Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information

A Robust Heterogeneous Co-MOFs Catalyst in Azide-alkynes Cycloaddition and Friedel-Crafts Reactions as well as Hydrosilylation of Alkynes

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Section 1. Supporting information for 1-2

Crystal structure determination.

Single crystals of **1-2** were chosen under an optical microscope and mounted on a glass fiber for data collection. All reflection data were collected on an Agilent Supernova diffractometer (Mo, λ= 0.71073 Å) at room temperature. The data integration and reduction were processed using CrysAlisPro software. The structures were solved by direct methods using ShelXS and refined using a full-matrix least-squares technique within ShelXL 2015 and OLEX-II Program.[1] All non-hydrogen atoms were refined anisotropically until convergence is reached. Hydrogen atoms attached to the organic moieties present in all compounds are either located from the difference Fourier map or stereochemically fixed. Guest molecules in **1** and **2** are significantly disordered and could not be modeled properly due to the lack of well define atomic, positions, and PLATON/SQUEEZE was employed to remove these electron densities. The Squeeze procedure is a widely used and accepted method that corrects diffraction data for structures affected by the presence of heavily disordered solvent. However, the use of Squeeze does not impact the framework atoms. Summary of crystallographic

data and details of data collection for **1** and **2** are given in Table S1. Selected bond lengths and angles for **1-2** are collected in Table S2. Crystallographic data for the structural analyses has been deposited at the Cambridge Crystallo-graphic Data Centre (CCDC reference numbers: (1977363-1977364).

Table S1. Crystallographic data and structure refinement parameters for 1-2.

Complex	**1**	**2**
Empirical formula	$C_{16}H_{13}Co_2N_5O_6$	$C_{16}H_{13}Co_2N_5O_6$
Formula weight (M)	489.16	489.16
Crystal system	Hexagonal	Hexagonal
Space group	$P6_3$	$P6_3$
a (Å)	21.6539 (9)	21.6328 (9)
b (Å)	—	—
c (Å)	8.3373 (3)	8.3468 (4)
α (°)	90.00	90.00
β (°)	90.00	90.00
γ (°)	120.00	120.00
V/(Å3)	3385.5 (2)	3382.8 (3)
Z	6	6
Dc(Mg cm-3)	1.434	1.456
F(000)	1464.0	1492
θ range for data collection (°)	3.9–28.3°	3.8-28.3
Reflections collected /	20859/4411	20766/4521
unique	[R(int) =0.046]	[R(int) =0.058]
Goodness-of-fit on F2	1.052	0.97
Final R indices [I > 2σ(I)]	R1 = 0.0241	R1 = 0.0327
	ωR2= 0.0563	ωR2= 0.0631
R indices (all data)	R1 = 0.0284	R1 = 0.0416

	ωR2= 0.0587		ωR2= 0.0658

Table S2. Selected bond lengths (Å) and angles (º) for 1-2

Complex 1			
Co1—O1	2.119 (3)	Co2—O3	2.012 (3)
Co1—O3	2.003 (3)	Co2—O6	2.142 (3)
Co1—O2A	2.371 (3)	Co2—O4	2.104 (3)
Co1—O5A	2.015 (3)	Co2—O2A	2.268 (3)
Co1—N3	2.114 (3)	Co2—N4	2.129 (3)
Co1—N5B	2.112 (3)	Co2—N1C	2.136 (3)
O1—Co1—O2A	90.04 (10)	O3—Co2—O6	162.39 (11)
O3—Co1—O1	80.16 (10)	O3—Co2—O4	92.49 (11)
O3—Co1—O2A	76.39 (10)	O3—Co2—O2A	78.65 (10)
O3—Co1—O5A	162.87 (11)	O3—Co2—N4	88.35 (11)
O3—Co1—N3	90.35 (11)	O3—Co2—N1C	98.68 (12)
O3—Co1—N5B	97.74 (12)	O6—Co2—O2A	85.40 (10)
O5A—Co1—O1	87.00 (11)	O4—Co2—O6	80.24 (12)
O5A—Co1—O2A	92.45 (10)	O4—Co2—O2A	90.94 (11)

O5A—Co1—N3	101.42 (13)	O4—Co2—N4	176.24 (12)
O5A—Co1—N5B	93.49 (12)	O4—Co2—N1C	89.81 (13)
N3—Co1—O1	169.62 (11)	N4—Co2—O6	97.93 (12)
N3—Co1—O2A	83.60 (10)	N4—Co2—O2A	85.63 (11)
N5B—Co1—O1	89.85 (12)	N4—Co2—N1C	93.69 (12)
N5B—Co1—O2A	174.05 (11)	N1C—Co2—O6	97.33 (12)
N5B—Co1—N3	95.62 (12)	N1C—Co2—O2A	177.26 (11)
Complex 2			
Co1—O1	2.121 (3)	Co2—O2A	2.269 (3)
Co1—O2A	2.372 (3)	Co2—O3	2.009 (3)
Co1—O3	2.006 (3)	Co2—O4	2.092 (3)
Co1—O5A	2.012 (3)	Co2—O6	2.130 (5)
Co1—N3	2.109 (4)	Co2—N1C	2.135 (4)
Co1—N5B	2.118 (4)	Co2—N4	2.128 (4)
O1—Co1—O2A	89.92 (12)	O3—Co2—O2A	78.86 (12)
O3—Co1—O1	80.08 (12)	O3—Co2—O4	92.38 (13)

O3—Co1—O2A	76.47 (12)	O3—Co2—O6	162.73 (15)
O3—Co1—O5A	162.82 (14)	O3—Co2—N1C	98.52 (14)
O3—Co1—N3	90.52 (13)	O3—Co2—N4	88.56 (13)
O3—Co1—N5B	97.62 (14)	O4—Co2—O2A	90.81 (14)
O5A—Co1—O1	87.04 (13)	O4—Co2—O6	80.25 (18)
O5A—Co1—O2A	92.30 (12)	O4—Co2—N1C	90.31 (15)
O5A—Co1—N3	101.25 (15)	O4—Co2—N4	175.93 (15)
O5A—Co1—N5B	93.68 (15)	O6—Co2—O2A	85.61 (15)
N3—Co1—O1	169.63 (13)	O6—Co2—N1C	97.11 (17)
N3—Co1—O2A	83.58 (13)	N1C—Co2—O2A	177.19 (14)
N3—Co1—N5B	95.60 (15)	N4—Co2—O2A	85.49 (13)
N5B—Co1—O1	90.02 (14)	N4—Co2—O6	97.76 (18)
N5B—Co1—O2A	174.01 (14)	N4—Co2—N1C	93.47 (14)

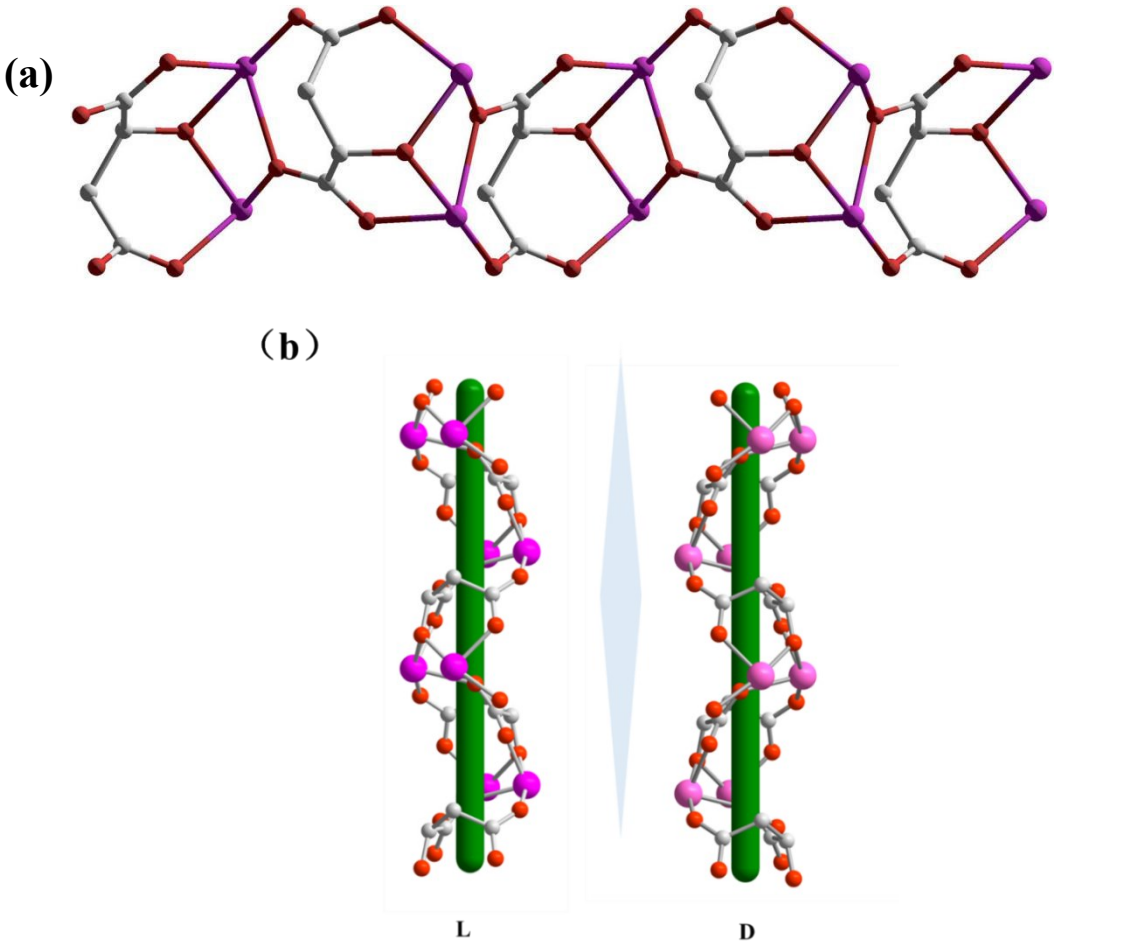


Figure S1. (a) the structure of **1** showing the 1D [Co(L-mac)] chain; (b) the enantiomeric [Co(L-mac)] and [Co(D-mac)] chain in **1** and **2**, respectively.

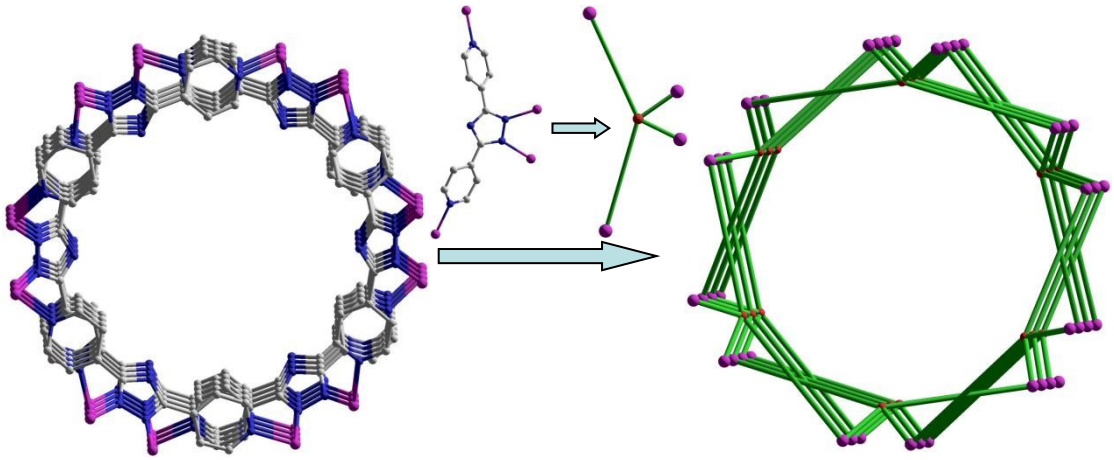


Figure S2. the 1D [Co(4,4´-bpt)] chain and its schematic description.

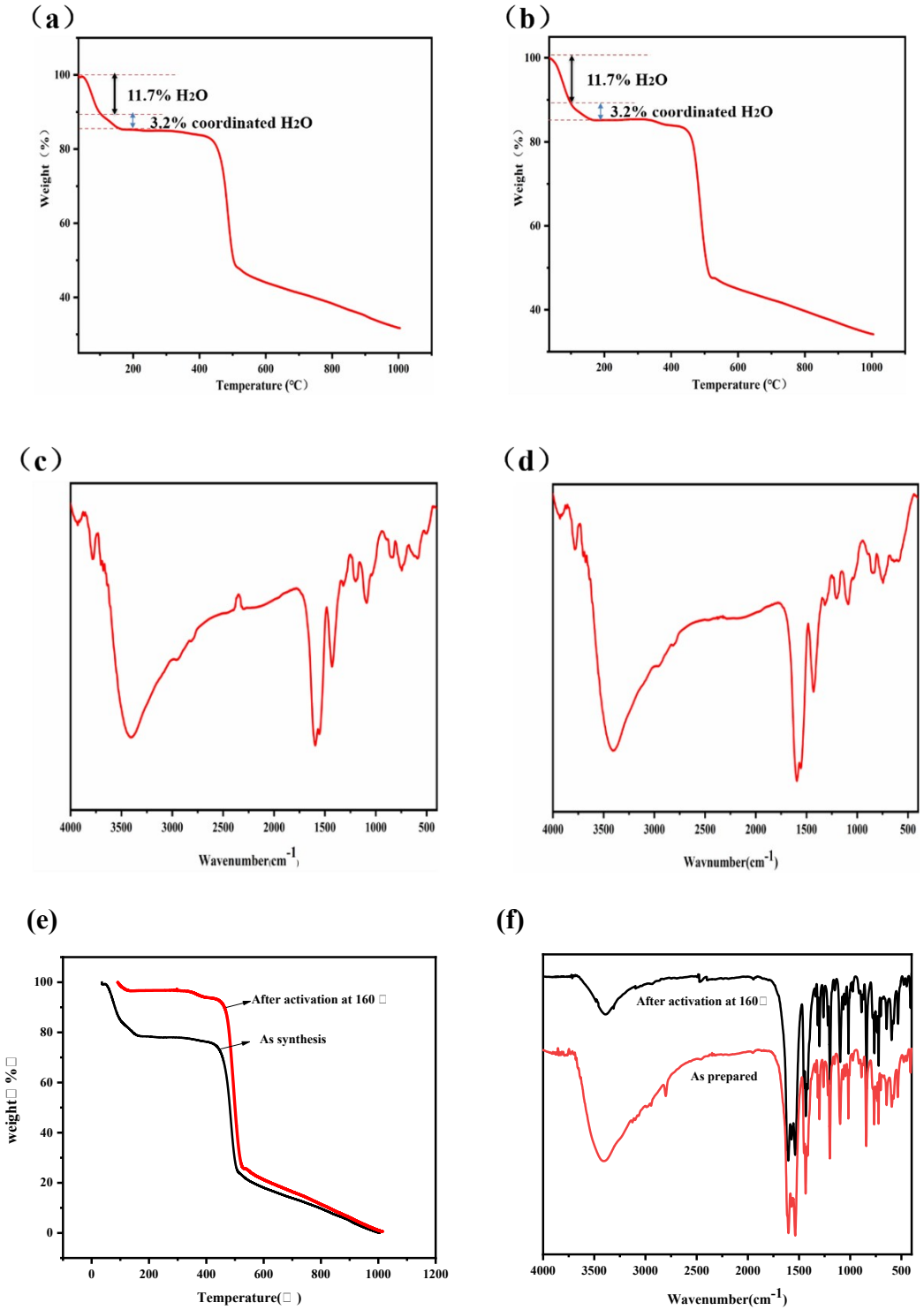


Figure S3. the Thermogravimetric analyses (TGA) curves (a-b, e) and the FTIR spectra (c-d, f) of **1-2** recorded in KBr palates.

