Asymmetric Cross-Dehydrogenative Coupling Enabled by the Design and Application of Chiral Triazole-Containing Phosphoric Acids

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Supporting Information

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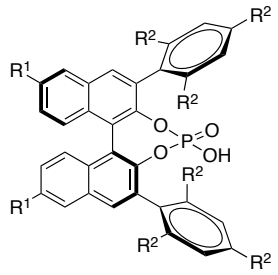
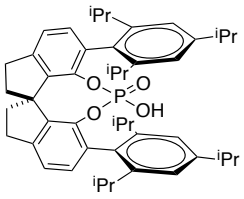
General Information

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Enantioselective cross-dehydrogenative coupling (CDC) reactions were run in 2 dram (15 X 60 mm) vials equipped with a screw cap and stirred using a magnetic Teflon stir bar (1/2" X 5/16"), placed on the surface of a magnetic stir plate. Due to the heterogeneous nature of these reactions, it was important that fast and efficient stirring be maintained over the course of the reaction in order to obtain optimal results. Tetrahydrofuran, dichloromethane, diethyl ether, toluene, triethylamine and N,N-dimethylformamide were purified by passage through an activated alumina column under argon. Thin-layer chromatography (TLC) analysis of reaction mixtures was performed using Merck silica gel 60 F254 TLC plates, and visualized under UV or by staining with ceric ammonium molybdate or $KMNO_4$. Column chromatography was performed on Merck Silica Gel 60 Å, 230 X 400 mesh. Nuclear magnetic resonance (NMR) spectra were recorded using Bruker AV-600, AV-500, DRX-500, AVQ-400, AVB-400 and AV-300 spectrometers. ^{1}H and ^{13}C chemical shifts are reported in ppm downfield of tetramethylsilane and referenced to residual solvent peak ($CHCl_3$; $\delta H = 7.26$ ppm and $\delta C = 77.0$ ppm, DMSO; $\delta H = 2.50$ and $\delta C = 39.5$ ppm). Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, app t = apparent triplet, m = multiplet, br = broad resonance. Solvent abbreviations are reported as follows: EtOAc = ethyl acetate, hex = hexanes, DCM = dichloromethane, Et_2O = diethyl ether, MeOH = methanol, THF = tetrahydrofuran, DMF = N,N-dimethylformamide, Et_3N = triethylamine. Mass spectral data were obtained from the Micro-Mass/Analytical Facility operated by the College of Chemistry, University of California, Berkeley. Enantiomeric excesses were measured on a Shimadzu VP Series Chiral HPLC using Chiralpak IA, IB, or IC columns. The syntheses of TRIP[1], C_8-TRIP[2], TCYP[3], STRIP[4], and VAPOL PA[5] have been previously reported. **Caution:** Although we have not experienced any problems during the preparation and handling of the azides reported herein, appropriate safety precautions should be taken due to the explosive nature of organic azides, including the use of a blast shield during any manipulations involving azides. Azides **S3b**[6] and **S3l**[7] have been previously reported. Azide **S3c** was prepared by the method of Zhang,[6] **S3d**, **S3e** and **S3f** by the method of Guo,[8] and **S3g**, **S3h**, **S3i**, **S3j** and **S3k** by the method of Tor.[9] All azides were used directly without further purification. Racemic CDC products were synthesized by carrying out the reactions in toluene in the absence of catalyst.

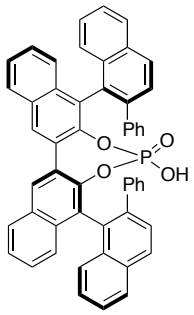
Optimization of Catalyst, Oxidant, Solvent and Base on Substrate 5a



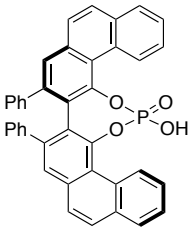
(***S***)-**TRIP**: R^1= H, R^2= ^{i}Pr
(***S***)-**C8-TRIP**: R^1= C_8H_{17}, R^2= ^{i}Pr
(***S***)-**TCYP**: R^1= H, R^2= C_6H_{11}



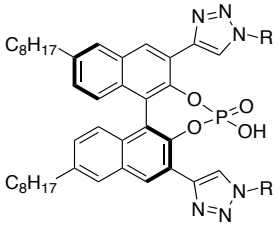
(***R***)-**STRIP**



(***R,R***)-**Ph-DAP**

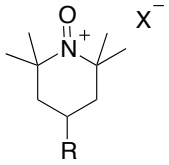


(***S***)-**VAPOL PA**

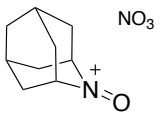


9

9a	R = Bn[a]	**9g**	R = 2,4,6-$(Me)_3C_6H_3$
9b	R = $CH(Ph)_2$	**9h**	R = 2,4,6-$(^iPr)_3C_6H_3$
9c	R = $CH(1\text{-Naph})_2$	**9i**	R = 2,4,6-$(c\text{-}C_6H_{11})_3C_6H_3$
9d	R = 1-naphthyl	**9j**	R = 4-$(^tBu)C_6H_5$
9e	R = 9-anthracyl	**9k**	R = 3,5-$(^tBu)_2C_6H_4$
9f	R = 1-pyrenyl	**9l**	R = 1-adamantyl

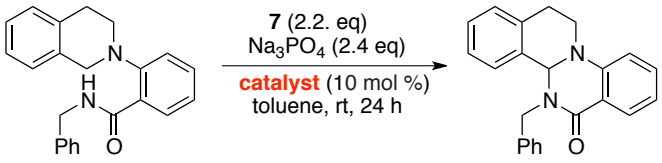


[O]-1: R = H, X = BF_4
[O]-2: R = NHAc, X= NO_3
7: R = NHAc, X = BF_4



[O]-3

Table S1. Catalyst Optimization on Substrate 5a

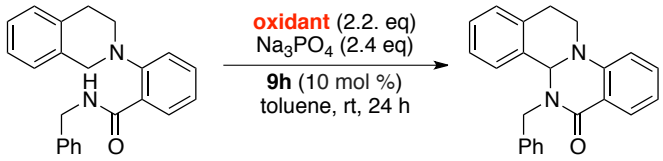


5a **6a**

Entry	catalyst	conversion (%)[a]	ee (%)[b]
1	(*S*)-C8-TRIP	86	8
2	(*S*)-TCYP	95	16
3	(*R*)-STRIP	64	30
4	(*R*,*R*)-Ph-DAP	69	-10[c]
5	(*S*)-VAPOL PA	97	31
6	**9a**	97	-70
7	**9b**	99	-69
8	**9c**	75	-52
9	**9d**	97	-63
10	**9e**	92	-41
11	**9f**	77	56
12	**9g**	92	-78
13	**9h**	92	-80
14	**9i**	91	-77
15	**9j**	91	-37
16	**9k**	92	-50
17	**9l**	75	-81

[a] Determined by HPLC using 1,4-dinitrobenzene internal standard. [b]Determined by chiral HPLC. [c]Negative sign indicates that opposite enantiomer predominates.

Table S2. Oxidant Optimiazation on Substrate 5a

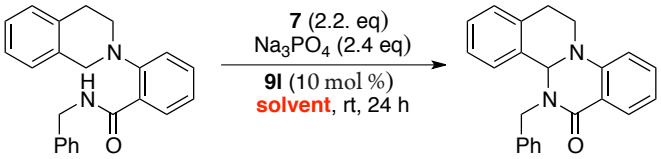


5a **6a**

Entry	Oxidant	Conversion (%)[a]	ee (%)[b]
1	**[O]-1**	95	79
2	**[O]-2**	88	78
3	**7**	72	79
4	**[O]-3**	32	56
5	DDQ	0	nd
6	TBHP	4	0

[a]Determined by HPLC using using 1,4-dinitrobenzene internal standard. [b]Determined by chiral HPLC. DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. TBHP = *tert*-butyl hydroperoxide.

Table S3. Solvent Optimization on Substrate 5a

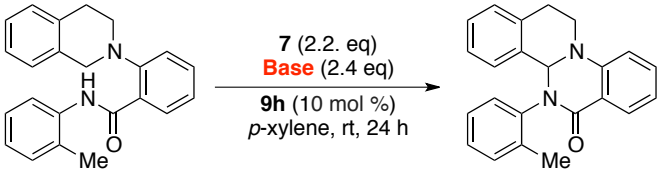


5a **6a**

Entry	Solvent	Conversion[a]	ee (%)[b]
1	hexanes	91	27
2	Et_2O	86	78
3	THF	95	55
4	MeCN	69	4
5	DCM	43	18
6	benzene	96	73
7	toluene	93	79
8	*o*-xylene	95	82
9	*m*-xylene	95	81
10	*p*-xylene	94	82
11	xylenes	95	81
12	mesitylene	92	84
13	triethylbenzene	80	80
14	triisopropylbenzene	98	80
15	fluorobenzene	92	61
16	hexafluorobenzene	39	76
17	*p*-xylene	91 (*83*)[c]	84

[a]Determined by HPLC using 1,4-dinitrobenzene internal standard. [b]Determined by chiral HPLC. [c]Performed on 0.1 mmol scale. Value in parenthases reflects isolated yield

Table S4. Base Optimization on Substrate 5h



5h **6h**

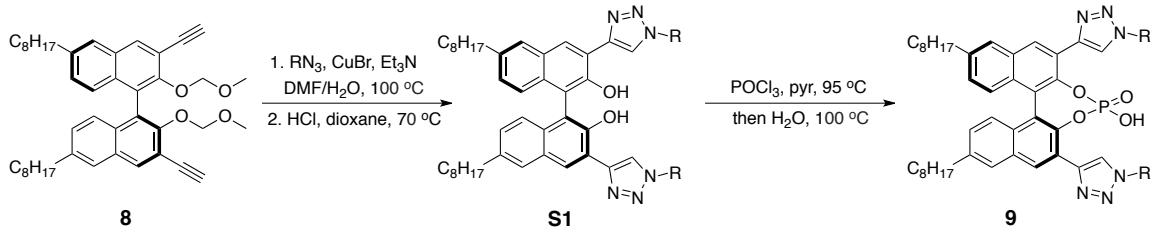
Entry	Base	Yield (%)[a]	ee (%)[b]
1	Na_3PO_4	**65**	**90**
2	Na_2HPO_4	38	88
3	Na_2CO_3	24	88
4	$NaHCO_3$	21	88
5	K_2CO_3	47	88
6	Li_2CO_3	29	82

[a]Isolated yield [b]Determined by chiral HPLC

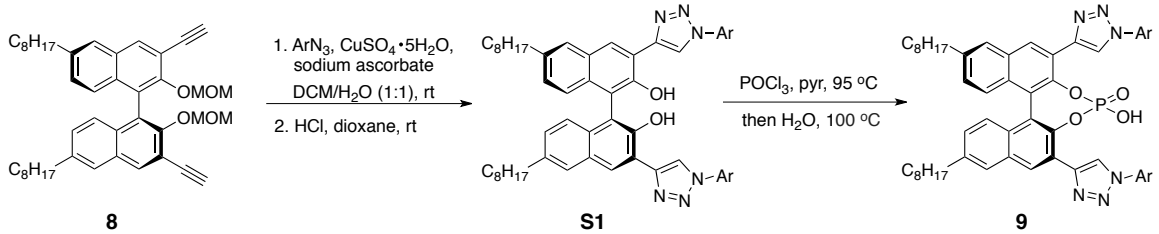
Synthesis of Catalysts

Compounds **9a-l** were synthesized according to the reaction sequences depicted in Schemes S1 and S2.

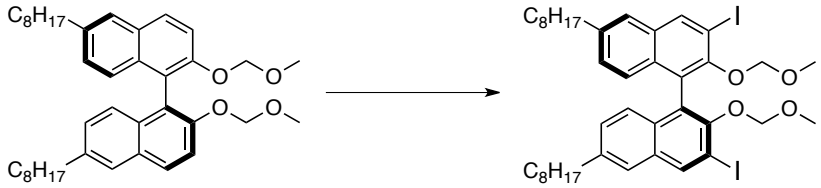
Scheme S1. Synthesis of Catalysts 9a-c and 9g-l



Scheme S2. Synthesis of Catalysts 9d-f



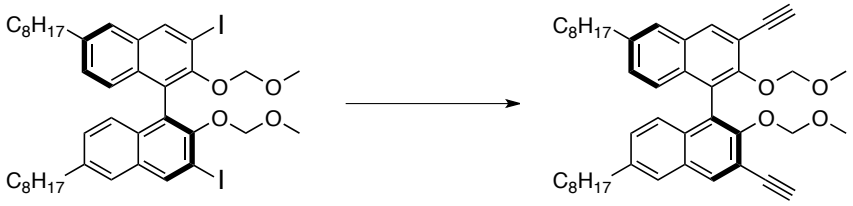
(*S*)-3,3'-diiodo-2,2'-bis(methoxymethyl)-6,6'-dioctyl-1,1'-binaphthalene (S2)



A magnetically stirred solution of (*S*)-2,2'-bis(methoxymethyl)-6,6'-dioctyl-1,1'-binaphthalene[10] (31.35 g, 52.35 mmol) in THF (500 mL) was cooled to -78 °C and *n*-butyllithium (2.5 M solution in hexanes, 73 mL, 183.2 mmol) was added dropwise over the course of 15 min. After 30 min, the solution was warmed to 0 °C and stirred at this temperature for 2 h. The dark brown reaction mixture was then cooled to -78 °C and iodine (49.82 g, 196.31 mmol) was added as a single portion. The solution was warmed to room temperature and stirred for an additional 2 h at which point saturated aqueous $Na_2S_2O_3$ (200 mL) was carefully added and the resulting mixture was allowed to stir at room temperature for 30 min. The mixture was extracted with EtOAc (2 X 200 mL) and

the organic extracts were washed with H_2O (200 mL) and brine (100 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the crude residue by column chromatography on silica gel using Hex/Et_2O as eluent (20:1) afforded the title compound (33.22 g, 39.05 mmol, 75 % yield) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.54 (s, 2H), 7.17 (d, *J* = 9.0 Hz, 2H), 7.11 (d, *J* = 9.0 Hz, 2H), 4.81 (d, *J* = 5.7 Hz, 2H), 4.70 (d, *J* = 5.6 Hz, 2H), 2.73 (t, *J* = 7.7 Hz, 4H), 2.62 (s, 6H), 1.74 - 1.63 (m, 4H), 1.39 - 1.22 (m, 20H), 0.89 (t, *J* = 6.7 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.33, 140.58, 139.40, 132.47, 132.23, 128.76, 126.41, 126.23, 125.00, 99.35, 92.31, 56.53, 35.84, 31.89, 31.10, 29.48, 29.37, 29.27, 22.69, 14.15. **HRMS** (EI) found $[M+Na]^+$ 873.1852, $C_{40}H_{52}O_4I_2Na$ requires 873.1847.

(*S*)-3,3'-diethynyl-2,2'-bis(methoxymethyl)-6,6'-dioctyl-1,1'-binaphthalene (8)



To a magnetically stirred solution of (*S*)-3,3'-diiodo-2,2'-bis(methoxymethyl)-6,6'-dioctyl-1,1'-binaphthalene (**S2**, 18.22 g, 21.42 mmol) in toluene (110 mL) and Et_3N (110 mL) were added bis(triphenylphosphine)palladium (II) dichloride (0.601 g, 0.857 mmol) and copper (I) bromide (1.63 g, 8.57 mmol). After degassing this solution under vacuum (3 x 30 s), trimethylsilylacetylene (9.76 mL, 68.54 mmol) was added. The reaction mixture was stirred at 50 ^oC for 12 h at which point TLC indicated complete consumption of the starting material. After cooling to room temperature, the reaction mixture was diluted with Et_2O (150 mL), filtered through Celite and concentrated *in vacuo*. The crude residue was taken up in MeOH (455 mL) and DCM (45 mL). To this vigorously-stirred solution was added K_2CO_3 (29.6 g, 214.2 mmol). The reaction mixture was stirred at room temperature for 1 h at which point TLC indicated consumption of the starting material. The reaction mixture was filtered through Celite and the filtrate partitioned between H_2O (200 mL) and DCM (200 mL). The organic phase was separated and the aqueous phase was extracted with DCM (3 x 50 mL). The combined organic extracts were washed with saturated aqueous NH_4Cl, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel using Hex/Et_2O as eluent (20:1) to give the title compound (10.15 g, 15.64 mmol, 73 % yield over 2 steps) as a viscous, brown oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.14 (s, 2H), 7.61 (s, 2H), 7.19 (d, *J* = 9.0 Hz, 2H), 7.16 (d, *J* = 9.0 Hz, 2H), 5.09 (d, *J* = 6.0 Hz, 2H), 4.90 (d, *J* = 6.0 Hz, 2H), 3.34 (s, 2H), 2.74 (t, *J* = 7.8 Hz, 4H), 2.57 (s, 6H), 1.72 - 1.63 (m, 4H), 1.45 - 1.21 (m, 20H), 0.90 (t, *J* = 6.8 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.66, 140.24,

134.64, 132.41, 130.32, 129.15, 126.40, 125.87, 125.74, 116.04, 98.84, 81.30, 80.82, 56.06, 35.83, 31.89, 31.14, 29.48, 29.36, 29.28, 22.69, 14.13. **HRMS** (EI) found $[M]^+$ 646.4031, $C_{44}H_{54}O_4$ requires 646.4022.

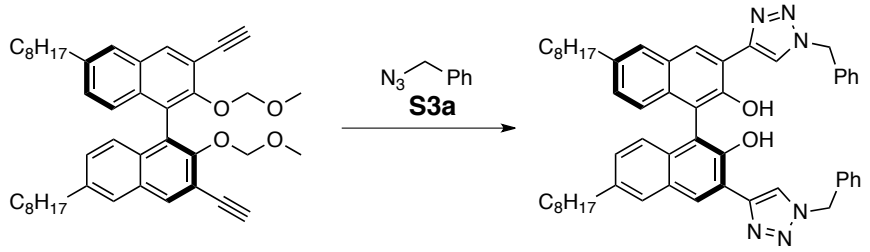
General Procedure A: Synthesis of triazolyl diols S1a-c and S1g-l:
To a magnetically stirred solution of *bis*-alkyne **8** (1.0 equiv) in DMF (0.05 M) were added copper (I) bromide (0.25 equiv.), Et_3N (2.0 equiv.), H_2O (4.0 equiv), and azide **S3** (2.2 equiv.). The reaction mixture was degassed under vacuum (3 X 30 s), and then heated for 12 h at 100 ^oC under an atmosphere of N_2. Upon complete consumption of the starting material, as judged by TLC, the reaction mixture was allowed to cool to room temperature and diluted with saturated aqueous NH_4Cl. The aqueous layer was extracted with ethyl acetate (x3) and the combined organic extracts were washed with H_2O (x4), dried (Na_2SO_4) and concentrated *in vacuo*. The crude residue was dissolved in 1,4-dioxane (0.05 M), concentrated HCl (2 mL) was added, and the mixture was heated at 70 ^oC. Upon complete consumption of the starting material as judged by TLC, the reaction mixture was allowed to cool to room temperature and then concentrated *in vacuo*. The residue was partitioned between DCM and saturated aqueous $NaHCO_3$. The aqueous layer was extracted with DCM (x3) and the combined organics were dried (Na_2SO_4) and concentrated *in vacuo*. The crude residue was purified by column chromatography (EtOAc/Hex).

General Procedure B: Synthesis of triazolyl diols S1d-f:
i. Preparation of azides: To a magnetically stirred solution of sodium azide (3.2 equiv.) and copper sulfate pentahydrate (0.3 equiv.) in MeOH (0.4 M) was added the appropriate boronic acid (3 equiv.). The brown suspension was stirred at room temperature for 3 h under air and then diluted with EtOAc and saturated aqueous sodium bicarbonate. The organic layer was separated and the aqueous layer was extracted with EtOAc (3x). The combined organic layers were concentrated in *vacuo* to furnish a crude oil, which was directly taken forward in the next step without further purification.
ii. Copper Catalyzed Alkyne-Azide Cycloaddition (CuAAC): The crude azide **S3** was dissolved in DCM and transferred to a magnetically stirred solution of *bis*-alkyne **8** (1.0 equiv) in DCM/H_2O (1:1, v/v, 0.05 M). Then $CuSO_4 \cdot 5H_2O$ (0.3 equiv.) and sodium ascorbate (1 equiv.) were successively added and the mixture was stirred at room temperature under an atmosphere of N_2. Every 24 h, sodium ascorbate (0.5 equiv.) was added until complete disappearance of *bis*-alkyne and mono-triazole product as judged by TLC (EtOAc/Hex). The reaction mixture was diluted with DCM, washed with saturated aqueous sodium bicarbonate and extracted with EtOAc (x3). The combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated *in vacuo*. The crude residue was purified by flash column chromatography using EtOAc/Hex as eluent.

iii. MOM Deprotection: To a magnetically stirred solution of MOM-protected intermediate **S1-i** in 1,4-dioxane (0.025 M) was added concentrated HCl (2 mL) and the mixture was stirred at room temperature overnight. Upon complete consumption of the starting material, as judged by TLC, the reaction mixture was concentrated *in vacuo*. The residue was partitioned between DCM and saturated aqueous $NaHCO_3$. The aqueous layer was extracted with DCM (x3) and the combined organic layers were dried (Na_2SO_4) and concentrated *in vacuo*. The crude residue was purified by column chromatography using EtOAc/Hex as eluent or by recrystallization from $CHCl_3$/Hex.

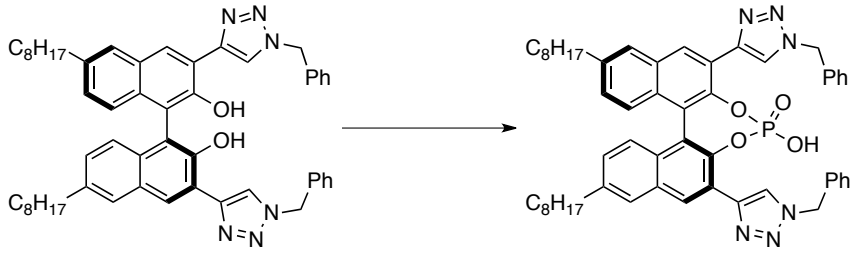
General Procedure C: Synthesis of phosphoric acids:
To a magnetically stirred solution of triazolyl diol **S1** in pyridine (0.05 M) was added phosphorus (V) oxychloride (2.0 equiv.) and the reaction mixture was heated at 95 ^oC under and atmosphere of N_2. Upon complete consumption of the starting material, as judged by TLC, the reaction mixture was allowed to cool to room temperature. H_2O (5 mL) was added and the mixture was stirred at 100 ^oC. Upon complete consumption of the intermediate, as judged by TLC, the reaction mixture was diluted with DCM (20 mL) and washed with 3N HCl (3 x 20 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated *in vacuo*. The crude residue was purified by column chromatography (DCM/MeOH or EtOAc/Hex/TFA).

(*S*)-3,3'-bis(1-benzyl-1*H*-1,2,3-triazol-4-yl)-6,6'-dioctyl-[1,1'-binaphthalene]-2,2'-diol (S1a)



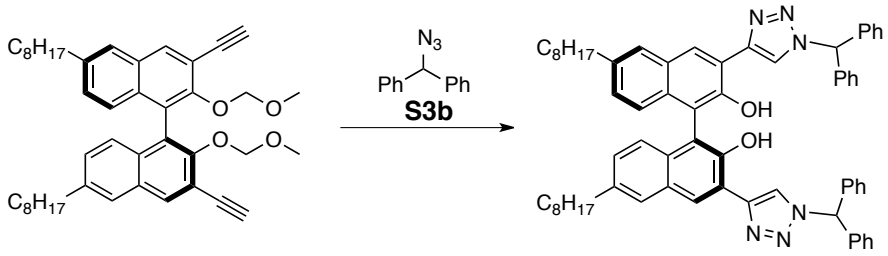
Subjection of *bis*-alkyne **8** (0.636 g, 0.980 mmol) and azide **S3a** (0.287 g, 2.16 mmol) to General Procedure A gave the title compound (0.597 g, 0.724 mmol, 74 % yield) as a yellow solid after purification by column chromatography on silica gel using Hex:EtOAc as eluent (3:2). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.98 (s, 2H), 8.16 (s, 2H), 8.00 (s, 2H), 7.58 (s, 2H), 7.44 - 7.35 (m, 6H), 7.35 - 7.25 (m, 4H), 7.17 (d, J = 8.5 Hz, 2H), 7.10 (d, J = 8.5 Hz, 2H), 5.54 (s, 4H), 2.69 (t, J = 7.7 Hz, 4H), 1.75 - 1.61 (m, 4H), 1.43 - 1.15 (m, 20H), 0.91 (t, J = 6.7 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.27, 147.20, 138.09, 134.39, 132.31, 129.18, 128.86, 128.71, 128.53, 128.14, 126.55, 125.81, 124.72, 120.84, 116.93, 116.56, 54.44, 35.85, 31.94, 31.31, 29.56, 29.46, 29.32, 22.71, 14.16. **HRMS** (ESI) found $[M+H]^+$ 825.4856, $C_{54}H_{61}N_6O_2$ requires 825.4851.

(4*R*,11b*S*)-2,6-bis(1-benzyl-1*H*-1,2,3-triazol-4-yl)-4-hydroxy-9,14-dioctyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (9a)



Subjection of diol **S1a** (0.500 g, 0.606 mmol) to General Procedure C gave the title compound (0.498 g, 0.561 mmol, 93 % yield) as a yellow solid after purification by column chromatography on silica gel using DCM/MeOH as eluent (20:1 to 10:1). **^{1}H NMR** (500 MHz, $CDCl_3$: DMSO, 1:1) δ 8.82 (s, 2H), 8.72 (s, 2H), 7.94 (s, 2H), 7.30 - 7.23 (m, 8H), 7.18 (d, *J* = 8.7 Hz, 4H), 7.05 (d, *J* = 8.6 Hz, 2H), 5.70 (d, *J* = 15.5 Hz, 2H), 5.65 (d, *J* = 16.0 Hz, 2H), 2.71 (t, *J* = 7.6 Hz, 4H), 1.80 - 1.56 (m, 4H), 1.40 - 1.14 (m, 20H), 0.82 (t, *J* = 6.7 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$: DMSO, 1:1) δ 144.20 (d, *J* = 8.9 Hz), 142.18, 140.34, 136.16, 131.31, 130.25, 128.86, 128.50, 128.14, 127.90, 127.54, 127.17, 126.52, 124.96, 123.24, 122.73, 53.23, 35.63, 31.80, 31.11, 29.39, 29.29, 29.18, 22.61, 14.34. **^{31}P NMR** (243 MHz, $CDCl_3$: DMSO, 1:1) δ 0.95. **HRMS** (ESI) found $[M-H]^-$ 885.4252, $C_{54}H_{58}N_6O_4P_1$ requires 885.4263.

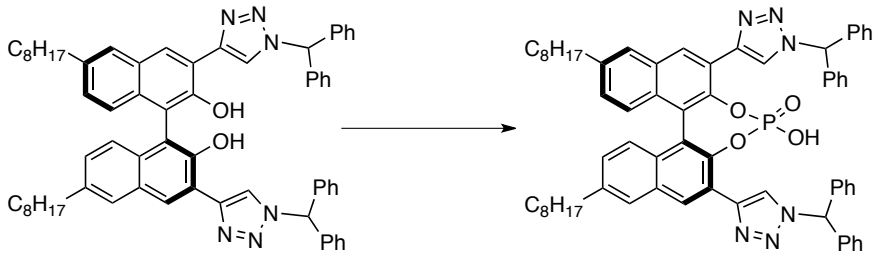
(*S*)-3,3'-bis(1-benzhydryl-1*H*-1,2,3-triazol-4-yl)-6,6'-dioctyl-[1,1'-binaphthalene]-2,2'-diol (S1b)



Subjection of *bis*-alkyne **8** (0.500 g, 0.771 mmol) and azide **S3b** (0.354 g, 1.69 mmol) to General Procedure A gave the title compound (0.390 g, 0.399 mmol, 52 % yield) as a yellow solid after purification by column chromatography on silica gel using Hex/EtOAc as eluent (9:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.76 (s, 2H), 8.29 (s, 2H), 8.02 (s, 2H), 7.65 (s, 2H), 7.53 - 7.33 (m, 12H), 7.30 - 7.16 (m, 12H), 7.13 (d, *J* = 8.5 Hz, 2H), 2.73 (t, *J* = 7.2 Hz, 4H), 1.79 - 1.57 (m, 4H), 1.50 - 1.19 (m, 20H), 0.93 (t, *J* = 6.3 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.26, 146.62, 138.13, 137.81, 132.38, 129.12, 129.10, 128.84, 128.80, 128.61, 128.23, 128.14, 126.57, 125.93, 124.75, 121.07, 117.10, 116.44,

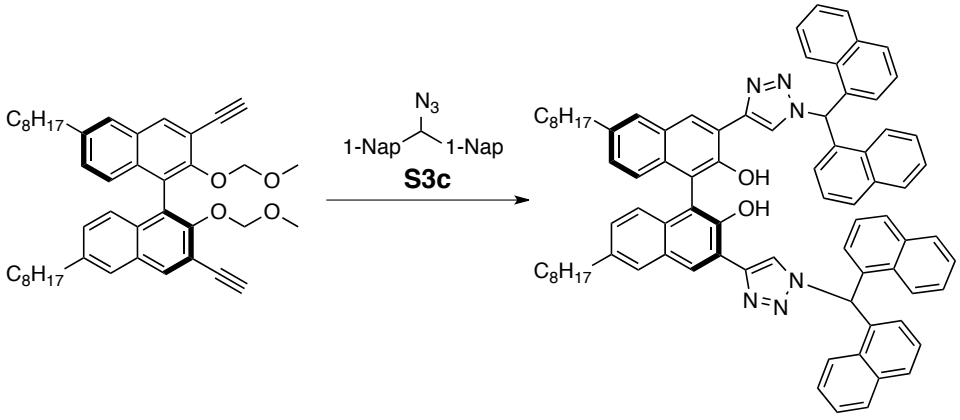
68.54, 35.87, 31.97, 31.29, 29.59, 29.43, 29.34, 22.75, 14.21. **HRMS** (ESI) found $[M+H]^+$ 977.5475, $C_{66}H_{69}N_6O_2$ requires 977.5477.

(4*R*,11b*S*)-2,6-bis(1-benzhydryl-1*H*-1,2,3-triazol-4-yl)-4-hydroxy-9,14-dioctyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (9b)



Subjection of diol **S1b** (0.380 g, 0.388 mmol) to General Procedure C gave the title compound (0.351 g, 0.338 mmol, 87 % yield) as a yellow solid after purification by column chromatography on silica gel using DCM/MeOH as eluent (20:1 to 10:1). **^{1}H NMR** (500 MHz, DMSO, 1:1) δ 8.78 (s, 2H), 8.68 (s, 2H), 7.94 (s, 2H), 7.46 (s, 2H), 7.42 - 7.11 (m, 20H), 7.06 (d, *J* = 8.8 Hz, 2H), 2.85 - 2.62 (m, 4H), 1.76 - 1.55 (m, 4H), 1.39 - 1.09 (m, 20H), 0.83 (t, *J* = 6.7 Hz, 6H). **^{13}C NMR** (151 MHz, DMSO) δ 144.79(d, *J* = 10.0 Hz), 140.12, 139.30, 139.15, 131.12, 130.25, 129.07, 128.63, 128.54, 128.44, 128.24, 127.55, 127.46, 127.40, 126.34, 125.28, 123.49, 123.48, 122.77, 122.75, 66.92, 35.35, 31.67, 30.93, 29.24, 29.13, 29.06, 22.49, 14.35. **^{31}P NMR** (202 MHz, DMSO) δ 2.37. **HRMS** (ESI) found $[M+H]^+$ 1039.5036, $C_{66}H_{68}N_6O_4P_1$ requires 1039.5034.

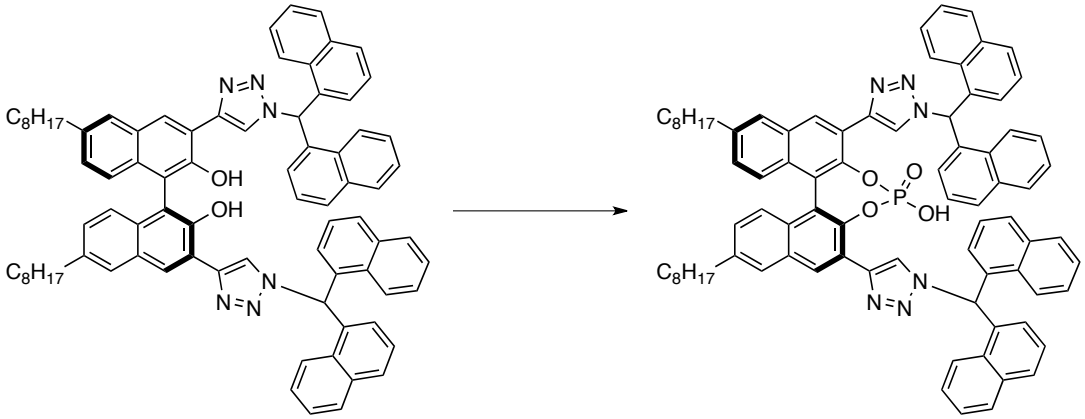
(*S*)-3,3'-bis(1-(di(naphthalen-1-yl)methyl)-1*H*-1,2,3-triazol-4-yl)-6,6'-dioctyl-[1,1'-binaphthalene]-2,2'-diol (S1c)



Subjection of *bis*-alkyne **8** (0.500 g, 0.771 mmol) and azide **S3c** (0.524 g, 1.69 mmol) to General Procedure A gave the title compound (0.706 g, 0.600 mmol, 78 % yield) as a brown solid after purification by column chromatography on silica gel using Hex/EtOAc

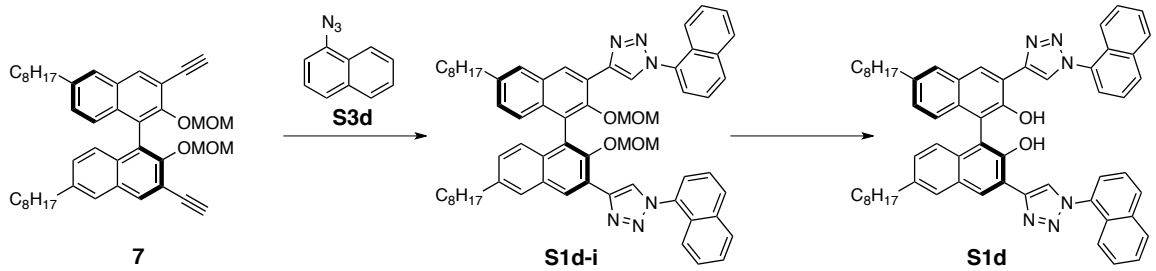
as eluent (4:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.84 (s, 2H), 8.71 (s, 2H), 8.21 (s, 2H), 8.04 - 7.85 (m, 14H), 7.62 - 7.54 (m, 6H), 7.54 - 7.47 (m, 4H), 7.44 (app t, *J* = 7.2 Hz, 4H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 7.03 (dd, *J* = 16.2, 7.0 Hz, 4H), 2.70 (t, *J* = 7.2 Hz, 4H), 1.76 - 1.61 (m, 4H), 1.45 - 1.24 (m, 20H), 0.94 (t, *J* = 6.7 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.21, 146.61, 138.08, 134.06, 134.04, 133.31, 133.28, 132.39, 130.72, 130.67, 129.99, 129.95, 129.19, 129.17, 128.80, 128.54, 127.55, 127.52, 126.49, 126.46, 126.44, 126.39, 126.23, 125.90, 125.44, 124.71, 122.82, 121.89, 116.95, 116.51, 62.75, 35.84, 31.97, 31.24, 29.58, 29.38, 29.33, 22.75, 14.21. **HRMS** (ESI) found $[M+H]^+$ 1176.6118, $C_{82}H_{77}N_6O_4$ requires 1177.6103.

(4*R*,11b*S*)-2,6-bis(1-(di(naphthalen-1-yl)methyl)-1*H*-1,2,3-triazol-4-yl)-4-hydroxy-9,14-dioctyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (9c)



Subjection of diol **S1c** (0.280 g, 0.236 mmol) to General Procedure C gave the title compound (0.132 g, 0.106 mmol, 45 % yield) as a beige solid after purification by column chromatography on silica gel using DCM/MeOH as eluent (20:1). **^{1}H NMR** (500 MHz, $CDCl_3$: DMSO, 1:1) δ 8.76 (s, 2H), 8.49 (s, 2H), 8.02 (d, *J* = 6.3 Hz, 2H), 7.99 - 7.81 (m, 10H), 7.76 (s, 2H), 7.56 - 7.44 (m, 6H), 7.40 (app t, *J* = 6.9 Hz, 4H), 7.35 (app t, *J* = 7.2 Hz, 2H), 7.08 (app s, 4H), 7.06 - 6.92 (m, 4H), 2.69 (t, *J* = 7.7 Hz, 4H), 1.72 - 1.55 (m, 4H), 1.37 - 1.15 (m, 20H), 0.84 (t, *J* = 6.5 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$: DMSO, 1:1) δ 143.73 (d, *J* = 9.9 Hz), 142.08, 140.60, 134.31, 133.94, 133.87, 131.39, 130.76, 130.57, 130.24, 129.69, 129.37, 129.17, 129.14, 129.00, 128.64, 127.99, 127.49, 127.24, 127.11, 126.82, 126.54, 126.45, 126.33, 126.18, 125.69, 125.68, 125.34, 123.30, 123.04, 122.88, 122.59, 61.75, 35.65, 31.80, 31.06, 29.38, 29.28, 29.20, 22.62, 14.31. **^{31}P NMR** (202 MHz, $CDCl_3$: DMSO, 1:1) δ 1.35. **HRMS** (ESI) found $[M-H]^-$ 1237.5513, $C_{82}H_{74}N_6O_4P_1$ requires 1237.5515.

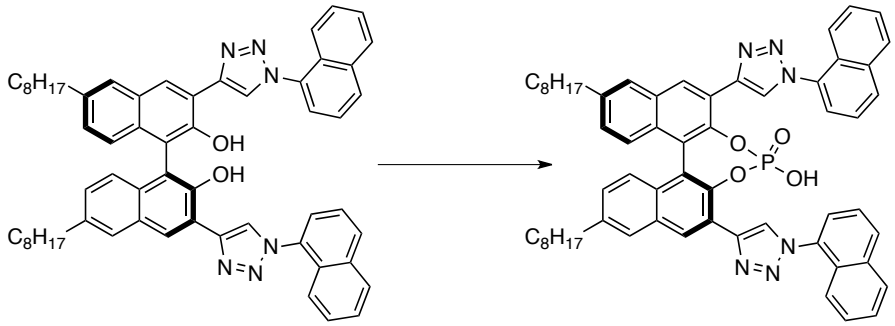
(*S*)-3,3'-bis(1-(naphthalen-1-yl)-1*H*-1,2,3-triazol-4-yl)-6,6'-dioctyl-[1,1'-binaphthalene]-2,2'-diol (S1d)



Subjection of *bis*-alkyne **8** (0.500 g, 0.773 mmol) to General Procedure Bi-Bii, gave intermediate **S1d-i** (0.585 g, 0.594 mmol, 77 % yield) as an orange solid after purification by column chromatography on silica gel using Hex/Et_2O as eluent (5:2). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.04 (s, 2H), 8.71 (s, 2H), 8.02 (d, *J* = 7.6 Hz, 2H), 7.96 (d, *J* = 7.6 Hz, 2H), 7.83 (s, 2H), 7.79 (d, *J* = 7.6 Hz, 2H), 7.65 (d, *J* = 7.2 Hz, 2H), 7.60 – 7.52 (m, 6H), 7.26 (d, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 2H), 4.67 (d, *J* = 4.8 Hz, 2H), 4.45 (d, *J* = 4.8 Hz, 2H), 2.78 (t, *J* = 7.8 Hz, 4H), 2.69 (s, 6H), 1.76-1.69 (m, 4H), 1.43-1.21 (m, 20H), 0.88 (t, *J* = 6.7 Hz, 6H).

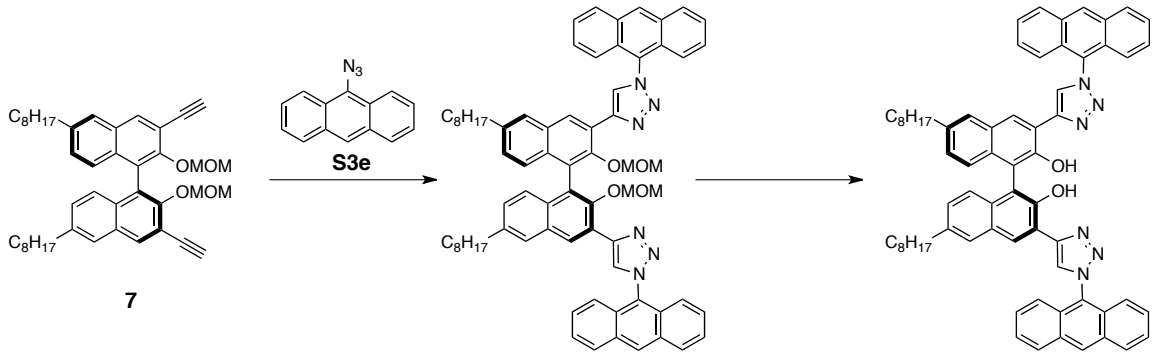
Subjection of **S1d-i (**0.530 g, 0.538 mmol) to General Procedure Biii gave the title compound **(**0.480 g, 0.535 mmol, 99 % yield) as a brown solid after purification by column chromatography on silica gel using EtOAc/Hex as eluent (0 to 40 %). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.45 (s, 2H), 8.49 (d, *J* = 11.8 Hz, 4H), 8.05 (d, *J* = 8.2 Hz, 2H), 7.98 (d, *J* = 7.5 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.70 (s, 2H), 7.65 (d, *J* = 7.0 Hz, 2H), 7.63 - 7.53 (m, 6H), 7.26 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 8.8 Hz, 2H), 2.75 (t, *J* = 7.7 Hz, 4H), 1.79 - 1.64 (m, 4H), 1.54 - 1.14 (m, 20H), 0.92 (t, *J* = 6.7 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.20, 146.34, 138.38, 134.17, 133.48, 132.40, 130.66, 128.96, 128.81, 128.46, 128.34, 128.09, 127.19, 126.78, 126.45, 125.04, 124.75, 123.92, 123.71, 122.29, 117.13, 116.10, 35.91, 31.96, 31.36, 29.59, 29.50, 29.35, 22.73, 14.18. **HRMS** (ESI) found $[M+H]^+$ 897.4861, $C_{60}H_{61}N_6O_2$ requires 897.4851.

(4*R*,11b*S*)-4-hydroxy-2,6-bis(1-(naphthalen-1-yl)-1*H*-1,2,3-triazol-4-yl)-9,14-dioctyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (9d)



Subjection of diol **S1d** (0.090 g, 0.100 mmol) to General Procedure C gave the title compound (0.041 g, 0.043 mmol, 43 % yield) as a yellow solid after purification by column chromatography on silica gel using DCM/MeOH as eluent (20:1). **^{1}H NMR** (500 MHz, DMSO) δ 9.15 (s, 2H), 8.82 (s, 2H), 8.22 (d, *J* = 8.2 Hz, 2H), 8.14 (d, *J* = 8.1 Hz, 2H), 7.98 (s, 2H), 7.81 (d, *J* = 7.1 Hz, 2H), 7.73 (app t, *J* = 7.7 Hz, 2H), 7.70 - 7.63 (m, 4H), 7.63 - 7.43 (m, 2H), 7.22 (d, *J* = 8.9 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 2.76 (t, *J* = 7.6 Hz, 4H), 1.81 - 1.59 (m, 4H), 1.44 - 1.15 (m, 20H), 0.86 (t, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, DMSO) δ 164.54, 145.99, 145.96, 139.85, 134.08, 133.78, 130.91, 130.71, 130.41, 128.55, 128.27, 128.16, 128.10, 127.59, 127.30, 127.02, 126.63, 125.43, 123.74, 123.64, 123.18, 122.67, 35.70, 31.84, 31.21, 29.44, 29.38, 29.26, 22.66, 14.37. **^{31}P NMR** (162 MHz, DMSO) δ 4.52. **HRMS** (ESI) found $[M-H]^-$ 957.4247, $C_{60}H_{58}N_6O_4P_1$ requires 957.4263.

(*S*)-3,3'-bis(1-(anthracen-9-yl)-1*H*-1,2,3-triazol-4-yl)-6,6'-dioctyl-[1,1'-binaphthalene]-2,2'-diol (S1e)

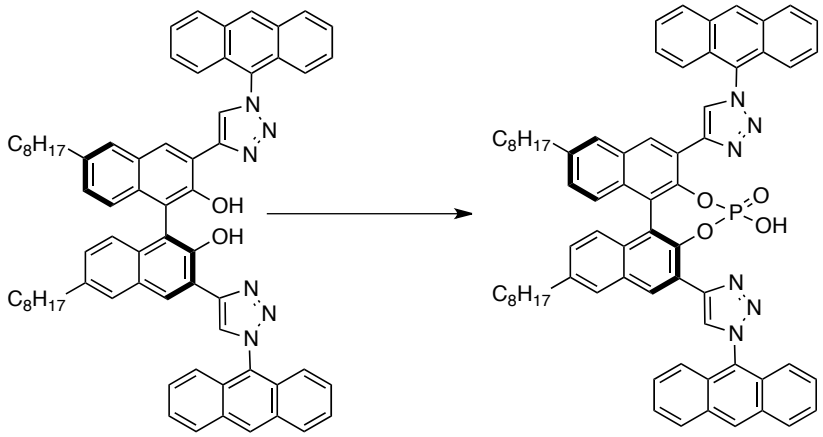


Subjection of *bis*-alkyne **8** (0.500 g, 0.773 mmol) to General Procedure Bi-Bii, gave intermediate **S1e-i** (0.639 g, 0.589 mmol, 76 % yield) as a yellow solid after purification by flash column chromatography on silica gel using EtOAc/Hex as eluent (0 to 25 %). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.11 (s, 2H), 8.72 (s, 2H), 8.66 (s, 2H), 8.15 - 7.99 (m, 4H), 7.85 (s, 2H), 7.57 - 7.38 (m, 12H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.22 (d, *J* = 8.8 Hz, 2H), 4.67 (d, *J* = 5.1 Hz, 2H), 4.50 (d, *J* = 5.1 Hz, 2H), 2.79 (t, *J* = 7.7 Hz, 4H), 2.67 (s, 6H), 1.81 - 1.67 (m, 4H), 1.49 - 1.20 (m, 20H), 0.88 (t, *J* = 6.8 Hz, 6H).

Subjection of **S1e-i (**0.300 g, 0.276 mmol) to General Procedure Biii gave the title compound (0.273 g, 0.274 mmol, 99 %) as an orange solid after recrystallization from $CHCl_3$/Hex. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.47 (s, 2H), 8.73 (s, 2H), 8.58 (s, 2H), 8.56 (s, 2H), 8.20 - 8.08 (m, 4H), 7.71 (d, *J* = 1.4 Hz, 2H), 7.65 - 7.51 (m, 8H), 7.45 (dd, *J* = 10.3, 7.2 Hz, 4H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 2.74 (t, *J* = 7.7 Hz,

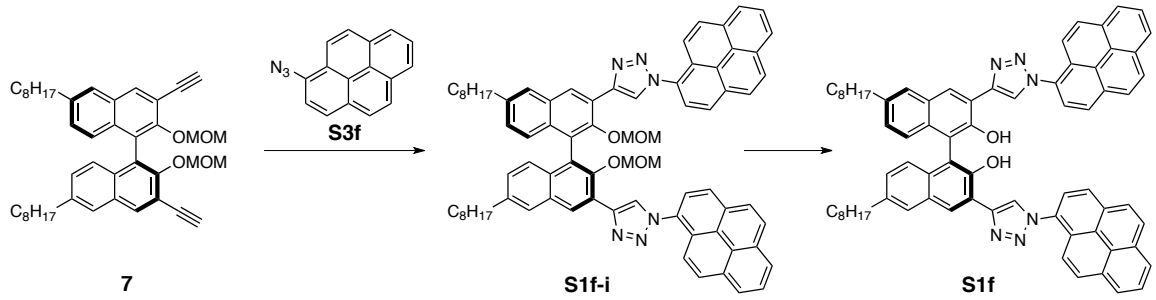
4H), 1.82 - 1.61 (m, 4H), 1.46 - 1.18 (m, 20H), 0.86 (t, *J* = 6.0 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 150.26, 146.55, 138.40, 132.48, 131.11, 130.04, 129.01, 128.83, 128.40, 128.28, 128.21, 127.96, 126.72, 126.48, 126.02, 125.61, 124.78, 121.97, 117.11, 116.21, 35.86, 31.89, 31.28, 29.52, 29.41, 29.27, 22.66, 14.10. **HRMS** (ESI) found $[M-H]^-$ 997.5184, $C_{68}H_{65}N_6O_2$ requires 997.5164.

(4*R*,11b*S*)-2,6-bis(1-(anthracen-9-yl)-1*H*-1,2,3-triazol-4-yl)-4-hydroxy-9,14-dioctyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (9e)



Subjection of diol **S1e** (0.150 g, 0.150 mmol) to General Procedure C gave the title compound **(**0.136 g, 0.128 mmol, 85 % yield) as a yellow solid after purification by column chromatography on silica gel using DCM/MeOH as eluent (30:1 to 20:1). **^{1}H NMR** (600 MHz, DMSO) δ 9.04 (s, 2H), 8.98 (d, *J* = 10.1 Hz, 4H), 8.26 (d, *J* = 8.3 Hz, 4H), 8.03 (s, 2H), 7.67 - 7.51 (m, 8H), 7.38 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.7 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 2.75 (t, *J* = 7.5 Hz, 4H), 1.77 - 1.58 (m, 4H), 1.42 - 1.10 (m, 20H), 0.83 (t, *J* = 6.6 Hz, 6H). **^{13}C NMR** (151 MHz, DMSO) δ 144.78 (d, *J* = 9.5 Hz), 142.44, 139.86, 130.86, 130.69, 130.13, 129.98, 128.71, 128.55, 128.46, 128.40, 127.81, 127.78, 127.59, 127.11, 126.16, 126.06, 122.95, 122.57, 121.61, 54.90, 35.00, 31.28, 30.57, 28.87, 28.76, 28.69, 22.10, 13.93. **^{31}P NMR** (162 MHz, DMSO) δ 2.93. **HRMS** (ESI) found $[M-H]^-$ 1057.4543, $C_{68}H_{62}N_6O_2P$ requires 1057.4552.

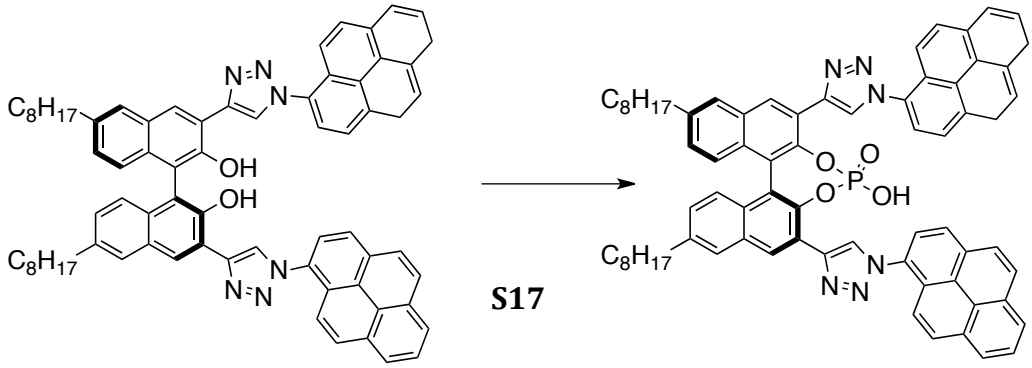
(*S*)-6,6'-dioctyl-3,3'-bis(1-(pyren-2-yl)-1*H*-1,2,3-triazol-4-yl)-[1,1'-binaphthalene]-2,2'-diol (S1f)



Subjection of *bis*-alkyne **8** (0.200 g, 0.309 mmol) to General Procedure Bi-Bii, gave intermediate **S1f-i** (0.235 g, 0.207 mmol, 67 % yield) as a dark green solid after purification by column chromatography on silica gel using Et_2O/Hex as eluent (0 to 50 %). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.09 (s, 2H), 8.87 (s, 2H), 8.34 - 8.25 (m, 4H), 8.25 - 8.19 (m, 2H), 8.18 (s, 2H), 8.16 - 8.10 (m, 6H), 8.10 - 7.99 (m, 4H), 7.86 (s, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 4.73 (d, *J* = 5.0 Hz, 2H), 4.51 (d, *J* = 5.0 Hz, 2H), 2.80 (t, *J* = 7.6 Hz, 4H), 2.74 (s, 6H), 1.85 - 1.67 (m, 4H), 1.48 - 1.19 (m, 20H), 0.89 (t, *J* = 6.5 Hz, 6H).

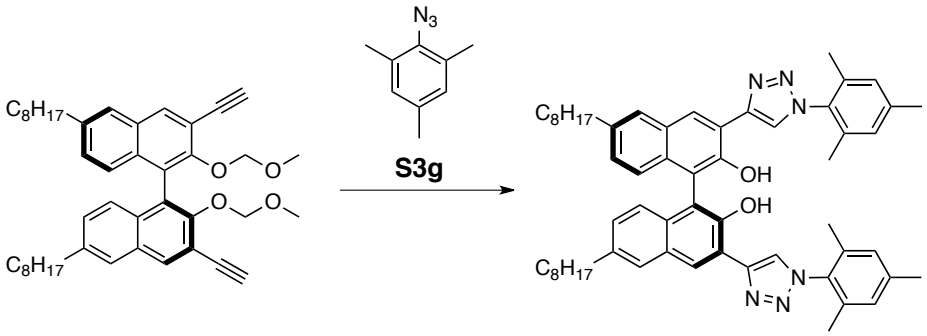
Subjection of **S1f-i** (0.200 g, 0.176 mmol) to General Procedure Biii gave the title compound **(**0.183 g, 0.175 mmol, 99 % yield) as a green solid after purification by column chromatography on silica gel using EtOAc/Hex as eluent (0 to 40 %). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.36 (s, 2H), 8.65 (s, 2H), 8.56 (s, 2H), 8.38 - 8.05 (m, 16H), 7.96 (d, *J* = 9.2 Hz, 2H), 7.72 (s, 2H), 7.27 (d, *J* = 8.7 Hz 2H), 7.18 (d, *J* = 8.7 Hz, 2H), 2.73 (t, *J* = 7.7 Hz, 4H), 1.79 - 1.62 (m, 4H), 1.44 - 1.14 (m, 20H), 0.86 (t, *J* = 6.4 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.40, 146.50, 138.33, 132.54, 132.14, 130.90, 130.43, 129.92, 129.70, 128.95, 128.89, 126.86, 126.82, 126.66, 126.55, 126.37, 126.04, 125.83, 124.87, 124.76, 124.66, 124.31, 123.87, 123.17, 120.86, 117.23, 116.39, 35.95, 32.01, 31.41, 29.65, 29.60, 29.41, 22.78, 14.25. **HRMS** (ESI) found $[M+H]^+$ 1045.5168, $C_{72}H_{65}N_6O_2$ requires 1045.5164.

(4*R*,11c*S*)-2-(1-(4,6-dihydropyren-1-yl)-1*H*-1,2,3-triazol-4-yl)-4-hydroxy-9,14-dioctyl-6-(1-(pyren-1-yl)-1*H*-1,2,3-triazol-4-yl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (9f)



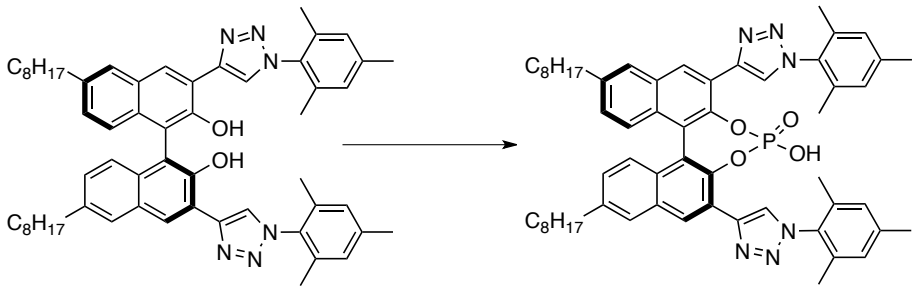
Subjection of diol **S1f** (0.150 g, 0.143 mmol) to General Procedure C gave the title compound (0.105 g, 0.095 mmol, 66 % yield) as a green solid after purification by column chromatography on silica gel using MeOH/DCM as eluent (0 to 5 %). **^{1}H NMR** (400 MHz, DMSO) δ 9.28 (s, 2H), 8.90 (s, 2H), 8.50 (d, *J* = 7.6 Hz, 2H), 8.44 (d, *J* = 7.4 Hz, 2H), 8.41 - 8.22 (m, 10H), 8.16 (t, *J* = 7.6 Hz, 2H), 8.02 (s, 2H), 7.96 (d, *J* = 9.3 Hz, 2H), 7.26 (d, *J* = 8.7 Hz, 2H), 7.17 (d, *J* = 8.7 Hz, 2H), 2.78 (t, *J* = 7.5 Hz, 4H), 1.85 ? 1.60 (m, 4H), 1.47 - 1.14 (m, 20H), 0.86 (t, *J* = 5.8 Hz, 6H). **^{13}C NMR** (151 MHz, DMSO) δ 145.43 (d, *J* = 7.9 Hz), 142.64, 139.45, 131.58, 130.59, 130.19, 130.02, 129.99, 129.70, 128.73, 128.15, 127.41, 126.99, 126.48, 126.07, 126.03, 125.14, 125.07, 124.00, 123.51, 123.19, 122.68, 120.76, 34.97, 31.25, 30.55, 28.84, 28.76, 28.66, 22.07, 13.93. **^{31}P NMR** (162 MHz, DMSO) δ 4.13. **HRMS** (ESI) found $[M-H]^-$ 1105.4553, $C_{72}H_{62}N_6O_4P$ requires 1105.4576.

(*S*)-3,3'-Bis(1-mesityl-1*H*-1,2,3-triazol-4-yl)-6,6'-dioctyl-[1,1'-binaphthalene]-2,2'-diol (S1g)



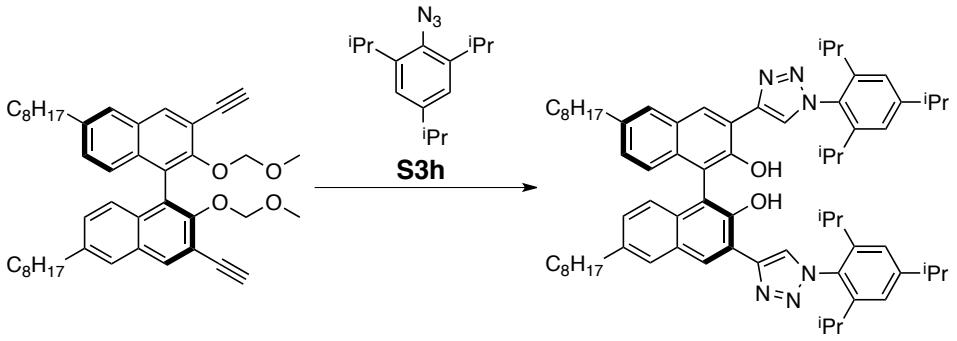
Subjection of *bis*-alkyne **8** (0.783 g, 1.20 mmol) and azide **S3g** (0.426 g, 2.64 mmol) to General Procedure A gave the title compound (0.157 g, 0.178 mmol, 15 % yield) as a yellow solid after purification by column chromatography on silica gel using Hex/EtOAc as eluent (4:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.69 (s, 2H), 8.43 (s, 2H), 8.21 (s, 2H), 7.70 (s, 2H), 7.22 (d, *J*= 8.5 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.06 (s, 4H), 2.81 - 2.67 (m, 4H), 2.41 (s, 6H), 2.07 (s, 12H), 1.79 - 1.64 (m, 4H), 1.42 - 1.21 (m, 20H), 0.89 (t, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.23, 146.58, 140.33, 138.27, 135.11, 133.28, 132.38, 129.20, 128.87, 128.68, 126.58, 126.04, 124.75, 122.85, 117.11, 116.34, 35.87, 31.92, 31.31, 29.55, 29.41, 29.31, 22.70, 21.21, 17.39, 14.14. **HRMS** (ESI) found $[M+H]^+$ 881.5472, $C_{58}H_{69}O_2N_6$ requires 881.5477.

(4*R*,11b*S*)-4-Hydroxy-2,6-bis(1-mesityl-1*H*-1,2,3-triazol-4-yl)-9,14-dioctyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (9g)



Subjection of diol **S1g** (0.143 g, 0.162 mmol) to General Procedure C gave the title compound (0.113 g, 0.119 mmol, 74 % yield) as a yellow solid after purification by column chromatography on silica gel using DCM/MeOH as eluent (20:1 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$: DMSO, 1:1) δ 8.75 (s, 2H), 8.69 (s, 2H), 7.92 (s, 2H), 7.17 (d, *J* = 8.7 Hz, 2H), 7.10 (s, 4H), 7.06 (d, *J* = 8.5 Hz, 2H), 2.88 - 2.58 (m, 4H), 2.31 (s, 6H), 1.94 (s, 12H), 1.75 - 1.49 (m, 4H), 1.42 - 1.05 (m, 20H), 0.81 (t, *J* = 6.4 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$: DMSO, 1:1) δ 145.57 (d, *J* = 8.9 Hz), 139.81, 139.74, 134.99, 133.78, 131.85, 131.02, 130.52, 129.18, 128.18, 127.36, 127.08, 126.59, 123.66, 123.04.**^{31}P NMR** (162 MHz, $CDCl_3$: DMSO, 1:1) δ 3.26. **HRMS** (ESI) found $[M-H]^-$ 941.4854, $C_{58}H_{66}O_4N_6P_1$ requires 941.4889.

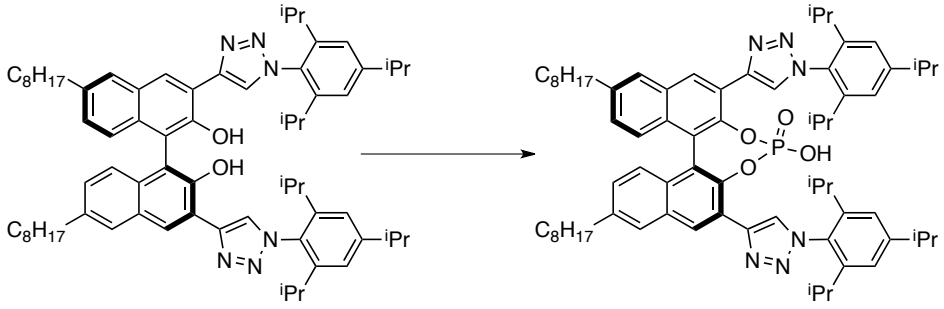
(*S*)-6,6'-Dioctyl-3,3'-bis(1-(2,4,6-triisopropylphenyl)-1*H*-1,2,3-triazol-4-yl)-[1,1'-binaphthalene]-2,2'-diol (S1h)



Subjection of *bis*-alkyne **8** (0.320 g, 0.494 mmol) and azide **S3h** (0.267 g, 1.09 mmol) to General Procedure A gave the title compound (0.328 g, 0.313 mmol, 63 % yield) as a yellow solid after purification by column chromatography on silica gel using Hex/EtOAc as eluent (4:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.84 (s, 2H), 8.42 (s, 2H), 8.23 (s, 2H), 7.71 (s, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.19 (s, 4H), 7.16 (d, *J* = 8.5 Hz, 2H), 3.03 (sept, *J* = 7. 0 Hz, 2H), 2.79 - 2.71 (m, 4H), 2.48 - 2.26 (m, 4H), 1.77 - 1.65 (m, 4H), 1.35 (d, *J* = 6.8 Hz, 24H), 1.31 (d, *J* = 6.8 Hz, 12H), 1.24 - 1.18 (m, 20H), 0.90 (t, *J* = 6.7 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.81, 150.35, 146.48, 145.86, 145.77, 138.26, 132.49,

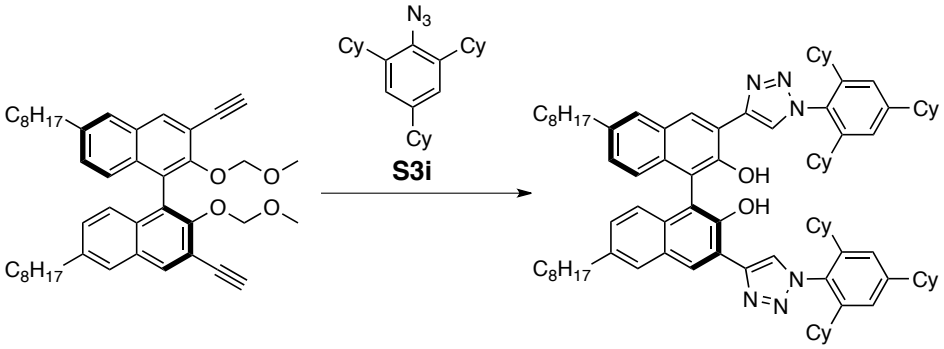
130.78, 128.88, 128.68, 126.59, 126.01, 124.81, 123.89, 121.90, 121.87, 117.10, 116.57, 35.91, 34.56, 31.95, 31.36, 29.58, 29.43, 29.33, 28.58, 28.55, 24.36, 24.31, 24.16, 24.05, 22.73, 14.18. **HRMS** (ESI) found $[M+H]^+$ 1049.7347, $C_{70}H_{93}O_2N_6$ requires 1049.7355.

(4*R*,11b*S*)-4-Hydroxy-9,14-dioctyl-2,6-bis(1-(2,4,6-triisopropylphenyl)-1*H*-1,2,3-triazol-4-yl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (9h)



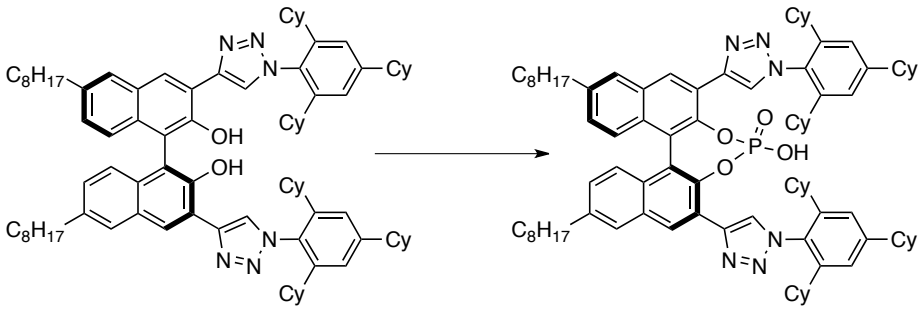
Subjection of diol **S1h** (0.230 g, 0.219 mmol) to General Procedure C gave the title compound (0.240 g, 0.216 mmol, 99 % yield) as an orange solid after purification by column chromatography on silica gel using Hex/EtOAc (1:1) with 1 % TFA as eluent. **^{1}H NMR** (400 MHz, DMSO) δ 8.79 (s, 2H), 8.73 (s, 2H), 7.92 (s, 2H), 7.22 (s, 4H), 7.17 (d, *J* = 8.7 Hz, 2H), 7.05 (d, *J* = 8.7 Hz, 2H), 2.95 (sept, *J* = 6.8 Hz, 2H), 2.81 - 2.66 (m, 4H), 2.35 - 2.20 (m, 2H), 2.20 - 2.07 (m, 2H), 1.81 - 1.50 (m, 4H), 1.46 - 1.16 (m, 26H), 1.16 - 0.91 (m, 20H), 0.81 (t, *J* = 6.5 Hz, 6H). **^{13}C NMR** (151 MHz, DMSO) δ 151.71 (d, *J* = 3.6 Hz), 145.69, 145.59, 139.89, 131.24, 131.01, 130.44, 128.51, 128.34, 127.63, 127.39, 126.42, 123.58, 122.94, 122.07, 122.05, 35.38, 34.22, 31.68, 30.97, 29.26, 29.14, 29.09, 28.53, 28.45, 24.30, 24.26, 24.23, 24.14, 22.50, 14.35. **^{31}P NMR** (162 MHz, DMSO) δ 4.20. **HRMS** (ESI) found $[M+H]^+$ 1111.6904, $C_{70}H_{92}O_4N_6P_1$ requires 1111.6912.

(*S*)-6,6'-Dioctyl-3,3'-bis(1-(2,4,6-tricyclohexylphenyl)-1*H*-1,2,3-triazol-4-yl)-[1,1'-binaphthalene]-2,2'-diol (S1i)



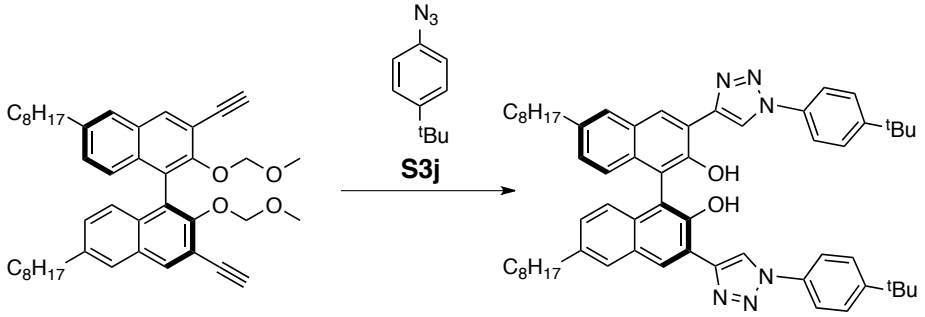
Subjection of *bis*-alkyne **8** (0.380 g, 0.586 mmol) and azide **S3i** (0.472 g, 1.29 mmol) to General Procedure A gave the title compound (0.300 g, 0.232 mmol, 40 % yield) as a yellow solid after purification by column chromatography on silica gel using Hex/Et_2O as eluent (20:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 10.25 (s, 2H), 8.34 (s, 2H), 8.16 (s, 2H), 7.69 (s, 2H), 7.24 (d, *J*= 8 Hz 2H), 7.17-7.13 (m, 6H), 2.72 (app t, *J*=8 Hz, 4H), 2.63-2.34 (m, 6H), 1.47-1.19 (m, 86H), 0.87 (t, *J*= 8 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.58, 150.54, 146.61, 144.87, 144.75, 138.18, 132.52, 130.85, 128.82, 128.56, 126.50, 125.80, 124.85, 123.44, 123.03, 122.99, 117.06, 116.90, 44.95, 39.17, 35.90, 34.87, 34.70, 34.66, 34.46, 33.15, 31.93, 31.35, 29.55, 29.39, 29.30, 27.27, 27.12, 26.88, 26.67, 26.59, 26.54, 26.50, 26.46, 26.29, 26.13, 25.95, 22.70, 14.14. **HRMS** (ESI) found $[M+H]^+$ 1289.9248, $C_{88}H_{117}O_2N_6$ requires 1289.9233.

(4*R*,11b*S*)-4-Hydroxy-9,14-dioctyl-2,6-bis(1-(2,4,6-tricyclohexylphenyl)-1*H*-1,2,3-triazol-4-yl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (9i)



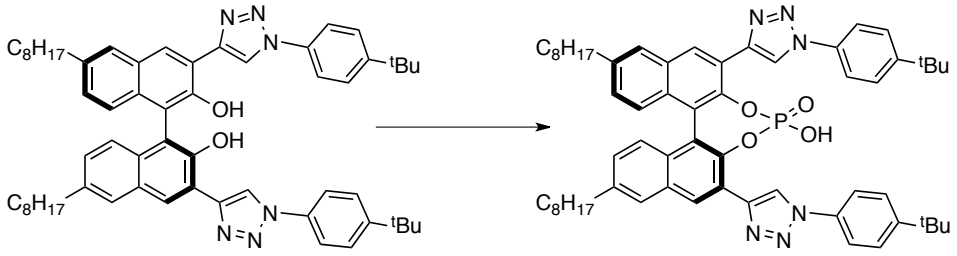
Subjection of diol **S3i** (0.271 g, 0.210 mmol) to General Procedure C gave the title compound (0.250 g, 0.185 mmol, 88 % yield) as a beige solid after purification by column chromatography on silica gel using Hex/EtOAc (1:1) with 0.5 % TFA as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$: DMSO, 1:1) δ 8.76 (s, 2H), 8.74 (s, 2H), 7.96 (s, 2H), 7.19 - 7.13 (m, 4H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.03 (s, 2H) 2.92 - 2.66 (m, 4H), 2.65 - 2.50 (m, 6H), 2.05 - 0.89 (m, 84H), 0.81 (t, *J* = 6.4 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$: DMSO, 1:1) δ 148.22, 142.82, 142.62, 137.95, 129.57, 129.15, 128.55, 126.31, 126.01, 125.10, 124.73, 121.69, 121.35, 120.99, 120.92, 120.83, 42.76, 42.31, 37.15, 36.90, 35.73, 33.65, 32.74, 32.41, 32.38, 32.32, 31.99, 31.98, 31.92, 29.81, 29.13, 27.40, 27.26, 27.21, 24.83, 24.78, 24.74, 24.64, 24.44, 24.03, 24.00, 23.95, 23.83, 20.62, 12.35. **^{31}P NMR** (162 MHz, $CDCl_3$: DMSO, 1:1) δ 9.16. **HRMS** (ESI) found $[M-H]^-$ 1349.8649, $C_{88}H_{114}O_2N_6P_1$ requires 1349.8645.

(*S*)-3,3'-bis(1-(4-(*tert*-butyl)phenyl)-1*H*-1,2,3-triazol-4-yl)-6,6'-dioctyl-[1,1'-binaphthalene]-2,2'-diol (S1j)



Subjection of *bis*-alkyne **8** (0.351 g, 0.541 mmol) and azide **S3j** (0.209 g, 1.19 mmol) to General Procedure A gave the title compound (0.210 g, 0.231 mmol, 43 % yield) as a yellow solid after purification by column chromatography on silica gel using Hex/EtOAc as eluent (10:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.30 (s, 2H), 8.55 (s, 2H), 8.46 (s, 2H), 7.76 (d, *J* = 8.3 Hz, 4H), 7.69 (s, 2H), 7.58 (d, *J* = 8.4 Hz, 4H), 7.18 (d, *J* = 9.1 Hz, 2H), 7.13 (d, *J* = 9.1 Hz, 2H), 2.72 (t, *J* = 6.0 Hz, 4H), 1.76 - 1.62 (m, 4H), 1.40 (s, 18H), 1.37 - 1.20 (m, 20H), 0.89 (t, *J* = 6.5 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.55, 152.47, 150.10, 138.36, 134.46, 132.28, 128.93, 128.75, 126.74, 126.69, 126.29, 124.69, 120.40, 119.19, 117.15, 115.93, 35.87, 34.86, 31.93, 31.31, 31.29, 29.55, 29.45, 29.31, 22.70, 14.15. **HRMS** (ESI) found $[M+H]^+$ 909.5801, $C_{60}H_{73}N_6O_2$ requires 909.5790.

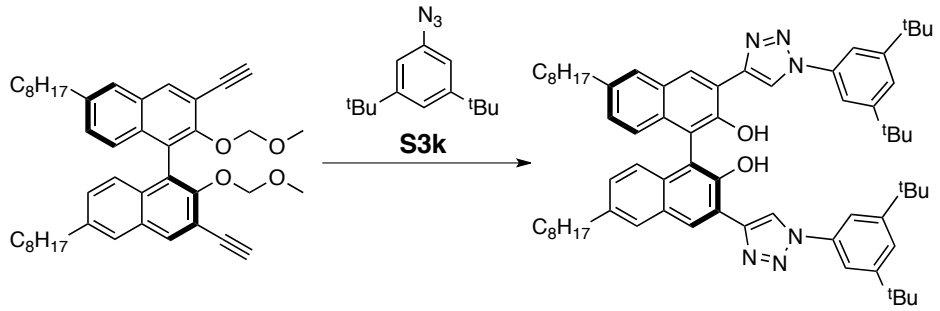
(4*R*,11b*S*)-2,6-bis(1-(4-(*tert*-butyl)phenyl)-1*H*-1,2,3-triazol-4-yl)-4-hydroxy-9,14-dioctyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (9j)



Subjection of diol **S1j** (0.181 g, 0.200 mmol) to General Procedure C gave the title compound **(**0.151 g, 0.155 mmol, 78 % yield) as a brown solid after purification by column chromatography on silica gel using Hex/EtOAc (1:1) with 1 % TFA as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$: DMSO, 1:1) δ 8.98 (s, 2H), 8.73 (s, 2H), 7.79 (s, 2H), 7.69 (d, *J* = 8.4 Hz, 4H), 7.40 (d, *J* = 8.1 Hz, 4H), 7.11 (s, 4H), 2.72 (t, *J* = 7.6 Hz, 4H), 1.77 - 1.55 (m, 4H), 1.45 - 1.08 (m, 38H), 0.85 (t, *J* = 6.3 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$: DMSO, 1:1) δ 164.54, 151.64, 144.42 (d, *J* = 7.6 Hz), 143.06, 140.32, 134.55, 131.23, 130.41, 128.54, 128.19, 127.15, 126.67, 122.97, 122.76, 122.25, 120.11, 35.68,

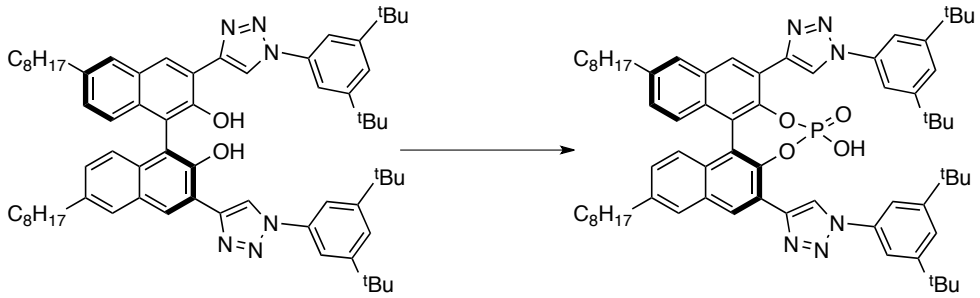
34.72, 31.83, 31.32, 31.10, 29.43, 29.38, 29.24, 22.64, 14.33. **^{31}P NMR** (202 MHz, $CDCl_3$: DMSO, 1:1) δ 3.50. **HRMS** (ESI) found $[M+H]^+$ 971.5355, $C_{60}H_{72}N_6O_4P_1$ requires 971.5347.

(*S*)-3,3'-bis(1-(3,5-di-*tert*-butylphenyl)-1*H*-1,2,3-triazol-4-yl)-6,6'-dioctyl-[1,1'-binaphthalene]-2,2'-diol (S1k)



Subjection of *bis*-alkyne **8** (0.500 g, 0.771 mmol) and azide **S3k** (0.391 g, 1.69 mmol) to General Procedure A gave the title compound (0.409 g, 0.400 mmol, 52 % yield) as a yellow solid after purification by column chromatography on silica gel using Hex/EtOAc as eluent (20:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.60 (s, 2H), 8.56 (s, 2H), 8.43 (s, 2H), 7.67 (s, 2H), 7.63 (s, 4H), 7.56 (s, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 2.71 (app t, *J* = 7.4 Hz, 4H), 1.79 - 1.58 (m, 4H), 1.48 - 1.17 (m, 56H), 0.87 (t, *J* = 6.7 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 153.22, 150.49, 147.26, 138.49, 136.89, 132.60, 129.09, 129.02, 126.95, 126.42, 124.93, 123.57, 119.75, 117.35, 116.47, 115.87, 36.13, 35.49, 32.20, 31.64, 31.56, 29.82, 29.71, 29.58, 22.96, 14.42. **HRMS** (ESI) found $[M+H]^+$ 1021.7058, $C_{68}H_{89}N_6O_2$ requires 1021.7042.

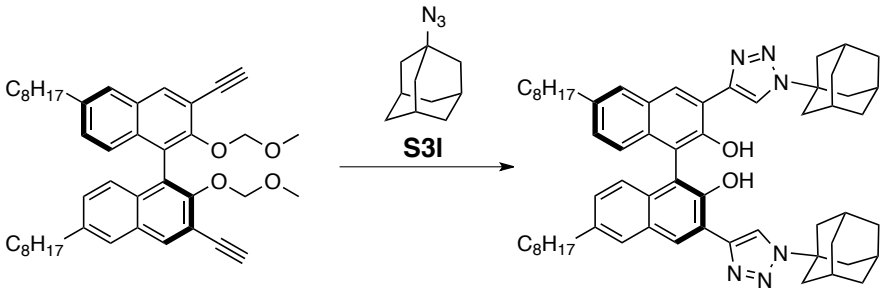
(4*R*,11b*S*)-2,6-bis(1-(3,5-di-*tert*-butylphenyl)-1*H*-1,2,3-triazol-4-yl)-4-hydroxy-9,14-dioctyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (9k)



Subjection of diol **S1k** (0.352 g, 0.345 mmol) to General Procedure C gave the title compound (0.341 g, 0.315 mmol, 91 % yield) as a brown solid after purification by

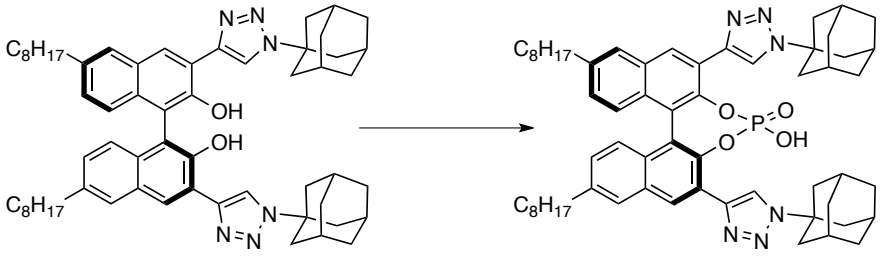
column chromatography on silica gel using Hex/EtOAc (1:1) with 1 % TFA as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$: DMSO, 1:1) δ 9.01 (s, 2H), 8.80 (s, 2H), 7.85 (s, 2H), 7.64 (s, 4H), 7.50 (s, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.17 (t, *J* = 8.5 Hz, 2H), 2.74 (t, *J* = 7.2 Hz, 4H), 1.80 - 1.62 (m, 4H), 1.45 - 1.08 (m, 56H), 0.84 (t, *J* = 6.1 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$: DMSO, 1:1) δ 152.83, 144.05 (d, *J* = 8.9 Hz), 143.04, 140.63, 136.85, 131.44, 130.42, 128.75, 128.35, 127.22, 126.61, 122.95, 122.84, 122.73, 115.40, 35.70, 35.24, 31.82, 31.47, 31.11, 29.41, 29.33, 29.22, 22.63, 14.31. **^{31}P NMR** (202 MHz, $CDCl_3$: DMSO, 1:1) δ 2.35. **HRMS** (ESI) found $[M+H]^+$ 1083.6586, $C_{68}H_{88}N_6O_4P_1$ requires 1083.6599.

(*S*)-3,3'-bis(adamantan-1-yl-1*H*-1,2,3-triazol-4-yl)-6,6'-dioctyl-[1,1'-binaphthalene]-2,2'-diol (S1l)



Subjection of *bis*-alkyne **8** (1.00 g, 1.54 mmol) and azide **S3l** (0.601 g, 3.39 mmol) to General Procedure A gave the title compound (0.900 g, 0.981 mmol, 64 % yield) as a brown solid after purification by column chromatography on silica gel using Hex/EtOAc as eluent (10:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 10.16 (s, 2H), 8.21 (s, 2H), 8.17 (s, 2H), 7.59 (s, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 7.05 (d, *J* = 8.7 Hz, 2H), 2.82 - 2.58 (m, 4H), 2.43 - 2.24 (m, 18H), 1.82 (s, 12H), 1.49 - 1.04 (m, 20H), 0.85 (t, *J* = 6.3 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.59, 146.30, 137.65, 132.33, 128.52, 128.29, 126.43, 125.27, 124.79, 117.32, 117.15, 117.05, 60.23, 59.06, 42.92, 41.56, 35.93, 35.86, 35.81, 31.97, 31.38, 29.84, 29.76, 29.62, 29.55, 29.50, 29.36, 22.74, 14.19. **HRMS** (ESI) found $[M+H]^+$ 913.6100, $C_{60}H_{77}O_2N_6$ requires 913.6103.

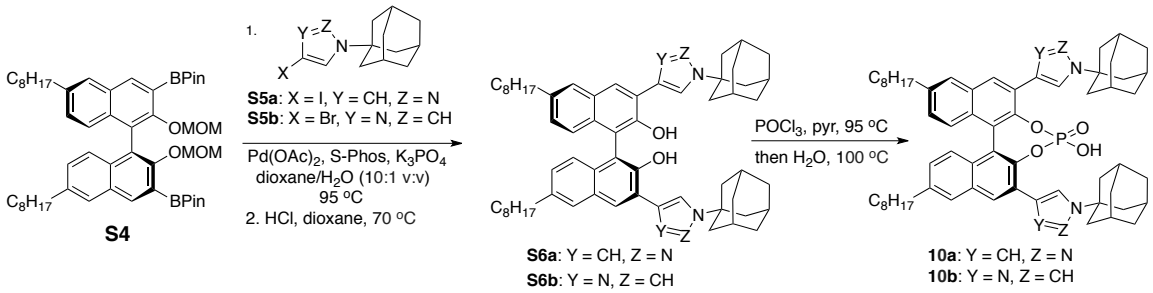
(4*R*,11b*S*)-4-hydroxy-2,6-bis(adamantan-1-yl-1*H*-1,2,3-triazol-4-yl)-9,14-dioctyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (9l)



Subjection of diol **S1l** (0.850 g, 0.927 mmol) to General Procedure C gave the title compound (0.882 g, 0.905 mmol, 98 % yield) as a brown solid after purification by column chromatography on silica gel using DCM/MeOH as eluent. (20:1). **^{1}H NMR** (500 MHz, $CDCl_3$: DMSO, 1:1) δ 8.70 (s, 2H), 8.56 (s, 2H), 7.80 (s, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 2.81 - 2.62 (m, 4H), 2.34 - 2.13 (m, 18H), 1.77 (s, 12H), 1.70 - 1.52 (m, 4H), 1.44 – 1.11 (m, 20H), 0.83 (t, *J* = 6.7 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$: DMSO, 1:1) δ 144.00 (d, *J* = 9.6 Hz), 141.28, 140.44, 131.35, 130.19, 128.54, 128.07, 127.15, 126.57, 123.23, 122.58, 120.91, 59.75, 42.87, 35.84, 35.62, 31.79, 31.09, 29.39, 29.37, 29.31, 29.19, 22.61, 14.33. **^{31}P NMR** (202 MHz, $CDCl_3$: DMSO, 1:1) δ 2.91. **HRMS** (ESI) found $[M+H]^+$ 975.5638, $C_{60}H_{76}O_2N_6P_1$ requires 975.5660.

