Supporting Information

Ru^{II}-amidobis(phosphine) catalyzed alkylation of indole and epoxide opening followed by α-alkylation through alcohol oxidation

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Crystal structure determination of of [PNP-Ru]

Single crystals of **[PNP-Ru]** was mounted in a Cryoloop with a drop of paratone oil and placed in the cold nitrogen stream on a Bruker D8 Venture diffractometer. The data collections were performed using Bruker D8 Venture diffractometer with a graphite monochromated Mo Kα radiation source (λα = 0.71073 Å) at 100 K to 256 K. CrysalisPro Red 171.41_64.93a software was used to reduce the data. The structure was solved using Olex2 1.5[1] with the ShelXT[2] structure solution program using intrinsic phasing and refined with SHELXL[2] refinement package using least-squares minimization. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the attached non-hydrogen atoms. The details of X-ray structural determination is given in Table S1. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC: 2475197.

Table S1. Crystallographic data for [PNP-Ru] complex

Code	**[PNP-Ru].CH_2Cl_2**
Empirical formula	$C_{48}H_{38}Cl_3N_3OP_2Ru$
Formula weight	942.17
Temperature/K	293(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	27.8316(15)
b/Å	18.4858(8)
c/Å	19.7674(10)
α/°	90
β/°	108.705(6)
γ/°	90
Volume/$Å^3$	9633.0(9)
Z	8
$\rho_{calc}g/cm^3$	1.299
μ/mm^{-1}	5.078
F(000)	3840.0
Crystal size/mm^3	0.086 × 0.065 × 0.043
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.84 to 146.158
Index ranges	-33 ≤ h ≤ 33, -21 ≤ k ≤ 18, -24 ≤ l ≤ 24
Reflections collected	57040
Independent reflections	9476 [R_{int} = 0.3449]
Data/restraints/parameters	9476/0/523
Goodness-of-fit on F^2	0.999
Final R indexes [I>=2σ (I)]	R_1 = 0.1211, wR_2 = 0.2954
Final R indexes [all data]	R_1 = 0.1767, wR_2 = 0.3620

Molecular Structure of [PNP-Ru]

The solid-state structure of **[PNP-Ru]** is depicted in Figure S1, with detailed crystallographic parameters provided in Table S1. The Ru(II) center in **[PNP-Ru]** features a distorted octahedral geometry. The coordination sphere is anchored by a tridentate PNP pincer ligand, in which the bisphosphine moiety chelates the metal through two phosphorus atoms, while the amide nitrogen (N1) provides additional stabilization. Complementing this, a bidentate 2,2'-bipyridine ligand

coordinates via its two nitrogen donors (N2 and N3), forming a five-membered chelate ring that contributes to the observed distortion. The remaining coordination site is occupied by a chloride ligand, completing the six-coordinate environment around ruthenium.

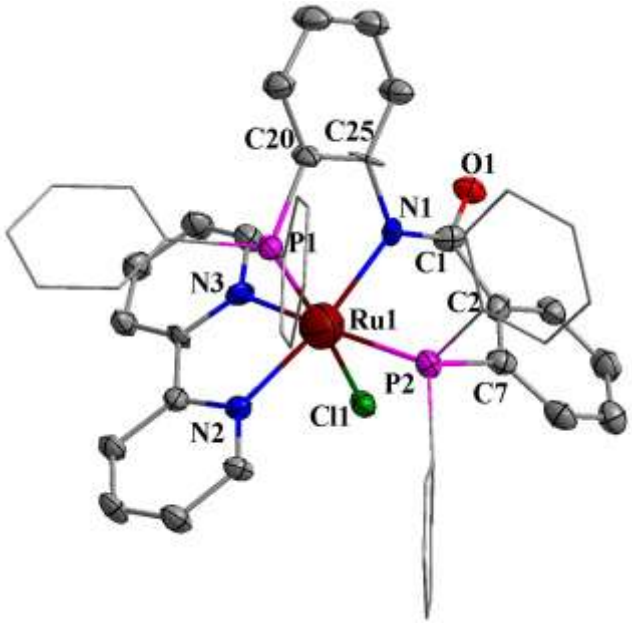

Figure S1. Molecular structure of **[PNP-Ru]** with 35% probability displacement ellipsoids. Hydrogen atoms and solvent molecules were omitted for clarity. Selected bond lengths (Å): Ru1−Cl1 2.482(2), Ru1−P1 2.218(3), Ru1−P2 2.282(3), Ru1−N1 2.120(8), Ru1−N2 2.073(8) and Ru1−N3 2.092(8). Selected bond angles (◦): N2−Ru1−N1 170.6(3), N2−Ru1−N3 77.0(3), N1−Ru1−P1 83.2(2), N1−Ru1−P2 80.7(2), N3−Ru1−P1 89.7(3), N3−Ru1−P2 168.0(3).

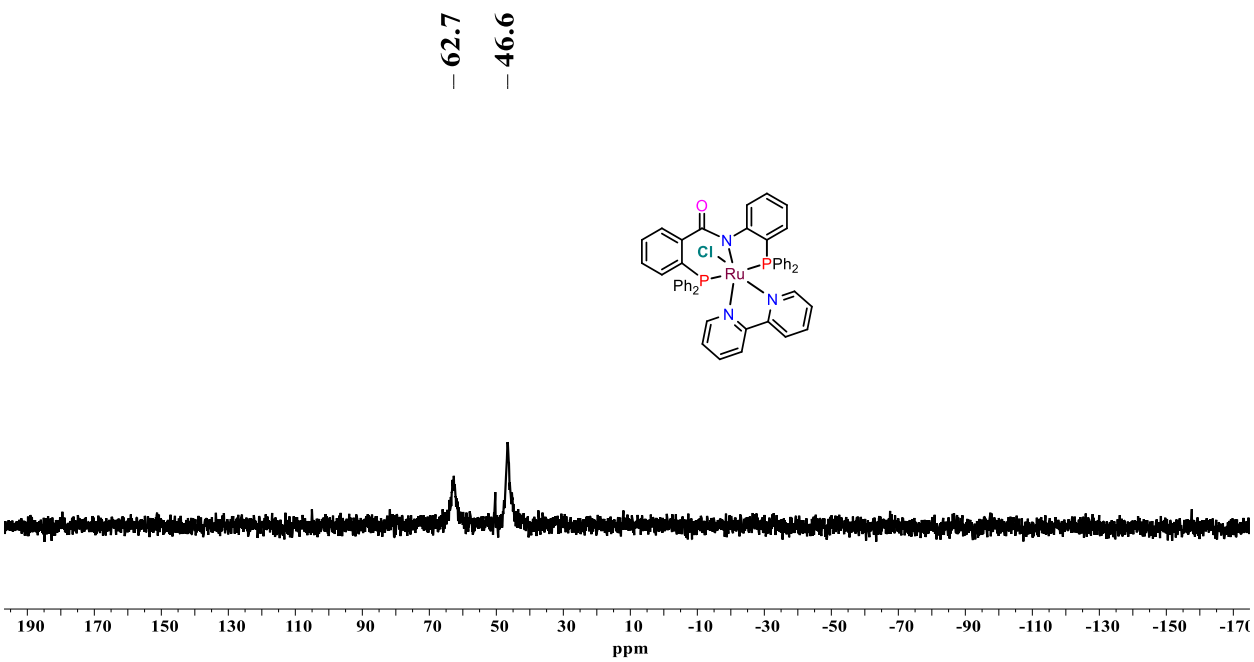

Figure S2: $^{31}P\{^{1}H\}$ NMR spectrum of **[PNP-Ru]** in $CDCl_3$ (202 MHz).

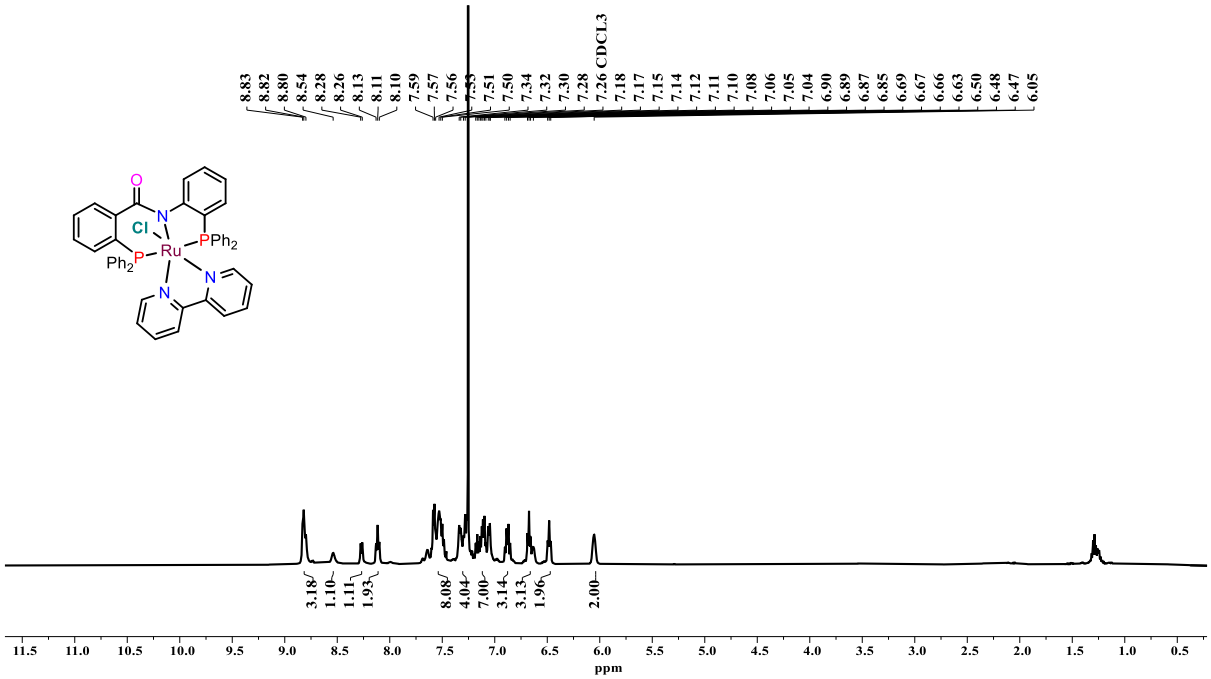

Figure S3. ^{1}H NMR spectrum of **[PNP-Ru]** in $CDCl_3$ (500 MHz).

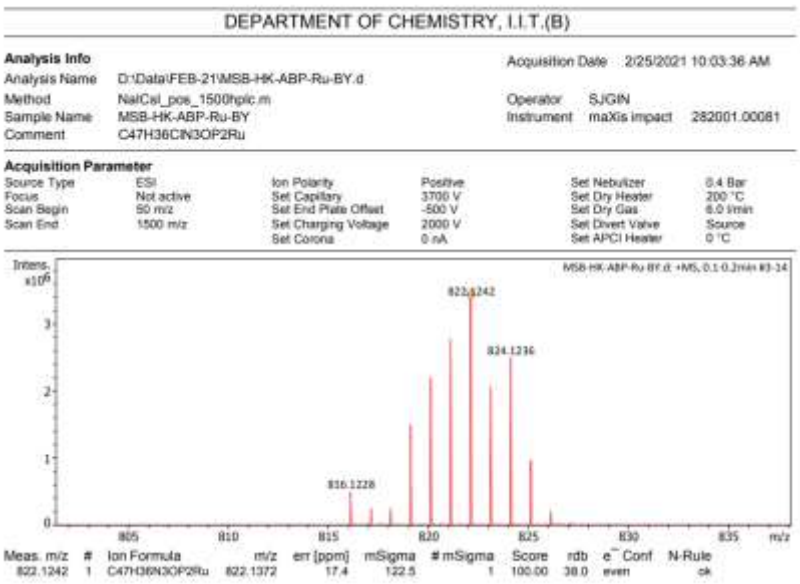

Figure S4. HRMS spectrum of **[PNP-Ru]**.

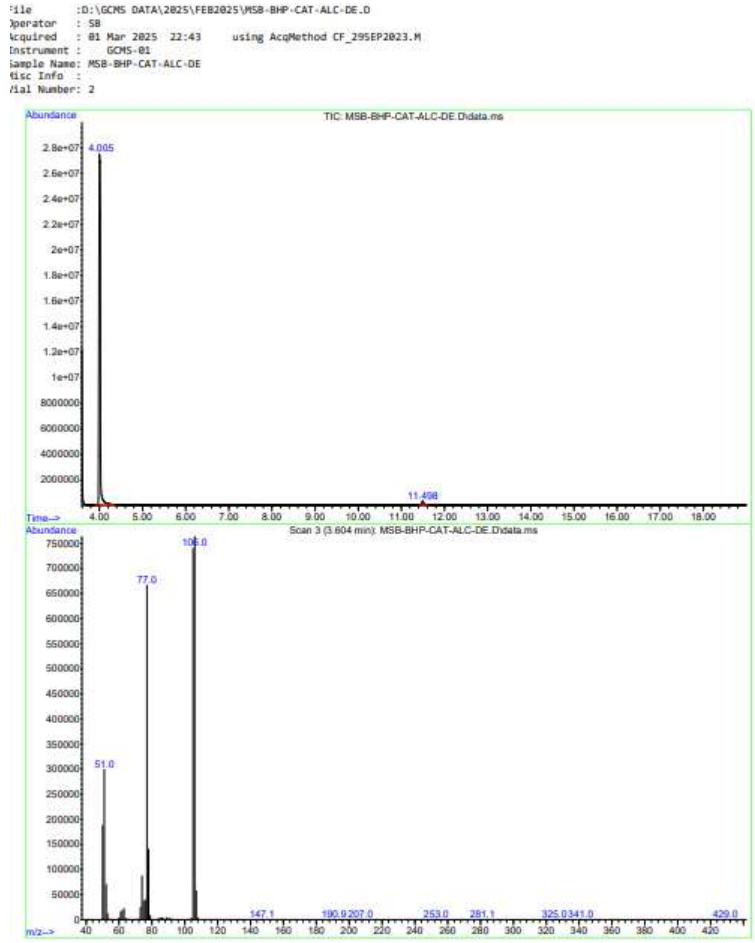

Figure S5. GC-MS for benzaldehyde formation.

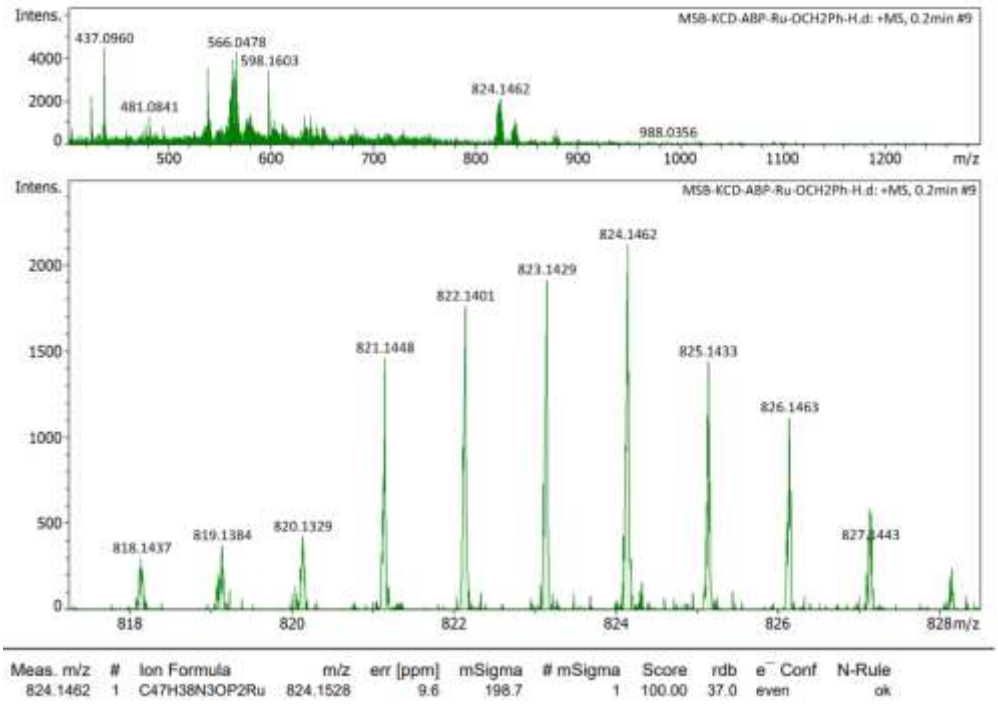

Figure S6. HRMS for Ru-H species.

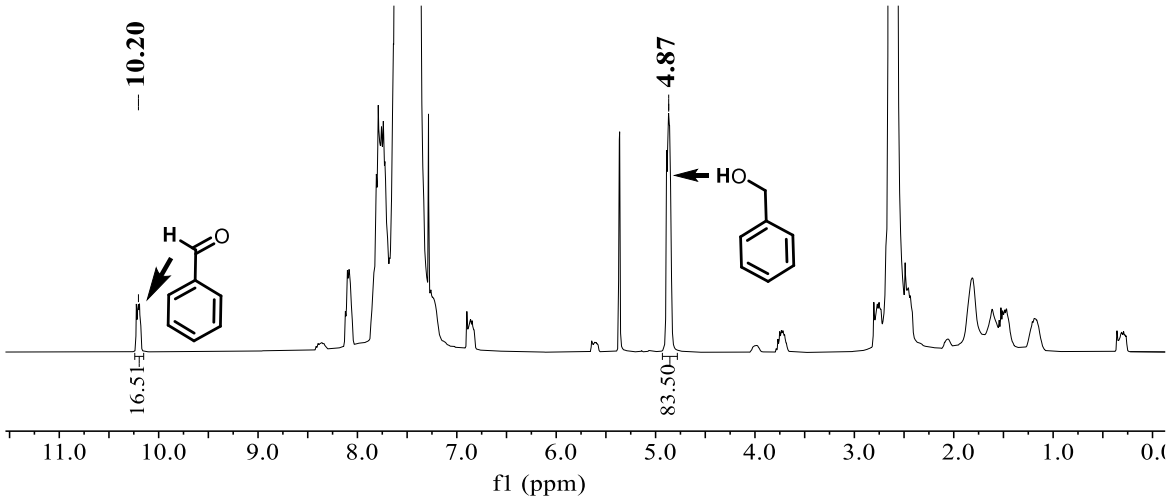

Figure S7. ^{1}H NMR spectrum for reaction mixture of oxidation of benzyl alcohol, reaction catalysed by **17**

peak #	R.T. min	first scan	max scan	last scan	PK TF	peak height	corr. area	corr. % max.	% of total
1	6.378	329	333	374	M	61509304	927612969	50.62%	26.691%
2	6.931	396	399	420	M	48017858	715378709	39.04%	20.584%
3	7.153	420	425	456	M2	68590700	1832376021	100.00%	52.725%

Sum of corrected areas: 3475367699

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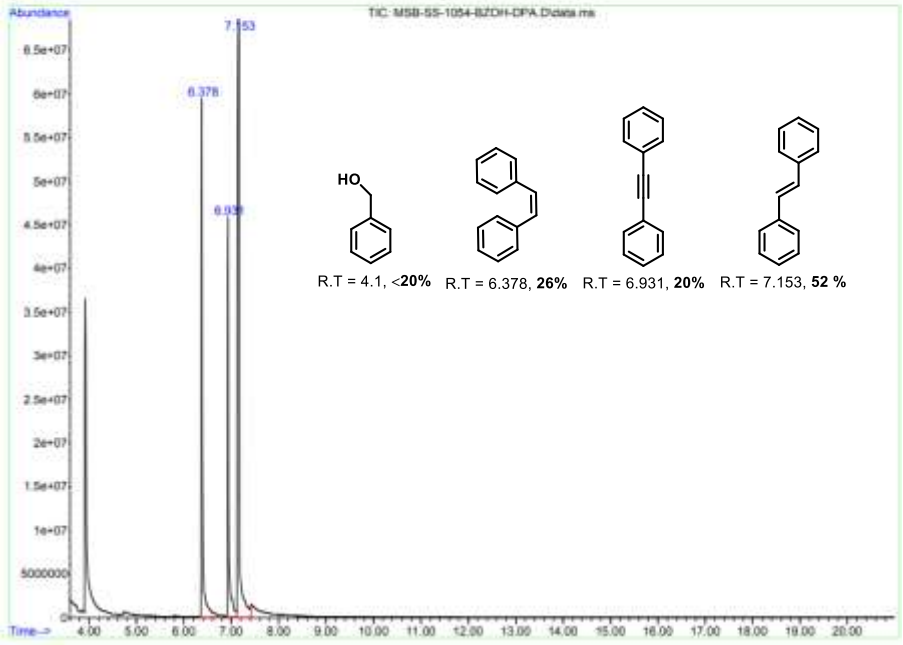


Figure S8. GCMS spectrum indicates the retention time (R.T).

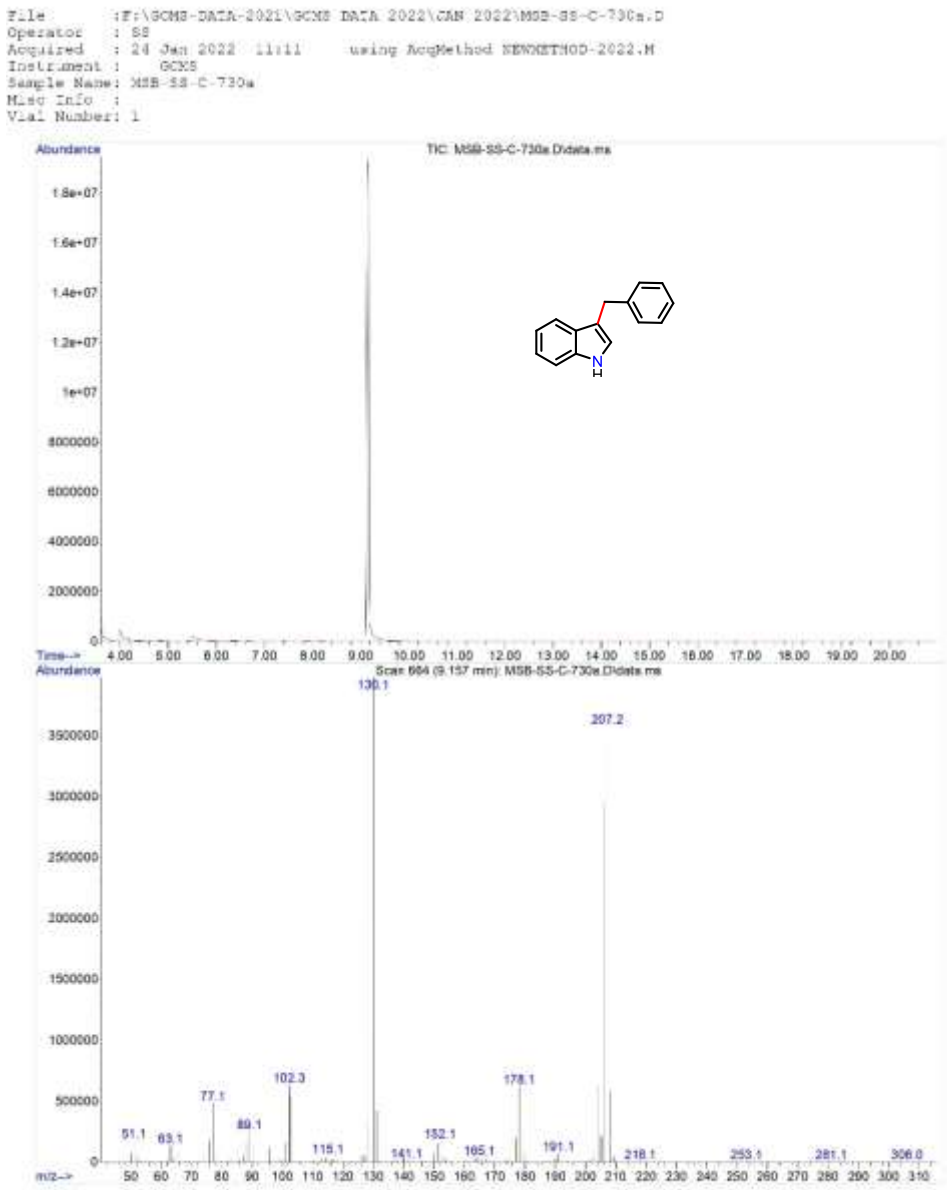


Figure S9. GCMS conversion of mono-indole ($\mathbf{I_1}$)

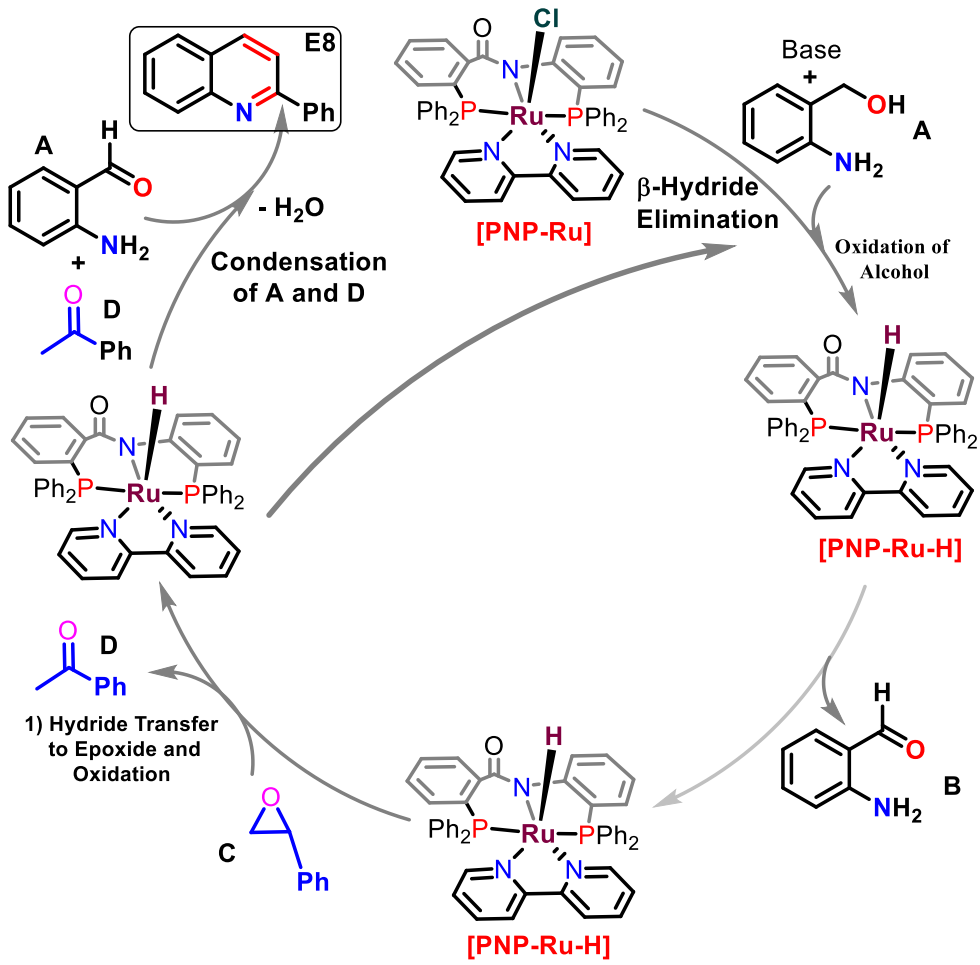
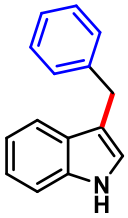


Figure S10. Plausible mechanism for quinoline synthesis through epoxide opening

The plausible mechanism of the dehydrogenative synthesis of quinoline initiated by **[PNP-Ru]**. 2-amino benzyl alcohol **A** in presence of base reacts with [PNP-Ru-H] at thermal condition, which leads to 2-amino benzaldehyde **B** and **[PNP-Ru-H]** species via β-hydride elimination process. Further, styrene epoxide **C** reacts with the **[PNP-Ru-H]** species, which transfers hydride at primary position of styrene epoxide followed by oxidation gives acetophenone **D** via *β*-hydride elimination process. In situ, both 2-amino benzaldehyde and acetophenone reacts together to form a 2-phenyl quinoline **E8** by condensation process.

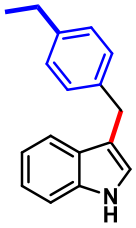
Spectral data of catalytic products

3-benzyl-1H-indole (I_1)



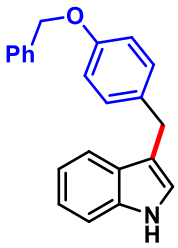
The reaction of indole (100 mg, 0.854 mmol, 1 equiv.), benzyl alcohol (92.3 mg, 0.854 mmol, 1 equiv.), KO^{t}Bu (95.8 mg, 1 mmol, 1 equiv.), cat. **[PNP-Ru]** (0.73 mg, 0.000854 mmol, 0.1 mol %), afforded 170 mg, **I_1** in 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.55 (t, J = 8.4 Hz, 1H), 7.37 (d, J = 8.2 Hz, 1H), 7.33 – 7.27 (m, 3H), 7.24 – 7.17 (m, 2H), 7.16 – 7.05 (m, 1H), 6.92 (d, J = 1.3 Hz, 1H), 4.13 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 136.6, 128.8, 128.5, 127.6, 126.0, 122.4, 122.2, 119.5, 119.3, 116.0, 111.2, 31.7. *m/z* calcd for $C_{15}H_{14}N$: 208.1121 $(M+H)^+$; found: 208.1119

3-(4-ethylbenzyl)-1H-indole (I_2)



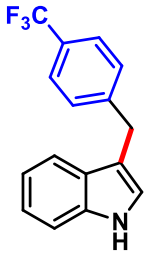
The reaction of indole (100 mg, 0.854 mmol, 1 equiv.), 4-ethyl benzyl alcohol (116.5 mg, 0.854 mmol, 1 equiv.), KO^{t}Bu (95.8 mg, 1 mmol, 1 equiv.), cat. **[PNP-Ru]** (0.73 mg, 0.000854 mmol, 0.1 mol %), afforded 190 mg, **I_2** in 95% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.55 (dd, J = 7.9, 1.0 Hz, 1H), 7.36 (d, J = 8.1 Hz, 1H), 7.24 – 7.16 (m, 3H), 7.16 – 7.06 (m, 3H), 6.94 – 6.90 (m, 1H), 4.10 (s, 2H), 2.62 (q, J = 7.6 Hz, 2H), 1.23 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 138.4, 136.5, 128.6, 127.8, 127.5, 122.3, 122.0, 119.3, 119.2, 116.1, 111.0, 31.2, 28.5, 15.7. *m/z* calcd for $C_{17}H_{17}N$: 236.1434 $[M+H]^+$; found: 236.1432.

3-(4-(benzyloxy)benzyl)-1H-indole (I_3)



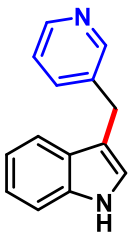
The reaction of indole (100 mg, 0.854 mmol, 1 equiv.), 4-benzyloxy benzyl alcohol (150.138 mg, 0.854 mmol, 1 equiv.), KO^{t}Bu (95.8 mg, 1 mmol, 1 equiv.), cat. **[PNP-Ru]** (0.73 mg, 0.000854 mmol, 0.1 mol %), afforded 238 mg, **I_3** in 89% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.55 (d, J = 7.9 Hz, 1H), 7.45 (d, J = 6.9 Hz, 2H), 7.43 – 7.37 (m, 2H), 7.37 – 7.32 (m, 1H), 7.22 (dd, J = 11.2, 8.2 Hz, 2H), 7.15 – 7.07 (m, 1H), 6.93 (d, J = 8.5 Hz, 3H), 5.06 (s, 2H), 4.09 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.1, 137.3, 136.5, 133.6, 129.6, 128.6, 127.9, 127.5, 127.5, 122.2, 122.0, 119.3, 119.2, 116.3, 114.7, 111.0, 70.1, 30.7. *m/z* calcd for $C_{22}H_{19}NO$: 314.1539 $[M+H]^+$; found: 314.1539.

3-(4-(trifluoromethyl)benzyl)-1H-indole (I_4)



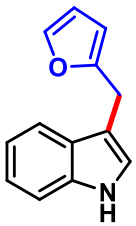
The reaction of indole (100 mg, 0.854 mmol, 1 equiv.), 4-CF_3-benzyl alcohol (182.4 mg, 0.854 mmol, 1 equiv.), KO^{t}Bu (95.8 mg, 1 mmol, 1 equiv.), cat. **[PNP-Ru]** (0.73 mg, 0.000854 mmol, 0.1 mol %), afforded 227 mg, **I_4** in 97% yield. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.28. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.54 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 7.9 Hz, 1H), 7.43 – 7.35 (m, 3H), 7.26 – 7.15 (m, 1H), 7.15 – 7.06 (m, 1H), 6.96 (d, J = 2.4 Hz, 1H), 4.19 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 136.5, 128.9, 128.2, 127.3, 125.3 (q, $^3J_{C–F}$ = 4 Hz), 124.4 (q, $^1J_{C-F}$ = 270 Hz), 122.5, 122.3, 119.6, 119.0, 114.7, 111.2, 31.5. *m/z* calcd for $C_{16}H_{12}F_3N$: 276.0995 $[M+H]^+$; found: 276.0989.

3-(pyridin-3-ylmethyl)-1H-indole (I_5)



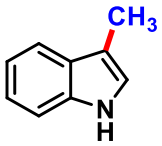
The reaction of indole (100 mg, 0.854 mmol, 1 equiv.), 3-pyridyl methanol (93 mg, 0.854 mmol, 1 equiv.), KO^{t}Bu (95.8 mg, 1 mmol, 1 equiv.), cat. **[PNP-Ru]** (0.73 mg, 0.000854 mmol, 0.1 mol %), afforded 160 mg, **I_5** in 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.46 (s, 1H), 8.16 (s, 1H), 7.62 – 7.53 (m, 1H), 7.49 (d, J = 7.9 Hz, 1H), 7.40 – 7.33 (m, 1H), 7.24 – 7.15 (m, 2H), 7.09 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 6.94 (d, J = 1.0 Hz, 1H), 4.12 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 147.4, 136.5, 136.2, 128.8, 127.1, 123.4, 122.5, 122.3, 122.3, 119.6, 118.9, 111.2, 28.9.*m/z* calcd for $C_{14}H_{13}N_2$:209.1073 $[M+H]^+$; found: 209.1088.

3-(furan-2-ylmethyl)-1H-indole (I_6)



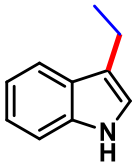
The reaction of indole (100 mg, 0.854 mmol, 1 equiv.), furfuryl alcohol (83.7 mg, 0.854 mmol, 1 equiv.), KO^{t}Bu (95.8 mg, 1 mmol, 1 equiv.), cat. **[PNP-Ru]** (0.73 mg, 0.000854 mmol, 0.1 mol %), afforded 161 mg, **I_6** in 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 2H), 7.59 (dd, J = 7.9, 1.1 Hz, 1H), 7.41 – 7.30 (m, 1H), 7.21 (t, J = 8.2 Hz, 2H), 7.13 (t, J = 6.9 Hz, 1H), 7.05 (d, J = 1.2 Hz, 1H), 6.33 – 6.27 (m, 1H), 6.04 (d, J = 3.2 Hz, 1H), 4.14 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.16, 142.69, 141.29, 136.55, 126.79, 123.19, 121.99, 119.71, 119.39, 117.10, 111.25, 110.46, 110.24, 106.68, 34.15. *m/z* calcd. for $C_{13}H_{11}NO$:196.0762 $[M^+]$; found: 196.0753.

