Electronic Supplementary Information

Organohalides-Catalyzed Dehydrative O-Alkylation between Alcohols: A Facile Etherification Method for Aliphatic Ether Synthesis

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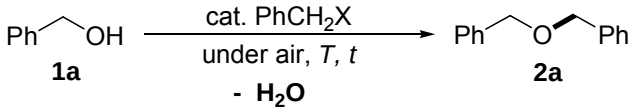
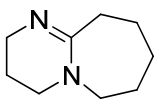
Detailed Condition Screening Tables and Detailed Summary Tables of the Etherification Reactions

Table S1. Detailed Condition Screening and Optimization for Benzyl Halide-Catalyzed O-Alkylative Homo-Etherification Reaction of Benzyl Alcohol.[a]



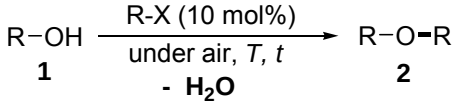
run	cat. (mol%), additive (mol%)	T (^{o}C)	t (h)	yield%[b]
1	-	120	24	0
2	$PhCH_2Br$ (1)	120	24	41
3	$PhCH_2Br$ (10)	30	8	0
4	$PhCH_2Br$ (10)	60	8	3
5	$PhCH_2Br$ (10)	100	8	20
6	$PhCH_2Br$ (10)	120	8	38
7	***$PhCH_2Br$ (10)***	***120***	***24***	***>99 (97)***
8	$PhCH_2Br$ (5)	120	24	71
9	$PhCH_2Br$ (8)	120	24	81
10	$PhCH_2Cl$ (10)	120	24	18
11[c,d]	$PhCH_2Br$ (10), DBU (10), toluene	120	24	0
12[c,d]	$PhCH_2Br$ (10), $NaHCO_3$ (10), toluene	120	24	<5
13[d]	$PhCH_2Br$ (10)	120	24	(93)
14[c,d]	$PhCH_2Br$ (10), toluene	120	24	(51)
15[c,e]	HBr (10), toluene	120	24	(57)
16[e]	HBr	120	24	(60)
17	NaBr (10 mol%), H_2SO_4 (10-15 mol%)	120	24	(9)
18	NaBr (10 mol%), H_3PO_4 (10-15 mol%)	120	24	(17)

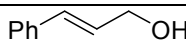
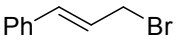
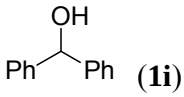
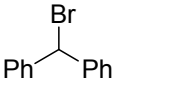
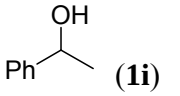
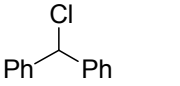
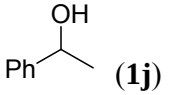
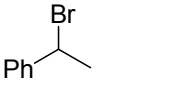
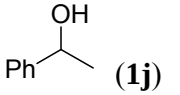
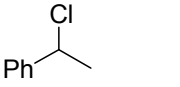
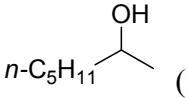
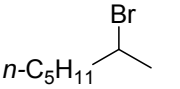
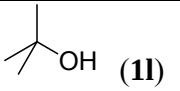
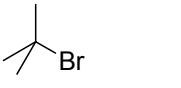
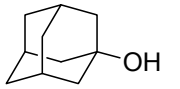
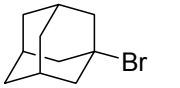
[a] Unless otherwise noted, the neat mixture of $PhCH_2OH$ **1a** (10 mmol) and different loadings of catalyst $PhCH_2X$ was directly sealed under air in a Schlenk tube (20 mL). The reaction was then heated and monitored by GC-MS and TLC analysis. [b] GC yields (isolated yields in parenthesis) based on **1a**. [c] The reactions used 4 mmol **1a** and 0.5 mL dry toluene (dried over CaH_2 by heating, redistilled under vacuum, and then collected and stored in a sealed Schlenk flask under nitrogen). [d] Using 10 mol% dry $PhCH_2Br$ (dried over $CaCl_2$ by heating, redistilled under vacuum, and then collected and stored in a sealed Schlenk flask under nitrogen). [e] HBr (33 wt% in acetic acid) was used.



DBU：1,8-Diazabicyclo[5,4,0]-undec-7-ene

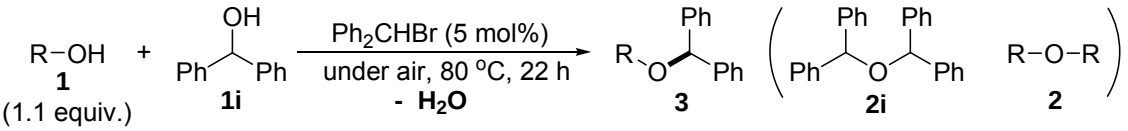
Table S2. Organohalide-Catalyzed O-Alkylative Homo-Etherification of Alcohols for Symmetrical Dialkyl Ether Synthesis.[a]

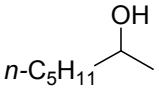
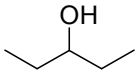
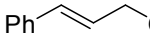


run	ROH (**1**)	organohalide RX	*T*, *t*	**2**: yield%[b]
1	$PhCH_2OH$ (**1a**)	$PhCH_2Br$	120 °C, 24 h	**2a**: >99 (97)
2	4-$MeC_6H_4CH_2OH$ (**1b**)	4-$MeC_6H_4CH_2Br$	120 °C, 24 h	**2b**: >99 (96)
3	4-$FC_6H_4CH_2OH$ (**1c**)	4-$FC_6H_4CH_2Br$	120 °C, 24 h	**2c**: >99 (88)
4	*n*-$C_5H_{11}OH$ (**1d**)	*n*-$C_5H_{11}I$	150 °C, 48 h	**2d**: 80 (65)
5	*n*-$C_6H_{13}OH$ (**1e**)	*n*-$C_6H_{13}I$	150 °C, 48 h	**2e**: 85 (60)
6	*n*-$C_7H_{15}OH$ (**1f**)	*n*-$C_7H_{15}Br$	150 °C, 30 h	**2f**: 45
7		*n*-$C_7H_{15}I$	150 °C, 30 h	**2f**: 85 (63)
8	*n*-$C_8H_{17}OH$ (**1g**)	*n*-$C_8H_{17}Br$	150 °C, 30 h	**2g**: 20
9		*n*-$C_8H_{17}I$	150 °C, 30 h	**2g**: 73 (64)
10[c]	 (**1h**)		60 °C, 16 h	**2h**: 75 (58)
16[d]	 (**1i**)		30 °C, 13 h	**2i**: 6
17[d]			60 °C, 13 h	**2i**: 69
18			80 °C, 13 h	**2i**: >99 (98)
19	 (**1i**)		80 °C, 13 h	**2i**: >99 (94)
11	 (**1j**)		30 °C, 24 h	**2j**: 8
12			90 °C, 24 h	**2j**: 56
13			90 °C, 24 h	**2j**: >99 (89)
14	 (**1j**)		90 °C, 24 h	**2j**: 80 (71)
15	 (**1k**)		150 °C, 40 h	**2k**: 26 (20)
20	 (**1l**)		150 °C, 40 h	NR[e]
21	 (**1m**)		150 °C, 40 h	NR[e]

[a] See Table S1 for similar conditions. [b] GC yields (isolated yields in parenthesis) based on **1**. [c] Unidentified byproducts were observed. [d] Dioxane (0.5 mL) was added to dissolve the solid alcohol. [e] No reaction.

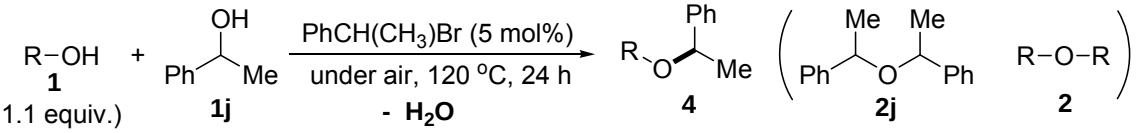
Table S3. Diphenylmethyl Bromide-Catalyzed O-Alkylative Cross-Etherification of Alcohols with Diphenylmethanol for Unsymmetrical Dialkyl Ether Synthesis.[a]

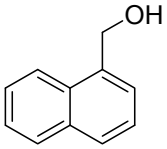
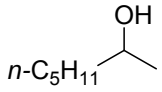
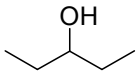


run	ROH	conditions[a]	**3** : **2i** : **2**[b]	**3**: yield%[c]
1	$PhCH_2OH$	80 °C, 22 h	96:4:0	**3a**: 96 (90)
2		100 °C, 22 h	94:6:0	**3a**: 94 (86)
3		Ph_2CHCl (5 mol%) 80 °C, 22 h	81:5:0[d]	**3a**: 81 (75)
4		$PhCH_2Br$ (5 mol%) 80 °C, 22 h	93:6:1	**3a**: 93 (84)
5	4-$MeC_6H_4CH_2OH$	80 °C, 22 h	95:5:0	**3b**: 95 (90)
6	4-$FC_6H_4CH_2OH$	80 °C, 22 h	94:6:0	**3c**: 94 (90)
7	4-$ClC_6H_4CH_2OH$	80 °C, 22 h	95:5:0	**3d**: 95 (92)
8	4-$BrC_6H_4CH_2OH$	80 °C, 22 h	95:5:0	**3e**: 95 (91)
9	4-$NO_2C_6H_4CH_2OH$	80 °C, 22 h	96:4:0	**3f**: 96 (94)
10	CH_3CH_2OH	73 °C, 22 h	95:5:0	**3g**: 95 (94)
11	*n*-C_4H_9OH	80 °C, 22 h	96:4:0	**3h**: 96 (93)
12	*n*-$C_5H_{11}OH$	80 °C, 22 h	97:3:0	**3i**: 97 (92)
13	*n*-$C_6H_{13}OH$	80 °C, 22 h	96:4:0	**3j**: 96 (94)
14	*n*-$C_7H_{15}OH$	80 °C, 22 h	93:7:0	**3k**: 93 (92)
15	*n*-$C_8H_{17}OH$	80 °C, 22 h	93:7:0	**3l**: 93 (91)
16	$Ph(CH_2)_2OH$	80 °C, 22 h	97:3:0	**3m**: 97 (96)
17	$Ph(CH_2)_3OH$	80 °C, 22 h	96:4:0	**3n**: 96 (94)
18	 (3 equiv.)	80 °C, 22 h	90:10:0	**3o**: 90 (80)
19		80 °C, 22 h (1 equiv. **1k**)	81:19:0	**3p**: 81
21		80 °C, 22 h (3 equiv. **1k**)	95:5:0	**3p**: 95 (92)
22		80 °C, 22 h (5 equiv. **1k**)	97:3:0	**3p**: 97
23	 (3 equiv.)	80 °C, 22 h	97:3:0	**3q**: 97 (91)
24		80 °C, 22 h	75:25:0	**3r**: 75 (64)

[a] Unless otherwise noted, the neat mixture of ROH (5.5 mmol, 1.1 equiv.), Ph_2CHOH **1i** (5 mmol), and Ph_2CHBr (5 mol%) was directly sealed under air in a Schlenk tube (20 mL). The reaction was then heated and monitored by GC-MS and TLC analysis. [b] Product ratios determined by GC-MS analysis. [c] GC yields (isolated yields in parenthesis) based on the less-usesd alcohols. [d] Unidentified byproducts were observed.

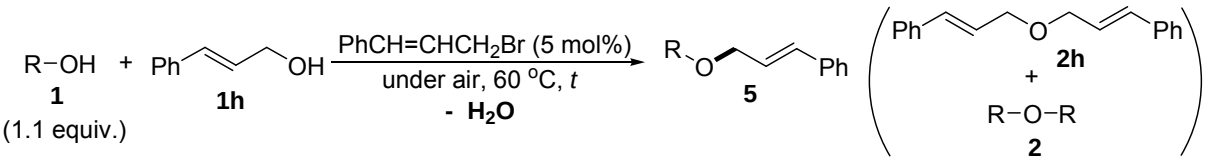
Table S4. 1-Phenylethyl Bromide-Catalyzed O-Alkylative Cross-Etherification of Alcohols with 1-Phenylethanol for Unsymmetrical Dialkyl Ether Synthesis.[a]



run	ROH	conditions[a]	**4** : **2j** : **2**[b]	**4**: yield%[c]
1	$PhCH_2OH$	60 °C, 24 h	66:34:0	**4a**: 66 (50)
2		90 °C, 24 h	71:29:0	**4a**: 71 (64)
3		120 °C, 24 h	94:6:0	**4a**: 94 (81)
4	4-$MeC_6H_4CH_2OH$	120 °C, 24 h	70:19:11	**4b**: 70 (66)
5	4-$FC_6H_4CH_2OH$	120 °C, 24 h	82:18:0	**4c**: 82 (66)
6	4-$ClC_6H_4CH_2OH$	120 °C, 24 h	82:18:0	**4d**: 82 (66)
7	4-$BrC_6H_4CH_2OH$	120 °C, 24 h	87:13:0	**4e**: 87 (66)
8		120 °C, 24 h	81:19:0	**4f**: 81 (67)
9	C_2H_5OH	120 °C, 24 h	87:0:0[d]	**4g**: 87 (76)
10	*n*-$C_5H_{11}OH$	120 °C, 24 h	85:15:0	**4h**: 85 (83)
11	*n*-$C_6H_{13}OH$	120 °C, 24 h	92:8:0	**4i**: 92 (86)
12	*n*-$C_7H_{15}OH$	120 °C, 24 h	>99:0:0	**4j**: >99 (82)
13	$Ph(CH_2)_2OH$	120 °C, 24 h	>99:0:0	**4k**: >99 (80)
14	$Ph(CH_2)_3OH$	120 °C, 24 h	95:5:0	**4l**: 95 (75)
15	 (3 equiv.)	120 °C, 38 h	82:0:0[d]	**4m**: 82 (66)
16	 (3 equiv.)	120 °C, 38 h	71:8:0[d]	**4n**: 71 (52)

[a] Unless otherwise noted, the neat mixture of ROH (5.5 mmol, 1.1 equiv.), $PhCH(CH_3)OH$ **2j** (5 mmol), and $PhCH(CH_3)Br$ (5 mol%) was directly sealed under air in a Schlenk tube (20 mL). The reaction was then heated and monitored by GC-MS and TLC analysis. [b] Product ratios determined by GC-MS analysis. [c] GC yields (isolated yields in parenthesis) based on the less alcohols. [d] Unidentified byproducts were observed.

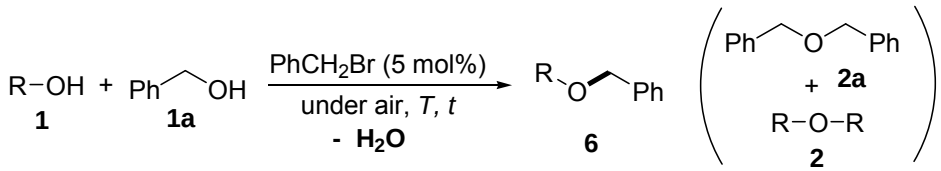
Table S5. Cinnamyl Bromide-Catalyzed O-Alkylative Cross-Etherification of Alcohols with Cinnamyl Alcohol for Unsymmetrical Dialkyl Ether Synthesis.[a]



run	ROH	*T, t*	**5** : **2h** : **2**[b]	ether: yield%[c]
1	$PhCH_2OH$	60 °C, 24 h	69:14:0[d]	**5a**: 69
2		60 °C, 46 h	82:18:0	**5a**: 82 (75)
3	*n*-$C_5H_{11}OH$	60 °C, 24 h	65:8:0[d,e]	**5b**: 65
4		60 °C, 46 h	72:10:0[e]	**5b**: 72 (56)

[a] The neat mixture of ROH **1** (5.5 mmol, 1.1 equiv.), $PhCH=CHCH_2OH$ **1h** (5 mmol), and $PhCH=CHCH_2Br$ (5 mol%) was directly sealed under air in a Schlenk tube (20 mL). The reaction was then heated and monitored by GC-MS and TLC analysis. [b] Product ratios determined by GC-MS analysis. [c] GC yields (isolated yields in parenthesis) based on **1h**. [d] Reactions incomplete. [e] Unidentified byproducts were observed.

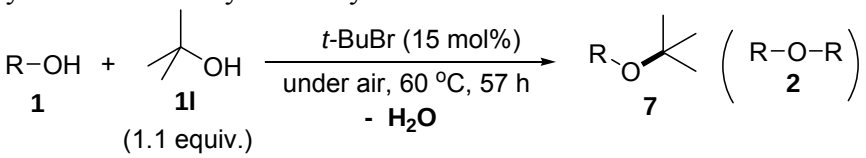
Table S6. Benzyl Bromide-Catalyzed O-Alkylative Cross-Etherification of Alcohols with Benzyl Alcohol for Unsymmetrical Dialkyl Ether Synthesis.[a]



run	ROH	*T, t*	**6** : **2a** : **2**[b]	ether: yield%[c]
1	4-$MeOC_6H_4CH_2OH$ (1.2 equiv.)	120 °C, 32 h	59:12:29	**6a**: 59 (50)
2	*n*-$C_7H_{15}OH$ (3 equiv.)	140 °C, 24 h	76:13:11	**6b**: 47 (35)[d]

[a] The neat mixture of ROH **1**, $PhCH_2OH$ **1a** (5 mmol), and $PhCH_2Br$ (5 mol%) was directly sealed under air in a Schlenk tube (20 mL). The reaction was then heated and monitored by GC-MS and TLC analysis. [b] Product ratios determined by GC-MS analysis. [c] GC yields (isolated yields in parenthesis) based on **1a**. [d] The reaction was incomplete.

Table S7. *t*-Butyl Bromide-Catalyzed O-Alkylative Cross-Etherification of Alcohols with *t*-Butyl Alcohol for Unsymmetrical Dialkyl Ether Synthesis.[a]



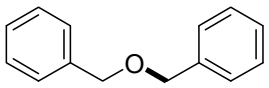
run	ROH	*T, t*	**7** : **2**[b]	**7**: yield%[c]
1	$PhCH_2OH$	60 °C, 32 h	100:0	**7a**: 55[d]
2		60 °C, 57 h	100:0	**7a**: 64 (57)[d]
3	*n*-$C_7H_{15}OH$	60 °C, 32 h	100:0	**7b**: 77[d]
4		60 °C, 57 h	100:0	**7b**: 82 (63)[d]

[a] The neat mixture of ROH **1** (5 mmol), *t*-BuOH (5.5 mmol, 1.1 equiv.), and *t*-BuBr (15 mol%) was directly sealed under air in a Schlenk tube (20 mL). The reaction was then heated and monitored by GC-MS and TLC analysis. [b] Product ratios determined by GC-MS analysis. [c] GC yields (isolated yields in parenthesis) based on **1**. [d] Reactions incomplete.

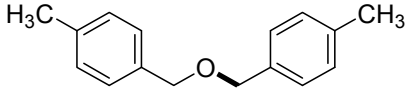
Experimental

General. Unless otherwise noted, alcohols, organohalides, and other reagents used in the work including (*S*)-PhCH(CH_3)OH ((*S*)-**1j**, 98% *ee*) were all purchased and used without further purification. Except the large scale reaction, all the reactions were directly sealed under air in a 20 mL Schlenk tube and then heated and monitored by TLC and/or GC-MS. Dry $PhCH_2Br$ was obtained by a standard procedure: firstly dried over $CaCl_2$ by heating, and then redistilled under vacuum and collected and stored in a sealed Schlenk flask under nitrogen. Dry toluene was obtained similarly: firstly dried over CaH_2 by heating, and then redistilled under vacuum and collected and stored in a sealed Schlenk flask under nitrogen. The products were purified by column chromatography on silica gel using petroleum ether and ethyl acetate as the eluent. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III AV500 instrument (500 MHz for ^1H and 125 MHz for ^{13}C NMR spectroscopy) or a Bruker Avance-1B 300 instrument (300 MHz for ^1H NMR spectroscopy) by using $CDCl_3$ as the solvent. Chemical shift values for ^1H and ^{13}C NMR were referred to internal Me_4Si (0 ppm). Mass spectra were measured on a Shimadzu GCMS-QP2010 Plus or a Shimadzu GCMS-QP2010 Ultra spectrometer (EI). HRMS (ESI) analysis was measured on a Bruker microOTOF-Q II instrument. The optical rotatory power of diasteoromers of product **2j** was recorded with an Optical Activity LTD polAAr 3005 automatic Polarimeter.

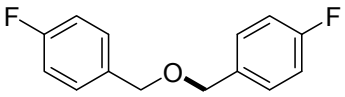
Typical Procedure for Organohalides-Catalyzed *O*-Alkylative Homo-Etherification Reaction of Alcohols for the Synthesis of Symmetrical Aliphatic Ethers. The mixture of benzyl alcohol **1a** (1.04 mL, 10 mmol) and benzyl bromide (0.12 mL, 1.0 mmol, 10 mol%) was sealed under air in a 20 mL Schlenk tube, stirred at 120 ^oC for 24 h, and then monitored by TLC and/or GC-MS. After completion of the reaction, the mixture was directly purified, without any workup, through a silica gel column using ethyl acetate and petroleum ether as the eluent, giving dibenzyl ether **2a** in 97% isolated yield.



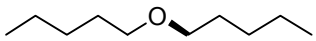
Dibenzyl ether (2a). Colorless liquid. ^1H NMR (500 MHz, $CDCl_3$): δ 7.39-7.35 (m, 8H), 7.32-7.28 (m, 2H), 4.57 (s, 4H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 138.3, 128.4, 127.8, 127.6, 72.1. MS (EI): *m/z* (%) 198 (0.02, M^+), 107 (14), 92 (100), 91 (81), 79 (15), 77 (13), 65 (17). This compound was known: Jereb, M.; Vražič, D.; Zupan, M. *Tetrahedron Lett*. **2009**, *50*, 2347.



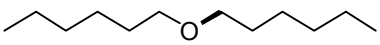
Bis(*p*-methylphenylmethyl) ether (2b). Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 (d, J = 8.0 Hz, 4H), 7.16 (d, J = 8.0 Hz, 4H), 4.50 (s, 4H), 2.35 (s, 6H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 137.2, 135.3, 129.0, 127.9, 71.8, 21.1. MS (EI): *m/z* (%) 226 (0.22, M^+), 121 (11), 106 (100), 105 (59), 91 (49), 79 (13), 77 (18). This compound was known: Zhu, Z. L.; Espenson, J. H. *J. Org. Chem*. **1996**, *61*, 324.



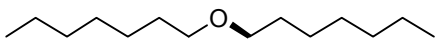
Bis(*p*-fluorophenylmethyl) ether (2c). Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34-7.31 (m, 4H), 7.06-7.03 (m, 4H), 4.51 (s, 4H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 162.4 (d, $J_{C\text{-}F}$ = 245.0 Hz), 133.8 (d, $J_{C\text{-}F}$ = 3.1 Hz), 129.5 (d, $J_{C\text{-}F}$ = 8.2 Hz), 115.3 (d, $J_{C\text{-}F}$ = 21.3 Hz), 71.4. MS (EI): *m/z* (%) 234 (0.37, M^+), 138 (7), 125 (19), 110 (76), 109 (100), 97 (15), 83 (16). This compound was known: Bach, P.; Albright, A.; Laali, K. K. *Eur. J. Org. Chem.* **2009**, 1961.



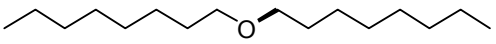
Dipentyl ether (2d). Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.39 (t, J = 6.8 Hz, 4H), 1.60-1.55 (m, 4H), 1.33-1.31 (m, 8H), 0.90 (t, J = 7.0 Hz, 6H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 71.0, 29.5, 28.4, 22.6, 14.1. MS (EI): *m/z* (%) 158 (1.52, M^+), 129 (3), 115 (1), 101 (6), 71 (100), 70 (46), 69 (22), 55 (12). This compound was known: Zhang, Y.-J.; Dayoub, W.; Chen, G.-R. Lemaire, M. *Tetrahedron*, **2012**, *68*, 7400.



Dihexyl ether (2e). Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.39 (t, J = 6.8 Hz, 4H), 1.59-1.54 (m, 4H), 1.34-1.29 (m, 12H), 0.89 (t, J = 7.0 Hz, 6H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 71.0, 31.7, 29.8, 25.9, 22.6, 14.1. MS (EI): *m/z* (%) 186 (0.13, M^+), 115 (2), 103 (5), 85 (100), 69 (16), 57 (23), 56 (41). This compound was known: Makowski, P.; Rothe, R.; Thomas, A.; Niederberger, M.; Goettmann, F. *Green Chem*. **2009**, *11*, 34.

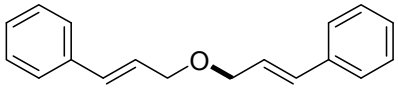


Diheptyl ether (2f). Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.39 (t, J = 6.8 Hz, 4H), 1.59-1.54 (m, 4H), 1.30-1.28 (m, 16H), 0.88 (t, J = 7.0 Hz, 6H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 71.0, 31.8, 29.8, 29.2, 26.2, 22.6, 14.1. MS (EI): *m/z* (%) 214 (0.07, M^+), 99 (13), 98 (13), 97 (15), 70 (29), 57 (100), 56 (15), 55 (14). This compound was known: Zolfigol, M. A.; Mohammadpoor-Baltork, I.; Mirjalili, B. F.; Bamoniri, A. *Synlett,* **2003**, *(12),* 1877.

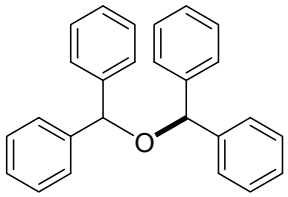


Dioctyl ether (2g). Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.39 (t, J = 6.8 Hz, 4H), 1.58-1.54 (m, 4H), 1.30-1.26 (m, 20H), 0.88 (t, J = 7.0 Hz, 6H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ

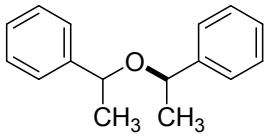
71.0, 31.8, 29.8, 29.5, 29.3, 26.2, 22.7, 14.1. MS (EI): *m/z* (%) 242 (0.05, M^+), 112 (17), 84 (34), 71 (100), 69 (36), 57 (94). This compound was known: Zolfigol, M. A.; Mohammadpoor-Baltork, I.; Habibi, D.; Mirjalili, B. F.; Bamoniri, A. *Tetrahedron Lett*. **2003**, *44*, 8165.



Dicinnamyl ether (2h). Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, J = 7.5 Hz, 4H), 7.33-7.29 (m, 4H), 7.25-7.22 (m, 2H), 6.63 (d, J = 16.0 Hz, 2H), 6.32 (dt, J = 6.0 Hz, J = 16.0 Hz, 2H), 4.20 (dd, J = 1.5 Hz, J = 6.0 Hz, 4H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 136.7, 132.5, 128.5, 127.6, 126.5, 126.0, 70.7. MS (EI): *m/z* (%) 250 (0.01, M^+), 155 (13), 154 (100), 153 (39), 152 (27), 76 (10). This compound was known: Kayaki, Y.; Koda, T.; Ikariya, T. *J. Org. Chem*. **2004**, *69*, 2595.

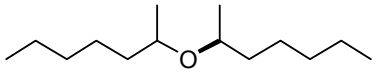


Bis(diphenylmethyl) ether (2i). White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (d, J = 7.5 Hz 8H), 7.31 (t, J = 7.5 Hz, 8H), 7.25 (t, J = 7.0 Hz, 4H), 5.40 (s, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 142.2, 128.4, 127.4, 127.2, 80.0. MS (EI): *m/z* (%) 350 (0.38, M^+), 207 (15), 183 (64), 168 (69), 165 (42), 152 (22), 106 (36), 105 (76), 91 (25), 77 (22). This compound was known: Le Bras, J.; Muzart, J. *Tetrahedron,* **2007**, *63*, 7942.



(*RR/SS/RS/SR* ~1/1/1/1 mixtures)

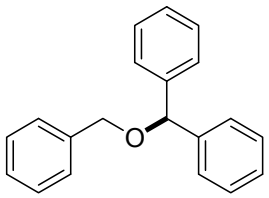
Bis(1-phenylethyl) ether (2j). Colorless liquid. The NMR spectra are of a 50/50 mixture of dl and meso isomers. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39-7.29 (m, 10+10H), 4.55 (q, J = 6.5 Hz, 1+1H), 4.26 (q, J = 6.5 Hz, 1+1H), 1.48 (d, J = 6.5 Hz, 3+3H), 1.40 (d, J = 6.5 Hz, 3+3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 144.2 (or 144.1), 128.4 (or 128.2), 127.4 (or 127.1), 126.3 (or 126.2), 74.6 (or 74.4), 24.7 (or 23.0). MS (EI): *m/z* (%) 226 (0.01, M^+), 121 (23), 106 (28), 105 (100), 91 (7), 79 (10), 77 (12). The above characterizations of **2j** are in agreement with the literature data: (a) Yu, J.-J.; Wang, L.-M.; Guo, F.-L.; Liu, J.-Q.; Liu, Y.; Jiao, N. *Synth. Commun.* **2011**, *41*, 1609. (b) Noji, M.; Ohno, T.; Fuji , K.; Futaba, N.; Tajima, H.; Ishii, K. *J. Org. Chem.* **2003**, *68*, 9340.



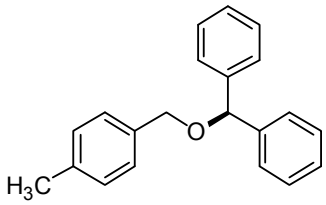
(RR/SS/RS/SR ~1/1/1/1 mixtures)

Bis(2-heptyl) ether (2k). Colorless liquid. The NMR spectra are of a 50/50 mixture of dl and meso isomers. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.44-3.37 (m, 2+2H), 1.50-1.46 (m, 2+2H), 1.39-1.28 (m, 14+14H), 1.12-1.09 (m, 6+6H), 0.90-0.87 (m, 6+6H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 73.4 (or 73.0), 37.5 (or 37.2), 32.1 (or 32.0), 25.5 (or 25.4), 22.7, 21.1 (or 20.5), 14.09 (or 14.07). MS (EI): *m/z* (%) 214 (0.11, M^+), 143 (31), 125 (11), 99 (58), 57 (100), 55 (12). This compound was known: Adams, J. M.; Ballantine, J. A.; Graham, S. H.; Laub, R. J.; Purnell, J. H.; Reid, Paul, I.; Shaman, W. Y. M.; Thomas, J. M. *Angew. Chem.* **1978**, *90*, 290.

Typical Procedure for Ph_2CHBr-Catalyzed *O*-Alkylative Cross-Etherification Reaction of Benzhydrol with Alcohols for Synthesis of Unsymmetrical Aliphatic Ethers. The mixture of benzhydrol **1i** (0.921 g, 5 mmol), benzyl alcohol **1a** (0.57 mL, 5.5 mmol, 1.1 equiv.) and diphenylmethyl bromide (0.0618 g, 0.25 mmol, 5 mol%) was sealed under air in a 20 mL Schlenk tube, stirred at 80 ^{o}C for 22 h, and then monitored by TLC and/or GC-MS. After completion of the reaction, the mixture was directly purified, without any workup, through a silica gel column using ethyl acetate and petroleum ether as the eluent, giving benzyl diphenylmethyl ether **3a** in 90% isolated yield.

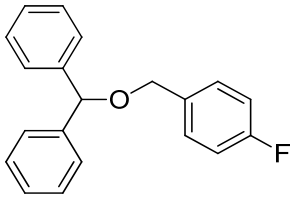


Benzyl diphenylmethyl ether (3a). Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.17 (m, 15H), 5.43 (s, 1H), 4.53 (s, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 142.2, 138.5, 128.5, 128.4, 127.8, 127.6, 127.5, 127.2, 82.6, 70.6. MS (EI): *m/z* (%) 274 (0.02, M^+), 183 (100), 168 (49), 167 (83), 165 (38), 152 (24), 105 (64), 92 (31), 91 (95), 77 (27). This compound was known: Stanescu, M. A.; Varma, R. S. *Tetrahedron Lett.* **2002**, *43*, 7307.

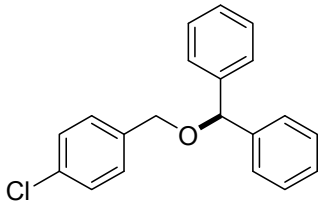


(*p*-Methylphenyl)methyl diphenylmethyl ether (3b). White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38-7.36 (m, 4H), 7.33-7.30 (m, 4H), 7.26-7.21 (m, 4H), 7.15 (d, J = 7.5 Hz, 2H), 5.43 (s, 1H), 4.50 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 142.2, 137.2, 135.3, 129.0, 128.3, 127.8, 127.4, 127.1, 82.2, 70.3, 21.2. MS (EI): *m/z* (%) 288 (0.20, M^+), 183 (63), 168 (68), 167 (100), 165

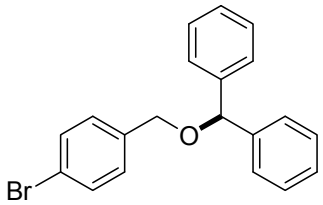
(42), 152 (22), 106 (37), 105 (76), 91 (25). HRMS Calcd for $C_{21}H_{20}NaO$ (M+Na): 311.1406; found: 311.1414.



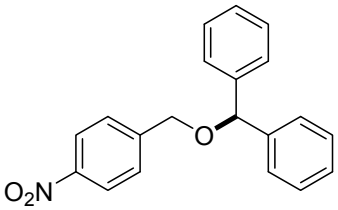
(*p*-Fluorophenyl)methyl diphenylmethyl ether (3c). Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39-7.33 (m, 10H), 7.29-7.26 (m, 2H), 7.06-7.02 (m, 2H), 5.44 (s, 1H), 4.51 (s, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 162.3 (d, $J_{C\text{-}F}$ = 244.8 Hz), 142.0, 134.1 (d, $J_{C\text{-}F}$ = 3.0 Hz), 129.4 (d, $J_{C\text{-}F}$ = 8.0 Hz), 128.4, 127.5, 127.1, 115.2 (d, $J_{C\text{-}F}$ = 21.3 Hz), 82.5, 69.8. MS (EI): *m/z* (%) 292 (0.15, M^+), 183 (54), 168 (93), 167 (100), 165 (44), 152 (24), 109 (69), 105 (49), 77 (20). This compound was known: Stanescu, M. A.; Varma, R. S. *Tetrahedron Lett*. **2002**, *43*, 7307.



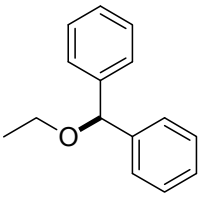
(*p*-Chlorophenyl)methyl diphenylmethyl ether (3d). White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.23 (m, 14H), 5.41 (s, 1H), 4.48 (s, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 141.9, 136.9, 133.2, 129.0, 128.5, 128.4, 127.5, 127.0, 82.6, 69.7. MS (EI): *m/z* (%) 309 (M+1), 308 (0.03, M^+), 183 (62), 168 (86), 167 (100), 165 (40), 152 (21), 125 (40), 105 (42), 89 (10), 77 (19). This compound was known: Stanescu, M. A.; Varma, R. S. *Tetrahedron Lett*. **2002**, *43*, 7307.



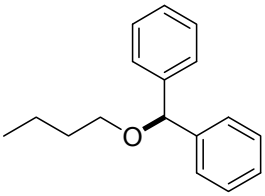
(*p*-Bromophenyl)methyl diphenylmethyl ether (3e). White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 (d, J = 8.5 Hz, 2H), 7.38-7.33 (m, 8H), 7.29-7.24 (m, 4H), 5.43 (s, 1H), 4.50 (s, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 141.9, 137.4, 131.5, 129.3, 128.4, 127.6, 127.0, 121.4, 82.7, 69.8. MS (EI): *m/z* (%) 353 (M+1), 352 (0.05, M^+), 184 (40), 183 (15), 165 (11), 105 (100), 79 (26), 78 (34), 77 (50), 51 (15). This compound was known: Gharib, A.; Pesyan, N. N.; Jahangir, M.; Roshani, M.; Scheeren, J. W. *Bulg. Chem. Commun*. **2012**, *44*, 11.



