Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supplementary Information for

Inversion of circularly polarized luminescence by electric current flow during transition

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1. General Considerations

Reagents and reactions

All moisture-sensitive reactions were conducted in dry flasks under a nitrogen atmosphere, using solvents dried over activated molecular sieves 4 Å or 5 Å. Reactions were monitored by thin-layer chromatography (TLC; Silica gel 60 F254, Merck) using one or a combination of the following methods: 1) observation under UV light (254 nm / 365 nm), 2) staining with phosphomolybdic acid solution. 3) heating on a hot plate. Normal-phase column chromatography was performed using SiliaFlash (R) F60 (SiliCycle). Silica gel 60 F_{254} (Merck) was used for preparative TLC. Gel permeation chromatography (GPC) was conducted using an LC-2000 plus system (JASCO, pump: PU-2086; UV detector: UV-2075; RI detector: RI-2031) with two connected columns, GPCH-2001 (20×500 nm, Showa Denko) and GPCH-2002 (20×500 nm, Showa Denko).

Analysis

The circularly polarized luminescence (CPL) spectra were measured using a JASCO CPL-200 spectrofluoropolarimeter (Tokyo, Japan). Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECZS 400 instrument. For ^{1}H NMR, chloroform (7.26 ppm) or tetramethylsilane (0.00 ppm) were used as internal standards, and for ^{13}C NMR, chloroform (77.16 ppm) was used as an internal standard when using deuterated chloroform. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are given in Hz. Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, quin = quintet, m = multiplet, dd = double doublet, ddd = double double doublet, br = broad. Melting points were measured using a micro melting point apparatus MP-J3 (Yanaco Scientific Instruments) and are uncorrected. High-resolution mass spectrometry (HRMS) was performed using a Bruker solariX (FT-ICR-MS), Shimadzu LCMS-IT-TOF and Aglient 6230 LC/TOF. Specific rotations were measured with JASCO P-2200 polarimeter, and are reported as follows: $[\alpha]_D^t$ (solvent, concentration).

2. Supplementary Photophysical Properties

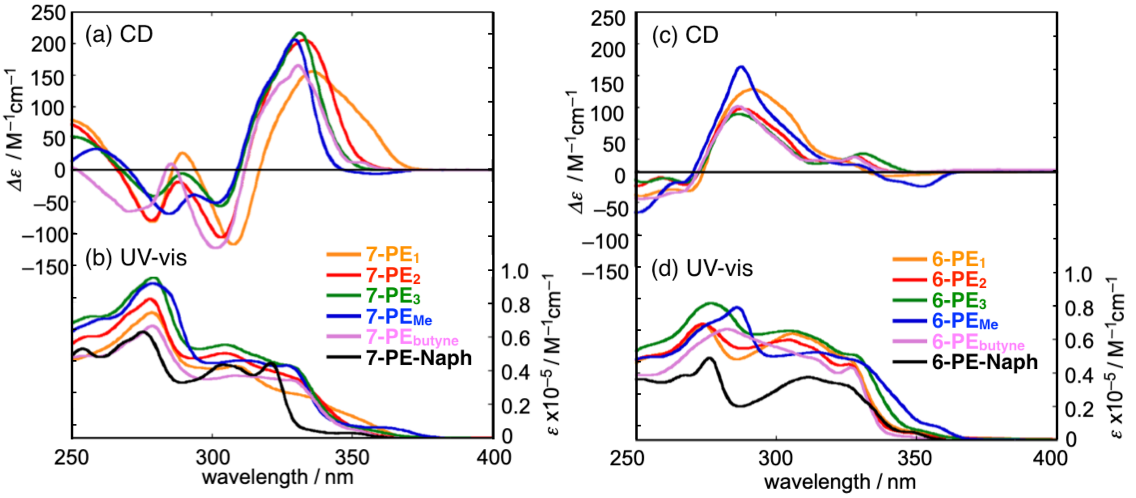
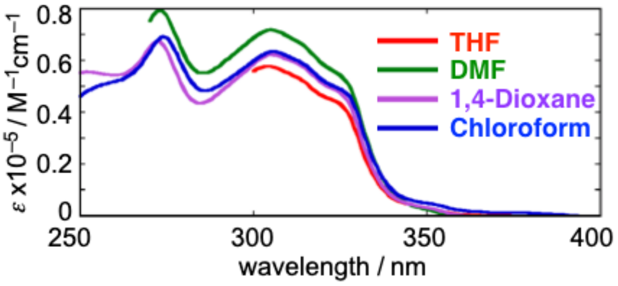


Figure S1. (a) CD spectra of **7-PE$_n$**, (b) UV-Vis absorption of **7-PE$_n$** and **7-PE-Naph**, (c) CD spectra of **6-PA$_n$** and (d) UV-Vis absorption of **6-PA$_n$** and **6-PE-Naph**. Conditions: 1.0×10^{-5} M in $CHCl_3$, 25 °C.

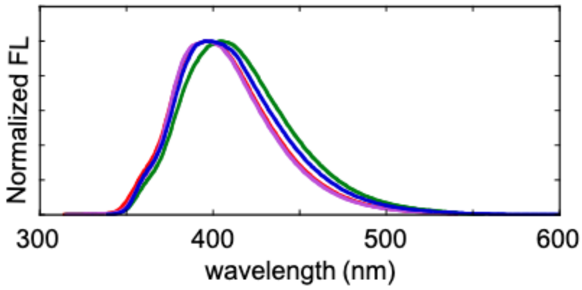
compound	λ_{em} (nm)	Φ (%)	τ (ns)	k_f / 10^{-8}	k_{nr} / 10^{-8}	g_{lum} (exp)
7-PE$_1$	407	37	4.1	0.90	1.53	5.6×10^{-3}
7-PE$_2$	381	39	4.6	0.85	1.33	3.2×10^{-3}
7-PE$_3$	392	34	5.1	0.67	1.29	0.68×10^{-3}
7-PE$_{Me}$	391	37	4.1	0.90	1.54	0.88×10^{-3}
7-PE$_{butyne}$	354, 377	54	5.0	1.08	0.92	3.04×10^{-3}
7-PE-Naph	373	28	8.9	0.31	0.81	–
6-PE$_1$	398	36	3.2	1.12	2.01	-1.8×10^{-3}
6-PE$_2$	360, 373	26	6.9	0.37	1.07	-0.78×10^{-3}
6-PE$_3$	370, 381	35	5.1	0.69	1.27	-0.50×10^{-3}
6-PE$_{Me}$	369, 383	35	3.7	0.94	1.74	-0.58×10^{-3}
6-PE$_{butyne}$	354, 370	24	8.5	0.28	0.89	-0.49×10^{-3}
6-PE-Naph	363	43	5.0	0.86	1.14	–

Table S1. Summary of photophysical properties of **7-PE$_n$**, **6-PE$_n$**, **7-PE-Naph** and **6-PE-Naph**. λ_{em} : Emission maximum. Φ : Fluorescence quantum yield. τ : Fluorescence lifetime. k_f : Fluorescence radiative rate constant. k_{nr} : Non-radiative rate constant. g_{lum} (exp) : Experimentally obtained dissymmetry (g_{lum}) value. Conditions: 1.0×10^{-5} M in $CHCl_3$, 25 °C.

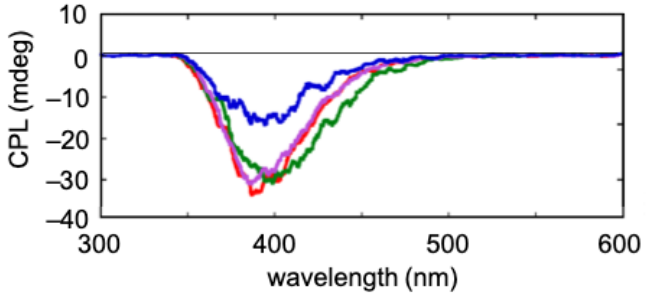
(a) UV-Vis spectra



(b) FL spectra



(c) CPL spectra



(d) Chiroptical properties

solvent	g_{lum}
THF	-2.13×10^{-3}
DMF	-1.99×10^{-3}
1,4-Dioxane	-2.16×10^{-3}
Chloroform	-1.80×10^{-3}

Figure S2. Solvent effects in (a) UV-Vis, (b) FL and (c) CPL spectra, and (d) dissymmetry (g_{lum}) value of **6-PE$_1$**. Conditions: 1.0×10^{-5} M, 25 °C.

3. Transition Dipole Moments and Expected Electric Currents

Table S2. Characteristic features relevant to the electronic transition from the excited to the ground state ($S_1 \rightarrow S_0$) calculated at the TD-DFT/CAM-B3LYP/ccpvtz level.

Compound	ϕ_{ex} (°)	μ (10^{-18} esu·cm)	m (10^{-20} esu·cm)	$\theta_{\mu m}$ (°)	g_{lum} (calc)	g_{lum} (exp)	g_{abs} (calc)
3-PE$_1$	44.5	4.25	0.313	108	-0.46×10^{-3}	-1.5×10^{-3}	6.9×10^{-3}
4-PE$_1$	44.2	12.1	0.634	113	-0.42×10^{-3}	-0.52×10^{-3}	-0.39×10^{-3}
5-PE$_1$	47.0	9.84	1.15	124	-1.3×10^{-3}	-1.9×10^{-3}	-1.1×10^{-3}
6-PE$_1$	33.2	5.09	3.42	96	-1.4×10^{-3}	-1.8×10^{-3}	-1.4×10^{-3}
7-PE$_1$	38.7	4.59	5.42	57	12.9×10^{-3}	5.6×10^{-3}	18.1×10^{-3}
8-PE$_1$	47.3	5.20	0.880	117	-1.6×10^{-3}	-1.8×10^{-3}	-1.2×10^{-3}

ϕ_{ex}: Dihedral angle of the binaphthyl in the excited state.

μ: Electric transition dipole moment in the excited state.

m: Magnetic transition dipole moment in the excited state.

$\theta_{\mu m}$: Angle of vectors between μ and m.

g_{lum} (calc): Theoretically calculated g_{lum} value.

g_{lum} (exp): Experimentally observed g_{lum} value.

g_{abs} (calc): Theoretically calculated g_{lum} value for the transition from the ground state to the excited state ($S_0 \rightarrow S_1$) calculated at the TD-DFT/B3LYP/6-31G+(d,p).

The structural optimization in the excited states and calculation of the electric (μ) and magnetic (m) transition dipole moments for compounds **3-PE$_1$**, **4-PE$_1$**, **5-PE$_1$** and **8-PE$_1$** were conducted using Time-Dependent Density Functional Theory (TD-DFT) at the CAM-b3LYP/ccpvtz level.

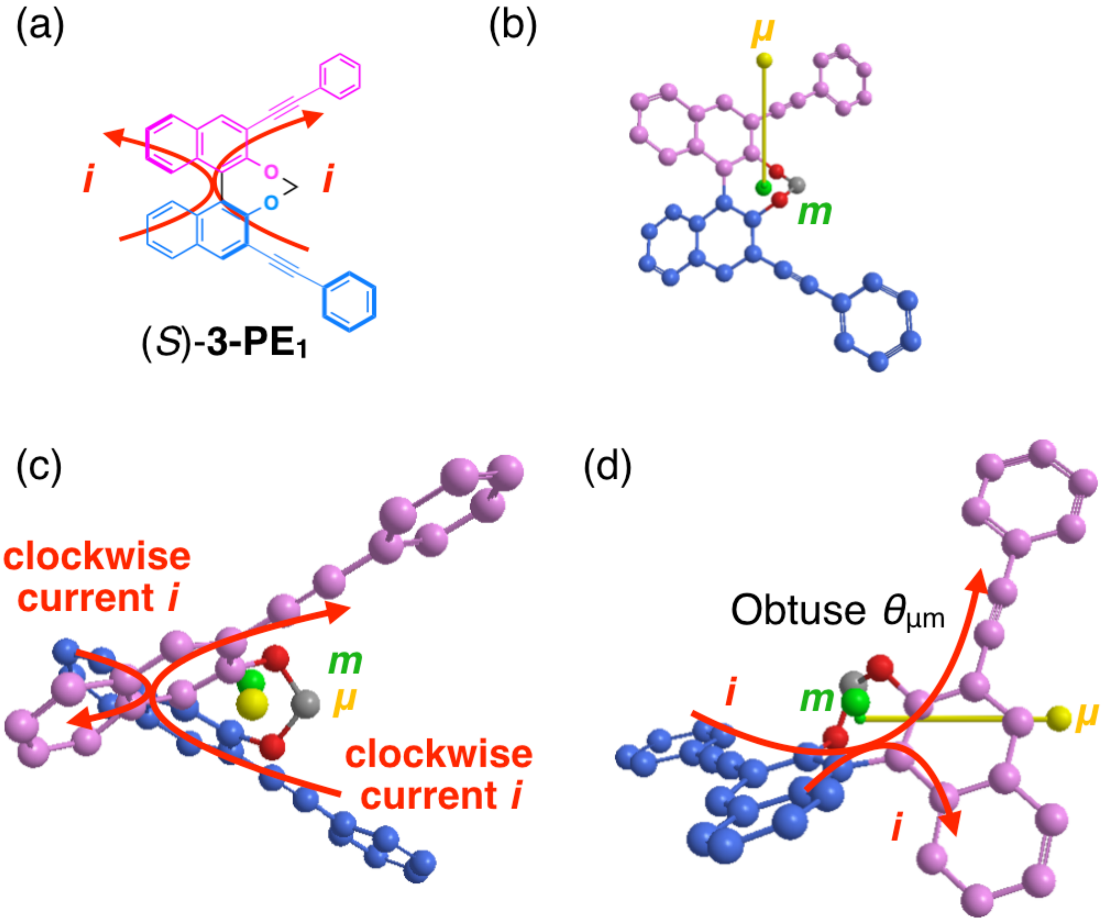


Figure S3. (a) Expected electric current flow (i is shown in red) for the $S_1 \rightarrow S_0$ transitions for (S)-**3-PE$_1$**. (b) Electric (μ is shown in yellow) and magnetic (m is shown in green) transition dipole moments for the $S_1 \rightarrow S_0$ transitions for (S)-**3-PE$_1$**. For clarity, the relative length of m is magnified by 137 times compared with that of μ. (c) Top view from the direction of μ. The current flows clockwise relative to the origin-μ axis. (d) Side view from the direction of μ. The $\theta_{\mu m}$ is obtuse.

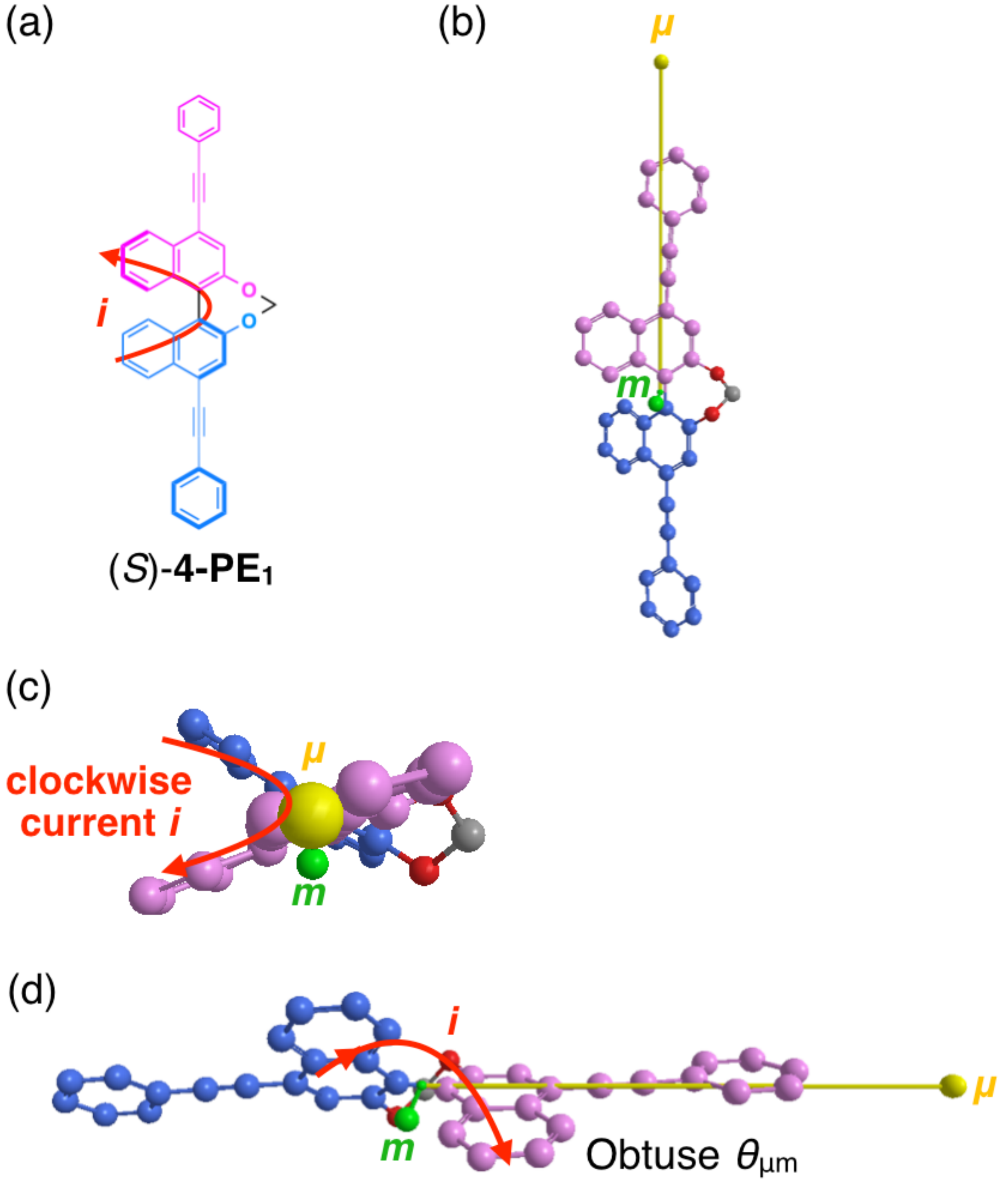


Figure S4. (a) Expected electric current flow (*i* is shown in red) for the $S_1 \rightarrow S_0$ transitions for (*S*)-**4-PE**$_1$. (b) Electric (μ is shown in yellow) and magnetic (*m* is shown in green) transition dipole moments for the $S_1 \rightarrow S_0$ transitions for (*S*)-**4-PE**$_1$. For clarity, the relative length of *m* is magnified by 137 times compared with that of μ. (c) Top view from the direction of μ. The current flows clockwise relative to the origin-μ axis. (d) Side view from the direction of μ. The $\theta_{\mu m}$ is clearly obtuse.

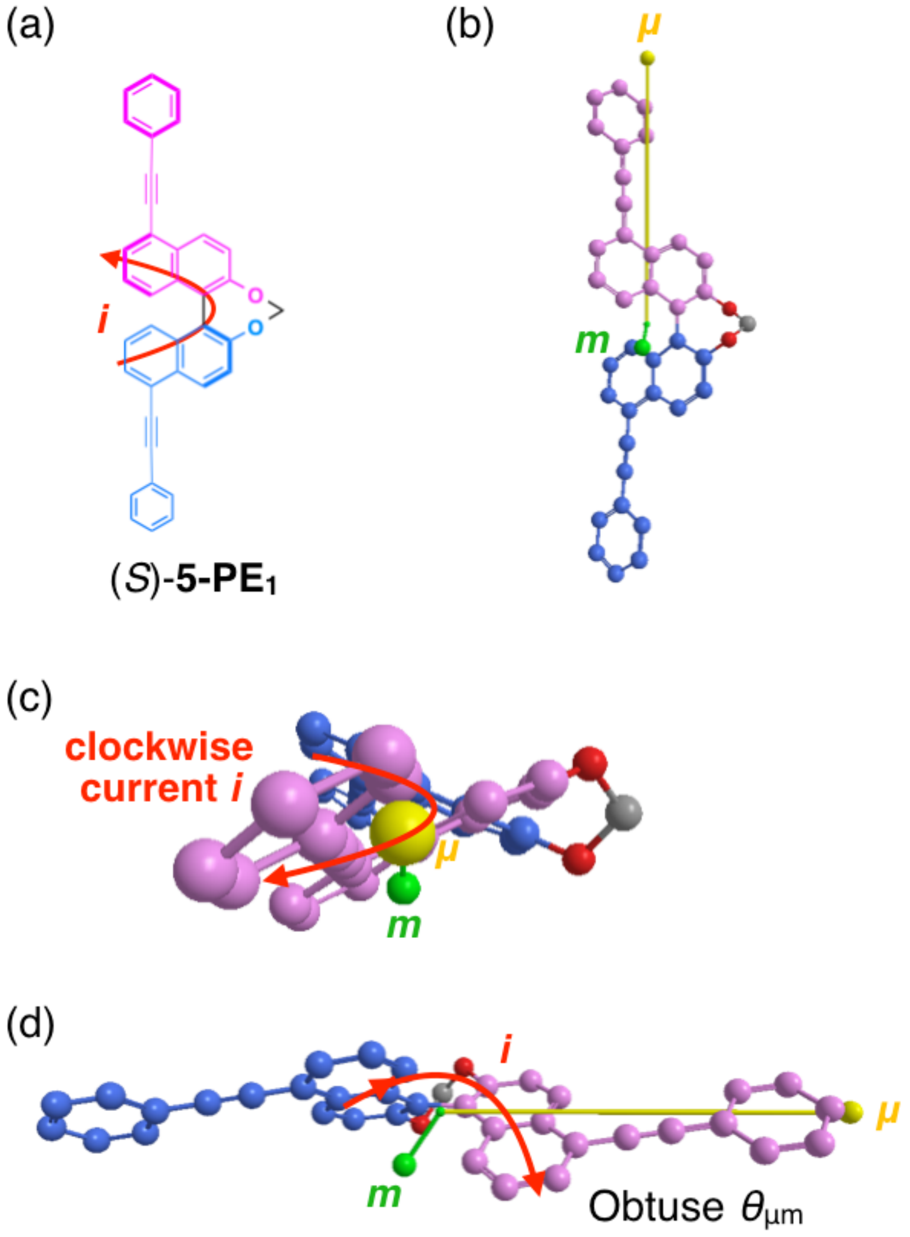


Figure S5. (a) Expected electric current flow (*i* is shown in red) for the $S_1 \rightarrow S_0$ transitions for (*S*)-**5-PE$_1$**. (b) Electric (*μ* is shown in yellow) and magnetic (*m* is shown in green) transition dipole moments for the $S_1 \rightarrow S_0$ transitions for (*S*)-**5-PE$_1$**. For clarity, the relative length of *m* is magnified by 137 times compared with that of *μ*. (c) Top view from the direction of *μ*. The current flows clockwise relative to the origin-*μ* axis. (d) Side view from the direction of *μ*. The $\theta_{\mu m}$ is clearly obtuse.

