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Mechanochemical Arylative Detrifluoromethylation of Trifluoromethylarenes

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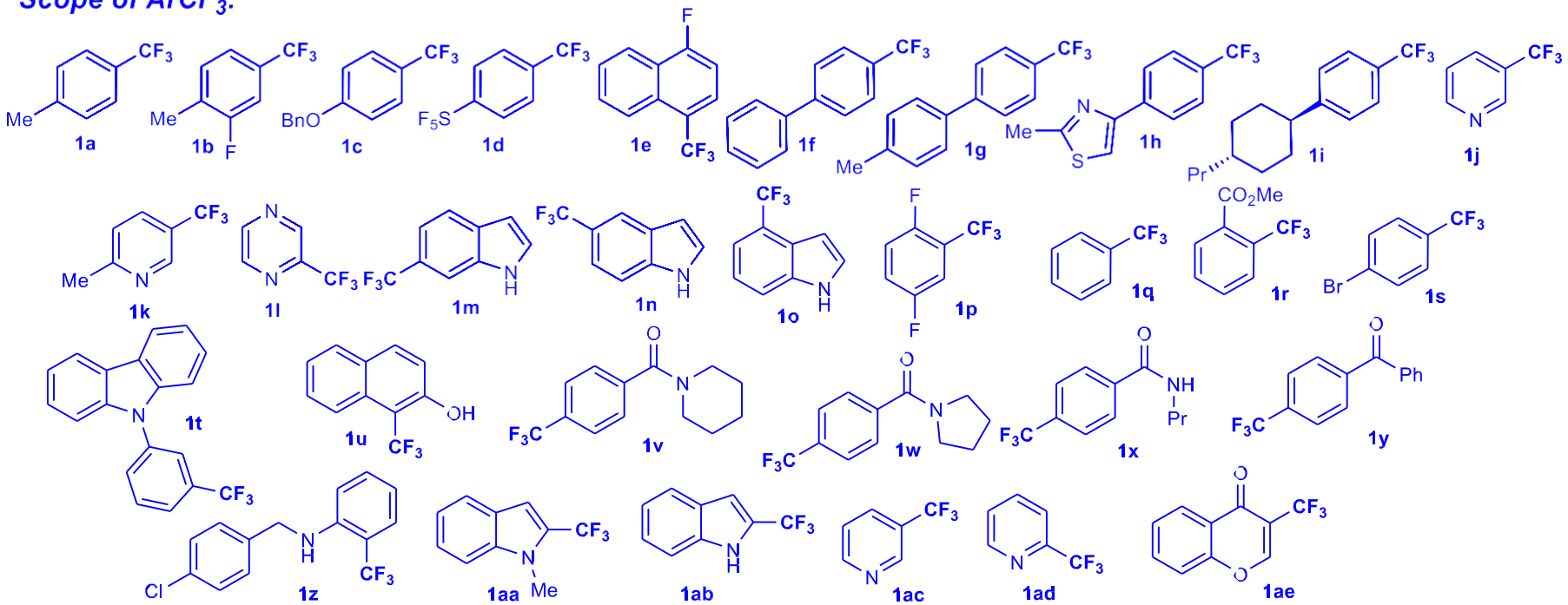
(A) Experimental Section.

Commercially available starting materials, reagents, catalysts, anhydrous and degassed solvents were used without further purification. Flash column chromatography was performed with Merck Silica gel 60 (230-400 mesh). The solvents for column chromatography were distilled before the use. Thin layer chromatography was carried out using Merck TLC Silica gel 60 F_{254} and visualized by short-wavelength ultraviolet light or by treatment with potassium permanganate ($KMnO_4$) stain. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker 250, 400 and 500 MHz at 20ºC. All ^1H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals for $CHCl_3$ (7.26 ppm) and DMSO (2.50 ppm). All $^{13}C\{^1H\}$ NMR spectra were reported in ppm relative to residual $CHCl_3$ (77.00 ppm) or DMSO (39.70 ppm) and were obtained with ^1H decoupling. Coupling constants, *J*, are reported in Hertz (Hz). Gas chromatographic analyses was performed on Gas Chromatograph Mass Spectrometer GCMS-QP2010 Ultra instrument. Mechanochemical synthesis was performed using the Retsch MM400 mill using the standard kit. Liquid chemicals were dosed using gas tight micro syringes. Isolation of obtained compounds was achieved by column chromatography on Silica gel. All commercially available compounds were purchased from appropriate vendors.

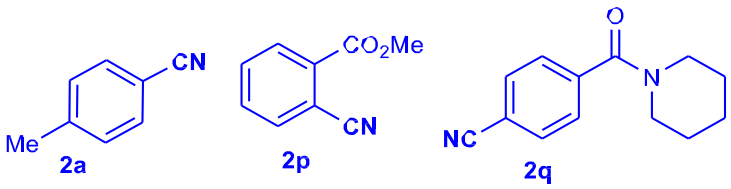
A-1. Scope of substrates used.

Scope of $ArCF_3$:



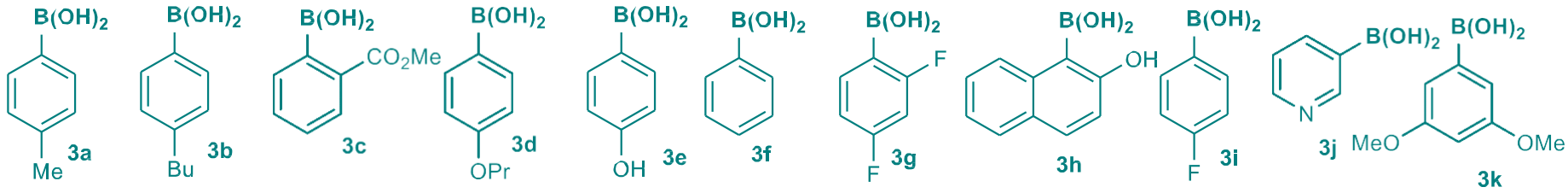
Scheme S1. List of $ArCF_3$ used.

Scope of benzonitriles:



Scheme S2. Nitriles used in this study.

Scope of boronic acids:



Scheme S3. List of boronic acids used.

A-2. Reaction condition screening.

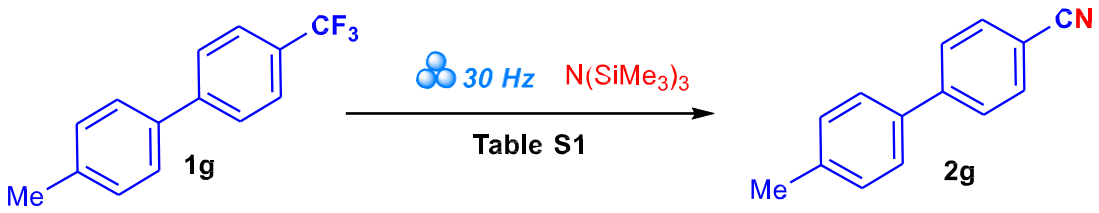


Table S1			
Entr.	Reaction components	Frequency/Time	Yield (%) **2g**
1	$ArCF_3$ (1 equiv.), $N(SiMe_3)_3$ (1.3 equiv.), ZrO_2 (1 equiv.), $NaHCO_3$ (4 equiv.), r.t.	30Hz/60min	0
2	$ArCF_3$ (1 equiv.), $N(SiMe_3)_3$ (1.3 equiv.), ZrN (1 equiv.), $NaHCO_3$ (4 equiv.), r.t.	30Hz/60min	0
3	$ArCF_3$ (1 equiv.), $N(SiMe_3)_3$ (1.3 equiv.), La_2O_3 (1 equiv.), $NaHCO_3$ (4 equiv.), r.t.	30Hz/60min	37
4	$ArCF_3$ (1 equiv.), $N(SiMe_3)_3$ (1.3 equiv.), Dy_2O_3 (1 equiv.), $NaHCO_3$ (4 equiv.), r.t.	30Hz/60min	32
5	**$ArCF_3$ (1 equiv.), $N(SiMe_3)_3$ (1.3 equiv.), Yb_2O_3 (1 equiv.), $NaHCO_3$ (4 equiv.), r.t.**	**30Hz/60min**	**95**
6	$ArCF_3$ (1 equiv.), $N(SiMe_3)_3$ (1.3 equiv.), Eu_2O_3 (1 equiv.), $NaHCO_3$ (4 equiv.), r.t.	30Hz/60min	14
7	$ArCF_3$ (1 equiv.), $N(SiMe_3)_3$ (1.3 equiv.), Ce_2O_3 (1 equiv.), $NaHCO_3$ (4 equiv.), r.t.	30Hz/60min	17

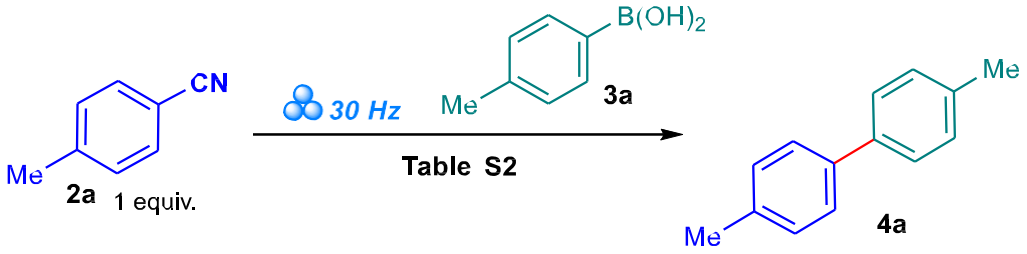


Table S2			
Entr.	Reaction components	Frequency/Time	Yield (%) **4a**
1	$ArB(OH)_2$ (1.2 equiv.), $NiCl_2$ (0.1 equiv.), dppe (0.1 equiv.), Na_2CO_3 (2 equiv.), r.t.	30Hz/60min	0
2	$ArB(OH)_2$ (1.2 equiv.), $NiCl_2$ (0.1 equiv.), dppp (0.1 equiv.), Na_2CO_3 (2 equiv.), r.t.	30Hz/60min	0
3	$ArB(OH)_2$ (1.2 equiv.), $NiBr_2$ (0.1 equiv.), dppe (0.1 equiv.), Na_2CO_3 (2 equiv.), r.t.	30Hz/60min	11
4	$ArB(OH)_2$ (1.2 equiv.), $NiBr_2$ (0.1 equiv.), dppp (0.1 equiv.), Na_2CO_3 (2 equiv.), r.t.	30Hz/60min	13

5	$ArB(OH)_2$ (1.2 equiv.), $NiCl_2$ (0.1 equiv.), PCy_3 (0.3 equiv.), Na_2CO_3 (2 equiv.), r.t.	30Hz/60min	27
6	$ArB(OH)_2$ (1.2 equiv.), $NiBr_2$ (0.1 equiv.), 1,1'-bis(dialkyl/diarylphosphino)ferrocene (0.1 equiv.), Na_2CO_3 (2 equiv.), r.t.	30Hz/60min	45
7	$ArB(OH)_2$ (1.2 equiv.), $Ni[PCy_3]_2Br_2$ (0.1 equiv.), Na_2CO_3 (2 equiv.), r.t.	30Hz/60min	71
8	**$ArB(OH)_2$ (1.2 equiv.), $NiBr_2$ (0.1 equiv.), PCy_3 (0.3 equiv.), Na_2CO_3 (2 equiv.), r.t.**	**30Hz/60min**	**91**
9	$ArB(OH)_2$ (1.5 equiv.), $NiBr_2$ (0.1 equiv.), PCy_3 (0.3 equiv.), Na_2CO_3 (2 equiv.), r.t.	30Hz/60min	92

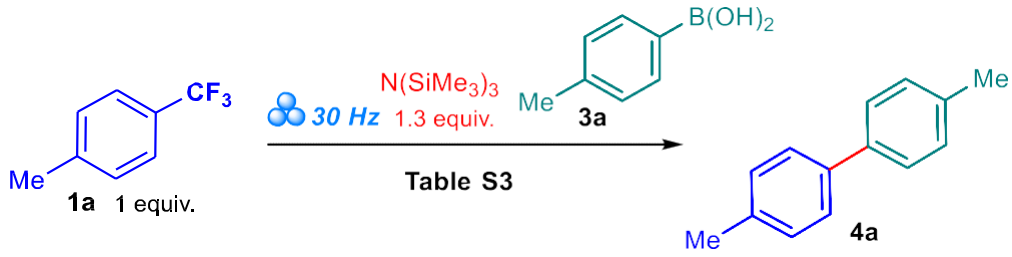


Table S3

Entr.	Reaction components	Frequency/Time	Yield (%) **4a**
1	**$ArB(OH)_2$ (1.2 equiv.), $NiBr_2$ (0.1 equiv.), PCy_3 (0.3 equiv.), Yb_2O_3 (1 equiv.), Na_2CO_3 (4 equiv.), r.t.**	**30Hz/90min**	**87**
2	$ArB(OH)_2$ (1.5 equiv.), $NiBr_2$ (0.1 equiv.), PCy_3 (0.3 equiv.), Yb_2O_3 (1 equiv.), Na_2CO_3 (4 equiv.), r.t.	30Hz/90min	72
3	$ArB(OH)_2$ (1.2 equiv.), $Ni[PCy_3]_2Br_2$ (0.1 equiv.), Na_2CO_3 (2 equiv.), r.t.	30Hz/90min	53

A-3. Reaction procedure with optimised reaction conditions.

General procedure for the synthesis of nitriles 2 starting from trifluoromethyl arenes 1:

In air, to 5 mL grinding vessel (made of stainless) equipped with two balls (made of stainless, diameter: 5 mm) was placed consequently $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), $NaHCO_3$ (336 mg, 4 mmol, 4 equiv.); then the appropriate CF_3 substrate (1 mmol, 1 equiv.) was added and the reaction vessel was properly capped. Finally, the reaction vessel was installed on the mill and subjected to milling at 30 Hz for 60 minutes at room temperature. After completion of the reaction, the resulted crude was directly subjected to gradient flash chromatography on silica gel to isolate the desired nitrile derivative.
The gram scale synthesis was performed on 10 mmol of the starting nitro substrate in a 25 mL grinding vessel by using three 10 mm balls.

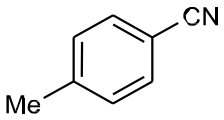
General procedure for the synthesis of biphenyls 4 starting from nitriles 2:

In glovebox under the Ar atmosphere, to 5 mL grinding vessel (made of stainless) equipped with two balls (made of stainless, diameter: 5 mm) was placed consequently Na_2CO_3 (212 mg, 2 mmol, 2 equiv.), $NiBr_2$ (22 mg, 0.1 mmol, 0.1 equiv.), PCy_3 (84 mg, 0.3 mmol, 0.3 equiv.); then the appropriate nitrile (1 mmol, 1 equiv.) and the appropriate boronic acid (1.2 mmol, 1.2 equiv.) was added and the reaction vessel was properly capped. Finally, the reaction vessel was installed on the mill and subjected to milling at 30 Hz for 60 minutes at room temperature. After completion of the reaction, the resulted crude was directly subjected to gradient flash chromatography on silica gel to isolate the desired biphenyl derivative.
The gram scale synthesis was performed on 10 mmol of the starting nitro substrate in a 25 mL grinding vessel by using three 10 mm balls.

General procedure for the synthesis of biphenyls 4 starting from trifluoromethyl arenes 1:

In glovebox under the Ar atmosphere, to 5 mL grinding vessel (made of stainless) equipped with two balls (made of stainless, diameter: 5 mm) was placed consequently $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), Na_2CO_3 (424 mg, 4 mmol, 4 equiv.), $NiBr_2$ (22 mg, 0.1 mmol, 0.1 equiv.), PCy_3 (84 mg, 0.3 mmol, 0.3 equiv.); then the appropriate CF_3 substrate (1 mmol, 1 equiv.) and the appropriate boronic acid (1.2 mmol, 1.2 equiv.) was added and the reaction vessel was properly capped. Finally, the reaction vessel was installed on the mill and subjected to milling at 30 Hz for 90 minutes at room temperature. After completion of the reaction, the resulted crude was directly subjected to gradient flash chromatography on silica gel to isolate the desired biphenyl derivative.
The gram scale synthesis was performed on 10 mmol of the starting nitro substrate in a 25 mL grinding vessel by using three 10 mm balls.

(B) Characterization of products



4-methylbenzonitrile 2a.

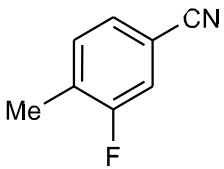
The title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), $NaHCO_3$ (336 mg, 4 mmol, 4 equiv.) and appropriate CF_3 substrate **1a** (160 mg, 1 mmol, 1 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired nitrile **2a** (106 mg, 0.91 mmol, 91%). The gram scale synthesis was performed on 10 mmol of the starting **1a** and the nitrile **2a** was prepared in 87% yield (1.01 g, 8.7 mmol).

Low melting white solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 2.36 (s, 3H, Me), 7.21 (d, 2H, ^3J = 8.2 Hz, CH_{Ar}), 7.46 (d, 2H, ^3J = 8.2 Hz, CH_{Ar}).

^{13}C NMR (126 MHz, $CDCl_3$): δ 21.5, 108.9, 117.9, 129.6, 131.7, 143.5.

MS (GC, 70eV): m/z (%) = 117 (M^+, 100), 90 (38).

Anal. calcd. for C_8H_7N: C 82.02; H, 6.02; N 11.96. Found: C 82.19; H, 6.30; N 11.51.



3-fluoro-4-methylbenzonitrile 2b.

The title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), $NaHCO_3$ (336 mg, 4 mmol, 4 equiv.) and appropriate CF_3 substrate **1b** (178 mg, 1 mmol, 1 equiv.). The purification was accomplished by column chromatography

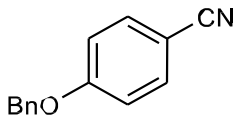
on silica gel to provide the desired nitrile **2b** (121 mg, 0.90 mmol, 90%). The gram scale synthesis was performed on 10 mmol of the starting **1b** and the nitrile **2b** was prepared in 82% yield (1.10 g, 8.2 mmol).

White solid, mp 83 - 84 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 2.34 (d, 3H, ^4J = 1.8 Hz, Me), 7.28 – 7.31 (m, 2H, CH_{Ar}), 7.35 (dd, 1H, ^3J = 7.8 Hz, ^4J = 1.3 Hz, CH_{Ar}).

^{13}C NMR (126 MHz, $CDCl_3$): δ 14.9, 110.9 (d, J_{CF} = 10.2 Hz), 117.8 (d, J_{CF} = 3.0 Hz), 118.1 (d, J_{CF} = 25.7 Hz), 127.9 (d, J_{CF} = 3.8 Hz), 131.3 (d, J_{CF} = 16.9 Hz), 132.4 (d, J_{CF} = 5.5 Hz), 160.7 (d, $^1J_{CF}$ = 251.7 Hz).

MS (GC, 70eV): m/z (%) = 135 (M^+, 100), 108 (34).

Anal. calcd. for C_8H_6NF: C 71.10; H, 4.48; N 10.36. Found: C 71.23; H, 4.43; N 10.42.



4-(benzyloxy)benzonitrile 2c.

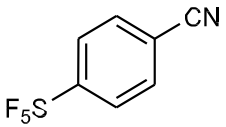
The title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), $NaHCO_3$ (336 mg, 4 mmol, 4 equiv.) and appropriate CF_3 substrate **1c** (252 mg, 1 mmol, 1 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired nitrile **2c** (186 mg, 0.89 mmol, 89%).

White solid, mp 94 - 96 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 5.12 (s, 2H, CH_2), 7.02 (d, 2H, ^3J = 8.8 Hz, CH_{Ar}), 7.36 – 7.39 (m, 3H, CH_{Ar}), 7.41 (d, 2H, J = 4.8 Hz, CH_{Ar}), 7.58 (dd, 2H, ^3J = 8.8 Hz, ^4J = 1.8 Hz, CH_{Ar}).

^{13}C NMR (126 MHz, $CDCl_3$): δ 70.2, 104.2, 115.5, 119.1, 127.4, 128.4, 128.7, 134.0, 135.7, 161.9.

MS (GC, 70eV): m/z (%) = 209 (M^+, 4), 91 (100).

Anal. calcd. for $C_{14}H_{11}NO$: C 80.36; H, 5.30; N 6.69. Found: C 80.46; H, 5.28; N 6.73.



4-(pentafluoro-l6-sulfanyl)benzonitrile 2d.

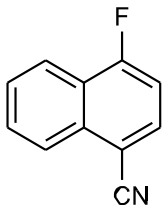
The title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), $NaHCO_3$ (336 mg, 4 mmol, 4 equiv.) and appropriate CF_3 substrate **1d** (272 mg, 1 mmol, 1 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired nitrile **2d** (183 mg, 0.80 mmol, 80%).

Yellowish solid, mp 103 - 104 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.79 (d, 2H, ^3J = 8.5 Hz, CH_{Ar}), 7.89 (d, 2H, ^3J = 8.7 Hz, CH_{Ar}).

^{13}C NMR (126 MHz, $CDCl_3$): δ 115.9, 116.9, 127.0 (m), 132.7, 156.5 (q, $^2J_{CF}$ = 19.5 Hz).

MS (GC, 70eV): m/z (%) = 229 (M^+, 100), 121 (80), 102 (67).

Anal. calcd. for $C_7H_4NSF_5$: C 36.69; H, 1.76; N 6.11. Found: C 36.61; H, 1.63; N 6.19.



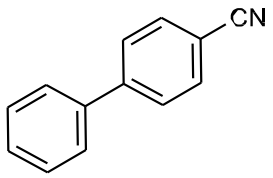
4-fluoro-1-naphthonitrile 2e.

The title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), $NaHCO_3$ (336 mg, 4 mmol, 4 equiv.) and appropriate CF_3 substrate **1e** (214 mg, 1 mmol, 1 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired nitrile **2e** (150 mg, 0.88 mmol, 88%).

White solid, mp 89 - 91 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.11 – 7.15 (m, 1H, CH_{Ar}), 7.60 – 7.63 (m, 1H, CH_{Ar}), 7.67 – 7.70 (m, 1H, CH_{Ar}), 7.80 – 7.83 (m, 1H, CH_{Ar}), 8.07 (dd, 1H, ^3J = 8.3 Hz, ^4J = 2.3 Hz, CH_{Ar}), 8.13 (d, 1H, ^3J = 8.3 Hz, CH_{Ar}).

^{13}C NMR (126 MHz, $CDCl_3$): δ 106.0 (d, J_{CF} = 4.3 Hz), 109.3 (d, J_{CF} = 21.6 Hz), 117.0, 121.0 (d, J_{CF} = 4.6 Hz), 123.2 (d, J_{CF} = 16.9 Hz), 124.8, 127.7, 129.4, 133.1(d, J_{CF} = 10.6 Hz), 133.9 (d, J_{CF} = 6.6 Hz), 161.3 (d, $^1J_{CF}$ = 263.2 Hz).

Anal. calcd. for $C_{11}H_6NF$: C 77.19; H, 3.53; N 8.18. Found: C 77.23; H, 3.48; N 8.21.



[1,1'-biphenyl]-4-carbonitrile 2f.

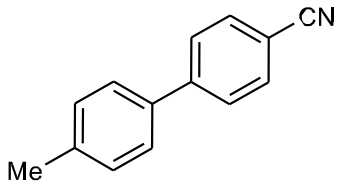
The title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), $NaHCO_3$ (336 mg, 4 mmol, 4 equiv.) and appropriate CF_3 substrate **1f** (222 mg, 1 mmol, 1 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired nitrile **2f** (168 mg, 0.94 mmol, 94%).

White solid, mp 85 - 87 °C. **^{1}H NMR** (500 MHz, DMSO-d_6): δ 7.42 – 7.45 (m, 1H, CH_{Ar}), 7.49 – 7.52 (m, 2H, CH_{Ar}), 7.18 – 7.73 (m, 2H, CH_{Ar}), 7.85 – 7.86 (m, 2H, CH_{Ar}), 7.90 – 7.91 (m, 2H, CH_{Ar}).

^{13}C NMR (126 MHz, DMSO-d_6): δ 110.0, 118.9, 127.1, 127.6, 128.7, 129.2, 132.8, 138.3, 144.6.

MS (GC, 70eV): m/z (%) = 179 (M^+, 100), 151 (13).

Anal. calcd. for $C_{13}H_9N$: C 87.12; H, 5.06; N 7.82. Found: C 87.31; H, 5.11; N 7.58.



4'-methyl-[1,1'-biphenyl]-4-carbonitrile 2g.

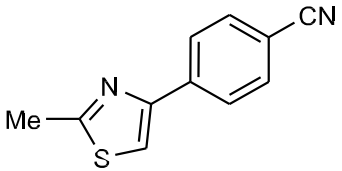
The title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), $NaHCO_3$ (336 mg, 4 mmol, 4 equiv.) and appropriate CF_3 substrate **1g** (236 mg, 1 mmol, 1 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired nitrile **2g** (183 mg, 0.95 mmol, 95%).

White solid, mp 110 - 111 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 2.42 (s, 3H, Me), 7.29 (d, 2H, ^{3}J = 7.09 Hz, CH_{Ar}), 7.50 (d, 2H, ^{3}J = 8.1 Hz, CH_{Ar}), 7.66 (d, 2H, ^{3}J = 8.5 Hz, CH_{Ar}), 7.70 (d, 2H, ^{3}J = 8.6 Hz, CH_{Ar}).

^{13}C NMR (126 MHz, $CDCl_3$): δ 21.1, 110.4, 119.0, 127.0, 127.4, 129.8, 132.5, 136.2, 138.7, 145.5.

MS (GC, 70eV): m/z (%) = 193 (M^+, 100), 151 (13).

Anal. calcd. for $C_{14}H_{11}N$: C 87.01; H, 5.74; N 7.25. Found: C 87.31; H, 5.11; N 7.58.



4-(2-methylthiazol-4-yl)benzonitrile 2h.

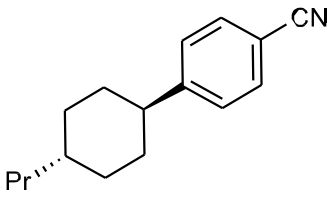
The title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), $NaHCO_3$ (336 mg, 4 mmol, 4 equiv.) and appropriate CF_3 substrate **1h** (243 mg, 1 mmol, 1 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired nitrile **2h** (174 mg, 0.87 mmol, 87%).

Yellowish solid, mp 154 - 155 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 2.78 (s, 3H, Me), 7.46 (s, 1H, CH_{Ar}), 7.68 (d, 2H, ^{3}J = 8.7 Hz, CH_{Ar}), 7.98 (d, 2H, ^{3}J = 8.5 Hz, CH_{Ar}), 7.70 (d, 2H, ^{3}J = 8.7 Hz, CH_{Ar}).

^{13}C NMR (126 MHz, $CDCl_3$): δ 19.3, 111.2, 115.2, 118.9, 126.7, 132.6, 138.5, 153.1, 166.6.

MS (GC, 70eV): m/z (%) = 200 (M^+, 69), 159 (100).

Anal. calcd. for $C_{11}H_8N_2S$: C 65.98; H, 4.03; N 13.99. Found: C 66.06; H, 4.09; N 14.07.



4-((1s,4r)-4-propylcyclohexyl)benzonitrile 2i.

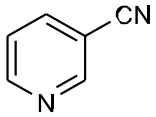
The title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), $NaHCO_3$ (336 mg, 4 mmol, 4 equiv.) and appropriate CF_3 substrate **1i** (270 mg, 1 mmol, 1 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired nitrile **2i** (193 mg, 0.85 mmol, 85%).

White solid, mp 45 - 46 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 0.90 (t, 3H, CH_3), 1.04 – 1.10 (m, 2H, Cy), 1.20 – 1.45 (m, 7H, Cy), 1.86 (br, s, 2H, CH_2), 1.89 (br, s, 2H, CH_2), 2.51 (tt, 1H, ^3J = 12.7 Hz, ^4J = 3.0 Hz, Cy), 7.29 (d, 2H, ^3J = 8.2 Hz, CH_{Ar}), 7.56 (d, 2H, ^3J = 8.2 Hz, CH_{Ar}).

^{13}C NMR (126 MHz, $CDCl_3$): δ 14.4, 20.0, 33.2, 33.9, 36.9, 39.6, 44.8, 109.6, 119.2, 127.7, 132.2, 153.4.

MS (GC, 70eV): m/z (%) = 227 (M^+, 93), 142 (50), 129 (100), 122 (44), 116 (87).

Anal. calcd. for $C_{16}H_{21}N$: C 84.53; H, 9.31; N 6.16. Found: C 84.63; H, 9.26; N 6.11.



nicotinonitrile 2j.

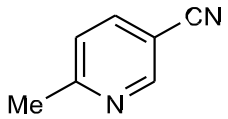
The title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), $NaHCO_3$ (336 mg, 4 mmol, 4 equiv.) and appropriate CF_3 substrate **1j** (147 mg, 1 mmol, 1 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired nitrile **2j** (83 mg, 0.80 mmol, 80%).

Yellowish solid, mp 49 - 50 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.39 – 7.42 (m, 1H, CH_{Ar}), 7.92 – 7.95 (m, 1H, CH_{Ar}), 8.76 – 8.77 (m, 1H, CH_{Ar}), 8.83 (s, 1H, CH_{Ar}).

^{13}C NMR (126 MHz, $CDCl_3$): δ 110.1, 116.6, 123.7, 139.3, 152.5, 153.0.

MS (GC, 70eV): m/z (%) = 104 (M^+, 100), 77 (65).

Anal. calcd. for $C_6H_4N_2$: C 69.22; H, 3.87; N 26.91. Found: C 69.31; H, 3.79; N 26.90.



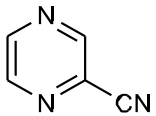
6-methylnicotinonitrile 2k.

The title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), $NaHCO_3$ (336 mg, 4 mmol, 4 equiv.) and appropriate CF_3 substrate **1k** (161 mg, 1 mmol, 1 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired nitrile **2k** (97 mg, 0.82 mmol, 82%).

Yellowish solid, mp 84 - 86 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 2.54 (s, 3H, Me), 7.21 (d, 1H, ^3J = 8.1 Hz, CH_{Ar}), 7.76 (dd, 1H, ^3J = 8.2 Hz, ^4J = 2.0 Hz, CH_{Ar}), 8.66 (s, 1H, CH_{Ar}).

^{13}C NMR (126 MHz, $CDCl_3$): δ 24.7, 106.7, 116.7, 123.1, 139.0, 151.7, 162.9.

Anal. calcd. for $C_7H_6N_2$: C 71.17; H, 5.12; N 23.71. Found: C 71.23; H, 5.19; N 23.58.



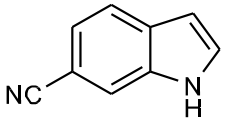
pyrazine-2-carbonitrile 2l.

The title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), $NaHCO_3$ (336 mg, 4 mmol, 4 equiv.) and appropriate CF_3 substrate **1l** (148 mg, 1 mmol, 1 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired nitrile **2l** (83 mg, 0.79 mmol, 79%).

Colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.67 (br. s, 1H, CH_{Ar}), 7.75 (d, 1H, ^4J = 2.4 Hz, CH_{Ar}), 8.86 (s, 1H, CH_{Ar}).

^{13}C NMR (126 MHz, $CDCl_3$): δ 115.1, 130.5, 145.3, 147.3, 148.0.

Anal. calcd. for $C_5H_3N_3$: C 57.14; H, 2.88; N 39.98. Found: C 57.23; H, 2.61; N 40.16.



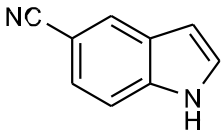
1H-indole-6-carbonitrile 2m.

The title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), $NaHCO_3$ (336 mg, 4 mmol, 4 equiv.) and appropriate CF_3 substrate **1m** (185 mg, 1 mmol, 1 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired nitrile **2m** (116 mg, 0.82 mmol, 82%).

Yellow solid, mp 126 - 127 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 6.63 (s, 1H, CH_{Ar}), 7.35 (d, 1H, ^3J = 8.4 Hz, CH_{Ar}), 7.43 (s, 1H, CH_{Ar}), 7.70 (d, 1H, ^3J = 8.4 Hz, CH_{Ar}), 7.78 (s, 1H, CH_{Ar}), 8.78 (br. s, 1H, NH).

^{13}C NMR (126 MHz, $CDCl_3$): δ 103.3, 104.0, 116.1, 120.8, 121.5, 122.6, 128.2, 131.2, 134.6.

HRMS (TOF MS ES+) m/z: $[M + H]^+$: Calcd for $C_9H_7N_2$ 143.0615. Found 143.0609.



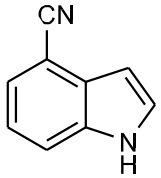
1H-indole-5-carbonitrile 2n.

The title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), $NaHCO_3$ (336 mg, 4 mmol, 4 equiv.) and appropriate CF_3 substrate **1n** (185 mg, 1 mmol, 1 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired nitrile **2n** (113 mg, 0.80 mmol, 80%).

Yellowish solid, mp 106 - 107 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 6.62 (s, 1H, CH_{Ar}), 7.36 (t, 1H, ^4J = 2.7 Hz, CH_{Ar}), 7.41 (dd, 1H, ^3J = 8.6 Hz, ^4J = 1.4 Hz, CH_{Ar}), 7.50 (d, 1H, ^3J = 8.6 Hz, CH_{Ar}), 7.99 (s, 1H, CH_{Ar}), 9.07 (br. s, 1H, NH).

^{13}C NMR (126 MHz, $CDCl_3$): δ 102.1, 103.0, 121.0, 124.5, 126.2, 126.7, 127.5, 137.5.

Anal. calcd. for $C_9H_6N_2$: C 76.04; H, 4.25; N 19.71. Found: C 75.96; H, 4.12; N 19.92.



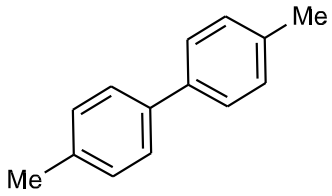
1H-indole-4-carbonitrile 2o.

The title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), $NaHCO_3$ (348 mg, 4 mmol, 4 equiv.) and appropriate CF_3 substrate **1o** (185 mg, 1 mmol, 1 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired nitrile **2o** (119 mg, 0.84 mmol, 84%).

Yellowish solid, mp 118 - 120 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 6.75 (s, 1H, CH_{Ar}), 7.22 (t, 1H, ^3J = 7.4 Hz, CH_{Ar}), 7.41 (d, 1H, ^4J = 2.8 Hz, CH_{Ar}), 7.47 (d, 1H, ^3J = 7.4 Hz, CH_{Ar}), 7.67 (d, 1H, ^3J = 8.2 Hz, CH_{Ar}), 8.94 (br. s, 1H, NH).

^{13}C NMR (126 MHz, $CDCl_3$): δ 116.2, 119.0, 121.4, 125.2, 127.1, 129.1, 135.5.

Anal. calcd. for $C_9H_6N_2$: C 76.04; H, 4.25; N 19.71. Found: C 76.16; H, 4.29; N 19.55.



4,4'-dimethyl-1,1'-biphenyl 4a.

The title compound was prepared starting from Na_2CO_3 (212 mg, 2 mmol, 2 equiv.), $NiBr_2$ (22 mg, 0.1 mmol, 0.1 equiv.), PCy_3 (83 mg, 0.3 mmol, 0.3 equiv.), nitrile **2a** (117 mg, 1 mmol, 1 equiv.) and boronic acid **3a** (136 mg, 1.2 mmol, 1.2 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired biphenyl **4a** (165 mg, 0.91 mmol, 91%). The gram scale synthesis was performed on 10 mmol of the starting nitrile **2a** and the biphenyl **4a** was prepared in 83% yield (1.51 g, 8.3 mmol).

Alternatively, the title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), Na_2CO_3 (424 mg, 4 mmol, 4 equiv.), $NiBr_2$ (22 mg, 0.1 mmol, 0.1 equiv.), PCy_3 (83 mg, 0.3 mmol, 0.3 equiv.), CF_3 substrate **1a** (160 mg, 1 mmol, 1

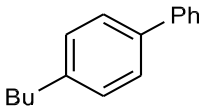
equiv.) and boronic acid **3a** (163 mg, 1.2 mmol, 1.2 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired biphenyl **4a** (158 mg, 0.87 mmol, 87%). The gram scale synthesis was performed on 10 mmol of the starting **1a** and the biphenyl **4a** was prepared in 80% yield (1.45 g, 8.0 mmol).

White solid, mp 118 - 119 °C. **^{1}H NMR** (500 MHz, DMSO-d_6): δ 2.33 (s, 6H, 2xMe), 7.24 (d, 4H, ^{3}J = 7.2 Hz, CH_{Ar}), 7.51 (d, 4H, ^{3}J = 8.1 Hz, CH_{Ar}).

^{13}C NMR (126 MHz, DMSO-d_6): δ 20.6, 126.2, 129.4, 136.3, 137.2.

MS (GC, 70eV): m/z (%) = 182 (M^+, 100), 167 (68), 152 (14).

Anal. calcd. for $C_{14}H_{14}$: C 92.26; H, 7.74. Found: C 92.33; H, 7.67.



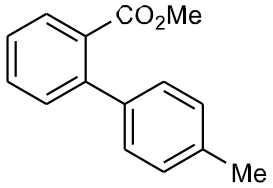
4-butyl-1,1'-biphenyl 4b.

The title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), Na_2CO_3 (424 mg, 4 mmol, 4 equiv.), $NiBr_2$ (22 mg, 0.1 mmol, 0.1 equiv.), PCy_3 (83 mg, 0.3 mmol, 0.3 equiv.), CF_3 substrate **1q** (146 mg, 1 mmol, 1 equiv.) and boronic acid **3b** (214 mg, 1.2 mmol, 1.2 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired biphenyl **4b** (155 mg, 0.74 mmol, 74%).

Colorless liquid. **^{1}H NMR** (500 MHz, DMSO-d_6): δ 0.89 (t, 3H, ^{3}J = 7.7 Hz, Me), 1.29 – 1.33 (m, 2H, CH_2), 1.55 – 1.57 (m, 2H, CH_2), 2.59 (t, 2H, ^{3}J = 7.8 Hz, CH_2), 7.25 (d, 2H, ^{3}J = 7.3 Hz, CH_{Ar}), 7.33 (t, 1H, ^{3}J = 7.3 Hz, CH_{Ar}), 7.45 (t, 2H, ^{3}J = 7.3 Hz, CH_{Ar}), 7.55 (d, 2H, ^{3}J = 7.8 Hz, CH_{Ar}), 7.62 (d, 2H, ^{3}J = 7.8 Hz, CH_{Ar}).

^{13}C NMR (126 MHz, DMSO-d_6): δ 13.8, 21.8, 33.1, 34.5, 126.4, 126.5, 127.1, 128.8, 137.5, 140.1, 141.6.

Anal. calcd. for $C_{14}H_{14}$: C 91.37; H, 8.63. Found: C 91.29; H, 8.71.



methyl 4'-methyl-[1,1'-biphenyl]-2-carboxylate 4c.

The title compound was prepared starting from Na_2CO_3 (212 mg, 2 mmol, 2 equiv.), $NiBr_2$ (22 mg, 0.1 mmol, 0.1 equiv.), PCy_3 (83 mg, 0.3 mmol, 0.3 equiv.), nitrile **2p** (166 mg, 1 mmol, 1 equiv.) and boronic acid **3a** (163 mg, 1.2 mmol, 1.2 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired biphenyl **4c** (165 mg, 0.73 mmol, 73%).

Alternatively, the title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), Na_2CO_3 (424 mg, 4 mmol, 4 equiv.), $NiBr_2$ (22 mg, 0.1 mmol, 0.1 equiv.), PCy_3 (83 mg, 0.3 mmol, 0.3 equiv.), CF_3 substrate **1r** (204 mg, 1 mmol, 1 equiv.) and boronic acid **3a** (163 mg, 1.2 mmol, 1.2 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired biphenyl **4c** (144 mg, 0.64 mmol, 64%).

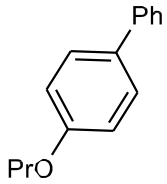
Alternatively, title compound was prepared starting from Na_2CO_3 (212 mg, 2 mmol, 2 equiv.), $NiBr_2$ (22 mg, 0.1 mmol, 0.1 equiv.), PCy_3 (83 mg, 0.3 mmol, 0.3 equiv.), nitrile **2a** (117 mg, 1 mmol, 1 equiv.) and boronic acid **3c** (216 mg, 1.2 mmol, 1.2 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired biphenyl **4c** (169 mg, 0.75 mmol, 75%).

Alternatively, the title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), Na_2CO_3 (424 mg, 4 mmol, 4 equiv.), $NiBr_2$ (22 mg, 0.1 mmol, 0.1 equiv.), PCy_3 (83 mg, 0.3 mmol, 0.3 equiv.), CF_3 substrate **1a** (160 mg, 1 mmol, 1 equiv.) and boronic acid **3c** (216 mg, 1.2 mmol, 1.2 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired biphenyl **4c** (150 mg, 0.65 mmol, 65%).

White solid, mp 60 - 61 °C. **^{1}H NMR** (500 MHz, DMSO-d_6): δ 2.34 (s, 3H, Me), 3.59 (s, 3H, OMe), 7.17 (d, 2H, ^3J = 8.1 Hz, CH_{Ar}), 7.22 (d, 2H, ^3J = 7.8 Hz, CH_{Ar}), 7.40 (d, 1H, ^3J = 7.7 Hz, CH_{Ar}), 7.46 (t, 1H, ^3J = 7.5 Hz, CH_{Ar}), 7.59 (dd, 1H, ^3J = 7.4 Hz, ^4J = 1.1 Hz, CH_{Ar}), 7.70 (d, 1H, ^3J = 7.7 Hz, CH_{Ar}).

^{13}C NMR (126 MHz, DMSO-d_6): δ 20.7, 51.9, 127.2, 128.0, 128.9, 129.1, 130.4, 130.9, 131.4, 136.6, 137.5, 141.0, 168.8.

Anal. calcd. for $C_{15}H_{14}O_2$: C 79.62; H, 6.24. Found: C 79.83; H, 6.11.



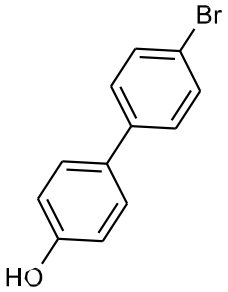
4-propoxy-1,1'-biphenyl 4d.

The title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), Na_2CO_3 (424 mg, 4 mmol, 4 equiv.), $NiBr_2$ (22 mg, 0.1 mmol, 0.1 equiv.), PCy_3 (83 mg, 0.3 mmol, 0.3 equiv.), CF_3 substrate **1q** (146 mg, 1 mmol, 1 equiv.) and boronic acid **3d** (216 mg, 1.2 mmol, 1.2 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired biphenyl **4d** (176 mg, 0.83 mmol, 83%).

White solid, mp 76 - 77 °C. **^{1}H NMR** (500 MHz, DMSO-*d_6*): δ 1.04 (t, 3H, ^3J = 7.7 Hz, Me), 1.79 – 1.83 (m, 2H, CH_2), 2.98 (t, 2H, ^3J = 7.5 Hz, OCH_2), 7.39 – 7.42 (m, 1H, CH_{Ar}), 7.46 – 7.49 (m, 2H, CH_{Ar}), 7.62 – 7.64 (m, 2H, CH_{Ar}), 7.68 (dt, 1H, ^3J = 8.5 Hz, ^4J = 1.8 Hz, CH_{Ar}), 8.04 (dt, 1H, ^3J = 8.5 Hz, ^4J = 1.7 Hz, CH_{Ar}).

^{13}C NMR (126 MHz, DMSO-*d_6*): δ 13.9, 17.7, 40.5, 127.1, 127.2, 128.1, 128.6, 128.9, 135.7, 139.8, 145.4, 199.9.

Anal. calcd. for $C_{15}H_{16}O$: C 84.87; H, 7.60. Found: C 84.96; H, 7.32.



4'-bromo-[1,1'-biphenyl]-4-ol 4e.

The title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), Na_2CO_3 (424 mg, 4 mmol, 4 equiv.), $NiBr_2$ (22 mg, 0.1 mmol, 0.1 equiv.), PCy_3 (83 mg, 0.3 mmol, 0.3 equiv.), CF_3 substrate **1s** (225 mg, 1 mmol, 1 equiv.) and boronic

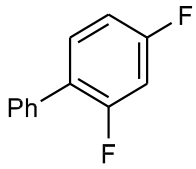
acid **3e** (165 mg, 1.2 mmol, 1.2 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired biphenyl **4e** (193 mg, 0.78 mmol, 78%).

Yellow solid, mp 164 - 166 °C. **^{1}H NMR** (500 MHz, DMSO-d_6): 6.85 (d, 2H, ^3J = 7.9 Hz, CH_{Ar}), 7.47 (d, 2H, ^3J = 7.9 Hz, CH_{Ar}), 7.51 (d, 2H, ^3J = 7.6 Hz, CH_{Ar}), 7.56 (d, 2H, ^3J = 8.0 Hz, CH_{Ar}).

^{13}C NMR (126 MHz, DMSO-d_6): δ 115.8, 119.6, 127.7, 128.0, 129.5, 131.6, 139.4, 157.5.

MS (GC, 70eV): m/z (%) = 249 (90), 248 (M^+, 100), 168 (13), 141 (34), 139 (23).

Anal. calcd. for $C_{12}H_9BrO$: C 57.86; H, 3.64. Found: C 58.01; H, 3.59.



2,4-difluoro-1,1'-biphenyl 4f.

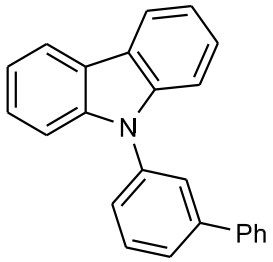
The title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), Na_2CO_3 (424 mg, 4 mmol, 4 equiv.), $NiBr_2$ (22 mg, 0.1 mmol, 0.1 equiv.), PCy_3 (83 mg, 0.3 mmol, 0.3 equiv.), CF_3 substrate **1p** (182 mg, 1 mmol, 1 equiv.) and boronic acid **3f** (146 mg, 1.2 mmol, 1.2 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired biphenyl **4f** (167 mg, 0.88 mmol, 88%).

Alternatively, the title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), Na_2CO_3 (424 mg, 4 mmol, 4 equiv.), $NiBr_2$ (22 mg, 0.1 mmol, 0.1 equiv.), PCy_3 (83 mg, 0.3 mmol, 0.3 equiv.), CF_3 substrate **1q** (146 mg, 1 mmol, 1 equiv.) and boronic acid **3g** (190 mg, 1.2 mmol, 1.2 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired biphenyl **4f** (163 mg, 0.86 mmol, 86%).

White solid, mp 61 - 63 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): 6.91 – 6.99 (m, 2H, CH_{Ar}), 7.37 – 7.42 (m, 2H, CH_{Ar}), 7.44 – 7.47 (m, 2H, CH_{Ar}), 7.51 (d, 2H, ^3J = 7.4 Hz, CH_{Ar}).

^{13}C NMR (126 MHz, $CDCl_3$): δ 104.4 (t, J_{CF} = 26.1 Hz), 111.5 (d, J_{CF} = 21.0 Hz, J_{CF} = 3.9 Hz), 125.4 (m), 127.7, 128.5, 128.9, 131.4 (m), 135.0, 159.7 (dd, $^1J_{CF}$ = 250.0 Hz, J_{CF} = 11.4 Hz), 162.2 (dd, $^1J_{CF}$ = 249.1 Hz, J_{CF} = 11.4 Hz).

HRMS (TOF MS ES+) m/z: $[M]^+$: Calcd for $C_{12}H_8F_2$ 190.0591. Found 190.0594.



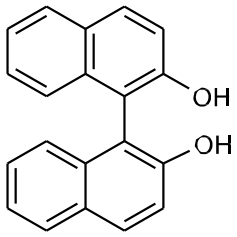
9-([1,1'-biphenyl]-3-yl)-9H-carbazole 4g.

The title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), Na_2CO_3 (424 mg, 4 mmol, 4 equiv.), $NiBr_2$ (22 mg, 0.1 mmol, 0.1 equiv.), PCy_3 (83 mg, 0.3 mmol, 0.3 equiv.), CF_3 substrate **1t** (311 mg, 1 mmol, 1 equiv.) and boronic acid **3f** (146 mg, 1.2 mmol, 1.2 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired biphenyl **4g** (252 mg, 0.79 mmol, 79%). The gram scale synthesis was performed on 10 mmol of the starting CF_3 substrate **1t** and the biphenyl **4g** was prepared in 73% yield (2.32 g, 7.3 mmol).

White solid, mp 128 - 129 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): 7.33 – 7.36 (t, 2H, ^3J = 7.7 Hz, CH_{Ar}), 7.42 – 7.54 (m, 7H, CH_{Ar}), 7.58 (d, 1H, ^3J = 7.3 Hz, CH_{Ar}), 7.69 (d, 3H, ^3J = 8.8 Hz, CH_{Ar}), 7.72 – 7.73 (m, 1H, CH_{Ar}), 7.85 (s, 1H, CH_{Ar}), 8.21 (d, 2H, ^3J = 7.7 Hz, CH_{Ar}).