Compounds 11a and 11b were prepared according to the reaction sequence depicted in Scheme S3.

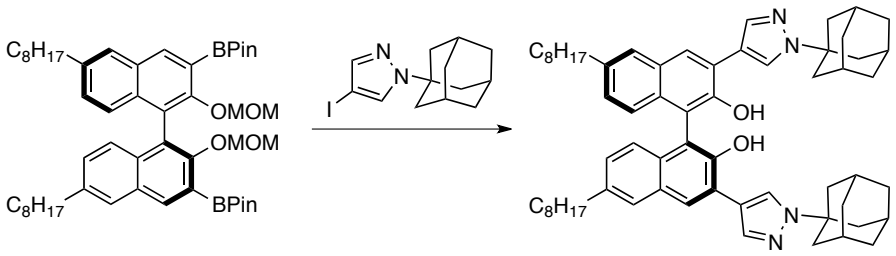
Scheme S3. Synthesis of Catalysts 10a-b



1-((3*s*,5*s*,7*s*)-adamantan-1-yl)-4-iodo-1*H*-pyrazole (S5a)[11]

To magnetically stirred solution of iodic acid (0.176 g, 1.0 mmol) and iodine (0.302 g, 1.19 mmol) in carbon tetrachloride (0.5 mL), water (1 mL) and acetic acid (1 mL) was added 1-((3*s*,5*s*,7*s*)-adamantan-1-yl)-1*H*-pyrazole (0.750 g, 3.71 mmol).[12] The reaction mixture was heated at 50 ^{o}C for 12 h at which point TLC indicated complete consumption of the starting material. After being allowed to cool to room temperature, the reaction mixture was diluted with saturated aqueous Na_2SO_3 (3 mL) and then basified by 1 N NaOH. The resulting suspension was extracted with EtOAc (3 X 20 mL), dried and concentrated *in vacuo* to afford the title compound (0.925 g, 2.83 mmol, 76 % yield) as a white semi-solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.54 (s, 1H), 2.24 (s, 3H), 2.15 - 2.09 (m, 6H), 1.79 - 1.73 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.40, 129.61, 59.36, 54.96, 42.72, 36.05, 29.53. **HRMS** (ESI) found $[M+H]^+$ 329.0512, $C_{13}H_{18}N_2I$ requires 329.0509.

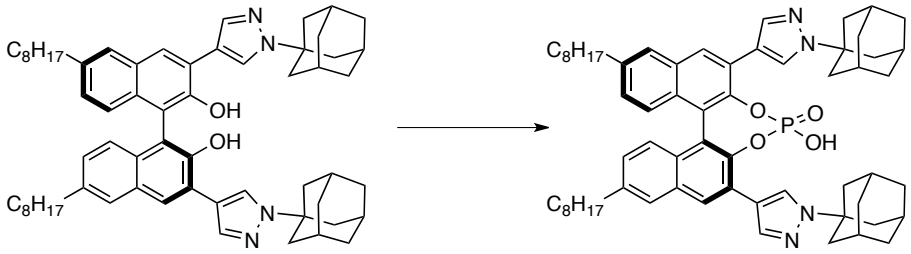
(*S*)-3,3'-bis(adamantan-1-yl-1*H*-pyrazol-4-yl)-6,6'-dioctyl-[1,1'-binaphthalene]-2,2'-diol (S6a)



To a magnetically stirred solution of *bis*-boronate ester **S4** (0.868 g, 1.02 mmol) and pyrazole **S5a** (0.900 g, 2.75 mmol) in 1,4-dioxane/H_2O (6.2/0.6 mL) were added $Pd(OAc)_2$ (0.011 g, 0.051 mmol), S-Phos (0.042 g, 0.102 mmol), and K_3PO_4 (0.650 g, 3.06 mmol). The reaction mixture was degassed under vacuum (3 X 30 s) and stirred at 95 ^{o}C for 15 h. The reaction mixture was allowed to cool to room temperature and then filtered through celite, dried (Na_2SO_4) and concentrated *in vacuo*. The crude residue was dissolved in 1,4-dioxane (20 mL) and concentrated HCl (2 mL) was added. The reaction mixture was stirred at 70 ^{o}C for 2 h, and then allowed to cool to room temperature and concentrated *in vacuo*. The residue was dissolved in DCM and washed with saturated aqueous Na_2CO_3 (20 mL), H_2O (20 mL) and brine (20 mL). The organic extracts were dried (Na_2SO_4) and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel using Hex/EtOAc as eluent (20:1 to 10:1) to afford the title compound (0.275 g, 0.302 mmol, 30 % yield) as a yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (s, 2H), 8.15 (s, 2H), 8.08 (s, 2H), 7.69 (s, 2H), 7.17 - 6.99 (m, 4H), 5.73 (s, 2H), 2.77 - 2.68 (m, 4H), 2.31 - 2.13 (m, 18H), 1.84 - 1.67 (m, 16H), 1.44 - 1.24 (m, 20H), 0.90 (t, *J* = 6.5 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.52, 138.87, 137.47,

130.24, 129.76, 128.32, 126.71, 126.45, 125.26, 124.07, 122.07, 116.97, 111.95, 58.63, 42.83, 36.16, 35.92, 31.94, 31.42, 29.57, 29.54, 29.45, 29.32, 22.72, 14.17. **HRMS** (ESI) found $[M-H]^-$ 909.6046, $C_{62}H_{77}N_4O_2$ requires 909.6052.

(4*R*,11b*S*)-4-hydroxy-2,6-bis(adamantan-1-yl-1*H*-pyrazol-4-yl)-9,14-dioctyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (10a)

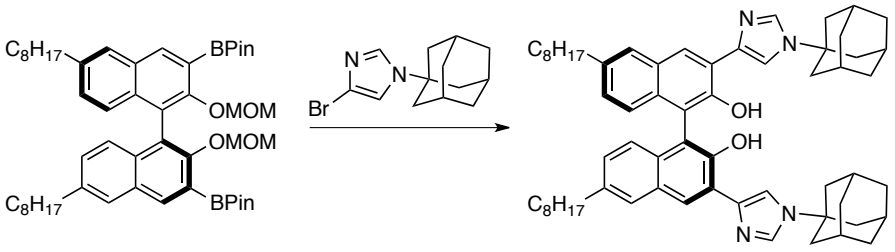


Subjection of diol **S6a** (0.080 g, 0.088 mmol) to General Procedure C gave the title compound (0.078 g, 0.080 mmol, 91 % yield) as a dark-yellow solid. **^{1}H NMR** (400 MHz, DMSO) δ 8.32 (s, 2H), 8.14 (s, 2H), 8.04 (s, 2H), 7.66 (s, 2H), 7.01 (s, 4H), 2.65 (t, *J* = 7.6 Hz, 4H), 2.28 - 2.07 (m, 18H), 1.80 - 1.67 (m, 12H), 1.67 - 1.49 (m, 4H), 1.35 - 1.14 (m, 20H), 0.80 (t, *J* = 6.5 Hz, 6H). **^{13}C NMR** (126 MHz, DMSO) δ 164.54, 144.21 (d, *J* = 9.6 Hz), 140.11, 137.88, 131.65, 129.37, 127.68, 127.22, 126.56, 126.45, 125.59, 125.42, 122.68, 116.64, 58.62, 42.82, 36.12, 35.66, 31.81, 31.07, 29.47, 29.44, 29.40, 29.28, 29.20, 22.62, 14.34. **^{31}P NMR** (162 MHz, DMSO) δ 1.91. **HRMS** (ESI) found $[M-H]^-$ 971.5584, $C_{62}H_{76}N_4O_4P_1$ requires 971.5610.

1-((3*s*,5*s*,7*s*)-adamantan-1-yl)-4-bromo-1*H*-imidazole (S5b)

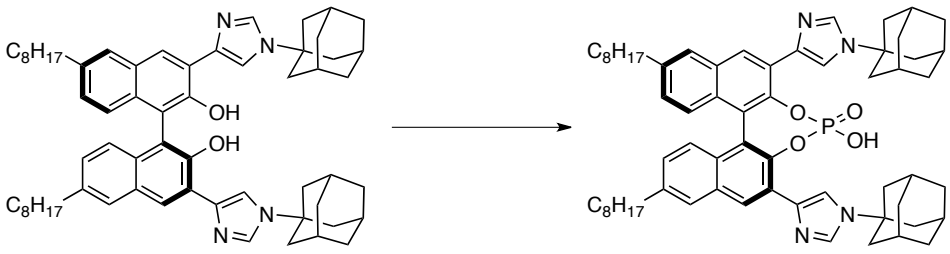
To a magnetically stirred solution of 1-((1*r*,3*R*,5*S*)-adamantan-1-yl)-1*H*-imidazole[13] (0.782 g, 3.87 mmol) in DMF (40 mL) was added N-bromosuccinimide (0.757 g, 4.25 mmol) and the reaction mixture was stirred at room temperature for 24 h. The crude reaction mixture was poured into H_2O (50 mL) and extracted with EtOAc (50 mL). The organic extracts were washed with H_2O (4 X 50 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the crude residue by column chromatography on silica gel using Hex/EtOAc as eluent (3:1) afforded the title compound (0.400 g, 1.42 mmol, 37 % yield) as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.45 (s, 1H), 6.99 (s, 1H), 2.19 (s, 3H), 2.01 (s, 6H), 1.72 (dd, *J* = 34.6, 12.9 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 133.16, 114.93, 114.72, 56.06, 43.49, 35.76, 29.34. **HRMS** (ESI) found $[M+H]^+$ 281.0649, $C_{13}H_{18}N_2Br$ requires 281.0648.

(*S*)-3,3'-bis(adamantan-1-yl-1*H*-imidazol-4-yl)-6,6'-dioctyl-[1,1'-binaphthalene]-2,2'-diol (S6b)



To a magnetically stirred solution of *bis*-boronate ester **S4** (0.408 g, 0.479 mmol) and imidazole **S5b** (0.363 g, 1.29 mmol) in 1,4-dioxane/H_2O (6.2/0.6 mL) were added $Pd(OAc)_2$ (0.011 g, 0.051 mmol), S-Phos (0.042 g, 0.102 mmol), and K_3PO_4 (0.650 g, 3.06 mmol). The reaction mixture was degassed under vacuum (3 x 30 s) and stirred at 95 ^oC for 15 h. The reaction mixture was allowed to cool to room temperature and then filtered through Celite, dried (Na_2SO_4) and concentrated *in vacuo*. The crude residue was dissolved in 1,4-dioxane (20 mL) and concentrated HCl (2 mL) was added. The reaction mixture was stirred at 70 ^oC for 2 h, and the allowed to cool to room temperature and concentrated *in vacuo*. The residue was dissolved in DCM and washed with saturated aqueous Na_2CO_3 (20 mL), H_2O (20 mL) and brine (20 mL). The organic extracts were dried (Na_2SO_4) and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel using Hex/EtOAc as eluent (20:1 to 10:1) to afford the title compound (0.275 g, 0.302 mmol, 30 % yield) as a yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 (s, 2H), 7.67 (s, 2H), 7.66 (s, 2H), 7.59 (s, 2H), 7.20 (d, J = 8.6 Hz, 2H), 7.03 (d, J = 8.6 Hz, 2H), 2.71 (t, J = 7.7 Hz, 4H), 2.29 (s, 6H), 2.18 (s, 12H), 1.90 - 1.76 (m, 12H), 1.73 - 1.62 (m, 4H), 1.49 - 1.23 (m, 20H), 0.91 (t, J = 6.3 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.70, 141.09, 136.92, 132.10, 131.41, 128.35, 127.39, 126.03, 124.98, 122.95, 119.71, 117.33, 111.65, 55.83, 43.80, 35.95, 35.84, 31.96, 31.37, 29.60, 29.51, 29.47, 29.33, 22.72, 14.15. **HRMS** (ESI) found $[M+H]^+$ 911.6201, $C_{62}H_{79}N_4O_2$ requires 911.6198.

(4*R*,11b*S*)-4-hydroxy-2,6-bis(adamantan-1-yl-1*H*-imidazol-4-yl)-9,14-dioctyldinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine 4-oxide (10b)

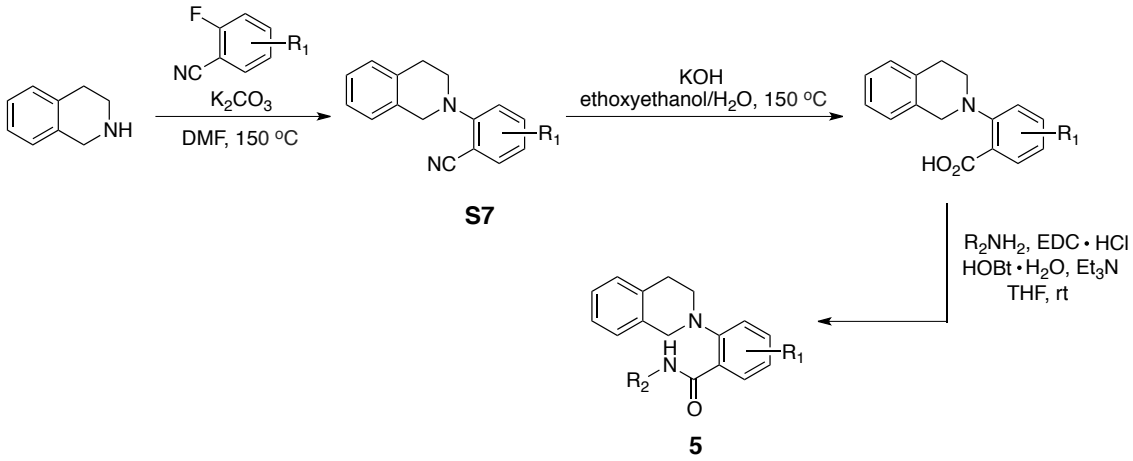


Subjection of diol **S6b** (0.051 g, 0.056 mmol) to General Procedure C gave the title compound (0.013 g, 0.013 mmol, 23 % yield) as a dark-yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$: DMSO, 1:1) δ 8.37 (s, 2H), 8.09 (s, 2H), 7.93 (s, 2H), 7.60 (s, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 2.64 (t, *J* = 7.8 Hz, 4H), 2.26 (s, 6H), 2.18 (s, 12H), 1.82 - 1.68 (m, 12H), 1.67 - 1.53 (m, 4H), 1.36 - 1.12 (m, 20H), 0.81 (t, *J* = 6.6 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$: DMSO, 1:1) δ 151.79, 140.30, 136.78, 132.44, 131.85, 128.21, 127.20, 124.86, 122.82, 119.77, 117.36, 113.17, 99.99, 56.18, 43.41, 35.86, 35.68, 31.81, 31.37, 29.48, 29.42, 29.29, 29.19, 22.59, 14.33. **^{31}P NMR** (202 MHz, $CDCl_3$: DMSO, 1:1) δ 9.12. **HRMS** (ESI) found $[M+H]^+$ 973.5771, $C_{62}H_{78}N_4O_4P$ requires 973.5755.

Synthesis of Substrates

Compounds **5a-r** were prepared according to the reaction sequence depicted in Scheme S4. Compounds **5a-m** and **5q-r** were prepared from known compound 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)benzoic acid.[14]

Scheme S4. Synthesis of Substrates 5



General Procedure D: Synthesis of Compounds 5a-m and 5q-r

To a magnetically stirred solution of 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)benzoic acid (1. 0 equiv.) in THF (0.1 M) were added N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (1.2 equiv.), 1-hydroxybenzotriazole hydrate (1.2 equiv.), triethylamine (1.3 equiv.), and the appropriate primary amine (1.2 equiv.) in succession and the reaction mixture was stirred at room temperature. Upon complete consumption of the starting material, as judged by TLC, the reaction mixture was filtered through silica gel

using EtOAc/Hex (1:1) as eluent. The resulting filtrate was concentrated *in vacuo*. The crude residue was purified by column chromatography or recrystallization.

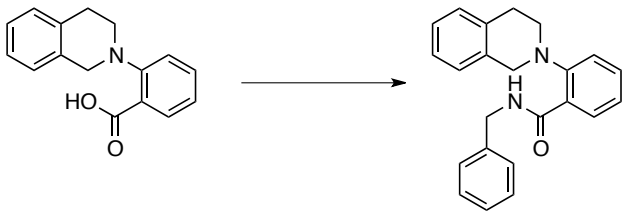
General Procedure E: Synthesis of N-arylated tetrahydroisoquinolines S7

To a magnetically stirred solution of 1,2,3,4-tetrahydroisoquinoline (2.0 equiv.) in DMF (2.0 M) was added K_2CO_3 (2.0 equiv.) followed by the appropriate 2-fluorobenzonitrile (1.0 equiv.). The reaction mixture was heated at 150 ^oC until TLC indicated complete consumption of the starting material. After being allowed to cool to room temperature, the reaction mixture was diluted with EtOAc, extracted with saturated aqueous NH_4Cl, washed with H_2O (x 4), dried (Na_2SO_4) and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel using EtOAc/Hex as eluent.

General Procedure F: Synthesis of Compounds 5n-p

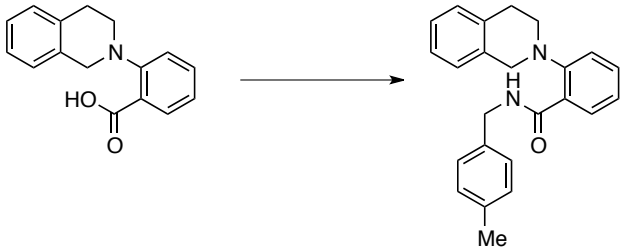
To a magnetically stirred solution of N-arylated 1,2,3,4-tetrahydroisoquinoline derivative **S7** (1.0 equiv.) in ethoxyethanol/H_2O (8:1 v:v, 1.0 M) was added freshly-ground KOH (6.0 equiv.). The reaction mixture was heated at 150 ^oC for 2h, at which point a precipitate was observed. The reaction mixture was allowed to cool to room temperature and the solid was filtered and dissolved in H_2O. This solution was acidified to pH = 7 using 3N HCl and extracted with DCM (x 2), dried (Na_2SO_4), and concentrated *in vacuo* to afford the crude carboxylic acid. Assuming quantitative yield, the crude product was dissolved in THF (0.1 M). To this magnetically stirred solution were added N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (1.2 equiv.), 1-hydroxybenzotriazole hydrate (1.2 equiv.), triethylamine (1.3 equiv.), and the appropriate primary amine (1.2 equiv.) in succession and the reaction mixture was stirred at room temperature. Upon complete consumption of the starting material, as judged by TLC, the reaction mixture was filtered through silica gel using EtOAc/Hex (1:1) as eluent. The resulting filtrate was concentrated *in vacuo*. The crude residue was purified by column chromatography or recrystallization.

***N*-benzyl-2-(3,4-dihydroisoquinolin-2(1*H*)-yl)benzamide (5a)**



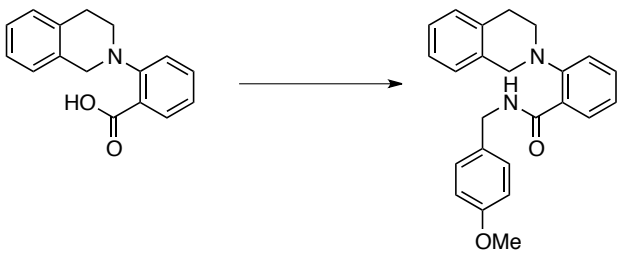
Subjection of 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)benzoic acid (1.00 g, 3.94 mmol) to General Procedure D gave the title compound (1.02 g, 2.98 mmol, 76 % yield) as a white solid after purification by column chromatography on silica gel using Hex/EtOAc as eluent (9:1). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 10.21 (s, 1H), 8.28 (d, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.32 - 7.24 (m, 2H), 7.23 - 7.11 (m, 3H), 7.11 - 7.04 (m, 3H), 7.03 - 6.96 (m, 3H), 4.48 (d, *J* = 5.1 Hz, 2H), 4.08 (s, 2H), 3.26 (t, *J* = 5.8 Hz, 2H), 2.76 (t, *J* = 5.8 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.03, 151.23, 137.99, 133.78, 133.40, 132.17, 131.64, 129.02, 128.49, 127.96, 127.88, 127.14, 126.70, 126.31, 126.10, 125.18, 121.00, 56.77, 50.40, 44.06, 29.24. **HRMS** (ESI) found $[M+H]^+$ 343.1800, $C_{23}H_{23}N_2O$ requires 343.1805.

2-(3,4-dihydroisoquinolin-2(1*H*)-yl)-*N*-(4-methylbenzyl)benzamide (5b)



Subjection of 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)benzoic acid (1.00 g, 3.94 mmol) to General Procedure D gave the title compound (0.587 g, 1.65 mmol, 42 % yield) as a white solid after recrystallization from hot EtOAc. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.18 (s, 1H), 8.29 (d, *J* = 9.3 Hz, 1H), 7.48 (app t, *J* = 7.6 Hz, 1H), 7.33 - 7.15 (m, 4H), 7.06 (d, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 7.2 Hz, 1H), 6.91 (d, *J* = 13.0 Hz, 2H), 6.88 (d, *J* = 13.0 Hz, 2H) 4.45 (d, *J* = 5.0 Hz, 2H), 4.08 (s, 2H), 3.27 (t, *J* = 5.9 Hz, 2H), 2.78 (t, *J* = 5.9 Hz, 2H), 2.28 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.91, 151.23, 136.65, 134.88, 133.76, 133.42, 132.12, 131.61, 129.15, 128.91, 128.01, 127.85, 126.55, 126.29, 126.01, 125.16, 121.01, 56.70, 50.37, 43.83, 29.26, 21.13. **HRMS** (ESI) found $[M+H]^+$ 357.1958, $C_{24}H_{25}N_2O$ requires 357.1961.

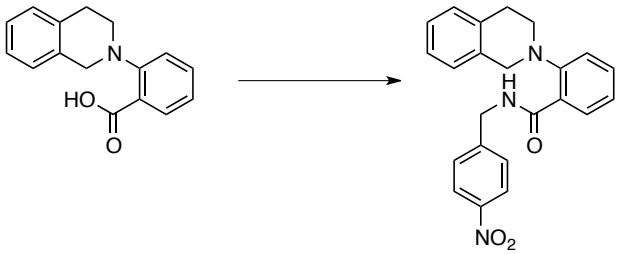
2-(3,4-dihydroisoquinolin-2(1*H*)-yl)-*N*-(4-methoxybenzyl)benzamide (5c)



Subjection of 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)benzoic acid (1.00 g, 3.94 mmol) to General Procedure D gave the title compound (0.680 g, 1.82 mmol, 46 % yield) as a

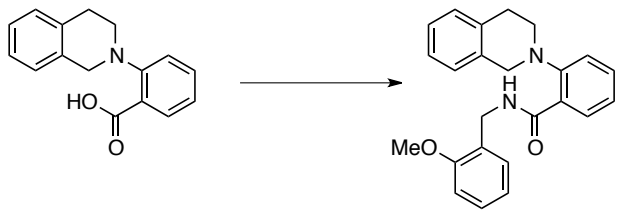
white solid after recrystallization from hot EtOAc. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.17 (s, 1H), 8.29 (d, *J* = 9.1 Hz, 1H), 7.48 (app t, *J* = 7.6 Hz, 1H), 7.34 - 7.15 (m, 4H), 7.08 (d, *J* = 7.2 Hz, 1H), 7.00 (d, *J* = 7.3 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.60 (d, *J* = 8.5 Hz, 2H), 4.43 (d, *J* = 5.0 Hz, 2H), 4.07 (s, 2H), 3.80 (s, 3H), 3.27 (t, *J* = 5.8 Hz, 2H), 2.78 (t, *J* = 5.7 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.85, 158.60, 151.22, 133.79, 133.44, 132.12, 131.58, 130.06, 129.17, 128.95, 128.00, 126.62, 126.30, 126.03, 125.17, 120.99, 113.81, 56.80, 55.18, 50.27, 43.50, 29.31. **HRMS** (ESI) found $[M+H]^+$ 373.1906, $C_{24}H_{25}N_2O_2$ requires 373.1911.

2-(3,4-dihydroisoquinolin-2(1*H*)-yl)-*N*-(4-nitrobenzyl)benzamide (5d)



Subjection of 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)benzoic acid (1.00 g, 3.94 mmol) to General Procedure D gave the title compound (0.473 g, 1.22 mmol, 31 % yield) as a white solid after recrystallization from hot EtOAc. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.58 (s, 1H), 8.30 (d, *J* = 7.8 Hz, 1H), 7.91 (d, *J* = 8.6 Hz, 2H), 7.53 (app t, *J* = 7.6 Hz, 1H), 7.36 - 7.29 (m, 2H), 7.23 - 7.12 (m, 4H), 7.05 (d, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 4.57 (d, *J* = 5.4 Hz, 2H), 4.02 (s, 2H), 3.32 (t, *J* = 5.9 Hz, 2H), 2.86 (t, *J* = 5.9 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.16, 151.28, 147.00, 145.50, 133.48, 133.01, 132.60, 131.62, 128.92, 128.57, 127.51, 126.90, 126.28, 126.18, 125.57, 123.71, 121.35, 57.27, 50.11, 43.27, 29.58. **HRMS** (ESI) found $[M+H]^+$ 388.1651, $C_{23}H_{22}N_3O_3$ requires 388.1656.

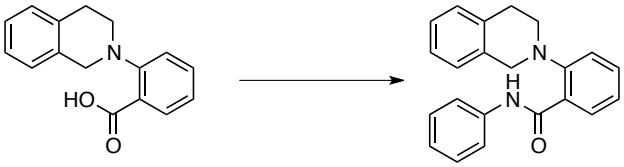
2-(3,4-dihydroisoquinolin-2(1*H*)-yl)-*N*-(2-methoxybenzyl)benzamide (5e)



Subjection of 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)benzoic acid (1.00 g, 3.94 mmol) to General Procedure D gave the title compound (0.251 g, 0.673 mmol, 17 % yield) as a white solid after recrystallization from hot EtOAc. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.98

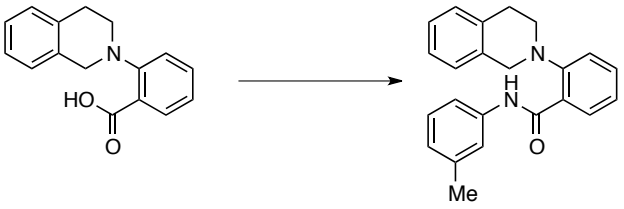
(s, 1H), 8.26 (d, *J* = 8.1 Hz, 1H), 7.45 (app t, *J* = 7.7 Hz, 1H), 7.31 - 7.24 (m, 2H), 7.24 - 7.12 (m, 4H), 7.08 (d, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 7.7 Hz, 1H), 6.79 (app t, *J* = 7.4 Hz, 1H), 6.61 (d, *J* = 8.1 Hz, 1H), 4.58 (d, *J* = 5.5 Hz, 2H), 4.13 (s, 2H), 3.42 (s, 3H), 3.23 (t, *J* = 5.8 Hz, 2H), 2.76 (t, *J* = 5.9 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.04, 157.41, 151.10, 134.05, 133.62, 131.86, 131.75, 129.87, 129.02, 128.63, 128.30, 126.44, 126.31, 126.23, 126.00, 124.80, 120.54, 120.44, 110.13, 55.24, 54.77, 51.59, 39.07, 28.97. **HRMS** (ESI) found $[M+H]^+$ 373.1906, $C_{24}H_{25}N_2O_2$ requires 373.1911.

2-(3,4-dihydroisoquinolin-2(1*H*)-yl)-*N*-phenylbenzamide (5f)



Subjection of 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)benzoic acid (0.506 g, 2.0 mmol) to General Procedure D gave the title compound (0.500 g, 0.673 mmol, 76 % yield) as a white solid after purification by column chromatography on silica gel using Hex/EtOAc as eluent (10:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 12.51 (s, 1H), 8.41 (d, *J* = 7.5 Hz, 1H), 7.56 (app t, *J* = 8.4 Hz, 1H), 7.43 - 7.35 (m, 2H), 7.35 - 7.25 (m, 4H), 7.25 - 7.14 (m, 3H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 4.23 (s, 2H), 3.46 (t, *J* = 6.0 Hz, 2H), 3.20 (t, *J* = 6.0 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.84, 150.90, 138.72, 133.77, 133.13, 132.61, 131.93, 129.05, 128.91, 128.12, 127.15, 126.78, 126.32, 125.71, 123.59, 121.43, 119.60, 56.75, 51.14, 29.41. **HRMS** (ESI) found $[M+H]^+$ 329.1647, $C_{22}H_{21}N_2O_1$ requires 329.1648.

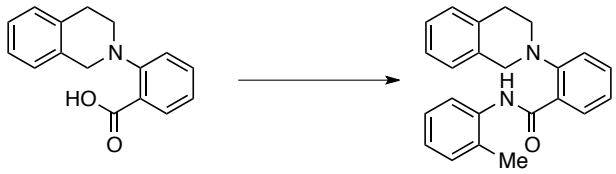
2-(3,4-dihydroisoquinolin-2(1*H*)-yl)-*N*-(*m*-tolyl)benzamide (5g)



Subjection of 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)benzoic acid (1.00 g, 3.94 mmol) to General Procedure D gave the title compound (0.785 g, 2.29 mmol, 58 % yield) as a white solid after recrystallization from hot EtOAc. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 12.52 (s, 1H), 8.41 (d, *J* = 6.6 Hz, 1H), 7.56 (app t, *J* = 7.6 Hz, 1H), 7.42 - 7.35 (m, 2H), 7.35 - 7.27 (m, 2H), 7.27 - 7.16 (m, 2H), 7.12 - 7.03 (m, 2H), 6.93 (s, 1H), 6.83 (d, *J* = 7.4 Hz, 1H), 4.22 (s, 2H), 3.47 (t, *J* = 5.9 Hz, 2H), 3.21 (t, *J* = 6.0 Hz, 2H), 2.18 (s, 3H). **^{13}C**

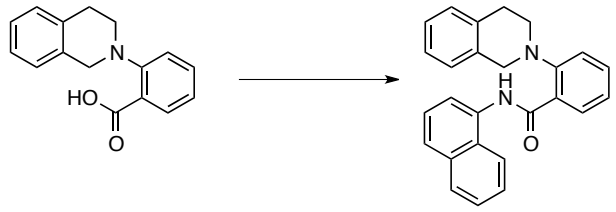
NMR (126 MHz, $CDCl_3$) δ 163.71, 150.88, 138.64, 138.61, 133.86, 133.25, 132.57, 131.90, 129.01, 128.74, 128.18, 127.20, 126.89, 126.26, 125.74, 124.39, 121.48, 120.25, 116.77, 56.95, 50.98, 29.44, 21.44. **HRMS** (ESI) found $[M+H]^+$ 343.1803, $C_{23}H_{23}N_2O_1$ requires 343.1805.

2-(3,4-dihydroisoquinolin-2(1*H*)-yl)-*N*-(*o*-tolyl)benzamide (5h)



Subjection of 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)benzoic acid (1.00 g, 3.94 mmol) to General Procedure D gave the title compound (0.695 g, 2.03 mmol, 52 % yield) as a white solid after purification by column chromatography on silica gel using Hex/EtOAc as eluent (4:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 11.57 (s, 1H), 8.37 (d, *J* = 7.7 Hz, 1H), 8.13 (d, *J* = 8.1 Hz, 1H), 7.53 (app t, *J* = 7.6 Hz, 1H), 7.40 - 7.32 (m, 2H), 7.26 - 7.20 (m, 3H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.15 - 7.07 (m, 2H), 7.04 (app t, *J* = 7.3 Hz, 1H), 4.36 (s, 2H), 3.45 (t, *J* = 5.9 Hz, 2H), 3.02 (t, *J* = 5.9 Hz, 2H), 1.98 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.56, 150.73, 136.58, 133.73, 133.39, 132.45, 132.16, 130.33, 128.97, 128.63, 128.51, 126.95, 126.57, 126.41, 126.36, 125.36, 124.39, 122.77, 121.04, 55.60, 52.11, 28.58, 17.60. **HRMS** (ESI) found $[M+H]^+$ 343.1802, $C_{23}H_{23}N_2O$ requires 343.1805.

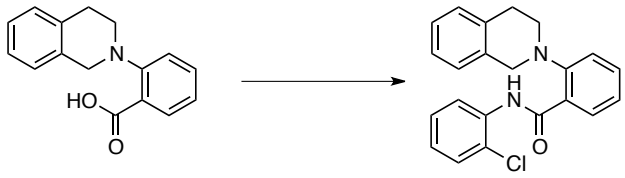
2-(3,4-dihydroisoquinolin-2(1*H*)-yl)-*N*-(naphthalen-1-yl)benzamide (5i)



Subjection of 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)benzoic acid (0.500 g, 1.97 mmol) to General Procedure D gave the title compound (0.304 g, 0.803 mmol, 41 % yield) as a white solid after recrystallization from hot EtOAc. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 12.61 (s, 1H), 8.45 (d, *J* = 7.8 Hz, 2H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.63 - 7.52 (m, 3H), 7.47 (app t, *J* = 7.9 Hz, 2H), 7.39 (app t, *J* = 7.5 Hz, 1H), 7.33 - 7.14 (m, 4H), 7.06 (d, *J* = 6.7 Hz, 1H), 6.63 (app t, *J* = 7.7 Hz, 1H), 4.45 (s, 2H), 3.43 (t, *J* = 5.9 Hz, 2H), 2.98 (t, *J* = 6.0 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.62, 151.12, 133.90, 133.71, 133.70,

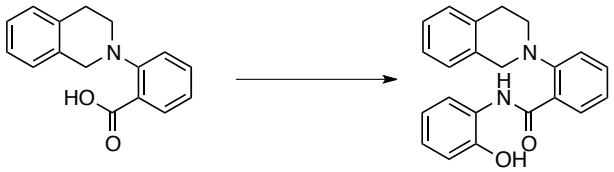
133.51, 132.65, 132.29, 129.20, 128.74, 128.48, 126.98, 126.51, 126.41, 126.00, 125.86, 125.58, 125.26, 124.26, 121.54, 120.97, 118.62, 55.86, 52.52, 29.18. **HRMS** (ESI) found $[M+H]^+$ 379.1801, $C_{26}H_{23}N_2O$ requires 379.1805.

_N_-(2-chlorophenyl)-2-(3,4-dihydroisoquinolin-2(1_H_)-yl)benzamide (5j)



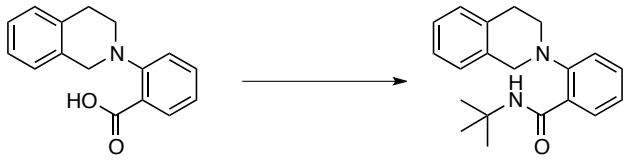
Subjection of 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)benzoic acid (0.500 g, 1.97 mmol) to General Procedure D gave the title compound (0.204 g, 0.562 mmol, 29 % yield) as a white solid after recrystallization from hot EtOAc. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 12.21 (s, 1H), 8.63 (d, *J* = 8.2 Hz, 1H), 8.28 (d, *J* = 7.8 Hz, 1H), 7.46 (app t, *J* = 7.5 Hz, 1H), 7.34 - 7.22 (m, 4H), 7.22 - 7.04 (m, 4H), 6.98 (app t, *J* = 6.9 Hz, 1H), 4.38 (s, 2H), 3.42 (t, *J* = 5.9 Hz, 2H), 2.94 (t, *J* = 5.9 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.82, 150.88, 135.83, 134.00, 133.98, 132.64, 132.15, 129.12, 128.88, 128.14, 127.47, 126.62, 126.26, 126.12, 125.13, 124.23, 123.15, 122.50, 121.49, 54.93, 52.12, 27.76. **HRMS** (ESI) found $[M+H]^+$ 363.1258, $C_{22}H_{20}N_2OCl$ requires 363.1259.

2-(3,4-dihydroisoquinolin-2(1_H_)-yl)-_N_-(2-hydroxyphenyl)benzamide (5k)



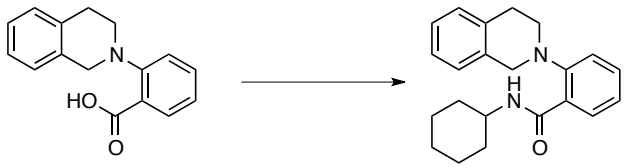
Subjection of 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)benzoic acid (0.415 g, 1.65 mmol) to General Procedure D gave the title compound (0.335 g, 0.973 mmol, 59 % yield) as a white solid after recrystallization from hot EtOAc. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 13.23 (s, 1H), 9.98 (s, 1H), 8.41 (d, *J* = 7.8 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.50 - 7.36 (m, 2H), 7.35 - 7.20 (m, 3H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.08 - 6.92 (m, 2H), 6.52 (app t, *J* = 8.0 Hz, 1H), 6.10 (d, *J* = 7.8 Hz, 1H), 4.24 (s, 2H), 3.49 (t, *J* = 5.9 Hz, 2H), 3.18 (t, *J* = 5.9 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.87, 151.44, 149.33, 133.47, 133.36, 133.05, 132.04, 129.16, 127.30, 126.84, 126.72, 126.43, 126.23, 126.15, 126.00, 122.08, 121.99, 120.04, 119.97, 57.26, 50.56, 29.32. **HRMS** (ESI) found $[M+H]^+$ 345.1592, $C_{22}H_{21}N_2O_2$ requires 345.1598.

_N_-(_tert_-butyl)-2-(3,4-dihydroisoquinolin-2(1_H_)-yl)benzamide (5l)



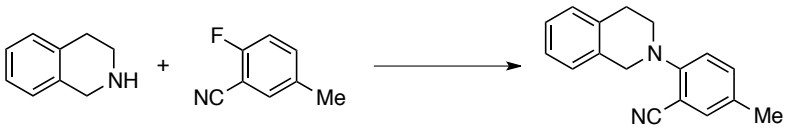
Subjection of 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)benzoic acid (0.500 g, 1.97 mmol) to General Procedure D gave the title compound (0.391 g, 1.27 mmol, 64 % yield) as a white solid after purification by column chromatography on silica gel using Hex/EtOAc as eluent (9:1 to 4:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.82 (s, 1H), 8.21 (d, *J* = 9.3 Hz, 1H), 7.46 (app t, *J* = 8.4 Hz, 1H), 7.30 - 7.17 (m, 5H), 7.07 (d, *J* = 7.2 Hz, 1H), 4.09 (s, 2H), 3.43 (t, *J* = 5.9 Hz, 2H), 3.12 (t, *J* = 6.0 Hz, 2H), 1.17 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.01, 150.79, 134.03, 133.51, 131.77, 131.31, 129.08, 128.89, 126.92, 126.35, 126.11, 124.95, 120.43, 57.98, 50.57, 49.28, 29.69, 28.33. **HRMS** (ESI) found $[M+H]^+$ 309.1959, $C_{20}H_{25}N_2O$ requires 309.1961.

_N_-cyclohexyl-2-(3,4-dihydroisoquinolin-2(1_H_)-yl)benzamide (5m)



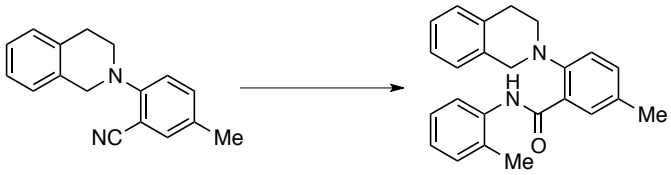
Subjection of 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)benzoic acid (0.500 g, 1.97 mmol) to General Procedure D gave the title compound (0.425 g, 1.23 mmol, 63 % yield) as a white solid after purification by column chromatography on silica gel using Hex/EtOAc as eluent (9:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.83 (d, *J* = 8.0 Hz, 1H), 8.25 (d, *J* = 6.2 Hz, 1H), 7.46 (app t, 1H), 7.32 - 7.14 (m, 5H), 7.04 (d, *J* = 7.4 Hz, 1H), 4.10 (s, 2H), 3.93 - 3.77 (m, 1H), 3.40 (t, *J* = 5.9 Hz, 2H), 3.10 (t, *J* = 5.9 Hz, 2H), 1.88 - 1.66 (m, 2H), 1.57 - 1.38 (m, 3H), 1.33 - 1.12 (m, 2H), 1.02 - 0.87 (m, 1H), 0.82 (app q, *J* = 12.7 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.05, 151.04, 134.06, 133.45, 131.92, 131.60, 128.91, 128.31, 126.82, 126.44, 126.04, 125.01, 120.83, 57.57, 49.68, 47.94, 32.56, 29.57, 25.58, 24.61. **HRMS** (ESI) found $[MH]^+$ 335.2119, $C_{22}H_{27}N_2O$ requires 335.2118.

2-(3,4-dihydroisoquinolin-2(1_H_)-yl)-5-methylbenzonitrile (S7n)



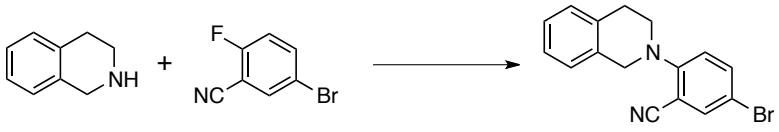
Subjection of 1,2,3,4-tetrahydroisoquinoline (6.70 g, 50.3 mmol)and 2-fluoro-5-methylbenzonitrile (3.4 g, 25.2 mmol) to General Procedure E gave the title compound (3.28 g, 13.2 mmol, 52 % yield) as a colorless oil after purification by column chromatography on silica gel using Hex/EtOAc as eluent (9:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.24 - 7.17 (m, 3H), 7.17 - 7.12 (m, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 4.37 (s, 2H), 3.62 (t, *J* = 5.8 Hz, 2H), 3.10 (t, *J* = 5.8 Hz, 2H), 2.33 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.12, 134.53, 134.51, 133.93, 133.39, 131.00, 129.01, 126.53, 126.39, 126.01, 118.83, 118.39, 104.88, 52.55, 51.20, 29.34, 20.24. **HRMS** (ESI) found $[M-H]^-$ 247.1229, $C_{17}H_{15}N_2$ requires 247.1230.

2-(3,4-dihydroisoquinolin-2(1*H*)-yl)-5-methyl-*N*-(*o*-tolyl)benzamide (5n)



Subjection of nitrile **S7n** (0.954 g, 3.84 mmol) to General Procedure F gave the title compound (0.306 g, 0.858 mmol, 22 % yield) as a white solid after purification by column chromatography on silica gel using Hex/EtOAc as eluent (9:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 11.72 (s, 1H), 8.19 (s, 1H), 8.10 (d, *J* = 8.1 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.28 - 7.25 (m, 1H), 7.24 - 7.18 (m, 3H), 7.16 (d, *J* = 6.4 Hz, 1H), 7.10 (app t, *J* = 7.9 Hz, 2H), 7.03 (app t, *J* = 7.3 Hz, 1H), 4.31 (s, 2H), 3.40 (t, *J* = 5.9 Hz, 2H), 3.01 (t, *J* = 5.9 Hz, 2H), 2.43 (s, 3H), 1.96 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.60, 148.38, 136.67, 135.16, 133.90, 133.42, 132.99, 132.49, 130.30, 128.94, 128.71, 128.14, 126.86, 126.51, 126.40, 126.30, 124.31, 122.85, 121.12, 55.79, 52.07, 28.70, 20.84, 17.61. **HRMS** (ESI) found $[M+H]^+$ 357.1958, $C_{24}H_{25}N_2O$ requires 357.1961.

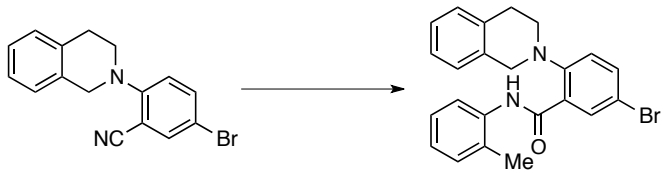
5-bromo-2-(3,4-dihydroisoquinolin-2(1*H*)-yl)benzonitrile (S7o)



Subjection of 1,2,3,4-tetrahydroisoquinoline (1.82 g, 13.7 mmol) and 5-bromo-2-fluorobenzonitrile (1.3 g, 6.50 mmol) to General Procedure E gave the title compound (1.44 g, 4.61 mmol, 71 % yield) as a yellow oil after purification by column chromatography on silica gel using Hex/EtOAc as eluent (20:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.56 (d, *J* = 11.1 Hz, 1H), 7.27 - 7.18 (m, 3H), 7.17 - 7.11 (m,

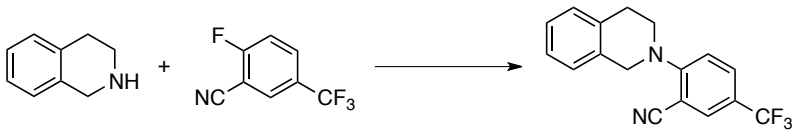
1H), 6.96 (d, *J* = 8.9 Hz, 1H), 4.42 (s, 2H), 3.69 (t, *J* = 5.8 Hz, 2H), 3.10 (t, *J* = 5.8 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 154.00, 136.65, 136.61, 134.37, 133.27, 129.01, 126.78, 126.35, 126.22, 119.67, 117.51, 112.21, 105.52, 52.14, 50.66, 29.17. **HRMS** (ESI) found $[M-H]^-$ 311.0177, $C_{16}H_{12}N_2Br$ requires 379.0178.

5-bromo-2-(3,4-dihydroisoquinolin-2(1*H*)-yl)-*N*-(*o*-tolyl)benzamide (5o)



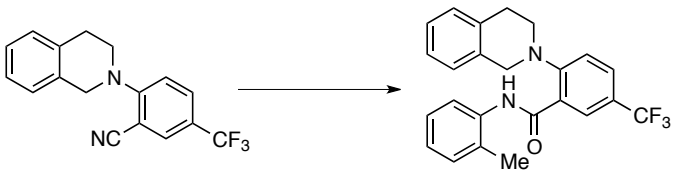
Subjection of nitrile **S7o** (0.406 g, 1.3 mmol) to General Procedure F gave the title compound (0.444 g, 1.05 mmol, 81 % yield) as a white solid after purification by column chromatography on silica gel using Hex/EtOAc as eluent (9:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 11.40 (s, 1H), 8.47 (s, 1H), 8.07 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.27 - 7.20 (m, 4H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.14 - 7.08 (m, 2H), 7.05 (d, *J* = 7.3 Hz, 1H), 4.32 (s, 2H), 3.42 (t, *J* = 5.9 Hz, 2H), 3.00 (t, *J* = 5.9 Hz, 2H), 1.97 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.04, 149.70, 136.26, 135.14, 134.92, 133.35, 133.22, 130.40, 129.00, 128.61, 127.07, 126.64, 126.47, 126.38, 124.65, 122.94, 122.70, 118.76, 55.55, 52.01, 28.38, 17.57. **HRMS** (ESI) found $[M+H]^+$ 421. 0908, $C_{23}H_{22}N_2OBr$ requires 421.0910.

2-(3,4-dihydroisoquinolin-2(1*H*)-yl)-5-(trifluoromethyl)benzonitrile (S7p)



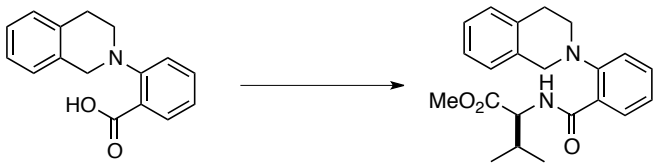
Subjection of 1,2,3,4-tetrahydroisoquinoline (4.62 g, 34.7 mmol) and 2-fluoro-5-(trifluoromethyl)benzonitrile (3.12 g, 16.5 mmol) to General Procedure E gave the title compound (4.89 g, 16.17 mmol, 98 % yield) as a yellow oil after purification by column chromatography on silica gel using Hex/EtOAc as eluent (20:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.68 (d, *J* = 9.9 Hz, 1H), 7.27 - 7.21 (m, 3H), 7.21 - 7.14 (m, 1H), 7.12 (d, *J* = 8.9 Hz, 1H), 4.57 (s, 2H), 3.84 (t, *J* = 5.8 Hz, 2H), 3.13 (t, *J* = 5.8 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.43, 134.40, 132.91, 132.38, 132.34, 130.44, 130.41, 128.91, 126.98, 126.41, 126.35, 118.06, 117.40, 101.80, 51.73, 49.82, 29.14. **HRMS** (ESI) found $[M+H]^+$ 303.1103, $C_{17}H_{14}N_2F_3$ requires 303.1104.

2-(3,4-dihydroisoquinolin-2(1*H*)-yl)-*N*-(*o*-tolyl)-5-(trifluoromethyl)benzamide (5p)



Subjection of nitrile **S7p** (0.320 g, 1.06 mmol) to General Procedure F gave the title compound (0.100 g, 0.243 mmol, 23 % yield) as a yellow oil after purification by column chromatography on silica gel using Hex/EtOAc as eluent (9:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.98 (s, 1H), 8.57 (s, 1H), 8.14 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.28 - 7.20 (m, 3H), 7.20 - 7.09 (m, 3H), 7.06 (app t, *J* = 7.3 Hz, 1H), 4.39 (s, 2H), 3.51 (t, *J* = 5.9 Hz, 2H), 3.00 (t, *J* = 5.9 Hz, 2H), 2.01 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.37, 153.35, 136.16, 133.22, 133.04, 130.45, 129.54, 129.51, 129.09, 129.01, 128.99, 128.96, 128.28, 127.18, 126.74, 126.56, 126.37, 124.70, 122.38, 121.05, 55.12, 52.09, 28.15, 17.52. **HRMS** (ESI) found $[M+H]^+$ 411.1677, $C_{24}H_{22}N_2O_1F_3$ requires 411.1679.

(*S*)-methyl 2-(2-(3,4-dihydroisoquinolin-2(1*H*)-yl)benzamido)-3-methylbutanoate (5q)



Subjection of 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)benzoic acid (0.500 g, 1.97 mmol) to General Procedure D gave the title compound (0.662 g, 1.81 mmol, 92 % yield) as a white solid after recrystallization from hot EtOH. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.59 (d, *J* = 8.3 Hz, 1H), 8.29 (d, *J* = 7.8 Hz, 1H), 7.62 - 7.40 (m, 1H), 7.38 - 7.29 (m, 2H), 7.24 - 7.12 (m, 3H), 7.06 (d, *J* = 7.2 Hz, 1H), 4.64 (t, *J* = 6.6 Hz, 1H), 4.26 (d, *J* = 15.4 Hz, 1H), 4.13 (d, *J* = 15.1 Hz, 1H), 3.59 (s, 3H), 3.51 - 3.35 (m, 2H), 3.22 (dd, *J* = 14.5, 7.7 Hz, 1H), 3.16 - 2.97 (m, 1H), 1.94 (h, *J* = 7.1 Hz, 1H), 0.79 (d, *J* = 6.8 Hz, 3H), 0.63 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.40, 166.18, 151.71, 134.06, 133.71, 132.46, 131.77, 128.86, 127.68, 126.69, 126.44, 125.97, 125.44, 121.70, 57.94, 57.41, 51.77, 50.21, 30.77, 29.21, 19.00, 17.80. **HRMS** (ESI) found $[M+H]^+$ 367.2081, $C_{22}H_{26}N_2O_3$ requires 367.2016.

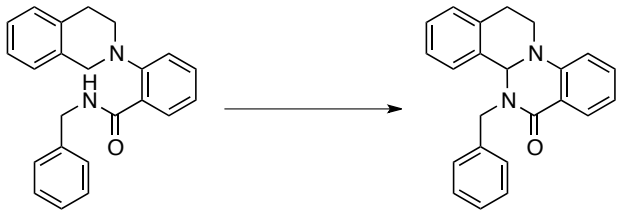
Synthesis of Products

General Procedure G: Asymmetric Amidation

To the catalyst **9** (0.005 mmol) in a 2 dram (15 X 60 mm) vial equipped with a Teflon stir bar (1/2" X 5/16") were added substrate **5** (0.1 mmol), Na_3PO_4 (0.24 mmol), 4-acetamido-2,2,6,6-tetramethyl-1-oxopiperidinium tetrafluoroborate (**7**, 0.22 mmol), and *p*-xylene (4 mL) in succession. The vial was fitted with a screw cap and the reaction mixture was stirred rapidly at room temperature for 48 h with the vial standing on the stir plate. After this time, the reaction mixture was diluted with saturated aqueous Na_2SO_3 (2 mL) and the contents were shaken vigorously. This mixture was extracted with EtOAc (3 X 2 mL) and the organic extracts were dried with Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by flash column chromatography. Due to the heterogeneous nature of the reaction mixture, it is essential that fast and efficient stirring be maintained in order to achieve reliable results.

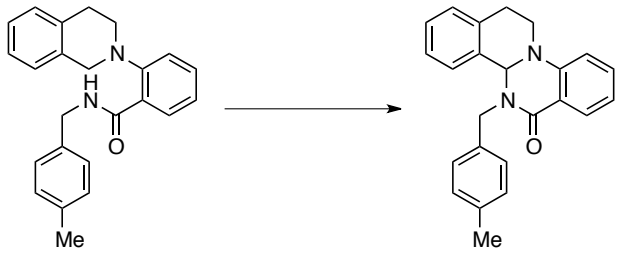
Preparation of reagents: Crystalline 4-acetamido-2,2,6,6-tetramethyl-1-oxopiperidinium tetrafluoroborate was ground with a mortar and pestle into a fine, light-yellow powder prior to use. Anhydrous Na_3PO_4 was ground with a mortar and pestle and dried at 80 ^oC under vacuum for 30 min prior to use.

5-benzyl-12,13-dihydro-4b*H*-isoquinolino[2,1-*a*]quinazolin-6(5*H*)-one (6a)



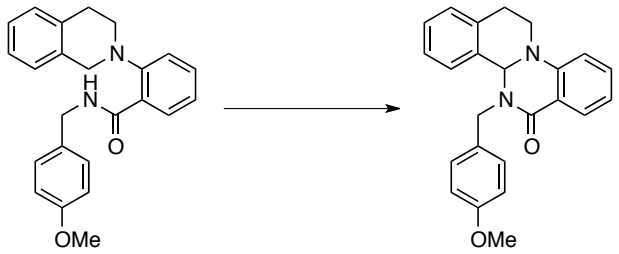
Subjection of **5a** (34 mg, 0.1 mmol) to General Procedure G gave the title compound (28 mg, 0.083 mmol, 83 % yield) as a white powder after purification by column chromatography on silica gel using Hex/EtOAc as eluent (4:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 6.7 Hz, 1H), 7.36 (app t, *J* = 7.8 Hz, 1H), 7.34 - 7.24 (m, 6H), 7.24 - 7.16 (m, 2H), 7.04 (d, *J* = 7.0 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 1H), 6.88 (app t, *J* = 7.5 Hz, 1H), 5.82-5.71 (m, 1H), 5.69 (s, 1H), 4.39 (d, *J* = 15.3 Hz, 1H), 4.11 - 3.96 (m, 1H), 3.53 (ddd, *J* = 14.0, 11.0, 5.7 Hz, 1H), 3.21 - 3.02 (m, 1H), 2.73 (dd, *J* = 16.3, 4.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.45, 147.45, 137.23, 134.75, 133.37, 129.48, 129.22, 129.04, 128.63, 128.25, 127.63, 127.45, 126.20, 125.88, 119.41, 113.65, 109.08, 71.67, 49.64, 44.58, 29.73. **HRMS** (ESI) found $[M+H]^+$ 341.1649, $C_{23}H_{21}N_2O$ requires 341.1648. **HPLC** (Chiralpak IC column, 75:25 hexanes/isopropanol, 1 mL/min); t_r = 18.8 min (minor), 22.5 min (major); 84 % ee.

5-(4-methylbenzyl)-12,13-dihydro-4b*H*-isoquinolino[2,1-*a*]quinazolin-6(5*H*)-one (6b)



Subjection of **5b** (36 mg, 0.1 mmol) to General Procedure G gave the title compound (29 mg, 0.081 mmol, 81 % yield) as a white powder after purification by column chromatography on silica gel using Hex/EtOAc as eluent (4:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.3 Hz, 1H), 7.35 (app t, *J* = 7.7 Hz, 1H), 7.33 - 7.26 (m, 1H), 7.26 - 7.17 (m, 4H), 7.17 - 7.10 (m, 2H), 7.04 (d, *J* = 6.9 Hz, 1H), 6.95 - 6.84 (m, 2H), 5.92 - 5.71 (m, 1H), 5.68 (s, 1H), 4.31 (d, *J* = 14.9 Hz, 1H), 4.03 (dd, *J* = 13.3, 5.0 Hz, 1H), 3.53 (ddd, *J* = 14.6, 11.3, 5.7 Hz, 1H), 3.21 - 3.09 (m, 1H), 2.73 (dd, *J* = 16.9, 4.4 Hz, 1H), 2.35 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.34, 151.19, 147.36, 137.15, 134.72, 134.14, 133.34, 132.11, 131.62, 129.45, 129.34, 129.24, 129.14, 128.18, 127.85, 127.72, 126.19, 121.00, 119.29, 71.52, 50.48, 44.57, 24.08, 21.16. **HRMS** (ESI) found $[M+H]^+$ 355.1804, $C_{24}H_{23}N_2O$ requires 355.1805. **HPLC** (Chiralpak IC column, 70:30 hexanes/isopropanol, 1 mL/min); t_r = 19.9 min (minor), 28.5 min (major); 87 % ee.

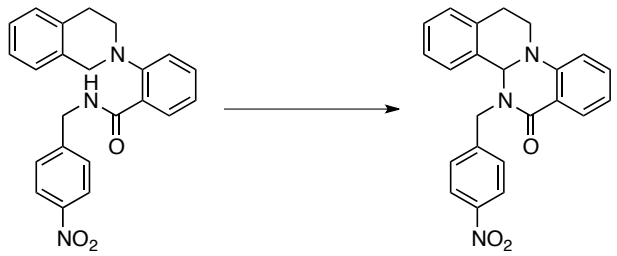
5-(4-methoxybenzyl)-12,13-dihydro-4b*H*-isoquinolino[2,1-*a*]quinazolin-6(5*H*)-one (6c)



Subjection of **5c** (37 mg, 0.1 mmol) to General Procedure G gave the title compound (33 mg, 0.089 mmol, 89 % yield) as a white powder after purification by column chromatography on silica gel using Hex/EtOAc as eluent (4:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.4 Hz, 1H), 7.35 (app t, *J* = 7.3 Hz, 1H), 7.32 - 7.11 (m, 5H), 7.04 (d, *J* = 7.0 Hz, 2H), 6.92 - 6.82 (m, 4H), 5.83 - 5.49 (m, 2H), 4.32 (d, *J* = 14.5 Hz, 1H), 4.06 - 3.96 (m, 1H), 3.80 (s, 3H), 3.52 (ddd, *J* = 16.3, 12.8, 5.7 Hz, 1H), 3.23 - 3.04 (m, 1H), 2.73 (dd, *J* = 17.0, 4.2 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 163.31, 158.99, 147.34, 134.73, 133.27, 129.38, 129.27, 129.16, 129.08, 128.15, 126.76, 126.14, 125.86,

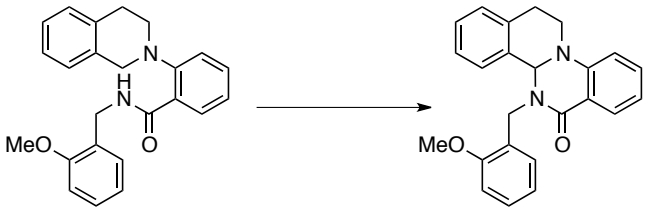
119.31, 113.98, 113.55, 71.37, 55.23, 48.88, 44.53, 24.33. **HRMS** (ESI) found $[M+H]^+$ 371.1756, $C_{24}H_{223}N_2O_2$ requires 371.1754. **HPLC** (Chiralpak IC column, 70:30 hexanes/isopropanol, 1 mL/min); t_r = 23.2 min (minor), 28.6 min (major); 86 % ee.

5-(4-nitrobenzyl)-12,13-dihydro-4b*H*-isoquinolino[2,1-*a*]quinazolin-6(5*H*)-one (6d)



Subjection of **5d** (37 mg, 0.1 mmol) to General Procedure G gave the title compound (35 mg, 0.090 mmol, 90 % yield) as a yellow powder after purification by column chromatography on silica gel using Hex/EtOAc as eluent (3:2). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 2H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.47 - 7.34 (m, 3H), 7.28 - 7.17 (m, 3H), 7.07 (d, *J* = 7.0 Hz, 1H), 7.00 - 6.87 (m, 2H), 5.74 (s, 1H), 5.66 - 5.34 (m, 1H), 4.61 (d, *J* = 16.5 Hz, 1H), 4.02 - 3.92 (m, 1H), 3.58 - 3.45 (m, 1H), 3.13 - 2.97 (m, 1H), 2.82 - 2.73 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.92, 147.87, 147.26, 145.19, 135.15, 133.74, 129.53, 129.30, 128.73, 128.56, 128.15, 126.37, 123.79, 123.51, 120.06, 118.69, 114.38, 72.15, 48.56, 44.66, 25.41. **HRMS** (ESI) found $[M+H]^+$ 386.1501, $C_{23}H_{20}N_3O_3$ requires 386.1499. **HPLC** (Chiralpak IC column, 70:30 hexanes/isopropanol, 1 mL/min); t_r = 30.8 min (minor), 39.9 min (major); 88 % ee.

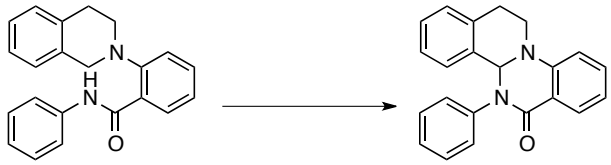
5-(2-methoxybenzyl)-12,13-dihydro-4b*H*-isoquinolino[2,1-*a*]quinazolin-6(5*H*)-one (6e)



Subjection of **5e** (37 mg, 0.1 mmol) to General Procedure G gave the title compound (30 mg, 0.081 mmol, 81 % yield) as a white powder after purification by column chromatography on silica gel using Hex/EtOAc as eluent (1:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.7 Hz, 1H), 7.50 (d, *J* = 7.4 Hz, 1H), 7.37 - 7.30 (m, 2H), 7.25 (d, *J* = 7.5 Hz, 1H), 7.17 (app p, *J* = 7.2 Hz, 2H), 7.03 (d, *J* = 6.8 Hz, 1H), 6.96 (app t, *J* =

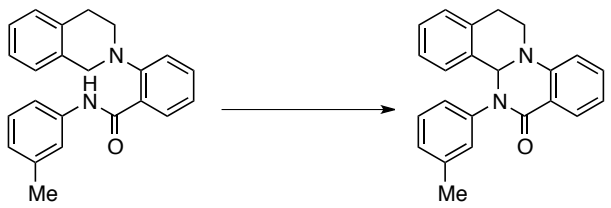
7.5 Hz, 1H), 6.90 (d, *J* = 8.5 Hz, 1H), 6.88 (d, *J* = 8.5 Hz, 1H), 6.82 (app t, *J* = 7.5 Hz, 1H), 5.82 (s, 1H), 5.68 (d, *J* = 15.7 Hz, 1H), 4.48 (d, *J* = 15.7 Hz, 1H), 4.17 (dd, *J* = 14.4, 6.3 Hz, 1H), 3.82 (s, 3H), 3.62 (ddd, *J* = 14.5, 11.8, 5.8 Hz, 1H), 3.25 (ddd, *J* = 17.9, 11.0, 6.6 Hz, 1H), 2.74 (dd, *J* = 17.0, 5.3 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.54, 163.28, 157.36, 147.19, 134.36, 133.24, 129.37, 129.16, 128.92, 128.48, 127.97, 126.18, 125.62, 125.26, 120.79, 119.00, 118.34, 113.06, 110.16, 72.60, 55.29, 45.75, 44.66, 23.99. **HRMS** (ESI) found $[M+H]^+$ 371.1756, $C_{24}H_{23}N_2O_2$ requires 371.1754. **HPLC** (Chiralpak IC column, 75:25 hexanes/isopropanol, 1 mL/min); t_r = 24.1 min (minor), 28.4 min (major); 94 % ee.

5-phenyl-12,13-dihydro-4b*H*-isoquinolino[2,1-*a*]quinazolin-6(5*H*)-one (6f)



Subjection of **5f** (33 mg, 0.1 mmol) to General Procedure G gave the title compound (28 mg, 0.086 mmol, 86 % yield) as a white powder after purification by column chromatography on silica gel using Hex/EtOAc as eluent (4:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.7 Hz, 1H), 7.52 (d, *J* = 7.9 Hz, 2H), 7.44 - 7.31 (m, 4H), 7.23 (app t, *J* = 7.4 Hz, 1H), 7.17 (app t, *J* = 7.4 Hz, 1H), 7.13 - 7.05 (m, 2H), 7.01 (d, *J* = 8.3 Hz, 1H), 6.90 (app t, *J* = 7.5 Hz, 1H), 6.19 (s, 1H), 4.26 (dd, *J* = 14.0, 6.2 Hz, 1H), 3.75 (ddd, *J* = 14.4, 11.3, 5.8 Hz, 1H), 3.32 (ddd, *J* = 17.5, 11.1, 6.9 Hz, 1H), 2.86 (dd, *J* = 17.1, 5.0 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.80, 147.40, 141.67, 135.66, 134.38, 133.77, 129.91, 129.14, 128.87, 128.19, 127.21, 126.16, 125.87, 125.01, 119.67, 119.16, 114.06, 75.34, 45.09, 24.58. **HRMS** (ESI) found $[M+H]^+$ 327.1492, $C_{22}H_{19}N_2O_1$ requires 327.1492. **HPLC** (Chiralpak IA column, 70:30 hexanes/isopropanol, 1 mL/min); t_r = 10.1 min (minor), 15.6 min (major); 63 % ee.

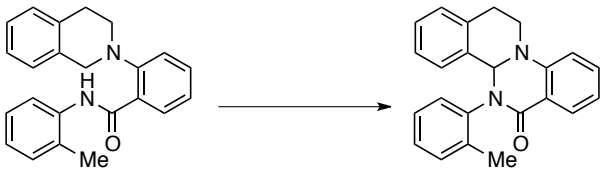
5-(*m*-tolyl)-12,13-dihydro-4b*H*-isoquinolino[2,1-*a*]quinazolin-6(5*H*)-one (6g)



Subjection of **5g** (34 mg, 0.1 mmol) to General Procedure G gave the title compound (31 mg, 0.091 mmol, 91 % yield) as a white powder after purification by column chromatography on silica gel using Hex/EtOAc as eluent (4:1). **^{1}H NMR** (500 MHz,

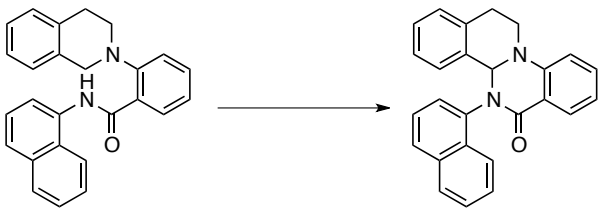
$CDCl_3$) δ 8.01 (d, *J* = 7.0 Hz, 1H), 7.46 - 7.35 (m, 3H), 7.34 - 7.26 (m, 2H), 7.18 (app t, *J* = 7.3 Hz, 1H), 7.11 (app t, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 7.0 Hz, 2H), 7.00 (d, *J* = 8.3 Hz, 1H), 6.89 (app t, *J* = 7.5 Hz, 1H), 6.17 (s, 1H), 4.27 (dd, *J* = 14.4, 6.1 Hz, 1H), 3.76 (ddd, *J* = 14.5, 11.5, 5.9 Hz, 1H), 3.32 (ddd, *J* = 17.6, 11.1, 6.9 Hz, 1H), 2.85 (dd, *J* = 17.1, 5.2 Hz, 1H), 2.39 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.78, 147.32, 141.73, 138.74, 135.94, 134.34, 133.72, 129.89, 129.13, 128.70, 128.15, 127.14, 126.71, 126.16, 125.67, 121.81, 119.58, 119.17, 113.94, 75.45, 45.09, 24.42, 21.52. **HRMS** (ESI) found $[M+H]^+$ 341.1647, $C_{23}H_{21}N_2O$ requires 341.1648. **HPLC** (Chiralpak IC column, 70:30 hexanes/isopropanol, 1 mL/min); t_r = 17.4 min (minor), 48.0 min (major); 60 % ee.

5-(*o*-tolyl)-12,13-dihydro-4b*H*-isoquinolino[2,1-*a*]quinazolin-6(5*H*)-one (6h)



Subjection of **5h** (34 mg, 0.1 mmol) to General Procedure G gave the title compound (22 mg, 0.065 mmol, 65 % yield) as a white powder after purification by column chromatography on silica gel using Hex/EtOAc as eluent (4:1). **^{1}H NMR** (500 MHz, $CDCl_3$, major rotamer) δ 8.08 (d, *J* = 7.7 Hz, 1H), 7.46 (app t, *J* = 7.7 Hz, 1H), 7.23 - 7.10 (m, 4H), 7.10 - 7.04 (m, 4H), 7.03 - 6.96 (m, 2H), 6.00 (s, 1H), 4.16 - 4.06 (m, 1H), 3.61 (ddd, *J* = 13.7, 9.1, 5.9 Hz, 1H), 3.36 - 3.19 (m, 1H), 3.03 - 2.89 (m, 1H), 2.44 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.90, 148.62, 139.53, 136.40, 134.67, 133.58, 133.50, 130.94, 129.69, 128.83, 128.28, 128.19, 127.65, 127.42, 126.30, 125.88, 120.58, 120.38, 115.72, 74.10, 44.98, 26.62, 18.91. **HRMS** (ESI) found $[M+H]^+$ 341.1648, $C_{23}H_{21}N_2O$ requires 341.1648. **HPLC** (Chiralpak IA column, 70:30 hexanes/isopropanol, 1 mL/min); t_r = 8.5 min (minor), 10.8 min (major); 91 % ee.

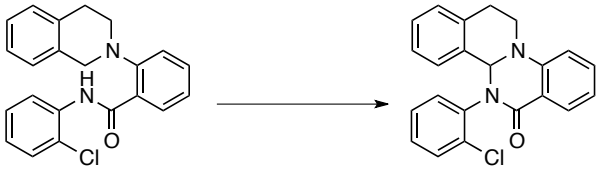
5-(naphthalen-1-yl)-12,13-dihydro-4b*H*-isoquinolino[2,1-*a*]quinazolin-6(5*H*)-one (6i)



Subjection of **5i** (38 mg, 0.1 mmol) to General Procedure G gave the title compound (26 mg, 0.069 mmol, 69 % yield) as a white powder after purification by column chromatography on silica gel using Hex/EtOAc as eluent (4:1). **^{1}H NMR** (500 MHz,

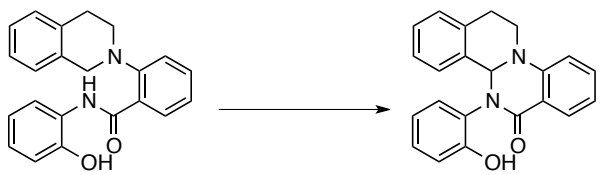
$CDCl_3$) δ 8.25 (d, *J* = 8.3 Hz, 1H), 8.12 (d, *J* = 7.7 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.61 (app t, *J* = 7.6 Hz, 1H), 7.58 - 7.52 (m, 2H), 7.49 (app t, *J* = 7.8 Hz, 1H), 7.43 (app t, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.17 - 7.04 (m, 3H), 7.02 (app t, *J* = 7.5 Hz, 1H), 6.91 (app t, *J* = 7.7 Hz, 1H), 6.21 (s, 1H), 4.22 (ddd, *J* = 12.2, 6.3, 3.7 Hz, 1H), 3.66 (ddd, *J* = 14.0, 9.9, 5.6 Hz, 1H), 3.32 (ddd, *J* = 16.2, 9.9, 6.2 Hz, 1H), 2.99 - 2.87 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.48, 148.54, 137.30, 134.70, 134.46, 133.70, 130.48, 129.92, 128.91, 128.73, 128.15, 128.10, 127.15, 127.13, 127.02, 126.14, 125.79, 125.24, 123.46, 120.44, 119.91, 115.39, 74.58, 45.06, 26.09. **HRMS** (ESI) found $[M+Na]^+$ 399.1472, $C_{26}H_{22}N_2O_1Na_1$ requires 399.1468. **HPLC** (Chiralpak IA column, 70:30 hexanes/isopropanol, 1 mL/min); t_r = 13.7 min (minor), 16.5 min (major); 82 % ee.

5-(2-chlorophenyl)-12,13-dihydro-4b*H*-isoquinolino[2,1-*a*]quinazolin-6(5*H*)-one (6j)



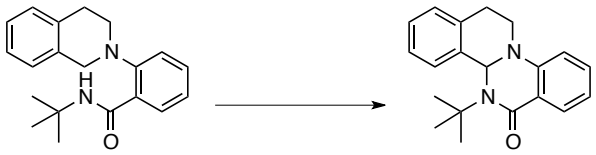
Subjection of **5j** (36 mg, 0.1 mmol) to General Procedure G gave the title compound (15 mg, 0.042 mmol, 42 % yield) as a white powder after purification by column chromatography on silica gel using Hex/EtOAc as eluent (4:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 6.9 Hz, 1H), 7.52 (app t, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.19 - 7.07 (m, 6H), 7.07 - 6.95 (m, 2H), 6.95 - 6.75 (m, 3H), 6.24 (s, 1H), 4.03 - 3.89 (m, 1H), 3.54 (dd, *J* = 12.1, 6.4 Hz, 1H), 3.31 - 3.15 (m, 1H), 3.11 (dd, *J* = 14.2, 7.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.55, 163.52, 149.59, 137.32, 134.91, 134.52, 133.63, 131.06, 130.75, 129.83, 129.61, 129.16, 128.73, 128.52, 127.09, 125.87, 121.84, 121.27, 118.06, 72.44, 45.44, 28.65. **HRMS** (ESI) found $[M-H]^-$ 359.0945 $C_{22}H_{16}N_2OCl$ requires 359.0946. **HPLC** (Chiralpak IA column, 70:30 hexanes/isopropanol, 1 mL/min); t_r = 8.0 min (minor), 12.5 min (major); 87 % ee.

5-(2-hydroxyphenyl)-12,13-dihydro-4b*H*-isoquinolino[2,1-*a*]quinazolin-6(5*H*)-one (6k)



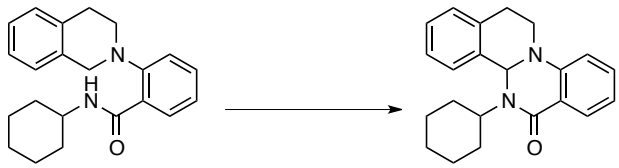
Subjection of **5k** (34 mg, 0.1 mmol) to General Procedure G gave the title compound (13 mg, 0.038 mmol, 38 % yield) as a white powder after purification by column chromatography on silica gel using Hex/EtOAc as eluent (4:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.35 (br s, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.48 - 7.33 (m, 2H), 7.33 - 6.74 (m, 9H), 6.32 (s, 1H), 4.31 (dd, *J* = 14.4, 6.6 Hz, 1H), 3.75 (ddd, *J* = 14.4, 12.4, 5.5 Hz, 1H), 3.31 (ddd, *J* = 18.0, 11.9, 6.8 Hz, 1H), 2.77 (dd, *J* = 17.2, 5.0 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.76, 152.02, 147.84, 134.70, 133.76, 130.18, 129.04, 128.64, 128.32, 128.28, 126.63, 126.52, 126.41, 125.44, 121.43, 120.84, 119.70, 117.39, 113.64, 44.95, 29.72, 24.19. **HRMS** (ESI) found $[M+H]^+$ 343.1439, $C_{22}H_{19}N_2O_2$ requires 343.1441. **HPLC** (Chiralpak IA column, 70:30 hexanes/isopropanol, 1 mL/min); t_r = 8.8 min (minor), 10.8 min (major); 80 % ee.

5-(*tert*-butyl)-12,13-dihydro-4b*H*-isoquinolino[2,1-*a*]quinazolin-6(5*H*)-one (6l)



Subjection of **5l** (31 mg, 0.1 mmol) to General Procedure G gave the title compound (25 mg, 0.082 mmol, 82 % yield) as a white powder after purification by column chromatography on silica gel using Hex/EtOAc as eluent (4:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.8 Hz, 0H), 7.47 - 7.32 (m, 1H), 7.25 (app t, *J* = 7.7 Hz, 1H), 7.19 - 7.04 (m, 2H), 7.01 - 6.92 (m, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.74 (app t, *J* = 7.5 Hz, 0H), 5.93 (s, 1H), 4.24 (dd, *J* = 14.8, 7.3 Hz, 1H), 3.77 (ddd, *J* = 14.9, 11.8, 6.3 Hz, 1H), 3.26 (ddd, *J* = 18.7, 11.8, 7.5 Hz, 1H), 2.72 (dd, *J* = 17.3, 6.1 Hz, 1H), 1.71 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.90, 146.71, 138.08, 134.17, 132.78, 129.16, 129.12, 127.64, 126.31, 126.00, 120.86, 119.04, 112.95, 70.62, 58.19, 45.33, 29.47, 23.53. **HRMS** (ESI) found $[M+H]^+$ 307.1805, $C_{20}H_{23}N_2O$ requires 307.1805. **HPLC** (Chiralpak IA column, 95:05 hexanes/isopropanol, 1 mL/min); t_r = 21.4 min (minor), 22.8 min (major); 73 % ee.

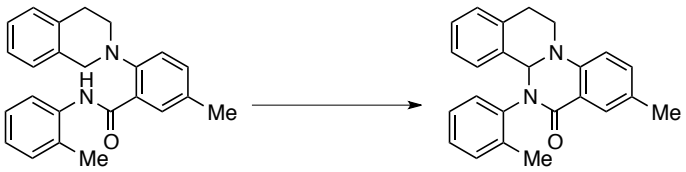
5-cyclohexyl-12,13-dihydro-4b*H*-isoquinolino[2,1-*a*]quinazolin-6(5*H*)-one (6m)



Subjection of **5m** (34 mg, 0.1 mmol) to General Procedure G gave the title compound (32 mg, 0.094 mmol, 94 % yield) as a white powder after purification by column chromatography on silica gel using Hex/EtOAc as eluent (9:1). **^{1}H NMR** (500 MHz,

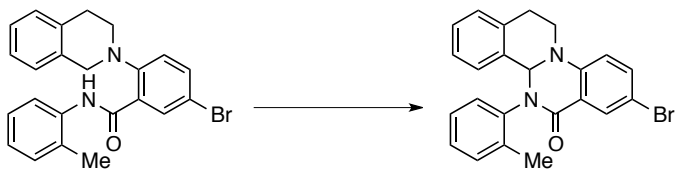
$CDCl_3$) δ 7.86 (d, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.28 (app t, *J* = 8.3 Hz, 1H), 7.16 - 7.07 (m, 2H), 6.99 (d, *J* = 7.1 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 6.78 (app t, *J* = 7.5 Hz, 1H), 5.68 (s, 1H), 4.69 (br s, 1H), 4.24 (dd, *J* = 14.7, 7.3 Hz, 1H), 3.81 (ddd, *J* = 14.7, 11.5, 6.5 Hz, 1H), 3.28 (ddd, *J* = 18.3, 11.4, 7.5 Hz, 1H), 2.80 (dd, *J* = 17.3, 6.3 Hz, 1H), 2.24 - 2.13 (m, 1H), 2.12 - 1.97 (m, 1H), 1.96 - 1.81 (m, 2H), 1.80 - 1.66 (m, 2H), 1.62 - 1.41 (m, 3H), 1.21 - 1.07 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.33, 146.94, 134.27, 133.04, 129.40, 129.01, 127.77, 126.47, 125.81, 119.48, 119.05, 113.08, 99.77, 68.78, 54.50, 44.84, 32.42, 30.79, 25.92, 25.90, 25.53. **HRMS** (ESI) found $[M+H]^+$ 333.1963, $C_{22}H_{25}N_2O$ requires 333.1961. **HPLC** (Chiralpak IA column, 80:20 hexanes/isopropanol, 1 mL/min); t_r = 12.2 min (minor), 15.6 min (major); 80 % ee.

8-methyl-5-(*o*-tolyl)-12,13-dihydro-4b*H*-isoquinolino[2,1-*a*]quinazolin-6(5*H*)-one (6n)



Subjection of **5n** (36 mg, 0.1 mmol) to General Procedure G gave the title compound (26 mg, 0.073 mmol, 73 % yield) as a white powder after purification by column chromatography on silica gel using Hex/EtOAc as eluent (4:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.19 - 7.07 (m, 5H), 7.07 – 6.93 (m, 5H), 5.95 (s, 1H), 4.08 - 3.91 (m, 1H), 3.54 (ddd, *J* = 13.6, 8.2, 6.0 Hz, 1H), 3.28 - 3.11 (m, 1H), 3.07 - 2.88 (m, 1H), 2.40 (s, 3H), 2.31 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.54, 162.97, 146.54, 139.47, 136.54, 134.59, 134.40, 130.86, 130.63, 129.57, 128.80, 128.24, 128.14, 127.83, 127.34, 126.28, 125.74, 120.77, 116.73, 74.09, 45.14, 26.72, 20.60, 18.91. **HRMS** (ESI) found $[M+H]^+$ 355.1806, $C_{24}H_{23}N_2O$ requires 355.1805. **HPLC** (Chiralpak IA column, 80:20 hexanes/isopropanol, 1 mL/min); t_r = 11.1 min (minor), 13.4 min (major); 90 % ee.

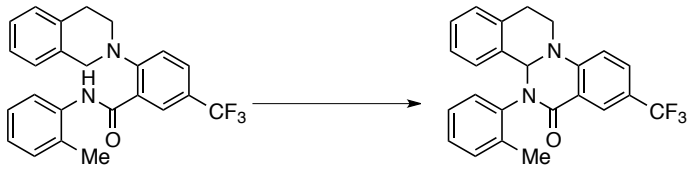
8-bromo-5-(*o*-tolyl)-12,13-dihydro-4b*H*-isoquinolino[2,1-*a*]quinazolin-6(5*H*)-one (6o)



Subjection of **5o** (42 mg, 0.1 mmol) to General Procedure G gave the title compound (23 mg, 0.055 mmol, 55 % yield) as a white powder after purification by column

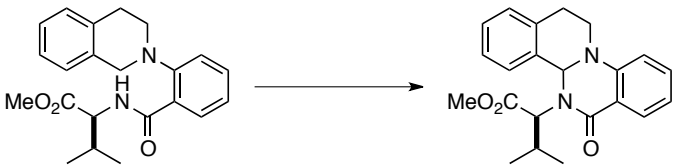
chromatography on silica gel using Hex/EtOAc as eluent (4:1). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.48 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.23 - 6.96 (m, 8H), 6.90 (d, *J* = 8.7 Hz, 1H), 5.93 (s, 1H), 4.04 (ddd, *J* = 13.4, 6.5, 4.1 Hz, 1H), 3.59 (ddd, *J* = 13.5, 9.8, 5.7 Hz, 1H), 3.22 (ddd, *J* = 16.0, 9.6, 6.2 Hz, 1H), 3.05 - 2.83 (m, 1H), 2.38 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.52, 161.67, 147.41, 139.36, 136.20, 134.45, 133.52, 132.23, 131.08, 128.93, 128.40, 128.00, 127.61, 127.49, 126.43, 126.06, 121.68, 117.17, 112.80, 74.28, 45.03, 26.30, 18.88. **HRMS** (ESI) found $[M+H]^+$ 419.0755, $C_{23}H_{20}N_2O_1Br_1$ requires 419.0754. **HPLC** (Chiralpak IA column, 80:20 hexanes/isopropanol, 0.75 mL/min); t_r = 20.5 min (major), 21.8 min (minor); 93 % ee.

5-(*o*-tolyl)-8-(trifluoromethyl)-12,13-dihydro-4b*H*-isoquinolino[2,1-*a*]quinazolin-6(5*H*)-one (6p)



Subjection of **5p** (41 mg, 0.1 mmol) to General Procedure G gave the title compound (28 mg, 0.069 mmol, 69 % yield) as a white powder after purification by column chromatography on silica gel using Hex/EtOAc as eluent (4:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.32 (dd, *J* = 12.4, 7.9 Hz, 2H), 7.24 - 7.16 (m, 3H), 7.16 - 7.03 (m, 4H), 6.00 (s, 1H), 4.25 - 4.12 (m, 1H), 3.80 - 3.63 (m, 1H), 3.31 (ddd, *J* = 16.9, 11.1, 6.6 Hz, 1H), 2.94 (ddd, *J* = 16.3, 4.8, 2.6 Hz, 1H), 2.42 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.64, 161.87, 150.52, 139.48, 135.96, 134.49, 133.88, 131.18, 130.20, 130.17, 128.98, 128.52, 127.97, 127.74, 127.44 (q, *J* = 3.8 Hz), 127.20, 126.50, 126.28, 118.86, 114.16, 74.37, 44.95, 26.25, 18.85. **HRMS** (ESI) found $[M+H]^+$ 409.1525, $C_{24}H_{20}N_2O_1F_3$ requires 409.1522. **HPLC** (Chiralpak IC column, 80:20 hexanes/isopropanol, 1 mL/min); t_r = 21.1 min (minor), 23.9 min (major); 90 % ee.