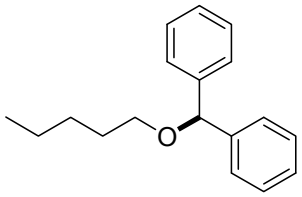
(*p*-Nitrophenyl)methyl diphenylmethyl ether (3f). White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (d, J = 9.0 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H), 7.40-7.33 (m, 8H), 7.29-7.23 (m, 2H), 5.47 (s, 1H), 4.62 (s, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 147.3, 146.0, 141.5, 128.5, 127.73, 127.67, 126.9, 123.6, 83.4, 69.4. MS (EI): *m/z* (%) 319 (0.46, M^+), 206 (12), 183 (71), 168 (61), 167 (100), 165 (47), 152 (26), 136 (19), 106 (37), 104 (74). This compound was known: Cast, J.; Stevens, T. S.; Holmes, J. *J. Chem. Soc*. **1960**, 3521.



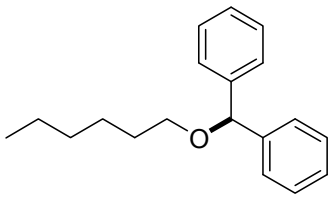
Ethyl diphenylmethyl ether (3g). Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.30 (m, 8H), 7.24-7.22 (m, 2H), 5.36 (s, 1H), 3.52 (q, J = 7.0 Hz, 2H), 1.27 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 142.5, 128.3, 127.3, 126.9, 83.5, 64.5, 15.3. MS (EI): *m/z* (%) 212 (36.26, M^+), 183 (13), 168 (54), 167 (100), 165 (46), 152 (20), 135 (41), 105 (43), 77 (26). This compound was known: Bikard, Y.; Weibel, J.-M.; Sirlin, C.; Dupuis, L.; Loeffler, J.-P.; Pale, P. *Tetrahedron Lett*. **2007**, *48*, 8895.



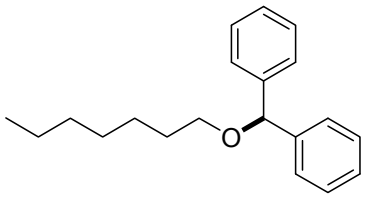
***n*-Butyl diphenylmethyl ether (3h).** Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.30 (m, 8H), 7.26-7.23 (m, 2H), 5.34 (s, 1H), 3.46 (t, J = 6.5 Hz, 2H), 1.67-1.61 (m, 2H), 1.47-1.40 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 142.7, 128.3, 127.3, 126.9, 83.6, 68.9, 32.0, 19.5, 13.9. MS (EI): *m/z* (%) 240 (10.53, M^+), 168 (51), 167 (100), 165 (36), 163 (15), 152 (19), 107 (35), 105 (27), 77 (14). This compound was known: Onishi, Y.; Nishimoto, Y.; Yasuda, M.; Baba, A. *Chem. Lett*. **2011**, *40*, 1223.



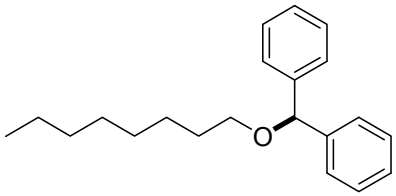
***n*-Pentyl diphenylmethyl ether (3i).** Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.30 (m, 8H), 7.26-7.22 (m, 2H), 5.34 (s, 1H), 3.45 (t, J = 6.5 Hz, 2H), 1.69-1.63 (m, 2H), 1.41-1.27 (m, 4H), 0.90 (t, J = 7.3 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 142.7, 128.3, 127.3, 126.9, 83.6, 69.3, 29.6, 28.4, 22.5, 14.0. MS (EI): *m/z* (%) 254 (5.62, M^+), 177 (11), 168 (50), 167 (100), 165 (32), 152 (18), 107 (34), 105 (26), 77 (11). This compound was known: Stanescu, M. A.; Varma, R. S. *Tetrahedron. Lett*. **2002**, *43*, 7307.



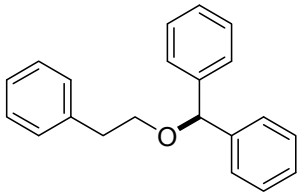
***n*-Hexyl diphenylmethyl ether (3j).** Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.30 (m, 8H), 7.26-7.22 (m, 2H), 5.34 (s, 1H), 3.45 (t, J = 6.5 Hz, 2H), 1.68-1.62 (m, 2H), 1.42-1.36 (m, 2H), 1.34-1.27 (m, 4H), 0.89 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 142.7, 128.3, 127.3, 127.0, 83.6, 69.3, 31.7, 29.8, 25.9, 22.6, 14.0. MS (EI): *m/z* (%) 268 (4.42, M^+), 191 (10), 168 (45), 167 (100), 165 (26), 152 (15), 107 (39), 105 (29), 77 (10). This compound was known: Dzhemilev, U. M.; Kutepov, B. I.; Grigor'eva, N. G.; Talipova, R. R.; Bubennov, S. V.; Yamali, E. I. *RU2404957* (in Russ.) C2, **2010**, 20101127.



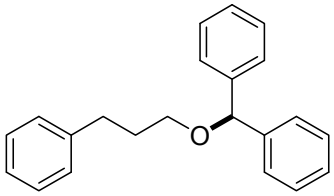
***n*-Heptyl diphenylmethyl ether (3k).** Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.30 (m, 8H), 7.26-7.22 (m, 2H), 5.34 (s, 1H), 3.45 (t, J = 6.5 Hz, 2H), 1.68-1.62 (m, 2H), 1.40-1.35 (m, 2H), 1.32-1.25 (m, 6H), 0.88 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 142.7, 128.3, 127.3, 127.0, 83.6, 69.3, 31.8, 29.9, 29.1, 26.2, 22.6, 14.1. MS (EI): *m/z* (%) 282 (2.39, M^+), 168 (45), 167 (100), 165 (25), 152 (16), 115 (12), 107 (30), 105 (22), 57 (7). This compound was known: Thiemann, T. *Lett. Org. Chem*. **2009**, *6*, 515.



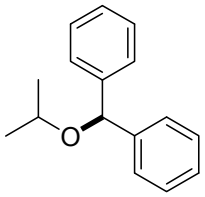
***n*-Octyl diphenylmethyl ether (3l).** Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.30 (m, 8H), 7.26-7.22 (m, 2H), 5.33 (s, 1H), 3.44 (t, J = 6.5 Hz, 2H), 1.67-1.61 (m, 2H), 1.37-1.25 (m, 10H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 142.7, 128.3, 127.3, 126.9, 83.6, 69.2, 31.8, 29.9, 29.4, 29.3, 26.2, 22.6, 14.1. MS (EI): *m/z* (%) 296 (1.77, M^+), 219 (6), 183 (5), 168 (45), 167 (100), 165 (22), 152 (12), 107 (21), 105 (16). This compound was known: Paredes, R.; Perez, R. L. *Tetrahedron Lett*. **1998**, *39*, 2037.



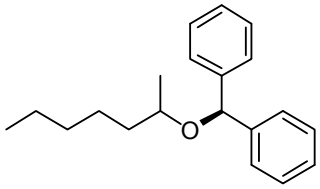
2-Phenylethyl diphenylmethyl ether (3m). White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30-7.22 (m, 15H), 5.36 (s, 1H), 3.67 (t, J = 7.0 Hz, 2H), 2.98 (t, J = 7.3 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 142.3, 139.1, 129.0, 128.3, 128.2, 127.3, 126.9, 126.1, 83.7, 70.0, 36.5. MS (EI): *m/z* (%) 288 (10.34, M^+), 183 (18), 168 (16), 167 (100), 165 (22), 105 (12), 77 (7). This compound was known: Gharib, A.; Pesyan, N. N.; Jahangir, M.; Roshani, M.; Scheeren, J. W. *Bulg. Chem. Commun*. **2012**, *44*, 11.



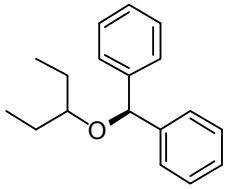
3-Phenylpropyl diphenylmethyl ether (3n). White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.31 (m, 8H), 7.27-7.25 (m, 4H), 7.19-7.17 (m, 3H), 5.34 (s, 1H), 3.49 (t, J = 6.3 Hz, 2H), 2.76 (t, J = 7.8 Hz, 2H), 2.00-1.96 (m, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 142.5, 142.0, 128.5, 128.33, 128.27, 127.3, 127.0, 125.7, 83.6, 68.3, 32.5, 31.5. MS (EI): *m/z* (%) 302 (2.07, M^+), 183 (14), 168 (21), 167 (100), 165 (16), 105 (11), 91 (23). This compound was known: Gharib, A.; Pesyan, N. N.; Jahangir, M.; Roshani, M.; Scheeren, J. W. *Bulg. Chem. Commun*. **2012**, *44*, 11.



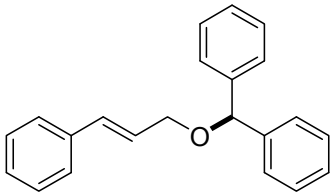
Isopropyl diphenylmethyl ether (3o). Colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.29 (m, 10H), 5.50 (s, 1H), 3.70-3.63 (m, 1H), 1.22 (d, J = 6.5 Hz, 6H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 142.5, 127.8, 126.7, 126.6, 80.0, 68.6, 21.8. MS (EI): *m/z* (%) 226 (8.14, M^+), 183 (10), 168 (86), 167 (100), 152 (18), 107 (61), 79 (15), 77 (19). This compound was known: Venkateswara Rao, K. T.; Rao, P. S. N.; Sai Prasad, P. S.; Lingaiah, N. *Catalysis Commun*. **2009**, *10*, 1394-1397.



2-Heptyl diphenylmethyl ether (3p). Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30-7.13 (m, 10H), 5.41 (s, 1H), 3.47-3.37 (m, 1H), 1.62-1.53 (m, 1H), 1.42-1.14 (m, 7H), 1.10 (d, J = 6.0 Hz, 3H), 0.79 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 138.3, 127.8, 127.1, 126.9, 72.3, 70.1, 31.3, 29.3, 28.6, 25.7, 22.1, 13.5. MS (EI): *m/z* (%) 282 (0.30, M^+), 168 (29), 107 (11), 105 (9). HRMS Calcd for $C_{20}H_{26}NaO$ (M+Na): 305.1876; found: 305.1869.



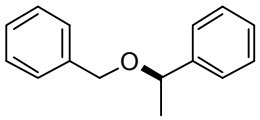
3-Pentyl diphenylmethyl ether (3q). Colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.22 (m, 10H), 5.47 (s, 1H), 3.31-3.27 (m, 1H), 1.59-1.53 (m, 4H), 0.86 (t, J = 7.5 Hz, 6H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 143.3, 128.2, 127.3, 127.1, 80.5, 78.7, 25.6, 9.4. MS (EI): *m/z* (%) 254 (0.43, M^+), 168 (25), 167 (100), 152 (9), 107 (6), 77 (3). This compound was known: Stanescu, M. A.; Varma, R. S. *Tetrahedron Lett.* **2002**, *43*, 7307-7309.



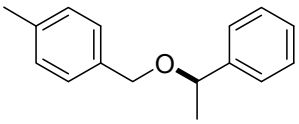
Cinnamyl diphenylmethyl ether (3r). Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40-7.20 (m, 15H), 6.60 (d, J = 16.0 Hz, 1H), 6.35 (dt, J = 6.0 Hz, J = 16.0 Hz, 1H), 5.48 (s, 1H), 4.18 (dd, J = 1.5 Hz, J = 6.0 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 142.1, 136.7, 132.3, 128.5, 128.4, 127.6,

127.4, 127.0, 126.4, 126.1, 82.6, 69.3. MS (EI): *m/z* (%) 300 (0.06, M^+), 168 (18), 167 (100), 165 (24), 152 (16), 118 (36), 117 (15), 115 (12), 77 (10). This compound was known: Wagh, Y. S.; Sawant, D. N.; Tambade, P. J.; Dhake, K. P.; Bhanage, B. M. *Tetrahedron*, **2011**, *67*, 2414.

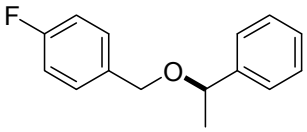
Typical Procedure for 1-Phenylethyl Bromide-Catalyzed *O*-Alkylative Cross-Etherification Reaction of 1-Phenyl ethanol with Alcohols for Synthesis of Unsymmetrical Aliphatic Ethers. The mixture of 1-phenyl ethanol **1j** (0.60 mL, 5 mmol), benzyl alcohol **1a** (0.57 mL, 5.5 mmol, 1.1 equiv.), and 1-phenylethyl bromide (0.034 mL, 0.25 mmol, 5 mol%) was sealed under air in a 20 mL Schlenk tube, stirred at 120 ^oC for 24 h, and then monitored by TLC and/or GC-MS. After completion of the reaction, the mixture was directly purified, without any workup, through a silica gel column using ethyl acetate and petroleum ether as the eluent, giving benzyl 1-phenylethyl ether **4a** in 81% isolated yield.



Benzyl 1-phenylethyl ether (4a). Colorless liquid. ^1H NMR (500 MHz, $CDCl_3$): δ 7.38-7.27 (m, 10H), 4.51 (q, J = 6.5 Hz, 1H), 4.46 (d, J = 11.5 Hz, 1H), 4.31 (d, J = 12.0 Hz, 1H), 1.49 (d, J = 6.5 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 143.7, 138.6, 128.5, 128.3, 127.7, 127.48, 127.45, 126.3, 77.2, 70.3, 24.2. MS (EI): *m/z* (%) 212 (0.01, M^+), 121 (14), 106 (51), 105 (35), 92 (19), 91 (100), 77 (12), 65 (7). This compound was known: Rahaim, R. J.; Maleczka, R. E. *Org. Lett*. **2011**, *13*, 584.

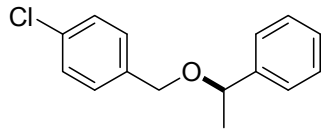


(*p*-Methylphenyl)methyl 1-phenylethyl ether (4b). Colorless liquid. ^1H NMR (500 MHz, $CDCl_3$): δ 7.40-7.36 (m, 4H), 7.32-7.28 (m, 1H), 7.21 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 4.49 (q, J = 6.5 Hz, 1H), 4.42 (d, J = 11.5 Hz, 1H), 4.25 (d, J = 12.0 Hz, 1H), 2.35 (s, 3H), 1.47 (d, J = 6.5 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 143.8, 137.1, 135.6, 129.0, 128.4, 127.8, 127.4, 126.3, 76.9, 70.1, 24.2, 21.1. MS (EI): *m/z* (%) 226 (0.08, M^+), 121 (36), 106 (53), 105 (100), 91 (28), 79 (12), 77 (16). HRMS Calcd for $C_{16}H_{18}NaO$ (M+Na): 249.1250; found: 249.1266.

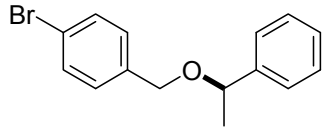


(*p*-Fluorophenyl)methyl 1-phenylethyl ether (4c). Colorless liquid. ^1H NMR (500 MHz, $CDCl_3$): δ 7.40-7.35 (m, 4H), 7.32-7.26 (m, 3H), 7.04-7.00 (m, 2H), 4.49 (q, J = 6.5 Hz, 1H), 4.40 (d, J = 11.5 Hz, 1H), 4.27 (d, J = 11.5 Hz, 1H), 1.49 (d, J = 6.5 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 162.3

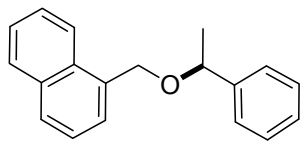
(d, $J_{C\text{-}F}$ = 244.5 Hz), 143.6, 134.4 (d, $J_{C\text{-}F}$ = 3.1 Hz), 129.4 (d, $J_{C\text{-}F}$ = 8.0 Hz), 128.5, 127.6, 126.3, 115.2 (d, $J_{C\text{-}F}$ = 21.3 Hz), 77.3, 69.6, 24.1. MS (EI): *m/z* (%) 230 (0.03, M^+), 110 (12), 109 (100), 106 (63), 105 (35), 91 (16), 77 (12). HRMS Calcd for $C_{15}H_{15}FNaO$ (M+Na): 253.0999; found: 253.1003 .



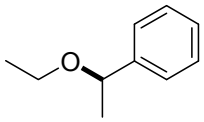
(*p*-Chlorophenyl)methyl 1-phenylethyl ether (4d). Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39-7.34 (m, 4H), 7.32-7.29 (m, 3H), 7.26-7.24 (m, 2H), 4.48 (q, *J* = 6.5 Hz, 1H), 4.40 (d, *J* = 12.0 Hz, 1H), 4.27 (d, *J* = 12.0 Hz, 1H), 1.49 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 143.4, 137.1, 133.2, 129.0, 128.53, 128.48, 127.6, 126.3, 77.4, 69.5, 24.1. MS (EI): *m/z* (%) 247 (M+1), 246 (0.07, M^+), 127 (33), 126 (11), 125 (97), 106 (100), 105 (59), 91 (32), 89 (13), 79 (10), 77 (20). HRMS Calcd for $C_{15}H_{15}ClNaO$ (M+Na): 269.0704; found: 269.0693.



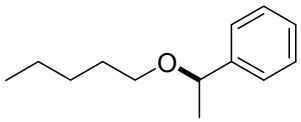
(*p*-Bromophenyl)methyl 1-phenylethyl ether (4e). Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47-7.45 (m, 2H), 7.39-7.34 (m, 4H), 7.32-7.29 (m, 1H), 7.19 (d, *J* = 8.5 Hz, 2H), 4.48 (q, *J* = 6.5 Hz, 1H), 4.38 (d, *J* = 12.0 Hz, 1H), 4.25 (d, *J* = 12.5 Hz, 1H), 1.49 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 143.4, 137.6, 131.4, 129.3, 128.5, 127.6, 126.3, 121.3, 77.4, 69.5, 24.1. MS (EI): *m/z* (%) 291 (M+1), 290 (0.03, M^+), 171 (53), 169 (54), 106 (100), 105 (53), 91 (31), 90 (18), 89 (12), 77 (18). HRMS Calcd for $C_{15}H_{15}BrNaO$ (M+Na): 313.0198; found: 313.0183.



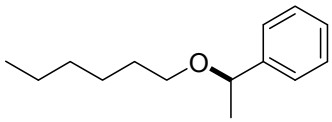
(1-Naphthyl)methyl 1-phenylethyl ether (4f). Colorless liquid. ^{1}H NMR (500 MHz,$CDCl_3$): δ 8.07-8.05 (m, 1H), 7.88-7.86 (m, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.53-7.49 (m, 2H), 7.46-7.41 (m, 5H), 7.37-7.30 (m, 2H), 4.92 (d, *J* = 12.0 Hz, 1H), 4.74 (d, *J* = 12.0 Hz, 1H), 4.60 (q, *J* = 6.5 Hz, 1H), 1.51 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 143.6, 134.0, 133.7, 131.7, 128.51, 128.47, 128.4, 127.6, 126.4, 126.3, 126.0, 125.7, 125.2, 124.0, 77.4, 68.8, 24.2. MS (EI): *m/z* (%) 262 (6.94, M^+), 142 (100), 141 (66), 129 (29), 115 (30), 106 (24), 105 (50), 91 (21), 77 (30). HRMS Calcd for $C_{19}H_{18}NaO$ (M+Na): 285.1250; found: 285.1255.



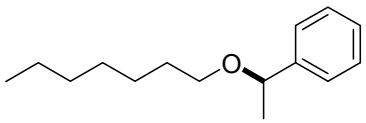
Ethyl 1-phenylethyl ether (4g). Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.29 (m, 5H), 4.40 (q, J = 6.5 Hz, 1H), 3.35 (q, J = 7.0 Hz, 2H), 1.44 (d, J = 6.5 Hz, 3H), 1.19 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 144.2, 128.4, 127.3, 126.1, 77.7, 63.9, 24.2, 15.4. MS (EI): *m/z* (%) 150 (1.97, M^+), 135 (100), 106 (66), 105 (49), 79 (51), 77 (26). This compound was known: Podder, S.; Choudhury, J.; Roy, S. *J. Org. Chem*. **2007**, *72*, 3129.



***n*-Pentyl 1-phenylethyl ether (4h).** Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.30 (m, 4H), 7.28-7.26 (m, 1H), 4.40 (q, J = 6.5 Hz, 1H), 3.28 (t, J = 6.8 Hz, 2H), 1.59-1.55 (m, 2H), 1.43 (d, J = 6.5 Hz, 3H), 1.34-1.26 (m, 4H), 0.89-0.86 (m, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 144.3, 128.3, 127.2, 126.1, 77.9, 68.8, 29.6, 28.4, 24.2, 22.5, 14.0. MS (EI): *m/z* (%) 192 (0.16, M^+), 177 (37), 107 (100), 106 (21), 105 (77), 79 (21), 77 (12). This compound was known: Ke, F.; Li, Z.-K.; Xiang, H.-F.; Zhou, X.-G. *Tetrahedron Lett*. **2011**, *52*, 318.

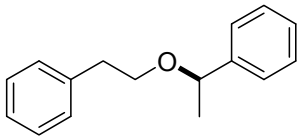


***n*-Hexyl 1-phenylethyl ether (4i).** Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35-7.30 (m, 4H), 7.27-7.24 (m, 1H), 4.38 (q, J = 6.5 Hz, 1H), 3.28 (t, J = 6.8 Hz, 2H), 1.57-1.53 (m, 2H), 1.43 (d, J = 6.5 Hz, 3H), 1.33-1.23 (m, 6H), 0.87 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 144.3, 128.3, 127.2, 126.1, 77.9, 68.8, 31.7, 29.9, 25.9, 24.2, 22.6, 14.0. MS (EI): *m/z* (%) 206 (0.14, M^+), 191 (31), 107 (100), 106 (21), 105 (73), 79 (16), 77 (9). This compound was known: Dzhemilev, U. M.; Kutepov, B. I.; Grigor'eva, N. G.; Talipova, R. R.; Bubennov, S. V.; Yamali, E. I. *RU2404957* (in Russ.) C2, **2010**, 20101127.

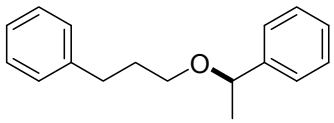


***n*-Heptyl 1-phenylethyl ether (4j).** Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.25 (m, 5H), 4.38 (q, J = 6.5 Hz, 1H), 3.29 (t, J = 6.8 Hz, 2H), 1.59-1.54 (m, 2H), 1.44 (d, J = 6.5 Hz, 3H), 1.33-1.26 (m, 8H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 144.3, 128.3, 127.2, 126.1, 77.9, 68.8, 31.8, 30.0, 29.1, 26.1, 24.2, 22.6, 14.1. MS (EI): *m/z* (%) 220 (0.18, M^+), 205 (41), 107 (100), 106 (21), 105 (75), 79 (18), 77 (11), 57 (19). Dzhemilev, U. M.; Kutepov, B. I.;

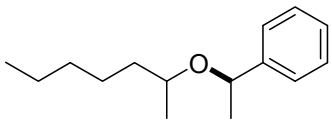
Grigor'eva, N. G.; Talipova, R. R.; Bubennov, S. V. *RU2384560* (in Russ.) C1, **2010**, 20100320.



2-Phenylethyl 1-phenylethyl ether (4k). Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32-7.29 (m, 2H), 7.26-7.22 (m, 5H), 7.20-7.17 (m, 3H), 4.40 (q, J = 6.5 Hz, 1H), 3.51 (t, J = 7.5 Hz, 2H), 2.93-2.83 (m, 2H), 1.43 (d, J = 6.5 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 143.9, 139.0, 128.9, 128.3, 128.2, 127.3, 126.09, 126.06, 78.1, 69.6, 36.5, 24.1. MS (EI): *m/z* (%) 226 (5.63, M^+), 106 (11), 105 (100), 104 (14), 79 (10). This compound was known: Rosenfeld, D. C.; Shekhar, S.; Takemiya, A.; Utsunomiya, M.; Hartwig, J. F. *Org. Lett.* **2006**, *8*, 4179.

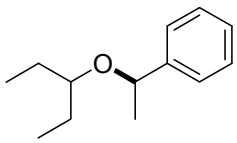


3-Phenylpropyl 1-phenylethyl ether (4l). Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.32 (m, 4H), 7.29-7.25 (m, 3H), 7.19-7.15 (m, 3H), 4.39 (q, J = 6.5 Hz, 1H), 3.34-3.32 (m, 2H), 2.75-2.61 (m, 2H), 1.92-1.86 (m, 2H), 1.46 (d, J = 6.5 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 144.1, 142.1, 128.43, 128.36, 128.2, 127.3, 126.1, 125.7, 78.0, 67.8, 32.4, 31.5, 24.1. MS (EI): *m/z* (%) 240 (0.56, M^+), 135 (21), 134 (25), 105 (100), 104 (17), 91 (72), 77 (11). This compound was known: Iwanami, K.; Yano, K.; Oriyama, T. *Chem. Lett*. **2007**, *36*, 38.



(*RR/SS/RS/SR* ~1/1/1/1 mixtures)

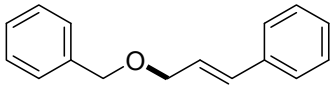
1-Phenylethyl 2-heptyl ether (4m). Colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27-7.17 (m, 5H+5H), 4.47-4.42 (m, 1H+1H), 3.34-3.27 (m, 1H) or 3.23-3.17 (m, 1H), 1.49-1.11 (m, 11H+11H), 1.05 (d, J = 6.0 Hz, 3H) or 0.96 (d, J = 6.5 Hz, 3H), 0.83 (t, J = 7.0 Hz, 3H) or 0.76 (t, J = 7.3 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 145.1 (144.6), 128.3 (128.2), 127.2 (127.1), 126.5 (126.2), 75.4 (74.5), 73.2 (71.9), 37.5 (36.0), 32.1 (31.8), 25.3 (25.0), 24.7 (24.4), 22.7 (22.6), 20.8 (19.3), 14.05 (14.00). MS (EI): *m/z* (%) 220 (0.01, M^+), 205 (9), 107 (31), 105 (100), 77 (6). HRMS Calcd for $C_{15}H_{24}NaO$ (M+Na): 243.1719; found: 243.1711.



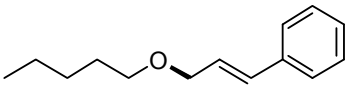
1-Phenylethyl 3-pentyl ether (4n). Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34-7.26 (m, 5H), 4.50 (q, J = 6.3 Hz, 1H), 3.12 (t, J = 5.8 Hz, 1H), 1.57-1.36 (m, 7H), 0.90 (t, J = 7.5 Hz, 3H),

0.77 (t, J = 7.5 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 144.3, 127.7, 126.7, 126.0, 78.2, 74.6, 26.1, 24.7, 23.8, 9.4, 8.5. MS (EI): *m/z* (%) 178 (0.87, M^+), 177 (7), 163 (10), 107 (14), 105 (100), 79 (8). HRMS Calcd for $C_{13}H_{20}NaO$ (M+Na): 215.1406; found: 215.1397.

Typical Procedure for Cinnamyl Bromide-Catalyzed *O*-Alkylative Cross-Etherifiaction Reaction of Cinnamyl Alcohol with Alcohols for Synthesis of Unsymmetrical Aliphatic Ethers. The mixture of cinnamyl alcohol **1h** (0.671 g, 5 mmol), benzyl alcohol **1a** (0.57 mL, 5.5 mmol, 1.1 equiv) and cinnamyl bromide (0.0493 g, 0.25 mmol, 5 mol%) was sealed under air in a 20 mL Schlenk tube, stirred at 60 ^{o}C for 46 h, and then monitored by TLC and/or GC-MS. After completion of the reaction, the mixture was directly purified, without any workup, through a silica gel column using ethyl acetate and petroleum ether as the eluent, giving benzyl cinnamyl ether **5a** in 75% isolated yield.



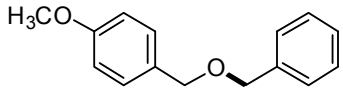
Benzyl cinnamyl ether (5a). Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42-7.27 (m, 10H), 6.65 (d, J = 15.5 Hz, 1H), 6.35 (dt, J = 6.0 Hz, J = 16 Hz, 1H), 4.60 (s, 2H), 4.22 (dd, J = 1.5 Hz, J = 6.0 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 138.2, 136.7, 132.5, 128.5, 128.4, 127.8, 127.65, 127.62, 126.5, 126.1, 72.1, 70.7. MS (EI): *m/z* (%) 224 (12.82, M^+), 223 (80), 195 (22), 152 (26), 119 (14). This compound was known: Billard, F.; Robiette, R.; Pospisil, J. *J. Org. Chem*. **2012**, *77*, 6358.



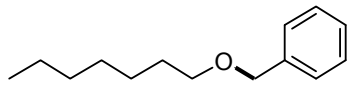
***n*-Pentyl cinnamyl ether (5b).** Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40-7.38 (m, 2H), 7.34-7.30 (m, 2H), 7.25-7.22 (m, 1H), 6.61 (d, J = 16.0 Hz, 1H), 6.31 (dt, J = 6.0 Hz, J = 16.0 Hz, 1H), 4.14 (dd, J =1.5 Hz, J = 6.0 Hz, 2H), 3.48 (t, J = 7.0 Hz, 2H), 1.64-1.60 (m, 2H), 1.37-1.34 (m, 4H), 0.91 (t, J = 6.8 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 136.8, 132.1, 128.5, 127.6, 126.8, 126.4, 71.4, 70.6, 29.5, 28.4, 22.6, 14.0. MS (EI): *m/z* (%) 206 (M+2), 204 (1.28, M^+), 190 (31), 133 (26), 117 (62), 115 (62), 92 (100), 91 (43), 78 (28).

Typical Procedure for Benzyl Bromide-Catalyzed *O*-Alkylative Cross-Etherifiaction Reaction of Benzyl Alcohol with Alcohols for Synthesis of Unsymmetrical Aliphatic Ethers. The mixture of benzyl alcohol **1a** (0.52 mL, 5.0 mmol), (4-methoxyphenyl)methanol (0.74 mL, 6.0 mmol, 1.2 equiv) and benzyl bromide (0.03 mL, 0.25 mmol, 5 mol%) was sealed under air in a 20 mL Schlenk

tube, stirred at 120 °C for 32 h, and then monitored by TLC and/or GC-MS. After completion of the reaction, the mixture was directly purified, without any workup, through a silica gel column using ethyl acetate and petroleum ether as the eluent, giving benzyl (*p*-methoxylphenyl)methyl ether 6**a** in 50% isolated yield.

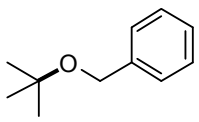


Benzyl (*p*-methoxylphenyl)methyl ether (6a). Colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39-7.28 (m, 7H), 6.92-6.86 (m, 2H), 4.56 (S, 2H), 4.52 (S, 2H), 3.84 (s, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): 159.3, 138.4, 130.4, 129.4, 128.4, 127.8, 127. 6, 113.8, 71.84, 71.79, 55.3. MS (EI): *m/z* (%) 228 (13.32, M^+), 137 (98), 121 (100), 109 (19), 91 (50), 77(19). This compound was known: Zeng, C. -C.; Zhang, N. -T.; Lam, C. M.; Little, R. D. *Org. Lett*. **2012**, *14*, 1314-1317.

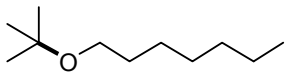


Benzyl 1-heptyl ether (6b). Colourless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.27 (m, 5H), 4.51 (s, 2H), 3.46 (t, J = 6.8 Hz, 2H), 1.64-1.59 (m, 2H), 1.37-1.26 (m, 8H), 0. 88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 138.7, 128.3, 127.6, 127.5, 72.9, 70.5, 31.8, 29.8, 29.2, 26.2, 22.6, 14.1. MS (EI): *m/z* (%) 206 (12.82, M^+), 97 (16), 92 (79), 91 (100), 55 (18). This compound was known: Zhou, J. R. Fu, G. C. *J. Am. Chem. Soc*. **2003**, *125*, 12527-12530.

Typical Procedure for *t*-Butyl Bromide-Catalyzed *O*-Alkylative Cross-Etherifiaction Reaction of *t*-Butyl Alcohol with Alcohols for Synthesis of Unsymmetrical Aliphatic Ethers. The mixture of *t*-butyl alcohol **1l** (0.46 mL, 5 mmol), benzyl alcohol **1a** (0.57 mL, 5.5 mmol, 1.1 equiv) and *t*-butyl bromide (0.028 mL, 0.25 mmol, 5 mol%) was sealed under air in a 20 mL Schlenk tube, stirred at 60 °C for 57 h, and then monitored by TLC and/or GC-MS. After completion of the reaction, the mixture was directly purified, without any workup, through a silica gel column using ethyl acetate and petroleum ether as the eluent, giving Benzyl *t*-butyl ether 7**a** in 57% isolated yield.

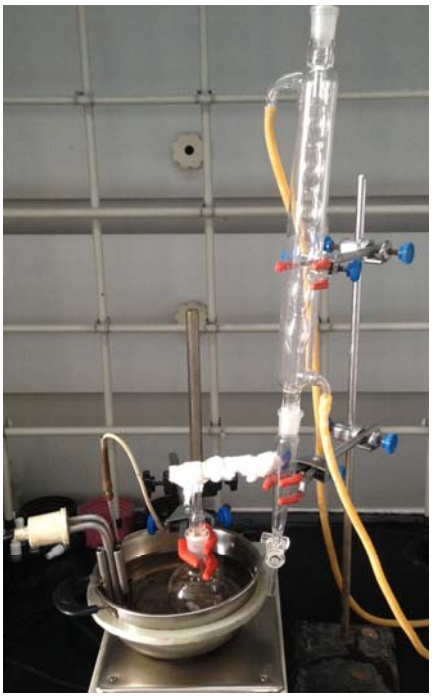


Benzyl *t*-butyl ether (7a). Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.32 (m, 5H), 4.45 (s, 2H), 1.30 (s, 9H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 139.9, 128.3, 127.4, 127.1, 73.4, 64.1, 27.7. MS (EI): *m/z* (%) 164 (2.45, M^+), 149 (25), 107 (6), 91 (100), 79 (9), 57 (19). This compound was known: Cui, X. J.; Zhang, S. G.; Shi, F.; Zhang, Q. H.; Ma, X. Y.; Lu, L. J.; Deng, Y. Q. *ChemSusChem*, **2010**, *3*, 1043.



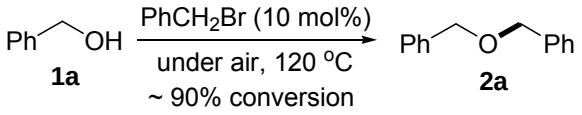
***n*-Heptyl *t*-butyl ether (7b).** Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.32 (t, J = 7.0 Hz, 2H), 1.54-1.49 (m, 2H), 1.30-1.28 (m, 8H), 1.19 (s, 9H), 0.88 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 72.4, 61.7, 31.9, 30.7, 29.2, 27.6, 26.2, 22.6, 14.1. MS (EI): *m/z* (%) 172 (0.08, M^+), 157 (30), 97 (3), 87 (4), 59 (100), 58 (6), 57 (93). This compound was known: Hartz, N.; Prakash, G. K. S.; Olah, G. A. *Synlett*, **1992**, *(7)*, 569.

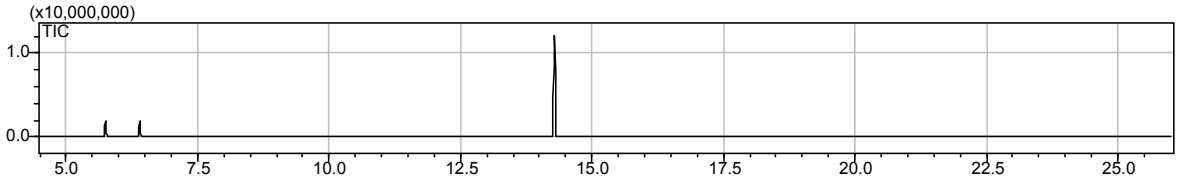
Large Scale Reaction of Benzyl alcohol (1a) Catalyzed by Benzyl Bromide for Dibenzyl Ether (2a) Preparation (eq. 5 in the text). As shown by the picture below, to a 100 mL round-bottomed flask equipped with a water separator and a condenser open to air were added 50 mL benzyl alcohol **1a** (484 mmol) and $PhCH_2Br$ (6 mL, 50.5 mmol, 10.4 mol%). The mixture was then directly heated under air at 120 ^{o}C. During the heating byproduct water was obviously generated and easily collected in the water separator. GC analysis showed 90% conversion of **1a** after 34 h's heating at 120 ^{o}C. The condenser and the water separator were then removed and the reaction subjected to distillation under reduced pressure. A careful vacuum distillation of the reaction mixture afforded 83% isolated yield of pure benzyl ether **2a**.