3-methyl-1H-indole (I_7)



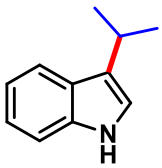
The reaction of indole (100 mg, 0.854 mmol, 1 equiv.), methanol (1 mL), KO^{t}Bu (95.8 mg, 1 mmol, 1 equiv.), cat. **[PNP-Ru]** (0.73 mg, 0.000854 mmol, 0.1 mol %), afforded 64 mg, **I_7** in 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.64 – 7.57 (m, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.23 – 7.18 (m, 1H), 7.18 – 7.08 (m, 1H), 6.98 (d, J = 1.2 Hz, 1H), 2.36 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.3, 128.3, 121.9, 121.6, 119.1, 118.8, 111.8, 110.9, 9.7.*m/z* calcd for $C_9H_{10}N$: 132.0808 $[M+H]^+$; found: 132.0506.

3-ethyl-1H-indole (I_8)



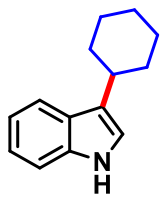
The reaction of indole (100 mg, 0.854 mmol, 1 equiv.), ethyl alcohol (1 mL), KO^{t}Bu (95.8 mg, 1 mmol, 1 equiv.), cat. **[PNP-Ru]** (0.73 mg, 0.000854 mmol, 0.1 mol %), afforded 77 mg, **I_8** in 62% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 8.1 Hz, 1H), 7.28 – 7.18 (m, 1H), 7.14 (ddd, J = 7.9, 6.9, 1.1 Hz, 1H), 7.00 – 6.94 (m, 1H), 2.82 (q, J = 7.3 Hz, 2H), 1.37 (t, J = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.4, 127.5, 121.9, 120.5, 119.1, 119.0, 111.1, 109.2, 18.4, 14.5. *m/z* calcd for $C_{10}H_{12}N$:146.0964 $[M+H]^+$; found: 146.0960.

3-isopropyl-1H-indole (I_9)



The reaction of indole (100 mg, 0.854 mmol, 1 equiv.), propan-2-ol (1 mL), KO^{t}Bu (95.8 mg, 1 mmol, 1 equiv.), cat. **[PNP-Ru]** (0.73 mg, 0.000854 mmol, 0.1 mol %), afforded 90 mg, **I_9** in 66% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.67 (d, J = 7.6 Hz, 1H), 7.39 – 7.33 (m, 1H), 7.22 – 7.17 (m, 1H), 7.12 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H), 6.96 (d, J = 1.8 Hz, 1H), 3.22 (h, J = 6.6 Hz, 1H), 1.38 (d, J = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.6, 126.8, 124.1, 121.8, 119.4, 119.2, 119.0, 111.1, 25.5, 23.3. *m/z* calcd for $C_{11}H_{14}N$: 160.1121 $[M+H]^+$; found: 160.1116.

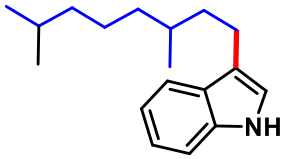
3-cyclohexyl-1H-indole (I_{10})



The reaction of indole (100 mg, 0.854 mmol, 1 equiv.), cyclohexanol (1mL), KO^{t}Bu (95.8 mg, 1 mmol, 1 equiv.), cat. **[PNP-Ru]** (0.73 mg, 0.000854 mmol, 0.1 mol %), afforded 115 mg, **I_{10}** in 68% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.66 (d, J = 7.9 Hz, 1H), 7.40 – 7.29 (m, 1H), 7.17 (td, J = 7.6, 1.2 Hz,

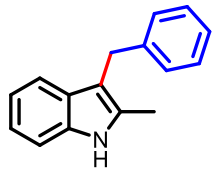
1H), 7.10 (ddd, *J* = 8.1, 6.9, 1.0 Hz, 1H), 6.95 (d, *J* = 1.9 Hz, 1H), 2.84 (tt, *J* = 8.0, 3.9 Hz, 1H), 2.13 – 1.98 (m, 2H), 1.81 – 1.72 (m, 2H), 1.50 – 1.41 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.4, 126.8, 123.3, 121.8, 119.4, 118.9, 111.1, 35.5, 34.1, 26.9, 26.6. *m/z* calcd for $C_{14}H_{18}N$: 200.1434 $[M+H]^+$; found: 200.1429.

3-(3,7-dimethyloctyl)-1H-indole (I_{11})



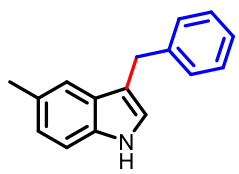
The reaction of indole (100 mg, 0.854 mmol, 1 equiv.), 3,7-dimethyl-1-octanol (135.5 mg, 0.854 mmol, 1 equiv.), KO^{t}Bu (95.8 mg, 1 mmol, 1 equiv.), cat. **[PNP-Ru]** (0.73 mg, 0.000854 mmol, 0.1 mol %), afforded 158 mg, **I_{11}** in 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.65 (d, *J* = 7.7 Hz,1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.21 (ddt, *J* = 6.9, 5.2, 1.5 Hz, 1H), 7.15 (dddd, *J* = 8.7, 7.1, 3.7, 1.5 Hz,1H), 6.97 (s, 1H), 2.89 – 2.66 (m, 2H), 1.83 – 1.70 (m, 1H), 1.59 (s, 3H), 1.46 – 1.16 (m, 6H), 1.02 – 0.99 (m, 3H), 0.94 – 0.85 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.4, 127.7, 121.9, 120.8, 119.1, 119.0, 117.5, 111.0, 39.4, 37.5, 37.3, 32.8, 28.0, 24.8, 22.8, 22.7, 22.7, 19.7. *m/z* calcd for $C_{18}H_{28}N$: 258.2216 $[M+H]^+$; found: 258.2218

3-benzyl-2-methyl-1H-indole (I_{12})[3]



The reaction of 2-methyl-1H-indole (100 mg, 0.76 mmol, 1 equiv.), benzyl alcohol (82.4 mg, 0.76 mmol, 1 equiv.), KO^{t}Bu (85.27 mg, 0.76 mmol, 1 equiv.), cat. **[PNP-Ru]** (0.65 mg, 0.00076 mmol, 0.1 mol %), afforded 129 mg, **I_{12}** in 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (s, 1H), 7.45 (dd, *J* = 7.0, 2.0 Hz, 1H), 7.37 – 7.31 (m, 4H), 7.28 – 7.24 (m, 1H), 7.07 (qd, *J* = 7.2, 1.7 Hz, 2H), 6.94 – 6.91 (m, 1H), 4.18 (d, *J* = 1.1 Hz, 2H), 2.52 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.4, 136.1, 128.8, 128.4, 127.1, 125.9, 122.6, 122.2, 120.3, 119.7, 117.0, 116.3, 31.8, 16.7.

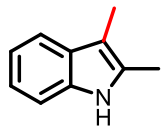
3-benzyl-5-methyl-1H-indole(I_{13})[3]



The reaction of 5-methyl-1H-indole (100 mg, 0.76 mmol, 1 equiv.), benzyl alcohol (82.4 mg, 0.76 mmol, 1 equiv.), KO^{t}Bu (85.27 mg, 0.76 mmol, 1 equiv.), cat. **[PNP-Ru]** (0.65 mg, 0.00076 mmol, 0.1 mol %), afforded 136 mg, **I_{13}** in 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (s, 1H), 7.33 (d, *J* = 10.4 Hz, 5H), 7.28 (d, *J* = 1.3 Hz, 1H), 7.22 (dq, *J* = 8.9, 3.9 Hz, 1H), 7.04 (d, *J*

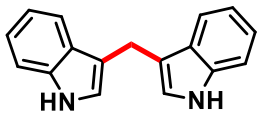
= 8.3 Hz, 1H), 6.89 (d, *J* = 2.3 Hz, 1H), 4.12 (s, 2H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.3, 134.8, 128.7, 128.6, 128.3, 127.7, 125.8, 123.7, 122.5, 118.7, 115.3, 110.7, 31.5, 21.5.

2,3-dimethyl-1H-indole (I_{14})[4]



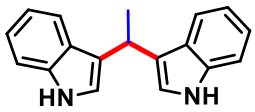
The reaction of 2-methyl-1H-indole (100 mg, 0.762 mmol, 1 equiv.), methanol (1 mL), KO^{t}Bu (85.5 mg, 1 mmol, 1 equiv.), cat. **[PNP-Ru]** (0.65 mg, 0.000762 mmol, 0.1 mol %), afforded 56 mg, **I_{14}** in 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (s, 1H), 7.50 (d, *J* = 11.0 Hz, 1H), 7.26 (dd, *J* = 7.2, 2.4 Hz, 1H), 7.19 – 7.07 (m, 2H), 2.37 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 135.2, 130.7, 129.4, 120.9, 119.0, 118.0, 110.0, 107.1, 11.6, 8.5.

di(1H-indol-3-yl) methane (I_{15})



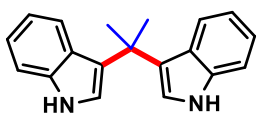
The reaction of indole (200 mg, 1.708 mmol, 2 equiv.), methanol (27.4 mg, 0.854 mmol, 1 equiv.), KO^{t}Bu (95.8 mg, 1 mmol, 1 equiv.), cat. **[PNP-Ru]** (0.73 mg, 0.000854 mmol, 0.1 mol %), afforded 179 mg, **I_{15}** in 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 2H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.20 (td, *J* = 7.6, 1.2 Hz, 2H), 7.14 – 7.06 (m, 2H), 6.93 (s, 1H), 4.26 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5, 127.6, 122.2, 121.9, 119.2, 119.2, 115.7, 111.0, 21.2.

3,3'-(ethane-1,1-diyl)bis(1H-indole) (I_{16})



The reaction of indole (200 mg, 1.708 mmol, 2 equiv.), ethanol (39.3 mg, 0.854 mmol, 1 equiv.), KO^{t}Bu (95.8 mg, 1 mmol, 1 equiv.), cat. **[PNP-Ru]** (0.73 mg, 0.000854 mmol, 0.1 mol %), afforded 177 mg, **I_{16}** in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (s, 2H), 7.60 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.19 (t, *J* = 7.6 Hz, 2H), 7.07 (t, *J* = 7.5 Hz, 2H), 6.89 (d, *J* = 2.4 Hz, 2H), 4.70 (q, *J* = 7.1 Hz, 1H), 1.83 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.7, 126.9, 121.8, 121.7, 121.3, 119.8, 119.0, 111.1, 28.2, 21.8. *m/z* calcd for $C_{18}H_{16}N_2$: 260.1313 $[M]^+$; found: 260.1261.

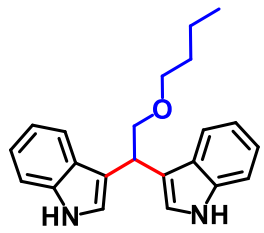
3,3'-(2-methylpropane-1,1-diyl)bis(1H-indole) (I_{17})



The reaction of indole (200 mg, 1.708 mmol, 2 equiv.), propan-1-ol (51 mg, 0.854 mmol, 1 equiv.), KO^{t}Bu (95.8 mg, 1 mmol, 1 equiv.), cat. **[PNP-Ru]** (0.73 mg, 0.000854 mmol, 0.1 mol %), afforded 181 mg, **I_{17}** in 78% yield.

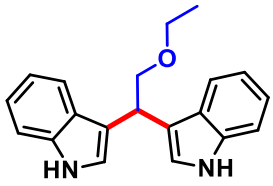
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (s, 2H), 7.43 (d, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.15 – 7.03 (m, 4H), 6.90 (ddt, *J* = 7.9, 5.8, 0.9 Hz, 2H), 1.94 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1, 126.4, 125.5, 121.4, 121.3, 120.5, 118.7, 111.1, 34.9, 30.0. *m/z* calcd for $C_{19}H_{18}N_2$: 274.147 $[M]^+$; found: 274.1455.

3,3'-(2-butoxyethane-1,1-diyl)bis(1H-indole) (I_{18})



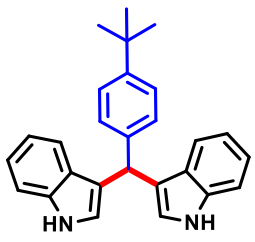
The reaction of indole (200 mg, 1.708 mmol, 2 equiv.), n-butoxyethanol (101 mg, 0.854 mmol, 1 equiv.), KO^{t}Bu (95.8 mg, 1 mmol, 1 equiv.), cat. **[PNP-Ru]** (0.73 mg, 0.000854 mmol, 0.1 mol %), afforded 230 mg, **I_{18}** in 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 2H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.16 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 2H), 7.11 – 6.93 (m, 4H), 4.87 (t, *J* = 6.6 Hz, 1H), 4.09 (d, *J* = 6.6 Hz, 2H), 3.51 (t, *J* = 6.6 Hz, 2H), 1.64 – 1.49 (m, 2H), 1.42 – 1.21 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5, 127.2, 122.4, 121.8, 119.6, 119.1, 117.4, 111.0, 74.4, 70.9, 34.5, 31.8, 19.4, 13.9. *m/z* calcd for $C_{22}H_{25}N_2O$: 333.1961 $[M+H]^+$; found: 333.1935.

3,3'-(2-ethoxyethane-1,1-diyl)bis(1H-indole) (I_{19})



The reaction of indole (200 mg, 1.708 mmol, 2 equiv.), ethoxy ethanol (76.9 mg, 0.854 mmol, 1 equiv.), KO^{t}Bu (95.8 mg, 1 mmol, 1 equiv.), cat. **[PNP-Ru]** (0.73 mg, 0.000854 mmol, 0.1 mol %), afforded 215 mg, **I_{19}** in 83% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 2H), 7.60 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.20 – 7.13 (m, 2H), 7.09 – 7.02 (m, 2H), 6.96 (d, *J* = 2.4 Hz, 2H), 4.88 (t, *J* = 6.7 Hz, 1H), 4.11 (d, *J* = 6.7 Hz, 2H), 3.60 (q, *J* = 7.0 Hz, 2H), 1.21 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5, 127.2, 122.4, 121.8, 119.6, 119.1, 117.3, 111.1, 74.1, 66.4, 34.6, 15.2. *m/z* calcd for $C_{20}H_{21}N_2O$: 305.1648 $[M+H]^+$; found: 305.1638.

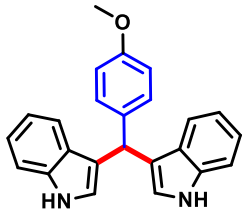
3,3'-((4-(tert-butyl)phenyl)methylene)bis(1H-indole) (I_{20})



The reaction of indole (200 mg, 1.708 mmol, 2 equiv.), 4-tert-butyl benzyl alcohol (140 mg, 0.854 mmol, 1 equiv.), KO^{t}Bu (95.8 mg, 1 mmol, 1 equiv.), cat. **[PNP-Ru]** (0.73 mg, 0.000854 mmol, 0.1 mol %), afforded 242 mg, **I_{20}** in 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 2H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.34 (dd, *J* = 8.2, 0.9 Hz, 2H), 7.25 (s, 4H), 7.15 (ddd, *J* = 8.2, 7.0,

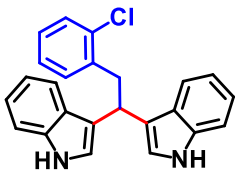
1.2 Hz, 2H), 6.99 (ddd, J = 8.0, 7.0, 1.0 Hz, 2H), 6.70 – 6.64 (m, 2H), 5.85 (s, 1H), 1.28 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.7, 140.8, 136.7, 128.2, 127.2, 125.0, 123.5, 121.9, 120.0, 119.1, 111.0, 39.7, 34.4, 31.5. m/z calcd for $C_{18}H_{16}N_2$: 260.1313 $[M+H]^+$; found: 260.1301.

3,3'-((4-methoxyphenyl)methylene)bis(1H-indole) (I_{21})



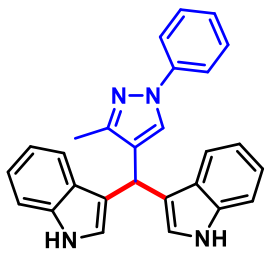
The reaction of indole (200 mg, 1.708 mmol, 2 equiv.), 4-methoxy benzyl alcohol (117.99 mg, 0.854 mmol, 1 equiv.), KO^{t}Bu (95.8 mg, 1 mmol, 1 equiv.), cat. **[PNP-Ru]** (0.73 mg, 0.000854 mmol, 0.1 mol %), afforded 204 mg, **I_{21}** in 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 7.31 – 7.24 (m, 2H), 7.19 (q, J = 7.0 Hz, 2H), 7.02 (td, J = 7.5, 1.0 Hz, 2H), 6.89 – 6.80 (m, 1H), 6.65 (s, 2H), 5.86 (s, 1H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 136.7, 129.6, 127.1, 123.5, 121.9, 120.0, 119.2, 113.6, 111.0, 55.2, 39.4.

3,3'-(2-(2-chlorophenyl)ethane-1,1-diyl)bis(1H-indole) (I_{22})



The reaction of indole (200 mg, 1.708 mmol, 2 equiv.), 2-chlorophenyl)methanol (133 mg, 0.854 mmol, 1 equiv.), KO^{t}Bu (95.8 mg, 1 mmol, 1 equiv.), cat. **[PNP-Ru]** (0.73 mg, 0.000854 mmol, 0.1 mol %), afforded 258 mg, **I_{22}** in 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (s, 2H), 7.60 (d, J = 7.9 Hz, 2H), 7.32 (d, J = 8.2 Hz, 3H), 7.15 (ddd, J = 8.2, 7.0, 1.2 Hz, 2H), 7.07 – 6.98 (m,3 H), 6.97 (d, J = 2.0 Hz, 2H), 6.92 – 6.80 (m, 2H), 4.97 (t, J = 7.7 Hz, 1H), 3.67 (d, J = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.4, 136.6, 134.1, 131.3, 129.2, 127.2, 127.1, 126.2, 122.0, 121.8, 119.8, 119.3, 119.1, 111.1, 39.4, 34.1.

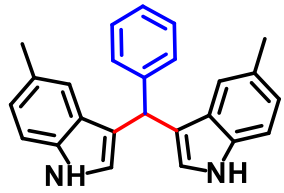
3,3'-((3-methyl-1-phenyl-1H-pyrazol-4-yl)methylene)bis(1H-indole) (I_{23})



The reaction of indole (200 mg, 1.708 mmol, 2 equiv.), 1-phenyl-4-methyl-1H- imidazole (160.75 mg, 0.854 mmol, 1 equiv.), KO^{t}Bu (95.8 mg, 1 mmol, 1 equiv.), cat. **[PNP-Ru]** (0.73 mg, 0.000854 mmol, 0.1 mol %), afforded 240 mg, **I_{23}** in 70% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97 (s, 2H), 7.53 (d, J = 8.0 Hz, 2H), 7.49 – 7.43 (m, 3H), 7.38 (d, J = 8.2 Hz, 2H), 7.33 (t, J = 7.8 Hz, 2H), 7.17 (dt, J = 15.1, 7.5 Hz, 3H), 7.03 (t, J = 7.5 Hz, 2H), 6.79 (d, J = 2.4 Hz, 2H), 5.78 (s, 1H), 2.25 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 149.1, 136.8, 129.2,

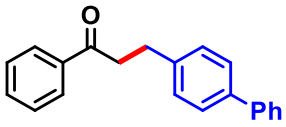
126.8, 126.7, 125.4, 124.8, 123.1, 122.0, 119.9, 119.3, 118.9, 118.3, 111.1, 109.6, 30.1, 12.3. *m/z* calcd for $C_{27}H_{23}N_4$: 403.1917 $[M+H]^+$; found: 403.1911.

3,3'-(phenylmethylene)bis(5-methyl-1H-indole) (I_{24})[5]



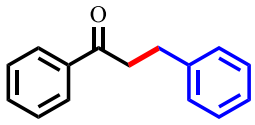
The reaction of 5-methyl-1H-indole (200 mg, 1.56 mmol, 2 equiv.), benzyl alcohol (82.4 mg, 0.76 mmol, 1 equiv.), KO^{t}Bu (85.27 mg, 0.76 mmol, 1 equiv.), cat. **[PNP-Ru]** (0.65 mg, 0.00076 mmol, 0.1 mol %), afforded 213 mg, **I_{24}** in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (s, 2H), 7.35 – 7.32 (m, 2H), 7.30 – 7.27 (m, 2H), 7.26 (d, *J* = 1.2 Hz, 2H), 7.23 – 7.20 (m, 1H), 7.20 – 7.18 (m, 2H), 7.00 (dd, *J* = 8.3, 1.6 Hz, 2H), 6.59 (dd, *J* = 2.5, 1.1 Hz, 2H), 5.83 (s, 1H), 2.35 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.2, 135.0, 128.7, 128.4, 128.2, 127.3, 126.0, 123.9, 123.5, 119.5, 119.3, 110.7, 40.0, 21.5.

3-([1,1'-biphenyl]-4-yl)-1-phenylpropan-1-one (E_1)



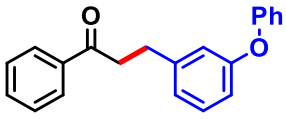
The reaction of styryl oxide (100 mg, 0.832 mmol, 1 equiv.), 4-phenyl benzyl alcohol (168.6 mg, 0.91 mmol, 1.1 equiv.), Cs_2CO_3 (271.1 mg, 0.834 mmol, 1 equiv.), cat. **[PNP-Ru]** (3.6 mg, 0.0042 mmol, 0.5 mol %), afforded 214 mg, **E_1** in 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (dt, *J* = 7.1, 1.4 Hz, 2H), 7.64 – 7.52 (m, 5H), 7.51 – 7.39 (m, 4H), 7.35 (t, *J* = 3.8 Hz, 3H), 3.36 (dd, *J* = 8.5, 6.9 Hz, 2H), 3.13 (dd, *J* = 8.4, 6.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.2, 141.0, 140.4, 139.2, 136.9, 133.1, 128.9, 128.8, 128.7, 128.1, 127.3, 127.1, 127.0, 40.4, 29.8.

1,3-diphenylpropan-1-one (E_2)



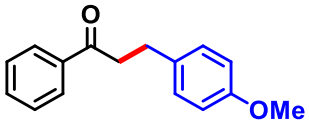
The reaction of styryl oxide (100 mg, 0.832 mmol, 1 equiv.), benzyl alcohol (98.3 mg, 0.91 mmol, 1.1 equiv.), Cs_2CO_3 (271.1 mg, 0.834 mmol, 1 equiv.), cat. **[PNP-Ru]** (3.6 mg, 0.0042 mmol, 0.5 mol %), afforded 166 mg, **E_2** in 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 9.7 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.21 (dd, *J* = 14.9, 6.4 Hz, 4H), 7.15 (t, *J* = 6.9 Hz, 1H), 3.29 – 3.20 (m, 2H), 3.12 – 2.97 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.3, 141.3, 139.5, 136.9, 133.1, 132.8, 129.0, 128.6, 128.6, 128.5, 128.4, 128.1, 128.1, 126.3, 126.2, 77.4, 77.1, 76.7, 40.5, 38.2, 30.2, 29.7.

3-(3-phenoxyphenyl)-1-phenylpropan-1-one (E_3)



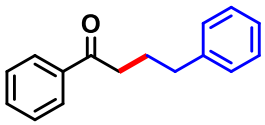
The reaction of styryl oxide (100 mg, 0.832 mmol, 1 equiv.), 3-phenoxy benzyl alcohol (200.2 mg, 0.91 mmol, 1.1 equiv.), Cs_2CO_3 (271.1 mg, 0.834 mmol, 1 equiv.), cat. **[PNP-Ru]** (3.6 mg, 0.0042 mmol, 0.5 mol %), afforded 239 mg, **E_3** in 93% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.4 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.41 – 7.32 (m, 2H), 7.31 – 7.24 (m, 1H), 7.02 (d, *J* = 7.9 Hz, 3H), 6.94 (d, *J* = 2.1 Hz, 1H), 6.91 – 6.82 (m, 1H), 3.32 (t, *J* = 7.7 Hz, 2H), 3.07 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 199.1, 157.4, 143.4, 133.1, 129.8, 128.6, 128.1, 123.4, 118.9, 116.5, 40.2, 30.0.

3-(4-methoxyphenyl)-1-phenylpropan-1-one (E_4)



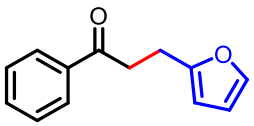
The reaction of styryl oxide (100 mg, 0.832 mmol, 1 equiv.), 4-methoxy benzyl alcohol (115 mg, 0.91 mmol, 1.1 equiv.), Cs_2CO_3 (271.1 mg, 0.834 mmol, 1 equiv.), cat. **[PNP-Ru]** (3.6 mg, 0.0042 mmol, 0.5 mol %), afforded 231 mg, **E_4** in 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 – 7.89 (m, 2H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.45 (ddd, *J* = 8.2, 6.5, 1.3 Hz, 2H), 7.20 – 7.07 (m, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 3.27 (dd, *J* = 8.5, 7.0 Hz, 2H), 3.02 (dd, *J* = 8.4, 6.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.4, 158.0, 136.9, 133.3, 133.1, 129.4, 128.6, 128.1, 114.0, 55.3, 40.7, 29.3.

1,4-diphenylbutan-1-one (E_5)



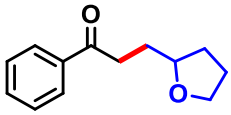
The reaction of styryl oxide (100 mg, 0.832 mmol, 1 equiv.), ethan-1-pheyl-2-ol (115 mg, 0.91 mmol, 1.1 equiv.), Cs_2CO_3 (271.1 mg, 0.834 mmol, 1 equiv.), cat. **[PNP-Ru]** (3.6 mg, 0.0042 mmol, 0.5 mol %), afforded 167 mg, **E_5** in 90 % yield.^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.51 – 7.45 (m,3H), 7.35 – 7.30 (m, 3H), 7.24 (d, *J* = 7.4 Hz, 2H), 3.01 (t, *J* = 7.3 Hz, 2H), 2.75 (d, *J* = 7.6 Hz, 2H), 2.30 – 2.00 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 200.2, 133.0, 130.0, 129.0, 129.0, 128.6, 128.5, 128.4, 128.0, 37.7, 35.2, 25.7.

3-(furan-2-yl)-1-phenylpropan-1-one (E_6)



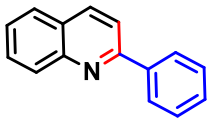
The reaction of styryl oxide (100 mg, 0.832 mmol, 1 equiv.), furfuryl alcohol (89.8 mg, 0.91 mmol, 1.1 equiv.), Cs_2CO_3 (271.1 mg, 0.834 mmol, 1 equiv.), cat. **[PNP-Ru]** (3.6 mg, 0.0042 mmol, 0.5 mol %), afforded 148 mg, **E_6** in 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 – 7.88 (m, 1H), 7.66 – 7.54 (m, 1H), 7.47 (dd, *J* = 8.4, 7.0 Hz, 1H), 7.31 (d, *J* = 1.8 Hz, 0H), 6.29 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.10 – 5.98 (m, 1H), 3.34 (dd, *J* = 8.3, 6.7 Hz, 1H), 3.10 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.7, 154.8, 141.1, 136.7, 133.2, 128.6, 128.0, 110.3, 105.3, 36.9, 22.5.

1-phenyl-3-(tetrahydrofuran-2-yl)propan-1-one (E_7)



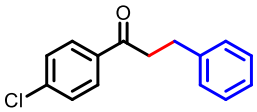
The reaction of styryl oxide (100 mg, 0.832 mmol, 1 equiv.), (tetrahydrofuran-2-yl)methanol (93.4 mg, 0.91 mmol, 1.1 equiv.), Cs_2CO_3 (271.1 mg, 0.834 mmol, 1 equiv.), cat. **[PNP-Ru]** (3.6 mg, 0.0042 mmol, 0.5 mol %), afforded 138 mg, **E_7** in 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 – 7.85 (m, 2H), 7.59 – 7.52 (m, 1H), 7.45 (dd, *J* = 8.4, 6.9 Hz, 2H), 3.88 – 3.82 (m, 1H), 3.73 (td, *J* = 8.0, 6.3 Hz, 1H), 3.17 (ddd, *J* = 17.3, 9.1, 5.5 Hz, 1H), 3.06 (ddd, *J* = 17.3, 8.9, 6.2 Hz, 1H), 2.08 – 1.96 (m, 2H), 1.89 (dddd, *J* = 17.1, 14.2, 8.8, 6.2 Hz, 3H), 1.53 (ddt, *J* = 11.9, 8.7, 7.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.1, 137.0, 132.9, 128.6, 128.1, 78.5, 67.7, 35.5, 31.5, 30.0, 25.7.

2-phenylquinoline (E_8)



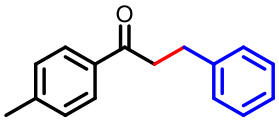
The reaction of styryl oxide (97.2 mg, 0.812 mmol, 1 equiv.), 2-amino-benzyl alcohol (89.8 mg, 0.812 mmol, 1 equiv.), Cs_2CO_3 (271.1 mg, 0.834 mmol, 1 equiv.), cat. **[PNP-Ru]** (3.6 mg, 0.0042 mmol, 0.5 mol %), afforded 150 mg, **E_8** in 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 – 8.12 (m, 4H), 7.88 (d, *J* = 8.6 Hz, 1H), 7.83 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.74 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.59 – 7.50 (m, 3H), 7.48 (ddt, *J* = 7.2, 4.7, 2.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.4, 148.3, 139.7, 136.8, 129.8, 129.7, 129.3, 128.9, 128.5, 127.6, 127.5, 127.2, 126.9, 126.3, 119.1.

1-(4-chlorophenyl)-3-phenylpropan-1-one (E_9)



The reaction of 4-chloro styryl oxide (100 mg, 0.647 mmol, 1 equiv.), benzyl alcohol (76.94 mg, 0.711 mmol, 1.1 equiv.), Cs_2CO_3 (210.8 mg, 0.647 mmol, 1 equiv.), cat. **[PNP-Ru]** (2.77 mg, 0.0032 mmol, 0.5 mol %), afforded 131 mg, **E_9** in 83% yield.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 8.1 Hz, 2H), 7.43 (d, J = 8.1 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.22 (d, J = 8.8 Hz, 2H), 7.20 – 7.09 (m, 1H), 3.27 (t, J = 7.6 Hz, 2H), 3.06 (t, J = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.0, 141.1, 139.5, 135.2, 129.5, 129.0, 128.9, 128.6, 128.5, 128.4, 126.2, 40.4, 30.1.

3-phenyl-1-(p-tolyl)propan-1-one (E_{10})



The reaction of 4-methyl styryl oxide (100 mg, 0.745 mmol, 1 equiv.), benzyl alcohol (88.6 mg, 0.82 mmol, 1.1 equiv.), Cs_2CO_3 (242.7 mg, 0.745 mmol, 1 equiv.), cat. **[PNP-Ru]** (3.17 mg, 0.0037 mmol, 0.5 mol %), afforded 148 mg, **E_{10}** in 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J = 8.3 Hz, 2H), 7.37 – 7.26 (m, 5H), 7.25 – 7.20 (m, 2H), 3.32 – 3.26 (m, 2H), 3.08 (dd, J = 8.6, 6.8 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.9, 143.9, 141.4, 134.4, 129.3, 128.5, 128.5, 128.2, 126.1, 40.4, 30.2, 21.7.

NMR spectra of catalytic products

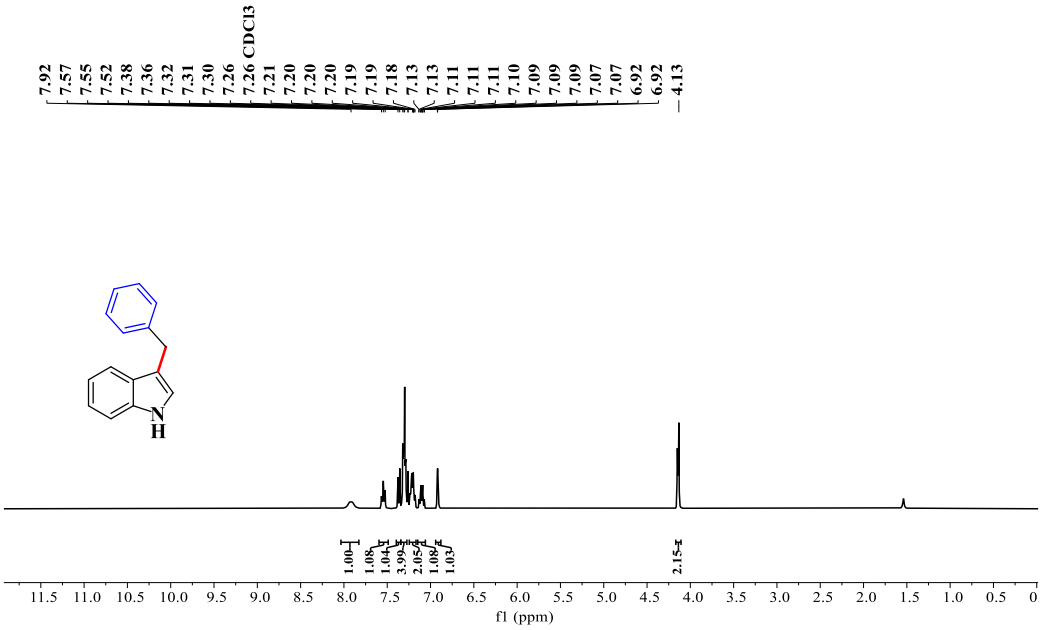


Figure S11. ^{1}H NMR spectrum of $\mathbf{I_1}$ (400 MHz).

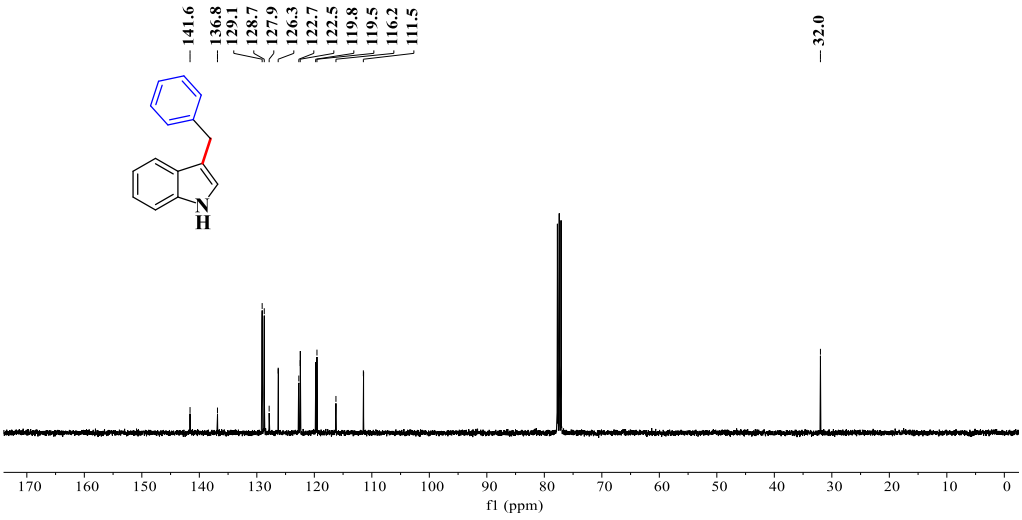


Figure S12. ^{13}C NMR spectrum of $\mathbf{I_1}$ (101 MHz).

