Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Nickel-catalyzed tandem isomerization/*anti*-Markovnikov hydroarylation of unactivated internal alkenes with heteroarenes†

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General Information:

Unless mentioned otherwise, all manipulations were performed using standard Schlenk techniques or in an N_2-filled glovebox. Solvents (THF, toluene, and *n*-hexane) were distilled from Na/benzophenone under pure argon prior to use. 1,3-Bis(4-methoxy-2,6-dimethylphenyl)imidazol-2-ylidene (IMXy) was prepared according to the reported procedures in the literature.[1] Heteroleptic Ni(II) complexes Ni(IMes)[P(OEt)$_3$]Br$_2$ and Ni(IPr^{*OMe})[P(OEt)$_3$]Br$_2$ were prepared by our lab's reported procedure.[2] 2-deutro-*N*-methylbenzimidazole ***d*-2a**,[3] and internal alkenes **3h**,[4] **3i**,[5] **3k**[6] were prepared according to reported methods. Other commercially available reagents were purchased from Acros, Sigma-Aldrich, TCI, and Alfa Aesar Chemical Company and were used as received. Unless otherwise stated, ^{1}H NMR spectra were recorded on a BRUKER AVANCE III HD (400 MHz) spectrometer at 25 °C. Chemical shifts are reported in ppm from tetramethylsilane with solvent resonance as an internal standard ($CDCl_3$: δ 7.26). Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. ^{13}C NMR spectra were recorded on a BRUKER AVANCE III HD (100 MHz) spectrometer at 25 °C with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.16). ^{19}F NMR spectra were recorded on a BRUKER AVANCE III HD (376 MHz) spectrometer at 25 °C. ^{31}P NMR spectra were recorded on a BRUKER AVANCE III HD (162 MHz, $CDCl_3$) spectrometer at 25 °C. ^{2}H NMR spectra were recorded on a BRUKER AVANCE III HD (61 MHz, $CDCl_3$) spectrometer at 25 °C. Gas chromatographic (GC) analysis was performed on a Thermo Fisher Trace 1300 instrument or Agilent GC-6891N instrument [Column Type: TG-5MA (30m × 0.32 mm i.d.); Temperature monitoring: 300 ^{o}C; Temperature injecting: 80 ^{o}C (2 min)//20 ^{o}C/min//240 ^{o}C (2 min//10) (2 min ^{o}C / min //300 ^{o}C (2 min)]. Melting points were determined on a Yu Hua X-4 device and were unchecked. High-resolution mass spectra (HRMS) were obtained using Bruker micro TOF-Q (III) device with ESI source, GCT-TOF device with E.I. source or GCT-TOF device with CI source. Elemental analyses were performed on a Carlo-Erba EA-1110 instrument (Atlanta, GA).

Experimental procedure and characterization data of complex 1

Ni(IMXy)[P(OEt)$_3$]Br$_2$ (1) A Schlenk flask was charged with Ni[P(OEt)$_3$]$_2$Br$_2$ (1.21 g, 2.27 mmol), dry THF (10 mL), and a stir bar. To this solution, IMXy (0.67 g, 2.27 mmol) in dry THF (15 mL) was added at room temperature. The color of the mixture immediately turned dark red. The solution was then stirred for 4 h at room temperature. Volatiles were removed in vacuo. The residue was washed with hexane (3×3 mL), extracted with THF (3×10 mL), and recrystallized from concentrated THF/hexane solution at 0 °C. The product was precipitated as a red microcrystalline solid with a yield of 80% (1.15 g). mp: 170 – 171 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 1H, NC*H*=CHN), 7.22 – 7.18 (m, 1H, NCH=C*H*N), 6.80 (s, 4H, *meta*-C*H*$_{\text{-Ph}}$), 4.06 (q, *J* = 7.0 Hz, 6H, O(C*H*$_2$CH$_3$), 3.90 (s, 6H, *para*-OC*H*$_{\text{3-Ph}}$), 2.38 (d, *J* = 4.4 Hz, 12H, *ortho*-C*H*$_{\text{3-Ph}}$), 1.23 (t, *J* = 7.0 Hz, 9H, O(CH$_2$C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5 (N*C*N), 138.2, 138.0, 131.9, 115.3, 113.4, 62.1, 55.3, 20.4, 16.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ 99.89. Anal. Calcd for $C_{27}H_{39}Br_2N_2NiO_5P$: C, 44.91; H, 5.72; N, 3.87. Found: C, 45.34; H, 5.75; N, 3.88.

Copies of NMR spectra for complex 1

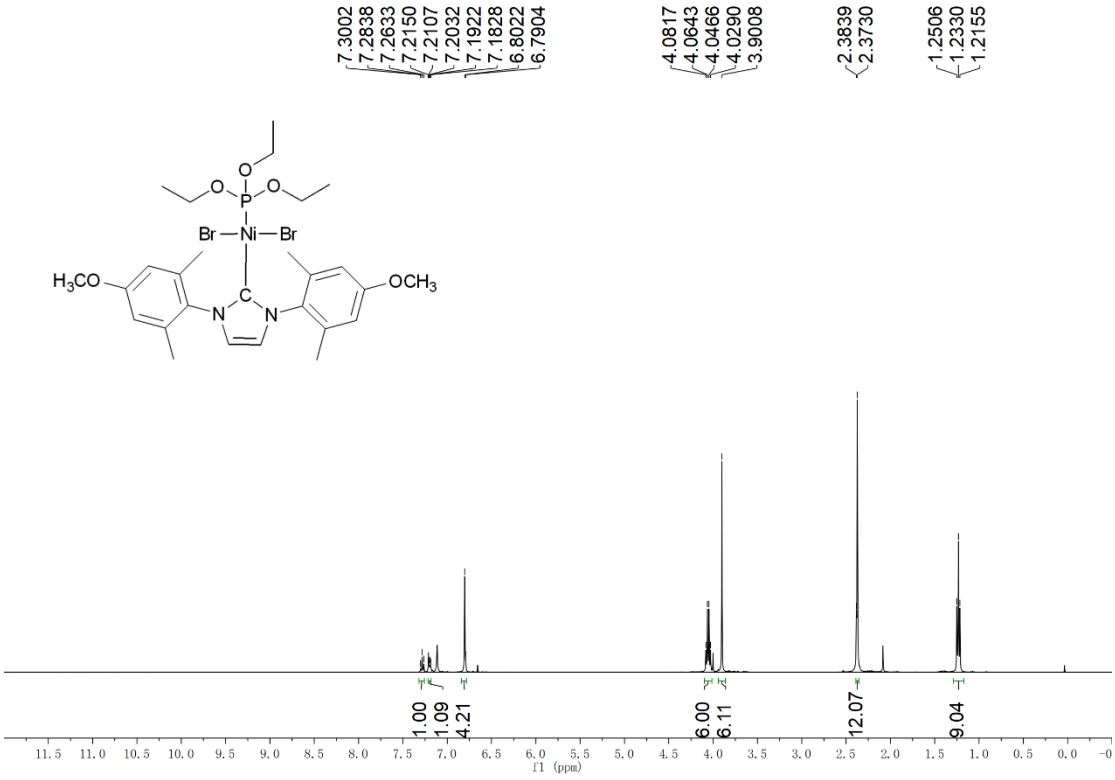


Figure S1. ^{1}H NMR spectrum of complex **1** (400 MHz, $CDCl_3$).

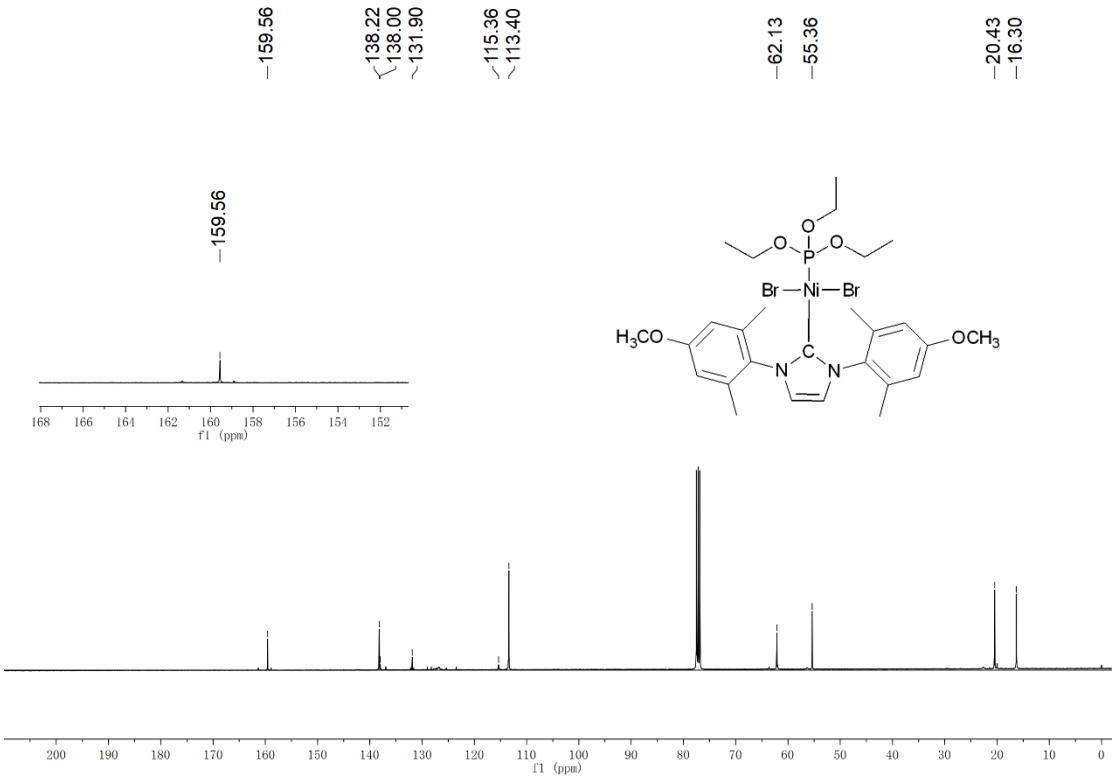


Figure S2. ^{13}C NMR spectrum of complex **1** (100 MHz, $CDCl_3$).

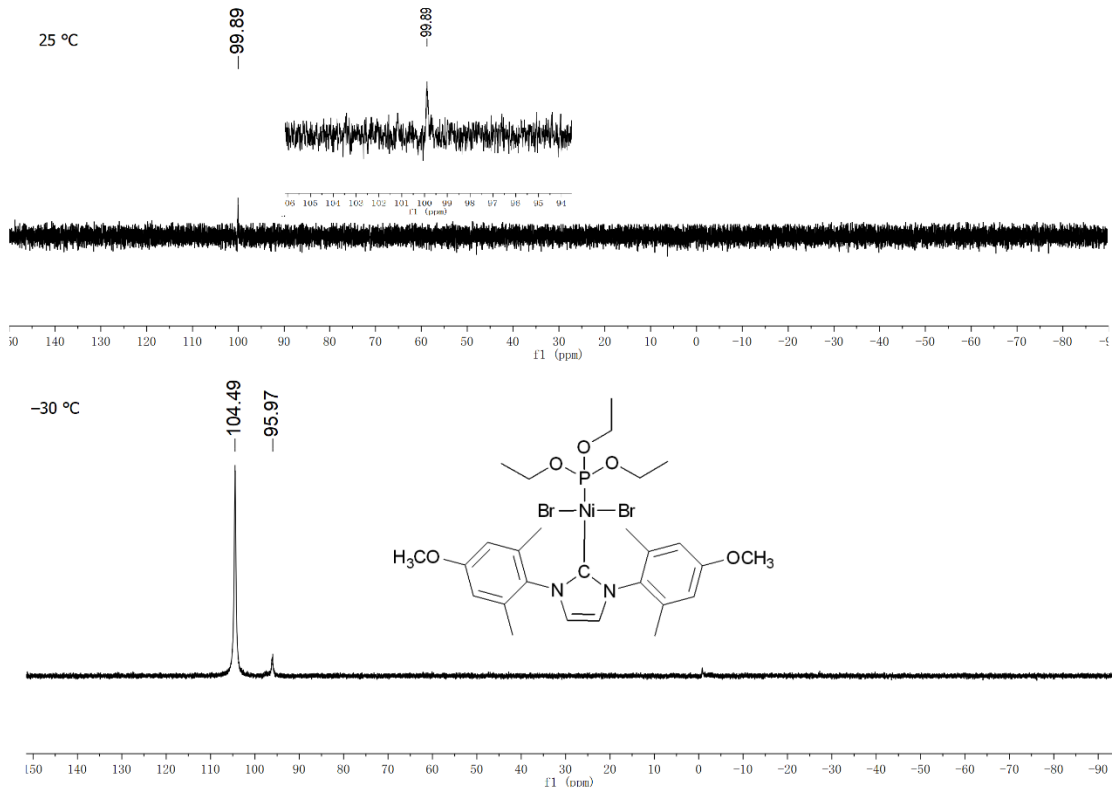


Figure S3. Variable-temperature ^{31}P NMR spectra of complex **1** (162 MHz, $CDCl_3$).

Table S1. X-ray crystallographic data for complex 1

Compound	**1**
Empirical formula	$C_{27}H_{39}Br_2N_2NiO_5P$
Formula weight	721.10
Temperature / K	120.01
Radiation used	Mo-Kα
Crystal system	triclinic
Space group	P-1
a / Å	8.3774(3)
b / Å	9.8859(4)
c / Å	18.6847(7)
α / °	97.9650(10)
β / °	97.3620(10)
γ / °	92.3300(10)
Volume/ $Å^3$	1517.18(10)
Z	2
D_c g /cm^3	1.578
μ / mm^{-1}	3.364
F(000)	736.0
Crystal size/ mm^3	0.15 × 0.15 × 0.1
θ range/ °	6.25 to 55.024
Index ranges	-10 h ⩽ 10, -12 ⩽ k ⩽ 12, -24 ⩽ l ⩽ 24
Reflections collected	32590
Independent reflections, R_{int}	6894, 0.0568,
Data / restraints / parameters	6894/0/352
Goodness-of-fit on F^2	1.022
R_1, wR_2 [I > = 2σ (I)]	R_1 = 0.0291, wR_2 = 0.0781
R_1, wR_2 (all data)	R_1 = 0.0322, wR_2 = 0.0802

Table S2. Bond length (Å) and bond angle (°) data for complex 1

Bond lengths (Å)	1
Ni(1)-P(1)	2.202(5)
Ni(1)-C(1)	1.926(2)
Ni(1)-Br(1)	2.314(3)
Ni(1)-Br(2)	2.290(3)
Bond angles (°)	
C(1)-Ni(1)-P(1)	173.86(5)
C(1)-Ni(1)-Br(1)	90.90(5)
C(1)-Ni(1)-Br(2)	90.47(5)
P(1)-Ni(1)-Br(1)	86.289(2)
P(1)-Ni(1)-Br(2)	92.719(2)

Calculation of percent buried volume (%V_{Bur}) of complex 1

Calculation of the percent buried volume (%V_{Bur}) of complex **1** was performed with the SambVca 2.0 web tool. The result calculation and the steric map are given below.

%V Free	**%V Buried**	% V Tot/V Ex
65.1	**34.9**	99.9

Quadrant	V f	V b	V t	%V f	**%V b**
SW	30.3	14.6	44.9	**67.5**	32.5
NW	29.4	15.4	44.9	**65.6**	34.4
NE	29.8	15.0	44.9	**66.5**	33.5
SE	27.2	17.6	44.9	**60.7**	39.3

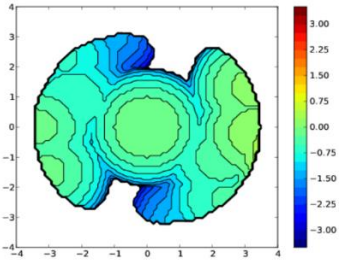


Figure S4. Steric Map

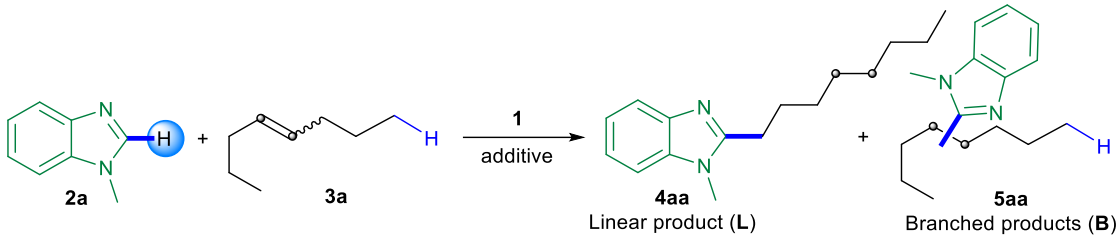
Experimental procedures for hydroarylation reactions

General Procedure for tandem isomerization/*anti*-Markovnikov hydroarylation of unactivated internal alkenes. To a reaction vial was added complex **1** (7 mg，0.01 mmol), KOEt (21 mg，0.25 mmol, 0.5 equiv), heteroarenes (0.50 mmol, 1 equiv), alkenes (0.75 mmol, 1.5 equiv), and toluene (1.5 mL) in the glove box. The vial was screw-capped and taken outside the glove box. The mixture was stirred for 36 h at 100 ℃. After cooling to room temperature, the reaction was quenched by adding water (0.5 mL). Additionally, reaction mixtures of iminoindoles (**2ap**, **2aq**) were treated with 2 molar HCl (1 mL) to deprotect aldehyde/ketonic functional groups. The resulting mixture was extracted with ethyl acetate (3×3 mL), dried over anhydrate $MgSO_4$, filtered, and concentrated. Yields and regioselectivities (**L**:**B**) were determined by GC analysis using *n*-hexadecane as an internal standard. The residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether as eluents to give the desired products.

The reaction procedure for scale-up regioconvergent tandem isomerization/*anti*-markovnikov hydroarylation of alkenes mixtures. To a reaction vial was added complex **1** (144 mg, 0.20 mmol), KOEt (420 mg, 5 mmol, 0.5 equiv), *N*-methylbenzimidazole (**2a**, 1.32 g, 10 mmol, 1 equiv), the mixture of five alkenes (1:1:1:1:1) (2.4 mL, 15 mmol, 1.5 equiv), and toluene (5 mL) in the glove box. The vial was screw-capped and taken outside the glove box. The mixture was stirred for 36 h at 100 ℃. After cooling to room temperature, the reaction was quenched by adding water (5 mL). The resulting mixture was extracted with ethyl acetate (15×3 mL), dried over anhydrate $MgSO_4$, filtered, and concentrated. The regioselectivities (**L**:**B**) were determined by GC analysis using *n*-hexadecane as an internal standard. The residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (1:2) as eluents to give the desired product (**5aa**) in a 94% (2.29 g) yield.

Additional data for optimization of reaction conditions

Table S3. Optimization of reaction conditions for tandem isomerization/*anti*-Markovnikov hydroarylation of *trans*-4-octene with *N*-methylbenzimidazole[a]

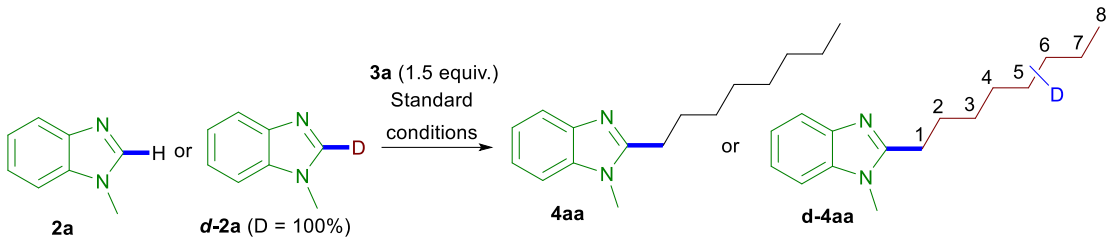


entry	additive	**4aa** (%)	**L**:**B**
1	NaO^{t}Bu	93	95:5
2	KO^{t}Bu	65	95:5
3	NaOEt	70	95:5
4	**KOEt**	**97(95)**[b]	**95:5**
5	NaOMe	20	95:5
6	KOMe	24	95:5
7	NaOAc	0	--
8	Na_2CO_3	0	--
9	K_2CO_3	0	--
10	K_3PO_4	trace	--
11	Mg	7	--
12	Zn	0	--
13	Mn	0	--
14[c]	KOEt	31	95:5
15[d]	KOEt	25	95:5
16[e]	KOEt	65	95:5
17[f]	KOEt	27	95:5

[a]Conditions: **1** (2 mol %), **2a** (0.5 mmol), **3a** (0.75 mmol), additive (0.5 equiv), toluene (1.5 mL), 100 °C, 36 h under Ar. Yields and regioselectivities (**L**:**B**) were determined by GC analysis using *n*-hexadecane as the internal standard (two runs average). [b]Isolated yield. [c]130 °C instead of 100 °C. [d]90 °C instead of 100 °C. [e]THF (1.5 mL) as solvent. [f]*n*-hexane (1.5 mL) as a solvent.

Mechanistic experiments

Measurement of the kinetic isotope effect from single-component two parallel reactions



To a reaction vial was added complex **1** (7 mg，0.010 mmol), KOEt (21 mg，0.25 mmol), *N*-methylbenzimidazole (**2a** or ***d*-2a**, 0.066g, 0.50 mmol), trans-4-octene (**3a**) (84 μL, 0.75 mmol), and toluene (1.5 mL) in the glove box. The vial was screw-capped and taken outside the glove box. The reaction mixture was stirred at 100 ℃ for the indicated time (1, 2, 3, 4, 5, and 6 h, two parallel runs). After cooling to room temperature, the reaction was quenched by adding water (0.5 mL). The resulting mixture was extracted with ethyl acetate (3×3 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated. Yields were determined by GC analysis using *n*-hexadecane as an internal standard. For **2a**, y = 3.56x, for ***d*-2a**, y = 1.91x. The KIE value of 1.86 was calculated by comparing the relative initial rates.

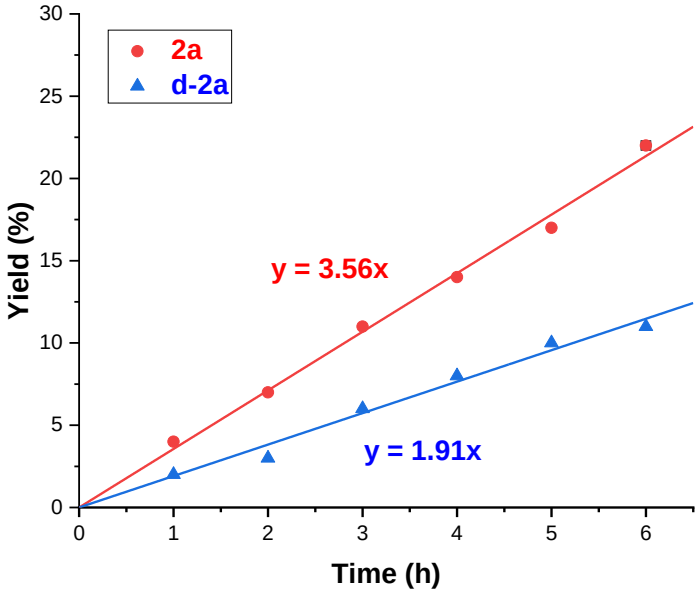
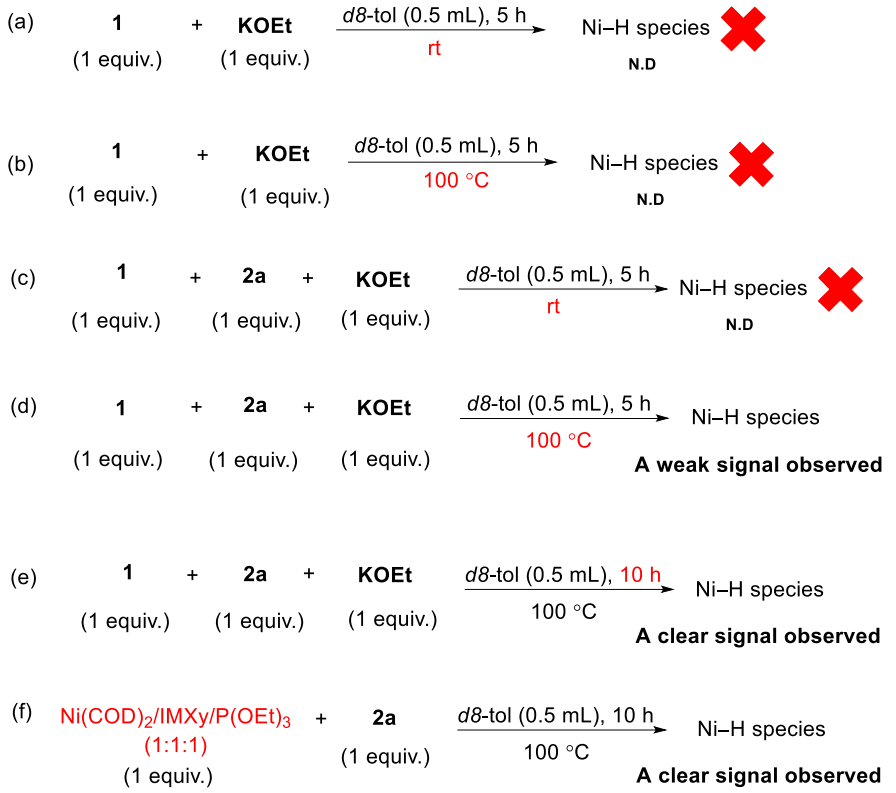


Figure S5. Parallel KIE experiment result: KH/KD = 1.86.

Scheme S1. ^{1}H NMR monitoring of *in situ* generation of Ni–H species



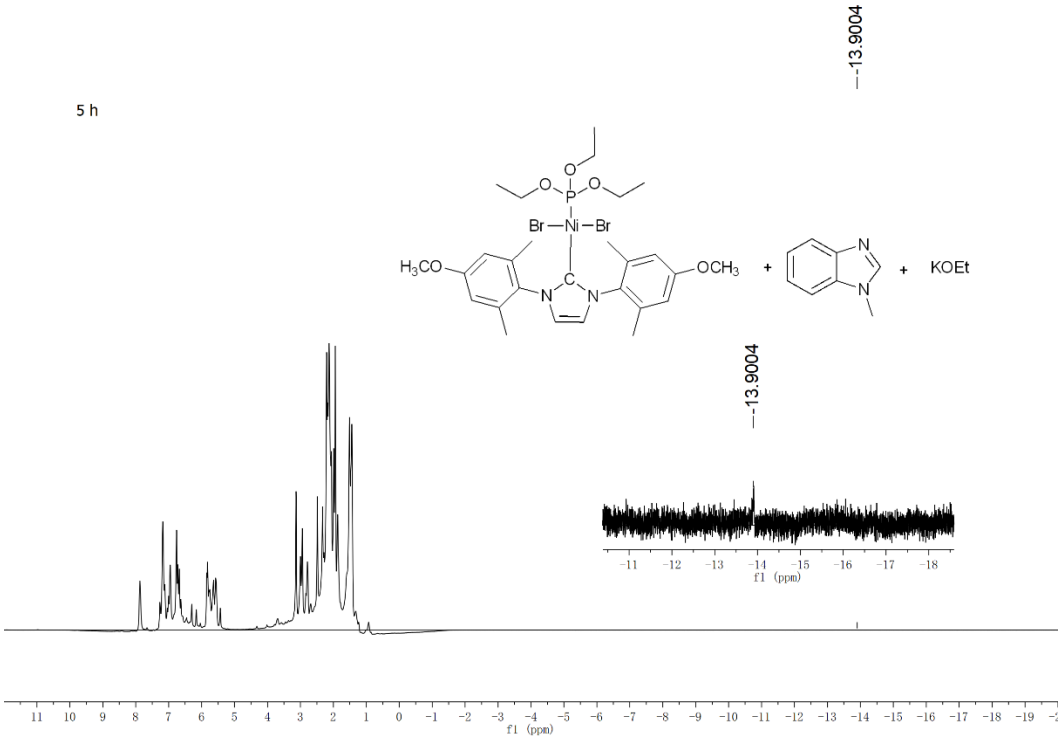


Figure S6. ^{1}H NMR spectrum of complex **1** + **2a** + KOEt (Scheme S1d, 400 MHz, $CDCl_3$).

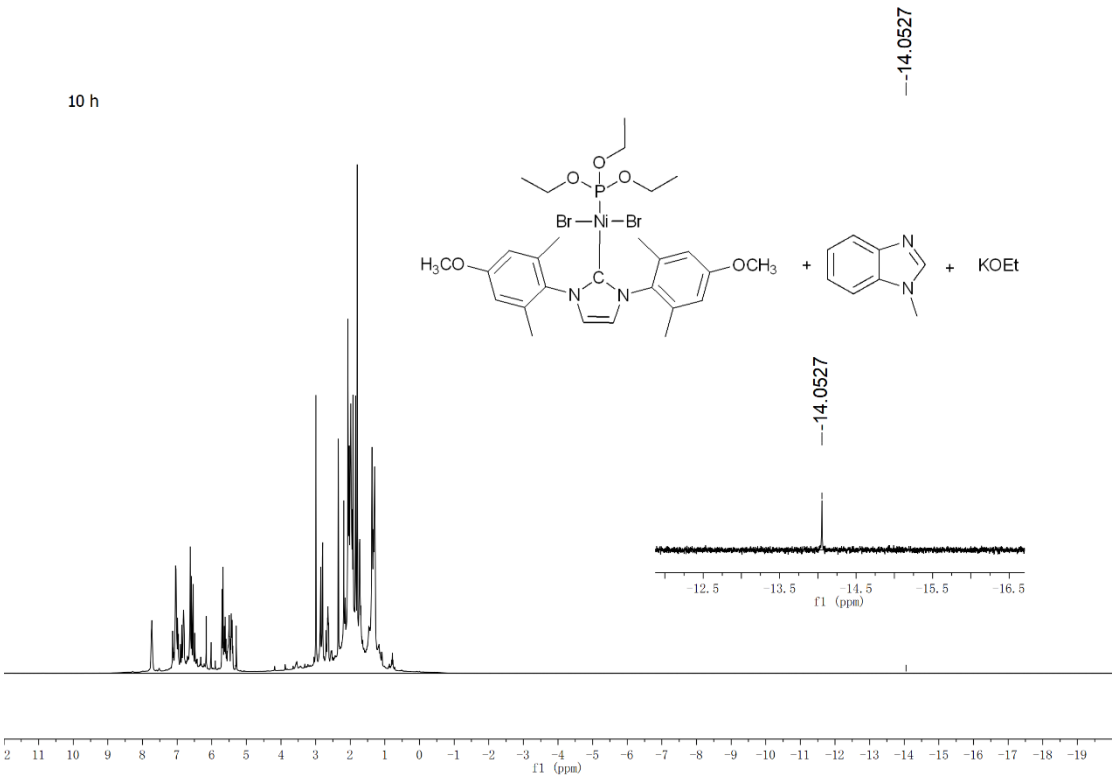


Figure S7. ^{1}H NMR spectrum of complex **1** + **2a** + KOEt (Scheme S1e, 400 MHz, $CDCl_3$).

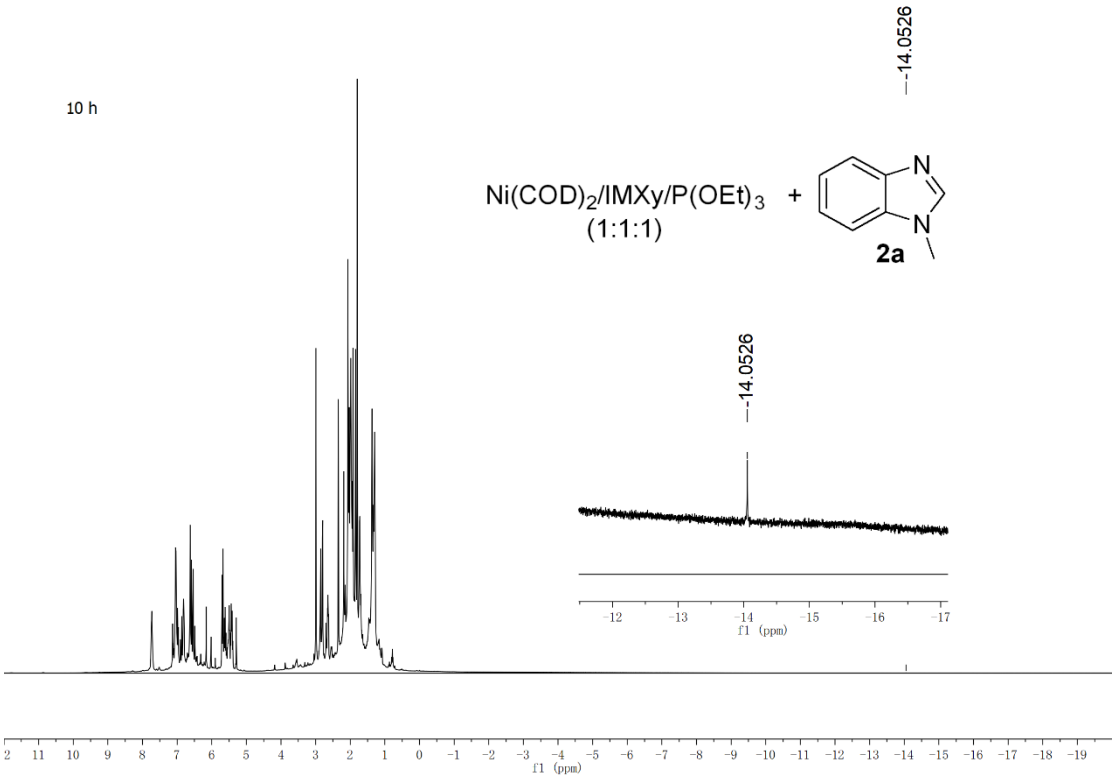
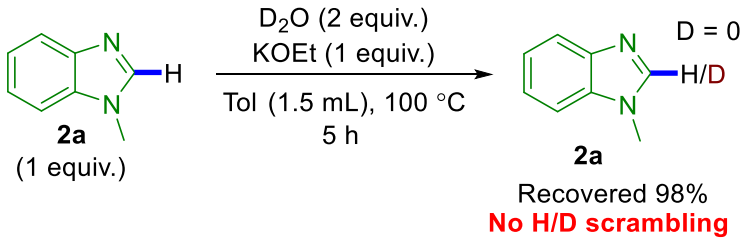
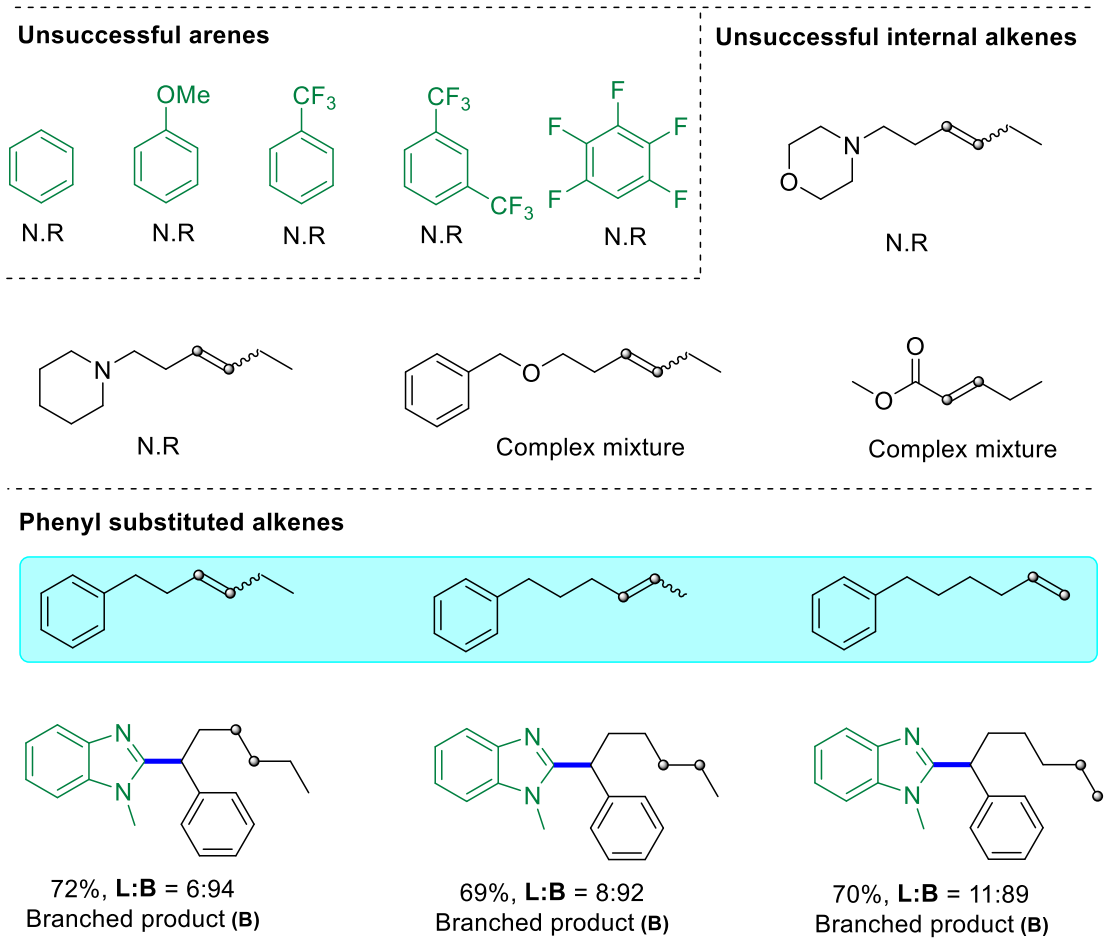


Figure S8. ^{1}H NMR spectrum of $Ni(COD)_2$/IMXy/$P(OEt)_3$ (1:1:1) + **2a** (Scheme S1f, 400 MHz, $CDCl_3$).

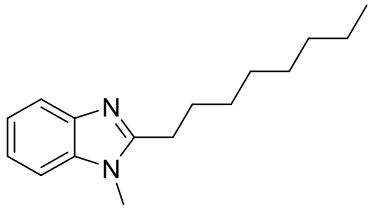
Scheme S2. Control experiment



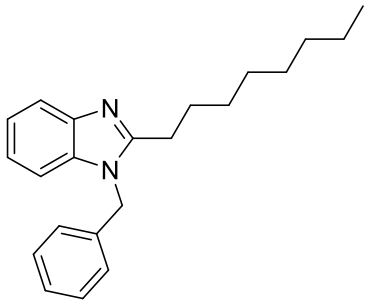
Scheme S3. Unsuccessful substrates



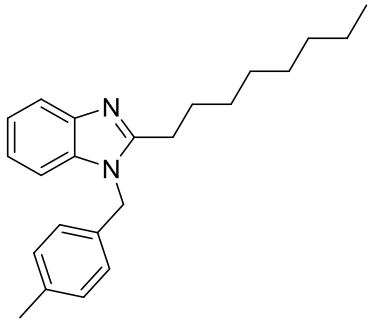
Spectral data of hydroarylation products



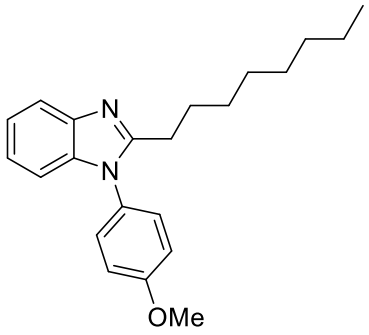
1-methyl-2-octyl-1*H*-benzo[*d*]imidazole (4aa) Yellow oil, EtOAc/PE (1:2) as the eluent, (117 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 1H), 7.31 – 7.22 (m, 3H), 3.72 (s, 3H), 2.87 (t, *J* = 7.8 Hz, 2H), 1.92 – 1.81 (m, 2H), 1.47 – 1.41 (m, 2H), 1.38 – 1.27 (m, 8H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 142.5, 135.7, 121.8, 121.6, 119.0, 108.8, 31.8, 29.6, 29.3, 29.2, 29.1, 27.6, 27.5, 22.6, 14.1. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{25}N_2$: 245.2012, Found: 245.2012.



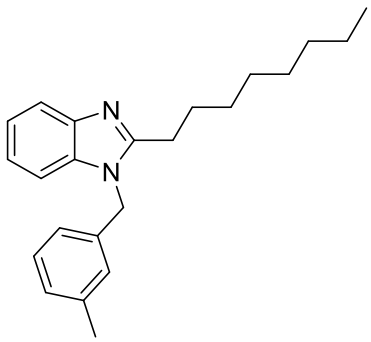
1-benzyl-2-octyl-1*H*-benzo[*d*]imidazole (4ba) Colorless oil, EtOAc/PE (1:4) as the eluent, (149 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 7.3 Hz, 4H), 7.20 (d, *J* = 4.0 Hz, 2H), 7.05 (d, *J* = 6.8 Hz, 2H), 5.32 (s, 2H), 2.84 (t, *J* = 7.4 Hz, 2H), 1.90 – 1.79 (m, 2H), 1.45 – 1.36 (m, 2H), 1.33 – 1.22 (m, 8H), 0.89 (t, *J* = 5.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 142.6, 136.1, 135.4, 128.9, 127.8, 126.1, 122.2, 121.9, 119.2, 109.4, 46.8, 31.8, 29.4, 29.2, 29.1, 27.6, 27.6, 22.6, 14.1. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{29}N_2$: 321.2325, Found: 321.2327.



1-(4-methylbenzyl)-2-octyl-1*H*-benzo[*d*]imidazole (4ca) Colorless oil, EtOAc/PE (1:4) as the eluent, (131 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 9.0 Hz, 1H), 7.18 (d, *J* = 3.4 Hz, 1H), 7.13 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 6.6 Hz, 2H), 6.85 (d, *J* = 6.3 Hz, 2H), 5.22 (s, 2H), 2.75 (t, *J* = 6.3 Hz, 2H), 2.23 (s, 3H), 1.79 – 1.69 (m, 2H), 1.33 – 1.27 (m, 2H), 1.20 – 1.10 (m, 8H), 0.79 (t, *J* = 5.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 142.6, 137.6, 135.3, 133.0, 129.6, 126.1, 122.2, 121.9, 119.2, 109.5, 46.7, 31.8, 29.4, 29.2, 29.1, 27.7, 27.6, 22.6, 21.0, 14.1. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{31}N_2$: 335.2482, Found: 335.2476.

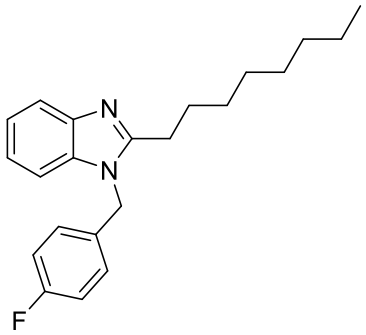


1-(4-methoxyphenyl)-2-octyl-1*H*-benzo[*d*]imidazole (4da) White solid, mp: 120 – 121 ℃, EtOAc/PE (1:2) as the eluent, (151 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 1H), 7.31 – 7.27 (m, 3H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.09 (dd, *J* = 8.1, 4.5 Hz, 3H), 3.93 (s, 3H), 2.76 (t, *J* = 7.8 Hz, 2H), 1.83 – 1.74 (m, 2H), 1.28 (m, 10H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 155.8, 142.4, 136.8, 129.5, 128.6, 122.4, 122.1, 119.0, 115.0, 109.9, 55.6, 31.8, 29.3, 29.1, 29.0, 27.8, 27.6, 22.6, 14.0. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{29}N_2O$: 337.2074, Found: 337.2080.