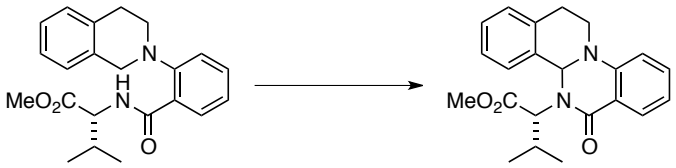
(2*S*)-methyl 3-methyl-2-(6-oxo-12,13-dihydro-4b*H*-isoquinolino[2,1-*a*]quinazolin-5(6*H*)-yl)butanoate (6q)



Subjection of **5q** (36 mg, 0.1 mmol) to General Procedure G gave the title compound (32 mg, 0.088 mmol, 88 % yield) as a 7:1 mixture of diastereomers in favor of diastereomer

1. The two diastereomers were separable by column chromatography on silica gel using Hex/EtOAc as eluent (10:1).

(2*R*)-methyl 3-methyl-2-(6-oxo-12,13-dihydro-4b*H*-isoquinolino[2,1-*a*]quinazolin-5(6*H*)-yl)butanoate (6r)



Subjection of **5r** (36 mg, 0.1 mmol) to General Procedure G gave the title compound (33 mg, 0.091 mmol, 91 % yield) as a 3:1 mixture of diastereomers in favor of diastereomer 2. The two diastereomers were separable by column chromatography on silica gel using Hex/EtOAc as eluent (10:1).

Diastereomer # 1

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.7 Hz, 1H), 7.31 (app t, *J* = 7.7 Hz, 1H), 7.16 - 6.95 (m, 4H), 6.91 (d, *J* = 8.3 Hz, 1H), 6.80 (app t, *J* = 7.0 Hz, 1H), 6.02 (s, 1H), 5.34 (br s, 1H), 4.32 - 4.16 (m, 1H), 3.86-3.69 (m, 1H), 3.75 (s, 3H), 3.24 (ddd, *J* = 17.9, 11.2, 7.4 Hz, 1H), 2.89 - 2.74 (m, 1H), 2.50 - 2.25 (m, 1H), 1.11 - 0.88 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.48, 164.54, 147.41, 134.24, 133.56, 129.91, 129.18, 127.85, 125.70, 119.15, 118.47, 113.48, 69.11, 62.16, 52.00, 44.78, 30.11, 19.45, 19.09. **HRMS** (ESI) found $[M+H]^+$ 365.1861, $C_{22}H_{25}N_2O_3$ requires 365.1860.

Diastereomer # 2

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.35 (app t, *J* = 7.8 Hz, 1H), 7.25 - 7.15 (m, 2H), 7.15 - 7.00 (m, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.90 - 6.74 (m, 1H), 5.81 (s, 1H), 4.33 - 4.08 (m, 1H), 4.06 - 3.76 (m, 4H), 3.72 - 3.58 (m, 1H), 3.32 (ddd, *J* = 17.5, 11.2, 6.9 Hz, 1H), 2.81 (dd, *J* = 18.8, 5.7 Hz, 1H), 2.70 - 2.54 (m, 1H), 1.18 (d, *J* = 6.7 Hz, 3H), 1.13 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.60, 164.59, 163.37, 147.58, 134.67, 133.45, 129.40, 129.23, 126.26, 119.58, 73.74, 66.41, 52.12, 45.22, 29.73, 29.25, 20.67, 19.93. **HRMS** (ESI) found $[M+H]^+$ 365.1862, $C_{22}H_{25}N_2O_3$ requires 365.1860.

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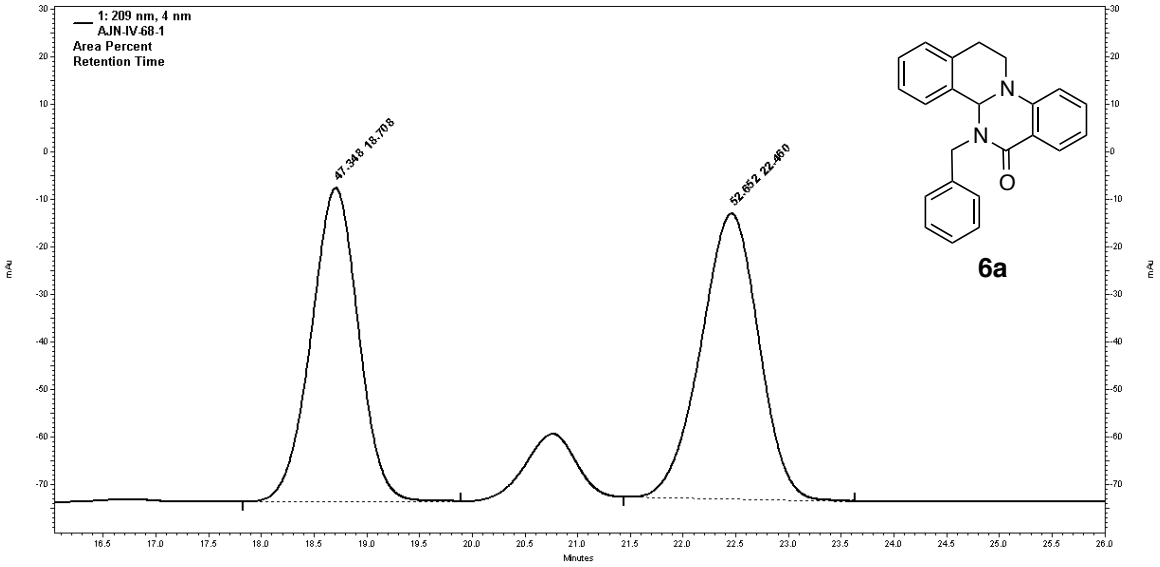
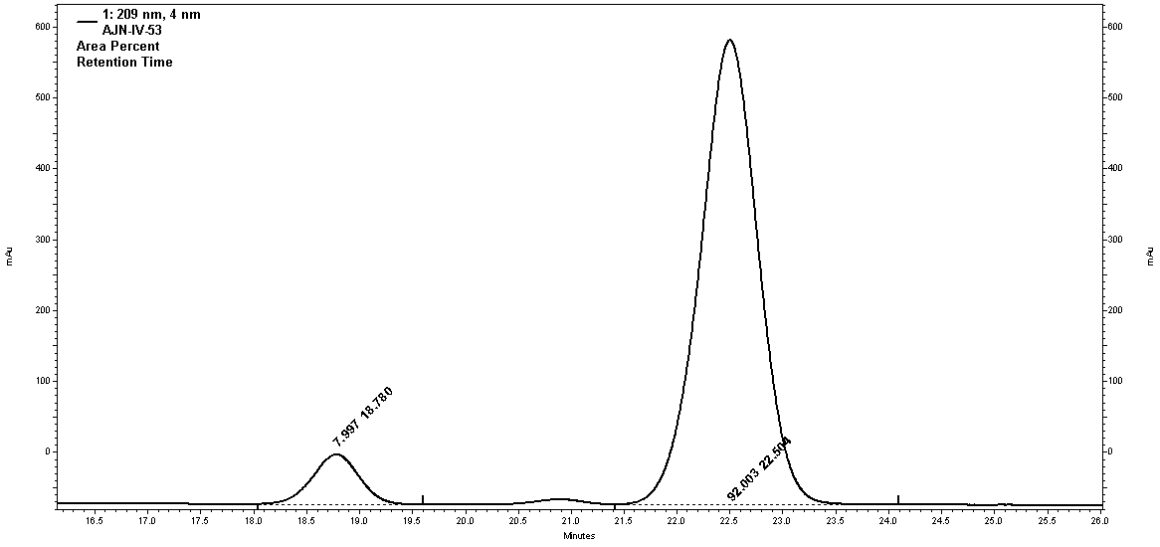
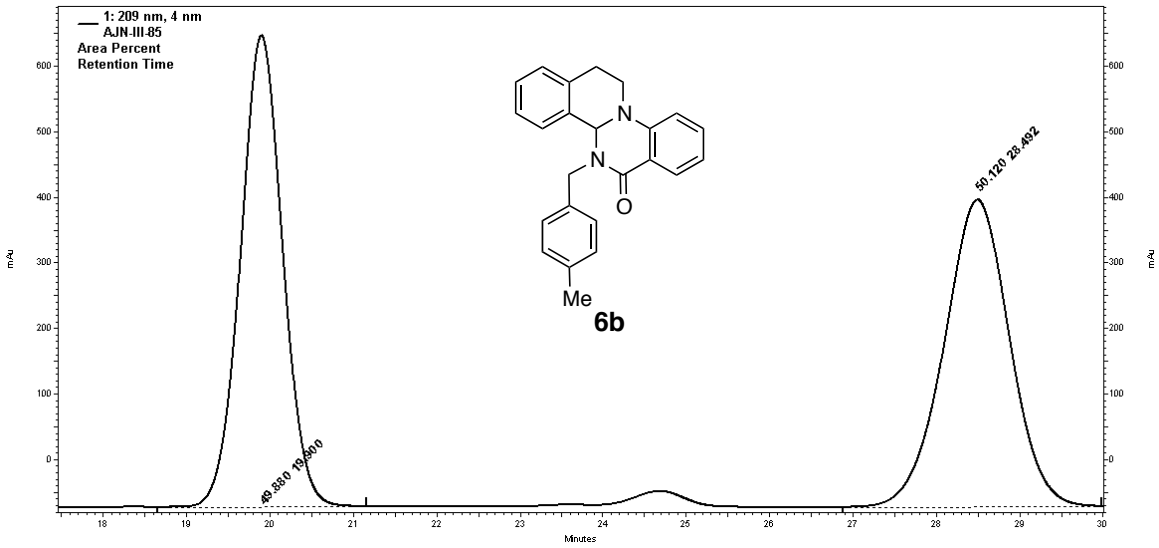


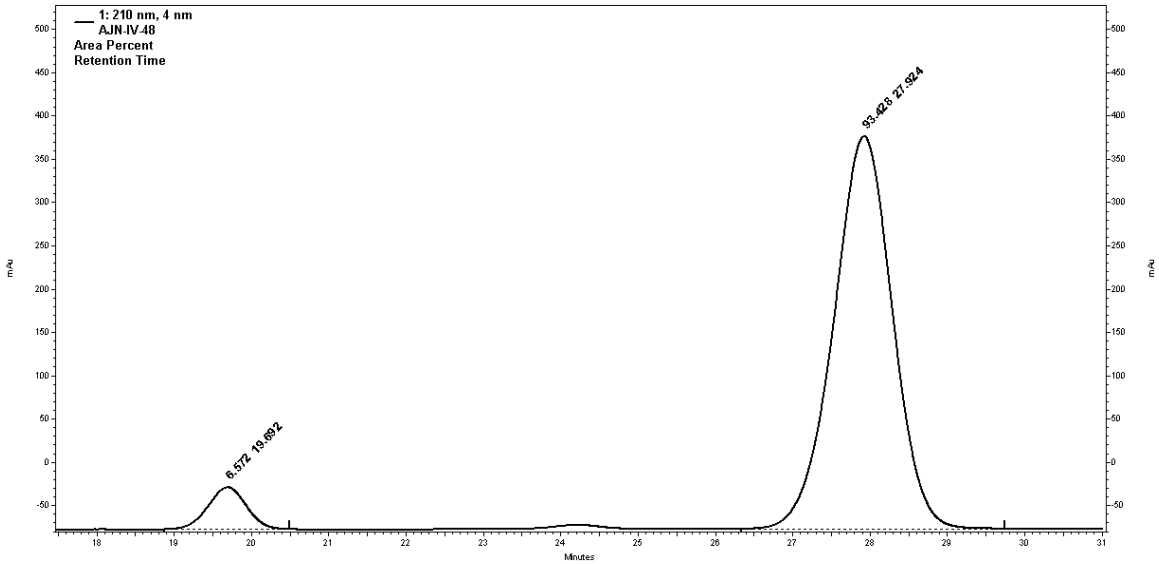
Peak #1	Retention Time (min)	Area Percent
1	18.8	47.34
2	22.5	52.65



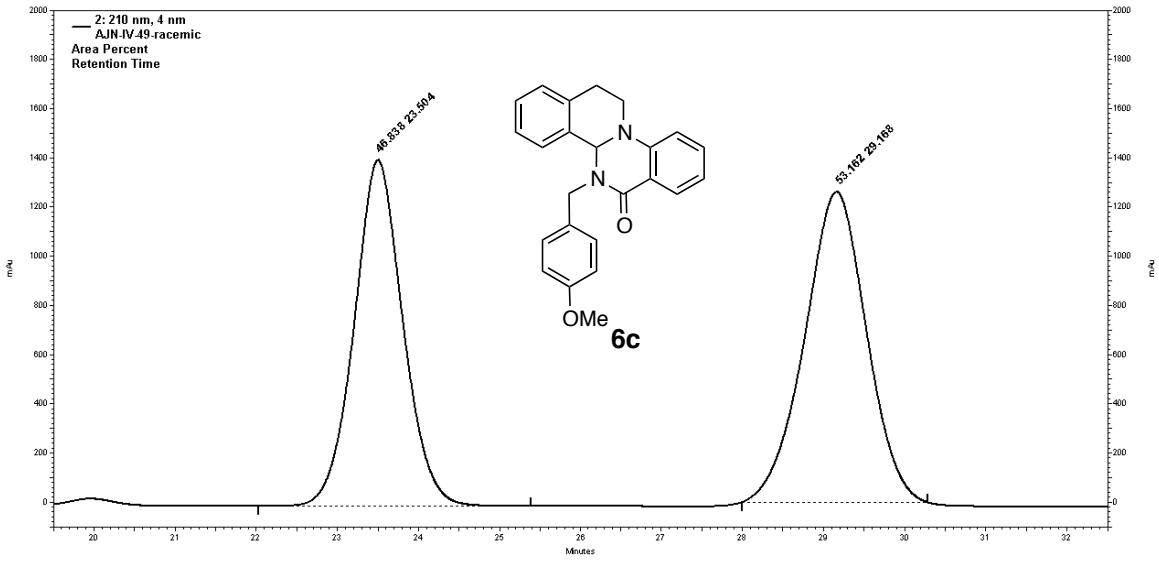
Peak #1	Retention Time (min)	Area Percent
1	18.7	8.00
2	22.5	92.00



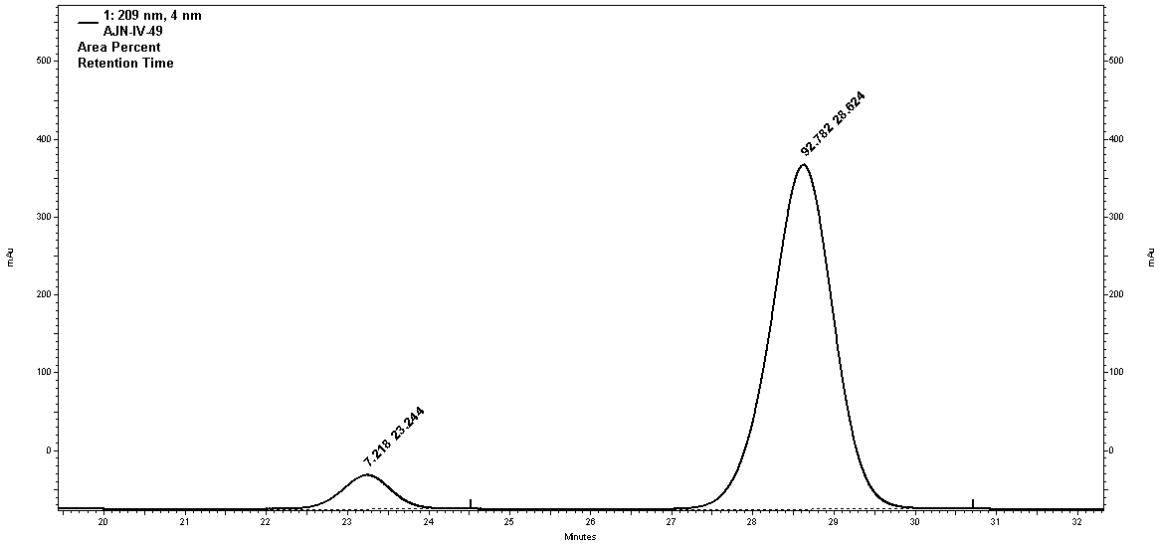
Peak #1	Retention Time (min)	Area Percent
1	19.9	49.88
2	28.5	50.12



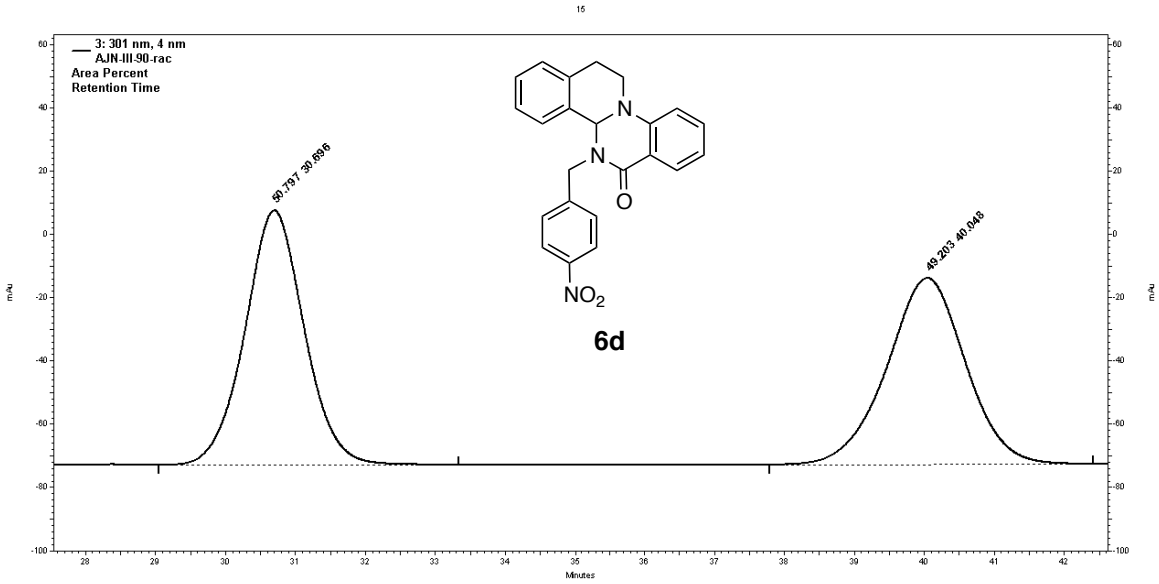
Peak #1	Retention Time (min)	Area Percent
1	19.7	6.57
2	27.9	93.43



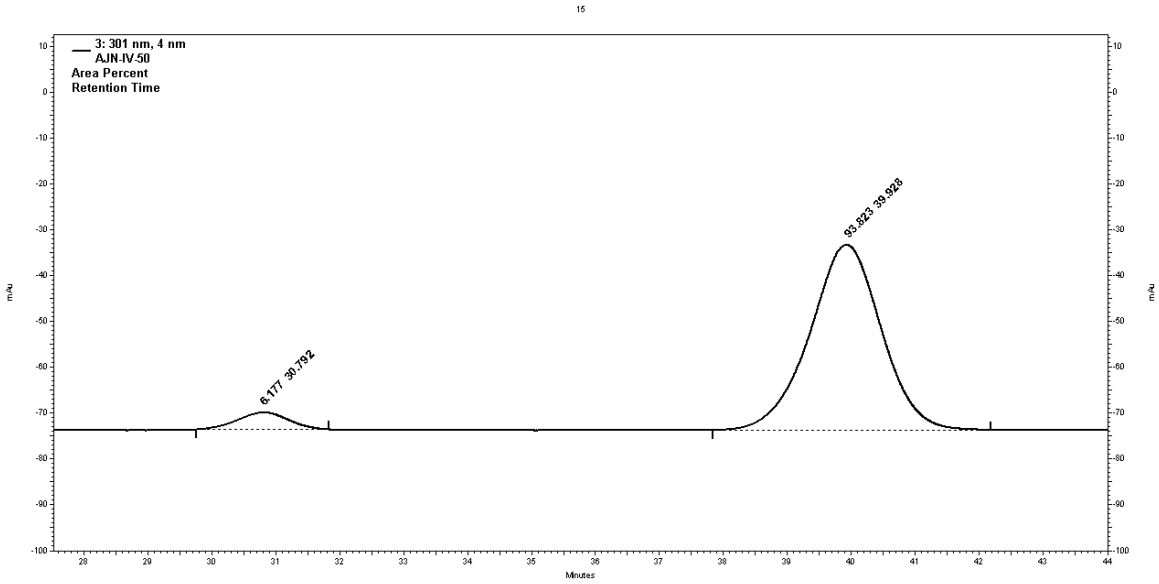
Peak #1	Retention Time (min)	Area Percent
1	23.5	46.83
2	29.2	53.17



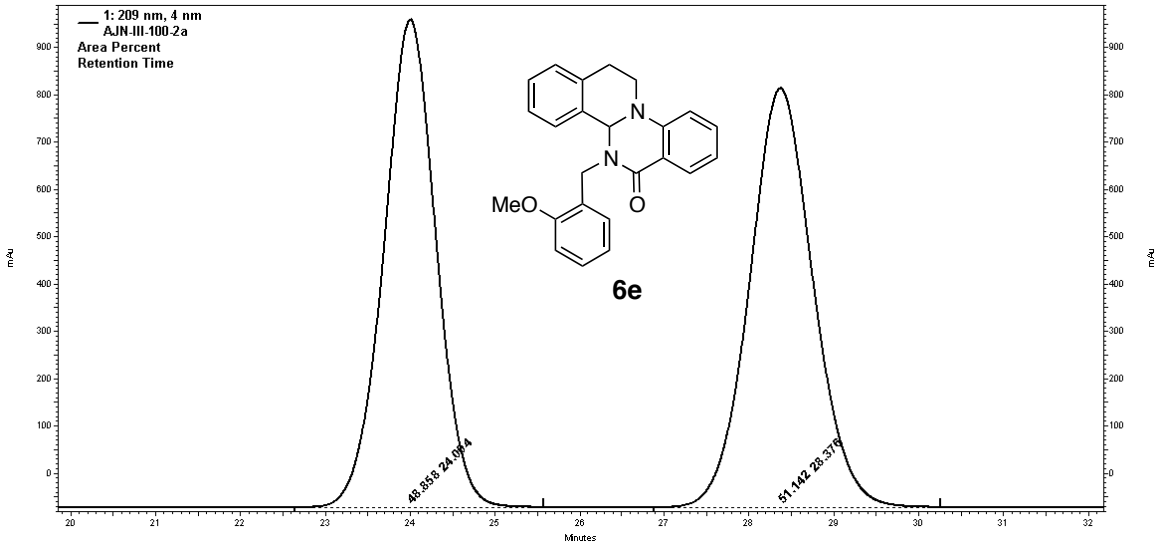
Peak #1	Retention Time (min)	Area Percent
1	23.2	7.22
2	28.6	92.78



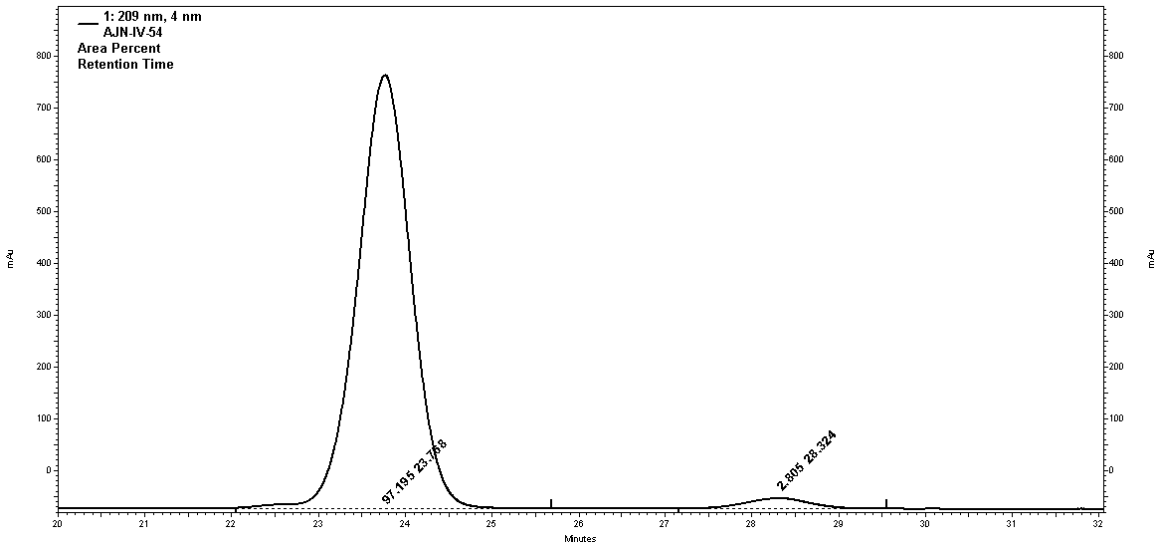
Peak #1	Retention Time (min)	Area Percent
1	30.7	50.80
2	40.0	49.20



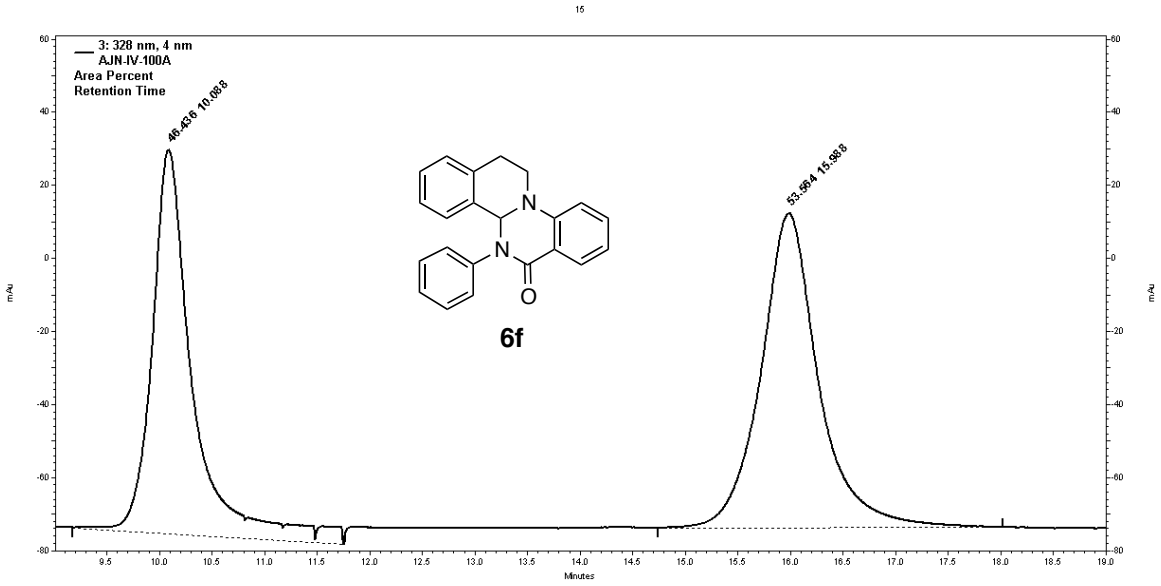
Peak #1	Retention Time (min)	Area Percent
1	30.8	6.18
2	39.9	93.82



Peak #1	Retention Time (min)	Area Percent
1	24.1	48.86
2	28.4	51.14

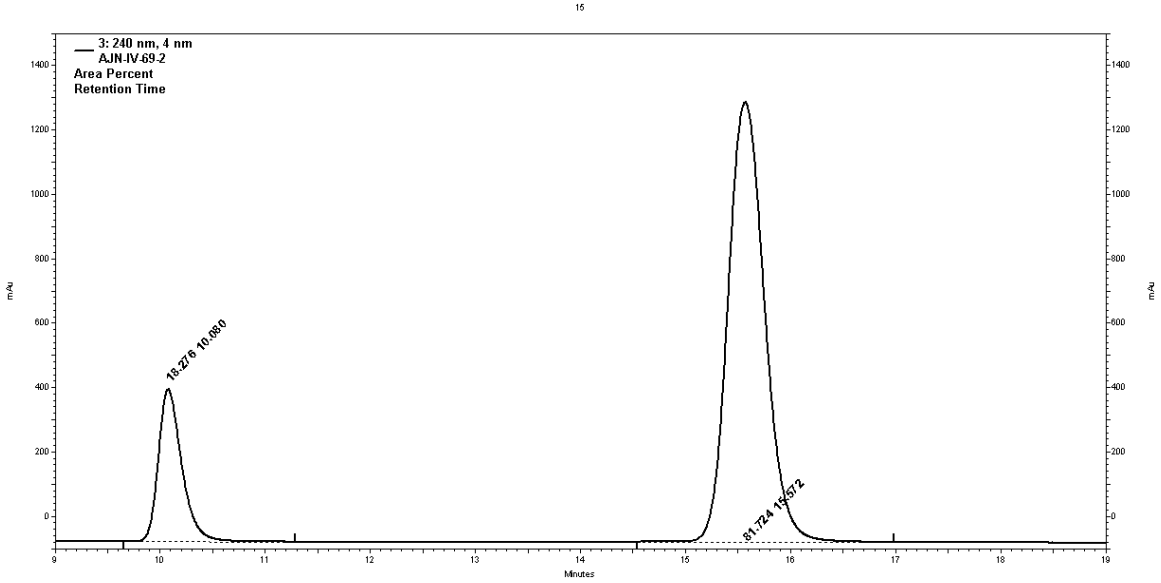


Peak #1	Retention Time (min)	Area Percent
1	23.8	97.20
2	28.3	2.80

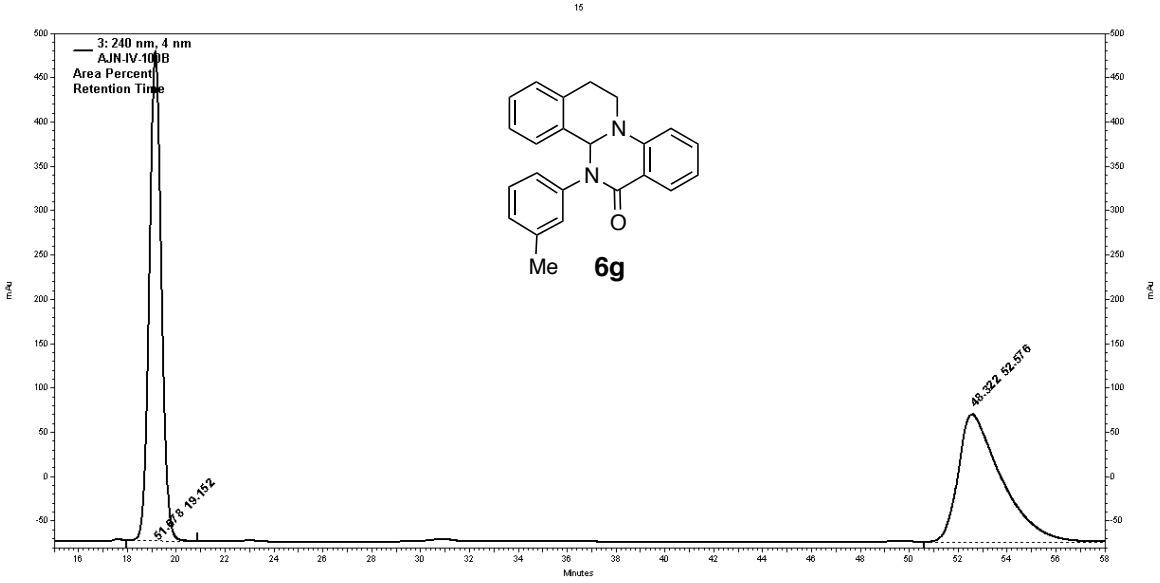


6f

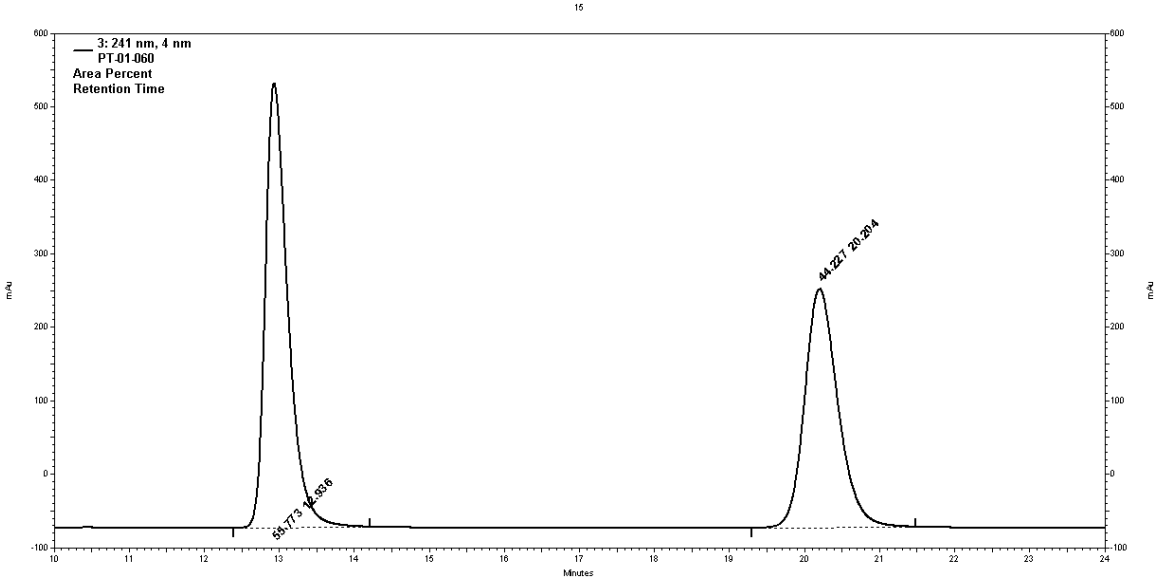
Peak #1	Retention Time (min)	Area Percent
1	10.1	46.43
2	16.0	53.56



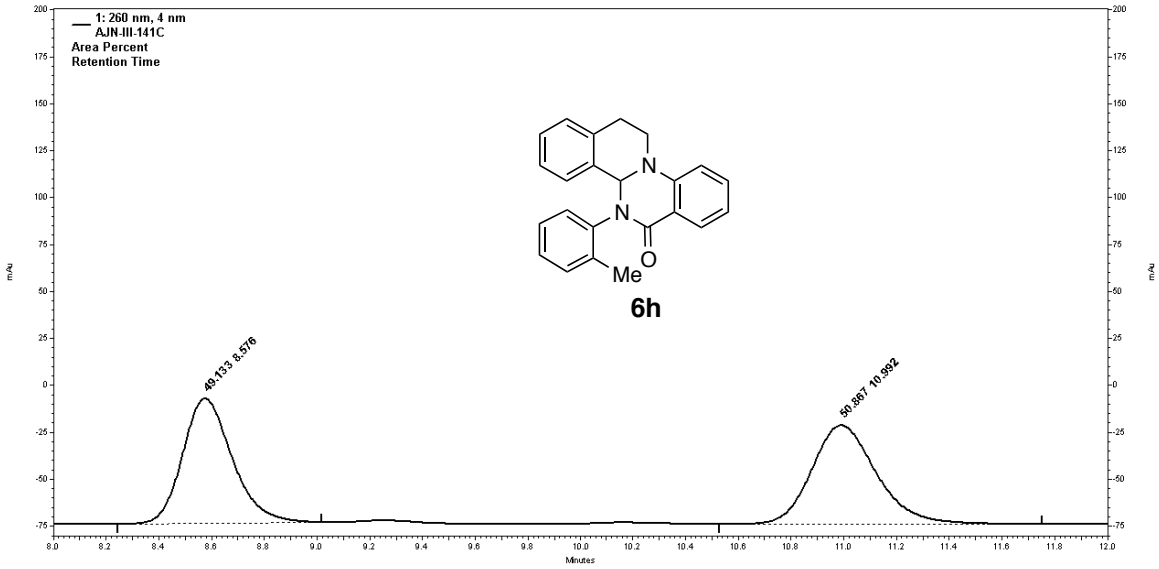
Peak #1	Retention Time (min)	Area Percent
1	10.1	18.28
2	15.6	81.72



Peak #1	Retention Time (min)	Area Percent
1	19.2	51.68
2	52.6	48.32

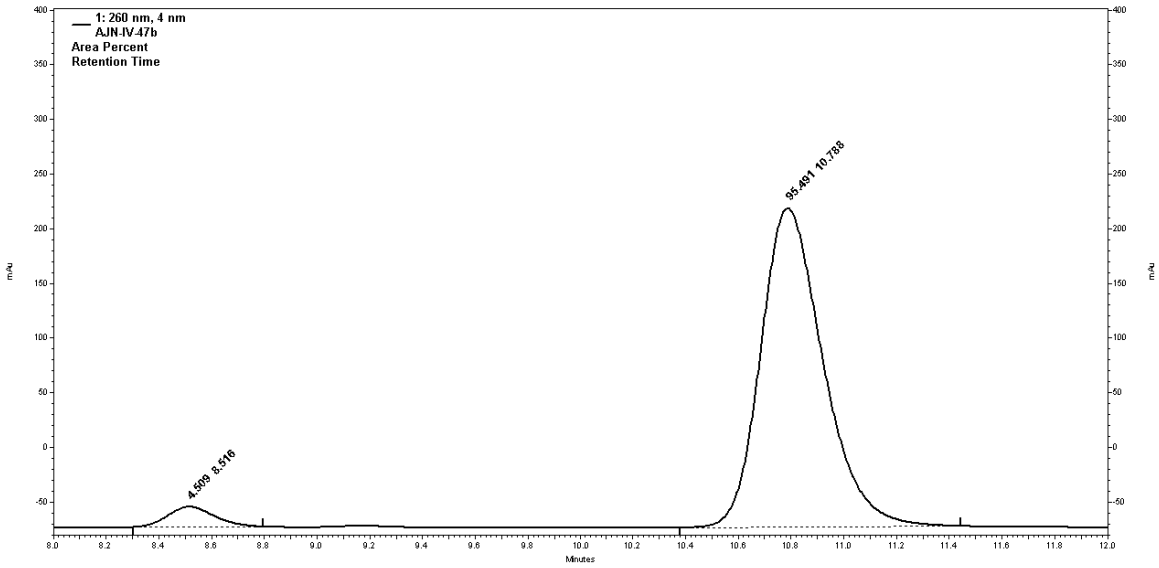


Peak #1	Retention Time (min)	Area Percent
1	17.4	79.76
2	48.0	20.24

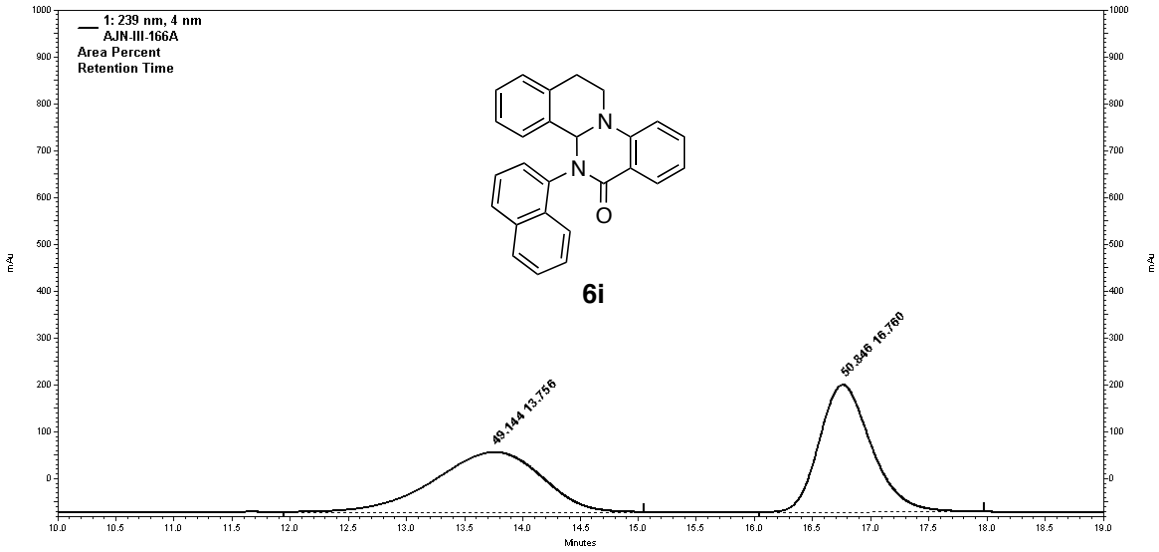


6h

Peak #1	Retention Time (min)	Area Percent
1	8.6	49.13
2	11.0	50.87

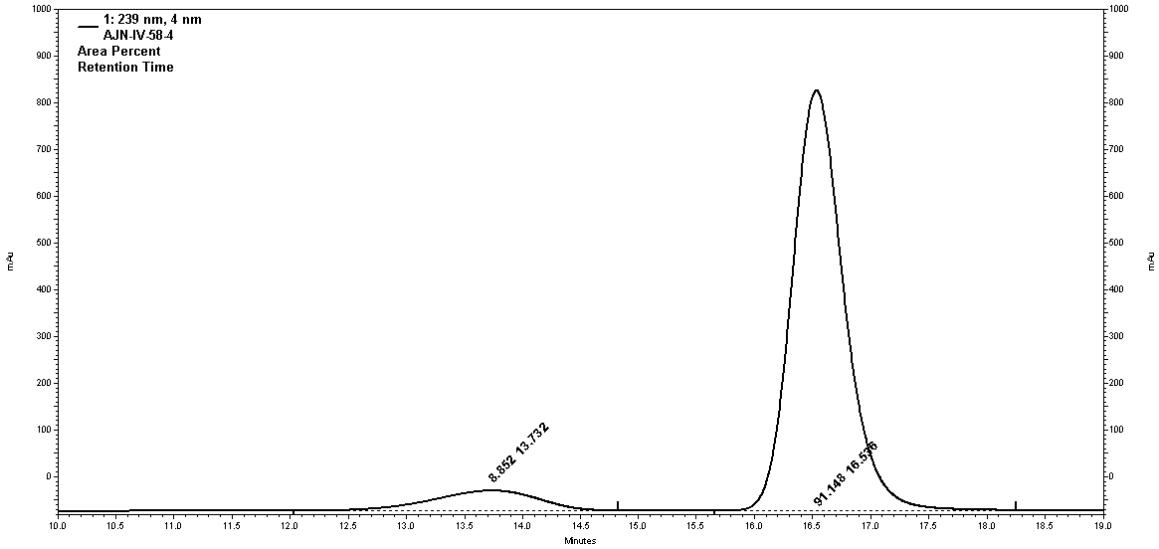


Peak #1	Retention Time (min)	Area Percent
1	8.5	4.51
2	10.8	95.49

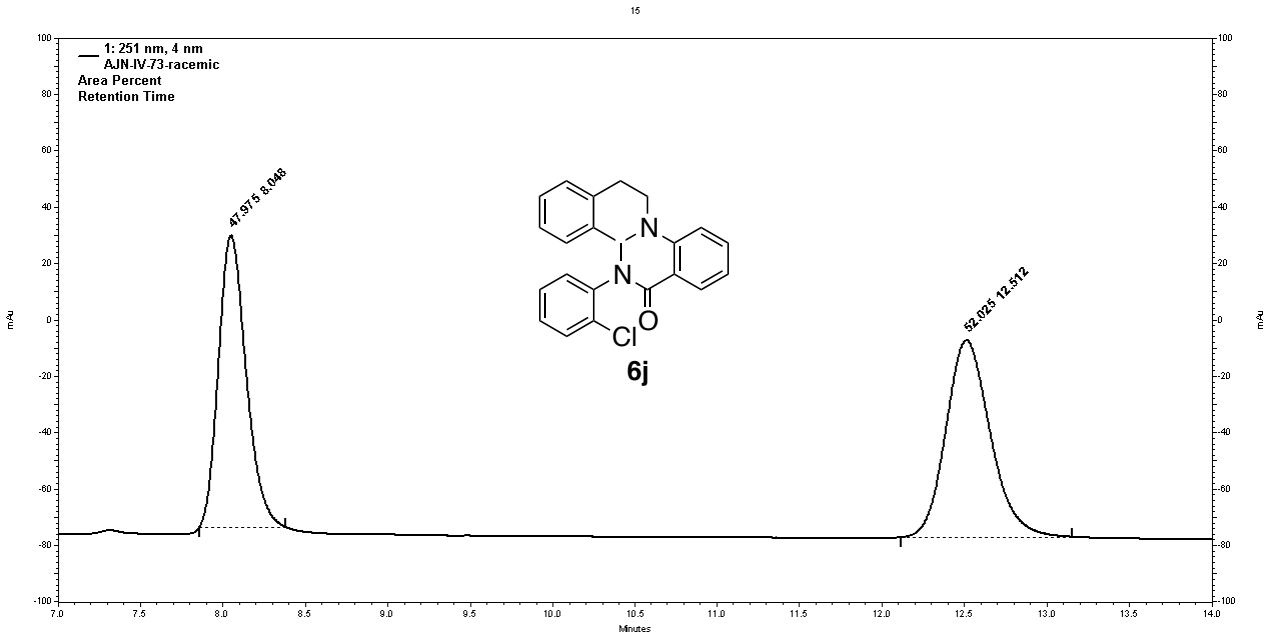


6i

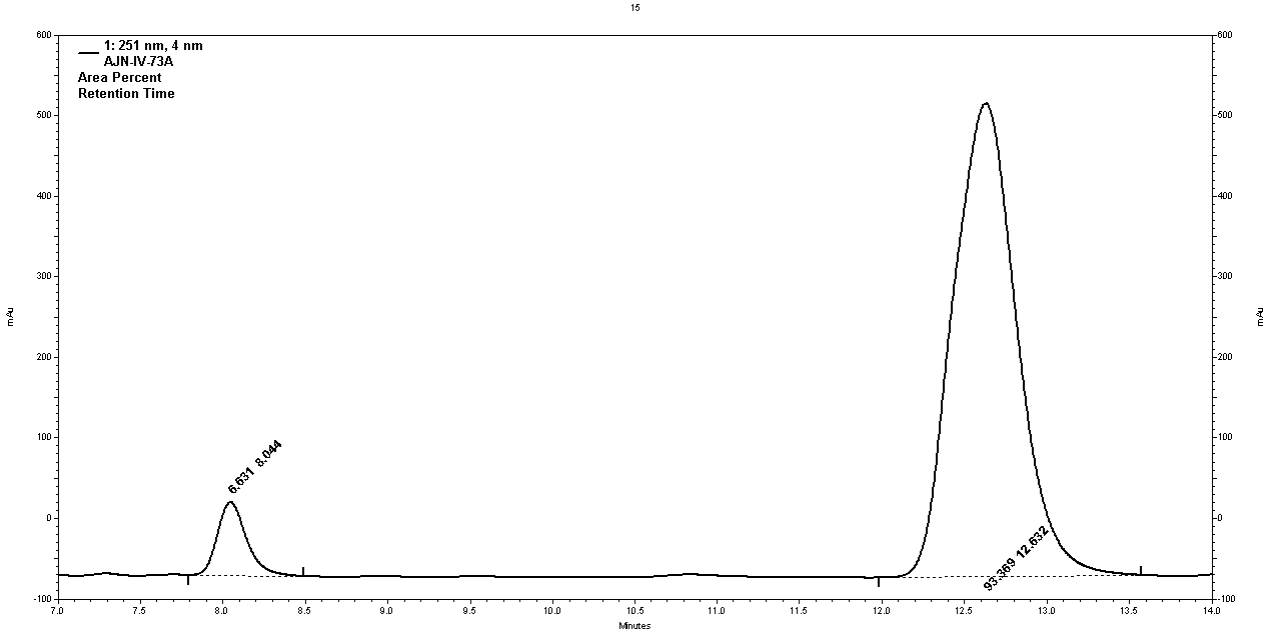
Peak #1	Retention Time (min)	Area Percent
1	13.8	49.14
2	16.8	50.85



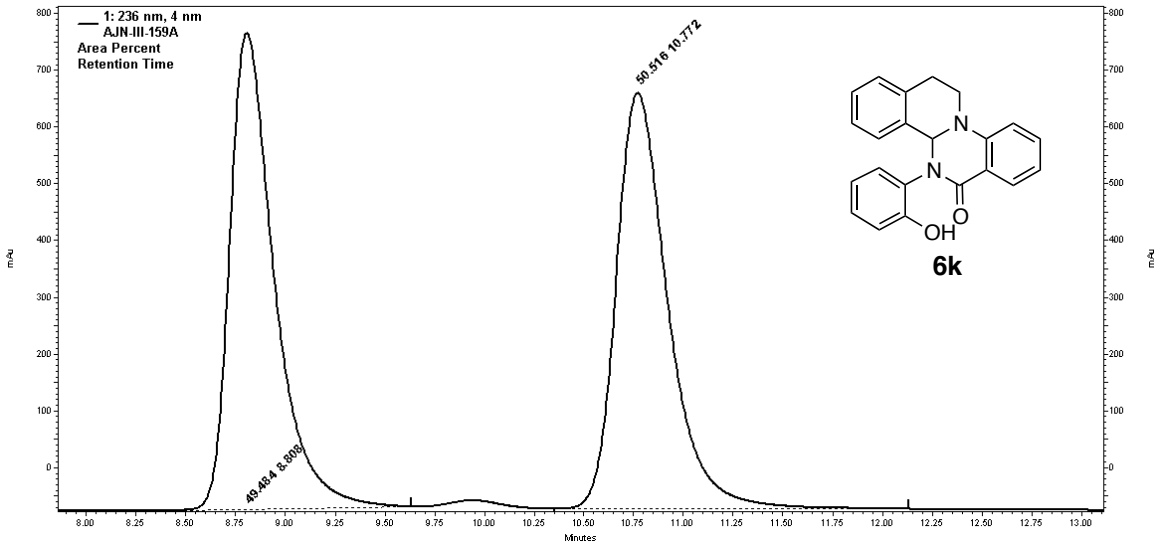
Peak #1	Retention Time (min)	Area Percent
1	13.7	8.85
2	16.5	91.15



Peak #1	Retention Time (min)	Area Percent
1	8.0	48.98
2	12.5	52.03

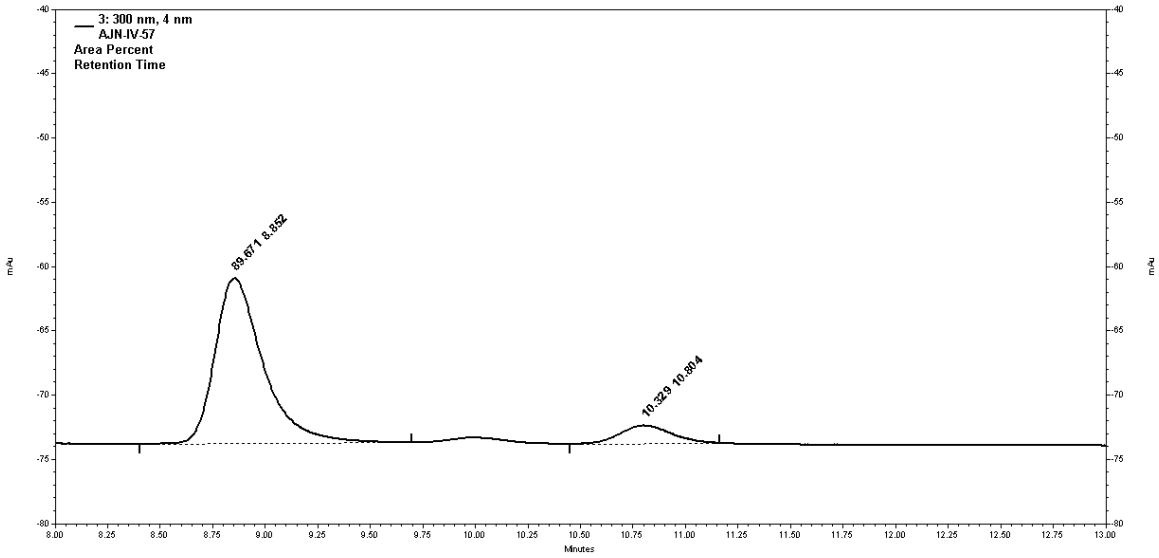


Peak #1	Retention Time (min)	Area Percent
1	8.0	6.63
2	12.6	93.37

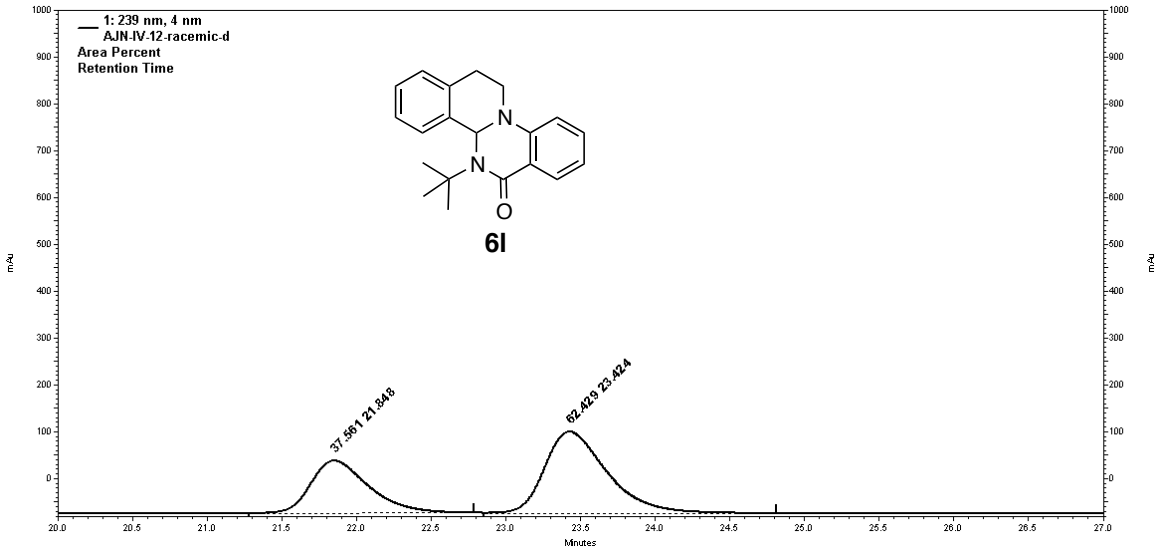


6k

Peak #1	Retention Time (min)	Area Percent
1	8.8	49.48
2	10.8	50.52

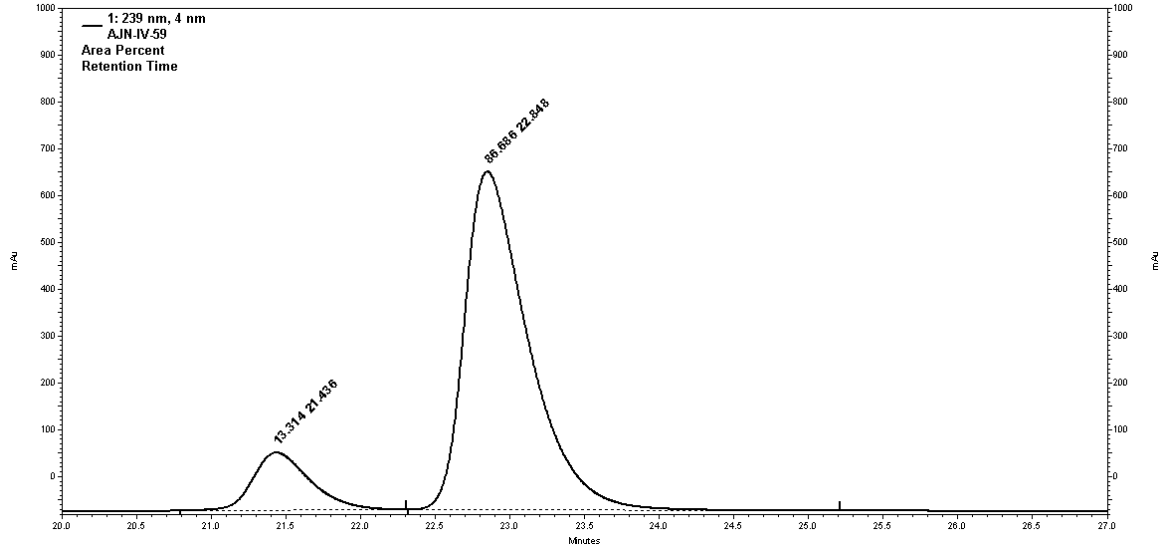


Peak #1	Retention Time (min)	Area Percent
1	8.9	89.67
2	10.8	10.33

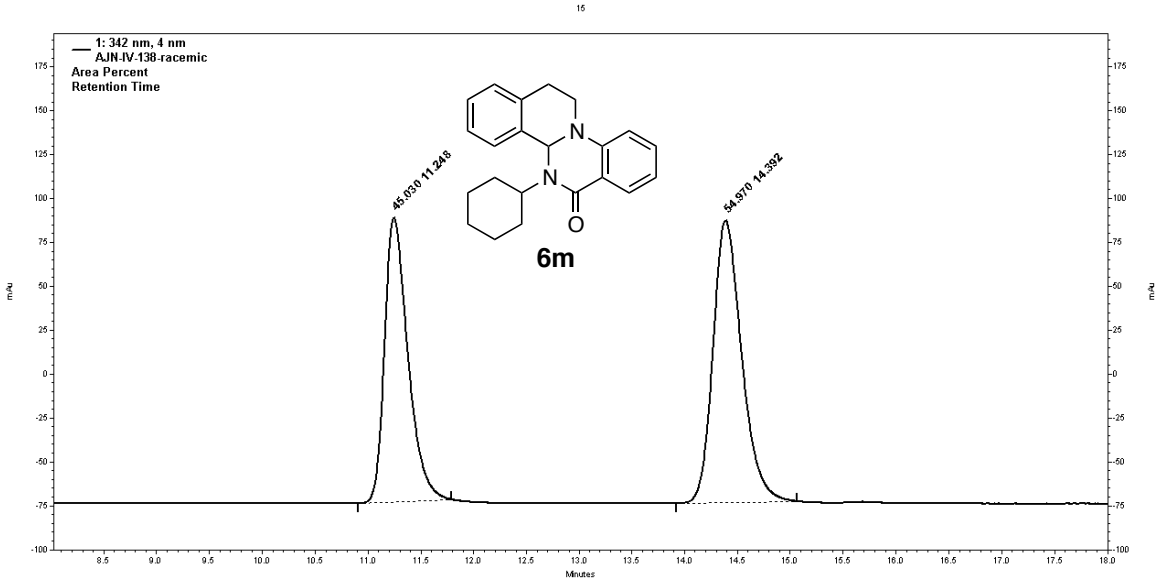


6l

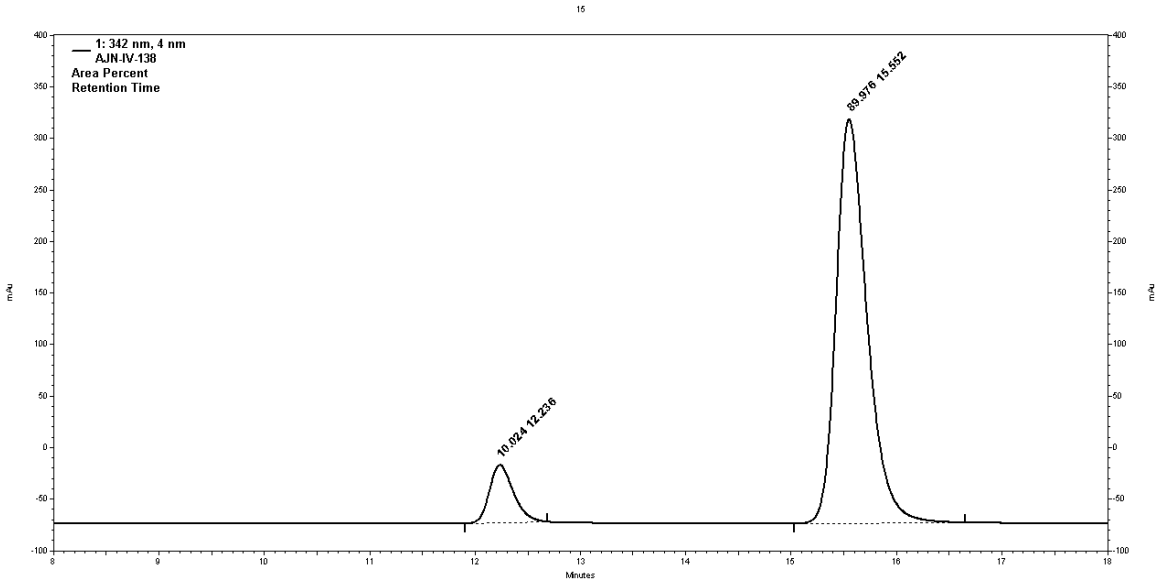
Peak #1	Retention Time (min)	Area Percent
1	21.8	37.56
2	23.4	62.43



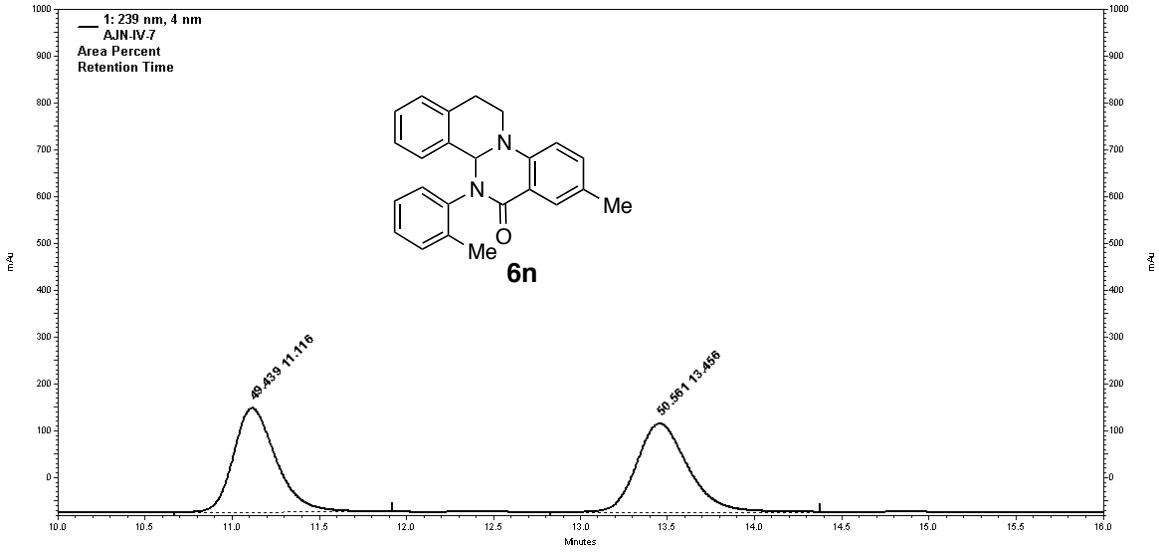
Peak #1	Retention Time (min)	Area Percent
1	21.4	13.31
2	22.8	86.61



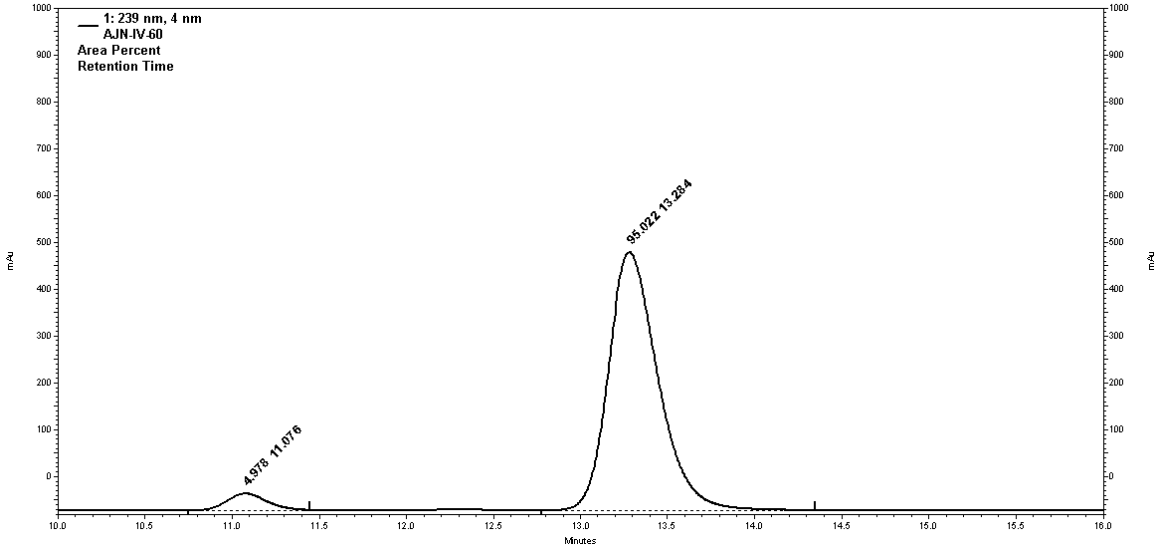
Peak #1	Retention Time (min)	Area Percent
1	11.2	45.03
2	14.4	54.97



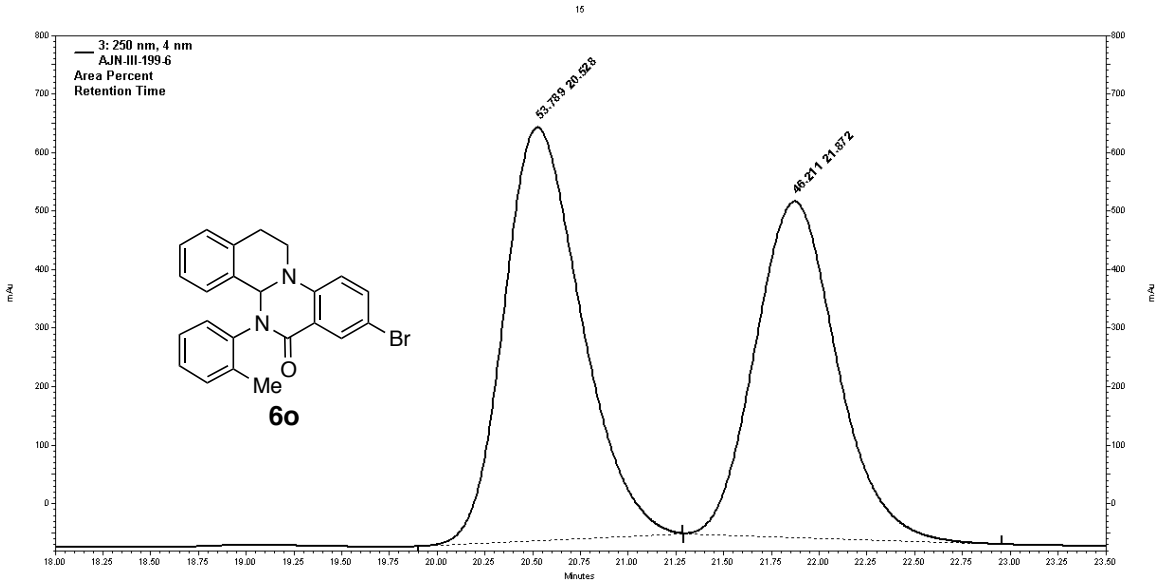
Peak #1	Retention Time (min)	Area Percent
1	12.2	10.02
2	15.6	89.98



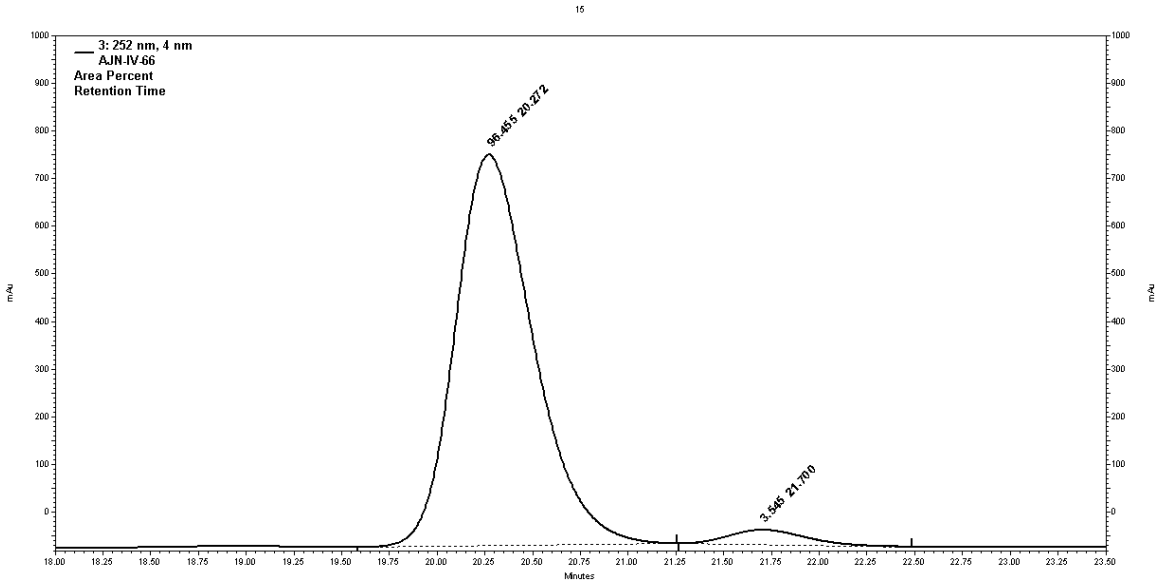
Peak #1	Retention Time (min)	Area Percent
1	11.1	49.44
2	13.5	50.56



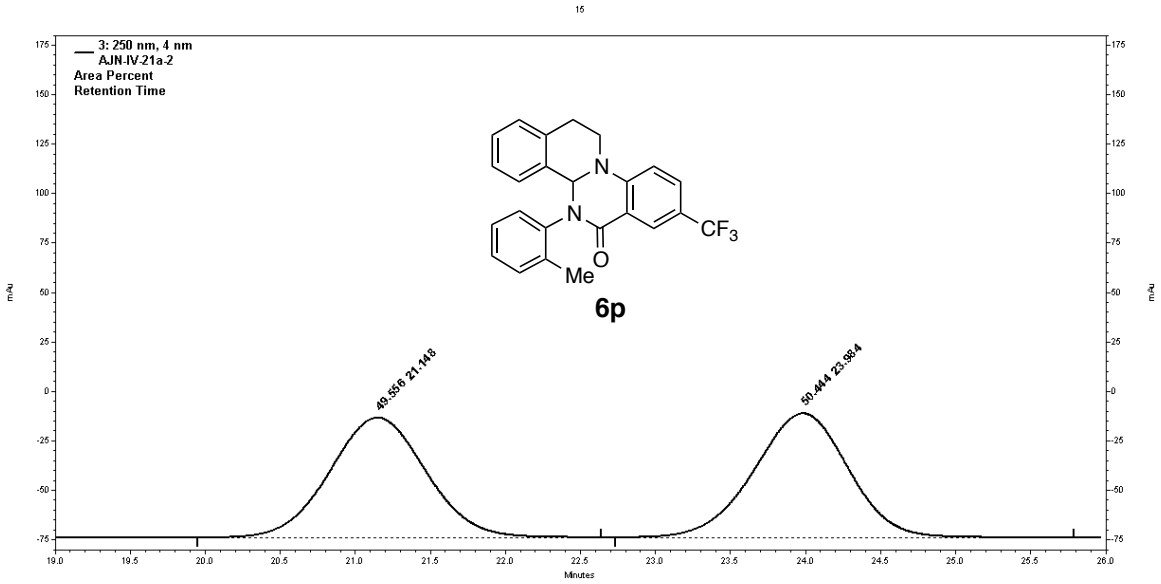
Peak #1	Retention Time (min)	Area Percent
1	11.1	4.98
2	13.3	95.02



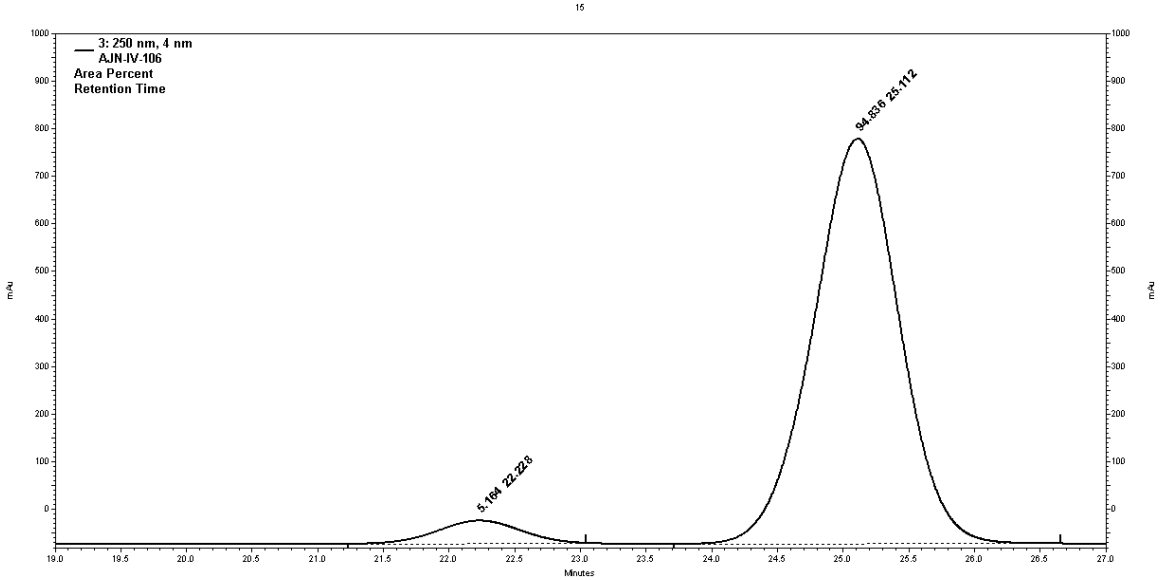
Peak #1	Retention Time (min)	Area Percent
1	20.5	53.79
2	21.9	46.21



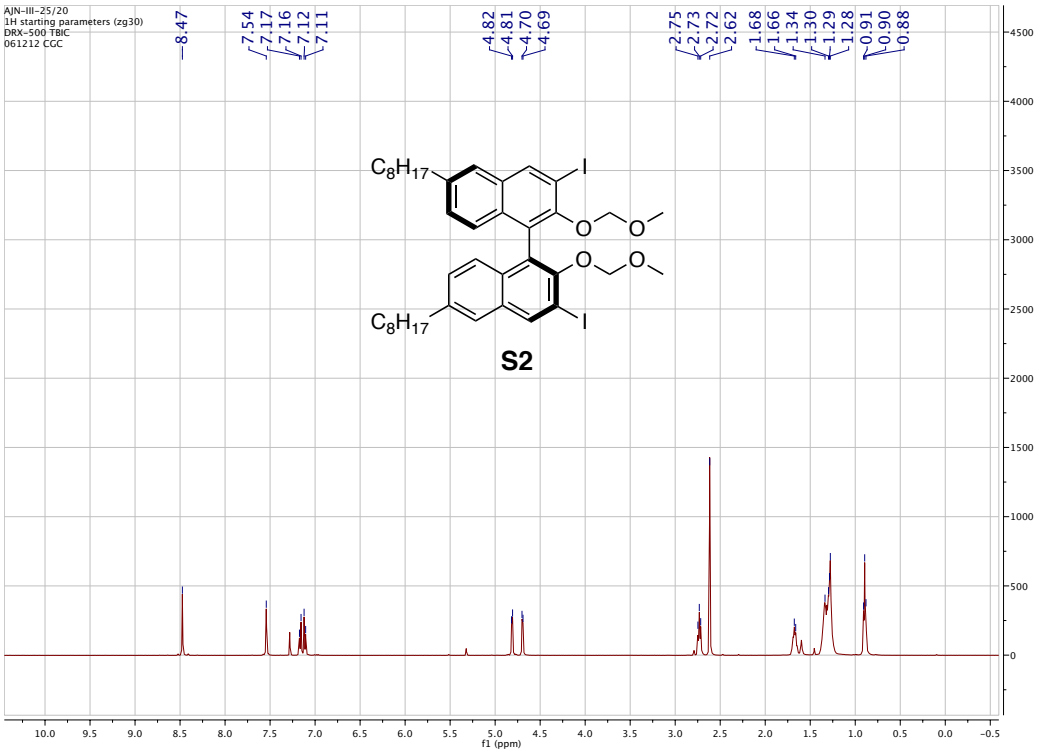
Peak #1	Retention Time (min)	Area Percent
1	20.3	96.46
2	21.7	3.54



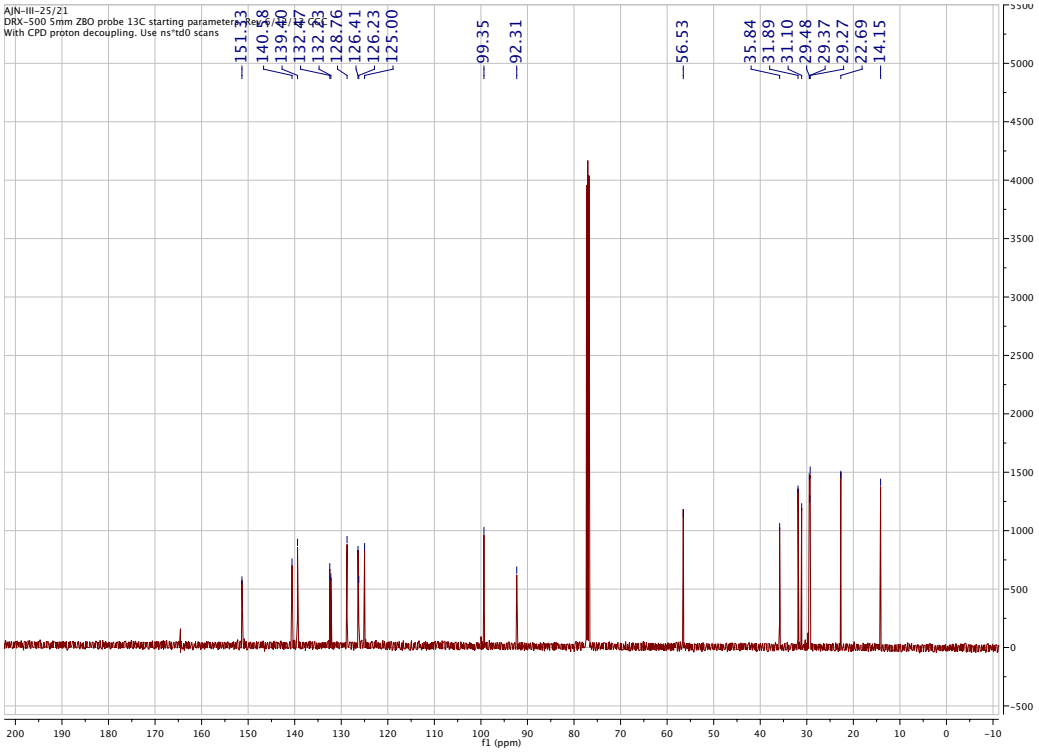
Peak #1	Retention Time (min)	Area Percent
1	21.1	49.56
2	24.0	50.44

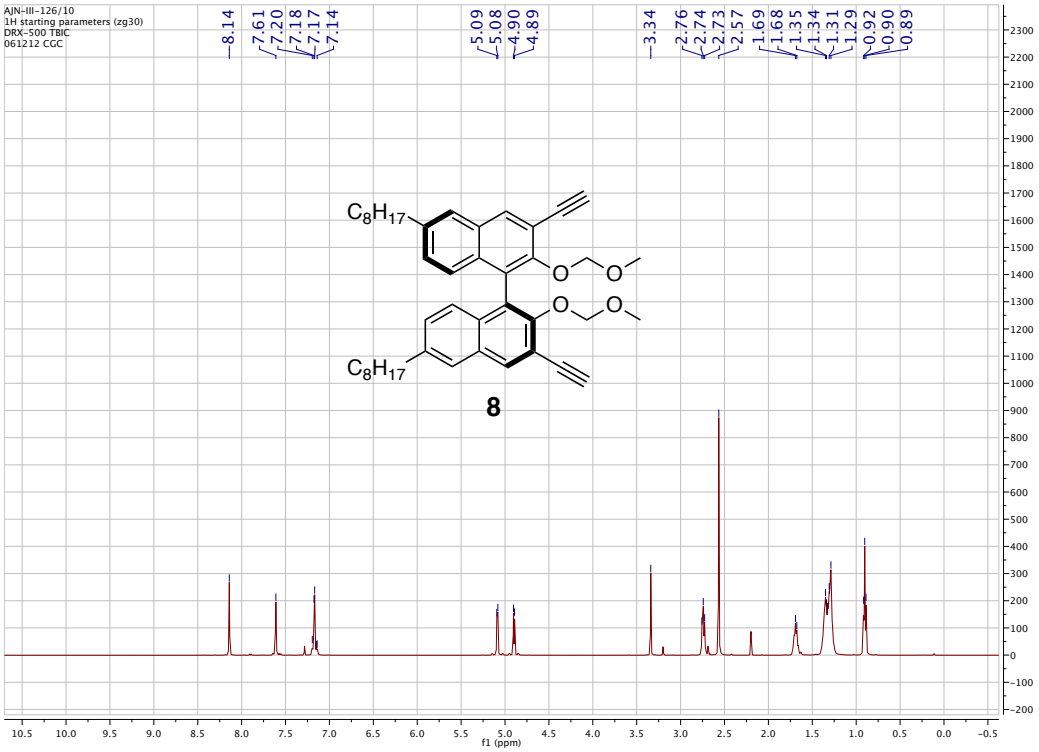


Peak #1	Retention Time (min)	Area Percent
1	22.2	5.16
2	25.1	94.84

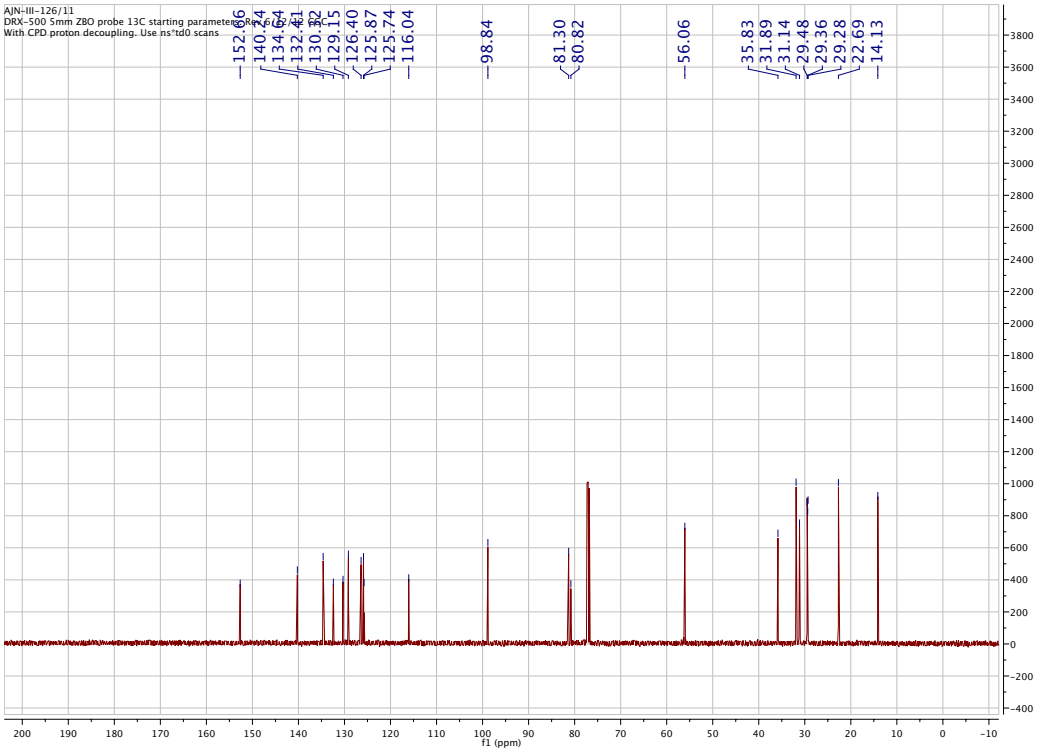

AJN-III-25/20
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
8.47
7.54
7.17
7.16
7.12
7.11
4.82
4.81
4.70
4.69
2.75
2.73
2.72
2.62
1.68
1.66
1.34
1.30
1.29
1.28
0.91
0.90
0.88
C8H17
I
O
O
O
O
C8H17
I
f1 (ppm)