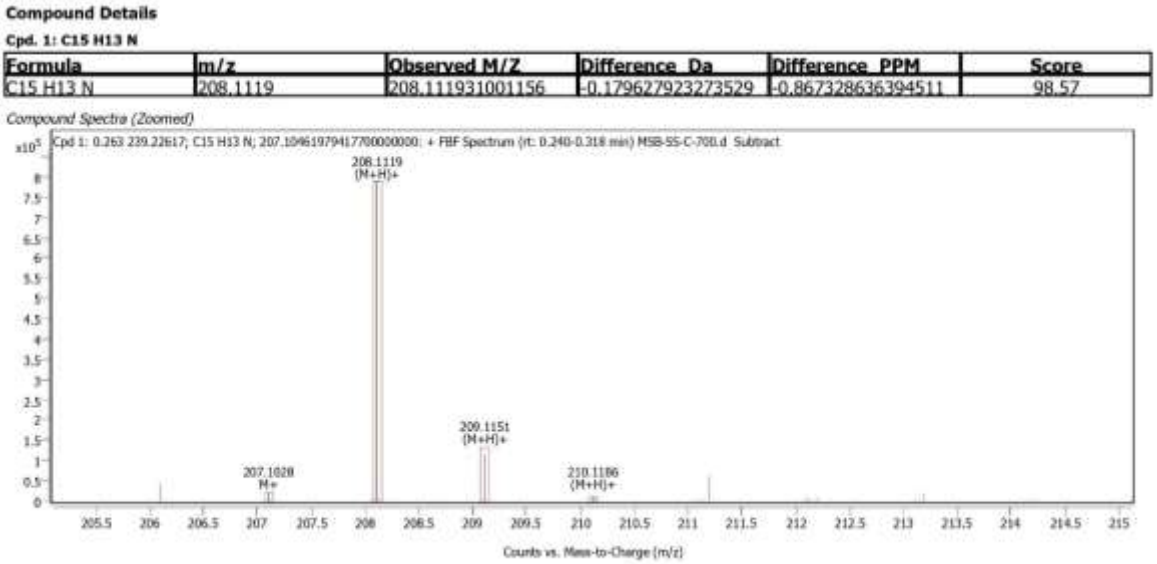


Figure S13. HRMS spectrum of $\mathbf{I_1}$.

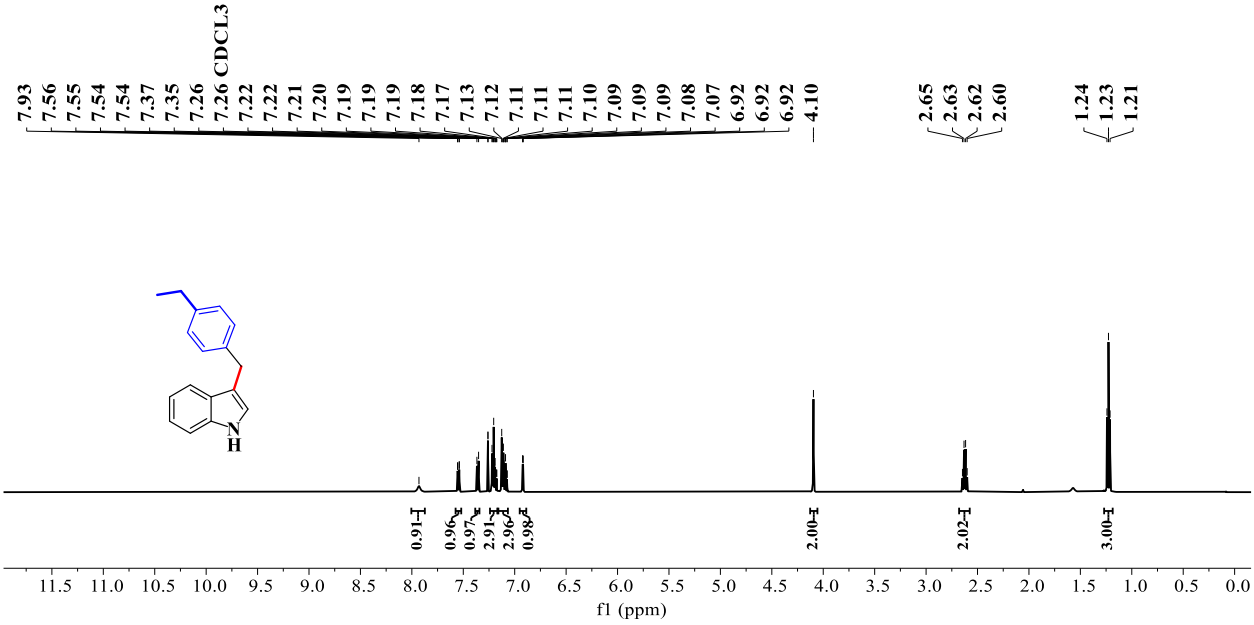


Figure S14. ^{1}H NMR spectrum of $\mathbf{I_2}$ (500 MHz).

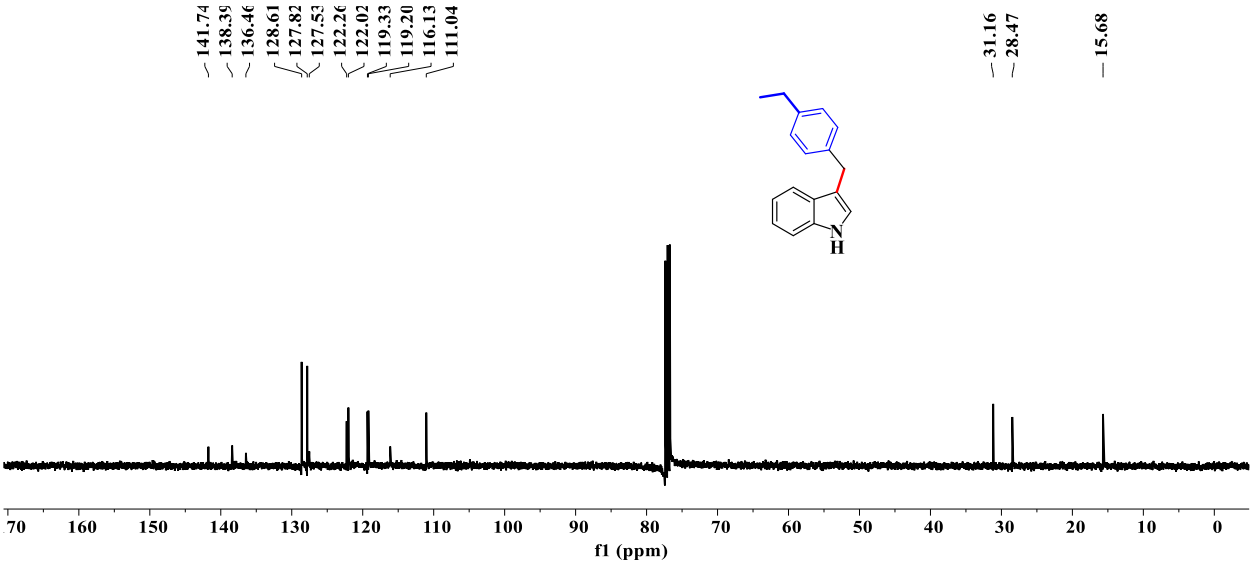


Figure S15. ^{13}C NMR spectrum of $\mathbf{I_2}$ (101 MHz).

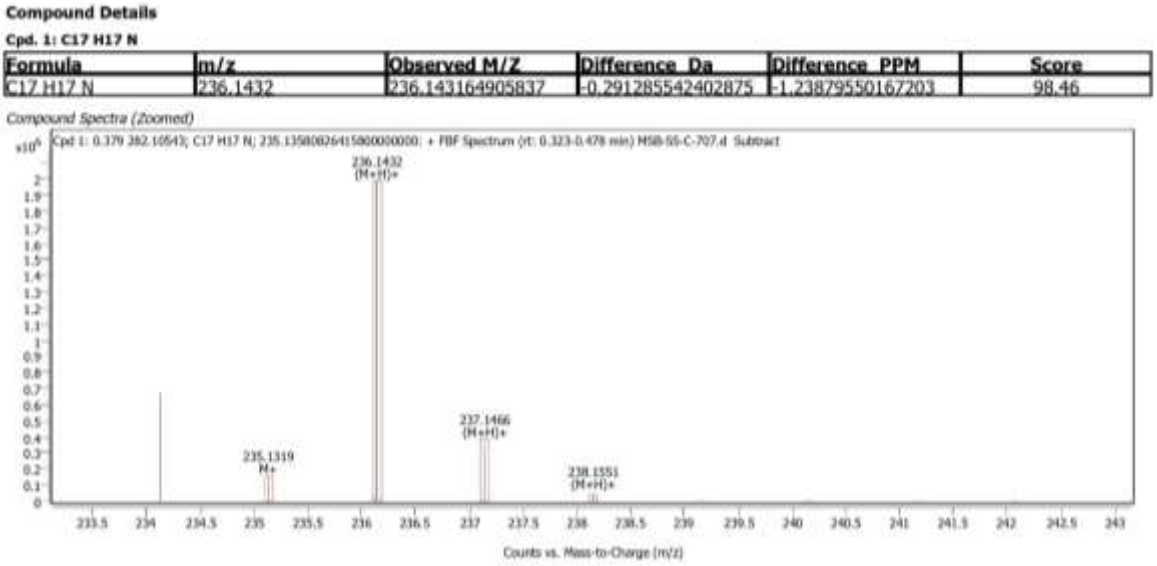


Figure S16. HRMS spectrum of $\mathbf{I_2}$.

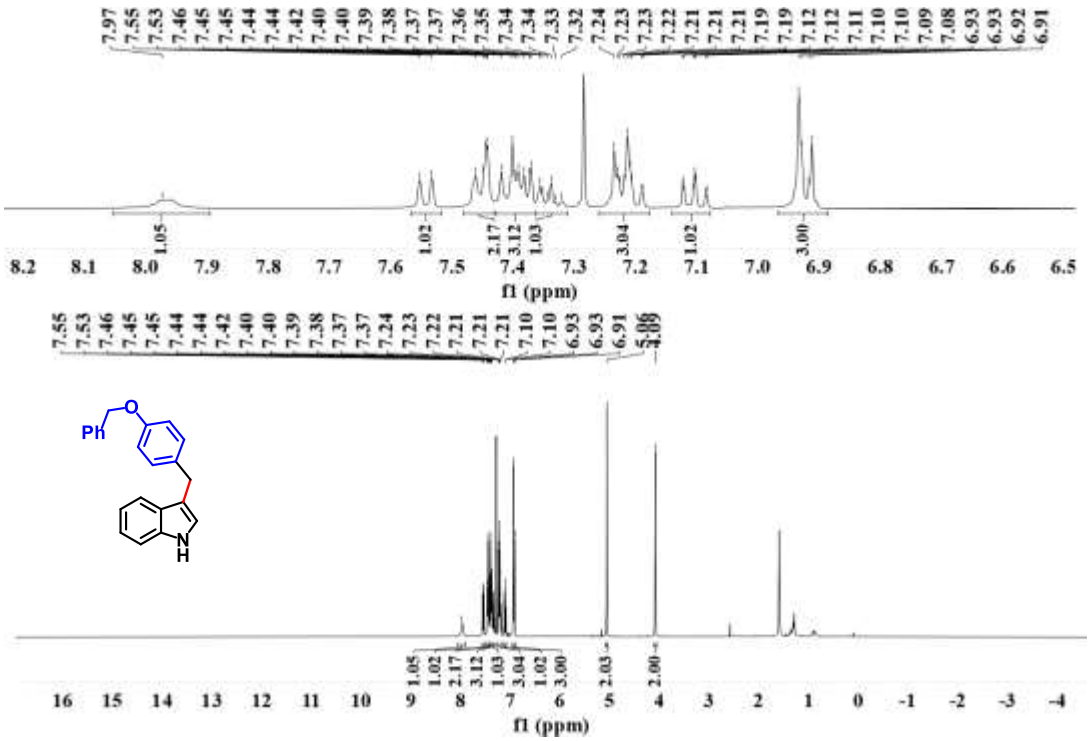


Figure S17. ^{1}H NMR spectrum of **I_3** (500 MHz).

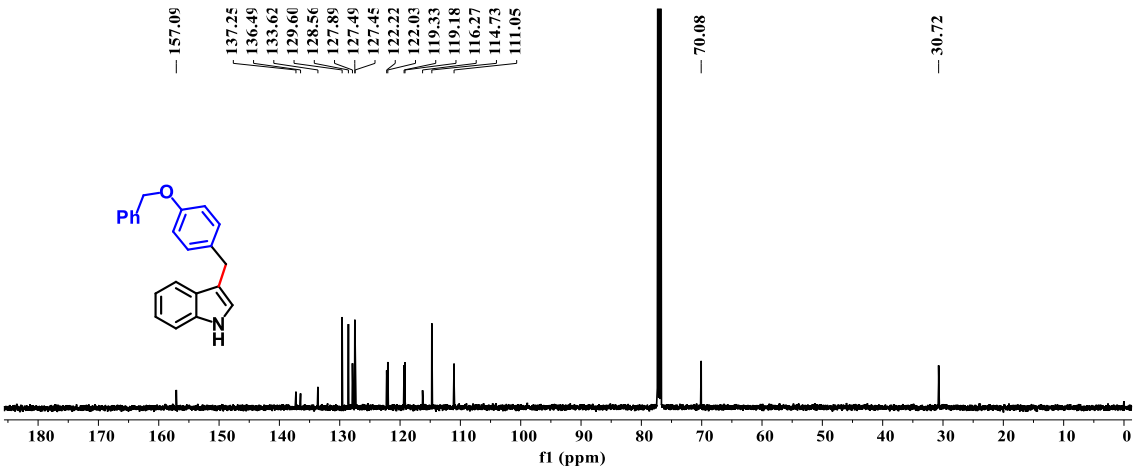


Figure S18. ^{13}C NMR spectrum of **I_3** (126 MHz).

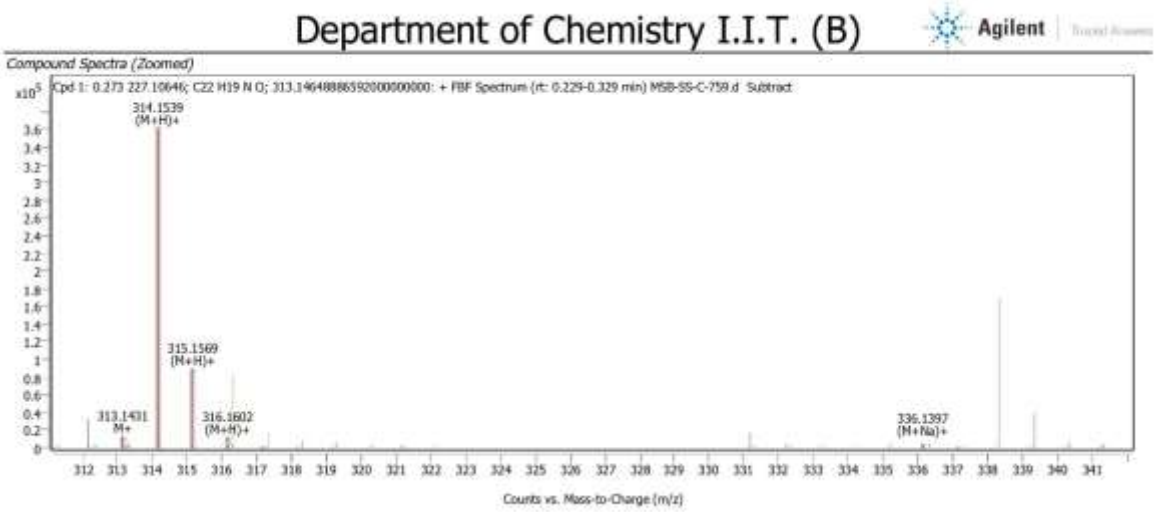


Figure S19. HRMS spectrum of **I_3**.

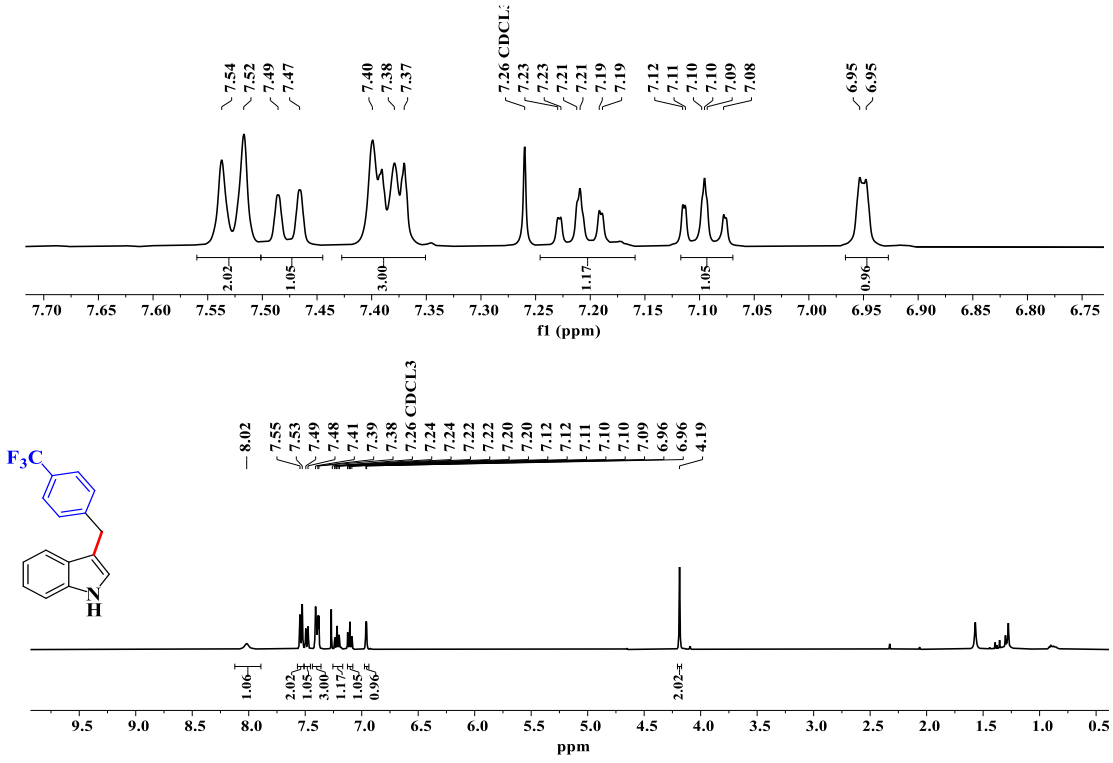


Figure S20. ^{1}H NMR spectrum of **I_4** (400 MHz).

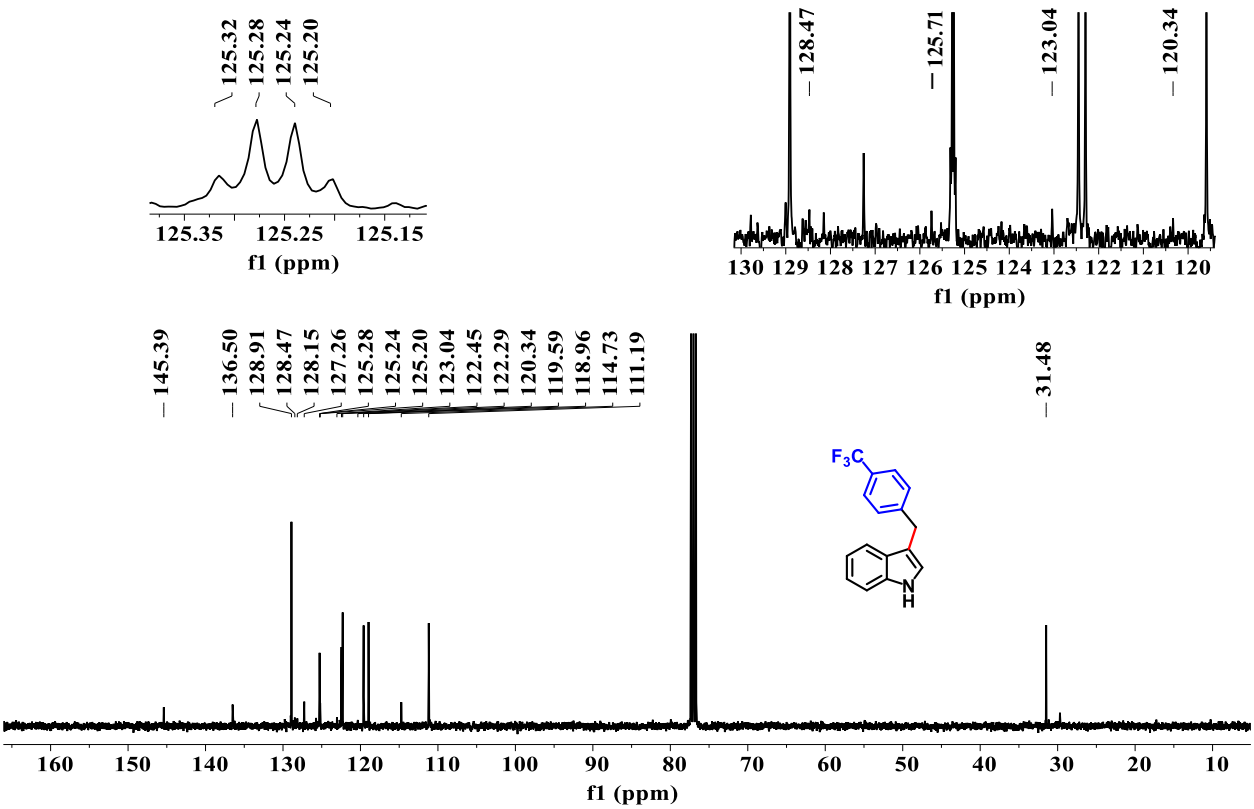


Figure S21. ^{13}C NMR spectrum of **I$_4$** (101 MHz).

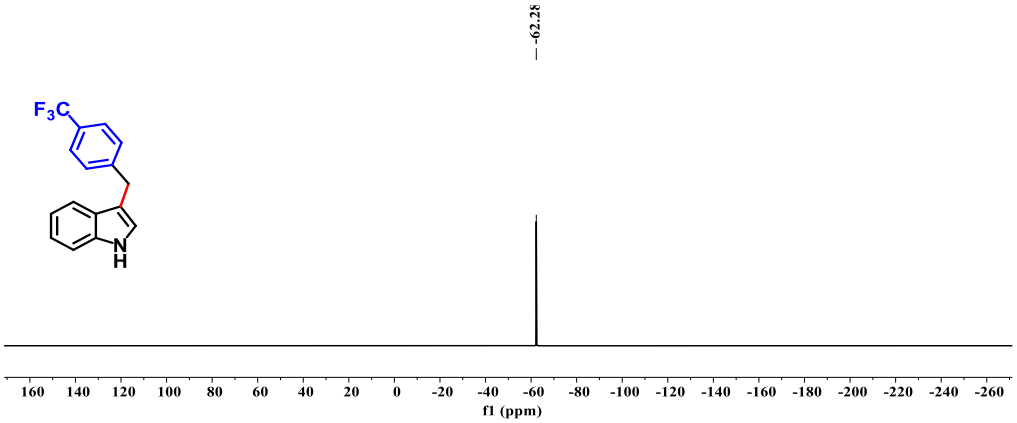


Figure S22. ^{19}F NMR spectrum of **I$_4$** (376 MHz).

Compound Details

Cpd. 1: C16 H12 F3 N

Formula	m/z	Observed M/Z	Difference Da	Difference PPM	Score
C16 H12 F3 N	276.0989	276.098905581918	-0.607712839553187	-2.20912434056955	98.78

Compound Spectra (Zoomed)

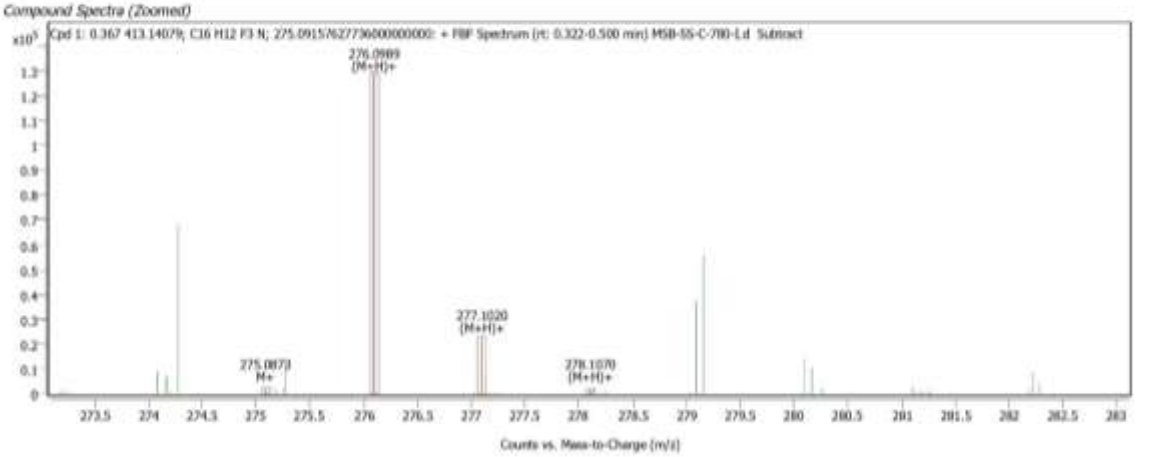


Figure S23. HRMS spectrum of **I_4**.

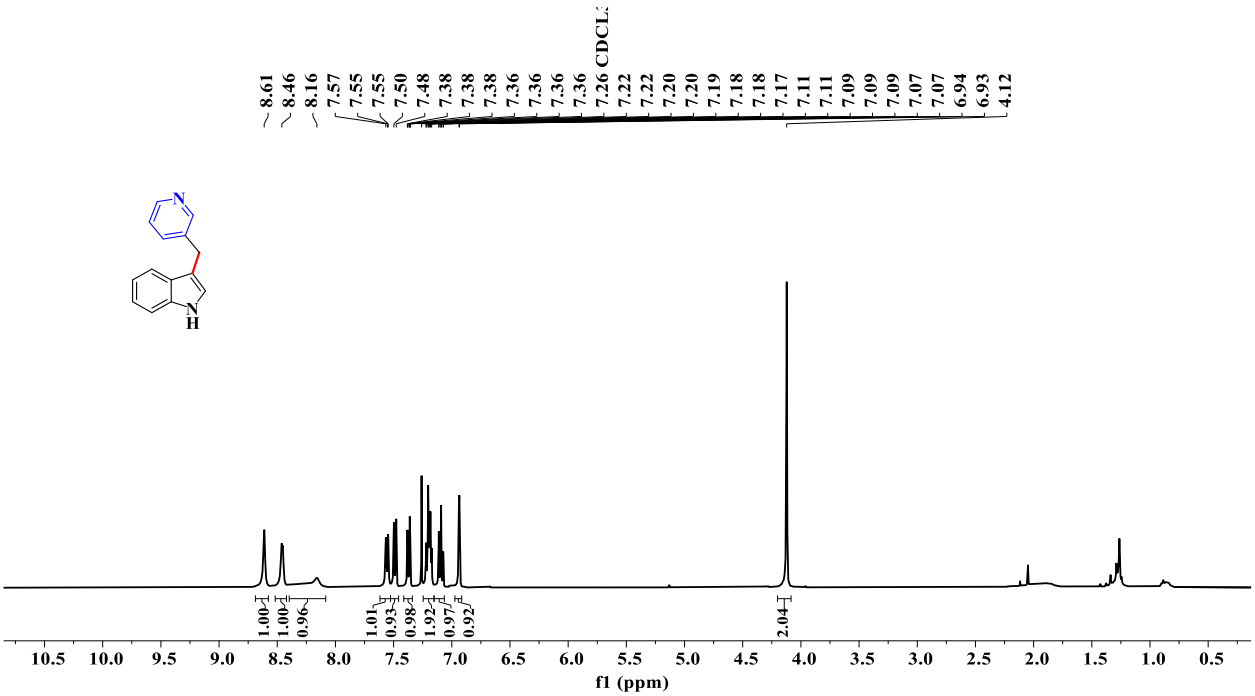


Figure S24. ^{1}H NMR spectrum of **I_5** (400 MHz).

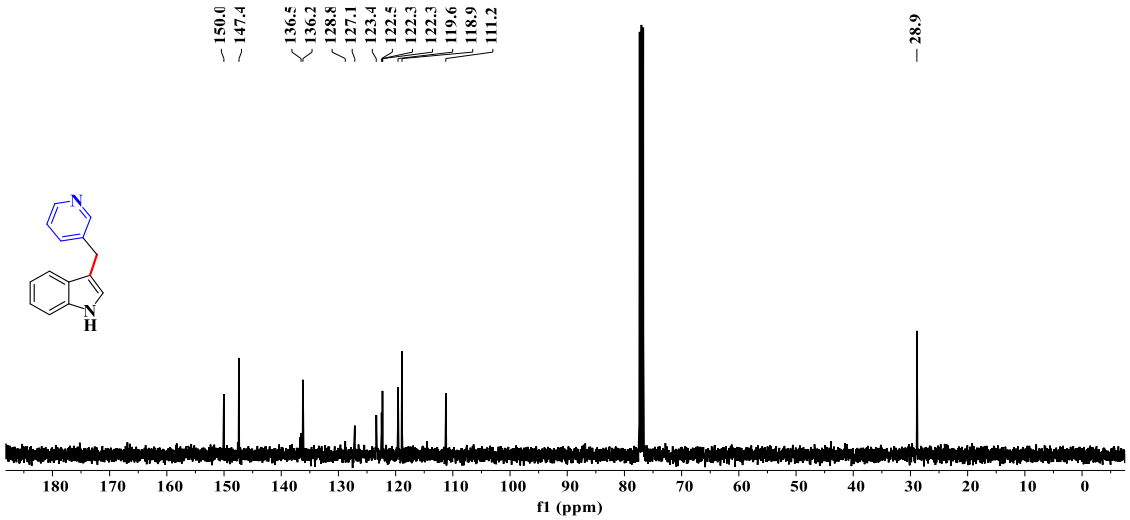


Figure S25. ^{13}C NMR spectrum of **I_5** (101 MHz).

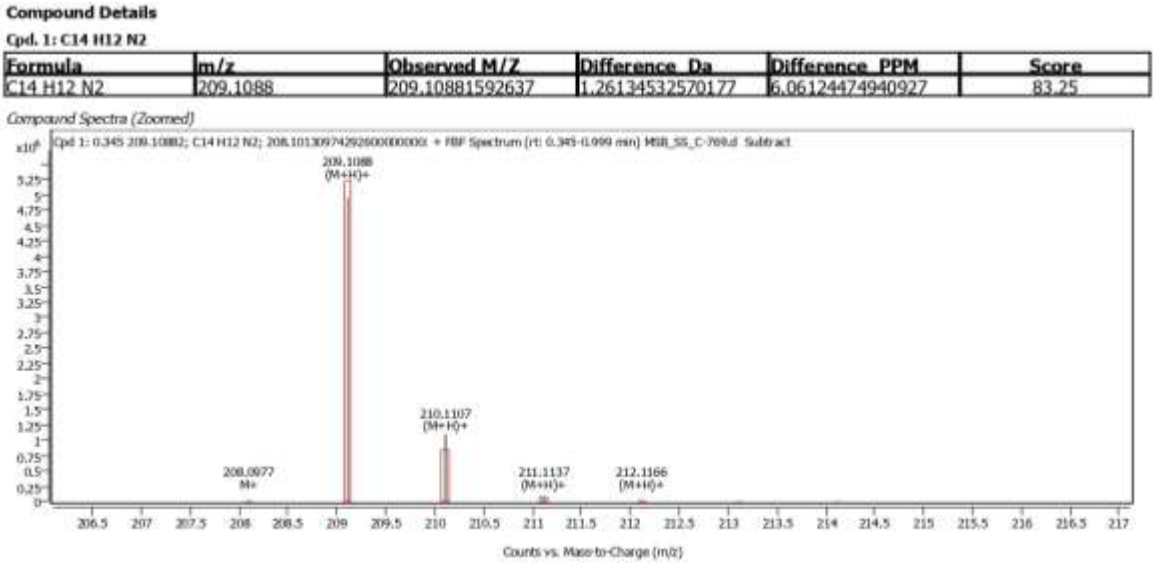


Figure S26. HRMS spectrum of **I_5**.

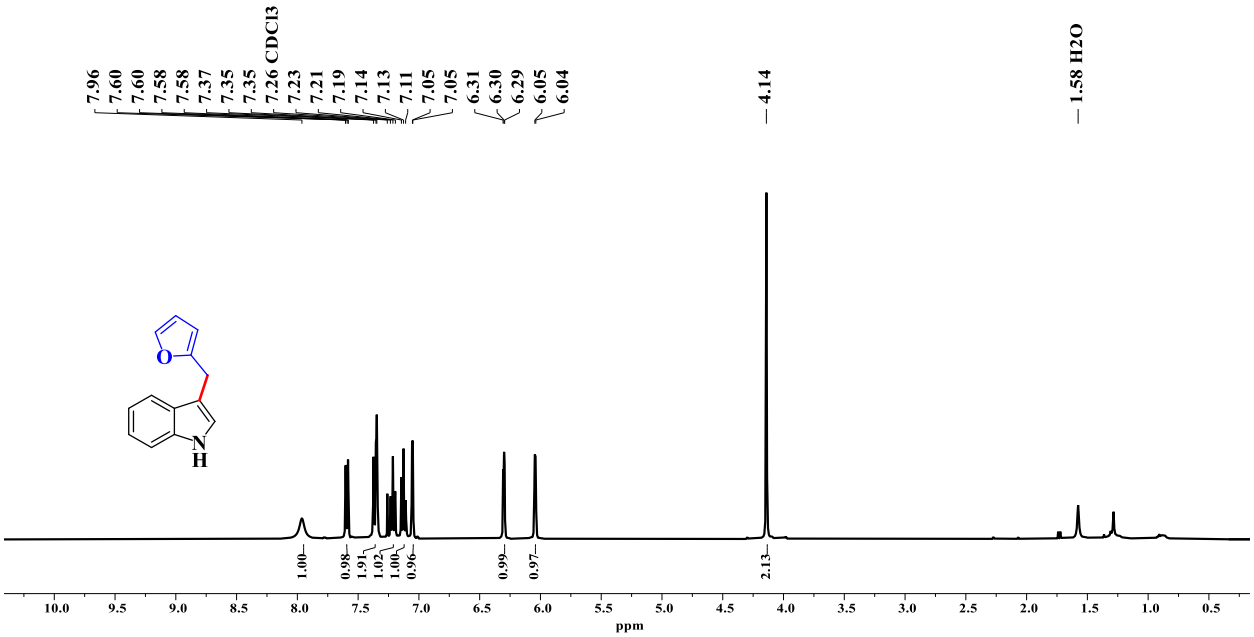


Figure S27. ^{1}H NMR spectrum of $\mathbf{I_6}$ (400 MHz).