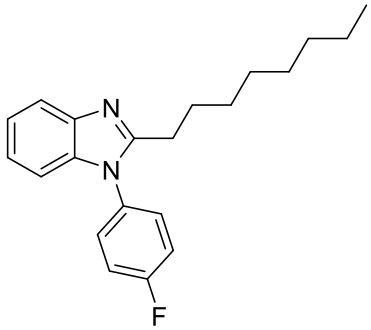


1-(3-methylbenzyl)-2-octyl-1*H*-benzo[*d*]imidazole (4ea) Colorless oil, EtOAc/PE (1:4) as the eluent, (125 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dt, *J* =

7.8, 1.1 Hz, 1H), 7.26 – 7.11 (m, 4H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.87 – 6.77 (m, 2H), 5.24 (s, 2H), 2.80 (t, *J* = 7.8, Hz, 2H), 2.25 (s, 3H), 1.86 – 1.79 (m, 2H), 1.40 – 1.33 (m, 2H), 1.30 – 1.20 (m, 8H), 0.86 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 142.6, 138.7, 136.0, 135.4, 128.8, 128.6, 126.7, 123.2, 122.2, 121.9, 119.2, 109.5, 67.9, 46.8, 31.8, 29.4, 29.2, 27.6, 27.6, 22.6, 21.3, 14.1. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{31}N_2$: 335.2482, Found: 335.2477.

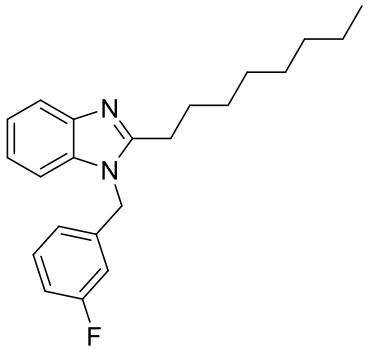


1-(4-fluorobenzyl)-2-octyl-1*H*-benzo[*d*]imidazole (4fa) Yellow oil, EtOAc/PE (1:2) as the eluent, (113 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.8 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.19 – 7.12 (m, 2H), 7.07 – 6.90 (m, 4H), 5.22 (s, 2H), 2.78 (t, *J* = 7.78 Hz, 2H), 1.88 – 1.76 (m, 2H), 1.34 – 1.41 (m, 2H), 1.31 – 1.20 (m, 8H), 0.87 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, *J* = 246.7 Hz), 155.3, 142.7, 135.2, 131.8, 127.7, 126.1, 122.1 (d, *J* = 27.5 Hz), 119.3, 115.8 (d, *J* = 21.7 Hz), 109.3, 46.1, 31.8, 29.4, 29.4, 29.2, 29.1, 27.6, 22.6, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.15. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{28}N_2F$: 339.2231, Found: 339.2240.

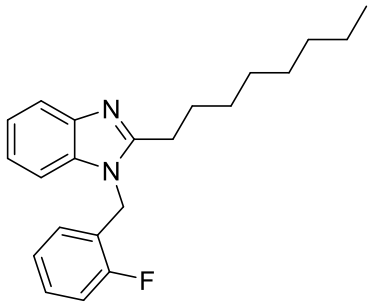


1-(4-fluorophenyl)-2-octyl-1*H*-benzo[*d*]imidazole (4ga) Brown solid, mp: 129 – 130 ℃. EtOAc/PE (1:2) as the eluent, (95 mg, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 1H), 7.36 – 7.27 (m, 2H), 7.25 (t, *J* = 8.4 Hz, 3H), 7.20 – 7.15 (m,

1H), 7.04 (d, *J* = 8.0 Hz, 1H), 2.80 – 2.68 (t, *J* = 7.8 Hz, 2H), 1.84 – 1.70 (m, 2H), 1.37 – 1.17 (m, 10H), 0.85 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, *J* = 249.5 Hz), 155.3, 142.5, 136.6, 132.0 (d, *J* = 3.3 Hz), 129.2 (d, *J* = 8.8 Hz), 122.5 (d, *J* = 21.9 Hz), 119.1, 116.9 (d, *J* = 22.9 Hz), 109.7, 31.7, 29.3, 29.1, 29.0, 27.7, 27.6, 22.6, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.64. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{26}N_2F$: 325.2075, Found: 325.2064.

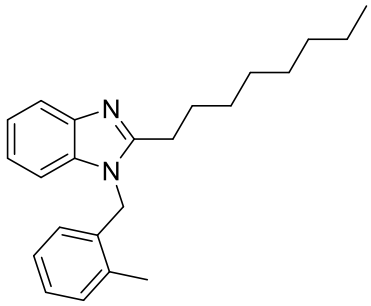


1-(3-fluorobenzyl)-2-octyl-1*H*-benzo[*d*]imidazole (4ha) Yellow oil, EtOAc/PE (1:2) as the eluent, (108 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.8 Hz, 1H), 7.33 – 7.16 (m, 4H), 7.16 – 7.07 (m, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.74 – 6.62 (m, 1H), 5.37 (s, 2H), 2.86 (t, *J* = 7.8 Hz, 2H), 1.91 – 1.77 (m, 2H), 1.47 – 1.35 (m, 2H), 1.35 – 1.23 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0 (d, *J* = 246.4 Hz), 155.5, 142.7, 135.2, 129.6 (d, *J* = 8.1 Hz), 127.7 (d, *J* = 3.7 Hz), 126.1, 124.6 (d, *J* = 3.6 Hz), 123.2 (d, *J* = 14.2 Hz), 122.2 (d, *J* = 25.7 Hz), 119.3, 115.5 (d, *J* = 20.9 Hz), 109.3, 40.7, 40.7, 31.8, 29.4, 29.2, 29.1, 27.6, 22.6, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.24. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{28}N_2F$: 339.2231, Found: 339.2241.

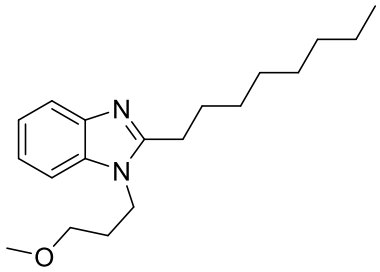


1-(2-fluorobenzyl)-2-octyl-1*H*-benzo[*d*]imidazole (4ia) Yellow oil, EtOAc/PE (1:2) as the eluent, (48 mg, 28% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.5 Hz, 1H), 7.36 – 7.06 (m, 5H), 7.05 – 6.91 (m, 1H), 6.75 (dd, *J* = 26.3, 8.2 Hz, 1H), 5.28 (s,

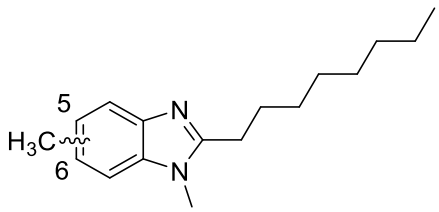
2H), 2.80 (t, *J* = 9.7 Hz, 2H), 1.89 – 1.74 (m, 2H), 1.39 – 1.21 (m, 10H), 0.85 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1 (d, *J* = 247.5 Hz), 155.4, 142.6, 138.7 (d, *J* = 6.9 Hz), 135.2, 130.6, 128.9, 126.1, 122.2 (d, *J* = 26.5 Hz), 119.3 (d, *J* = 14.0 Hz), 114.9 (d, *J* = 21.1 Hz), 113.2 (d, *J* = 22.3 Hz), 109.3, 46.3, 46.3, 31.8, 29.4, 29.1, 27.6, 27.5, 22.6, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.77. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{28}N_2F$: 339.2231, Found: 339.2236.



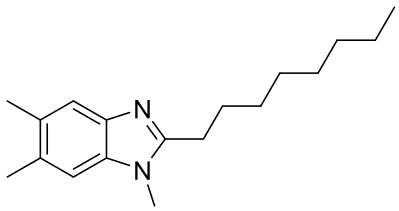
1-(2-methylbenzyl)-2-octyl-1*H*-benzo[*d*]imidazole (4ja) Colorless oil, EtOAc/PE (1:4) as the eluent, (trace yield). HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{31}N_2$: 335.2482, Found: 335.2477.



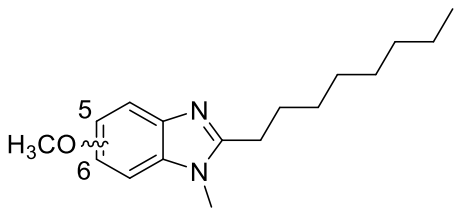
1-(3-methoxypropyl)-2-octyl-1*H*-benzo[*d*]imidazole (4ka) Colorless oil, EtOAc/PE (1:4) as the eluent, (132 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (q, *J* = 3.8 Hz, 1H), 7.34 – 7.24 (m, 1H), 7.19 (dt, *J* = 7.4, 3.6 Hz, 2H), 4.19 (t, *J* = 6.6 Hz, 2H), 3.31 (s, 3H), 3.28 – 3.20 (m, 2H), 2.84 (t, *J* = 10.0 Hz, 2H), 2.06 – 1.93 (m, 2H), 1.93 – 1.81 (m, 2H), 1.50 – 1.40 (m, 2H), 1.39 – 1.21 (m, 8H), 0.88 (t, *J* = 5.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 142.7, 135.0, 121.8, 121.6, 119.0, 109.2, 68.5, 58.5, 58.5, 40.1, 31.8, 29.7, 29.5, 29.3, 27.8, 27.1, 22.6, 14.0. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{31}N_2O$: 303.2431, Found: 303.2431.



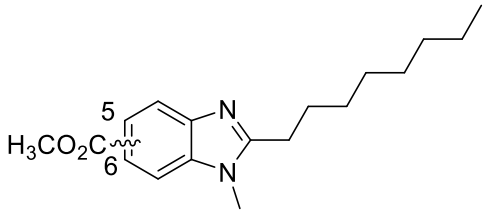
1,5/6-dimethyl-2-octyl-1*H*-benzo[*d*]imidazole (4la, two isomers mixture**)** Yellow oil, EtOAc/PE (1:4) as the eluent, (154 mg, 87% yield). **1,5-dimethyl-2-octyl-1*H*-benzo[*d*]imidazole:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.2 Hz, 1H), 7.09 – 7.06 (m, 2H), 3.67 (s, 3H), 2.89 – 2.80 (m, 2H), 2.48 (s, 3H), 1.91 – 1.79 (m, 2H), 1.49 – 1.41 (m, 2H), 1.37 – 1.26 (m, 8H), 0.93 – 0.86 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.97, 140.5,135.9, 131.3, 123.2, 118.5, 108.3, 31.8, 29.7, 29.6, 29.2, 27.7, 27.5, 21.7, 21.7, 21.5, 14.1. **1,6-dimethyl-2-octyl-1*H*-benzo[*d*]imidazole:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 1H), 7.51 (s, 1H), 7.05 (d, *J* = 2.3 Hz, 1H), 3.68 (s, 3H), 2.89 – 2.80 (m, 2H), 2.50 (s, 3H), 1.91 – 1.79 (m, 2H), 1.49 – 1.41 (m, 2H), 1.37 – 1.26 (m, 8H), 0.93 – 0.86 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 142.7, 135.9, 131.8, 123.2, 118.9, 108.9, 31.8, 29.7, 29.6, 29.5, 27.7, 27.5, 22.6, 21.7, 21.5, 14.1. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{27}N_2$: 259.2169, Found: 259.2162.



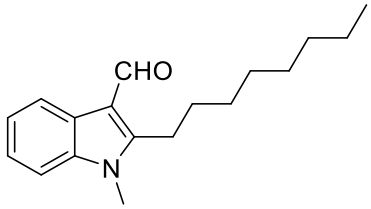
1,5,6-trimethyl-2-octyl-1*H*-benzo[*d*]imidazole (4ma) Off white solid, mp: 84 – 85 °C. EtOAc/PE (1:4) as the eluent, (162 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.02 (s, 1H), 3.63 (s, 3H), 2.80 (t, *J* = 7.7 Hz, 2H), 2.37 (s, 3H), 2.35 (s, 3H), 1.86 – 1.77 (m, 2H), 1.45 – 1.37 (m, 2H), 1.34 – 1.21 (m, 8H), 0.87 (t, *J* = 5.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 141.0, 134.2, 130.8, 130.3, 119.2, 109.2, 31.8, 29.6, 29.5, 29.3, 29.2, 27.8, 27.5, 22.6, 20.5, 20.2, 14.1. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{29}N_2$: 273.2325, Found: 273.2319.



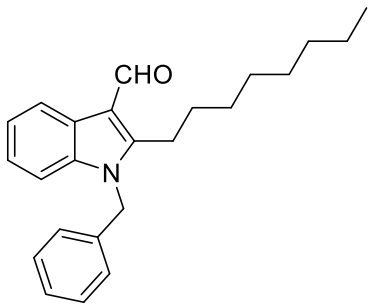
5/6-methoxy-1-methyl-2-octyl-1*H*-benzo[*d*]imidazole (4na, two isomers mixture**)** Off white solid, mp: 92 – 93 ℃. EtOAc/PE (1:2) as the eluent, (121 mg, 88% yield). **5-methoxy-1-methyl-2-octyl-1*H*-benzo[*d*]imidazole:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.7 Hz, 1H), 6.92 – 6.83 (m, 2H), 3.84 (s, 3H), 3.66 (s, 3H), 2.87 – 2.79 (m, 2H), 1.90 – 1.80 (m, 2H), 1.48 – 1.40 (m, 2H), 1.37 – 1.24 (m, 8H), 0.91 – 0.85 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 154.6, 130.3, 119.4, 109.1, 101.6, 93.1, 55.9, 55.8, 31.8, 29.7, 29.1, 27.7, 27.6, 27.5, 22.6, 14.1. **6-methoxy-1-methyl-2-octyl-1*H*-benzo[*d*]imidazole:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.7 Hz, 1H), 7.23 (d, *J* = 2.3 Hz, 1H), 6.75 (d, *J* = 2.4 Hz, 1H), 3.86 (s, 3H), 3.68 (s, 3H), 2.87 – 2.79 (m, 2H), 1.90 – 1.80 (m, 2H), 1.48 – 1.40 (m, 2H), 1.37 – 1.24 (m, 8H), 0.91 – 0.85 (m, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 155.6, 143.0, 111.6, 110.4, 101.6, 93.1, 55.9, 55.8, 31.8, 29.7, 29.5, 27.7, 27.6, 27.5, 22.6, 14.1. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{27}N_2O$: 275.2180, Found: 275.2182.



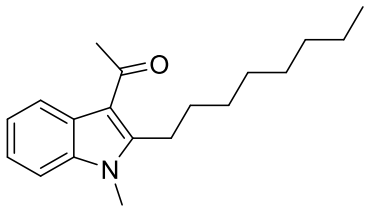
Methyl 1-methyl-2-octyl-1*H*-benzo[*d*]imidazole-5/6-carboxylate (4oa, two isomers mixture**)** Off white solid, mp: 103 – 104 ℃. EtOAc/PE (1:4) as the eluent, (118 mg, 78% yield). **Methyl 1-methyl-2-octyl-1*H*-benzo[*d*]imidazole-5-carboxylate:** ^{1}H NMR (400 MHz, $CDCl_3$) 8.05 (t, *J* = 11.1 Hz, 1H), 7.95 (q, *J* = 8.6, 7.7 Hz, 2H), 3.93 (s, 3H), 3.73 (s, 3H), 2.97 – 2.79 (m, 2H), 1.95 – 1.76 (m, 2H), 1.44 – 1.21 (m, 10H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 157.3, 142.1, 123.9, 123.4, 118.6, 108.5, 52.0, 51.9, 31.8, 29.9, 29.1, 27.6, 27.4, 22.6, 14.4, 14.0. **Methyl 1-methyl-2-octyl-1*H*-benzo[*d*]imidazole-6-carboxylate:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 – 8.29 (m, 1H), 7.71 (q, *J* = 7.6 Hz, 1H), 7.39 – 7.16 (m, 1H), 3.94 (s, 3H), 3.77 (s, 3H), 2.97 – 2.79 (m, 2H), 1.95 – 1.76 (m, 2H), 1.44 – 1.21 (m, 10H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 158.4, 146.1, 135.4, 123.7, 121.3, 111.2, 52.0, 51.9, 31.8, 29.9, 29.1, 27.6, 27.4, 22.6, 14.4, 14.0. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{27}N_2O_2$: 303.2067, Found: 303.2067.



1-methyl-2-octyl-1*H*-indole-3-carbaldehyde (4pa) Yellow oil, EtOAc/PE (1:10) as the eluent, (129 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.31 – 8.22 (m, 1H), 7.26 (d, *J* = 3.2 Hz, 3H), 3.65 (s, 3H), 2.99 (t, *J* = 7.8 Hz, 2H), 1.69 – 1.57 (m, 2H), 1.45 – 1.34 (m, 2H), 1.35 – 1.22 (m, 8H), 0.87 (t, *J* = 6.9, Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.2, 171.0, 152.3, 151.0, 136.7, 127.1, 113.9, 109.2, 102.7, 50.7, 31.9, 30.1, 29.2, 29.1, 25.6, 24.4, 22.6, 14.0. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{26}NO$: 272.2009, Found: 272.2015.

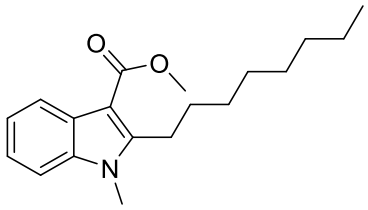


1-benzyl-2-octyl-1*H*-indole-3-carbaldehyde (4qa) Yellow oil, EtOAc/PE (1:10) as the eluent, (161 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.22 (s, 1H), 8.32 (d, *J* = 8.8 Hz, 1H), 7.29 (dd, *J* = 7.8, 5.3 Hz, 4H), 7.20 (q, *J* = 4.8, 4.1 Hz, 2H), 6.99 (dd, *J* = 7.6, 1.9 Hz, 2H), 5.37 (s, 2H), 3.04 (t, *J* = 7.9 Hz, 2H), 1.64 – 1.52 (m, 2H), 1.40 – 1.33 (m, 2H), 1.29 – 1.21 (m, 8H), 0.86 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.4, 152.1, 136.8, 136.0, 129.0, 127.9, 127.1, 125.8, 123.4, 123.0, 121.1, 114.4, 110.0, 46.7, 31.7, 30.5, 29.4, 29.1, 29.0, 24.7, 22.6, 14.0. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{30}NO$: 348.2322, Found: 348.2311.

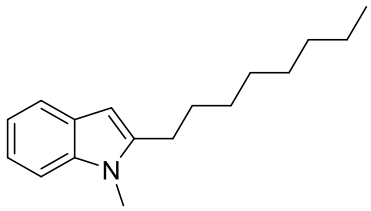


1-(1-methyl-2-octyl-1*H*-indol-3-yl)ethan-1-one (4ra) Yellow oil, EtOAc/PE (1:10) as the eluent, (118 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 6.6, 2.3

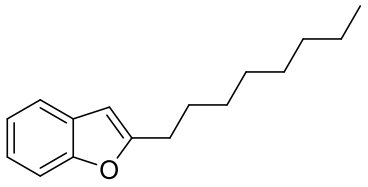
Hz, 1H), 7.37 – 7.32 (m, 1H), 7.27 (d, *J* = 4.0 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 3.73 (s, 3H), 3.19 (t, *J* = 7.8 Hz, 2H), 2.69 (s, 3H), 1.65 – 1.59 (m, 2H), 1.52 – 1.40 (m, 2H), 1.36 – 1.25 (m, 8H), 0.87 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 149.7, 136.6, 129.5, 128.5, 121.9, 120.7, 113.4, 109.6, 31.8, 31.7, 29.8, 29.4, 29.4, 29.2, 29.1, 26.1, 22.6, 14.1. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{28}NO$: 286.2165, Found: 286.2163.



Methyl 1-methyl-2-octyl-1*H*-indole-3-carboxylate (4sa) Yellow oil, EtOAc/PE (1:10) as the eluent, (82 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.09 (m, 1H), 7.32 – 7.29 (m, 1H), 7.25 – 7.21 (m, 2H), 3.93 (s, 3H), 3.72 (s, 3H), 3.20 (t, *J* = 7.9 Hz, 2H), 1.65 – 1.61 (m, 2H), 1.50 – 1.39 (m, 2H), 1.34 – 1.26 (m, 8H), 0.87 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 149.8, 136.5, 126.6, 122.0, 121.7, 121.5, 109.1, 103.2, 50.6, 31.8, 29.8, 29.4, 29.2, 27.2, 25.6, 22.6, 14.6, 14.1. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{28}NO_2$: 302.2125, Found: 302.2126.

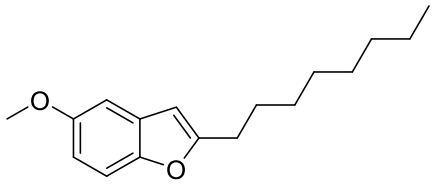


1-methyl-2-octyl-1*H*-indole (4ta)[7] Colorless oil, PE as the eluent, (30 mg, 25% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.05 (m, 3H), 7.02 (s, 2H), 2.57 (t, *J* = 7.8 Hz, 2H), 2.35 (s, 3H), 1.66 – 1.59 (m, 2H), 1.36 – 1.27 (m, 10H), 0.90 (t, *J* = 6.5 Hz, 3H).

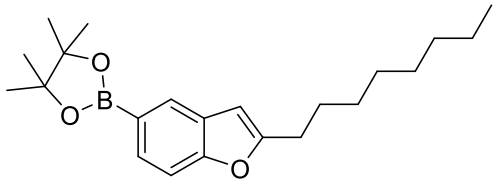


2-octylbenzofuran (4ua)[8] Colorless oil, PE as the eluent (101 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 1H), 7.48 (d, *J* = 6.1 Hz, 1H), 7.27 – 7.21

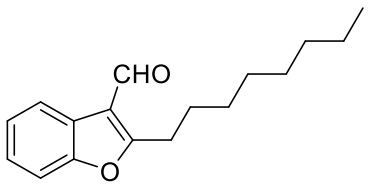
(m, 2H), 6.43 (s, 1H), 2.82 (t, *J* = 7.6 Hz, 2H), 1.87 – 1.75 (m, 2H), 1.47 – 1.33 (m, 10H), 0.95 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 154.6, 129.0, 123.0, 122.3, 120.1, 110.7, 101.7, 31.9, 31.8, 29.3, 29.2, 28.5, 27.7, 22.7, 14.1.



5-methoxy-2-octylbenzofuran (4va) Colorless oil, PE as the eluent, (109 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.23 (m, 1H), 6.95 (t, *J* = 3.3 Hz, 1H), 6.79 (dd, *J* = 9.0, 3.1 Hz, 1H), 6.30 (d, *J* = 3.4 Hz, 1H), 3.81 (s, 3H), 2.72 (t, *J* = 7.3 Hz, 2H), 1.83 – 1.65 (m, 2H), 1.42 – 1.25 (m, 10H), 0.88 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 155.7, 149.6, 129.6, 129.4, 111.3, 103.2, 101.9, 55.9, 35.5, 33.7, 31.8, 28.5, 27.7, 27.1, 22.6, 14.1. HRMS (EI) Calcd for $C_{17}H_{24}O_2$: 260.1776, Found: 260.1776.

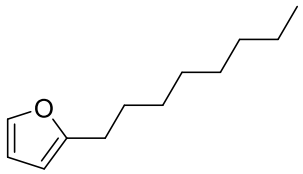


4,4,5,5-tetramethyl-2-(2-octylbenzofuran-5-yl)-1,3,2-dioxaborolane (4wa) Colorless oil, EtOAc/PE (1:20) as the eluent, (142 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (t, *J* = 1.0 Hz, 1H), 7.72 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.44 (dd, *J* = 8.1, 0.9 Hz, 1H), 6.40 (d, *J* = 1.1 Hz, 1H), 2.79 (t, *J* = 7.6 Hz, 2H), 1.82 – 1.73 (m, 2H), 1.41 – 1.42 (m, 2H), 1.40 (s, 12H), 1.37 – 1.29 (m, 8H), 0.92 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 156.8, 129.7, 128.7, 127.5, 110.2, 101.8, 83.6, 31.8, 29.3, 29.3, 29.2, 28.4, 27.6, 24.9, 22.7, 14.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.65. HRMS (EI) Calcd for $C_{22}H_{33}BO_3$: 356.2523, Found: 356.2523.

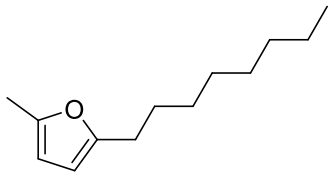


2-octylbenzofuran-3-carbaldehyde (4xa) Colorless oil, EtOAc/PE (1:20) as the eluent, (107 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.22 (s, 1H), 8.13 (dd, *J*

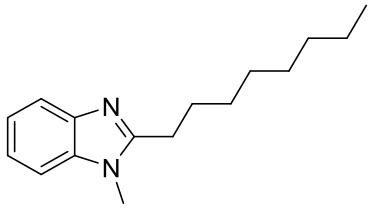
= 5.2, 3.7 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.33 – 7.31 (m, 1H), 7.21 – 7.10 (m, 1H), 3.09 (t, *J* = 7.5 Hz, 2H), 1.90 – 1.77 (m, 2H), 1.44 – 1.37 (m, 2H), 1.33 – 1.21 (m, 8H), 0.87 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.9, 170.7, 153.9, 129.7, 128.1, 125.1, 121.7, 117.6, 110.9, 31.8, 29.1, 29.1, 29.1, 28.3, 27.1, 22.6, 14.0. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{23}O_2$: 259.1693, Found: 259.1685.



2-octylfuran (4ya)[8] Colorless oil, PE as the eluent, (77 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 1.9 Hz, 1H), 6.27 (dd, *J* = 3.2, 1.9 Hz, 1H), 5.96 (d, *J* = 3.2 Hz, 1H), 2.61 – 2.55 (m, 2H), 1.66 – 1.60 (m, 2H), 1.35 – 1.28 (m, 10H), 0.87 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 154.6, 110.0, 104.5, 31.8, 29.3, 29.2, 28.1, 28.0, 28.0, 22.6, 14.1.

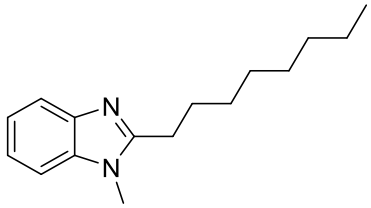


2-methyl-5-octylfuran (4za)[9] Colorless oil, PE as the eluent, (88 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (s, 0.37H), 6.99 (s, 0.61H), 5.83 (s, 1H), 2.55 (t, *J* = 7.6 Hz, 2H), 2.32 (s, 1H), 2.25 (s, 2H), 1.64 – 1.55 (m, 2H), 1.34 – 1.23 (m, 10H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 150.0, 105.7, 105.0, 35.9, 31.8, 29.3, 29.2, 28.2, 28.0, 22.6, 14.1, 13.5.

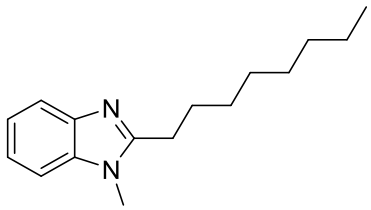


1-methyl-2-octyl-1*H*-benzo[*d*]imidazole (6ab) Yellow oil, EtOAc/PE (1:2) as the eluent, (112 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 1H), 7.31 – 7.22 (m, 3H), 3.72 (s, 3H), 2.87 (t, *J* = 7.8 Hz, 2H), 1.92 – 1.81 (m, 2H), 1.47 – 1.41 (m, 2H), 1.38 – 1.27 (m, 8H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

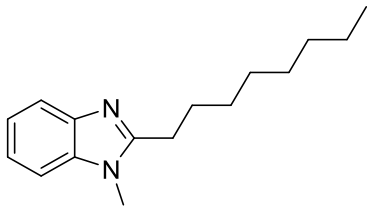
155.4, 142.5, 135.7, 121.8, 121.6, 119.0, 108.8, 31.8, 29.6, 29.3, 29.2, 29.1, 27.6, 27.5, 22.6, 14.1. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{25}N_2$: 245.2012, Found: 245.2012.



1-methyl-2-octyl-1*H*-benzo[*d*]imidazole (6ac) Yellow oil, EtOAc/PE (1:2) as the eluent, (115 mg, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 1H), 7.31 – 7.22 (m, 3H), 3.72 (s, 3H), 2.87 (t, *J* = 7.8 Hz, 2H), 1.92 – 1.81 (m, 2H), 1.47 – 1.41 (m, 2H), 1.38 – 1.27 (m, 8H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 142.5, 135.7, 121.8, 121.6, 119.0, 108.8, 31.8, 29.6, 29.3, 29.2, 29.1, 27.6, 27.5, 22.6, 14.1. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{25}N_2$: 245.2012, Found: 245.2012.

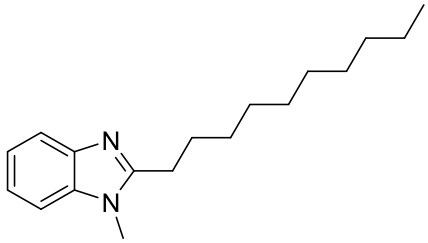


1-methyl-2-octyl-1*H*-benzo[*d*]imidazole (6ad) Yellow oil, EtOAc/PE (1:2) as the eluent, (113 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 1H), 7.31 – 7.22 (m, 3H), 3.72 (s, 3H), 2.87 (t, *J* = 7.8 Hz, 2H), 1.92 – 1.81 (m, 2H), 1.47 – 1.41 (m, 2H), 1.38 – 1.27 (m, 8H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 142.5, 135.7, 121.8, 121.6, 119.0, 108.8, 31.8, 29.6, 29.3, 29.2, 29.1, 27.6, 27.5, 22.6, 14.1. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{25}N_2$: 245.2012, Found: 245.2012.

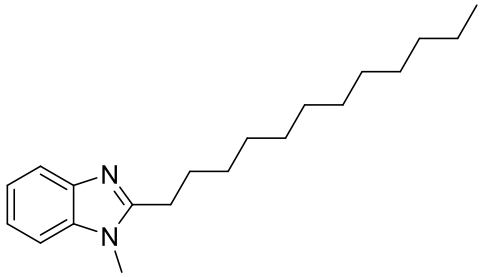


1-methyl-2-octyl-1*H*-benzo[*d*]imidazole (6ae) Yellow oil, EtOAc/PE (1:2) as the eluent, (117 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 1H), 7.31 – 7.22 (m, 3H), 3.72 (s, 3H), 2.87 (t, *J* = 7.8 Hz, 2H), 1.92 – 1.81 (m, 2H), 1.47 – 1.41 (m, 2H), 1.38 – 1.27 (m, 8H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

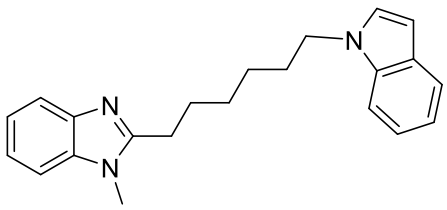
155.4, 142.5, 135.7, 121.8, 121.6, 119.0, 108.8, 31.8, 29.6, 29.3, 29.2, 29.1, 27.6, 27.5, 22.6, 14.1. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{25}N_2$: 245.2012, Found: 245.2012.



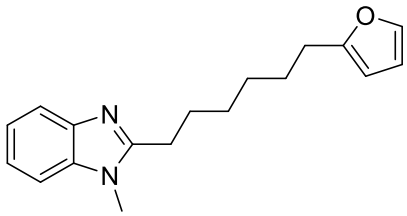
2-decyl-1-methyl-1*H*-benzo[*d*]imidazole (6af) Yellow oil, EtOAc/PE (1:4) as the eluent, (125 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.66 (m, 1H), 7.34 – 7.14 (m, 3H), 3.69 (s, 3H), 2.85 (t, *J* = 7.8 Hz, 2H), 1.95 – 1.80 (m, 2H), 1.50 – 1.41 (m, 2H), 1.39 – 1.21 (m, 12H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 142.6, 135.7, 121.8, 121.6, 119.1, 108.8, 31.9, 29.6, 29.5, 29.5, 29.3, 29.3, 29.3, 27.6, 27.5, 22.6, 14.1. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{29}N_2$: 273.2325, Found: 273.2329.



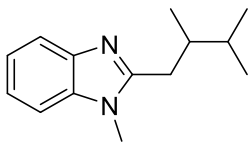
2-dodecyl-1-methyl-1*H*-benzo[*d*]imidazole (6ag) Yellow oil, EtOAc/PE (1:4) as the eluent, (123 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 1H), 7.26 – 7.19 (m, 3H), 3.66 (s, 3H), 2.83 (t, *J* = 7.8 Hz, 2H), 1.92 – 1.80 (m, 2H), 1.50 – 1.40 (m, 2H), 1.37 – 1.22 (m, 16H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 142.5, 135.7, 121.8, 121.6, 119.0, 108.8, 31.9, 29.6, 29.6, 29.6, 29.6, 29.5, 29.5, 29.3, 29.3, 27.6, 27.5, 22.7, 14.1. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{33}N_2$: 301.2638, Found: 301.2638.



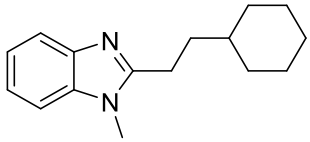
2-(6-(1*H*-indol-1-yl)hexyl)-1-methyl-1*H*-benzo[*d*]imidazole (6ah) Yellow oil, EtOAc/PE (1:2) as the eluent, (124 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 6.1, 2.7 Hz, 1H), 7.61 (d, *J* = 8.9 Hz, 1H), 7.31 (d, *J* = 8.3 Hz, 1H), 7.26 – 7.14 (m, 4H), 7.10 – 7.04 (m, 2H), 6.46 (d, *J* = 4.0 Hz, 1H), 4.09 (t, *J* = 7.0 Hz, 2H), 3.61 (s, 3H), 2.79 (t, *J* = 7.7 Hz, 2H), 1.90 – 1.78 (m, 4H), 1.48 – 1.34 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 142.5, 135.9, 135.7, 128.6, 127.8, 122.0, 121.8, 121.3, 120.9, 119.1, 119.1, 109.4, 108.9, 100.9, 46.2, 30.0, 29.6, 28.9, 27.3, 27.3, 26.7. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{26}N_3$: 332.2121, Found: 332.2127.



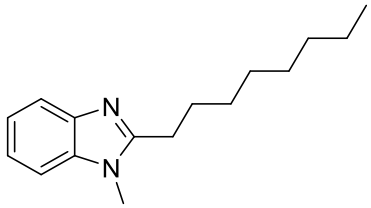
2-(6-(furan-2-yl)hexyl)-1-methyl-1*H*-benzo[*d*]imidazole (6ai) Yellow oil, EtOAc/PE (1:2) as the eluent, (84 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.70 (m, 1H), 7.28 (d, *J* = 3.2 Hz, 1H), 7.24 – 7.21 (m, 2H), 6.25 (d, *J* = 3.2 Hz, 1H), 5.95 (d, *J* = 3.7 Hz, 1H), 5.83 (d, *J* = 4.2 Hz, 1H), 3.69 (s, 3H), 2.86 (t, *J* = 7.8 Hz, 2H), 2.64 – 2.54 (m, 2H), 1.93 – 1.83 (m, 2H), 1.65 (t, *J* = 8.5 Hz, 2H), 1.51 – 1.37 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 155.3, 142.4, 140.6, 135.7, 122.0, 121.8, 119.0, 110.0, 108.8, 104.6, 29.7, 29.1, 28.8, 28.0, 27.8, 27.5, 27.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{23}N_2O$: 283.1805, Found: 283.1804.



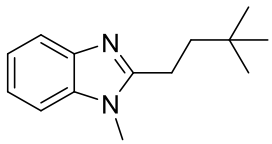
2-(2,3-dimethylbutyl)-1-methyl-1*H*-benzo[*d*]imidazole (6aj) Yellow oil, EtOAc/PE (1:2) as the eluent, (67 mg, 62% yield**).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.71 (m, 1H), 7.34 – 7.30 (m, 1H), 7.28 – 7.25 (m, 2H), 3.76 (s, 3H), 2.98 (dd, *J* = 14.5, 5.0 Hz, 1H), 2.68 (dd, *J* = 14.5, 9.9 Hz, 1H), 2.09 – 2.04 (m, 1H), 1.74 (td, *J* = 6.8, 4.5 Hz, 1H), 0.99 (dd, *J* = 6.8, 4.9 Hz, 6H), 0.92 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 142.9, 135.7, 121.9, 121.8, 119.1, 108.8, 38.3, 32.3, 31.9, 29.9, 20.0, 18.1, 15.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{21}N_2$: 217.1699, Found: 217.1696.



2-(2-cyclohexylethyl)-1-methyl-1*H*-benzo[*d*]imidazole (6ak) Off white solid, mp: 49 – 50 °C. EtOAc/PE (1:4) as the eluent, (82 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 1H), 7.26 – 7.16 (m, 3H), 3.64 (s, 3H), 2.83 (t, *J* = 8.2 Hz, 2H), 1.86 – 1.64 (m, 7H), 1.41 – 1.15 (m, 4H), 1.06 – 0.93 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 142.5, 135.7, 121.8, 121.6, 119.0, 108.8, 37.5, 35.0, 33.1, 29.6, 26.5, 26.2, 25.0. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{23}N_2$: 243.1856, Found: 243.1866.



1-methyl-2-octyl-1*H*-benzo[*d*]imidazole (6al) Yellow oil, EtOAc/PE (1:2) as the eluent, (115 mg, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 1H), 7.31 – 7.22 (m, 3H), 3.72 (s, 3H), 2.87 (t, *J* = 7.8 Hz, 2H), 1.92 – 1.81 (m, 2H), 1.47 – 1.41 (m, 2H), 1.38 – 1.27 (m, 8H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 142.5, 135.7, 121.8, 121.6, 119.0, 108.8, 31.8, 29.6, 29.3, 29.2, 29.1, 27.6, 27.5, 22.6, 14.1. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{25}N_2$: 245.2012, Found: 245.2012.



2-(3,3-dimethylbutyl)-1-methyl-1*H*-benzo[*d*]imidazole (6am) Yellow oil, EtOAc/PE (1:4) as the eluent, (82 mg, 77% yield). mp: 62 – 63 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.36 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.31 (td, *J* = 7.5, 1.5 Hz, 1H), 7.21 (td, *J* = 7.5, 1.6 Hz, 1H), 3.80 (s, 3H), 2.66 – 2.58 (m, 2H), 1.91 – 1.78 (m, 1H), 1.73 – 1.59 (m, *J* = 6.9 Hz, 1H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.85 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 142.4, 135.7, 121.9, 121.7, 119.0, 108.8, 41.4, 30.4, 29.6, 29.1, 22.9. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{21}N_2$: 217.1699, Found: 217.1696.

Copies of NMR spectra for hydroarylation products

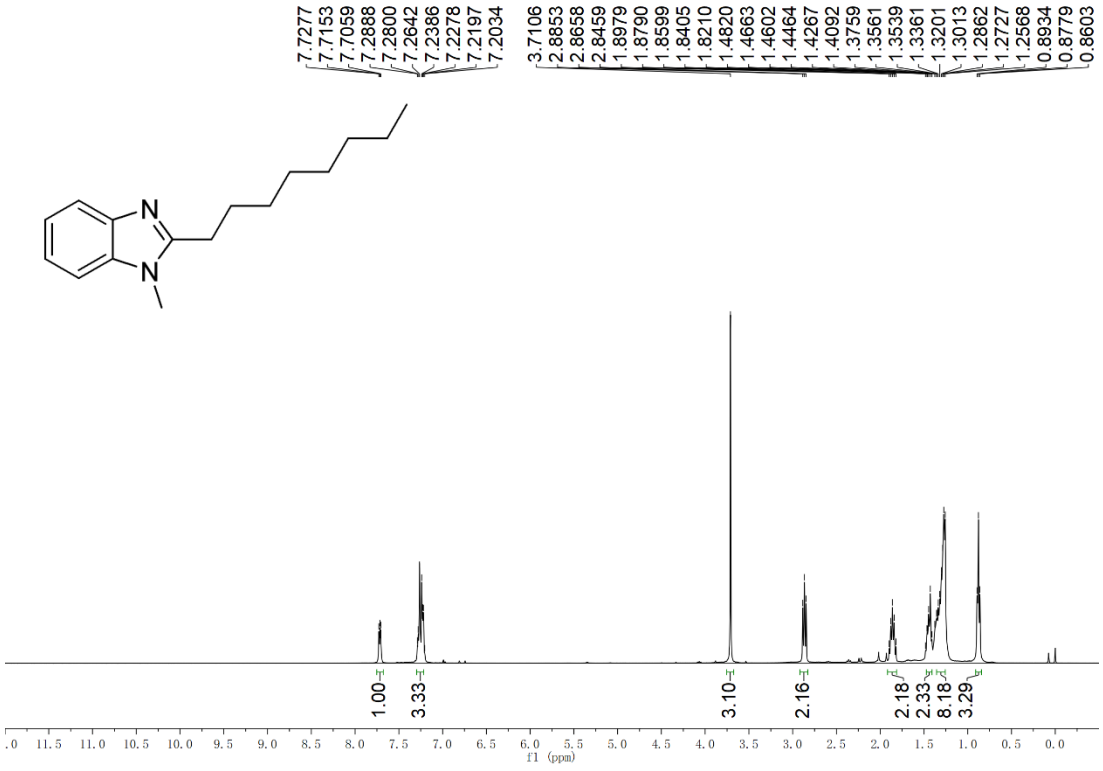


Figure S9. ^{1}H NMR spectrum of compound **4aa** (400 MHz, $CDCl_3$).

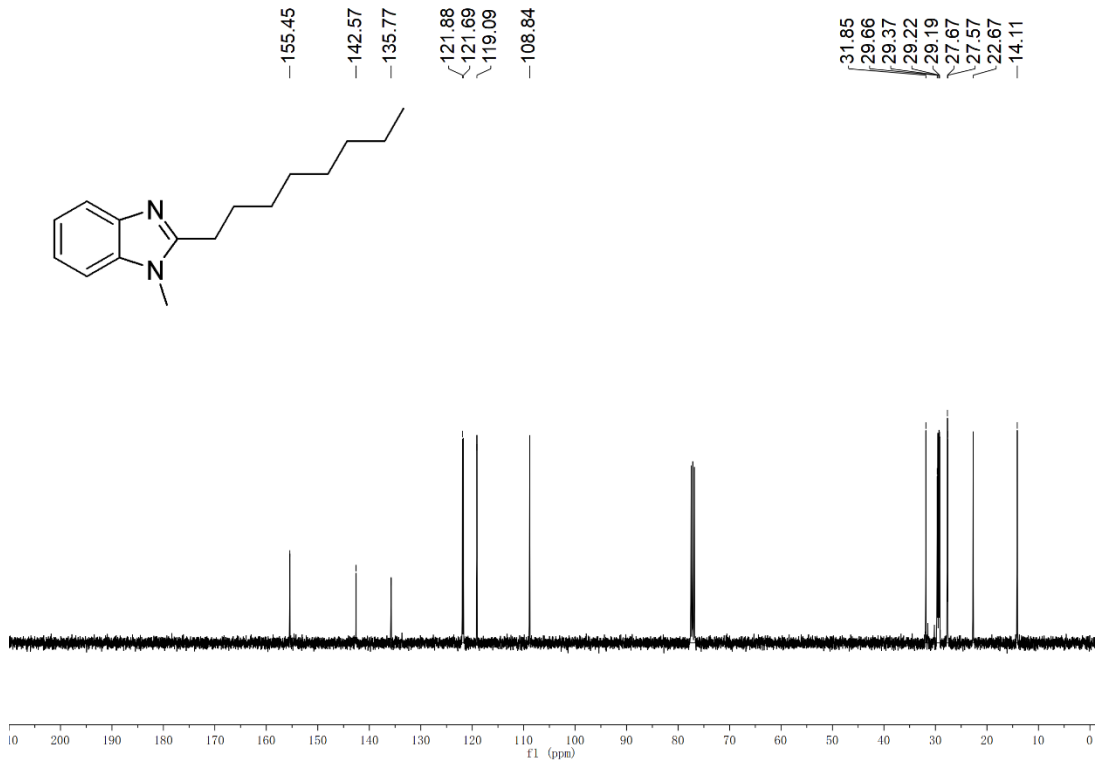


Figure S10. ^{13}C NMR spectrum of compound **4aa** (100 MHz, $CDCl_3$).