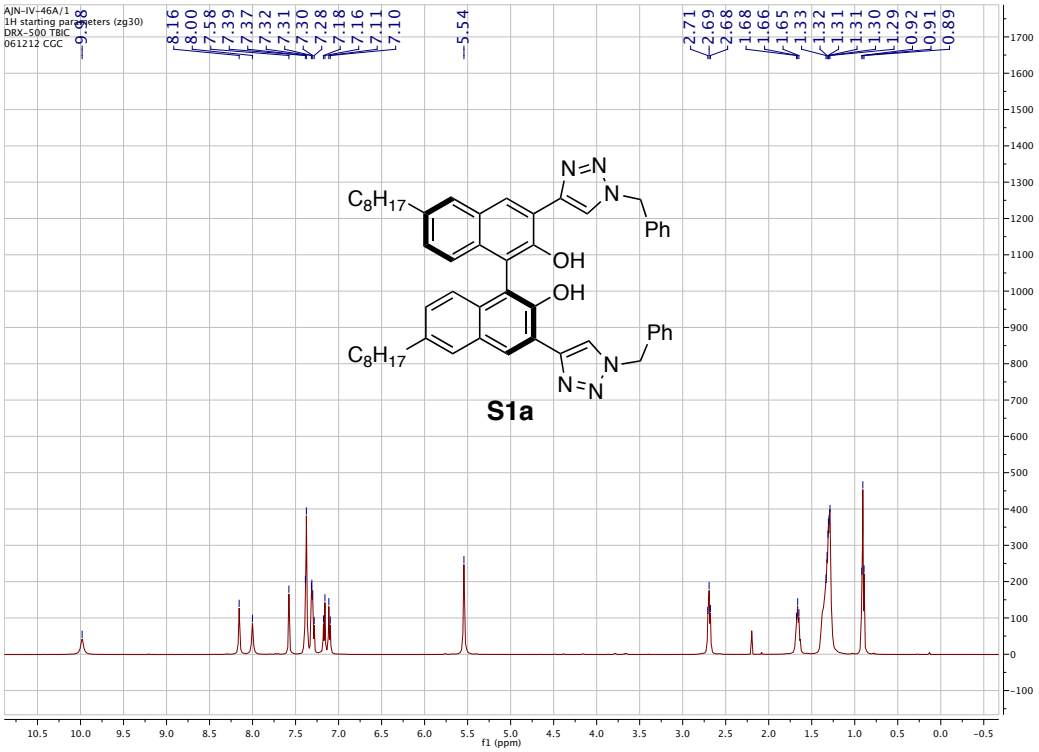
S2

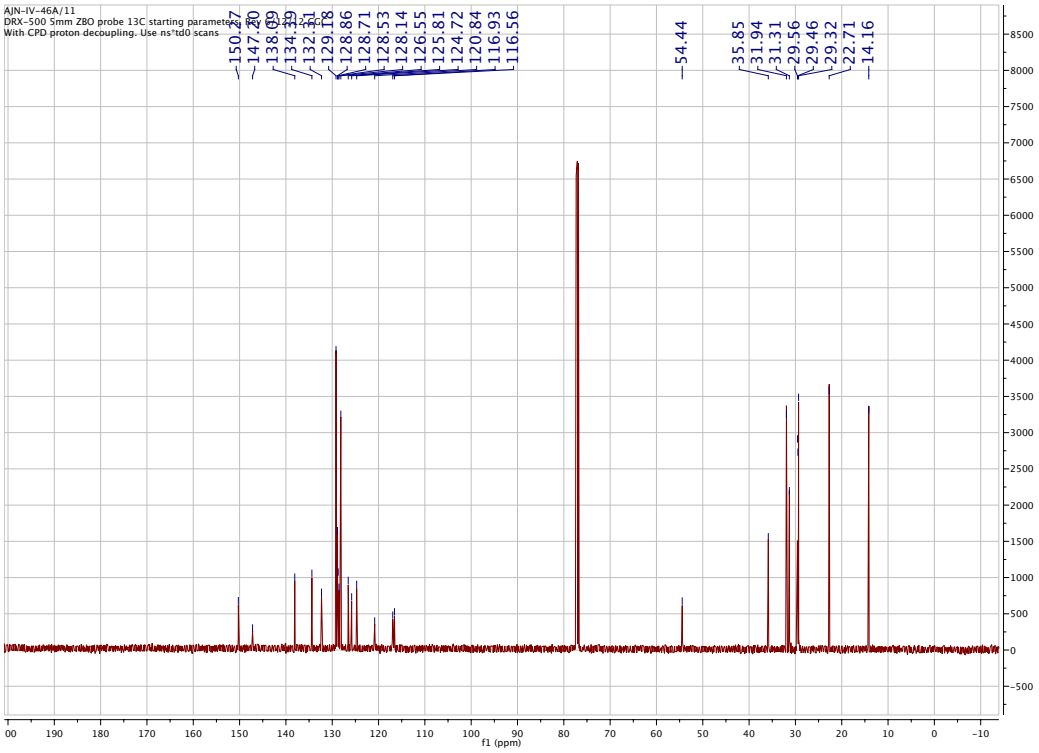

AJN-III-25/21
DRX-500 5mm ZBO probe 13C starting parameters
With CPD proton decoupling. Use ns*td0 scans
151.33
140.88
139.20
132.47
132.23
128.76
126.41
126.23
125.00
99.35
92.31
56.53
35.84
31.89
31.10
29.48
29.37
29.27
22.69
14.15
f1 (ppm)

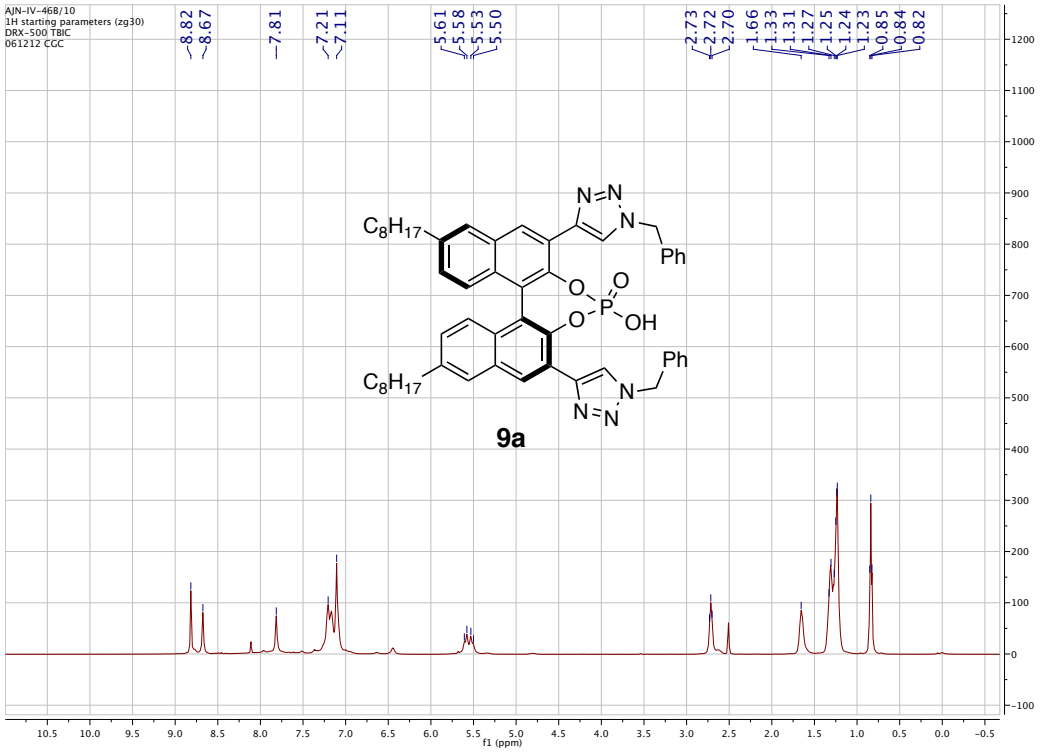

AJN-III-126/10
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
8.14
7.61
7.20
7.18
7.17
7.14
5.09
5.08
4.90
4.89
3.34
2.76
2.74
2.73
2.57
1.69
1.68
1.35
1.34
1.31
1.29
0.92
0.90
0.89
C8H17
O
O
O
O
C8H17
f1 (ppm)

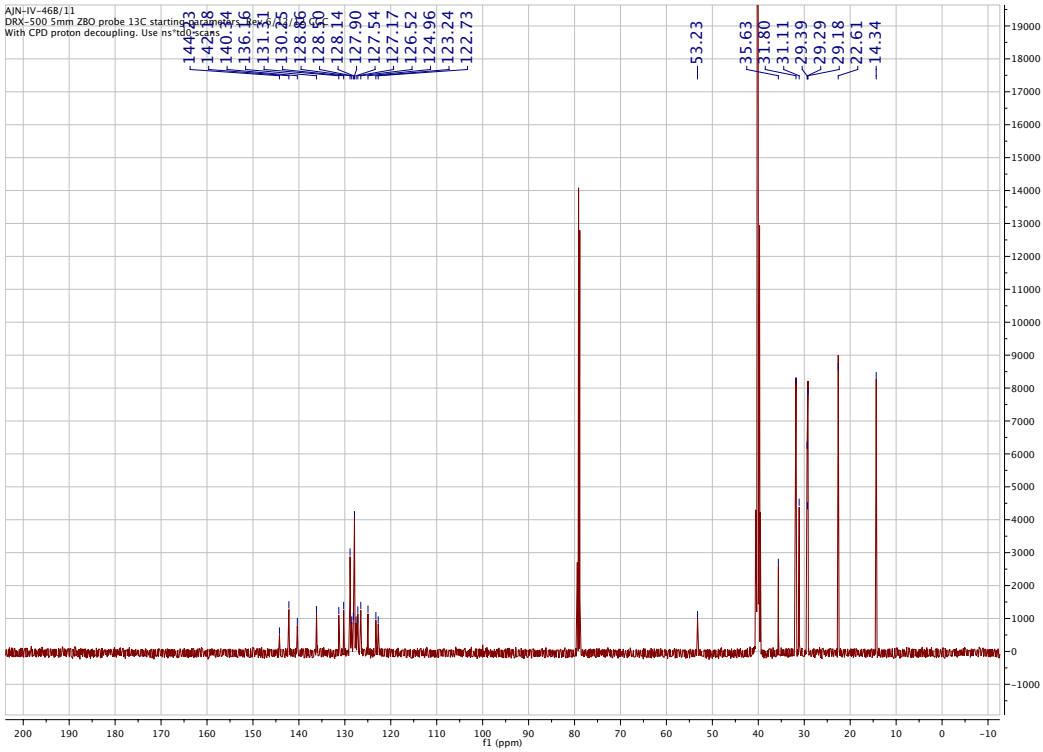
8

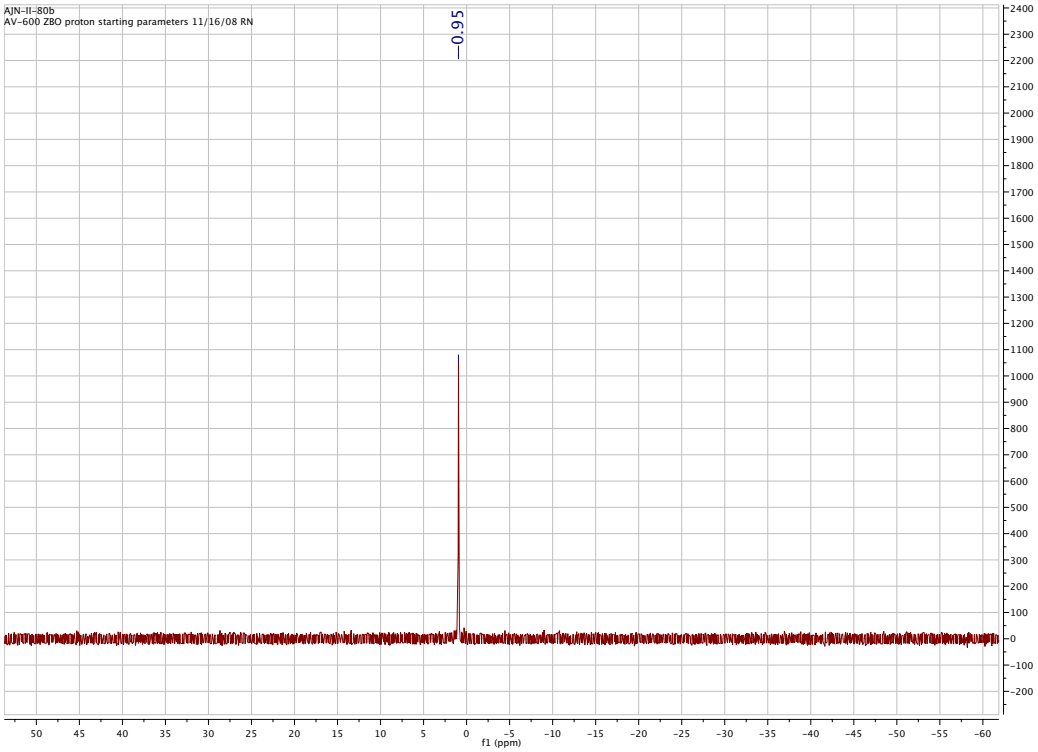

AJN-III-126/11
DRX-500 5mm ZBO probe 13C starting parameters (zgpg30)
With CPD proton decoupling. Use ns*td0 scans
152.66
140.74
134.64
132.41
130.32
129.15
126.40
125.87
125.74
116.04
98.84
81.30
80.82
56.06
35.83
31.89
31.14
29.48
29.36
29.28
22.69
14.13
f1 (ppm)

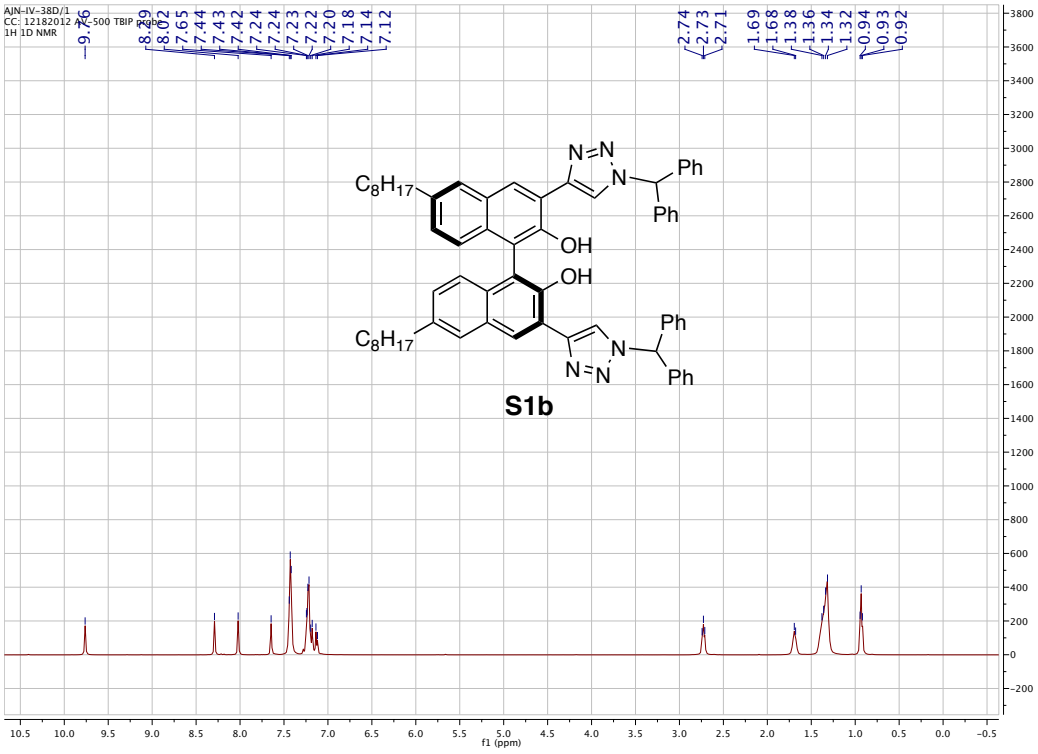

AJN-IV-46A/1
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
9.98
8.16
8.00
7.58
7.39
7.37
7.32
7.31
7.30
7.28
7.18
7.16
7.11
7.10
5.54
2.71
2.69
2.68
1.68
1.66
1.65
1.33
1.32
1.31
1.31
1.30
1.29
0.92
0.91
0.89
f1 (ppm)


AJN-IV-46A/11
DRX-500 5mm ZBO probe 13C starting parameters (zgpg30)
With CPD proton decoupling. Use ns*td0 scans
150.27
147.20
138.09
134.19
132.21
129.18
128.86
128.71
128.53
128.14
126.55
125.81
124.72
120.84
116.93
116.56
54.44
35.85
31.94
31.31
29.56
29.46
29.32
22.71
14.16
f1 (ppm)

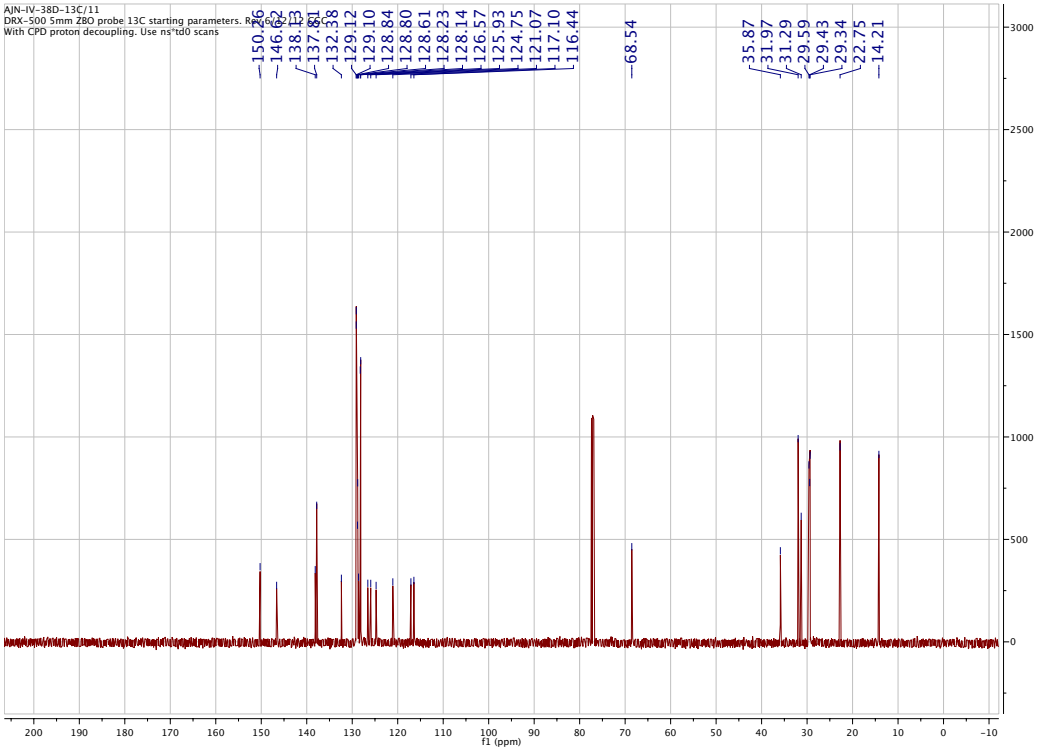

AJN-IV-468/10
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
8.82
8.67
7.81
7.21
7.11
5.61
5.58
5.53
5.50
2.73
2.72
2.70
1.66
1.33
1.31
1.27
1.25
1.24
1.23
0.85
0.84
0.82
C8H17
N=N
N
Ph
O
P
OH
9a
f1 (ppm)

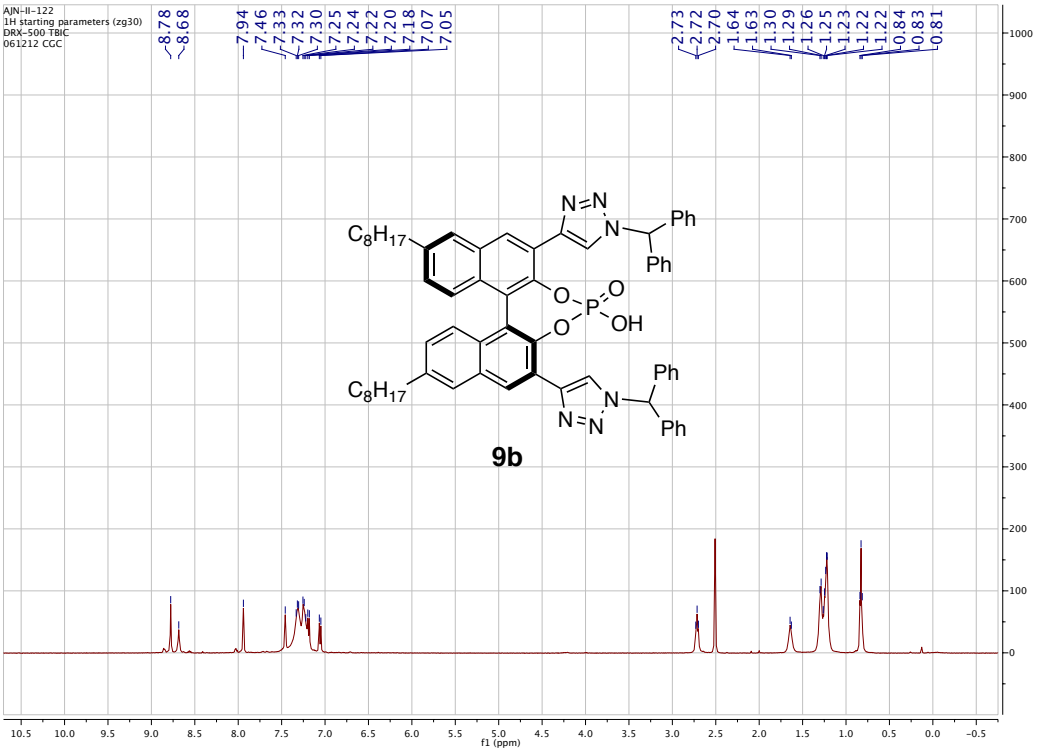

AJN-IV-468/11
DRX-500 5mm ZBO probe 13C starting parameters
With CPD proton decoupling. Use ns*td0 scans
144.23
142.89
140.44
136.16
131.71
130.25
128.86
128.60
128.14
127.90
127.54
127.17
126.52
124.96
123.24
122.73
53.23
35.63
31.80
31.11
29.39
29.29
29.18
22.61
14.34
f1 (ppm)

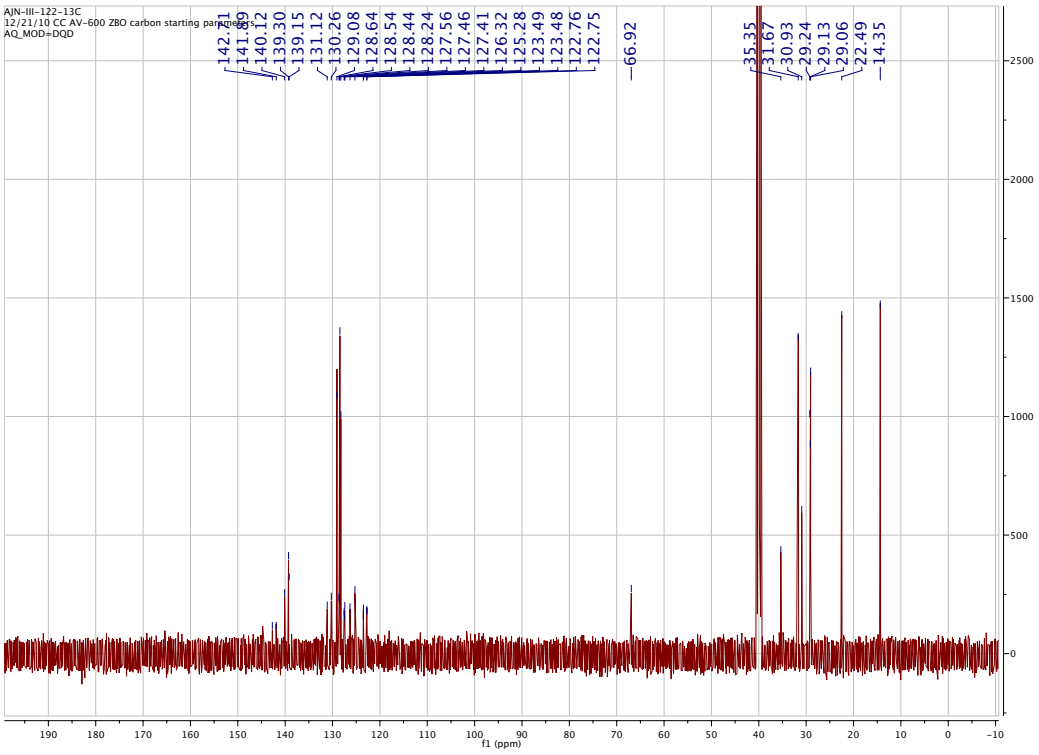

AJN-II-80b
AV-600 ZBO proton starting parameters 11/16/08 RN
0.95
f1 (ppm)

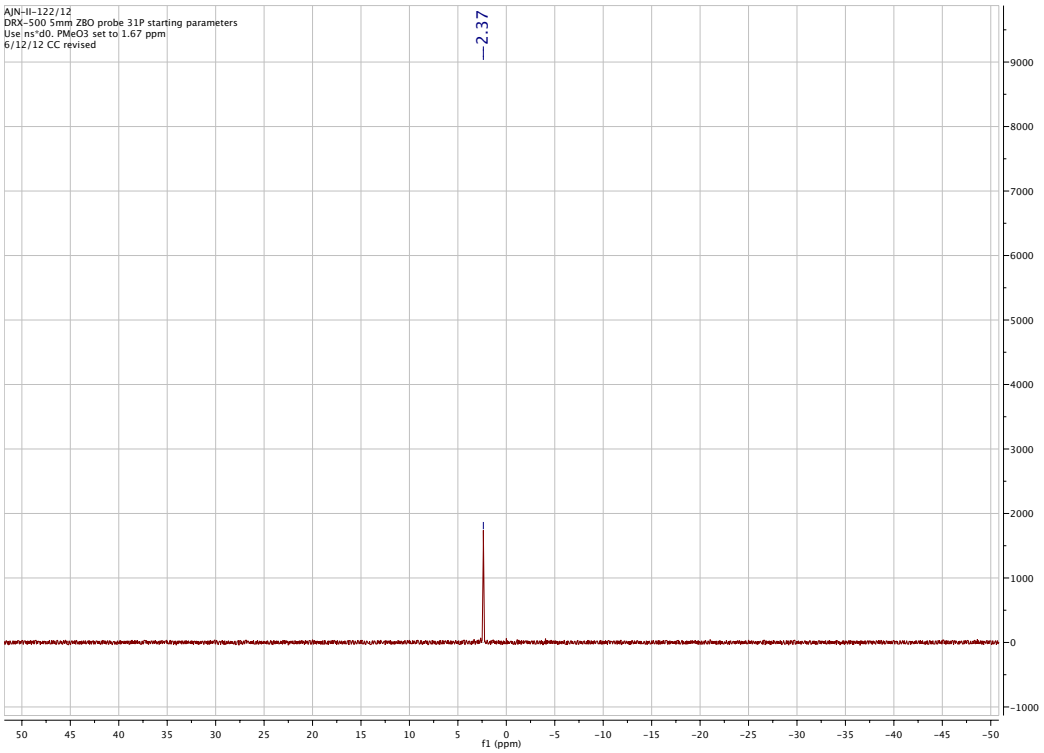

AJN-IV-38D/1
CC: 12182012 AV-500 TBIP probe
1H 1D NMR
9.76
8.09
8.02
7.65
7.44
7.43
7.42
7.24
7.24
7.23
7.22
7.20
7.18
7.14
7.12
2.74
2.73
2.71
1.69
1.68
1.38
1.36
1.34
1.32
0.94
0.93
0.92
N=N
N
Ph
Ph
C8H17
OH
OH
C8H17
Ph
N
N=N
Ph
f1 (ppm)

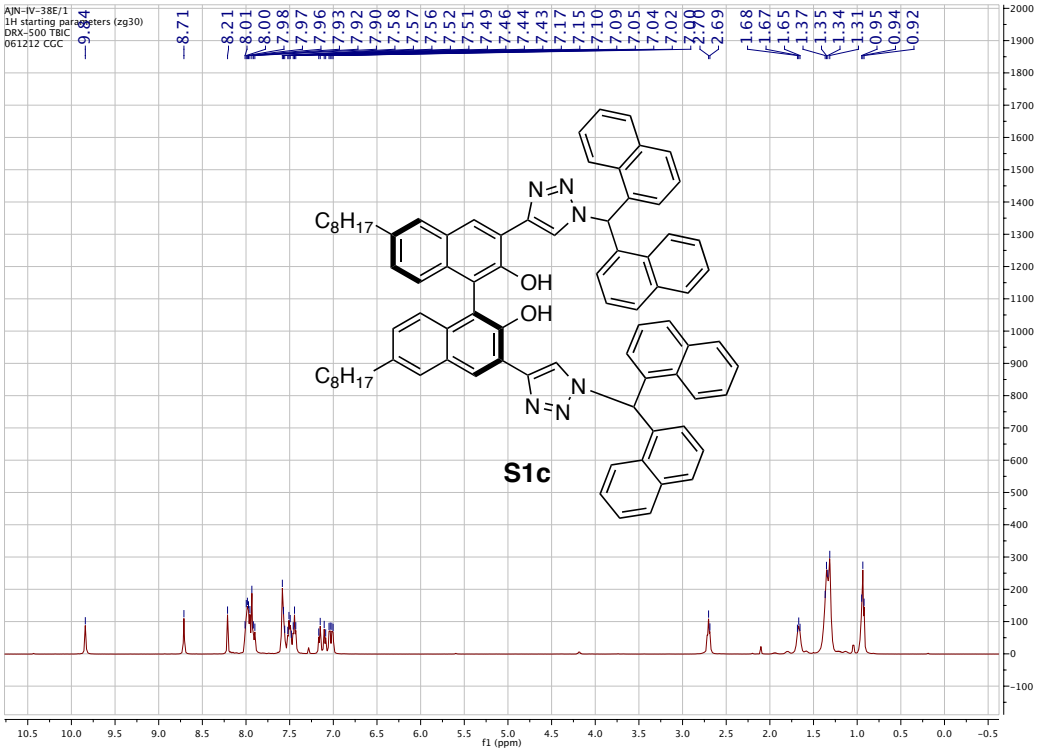
S1b

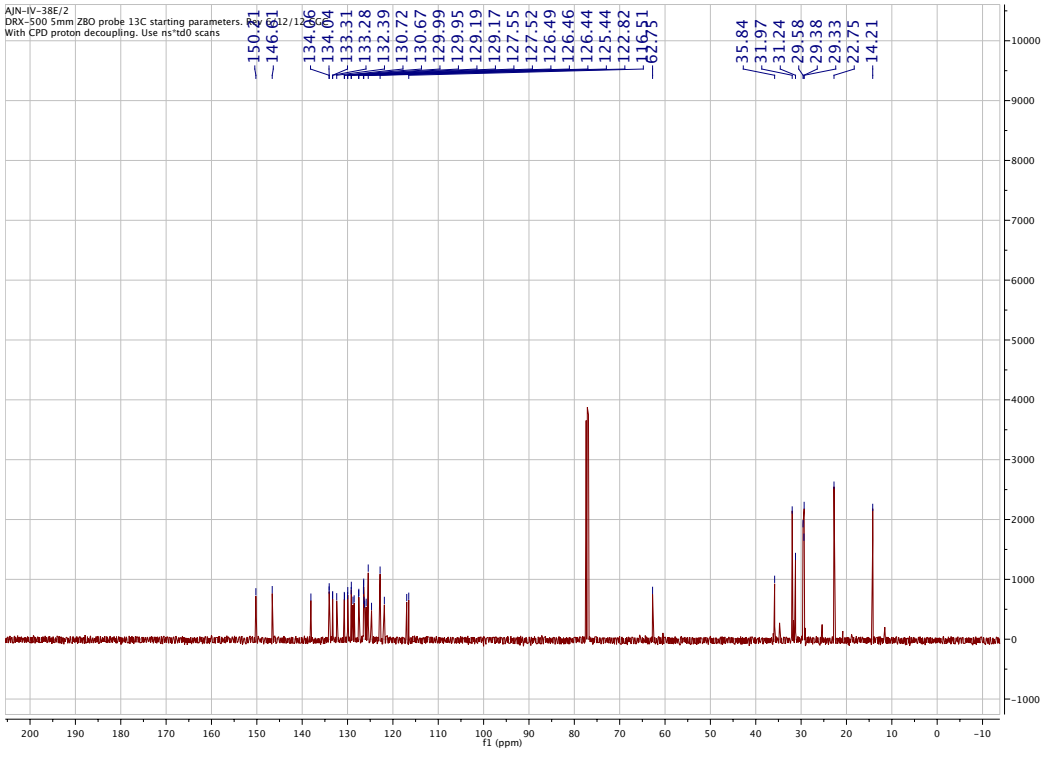

AJN-IV-38D-13C/11
DRX-500 5mm ZBO probe 13C starting parameters. Rev. 6.2
With CPD proton decoupling. Use ns*td0 scans
150.76
146.62
138.13
137.61
132.38
129.12
129.10
128.84
128.80
128.61
128.23
128.14
126.57
125.93
124.75
121.07
117.10
116.44
68.54
35.87
31.97
31.29
29.59
29.43
29.34
22.75
14.21
f1 (ppm)

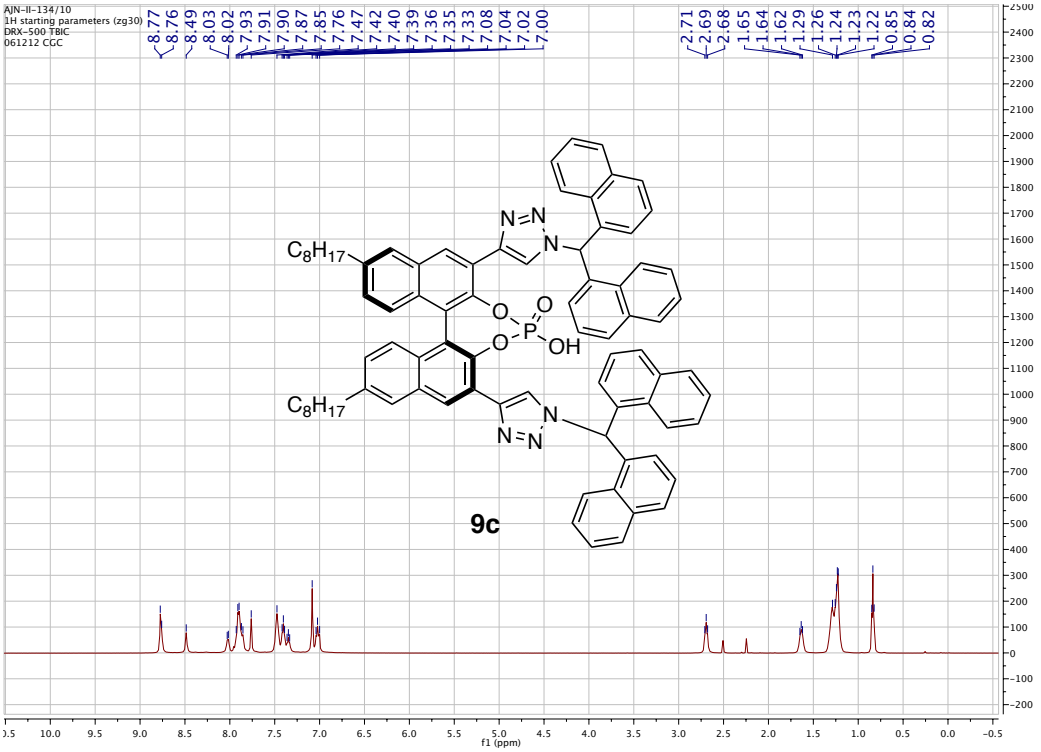

AJN-II-122
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
8.78
8.68
7.94
7.46
7.33
7.32
7.30
7.25
7.24
7.22
7.20
7.18
7.07
7.05
2.73
2.72
2.70
1.64
1.63
1.30
1.29
1.26
1.25
1.23
1.22
1.22
0.84
0.83
0.81
f1 (ppm)

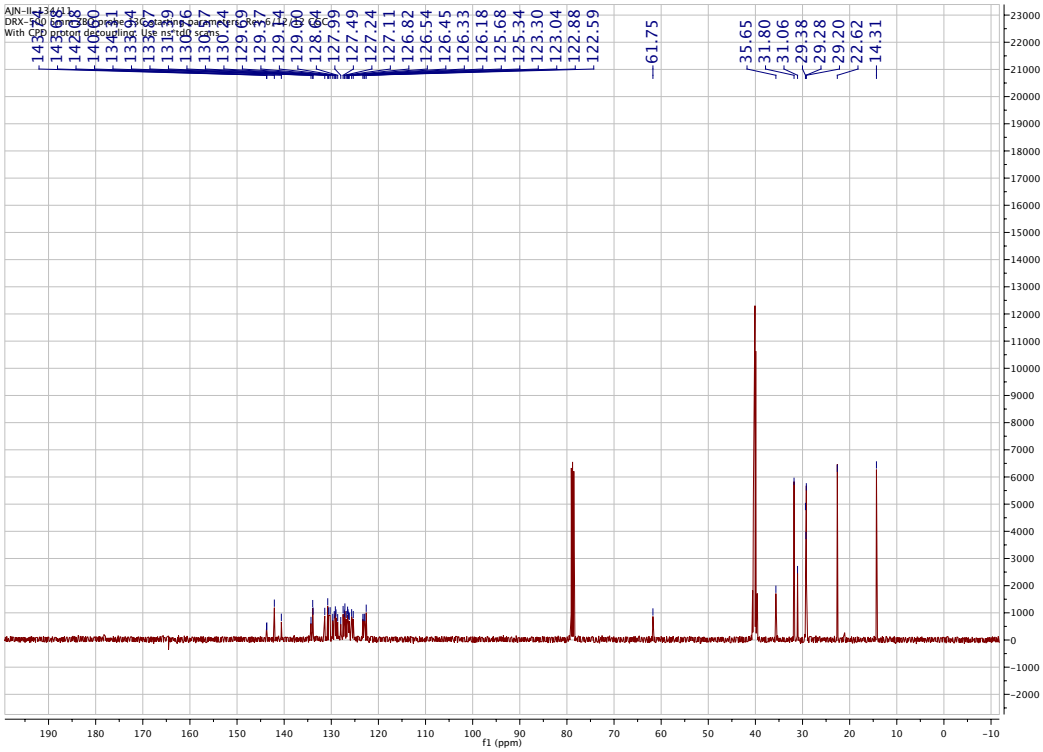

AJN-III-122-13C
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
142.71
141.69
140.12
139.30
139.15
131.12
130.26
129.08
128.64
128.54
128.44
128.24
127.56
127.46
127.41
126.32
125.28
123.49
123.48
122.76
122.75
66.92
35.35
31.67
30.93
29.24
29.13
29.06
22.49
14.35
f1 (ppm)

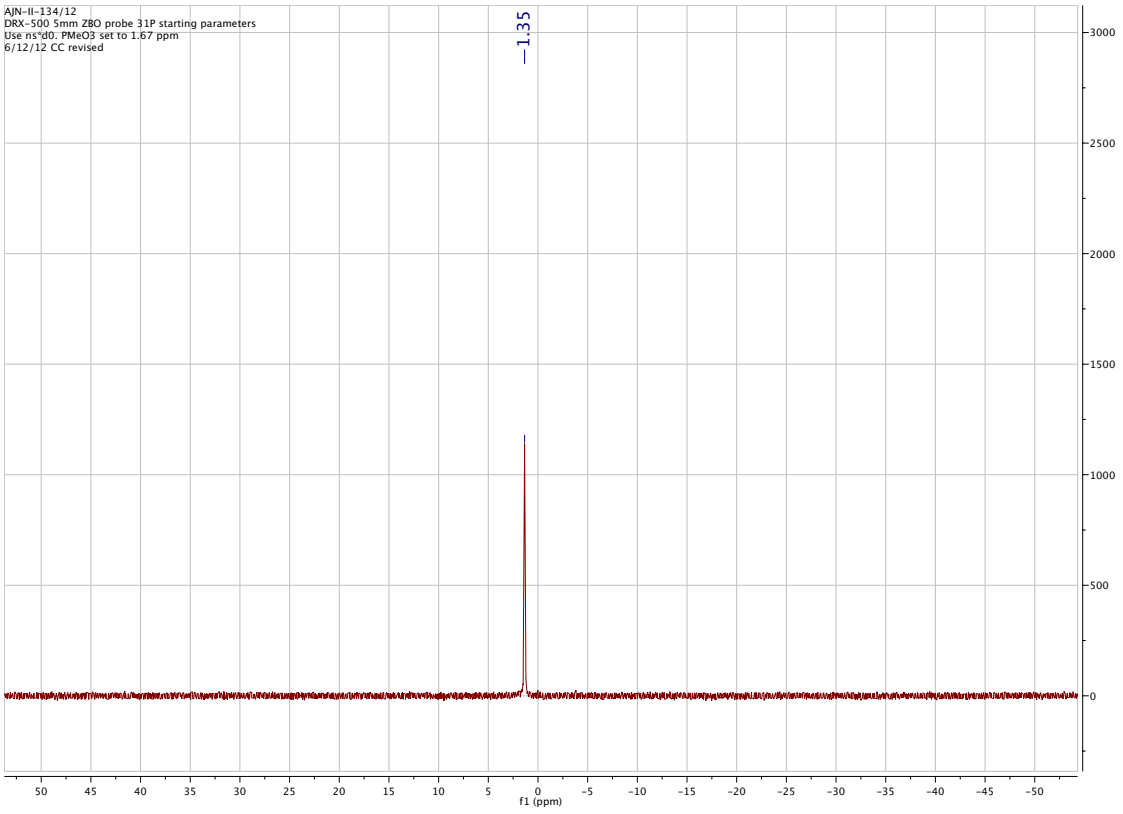

AJN-II-122/12
DRX-500 5mm ZBO probe 31P starting parameters
Use ns*d0. PMeO3 set to 1.67 ppm
6/12/12 CC revised
2.37
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
f1 (ppm)

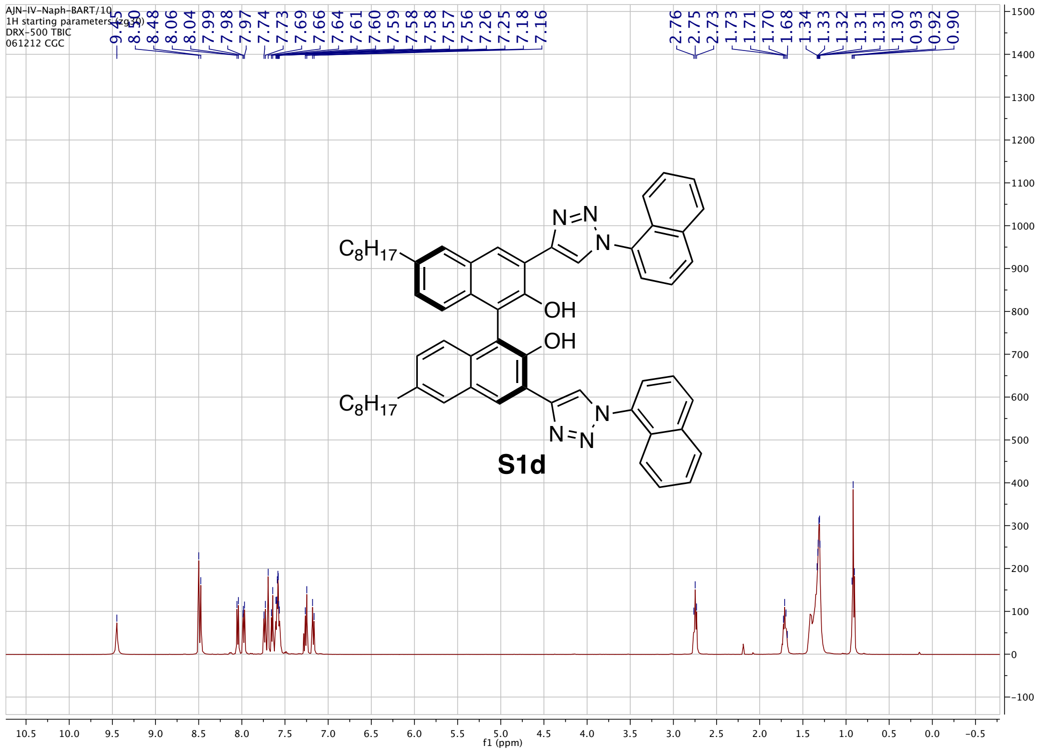

AJN-IV-38E/1
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
9.64
8.71
8.21
8.01
8.00
7.98
7.97
7.96
7.93
7.92
7.90
7.58
7.57
7.56
7.52
7.51
7.49
7.46
7.44
7.43
7.17
7.15
7.10
7.09
7.05
7.04
7.02
7.00
2.70
2.69
1.68
1.67
1.65
1.37
1.35
1.34
1.31
0.95
0.94
0.92
C8H17
OH
OH
C8H17
N=N
N
N
N=N
S1c
f1 (ppm)

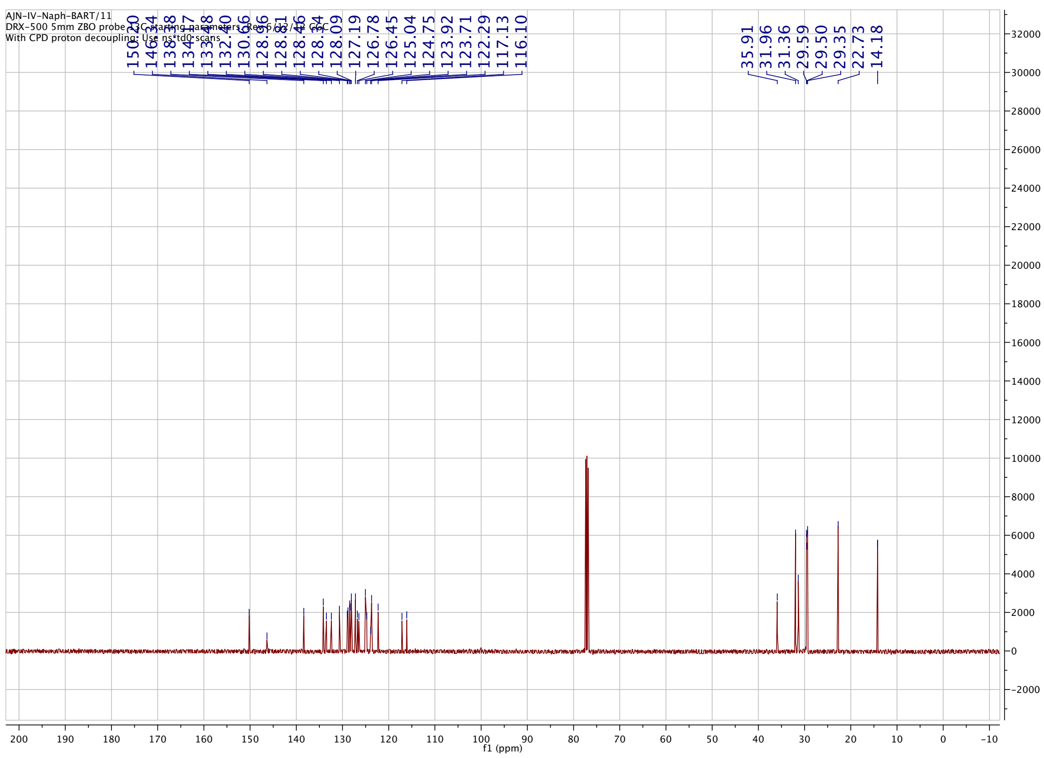

AJN-IV-38E/2
DRX-500 5mm ZBO probe 13C starting parameters
With CPD proton decoupling. Use ns*td0 scans
150.21
146.61
134.66
134.04
133.31
133.28
132.39
130.72
130.67
129.99
129.95
129.19
129.17
127.55
127.52
126.49
126.46
126.44
125.44
122.82
116.51
62.73
35.84
31.97
31.24
29.58
29.38
29.33
22.75
14.21
f1 (ppm)

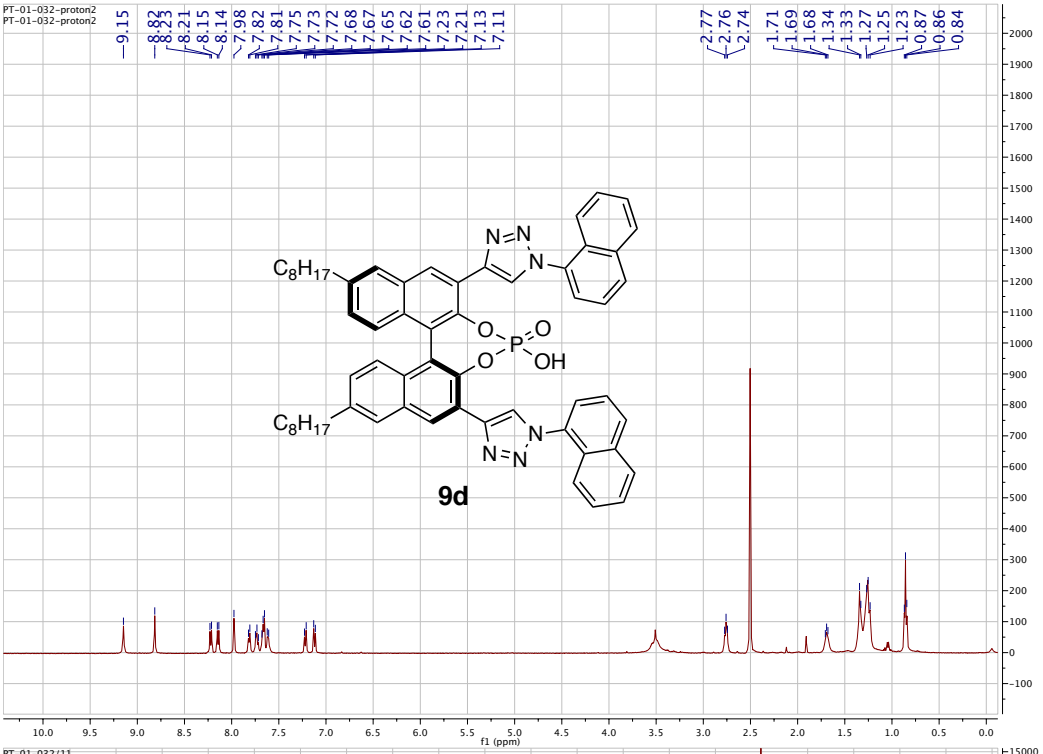

AJN-II-134/10
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
8.77
8.76
8.49
8.03
8.02
7.93
7.91
7.90
7.87
7.85
7.76
7.47
7.42
7.40
7.39
7.36
7.35
7.33
7.08
7.04
7.02
7.00
2.71
2.69
2.68
1.65
1.64
1.62
1.29
1.26
1.24
1.23
1.22
0.85
0.84
0.82
C8H17
C8H17
O
O
P
O
OH
N
N
N
N
9c
f1 (ppm)

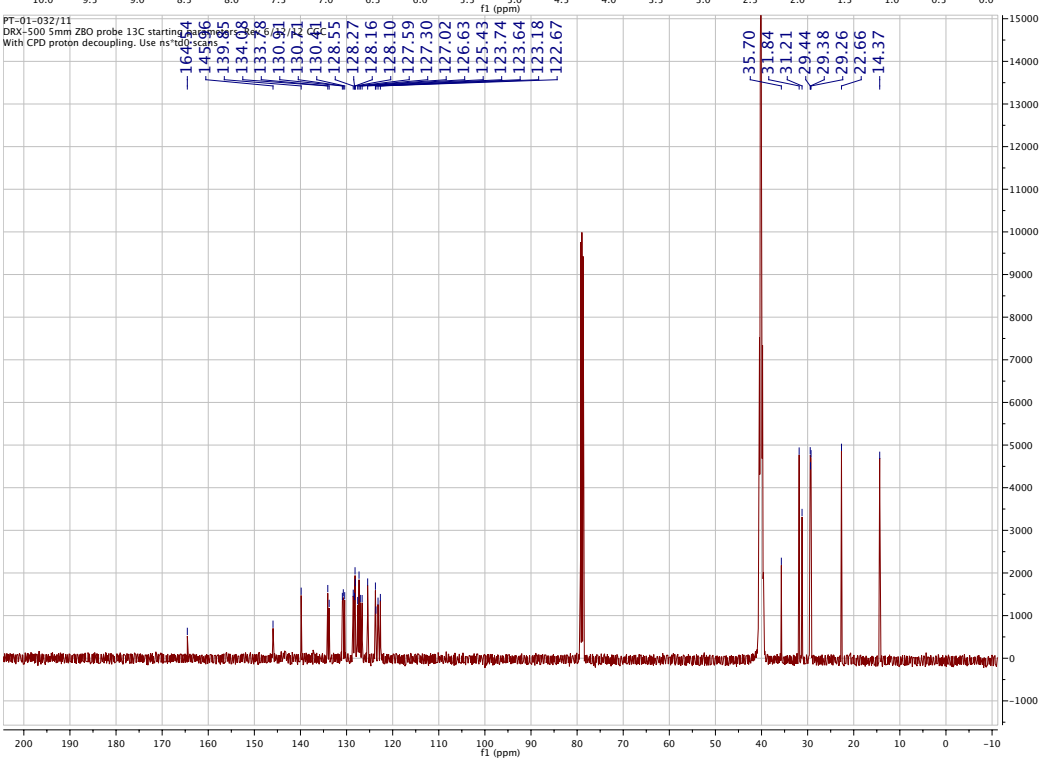

61.75
35.65
31.80
31.06
29.38
29.28
29.20
22.62
14.31
f1 (ppm)

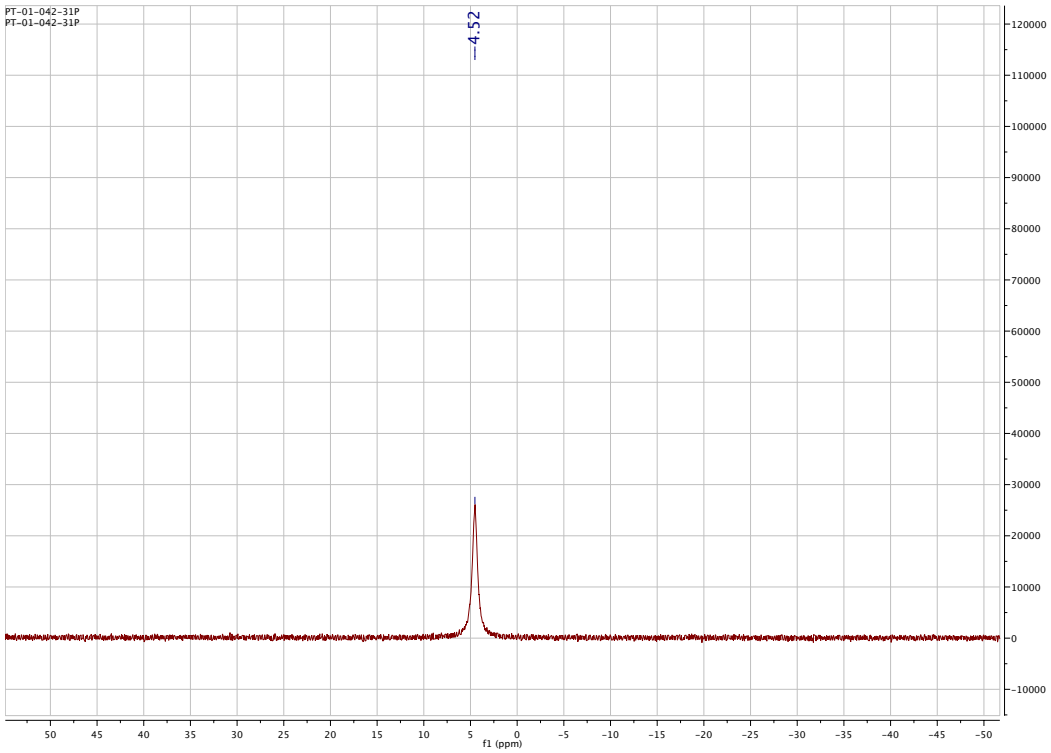

AJN-II-134/12
DRX-500 5mm ZBO probe 31P starting parameters
Use ns*d0. PMeO3 set to 1.67 ppm
6/12/12 CC revised
1.35
3000
2500
2000
1500
1000
500
0
50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
f1 (ppm)

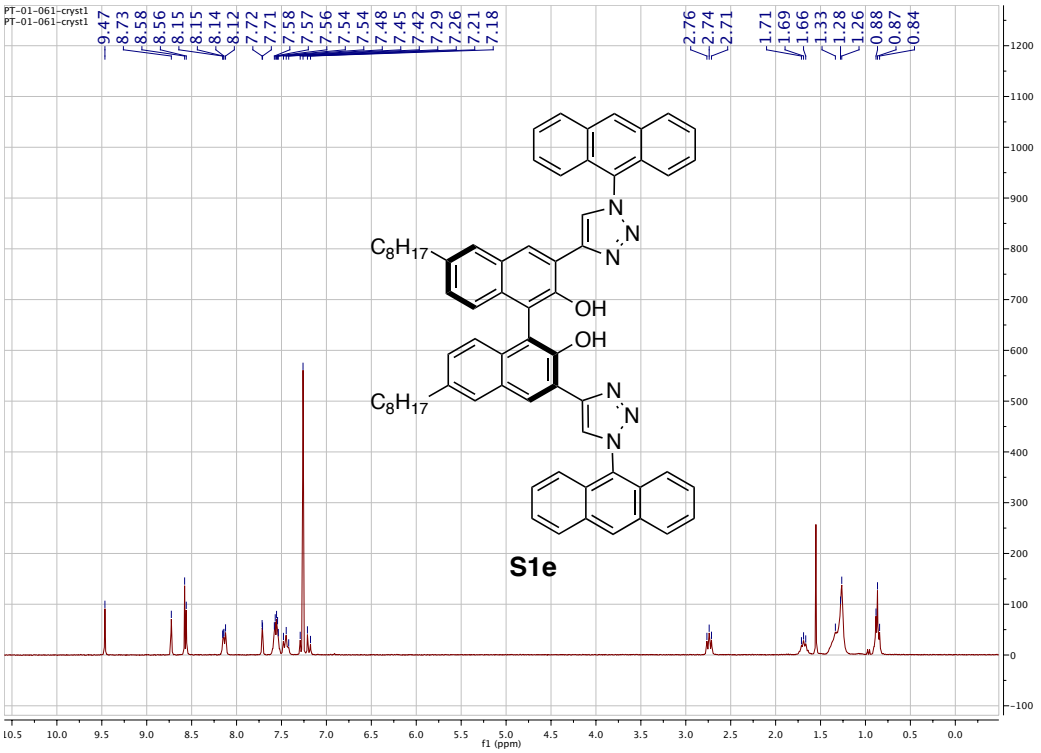

AJN-IV-Naph-BART/10
1H starting parameters
DRX-500 TBIC
061212 CGC
9.45
8.48
8.06
8.04
7.99
7.98
7.97
7.74
7.73
7.69
7.66
7.64
7.61
7.60
7.59
7.58
7.58
7.57
7.56
7.26
7.25
7.18
7.16
2.76
2.75
2.73
1.73
1.71
1.70
1.68
1.34
1.33
1.32
1.31
1.31
1.30
0.93
0.92
0.90
C_8H_{17}
N
OH
S1d
f1 (ppm)

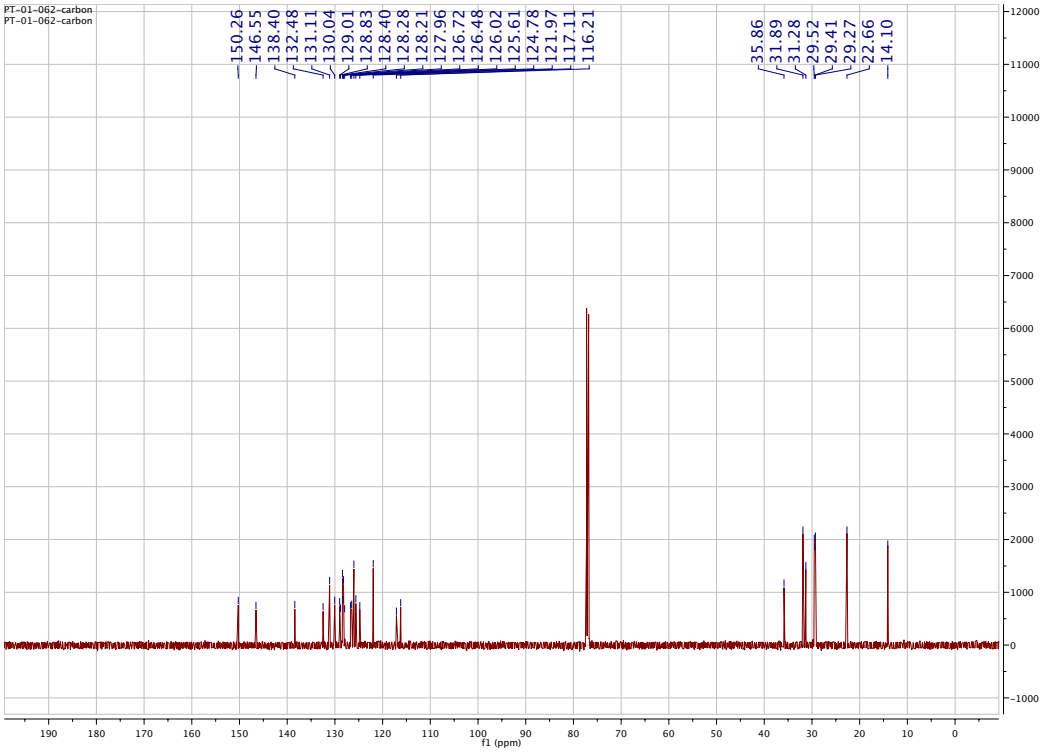

AJN-IV-Naph-BART/11
DRX-500 5mm ZBO probe 13C starting parameters
With CPD proton decoupling
127.19
126.78
126.45
125.04
124.75
123.92
123.71
122.29
117.13
116.10
35.91
31.96
31.36
29.59
29.50
29.35
22.73
14.18
f1 (ppm)

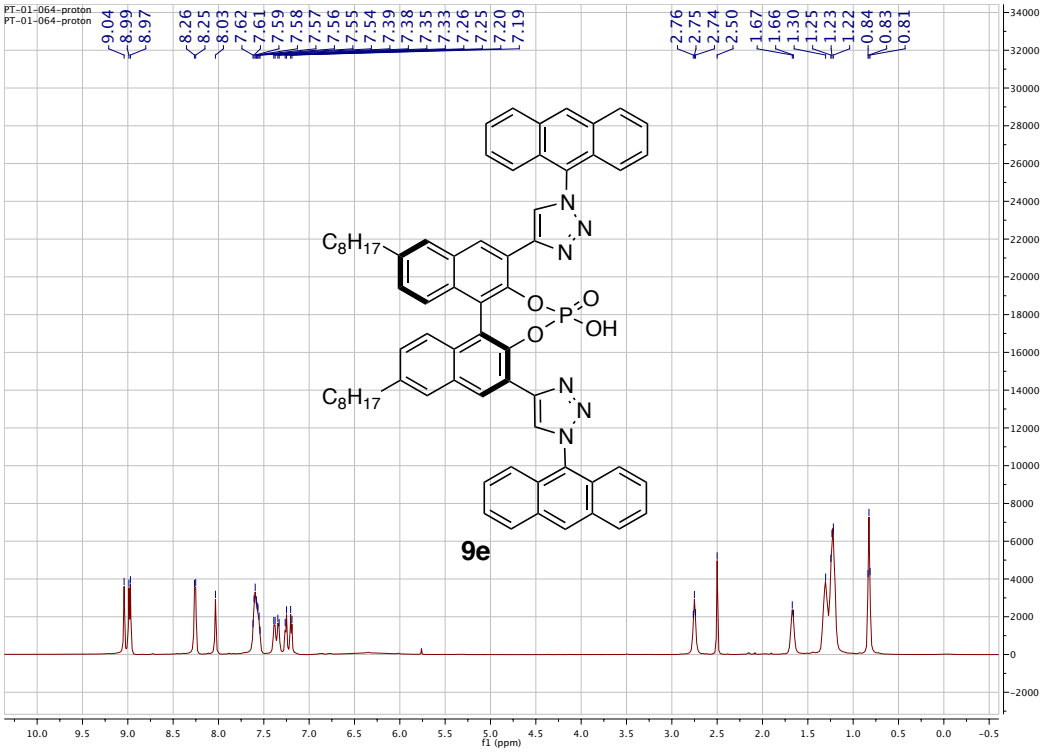

PT-01-032-proton2
PT-01-032-proton2
9.15
8.82
8.23
8.21
8.15
8.14
7.98
7.82
7.81
7.75
7.73
7.72
7.68
7.67
7.65
7.62
7.61
7.23
7.21
7.13
7.11
2.77
2.76
2.74
1.71
1.69
1.68
1.34
1.33
1.27
1.25
1.23
0.87
0.86
0.84
C8H17
N=N
N
O
P
O
OH
C8H17
N
N=N
9d
f1 (ppm)

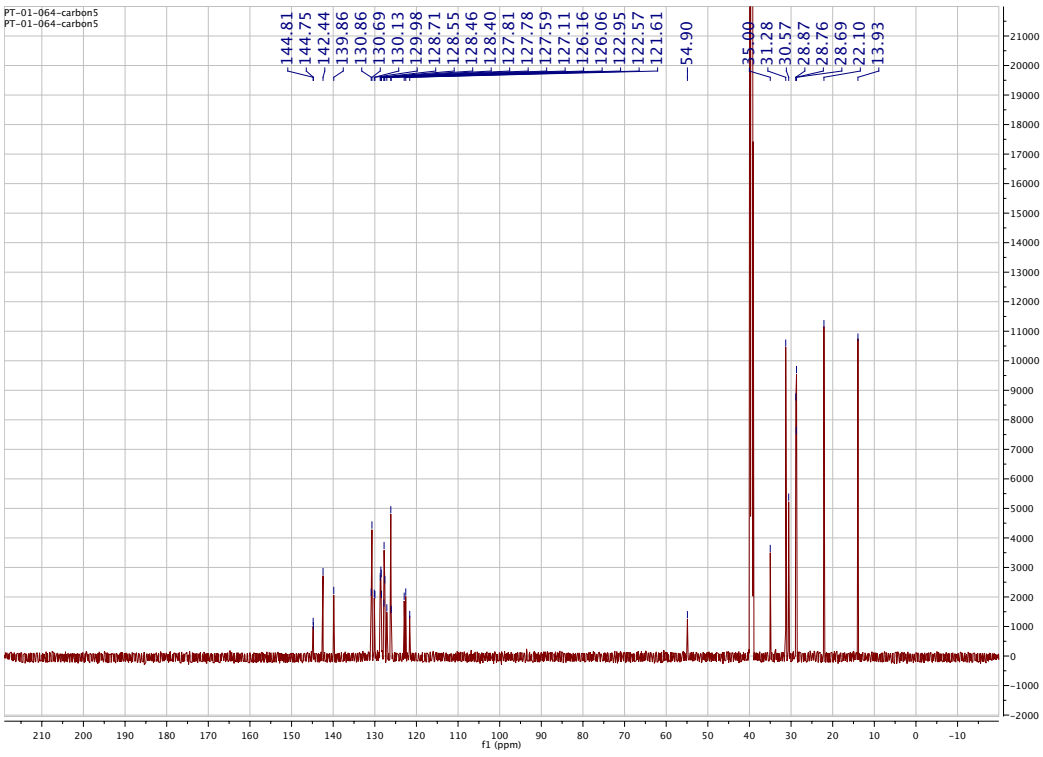

PT-01-032/11
DRX-500 5mm ZBO probe 13C starting sample
With CPD proton decoupling. Use ns*ds>scans
164.44
145.96
139.05
134.08
133.68
130.91
130.71
130.41
128.55
128.27
128.16
128.10
127.59
127.30
127.02
126.63
125.43
123.74
123.64
123.18
122.67
35.70
31.84
31.21
29.44
29.38
29.26
22.66
14.37
f1 (ppm)

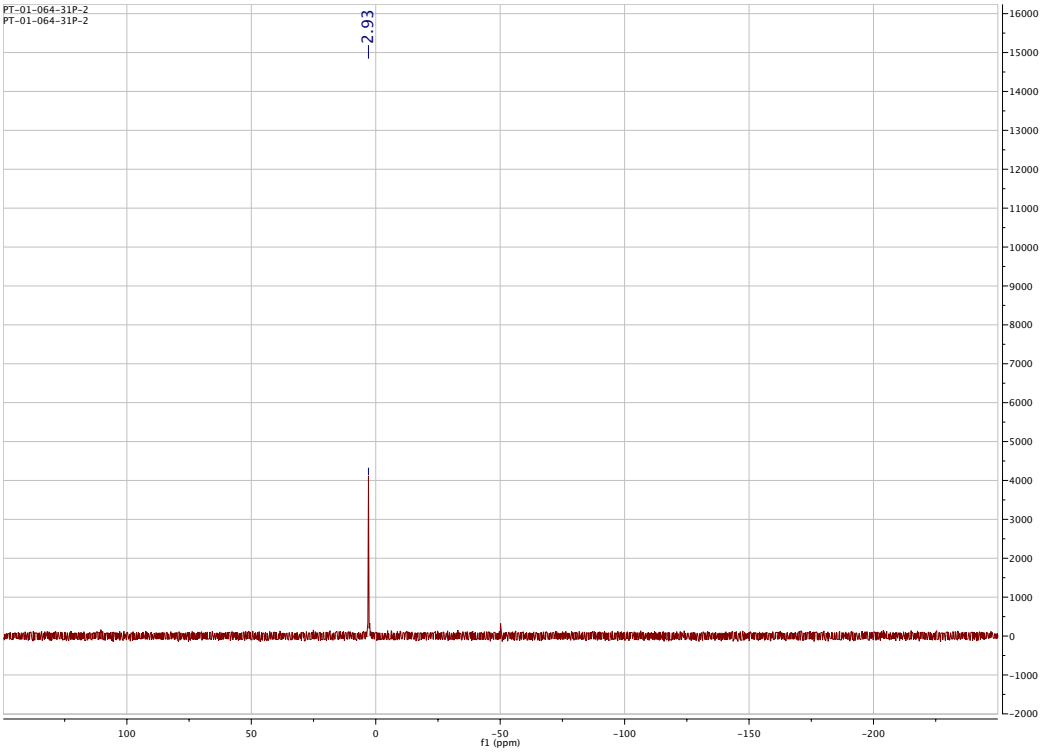

PT-01-042-31P
PT-01-042-31P
4.52
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
f1 (ppm)

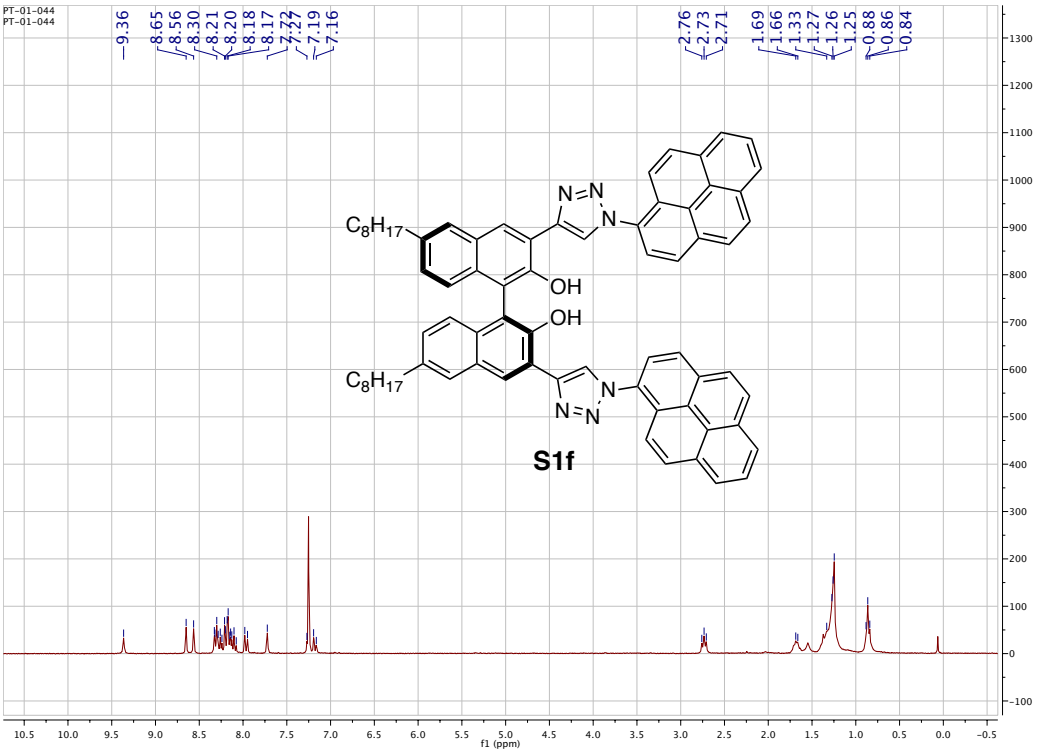

PT-01-061-cryst1
PT-01-061-cryst1
9.47
8.73
8.58
8.56
8.15
8.15
8.14
8.12
7.72
7.71
7.58
7.57
7.56
7.54
7.54
7.48
7.45
7.42
7.29
7.26
7.21
7.18
2.76
2.74
2.71
1.71
1.69
1.66
1.33
1.28
1.26
0.88
0.87
0.84
C8H17
OH
OH
C8H17
N
N
N
N
N
N
S1e
f1 (ppm)

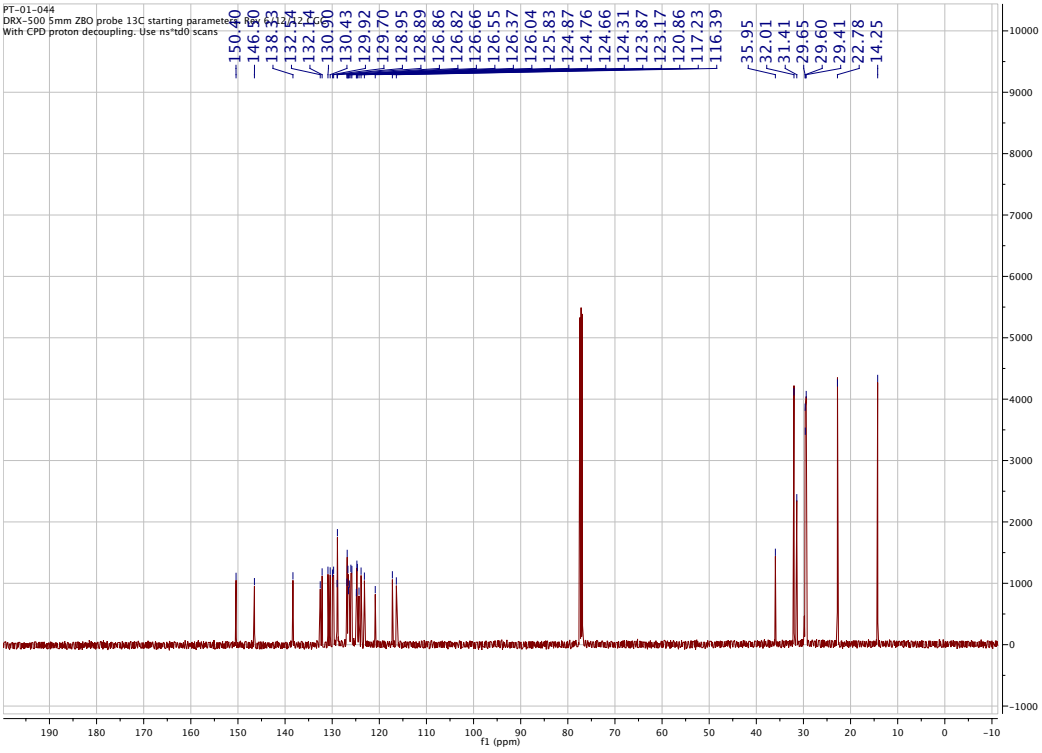

PT-01-062-carbon
PT-01-062-carbon
150.26
146.55
138.40
132.48
131.11
130.04
129.01
128.83
128.40
128.28
128.21
127.96
126.72
126.48
126.02
125.61
124.78
121.97
117.11
116.21
35.86
31.89
31.28
29.52
29.41
29.27
22.66
14.10
f1 (ppm)

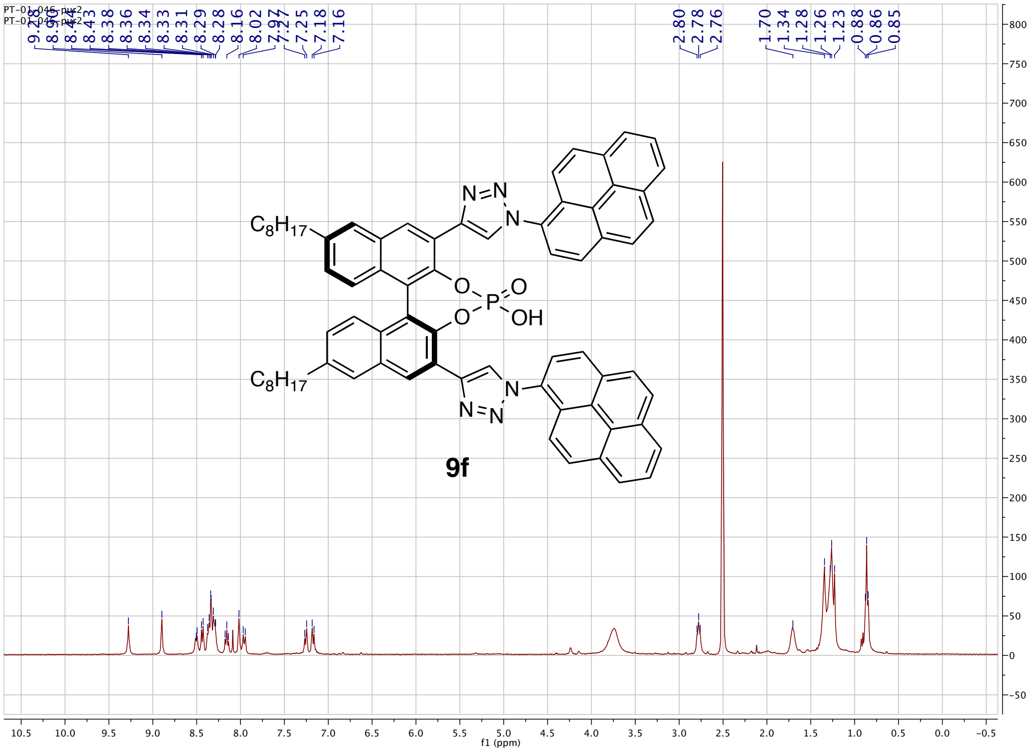

PT-01-064-proton
PT-01-064-proton
9.04
8.99
8.97
8.26
8.25
8.03
7.62
7.61
7.59
7.58
7.57
7.56
7.55
7.54
7.39
7.38
7.35
7.33
7.26
7.25
7.20
7.19
2.76
2.75
2.74
2.50
1.67
1.66
1.30
1.25
1.23
1.22
0.84
0.83
0.81
C8H17
C8H17
O
P
O
OH
N
N
N
N
N
N
9e
f1 (ppm)

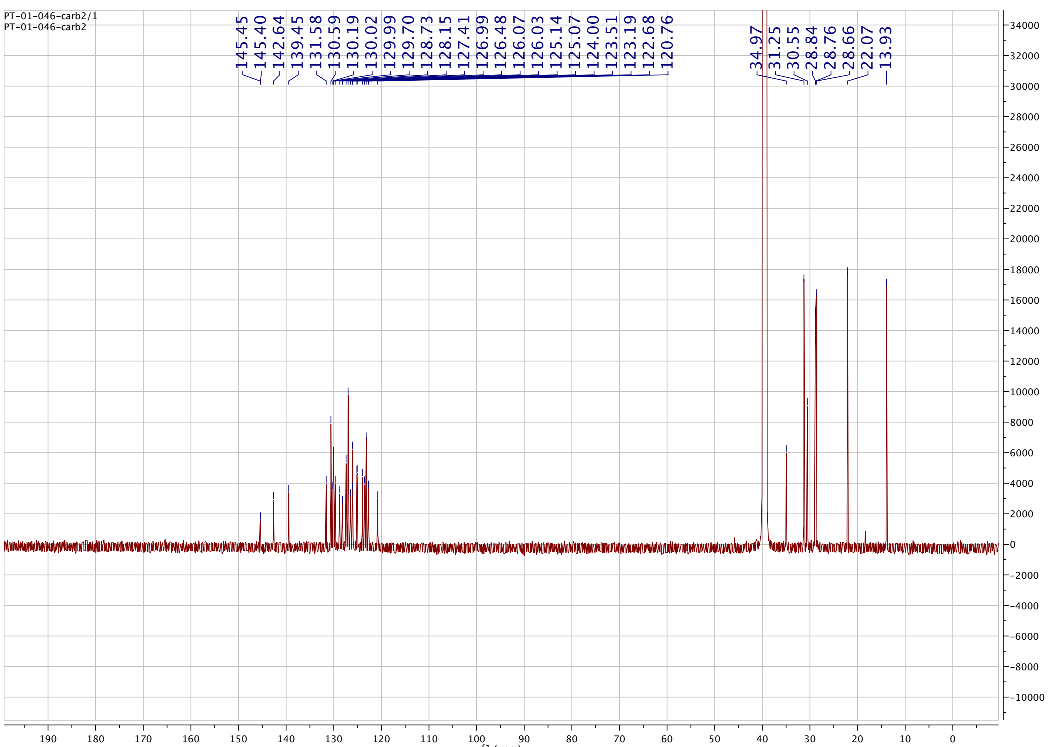

PT-01-064-carbon5
PT-01-064-carbon5
144.81
144.75
142.44
139.86
130.86
130.69
130.13
129.98
128.71
128.55
128.46
128.40
127.81
127.78
127.59
127.11
126.16
126.06
122.95
122.57
121.61
54.90
35.00
31.28
30.57
28.87
28.76
28.69
22.10
13.93
f1 (ppm)

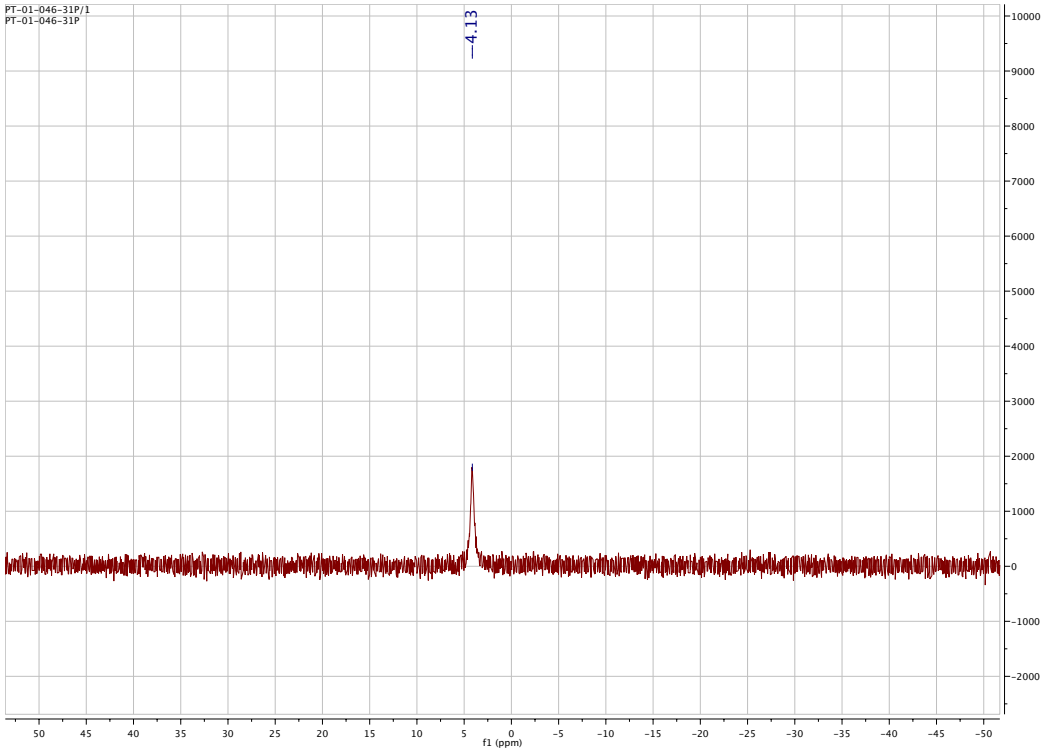

PT-01-064-31P-2
PT-01-064-31P-2
2.93
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
100
50
0
-50
-100
-150
-200
f1 (ppm)

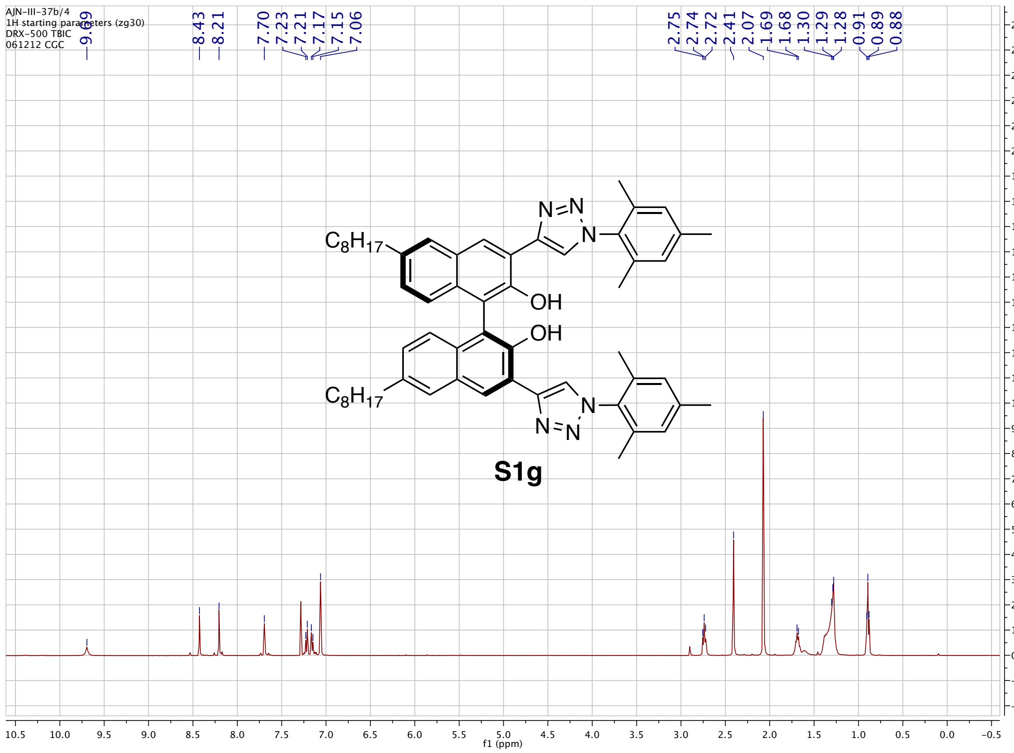

PT-01-044
PT-01-044
9.36
8.65
8.56
8.30
8.21
8.20
8.18
8.17
7.22
7.19
7.16
2.76
2.73
2.71
1.69
1.66
1.33
1.27
1.26
1.25
0.88
0.86
0.84
C8H17
OH
OH
C8H17
S1f
f1 (ppm)