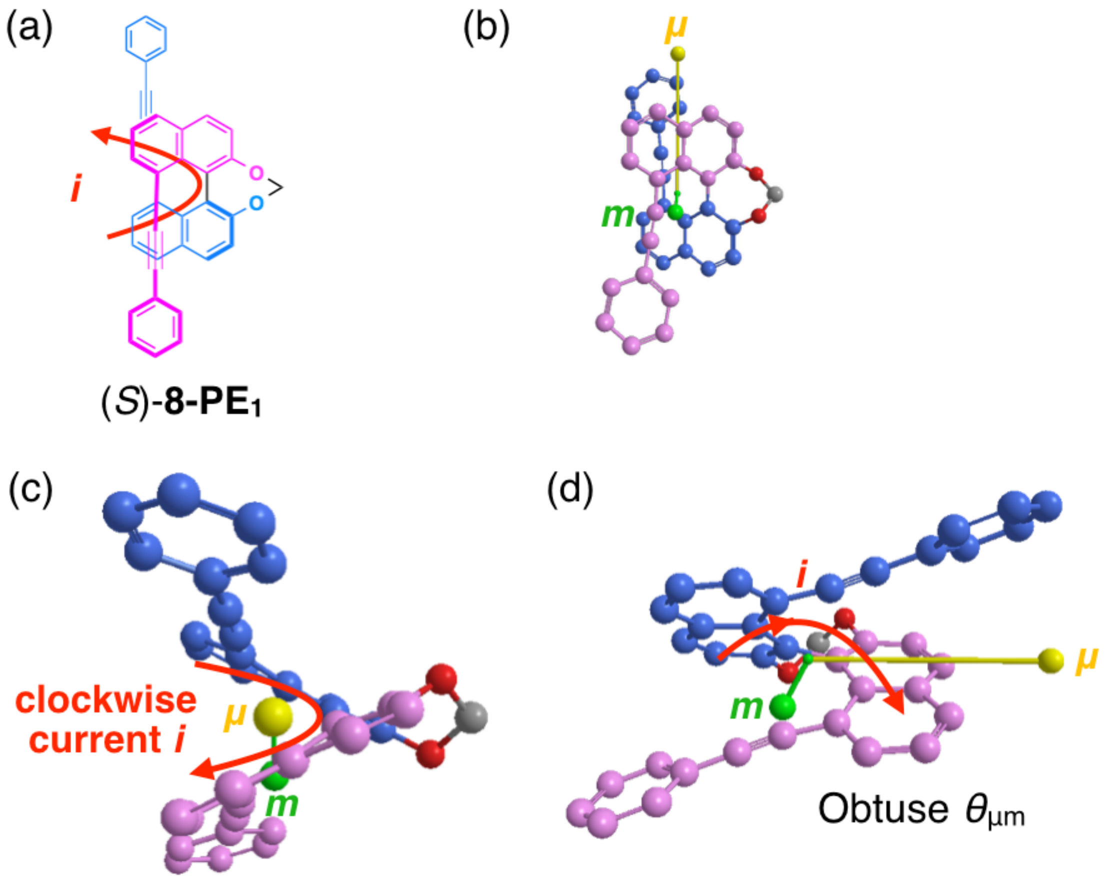


Figure S6. (a) Expected electric current flow (*i* is shown in red) for the $S_1 \rightarrow S_0$ transitions for (*S*)-**8-PE$_1$**. (b) Electric (μ is shown in yellow) and magnetic (m is shown in green) transition dipole moments for the $S_1 \rightarrow S_0$ transitions for (*S*)-**8-PE$_1$**. For clarity, the relative length of m is magnified by 137 times compared with that of μ. (c) Top view from the direction of μ. The current flows clockwise relative to the origin-μ axis. (d) Side view from the direction of μ. The $\theta_{\mu m}$ is clearly obtuse.

4. Computational Data

Table S3. Atomic coordinate of optimized structure of (*S*)-**7-PE**$_1$ in the excited state.
The origin, μ, and m are represented by replacing the atoms F, X, and W, respectively.

Compound: (*S*)-**7-PE**$_1$

Method: Time-dependent approximate coupled cluster calculations at the RI-CC2/def2-TZVP level

Energy: –1570.3224574584 hartree

F	0.0	0.0	0.0
X	2.392723202	-4.797788909	4.020134801
W	-1.152890749	4.45118932	8.705194258
C	-1.5931768	2.7498860	-1.3302891
C	-0.9572192	1.4827907	-1.4100746
C	-1.6719002	0.3246129	-0.9957039
C	-2.9012577	0.4057535	-0.3559870
C	-3.5512848	1.6995243	-0.3028371
C	-2.8608358	2.8408146	-0.8071136
C	-3.5715051	-0.7652970	0.2098926
C	-4.9089136	-0.5582501	0.6847378
C	-5.5152183	0.6817679	0.7029339
C	-4.8398001	1.8135531	0.2124925
C	-2.9983486	-2.0637512	0.3530779
C	-1.6164231	-2.3491913	0.7405163
C	-1.1287485	-3.7130726	0.7023259
C	-1.9919235	-4.7553808	0.3744608
C	-3.3375774	-4.4956789	0.0592415
C	-3.8211511	-3.2028099	0.0662674
C	-0.7507603	-1.3646135	1.1973121
C	0.6290328	-1.6197488	1.4309704
C	1.1029640	-2.9567558	1.3660283
C	0.2358672	-3.9681894	1.0283340
O	-5.0883450	-2.9982820	-0.4445904
O	-5.5428915	-1.5824927	1.3607121
C	-6.0369101	-2.6025121	0.5209570
C	1.4906817	-0.5341698	1.5697607
C	0.3894253	1.3480912	-1.7391086

C	1.6176031	1.1840730	-1.8347849
C	2.2197459	0.4696942	1.4985301
C	2.9894300	0.9020328	-1.7845200
C	2.9396904	1.6508770	1.2725907
C	4.3460328	1.7005147	1.3994865
C	5.0290034	2.8683926	1.0886655
C	4.3343973	3.9979351	0.6397886
C	2.9417943	3.9609419	0.5228805
C	2.2413649	2.8018755	0.8358233
C	3.4074808	-0.3691004	-1.3233744
C	4.7626119	-0.6441902	-1.1814943
C	5.7170383	0.3280120	-1.4943967
C	5.3101987	1.5811480	-1.9682483
C	3.9611248	1.8748427	-2.1103470
H	-1.0611744	3.6338829	-1.6682366
H	-1.1853065	-0.6376979	-1.1225757
H	-3.3607974	3.8048321	-0.7525423
H	-6.4973320	0.7670539	1.1575406
H	-5.3203312	2.7880961	0.2389472
H	-1.6159545	-5.7750491	0.3577796
H	-4.0056232	-5.2928674	-0.2516918
H	-1.0983568	-0.3423052	1.3112086
H	2.1502483	-3.1598476	1.5676977
H	0.5864917	-4.9966118	0.9872702
H	4.8775359	0.8158217	1.7345550
H	6.1095463	2.9000067	1.1855521
H	4.8762023	4.9056954	0.3944254
H	2.4015896	4.8390745	0.1830337
H	1.1601373	2.7575596	0.7440505
H	2.6552172	-1.1130294	-1.0782301
H	5.0774677	-1.6189383	-0.8221045
H	6.7737711	0.1079860	-1.3816231
H	6.0521787	2.3331702	-2.2169433
H	3.6362228	2.8482629	-2.4629537
H	-6.2903701	-3.4259641	1.1955629
H	-6.9026602	-2.2627785	-0.0556389

Table S4. Atomic coordinate of optimized structure of (*S*)-**6-PE$_1$** in the excited state.
The origin, μ, and *m* are represented by replacing the atoms F, X, and W, respectively.

Compound: (*S*)-**6-PE$_1$**

Method: Time-dependent approximate coupled cluster calculations at the RI-CC2/def2-TZVP level

Energy: –1570.3056391648 hartree

F	0.0	0.0	0.0
X	-11.80419394	4.531878535	3.550830721
W	-0.26188213	0.916222888	-4.204782331
C	-2.7305688	1.1446613	-0.2773476
C	-1.7493127	0.5040052	-1.0732423
C	-1.7079828	-0.8782501	-1.1392797
C	-2.6262484	-1.6809820	-0.4252261
C	-3.7096353	-1.0305728	0.2599884
C	-3.7156158	0.3643483	0.3600606
C	-2.4780193	-3.1149104	-0.3876005
C	-3.6759544	-3.8352736	-0.0129854
C	-4.7779676	-3.1825129	0.5674027
C	-4.7727402	-1.8143371	0.7741122
C	-1.2110261	-3.7006174	-0.6931643
C	0.0329860	-3.0266545	-0.3544113
C	1.1949481	-3.2513181	-1.1752690
C	1.1404195	-4.2275190	-2.1976268
C	0.0184387	-5.0653776	-2.3341008
C	-1.1011586	-4.8364261	-1.5643724
C	0.1492594	-2.1791046	0.7584745
C	1.3236663	-1.4767437	1.0218239
C	2.4366267	-1.6114930	0.1681917
C	2.3638710	-2.5049430	-0.9133436
C	-2.7511226	2.5483970	-0.1526525
C	3.6161067	-0.8651637	0.4088512
O	-2.1909499	-5.6798556	-1.7171545
O	-3.8411945	-5.1650601	-0.1074493
C	4.6409368	-0.2124783	0.6184241
C	-2.7581521	3.7773098	-0.0473435

C	-2.7592133	5.1888288	0.0736850
C	5.8198071	0.5392826	0.8584316
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C	8.0846731	1.1596730	0.2416212
C	8.1534750	2.0281475	1.3328743
C	7.0558882	2.1522975	2.1870765
C	5.8971662	1.4166821	1.9561030
C	-1.7449965	5.9526912	-0.5334368
C	-1.7486109	7.3384788	-0.4116282
C	-2.7568996	7.9788637	0.3121267
C	-3.7662531	7.2266448	0.9171392
C	-3.7719581	5.8403251	0.8019137
C	-2.7487517	-6.0259596	-0.4961221
H	-1.0385703	1.1057201	-1.6294534
H	-0.9625986	-1.3629173	-1.7637702
H	-4.5035091	0.8607237	0.9215673
H	-5.6083709	-3.8035086	0.8872242
H	-5.5985463	-1.3294284	1.2868659
H	2.0220134	-4.4016077	-2.8091000
H	0.0171224	-5.9042429	-3.0235890
H	-0.7070305	-2.0519889	1.4179592
H	1.3877971	-0.8173698	1.8819538
H	3.2334358	-2.6383362	-1.5528964
H	6.8722962	-0.2567658	-0.8438127
H	8.9340537	1.0580490	-0.4256989
H	9.0547939	2.6028525	1.5162473
H	7.1029191	2.8248002	3.0371644
H	5.0419528	1.5093639	2.6171545
H	-0.9652052	5.4466694	-1.0925123
H	-0.9634704	7.9207110	-0.8815368
H	-2.7558639	9.0594133	0.4046609
H	-4.5499080	7.7221936	1.4798540
H	-4.5518113	5.2481254	1.2687079
H	-1.9970743	-6.0107559	0.3010401
H	-3.2288232	-6.9964405	-0.6049397

Table S5. Atomic coordinate of optimized structure of (*S*)-**6-PE$_{\mathbf{Me}}$** in the excited state.

Compound: (*S*)-**6-PE$_{\mathbf{Me}}$**

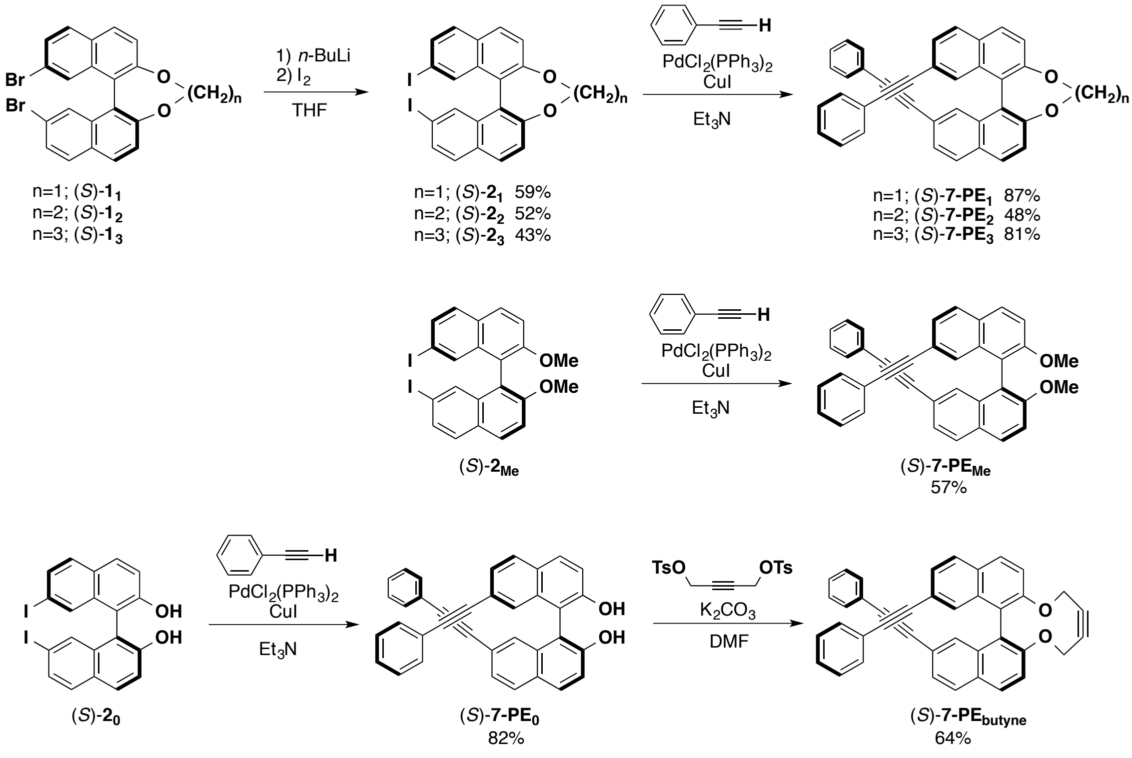
Method: Time-dependent approximate coupled cluster calculations at the RI-CC2/def2-TZVP level

Energy: –1610.7120760722 hartree

C	-2.4803896	2.5376033	-0.3059643
C	-1.4937511	1.8642816	-1.0495276
C	-1.4123762	0.4640860	-0.9775875
C	-2.2881213	-0.2835938	-0.1642343
C	-3.3451681	0.3965561	0.5728993
C	-3.4051782	1.7970197	0.4999942
C	-2.1995003	-1.6909095	-0.0454128
C	-3.1714099	-2.4023839	0.7380500
C	-4.2344399	-1.7598247	1.3982207
C	-4.2793558	-0.3545958	1.3251549
C	-1.1456376	-2.4521730	-0.7123672
C	0.2238628	-2.2886558	-0.3637150
C	1.2306992	-3.0344899	-1.0585595
C	0.8351018	-3.9293748	-2.0792770
C	-0.4962970	-4.0890747	-2.4120191
C	-1.4875488	-3.3465280	-1.7354816
C	0.6304499	-1.4270286	0.6882182
C	1.9603829	-1.2864548	1.0135686
C	2.9672045	-2.0063673	0.3090524
C	2.5887020	-2.8723925	-0.7103584
C	-2.5791698	3.9339299	-0.3496986
C	4.3320504	-1.8400449	0.6558680
O	-2.8134946	-3.4069499	-2.0449703
O	-2.9270137	-3.7196900	0.8232906
C	5.5134789	-1.6855872	0.9677299
C	-2.6855894	5.1670366	-0.3738765
C	-2.7957200	6.5743906	-0.4079166
C	6.8766111	-1.5092412	1.3235841
C	7.8868750	-2.2222798	0.6530375
C	9.2217273	-2.0455665	1.0054166
C	9.5700920	-1.1598324	2.0269720
C	8.5727359	-0.4485379	2.6969308

C	7.2351905	-0.6185752	2.3516225
C	-1.9059465	7.3420345	-1.1865611
C	-2.0191768	8.7276685	-1.2162337
C	-3.0143291	9.3706225	-0.4756709
C	-3.9003542	8.6174382	0.2988019
C	-3.7967696	7.2312356	0.3361749
C	-3.8627288	-4.5221277	1.5609791
C	-3.1931040	-4.2883758	-3.0990516
H	-0.8112685	2.4327903	-1.6719494
H	-0.6609538	-0.0633216	-1.5587963
H	-4.1701959	2.3385762	1.0510654
H	-4.9423297	-2.3025907	2.0095022
H	-5.0653131	0.1834689	1.8501295
H	1.5962304	-4.4975220	-2.6075355
H	-0.7638814	-4.7757961	-3.2059246
H	-0.1252933	-0.8739069	1.2378479
H	2.2601284	-0.6220852	1.8178523
H	3.3474358	-3.4375021	-1.2461098
H	7.6100342	-2.9089853	-0.1398436
H	9.9926162	-2.6004489	0.4813341
H	10.6112630	-1.0246969	2.2988615
H	8.8378114	0.2413313	3.4910389
H	6.4559571	-0.0684440	2.8683170
H	-1.1358064	6.8353137	-1.7584120
H	-1.3295150	9.3094751	-1.8184393
H	-3.0986945	10.4516092	-0.5017612
H	-4.6741523	9.1134788	0.8749915
H	-4.4808159	6.6393836	0.9351766
H	-3.4961253	-5.5413979	1.4699012
H	-3.8781444	-4.2166357	2.6088156
H	-4.8596793	-4.4325390	1.1252737
H	-4.2719597	-4.1819482	-3.1900056
H	-2.7163734	-4.0051818	-4.0417887
H	-2.9435684	-5.3256720	-2.8566240

5. Syntheses of Compounds



Scheme S1. Synthetic route for **7-PE$_n$**

General procedures for the conversion of bromo derivatives to iodine derivatives

(*S*)-**2$_1$**

Compound (*S*)-**1$_1$** (115 mg, 0.25 mmol, 1.0 equiv.) was stirred under N_2 at –78 °C in THF (5 mL) while a *n*-hexane solution of *n*-BuLi (336 μL, 0.53 mmol, 2.1 equiv.) was added dropwise. After 45 minutes, a THF solution of iodine (135 mg, 0.53 mmol, 2.1 equiv.) was added dropwise at –78 °C, and the mixture was stirred for 15 min. The reaction mixture was quenched with an aqueous solution of $Na_2S_2O_3$, followed by extraction with AcOEt. The organic layer was washed with water (twice) and brine, dried over Na_2SO_4, filtered, and evaporated to dryness under a reduced pressure. The crude product was purified by column chromatography (SiO_2, Hexane/AcOEt 5/1) to afford compound (*S*)-**2$_1$** (82 mg, 59% yield) as a white solid. M.p. 197–199 °C. $[\alpha]_D^{24}$ +925.00 ($CHCl_3$, c = 0.0535 g/dL). ^1H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 8.7 Hz, 2H), 7.88 (d, J = 1.4 Hz, 2H), 7.73 (dd, J = 8.7, 1.8 Hz, 2H), 7.67 (d, J = 8.7 Hz, 2H), 7.48 (d, J = 8.7 Hz, 2H), 5.68 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0, 135.5, 134.0, 133.4, 130.8, 130.7, 130.1, 124.7, 121.8, 103.4, 92.8. HRMS (ESI): m/z calcd for $C_{21}H_{12}I_2O_2Na$ $[M+Na]^+$: 572.88189, found 572.88353.