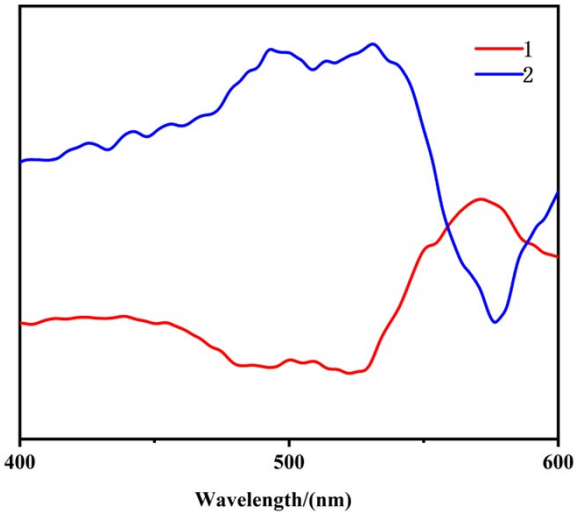
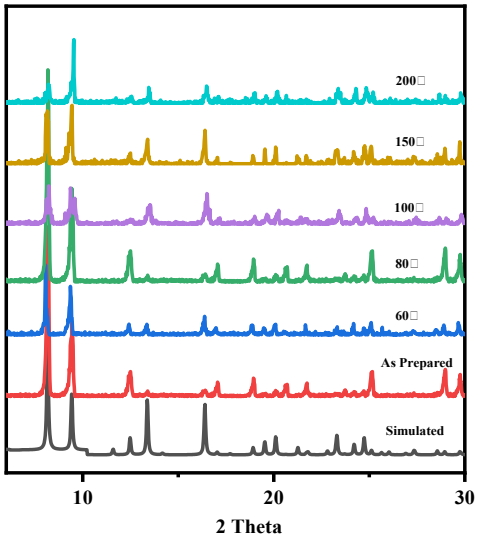
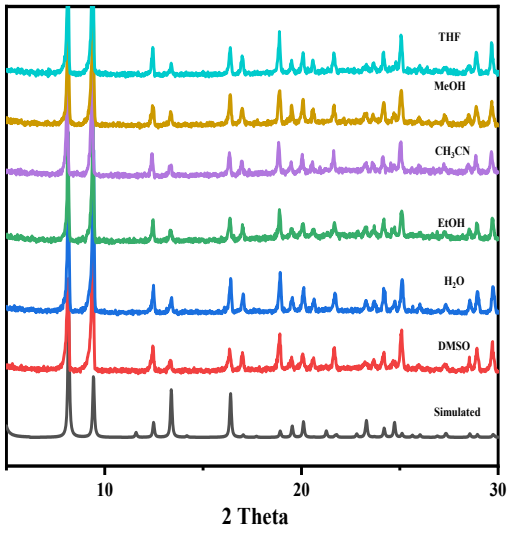


Figure S4. the Solid-state CD spectra of **1** (red line) and **2** (blue line).

(a)



(b)



(c)

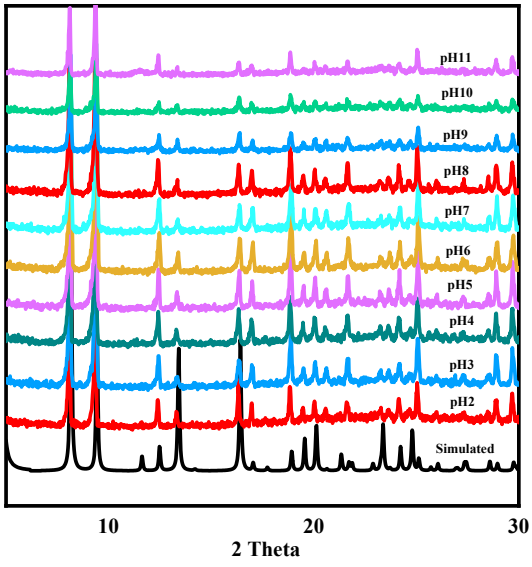


Figure S5. The XRD patterns of **2** at different temperatures (a), after immersing in different solvents (b) and different acid/base condition (c).

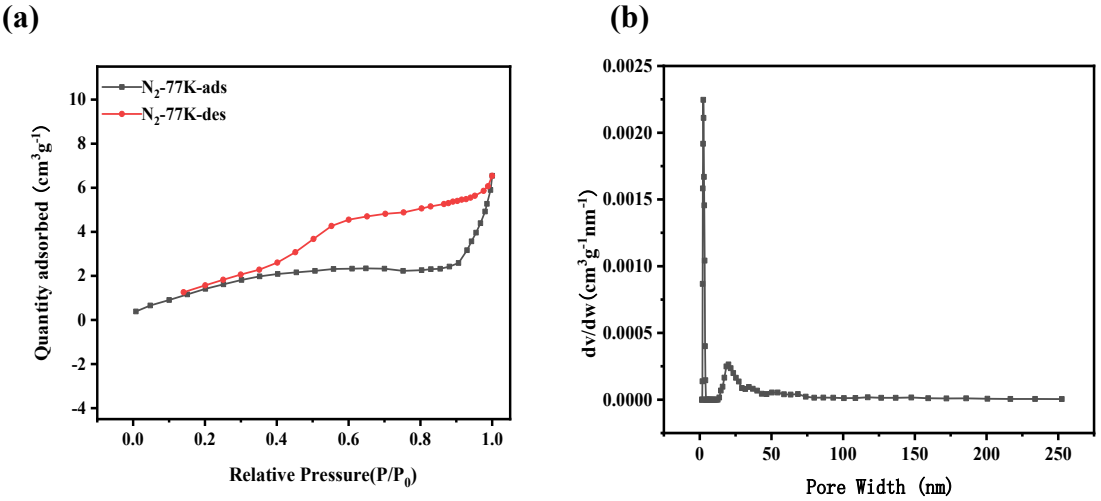


Figure S6. N_2 adsorption–desorption isotherms at 77 K(left) and porous size distribution (PSD) curve calculated from N_2 adsorption isotherm using the HorvathKawazoe model(right).

Section 2. Supporting information for Azide-alkynes Cycloaddition Reactions Catalyzed by 1

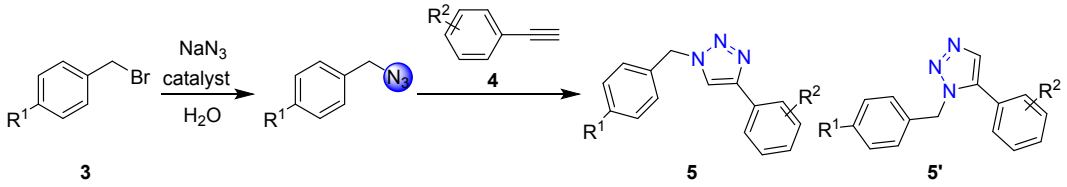


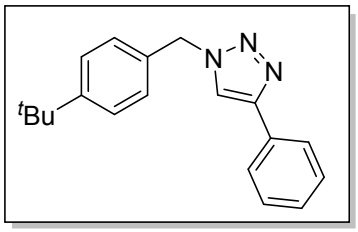
Table S3. Screening of temperatures [a]

Entry	T (℃)	t/h	Isolated yield of **5**+**5'**
1	60	6	68
2	50	6	57
3	70	6	67
4	80	6	68
5	60	5	64
6	60	7	68

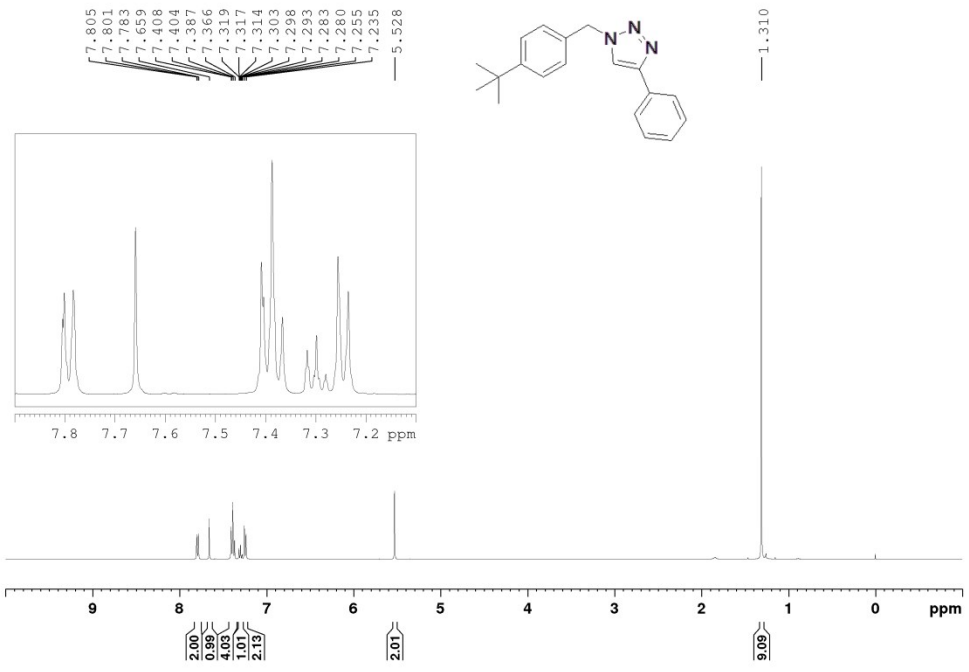
[a] Reaction conditions: benzyl bromide (1 mmol), NaN_3 (1.5 mmol), H_2O (2 mL), Co-MOF (0.02 mmol), *p*-methyl phenylacetylene (1.5 mmol) and reaction 6 h.

On the basis of the above observation, the activity of **1** was first examined in which the azidation of benzyl bromine with NaN_3 in aqueous solution was chosen as a model reaction to optimize the reaction conditions. As show in Table S3, we screened the reaction temperature with (bromomethyl) benzene and 1-ethynyl-4-methylbenzene as substrates. The performance of **1** in the model azidation experiment exhibited that there was no significant correlation with temperature in a small range. For example, 1,2,3-triazole was obtained in an isolated yield of 68 % at 60 ℃ and 80 ℃. (entries 1 and 4, Table S3). Besides, a 57 % conversion was obtained when the action temperature down to 50 ℃. This suggests that the yield decreased slightly when the temperature was lowered (entry 2, Table S3); What is more, the yield did not increase significantly when

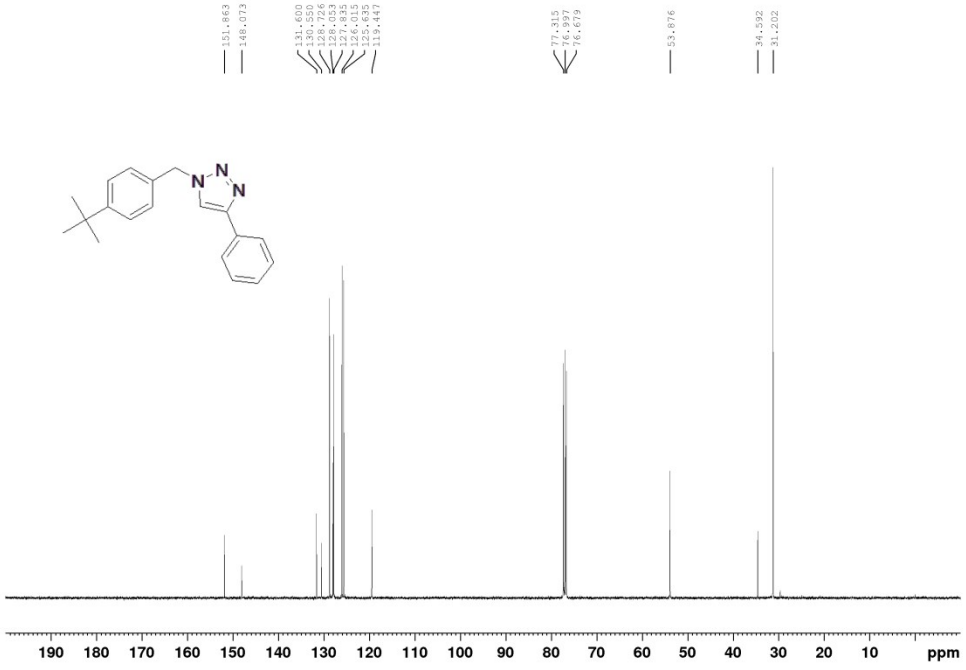
the temperature was increased (entries 3-4, Table S3). The reaction temperature was controlled to 60 °C, we shortened the reaction time to 5 h, and the yield was 64% (entries 5, Table S3). When the reaction time was extended to 7 hours, the yield was 68% (entries 6, Table S3). Our optimized condition is to react at 60 °C for 6 h.



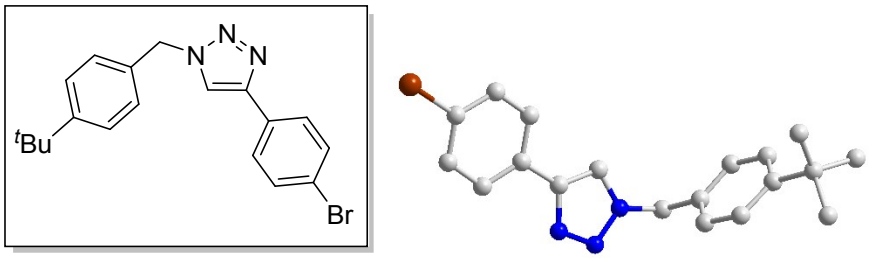
1-(4-(*tert*-butyl)benzyl)-4-phenyl-1*H*-1,2,3-triazole. White solid, 74% yield, mp 161-163 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.75 (m, 2H), 7.66 (s, 1H), 7.44-7.34 (m, 4H), 7.33-7.27 (m, 1H), 7.27-7.22 (2, H), 5.53 (s, 2H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.86, 148.07, 131.60, 130.55, 128.73, 128.05, 127.84, 126.02, 125.64, 119.45, 53.88, 34.59, 31.20. HRMS (ESI) *m/z* Calculated for $C_{19}H_{21}N_3$ $[M+H]^+$ 292.1808, found: 292.1812.



