Electronic Supporting Information(ESI) for:

Synthesis of Axially Chiral Heterobiaryl Alkynes *via* Dynamic Kinetic Asymmetric Alkynylation

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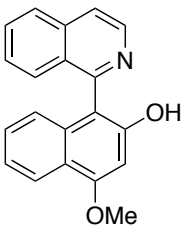
General Information.

^{1}H NMR spectra were recorded at 300 MHz or 400 MHz; ^{13}C NMR spectra were recorded at 75 MHz or 100 MHz with the solvent peak used as the internal reference (7.26 and 77.0 ppm for ^{1}H and ^{13}C respectively for $CDCl_3$; Column chromatography was performed on silica gel (Merck Kieselgel 60). Analytical TLC was performed on aluminum backed plates (1.5 × 5 cm) pre-coated (0.25 mm) with silica gel (Merck, Silica Gel 60 F_{254}). Compounds were visualized by exposure to UV light or by dipping the plates in a solution of 5% $(NH_4)_2Mo_7O_{24}\cdot 4\ H_2O$ in 95% EtOH (w/v) or followed by heating.

Purging refers to an evacuation/argon refilling procedure carried out three times. Anhydrous 1,4-dioxane, DME and THF were obtained by distillation from sodium using benzophenone as indicator. MeCN was dried by passage through solvent-purification columns containing activated alumina. Anhydrous DIPEA and Et_3N were obtained by distillation from CaH_2. $Pd(OAc)_2$, $Pd(dba)_2$, $Pd_2(dba)_3$, ligands **L1-L6**, **L9,** anhydrous DMSO and terminal alkynes **a-q** were purchased from Aldrich, **L7**[1] and **L8**[2] were prepared following described procedures. Triflates **(±)-1C** and **1E**[3] and nonaflate **1D**[4] were synthesized according to literature procedures.

Preparation of 1-(Isoquinolin-1-yl)-4-methoxynaphthalen-2-ol.

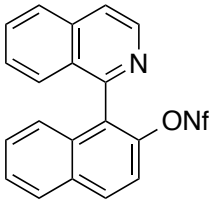


A solution of boronic acid pinacol ester[5] (1.9 g, 5.0 mmol) in THF (50 mL) was treated with a 1:1 mixture of H_2O_2 (30%)/NaOH (20 mL, 2M, aq.). After stirring for 30 min at room temperature, the reaction mixture was diluted with CH_2Cl_2 (5 mL) and washed with NH_4Cl (aq.) The organic layer was dried over $MgSO_4$, filtered, concentrated, and the residue was purified by flash chromatography on silica gel (1:1 EtOAc/*n*-hexane) to give the corresponding alcohol (1.28 g, 85 %) as a yellow amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (d, *J* = 5.7 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.72-7.67 (m, 2H), 7.65 (d, *J* = 8.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 7.9 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.34 (s, 1H), 3.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2, 157.2, 154.9, 141.2, 137.1, 133.8, 130.7, 128.6, 128.5, 127.2, 126.9, 126.8, 124.5, 122.4, 121.2, 120.4, 110.5, 98.3, 55.3. HRMS(EI) calcd. for $C_{20}H_{15}NO_2$ (M^+) 301.1103. Found 301.1108.

Synthesis of Nonaflates 1A,C,E. General procedure.

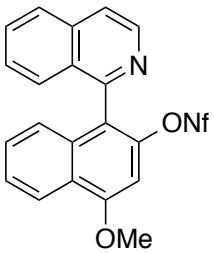
Following a described procedure,[6] over a suspension of alcohol precursor (1.0 equiv) and K_2CO_3 (1.5 equiv) in dry acetonitrile (0.5 M), perfluorobutanesulfonyl fluoride (90%, 1.2 equiv) was added in one portion, and the resulting mixture was vigorously stirred for 24 h. After completion (TLC checking), the reaction mixture was filtered through a Celite pad, the solvent was removed in vacuum, and the residue was purified by flash column chromatography over silica gel.

1-(Isoquinolin-1-yl)naphthalen-2-yl nonaflate 1A.



Following the general procedure starting from 1-(isoquinolin-1-yl)naphthalen-2-ol[7] (1.35 g, 4.98 mmol), column chromatography (85:15 *n*-hexane/AcOEt) afforded **1A** (2.22 g, 80%) as a white foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (d, *J* = 5.7 Hz, 1H), 8.10 (d, *J* = 9.1 Hz, 1H), 7.98 (dd, *J* = 13.2, 8.3 Hz, 2H), 7.83 (d, *J* = 5.7 Hz, 1H), 7.72 (dt, *J* = 8.2, 4.0 Hz, 1H), 7.65-7.52 (m, 2H), 7.49-7.36 (m, 3H), 7.31-7.21 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.0, 145.0, 142.6, 136.3, 133.2, 132.5, 131.2, 130.5, 129.4, 128.4, 128.2, 127.8, 127.7, 127.1, 127.0, 126.7, 126.5, 121.2, 119.5, (nanoflate group not observed). ^{19}F NMR (377 MHz, $CDCl_3$): –80.8 (t, $J_{F\text{-}P}$ = 11 Hz), –110.2 (t, $J_{F\text{-}P}$ = 15 Hz), –121.2 (m), –126.0 (m).

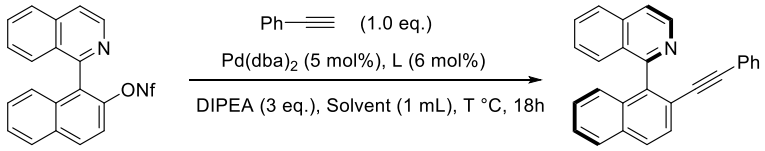
1-(Isoquinolin-1-yl)-4-methoxynaphthalen-2-yl 1E



Following the general procedure starting from 1-(isoquinolin-1-yl)-4-methoxynaphthalen-2-ol[4] (393 mg, 1.30 mmol), column chromatography (85:15 *n*-hexane/AcOEt) afforded **1B** (571 mg, 75%) as a white foam. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (d, *J* = 5.6 Hz, 1H), 8.38 (d, *J* = 8.5 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 5.7 Hz, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.57-7.35 (m, 4H), 7.22 (d, *J* = 8.5 Hz, 1H), 6.91 (s, 1H), 4.13 (d, *J* = 1.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.5, 154.2, 145.2, 142.6, 136.4, 133.4, 130.4, 128.8, 128.4, 127.5, 127.0, 126.9, 126.4, 126.3, 124.8, 122.4, 121.6, 121.0, 98.3, 56.1, (nanoflate group not observed). ^{19}F NMR (377 MHz, $CDCl_3$): –80.7 (t, $J_{F\text{-}P}$ = 11 Hz), –110.4 (m), –121.2 (m), –126.0 (m).

Full screening results

Table S1. Additional conditions and ligands screened for the dynamic kinetic asymmetric alkynylation.



rac-**1A** (+)-**2A**

Entry[a]	Ligand	Solvent/ T °C	Variations in the reaction conditions	Conv. (%)[b]	*ee* (%)[c]
1	(*R*)-BINAP **L1**	Dioxane, 70		62	38
2	(*R*)-BINAP **L1**	Dioxane, 60		46	70
3	(*R*)-BINAP **L1**	THF, 60		38	68
4	(*R*)-BINAP **L1**	DME, 60		43	66
5	(*R*)-BINAP **L1**	Toluene, 60		43	64
6	(*R*)-BINAP **L1**	CH_3CN, 60		10	66
7	(*R*)-BINAP **L1**	DMF, 60		28	65
8	(*R*)-BINAP **L1**	DMSO, 60		90	68
9	(*R*)-Tol-BINAP **L2**	DMSO, 60		75	72
10	(*R*)-DM-BINAP	DMSO, 60		45	60
11	(*R*)-H8-BINAP **L3**	DMSO, 60		77	68
12	(*R*)-Tol-SDP **L4**	DMSO, 60		90	18
13	(*R*)-MeO-BIPHEP **L5**	DMSO, 60		44	68
14	(R)-DM-SEGPHOS **L6**	DMSO, 60		22	82
15	(R,R)-Me-DUPHOS	DMSO, 60		<5	-
16	Josiphos SL-J002-1	DMSO, 60		18	80
17	(*S*)-QUINAP **L10**	DMSO, 60		full	86
18	(*S*)-*p*-MeQUINAP4	DMSO, 60		full	86
19	(*S*)-*p*-FQUINAP[4] **L11**	DMSO, 60		full	90
20	(*S*)-*p*-OMeQUINAP[4]	DMSO, 60		full	76
21	(*S*)-*p*-CyQUINAP	DMSO, 60		full	58
22	(*S*)-*t*BuQUINAP	DMSO, 60		full	0
23	(*S*)-*i*BuQUINAP	DMSO, 60		full	42
24	(*S*)-*QNZ*-QUINAP[4]	DMSO, 60		full	85
25	(*R*)-Ph-Garphos	DMSO, 60		45	74
26	(*S*)-2-Furyl-MeOBIPHEP	DMSO, 60		47	8

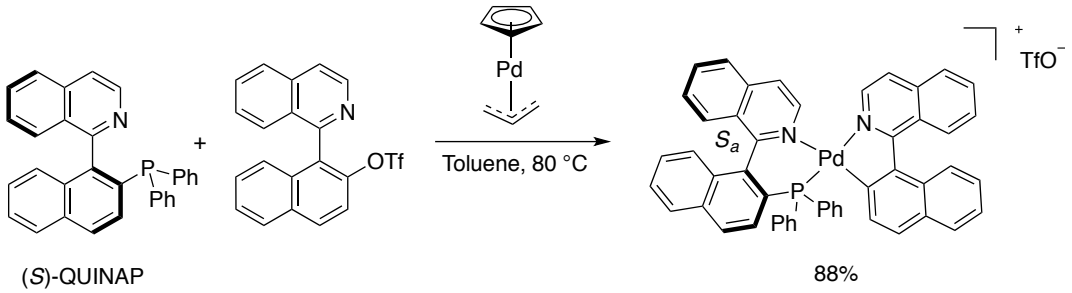
27	Phosphinohydrazone **L8**	DMSO, 60		full	0
28	SL-J001_1 (Taniaphos)	DMSO, 60		15	54
29	SL-J003_1	DMSO, 60		0	-
30	SL-J005_1 **L9**	DMSO, 60		73	90
31	SL-M001_1	DMSO, 60		full	22
32	Taddol-P-NMe_2 **L7**	DMSO, 60		full	30
33	SL-W001-1	DMSO, 60		85	12
34	(*S*)-QUINAP **L10**	DMSO, 50		full	92
35	(*S*)-*p*-FQUINAP **L11**	DMSO, 50		full	92
36	SL-J005_1 **L9**	DMSO, 50		57	88
37	(*S*)-QUINAP **L10**	DMSO, 40		full	94
38	(*S*)-*p*-FQUINAP	DMSO, 40		full	93.5
39	(*S*)-QUINAP	DMSO, 30		>95	93
40	(*S*)-QUINAP	DMSO, 40	[Pd-L] (5 mol %)	full	94
41	(*S*)-QUINAP	THF, 40	[Pd-L] (5 mol %)	60	86
42	(*S*)-QUINAP	dioxane, 40	[Pd-L] (5 mol %)	73	95
43	(*S*)-QUINAP	toluene, 40	[Pd-L] (5 mol %)	50	94
44	(*S*)-QUINAP	DME, 40	[Pd-L] (5 mol %)	70	90
45	(*S*)-QUINAP	DMSO, 40	[Pd-L] (5 mol %) Et_3N	full	96
46	(*S*)-QUINAP	DMSO, 40	*i*Pr_2N	full	96
47	(*S*)-QUINAP	DMSO, 40	pyrrolidine	full	70
48	(*S*)-QUINAP	DMSO, 40	DBU	0	-
49	(*S*)-QUINAP	DMSO, 40	DABCO	76	95
50	(*S*)-QUINAP	DMSO, 40	$Pd_2(dba)_3$	full	96

[a]Conditions: 0.1 mmol of *rac*-**1A**, 0.2 mmol of phenylacetylene. [b]Determined by ^1H NMR spectroscopy. [c]Determined by chiral HPLC analysis

Reactivity studies using an oxidative addition intermediate OAI$^+$(OTf$^-$).

An oxidative addition intermediate **OAI$^+$(OTf$^-$)** has been prepared by reaction of 1-(isoquinolin-1-yl)naphthalene-2-yl triflate[3b] with **L10** and [Pd(Cp) (allyl)] in 88% yield after crystallization (Scheme S1). Reaction of this mixture with alkyne **2q** led to the expected product (*R*)-**3Aq** in 68% ee.

Isolation of the OA intermediate OAI$^+$(OTf$^-$).



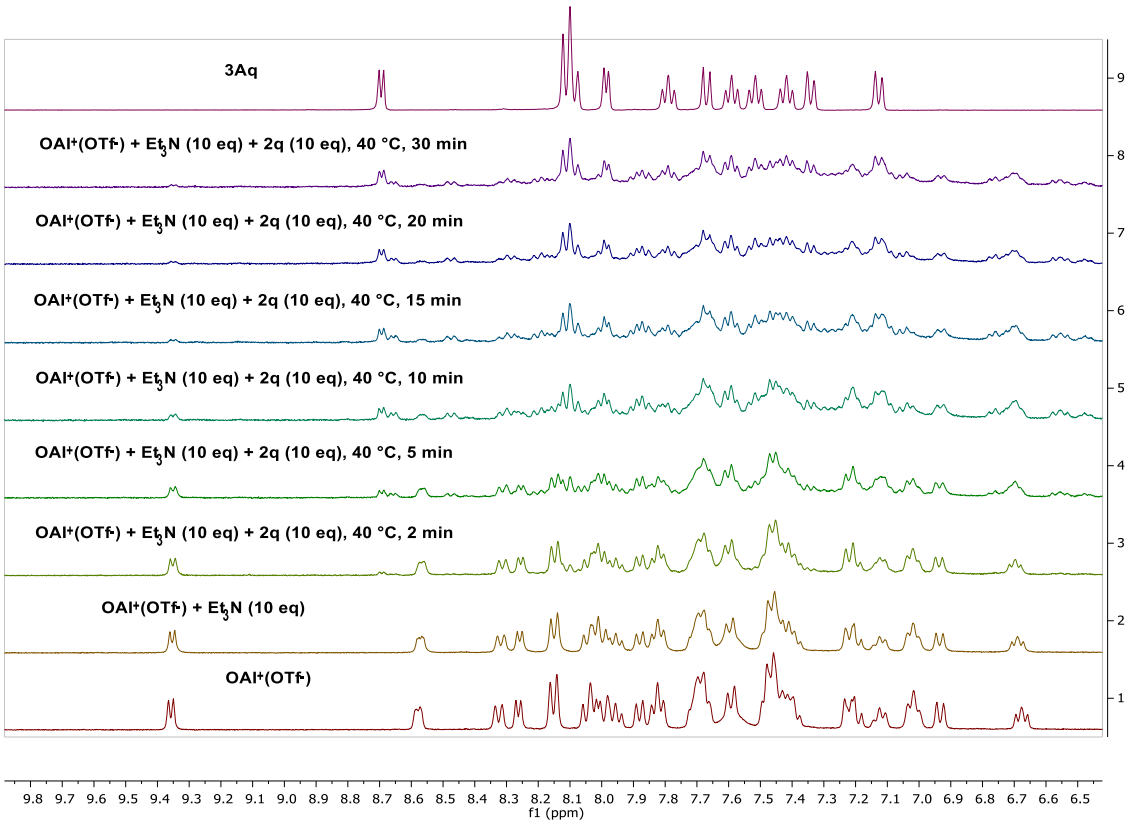
Scheme S1

A dried and deoxygenated Schlenk was charged with (*S*)-QUINAP **L10** (0.087 mmol, 38.4 mg) and 1-(isoquinolin-1-yl)naphthalene-2-yl triflate (0.087 mmol, 35.1 mg). After three cycles of vacuum-N_2, [Pd(Cp)(allyl)] (0.087 mmol, 18.4 mg) and dry and deoxygenated toluene (2.6 mL) were added. The reaction mixture was stirred overnight at 80 °C and a green precipitated was formed. The mixture was concentrated to dryness and the resulting residue (127.2 mg) was crystallized by slow diffusion of *n*-hexane into a solution of the reaction crude in THF to give **OAI$^+$(OTf$^-$)** as pale yellow prisms suitable for X-Ray analysis (76 mg, 88%). M.P. = 170-172 °C (dec.). $[\alpha]^{20}_D$= –71.2° (*c* 0.1, $CHCl_3$). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): A curved baseline was observed. δ 9.15 (d, 1H, *J* = 6.2 Hz), 8.41 (d, 1H, $J_{H,H}$ = 6.2 Hz and $J_{H,P}$ = 2.7 Hz), 8.09 (d, 1H, *J* = 8.7 Hz), 8.07 (d, 1H, *J* = 8.7 Hz), 8.02-7.94 (m, 3H), 7.86-7.82 (m, 2H), 7.78-7.70 (m, 4H), 7.66-7.61 (m, 3H), 7.59-7.53 (m, 3H), 7.44-7.30 (m, 8H), 7.23 (t, 1H, $J_{H,H}$ = $J_{H,P}$ = 8.7 Hz), 7.16 (d, 1H, *J* = 8.7 Hz), 7.05-7.00 (m, 2H), 6.95-6.92 (m, 2H), 6.75 (dd, 1H, $J_{H,H}$ = 8.3 Hz and $J_{H,P}$ = 6.3 Hz). ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): δ 167.8 (d, $J_{C,P}$ = 3 Hz), 158.2 (d, $J_{C,P}$ = 8 Hz), 156.7 (d, $J_{C,P}$ = 5 Hz), 143.8 (d, $J_{C,P}$ = 2 Hz), 141.7, 141.3, 140.1 (d, $J_{C,P}$ = 13 Hz), 138.9, 137.2, 136.8 (d, $J_{C,P}$ = 12 Hz), 136.0 (br s), 134.7 (d, $J_{C,P}$ = 2 Hz), 134.3, 134.2, 133.6, 133.6, 133.5, 133.2 133.1 (d, $J_{C,P}$ = 9 Hz), 132.7, 132.4 (d, $J_{C,P}$ = 3 Hz), 131.9, 131.8, 130.5, 130.2 (d, $J_{C,P}$ = 6 Hz), 130.0, 129.9, 129.2, 129.1, 129.1, 129.0, 128.9, 128.8, 128.7, 128.3, 128.2, 127.7, 127.6,

127.3 (d, $J_{C,P}$ = 7 Hz), 126.8 (d, $J_{C,P}$ = 15 Hz), 126.5, 126.4, 126.2, 125.8, 125.8, 125.0 (d, $J_{C,P}$ = 50 Hz), 123.3 (d, $J_{C,P}$ = 54 Hz), 122.0 (d, $J_{C,P}$ = 3 Hz), 121.6 (q, $J_{C,F}$ = 319 Hz). ^{31}P NMR (161.7 MHz, CD_2Cl_2): δ +42.6. ^{19}F NMR (377 MHz, CD_2Cl_2): δ –78.8. HRMS (ESI) *m/z* calcd for $C_{50}H_{34}N_2PPd$ (M^+) 799.1489, found 799.1468.

Reaction of the OAI$^+$(OTf$^-$) with ethynyltrimethylsilane 2q (Graph S1).

A Young's NMR tube was charged with a solution of **OAI$^+$(OTf$^-$)** (4.9 mg, 5 μmol) in DMSO-d_6 (0.5 mL) (^{1}H NMR spectra 1). Et_3N (10 eq) was added and the resulting mixture was warmed at 40 °C (^{1}H NMR spectra 2). Then alkyne **2q** (10 eq) was added and a series of ^{1}H NMR spectra were recorded every 5 min at the same temperature (^{1}H NMR spectra 3-8, Graph S1).



Graph S1

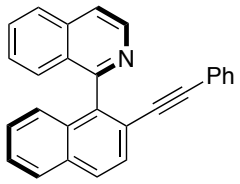
Dynamic Kinetic Asymmetric alkynylation employing Quinap ligand L10.

General procedure: A flamed-dried Schlenk tube was charged with the corresponding nonaflate **(±)-1A, 1C, 1E** or triflate **(±)-1B, 1D** (0.1 mmol), $Pd(AcO)_2$ (5 mol%, 1.1 mg) and (S)-QUINAP ligand **L10** (6 mol%, 2.7 mg). After three cycles of vacuum-argon, dry DMSO (1 mL) was added and the resulting mixture was stirred for 5 min at room temperature. Then Et_3N (0.3 mmol, 42 μL) and the corresponding alkyne **2a-q** (0.2 mmol) were sequentially added and the resulting mixture was stirred at 40 °C for 18 hours. The reaction crude was allowed to reach room temperature, water (5 mL) was added and the resulting mixture was extracted with AcOEt (4 × 3 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, concentrated, and the residue was purified by column chromatography on silica gel using CH_2Cl_2/AcOEt mixtures.

*Note: The racemic products were prepared by heating at 60 °C a mixture of the corresponding starting nonaflate **(±)-1A, 1C, 1E** or triflate **(±)-1B, 1D** (0.1 mmol), Et_3N (0.3 mmol) and alkyne (0.2 mmol) in DMSO (1 mL), using (±)-BINAP (12 mol%)/$Pd(AcO)_2$ (10 mol%) as the catalyst. For the synthesis of **3Af,** racemic (±)-QUINAP was used instead (±)-BINAP.*

Yields, solvent used for chromatography, and characterization data for products **3Aa-3Eq, 4A-C, 5-7** are as follows:

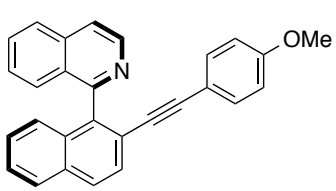
(*R*)-1-(2-(Phenylethynyl)naphthalen-1-yl)isoquinoline (3Aa, Table 2).



Following the general procedure using nonaflate **1A** and ethynylbenzene **2a**, purification by flash chromatography (CH_2Cl_2→25:1 CH_2Cl_2/EtOAc) afforded **3Aa** (35 mg, 99%) as a light yellow solid. M. p. 159-162 °C. $[\alpha]^{20}_D$ +494.8 (*c* 0.49, $CHCl_3$) for 97 % ee. ^1H NMR (400 MHz, $CDCl_3$): δ 8.77 (d, *J* = 5.7 Hz, 1H), 7.98 (dd, *J* = 8.4, 2.4 Hz, 2H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 5.7 Hz, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.70 (ddd, *J* = 8.2, 6.7, 1.2 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.49 (ddd, *J* = 8.1, 6.6, 1.3 Hz, 1H), 7.43 (ddd, *J* = 8.3, 6.8, 1.2 Hz, 1H), 7.35 (ddd, *J* = 8.1, 6.6, 1.3 Hz, 1H), 7.29 (*br* d, *J* = 8.3 Hz 1H), 7.18-7.07 (m, 3H), 6.78-6.74 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 142.5, 139.8, 136.2, 133.1, 132.4, 131.2, 130.2, 128.6, 128.3, 128.1, 128.0 (2C), 127.9, 127.5, 127.3, 126.9, 126.8, 126.6, 126.2, 122.9, 121.1, 120.3, 94.1, 88.9. HRMS (ESI) calcd. for $C_{27}H_{18}N$ (M +

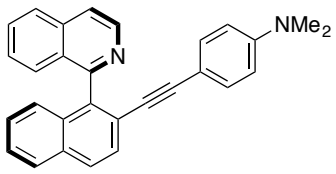
H^+) 356.1434. Found 356.1430. HPLC (AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min): t_R 12.07 min (major) and 14.46 min (minor).

(*R*)-1-(2-((4-Methoxyphenyl)ethynyl)naphthalen-1-yl)isoquinoline (3Ab, Table 2).



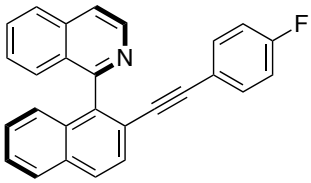
Following the general procedure using nonaflate **1A** and 1-ethynyl-4-methoxybenzene **2b**, purification by flash chromatography (CH_2Cl_2→20:1 CH_2Cl_2/EtOAc) afforded **3Ab** (38 mg, 99%) as a yellow amorphous solid. $[\alpha]^{20}_D$ +405.2 (*c* 0.51, $CHCl_3$) for 95 % ee. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (d, *J* = 5.7 Hz, 1H), 7.96 (d, *J* = 8.6 Hz, 2H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 5.7 Hz, 1H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 9.5 Hz, 1H), 6.69 (d, *J* = 8.8 Hz, 2H), 6.63 (d, *J* = 8.8 Hz, 2H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 159.4, 142.5, 139.4, 136.2, 132.9, 132.6, 132.4, 130.2, 128.5, 128.3, 128.0 (2C), 127.6, 127.3, 126.9, 126.7, 126.4, 126.1, 121.4, 120.2, 115.0, 113.6, 94.2, 87.7, 55.2. HRMS (ESI) calcd. for $C_{28}H_{20}NO$ (M + H^+) 386.1539. Found 386.1534. HPLC (AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 10.61 min (minor) and 16.08 min (major).

(*R*)-4-((1-(Isoquinolin-1-yl)naphthalen-2-yl)ethynyl)-*N*,*N*-dimethylaniline (3Ac, Table 2).



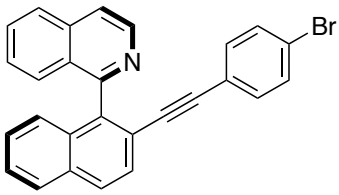
Following the general procedure using nonaflate **1A** and 4-ethynyl-*N*,*N*-dimethylaniline **2c**, purification by flash chromatography (CH_2Cl_2→10:1 CH_2Cl_2/EtOAc) afforded **3Ac** (38 mg, 95%) as a beige amorphous solid. $[\alpha]^{20}_D$ +669.2 (*c* 0.05, $CHCl_3$) for 88 % ee. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (dd, *J* = 5.9, 2.2 Hz, 1H), 7.95 (t, *J* = 7.6 Hz, 2H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.80 (dd, *J* = 5.8, 2.0 Hz, 1H), 7.71 (d, *J* = 8.9 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.49-7.38 (m, 2H), 7.32 (*br* t, *J* = 7.4 Hz, 1H), 7.27 (*br* d, *J* = 8.5 Hz, 1H), 6.63 (d, *J* = 7.3 Hz, 2H), 6.41 (d, *J* = 7.4 Hz, 2H), 2.88 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 149.8, 142.5, 138.8, 136.2, 132.7, 132.5, 132.3, 130.1, 128.4, 128.0 (2C), 127.7, 127.2, 126.7 (2C), 126.1, 126.0, 122.0, 120.1, 111.4, 109.7, 95.7, 87.1, 40.1. HRMS (ESI) calcd. for $C_{29}H_{23}N_2$ (M + H^+) 399.1856. Found 399.1851. HPLC (AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 9.06 min (minor) and 15.57 min (major).

(*R*)-1-(2-((4-Fluorophenyl)ethynyl)naphthalen-1-yl)isoquinoline (3Ad, Table 2).



Following the general procedure using nonaflate **1A** and 1-ethynyl-4-fluorobenzene **2d**, purification by flash chromatography (CH_2Cl_2→5:1 CH_2Cl_2/EtOAc) afforded **3Ad** (37 mg, 98%) as a clear viscous oil. $[\alpha]^{20}_D$ +214.5 (*c* 0.5, $CHCl_3$) for 95 % ee. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (d, *J* = 5.7 Hz, 1H), 7.97 (d, *J* = 8.6 Hz, 2H) 7.93 (d, *J* = 8.2 Hz, 1H), 7.81 (*br* d, *J* = 5.7 Hz, 1H), 7.76-7.65 (m, 2H), 7.58 (*br* dd, *J* = 8.5, 1.1 Hz, 1H), 7.50 (ddd, *J* = 8.1, 6.7, 1.3 Hz, 1H), 7.43 (ddd, *J* = 8.3, 6.8, 1.2 Hz, 1H), 7.35 (ddd, *J* = 8.1, 6.7, 1.3 Hz, 1H), 7.28 (*br* d, *J* = 8.4 Hz, 1H), 6.83-6.77 (m, 2H), 6.74-6.69 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2 (d, $^1J_{CF}$ = 249.4 Hz), 159.4, 142.6, 139.8, 136.2, 133.1, 133.0 (d, $^3J_{CF}$ = 8.4 Hz), 132.4, 130.3, 128.6, 128.3, 128.1, 127.9, 127.5, 127.3, 127.0, 126.8, 126.6, 126.2, 120.9, 120.3, 119.0 (d, $^4J_{CF}$ = 3.3 Hz), 115.3 (d, $^2J_{CF}$ = 22.2 Hz), 93.0, 88.6 (d, $^5J_{CF}$ = 1.3 Hz). ^{19}F NMR (377 MHz, $CDCl_3$) δ -111.0. HRMS (ESI) calcd. for $C_{27}H_{17}FN$ ($M + H^+$) 374.1340. Found 374.1335. HPLC (AD-H column, 80:20 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 7.08 min (minor) and 9.53 min (major).

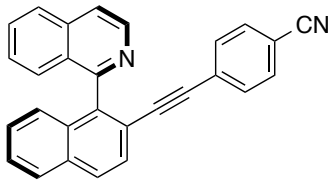
(*R*)-1-(2-((4-Bromophenyl)ethynyl)naphthalen-1-yl)isoquinoline (3Ae, Table 2).



Following the general procedure using nonaflate **1A** and 1-bromo-4-ethynylbenzene **2e**, purification by flash chromatography (CH_2Cl_2→5:1 CH_2Cl_2/EtOAc) afforded **3Ae** (40 mg, 92%) as a light yellow amorphous solid. $[\alpha]^{20}_D$ +146.7 (*c* 0.26, $CHCl_3$) for 94 % ee. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (d, *J* = 5.7 Hz, 1H), 7.98 (dd, *J* = 8.4, 3.1 Hz, 2H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 5.7 Hz, 1H), 7.75-7.67 (m, 2H), 7.58 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.50 (ddd, *J* = 8.1, 6.7, 1.3 Hz, 1H), 7.43 (ddd, *J* = 8.3, 6.8, 1.2 Hz, 1H), 7.35 (ddd, *J* = 8.1, 6.7, 1.3 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.25-7.21 (m, 2H), 6.62-6.54 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 142.4, 136.2, 133.2, 132.5, 132.3, 131.2, 130.3, 128.7, 128.3, 128.1, 127.9, 127.5, 127.4, 127.0, 126.8, 126.7, 126.2, 122.2, 121.8, 120.7, 120.3, 93.0, 90.0. HRMS (ESI) calcd. for $C_{27}H_{17}BrN$ ($M + H^+$) 434.0539. Found 434.0533. HPLC (AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 8.98 min (minor) and 14.77 min (major).

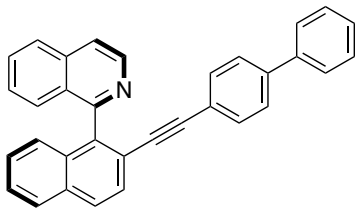
(*R*)-4-((1-(Isoquinolin-1-yl)naphthalen-2-yl)ethynyl)benzonitrile (3Af, Table 2).

Following the general procedure using nonaflate **1A** and 4-ethynylbenzonitrile **2f**,



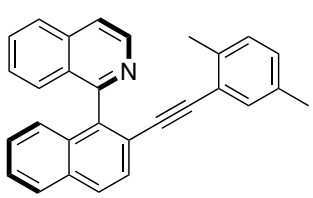
purification by flash chromatography (CH_2Cl_2→5:1 CH_2Cl_2/EtOAc) afforded **3Af** (35 mg, 92%) as a yellow foam. $[\alpha]^{20}_D$ +192.4 (*c* 0.20, $CHCl_3$) for 75 % ee. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (d, *J* = 5.7 Hz, 1H), 8.0 (d, *J* = 8.5 Hz, 1H), 7.99 (*br* d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.83 (dd, *J* = 5.7, 0.9 Hz, 1H), 7.75-7.69 (m, 2H), 7.57-7.50 (m, 2H), 7.43 (ddd, *J* = 8.2, 6.8, 1.1 Hz, 1H), 7.40-7.34 (m, 3H), 7.29 (*br* d, *J* = 8.7 Hz, 1H), 6.81-6.77 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 142.5, 140.7, 136.2, 133.5, 132.3, 131.7, 131.5, 130.4, 128.8, 128.2, 128.1, 127.8, 127.5, 127.3, 127.2, 127.1, 126.9, 126.3, 120.4, 119.9, 118.4, 111.1, 93.3, 92.2. HRMS (ESI) calcd. for $C_{28}H_{17}N_2$ (M + H^+) 381.1386. Found 381.1382. HPLC (AD-H column, 80:20 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 10.2 min (minor) and 19.5 min (major).

(*R*)-1-(2-([1,1'-Biphenyl]-4-ylethynyl)naphthalen-1-yl)isoquinoline (3Ag, Table 2).



Following the general procedure using nonaflate **1A** and 4-ethynyl-1,1'-biphenyl **2g**, purification by flash chromatography (CH_2Cl_2→5:1 CH_2Cl_2/EtOAc) afforded **3Ag** (38 mg, 88%) as a light brown foam. $[\alpha]^{20}_D$ +316.1.0 (*c* 0.51, $CHCl_3$) for 91 % ee. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (d, *J* = 5.7 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.94 (*br* d, *J* = 8.2 Hz, 1H), 7.83 (dd, *J* = 5.8, 0.9 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.71 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 7.61 (*br* dd, *J* = 8.5, 1.0 Hz, 1H), 7.52-7.47 (m, 3H), 7.47-7.36 (m, 3H), 7.36-7.31 (m, 4H), 7.29 (dd, *J* = 8.3, 1.2 Hz, 1H), 6.83-6.80 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 142.6, 140.7, 140.2, 139.9, 136.3, 133.1, 132.4, 131.6, 130.3, 128.8, 128.6, 128.4, 128.1, 128.0, 127.6, 127.5, 127.4, 126.9 (2C), 126.8, 126.6 (2C), 126.2, 121.8, 121.1, 120.3, 94.0, 89.6. HRMS (ESI) calcd. for $C_{33}H_{22}N$ (M + H^+) 432.1747. Found 432.1742. HPLC (AD-H column, 80:20 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 7.58 min (minor) and 12.05 min (major).

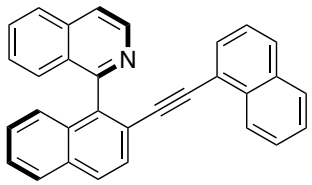
(*R*)-1-(2-((2,5-Dimethylphenyl)ethynyl)naphthalen-1-yl)isoquinoline (3Ah, Table 2).



Following the general procedure using nonaflate **1A** and 2-ethynyl-1,4-dimethylbenzene **2h**, purification by flash chromatography (CH_2Cl_2→5:1 CH_2Cl_2/EtOAc) afforded **3Ah** (36 mg, 94%) as a light yellow amorphous solid. $[\alpha]^{20}_D$ +303.2 (*c* 0.5, $CHCl_3$) for 92 % ee. ^{1}H NMR (400MHz, $CDCl_3$): δ 8.76 (d, *J* = 5.7 Hz, 1H), 7.98 (*br* d, *J* = 8.5 Hz, 1H), 7.94 (*br* t, *J* = 7.7 Hz, 2H), 7.81-7.75 (m, 2H), 7.68 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 7.59 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.48 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.42 (ddd, *J* = 8.3, 6.8, 1.2 Hz, 1H), 7.32 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.20 (*br* d, *J* = 8.4 Hz, 1H), 6.88 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.84 (*br* d, *J* = 7.8 Hz, 1H), 6.77 (*br* s, 1H), 2.17 (s, 3H), 1.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 142.7, 139.2, 136.7, 136.4, 134.6, 133.0, 132.5, 132.2, 130.2, 129.0, 128.9, 128.5 (2C), 128.4, 128.0, 127.5, 127.4, 126.9, 126.7, 126.5, 126.1, 122.5, 121.3, 120.3, 93.0, 92.3, 20.6, 19.2. HRMS (ESI) calcd. for $C_{29}H_{22}N$ (M + H^+) 384.1747. Found 384.1743. HPLC (AD-H column, 80:20 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 8.23 min (major) and 18.64 min (minor).

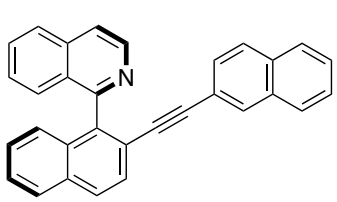
(*R*)-1-(2-(Naphthalen-1-ylethynyl)naphthalen-1-yl)isoquinoline (3Ai, Table 2).

Following the general procedure using nonaflate **1A** and 1-ethynylnaphthalene **2i**,



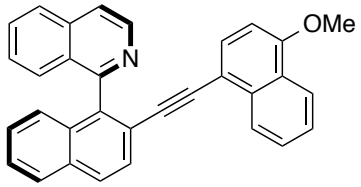
purification by flash chromatography (CH_2Cl_2→5:1 CH_2Cl_2/EtOAc) afforded **3Ai** (40 mg, 99%) as a yellow foam. $[\alpha]^{20}_D$ +371.0 (*c* 0.5, $CHCl_3$) for 94 % ee. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (d, *J* = 5.7 Hz, 1H), 8.02 (t, *J* = 8.2 Hz, 2H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.90-7.85 (m, 2H), 7.73-7.63 (m, 4H), 7.51 (ddd, *J* = 8.1, 6.7, 1.2 Hz, 1H), 7.44 (ddd, *J* = 8.3, 6.8, 1.2 Hz, 1H), 7.41-7.27 (m, 4H), 7.25 (*br* d, *J* = 9.3 Hz, 1H), 7.16 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 142.8, 139.5, 136.4, 133.1, 132.8, 132.5, 130.4, 130.2, 128.7, 128.5 (3C), 128.1, 127.9, 127.6, 127.5, 127.0, 126.8, 126.6, 126.2 (2C), 126.1, 125.8, 125.0, 121.2, 120.6, 120.4, 93.6, 92.0. HRMS (ESI) calcd. for $C_{31}H_{20}N$ (M + H^+) 406.1590. Found 406.1586. HPLC (AD-H column, 80:20 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 12.07 min (major) and 18.17 min (minor).

(*R*)-1-(2-(Naphthalen-2-ylethynyl)naphthalen-1-yl)isoquinoline (3Aj, Table 2).



Following the general procedure using nonaflate **1A** and 2-ethynylnaphthalene **2j**, purification by flash chromatography (CH_2Cl_2→5:1 CH_2Cl_2/EtOAc) afforded **3Aj** (40 mg, 99%) as a light yellow foam. $[\alpha]^{20}_D$ +207.6 (*c* 0.5, $CHCl_3$) for 94 % ee. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (d, *J* = 5.7 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.95 (*br* d, *J* = 8.2, 1H), 7.85 (dd, *J* = 5.8, 0.9 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.75-7.67 (m, 2H), 7.65 (*br* dd, *J* = 8.5, 1.0 Hz, 1H), 7.62-7.58 (m, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.51 (ddd, *J* = 8.2, 6.5, 1.5 Hz, 1H), 7.48-7.39 (m, 3H), 7.39-7.34 (m, 1H), 7.32 (*br* d, *J* = 7.8 Hz, 1H), 7.23 (*br* s, 1H), 6.76 (dd, *J* = 8.5, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 142.6, 140.0, 136.3, 133.2, 132.7, 132.6, 132.4, 131.1, 130.3, 128.6, 128.4, 128.1, 128.0, 127.9, 127.6 (3C), 127.5, 127.4, 127.0, 126.8, 126.6, 126.5, 126.3, 126.2, 121.1, 120.3, 120.2, 94.6, 89.4. HRMS (ESI) calcd. for $C_{31}H_{20}N$ (M + H^+) 406.1590. Found 406.1586. HPLC (AD-H column, 80:20 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 8.75 min (minor) and 12.53 min (major).

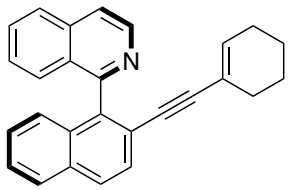
(*R*)-1-(2-((4-Methoxynaphthalen-1-yl)ethynyl)naphthalen-1-yl)isoquinoline (3Ak, Table 2).



Following the general procedure using nonaflate **1A** and 1-ethynyl-4-methoxynaphthalene **2k**, purification by flash chromatography (CH_2Cl_2→CH_2Cl_2/EtOAc 20:1) afforded **3Ak** (41 mg, 94%) as a beige solid. X-ray quality crystals (colorless prisms) were obtained by slow evaporation of a solution of **3Ak** in CH_2Cl_2. M. p. 220-222 °C (decomposition). $[\alpha]^{20}_D$ +387.3 (*c* 0.52, $CHCl_3$) for 89 % ee. ^{1}H NMR (400 MHz, $CDCl_3$). 8.83 (d, *J* = 5.7 Hz, 1H), 8.13 (d, *J* = 8.3, 1H), 8.02 (d, *J* = 3.9 Hz, 1H), 8.00 (d, *J* = 3.7 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.89-7.85 (m, 2H), 7.73-7.65 (m, 2H), 7.50 (ddd, *J* = 8.1, 6.7, 1.2 Hz, 1H), 7.44 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 7.41-7.32 (m, 2H), 7.29-7.22 (m, 2H), 7.18 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 6.82 (d, *J* = 8.3 Hz, 1H), 6.62 (d, *J* = 8.1 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 155.8, 142.8, 139.0, 136.4, 133.7, 132.9, 132.5, 130.9, 130.4, 128.6, 128.5, 128.0, 127.5 (2C), 126.9, 126.8, 126.7, 126.4, 126.1, 125.5, 125.3, 124.9, 121.9, 121.6, 120.3, 112.8, 103.4, 99.9, 92.5, 92.1, 55.5. HRMS (ESI)

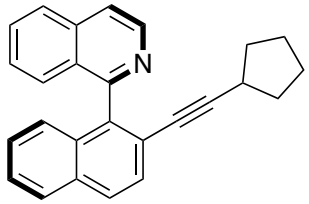
calcd. for $C_{32}H_{22}NO$ (M + H^+) 436.1696. Found 436.1693. HPLC (AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 18.65 min (major) and 21.13 min (minor).

(*R*)-1-(2-(Cyclohex-1-en-1-ylethynyl)naphthalen-1-yl) (3Al, Table 2).



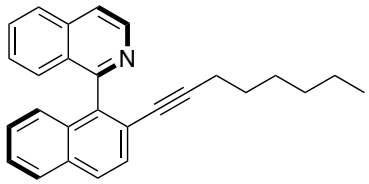
Following the general procedure using nonaflate **1A** and 1-ethynylcyclohex-1-ene **2l**, purification by flash chromatography (CH_2Cl_2→25:1 CH_2Cl_2/EtOAc) afforded **3Al** (28 mg, 78%) as light yellow amorphous solid. $[\alpha]^{20}_D$ +229.8 (*c* 0.51, $CHCl_3$) for 98 % ee. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (d, *J* = 5.7 Hz, 1H), 7.97-7.86 (m, 3H), 7.77 (d, *J* = 5.8 Hz, 1H), 7.68 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 7.63 (d, *J* = 8.6 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.48-7.38 (m, 2H), 7.31 (ddd, *J* = 8.2, 6.7, 1.2 Hz, 1H), 7.23 (d, *J* = 8.5 Hz, 1H), 5.55 (*br* t, *J* = 3.5 Hz, 1H), 1.96-1.85 (m, 2H), 1.46-1.33 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 142.5, 139.3, 136.2, 134.8, 132.8, 132.4, 130.1, 128.4, 128.3, 128.1, 128.0, 127.6, 127.2, 126.8, 126.7, 126.2, 126.1, 121.6, 120.4, 120.1, 96.1, 86.4, 28.3, 25.5, 22.0, 21.3. HRMS (ESI) calcd. for $C_{27}H_{22}N$ (M + H^+) 360.1747. Found 360.1742. HPLC (AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 9.28 min (minor) and 10.55 min (major).

(*R*)-1-(2-(Cyclopentylethynyl)naphthalen-1-yl)isoquinoline (3Am, Table 2).



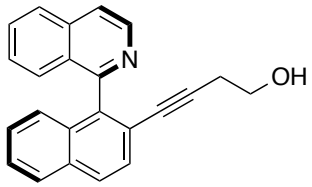
Following the general procedure using nonaflate **1A** and ethynylcyclopentane **3m**, purification by flash chromatography (CH_2Cl_2→25:1 CH_2Cl_2/EtOAc) afforded **3Am** (31 mg, 89%) as light yellow amorphous solid. $[\alpha]^{20}_D$ +110.0 (*c* 0.26, $CHCl_3$) for 96 % ee. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (d, *J* = 5.7 Hz, 1H), 7.95-7.86 (m, 3H), 7.76 (d, *J* = 5.7 Hz, 1H), 7.68 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.53 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.47-7.38 (m, 2H), 7.30 (ddd, *J* = 8.2, 6.7, 1.3 Hz, 1H), 7.22 (dd, *J* = 8.5, 1.1 Hz, 1H), 2.44-2.35 (m, 1H), 1.50-1.38 (m, 2H), 1.30-1.11 (m, 4H), 0.98-0.83 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 142.3, 139.3, 136.2, 132.7, 132.4, 130.1, 128.4, 128.3, 128.2, 127.9, 127.6, 127.1, 126.7, 126.6, 126.1, 125.9, 121.9, 120.0, 100.0, 79.4, 33.2, 33.2, 30.3, 24.4. HRMS (ESI) calcd. for $C_{26}H_{22}N$ (M + H^+) 348.1747. Found 348.1742. HPLC (AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 6.17 min (minor) and 7.01 min (major).

(*R*)-1-(2-(Oct-1-yn-1-yl)naphthalen-1-yl)isoquinoline (3An, Table 2).



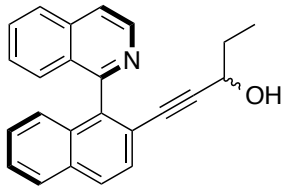
Following the general procedure using nonaflate **1A** and oct-1-yne **2n**, purification by flash chromatography (CH_2Cl_2→25:1 CH_2Cl_2/EtOAc) afforded **3An** (36 mg, 99%) as a yellow amorphous solid. $[\alpha]^{20}_D$ +1253.3 (*c* 0.51, $CHCl_3$) for 96 % ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 5.7 Hz, 1H), 8.05-7.92 (m, 3H), 7.84 (d, *J* = 5.7 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.60 (d, *J* = 8.5 Hz, 1H), 7.57-7.45 (m, 2H), 7.41-7.34 (m, 1H), 7.25 (d, *J* = 8.5 Hz, 1H), 2.05 (t, *J* = 6.8 Hz, 2H), 1.22 (q, *J* = 7.4 Hz, 2H), 1.11-0.96 (m, 4H), 0.95-0.84 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 142.5, 139.3, 136.2, 132.7, 132.4, 130.0, 128.5, 128.3, 127.9, 127.5, 127.1, 126.7, 126.1, 126.0, 121.8, 120.1, 95.4, 79.9, 31.2, 28.1, 27.9, 22.3, 19.1, 14.1. HRMS (ESI) calcd. for $C_{27}H_{26}N$ (M + H^+) 364.2060. Found 364.2053. HPLC (AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 5.40 min (minor) and 6.48 min (major).

(*R*)-4-(1-(Isoquinolin-1-yl)naphthalen-2-yl)but-3-yn-1-ol (3Ao, Table 2).



Following the general procedure using nonaflate **1A** and but-3-yn-1-ol **2o**, purification by flash chromatography (CH_2Cl_2→10:1 CH_2Cl_2/EtOAc) afforded **3Ao** (32 mg, 99%) as a white foam. $[\alpha]^{20}_D$ +84.2 (*c* 0.27, $CHCl_3$) for 96 % ee. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (d, *J* = 5.7 Hz, 1H), 7.96 (dt, *J* = 8.3, 1.0 Hz, 1H), 7.94-7.88 (m, 2H), 7.81 (dd, *J* = 5.8, 0.9 Hz, 1H), 7.71 (ddd, *J* = 8.2, 6.7, 1.4 Hz, 1H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.51-7.40 (m, 3H), 7.30 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.15 (*br* dd, *J* = 8.6, 1.0 Hz, 1H), 3.10 (t, *J* = 5.9 Hz, 2H), 2.20 (q, *J* = 6.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 142.3, 139.3, 136.2, 132.8, 132.2, 130.5, 128.6, 128.2, 128.1, 128.0, 127.5, 127.3, 127.0, 126.9, 126.4, 125.9, 121.1, 120.5, 91.6, 81.7, 60.6, 23.7. HRMS (ESI) calcd. for $C_{23}H_{18}NO$ (M + H^+) 324.1383. Found 324.1380. HPLC (AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 9.42 min (minor) and 10.42 min (major).

(*R,R*) and (*R,S*)-1-(1-(Isoquinolin-1-yl)naphthalen-2-yl)pent-1-yn-3-ol (3Ap, Table 2).

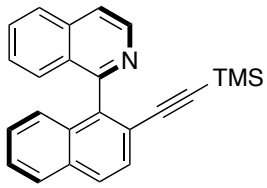


Following the general procedure using nonaflate **1A** and racemic pent-1-yn-3-ol **2p**, purification by flash chromatography (CH_2Cl_2→20:1 CH_2Cl_2/EtOAc) afforded **3Ap** (33 mg, 99%) as a 1:1 separable diastereomeric mixture and as a yellow foam. HRMS (ESI) calcd. for $C_{24}H_{20}NO$ ($M + H^+$) 338.1539. Found 338.1535.

Diastereomer 1 $[\alpha]^{20}_D$ +130.9 (*c* 0.16, $CHCl_3$) for 97 % ee. ^1H NMR (400 MHz, $CDCl_3$): δ 8.73 (d, *J* = 5.7 Hz, 1H), 7.98-7.88 (m, 3H), 7.78 (d, *J* = 5.8 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.53-7.40 (m, 3H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 8.5 Hz, 1H), 4.06 (dd, *J* = 7.0, 5.7 Hz, 1H), 1.28-1.02 (m, 3H), 0.40 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 142.2, 139.6, 136.3, 133.1, 132.3, 130.4, 128.7, 128.2, 128.1 (2C), 127.5, 127.4, 127.0, 126.8, 126.6, 126.1, 120.5, 120.4, 94.7, 84.0, 63.7, 30.3, 8.6. HPLC (AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 10.93 min (minor) and 11.89 min (major).

Diastereomer 2 $[\alpha]^{20}_D$ +105.0 (*c* 0.25, $CHCl_3$) for 97 % ee. ^1H NMR (400 MHz, $CDCl_3$): δ 8.73 (d, *J* = 5.7 Hz, 1H), 7.99-7.88 (m, 3H), 7.79 (d, *J* = 5.8 Hz, 1H), 7.70 (ddd, *J* = 8.1, 6.7, 1.3 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.52-7.45 (m, 2H), 7.45-7.39 (m, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 1H), 4.03 (t, *J* = 6.4 Hz, 1H), 1.35-1.05 (m, 3H), 0.40 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 142.1, 139.6, 136.3, 133.1, 132.2, 130.4, 128.7, 128.3, 128.2, 128.1, 127.5, 127.4, 127.0, 126.9, 126.7, 126.1, 120.5, 94.7, 84.0, 63.7, 30.3, 8.6. HPLC (AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 10.09 min (minor) and 12.33 min (major).

(*R*)-1-(2-((Trimethylsilyl)ethynyl)naphthalen-1-yl)isoquinoline (3Aq, Table 2).