Mechanistic Studies

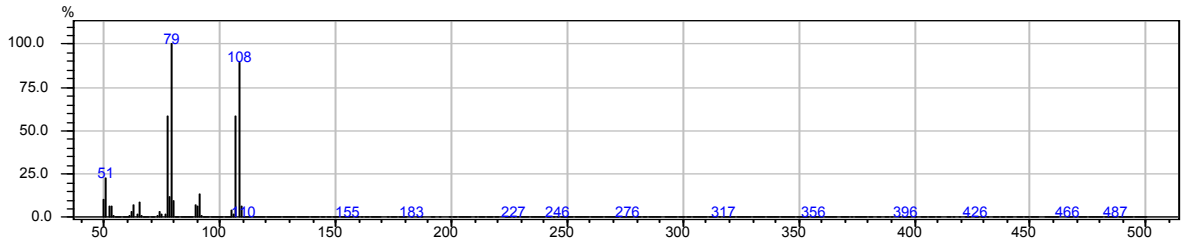
1. GC detection of considerable amounts of $PhCH_2Br$ (initial catalyst loading: 10 mol%) in an almost completed etherification reaction of benzyl alcohol (1a).



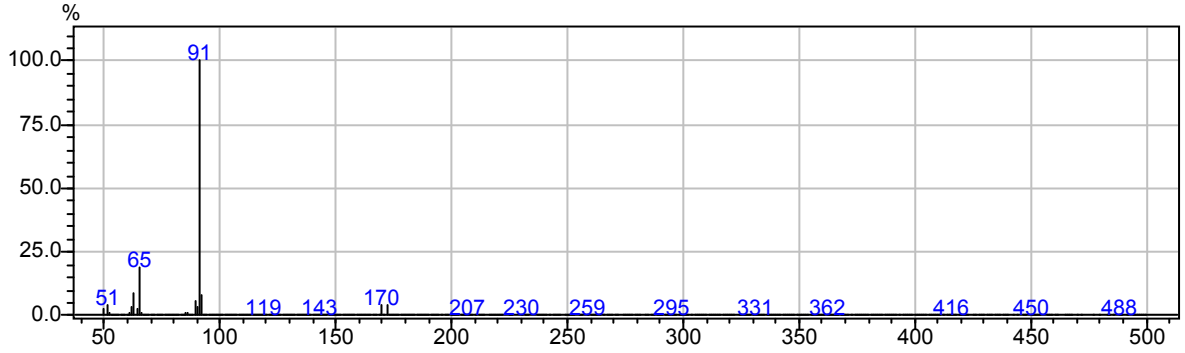


5.750	5.717	5.792	TIC	3048941	**9.78**	1961459	12.26	1.55	MI
6.401	6.375	6.442	TIC	2666968	**8.56**	1949246	12.18	1.36	MI
14.288	14.233	14.350	TIC	25447195	**81.66**	12088244	75.56	2.10	MI

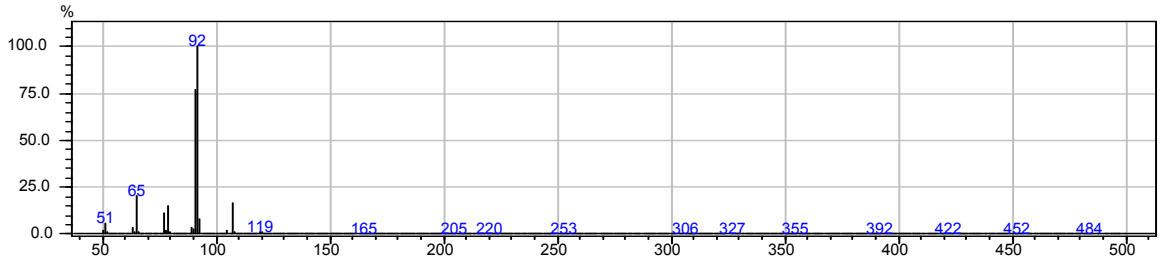
Time：5.75 min ($PhCH_2OH$ 1a, MW 108)



Time：6.40 min (catalyst $PhCH_2Br$, MW 170, 172)



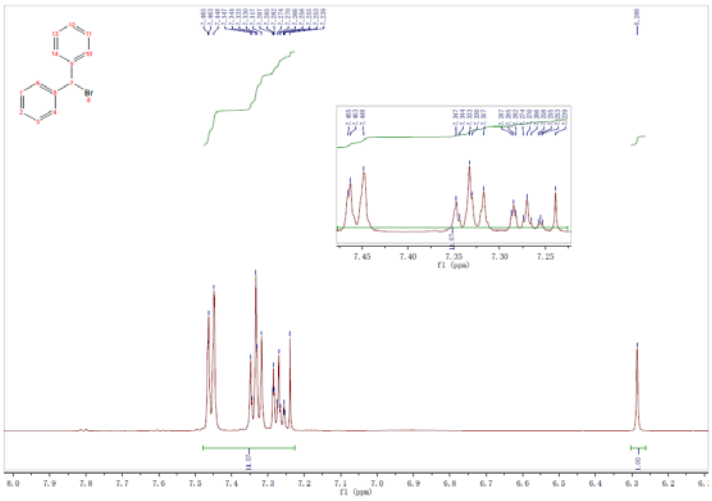
Time：14.28 min ($PhCH_2OCH_2Ph$ 2a)



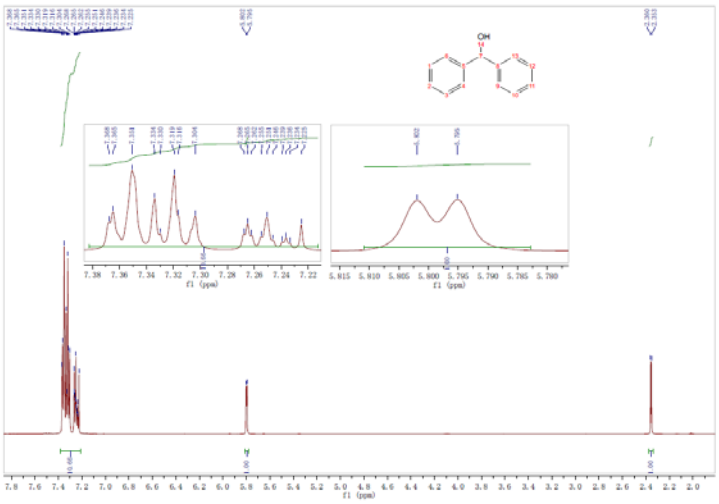
2. NMR detection of Ph_2CHBr in Ph_2CHBr-catalyzed cross-etherification reaction of benzyl alcohol (1a) and Ph_2CHOH (1i).

2.1 Standard ^1H NMR spectra of the involved compounds

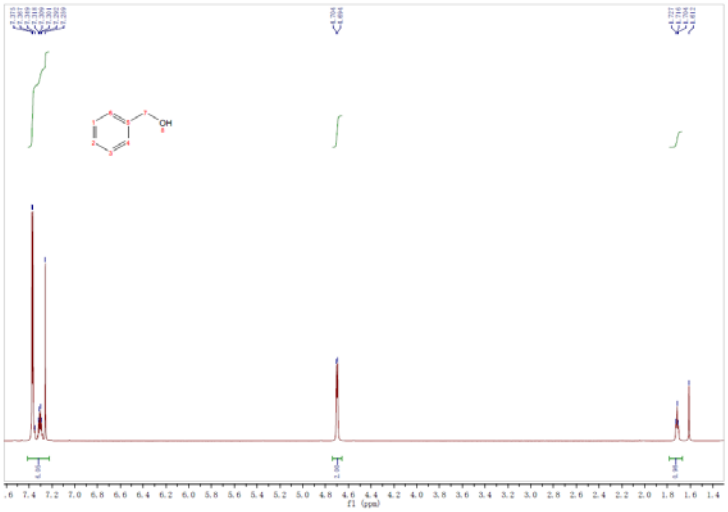
Ph_2CHBr:



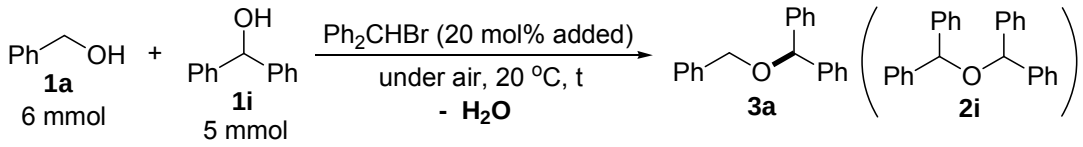
Ph_2CHOH:



$PhCH_2OH$:



2.2 Results for ^{1}H NMR analysis on variation of the components in Ph_2CHBr-catalyzed cross-etherification reaction of 1a and 1i. These data were then converted to the following figure using Microsoft Excel 2010.



run	NMR spectra No.	time	**3a**%	**1i** % (conversion)	Ph_2CHBr (mol%)
1	(1)	20 min	10	13	21
2	(2)	1 h	43	54	14
3	(3)	2 h	57	73	13
4	(4)	3 h	65	82	10
4	(5)	5 h	72	90	9

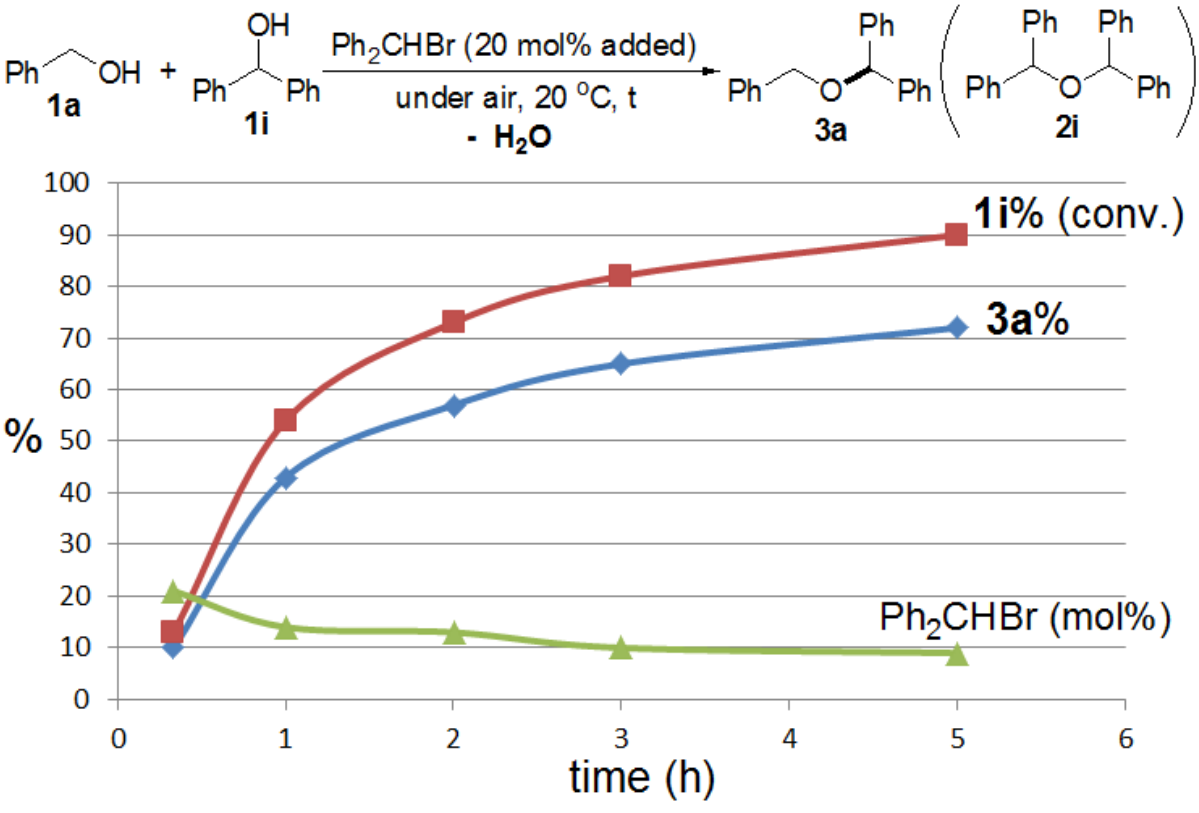
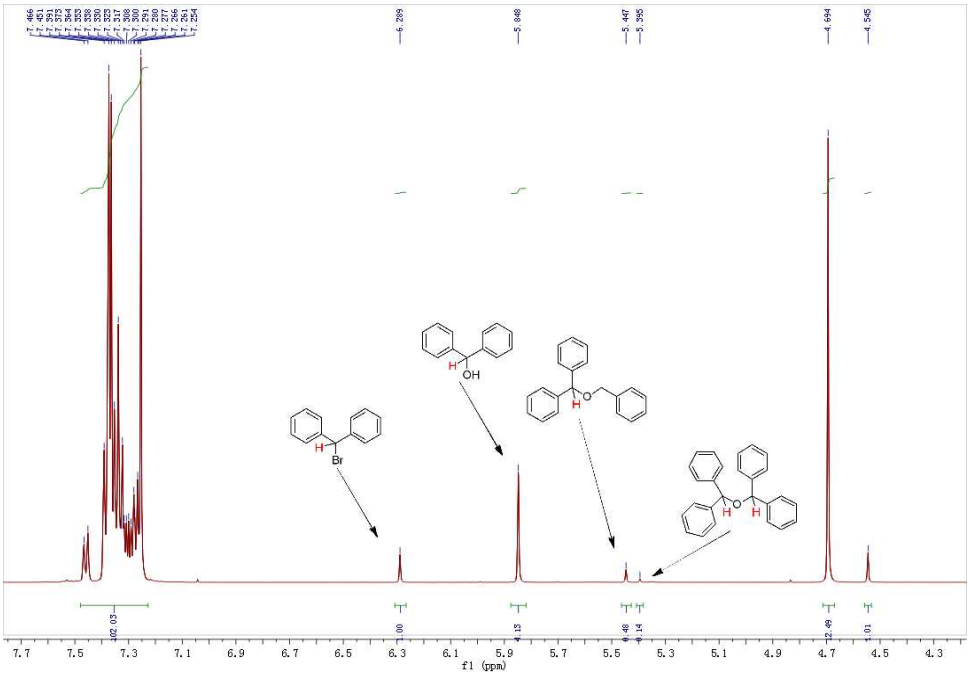


Figure. (Figure 1 in the text).

(1) ^{1}H NMR spectra of run 1: 20 ^{o}C, 20 min

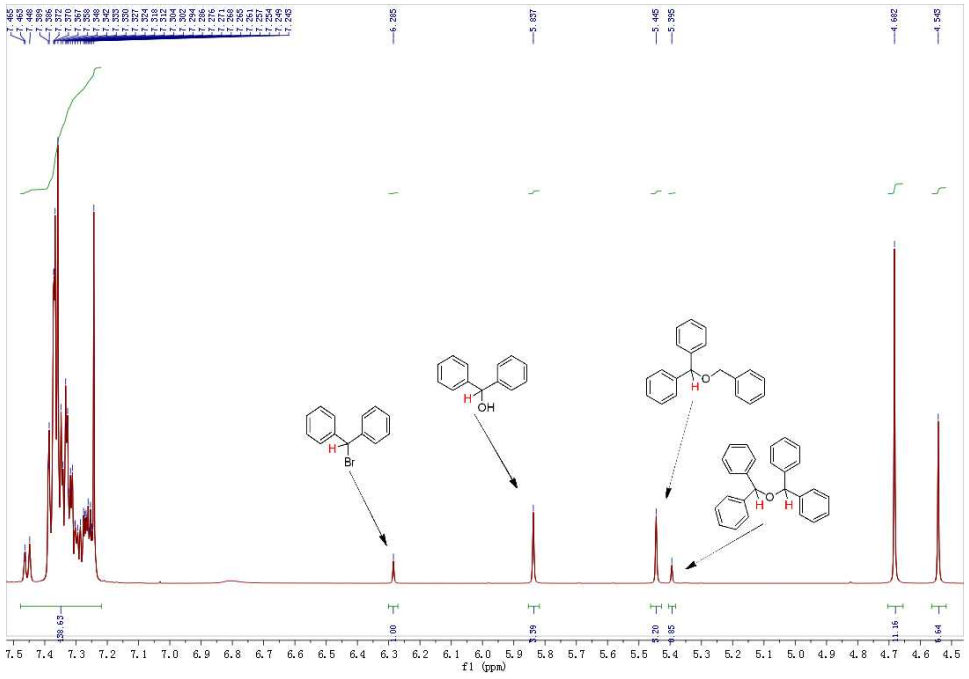


3a%: 0.48/(4.13+0.48+0.14) = 10%

1i% (conversion): (0.48 +0.14)/(4.13+0.48+0.14) = 13%

Ph_2CHBr (mol%): 1.00/(4.13+0.48+0.14) = 1/4.75 = 21 mol% (initial catalyst loading 20 mol%)

(2) ^{1}H NMR spectra of run 2: 20 ^{o}C, 1 h

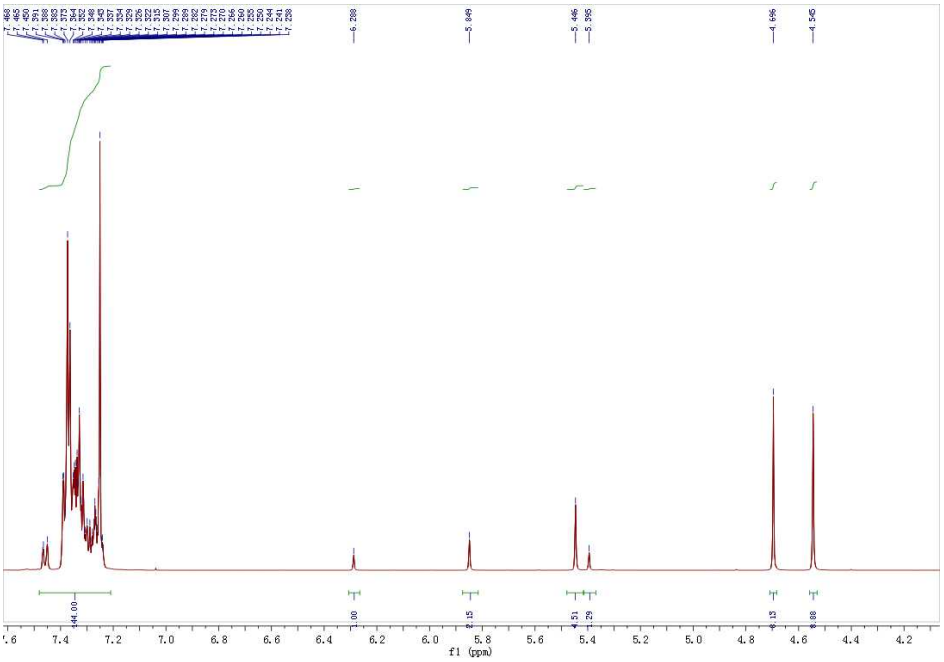


3a%: 3.20/(3.39+3.20+0.85) = 43%

1i% (conversion): (3.20 + 0.85)/(3.39+3.20+0.85) = 54%

Ph_2CHBr (mol%): 1/(3.39+3.20+0.85) = 1/7.44 = 14 mol%

(3) ^{1}H NMR spectra of run 3: 20 ^{o}C, 2 h

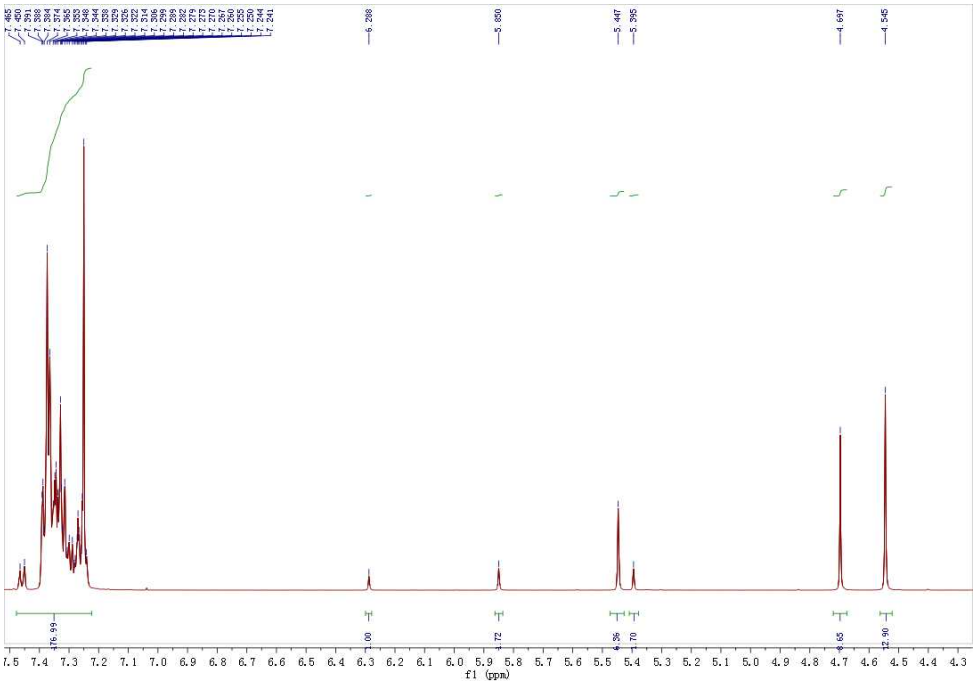


3a% = 4.51/(2.15+4.51+1.29) = 57%

1i% (conversion): (4.51 + 1.29) = 73%

Ph_2CHBr mol% = 1/(2.15+4.51+1.29)=1/7.95 = 13 mol%

(4) ^{1}H NMR spectra of run 4: 20 ^{o}C, 3 h

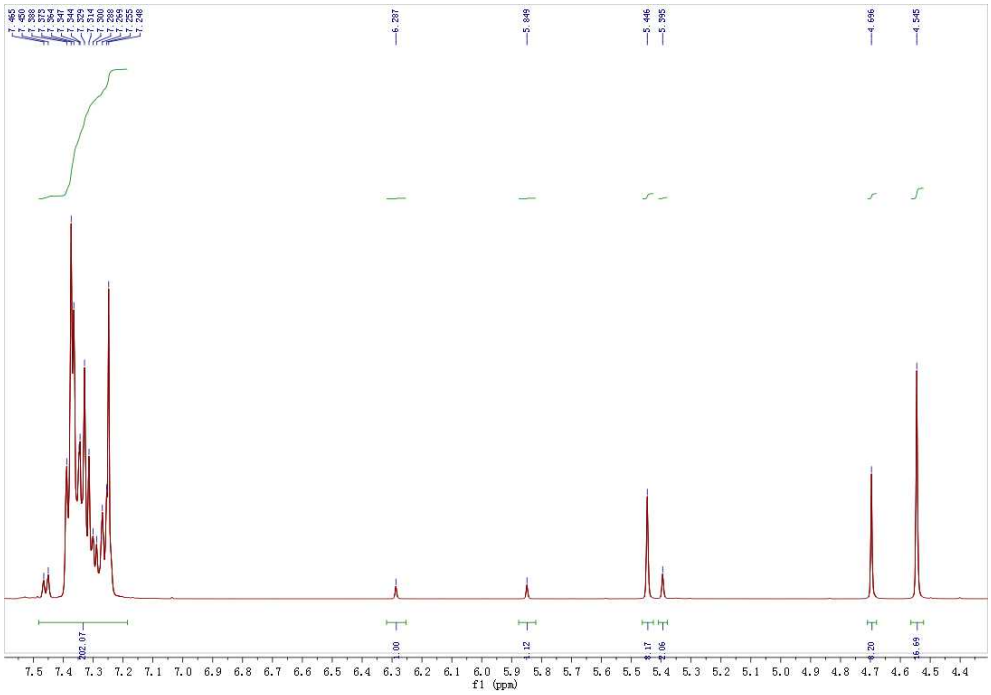


3a% = 6.36/(1.72+6.36+1.70) = 65%

1i% (conversion): (6.36 + 1.60)/(1.72+6.36+1.70) = 82%

Ph_2CHBr mol% = 1/(1.72+6.36+1.70) = 1/9.78 = 10 mol%

(5) ^{1}H NMR spectra of run 5: 20 ^{o}C, 5 h

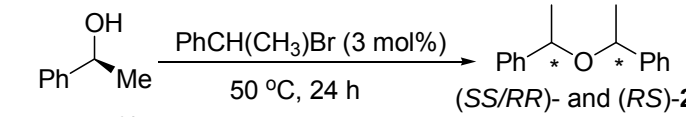


3a% = 8.17/(1.12+8.17+2.06) = 72%

1i% (conversion): (8.17 + 2.06)/(1.12+8.17+2.06) = 90%

Ph_2CHBr mol% = 1/(1.12+8.17+2.06) = 1/11.35 = 9 mol%

3. Racemic PhCH(CH_3)Br-catalyzed diastereo-selective homo-etherification reaction of optically active (*S*)-1-phenyl ethanol (1j, 98%*ee*) (eq. 6 in the text)



(*S*)-**1j**, 98% *ee*

(*SS/RR*)- and (*RS*)-**2j**

40%^{GC}, 15%^{isolated}

dr ((*SS*+*RR*)/RS): 59/41

$[\alpha]_D^{19.7}$ = - 176.5 (c = 0.00553, CH_2Cl_2)

(lit. data : (*S,S*)-**2j**, $[\alpha]_D^{20}$ = - 234; (*R,R*)-**2j**, $[\alpha]_D^{20}$ = + 224)

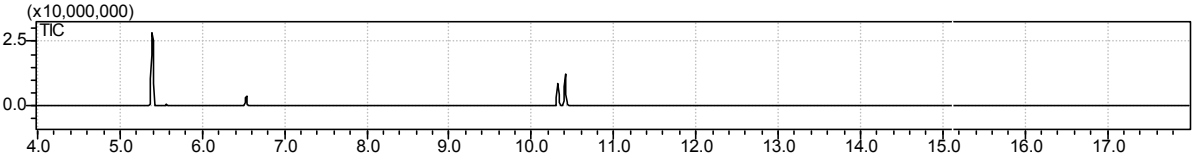
enantiomer ratio (*SS/RR*): ca. 88/12~89/11; ca. 76~78% *ee*

15% isolated yield (0.136 g) of **2j** was obtained in an 8 mmol reaction.
0.0938 g isolated **2j** was dissolved in 10 mL CH_2Cl_2, c_1 = 0.00938.

Optical rotatory power measured: α = -0.977 (L = 1 dm; T = 19.7 ℃; λ = 589 nm)

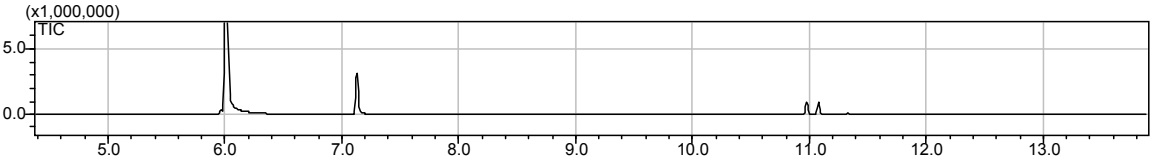
(*Eur. J. Org. Chem.* 2008, 4963: (*S,S*)-diasteoromer, $[\alpha]_D^{20}$ = - 234; (*R,R*)-, $[\alpha]_D^{20}$ = + 224).
Therefore, the mixture contains mainly the (*S,S*)-diasteoromer.
Then, c_2 = 0.00938*0.59 = 0.00553 (if 41% are the mixture of RR and SS isomers, then [α] will exceed the known value of 224 or 234).
Therefore, $[\alpha]_D^{19.7}$ = - 176.5 (c = 0.00553, CH_2Cl_2).
Therefore, enantiomer ratio *SS/RR*: ca. 88/12~89/11 (by comparison with the literature data). Enantiomeric excess is ca. 76~78%.

(1) GC spectra and data of the above reaction: 59/41 dr



5.394	5.350	5.425	TIC	48739446	60.48	28584120	57.98	1.70	MI
10.322	10.292	10.350	TIC	13101811	**16.26**	8485827	17.21	1.54	MI
10.410	10.383	10.458	TIC	18739662	**23.26**	12232992	24.81	1.53	MI

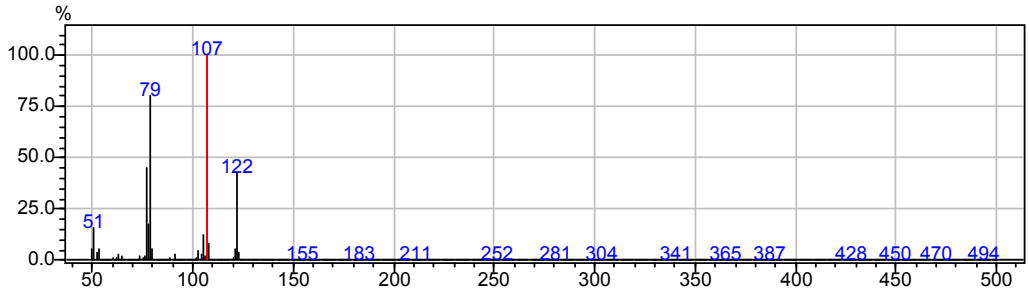
(2) GC spectra and data of a normal reaction using racemic 1j as the substrate:



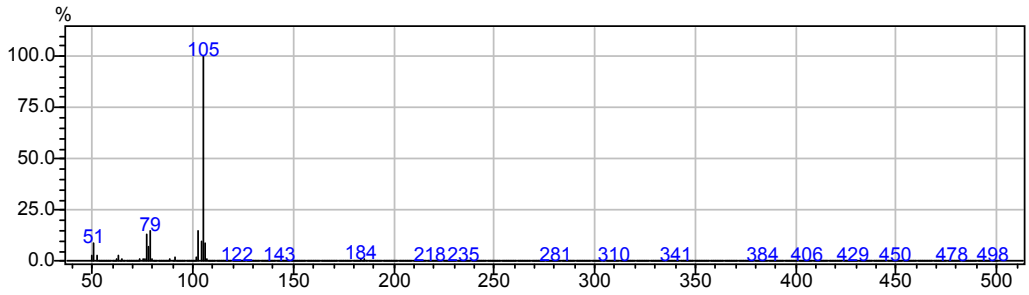
6.015	5.933	6.133	TIC	33707499	80.48	16895549	77.36	1.99	MI
7.131	7.092	7.183	TIC	5161344	12.32	3083563	14.12	1.67	MI
10.977	10.942	11.025	TIC	1468361	3.51	926689	4.24	1.58	MI
11.078	11.042	11.150	TIC	1545411	3.69	934374	4.28	1.65	MI

(3) MS spectra of the involved compounds:

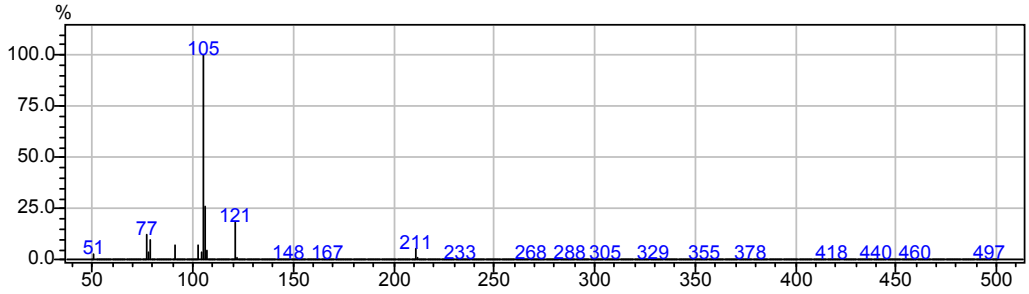
Retention Time：~5.4 or 6.0 min (1j, MW 122)



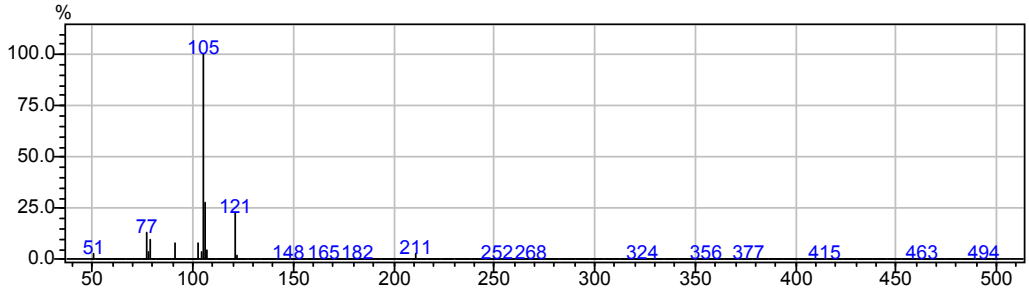
Retention Time：~6.5 or 7.1 min (catalyst, MW 184, 186)



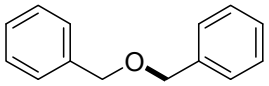
Retention Time: ~10.32 or 10.98 min (isomers of 2j, MW 226)



Retention Time: ~10.41 or 11.08 min (isomers of 2j, MW 226)