^{13}C NMR (126 MHz, $CDCl_3$): δ 109.8, 120.0, 120.3, 123.3, 125.7, 125.8, 126.0, 126.1, 127.1, 127.8, 128.9, 130.2, 138.2, 140.1, 140.8, 143.1.

Anal. calcd. for $C_{24}H_{17}N$: C 90.25; H, 5.36; N, 4.39. Found: C 90.33; H, 5.62; N 4.05.



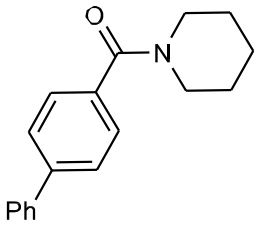
[1,1'-binaphthalene]-2,2'-diol 4h.

The title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), Na_2CO_3 (424 mg, 4 mmol, 4 equiv.), $NiBr_2$ (22 mg, 0.1 mmol, 0.1 equiv.), PCy_3 (83 mg, 0.3 mmol, 0.3 equiv.), CF_3 substrate **1u** (212 mg, 1 mmol, 1 equiv.) and boronic acid **3h** (226 mg, 1.2 mmol, 1.2 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired biaryl **4h** (183 mg, 0.64 mmol, 64%).

White solid, mp 205 - 208 °C. **^{1}H NMR** (500 MHz, DMSO-d_6): 6.98 (d, 2H, ^3J = 8.6 Hz, CH_{Ar}), 7.17 (dt, 2H, ^3J = 6.9 Hz, ^4J = 1.0 Hz, CH_{Ar}), 7.24 (dt, 2H, ^3J = 7.9 Hz, ^4J = 1.0 Hz, CH_{Ar}), 7.36 (d, 2H, ^3J = 8.8 Hz, CH_{Ar}), 7.87 (t, 4H, ^3J = 7.4 Hz, CH_{Ar}), 9.26 (s, 2H, 2xOH).

^{13}C NMR (126 MHz, DMSO-d_6): δ 115.5, 118.6, 122.3, 124.5, 125.9, 127.9, 128.1, 128.7, 134.2, 153.1.

Anal. calcd. for $C_{20}H_{14}O_2$: C 83.90; H, 4.93. Found: C 83.97; H, 5.03.



[1,1'-biphenyl]-4-yl(piperidin-1-yl)methanone 4i.

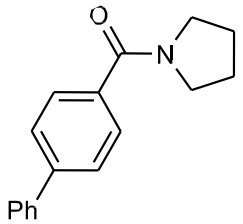
The title compound was prepared starting from Na_2CO_3 (212 mg, 2 mmol, 2 equiv.), $NiBr_2$ (22 mg, 0.1 mmol, 0.1 equiv.), PCy_3 (83 mg, 0.3 mmol, 0.3 equiv.), nitrile **2q** (214 mg, 1 mmol, 1 equiv.) and boronic acid **3f** (146 mg, 1.2 mmol, 1.2 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired biphenyl **4i** (235 mg, 0.89 mmol, 89%).

Alternatively, the title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), Na_2CO_3 (424 mg, 4 mmol, 4 equiv.), $NiBr_2$ (22 mg, 0.1 mmol, 0.1 equiv.), PCy_3 (83 mg, 0.3 mmol, 0.3 equiv.), CF_3 substrate **1v** (257 mg, 1 mmol, 1 equiv.) and boronic acid **3f** (146 mg, 1.2 mmol, 1.2 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired biphenyl **4i** (220 mg, 0.83 mmol, 83%).

White solid, mp 98 - 99 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): 1.61 – 1.69 (m, 6H, Piperidine), 3.40 – 3.70 (m, 4H, Piperidine), 7.37 (t, 1H, ^3J = 7.3 Hz, CH_{Ar}), 7.44 (d, 2H, ^3J = 7.6 Hz, CH_{Ar}), 7.47 (d, 2H, ^3J = 7.3 Hz, CH_{Ar}), 7.59 (d, 2H, ^3J = 7.3 Hz, CH_{Ar}), 7.61 (d, 2H, ^3J = 7.9 Hz, CH_{Ar}).

^{13}C NMR (126 MHz, $CDCl_3$): δ 24.6, 127.1, 127.4, 127.6, 128.8, 135.2, 140.3, 142.2, 170.1.

HRMS (TOF MS ES+) m/z: $[M + H]^+$: Calcd for $C_{18}H_{19}NO$ 266.1550. Found 266.1545.



[1,1'-biphenyl]-4-yl(pyrrolidin-1-yl)methanone 4j.

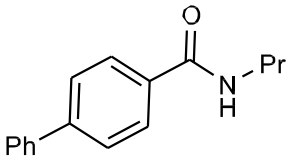
The title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), Na_2CO_3 (424 mg, 4 mmol, 4 equiv.), $NiBr_2$ (22 mg, 0.1 mmol, 0.1 equiv.), PCy_3 (83 mg, 0.3 mmol, 0.3 equiv.), CF_3 substrate **1w** (243 mg, 1 mmol, 1 equiv.) and boronic acid **3f** (146 mg, 1.2 mmol, 1.2 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired biphenyl **4j** (213 mg, 0.85 mmol, 85%). The gram scale synthesis was performed on 10 mmol of the starting **1x** and the biphenyl **4j** was prepared in 80% yield (2.01 g, 8.0 mmol).

White solid, mp 139 – 140 °C. **^{1}H NMR** (500 MHz, DMSO-d_6): 1.78 – 1.82 (m, 2H, Pyrrolidine), 1.83 – 1.87 (m, 2H, Pyrrolidine), 3.42 (t, 2H, ^3J = 6.4 Hz, Pyrrolidin), 3.48 (t, 2H, ^3J = 6.8 Hz, Pyrrolidine), 7.39 (t, 1H, ^3J = 7.2 Hz, CH_{Ar}), 7.48 (d, 2H, ^3J = 7.8 Hz, CH_{Ar}), 7.60 (d, 2H, ^3J = 8.1 Hz, CH_{Ar}), 7.70 (t, 4H, ^3J = 7.5 Hz, CH_{Ar}).

^{13}C NMR (126 MHz, DMSO-d_6): δ 23.9, 26.0, 46.0, 48.9, 126.4, 126.8, 127.8, 127.9, 129.0, 136.1, 139.3, 141.3.

MS (GC, 70eV): m/z (%) = 251 (M^+, 46), 181 (100), 152 (57.5).

Anal. calcd. for $C_{17}H_{17}NO$: C 81.24; H, 6.82. Found: C 82.52; H, 6.76.



N-propyl-[1,1'-biphenyl]-4-carboxamide 4k.

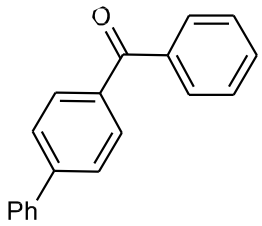
The title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), Na_2CO_3 (424 mg, 4 mmol, 4 equiv.), $NiBr_2$ (22 mg, 0.1 mmol, 0.1 equiv.), PCy_3 (83 mg, 0.3 mmol, 0.3 equiv.), CF_3 substrate **1x** (231 mg, 1 mmol, 1 equiv.) and boronic acid **3f** (146 mg, 1.2 mmol, 1.2 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired biphenyl **4k** (193 mg, 0.81 mmol, 81%).

White solid, mp 160 - 161 °C. **^{1}H NMR** (500 MHz, DMSO-d_6): 0.90 (t, 3H, CH_3), 1.53 – 1.58 (m, 2H, CH_2), 3.25 (q, 2H, ^3J = 6.6 Hz, CH_2N), 7.40 (t, 1H, ^3J = 7.2 Hz, CH_{Ar}), 7.48 (t, 2H, ^3J = 7.7 Hz, CH_{Ar}), 7.71 – 7.73 (m, 2H, CH_{Ar}), 7.75 (d, 2H, ^3J = 8.4 Hz, CH_{Ar}), 7.95 (d, 2H, ^3J = 8.2 Hz, CH_{Ar}).

^{13}C NMR (126 MHz, DMSO-d_6): δ 11.5, 22.5, 41.0, 126.5, 126.9, 127.8, 128.0, 129.0, 133.5, 139.2, 142.5, 165.8.

MS (GC, 70eV): m/z (%) = 239 (M^+, 36), 197 (19), 181 (100), 152 (44).

Anal. calcd. for $C_{16}H_{17}NO$: C 80.30; H, 7.16; N, 5.85. Found: C 80.36; H, 7.23; N, 5.91.



[1,1'-biphenyl]-4-yl(phenyl)methanone 4l.

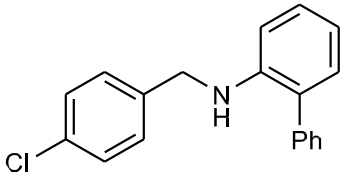
The title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), Na_2CO_3 (424 mg, 4 mmol, 4 equiv.), $NiBr_2$ (22 mg, 0.1 mmol, 0.1 equiv.), PCy_3 (83 mg, 0.3 mmol, 0.3 equiv.), CF_3 substrate **1y** (250 mg, 1 mmol, 1 equiv.) and boronic acid **3f** (146 mg, 1.2 mmol, 1.2 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired biphenyl **4l** (211 mg, 0.82 mmol, 82%).

White solid, mp 99 - 101 °C. **^{1}H NMR** (500 MHz, DMSO-d_6): δ 7.43 (t, 1H, ^3J = 7.4 Hz, CH_{Ar}), 7.51 (t, 2H, ^3J = 7.8 Hz, CH_{Ar}), 7.57 (t, 2H, ^3J = 8.1 Hz, CH_{Ar}), 7.70 (t, 2H, ^3J = 7.5 Hz, CH_{Ar}), 7.67 – 7.70 (m, 1H, CH_{Ar}), 7.76 (t, 4H, ^3J = 7.6 Hz, CH_{Ar}), 7.84 (q, 4H, ^3J = 6.0 Hz, CH_{Ar}).

^{13}C NMR (126 MHz, DMSO-d_6): δ 126.8, 127.0, 128.4, 128.6, 129.1, 129.6, 130.5, 132.6, 135.7, 137.2, 138.9, 144.2, 195.3.

MS (GC, 70eV): m/z (%) = 258 (M^+, 52), 181 (100), 152 (50).

Anal. calcd. for $C_{19}H_{14}O$: C 88.34; H, 5.46. Found: C 88.41; H, 5.55.



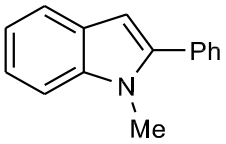
N-(4-chlorobenzyl)-[1,1'-biphenyl]-2-amine 4m.

The title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), Na_2CO_3 (424 mg, 4 mmol, 4 equiv.), $NiBr_2$ (22 mg, 0.1 mmol, 0.1 equiv.), PCy_3 (83 mg, 0.3 mmol, 0.3 equiv.), CF_3 substrate **1z** (286 mg, 1 mmol, 1 equiv.) and boronic acid **3f** (146 mg, 1.2 mmol, 1.2 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired biphenyl **4m** (231 mg, 0.79 mmol, 79%).

Yellowish solid, mp 154 - 155 °C. **^{1}H NMR** (500 MHz, *CDCl$_3$*): 4.33 (s, 2H, CH_2), 4.47 (br. s, 1H, NH), 6.63 (d, 1H, ^3J = 8.0 Hz, CH_{Ar}), 6.84 (t, 1H, ^3J = 7.2 Hz, CH_{Ar}), 7.17 (d, 1H, ^3J = 7.3 Hz, CH_{Ar}), 7.22 (t, 1H, ^3J = 7.0 Hz, CH_{Ar}), 7.28 (d, 2H, ^3J = 8.3 Hz, CH_{Ar}), 7.32 (d, 2H, ^3J = 8.5 Hz, CH_{Ar}), 7.36 – 7.42 (m, 1H, CH_{Ar}), 7.49 – 7.53 (m, 4H, CH_{Ar}).

^{13}C NMR (126 MHz, *CDCl$_3$*): δ 47.4, 110.7, 117.4, 127.3, 127.7, 128.3, 128.7, 129.0, 129.3, 130.2, 132.6, 138.0, 139.3, 144.5.

Anal. calcd. for $C_{19}H_{16}NCl$: C 77.68; H, 5.49; N, 4.77. Found: C 77.62; H, 5.29; N, 4.71.



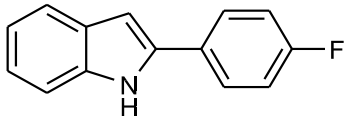
1-methyl-2-phenyl-1H-indole 4n.

The title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), Na_2CO_3 (424 mg, 4 mmol, 4 equiv.), $NiBr_2$ (22 mg, 0.1 mmol, 0.1 equiv.), PCy_3 (83 mg, 0.3 mmol, 0.3 equiv.), CF_3 substrate **1aa** (199 mg, 1 mmol, 1 equiv.) and boronic acid **3f** (146 mg, 1.2 mmol, 1.2 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired phenylindole **4n** (149 mg, 0.72 mmol, 72%).

Yellowish solid, mp 102 - 103 °C. **^{1}H NMR** (500 MHz, DMSO-d_6): δ 3.04 (s, 3H, Me), 6.73 (s, 1H, CH_{indole}), 7.31 (dt, 1H, ^3J = 7.1 Hz, ^4J = 0.8 Hz, CH_{Ar}), 7.40 (dt, 1H, ^3J = 7.3 Hz, ^4J = 0.8 Hz, CH_{Ar}), 7.49 (d, 1H, ^3J = 8.2 Hz, CH_{Ar}), 7.51 – 7.54 (m, 1H, CH_{Ar}), 7.59 (t, 2H, ^3J = 8.0 Hz, CH_{Ar}), 7.64 – 7.66 (m, 2H, CH_{Ar}), 7.80 (d, 1H, ^3J = 7.8 Hz, CH_{Ar}).

^{13}C NMR (126 MHz, DMSO-d_6): δ 31.1, 101.6, 109.6, 119.8, 120.4, 121.6, 127.8, 127.9, 128.4, 129.3, 132.8, 138.3, 141.5.

HRMS (TOF MS ES+) m/z: $[M + H]^+$: Calcd for $C_{15}H_{14}N$ 208.1131. Found 208.1126.



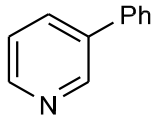
2-(4-fluorophenyl)-1H-indole 4o.

The title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), Na_2CO_3 (424 mg, 4 mmol, 4 equiv.), $NiBr_2$ (22 mg, 0.1 mmol, 0.1 equiv.), PCy_3 (83 mg, 0.3 mmol, 0.3 equiv.), CF_3 substrate **1ab** (185 mg, 1 mmol, 1 equiv.) and boronic acid **3i** (168 mg, 1.2 mmol, 1.2 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired phenylindole **4o** (158 mg, 0.75 mmol, 75%).

Yellowish solid, mp 190 - 192 °C. **^{1}H NMR** (500 MHz, DMSO-d_6): δ 6.85 (s, 1H, CH_{indole}), 7.01 (t, 1H, ^3J = 7.4 Hz, CH_{Ar}), 7.11 (t, 1H, ^3J = 7.3 Hz, CH_{Ar}), 7.31 (t, 2H, ^3J = 8.6 Hz, CH_{Ar}), 7.42 (d, 1H, ^3J = 8.0 Hz, CH_{Ar}), 7.53 (d, 1H, ^3J = 8.0 Hz, CH_{Ar}), 7.89 – 7.92 (m, 2H, CH_{Ar}), 11.6 (s, 1H, NH).

^{13}C NMR (126 MHz, DMSO-d_6): δ 98.7, 111.3, 115.8 (d, J_{CF} = 21.5 Hz), 119.4, 120.1, 121.6, 127.0 (d, J_{CF} = 7.9 Hz), 128.7, 128.9 (d, J_{CF} = 3.0 Hz), 137.0 (d, J_{CF} = 49.8 Hz), 161.6 (d, $^1J_{CF}$ = 247.4 Hz).

HRMS (TOF MS ES+) m/z: $[M + H]^+$: Calcd for $C_{14}H_{11}NF$ 212.0878. Found 212.0876.



3-phenylpyridine 4p.

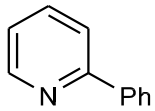
The title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), Na_2CO_3 (424 mg, 4 mmol, 4 equiv.), $NiBr_2$ (22 mg, 0.1 mmol, 0.1 equiv.), PCy_3 (83 mg, 0.3 mmol, 0.3 equiv.), CF_3 substrate **1q** (146 mg, 1 mmol, 1 equiv.) and boronic acid **3j** (147 mg, 1.2 mmol, 1.2 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired phenylpyridine **4p** (116 mg, 0.75 mmol, 75%).

Alternatively, the title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), Na_2CO_3 (424 mg, 4 mmol, 4 equiv.), $NiBr_2$ (22 mg, 0.1 mmol, 0.1 equiv.), PCy_3 (83 mg, 0.3 mmol, 0.3 equiv.), CF_3 substrate **1ac** (147 mg, 1 mmol, 1 equiv.) and boronic acid **3f** (146 mg, 1.2 mmol, 1.2 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired phenylpyridine **4p** (119 mg, 0.77 mmol, 77%).

Yellow solid. **^{1}H NMR** (500 MHz, DMSO-d_6): δ 7.28 – 7.31 (m, 1H, CH_{Ar}), 7.35 – 7.38 (m, 1H, CH_{Ar}), 7.43 (t, 2H, ^3J = 7.8 Hz, CH_{Ar}), 7.53 (d, 2H, ^3J = 8.6 Hz, CH_{Ar}), 7.42 (d, 1H, ^3J = 8.4 Hz, CH_{Ar}), 8.56 (dd, 1H, ^3J = 4.8 Hz, ^4J = 1.3 Hz, CH_{Ar}), 8.83 (d, 1H, ^4J = 2.2 Hz, CH_{Ar}).

^{13}C NMR (126 MHz, $CDCl_3$): δ 123.3, 126.9, 127.9, 128.8, 134.1, 136.3, 137.6, 148.1, 148.2.

HRMS (TOF MS ES+) m/z: $[M + H]^+$: Calcd for $C_{11}H_{10}N$ 156.0816. Found 156.0813.



2-phenylpyridine 4q.

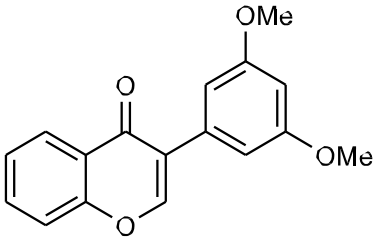
The title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), Na_2CO_3 (424 mg, 4 mmol, 4 equiv.), $NiBr_2$ (22 mg, 0.1 mmol, 0.1 equiv.), PCy_3 (83 mg, 0.3 mmol, 0.3 equiv.), CF_3 substrate **1ad** (147 mg, 1 mmol, 1 equiv.) and boronic

acid **3f** (146 mg, 1.2 mmol, 1.2 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired phenylpyridine **4p** (104 mg, 0.67 mmol, 67%).

Yellowish solid. **^{1}H NMR** (500 MHz, DMSO-d_6): δ 7.15 – 7.18 (m, 1H, CH_{Ar}), 7.41 (t, 1H, ^{3}J = 7.5 Hz, CH_{Ar}), 7.47 (t, 2H, ^{3}J = 7.8 Hz, CH_{Ar}), 7.66 – 7.68 (m, 2H, CH_{Ar}), 8.00 – 8.02 (m, 2H, CH_{Ar}), 8.69 (d, 1H, ^{3}J = 4.8 Hz, CH_{Ar}).

^{13}C NMR (126 MHz, $CDCl_3$): δ 120.3, 121.9, 126.7, 128.5, 128.8, 136.5, 139.2, 149.4, 157.2.

HRMS (TOF MS ES+) m/z: $[M + H]^+$: Calcd for $C_{11}H_{10}N$ 156.0816. Found 156.0813.



3-(3,5-dimethoxyphenyl)-4H-chromen-4-one 4r.

The title compound was prepared starting from $N(SiMe_3)_3$ (304 mg, 1.3 mmol, 1.3 equiv.), Yb_2O_3 (394 mg, 1 mmol, 1 equiv.), Na_2CO_3 (424 mg, 4 mmol, 4 equiv.), $NiBr_2$ (22 mg, 0.1 mmol, 0.1 equiv.), PCy_3 (83 mg, 0.3 mmol, 0.3 equiv.), CF_3 substrate **1ae** (214 mg, 1 mmol, 1 equiv.) and boronic acid **3k** (218 mg, 1.2 mmol, 1.2 equiv.). The purification was accomplished by column chromatography on silica gel to provide the desired 3-arylchromone **4r** (206 mg, 0.73 mmol, 73%).

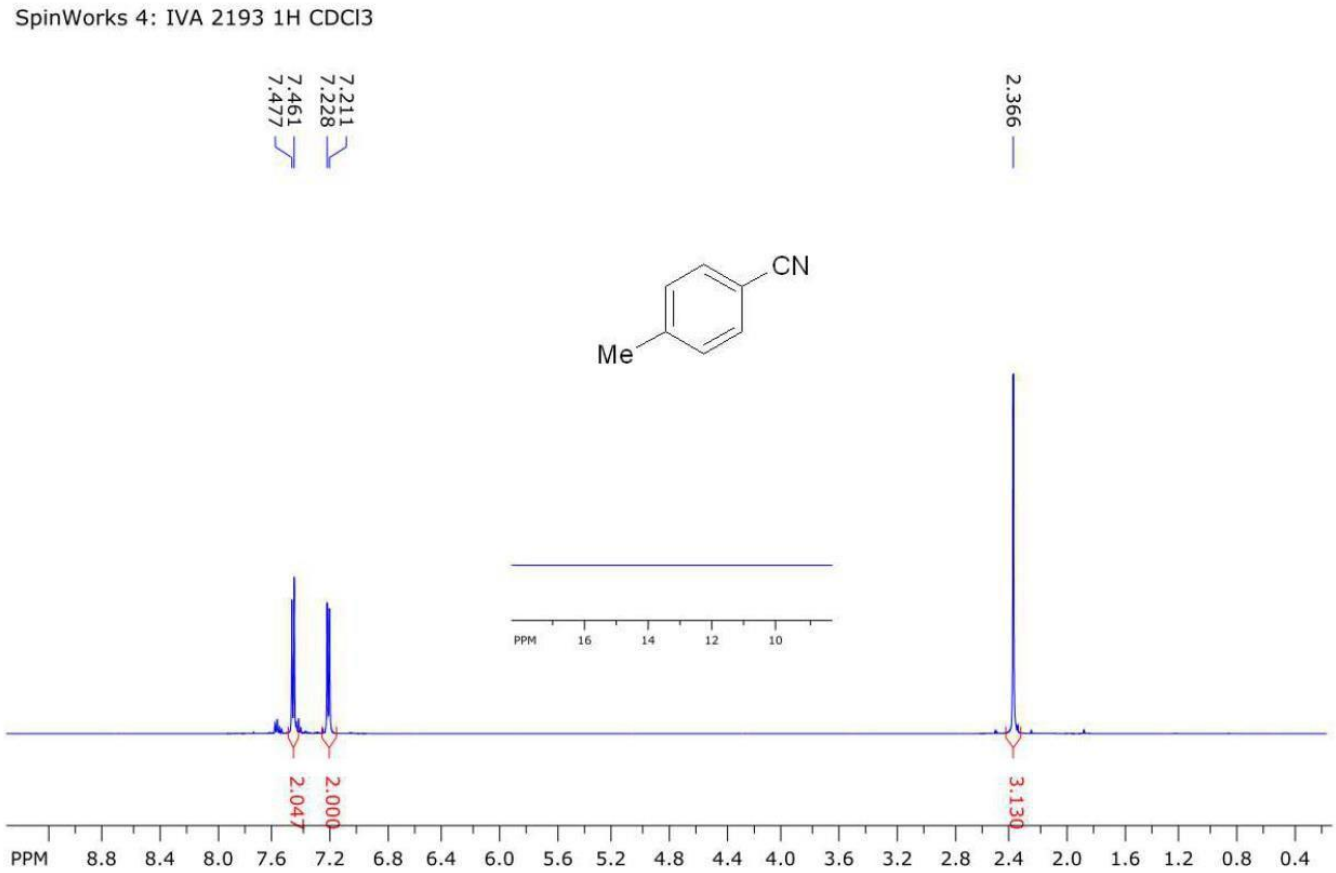
Yellow solid, mp 140 - 142 ^{o}C. **^{1}H NMR** (500 MHz, DMSO-d_6): δ 3.81 (s, 6H, 2xOMe), 6.48 (t, 1H, J = 2.4 Hz, CH_{Ar}), 6.72 (d, 2H, J = 2.4 Hz, CH_{Ar}), 7.42 (t, 1H, ^{3}J = 7.5 Hz, CH_{Ar}), 7.47 (d, 1H, ^{3}J = 8.3 Hz, CH_{Ar}), 7.66 – 7.68 (m, 2H, CH_{Ar}), 8.03 (s, 1H, CH_{Ar}), 8.30 (dd, 1H, ^{3}J = 7.9 Hz, ^{4}J = 1.8 Hz, CH_{Ar}).

^{13}C NMR (126 MHz, $CDCl_3$): δ 55.4, 100.5, 107.0, 124.5, 125.2, 125.2, 126.3, 133.6, 153.2, 156.0, 160.7, 176.1.

HRMS (TOF MS ES+) m/z: $[M + H]^+$: Calcd for $C_{17}H_{15}O_4$ 283.0970. Found 283.0979.

(C) Copies ^{1}H and ^{13}C NMR spectra.

Compound **2a**



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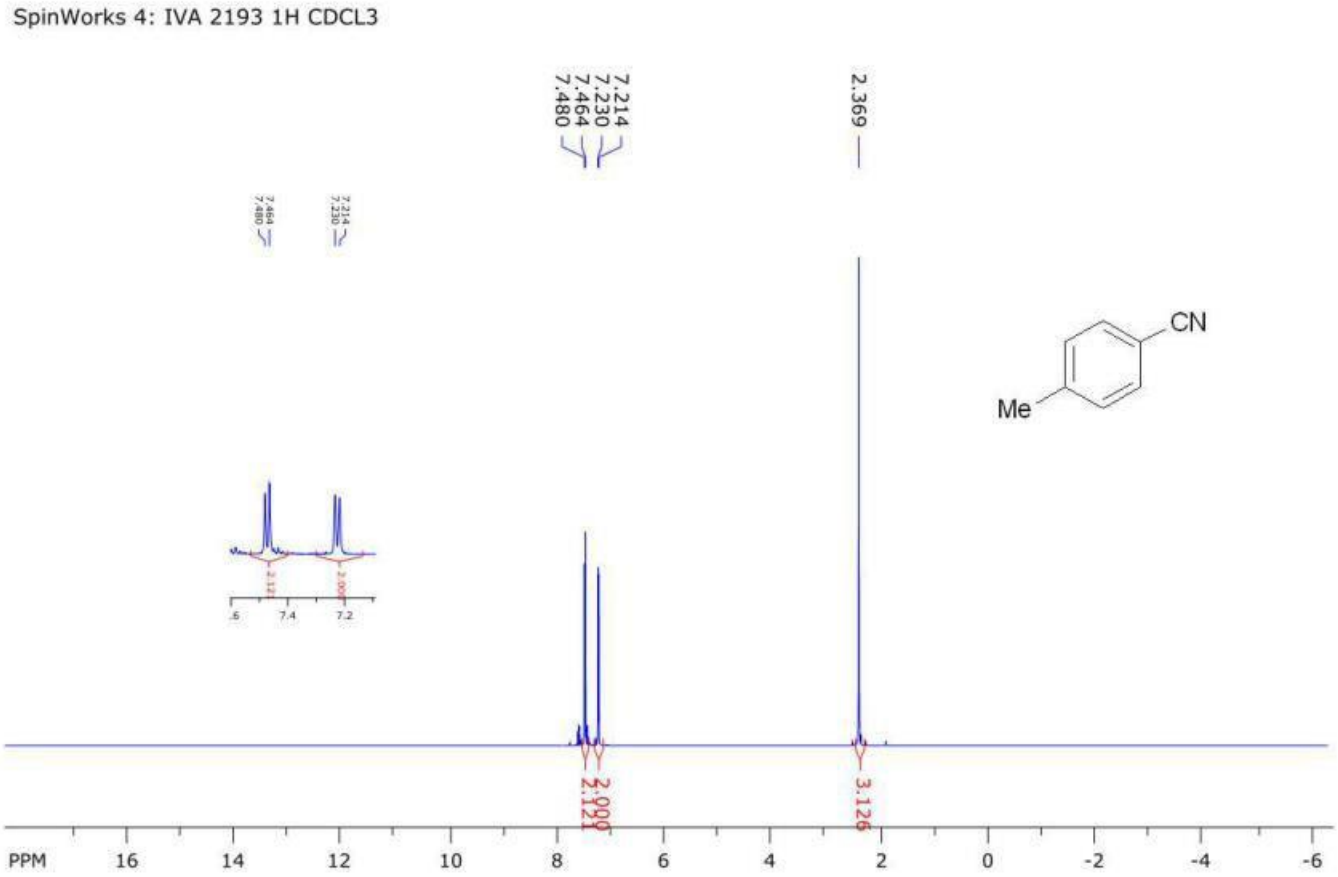
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 187.216 ppm/cm: 0.37433

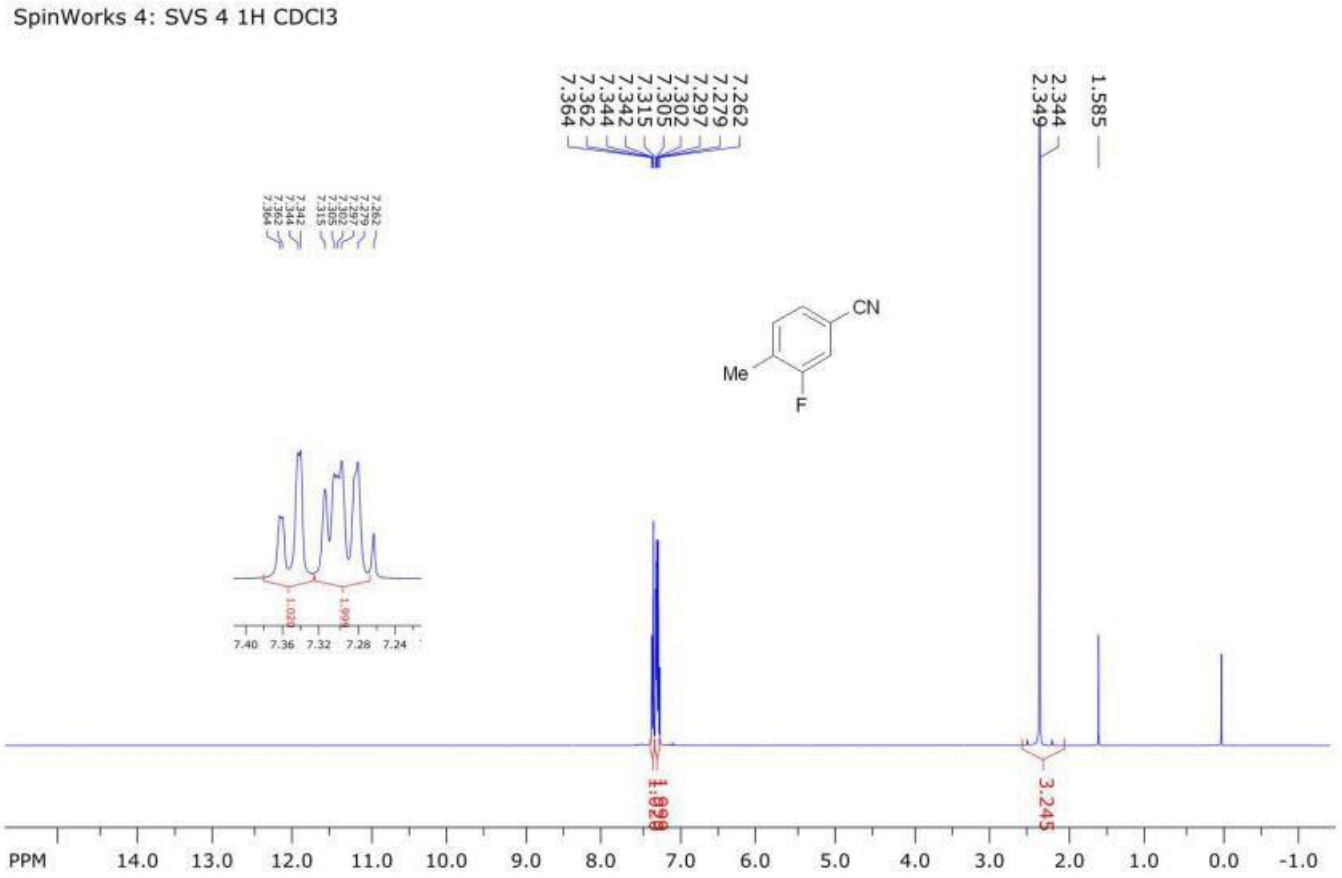
Compound **2a**



file: D:\NAPO\NMR\500-2\mkr10304\19\fid expt: <zg30>
transmitter freq.: 500.133001 MHz
time domain size: 65536 points
width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt
number of scans: 24

freq. of 0 ppm: 500.130021 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 493.421 ppm/cm: 0.98658

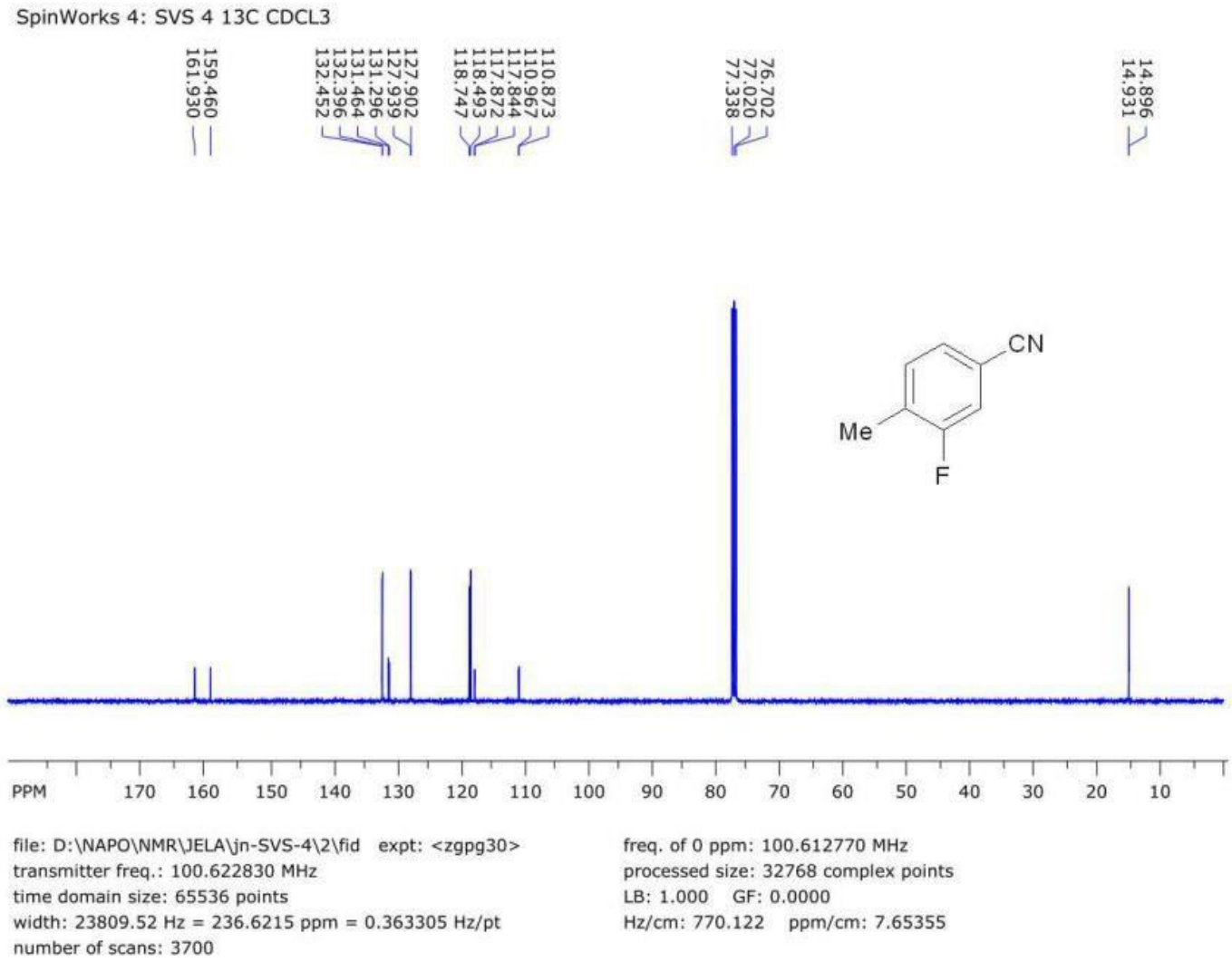
Compound **2b**



file: ...:\NAPO\NMR\JELA\nmr\jn-SVS-4\1\fid expt: <zg30>
transmitter freq.: 400.132471 MHz
time domain size: 65536 points
width: 8196.72 Hz = 20.4850 ppm = 0.125072 Hz/pt
number of scans: 16

freq. of 0 ppm: 400.130008 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 274.554 ppm/cm: 0.68616

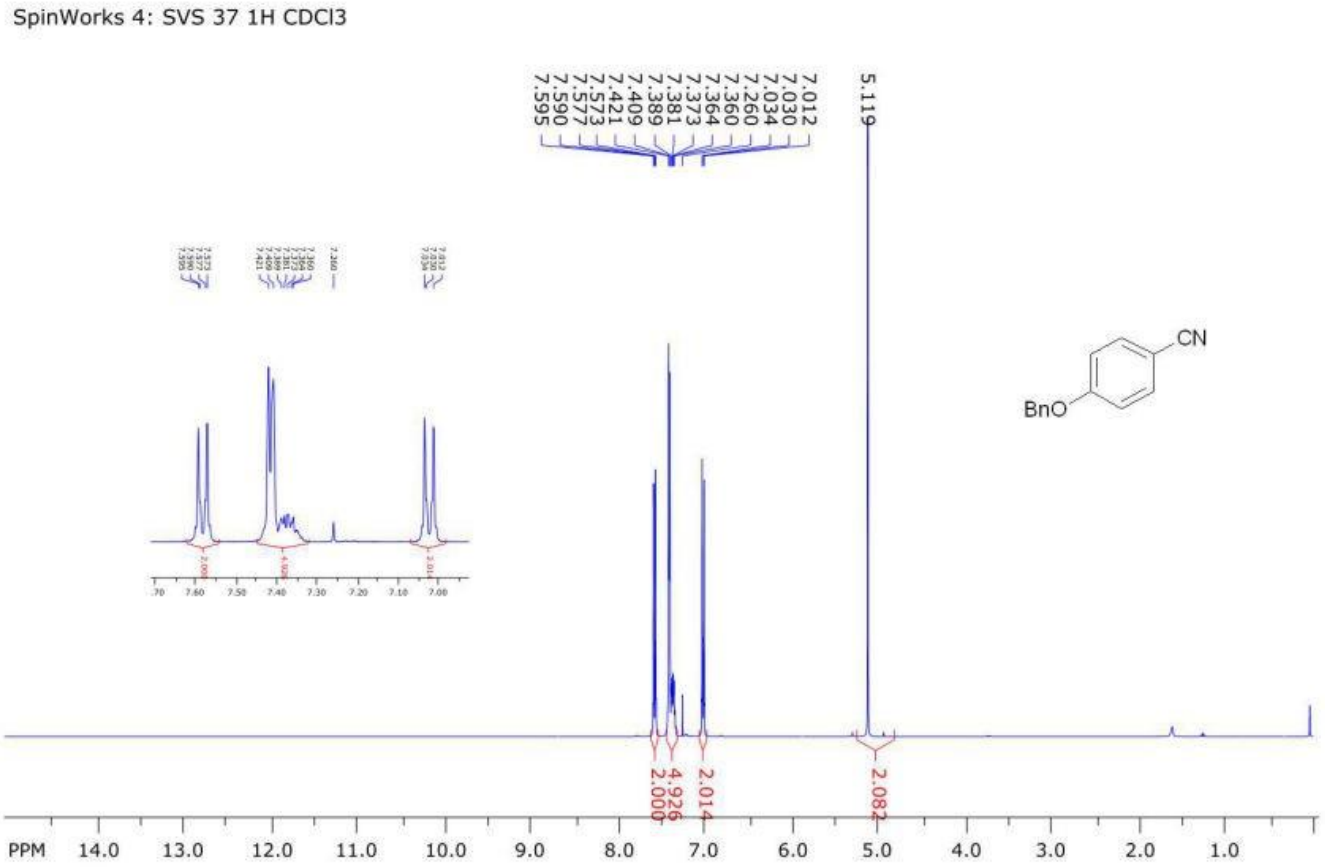
Compound **2b**



file: D:\NAPO\NMR\JELA\jn-SVS-4\2\fid expt: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 23809.52 Hz = 236.6215 ppm = 0.363305 Hz/pt
number of scans: 3700

freq. of 0 ppm: 100.612770 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 770.122 ppm/cm: 7.65355

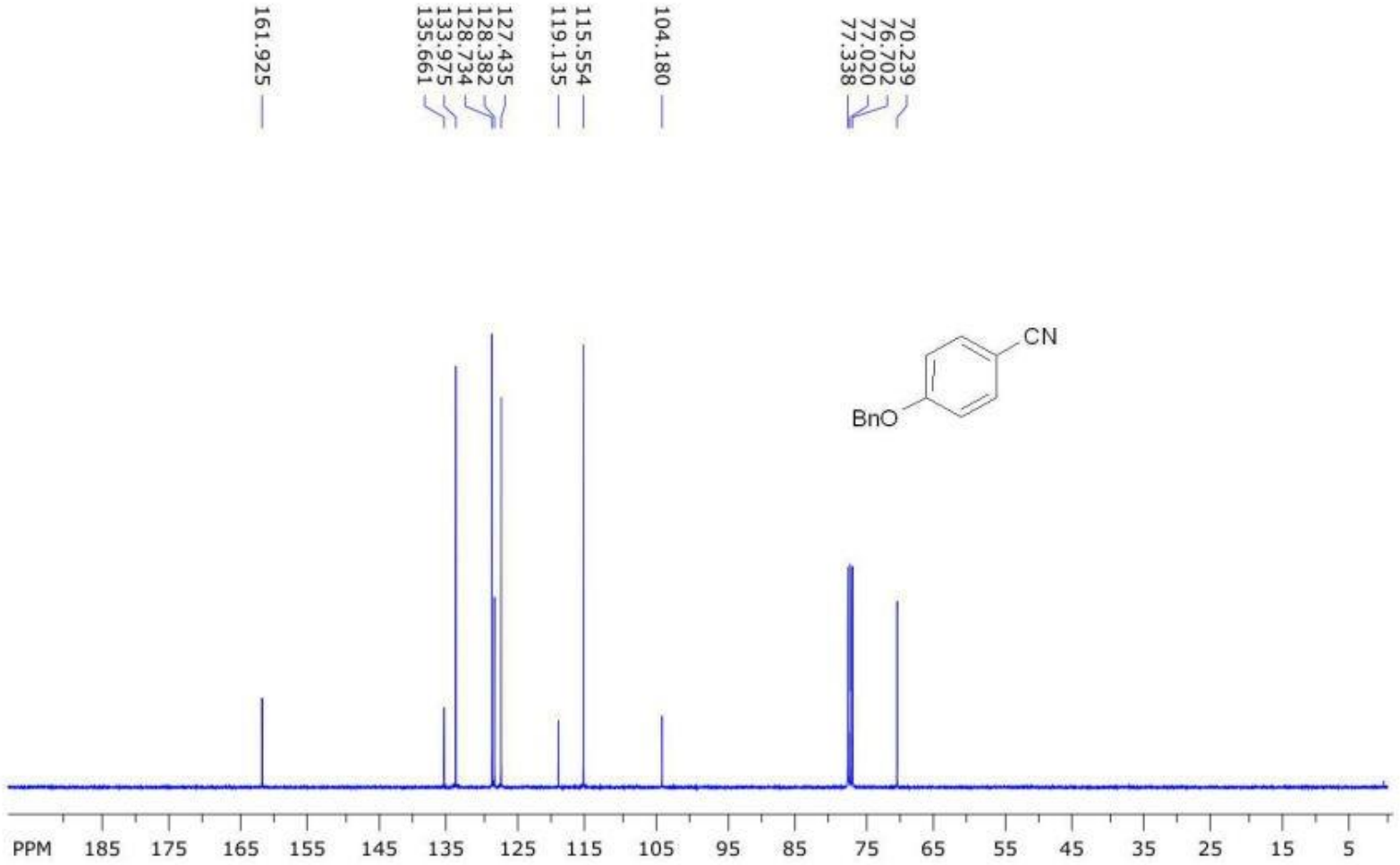
Compound **2c**



file: ...\NAPO\NMR\JELA\nmr\jn-SVS-37\1\fid expt: <zg30>
transmitter freq.: 400.132471 MHz
time domain size: 65536 points
width: 8196.72 Hz = 20.4850 ppm = 0.125072 Hz/pt
number of scans: 16

freq. of 0 ppm: 400.130009 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 242.275 ppm/cm: 0.60549

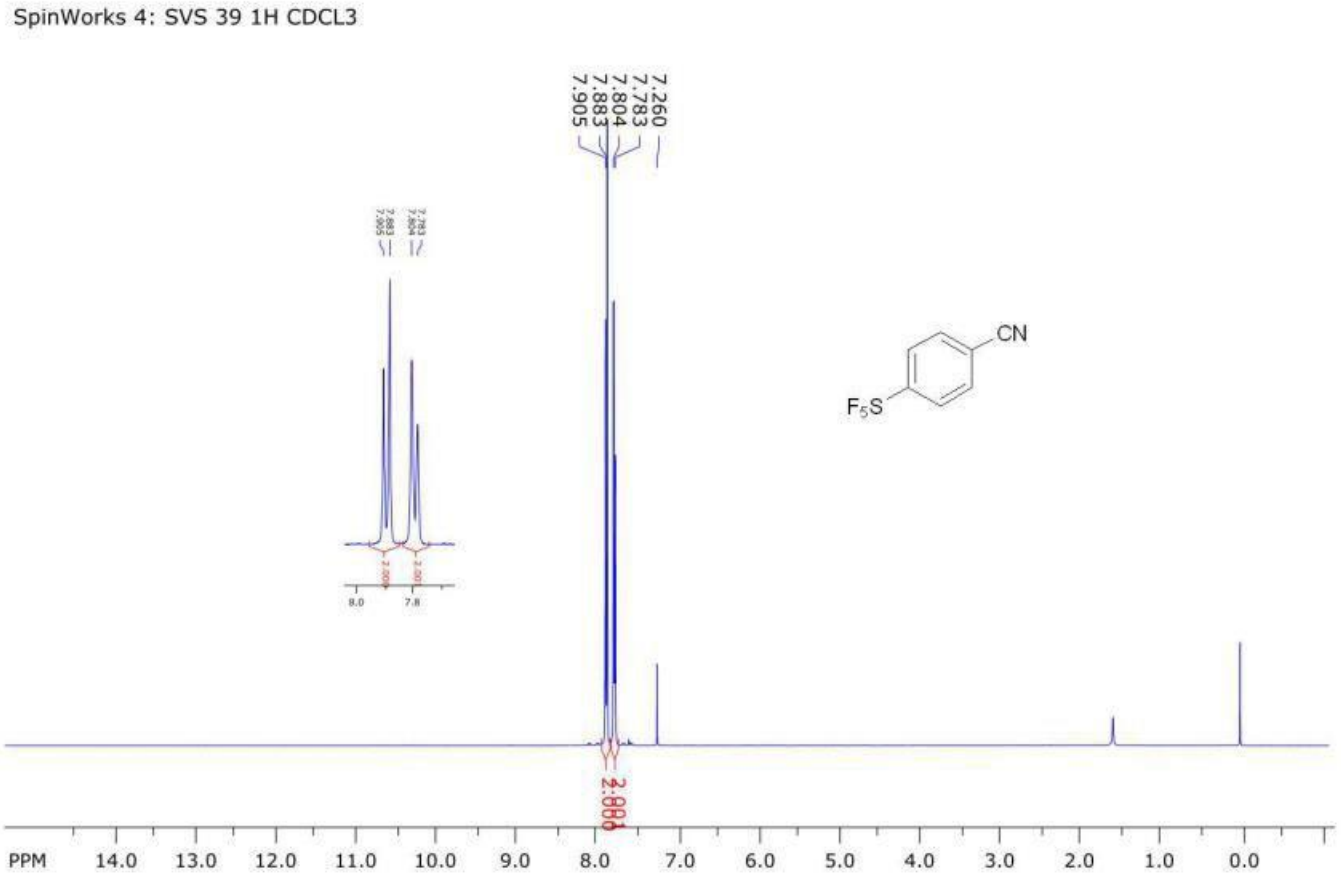
Compound **2c**



file: D:\NAPO\NMR\JELA\jn-SVS-37\2\fid expt: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 23809.52 Hz = 236.6215 ppm = 0.363305 Hz/pt
number of scans: 2215

freq. of 0 ppm: 100.612774 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 801.728 ppm/cm: 7.96765

