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Supporting Information

De Novo Endo-functionalized Organic Cages as Cooperative multi Hydorgen-bond-donating Catalysts

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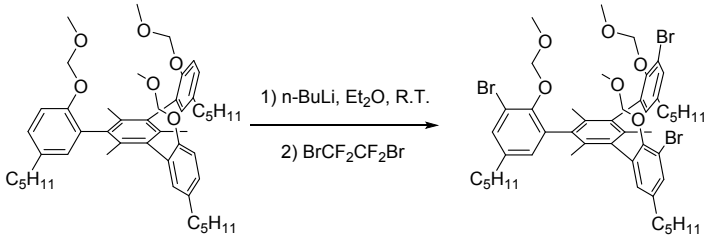
Materials and general methods

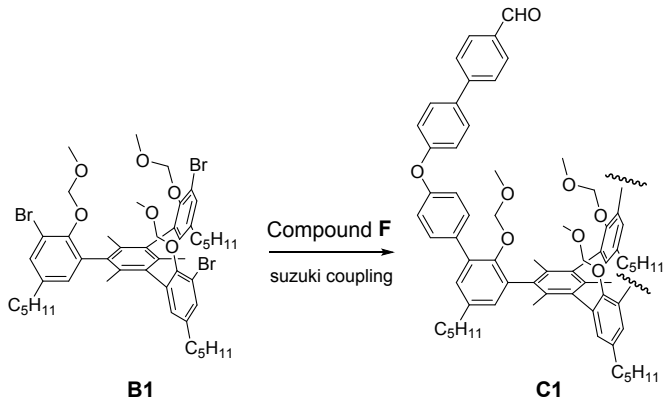
All the reagents and solvents are purchased from commercial sources and used without any purification unless anhydrous condition was noted. All reaction are reacted in a flame-dried glassware under nitrogen atmosphere except when aqueous solution were needed as reagents. NMR spectra were recorded on Bruker AM-300 spectrometers. The chemical shift (δ) values are given in ppm with TMS as internal standard. Coupling constants are recorded in Hz, and multiplicities are reported as follows: s, singlet; d, doublet, t, triplet; m, multiplet; dd, doublet of doublets; dt, doublet of triplets; br, broad. ESI-HRMS were recorded on a Waters Xevo Q-TOF MS and a Thermofisher LTQ Orbitrap Elite MS. 200-300 mesh silica gel was used for flash chromatography and was produced by Qingdao Marine Chemical Industrials. EI-HRMS were recorded on a Thermofisher MAT95XP MS. TLC and pre-TLC were carried out on precoated silica gel GF254 plates (Yantai Chemical Industrials) and the TLC spots were viewed at 254 nm. X-ray crystallographic analysis was carried out on a Agilent SuperNova, Dual, Cu at zero, AtlasS2 diffractometer with graphite monochromated Cu Kα radiation (λ = 1.54184 Å). Compound A1, A2, r1, r2[S1] and 1,3,5-tris-(aminomethyl)-2,4,6-triethylbenzene[S2] were synthesized and characterized as previous reports.

Synthesis of catalyst



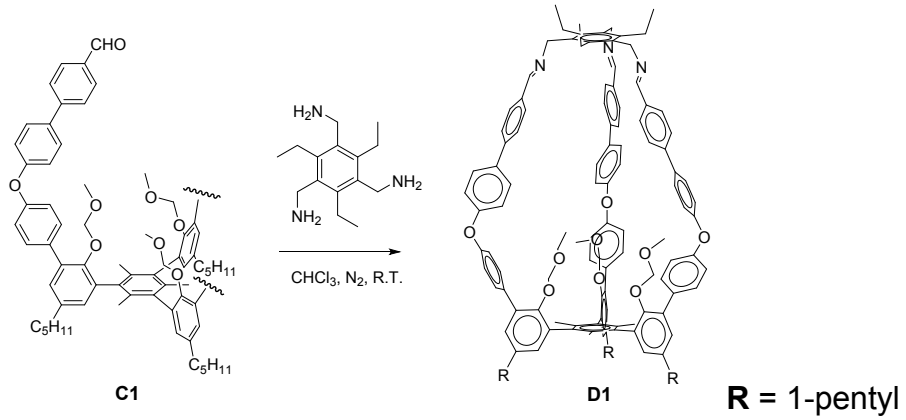
Compound B1. To a solution of compound A1 (138 mg, 0.19 mmol) in anhydrous Et_2O (10 mL) was added n-BuLi (2.4 M in hexane, 263 ul, 0.63 mmol) at 0 °C. The mixture was first stirred at room temperature for 4h, then move to a -78 °C bath. After slowly adding dibrometetrafluoroethane (136 ul, 1.14 mmol), the mixture was kept at -78 °C for 1h , then stirred at room temperature for addtional 24h. The mixture was quenched with sat. NH_4Cl aqueous solution and extracted with AcOEt (20 mL × 2), and the AcOEt extract was washed with brine and dried over Na_2SO_4. The evaporated residue was purified by column chromatography (silica gel, petroleum ether / Et_2O = 20:1) to give compound B1 (93 mg, 50%) as white solid.

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.39 (d, *J* = 2.1 Hz, 3H), 6.87 (d, *J* = 2.1 Hz, 3H), 4.65 (s, 6H), 3.49 (s, 9H), 2.55 (t, *J* = 7.5 Hz, 6H), 1.80 (s, 9H), 1.67 – 1.58 (m, 6H), 1.35 – 1.23 (m, 12H), 0.86 (t, *J* = 6.9 Hz, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 149.2, 140.4, 136.4, 135.9, 134.8, 132.5, 130.9, 118.1, 98.4, 58.0, 35.0, 31.4, 31.0, 22.6, 19.2, 14.1. ESI-HRMS *m/z* 995.2117 $[M+Na]^+$ (calcd. for $C_{48}H_{63}O_6Br_3Na$ $[M+Na]^+$ 995.2067)



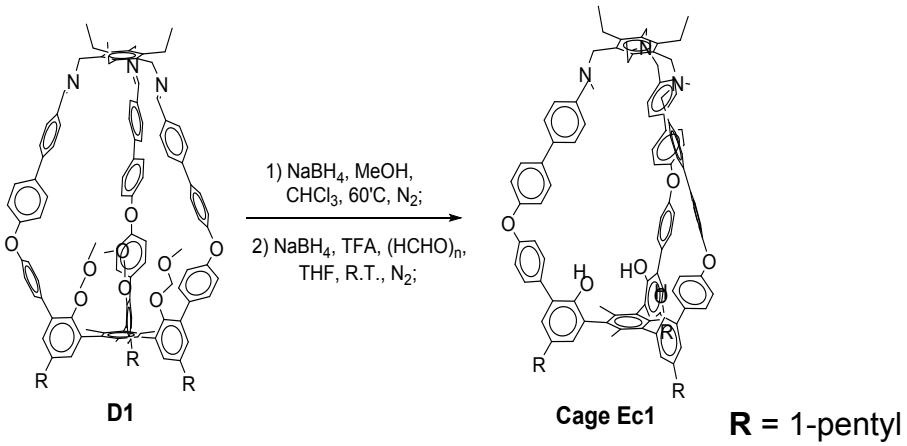
Compound C1. a mixture of compound B1 (120 mg, 0.12 mmol), compound F (295

mg, 0.74 mmol), $Pd(PPh_3)_4$ (28 mg, 0.024 mmol) and K_2CO_3 (66 mg, 0.48 mmol) in THF (5 mL)-water (0.5 mL) was refluxed for 48h. The resulted mixture was concentrated and then purified by column chromatography (silica gel, petroleum ether / AcOEt = 4:1) to afford compound C1 (112 mg, 60%) as pale-yellow solid. ^{1}H-NMR (300 MHz, Acetone-d6): δ 10.06 (s, 3H), 7.97 (d, *J* = 8.4 Hz, 6H), 7.85 (d, *J* = 8.3 Hz, 6H), 7.76 (d, *J* = 8.8 Hz, 6H), 7.66 (s, 6H), 7.24 (d, *J* = 2.2 Hz, 3H), 7.20 – 7.09 (m, 12H), 7.03 (d, *J* = 2.2 Hz, 3H), 4.45 (s, 6H), 2.84 (s, 9H), 2.69 (t, *J* = 7.6 Hz, 6H), 2.03 (s, 9H), 1.76 – 1.62 (m, 6H), 1.40 – 1.31 (m, 12H), 0.88 (t, *J* = 7.0 Hz, 9H). ^{13}C-NMR (75 MHz, Acetone-d6): δ 192.4, 159.1, 156.5, 150.4, 146.7, 139.7, 137.9, 136.4, 136.3, 136.0, 136.1, 135.2, 134.9, 132.3, 131.7, 130.9, 130.7, 129.7, 128.0, 119.8, 119.6, 99.0, 57.0, 35.8, 32.2, 32.1, 23.2, 19.7, 14.4. ESI-HRMS *m*/*z* 1577.7268 $[M+Na]^+$ (calcd. for $C_{105}H_{102}O_{12}Na$ $[M+Na]^+$ 1577.7264)



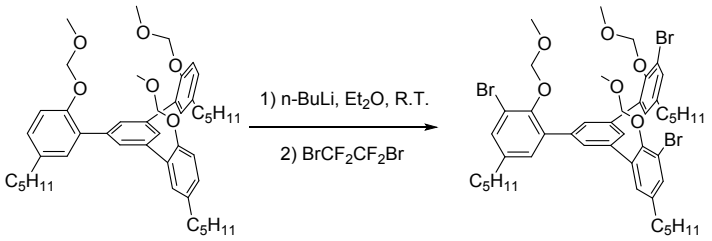
Compound D1. To a solution of compound C1 (16 mg, 0.01 mmol) in anhydrous $CHCl_3$ (3 mL) was added 1,3,5-Tris-(aminomethyl)-2,4,6-triethylbenzene (2.6 mg , 0.01 mmol in 1mL $CHCl_3$). The mixture was stirred at room temperature for 24h. After completely removing the solvent, the mixture was washed with a small portion of MeCN and EtOH to give compound D1 as white solid (17.6 mg , 95%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.22 (s, 3H), 7.74 (d, *J* = 8.1 Hz, 6H), 7.59 (d, *J* = 8.4 Hz, 6H), 7.52 (d, *J* = 8.1 Hz, 6H), 7.43 (d, *J* = 8.6 Hz, 6H), 7.21 (d, *J* = 1.4 Hz, 3H), 7.15 (d, *J* = 8.4 Hz, 6H), 7.09 (d, *J* = 1.4 Hz, 3H), 6.85 (d, *J* = 8.6 Hz, 6H), 4.98 (s, 6H), 4.32 (s, 6H), 2.85 (s, 9H), 2.79 – 2.66 (m, 12H), 2.00 (s, 9H), 1.75 – 1.64 (m, 6H), 1.41 – 1.28 (m, 21H), 0.91 (t, *J* = 6.4 Hz, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 160.0, 159.8, 154.5,

149.3, 143.7, 142.5, 139.1, 136.7, 136.3, 135.9, 135.4, 135.2, 134.7, 134.2, 132.6, 132.0, 130.5, 129.4, 128.8, 128.2, 126.8, 121.6, 116.7, 98.2, 56.7, 35.4, 31.6, 31.3, 22.7, 19.3, 16.0, 14.2. ESI-HRMS *m/z* 1772.9136 $[M+Na]^+$ (calcd. for $C_{120}H_{123}O_9N_3Na$ $[M+Na]^+$ 1772.9152); *m/z* 1750.9332 $[M+H]^+$ (calcd. for $C_{120}H_{124}O_9N_3$ $[M+H]^+$ 1750.9325)



Cage Ec1. Compound D1 (490 mg, 0.28 mmol) was first dissolved in a mixture of anhydrous chloroform and methanol (25 mL, v/v 1.5/1) at 0 °C. Sodium borohydride (960 mg, 25 mmol) was then slowly added to the cooled solution. The suspension was stirred at room temperature for 3 h, and then heated to 50 °C and stirred at this temperature for an additional 20 h to ensure the reduction was completed. The solvents were removed under vacuum. The residue was dissolved in chloroform (30 mL) and 10% aqueous NaOH (50 mL). The organic layer was separated and the aqueous phase was extracted with chloroform (3 × 50 mL). The combined organic layers were washed by brine and then water, dried over Na_2SO_4 and concentrated. The crude compound paraformaldehyde (191 mg, 6.3 mmol) and sodium borohydride (110 mg, 2.9 mmol) were suspended under argon in anhydrous THF (20 mL). TFA (5 mL, 64.9 mmol) was slowly added at room temperature. The mixture was stirred for 24 h at room temperature, then quenched by water (10 mL) and vigorously stirred for an additional 2 h. The mixture was subsequently extracted with AcOEt and washed by a 25% aqueous sodium bicarbonate solution (30 mL), brine (20 mL) and water (30 mL) to ensure organic phase was neutralized. The extraction was concentrated under

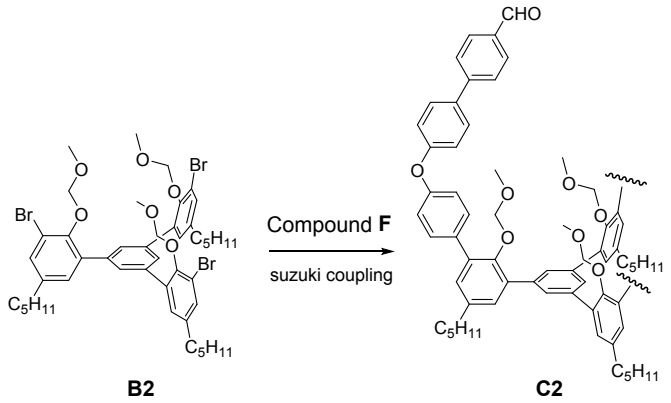
vacuum and then purified by column chromatography (silica gel, petroleum ether / AcOEt = 5:1) to afford Cage Ec1 (280 mg, 60%) as pale-yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.5 Hz, 6H), 7.41 (m, 12H), 7.27 (d, *J* = 7.9 Hz, 6H), 7.14 (d, *J* = 1.4 Hz, 3H), 7.06 (d, *J* = 8.6 Hz, 6H), 7.02 (d, *J* = 8.7 Hz, 6H), 6.98 (d, *J* = 1.4 Hz, 3H), 6.20 (s, 3H, -OH), 3.75 (s, 6H), 3.56 (s, 6H), 3.29 (q, *J* = 7.2 Hz, 6H), 2.63 (t, *J* = 7.5 Hz, 6H), 2.14 (s, 9H), 1.87 (s, 9H), 1.71 – 1.60 (m, 6H), 1.36 – 1.23 (m, 21H), 0.89 (t, *J* = 6.5 Hz, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 157.0, 156.5, 147.6, 144.8, 139.34, 139.30, 137.2, 136.6, 135.6, 135.2, 133.1, 132.2, 130.8, 129.4, 129.1, 129.0, 128.5, 127.9, 127.6, 126.9, 119.5, 119.0, 60.7, 55.5, 41.1, 35.3, 31.6, 31.4, 29.8, 22.2, 18.6, 16.2, 14.2. ESI-HRMS *m*/*z* 1666.9492 $[M+H]^+$ (calcd. for $C_{117}H_{124}O_6N_3$ $[M+H]^+$ 1666.9485)



A2 **B2**

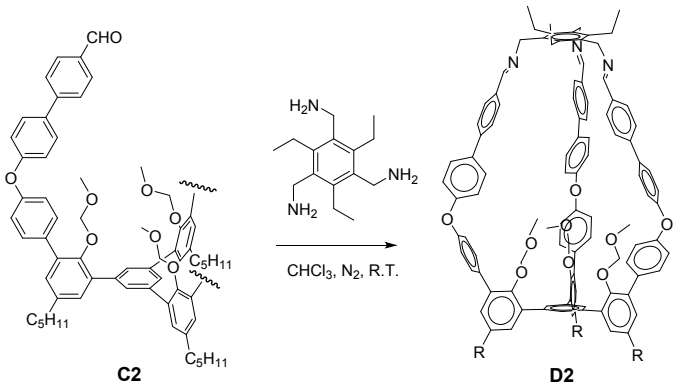
Compound B2. To a solution of compound A2 (209 mg, 0.30 mmol) in anhydrous Et_2O (20 mL) was added n-BuLi (2.4 M in hexane, 417ul, 1.0 mmol) at 0 °C. The mixture was first stirred at room temperature for 4h, then move to a -78 °C bath. After slowly addition of dibrometetrafluoroethane (143 ul, 1.20 mmol), the mixture was sitrred at -78 °C for 1h , then at room temperature for addtional 24h. The mixture was quenched with sat. NH_4Cl aqueous solution and extracted with AcOEt (20 mL × 2), and the AcOEt extract was washed with brine and dried over Na_2SO_4. The evaporated residue was purified by column chromatography (silica gel, petroleum ether / Et_2O = 20:1) to give compound B2 (98 mg, 35%) as white solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.71 (s, 3H), 7.40 (d, *J* = 2.1 Hz, 3H), 7.13 (d, *J* = 2.1 Hz, 3H), 4.78 (s, 6H), 3.30 (s, 9H), 2.58 (t, *J* = 7.7 Hz, 6H), 1.70 – 1.54 (m, 6H), 1.41 – 1.25 (m, 12H), 0.90 (t, *J* = 6.8 Hz, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 149.4, 140.8, 138.7, 136.3, 132.7, 130.5, 129.3, 118.1, 99.5, 57.9, 35.2, 31.6, 31.2, 22.6, 14.2. ESI-HRMS *m*/*z* 953.1610

$[M+Na]^+$ (calcd. for $C_{45}H_{56}O_6Br_3Na$ $[M+Na]^+$ 953.1598)



B2 **C2**

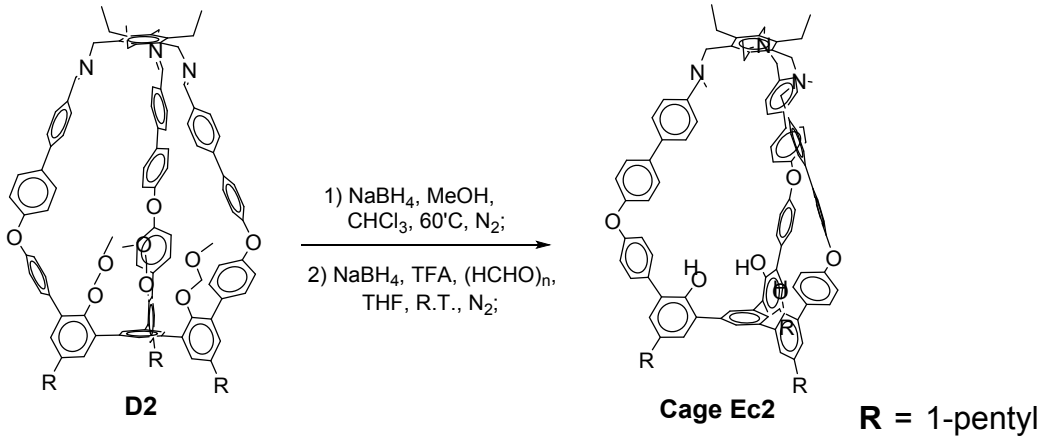
Compound C2. A mixture of compound B2 (140 mg, 0.15 mmol), compound F (360 mg, 0.90 mmol), $Pd(PPh_3)_4$ (35mg, 0.03 mmol) and K_2CO_3 (83 mg, 0.60 mmol) in THF (5 mL)-water (0.5 mL) was refluxed for 48h. The resulted mixture was concentrated and then purified by column chromatography (silica gel, petroleum ether / AcOEt = 4:1) to afford compound C2 (159 mg, 70%) as pale-yellow solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 10.05 (s, 3H), 7.95 (d, *J* = 8.4 Hz, 6H), 7.87 (s, 3H), 7.74 (d, *J* = 8.2 Hz, 6H), 7.64 (dd, *J* = 8.8, 2.4 Hz, 12H), 7.24 (d, *J* = 2.2 Hz, 3H), 7.20 (d, *J* = 2.2 Hz, 3H), 7.14 (dd, *J* = 8.7, 1.6 Hz, 12H), 4.47 (s, 6H), 2.79 (s, 9H), 2.70 – 2.66 (t, *J* = 7.5 Hz, 6H), 1.75 – 1.62 (m, 6H), 1.43 – 1.29 (m, 12H), 0.91 (t, *J* = 7.0 Hz, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 191.9, 158.1, 155.7, 149.6, 146.5, 139.34, 139.27, 135.52, 135.50, 135.0, 134.9, 134.6, 131.4, 130.5, 130.4, 130.2, 129.5, 128.8, 127.3, 119.0, 118.9, 99.0, 56.8, 35.4, 31.7, 31.3, 22.6, 14.1. ESI-HRMS *m*/*z* 1535.6809 $[M+Na]^+$ (calcd. for $C_{102}H_{96}O_{12}Na$ $[M+Na]^+$ 1535.6794)



C2 **D2**

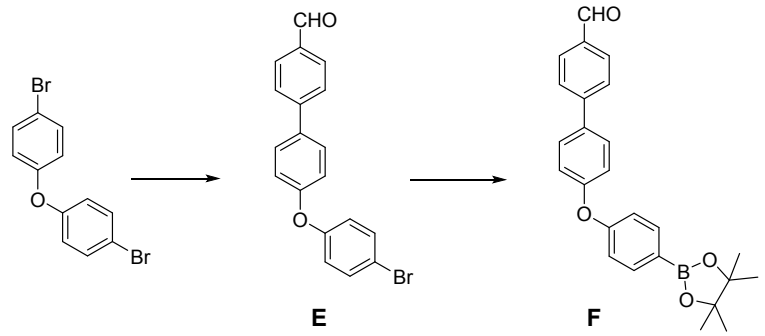
R = 1-pentyl

Compound D2. To a solution of compound C2 (151 mg, 0.1 mmol) in anhydrous $CHCl_3$ (20 mL) was added 1, 3, 5-Tris-(aminomethyl)-2, 4, 6-triethylbenzene (25 mg, 0.1 mmol in 10mL $CHCl_3$). The mixture was stirred at 40°C for 48h and then vaporized to a half volume for the reduction step.



Cage Ec2. The concentrated solution of compound D2 (15 mL) was first diluted with anhydrous methanol (7 mL) at 0 °C. Sodium borohydride (338 mg, 8.9 mmol) was then slowly added to the cooled solution. The suspension was stirred at room temperature for 3 h, and then heated to 50 °C and stirred at this temperature for an additional 20 h to ensure the reduction was completed. The solvents were removed under vacuum. The residue was dissolved in chloroform (30 mL) and 10% aqueous NaOH (50 mL). The organic layer was separated and the aqueous phase was extracted with chloroform (3 × 50 mL). The combined organic layers were washed by brine and then water, dried over Na_2SO_4 and concentrated. The crude compound, paraformaldehyde (68 mg, 2.25 mmol) and sodium borohydride (39 mg, 1.03 mmol) were suspended in anhydrous THF (20 mL). TFA (1.78 mL, 23 mmol) was slowly added at room temperature. After stirred for 24 h at room temperature, the mixture was quenched by water (10 mL) and vigorously stirred for an additional 2 h. Subsequently, the mixture was extracted with AcOEt and washed by a 25% aqueous sodium bicarbonate solution (30 mL), brine (20 mL) and water (30 mL) to ensure PH of organic layer was almost 7. The neutralized extraction was concentrated under vacuum and then purified by column chromatography (silica gel, petroleum ether / AcOEt = 5:1) to afford Cage Ec2 (64 mg, 40%) as pale-yellow solid. ^{1}H-NMR (300

MHz, CD_2Cl_2): δ 7.51-7.41 (m, 21H), 7.29 (d, *J* = 8.1 Hz, 6H), 7.16 (d, *J* = 2.0 Hz, 3H), 7.15 (d, *J* = 2.0 Hz, 3H), 7.02 (dd, *J* = 8.7, 2.4 Hz, 12H), 5.73 (s, 3H, -OH), 3.75 (s, 6H), 3.59 (s, 6H), 3.27 (q, *J* = 7.4 Hz, 6H), 2.64 (t, *J* = 6.9 Hz, 6H), 2.10 (s, 9H), 1.72 – 1.62 (m, 6H), 1.40 – 1.35 (m, 12H), 1.24 (t, *J* = 7.3 Hz, 9H), 0.92 (t, *J* = 7.0 Hz, 9H). ^{13}C-NMR (75 MHz, CD_2Cl_2): δ 157.5, 157.1, 148.3, 145.3, 139.6, 139.42, 139.35, 137.0, 135.4, 133.1, 132.5, 131.2, 130.8, 130.0, 129.8, 129.1, 128.9, 128.7, 128.1, 127.0, 120.0, 119.3, 61.6, 55.7, 41.0, 35.5, 32.0, 31.9, 23.0, 22.5, 16.3, 14.3. ESI-HRMS *m*/*z* 1624.9028 $[M+H]^+$ (calcd. for $C_{114}H_{118}O_6N_3$ $[M+H]^+$ 1624.9015)



Compound E. a mixture of 4, 4'-oxybis(bromobenzene) (2.0 g, 6 mmol), (4-formylphenyl) boronic acid (640 mg, 4.3 mmol), $Pd(PPh_3)_4$ (352 mg, 0.3 mmol) and K_2CO_3 (841 mg, 6mmol) in THF (50 mL)-water (20 mL) was refluxed for 24h. The resulted mixture was concentrated and then purified by column chromatography (silica gel, petroleum ether / DCM = 1:1) to afford compound E (860 mg, 57%) as white solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 10.06 (s, 1H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 8.9 Hz, 2H), 7.10 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 192.0, 157.6, 156.1, 146.5, 135.23, 135.16, 133.0, 130.5, 129.0, 127.5, 121.0, 119.3, 116.4. EI-HRMS *m*/*z* 352.0087 (calcd. for $C_{19}H_{13}O_2Br$ 352.0093)

Compound F. a mixture of compound E (850 mg, 2.4 mmol), bis(pinacolato)-diboron (673 mg, 2.65 mmol), $Pd_2(dba)_3$ (33 mg, 0.04 mmol), Cy_3P (24 mg, 0.08 mmol), KOAc (354 mg, 3.6 mmol) in dioxane (15 mL) was stirred at 80 °C for 24h. The resulted mixture was diluted with water (100 mL) and extracted with AcOEt (30

mL x 2). The AcOEt solution was washed with water, dried over Na_2SO_4 and evaporated. The residue was purified with column chromatography (silica gel, petroleum ether / AcOEt = 5:1) to afford compound F (672 mg, 70%) as yellow solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 10.05 (s, 1H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 7.05 (d, *J* = 8.6 Hz, 2H), 1.35 (s, 12H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 192.0, 159.7, 157.5, 146.6, 136.9, 135.1, 135.0, 130.5, 128.9, 127.5, 119.7, 118.3, 84.0, 25.0. ESI-HRMS *m*/*z* 401.1937 $[M+H]^+$ (calcd. for $C_{25}H_{26}O_4B$ $[M+H]^+$ 401.1919)

X-ray Crystal Data for Cage Ec1

Chemical formula	$C_{117}H_{123}N_3O_6 \cdot 3(CH_2Cl_2) \cdot 2(CH_3OH)$
M_r	1986.04
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	150
a, b, c (Å)	17.7964 (3), 20.6944 (5), 21.5845 (4)
α, β, γ (°)	109.368 (2), 106.354 (2), 104.440 (2)
V (Å^3)	6660.2 (3)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	1.55
Crystal size (mm)	0.80 × 0.60 × 0.45
Diffractometer	SuperNova, Dual, Cu at zero, AtlasS2
Absorption correction	Multi-scan *CrysAlis PRO* 1.171.38.43 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.726, 0.786
No. of measured, independent and observed [$I > 2s(I)$] reflections	44200, 22112, 18569
R_{int}	0.035
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.583
$R[F^2 > 2s(F^2)]$, $wR(F^2)$, S	0.076, 0.241, 1.05
No. of reflections	22112
No. of parameters	1325
No. of restraints	1152
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.15, -1.41

A clear, colorless needle-like specimen of cage **Ec1** was obtained from MeOH/CH_2Cl_2. Crystal data were obtained on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer employing graphite monochromated Cu $K\alpha$ radiation (λ = 1.54184 Å) at 150(10) K and operating in the muti-scan mode. The structure was solved by direct methods using Olex2[S10] and refined with full-matrix least-squares calculations on F^2 using SHELXL-14[S11]. Owing to the cavity structure of cage **Ec1**,

there were heavily disordered solvent molecules (MeOH and CH_2Cl_2) that could not be identified from different Fourier map. Accordingly, the SQUEEZE routine of PLATON[S12] was applied to remove the contributions to the scattering from the solvents. All non-hydrogen atoms were refined anisotropically. The hydrogen atom positions were geometrically idealized and allowed to ride on their parent atoms. Crystallographic data for cage **Ec1** have been deposited at the Cambridge Crystallographic Data Centre (deposition no. CCDC 1527258). Copies of these data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html

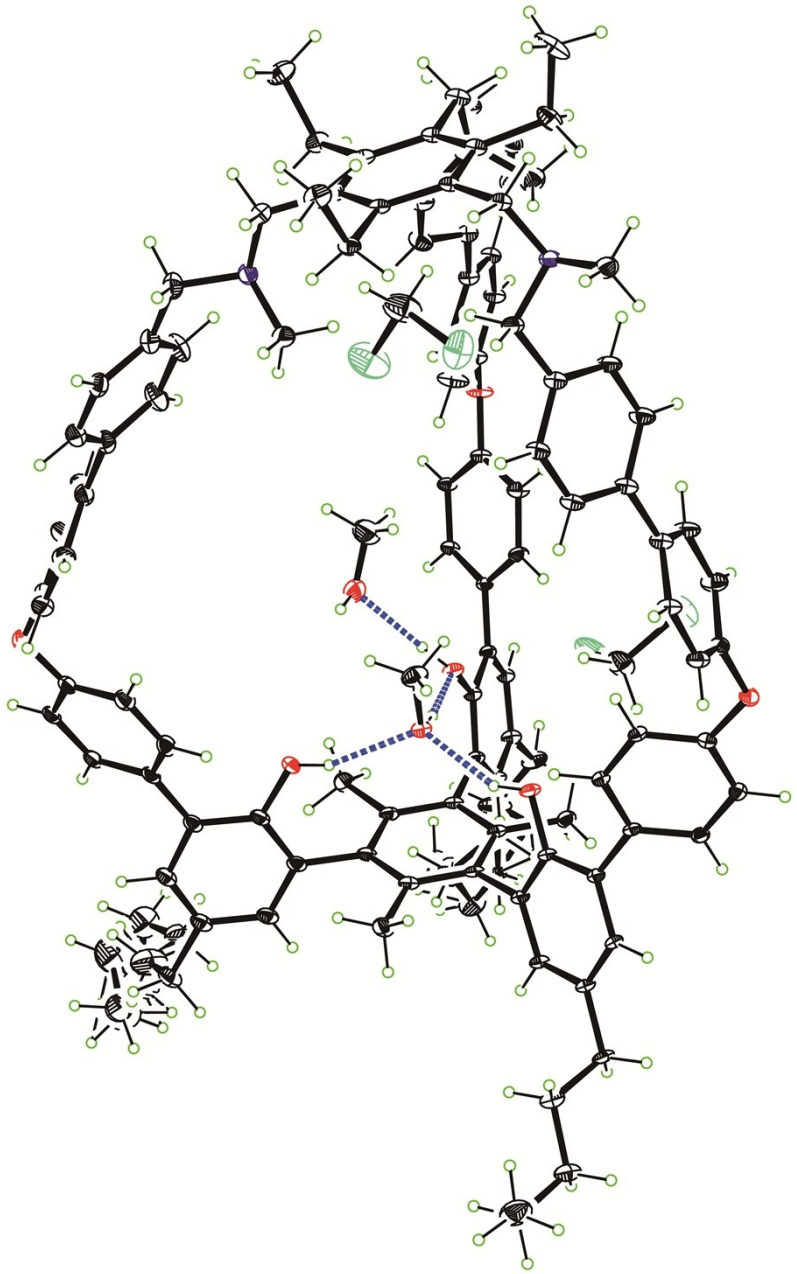
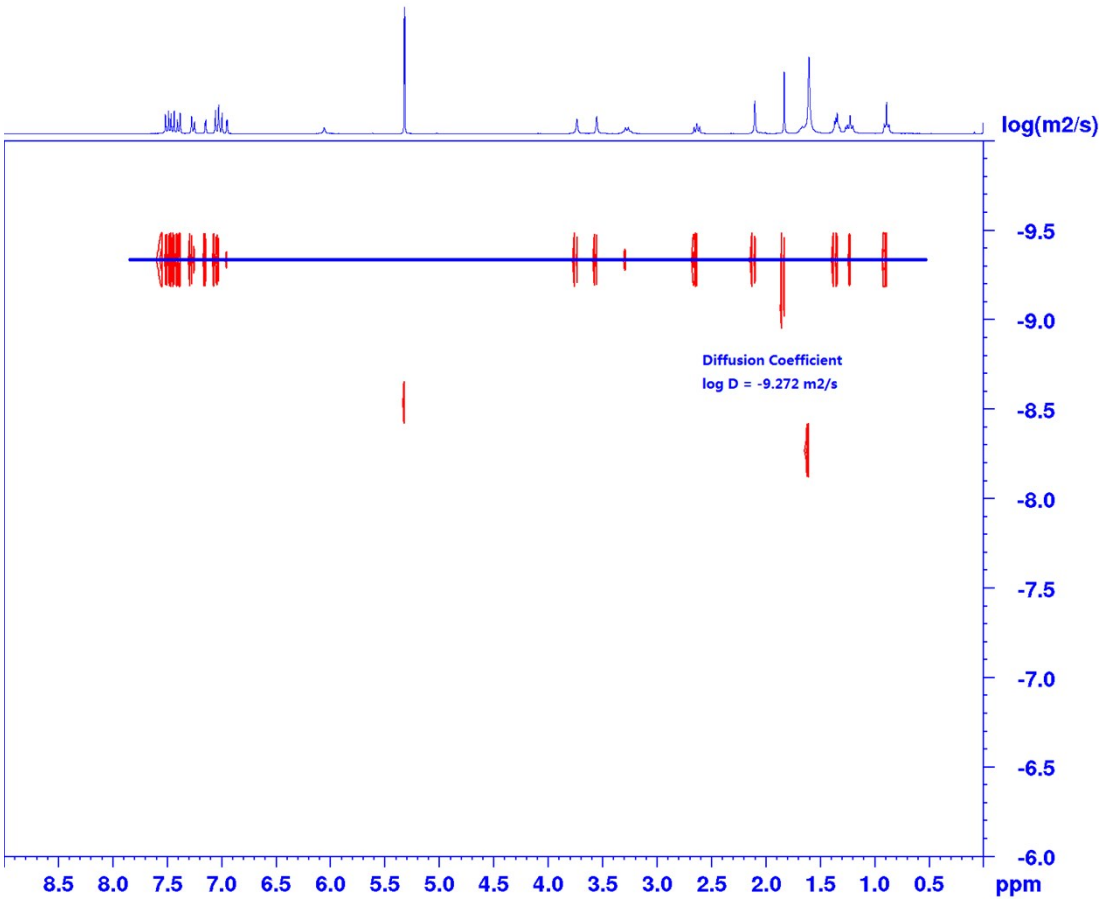