(*S*)-**2**$_2$

52% as a white solid. M.p. 214–216 °C. $[\alpha]_D^{24}$ +1109.09 ($CHCl_3$, *c* = 0.0995 g/dL). ^1H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 9.2 Hz, 2H), 7.68 (dd, *J* = 8.7, 1.8 Hz, 2H), 7.62 (d, *J* = 8.7 Hz, 2H), 7.58 (s, 2H), 7.45 (d, *J* = 8.7 Hz, 2H), 4.41 (dd, *J* = 19.7, 10.5 Hz, 2H), 4.15 (dd, *J* = 19.7, 10.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3, 135.4, 134.4, 133.8, 131.3, 129.9, 123.3, 122.8, 93.1, 73.1 (one signal overlapping). HRMS (ESI): m/z calcd for $C_{22}H_{14}I_2O_2Na$ $[M+Na]^+$: 586.89754, found 586.89755.

(*S*)-**2**$_3$

43% yield as a white solid. M.p. 151–153 °C. $[\alpha]_D^{24}$ +496.17 ($CHCl_3$, *c* = 0.326 g/dL). ^1H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.7 Hz, 2H), 7.65 (dd, *J* = 8.7, 1.8 Hz, 2H), 7.61 (d, *J* = 8.7 Hz, 2H), 7.58 (s, 2H), 7.45 (d, *J* = 9.2 Hz, 2H), 4.39–4.29 (m, 5H), 1.93 (quin, *J* = 5.03 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.5, 135.0, 134.4, 133.3, 130.2, 130.0, 129.3, 122.4, 119.9, 93.4, 72.2, 30.6. HRMS (ESI): m/z calcd for $C_{23}H_{16}I_2O_2$ $[M]^+$: 577.92342, found 577.92343.

General procedures for the introduction of phenylethynyl group via Sonogashira coupling

(*S*)-**7-PE**$_1$

Compounds (*S*)-**2**$_1$ (70 mg, 0.128 mmol, 1.0 equiv), $PdCl_2(PPh_3)_2$ (1.3 mg, 0.0019 mmol, 0.015 equiv.), and CuI (0.7 mg, 0.004 mmol, 0.030 eq.) were stirred in degassed Et_3N and then ethynylbenzene (42 µL, 0.384 mmol, 3.0 equiv.) was added dropwise. After 16 hours, the reaction mixture was quenched with water and filtered through Celite. The resulting mixture was extracted with AcOEt, and the organic layer was washed with water and brine, then dried over Na_2SO_4, filtered, and evaporated to dryness under a reduced pressure. The crude product was purified by column chromatography (SiO_2, Hexane/AcOEt 3/1) to afford compound (*S*)-**7-PE**$_1$ (55 mg, 87% yield) as a white solid. M.p. 220–222 °C. $[\alpha]_D^{25}$ +1891.08 ($CHCl_3$, *c* = 0.0705 g/dL). ^1H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.7 Hz, 2H), 7.91 (d, *J* = 8.7 Hz, 2H), 7.70 (s, 2H), 7.57 (dd, *J* = 8.7, 0.9 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.43–7.41 (m, 4H), 7.27–7.24 (m, 6H), 5.67 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 132.1, 131.8, 131.3, 130.5, 129.7, 128.7, 128.4, 128.2, 125.9, 123.2, 121.7, 121.5, 103.2, 90.2, 90.0 (one signal overlapping). HRMS (ESI): m/z calcd for $C_{37}H_{22}O_2$ $[M]^+$: 498.16143, found 498.16143.

(*S*)-**7-PE**$_2$

48% yield as a brown solid. M.p. 122–124 °C. $[\alpha]_D^{24}$ +1449.63 ($CHCl_3$, *c* = 0.0695 g/dL). ^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.7 Hz, 2H), 7.88 (d, *J* = 8.7 Hz, 2H), 7.53 (dd, *J* = 8.2, 1.8 Hz, 2H), 7.47 (t, *J* = 8.7 Hz, 2H), 7.44–7.41 (m, 6H), 7.27–7.25 (m, 6H), 4.41 (dd, *J* = 19.7, 10.5 Hz, 2H), 4.17 (dd, J = 19.7, 10.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3, 132.9, 131.7, 131.0, 130.6, 130.0, 128.4, 128.3, 128.0, 124.0, 123.3, 123.2, 121.6, 90.2, 90.0, 73.2 (one signal overlapping). HRMS (ESI): m/z calcd for $C_{38}H_{24}O_2$ $[M]^+$: 512.17708, found 512.17745.

(*S*)-7-PE$_3$

81% yield as a white solid. M.p. 140–142 °C. $[\alpha]_D^{24}$ +1118.05 ($CHCl_3$, c = 0.0590 g/dL). ^{1}H NMR (400 MHz, $CDCl_3$): δ NMR 7.96 (d, J = 8.7 Hz, 2H), 7.87 (d, J = 8.2 Hz, 2H), 7.50 (dd, J = 8.2, 1.4 Hz, 2H), 7.47 (d, J = 8.7 Hz, 2H), 7.44–7.41 (m, 6H), 7.27–7.25 (m, 6H), 4.36–4.34 (m, 4H), 1.94 (q, J = 5.0, 2H).^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 133.4, 131.7, 130.0, 129.9, 129.2, 128.5, 128.33, 128.27, 127.5, 123.8, 123.3, 121.6, 120.1, 90.3, 89.8, 72.3, 30.7. HRMS (ESI): m/z calcd for $C_{39}H_{26}O_2$ $[M]^+$: 526.19273, found 526.19273.

(*S*)-7-PE$_{Me}$

57% yield as a white solid. M.p. 236–237 °C. $[\alpha]_D^{25}$ +881.16 ($CHCl_3$, c = 0.0810 g/dL). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 9.2 Hz, 2H), 7.85 (d, J = 8.2 Hz, 2H), 7.48–7.43 (m, 8H), 7.30–7.26 (m, 8H), 3.77 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.6, 133.9, 131.7, 129.6, 128.71, 128.68, 128.4, 128.29, 128.27, 126.5, 123.3, 121.2, 119.1, 114.8, 90.5, 89.6, 56.9. HRMS (ESI): m/z calcd for $C_{38}H_{26}O_2Na$ $[M+Na]^+$: 537.18250, found 537.18250.

(*S*)-7-PE$_0$

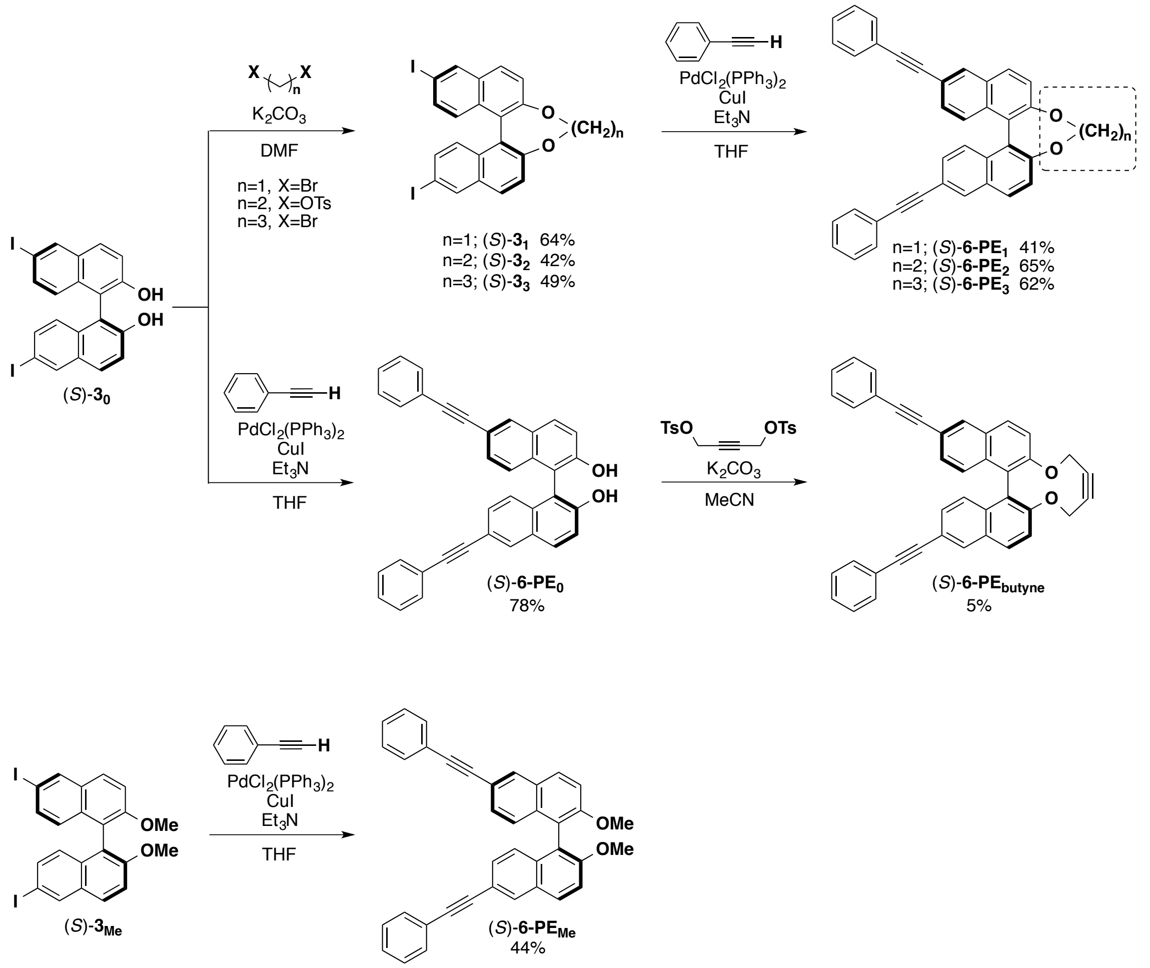
Compound (*S*)-**7-PE$_0$** was synthesized using a similar synthetic method as compound (*S*)-**7-PE$_1$**, except during the extraction step, where the organic layer was extracted with AcOEt and washed successively with water, HCl aqueous solution, water, and brine.

82% yield as a pale yellow amorphous. $[\alpha]_D^{25}$ +1138.01 ($CHCl_3$, c = 0.152 g/dL). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 8.7 Hz, 2H), 7.82 (d, J = 8.7 Hz, 2H), 7.47 (d, J = 8.2 Hz, 2H), 7.43–7.42 (m, 4H), 7.32–7.19 (m, 10H), 5.15 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.5, 133.3, 131.7, 131.6, 129.0, 128.7, 128.5, 128.4, 127.4, 127.1, 123.0, 122.5, 118.7, 110.4, 90.4, 89.8. HRMS (ESI): m/z calcd for $C_{36}H_{22}O_2Na$ $[M+Na]^+$: 509.15120, found 509.15055.

Procedures for the butynyl tethering of the hydroxy groups of binaphthol

(*S*)-**7-PE$_{\mathbf{butyne}}$**

Compounds (*S*)-**7-PE$_{\mathbf{0}}$** (160 mg, 0.33 mmol, 1.0 equiv.), 1,4-bis(tosyloxy)but-2-yne (142 mg, 0.36 mmol, 1.1 equiv.), and K_2CO_3 (136 mg, 0.99 mmol, 3.0 equiv.) were stirred in DMF (16 mL) at room temperature. After 20 hours, the reaction mixture was quenched with water and extracted with AcOEt, and the organic layer was washed with water and brine, then dried over Na_2SO_4, filtered, and evaporated to dryness under a reduced pressure. The crude product was purified by column chromatography (SiO_2, Hexane/AcOEt 3/1) to afford compound (*S*)-**7-PE$_{\mathbf{butyne}}$** (113 mg, 64% yield) as a white solid. M.p. 155–158 °C. $[\alpha]_D^{25}$ +572.05 ($CHCl_3$, *c* = 0.211 g/dL). ^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.7 Hz, 2H), 7,87 (d, *J* = 8.2 Hz, 2H), 7.56–7.53 (m, 2H), 7.49 (s, 2H), 7.45–7.43 (m, 6H), 7.27–7.25 (m, 6H), 4.50 (ddd, *J* = 38.9, 17.8, 3.2 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.3, 133.7, 131.7, 130.7, 130.4, 129.6, 128.4, 128.1, 127.4, 123.2, 122.1, 121.6, 90.31, 90.24, 88.2, 62.4 (two signals overlapping). HRMS (ESI): m/z calcd for $C_{40}H_{24}O_2Na$ $[M+Na]^+$: 559.16685, found 559.16764.



Scheme S2. Synthetic route for **6-PE**$_n$

Procedures for the linking (n=1, 2, 3) of the hydroxy group of binaphthol

(*S*)-**3**$_1$

To a DMF solution (20 mL) of (*S*)-**3**$_0$ (4.3 g, 8.0 mmol, 1.0 equiv.) was added K_2CO_3 (11 g, 80 mmol, 10 equiv.), followed by dibromomethane (8.7 mL, 125 mmol, 15 equiv.). The mixture was stirred at 85 °C under N_2 atmosphere for 5 hours, then water was added to quench the reaction. The mixture was extracted with AcOEt. The organic layer was washed with 1 M HCl aqueous solution, water (twice) and brine, then dried over Na_2SO_4, filtered, and evaporated to dryness under a reduced pressure. After purification by column chromatography (SiO_2, Hexane/AcOEt 10/1), compound (*S*)-**3**$_1$ was obtained (2.80 g, 64% yield) as a white solid. M.p. 203–205 °C. $[\alpha]_D^{23}$ +558.90 ($CHCl_3$, *c* = 0.136 g/dL). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 1.8 Hz, 2H), 7.86 (d, *J* = 8.7 Hz, 2H), 7.53 (dd, *J* = 9.2, 1.8 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.17 (d, *J* = 9.2 Hz, 2H), 5.69 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.8, 137.2, 134.8, 133.5, 130.9, 129.6, 128.3, 125.9, 122.1, 103.3, 90.8. HRMS (FAB): m/z calcd for $C_{21}H_{12}I_2O_2$ $[M]^+$: 549.89212, found 549.8927.

(*S*)-**3₂**

To a DMF solution (2 mL) of (*S*)-**3₀** (65 mg, 0.12 mmol, 1.0 equiv.) was added K_2CO_3 (82 mg, 0.60 mmol, 5.0 equiv.), followed by 1,2-bis(tosyloxy)ethane (59 mg, 0.16 mmol, 1.3 equiv.). The mixture was stirred at 60 °C under N_2 atmosphere for 18 hours, then water was added to quench the reaction. The mixture was extracted with AcOEt. The organic layer was washed with water (twice) and brine, then dried over Na_2SO_4, filtered, and evaporated to dryness under a reduced pressure. After purification by column chromatography (SiO_2, Hexane/AcOEt 10/1), compound (*S*)-**3₂** was obtained (29 mg, 42% yield) as a white solid. M.p. 182–184 °C. $[\alpha]_D^{22}$ +385.54 ($CHCl_3$, c = 0.137 g/dL). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J = 1.8 Hz, 2H), 7.86 (d, J = 8.7 Hz, 2H), 7.46 (dd, J = 8.7, 1.8 Hz, 2H), 7.44 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 9.2 Hz, 2H), 4.41 (dd, J = 19.7, 10.5 Hz, 2H), 4.16 (dd, J = 19.7, 10.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.1, 136.9, 135.0, 132.7, 131.8, 130.0, 128.6, 124.0, 123.7, 90.6, 73.0. HRMS (EI): m/z calcd for $C_{22}H_{14}I_2O_2$ $[M]^+$: 563.90777, found 563.9082.

(*S*)-**3₃**

To a DMF solution (2 mL) of (*S*)-**3₀** (40 mg, 0.075 mmol, 1.0 equiv.) was added K_2CO_3 (51 mg, 0.374 mmol, 5.0 equiv.), followed by 1,3-dibromopropane (76 μL, 0.75 mmol, 10 equiv.). The mixture was stirred at 70 °C under N_2 atmosphere for 2 hours, then 1 M HCl aqueous solution was added to quench the reaction. The mixture was extracted with AcOEt. The organic layer was washed with water (twice) and brine, then dried over Na_2SO_4, filtered, and evaporated to dryness under a reduced pressure. After purification by column chromatography (SiO_2, Hexane/AcOEt 10/1), compound (*S*)-**3₃** was obtained (21 mg, 49% yield) as a white solid. M.p. 210–212 °C. $[\alpha]_D^{23}$ +330.10 ($CHCl_3$, c = 0.0680 g/dL). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (s, 2H), 7.83 (d, J = 9.2 Hz, 2H), 7.48-7.44 (m, 4H), 6.94 (d, J = 9.2 Hz, 2H), 4.41–4.30 (m, 4H), 1.97–1.92 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.3, 137.0, 135.1, 132.21, 132.17, 129.0, 127.8, 123.6, 120.3, 89.8, 72.1, 30.7. HRMS (FT-ICR): m/z calcd for $C_{23}H_{16}I_2O_2$ $[M]^+$: 577.92342, found 577.9238.

Procedures for the introduction of phenylethynyl group via Sonogashira coupling

(*S*)-**6-PE₁**

Compound (*S*)-**6-PE₁** was synthesized using (*S*)-**3₁** as the starting material and following a similar synthetic method as compound (*S*)-**7-PE₁**.

41% as a pale yellowish white solid. M.p. 272–273 °C. $[\alpha]_D^{20}$ +882.63 ($CHCl_3$, c = 0.158 g/dL). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (s 2H), 7.98 (d, J = 8.7 Hz, 2H), 7.59–7.57 (m, 4H), 7.51 (d, J = 8.7 Hz, 2H), 7.47–7.41 (m, 4H), 7.38–7.36 (m, 6H), 5.72 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0, 132.0, 131.7, 131.5, 130.4, 128.8, 128.5, 126.9, 126.0, 123.2, 121.8, 120.0, 103.3, 90.2, 89.6 (two signals overlapping). HRMS (EI): m/z calcd for $C_{37}H_{23}O_2$ $[M+H]^+$: 499.1693, found 499.1679.

(*S*)-**6-PE$_2$**

Compound (*S*)-**3$_2$** (300 mg, 0.53 mmol, 1.0 equiv.), $PdCl_2(PPh_3)_2$ (112 mg, 0.16 mmol, 0.30 equiv.) and CuI (51 mg, 0.27 mmol, 0.50 equiv.) were sequentially added to a flask, followed by the addition of degassed THF (3 mL). Degassed Et_3N (371 μL, 2.7 mmol, 5.0 equiv.) was then added, followed by ethynylbenzene (175 μL, 1.6 mmol, 3.0 equiv.), and the mixture was stirred at room temperature for 5 hours. The reaction was quenched by the addition of water and AcOEt, followed by filtration through Celite. The organic layer was washed with water (3 times) and brine, dried over Na_2SO_4, filtered, and evaporated to dryness under a reduced pressure. After purification by column chromatography (SiO_2, Hexane/AcOEt 10/1), compound (*S*)-**6-PE$_2$** was obtained (179 mg, 65% yield) as a brown solid. M.p. 261 °C (decomposition). $[\alpha]_D^{22}$ +667.26 ($CHCl_3$, *c* = 0.0525 g/dL). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (s, 2H), 7.97 (d, *J* = 9.2 Hz, 2H), 7.57–7.55 (m, 4H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.35–7.34 (m, 8H), 7.20 (d, *J* = 8.7 Hz, 2H), 4.44 (dd, *J* = 20.1, 11.4 Hz, 2H), 4.20 (dd, *J* = 20.1, 11.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4, 132.4, 131.8, 131.7, 130.9, 130.8, 129.1, 128.5, 128.4, 127.2, 124.1, 123.41, 123.36, 119.8, 89.9, 89.7, 73.1. HRMS (EI): m/z calcd for $C_{38}H_{24}O_2$ $[M]^+$: 512.17708, found 512.1779.

(*S*)-**6-PE$_3$**

Compound (*S*)-**6-PE$_3$** was synthesized using (*S*)-**3$_3$** as the starting material and following a similar synthetic method as compound (*S*)-**6-PE$_2$**.