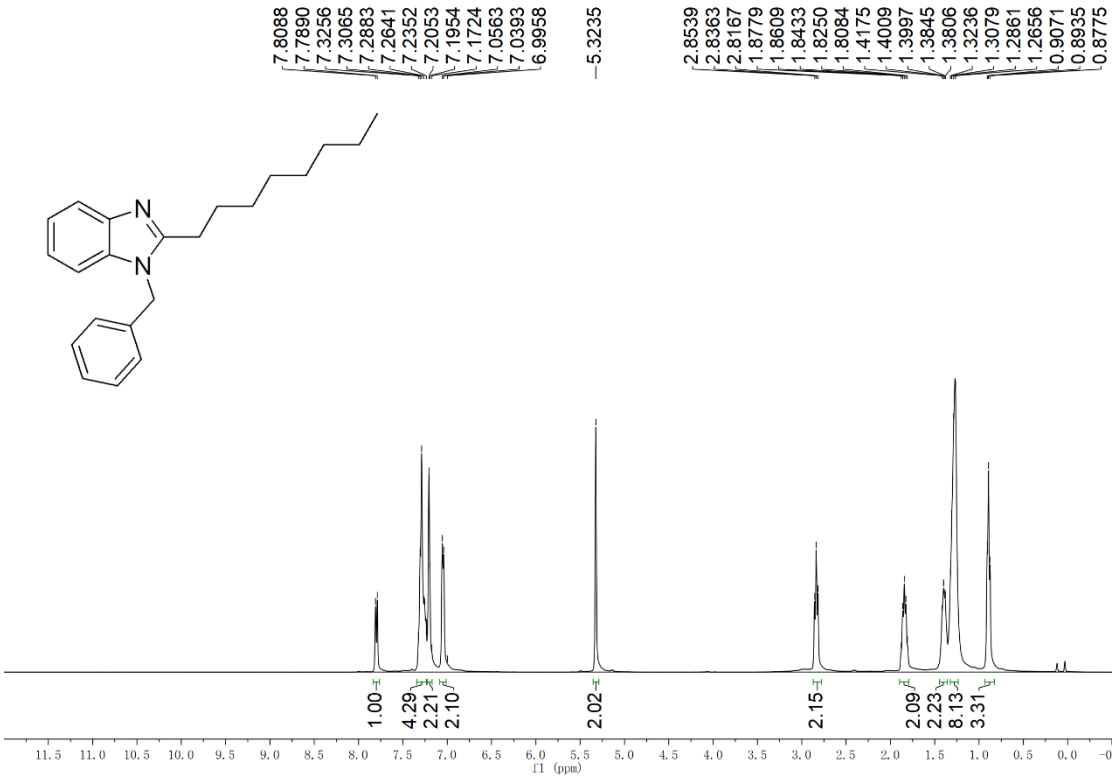


Figure S11. ^{1}H NMR spectrum of compound **4ba** (400 MHz, $CDCl_3$).

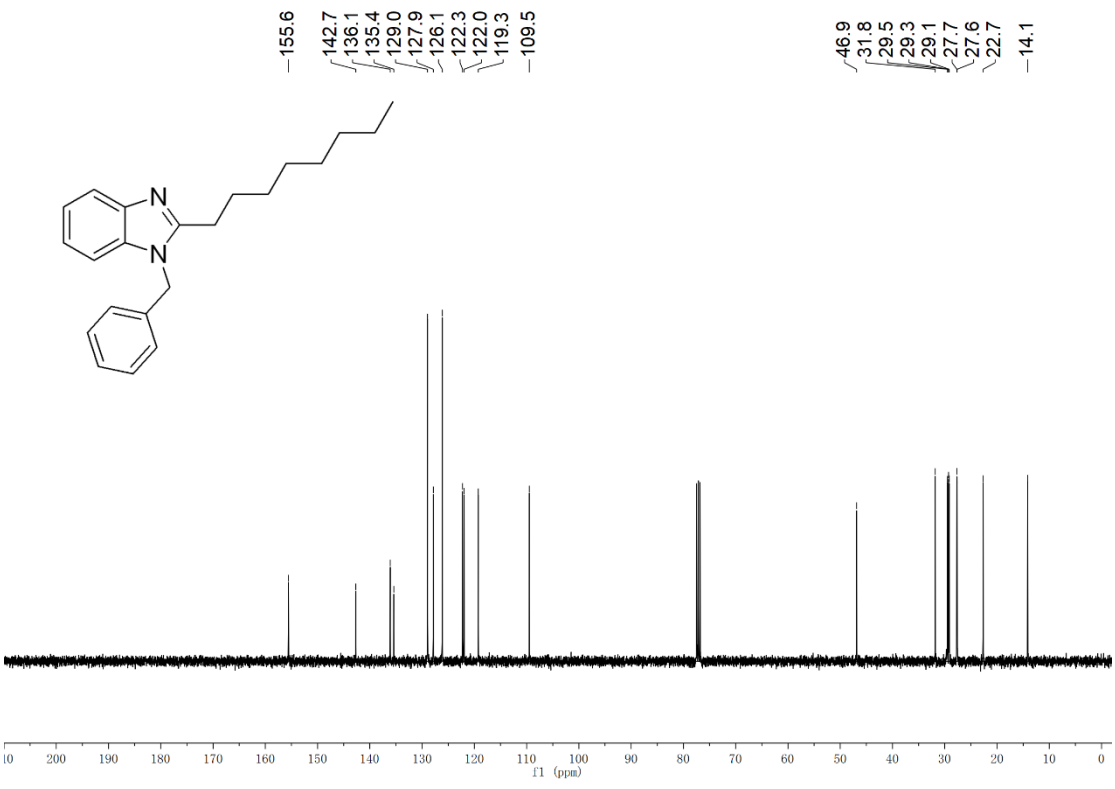


Figure S12. ^{13}C NMR spectrum of compound **4ba** (100 MHz, $CDCl_3$).

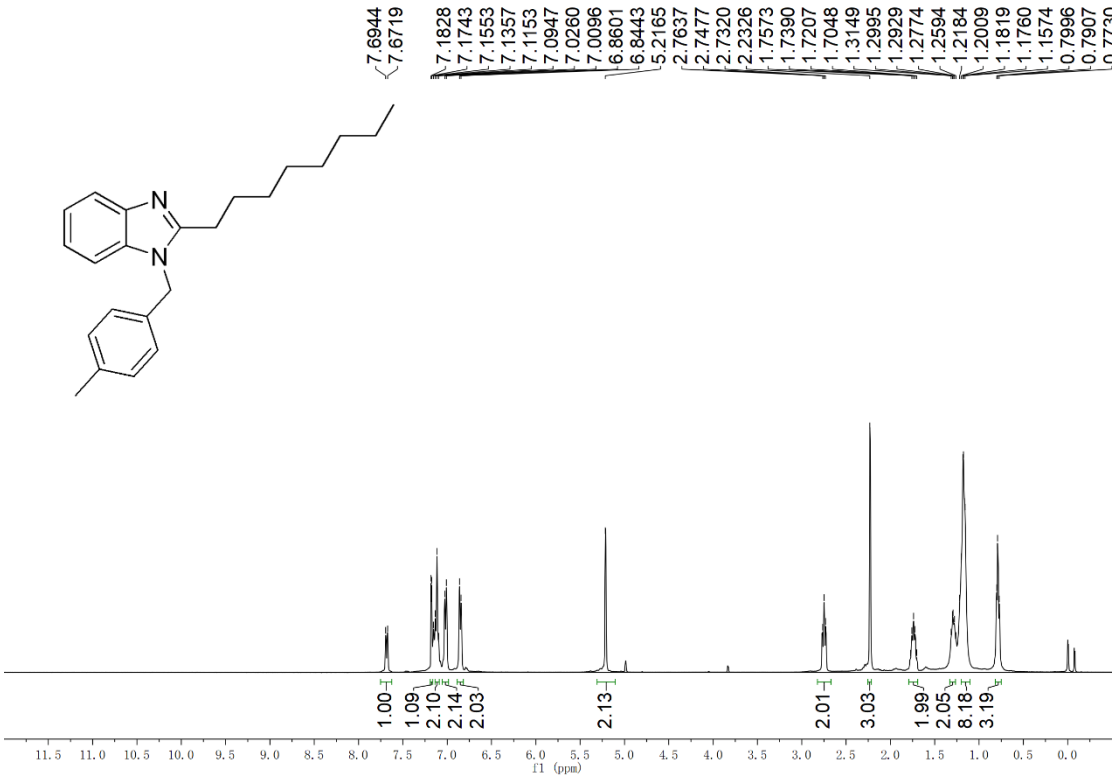


Figure S13. ^{1}H NMR spectrum of compound **4ca** (400 MHz, $CDCl_3$).

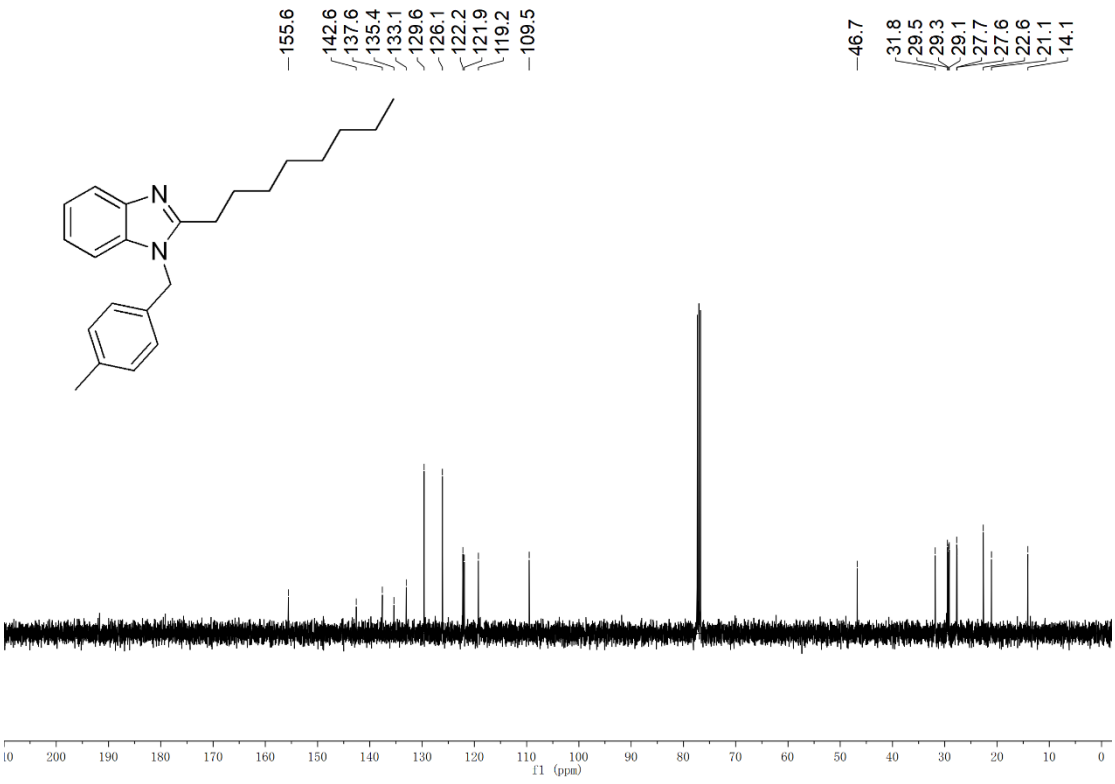


Figure S14. ^{13}C NMR spectrum of compound **4ca** (100 MHz, $CDCl_3$).

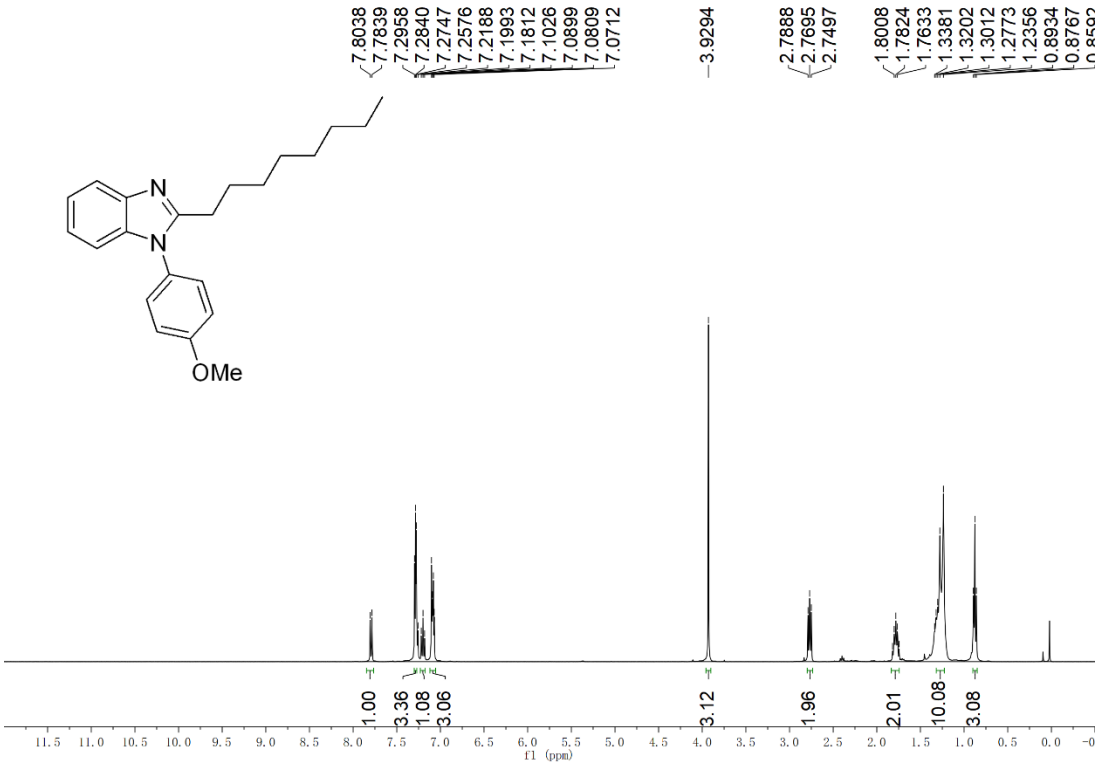


Figure S15. ^{1}H NMR spectrum of compound **4da** (400 MHz, $CDCl_3$).

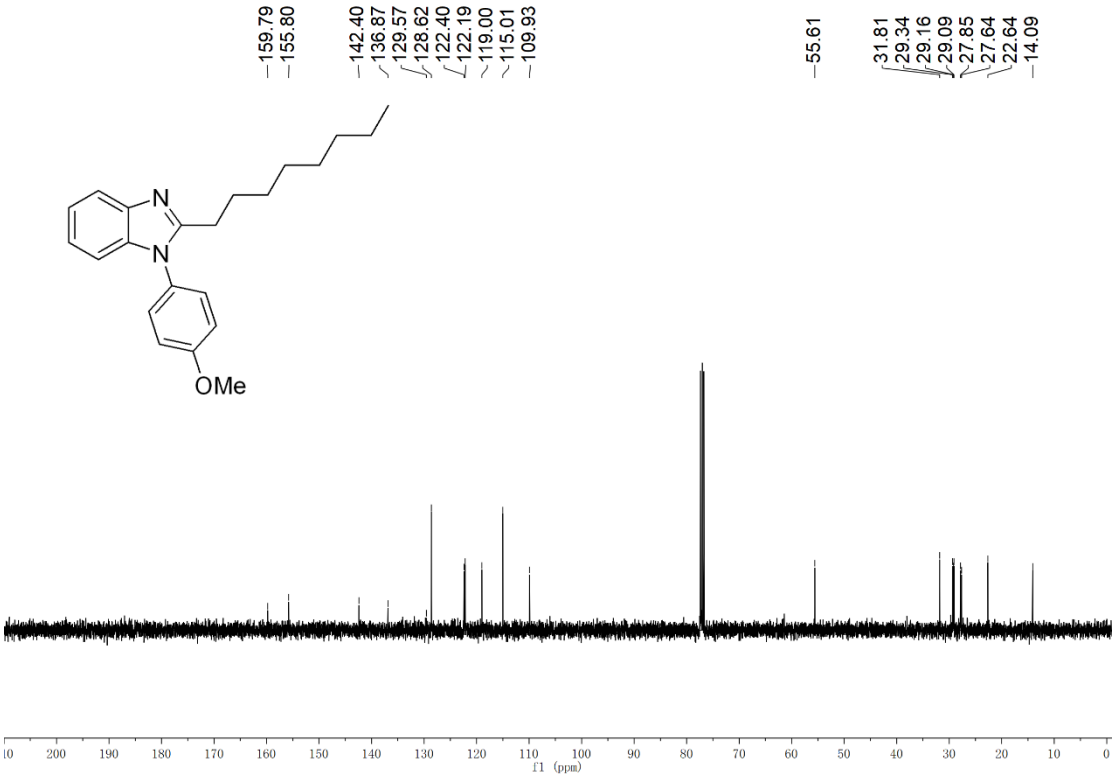


Figure S16. ^{13}C NMR spectrum of compound **4da** (100 MHz, $CDCl_3$).

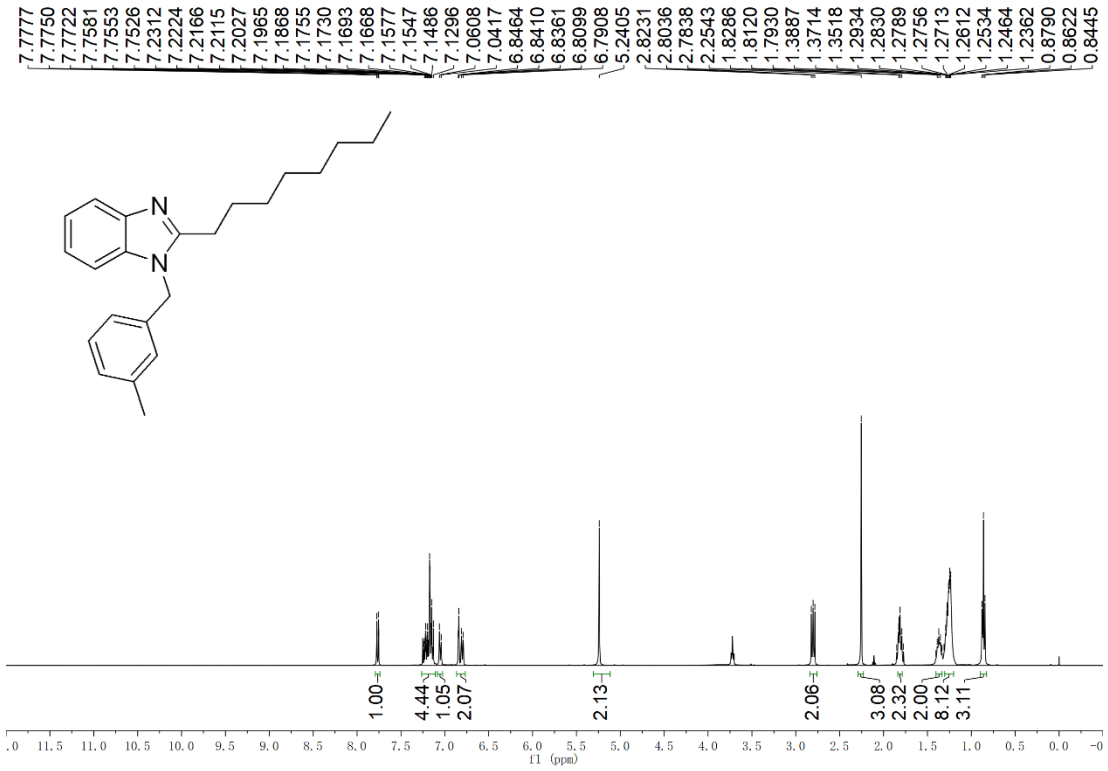


Figure S17. ^{1}H NMR spectrum of compound **4ea** (400 MHz, $CDCl_3$).

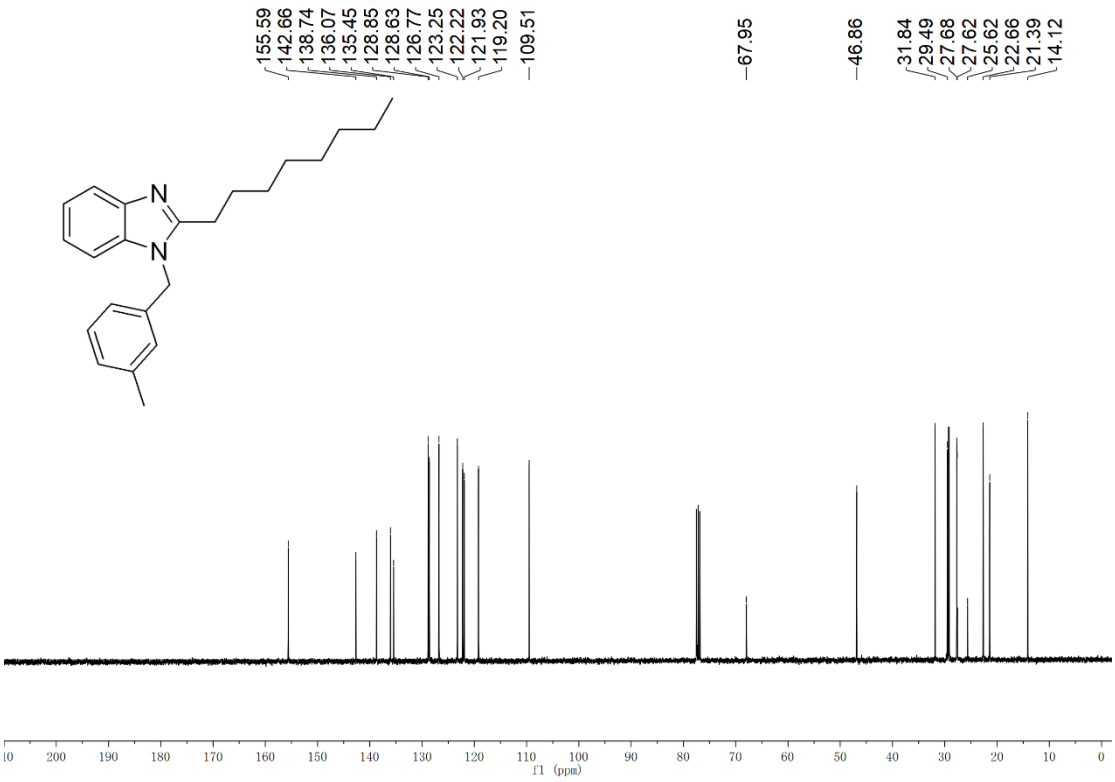


Figure S18. ^{13}C NMR spectrum of compound **4ea** (100 MHz, $CDCl_3$).

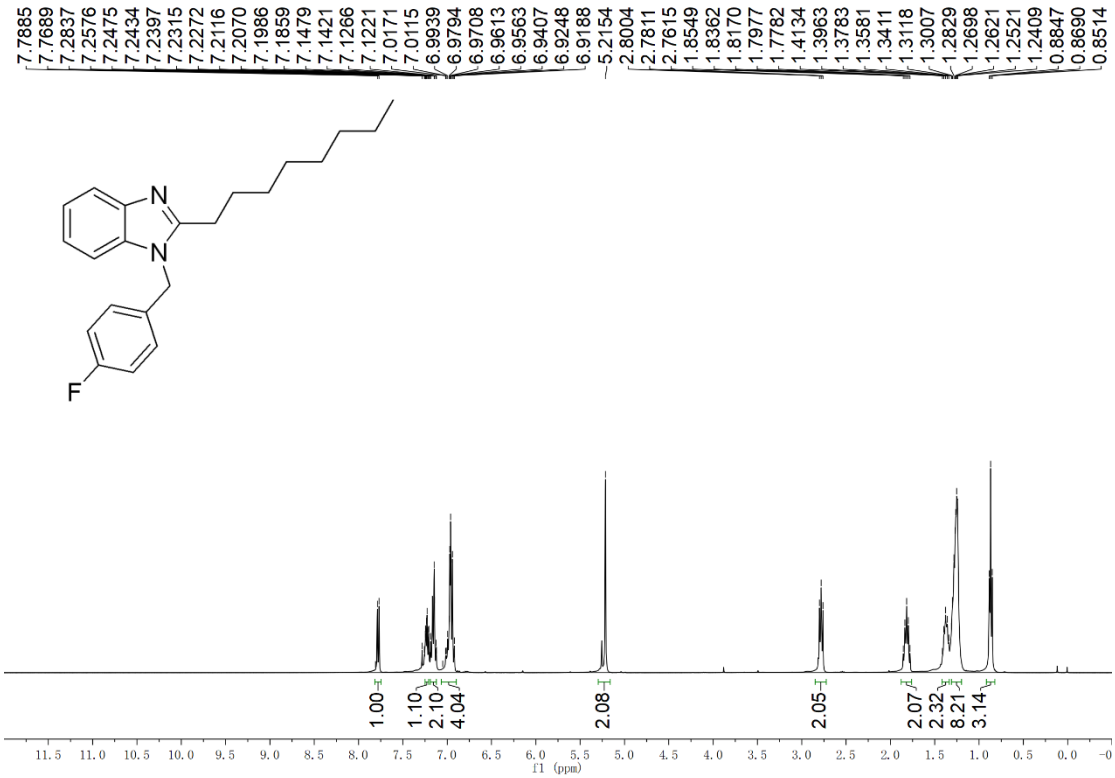


Figure S19. ^{1}H NMR spectrum of compound **4fa** (400 MHz, $CDCl_3$).

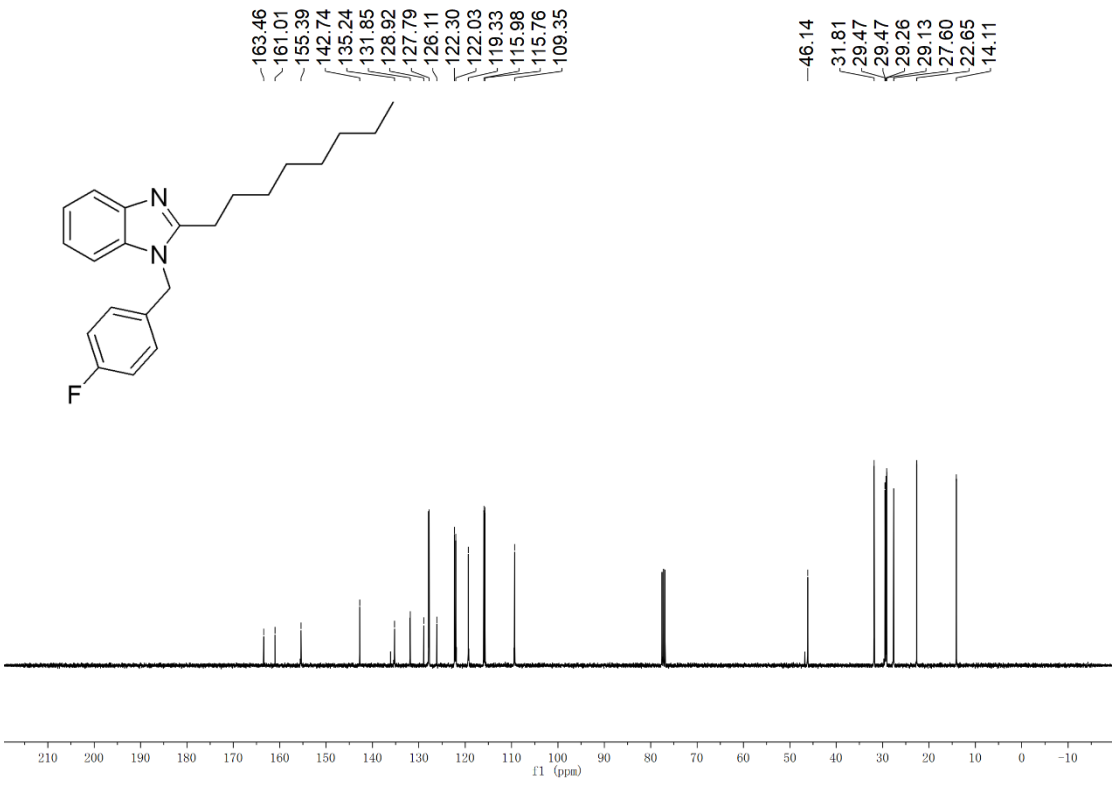


Figure S20. ^{13}C NMR spectrum of compound **4fa** (100 MHz, $CDCl_3$).

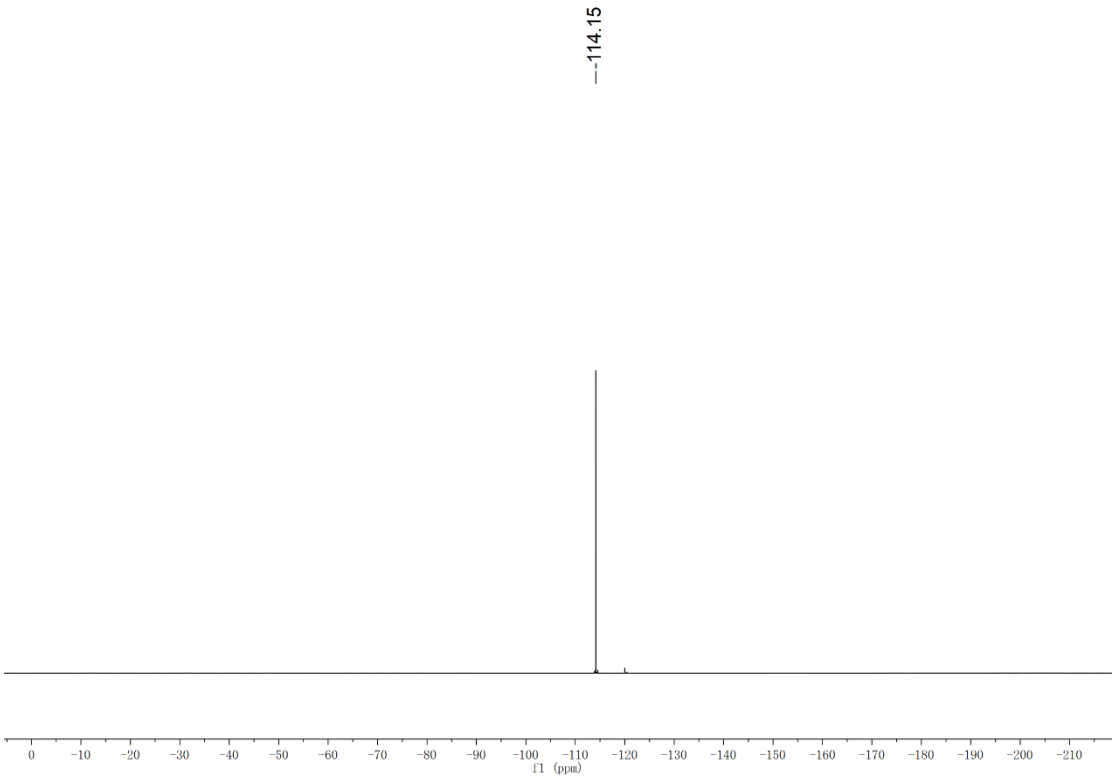


Figure S21. ^{19}F NMR spectrum of compound **4fa** (376 MHz, $CDCl_3$).

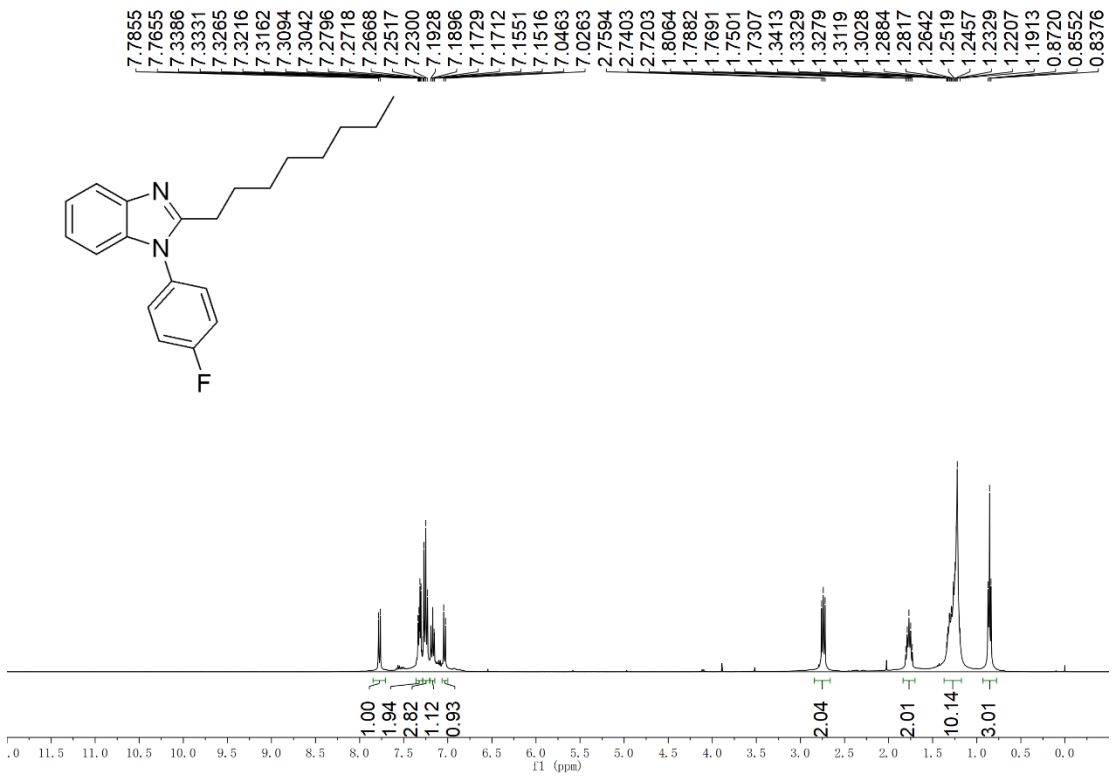


Figure S22. ^{1}H NMR spectrum of compound **4ga** (400 MHz, $CDCl_3$).

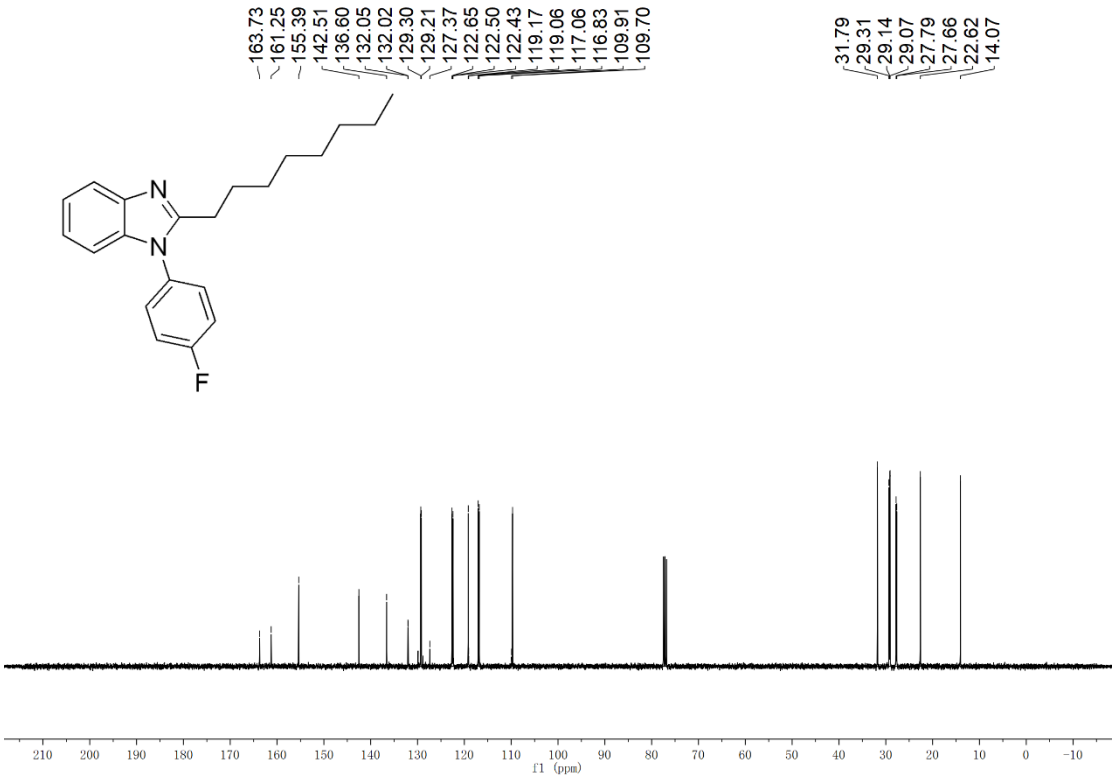


Figure S23. ^{13}C NMR spectrum of compound **4ga** (100 MHz, $CDCl_3$).

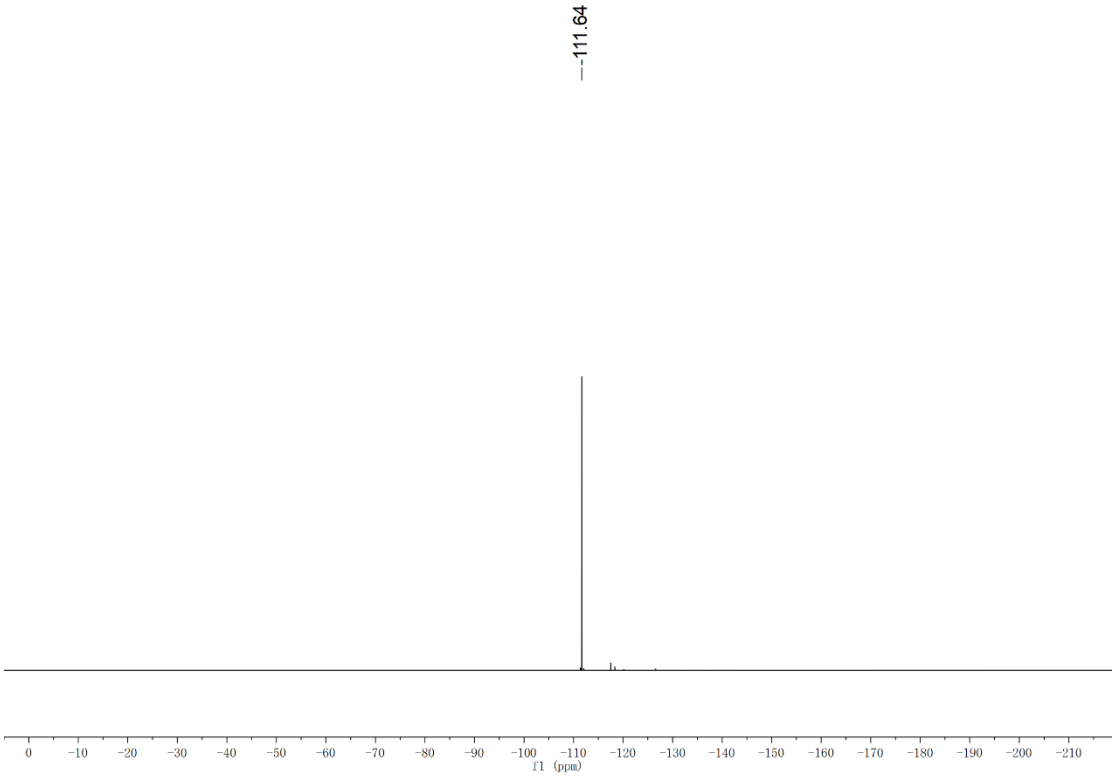


Figure S24. ^{19}F NMR spectrum of compound **4ga** (376 MHz, $CDCl_3$).

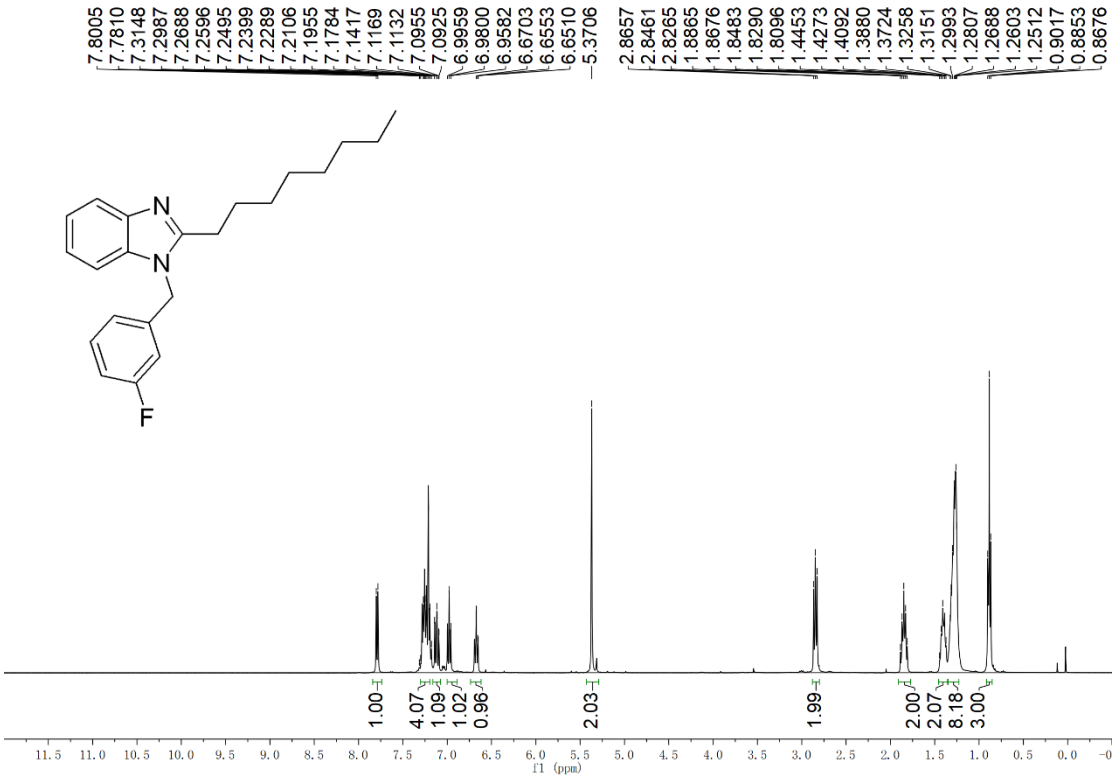


Figure S25. ^{1}H NMR spectrum of compound **4ha** (400 MHz, $CDCl_3$).