Figure S1. X-ray Crystal Structure of cage **Ec1**

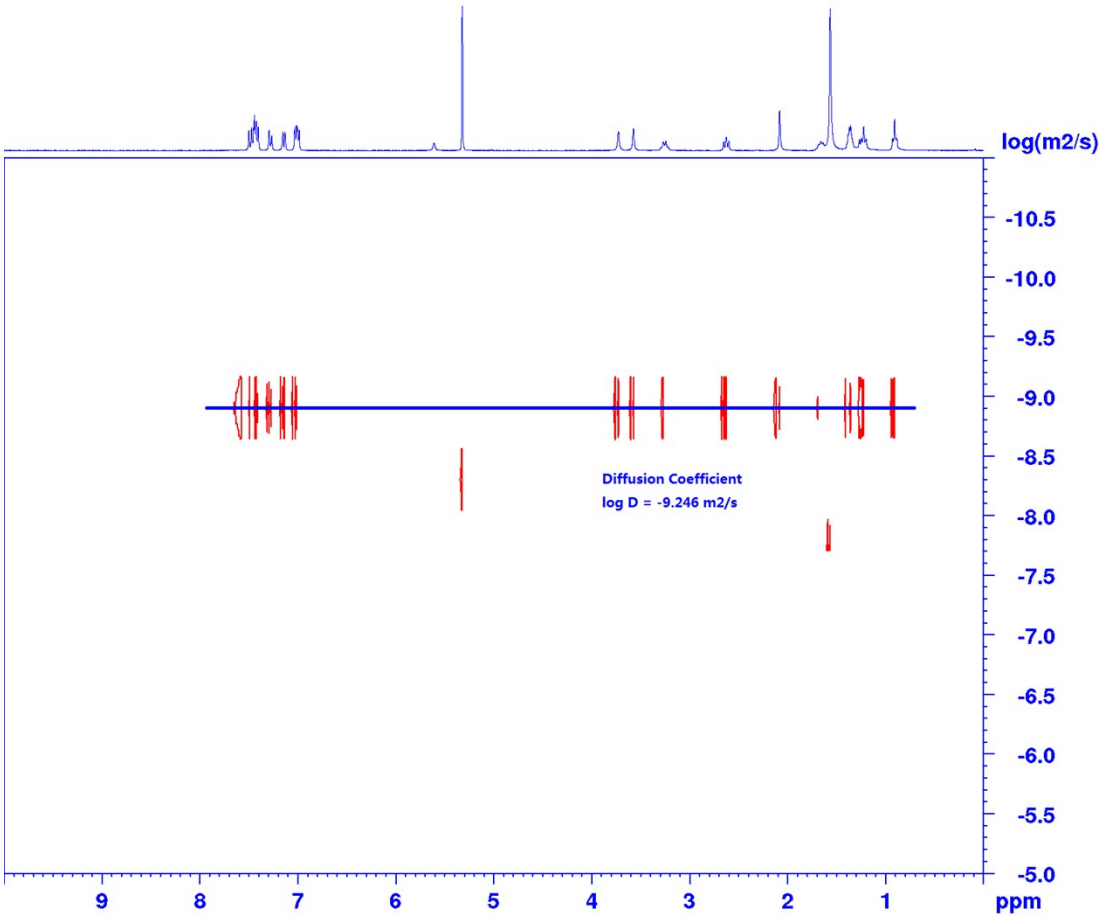
^{1}H-DOSY spectrum of Cage Ec1 in CD_2Cl_2 at 298K

According to Stokes-Einstein equation: D=KT/6πηr, the calculated molecular diameter of Cage Ec1 was 9.5 Å. (D: diffusion coefficient; K: the Boltzmann constant; T: absolute temperature; η: the fluid viscosity; r: hydrodynamic radius.)



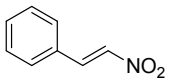
^{1}H-DOSY spectrum of Cage Ec2 in CD_2Cl_2 at 298K

According to Stokes-Einstein equation : D=KT/6πηr, the calculated molecular diameter of Cage Ec2 was 8.9 Å. (D: diffusion coefficient; K: the Boltzmann constant; T: absolute temperature; η: the fluid viscosity; r: hydrodynamic radius.)

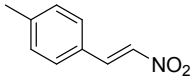


Synthesis of nitroalkene substrate

Different aldehyde (10 mmol) and nitromethane (30 mL) was introduced into a flask with a catalytic amount of ammonium acetate (3 mmol). The mixture was stirred at 100 °C for 5 h. The reaction system was cooled and quenched with water (200 mL), then extracted by ethyl acetate (50 mL × 3). The combined extraction was washed by brine, dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography (silica gel, petroleum ether / DCM = 2:1) to give desired product.

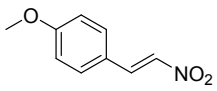


(E)-(2-nitrovinyl)benzene (1a) was purchased from commercial sources and used without further purification.



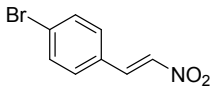
(E)-1-methyl-4-(2-nitrovinyl)benzene (1b) [S3]

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.99 (d, *J* = 13.7 Hz, 1H), 7.57 (d, *J* = 13.6 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 2.41 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 143.1, 139.2, 136.3, 130.2, 129.2, 127.3, 21.7.



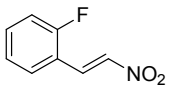
(E)-1-methoxy-4-(2-nitrovinyl)benzene (1c) [S3]

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.98 (d, *J* = 13.6 Hz, 1H), 7.56 – 7.46 (m, 3H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 163.1, 139.1, 135.1, 131.3, 122.6, 115.0, 55.6.



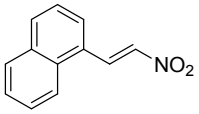
(E)-1-bromo-4-(2-nitrovinyl)benzene (1d) [S3]

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.95 (d, *J* = 13.7 Hz, 1H), 7.64 – 7.52 (m, 3H), 7.42 (d, *J* = 8.4 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 137.9, 137.6, 132.9, 130.5, 129.1, 126.9.



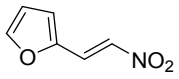
(E)-1-fluoro-2-(2-nitrovinyl)benzene (1e) [S3]

^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.05 (d, *J* = 13.8 Hz, 1H), 7.73 (d, *J* = 13.8 Hz, 1H), 7.58 – 7.41 (m, 2H), 7.29 – 7.11 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 163.6, 160.2, 139.4, 139.3, 133.8, 133.7, 132.5, 131.44, 131.40, 125.2, 125.1, 118.5, 118.4, 116.8, 116.5. ^{19}F-NMR (282 MHz, $CDCl_3$): δ -109.21 .



(E)-1-(2-nitrovinyl)naphthalene (1f) [S4]

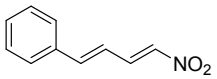
^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.84 (d, *J* = 13.4 Hz, 1H), 8.13 (d, *J* = 8.3 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 8.3 Hz, 1H), 7.75 (d, *J* = 7.2 Hz, 1H), 7.71 – 7.46 (m, 5H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 138.6, 136.2, 133.9, 132.7, 131.7, 129.2, 127.8, 127.1, 126.9, 126.5, 125.5, 123.1.



(E)-2-(2-nitrovinyl)furan (1g) [S5]

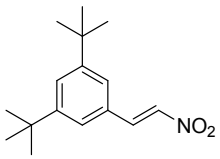
^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.77 (d, *J* = 13.2 Hz, 1H), 7.59 (d, *J* = 1.9 Hz, 1H), 7.51 (d, *J* = 13.2 Hz, 1H), 6.89 (d, *J* = 3.5 Hz, 1H), 6.57 (dd, *J* = 3.6, 1.9 Hz, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ 147.0, 146.7, 135.0, 125.5, 120.1, 113.5.



((1E,3E)-4-nitrobuta-1,3-dien-1-yl)benzene (1h) [S3]

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.78 (dd, *J* = 13.0, 11.5 Hz, 1H), 7.56 – 7.47 (m, 2H), 7.44 – 7.37 (m, 3H), 7.24 (d, *J* = 12.3 Hz, 1H), 7.16 (d, *J* = 15.6 Hz, 1H), 6.87 (dd, *J* = 15.5, 11.5 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 146.1, 139.3, 138.7, 135.2, 130.4, 129.1, 127.8, 120.7.

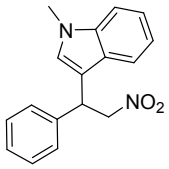


(E)-1,3-di-tert-butyl-5-(2-nitrovinyl)benzene (1i)

^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.04 (d, *J* = 13.6 Hz, 1H), 7.68 – 7.54 (m, 2H), 7.37 (d, *J* = 1.6 Hz, 2H), 1.35 (s, 18H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 152.2, 140.4, 136.7, 129.6, 126.9, 123.6, 35.0, 31.4. EI-HRMS *m*/*z* 261.1720 (calcd. for $C_{16}H_{23}O_2N$ 261.1723)

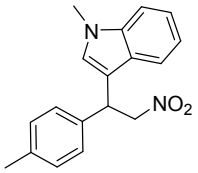
Typical experimental procedure for catalysis

To a solution of nitroalkene substrates (0.15 mmol) and N-methylindole (0.45 mmol) in 0.3 mL dry CH_2Cl_2, Cage (0.015mmol) was added. The reaction mixture was remained at room temperature and stirred for 168h. The solution was directly purified by short column chromatography as soon as possible (silica gel, petroleum ether / dichloromethane = 2:1 to 1:1) to obtain the products.



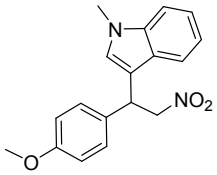
1-Methyl-3-(2-nitro-1-phenylethyl)-1H-indole (3a) [S6]

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.0 Hz, 1H), 7.40 – 7.27 (m, 6H), 7.23 (s, 1H), 7.11 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 6.89 (s, 1H), 5.22 (t, *J* = 8.0 Hz, 1H), 5.07 (dd, *J* = 12.5, 7.5 Hz, 1H), 4.95 (dd, *J* = 12.5, 8.5 Hz, 1H), 3.75 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 139.5, 137.4, 129.0, 127.8, 127.6, 126.6, 126.5, 122.3, 119.6, 119.1, 112.9, 109.6, 79.6, 41.6, 32.9.



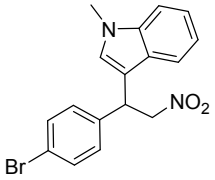
1-Methyl-3-(2-nitro-1-(p-tolyl)ethyl)-1H-indole (3b) [S7]

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.9 Hz, 1H), 7.27 (dd, *J* = 21.2, 5.6 Hz, 4H), 7.18 – 7.05 (m, 3H), 6.87 (s, 1H), 5.16 (t, *J* = 8.0 Hz, 1H), 5.05 (dd, *J* = 12.3, 7.4 Hz, 1H), 4.92 (dd, *J* = 12.3, 8.6 Hz, 1H), 3.75 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 137.4, 137.2, 136.4, 129.7, 127.7, 126.7, 126.4, 122.3, 119.5, 119.1, 113.1, 109.6, 79.8, 41.3, 32.9, 21.2.



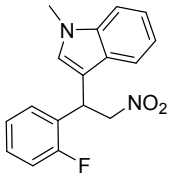
3-(1-(4-methoxyphenyl)-2-nitroethyl)-1-methyl-1H-indole (3c) [S6]

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.0 Hz, 1H), 7.34 – 7.20 (m, 4H), 7.09 (t, *J* = 7.0 Hz, 1H), 6.90 – 6.83 (m, 3H), 5.15 (t, *J* = 8.0 Hz, 1H), 5.04 (dd, *J* = 12.2, 7.3 Hz, 1H), 4.90 (dd, *J* = 12.2, 8.6 Hz, 1H), 3.78 (s, 3H), 3.75 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 159.0, 137.4, 131.5, 128.9, 126.6, 126.4, 122.3, 119.5, 119.1, 114.4, 113.2, 109.6, 79.9, 55.3, 40.9, 32.9.



3-(1-(4-bromophenyl)-2-nitroethyl)-1-methyl-1H-indole (3d) [S7]

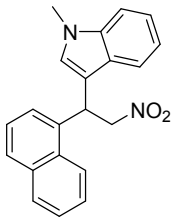
^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.52 – 7.40 (m, 3H), 7.37 – 7.21 (m, 4H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.88 (s, 1H), 5.23 – 5.12 (m, 1H), 5.06 (dd, *J* = 12.5, 7.2 Hz, 1H), 4.92 (dd, *J* = 12.4, 8.7 Hz, 1H), 3.78 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 138.6, 137.4, 132.14, 129.6, 126.43, 126.40, 122.5, 121.6, 119.7, 118.9, 112.3, 109.7, 79.31, 41.1, 33.0.



3-(1-(2-fluorophenyl)-2-nitroethyl)-1-methyl-1H-indole (3e) [S7]

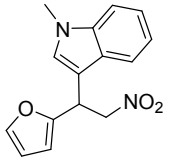
^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.0 Hz, 1H), 7.34 – 7.22 (m, 4H), 7.16 – 7.05 (m, 3H), 6.96 (s, 1H), 5.49 (t, *J* = 8.0 Hz, 1H), 5.12 – 4.99 (m, 2H), 3.75 (s, 3H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ 162.4, 159.1, 137.3, 129.6, 129.5, 129.4, 129.3, 126.7, 126.68, 126.6, 126.6, 126.4, 124.7, 124.6, 122.4, 119.7, 118.8, 116.3, 116.0, 111.4, 109.7, 78.15, 78.11, 35.6, 35.6, 33.0. ^{19}F-NMR (282 MHz, $CDCl_3$): δ -116.97.



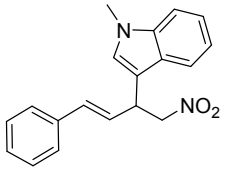
1-Methyl-3-(1-(naphthalen-1-yl)-2-nitroethyl)-1H-indole (3f) [S8]

^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.27 (d, *J* = 9.1 Hz, 1H), 7.93 – 7.86 (m, 1H), 7.80 (dd, *J* = 6.5, 2.8 Hz, 1H), 7.60 – 7.37 (m, 5H), 7.35 – 7.18 (m, 2H), 7.07 (t, *J* = 6.8 Hz, 1H), 7.07 (t, *J* = 6.8 Hz, 1H), 6.84 (s, 1H), 6.08 (t, *J* = 7.8 Hz, 1H), 5.11 (dd, *J* = 7.8, 1.2 Hz, 2H), 3.72 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 137.5, 134.9, 134.3, 131.3, 129.2, 128.4, 127.4, 126.9, 126.7, 126.0, 125.4, 124.6, 122.9, 122.3, 119.6, 119.0, 112.7, 109.7, 78.7, 37.0, 32.9.



3-(1-(furan-2-yl)-2-nitroethyl)-1-methyl-1H-indole (3g) [S6]

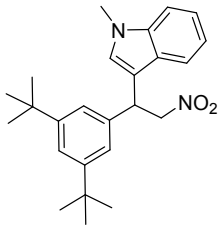
^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.9 Hz, 1H), 7.40 (d, *J* = 0.9 Hz, 1H), 7.37 – 7.22 (m, 2H), 7.19 – 7.09 (m, 1H), 6.99 (s, 1H), 6.32 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.18 (d, *J* = 3.2 Hz, 1H), 5.25 (t, *J* = 7.7 Hz, 1H), 5.05 (dd, *J* = 12.5, 8.1 Hz, 1H), 4.91 (dd, *J* = 12.5, 7.4 Hz, 1H), 3.76 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 152.5, 142.3, 137.2, 127.4, 126.3, 122.3, 119.7, 118.9, 110.6, 110.0, 109.8, 107.4, 78.1, 35.8, 32.9.



(E)-1-methyl-3-(1-nitro-4-phenylbut-3-en-2-yl)-1H-indole (3h) [S9]

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.0 Hz, 1H), 7.40 – 7.27 (m, 5H), 7.25 – 7.20 (m, 1H), 7.20 – 7.12 (m, 1H), 6.97 (s, 1H), 6.62 (d, *J* = 15.9 Hz, 1H), 6.43 (dd, *J* = 15.8, 7.2 Hz, 1H), 4.91 – 4.64 (m, 3H), 3.77 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ

137.4, 136.6, 132.5, 128.7, 127.9, 127.2, 126.6, 126.5, 126.4, 122.3, 119.6, 119.0, 111.5, 109.8, 79.5, 39.5, 32.9.



3-(1-(3,5-di-tert-butylphenyl)-2-nitroethyl)-1-methyl-1H-indole (3i)

^{1}H-NMR (300 MHz, CD_3CN): δ 7.60 (d, *J* = 8.0 Hz, 1H), 7.37 – 7.29 (m, 4H), 7.23 – 7.15 (m, 1H), 7.13 (s, 1H), 7.08 – 7.01 (m, 1H), 5.20 – 5.09 (m, 3H), 3.74 (s, 3H), 1.28 (s, 18H). ^{13}C-NMR (75 MHz, CD_3CN): δ 152.1, 140.6, 138.1, 127.6, 127.5, 123.1, 122.8, 122.1, 120.0, 119.7, 114.3, 110.7, 80.3, 42.7, 35.6, 33.2, 31.7. ESI-HRMS *m*/*z* 393.2547 $[M+H]^+$ (calcd. for $C_{25}H_{33}O_2N_2$ $[M+H]^+$ 393.2542)

Host-guest recognition experiments

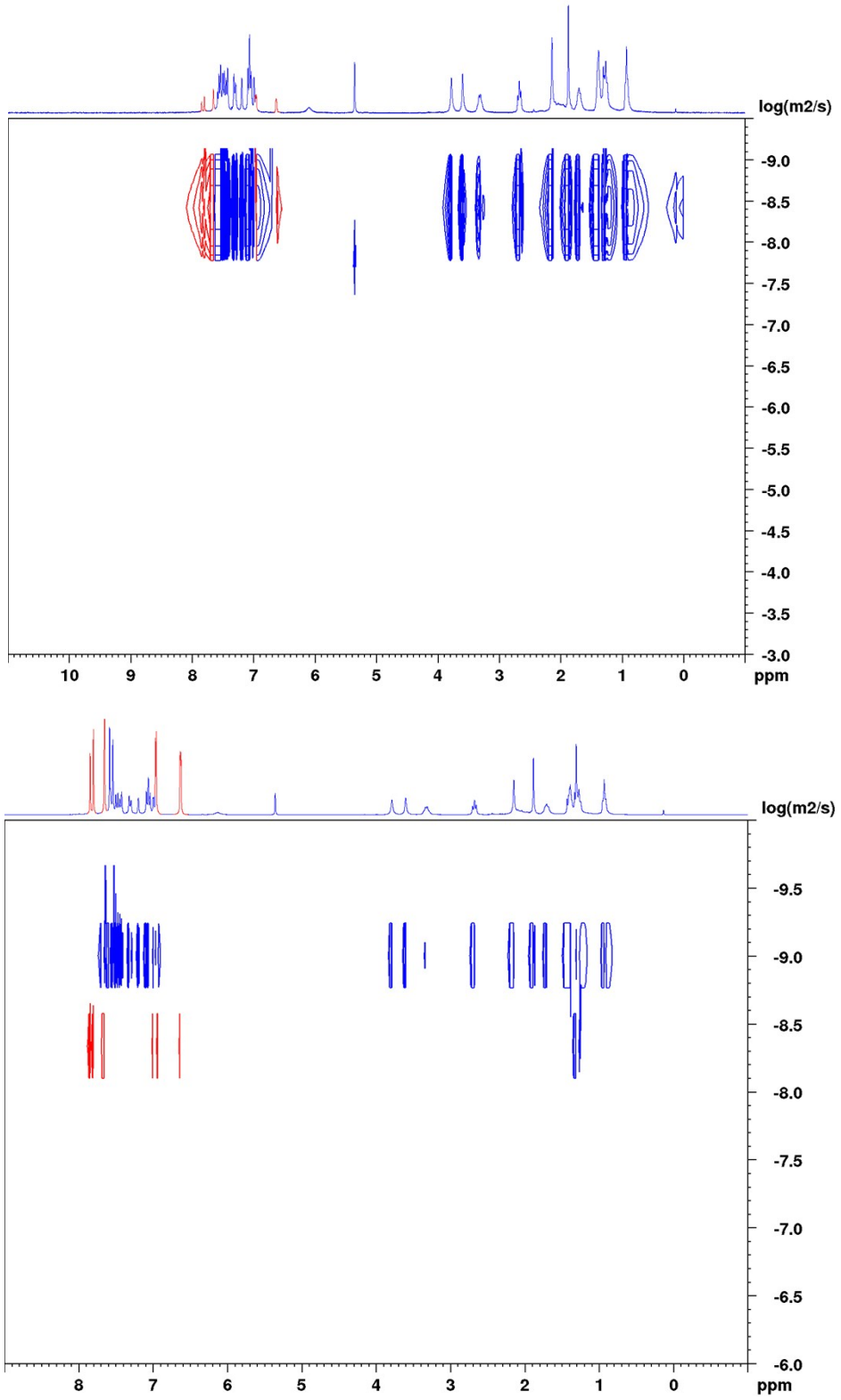


Figure S2. ^{1}H-DOSY spectra (300M, CD_2Cl_2) of Cage **Ec1** (blue, 1eq) with compound **1g** (red, 0.94eq top and 16 eq bottom) at 296K, which indicated **1g** was encapsulated by Cage **Ec1**.

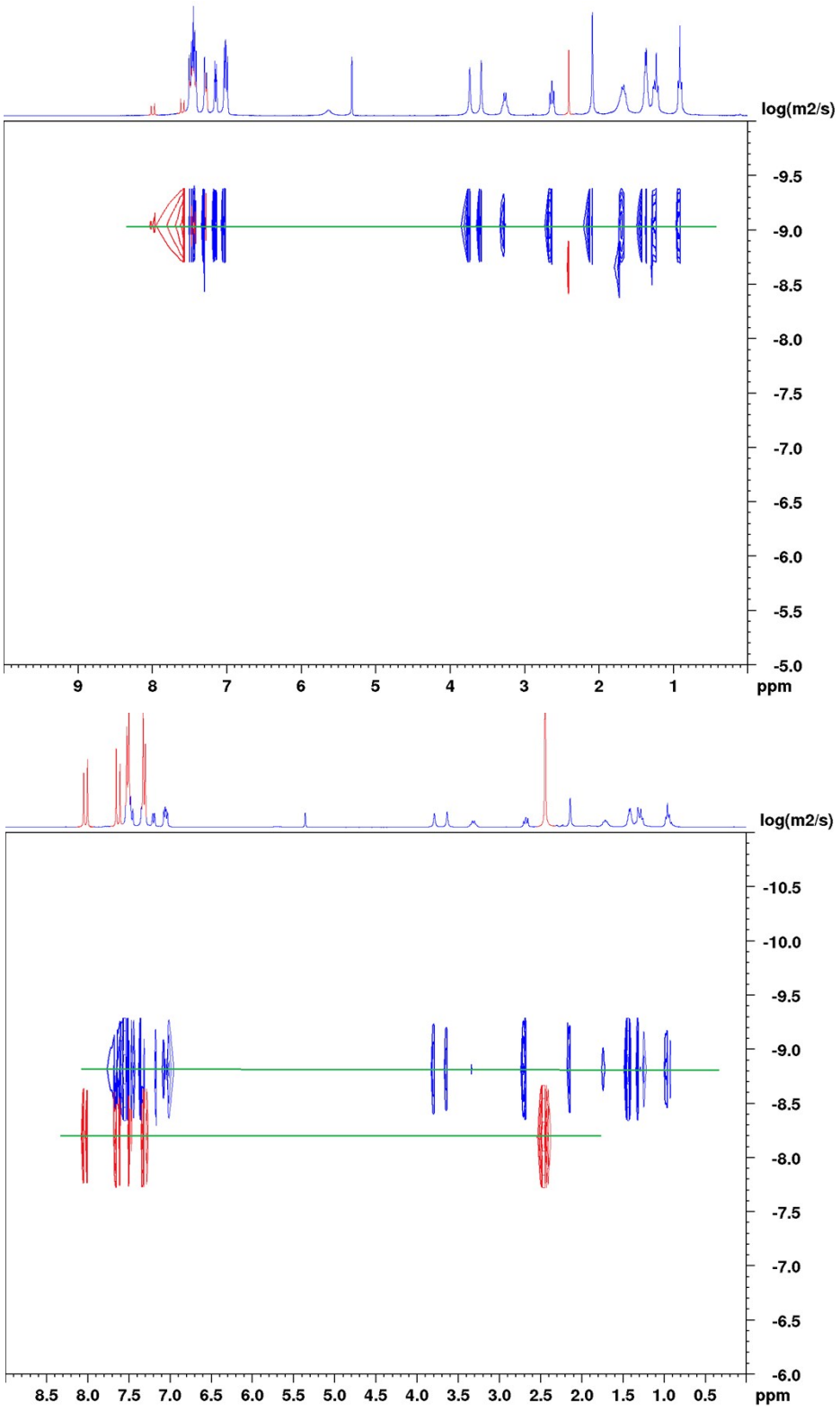


Figure S3. ^{1}H-DOSY spectra (300M, CD_2Cl_2) of Cage **Ec2** (blue, 1eq) with compound **1b** (red, 0.94eq top and 15 eq bottom) at 296K, which indicated **1b** was encapsulated by Cage **Ec2**.

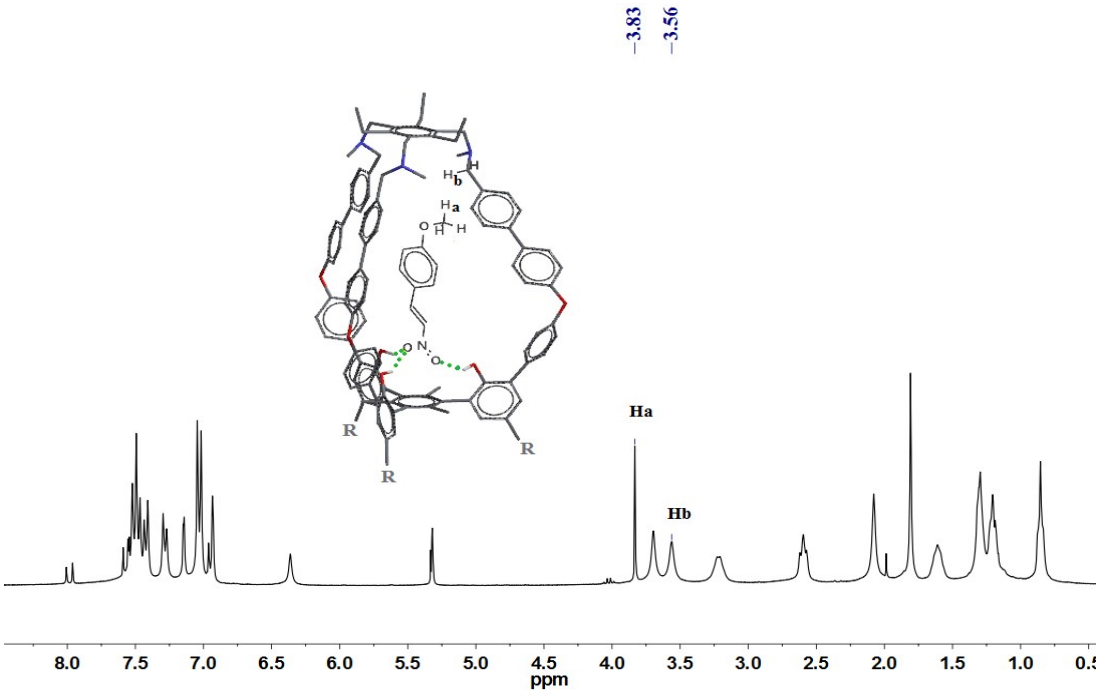


Figure S4. ^{1}H-NMR spectrum (300M, CD_2Cl_2) of [cage **Ec1** (1 eq) ⊃ **1c** (0.7 eq)] at 253K (R = 1-pentyl group)

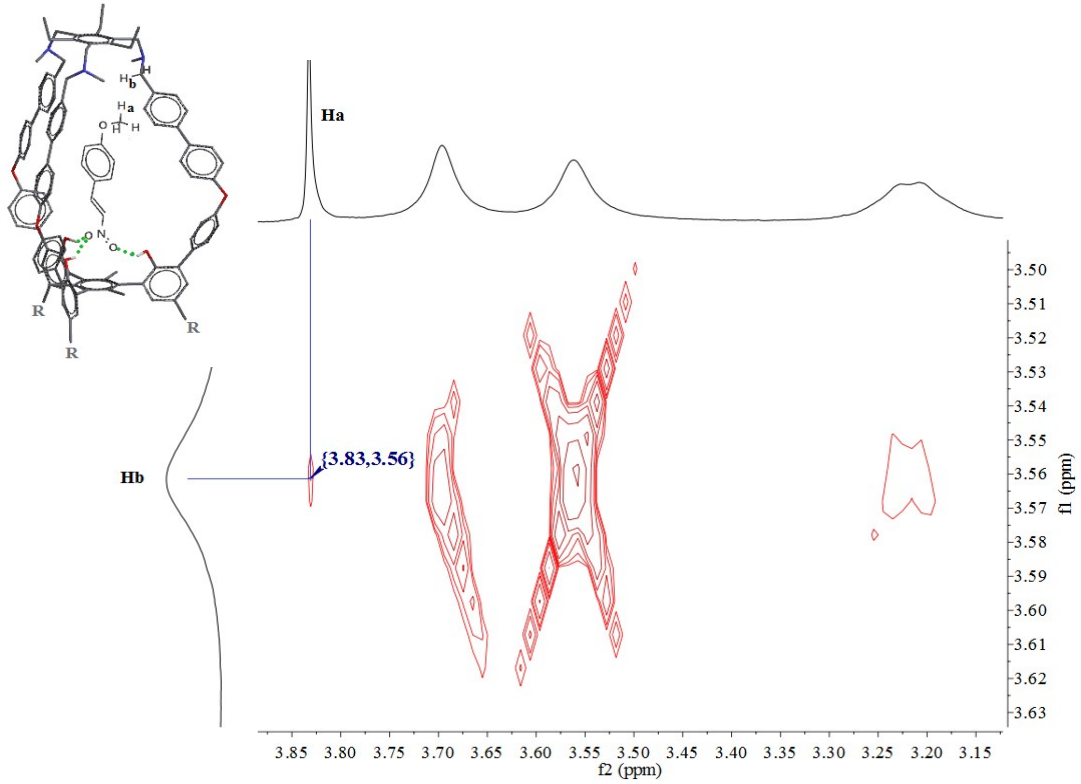


Figure S5. Expanded NOESY spectrum (300M, CD_2Cl_2) of [cage **Ec1** (1 eq) ⊃ **1c** (0.7 eq)] at 253K, which indicated **1c** was encapsulated by cage **Ec1** (R = 1-pentyl group). The spectrum was processed using MestReNova software package.