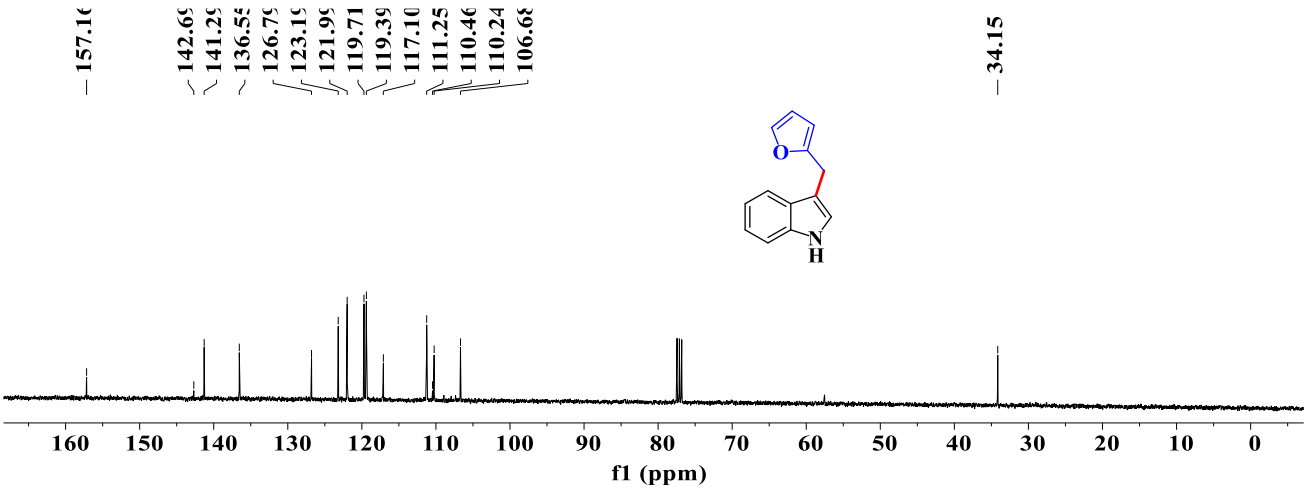


Figure S28. ^{13}C NMR spectrum of $\mathbf{I_6}$ (101 MHz).

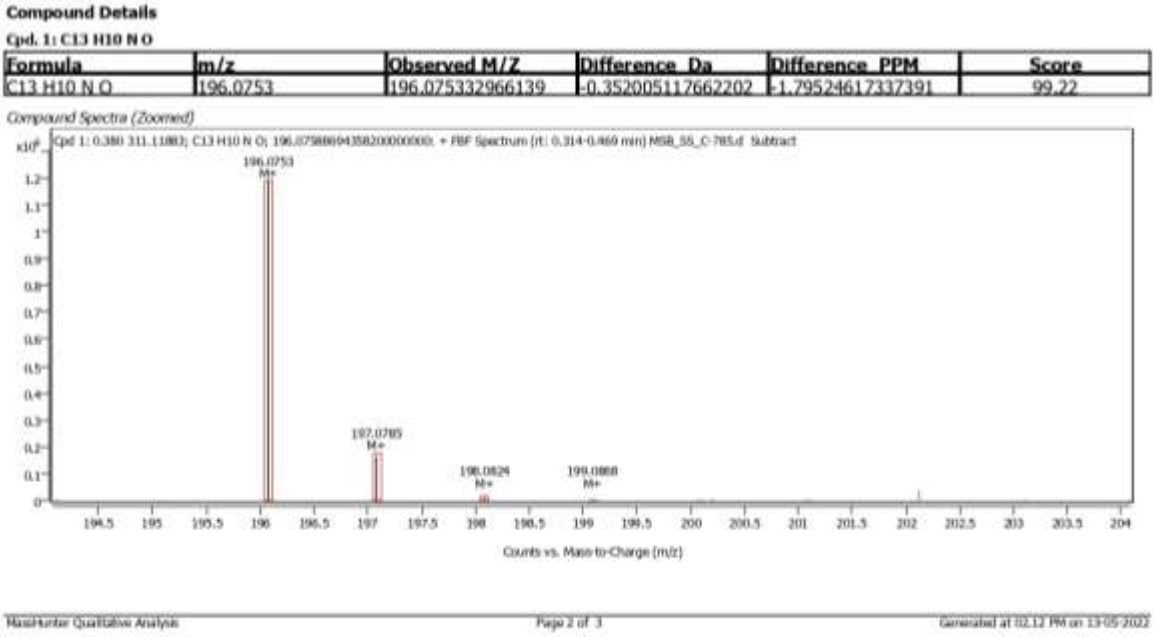


Figure S29. HRMS spectrum of **I_6**.

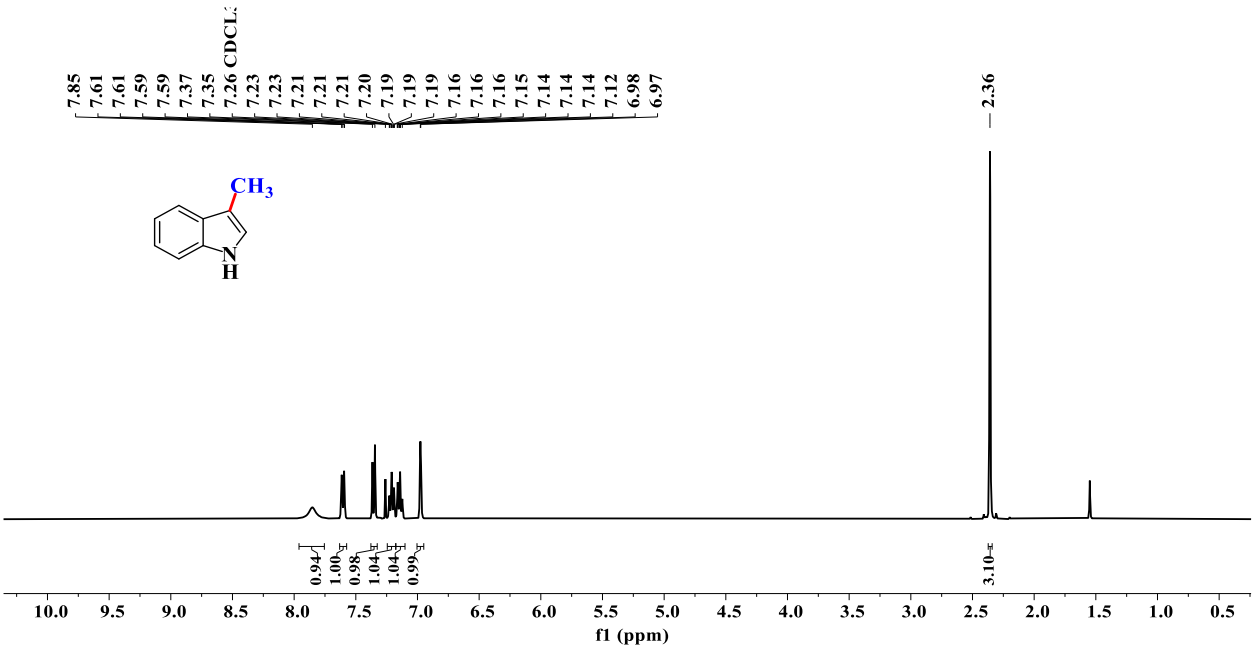


Figure S30. ^{1}H NMR spectrum of **I_7** (400 MHz).

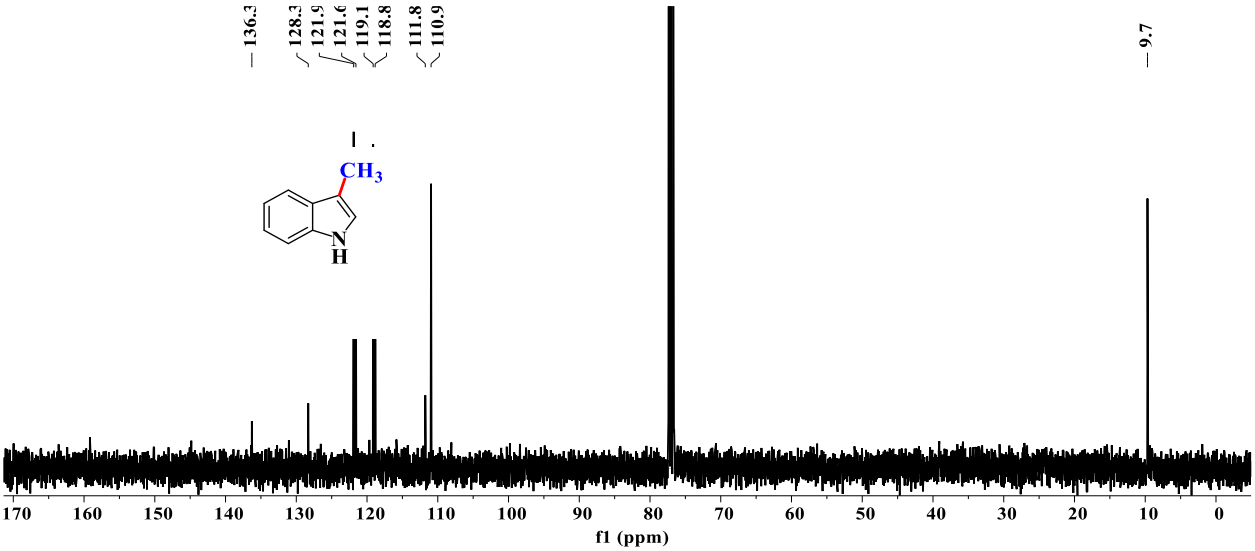


Figure S31. ^{13}C NMR spectrum of **I$_7$** (101 MHz).

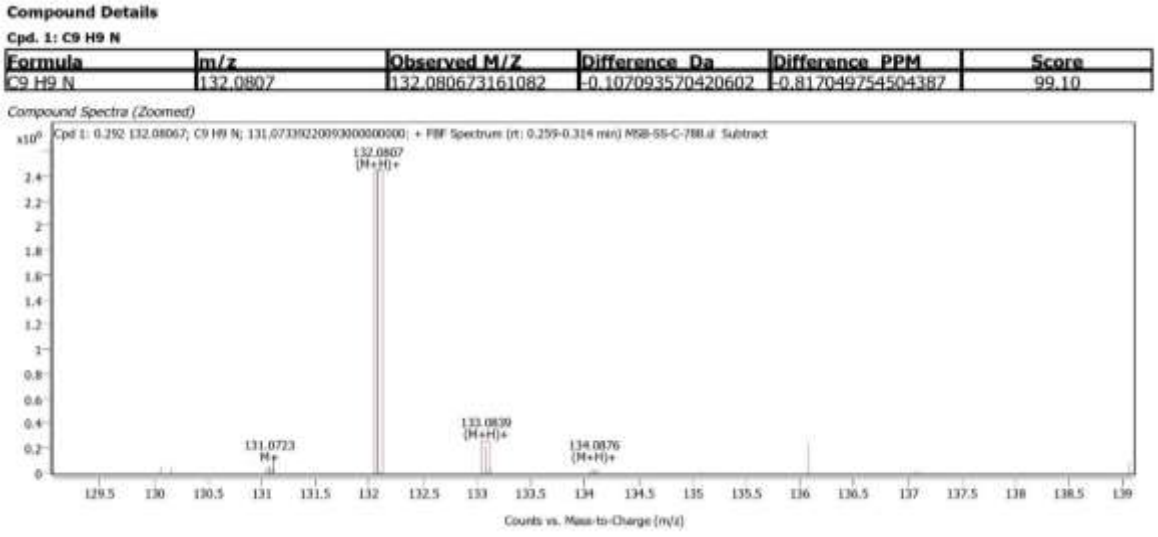


Figure S32. HRMS spectrum of **I$_7$**.

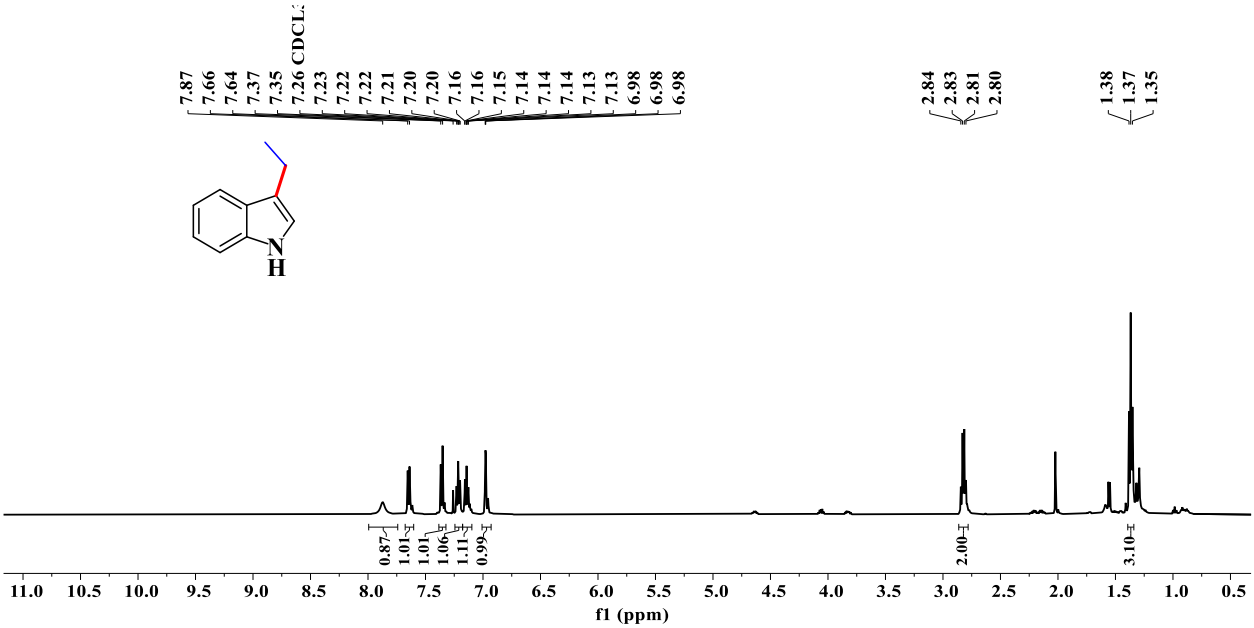


Figure S33. ^{1}H NMR spectrum of $\mathbf{I_8}$ (500 MHz).

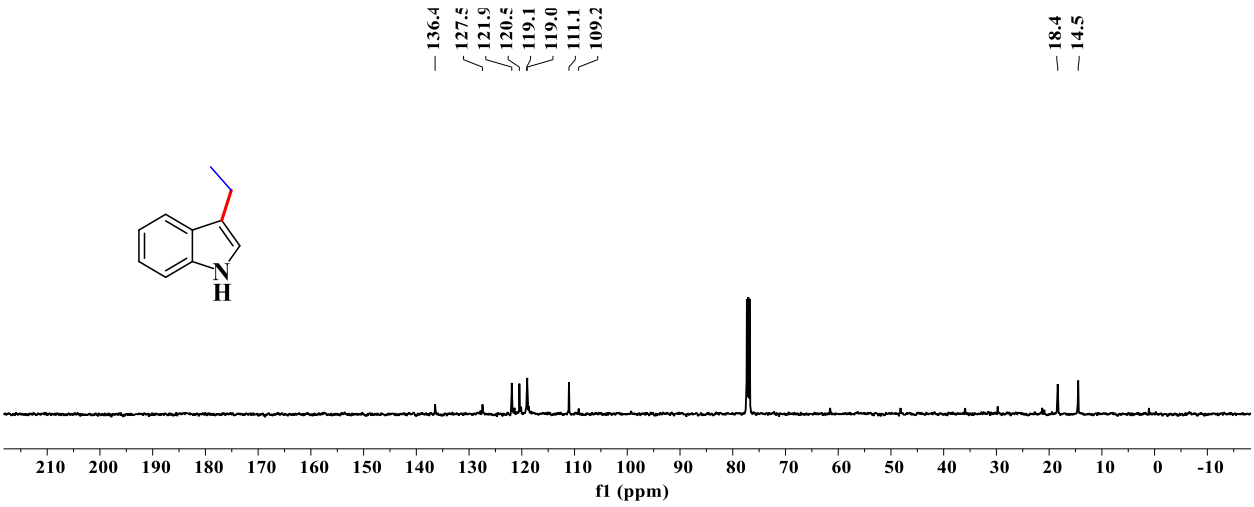


Figure S34. ^{13}C NMR spectrum of $\mathbf{I_8}$ (126 MHz).

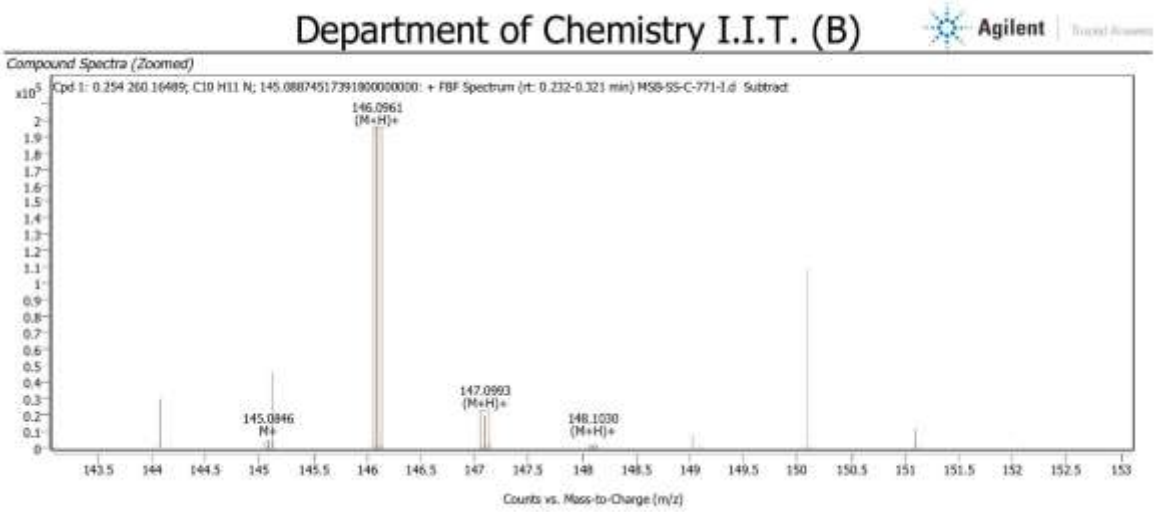


Figure S35. HRMS spectrum of **I8**.

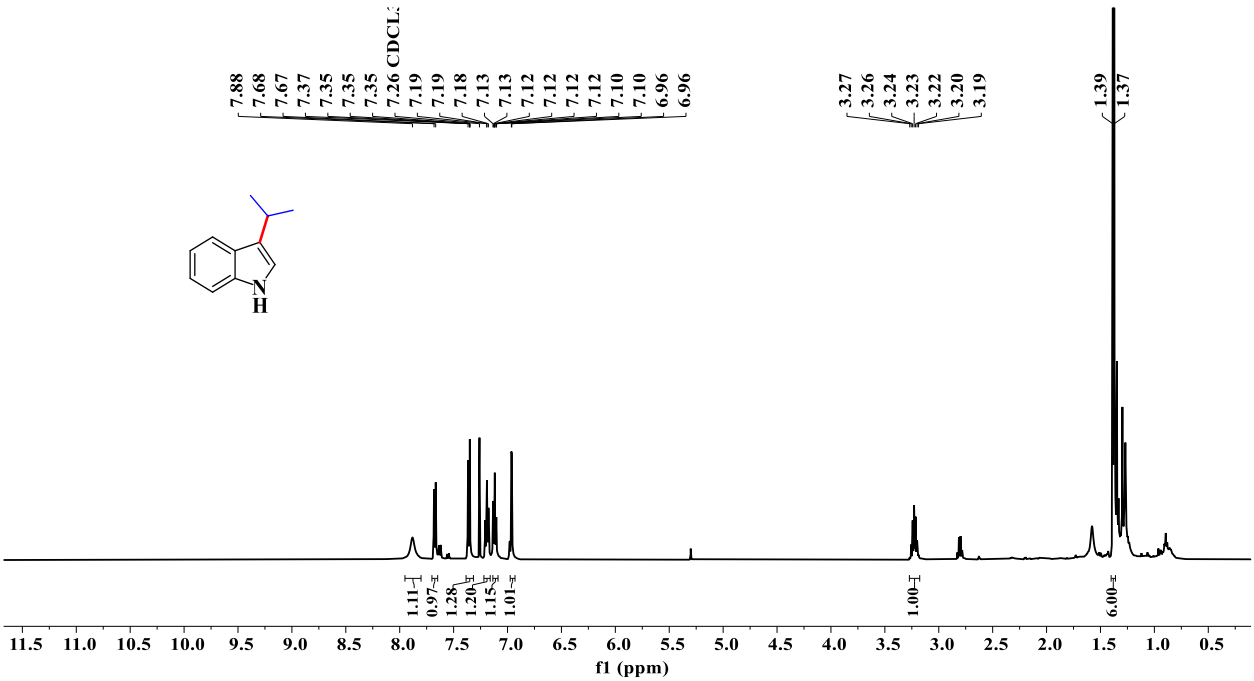


Figure S36. ^{1}H NMR spectrum of **I9** (500 MHz).

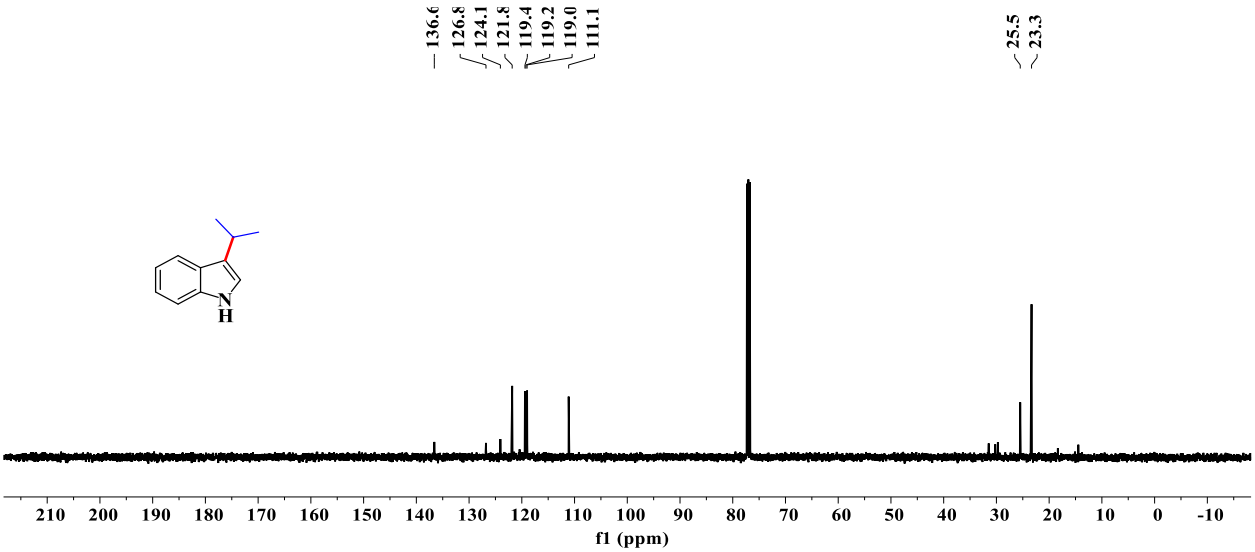


Figure S37. ^{13}C NMR spectrum of **I$_9$** (126 MHz).

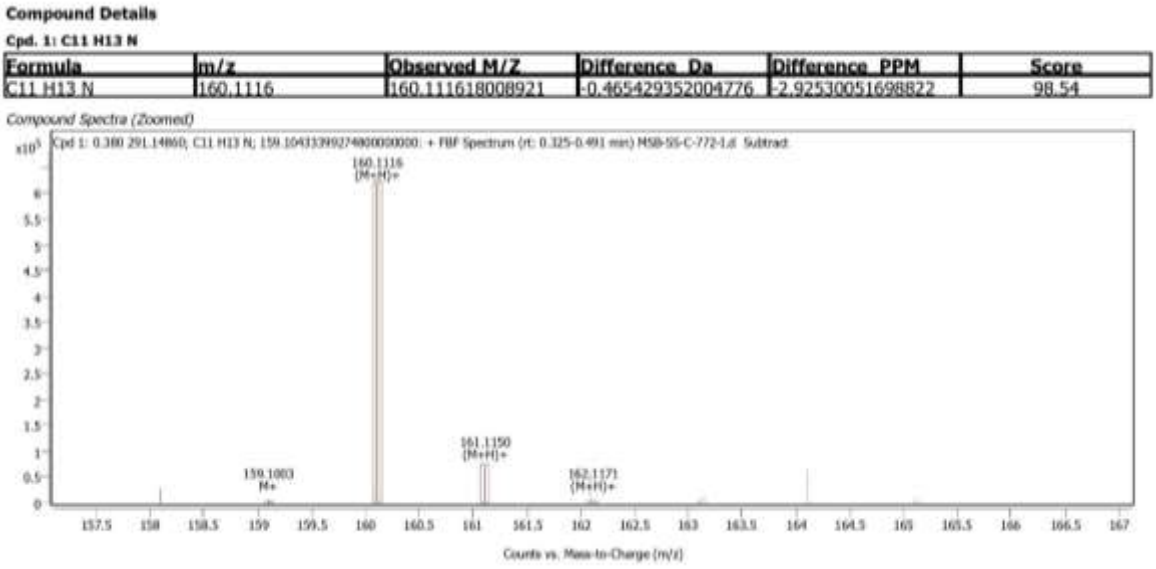


Figure S38. HRMS spectrum of **I$_9$**.

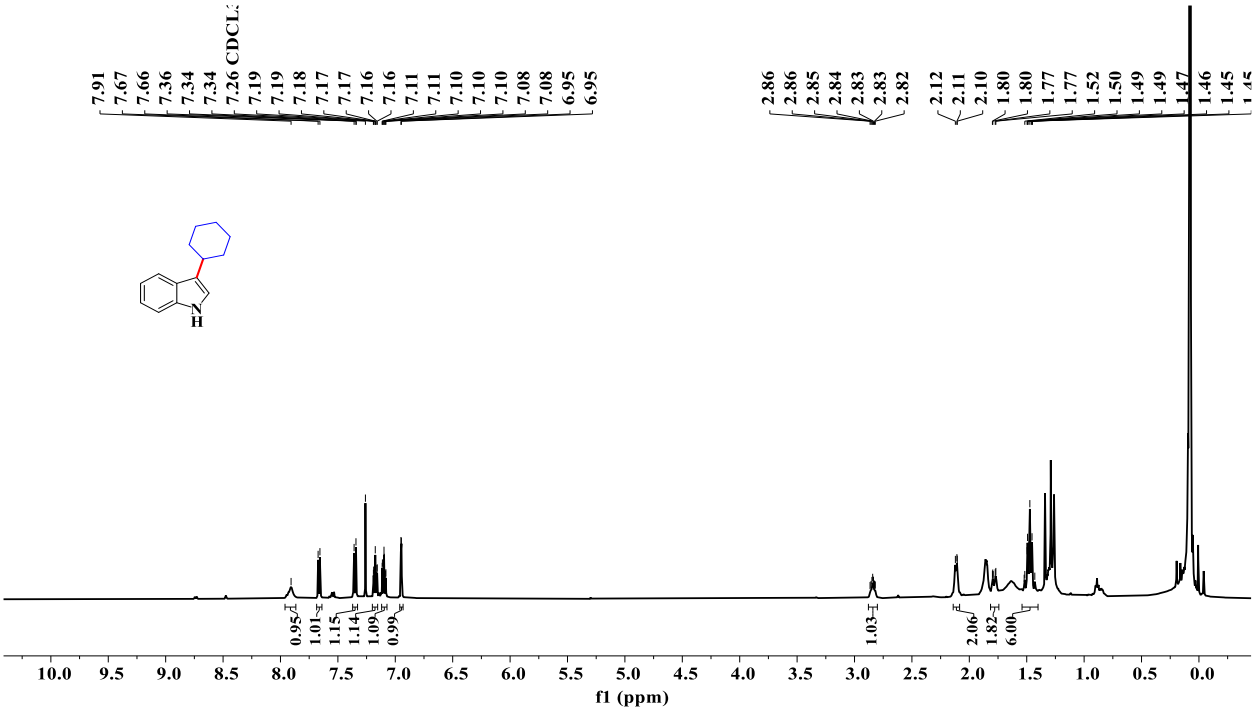


Figure S39. ^{1}H NMR spectrum of **I_{10}** (500 MHz).

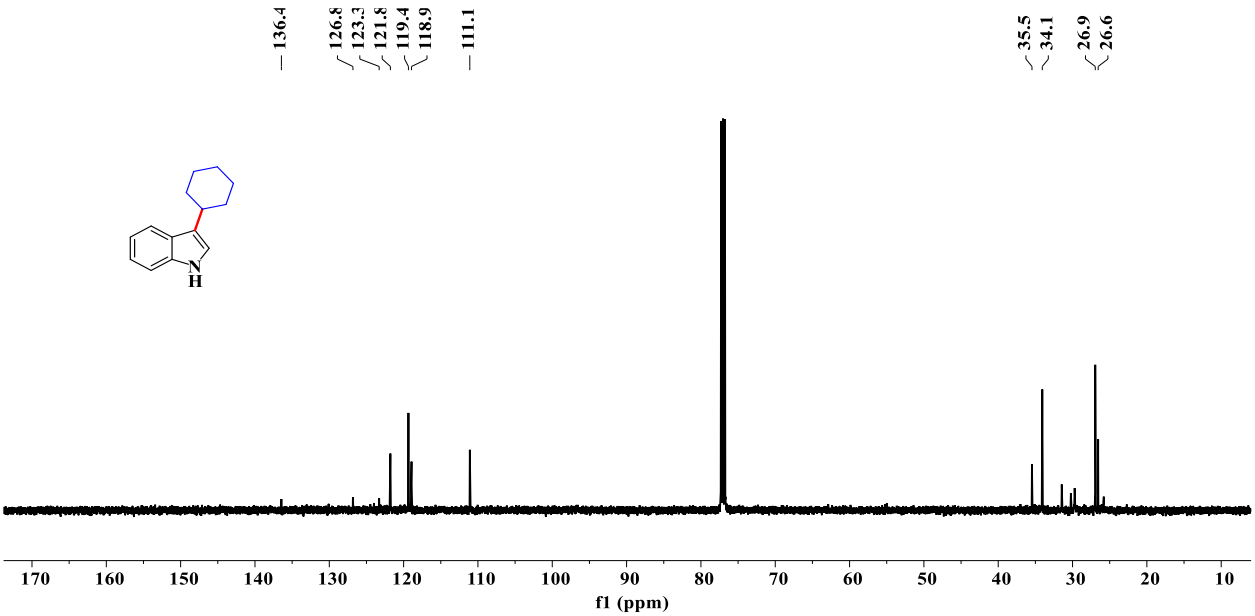


Figure S40. ^{13}C NMR spectrum of **I_{10}** (126 MHz).

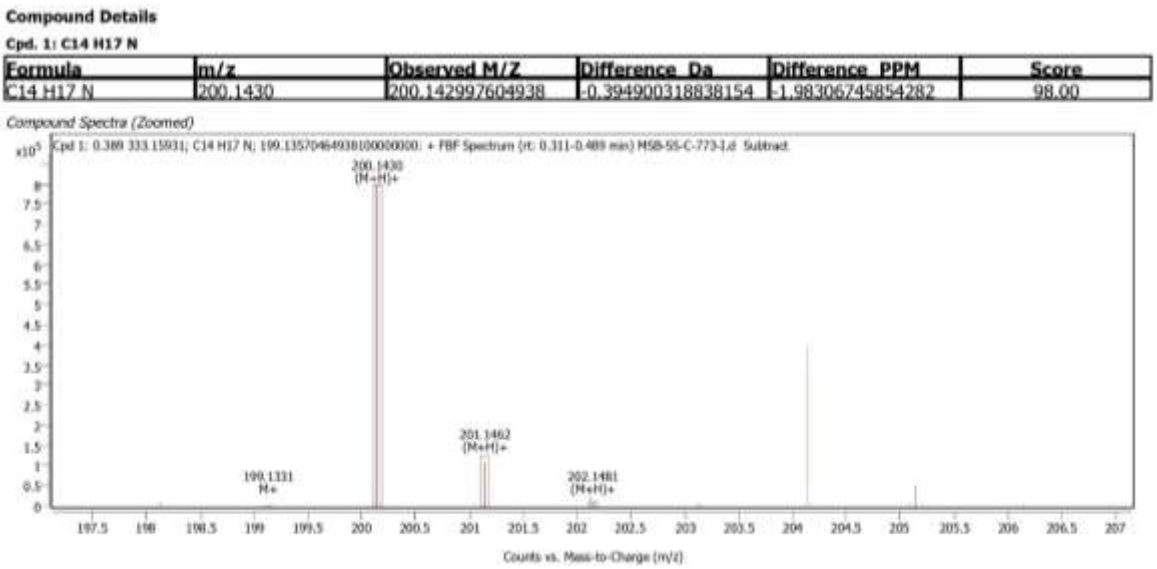


Figure S41. HRMS spectrum of **I_{10}**.

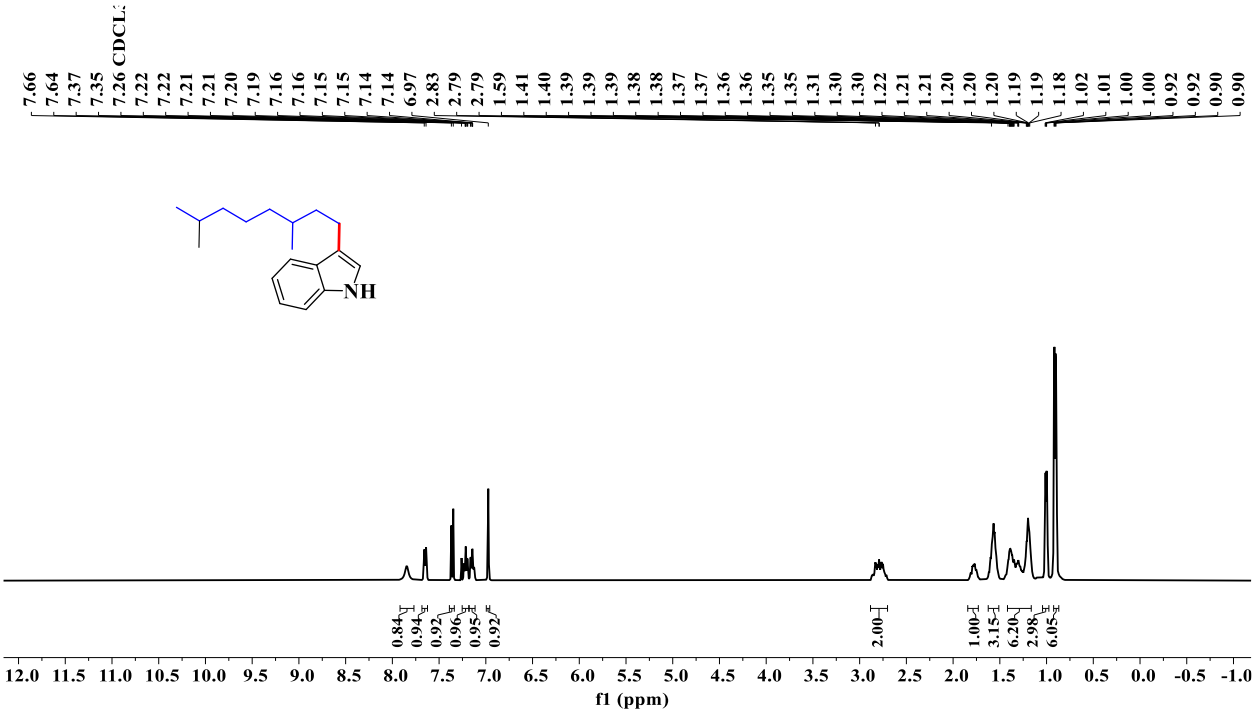


Figure S42. ^{1}H NMR spectrum of **I_{11}** (400 MHz).