62% as a brown solid. M.p. 234–239 °C. $[\alpha]_D^{21}$ +677.90 ($CHCl_3$, *c* = 0.0715 g/dL). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 2H), 7.95 (d, *J* = 9.2 Hz, 2H), 7.57–7.55 (m, 4H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.38–7.33 (m, 8H), 7.22 (d, *J* = 8.7 Hz, 2H), 4.43–4.37 (m, 4H), 2.00–1.98 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7, 132.9, 131.9, 131.8, 130.2, 129.9, 129.2, 128.5, 128.3, 126.3, 123.7, 123.5, 120.0, 119.1, 90.0, 89.6, 72.1, 30.7. HRMS (ESI): m/z calcd for $C_{39}H_{26}O_2Na$ $[M+Na]^+$: 549.18250, found 549.18506.

(*S*)-**6-PE$_{Me}$**

Compound (*S*)-**6-PE$_{Me}$** was synthesized using (*S*)-**3$_{Me}$** as the starting material and following a similar synthetic method as compound (*S*)-**7-PE$_1$**.

44% yield as a light yellowish white solid. M.p. 183–185 °C. $[\alpha]_D^{23}$ +326.36 ($CHCl_3$, *c* = 0.0945 g/dL). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 1.8 Hz, 2H), 7.97 (d, *J* = 9.2 Hz, 2H), 7.56-7.54 (m, 4H), 7.48 (d, *J* = 9.2 Hz, 2H), 7.35–7.31 (m, 8H), 7.07 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 133.5, 131.8, 131.7, 129.7, 129.1, 128.8, 128.5, 128.2, 125.4, 123.6, 119.2, 118.2, 114.6, 90.1, 89.3, 56.8. HRMS (ESI): m/z calcd for $C_{38}H_{26}O_2Na$ $[M+Na]^+$: 537.18250, found 537.18517.

(*S*)-**6-PE$_0$**

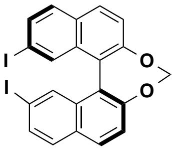
Compound (*S*)-**3$_0$** (1.4 g, 2.6 mmol, 1.0 equiv.), $PdCl_2(PPh_3)_2$ (91 mg, 0.13 mmol, 0.050 equiv.) and CuI (25 mg, 0.13 mmol, 0.050 equiv.) were sequentially added to a flask, followed by the addition of degassed THF (14 mL). Degassed Et_3N (1.8 mL, 1.3 mmol, 5.0 equiv.) was then added, followed by ethynylbenzene (600 μL, 5.5 mmol, 2.1 equiv.), and the mixture was stirred at room temperature for 2 hours. The reaction was quenched by the addition of 1 M HCl aqueous solution, followed by filtration through Celite. The mixture was extracted with AcOEt. The organic layer was washed with water (twice) and brine, dried over Na_2SO_4, filtered, and evaporated to dryness under a reduced pressure. After purification by column chromatography (SiO_2, Hexane/AcOEt 10/1), compound (*S*)-**6-PE$_0$** was obtained (987 mg, 78% yield) as yellow solid. M.p. 150–152 °C. $[\alpha]_D^{22}$ +472.18 ($CHCl_3$, *c* = 0.125 g/dL). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 1.4 Hz, 2H), 7.97 (d, *J* = 9.2 Hz, 2H), 7.43 (dd, *J* = 8.7, 1.8 Hz, 2H), 7.42 (d, *J* = 9.2 Hz, 2H), 7.38-7.34 (m, 6H), 7.11 (d, *J* = 8.7 Hz, 2H), 5.10 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.6, 133.0, 132.1, 131.8, 131.6, 130.3, 129.3, 128.5, 128.4, 124.4, 123.4, 119.1, 118.7, 110.8, 89.8, 89.6. HRMS (ESI): m/z calcd for $C_{37}H_{22}O_2Na$ $[M+Na]^+$: 509.15120, found 509.15340.

Procedures for the butynyl tethering of the hydroxy groups of binaphthol

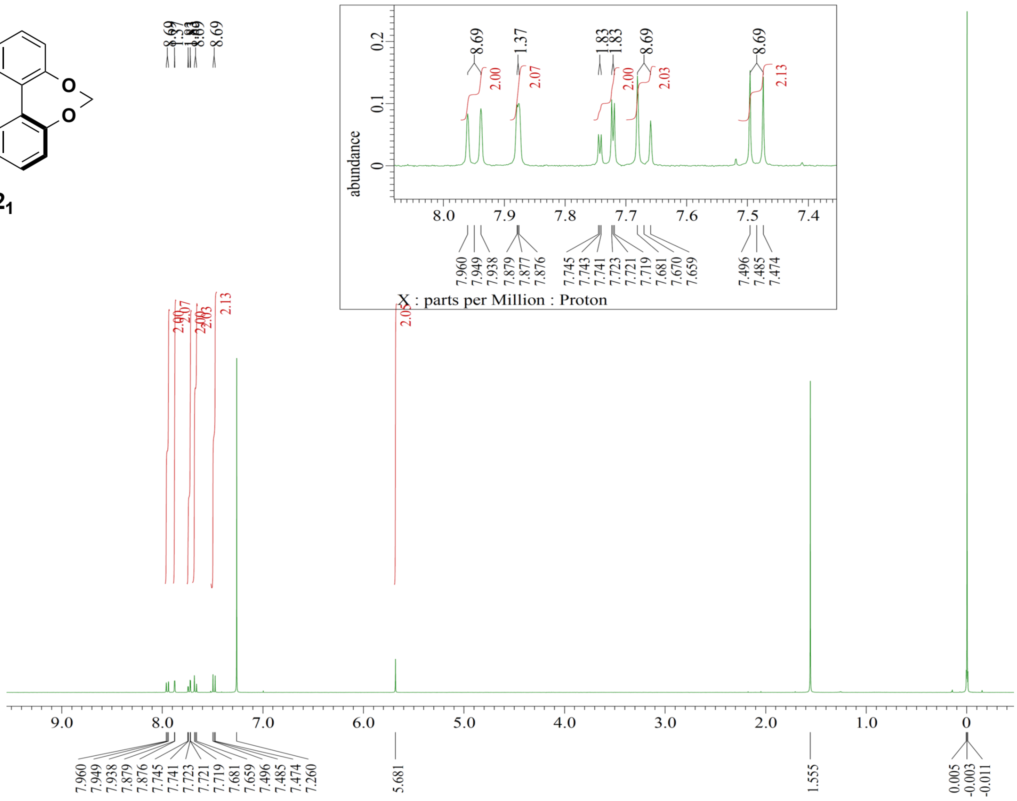
(*S*)-**6-PE$_{butyne}$**

Compounds (*S*)-**6-PE$_0$** (400 mg, 0.82 mmol, 1.0 equiv.) 1,4-bis(tosyloxy)but-2-yne (391 mg, 0.99 mmol, 1.2 equiv.), and K_2CO_3 (566 mg, 4.1 mmol, 5.0 equiv.) were stirred in acetonitrile (4 mL) at 50 °C. After 21 hours, the reaction mixture was quenched with 1 M HCl aqueous solution, and extracted with AcOEt. The organic layer was washed with water (twice) and brine, dried over Na_2SO_4, filtered, and evaporated to dryness under a reduced pressure. The crude product was subjected to column chromatography (SiO_2, Hexane/AcOEt 10/1), followed by further purification using a gel filtration column to afford compound (*S*)-**6-PE$_{butyne}$** (23 mg, 5% yield) as a white solid. M.p. 126–129 °C. $[\alpha]_D^{22}$ +359.08 ($CHCl_3$, *c* = 0.0500 g/dL). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 1.4 Hz, 2H), 8.01 (d, *J* = 8.7 Hz, 2H), 7.57–7.55 (m, 4H), 7.47–7.42 (m, 4H), 7.38–7.33 (m, 6H), 7.29 (d, *J* = 8.7 Hz, 2H), 4.52 (ddd, *J* = 34.3, 18.3, 3.7 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.4, 133.2, 131.8, 131.7, 131.0, 130.5, 129.4, 128.5, 128.4, 127.8, 126.4, 123.4, 122.1, 120.3, 89.9, 89.8, 88.1, 62.5. HRMS (ESI): m/z calcd for $C_{40}H_{24}O_2Na$ $[M+Na]^+$: 559.16685, found 559.16819.