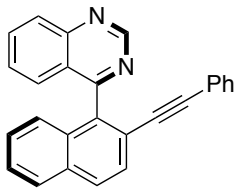


Following the general procedure using nonaflate **1A** and ethynyltrimethylsilane **2q**, purification by column chromatography (CH_2Cl_2→CH_2Cl_2/EtOAc 25:1) afforded **3Aq** (35 mg, 99%) as a beige amorphous solid. $[\alpha]^{20}_D$ +223.7 (*c* 0.50, $CHCl_3$) for 97 % ee. ^1H NMR (400 MHz, $CDCl_3$): δ 8.73 (*br* d, *J* = 5.7 Hz, 1H), 7.98-7.87 (m, 3H), 7.77 (d, *J* = 5.7 Hz, 1H), 7.69 (d, *J* = 7.2 Hz, 1H), 7.65 (d, *J* = 8.7 Hz, 1H), 7.53 (d, *J* = 8.5 Hz, 1H), 7.48 (*br* t,

J = 7.4 Hz, 1H), 7.41 (*br* t, *J* = 7.6 Hz, 1H), 7.33 (*br* t, *J* = 7.6 Hz, 1H), 7.27 (*br* d, *J* = 9.0 Hz, 1H), -0.27 (d, *J* = 1.2 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 142.4, 140.8, 136.2, 133.2, 132.2, 130.1, 128.4, 128.3, 128.0, 127.8, 127.5, 127.1, 126.9, 126.6 (2C), 126.2, 120.9, 120.1, 104.1, 99.4, -0.7. HRMS (ESI) calcd. for $C_{24}H_{22}NSi$ ($M + H^+$) 352.1516. Found 352.1511. HPLC (AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 4.47 min (minor) and 5.20 min (major).

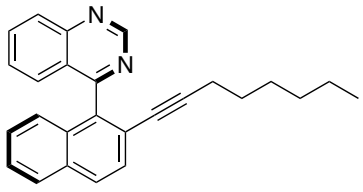
Reaction performed on a large scale: nonaflate ***1A*** *(1.11 g, 2.0 mmol), ethynyltrimethylsilane* ***2q*** *(295 mg, 424 μL, 3.0 mmol), $Pd(OAc)_2$, (1 mol%, 4.5 mg, 0.02 mmol), (S)-QUINAP (1.2 mol%, 10.5 mg, 0.024 mmol), Et_3N (405 mg, 558 μL, 4.0 mmol) in DMSO (4 mL). After deprotection with TBAF (2.1 mL, 1.0M) in THF (15 mL) at room temperature, the corresponding terminal alkyne* ***3Aq*** *was obtained in 80% yield (447 mg) and 97% ee.*

(*R*)-4-(2-(Phenylethynyl)naphthalen-1-yl)quinazoline. (3Ba, Table 3).



Following the general procedure using triflate **1B** and ethynylbenzene **2a**, purification by flash chromatography (CH_2Cl_2→25:1 CH_2Cl_2/EtOAc) afforded **3Ba** (35 mg, 99%) as a white amorphous solid. $[\alpha]^{20}_D$ +209.2 (*c* 0.05, $CHCl_3$) for 98 % ee. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.57 (s, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.98-7.90 (m, 2H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.64-7.60 (m, 1H), 7.56-7.47 (m, 2H), 7.39 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.29 (*br* d, *J* = 8.4 Hz, 1H), 7.21-7.08 (m, 3H), 6.81-6.75 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6, 155.0, 150.5, 137.0, 134.2, 133.0, 131.6, 131.2, 129.5, 128.7, 128.4, 128.3, 128.1 (2C), 128.0, 127.5, 127.3, 127.0, 125.7, 125.0, 122.4, 120.9, 94.9, 88.2. HRMS (ESI) calcd. for $C_{26}H_{17}N_2$ ($M + H^+$) 357.1386. Found 357.1382. HPLC (IA column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 9.20 min (major) and 11.63 min (minor).

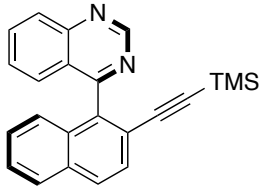
(*R*)-4-(2-(Oct-1-yn-1-yl)naphthalen-1-yl)quinazoline (3Bn, Table 3).



Following the general procedure using triflate **1B** and oct-1-yne **2n**, purification by flash chromatography (CH_2Cl_2→25:1 CH_2Cl_2/EtOAc) afforded **3Bn** (36 mg, 99%) as a light yellow

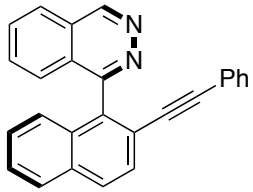
amorphous solid. $[\alpha]^{20}_D$ +124.9 (*c* 0.49, $CHCl_3$) for 97 % ee . ^1H NMR (400 MHz, $CDCl_3$): δ 9.52 (s, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 7.98-7.86 (m, 3H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.55-7.52 (m, 1H), 7.50-7.45 (m, 2H), 7.34 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.17 (*br* dd, *J* = 8.5, 0.9 Hz, 1H), 1.97 (td, *J* = 6.8, 1.3 Hz, 2H), 1.20-1.08 (m, 2H), 1.05-0.90 (m, 4H), 0.83 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.8, 154.9, 150.4, 136.6, 133.9, 132.5, 131.5, 129.2, 128.6, 128.5, 128.1, 127.7, 127.2 (2C), 126.4, 125.4, 125.0, 121.6, 96.5, 79.3, 31.1, 28.0, 27.9, 22.3, 19.1, 14.0. HRMS (ESI) calcd. for $C_{26}H_{25}N_2$ (M + H^+) 365.2012. Found 365.2007. HPLC (OJ-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 5.47 min (minor) and 9.03 min (major).

(*R*)-4-(2-((Trimethylsilyl)ethynyl)naphthalen-1-yl)quinazoline (3Bq, Table 3).



Following the general procedure using triflate **1B** and ethynyltrimethylsilane **2q**, purification by flash chromatography (CH_2Cl_2→5:1 CH_2Cl_2/EtOAc) afforded **3Bq** (33 mg, 94%) as a colorless viscous oil. $[\alpha]^{20}_D$ +325.0 (*c* 1.0, $CHCl_3$) for 96 % ee. ^1H NMR (400 MHz, $CDCl_3$): δ 9.52 (s, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 8.00-7.88 (m, 3H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.58-7.45 (m, 3H), 7.38 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.27 (*br* d, *J* = 9.1 Hz, 1H), -0.25 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 154.8, 150.4, 138.0, 134.0, 133.0, 131.4, 129.2, 128.6, 128.2, 127.8, 127.7, 127.3, 127.2, 127.0, 125.6, 125.0, 120.7, 103.3, 100.5, -0.8. HRMS (ESI) calcd. for $C_{23}H_{21}N_2Si$ (M + H^+) 353.1469. Found 353.1454. HPLC (IA column, 90:10 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 5.58 min (major) and 6.48 min (minor).

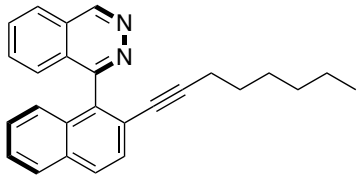
(*R*)-1-(2-(Phenylethynyl)naphthalen-1-yl)phthalazine (3Ca, Table 3).



Following the general procedure using nonaflate **1C** and ethynylbenzene **2a**, purification by flash chromatography (CH_2Cl_2→20:1 CH_2Cl_2/EtOAc) afforded **3Ca** (33 mg, 93%) as a light brown foam. $[\alpha]^{20}_D$ +79.5 (*c* 0.50, $CHCl_3$) for 94 % ee. ^1H NMR (400 MHz, $CDCl_3$): δ 9.72 (s, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.97-7.87 (m, 2H), 7.80-7.71 (m, 2H), 7.57 (*br* d, *J* = 8.3 Hz, 1H), 7.51 (ddd, *J* = 8.1, 6.6, 1.3 Hz, 1H), 7.37 (ddd, *J* = 8.1, 6.7, 1.3 Hz, 1H), 7.31 (dd, *J* = 8.6, 1.1 Hz, 1H), 7.19-7.06 (m, 3H), 6.81-6.75 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 150.8, 136.1, 133.0, 132.7, 132.5, 132.3,

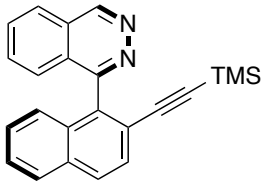
131.1, 129.3, 128.2, 128.1 (2C), 128.0, 127.2, 126.9, 126.8, 126.5, 126.3, 125.9, 122.5, 121.7, 94.8, 88.4. HRMS (ESI) calcd. for $C_{26}H_{17}N_2$ (M + H^+) 357.1386. Found 357.1382. HPLC (IA column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 17.16 min (major) and 24.76 min (minor).

(*R*)-1-(2-(Oct-1-yn-1-yl)naphthalen-1-yl)phthalazine (3Cn, Table 3).



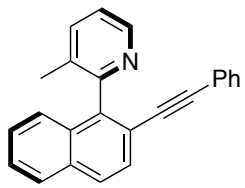
Following the general procedure using nonaflate **1C** and oct-1-yne **2n**, purification by flash chromatography (CH_2Cl_2→20:1 CH_2Cl_2/EtOAc) afforded **3Cn** (31 mg, 85%) as a light yellow foam. $[\alpha]^{20}_D$ +87.6 (*c* 0.48, $CHCl_3$) for 93 % ee. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.66 (d, *J* = 1.0 Hz, 1H), 8.07 (*br* d, *J* = 8.1, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.93-7.88 (m, 2H), 7.74 (ddd, *J* = 8.3, 7.0, 1.2 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.53-7.49 (m, 1H), 7.47 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.32 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.20 (dd, *J* = 8.5, 1.0 Hz, 1H), 1.94 (td, *J* = 6.9, 1.1 Hz, 2H), 1.17-1.05 (m, 2H), 1.01-0.86 (m, 4H), 0.84-0.75 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 150.7, 135.6, 132.6, 132.5, 132.4, 132.3 (2C), 129.1, 128.5, 128.0, 127.0 (2C), 126.5, 126.3, 125.7, 122.5, 96.3, 79.6, 31.1, 28.0, 27.9, 22.3, 19.1, 14.0. HRMS (ESI) calcd. for $C_{26}H_{25}N_2$ (M + H^+) 365.2012. Found 365.2006. HPLC (AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 10.00 min (major) and 11.56 min (minor).

(*R*)-1-(2-((Trimethylsilyl)ethynyl)naphthalen-1-yl)phthalazine (3Cq, Table 3).



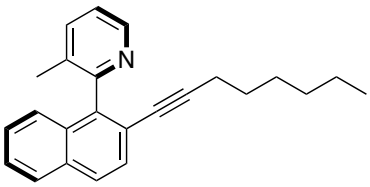
Following the general procedure using nonaflate **1C** and ethynyltrimethylsilane **2q**, purification by flash chromatography (CH_2Cl_2→3:1 CH_2Cl_2/EtOAc) afforded **3Cq** (32 mg, 91%) as a pale brown foam. $[\alpha]^{20}_D$ +318.5 (*c* 0.6, $CHCl_3$) for 92 % ee. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.66 (s, 1H), 8.08 (*br* d, *J* = 8.1, 1H), 7.97 (*br* d, *J* = 8.5 Hz, 1H), 7.95-7.89 (m, 2H), 7.75 (ddd, *J* = 8.3, 7.0, 1.2 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.57-7.46 (m, 2H), 7.41-7.28 (m, 2H), -0.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 150.7, 137.1, 133.2, 132.5, 132.4, 132.2, 129.2, 128.1, 127.9, 127.2, 126.9, 126.5, 126.3 (2C), 126.0, 121.5, 103.7, 100.3, -0.7. HRMS (ESI) calcd. for $C_{23}H_{21}N_2Si$ (M + H^+) 353.1469. Found 353.1455. HPLC (AD-H column, 90:10 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 10.58 min (major) and 16.18 min (minor).

(*R*)-3-Methyl-2-(2-(phenylethynyl)naphthalen-1-yl)pyridine (3Da, Table 3).



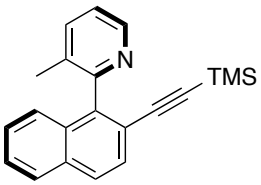
Following the general procedure using triflate **1D** and ethynylbenzene **2a**, purification by flash chromatography (CH_2Cl_2→25:1 CH_2Cl_2/EtOAc) afforded **3Da** (28 mg, 89%) as a white foam. $[\alpha]^{20}_D$ +28.8 (*c* 0.52, $CHCl_3$) for 95 % ee. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (dd, *J* = 4.9, 1.6 Hz, 1H), 7.90 (*br* d, *J* = 8.6 Hz, 2H), 7.73 (*br* d, *J* = 7.7 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.50 (ddd, *J* = 8.1, 6.7, 1.2 Hz, 1H), 7.42 (ddd, *J* = 8.2, 6.7, 1.3 Hz, 1H), 7.36 (dd, *J* = 7.7, 4.8 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.28-7.22 (m, 3H), 7.18-7.12 (m, 2H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.5, 147.0, 141.1, 137.6, 133.4, 133.2, 131.5, 131.4, 128.1 (3C), 126.9, 126.5, 125.7, 123.2, 122.6, 120.0, 93.0, 88.7, 18.6. HRMS (ESI) calcd. for $C_{24}H_{18}N$ (M + H^+) 320.1434. Found 320.1430. HPLC (AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 6.98 min (major) and 7.75 min (minor).

(*R*)-Methyl-2-(2-(oct-1-yn-1-yl)naphthalen-1-yl)pyridine (3Dn, Table 3).



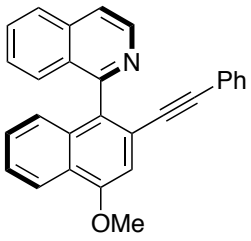
Following the general procedure using triflate **1D** and oct-1-yne **2n**, purification by flash chromatography (CH_2Cl_2→25:1 CH_2Cl_2/EtOAc) afforded **3Dn** (32 mg, 99%) as a white foam. $[\alpha]^{20}_D$ +71.6 (*c* 0.49, $CHCl_3$) for 88 % ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 4.9, 1.6 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.44 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.35 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.31-7.25 (m, 1H), 7.20 (d, *J* = 8.5 Hz, 1H), 2.19 (t, *J* = 6.8 Hz, 2H), 2.08 (s, 3H), 1.34-1.10 (m, 8H), 0.89 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 146.9, 140.4, 137.5, 133.2, 132.8, 131.6, 128.6, 128.0, 127.9, 126.6, 126.0, 125.5, 122.4, 120.8, 94.3, 79.6, 31.4, 28.4, 28.2, 22.5, 19.3, 18.6, 14.1. HRMS (ESI) calcd. for $C_{24}H_{26}N$ (M + H^+) 328.2060. Found 328.2055. HPLC (AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 4.24 min (minor) and 4.61 min (major).

(*R*)-3-Methyl-2-(2-((trimethylsilyl)ethynyl)naphthalen-1-yl)pyridine (3Dq, Table 3).



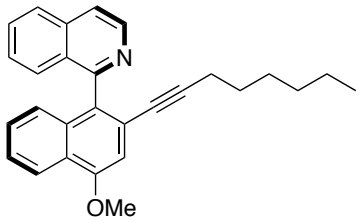
Following the general procedure using triflate **1D** and ethynyltrimethylsilane **2q**, purification by flash chromatography (CH_2Cl_2→25:1 CH_2Cl_2/EtOAc) afforded **3Dq** (30 mg, 96%) as a light yellow oil. $[\alpha]^{20}_D$ +79.8 (*c* 0.51, $CHCl_3$) for 90 % ee. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (ddd, *J* = 4.8, 1.4, 0.6 Hz, 1H), 7.86 (*br* d, *J* = 8.1 Hz, 1H), 7.83 (*br* d, *J* = 8.3 Hz, 1H), 7.66 (ddd, *J* = 7.7, 1.5, 0.7 Hz, 1H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.47 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1H), 7.38 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H), 7.31-7.25 (m, 2H), 2.08 (s, 3H), 0.01 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3, 146.9, 142.0, 137.4, 133.2, 133.2, 131.4, 128.1, 128.0, 127.9, 126.8, 126.5, 125.7, 122.5, 119.9, 104.0, 98.1, 18.5, -0.3. HRMS (ESI) calcd. for $C_{21}H_{22}NSi$ (M + H^+) 316.1516. Found 316.1512. HPLC (OJ-H column, 99:1 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 7.10 min (major) and 9.93 min (minor).

(*R*)-1-(4-Methoxy-2-(phenylethynyl)naphthalen-1-yl) (3Ea, Table 3).



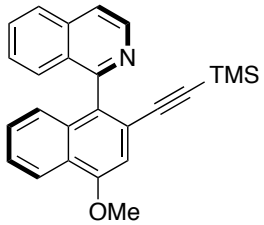
Following the general procedure using nonaflate **1E** and ethynylbenzene **2a**, purification by flash chromatography (CH_2Cl_2→20:1 CH_2Cl_2/EtOAc) afforded **3Ea** (37 mg, 96%) as a pale yellow solid. X-ray quality crystals (colorless prisms) were obtained by slow evaporation of a solution of **3Ea** in CH_2Cl_2. M. p. 155-160 °C (decomposition). $[\alpha]^{20}_D$ +436.4 (*c* 0.51, $CHCl_3$) for 95 % ee. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (d, *J* = 5.7 Hz, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 5.7 Hz, 1H), 7.68 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.49 (ddd, *J* = 8.2, 6.7, 1.2 Hz, 1H), 7.42 (ddd, *J* = 8.3, 6.8, 1.1 Hz, 1H), 7.36 (ddd, *J* = 8.2, 6.7, 1.3 Hz, 1H), 7.25 (*br* d, *J* = 8.4 Hz, 1H), 7.20-7.06 (m, 4H), 6.76 (d, *J* = 6.9 Hz, 2H), 4.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 155.4, 142.5, 136.3, 133.4, 132.7, 131.2, 130.2, 128.7, 128.0, 127.9, 127.7, 127.4, 127.2, 126.7, 126.0 (2C), 125.7, 122.9, 122.1, 121.0, 120.1, 105.8, 93.6, 89.3, 55.8. HRMS (ESI) calcd. for $C_{28}H_{20}NO$ (M + H^+) 386.1539. Found 386.1533. HPLC (AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R min 11.62 (minor) and min 16.23 (major).

(*R*)-1-(4-Methoxy-2-(oct-1-yn-1-yl)naphthalen-1-yl)isoquinoline (3En, Table 3).



Following the general procedure using nonaflate **1E** and oct-1-yne **2n**, purification by flash chromatography (CH_2Cl_2→CH_2Cl_2/EtOAc 20:1) afforded **3En** (34 mg, 86%) as a white foam. $[\alpha]^{20}_D$ +219.0 (*c* 0.50, $CHCl_3$) for 85 % ee. ^{1}H NMR (400MHz, $CDCl_3$): δ 8.72 (d, *J* = 5.7 Hz, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 5.8 Hz, 1H), 7.66 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.46-7.37 (m, 2H), 7.30 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.12 (*br* d, *J* = 8.5 Hz, 1H), 6.95 (s, 1H), 4.08 (s, 3H), 1.96 (td, *J* = 6.8, 2.1 Hz, 2H), 1.19-1.06 (m, 2H), 1.01-0.87 (m, 4H), 0.86-0.74 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 155.3, 142.4, 136.3, 133.4, 132.1, 130.0, 128.7, 127.7, 127.2, 127.0, 126.6, 125.8, 125.5, 125.2, 121.9, 121.7, 119.9, 106.3, 95.0, 80.2, 55.7, 31.2, 28.1, 27.9, 22.3, 19.1, 14.1. HRMS (ESI) calcd. for $C_{28}H_{28}NO$ (M + H^+) 394.2165. Found 394.2160. HPLC (AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 5.13 min (minor) and 10.03 min (major).

(*R*)-1-(4-Methoxy-2-((trimethylsilyl)ethynyl)naphthalen-1-yl)isoquinoline (3Eq, Table 3).

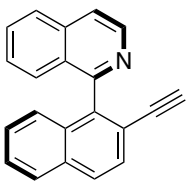


Following the general procedure using nonaflate **1E** and ethynyltrimethylsilane **2q**, purification by flash chromatography (CH_2Cl_2→20:1 CH_2Cl_2/EtOAc) afforded **3Eq** (37 mg, 97%) as a light yellow oil. $[\alpha]^{20}_D$ +229.9 (*c* 0.49, $CHCl_3$) for 92 % ee. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, *J* = 5.7 Hz, 1H), 8.32 (ddd, *J* = 8.5, 1.4, 0.7 Hz, 1H), 7.92 (*br* d, *J* = 8.3 Hz, 1H), 7.74 (dd, *J* = 5.7, 0.9 Hz, 1H), 7.67 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 7.57 (*br* dd, *J* = 8.5, 1.0 Hz, 1H), 7.47 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.41 (ddd, *J* = 8.3, 6.8, 1.2 Hz, 1H), 7.34 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.23 (ddd, *J* = 8.5, 1.3, 0.8 Hz, 1H), 6.98 (s, 1H), 4.08 (s, 3H), -0.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 155.3, 142.4, 136.3, 133.3, 132.1, 130.0, 128.7, 127.7, 127.3, 127.0, 126.6, 126.0 (2C), 125.7, 122.0, 120.8, 120.0, 105.6, 104.6, 98.8, 55.7, -0.7. HRMS (ESI) calcd. for $C_{25}H_{24}NOSi$ (M + H^+) 382.1622. Found 382.1617. HPLC (AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 4.31 min (minor) and 8.79 min (major).

Procedure for the cleavage of TMS-protected alkynes 3Aq, 3Bq, 3Cq.

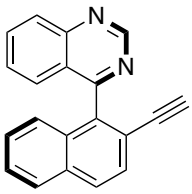
TBAF (1.0 M, 1.07 equiv.) was slowly added to a solution of the corresponding TMS-protected alkyne (1.00 equiv) in THF (5 mL/mmol) at room temperature and the solution was stirred for 30 min. Then, SiO_2 was added to the reaction crude and the solvents were removed under *vacuum*. The resulting solid was purified through a short pad of silica gel (5:1 CH_2Cl_2/AcOEt) to yield the corresponding pure terminal alkynes.

(*R*)-1-(2-Ethynylnaphthalen-1-yl)isoquinoline (4A, Table 2).



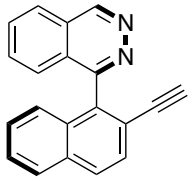
Following the general procedure using TMS-alkyne **3Aq** (91 mg, 0.26 mmol) afforded **4A** (68 mg, 94%) as a beige solid. M. p. 149-151 °C. $[\alpha]^{20}_D$ +81.8 (*c* 0.25, $CHCl_3$) for 97 % ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 5.7 Hz, 1H), 8.01-7.88 (m, 3H), 7.79 (d, *J* = 5.7 Hz, 1H), 7.75-7.64 (m, 2H), 7.54-7.37 (m, 3H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.14 (d, *J* = 8.5 Hz, 1H), 2.77 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 142.5, 140.5, 136.2, 133.2, 132.2, 130.3, 128.7, 128.6, 128.2, 128.0, 127.4, 127.2, 127.0, 126.9, 126.8, 126.2, 120.5, 119.8, 82.4, 81.3. HRMS (ESI) for calcd. $C_{21}H_{14}N$ for (M + H^+) 280.1121. Found 280.1120. HPLC (AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 7.84 min (minor) and 8.52 min (major).

(*R*)-4-(2-Ethynylnaphthalen-1-yl)quinazoline (4B, Table 3).



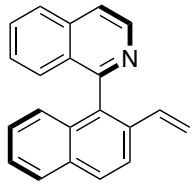
Following the general procedure using TMS-alkyne **3Bq** (33 mg, 0.094 mmol) afforded **4B** (26 mg, 99%) as a brown viscous oil. $[\alpha]^{20}_D$ +159.0 (*c* 0.7, $CHCl_3$) for 95% ee. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.68 (s, 1H), 8.09 (*br* d, *J* = 8.1, 1H), 7.99 (*br* d, *J* = 8.5, 1H), 7.96-7.88 (m, 2H), 7.77-7.70 (m, 2H), 7.51 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 7.45 (*br* dd, *J* = 8.3, 1.0 Hz, 1H), 7.34 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.18 (dd, *J* = 8.5, 1.0 Hz, 1H), 2.78 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 154.9, 150.5, 137.8, 134.1, 133.1, 131.4, 129.4, 128.7, 128.6, 128.2, 128.0, 127.4, 127.1, 126.9, 125.7, 124.9, 119.5, 82.3, 81.8. HRMS (ESI) calcd. for $C_{20}H_{13}N_2$ (M + H^+) 281.1073. Found 281.1063. HPLC (AS-H column, 90:10 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 9.04 min (major) and 9.87 min (minor).

(*R*)-1-(2-Ethynylnaphthalen-1-yl)phthalazine (3C, Table 3).



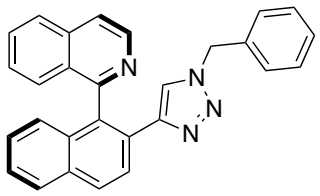
Following the general procedure using TMS-alkyne **3Cq** (32 mg, 0.091 mmol) afforded **4C** (23 mg, 90%) as a light brown amorphous solid. $[\alpha]^{20}_{D}$ +139.0 (*c* 0.7, $CHCl_3$) for 92 % ee. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.68 (s, 1H), 8.09 (*br* d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.97-7.87 (m, 2H), 7.79-7.68 (m, 2H), 7.45 (*br* dd, *J* = 8.4, 1.0 Hz, 1H), 7.34 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.34 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.18 (*br* dd, *J* = 8.5, 1.1 Hz, 1H), 2.78 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 151.0, 137.0, 133.2, 132.7, 132.5, 132.2, 129.3, 128.6, 128.1, 127.3, 127.0, 126.8, 126.5, 126.5, 125.9, 125.9, 120.4, 82.2, 82.0. HRMS (ESI) calcd. for $C_{20}H_{13}N_2$ (M + H^+) 281.1073. Found 281.1064. HPLC (AD-H column, 80:20 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 12.10 min (major) and 12.92 min (minor).

Preparation of (*R*)-1-(2-vinylnaphthalen-1-yl)isoquinoline (5, Scheme 2).



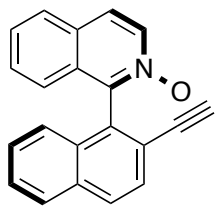
Following a described methodology,[8] a dried Schlenk tube was charged with IPrCuCl (2.7 mg, 5 mol%) and Na*t*BuO (0.5 mg, 5 mol%) and after cycles of vacuum-N_2 anhydrous THF (0.5 mL) was added. The resulting reaction mixture was stirred 1 hour at room temperature, and then the solvent was removed under vacuum and anhydrous toluene (1 mL) was added and the solution was transferred *via* cannula to a dried Schlenk tube containing **4A** (28 mg, 0.1 mmol). PMHS (0.12 mmol, 7.1 μL) and *t*BuOH (0.12 mmol, 11.5 μL) were added and the reaction mixture was stirred overnight at rt. Then, reaction crude was concentrated to dryness and purified by flash chromatography (5:1 *n*-hexane/EtOAc) to afford **5** (23 mg, 82%) as a viscous oil. $[\alpha]^{20}_{D}$ +10.0 (*c* 0.5, $CHCl_3$) for 97 % ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 5.7 Hz, 1H), 7.99-7.87 (m, 4H), 7.79 (*br* d, *J* = 5.7 Hz, 1H), 7.68 (ddd, *J* = 8.2, 6.1, 1.9 Hz, 1H), 7.45-7.35 (m, 3H), 7.27-7.21 (m, 1H), 7.01 (*br* dd, *J* = 8.5, 1.0 Hz, 1H), 6.27 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.80 (dd, *J* = 17.5, 0.9 Hz, 1H), 5.10 (dd, *J* = 11.0, 0.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 142.6, 136.1, 134.6, 134.5, 133.8, 133.1, 132.9, 130.4, 128.8 (2C), 127.9, 127.5, 127.4, 126.9, 126.5, 126.3, 125.8, 122.5, 120.2, 115.6. HRMS (ESI) calcd. for $C_{21}H_{16}N$ (M + H^+) 282.1277. Found 282.1278. HPLC (OD column, 90:10 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 8.32 min (minor) and 9.39 min (major).

Preparation of (*R*)-1-(2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)naphthalen-1-yl)isoquinoline (6, Scheme 2).



To a mixture of terminal alkyne **4A** (28 mg, 0.10 mmol) and benzyl azide (20 mg, 0.15 mmol) in *t*-BuOH (3 mL) and water (240 μL), a solution of $CuSO_4{\cdot}5H_2O$ (0.1 M in water, 100 μL, 0.01 mmol) and (*L*)-sodium ascorbate (0.1 M in water, 200 μL, 0.02 mmol) were then sequentially added. The resulting mixture was stirred at 35 °C for 5 h. The reaction mixture was allowed to reach room temperature, washed with a saturated aqueous solution of NH_3, and extracted with DCM (3× 5 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, concentrated to dryness, and the crude product was purified by column chromatography (CH_2Cl_2→3:1 CH_2Cl_2/EtOAc) affording **6** (31 mg, 76%) as a pale yellow solid. $[\alpha]^{20}_D$ +23.1 (*c* 0.26, $CHCl_3$) for 97 % ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 5.7 Hz, 1H), 8.42 (d, *J* = 8.7 Hz, 1H), 8.10 (d, *J* = 8.7 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 5.8 Hz, 1H), 7.59 (dd, *J* = 8.4, 6.6 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.34-7.17 (m, 6H), 7.11 (d, *J* = 8.5 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 2H), 5.92 (s, 1H), 5.21 (d, *J* = 14.9 Hz, 1H), 5.11 (d, *J* = 14.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 146.2, 142.1, 136.2, 134.1, 133.3, 133.2, 132.7, 130.5, 129.1, 128.8, 128.3, 128.1, 128.0, 127.9, 127.8, 127.5, 126.7, 126.7, 126.6, 126.1, 126.1, 125.7, 122.0, 120.6, 53.6. HRMS (ESI) calcd. for $C_{28}H_{21}N_4$ (M + H^+) 413.1761. Found 413.1753. HPLC (AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 20.51 min (minor) and 27.53 min (major).

Preparation of (*R*)-1-(2-Ethynylnaphthalen-1-yl)isoquinoline *N*-oxide (7, Scheme 2).

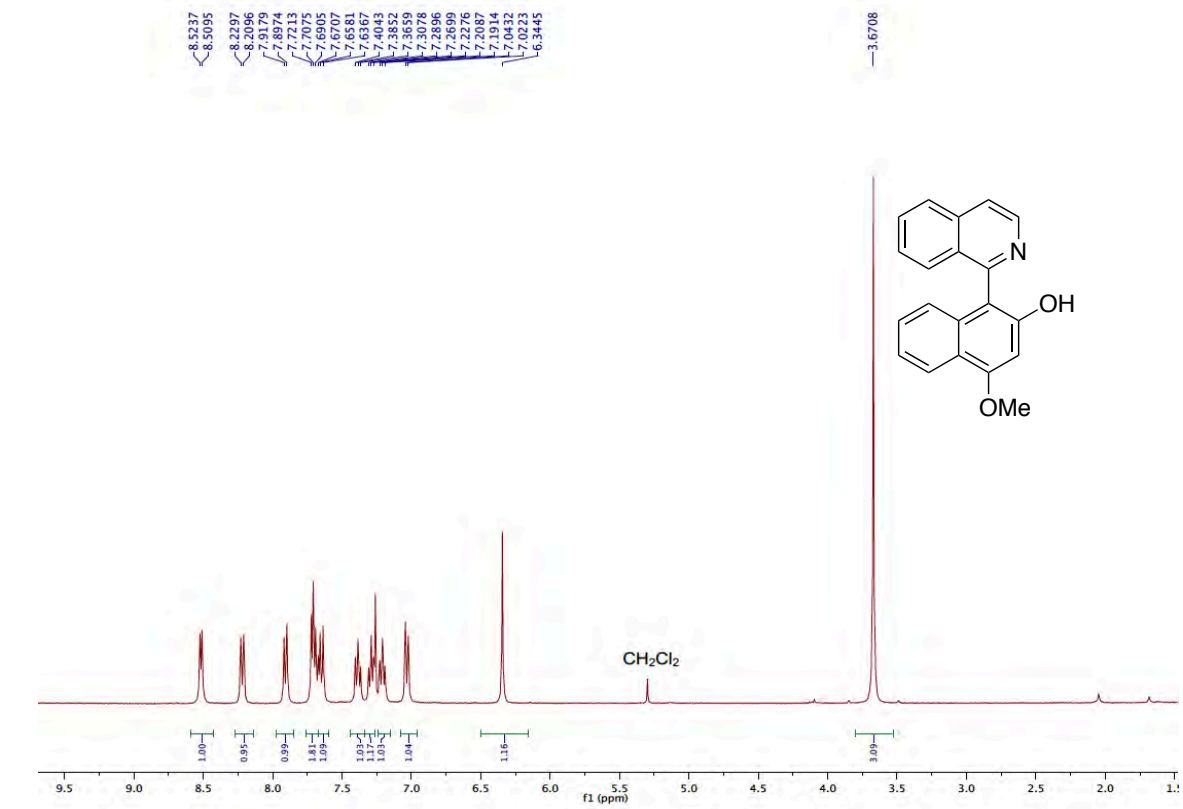


Over a cooled (0 °C) solution of (*R*)-**4A** (100 mg, 0.36 mmol, 97% ee) in THF (5 mL), *m*-CPBA acid (77%; 160 mg, 0.72 mmol,) was added in portions. The resulting mixture was warmed to rt and stirred for 3 hours. Then, CH_2Cl_2 (10 mL) was added and the mixture was washed once with saturated aqueous Na_2CO_3. The organic layer was dried over anhydrous Na_2SO_4, filtered, concentrated, and the resulting residue was purified by flash chromatography (CH_2Cl_2→5:1 EtOAc/MeOH) to afford (*R*)-**7** (100 mg, 94%) as a white foam. $[\alpha]^{20}_D$ +1.2 (*c* 1.0, $CHCl_3$) for 97 % ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 7.2

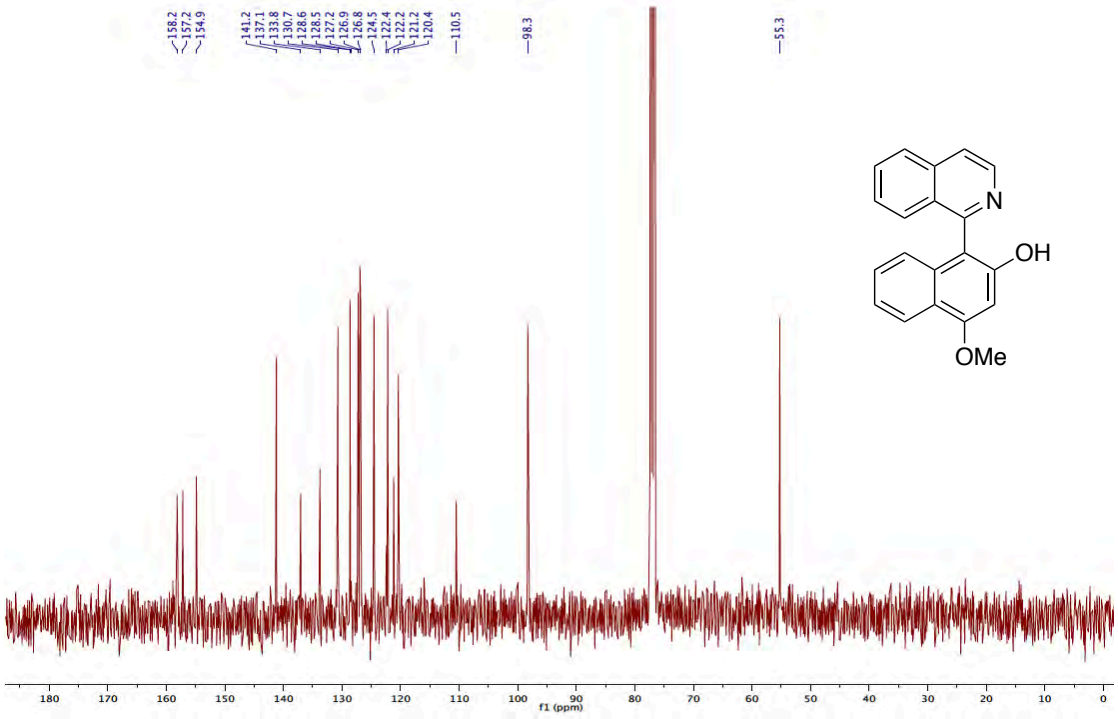
Hz, 1H), 8.00 (dd, *J* = 8.6, 0.8 Hz, 1H), 7.94 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.87 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.80 (d, *J* = 7.2 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.59-7.47 (m, 2H), 7.45-7.34 (m, 2H), 7.17 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.09 (dd, *J* = 8.5, 1.0 Hz, 1H), 2.86 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 137.5, 133.3, 132.7, 131.1, 129.9, 129.8, 129.4, 128.9, 128.7, 128.5, 128.4, 127.7, 127.2, 126.9, 125.0 (2C), 123.9, 120.9, 81.5 (2C). HRMS (ESI) calcd. for $C_{21}H_{14}NO$ ($M + H^+$) 296.1070. Found 296.1070. HPLC (AD-H column, 70:30 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min): t_R 9.44 min (minor) and 10.12 min (major).

NMR Spectra:

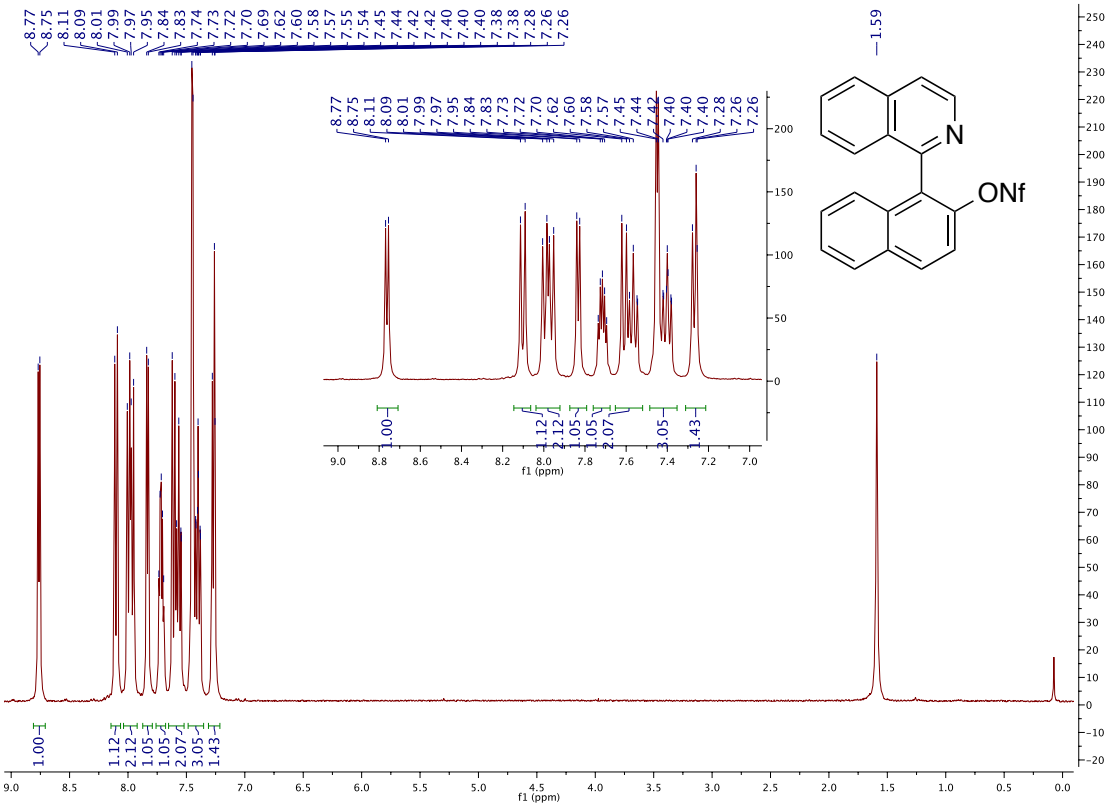
^{1}H NMR ($CDCl_3$, 400 MHz) of 1-(Isoquinolin-1-yl)-4-methoxynaphthalen-2-ol:



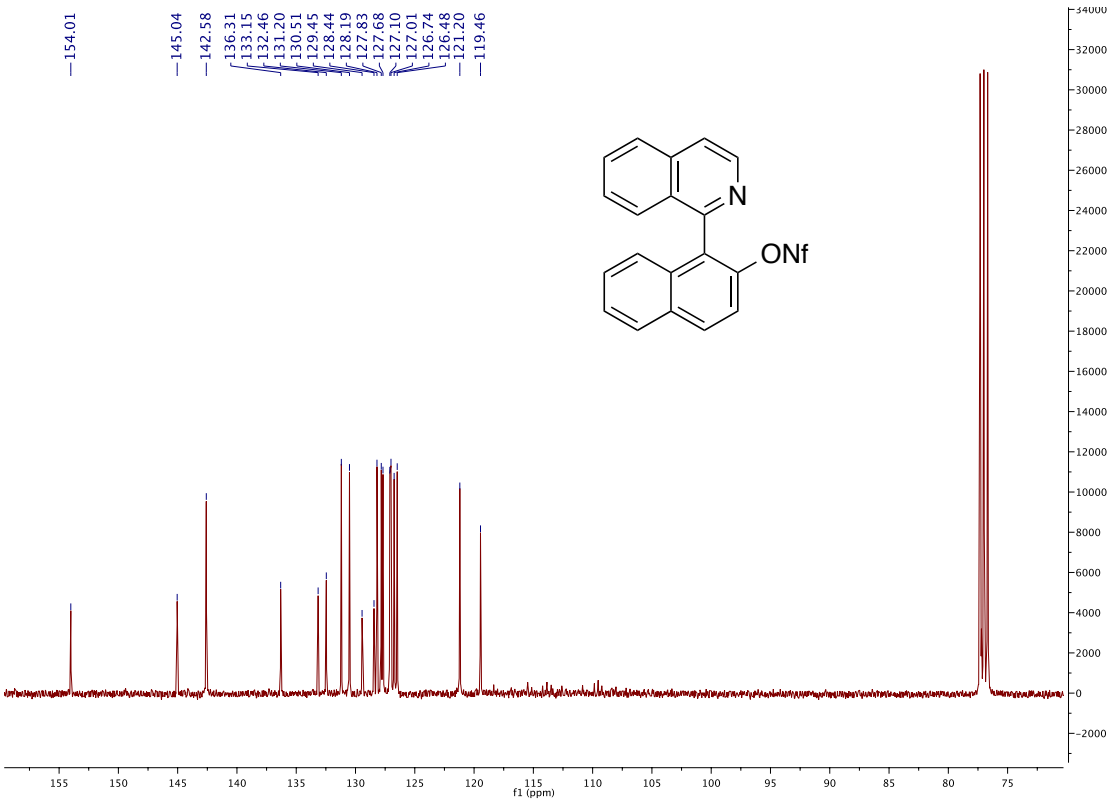
^{13}C NMR ($CDCl_3$, 100 MHz) of 1-(Isoquinolin-1-yl)-4-methoxynaphthalen-2-ol:



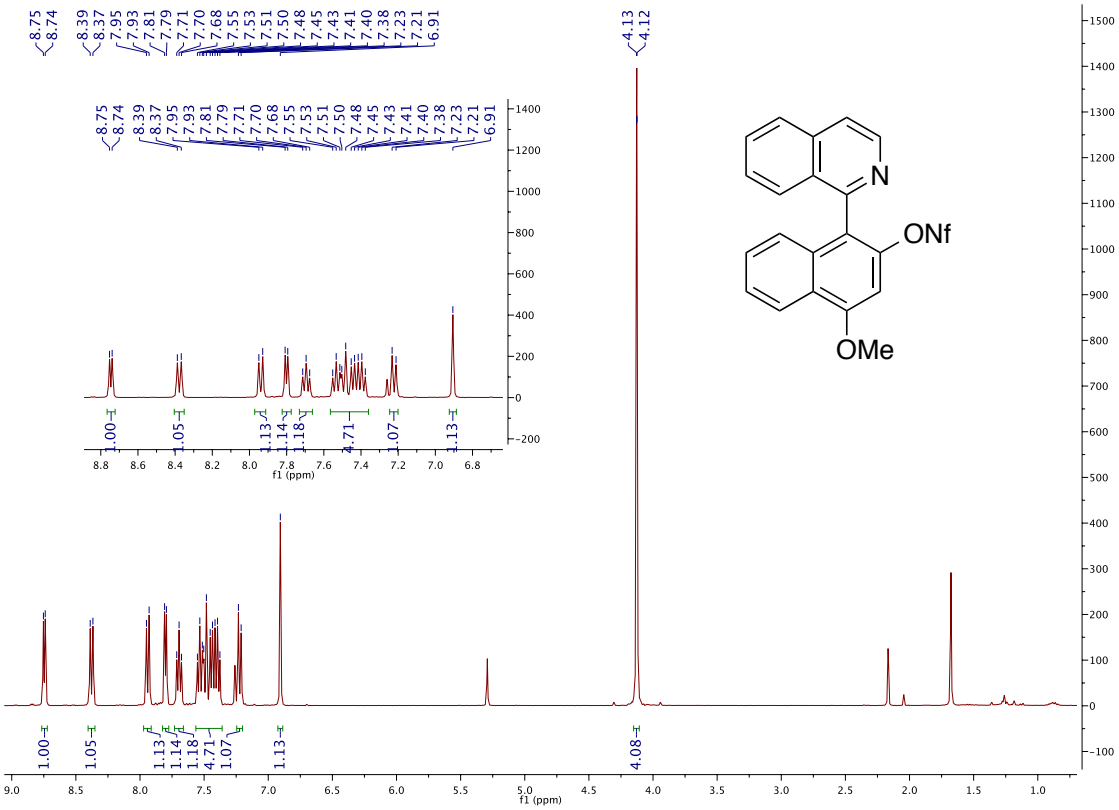
^{1}H NMR (400 MHz, $CDCl_3$) of **1A**



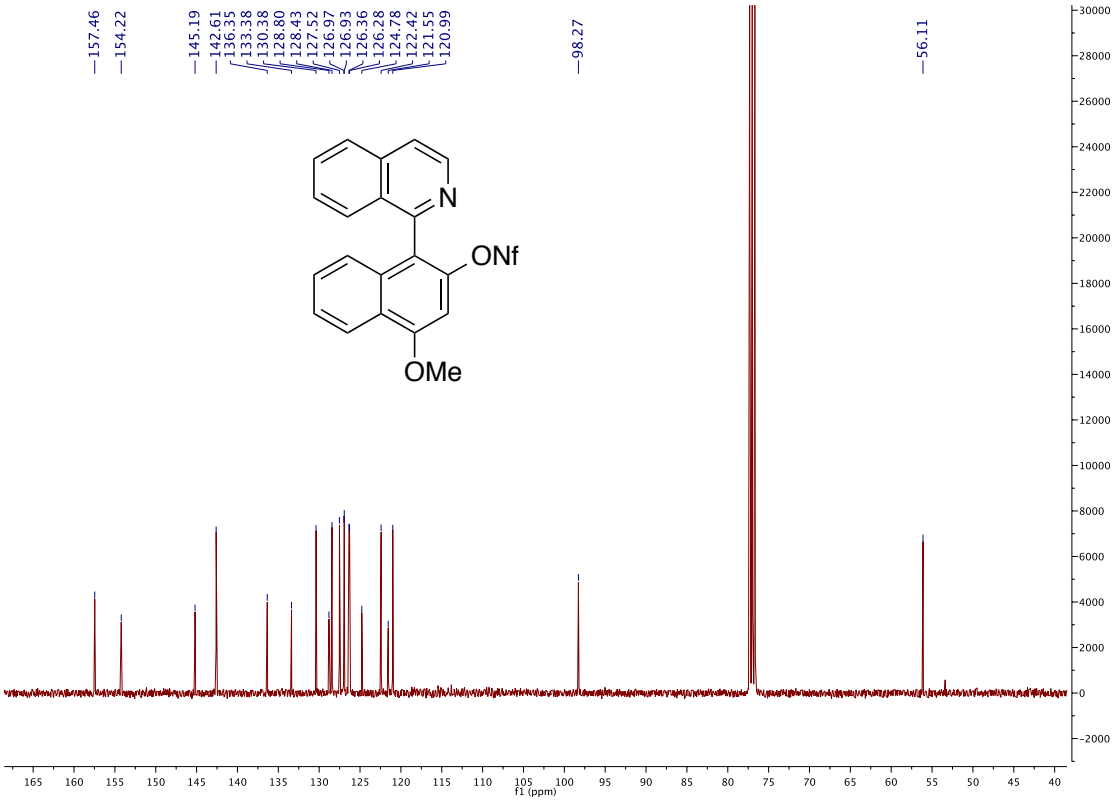
^{13}C NMR (100 MHz, $CDCl_3$) of **1A**