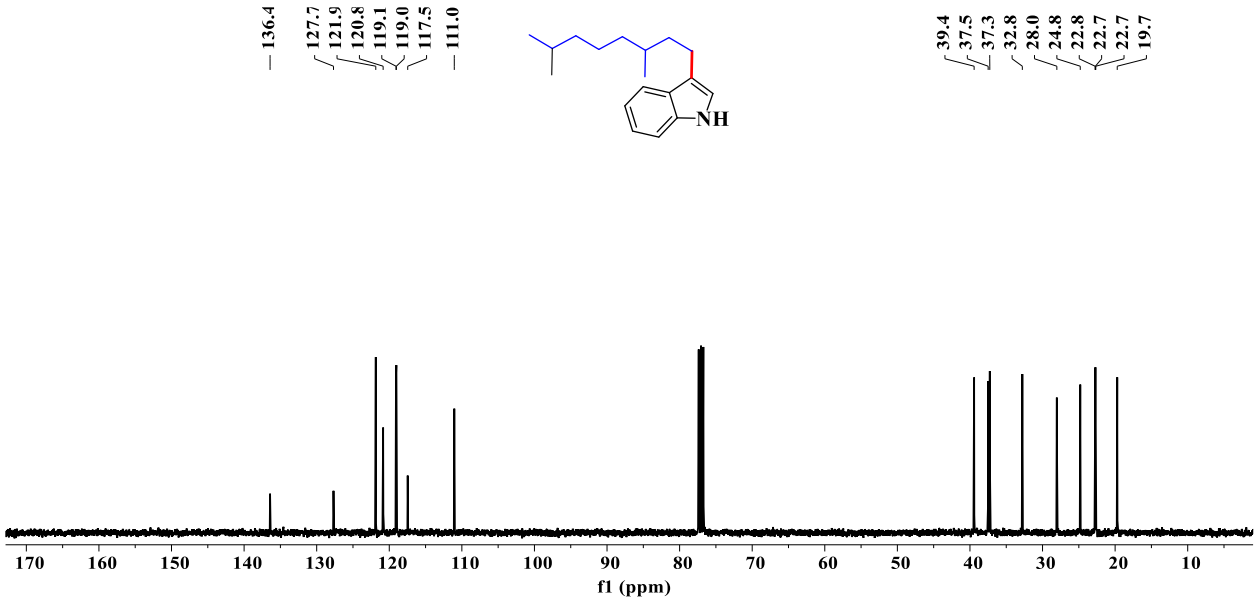


Figure S43. ^{13}C NMR spectrum of $\mathbf{I_{11}}$ (101 MHz).

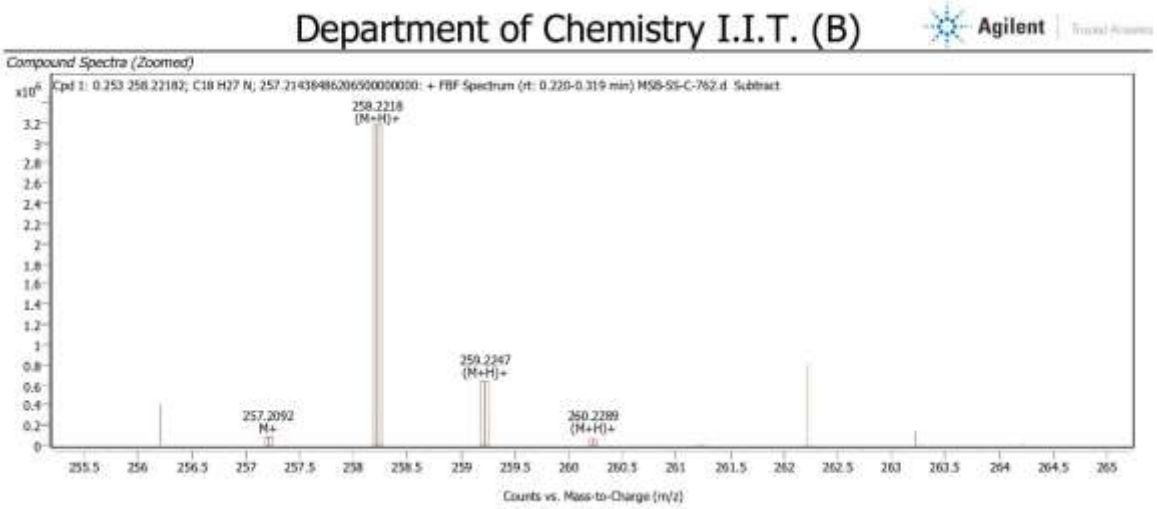


Figure S44. HRMS spectrum of $\mathbf{I_{11}}$.

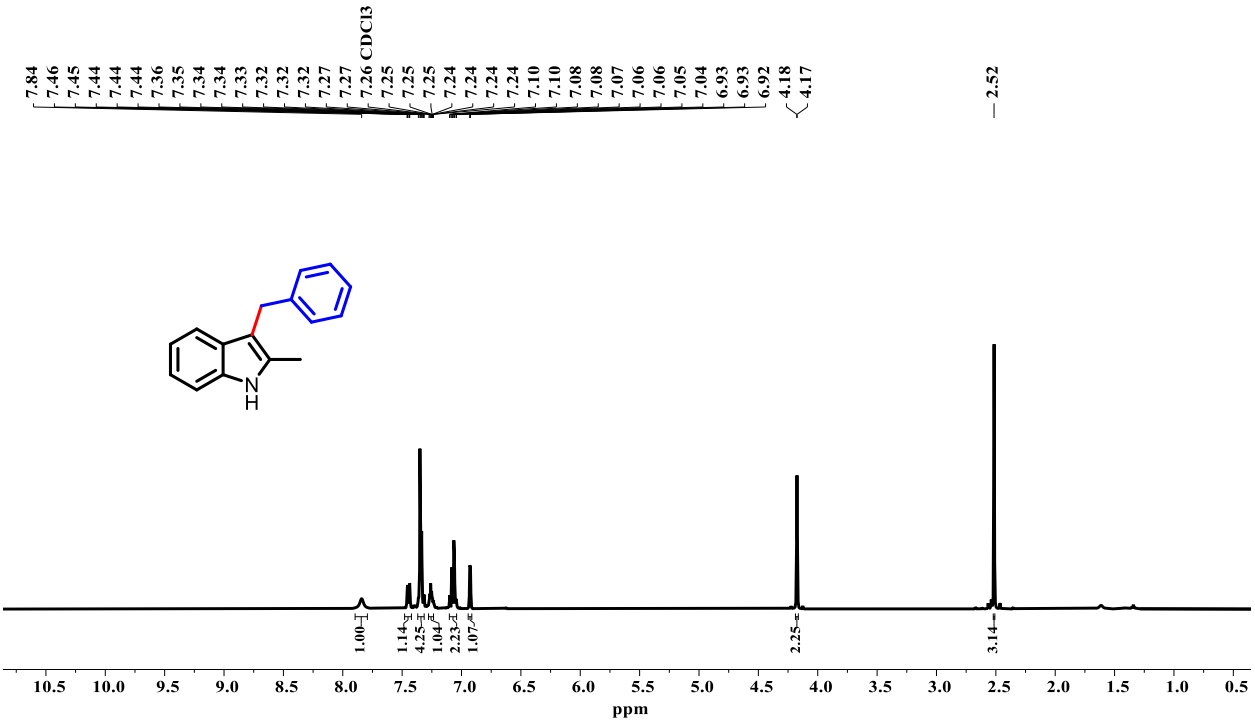


Figure S45. ^{1}H NMR spectrum of **I_{12}** (400 MHz).

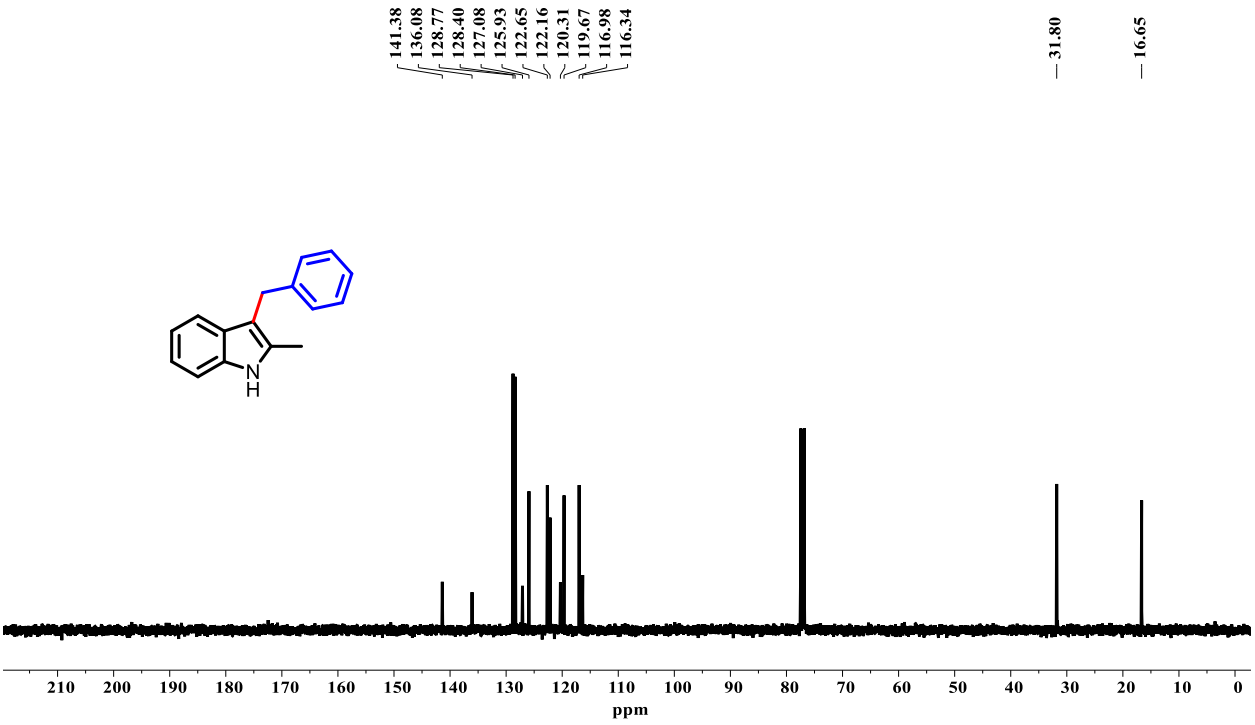


Figure S46. ^{13}C NMR spectrum of **I_{12}** (101 MHz).

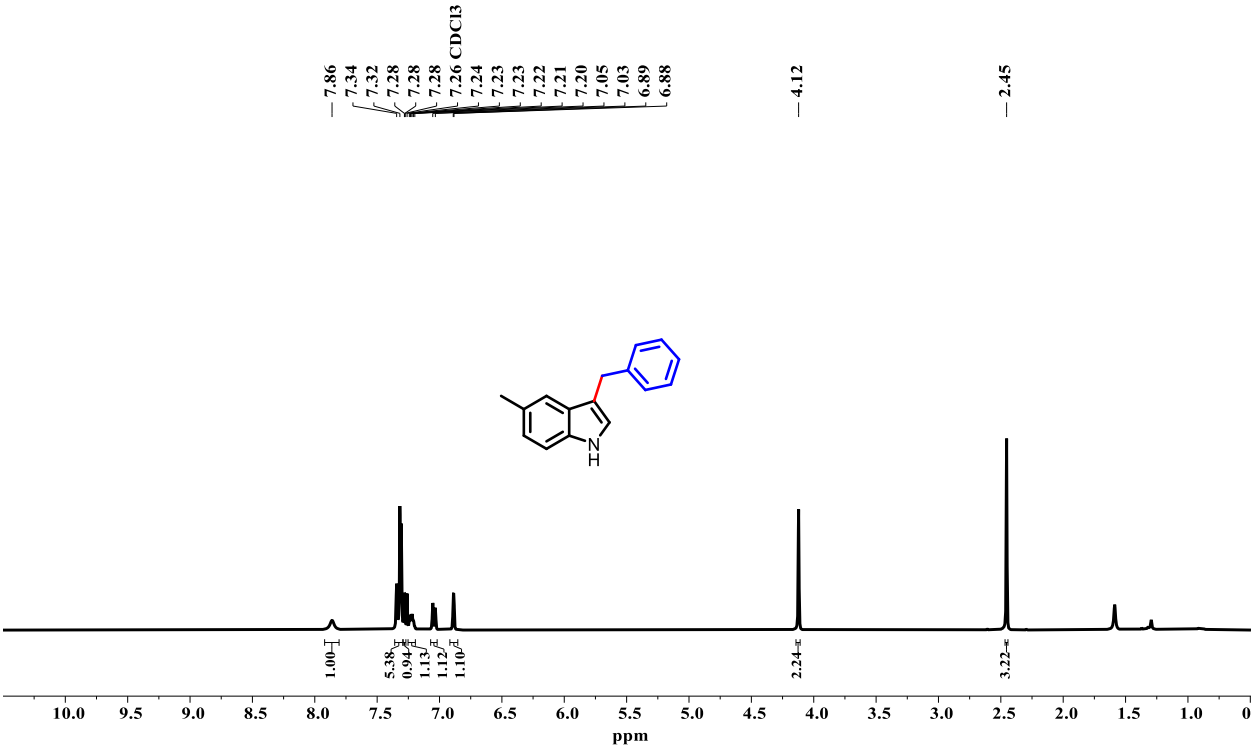


Figure S47. ^{1}H NMR spectrum of $\mathbf{I_{13}}$ (400 MHz).

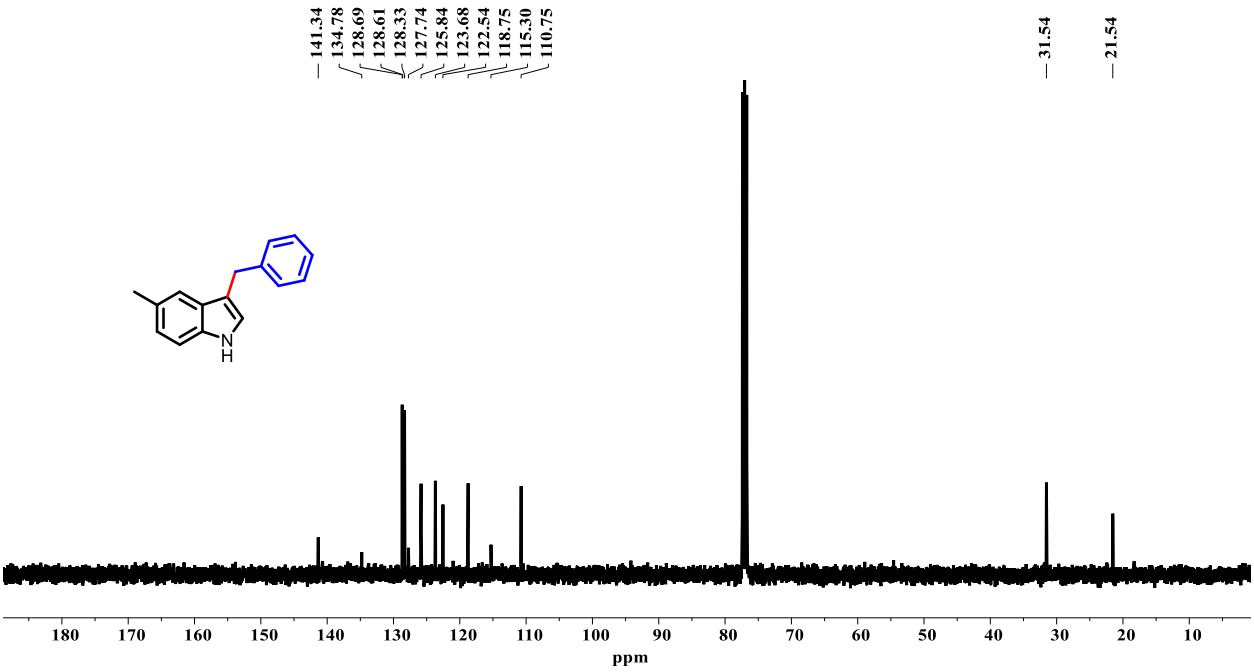


Figure S48. ^{13}C NMR spectrum of $\mathbf{I_{13}}$ (101 MHz).

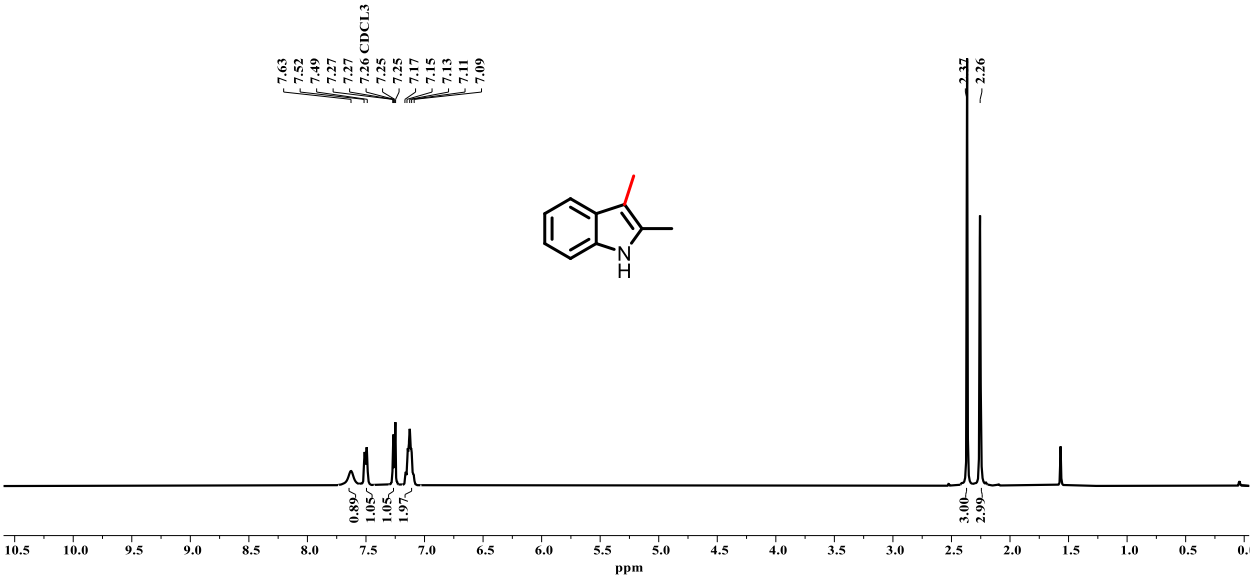


Figure S49. ^{1}H NMR spectrum of $\mathbf{I_{14}}$ (400 MHz).

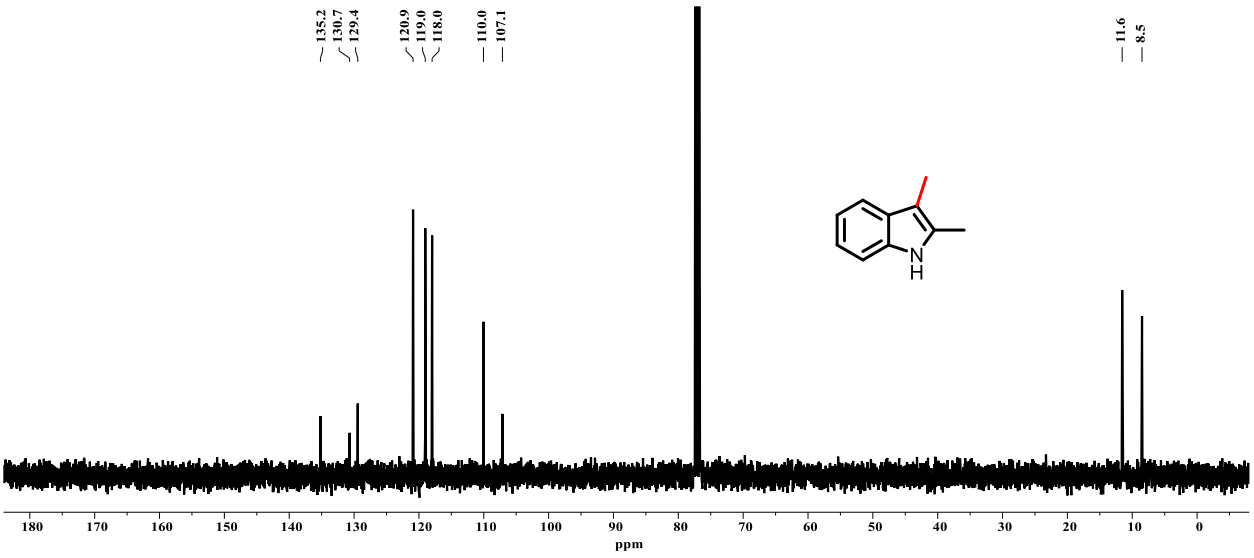


Figure S50. ^{13}C NMR spectrum of $\mathbf{I_{14}}$ (101 MHz).

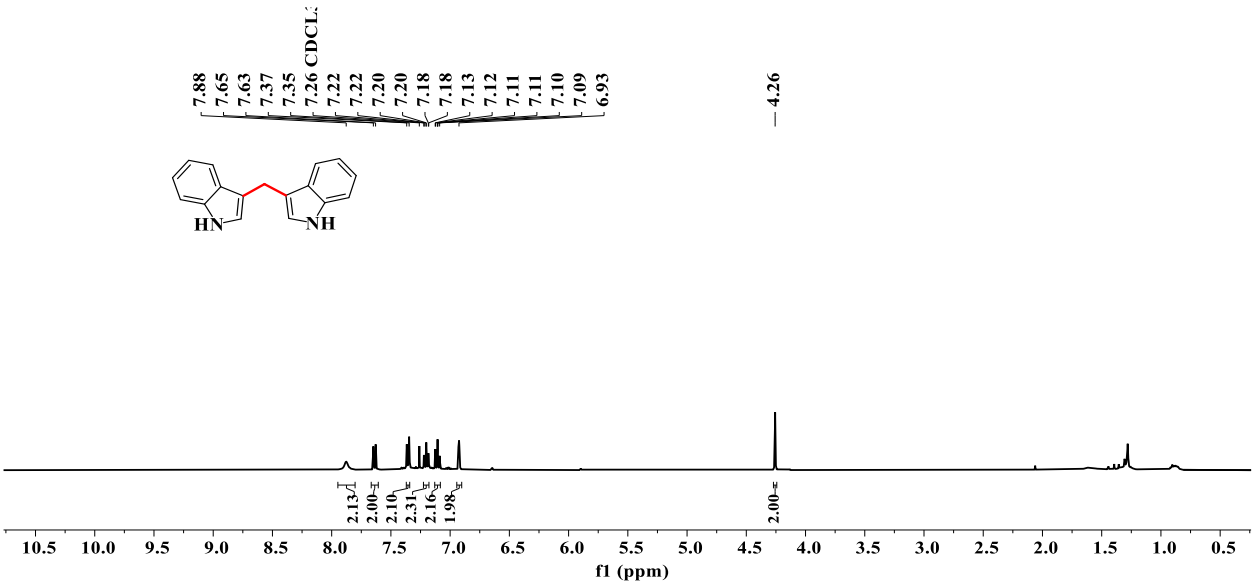


Figure S51. ^{1}H NMR spectrum of $\mathbf{I_{15}}$ (400 MHz).

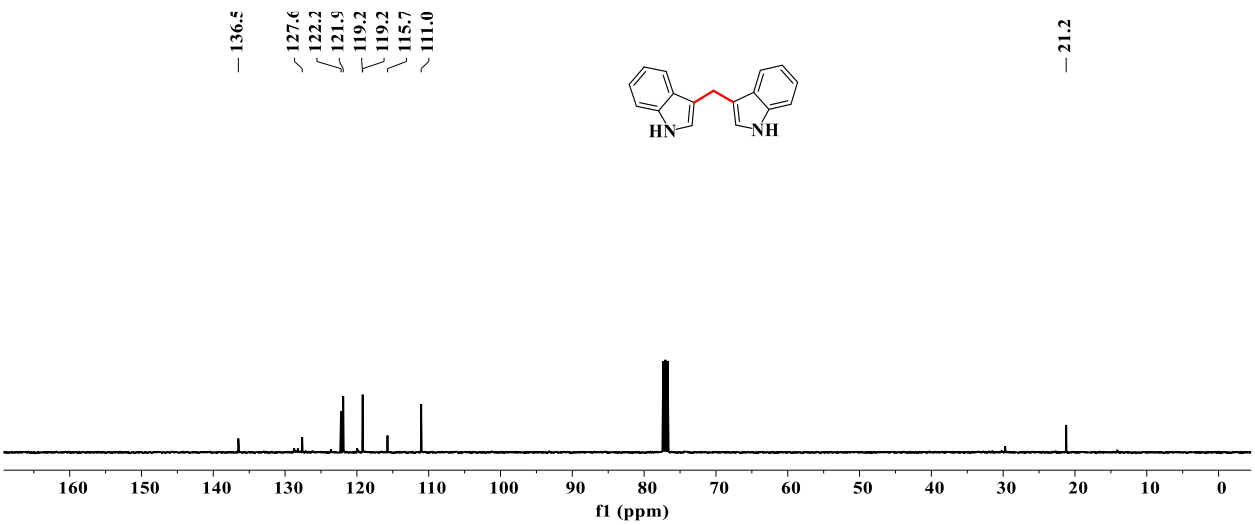


Figure S52. ^{13}C NMR spectrum of $\mathbf{I_{15}}$ (101 MHz).

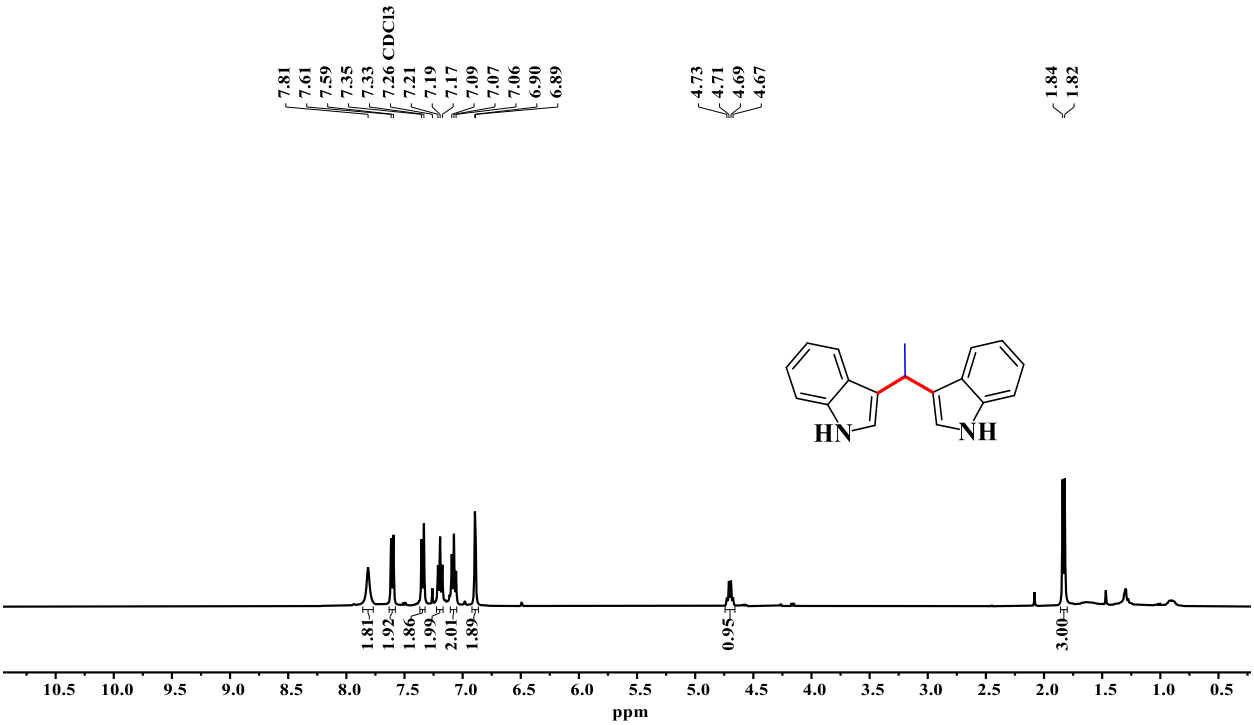


Figure S53. ^{1}H NMR spectrum of $\mathbf{I_{16}}$ (400 MHz).

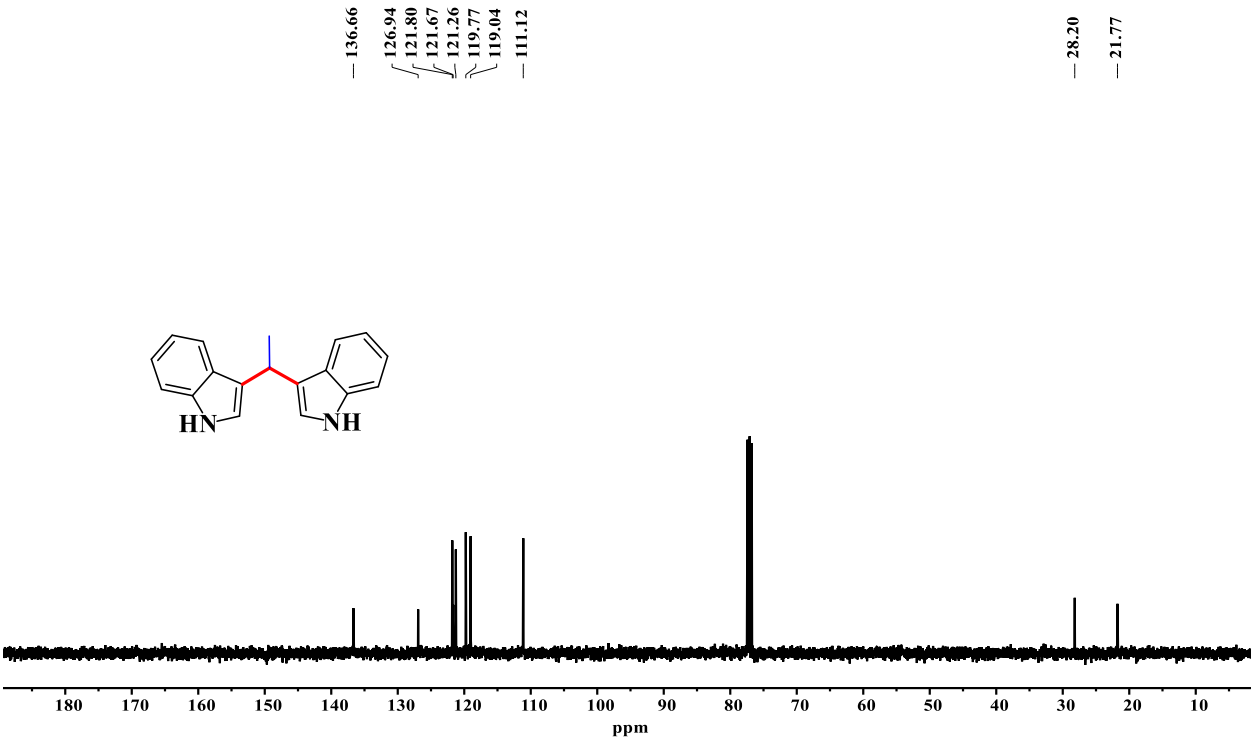


Figure S54. ^{13}C NMR spectrum of $\mathbf{I_{16}}$ (101 MHz).

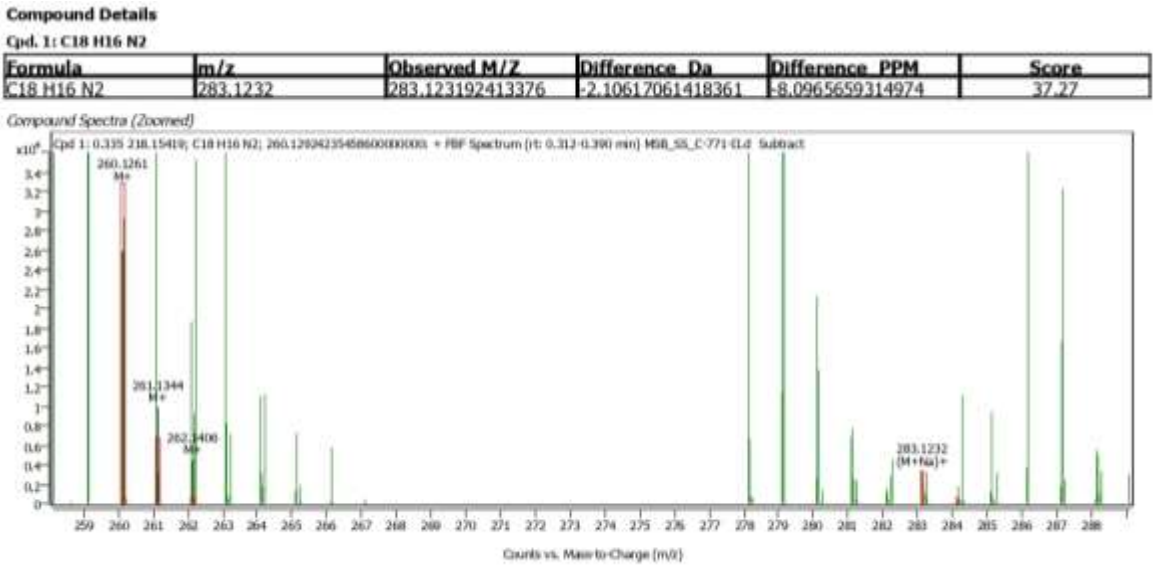


Figure S55. HRMS spectrum of $\mathbf{I_{16}}$.

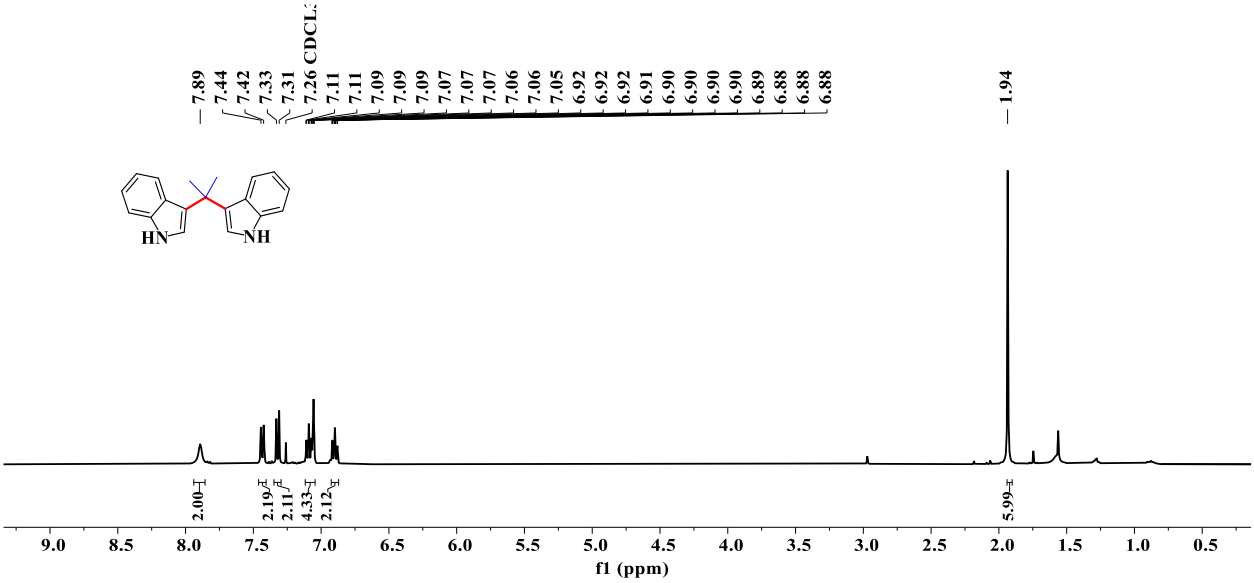


Figure S56. ^{1}H NMR spectrum of $\mathbf{I_{17}}$ (400 MHz).