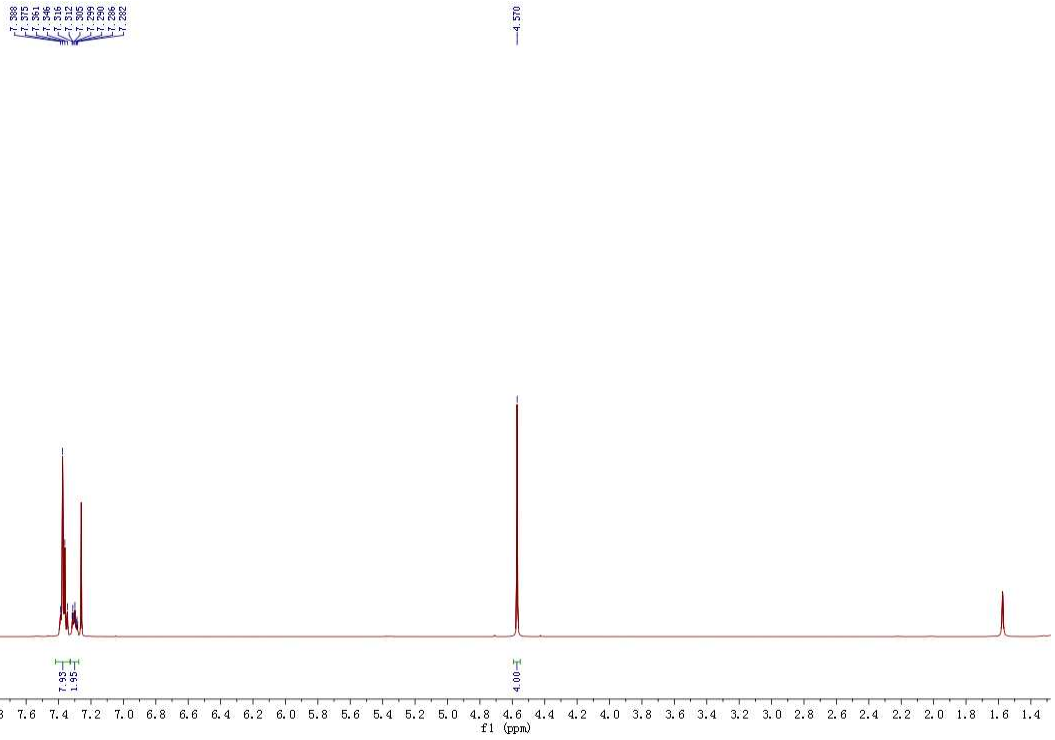


^{1}H and ^{13}C NMR Spectra of the Products

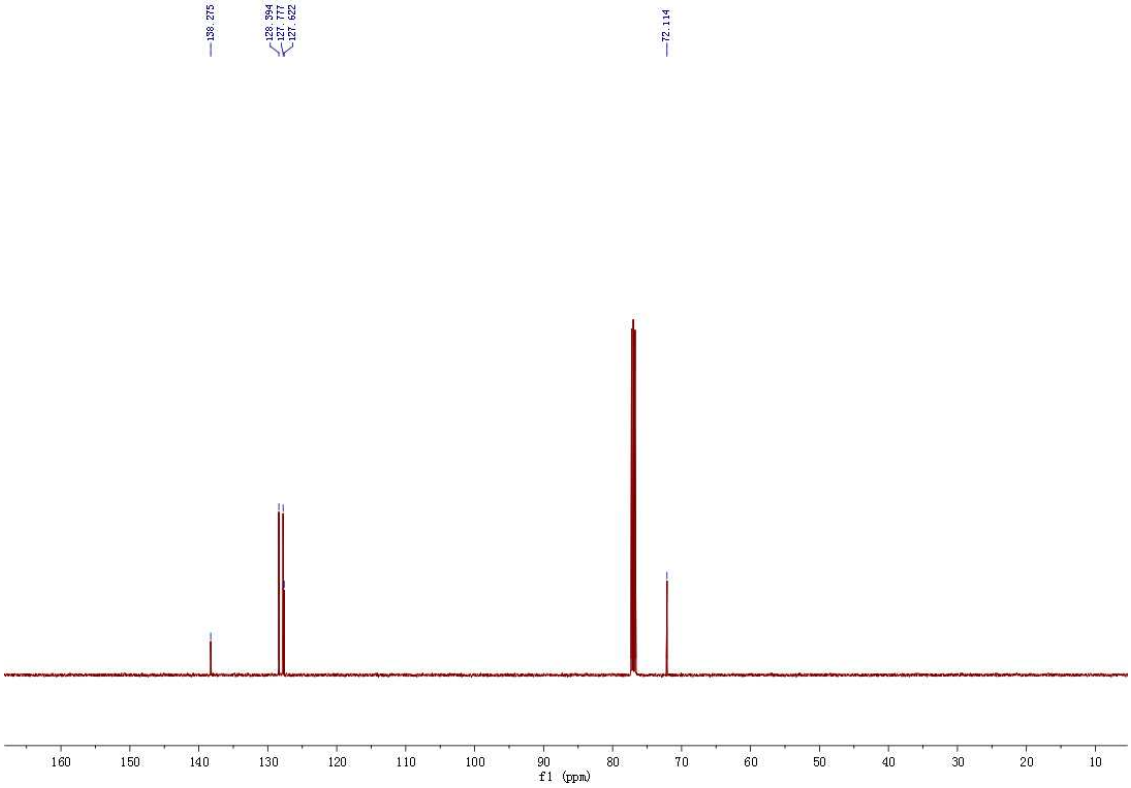


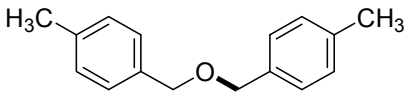
(2a)

^{1}H NMR



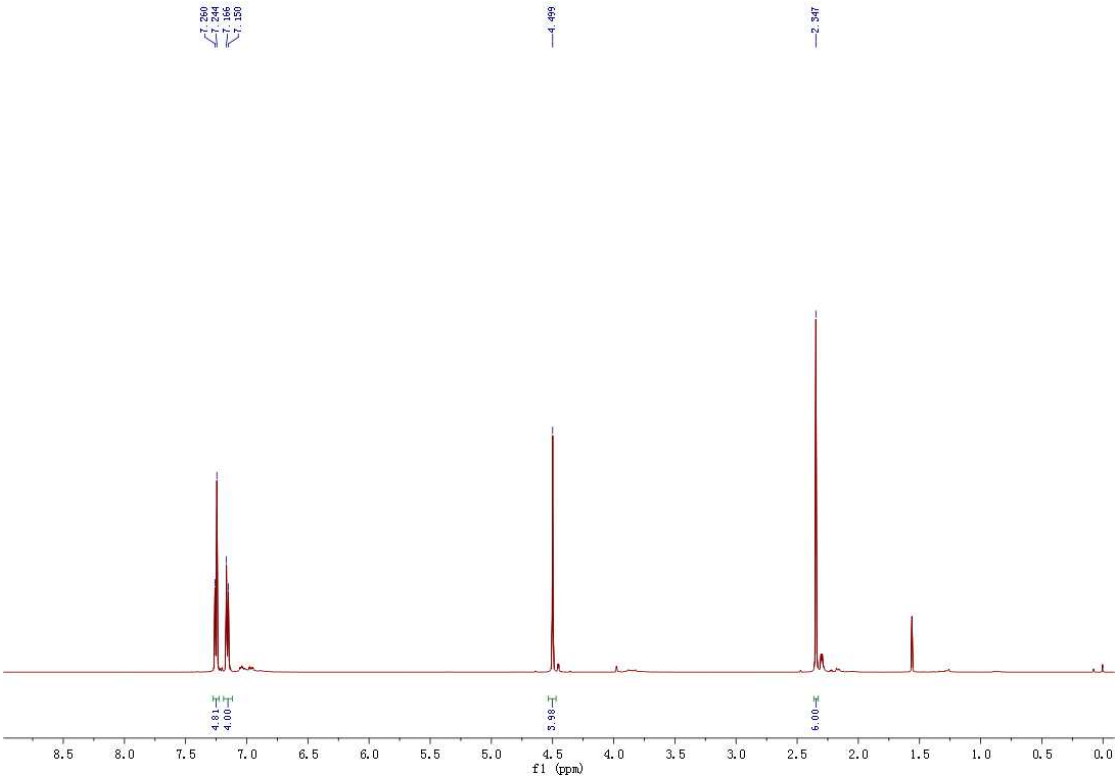
^{13}C NMR



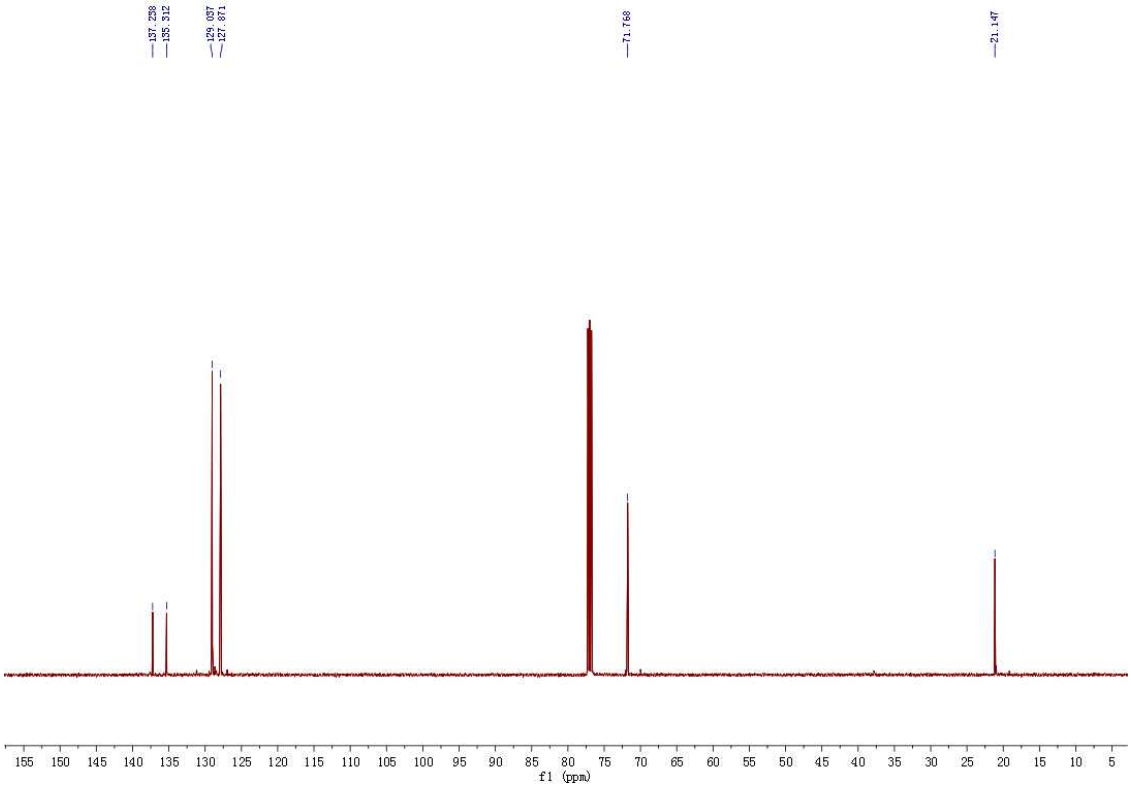


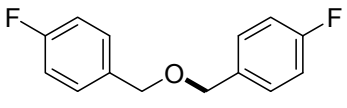
(2b)

^{1}H NMR



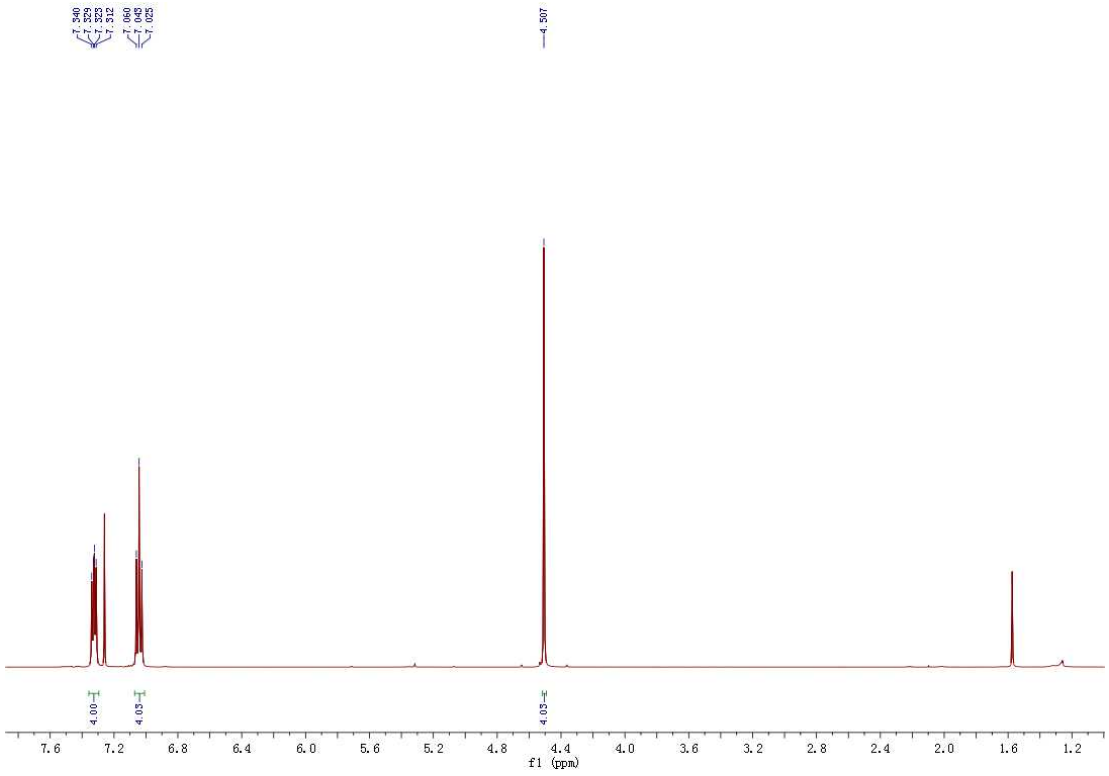
^{13}C NMR



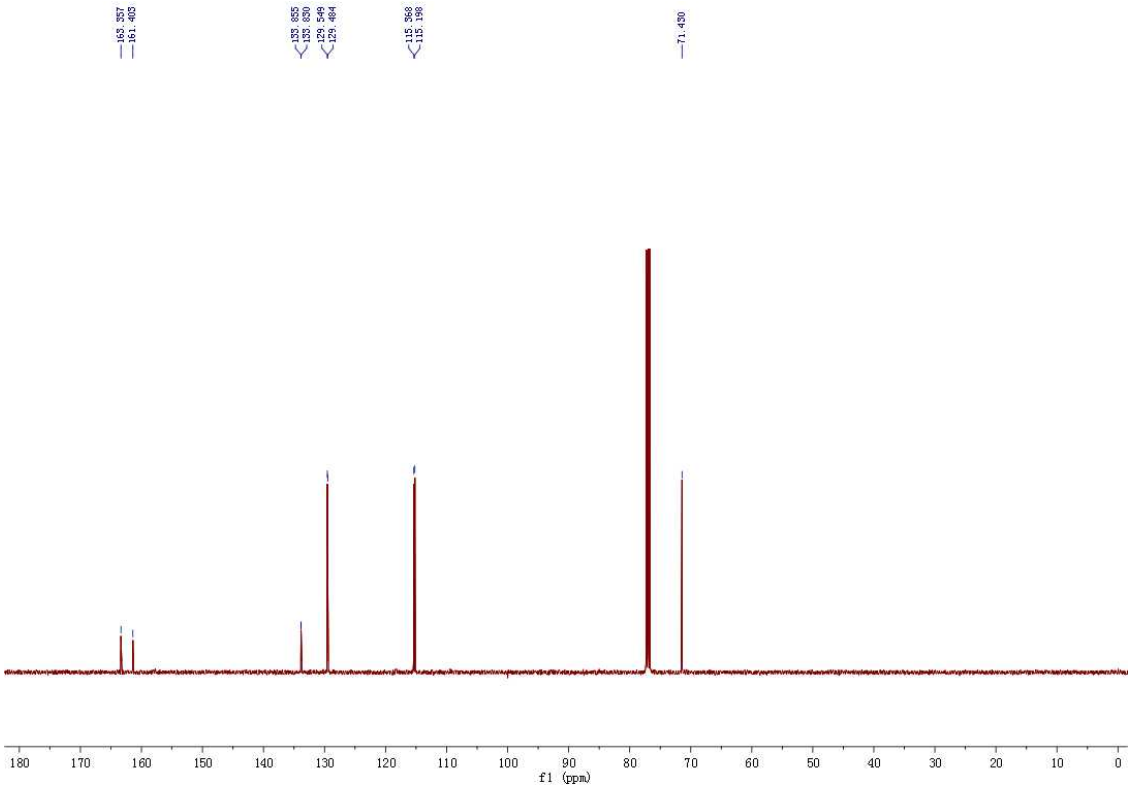


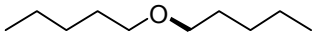
(2c)

^{1}H NMR



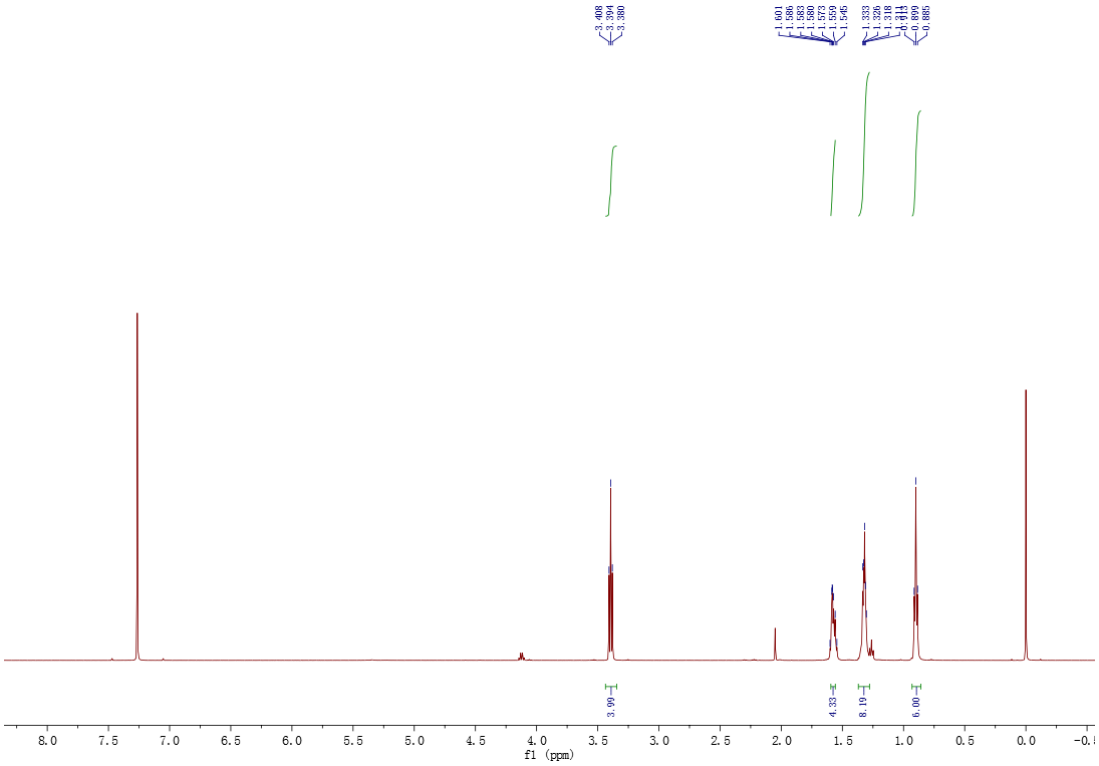
^{13}C NMR



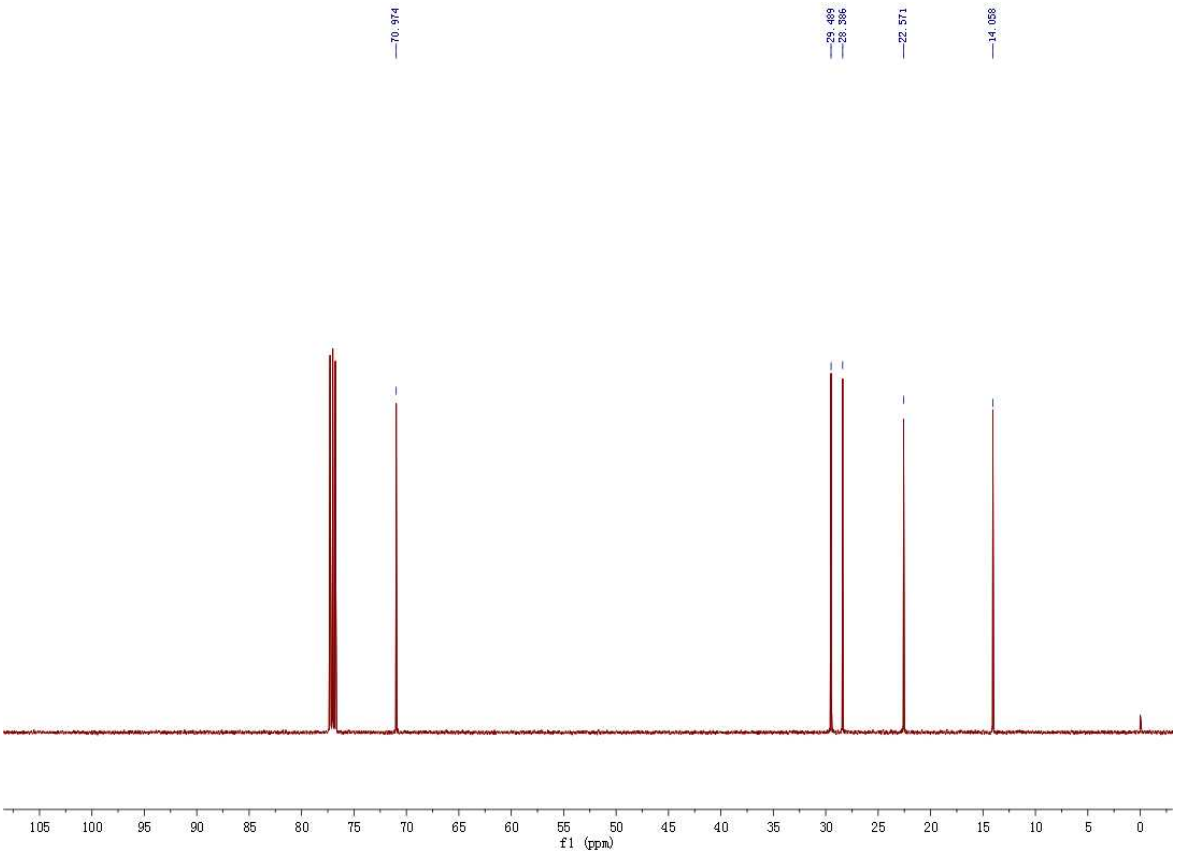


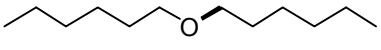
(2d)

^{1}H NMR



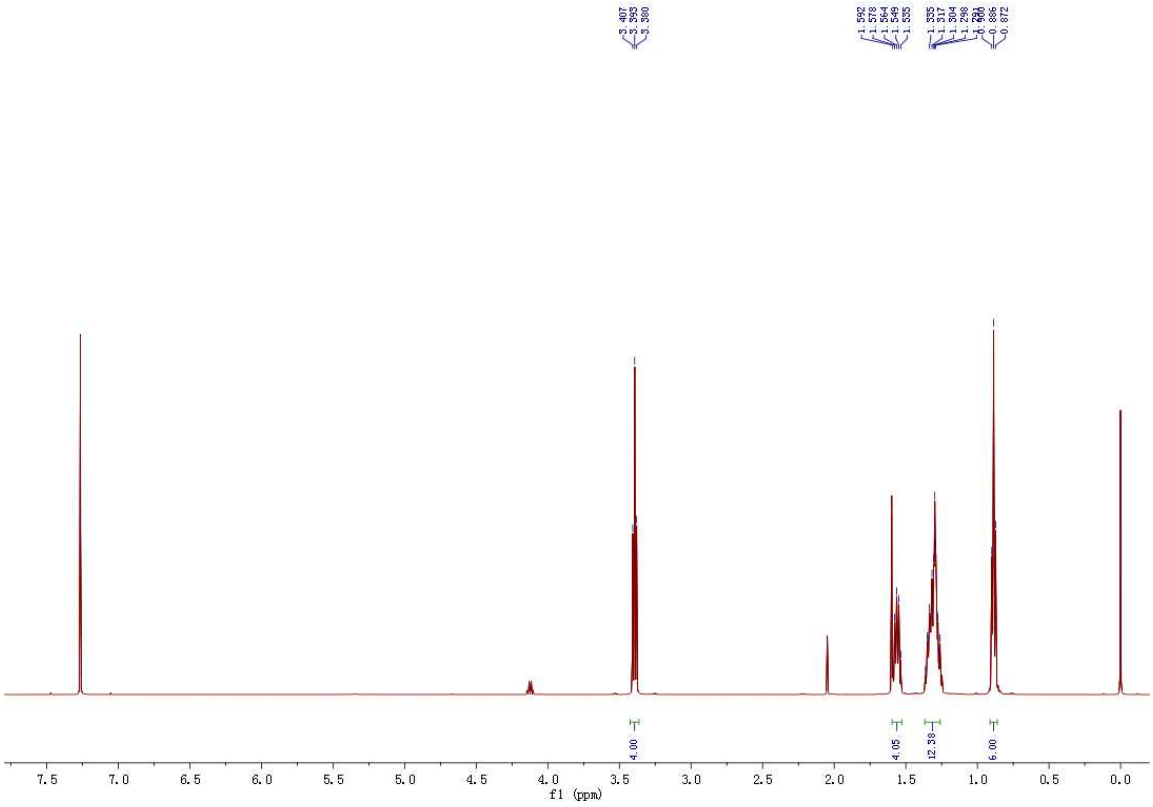
^{13}C NMR



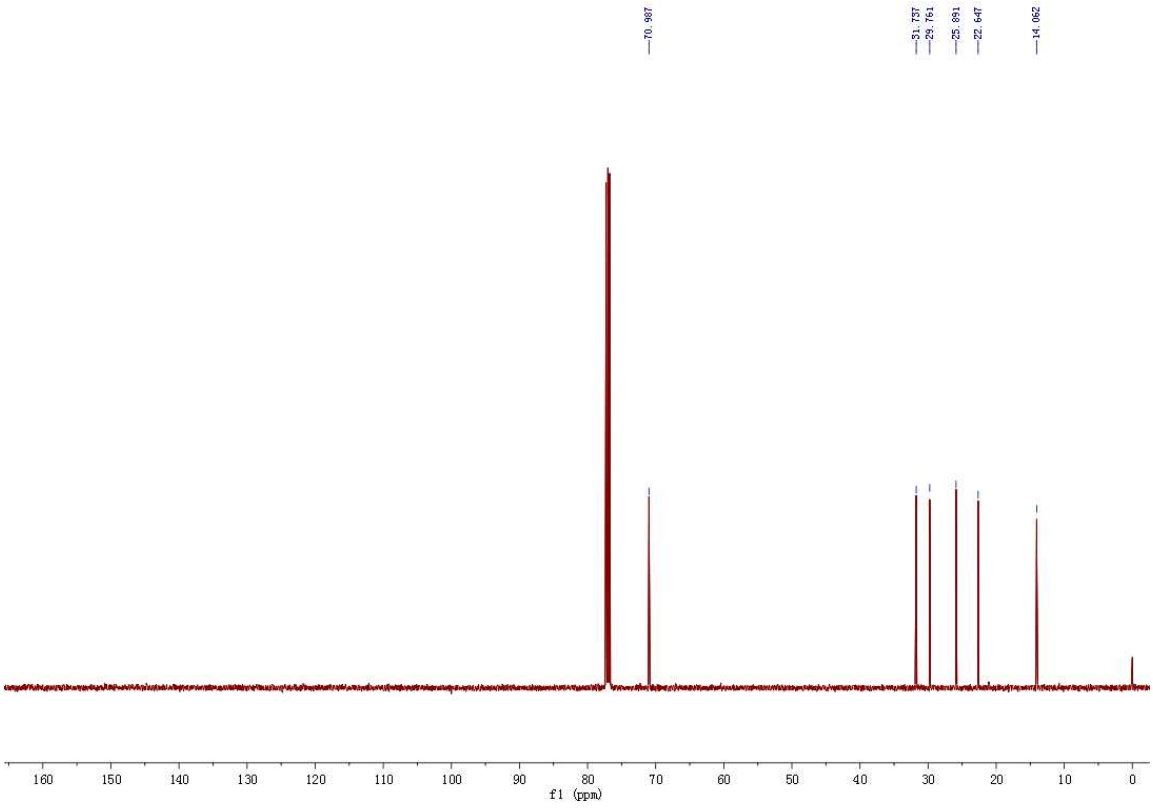


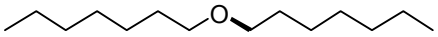
(2e)

^{1}H NMR



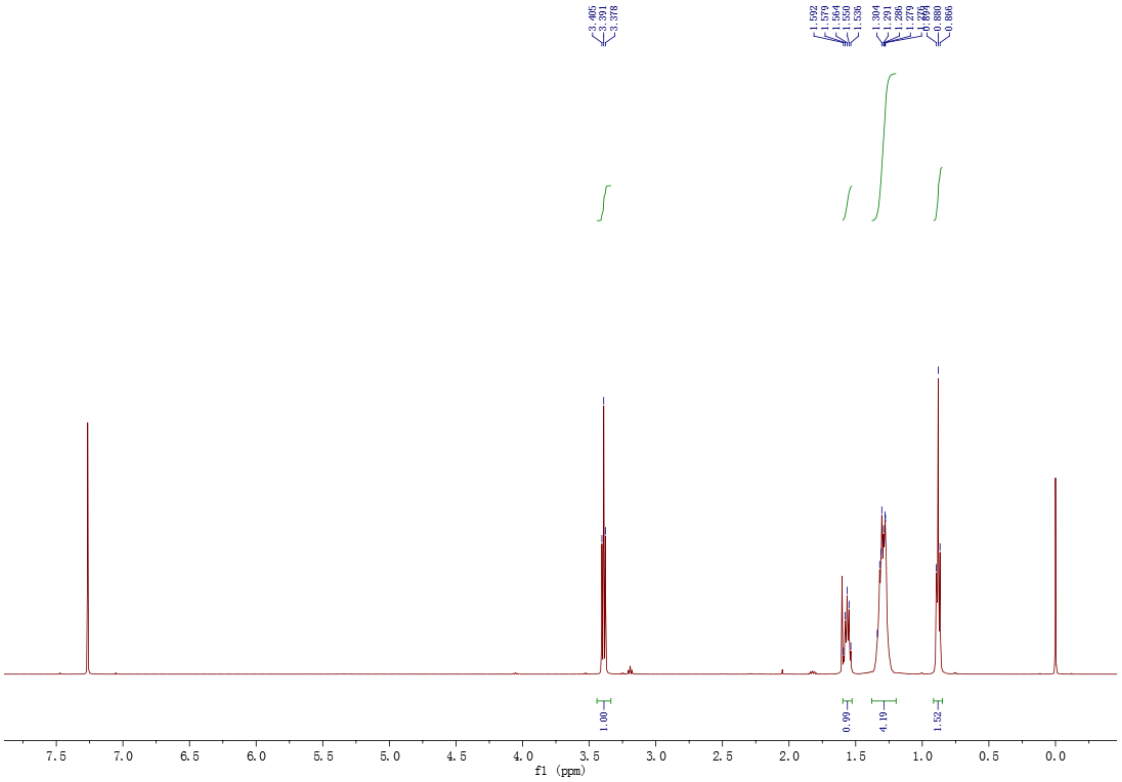
^{13}C NMR



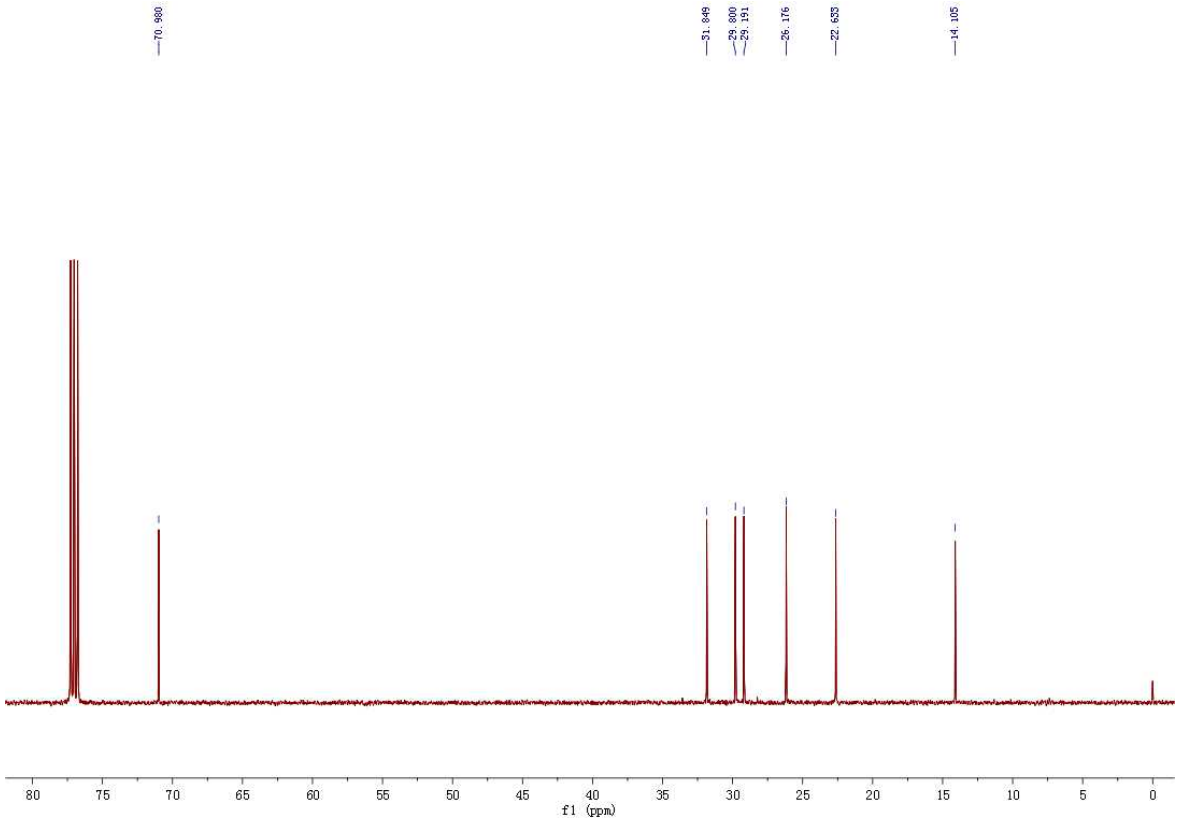


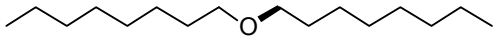
(2f)

^{1}H NMR



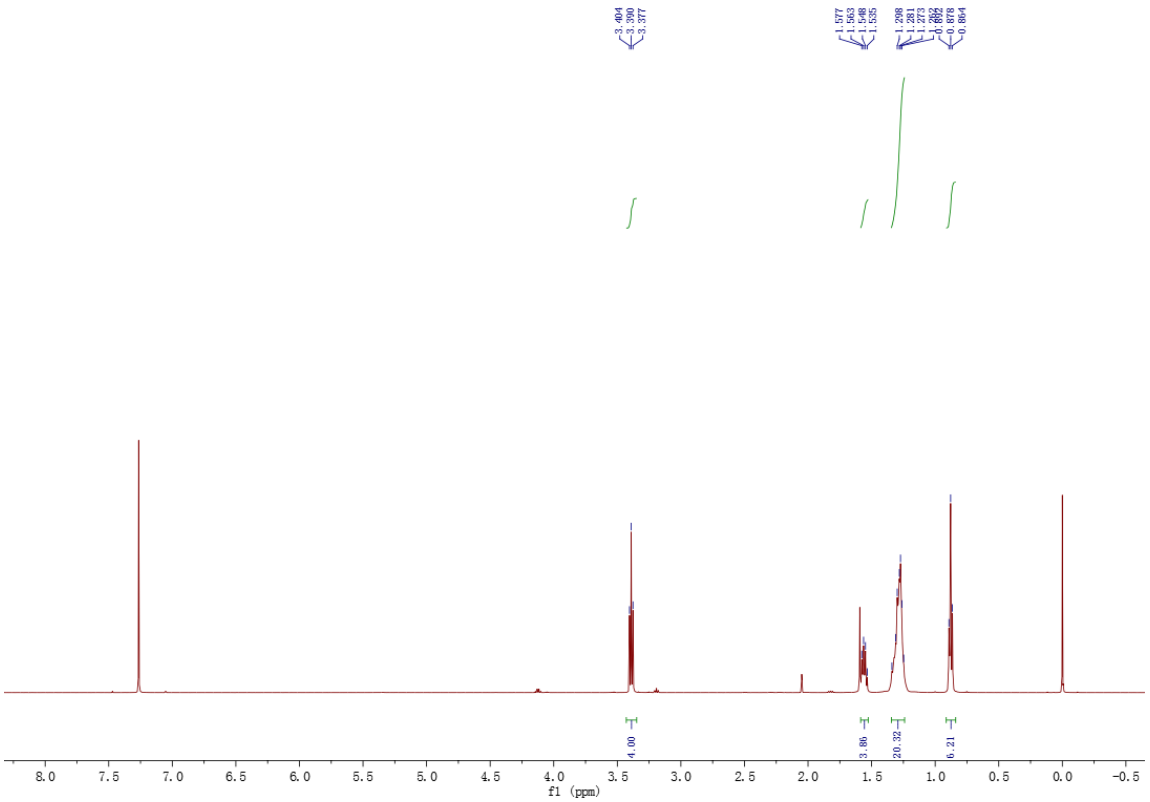
^{13}C NMR



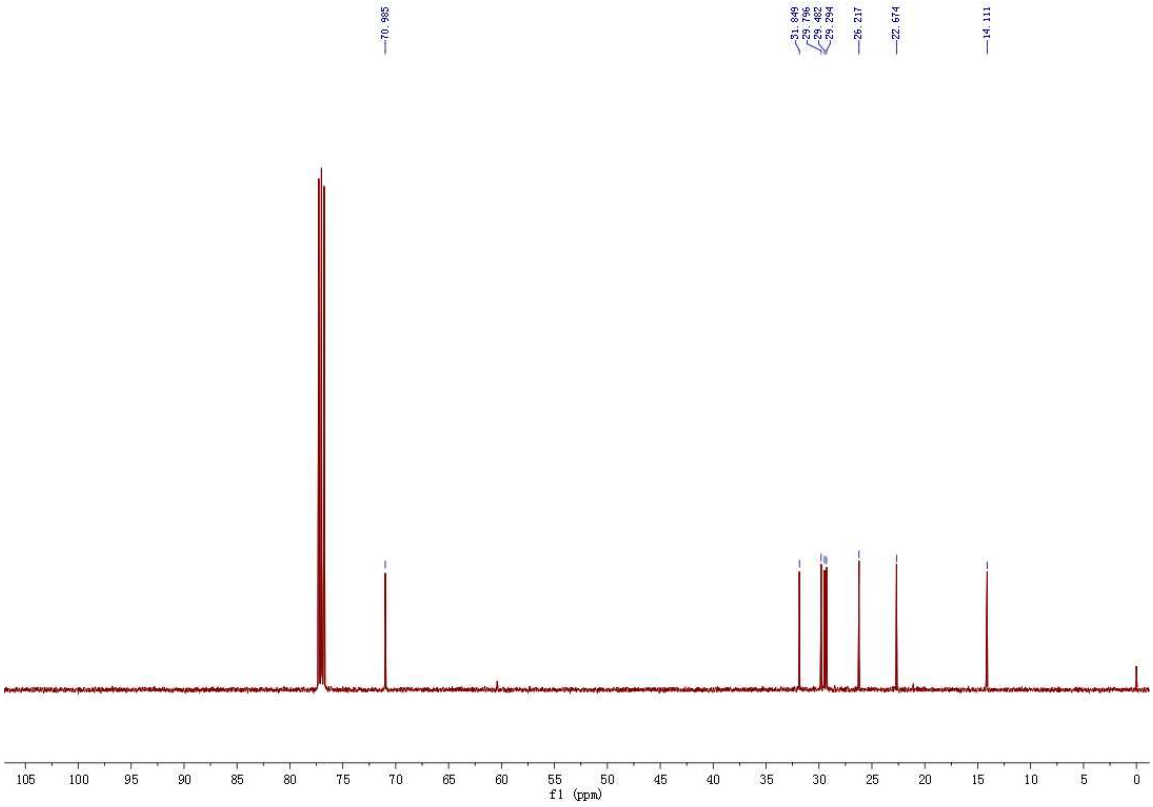


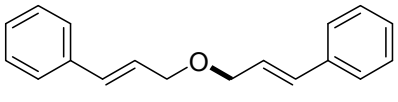
(2g)