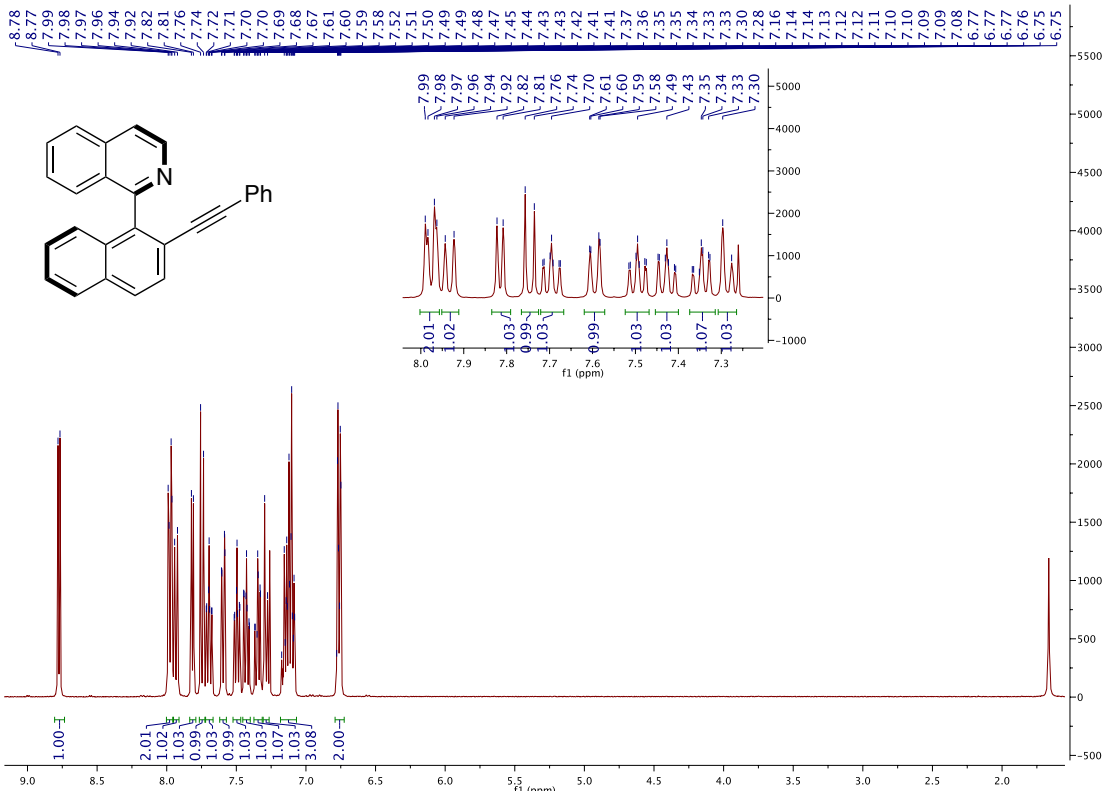
^{1}H NMR (400 MHz, $CDCl_3$) of **1E**



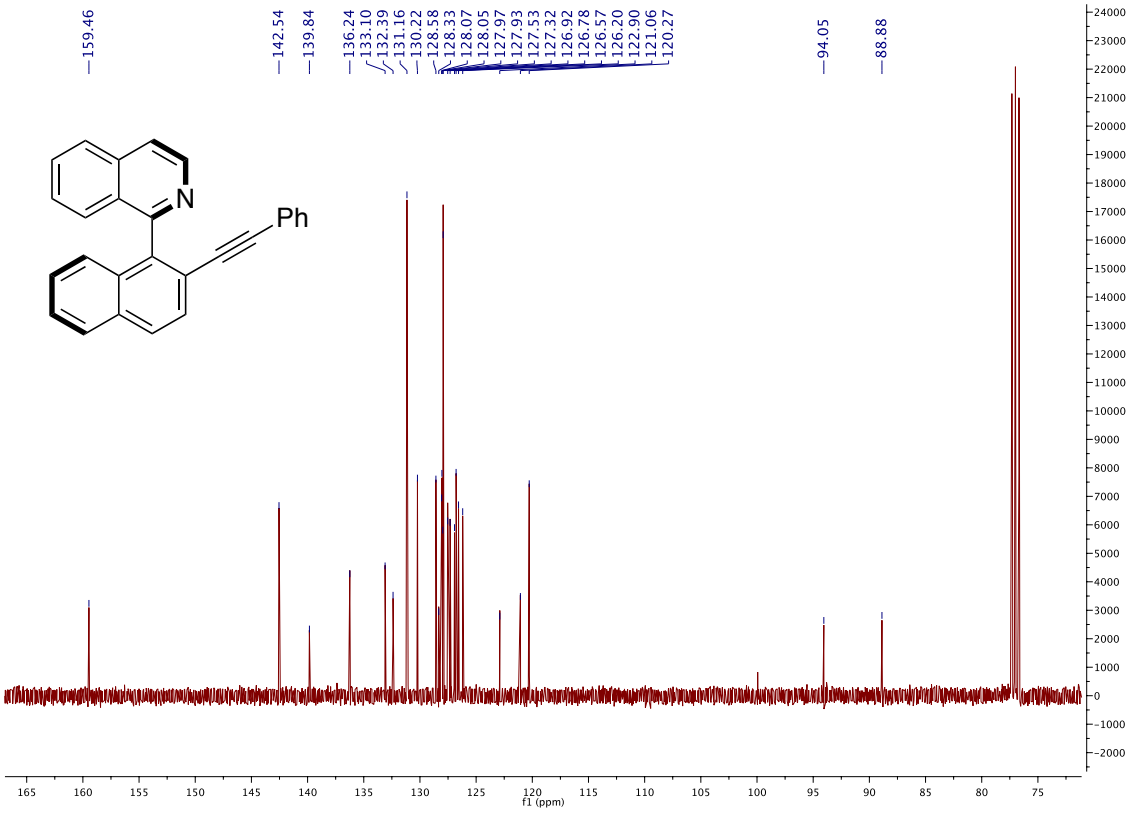
^{13}C NMR (100 MHz, $CDCl_3$) of **1E**



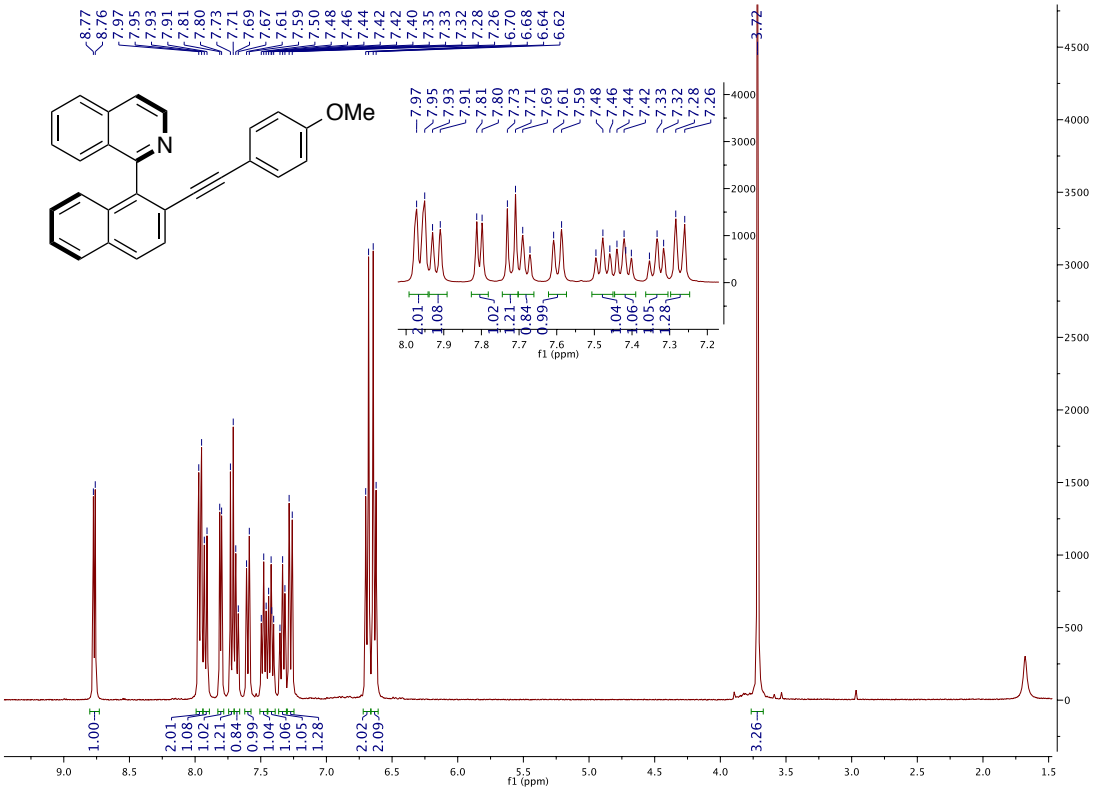
^{1}H NMR (400 MHz, $CDCl_3$) of **3Aa**



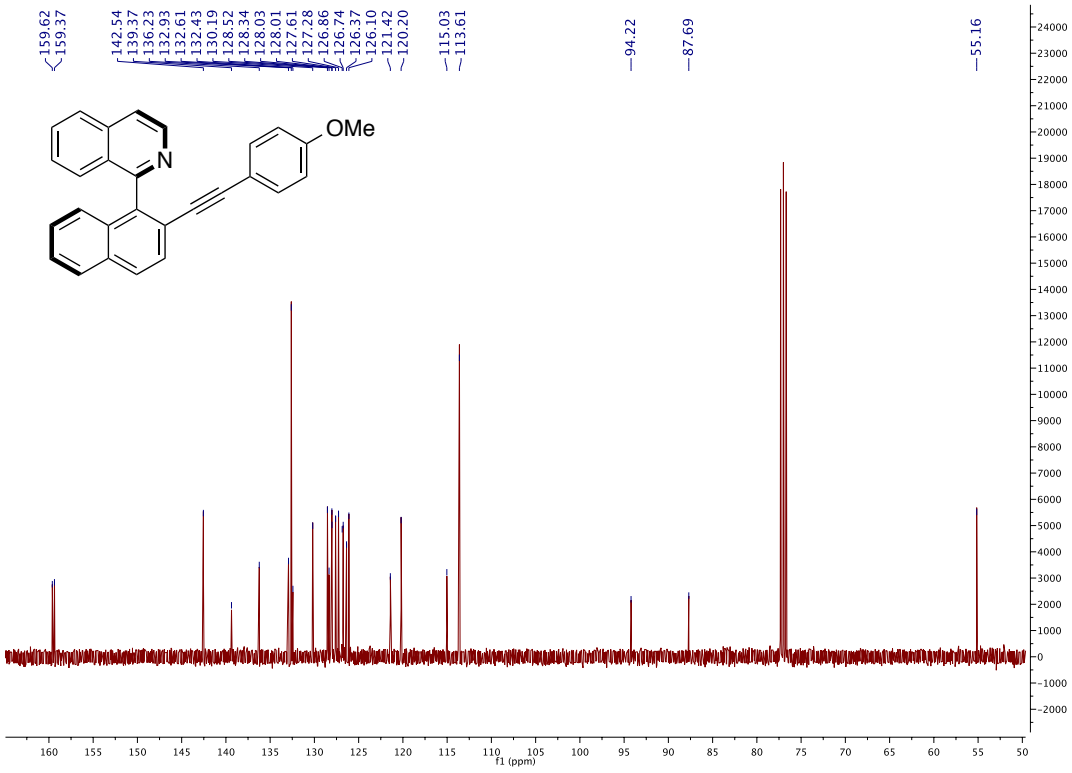
^{13}C NMR (100 MHz, $CDCl_3$) of **3Aa**



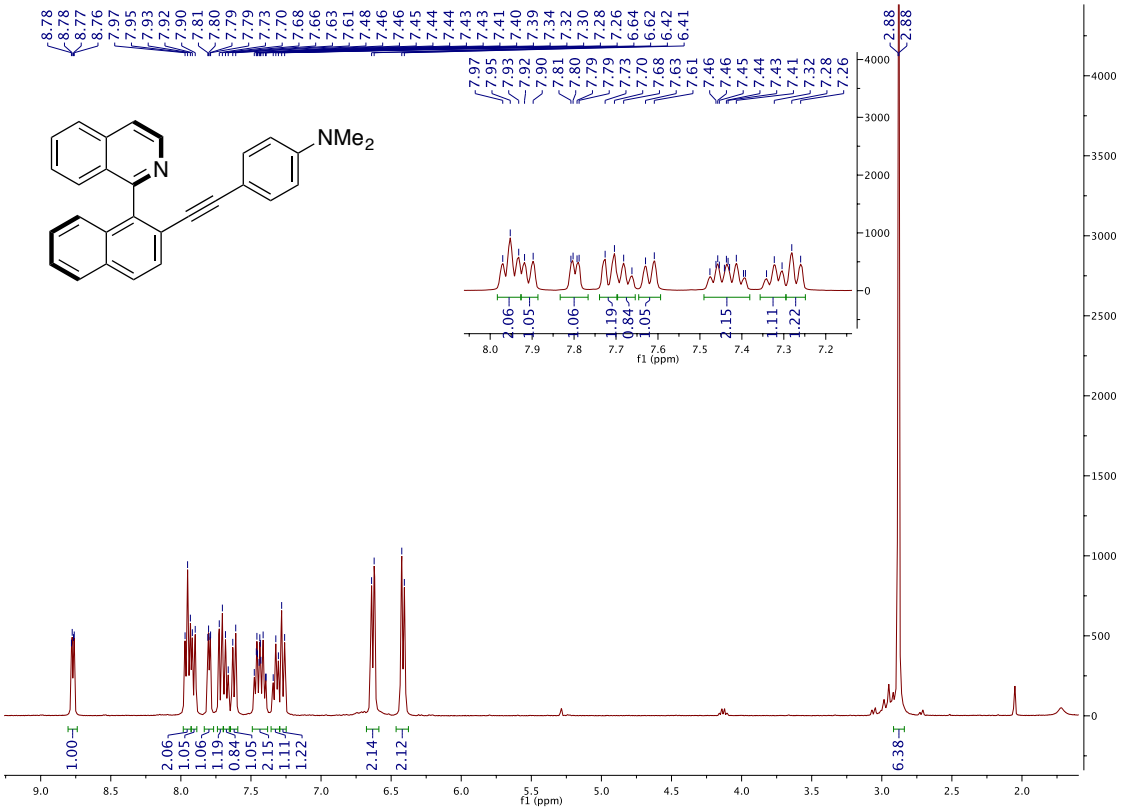
^{1}H NMR (400 MHz, $CDCl_3$) of **3Ab**



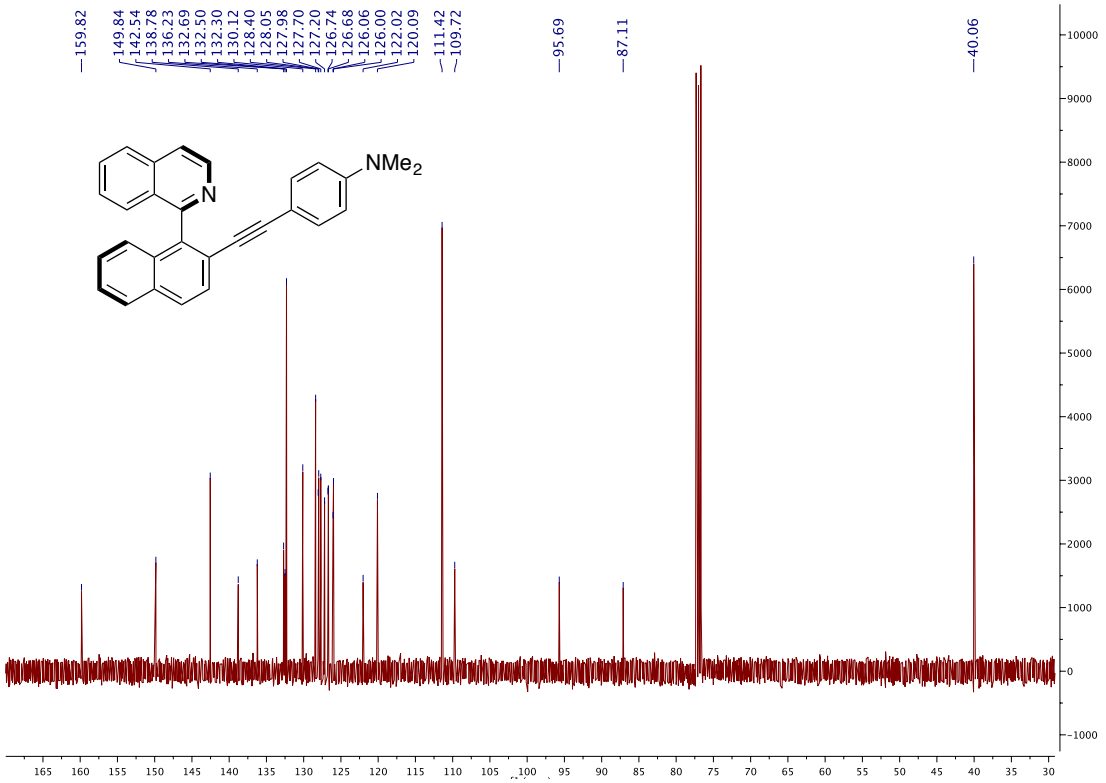
^{13}C NMR (100 MHz, $CDCl_3$) of **3Ab**



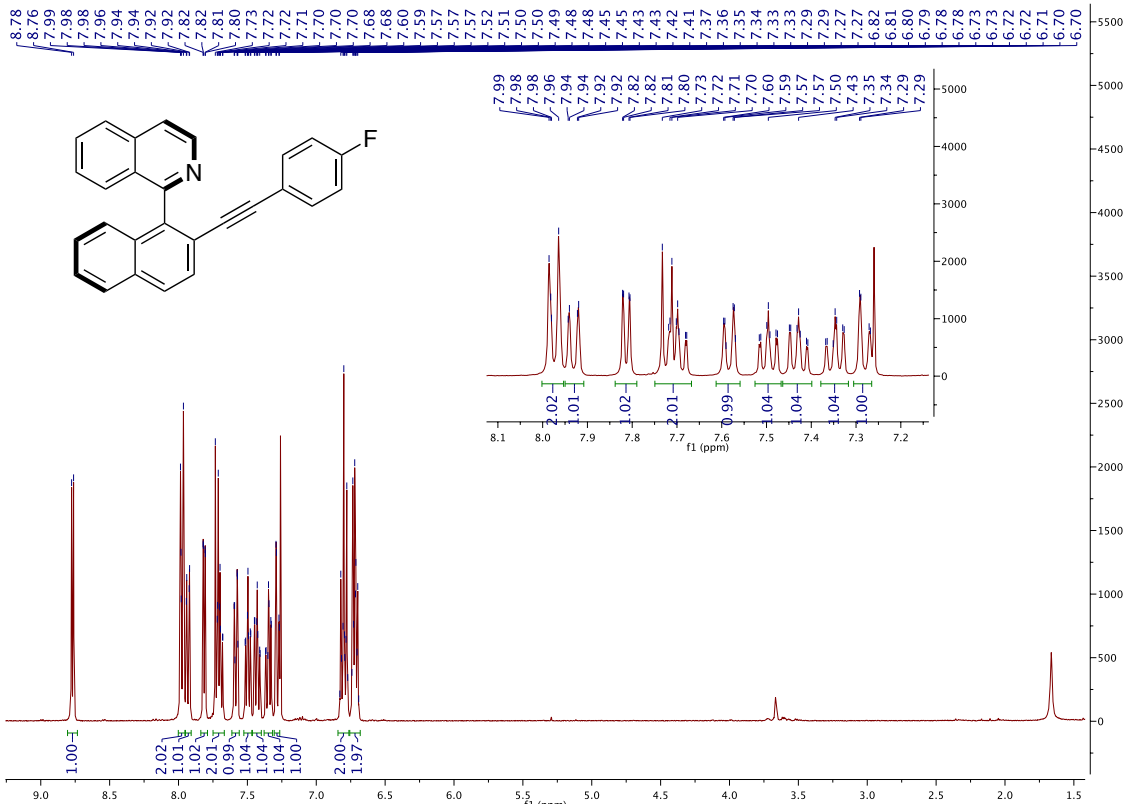
^{1}H NMR (400 MHz, $CDCl_3$) of **3Ac**



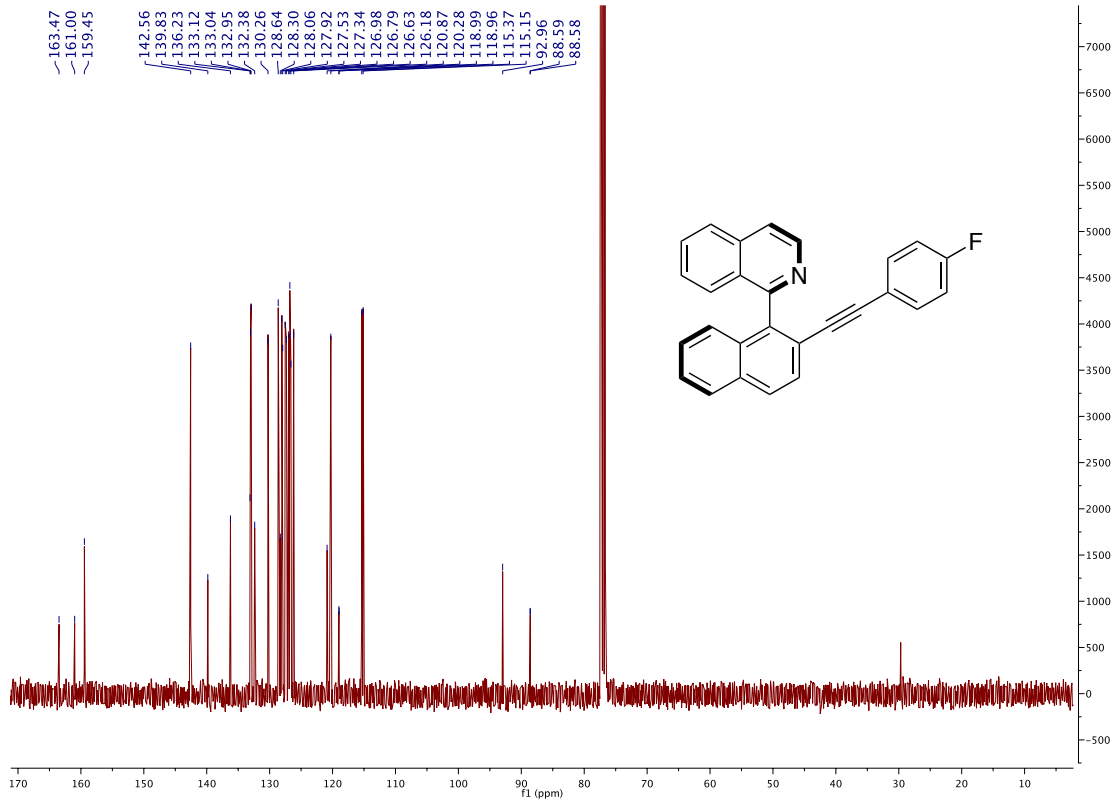
^{13}C NMR (100 MHz, $CDCl_3$) of **3Ac**



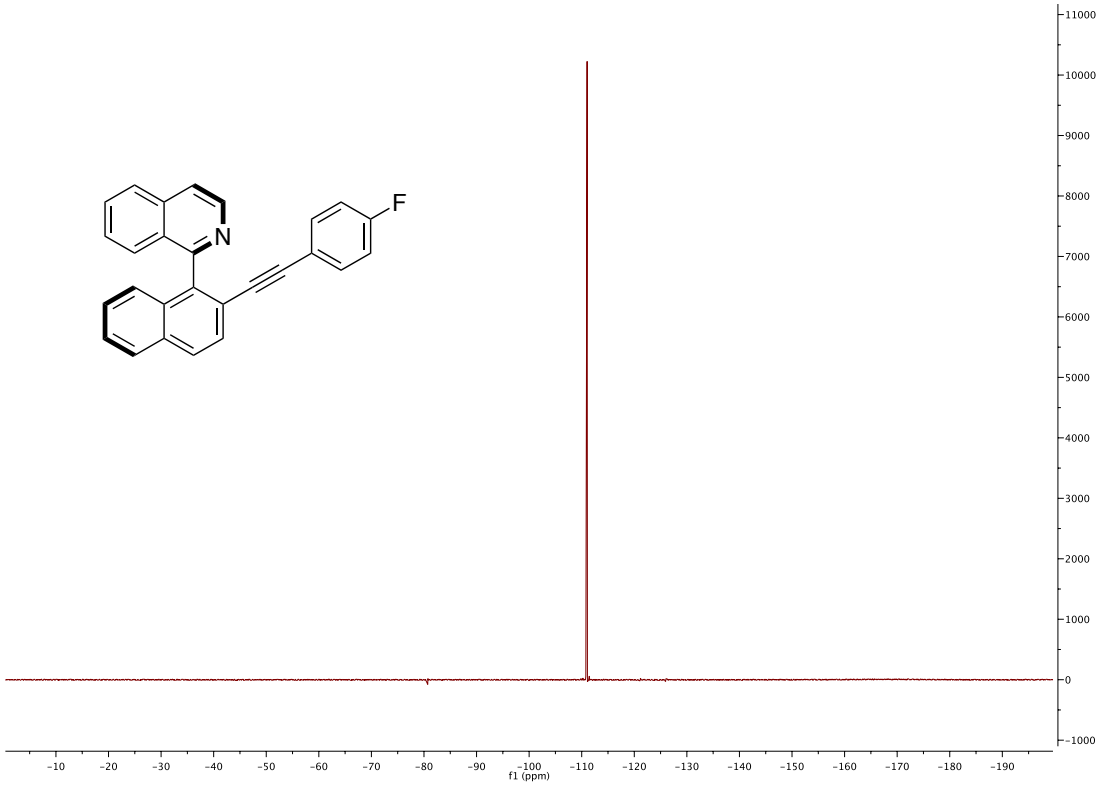
^{1}H NMR (400 MHz, $CDCl_3$) of **3Ad**



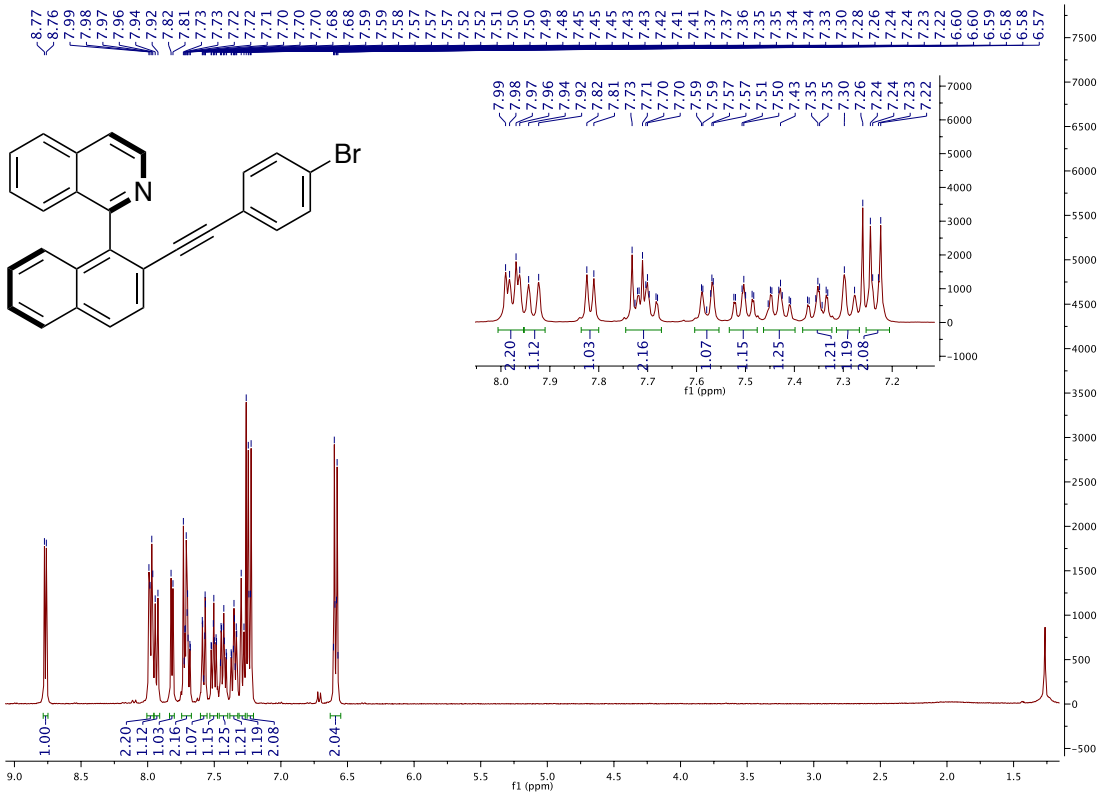
^{13}C NMR (100 MHz, $CDCl_3$) of **3Ad**



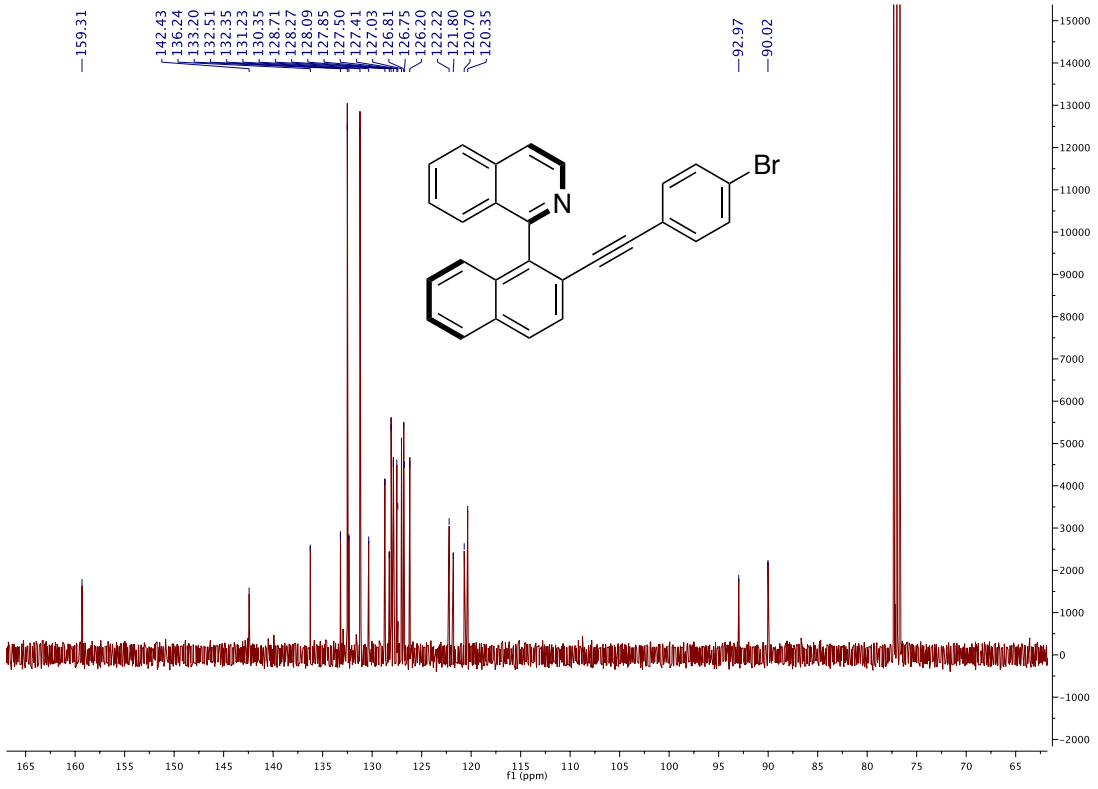
^{19}F NMR (377 MHz, $CDCl_3$) of **3Ad**



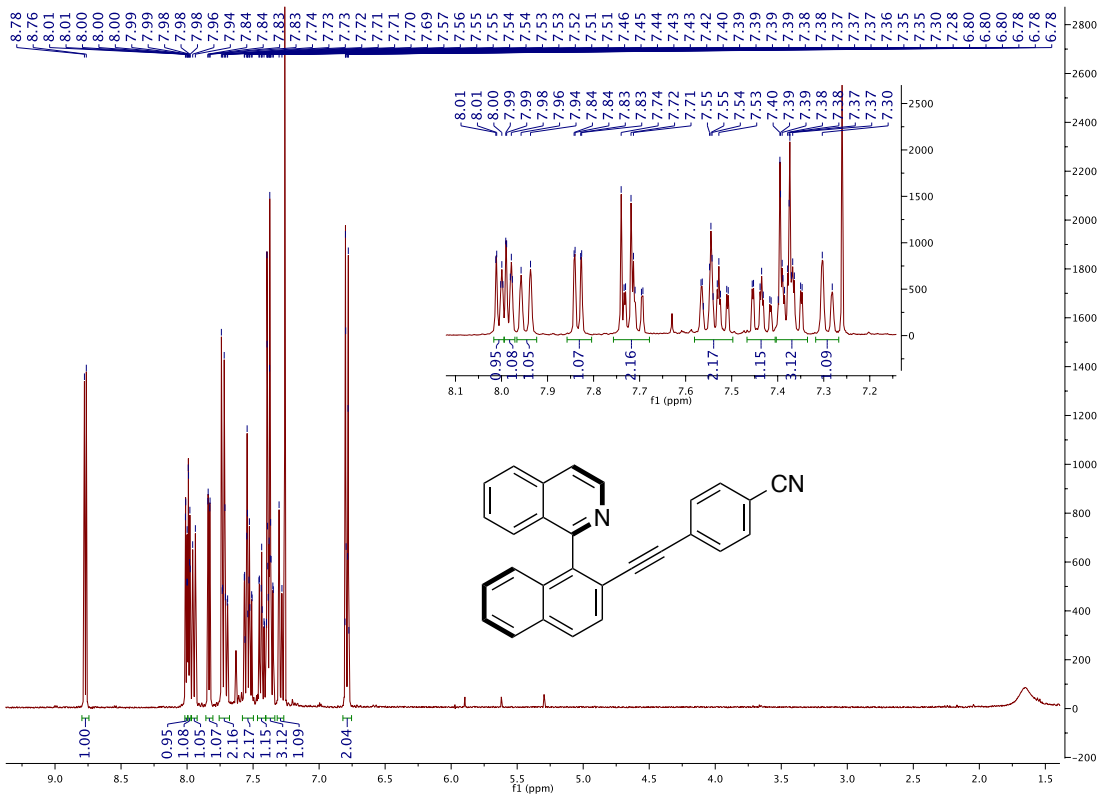
^{1}H NMR (400 MHz, $CDCl_3$) of **3Ae**



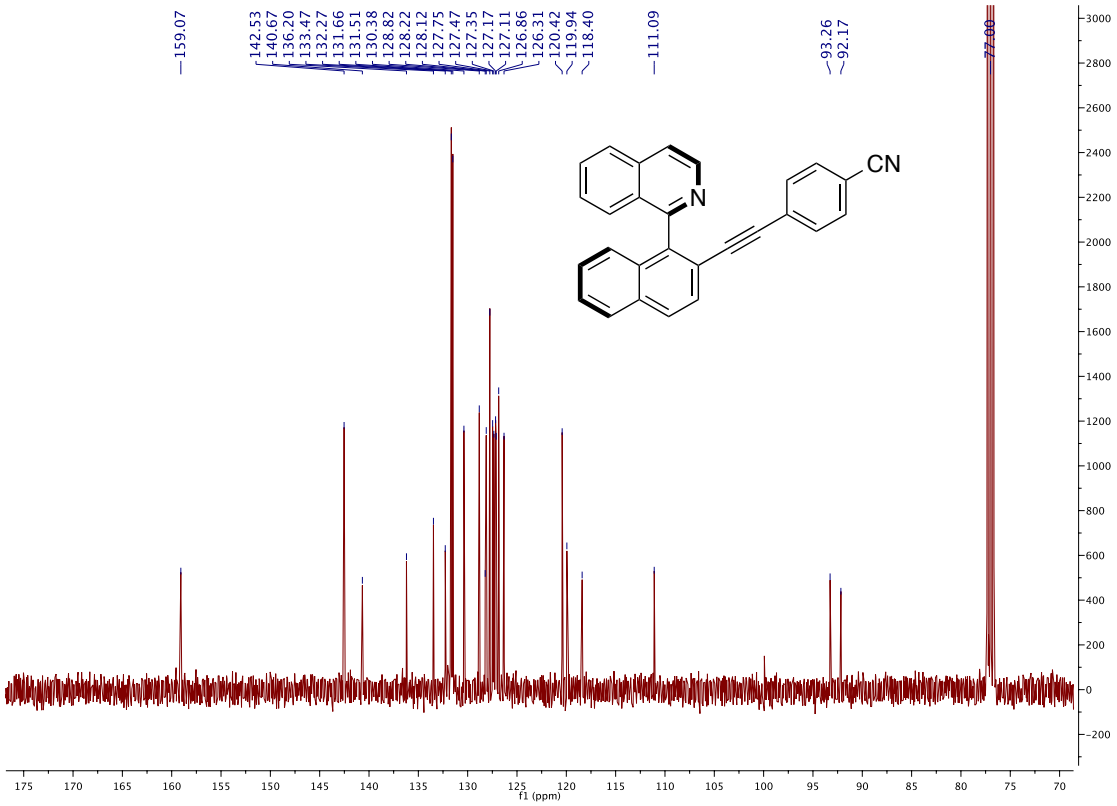
^{13}C NMR (100 MHz, $CDCl_3$) of **3Ae**



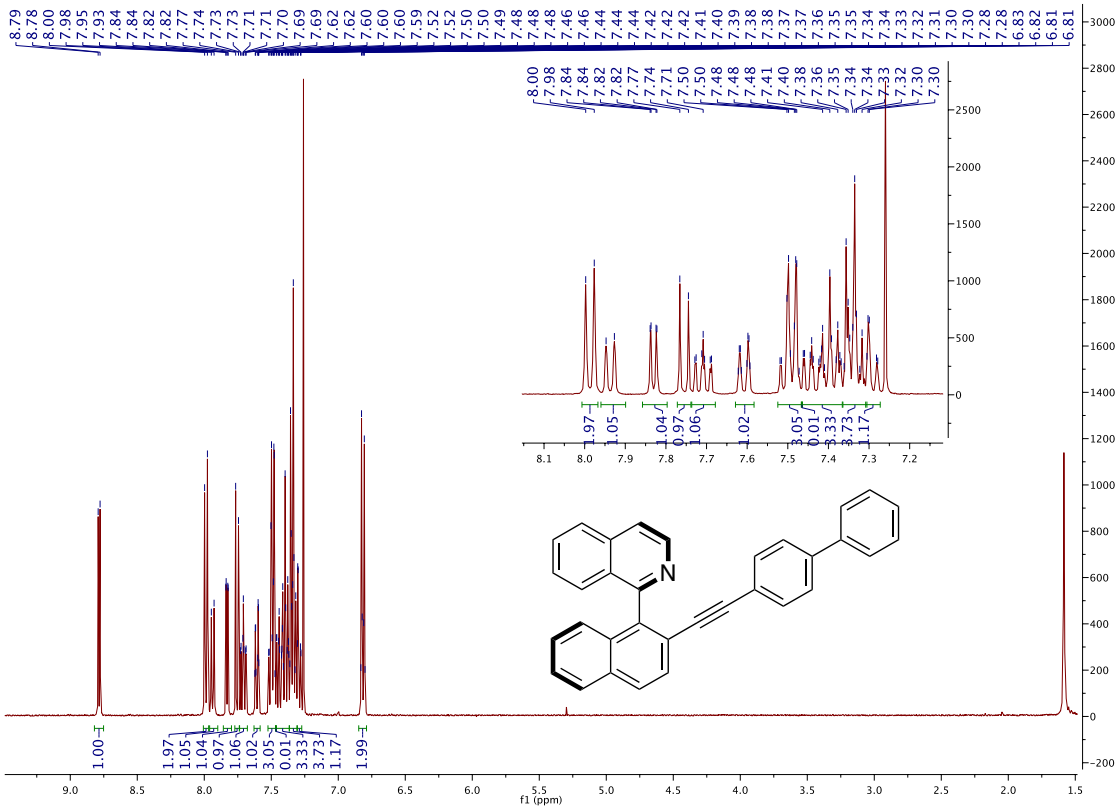
^{1}H NMR (400 MHz, $CDCl_3$) of **3Af**



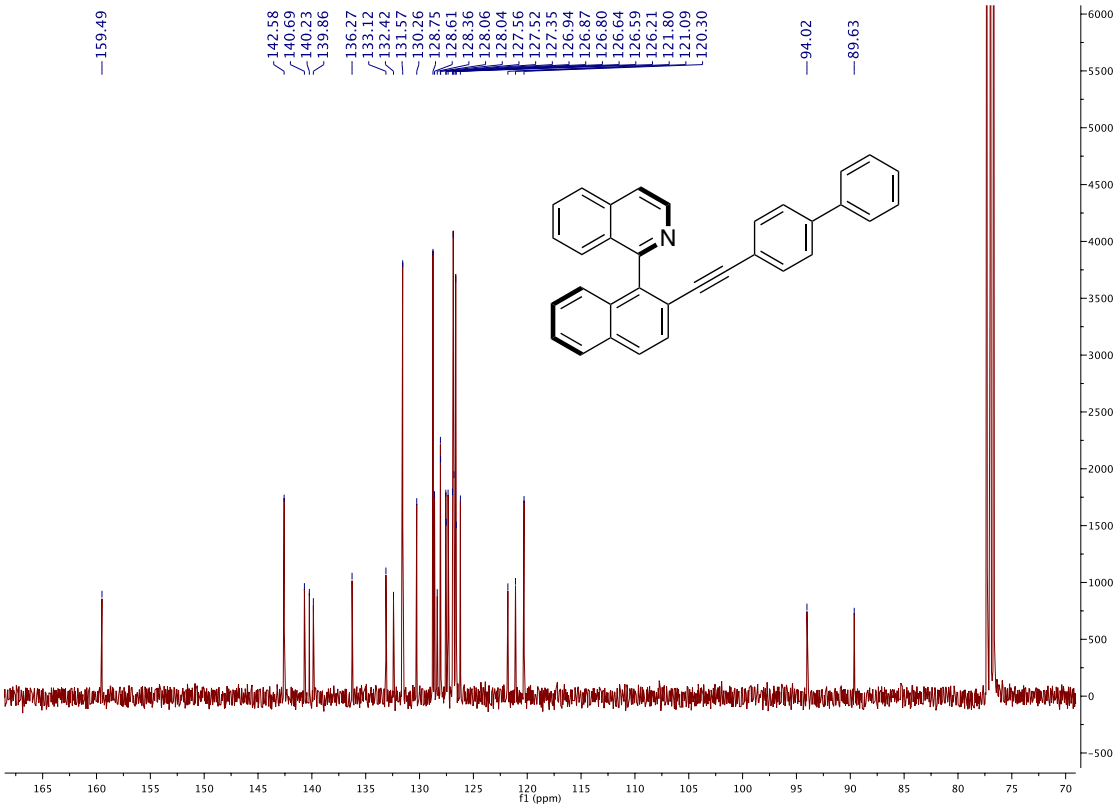
^{13}C NMR (100 MHz, $CDCl_3$) of **3Af**



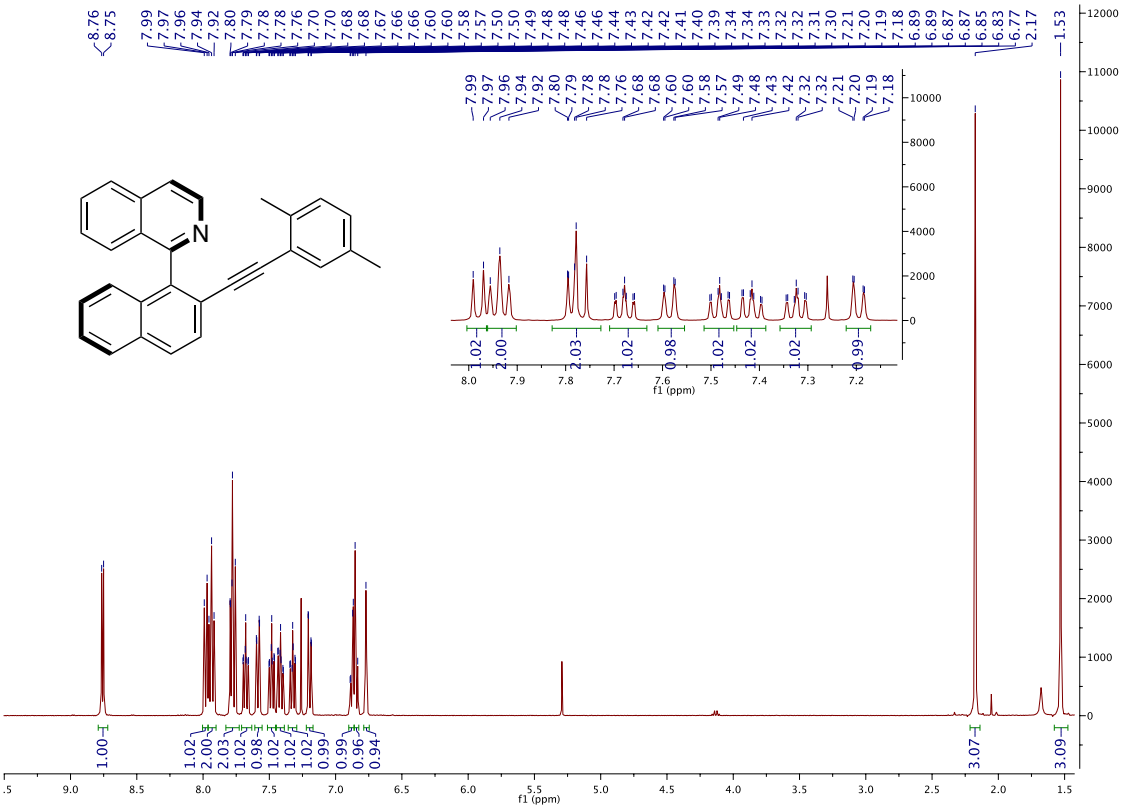
^{1}H NMR (400 MHz, $CDCl_3$) of **3Ag**



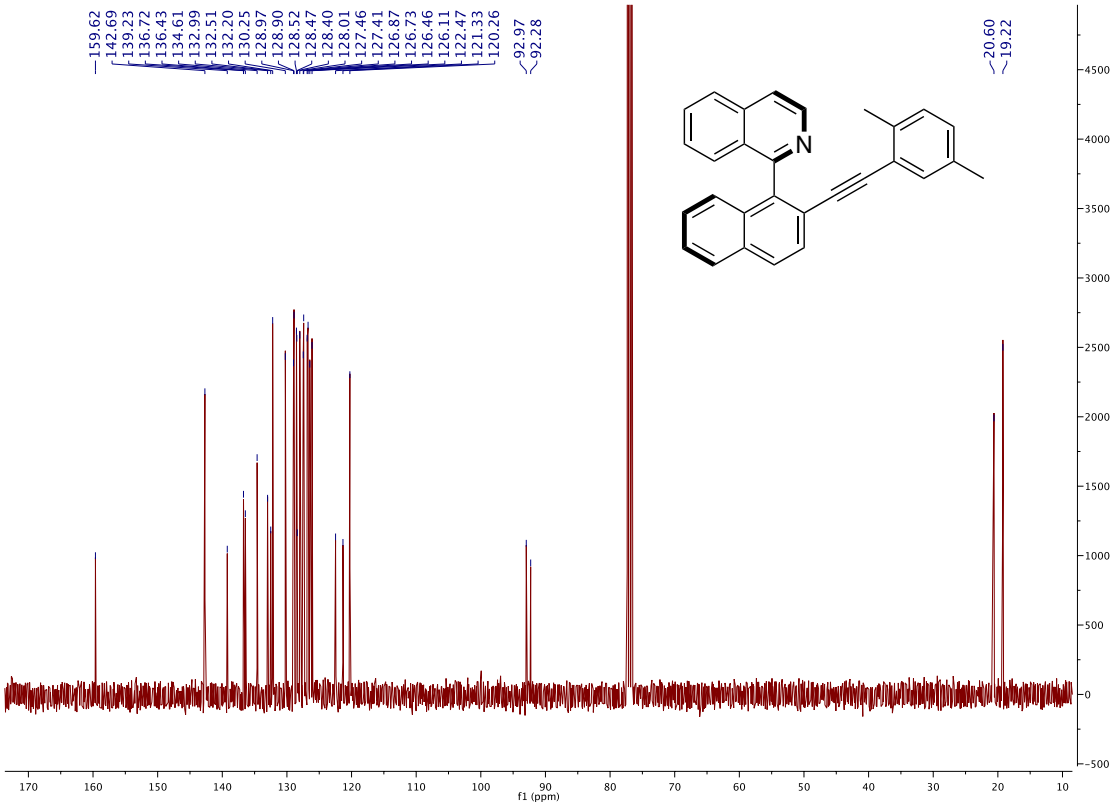
^{13}C NMR (100 MHz, $CDCl_3$) of **3Ag**



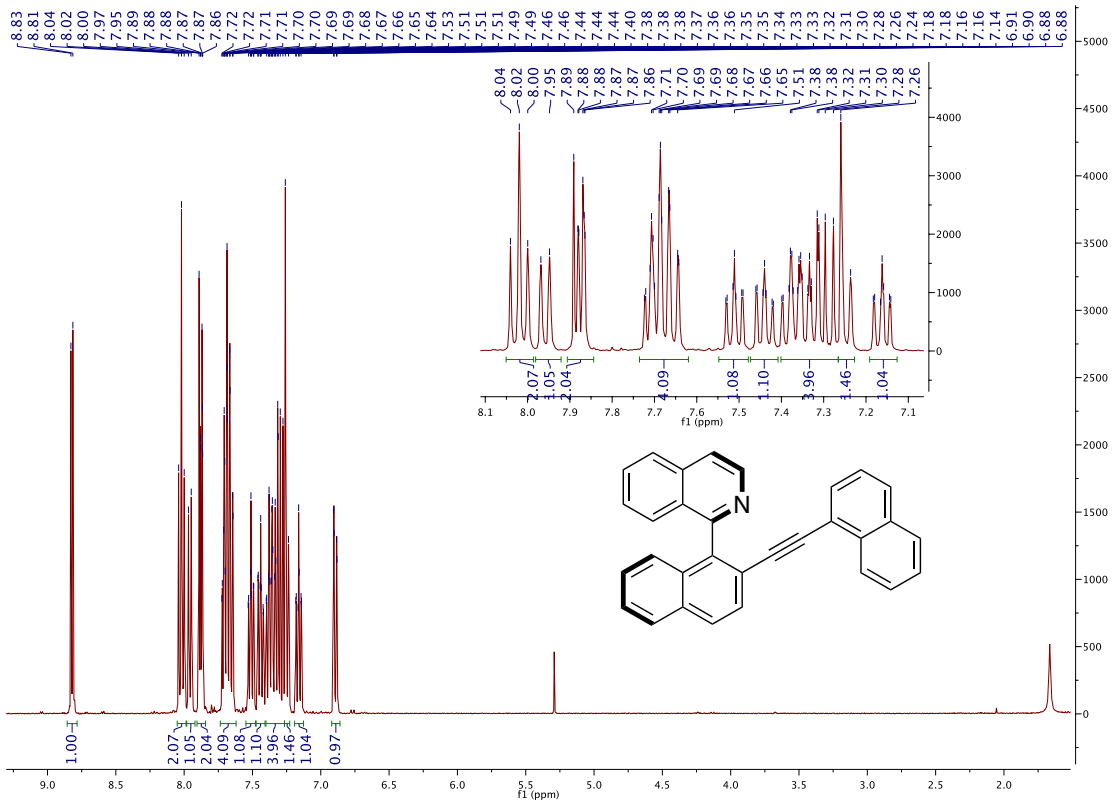
^{1}H NMR (400 MHz, $CDCl_3$) of **3Ah**



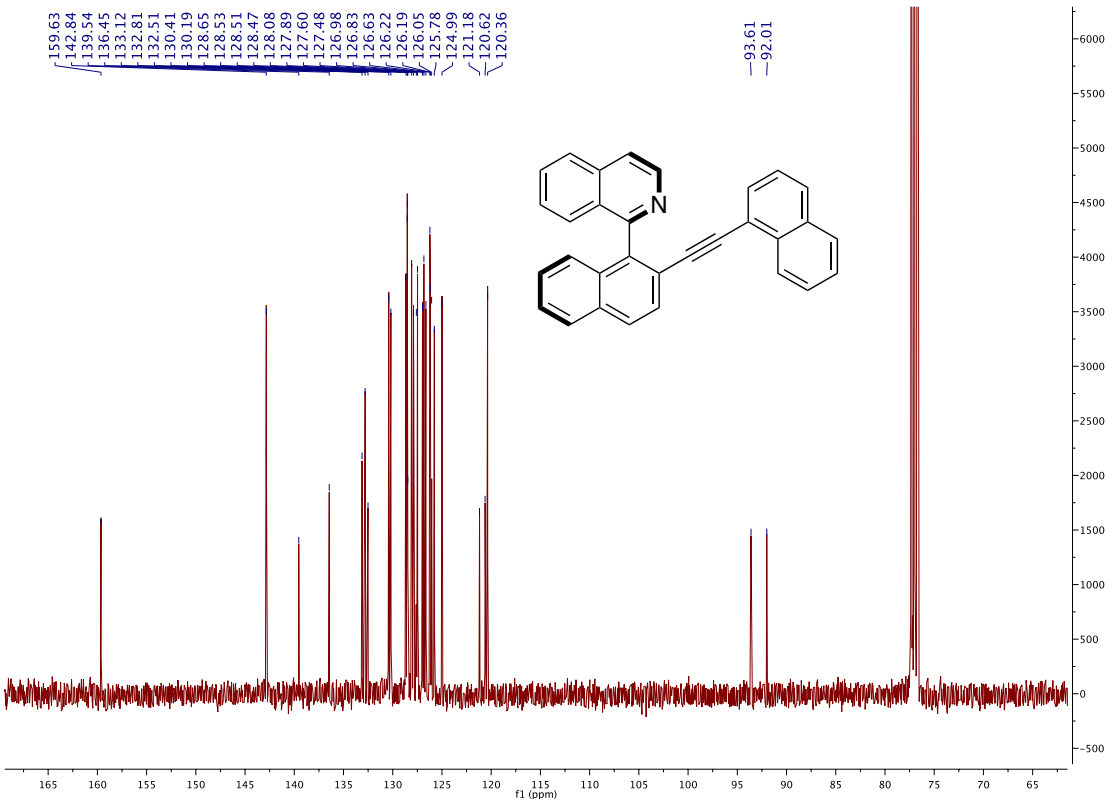
^{13}C NMR (100 MHz, $CDCl_3$) of **3Ah**



