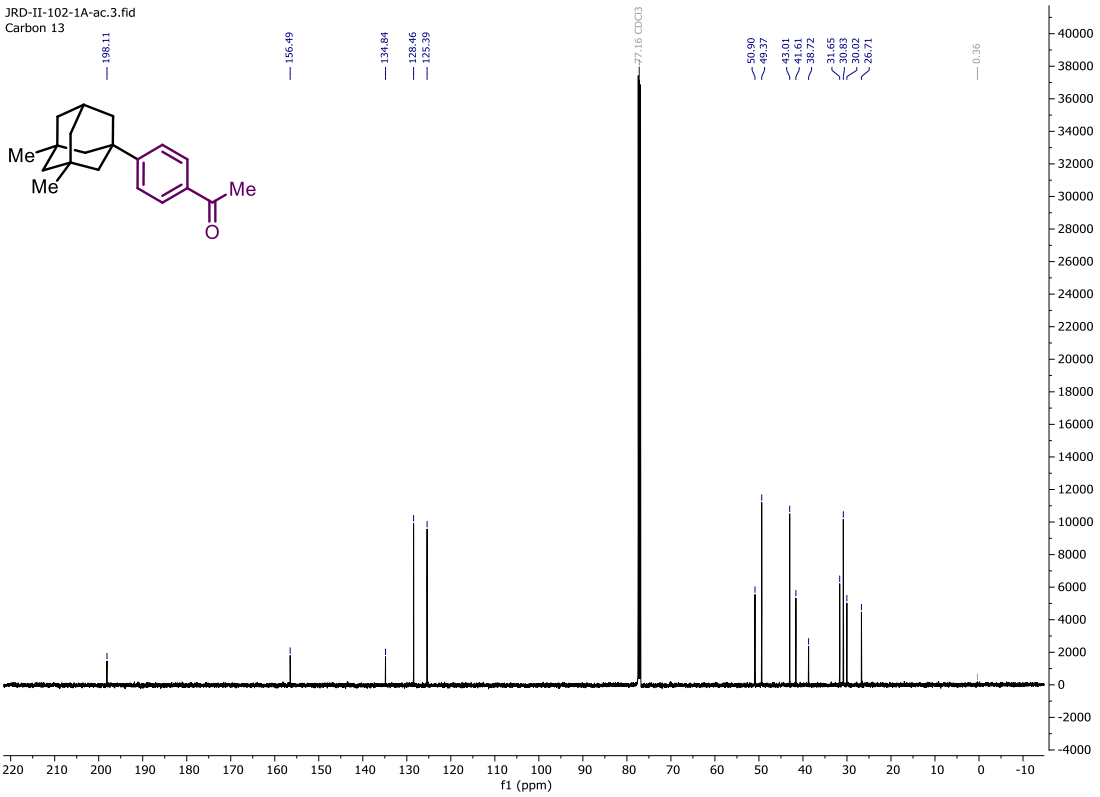

JRD-II-20-3-ac.1.fid
Proton
7.91
7.89
7.46
7.44
7.26 CDCl3
2.59
2.09
2.07
1.71
1.51
1.23
Me
Me
O
1.99
2.00
3.00
1.08
1.37
10.50
2.98
f1 (ppm)