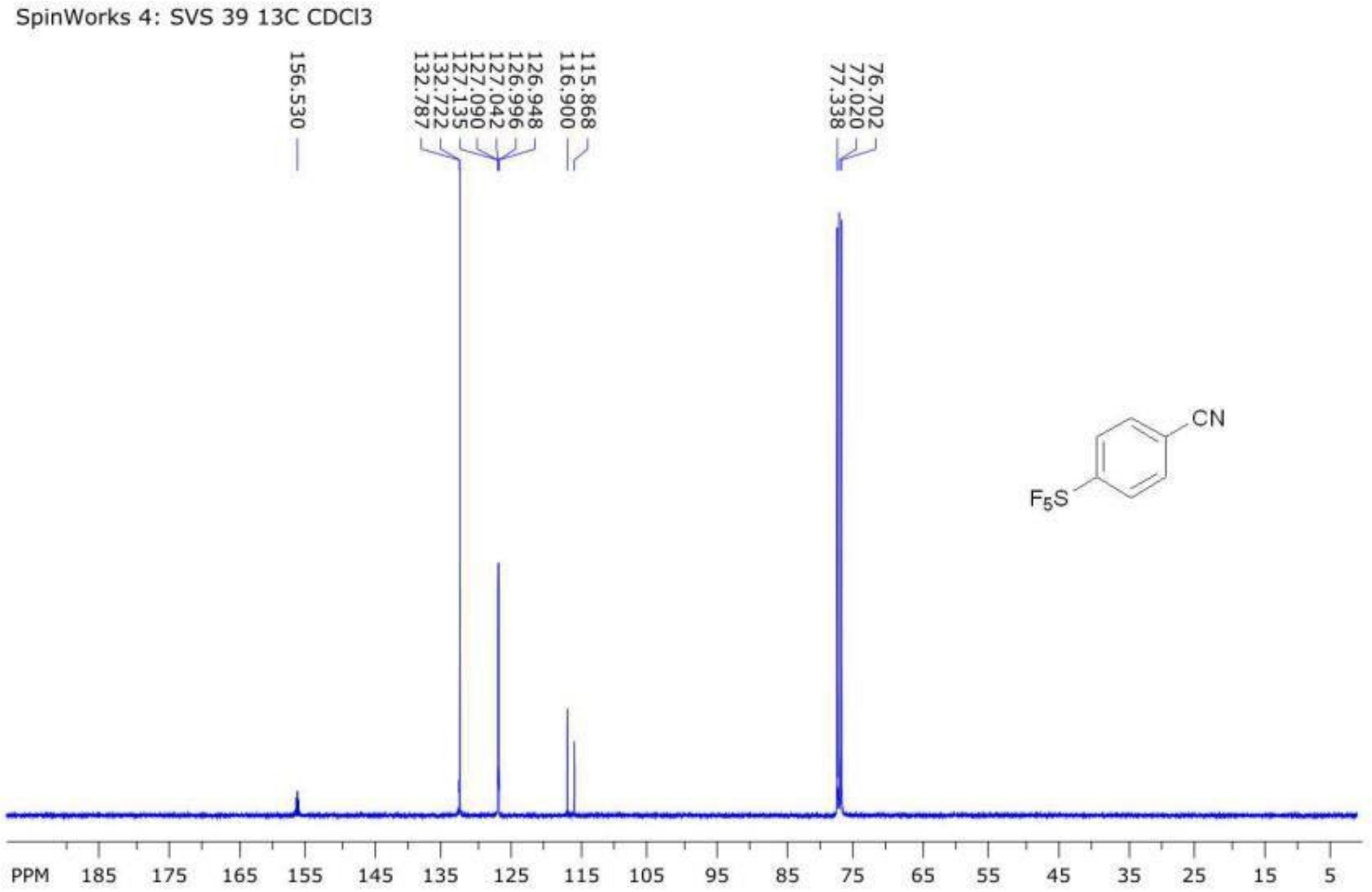
Compound **2d**



file: ...\NAPO\NMR\JELA\nmr\jn-SVS-39\1\fid expt: <zg30>
transmitter freq.: 400.132471 MHz
time domain size: 65536 points
width: 8196.72 Hz = 20.4850 ppm = 0.125072 Hz/pt
number of scans: 16

freq. of 0 ppm: 400.130009 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 264.399 ppm/cm: 0.66078

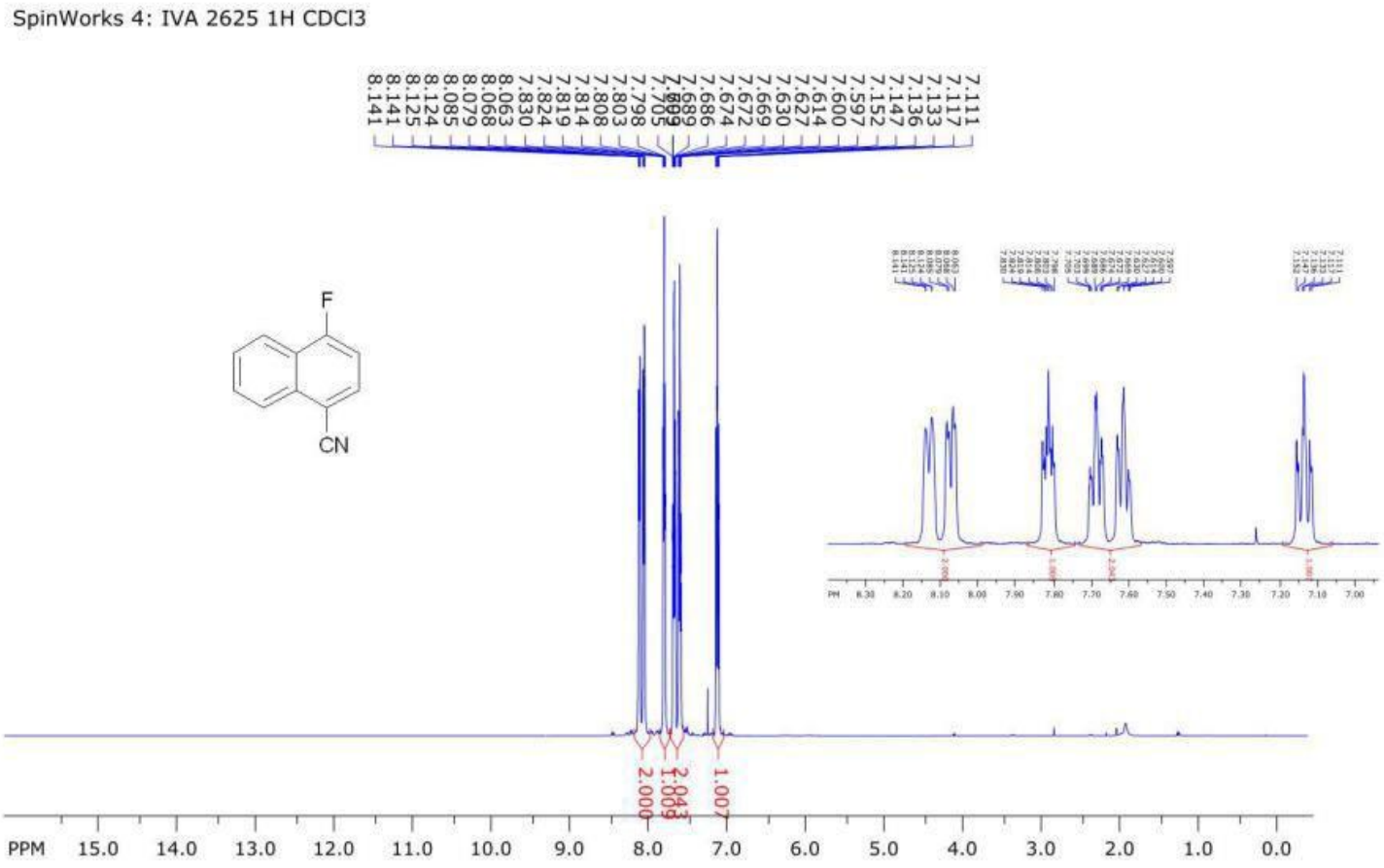
Compound **2d**



file: D:\NAPO\NMR\JELA\jn-SVS-39\2\fid expt: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 23809.52 Hz = 236.6215 ppm = 0.363305 Hz/pt
number of scans: 3700

freq. of 0 ppm: 100.612769 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 797.514 ppm/cm: 7.92577

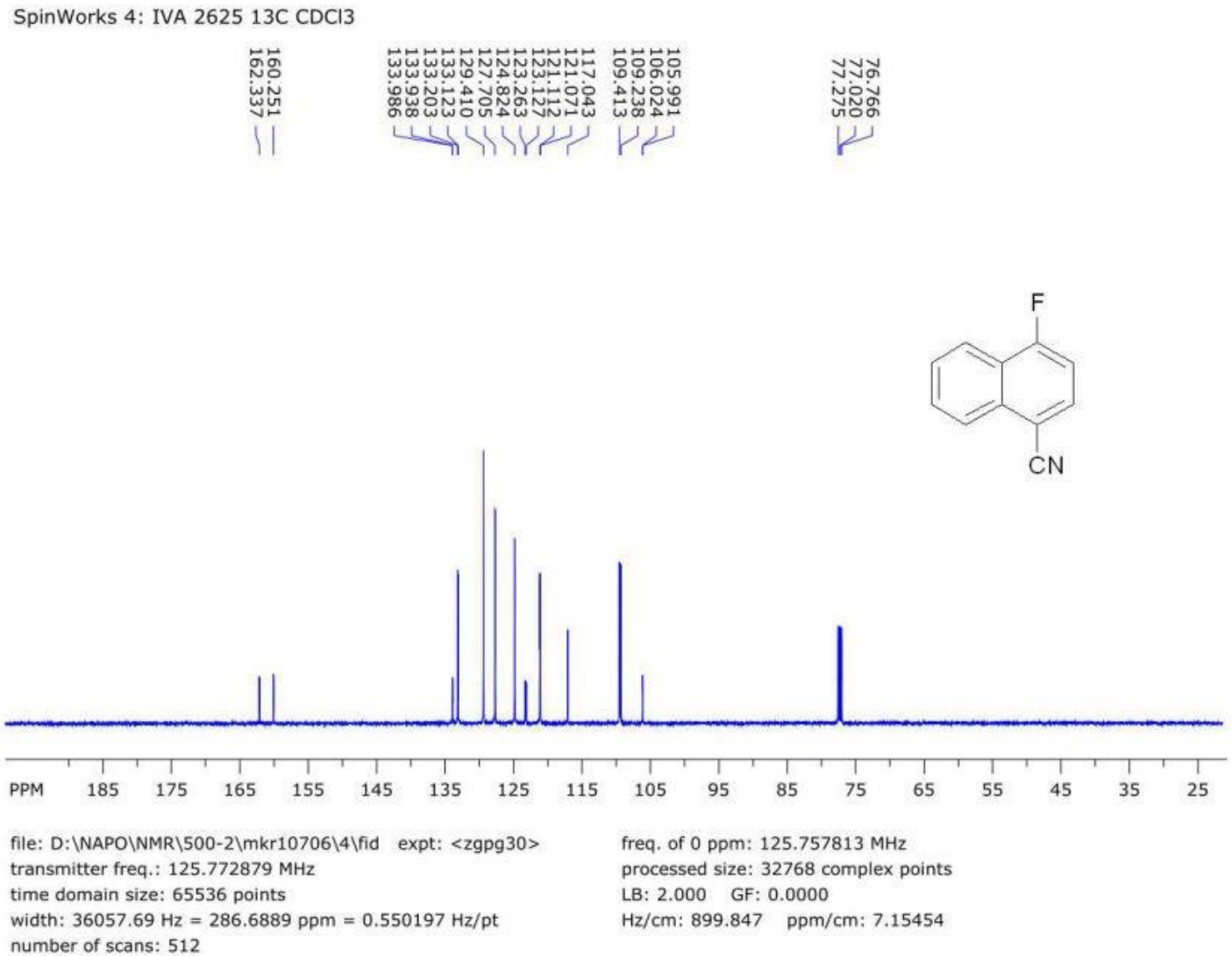
Compound **2e**



file: ...NAPO\NMR\500-2\mkr10706\3 2625\fid expt: <zg30>
transmitter freq.: 500.133001 MHz
time domain size: 65536 points
width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt
number of scans: 24

freq. of 0 ppm: 500.130023 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 334.042 ppm/cm: 0.66791

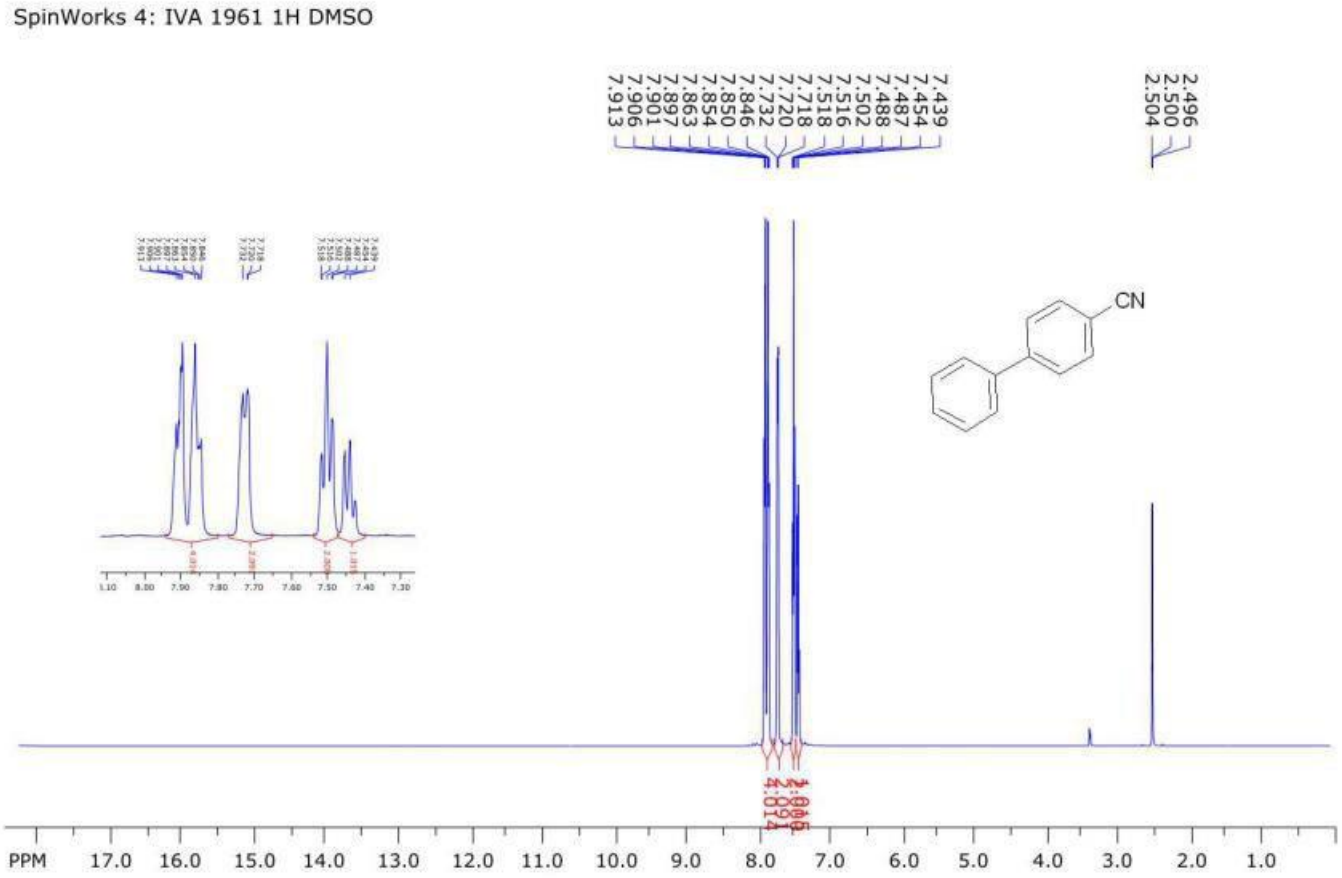
Compound **2e**



file: D:\NAPO\NMR\500-2\mkr10706\4\fid expt: <zgpg30>
transmitter freq.: 125.772879 MHz
time domain size: 65536 points
width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt
number of scans: 512

freq. of 0 ppm: 125.757813 MHz
processed size: 32768 complex points
LB: 2.000 GF: 0.0000
Hz/cm: 899.847 ppm/cm: 7.15454

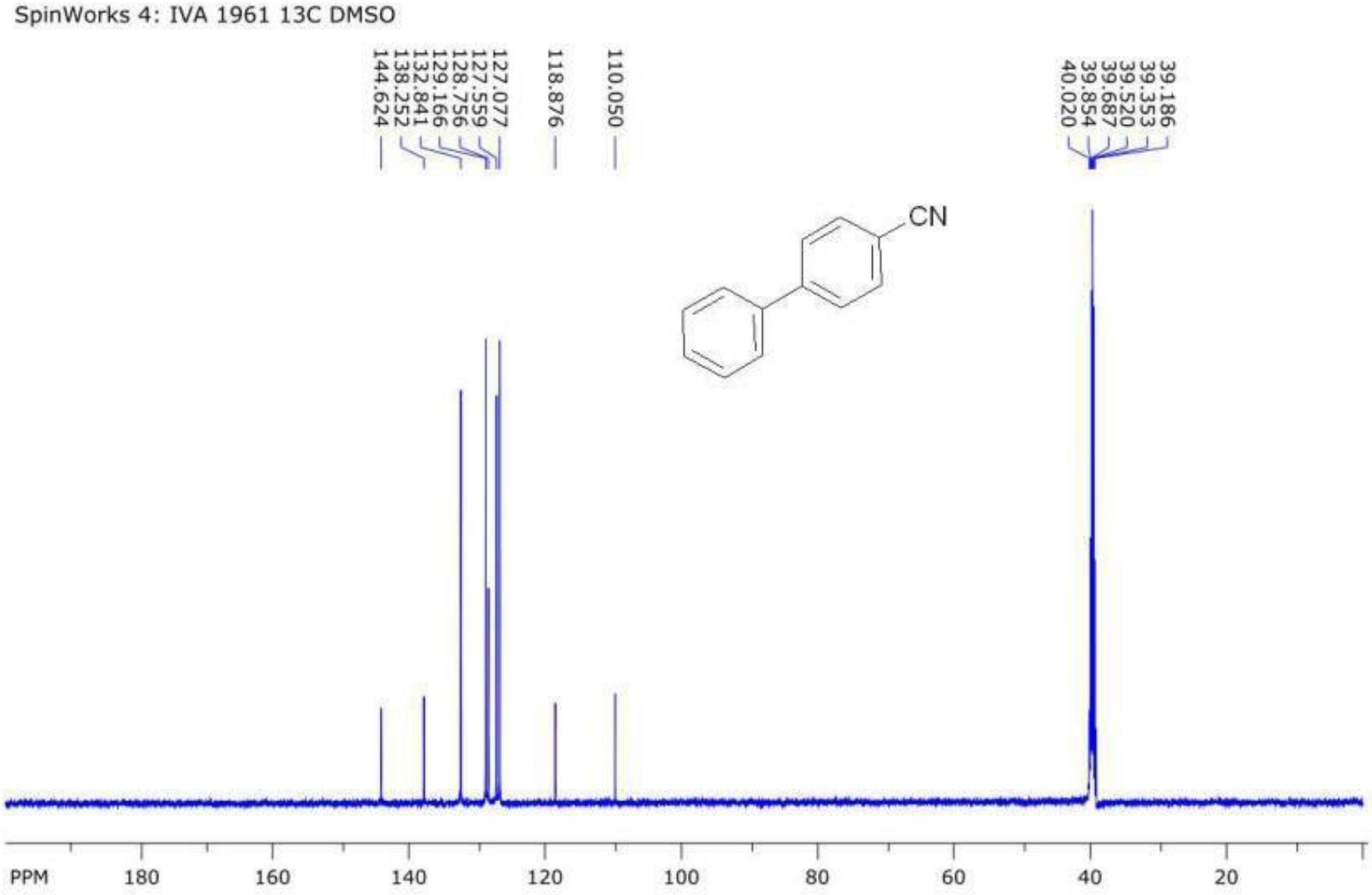
Compound **2f**



file: D:\NAPO\NMR\500-2\mkr12203\23\fid expt: <zg30>
transmitter freq.: 500.133001 MHz
time domain size: 65536 points
width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt
number of scans: 24

freq. of 0 ppm: 500.130005 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 370.066 ppm/cm: 0.73993

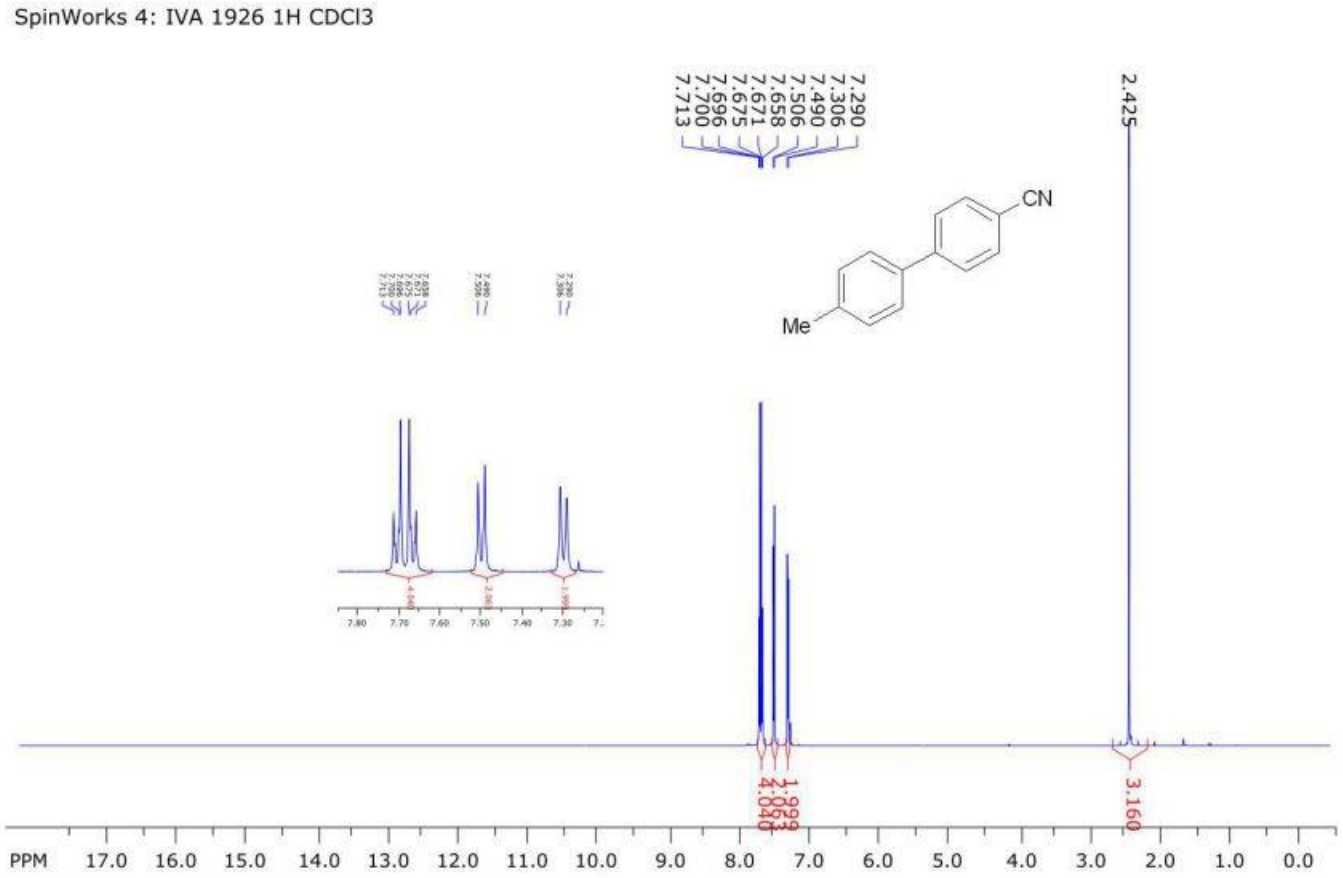
Compound **2f**



file: D:\NAPO\NMR\500-2\mkr12203\24\fid expt: <zgpg30>
transmitter freq.: 125.772879 MHz
time domain size: 65536 points
width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt
number of scans: 512

freq. of 0 ppm: 125.757846 MHz
processed size: 32768 complex points
LB: 2.000 GF: 0.0000
Hz/cm: 1008.339 ppm/cm: 8.01714

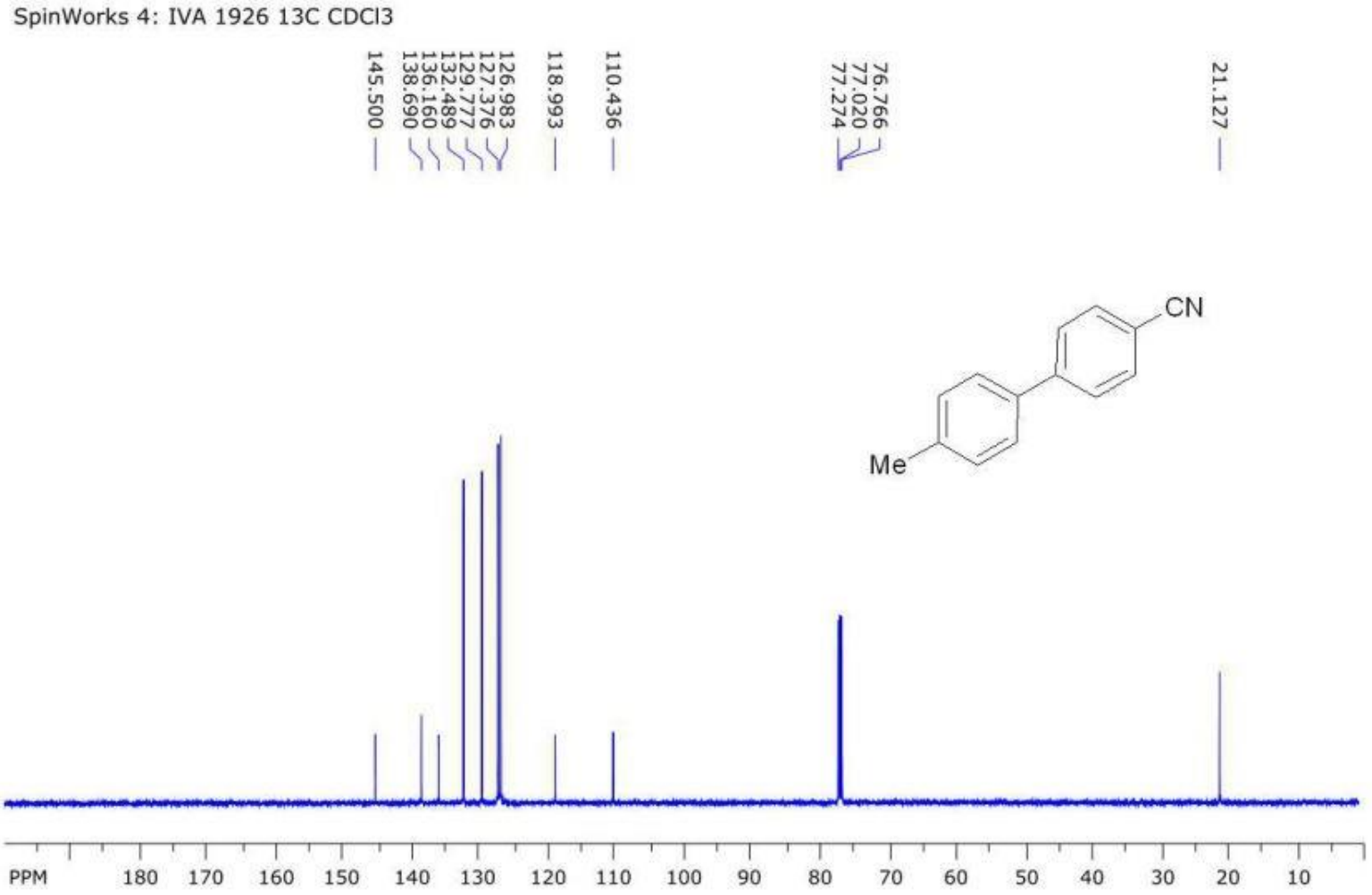
Compound **2g**



file: D:\NAPO\NMR\500-2\mkr11502\29\fid expt: <zg30>
transmitter freq.: 500.133001 MHz
time domain size: 65536 points
width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt
number of scans: 24

freq. of 0 ppm: 500.130023 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 378.799 ppm/cm: 0.75740

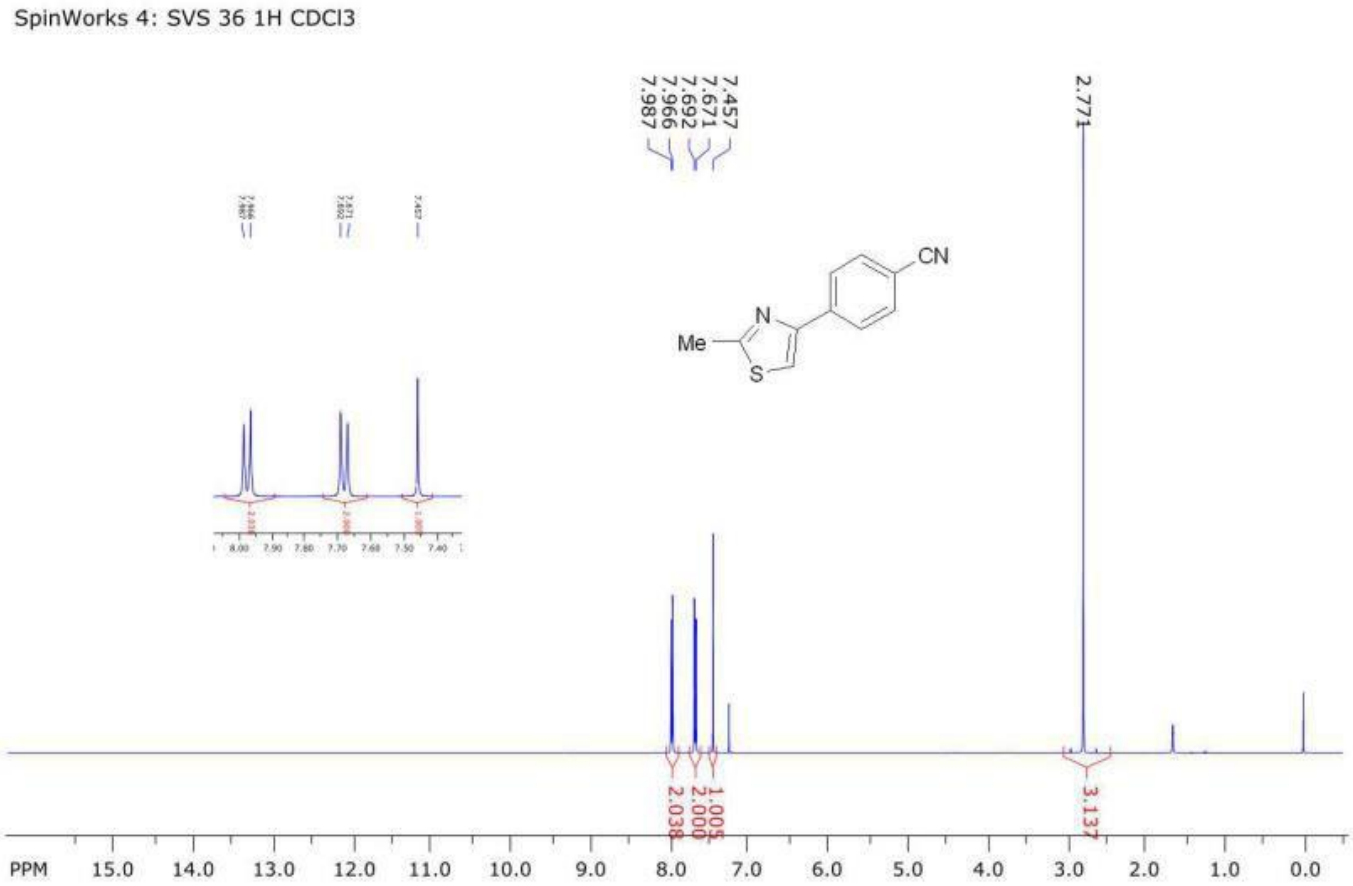
Compound **2g**



file: D:\NAPO\NMR\500-2\mkr11502\30\fid expt: <zgpg30>
transmitter freq.: 125.772879 MHz
time domain size: 65536 points
width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt
number of scans: 512

freq. of 0 ppm: 125.757802 MHz
processed size: 32768 complex points
LB: 2.000 GF: 0.0000
Hz/cm: 1003.553 ppm/cm: 7.97909

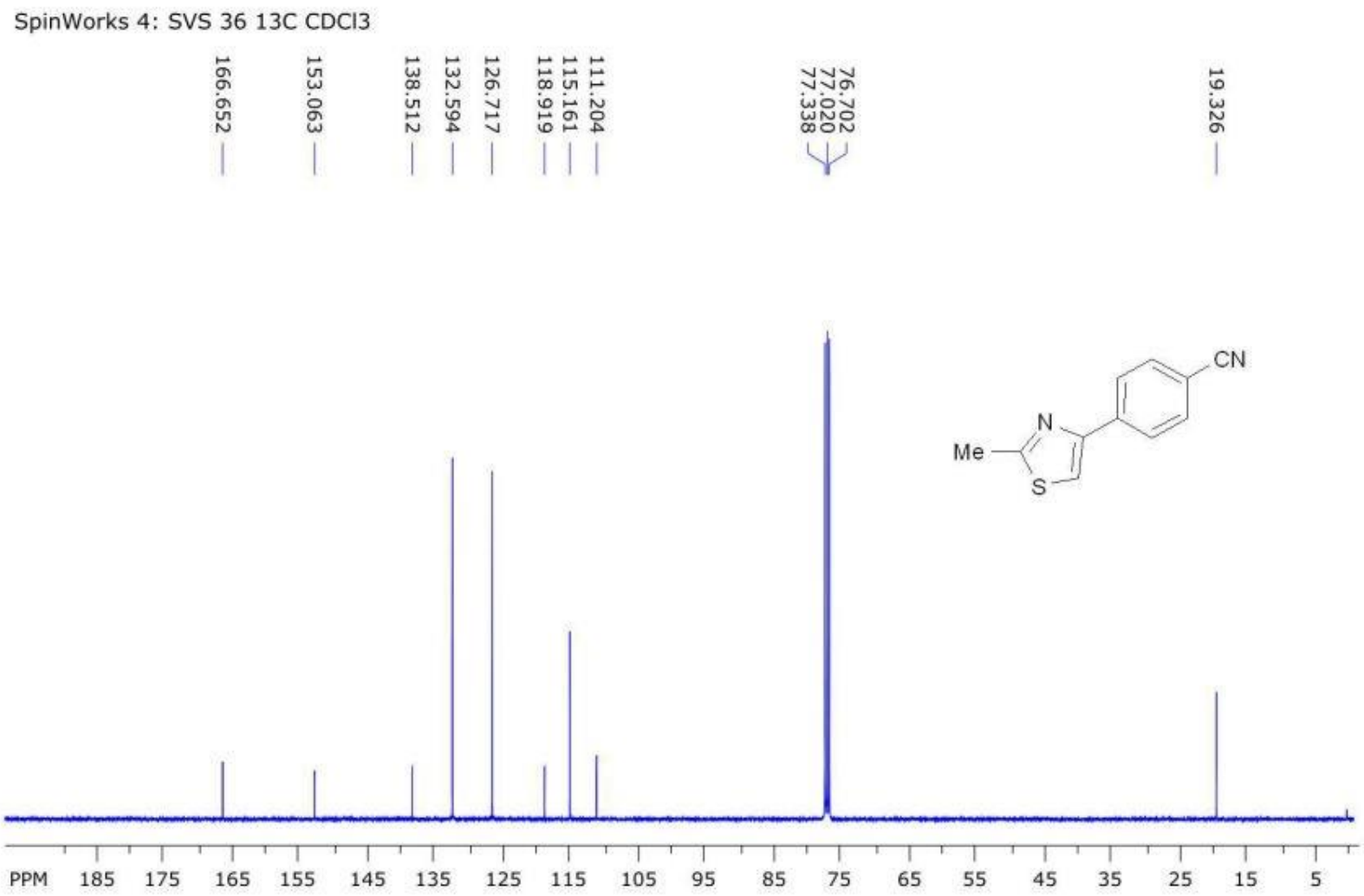
Compound **2h**



file: ...\NAPO\NMR\JELA\nmr\jn-SVS-36\1\fid expt: <zg30>
transmitter freq.: 400.132471 MHz
time domain size: 65536 points
width: 8196.72 Hz = 20.4850 ppm = 0.125072 Hz/pt
number of scans: 16

freq. of 0 ppm: 400.130012 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 270.927 ppm/cm: 0.67709

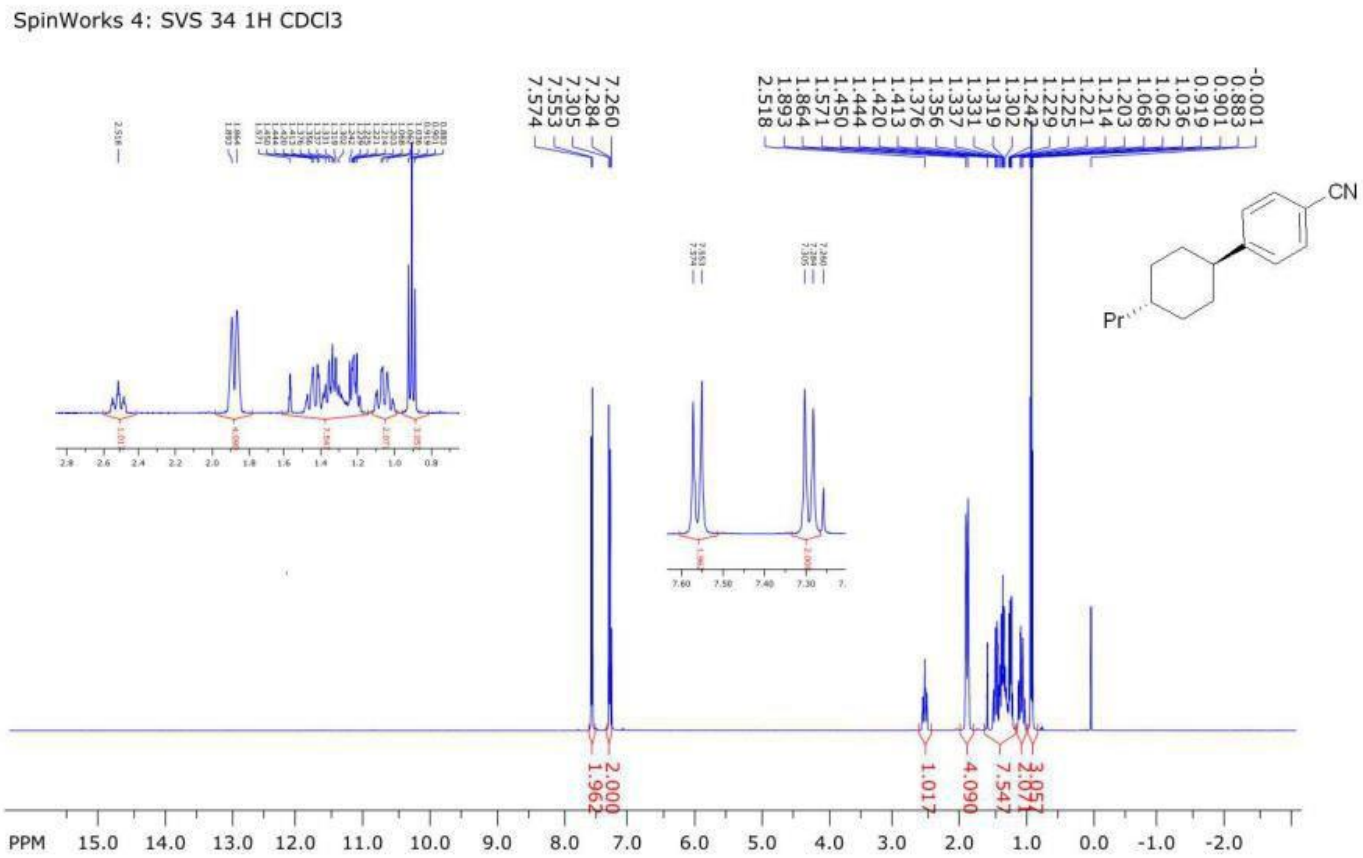
Compound **2h**



file: D:\NAPO\NMR\JELA\jn-SVS-36\2\fid expt: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 23809.52 Hz = 236.6215 ppm = 0.363305 Hz/pt
number of scans: 3700

freq. of 0 ppm: 100.612770 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 804.888 ppm/cm: 7.99906

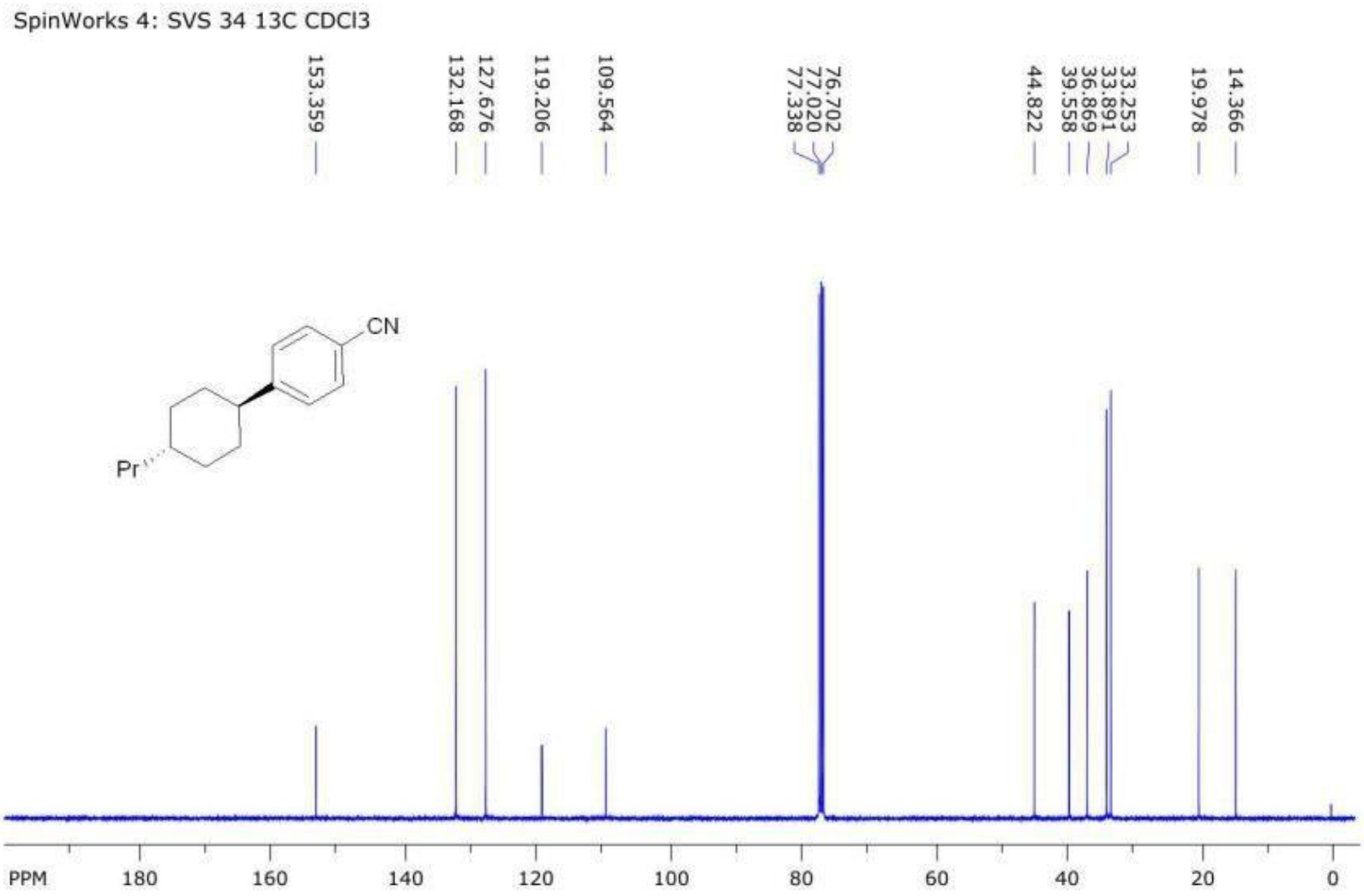
Compound **2i**



file: ...\NAPO\NMR\JELA\nmr\jn-SVS-34\1\fid expt: <zg30>
transmitter freq.: 400.132471 MHz
time domain size: 65536 points
width: 8196.72 Hz = 20.4850 ppm = 0.125072 Hz/pt
number of scans: 16

freq. of 0 ppm: 400.130009 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 313.361 ppm/cm: 0.78314

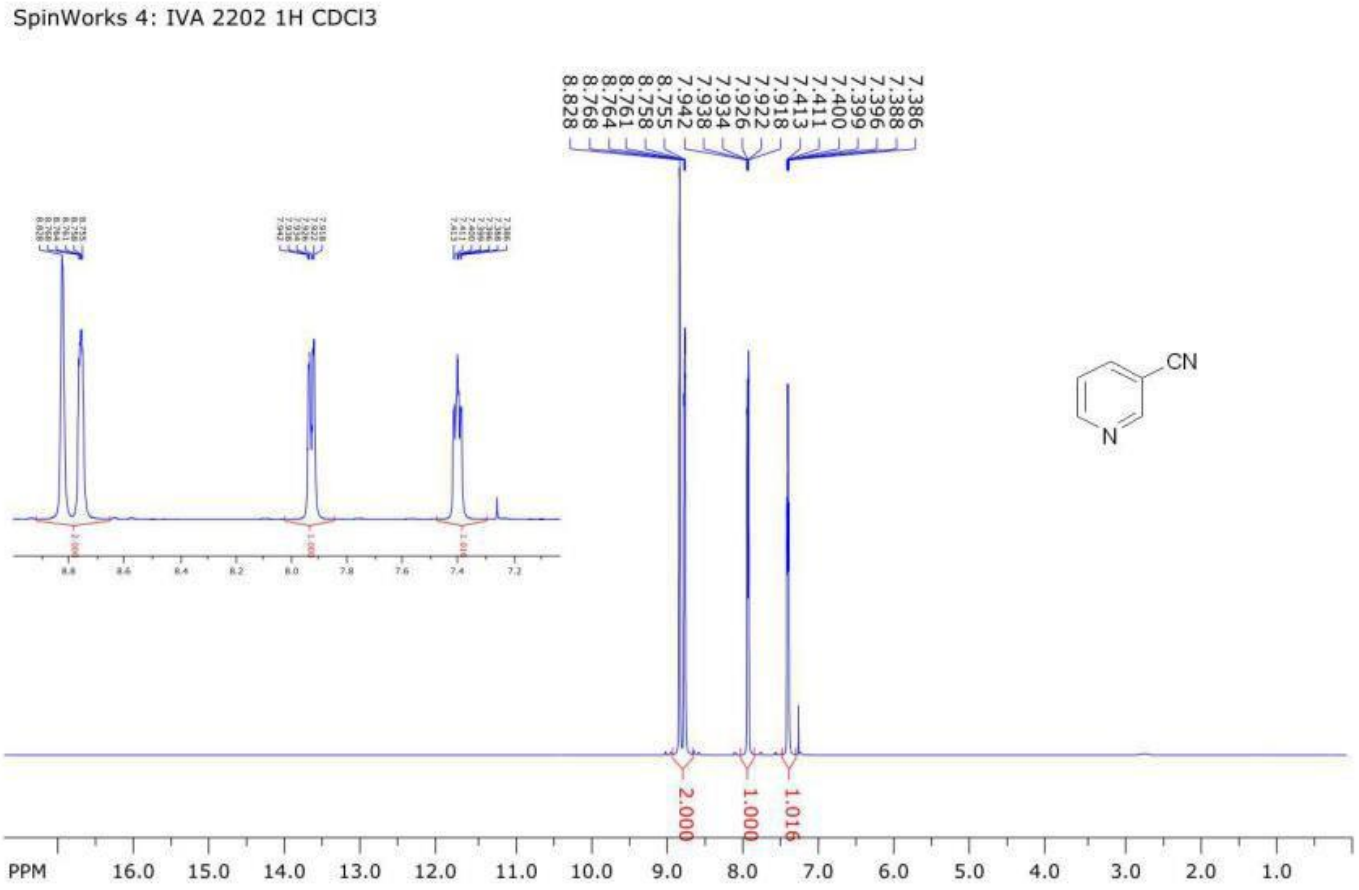
Compound **2i**



file: D:\NAPO\NMR\JELA\jn-SVS-34\2\fid expt: <zgpg30>
transmitter freq.: 100.622830 MHz
time domain size: 65536 points
width: 23809.52 Hz = 236.6215 ppm = 0.363305 Hz/pt
number of scans: 4000

freq. of 0 ppm: 100.612769 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000
Hz/cm: 821.184 ppm/cm: 8.16101