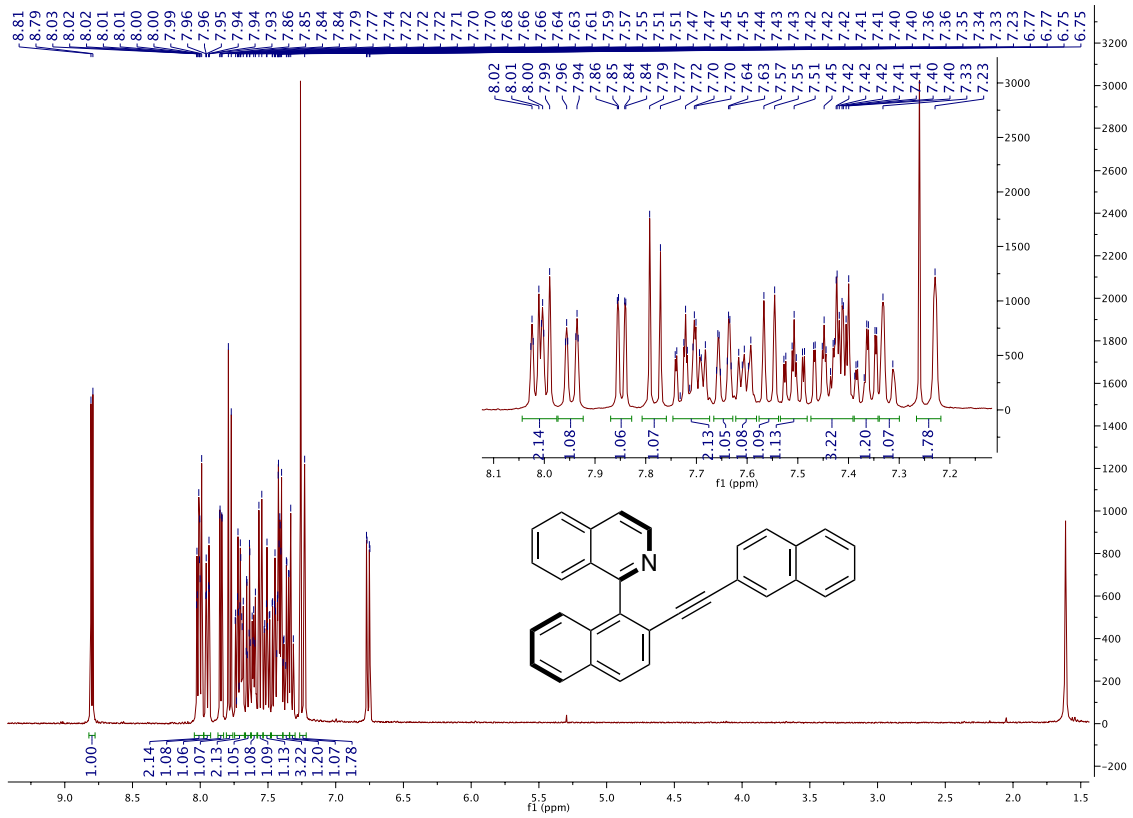
^{1}H NMR (400 MHz, $CDCl_3$) of **3Ai**



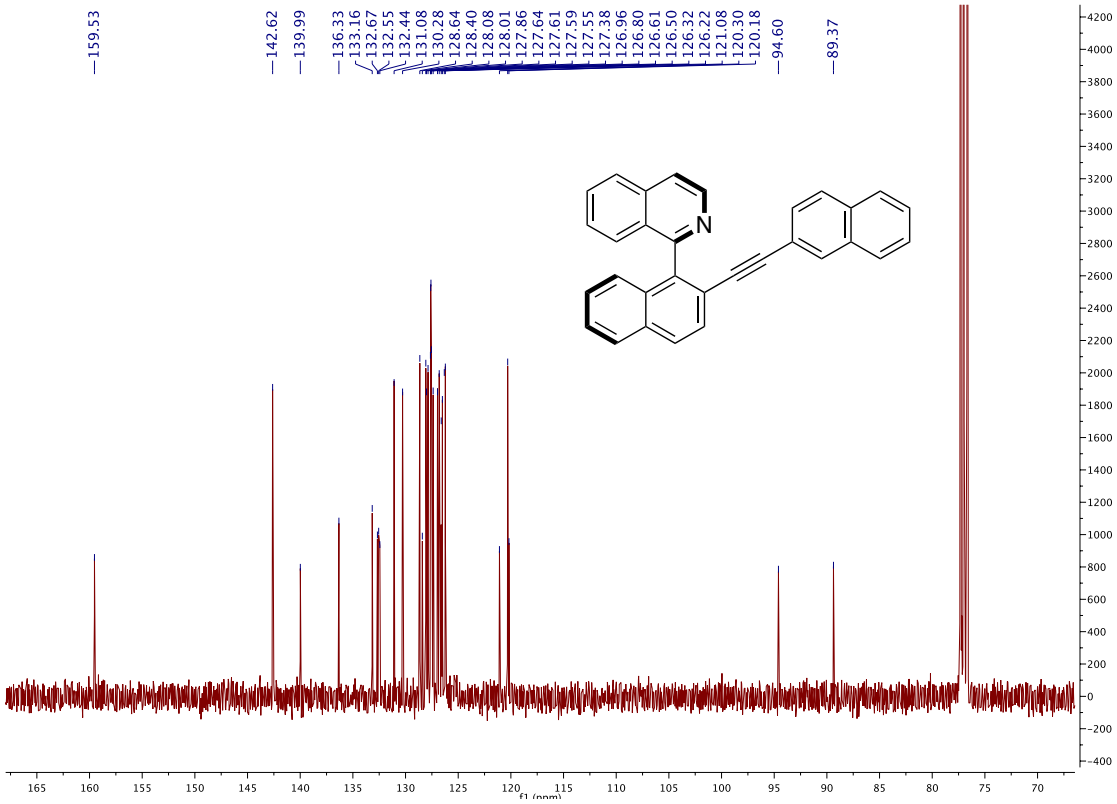
^{13}C NMR (100 MHz, $CDCl_3$) of **3Ai**



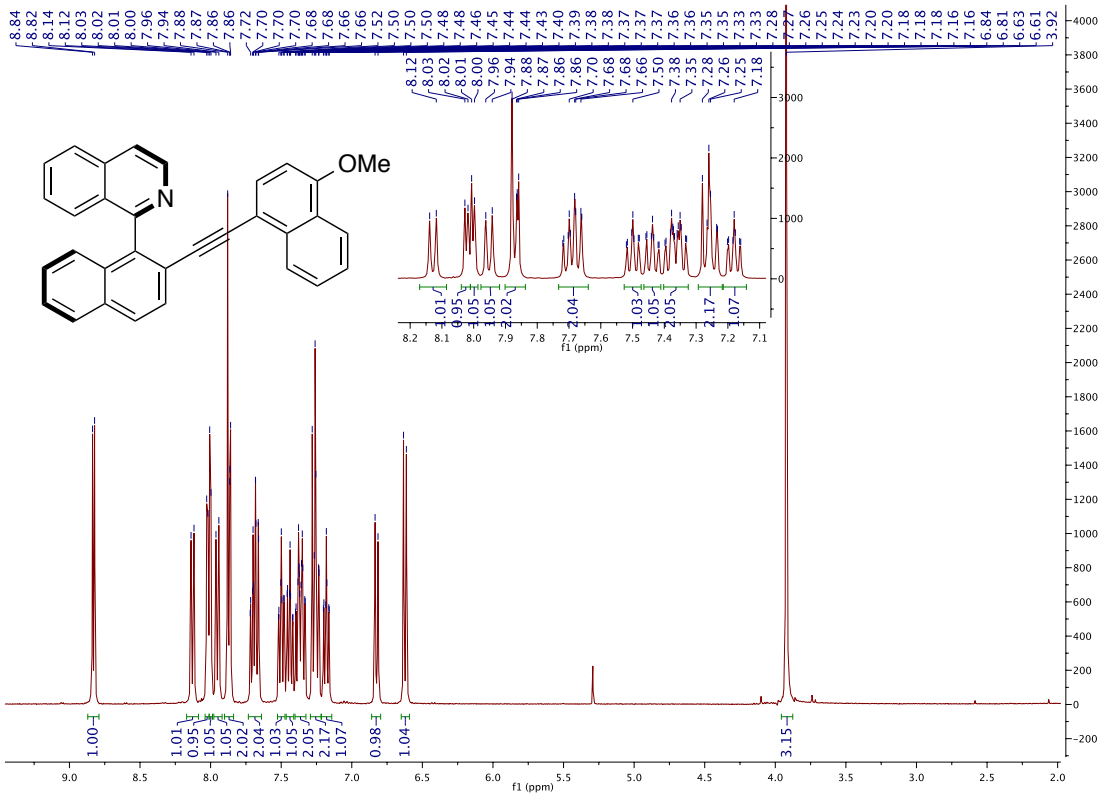
^{1}H NMR (400 MHz, $CDCl_3$) of **3Aj**



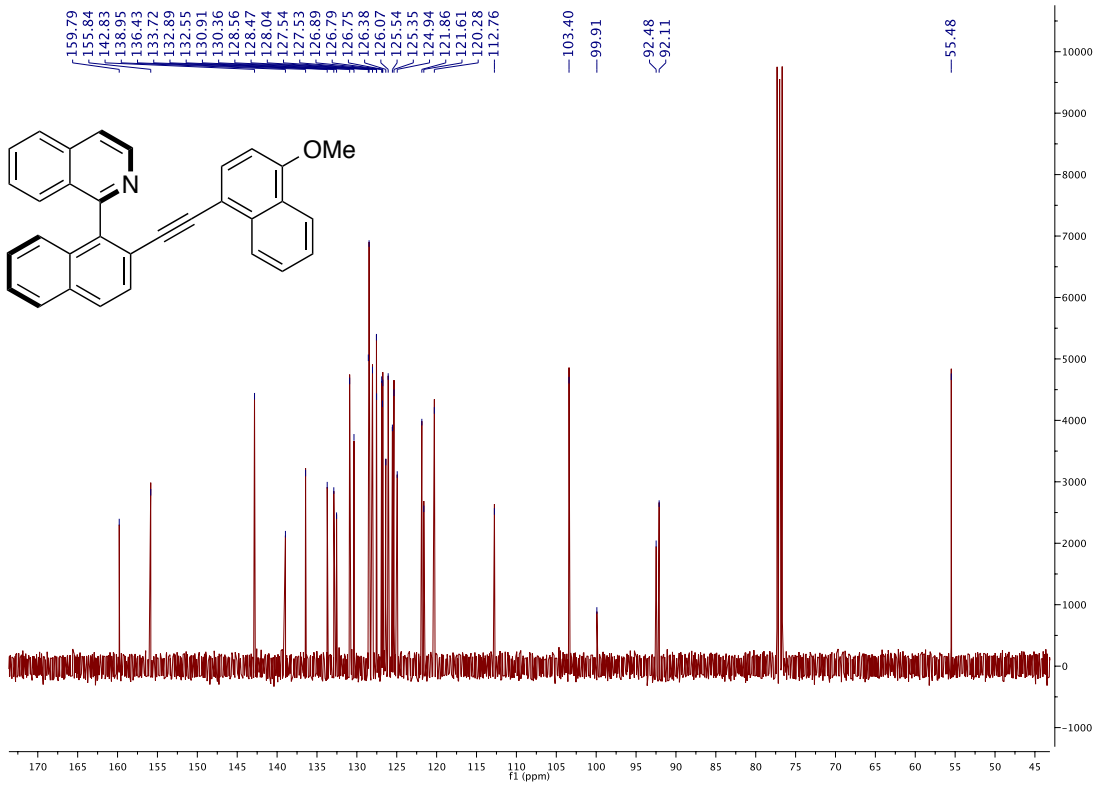
^{13}C NMR (100 MHz, $CDCl_3$) of **3Aj**



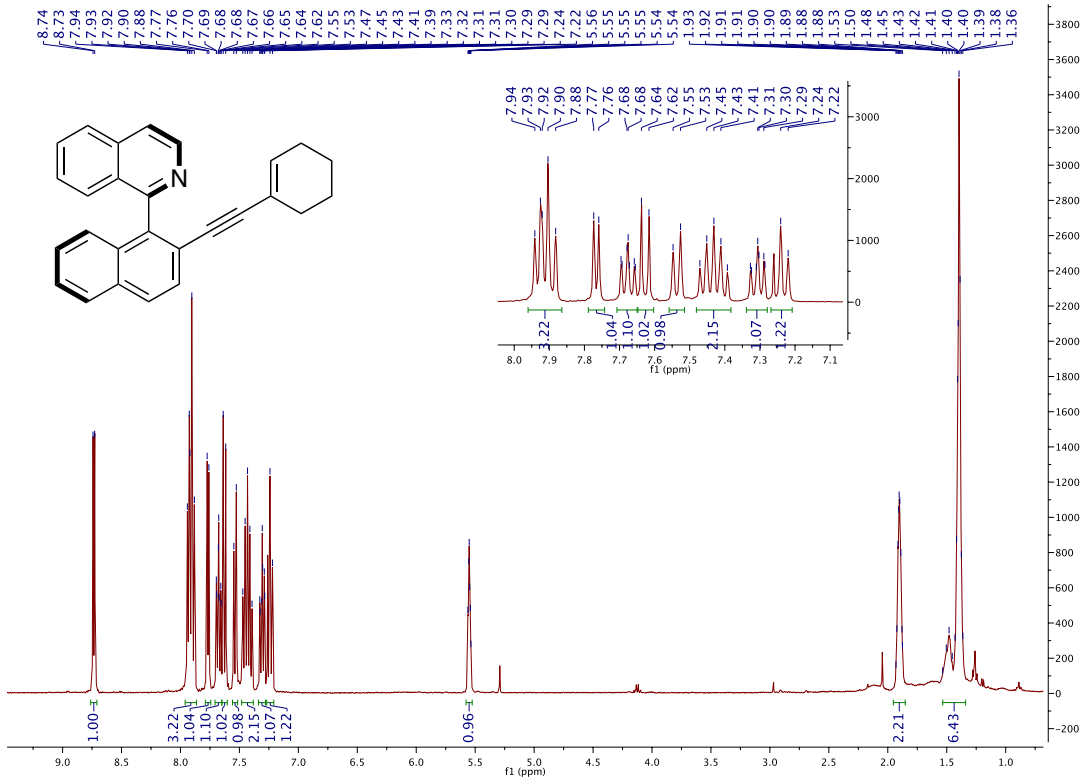
^{1}H NMR (400 MHz, $CDCl_3$) of **3Ak**



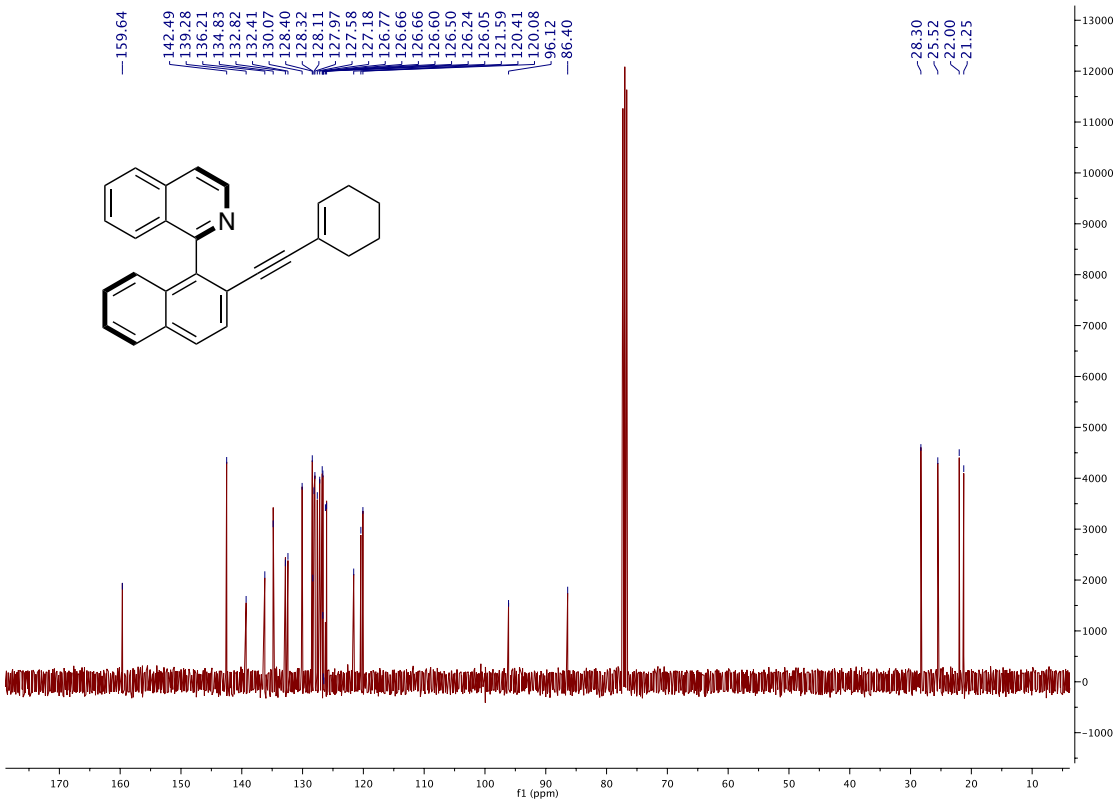
^{13}C NMR (100 MHz, $CDCl_3$) of **3Ak**



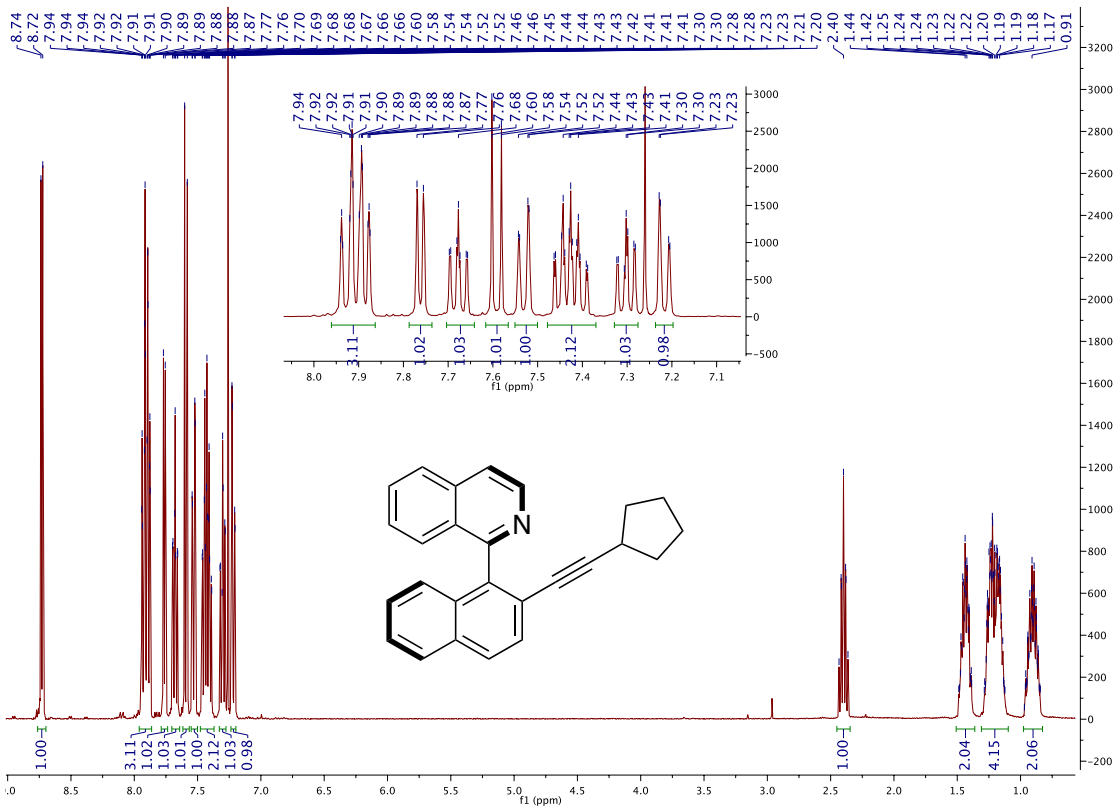
^{1}H NMR (400 MHz, $CDCl_3$) of **3Al**



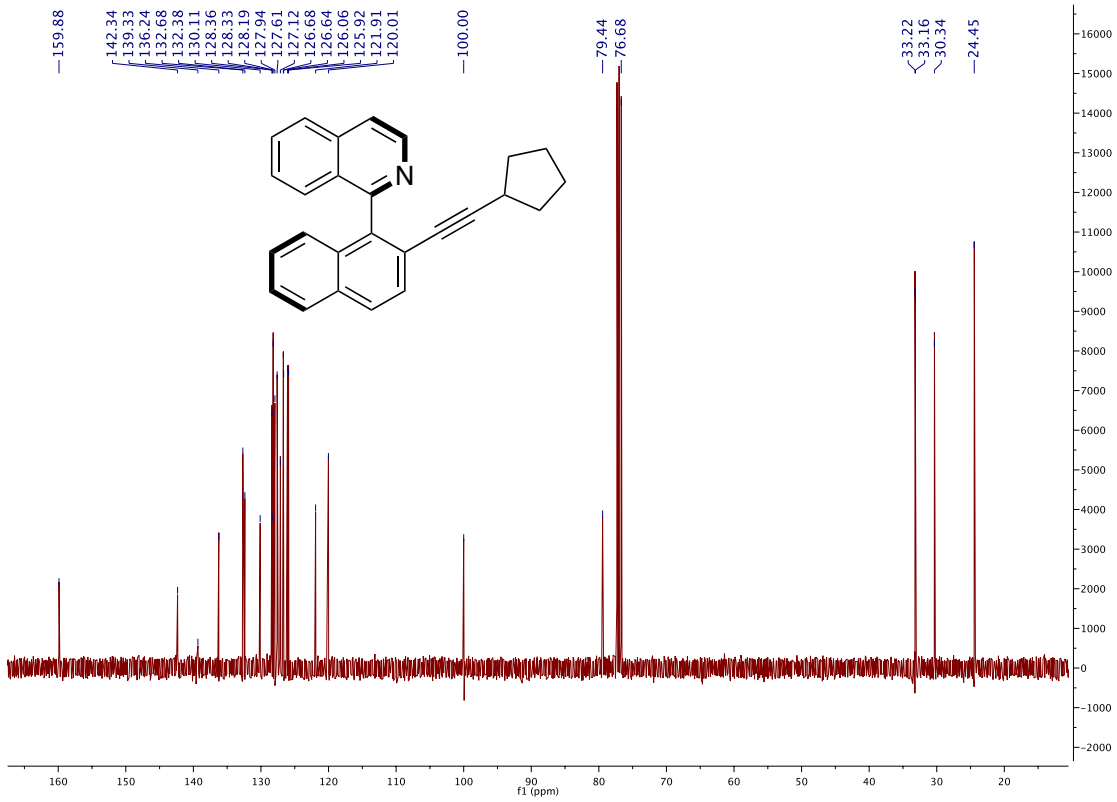
^{13}C NMR (100 MHz, $CDCl_3$) of **3Al**



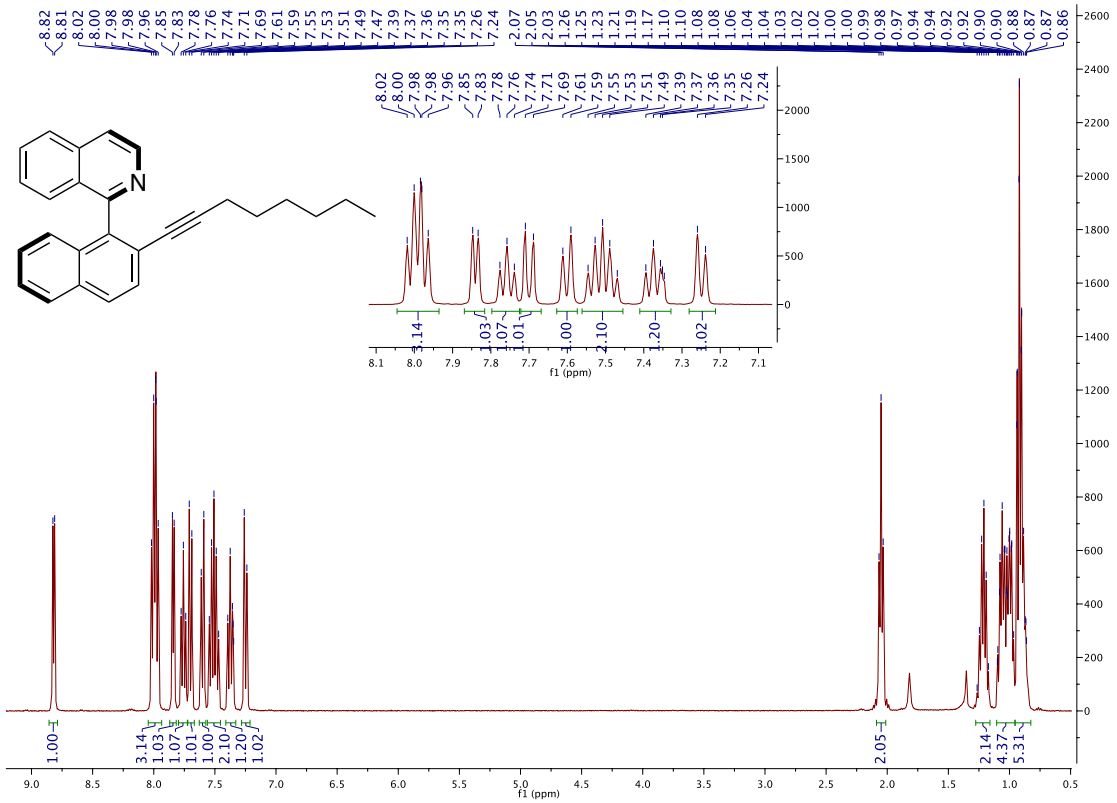
^{1}H NMR (400 MHz, $CDCl_3$) of **3Am**



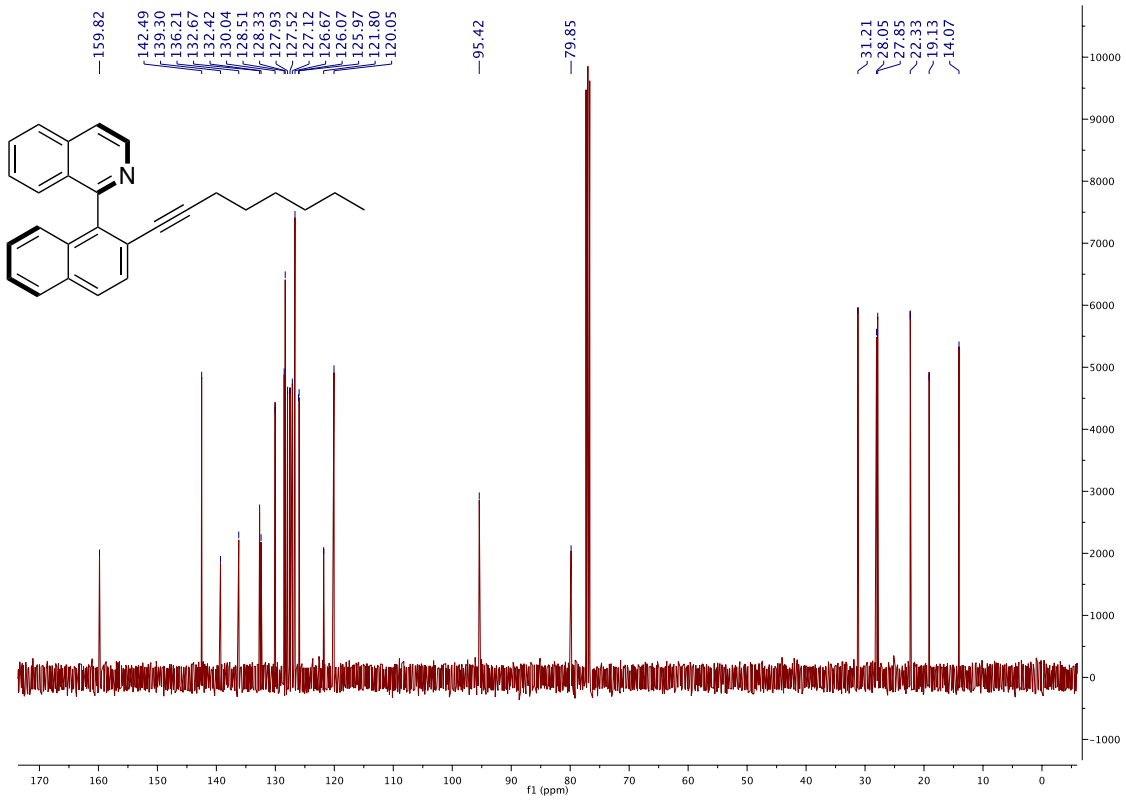
^{13}C NMR (100 MHz, $CDCl_3$) of **3Am**



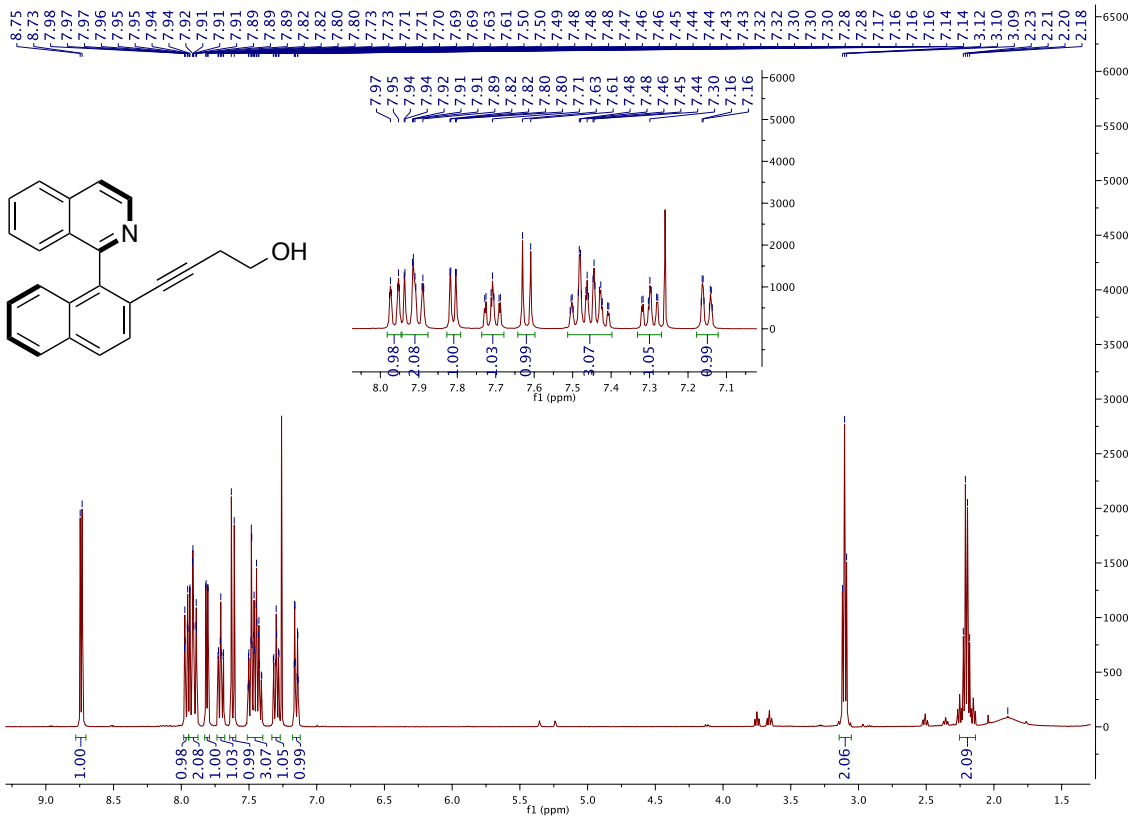
^{1}H NMR (400 MHz, $CDCl_3$) of **3An**



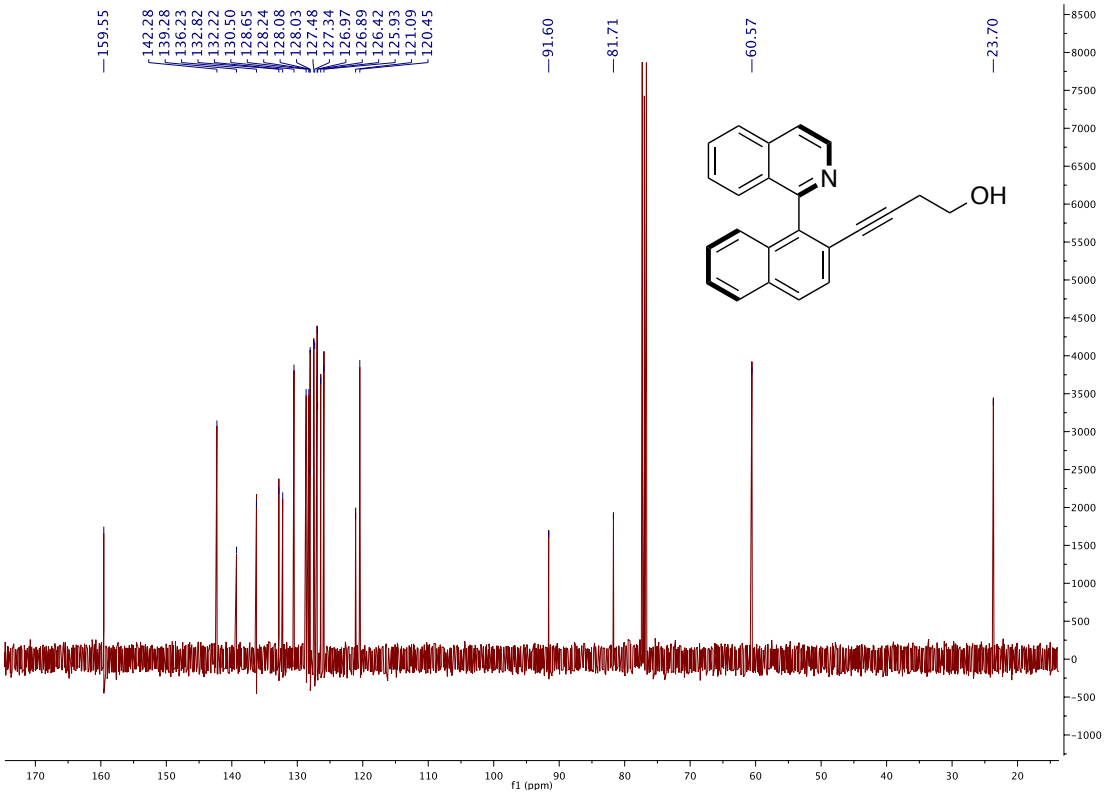
^{13}C NMR (100 MHz, $CDCl_3$) of **3An**



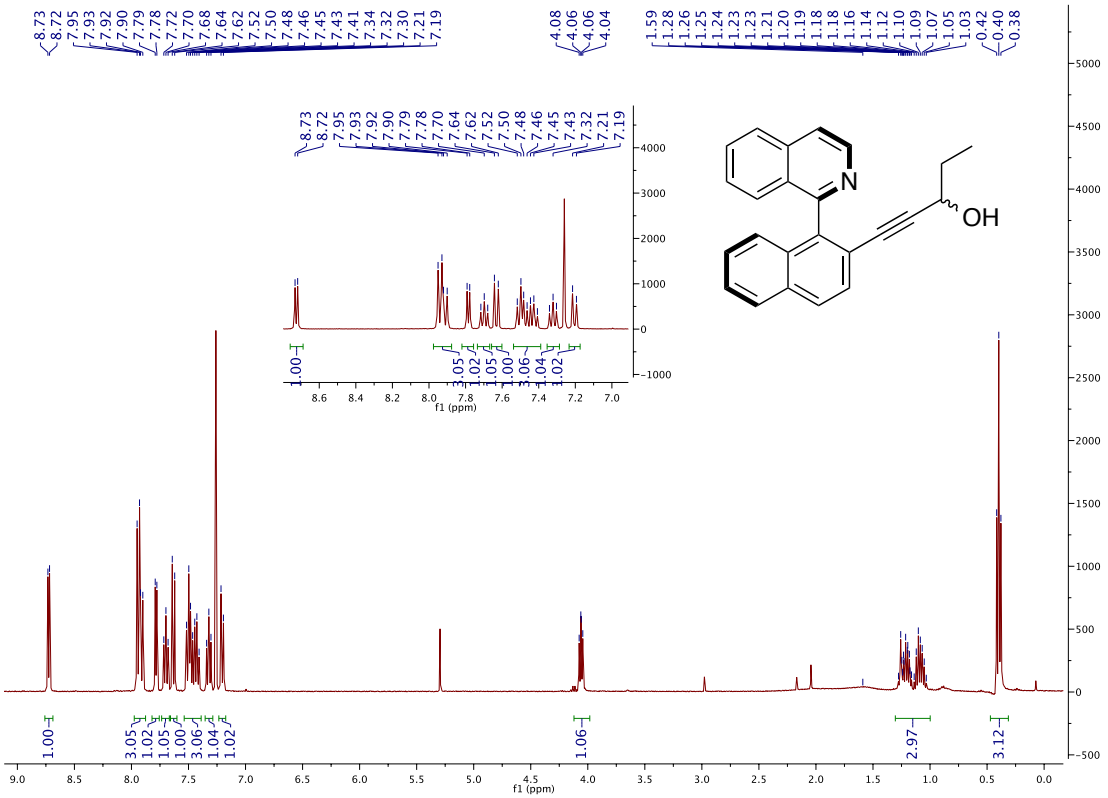
^{1}H NMR (400 MHz, $CDCl_3$) of **3Ao**



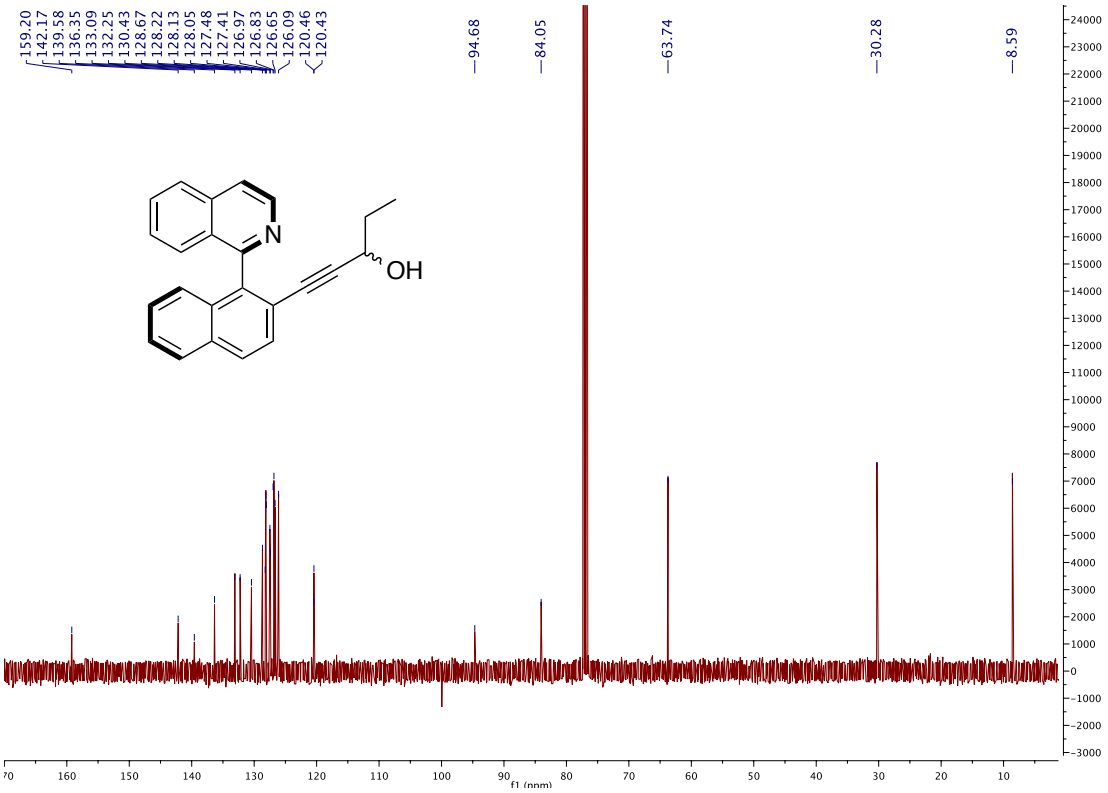
^{13}C NMR (100 MHz, $CDCl_3$) of **3Ao**



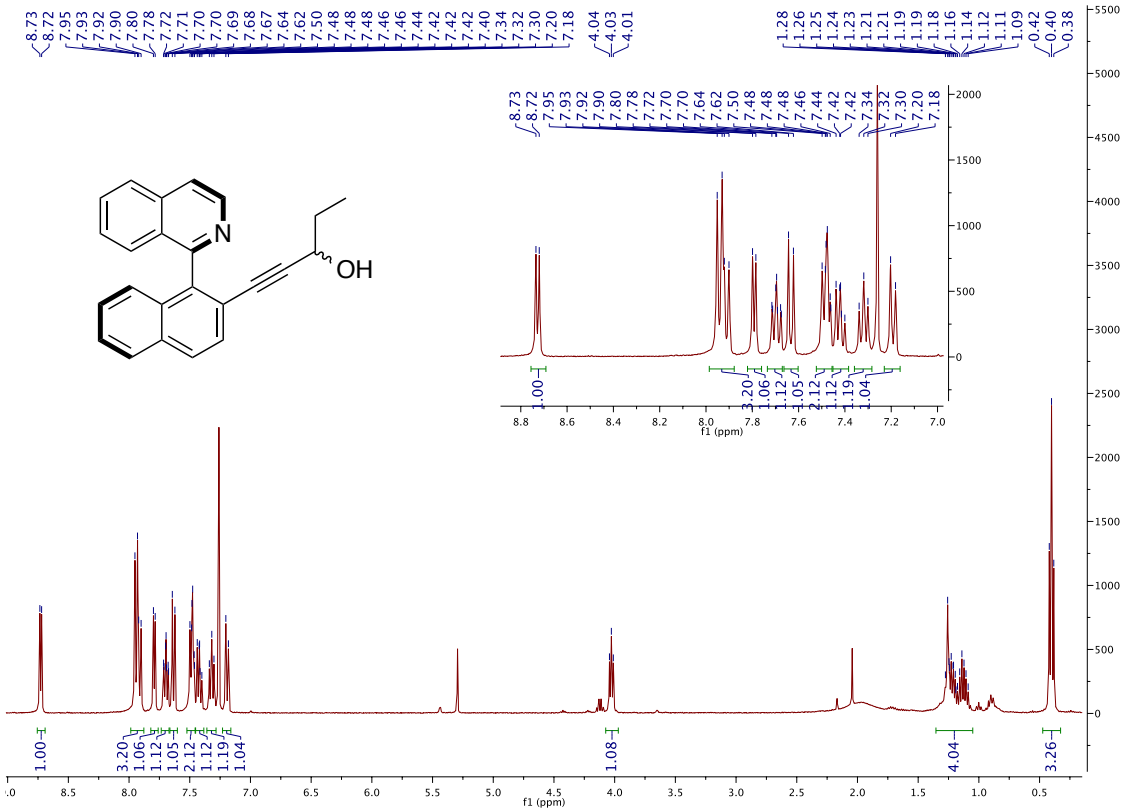
^{1}H NMR (400 MHz, $CDCl_3$) of **3Ap diast 1**



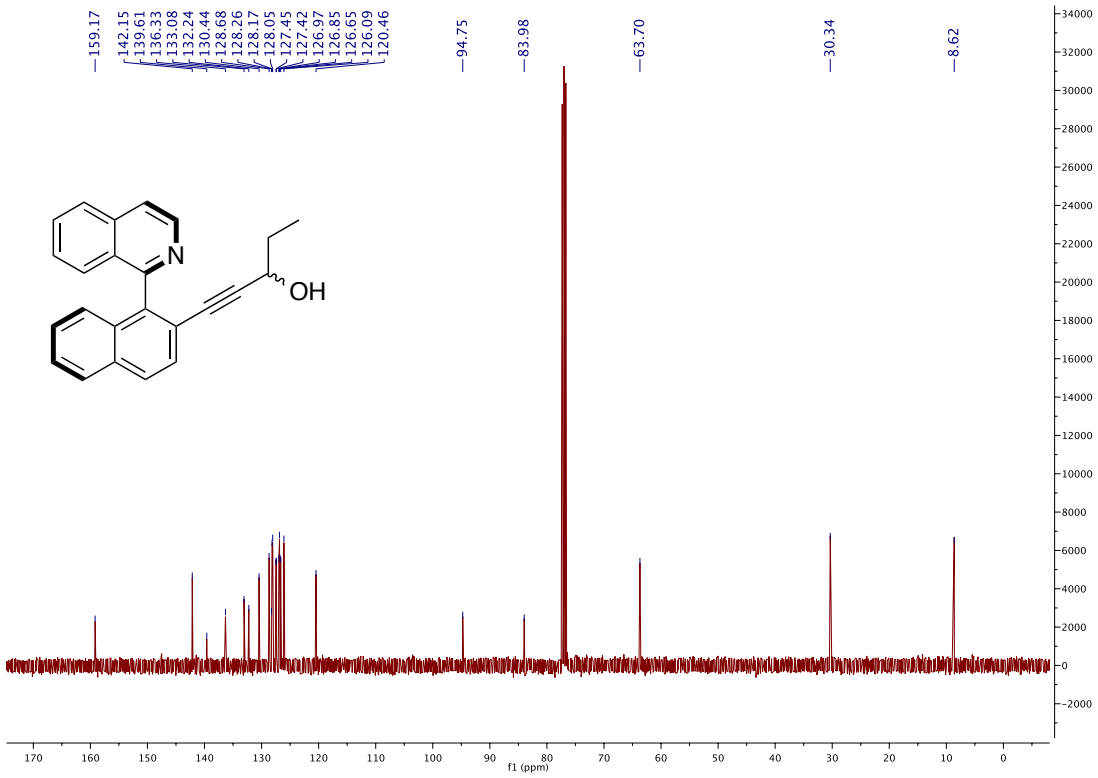
^{13}C NMR (100 MHz, $CDCl_3$) of **3Ap diast 1**



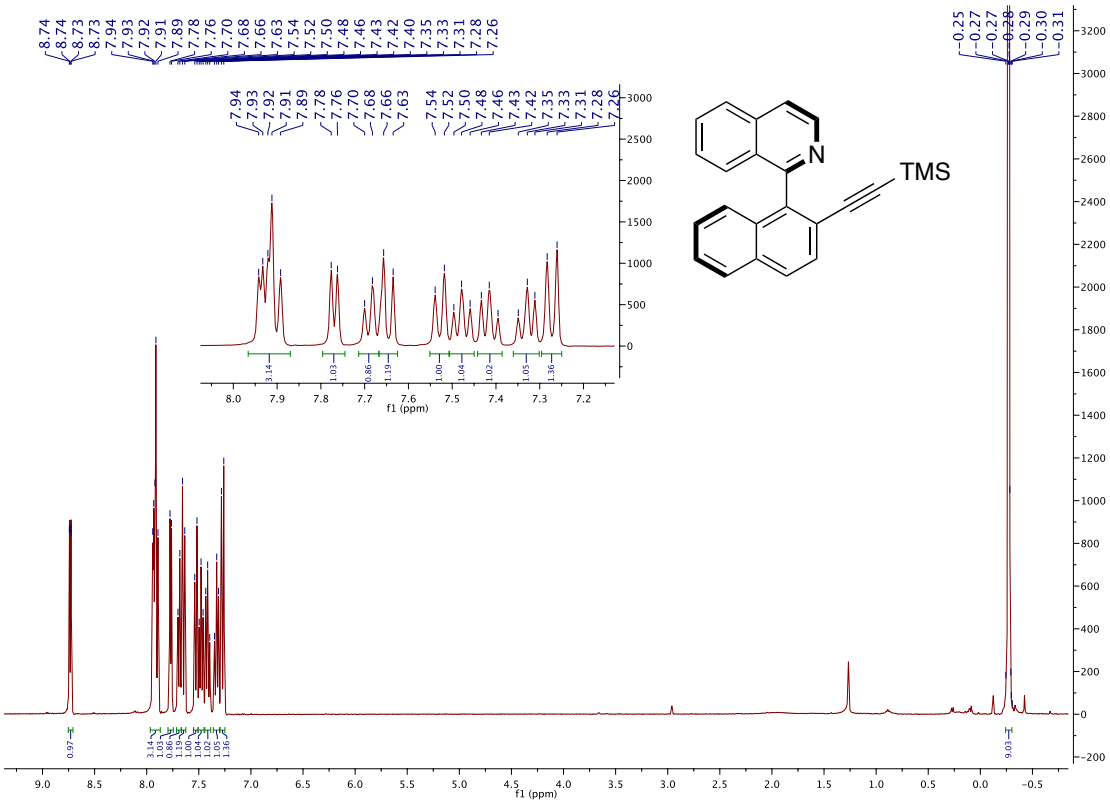
^{1}H NMR (400 MHz, $CDCl_3$) of **3Ap diast 2**



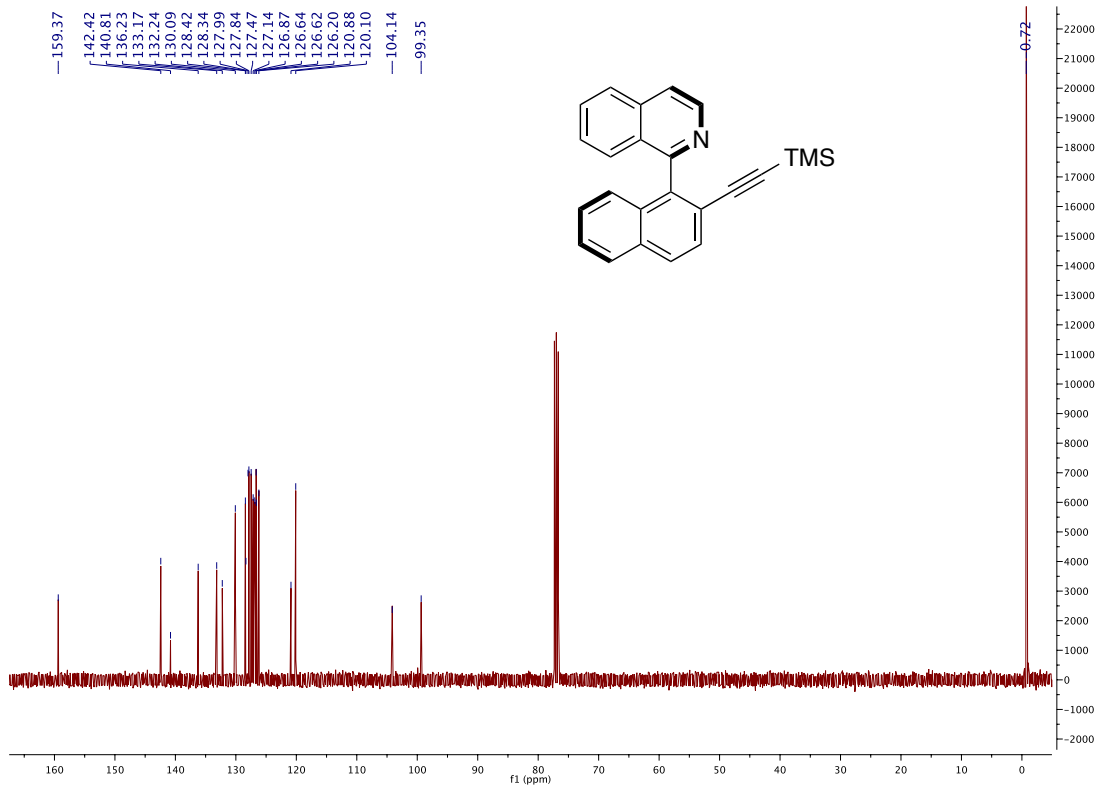
^{13}C NMR (100 MHz, $CDCl_3$) of **3Ap diast 2**