^{1}H NMR



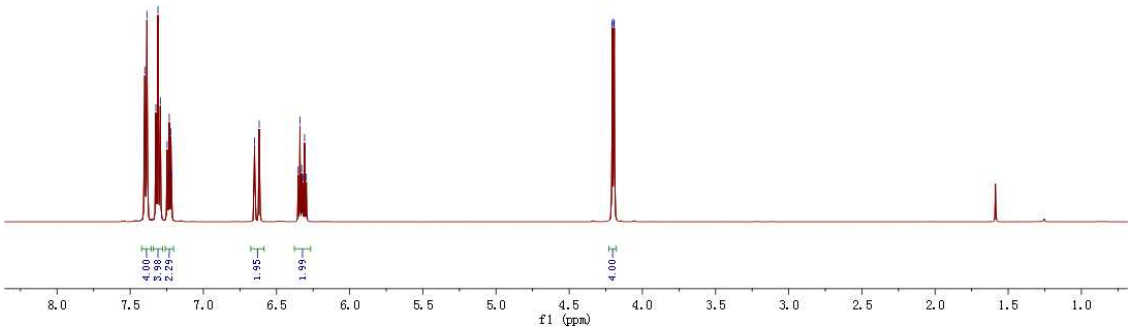
^{13}C NMR



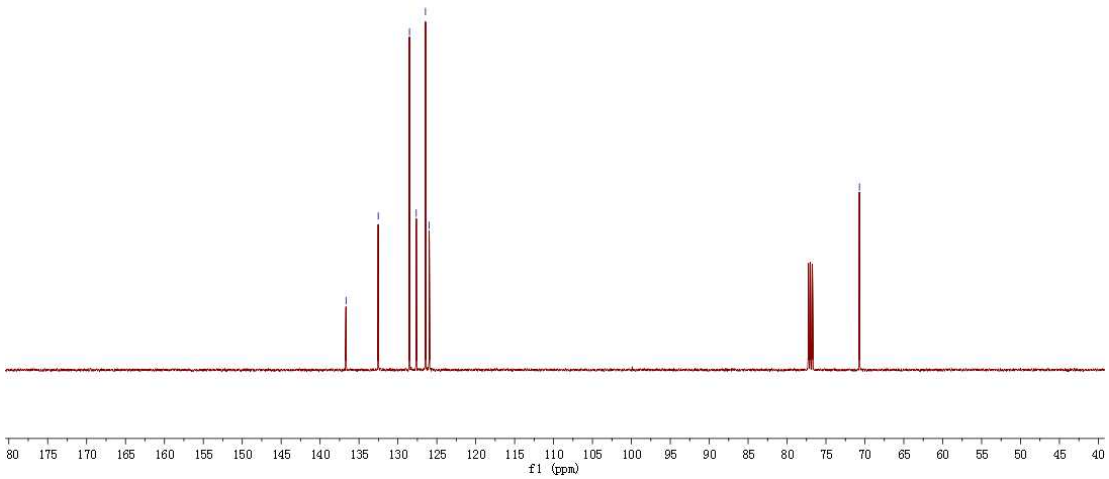


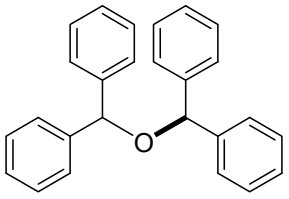
(2h)

^{1}H NMR



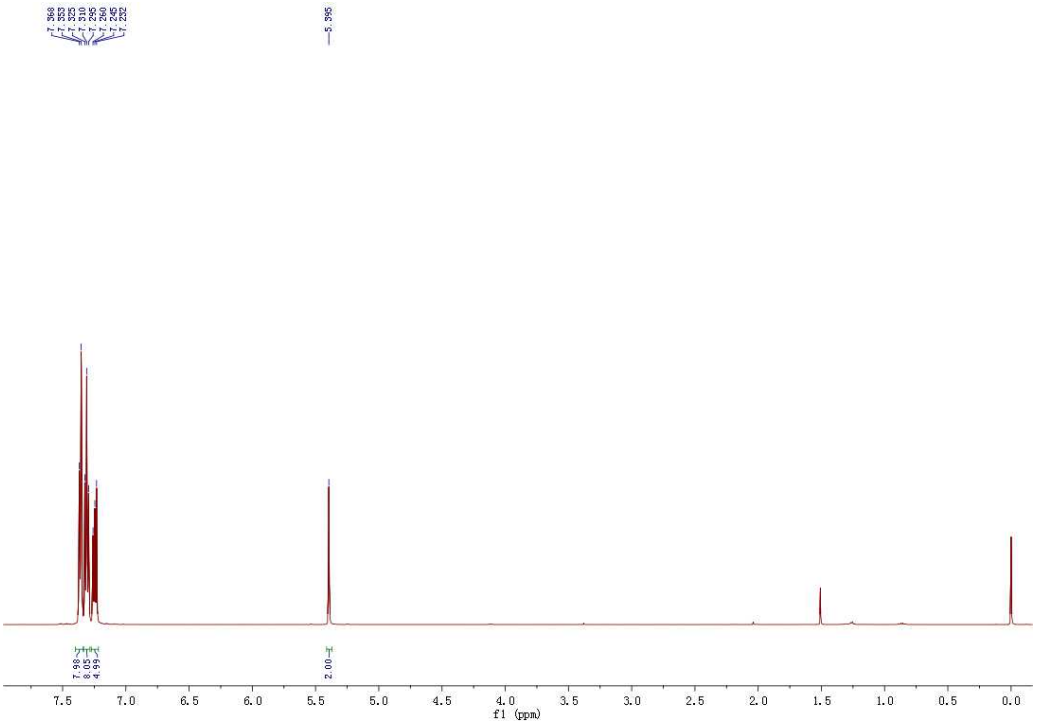
^{13}C NMR



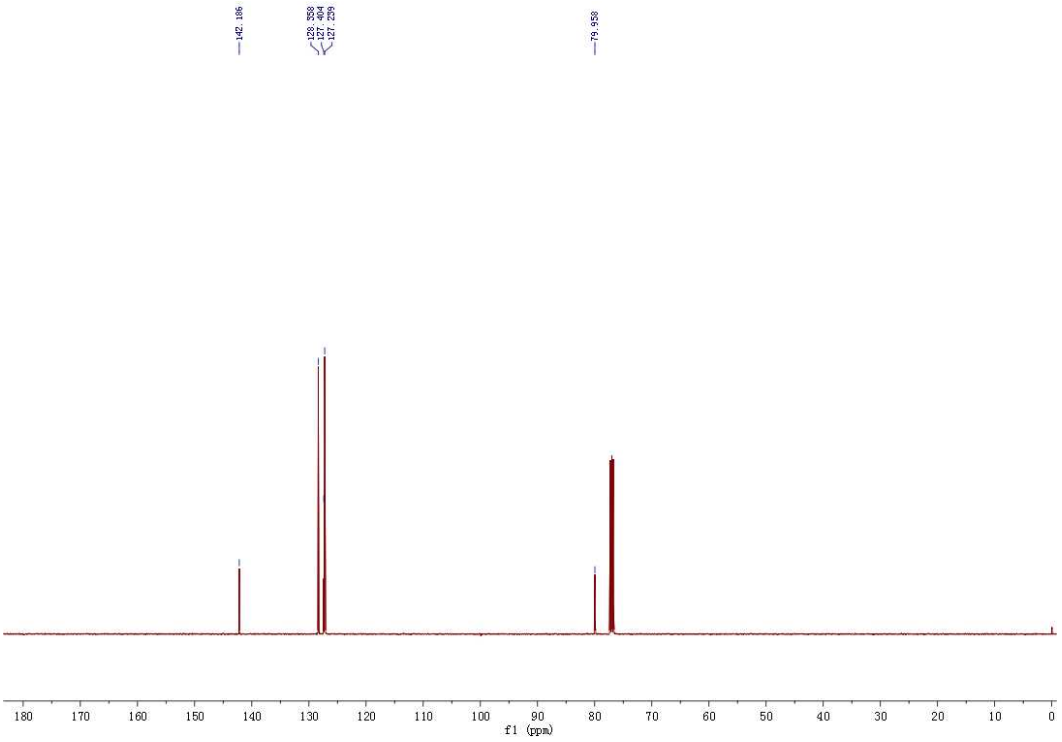


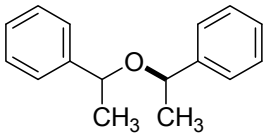
(2i)

^{1}H NMR



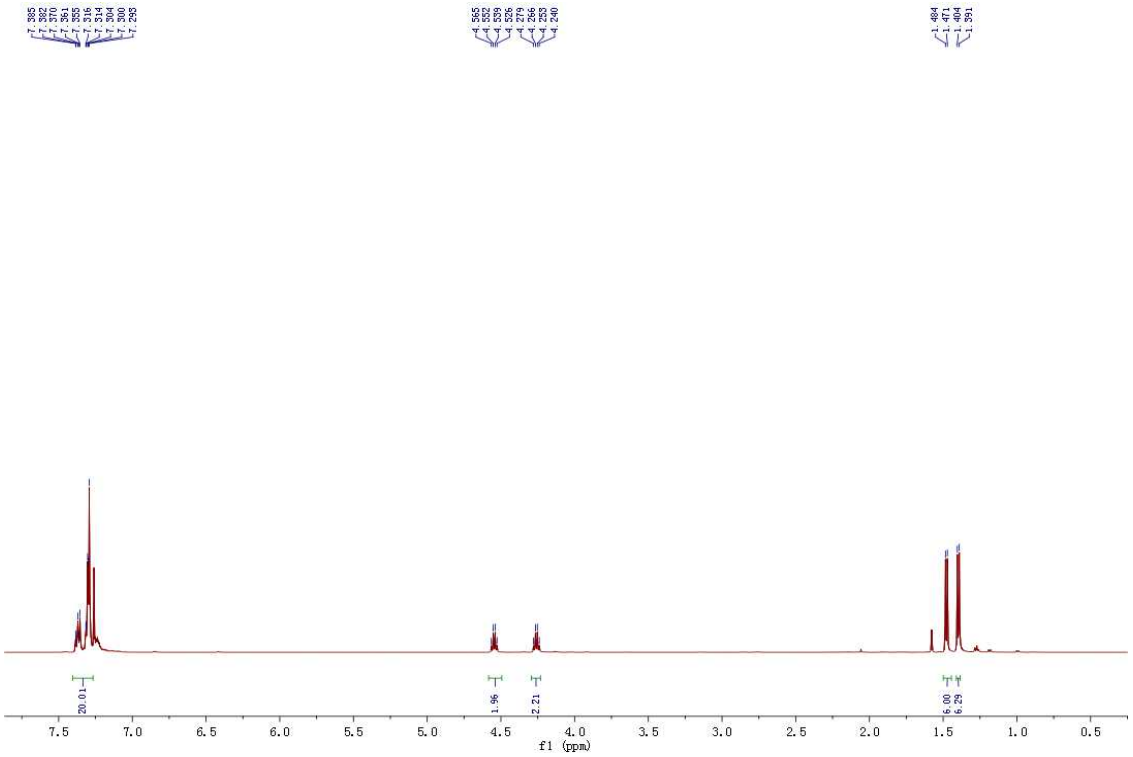
^{13}C NMR



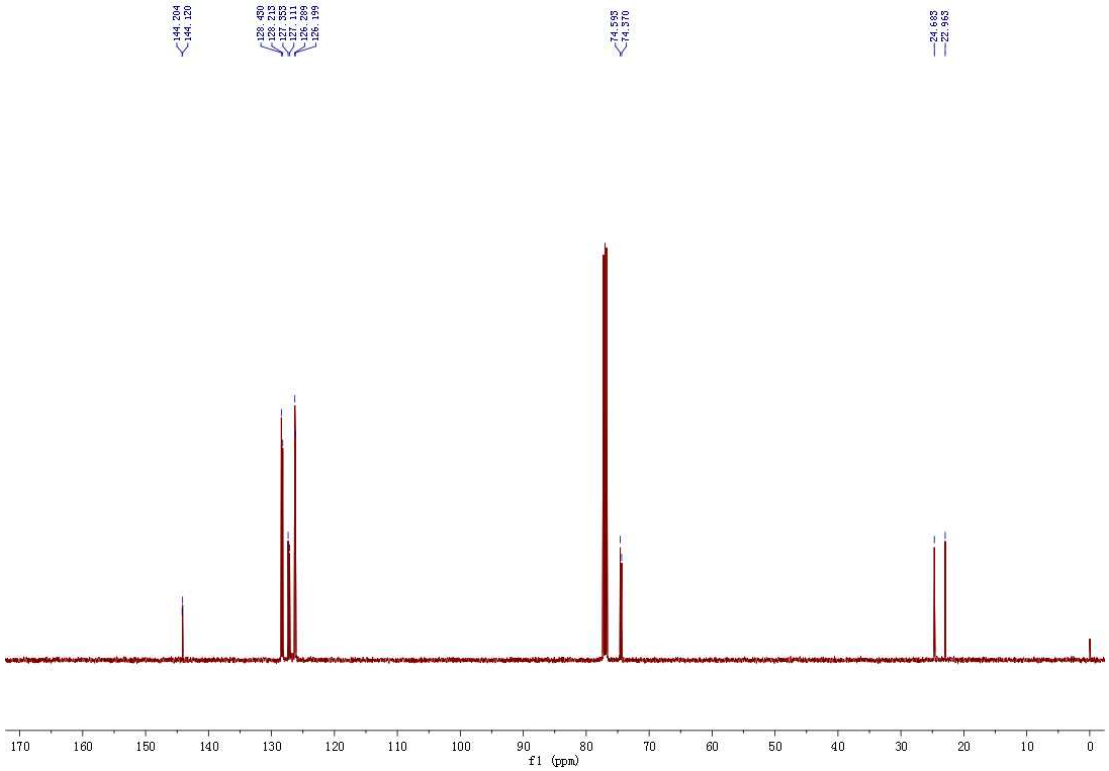


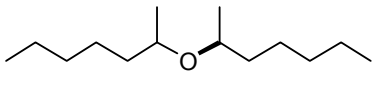
(2j)

^{1}H NMR



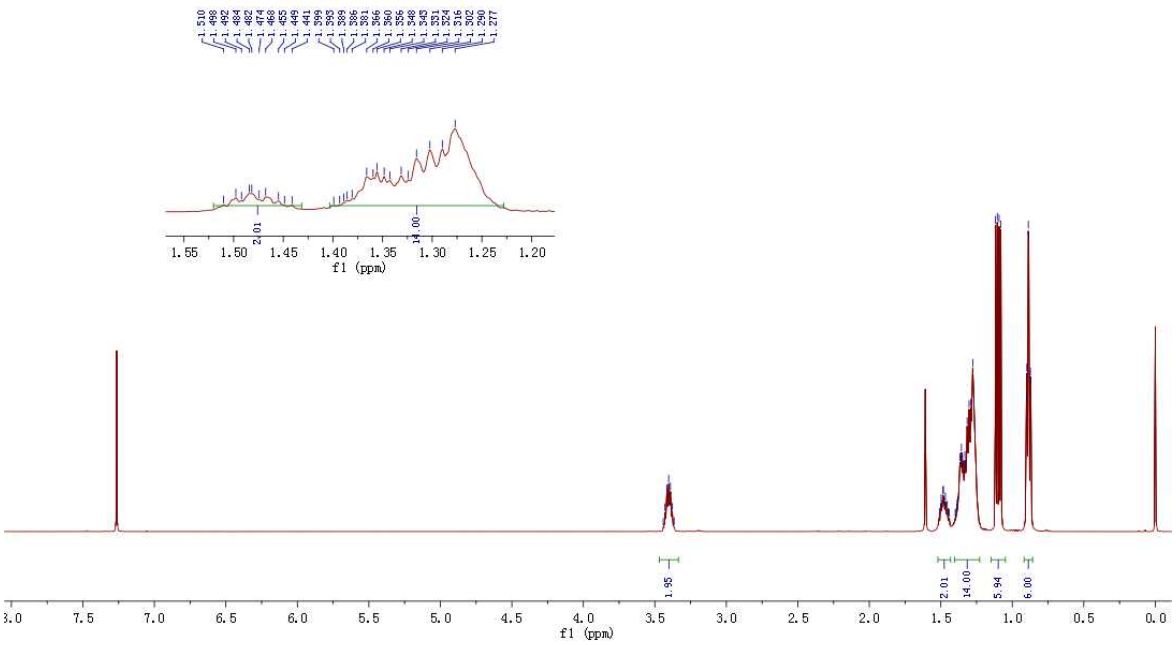
^{13}C NMR



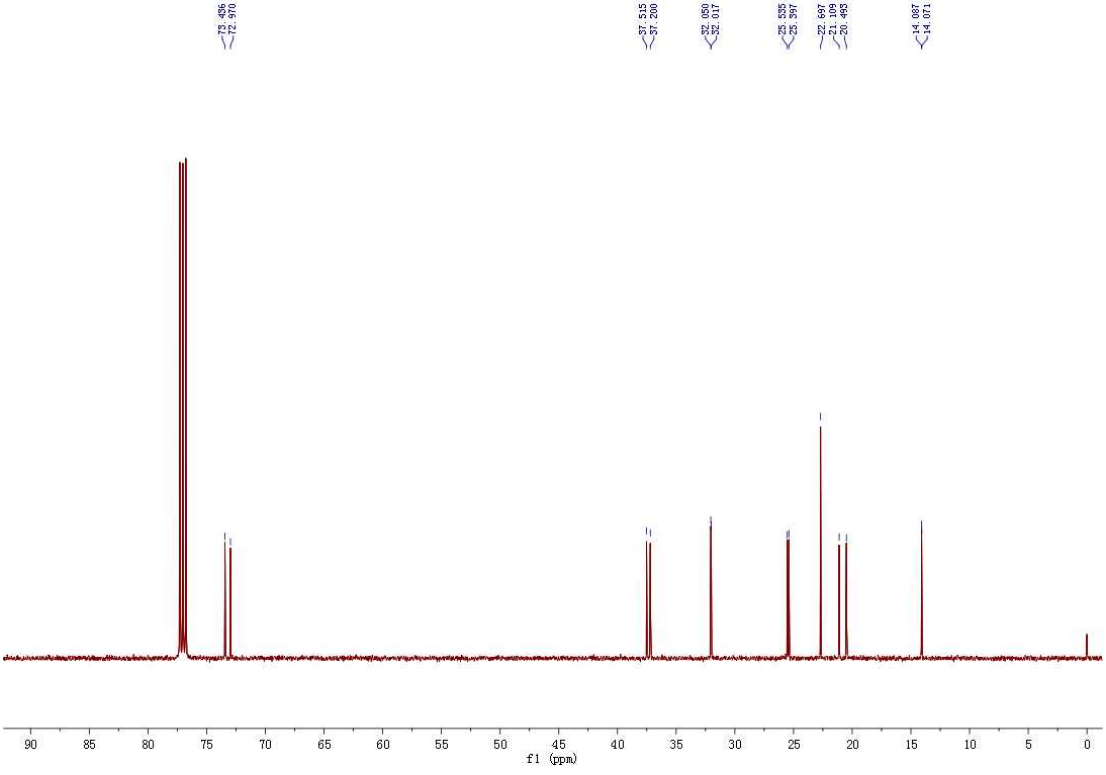


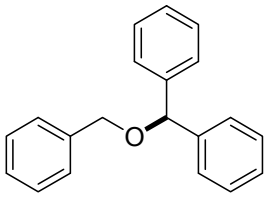
(2k)

^{1}H NMR



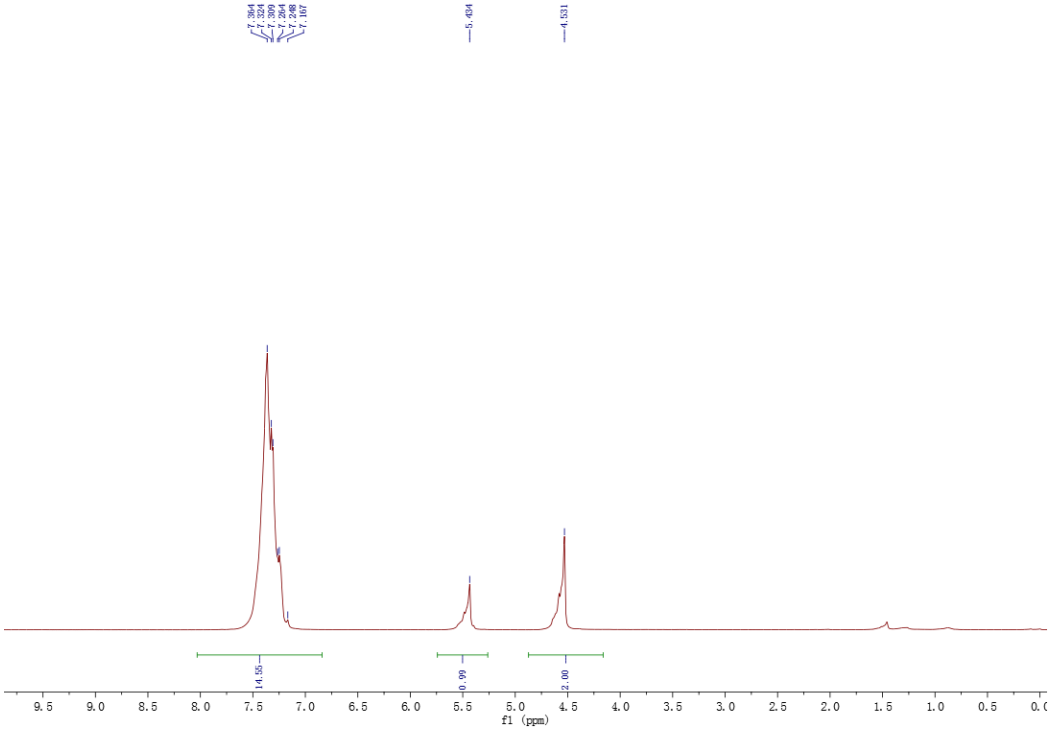
^{13}C NMR



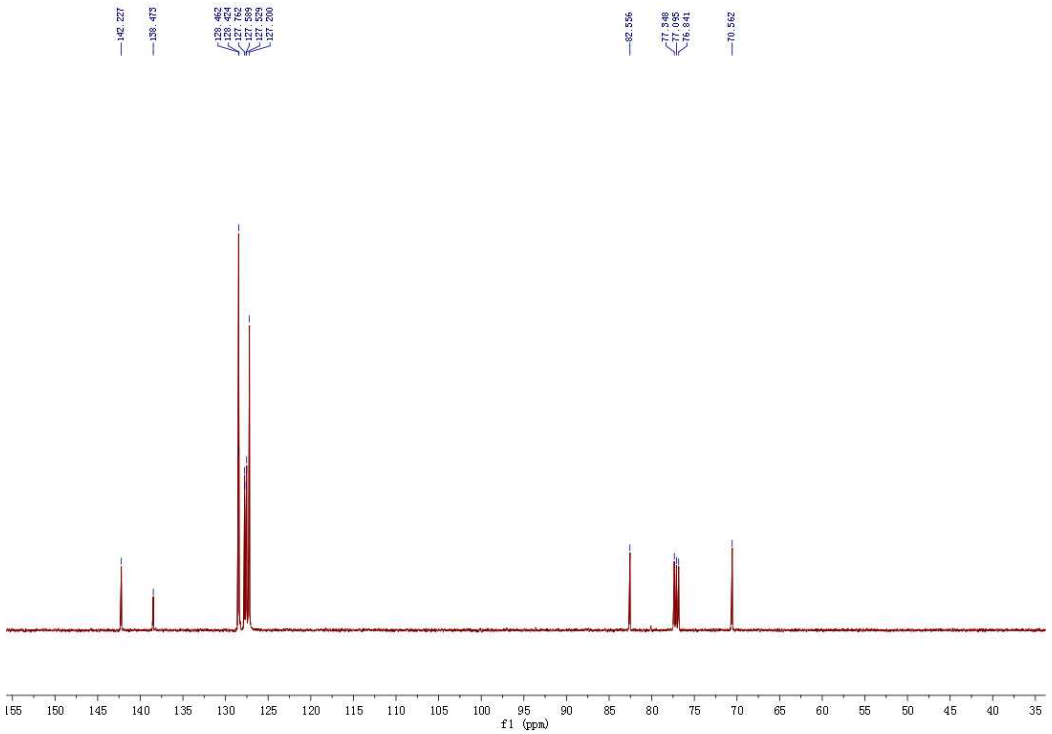


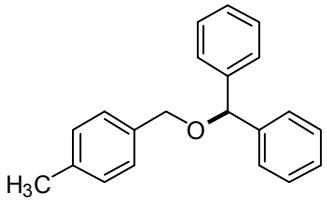
(3a)

^{1}H NMR



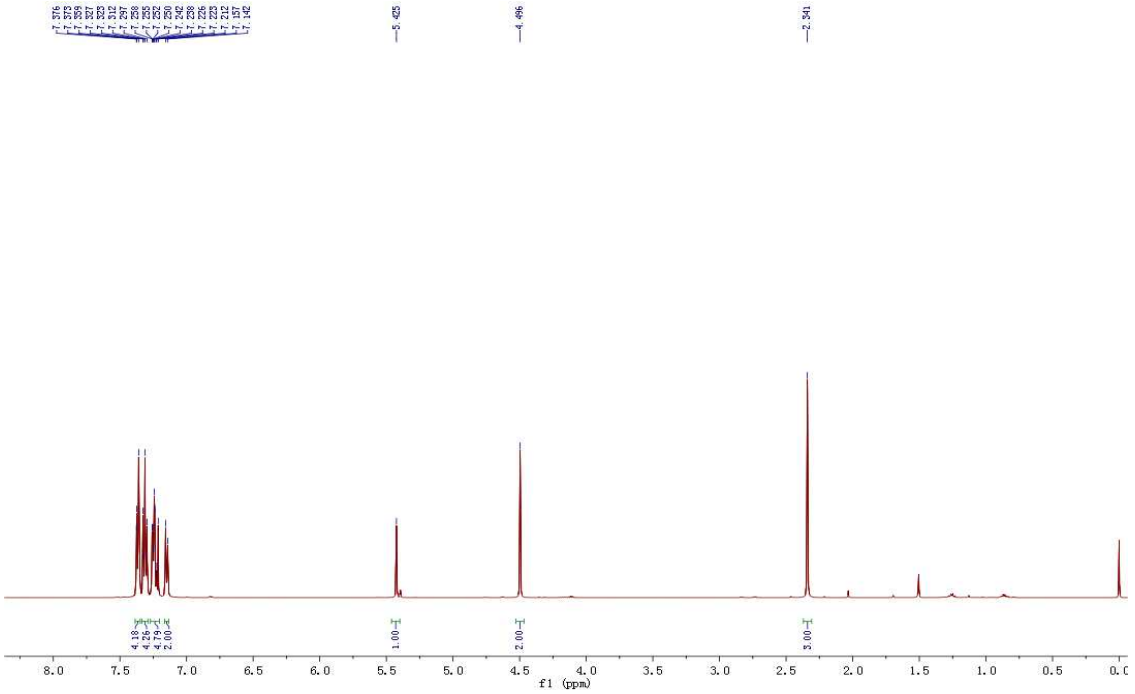
^{13}C NMR



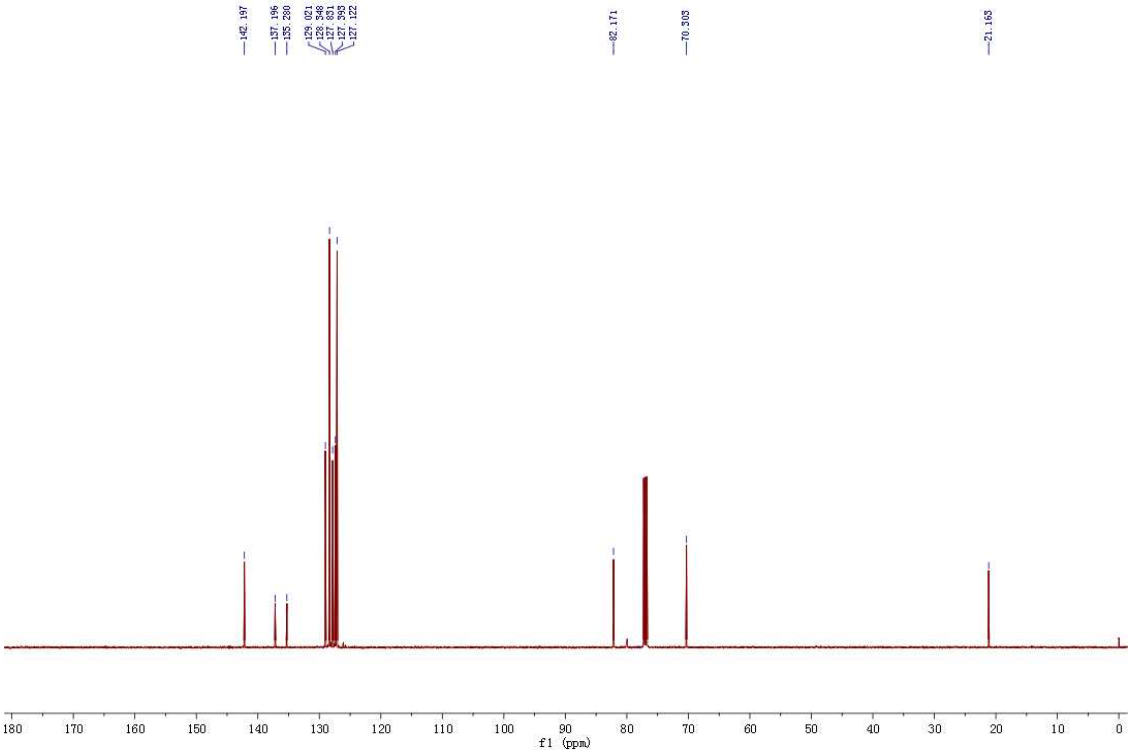


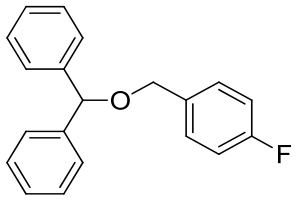
(3b)

^{1}H NMR



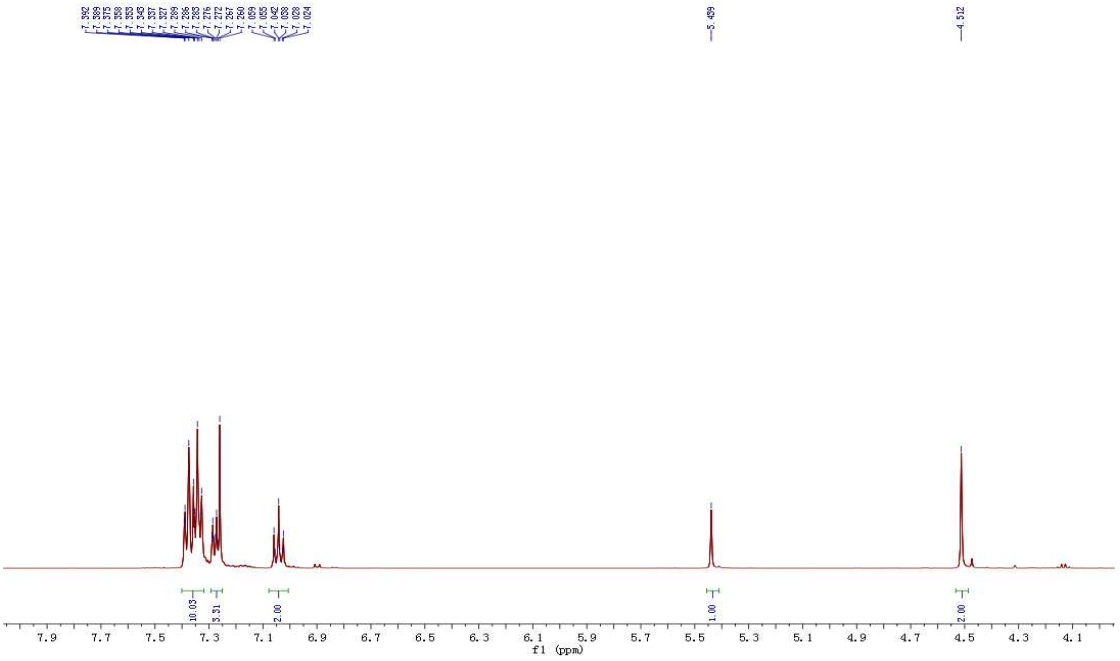
^{13}C NMR



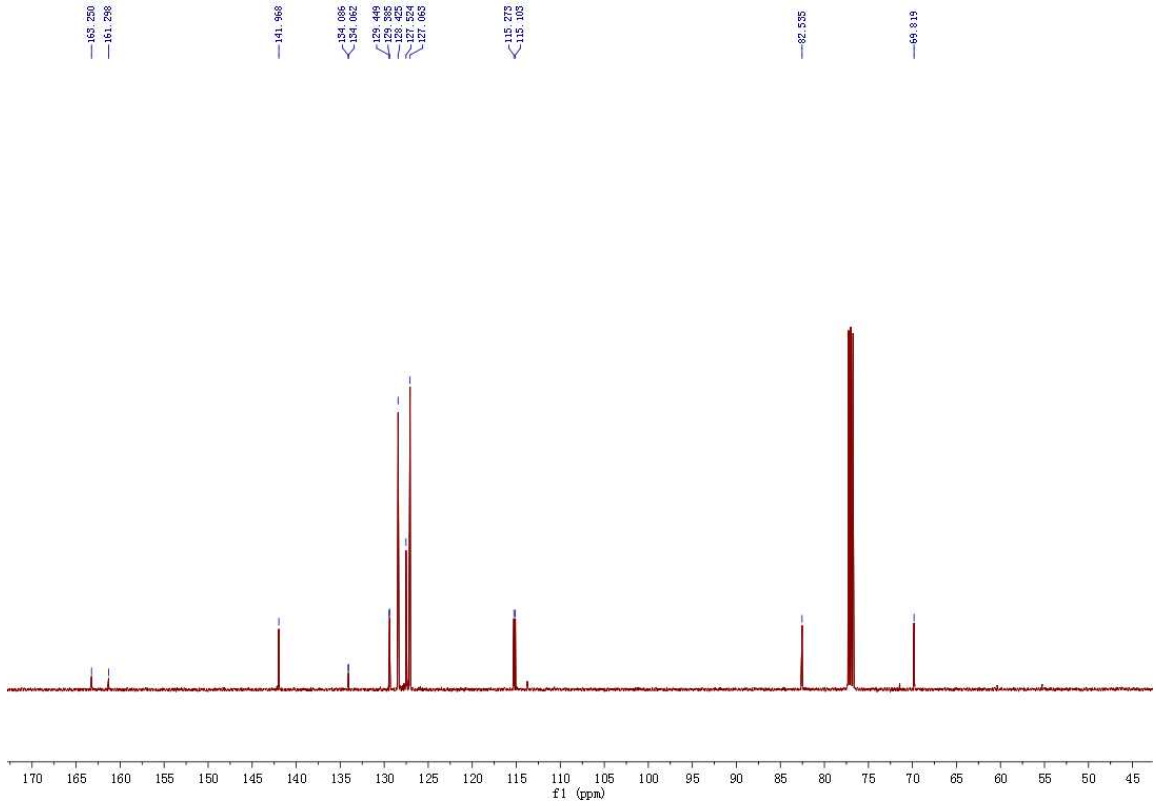


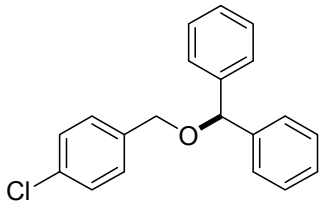
(3c)