Reusability studies of Cage Ec1 for the synthesis of Compound 3a

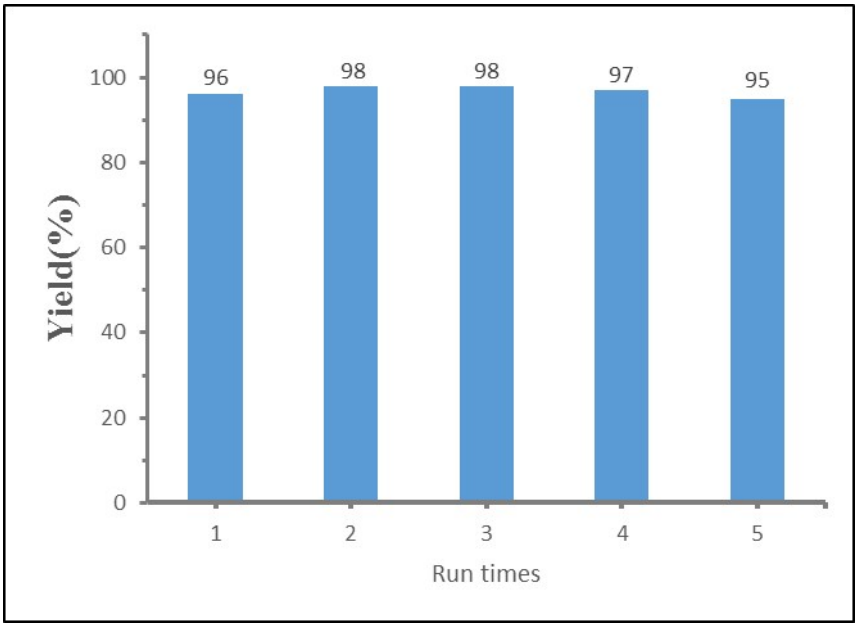


Figure S6. The recyclable results of Cage **Ec1** catalyzed Friedel-Crafts alkylation for 1-methylindole. The reaction were carried out with 1-methylindole (0.45 mmol), **1a** (0.15 mmol), Cage **Ec1** (10 mol%), dry dichloromethane (0.3 mL) for 168 h.

^{1}H-NMR spectra of fresh catalyst Cage Ec1 and reused catalyst

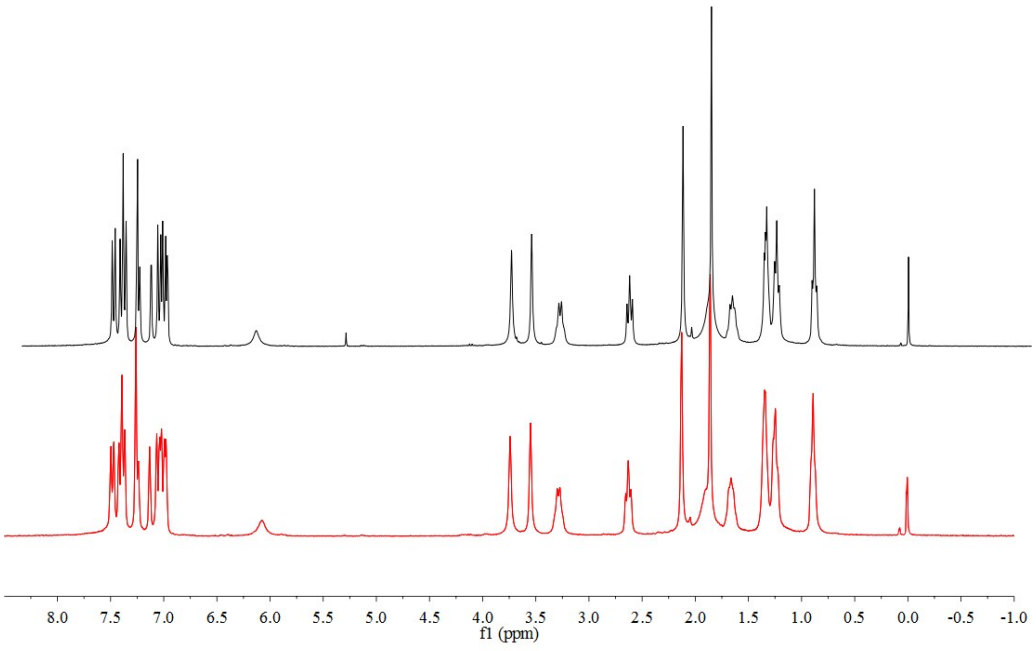


Figure S7. ^{1}H NMR spectra of fresh Cage **Ec1** (**black**) and reused Cage **Ec1** (red) in $CDCl_3$

Typical experimental procedure for situ catalysis in NMR tube

Freshly distilled N-methylindole (1.5 mmol) and β-nitrostyrene (0.5 mmol) were dissolved in 1 ml of dichloromethane-d2 and 0.3 ml portions of the solution were separately added to Cage **Ec1** and Cage **Ec2** (10 mol%) in NMR tubes. Then these tubes were sealed and monitored by ^{1}H-NMR at 23 ± 1 °C (i.e., ambient temperature) at intervals throughout the reaction time. The crude yield of product was caculated by integrating the product signals at δ 3.74 (s, 3 H) and 4.98 (dd, 1 H) and the methenyl group of the starting material at δ 8.09 (d, 1H).

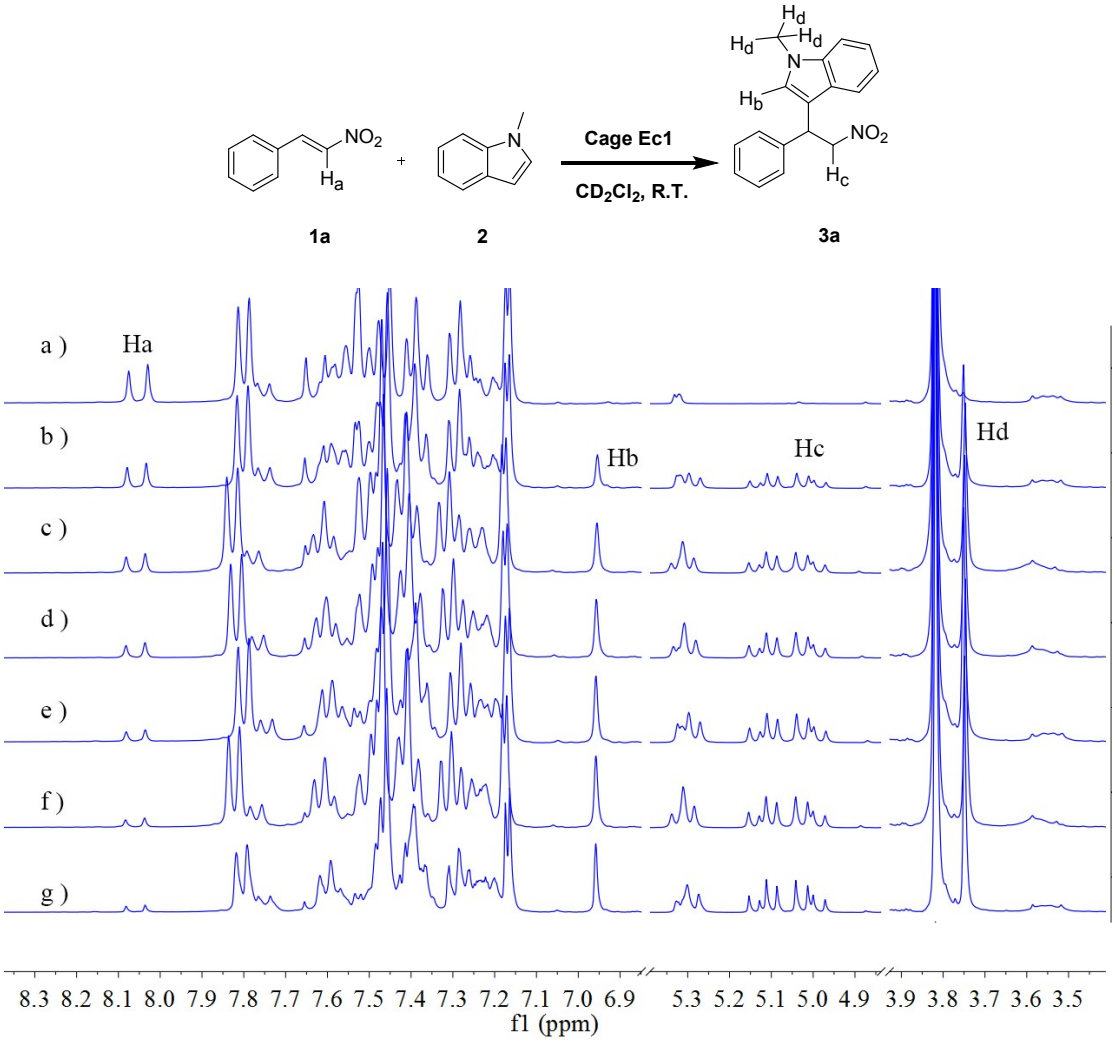


Figure S8. ^{1}H NMR spectra of Friedel-Crafts alkylation for compound **1a** (0.15 mmol) and 1-methylindole (0.45 mmol), Cage **Ec1** (10 mol%) in CD_2Cl_2 (0.3 mL) at time intervals a) 0.25h, b) 48 h, c) 72 h, d) 96h, e) 120h, f) 144h, h) 168h showing the buildup of product, and illustrating the lack of product inhibition.

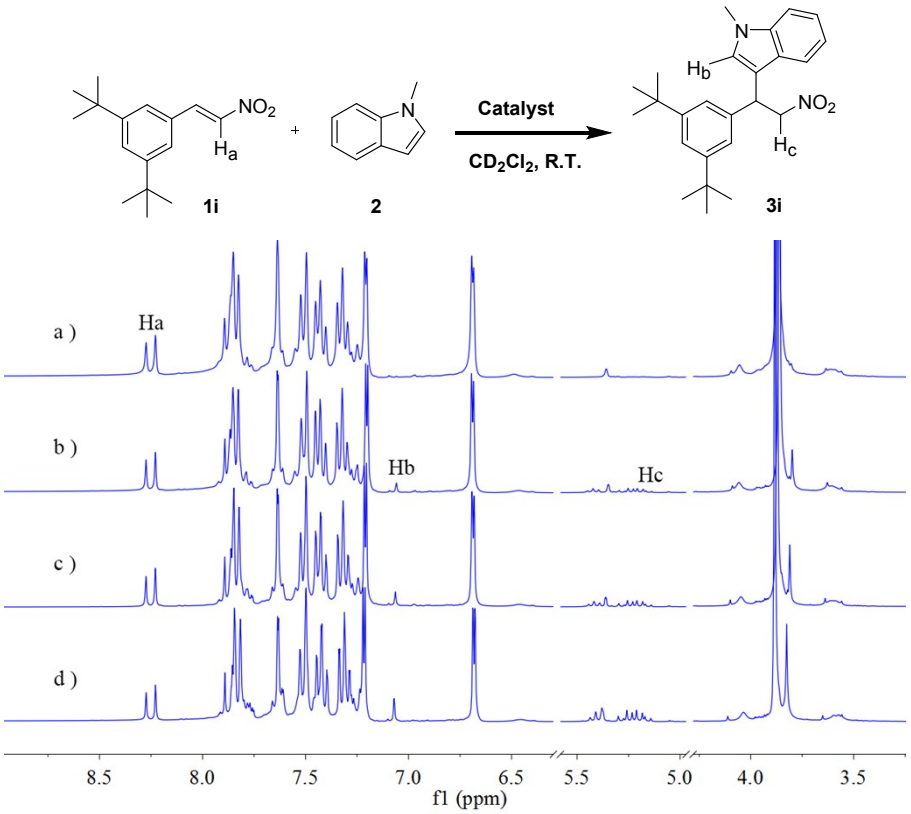


Figure S9. [1]H NMR spectra of Friedel-Crafts alkylation for steric bulk substrate compound **1i** (0.15 mmol) and 1-methylindole (0.45 mmol), Cage **Ec1** (10 mol%) in CD_2Cl_2 (0.3 mL) at time intervals a) 0.5h, b) 96 h, c) 144 h, d) 216h showing the buildup of product, and illustrating the size selectivity of Cage **Ec1**.

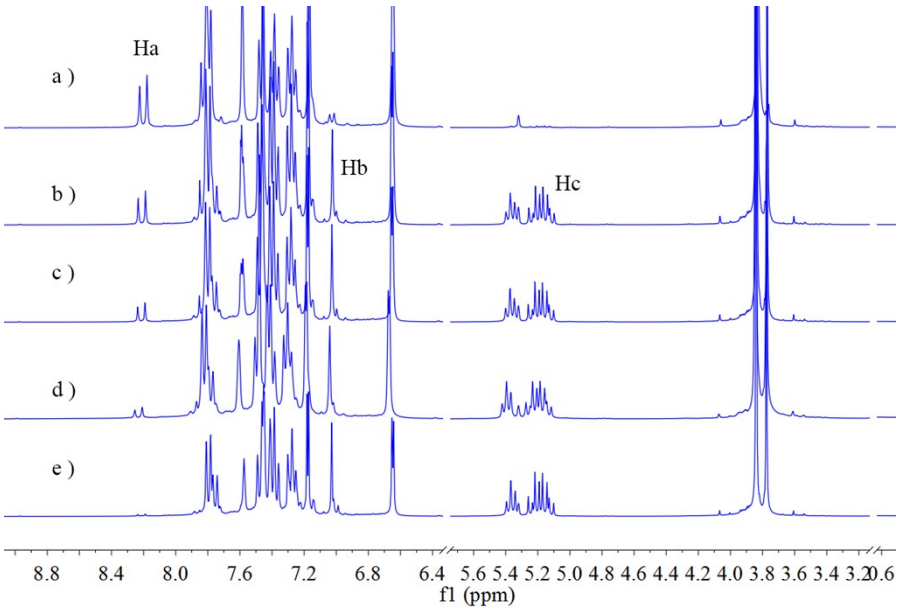


Figure S10. [1]H NMR spectra of Friedel-Crafts alkylation for steric bulk substrate compound **1i** (0.15 mmol) and 1-methylindole (0.45 mmol), the model catalyst **r1** (10 mol%) in CD_2Cl_2 (0.3 mL) at time intervals a) 0.5h, b) 41 h, c) 65 h, d) 95h, e) 142h showing the buildup of product, and further illustrating the size selectivity of Cage **Ec1**.

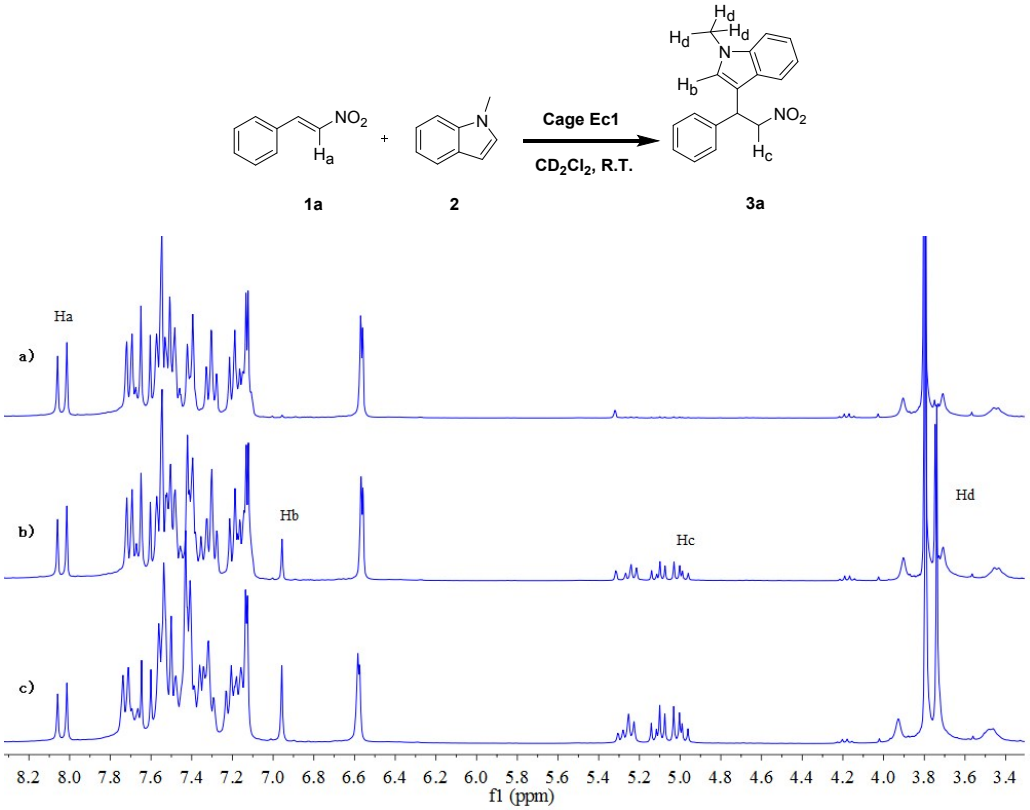


Figure S11. ^{1}H NMR spectra of Friedel-Crafts alkylation for compound **1a** (0.15 mmol) and 1-methylindole (0.23 mmol), Cage **Ec1** (10 mol%) in CD_2Cl_2 (0.3 mL) at R.T. and monitored at time intervals a) 0.25h, b) 71 h, c) 168h showing the buildup of product, and probably indicating the competitively inhibition of nitrostyrene (**1a**) to Cage **Ec1**.