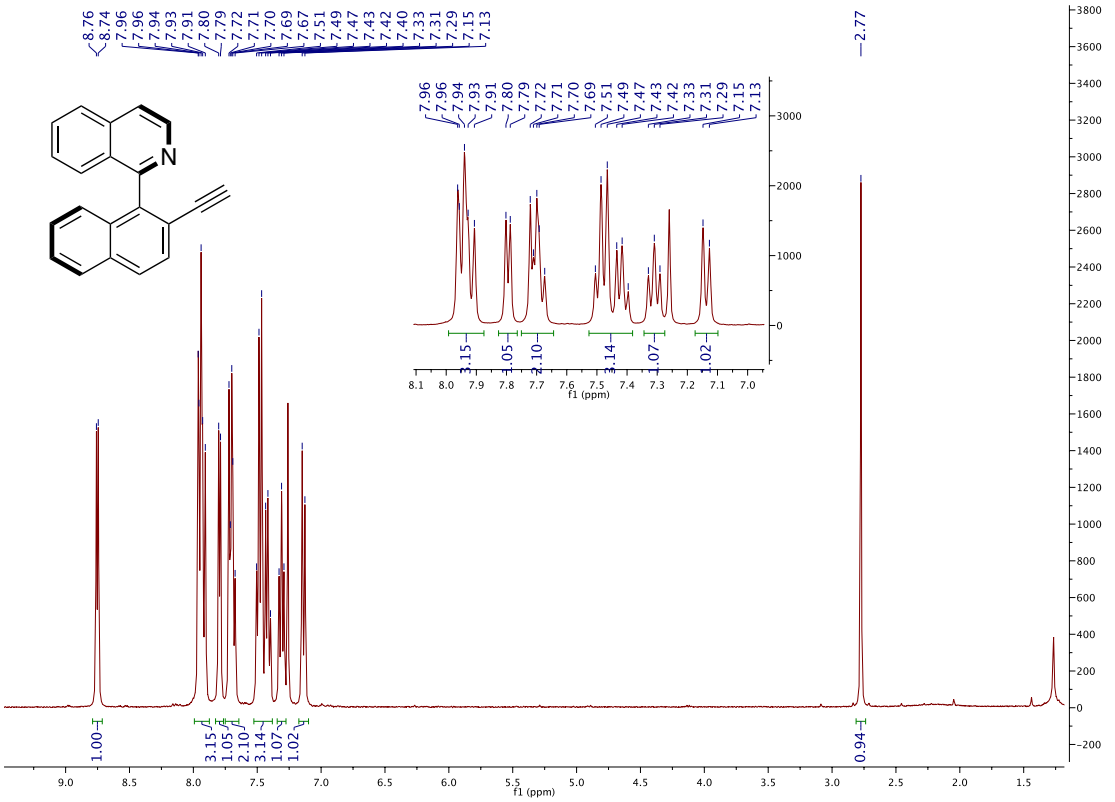
^{1}H NMR (400 MHz, $CDCl_3$) of **3Aq**



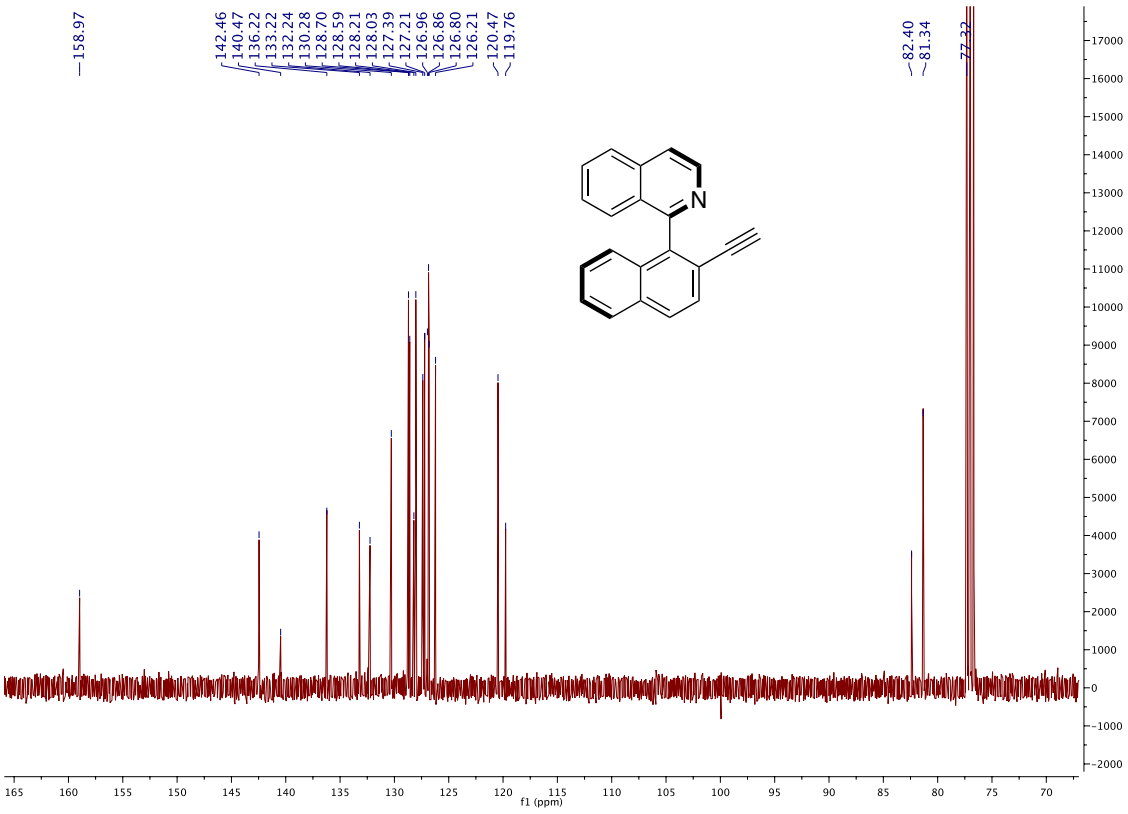
^{13}C NMR (100 MHz, $CDCl_3$) of **3Aq**



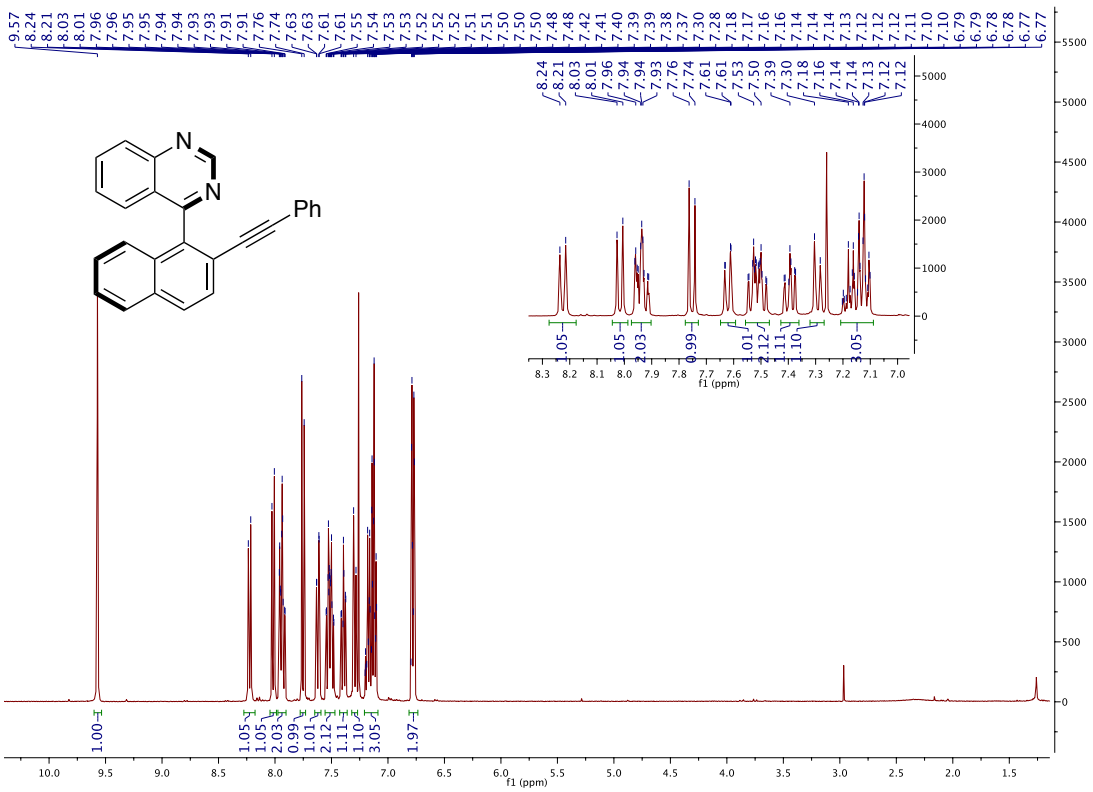
^{1}H NMR (400 MHz, $CDCl_3$) of **4A**



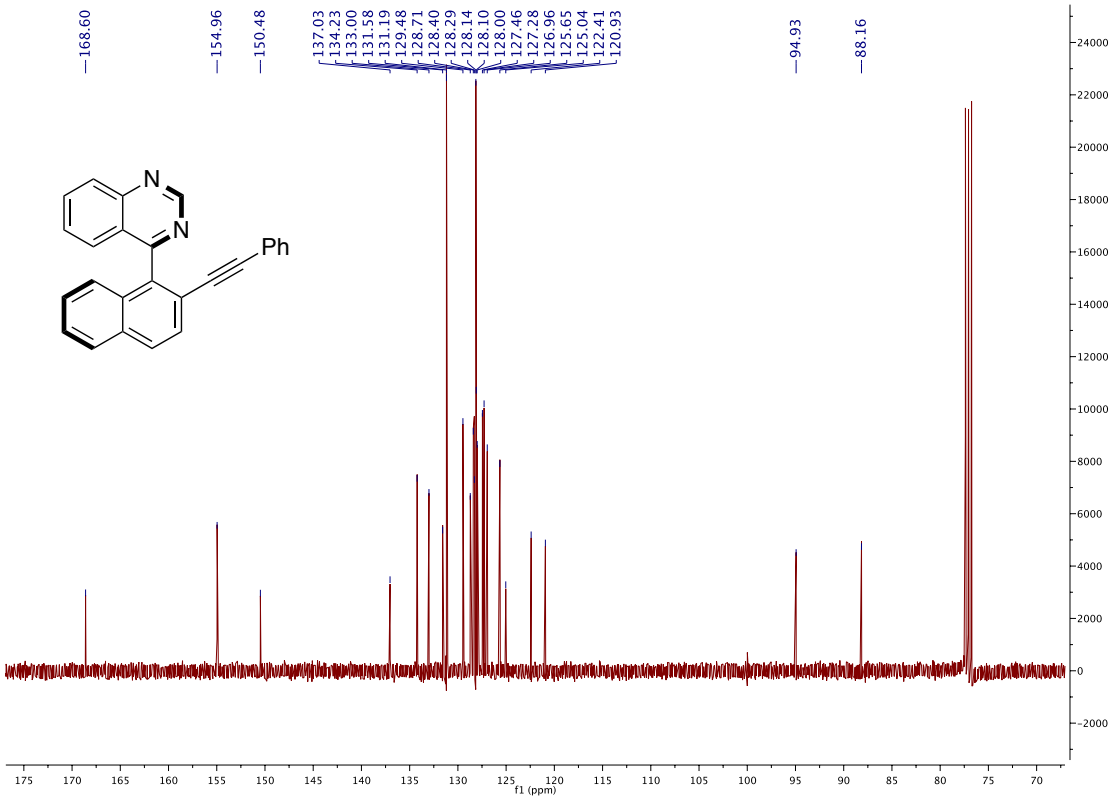
^{13}C NMR (100 MHz, $CDCl_3$) of **4A**



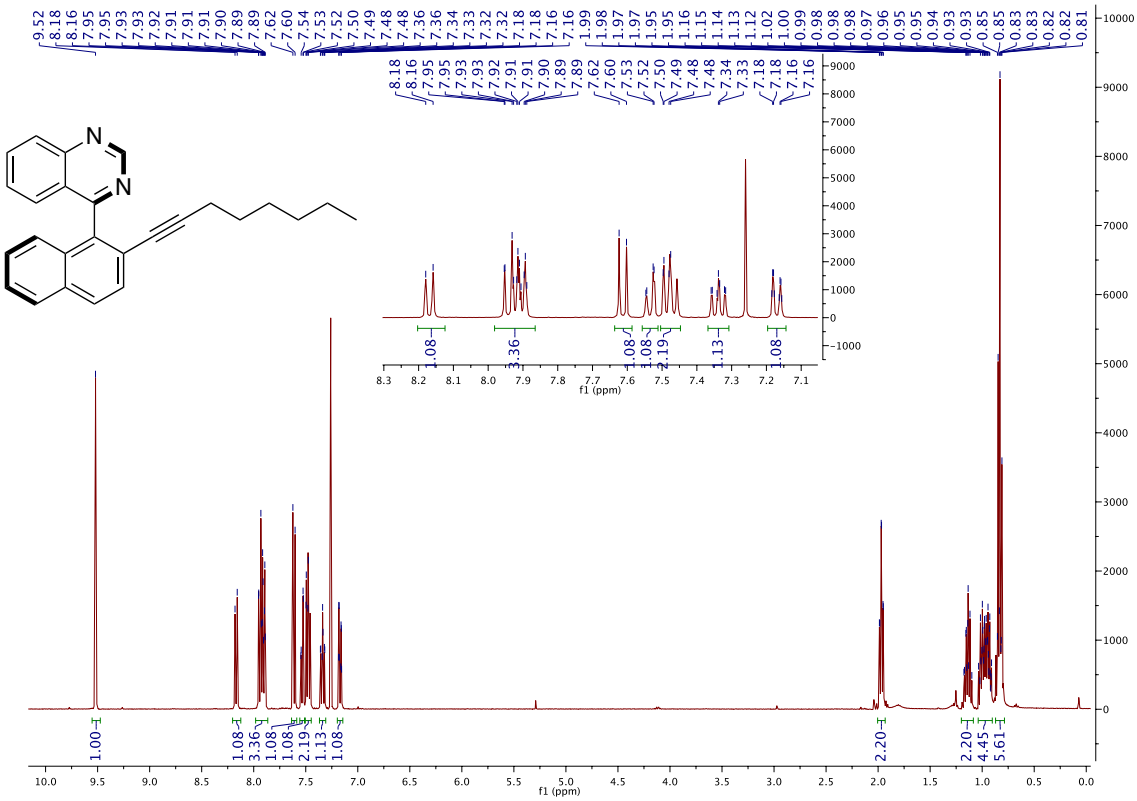
^{1}H NMR (400 MHz, $CDCl_3$) of **3Ba**



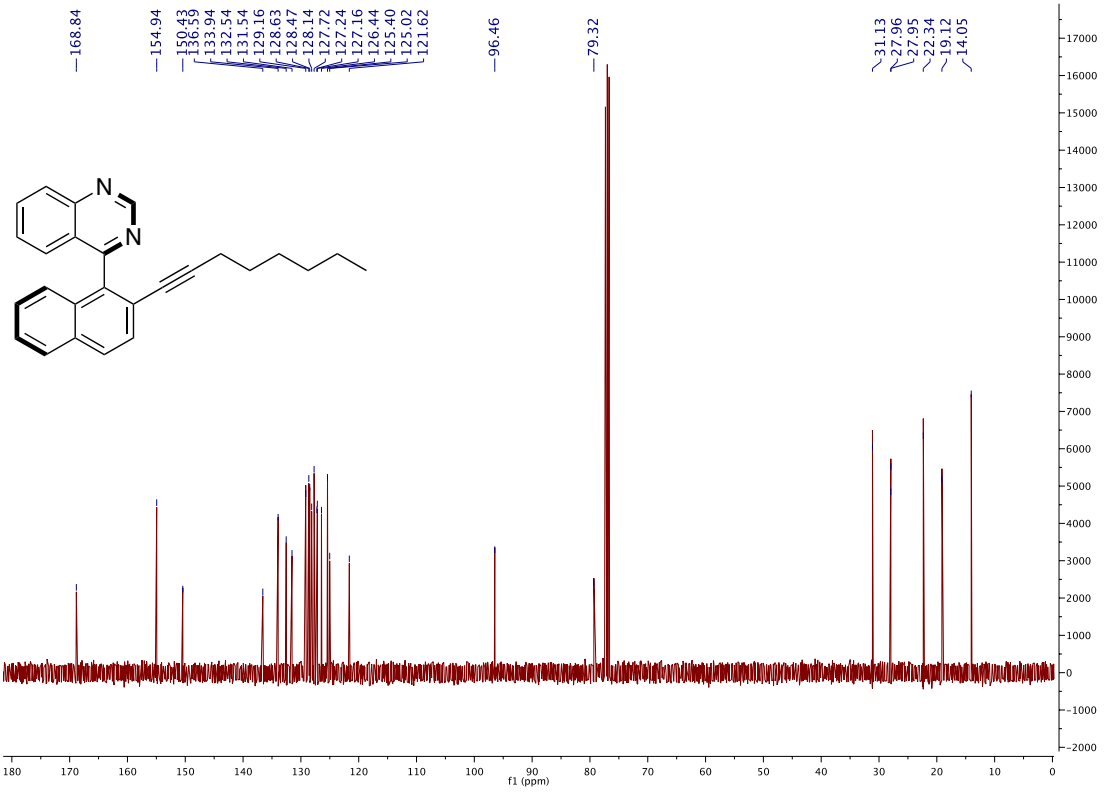
^{13}C NMR (100 MHz, $CDCl_3$) of **3Ba**



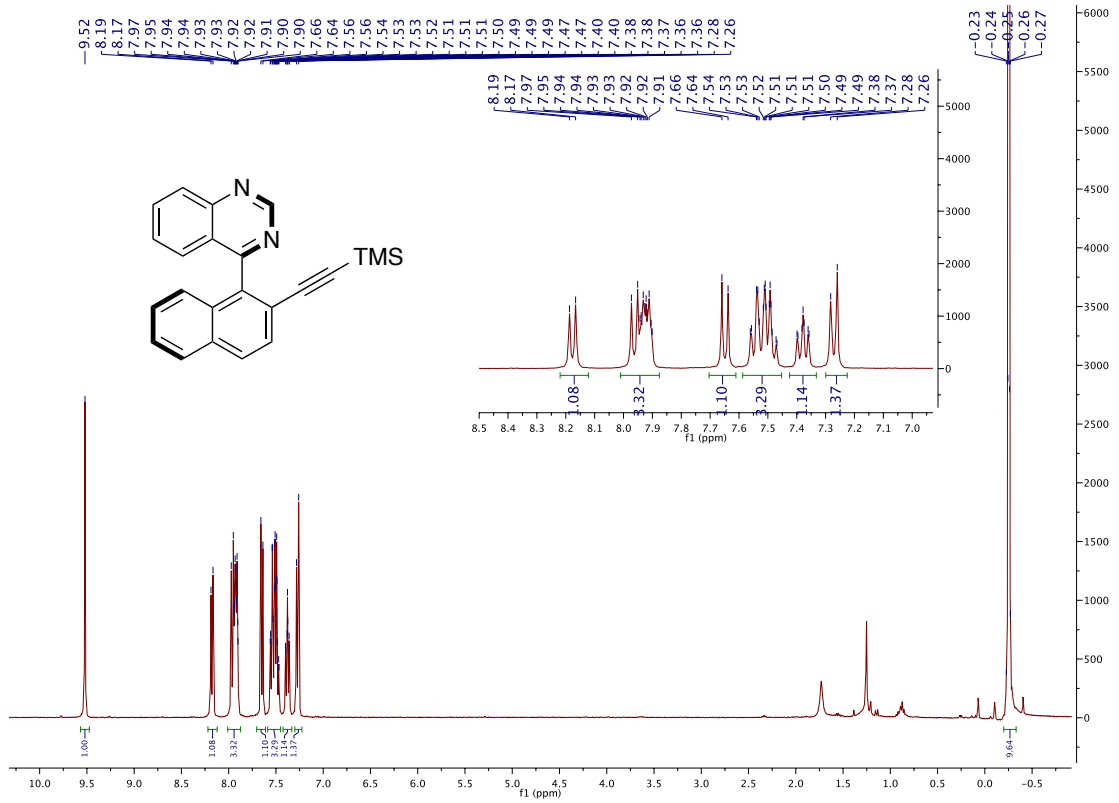
^{1}H NMR (400 MHz, $CDCl_3$) of **3Bn**



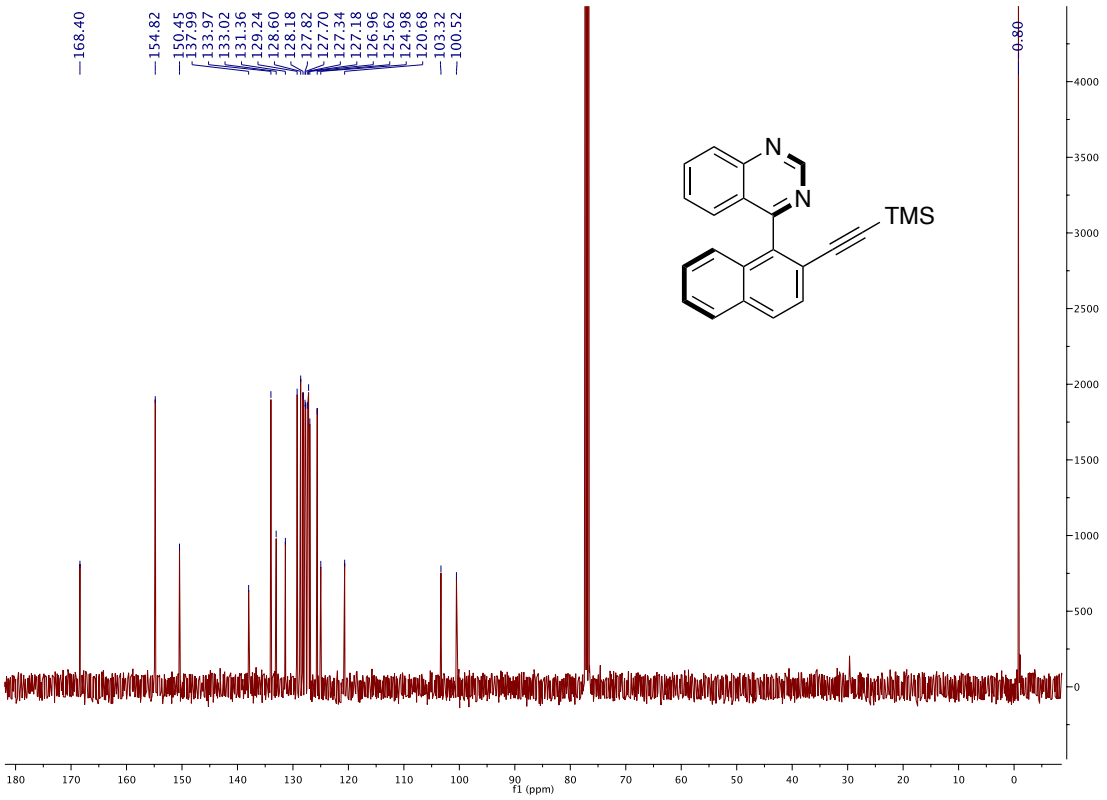
^{13}C NMR (100 MHz, $CDCl_3$) of **3Bn**



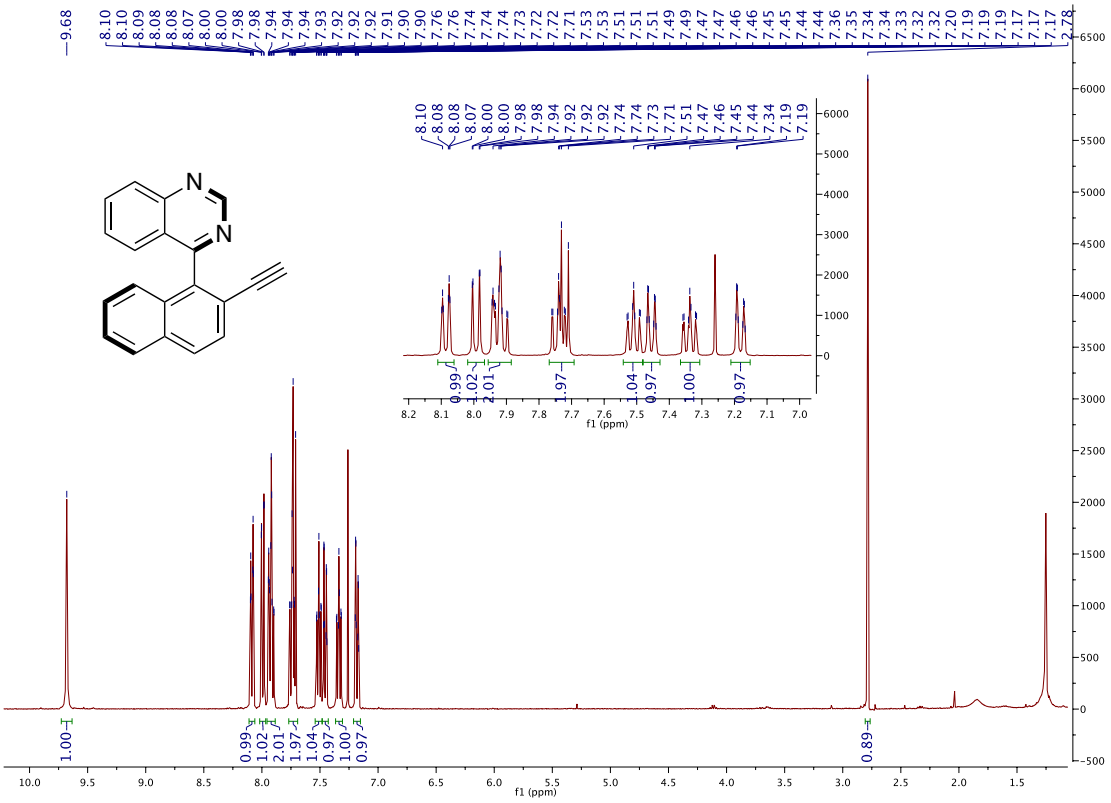
^{1}H NMR (400 MHz, $CDCl_3$) of **3Bq**



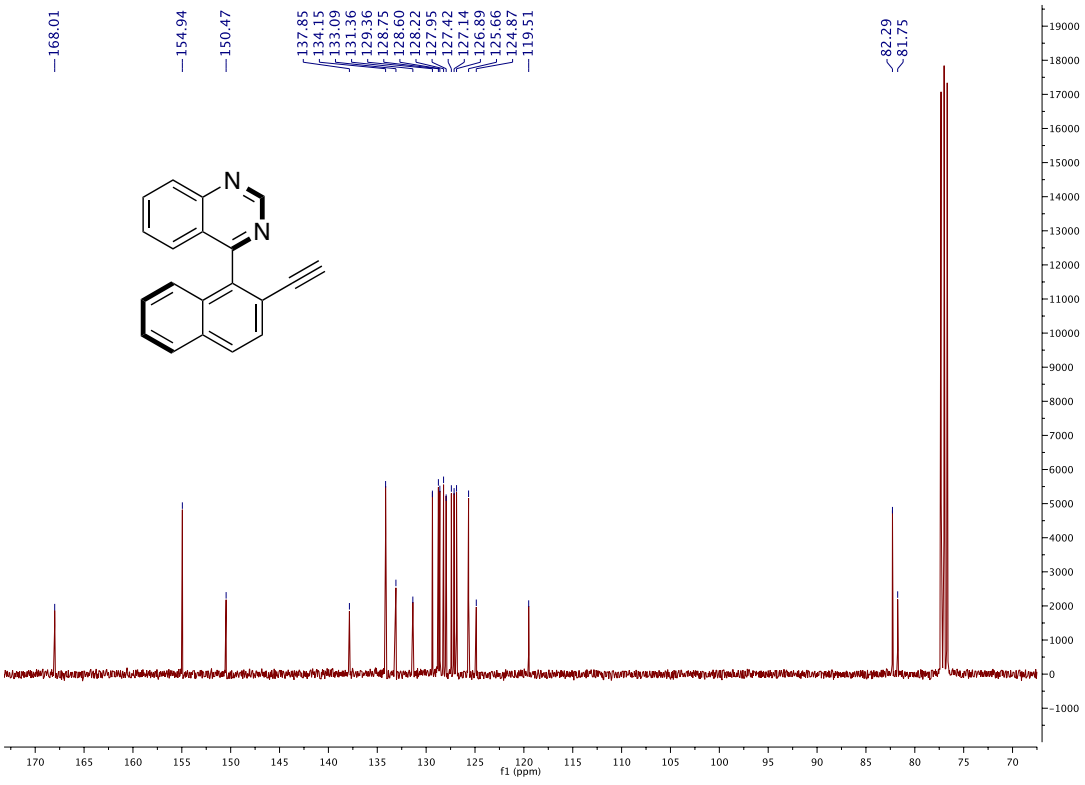
^{13}C NMR (100 MHz, $CDCl_3$) of **3Bq**



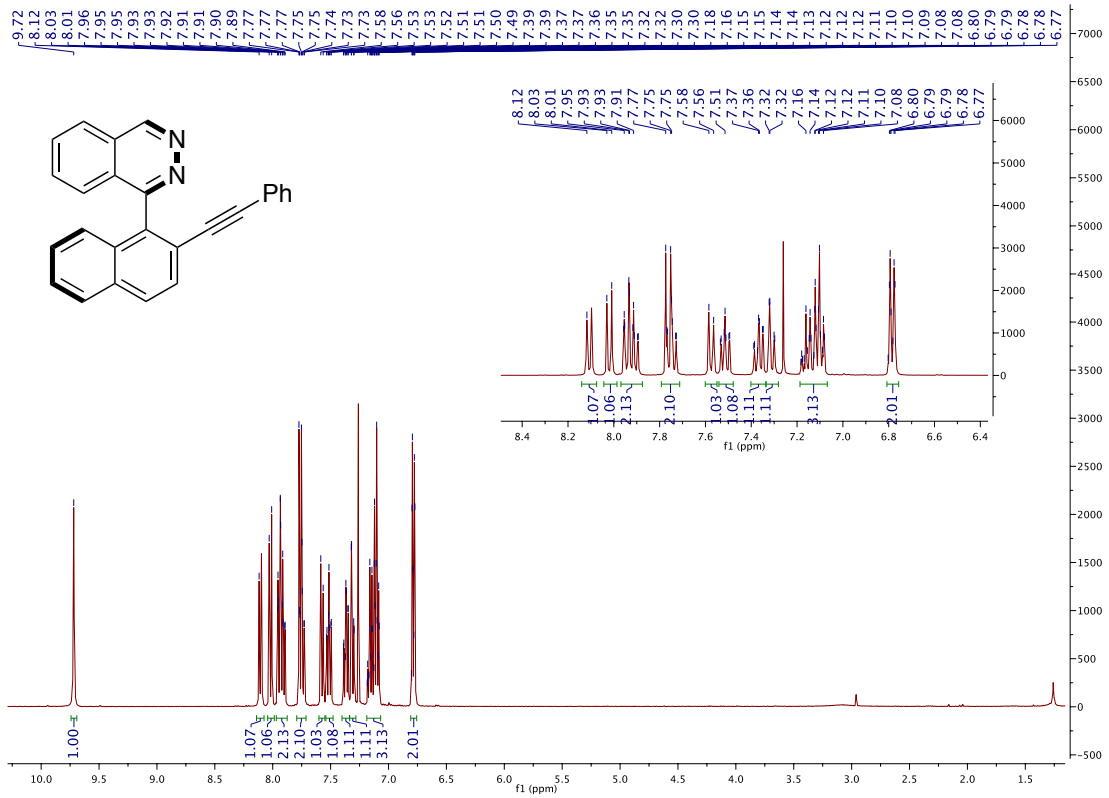
^{1}H NMR (400 MHz, $CDCl_3$) of **4B**



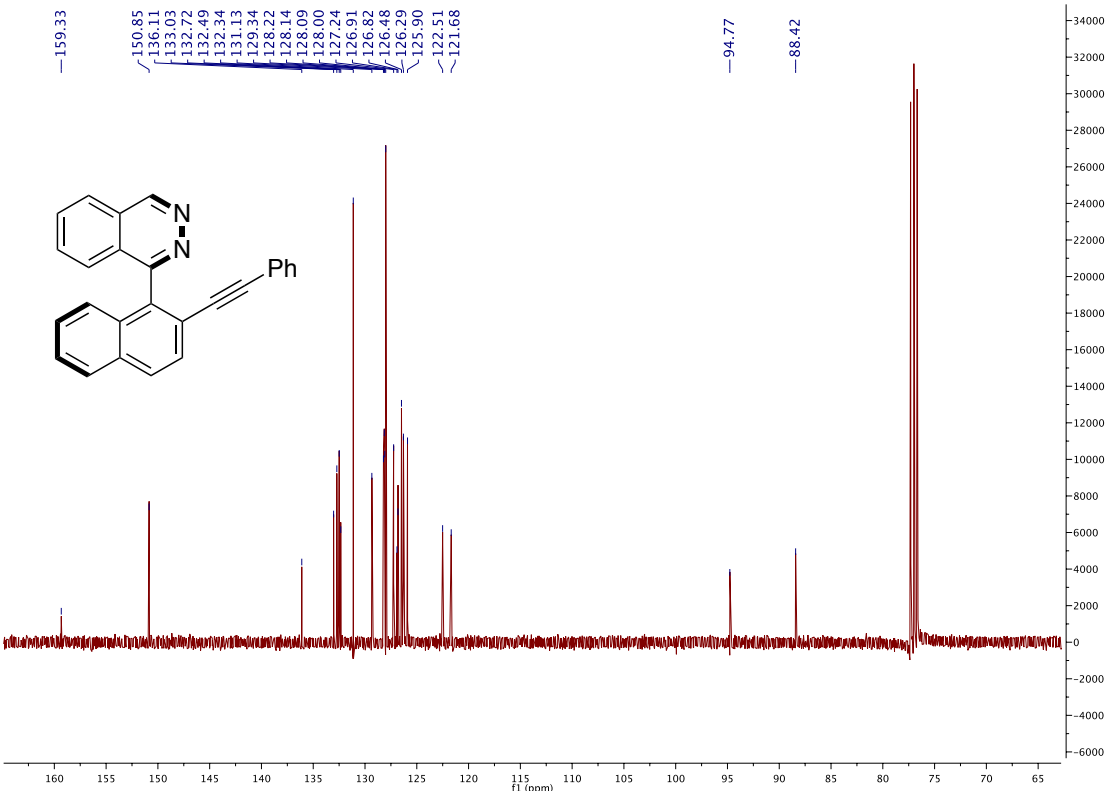
^{13}C NMR (100 MHz, $CDCl_3$) of **4B**



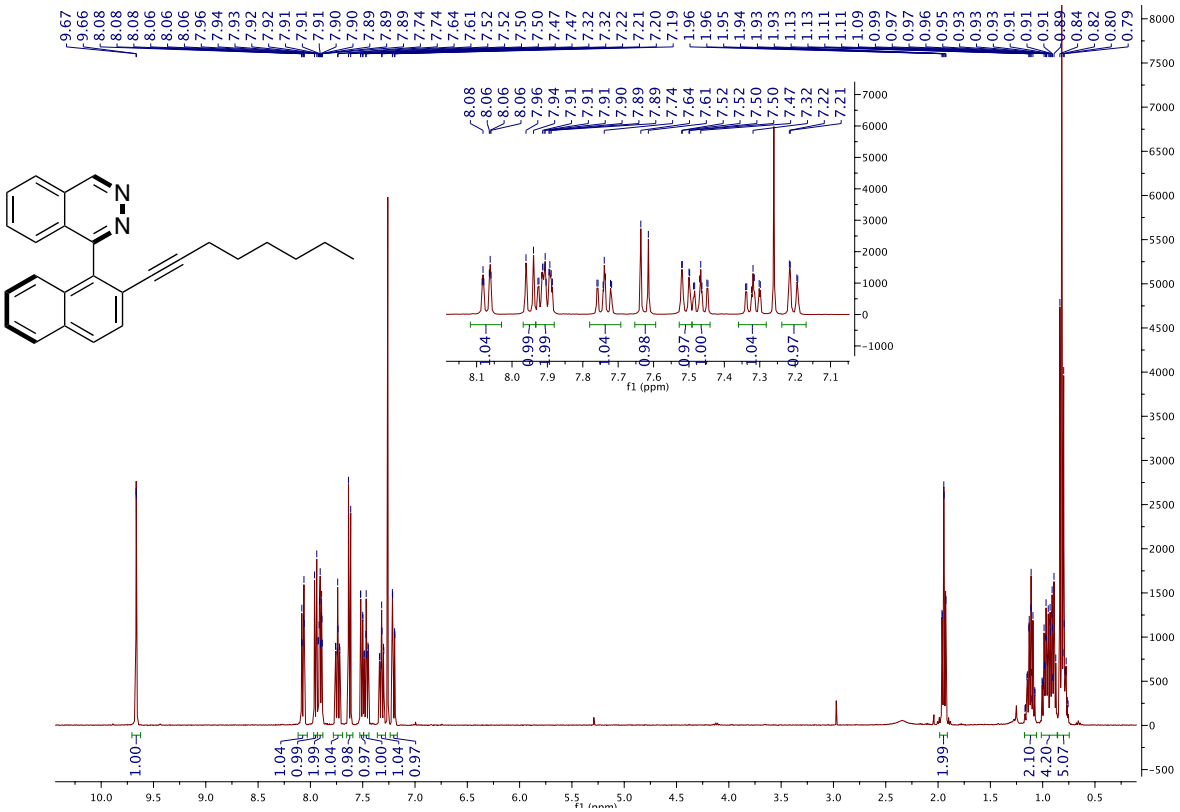
^{1}H NMR (400 MHz, $CDCl_3$) of **3Ca**



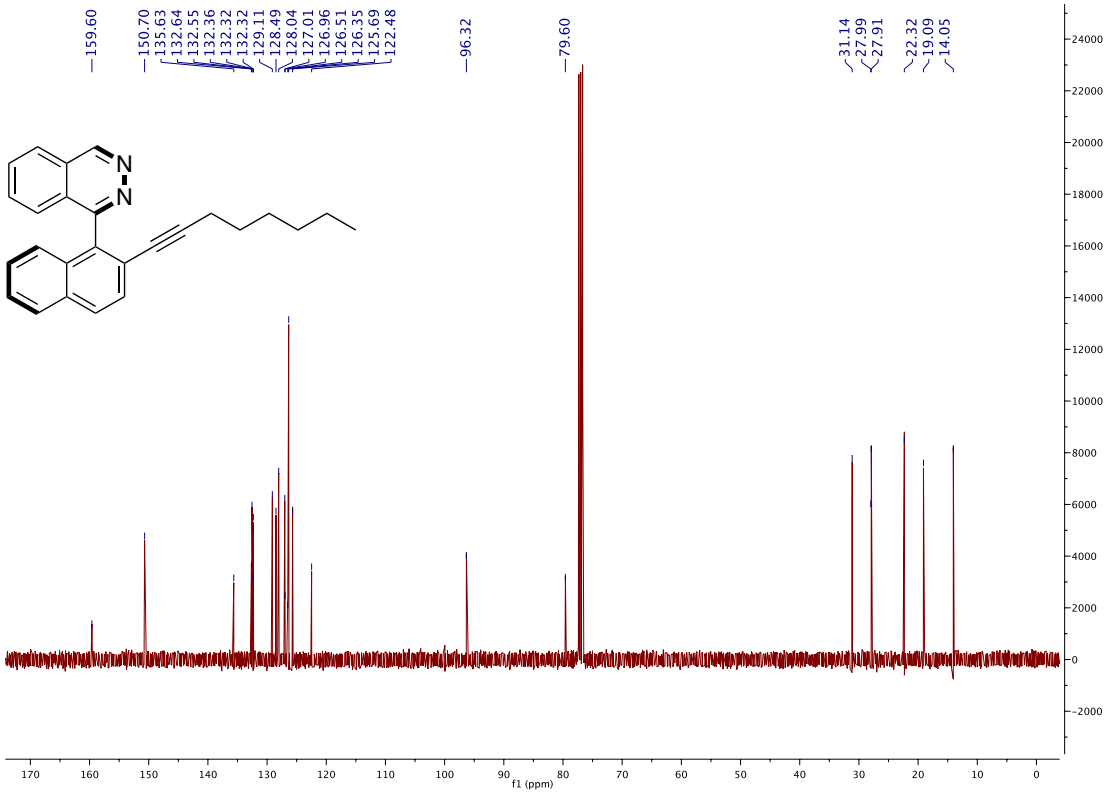
^{13}C NMR (100 MHz, $CDCl_3$) of **3Ca**



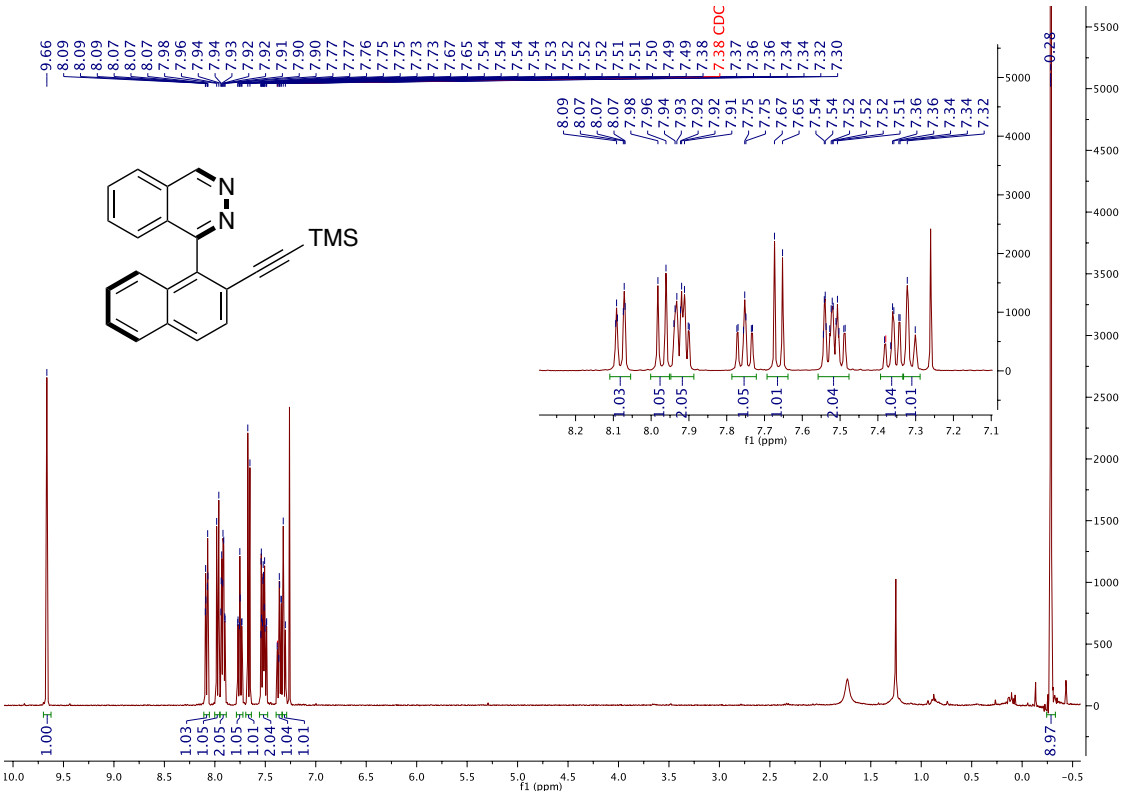
^{1}H NMR (400 MHz, $CDCl_3$) of **3Cn**



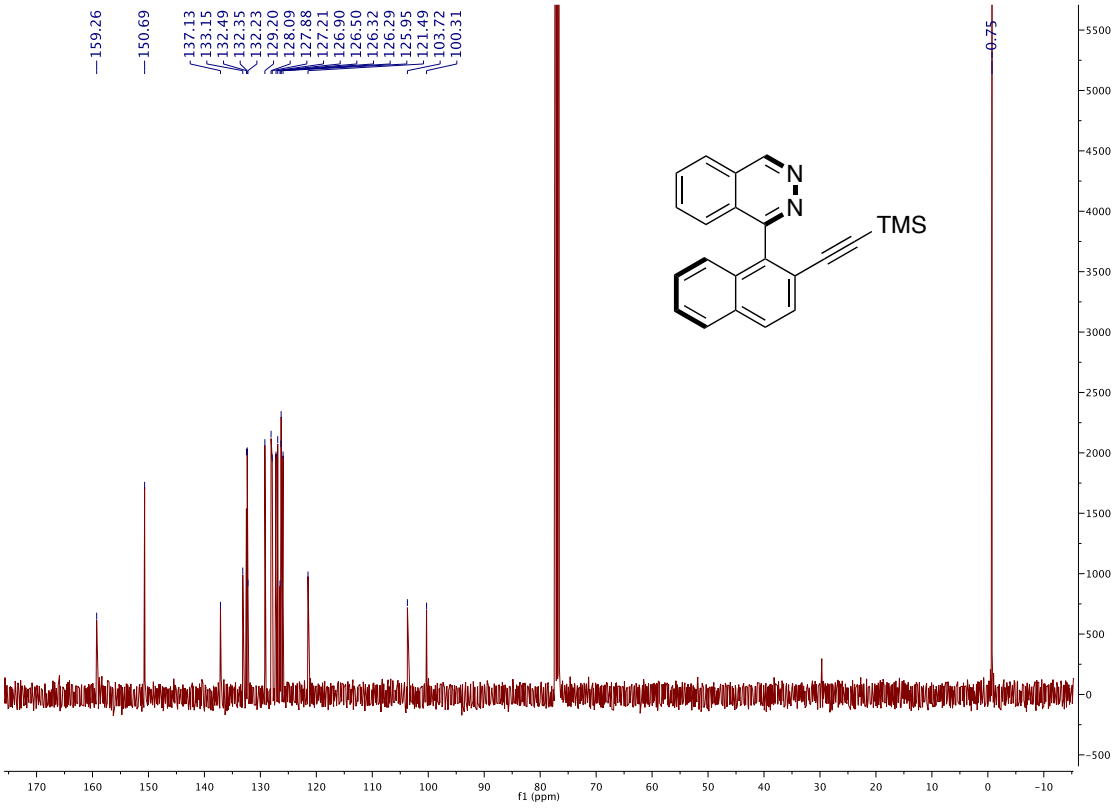
^{13}C NMR (100 MHz, $CDCl_3$) of **3Cn**



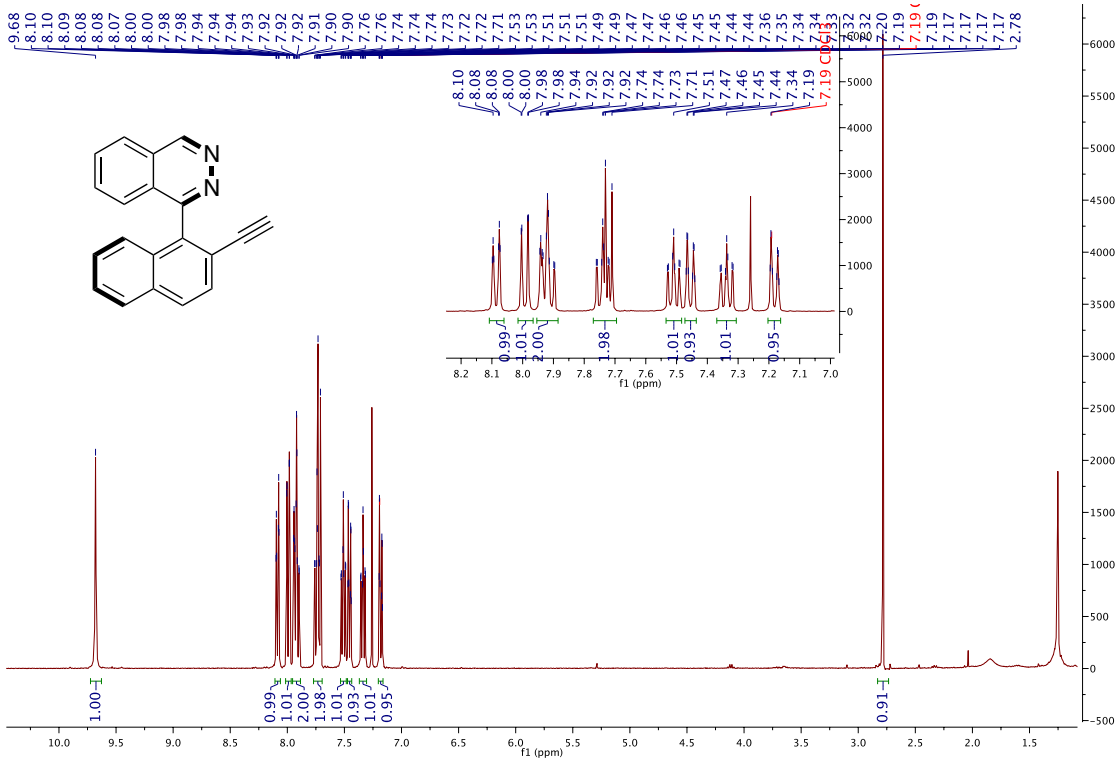
^{1}H NMR (400 MHz, $CDCl_3$) of **3Cq**



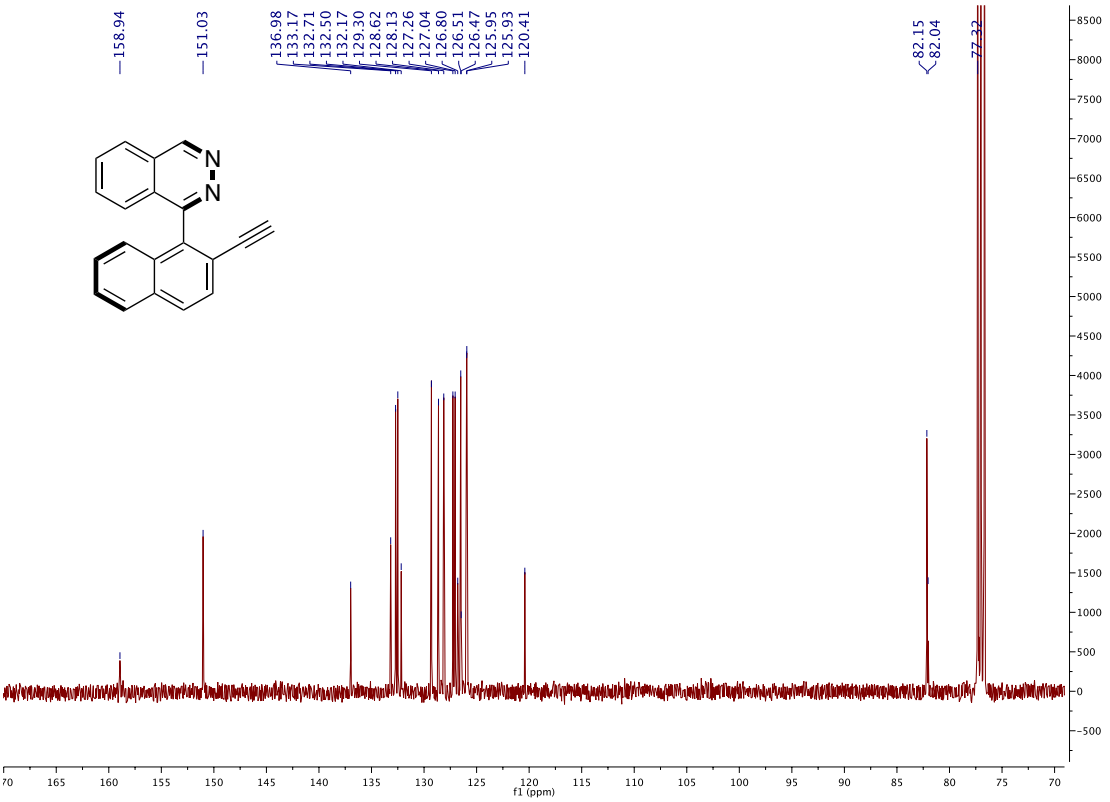
^{13}C NMR (100 MHz, $CDCl_3$) of **3Cq**