^{1}H NMR



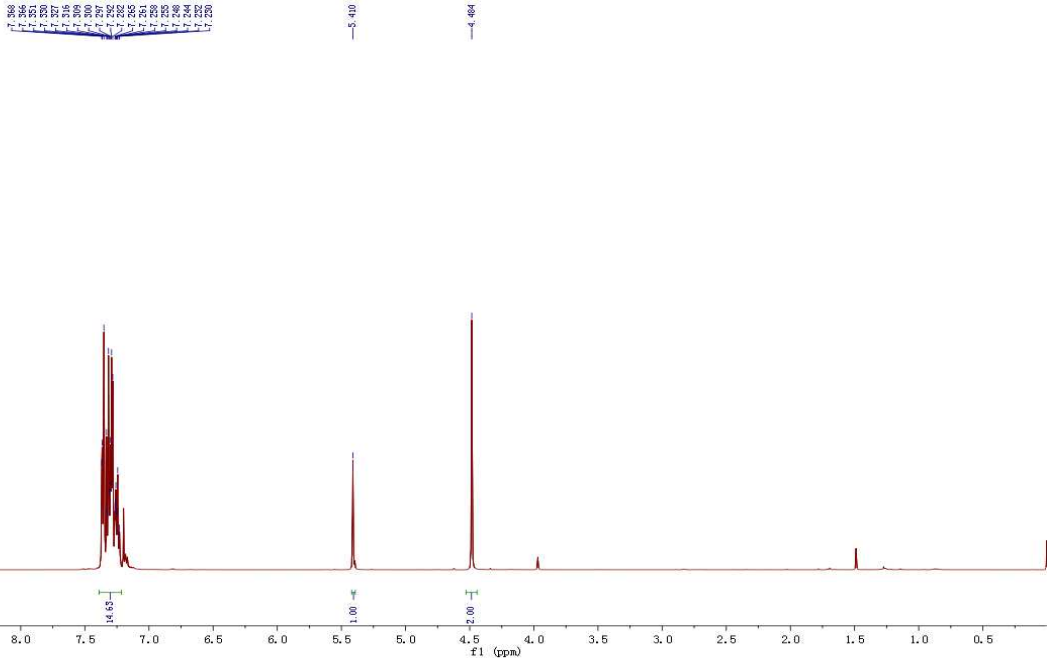
^{13}C NMR



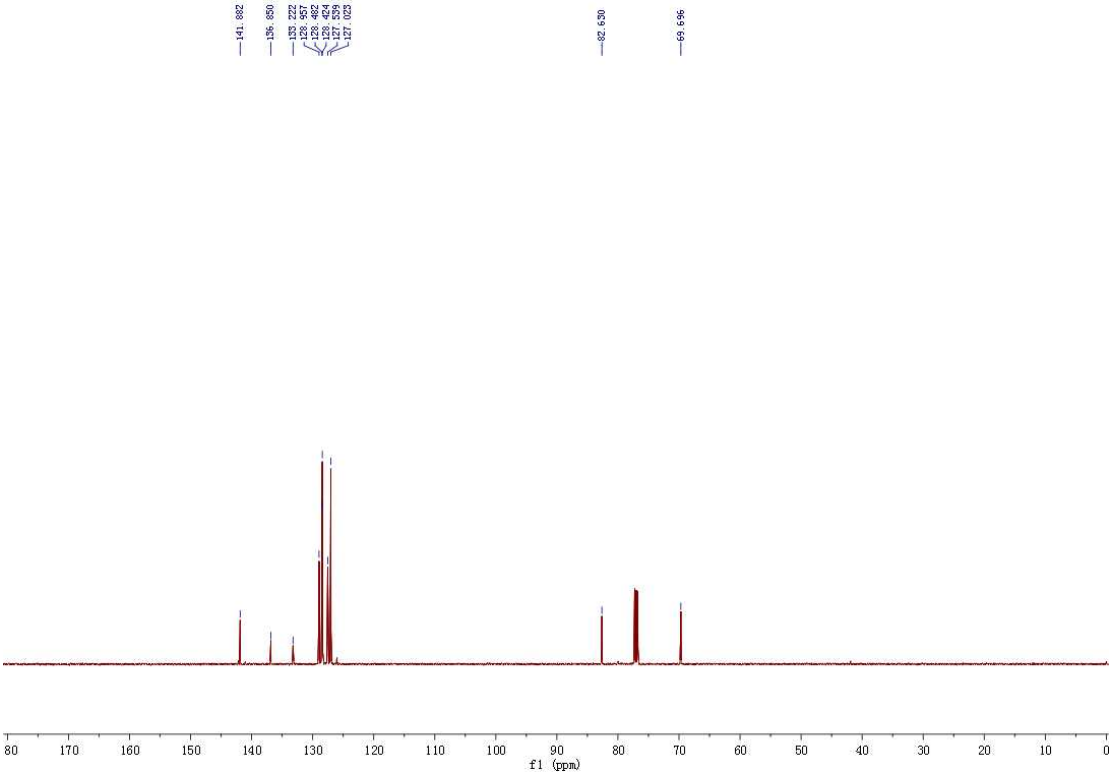


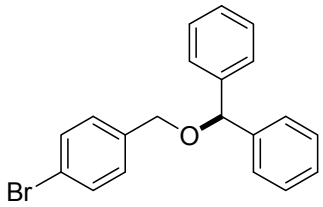
(3d)

^{1}H NMR



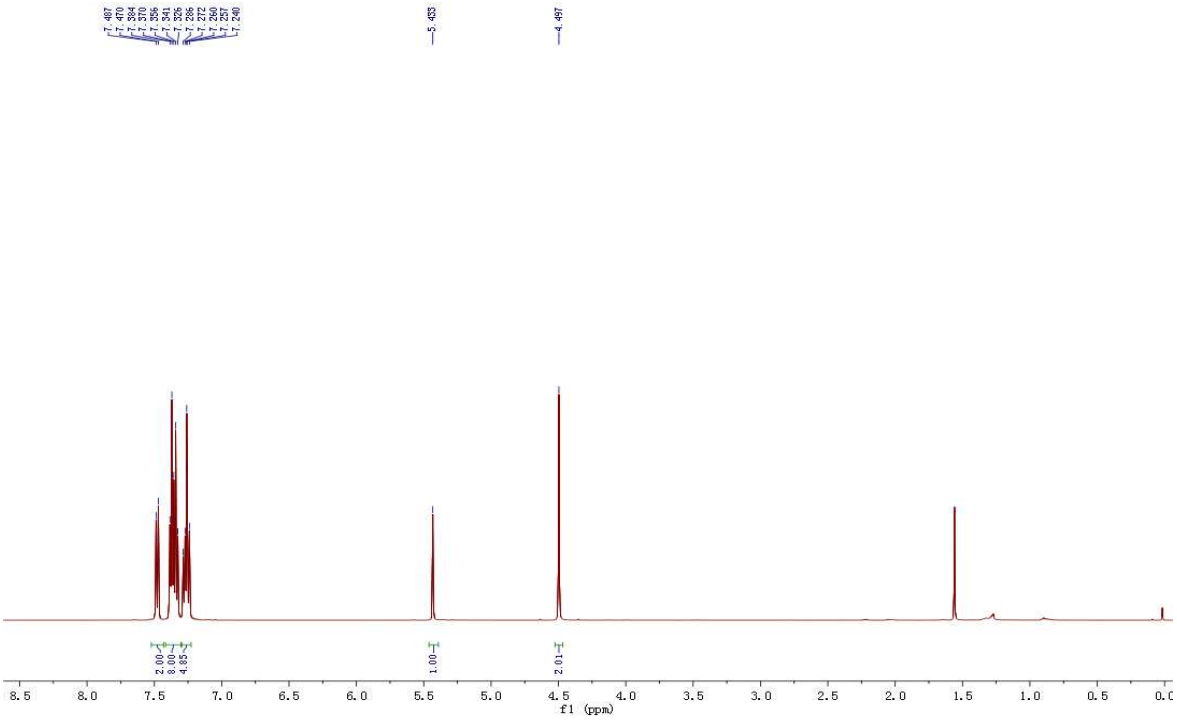
^{13}C NMR





(3e)

^{1}H NMR



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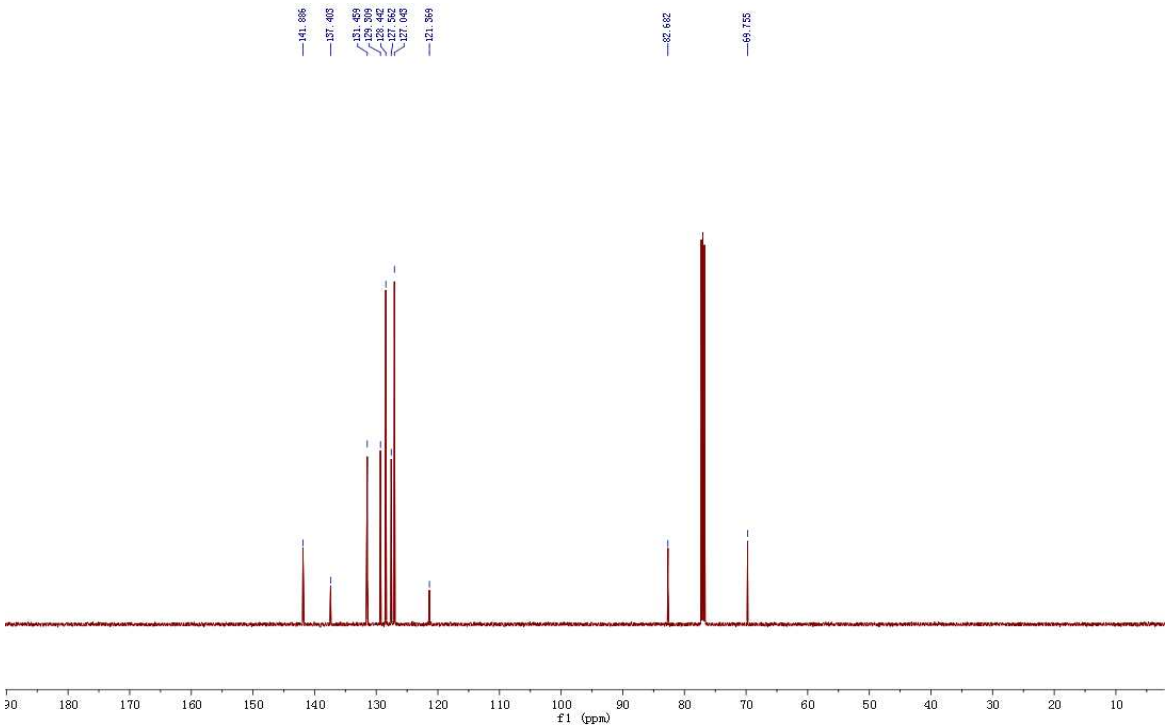
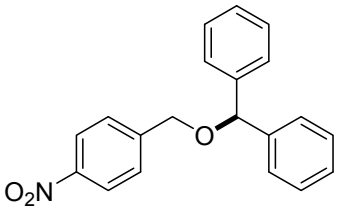
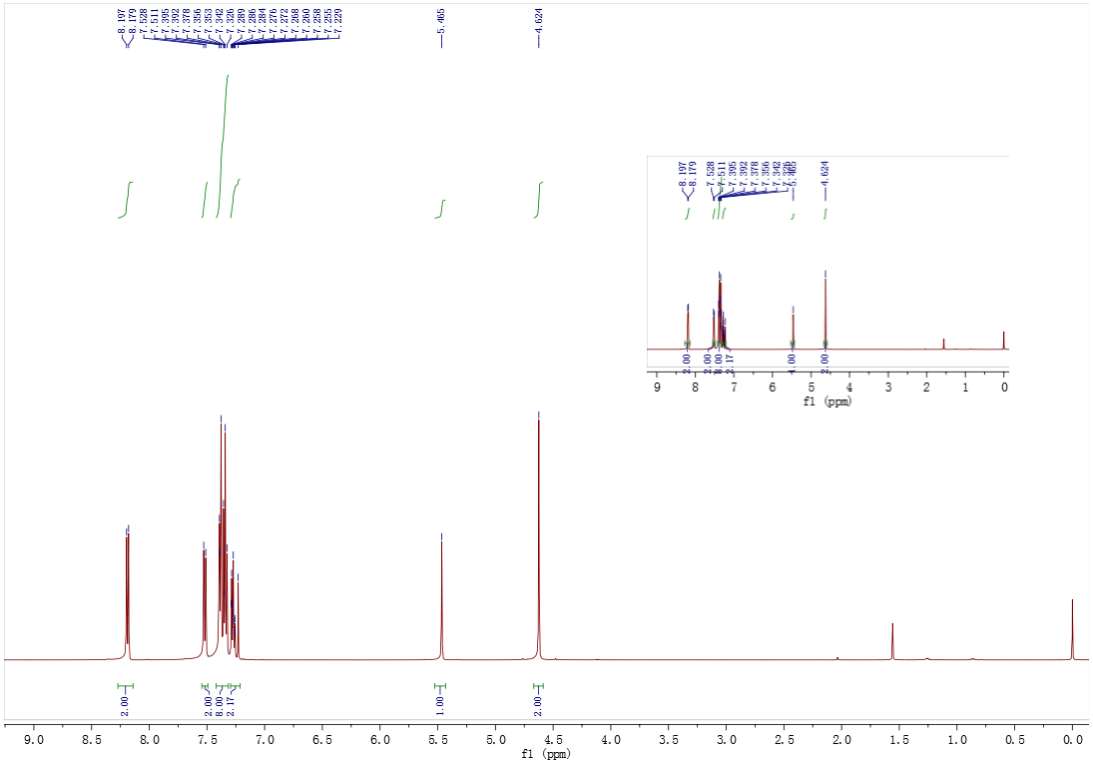




(3f)

^{1}H NMR



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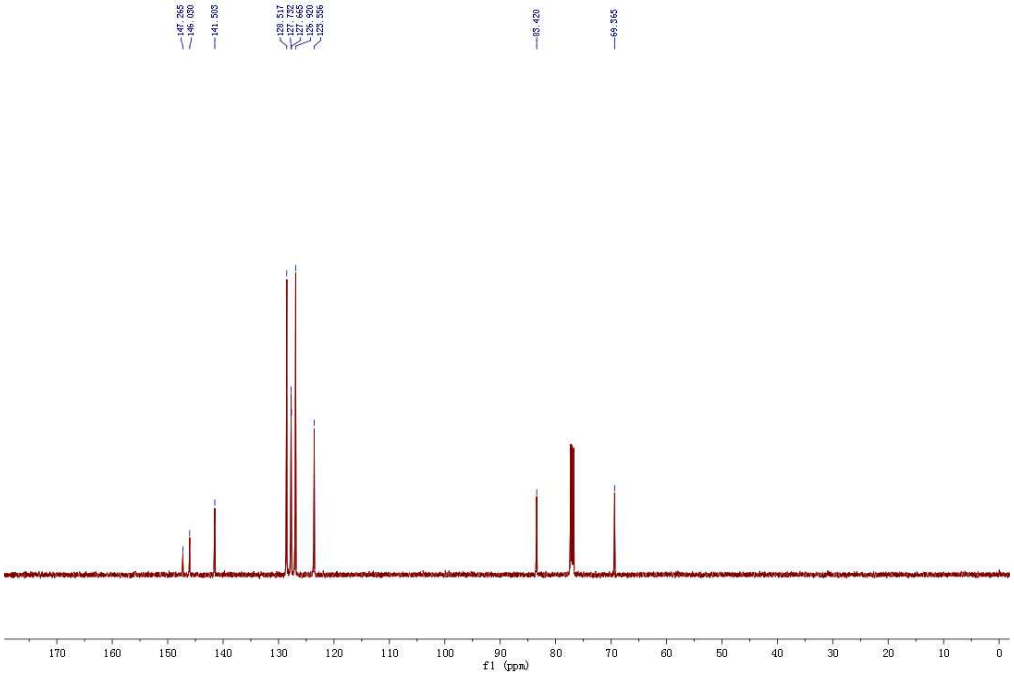
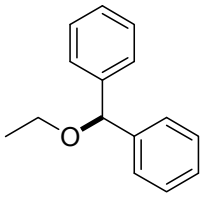
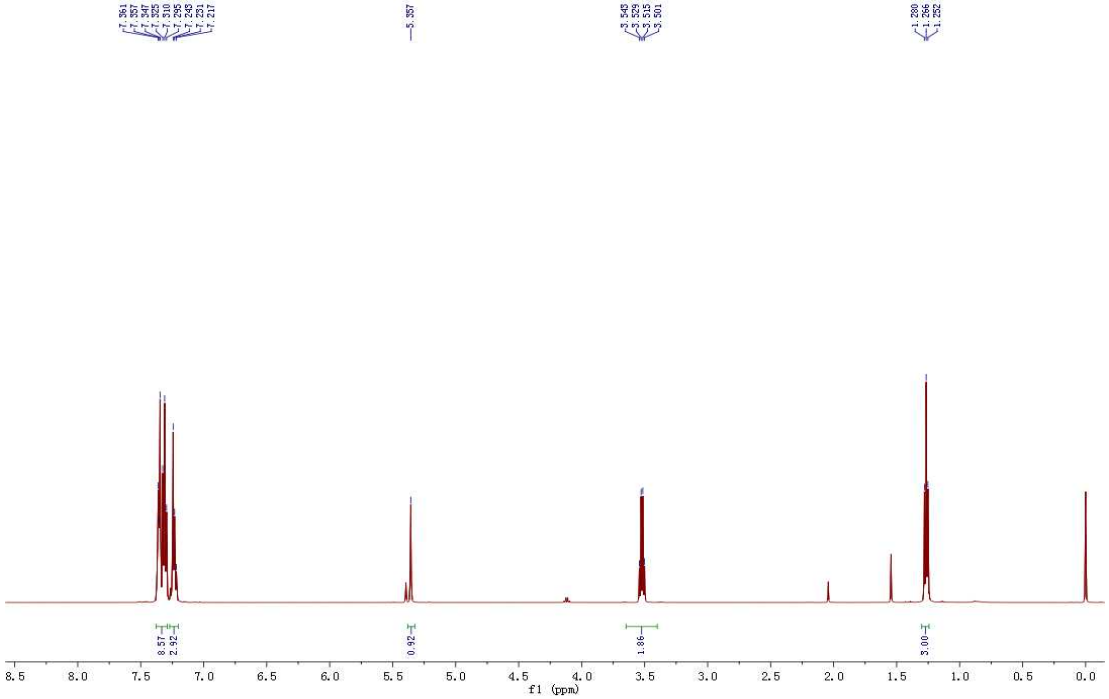




(3g)

^{1}H NMR



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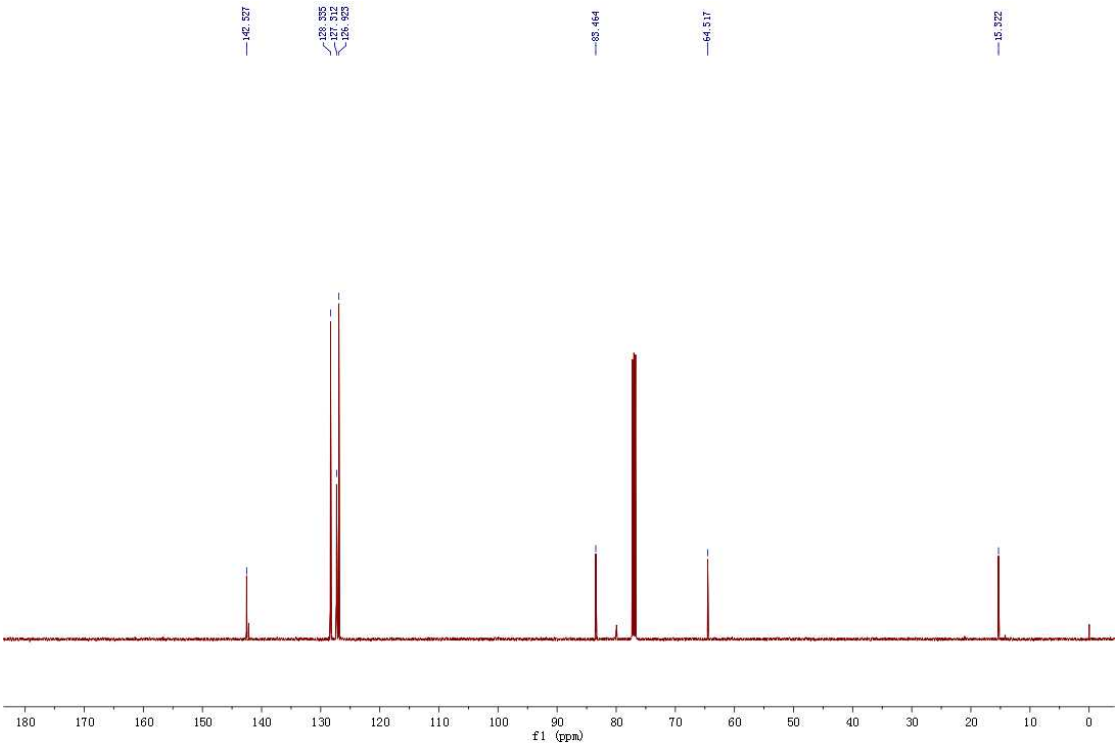
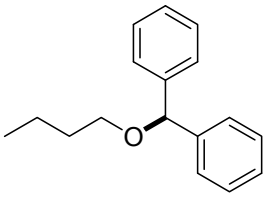
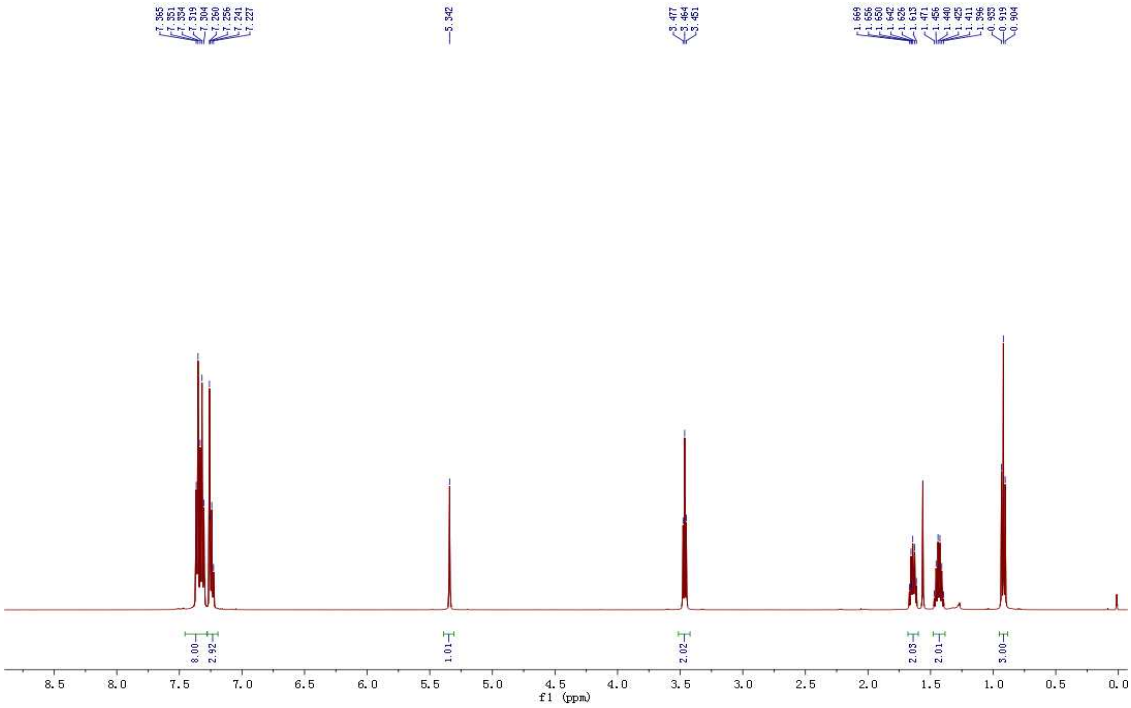




(3h)

^{1}H NMR



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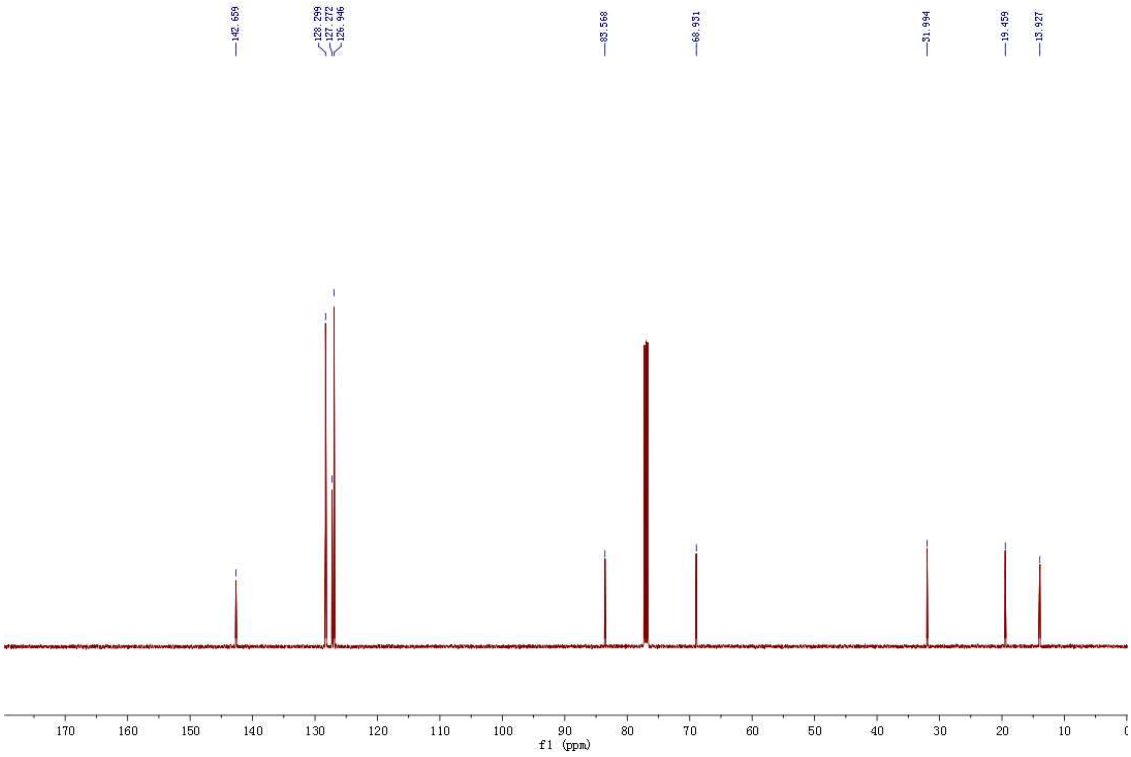
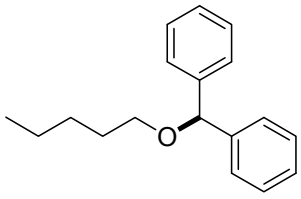
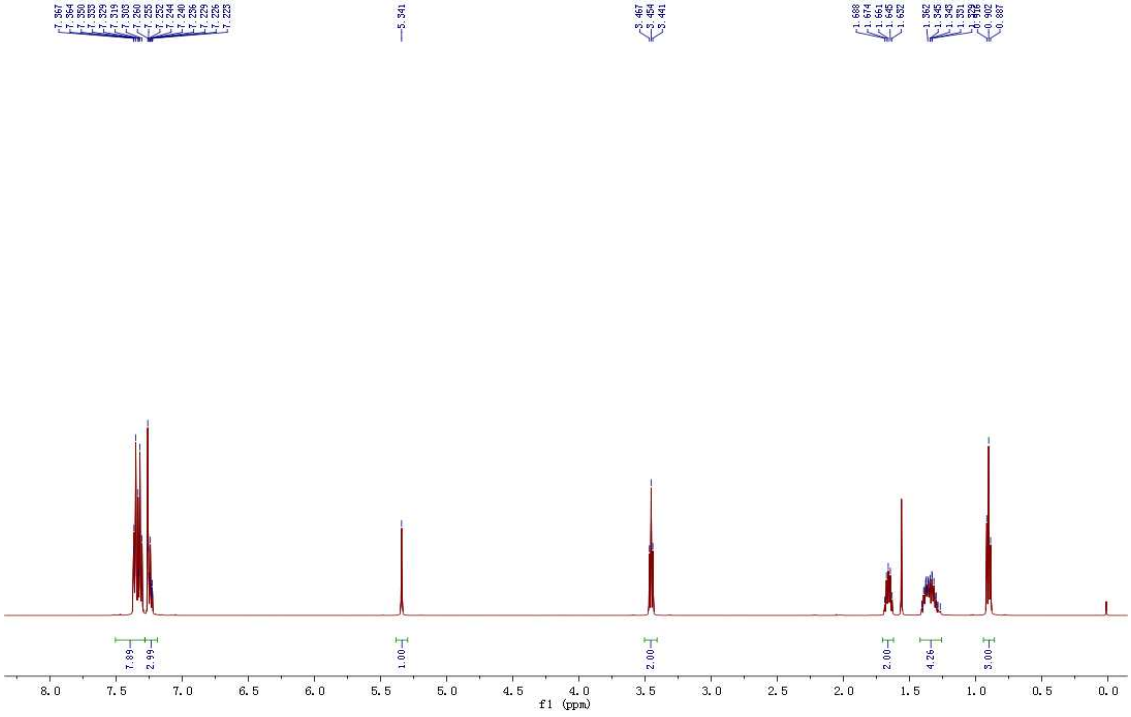


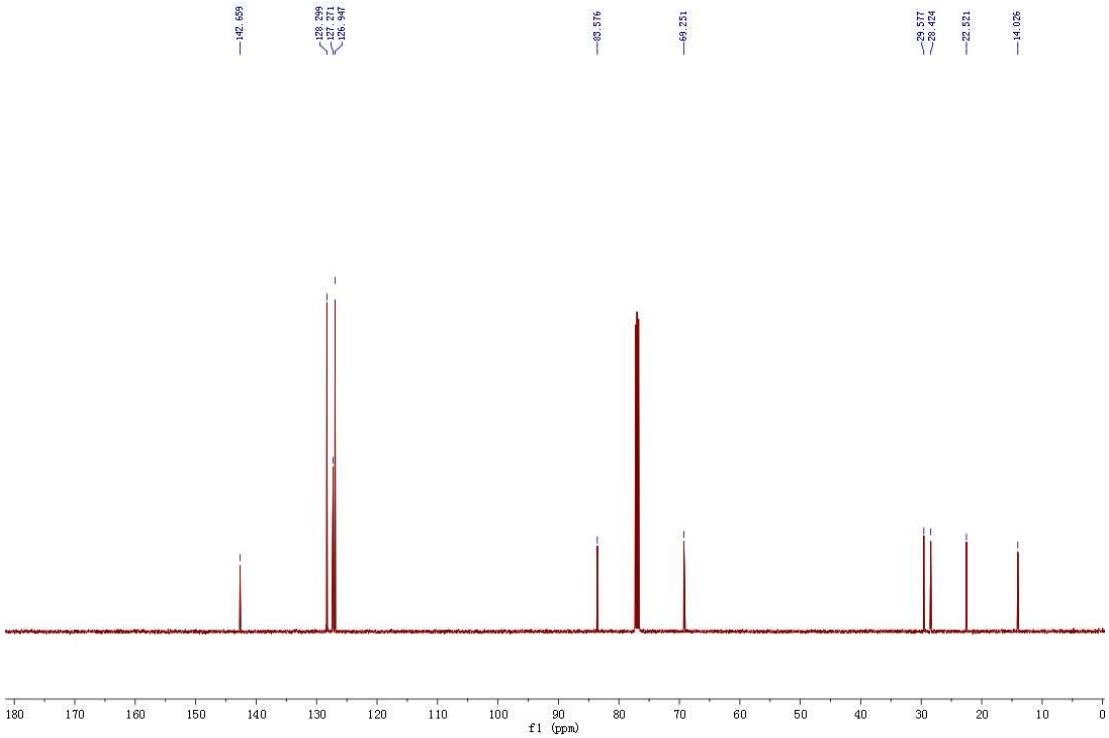


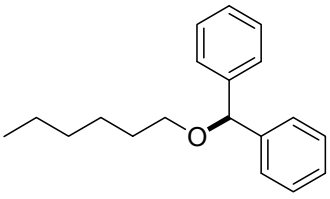
(3i)