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NMR spectra of catalysts

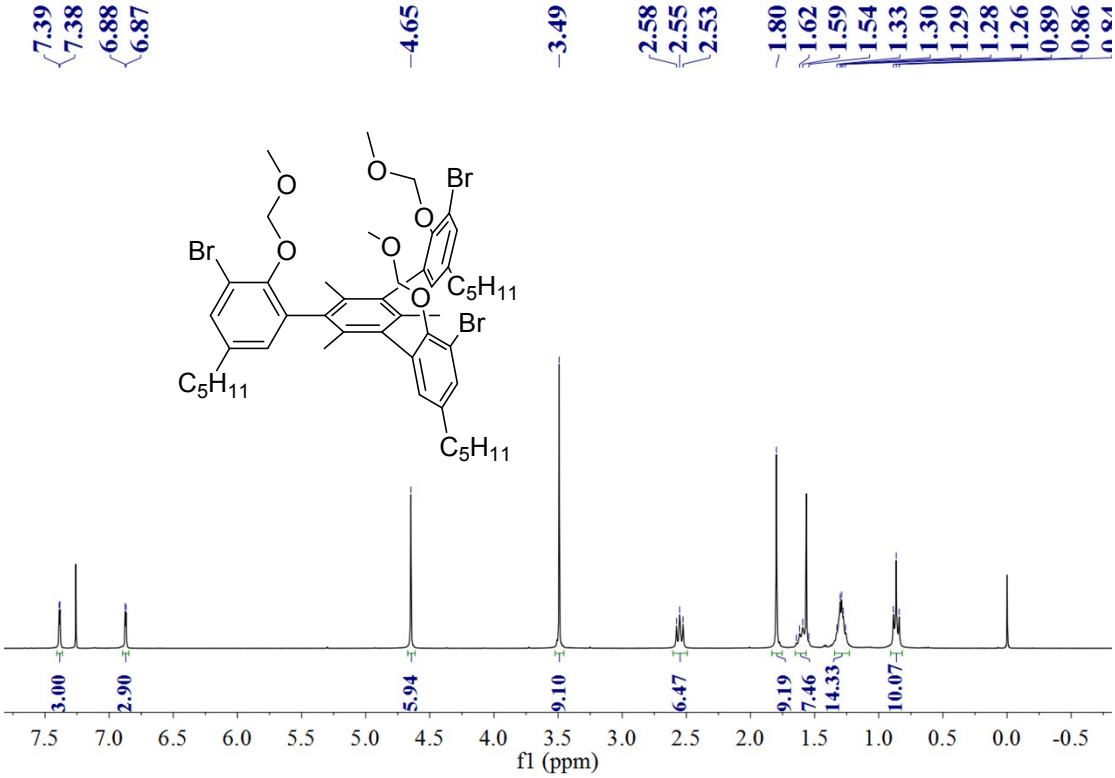

Figure S12. ^{1}H-spectrum of Compound B1 in $CDCl_3$

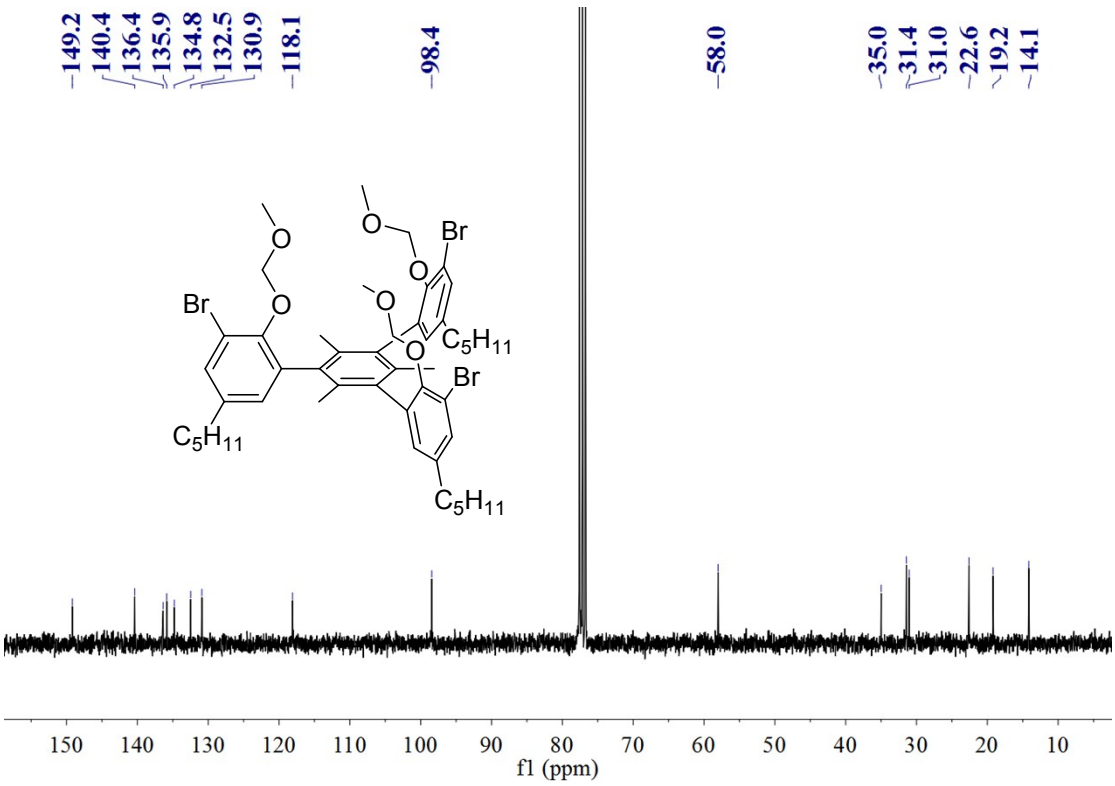

Figure S13. ^{13}C-spectrum of Compound B1 in $CDCl_3$

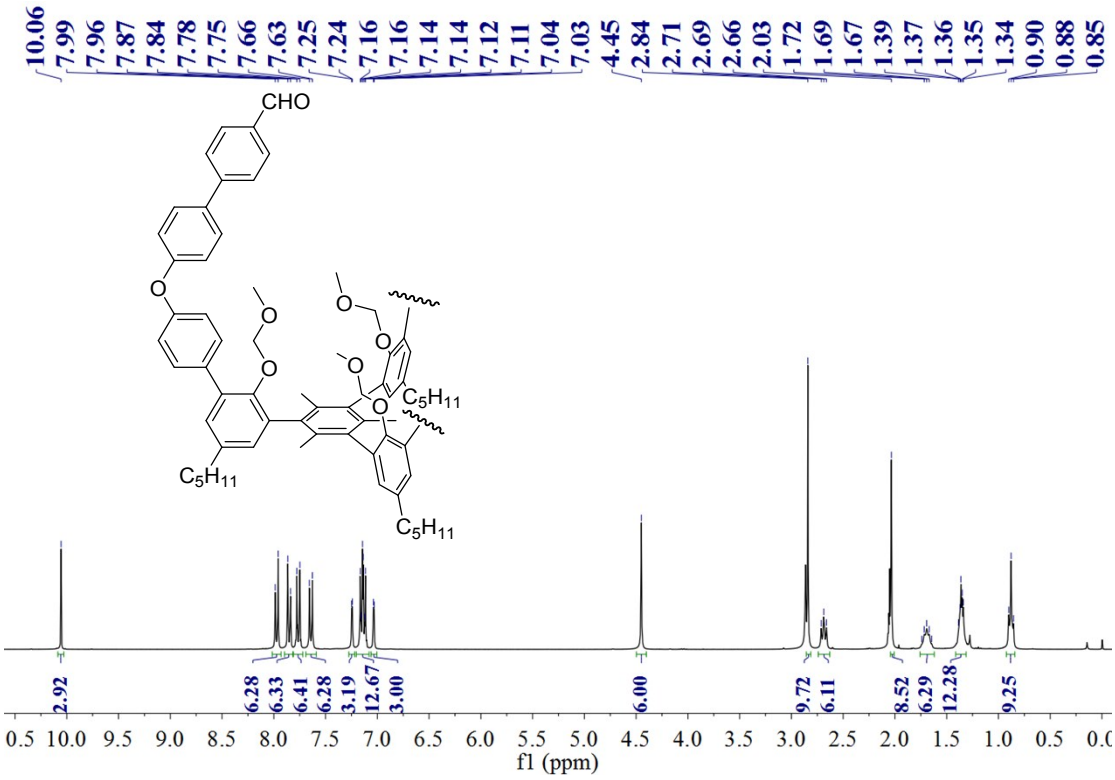

Figure S14. [1]H-spectrum of Compound C1 in acetone-d6

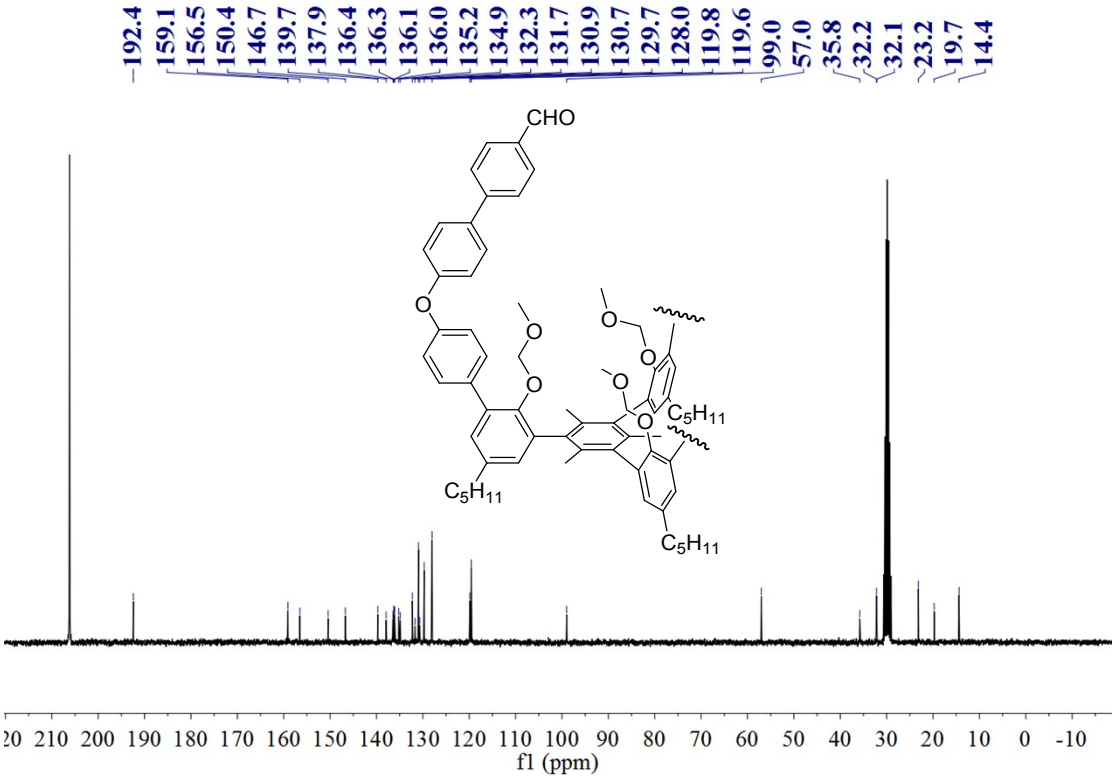

Figure S15. [13]C-spectrum of Compound C1 in acetone-d6

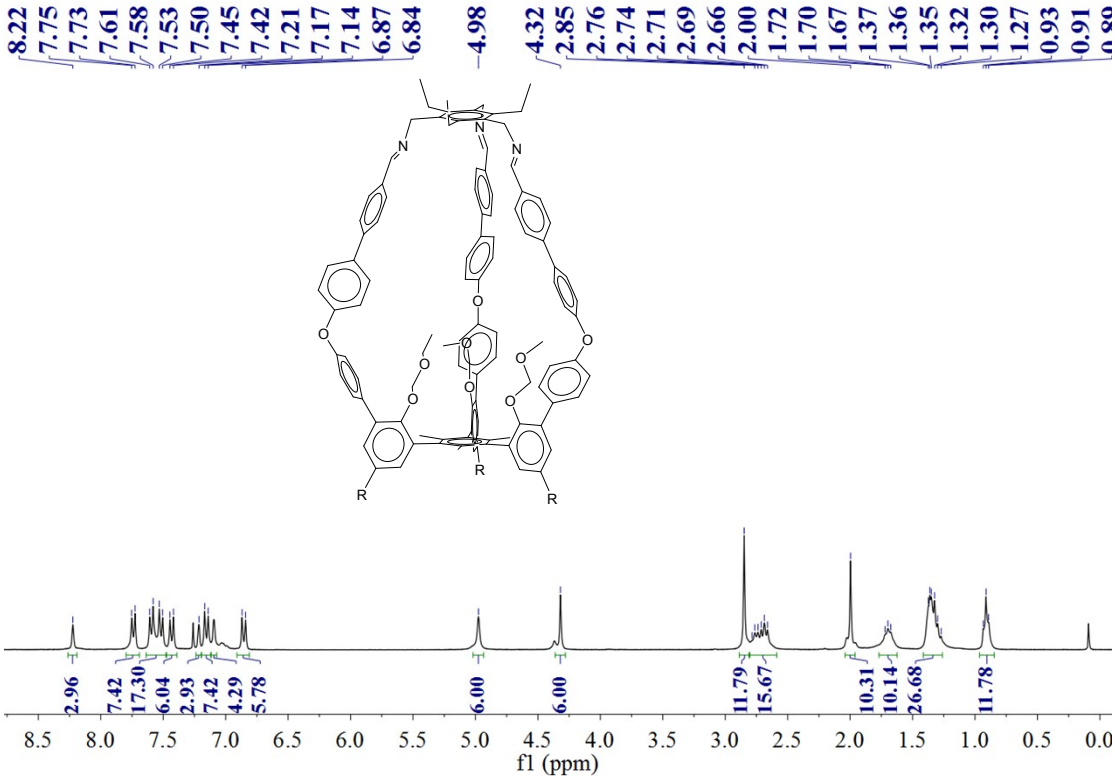

Figure S16. [1]H-spectrum of Compound D1 in CDCl3

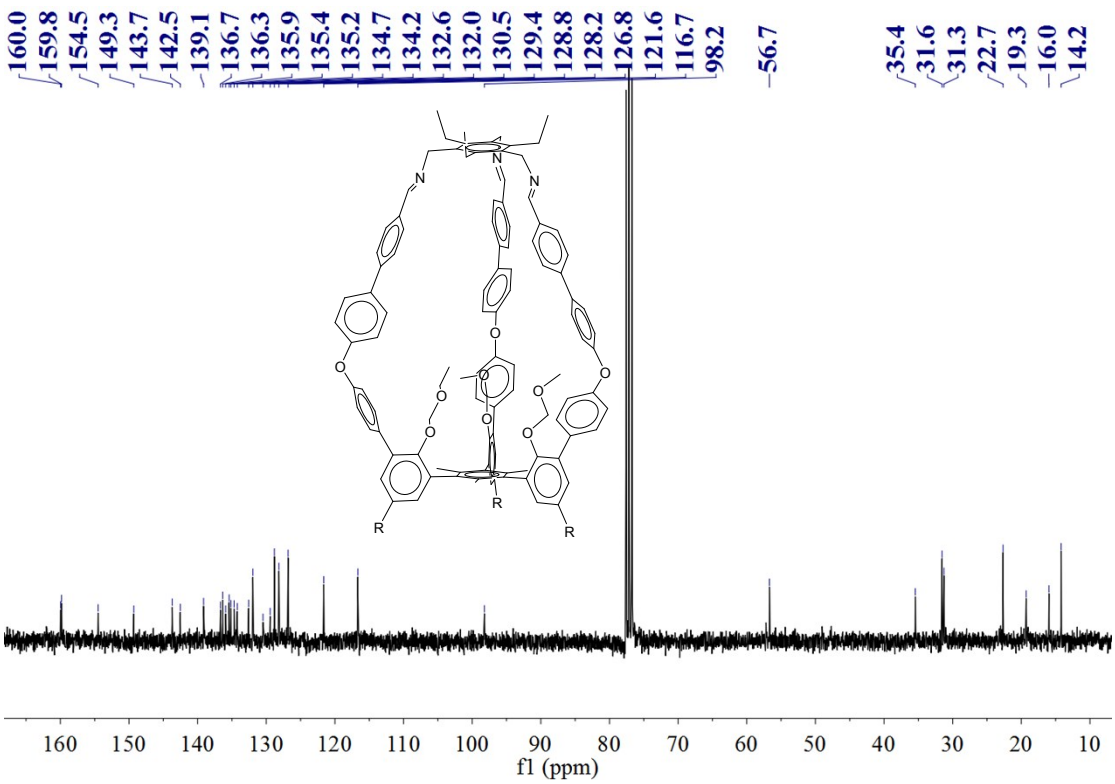

Figure S17. [13]C-spectrum of Compound D1 in $CDCl_3$

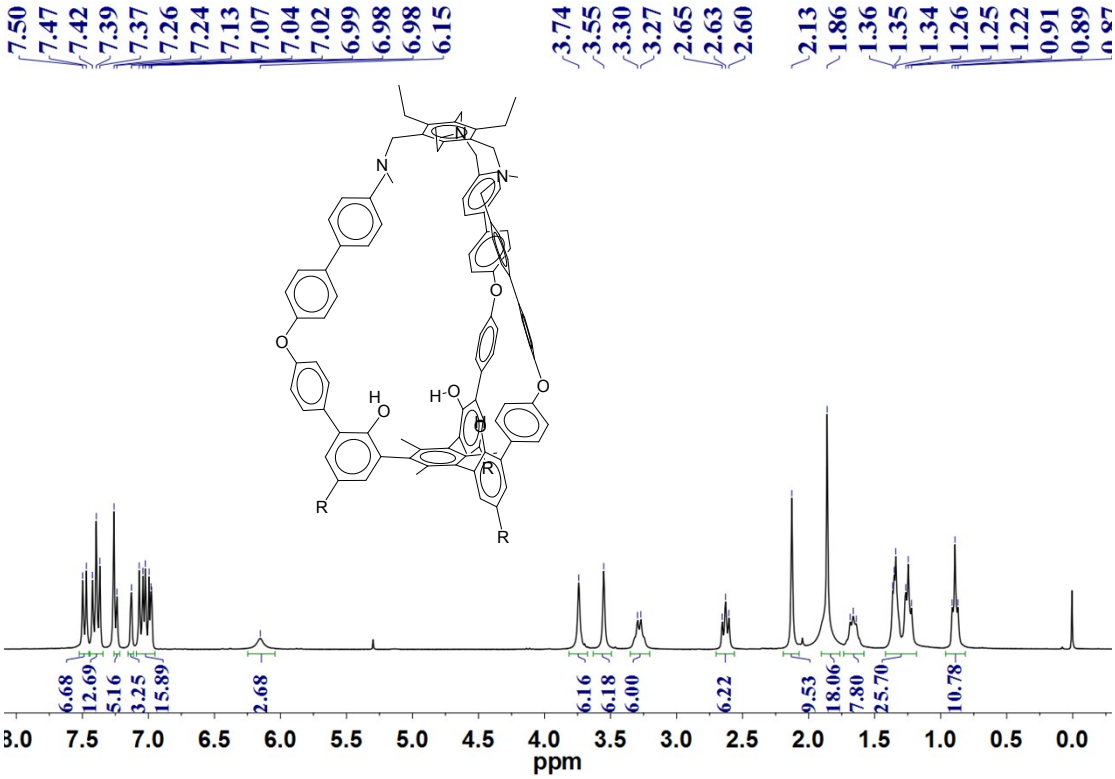

Figure S18. ^{1}H-spectrum of Cage **Ec1** in $CDCl_3$

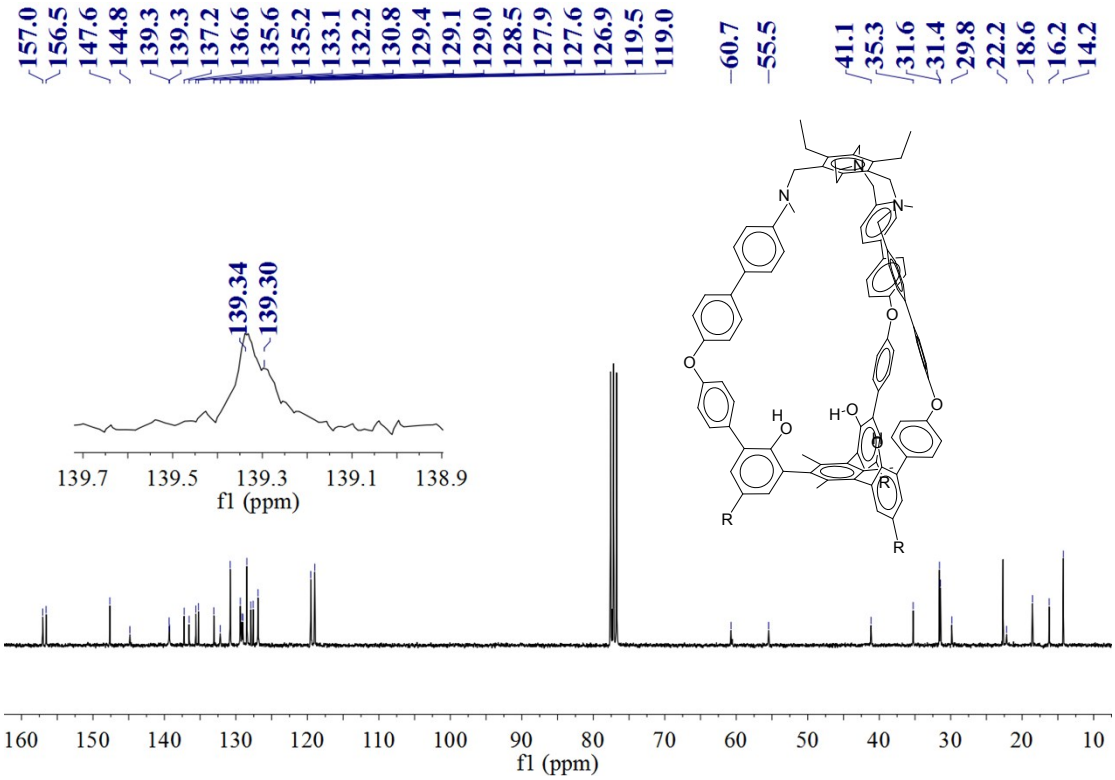

Figure S19. ^{13}C-spectrum of Cage **Ec1** in $CDCl_3$

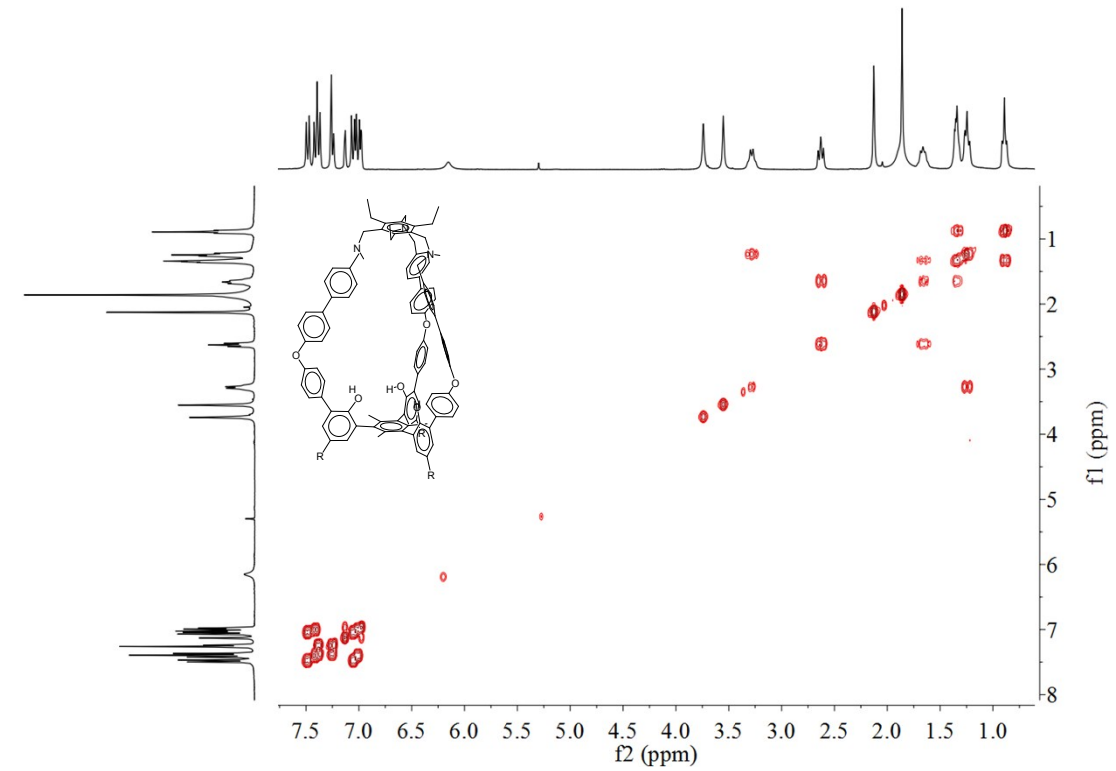

Figure S20. ^{1}H-^{1}H-COSY spectrum of Cage **Ec1** in $CDCl_3$

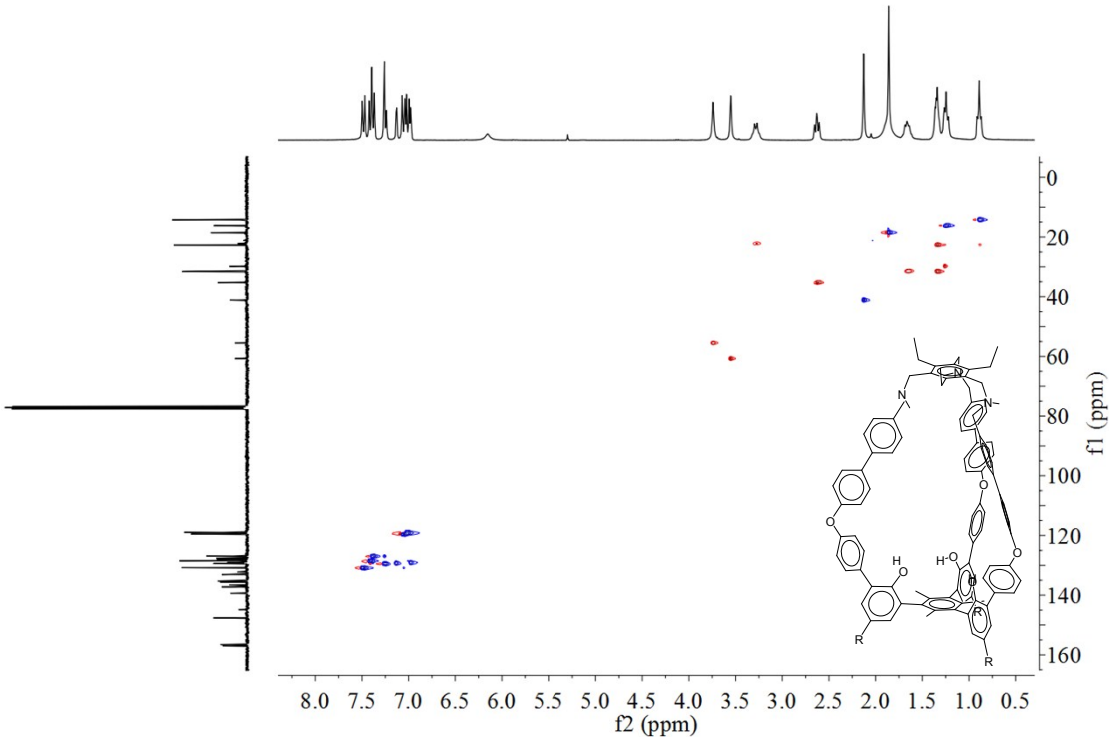

Figure S21. HSQC spectrum of Cage **Ec1** in $CDCl_3$

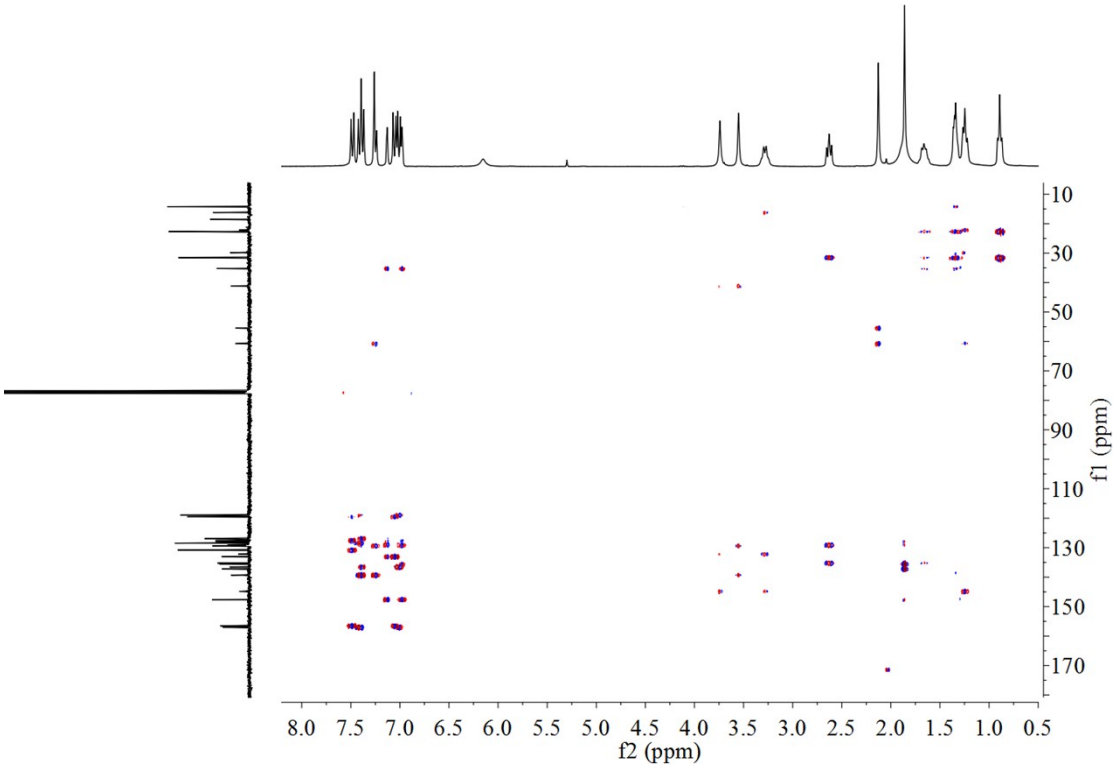

Figure S22. HMBC spectrum of Cage **Ec1** in $CDCl_3$

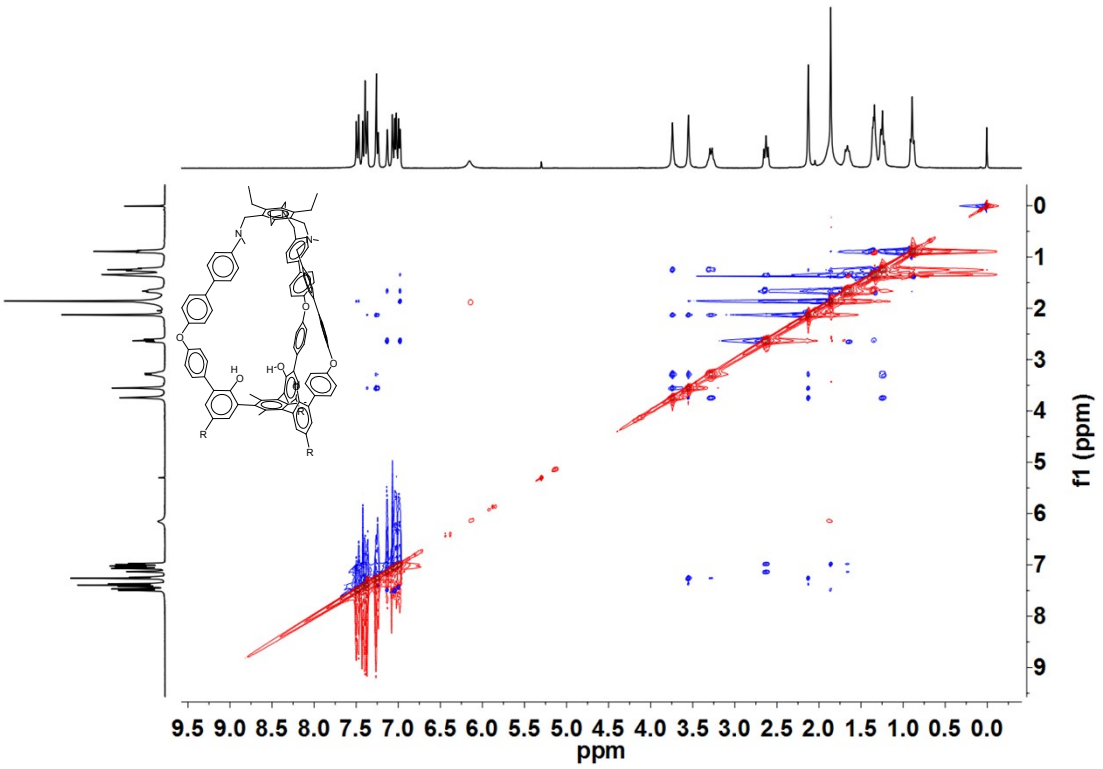

Figure S23. ROESY spectrum of Cage **Ec1** in $CDCl_3$

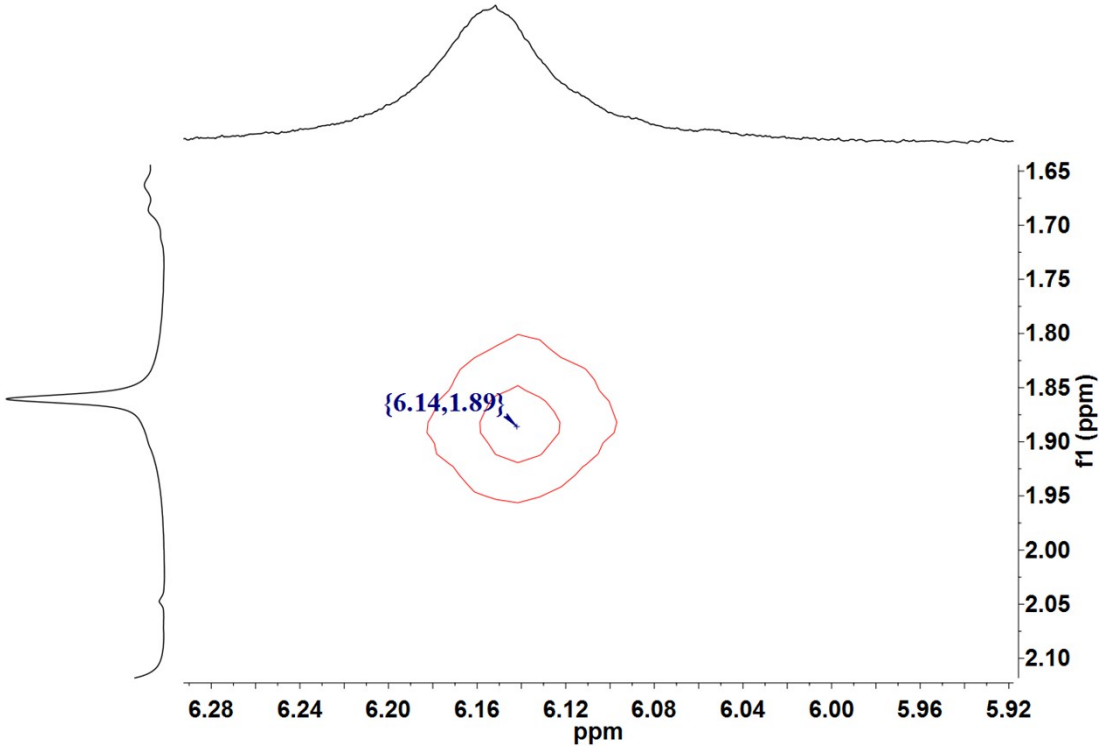

Figure S24. Expansion of ROESY spectrum of Cage **Ec1** in $CDCl_3$, which showed a water molecule bound with phenol hydroxyl group in the cavity.