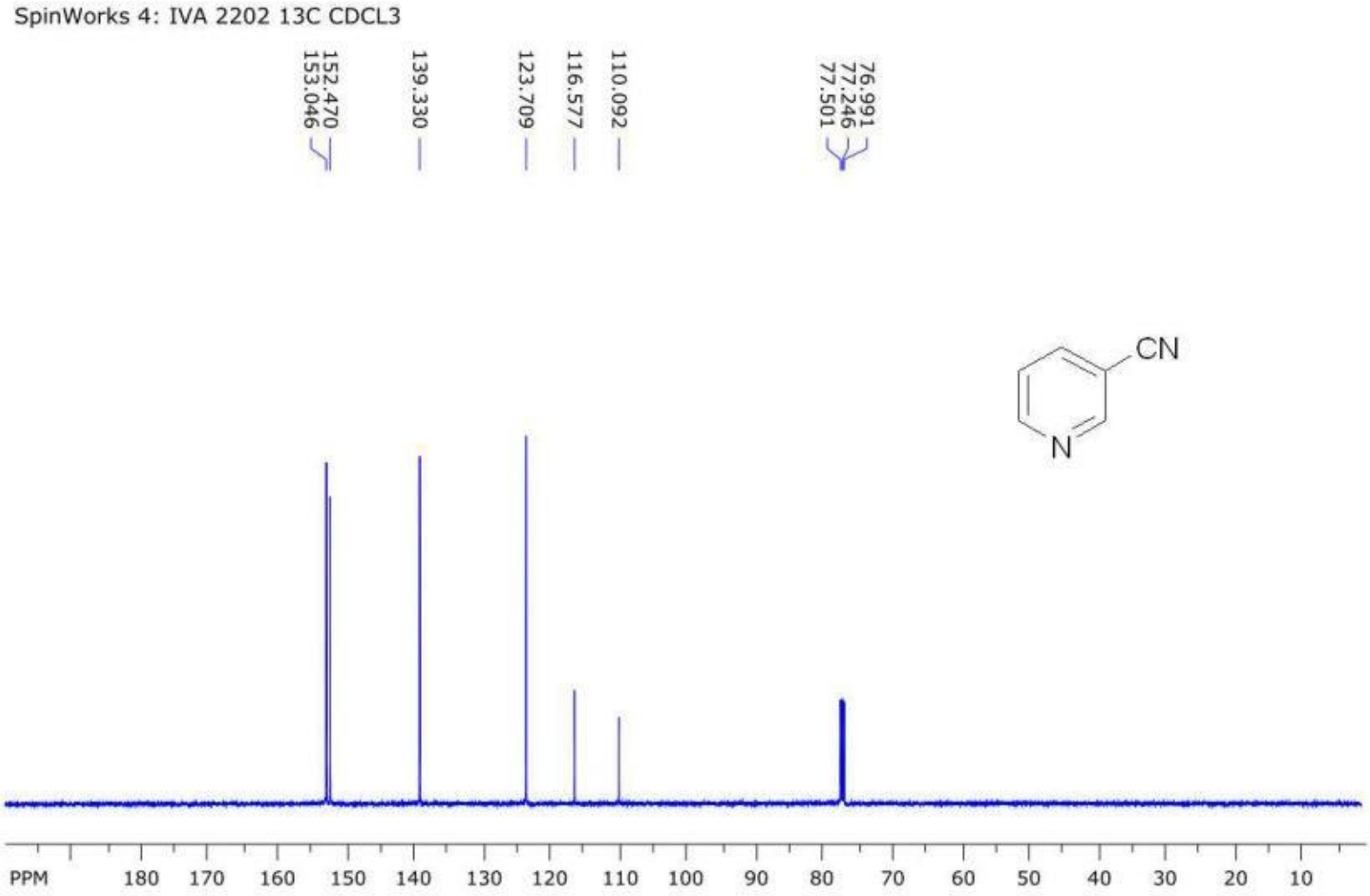
Compound **2j**



file: D:\NAPO\NMR\500-2\mkr11204\25\fid expt: <zg30>
transmitter freq.: 500.133001 MHz
time domain size: 65536 points
width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt
number of scans: 24

freq. of 0 ppm: 500.130025 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 354.237 ppm/cm: 0.70829

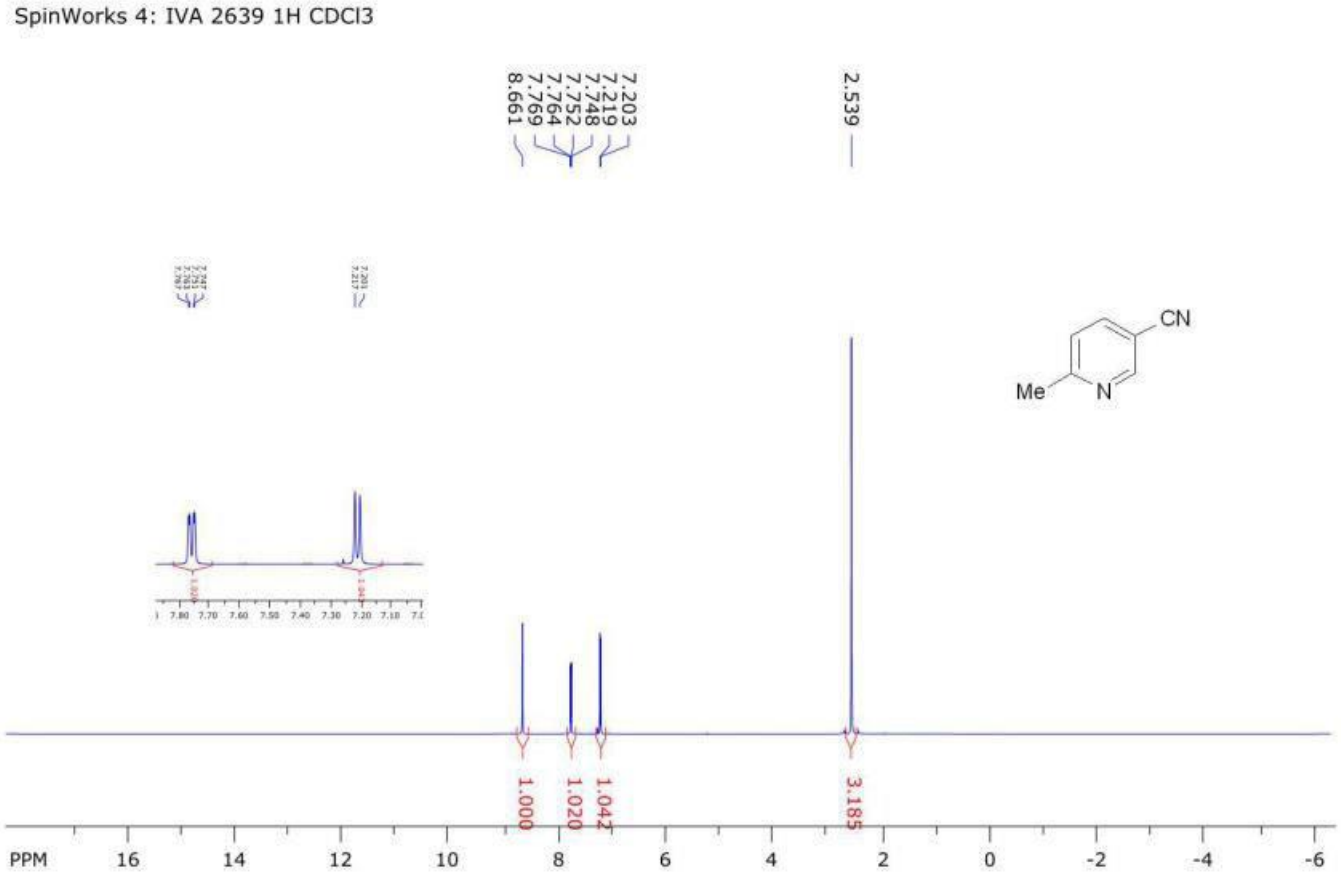
Compound **2j**



file: D:\NAPO\NMR\500-2\mkr11204\26\fid expt: <zgpg30>
transmitter freq.: 125.772879 MHz
time domain size: 65536 points
width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt
number of scans: 512

freq. of 0 ppm: 125.757789 MHz
processed size: 32768 complex points
LB: 2.000 GF: 0.0000
Hz/cm: 1001.957 ppm/cm: 7.96640

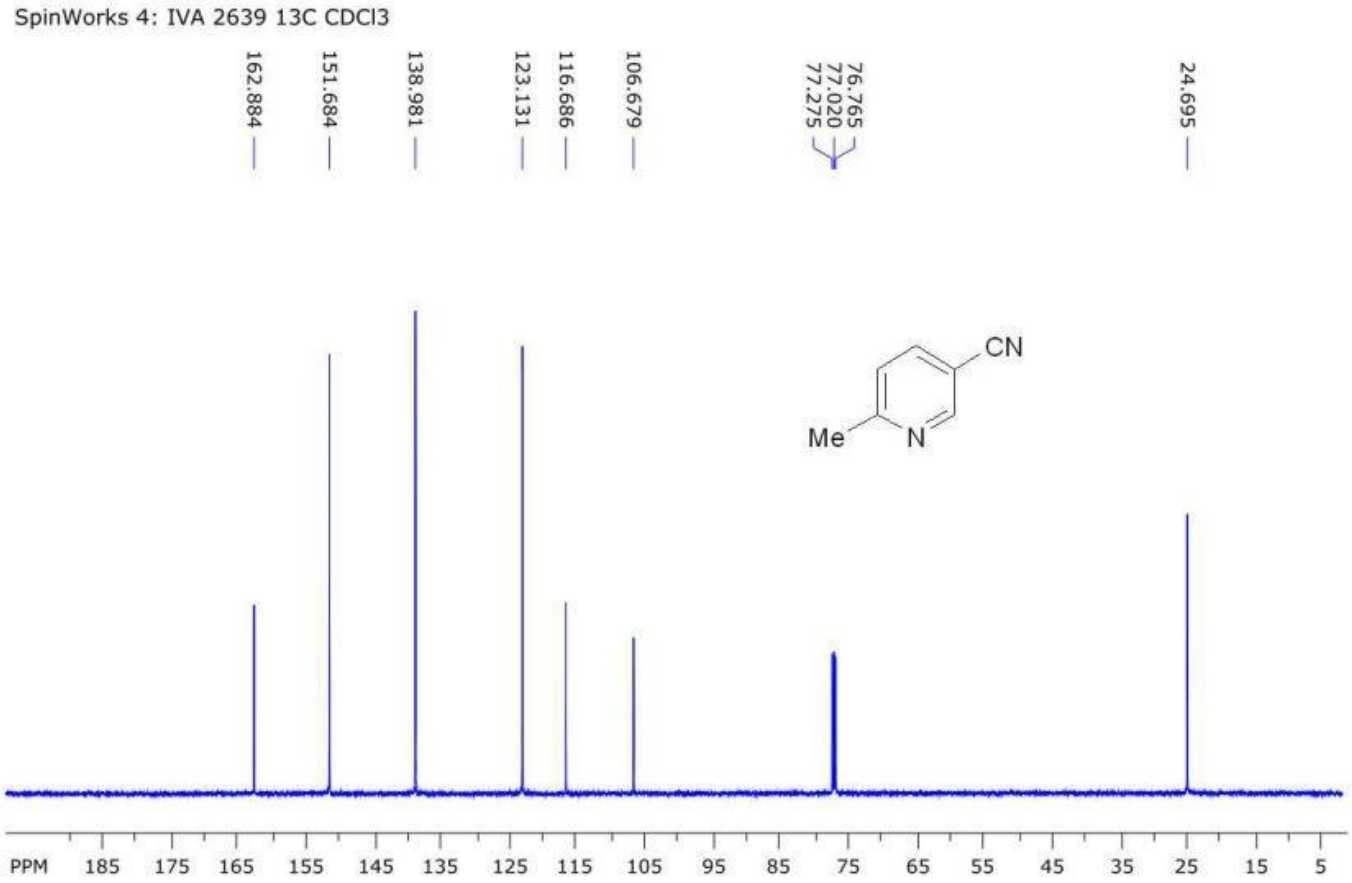
Compound **2k**



file: ...APO\NMR\500-2\mkr13105\11 2639\fid expt: <zg30>
transmitter freq.: 500.133001 MHz
time domain size: 65536 points
width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt
number of scans: 24

freq. of 0 ppm: 500.130024 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 493.421 ppm/cm: 0.98658

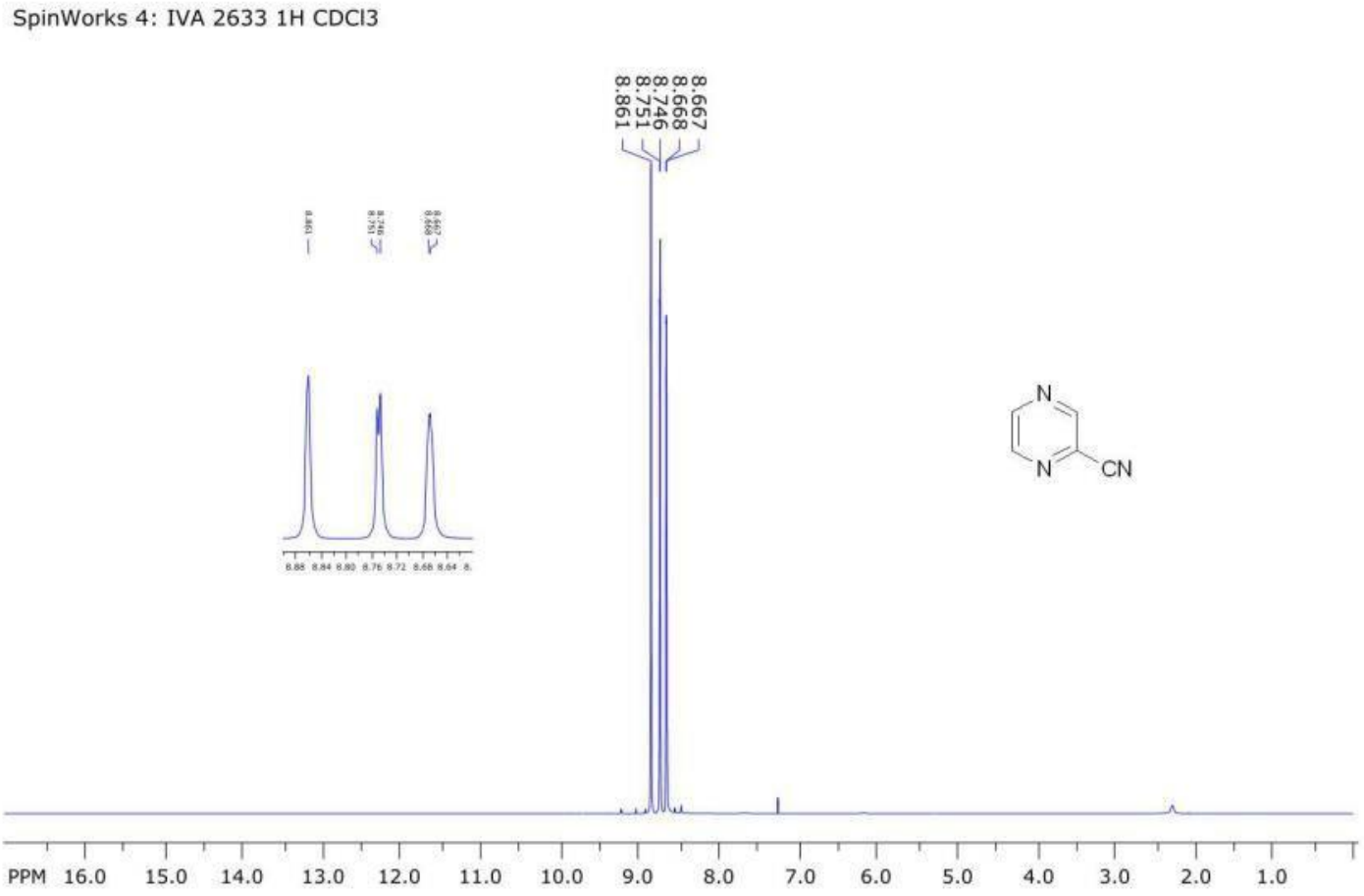
Compound **2k**



file: D:\NAPO\NMR\500-2\mkr13105\12\fid expt: <zgpg30>
transmitter freq.: 125.772879 MHz
time domain size: 65536 points
width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt
number of scans: 512

freq. of 0 ppm: 125.757818 MHz
processed size: 32768 complex points
LB: 2.000 GF: 0.0000
Hz/cm: 995.575 ppm/cm: 7.91566

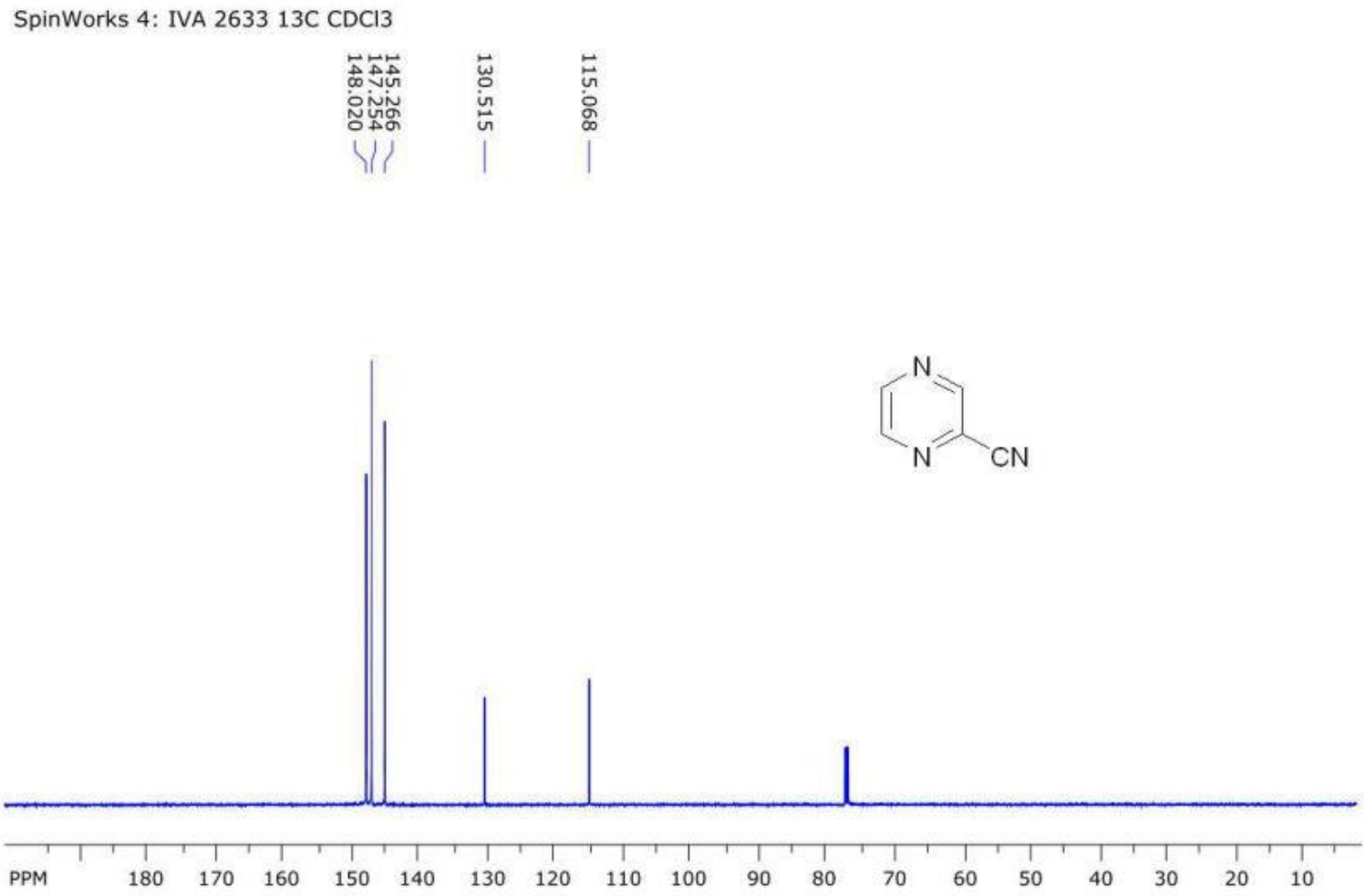
Compound **2l**



file: ...APO\NMR\500-2\mkr13105\27 2633\fid expt: <zg30>
transmitter freq.: 500.133001 MHz
time domain size: 65536 points
width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt
number of scans: 24

freq. of 0 ppm: 500.130025 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 341.683 ppm/cm: 0.68318

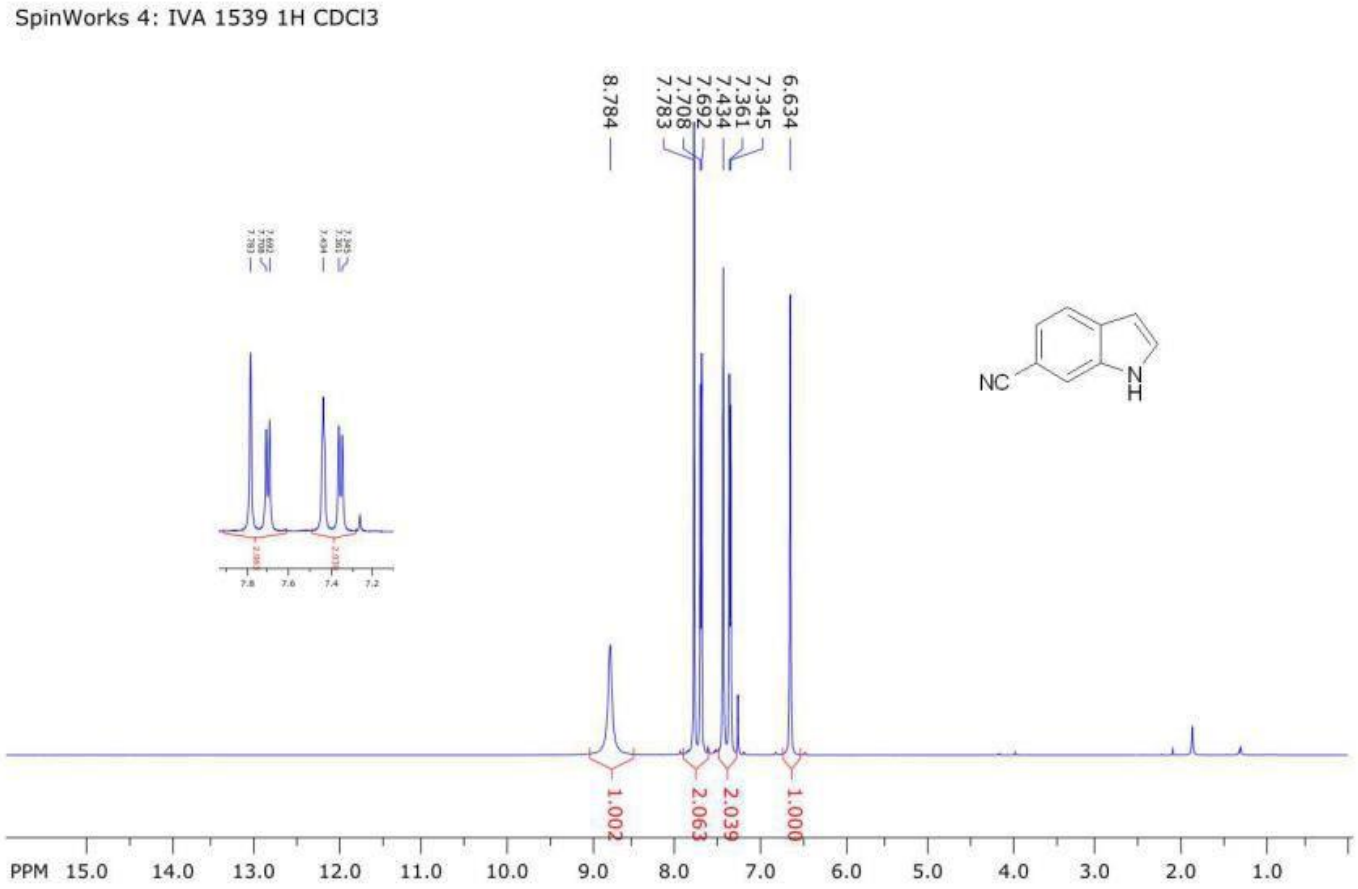
Compound **2l**



file: D:\NAPO\NMR\500-2\mkr13105\28\fid expt: <zgpg30>
transmitter freq.: 125.772879 MHz
time domain size: 65536 points
width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt
number of scans: 512

freq. of 0 ppm: 125.757830 MHz
processed size: 32768 complex points
LB: 2.000 GF: 0.0000
Hz/cm: 1005.148 ppm/cm: 7.99177

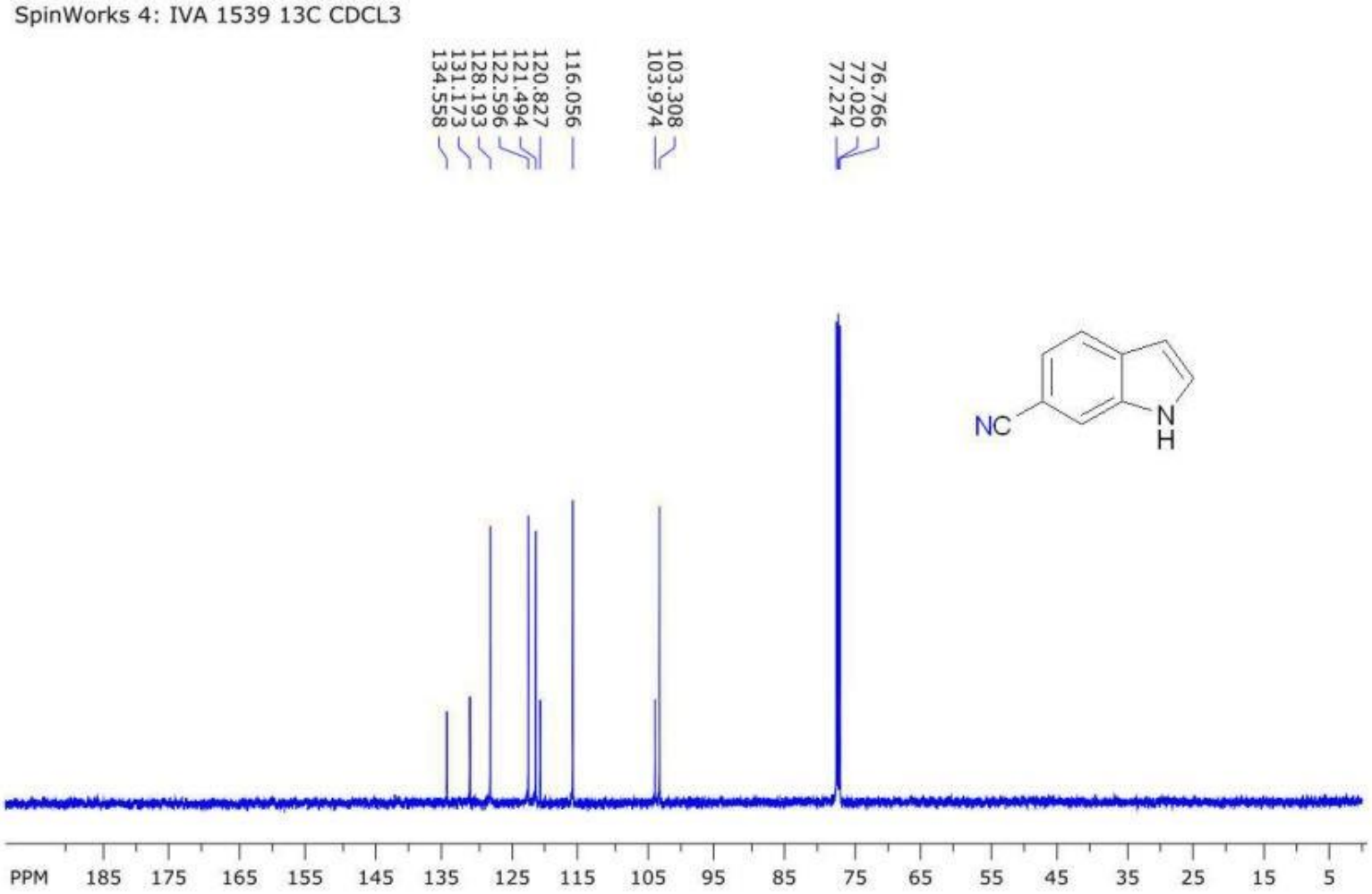
Compound **2m**



file: D:\NAPO\NMR\500-2\mkr100201\11\fid expt: <zg30>
transmitter freq.: 500.133001 MHz
time domain size: 65536 points
width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt
number of scans: 24

freq. of 0 ppm: 500.130023 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 320.396 ppm/cm: 0.64062

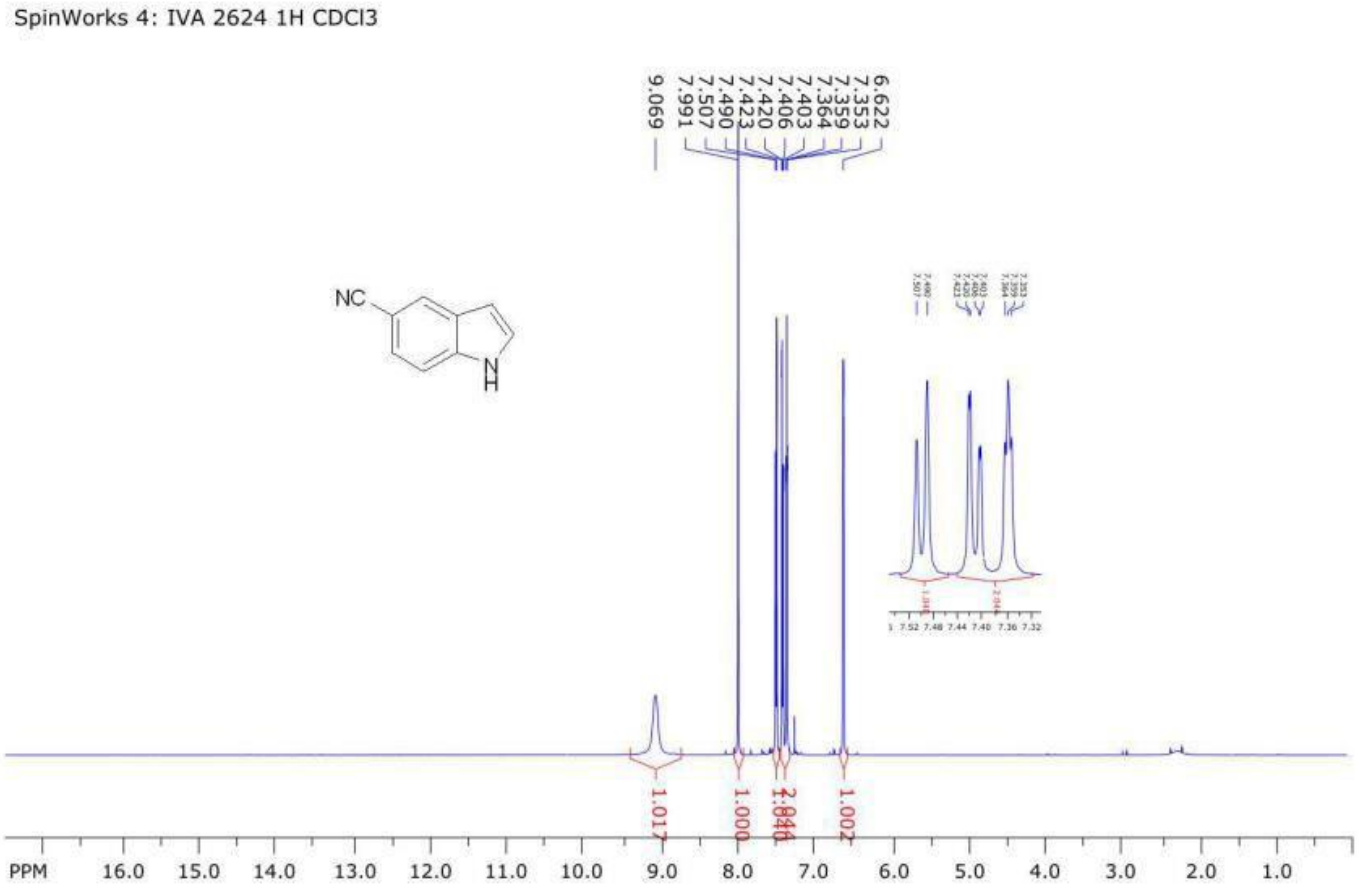
Compound **2m**



file: D:\NAPO\NMR\500-2\mkr100201\12\fid expt: <zgpg30>
transmitter freq.: 125.772879 MHz
time domain size: 65536 points
width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt
number of scans: 512

freq. of 0 ppm: 125.757800 MHz
processed size: 32768 complex points
LB: 2.000 GF: 0.0000
Hz/cm: 1003.553 ppm/cm: 7.97909

Compound **2n**

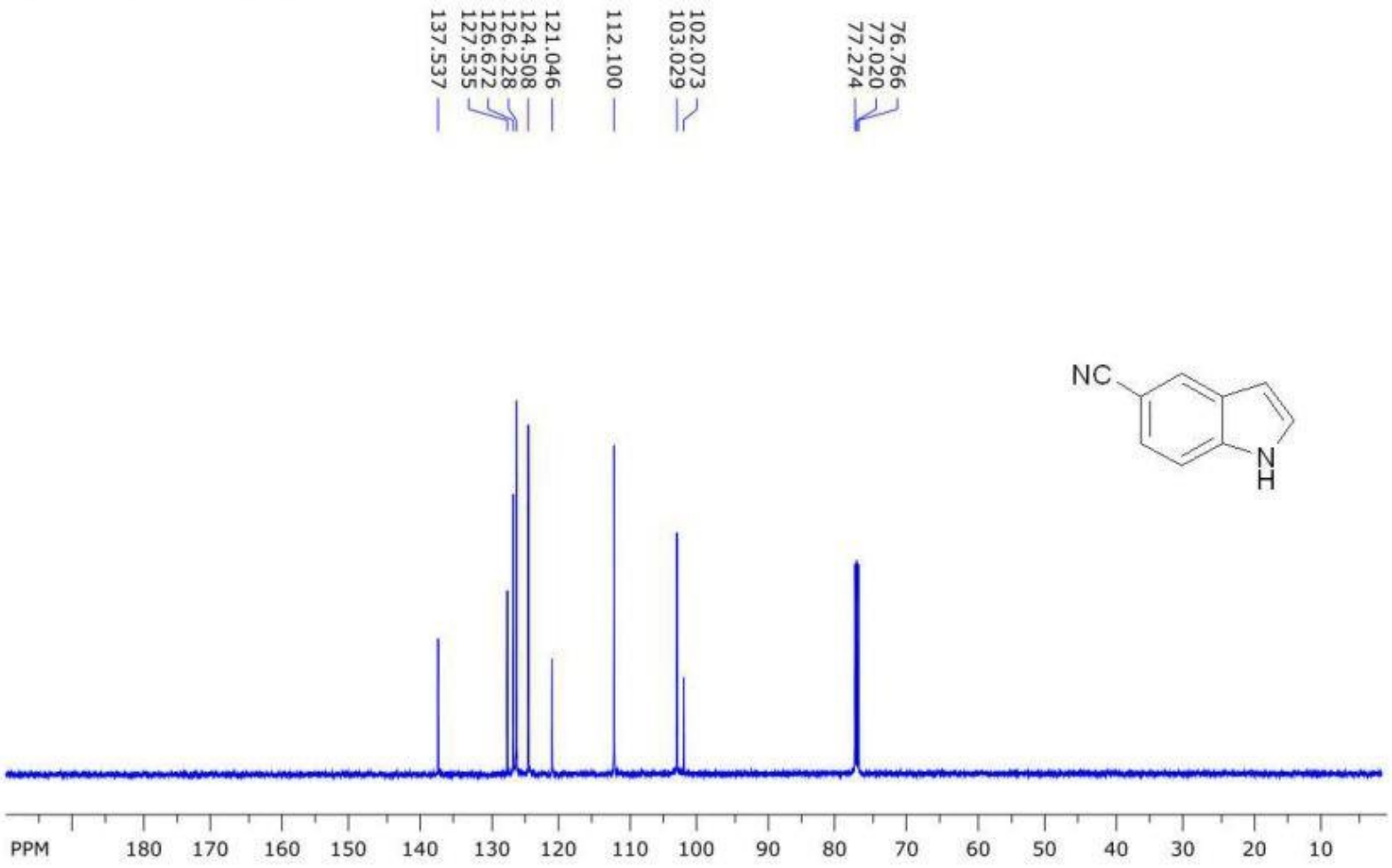


file: ...NMR\500-2\mkr12905\29 iva 2624\fid expt: <zg30>
transmitter freq.: 500.133001 MHz
time domain size: 65536 points
width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt
number of scans: 24

freq. of 0 ppm: 500.130024 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 349.870 ppm/cm: 0.69955

Compound **2n**

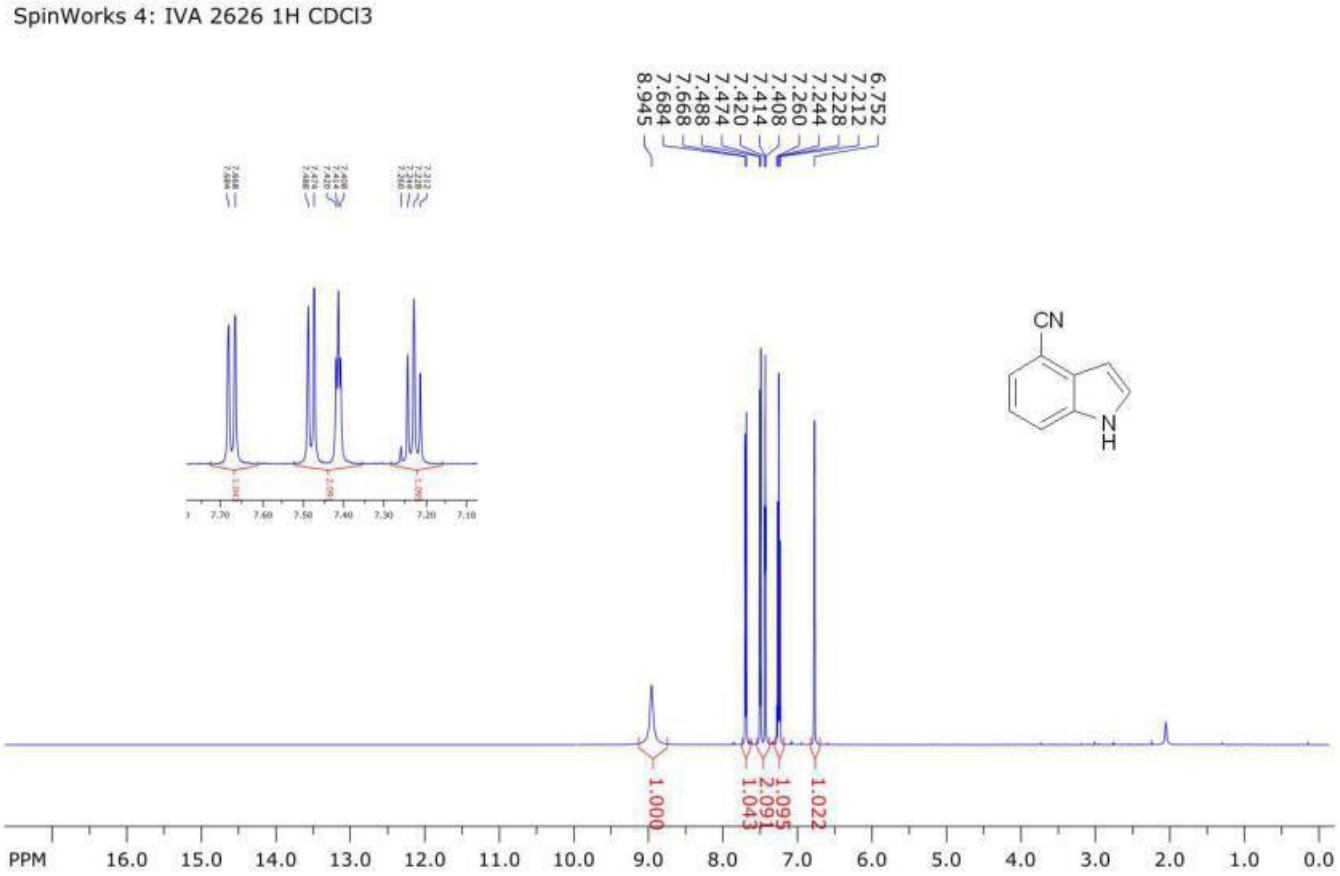
SpinWorks 4: IVA 2624 13C CDCl3



file: D:\NAPO\NMR\500-2\mkr12905\30\fid expt: <zgpg30>
transmitter freq.: 125.772879 MHz
time domain size: 65536 points
width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt
number of scans: 512

freq. of 0 ppm: 125.757813 MHz
processed size: 32768 complex points
LB: 2.000 GF: 0.0000
Hz/cm: 1000.362 ppm/cm: 7.95372

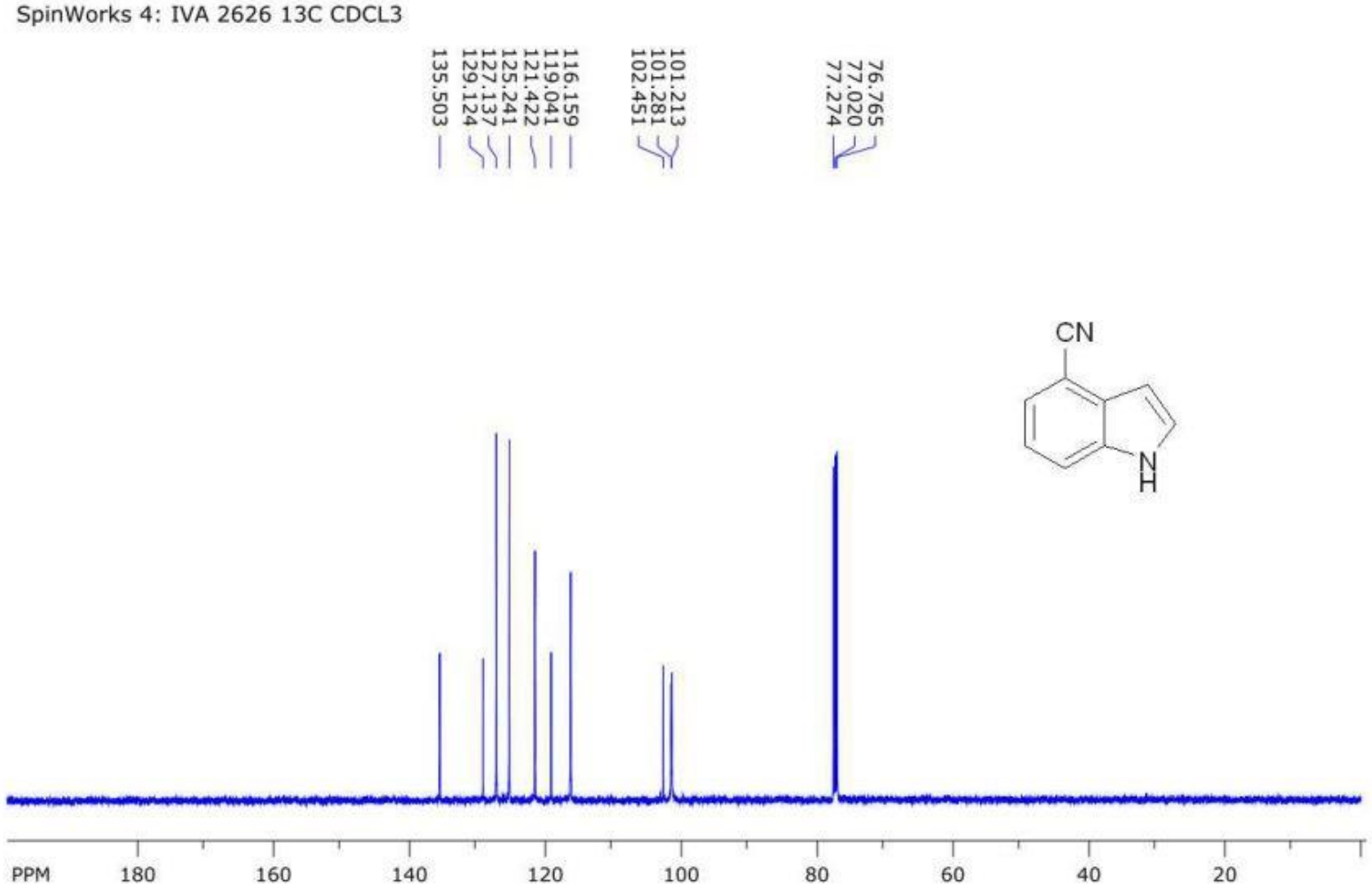
Compound **2o**



file: ...APO\NMR\500-2\mkr10706\11 2626\fid expt: <zg30>
transmitter freq.: 500.133001 MHz
time domain size: 65536 points
width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt
number of scans: 24

freq. of 0 ppm: 500.130023 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 356.966 ppm/cm: 0.71374

Compound **2o**

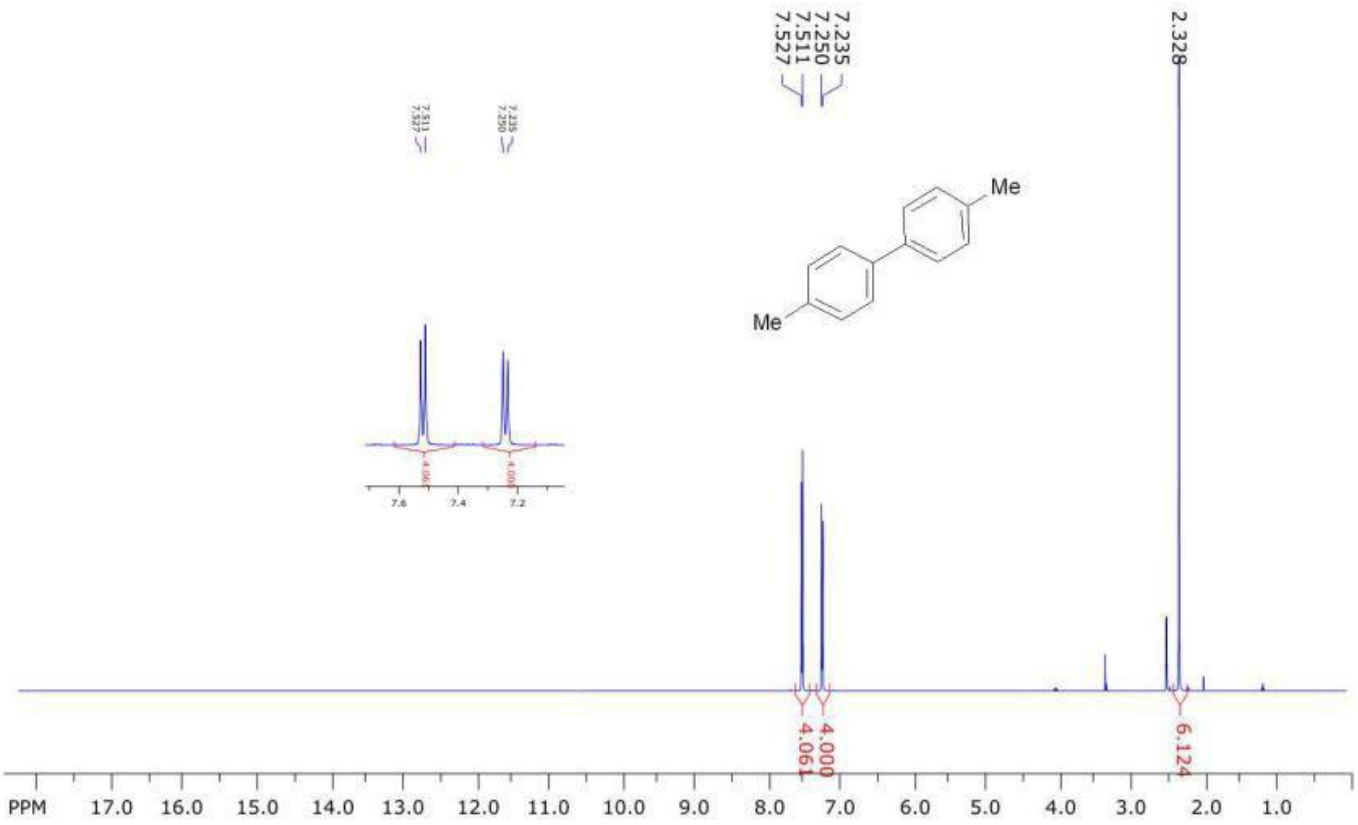


file: D:\NAPO\NMR\500-2\mkr10706\12\fid expt: <zgpg30>
transmitter freq.: 125.772879 MHz
time domain size: 65536 points
width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt
number of scans: 512

freq. of 0 ppm: 125.757806 MHz
processed size: 32768 complex points
LB: 2.000 GF: 0.0000
Hz/cm: 1006.744 ppm/cm: 8.00446