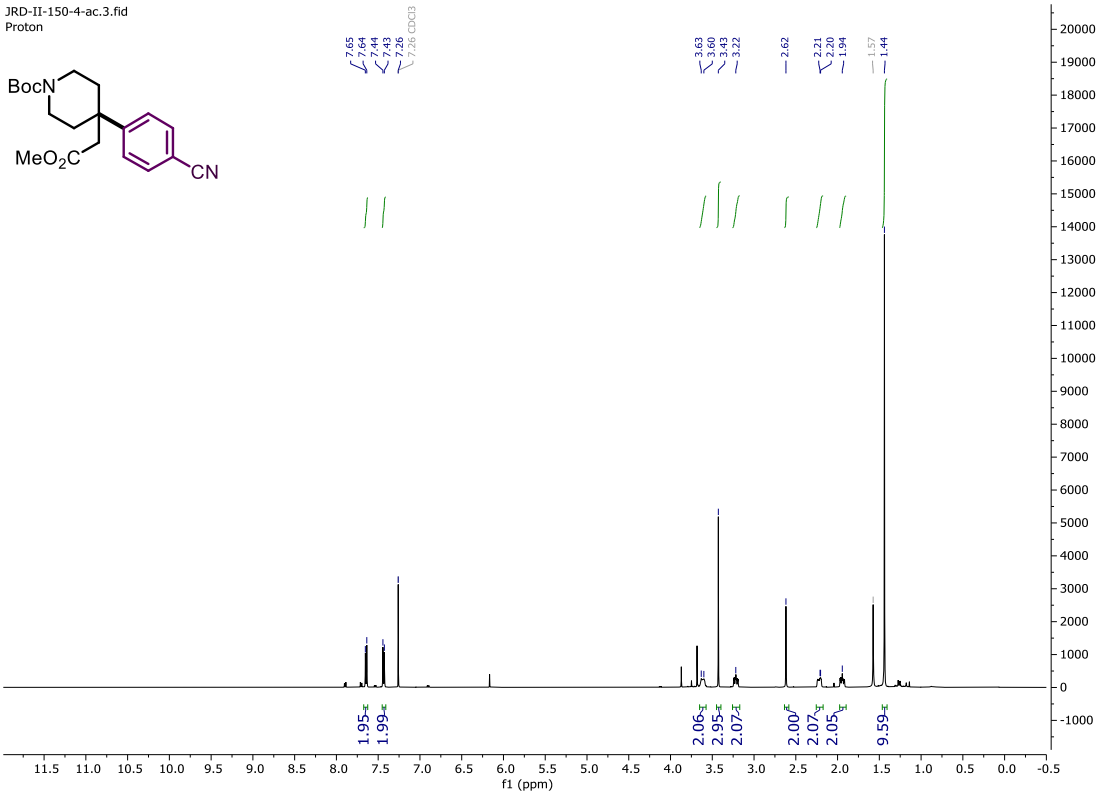

JRD-II-20-3-ac.2.fid
Carbon 13
198.05
157.20
134.55
128.45
126.38
77.16 CDCl3
41.92
40.80
32.38
30.02
26.69
23.82
Me
Me
O
f1 (ppm)