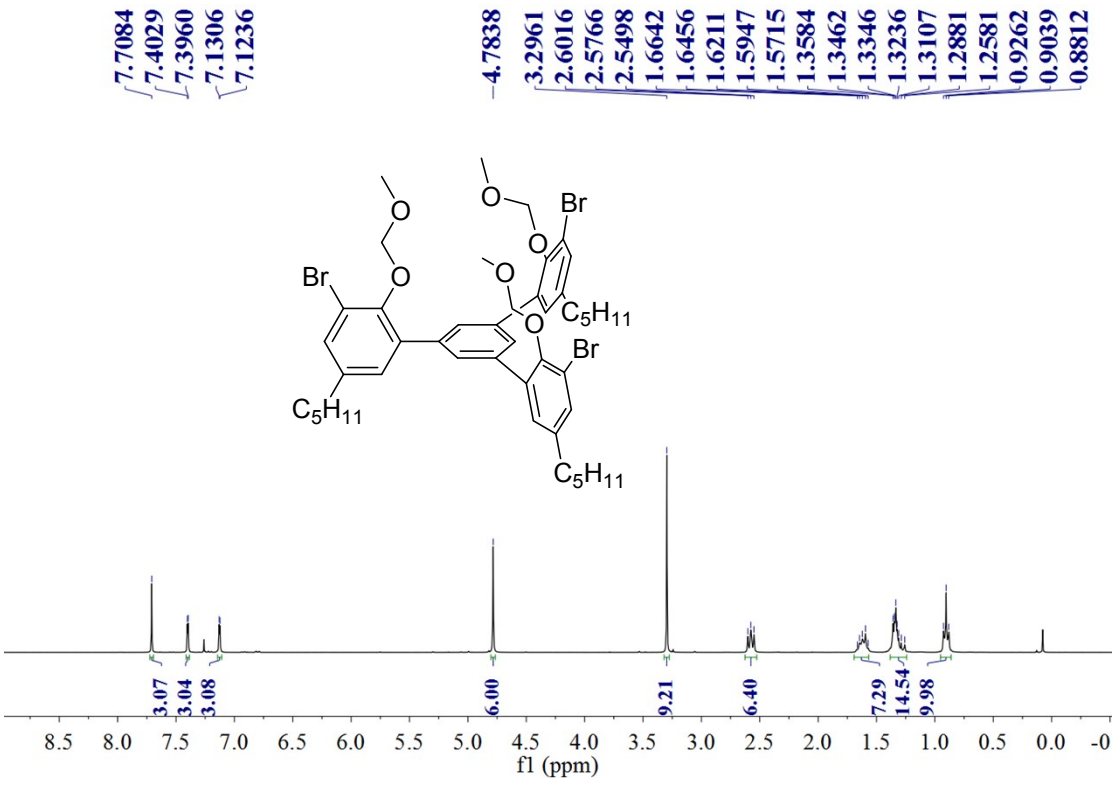

Figure S25. ^{1}H-NMR spectrum of Compound B2 in $CDCl_3$

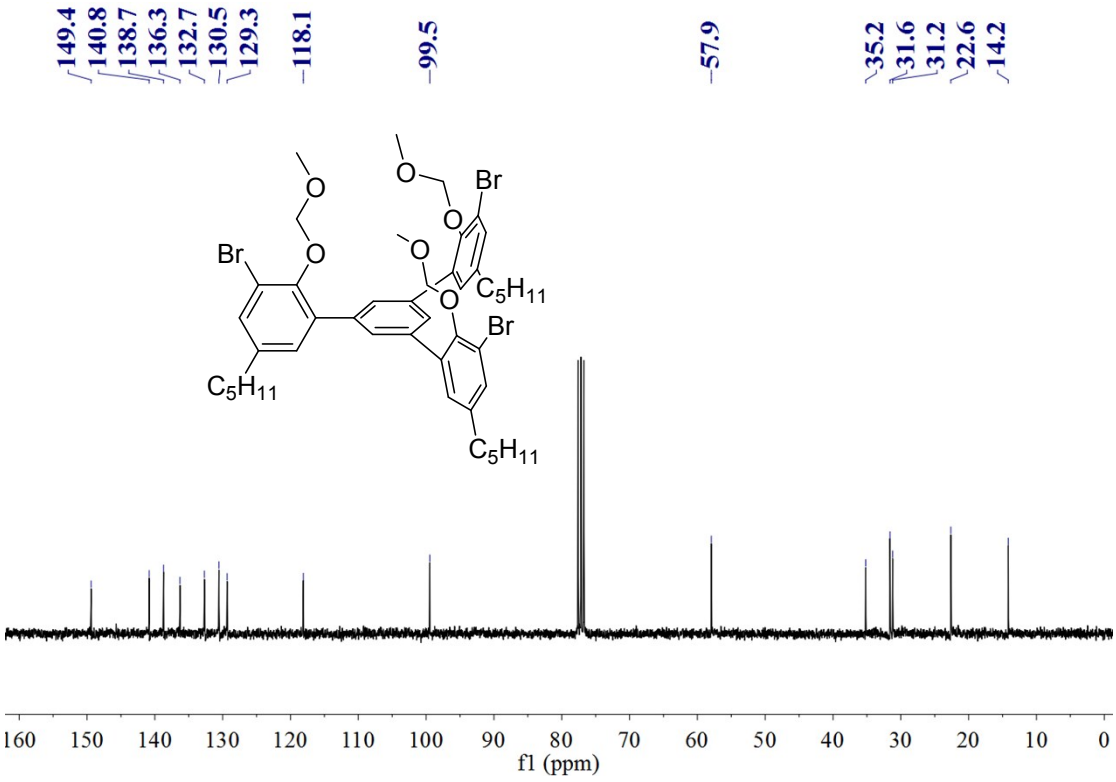

Figure S26. ^{13}C-NMR spectrum of Compound B2 in $CDCl_3$

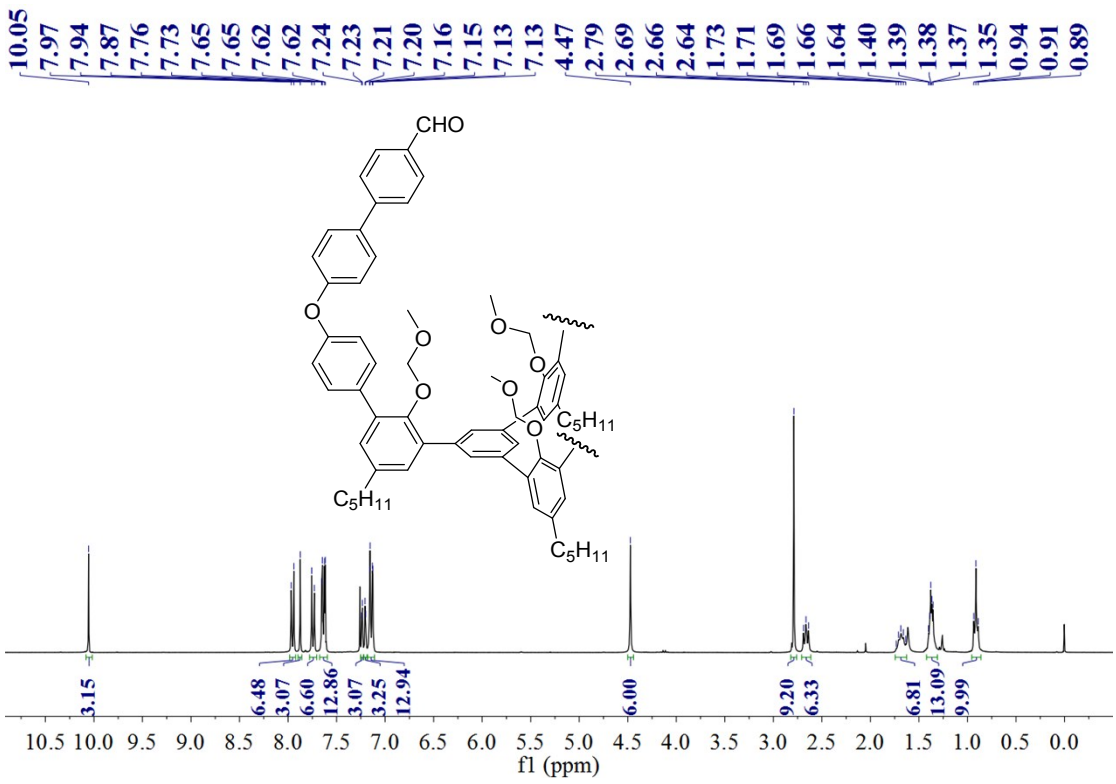

Figure S27. ^{1}H-NMR spectrum of Compound C2 in $CDCl_3$

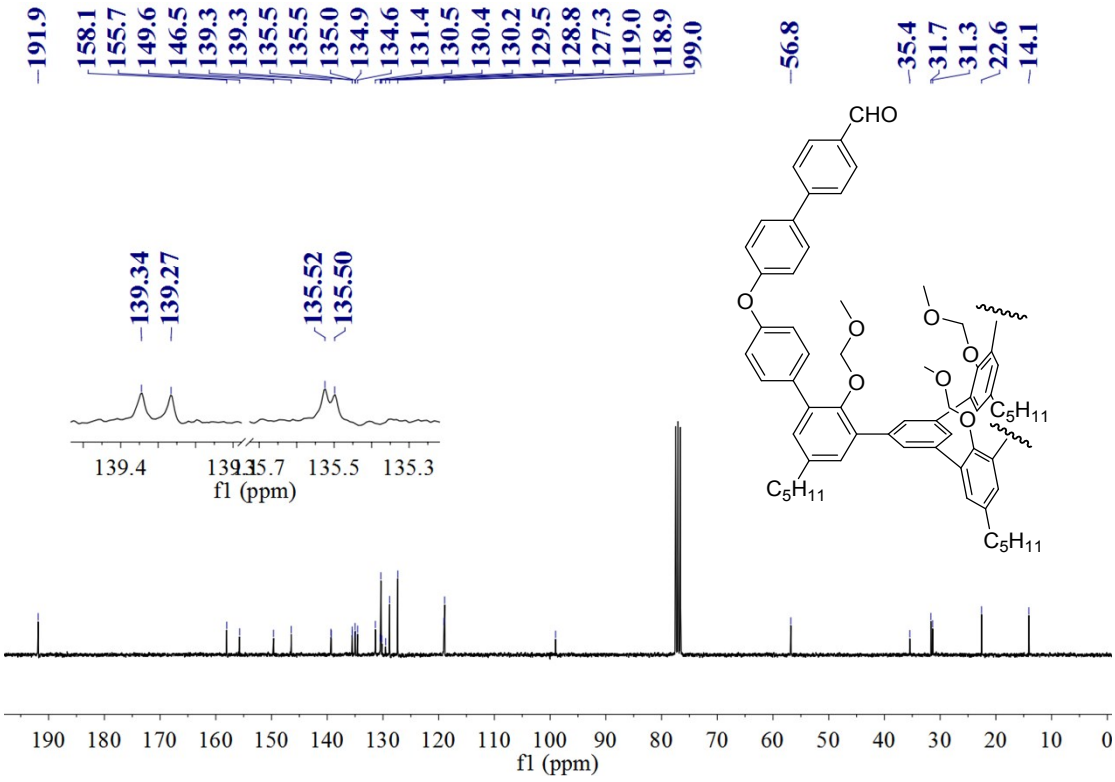

Figure S28. ^{13}C-NMR spectrum of Compound C2 in $CDCl_3$

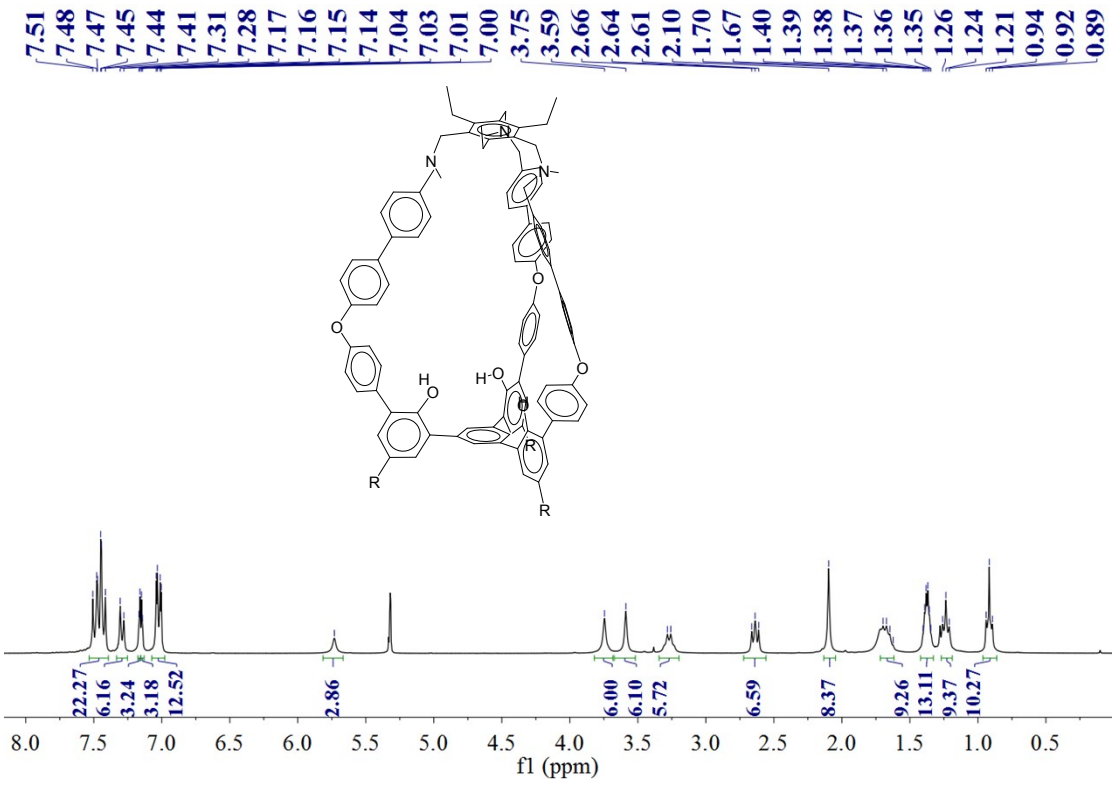

Figure S29. ^{1}H-NMR spectrum of Cage **Ec2** in CD_2Cl_2

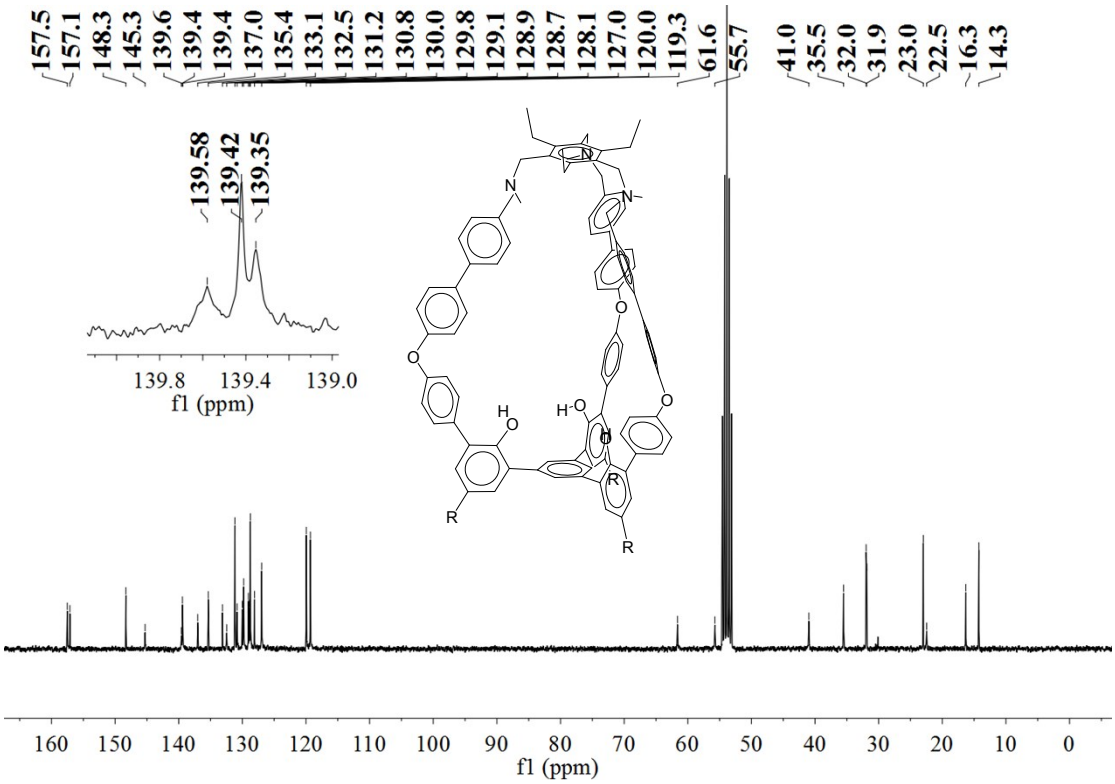

Figure S30. ^{13}C-NMR spectrum of Cage **Ec2** in CD_2Cl_2

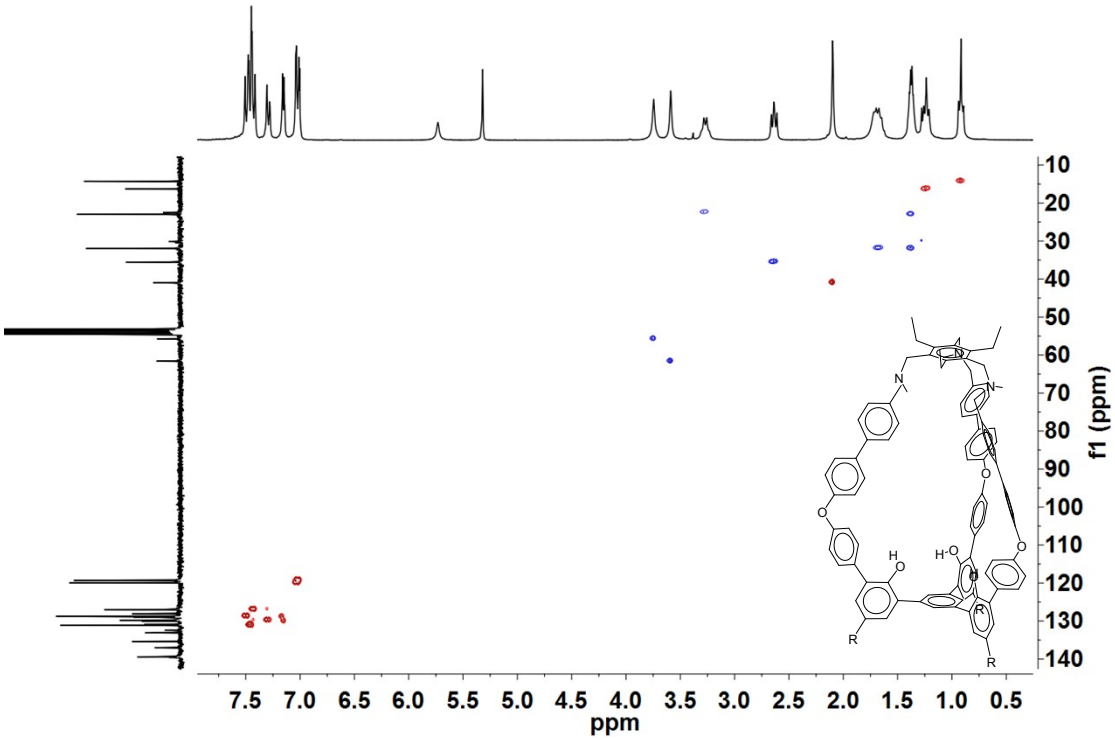

Figure S31. HSQC spectrum of Cage **Ec2** in CD_2Cl_2

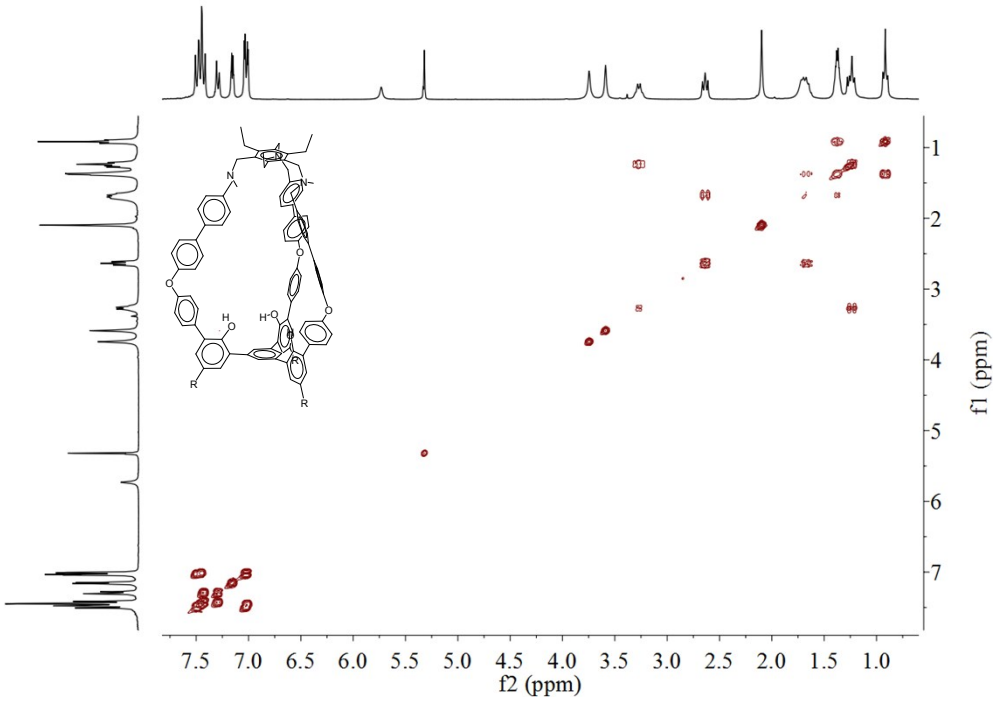

Figure S32. ^{1}H-^{1}H COSY spectrum of Cage **Ec2** in CD_2Cl_2

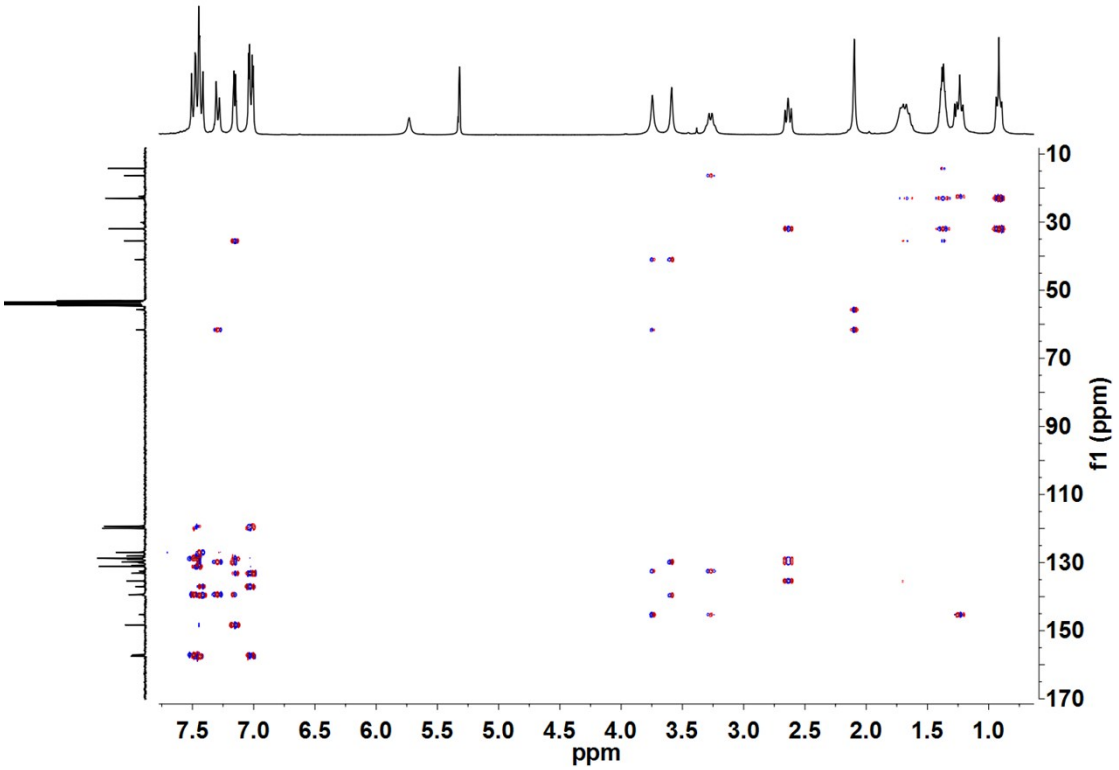

Figure S33. HMBC spectrum of Cage **Ec2** in CD_2Cl_2

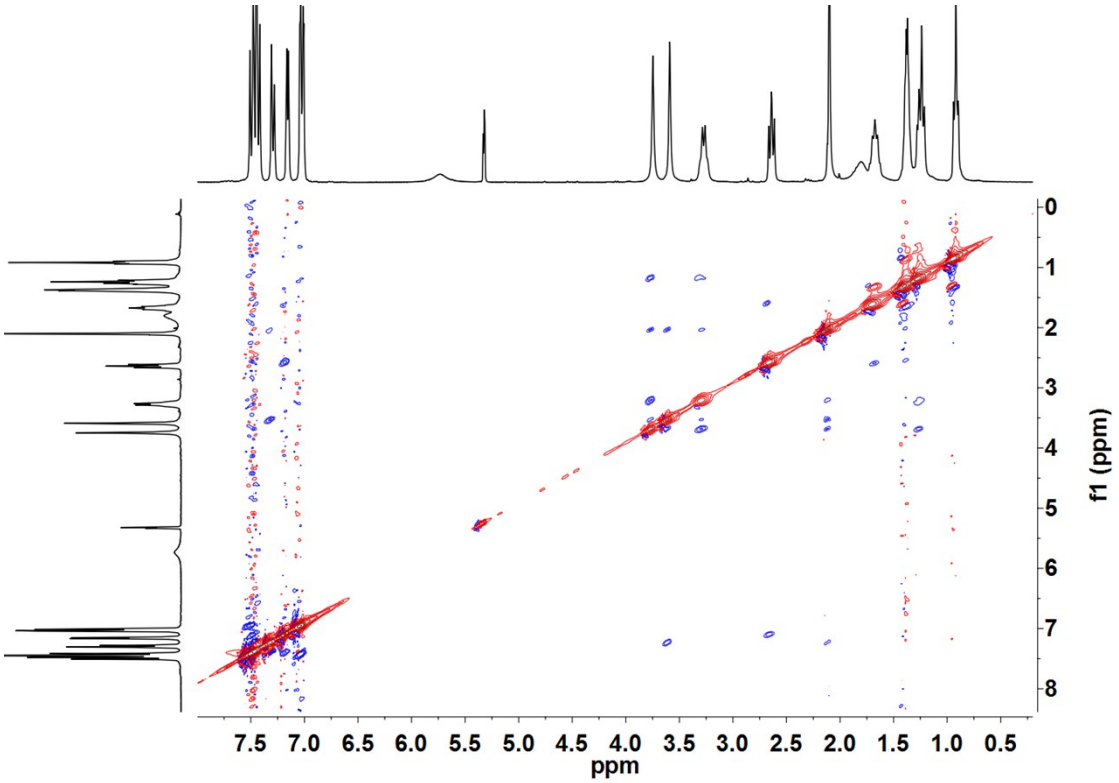

Figure S34. ROESY spectrum of Cage **Ec2** in CD_2Cl_2

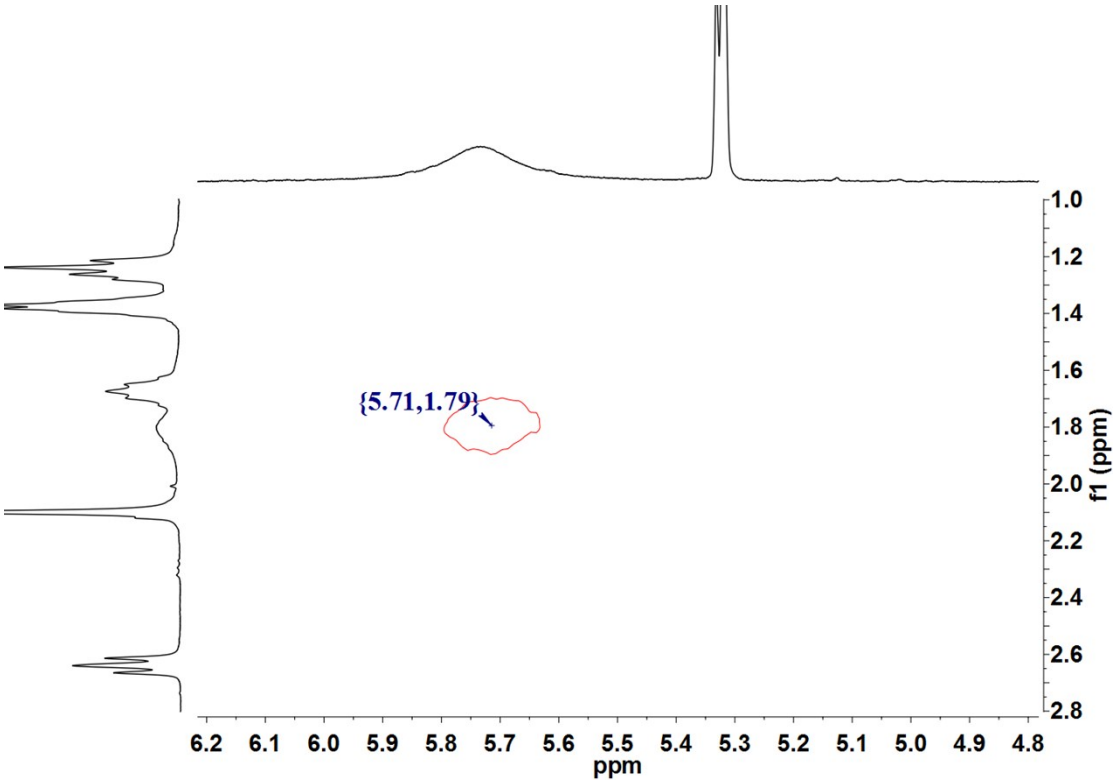

Figure S35. Enlarged ROESY spectrum of Cage **Ec2** in CD_2Cl_2, which also showed a water molecule bound with phenol hydroxyl group in the cavity.