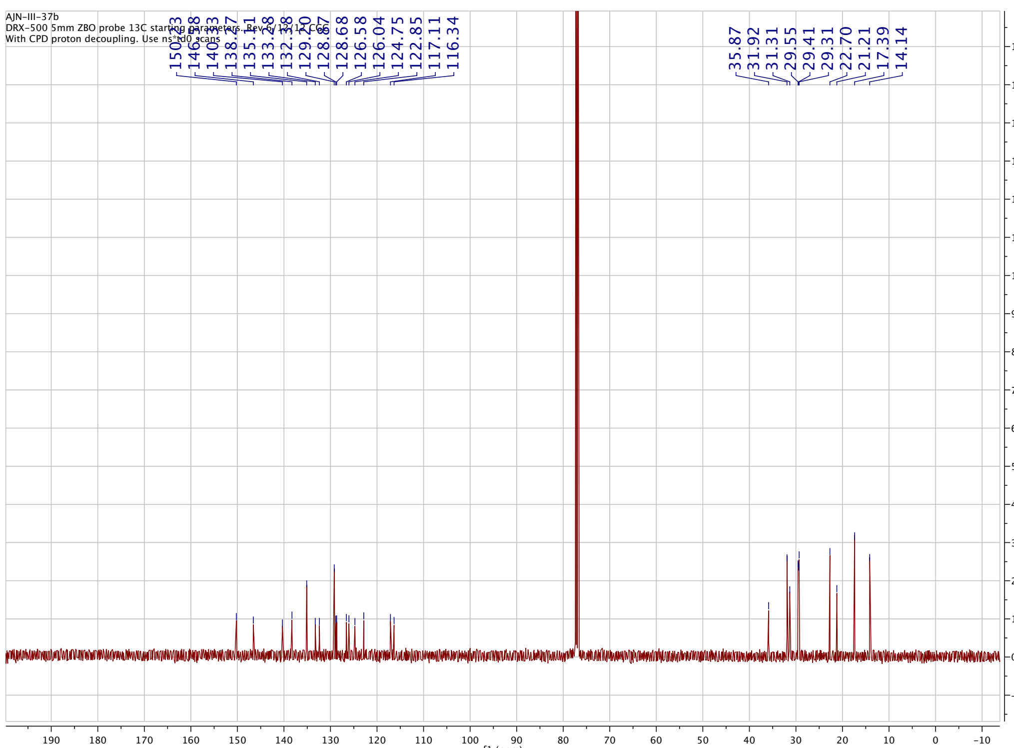

PT-01-044
DRX-500 5mm ZBO probe 13C starting parameter
With CPD proton decoupling. Use ns*td0 scans
150.40
146.20
138.23
132.44
132.14
130.90
130.43
129.92
129.70
128.95
128.89
126.86
126.82
126.66
126.55
126.37
126.04
125.83
124.87
124.76
124.66
124.31
123.87
123.17
120.86
117.23
116.39
35.95
32.01
31.41
29.65
29.60
29.41
22.78
14.25
f1 (ppm)

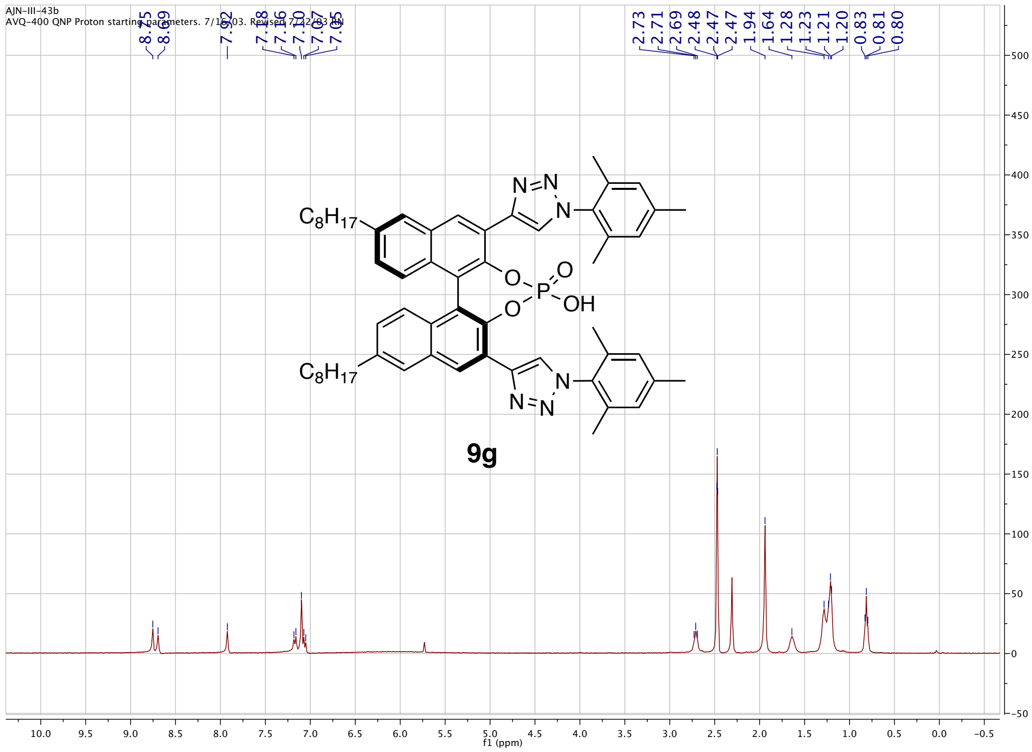

PT-01-046-pur2
8.44
8.43
8.38
8.36
8.34
8.33
8.31
8.29
8.28
8.16
8.02
7.97
7.27
7.25
7.18
7.16
2.80
2.78
2.76
1.70
1.34
1.28
1.26
1.23
0.88
0.86
0.85
C8H17
N=N
N
O
P
O
OH
9f
f1 (ppm)

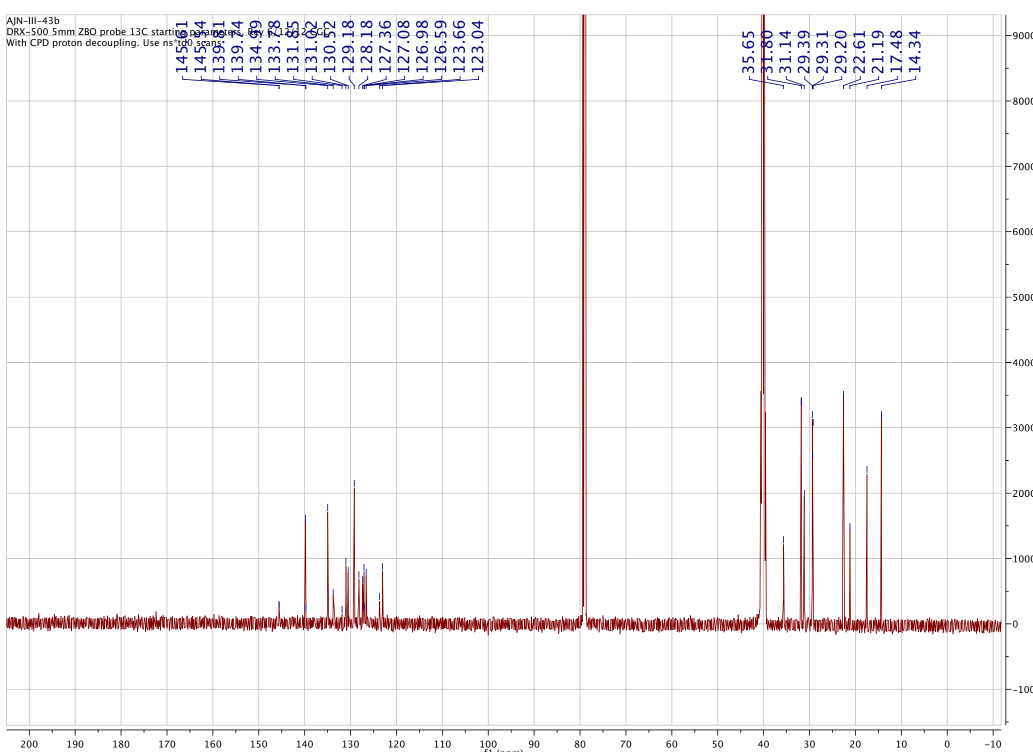

PT-01-046-carb2/1
PT-01-046-carb2
145.45
145.40
142.64
139.45
131.58
130.59
130.19
130.02
129.99
129.70
128.73
128.15
127.41
126.99
126.48
126.07
126.03
125.14
125.07
124.00
123.51
123.19
122.68
120.76
34.97
31.25
30.55
28.84
28.76
28.66
22.07
13.93
f1 (ppm)

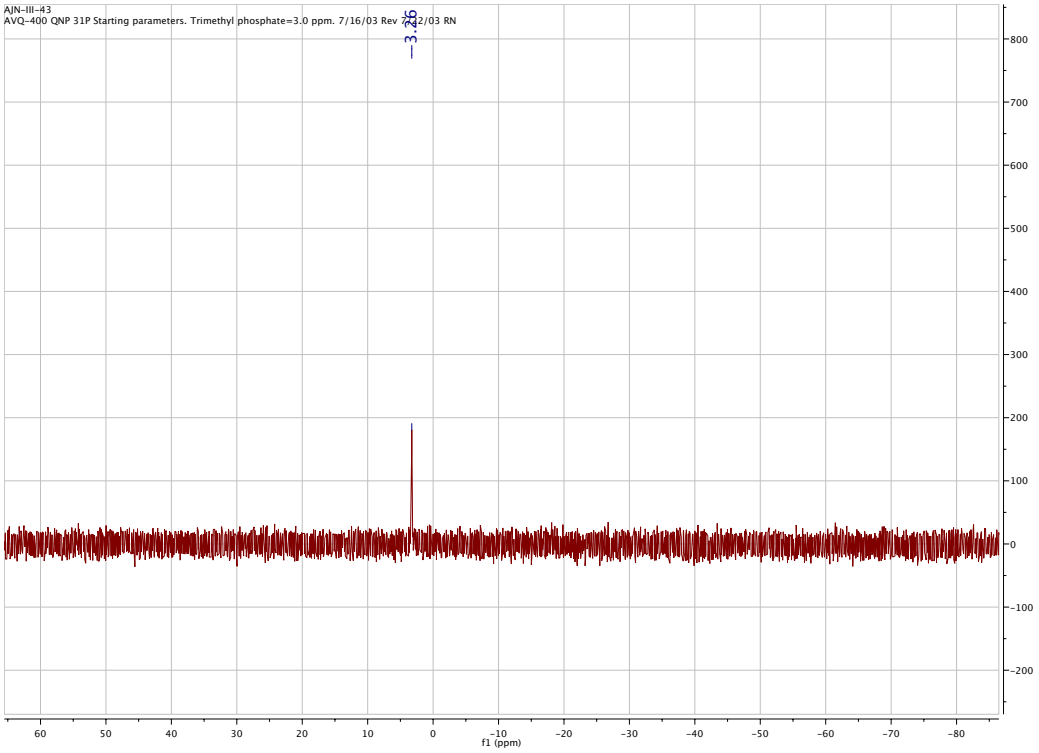

PT-01-046-31P/1
PT-01-046-31P
4.13
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

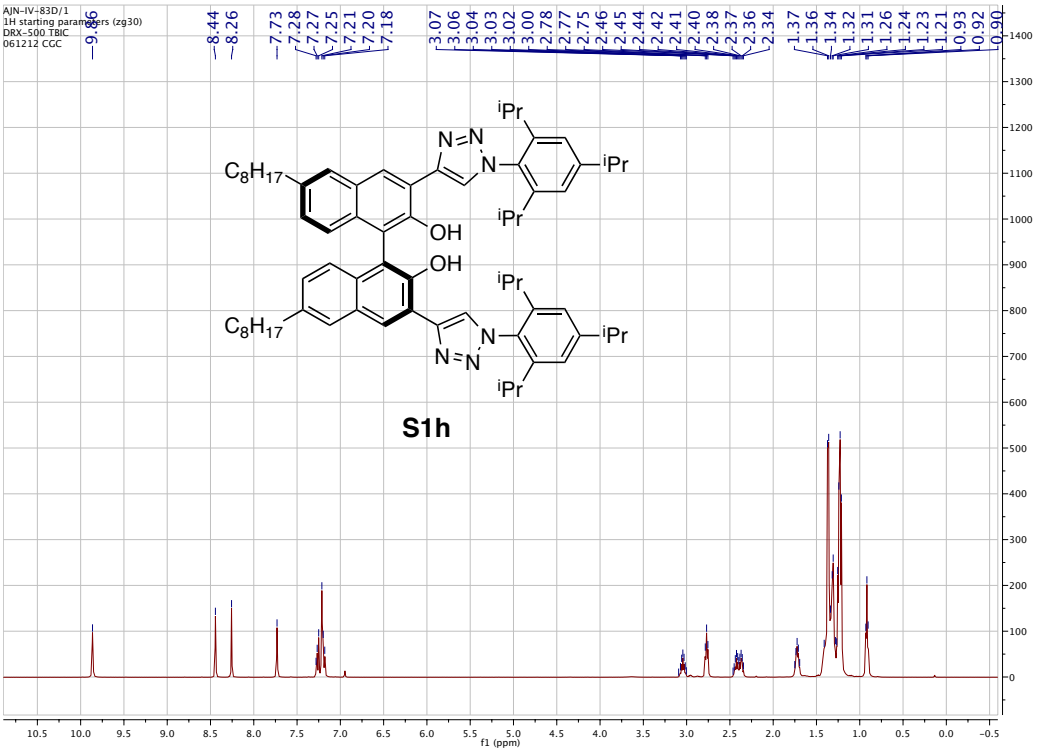

AJN-III-37b/4
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
9.69
8.43
8.21
7.70
7.23
7.21
7.17
7.15
7.06
2.75
2.74
2.72
2.41
2.07
1.69
1.68
1.30
1.29
1.28
0.91
0.89
0.88
S1g
f1 (ppm)

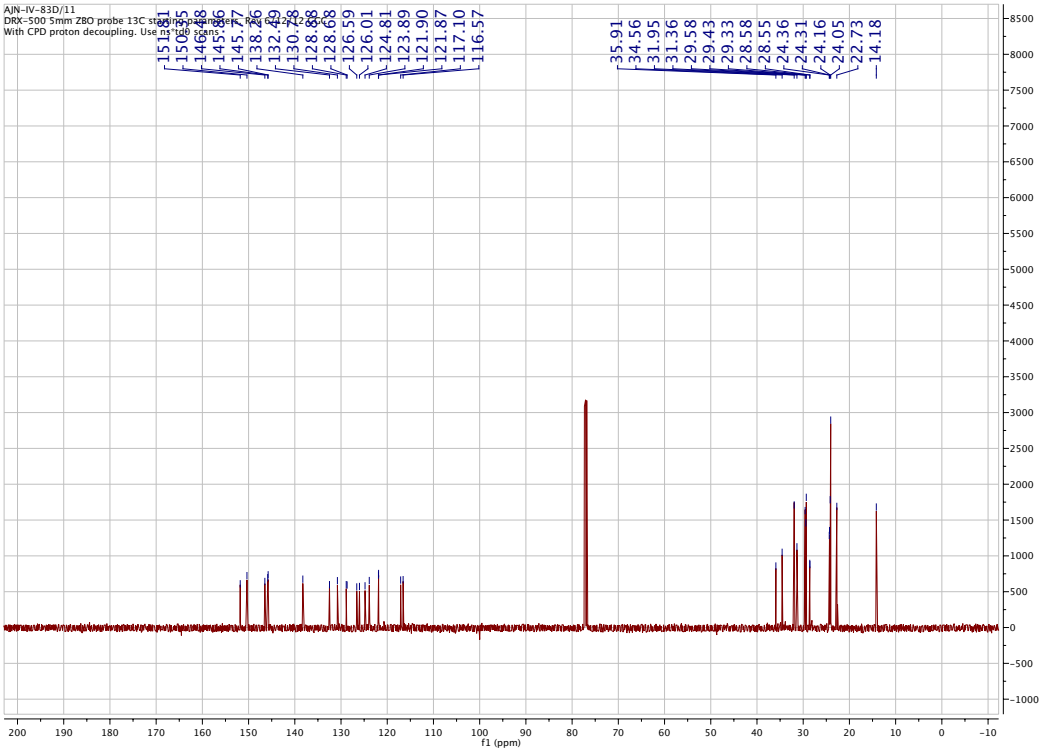

AJN-III-37b
DRX-500 5mm ZBO probe 13C starting parameters
With CPD proton decoupling. Use ns
150.13
146.58
140.03
138.17
135.11
133.18
132.38
129.20
128.87
128.68
126.58
126.04
124.75
122.85
117.11
116.34
35.87
31.92
31.31
29.55
29.41
29.31
22.70
21.21
17.39
14.14
f1 (ppm)

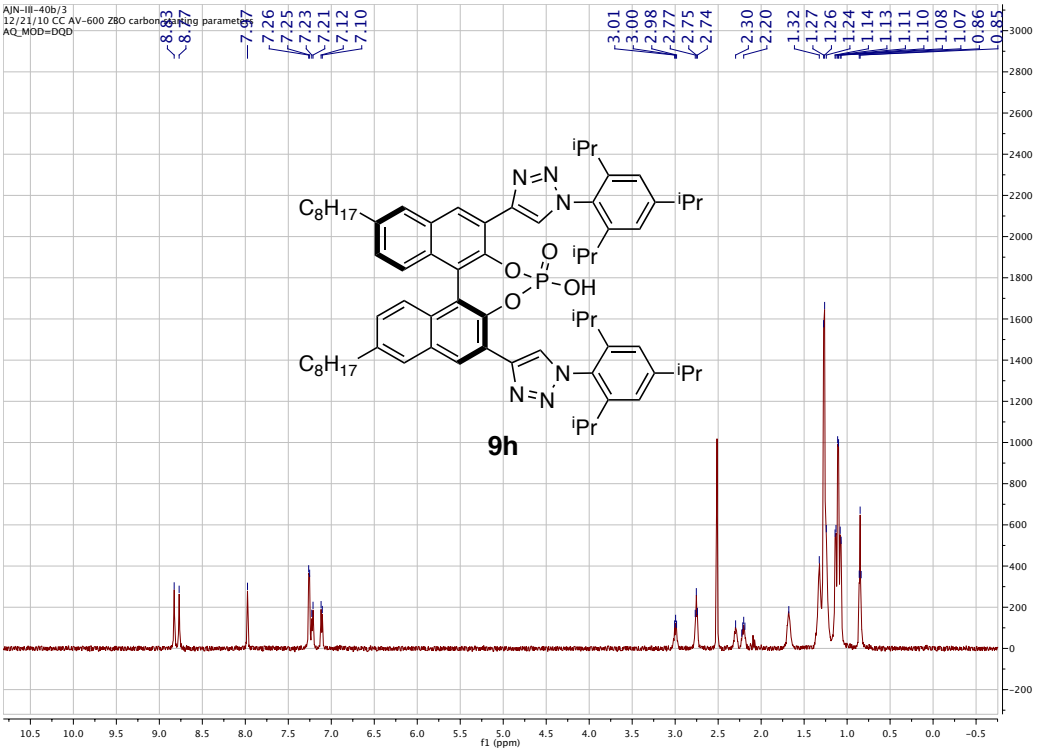

AJN-III-43b
AVQ-400 QNP Proton starting parameters.
8.75
8.69
7.92
7.18
7.16
7.10
7.07
7.05
2.73
2.71
2.69
2.48
2.47
2.47
1.94
1.64
1.28
1.23
1.21
1.20
0.83
0.81
0.80
C_8H_{17}
N
N
N
O
P
O
O
OH
9g
f1 (ppm)

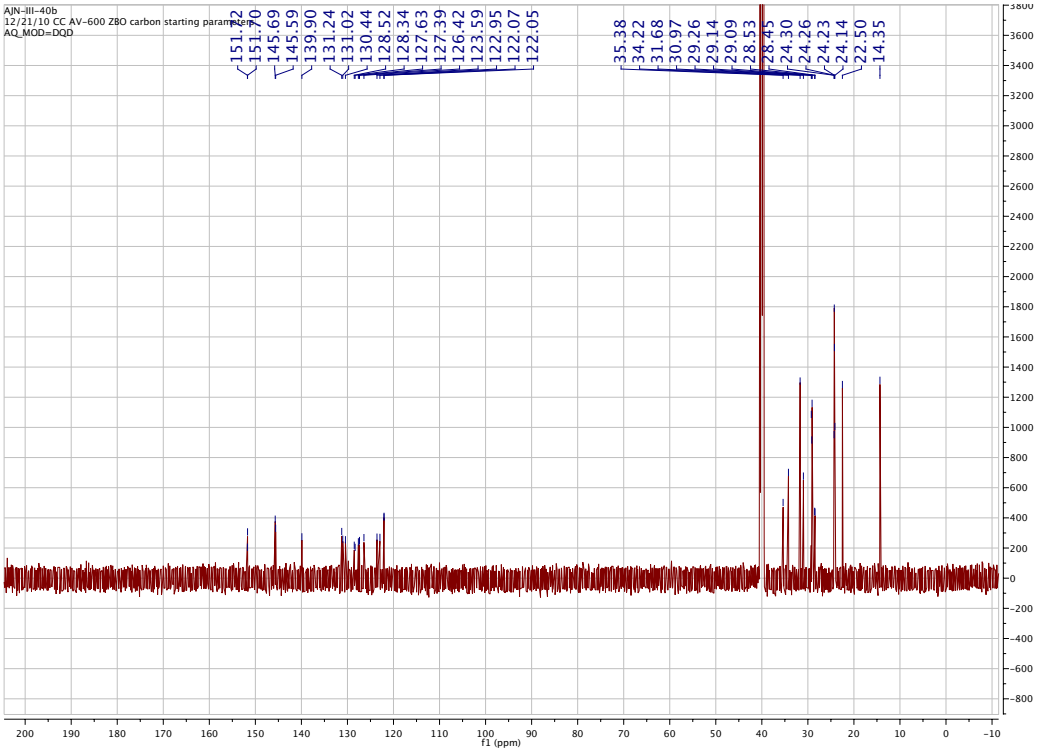

AJN-III-43b
DRX-500 5mm ZBO probe 13C starting parameters.
With CPD proton decoupling.
130.52
129.18
128.18
127.36
127.08
126.98
126.59
123.66
123.04
35.65
31.80
31.14
29.39
29.31
29.20
22.61
21.19
17.48
14.34
f1 (ppm)

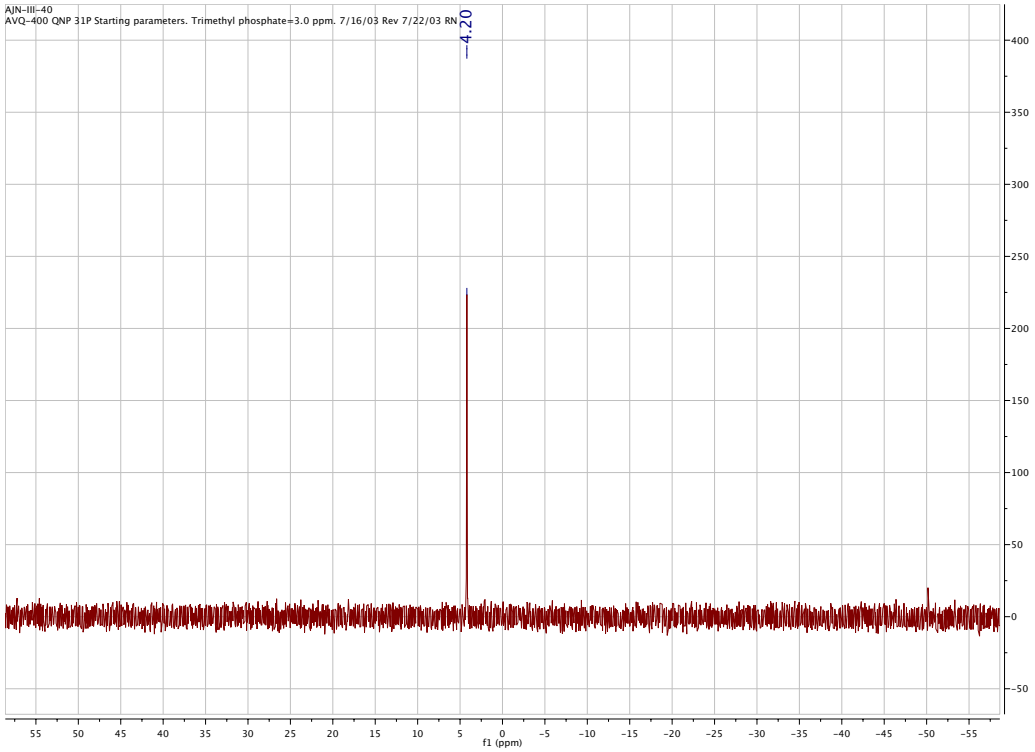

AJN-III-43
AVQ-400 QNP 31P Starting parameters. Trimethyl phosphate=3.0 ppm. 7/16/03 Rev 7/22/03 RN
3.25
800
700
600
500
400
300
200
100
0
-100
-200
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
f1 (ppm)

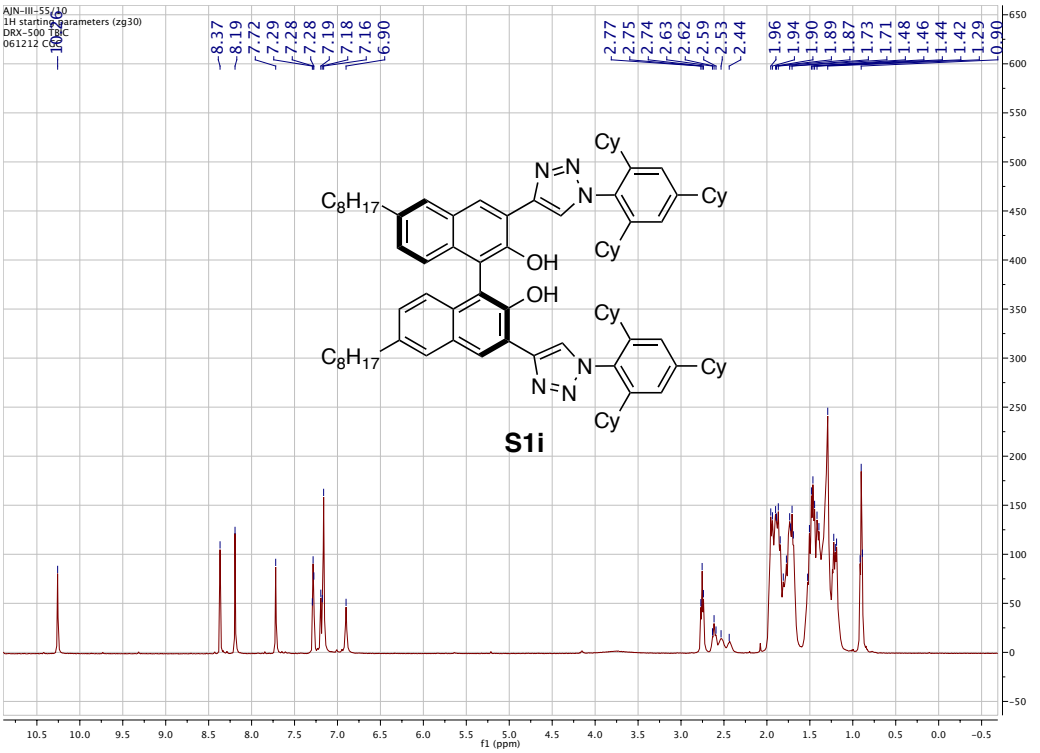

AJN-IV-83D/1
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
9.66
8.44
8.26
7.73
7.28
7.27
7.25
7.21
7.20
7.18
3.07
3.06
3.04
3.03
3.02
3.00
2.78
2.77
2.75
2.46
2.45
2.44
2.42
2.41
2.40
2.38
2.37
2.36
2.34
1.37
1.36
1.34
1.32
1.31
1.26
1.24
1.23
1.21
0.93
0.92
0.90
iPr
N=N
N
C8H17
OH
S1h
f1 (ppm)

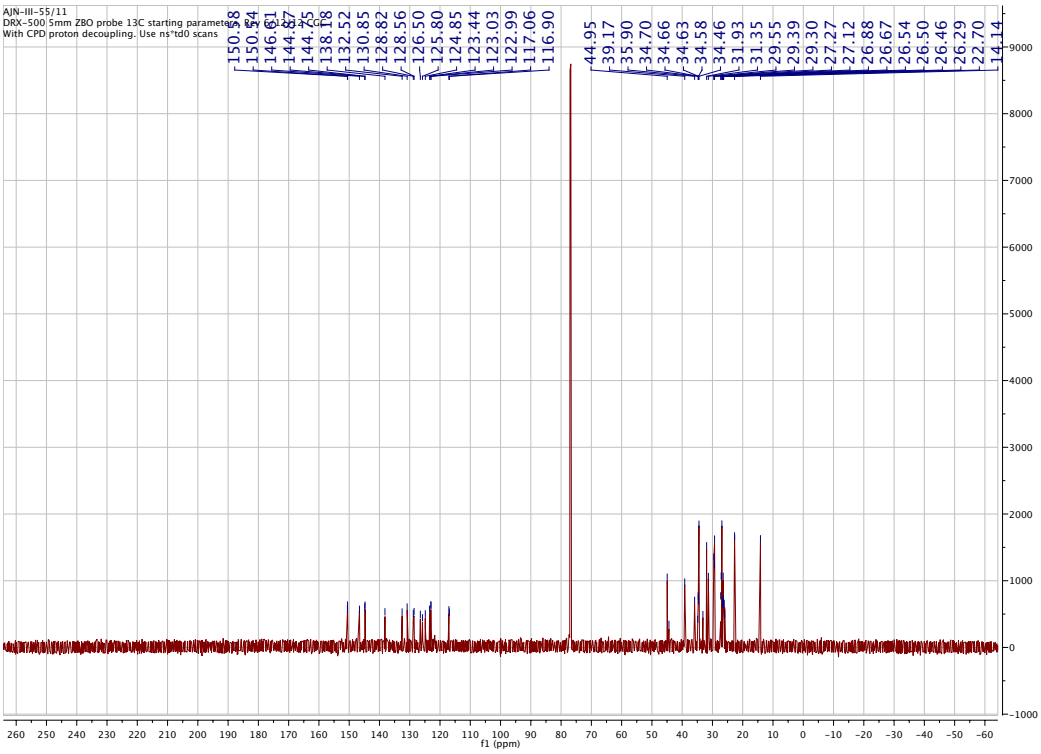

AJN-IV-83D/11
DRX-500 5mm Z8O probe 13C starting parameters
With CPD proton decoupling. Use ns*rd0 scans:
151.11
150.55
146.88
145.66
145.77
138.26
132.49
130.78
128.88
128.68
126.59
126.01
124.81
123.89
121.90
121.87
117.10
116.57
35.91
34.56
31.95
31.36
29.58
29.43
29.33
28.58
28.55
24.36
24.31
24.16
24.05
22.73
14.18
f1 (ppm)

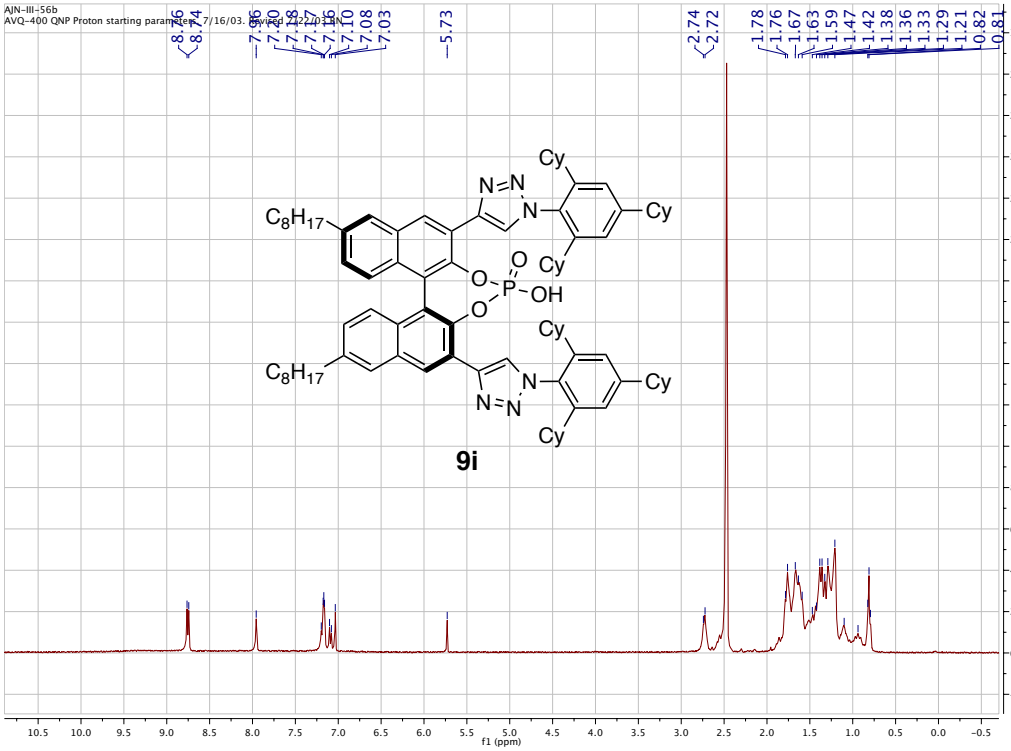

AJN-III-40b/3
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
8.83
8.17
7.97
7.26
7.25
7.23
7.21
7.12
7.10
3.01
3.00
2.98
2.77
2.75
2.74
2.30
2.20
1.32
1.27
1.26
1.24
1.14
1.13
1.11
1.10
1.08
1.07
0.86
0.85
iPr
N=N
N
iPr
iPr
C8H17
O
O
P
OH
O
iPr
C8H17
N
iPr
N=N
iPr
9h
f1 (ppm)

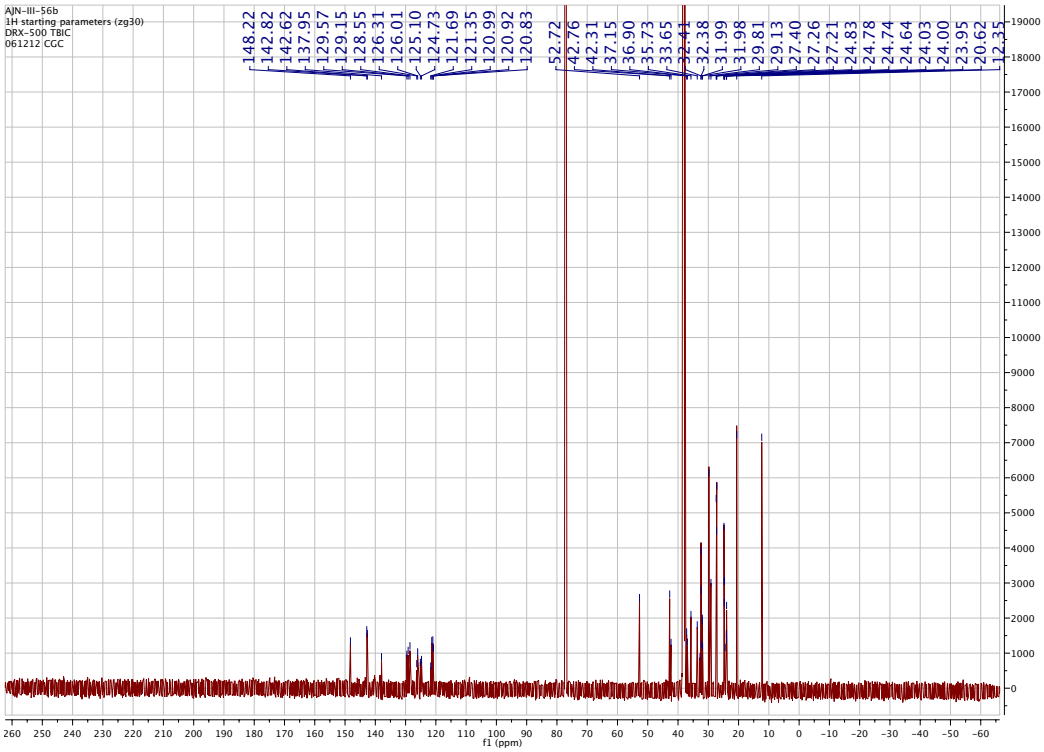

AJN-III-40b
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
151.82
151.70
145.69
145.59
139.90
131.24
131.02
130.44
128.52
128.34
127.63
127.39
126.42
123.59
122.95
122.07
122.05
35.38
34.22
31.68
30.97
29.26
29.14
29.09
28.53
28.45
24.30
24.26
24.23
24.14
22.50
14.35
f1 (ppm)

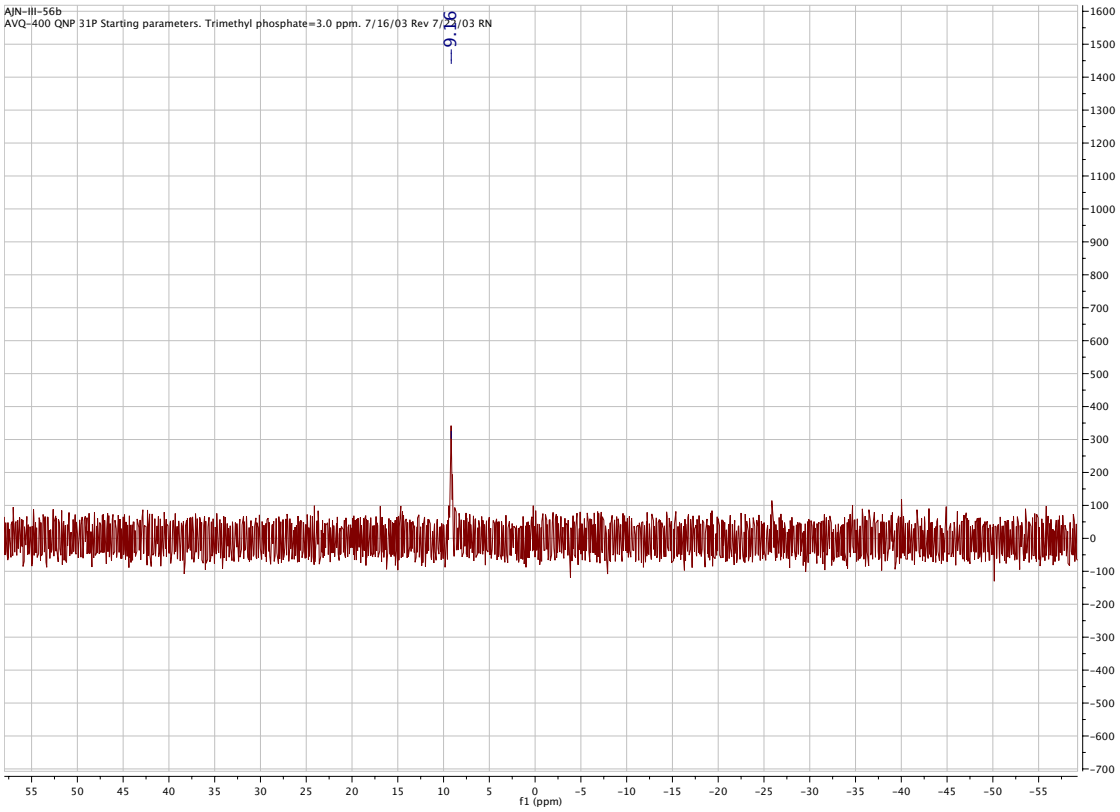

AJN-III-40
AVQ-400 QNP 31P Starting parameters. Trimethyl phosphate=3.0 ppm. 7/16/03 Rev 7/22/03 RN
4.20
400
350
300
250
200
150
100
50
0
-50
55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55
f1 (ppm)

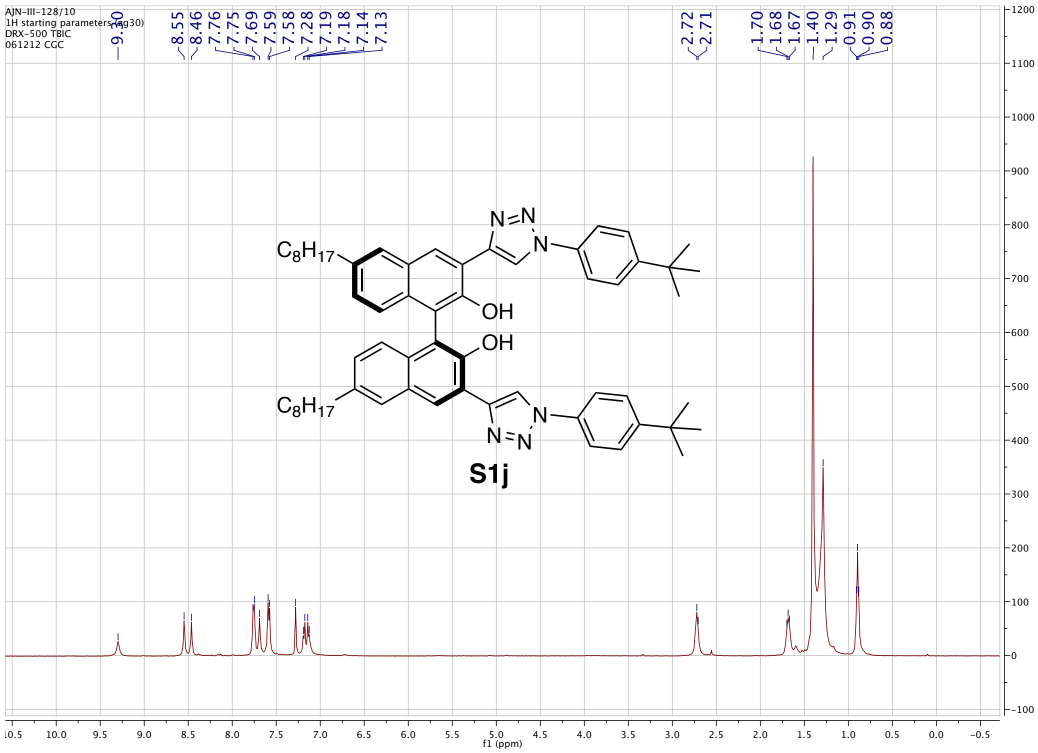

AJN-III-55/10
1H starting parameters (zg30)
DRX-500 TBIC
061212 CDCl3
8.37
8.19
7.72
7.29
7.28
7.28
7.19
7.18
7.16
6.90
2.77
2.75
2.74
2.63
2.62
2.59
2.53
2.44
1.96
1.94
1.90
1.89
1.87
1.73
1.71
1.48
1.46
1.44
1.42
1.29
0.90
Cy
Cy
Cy
Cy
Cy
Cy
N
N
N
N
OH
OH
C8H17
C8H17
S1i
f1 (ppm)

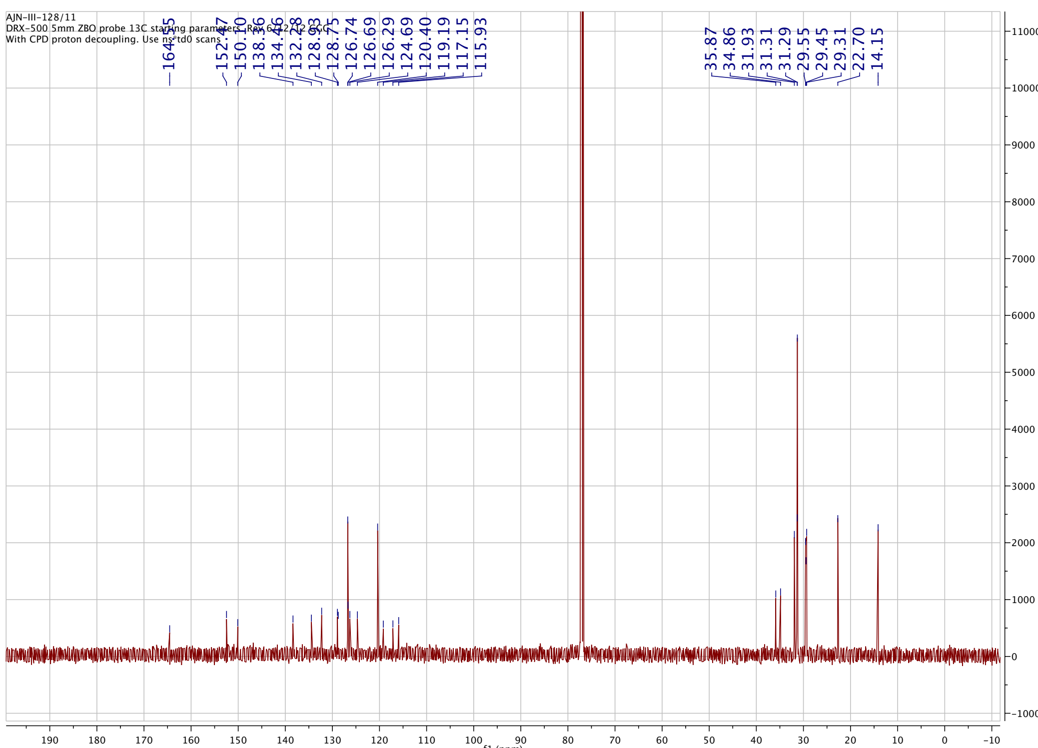

AJN-III-55/11
DRX-500 5mm ZBO probe 13C starting parameters
With CPD proton decoupling. Use ns*td0 scans
150.58
150.54
146.61
144.87
144.75
138.18
132.52
130.85
128.82
128.56
126.50
125.80
124.85
123.44
123.03
122.99
117.06
116.90
44.95
39.17
35.90
34.70
34.66
34.63
34.58
34.46
31.93
31.35
29.55
29.39
29.30
27.27
27.12
26.88
26.67
26.54
26.50
26.46
26.29
22.70
14.14
f1 (ppm)

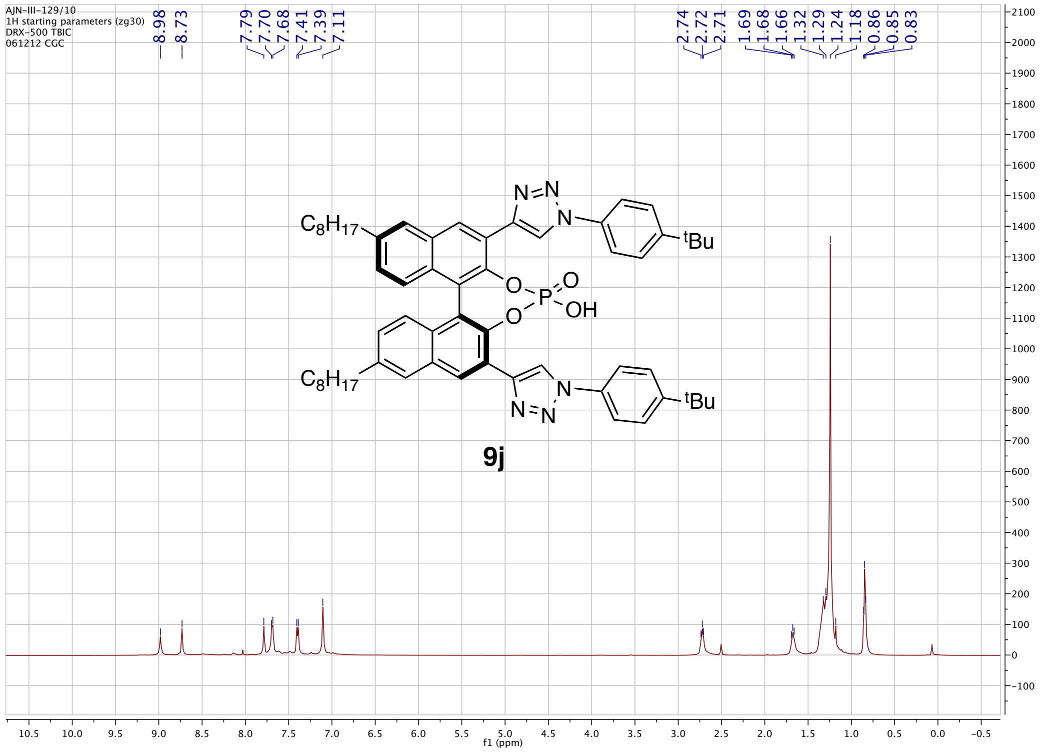

AJN-III-56b
AVQ-400 QNP Proton starting param
8.76
8.74
7.96
7.40
7.18
7.17
7.16
7.10
7.08
7.03
5.73
2.74
2.72
1.78
1.76
1.67
1.63
1.59
1.47
1.42
1.38
1.36
1.33
1.29
1.21
0.82
0.81
Cy
N=N
N
Cy
Cy
C8H17
O
O
P
OH
O
Cy
Cy
C8H17
N
N=N
Cy
Cy
9i
f1 (ppm)

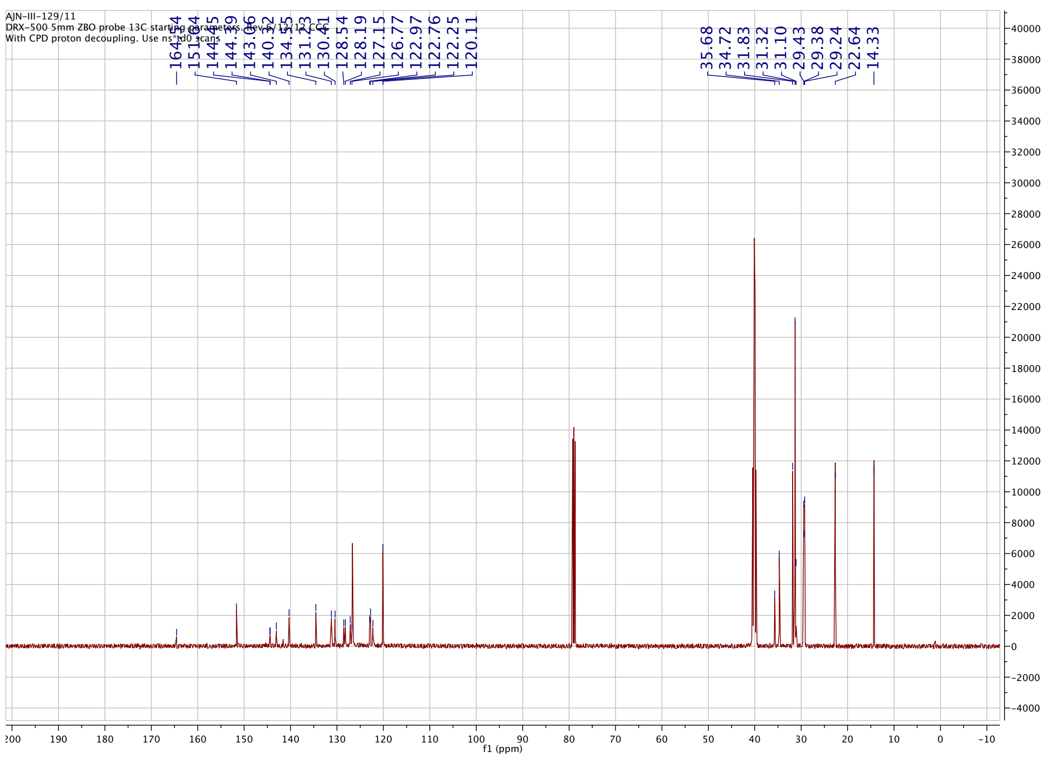

AJN-III-56b
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
148.22
142.82
142.62
137.95
129.57
129.15
128.55
126.31
126.01
125.10
124.73
121.69
121.35
120.99
120.92
120.83
52.72
42.76
42.31
37.15
36.90
35.73
33.65
32.41
32.38
31.99
31.98
29.81
29.13
27.40
27.26
27.21
24.83
24.78
24.74
24.64
24.03
24.00
23.95
20.62
12.35
f1 (ppm)

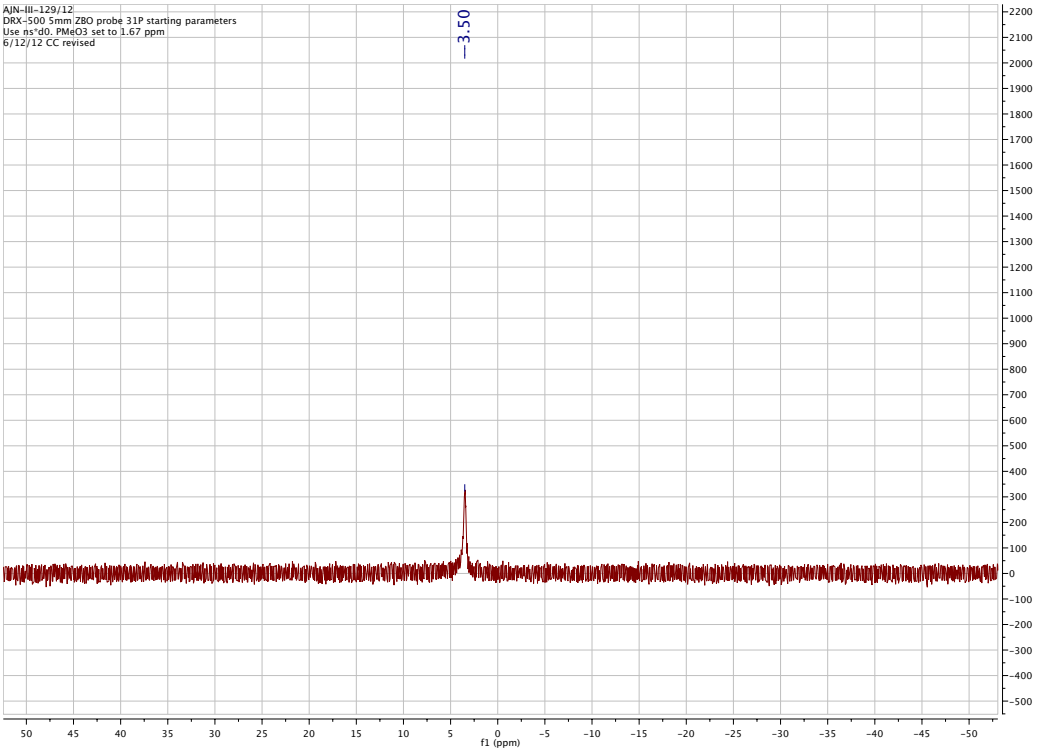

AJN-III-56b
AVQ-400 QNP 31P Starting parameters. Trimethyl phosphate=3.0 ppm. 7/16/03 Rev 7/24/03 RN
9.76
f1 (ppm)

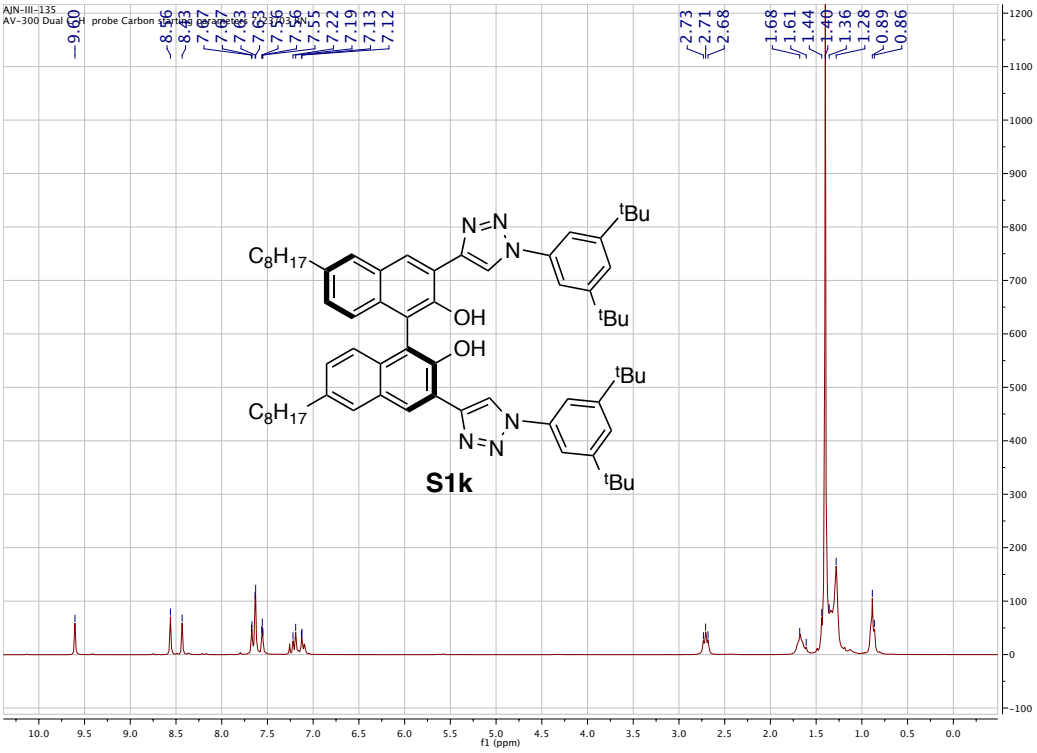

AJN-III-128/10
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
S1j
f1 (ppm)

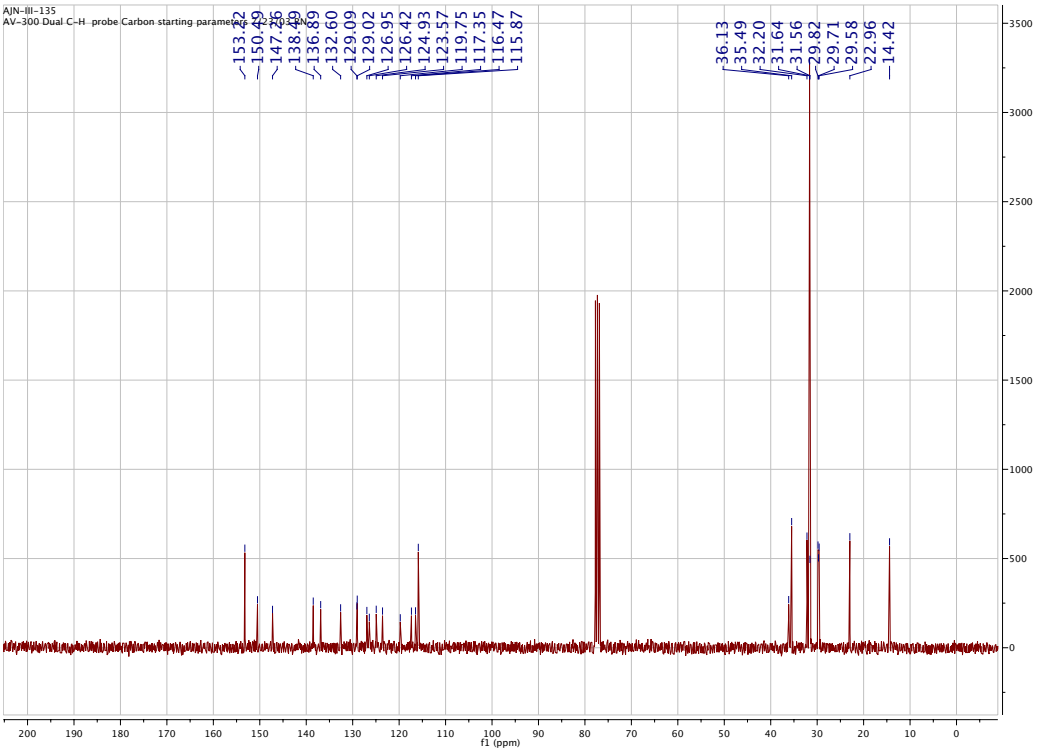

AJN-III-128/11
DRX-500 5mm ZBO probe 13C starting parameters
With CPD proton decoupling. Use ns*td0 scans
f1 (ppm)

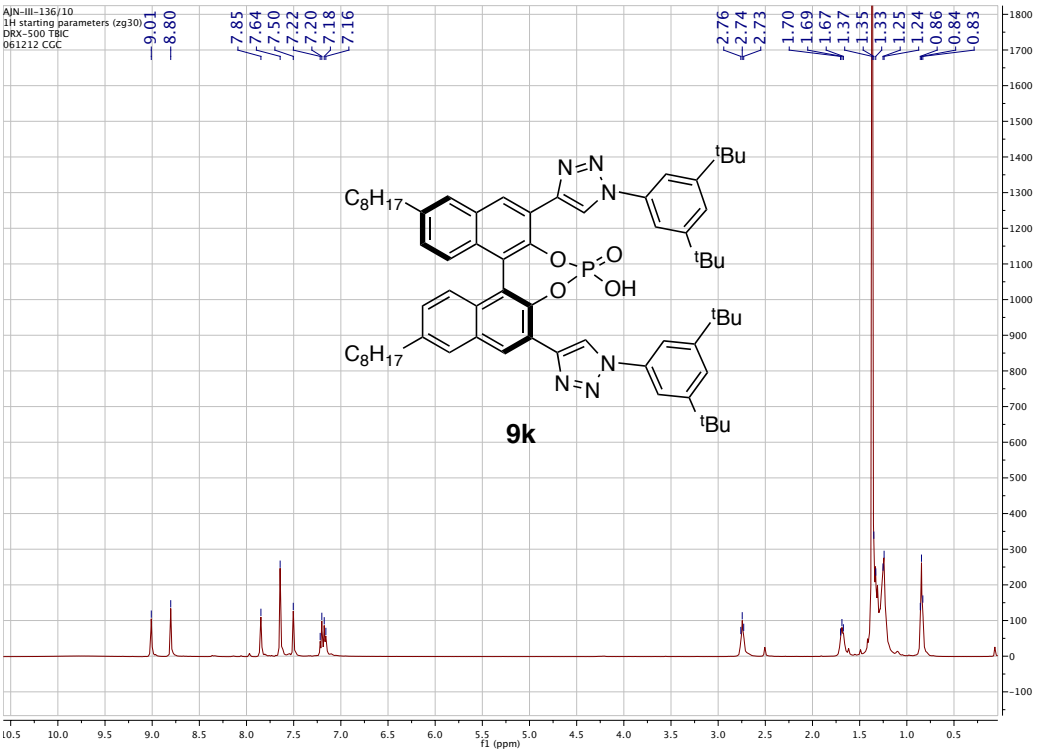


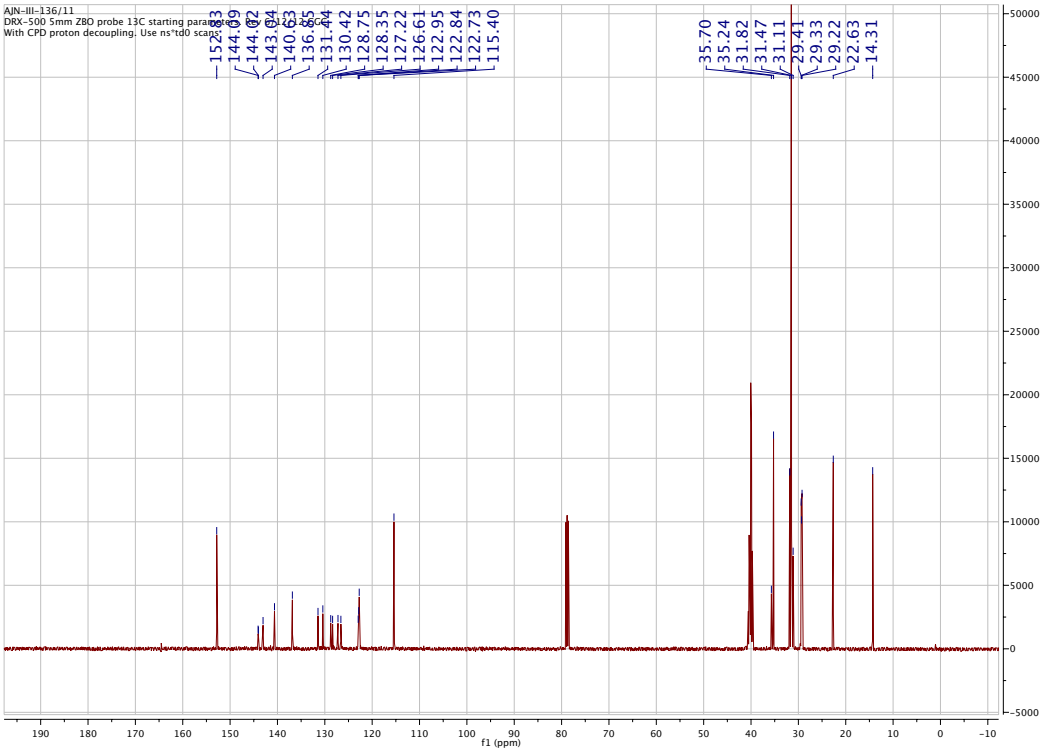


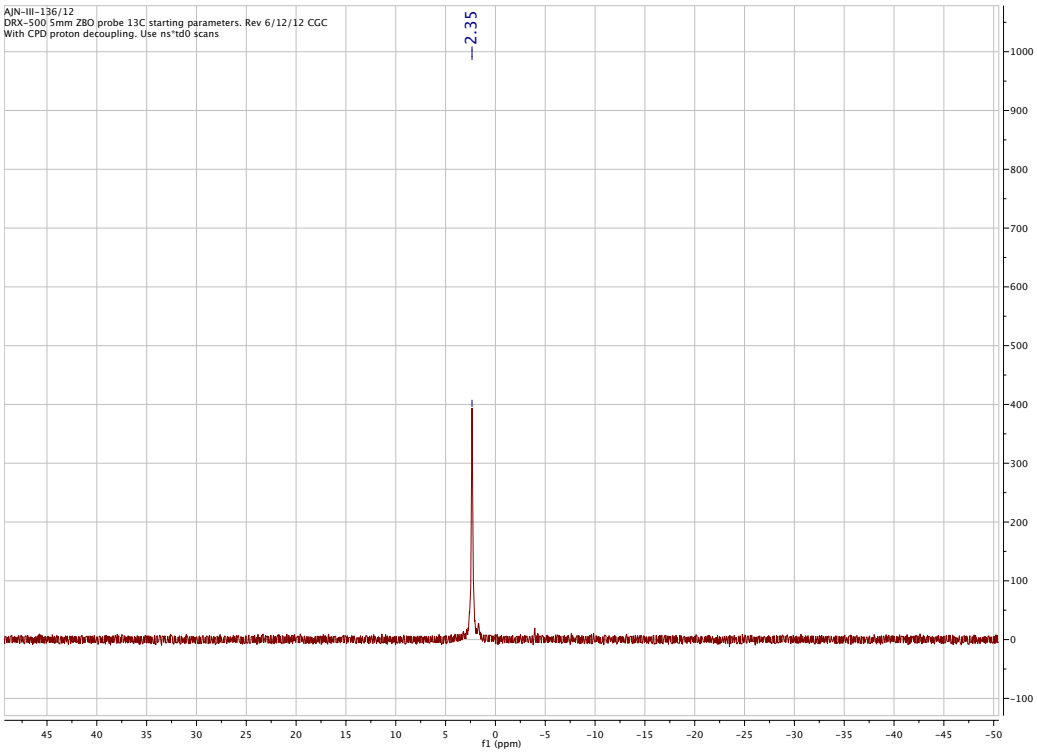

AJN-III-129/12
DRX-500 5mm ZBO probe 31P starting parameters
Use ns*d0. PMeO3 set to 1.67 ppm
6/12/12 CC revised
3.50
f1 (ppm)

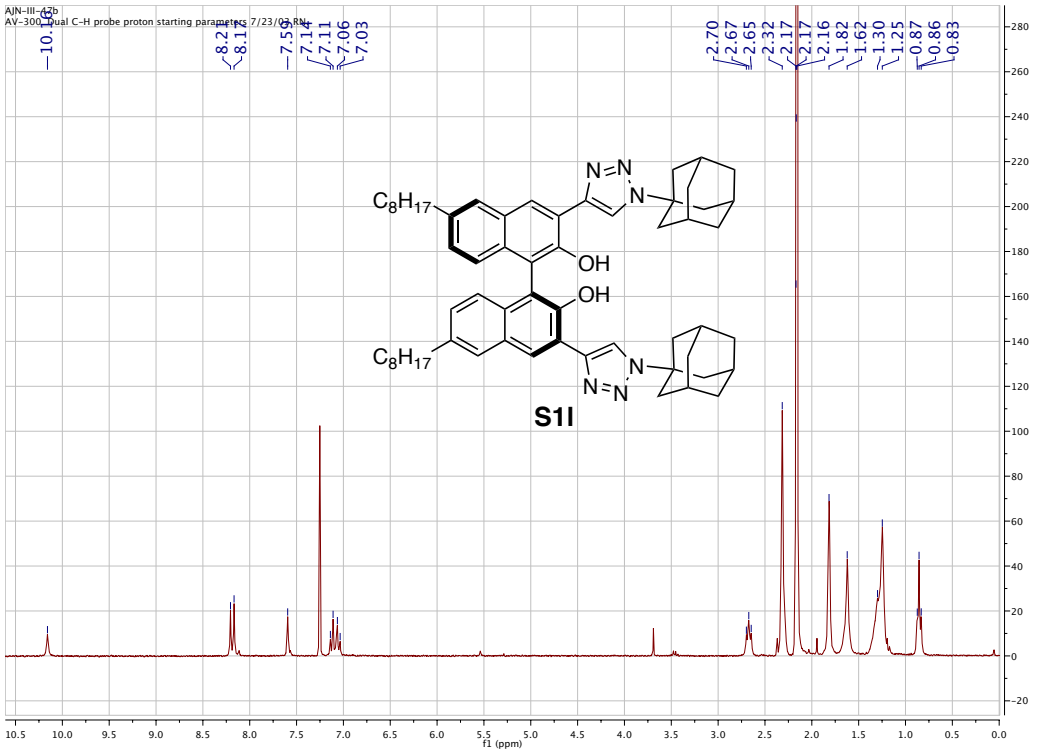

AJN-III-135
AV-300 Dual C-H probe Carbon starting parameters
9.60
8.46
8.43
7.67
7.47
7.43
7.63
7.56
7.46
7.55
7.22
7.19
7.13
7.12
2.73
2.71
2.68
1.68
1.61
1.44
1.40
1.36
1.28
0.89
0.86
N=N
N
tBu
tBu
C8H17
OH
OH
tBu
tBu
C8H17
N=N
N
S1k
f1 (ppm)

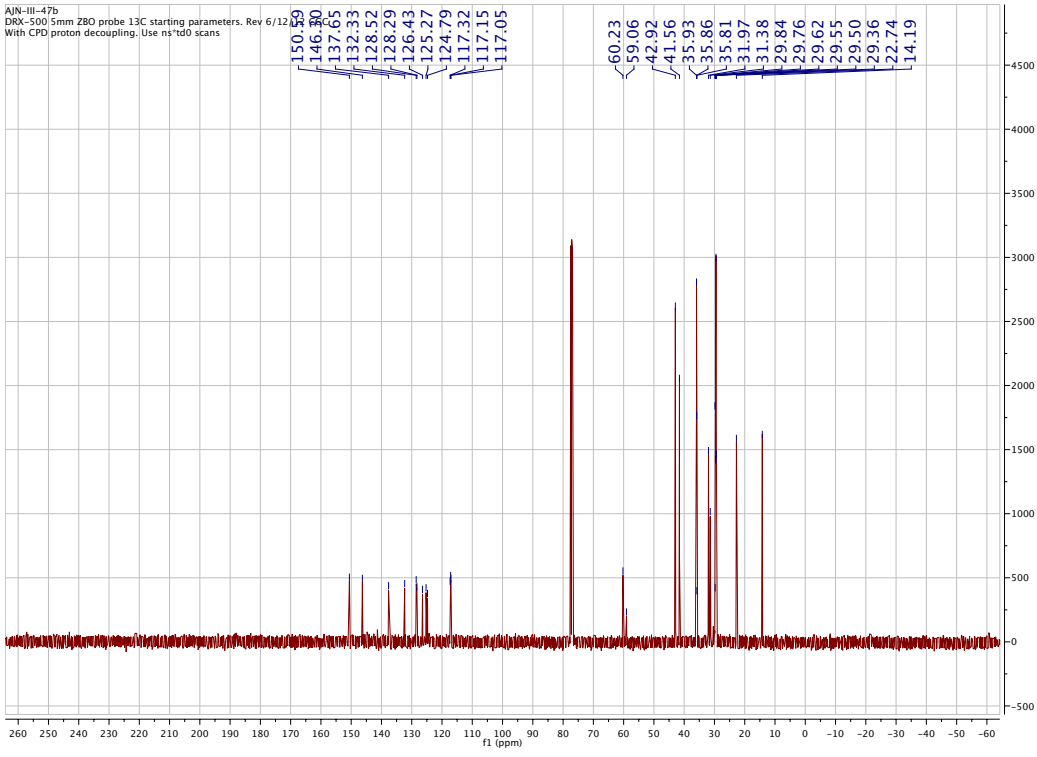

AJN-III-135
AV-300 Dual C-H probe Carbon starting parameters
153.22
150.49
147.26
138.99
136.89
132.60
129.09
129.02
126.95
126.42
124.93
123.57
119.75
117.35
116.47
115.87
36.13
35.49
32.20
31.64
31.56
29.82
29.71
29.58
22.96
14.42
f1 (ppm)

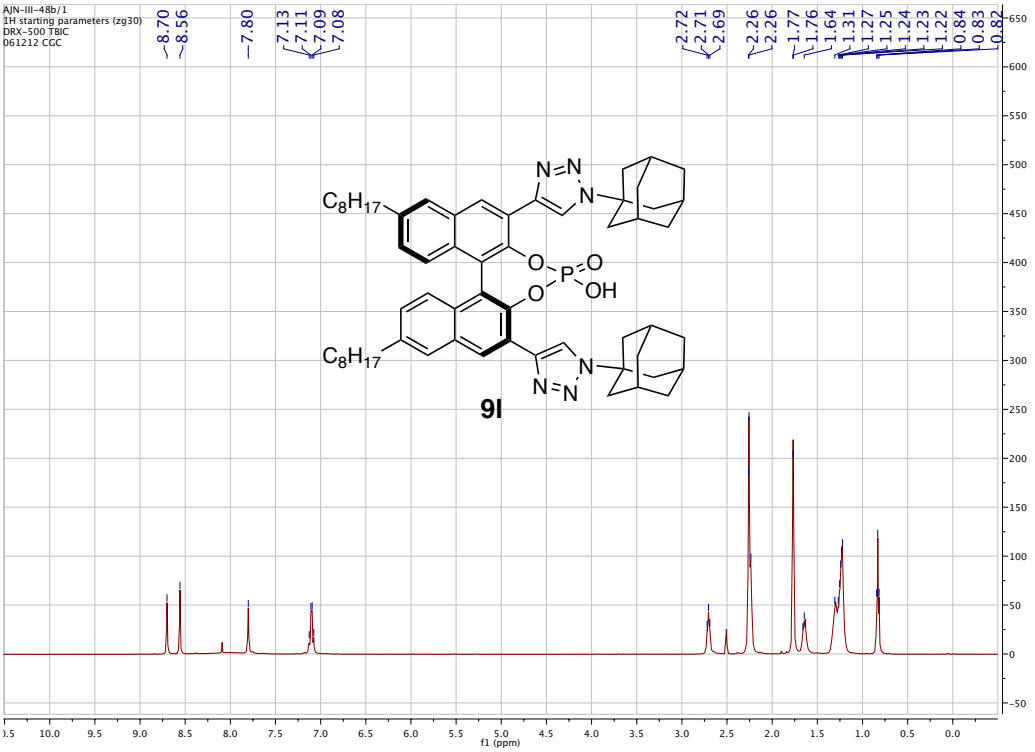

AJN-III-136/10
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
9.01
8.80
7.85
7.64
7.50
7.22
7.20
7.18
7.16
2.76
2.74
2.73
1.70
1.69
1.67
1.37
1.35
1.33
1.25
1.24
0.86
0.84
0.83
f1 (ppm)

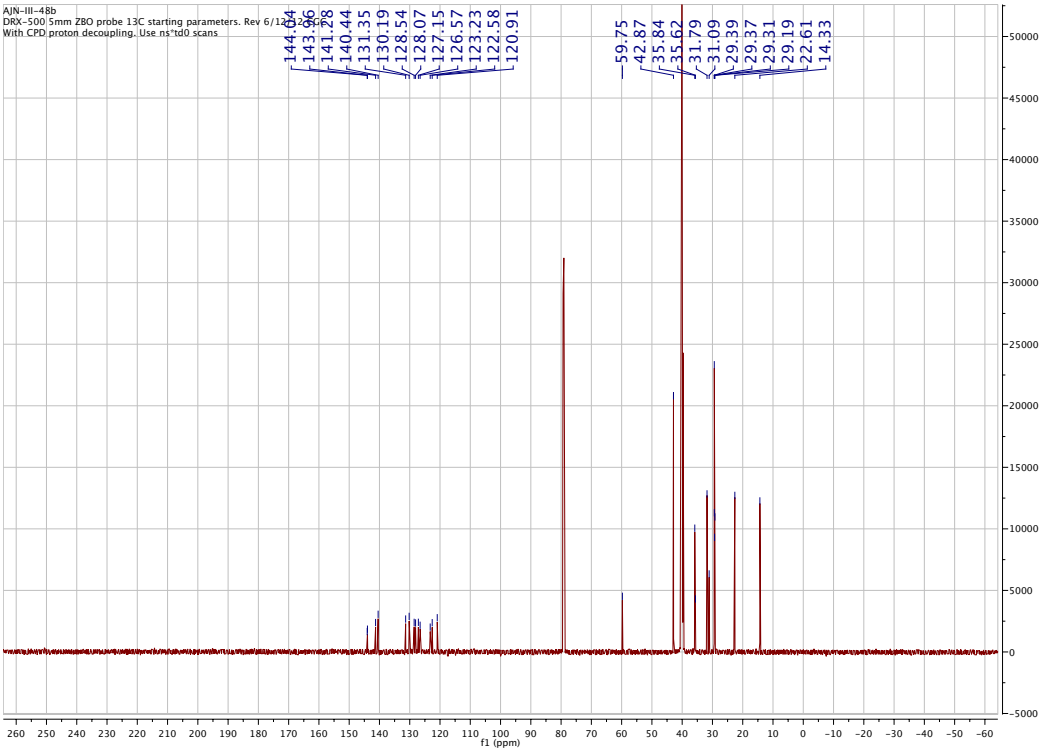

AJN-III-136/11
DRX-500 5mm ZBO probe 13C starting parameters (zgpg30)
With CPD proton decoupling. Use ns*td0 scans
152.23
144.09
144.02
143.64
140.23
136.65
131.44
130.42
128.75
128.35
127.22
126.61
122.95
122.84
122.73
115.40
35.70
35.24
31.82
31.47
31.11
29.41
29.33
29.22
22.63
14.31
f1 (ppm)

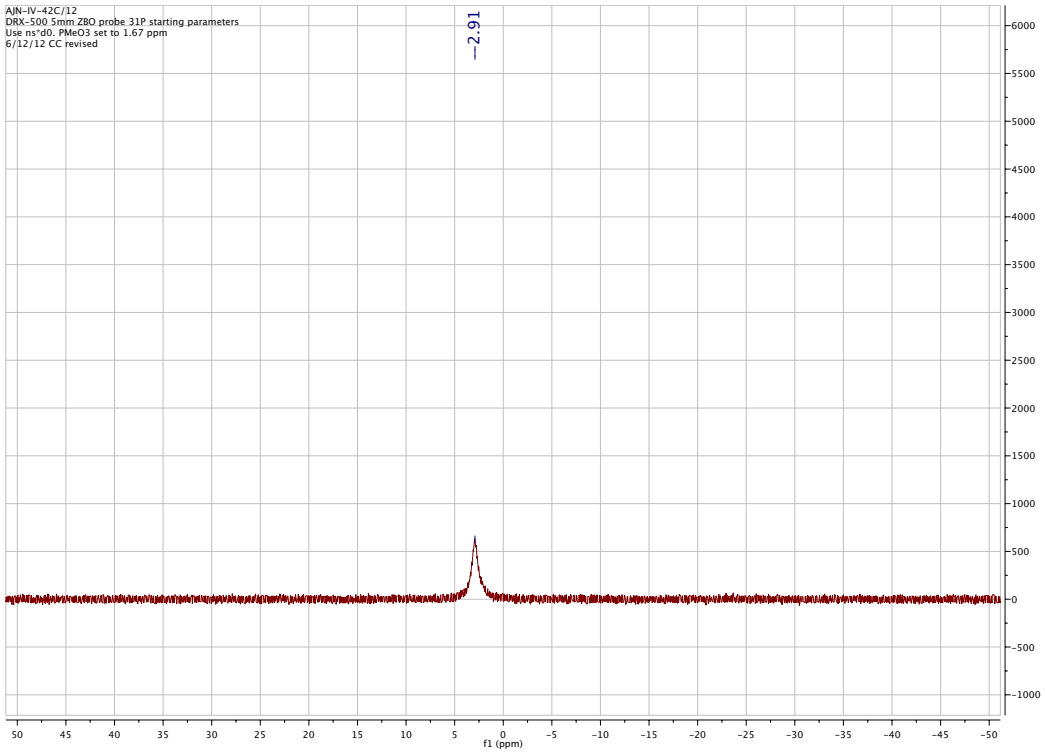

AJN-III-136/12
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12 CGC
With CPD proton decoupling. Use ns*td0 scans
2.35
1000
900
800
700
600
500
400
300
200
100
0
-100
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

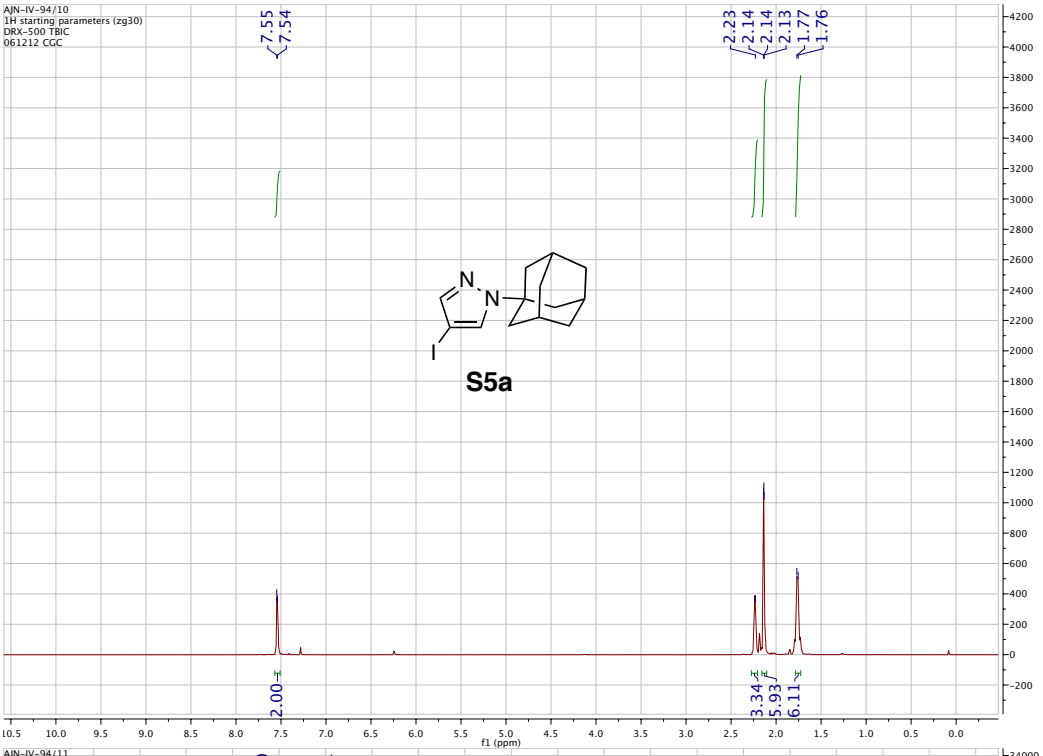

AJN-III-47b
AV-300 Dual C-H probe proton starting parameters 7/23/03 RN
10.16
8.21
8.11
7.59
7.14
7.11
7.06
7.03
2.70
2.67
2.65
2.32
2.17
2.17
2.16
1.82
1.62
1.30
1.25
0.87
0.86
0.83
C8H17
OH
OH
C8H17
N
N
N
N
S1l
f1 (ppm)


AJN-III-47b
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/02 RAC
With CPD proton decoupling. Use ns*td0 scans
150.29
146.80
137.65
132.33
128.52
128.29
126.43
125.27
124.79
117.32
117.15
117.05
60.23
59.06
42.92
41.56
35.93
35.86
35.81
31.97
31.38
29.84
29.76
29.62
29.55
29.50
29.36
22.74
14.19
f1 (ppm)