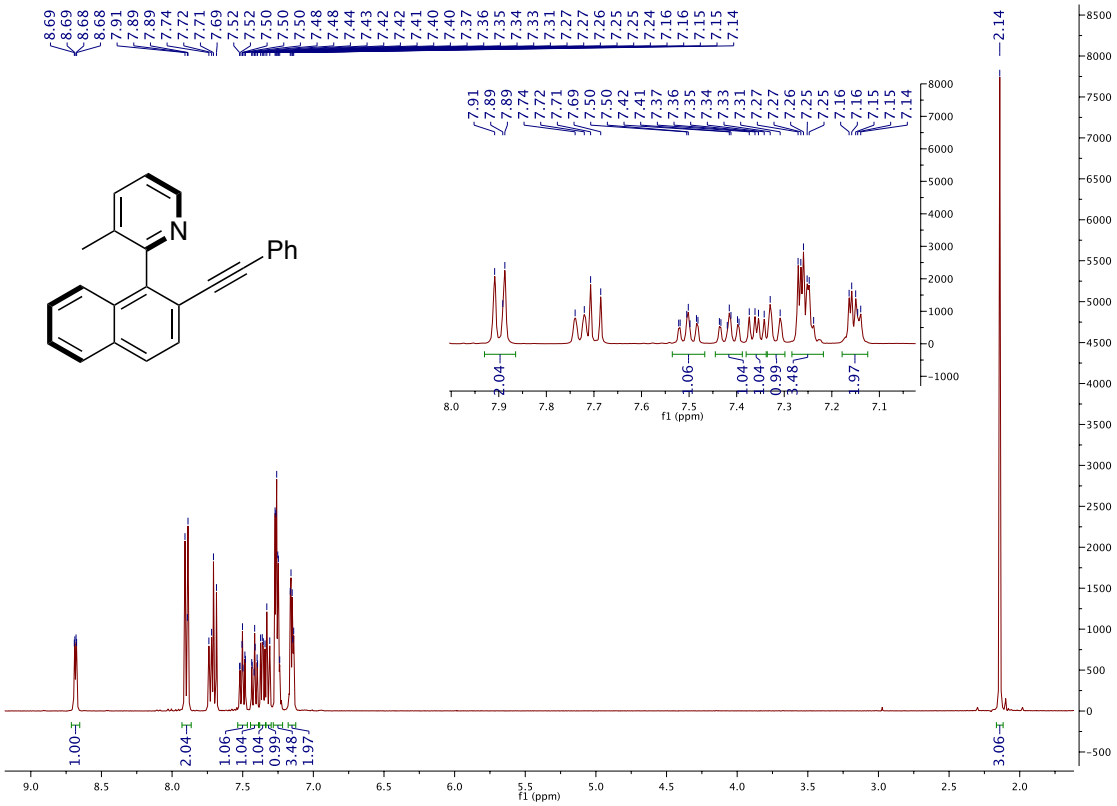
^{1}H NMR (400 MHz, $CDCl_3$) of **4C**



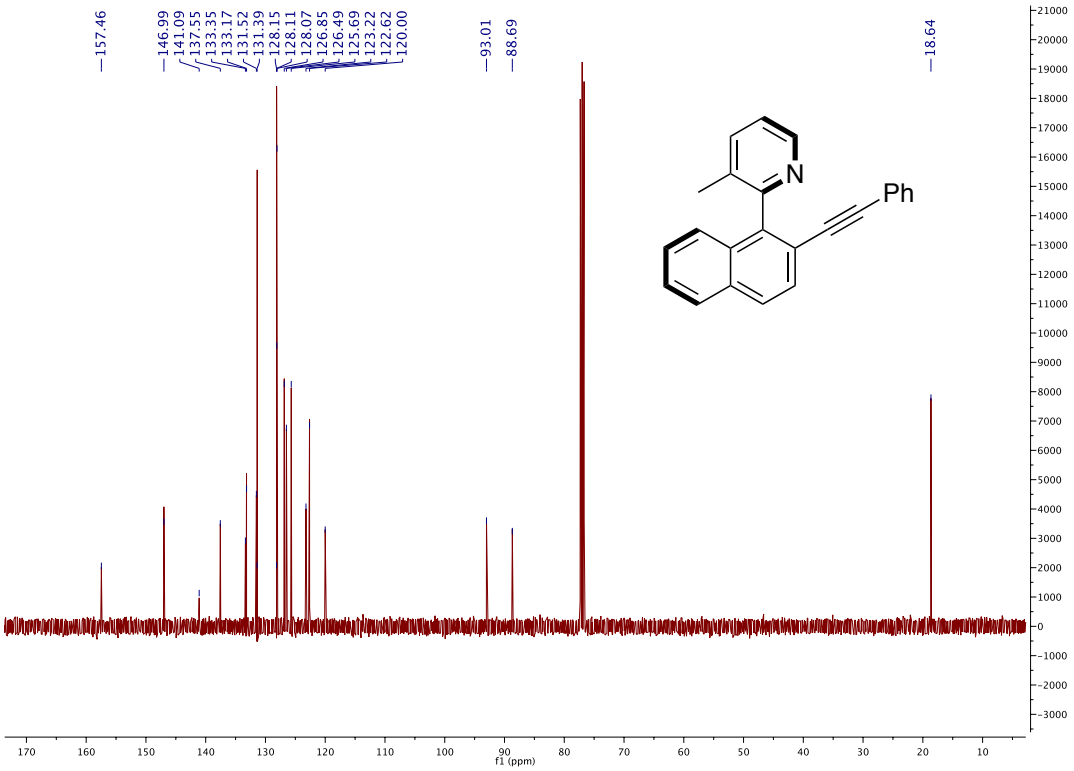
^{13}C NMR (100 MHz, $CDCl_3$) of **4C**



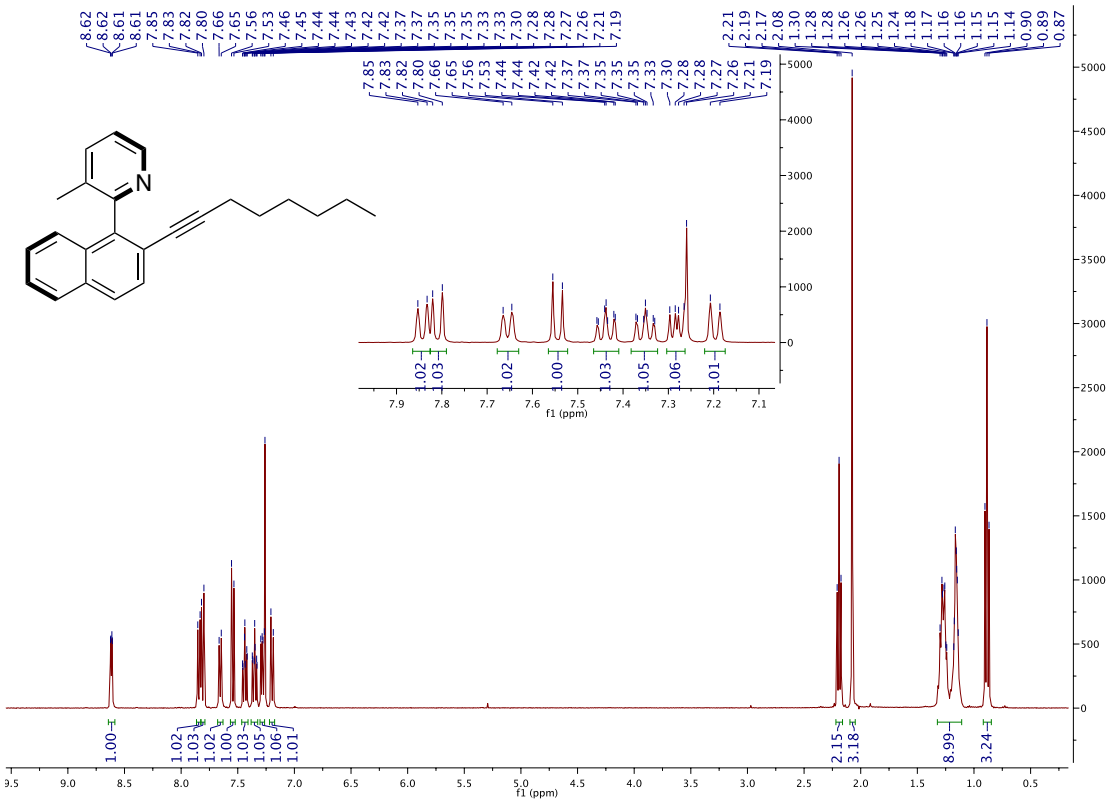
^{1}H NMR (400 MHz, $CDCl_3$) of **3Da**



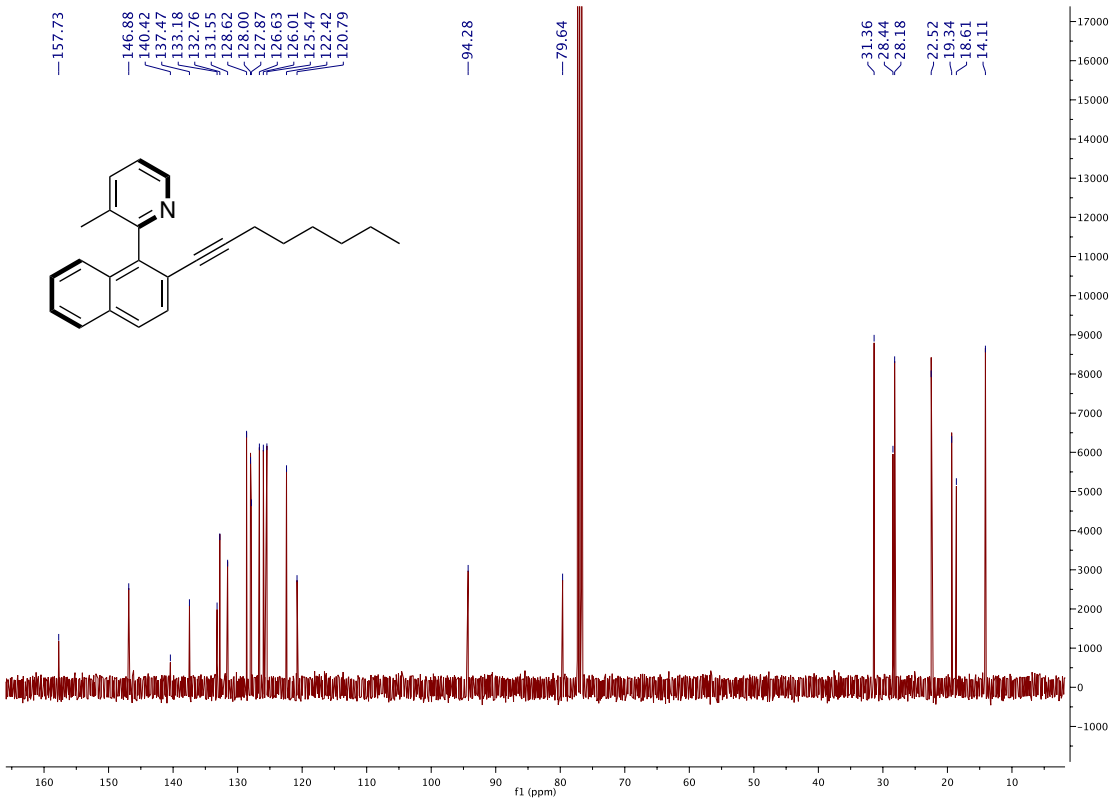
^{13}C NMR (100 MHz, $CDCl_3$) of **3Da**



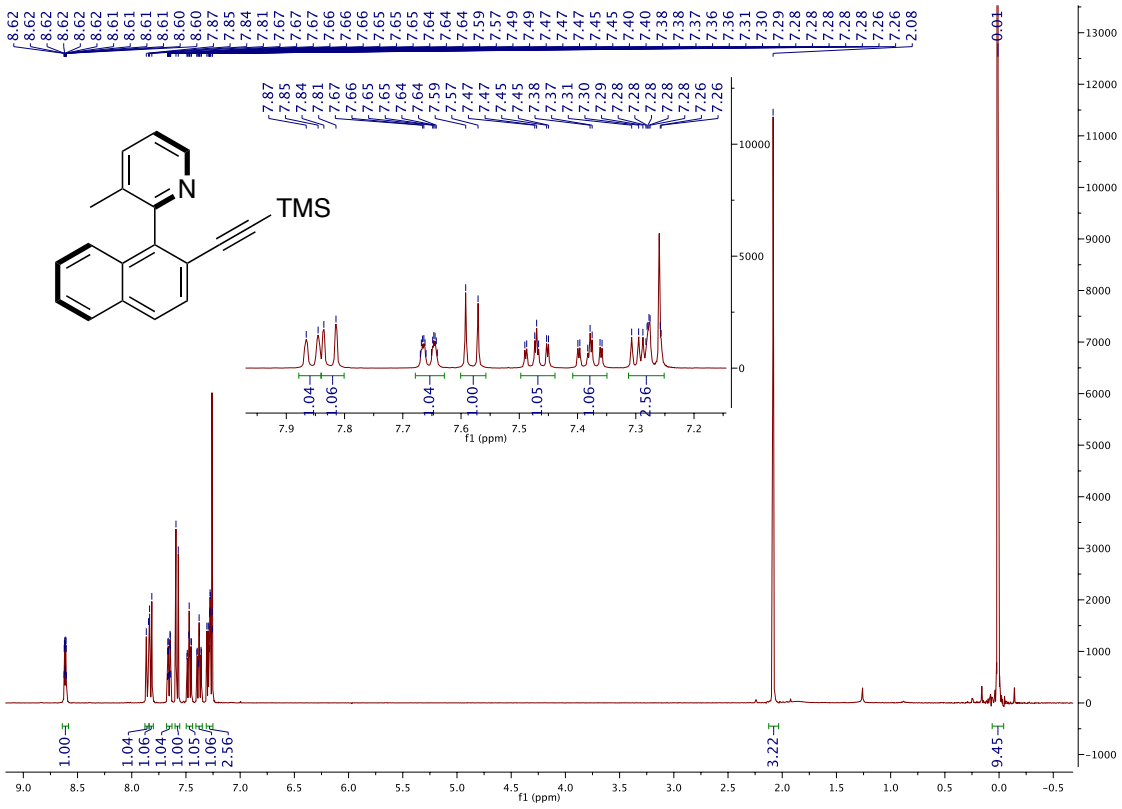
^{1}H NMR (400 MHz, $CDCl_3$) of **3Dn**



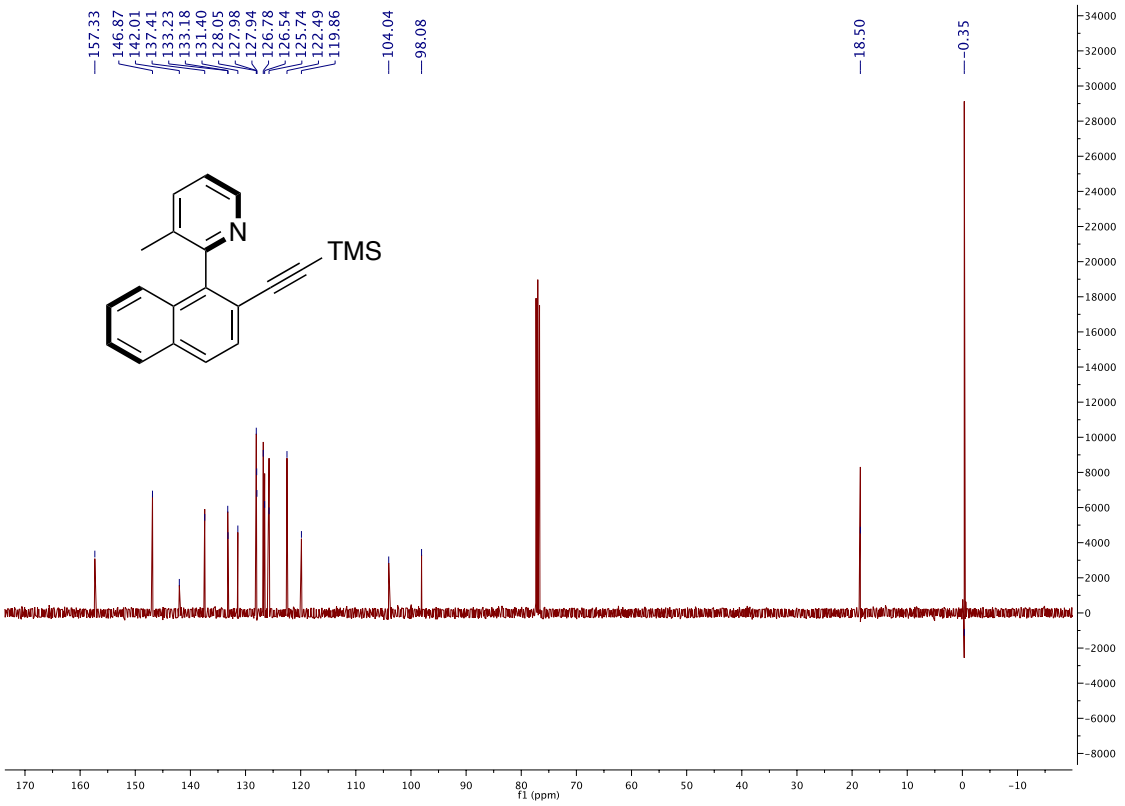
^{13}C NMR (100 MHz, $CDCl_3$) of **3Dn**



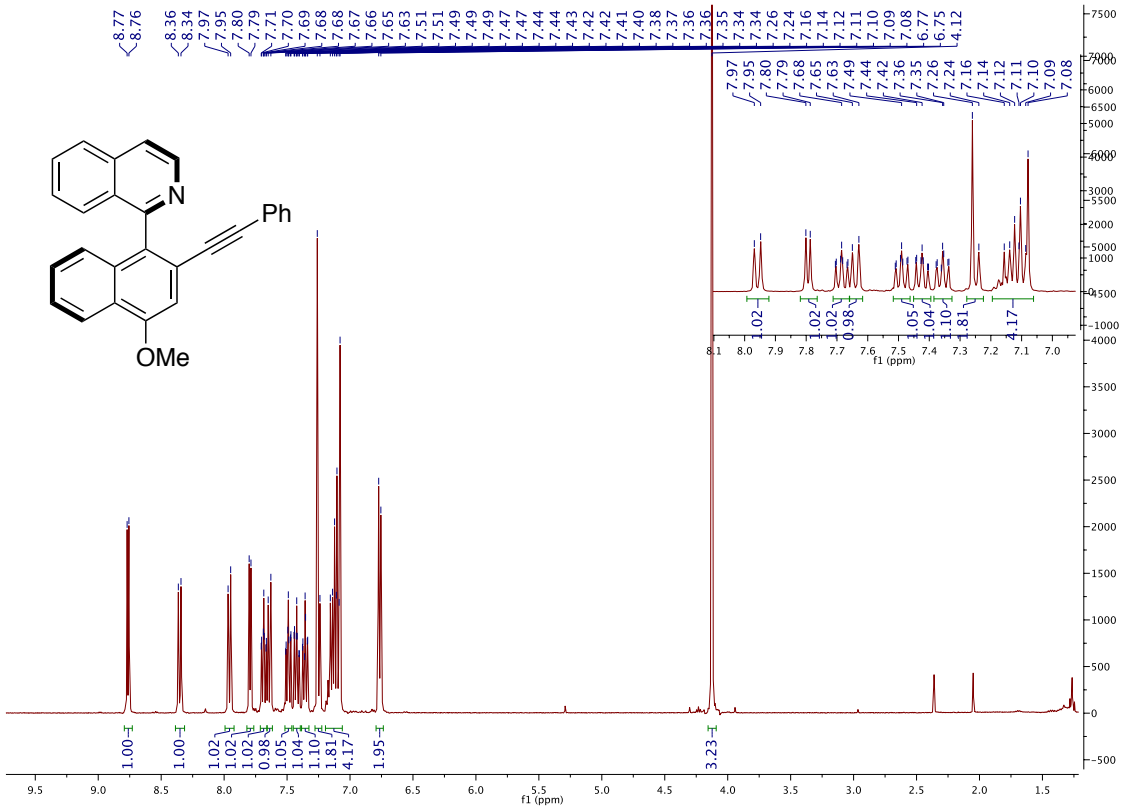
^{1}H NMR (400 MHz, $CDCl_3$) of **3Dq**



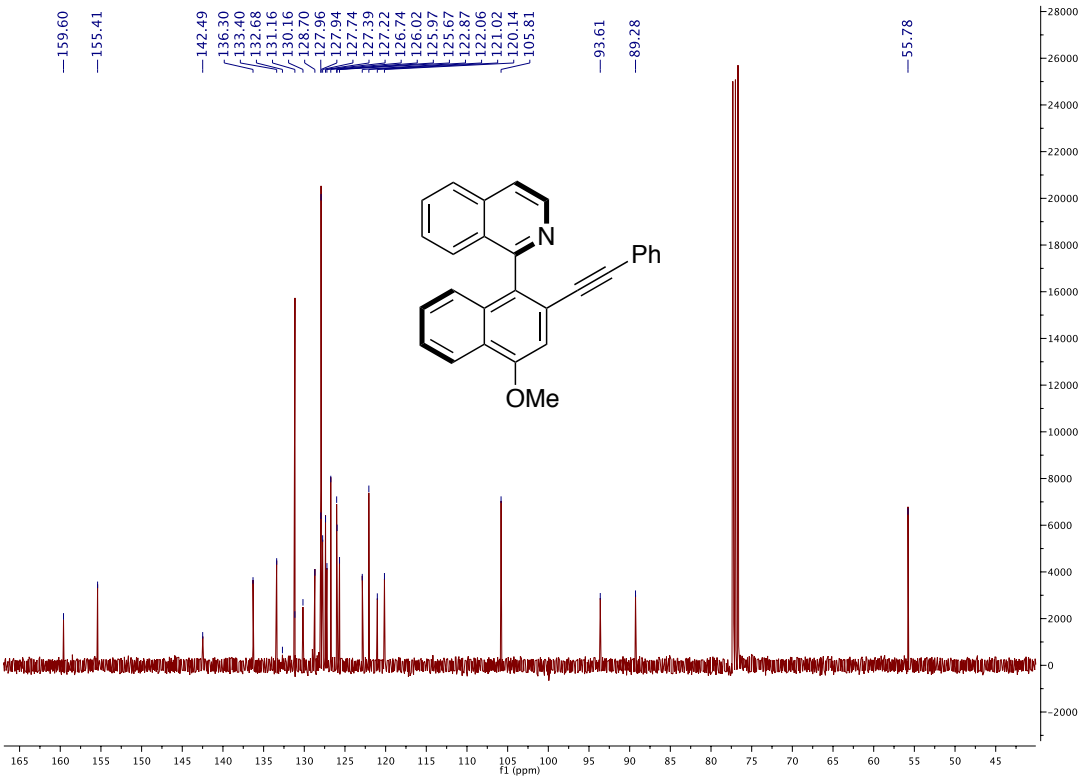
^{13}C NMR (100 MHz, $CDCl_3$) of **3Dq**



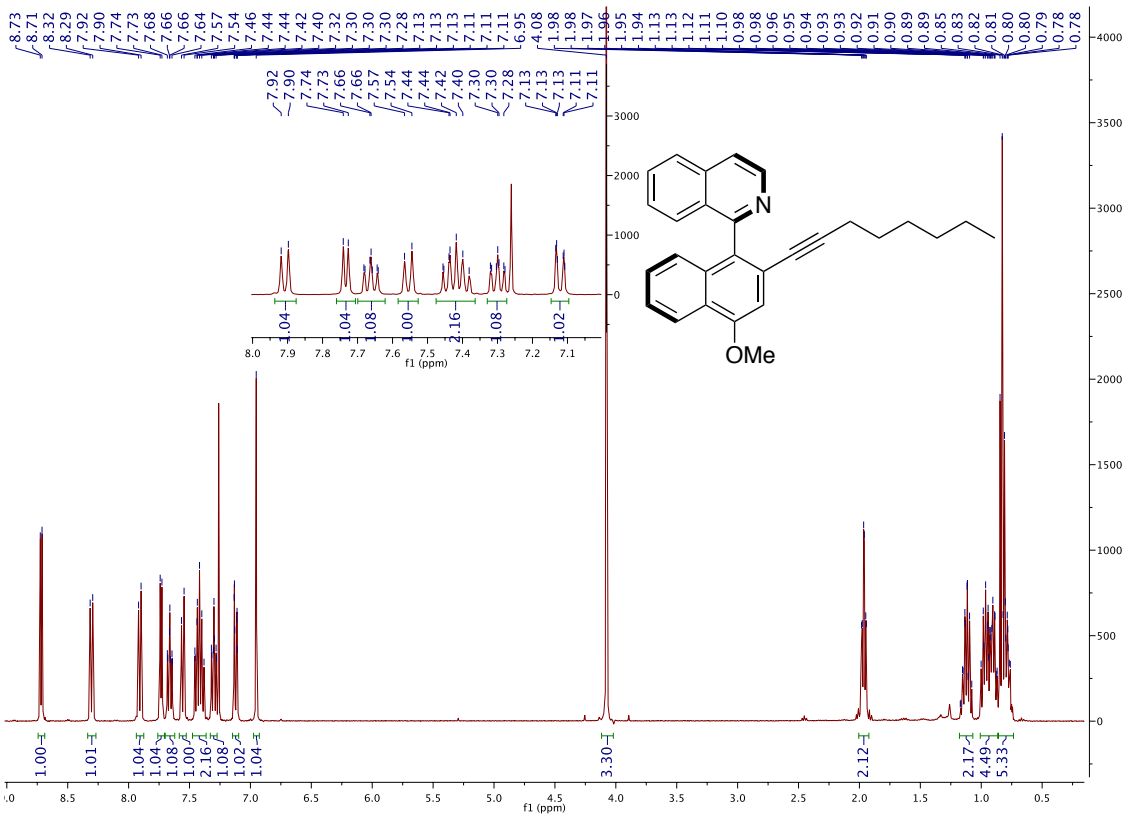
^{1}H NMR (400 MHz, $CDCl_3$) of **3Ea**



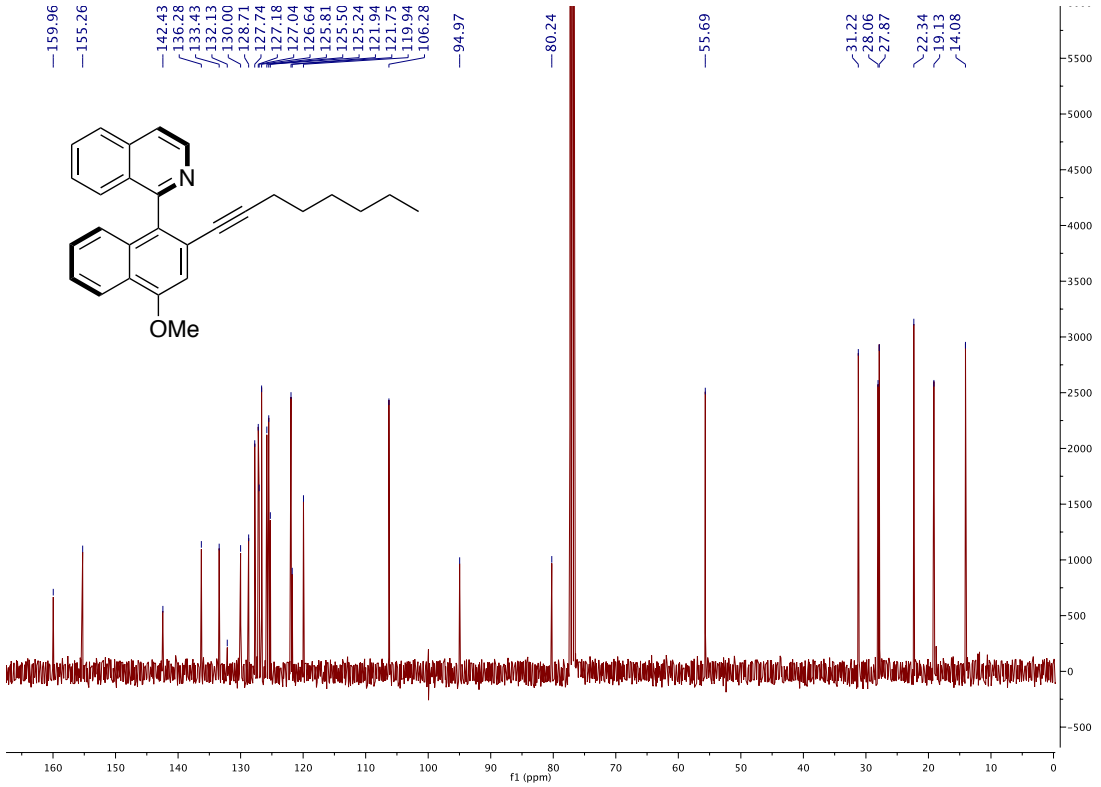
^{13}C NMR (100 MHz, $CDCl_3$) of **3Ea**



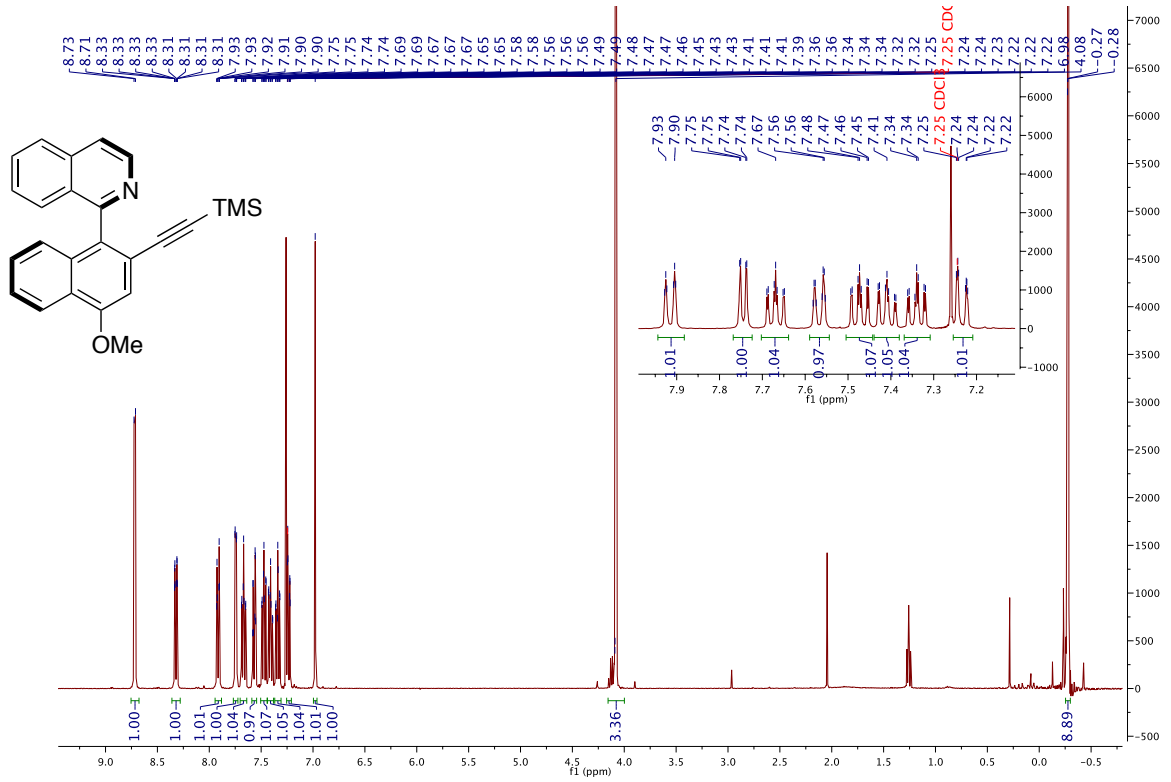
^{1}H NMR (400 MHz, $CDCl_3$) of **3En**



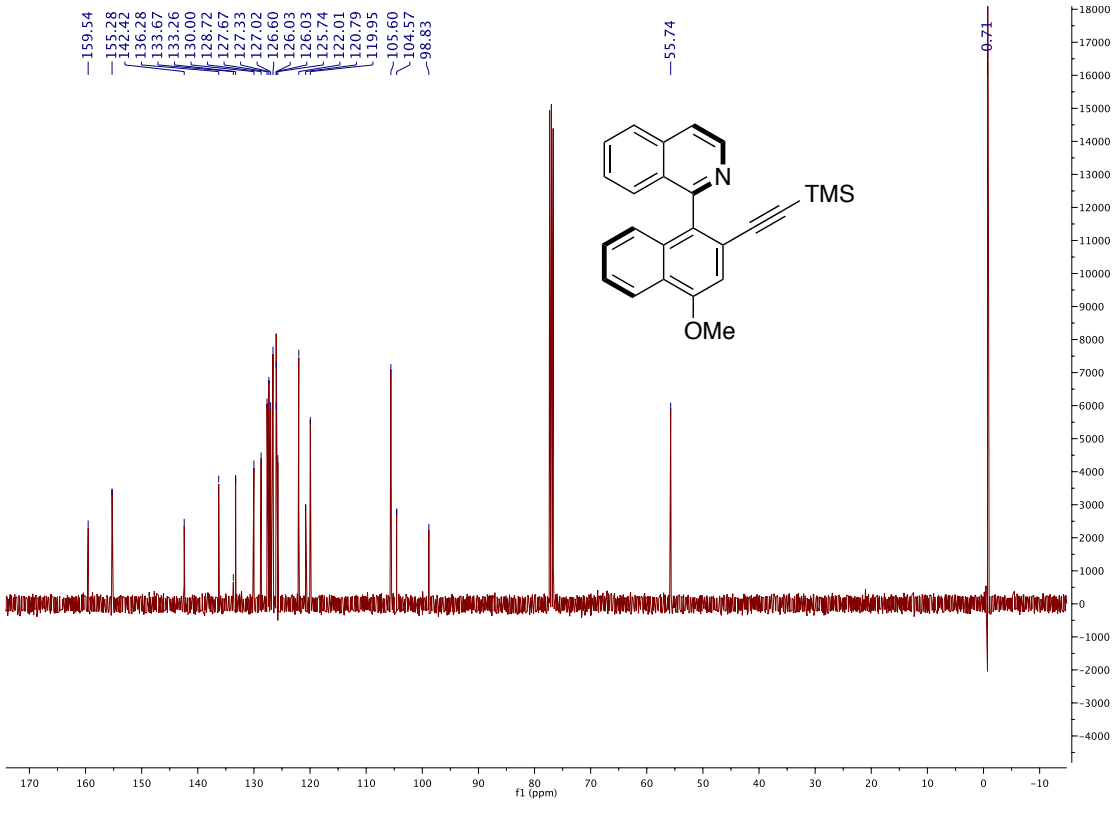
^{13}C NMR (100 MHz, $CDCl_3$) of **3En**



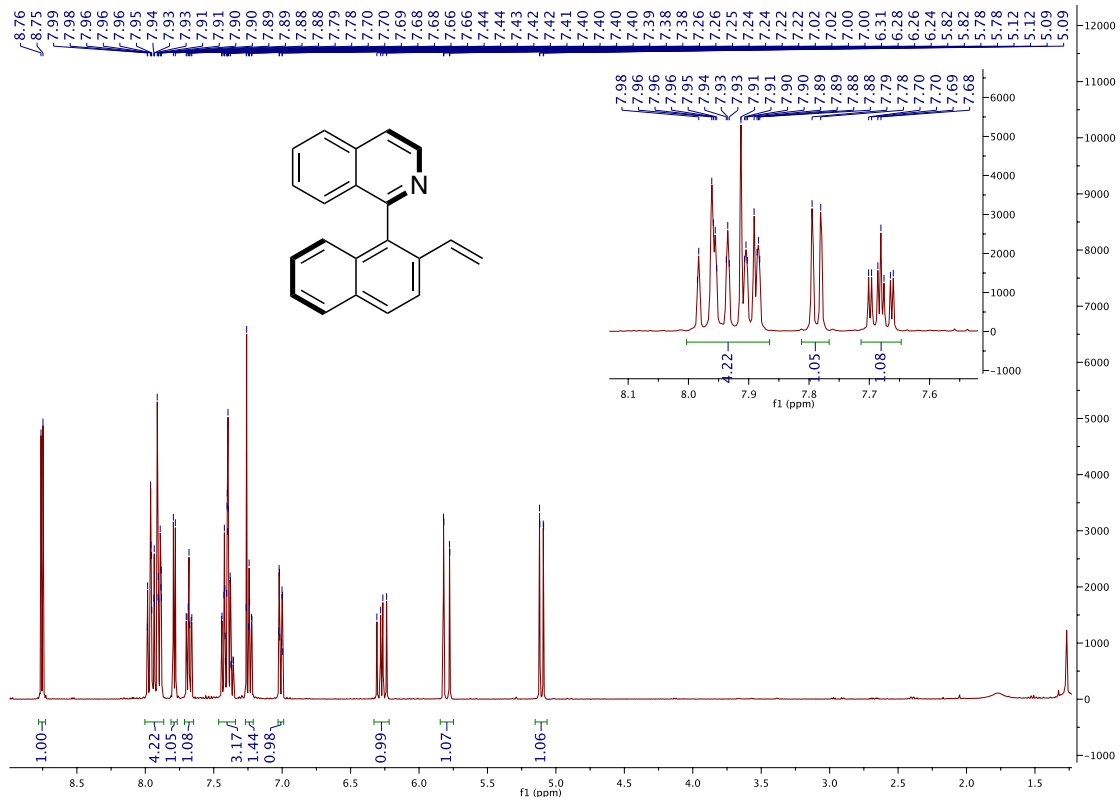
^{1}H NMR (400 MHz, $CDCl_3$) of **3Eq**



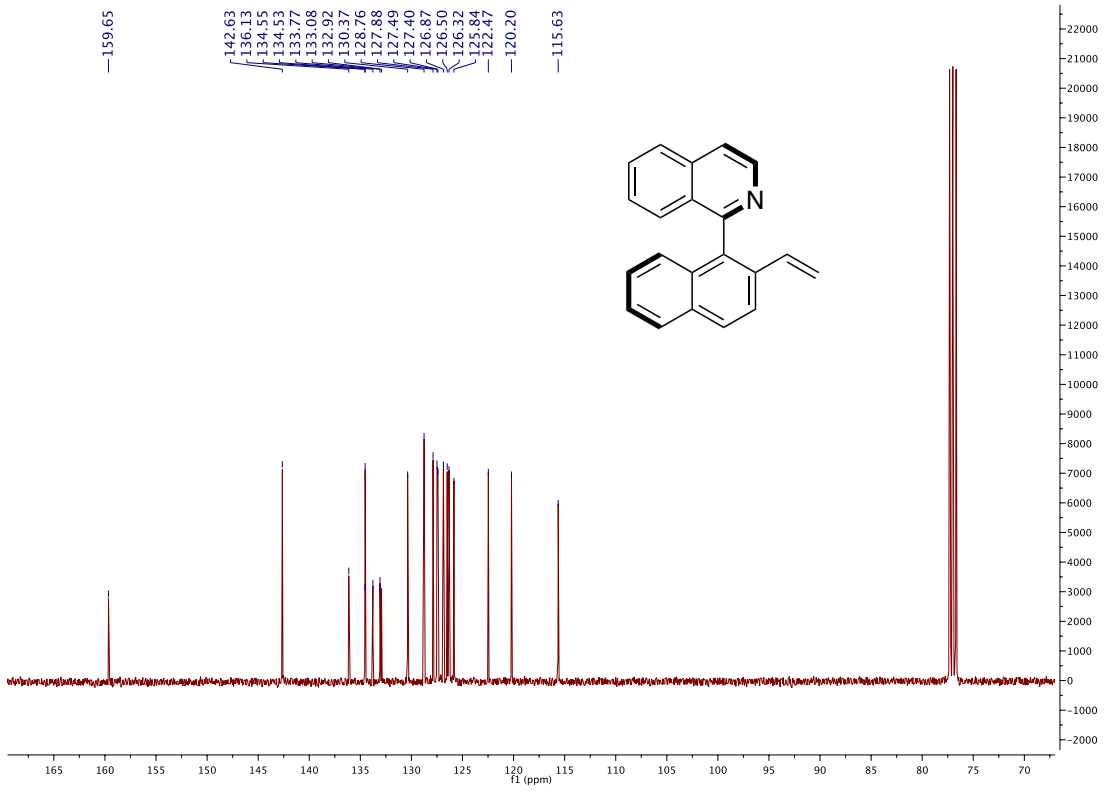
^{13}C NMR (100 MHz, $CDCl_3$) of **3Eq**



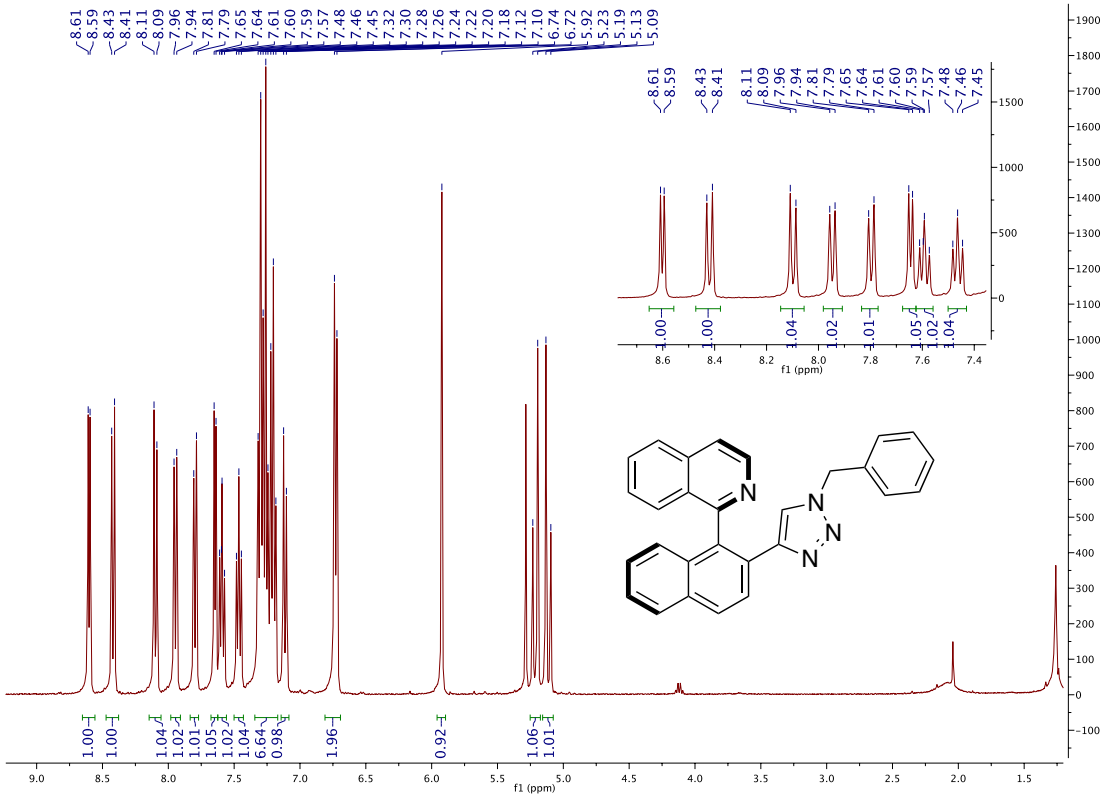
^{1}H NMR (400 MHz, $CDCl_3$) of **5**



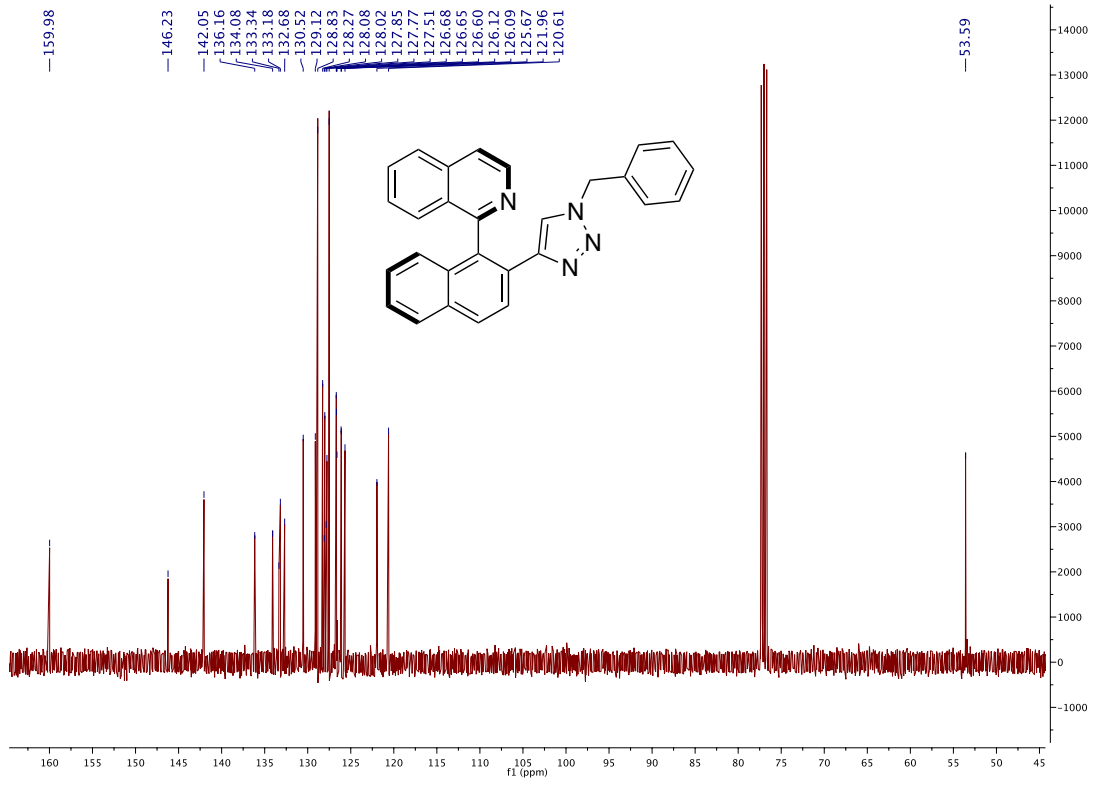
^{13}C NMR (100 MHz, $CDCl_3$) of **5**



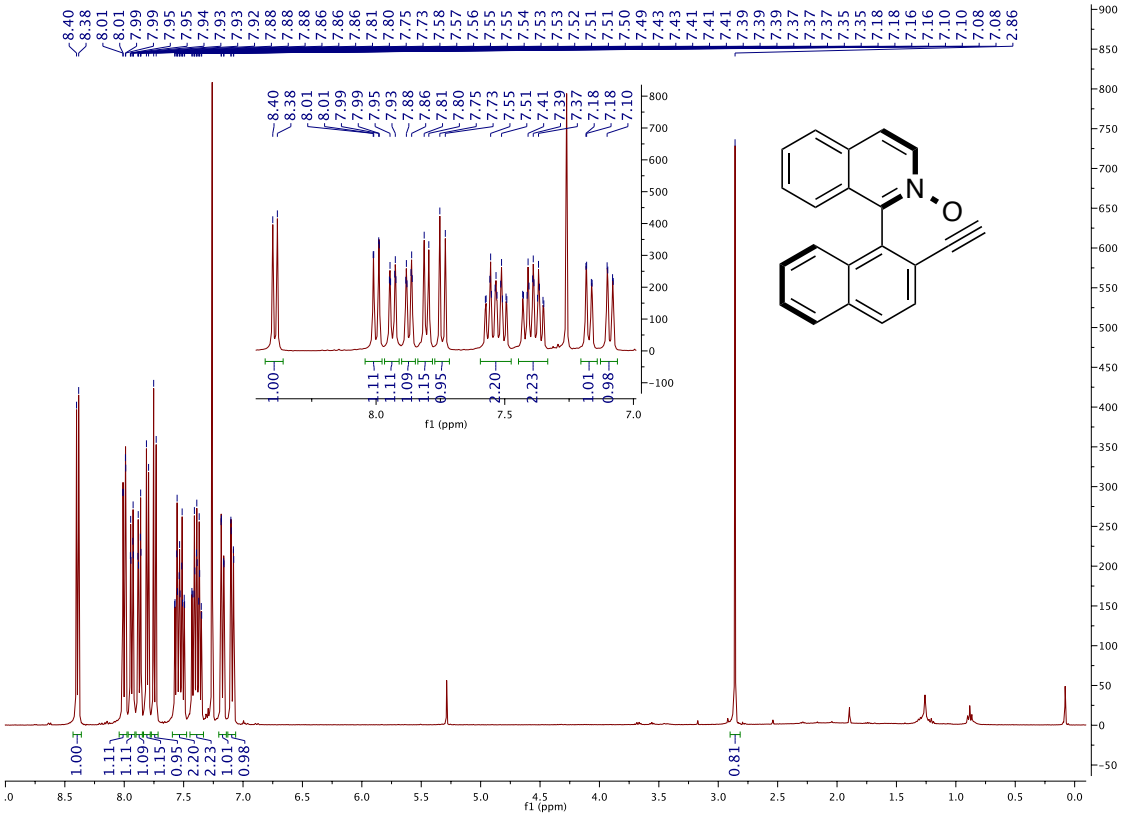
^{1}H NMR (400 MHz, $CDCl_3$) of **6**



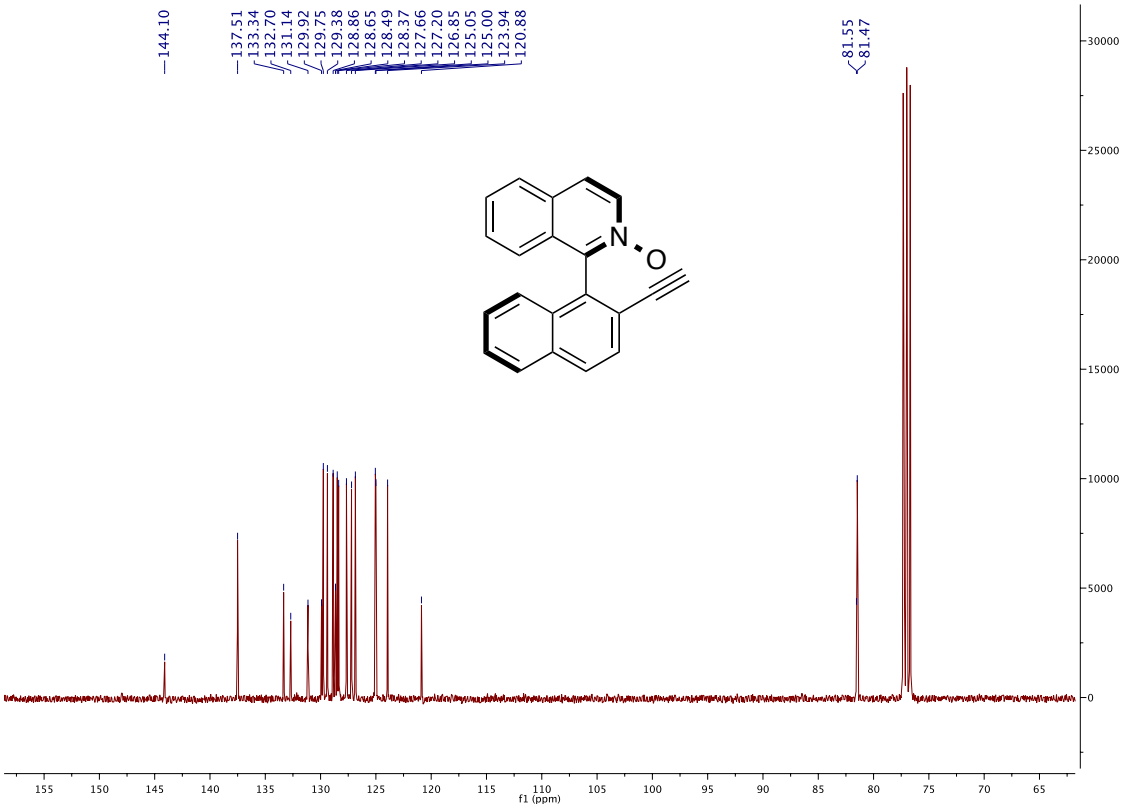
^{13}C NMR (100 MHz, $CDCl_3$) of **6**



^{1}H NMR (400 MHz, $CDCl_3$) of **7**

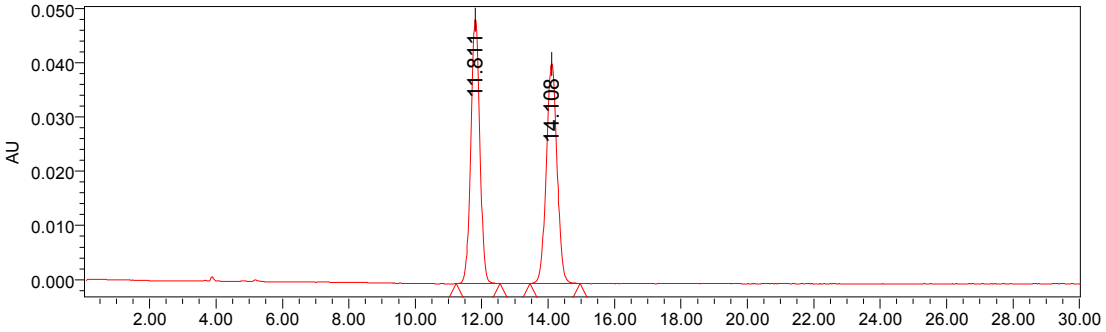


^{13}C NMR (100 MHz, $CDCl_3$) of **7**



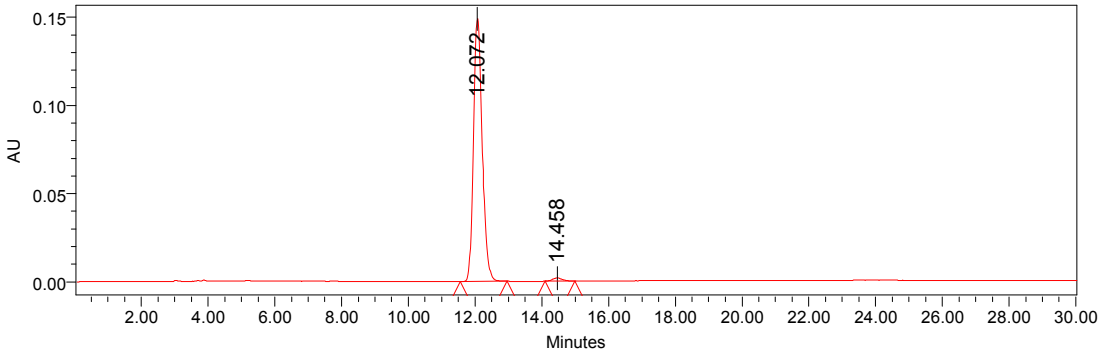
HPLC traces

Figure S1. Alkyne 3Aa racemic sample: AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min



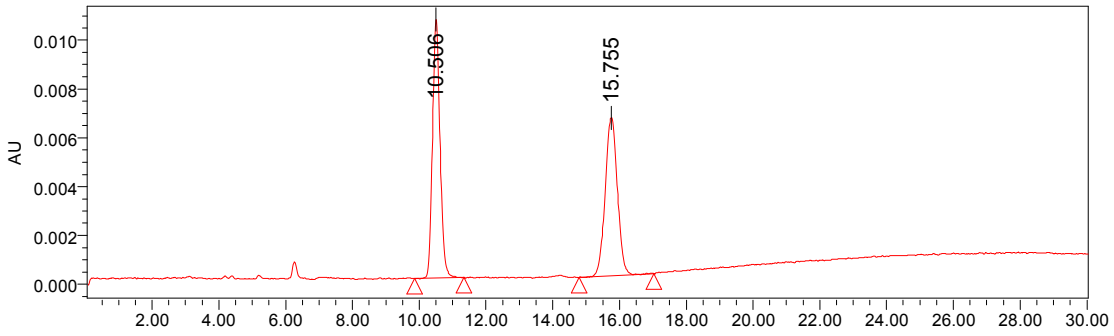
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 276.0 nm	11.811	906877	49.98	48698
2	PDA 276.0 nm	14.108	907703	50.02	40510

Figure S2. Alkyne 3Aa enantioriched sample: 97% ee.