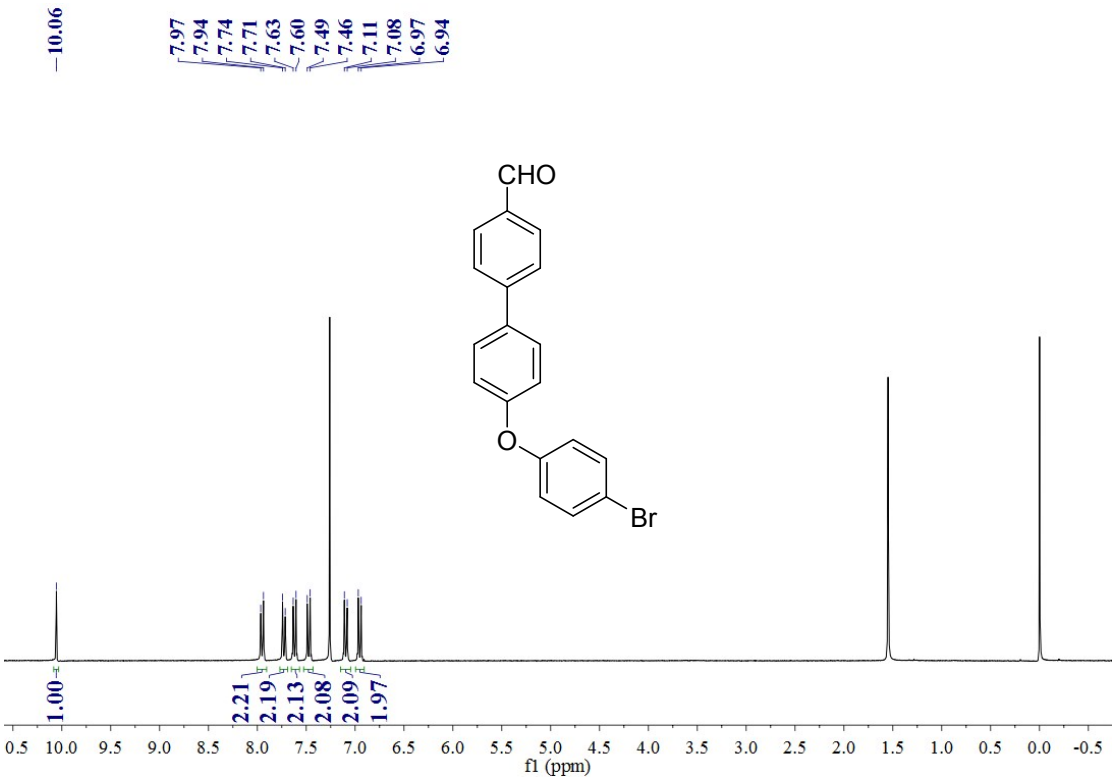

Figure S36. ^{1}H-spectrum of Compound E in $CDCl_3$

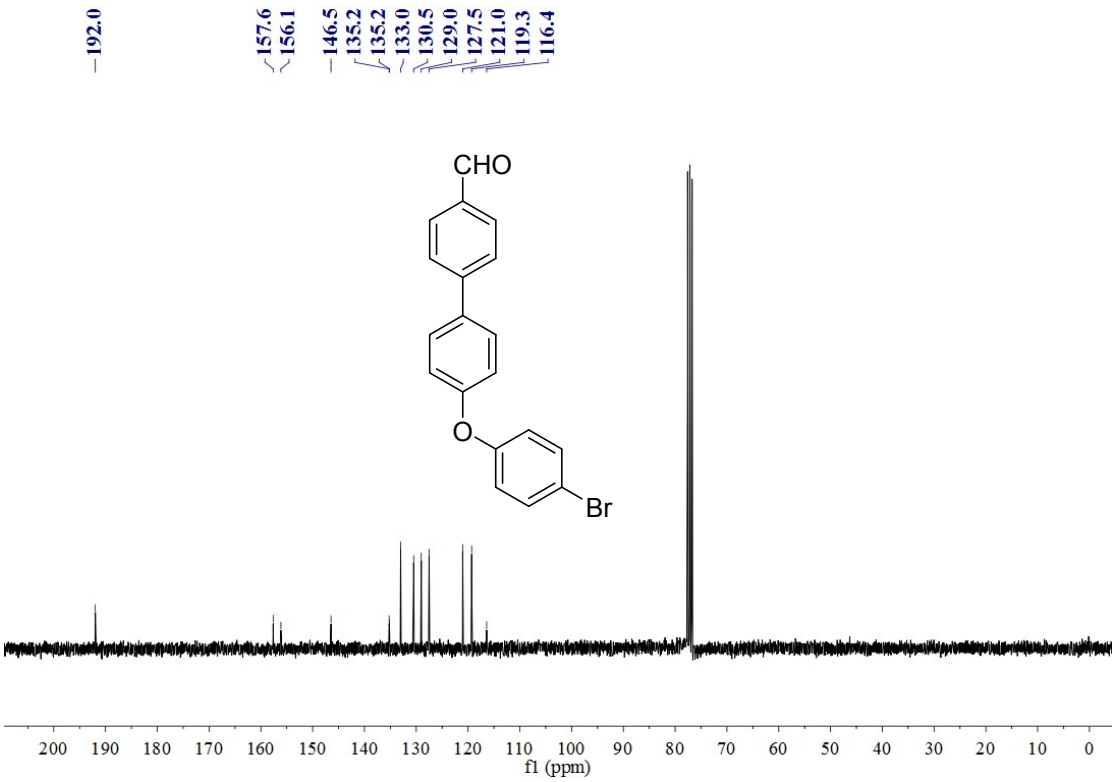

Figure S37. ^{13}C-spectrum of Compound E in $CDCl_3$

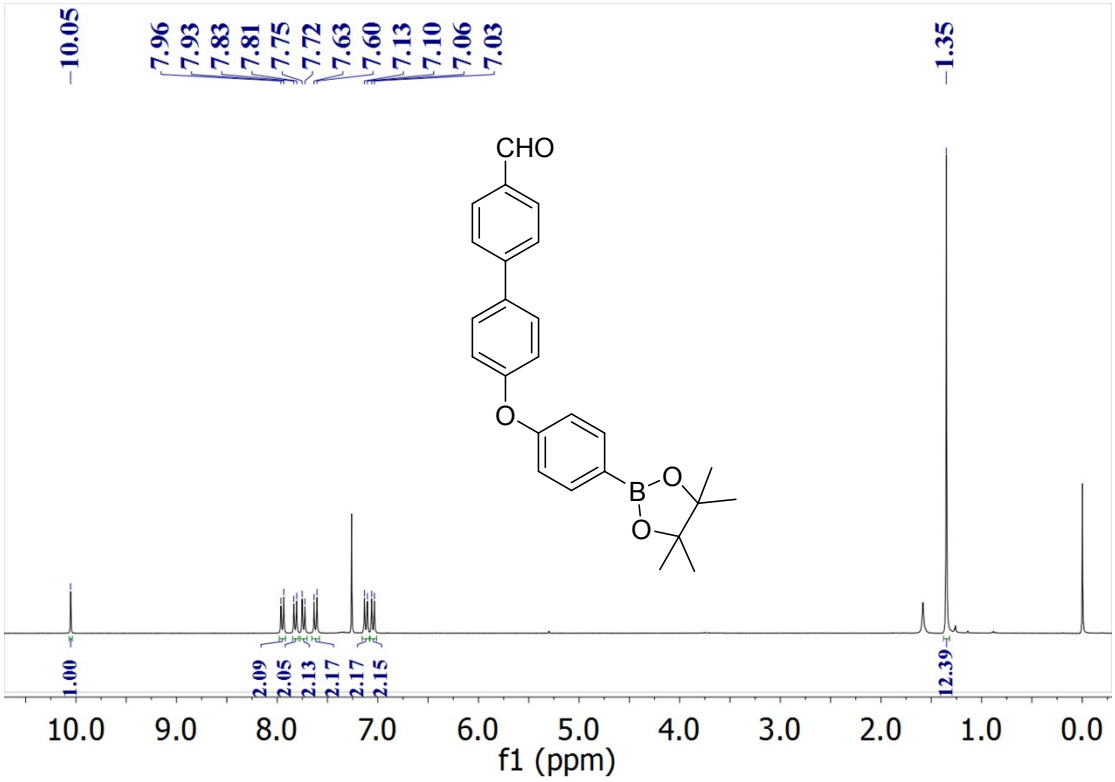

Figure S38. ^{1}H-spectrum of Compound F in $CDCl_3$

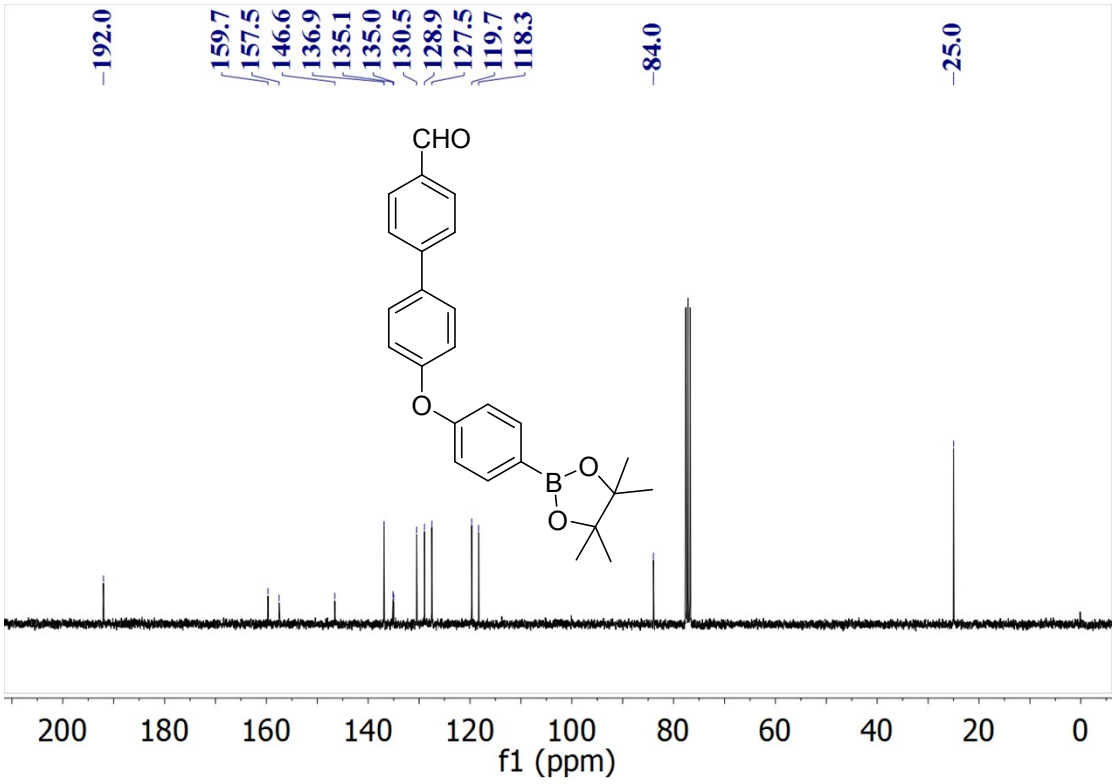

Figure S39. ^{13}C-spectrum of Compound F in $CDCl_3$

NMR spectra of Substrate

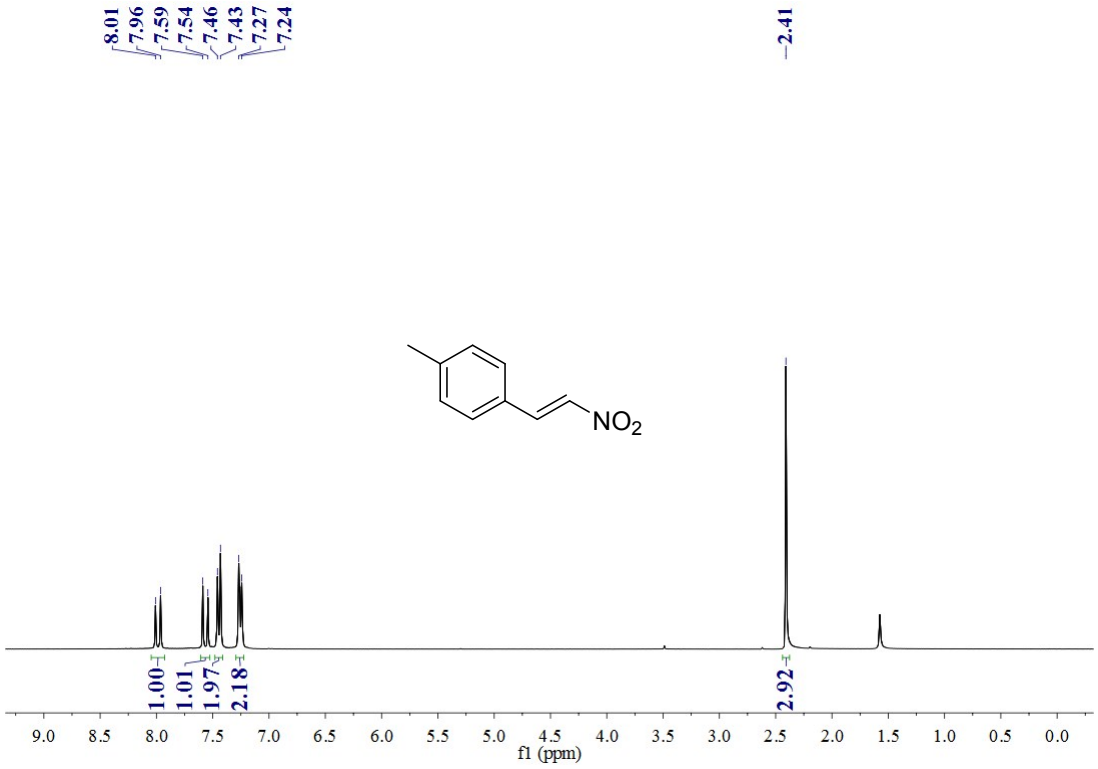

Figure S40. ^{1}H-NMR spectrum of Compound 1b in $CDCl_3$

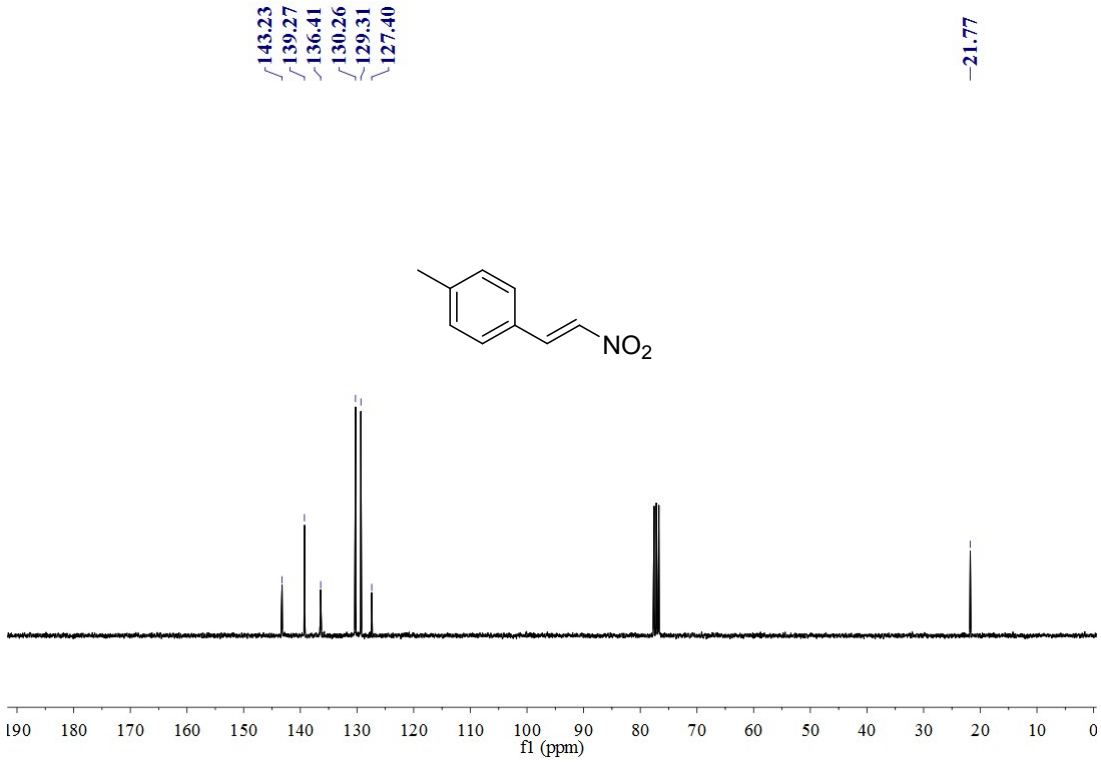

Figure S41. ^{13}C-NMR spectrum of Compound 1b in $CDCl_3$

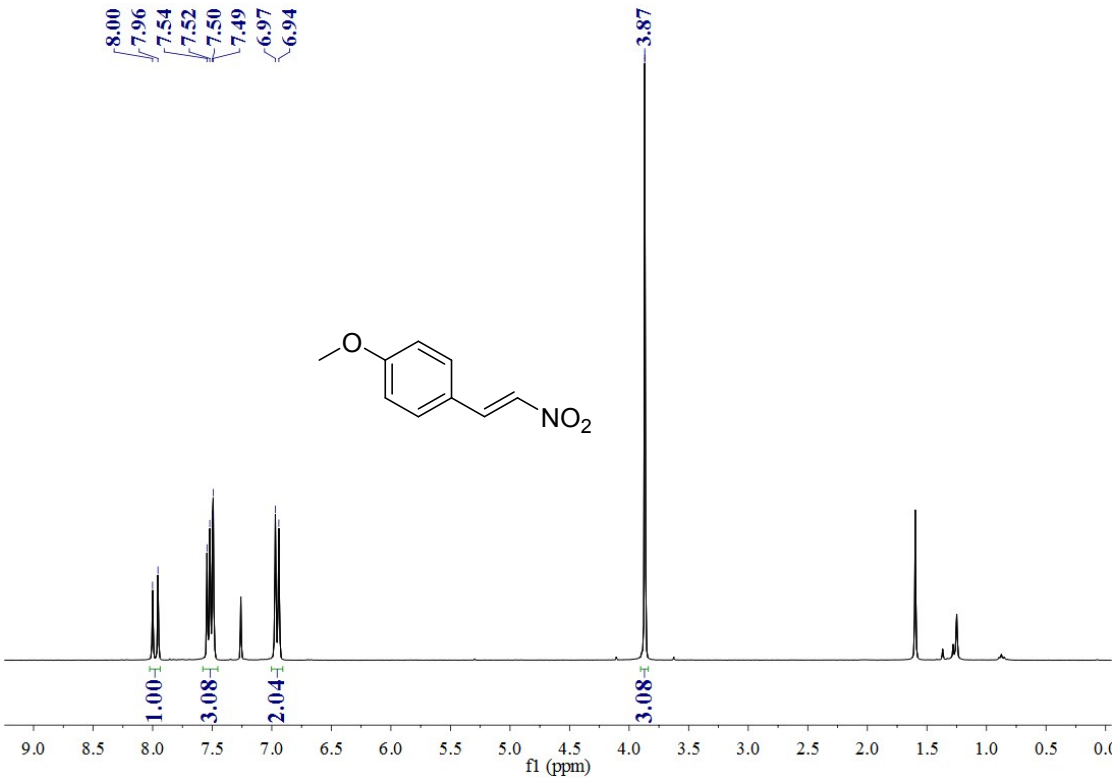

Figure S42. ^{1}H-NMR spectrum of Compound 1c in $CDCl_3$

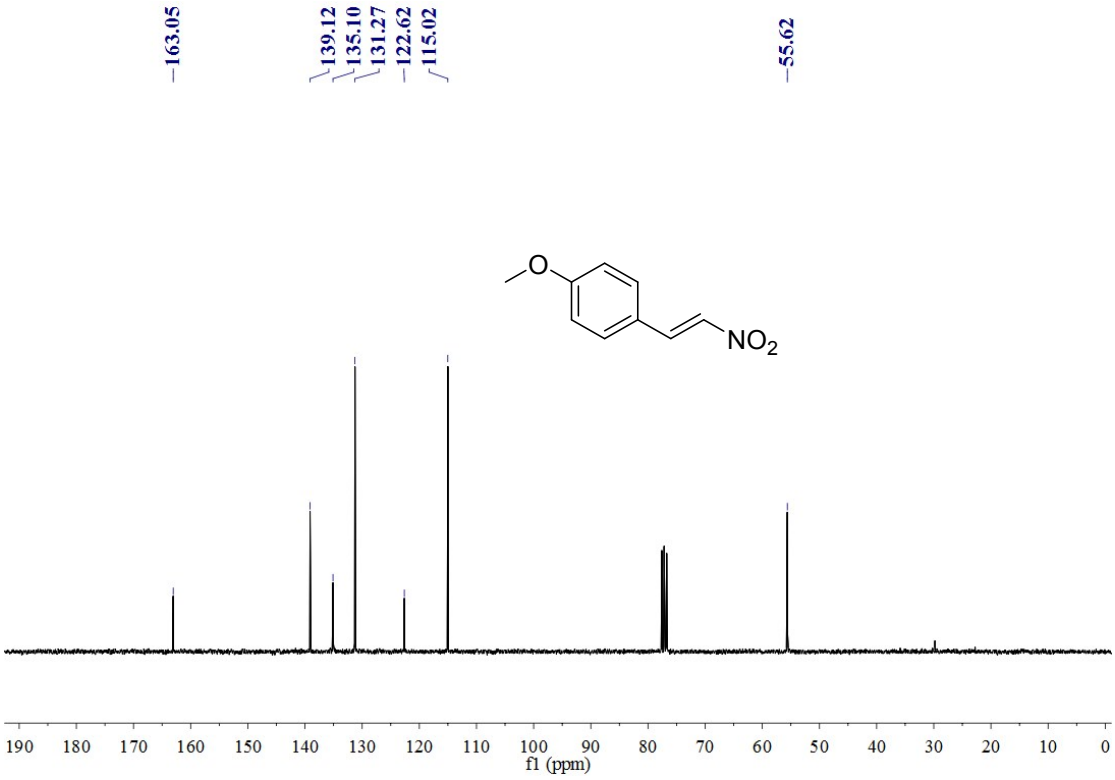

Figure S43. ^{13}C-NMR spectrum of Compound 1c in $CDCl_3$

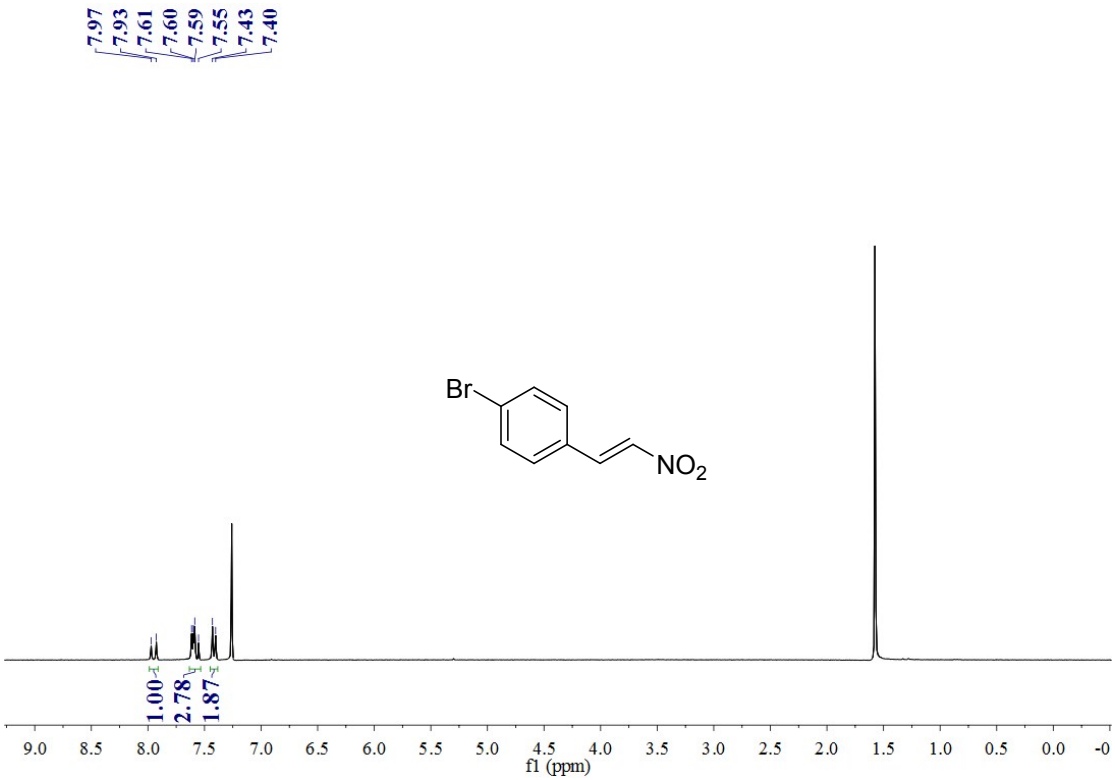

Figure S44. ^{1}H-NMR spectrum of Compound 1d in $CDCl_3$

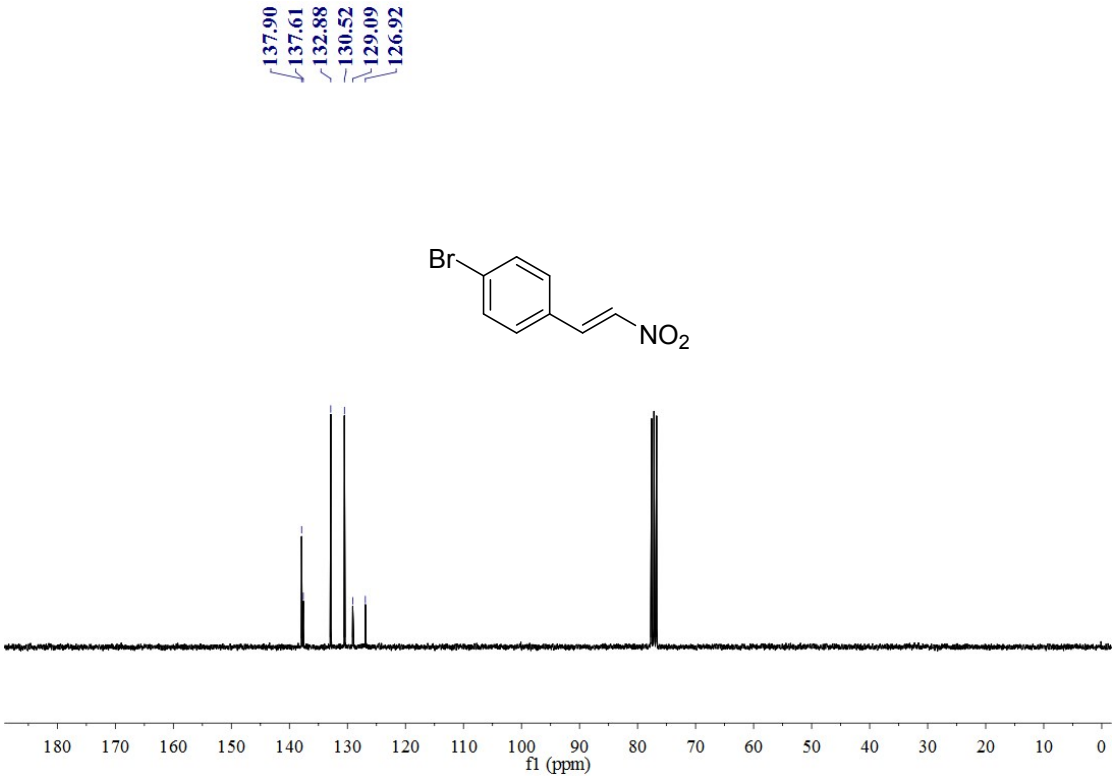

Figure S45. ^{13}C-NMR spectrum of Compound 1d in $CDCl_3$

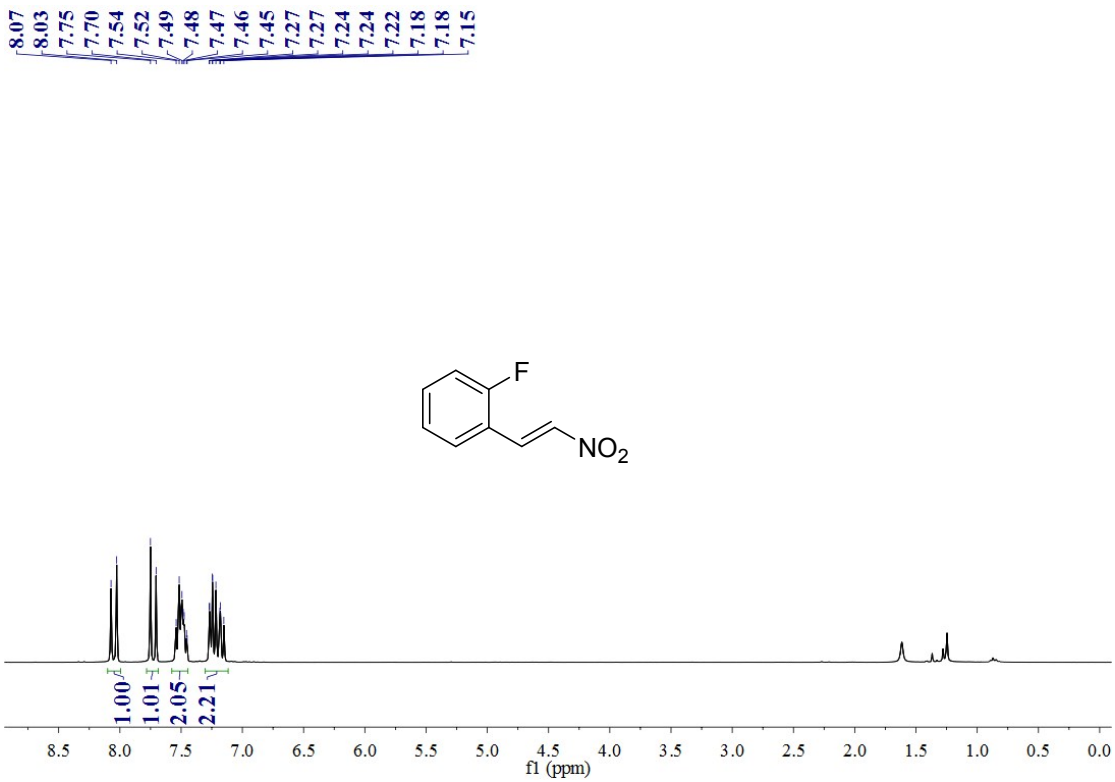