Compound **4a**

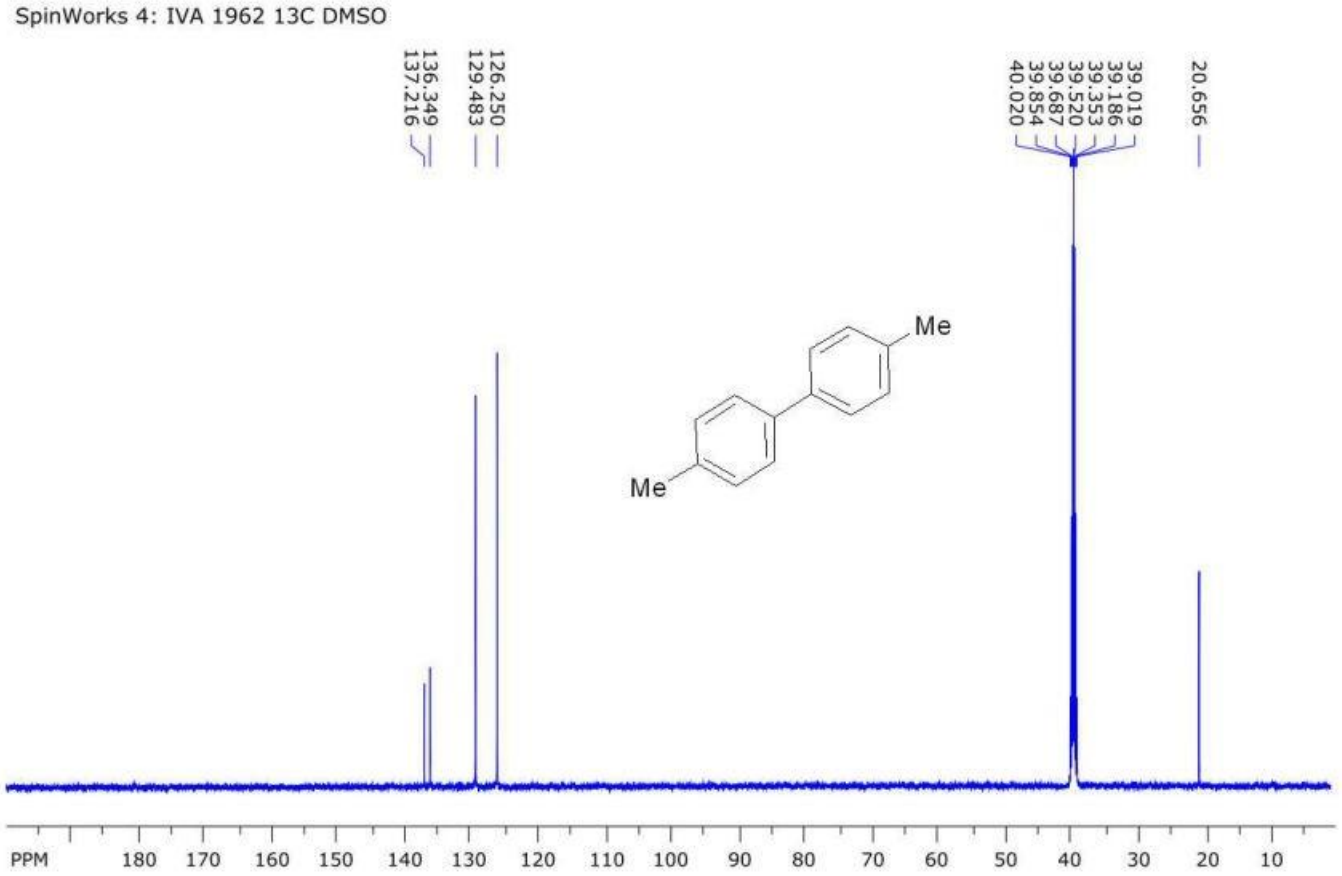
SpinWorks 4: IVA 1962 1H DMSO



file: D:\NAPO\NMR\500-2\mkr10103\15\fid expt: <zg30>
transmitter freq.: 500.133001 MHz
time domain size: 65536 points
width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt
number of scans: 24

freq. of 0 ppm: 500.130005 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 370.066 ppm/cm: 0.73993

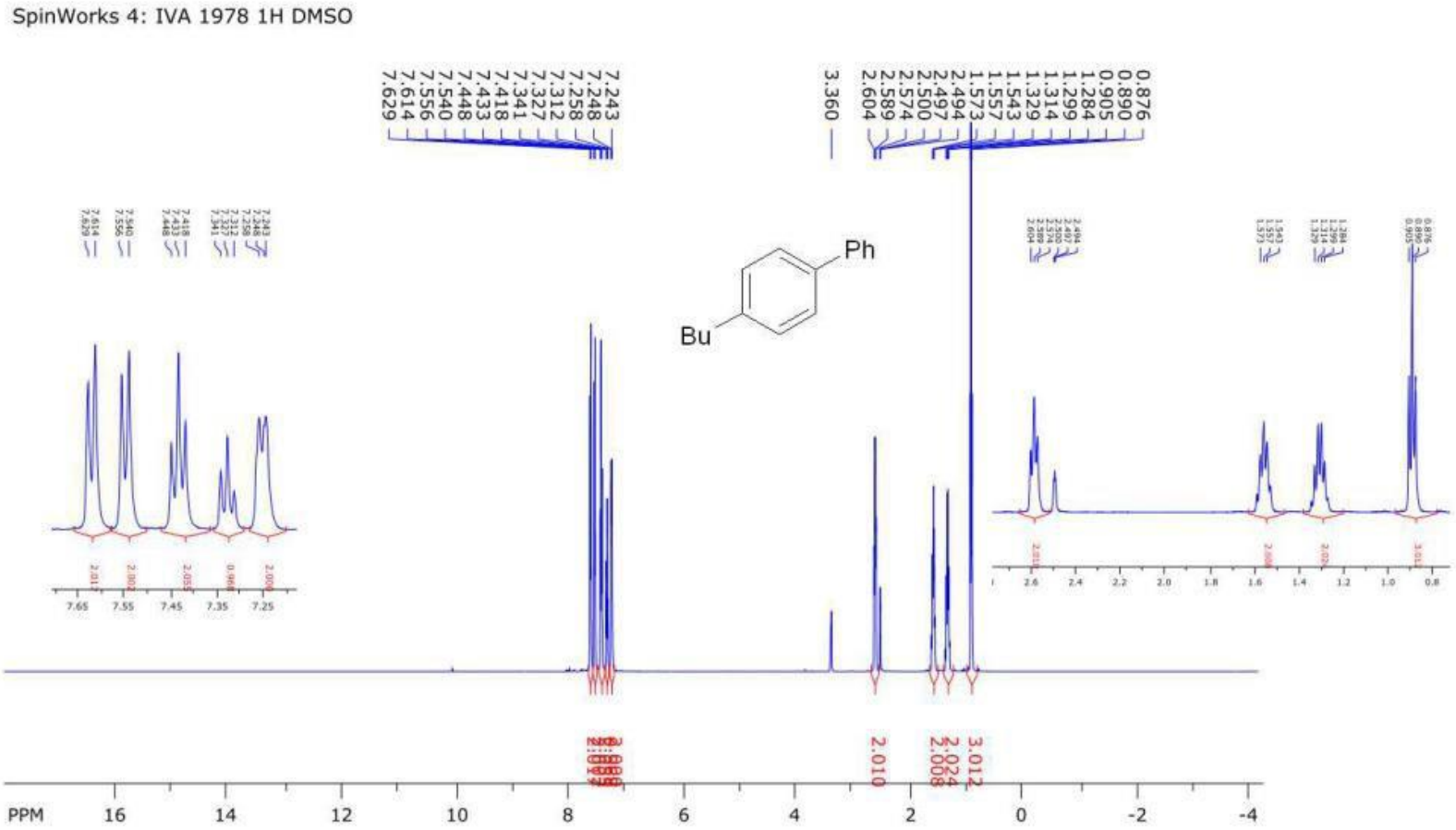
Compound **4a**



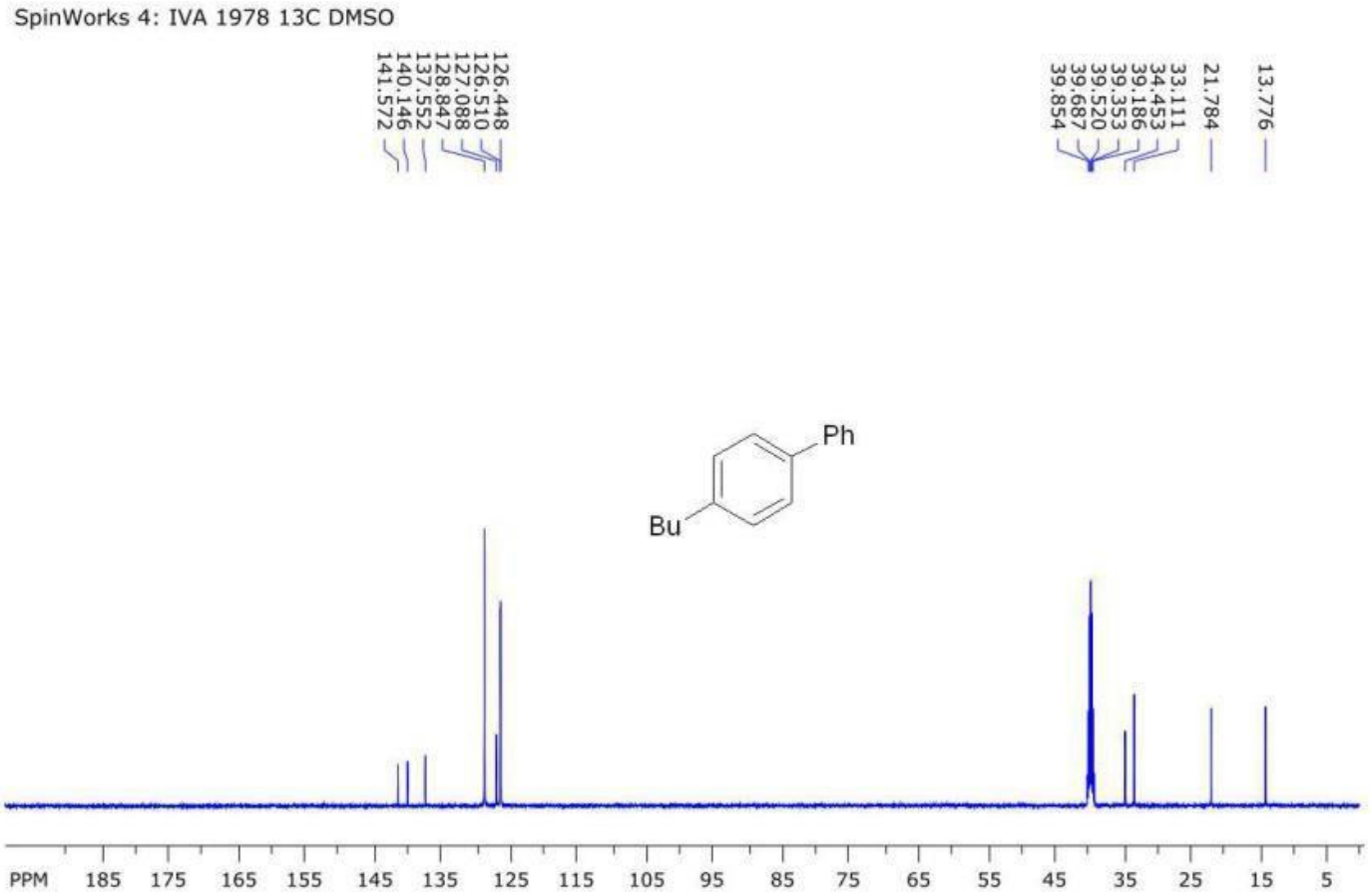
file: D:\NAPO\NMR\500-2\mkr10103\16\fid expt: <zgpg30>
transmitter freq.: 125.772879 MHz
time domain size: 65536 points
width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt
number of scans: 512

freq. of 0 ppm: 125.757845 MHz
processed size: 32768 complex points
LB: 2.000 GF: 0.0000
Hz/cm: 1001.957 ppm/cm: 7.96640

Compound **4b**


SpinWorks 4: IVA 1978 1H DMSO
Ph
Bu
PPM
file: ...NAPO\NMR\500-2\mkr12406\9 1978\fid expt: <zg30>
transmitter freq.: 500.133001 MHz
time domain size: 65536 points
width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt
number of scans: 24
freq. of 0 ppm: 500.130006 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 443.751 ppm/cm: 0.88727

Compound **4b**

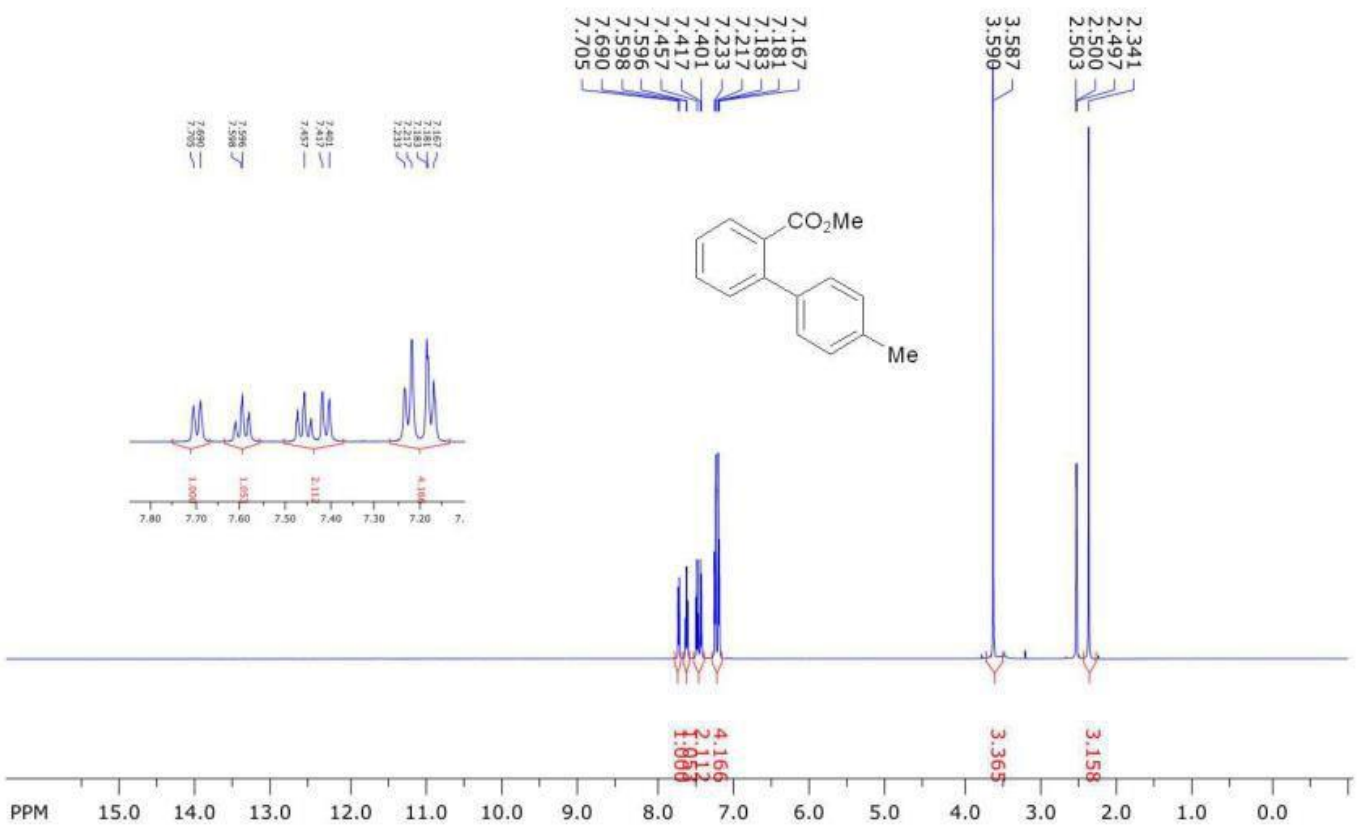


file: D:\NAPO\NMR\500-2\mkr12406\10\fid expt: <zgpg30>
transmitter freq.: 125.772879 MHz
time domain size: 65536 points
width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt
number of scans: 512

freq. of 0 ppm: 125.757846 MHz
processed size: 32768 complex points
LB: 2.000 GF: 0.0000
Hz/cm: 1003.553 ppm/cm: 7.97909

Compound **4c**

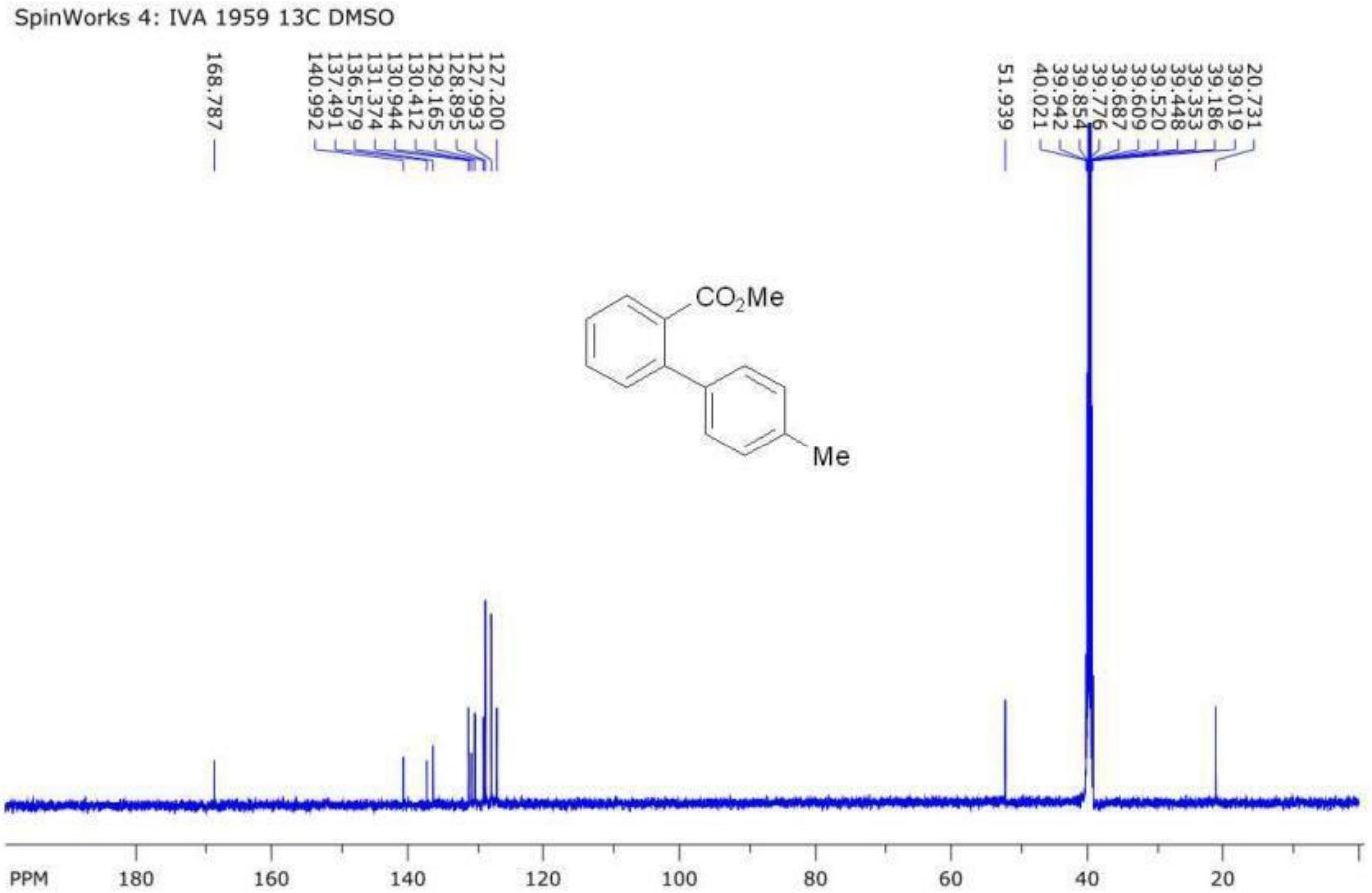
SpinWorks 4: IVA 1959 1H DMSO



file: D:\NAPO\NMR\500-2\mkr11903\17\fid expt: <zg30>
transmitter freq.: 500.133001 MHz
time domain size: 65536 points
width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt
number of scans: 24

freq. of 0 ppm: 500.130005 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 350.962 ppm/cm: 0.70174

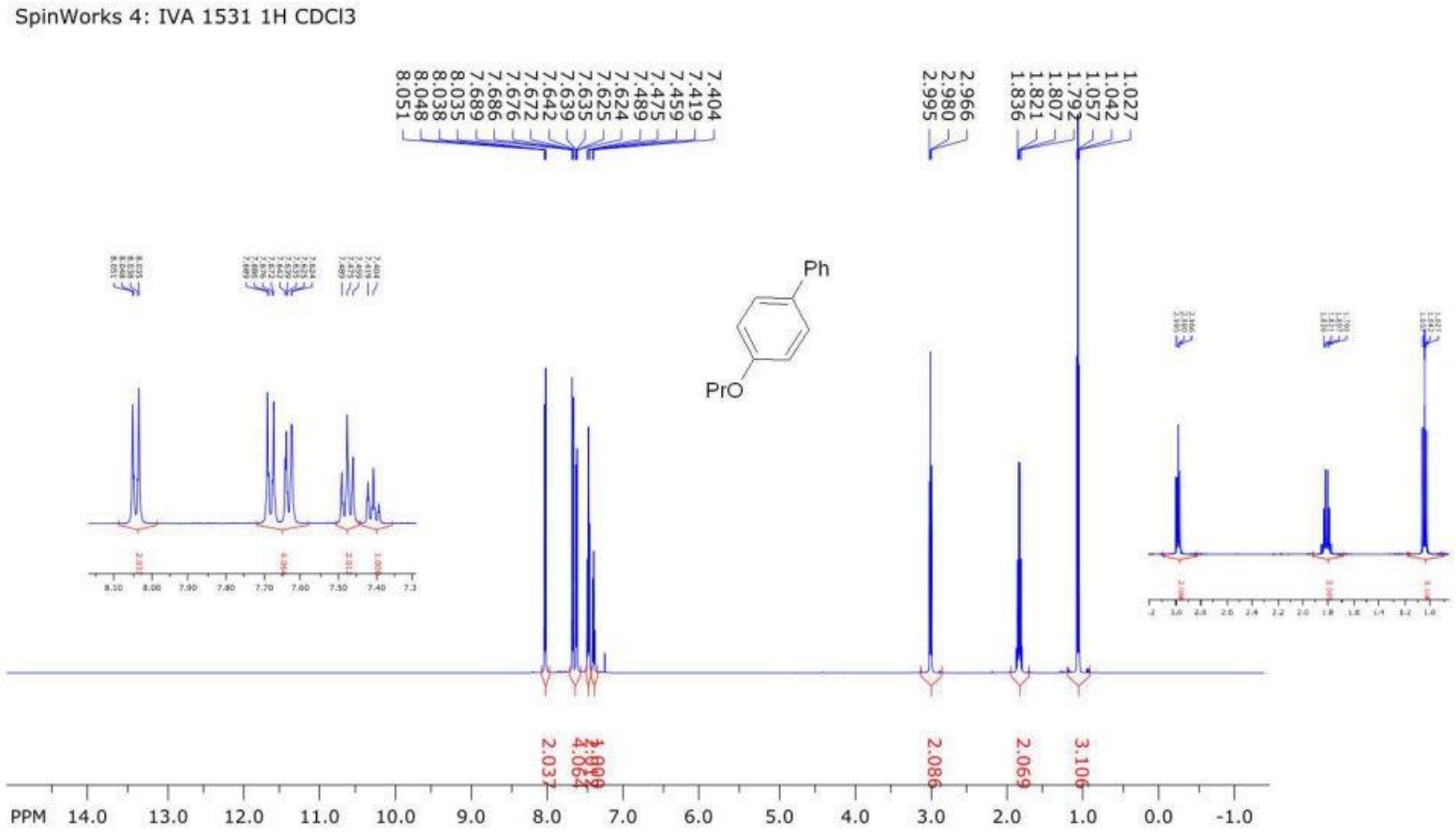
Compound **4c**



file: D:\NAPO\NMR\500-2\mkr11903\18\fid expt: <zgpg30>
transmitter freq.: 125.772879 MHz
time domain size: 65536 points
width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt
number of scans: 512

freq. of 0 ppm: 125.757844 MHz
processed size: 32768 complex points
LB: 2.000 GF: 0.0000
Hz/cm: 1006.744 ppm/cm: 8.00446

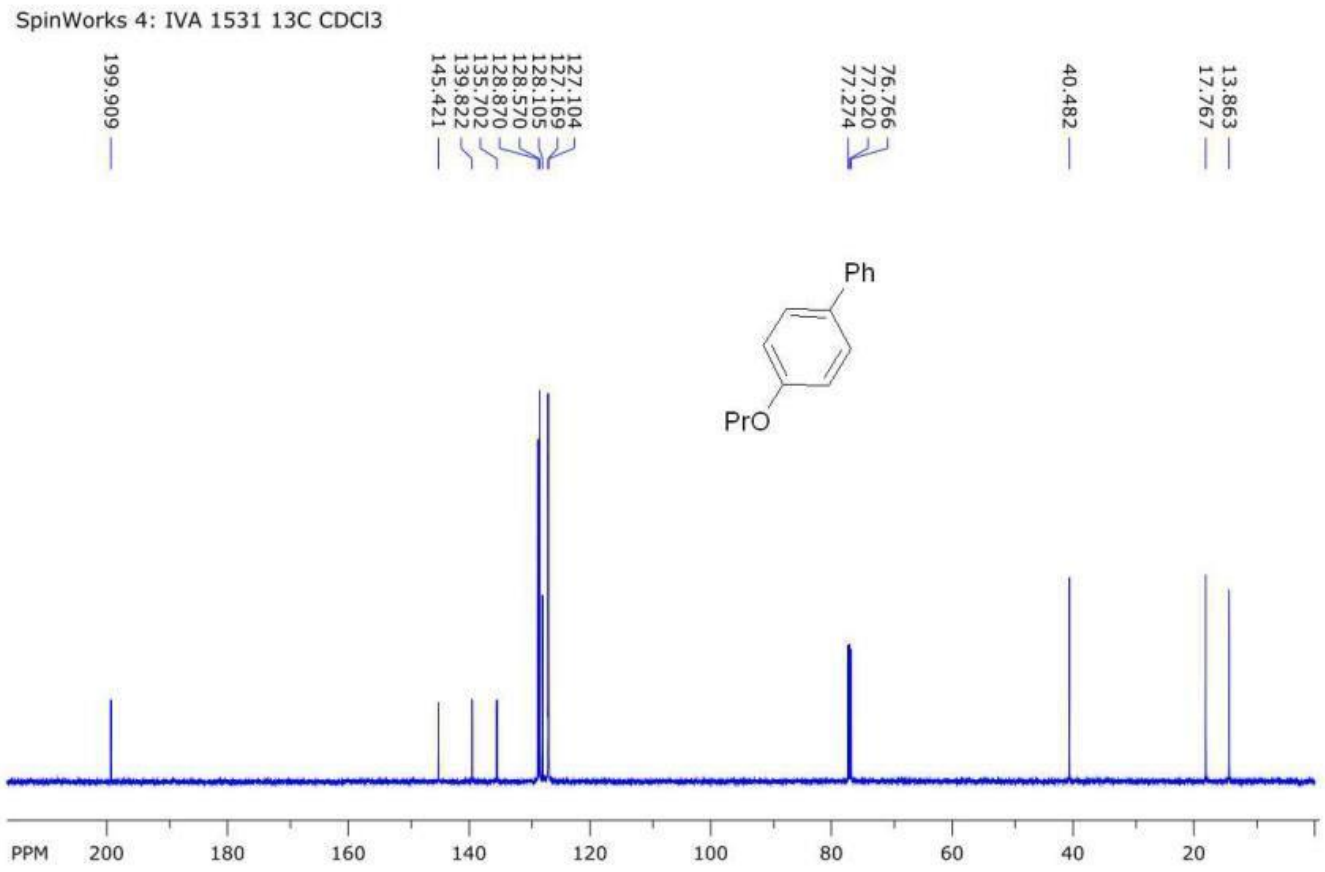
Compound **4d**



file: D:\NAPO\NMR\500-2\mkr21801\29\fid expt: <zg30>
transmitter freq.: 500.133001 MHz
time domain size: 65536 points
width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt
number of scans: 24

freq. of 0 ppm: 500.130023 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 330.767 ppm/cm: 0.66136

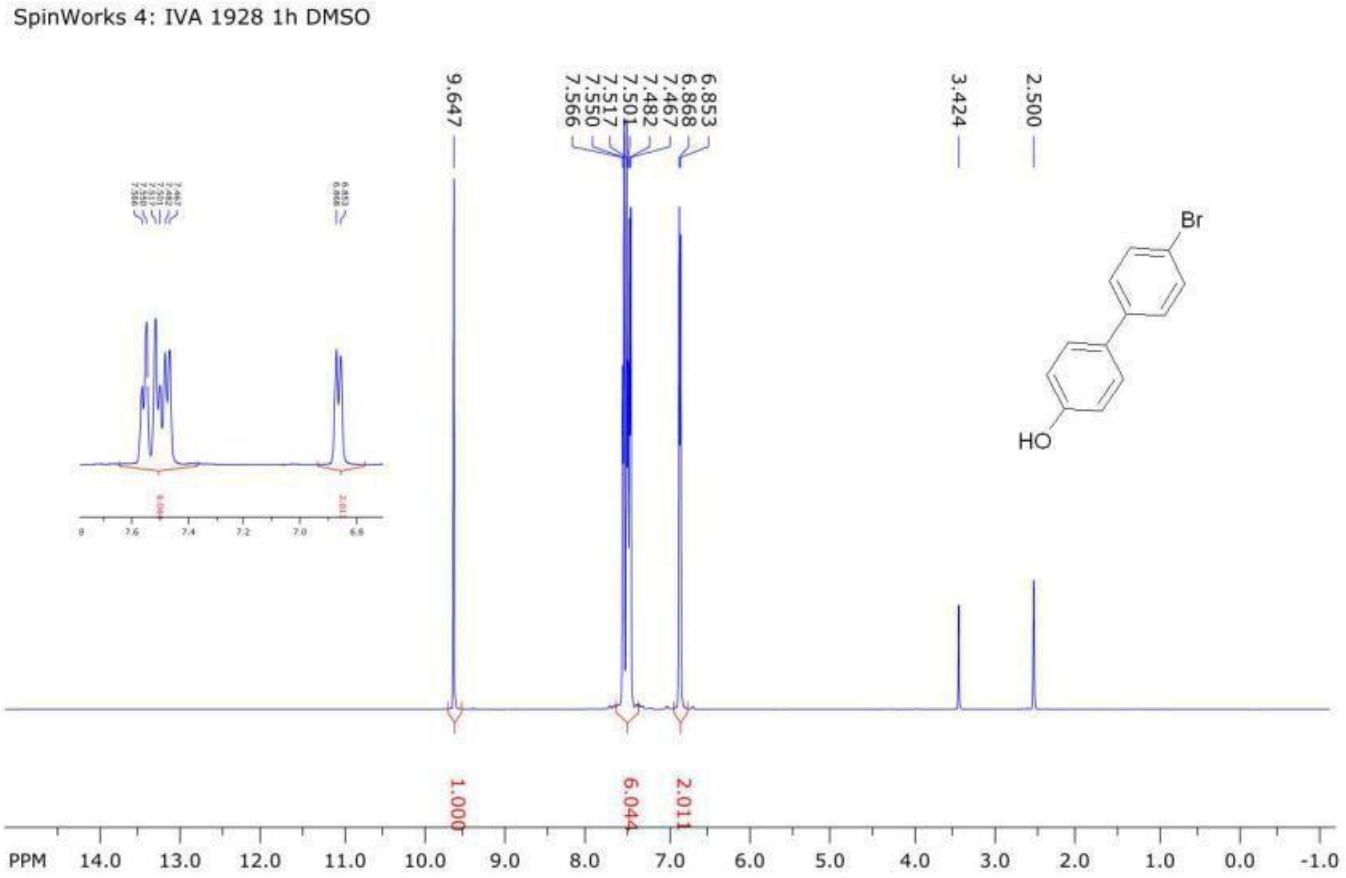
Compound **4d**



file: D:\NAPO\NMR\500-2\mkr21801\30\fid expt: <zgpg30>
transmitter freq.: 125.772879 MHz
time domain size: 65536 points
width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt
number of scans: 256

freq. of 0 ppm: 125.757804 MHz
processed size: 32768 complex points
LB: 2.000 GF: 0.0000
Hz/cm: 1094.495 ppm/cm: 8.70215

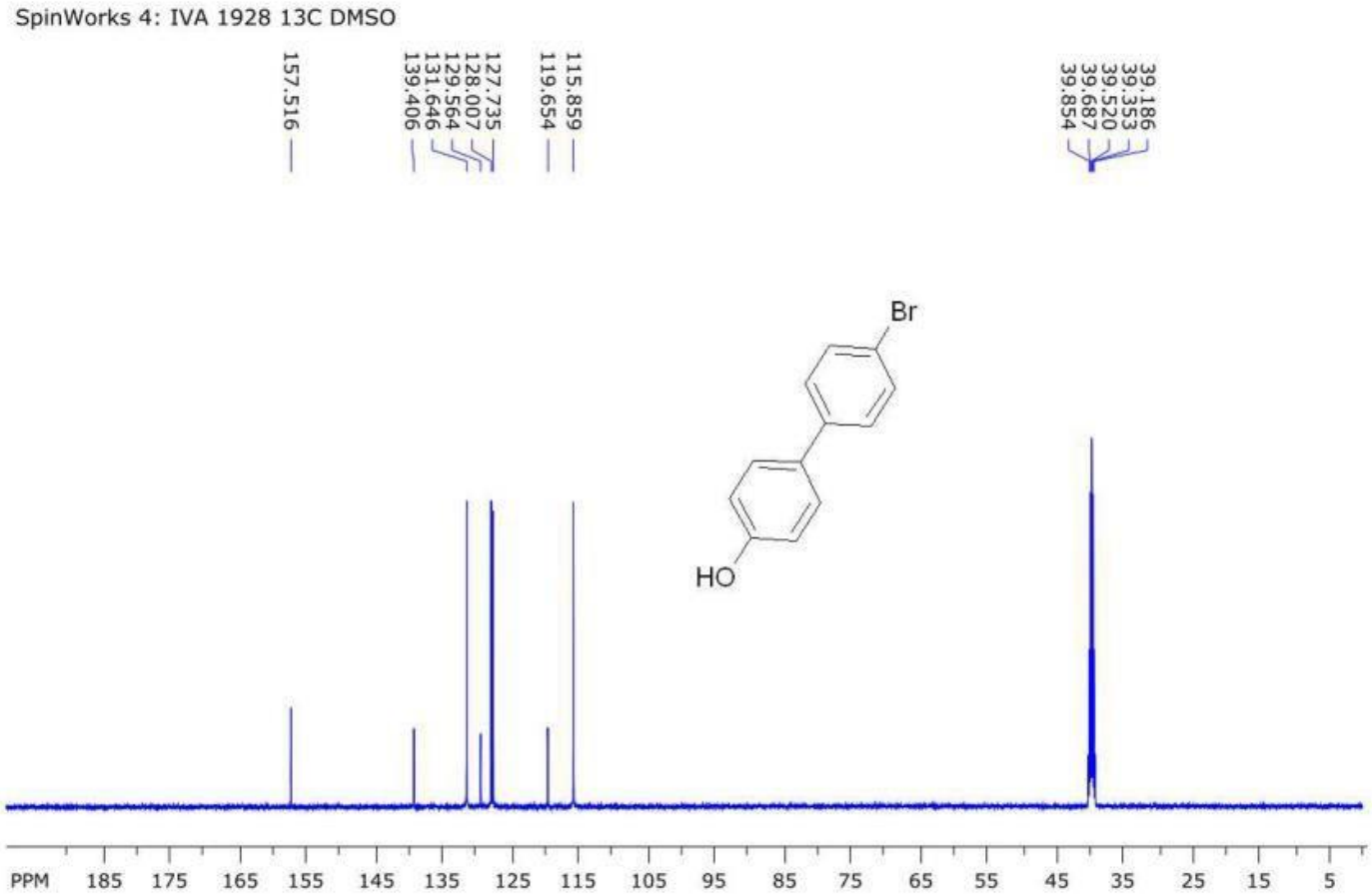
Compound **4e**



file: D:\NAPO\NMR\500-2\mkr11305\11\fid expt: <zg30>
transmitter freq.: 500.133001 MHz
time domain size: 65536 points
width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt
number of scans: 24

freq. of 0 ppm: 500.130004 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 326.946 ppm/cm: 0.65372

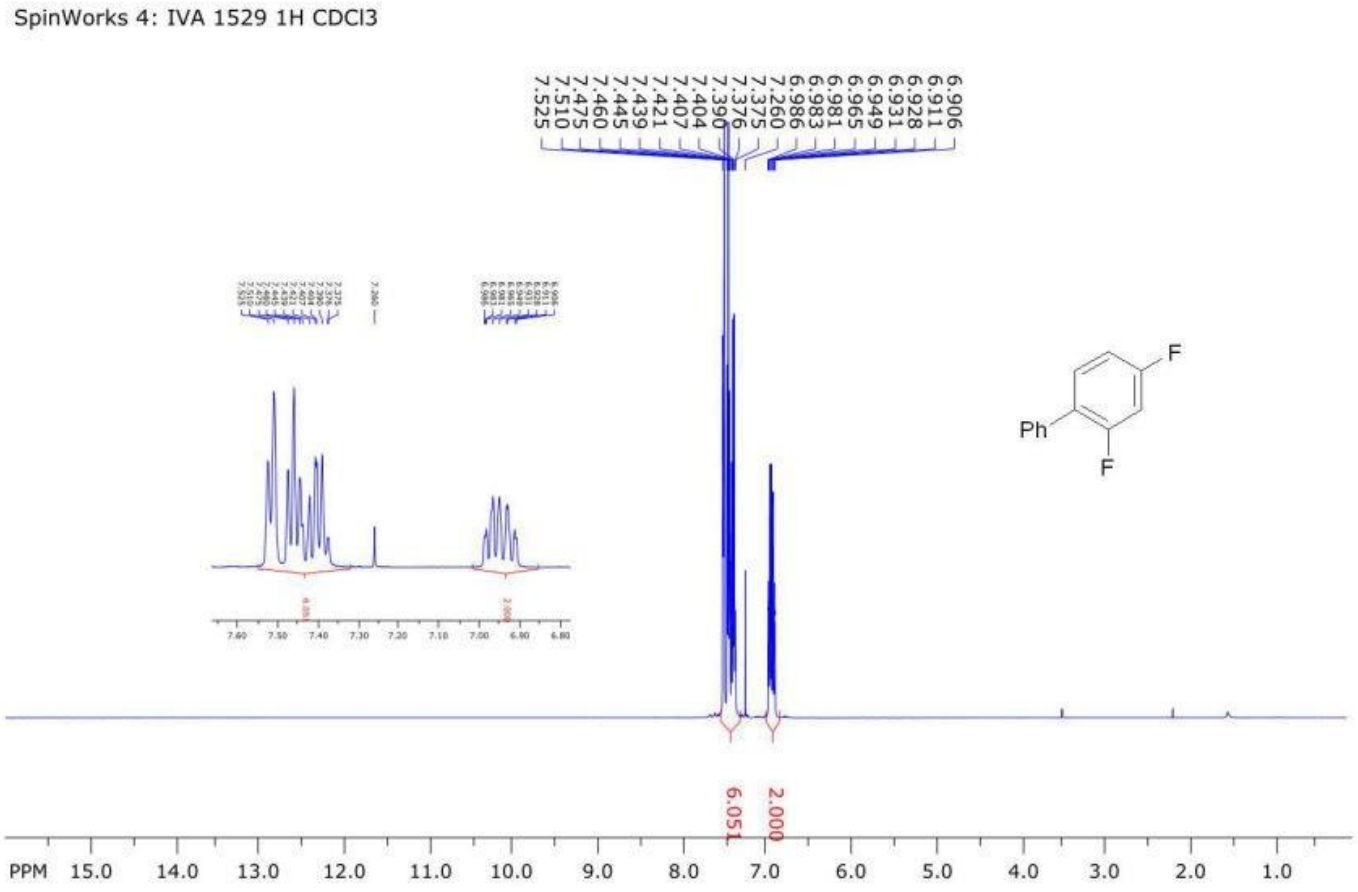
Compound **4e**



file: D:\NAPO\NMR\500-2\mkr11305\12\fid expt: <zgpg30>
transmitter freq.: 125.772879 MHz
time domain size: 65536 points
width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt
number of scans: 512

freq. of 0 ppm: 125.757842 MHz
processed size: 32768 complex points
LB: 2.000 GF: 0.0000
Hz/cm: 1005.148 ppm/cm: 7.99177

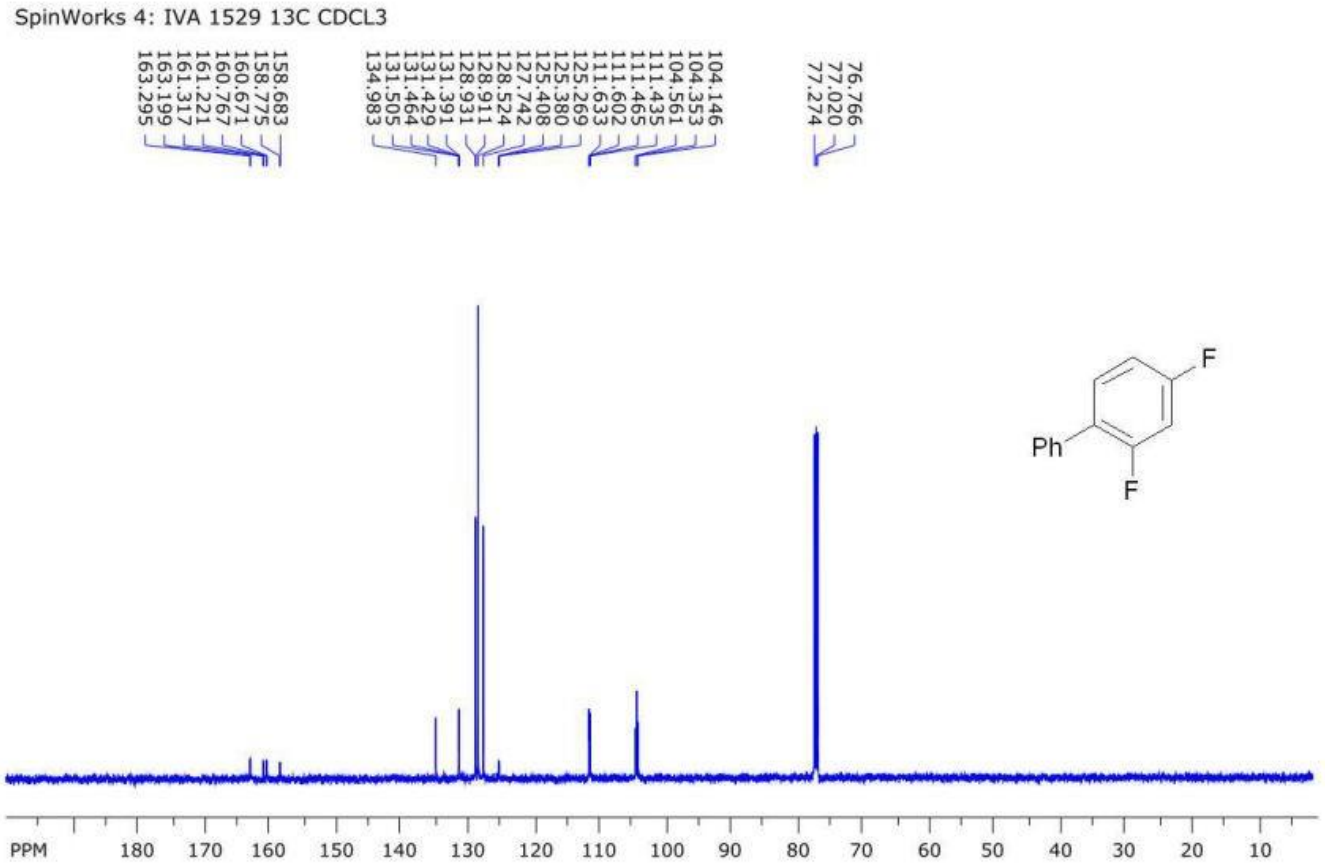
Compound **4f**



file: D:\NAPO\NMR\500-2\mkr100201\21\fid expt: <zg30>
transmitter freq.: 500.133001 MHz
time domain size: 65536 points
width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt
number of scans: 24

freq. of 0 ppm: 500.130023 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 318.759 ppm/cm: 0.63735

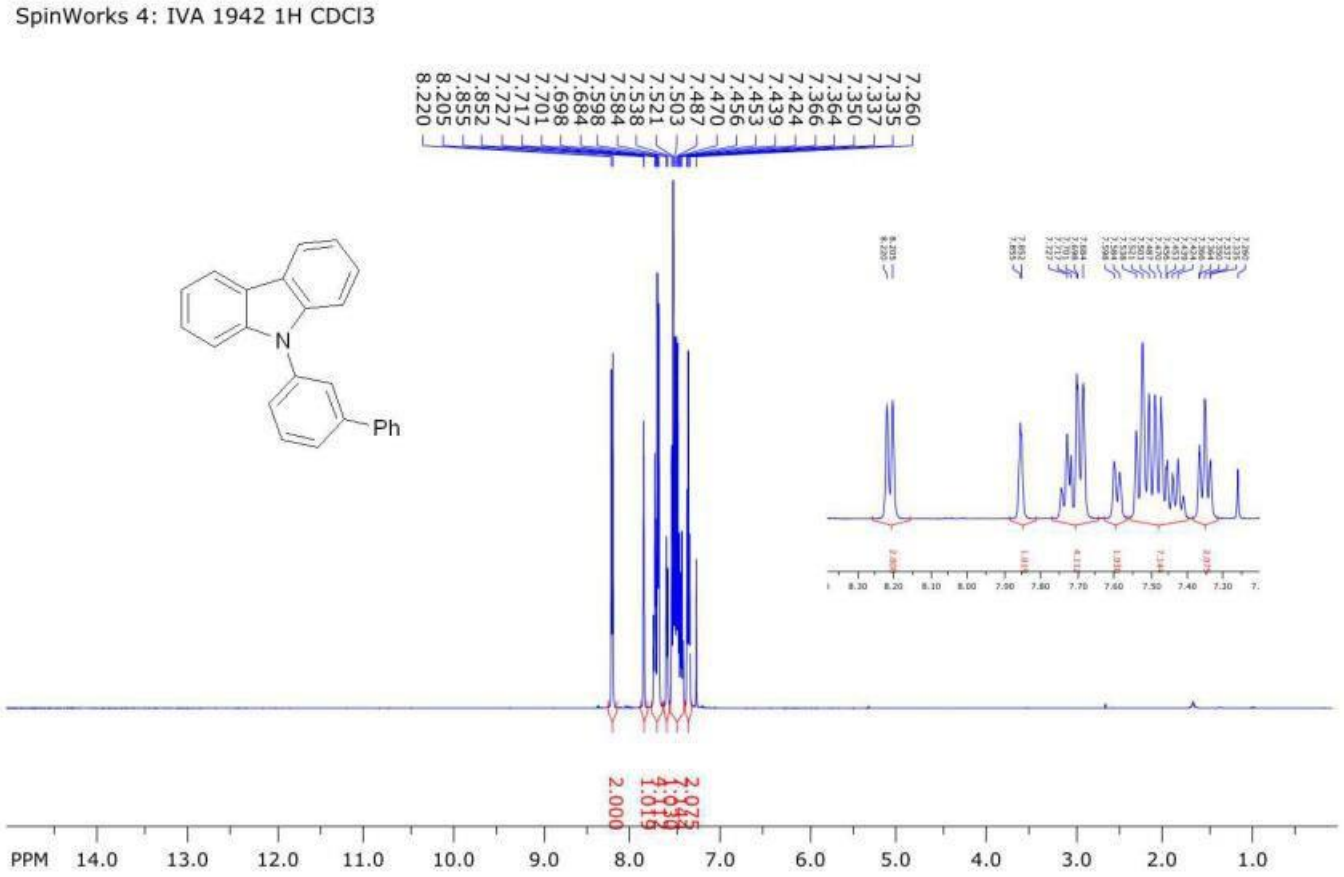
Compound **4f**



file: D:\NAPO\NMR\500-2\mkr100201\22\fid expt: <zgpg30>
transmitter freq.: 125.772879 MHz
time domain size: 65536 points
width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt
number of scans: 512

freq. of 0 ppm: 125.757793 MHz
processed size: 32768 complex points
LB: 2.000 GF: 0.0000
Hz/cm: 1001.957 ppm/cm: 7.96640