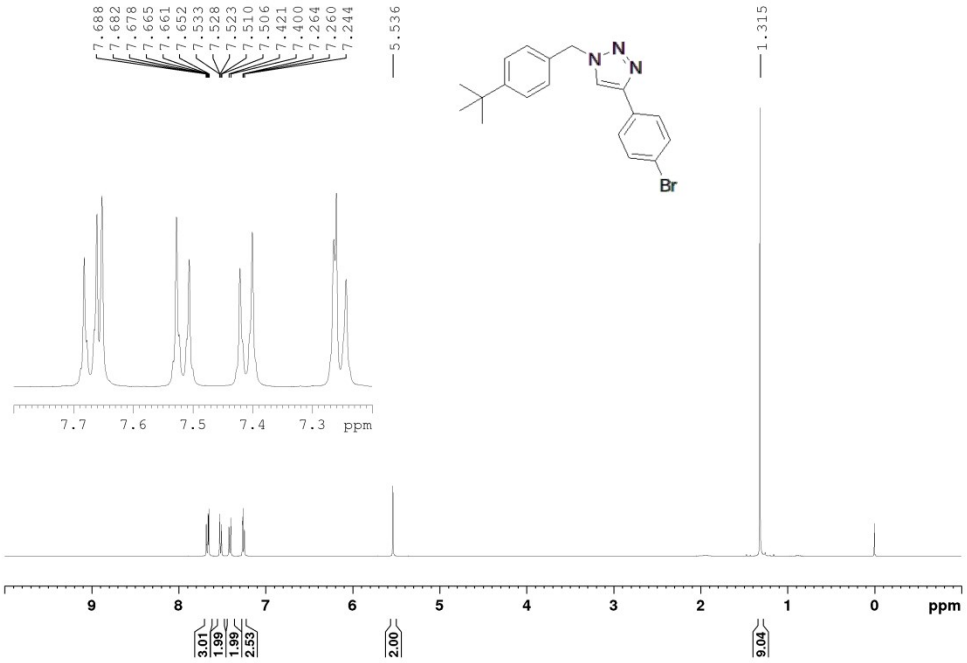
Spectrum of ^{1}H NMR



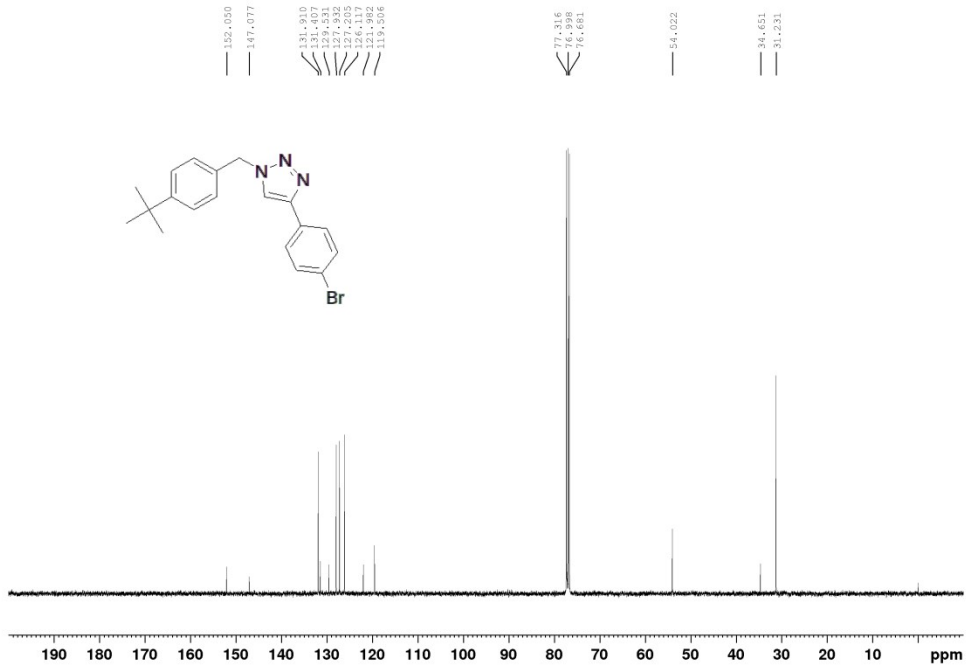
Spectrum of ^{13}C NMR



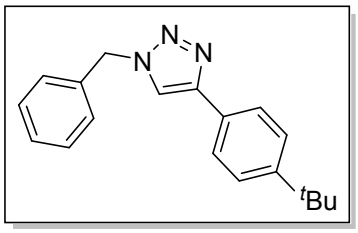
4-(4-bromophenyl)-1-(4-(*tert*-butyl)benzyl)-1*H*-1,2,3-triazole. White solid, 77% yield, mp 140-142 ℃**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.62 (m, 3H), 7.56-7.48 (m, 2H), 7.44-7.36 (m, 2H), 7.28-7.21 (m, 2H), 5.54 (s, 2H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.05, 147.08, 131.91, 131.41, 129.53, 127.93, 127.21, 126.12, 121.98, 129.51, 54.02, 34.65, 31.23. HRMS (ESI) *m/z* Calculated for $C_{19}H_{20}BrN_3$ $[M+H]^+$ 370.0913, found: 370.0916.



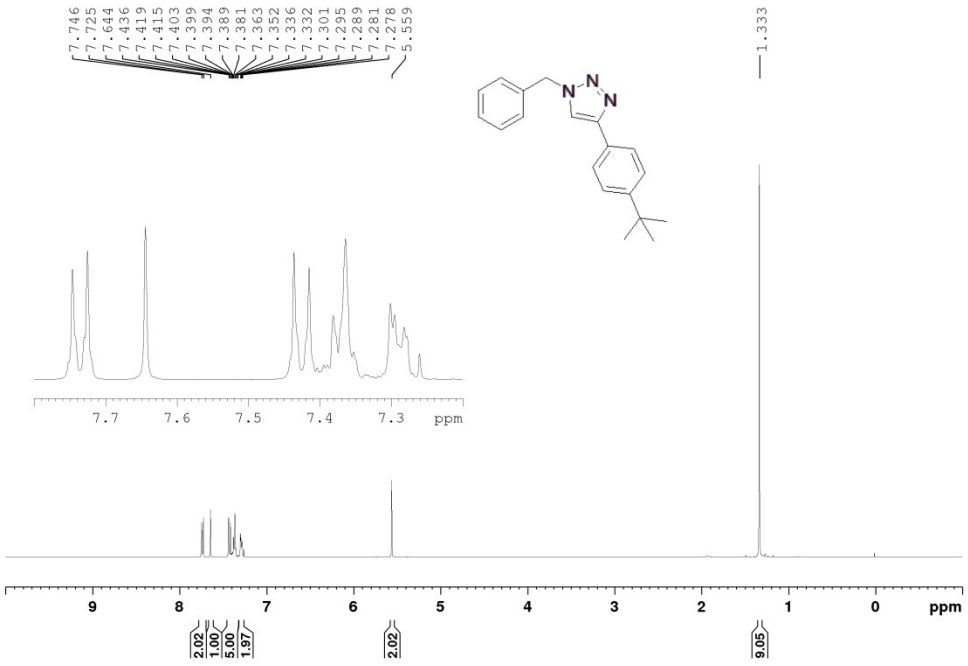
Spectrum of ^{1}H NMR



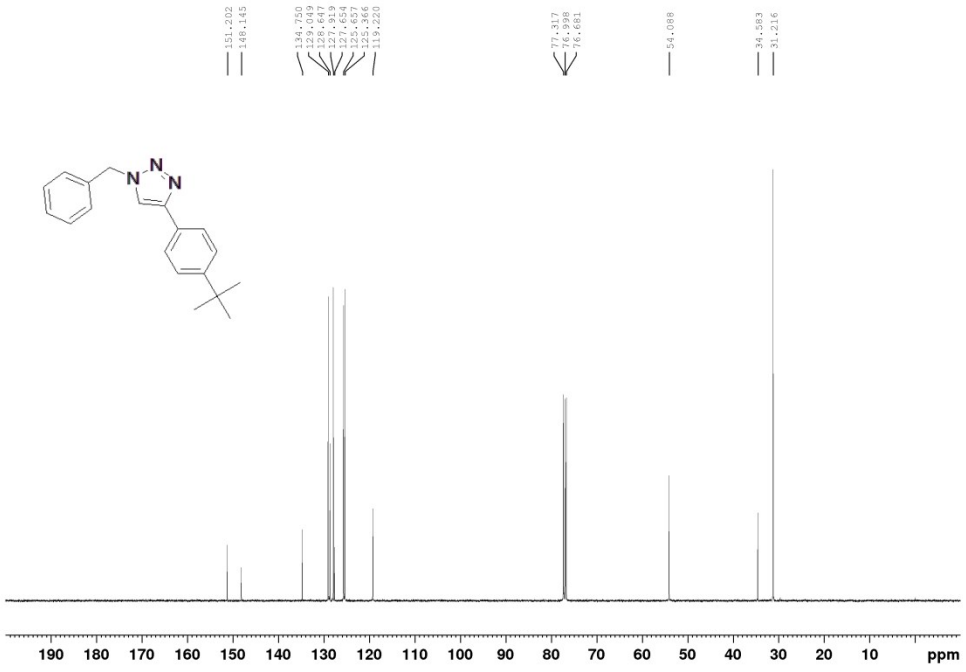
Spectrum of ^{13}C NMR



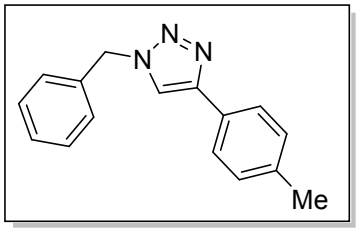
1-benzyl-4-(4-(*tert*-butyl)phenyl)-1*H*-1,2,3-triazole. White solid, 70% yield, mp 115-116 ℃**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.70 (m, 2H), 7.64 (s, 1H), 7.46-7.32 (m, 5H), 7.32-7.26 (m, 2H), 5.56 (s, 2H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.20, 148.15, 134.75, 129.05, 128.65, 127.92, 127.65, 125.66, 125.37, 119.22, 54.09, 34.58, 31.22. HRMS (ESI) *m/z* Calculated for $C_{19}H_{21}N_3$ $[M+H]^+$ 292.1808, found: 292.1812.



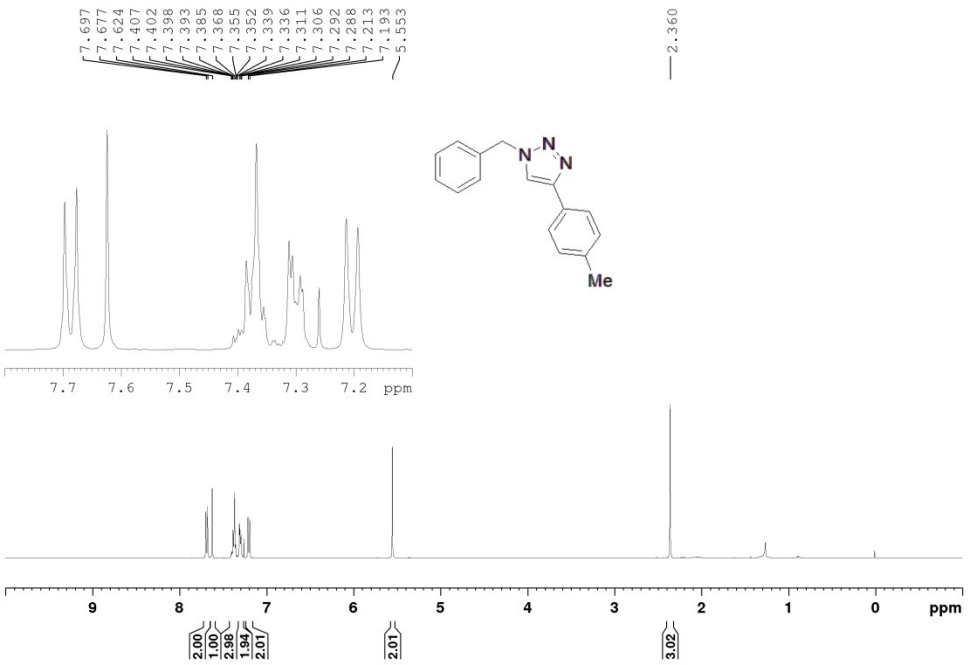
Spectrum of ^{1}H NMR



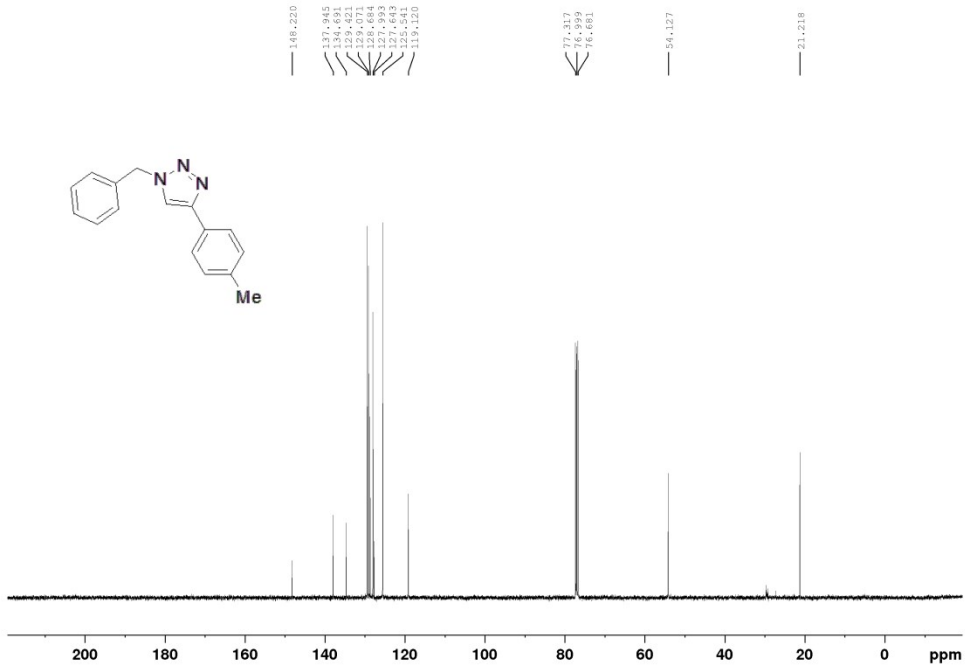
Spectrum of ^{13}C NMR



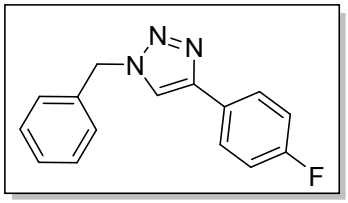
1-benzyl-4-(*p*-tolyl)-1*H*-1,2,3-triazole. White solid, 68% yield, mp 157-158 ℃**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.65 (m, 2H), 7.62 (s, 1H), 7.42-7.33 (m, 3H), 7.33-7.27 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.55 (s, 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.22, 137.94, 134.69, 129.42, 129.07, 128.68, 127.99, 127.64, 125.54, 119.12, 54.13, 21.22. HRMS (ESI) *m/z* Calculated for $C_{16}H_{15}N_3$ $[M+H]^+$ 250.1339, found: 250.1339.