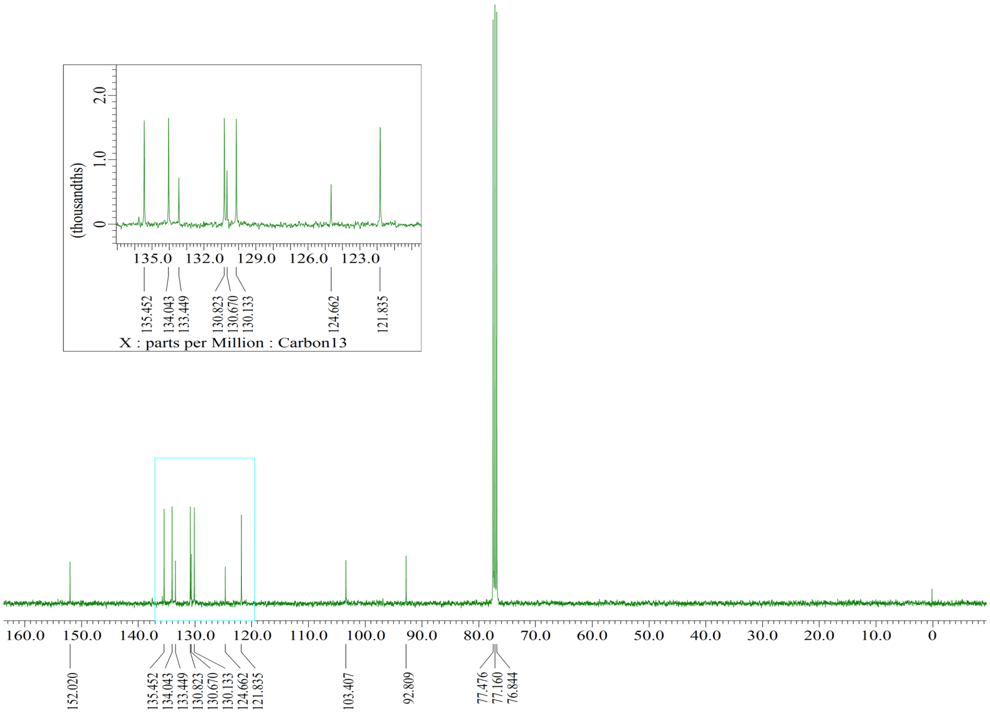
6. ^{1}H and ^{13}C NMR Spectroscopy



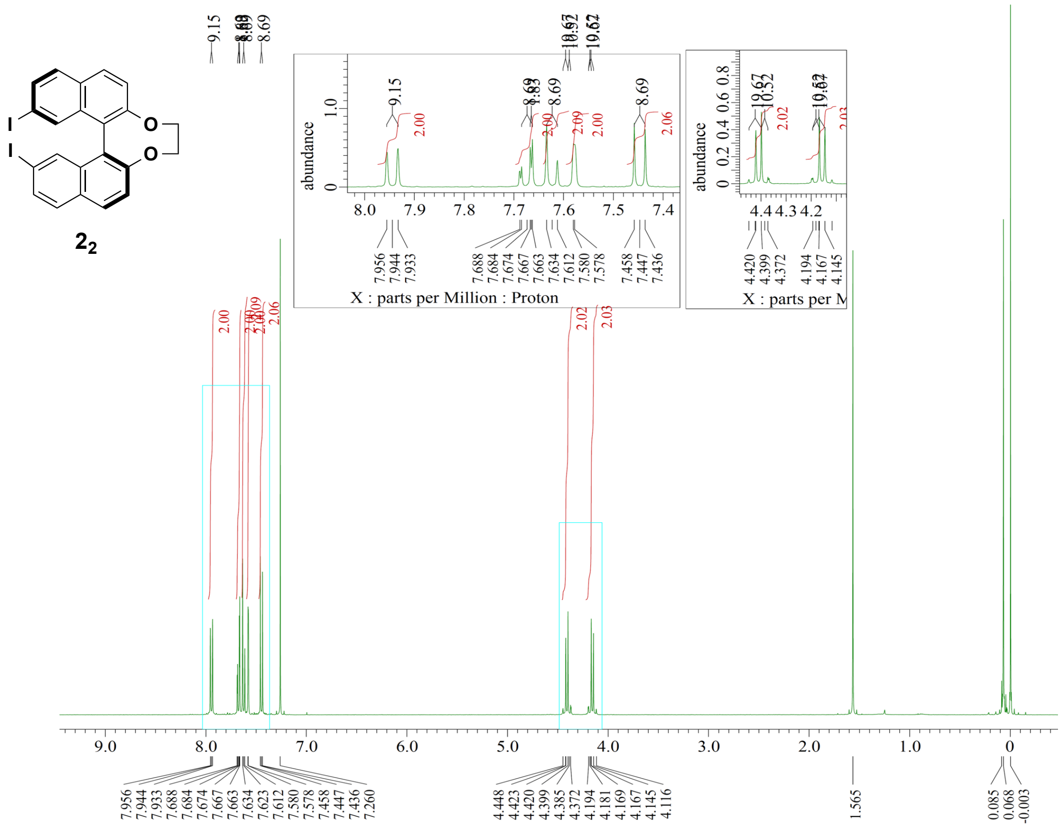
2_1



^{1}H NMR spectrum (400 MHz) of **2_1** in $CDCl_3$

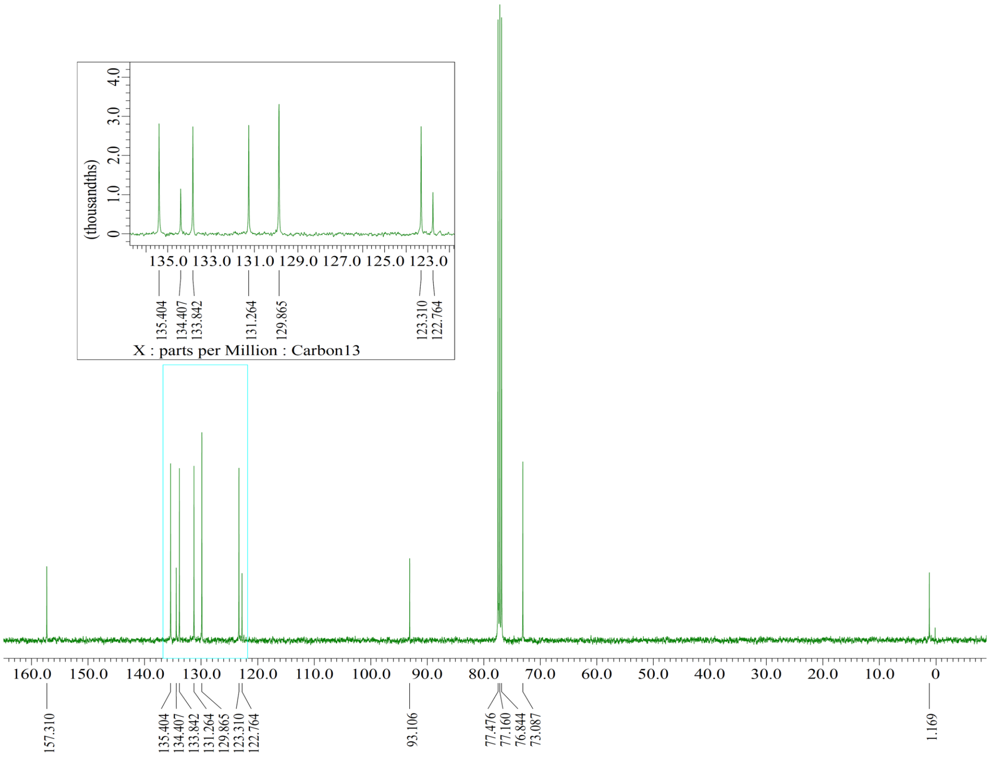


^{13}C NMR spectrum (100 MHz) of **2_1** in $CDCl_3$

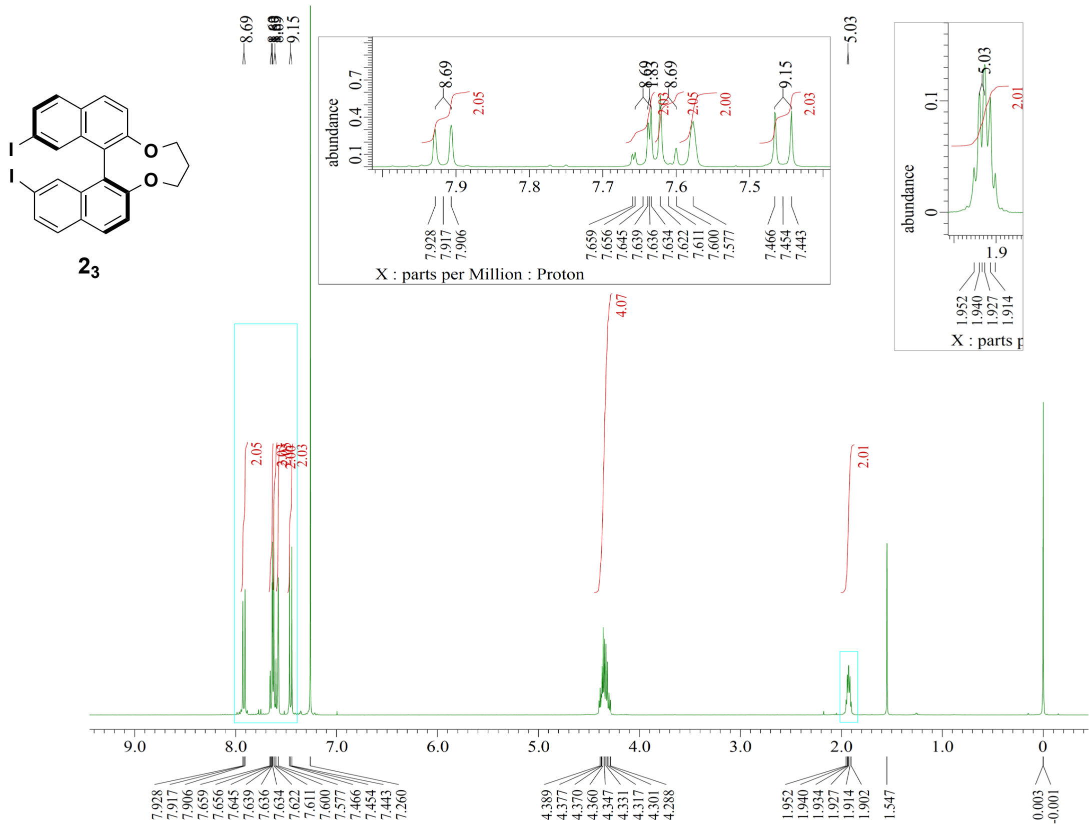


2$_2$

^{1}H NMR spectrum (400 MHz) of **2**$_2$ in CDCl$_3$

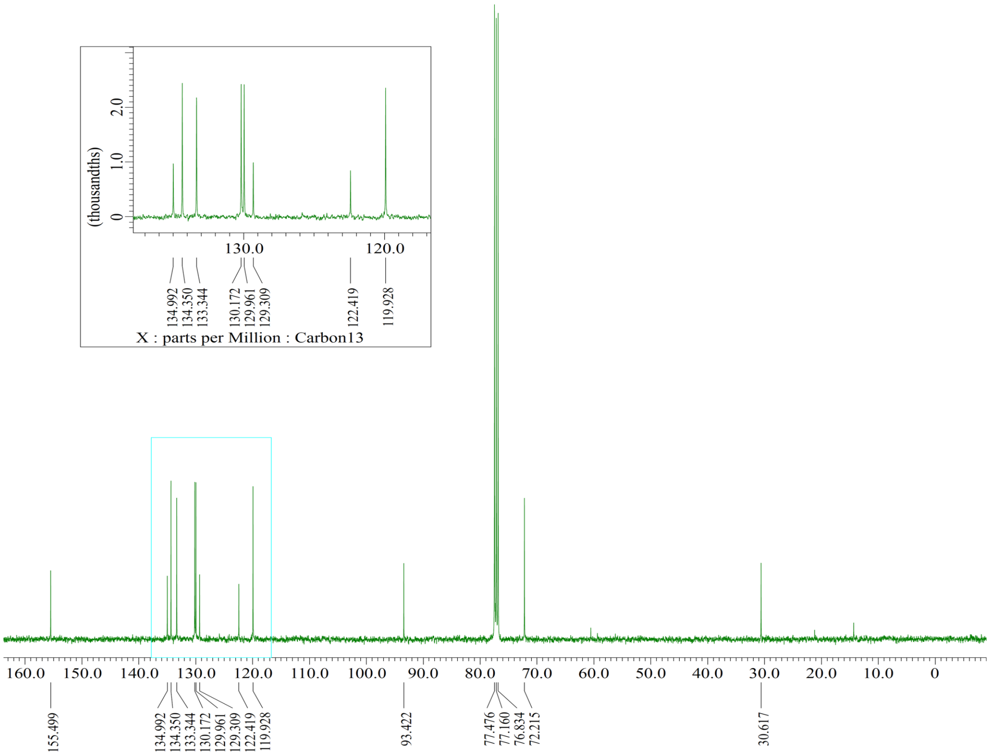


^{13}C NMR spectrum (100 MHz) of **2**$_2$ in CDCl$_3$

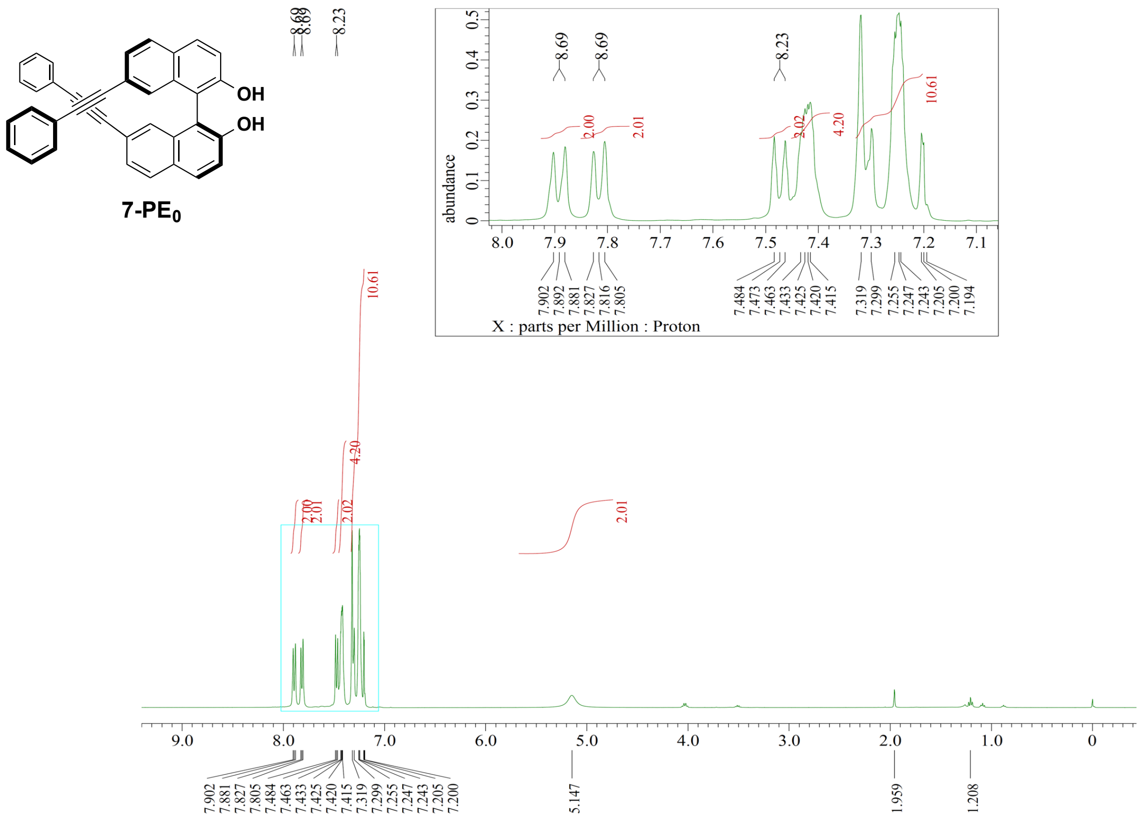


2$_3$

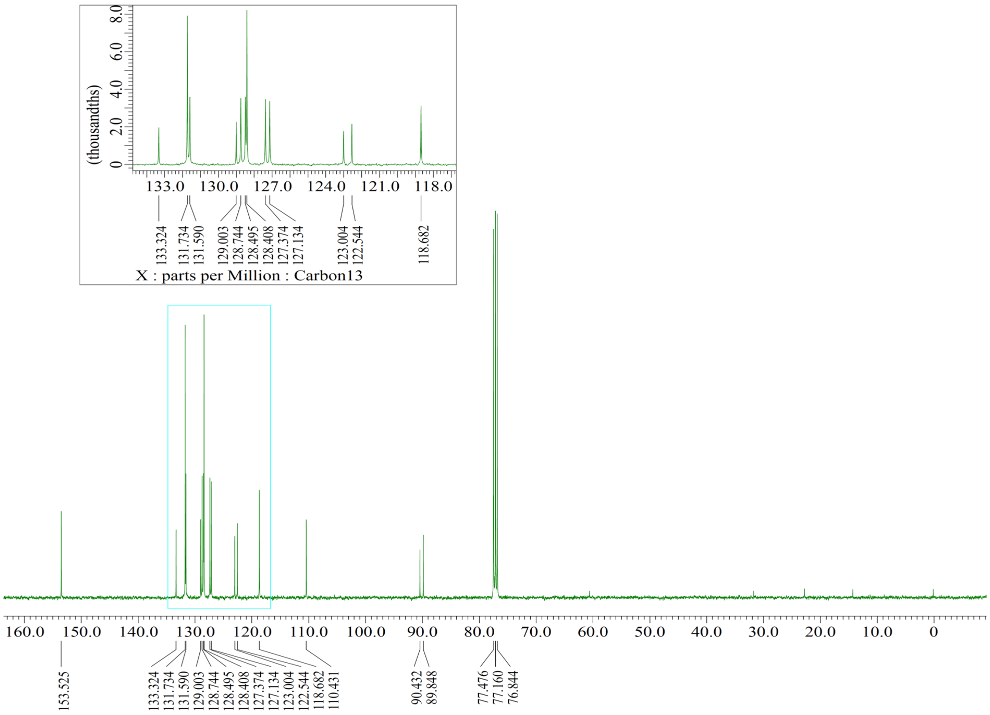
^{1}H NMR spectrum (400 MHz) of **2$_3$** in CDCl$_3$



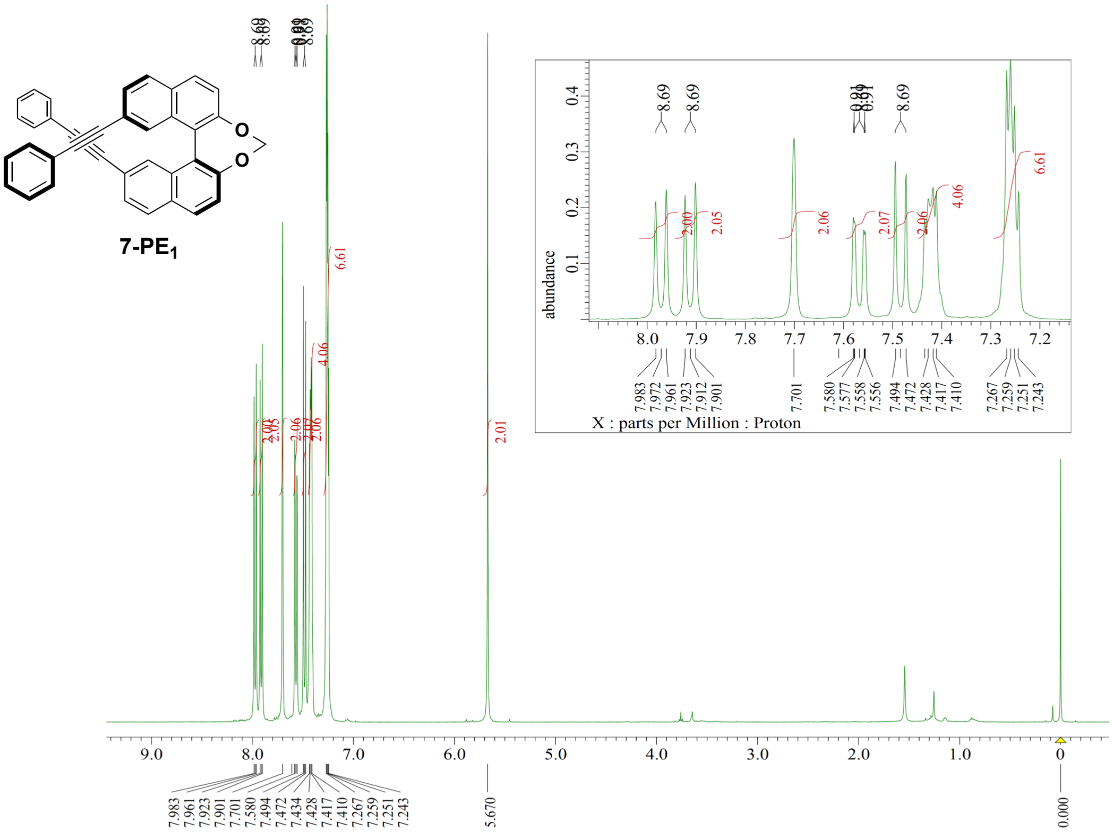
^{13}C NMR spectrum (100 MHz) of **2$_3$** in CDCl$_3$



^{1}H NMR spectrum (400 MHz) of **7-PE$_0$** in CDCl$_3$

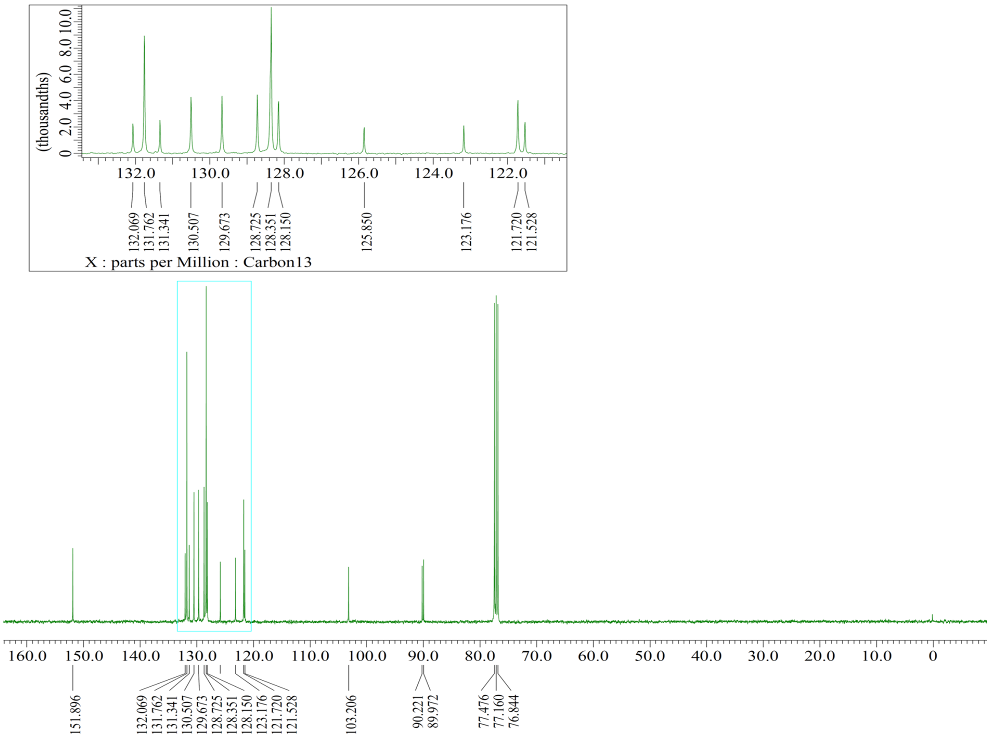


^{13}C NMR spectrum (100 MHz) of **7-PE$_0$** in CDCl$_3$

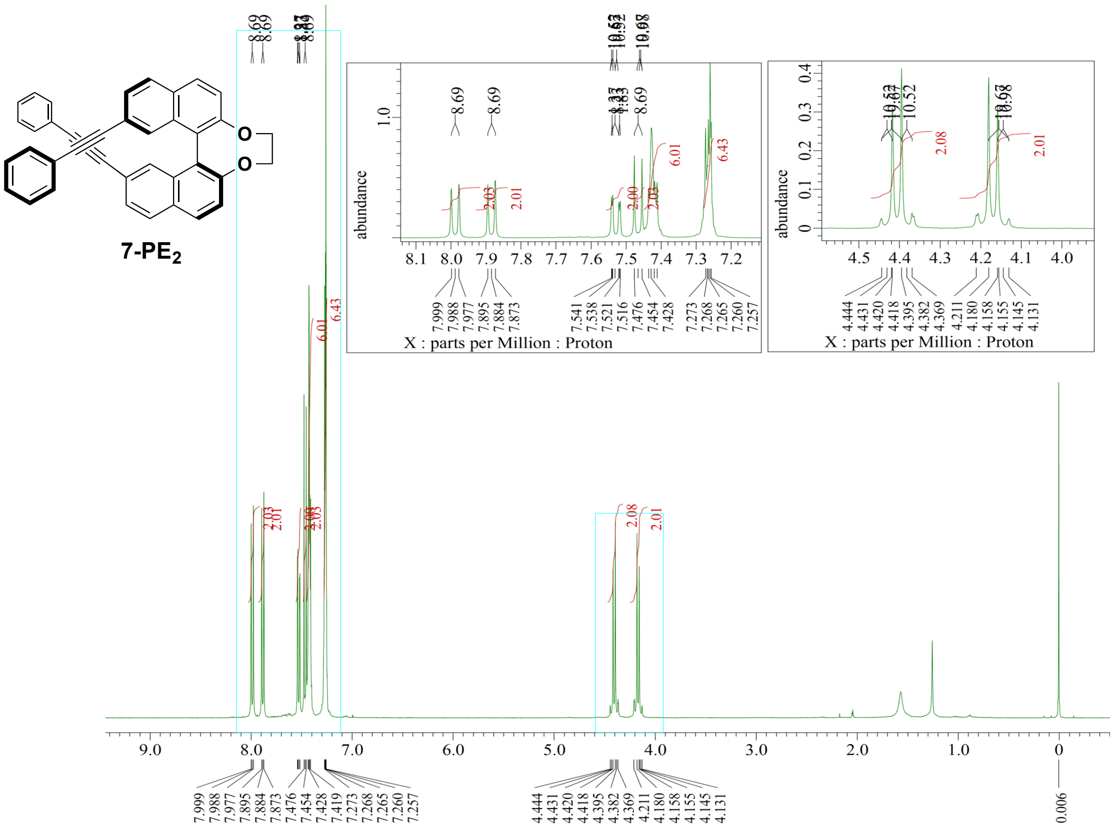


7-PE$_1$

^{1}H NMR spectrum (400 MHz) of **7-PE$_1$** in CDCl$_3$

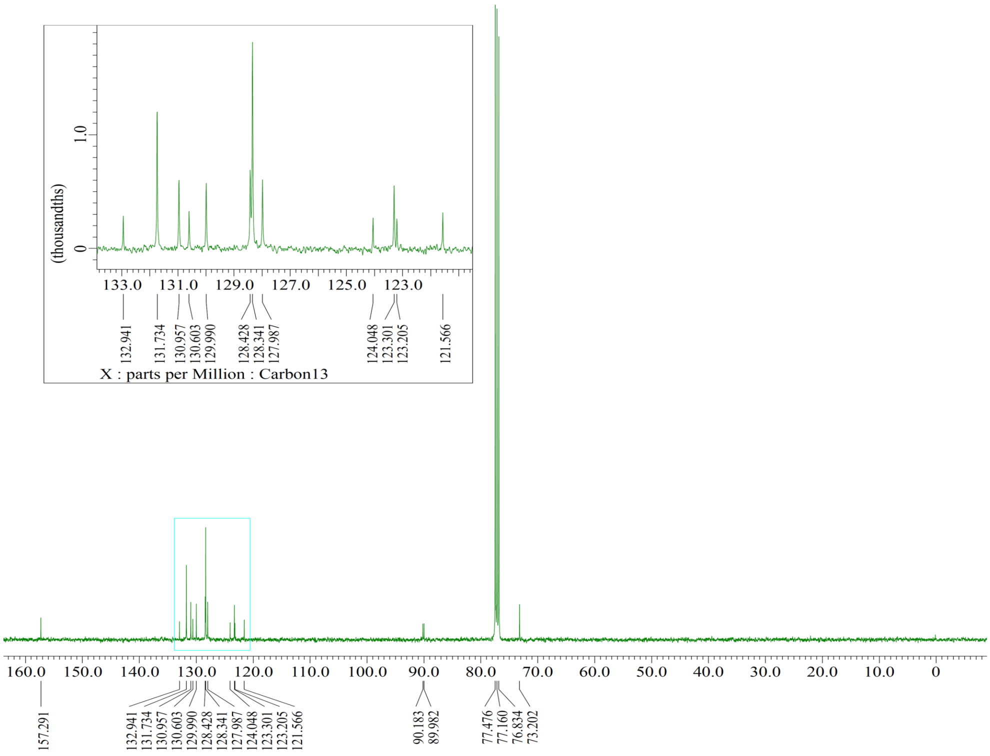


^{13}C NMR spectrum (100 MHz) of **7-PE$_1$** in CDCl$_3$

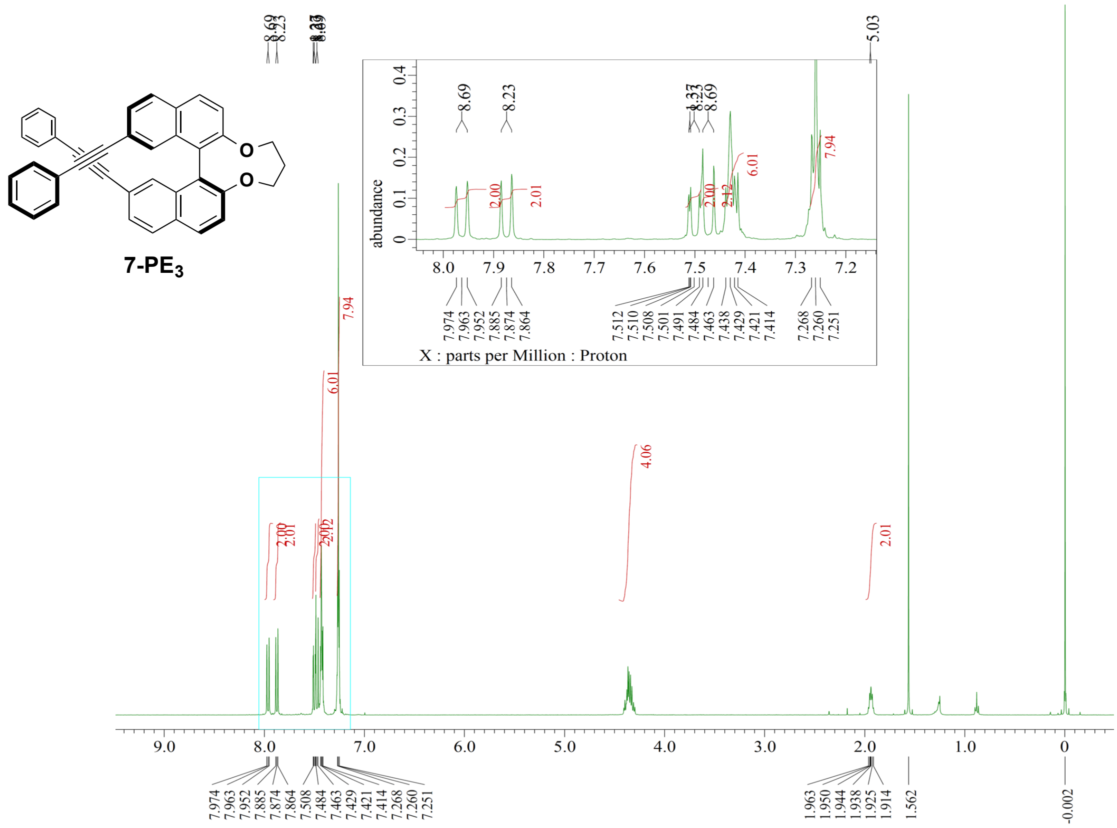


7-PE₂

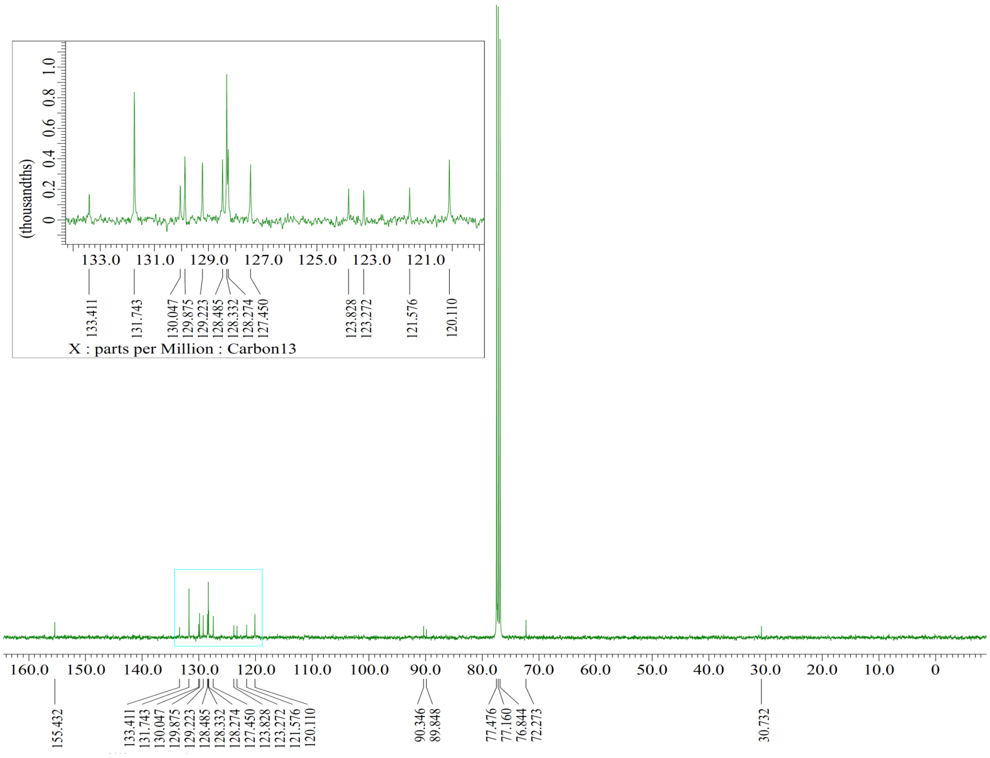
^{1}H NMR spectrum (400 MHz) of **7-PE₂** in CDCl₃