^{1}H NMR



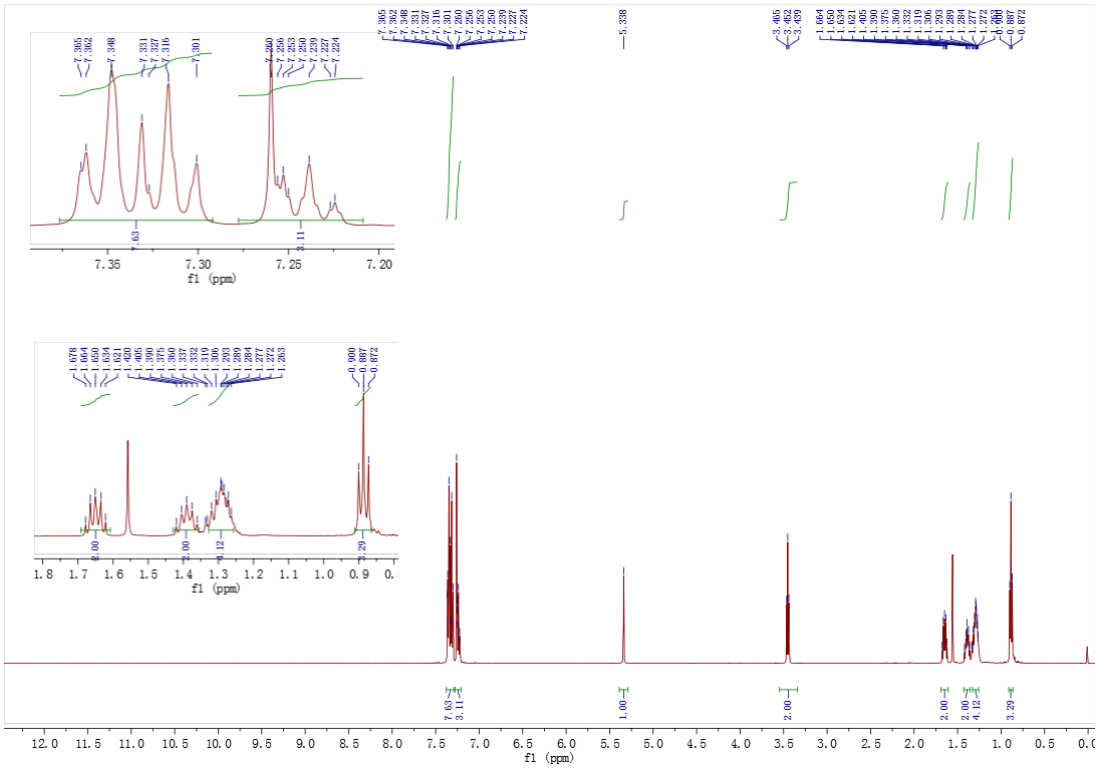
^{13}C NMR



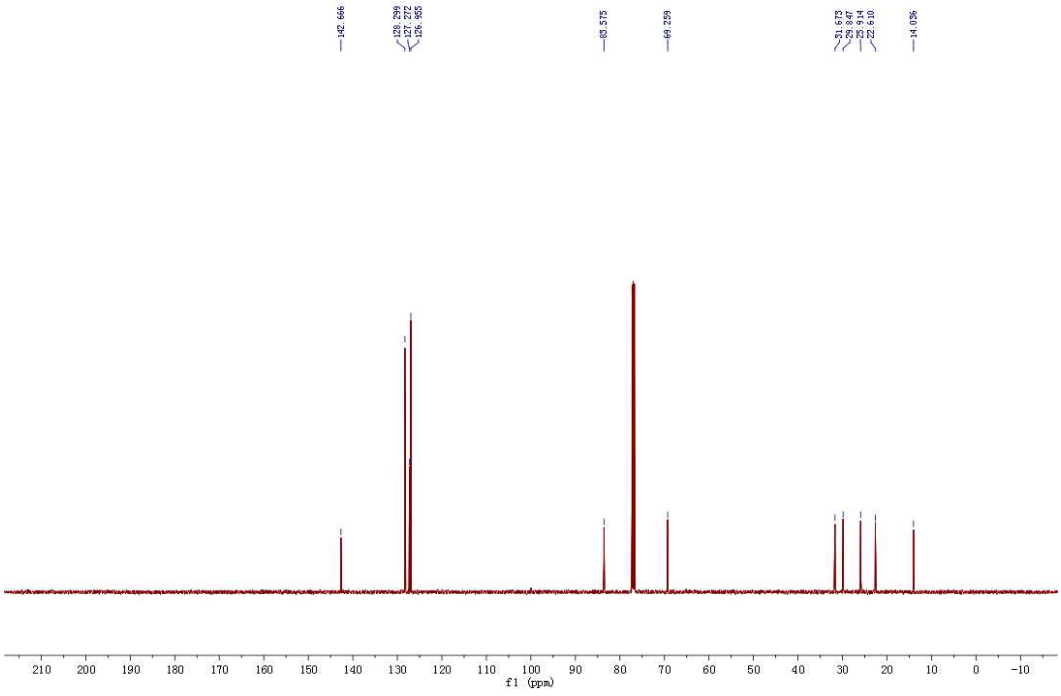


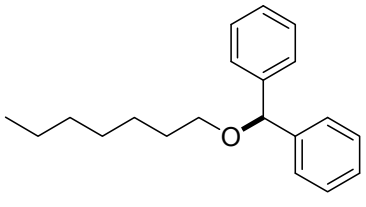
(3j)

^{1}H NMR



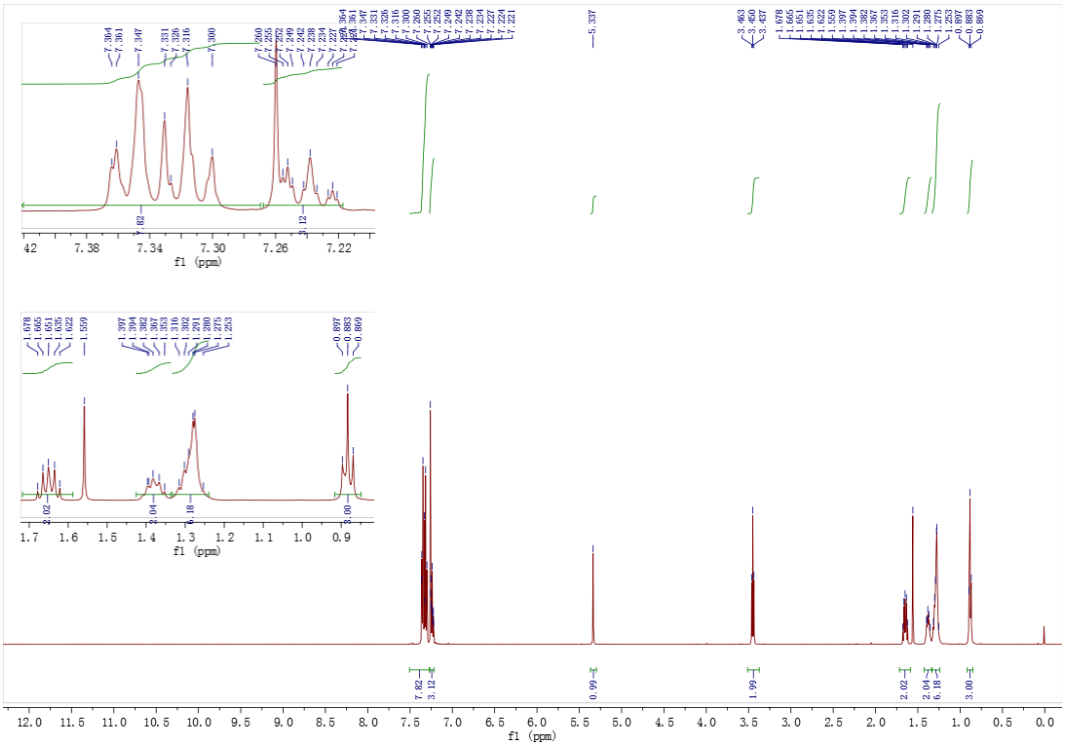
^{13}C NMR



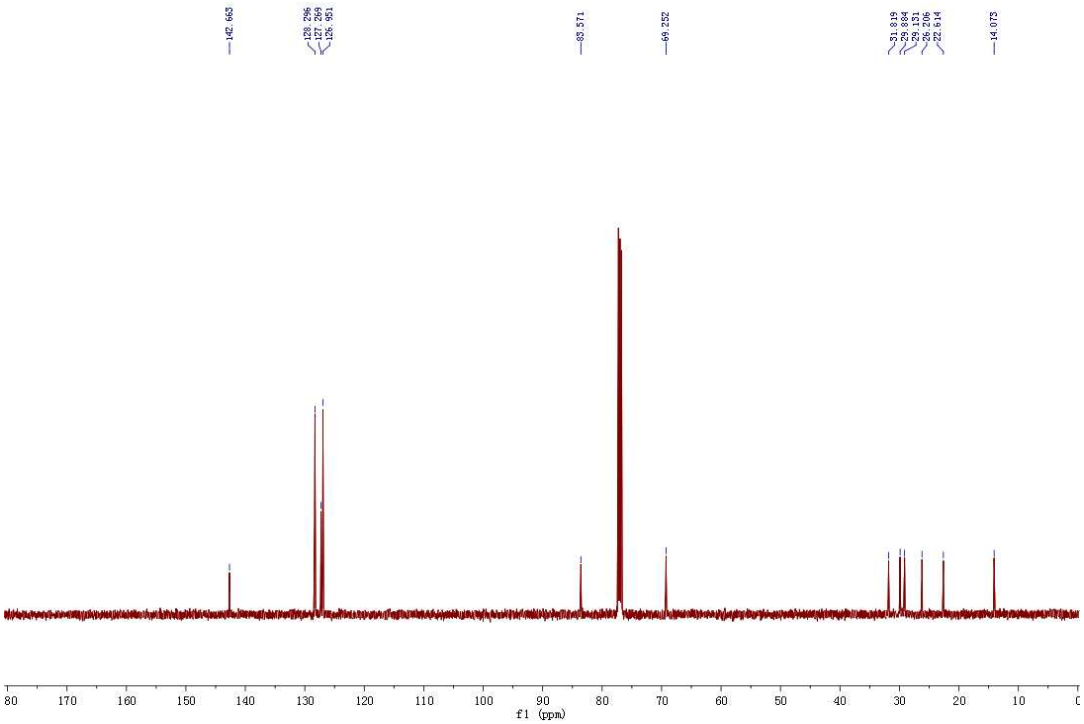


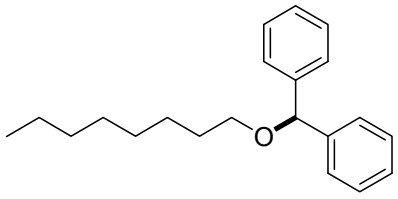
(3k)

^{1}H NMR



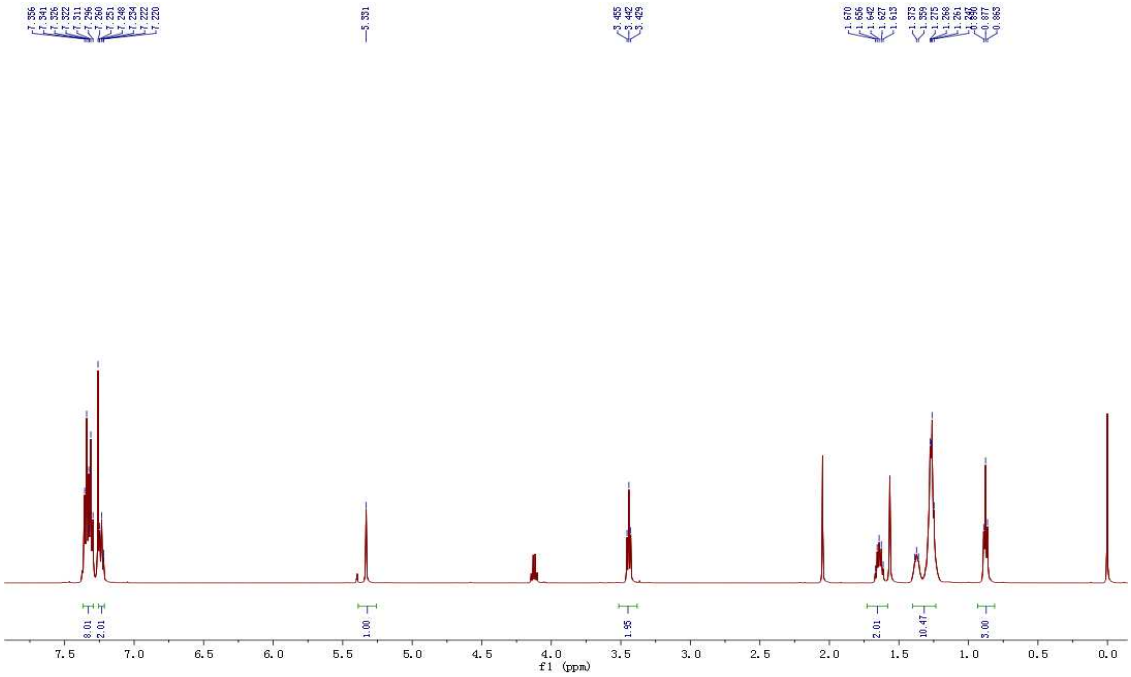
^{13}C NMR



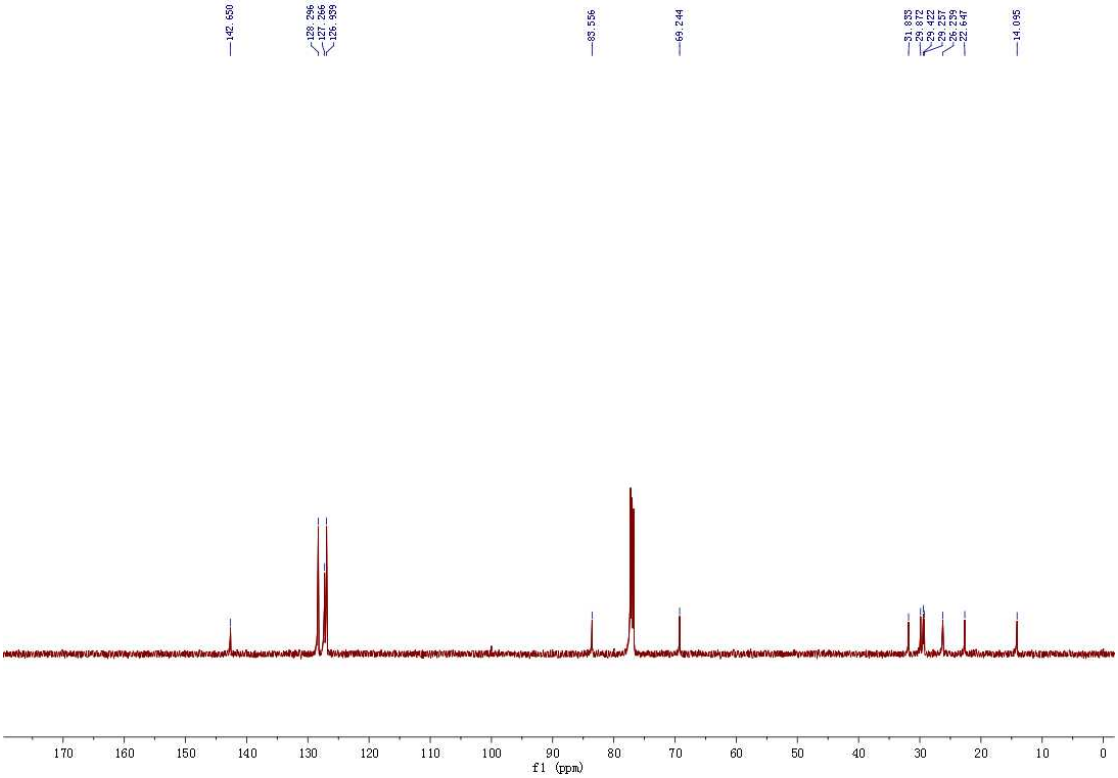


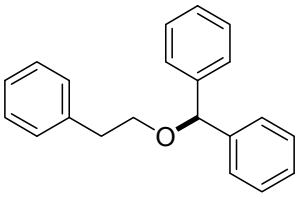
(3l)

^{1}H NMR



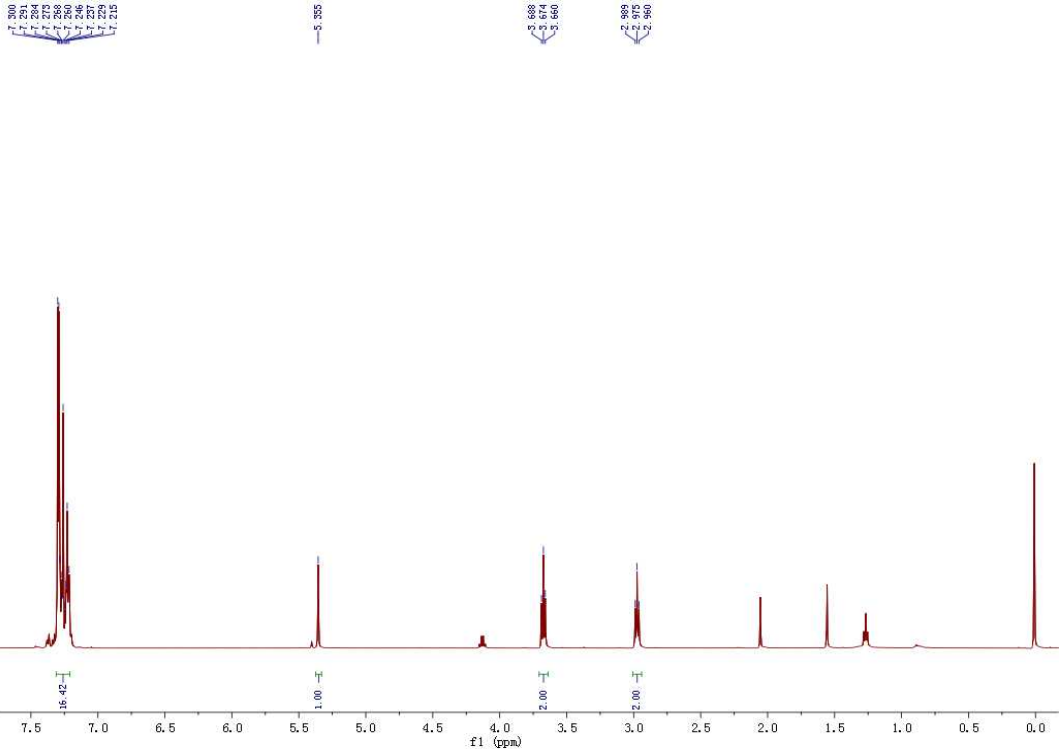
^{13}C NMR



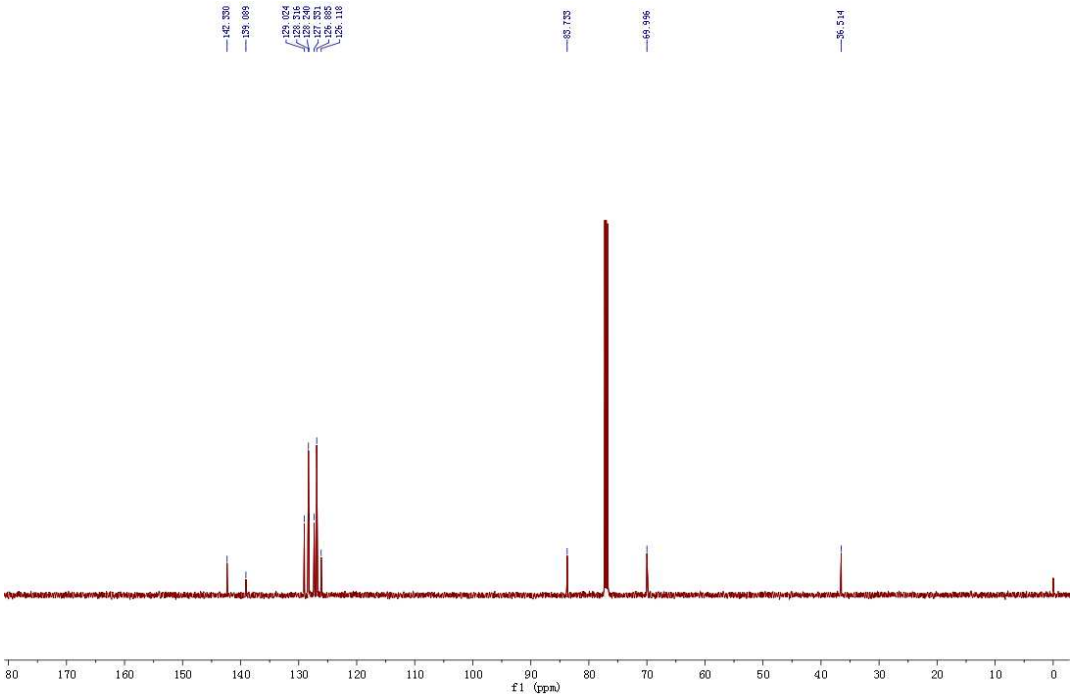


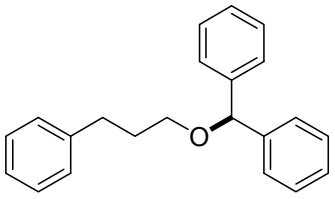
(3m)

^{1}H NMR



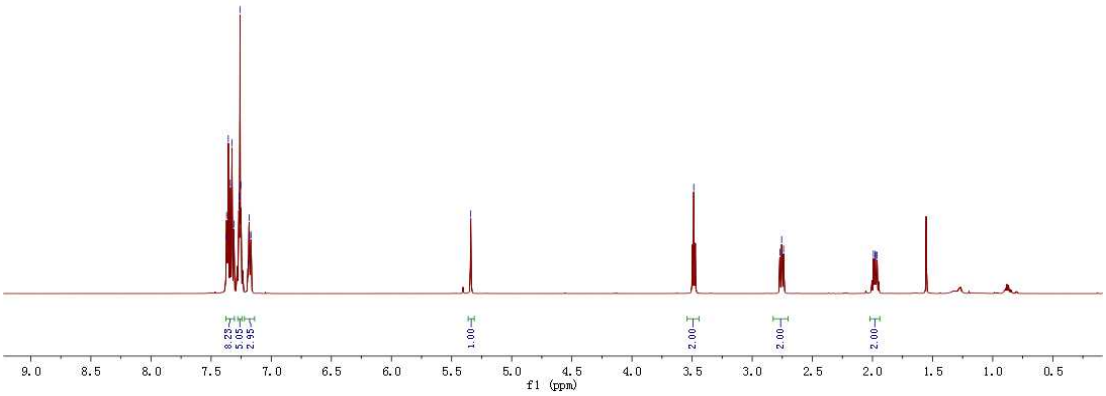
^{13}C NMR



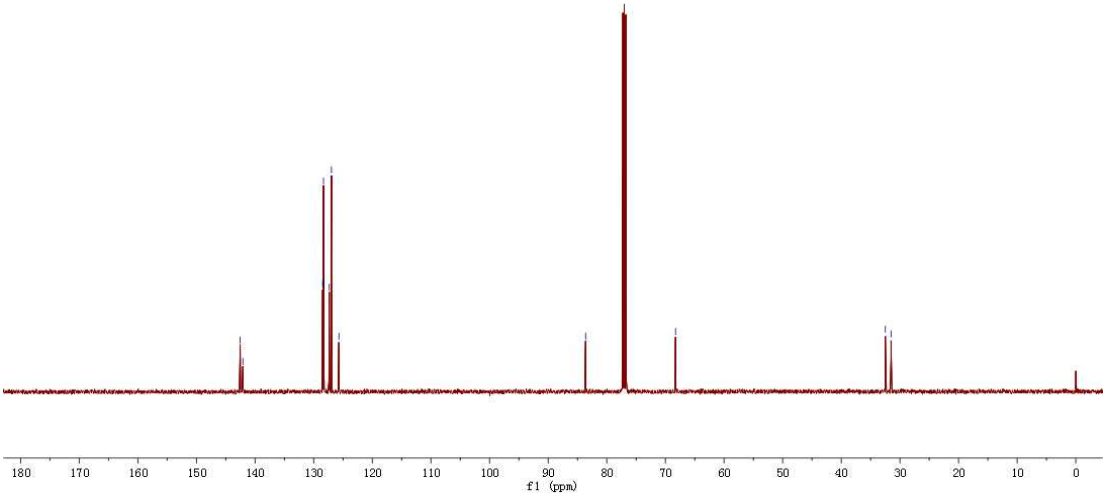


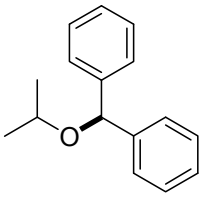
(3n)

^{1}H NMR



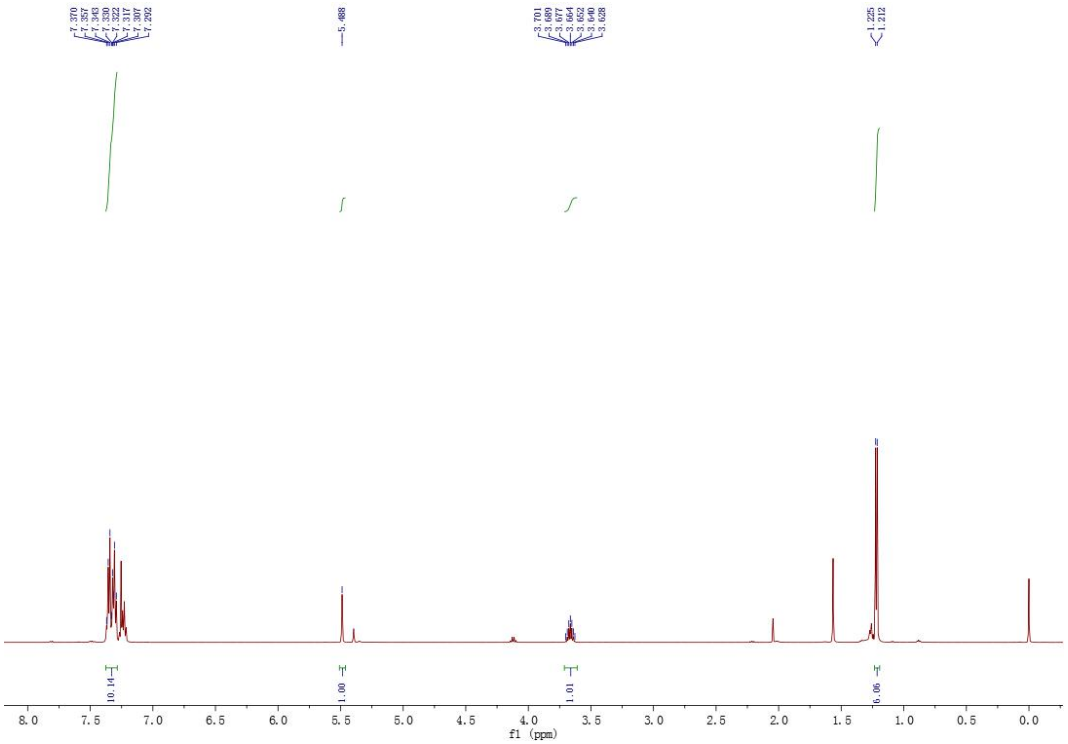
^{13}C NMR



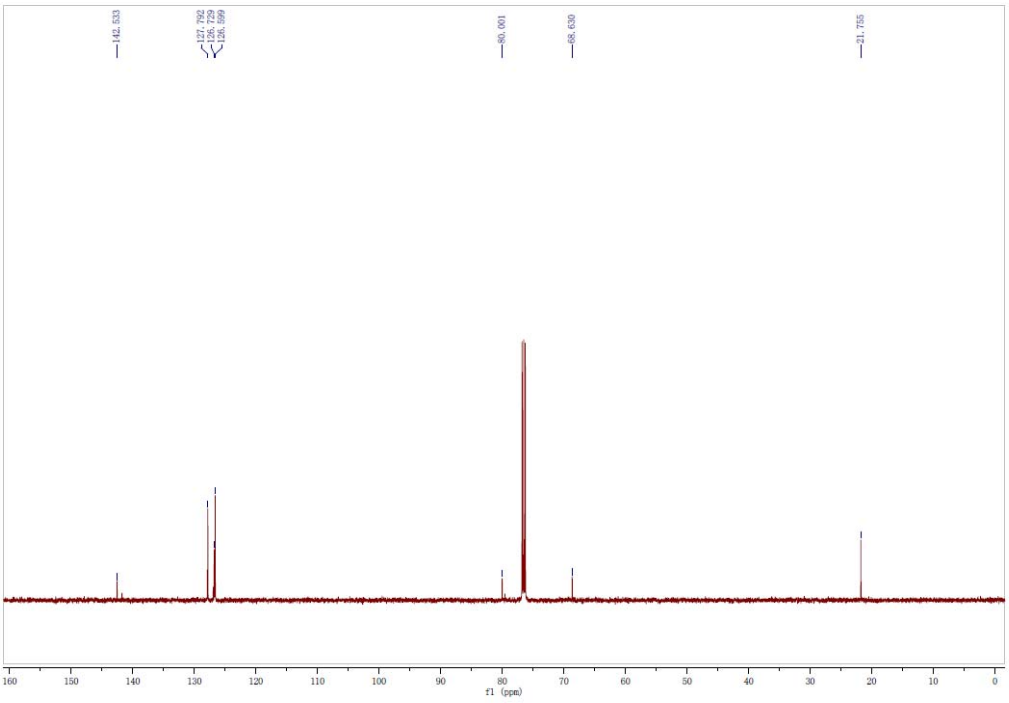


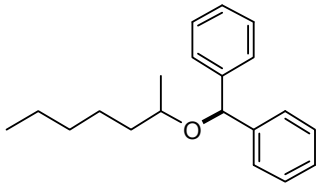
(3o)

^{1}H NMR



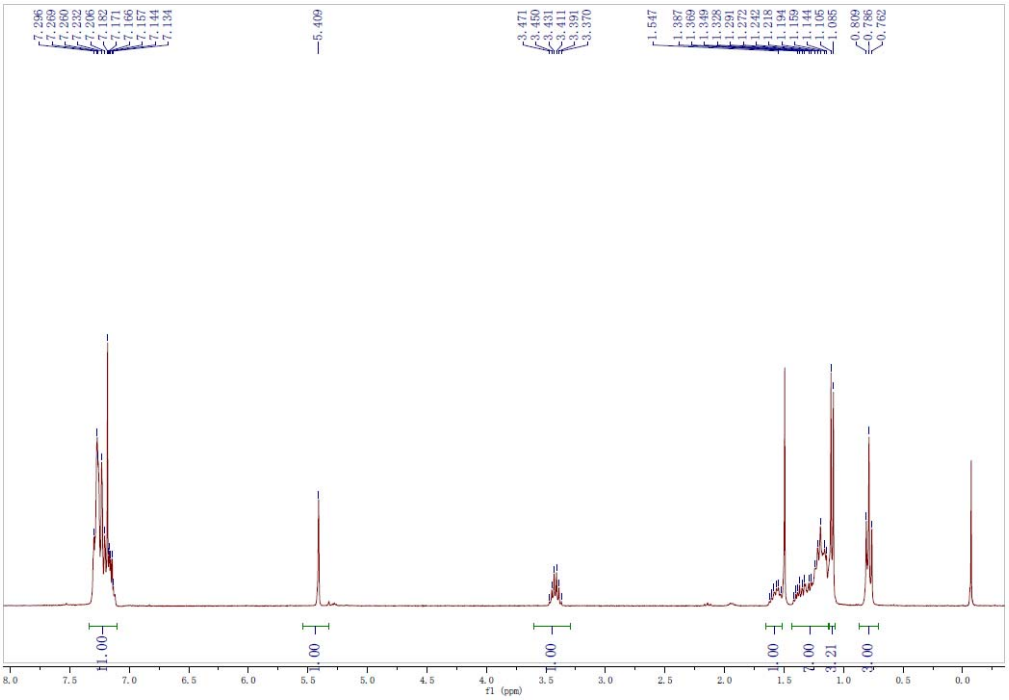
^{13}C NMR



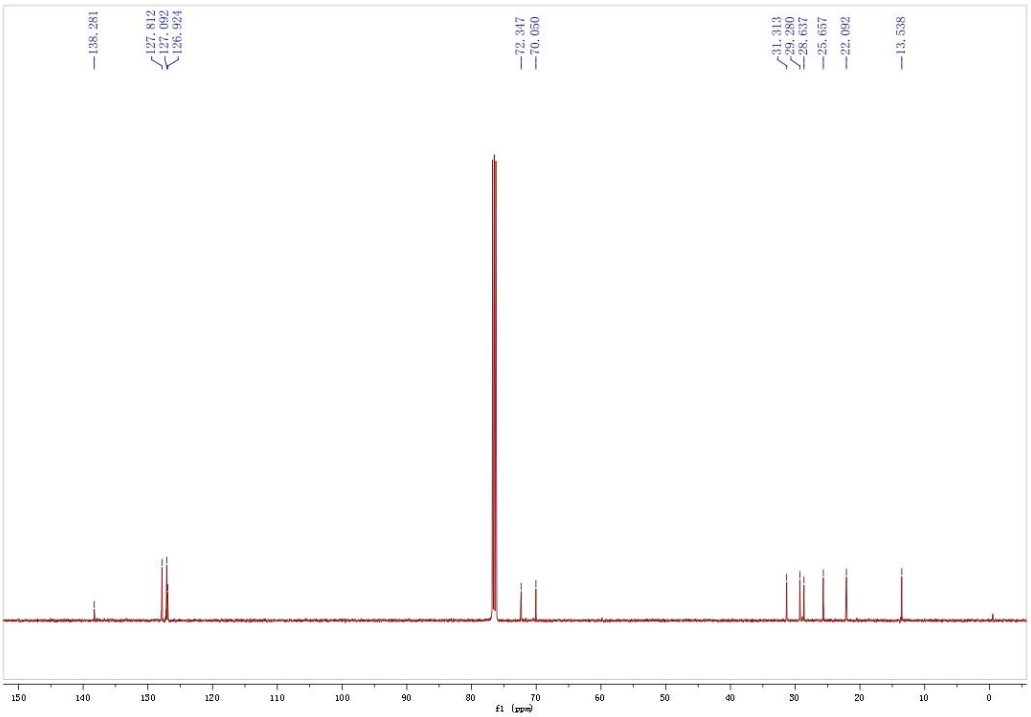


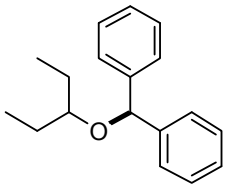
(3p)

^{1}H NMR



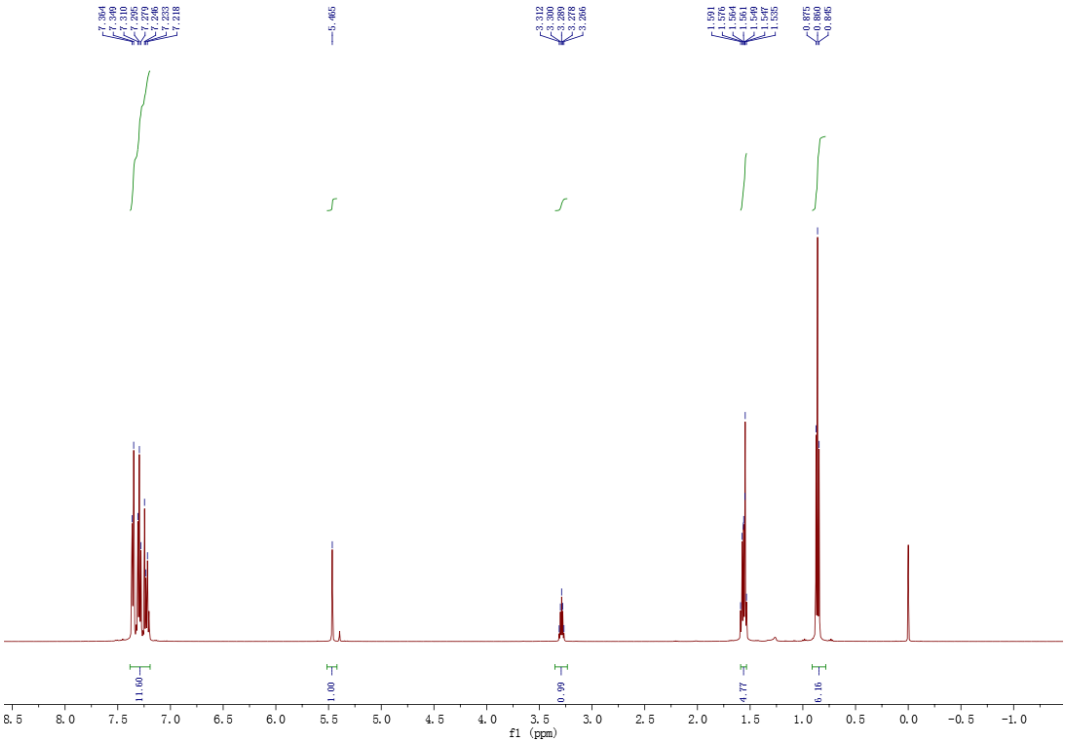
^{13}C NMR



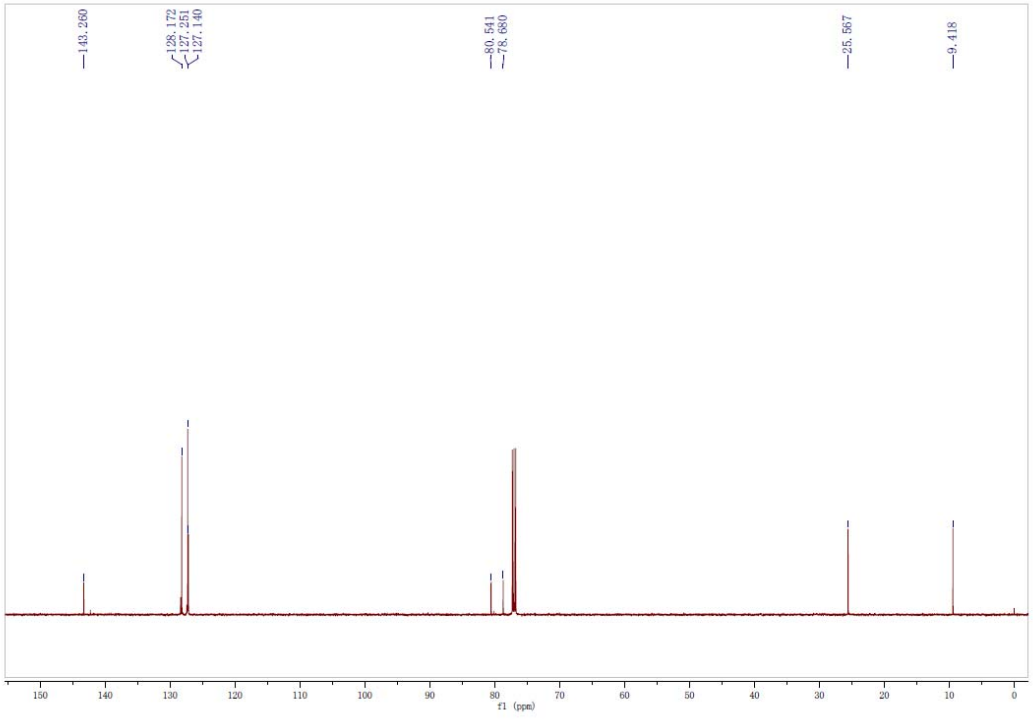


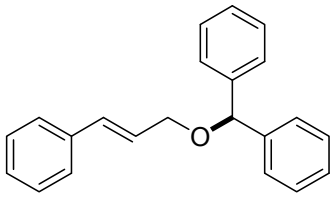
(3q)