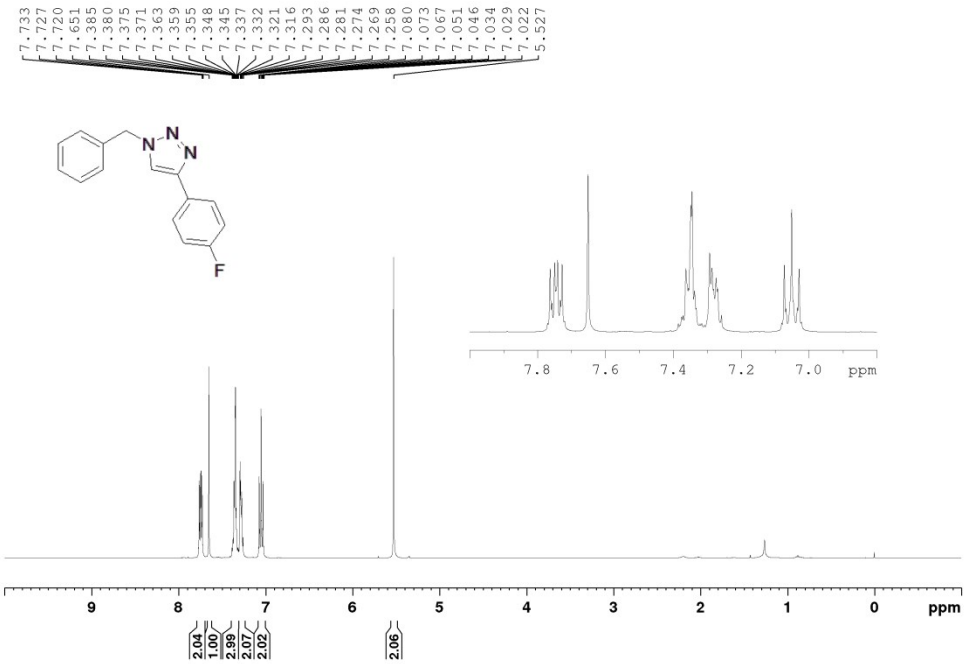
Spectrum of ^{1}H NMR



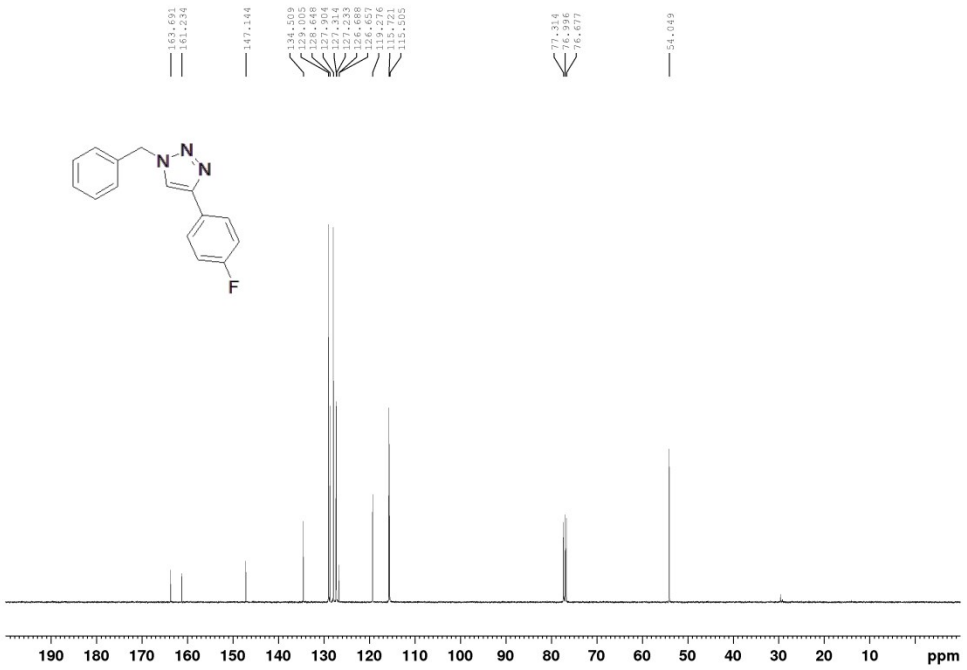
Spectrum of ^{13}C NMR



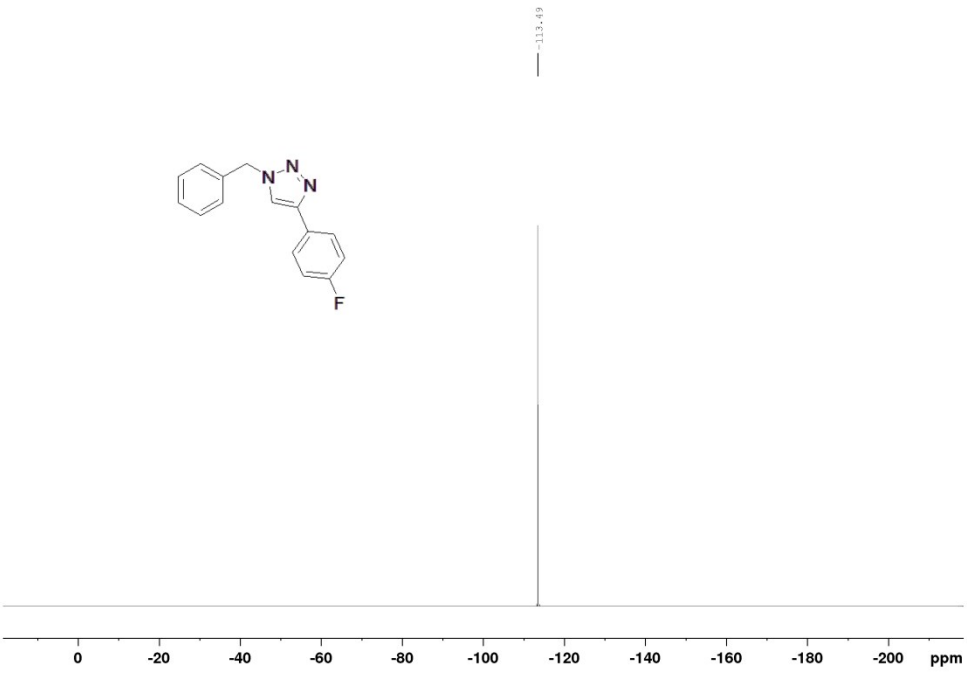
1-benzyl-4-(4-fluorophenyl)-1*H*-1,2,3-triazole. White solid, 71% yield, mp 111-112 ℃**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.70 (m, 2H), 7.65 (s, 1H), 7.40-7.31 (m, 3H), 7.31-7.24 (m, 2H), 7.09-7.00 (m, 2H), 5.53 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.69, 161.23, 147.14, 134.51, 129.01, 128.65, 127.90, 127.27 (d, *J*=8.1 Hz), 126.67 (d, *J*=3.1 Hz), 119.28, 115.61 (d, *J*=21.6Hz), 54.05. ^{19}F NMR (400 MHz, $CDCl_3$) δ -113.49. HRMS (ESI) *m/z* Calculated for $C_{15}H_{12}FN_3$ $[M+H]^+$ 254.1088, found: 254.1091.



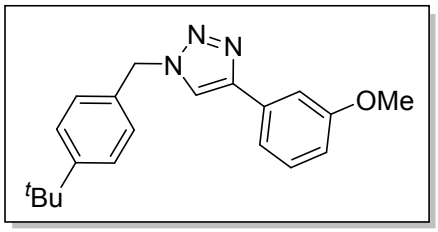
Spectrum of ^{1}H NMR



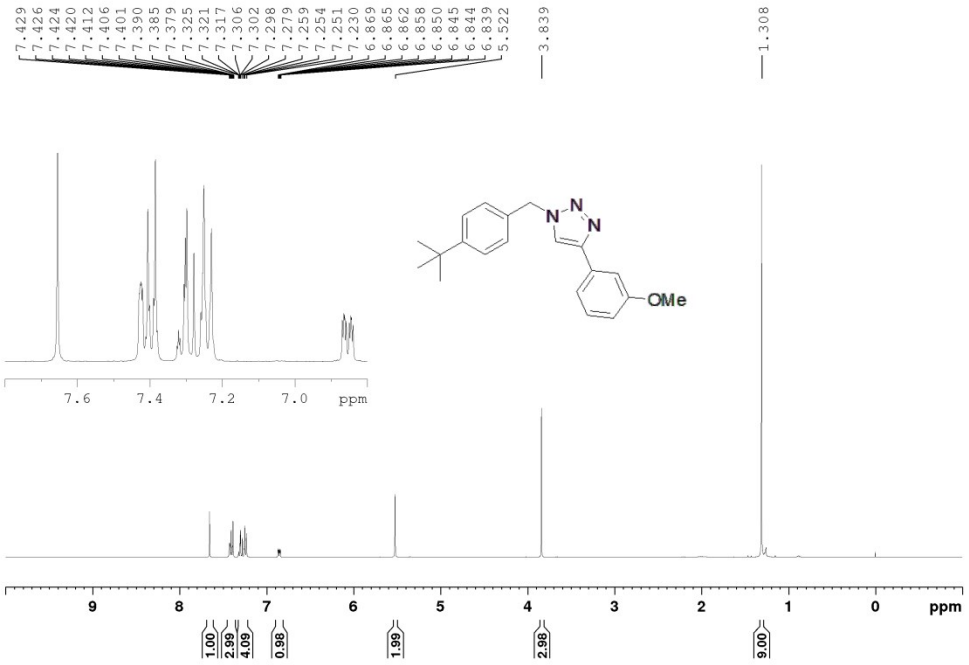
Spectrum of ^{13}C NMR



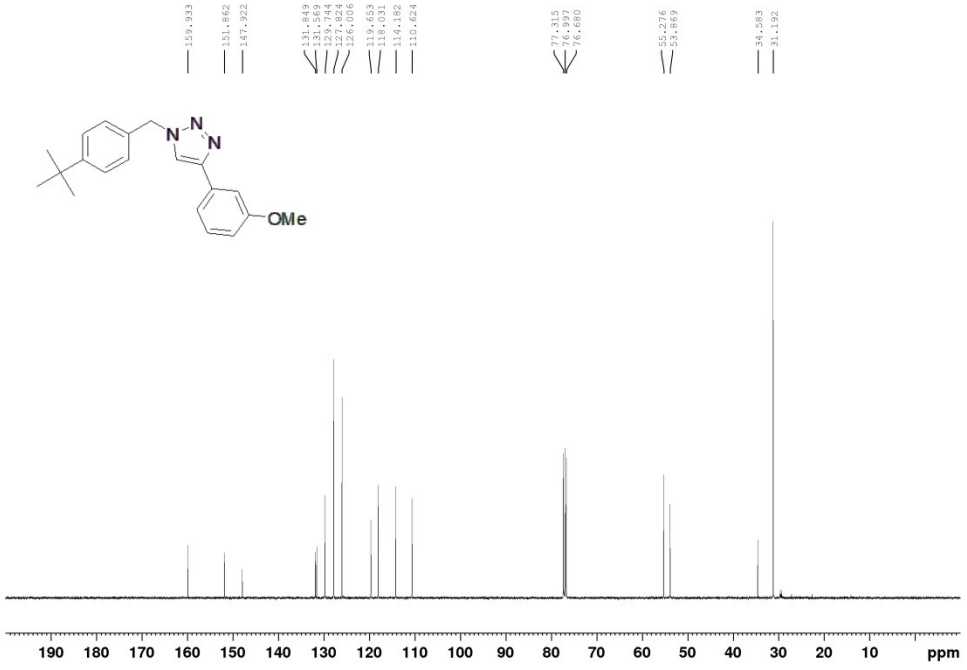
Spectrum of ^{19}F NMR



1-(4-(*tert*-butyl)benzyl)-4-(3-methoxyphenyl)-1*H*-1,2,3-triazole. Light yellow oil, 75% isolated yield**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.46-7.36 (m, 3H), 7.33-7.22 (m, 4H), 6.90-6.81 (m, 1H), 5.52 (s, 2H), 3.84 (s, 3H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.93, 151.86, 147.92, 131.85, 131.57, 129.74, 127.82, 126.01, 119.65, 118.03, 114.18, 110.62, 55.28, 53.87, 34.58, 31.19. HRMS (ESI) *m/z* Calculated for $C_{16}H_{24}N_3O$ $[M+H]^+$ 322.1914, found: 322.1920.



Spectrum of ^{1}H NMR

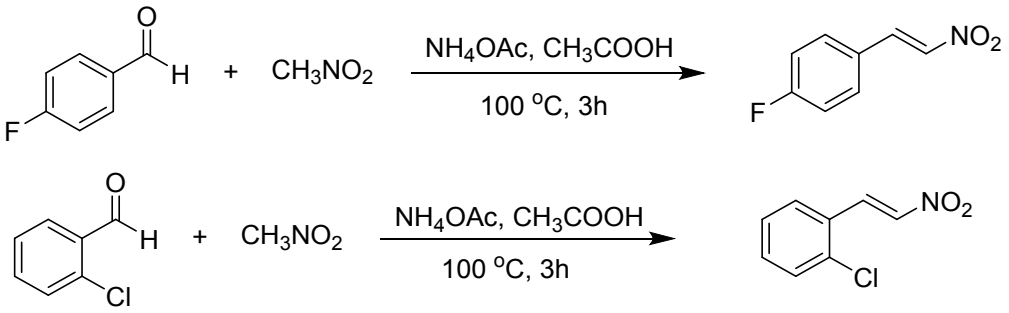


Spectrum of ^{13}C NMR

Figure S7. The products of azide-alkynes cycloaddition reaction

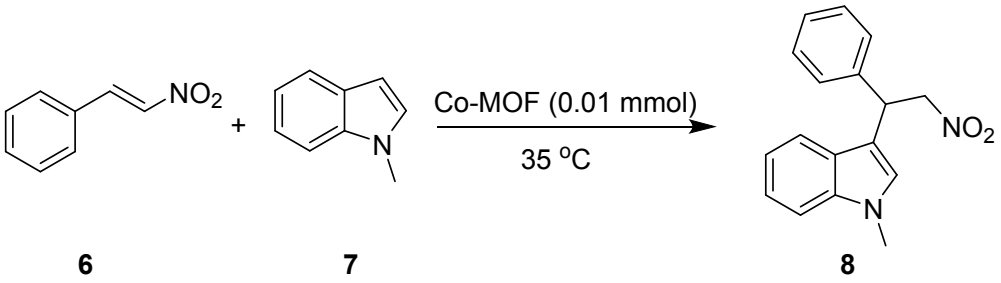
Section 3. Supporting information for Friedel–Crafts alkylation reaction of *trans-β*-Nitrostyrenes and Indoles Catalyzed by 1

Synthesis of the substrates of Friedel–Crafts alkylation reaction of *trans-β*-nitrostyrenes and indoles.



(*E*)-1-fluoro-4-(2-nitrovinyl)benzene (S1) and **(*E*)-1-chloro-2-(2-nitrovinyl) benzene (S2)** was prepared according to the literature.[2] Dissolve 4-fluorobenzaldehyde

(2 mmol, 256 mg), NH_4OAc (2 mmol, 155 mg) in 1 mL glacial acetic acid, add CH_3NO_2 (5 mmol, 610 mg) and react at 100 °C for 3 h. After the reaction was completed, the solvent was evaporated under reduced pressure. The crude product was extracted with 30 mL of water and CH_2Cl_2 (2 × 30 mL). The organic layers were combined, and the organic layers were washed with saturated brine, dried over anhydrous Na_2SO_4, and the solvent was evaporated. The product was recrystallized from hydro ethanol 2-3 times to obtain the product with a yield of 95 %.