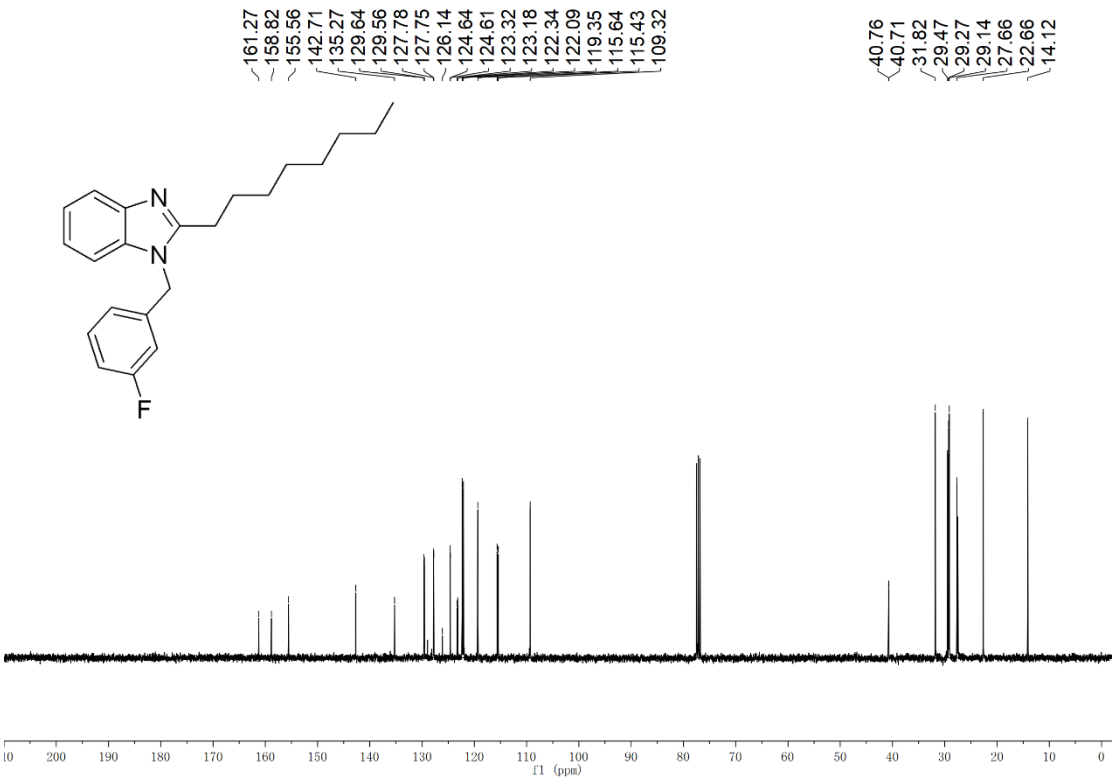


Figure S26. ^{13}C NMR spectrum of compound **4ha** (100 MHz, $CDCl_3$).

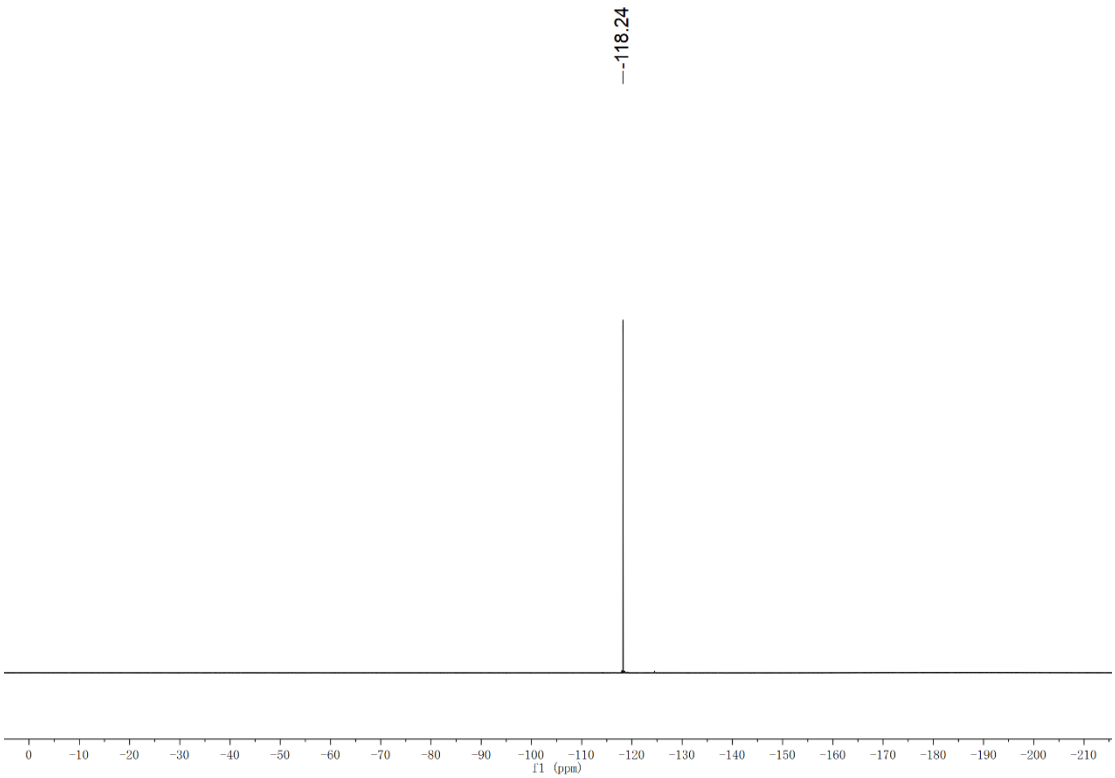


Figure S27. ^{19}F NMR spectrum of compound **4ha** (376 MHz, $CDCl_3$).

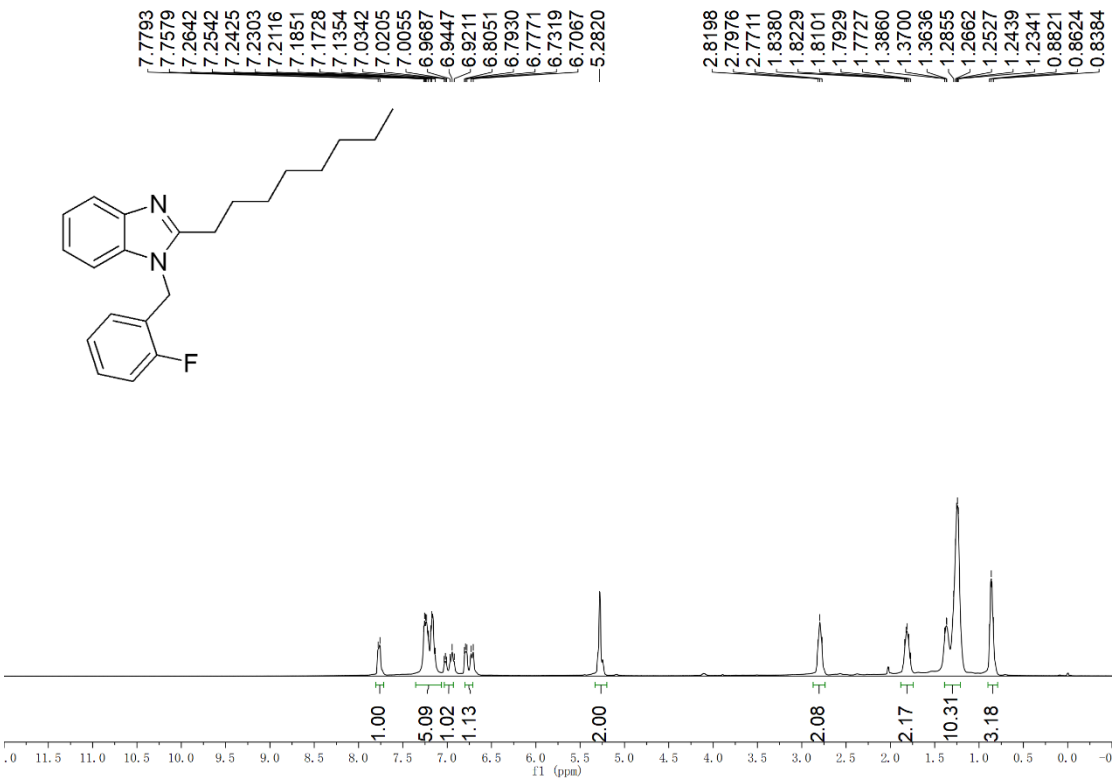


Figure S28. ^{1}H NMR spectrum of compound **4ia** (400 MHz, $CDCl_3$).

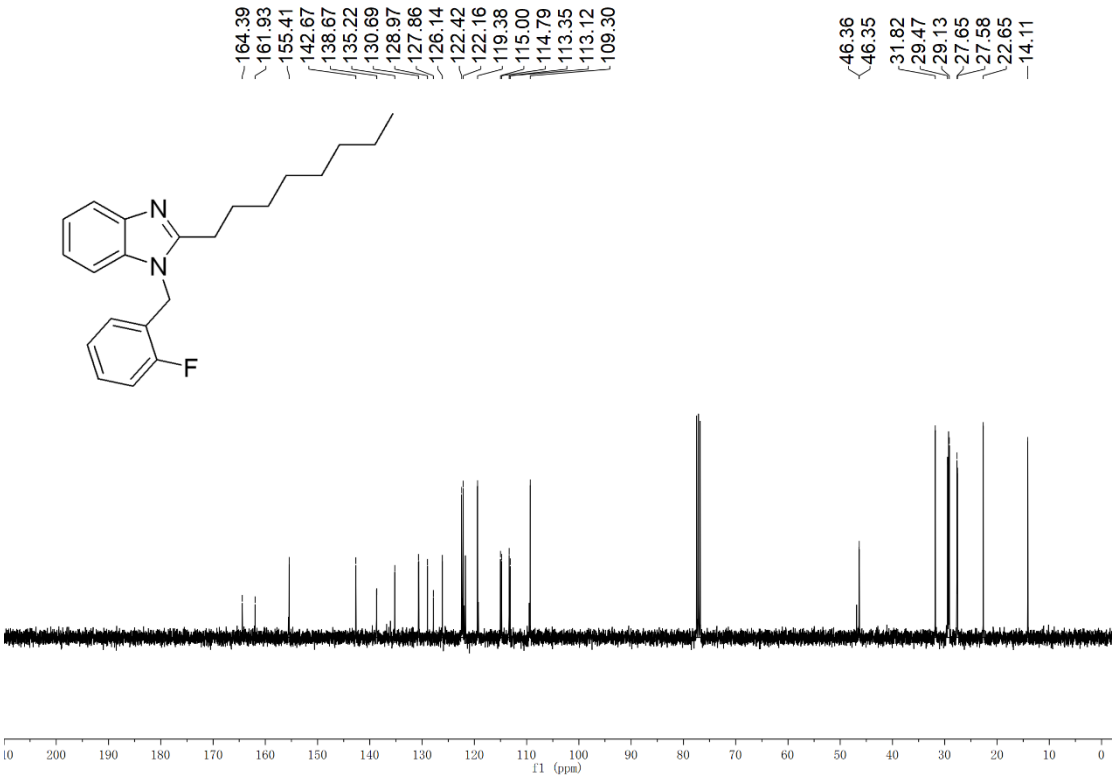


Figure S29. ^{13}C NMR spectrum of compound **4ia** (100 MHz, $CDCl_3$).

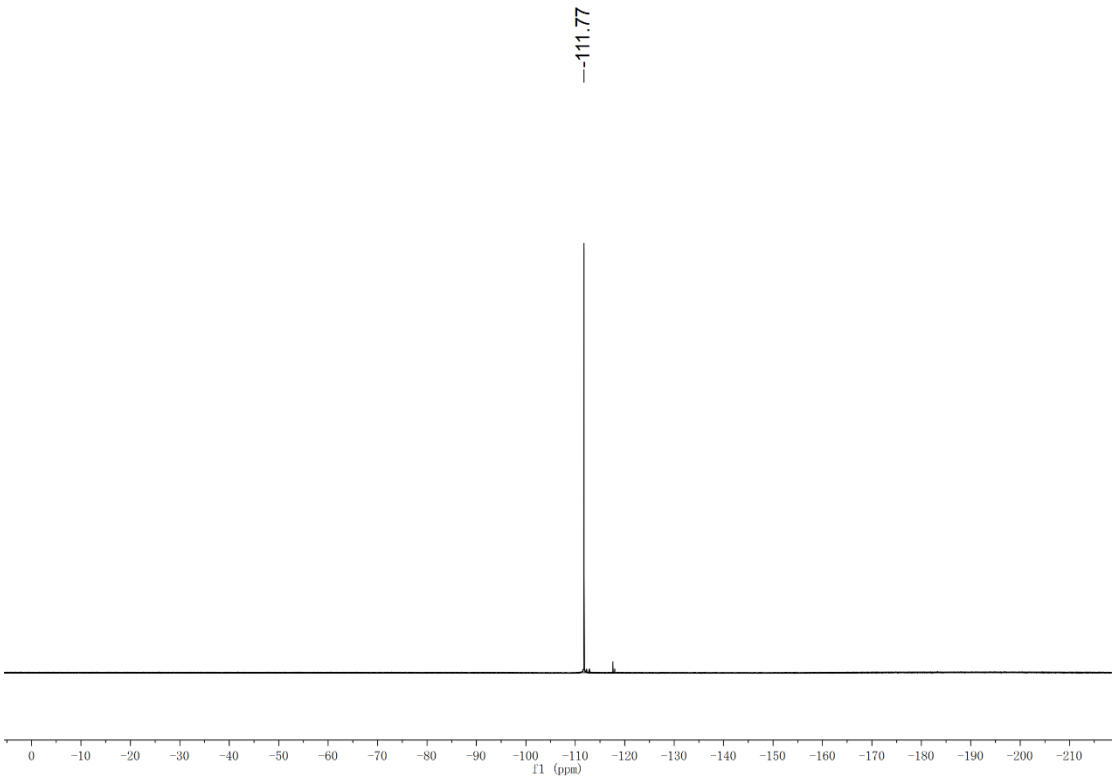


Figure S30. ^{19}F NMR spectrum of compound **4ia** (376 MHz, $CDCl_3$).

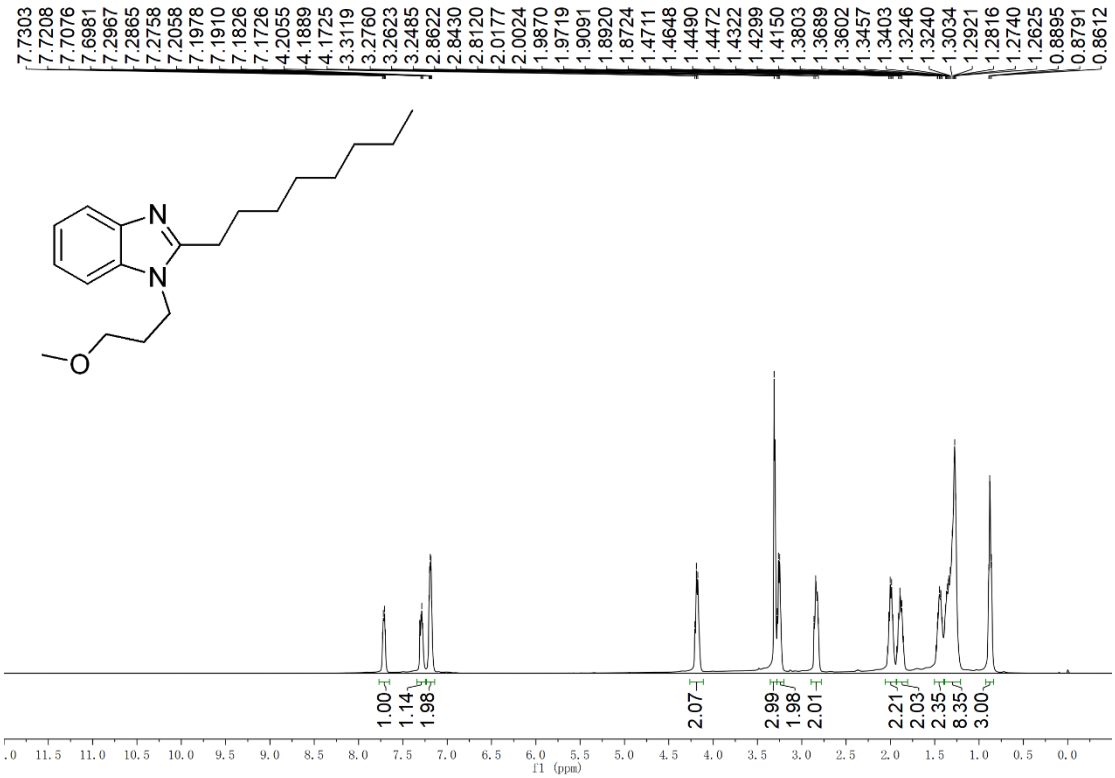


Figure S31. ^{1}H NMR spectrum of compound **4ka** (400 MHz, $CDCl_3$).

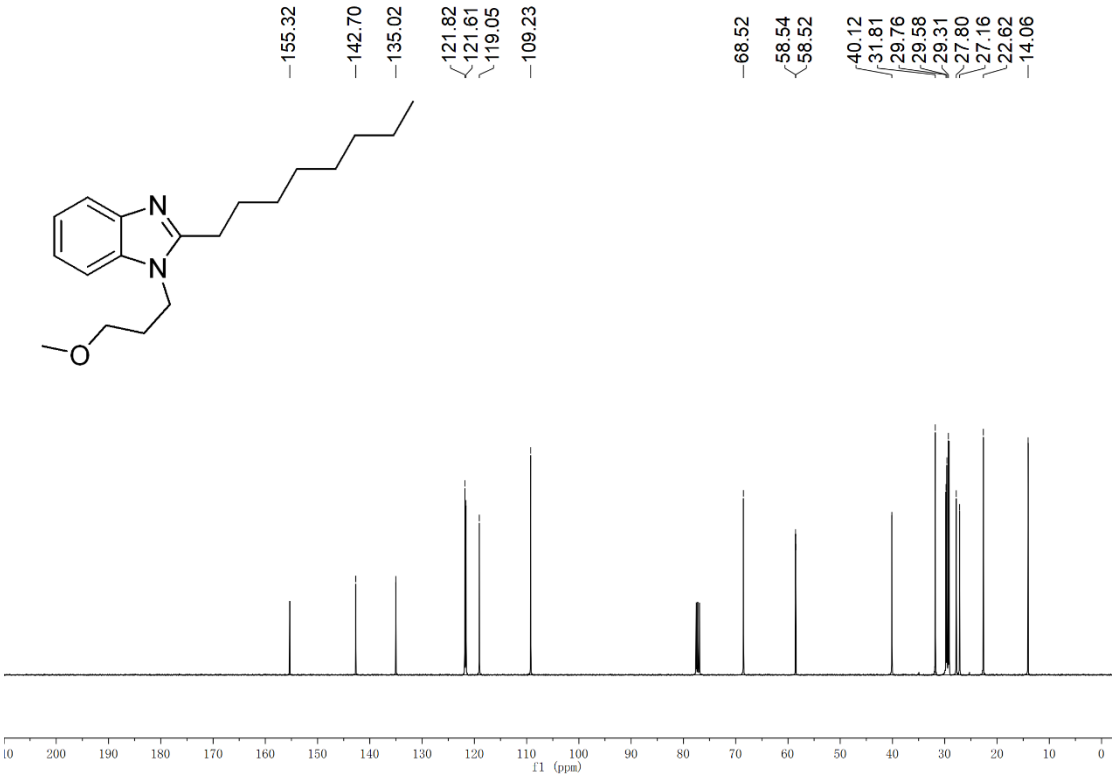


Figure S32. ^{13}C NMR spectrum of compound **4ka** (100 MHz, $CDCl_3$).

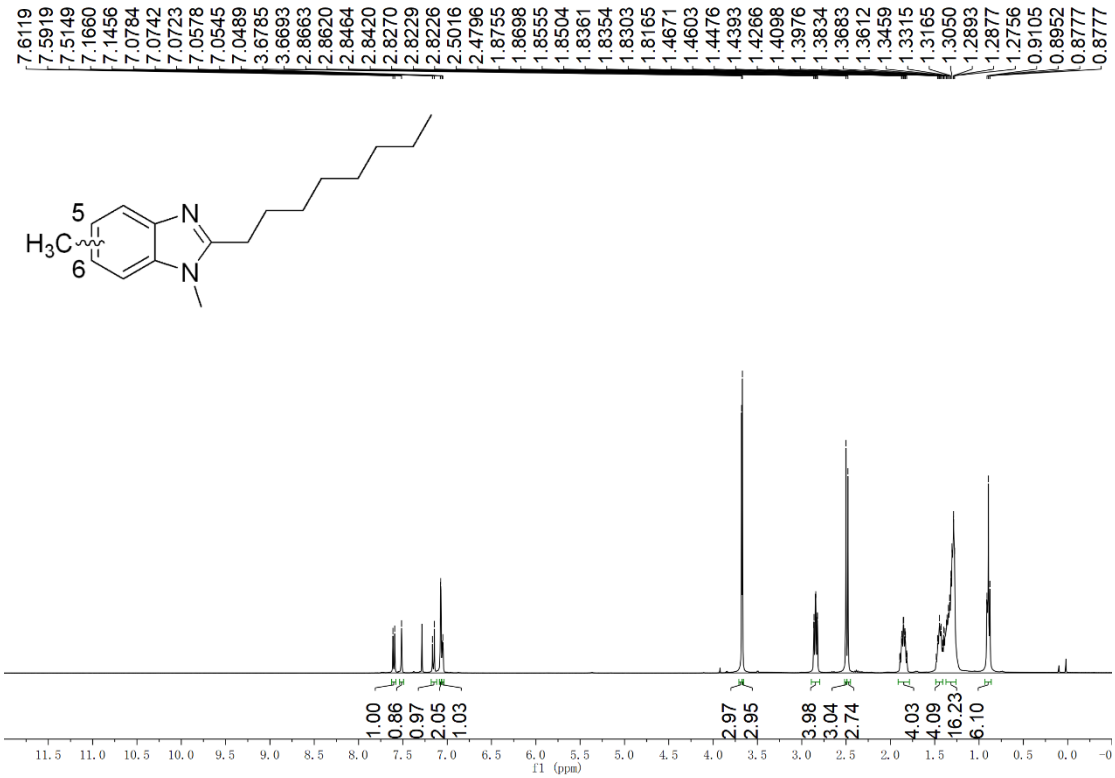


Figure S33. ^{1}H NMR spectrum of compound **4la** (400 MHz, $CDCl_3$).

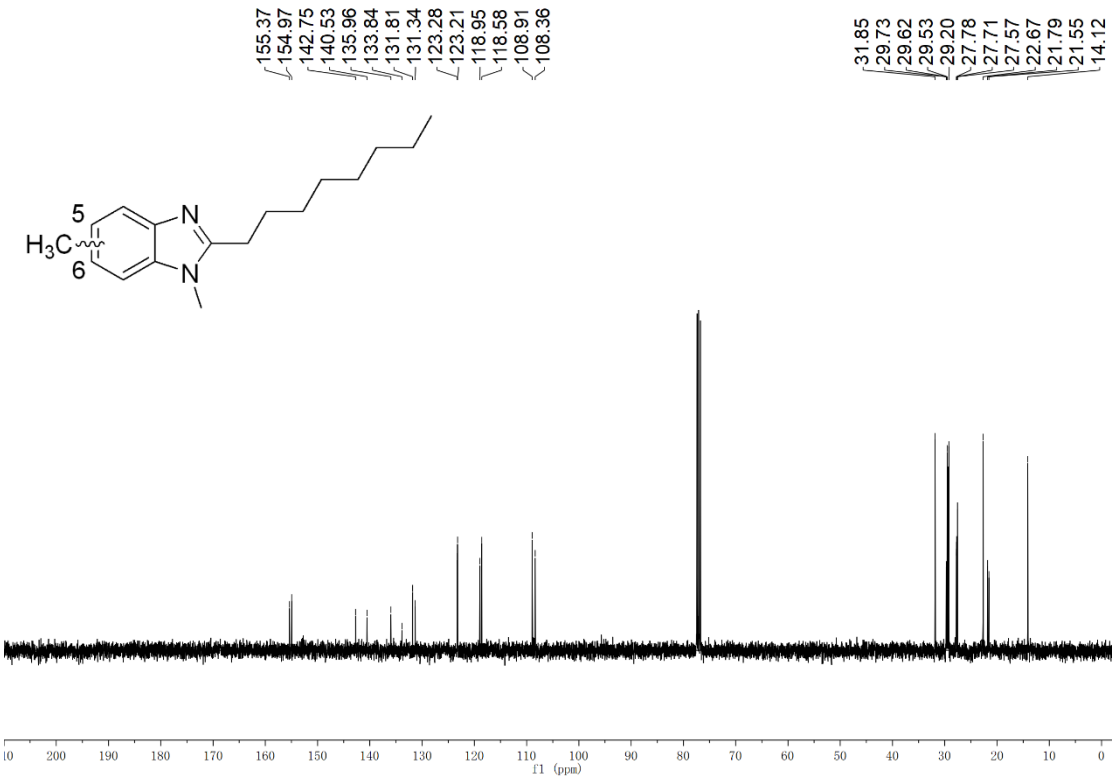


Figure S34. ^{13}C NMR spectrum of compound **4la** (100 MHz, $CDCl_3$).

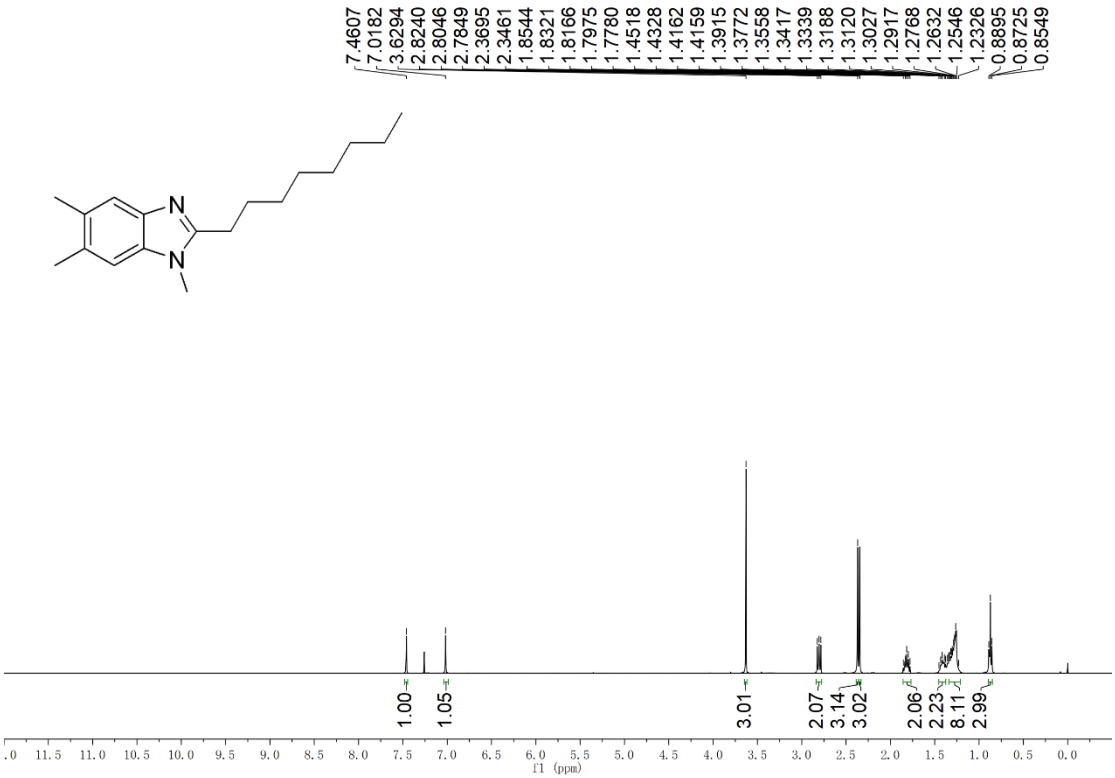


Figure S35. ^{1}H NMR spectrum of compound **4ma** (400 MHz, $CDCl_3$).

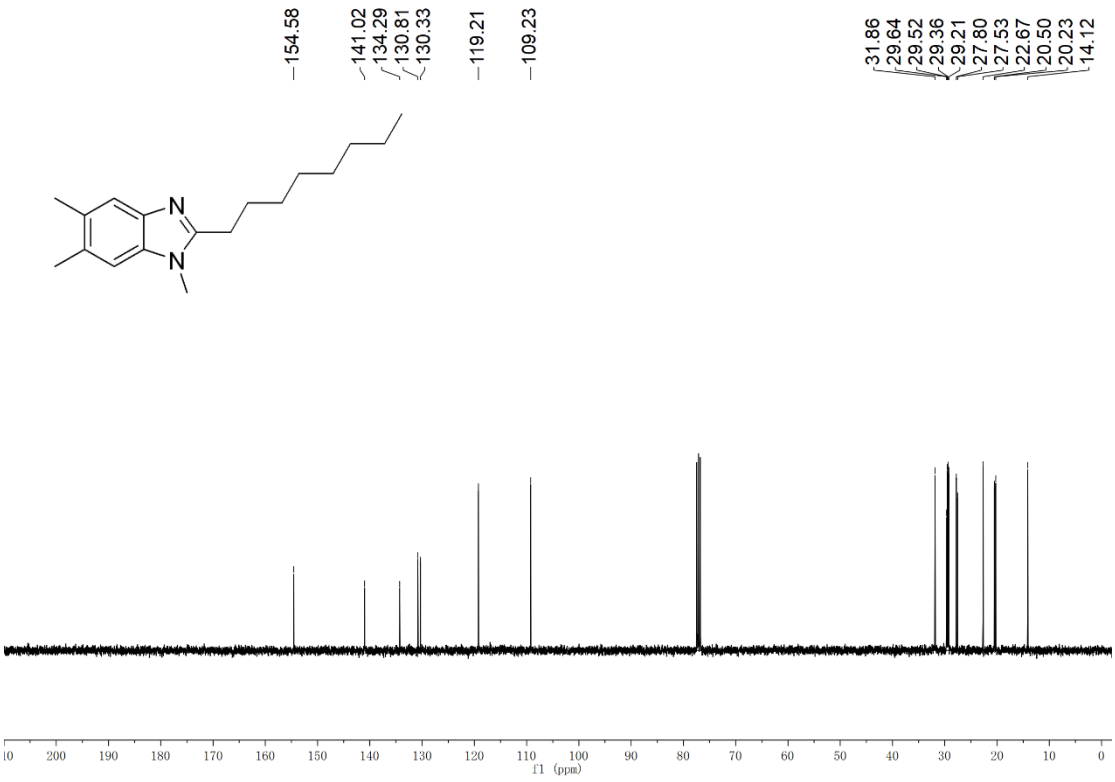


Figure S36. ^{13}C NMR spectrum of compound **4ma** (100 MHz, $CDCl_3$).

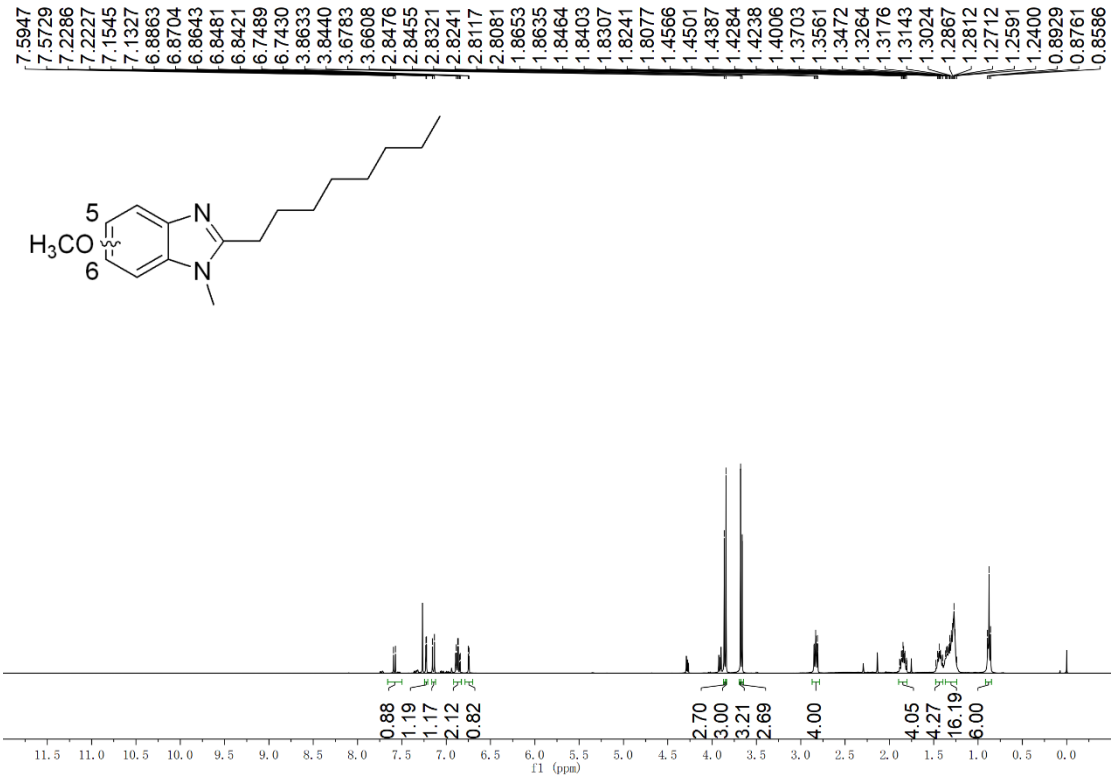


Figure S37. ^{1}H NMR spectrum of compound **4na** (400 MHz, $CDCl_3$).

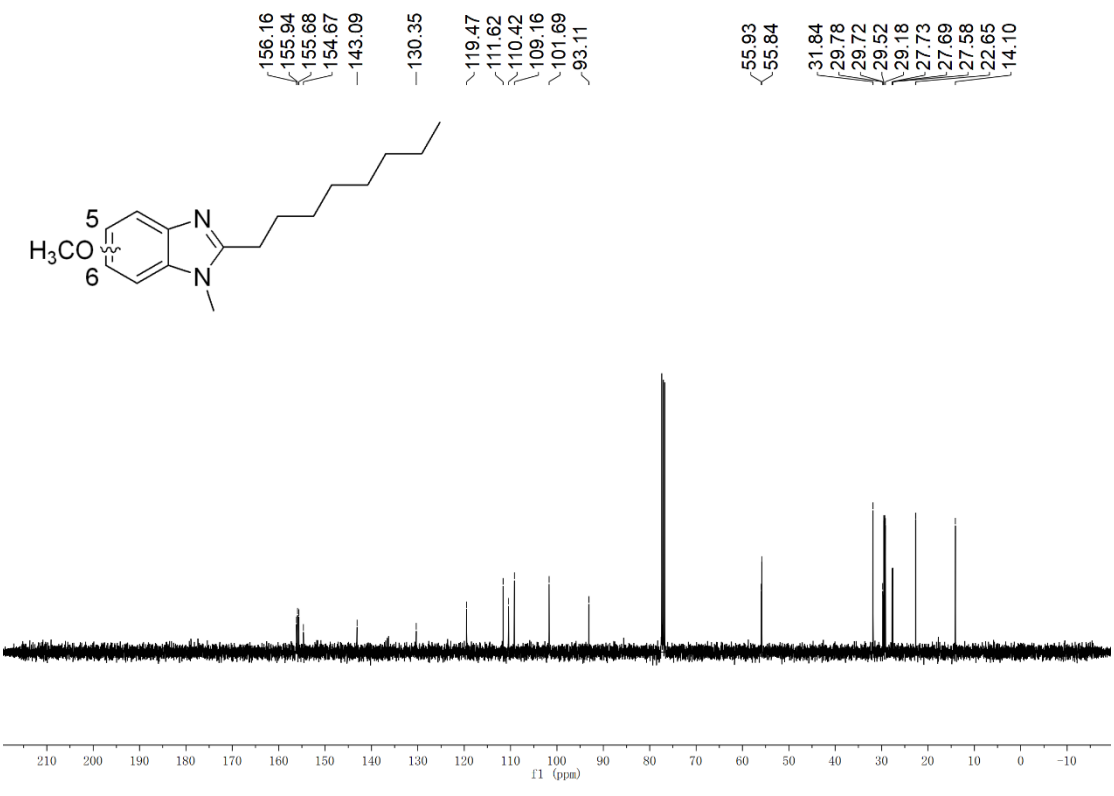


Figure S38. ^{13}C NMR spectrum of compound **4na** (100 MHz, $CDCl_3$).

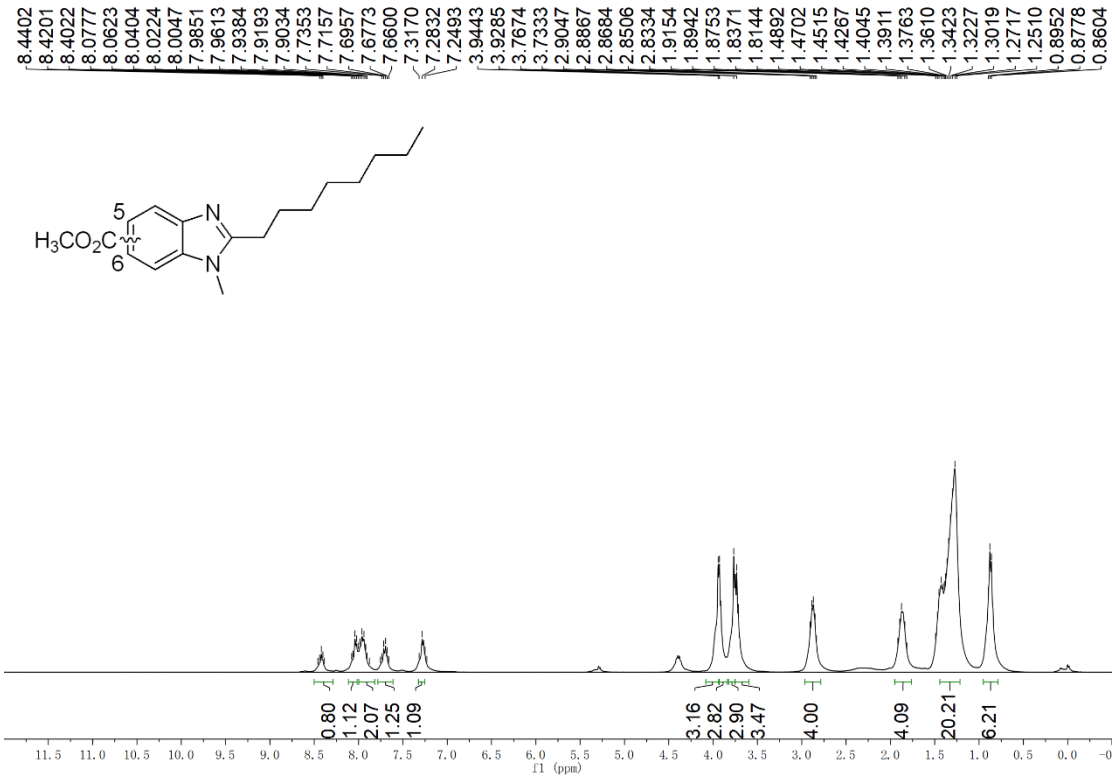


Figure S39. ^{1}H NMR spectrum of compound **4oa** (400 MHz, $CDCl_3$).

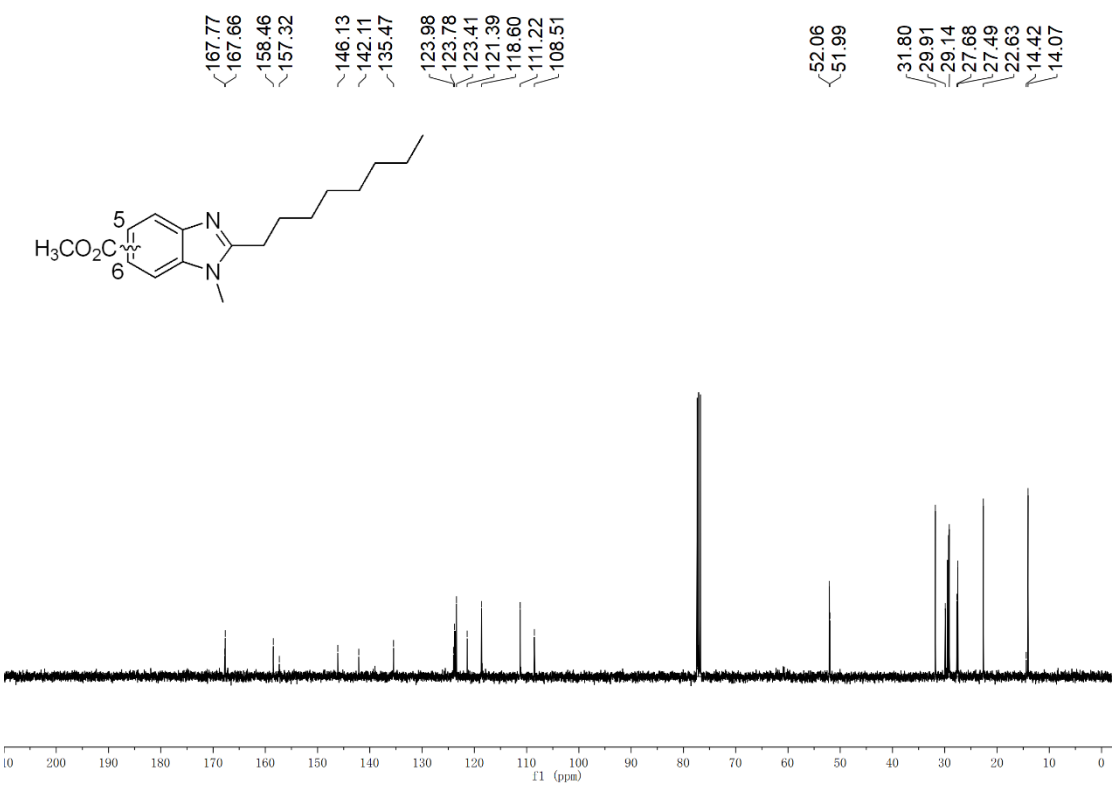


Figure S40. ^{13}C NMR spectrum of compound **4oa** (100 MHz, $CDCl_3$).