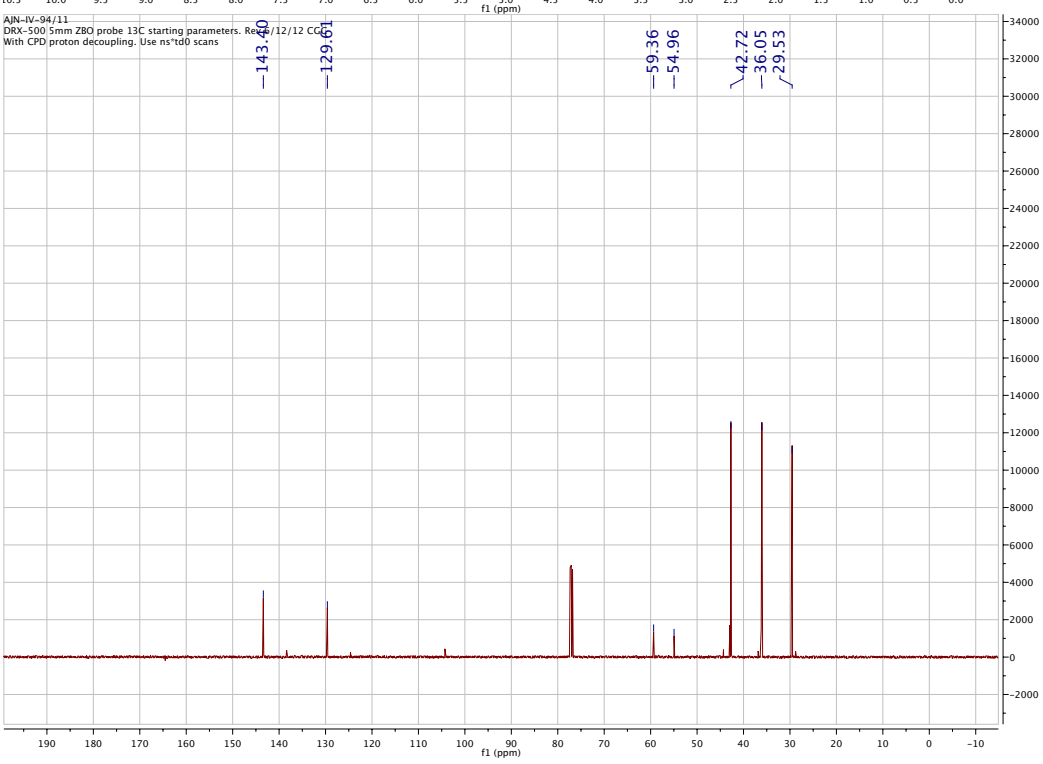

AJN-III-48b/1
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
8.70
8.56
7.80
7.13
7.11
7.09
7.08
2.72
2.71
2.69
2.26
2.26
1.77
1.76
1.64
1.31
1.27
1.25
1.24
1.23
1.22
0.84
0.83
0.82
C8H17
C8H17
O
P
O
OH
O
N
N
N
N
9l
f1 (ppm)

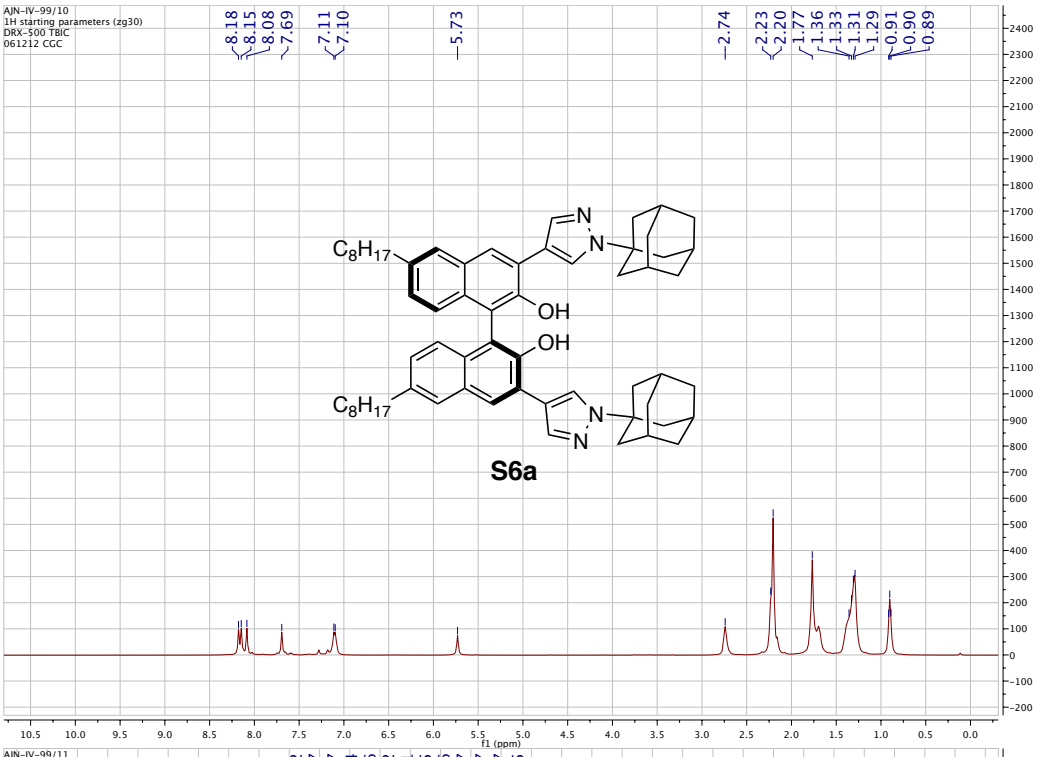

AJN-III-48b
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/2006
With CPD proton decoupling. Use ns*td0 scans
144.04
143.96
141.28
140.44
131.35
130.19
128.54
128.07
127.15
126.57
123.23
122.58
120.91
59.75
42.87
35.84
35.62
31.79
31.09
29.39
29.37
29.31
29.19
22.61
14.33
f1 (ppm)


AJN-IV-42C/12
DRX-500 5mm ZBO probe 31P starting parameters
Use ns*d0. PMeO3 set to 1.67 ppm
6/12/12 CC revised
2.91
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50
f1 (ppm)

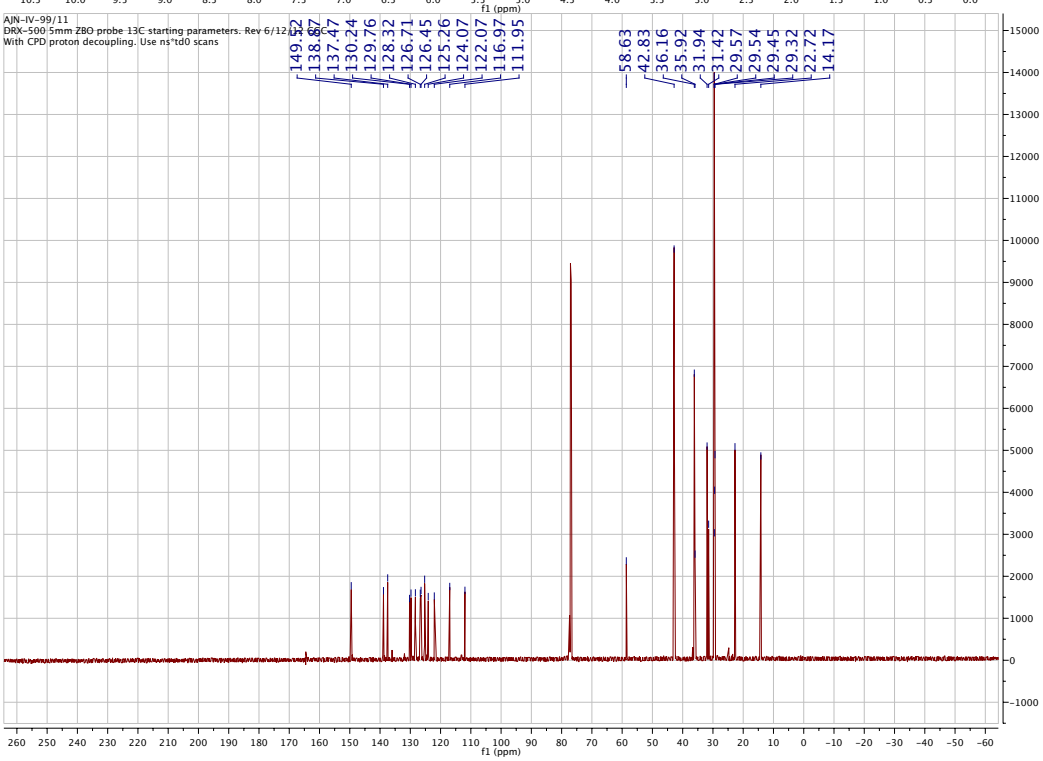

AJN-IV-94/10
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
7.55
7.54
2.23
2.14
2.14
2.13
1.77
1.76
N
N
I
2.00
3.34
5.93
6.11
f1 (ppm)

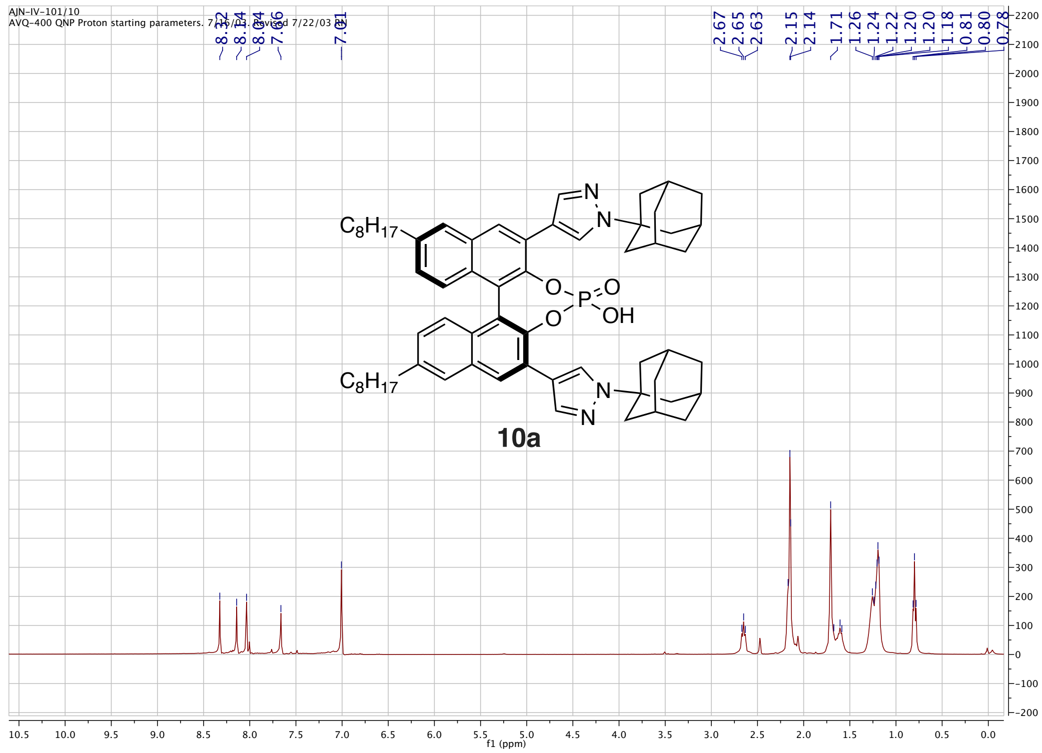
S5a

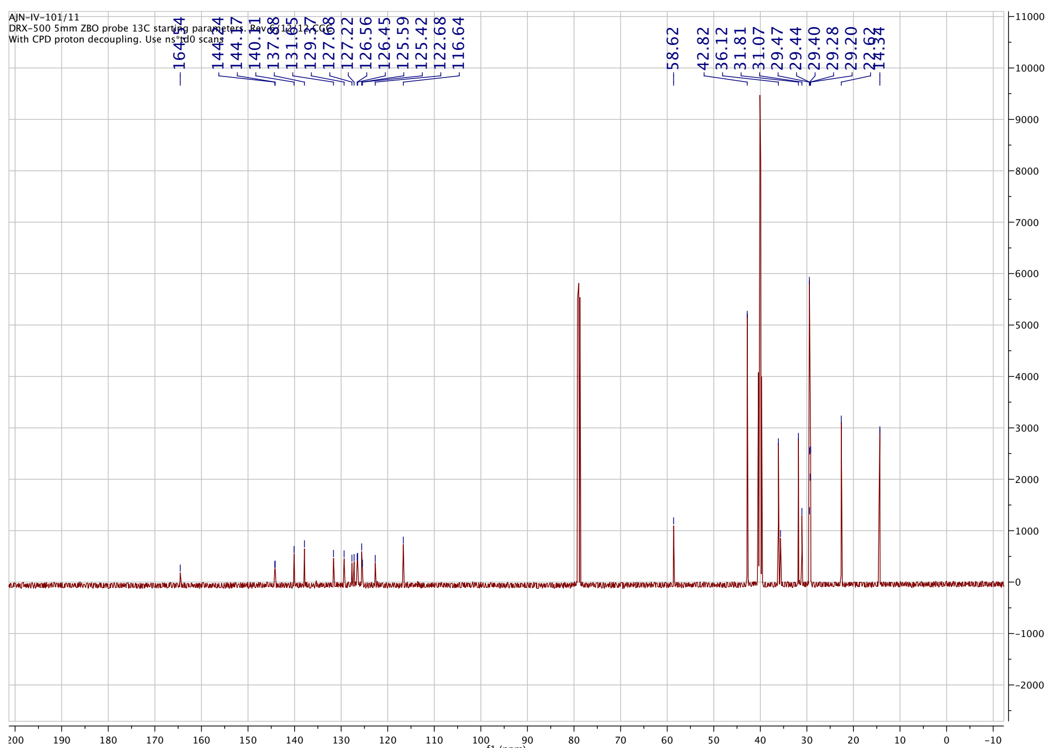

AJN-IV-94/11
DRX-500 5mm ZBO probe 13C starting parameters. Rege/12/12 CGC
With CPD proton decoupling. Use ns*td0 scans
143.40
129.61
59.36
54.96
42.72
36.05
29.53
f1 (ppm)

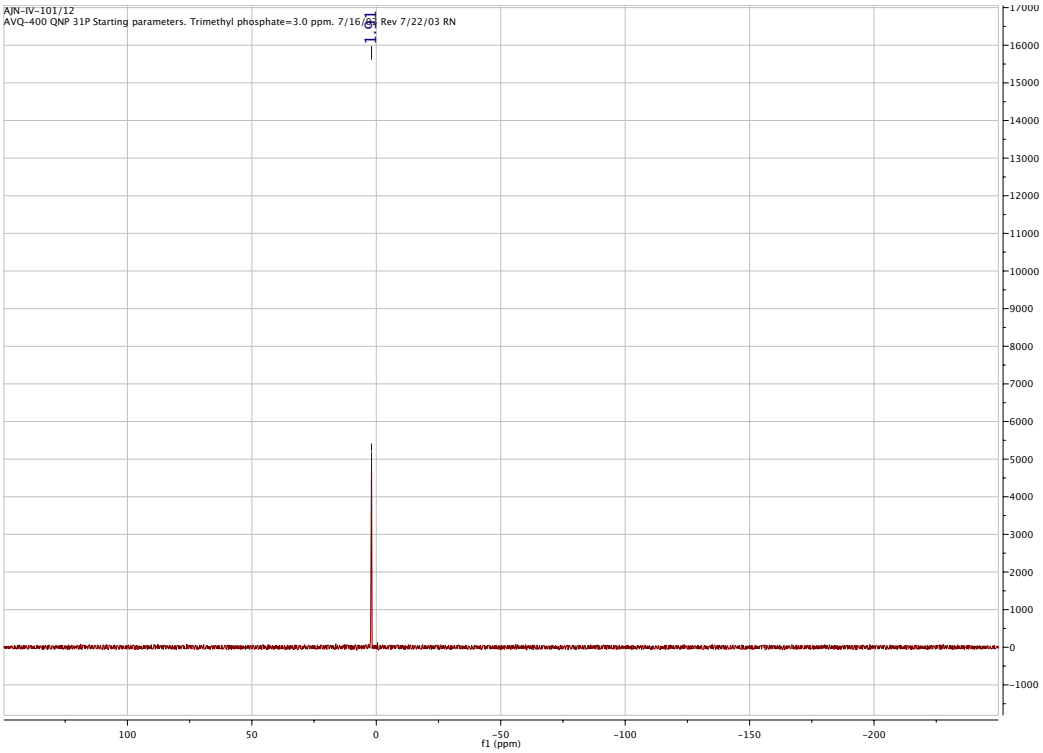

AJN-IV-99/10
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
8.18
8.15
8.08
7.69
7.11
7.10
5.73
2.74
2.23
2.20
1.77
1.36
1.33
1.31
1.29
0.91
0.90
0.89
C8H17
OH
OH
C8H17
N
N
N
N
f1 (ppm)

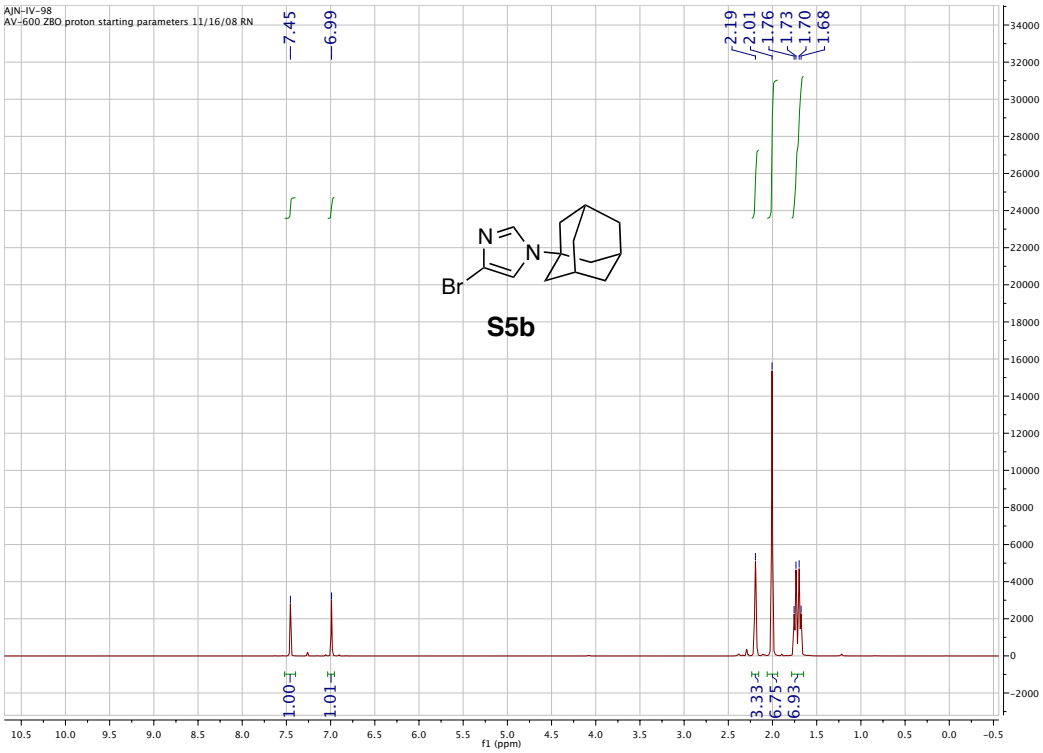
S6a


AJN-IV-99/11
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12
With CPD proton decoupling. Use ns*td0 scans
149.52
138.67
137.47
130.24
129.76
128.32
126.71
126.45
125.26
124.07
122.07
116.97
111.95
58.63
42.83
36.16
35.92
31.94
31.42
29.57
29.54
29.45
29.32
22.72
14.17
f1 (ppm)

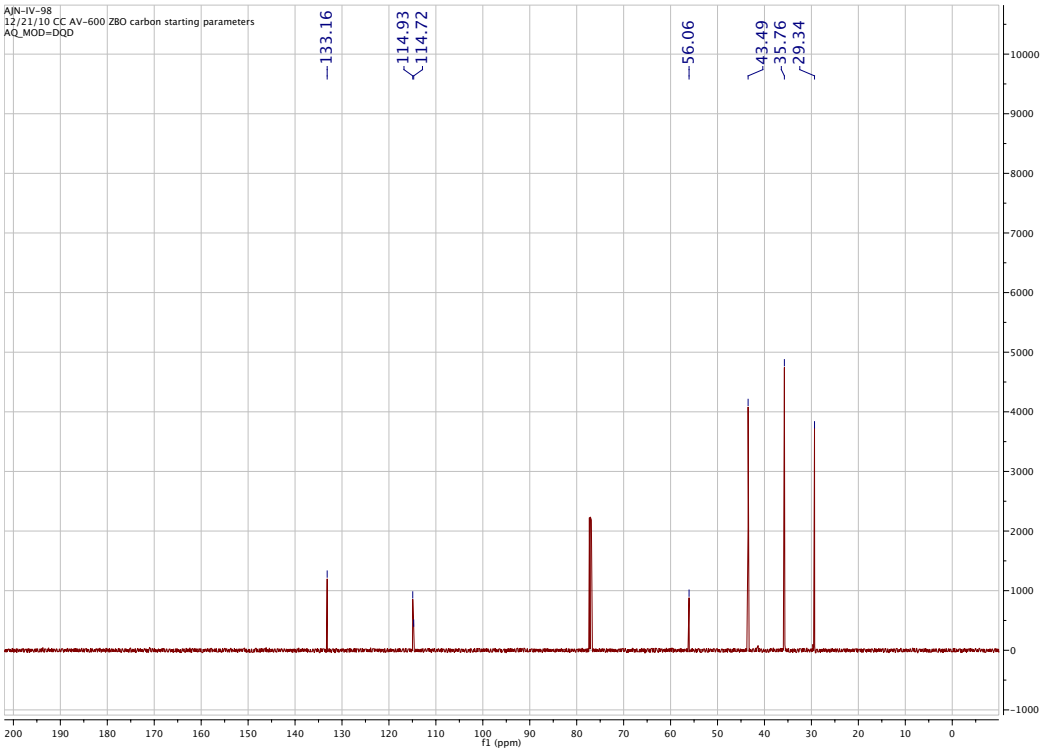

AJN-IV-101/10
AVQ-400 QNP Proton starting parameters.
8.32
8.14
8.04
7.66
7.01
2.67
2.65
2.63
2.15
2.14
1.71
1.26
1.24
1.22
1.20
1.20
1.18
0.81
0.80
0.78
C8H17
N
N
O
O
P
O
OH
10a
f1 (ppm)

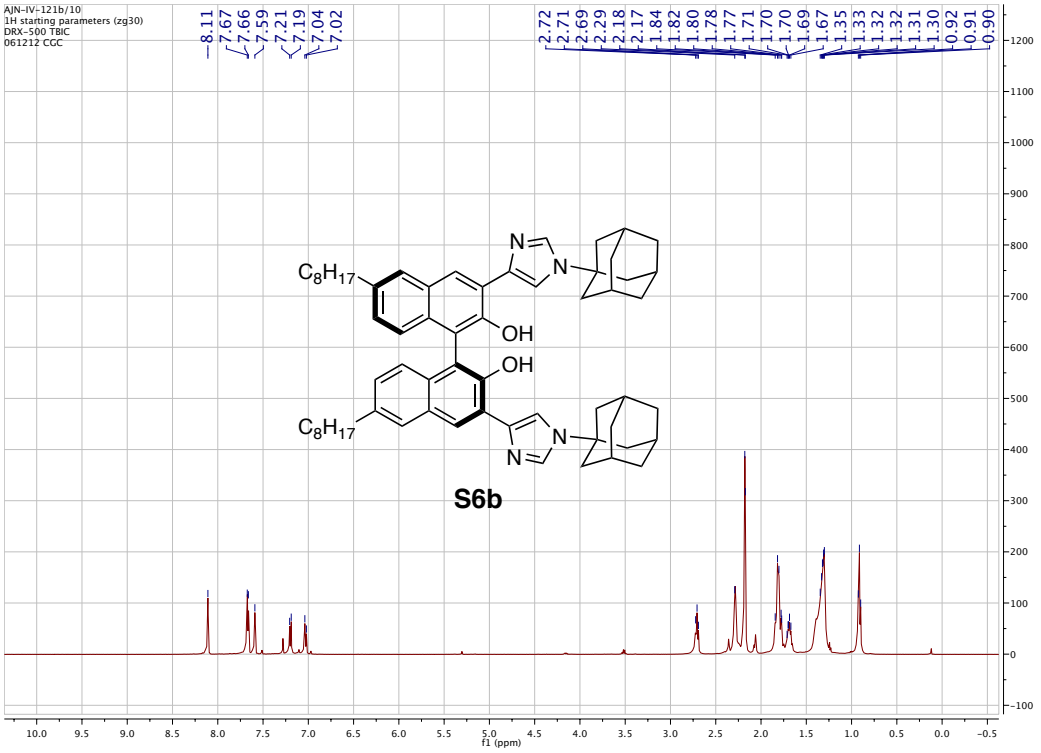

AJN-IV-101/11
DRX-500 5mm Z8O probe 13C starting parameters.
With CPD proton decoupling.
164.34
144.44
144.27
140.11
137.88
131.65
129.37
127.68
127.22
126.56
126.45
125.59
125.42
122.68
116.64
58.62
42.82
36.12
31.81
31.07
29.47
29.44
29.40
29.28
29.20
22.62
14.34
f1 (ppm)


AJN-IV-101/12
AVQ-400 QNP 31P Starting parameters. Trimethyl phosphate=3.0 ppm. 7/16/03 Rev 7/22/03 RN
-1.971
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
100
50
0
-50
-100
-150
-200
f1 (ppm)

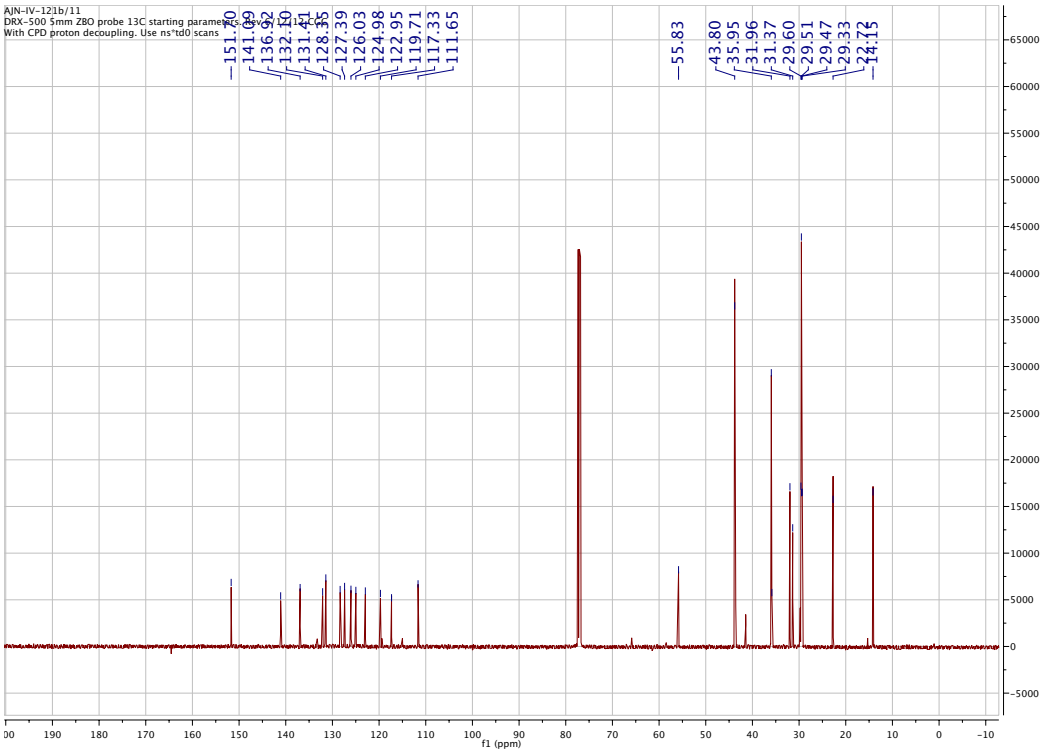

AJN-IV-98
AV-600 ZBO proton starting parameters 11/16/08 RN
7.45
6.99
2.19
2.01
1.76
1.73
1.70
1.68
N
N
Br
1.00
1.01
3.33
6.75
6.93
f1 (ppm)

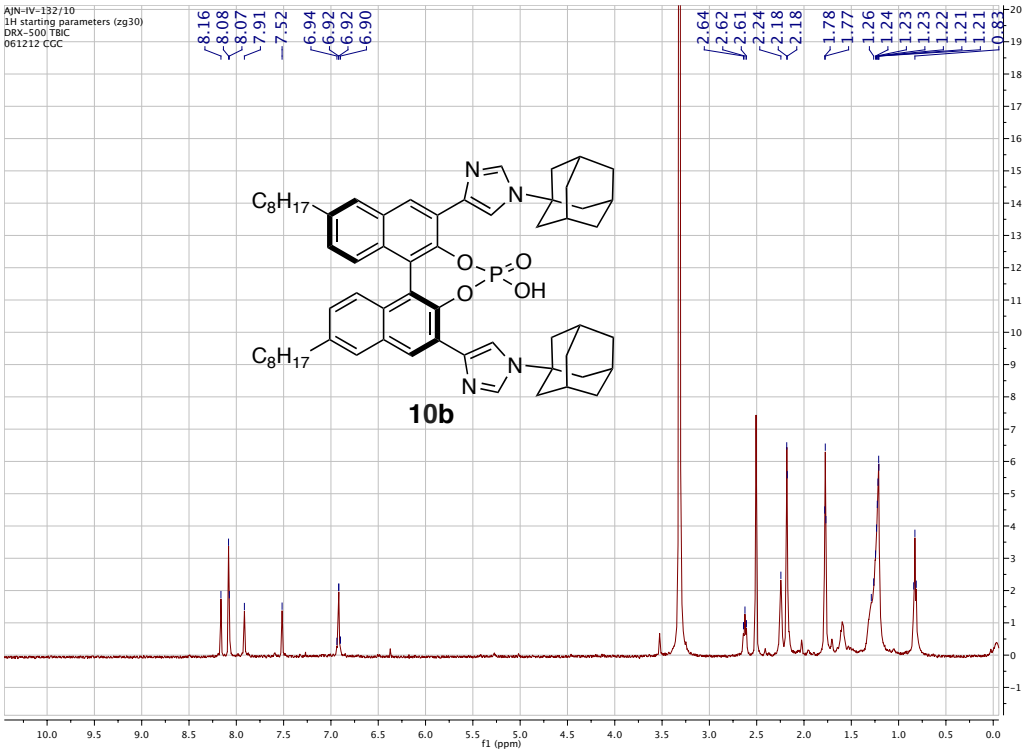
S5b

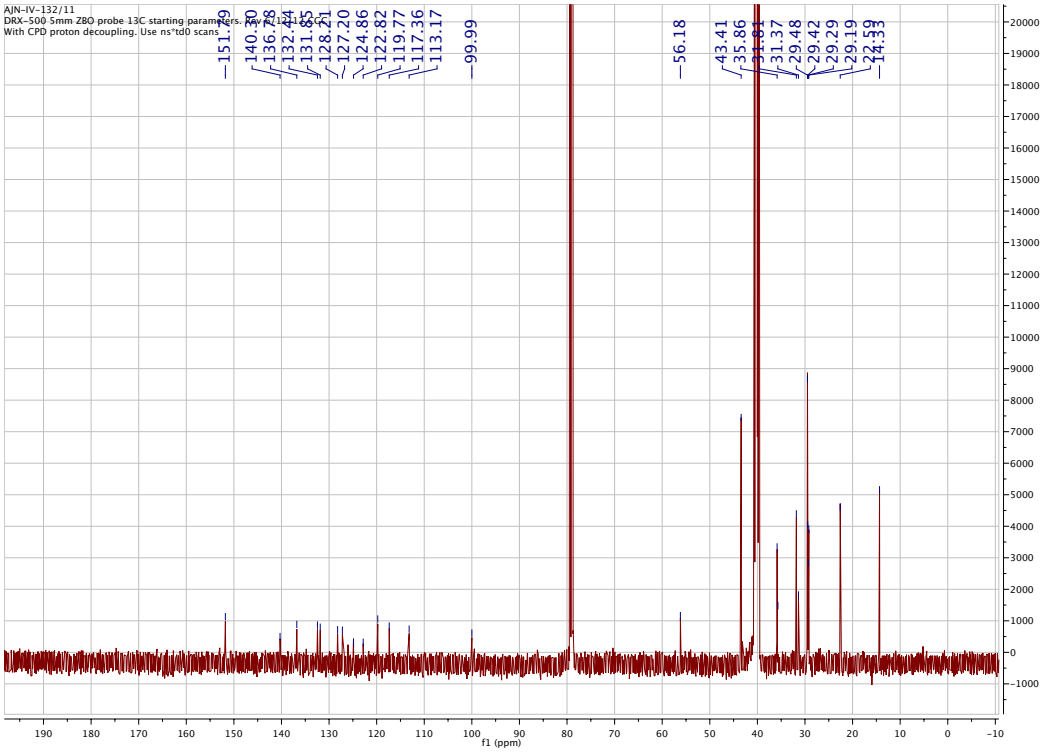

AJN-IV-98
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
133.16
114.93
114.72
56.06
43.49
35.76
29.34
f1 (ppm)

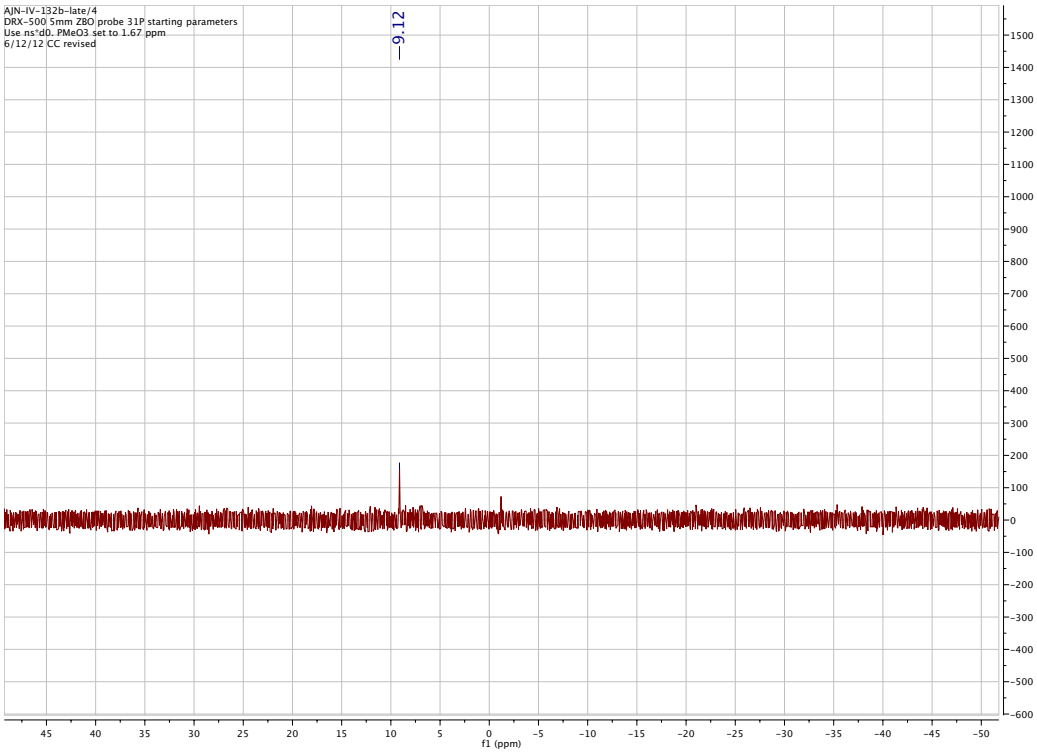

AJN-IV-121b/10
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
8.11
7.67
7.66
7.59
7.21
7.19
7.04
7.02
2.72
2.71
2.69
2.29
2.18
2.17
1.84
1.82
1.80
1.78
1.77
1.71
1.70
1.70
1.69
1.67
1.35
1.33
1.32
1.32
1.31
1.30
0.92
0.91
0.90
f1 (ppm)

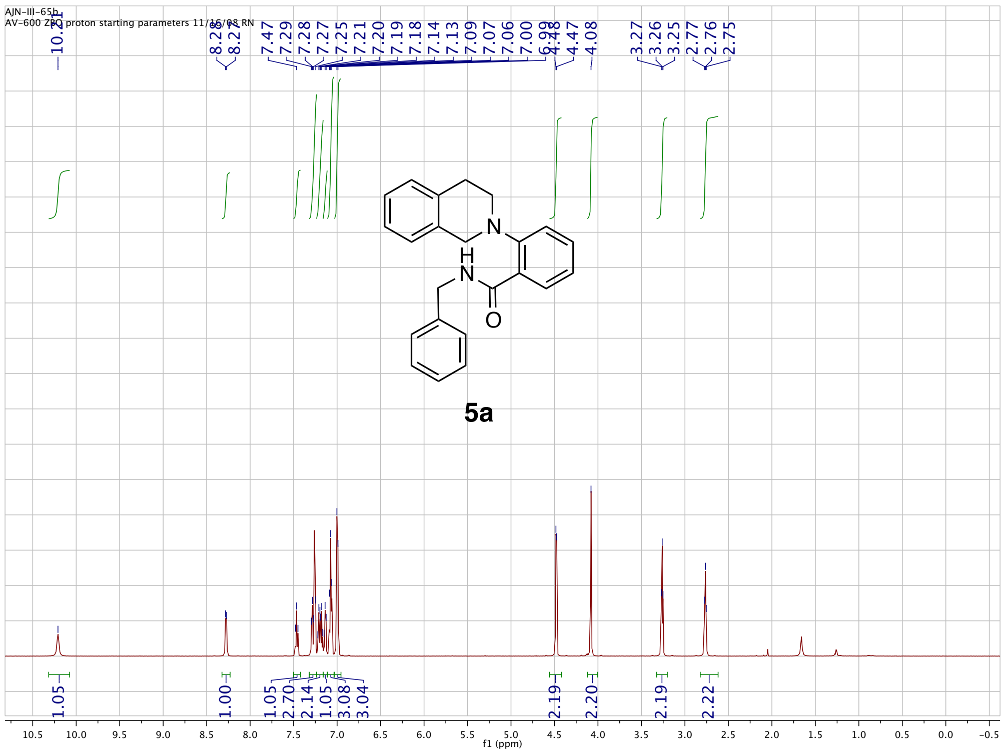
S6b

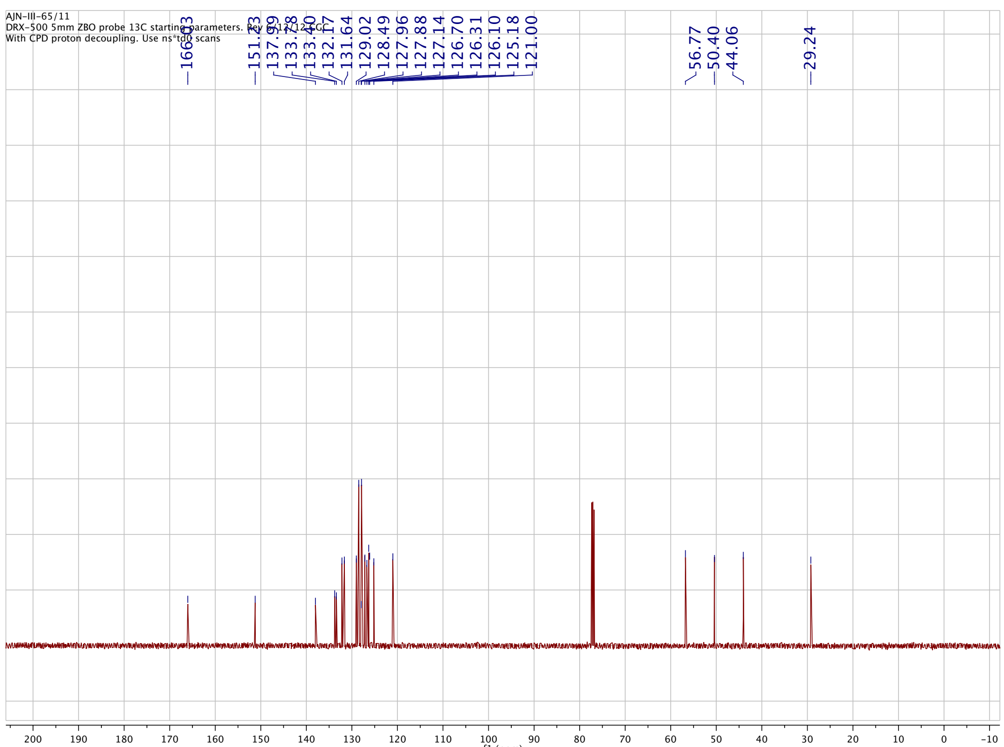

AJN-IV-121b/11
DRX-500 5mm ZBO probe 13C starting parameters
With CPD proton decoupling. Use ns*td0 scans
151.80
141.69
136.92
132.10
131.41
128.35
127.39
126.03
124.98
122.95
119.71
117.33
111.65
55.83
43.80
35.95
31.96
31.37
29.60
29.51
29.47
29.33
14.15
f1 (ppm)

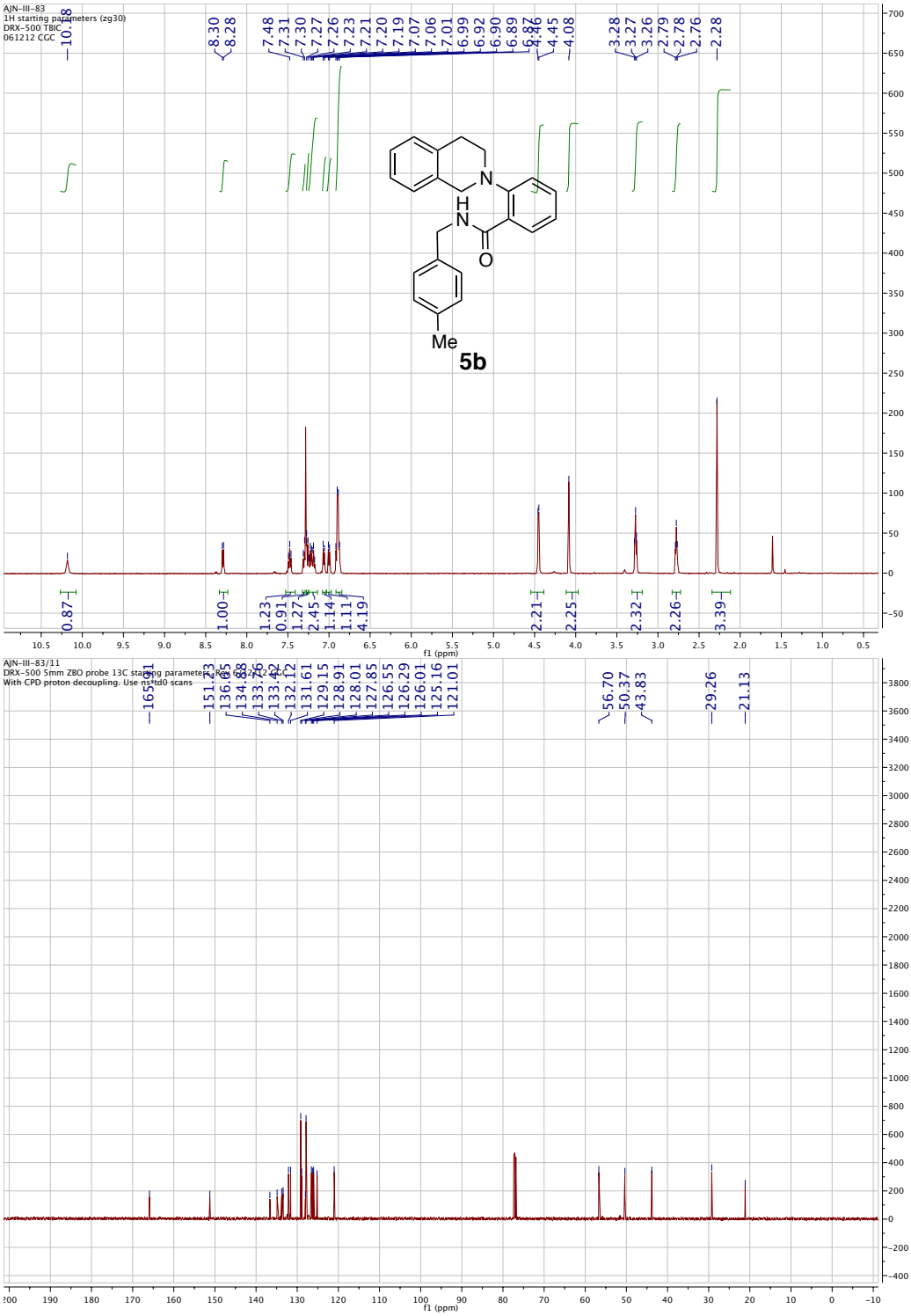

AJN-IV-132/10
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
8.16
8.08
8.07
7.91
7.52
6.94
6.92
6.92
6.90
2.64
2.62
2.61
2.24
2.18
2.18
1.78
1.77
1.26
1.24
1.23
1.23
1.22
1.21
1.21
0.83
C8H17
C8H17
O
P
O
O
OH
N
N
N
N
10b
f1 (ppm)

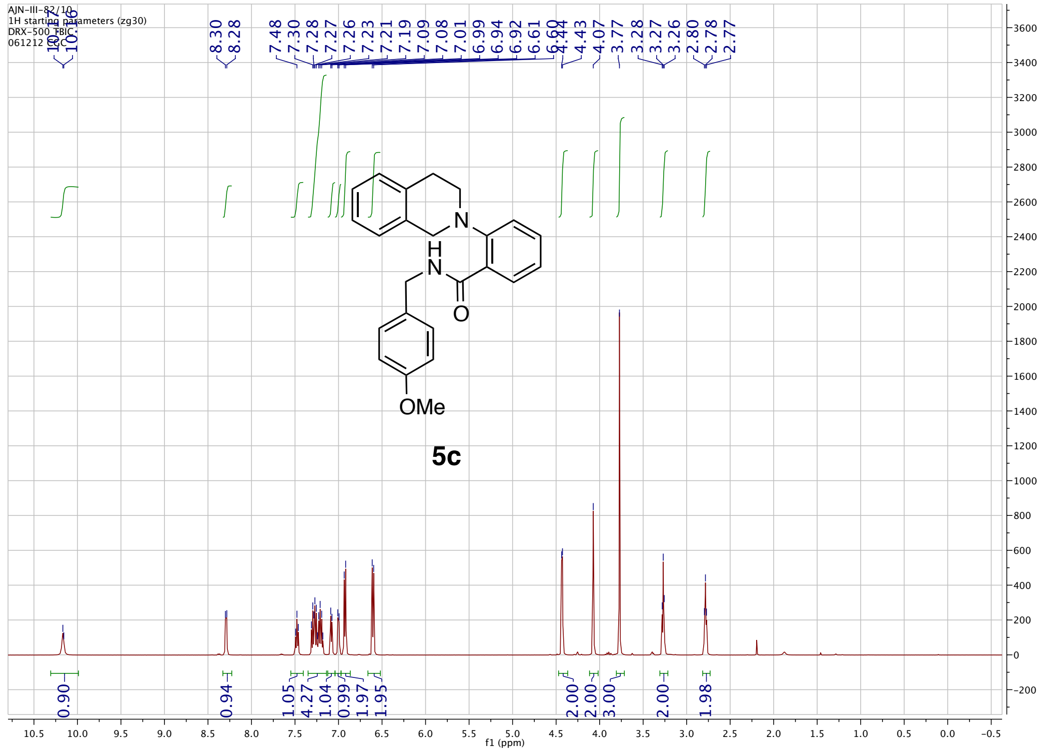

AJN-IV-132/11
DRX-500 5mm ZBO probe 13C starting parameters
With CPD proton decoupling. Use ns*td0 scans
151.29
140.30
136.78
132.44
131.85
128.21
127.20
124.86
122.82
119.77
117.36
113.17
99.99
56.18
43.41
35.86
31.81
31.37
29.48
29.42
29.29
29.19
22.59
14.33
f1 (ppm)

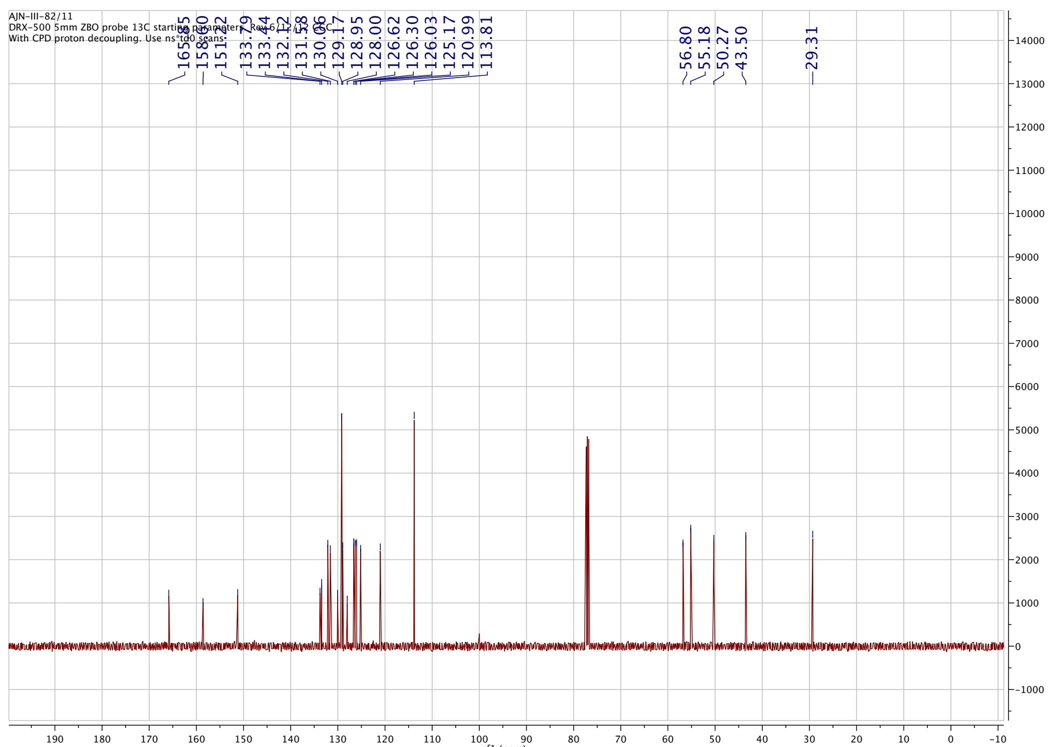

AJN-IV-132b-late/4
DRX-500 5mm ZBO probe 31P starting parameters
Use ns*d0. PMeO3 set to 1.67 ppm
6/12/12 CC revised
9.12
f1 (ppm)

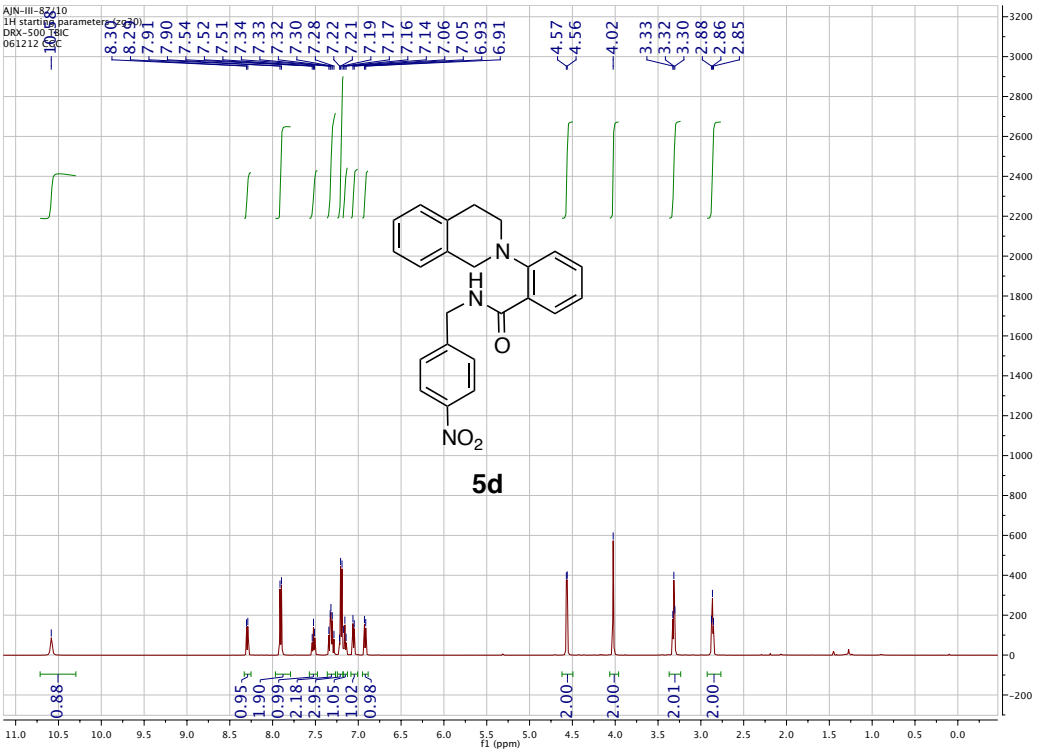

AJN-III-65b
AV-600 ZBO proton starting parameters 11/15/08 RN
5a
f1 (ppm)


AJN-III-65/11
DRX-500 5mm ZBO probe 13C starting parameters.
With CPD proton decoupling. Use ns*td0 scans
f1 (ppm)

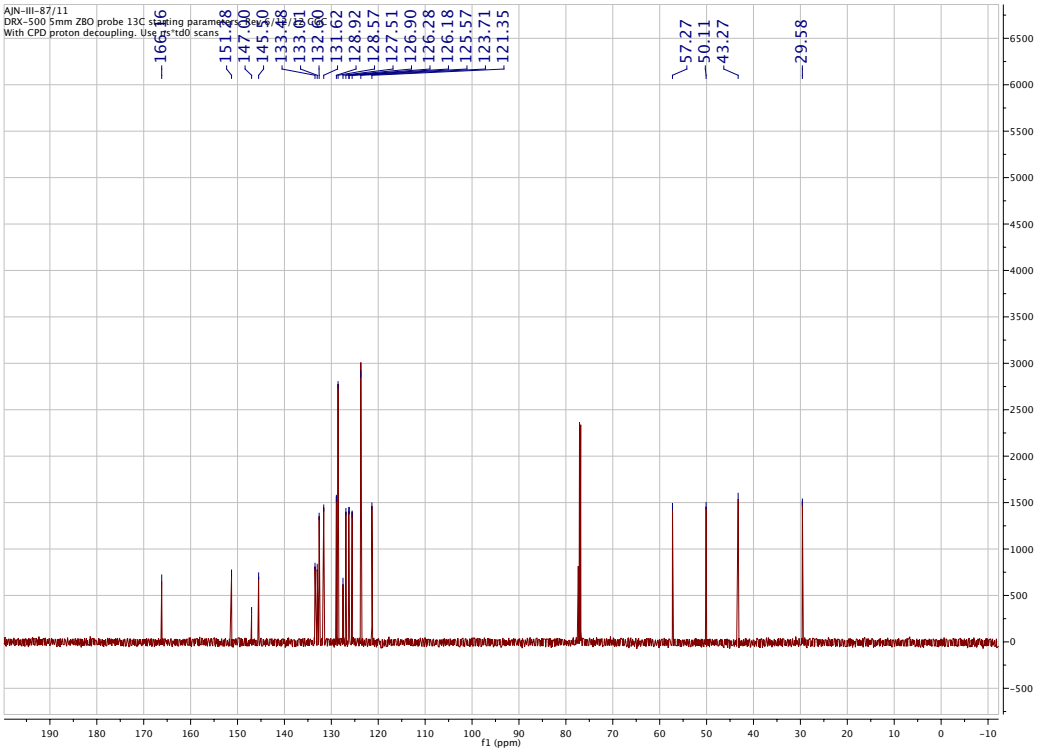

AJN-III-83
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
10.18
8.30
8.28
7.48
7.31
7.30
7.27
7.26
7.23
7.21
7.20
7.19
7.07
7.06
7.01
6.99
6.92
6.90
6.89
6.87
4.46
4.45
4.08
3.28
3.27
3.26
2.79
2.78
2.76
2.28
N
H
N
O
Me
5b
0.87
1.00
1.23
0.91
1.27
2.45
1.14
1.11
4.19
2.21
2.25
2.32
2.26
3.39
f1 (ppm)
AJN-III-83/11
DRX-500 5mm ZBO probe 13C starting parameters (zgpg30)
With CPD proton decoupling. Use ns*td0 scans
165.91
151.23
136.65
134.68
133.76
133.42
132.12
131.61
129.15
128.91
128.01
127.85
126.55
126.29
126.01
125.16
121.01
56.70
50.37
43.83
29.26
21.13
f1 (ppm)

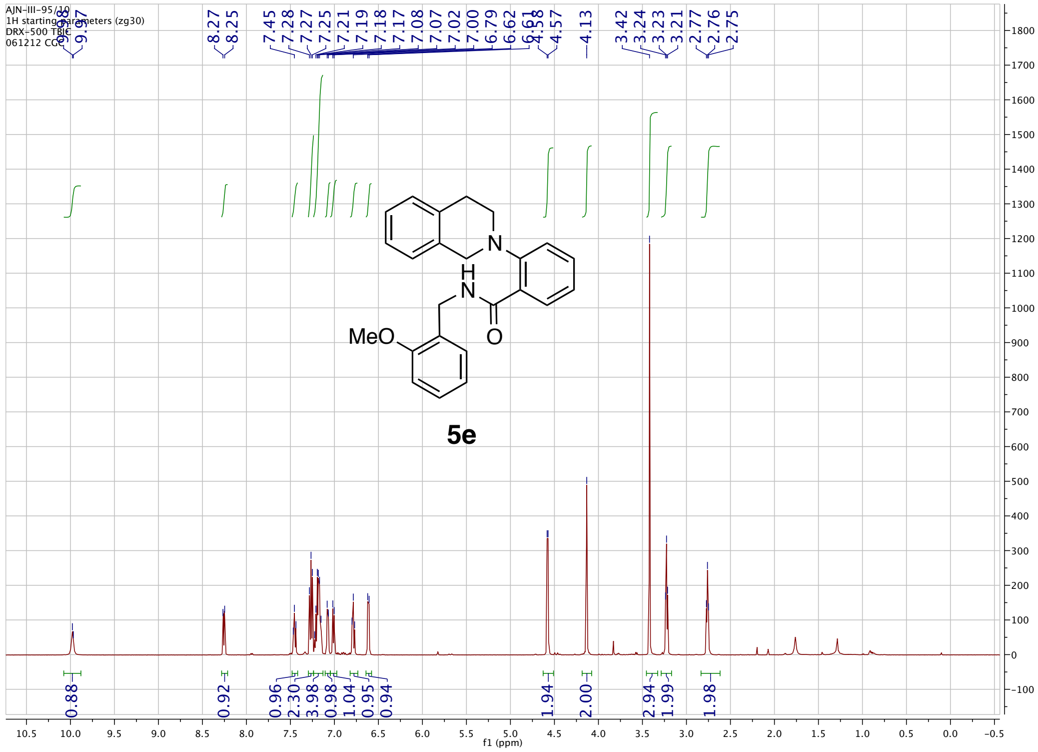

AJN-III-82/10
1H starting parameters (zg30)
DRX-500 FBIC
061212 CCC
5c
OMe
f1 (ppm)

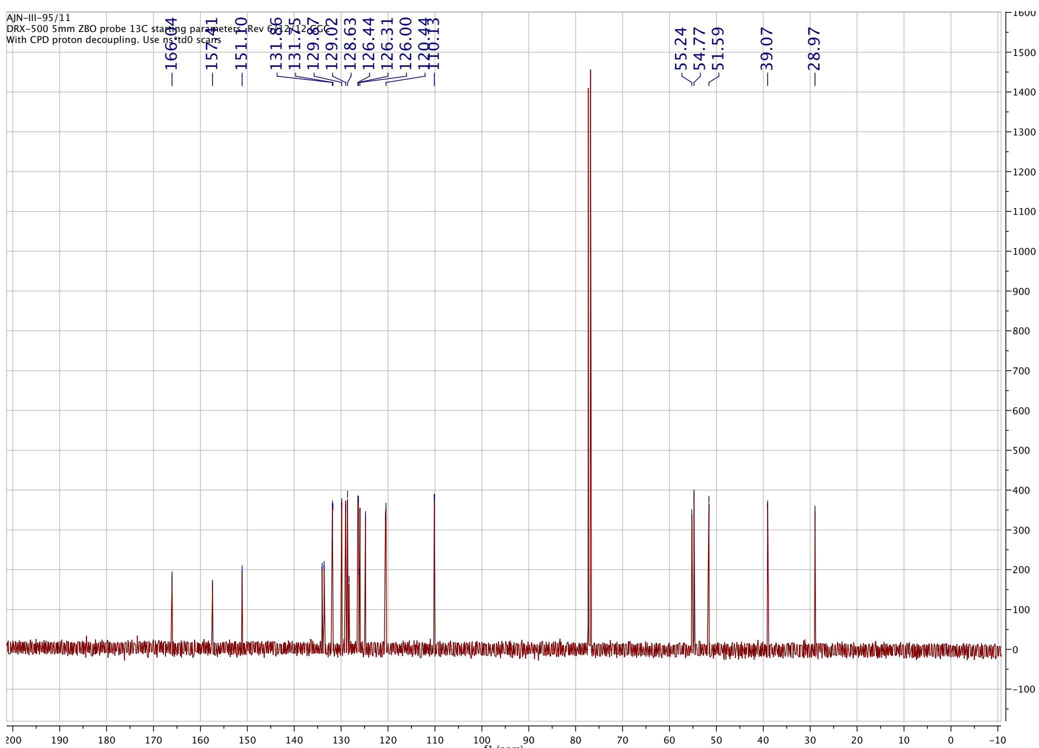

AJN-III-82/11
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12 CCC
With CPD proton decoupling. Use ns*td0 scans
f1 (ppm)

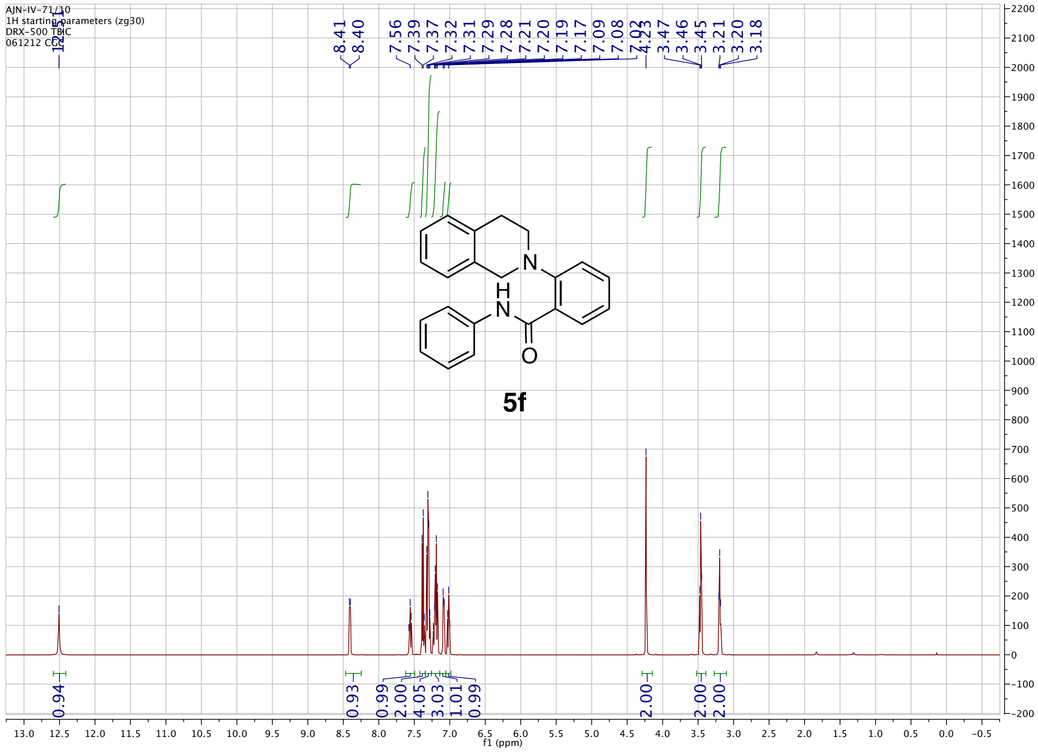

AJN-III-87/10
1H startup parameters (zg30)
DRX-500 TBIC
061212 SC
10.56
8.30
8.29
7.91
7.90
7.54
7.52
7.51
7.34
7.33
7.32
7.30
7.28
7.22
7.21
7.19
7.17
7.16
7.14
7.06
7.05
6.93
6.91
4.57
4.56
4.02
3.33
3.32
3.30
2.88
2.86
2.85
0.88
0.95
1.90
0.99
2.18
2.95
1.05
1.02
0.98
2.00
2.00
2.01
2.00
f1 (ppm)

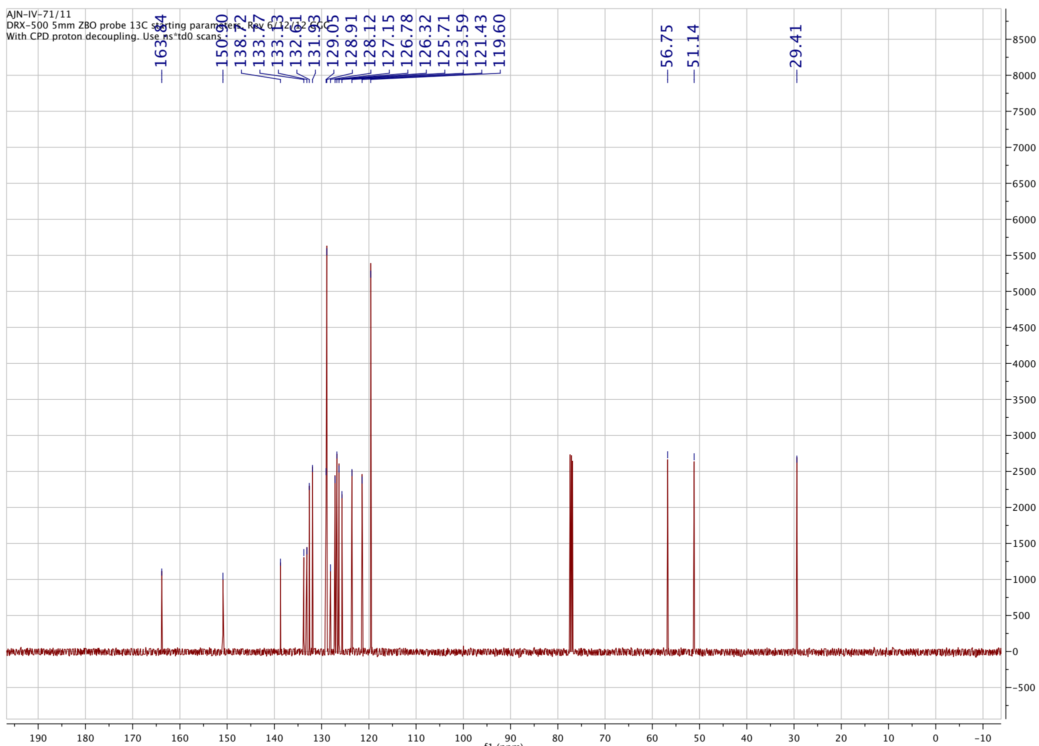
5d

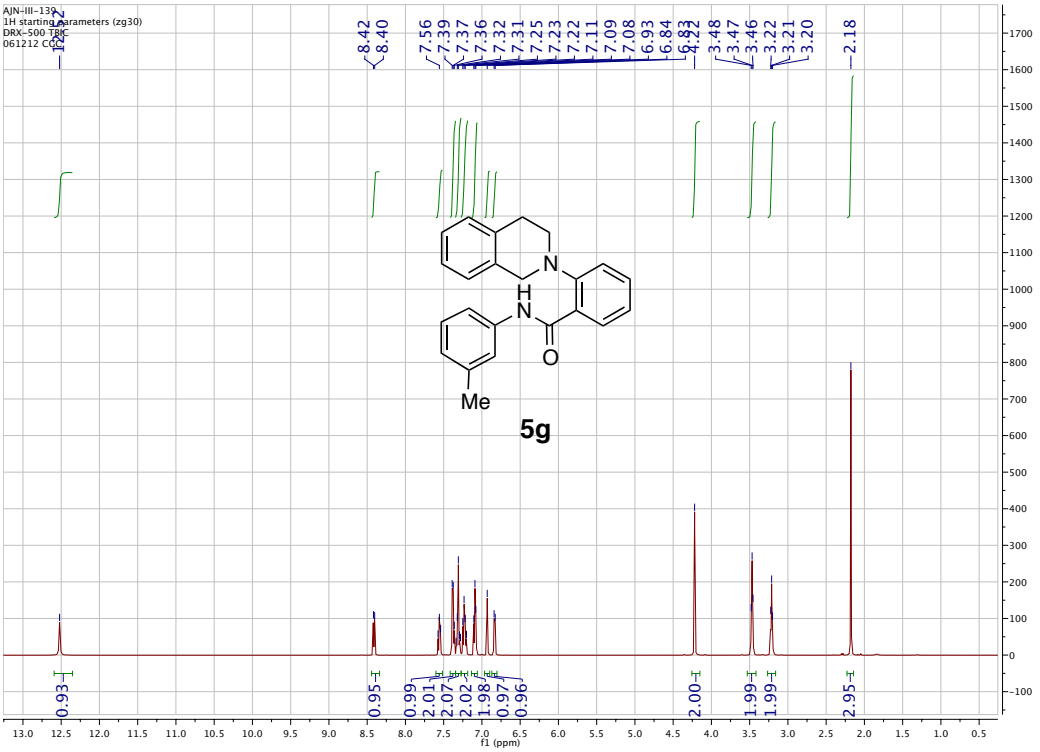

AJN-III-87/11
DRX-500 5mm ZBO probe 13C starting parameters (zgpg30)
With CPD proton decoupling. Use ns*td0 scans
166.16
151.88
147.00
145.50
133.48
133.01
132.60
131.62
128.92
128.57
127.51
126.90
126.28
126.18
125.57
123.71
121.35
57.27
50.11
43.27
29.58
f1 (ppm)

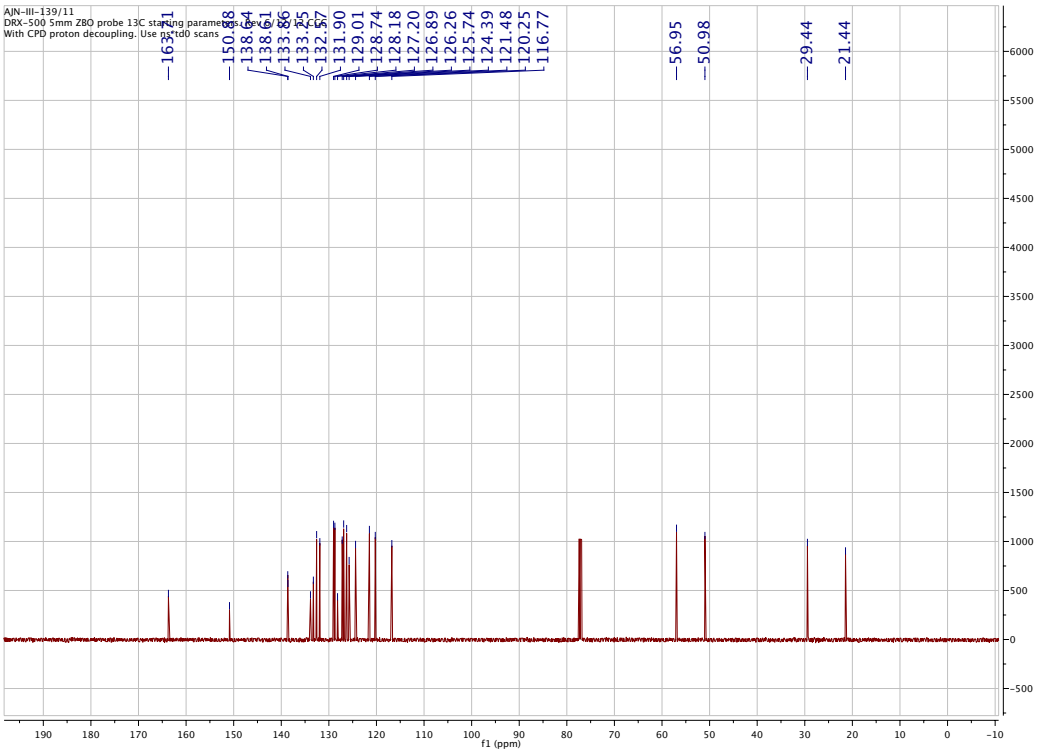

AJN-III-95/10
1H starting parameters (zg30)
DRX-500 TBIC
9.97
8.27
8.25
7.45
7.28
7.27
7.25
7.21
7.19
7.18
7.17
7.08
7.07
7.02
7.00
6.79
6.62
4.58
4.57
4.13
3.42
3.24
3.23
3.21
2.77
2.76
2.75
N
H
N
MeO
O
5e
0.88
0.92
0.96
2.30
3.98
0.98
1.04
0.95
0.94
1.94
2.00
2.94
1.99
1.98
f1 (ppm)


AJN-III-95/11
With CPD proton decoupling.
151.10
129.02
128.63
126.44
126.31
126.00
110.13
55.24
54.77
51.59
39.07
28.97
f1 (ppm)

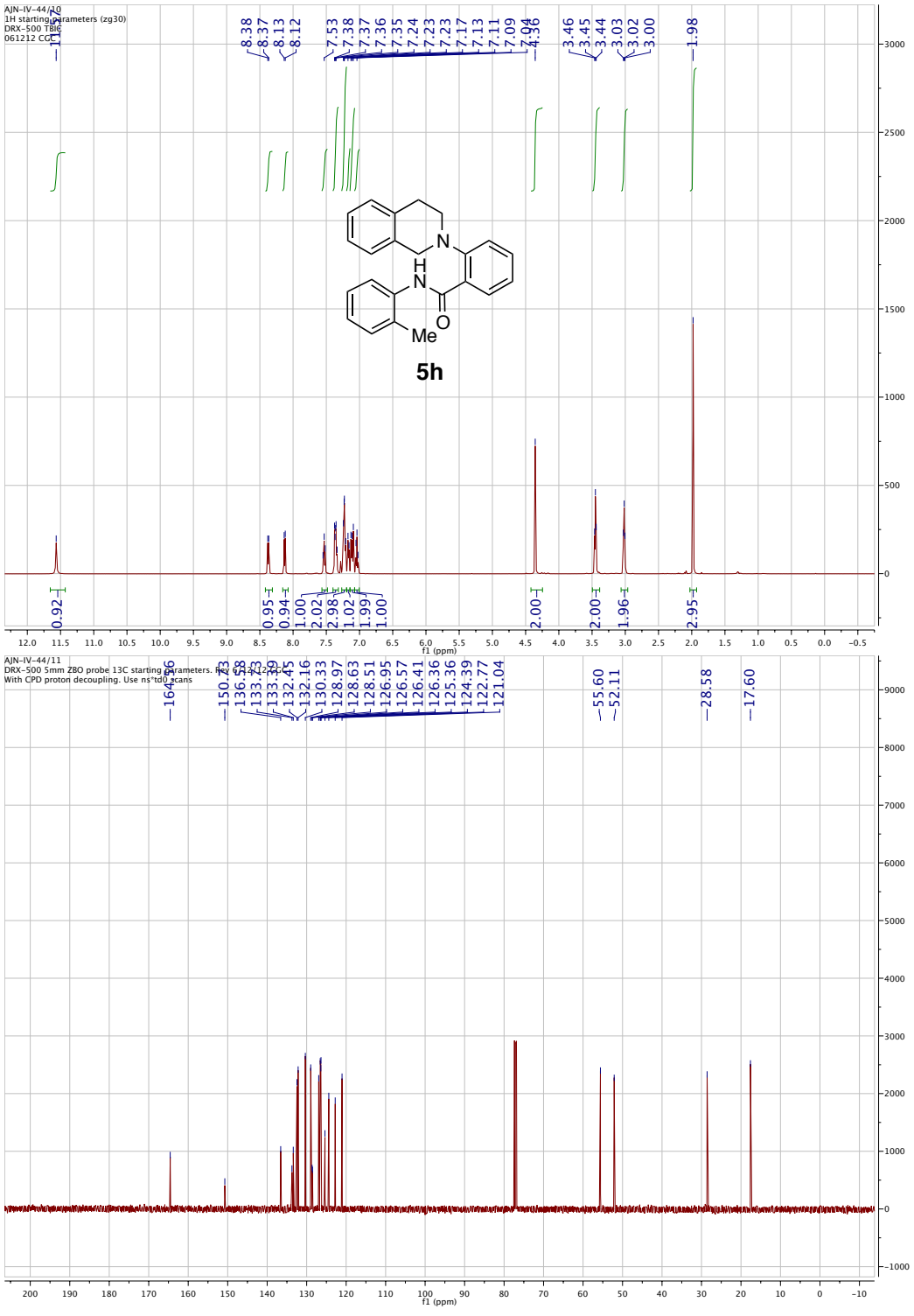

AJN-IV-71/10
1H starting parameters (zg30)
DRX-500 TBIC
061212 CDCl3
12.51
8.41
8.40
7.56
7.39
7.37
7.32
7.31
7.29
7.28
7.21
7.20
7.19
7.17
7.09
7.08
7.02
4.23
3.47
3.46
3.45
3.21
3.20
3.18
H
N
N
O
5f
0.94
0.93
0.99
2.00
4.05
3.03
1.01
0.99
2.00
2.00
2.00
f1 (ppm)

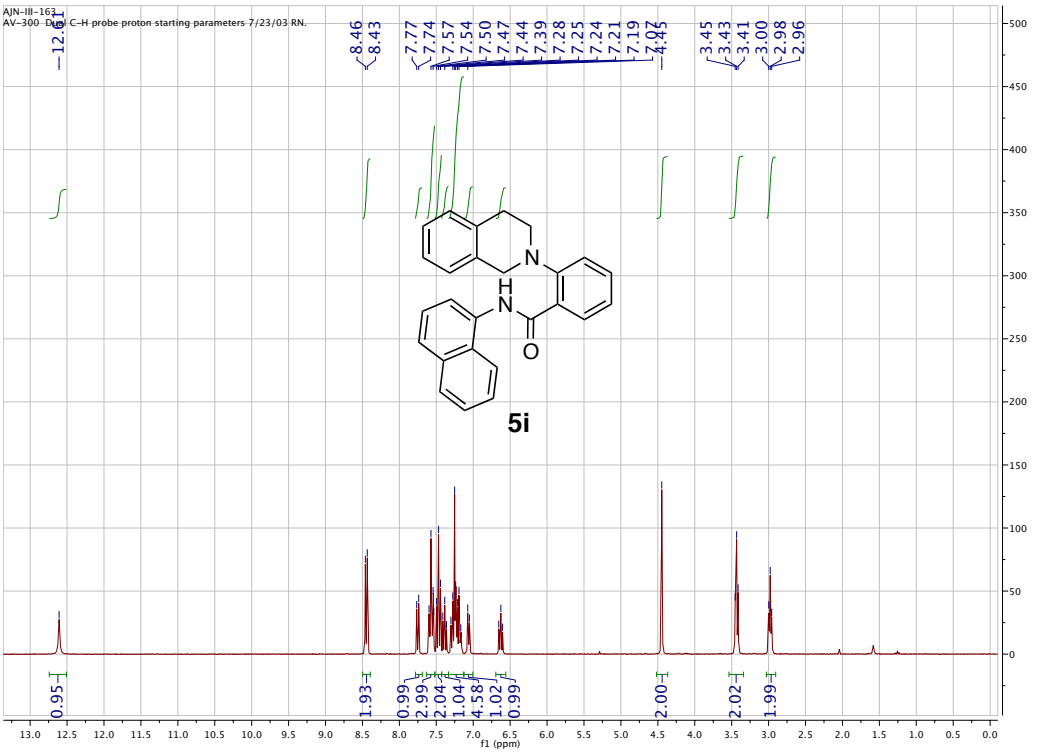

AJN-IV-71/11
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12 SGC
With CPD proton decoupling. Use ns*td0 scans.
163.64
150.90
138.72
133.77
133.13
132.61
131.93
129.05
128.91
128.12
127.15
126.78
126.32
125.71
123.59
121.43
119.60
56.75
51.14
29.41
f1 (ppm)

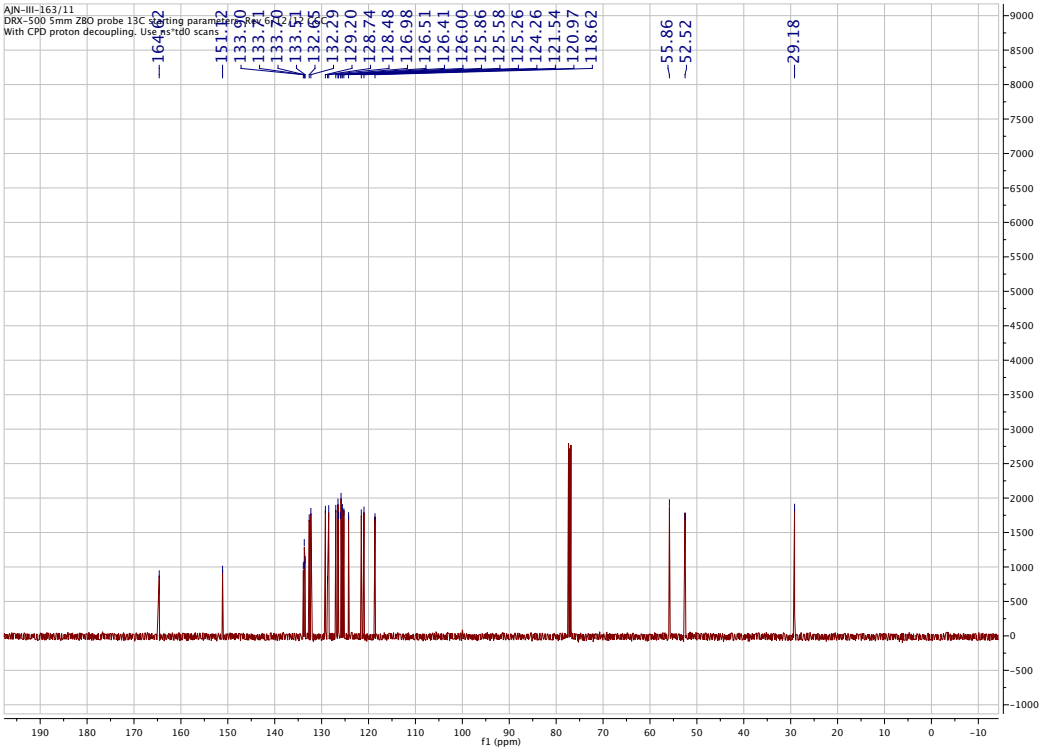

AJN-III-139
1H starting parameters (zg30)
DRX-500 TBIC
061212 CDCl3
8.42
8.40
7.56
7.39
7.37
7.36
7.32
7.31
7.25
7.23
7.22
7.11
7.09
7.08
6.93
6.84
6.83
4.22
3.48
3.47
3.46
3.22
3.21
3.20
2.18
0.93
0.95
0.99
2.01
2.07
2.02
1.98
0.97
0.96
2.00
1.99
1.99
2.95
f1 (ppm)

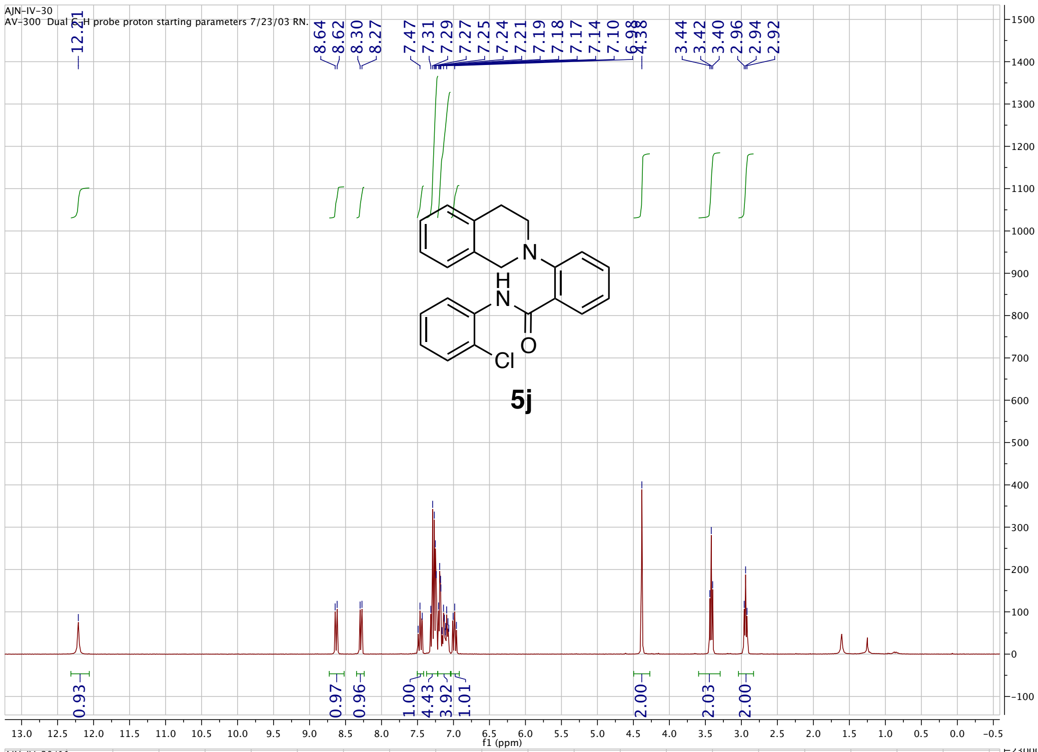

AJN-III-139/11
DRX-500 5mm ZBO probe 13C starting parameters (zgpg30)
With CPD proton decoupling. Use ns >td0 scans
162.11
150.08
138.64
138.61
133.66
133.55
132.67
131.90
129.01
128.74
128.18
127.20
126.89
126.26
125.74
124.39
121.48
120.25
116.77
56.95
50.98
29.44
21.44
f1 (ppm)