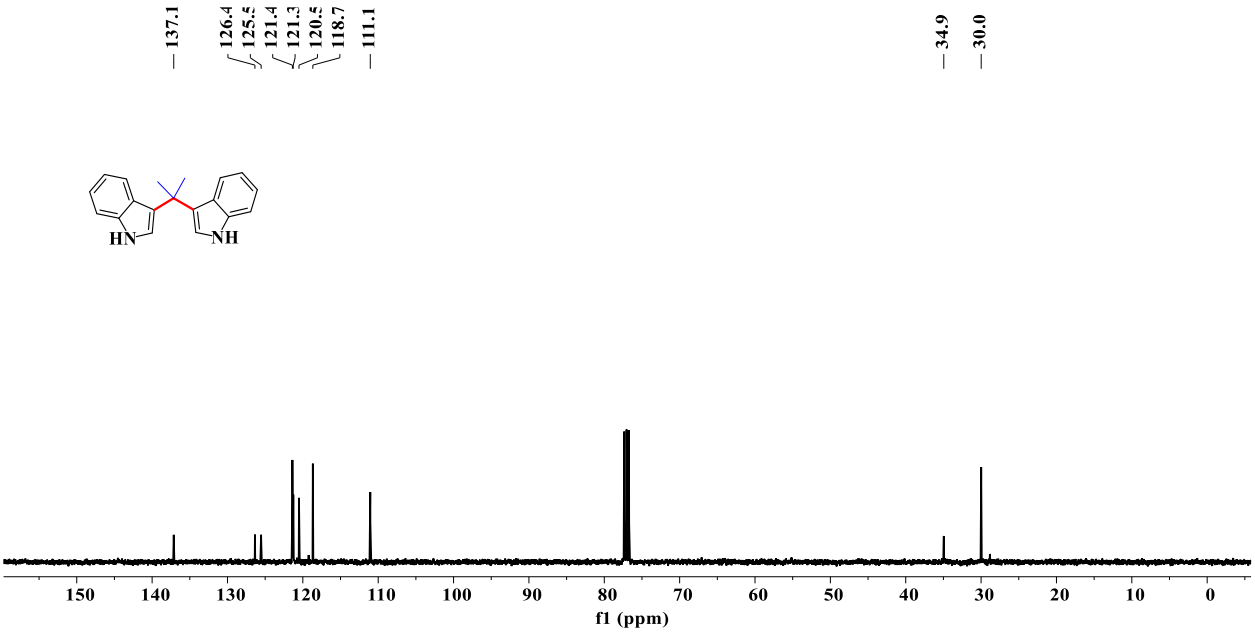


Figure S57. ^{13}C NMR spectrum of $\mathbf{I_{17}}$ (101 MHz)

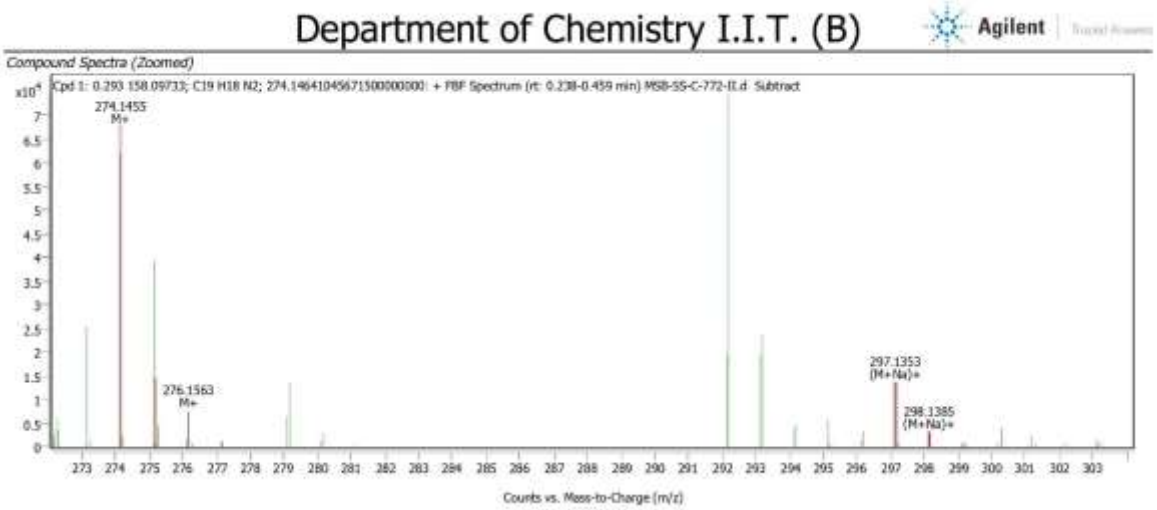


Figure S58. HRMS spectrum of $\mathbf{I_{17}}$.

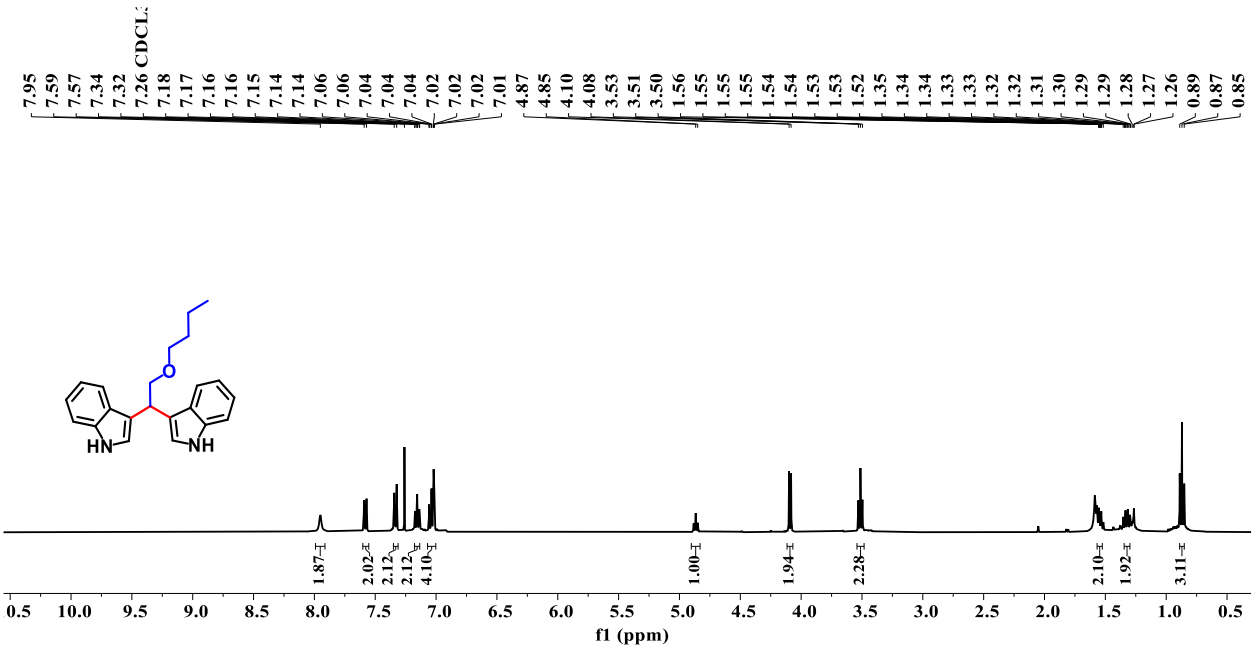


Figure S59. ^{1}H NMR spectrum of $\mathbf{I_{18}}$ (400 MHz).

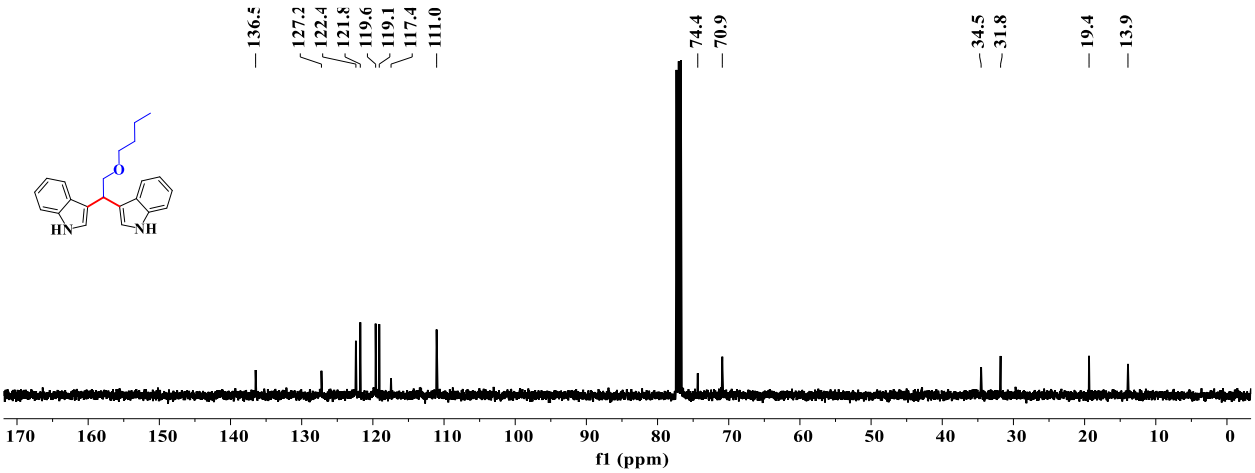


Figure S60. ^{13}C NMR spectrum of $\mathbf{I_{18}}$ (101 MHz).

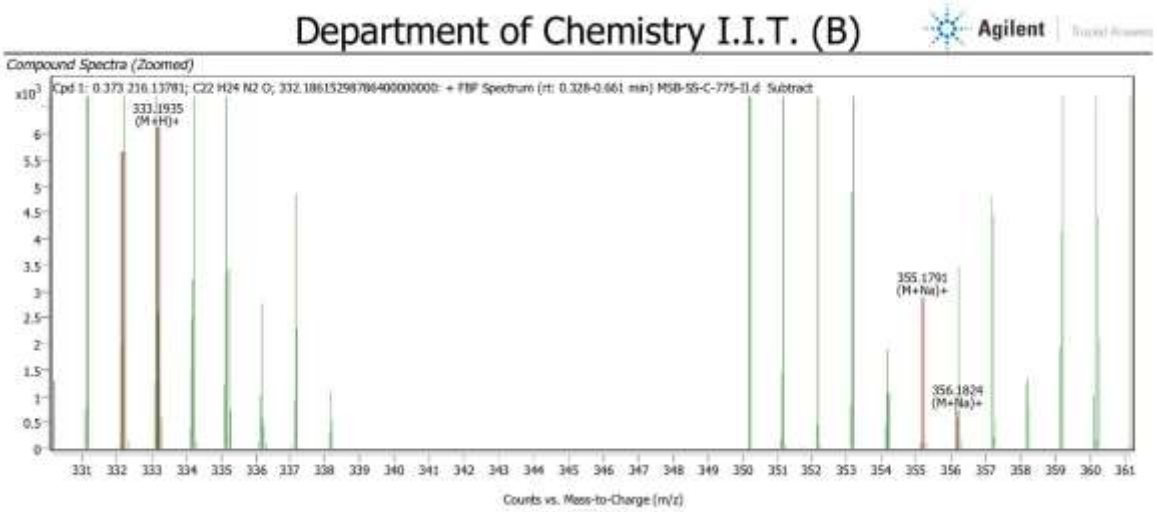


Figure S61. HRMS spectrum of $\mathbf{I_{18}}$.

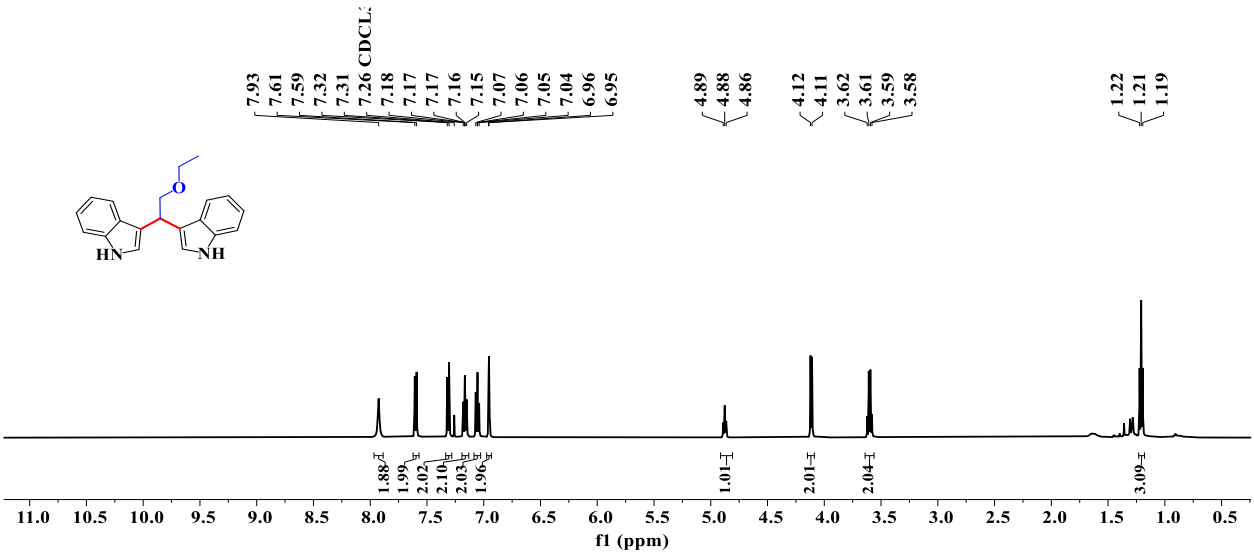


Figure S62. ^{1}H NMR spectrum of $\mathbf{I_{19}}$ (500 MHz).

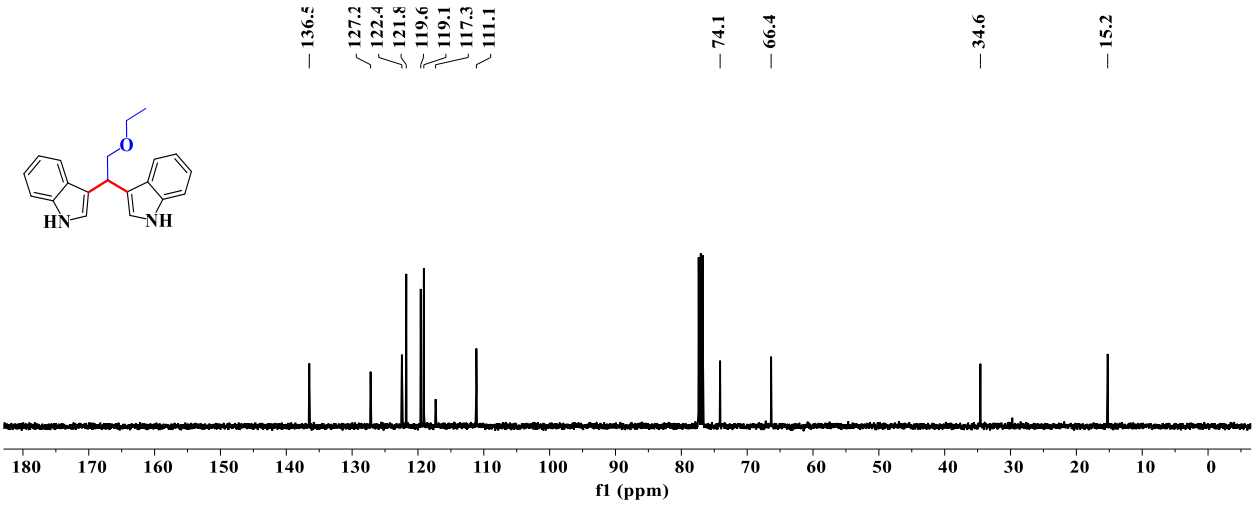


Figure S63. ^{13}C NMR spectrum of **I_{19}** (101 MHz).

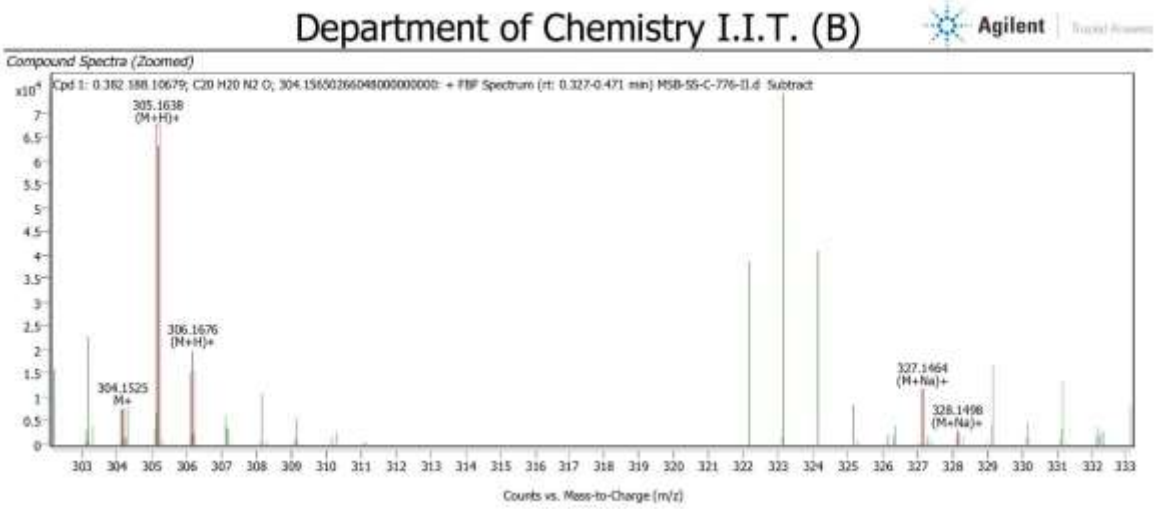


Figure S64. HRMS spectrum of **I_{19}**.

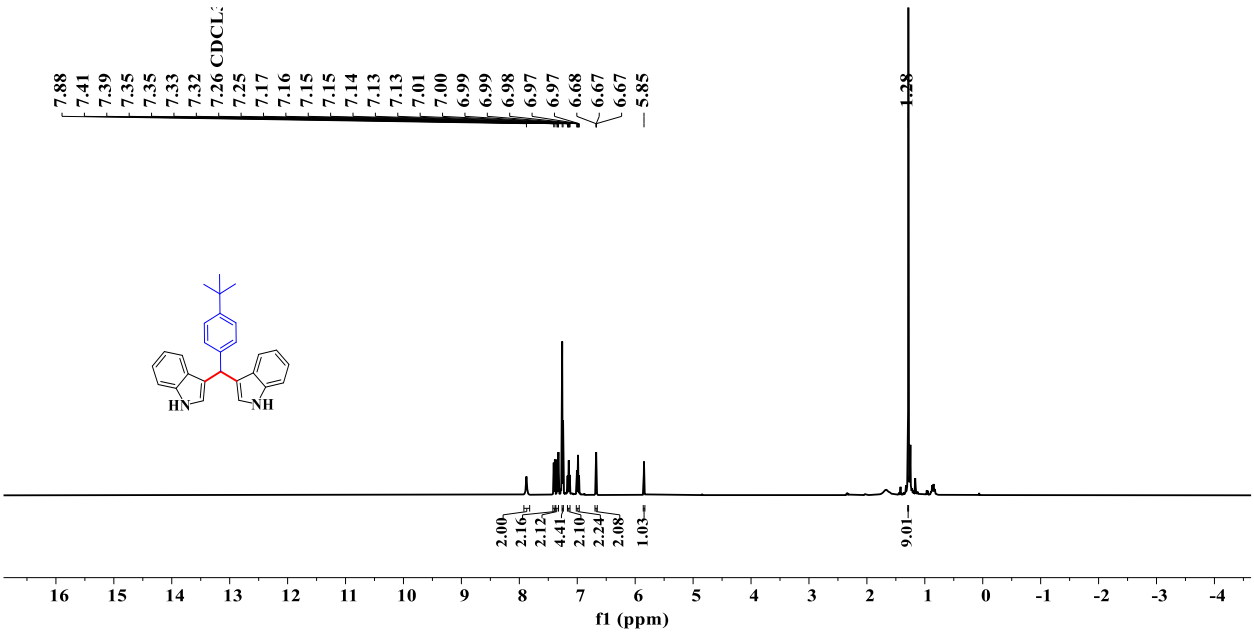


Figure S65. ^{1}H NMR spectrum of $\mathbf{I_{20}}$ (400 MHz).

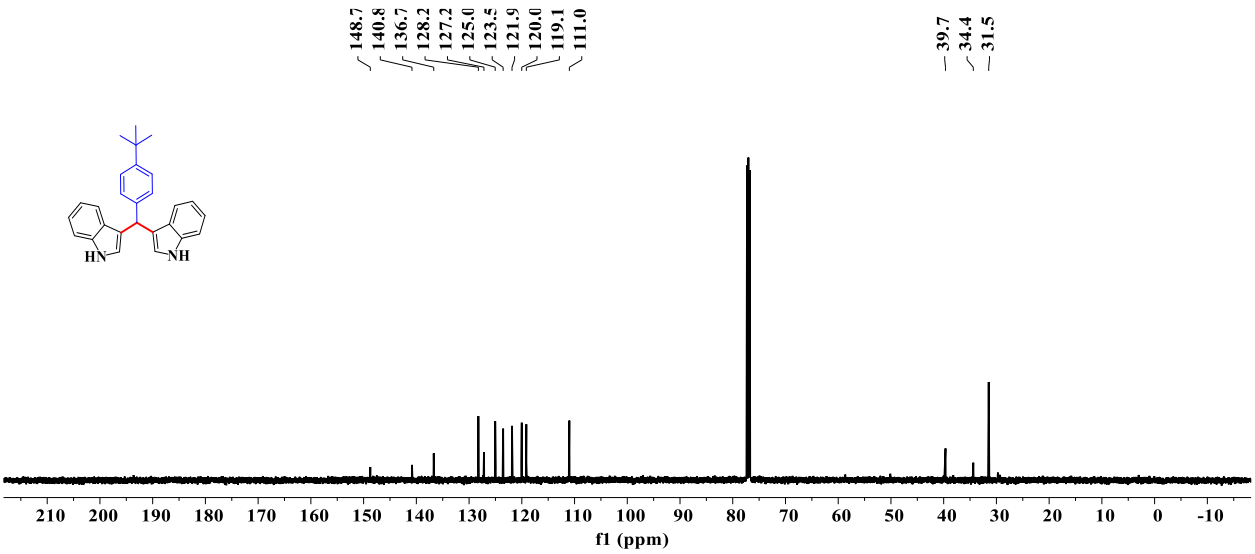


Figure S66. ^{13}C NMR spectrum of $\mathbf{I_{20}}$ (126 MHz).

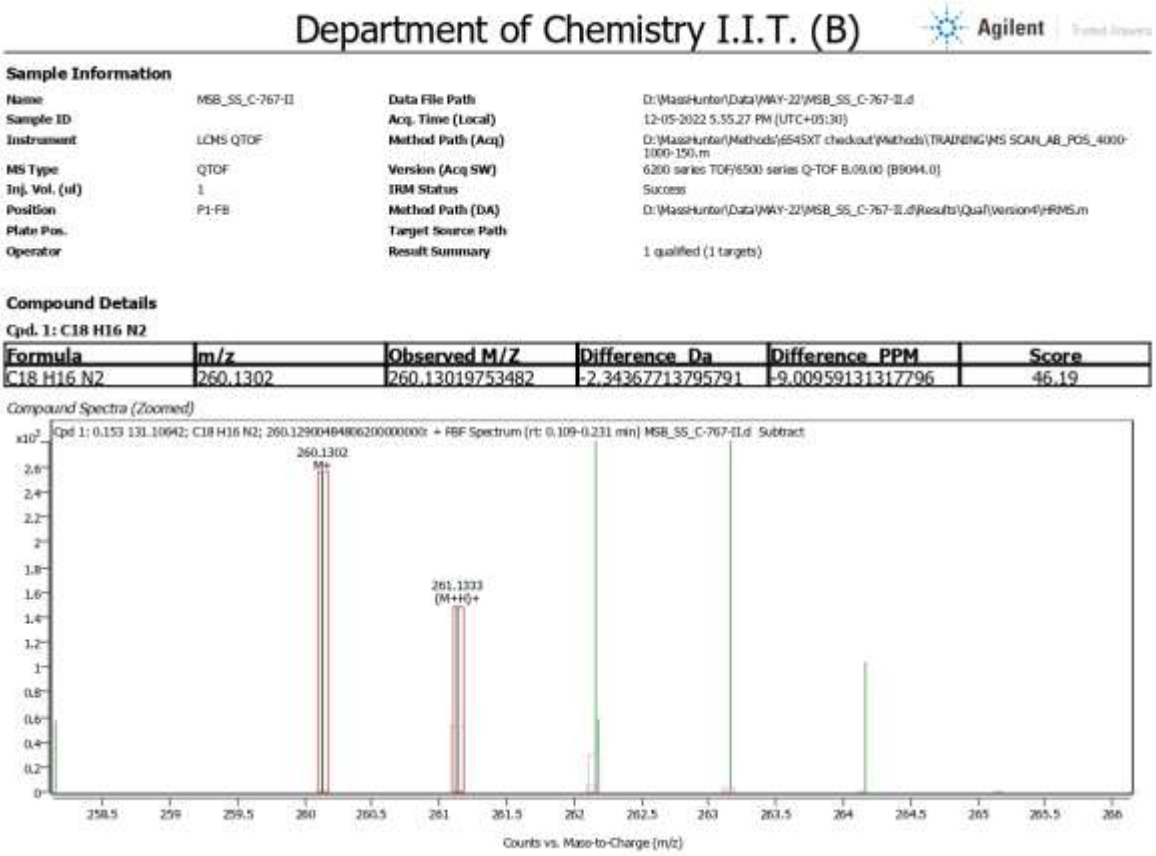


Figure S67. HRMS spectrum of **I_{20}**.

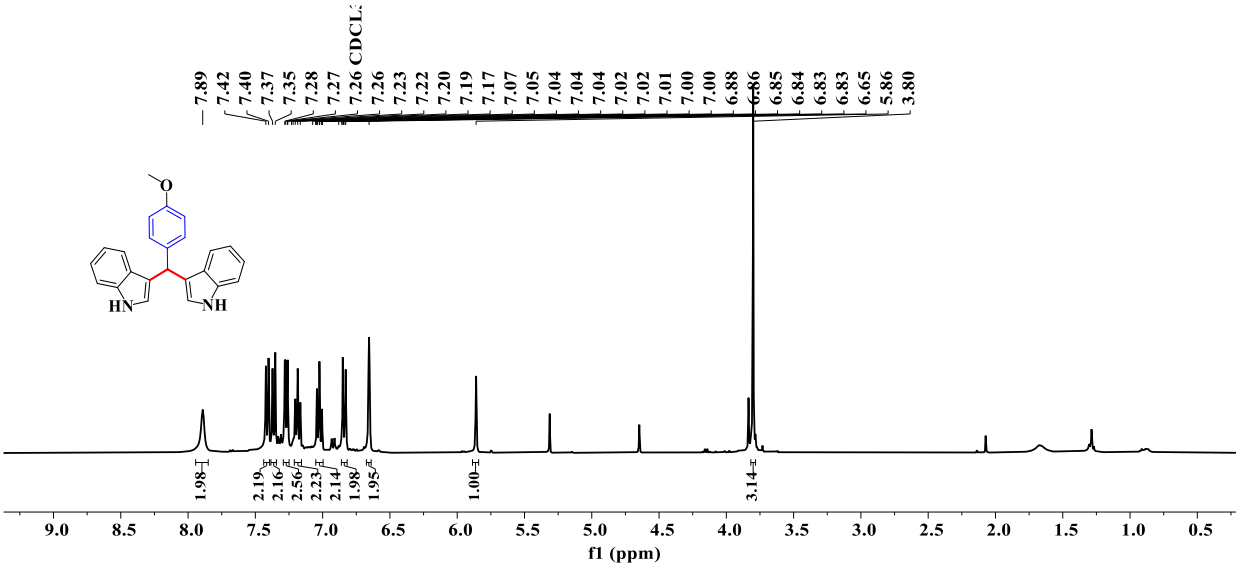


Figure S68. ^{1}H NMR spectrum of **I_{21}** (400 MHz).

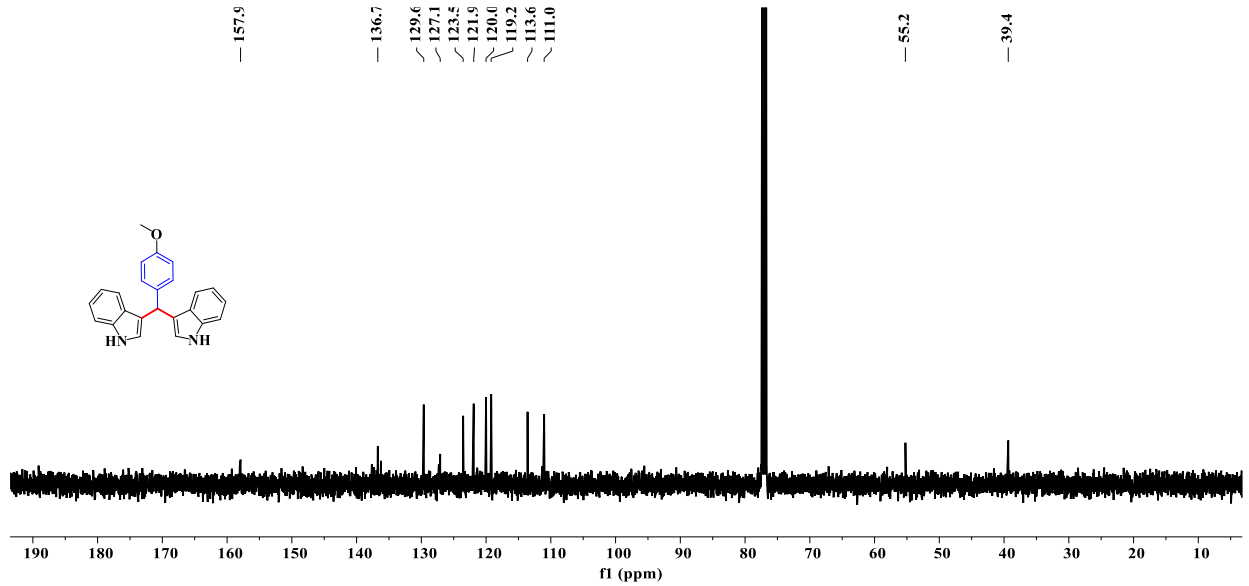


Figure S69. ^{13}C NMR spectrum of $\mathbf{I_{21}}$ (101 MHz).

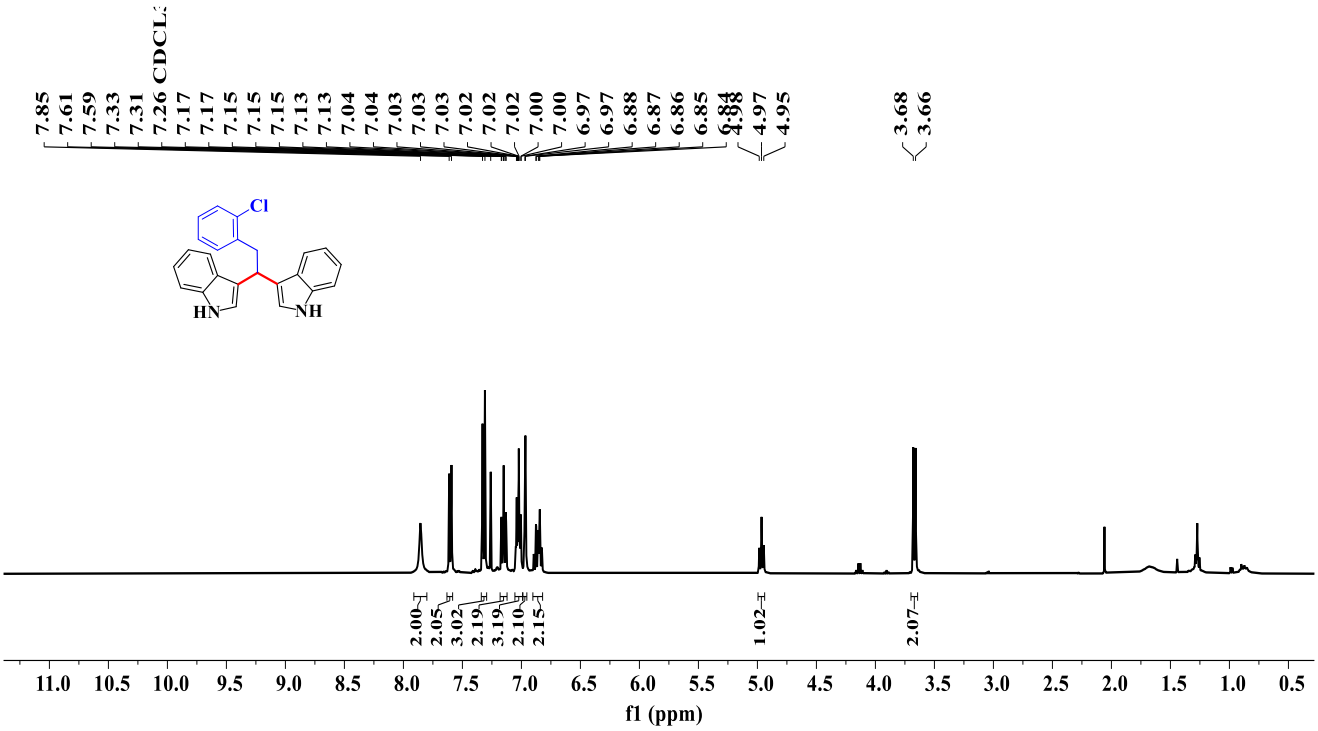


Figure S70. ^{1}H NMR spectrum of $\mathbf{I_{22}}$ (400 MHz).

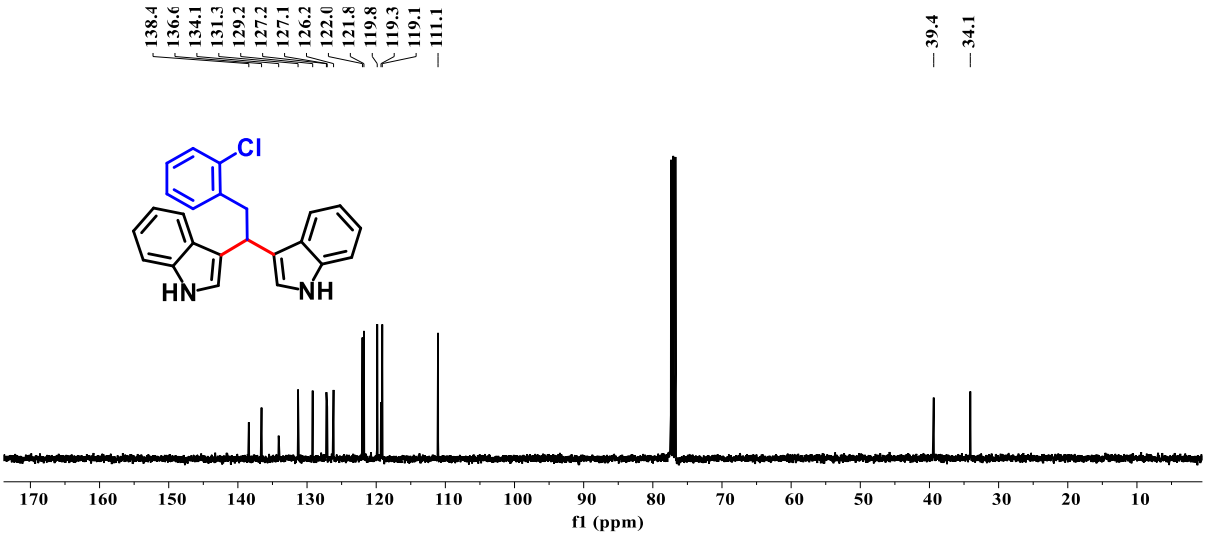


Figure S71. ^{13}C NMR spectrum $\mathbf{I_{22}}$ (101 MHz).