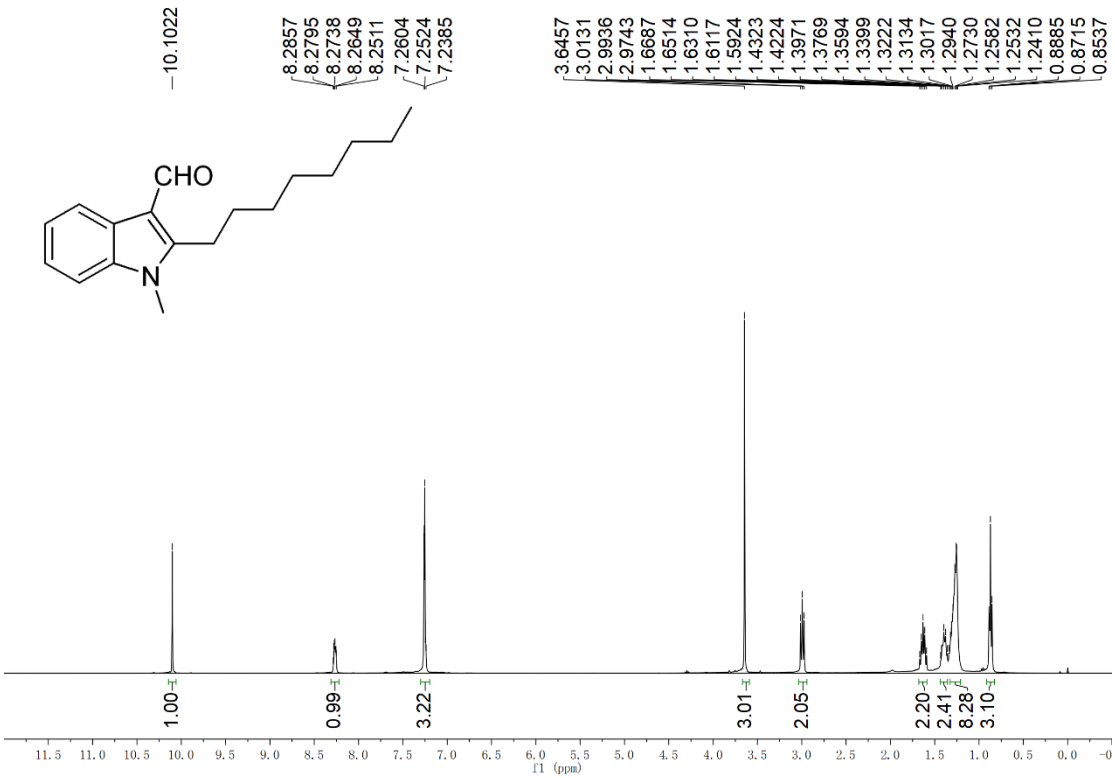


Figure S41. ^{1}H NMR spectrum of compound **4pa** (400 MHz, $CDCl_3$).

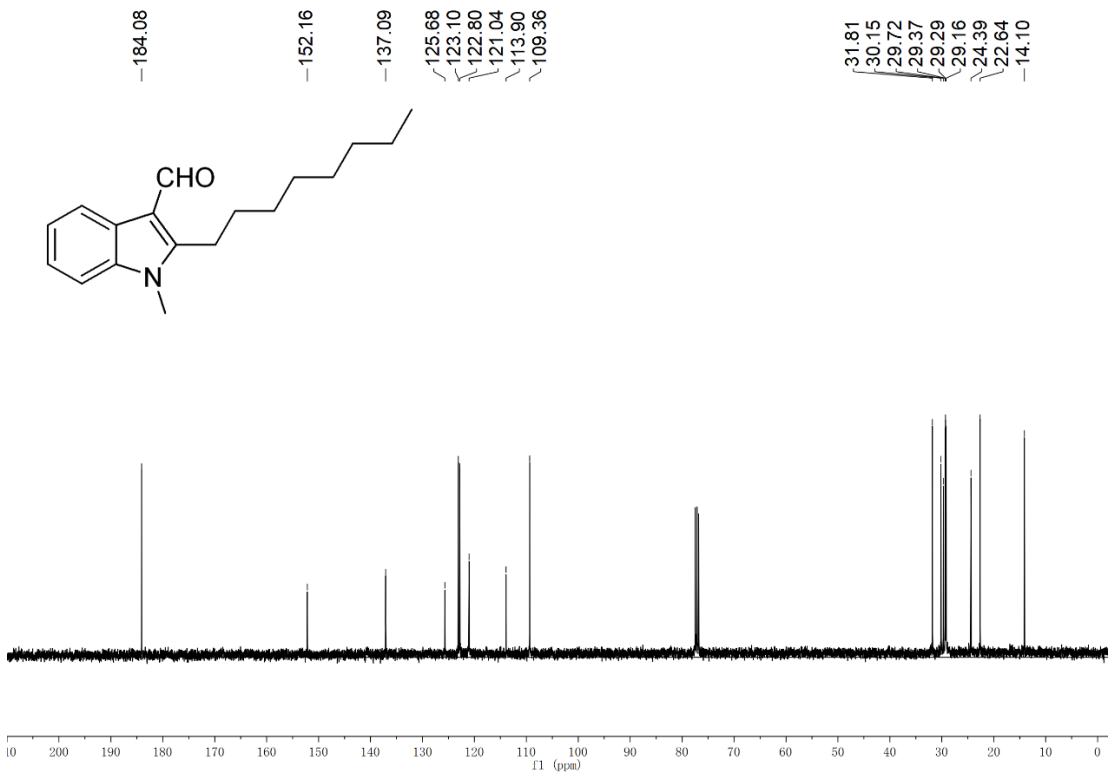


Figure S42. ^{13}C NMR spectrum of compound **4pa** (100 MHz, $CDCl_3$).

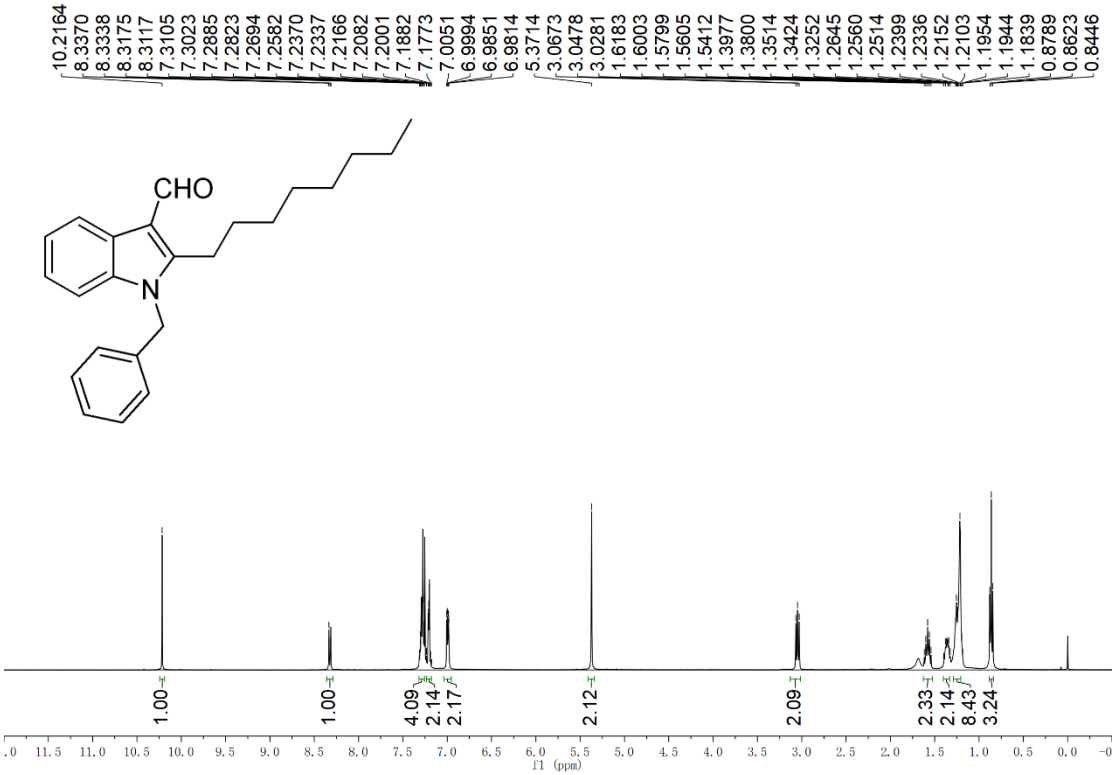


Figure S43. ^{1}H NMR spectrum of compound **4qa** (400 MHz, $CDCl_3$).

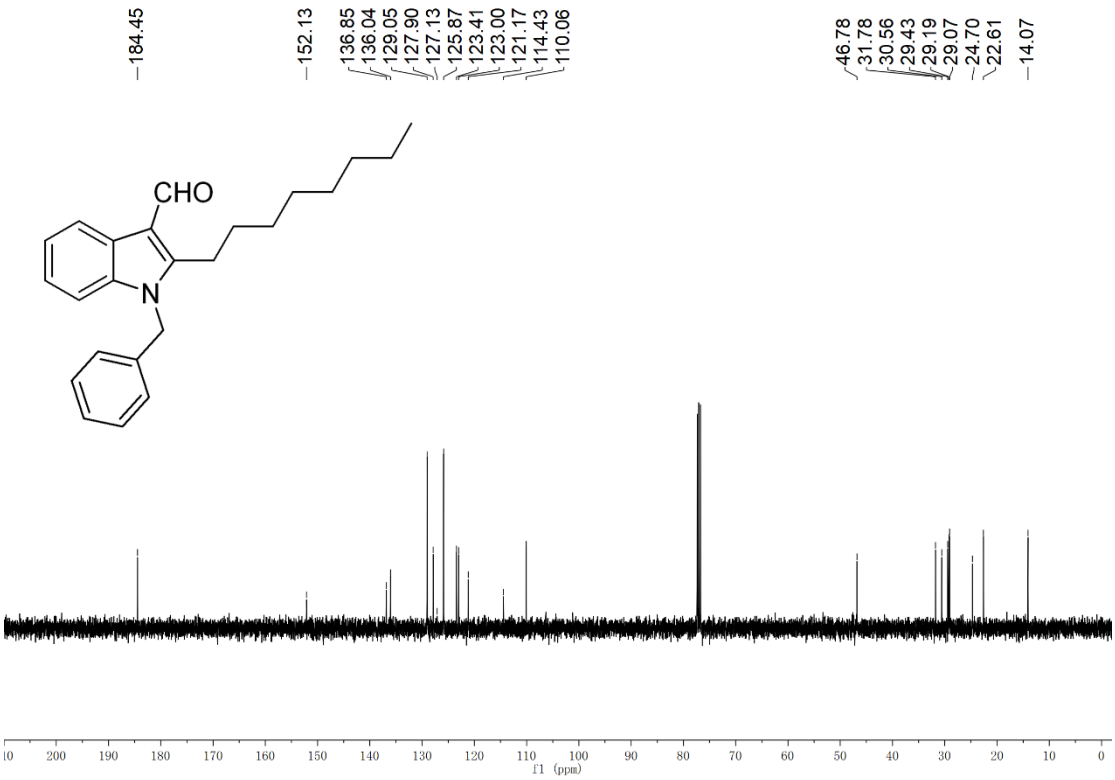


Figure S44. ^{13}C NMR spectrum of compound **4qa** (100 MHz, $CDCl_3$).

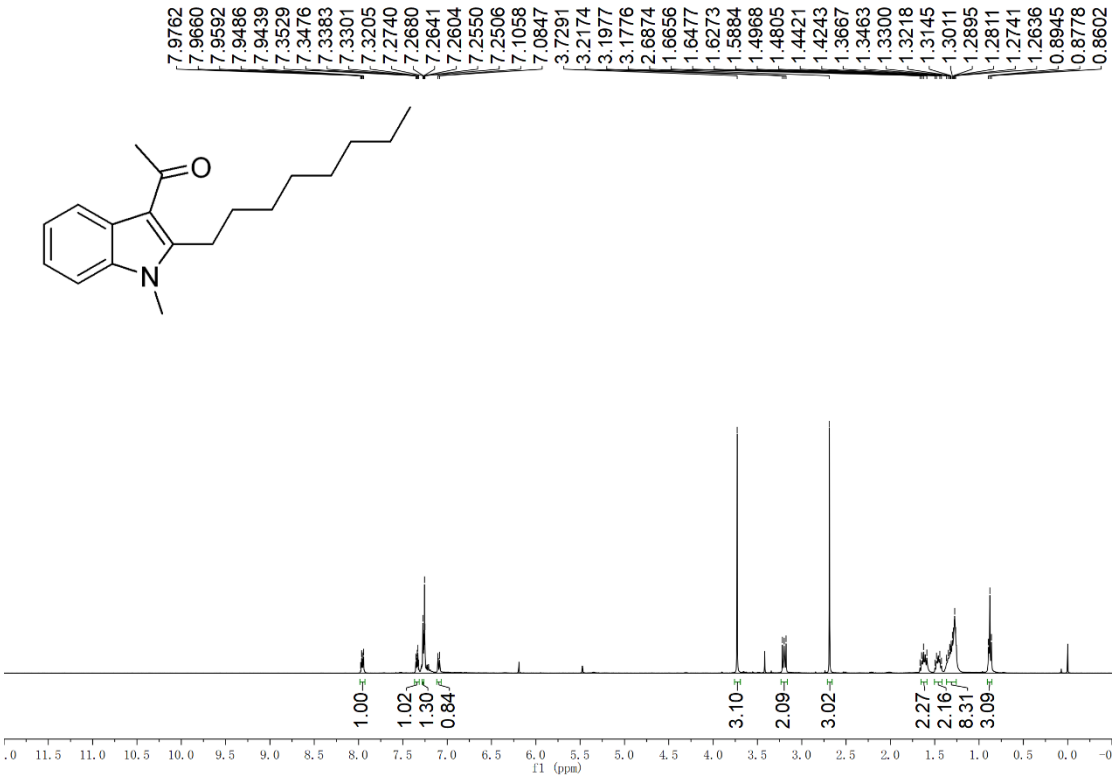


Figure S45. ^{1}H NMR spectrum of compound **4ra** (400 MHz, $CDCl_3$).

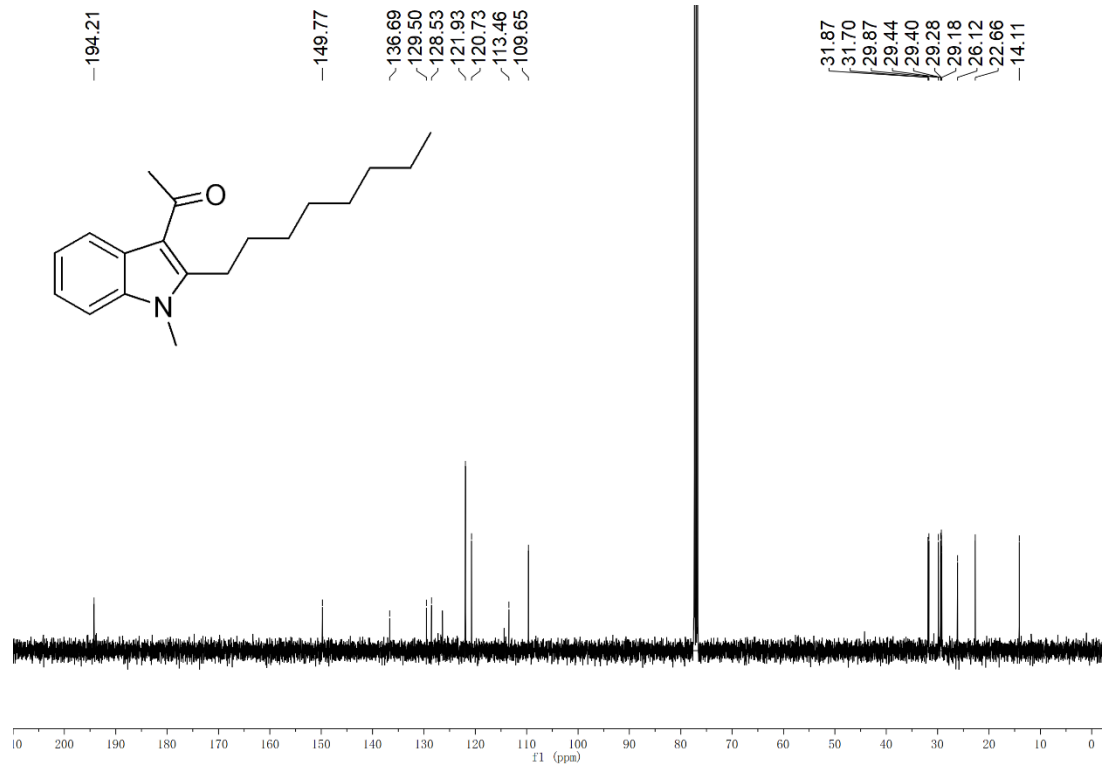


Figure S46. ^{13}C NMR spectrum of compound **4ra** (100 MHz, $CDCl_3$).

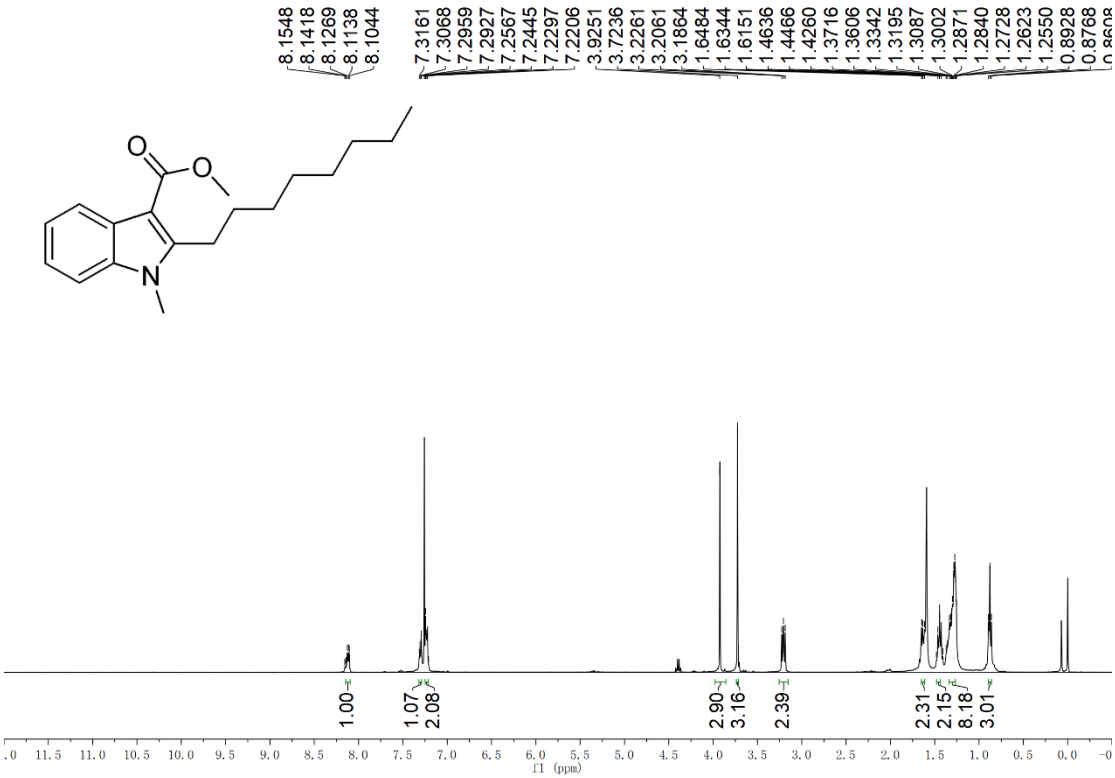


Figure S47. ^{1}H NMR spectrum of compound **4sa** (400 MHz, $CDCl_3$).

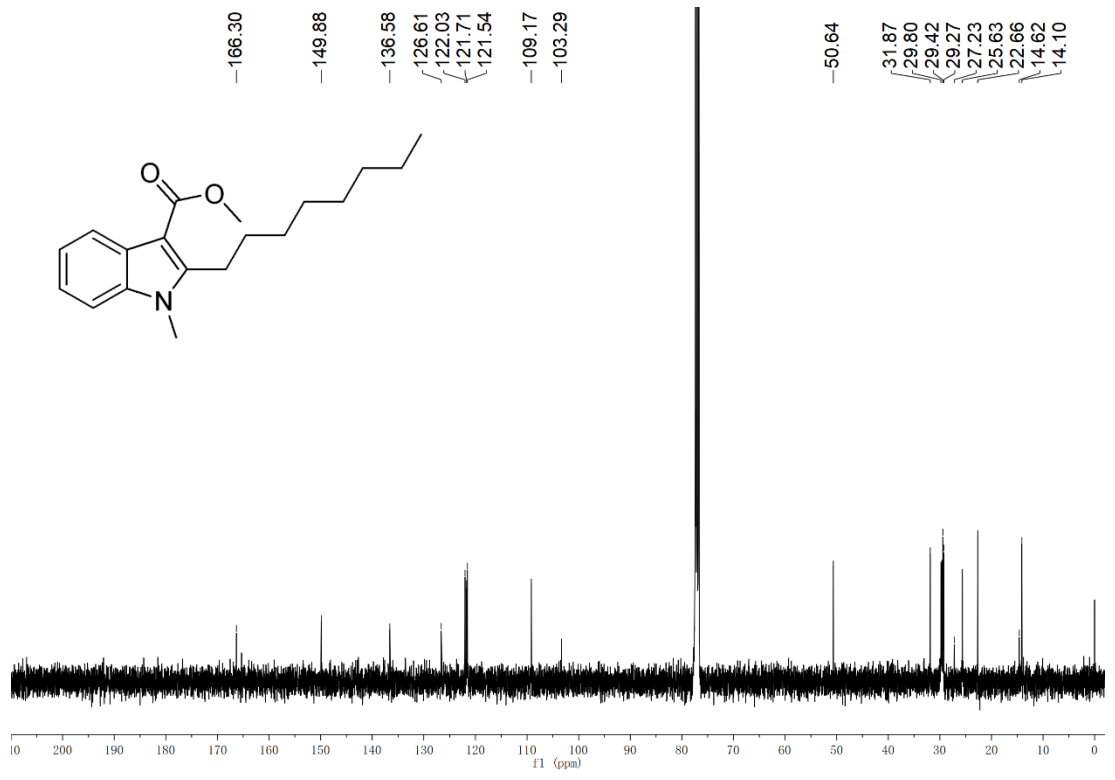


Figure S48. ^{13}C NMR spectrum of compound **4sa** (100 MHz, $CDCl_3$).

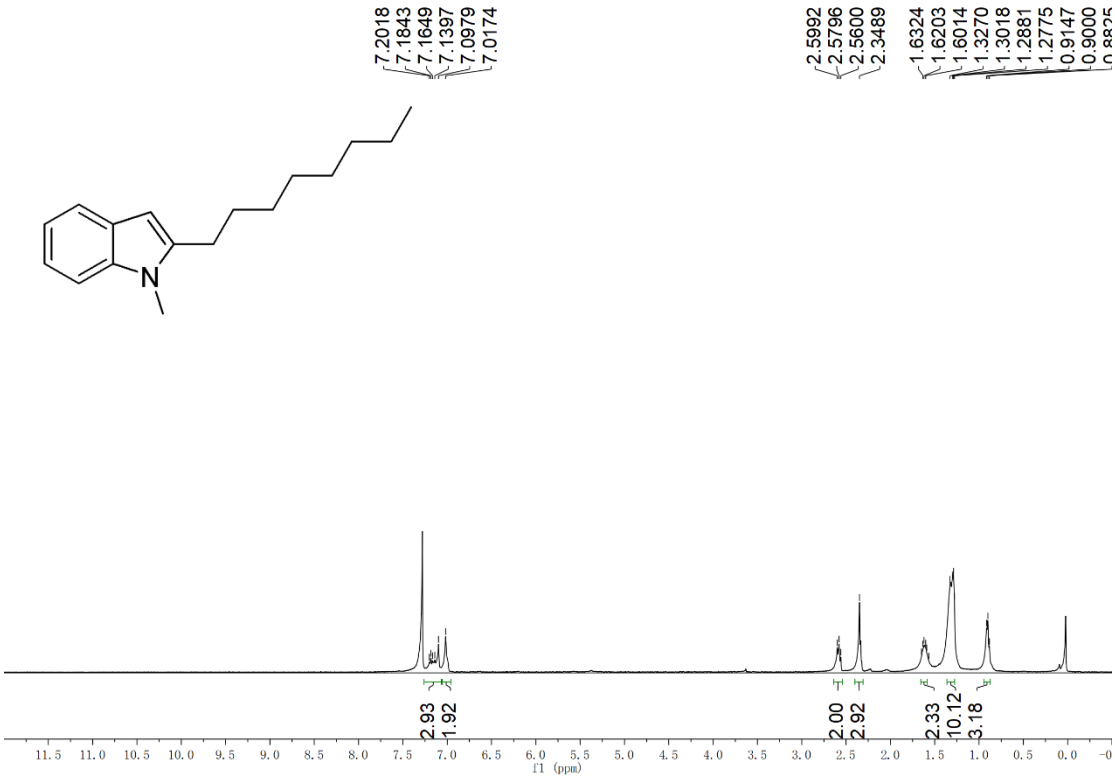


Figure S49. ^{1}H NMR spectrum of compound **4ta** (400 MHz, $CDCl_3$).

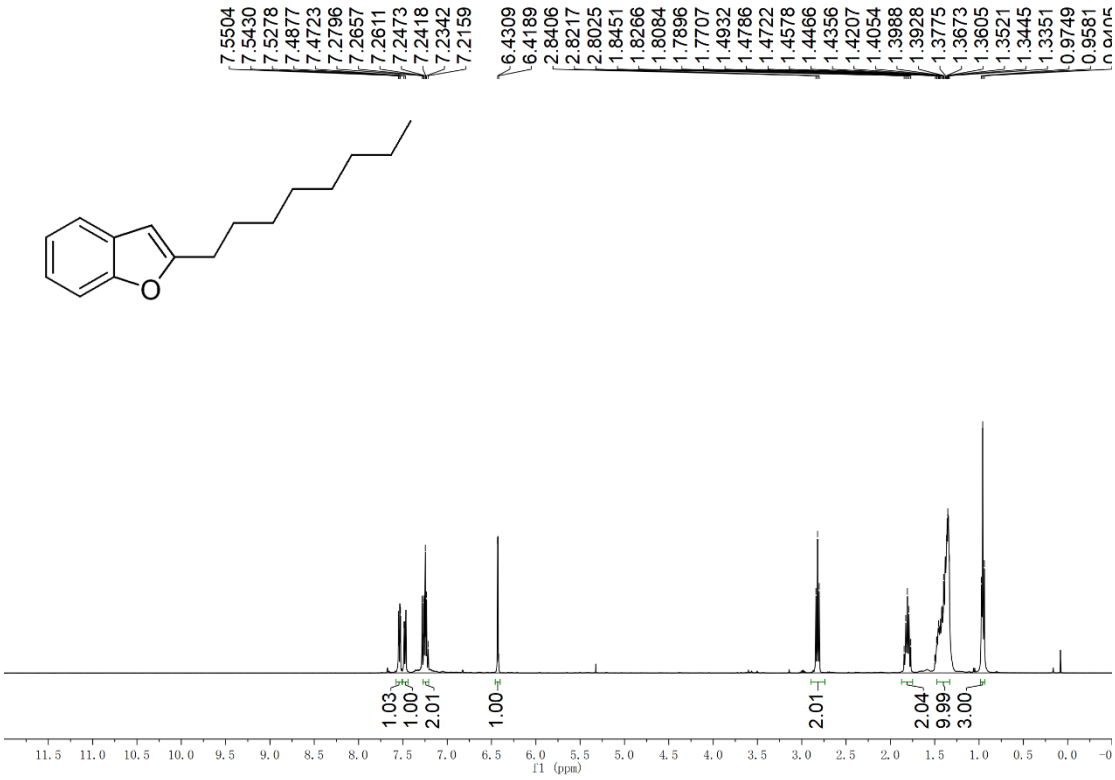


Figure S50. ^{1}H NMR spectrum of compound **4ua** (400 MHz, $CDCl_3$).

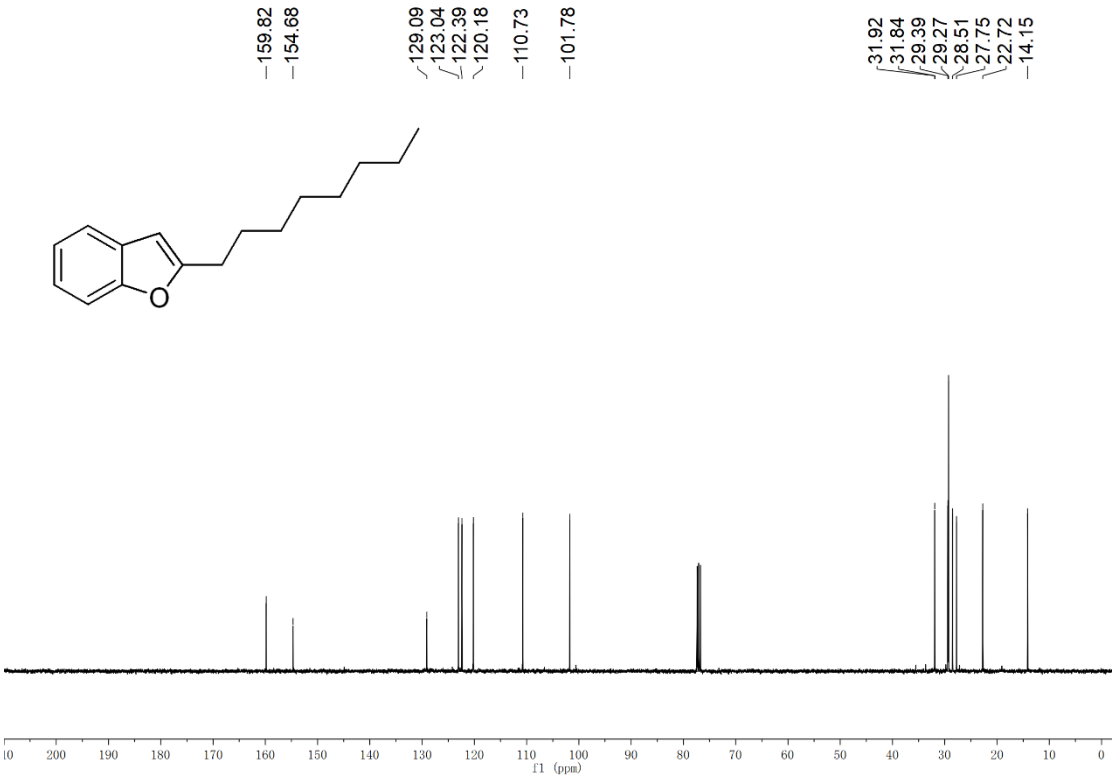


Figure S51. ^{13}C NMR spectrum of compound **4ua** (100 MHz, $CDCl_3$).

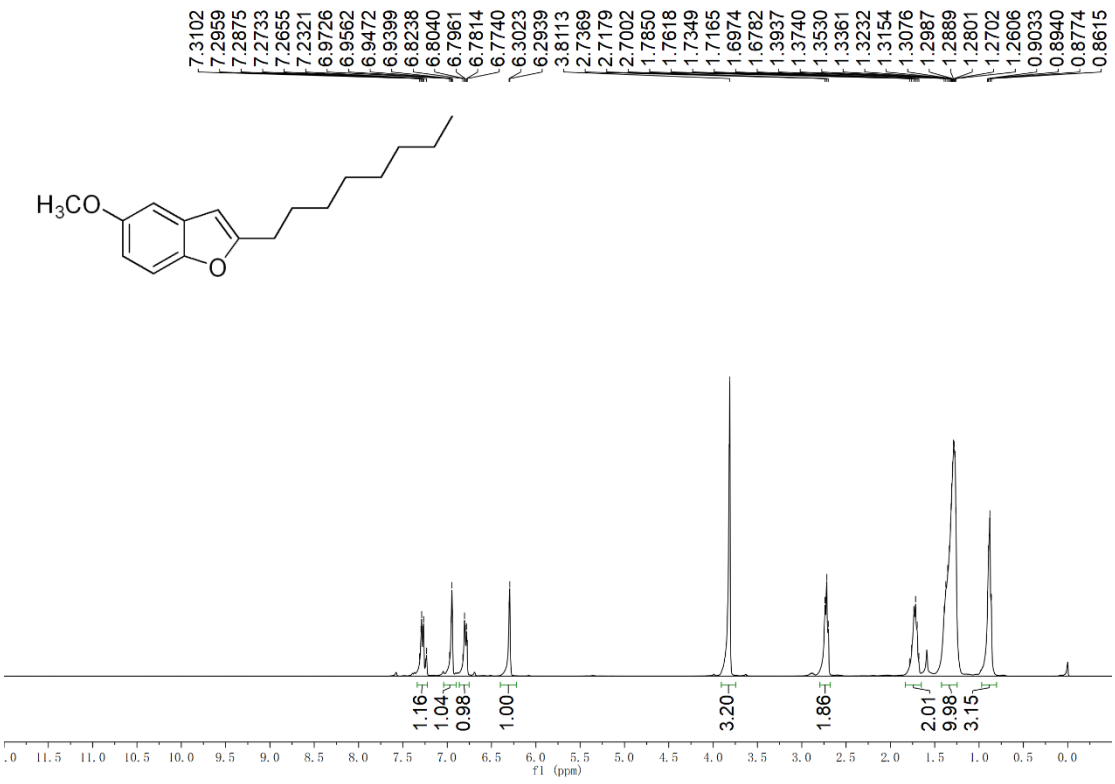


Figure S52. ^{1}H NMR spectrum of compound **4va** (400 MHz, $CDCl_3$).

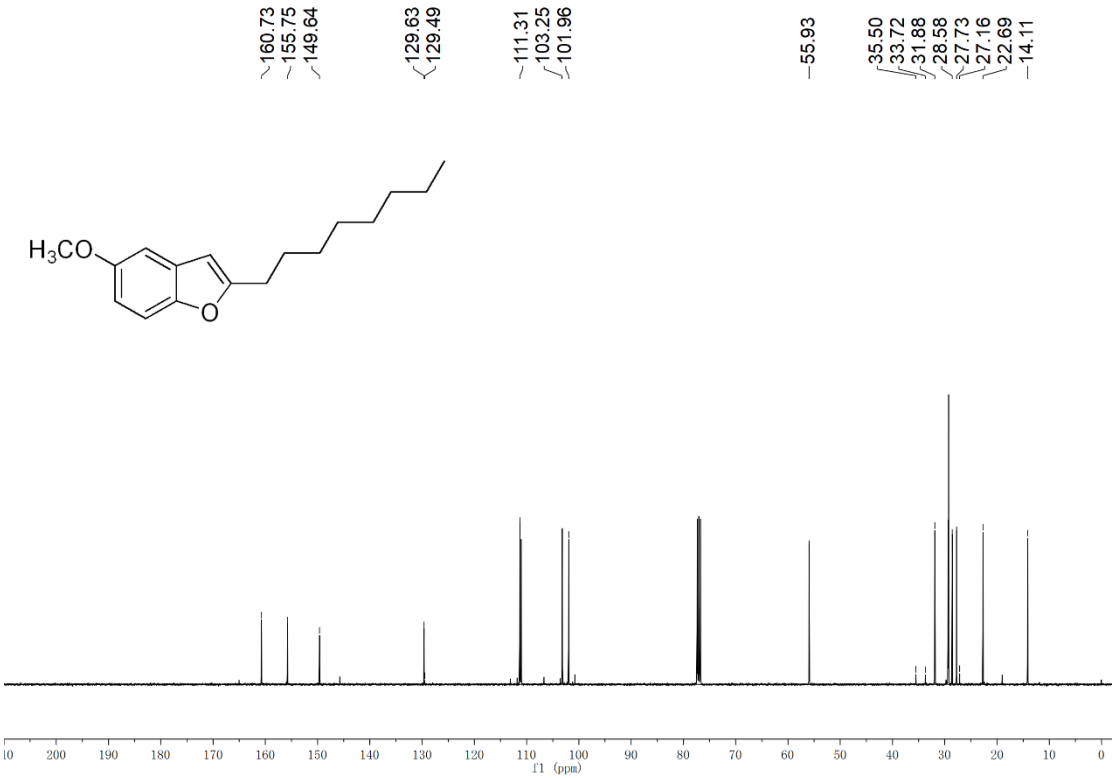


Figure S53. ^{13}C NMR spectrum of compound **4va** (100 MHz, $CDCl_3$).

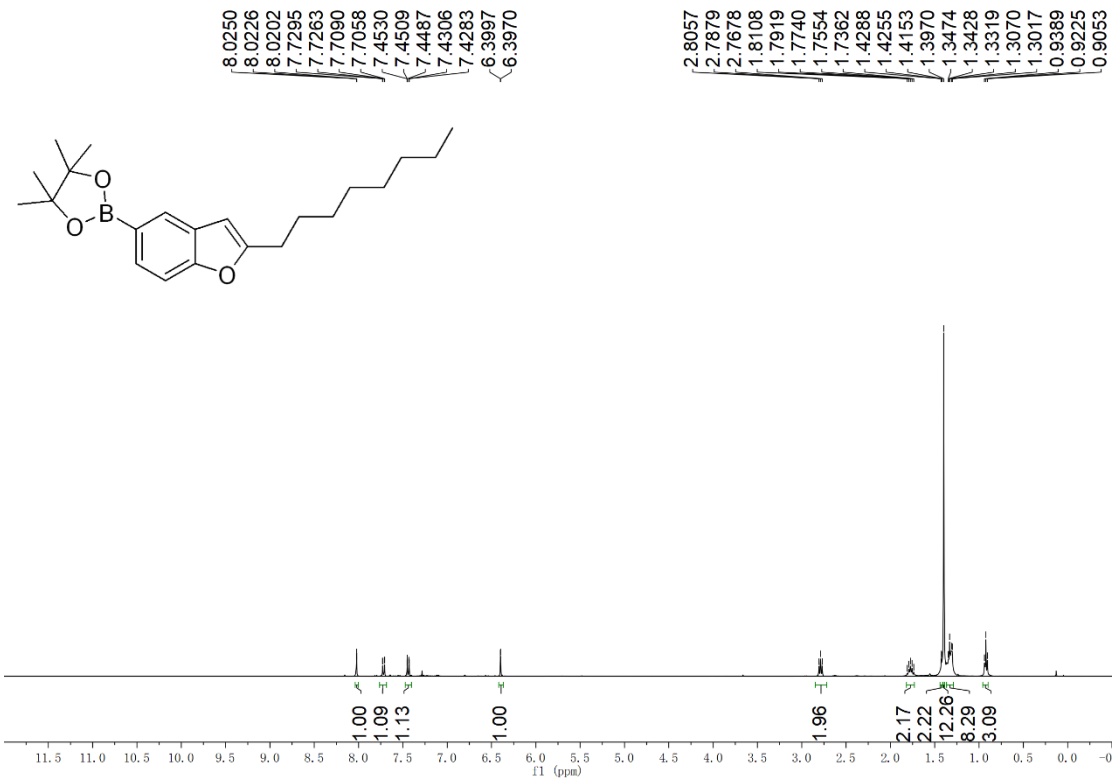


Figure S54. ^{1}H NMR spectrum of compound **4wa** (400 MHz, $CDCl_3$).

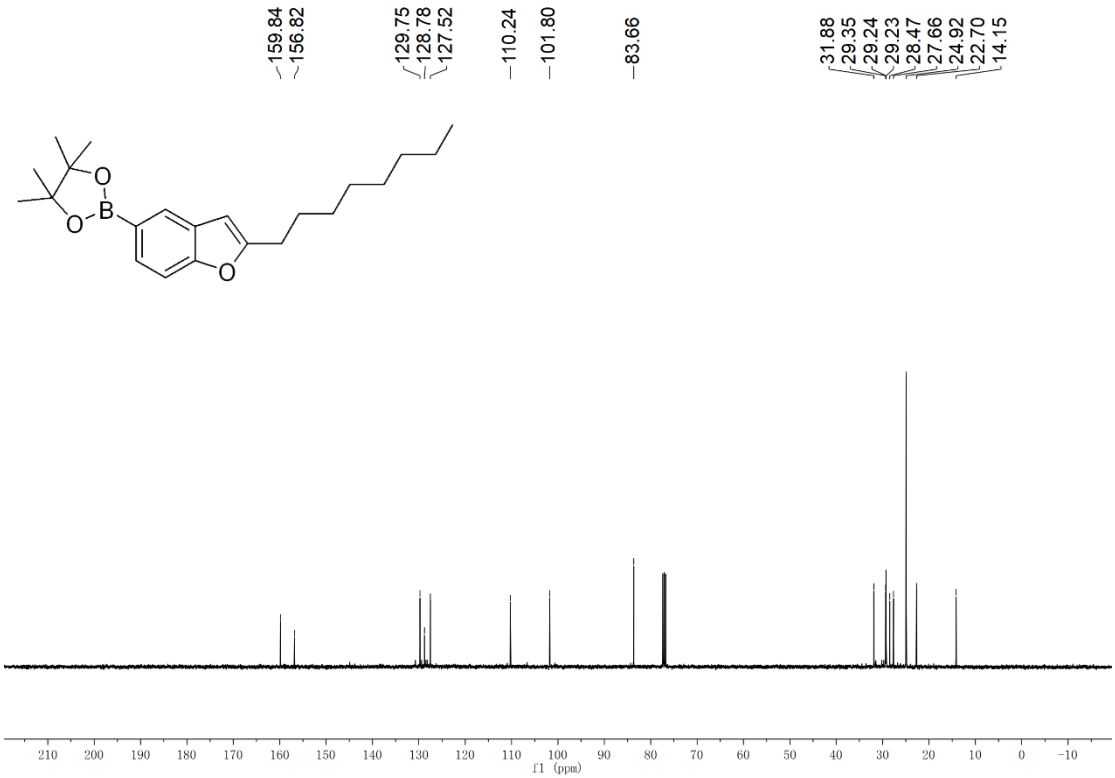


Figure S55. ^{13}C NMR spectrum of compound **4wa** (100 MHz, $CDCl_3$).

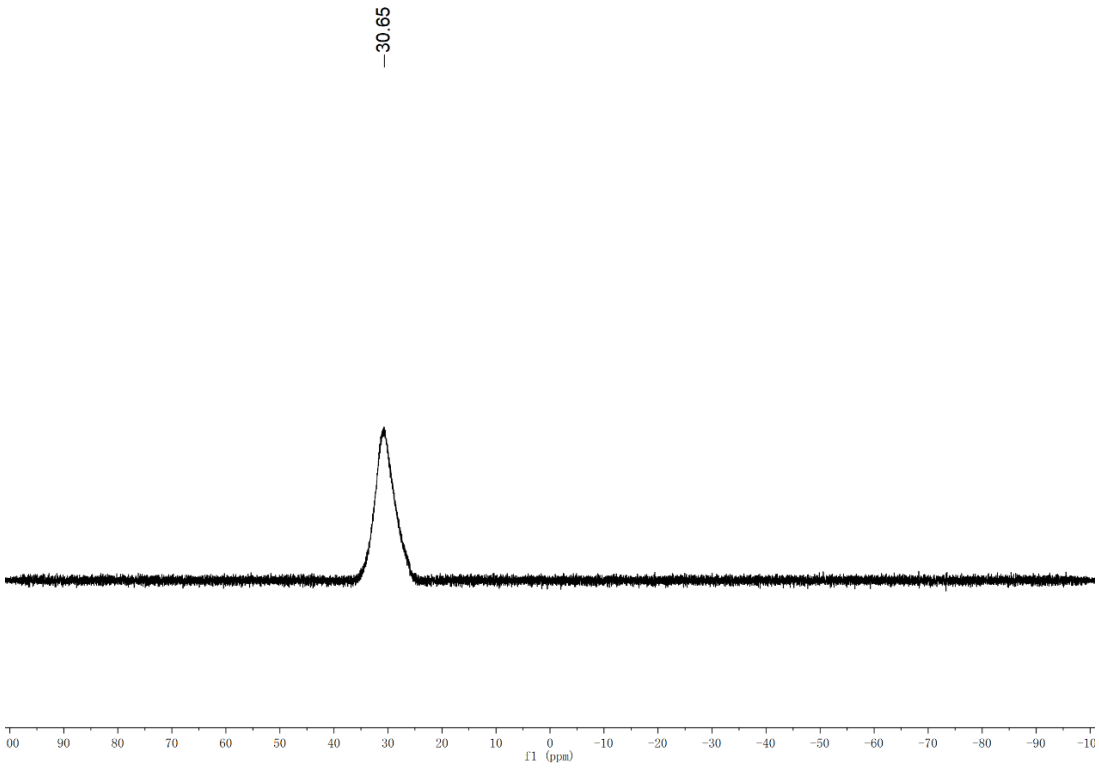


Figure S56. ^{11}B NMR spectrum of compound **4wa** (128 MHz, $CDCl_3$).