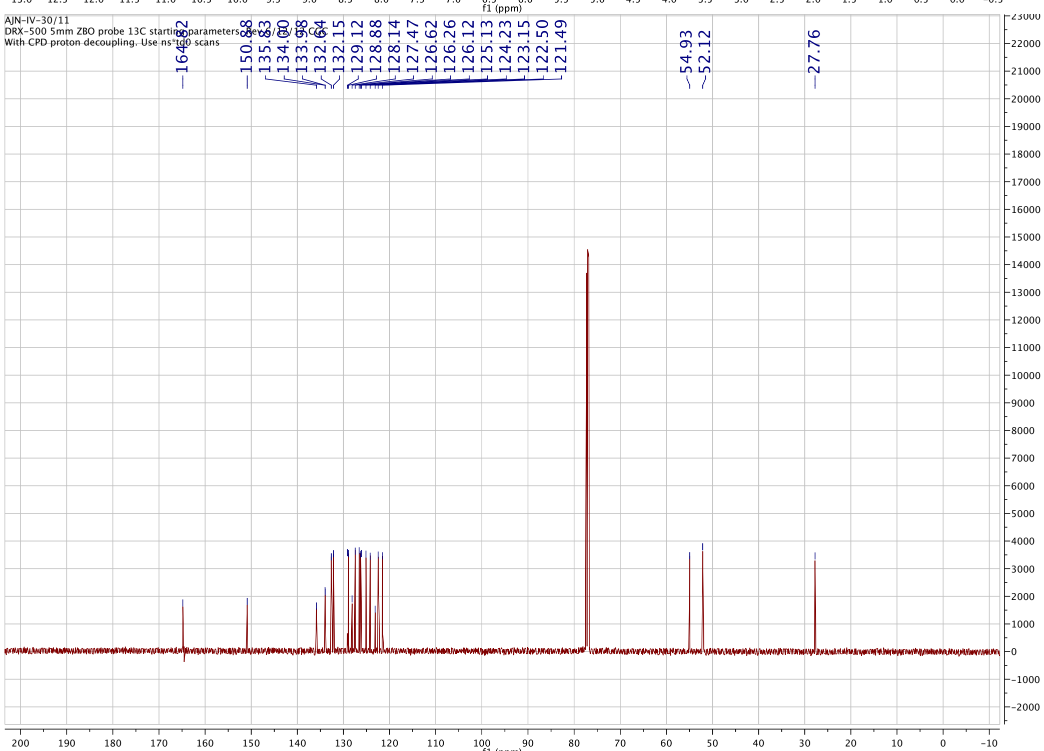
5g

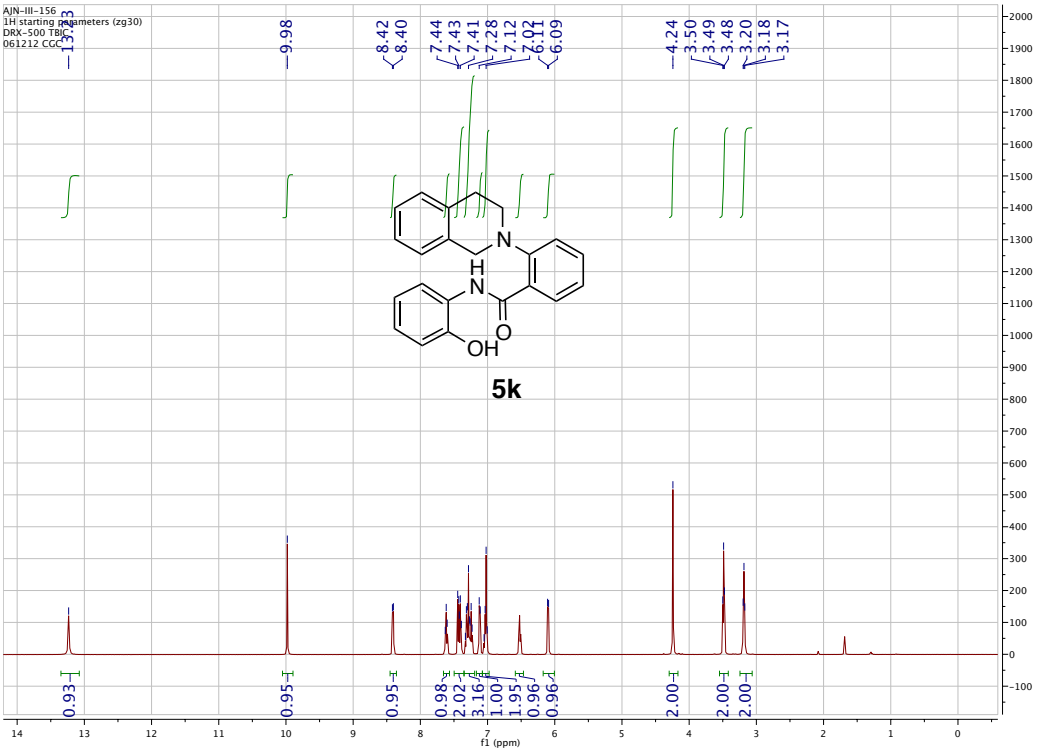

AJN-IV-44/10
1H starting parameters (zg30)
DRX-500 TBI
061212 CC
11.12
8.38
8.37
8.13
8.12
7.53
7.38
7.37
7.36
7.35
7.24
7.23
7.23
7.17
7.13
7.11
7.09
7.04
4.36
3.46
3.45
3.44
3.03
3.02
3.00
1.98
N
H
N
O
Me
5h
0.92
0.95
0.94
1.00
2.02
2.98
1.02
1.99
1.00
2.00
2.00
1.96
2.95
f1 (ppm)
AJN-IV-44/11
DRX-500 5mm ZBO probe 13C starting parameters.
With CPD proton decoupling. Use ns*td0 scans
164.96
150.23
136.58
133.73
133.39
132.45
132.16
130.33
128.97
128.63
128.51
126.95
126.57
126.41
126.36
125.36
124.39
122.77
121.04
55.60
52.11
28.58
17.60
f1 (ppm)

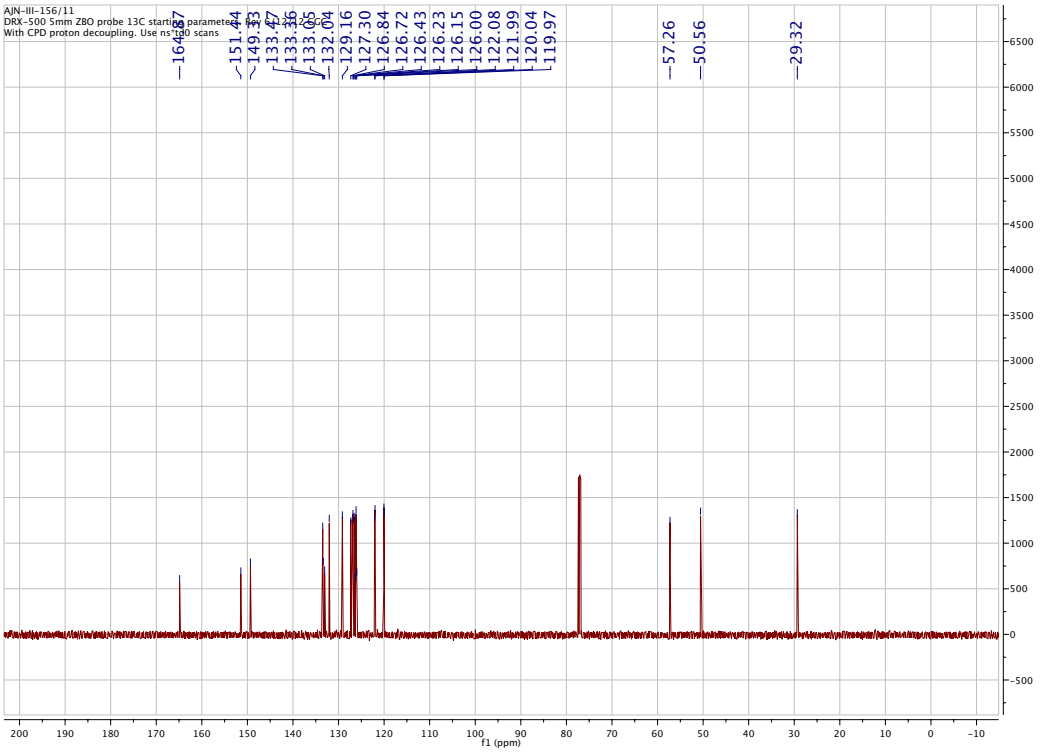

AJN-III-163
AV-300 Dual C-H probe proton starting parameters 7/23/03 RN.
12.41
8.46
8.43
7.77
7.74
7.57
7.54
7.50
7.47
7.44
7.39
7.28
7.25
7.24
7.21
7.19
7.07
4.45
3.45
3.43
3.41
3.00
2.98
2.96
N
H
N
O
5i
0.95
1.93
0.99
2.99
2.04
1.04
4.58
1.02
0.99
2.00
2.02
1.99
f1 (ppm)

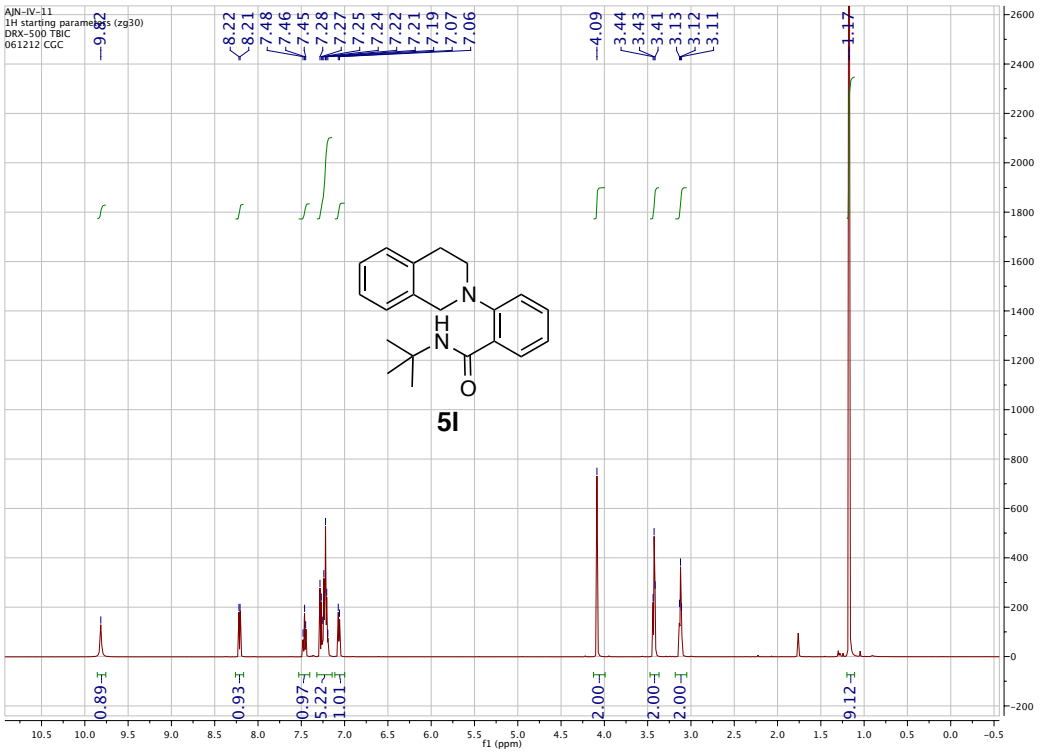

AJN-III-163/11
DRX-500 5mm ZBO probe 13C starting parameters 9/4/12 RK
With CPD proton decoupling. Use ns*td0 scans
164.62
151.22
133.40
133.31
133.20
133.11
132.65
132.29
129.20
128.74
128.48
126.98
126.51
126.41
126.00
125.86
125.58
125.26
124.26
121.54
120.97
118.62
55.86
52.52
29.18
f1 (ppm)


AJN-IV-30
AV-300 Dual 1H probe proton starting parameters 7/23/03 RN.
12.21
8.64
8.62
8.30
8.27
7.47
7.31
7.29
7.27
7.25
7.24
7.21
7.19
7.18
7.17
7.14
7.10
6.98
4.38
3.44
3.42
3.40
2.96
2.94
2.92
N
H
N
O
Cl
5j
0.93
0.97
0.96
1.00
4.43
3.92
1.01
2.00
2.03
2.00
f1 (ppm)

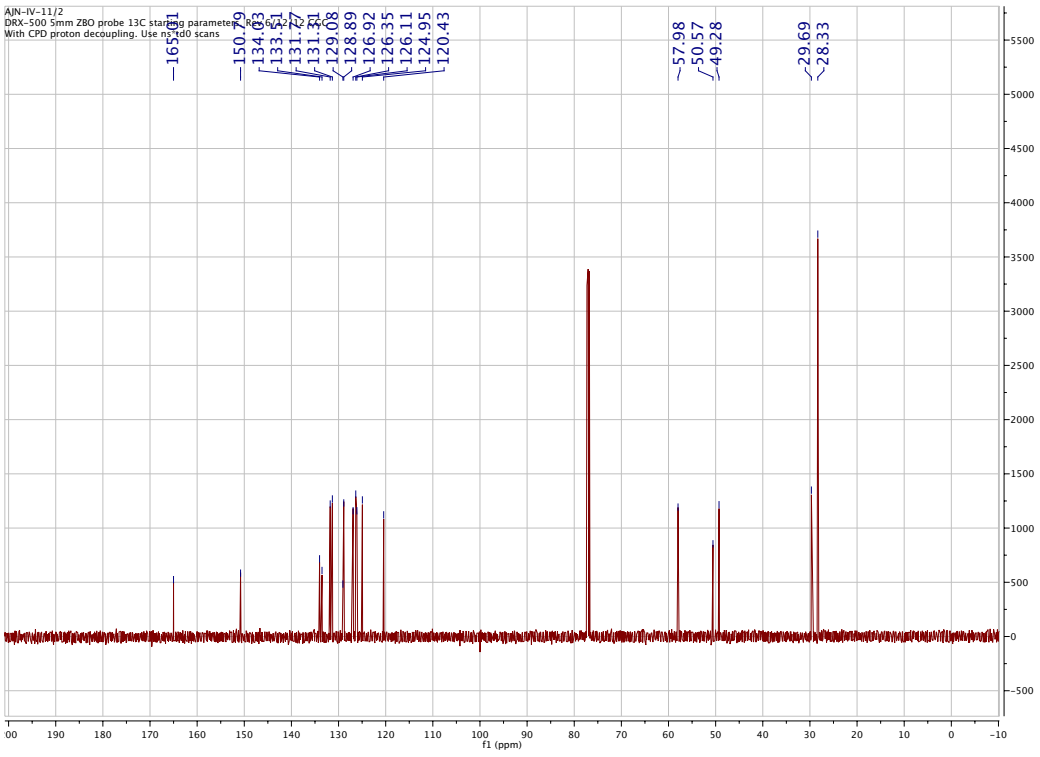

AJN-IV-30/11
DRX-500 5mm ZBO probe 13C starting parameters
With CPD proton decoupling. Use ns*100 scans
164.82
150.88
135.53
134.00
133.58
132.64
132.15
129.12
128.88
128.14
127.47
126.62
126.26
126.12
125.13
124.23
123.15
122.50
121.49
54.93
52.12
27.76
f1 (ppm)

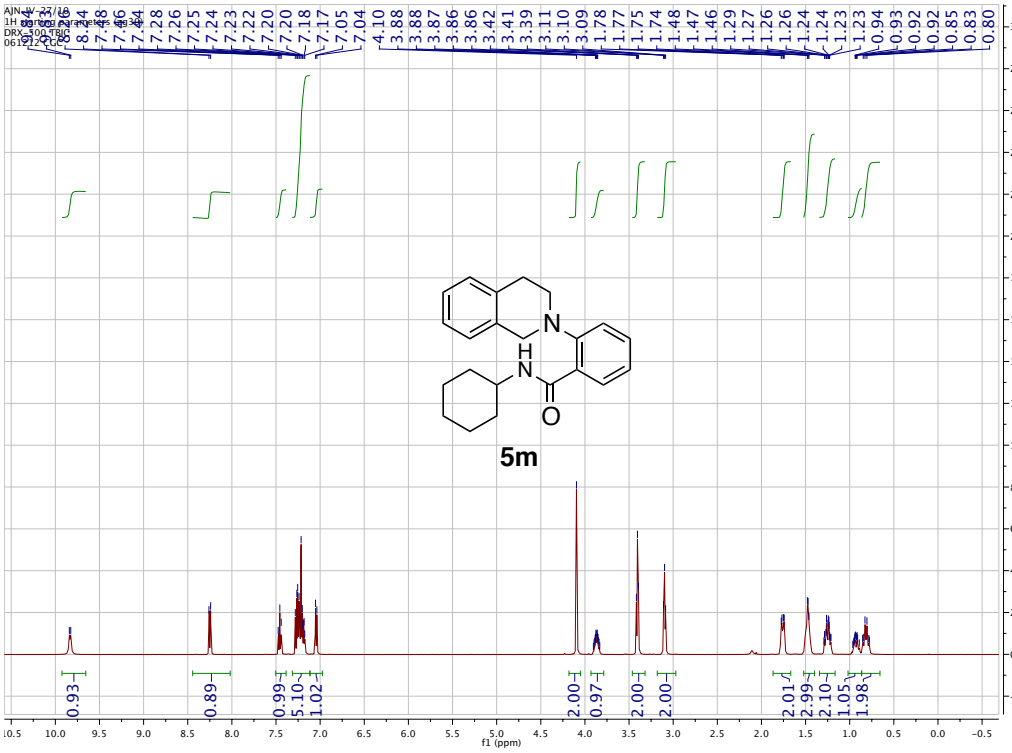

AJN-III-156
1H starting parameters (zg30)
DRX-500 TBI
061212 CGC
12.33
9.98
8.42
8.40
7.44
7.43
7.41
7.28
7.12
7.02
6.11
6.09
4.24
3.50
3.49
3.48
3.20
3.18
3.17
N
H
N
O
OH
5k
0.93
0.95
0.95
0.98
2.02
3.16
1.00
1.95
0.96
0.96
2.00
2.00
2.00
f1 (ppm)

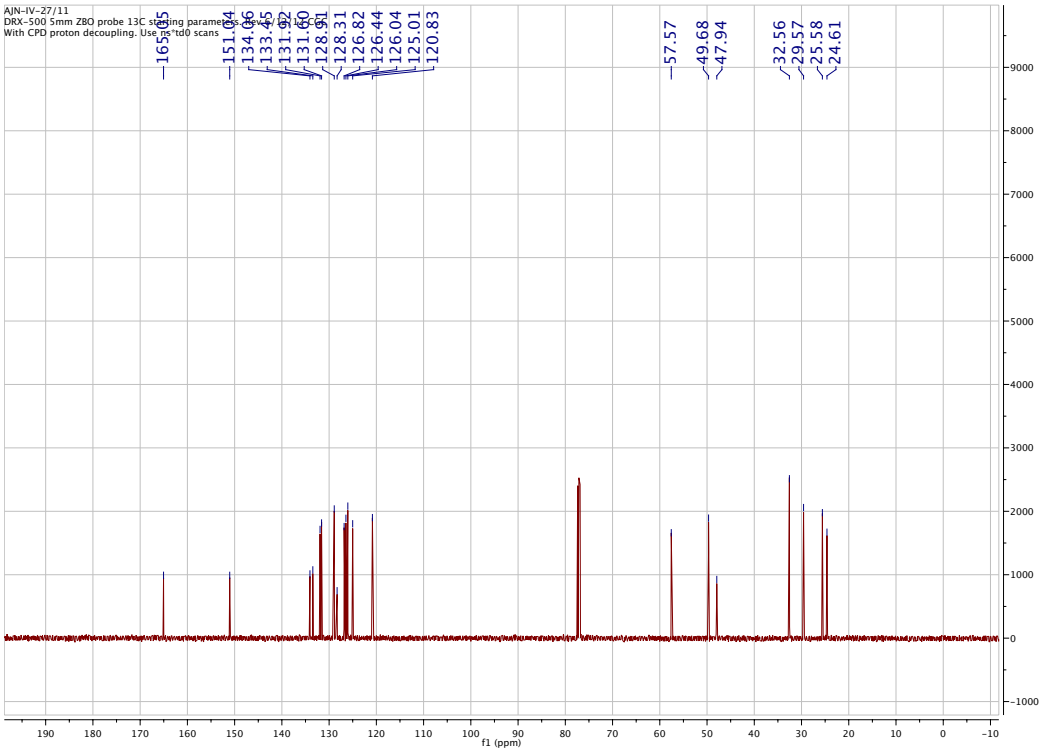

AJN-III-156/11
DRX-500 5mm ZBO probe 13C starting parameters (zgpg30)
With CPD proton decoupling. Use ns 4000 scans
164.87
151.44
149.33
133.47
133.36
133.05
132.04
129.16
127.30
126.84
126.72
126.43
126.23
126.15
126.00
122.08
121.99
120.04
119.97
57.26
50.56
29.32
f1 (ppm)

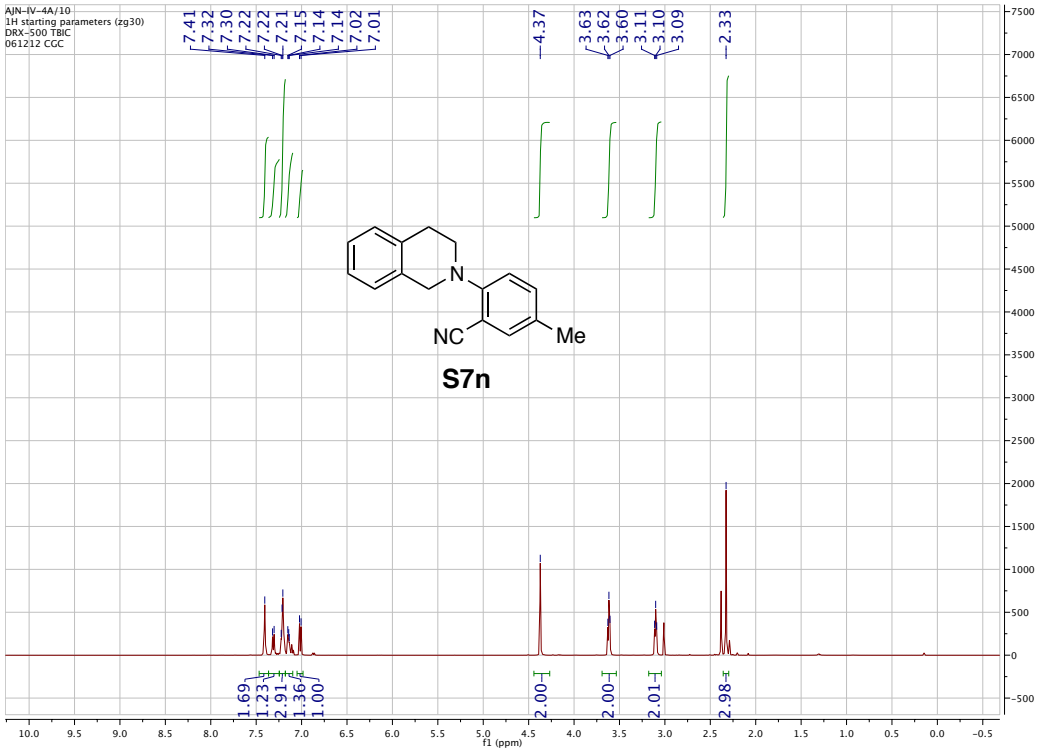

AJN-IV-11
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
9.82
8.22
8.21
7.48
7.46
7.45
7.28
7.27
7.25
7.24
7.22
7.21
7.19
7.07
7.06
4.09
3.44
3.43
3.41
3.13
3.12
3.11
1.17
0.89
0.93
0.97
5.22
1.01
2.00
2.00
2.00
9.12
f1 (ppm)

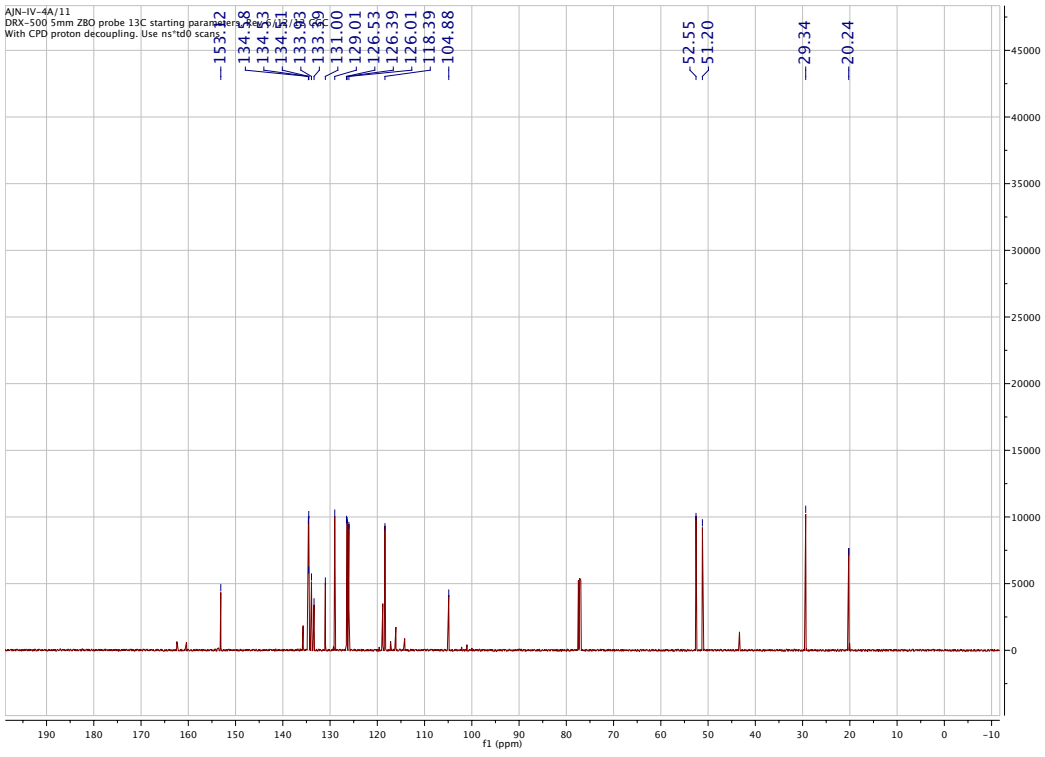
5l

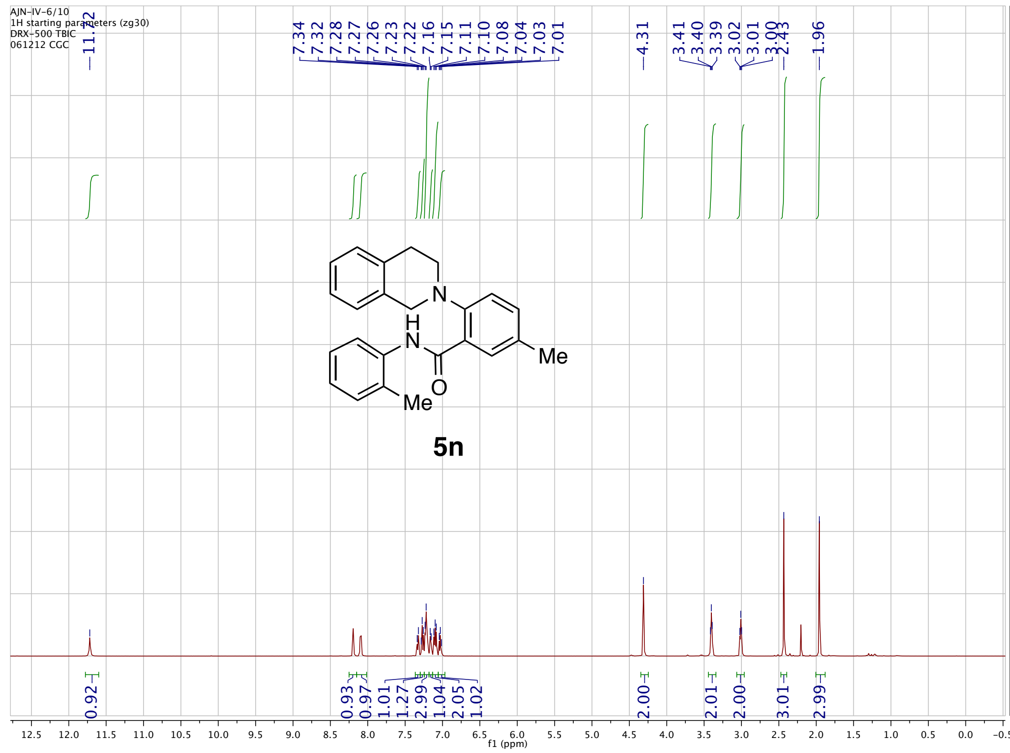

AJN-IV-11/2
DRX-500 5mm ZBO probe 13C starting parameters
With CPD proton decoupling. Use ns*td0 scans
165.11
150.29
134.03
133.21
131.77
131.21
129.08
128.89
126.92
126.35
126.11
124.95
120.43
57.98
50.57
49.28
29.69
28.33
f1 (ppm)

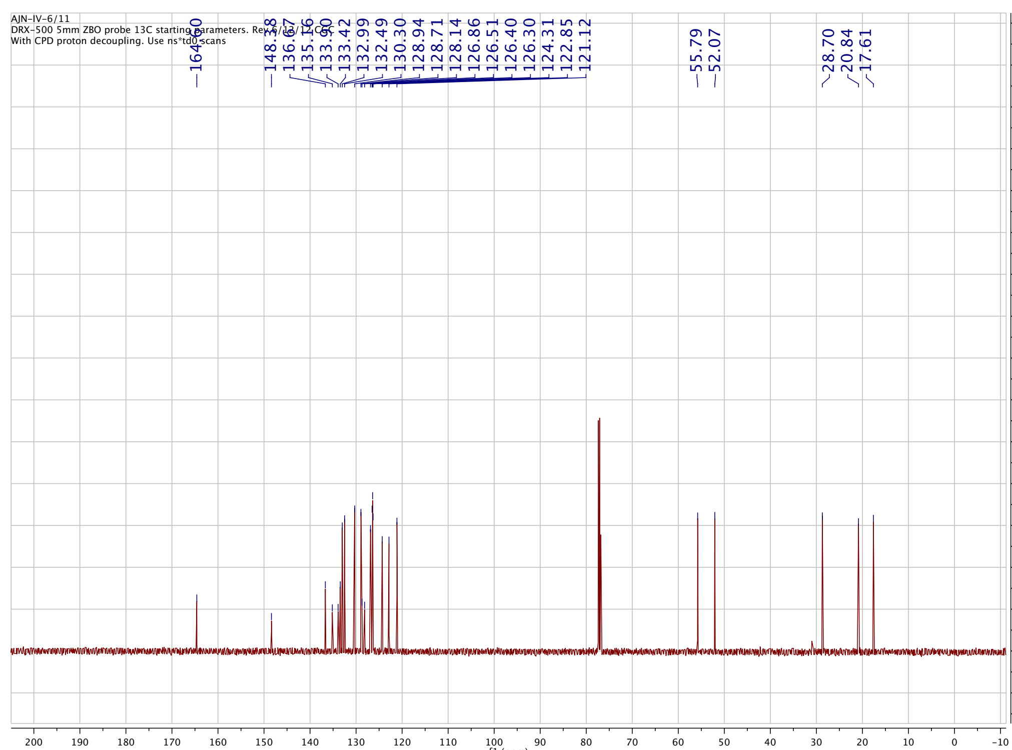

5m

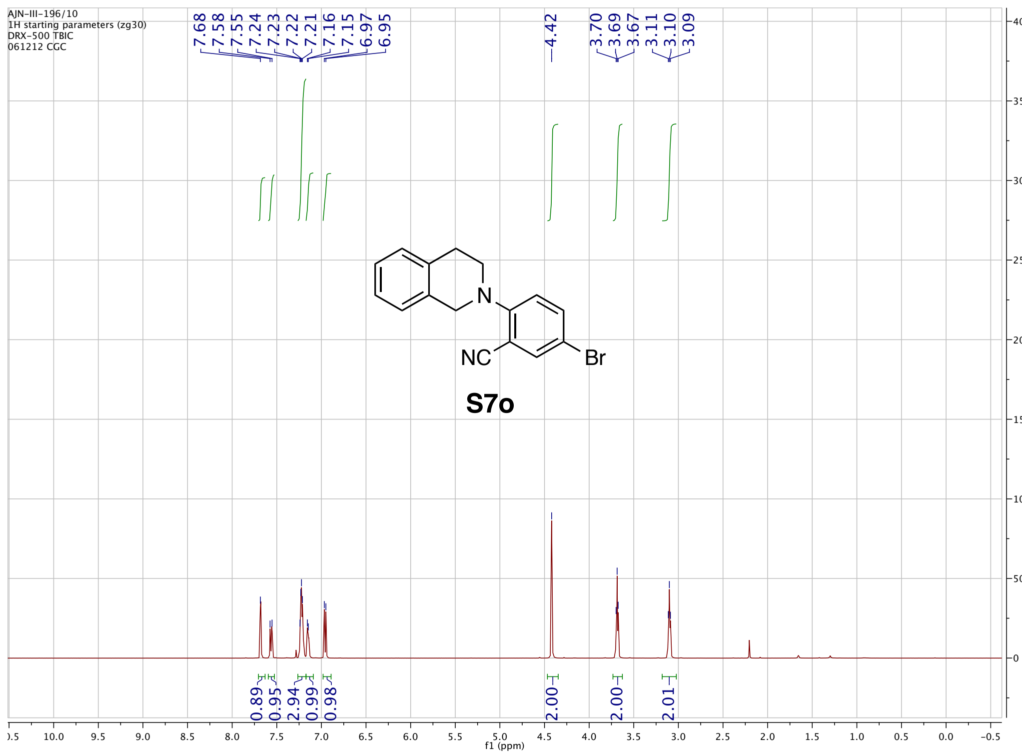


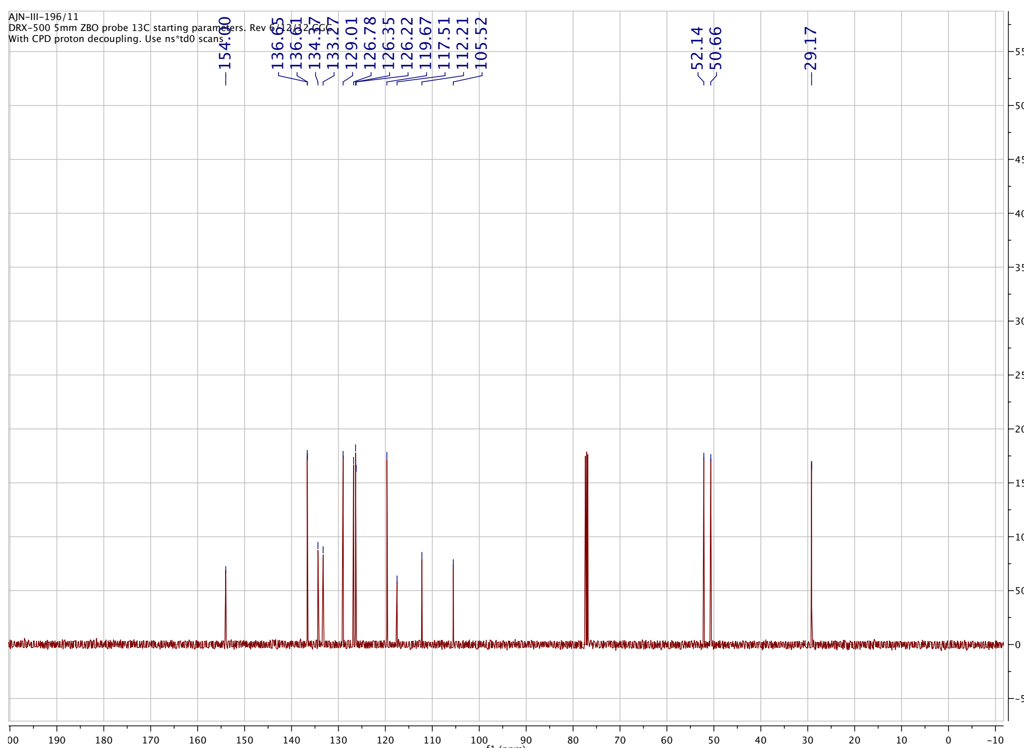

AJN-IV-4A/10
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
7.41
7.32
7.30
7.22
7.22
7.21
7.15
7.14
7.14
7.02
7.01
4.37
3.63
3.62
3.60
3.11
3.10
3.09
2.33
N
NC
Me
S7n
1.69
1.23
2.91
1.36
1.00
2.00
2.00
2.01
2.98
f1 (ppm)

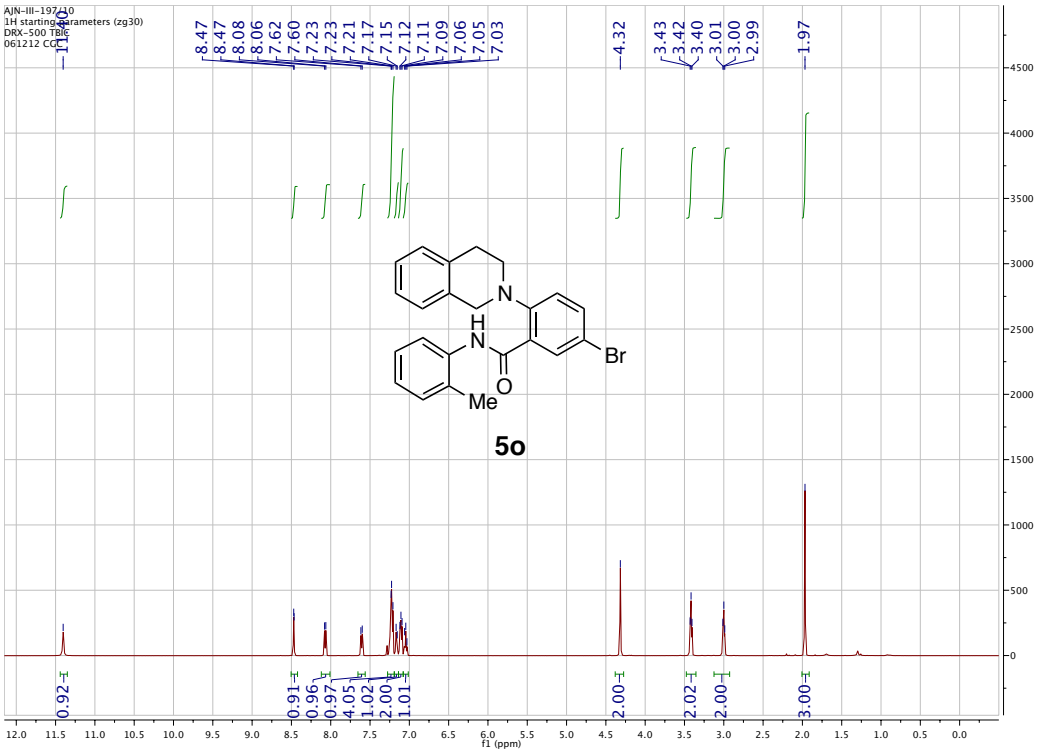

AJN-IV-4A/11
DRX-500 5mm ZBO probe 13C starting parameters (zgpg30)
With CPD proton decoupling. Use ns*td0 scans
153.42
134.58
134.53
134.51
133.63
133.49
131.00
129.01
126.53
126.39
126.01
118.39
104.88
52.55
51.20
29.34
20.24
f1 (ppm)

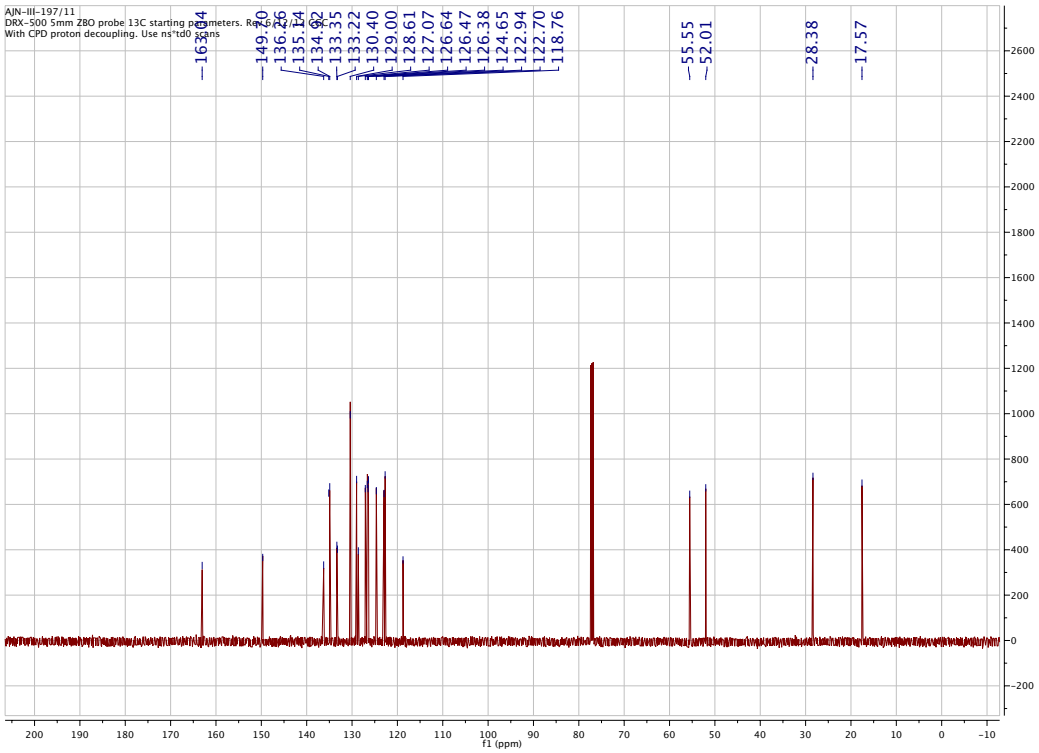

AJN-IV-6/10
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
5n
f1 (ppm)

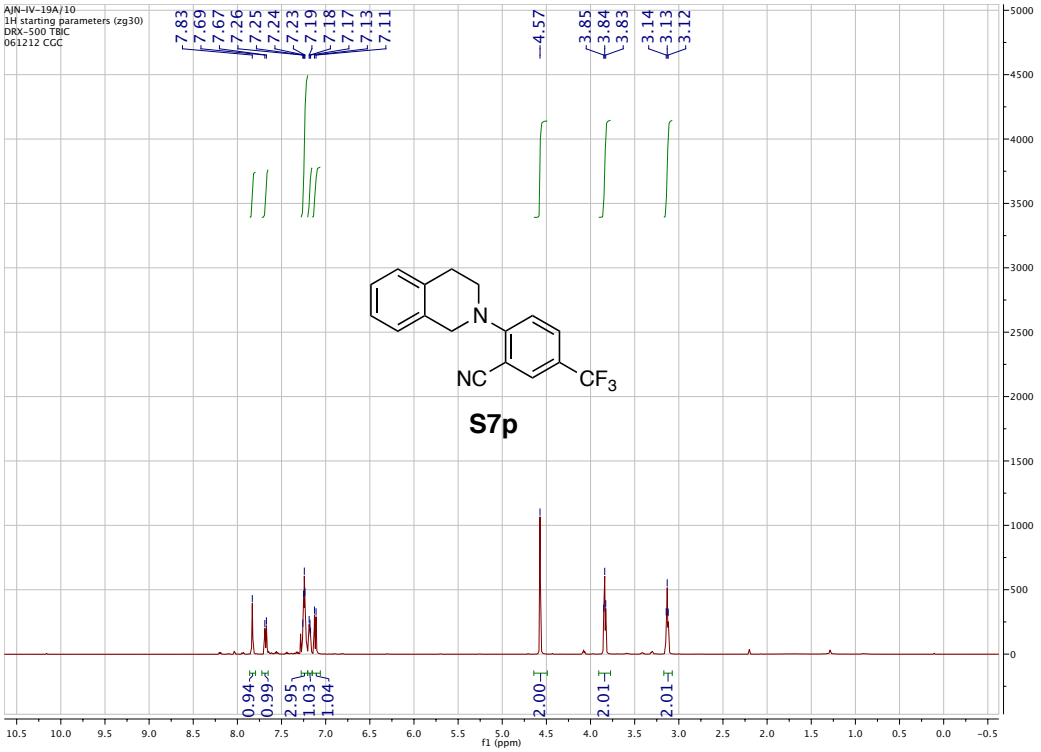

AJN-IV-6/11
DRX-500 5mm ZBO probe 13C starting parameters. Rev.6/15/12 CGC
With CPD proton decoupling. Use ns*td0 scans
f1 (ppm)

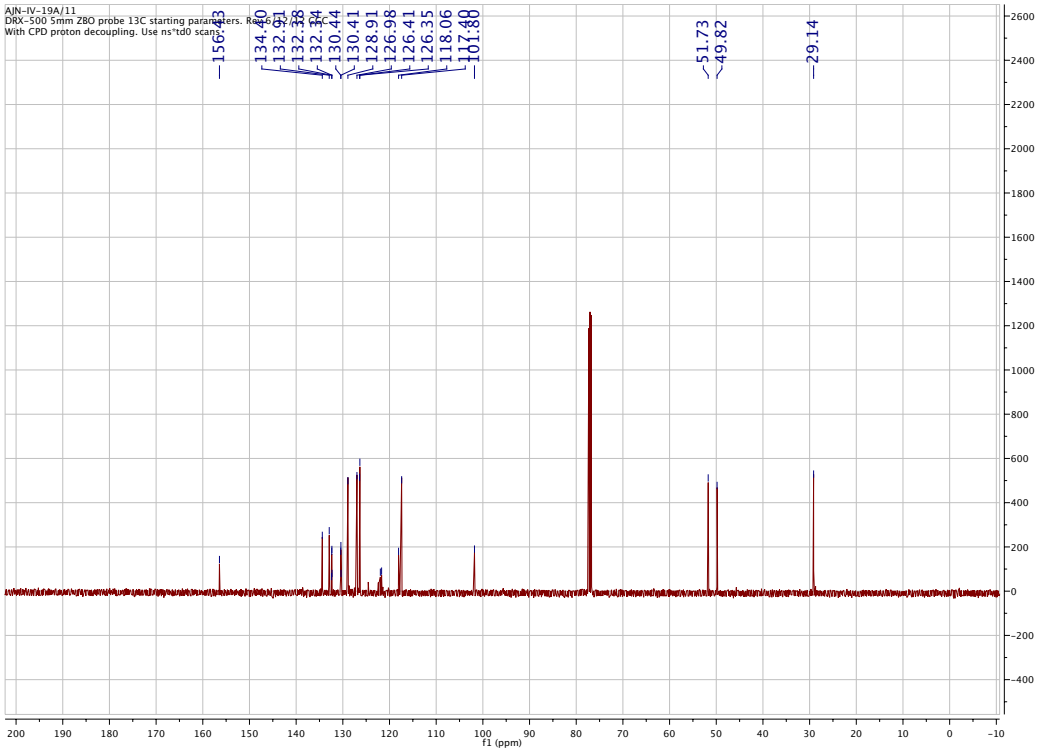

AJN-III-196/10
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
7.68 7.58 7.55 7.24 7.23 7.22 7.21 7.16 7.15 6.97 6.95
4.42
3.70 3.69 3.67 3.11 3.10 3.09
NC
N
Br
S7o
0.89 0.95 2.94 0.99 0.98
2.00 2.00 2.01
f1 (ppm)

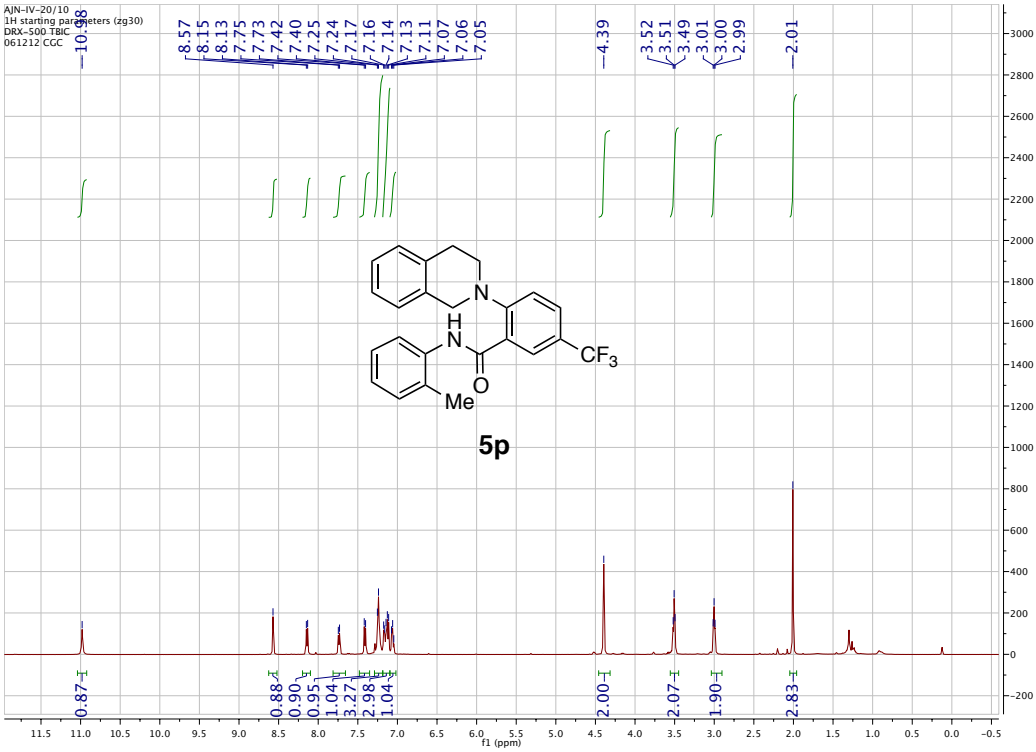

AJN-III-196/11
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6-12-12 CGC
With CPD proton decoupling. Use ns*td0 scans
154.00
136.65 136.61 134.37 133.27 129.01 126.78 126.35 126.22 119.67 117.51 112.21 105.52
52.14 50.66
29.17
f1 (ppm)

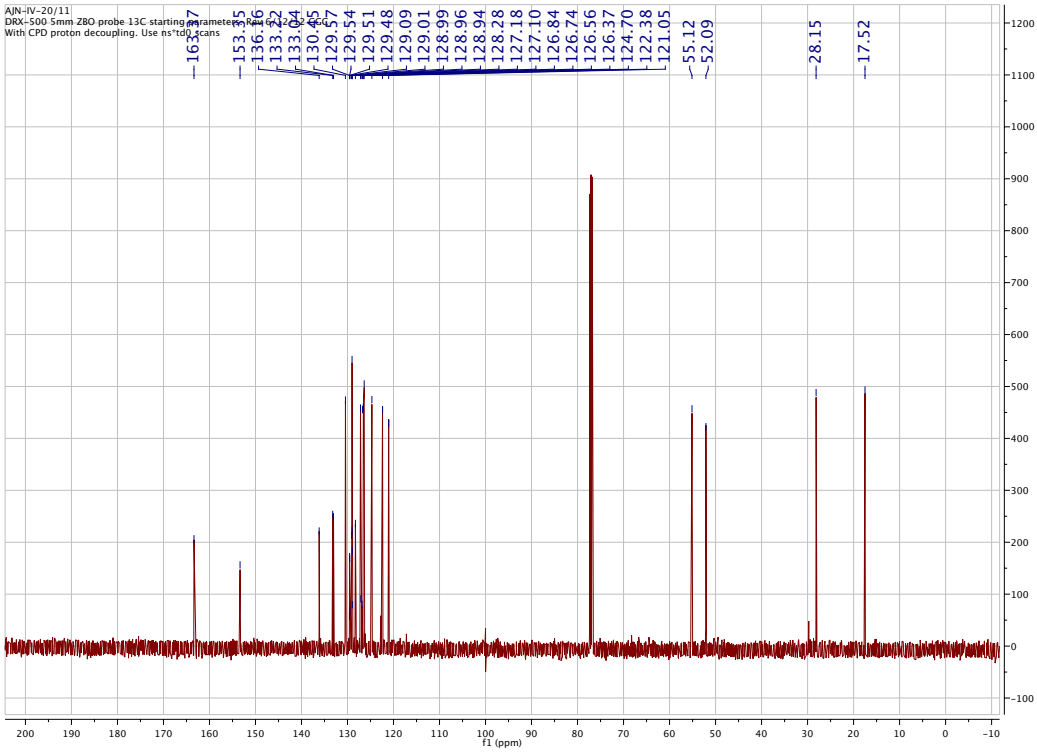

AJN-III-197/10
1H starting parameters (zg30)
DRX-500 TBI
061212 CC
11.97
8.47
8.47
8.08
8.06
7.62
7.60
7.23
7.23
7.21
7.17
7.15
7.12
7.11
7.09
7.06
7.05
7.03
4.32
3.43
3.42
3.40
3.01
3.00
2.99
1.97
N
H
N
O
Br
Me
5o
0.92
0.91
0.96
0.97
4.05
1.02
2.00
1.01
2.00
2.02
2.00
3.00
f1 (ppm)

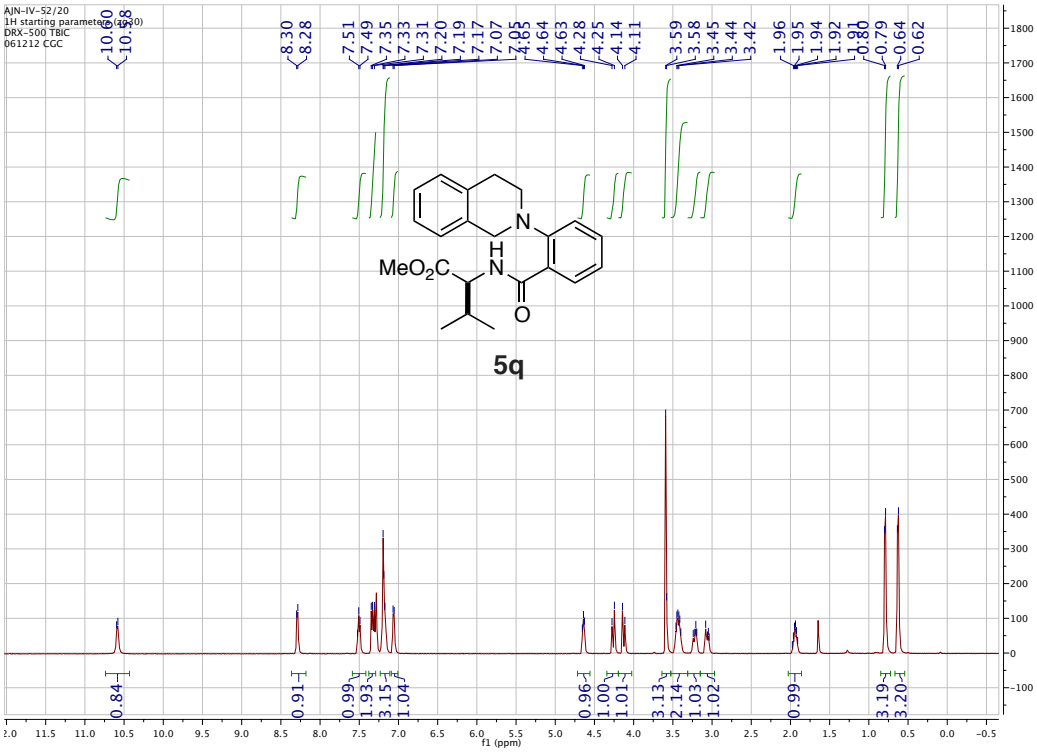

AJN-III-197/11
DRX-500 5mm ZBO probe 13C starting parameters. Re
With CPD proton decoupling. Use ns*td0 scans
163.04
149.70
136.26
135.14
134.62
133.35
133.22
130.40
129.00
128.61
127.07
126.64
126.47
126.38
124.65
122.94
122.70
118.76
55.55
52.01
28.38
17.57
f1 (ppm)

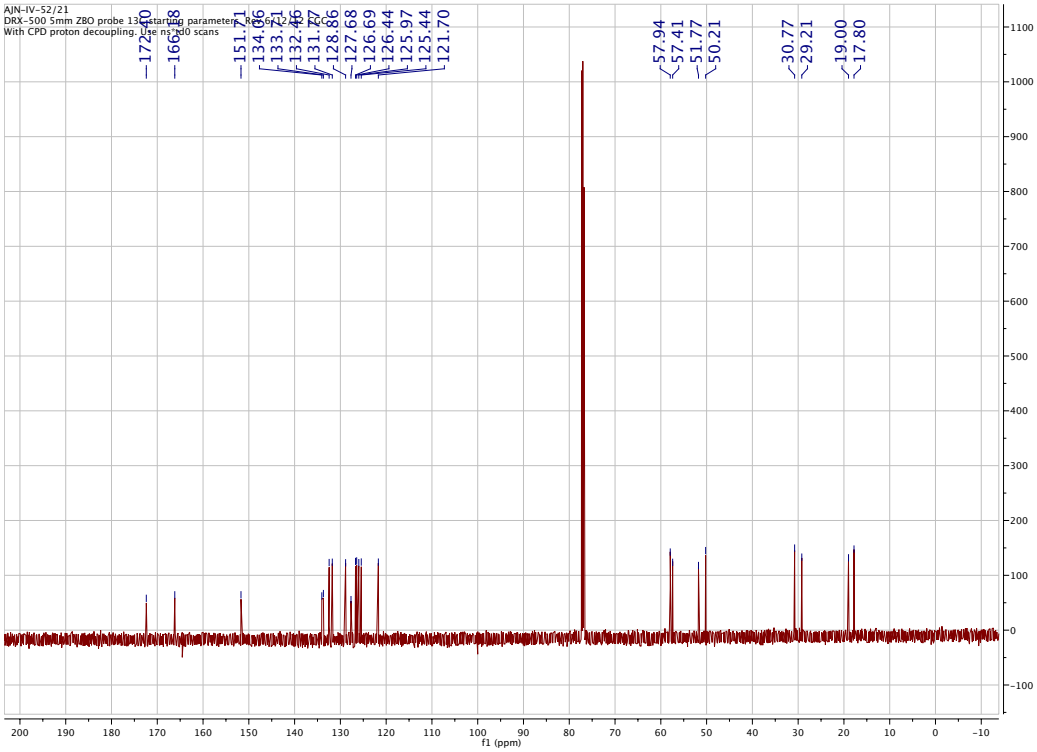

AJN-IV-19A/10
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
7.83
7.69
7.67
7.26
7.25
7.24
7.23
7.19
7.18
7.17
7.13
7.11
4.57
3.85
3.84
3.83
3.14
3.13
3.12
N
NC
CF3
S7p
0.94
0.99
2.95
1.03
1.04
2.00
2.01
2.01
f1 (ppm)

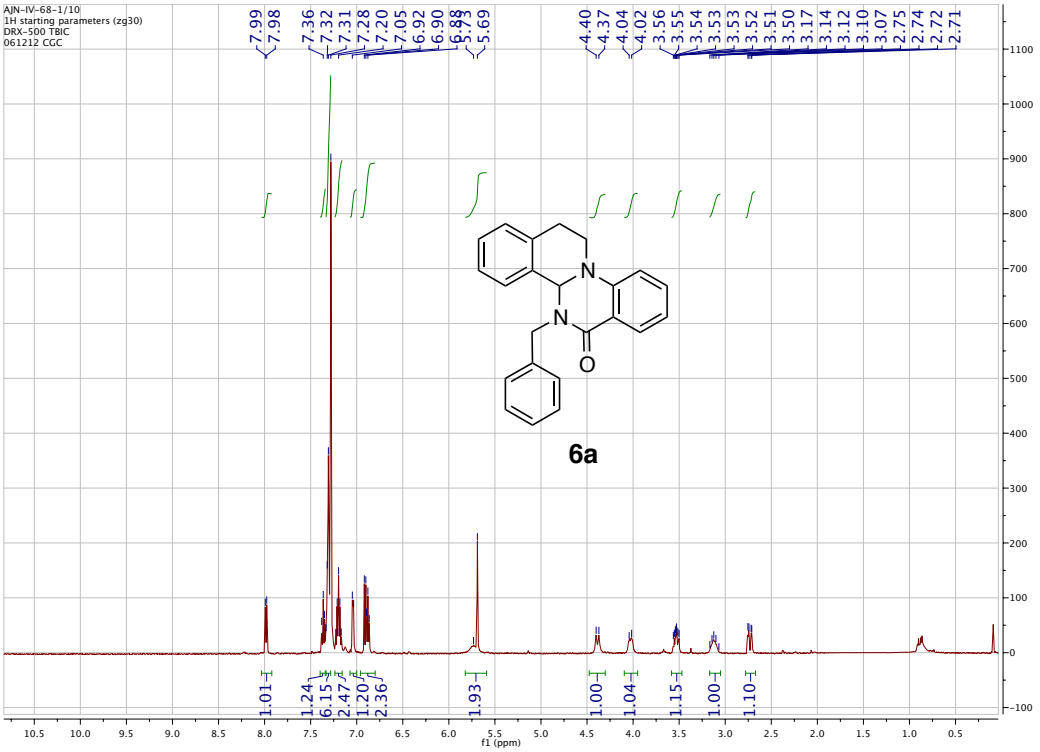

AJN-IV-19A/11
DRX-500 5mm ZBO probe 13C starting parameters. Ready for 13C
With CPD proton decoupling. Use ns*td0 scans.
156.23
134.40
132.91
132.38
132.34
130.44
130.41
128.91
126.98
126.41
126.35
118.06
117.40
101.80
51.73
49.82
29.14
f1 (ppm)

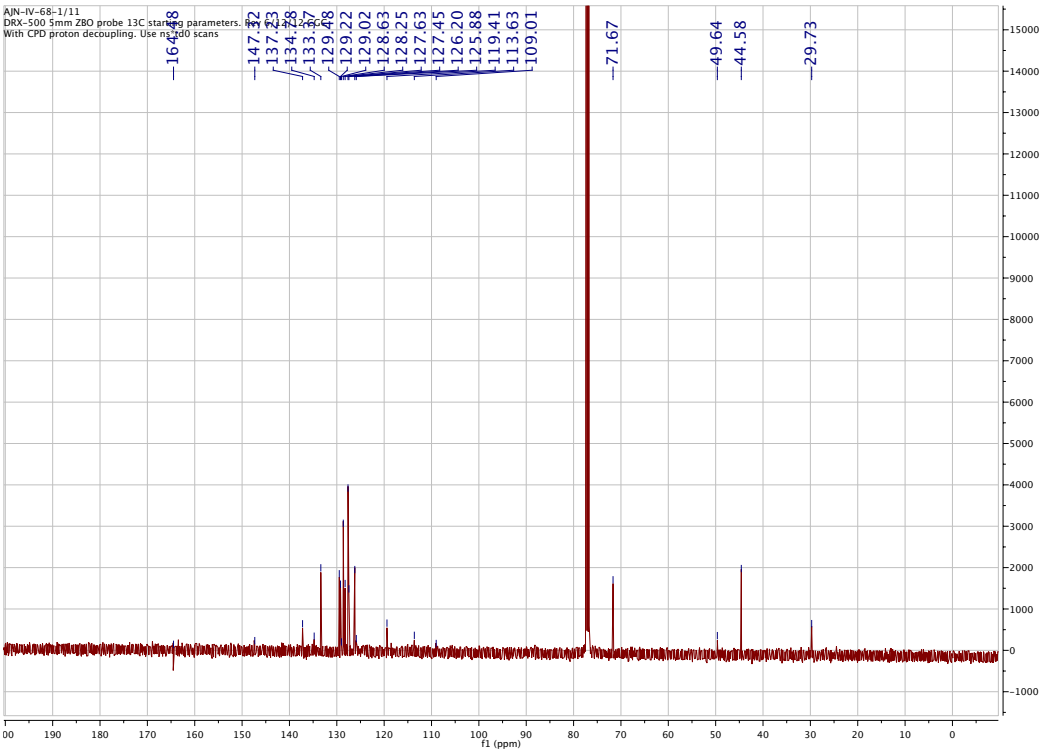

AJN-IV-20/10
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
10.98
8.57
8.15
8.13
7.75
7.73
7.42
7.40
7.25
7.24
7.17
7.16
7.14
7.13
7.11
7.07
7.06
7.05
4.39
3.52
3.51
3.49
3.01
3.00
2.99
2.01
N
H
N
O
CF3
Me
5p
0.87
0.88
0.90
0.95
1.04
3.27
2.98
1.04
2.00
2.07
1.90
2.83
f1 (ppm)


AJN-IV-20/11
DRX-500 5mm ZBO probe 13C starting parameters Raw 6 2012 CGC
With CPD proton decoupling. Use ns*td0 scans
163.37
153.45
136.46
133.22
133.04
130.65
129.57
129.54
129.51
129.48
129.09
129.01
128.99
128.96
128.94
128.28
127.18
127.10
126.84
126.74
126.56
126.37
124.70
122.38
121.05
55.12
52.09
28.15
17.52
f1 (ppm)

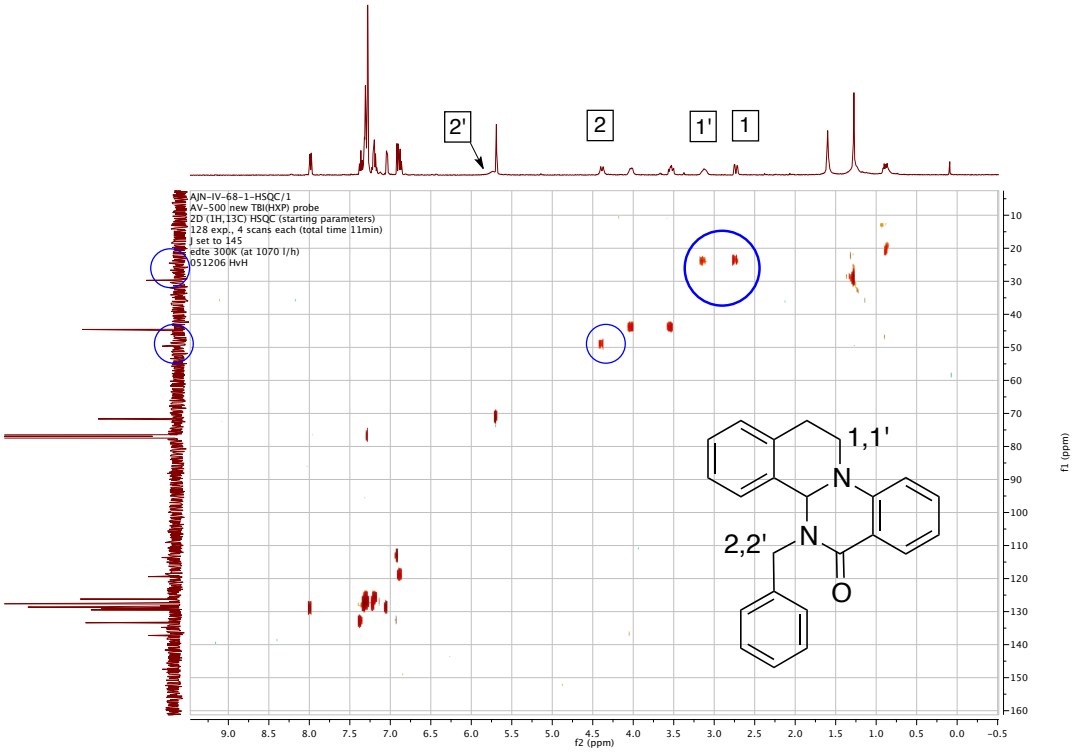

AJN-IV-52/20
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
10.60
10.58
8.30
8.28
7.51
7.49
7.35
7.33
7.31
7.20
7.19
7.17
7.07
7.05
4.65
4.64
4.63
4.28
4.25
4.14
4.11
3.59
3.58
3.45
3.44
3.42
1.96
1.95
1.94
1.92
1.91
0.80
0.79
0.64
0.62
MeO2C
H
N
N
O
5q
0.84
0.91
0.99
1.93
3.15
1.04
0.96
1.00
1.01
3.13
2.14
1.03
1.02
0.99
3.19
3.20
f1 (ppm)

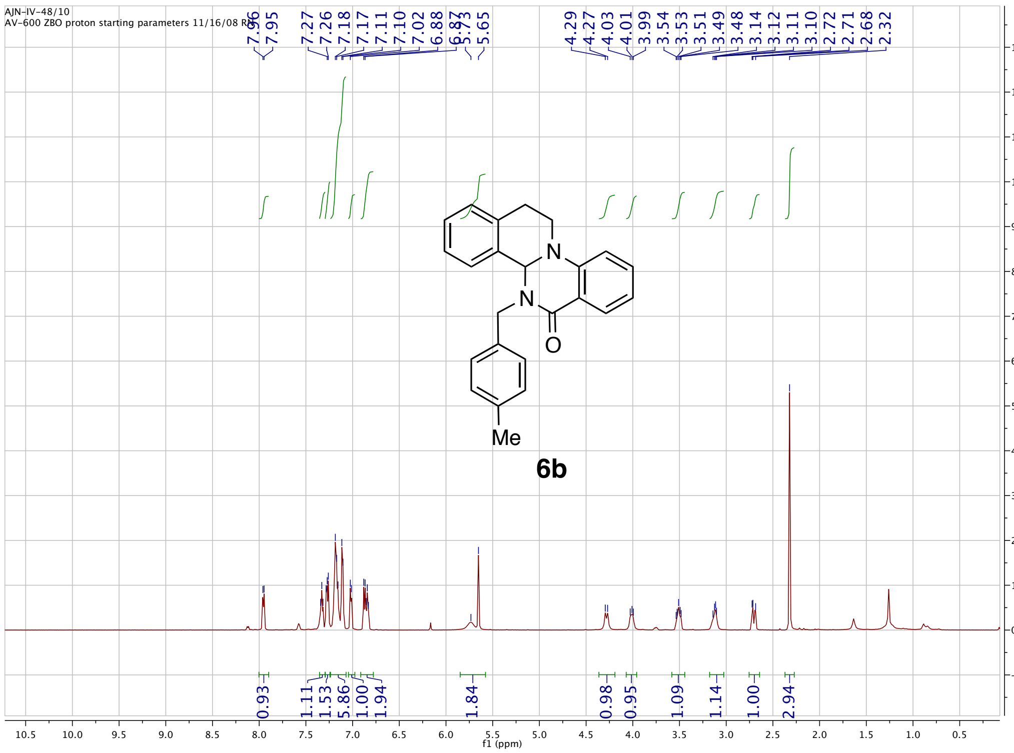

AJN-IV-52/21
DRX-500 5mm ZBO probe 13C starting parameters (zgpg30) CGC
With CPD proton decoupling. Use ns >d0 scans
172.00
166.68
151.71
134.86
133.71
132.46
131.87
128.86
127.68
126.69
126.44
125.97
125.44
121.70
57.94
57.41
51.77
50.21
30.77
29.21
19.00
17.80
f1 (ppm)

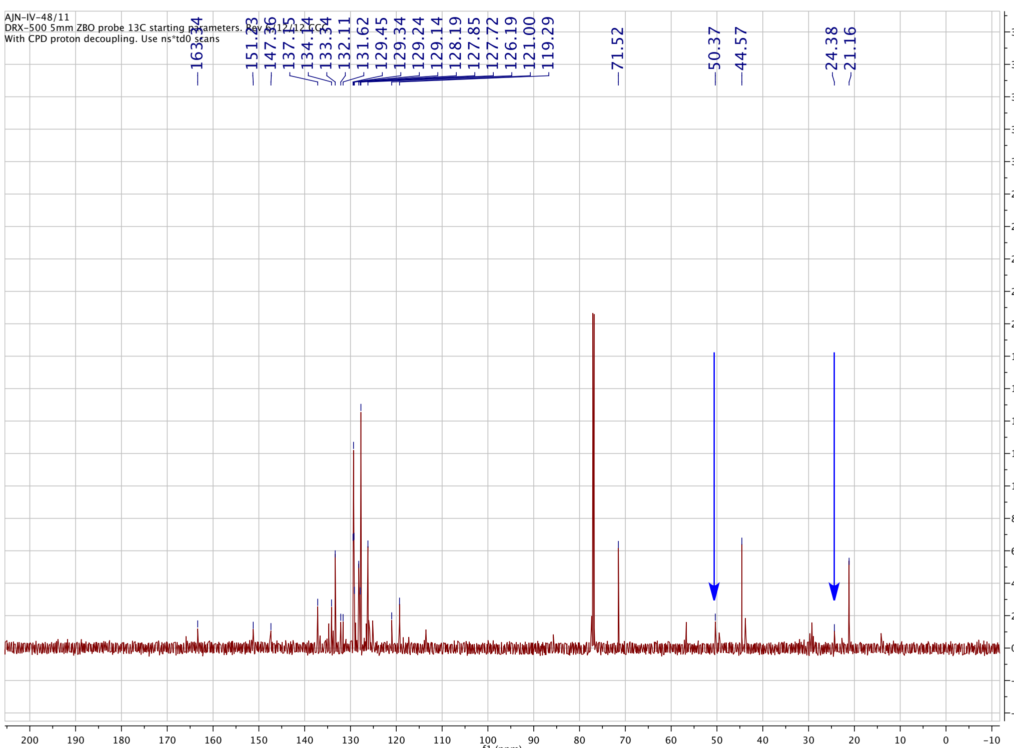

AJN-IV-68-1/10
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
7.99
7.98
7.36
7.32
7.31
7.28
7.20
7.05
6.92
6.90
6.88
6.73
5.69
4.40
4.37
4.04
4.02
3.56
3.55
3.54
3.53
3.53
3.52
3.51
3.50
3.17
3.14
3.12
3.10
3.07
2.75
2.74
2.72
2.71
1.01
1.24
6.15
2.47
1.20
2.36
1.93
1.00
1.04
1.15
1.00
1.10
N
N
O
6a
f1 (ppm)


AJN-IV-68-1/11
DRX-500 5mm ZBO probe 13C starting parameters.
With CPD proton decoupling. Use ns 7d0 scans
164.88
147.32
137.23
134.28
133.57
129.48
129.22
129.02
128.63
128.25
127.63
127.45
126.20
125.88
119.41
113.63
109.01
71.67
49.64
44.58
29.73
f1 (ppm)

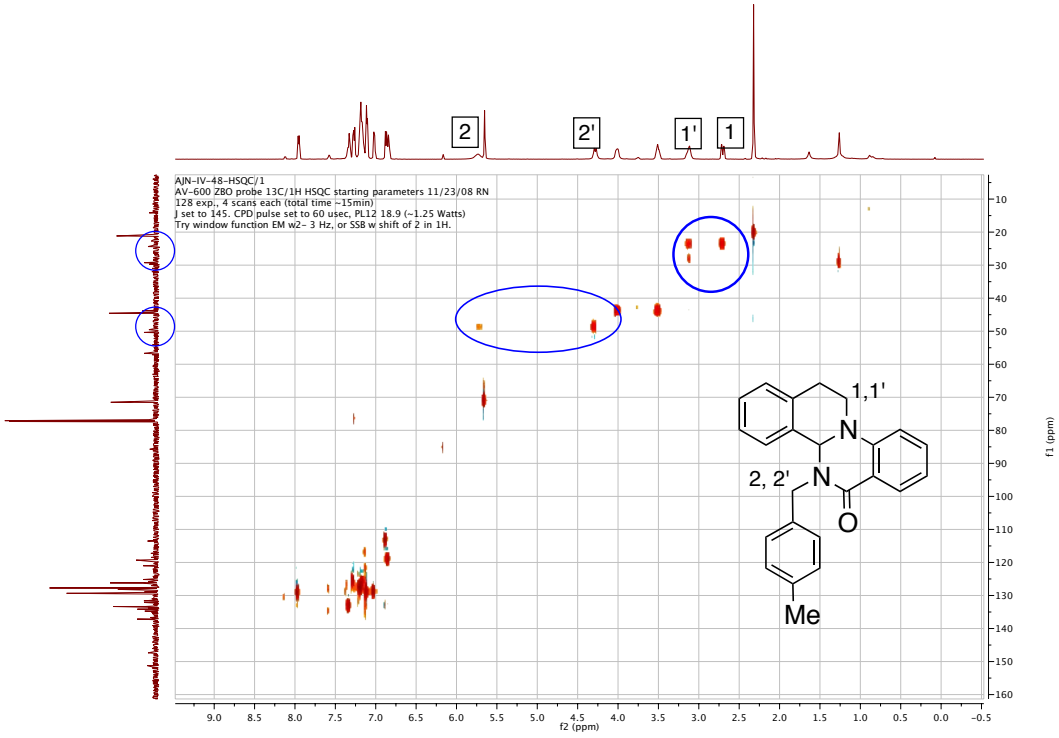
Only three of the five expected alkyl carbons show significant resonances in the ^{13}C NMR spectrum above. HSQC confirms that the remaining two carbons are present and correlate with diastereotopic sets 1,1' and 2,2', corresponding to tetrahydroisoquinoline methylene and benzylic protons respectively.

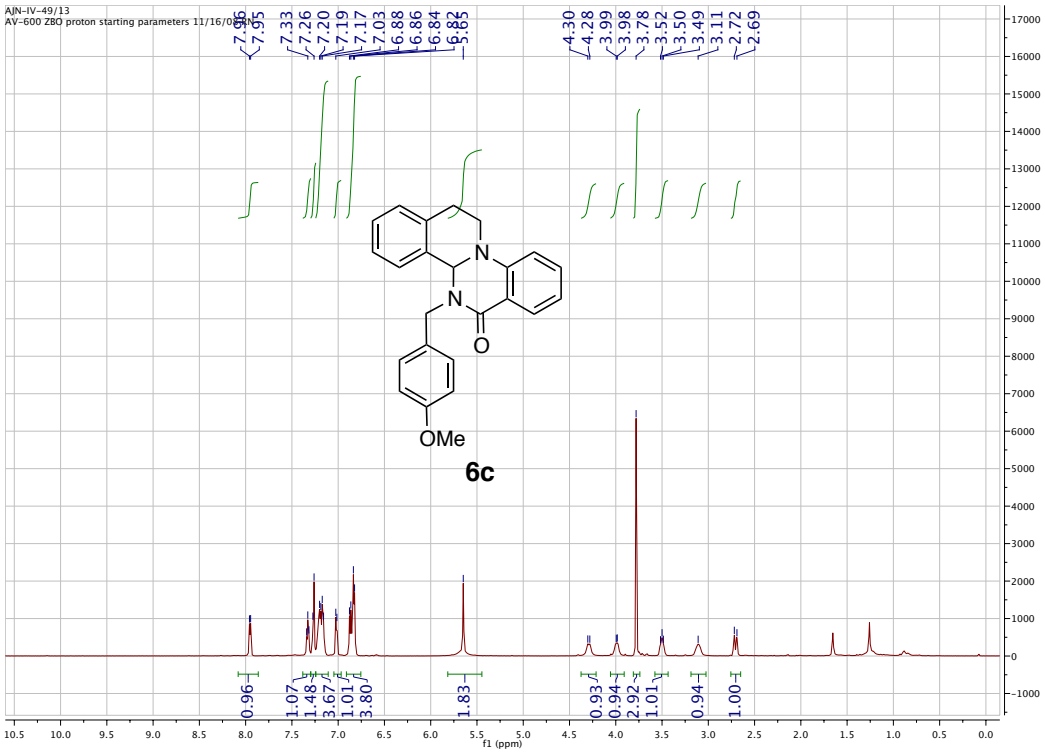


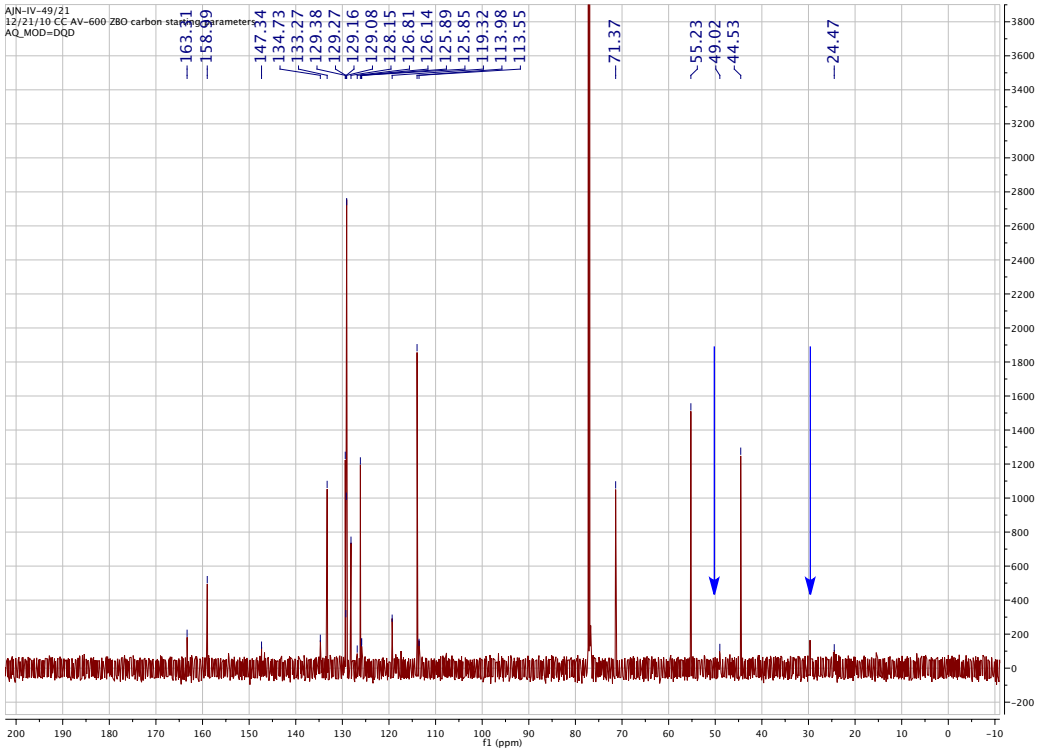

AJN-IV-48/10
AV-600 ZBO proton starting parameters 11/16/08 RK
7.96 7.95 7.27 7.26 7.18 7.17 7.11 7.10 7.02 6.88 6.87 5.73 5.65 4.29 4.27 4.03 4.01 3.99 3.54 3.53 3.51 3.49 3.48 3.14 3.12 3.11 3.10 2.72 2.71 2.68 2.32
0.93 1.11 1.53 5.86 1.00 1.94 1.84 0.98 0.95 1.09 1.14 1.00 2.94
N
N
O
Me
6b
f1 (ppm)


AJN-IV-48/11
DRX-500 5mm ZBO probe 13C starting parameters.
With CPD proton decoupling. Use ns*td0 scans
163.34 151.23 147.36 137.15 134.24 133.34 132.11 131.62 129.45 129.34 129.24 129.14 128.19 127.85 127.72 126.19 121.00 119.29 71.52 50.37 44.57 24.38 21.16
f1 (ppm)

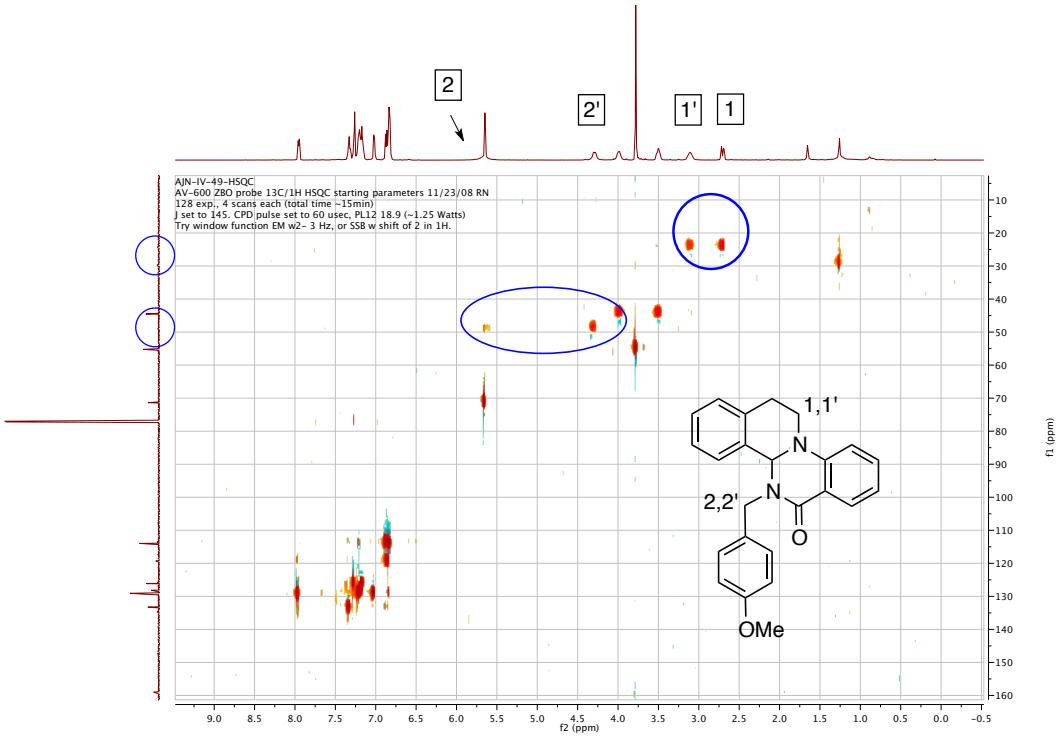
Only three of the five expected alkyl carbons show significant resonances in the ^{13}C NMR spectrum above. HSQC confirms that the remaining two carbons are present and correlate with diastereotopic sets 1,1' and 2,2', corresponding to tetrahydroisoquinoline methylene and benzylic protons respectively.