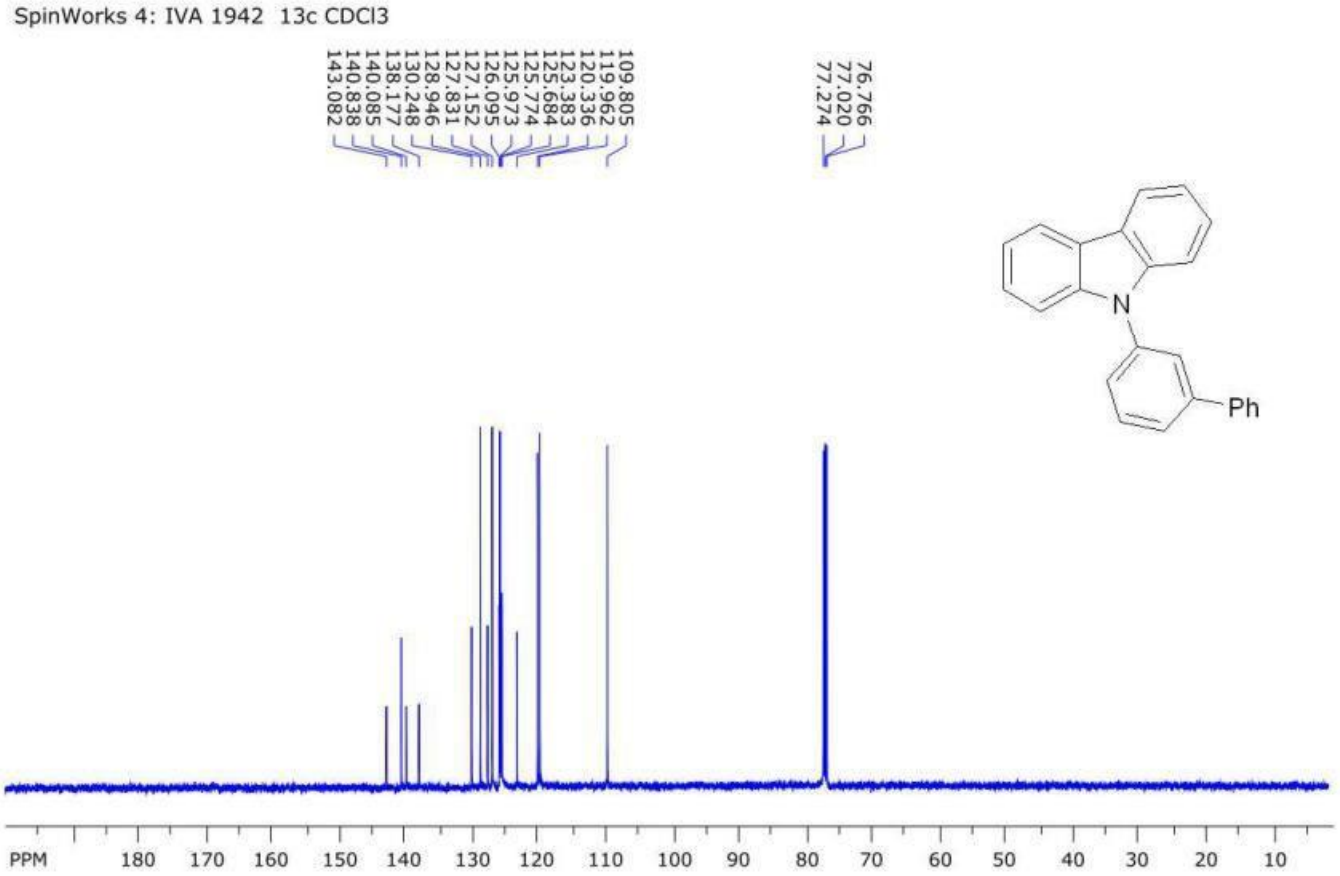
Compound **4g**



file: D:\NAPO\NMR\500-2\mkr12102\39\fid expt: <zg30>
transmitter freq.: 500.133001 MHz
time domain size: 65536 points
width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt
number of scans: 24

freq. of 0 ppm: 500.130023 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 300.201 ppm/cm: 0.60024

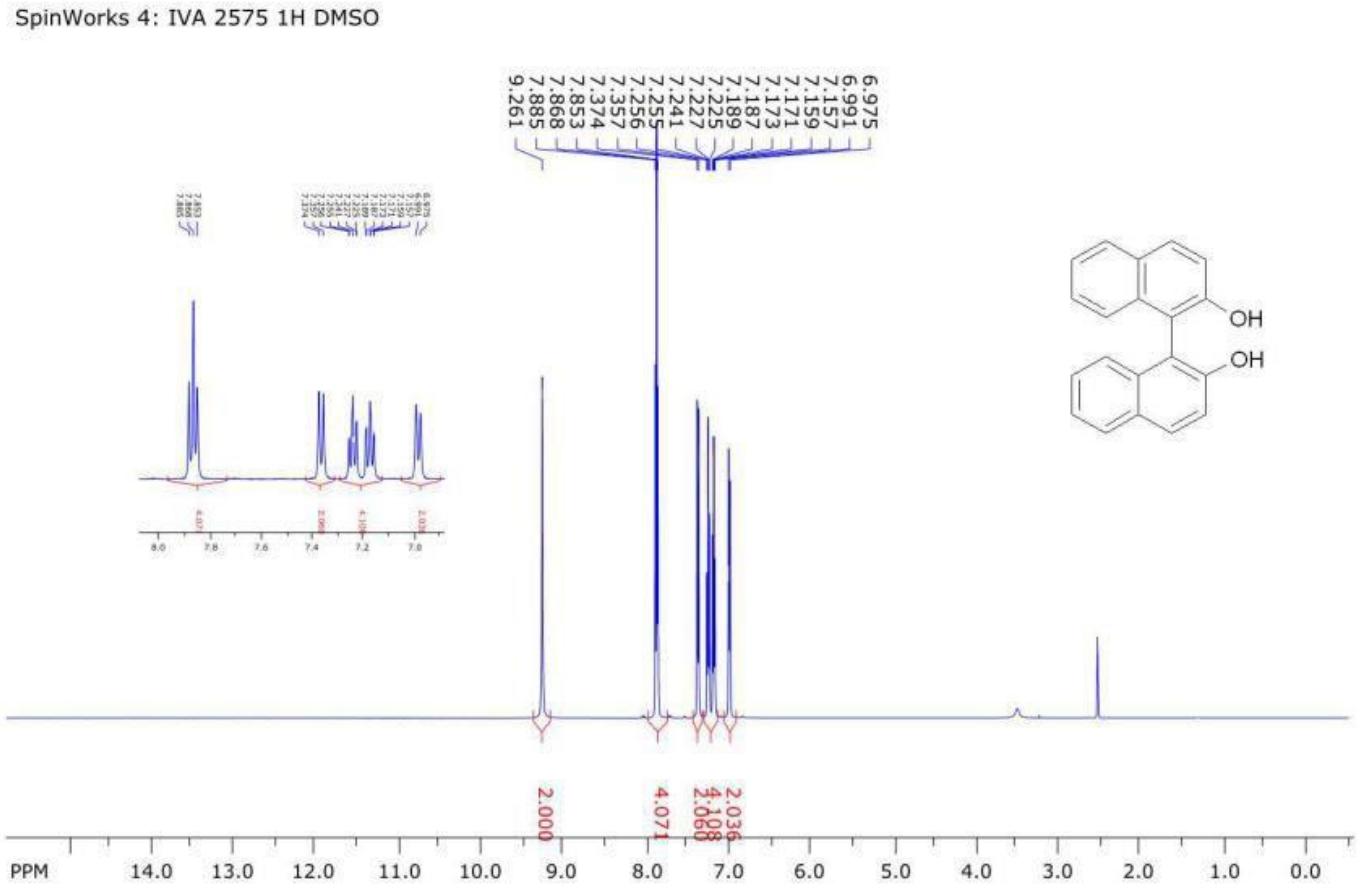
Compound **4g**



file: D:\NAPO\NMR\500-2\mkr12102\40\fid expt: <zgpg30>
transmitter freq.: 125.772879 MHz
time domain size: 65536 points
width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt
number of scans: 512

freq. of 0 ppm: 125.757800 MHz
processed size: 32768 complex points
LB: 2.000 GF: 0.0000
Hz/cm: 1001.957 ppm/cm: 7.96640

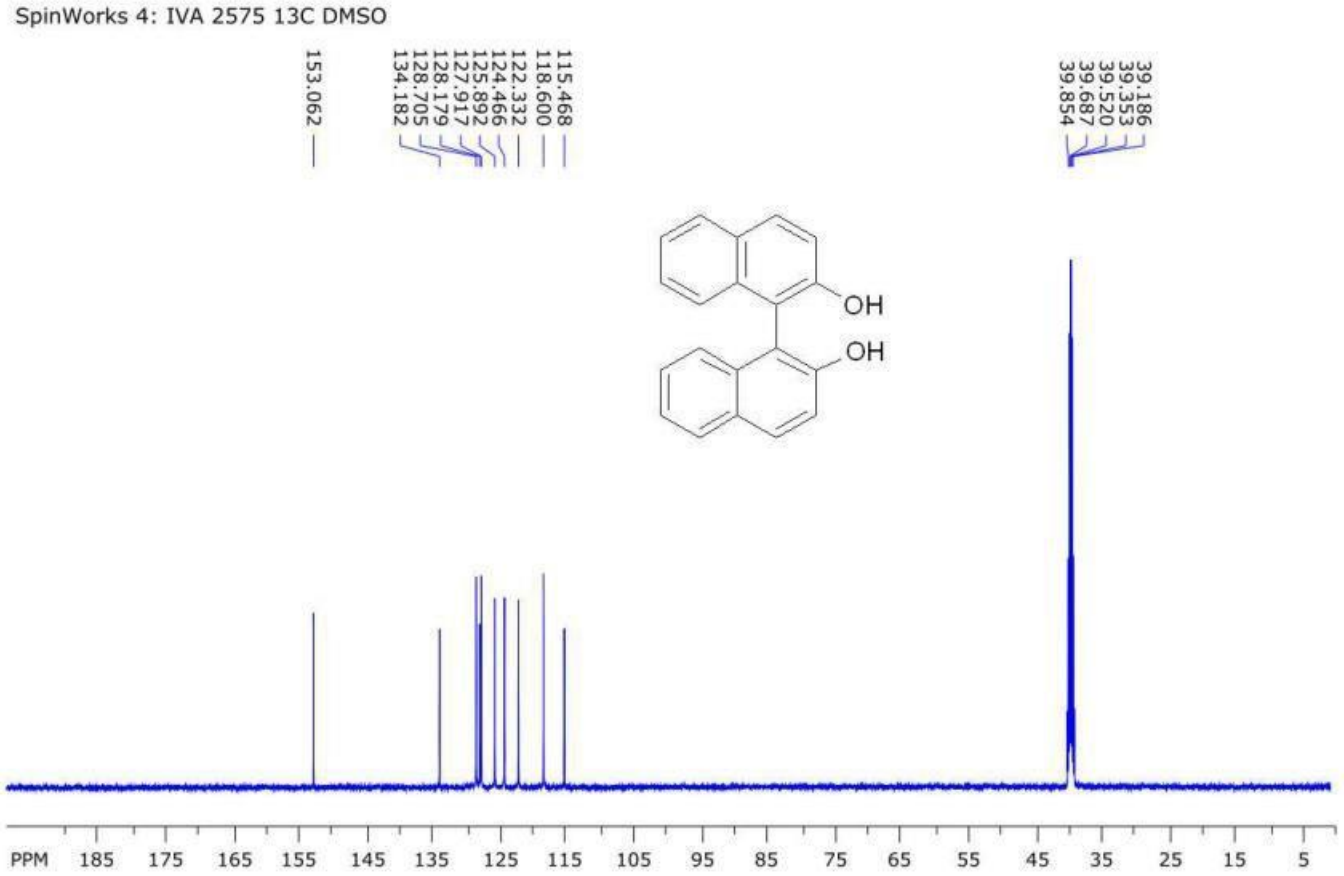
Compound **4h**



file: ...APO\NMR\500-2\mkr12506\23 2575\fid expt: <zg30>
transmitter freq.: 500.133001 MHz
time domain size: 65536 points
width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt
number of scans: 24

freq. of 0 ppm: 500.130004 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 326.946 ppm/cm: 0.65372

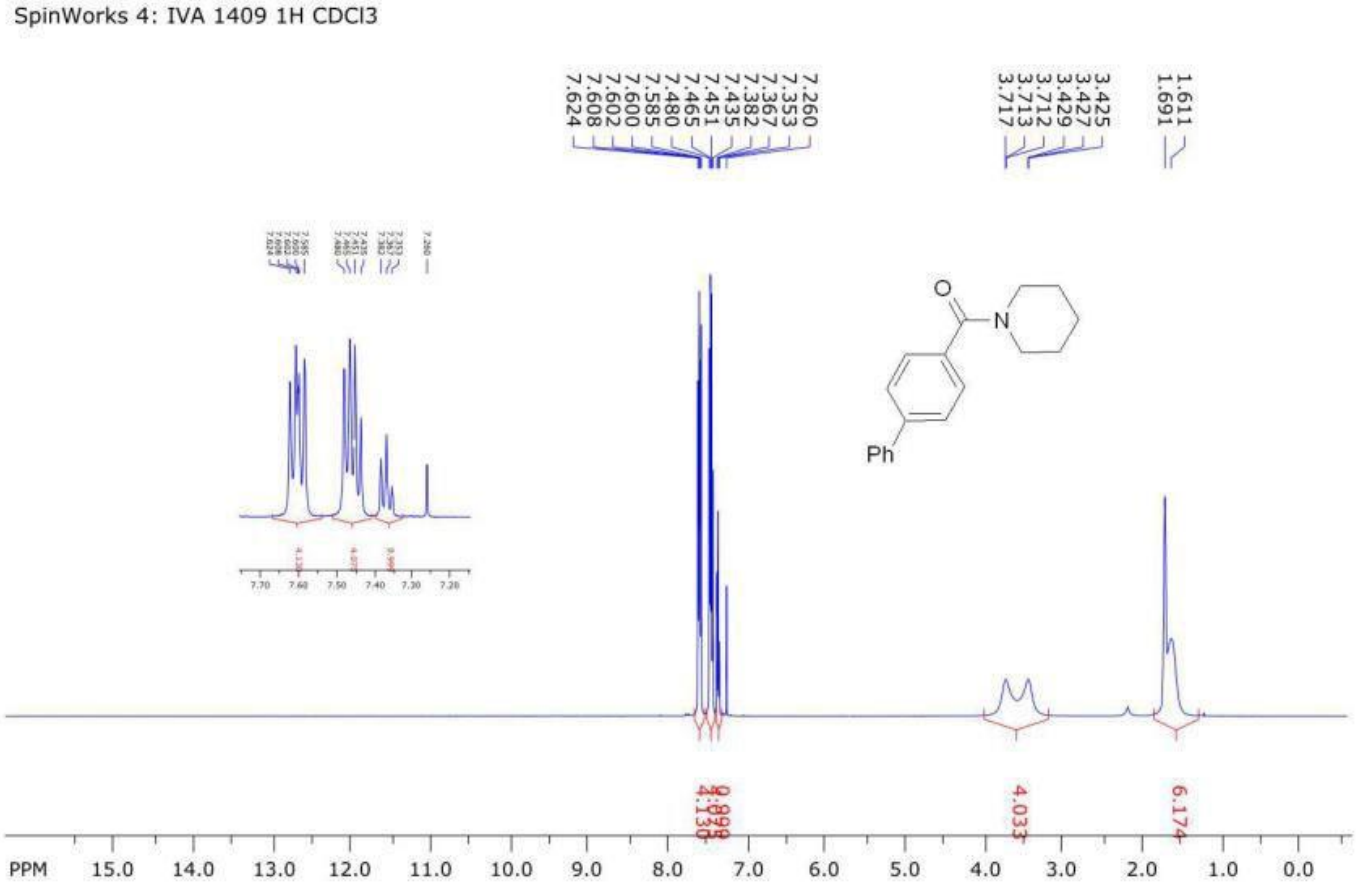
Compound **4h**



file: D:\NAPO\NMR\500-2\mkr12506\24\fid expt: <zgpg30>
transmitter freq.: 125.772879 MHz
time domain size: 65536 points
width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt
number of scans: 512

freq. of 0 ppm: 125.757842 MHz
processed size: 32768 complex points
LB: 2.000 GF: 0.0000
Hz/cm: 998.766 ppm/cm: 7.94103

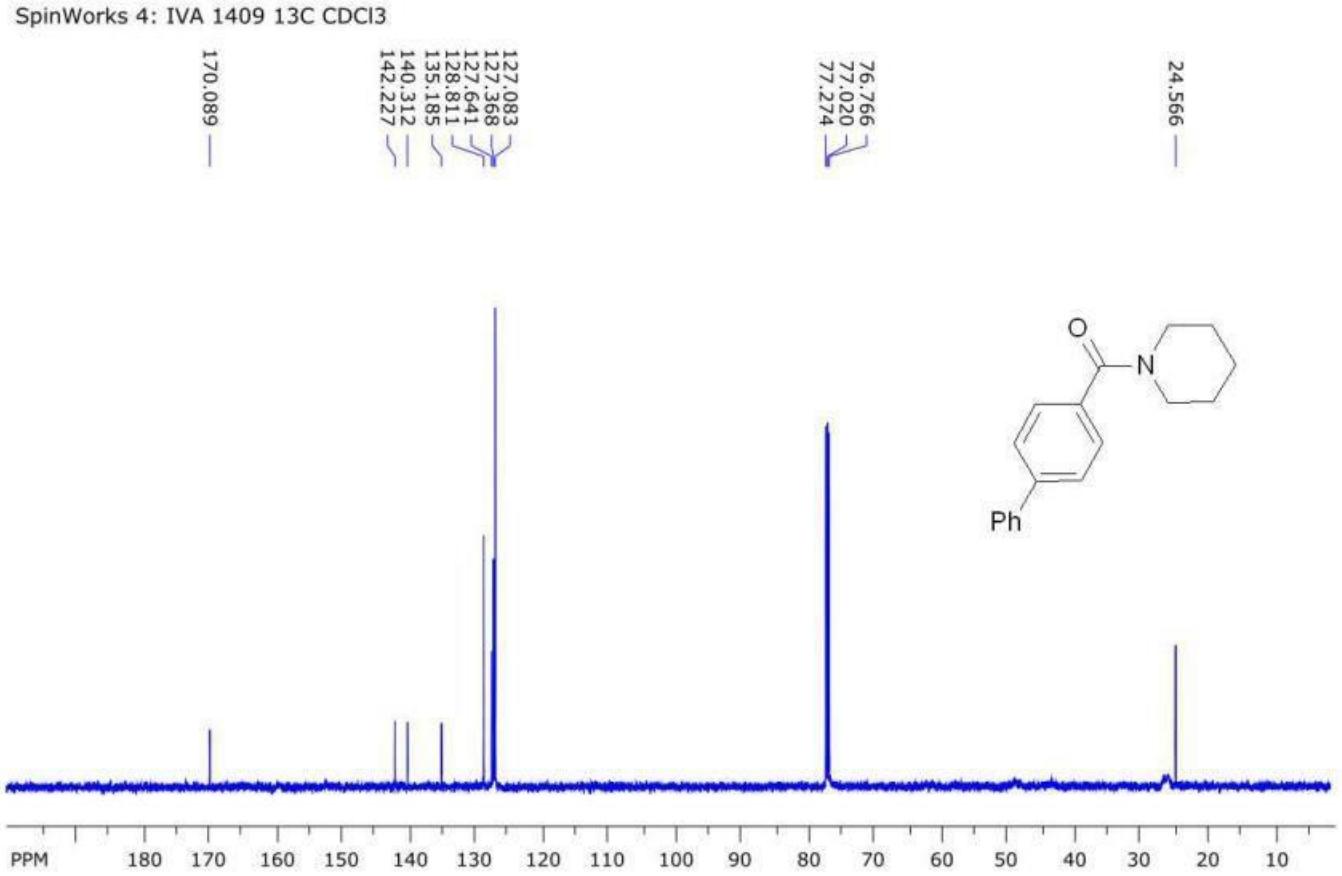
Compound **4i**



file: D:\NAPO\NMR\500-2\mkr11112\3\fid expt: <zg30>
transmitter freq.: 500.133001 MHz
time domain size: 65536 points
width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt
number of scans: 12

freq. of 0 ppm: 500.130023 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 341.137 ppm/cm: 0.68209

Compound **4i**

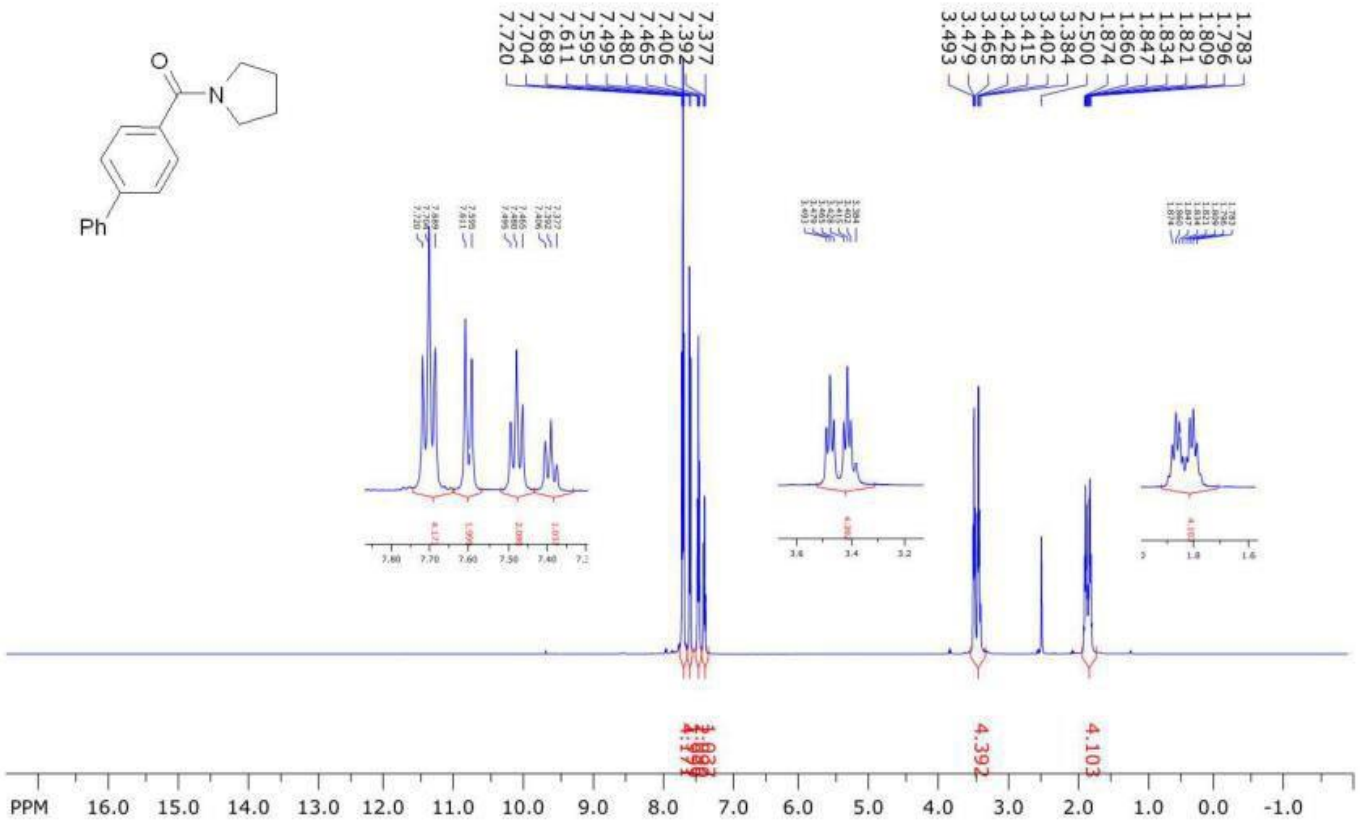


file: D:\NAPO\NMR\500-2\mkr11112\4\fid expt: <zgpg30>
transmitter freq.: 125.772879 MHz
time domain size: 65536 points
width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt
number of scans: 196

freq. of 0 ppm: 125.757800 MHz
processed size: 32768 complex points
LB: 2.000 GF: 0.0000
Hz/cm: 1003.553 ppm/cm: 7.97909

Compound **4j**

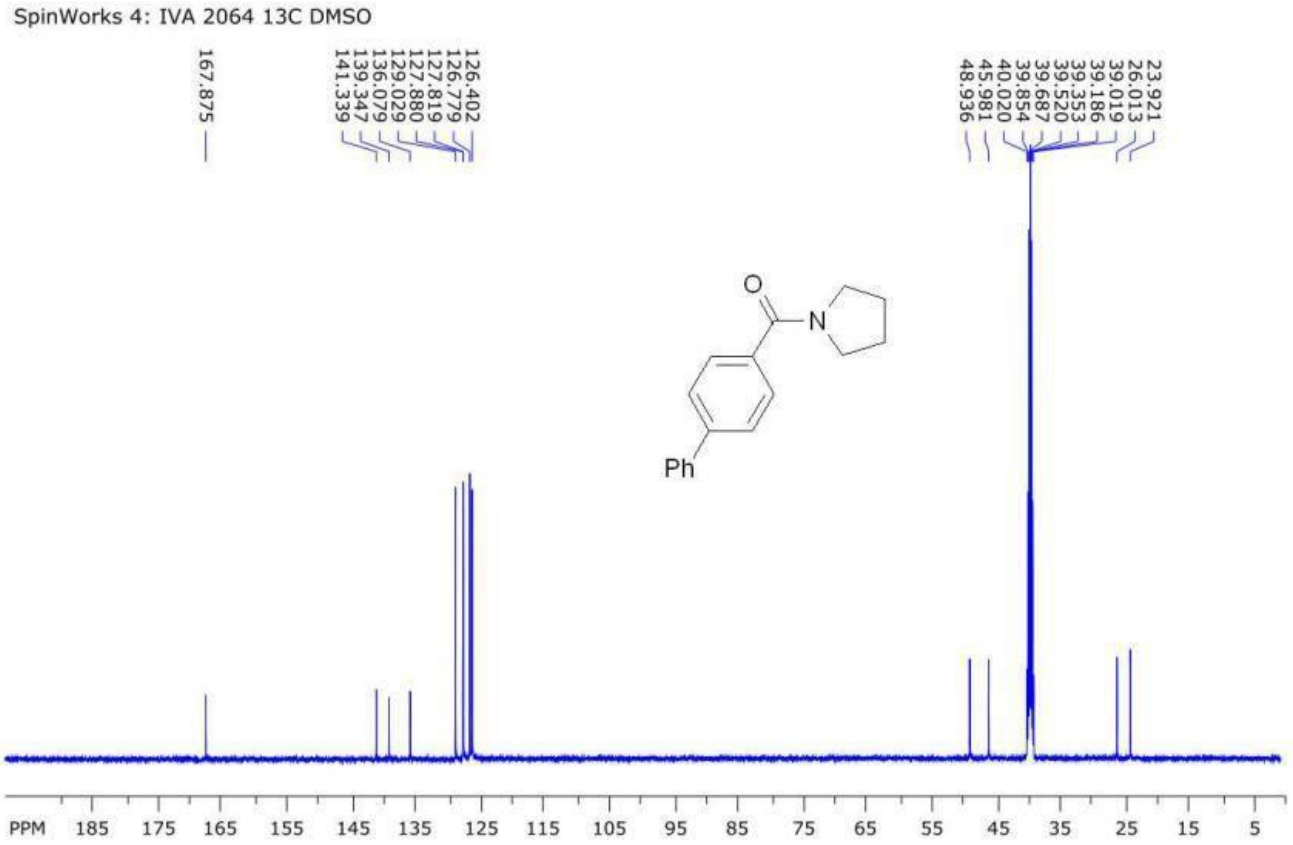
SpinWorks 4: IVA 2064 1H DMSO



file: ...APO\NMR\500-2\mkr12607\27 2064\fid expt: <zg30>
transmitter freq.: 500.133001 MHz
time domain size: 65536 points
width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt
number of scans: 24

freq. of 0 ppm: 500.130005 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 389.715 ppm/cm: 0.77922

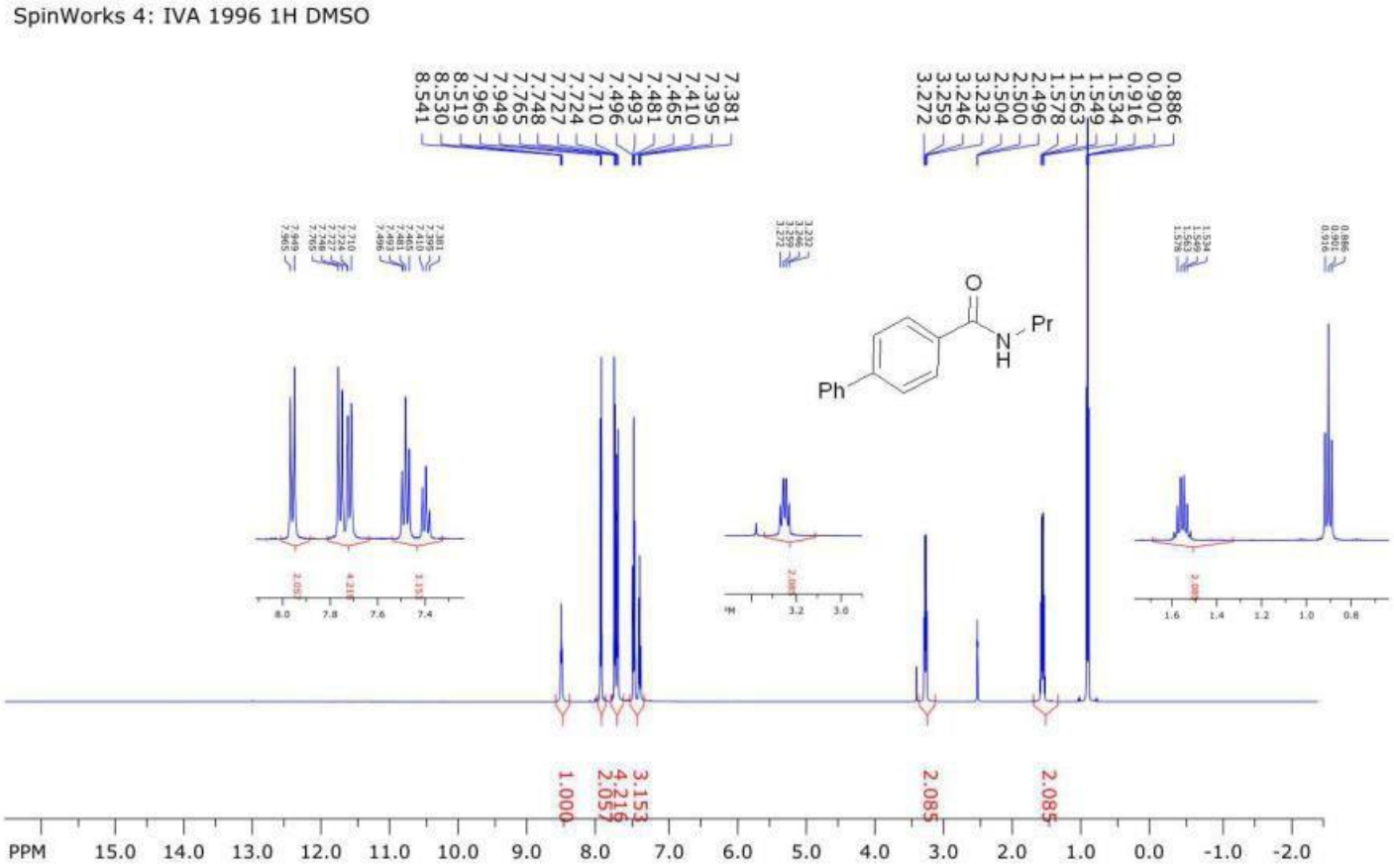
Compound **4j**



file: D:\NAPO\NMR\500-2\mkr12607\28\fid expt: <zgpg30>
transmitter freq.: 125.772879 MHz
time domain size: 65536 points
width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt
number of scans: 512

freq. of 0 ppm: 125.757845 MHz
processed size: 32768 complex points
LB: 2.000 GF: 0.0000
Hz/cm: 998.766 ppm/cm: 7.94103

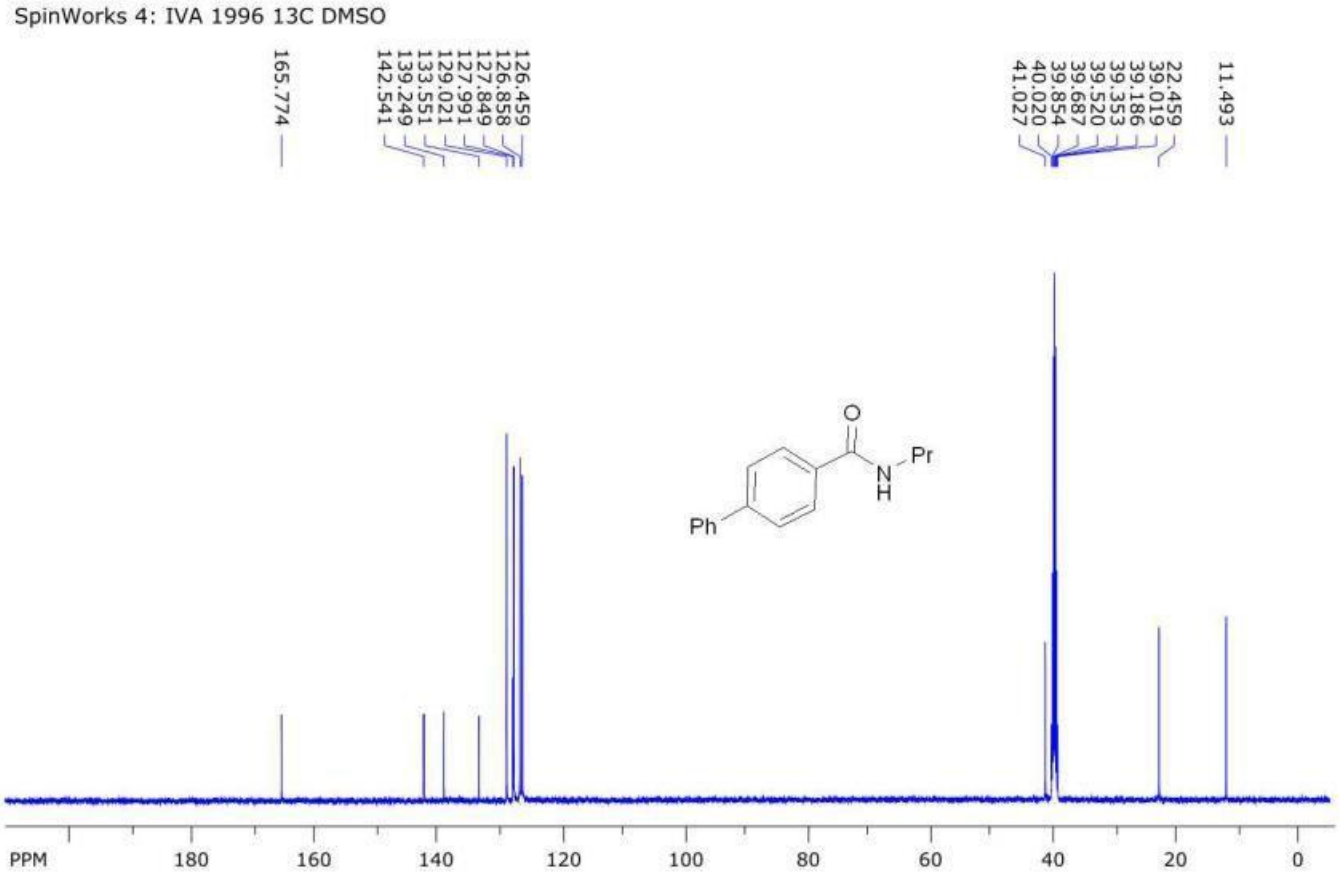
Compound **4k**



file: D:\NAPO\NMR\500-2\mkr10804\9\fid expt: <zg30>
transmitter freq.: 500.133001 MHz
time domain size: 65536 points
width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt
number of scans: 24

freq. of 0 ppm: 500.130005 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 380.982 ppm/cm: 0.76176

Compound **4k**

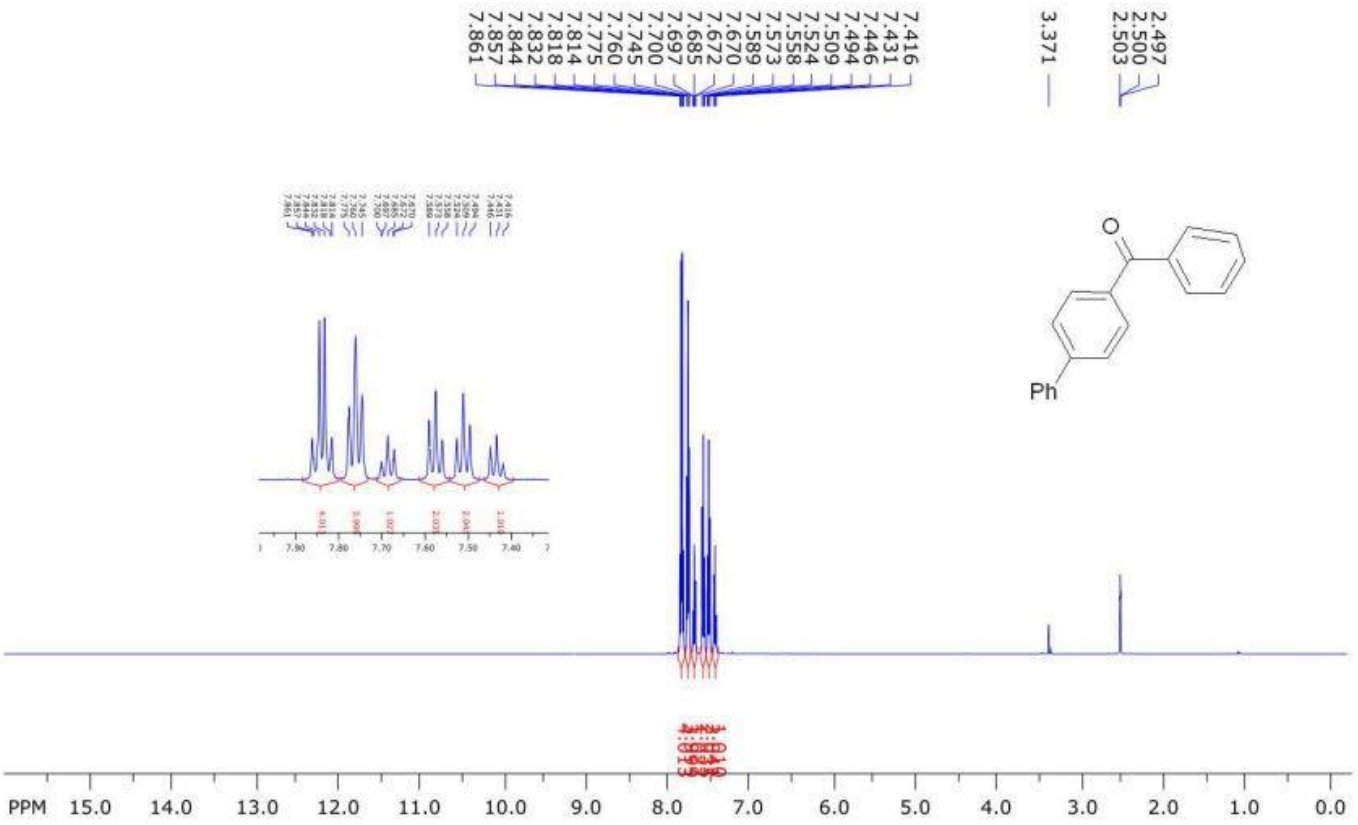


file: D:\NAPO\NMR\500-2\mkr10804\10\fid expt: <zgpg30>
transmitter freq.: 125.772879 MHz
time domain size: 65536 points
width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt
number of scans: 512

freq. of 0 ppm: 125.757844 MHz
processed size: 32768 complex points
LB: 2.000 GF: 0.0000
Hz/cm: 1088.113 ppm/cm: 8.65141

Compound **4l**

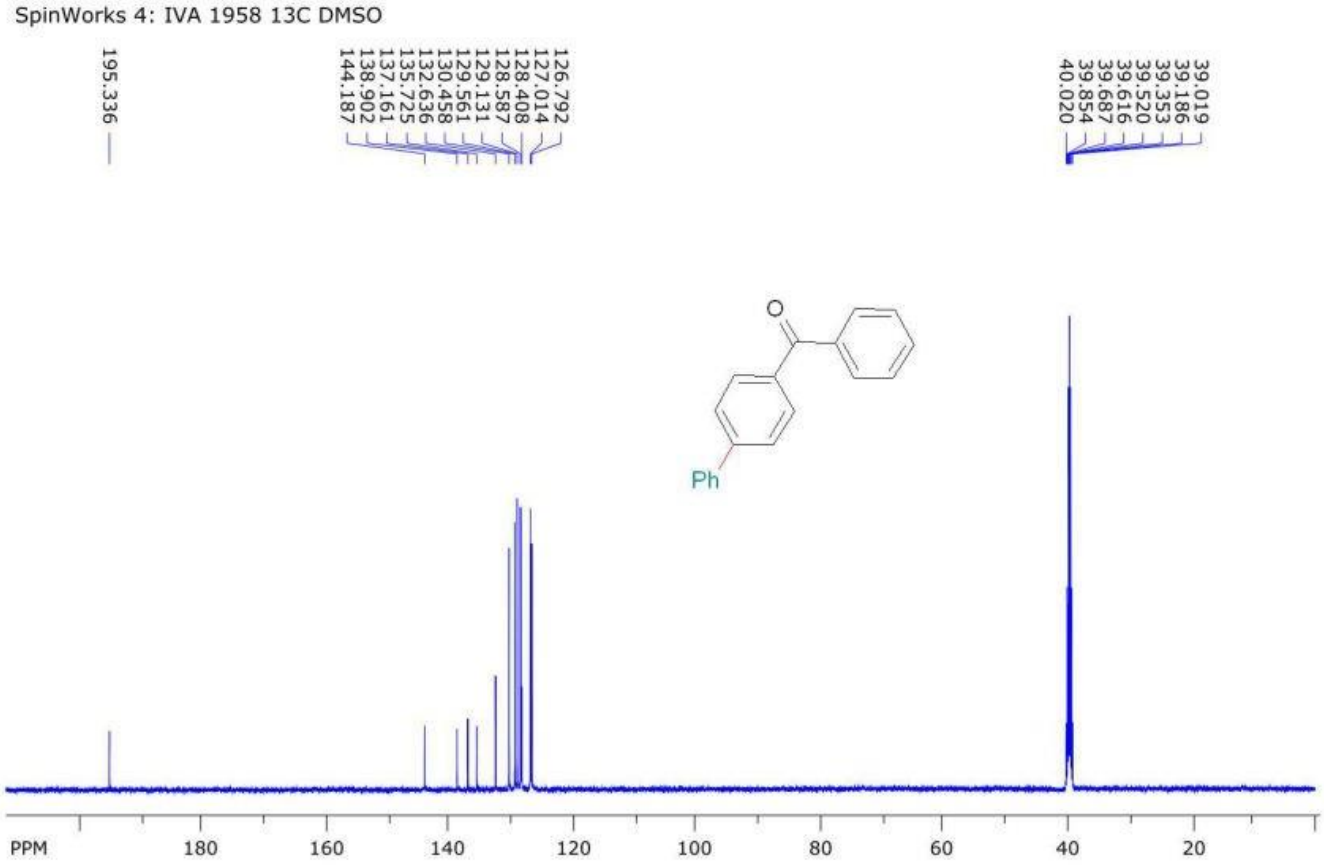
SpinWorks 4: IVA 1958 1H DMSO



file: D:\NAPO\NMR\500-2\mkr10103\3\fid expt: <zg30>
transmitter freq.: 500.133001 MHz
time domain size: 65536 points
width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt
number of scans: 24

freq. of 0 ppm: 500.130005 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 326.946 ppm/cm: 0.65372

Compound **4l**

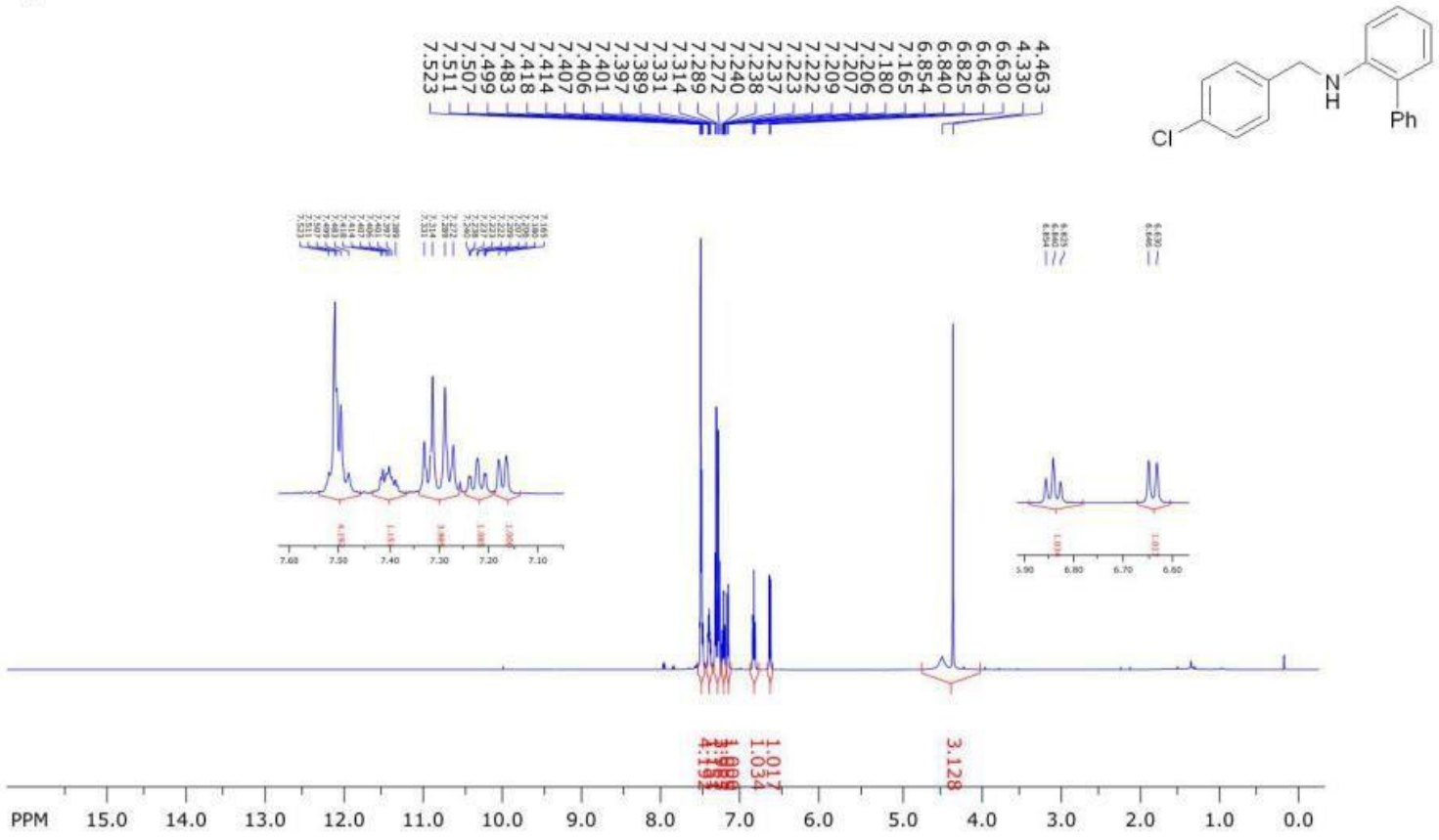


file: D:\NAPO\NMR\500-2\mkr10103\4\fid expt: <zgpg30>
transmitter freq.: 125.772879 MHz
time domain size: 65536 points
width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt
number of scans: 512

freq. of 0 ppm: 125.757846 MHz
processed size: 32768 complex points
LB: 2.000 GF: 0.0000
Hz/cm: 1068.967 ppm/cm: 8.49919