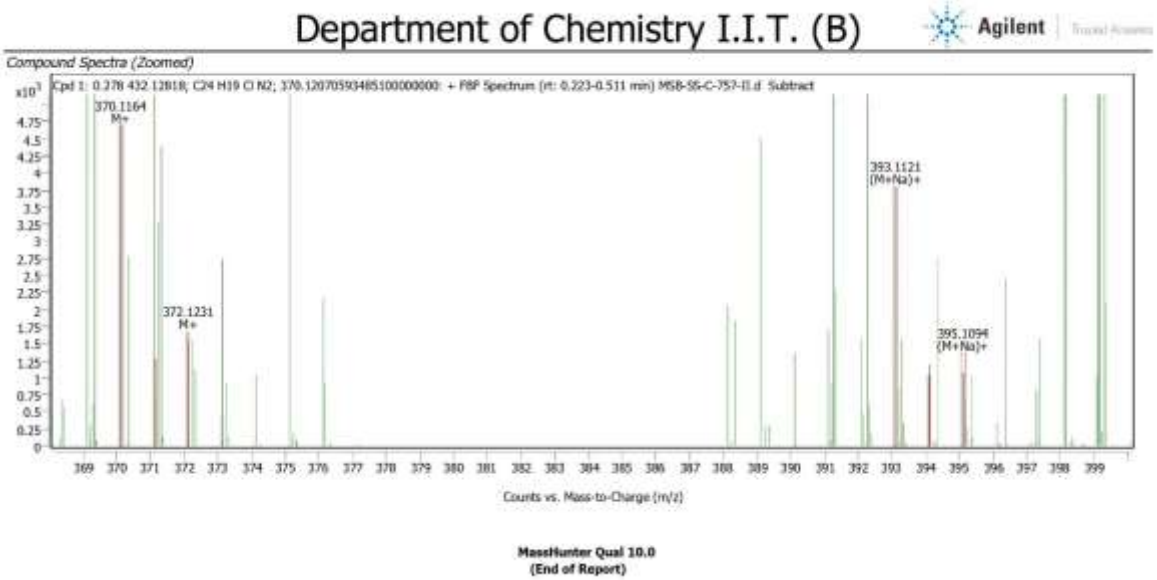


Figure S72. HRMS spectrum of $\mathbf{I_{22}}$.

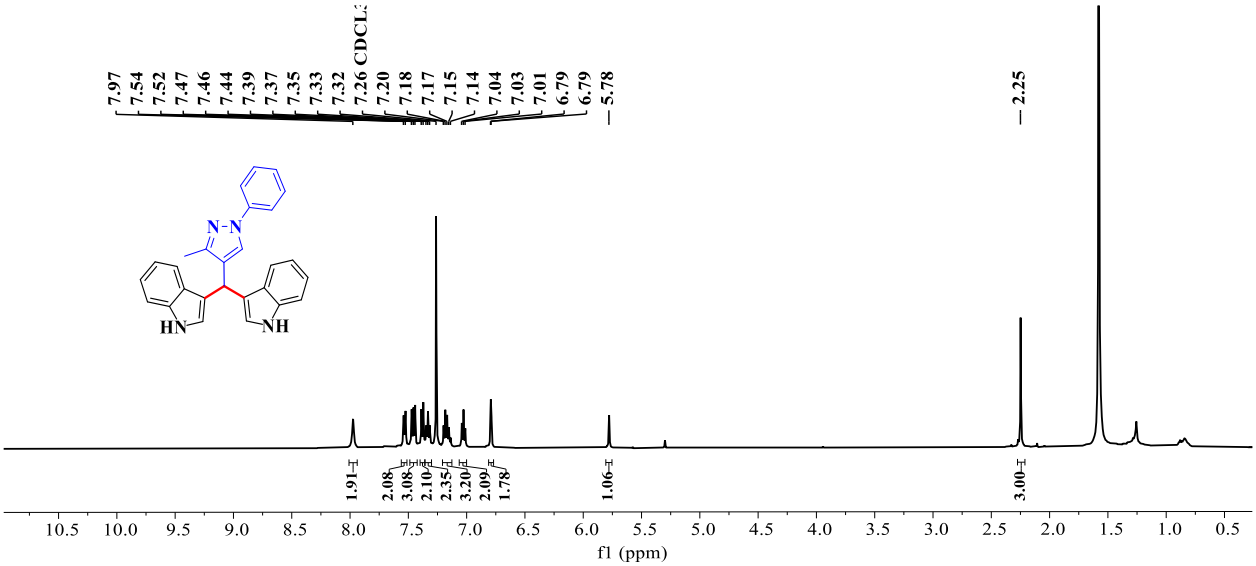


Figure S73. ^{1}H NMR spectrum of $\mathbf{I_{23}}$ (500 MHz).

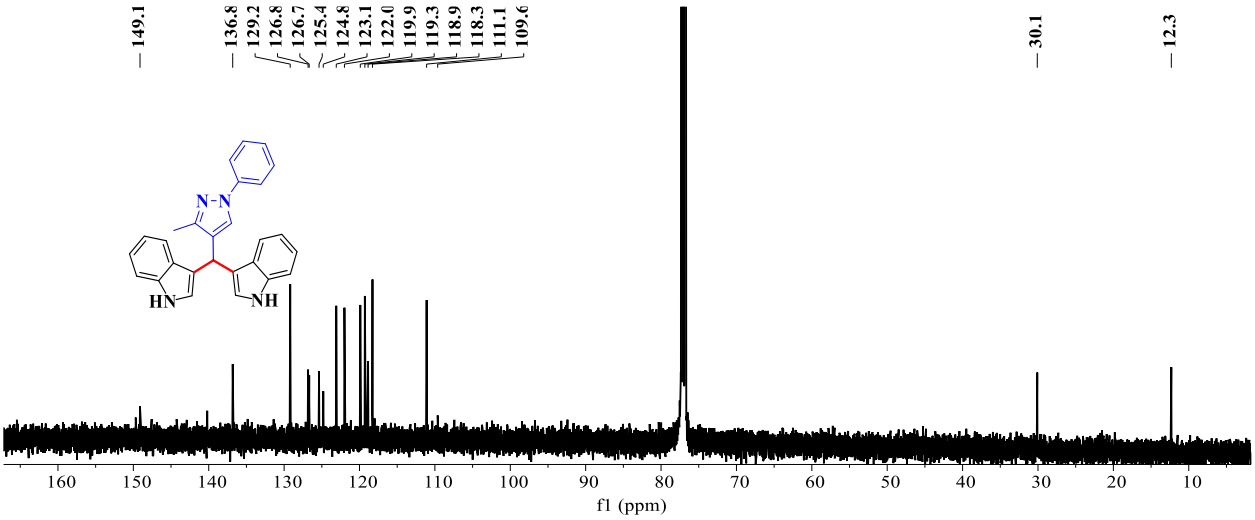


Figure S74. ^{13}C NMR spectrum of $\mathbf{I_{23}}$ (126 MHz).

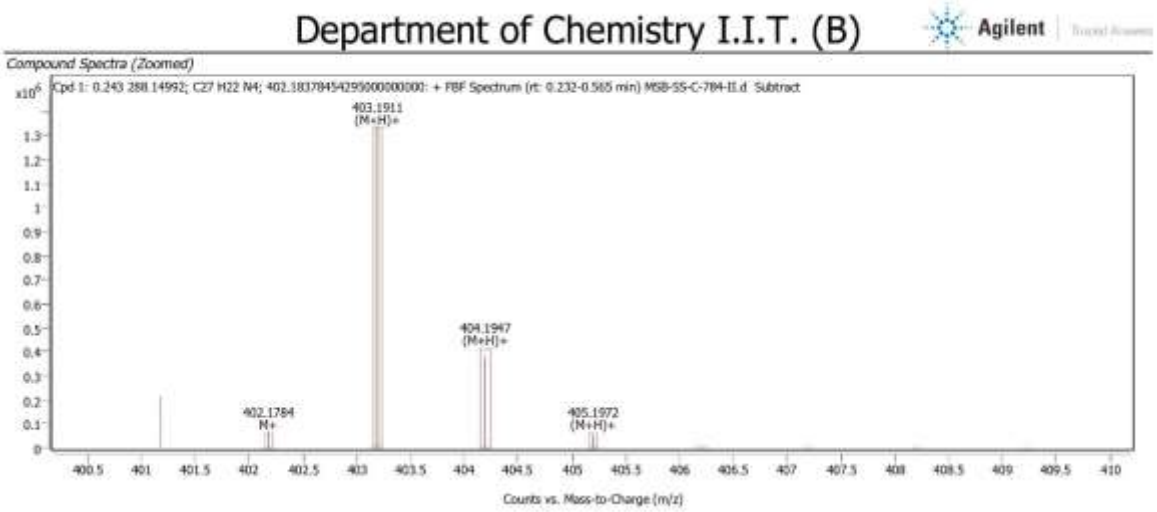


Figure S75. HRMS spectrum of **I_{23}**.

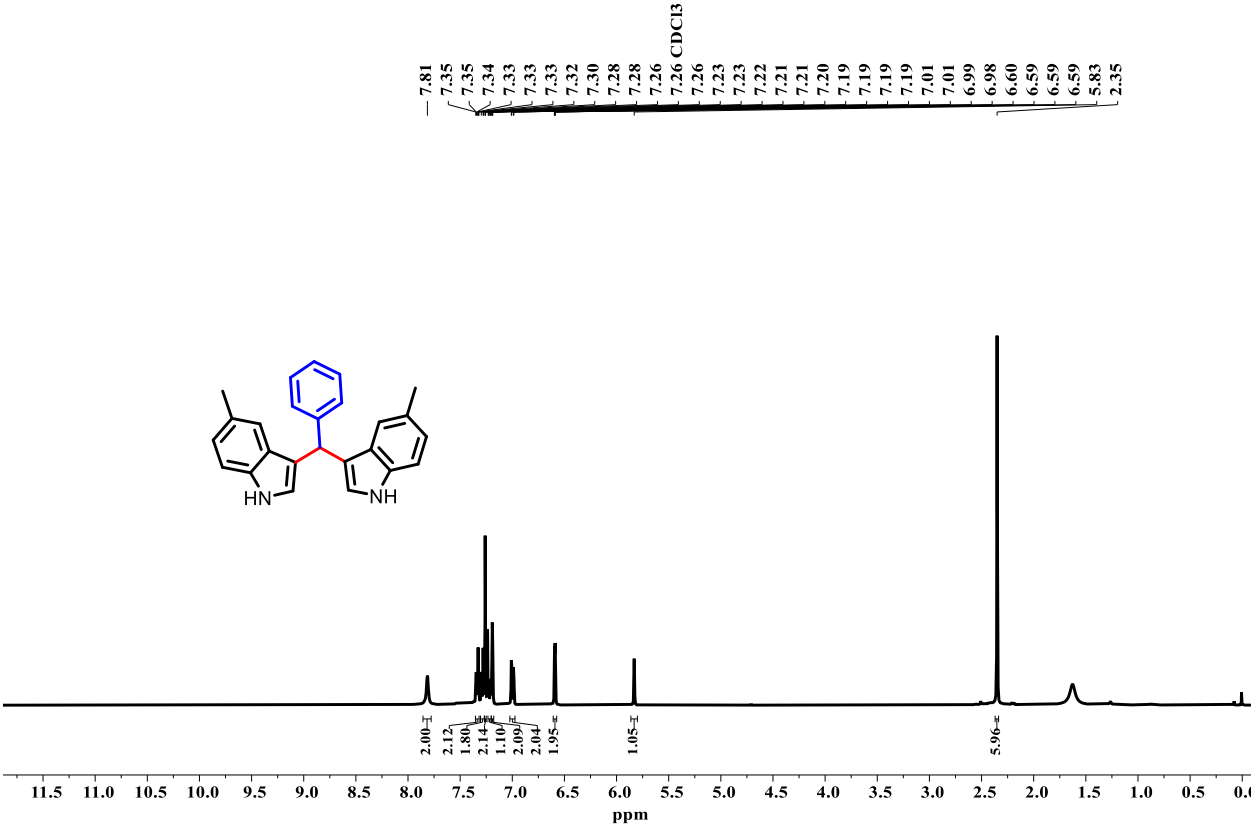


Figure S76. ^{1}H NMR spectrum of **I_{24}** (400 MHz).

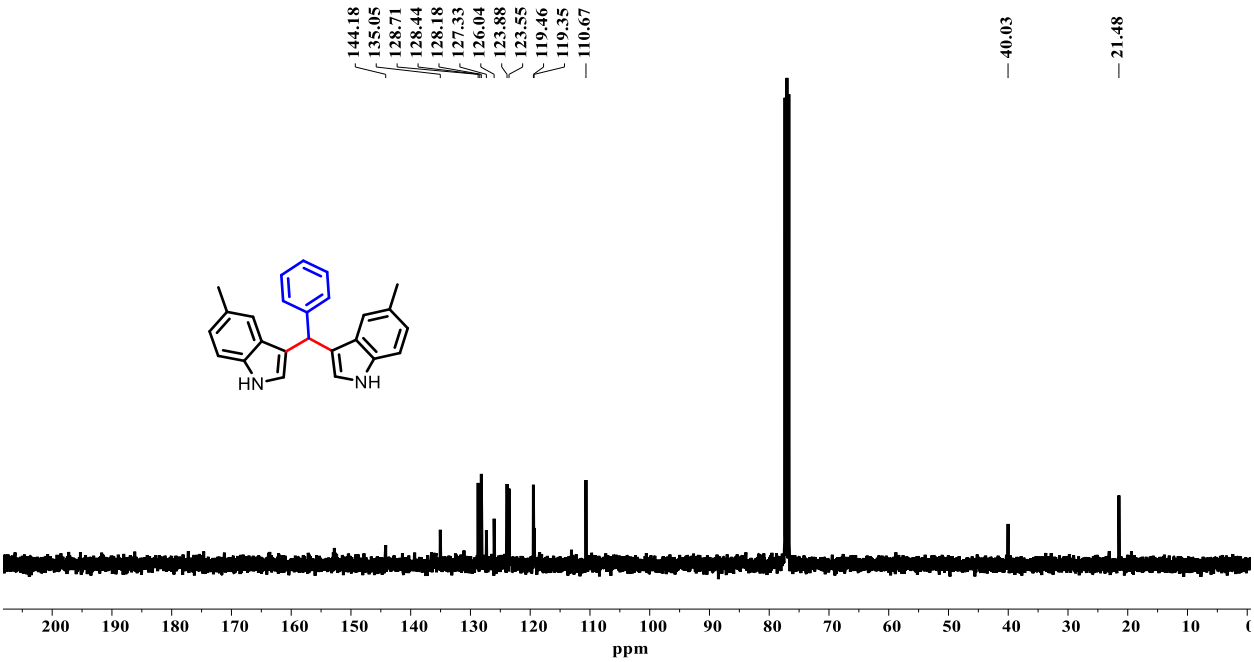


Figure S77. ^{13}C NMR spectrum of $\mathbf{I_{24}}$ (101 MHz).

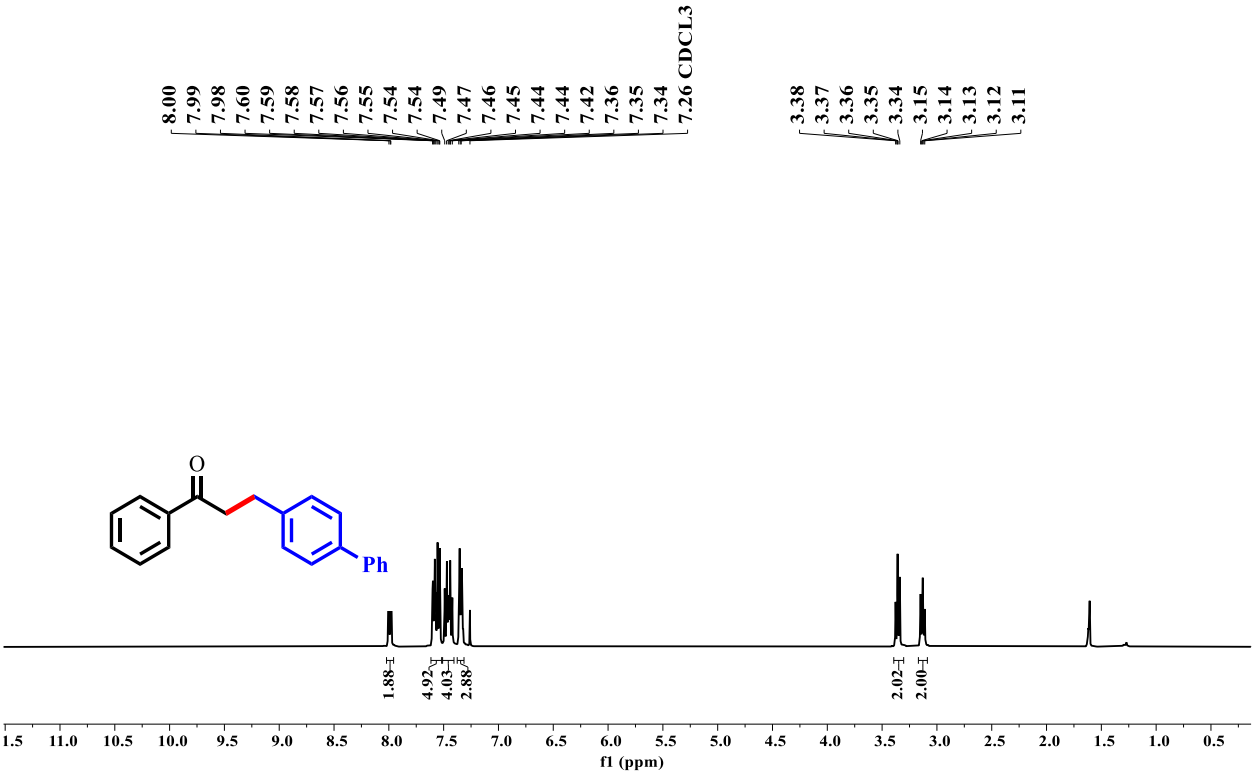


Figure S78. ^{1}H NMR spectrum of $\mathbf{E_1}$ (400 MHz).

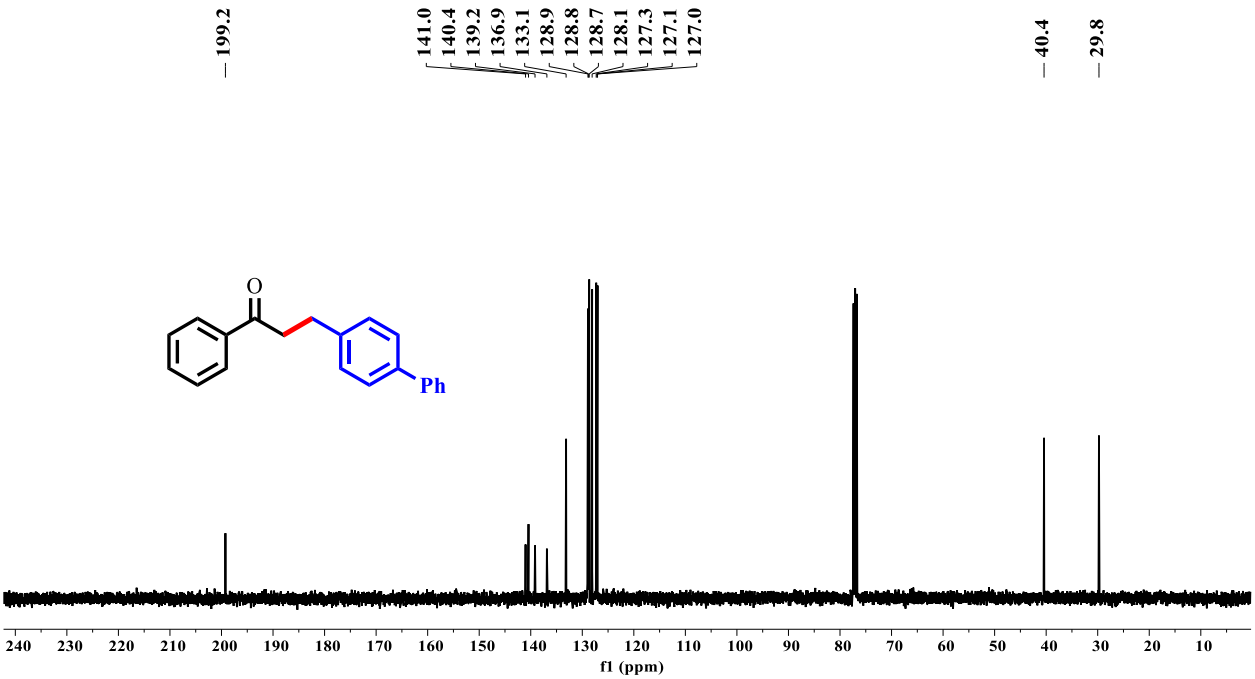


Figure S79. ^{13}C NMR spectrum $\mathbf{E_1}$ (101 MHz).

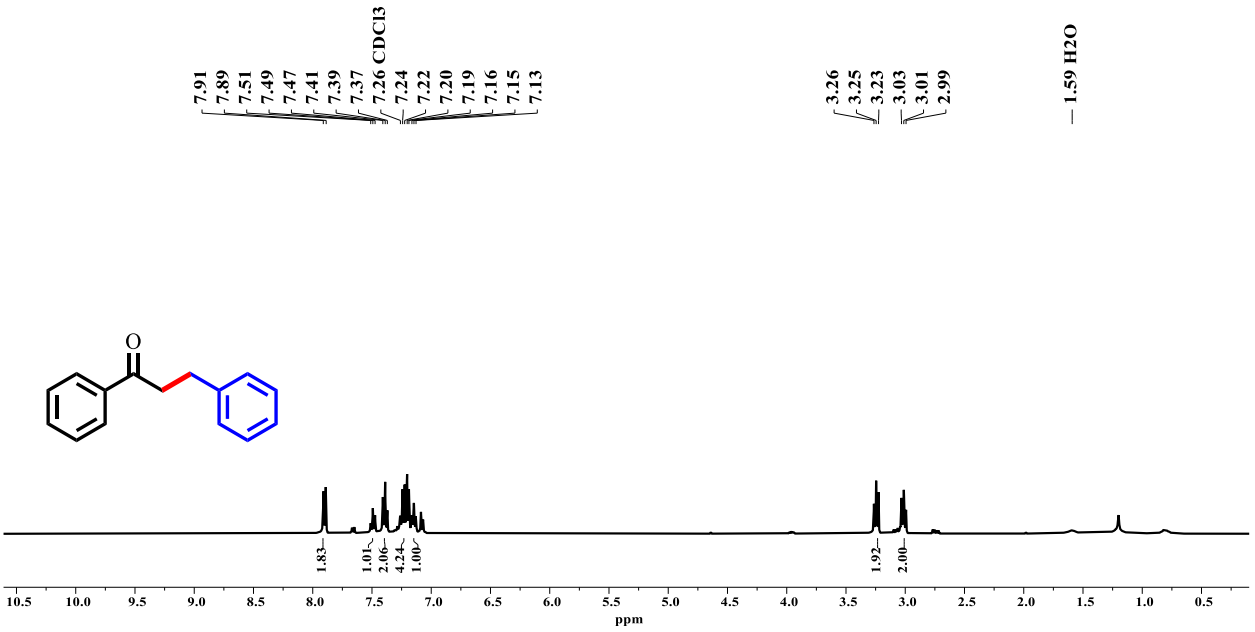


Figure S80. ^{1}H NMR spectrum of $\mathbf{E_2}$ (400 MHz).

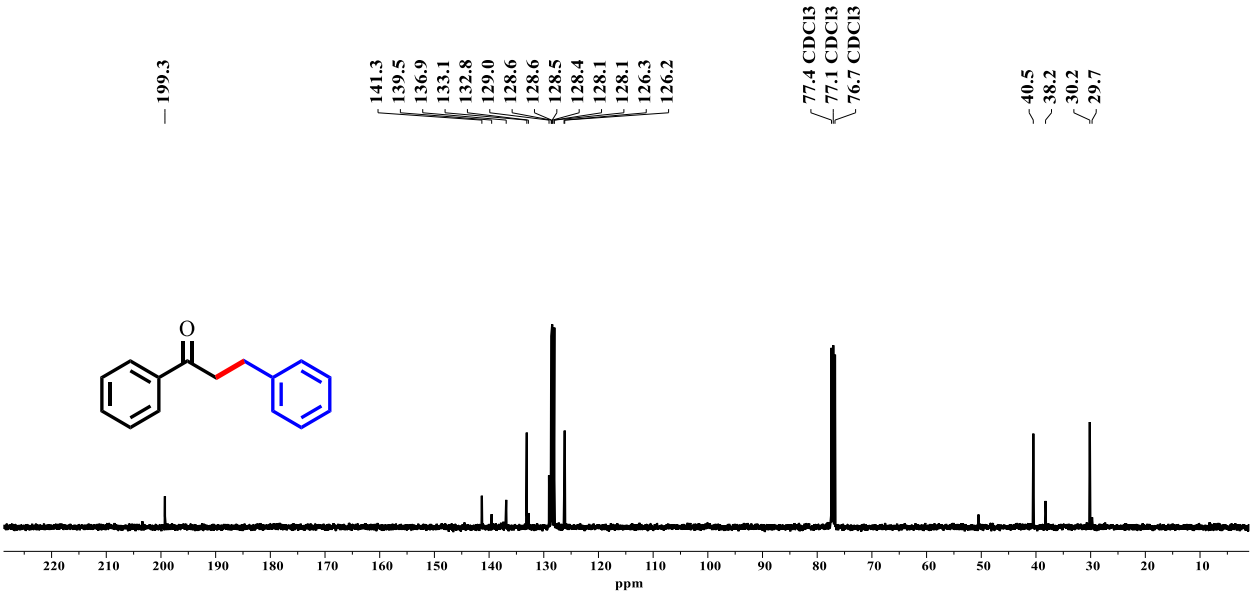


Figure S81. ^{13}C NMR spectrum **E₂** (101 MHz).

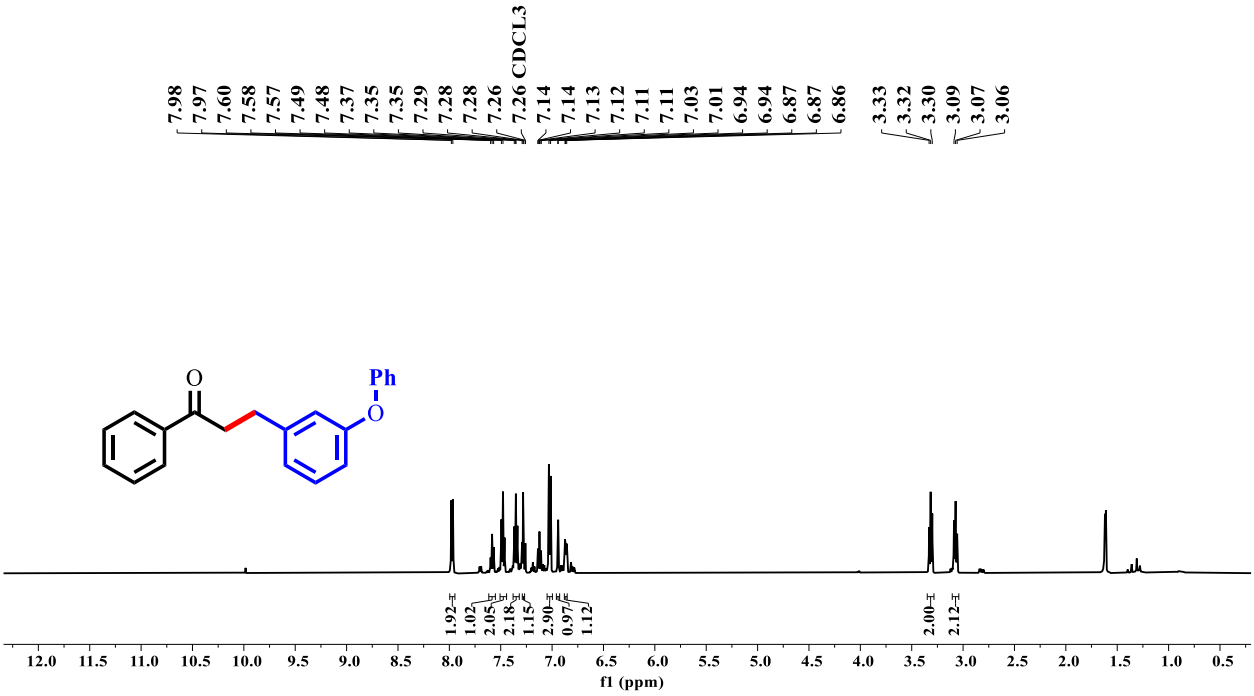


Figure S82. ^{1}H NMR spectrum of **E₃** (500 MHz).

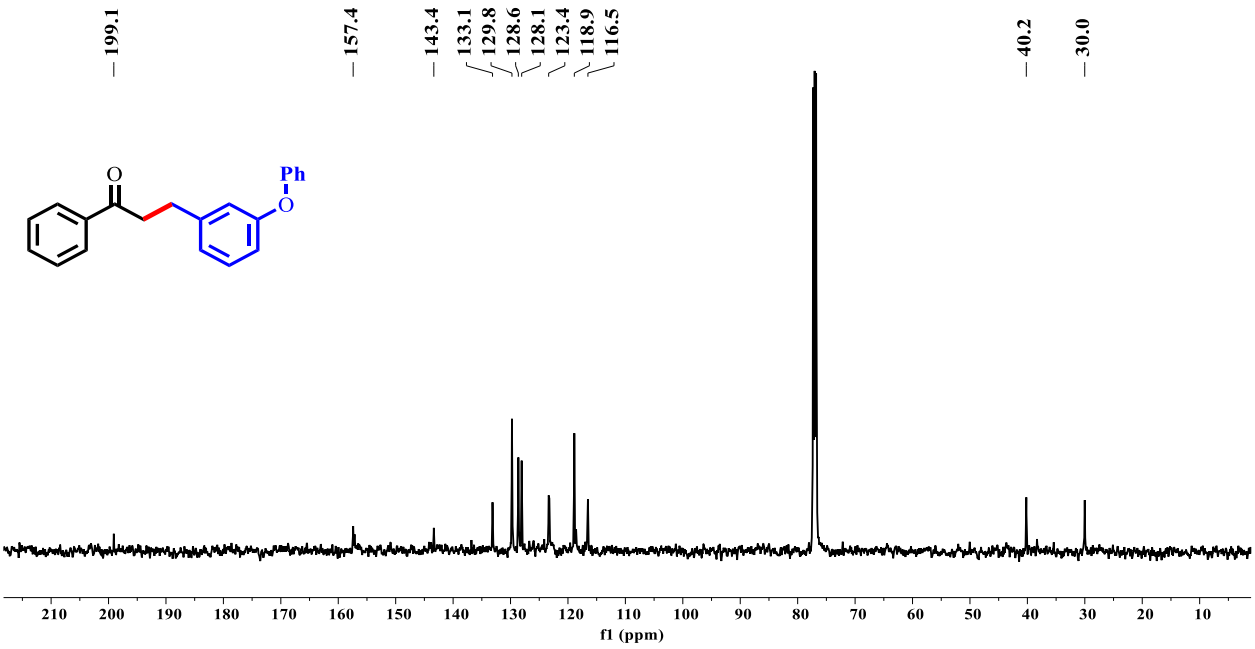


Figure S83. ^{13}C NMR spectrum **E$_3$** (126 MHz).

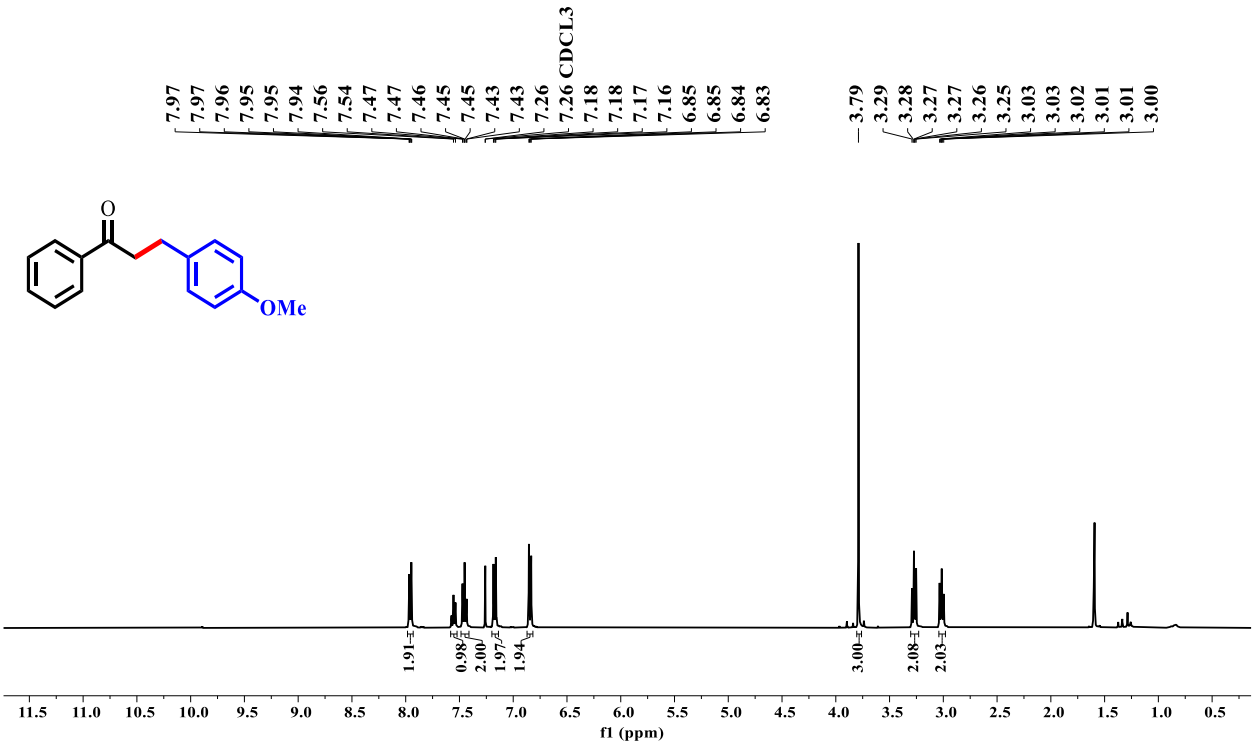


Figure S84.^{1}H NMR spectrum of **E$_4$** (400 MHz).