Figure S46. ^{1}H-NMR spectrum of Compound 1e in $CDCl_3$

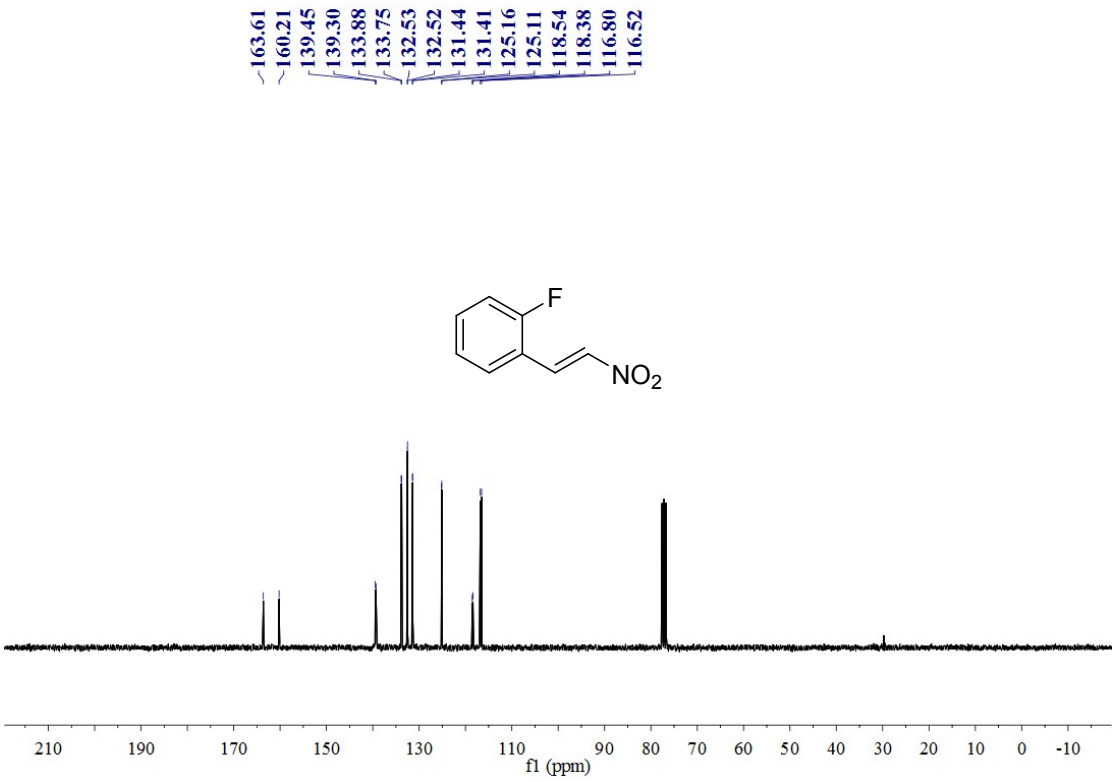

Figure S47. ^{13}C-NMR spectrum of Compound 1e in $CDCl_3$

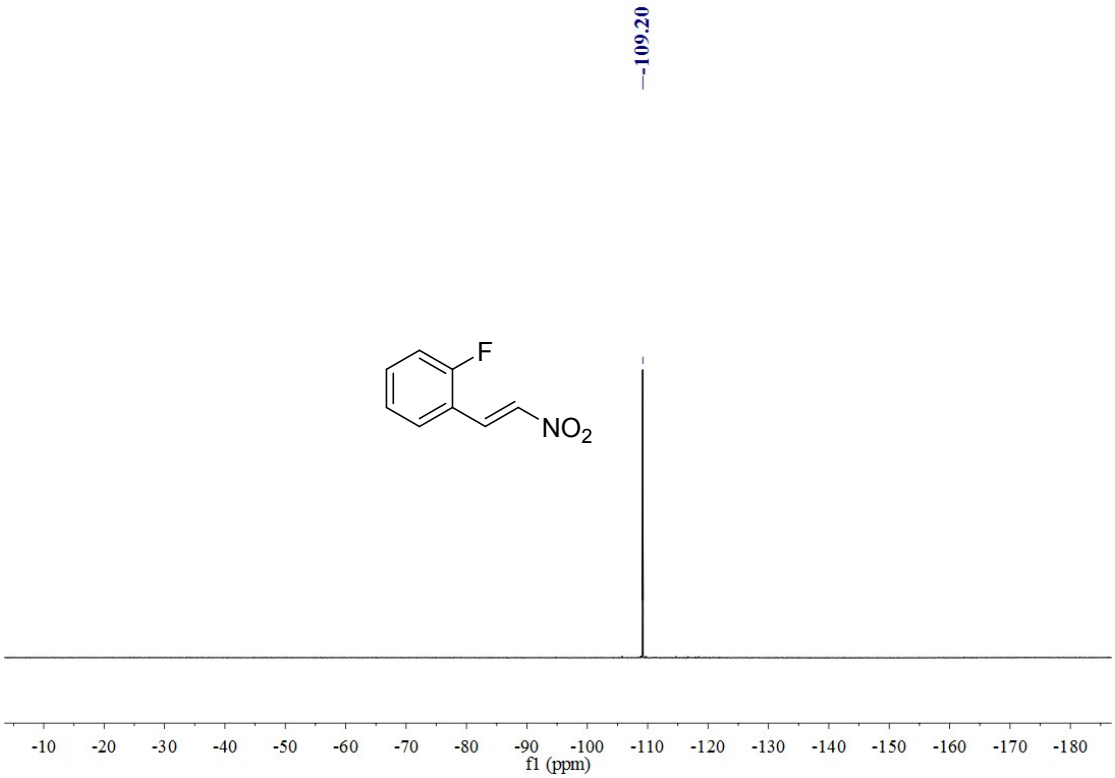

Figure S48. ^{19}F-NMR spectrum of Compound 1e in $CDCl_3$

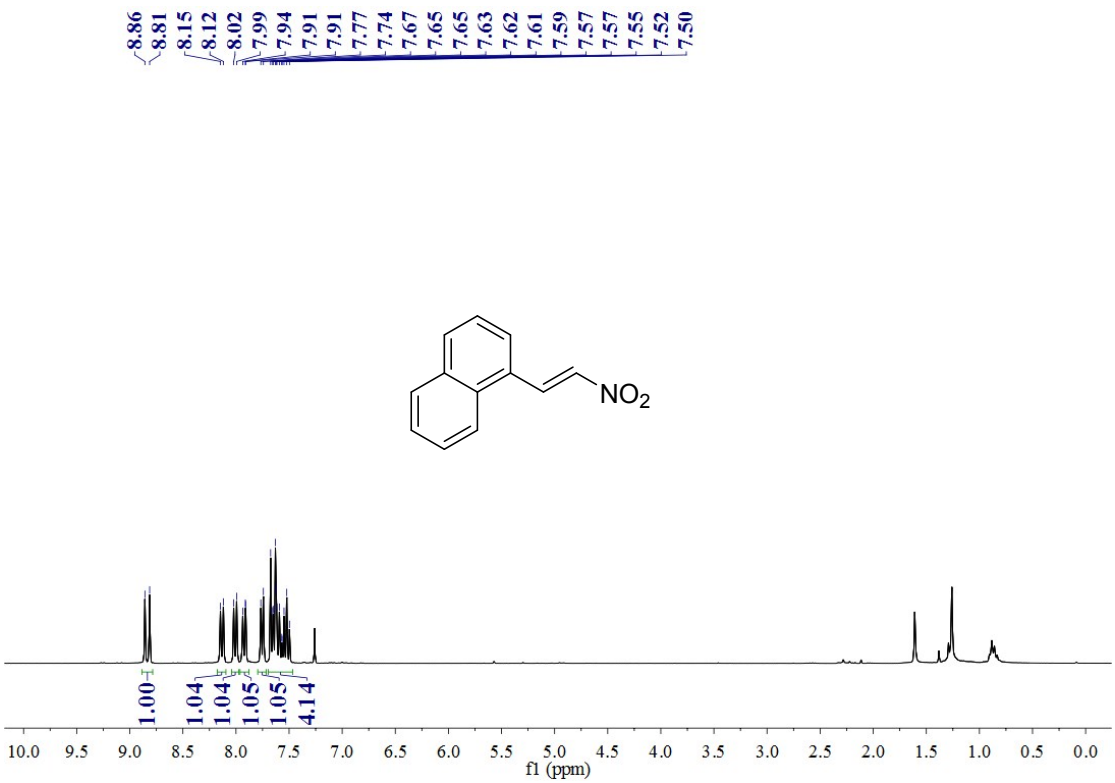

Figure S49. ^{1}H-NMR spectrum of Compound 1f in $CDCl_3$

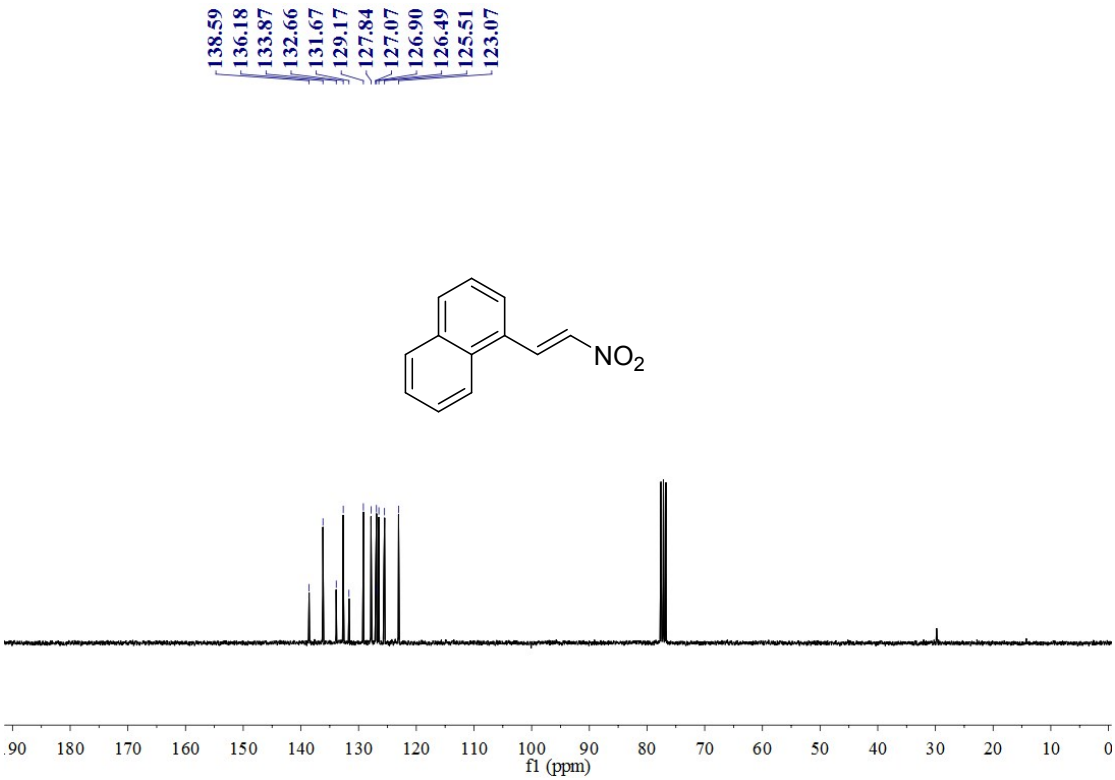

Figure S50. ^{13}C-NMR spectrum of Compound 1f in $CDCl_3$

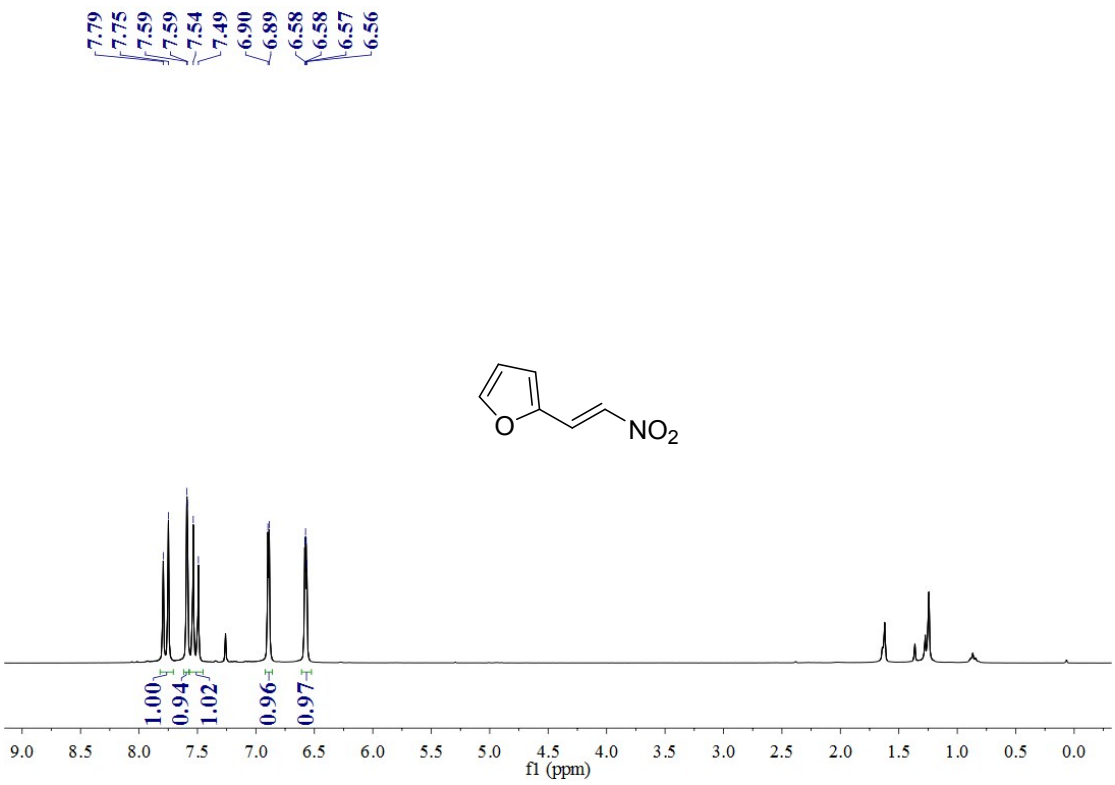

Figure S51. ^{1}H-NMR spectrum of Compound 1g in $CDCl_3$

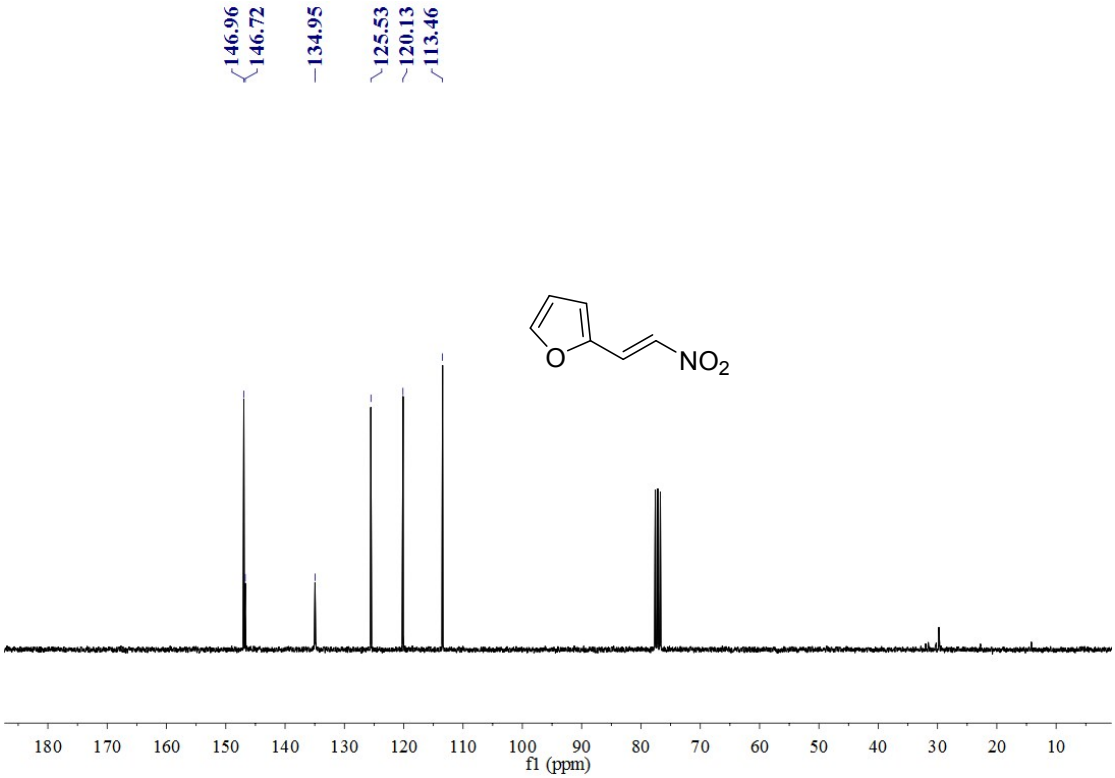

Figure S52. ^{13}C-NMR spectrum of Compound 1g in $CDCl_3$

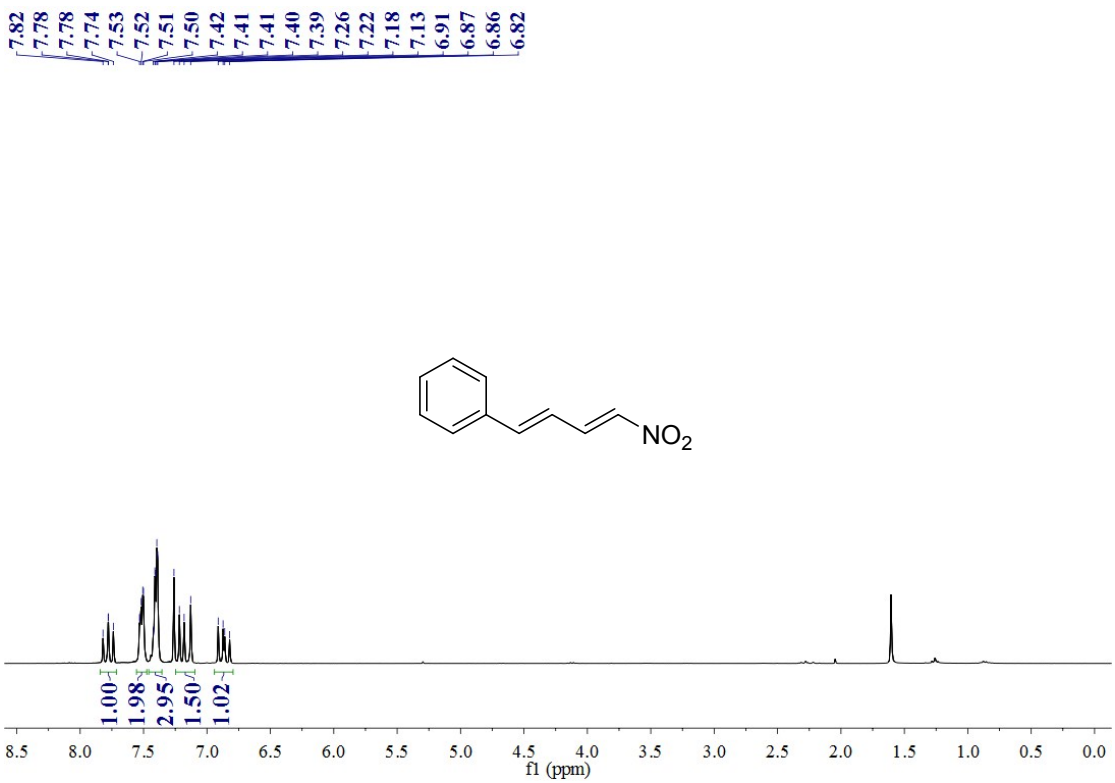

Figure S53. ^{1}H-NMR spectrum of Compound 1h in $CDCl_3$

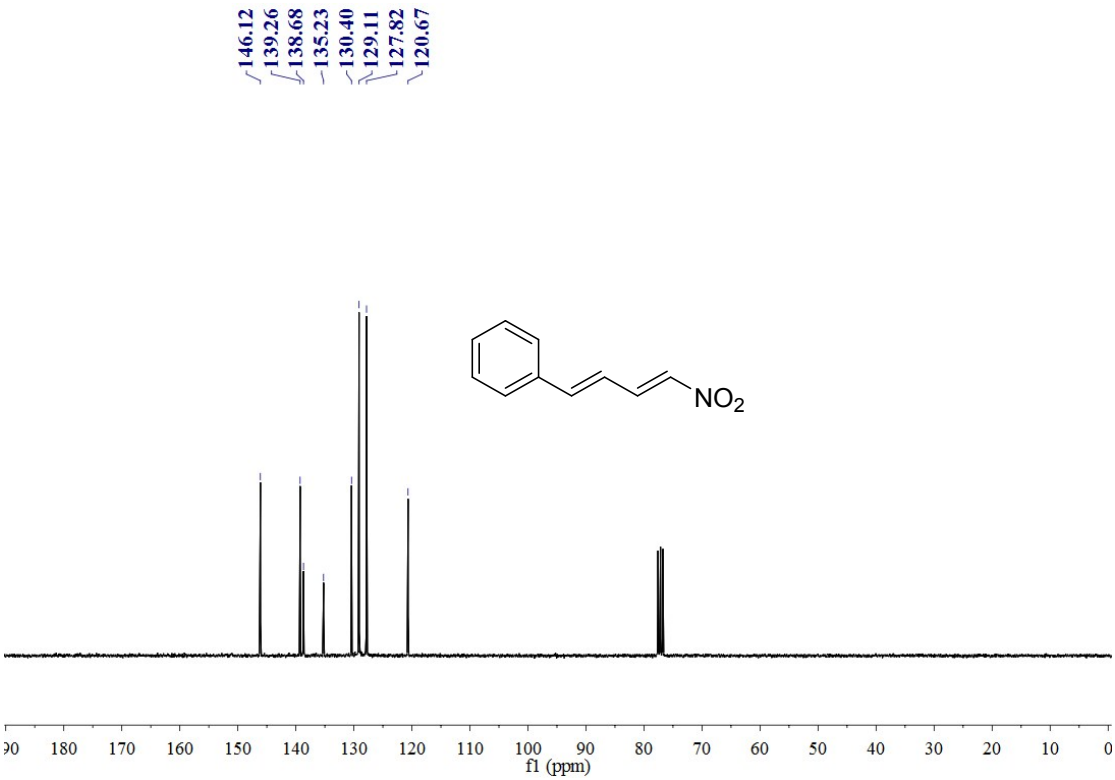

Figure S54. ^{13}C-NMR spectrum of Compound 1h in $CDCl_3$

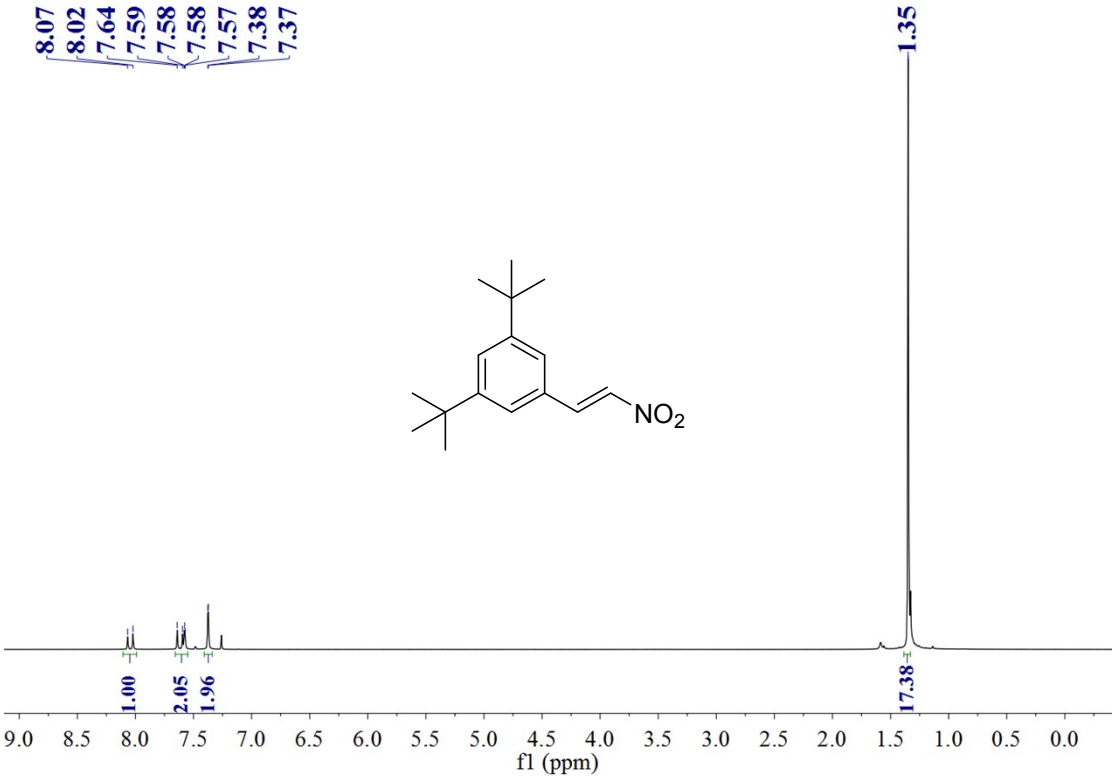

Figure S55. ^{1}H-NMR spectrum of Compound 1i in $CDCl_3$

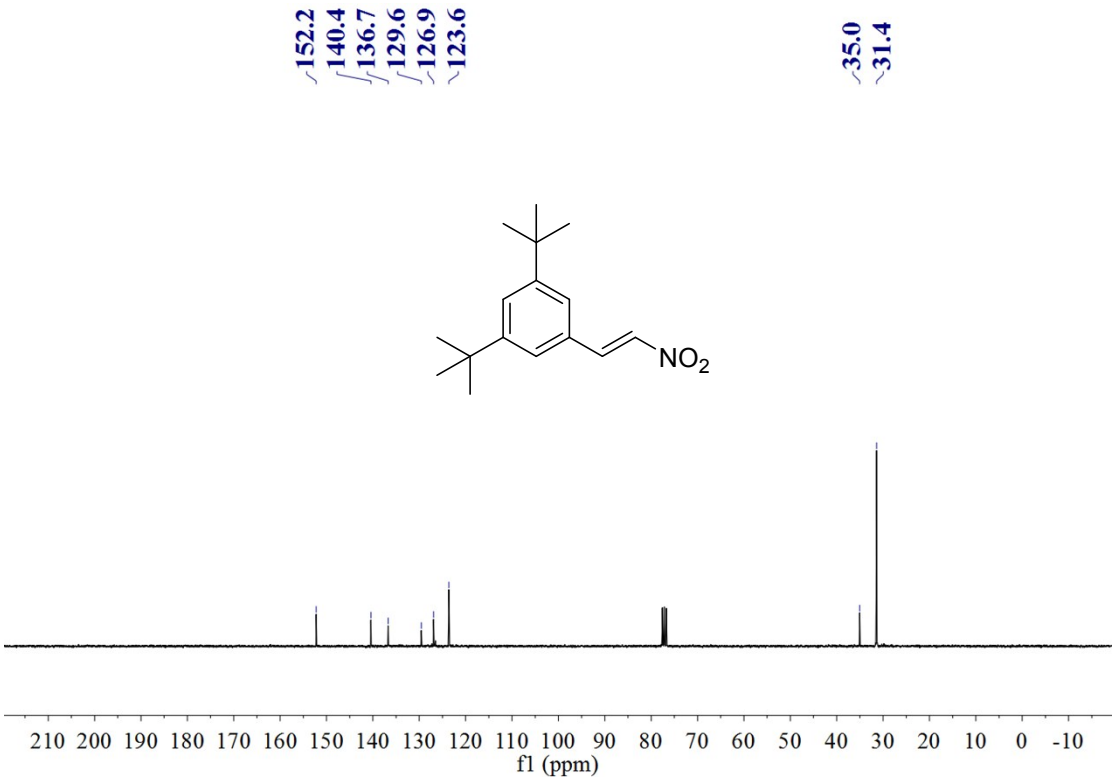

Figure S56. ^{13}C-NMR spectrum of Compound 1i in $CDCl_3$

NMR spectra of Products (3a-3i)