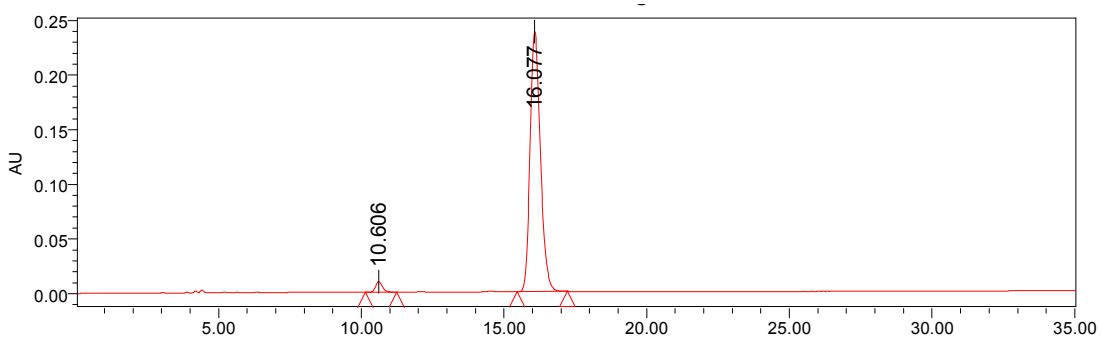
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 276.0 nm	12.072	2702149	98.64	148987
2	PDA 276.0 nm	14.458	37263	1.36	1792

Figure S3. Alkyne 3Ab racemic sample: AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min



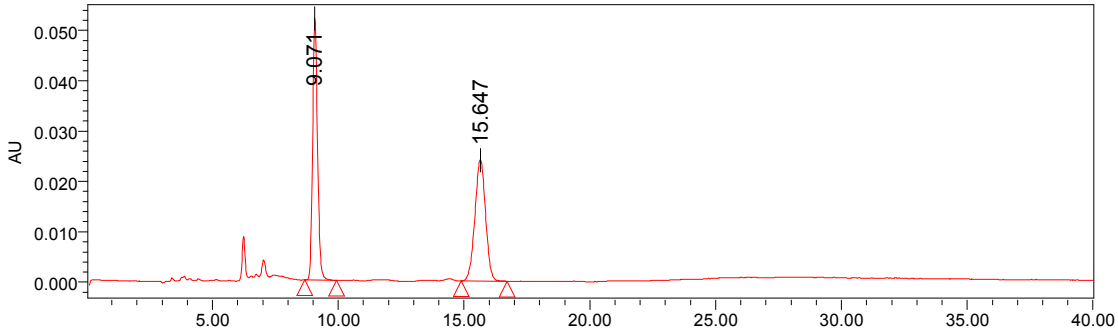
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 347.0 nm	10.506	165944	50.18	10615
2	PDA 347.0 nm	15.755	164779	49.82	6479

Figure S4. Alkyne 3Ab enantioriched sample: 95% ee.



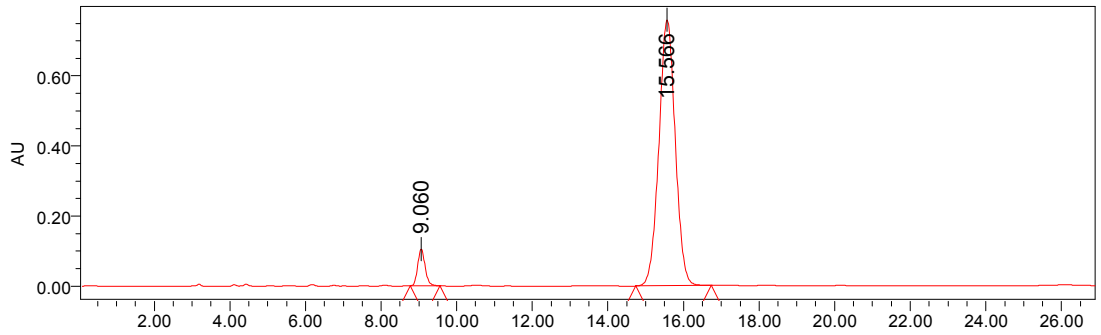
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 283.0 nm	10.606	160187	2.62	9773
2	PDA 283.0 nm	16.077	5954320	97.38	238432

Figure S5. Alkyne 3Ac racemic sample: AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min



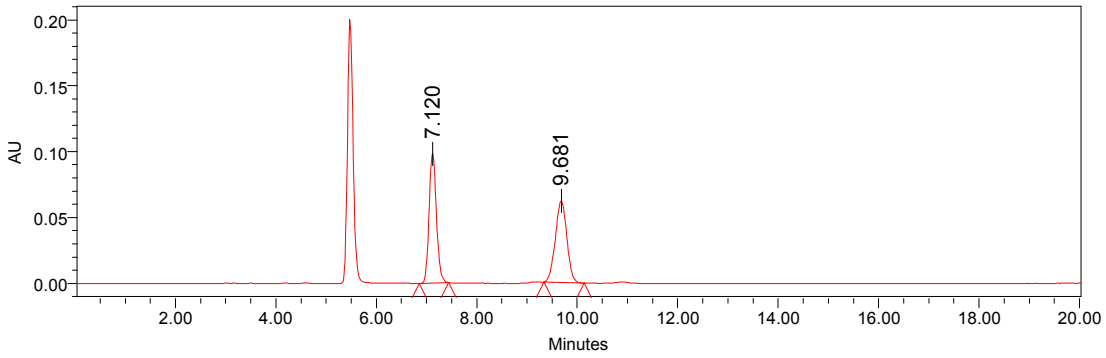
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 285.8 nm	9.071	709669	49.96	52037
2	PDA 285.8 nm	15.647	710786	50.04	24057

Figure S6. Alkyne 3Ac enantioriched sample: 88% ee.



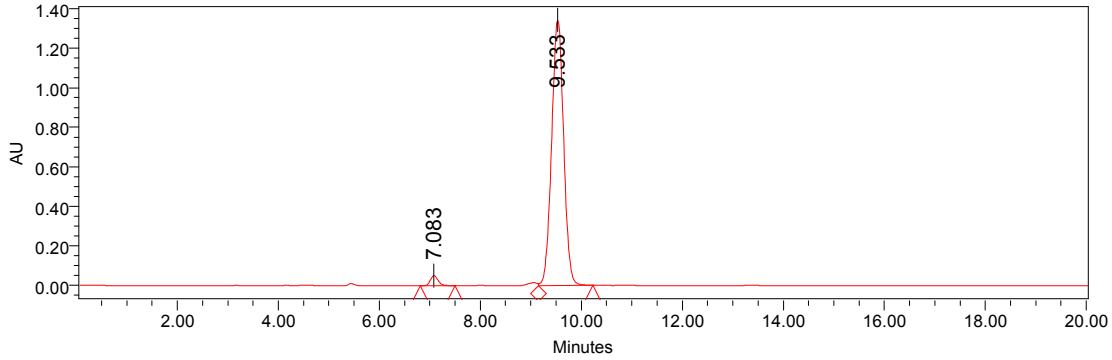
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 217.0 nm	9.060	1412494	5.83	104619
2	PDA 217.0 nm	15.566	22798629	94.17	759164

Figure S7. Alkyne 3Ad racemic sample: AD-H column, 80:20 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min



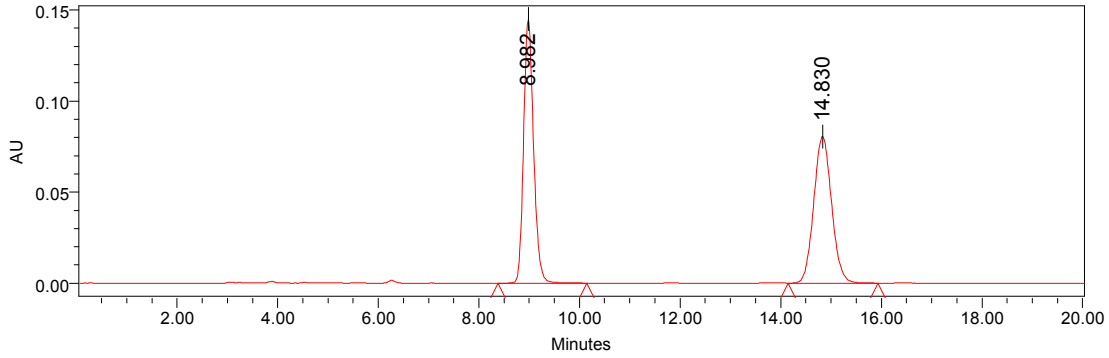
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 266.6 nm	7.120	999686	50.33	98606
2	PDA 266.6 nm	9.681	986740	49.67	62082

Figure S8. Alkyne 3Ad enantioriched sample: 95% ee.



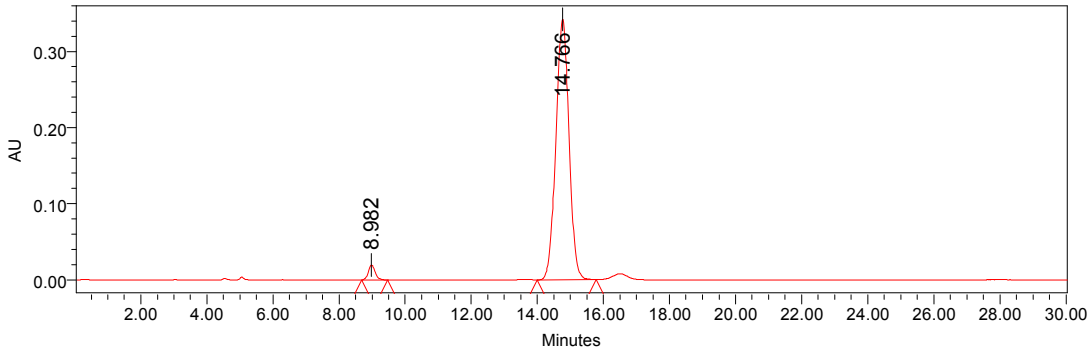
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 218.1 nm	7.083	532569	2.36	51143
2	PDA 218.1 nm	9.533	22036524	97.64	1343559

Figure S9. Alkyne 3Ae racemic sample: AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min



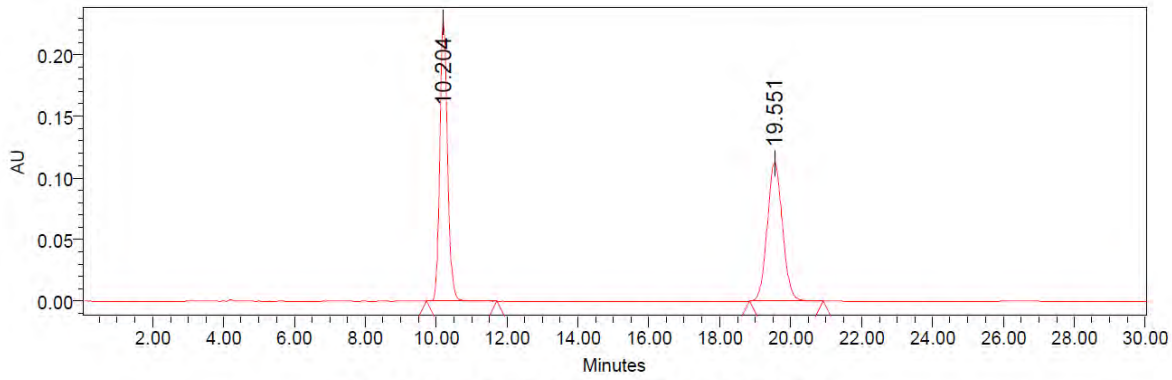
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 279.0 nm	8.982	1986069	50.10	144938
2	PDA 279.0 nm	14.830	1977831	49.90	80529

Figure S10. Alkyne 3Ae enantioriched sample: 94% ee.



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 279.0 nm	8.982	274783	2.83	19389
2	PDA 279.0 nm	14.766	9432618	97.17	342624

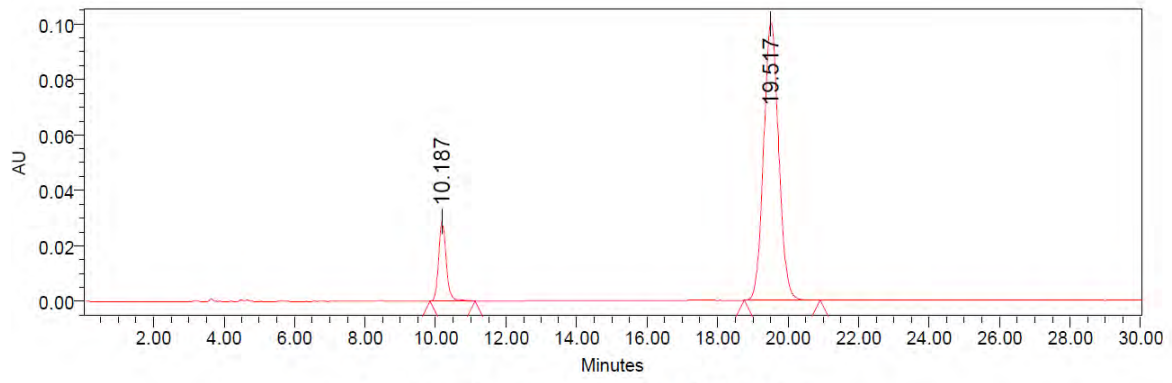
Figure S11. Alkyne 3Af racemic sample: AD-H column, 80:20 *n*-Hex/*i*-PrOH, 30 °C, 1mL/min.



Processed Channel: PDA 283.0 nm

	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 283.0 nm	10.204	3442094	50.66	227246
2	PDA 283.0 nm	19.551	3351942	49.34	112184

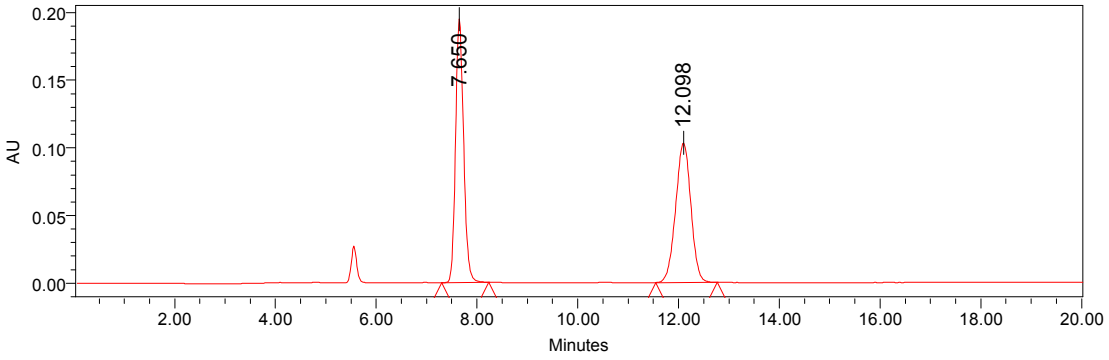
Figure S12. Alkyne 3Af enantioriched sample: 75% ee.



Processed Channel: PDA 283.0 nm

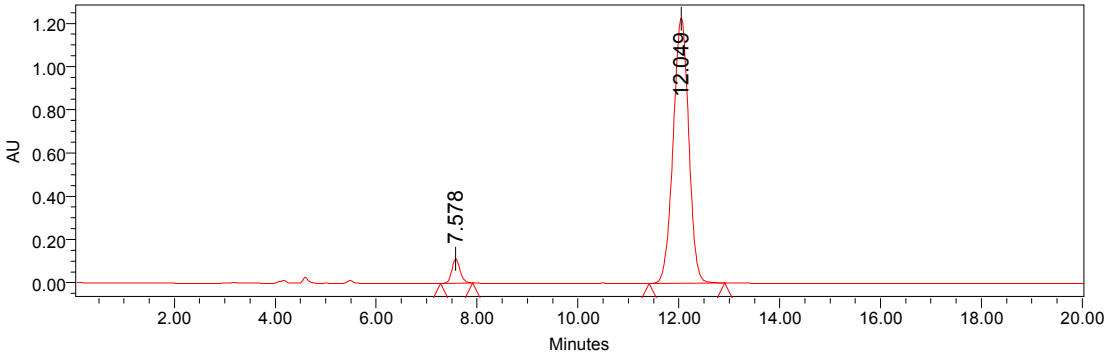
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 283.0 nm	10.187	428951	12.63	28590
2	PDA 283.0 nm	19.517	2968621	87.37	99895

Figure S13. Alkyne 3Ag racemic sample: AD-H column, 80:20 *n*-Hex/*i*-PrOH, 30 °C, 1mL/min.



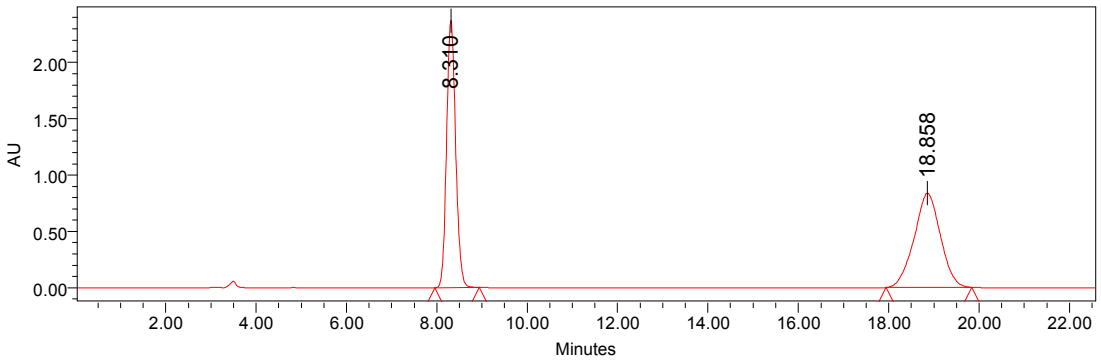
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 327.3 nm	7.650	2156984	49.98	194853
2	PDA 327.3 nm	12.098	2159072	50.02	103195

Figure S14. Alkyne 3Ag enantioriched sample: 91% ee.



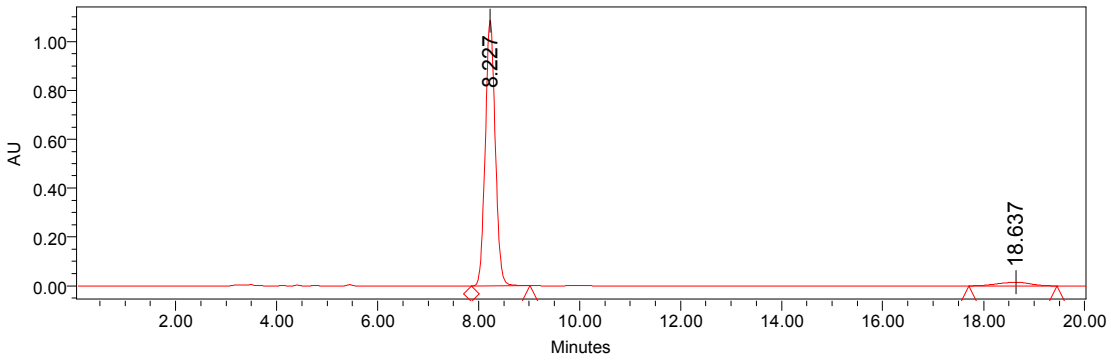
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 216.0 nm	7.578	1259550	4.58	112724
2	PDA 216.0 nm	12.049	26214642	95.42	1227137

Figure S15. Alkyne 3Ah racemic sample: AD-H column, 80:20 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min



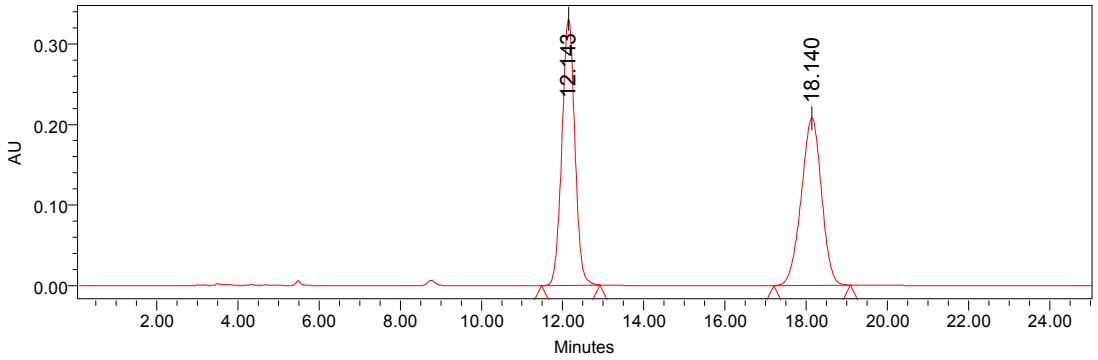
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 216.0 nm	8.310	33248136	49.61	2374737
2	PDA 216.0 nm	18.858	33773991	50.39	836482

Figure S16. Alkyne 3Ah enantioriched sample: 92% ee.



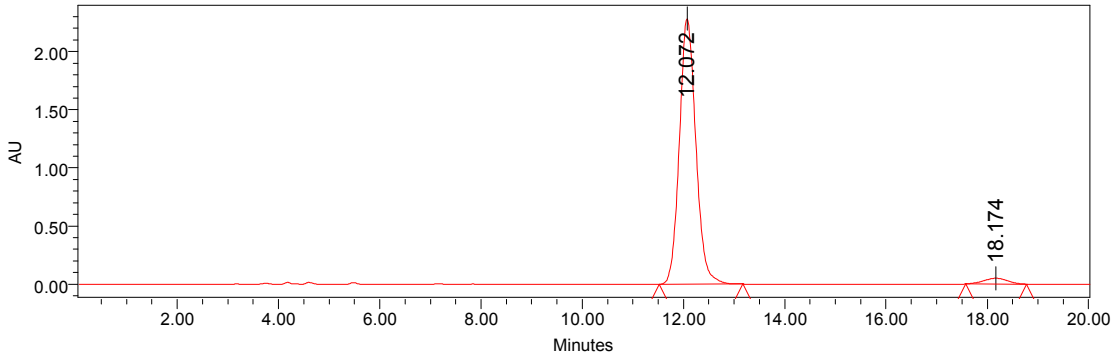
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 217.0 nm	8.227	14884286	95.89	1088553
2	PDA 217.0 nm	18.637	637476	4.11	14732

Figure S17. Alkyne 3Ai racemic sample: AD-H column, 80:20 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min



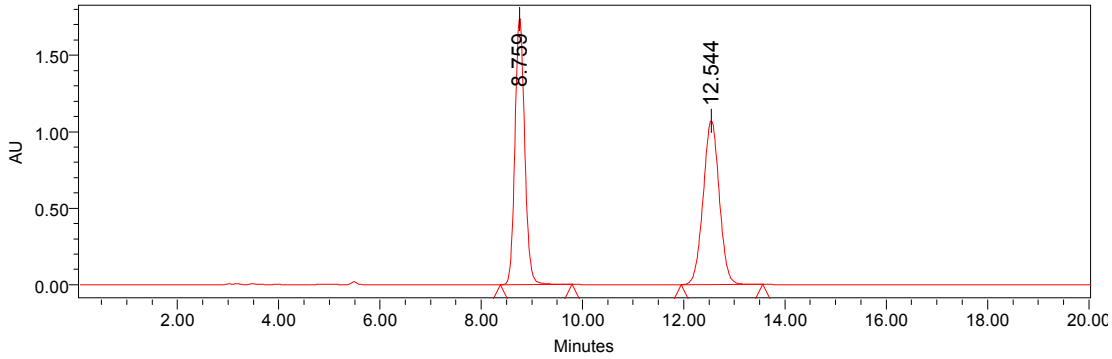
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 234.2 nm	12.143	7290186	50.33	331462
2	PDA 234.2 nm	18.140	7195899	49.67	207897

Figure S18. Alkyne 3Ai enantioriched sample: 94% ee.



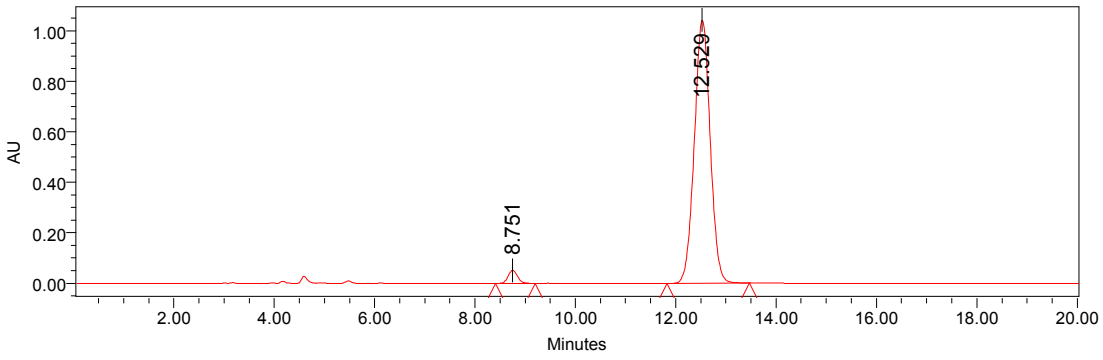
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 219.0 nm	12.072	51501913	96.98	2282808
2	PDA 219.0 nm	18.174	1601344	3.02	49056

Figure S19. Alkyne 3Aj racemic sample: AD-H column, 80:20 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min



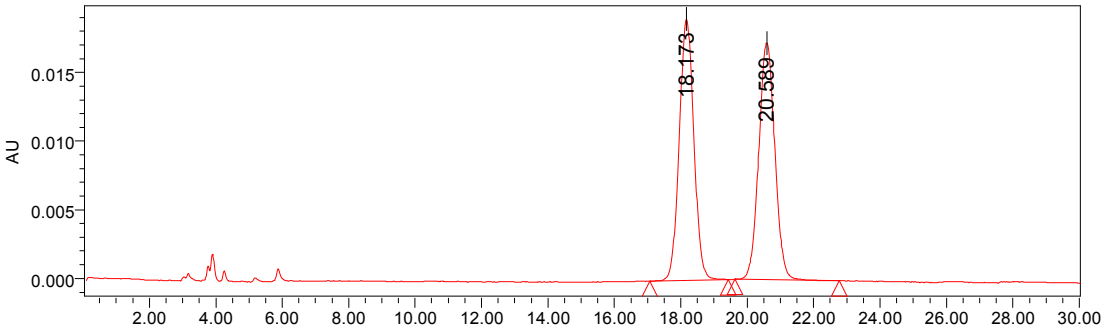
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 209.7 nm	8.759	23207477	49.58	1740744
2	PDA 209.7 nm	12.544	23599870	50.42	1070478

Figure S20. Alkyne 3Aj enantioriched sample: 94% ee.



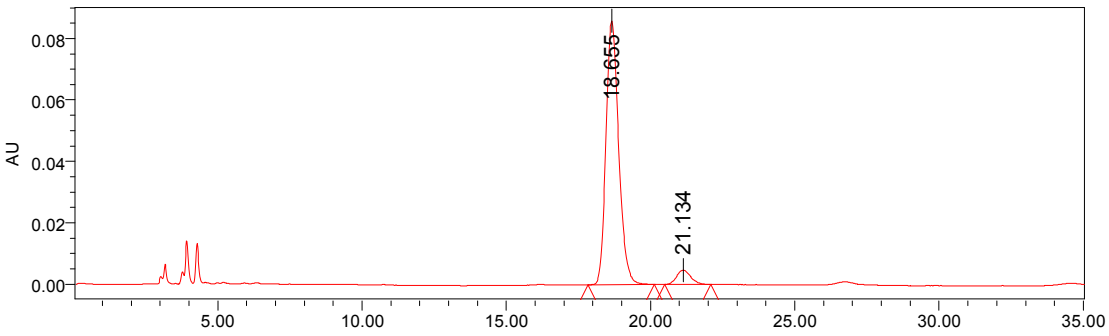
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 219.1 nm	8.751	673023	2.86	51754
2	PDA 219.1 nm	12.529	22825570	97.14	1042832

Figure S21. Alkyne 3Ak racemic sample: AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min



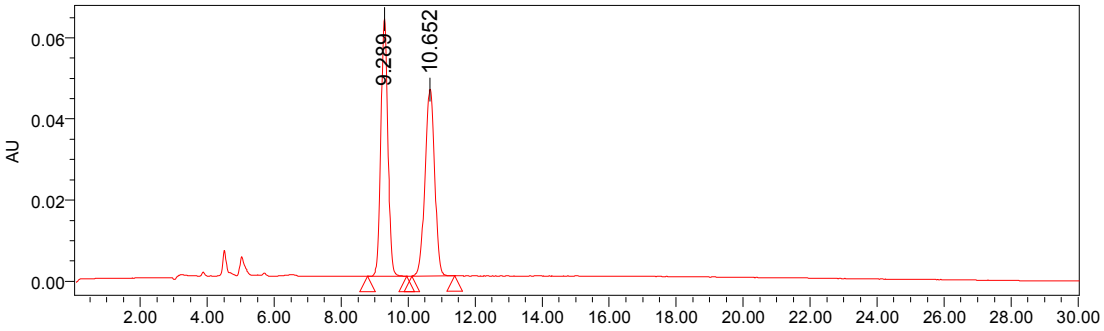
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 247.5 nm	18.173	579802	49.99	19027
2	PDA 247.5 nm	20.589	580104	50.01	17231

Figure S22. Alkyne 3Ak enantioriched sample: 89% ee.



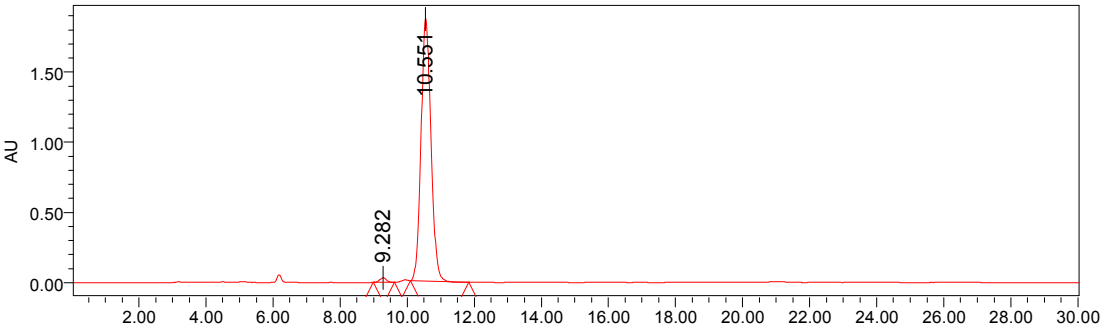
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 217.0 nm	18.655	2620882	94.38	85951
2	PDA 217.0 nm	21.134	155990	5.62	4651

Figure S23. Alkyne 3Al racemic sample: AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min



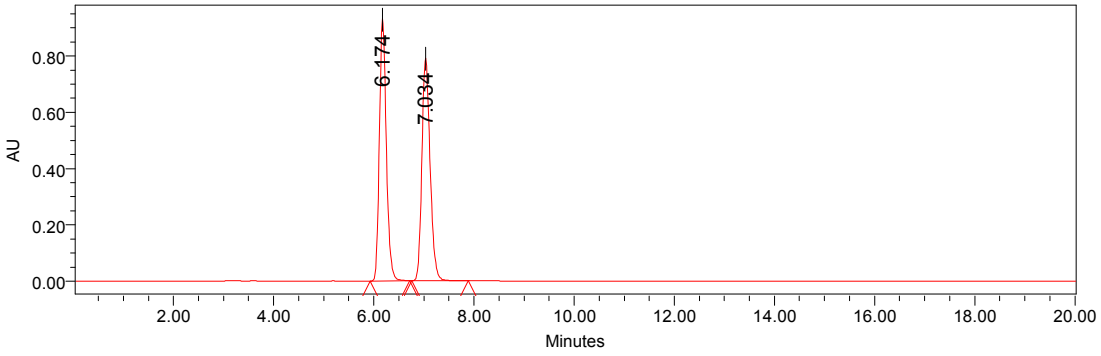
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 272.0 nm	9.289	923642	50.06	63485
2	PDA 272.0 nm	10.652	921435	49.94	46024

Figure S24. Alkyne 3Al enantioriched sample: 98% ee.



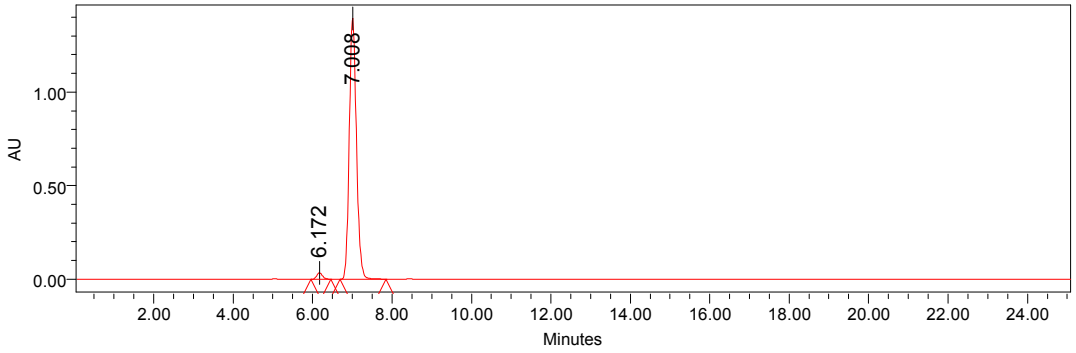
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 217.0 nm	9.282	468260	1.20	33476
2	PDA 217.0 nm	10.551	38451775	98.80	1872580

Figure S25. Alkyne 3Am racemic sample: AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min



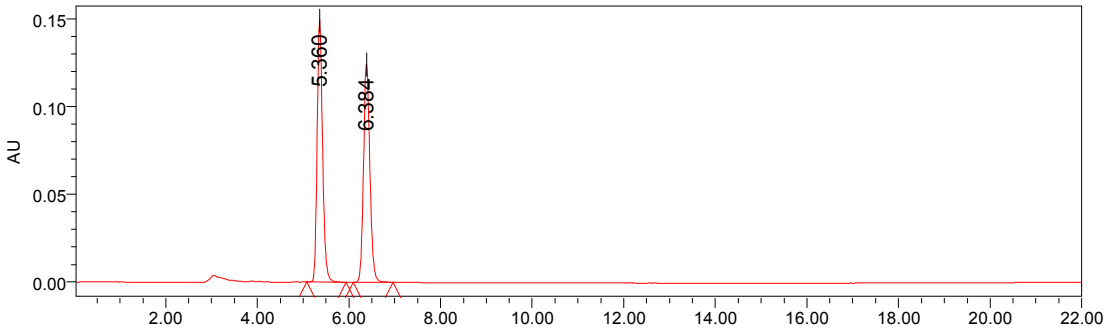
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 252.0 nm	6.174	9018972	49.94	933772
2	PDA 252.0 nm	7.034	9040391	50.06	790739

Figure S26. Alkyne 3Am enantioriched sample: 96% ee.



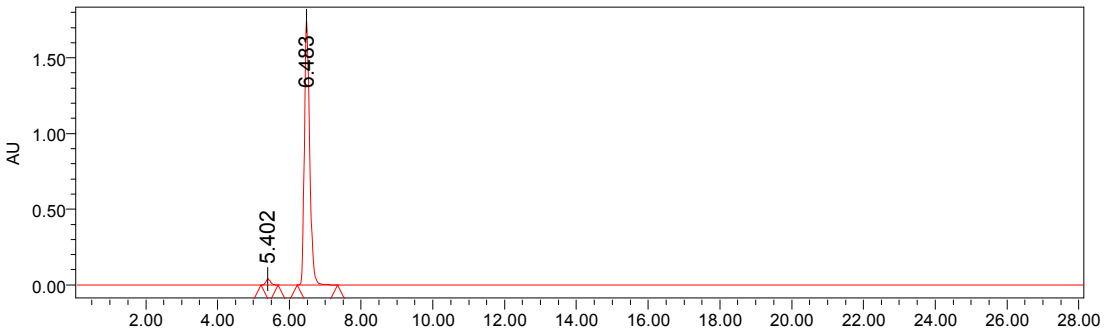
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 252.0 nm	6.172	344229	1.96	34707
2	PDA 252.0 nm	7.008	17262551	98.04	1396151

Figure S27. Alkyne 3An racemic sample: AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min



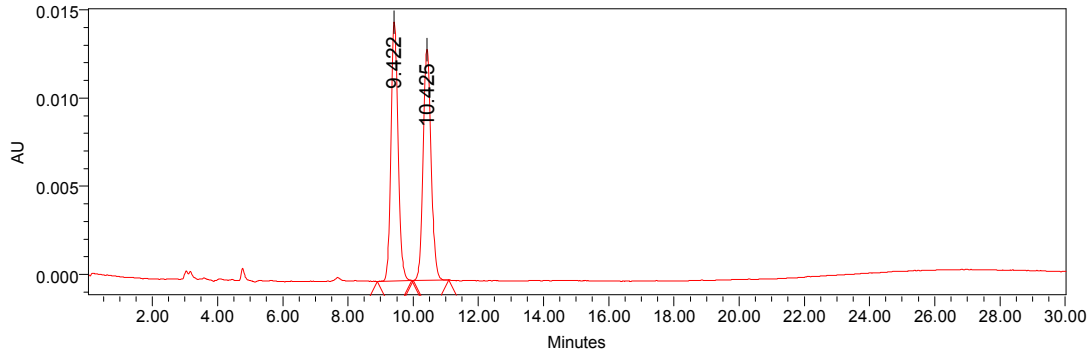
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 251.0 nm	5.360	1213614	50.01	149394
2	PDA 251.0 nm	6.384	1213339	49.99	124876

Figure S28. Alkyne 3An enantioriched sample: 96% ee.



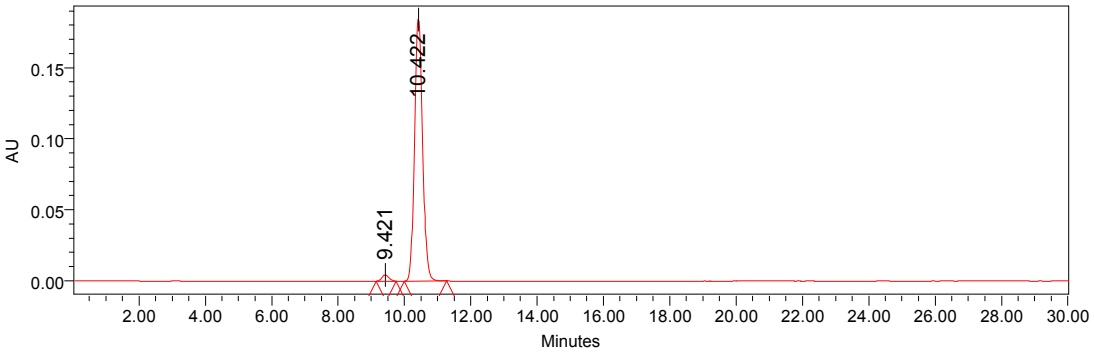
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 251.0 nm	5.402	335386	1.85	39969
2	PDA 251.0 nm	6.483	17841815	98.15	1744935

Figure S29. Alkyne 3Ao racemic sample: AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min



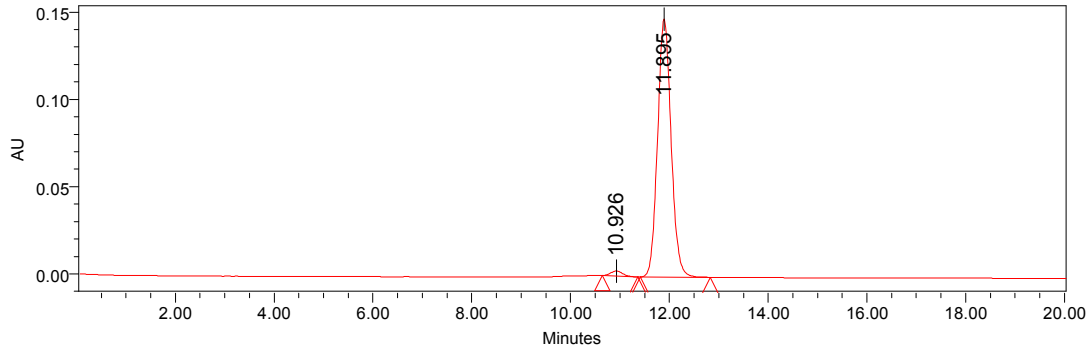
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 249.0 nm	9.422	221133	50.07	14691
2	PDA 249.0 nm	10.425	220552	49.93	13094

Figure S30. Alkyne 3Ao enantioriched sample: 96% ee.



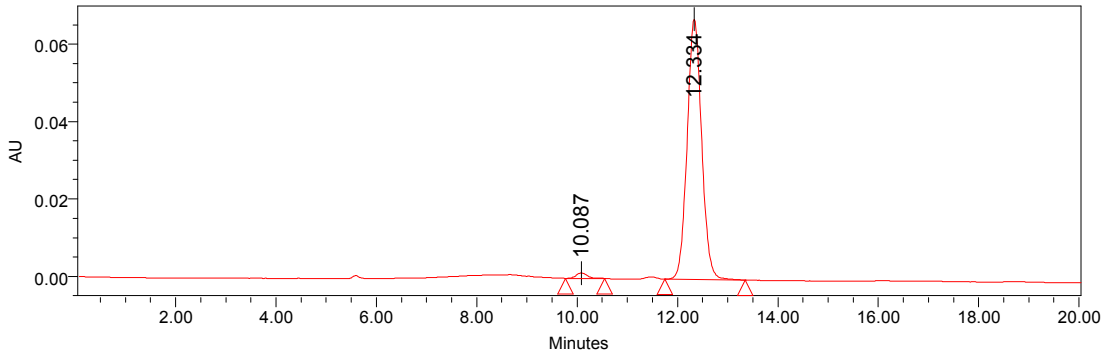
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 249.0 nm	9.421	62174	1.97	4292
2	PDA 249.0 nm	10.422	3088521	98.03	184406

Figure S31. Alkyne 3Ap diast 1 enantioriched sample: 97% ee. HPLC (AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min)



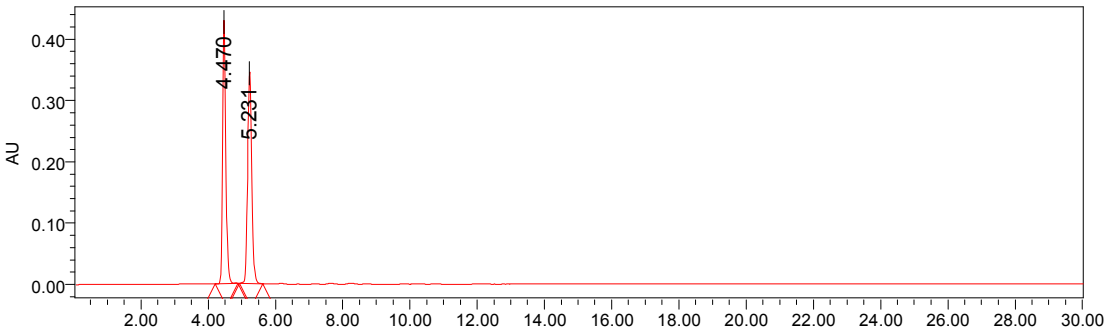
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 250.0 nm	10.926	46929	1.65	2858
2	PDA 250.0 nm	11.895	2805772	98.35	147812

Figure S32. Alkyne 3Ap diast 2 enantioriched sample: 97% ee. HPLC (AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min)



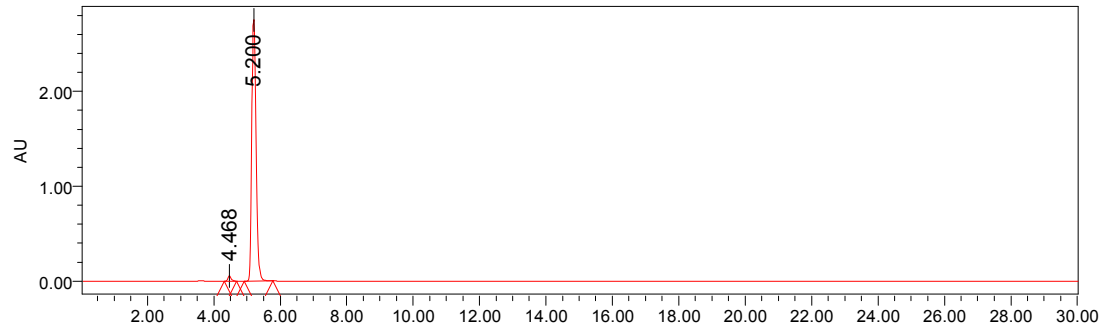
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 250.0 nm	10.087	22264	1.62	1415
2	PDA 250.0 nm	12.334	1351374	98.38	67255

Figure S33. Alkyne 3Aq racemic sample: AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min



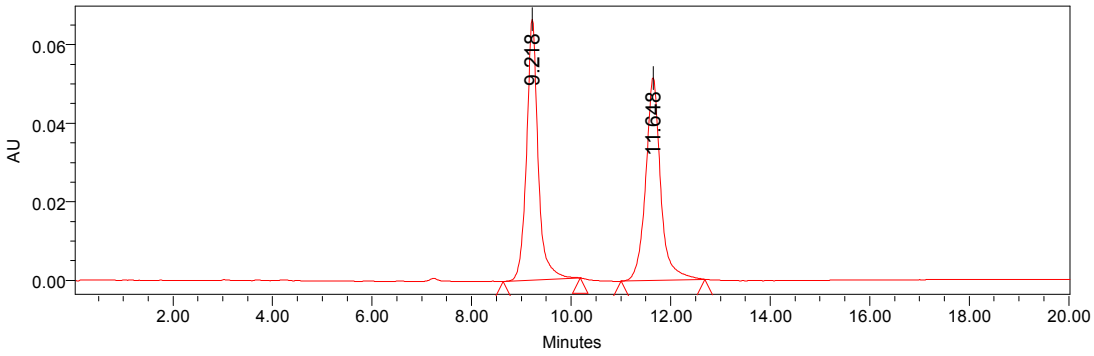
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 254.0 nm	4.470	2954809	50.04	428271
2	PDA 254.0 nm	5.231	2949713	49.96	345223

Figure S34. Alkyne 3Aq enantioriched sample: 97% ee.