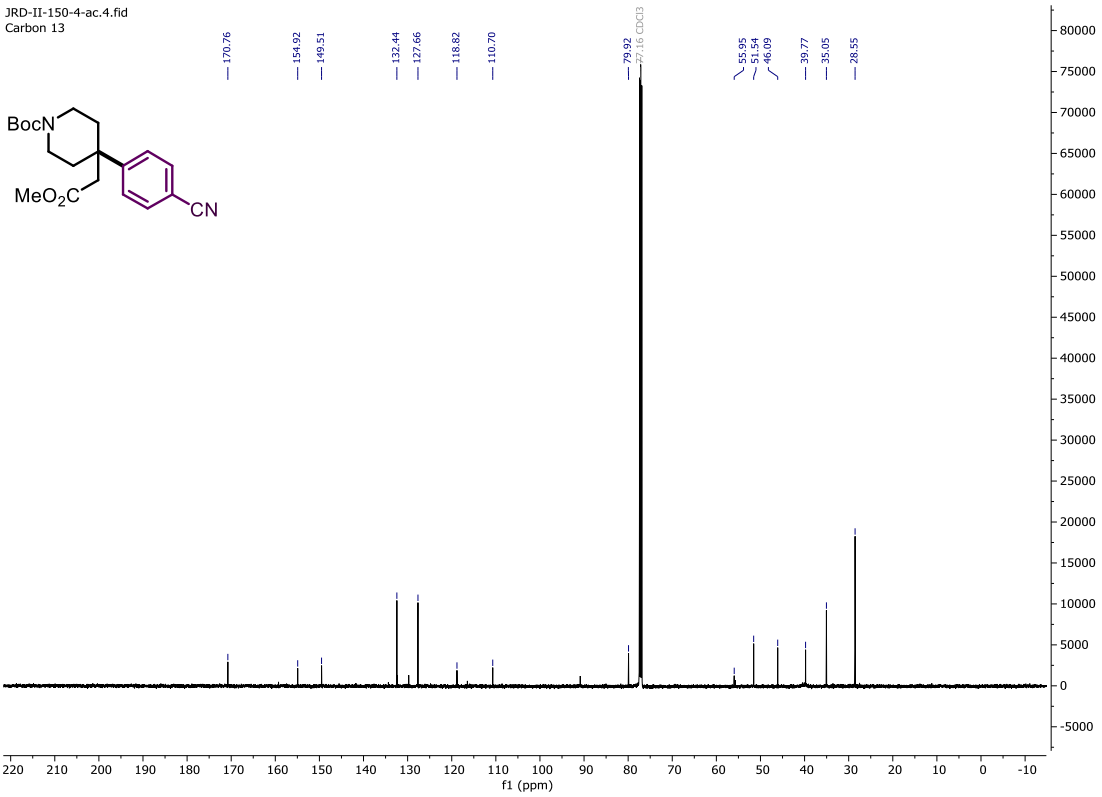

JRD-II-46-2-ac.1.fid
Proton
7.92
7.91
7.46
7.45
7.26 CDCl3
2.59
2.12
1.93
1.92
1.80
1.77
1.77
Me
O
2.00
2.02
3.04
3.06
6.06
6.15
f1 (ppm)

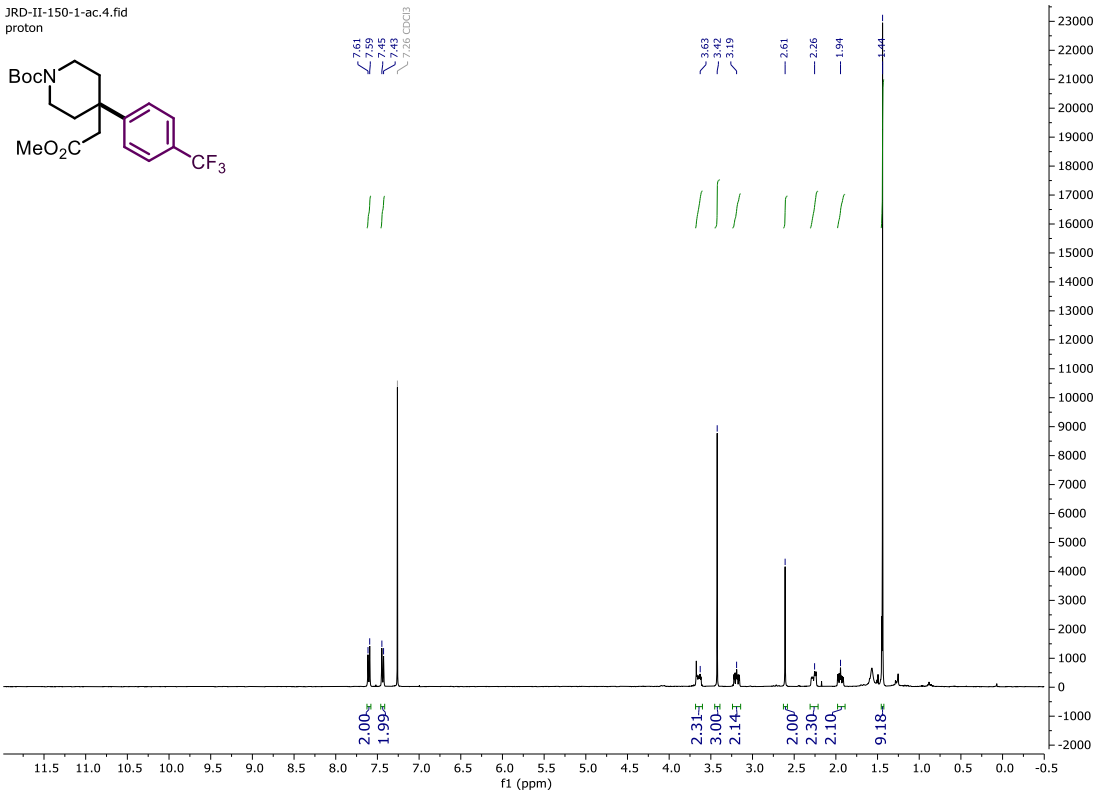

JRD-II-46-2-ac.2.fid
Carbon 13
198.10
157.08
134.79
128.47
125.27
77.16 CDCl3
43.02
36.84
36.80
28.94
26.71
Me
O
f1 (ppm)