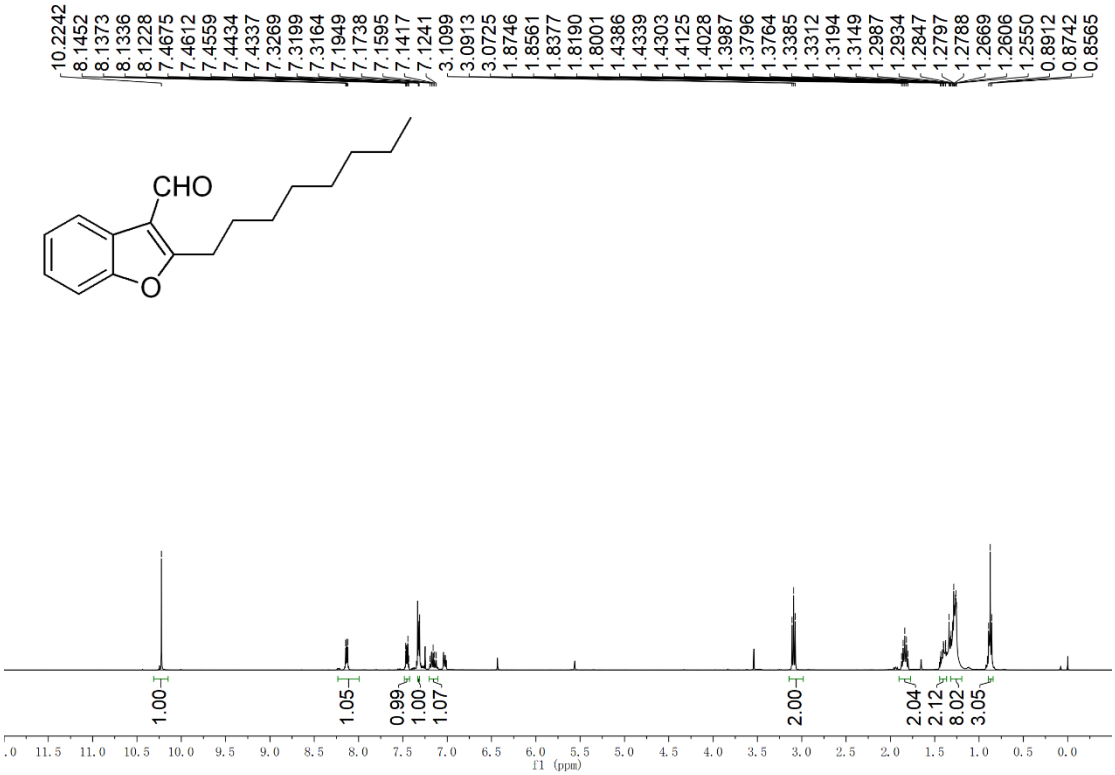


Figure S57. ^{1}H NMR spectrum of compound **4xa** (400 MHz, $CDCl_3$).

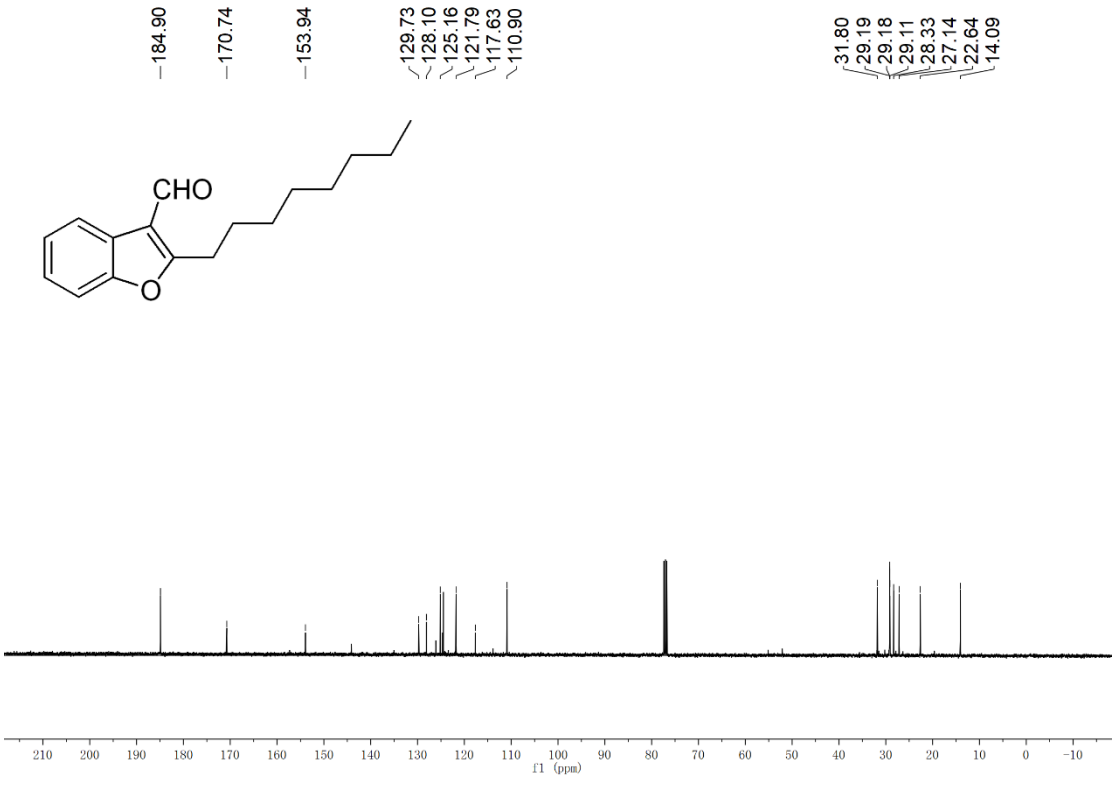


Figure S58. ^{13}C NMR spectrum of compound **4xa** (100 MHz, $CDCl_3$).

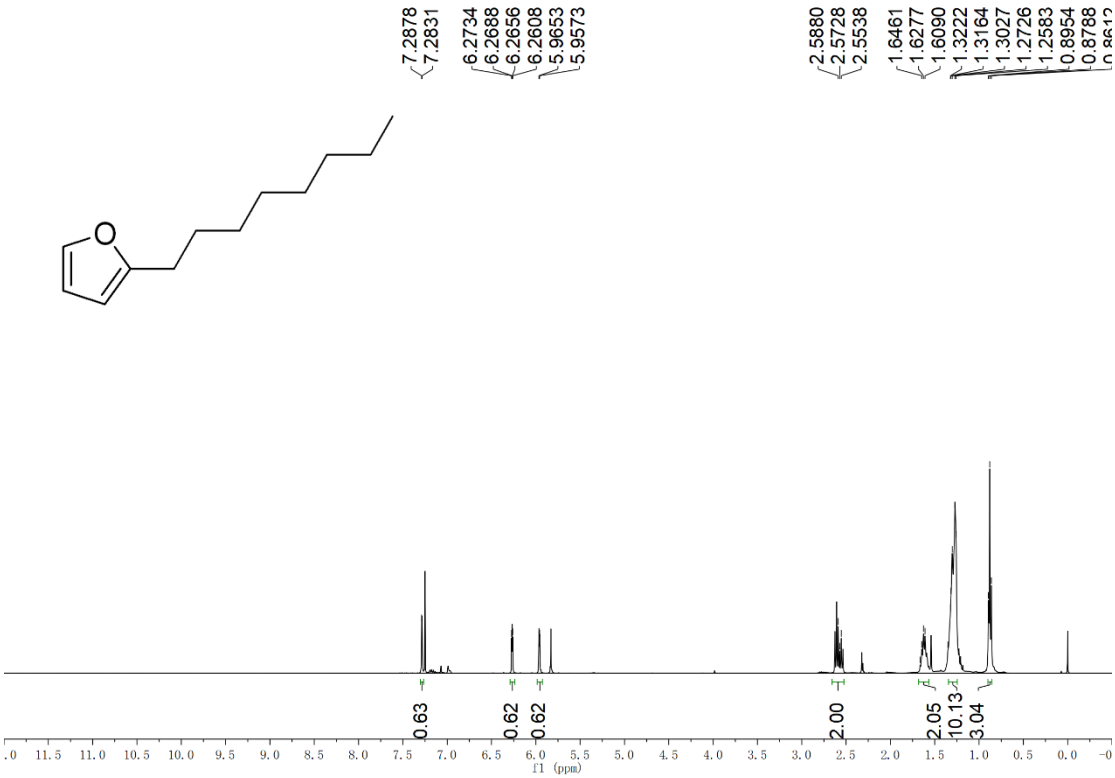


Figure S59. ^{1}H NMR spectrum of compound **4ya** (400 MHz, $CDCl_3$).

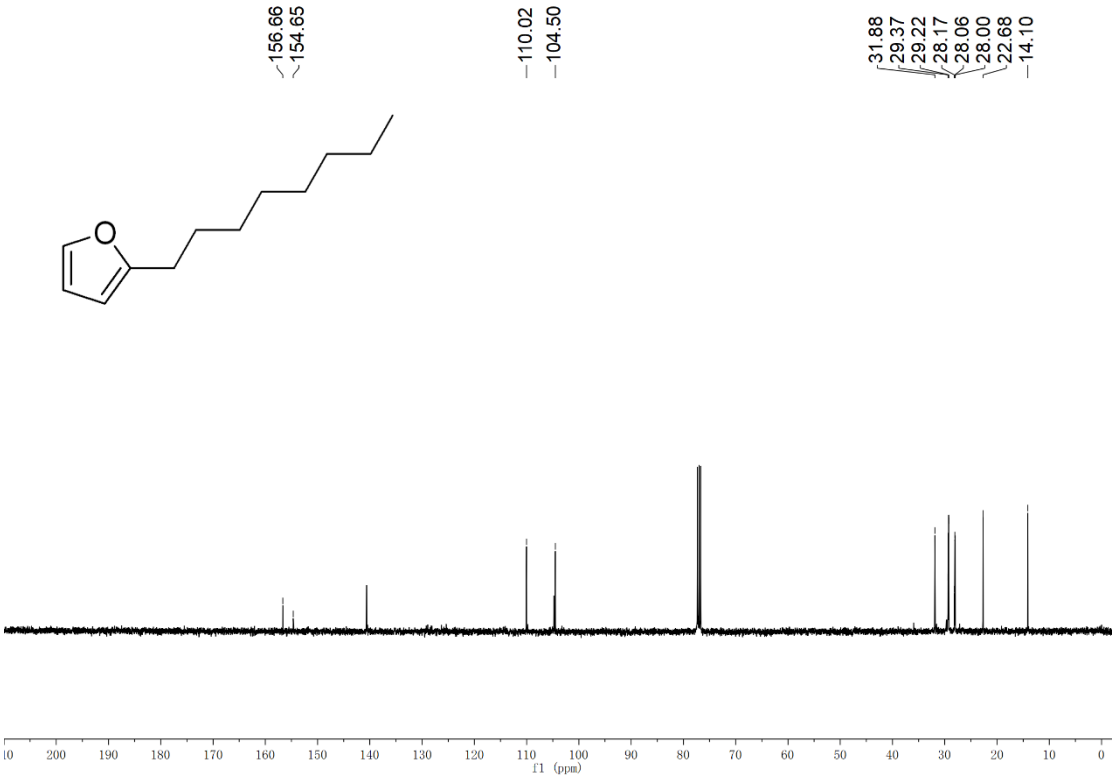


Figure S60. ^{13}C NMR spectrum of compound **4ya** (100 MHz, $CDCl_3$).

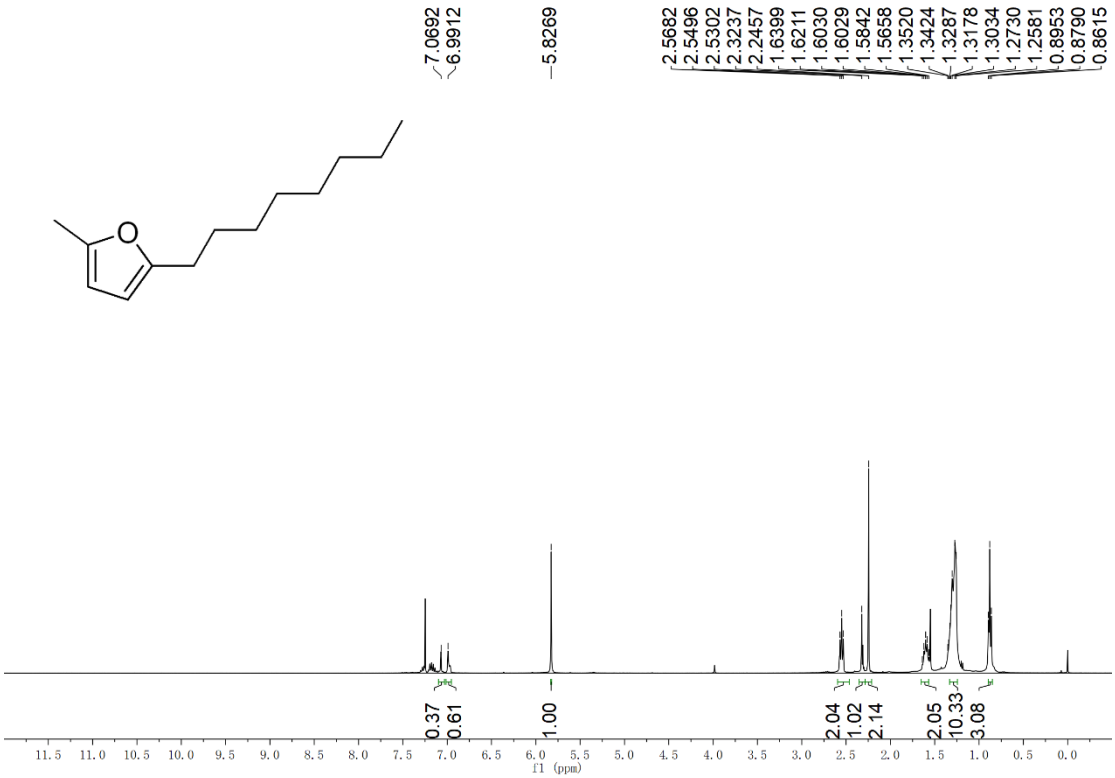


Figure S61. ^{1}H NMR spectrum of compound **4za** (400 MHz, $CDCl_3$).

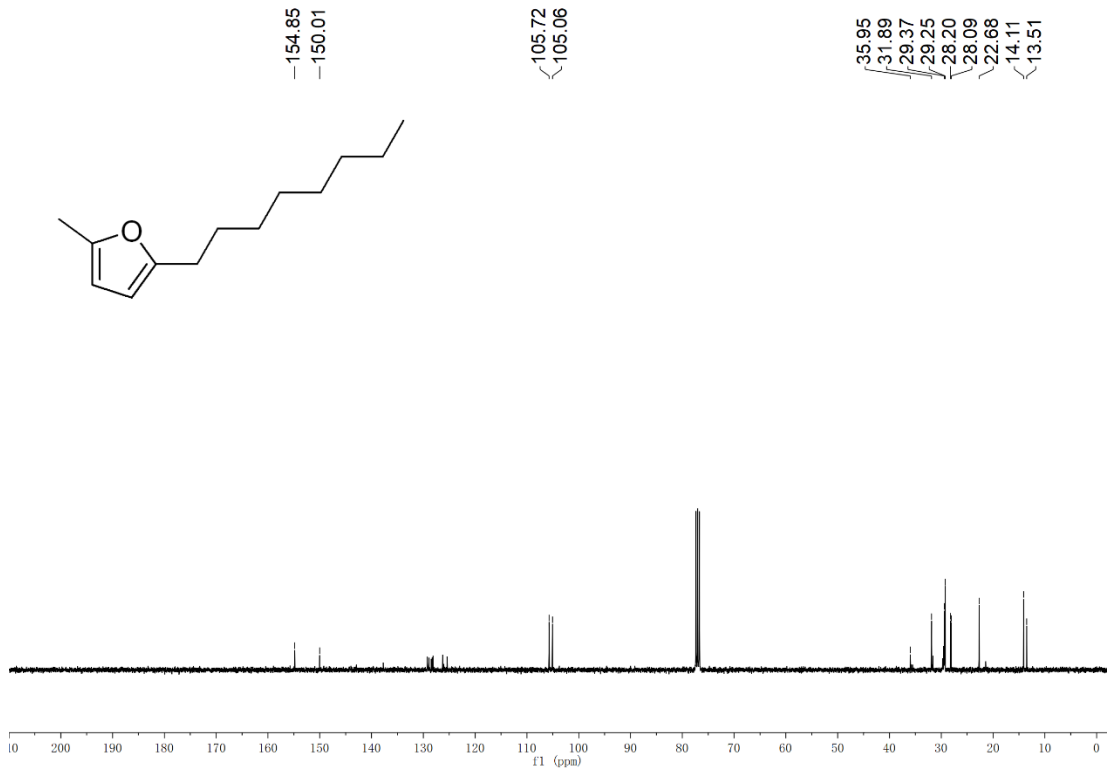


Figure S62. ^{13}C NMR spectrum of compound **4za** (100 MHz, $CDCl_3$, * = toluene)

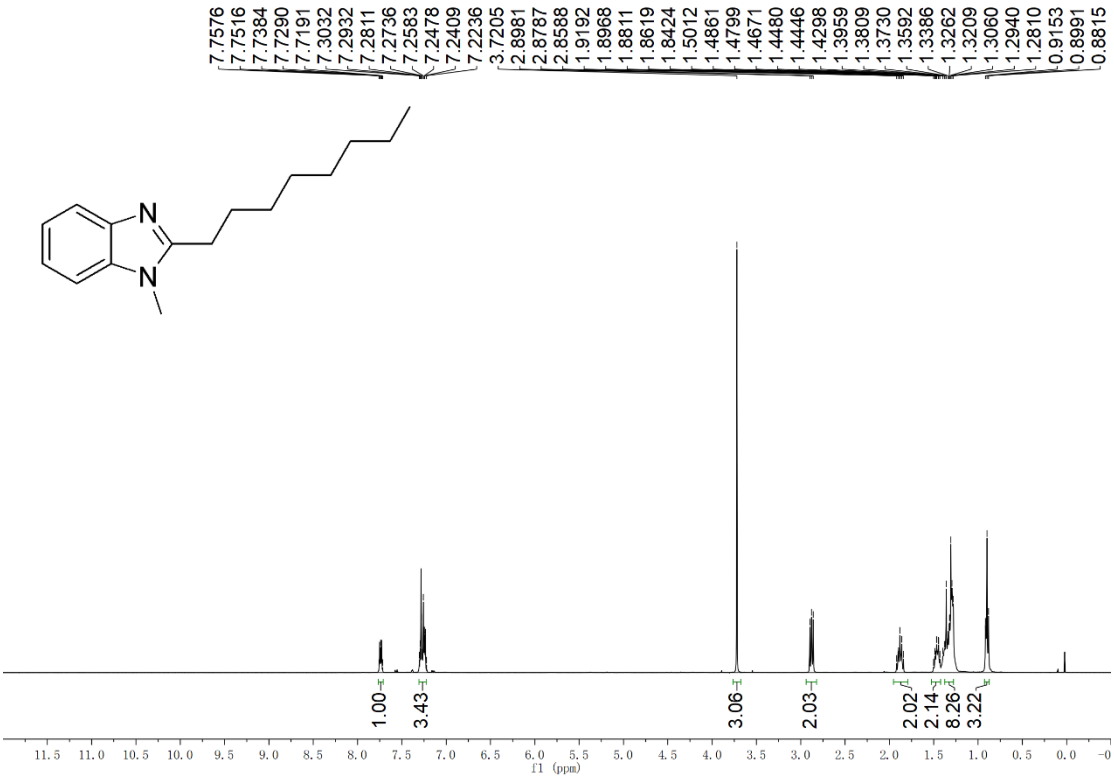


Figure S63. ^{1}H NMR spectrum of compound **6ab** (400 MHz, $CDCl_3$).

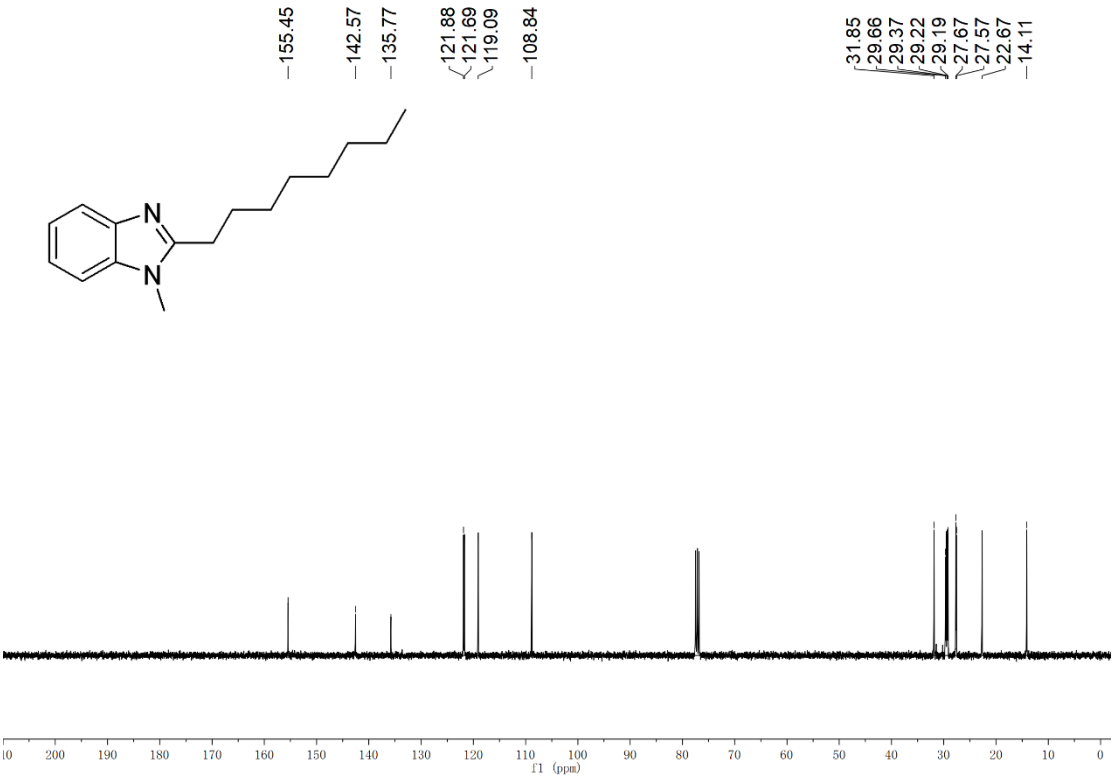


Figure S64. ^{13}C NMR spectrum of compound **6ab** (100 MHz, $CDCl_3$).

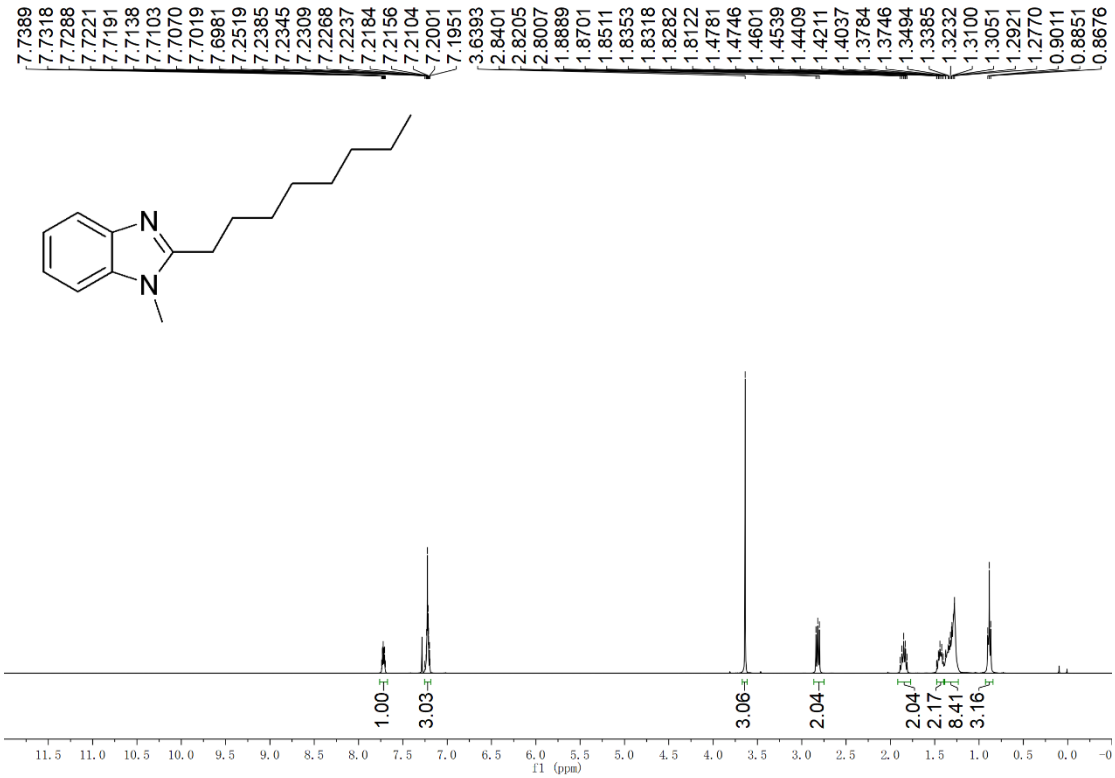


Figure S65. ^{1}H NMR spectrum of compound **6ac** (400 MHz, $CDCl_3$).

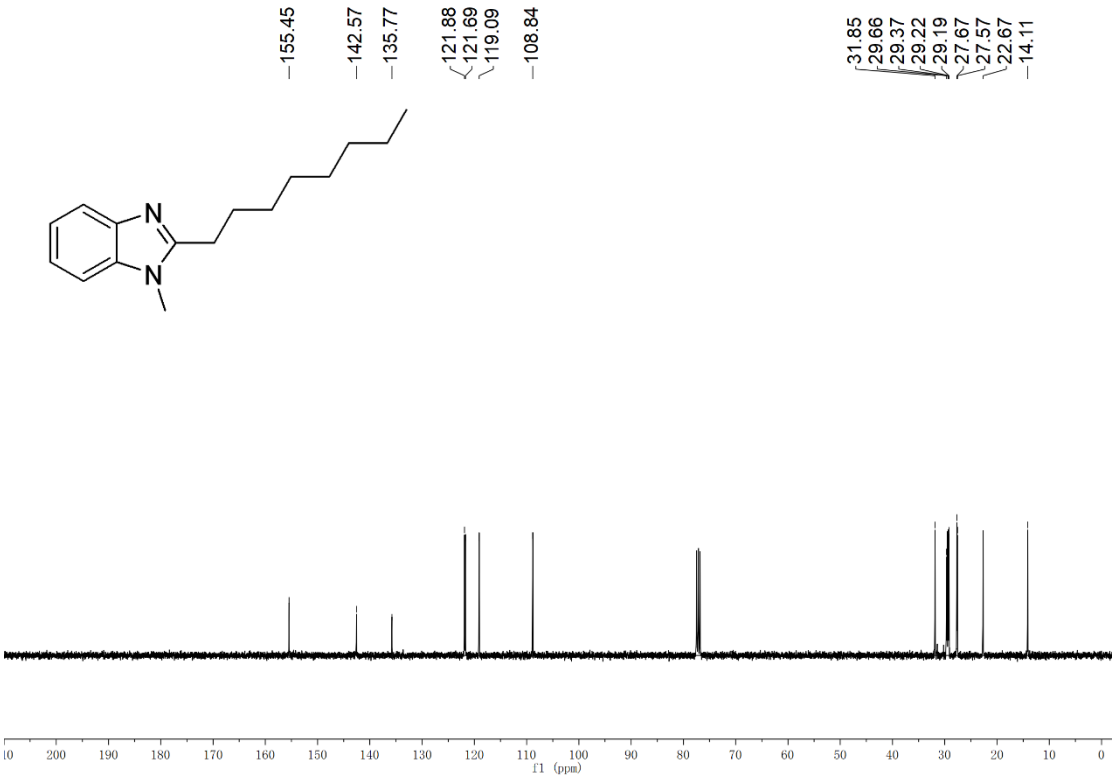


Figure S66. ^{13}C NMR spectrum of compound **6ac** (100 MHz, $CDCl_3$).

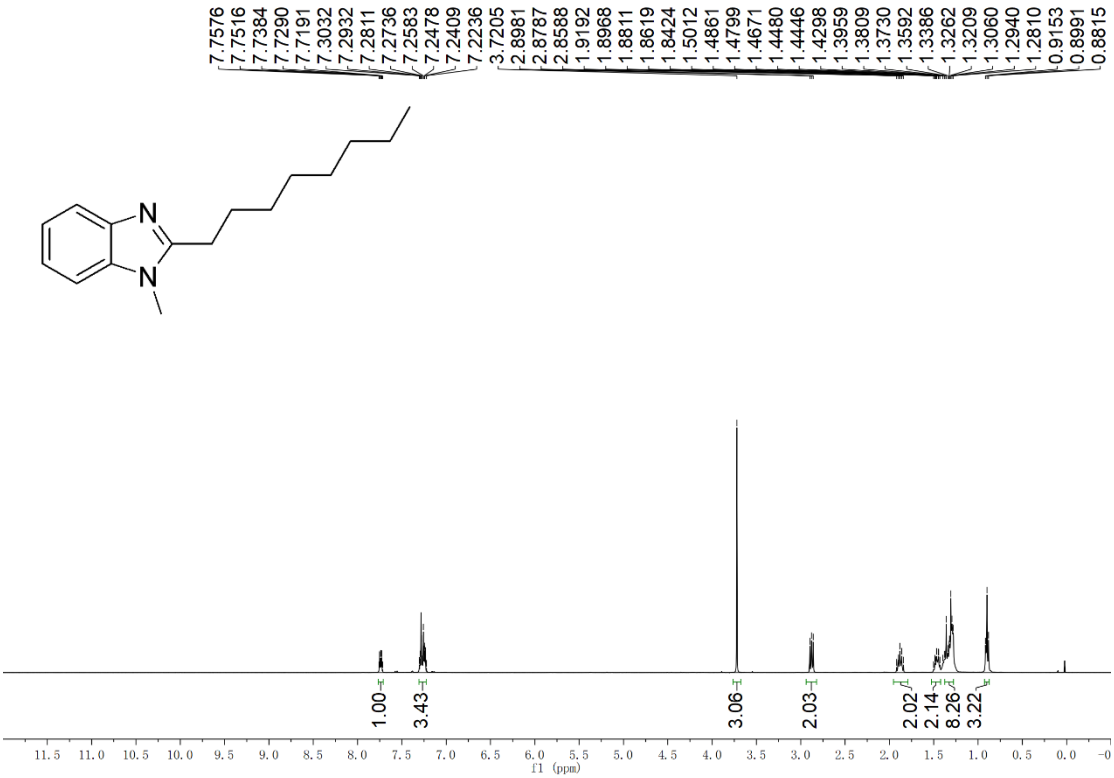


Figure S67. ^{1}H NMR spectrum of compound **6ad** (400 MHz, $CDCl_3$).

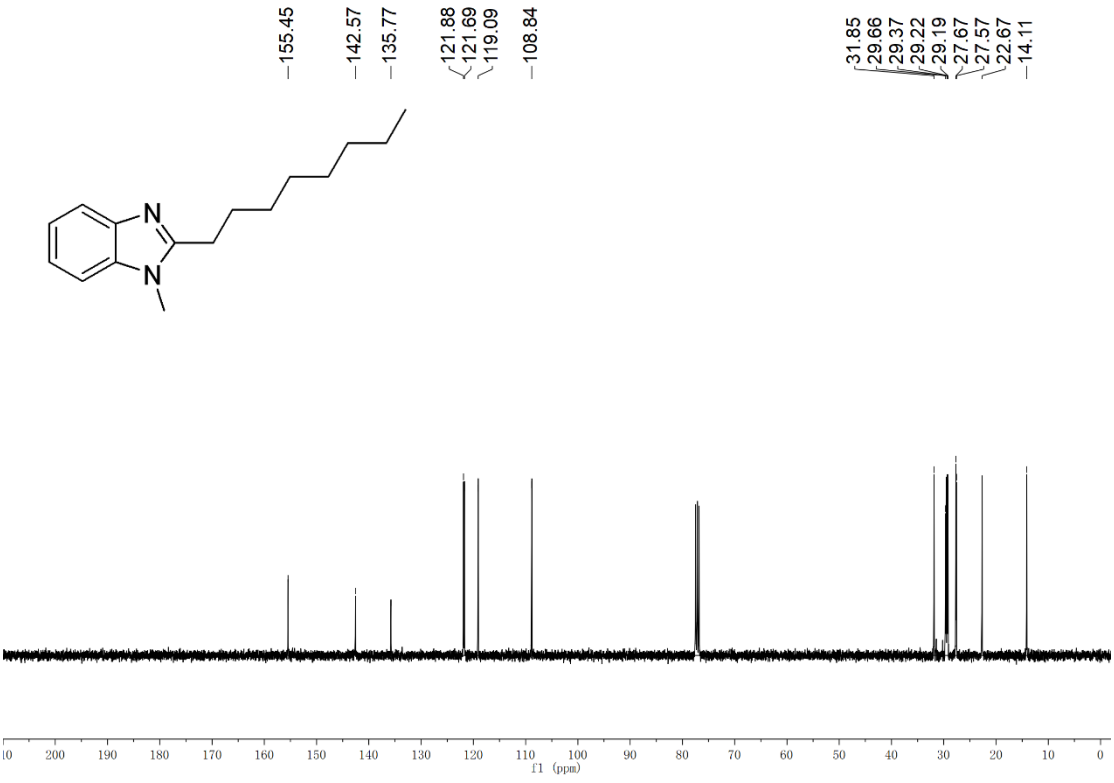


Figure S68. ^{13}C NMR spectrum of compound **6ad** (100 MHz, $CDCl_3$).

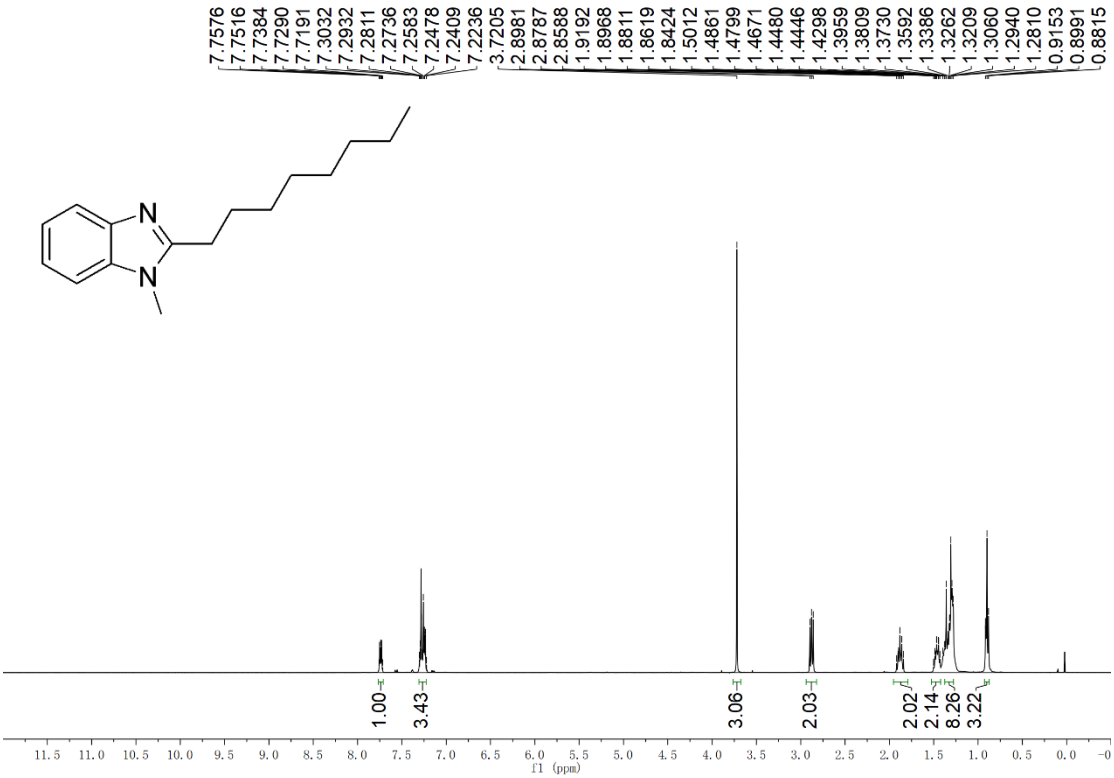


Figure S69. ^{1}H NMR spectrum of compound **6ae** (400 MHz, $CDCl_3$).

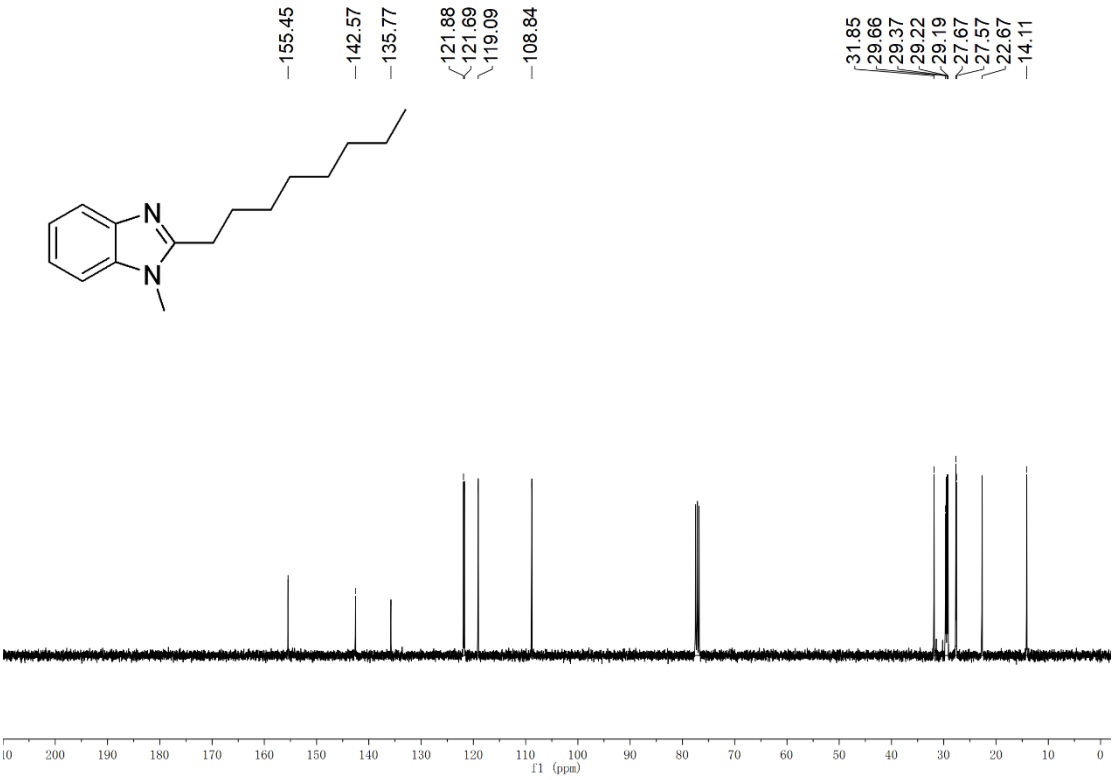


Figure S70. ^{13}C NMR spectrum of compound **6ae** (100 MHz, $CDCl_3$).

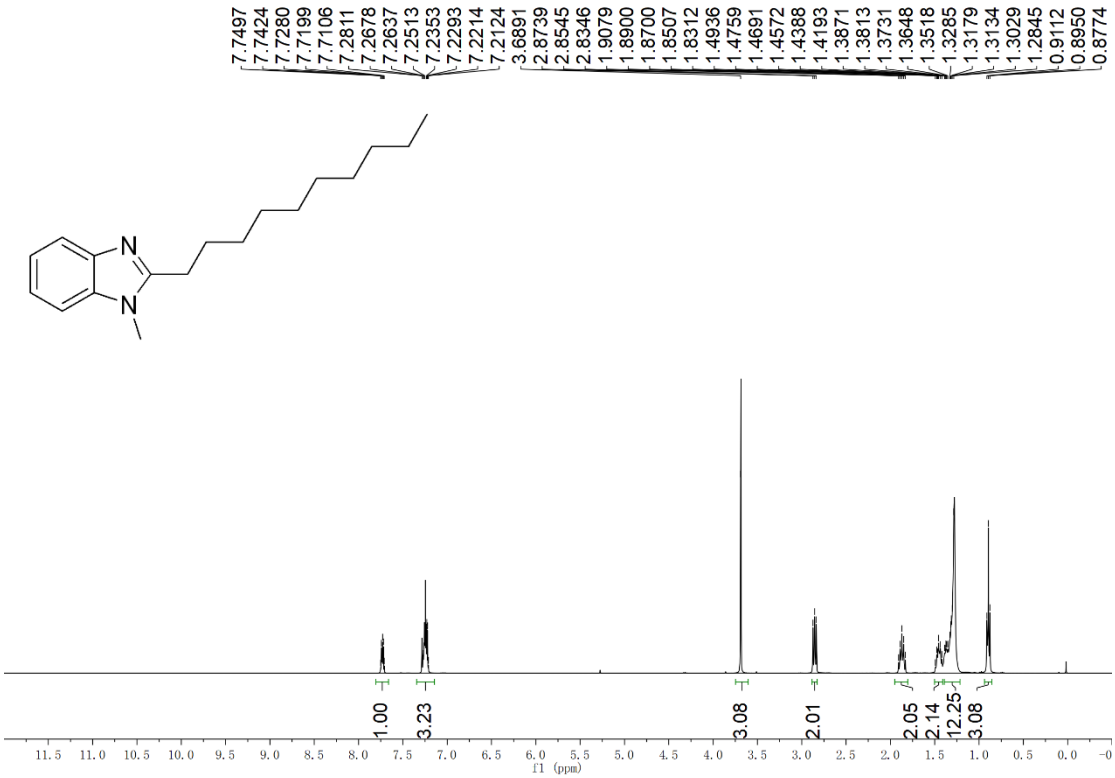


Figure S71. ^{1}H NMR spectrum of compound **6af** (400 MHz, $CDCl_3$).