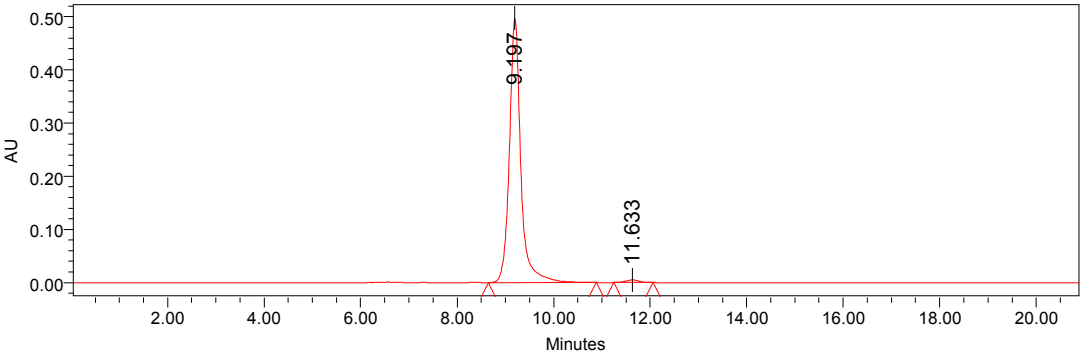
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 254.0 nm	4.468	371258	1.49	54874
2	PDA 254.0 nm	5.200	24600298	98.51	2754563

Figure S35. Alkyne 3Ba racemic sample: IA column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min



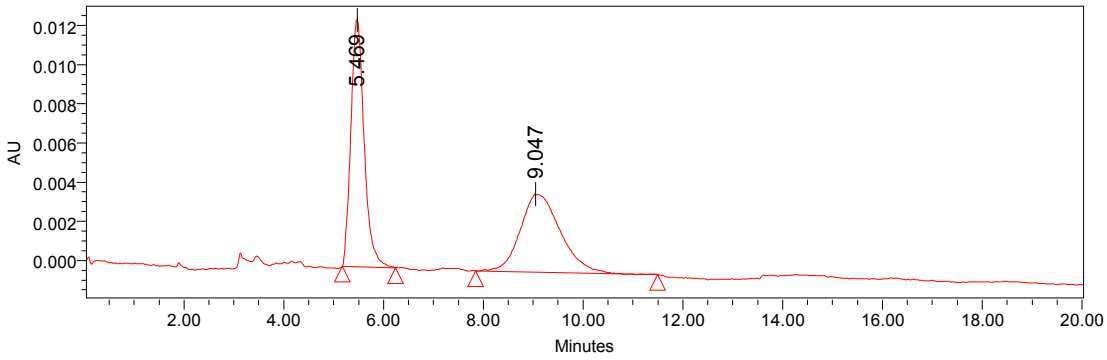
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 276.0 nm	9.218	1073105	49.99	66333
2	PDA 276.0 nm	11.648	1073432	50.01	51568

Figure S36. Alkyne 3Ba enantioriched sample: 98% ee.



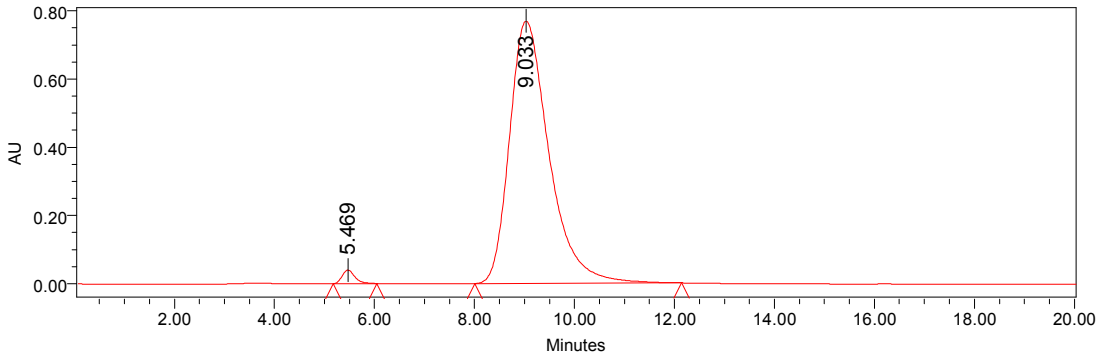
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 276.0 nm	9.197	8139837	98.92	497545
2	PDA 276.0 nm	11.633	88778	1.08	4813

Figure S37. Alkyne 3Bn racemic sample: OJ-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min



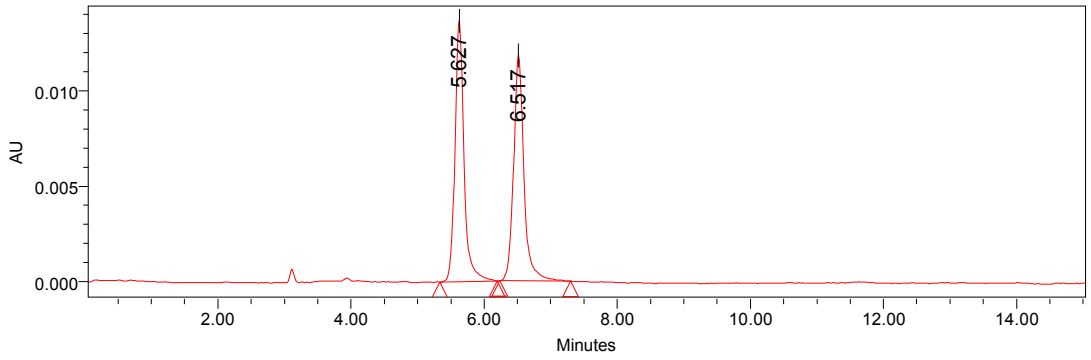
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 246.0 nm	5.469	232432	50.89	12632
2	PDA 246.0 nm	9.047	224288	49.11	3993

Figure S38. Alkyne 3Bn enantioriched sample: 97% ee.



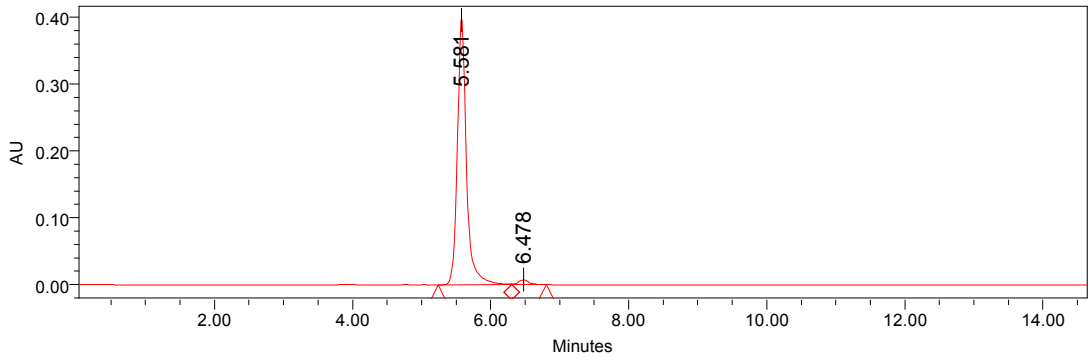
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 246.0 nm	5.469	697040	1.62	39884
2	PDA 246.0 nm	9.033	42324243	98.38	769914

Figure S39. Alkyne 3Bq racemic sample: IA column, 90:10 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min



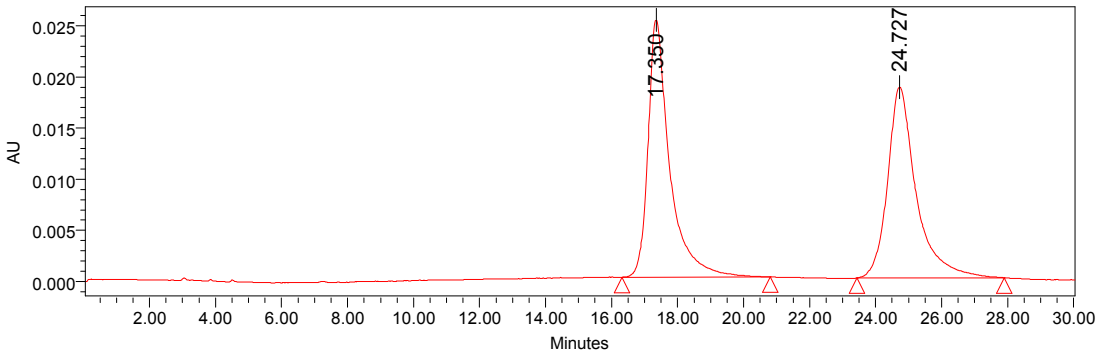
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 255.4 nm	5.627	129421	50.28	13746
2	PDA 255.4 nm	6.517	128004	49.72	11845

Figure S40. Alkyne 3Bq enantioriched sample: 96% ee.



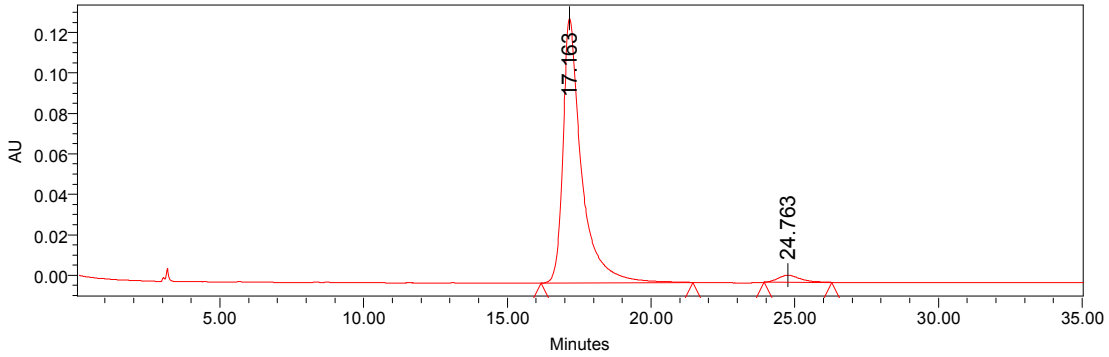
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 254.0 nm	5.581	3670945	97.94	398914
2	PDA 254.0 nm	6.478	77268	2.06	7429

Figure S41. Alkyne 3Ca racemic sample: IA column, *n*-Hex/*i*-PrOH 85:15, 30 °C, 1.0 mL/min



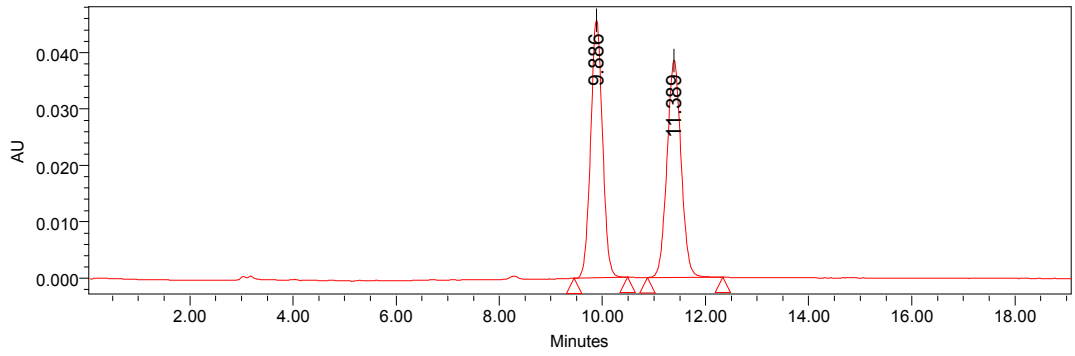
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 275.0 nm	17.350	1143709	50.49	25157
2	PDA 275.0 nm	24.727	1121650	49.51	18650

Figure S42. Alkyne 3Ca enantioriched sample: 94% ee.



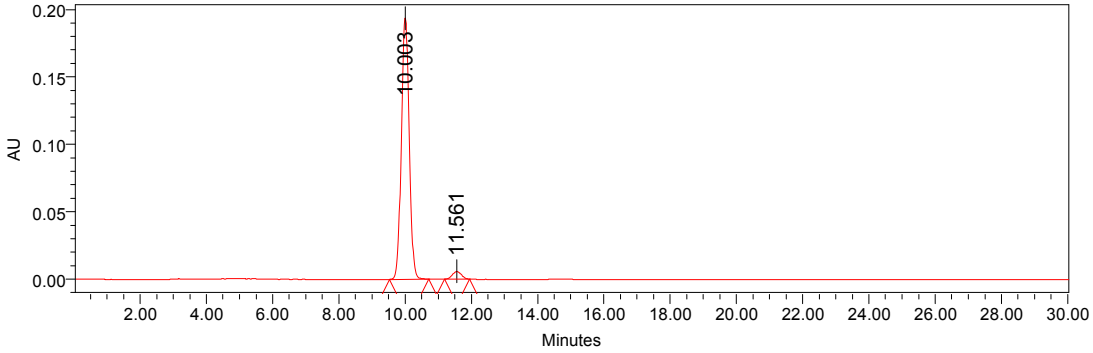
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 218.0 nm	17.163	5849676	96.87	130855
2	PDA 218.0 nm	24.763	188871	3.13	3514

Figure S43. Alkyne 3Cn racemic sample: AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min



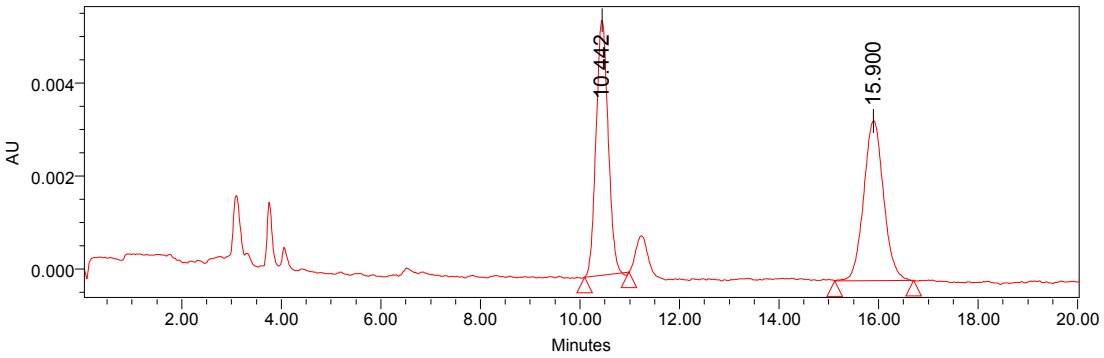
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 246.0 nm	9.886	727056	49.93	45722
2	PDA 246.0 nm	11.389	729218	50.07	38501

Figure S44. Alkyne 3Cn enantioriched sample: 93% ee.



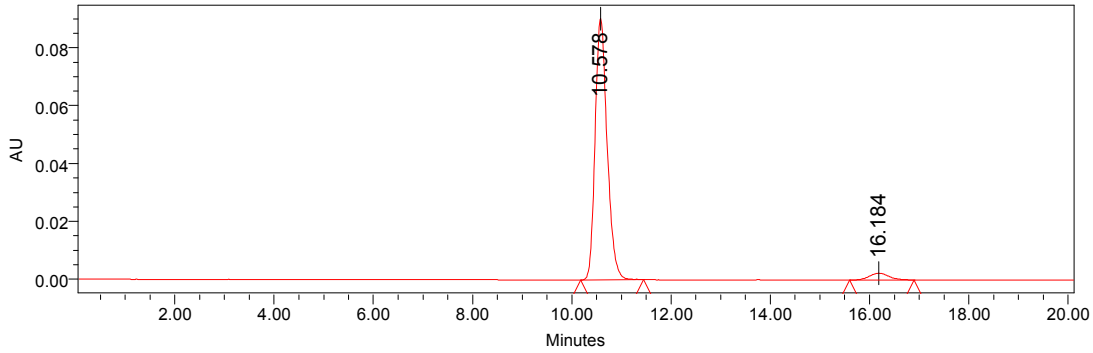
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 246.0 nm	10.003	3188608	96.72	194218
2	PDA 246.0 nm	11.561	108008	3.28	5736

Figure S45. Alkyne 3Cq racemic sample: AD-H column, 90:10 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min



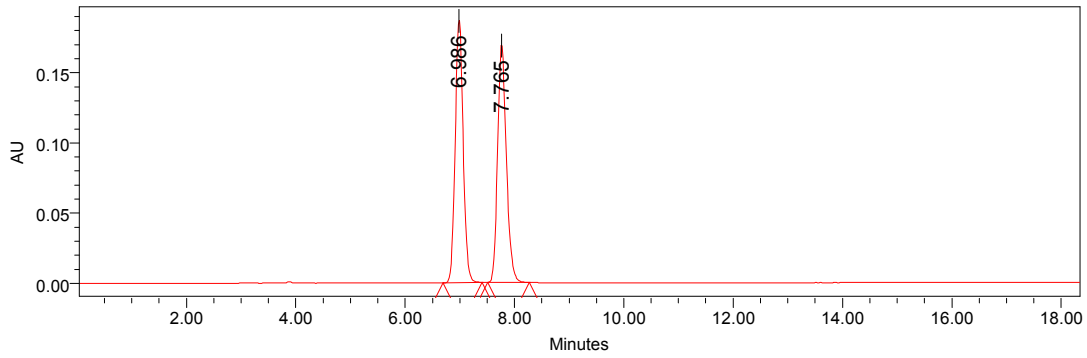
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 255.3 nm	10.442	92660	49.30	5495
2	PDA 255.3 nm	15.900	95302	50.70	3444

Figure S46. Alkyne 3Cq enantioriched sample: 92% ee.



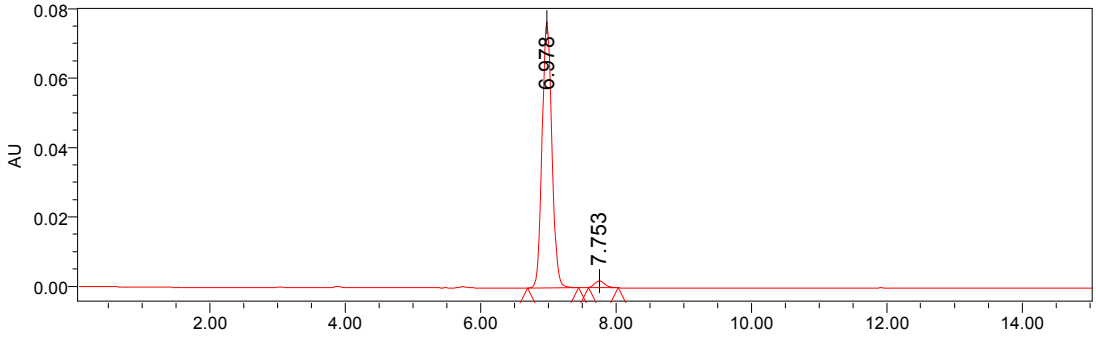
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 260.3 nm	10.578	1510913	96.03	90441
2	PDA 260.3 nm	16.184	62428	3.97	2333

Figure S47. Alkyne 3Da racemic sample: AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min



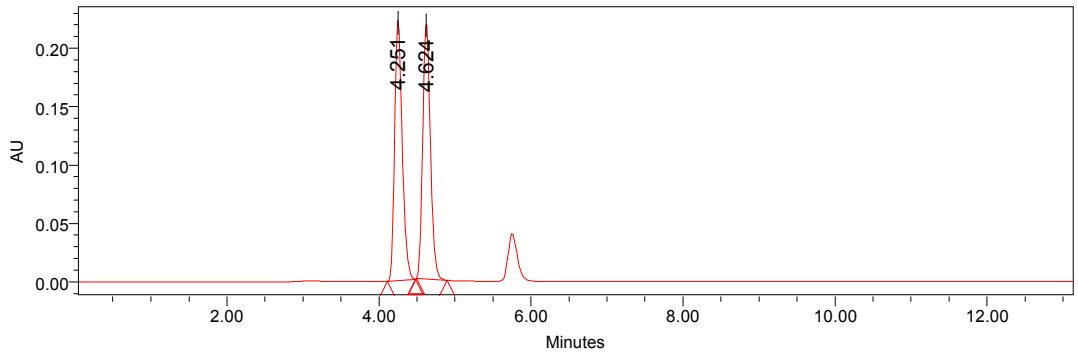
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 276.0 nm	6.986	1903644	50.01	187258
2	PDA 276.0 nm	7.765	1902650	49.99	169765

Figure S48. Alkyne 3Da enantioriched sample: 95% ee.



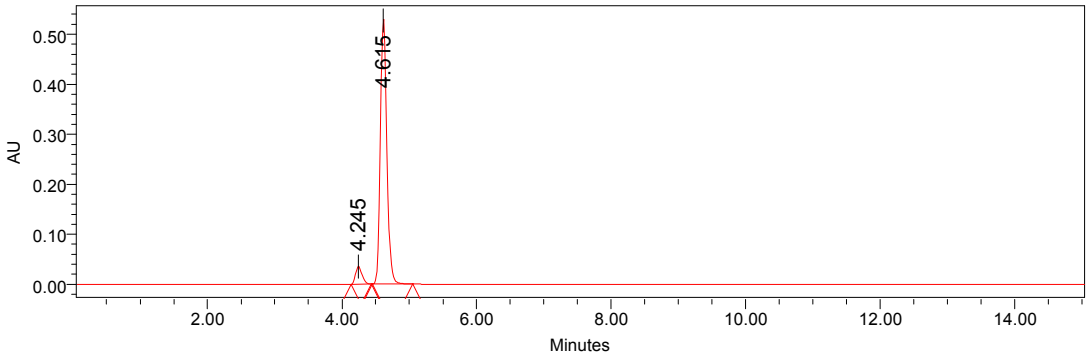
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 276.0 nm	6.978	761396	97.51	76567
2	PDA 276.0 nm	7.753	19476	2.49	1893

Figure S49. Alkyne 3Dn racemic sample: AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min



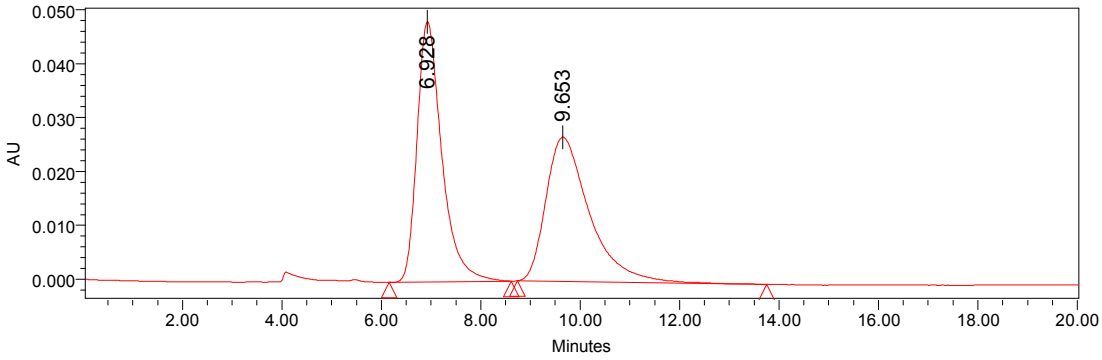
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 245.0 nm	4.251	1533751	50.20	222980
2	PDA 245.0 nm	4.624	1521799	49.80	218651

Figure S50. Alkyne 3Dn enantioriched sample: 88% ee.



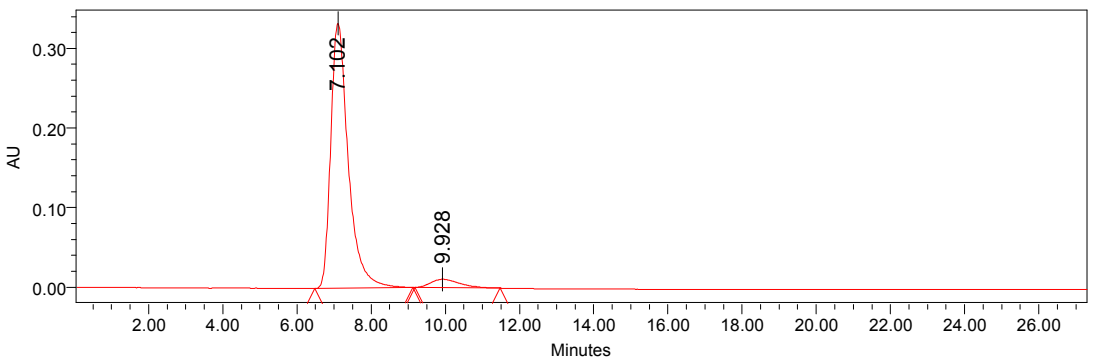
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 250.0 nm	4.245	231231	6.10	35471
2	PDA 250.0 nm	4.615	3561352	93.90	527630

Figure S51. Alkyne 3Dq racemic sample: OJ-H column, 99:1 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min



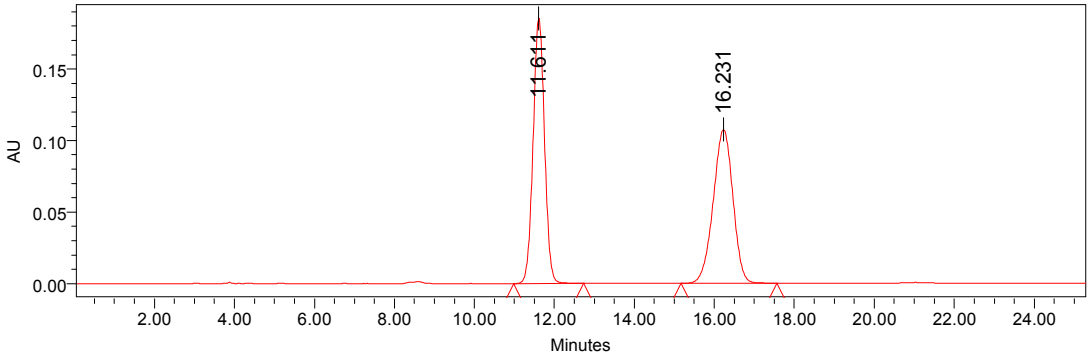
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 254.0 nm	6.928	1670737	50.59	48348
2	PDA 254.0 nm	9.653	1631902	49.41	26777

Figure S52. Alkyne 3Dq enantioriched sample: 90% ee.



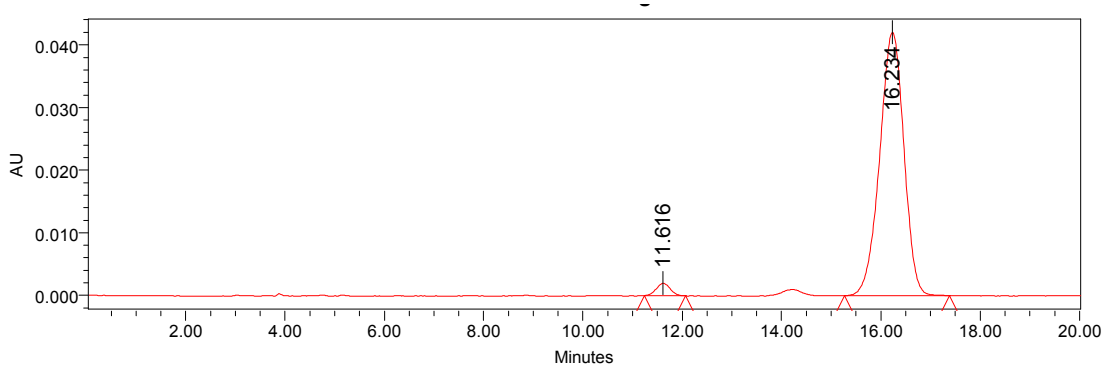
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 254.0 nm	7.102	10938282	95.03	333149
2	PDA 254.0 nm	9.928	571937	4.97	10490

Figure S53. Alkyne 3Ea racemic sample: AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min



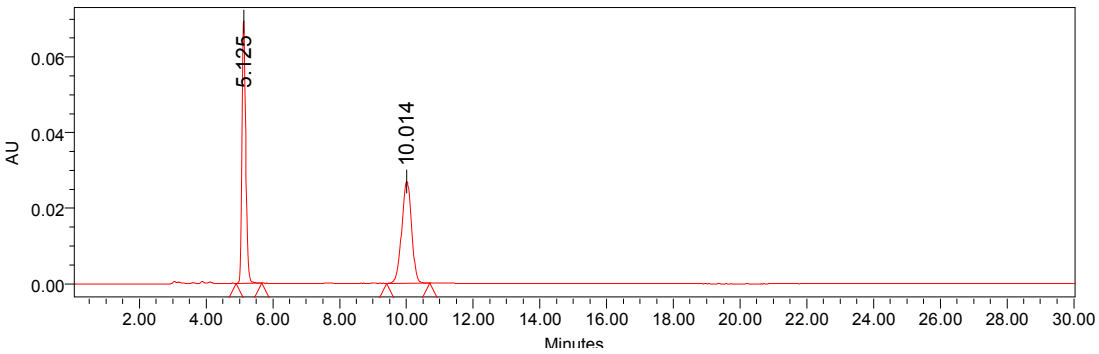
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 284.0 nm	11.611	3671082	49.98	185636
2	PDA 284.0 nm	16.231	3673301	50.02	107401

Figure S54. Alkyne 3Ea enantioriched sample: 95% ee.



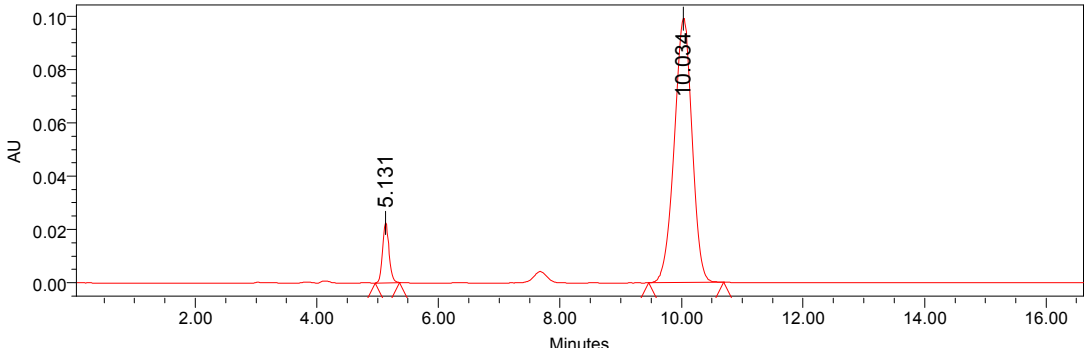
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 284.0 nm	11.616	38350	2.63	1984
2	PDA 284.0 nm	16.234	1422553	97.37	42049

Figure S55. Alkyne 3En racemic sample: AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min



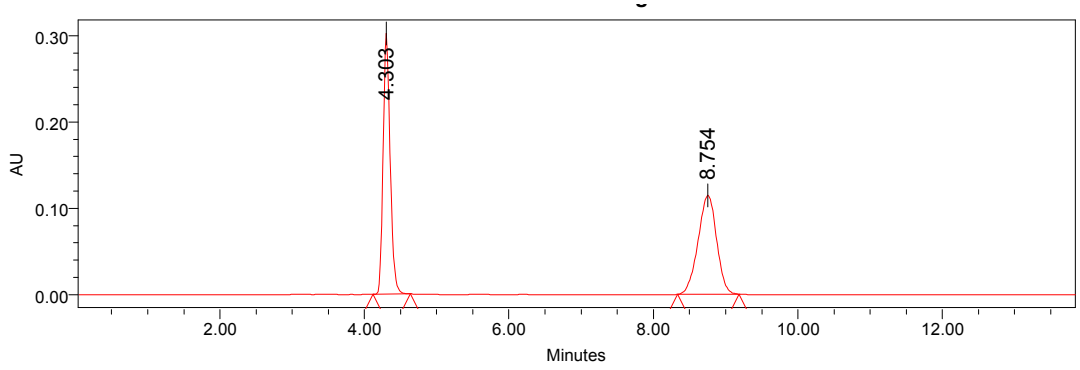
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 252.0 nm	5.125	554047	50.10	69746
2	PDA 252.0 nm	10.014	551890	49.90	26898

Figure S56. Alkyne 3En enantioriched sample: 85% ee.



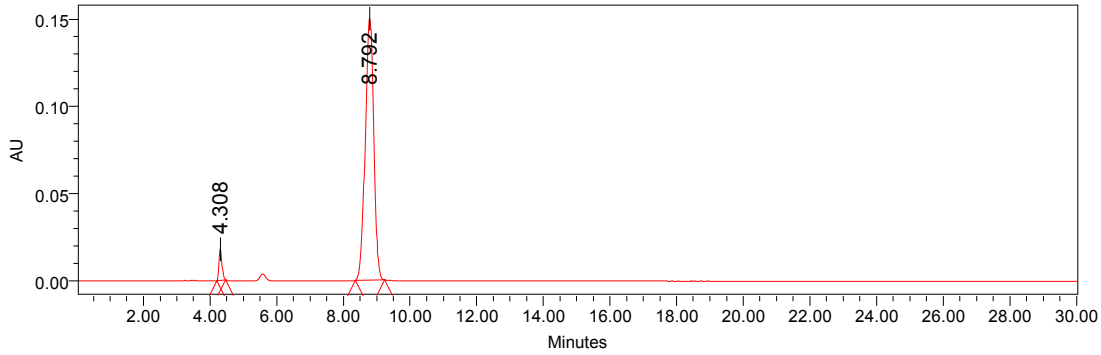
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 252.0 nm	5.131	169785	7.74	22552
2	PDA 252.0 nm	10.034	2024668	92.26	99255

Figure S57. Alkyne 3Eq racemic sample: AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min



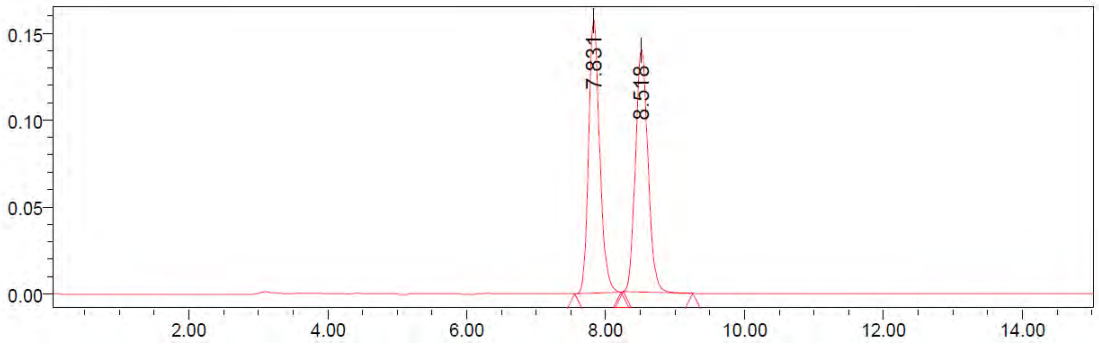
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 259.0 nm	4.303	2051486	50.12	300974
2	PDA 259.0 nm	8.754	2041736	49.88	114634

Figure S58. Alkyne 3Eq enantioriched sample: 92% ee.



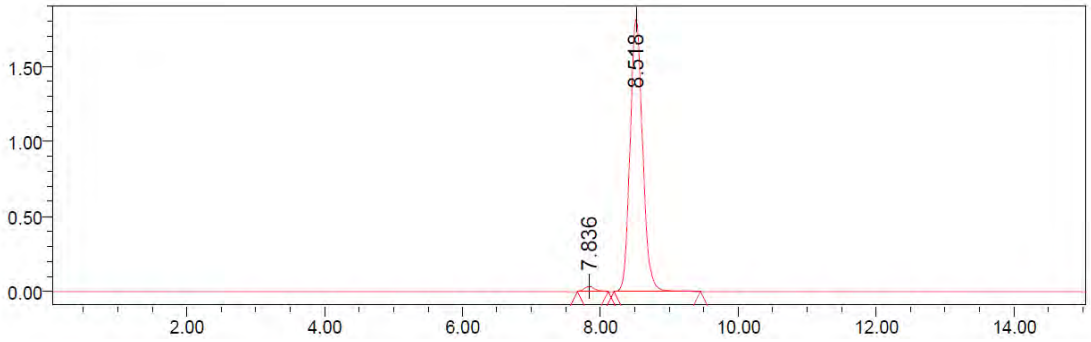
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 259.0 nm	4.308	115389	4.15	18089
2	PDA 259.0 nm	8.792	2663507	95.85	150288

Figure S59. Alkyne 4A racemic sample: AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min



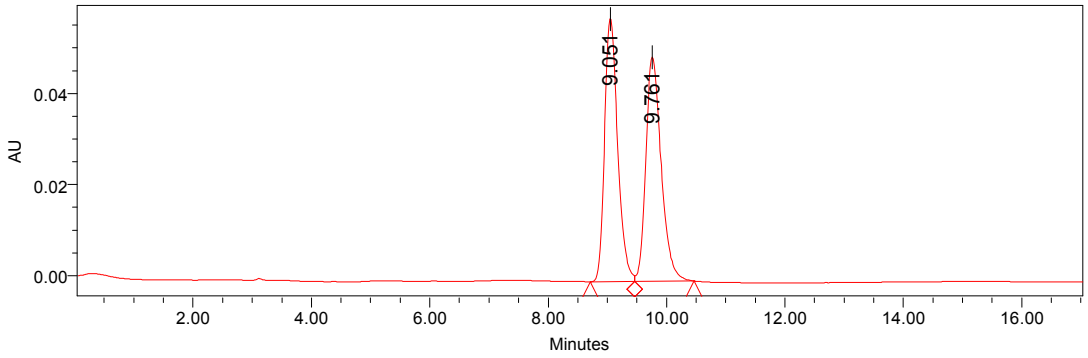
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 246.0 nm	7.831	1748065	50.01	157639
2	PDA 246.0 nm	8.518	1747665	49.99	139488

Figure S60. Alkyne 4A enantioriched sample: 97% ee. AD-H column, 85:15 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min



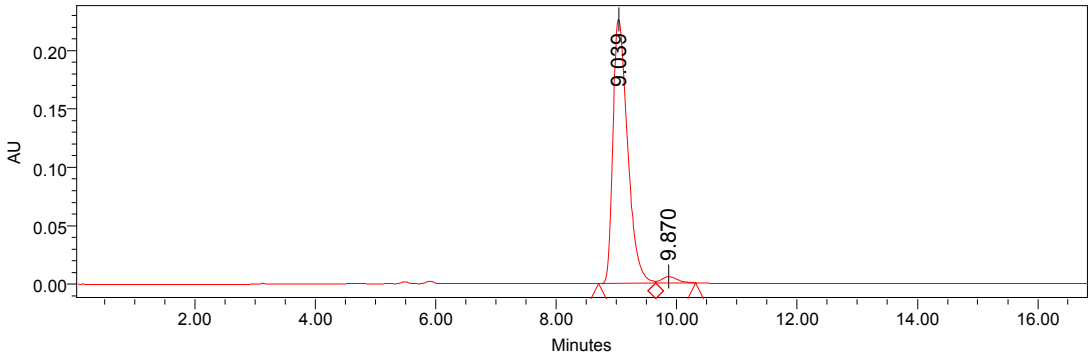
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 246.0 nm	7.836	336205	1.45	32389
2	PDA 246.0 nm	8.518	22794678	98.55	1811892

Figure S61. Alkyne 4B racemic sample: AS-H column, 90:10 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min



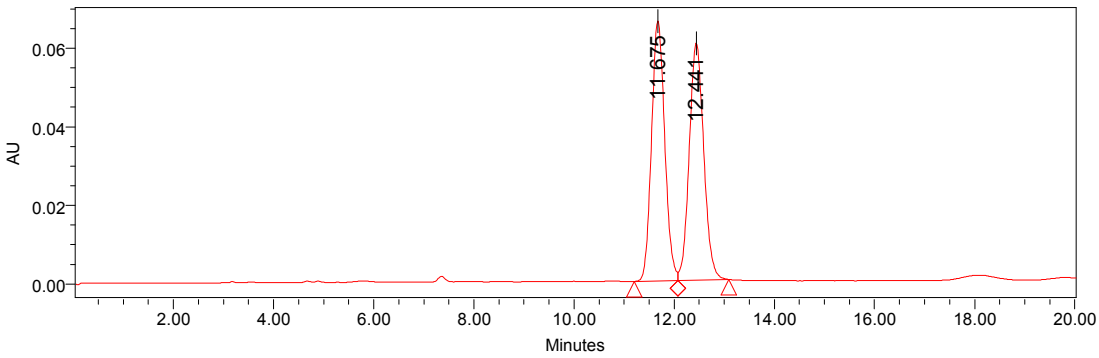
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 244.6 nm	9.051	883588	49.88	57916
2	PDA 244.6 nm	9.761	887805	50.12	49297

Figure S62. Alkyne 4B enantioriched sample: 95% ee.



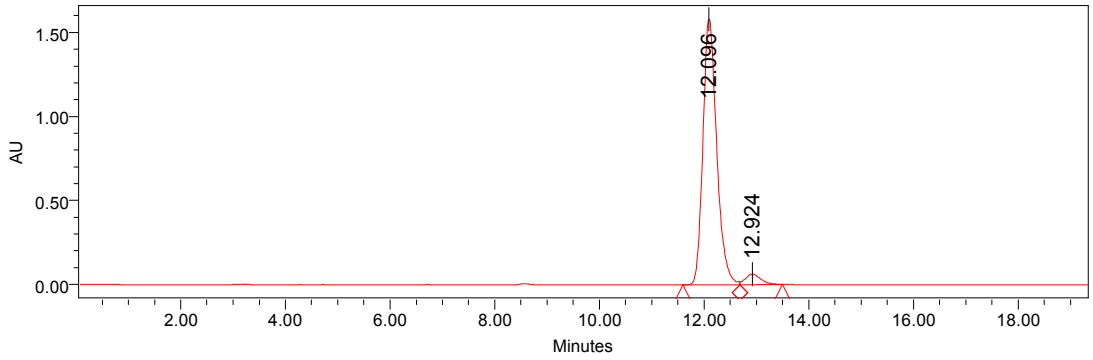
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 273.9 nm	9.039	3814072	97.42	226640
2	PDA 273.9 nm	9.870	101209	2.58	5485

Figure S63. Alkyne 4C racemic sample: AD-H column, 80:20 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min



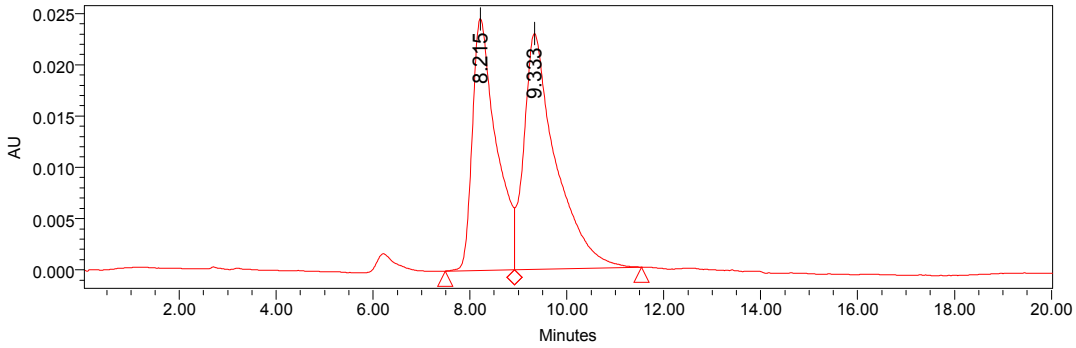
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 242.3 nm	11.675	1208774	49.94	66189
2	PDA 242.3 nm	12.441	1211603	50.06	60265

Figure S64. Alkyne 4C enantioriched sample: 92% ee.



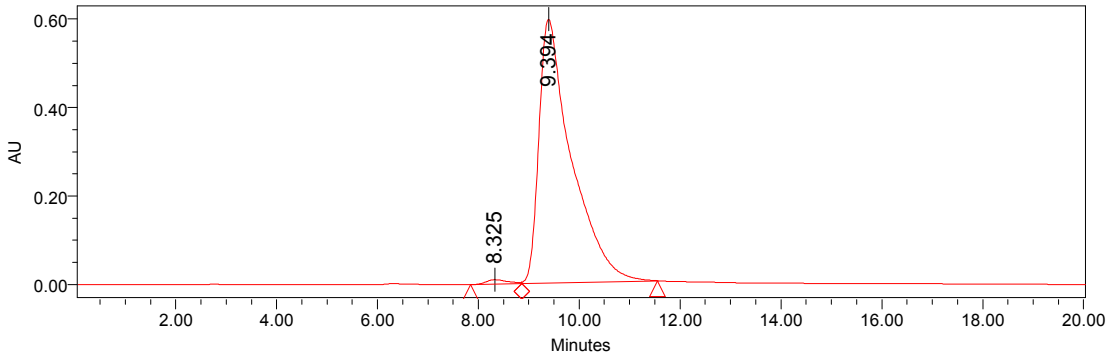
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 219.1 nm	12.096	28855868	95.85	1583123
2	PDA 219.1 nm	12.924	1248875	4.15	61685

Figure S65. Alkene 5 racemic sample: OD column, 90:10 *n*-Hex/*i*-PrOH, 30 °C, 1 mL/min



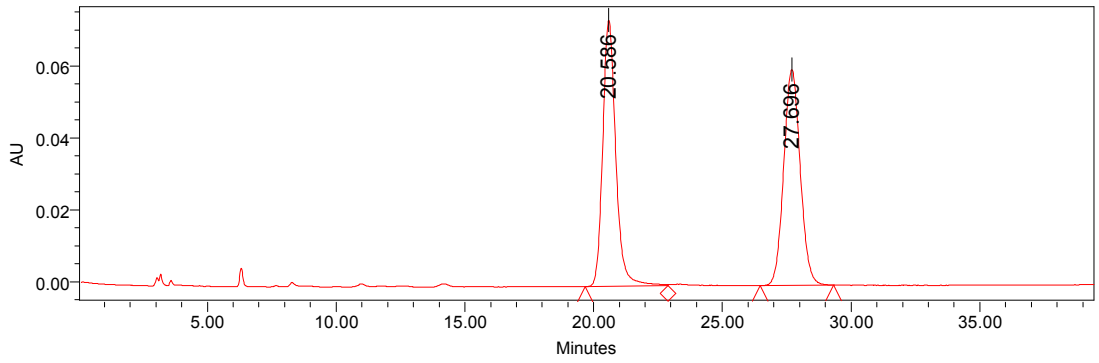
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 257.4 nm	8.215	837605	44.44	24569
2	PDA 257.4 nm	9.333	1047007	55.56	23002

Figure S66. Alkene 5 enantioriched sample: 97% ee.



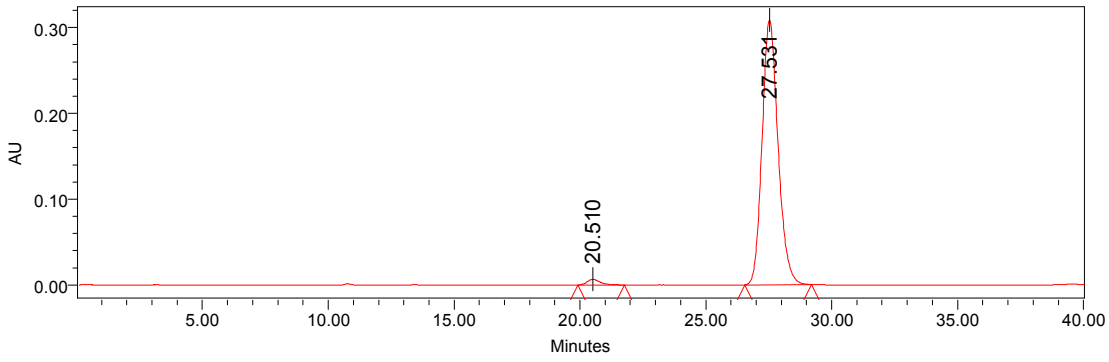
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 247.9 nm	8.325	286085	1.06	9946
2	PDA 247.9 nm	9.394	26666475	98.94	596370

Figure S67. Compound 6 racemic sample: AD-H column, *n*-Hex/*i*-PrOH 85:15, 30 °C, 1.0 mL/min



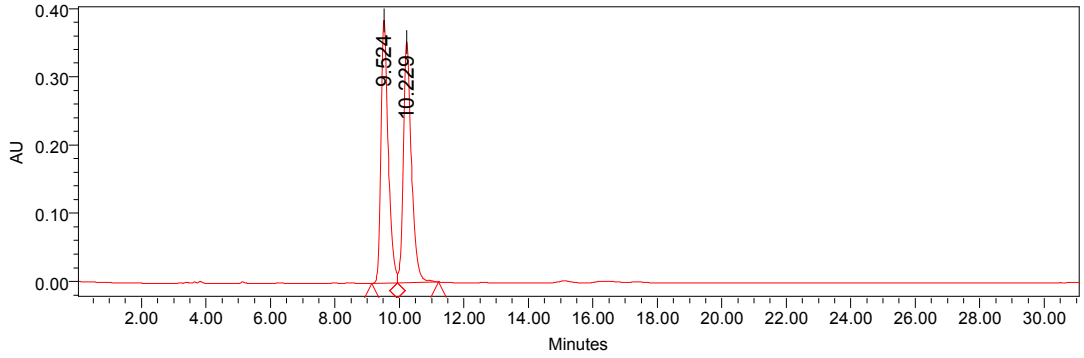
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 218.3 nm	20.586	2610370	49.45	74050
2	PDA 218.3 nm	27.696	2668739	50.55	59986

Figure S68. Compound 6 enantioriched sample: 97% ee.



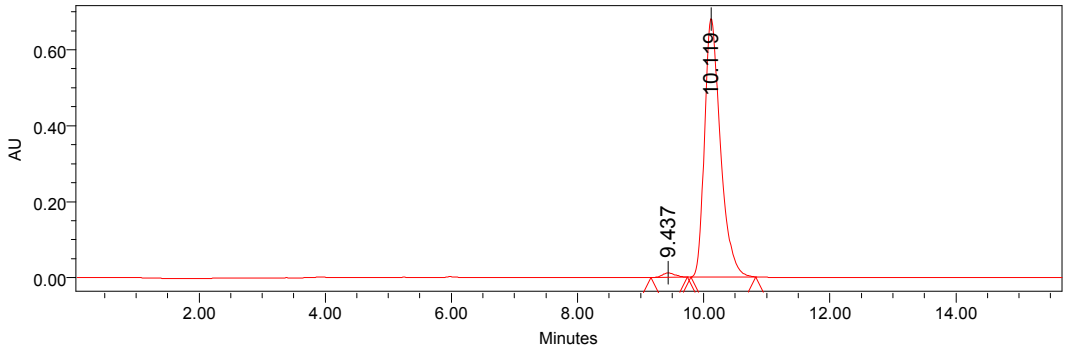
	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 245.0 nm	20.510	229554	1.66	6524
2	PDA 245.0 nm	27.531	13590233	98.34	308562

Figure S69. Compound 7 racemic sample: AD-H column, 70:30 *n*-Hex/*i*-PrOH, 30 °C, 1.0 mL/min



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 219.0 nm	9.524	6111386	49.55	385522
2	PDA 219.0 nm	10.229	6223264	50.45	352982

Figure S70. Compound 7 enantioriched sample: 97% ee.



	Processed Channel	Retention Time (min)	Area	% Area	Height
1	PDA 242.6 nm	9.437	177069	1.46	12138
2	PDA 242.6 nm	10.119	11928061	98.54	682117

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