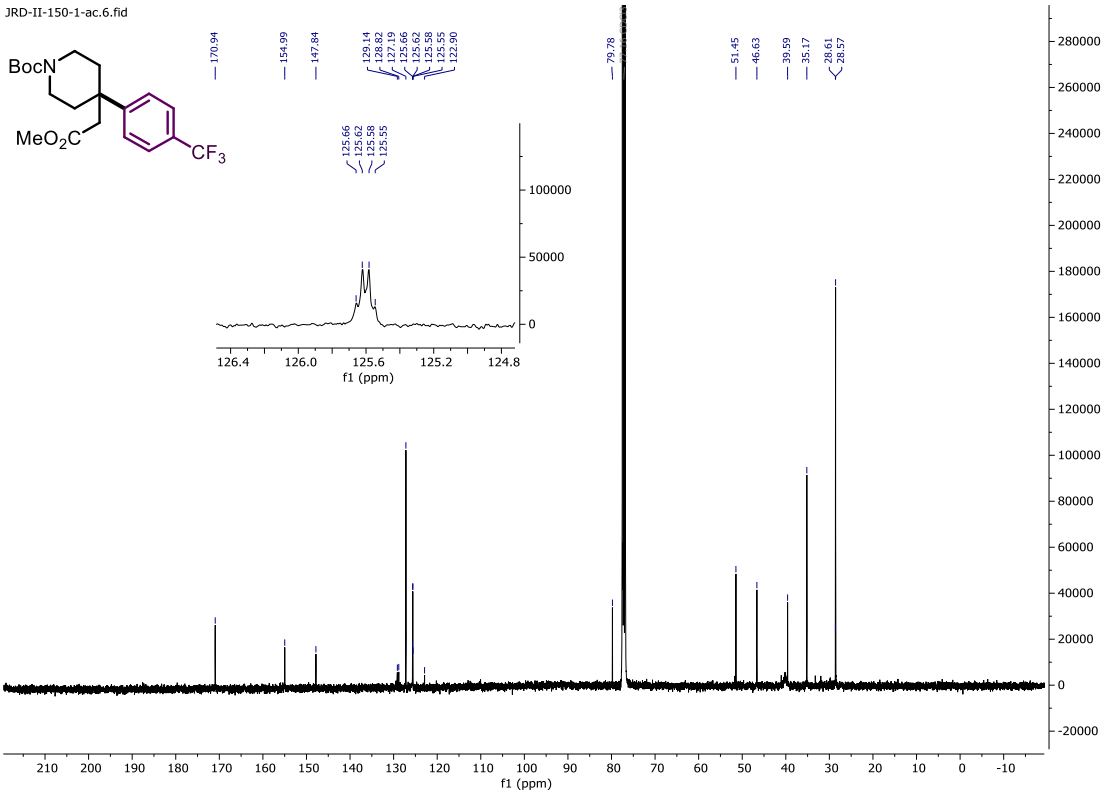

JRD-II-102-1A-ac.2.fid
Proton
7.91
7.90
7.46
7.44
7.26 CDCl3
2.58
2.20
1.75
1.75
1.55
1.55
1.55
1.42
1.41
1.24
0.89
Me
Me
Me
O
2.00
2.02
3.03
1.03
2.07
4.02
3.85
2.10
6.13
f1 (ppm)