6 **7** **8**

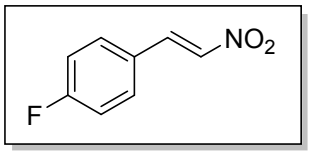
Table S4. Screening of solvent and reaction time [a]

entry	Solvent	t/ h	Isolated yield/%
1	DCM	24	64
2	Toulene	24	52
3	DCM	12	43
4	DCM	36	64
5	DCM	48	63

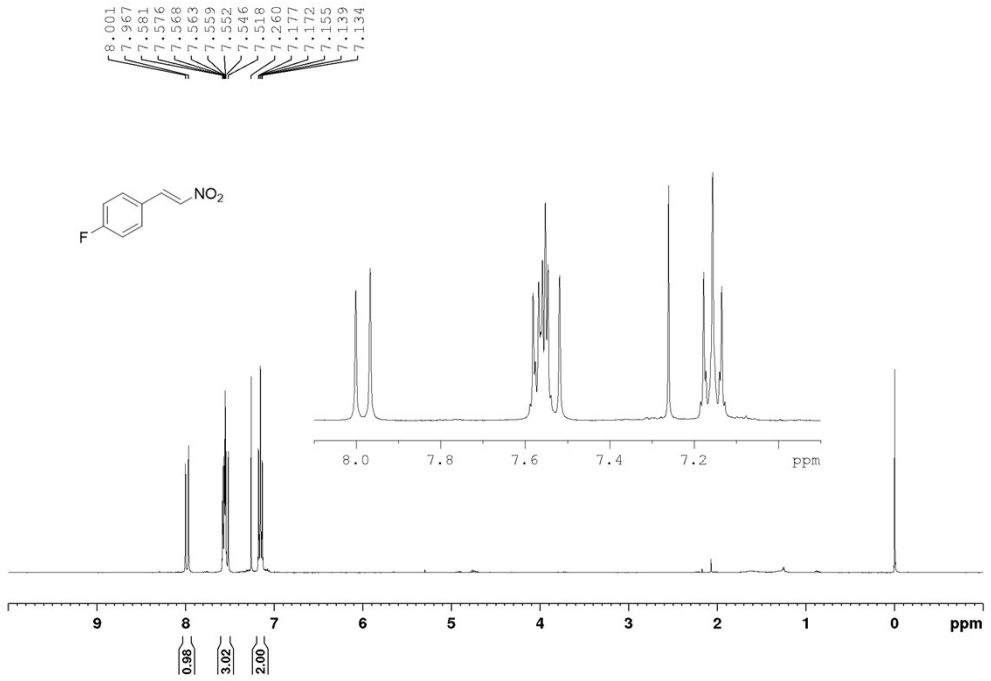
[a] Reaction conditions: *trans-β*-nitrostyrenes (0.2 mmol), indoles (0.3 mmol), solvent (1 mL), Co-MOF (0.01 mmol), 35 °C.

As shown in Table S4**,** when the reaction was carried out in the presence of **1** (0.01 mmol) at 35 °C in DCM under air atmosphere for 24 h, an isolated yield of 64 % was obtained (entry 1, Table S4). When toluene is used as the solvent, the yield drops to 52 % (entry 2, Table S4). Subsequently, with DCM as the solvent, we screened the reaction time. It seems that the longer reaction time (48 h, entry 5, Table S4) were not helpful

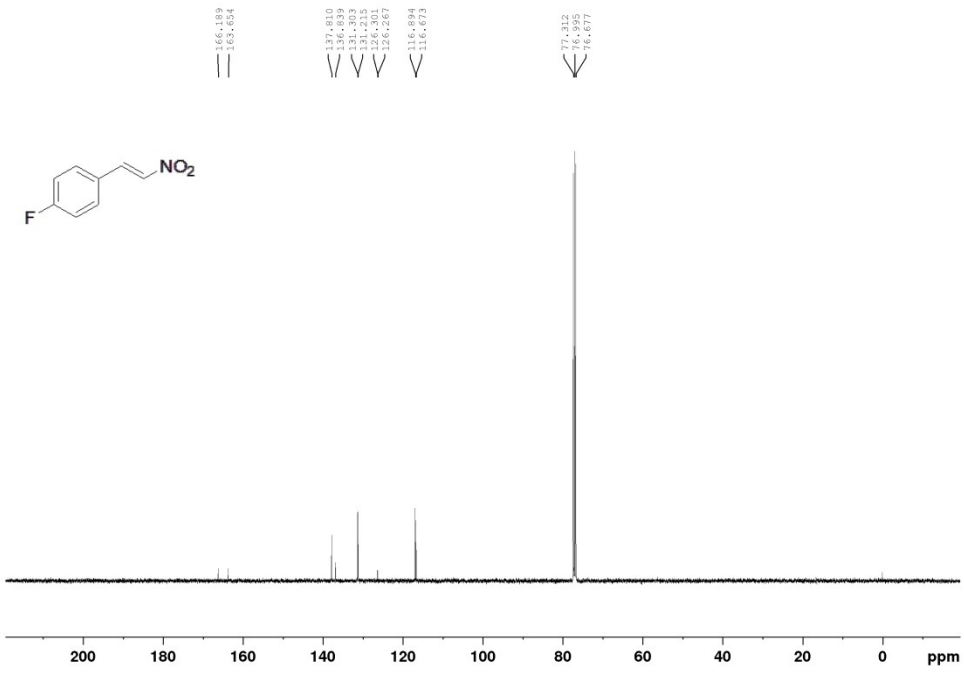
for the product generate. For instance, when the reaction time was reduced to 12 h, the yield was 43 % (entry 3, Table S4). The amount of product obtained did not increase significantly when the reaction time was extended (entries 4 and 5, Table S4).



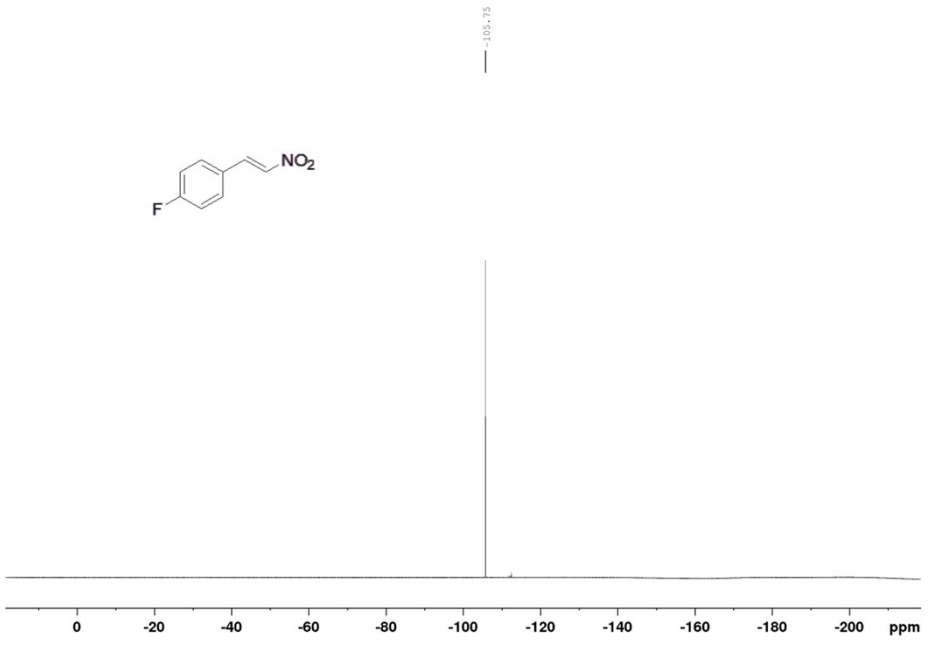
(*E*)-1-fluoro-4-(2-nitrovinyl)benzene.[3] 87% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J*=13.7 Hz, 1H), 7.59-7.51 (m, 3H), 7.19-7.12 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.19, 163.65, 137.81, 136.84, 131.26 (d, *J*=8.8 Hz), 126.28 (d, *J*=3.4 Hz), 116.89, 116.67. ^{19}F NMR (400 MHz, $CDCl_3$) δ -105.75.



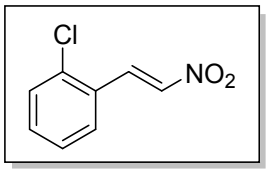
Spectrum of ^{1}H NMR



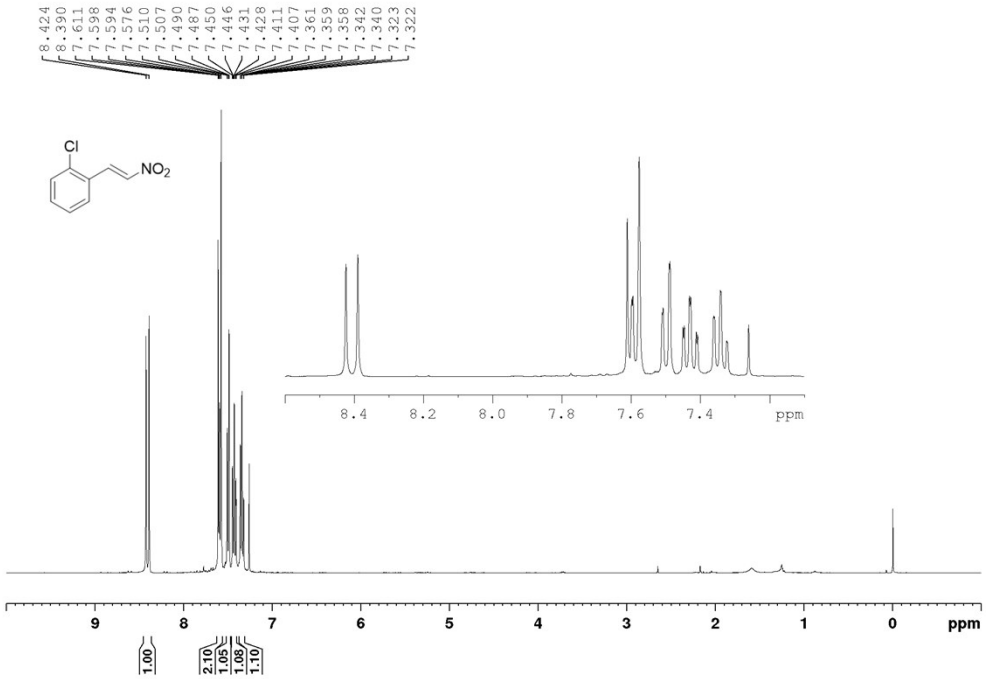
Spectrum of ^{13}C NMR



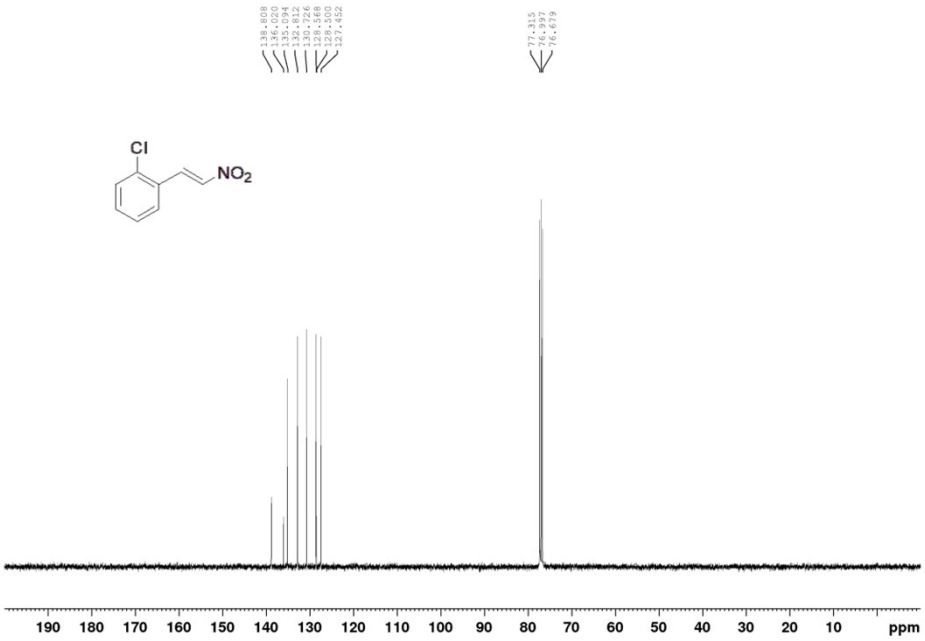
Spectrum of ^{19}F NMR



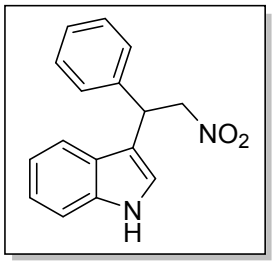
(*E*)-1-chloro-2-(2-nitrovinyl)benzene.[2] 84% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J*=13.7 Hz, 1H), 7.62-7.56 (m, 2H), 7.52-7.47 (m, 1H), 7.46-7.40 (m, 1H), 7.37-7.31 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.81, 136.02, 135.09, 132.81, 130.73, 128.57, 128.50, 127.45.



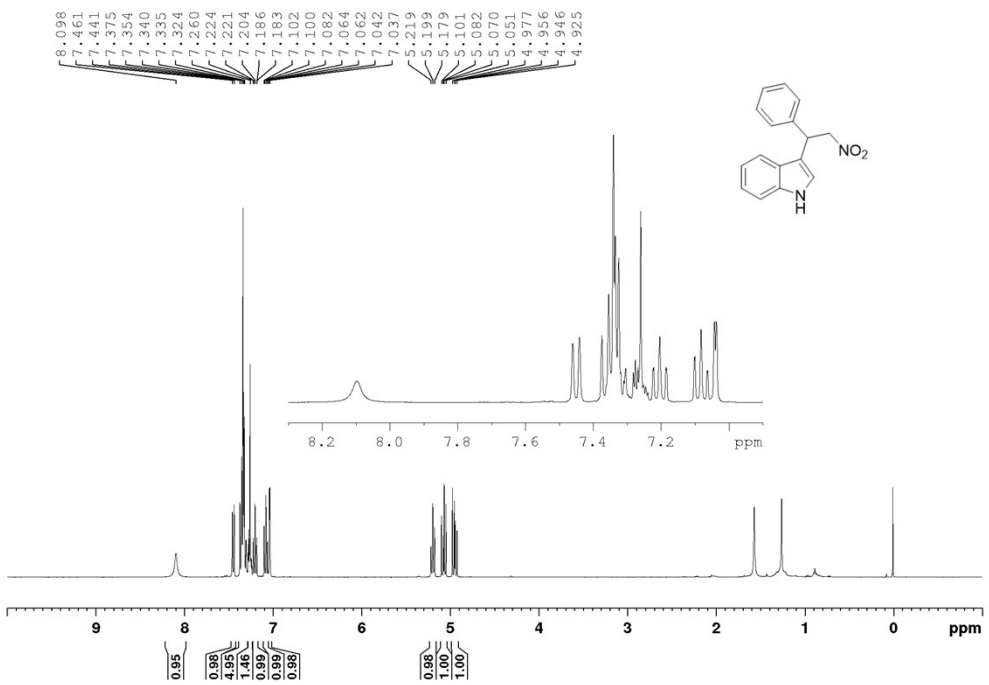
Spectrum of ^{1}H NMR



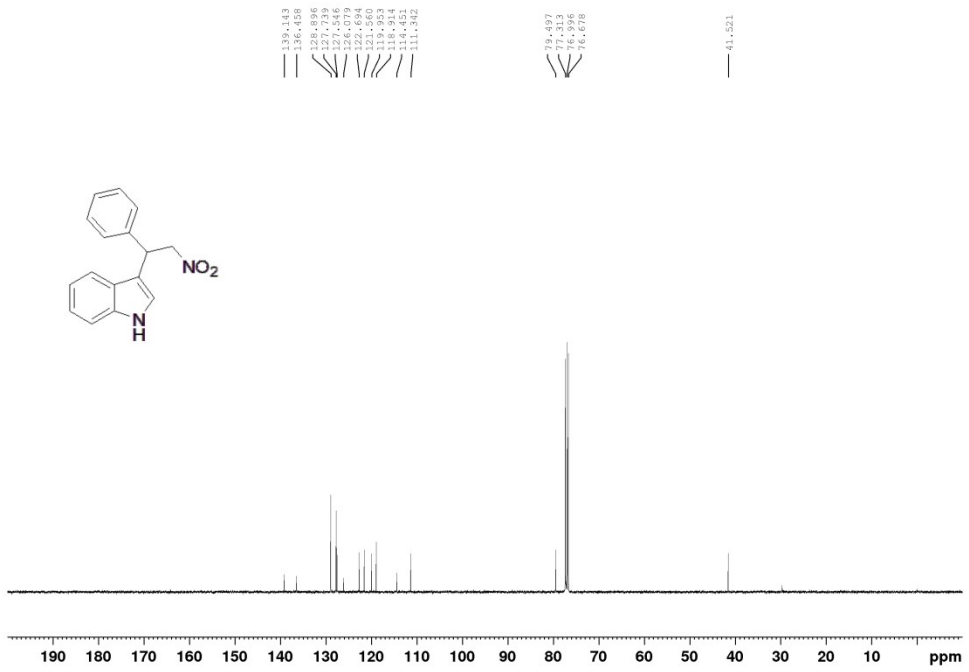
Spectrum of ^{13}C NMR



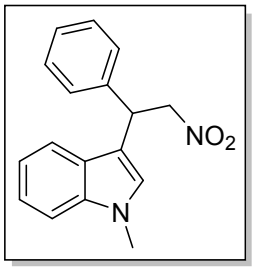
3-(2-nitro-1-phenylethyl)-1*H*-indole. Colorless oil, 43% isolated yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.45 (d, *J*=8.0 Hz, 1H), 7.39-7.29 (m, 5H), 7.29-7.24 (m, 1H), 7.23-7.17 (m, 1H), 7.11-7.06 (m, 1H), 7.04 (d, *J*=2.1 Hz, 1H) 5.20 (t, *J*=8.0 Hz, 1H), 5.11-5.04 (dd, *J*=12.5, 7.6 Hz, 1H), 4.95 (dd, *J*=12.5, 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.14, 136.46, 128.90, 127.74, 127.55, 126.08, 122.69, 121.56, 119.95, 118.91, 114.45, 111.32, 79.50, 41.52. HRMS (ESI) *m/z* Calculated for $C_{16}H_{14}N_2O_2$ $[M+H]^+$ 267.1228, found: 267.1131.