Compound **4m**

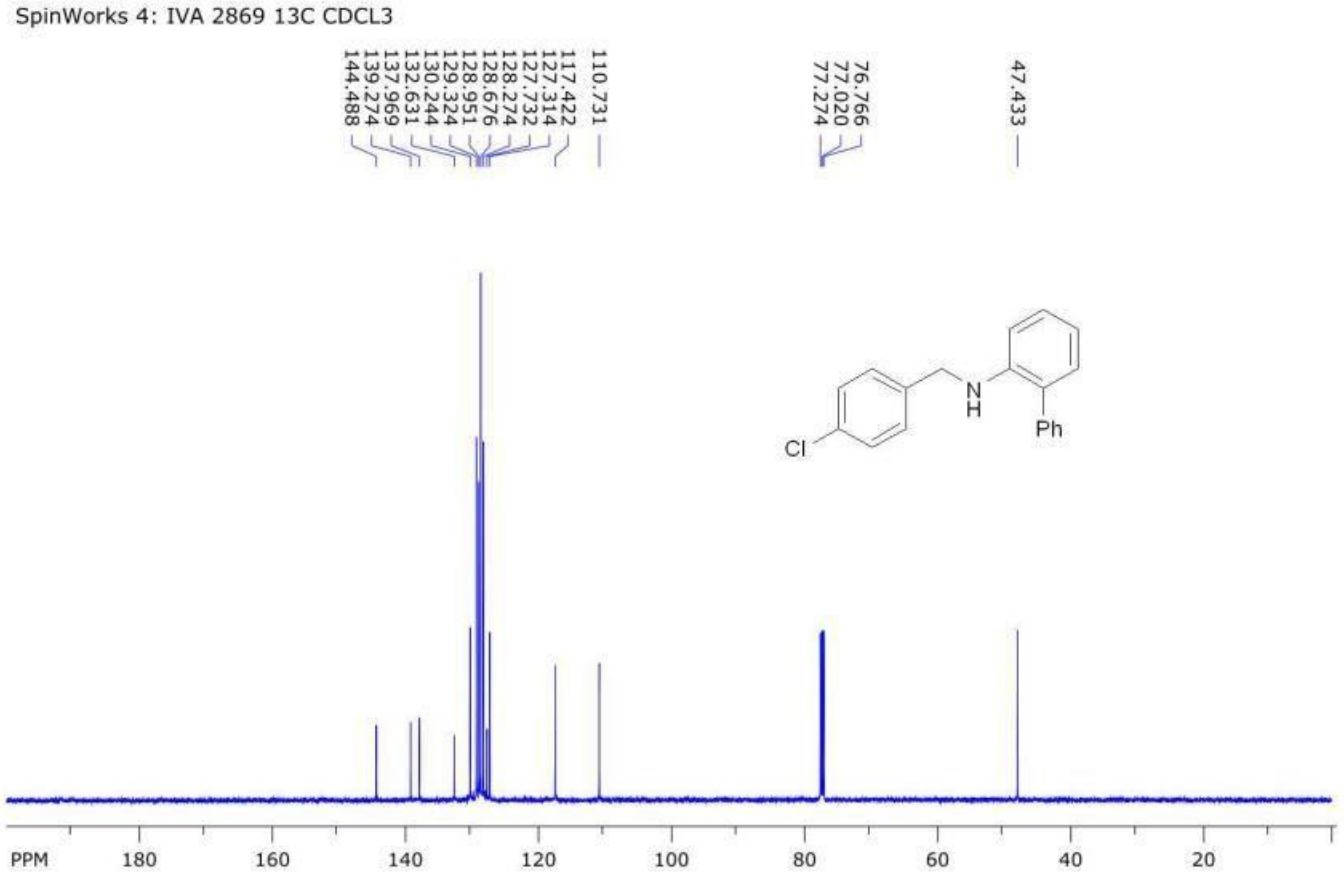
SpinWorks 4: IVA 2869 1H CDCl3



file: ...PO\NMR\500-2\mkr11706\9 2869-1\fid expt: <zg30>
transmitter freq.: 500.133001 MHz
time domain size: 65536 points
width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt
number of scans: 24

freq. of 0 ppm: 500.130024 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 331.313 ppm/cm: 0.66245

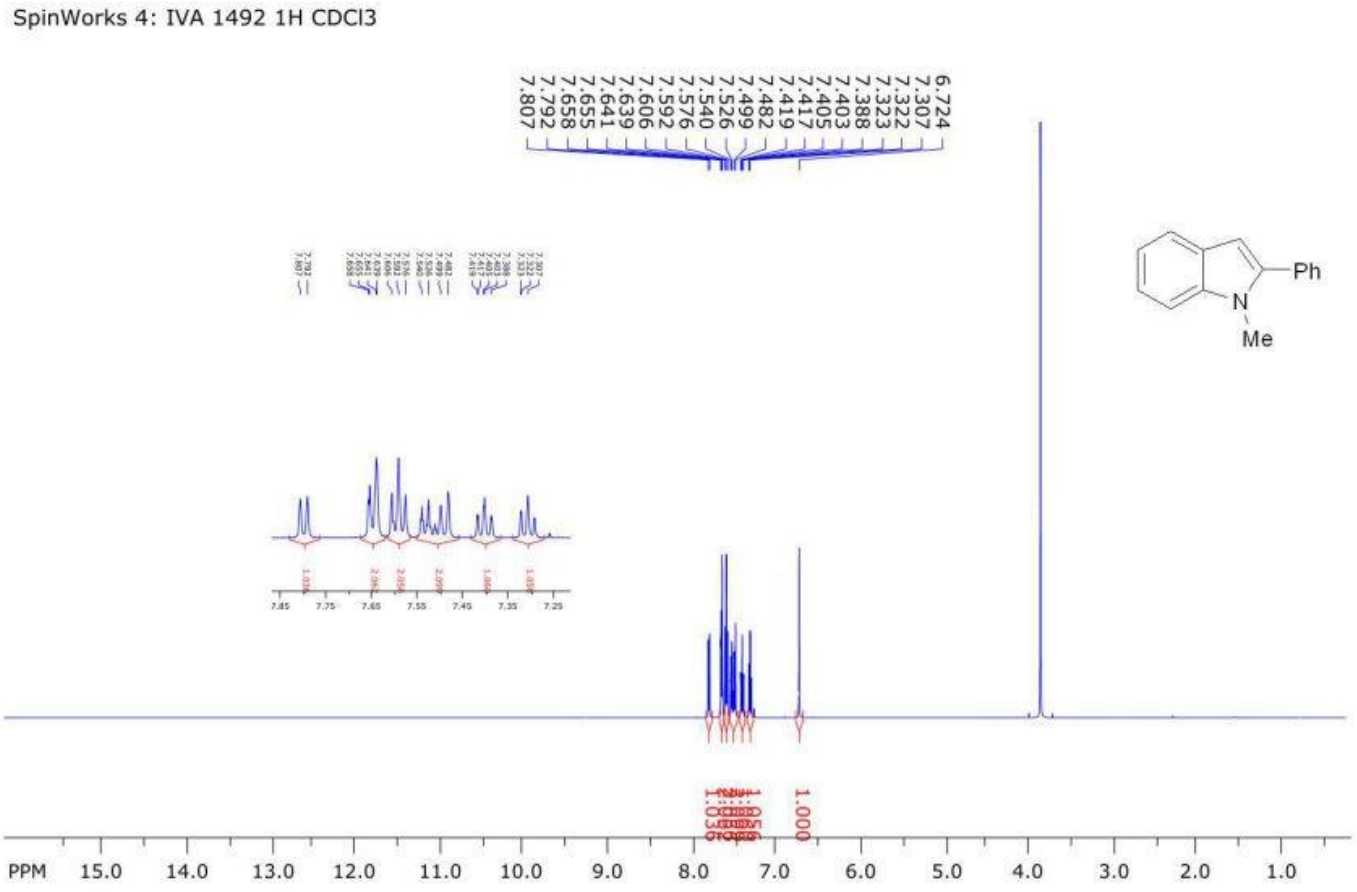
Compound **4m**



file: D:\NAPO\NMR\500-2\mkr11706\10\fid expt: <zgpg30>
transmitter freq.: 125.772879 MHz
time domain size: 65536 points
width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt
number of scans: 512

freq. of 0 ppm: 125.757804 MHz
processed size: 32768 complex points
LB: 2.000 GF: 0.0000
Hz/cm: 1008.339 ppm/cm: 8.01714

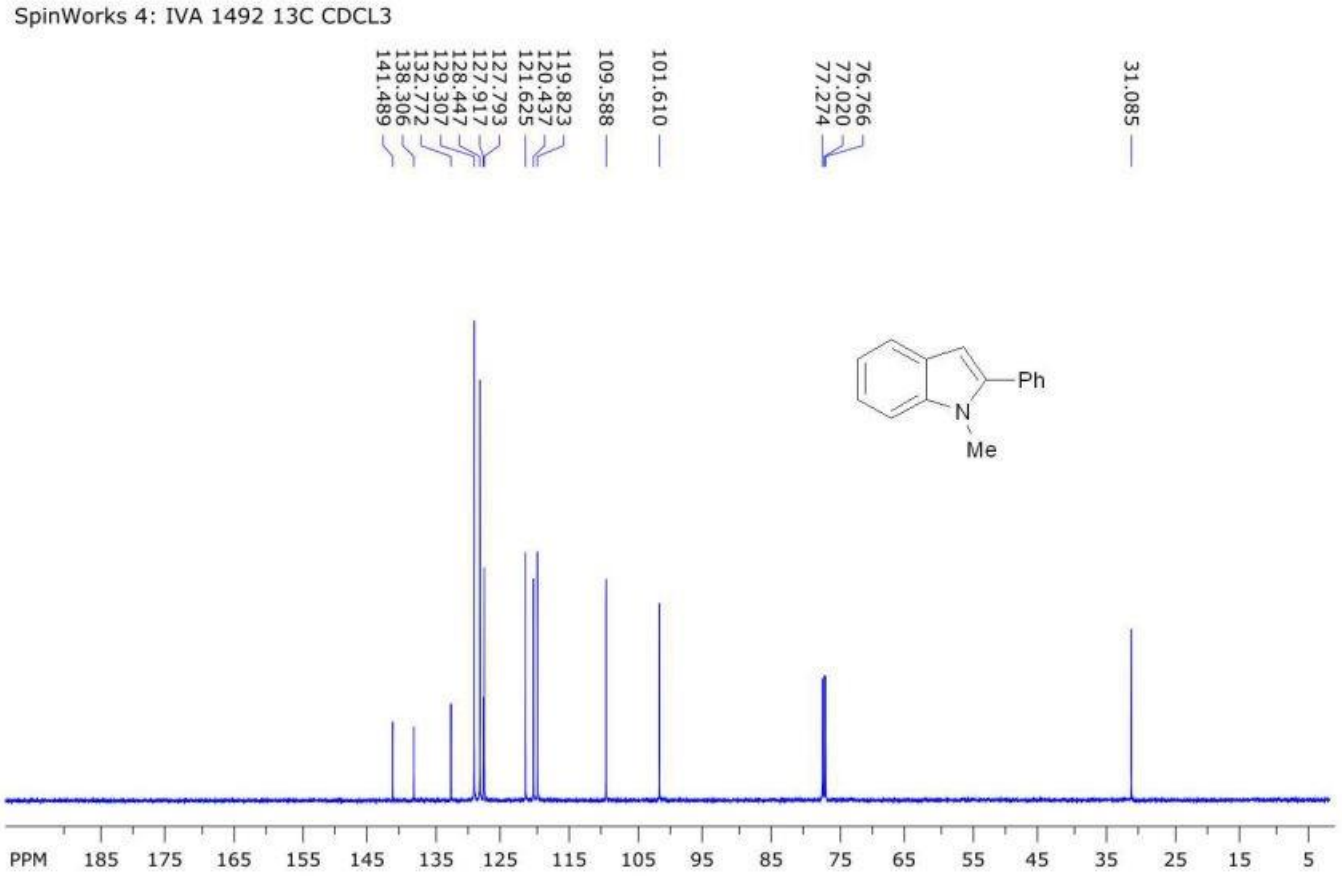
Compound **4n**



file: D:\NAPO\NMR\500-2\mkr100201\19\fid expt: <zg30>
transmitter freq.: 500.133001 MHz
time domain size: 65536 points
width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt
number of scans: 24

freq. of 0 ppm: 500.130023 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 320.396 ppm/cm: 0.64062

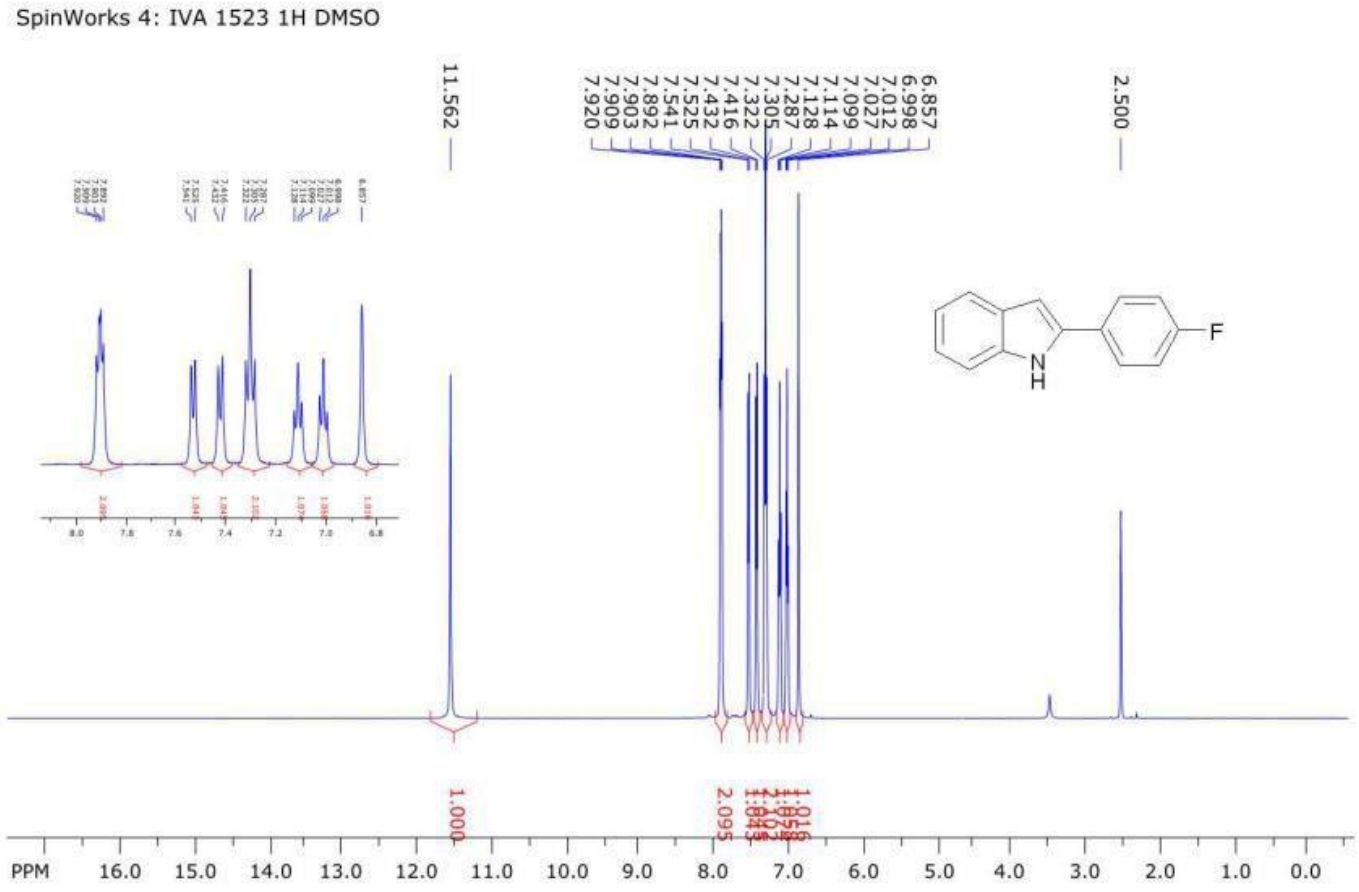
Compound **4n**



file: D:\NAPO\NMR\500-2\mkr100201\20\fid expt: <zgpg30>
transmitter freq.: 125.772879 MHz
time domain size: 65536 points
width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt
number of scans: 512

freq. of 0 ppm: 125.757818 MHz
processed size: 32768 complex points
LB: 2.000 GF: 0.0000
Hz/cm: 995.575 ppm/cm: 7.91566

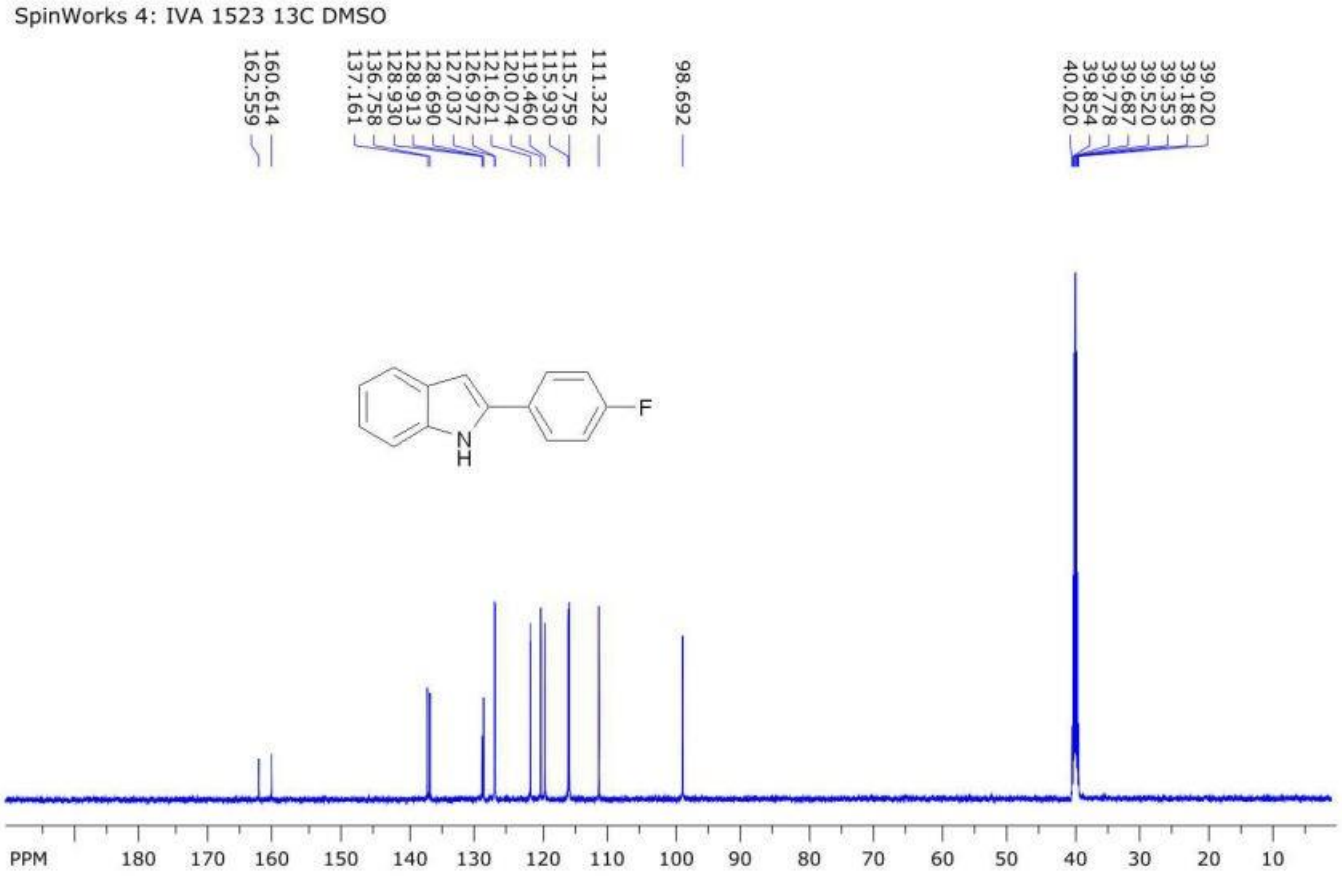
Compound **4o**



file: D:\NAPO\NMR\500-2\mkr11802\19\fid expt: <zg30>
transmitter freq.: 500.133001 MHz
time domain size: 65536 points
width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt
number of scans: 24

freq. of 0 ppm: 500.130004 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 362.970 ppm/cm: 0.72575

Compound **4o**

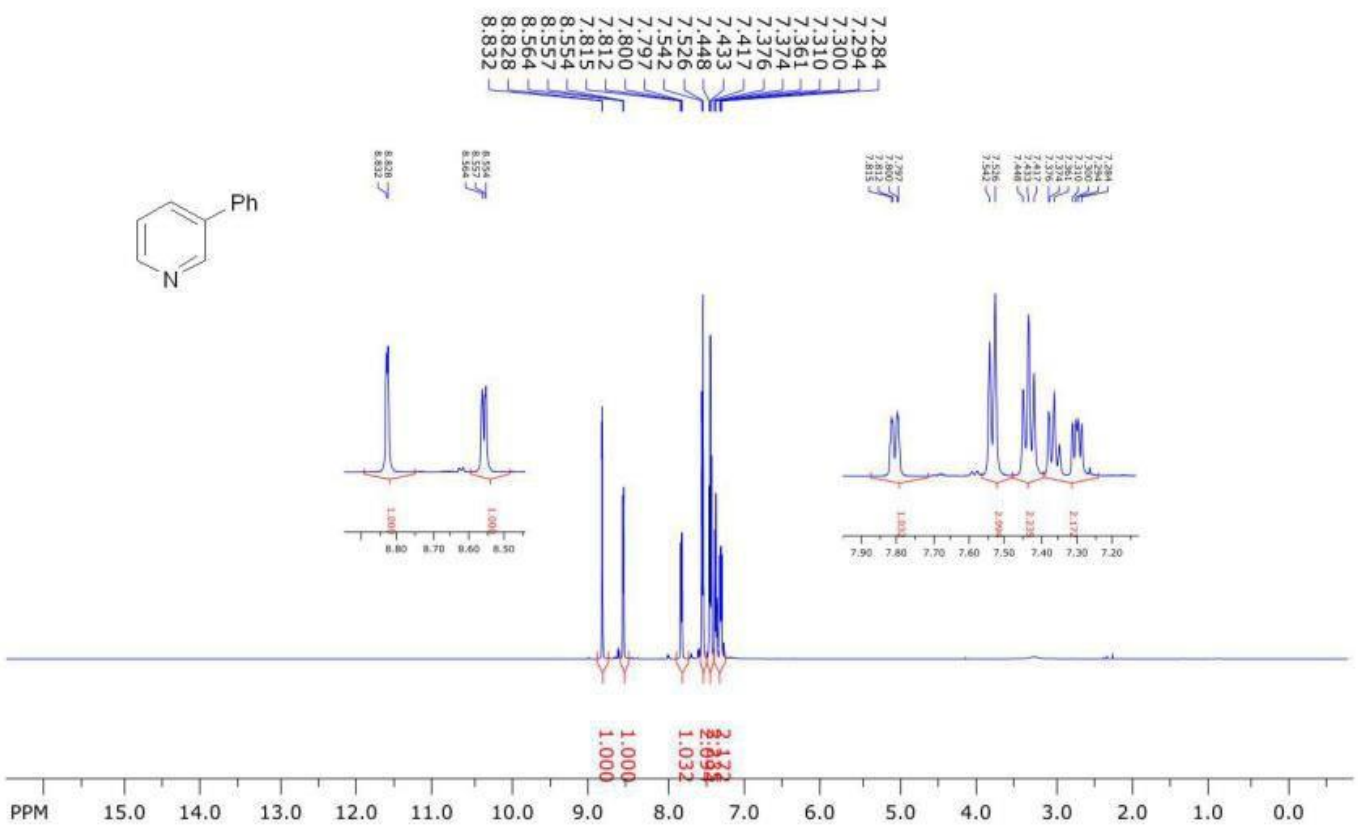


file: D:\NAPO\NMR\500-2\mkr11802\20\fid expt: <zgpg30>
transmitter freq.: 125.772879 MHz
time domain size: 65536 points
width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt
number of scans: 512

freq. of 0 ppm: 125.757842 MHz
processed size: 32768 complex points
LB: 2.000 GF: 0.0000
Hz/cm: 1005.148 ppm/cm: 7.99177

Compound **4p**

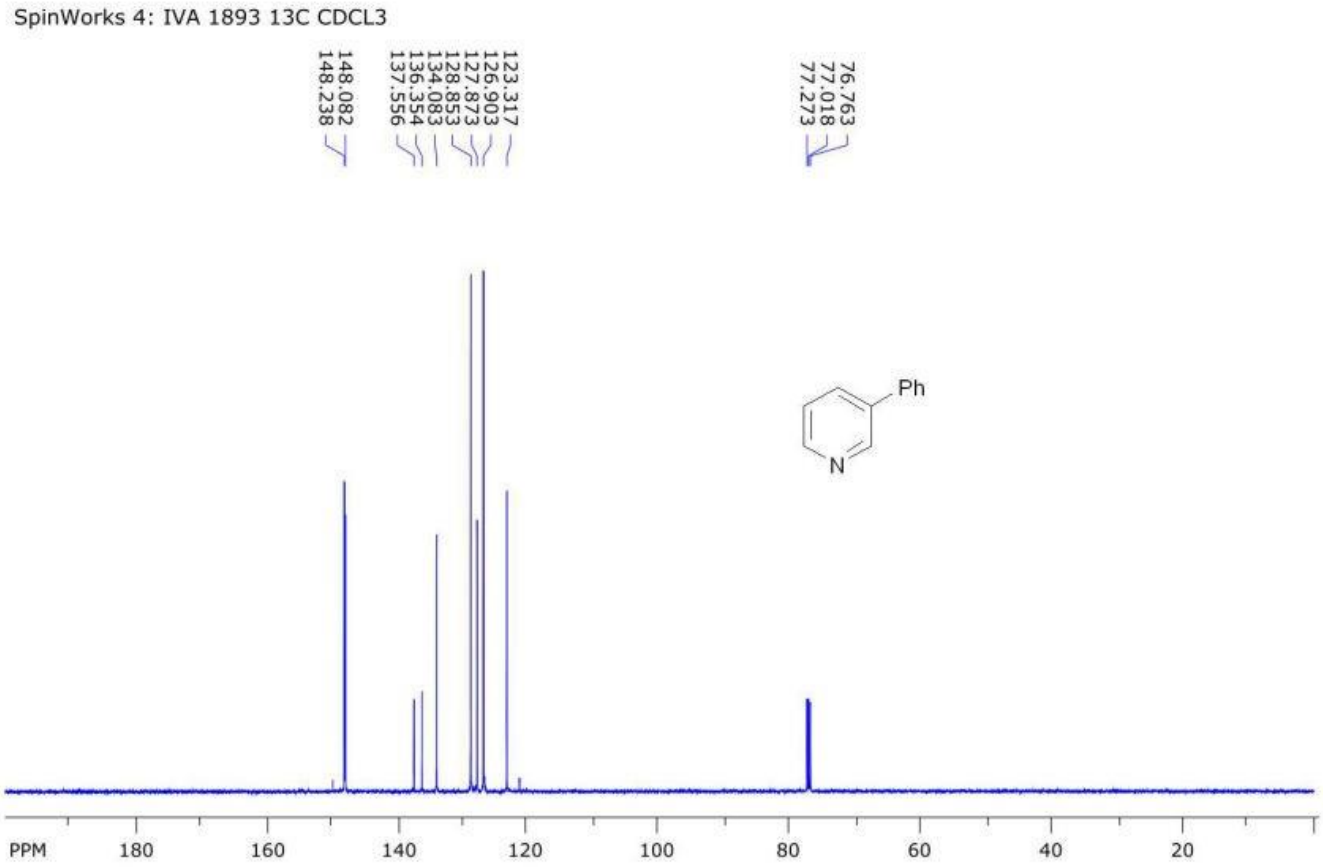
SpinWorks 4: IVA 1893 1H CDCl3



file: D:\NAPO\NMR\500-2\mkr10403\11\fid expt: <zg30>
transmitter freq.: 500.133001 MHz
time domain size: 65536 points
width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt
number of scans: 24

freq. of 0 ppm: 500.130023 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 347.141 ppm/cm: 0.69410

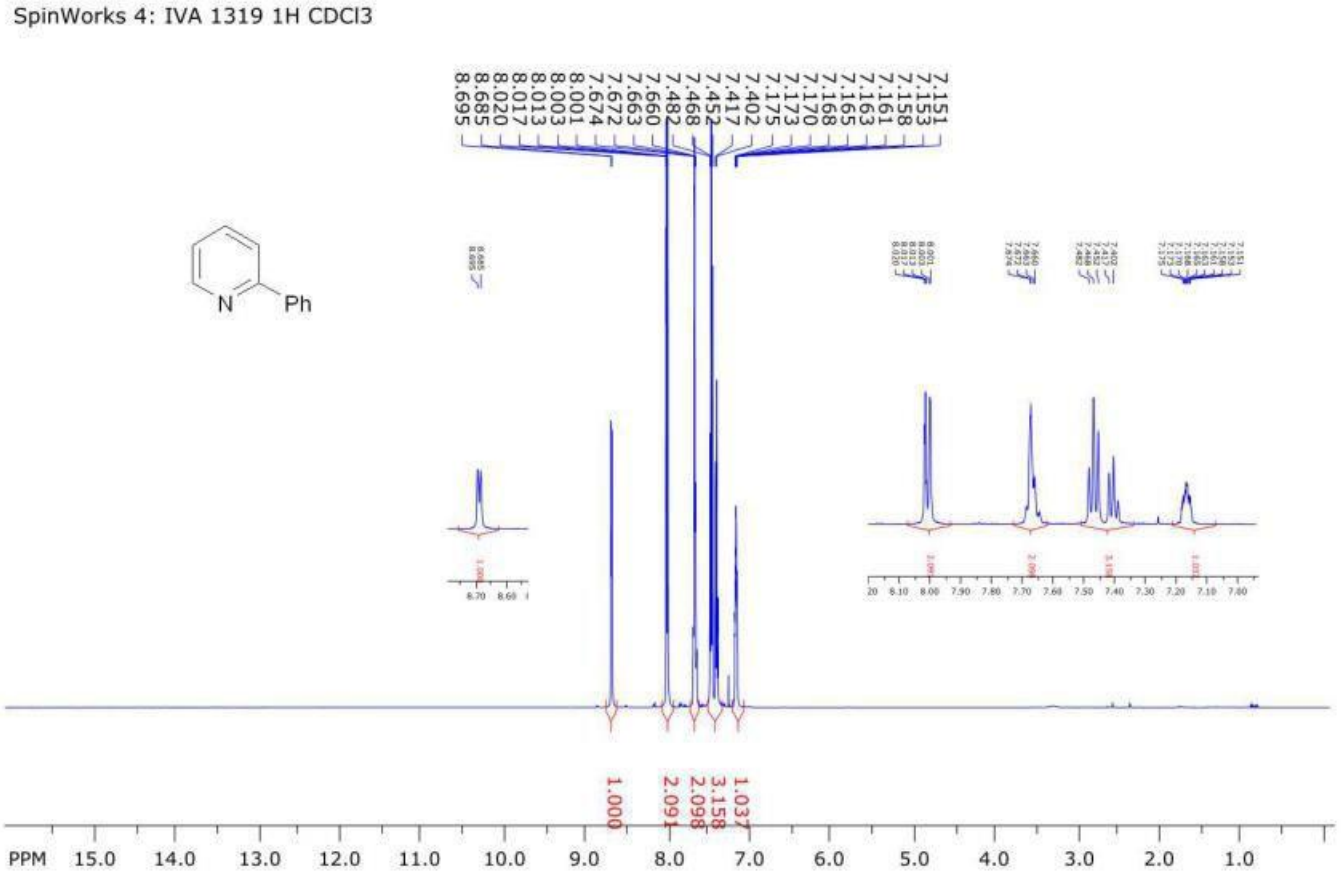
Compound **4p**



file: D:\NAPO\NMR\500-2\mkr10403\12\fid expt: <zgpg30>
transmitter freq.: 125.772879 MHz
time domain size: 65536 points
width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt
number of scans: 512

freq. of 0 ppm: 125.757820 MHz
processed size: 32768 complex points
LB: 2.000 GF: 0.0000
Hz/cm: 1009.934 ppm/cm: 8.02983

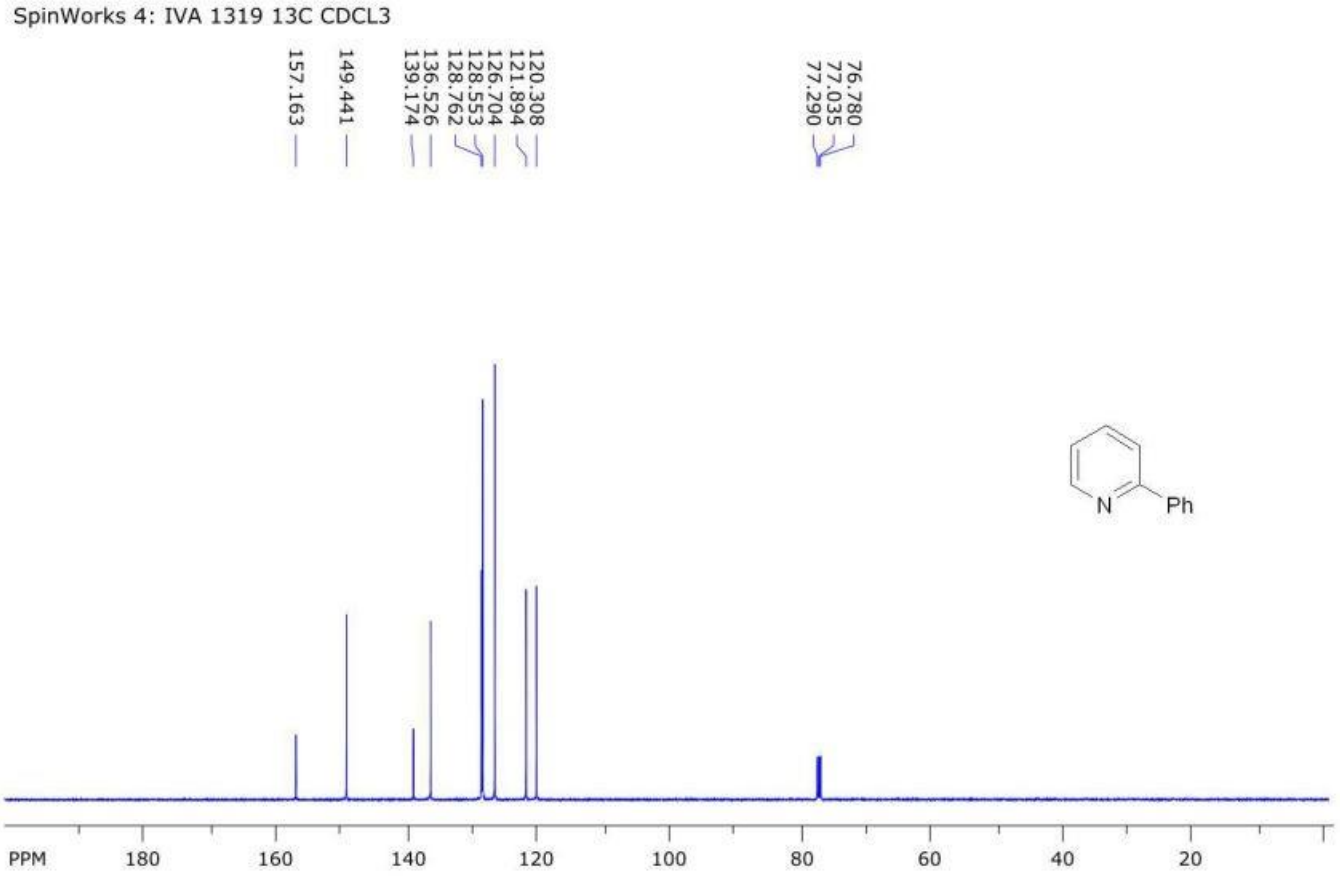
Compound **4q**



file: D:\NAPO\NMR\500-2\mkr12311\19\fid expt: <zg30>
transmitter freq.: 500.133001 MHz
time domain size: 65536 points
width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt
number of scans: 32

freq. of 0 ppm: 500.130025 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 324.763 ppm/cm: 0.64935

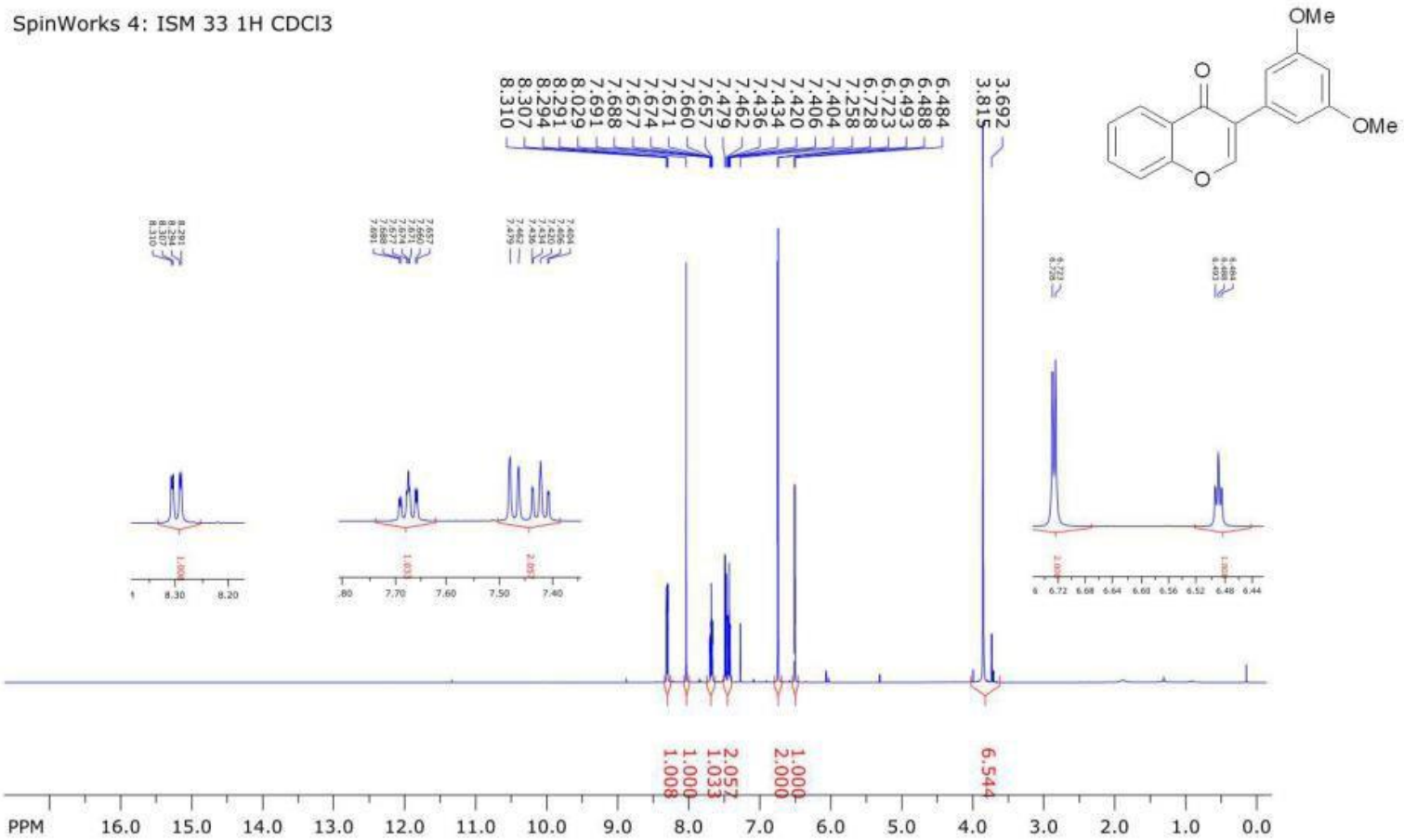
Compound **4q**



file: D:\NAPO\NMR\500-2\mkr12311\20\fid expt: <zgpg30>
transmitter freq.: 125.772879 MHz
time domain size: 65536 points
width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt
number of scans: 512

freq. of 0 ppm: 125.757821 MHz
processed size: 32768 complex points
LB: 2.000 GF: 0.0000
Hz/cm: 1021.103 ppm/cm: 8.11862

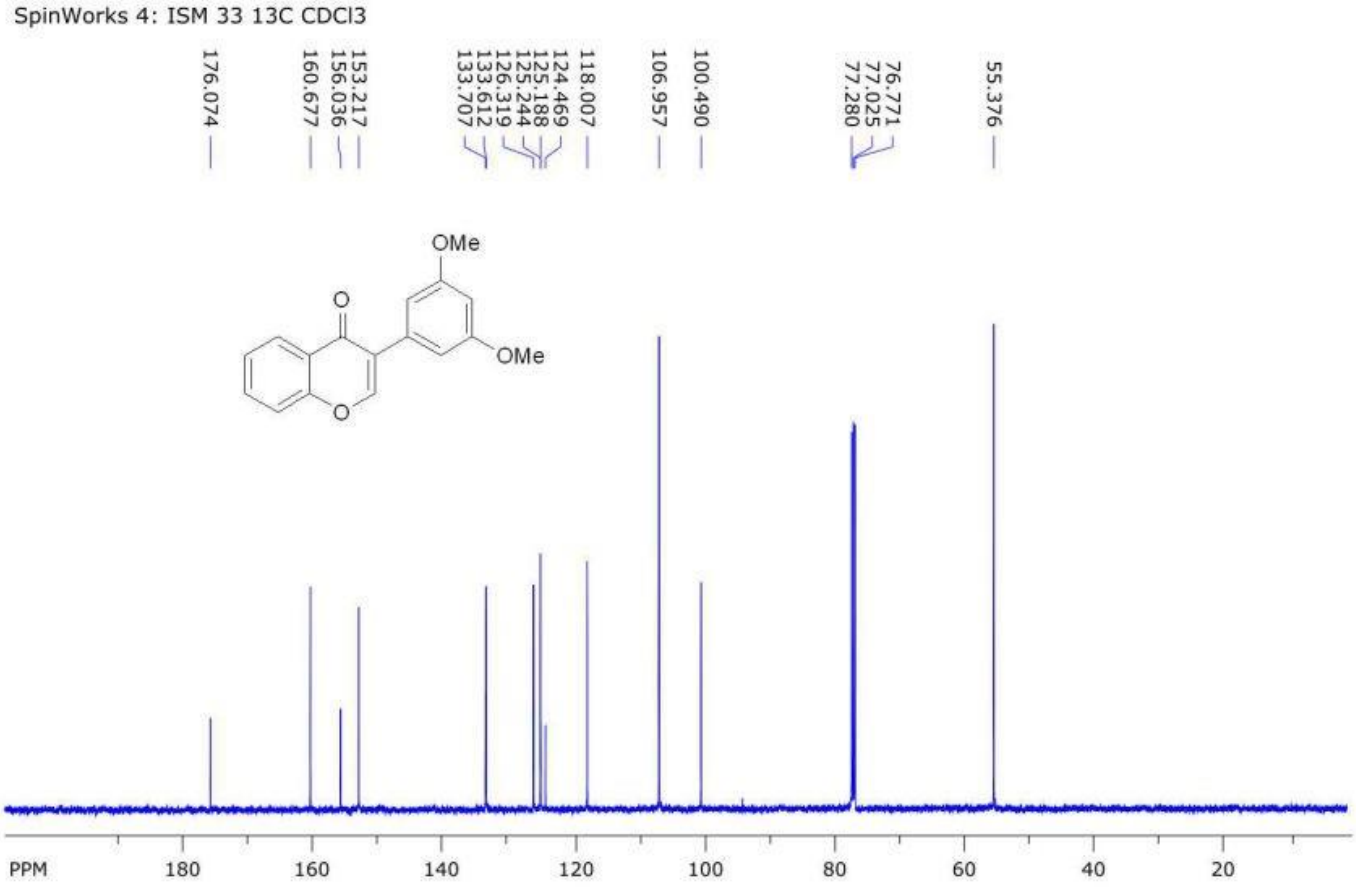
Compound **4r**



file: D:\NAPO\NMR\500-1\mkr11004\5\fid expt: <zg30>
transmitter freq.: 500.133001 MHz
time domain size: 65536 points
width: 12335.53 Hz = 24.6645 ppm = 0.188225 Hz/pt
number of scans: 24

freq. of 0 ppm: 500.130024 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 358.604 ppm/cm: 0.71702

Compound **4r**



file: D:\NAPO\NMR\500-1\mkr11004\6\fid expt: <zgpg30>
transmitter freq.: 125.772879 MHz
time domain size: 65536 points
width: 36057.69 Hz = 286.6889 ppm = 0.550197 Hz/pt
number of scans: 512

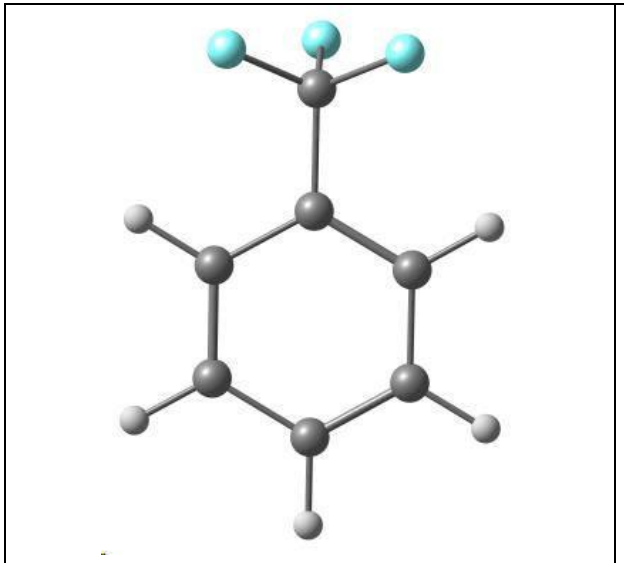
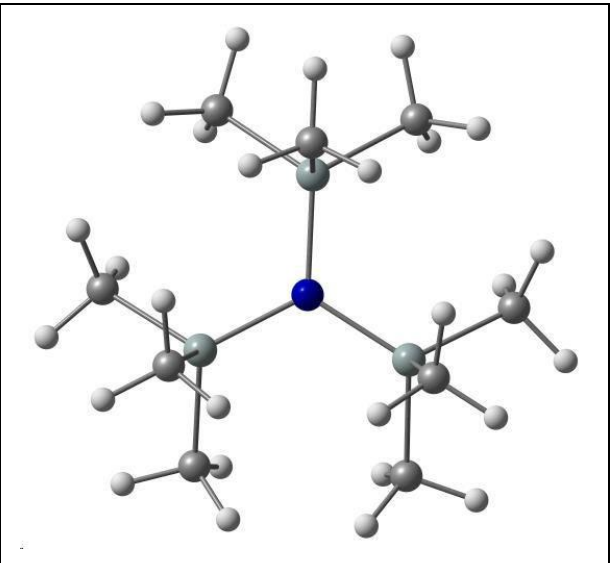
freq. of 0 ppm: 125.757800 MHz
processed size: 32768 complex points
LB: 2.000 GF: 0.0000
Hz/cm: 1040.248 ppm/cm: 8.27085

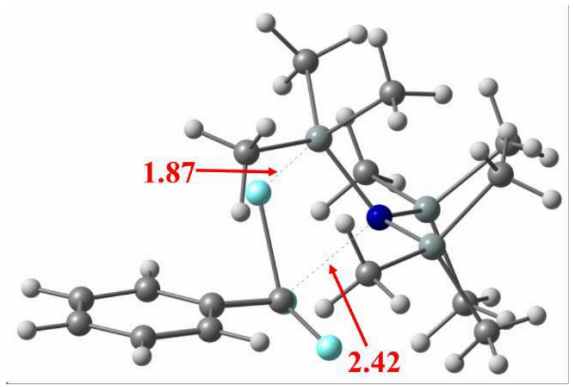
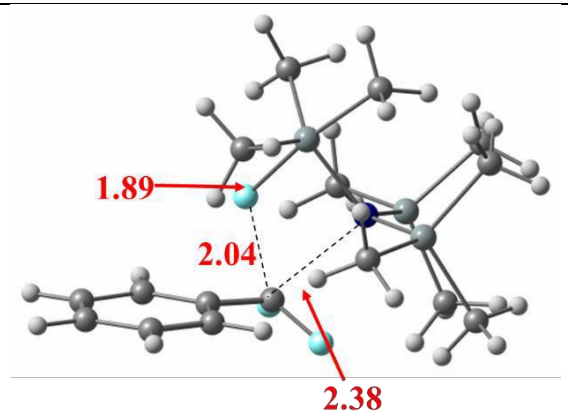
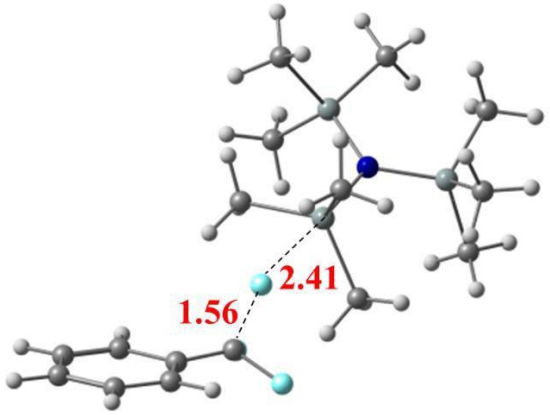
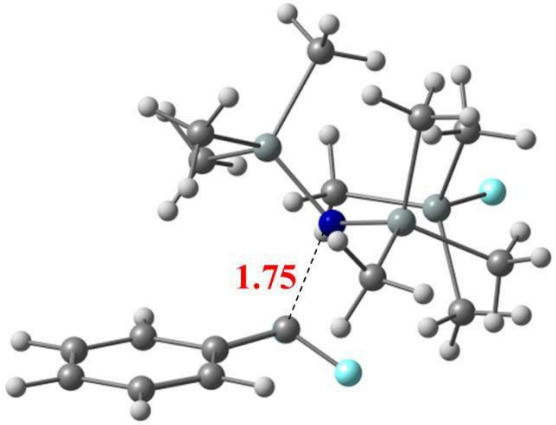
(D) Computational study