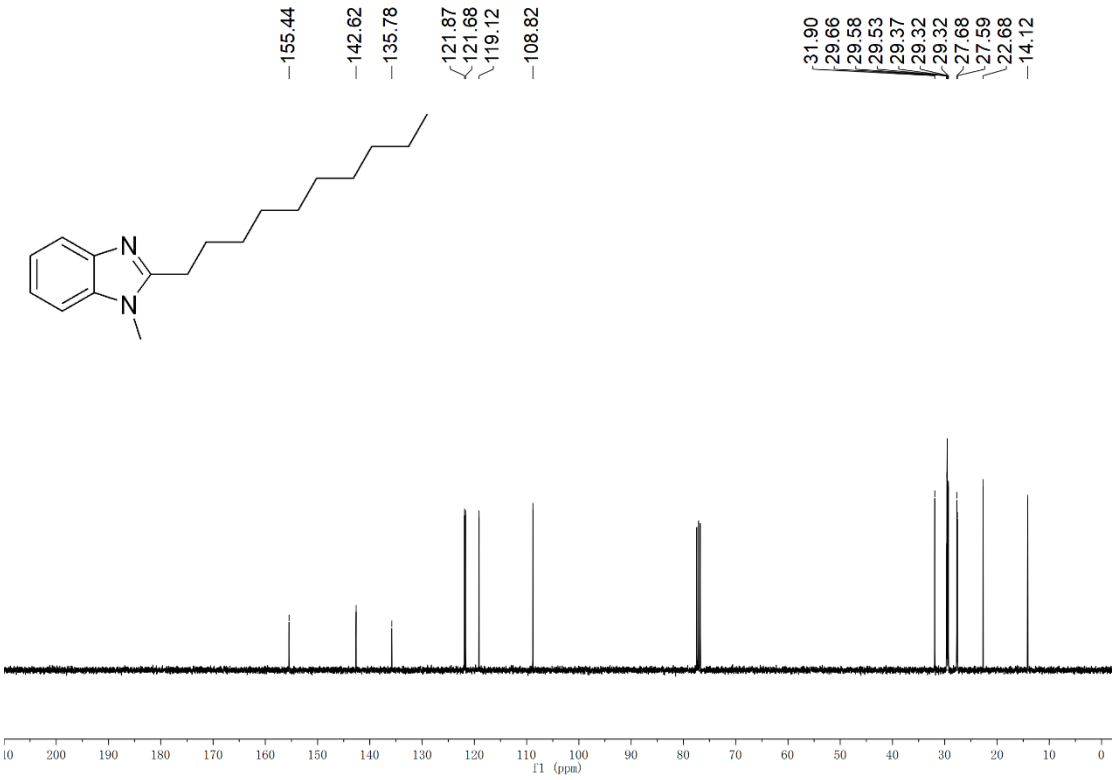


Figure S72. ^{13}C NMR spectrum of compound **6af** (100 MHz, $CDCl_3$).

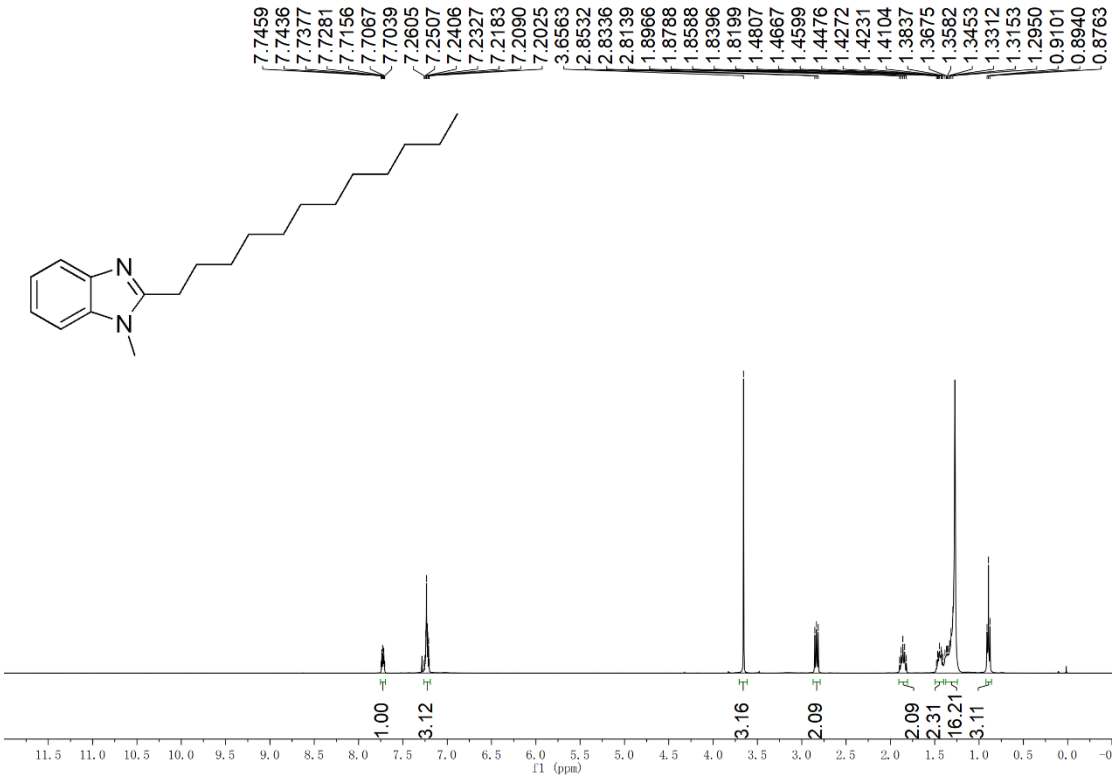


Figure S73. ^{1}H NMR spectrum of compound **6ag** (400 MHz, $CDCl_3$).

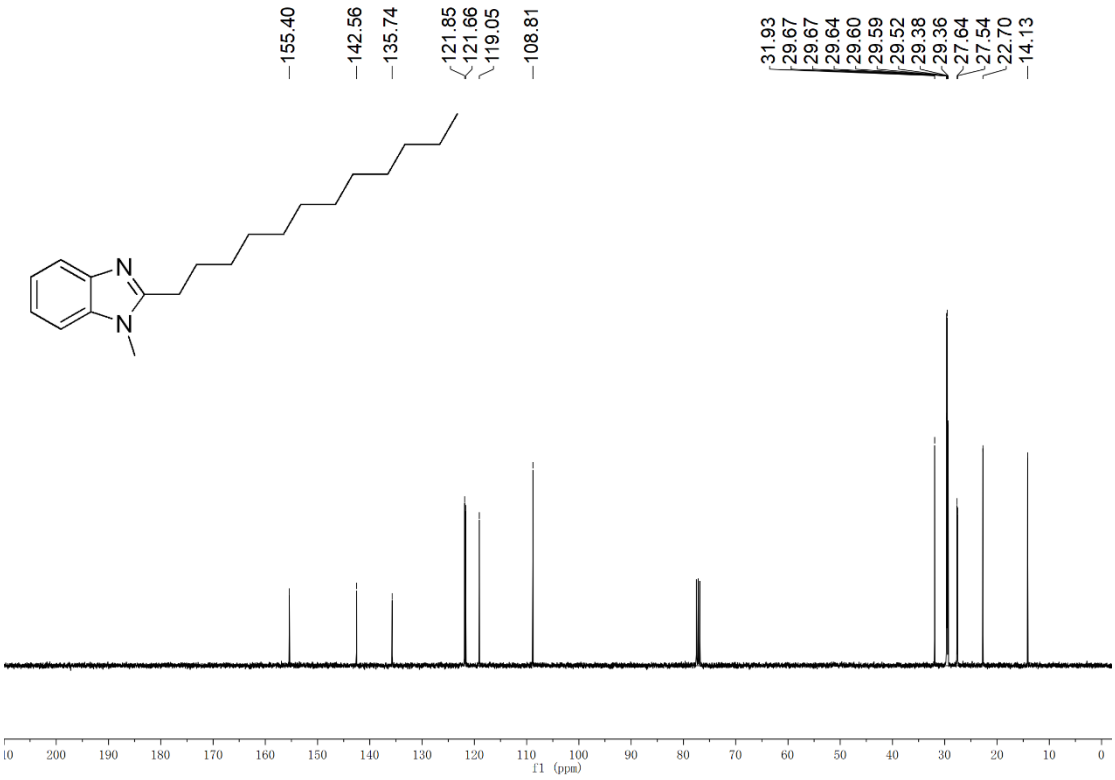


Figure S74. ^{13}C NMR spectrum of compound **6ag** (100 MHz, $CDCl_3$).

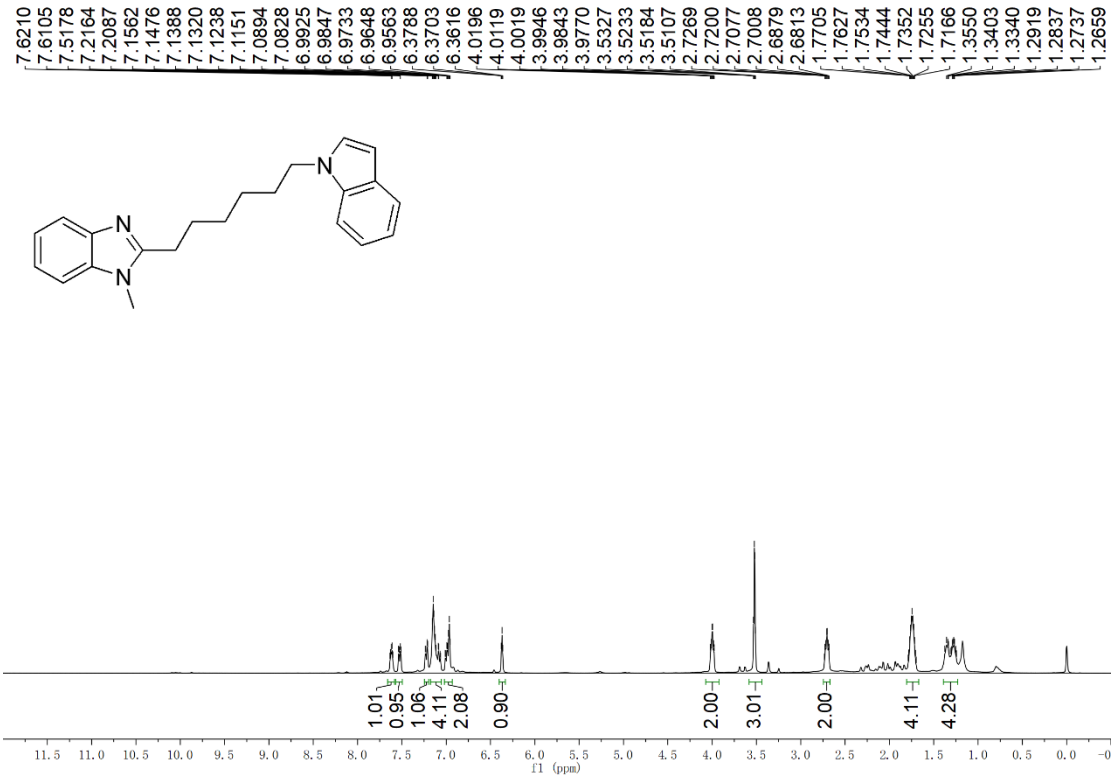


Figure S75. ^{1}H NMR spectrum of compound **6ah** (400 MHz, $CDCl_3$).

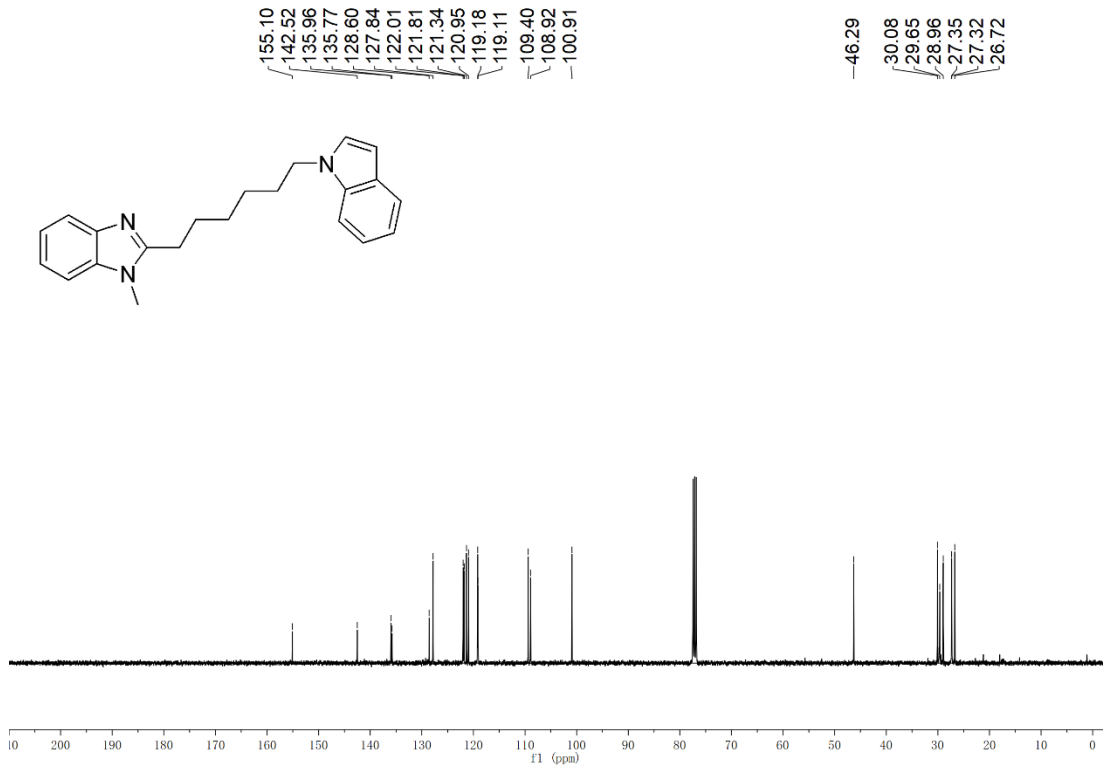


Figure S76. ^{13}C NMR spectrum of compound **6ah** (100 MHz, $CDCl_3$).

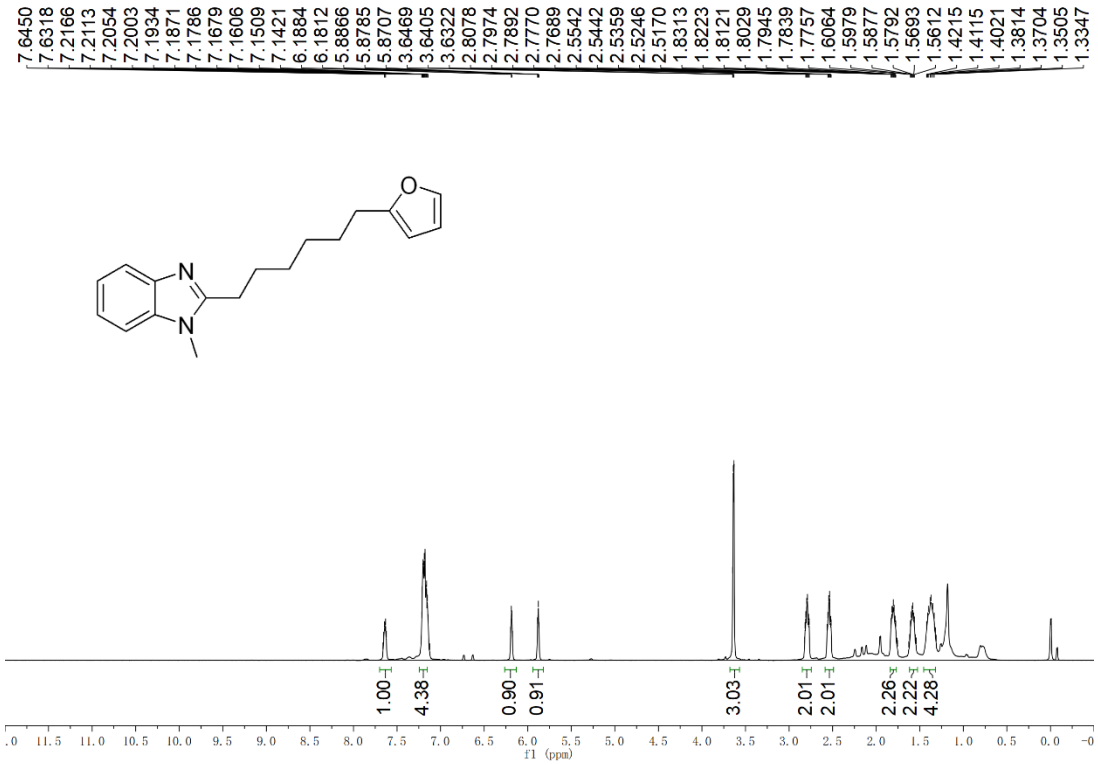


Figure S77. ^{1}H NMR spectrum of compound **6ai** (400 MHz, $CDCl_3$).

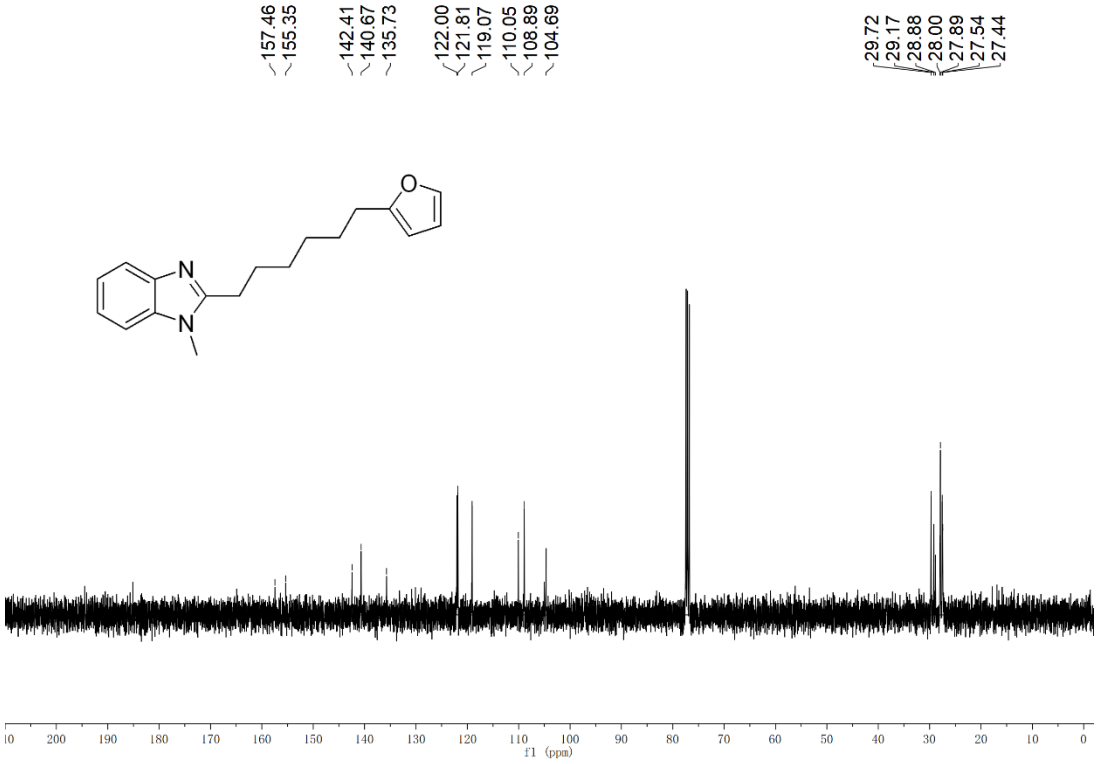


Figure S78. ^{13}C NMR spectrum of compound **6ai** (100 MHz, $CDCl_3$).

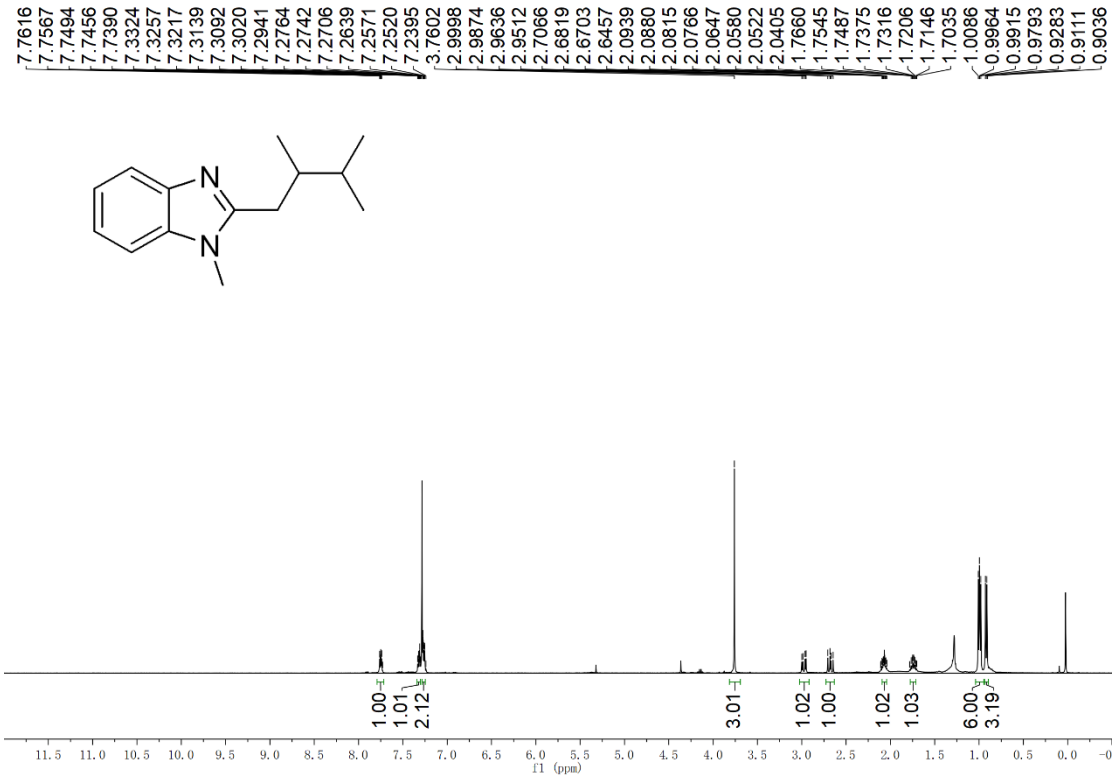


Figure S79. ^{1}H NMR spectrum of compound **6aj** (400 MHz, $CDCl_3$).

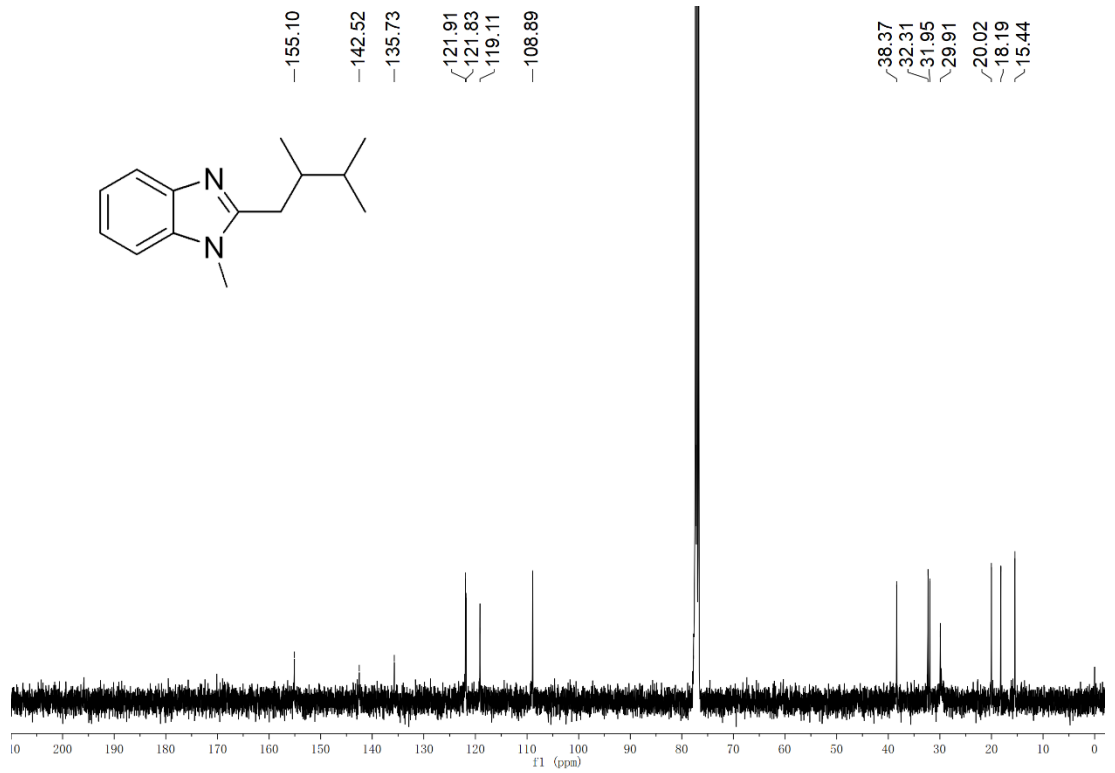


Figure S80. ^{13}C NMR spectrum of compound **6aj** (100 MHz, $CDCl_3$).

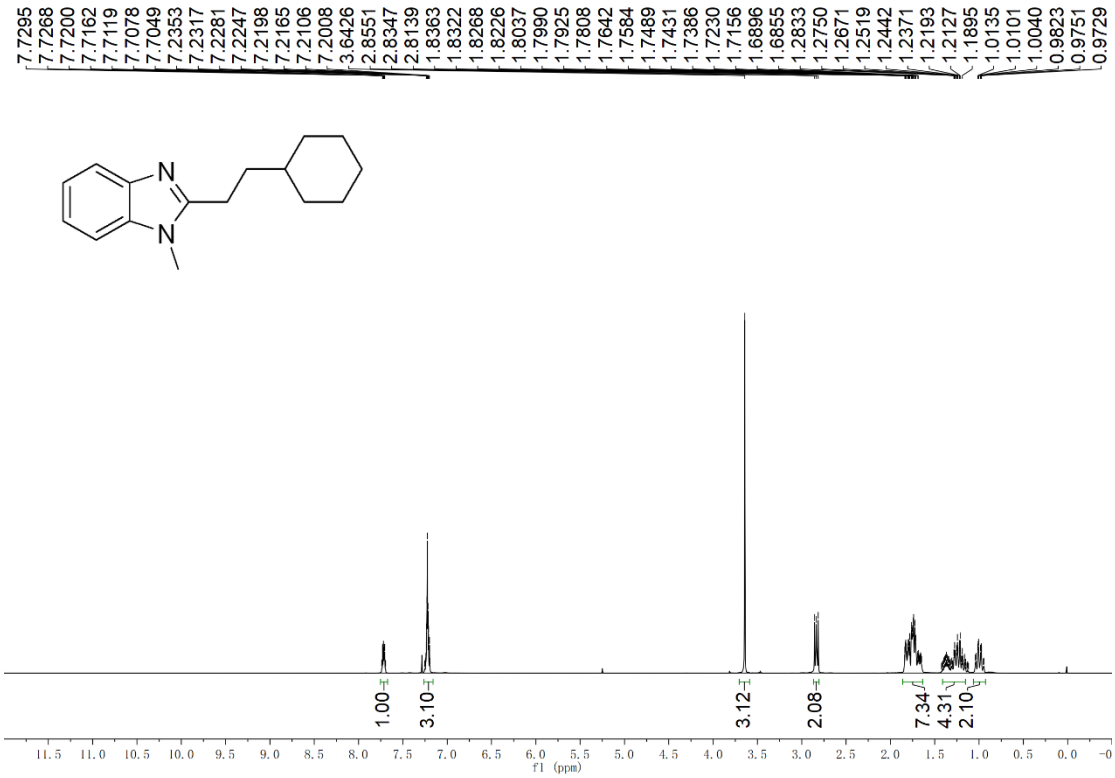


Figure S81. ^{1}H NMR spectrum of compound **6ak** (400 MHz, $CDCl_3$).

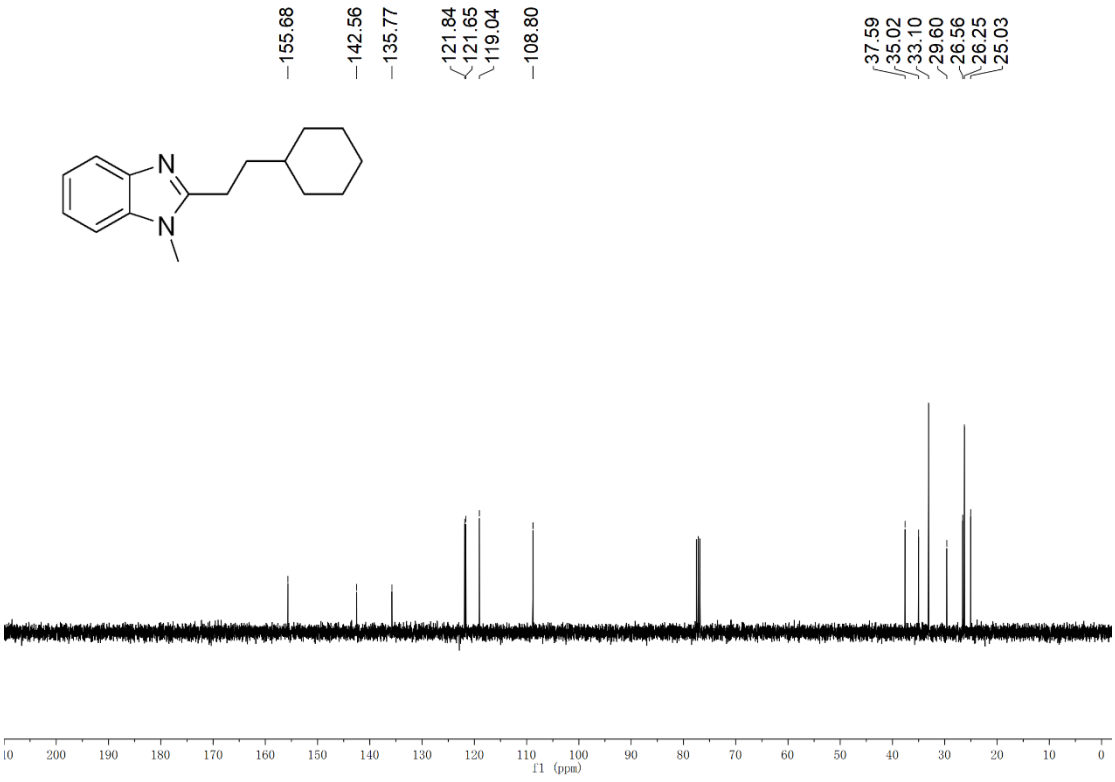


Figure S82. ^{13}C NMR spectrum of compound **6ak** (100 MHz, $CDCl_3$).

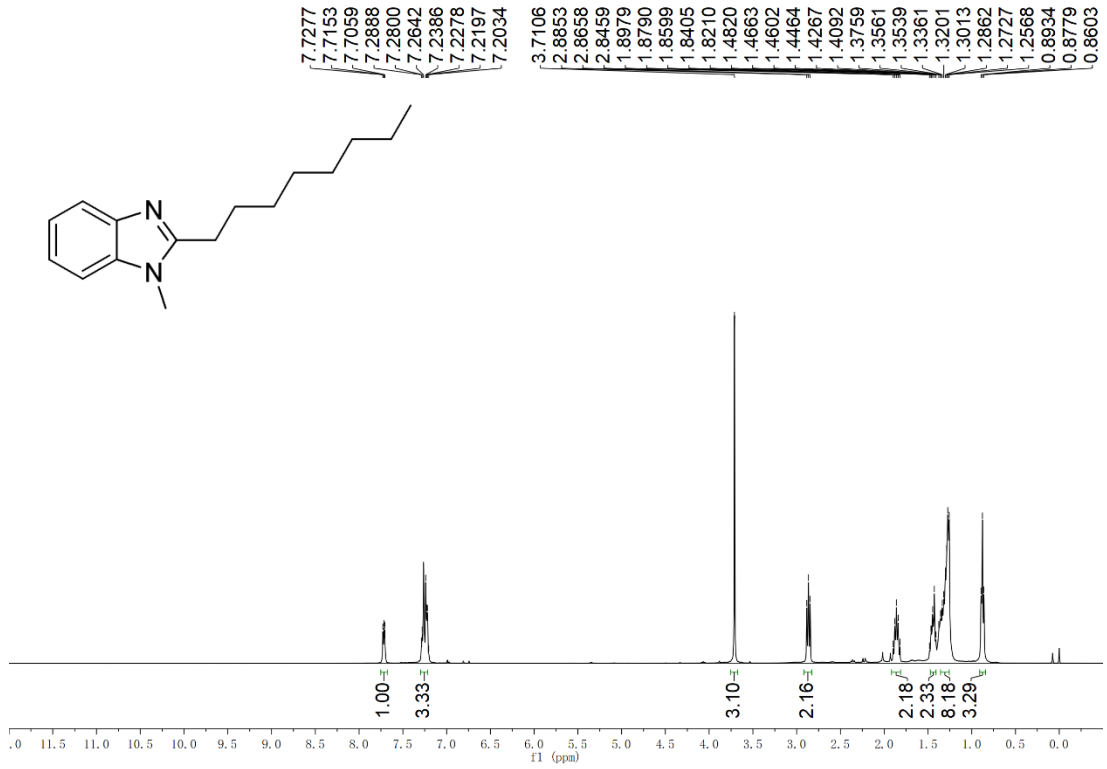


Figure S83. ^{1}H NMR spectrum of compound **6al** (400 MHz, $CDCl_3$).

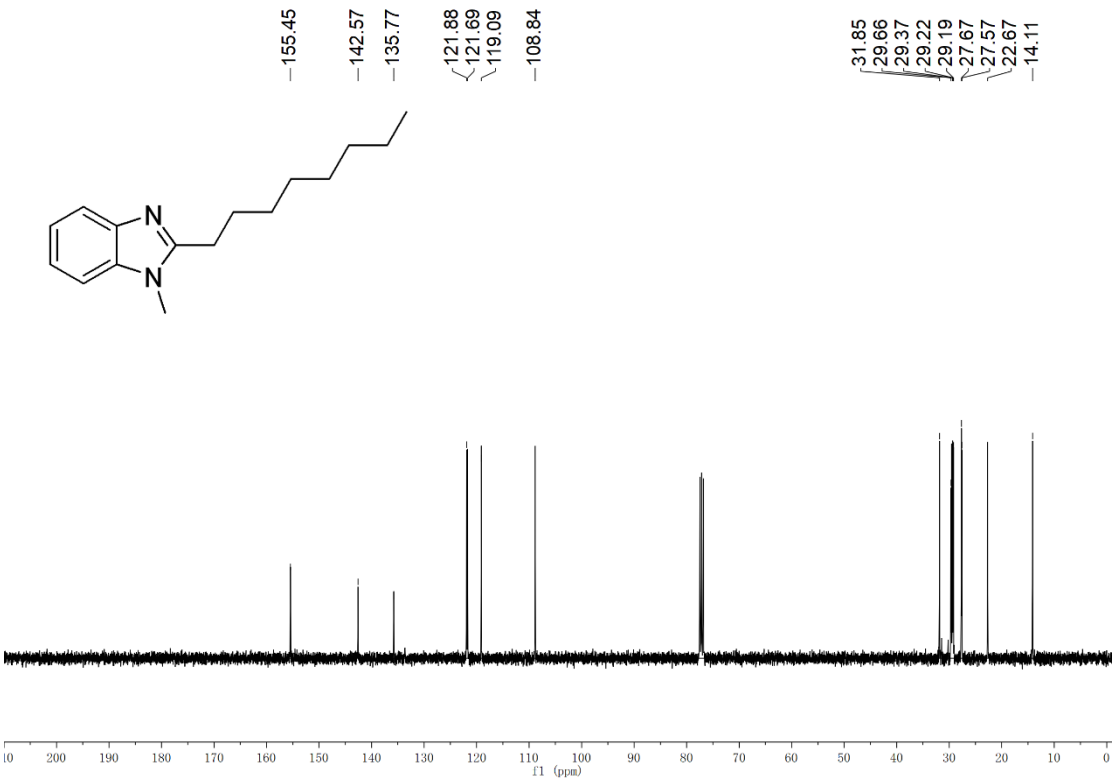


Figure S84. ^{13}C NMR spectrum of compound **6al** (100 MHz, $CDCl_3$).

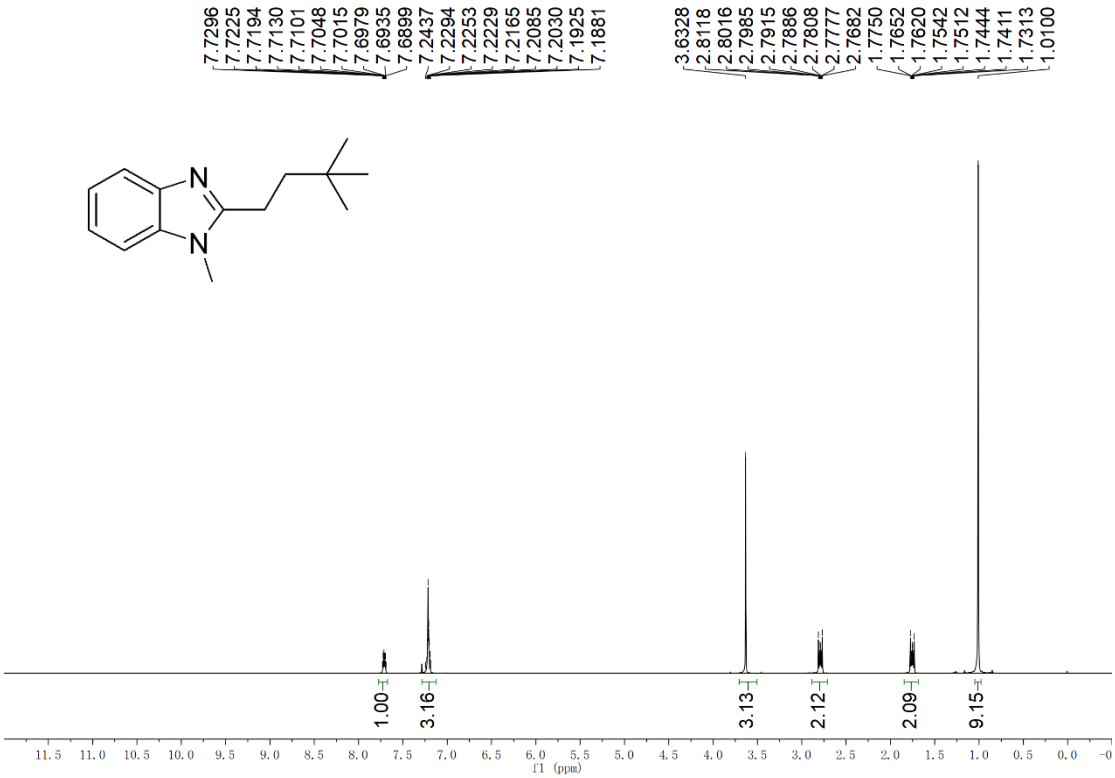


Figure S85. ^{1}H NMR spectrum of compound **6am** (400 MHz, $CDCl_3$).

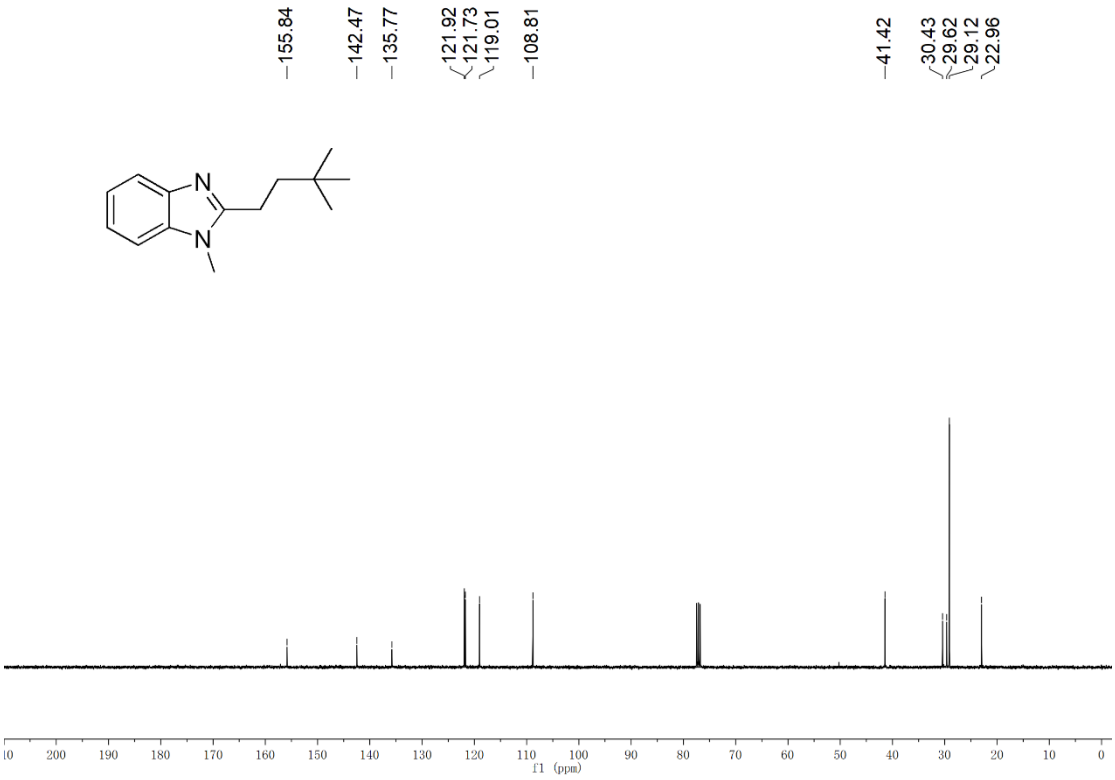


Figure S86. ^{13}C NMR spectrum of compound **6am** (100 MHz, $CDCl_3$).

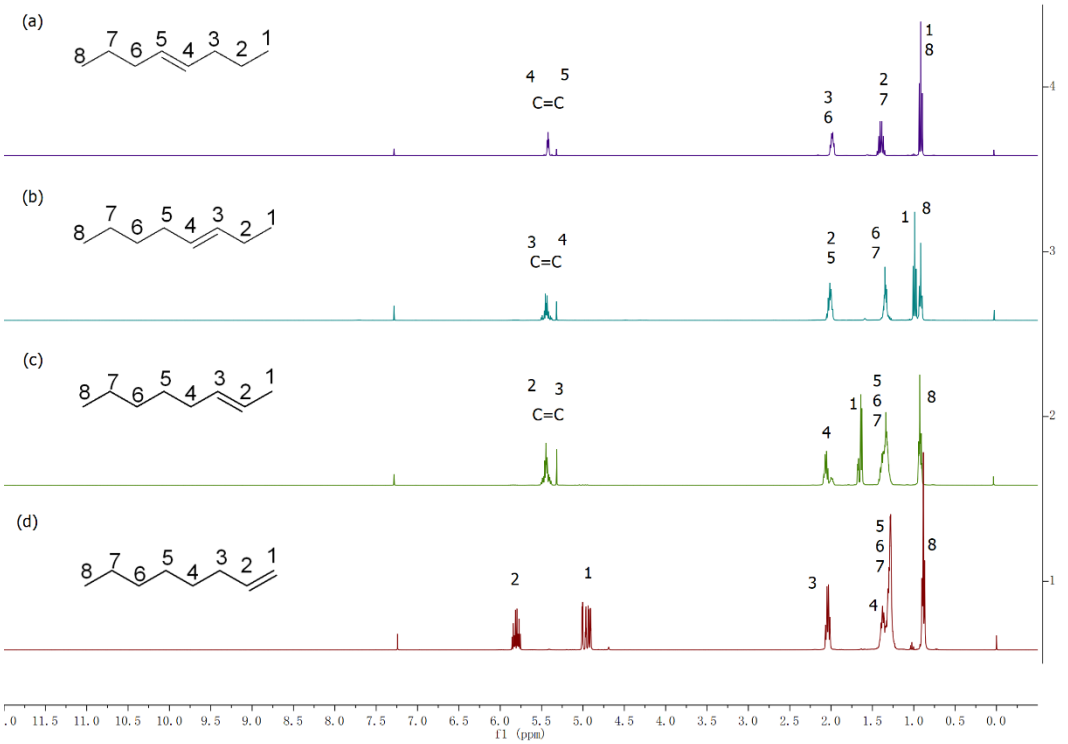


Figure S87. Stacked ^{1}H NMR spectra of commercially purchased 4-octene (a), 3-octene (b), 2-octene (c), and 1-octene (d) (400 MHz, $CDCl_3$).