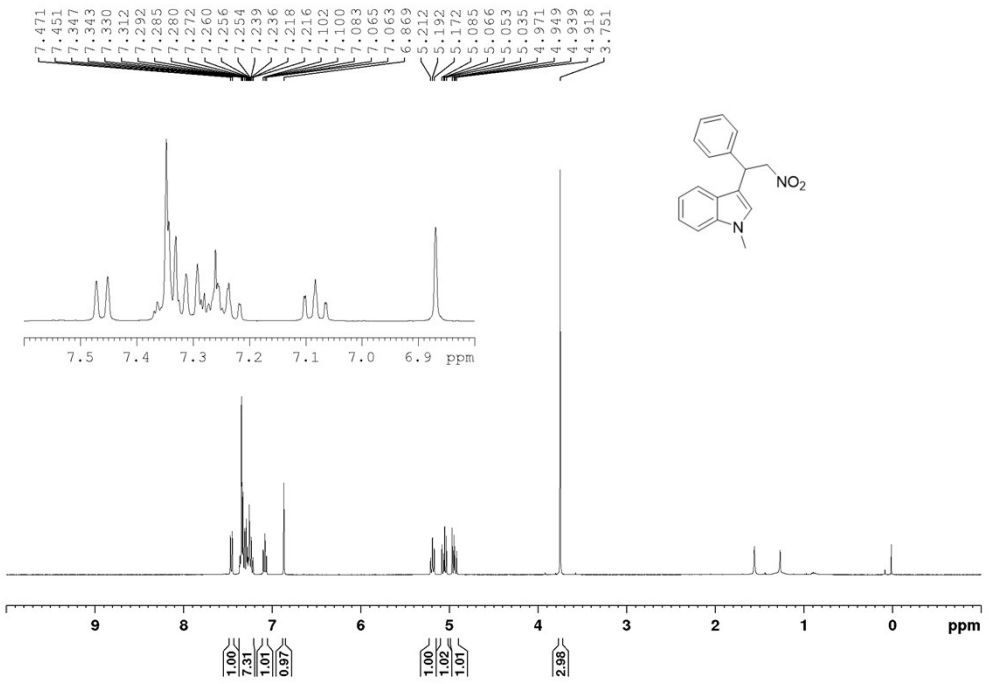
Spectrum of ^{1}H NMR



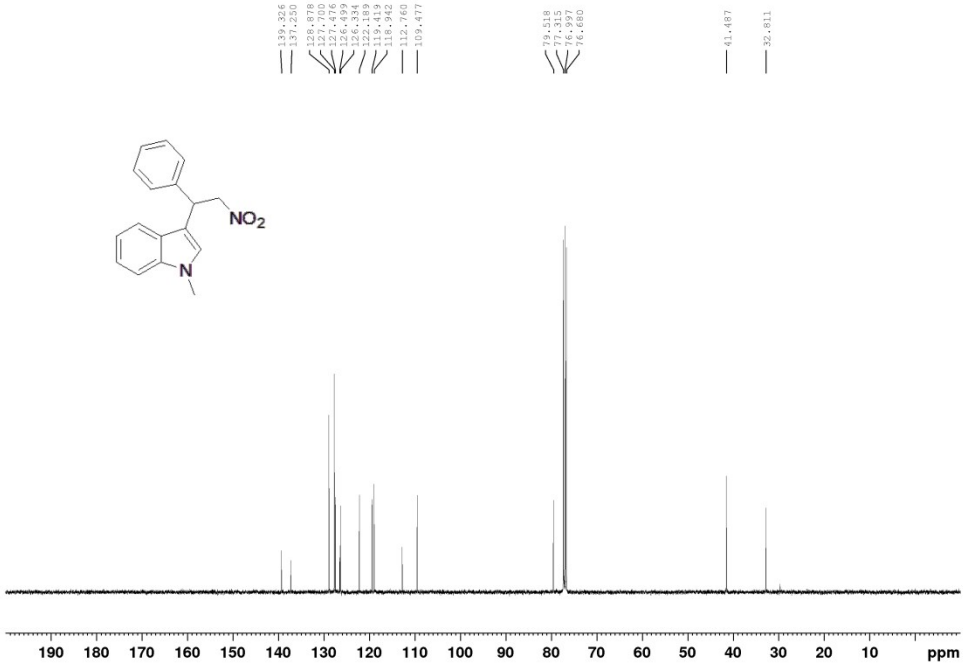
Spectrum of ^{13}C NMR



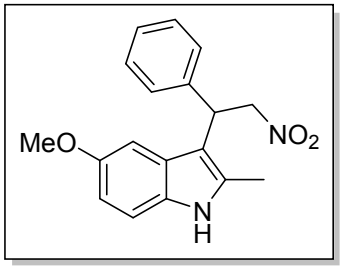
1-methyl-3-(2-nitro-1-phenylethyl)-1*H*-indole. Colorless oil, 64% isolated yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.44 (m, 1H), 7.37-7.21 (m, 7H), 7.11-7.05 (m, 1H), 6.86 (s, 1H), 5.19 (t, *J*=8.0 Hz,1H), 5.06 (dd, *J*=12.5, 7.5 Hz, 1H), 4.94 (dd, *J*=12.5, 8.5 Hz, 1H), 3.74 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.33, 137.25, 128.88, 127.70, 127.48, 126.50, 126.33, 122.19, 119.42, 118.94, 112.76, 109.48, 79.52, 41.49, 32.81. HRMS (ESI) *m/z* Calculated for $C_{17}H_{16}N_2O_2$ $[M+H]^+$ 281.1285, found: 281.1288.



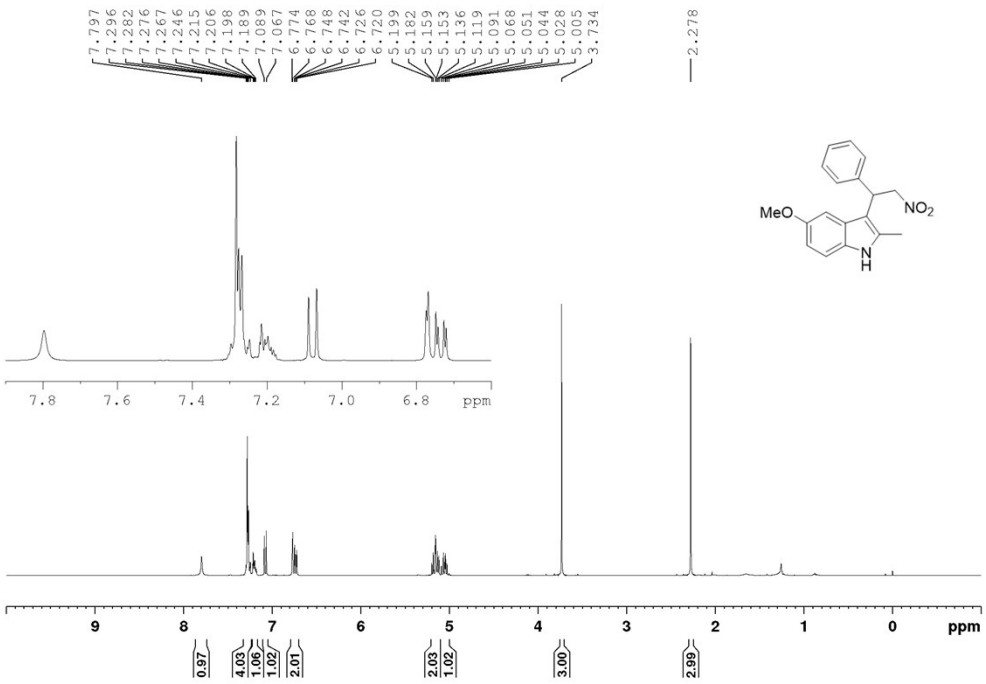
Spectrum of ^{1}H NMR



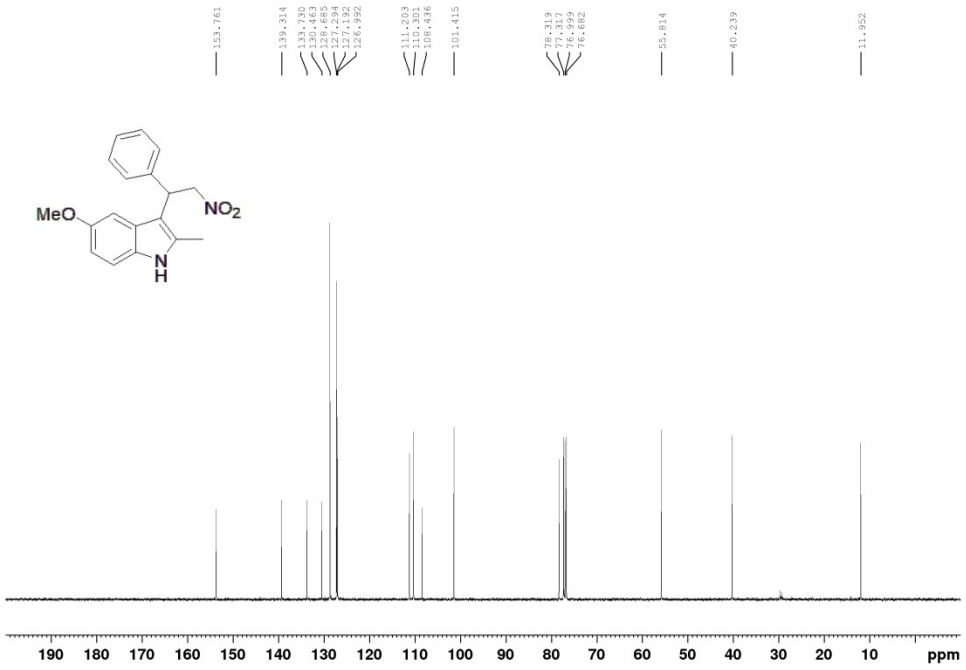
Spectrum of ^{13}C NMR



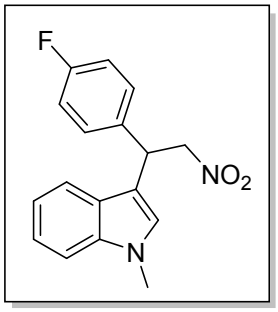
5-methoxy-2-methyl-3-(2-nitro-1-phenylethyl)-1*H*-indole. Colorless oil, 70% isolated yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.33-7.24 (m, 4H), 7.22-7.17 (m, 1H), 7.08 (d, J = 8.7 Hz, 1H), 6.79-6.70 (m, 2H), 5.21-5.10 (m, 2H), 5.10-5.00 (m, 1H), 3.73 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.76, 139.31, 133.73, 130.46, 128.69, 127.29, 127.19, 126.99, 111.20, 110.30, 108.44, 101.42, 78.32, 55.81, 40.24, 11.95. HRMS (ESI) *m/z* Calculated for $C_{18}H_{18}N_2O_3$ $[M+H]^+$ 311.1390, found: 311.1395.



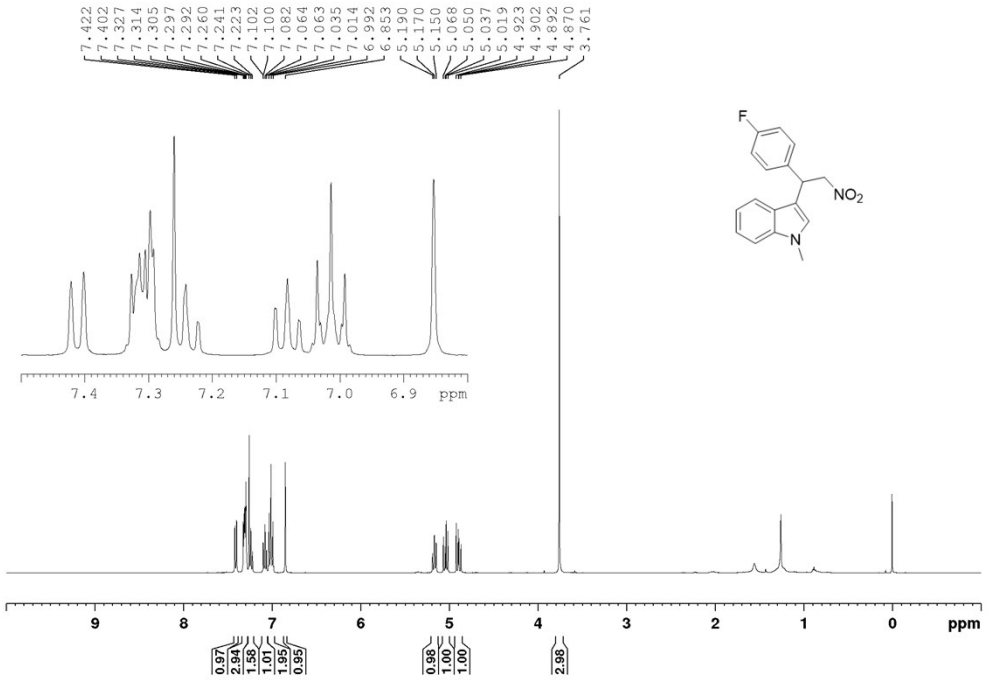
Spectrum of ^{1}H NMR



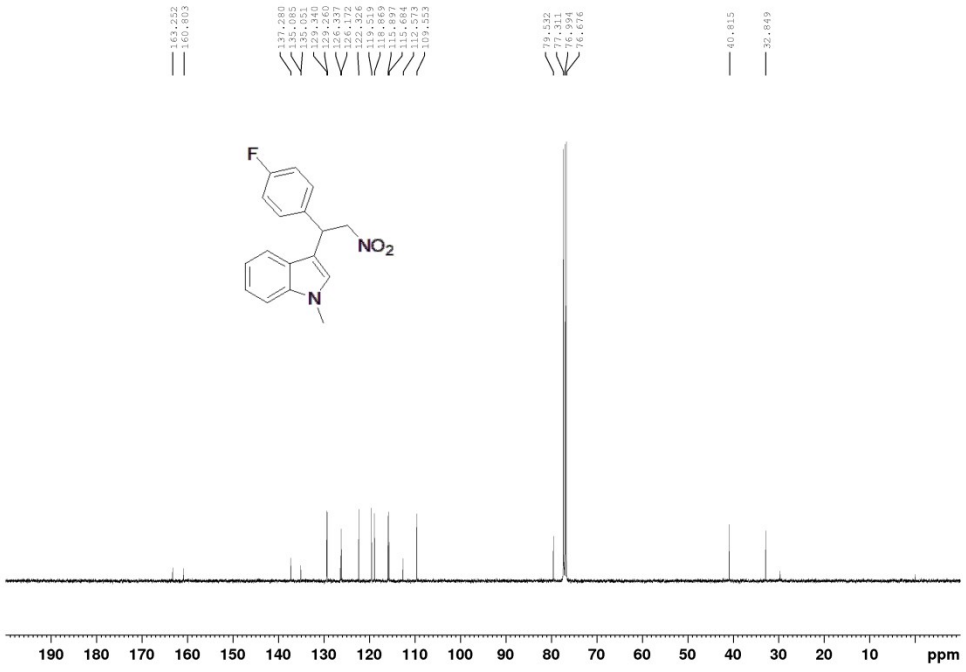
Spectrum of ^{13}C NMR Spectrum of ^{1}H NMR