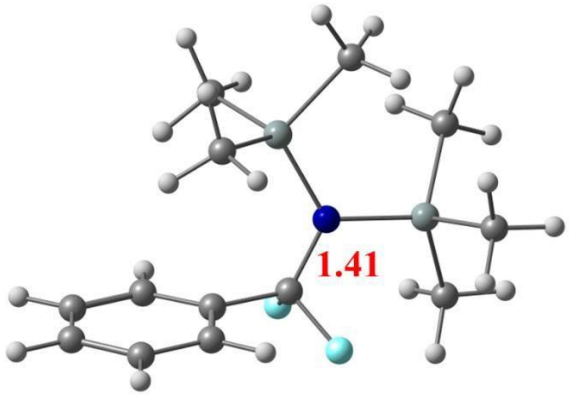
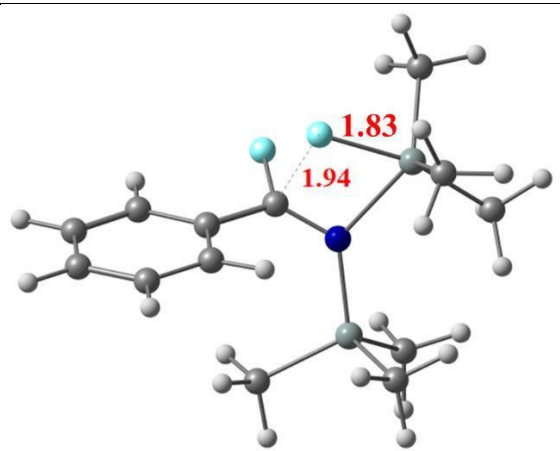
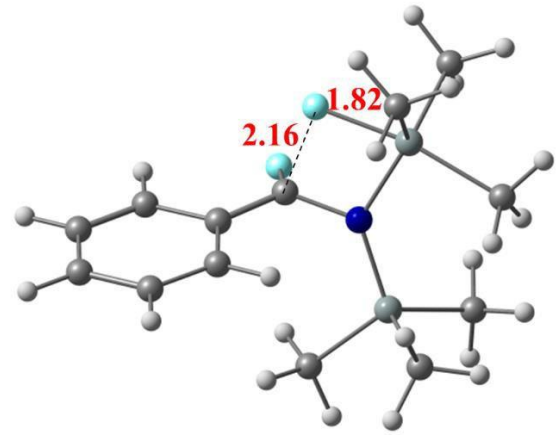
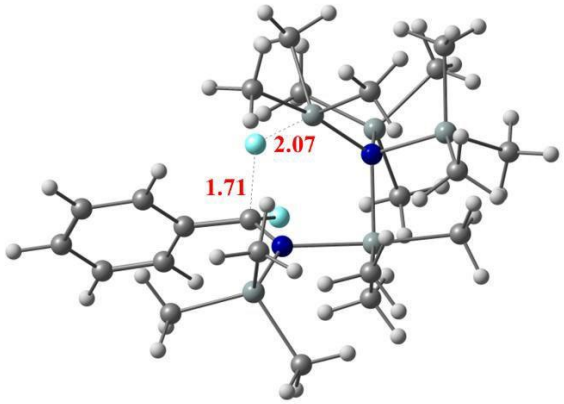
Computational methodology

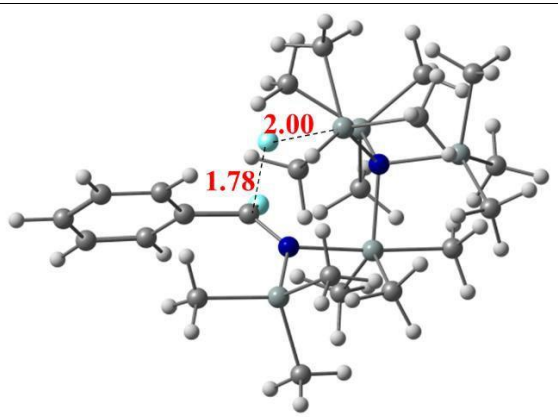
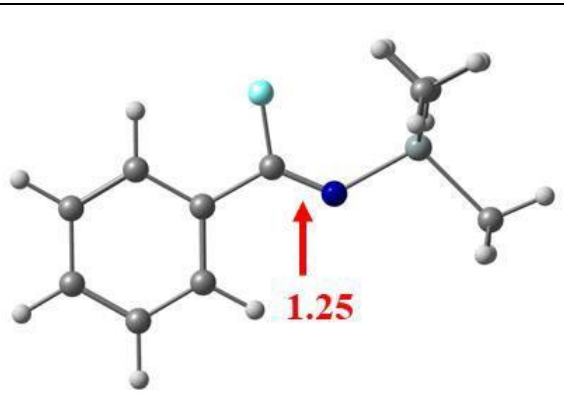
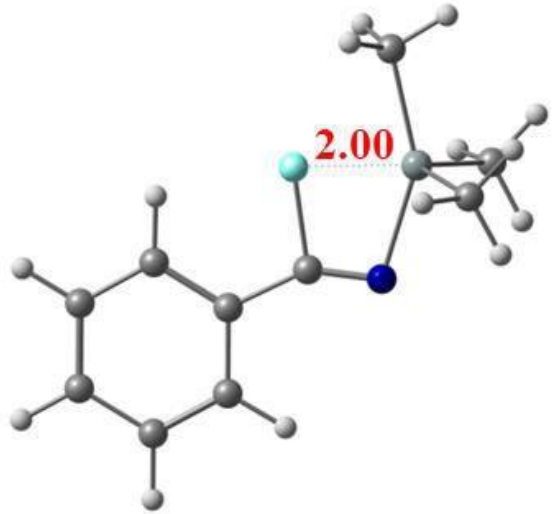
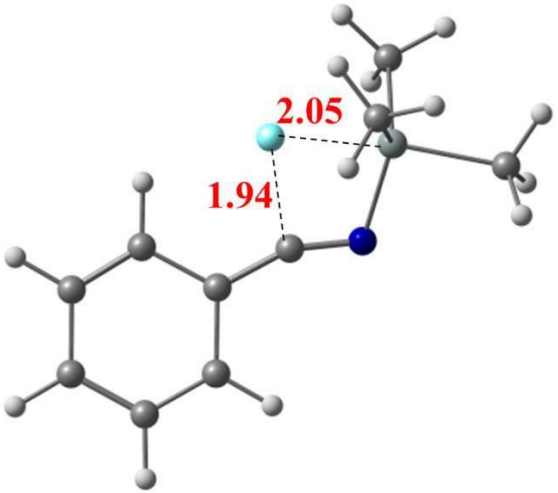
In current study, all the simulations of mechanistic part are performed using Gaussian09 software.[1] B3LYP/6-31G(d,p) level of theory is used to perform the geometry optimization of ground states as well as for transition states. B3LYP is a cost effective DFT functional which is not only reliable for mechanistic studies, but also frequently implemented for geometric optimization of various compounds.[2–4]
Nature of optimized structures is confirmed via frequency analysis i.e., absence of negative frequency confirms the true minima nature of reactants, intermediates, and products. On the other hand, transition states are confirmed from the presence of one imaginary frequency. Furthermore, imaginary frequency of transition states is also analyzed to validate that eigen vector of these states correspond to motion along the reaction coordinates.[5] All the energy values are reported in kcal/mol while bond distances for all structures are in angstrom (Å).

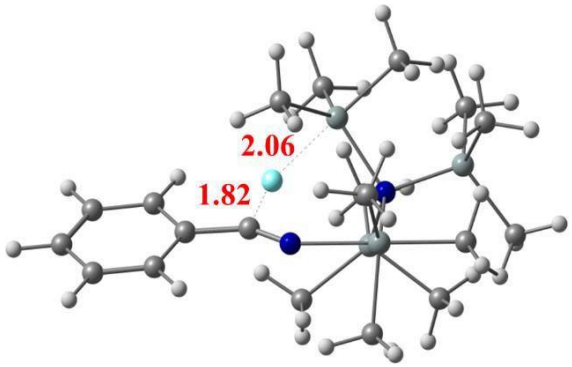
Cartesian Coordinates of optimized geometries

	
Trifluoromethylbenzene	**Tris(trimethylsilyl)amine**

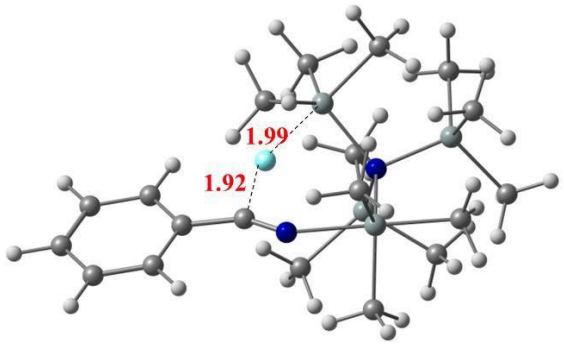
	
TS	**TS1$^{\bullet-}$**
	
TS1$^{\bullet-}$ (step I)	**TS1$^{\bullet-}$ (step II)**

	
Int1	**TS2**
	
TS2$^{\bullet-}$	**TS2'**

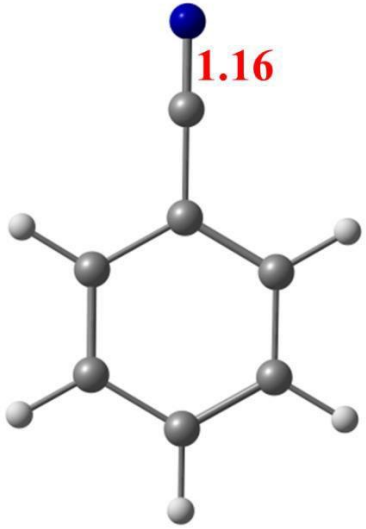
	
TS2'$^{\bullet-}$	**Int2**
	
TS3	**TS3$^{\bullet-}$**



TS3’



TS3’$^{\bullet-}$



Benzonitrile

Table S4: Summary of electronic energy (SCF energy), zero-point vibrational energy (ZPVE) and Gibbs free energy of optimized reacting species			
Optimized Geometry	SCF energy (au)	ZPVE (au)	Gibbs free energy (au)
Trifluoromethylbenzene	-569.29	-569.19	-569.22
Tris(trimethylsilyl)amine	-1282.66	-1282.32	-1282.36
TS1	-1851.84	-1851.29	-1851.35
$TS1^{\bullet-}$	-1851.78	-1851.30	-1851.35
$TS1^{\bullet-}$ (step I)	-1851.92	-1851.29	-1851.35
$TS1^{\bullet-}$ (step II)	-1851.95	-1851.26	-1851.34
Int1	-1106.84	-1106.68	-1106.72
TS2	-1106.79	-1106.64	-1106.68
$TS2^{\bullet-}$	-1106.11	-1106.93	-1106.97
TS2’	-2153.43	-2153.19	-2153.24
$TS2'^{\bullet-}$	-2153.36	-2153.03	-2153.07
Int2	-833.67	-833.54	-833.58
TS3	-833.62	-833.49	-833.53
$TS3^{\bullet-}$	-833.63	-833.52	-833.55
TS3’	-1762.24	-1762.09	-1762.13
$TS3'^{\bullet-}$	-1762.25	-1761.96	-1762.00
Benzonitrile	-324.50	-324.40	-324.43

Trifluoromethyl benzene

0 1

C -0.03418200 2.83637500 0.00000000

C	-0.03508700	2.13872200	-1.20921700
C	-0.03508700	0.74448100	-1.21200900
C	-0.03556900	0.04904200	0.00000000
C	-0.03508700	0.74448100	1.21200900
C	-0.03508700	2.13872200	1.20921700
H	-0.03587700	3.92244300	0.00000000
H	-0.03907000	2.67959000	-2.15068900
H	-0.04322800	0.19596700	-2.14763600
H	-0.04322800	0.19596700	2.14763600
H	-0.03907000	2.67959000	2.15068900
C	0.02352400	-1.45511600	0.00000000
F	-0.57682200	-1.98331200	1.09038900
F	-0.57682200	-1.98331200	-1.09038900
F	1.30030200	-1.90602100	0.00000000

Tris(trimethylsilyl)amine

0 1

N	0.00035600	0.00012500	-0.00038000
Si	-0.97372700	1.45852100	0.00003400
Si	-0.77653400	-1.57237700	0.00003100
Si	1.75015400	0.11381800	0.00003400
H	-0.71609000	2.29681200	-1.20101800

H	-2.40151900	1.04434400	-0.00050100
H	-0.71682900	2.29584600	1.20194100
H	-1.63199200	-1.76759800	-1.20068400
H	0.29543700	-2.60243400	-0.00116800
H	-1.62977100	-1.76829400	1.20223300
H	2.34724200	-0.52941500	-1.20055800
H	2.10603100	1.55724900	-0.00133500
H	2.34649500	-0.52685900	1.20236400

TS1

v_i = -326.77

Energy = -1851.84

0 1

C	5.06503300	0.41712400	0.10035300
C	4.17365300	1.42814300	-0.25744100
C	2.87245700	1.10834300	-0.63917900
C	2.46539100	-0.23180300	-0.63935300
C	3.35397500	-1.25087700	-0.25793300
C	4.65535800	-0.92160200	0.09137000
H	6.08053500	0.66876700	0.39020300
H	4.49030300	2.46573600	-0.24666600
H	2.17945200	1.88830600	-0.93088300

H	3.01327400	-2.27826000	-0.24092100
H	5.35111700	-1.70583900	0.37099100
C	1.12327300	-0.57277200	-1.11209600
F	0.85325400	-1.77817500	-1.52755200
F	0.83802800	-1.32056000	0.77003100
F	0.67417900	0.27220400	-2.01332400
N	-0.95227100	0.04623900	-0.02700700
Si	-2.09719200	-1.18032900	-0.58931200
Si	-1.43624600	1.71844900	-0.36609700
Si	-0.32969200	-0.21202000	1.71581200
C	-0.82360400	-1.81537800	2.68992300
H	-0.48877000	-2.67723900	2.15142300
H	-0.36702000	-1.79974000	3.65749100
H	-1.88743700	-1.85348300	2.79812400
C	-1.66030300	0.97909000	2.47365800
H	-1.71440000	0.82661100	3.53135500
H	-1.38622100	1.99376800	2.27313800
H	-2.61418300	0.77384400	2.03446700
C	1.22697400	0.80289900	2.27288300
H	1.57900100	0.42939900	3.21175200
H	1.99849700	0.70465500	1.53803700
H	0.96199700	1.83441800	2.37611100

C	0.08712000	2.88007800	-0.06019600
H	0.06329900	3.24187200	0.94650000
H	0.99175700	2.33168200	-0.22079900
H	0.04650900	3.70737100	-0.73757100
C	-2.92323800	2.32637800	0.72150500
H	-2.54936500	2.85468000	1.57357100
H	-3.54550700	2.97699900	0.14325300
H	-3.49498700	1.48275700	1.04755300
C	-1.95136200	1.84626600	-2.23208700
H	-1.95415900	2.87343800	-2.53176800
H	-1.25349700	1.30134600	-2.83287500
H	-2.93054100	1.43451000	-2.36079700
C	-3.85323100	-0.91229000	0.19048300
H	-4.32128000	-0.06587900	-0.26713900
H	-4.45287000	-1.78324000	0.02683900
H	-3.75408000	-0.73991600	1.24184200
C	-2.27957200	-1.04016400	-2.51562700
H	-3.08477800	-0.37571000	-2.75024400
H	-1.37057000	-0.66042900	-2.93325900
H	-2.48396000	-2.00704500	-2.92583000
C	-1.46466100	-2.95295500	-0.11888200
H	-0.39903300	-2.93772500	-0.02346800

H	-1.90174200	-3.25256900	0.81068300
H	-1.74433900	-3.64625400	-0.88439900

TS1$^{\bullet-}$

v_i = -351.19

Energy = -1851.78

-1 2

C	5.06281500	0.41850800	0.09793500
C	4.17079500	1.42699100	-0.26587400
C	2.87042400	1.10437800	-0.64675100
C	2.46383800	-0.23591900	-0.64048300
C	3.35258900	-1.25231600	-0.25249000
C	4.65362000	-0.92041900	0.09588800
H	6.07794600	0.67230000	0.38703700
H	4.48707300	2.46476000	-0.26063700
H	2.17691200	1.88228700	-0.94320700
H	3.01227600	-2.27971600	-0.22998600
H	5.34939200	-1.70317500	0.38079600
C	1.12297700	-0.57976900	-1.11271800
F	0.85309900	-1.78729100	-1.52164600
F	0.83589100	-1.31974400	0.77421200
F	0.67243500	0.26054900	-2.01725900
N	-0.95301700	0.04556800	-0.02794200

Si	-2.09777600	-1.18676800	-0.57694000
Si	-1.44034200	1.71498000	-0.37582000
Si	-0.32368200	-0.19828900	1.71436300
C	-1.45084900	-2.95655500	-0.11548800
H	-1.71309900	-3.17921000	0.89770000
H	-1.89591400	-3.67990900	-0.76631500
H	-0.38672400	-2.98666600	-0.22333700
C	-0.82284900	-1.79015600	2.70451000
H	-0.29915600	-2.63517500	2.30879600
H	-0.56764800	-1.66334200	3.73586300
H	-1.87705700	-1.94994000	2.61498100
C	-3.84586600	-0.92871100	0.22380100
H	-4.44157000	-0.30815000	-0.41254900
H	-4.32521900	-1.87734300	0.34716400
H	-3.73496200	-0.45830900	1.17843300
C	-1.64431500	1.00795700	2.46569400
H	-1.72009100	0.84191800	3.52001400
H	-1.34720900	2.01977100	2.28442100
H	-2.59403400	0.82748100	2.00704300
C	1.24052300	0.81326900	2.25622500
H	1.60614300	0.43321000	3.18723400
H	2.00142000	0.72060600	1.50966800

H	0.97673500	1.84391300	2.37063700
C	0.07773100	2.88238400	-0.06562600
H	0.03350900	3.71182700	-0.74013900
H	0.05211900	3.24057800	0.94231300
H	0.98485400	2.33862400	-0.22796400
C	-2.93658500	2.32213900	0.69945500
H	-2.57533100	2.93057600	1.50207600
H	-3.60434800	2.89485800	0.09036900
H	-3.45532200	1.47586000	1.09898400
C	-1.94443500	1.83397500	-2.24540000
H	-1.90346800	2.85538600	-2.56153600
H	-1.26826700	1.25075500	-2.83493600
H	-2.93959900	1.46141500	-2.37088900
C	-2.30385400	-1.04630300	-2.50084300
H	-3.09287600	-0.35948100	-2.72583200
H	-1.39041200	-0.69403100	-2.93261700
H	-2.54193500	-2.00792200	-2.90520100

TS1$^{\bullet-}$ (Step I)

v_i = -171.80

Energy = -1851.92

-1 2

C	5.36966100	1.03860000	-0.50767900

C	5.02621000	-0.25660500	-1.00640700
C	3.84092100	-0.85143900	-0.67628600
C	2.89326000	-0.20527700	0.22042800
C	3.25299900	1.11870200	0.70186500
C	4.45670100	1.69961200	0.35181700
H	6.31362700	1.50385800	-0.78173100
H	5.70250200	-0.76849500	-1.68766500
H	3.58225500	-1.82847200	-1.07579900
H	2.57119800	1.62738700	1.38086000
H	4.70881400	2.67215200	0.76660700
C	1.63659100	-0.75779900	0.46639900
F	0.98902800	-0.31399900	1.58937900
F	1.55409100	-2.12844000	0.43648800
F	0.50984900	-0.44939500	-0.56056200
N	-3.65342000	0.22047900	-0.14784400
Si	-4.71004300	-1.16118500	-0.01720300
Si	-4.18600000	1.87616900	-0.12666200
Si	-1.86790700	-0.10029400	-0.32933600
C	-1.13256974	1.64724887	0.08172731
H	-0.06563653	1.58274182	0.13063900
H	-1.41325677	2.34115478	-0.68287021
H	-1.51324351	1.98170056	1.02413357

C	-1.56428869	-1.52468397	0.95227593
H	-1.92462650	-2.44865970	0.55062245
H	-0.51637394	-1.60722105	1.15218170
H	-2.08440613	-1.30378796	1.86089180
C	-1.67231300	-0.65360548	-2.17844103
H	-0.64656504	-0.56641818	-2.47022775
H	-1.98720739	-1.67101338	-2.28150748
H	-2.27528749	-0.02856167	-2.80345463
C	-4.29842815	-2.49944663	-1.36004663
H	-5.09680565	-3.20993701	-1.41197728
H	-4.18060801	-2.02512676	-2.31190748
H	-3.39084616	-3.00138920	-1.09689536
C	-4.60069884	-2.06113091	1.69794749
H	-5.57523342	-2.39333478	1.98919125
H	-3.94592912	-2.90357955	1.61759259
H	-4.22062559	-1.38284008	2.43304332
C	-6.55896926	-0.62670507	-0.26093011
H	-7.18324085	-1.49567421	-0.26973971
H	-6.85336383	0.01582499	0.54242968
H	-6.66007126	-0.10547562	-1.18990710
C	-6.12454383	1.95096892	-0.11939581
H	-6.50331511	1.47029494	-0.99711151

H	-6.49750483	1.45115178	0.75007697
H	-6.44200795	2.97271568	-0.10714526
C	-3.58811467	2.85870838	1.43562782
H	-2.81898485	3.54628187	1.15175812
H	-4.41183043	3.39804544	1.85456442
H	-3.20376736	2.17371361	2.16223591
C	-3.59411305	2.88911566	-1.67172151
H	-4.30127935	3.66397341	-1.88246139
H	-2.63816016	3.32446000	-1.46793394
H	-3.51644666	2.23760037	-2.51694087

TS1$^{\bullet-}$ (Step II)

v_i = -334.33

Energy = -1851.95

-1 2

C	4.49531500	-0.40387900	0.23141800
C	3.94679000	0.78936500	-0.29871200
C	2.62034700	0.87767500	-0.66393100
C	1.73868400	-0.25491800	-0.52895700
C	2.30624000	-1.46254200	0.01615100
C	3.63767200	-1.51972600	0.37534800
H	5.53974900	-0.45844700	0.52423600
H	4.58762500	1.66086000	-0.43112600

H	2.23078400	1.80085400	-1.08198600
H	1.67558800	-2.34018300	0.11842300
H	4.03570000	-2.45510000	0.76810000
C	0.34159800	-0.14392400	-0.79235400
F	-0.27599100	-1.33491000	-1.05655000
F	0.02155900	0.74145400	-1.80751600
F	-5.07268268	-1.23638722	-0.62830301
N	-0.88693232	0.62441068	0.64530491
Si	-3.58790868	-0.62334122	-0.27624401
Si	-1.24601532	2.31899068	0.45005691
Si	-0.61305732	-0.00169532	2.24941691
C	0.30304736	3.42353057	0.07058829
H	0.97718174	2.88665391	-0.56360906
H	-0.01048030	4.32092839	-0.42061183
H	0.79682023	3.67221415	0.98669136
C	-2.53974093	2.67871721	-0.95011125
H	-2.75332545	3.72682138	-0.97766656
H	-2.13903925	2.37145311	-1.89347064
H	-3.44040750	2.13628290	-0.75145391
C	-2.00565700	3.05385112	2.07687117
H	-2.83468512	2.45251437	2.38672030
H	-1.26228551	3.06019164	2.84645459

H	-2.33897782	4.05415684	1.89470176
C	0.90232883	0.75111968	3.19835019
H	1.27275455	0.03625956	3.90309113
H	1.67467457	0.99633132	2.49959894
H	0.59536275	1.63598043	3.71574103
C	-0.36107479	-1.92420620	2.18572447
H	0.52696370	-2.14940872	1.63293928
H	-0.26759713	-2.30485001	3.18135101
H	-1.20361099	-2.37871337	1.70775377
C	-2.15157909	0.32423879	3.38533844
H	-2.01042048	1.23827804	3.92339651
H	-3.03164627	0.39822175	2.78126205
H	-2.26123629	-0.48401577	4.07786993
C	-2.64296982	-2.12101816	0.51600238
H	-2.58930659	-2.92286239	-0.19044371
H	-1.65332176	-1.81613925	0.78534526
H	-3.16510373	-2.45009080	1.39006610
C	-3.96958402	0.79180085	0.99469928
H	-3.05147502	1.22678735	1.33050072
H	-4.56855174	1.54267377	0.52318307
H	-4.49923689	0.38645759	1.83139795
C	-2.91278986	0.00993491	-1.98117096

H	-1.94398379	0.44253287	-1.84270142
H	-2.84262366	-0.81080137	-2.66408286
H	-3.57940296	0.74735429	-2.37707453

Int 1

0 1

C	3.73749500	-2.83638300	-0.38371100
C	3.77101100	-1.73803400	-1.24598300
C	2.86872700	-0.68994300	-1.07633400
C	1.92600200	-0.73594000	-0.04280300
C	1.88828100	-1.83807600	0.81528000
C	2.79693100	-2.88350300	0.64534000
H	4.44345000	-3.65128900	-0.51379300
H	4.50040100	-1.69707500	-2.04927100
H	2.89447700	0.16843400	-1.73989700
H	1.15680300	-1.87016900	1.61347100
H	2.76852900	-3.73438100	1.31928100
C	0.92132900	0.39311800	0.08487300
F	0.19773900	0.22675500	1.26075300
F	-0.02442800	0.25753900	-0.92915000
N	1.43490600	1.71377400	0.00082600
Si	2.56124500	2.28940200	1.23960500
Si	0.61976100	2.86548000	-1.06968300

C	-1.26485374	3.09811321	-0.67255698
H	-1.56989714	4.08395694	-0.95533011
H	-1.83619275	2.37736997	-1.21936674
H	-1.42792334	2.96132065	0.37605930
C	1.54239686	4.53705164	-0.72589334
H	2.58974305	4.40952239	-0.90394458
H	1.15987201	5.29585993	-1.37611231
H	1.38645177	4.82772150	0.29199278
C	0.83900146	2.39682102	-2.93941356
H	0.61702995	3.24784639	-3.54882679
H	1.84825818	2.08697793	-3.11347718
H	0.17263746	1.59715166	-3.18717944
C	3.96365626	3.32362351	0.38682806
H	3.79194118	4.36593362	0.55713244
H	4.91167783	3.04642984	0.79831169
H	3.96084431	3.12892797	-0.66530584
C	1.67327812	3.41889004	2.54320447
H	1.97101604	3.12792913	3.52889909
H	1.94584754	4.43983850	2.37506714
H	0.61321602	3.31186727	2.44464246
C	3.31690116	0.74648653	2.14071300
H	2.52703556	0.13737851	2.52801100

H	3.89848559	0.17716913	1.44606400
H	3.94196161	1.07392290	2.94506670

TS2

v_i = -361.60

Energy = -1106.79

0 1

C	3.68343200	0.35340300	0.50310500
C	3.40214500	-0.55743900	-0.51802400
C	2.08217500	-0.84863700	-0.84872100
C	1.03434200	-0.21224000	-0.16380800
C	1.32168100	0.69534900	0.86891800
C	2.64308500	0.97600300	1.19869600
H	4.71464300	0.57454900	0.76158000
H	4.21186500	-1.04193500	-1.05418500
H	1.85435000	-1.55493700	-1.63783500
H	0.50841200	1.15228600	1.42197900
H	2.86338800	1.67201300	2.00157400
C	-0.36389600	-0.49162500	-0.51107100
F	-1.06559900	-1.55459700	0.93702700
F	-0.48733400	-1.49748900	-1.38999700
N	-1.40329600	0.30954100	-0.35898400
Si	-2.64822100	-0.64669300	0.78342700

Si	-1.54677700	2.03087700	-0.68634700
C	-0.04964788	2.54198310	-1.80927841
H	0.79381752	2.77662526	-1.19412869
H	0.19946157	1.73167694	-2.46215544
H	-0.31648694	3.39954574	-2.39089963
C	-1.50874971	3.09435821	0.93573858
H	-0.68181106	3.77235456	0.89841016
H	-2.42039548	3.64806482	1.02065614
H	-1.40306880	2.44921419	1.78280454
C	-3.21675828	2.34572867	-1.62209854
H	-4.03125875	2.27468805	-0.93185061
H	-3.20270373	3.32288423	-2.05783868
H	-3.33738412	1.61326890	-2.39271654
C	-3.82294038	0.88346761	0.57789626
H	-3.32737382	1.76355774	0.93110321
H	-4.07266603	1.00515298	-0.45541385
H	-4.71669328	0.72564630	1.14463974
C	-2.79012903	-0.77096469	2.71423477
H	-3.78607223	-0.52144455	3.01546034
H	-2.56306910	-1.76933861	3.02502942
H	-2.09951456	-0.09065246	3.16714417
C	-3.60170479	-2.04523361	-0.16449325

H	-3.12950061	-2.98738909	0.02061826
H	-4.61499887	-2.08086068	0.17736319
H	-3.58650521	-1.83881076	-1.21428303

TS2$^{\bullet-}$

v_i = -506.96

Energy = -1106.11

-1 2

C	-3.74594200	0.38490200	-0.49124500
C	-3.42185000	-0.59587100	0.48655600
C	-2.09268700	-0.87423900	0.80236800
C	-0.99273900	-0.17239100	0.16443500
C	-1.35896600	0.80879900	-0.83984000
C	-2.69224700	1.07684100	-1.14960300
H	-4.77850800	0.59778300	-0.73407200
H	-4.22158000	-1.12784700	0.98714800
H	-1.86986700	-1.62518800	1.54942800
H	-0.57582300	1.34287000	-1.36168800
H	-2.93530500	1.81940100	-1.89966800
C	0.34892600	-0.50867100	0.42787600
F	1.06226700	-1.69683800	-0.59856000
F	0.54904500	-1.24000800	1.58181100
N	1.46645600	0.33486200	0.06530900

Si	2.48288900	-0.64123100	-0.99724400
Si	1.72310500	1.88353000	0.77044300
C	2.09396580	-0.90399660	-2.87960767
H	3.00908312	-0.92155009	-3.43382078
H	1.57941139	-1.83287397	-3.01121537
H	1.47889377	-0.10249305	-3.23199732
C	3.84449526	0.72343119	-1.21478824
H	3.40378349	1.60317837	-1.63516667
H	4.26968912	0.95821071	-0.26137923
H	4.61100191	0.36157864	-1.86780455
C	3.64938392	-2.04496747	-0.33966243
H	4.58079964	-2.01005889	-0.86515853
H	3.82441039	-1.90247855	0.70626426
H	3.18631749	-2.99659046	-0.49740645
C	1.80658617	3.30706552	-0.54491913
H	1.15230594	4.10163890	-0.25256569
H	2.80909174	3.67563918	-0.60844891
H	1.50440453	2.92906399	-1.49922574
C	3.39123479	1.98623726	1.75552889
H	4.16313929	2.35432075	1.11242860
H	3.27395837	2.64885383	2.58744566
H	3.65665730	1.01218495	2.11003276

C	0.30890702	2.33953491	2.01772148
H	-0.58786604	2.55717448	1.47612098
H	0.13586668	1.51523872	2.67764028
H	0.59872498	3.19769933	2.58733484

TS2'

v_i = -506.96

Energy = -2153.35

0 1

C	-5.03515300	-0.60621900	-0.33467100
C	-4.51889900	-0.77294700	0.95093100
C	-3.14945200	-0.63627900	1.17911700
C	-2.29287400	-0.31991900	0.11869200
C	-2.80970100	-0.16167800	-1.17218200
C	-4.17770900	-0.30316000	-1.39514500
H	-6.10146300	-0.71679500	-0.51172400
H	-5.18011600	-1.01485200	1.77827200
H	-2.74442900	-0.77275600	2.17637300
H	-2.13853000	0.05513300	-1.99602200
H	-4.57367400	-0.18384700	-2.39969700
C	-0.83615200	-0.11774800	0.40300800
F	-0.13260500	-1.00376700	-0.87701400
F	-0.41985600	-0.99010200	1.38578100

N	-0.21778500	1.04914600	0.44370900
Si	-0.93352300	2.61846500	0.05841200
H	-0.41508600	3.15147700	-1.22762900
H	-2.40905200	2.51719900	-0.01328000
H	-0.57537600	3.56633100	1.14231700
N	2.27668100	-0.25527600	-0.09859500
Si	4.08329100	0.12595100	-0.30931800
H	4.26014700	1.54774000	-0.66160300
H	4.82247400	-0.25823400	0.91335600
H	4.56489300	-0.75663900	-1.39991000
Si	2.24103700	-1.92575700	0.68732700
H	2.12954800	-1.74487000	2.15016000
H	1.20743900	-2.81393700	0.13940600
H	3.57046100	-2.51591900	0.38210400
H	2.73288900	0.44089800	-2.45106500
H	0.51262600	0.83567100	-2.19601600
H	1.48331600	-1.50816700	-2.50483800
Si	1.50903200	-0.18934000	-1.83011400
H	3.16167400	1.21461800	1.57906100
H	1.15136700	0.93938600	2.50969800
H	1.70657100	2.54769600	0.55057000
Si	1.69400800	1.18248700	1.14706800

TS2'$^{\bullet-}$

v_i = -265.78

Energy = -2153.36

-1 2

C	-5.23232500	0.72845300	-0.35397600
C	-4.83350400	-0.37157100	-1.10313300
C	-3.49292100	-0.76001500	-1.12816200
C	-2.54742000	-0.05955700	-0.36552300
C	-2.95572600	1.04097400	0.39416800
C	-4.29047600	1.43986700	0.39159200
H	-6.27126300	1.03723400	-0.35077900
H	-5.55207000	-0.93756100	-1.68780600
H	-3.17728000	-1.61221400	-1.72379100
H	-2.24675800	1.57093400	1.01783600
H	-4.59182100	2.30045800	0.98462700
C	-1.12506400	-0.53574700	-0.37099800
F	-0.25074000	0.97051900	-0.63373400
F	-0.79597100	-1.03359800	-1.60621000
N	-0.49999900	-1.12381000	0.62471600
Si	-1.10511700	-1.43071600	2.25287900
N	2.04129200	-0.29679100	-0.40797300
Si	3.85384400	-0.44673300	-0.03640400

Si	1.92662400	-0.25058700	-2.25632200
Si	1.43424500	1.31008400	0.44057300
Si	1.34205500	-1.99159400	0.32957400
C	1.53434600	2.86103400	-0.72103900
H	0.59924300	2.93183600	-1.30649000
H	1.70678400	3.77370800	-0.10987500
H	2.38976200	2.71355300	-1.40912900
C	3.09626300	1.53692500	1.42430900
H	3.53278100	0.55646500	1.74263800
H	3.79242900	2.03638000	0.72316500
H	2.91042500	2.11641500	2.33818900
C	0.12354500	1.37810400	1.87906900
H	0.47350400	2.03633000	2.70363300
H	-0.79982500	1.76443700	1.38712600
H	-0.04222900	0.36299700	2.28993800
C	0.09960547	-0.61115153	3.53372163
H	-0.30572536	-0.71081229	4.51894985
H	1.05193749	-1.09691483	3.48902548
H	0.21706434	0.42630020	3.29963337
C	-2.90237874	-0.73528304	2.47609024
H	-2.88375642	0.33191569	2.40098975
H	-3.53697910	-1.13549903	1.71319474

H	-3.27767350	-1.01870242	3.43719756
C	-1.10078052	-3.34661998	2.55766274
H	-0.13239646	-3.74156014	2.33148895
H	-1.33660318	-3.54531120	3.58226484
H	-1.83095018	-3.80969809	1.92733669
C	0.42378928	-3.34564360	-0.71298907
H	1.10236740	-3.77005791	-1.42313288
H	0.06299201	-4.11376128	-0.06128318
H	-0.40045752	-2.89993244	-1.22957281
C	1.41931357	-2.11740832	2.26394777
H	0.47721597	-1.82474348	2.67831404
H	1.63567580	-3.12624208	2.54739410
H	2.18766064	-1.47063176	2.63303158
C	4.11129905	-1.05359403	1.78816077
H	4.09830285	-2.12321586	1.81346370
H	5.05314262	-0.69963214	2.15222349
H	3.32444998	-0.67264594	2.40512681
C	4.65488645	1.30073271	-0.29773632
H	5.01641931	1.67102528	0.63878779
H	5.46878510	1.22042288	-0.98767784
H	3.92126678	1.97455799	-0.68845575
C	4.65519142	-1.67096269	-1.31025798

H	4.87230204	-1.14884443	-2.21863868
H	5.56096280	-2.06814159	-0.90193564
H	3.97428947	-2.47112128	-1.51278890
C	1.60627555	-2.05593917	-2.89010462
H	0.56842755	-2.29289515	-2.78229279
H	1.88292843	-2.12627918	-3.92132500
H	2.19078376	-2.74437827	-2.31625641
C	0.64320240	1.04538012	-2.91730478
H	1.12396066	1.99357900	-3.03850866
H	0.25855170	0.71737704	-3.86036247
H	-0.16077143	1.13997000	-2.21760568
C	3.69233654	0.32334527	-2.81887063
H	3.93087206	-0.12706643	-3.75968417
H	3.70585302	1.38849456	-2.91973827
H	4.41415654	0.02515779	-2.08746096
C	3.12524404	-2.69082327	0.02149079
H	3.34001841	-2.67089817	-1.02654307
H	3.83948503	-2.08889202	0.54344730
H	3.17973976	-3.69833686	0.37764605

Int2

0 1

C	-3.42419900	-0.34042000	-0.00004200

C	-2.91750000	0.96020700	-0.00008700
C	-1.54057400	1.17455100	-0.00005700
C	-0.66236300	0.08106100	0.00002000
C	-1.17564300	-1.22555000	0.00007000
C	-2.55093200	-1.43245800	0.00003700
H	-4.49783300	-0.50438700	-0.00006800
H	-3.59478000	1.80875100	-0.00014700
H	-1.14078300	2.18137200	-0.00009100
H	-0.48020700	-2.05760900	0.00013200
H	-2.94474200	-2.44424600	0.00007500
C	0.79924600	0.27271900	0.00005600
F	1.13390800	1.61033900	0.00014300
N	1.67748900	-0.62083500	0.00002000
Si	3.41304300	-0.36622600	-0.00007100
C	3.98365546	0.60385628	1.58010044
H	4.98994722	0.33188432	1.82157125
H	3.93428561	1.65569064	1.39008175
H	3.34145264	0.35903903	2.40018583
C	4.25912991	-2.11200287	-0.00031452
H	3.94818387	-2.65892805	-0.86581173
H	5.32237346	-1.99304856	-0.01653245
H	3.97348836	-2.64690855	0.88126635

C	3.98334459	0.60420654	-1.58013960
H	5.02069234	0.41380626	-1.76057624
H	3.40947921	0.28126890	-2.42351959
H	3.83440987	1.65278282	-1.42780373

TS3

v_i = -425.27

Energy = -833.62

0 1

C	3.43585500	-0.16294500	0.00007500
C	2.60784900	-1.28707600	0.00009400
C	1.22290000	-1.13965200	0.00003000
C	0.66732500	0.14709200	-0.00004400
C	1.49860200	1.28142600	-0.00007600
C	2.87993200	1.11948200	-0.00001500
H	4.51481100	-0.28475600	0.00012100
H	3.04074400	-2.28238700	0.00015000
H	0.56615800	-1.99999100	0.00001000
H	1.05155600	2.26970700	-0.00015300
H	3.52346700	1.99352400	-0.00004200
C	-0.76249400	0.38092600	-0.00009600
F	-1.55339700	-1.10826500	0.00015300

N	-1.66052400	1.18976900	-0.00021300
Si	-3.21796300	0.00540400	0.00000400
C	-3.93044595	0.78452648	1.62755929
H	-3.88280177	1.85150080	1.56278404
H	-4.94848924	0.47991368	1.75285451
H	-3.35301404	0.45188695	2.46471120
C	-3.93105759	0.78513745	-1.62699073
H	-3.37594227	0.42534989	-2.46800196
H	-4.95931712	0.50916335	-1.73385810
H	-3.85121795	1.85095816	-1.57647480
C	-3.98982183	-1.77443696	-0.00032688
H	-3.66843712	-2.30240961	-0.87374359
H	-3.66949471	-2.30227580	0.87355909
H	-5.05724948	-1.70028990	-0.00097864

TS3$^{\bullet-}$

v_i = -296.12

Energy = -833.631

-1 2

C	4.38597100	-0.10085600	0.10367700
C	3.53125900	-1.22503700	0.02403100
C	2.16488600	-1.09332700	-0.09943500
C	1.56022900	0.21267100	-0.15289000

C	2.43961000	1.35757700	-0.06211200
C	3.80307100	1.18379300	0.06121400
H	5.46108900	-0.22208300	0.20035800
H	3.95933000	-2.22605100	0.06505400
H	1.50338100	-1.94926600	-0.14287500
H	2.00823000	2.35372800	-0.09512100
H	4.44008600	2.06544300	0.12556400
C	0.20049900	0.41978600	-0.27972700
F	-0.68815000	-1.26916500	0.08333500
N	-0.83784300	1.05252900	-0.48962400
Si	-2.26202500	0.04561000	0.02585600
C	-2.46079600	-0.44433300	1.86161300
H	-3.37261900	-0.03796500	2.31517900
H	-2.45541000	-1.53241800	1.97712700
H	-1.60307700	-0.06649700	2.42971900
C	-3.56009000	1.48626200	-0.09784600
H	-3.58501400	1.91495600	-1.10844500
H	-4.57821700	1.14585400	0.14161300
H	-3.31795800	2.30567600	0.59222000
C	-2.97232000	-1.15384400	-1.27733700
H	-2.43569100	-1.00850900	-2.22232700
H	-2.81241300	-2.19371700	-0.97821900

H	-4.03903500	-0.98905800	-1.47159800

TS3'

v_i = -249.98

Energy = -1762.24

0 1

C	-5.19630700	-0.23627100	0.04699800
C	-4.69616600	1.06391200	-0.06334200
C	-3.32309400	1.28160600	-0.10611400
C	-2.43644100	0.18997700	-0.04042500
C	-2.93937800	-1.11380100	0.07198600
C	-4.31708800	-1.31827800	0.11499100
H	-6.26927600	-0.40415500	0.08043900
H	-5.37608300	1.90933500	-0.11565300
H	-2.92199800	2.28599100	-0.19142000
H	-2.24915000	-1.94338000	0.12758000
H	-4.70395100	-2.32950000	0.20187000
C	-1.02220800	0.51546400	-0.09121900
F	-0.22715600	-1.12092900	0.02478900
N	-0.22649200	1.38766800	-0.17046500
N	2.17634300	-0.05939400	0.03189200
Si	3.99768300	-0.14292000	-0.26336300
H	4.36355900	0.49744700	-1.53816600

H	4.72679000	0.43666500	0.88424900
H	4.30885700	-1.59580600	-0.29550000
Si	1.78397700	-0.56173100	1.75471600
H	2.83347700	0.08220600	2.58331500
H	0.48138300	-0.08664700	2.24174600
H	1.92399800	-2.03098100	1.84315900
H	2.55774600	-1.22597400	-2.20880300
H	0.37023000	-0.69176000	-2.19665700
H	1.34606000	-2.63980700	-0.83213000
Si	1.38037200	-1.22485600	-1.26246500
H	3.23277400	2.12166800	-0.05536500
H	1.37040600	2.67692700	1.04584100
H	1.54167600	2.35253600	-1.53758600
Si	1.72675500	1.86379500	-0.14940600

TS3'$^{\bullet-}$

v_i = -249.98

Energy = -1762.25

-1 2

C	5.39897500	0.30511700	0.14457500
C	4.98560200	-0.89142400	-0.44894000
C	3.63386900	-1.19295700	-0.53390100
C	2.67666400	-0.28989700	-0.02294000

C	3.09274400	0.90941000	0.57925100
C	4.44992000	1.19902200	0.65907900
H	6.45972600	0.54007100	0.21722400
H	5.71734100	-1.58264000	-0.85336900
H	3.29677900	-2.11704000	-0.99091500
H	2.34595900	1.58399800	0.96581000
H	4.77802300	2.12766700	1.12641000
C	1.30688300	-0.71417300	-0.16976600
F	0.35724400	0.76671800	0.59398000
N	0.53894900	-1.53084000	-0.53086700
N	-1.91660700	-0.46622100	0.28417100
Si	-3.75882000	-0.41046000	0.13582400
Si	-1.41053500	-0.60137700	2.05516400
Si	-1.26216200	1.16084800	-0.49277600
Si	-1.39948800	-2.12949900	-0.61567000
C	-1.32704400	2.69064700	0.71191200
H	-0.69943500	2.48438900	1.57890500
H	-0.92461900	3.56463600	0.14583500
H	-2.38118900	2.89165300	1.01602600
C	-2.87352600	1.57066700	-1.53965300
H	-3.41152400	0.67491300	-1.93923400
H	-3.54063900	2.13933500	-0.84656400

H	-2.55060100	2.19806800	-2.39248100
C	0.00643000	1.07613800	-1.97044000
H	0.15341900	2.13737000	-2.29877700
H	0.96375800	0.65214700	-1.64103500
H	-0.44219000	0.47577300	-2.81967300
C	-4.33302232	-0.74631515	-1.68656263
H	-4.85753758	-1.67795805	-1.72928560
H	-4.98062081	0.04264044	-2.00760041
H	-3.47760761	-0.78886747	-2.32793223
C	-4.26847879	1.37157775	0.70870216
H	-4.52819359	1.96038966	-0.14613628
H	-5.10978427	1.30770342	1.36674863
H	-3.44855882	1.82951625	1.22146289
C	-4.55175931	-1.68059144	1.36936094
H	-4.50841009	-1.28702237	2.36340532
H	-5.57244261	-1.85190968	1.09778100
H	-4.01176784	-2.60337841	1.32724904
C	-1.72163849	1.12487635	2.88393658
H	-1.94957138	0.98709087	3.92025785
H	-0.84389252	1.72941760	2.78911105
H	-2.54303955	1.61022900	2.39954716
C	-2.64462608	-1.89059875	2.81577327

H	-3.53890921	-1.38992027	3.12314721
H	-2.88471172	-2.63078162	2.08134273
H	-2.19091548	-2.36215970	3.66234103
C	0.38876615	-1.26930487	2.33798504
H	0.70574042	-1.03059705	3.33168816
H	0.40005143	-2.33099533	2.20537276
H	1.05290425	-0.81471525	1.63288302
C	-3.26451662	-2.65841798	-0.54142065
H	-3.73450170	-2.19145032	0.29879077
H	-3.75771023	-2.35381678	-1.44079720
H	-3.32998729	-3.72171011	-0.44130357
C	-0.73214291	-3.64724161	0.39165711
H	-0.82979194	-4.53608818	-0.19597920
H	0.29854982	-3.49022052	0.63231635
H	-1.29711503	-3.75252122	1.29422163
C	-1.23880964	-2.00392134	-2.54492185
H	-0.20874277	-1.88784502	-2.81023022
H	-1.62443724	-2.89542033	-2.99372126
H	-1.79462740	-1.15923676	-2.89488553

Benzonitrile

0 1

C	2.18023600	0.00000000	0.00000000

C	1.48383400	-1.21067300	0.00000000
C	0.09156900	-1.21743300	0.00000000
C	-0.60995200	0.00000000	0.00000000
C	0.09156900	1.21743300	0.00000000
C	1.48383400	1.21067300	0.00000000
H	3.26607400	0.00000000	0.00000000
H	2.02591200	-2.15115600	0.00000000
H	-0.45848600	-2.15226000	0.00000000
H	-0.45848600	2.15226000	0.00000000
H	2.02591200	2.15115600	0.00000000
C	-2.04487500	0.00000000	0.00000000
N	-3.20831600	0.00000000	0.00000000

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