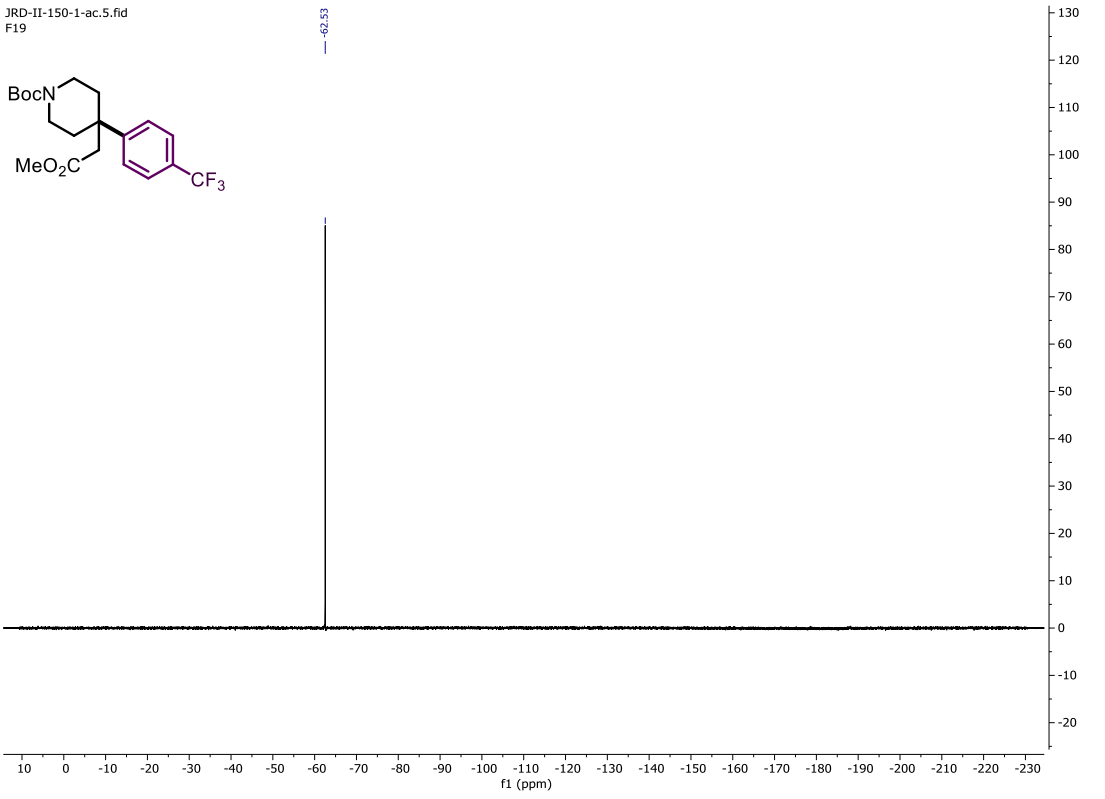

JRD-II-102-1A-ac.3.fid
Carbon 13
198.11
156.49
134.84
128.46
125.39
77.16 CDCl3
50.90
49.37
43.01
41.61
38.72
31.65
30.83
30.02
26.71
0.36
Me
Me
Me
O
f1 (ppm)