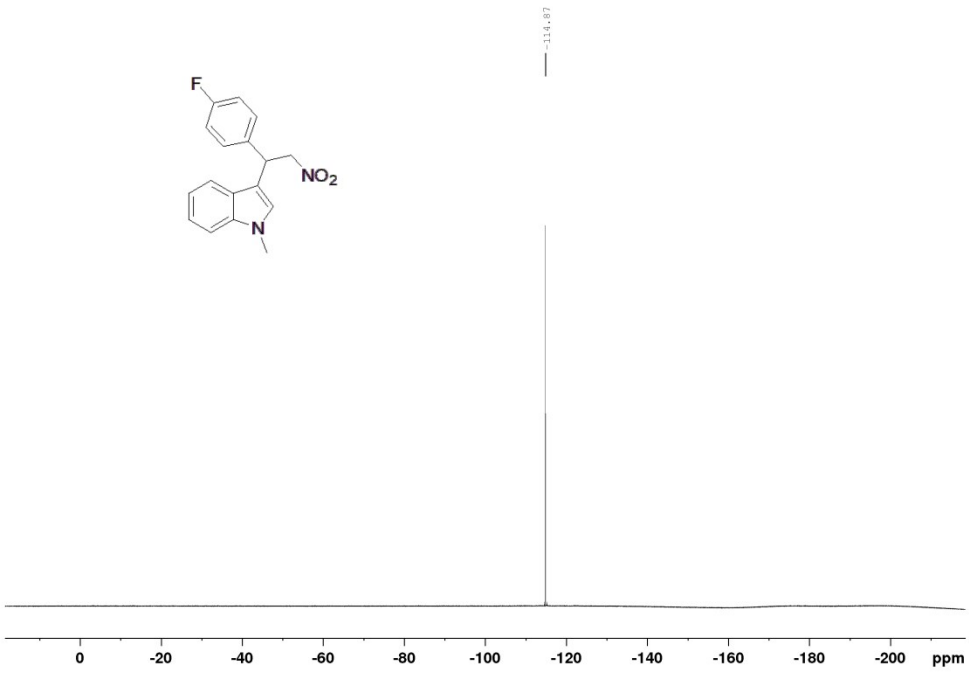
3-(1-(4-fluorophenyl)-2-nitroethyl)-1-methyl-1*H*-indole. Colorless oil, 40% isolated yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.0 Hz, 1H), 7.34-7.28 (m, 3H), 7.27-7.21 (m, 1H), 7.12-7.05 (m, 1H), 7.05-6.97 (m, 2H), 6.85 (s, 1H), 5.17 (t, *J* = 7.9 Hz, 1H), 5.04 (dd, *J* = 12.4, 7.3 Hz, 1H), 4.90 (dd, *J* = 12.4, 8.7 Hz, 1H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.25, 160.80, 137.28, 135.07 (d, *J*=3.4 Hz), 129.30 (d, *J*=8.1 Hz), 126.34, 126.17, 122.33, 119.52, 118.87, 115.90, 115.68, 112.57, 109.55, 79.53, 40.82, 32.85. ^{19}F NMR (400 MHz, $CDCl_3$) δ -114.87. HRMS (ESI) *m/z* Calculated for $C_{17}H_{15}FN_2O_2$ $[M+H]^+$ 299.1190, found: 299.1193.



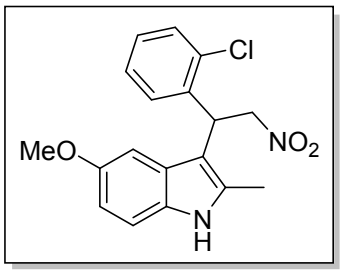
Spectrum of ^{1}H NMR



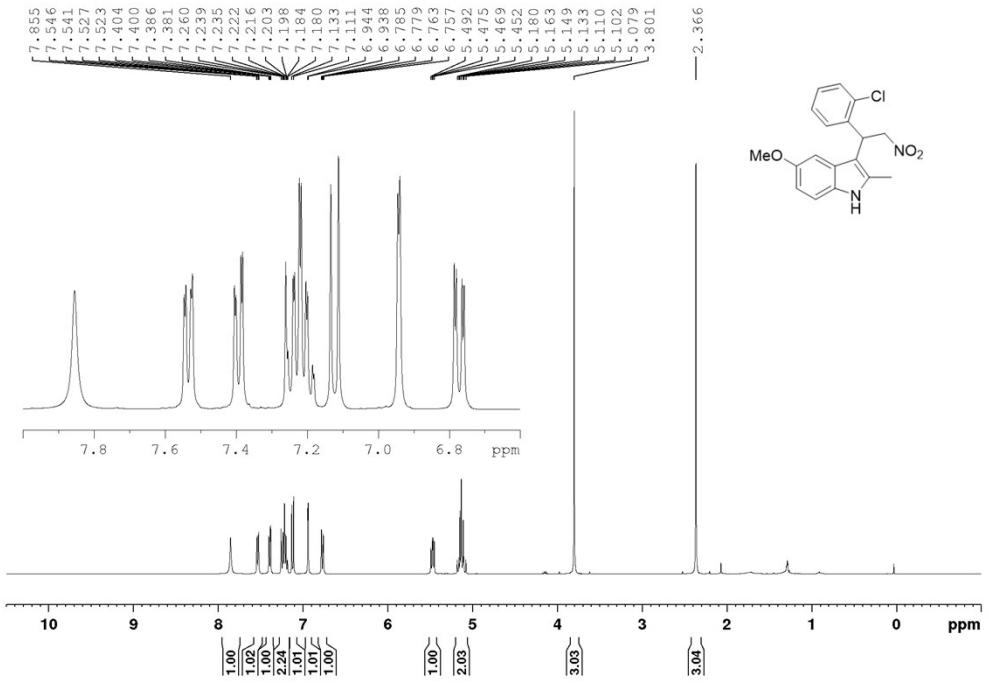
Spectrum of ^{13}C NMR



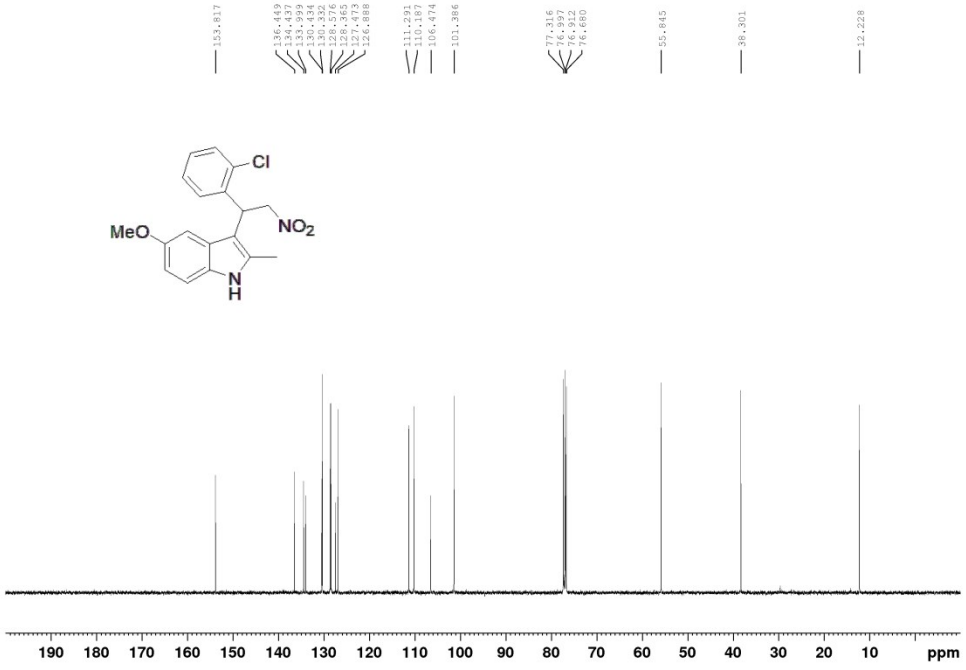
Spectrum of ^{19}F NMR



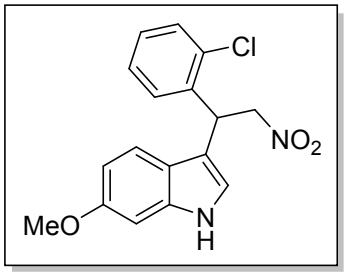
3-(1-(2-chlorophenyl)-2-nitroethyl)-5-methoxy-2-methyl-1*H*-indole. Colorless oil, 68% isolated yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.53 (dd, *J* = 7.4, 2.0 Hz, 1H), 7.40 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.28-7.16 (m, 2H), 7.10 (d, *J* = 8.7 Hz, 1H), 6.90 (d, *J* = 2.2 Hz, 1H), 6.77 (dd, *J* = 8.7, 2.3 Hz, 1H), 5.47 (dd, *J* = 9.2, 6.8 Hz, 1H), 5.20-5.06 (m, 2H), 3.80 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.82, 136.45, 134.44, 134.00, 130.43, 130.33, 128.58, 128.37, 127.47, 126.89, 111.29, 110.19, 106.47, 101.39, 76.91, 55.85, 38.30, 12.23. HRMS (ESI) *m/z* Calculated for $C_{18}H_{17}ClN_2O_3$ $[M+H]^+$ 345.1000, found: 345.1000.



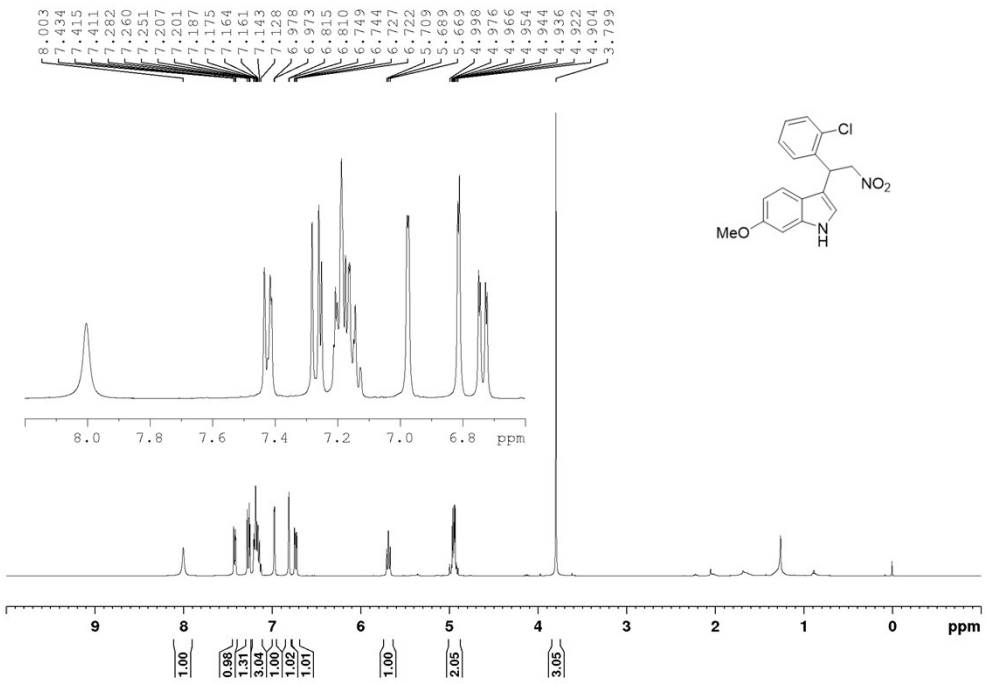
Spectrum of ^{1}H NMR



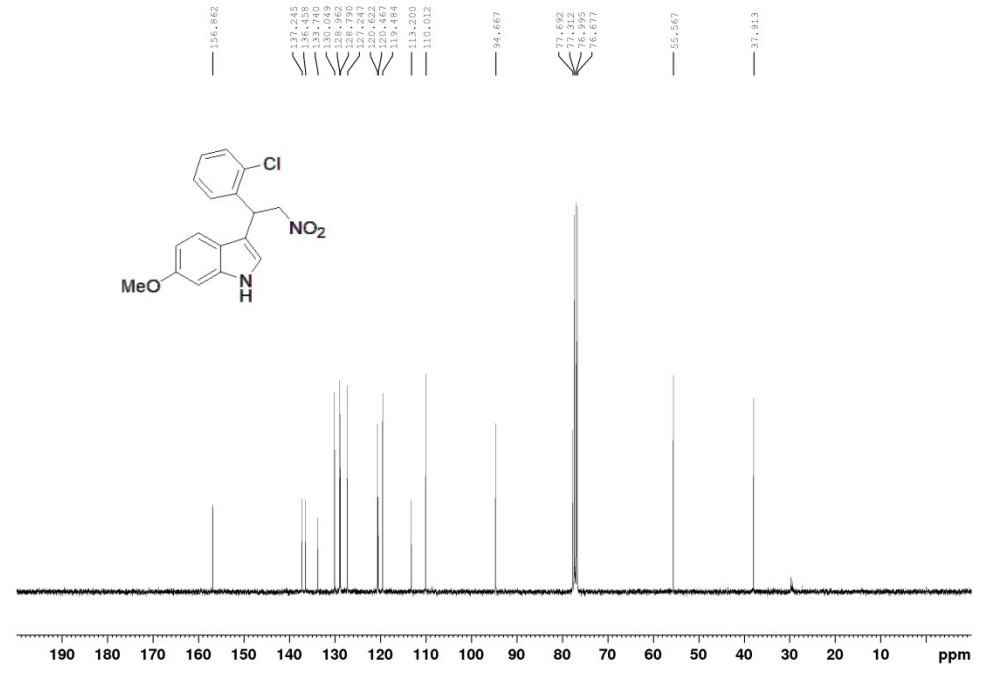
Spectrum of ^{13}C NMR



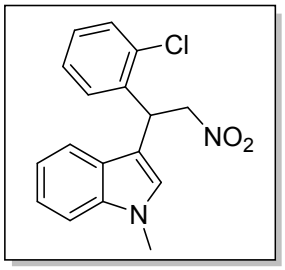
3-(1-(2-chlorophenyl)-2-nitroethyl)-6-methoxy-1*H*-indole. Colorless oil, 51% isolated yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.45-7.40 (m, 1H), 7.32-7.24 (m, 1H), 7.22-7.11 (m, 3H), 6.98 (d, J = 1.9 Hz, 1H), 6.81 (d, J = 1.9 Hz, 1H), 6.74 (dd, J = 8.7, 2.1 Hz, 1H), 5.69 (t, J = 7.8 Hz, 1H), 5.01-4.88 (m, 2H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.86, 137.25, 136.46, 133.74, 130.05, 128.96, 128.79, 127.25, 120.62, 120.47, 119.48, 113.20, 110.01, 94.67, 77.69, 55.57, 37.91. HRMS (ESI) *m/z* Calculated for $C_{17}H_{15}ClN_2O_3$ $[M+H]^+$ 331.0844, found: 331.0848.