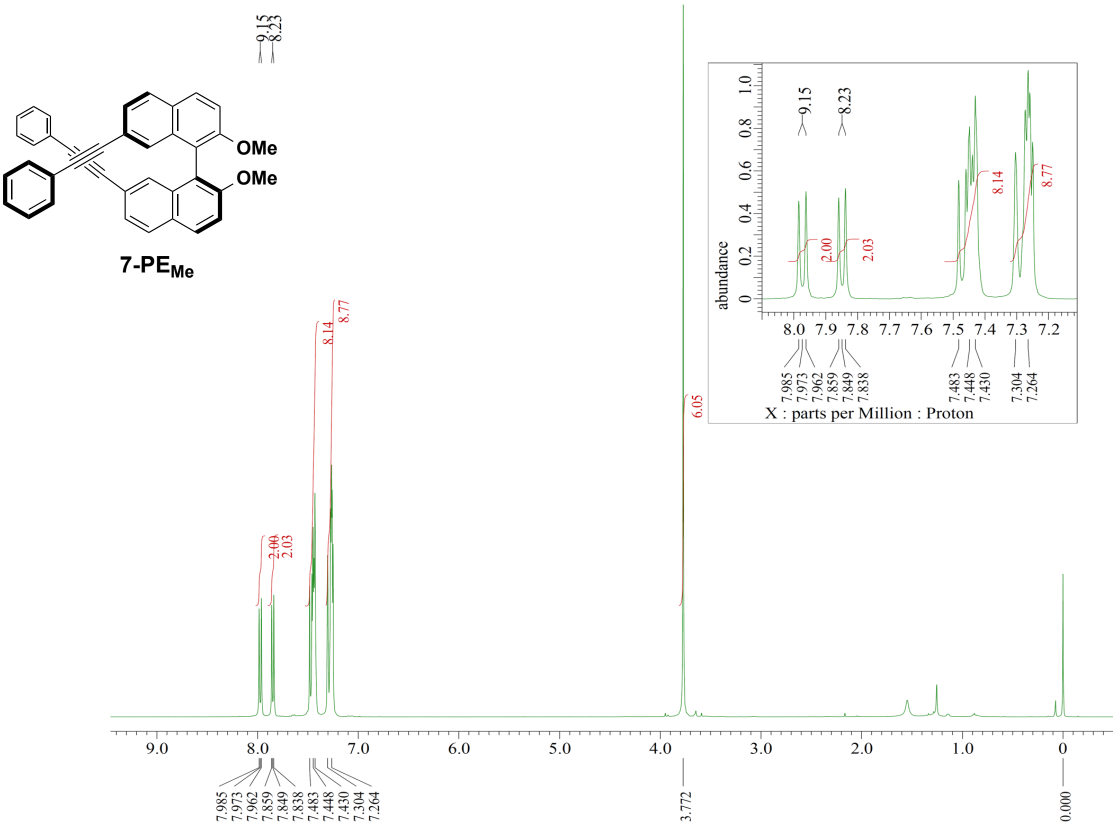
^{13}C NMR spectrum (100 MHz) of **7-PE₂** in CDCl₃



^{1}H NMR spectrum (400 MHz) of **7-PE$_3$** in CDCl$_3$

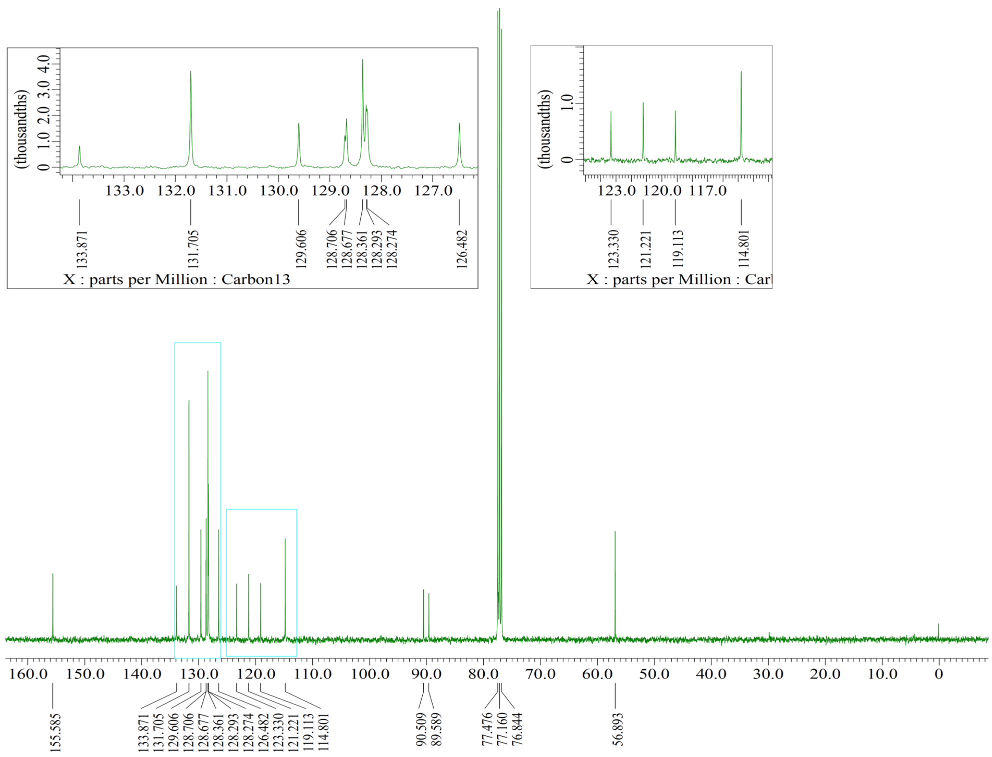


^{13}C NMR spectrum (100 MHz) of **7-PE$_3$** in CDCl$_3$

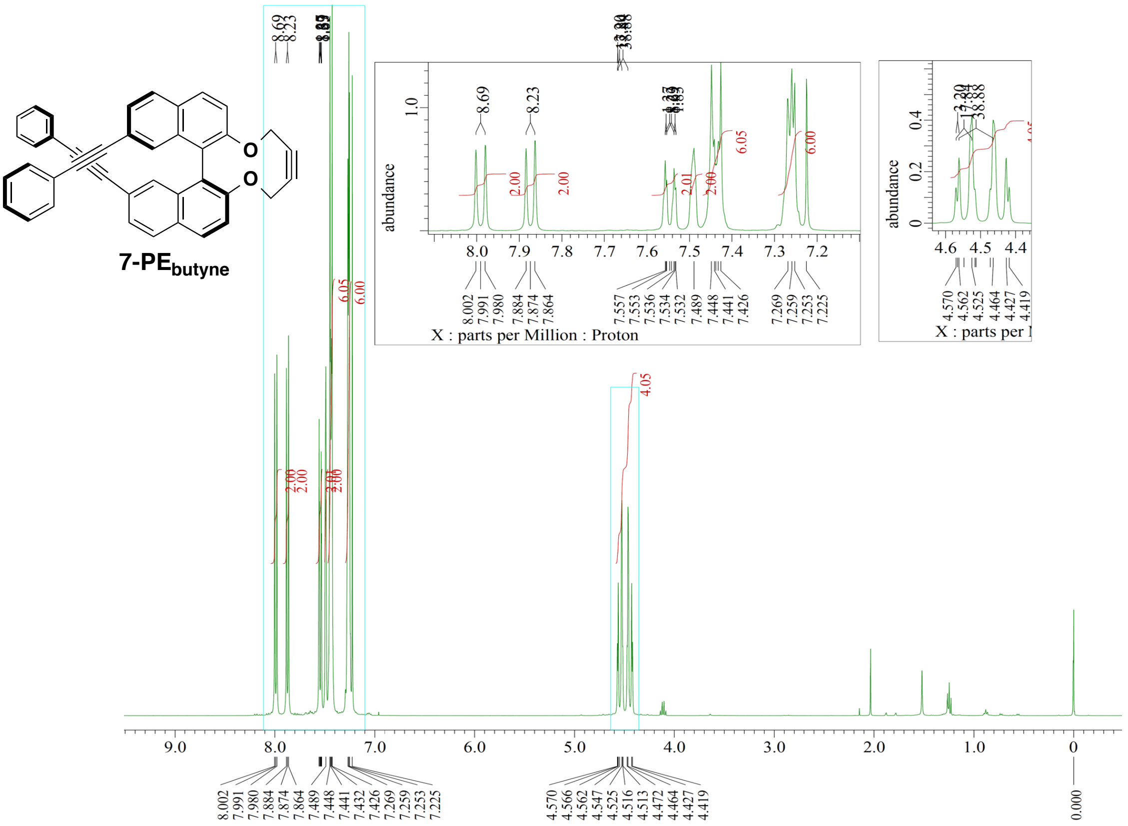


7-PE$_{Me}$

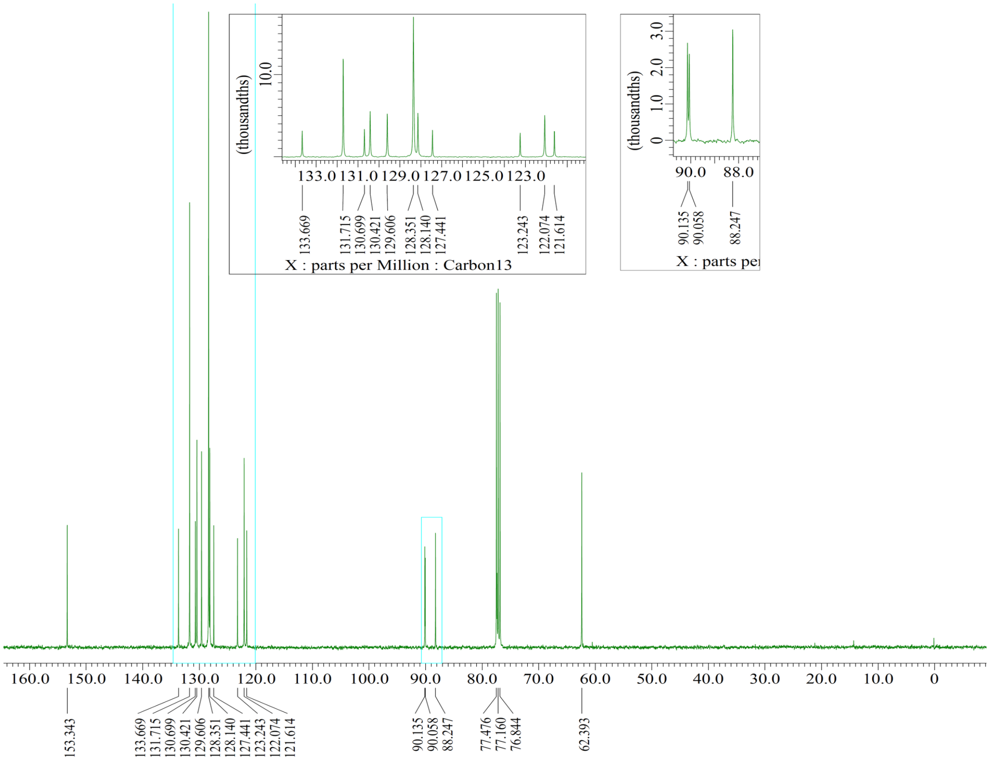
^{1}H NMR spectrum (400 MHz) of **7-PE$_{Me}$** in CDCl$_3$



^{13}C NMR spectrum (100 MHz) of **7-PE$_{Me}$** in CDCl$_3$



^{1}H NMR spectrum (400 MHz) of **7-PE$_{butyne}$** in CDCl$_3$



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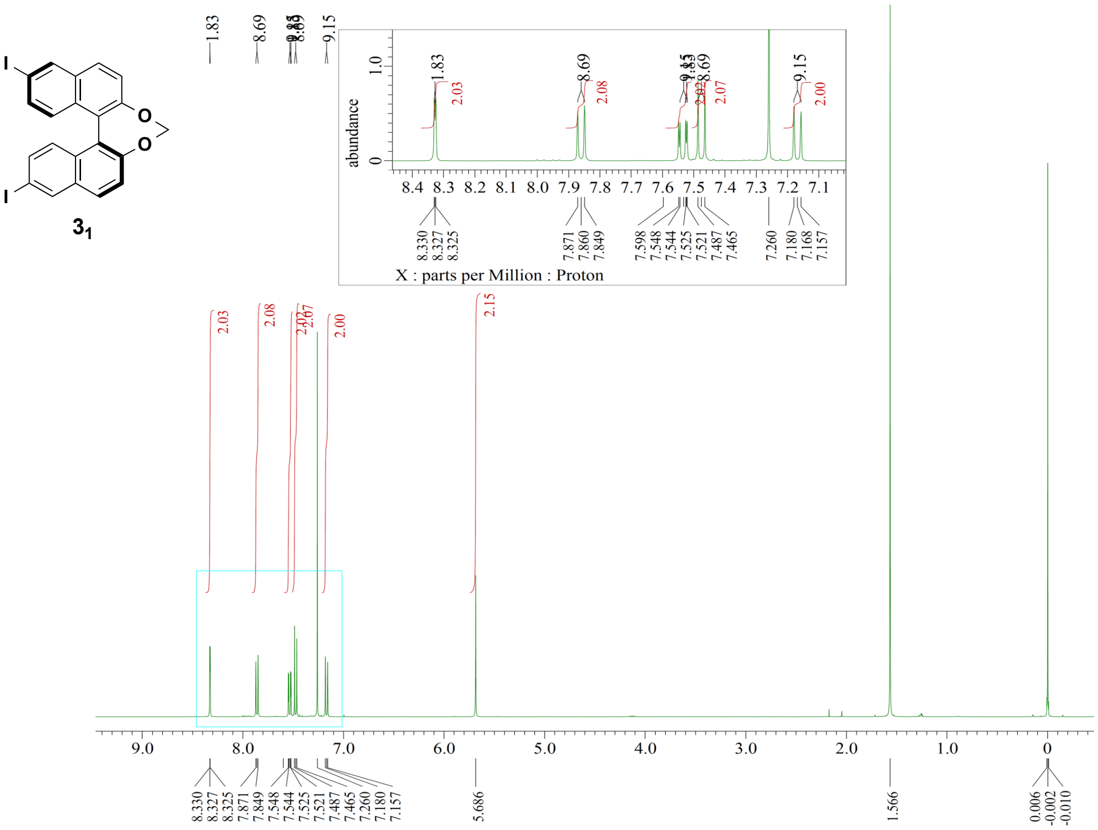
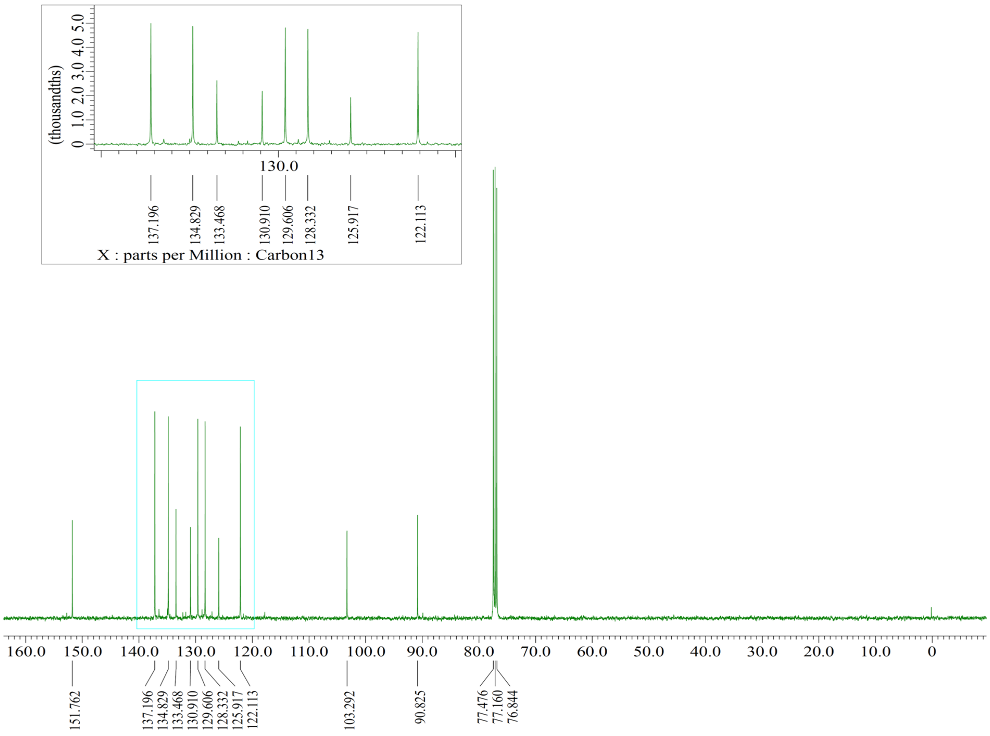
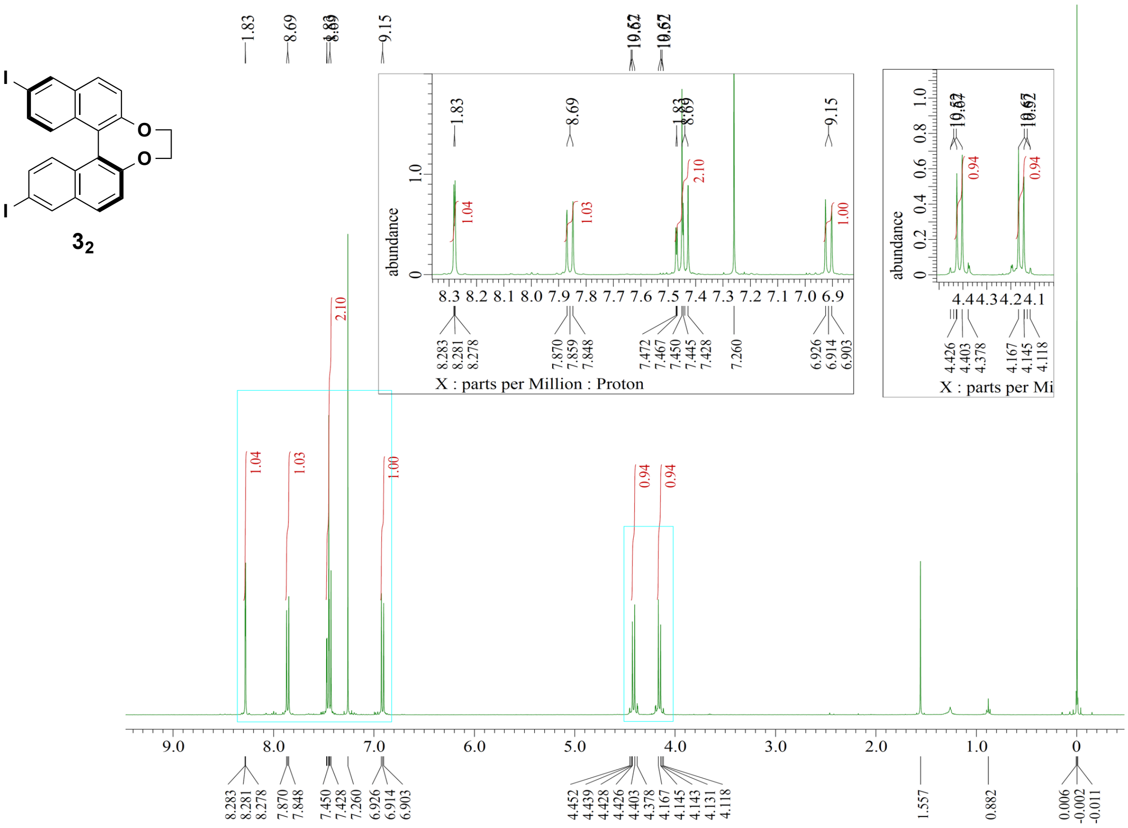