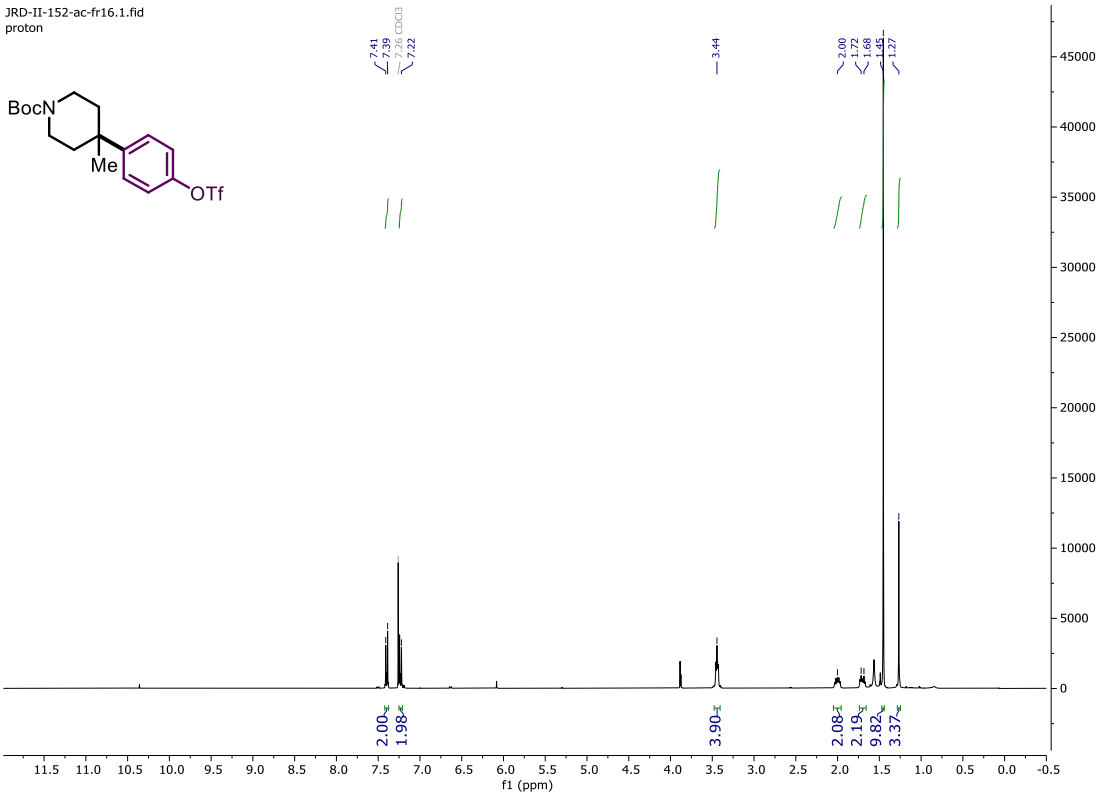

JRD-II-150-4-ac.3.fid
Proton
7.65
7.64
7.44
7.43
7.26
7.26 CDCl3
3.63
3.60
3.43
3.22
2.62
2.21
2.20
1.94
1.57
1.44
BocN
MeO2C
CN
1.95
1.99
2.06
2.95
2.07
2.00
2.07
2.05
9.59
f1 (ppm)