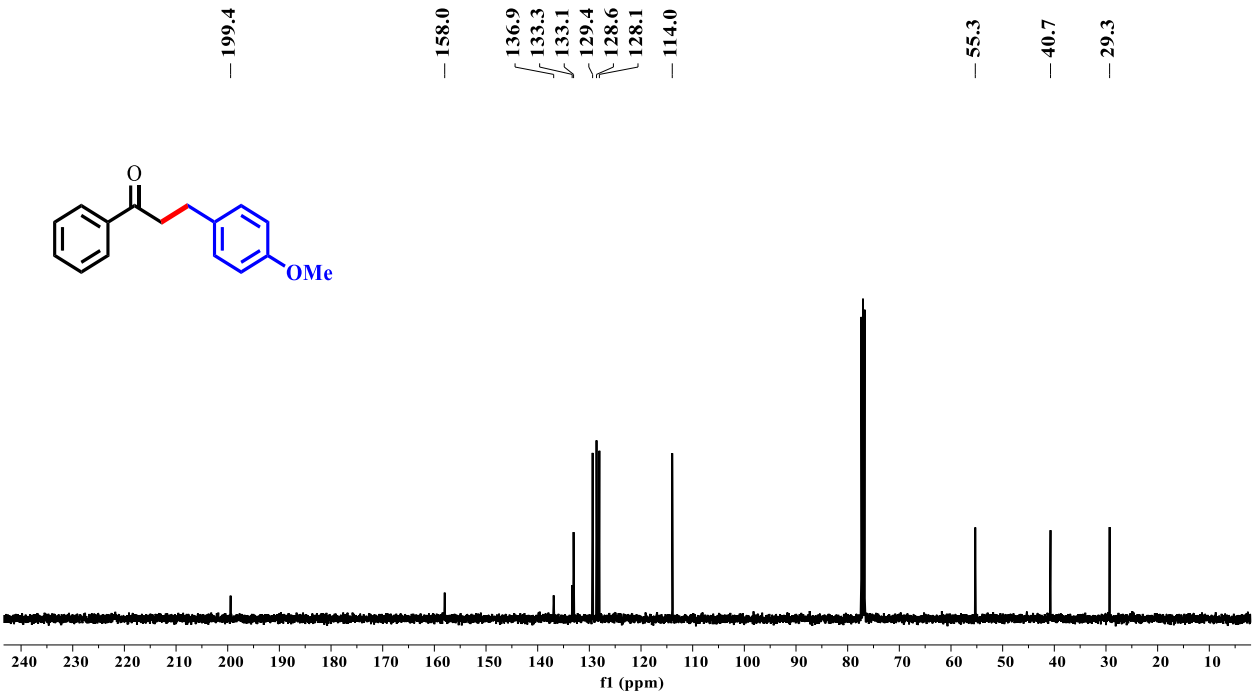


Figure S85. ^{13}C NMR spectrum **E$_4$** (101 MHz).

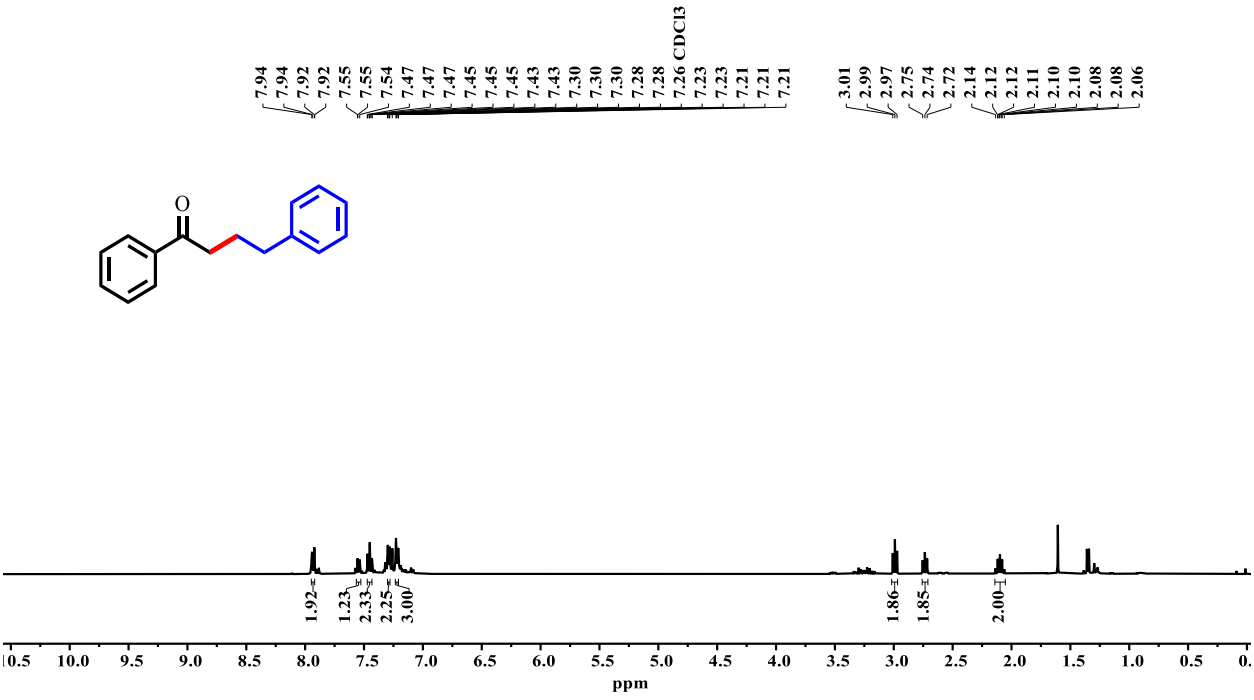


Figure S86. ^{1}H NMR spectrum of **E$_5$** (400 MHz).

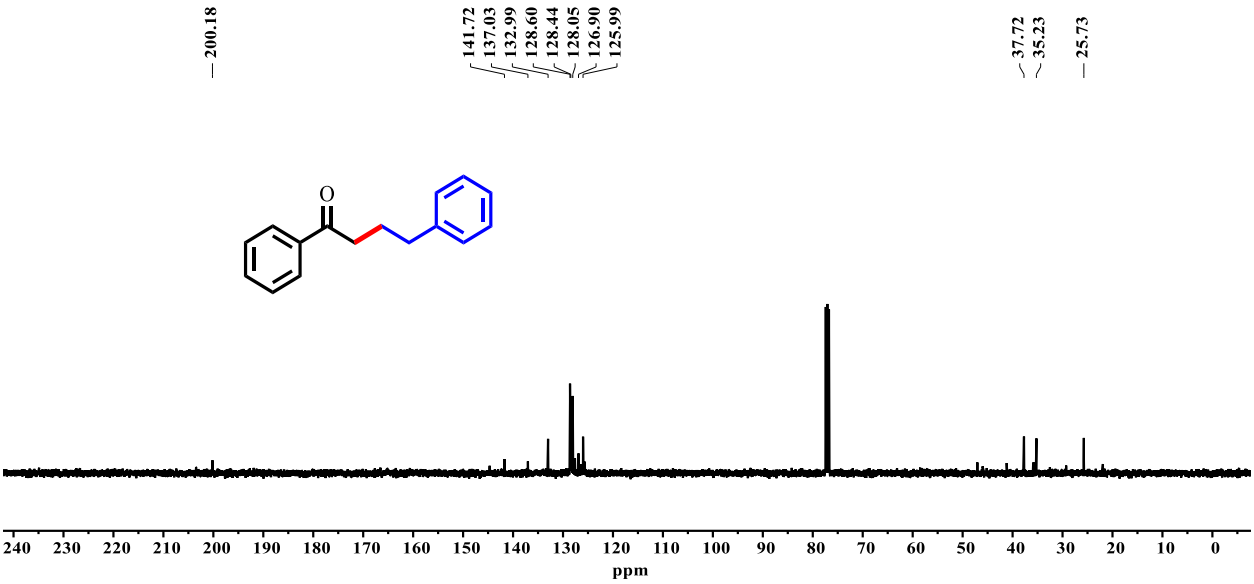


Figure S87. ^{13}C NMR spectrum **E$_5$** (101 MHz).

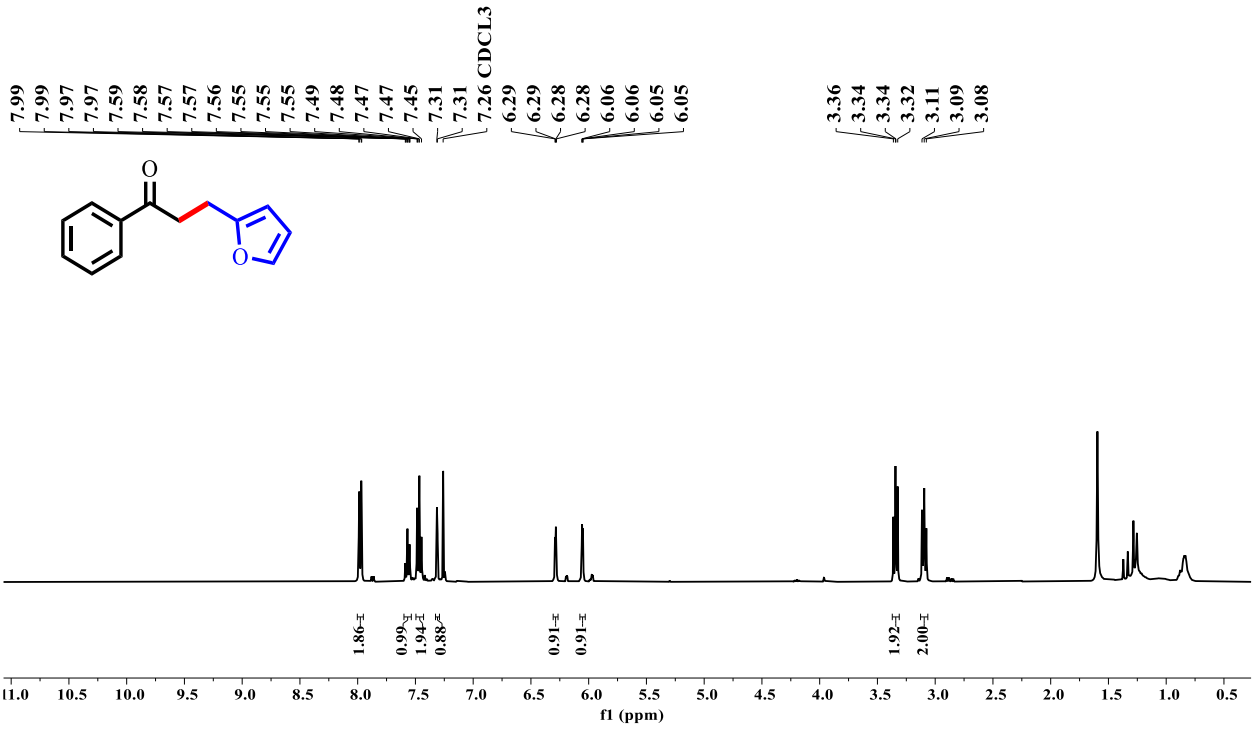


Figure S88. ^{1}H NMR spectrum of **E$_6$** (400 MHz).

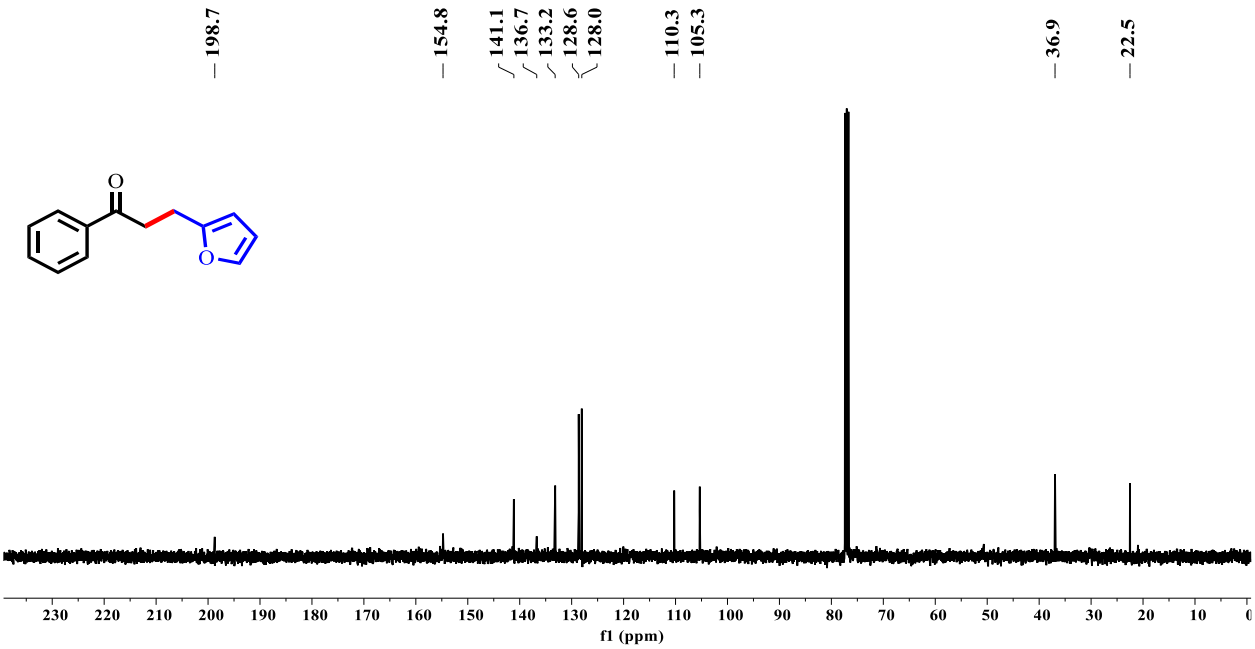


Figure S89. ^{13}C NMR spectrum **E$_6$** (101 MHz).

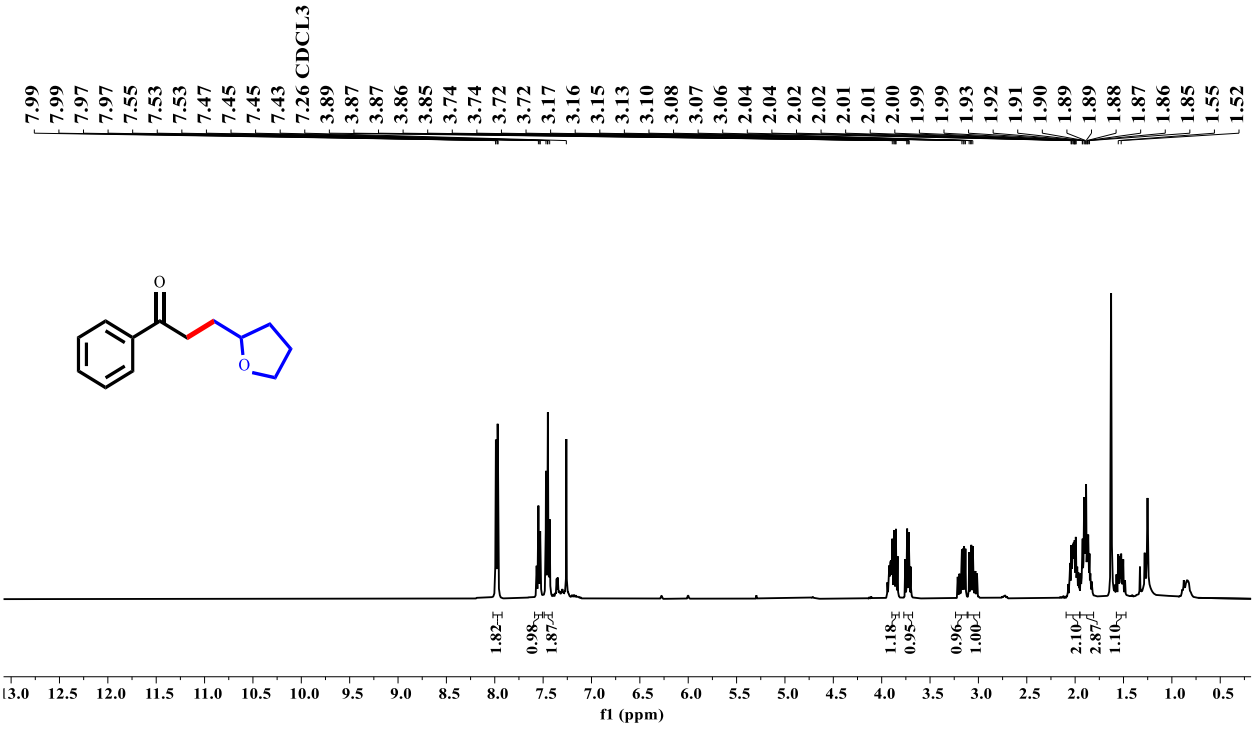


Figure S90. ^{1}H NMR spectrum of **E$_7$** (400 MHz).

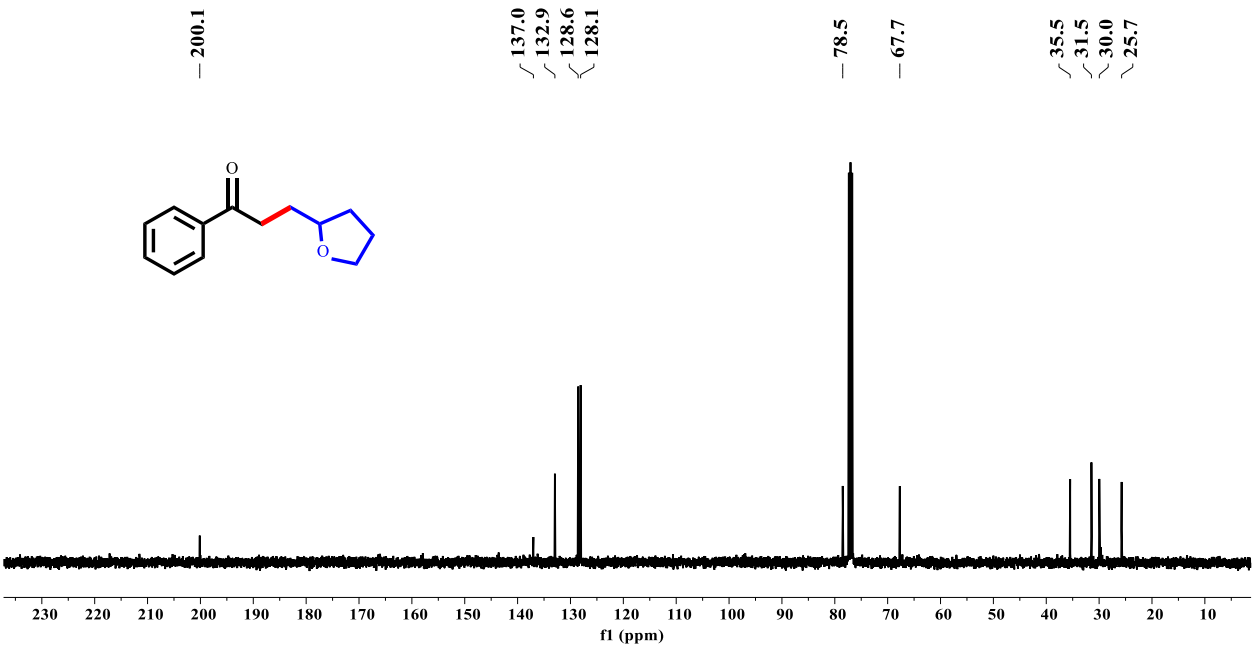


Figure S91. ^{13}C NMR spectrum **E$_7$** (101 MHz).

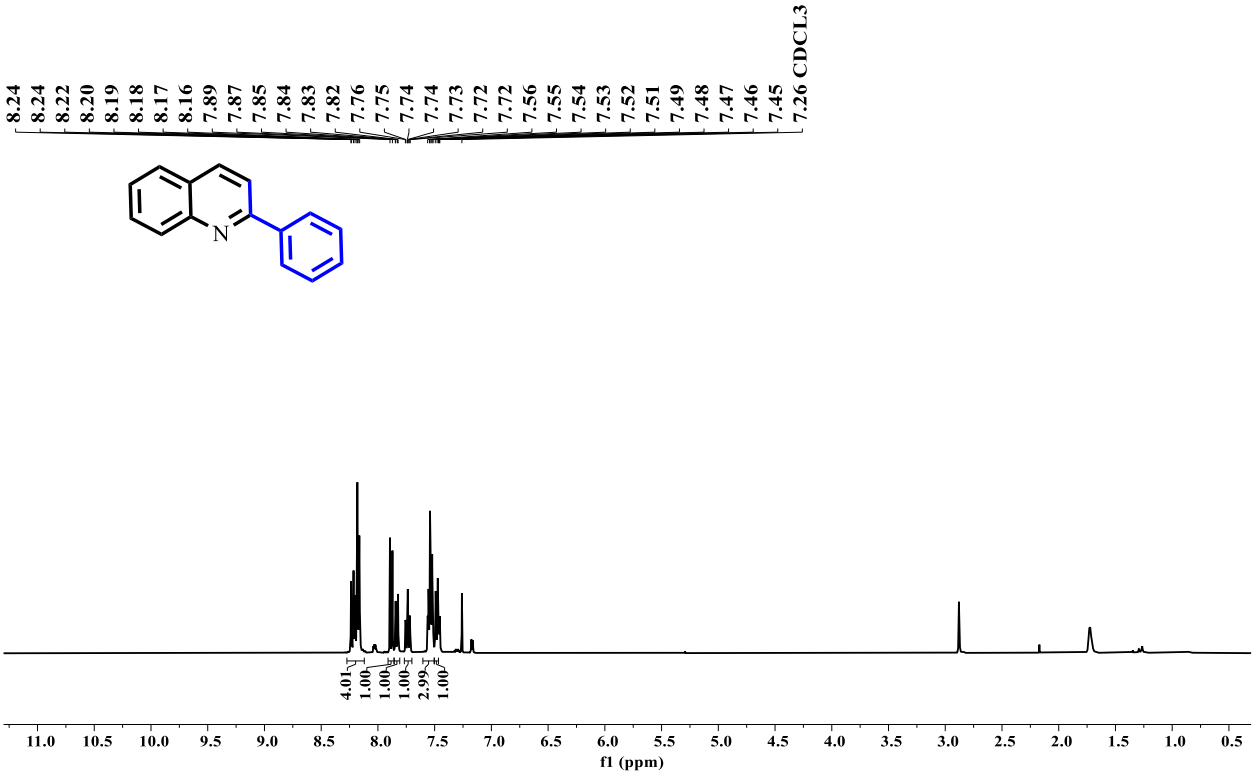


Figure S92. ^{1}H NMR spectrum of **E$_8$** (400 MHz).

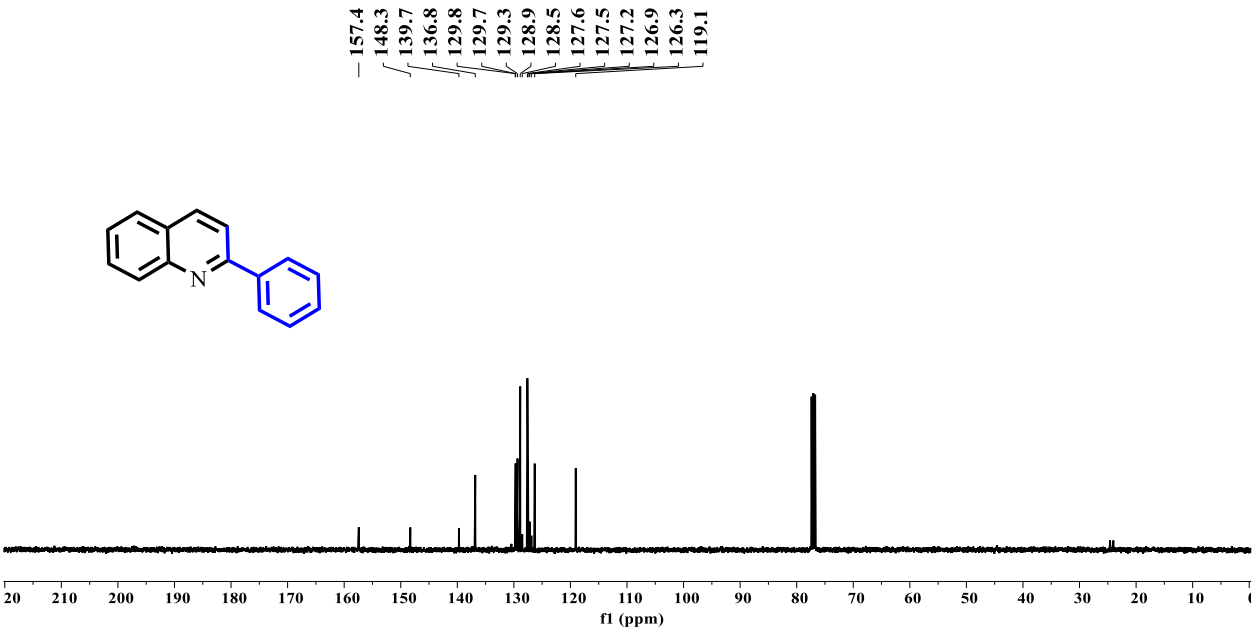


Figure S93. ^{13}C NMR spectrum **E$_8$** (101 MHz).

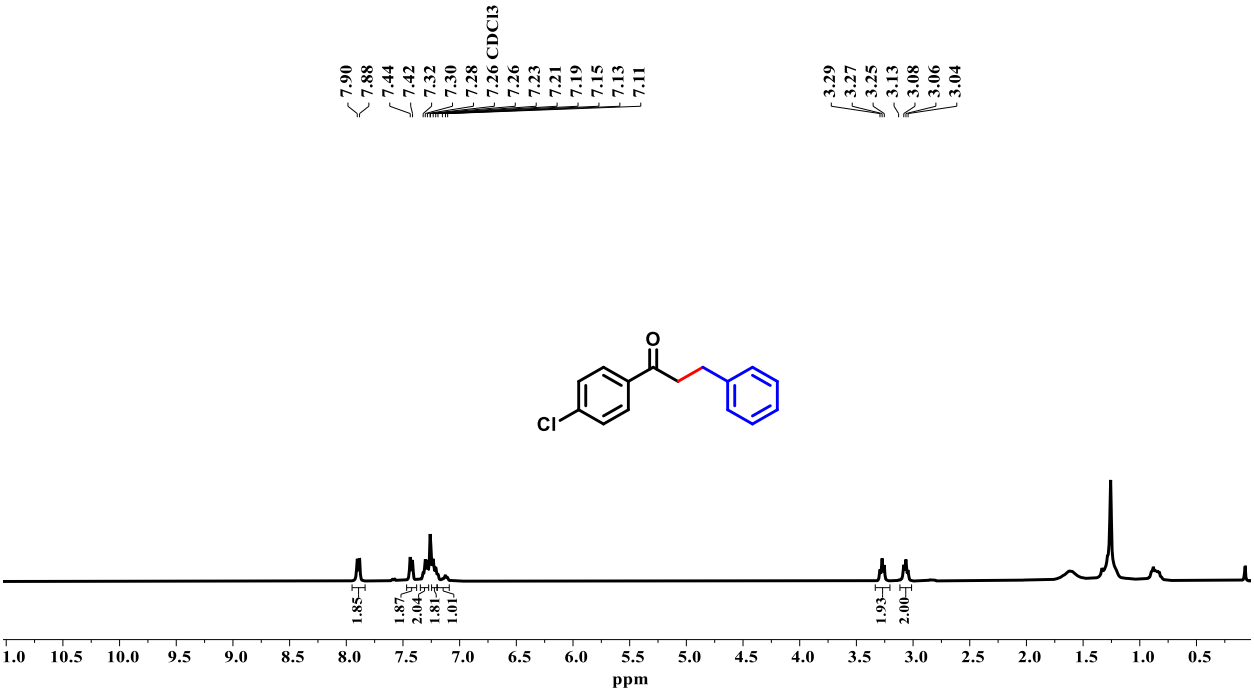


Figure S94. ^{1}H NMR spectrum of **E$_9$** (400 MHz).

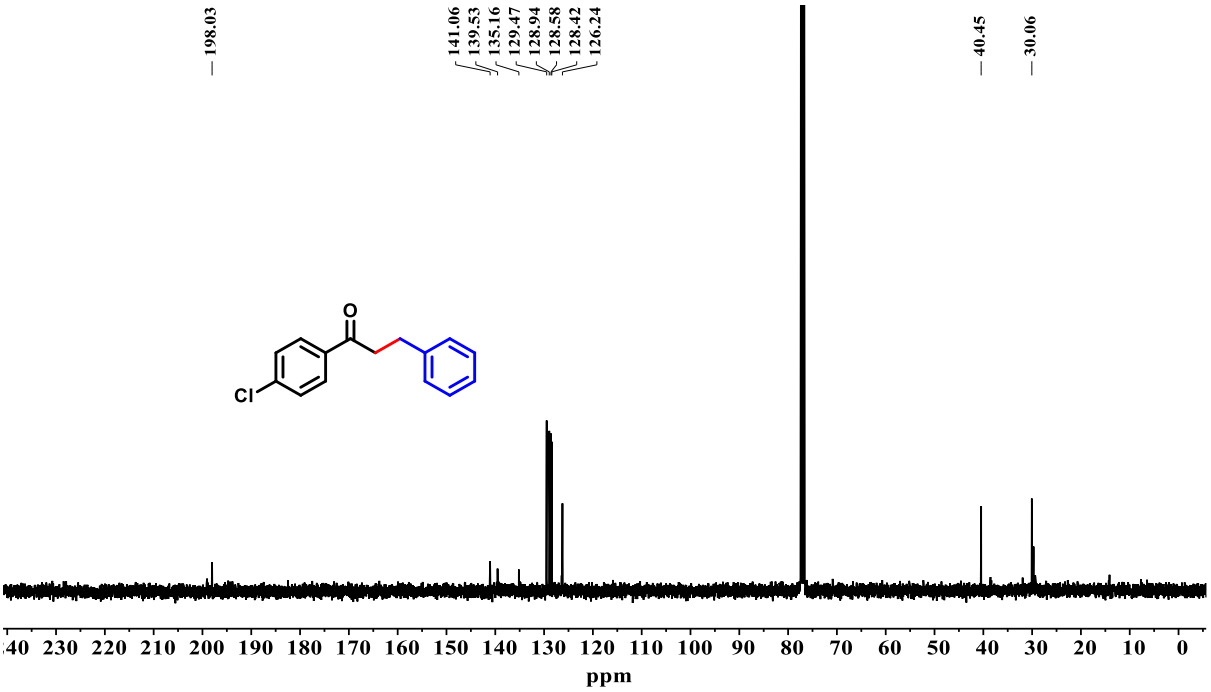


Figure S95. ^{13}C NMR spectrum **E9** (101 MHz).

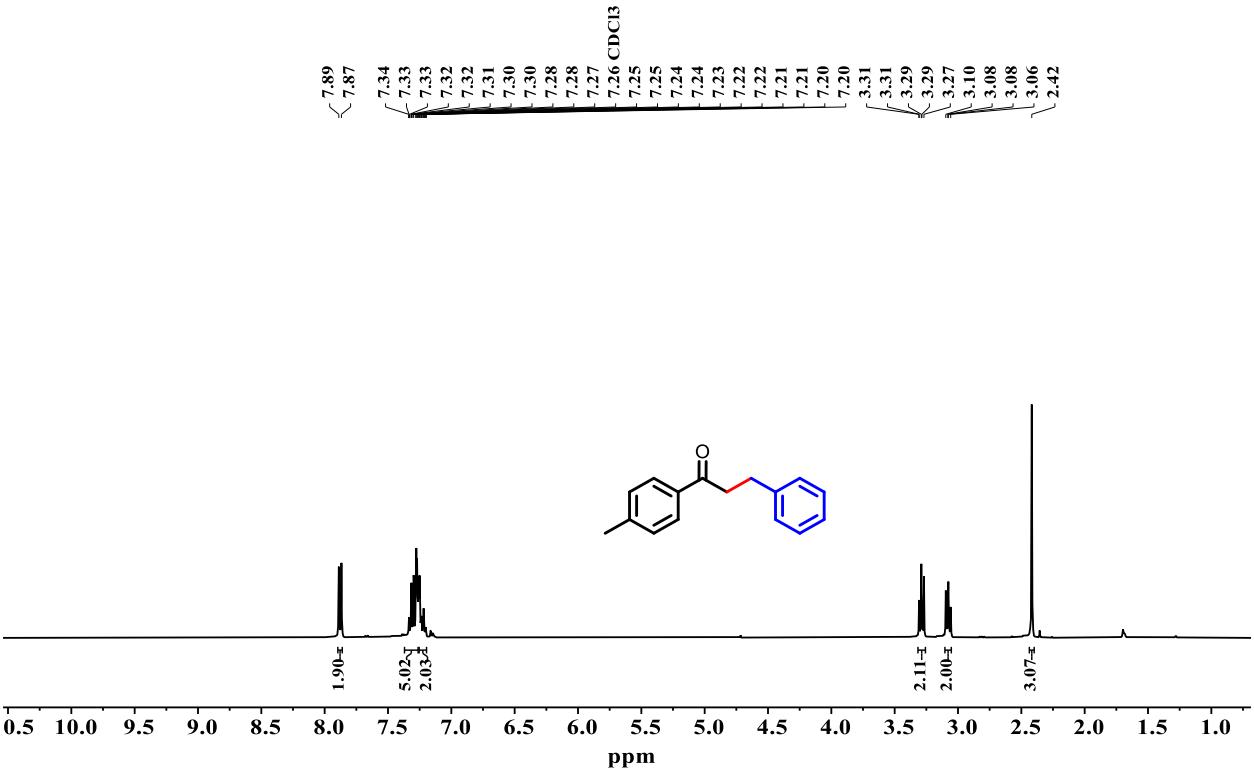


Figure S96. ^{1}H NMR spectrum of **E_{10}** in $CDCl_3$ (400 MHz).

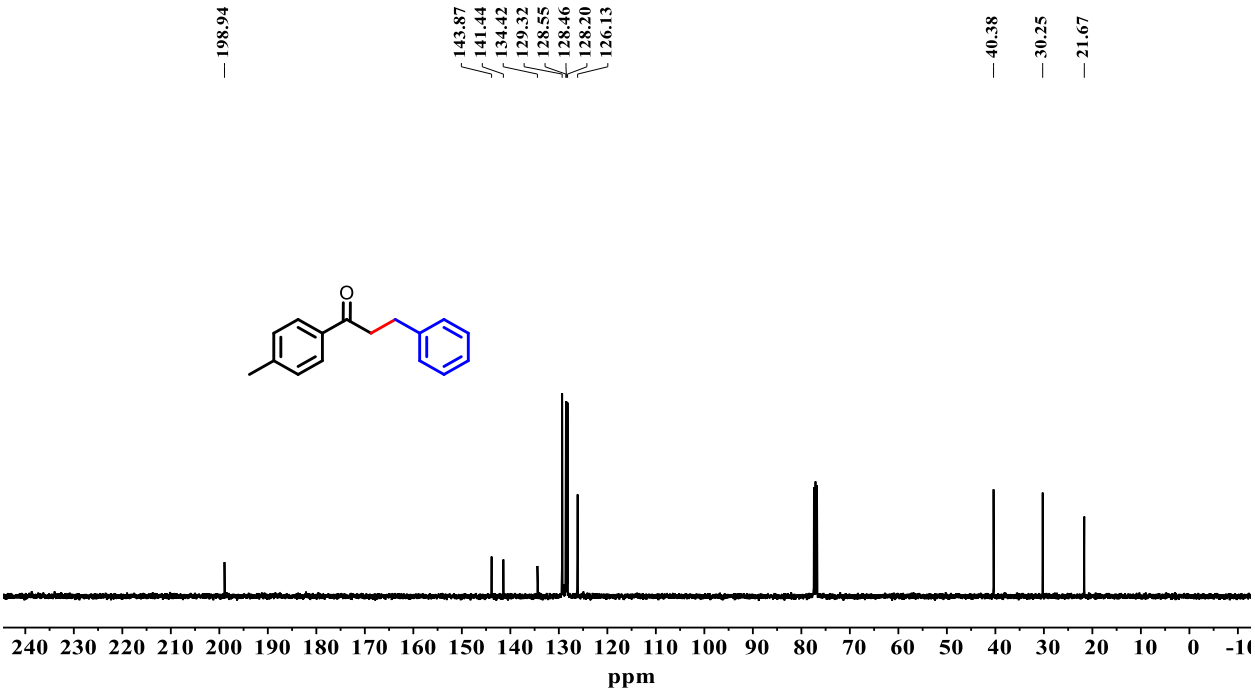


Figure S97. ^{13}C NMR spectrum of $\mathbf{E_{10}}$ in $CDCl_3$ (101 MHz).

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