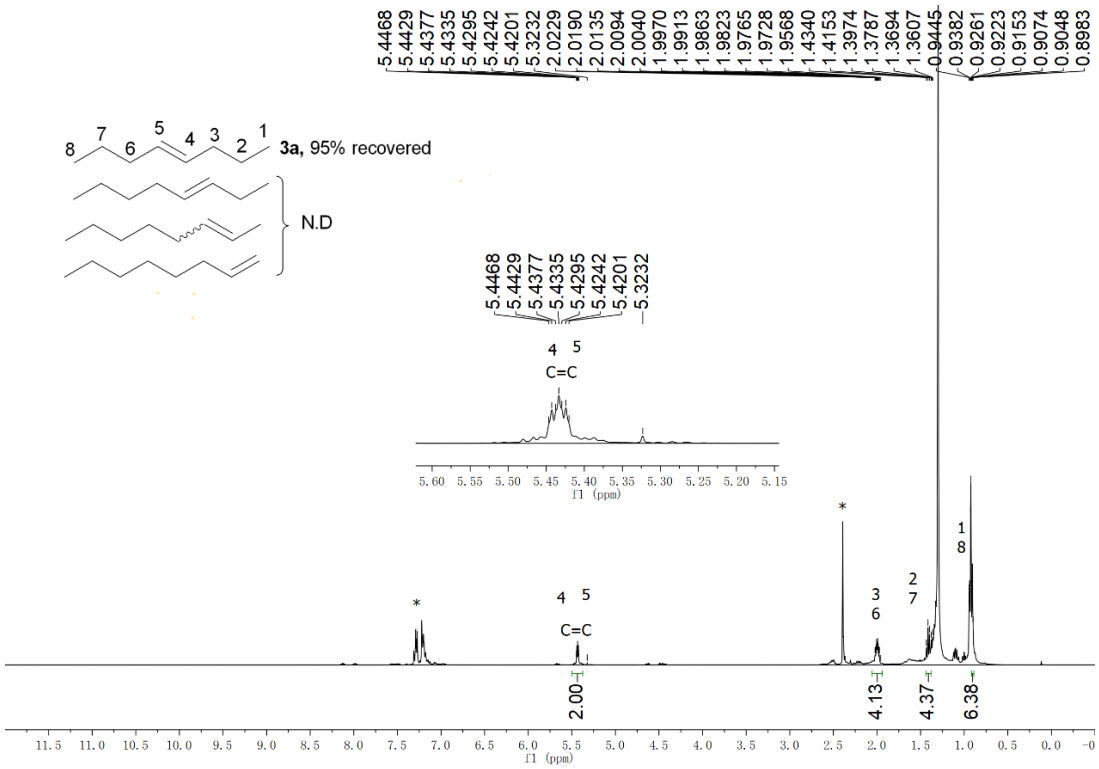


Figure S88. ^{1}H NMR spectrum of the recovered alkene from the tracing alkene isomerization reaction without *N*-methylbenzimidazole (**1 h**, 400 MHz, $CDCl_3$, * = C_7H_8).

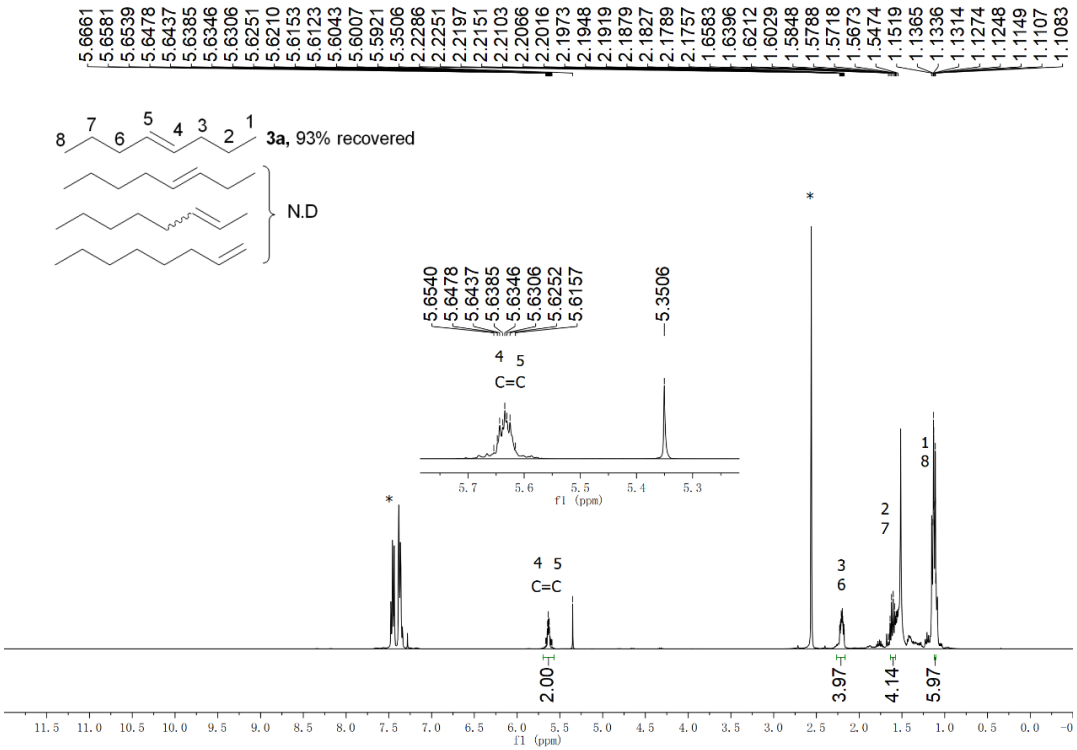


Figure S89. ^{1}H NMR spectrum of the recovered alkene from the tracing alkene isomerization reaction without *N*-methylbenzimidazole (**10 h**, 400 MHz, $CDCl_3$, * = C_7H_8).

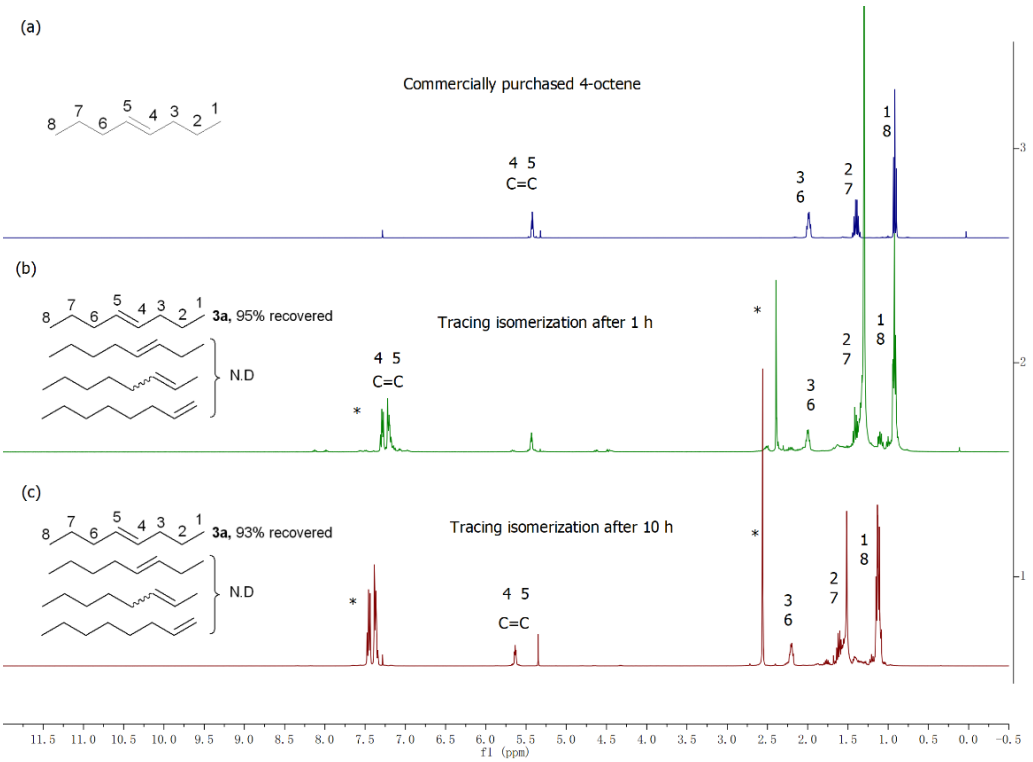


Figure S90. Stacked ^{1}H NMR spectra of commercially purchased 4-octene (a), recovered alkenes **3a** (b), and (c) from the tracing alkene isomerization reaction without *N*-methylbenzimidazole (400 MHz, $CDCl_3$, * = C_7H_8).

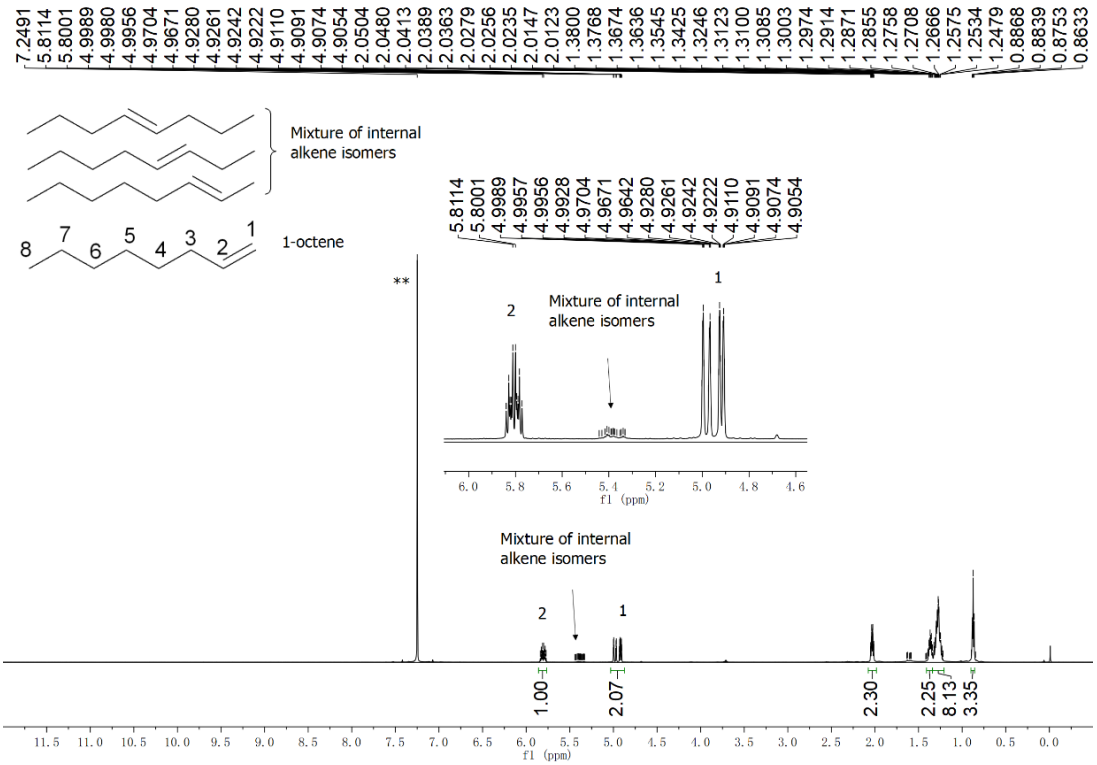


Figure S91. ^{1}H NMR spectrum of the isomerized alkenes mixture from the tracing alkene isomerization reaction with *N*-methylbenzimidazole (**1 h**, 400 MHz, $CDCl_3$, ** = $CHCl_3$).

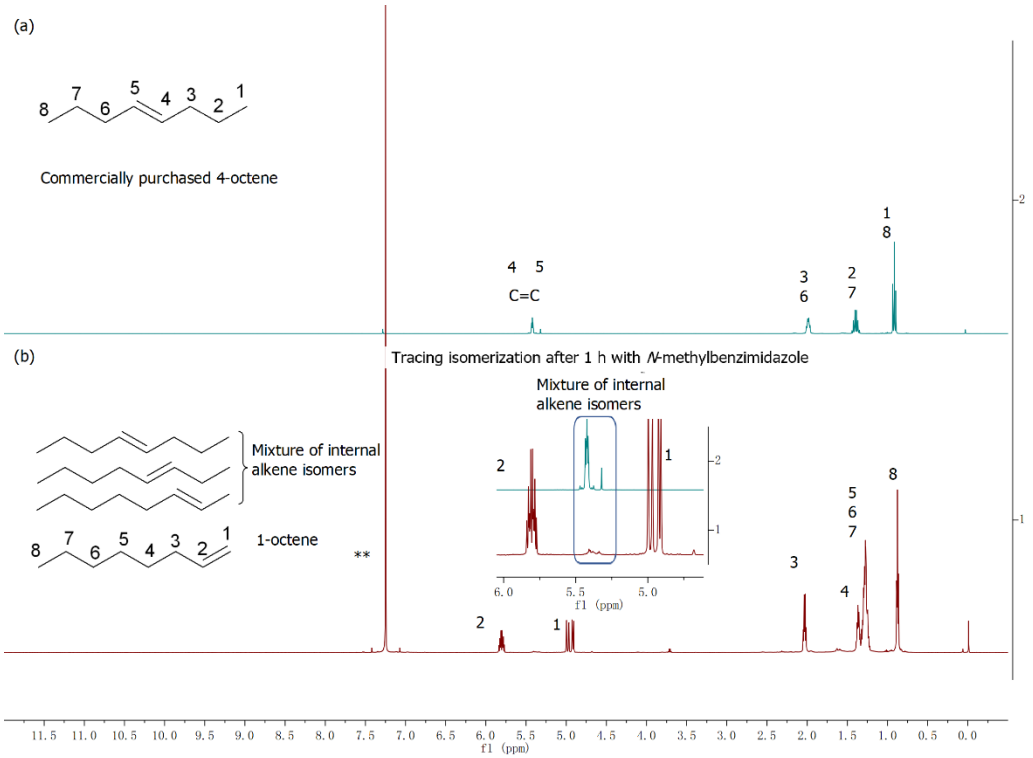


Figure S92. Stacked ^{1}H NMR spectra of commercially purchased 4-octene (a) and the isomerized alkenes mixture (b) from the tracing isomerization reaction with *N*-methyl-benzimidazole (400 MHz, $CDCl_3$, ** = $CDCl_3$).

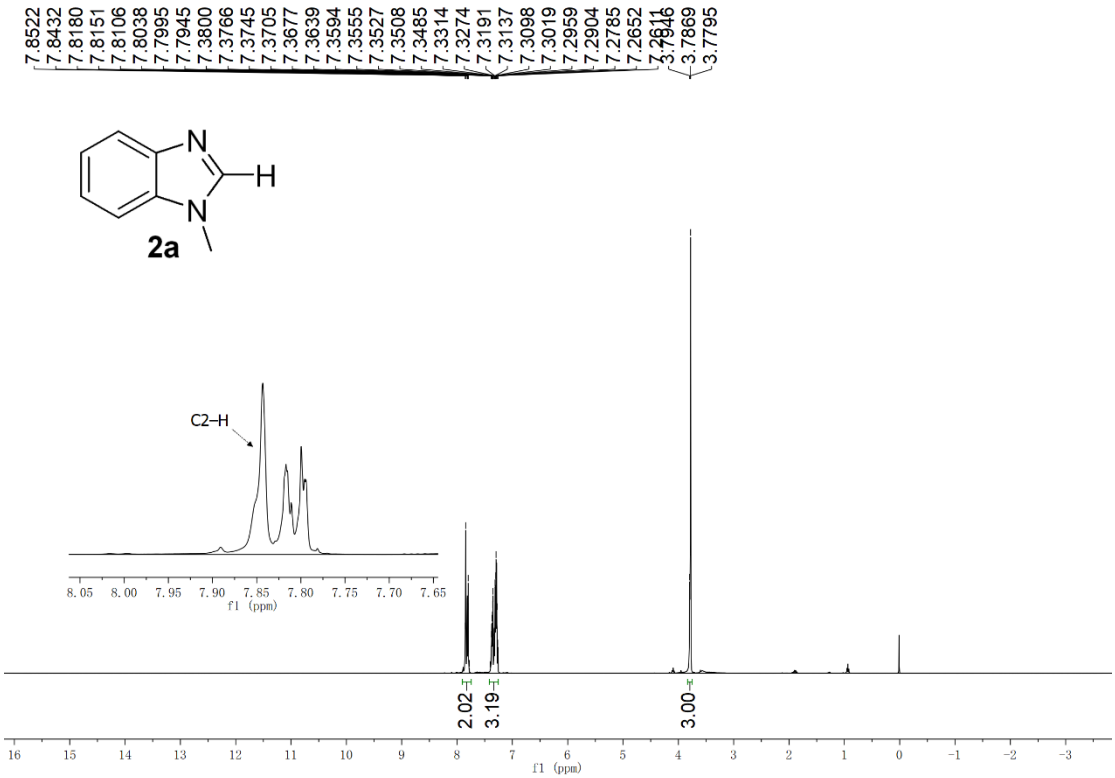


Figure S93. ^{1}H NMR spectrum of compound **2a** (400 MHz, $CDCl_3$).

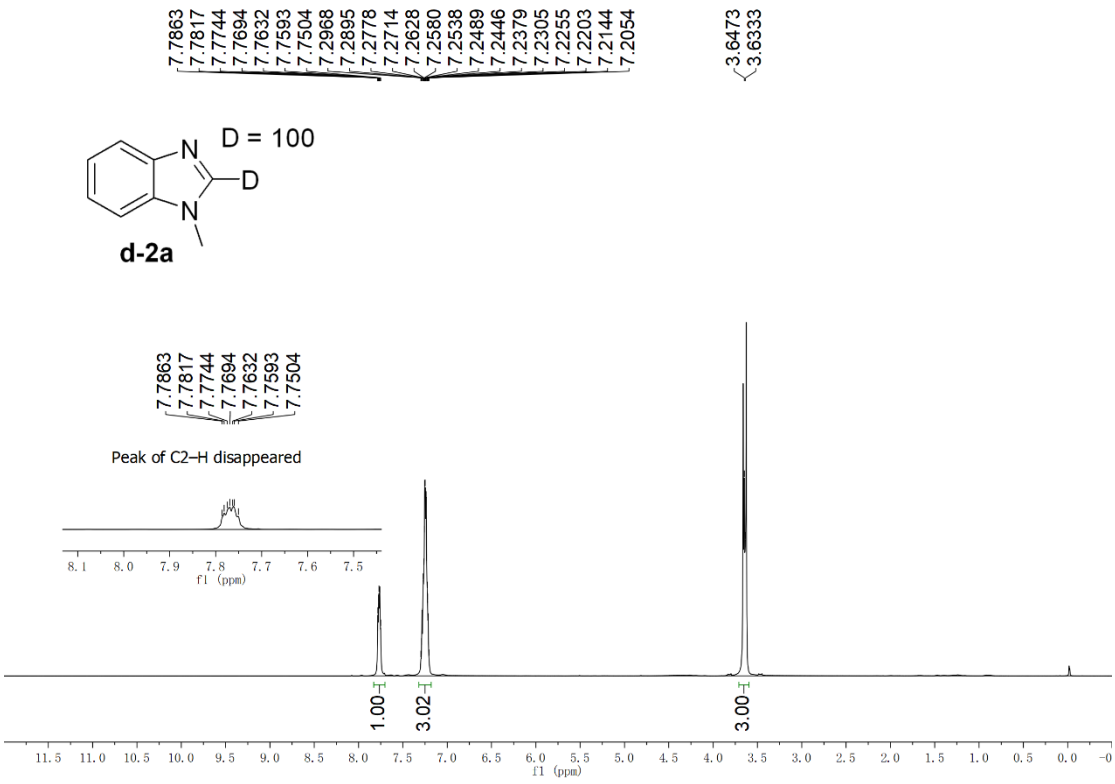


Figure S94. ^{1}H NMR spectrum of compound **d-2a** (400 MHz, $CDCl_3$).

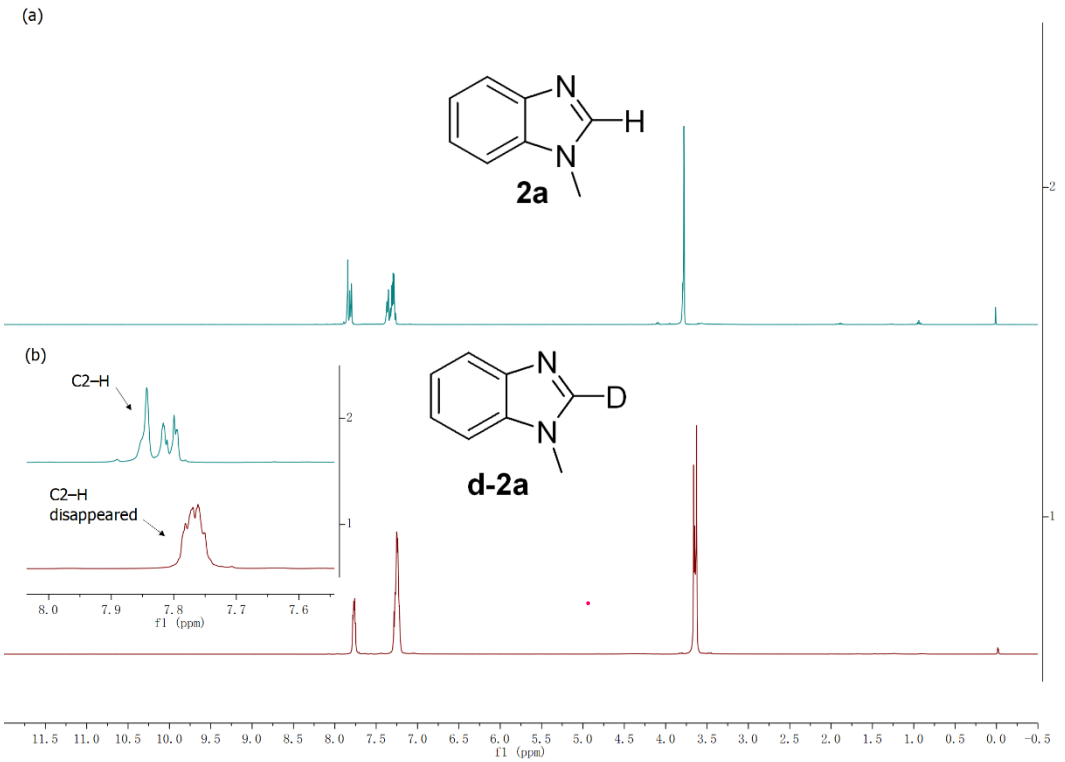


Figure S95. Stacked ^{1}H NMR spectra of compounds **2a** (a) and **d-2a** (b) (400 MHz, $CDCl_3$).

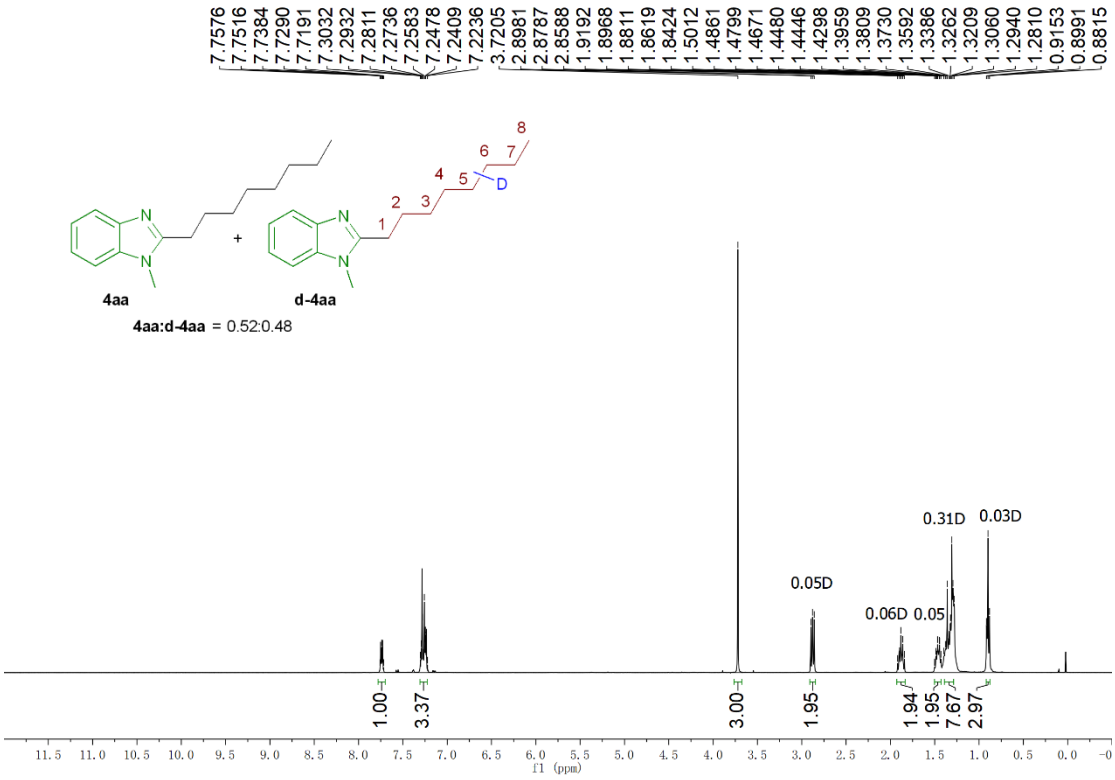


Figure S96. ^{1}H NMR spectrum of compound **4aa + d-4aa** from the KIE reaction (400 MHz, $CDCl_3$).

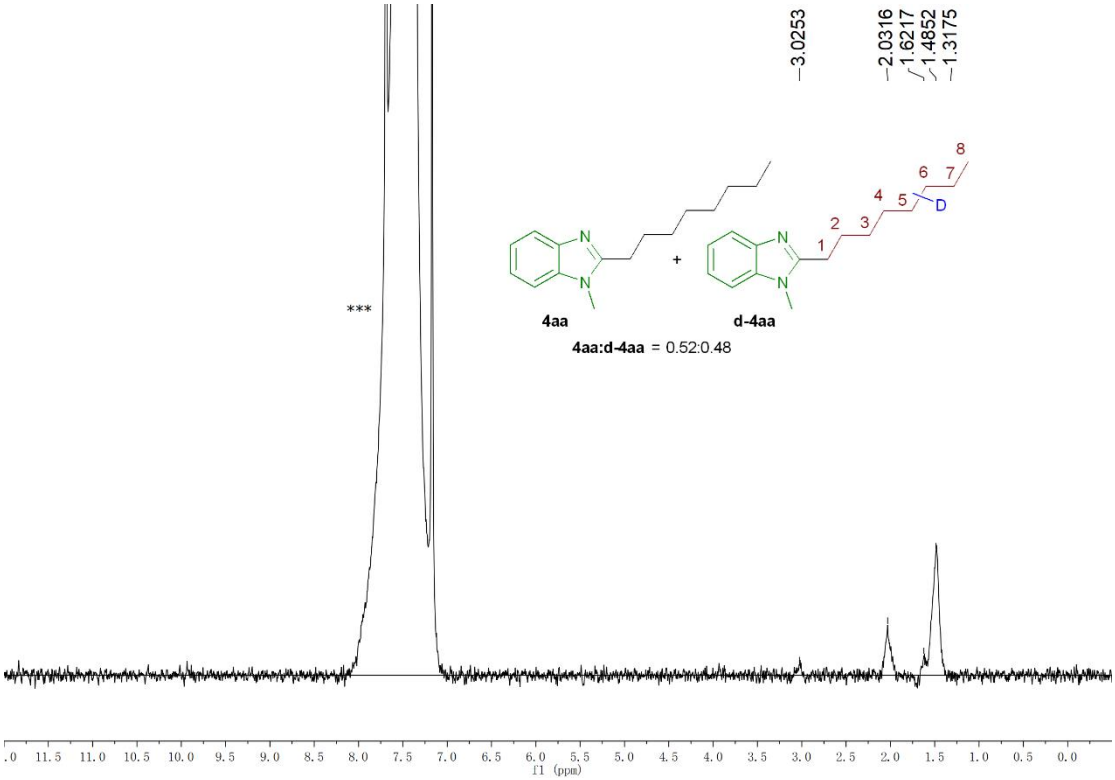


Figure S97. ^{2}H NMR spectrum of compound **4aa + d-4aa** from the KIE reaction (61 MHz, $CDCl_3$, *** = $CDCl_3$).

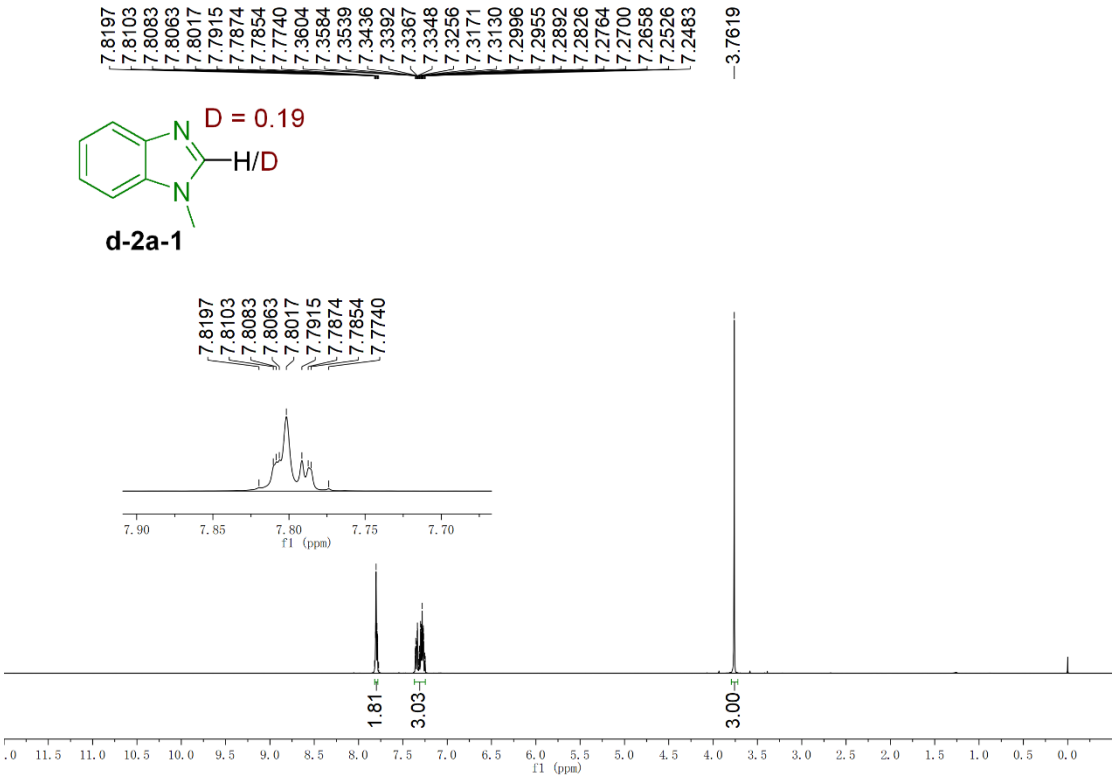


Figure S98. ^{1}H NMR spectrum of *N*-methylbenzimidazole **d-2a-1** from the H/D scrambling experiment using **4-octene** (400 MHz, $CDCl_3$).

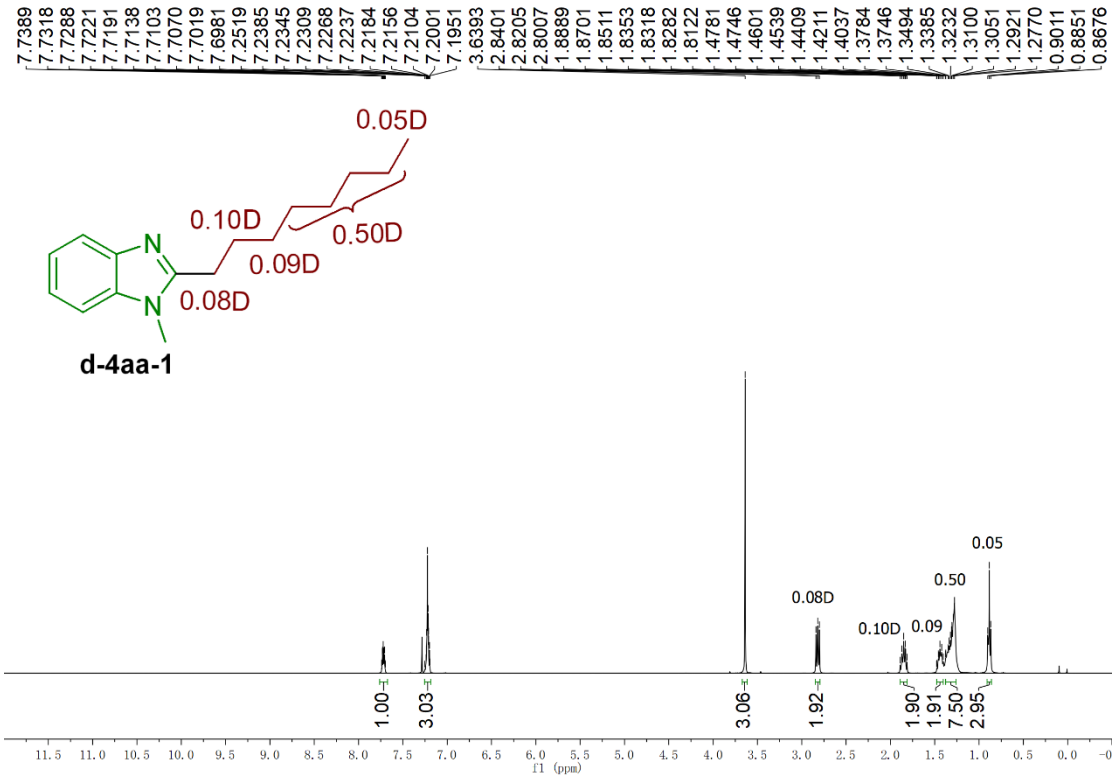


Figure S99. ^{1}H NMR spectrum of compound **d-4aa-1** from the H/D scrambling experiment using **4-octene** (400 MHz, $CDCl_3$).

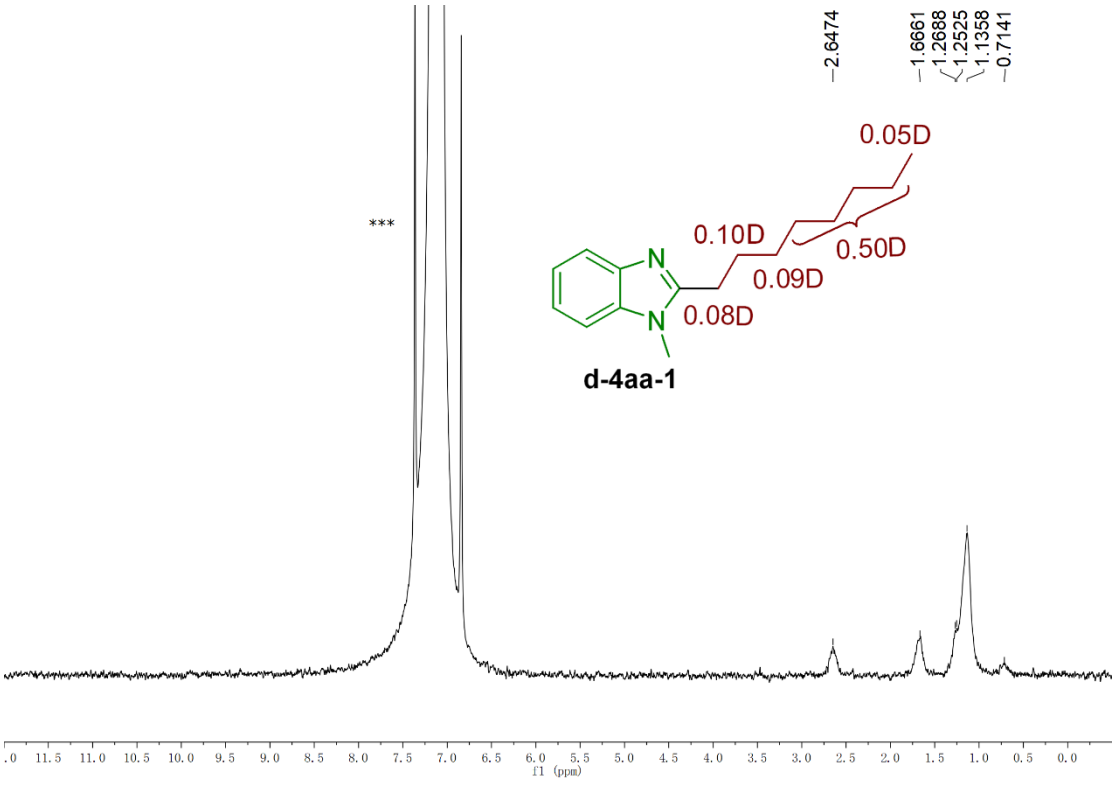


Figure S100. ^{2}H NMR spectrum of compound **d-4aa-1** from the H/D scrambling experiment using **4-octene** (61 MHz, $CDCl_3$, *** = $CDCl_3$).

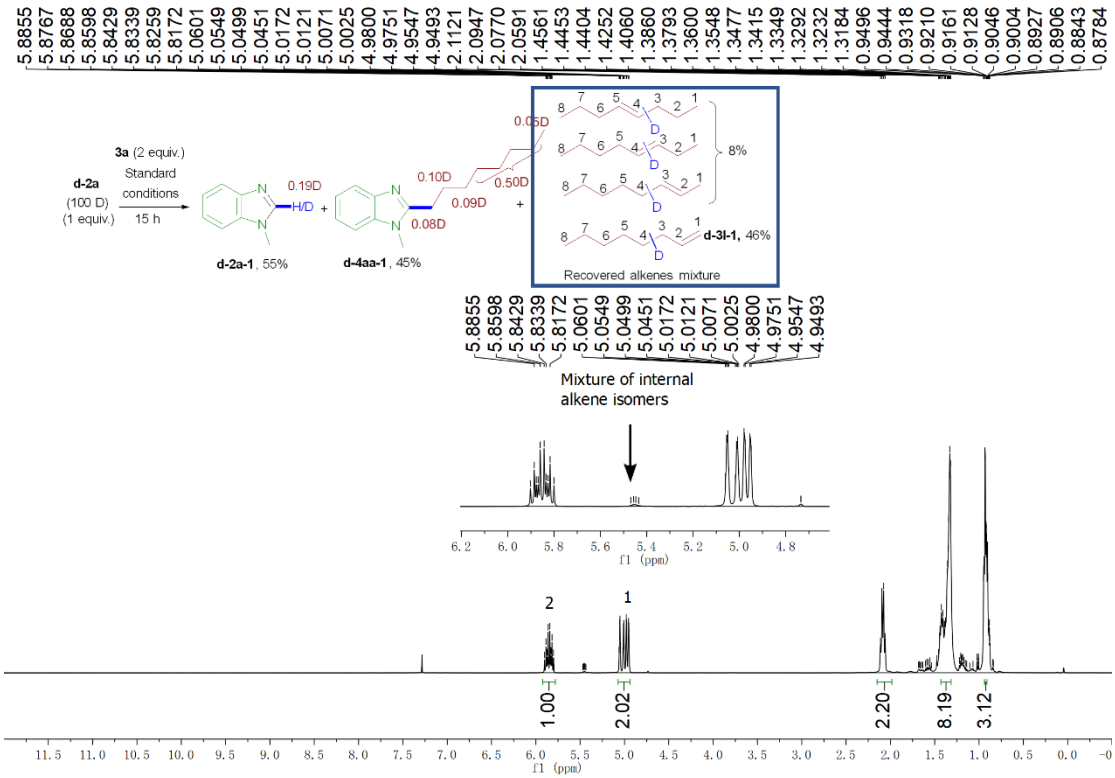


Figure S101. ^{1}H NMR spectrum of recovered alkenes mixture from the H/D scrambling experiment using **4-octene** (400 MHz, $CDCl_3$).

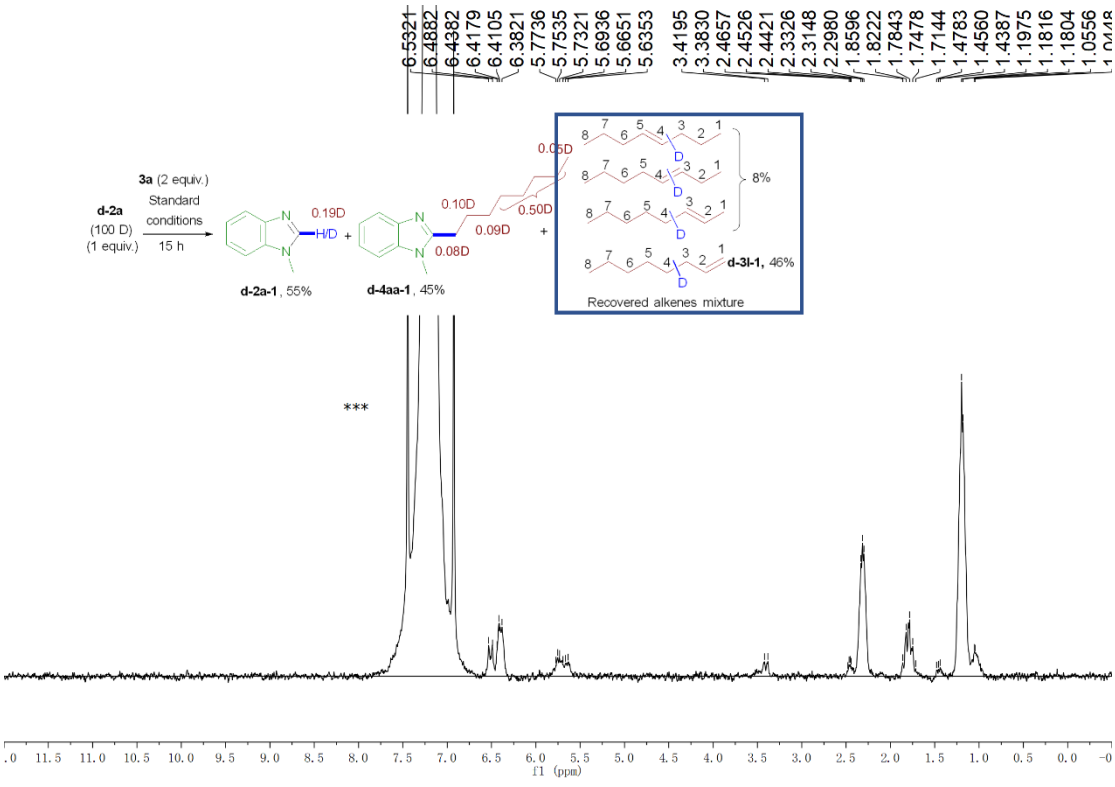


Figure S102. ^{2}H NMR spectrum of recovered alkenes mixture from the H/D scrambling experiment using **4-octene** (61 MHz, $CDCl_3$, *** = $CDCl_3$).

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