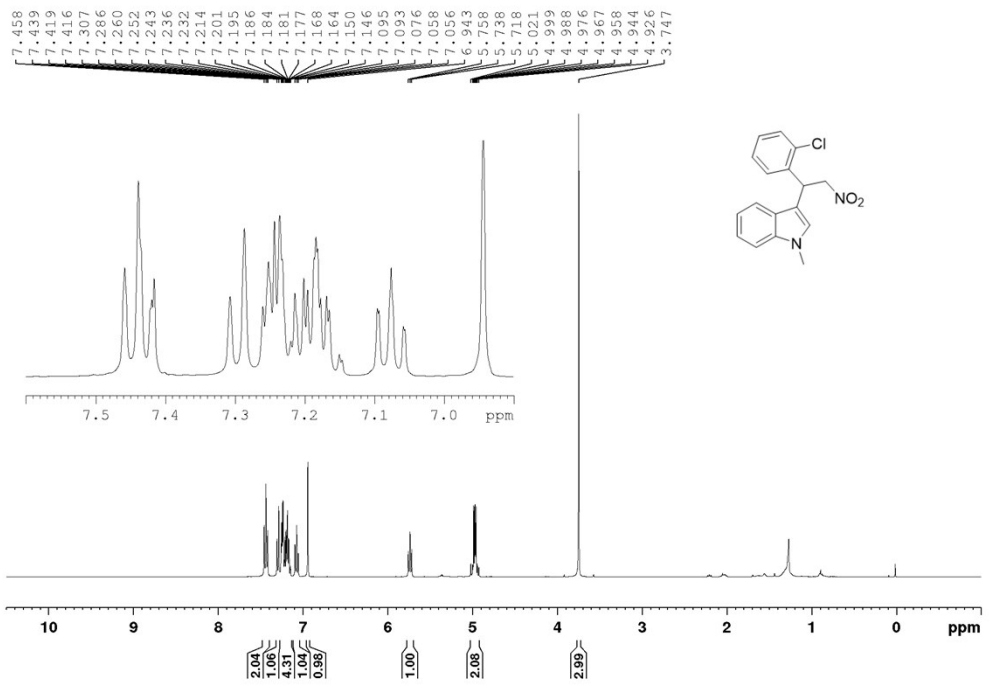
Spectrum of ^{1}H NMR



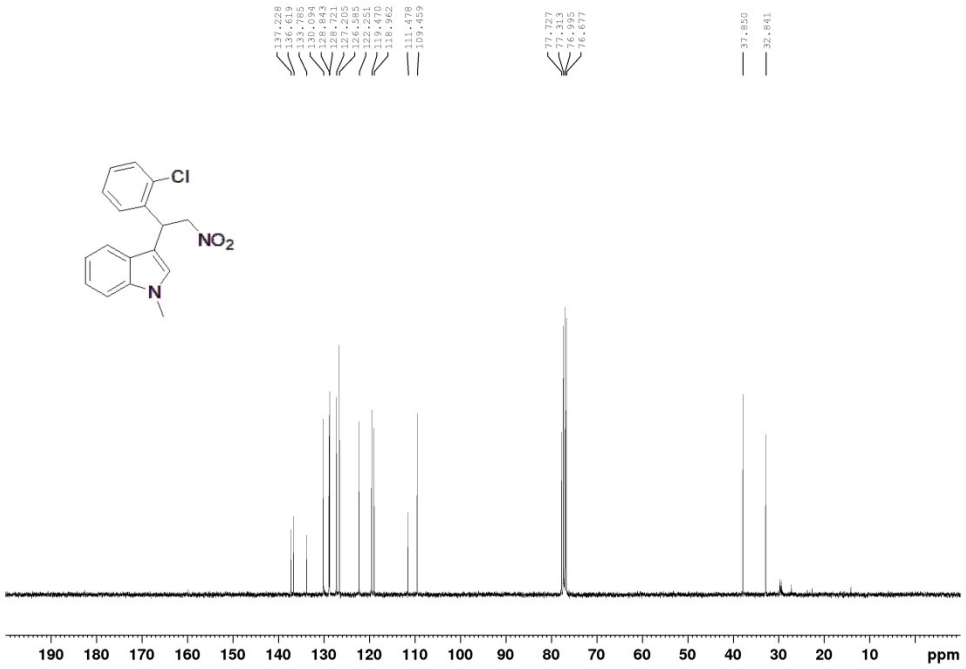
Spectrum of ^{13}C NMR



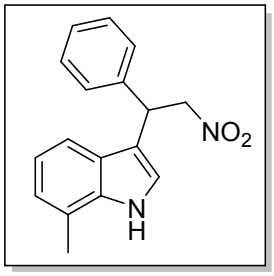
3-(1-(2-chlorophenyl)-2-nitroethyl)-1-methyl-1*H*-indole. Colorless oil, 63% isolated yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.40 (m, 2H), 7.32-7.27 (m, 1H), 7.27-7.14 (m, 4H), 7.12-7.04 (m, 1H), 6.94 (s, 1H), 5.74 (t, *J* = 7.9 Hz, 1H), 5.03-4.92 (m, 2H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.23, 136.62, 133.78, 130.09, 128.84, 128.72, 127.21, 126.58, 122.25, 119.47, 118.96, 111.48, 109.46, 77.73, 37.85, 32.84. HRMS (ESI) *m/z* Calculated for $C_{17}H_{15}ClN_2O_2$ $[M+H]^+$ 315.0895, found: 315.0894.



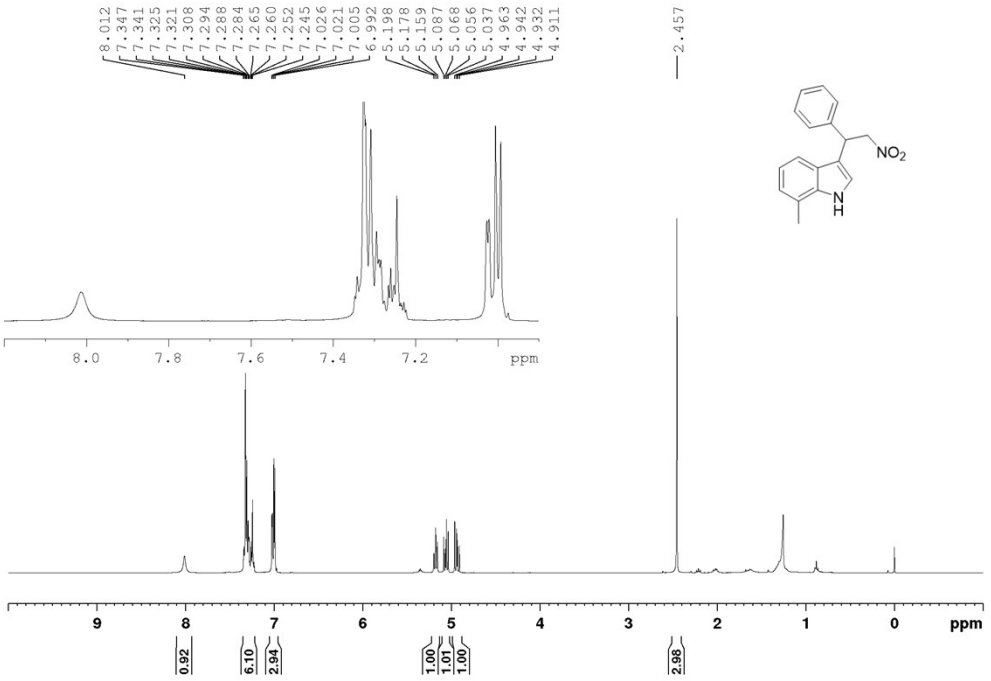
Spectrum of ^{1}H NMR



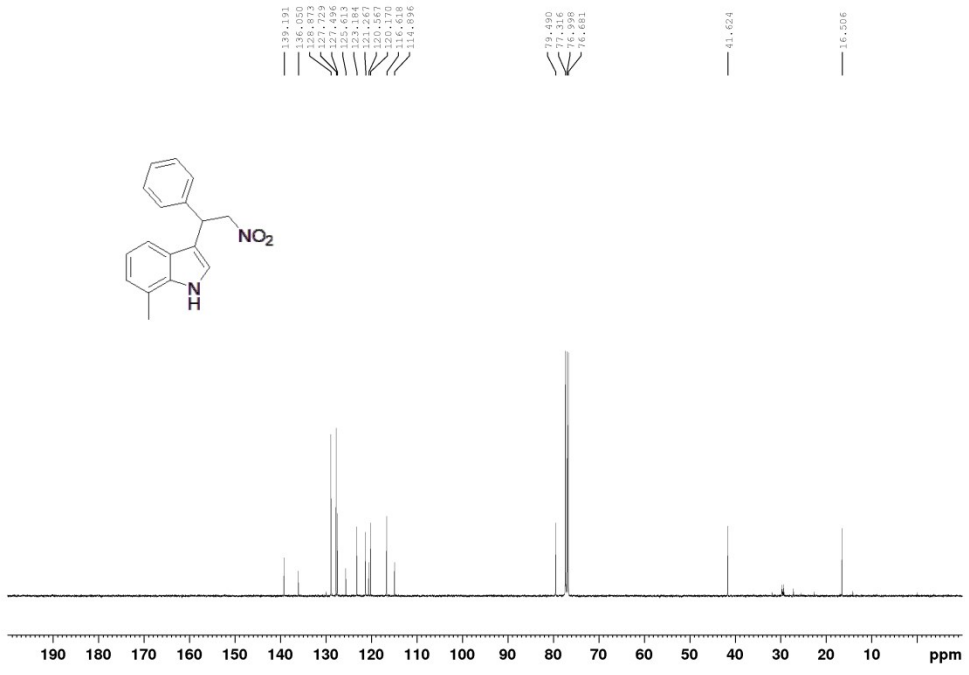
Spectrum of ^{13}C NMR



7-methyl-3-(2-nitro-1-phenylethyl)-1*H*-indole. Colorless oil, 45% isolated yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.35-7.22 (m, 6H), 7.01-6.96 (m, 3H), 5.18 (t, *J* = 8.0 Hz, 1H), 5.06 (dd, *J* = 12.4, 7.6 Hz, 1H), 4.94 (dd, *J* = 12.4, 8.4 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.19, 136.05, 128.87, 127.73, 127.50, 125.61, 123.18, 121.27, 120.57, 120.17, 116.62, 114.90, 79.49, 41.62, 16.51. HRMS (ESI) *m/z* Calculated for $C_{17}H_{16}N_2O_2$ $[M+H]^+$ 281.1285, found: 281.1288.



Spectrum of ^{1}H NMR



Spectrum of ^{13}C NMR

Figure S8. The substrates and products of Friedel-Crafts reaction

Section 4. Supporting information for Selective hydrosilylation of alkynes reaction catalyzed by 1

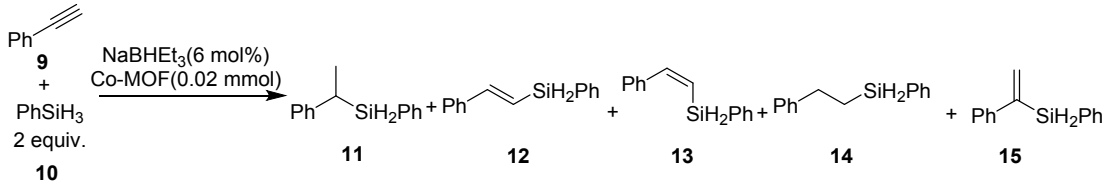


Table S5. Screening of solvent and temperatures [a]

entry	solvent	T/ ℃	Isolated yield of **11-15**/%[b]
1	THF	50	52
2	CH_3CN	50	43
3	Et_2O	50	47
4	Toluene	50	20
5	THF	60	50
6	THF	70	52

[a] Reaction conditions: phenylacetylene (1 mmol), $PhSiH_3$ (2 mmol), $NaBHEt_3$ (6 mol %), Co-MOF (0.02 mmol), 6 h.

The reaction yield was is not high when using THF as a solvent, as mentioned previously, we first screened the solvents and found that the commonly used solvents, acetonitrile, ether and toluene did not greatly improve the reaction yield (20 %-47 %, entries 2-4, Table S5). Subsequently, we screened the reaction temperature. Unfortunately, and the hydrosilylation yield also did not increase significantly when the reaction temperature was changed (entries 5 and 6, Table S5).

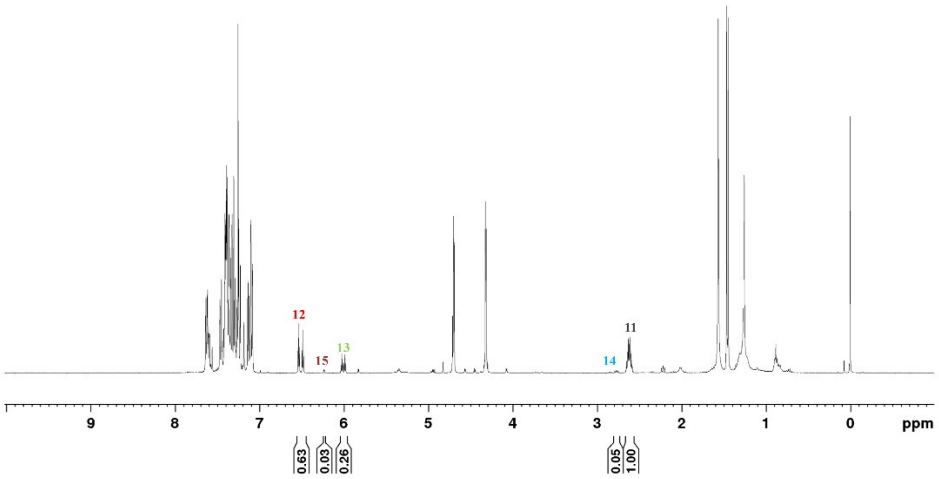


Figure S9. The products of hydrosilylation of alkynes reaction

The standard ^{1}H NMR of compounds **11-15** are obtained from the literature.[4-8]

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