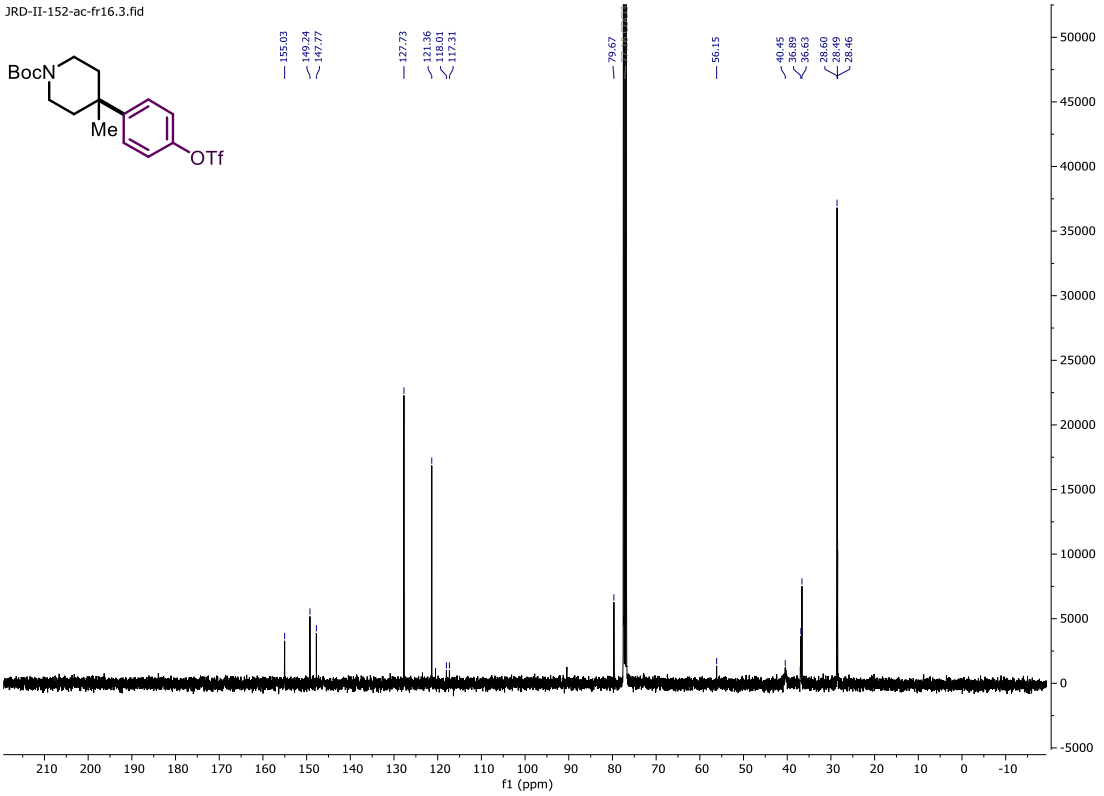

JRD-II-150-4-ac.4.fid
Carbon 13
BocN
MeO2C
CN
170.76
154.92
149.51
132.44
127.66
118.82
110.70
79.92
77.16 CDCl3
55.95
51.54
46.09
39.77
35.05
28.55
f1 (ppm)


JRD-II-150-1-ac.4.fid
proton
BocN
MeO2C
CF3
7.61
7.59
7.45
7.43
7.26 CDCl3
3.63
3.42
3.19
2.61
2.26
1.94
1.44
2.00
1.99
2.31
3.00
2.14
2.00
2.30
2.10
9.18
f1 (ppm)

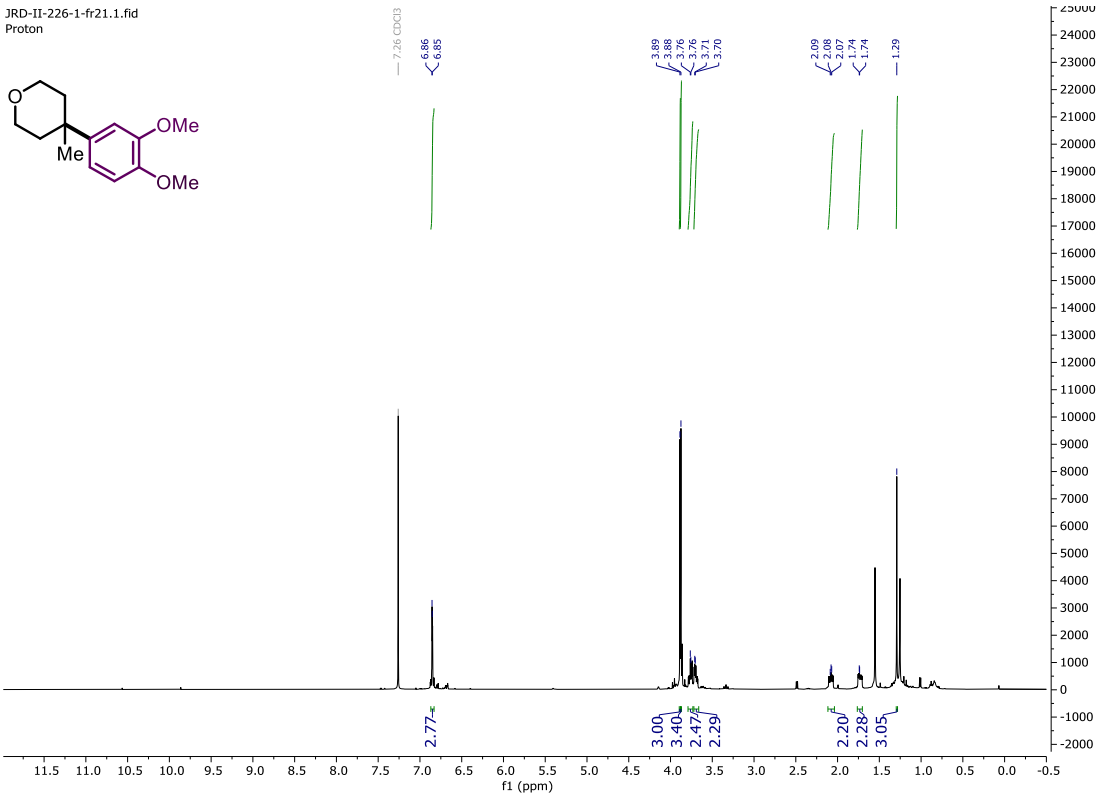

JRD-II-150-1-ac.6.fid
BocN
MeO2C
CF3
170.94
154.99
147.84
129.14
128.82
127.19
125.66
125.62
125.58
125.55
122.90
79.78
51.45
46.63
39.59
35.17
28.61
28.57
125.66
125.62
125.58
125.55
f1 (ppm)
f1 (ppm)