3_1

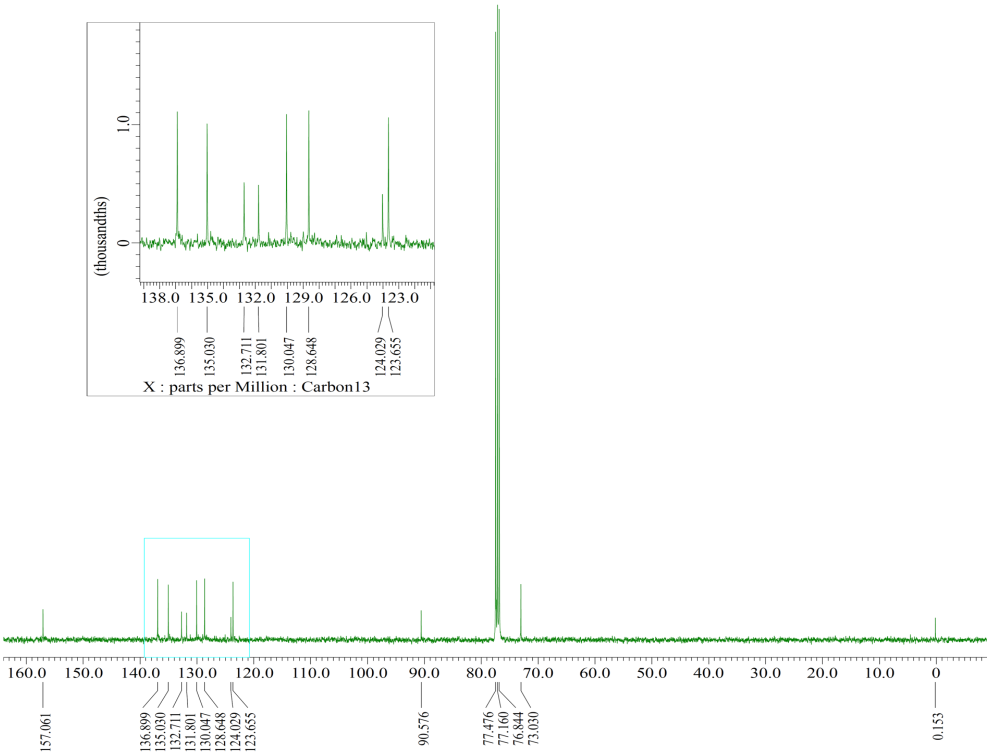
^{1}H NMR spectrum (400 MHz) of **3_1** in CDCl$_3$



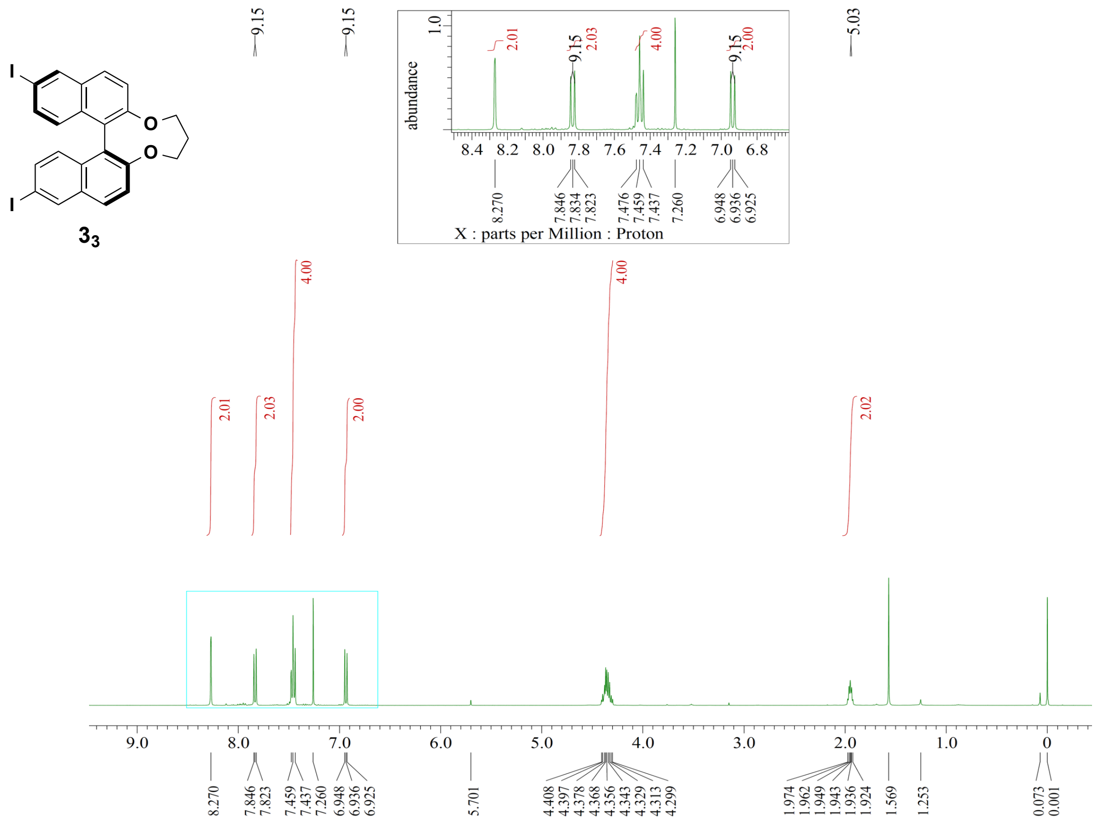
^{13}C NMR spectrum (100 MHz) of **3_1** in CDCl$_3$



^{1}H NMR spectrum (400 MHz) of $\mathbf{3_2}$ in $CDCl_3$

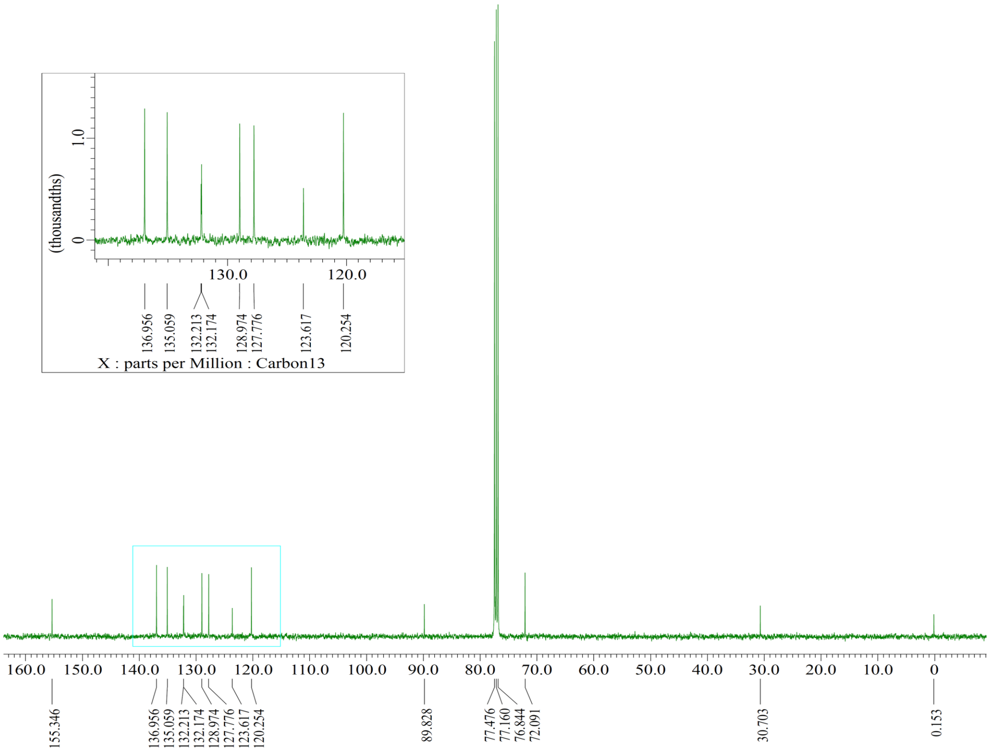


^{13}C NMR spectrum (100 MHz) of $\mathbf{3_2}$ in $CDCl_3$



3$_3$

^{1}H NMR spectrum (400 MHz) of **3$_3$** in CDCl$_3$



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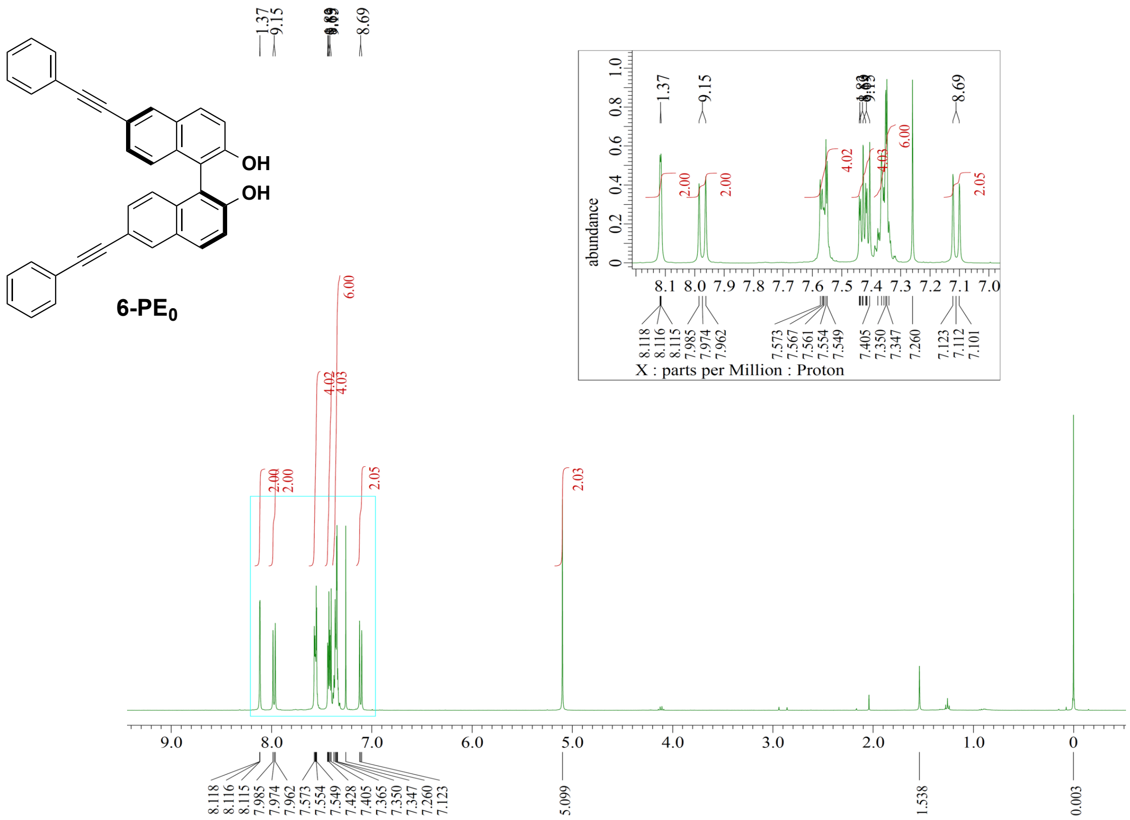
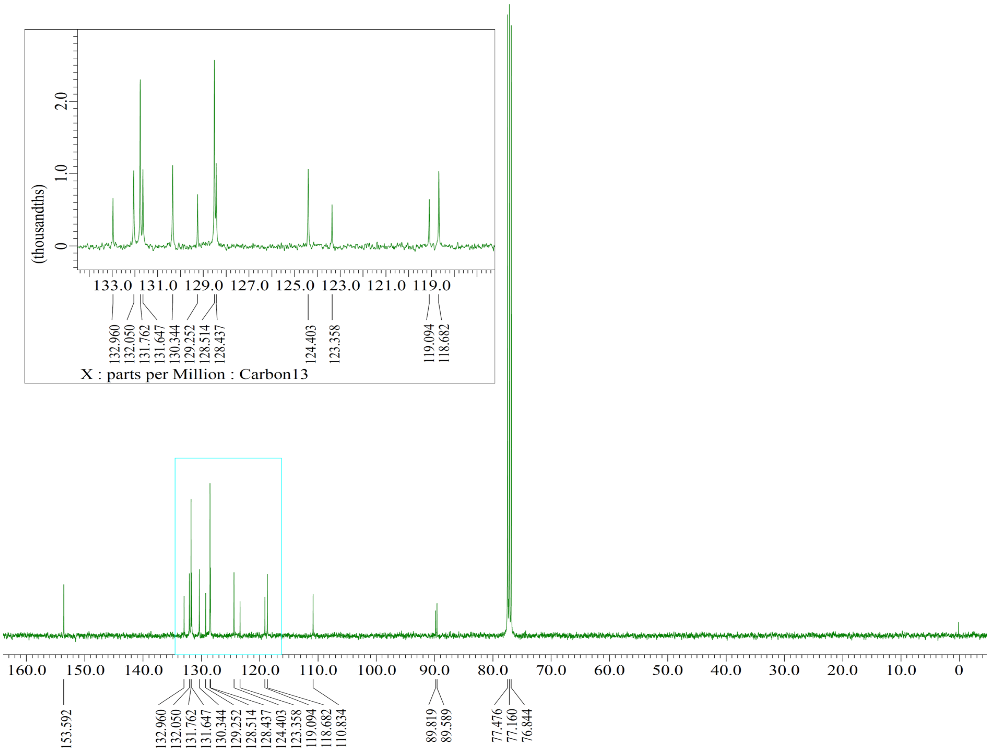


^{1}H NMR spectrum (400 MHz) of **6-PE$_0$** in CDCl$_3$



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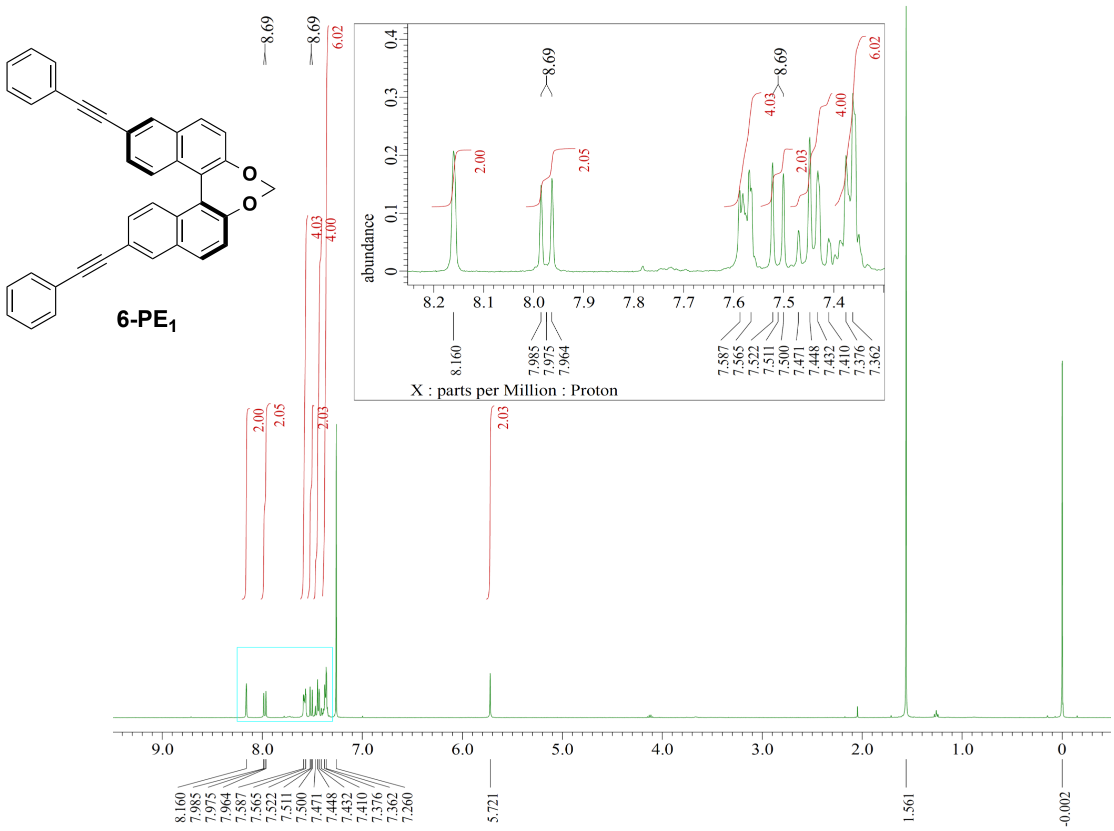
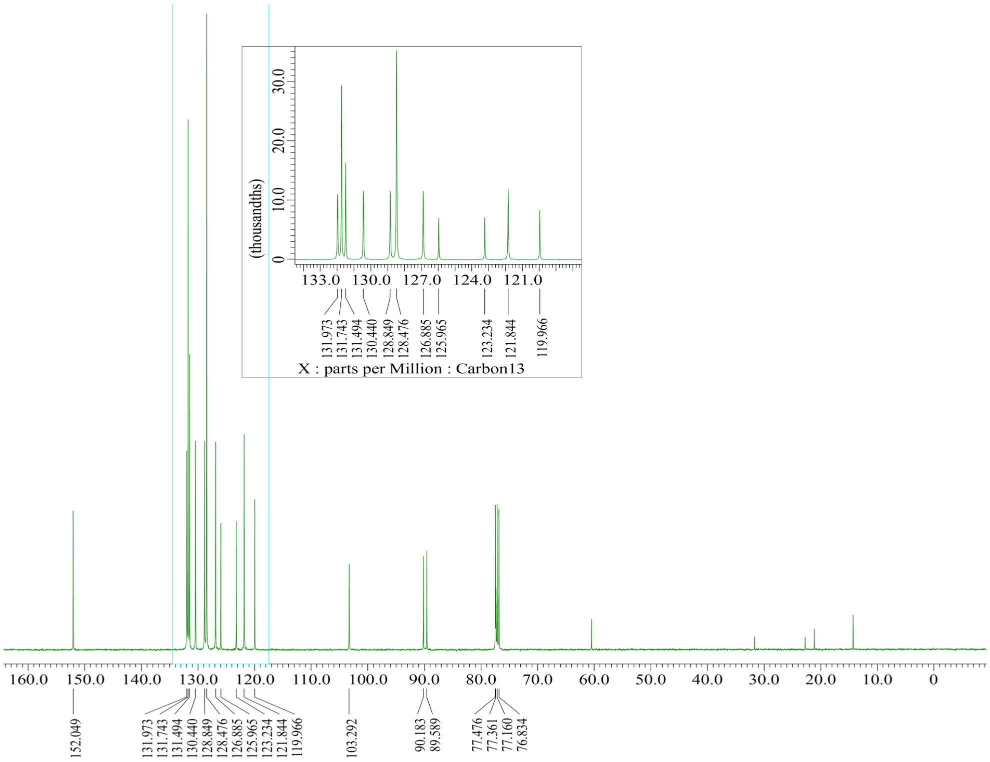
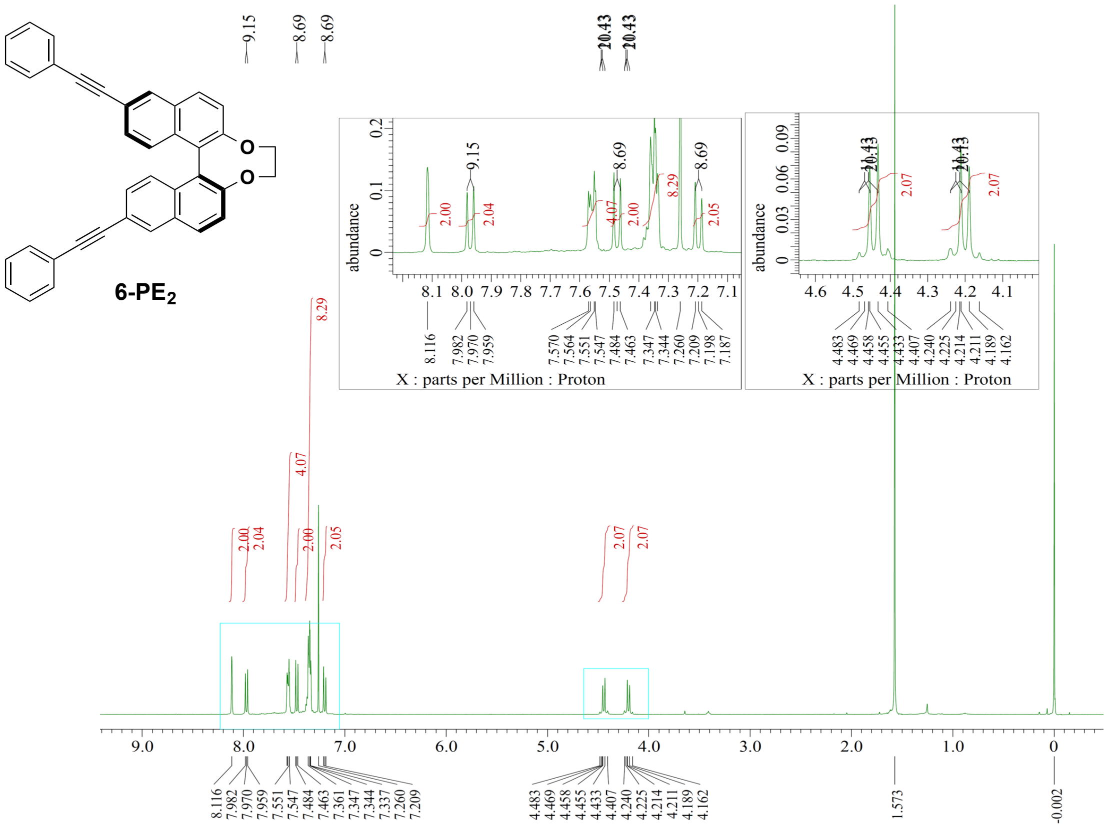