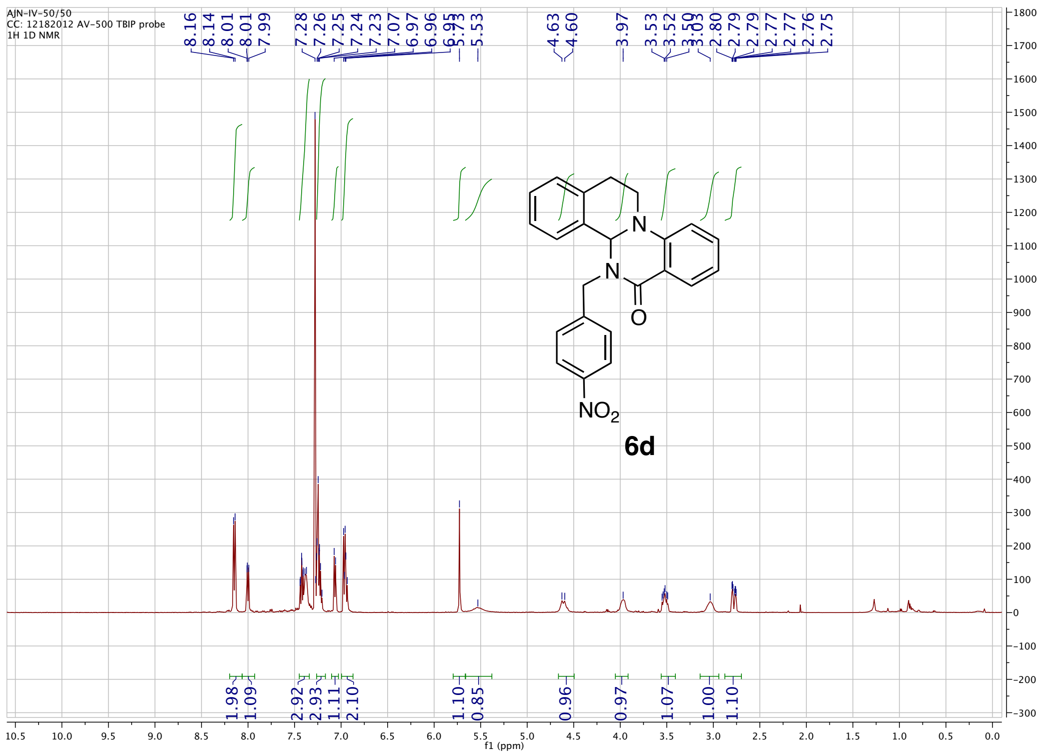


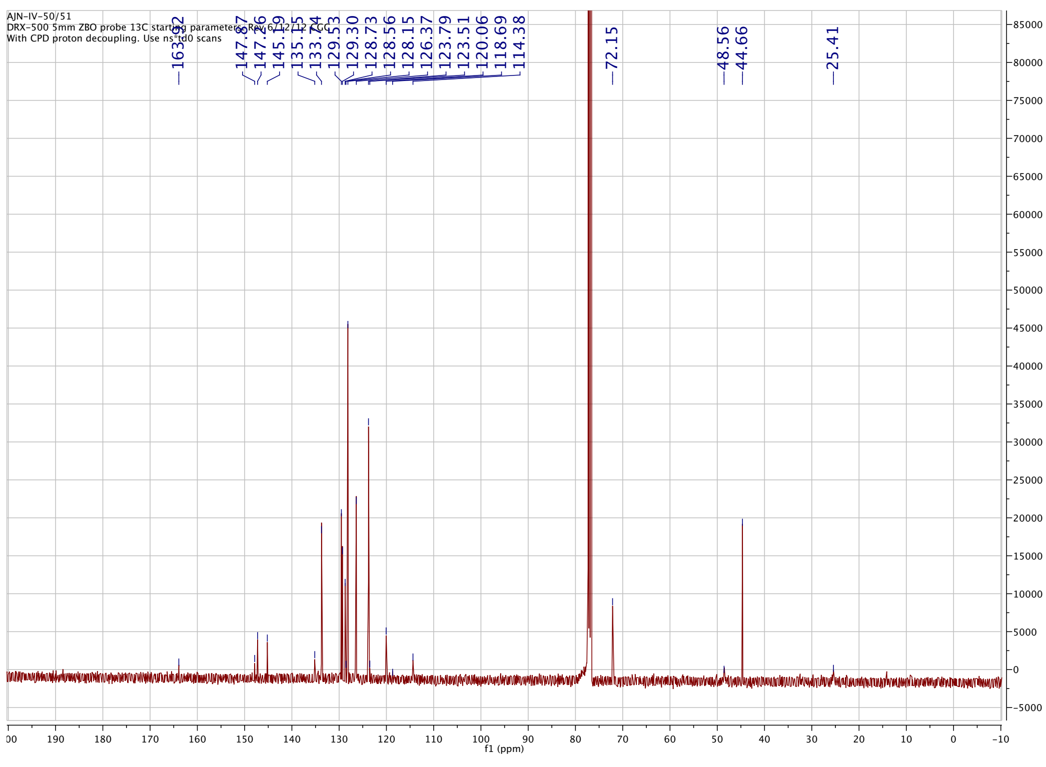

AJN-IV-49/13
AV-600 ZBO proton starting parameters 11/16/07
7.96
7.95
7.33
7.26
7.20
7.19
7.17
7.03
6.88
6.86
6.84
6.82
5.65
4.30
4.28
3.99
3.98
3.78
3.52
3.50
3.49
3.11
2.72
2.69
N
N
O
OMe
6c
0.96
1.07
1.48
3.67
1.01
3.80
1.83
0.93
0.94
2.92
1.01
0.94
1.00
f1 (ppm)


AJN-IV-49/21
12/21/10 CC AV-600 ZBO carbon starting parameters
AQ_MOD=DQD
163.41
158.99
147.34
134.73
133.27
129.38
129.27
129.16
129.08
128.15
126.81
126.14
125.89
125.85
119.32
113.98
113.55
71.37
55.23
49.02
44.53
24.47
f1 (ppm)

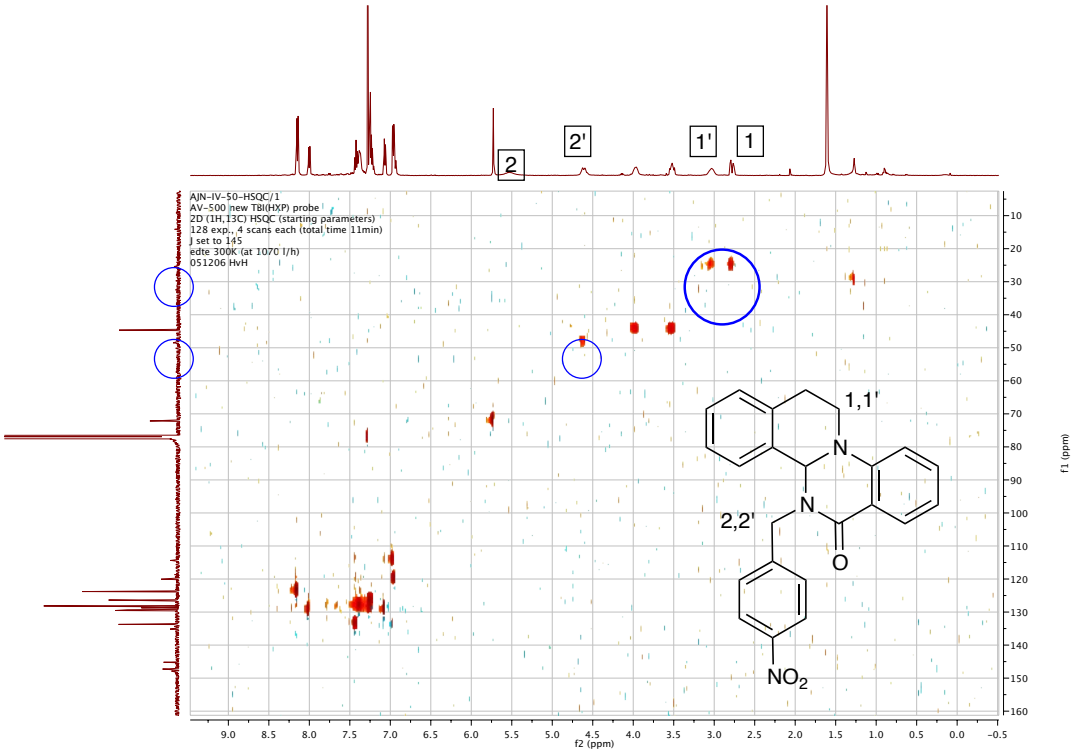
Only three of the five expected alkyl carbons show significant resonances in the ^{13}C NMR spectrum above. HSQC confirms that the remaining two carbons are present and correlate with diastereotopic proton sets 1,1’ and 2,2’, corresponding to tetrahydroisoquinoline methylene and benzylic protons respectively.

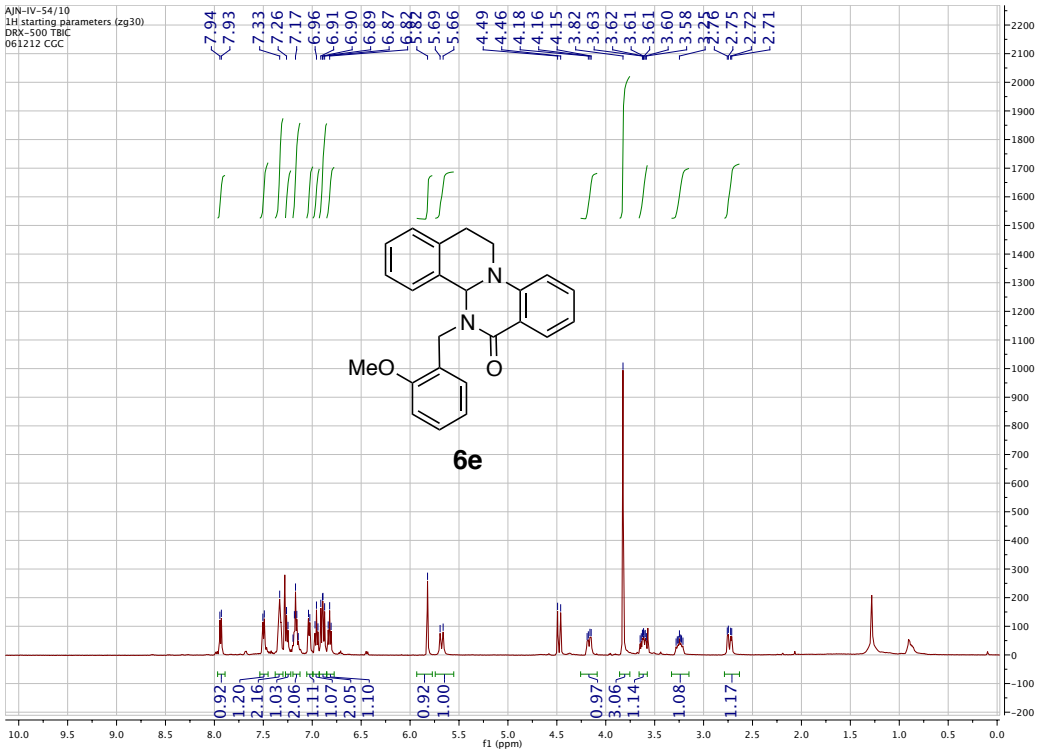


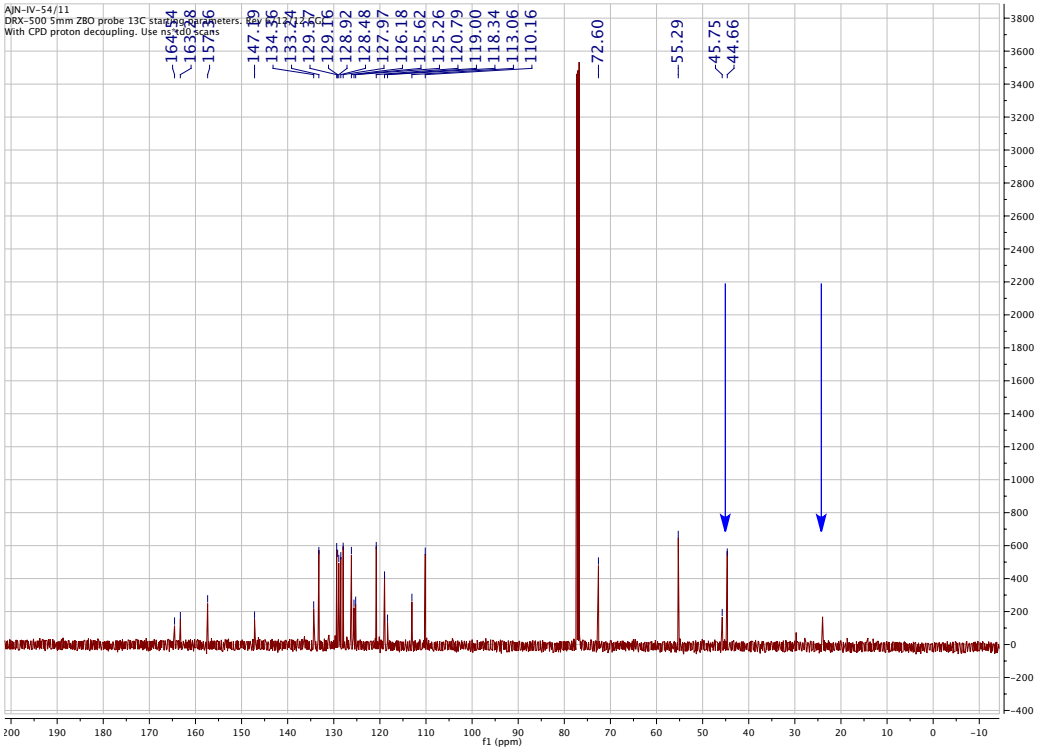




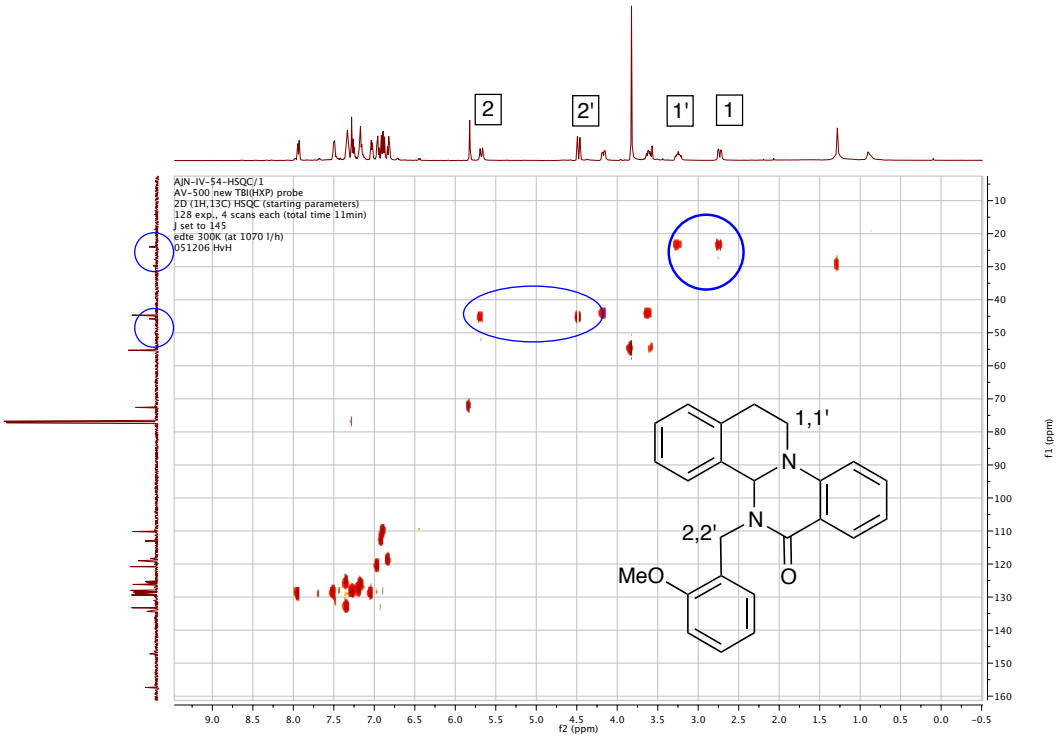
Only two of the four expected alkyl carbons show significant resonances in the ^{13}C NMR spectrum above. HSQC confirms that the remaining two carbons are present and correlate with diastereotopic proton sets 1,1' and 2,2', corresponding to tetrahydroisoquinoline methylene and benzylic protons respectively.

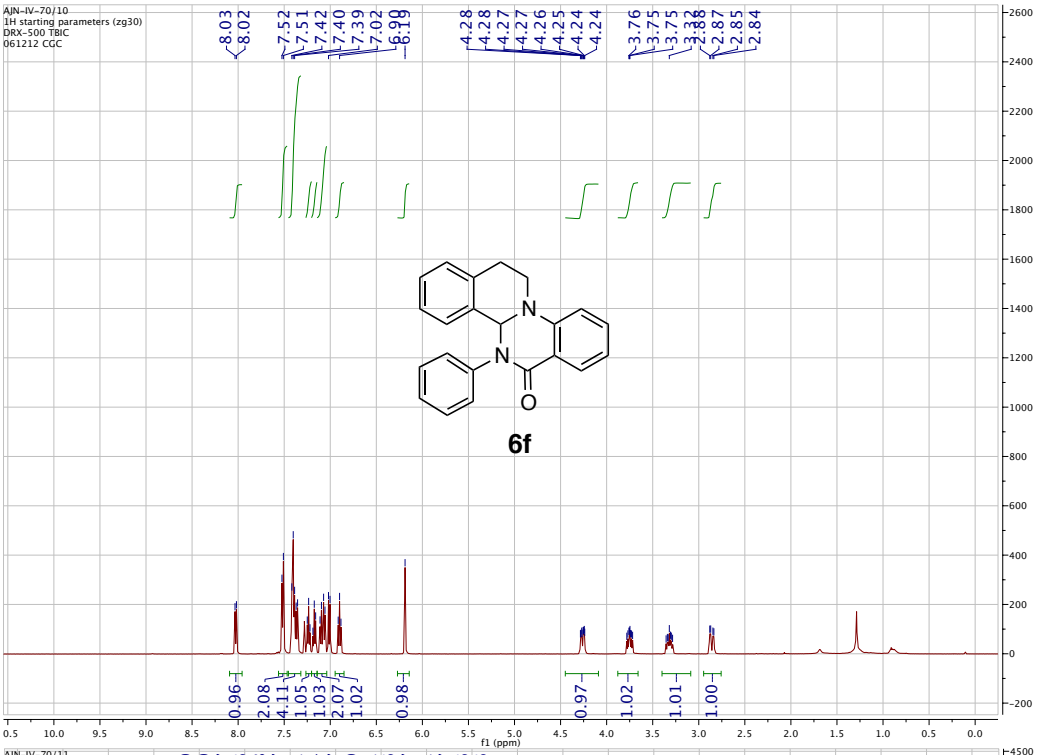


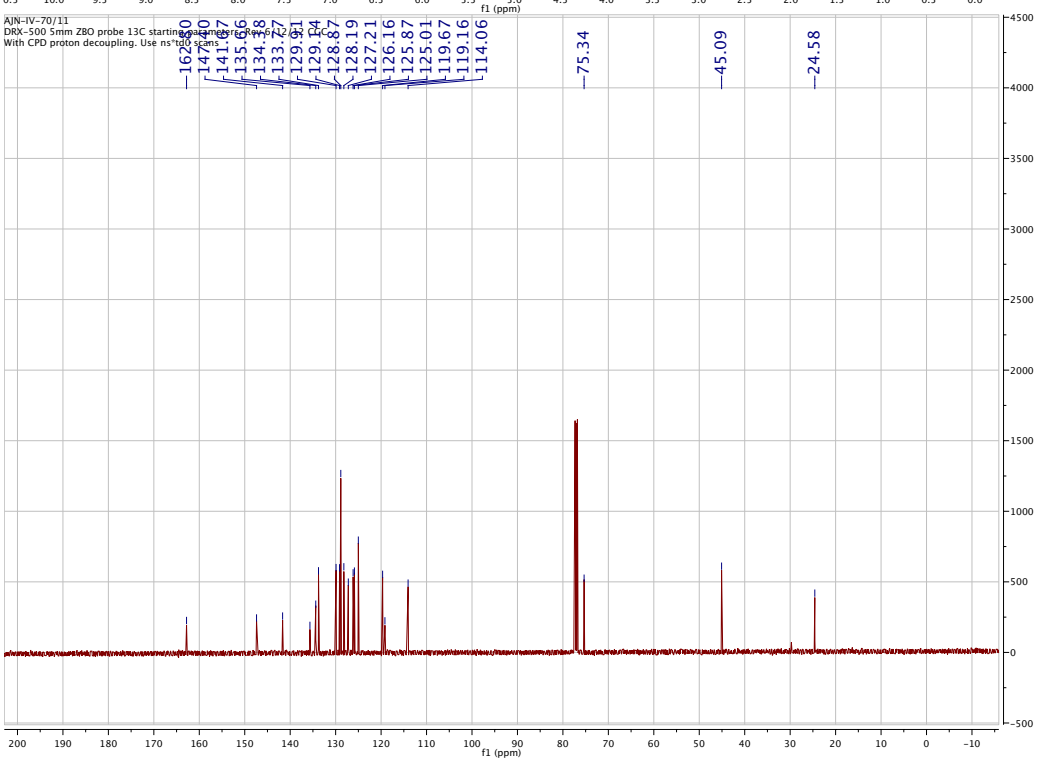

AJN-IV-54/10
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
7.94
7.93
7.33
7.26
7.17
6.96
6.91
6.90
6.89
6.87
6.82
5.69
5.66
4.49
4.46
4.18
4.16
4.15
3.82
3.63
3.62
3.61
3.61
3.60
3.58
3.25
2.76
2.75
2.72
2.71
N
N
O
MeO
6e
0.92
1.20
2.16
1.03
2.06
1.11
1.07
2.05
1.10
0.92
1.00
0.97
3.06
1.14
1.08
1.17
f1 (ppm)

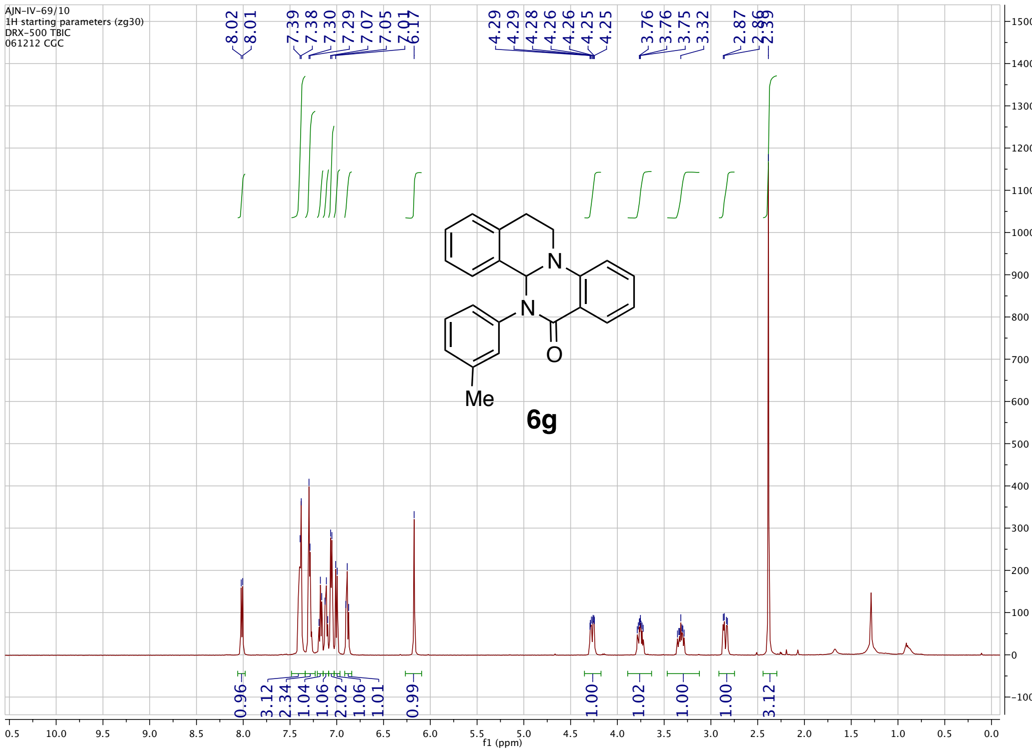

AJN-IV-54/11
DRX-500 5mm ZBO probe 13C standard parameters: zgpg30
With CPD proton decoupling. Use ns >d0 scans
164.54
163.88
157.66
147.89
134.36
133.24
129.47
129.40
128.92
128.48
127.97
126.18
125.62
125.26
120.79
119.00
118.34
113.06
110.16
72.60
55.29
45.75
44.66
f1 (ppm)

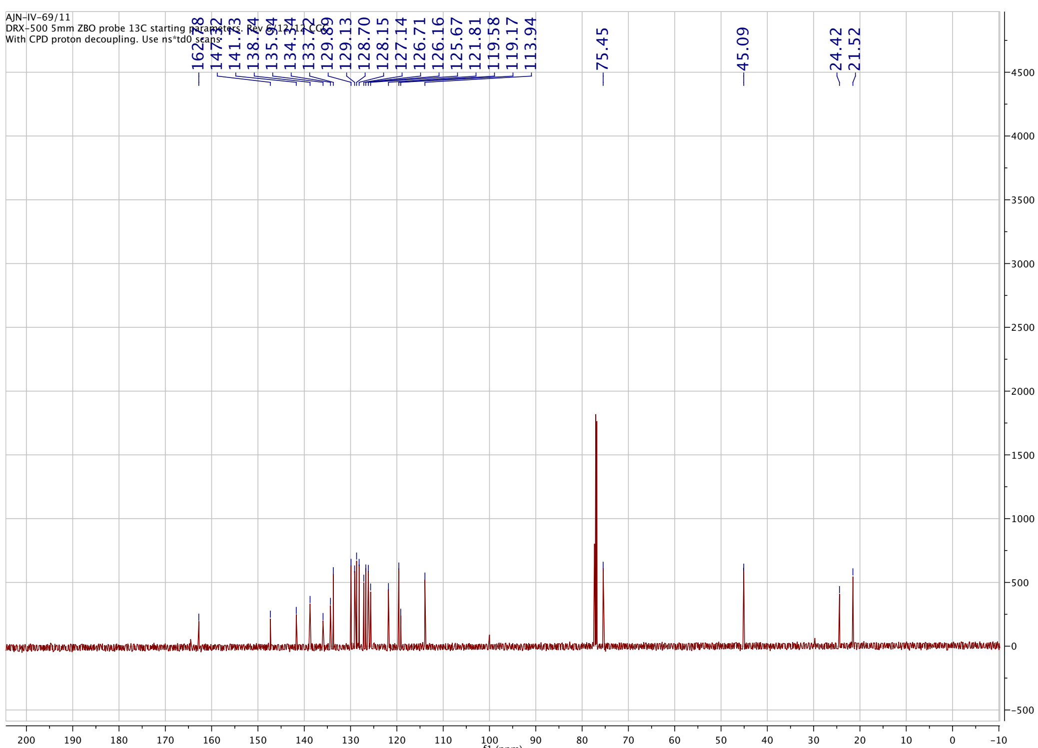
Only three of the five expected alkyl carbons show significant resonances in the ^{13}C NMR spectrum above. HSQC confirms that the remaining two carbons are present and correlate with diastereotopic proton sets 1,1' and 2,2', corresponding to tetrahydroisoquinoline methylene and benzylic protons respectively.

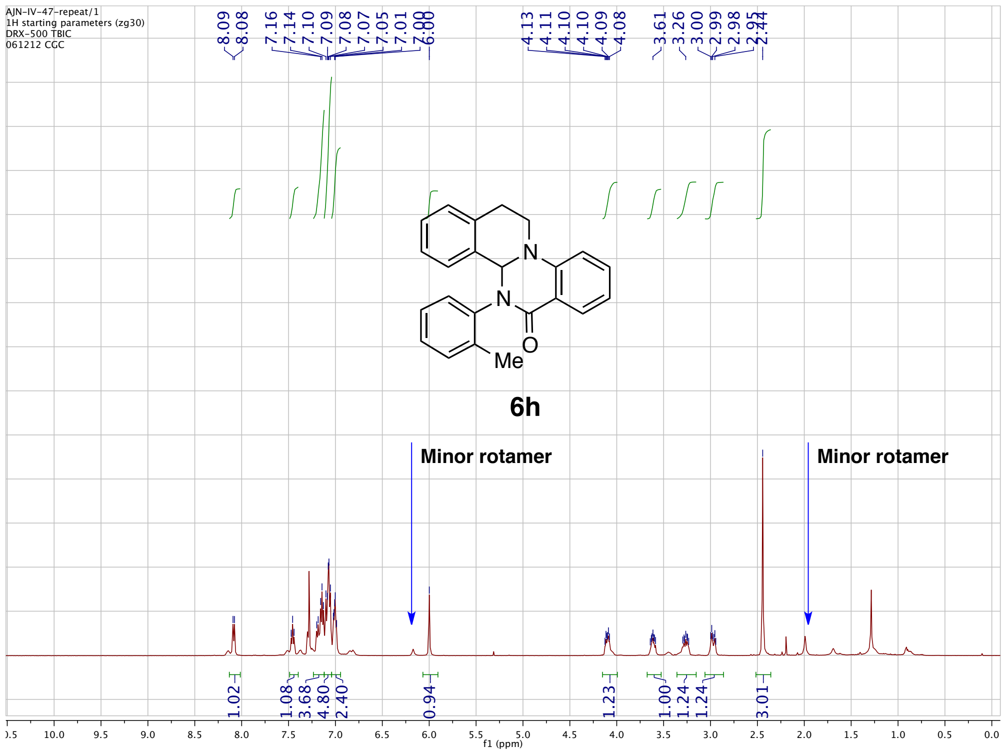


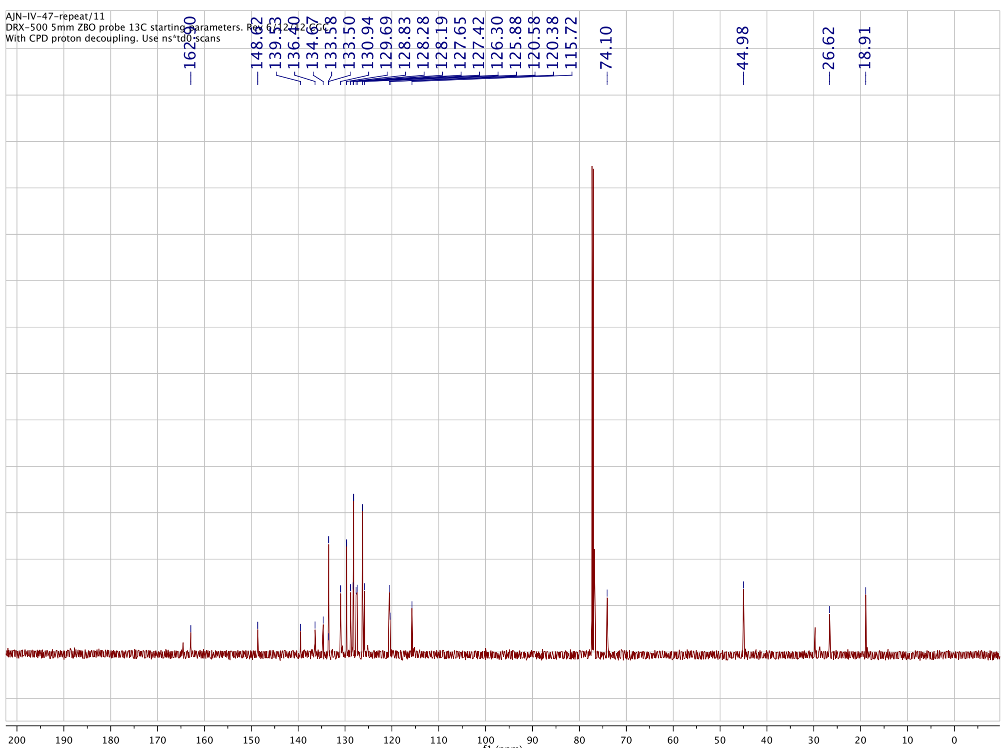

AJN-IV-70/10
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
8.03
8.02
7.52
7.51
7.42
7.40
7.39
7.02
6.99
6.98
4.28
4.28
4.27
4.27
4.26
4.25
4.24
4.24
3.76
3.75
3.75
3.74
2.87
2.85
2.84
N
N
O
6f
0.96
2.08
4.11
1.05
1.03
2.07
1.02
0.98
0.97
1.02
1.01
1.00
f1 (ppm)

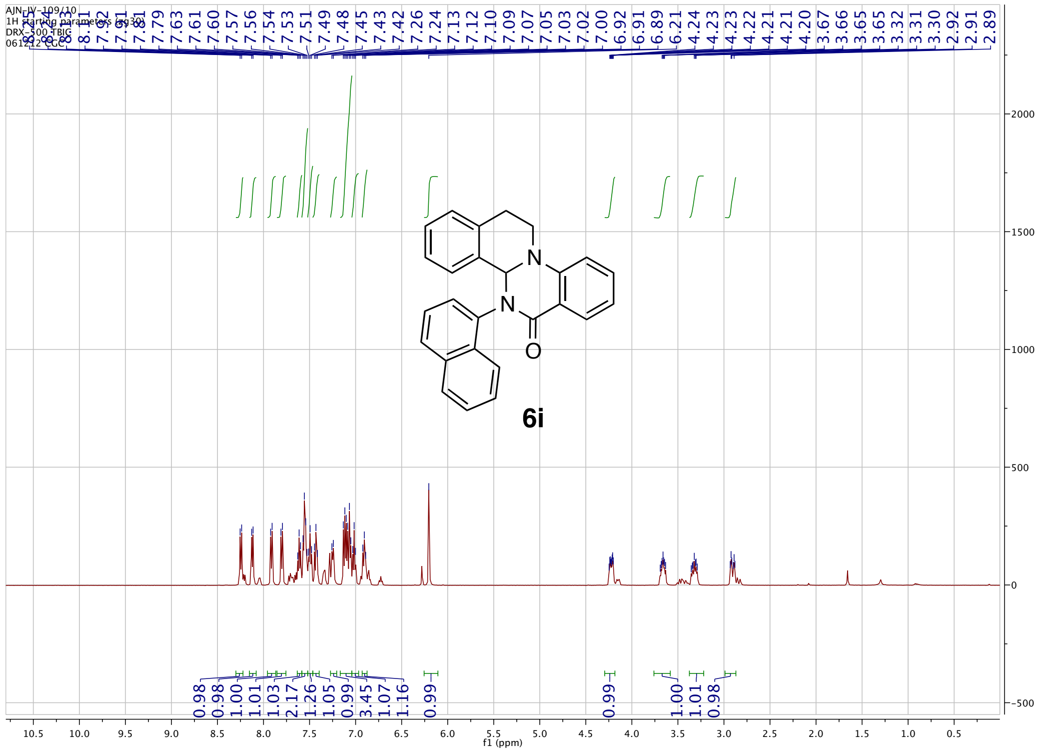

AJN-IV-70/11
DRX-500 5mm ZBO probe 13C starting parameters (zgpg)
With CPD proton decoupling. Use ns*td0 scans
162.60
147.80
141.77
135.66
134.38
133.27
129.41
129.24
128.87
128.19
127.21
126.16
125.87
125.01
119.67
119.16
114.06
75.34
45.09
24.58
f1 (ppm)

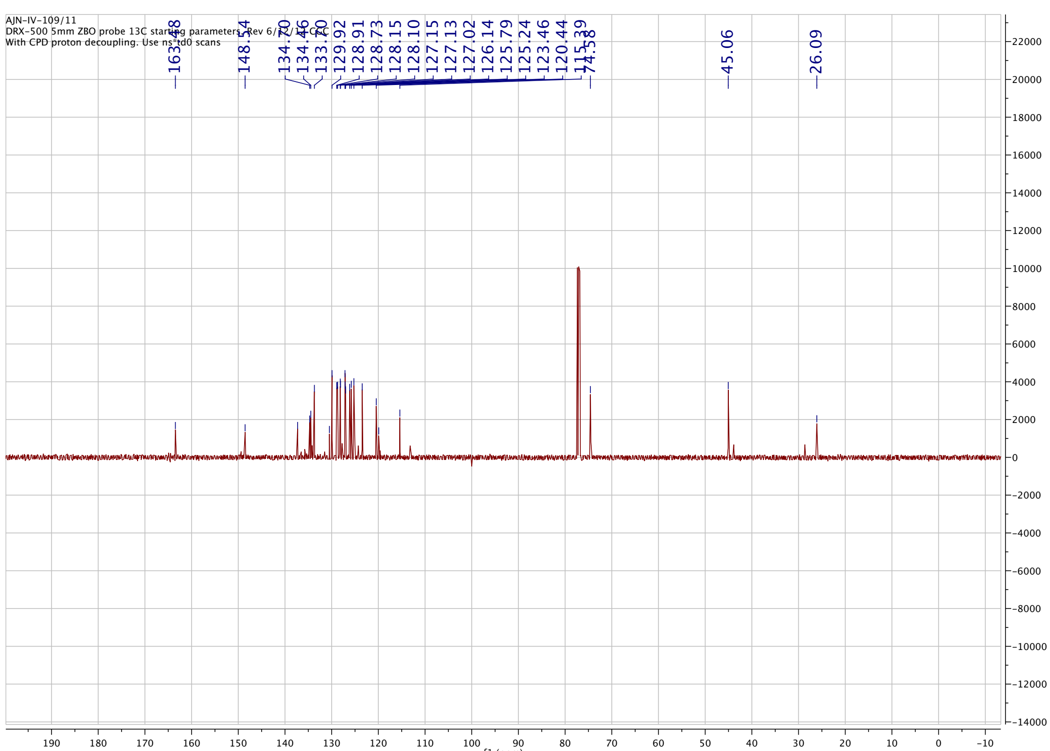

AJN-IV-69/10
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
8.02
8.01
7.39
7.38
7.30
7.29
7.07
7.05
7.01
6.17
4.29
4.29
4.28
4.26
4.26
4.25
4.25
3.76
3.76
3.75
3.32
2.87
2.86
2.39
N
N
O
Me
6g
0.96
3.12
2.34
1.04
1.06
2.02
1.06
1.01
0.99
1.00
1.02
1.00
1.00
3.12
f1 (ppm)

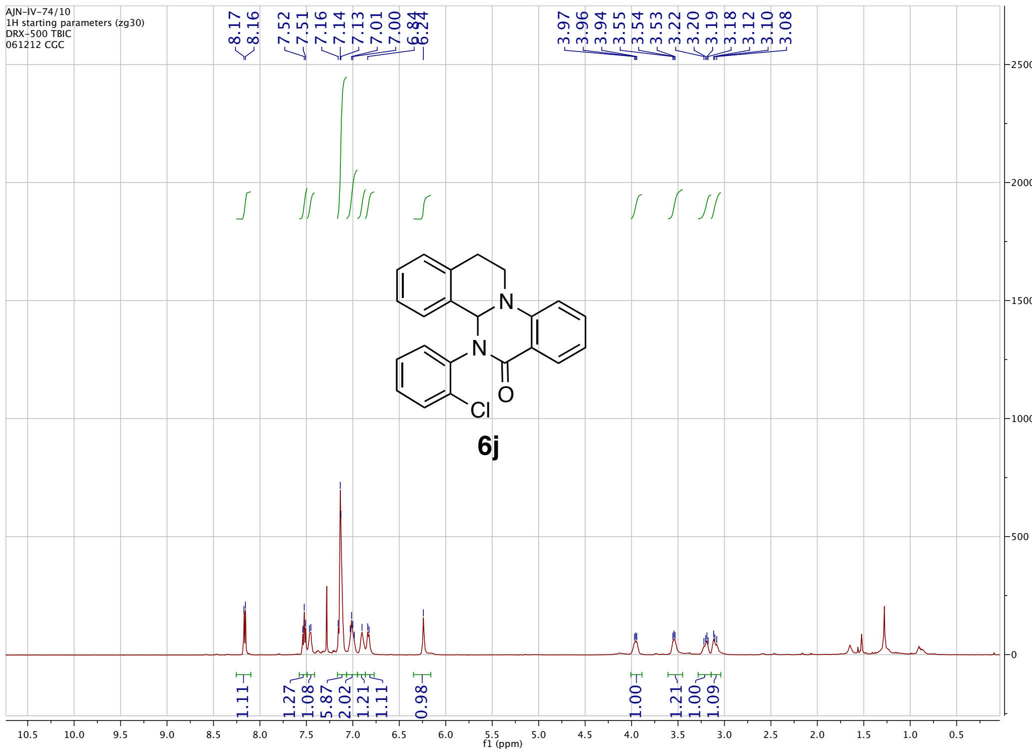

AJN-IV-69/11
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12 CGC
With CPD proton decoupling. Use ns*td0 scans
162.78
147.32
141.73
138.74
135.94
134.34
133.72
129.89
129.13
128.70
128.15
127.14
126.71
126.16
125.67
121.81
119.58
119.17
113.94
75.45
45.09
24.42
21.52
f1 (ppm)


AJN-IV-47-repeat/1
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
Me
N
N
O
6h
Minor rotamer
Minor rotamer
f1 (ppm)

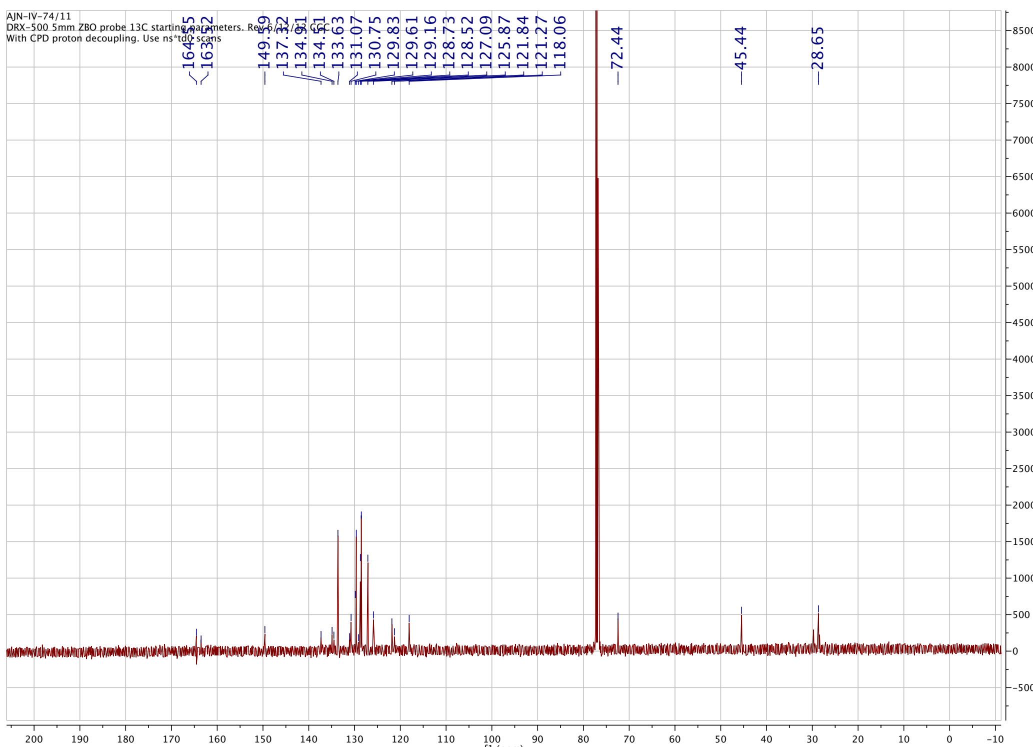

AJN-IV-47-repeat/11
DRX-500 5mm ZBO probe 13C starting parameters.
With CPD proton decoupling.
f1 (ppm)



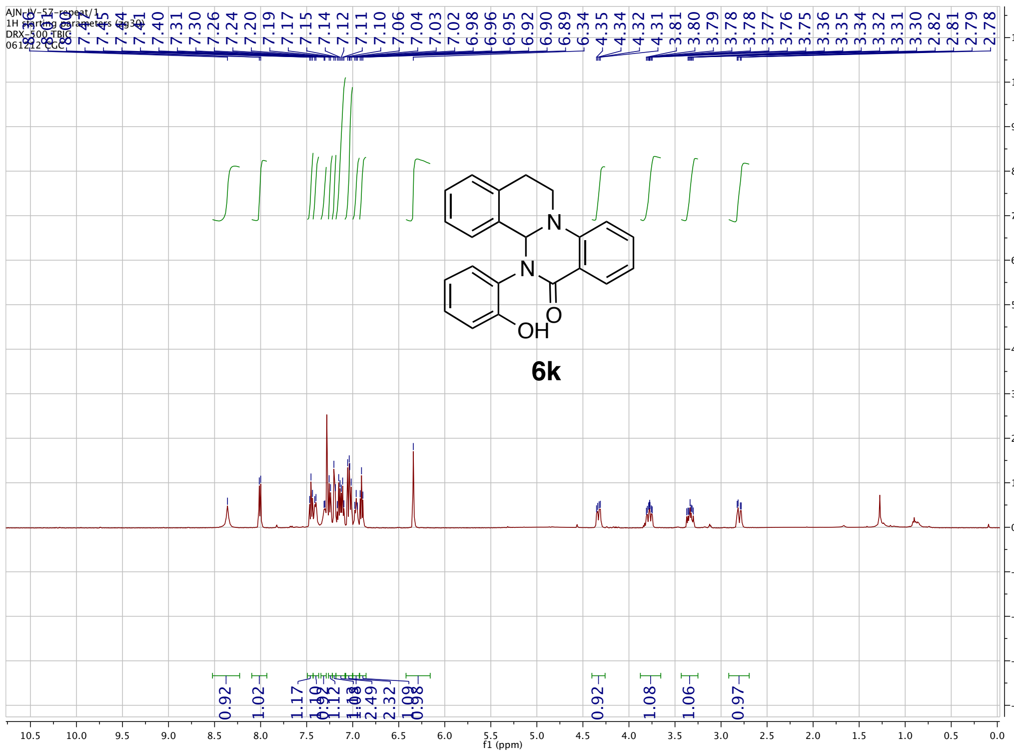


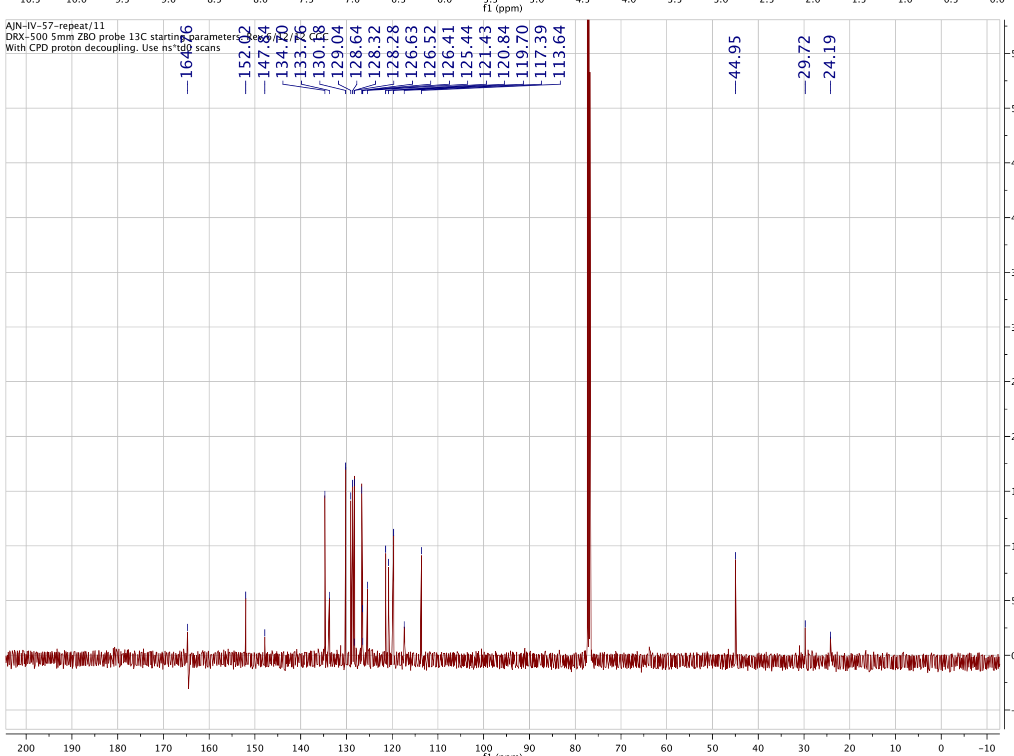


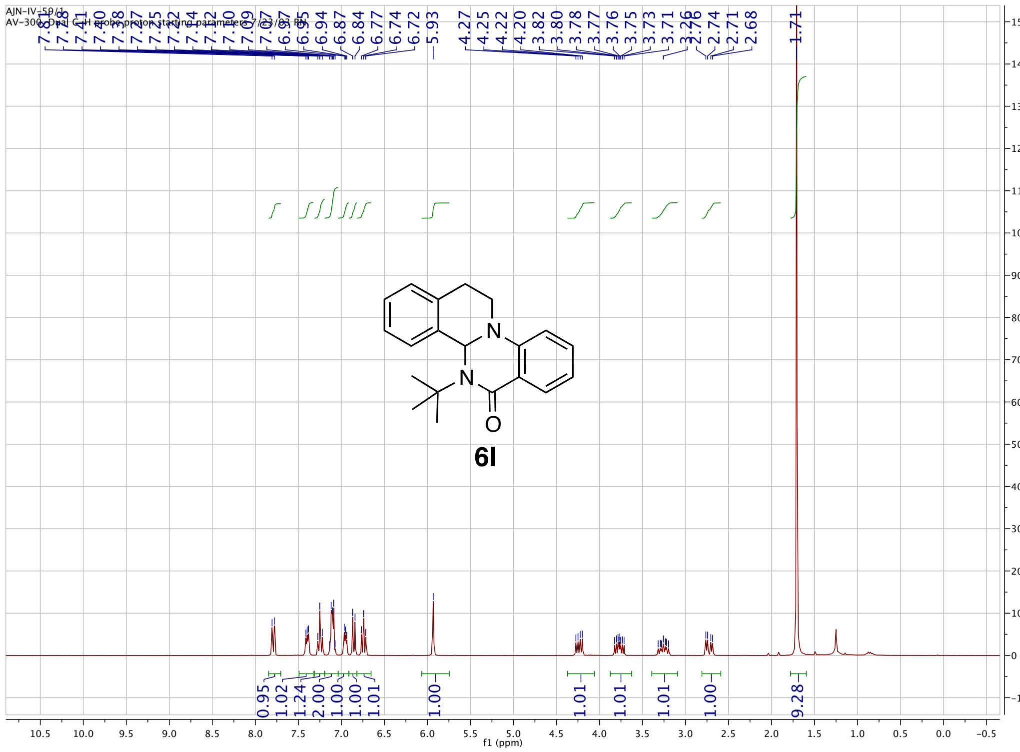
AJN-IV-74/10
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
6j
f1 (ppm)

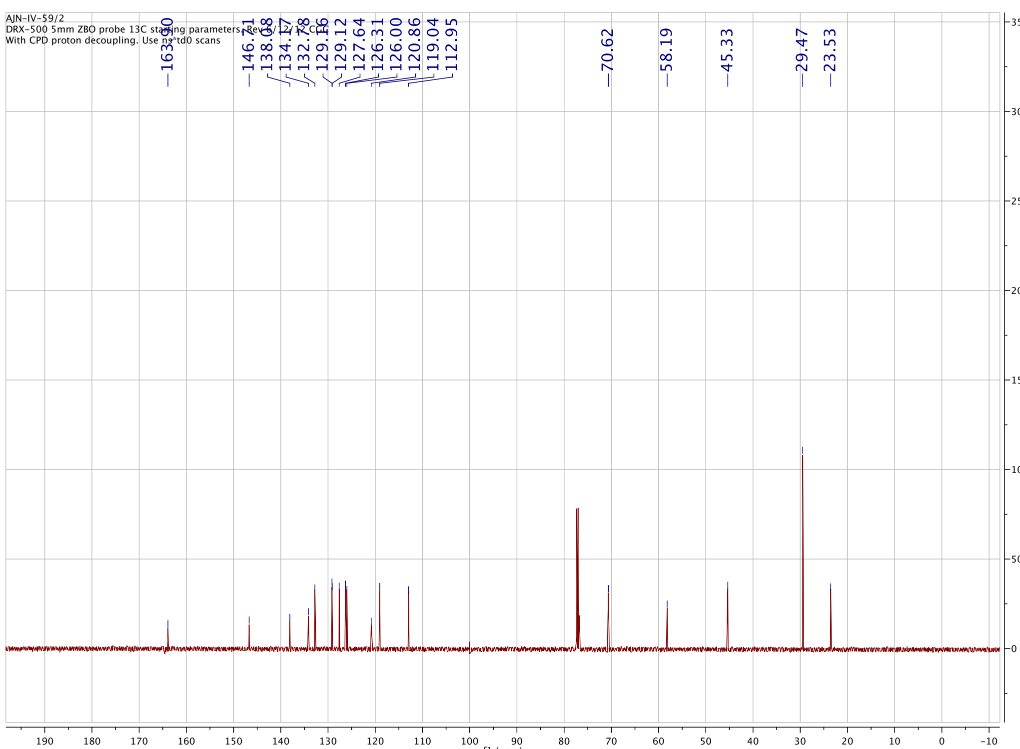


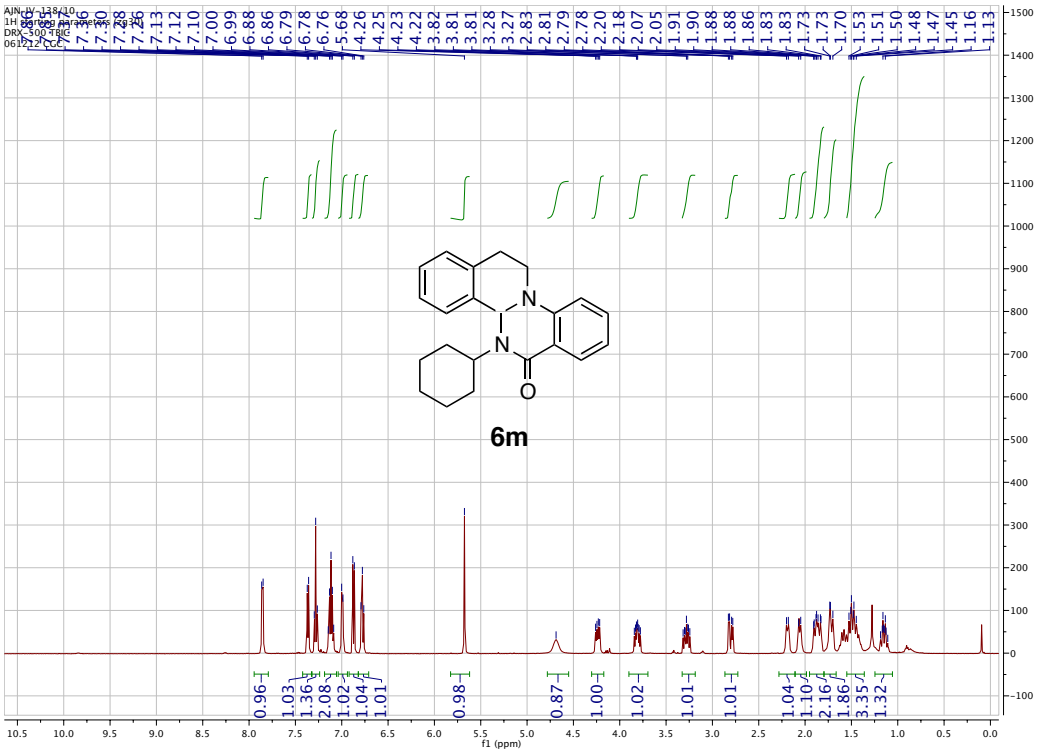
AJN-IV-74/11
With CPD proton decoupling. Use ns*td0 scans
f1 (ppm)

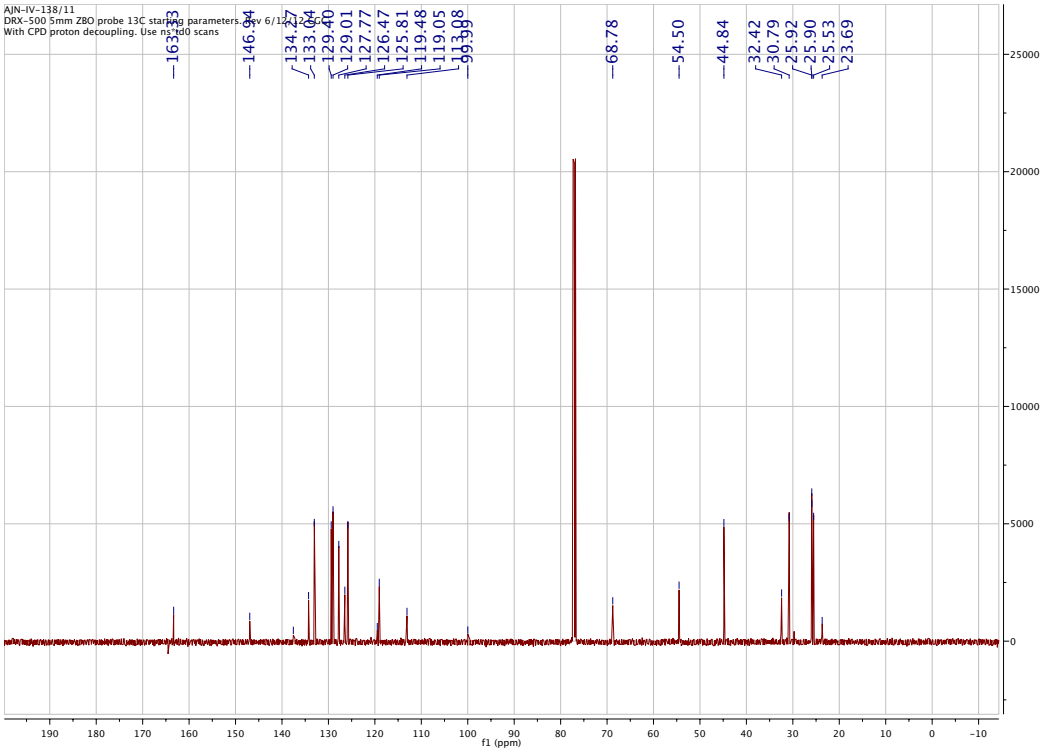

AJN-IV-57-repeat/1
1H starting parameters (zg30)
DRX-500 TBIG
061212 CCC
7.45 7.44 7.41 7.40 7.31 7.30 7.26 7.24 7.20 7.19 7.17 7.15 7.14 7.12 7.11 7.10 7.06 7.04 7.03 7.02 6.98 6.96 6.95 6.92 6.90 6.89 6.34 4.35 4.34 4.32 4.31 3.81 3.80 3.79 3.78 3.78 3.77 3.76 3.75 3.36 3.35 3.34 3.32 3.31 3.30 2.82 2.81 2.79 2.78
N
N
O
OH
6k
0.92 1.02 1.17 1.10 0.92 1.12 1.08 2.49 2.32 1.09 0.98 0.92 1.08 1.06 0.97
f1 (ppm)

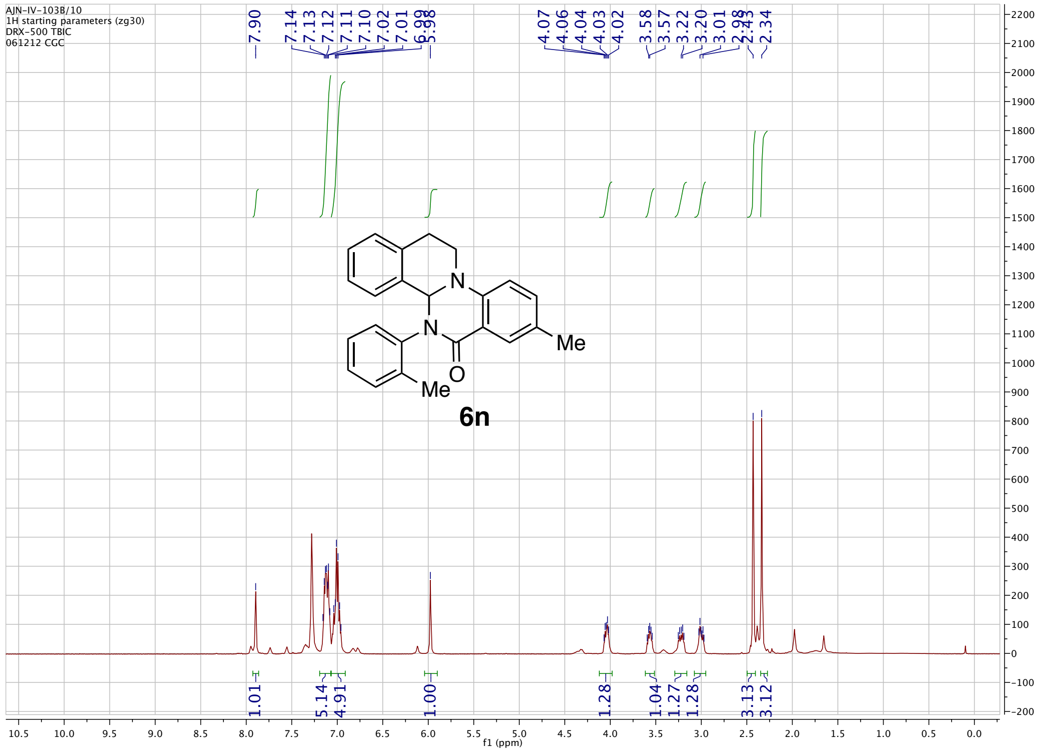

AJN-IV-57-repeat/11
DRX-500 5mm ZBO probe 13C starting parameters. Rev.6/12/12 CCC
With CPD proton decoupling. Use ns*td0 scans
152.02 147.84 134.10 133.76 130.18 129.04 128.64 128.32 128.28 126.63 126.52 126.41 125.44 121.43 120.84 119.70 117.39 113.64
44.95
29.72
24.19
f1 (ppm)

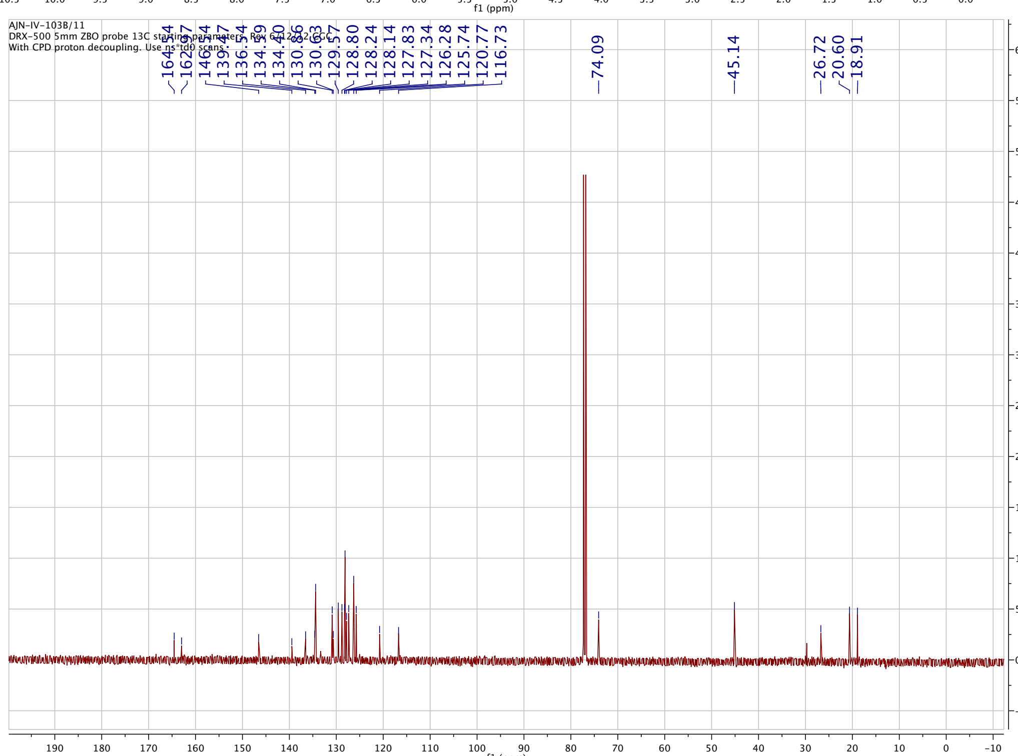

AJN-IV-59/1
6l
f1 (ppm)

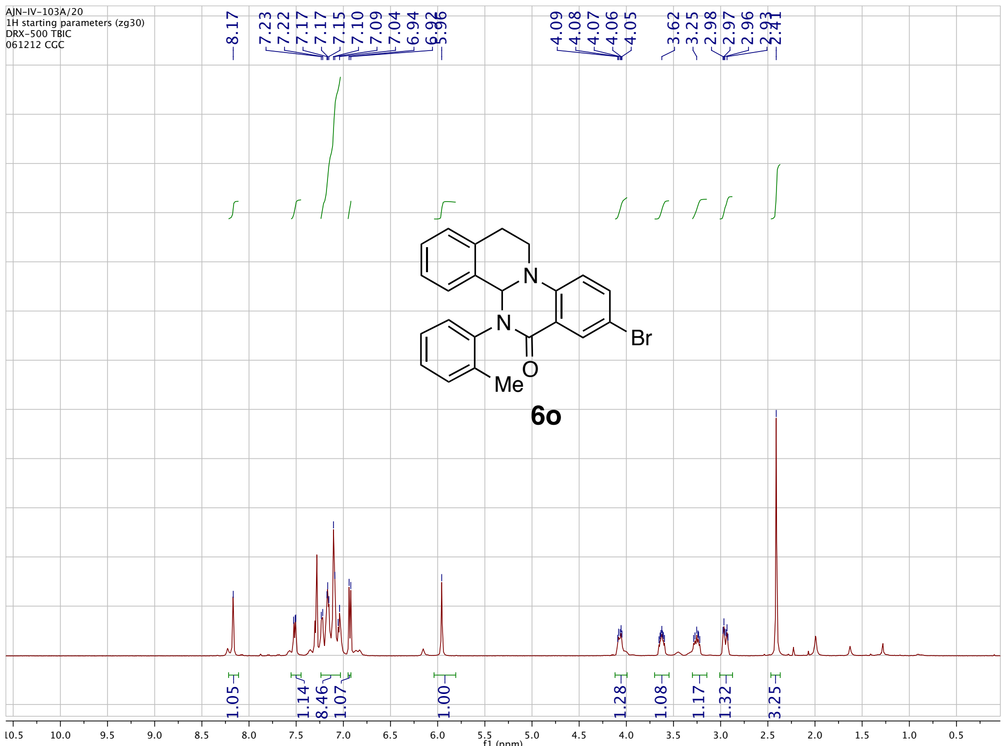

AJN-IV-59/2
DRX-500 5mm ZBO probe 13C starting parameters
With CPD proton decoupling. Use ns*td0 scans
146.11
138.08
134.17
132.78
129.16
129.12
127.64
126.31
126.00
120.86
119.04
112.95
70.62
58.19
45.33
29.47
23.53
f1 (ppm)

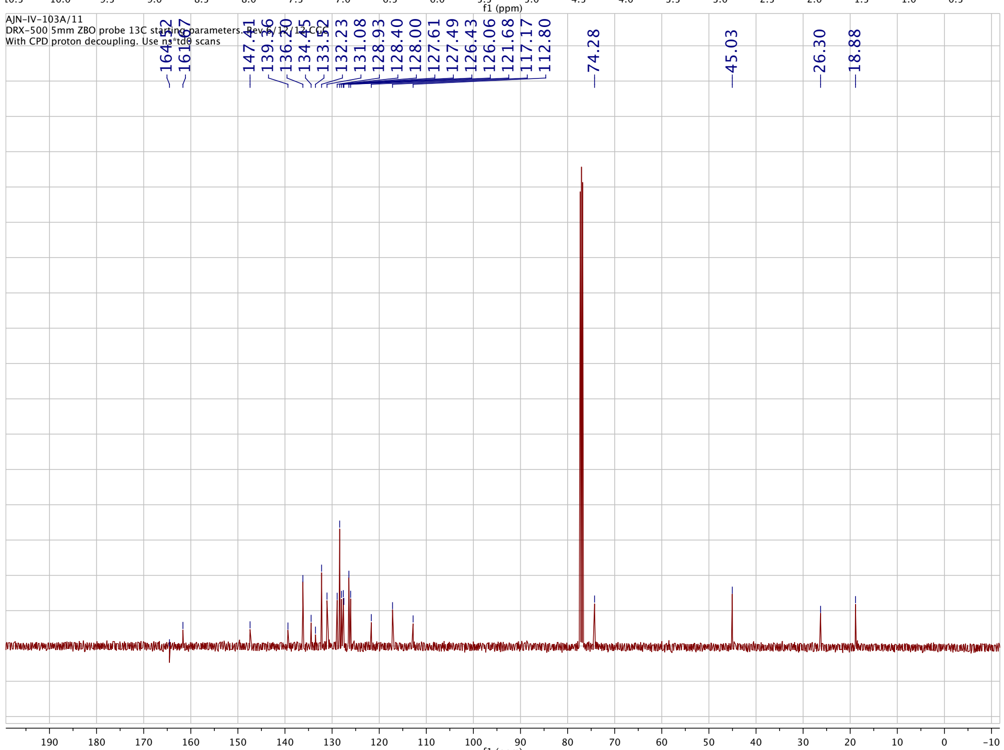

AJN-IV-138/10
7.46
7.40
7.28
7.26
7.13
7.12
7.10
7.00
6.99
6.88
6.86
6.79
6.78
6.76
5.68
4.26
4.25
4.23
4.22
3.82
3.81
3.81
3.28
3.27
2.83
2.81
2.79
2.78
2.20
2.18
2.07
2.05
1.91
1.90
1.88
1.88
1.86
1.83
1.83
1.73
1.73
1.70
1.53
1.51
1.50
1.48
1.47
1.45
1.16
1.13
N
N
O
6m
0.96
1.03
1.36
2.08
1.02
1.04
1.01
0.98
0.87
1.00
1.02
1.01
1.01
1.04
1.10
2.16
1.86
3.35
1.32
f1 (ppm)

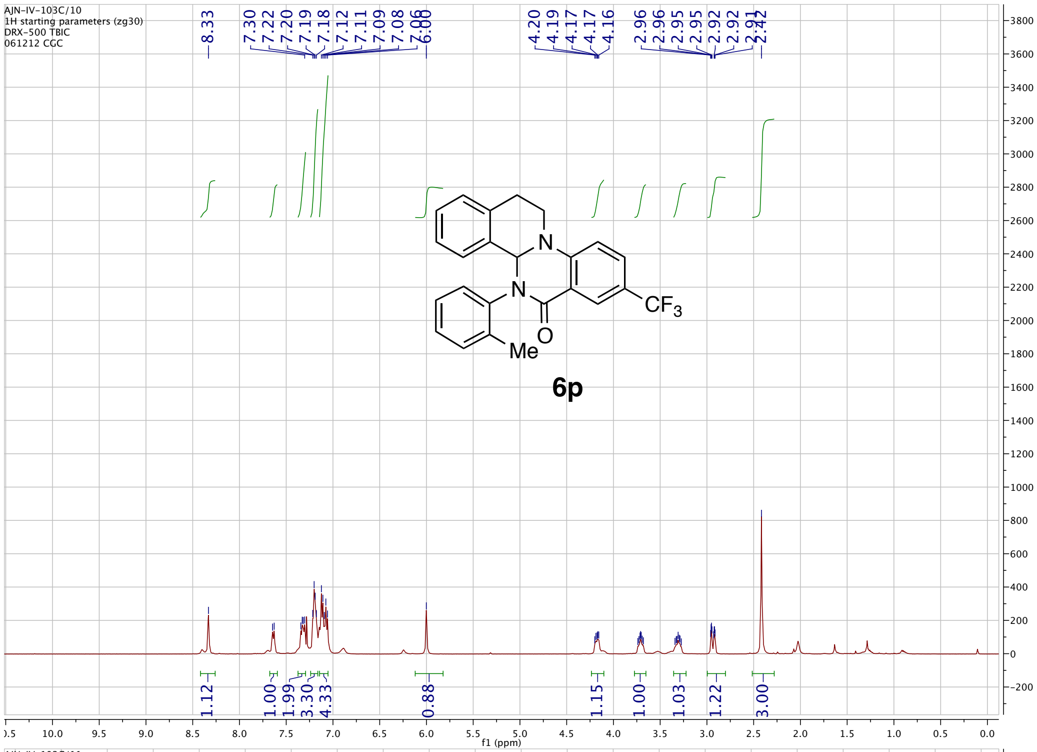

AJN-IV-138/11
DRX-500 5mm ZBO probe 13C starting parameters dev 6/12/12 cmc
With CPD proton decoupling. Use ns 1d0 scans
163.53
146.94
134.27
133.04
129.40
129.01
127.77
126.47
125.81
119.48
119.05
113.08
99.99
68.78
54.50
44.84
32.42
30.79
25.92
25.90
25.53
23.69
f1 (ppm)

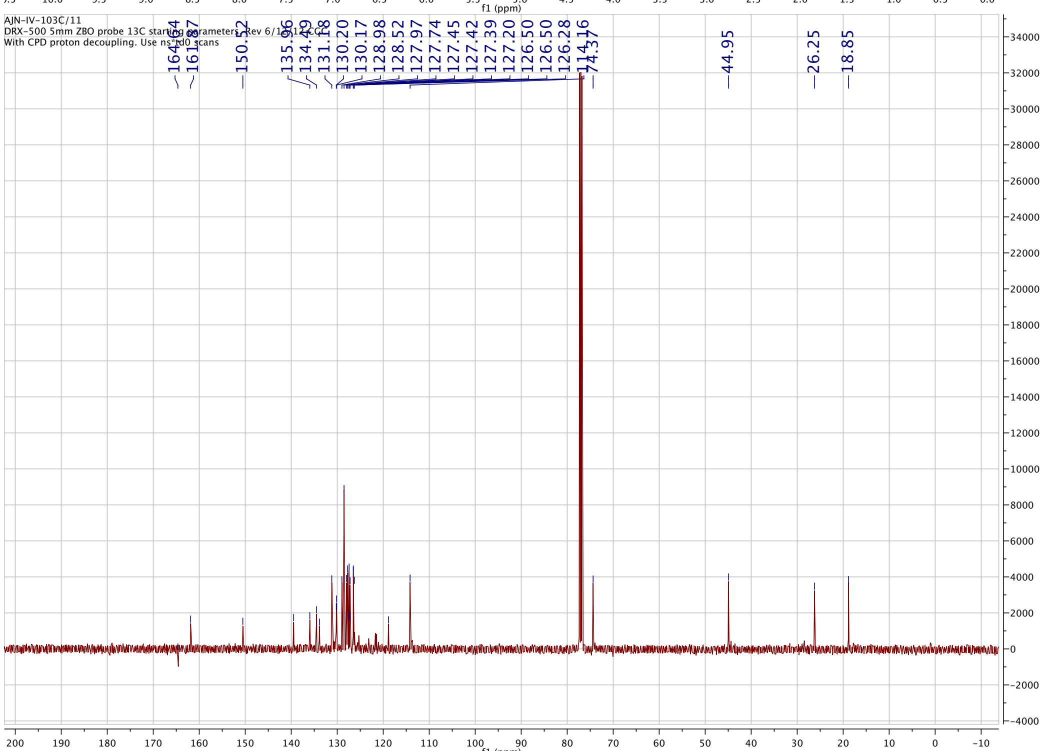

AJN-IV-103B/10
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
7.90
7.14
7.13
7.12
7.11
7.10
7.02
7.01
6.99
5.98
4.07
4.06
4.04
4.03
4.02
3.58
3.57
3.22
3.20
3.01
2.98
2.43
2.34
N
N
O
Me
Me
6n
1.01
5.14
4.91
1.00
1.28
1.04
1.27
1.28
3.13
3.12
f1 (ppm)

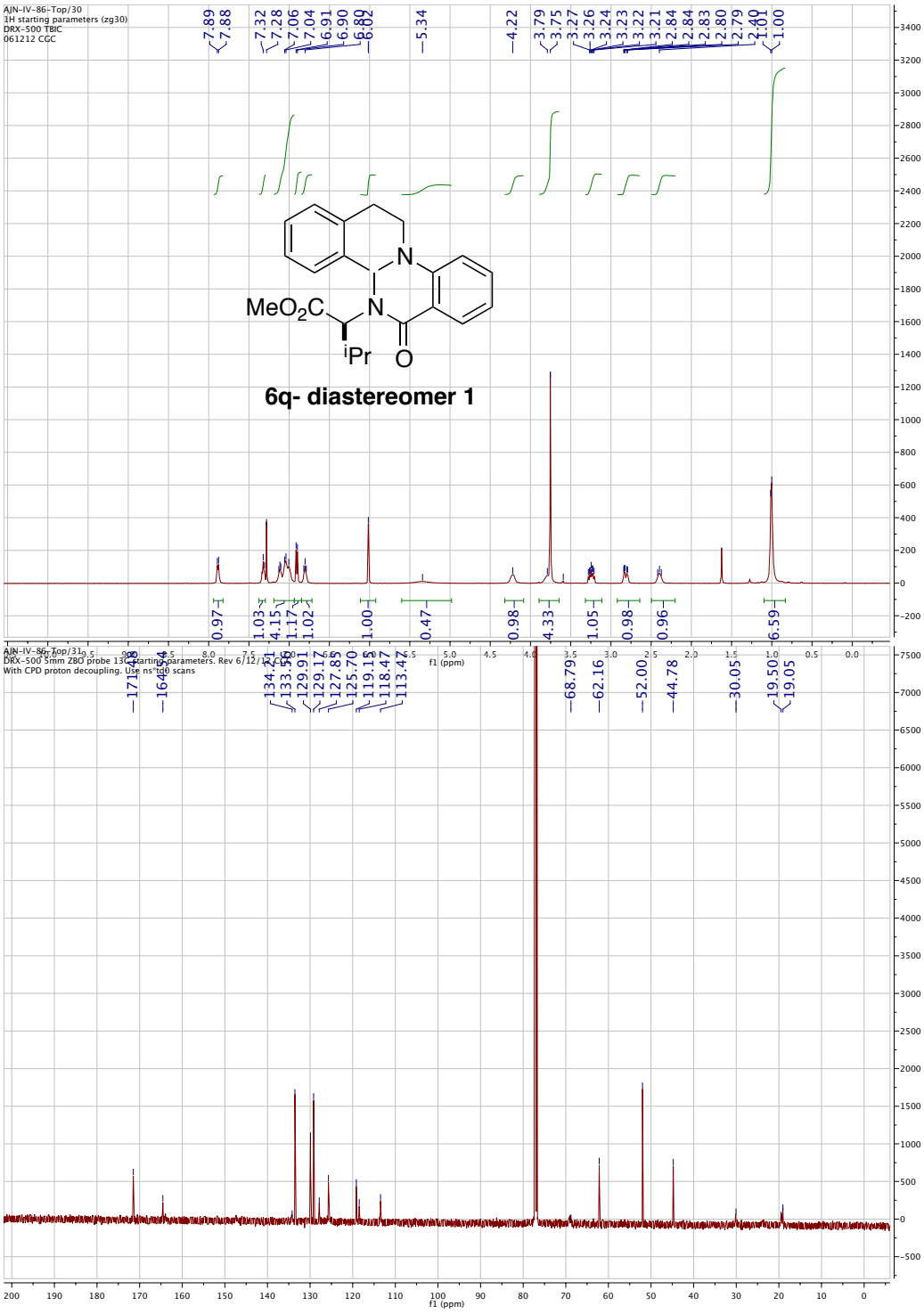

AJN-IV-103B/11
DRX-500 5mm ZBO probe 13C starting parameters
With CPD proton decoupling.
136.44
134.59
134.40
130.76
130.63
129.57
128.80
128.24
128.14
127.83
127.34
126.28
125.74
120.77
116.73
74.09
45.14
26.72
20.60
18.91
f1 (ppm)

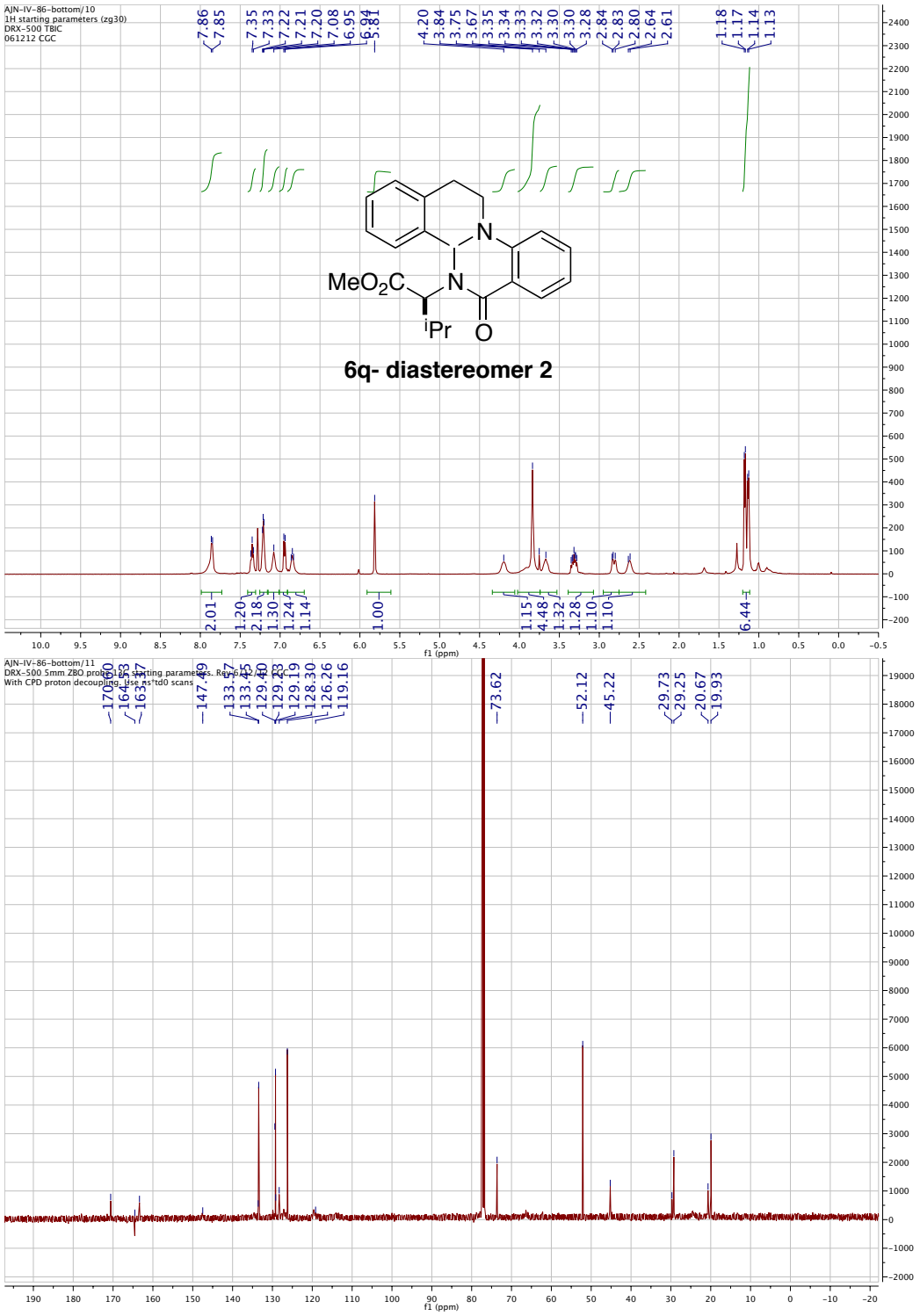

AJN-IV-103A/20
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
Br
N
N
O
Me
6o
f1 (ppm)


AJN-IV-103A/11
f1 (ppm)


AJN-IV-103C/10
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
8.33
7.30
7.22
7.20
7.19
7.18
7.12
7.11
7.09
7.08
7.06
6.00
4.20
4.19
4.17
4.17
4.16
2.96
2.96
2.95
2.95
2.92
2.92
2.91
2.42
N
N
CF3
O
Me
6p
1.12
1.00
1.99
3.30
4.33
0.88
1.15
1.00
1.03
1.22
3.00
f1 (ppm)


AJN-IV-103C/11
DRX-500 5mm ZBO probe 13C starting parameters, Rev 6/15/12 CGC
With CPD proton decoupling. Use ns*rd0 scans
150.52
135.96
134.49
131.18
130.20
130.17
128.98
128.52
127.97
127.74
127.45
127.42
127.39
127.20
126.50
126.50
126.28
114.16
74.37
44.95
26.25
18.85
f1 (ppm)


AJN-IV-86-Top/30
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
7.89
7.88
7.32
7.28
7.06
7.04
6.91
6.90
6.80
6.02
5.34
4.22
3.79
3.75
3.27
3.26
3.24
3.23
3.22
3.21
2.84
2.84
2.83
2.80
2.79
1.41
1.00
MeO2C
N
N
iPr
O
6q- diastereomer 1
0.97
1.03
4.15
1.17
1.02
1.00
0.47
0.98
4.33
1.05
0.98
0.96
6.59
AJN-IV-86-Top/31
DRX-500 5mm ZBO probe 13C starting parameters. Rev 6/12/12 CGC
With CPD proton decoupling. Use ns 160 scans
f1 (ppm)
171.48
164.54
134.21
133.50
129.91
129.17
127.85
125.70
119.15
118.47
113.47
68.79
62.16
52.00
44.78
30.05
19.50
19.05


AJN-IV-86-bottom/10
1H starting parameters (zg30)
DRX-500 TBIC
061212 CGC
7.86
7.85
7.35
7.33
7.22
7.21
7.20
7.08
6.95
6.94
5.81
4.20
3.84
3.75
3.67
3.35
3.34
3.33
3.32
3.30
3.28
2.84
2.83
2.80
2.64
2.61
1.18
1.17
1.14
1.13
N
MeO2C
N
iPr
O
6q- diastereomer 2
2.01
1.20
2.18
1.30
1.24
1.14
1.00
1.15
4.48
1.32
1.28
1.10
1.10
6.44
f1 (ppm)
AJN-IV-86-bottom/11
DRX-500 5mm ZBO proton starting parameters. Rev.6
With CPD proton decoupling. use ns*td0 scans
170.60
164.53
163.87
147.49
133.67
133.45
129.40
129.23
129.19
128.30
126.26
119.16
73.62
52.12
45.22
29.73
29.25
20.67
19.93
f1 (ppm)