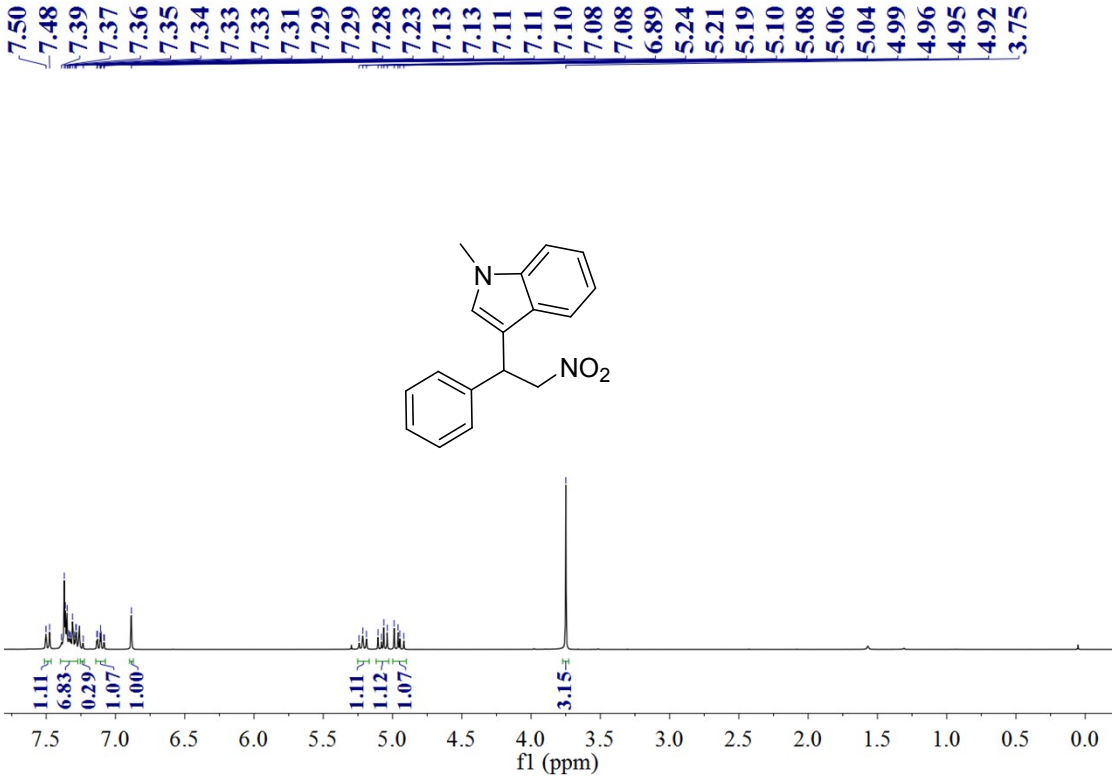

Figure S57. ^{1}H-NMR spectrum of Compound 3a in $CDCl_3$

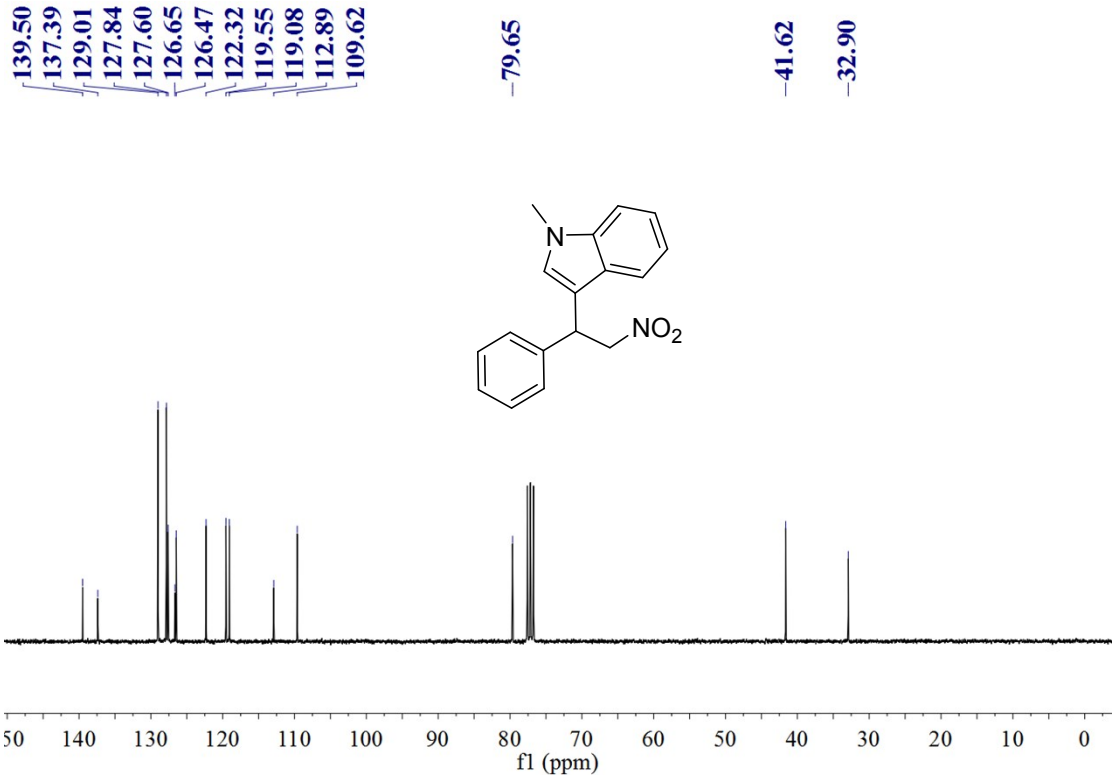

Figure S58. ^{13}C-NMR spectrum of Compound 3a in $CDCl_3$

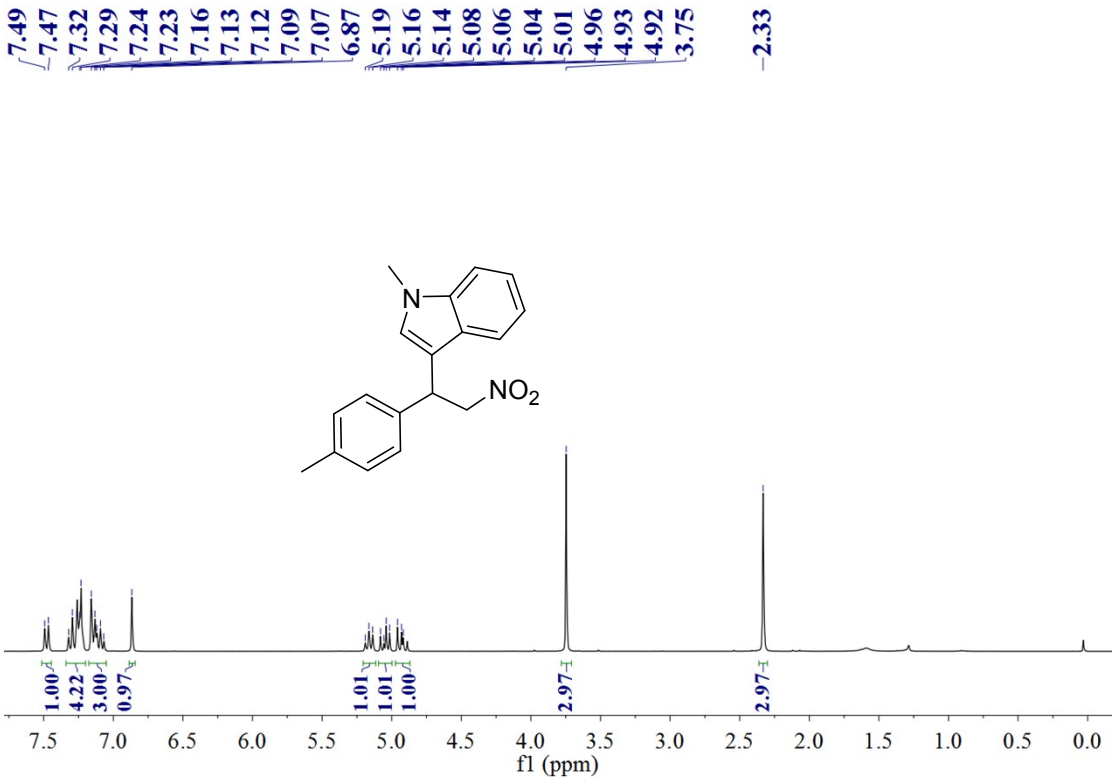

Figure S59. ^{1}H-NMR spectrum of Compound 3b in $CDCl_3$

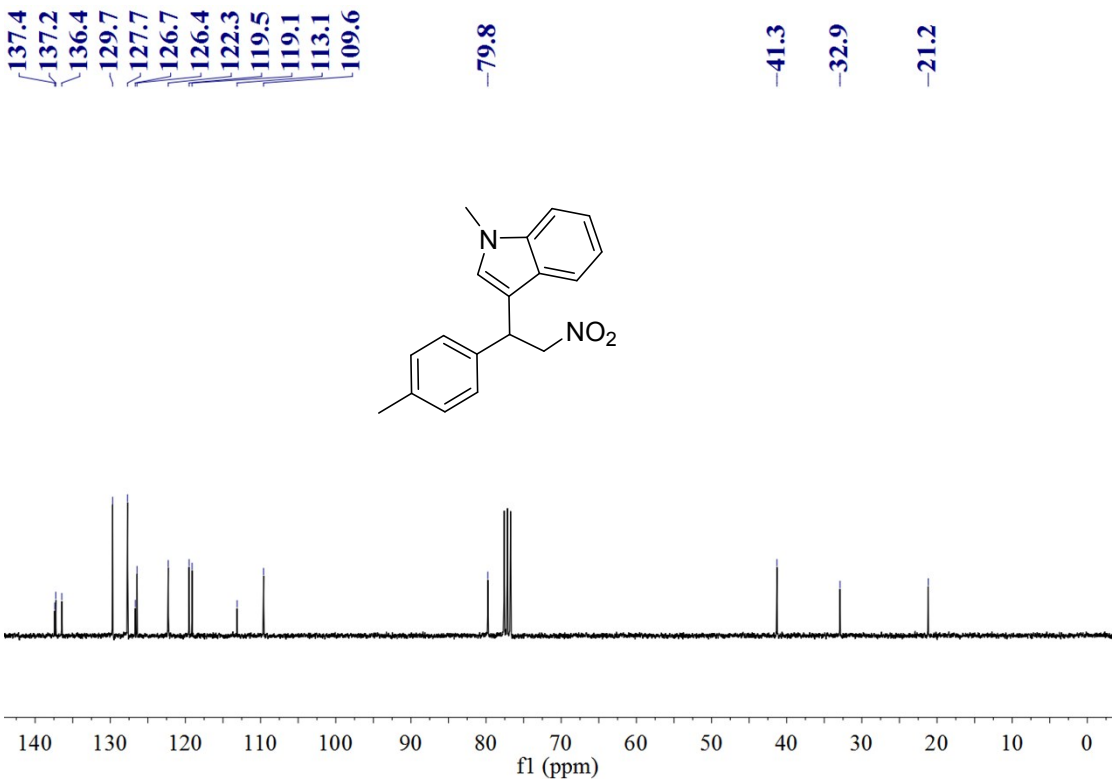

Figure S60. ^{13}C-NMR spectrum of Compound 3b in $CDCl_3$

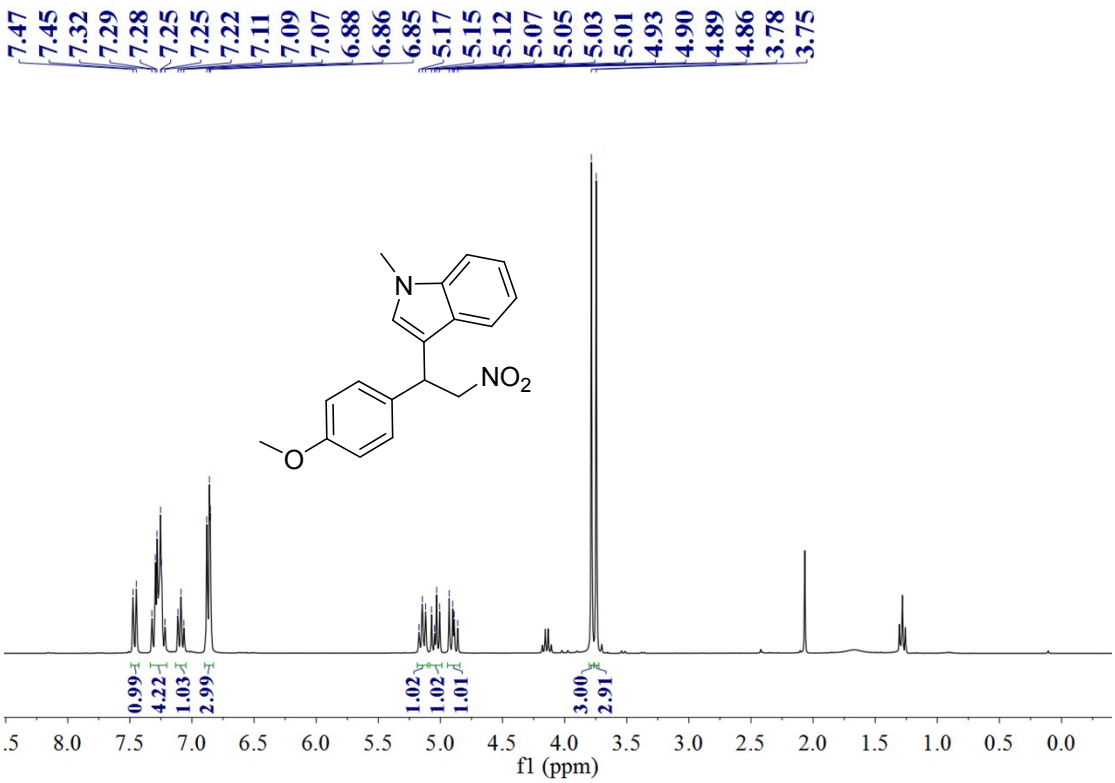

Figure S61. ^{1}H-NMR spectrum of Compound 3c in $CDCl_3$

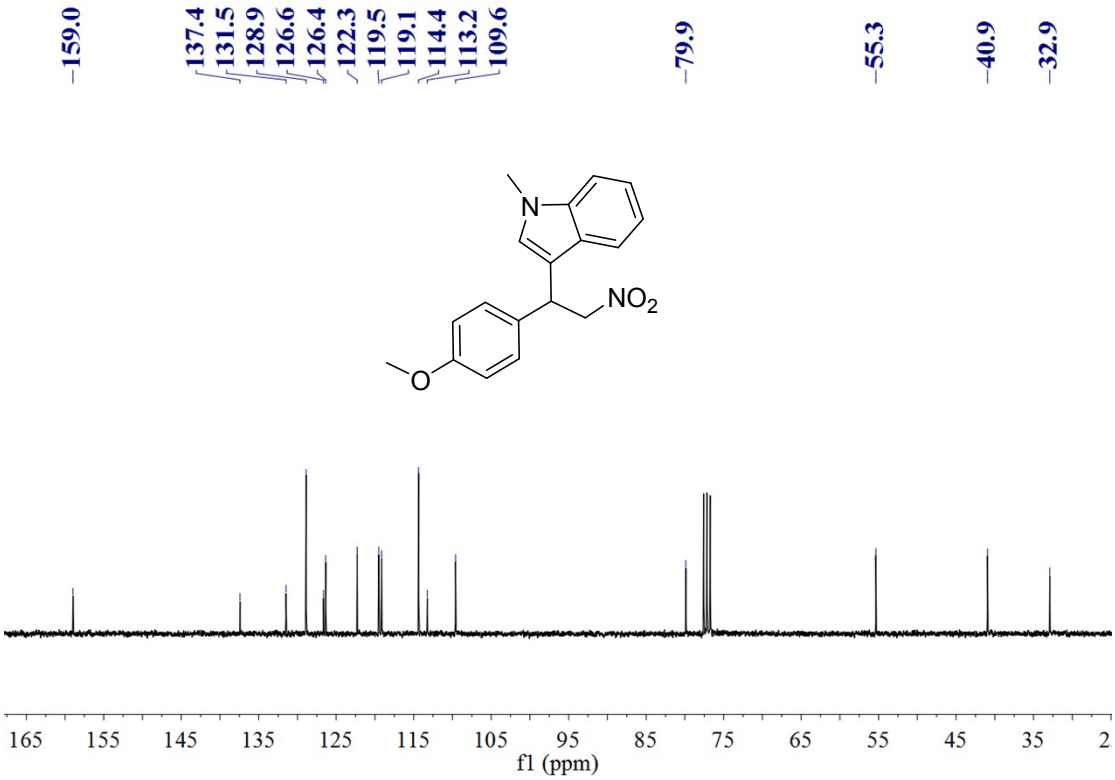

Figure S62. ^{13}C-NMR spectrum of Compound 3c in $CDCl_3$

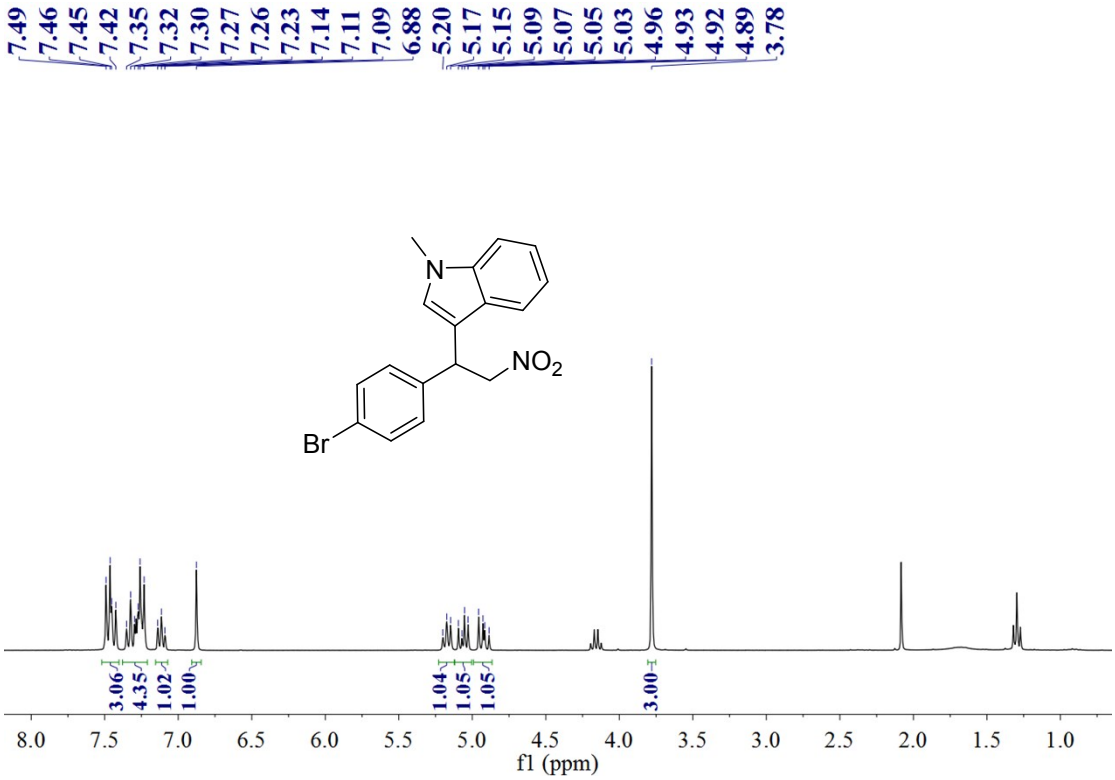

Figure S63. ^{1}H-NMR spectrum of Compound 3d in $CDCl_3$

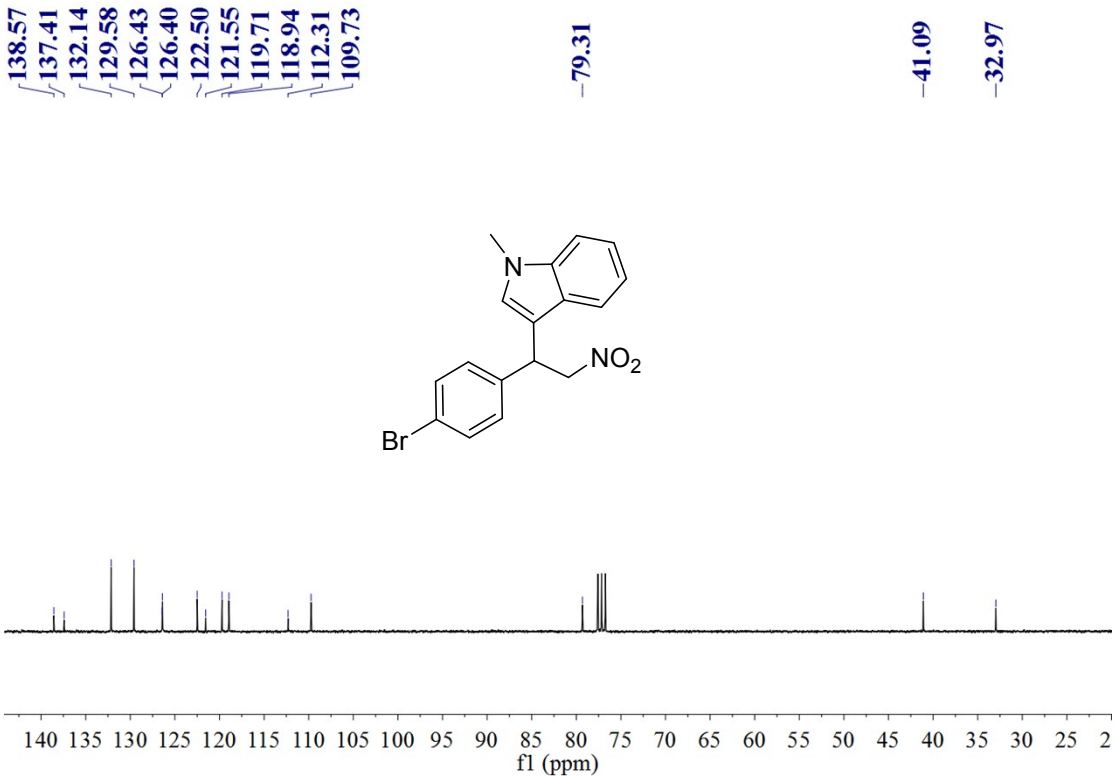

Figure S64. ^{13}C-NMR spectrum of Compound 3d in $CDCl_3$

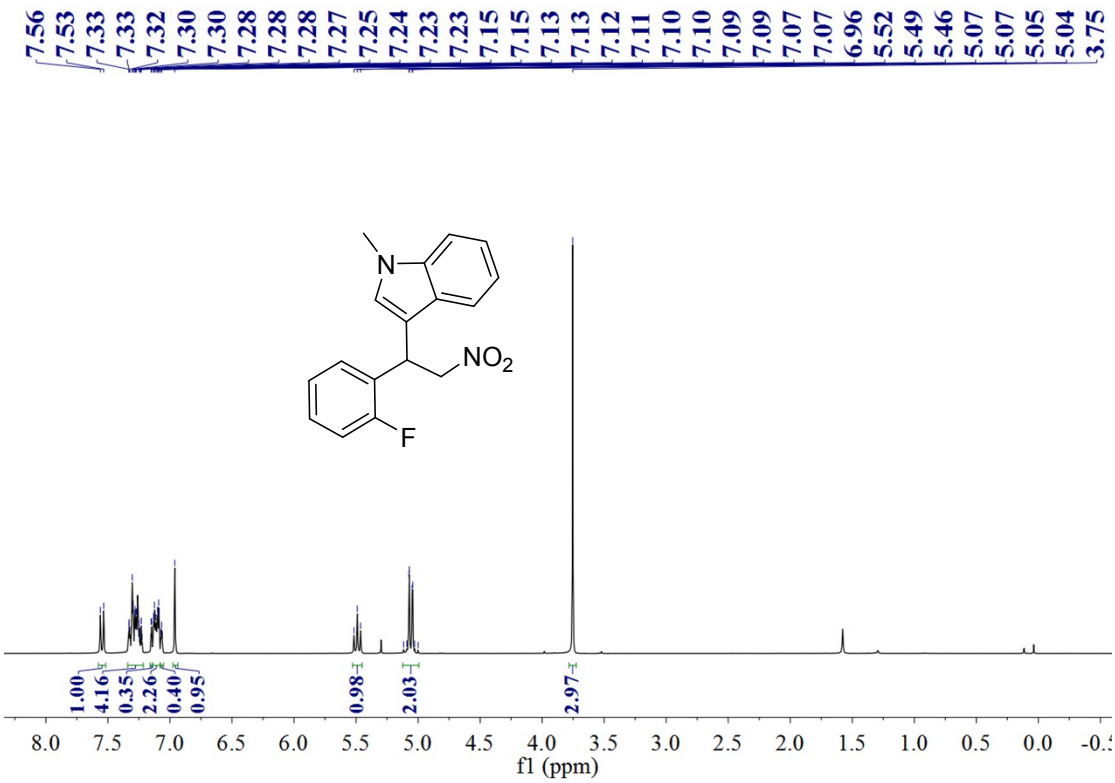

Figure S65. ^{1}H-NMR spectrum of Compound 3e in $CDCl_3$

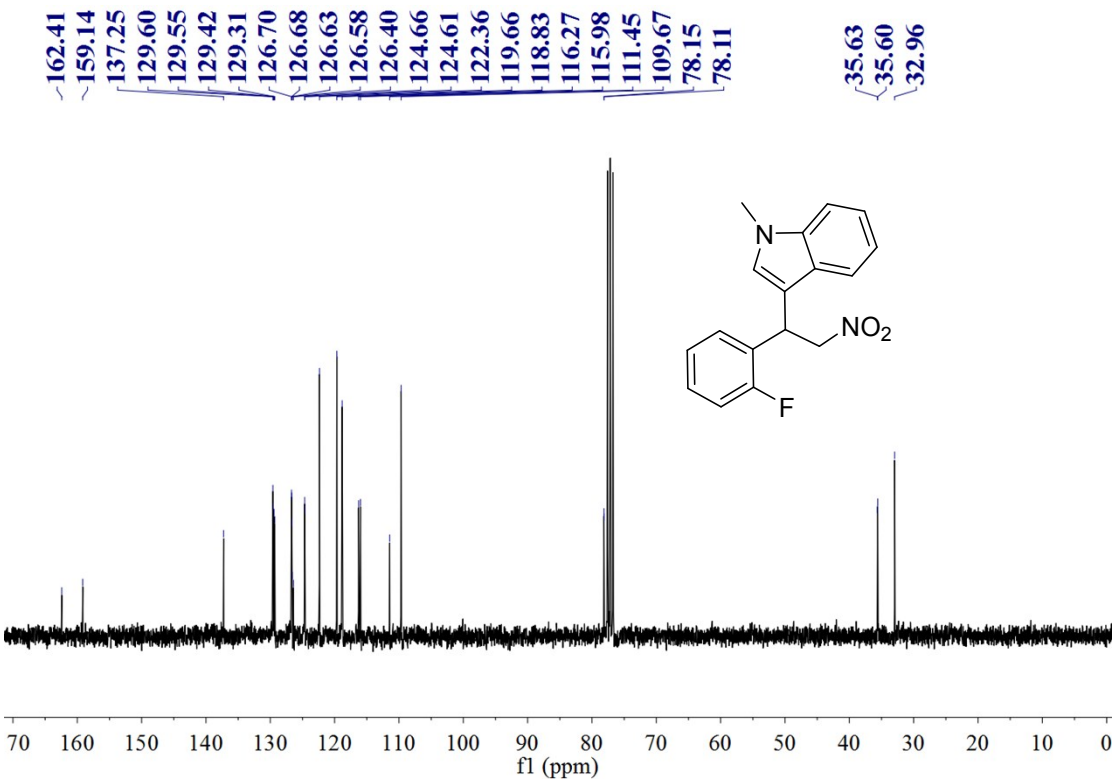

Figure S66. ^{13}C-NMR spectrum of Compound 3e in $CDCl_3$

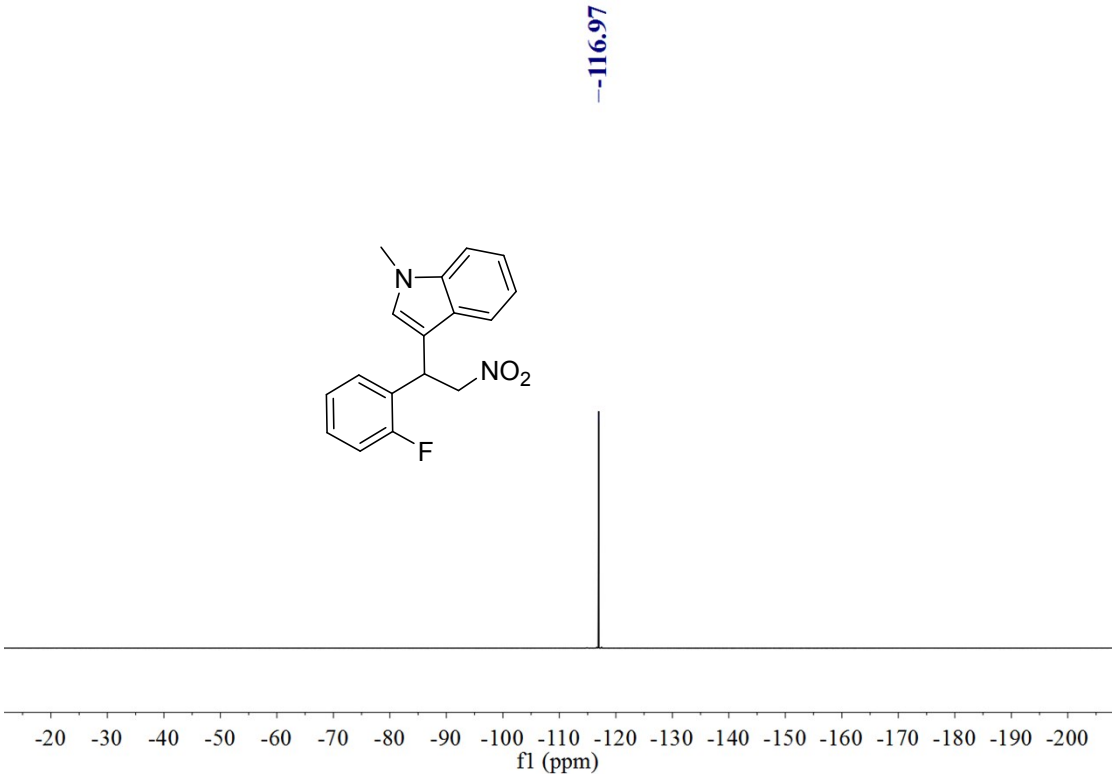

Figure S67. ^{19}F-NMR spectrum of Compound 3e in $CDCl_3$

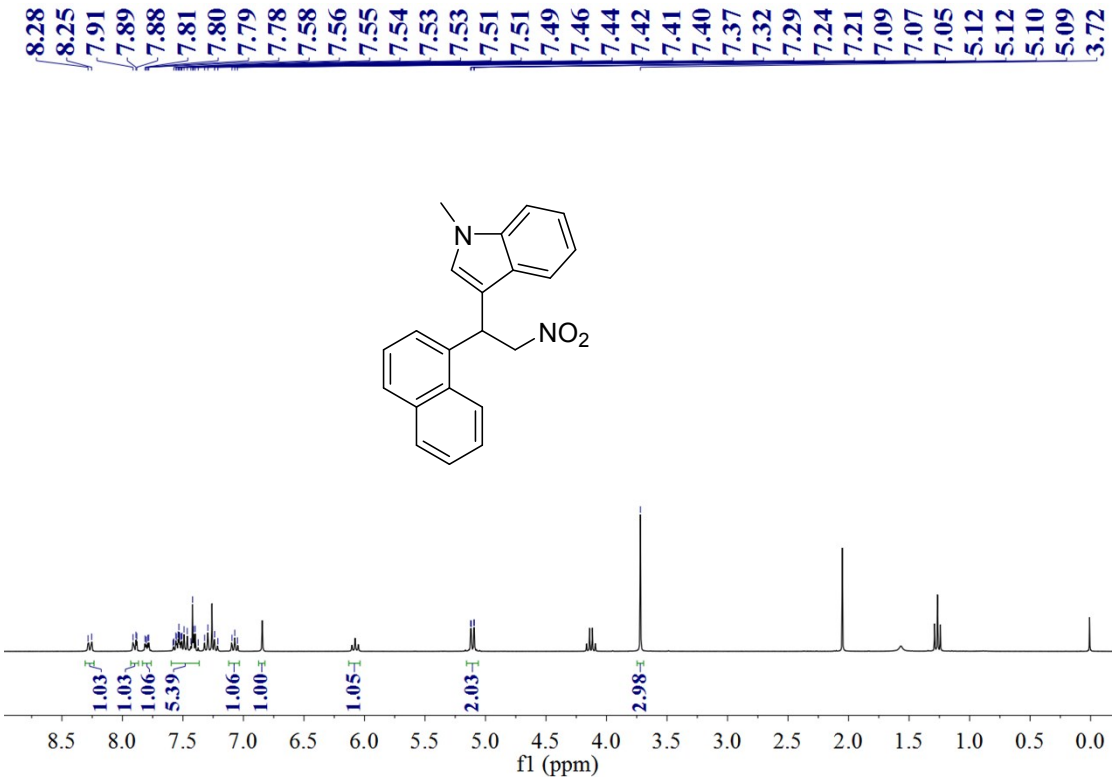

Figure S68. ^{1}H-NMR spectrum of Compound 3f in $CDCl_3$

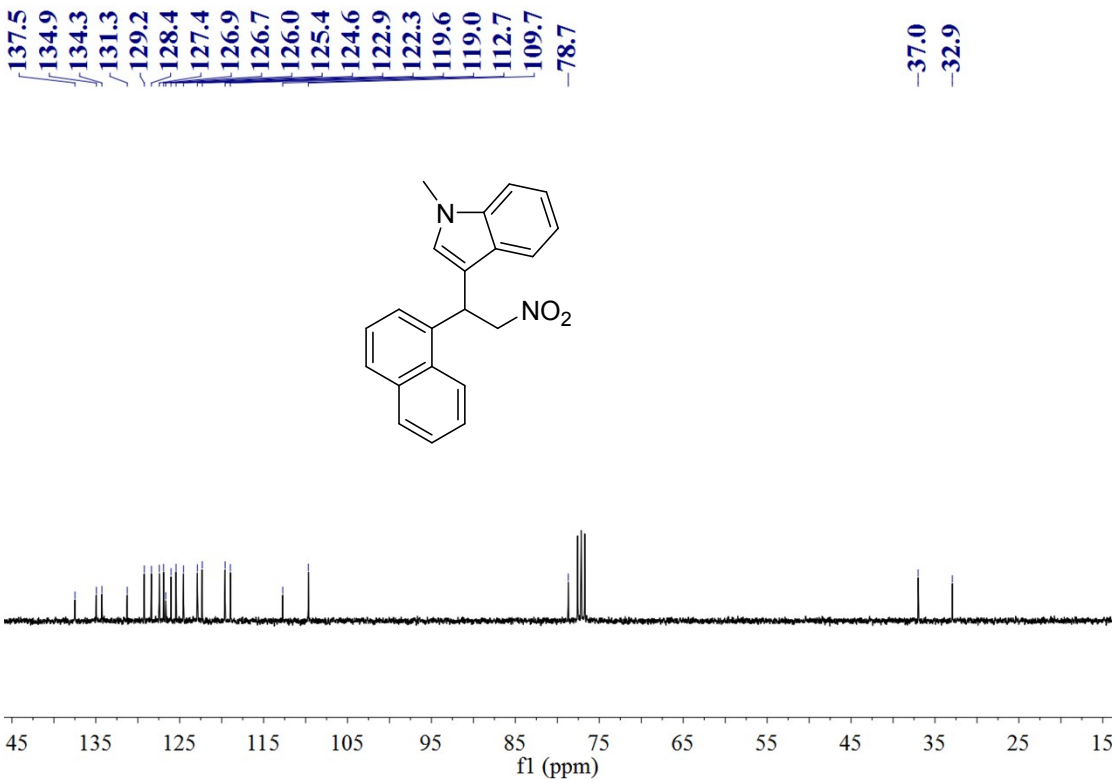

Figure S69. ^{13}C-NMR spectrum of Compound 3f in $CDCl_3$

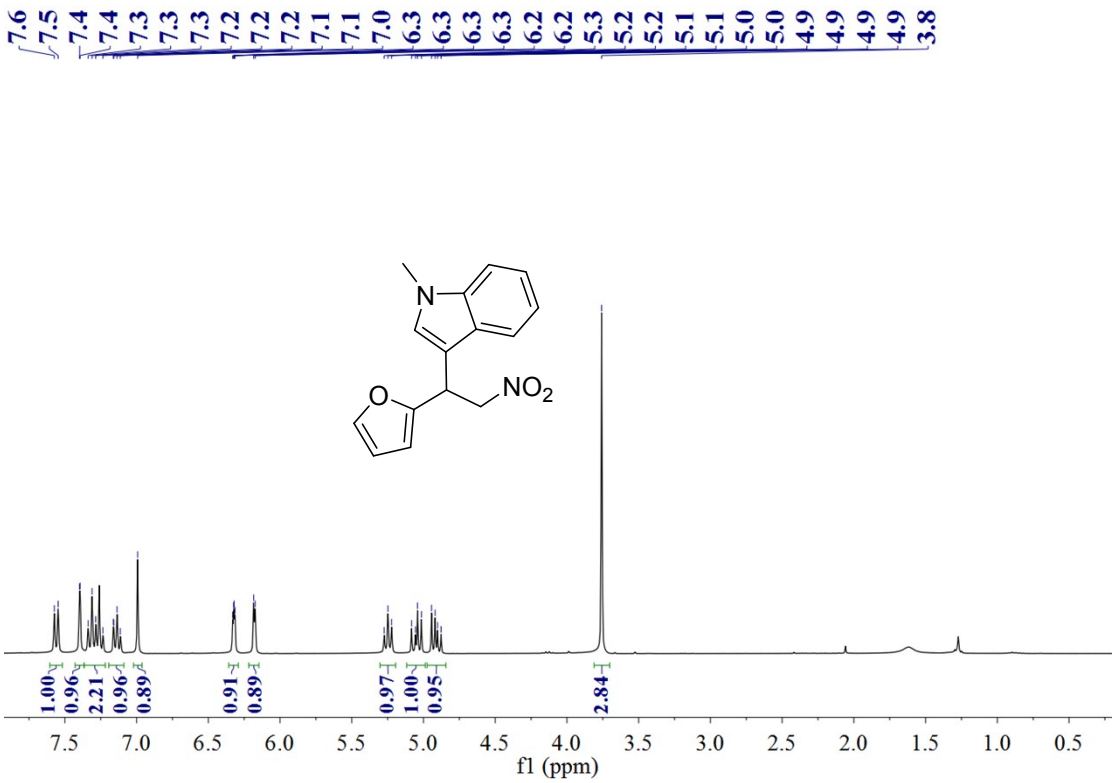

Figure S70. ^{1}H-NMR spectrum of Compound 3g in $CDCl_3$

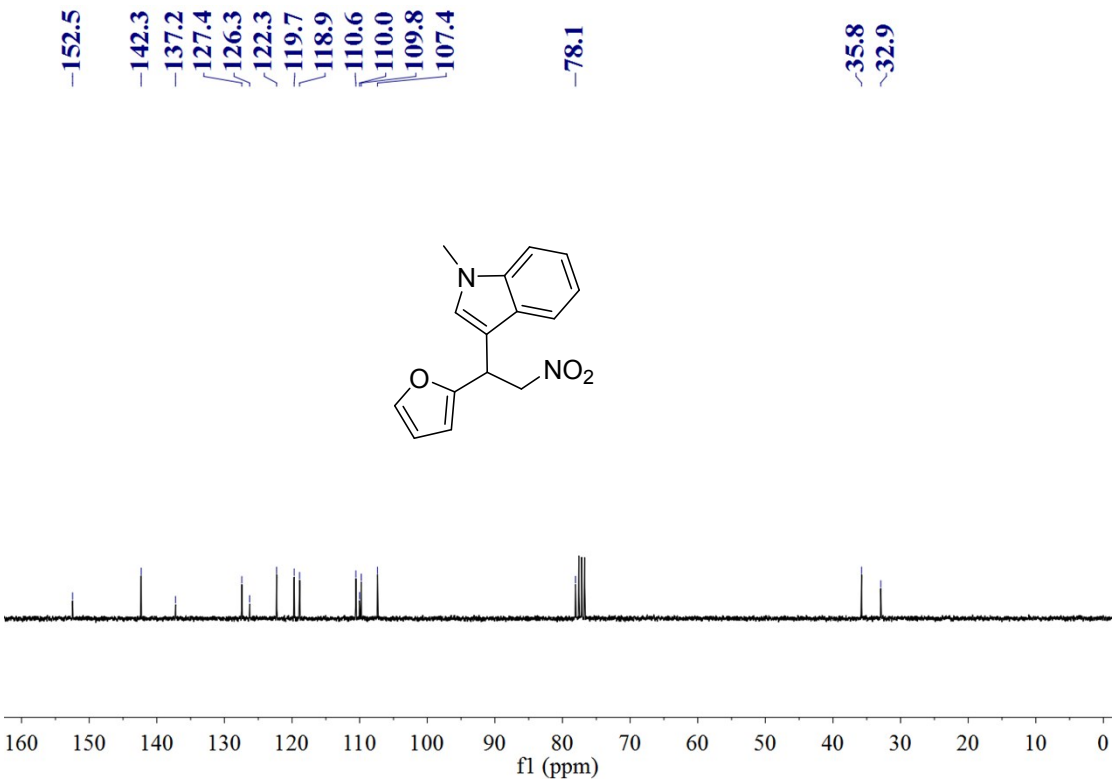

Figure S71. ^{13}C-NMR spectrum of Compound 3g in $CDCl_3$

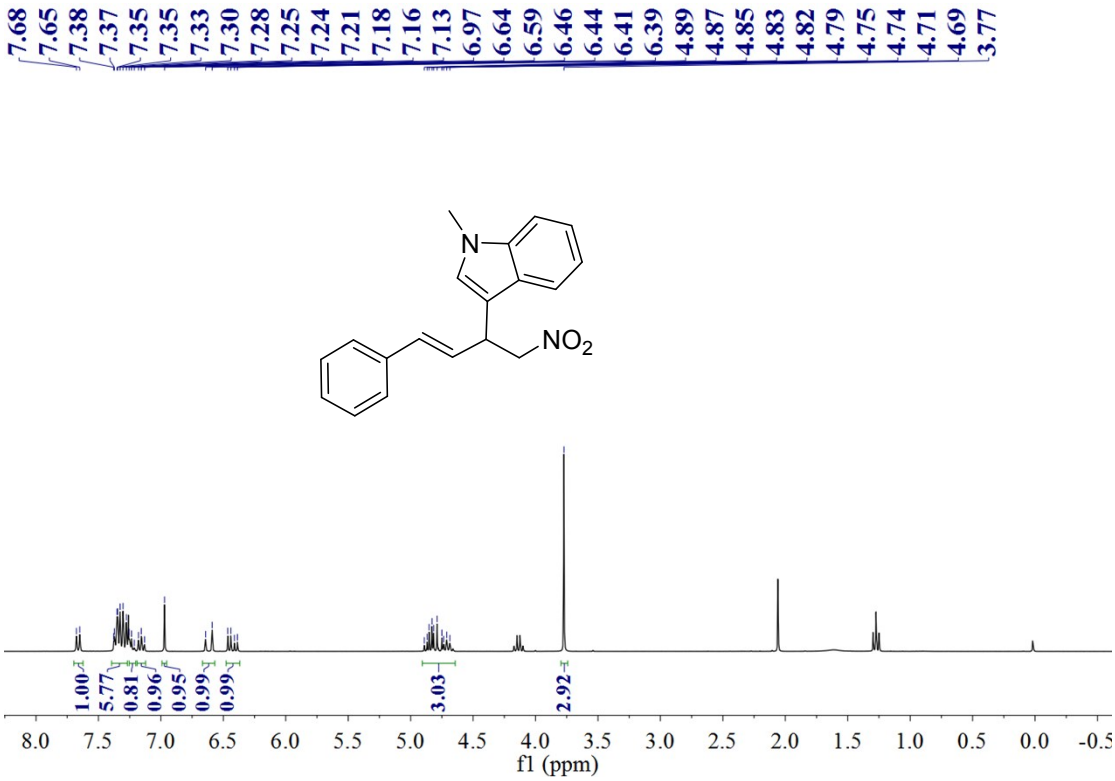

Figure S72. ^{1}H-NMR spectrum of Compound 3h in $CDCl_3$

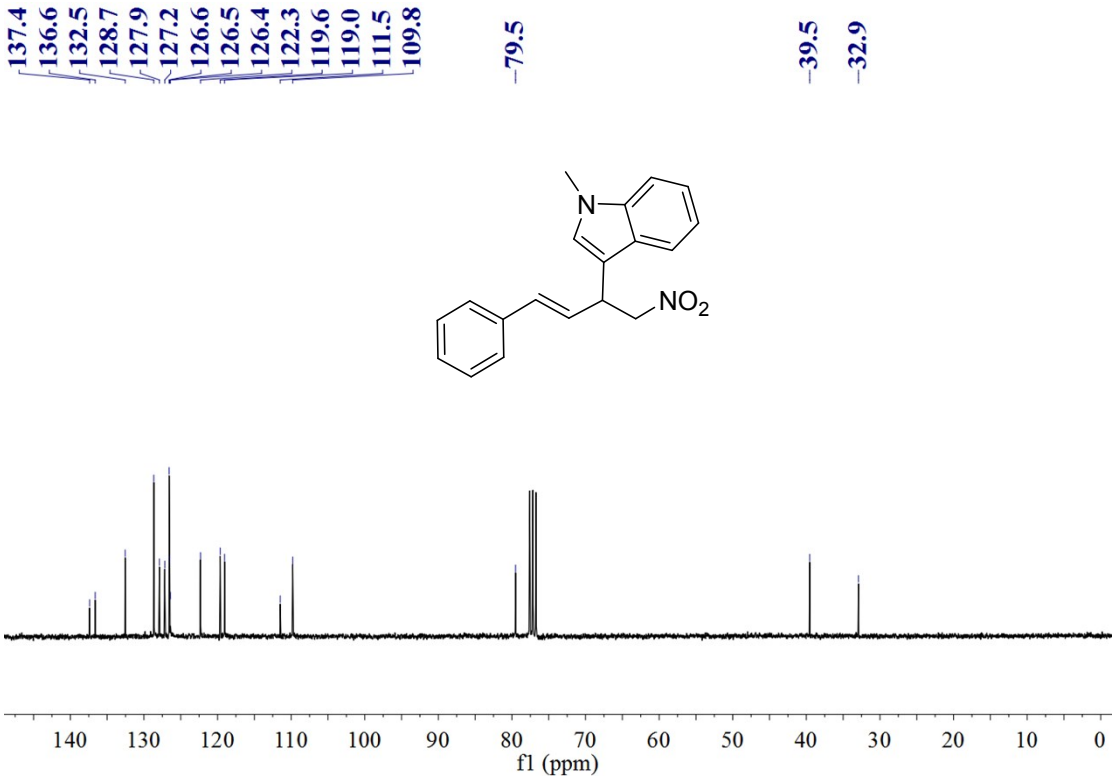

Figure S73. ^{13}C-NMR spectrum of Compound 3h in $CDCl_3$

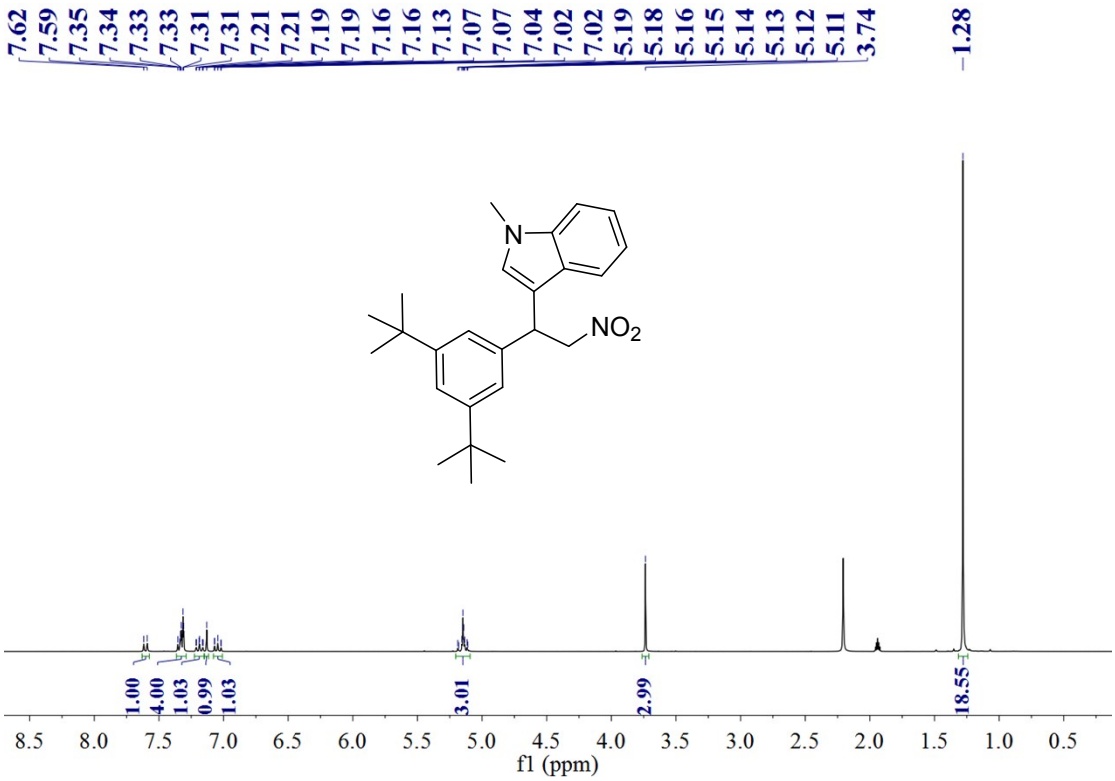

Figure S74. ^{1}H-NMR spectrum of Compound 3i in CD_3CN

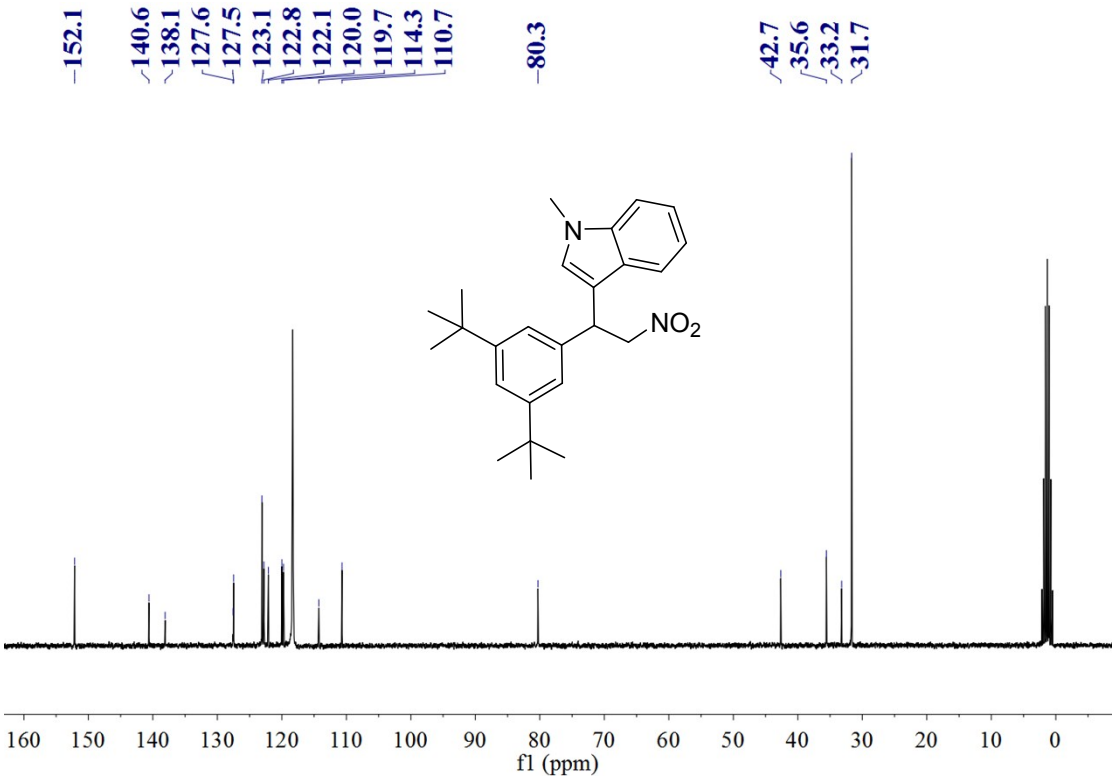

Figure S75. ^{13}C-NMR spectrum of Compound 3i in CD_3CN