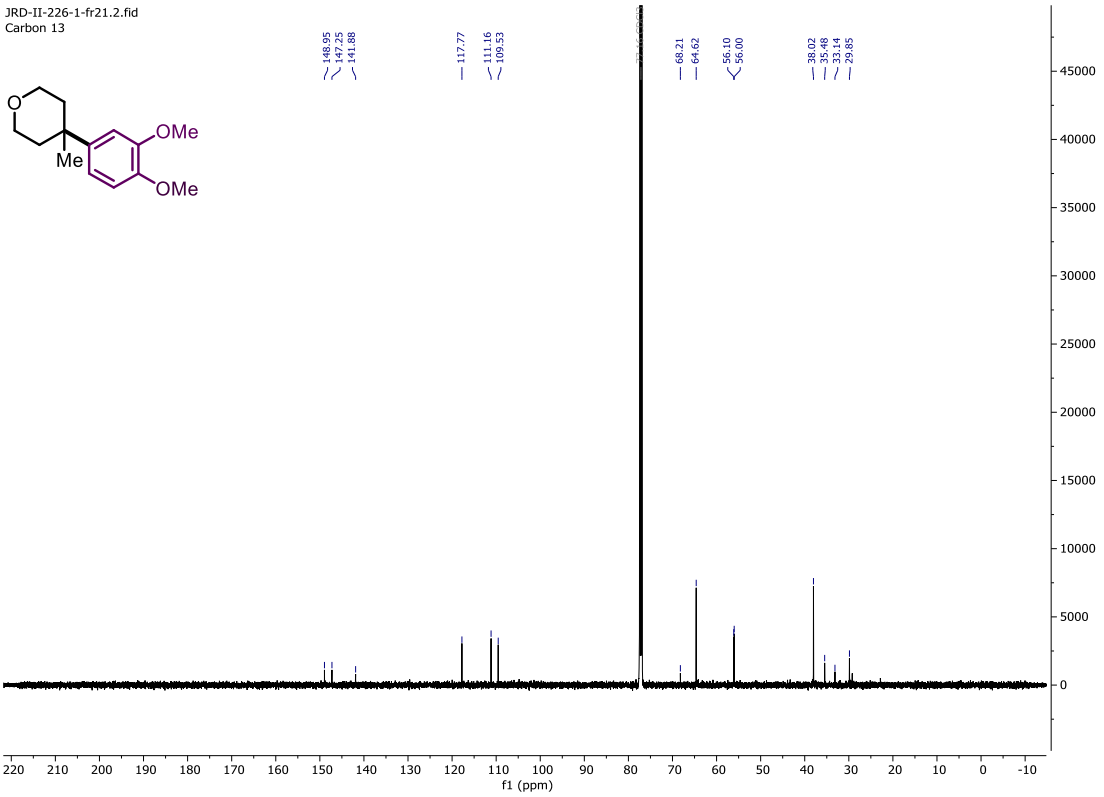

JRD-II-150-1-ac.5.fid
F19
BocN
MeO2C
CF3
-62.53
f1 (ppm)


JRD-II-152-ac-fr16.1.fid
proton
BocN
Me
OTf
7.41
7.39
7.26 CDCl3
7.22
3.44
2.00
1.72
1.68
1.45
1.27
2.00
1.98
3.90
2.08
2.19
9.82
3.37
f1 (ppm)


JRD-II-152-ac-fr16.3.fid
BocN
Me
OTf
155.03
149.24
147.77
127.73
121.36
118.01
117.31
79.67
56.15
40.45
36.89
36.63
28.60
28.49
28.46
f1 (ppm)


JRD-II-152-ac-fr16.2.fid
F19
BocN
Me
OTf
-72.89
f1 (ppm)


JRD-II-226-1-fr21.1.fid
Proton
O
Me
OMe
OMe
7.26 CDCl3
6.86
6.85
3.89
3.88
3.76
3.75
3.71
3.70
2.09
2.08
2.07
1.74
1.74
1.29
2.77
3.00
3.40
2.47
2.29
2.20
2.28
3.05
f1 (ppm)



9. References

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