6-PE$_1$

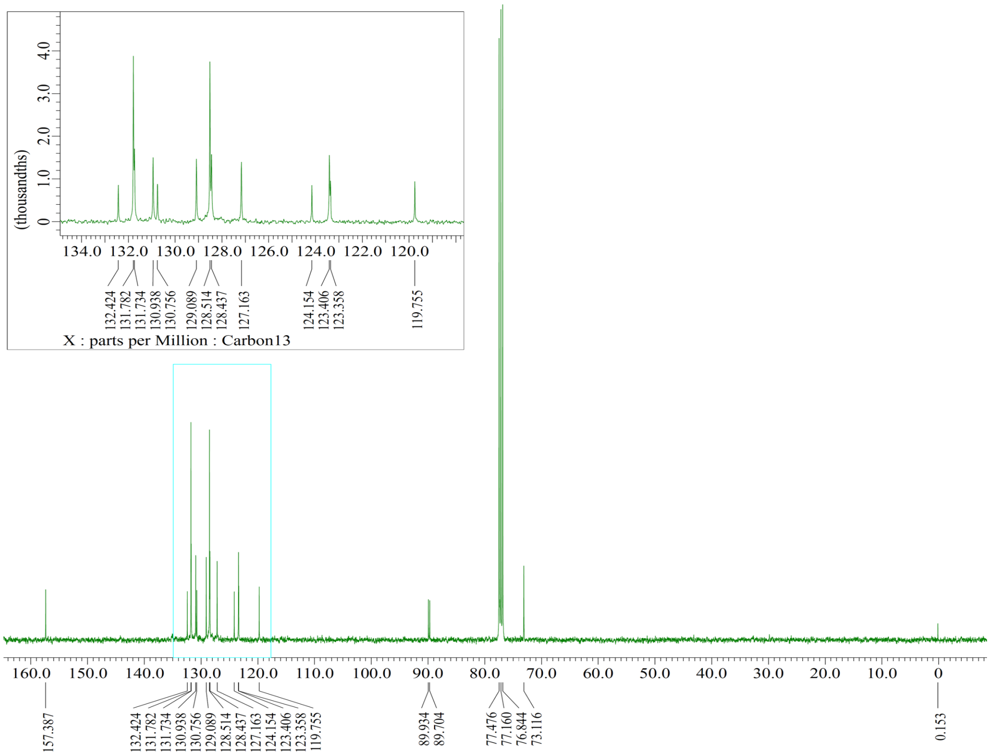
^{1}H NMR spectrum (400 MHz) of **6-PE$_1$** in CDCl$_3$



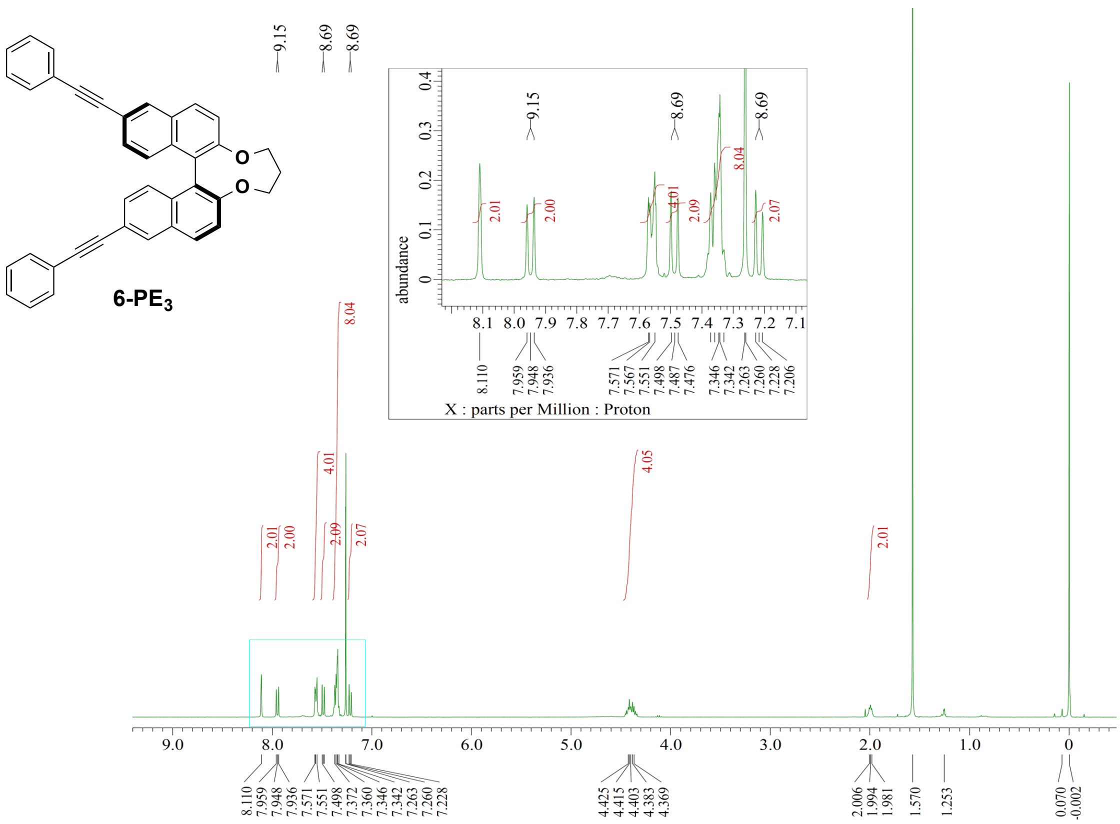
^{13}C NMR spectrum (100 MHz) of **6-PE$_1$** in CDCl$_3$



^{1}H NMR spectrum (400 MHz) of **6-PE$_2$** in CDCl$_3$



^{13}C NMR spectrum (100 MHz) of **6-PE$_2$** in CDCl$_3$



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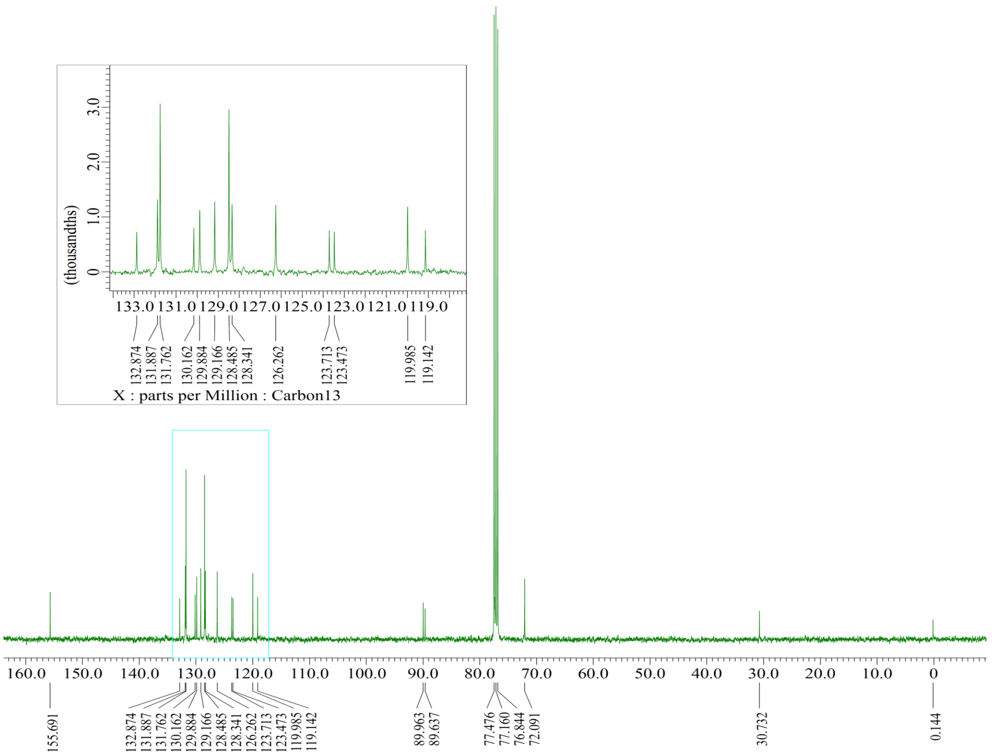
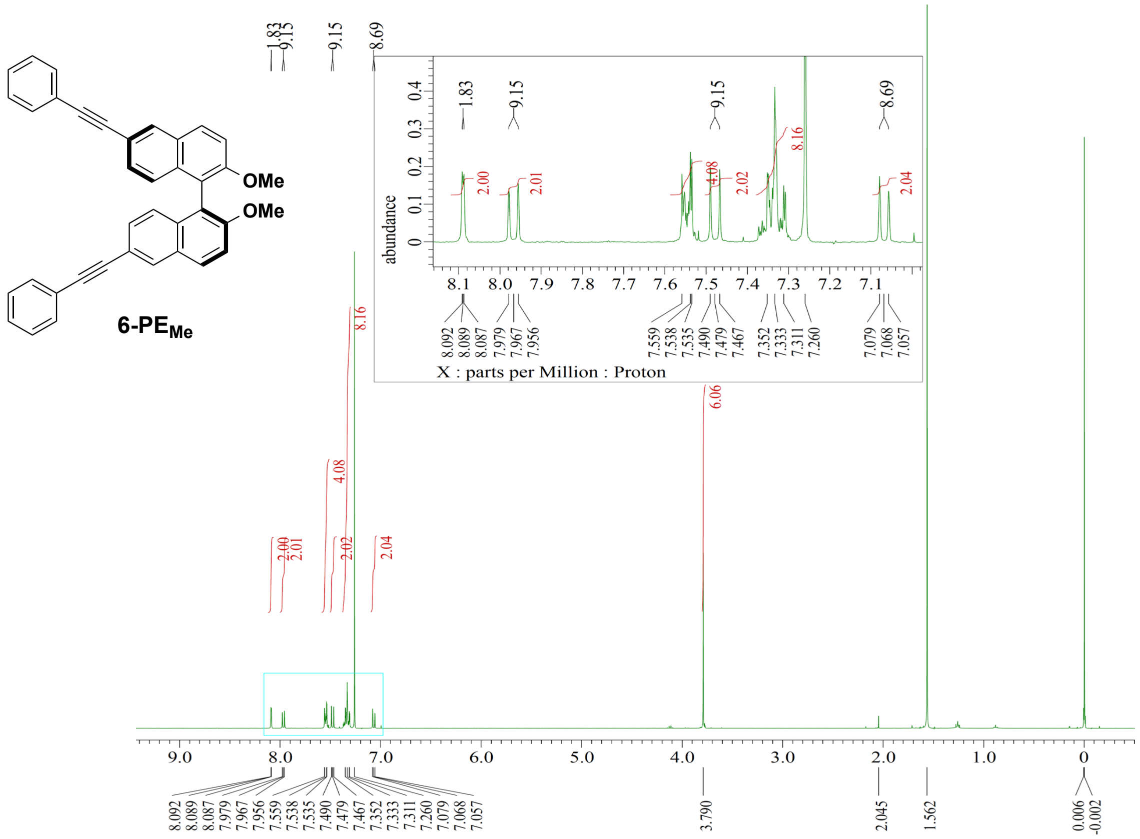
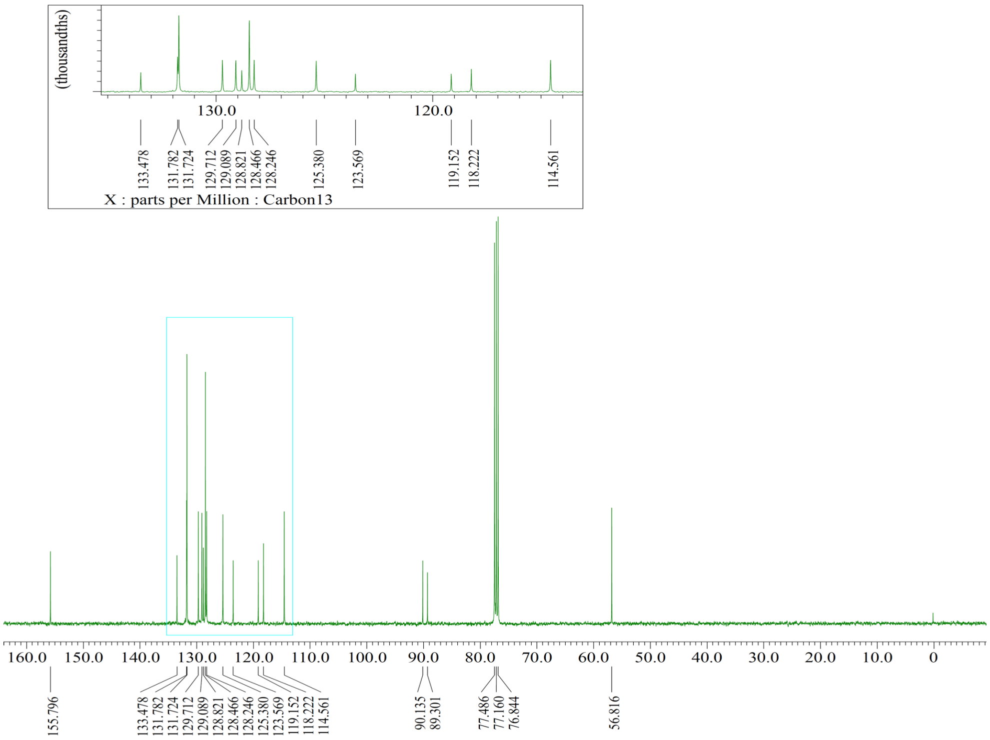


^{13}C NMR spectrum (100 MHz) of **6-PE$_3$** in CDCl$_3$



^{1}H NMR spectrum (400 MHz) of **6-PE$_{Me}$** in CDCl$_3$



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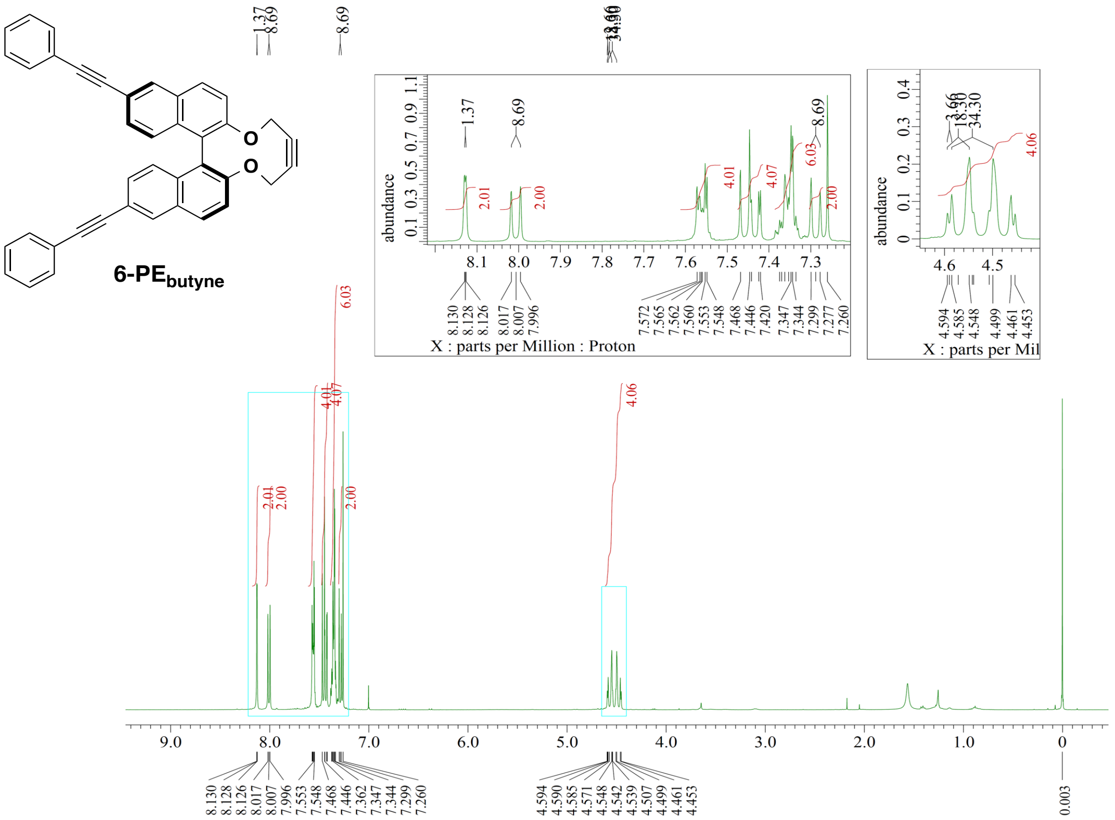
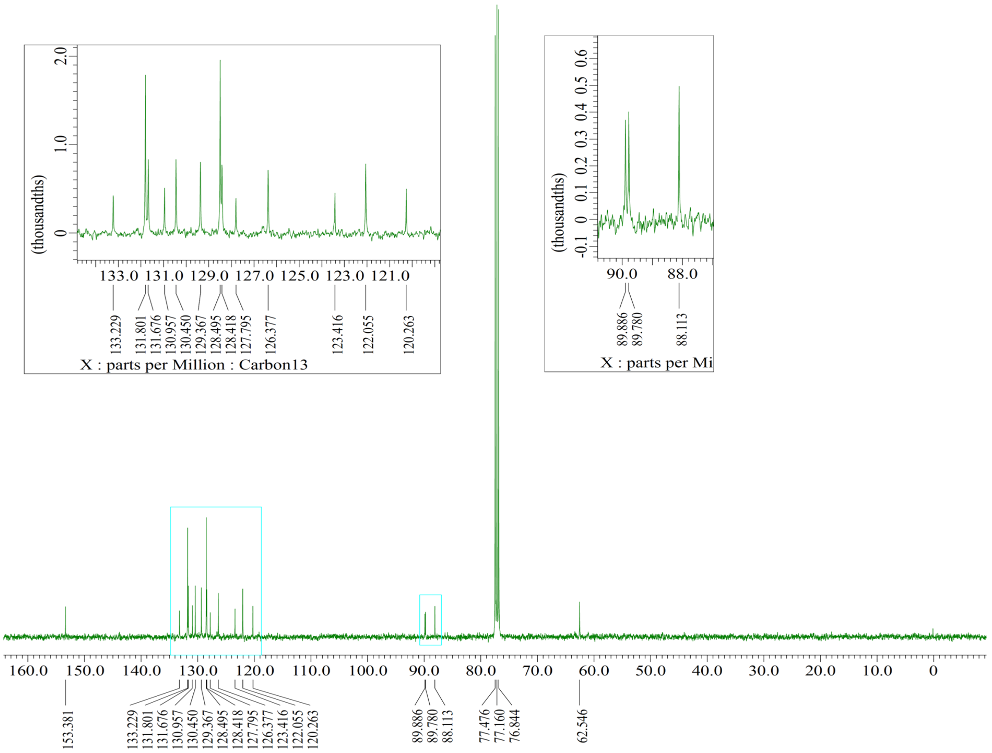


^{1}H NMR spectrum (400 MHz) of **6-PE$_{\text{butyne}}$** in $CDCl_3$



^{13}C NMR spectrum (100 MHz) of **6-PE$_{\text{butyne}}$** in $CDCl_3$