^{1}H NMR



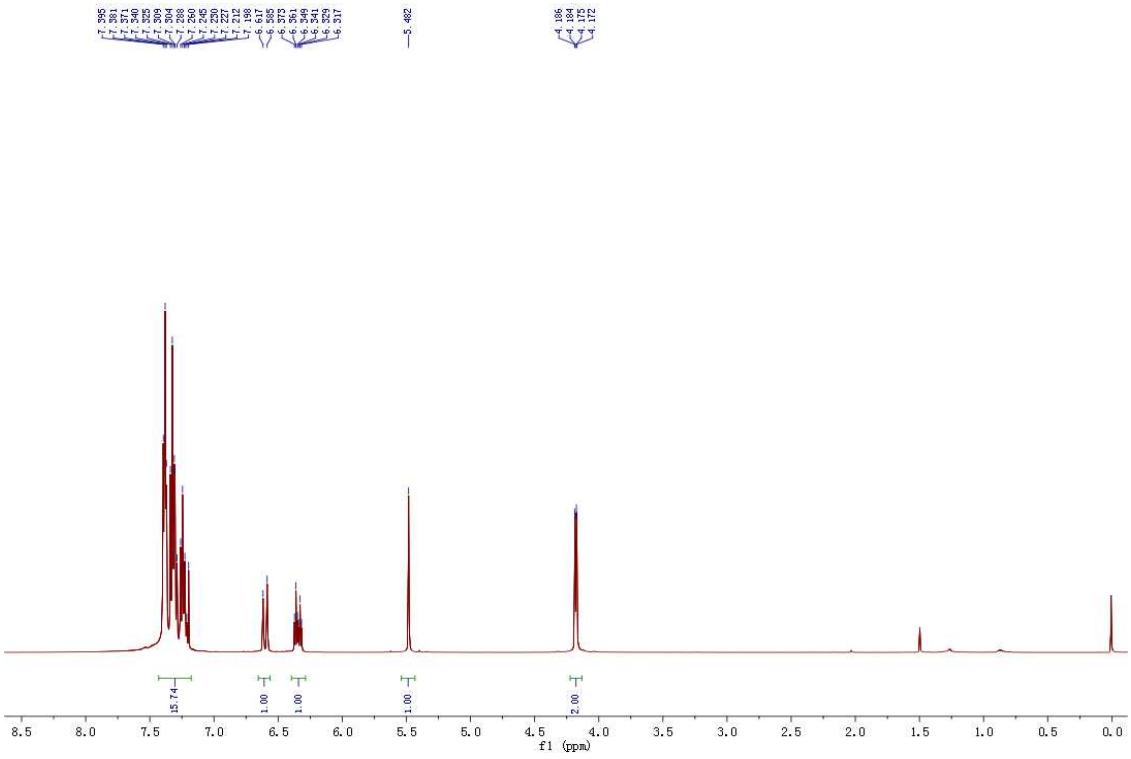
^{13}C NMR



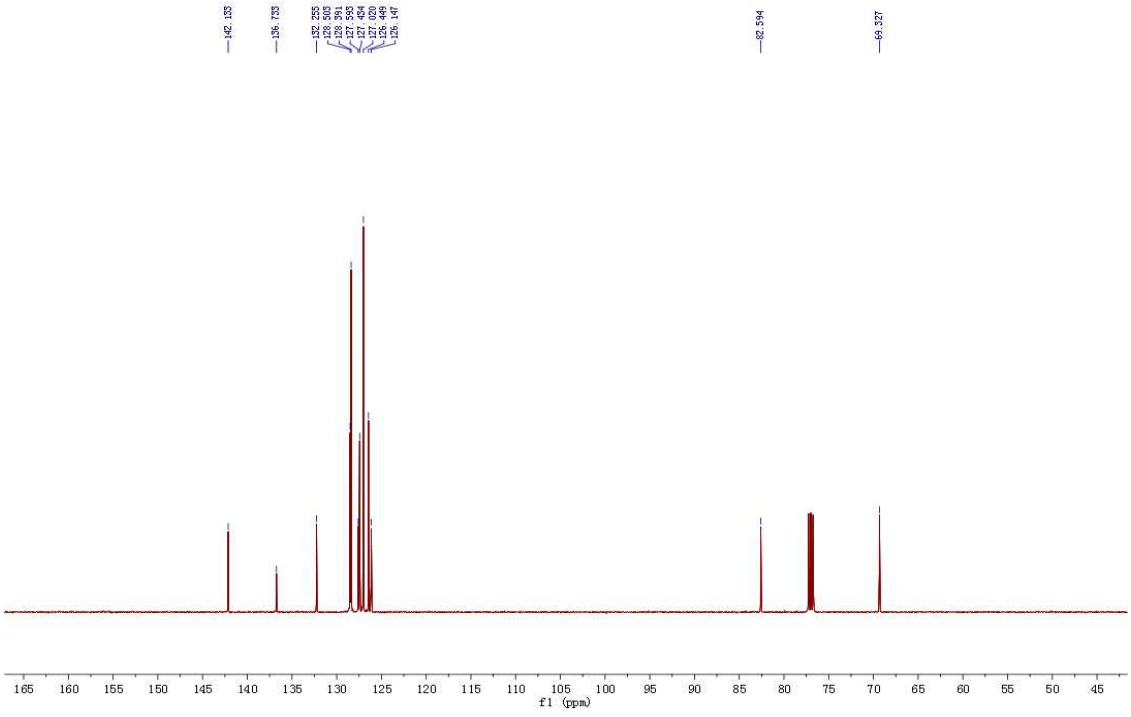


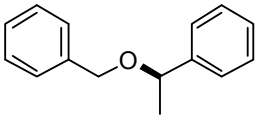
(3r)

^{1}H NMR



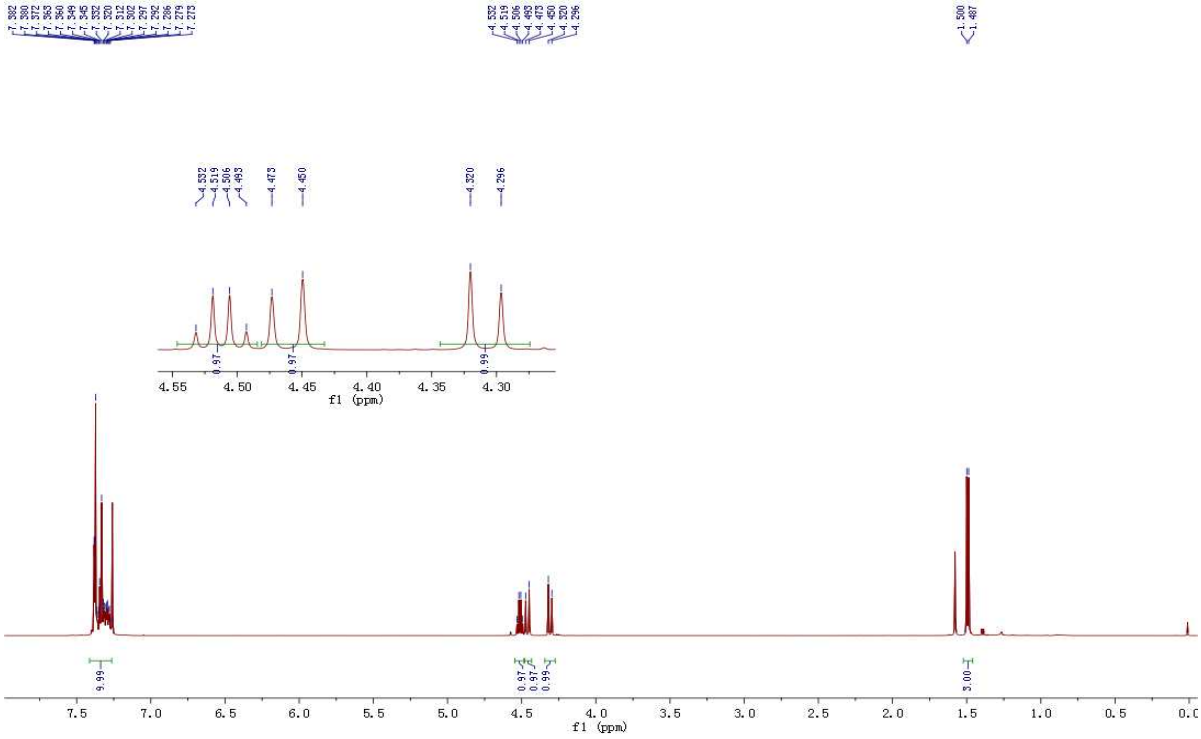
^{13}C NMR



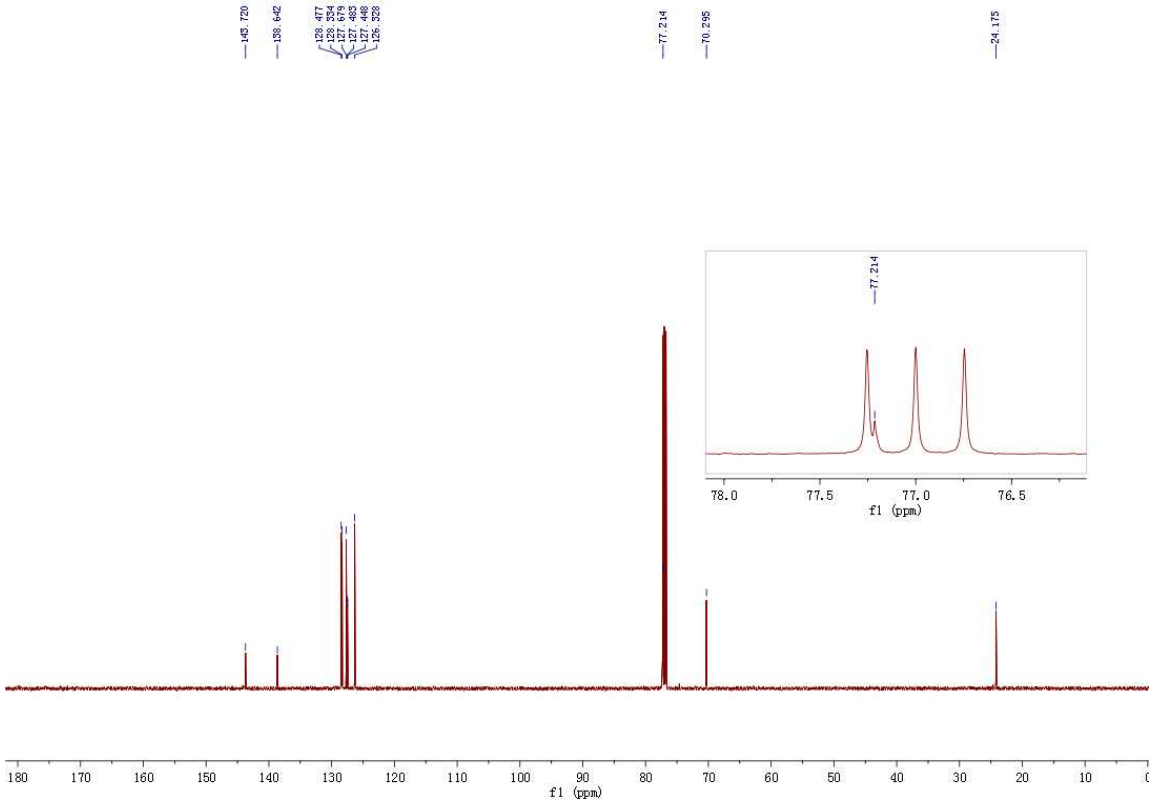


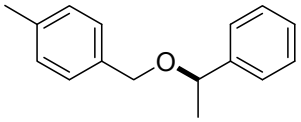
(4a)

^{1}H NMR



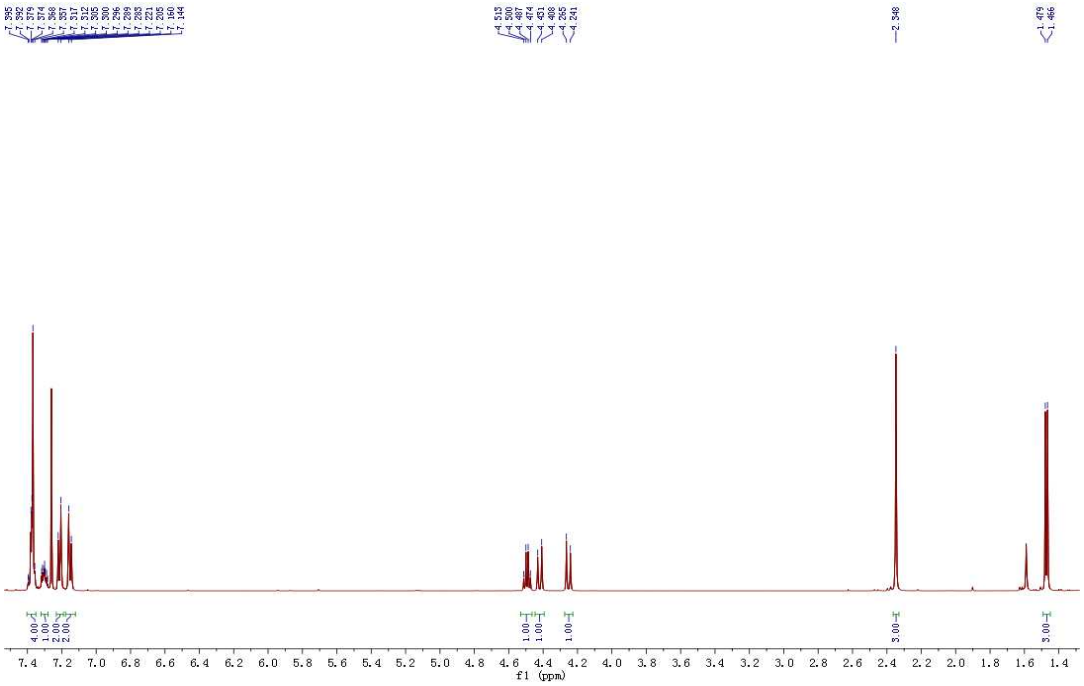
^{13}C NMR



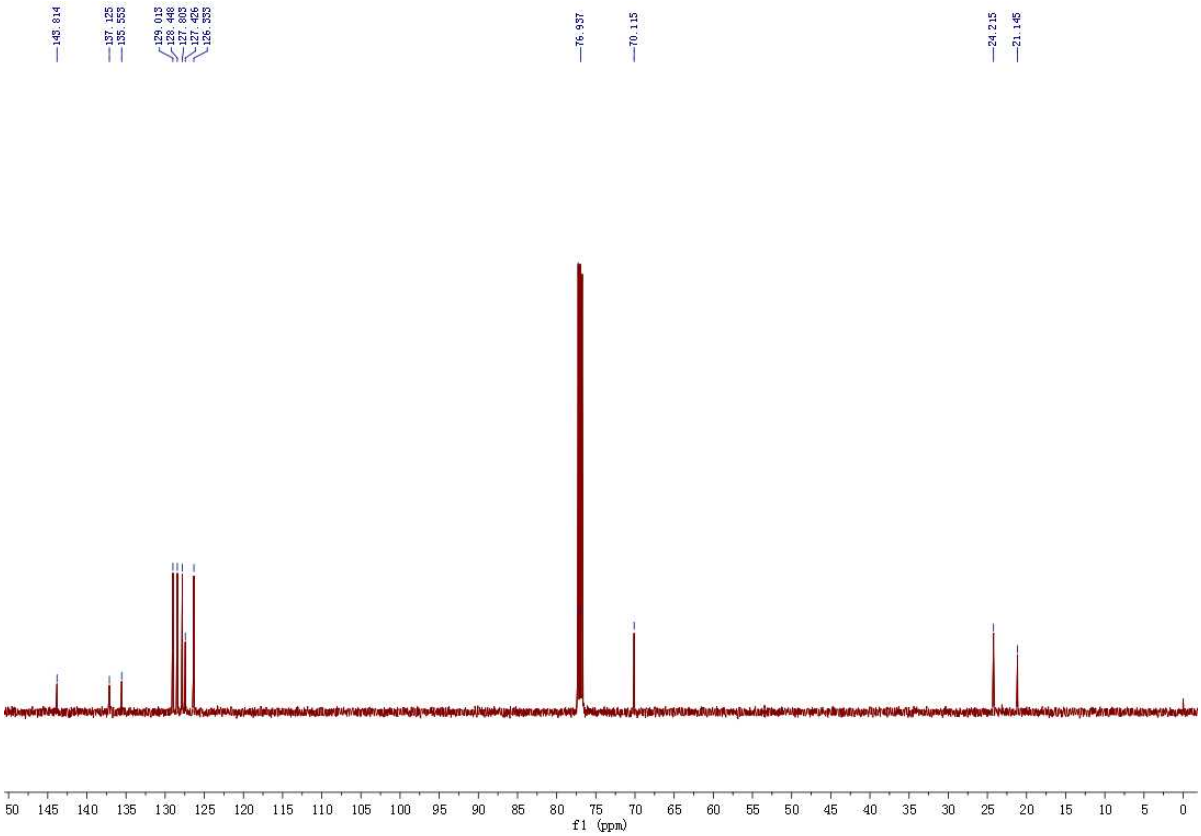


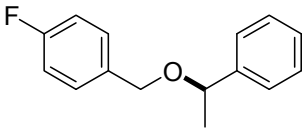
(4b)

^{1}H NMR



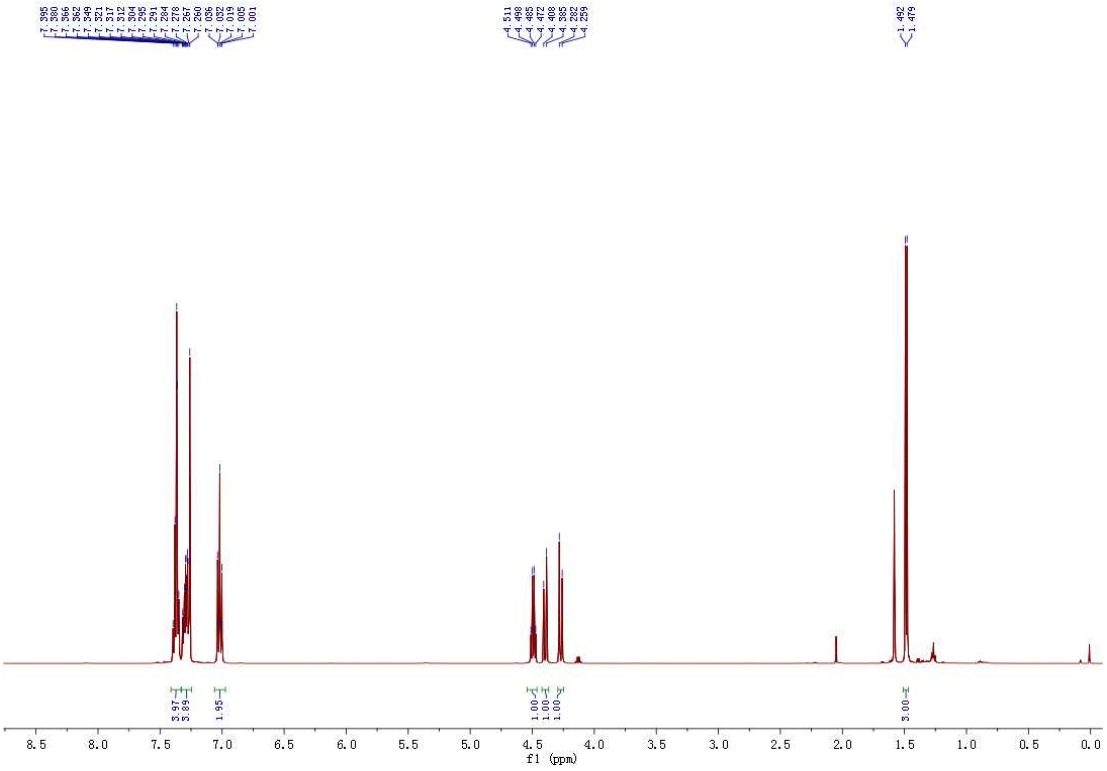
^{13}C NMR



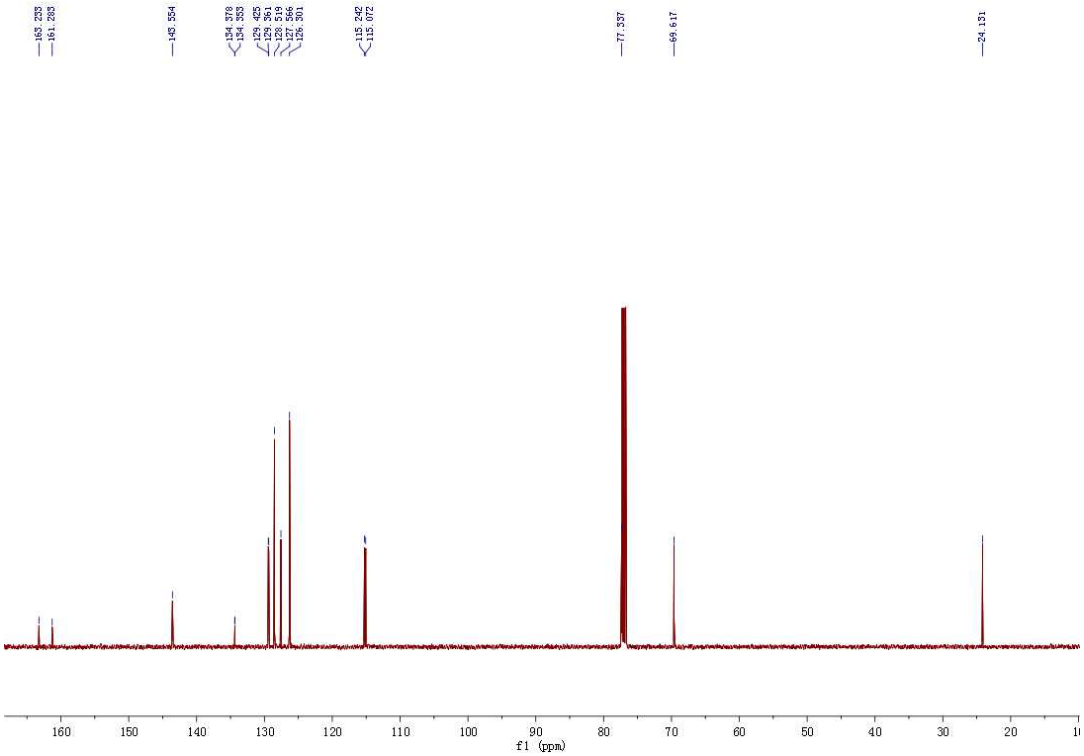


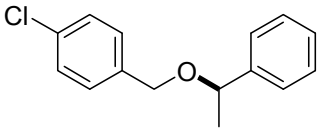
(4c)

^{1}H NMR



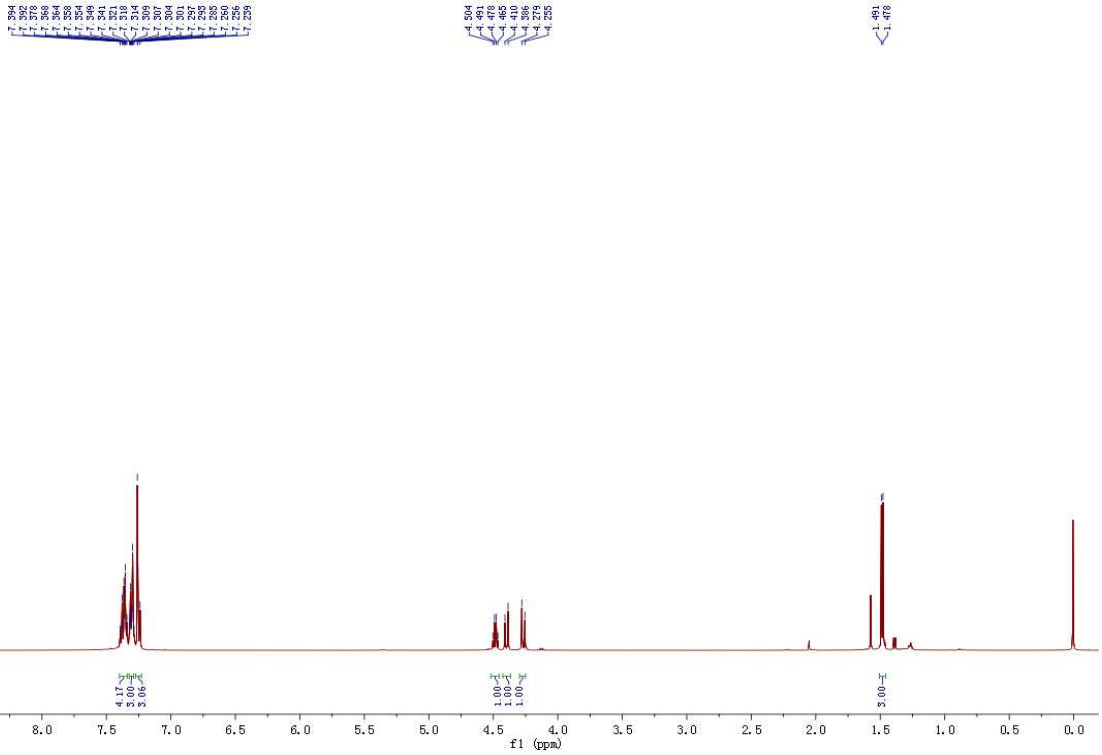
^{13}C NMR



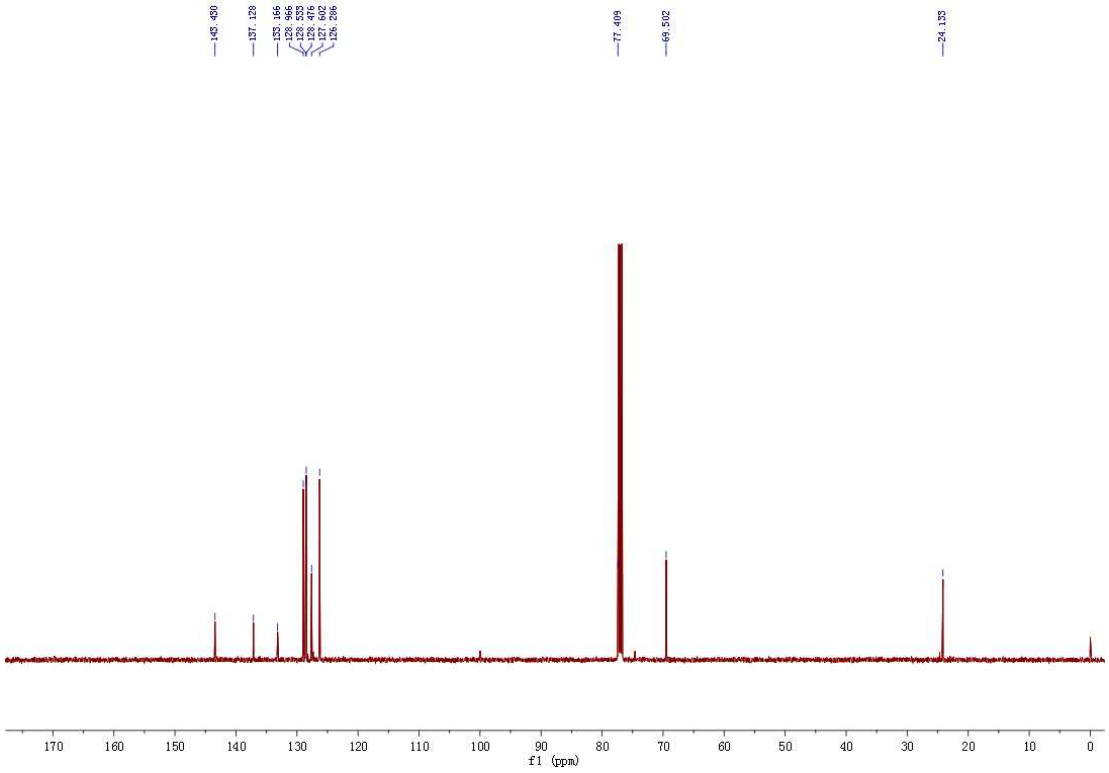


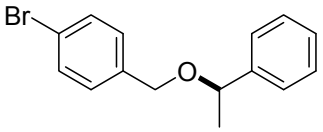
(4d)

^{1}H NMR



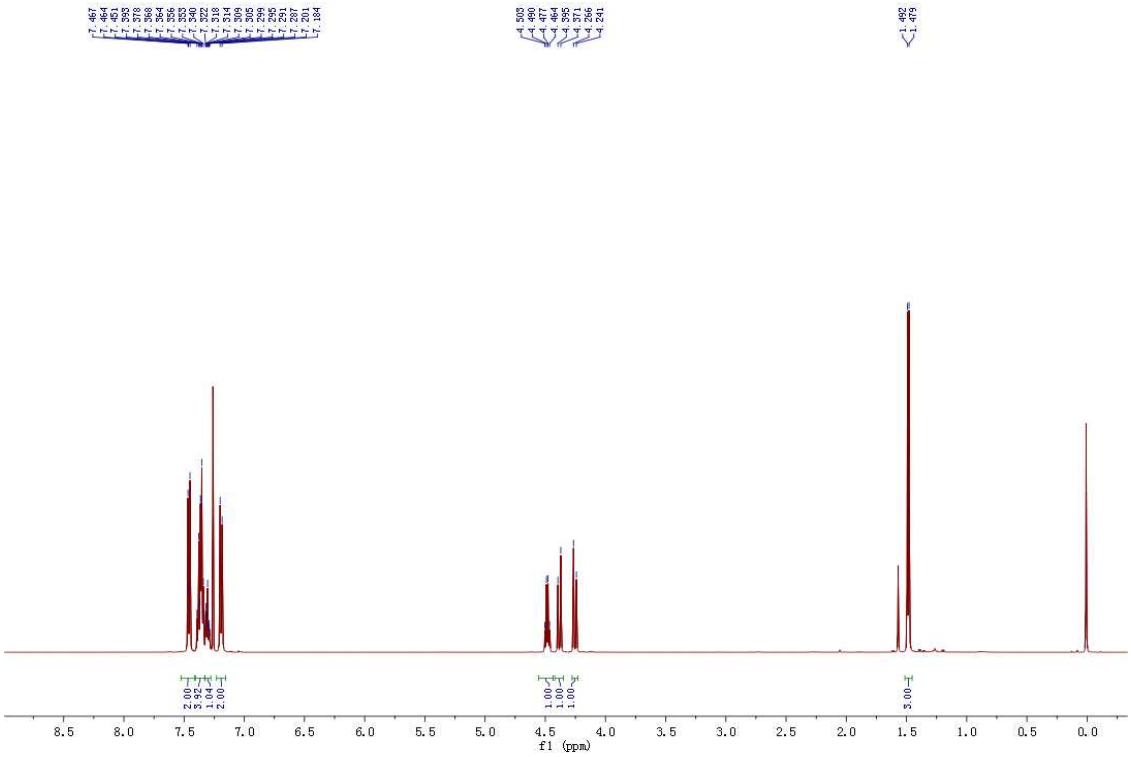
^{13}C NMR



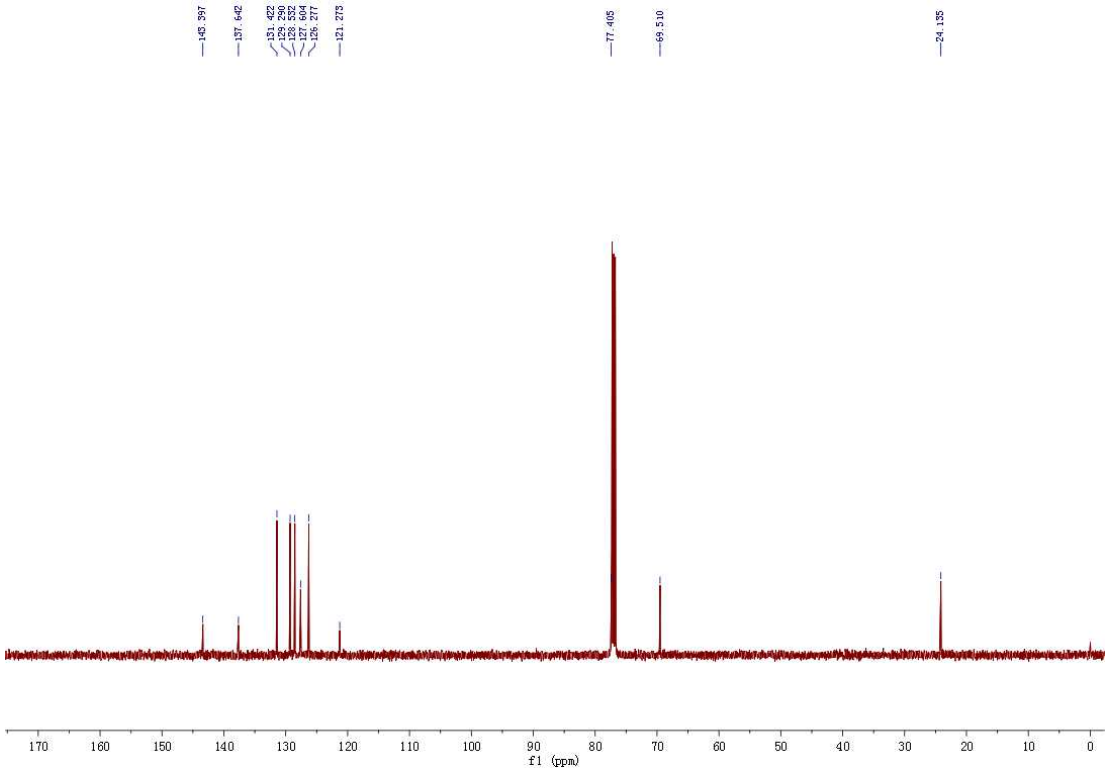


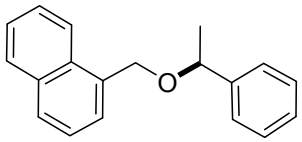
(4e)

^{1}H NMR



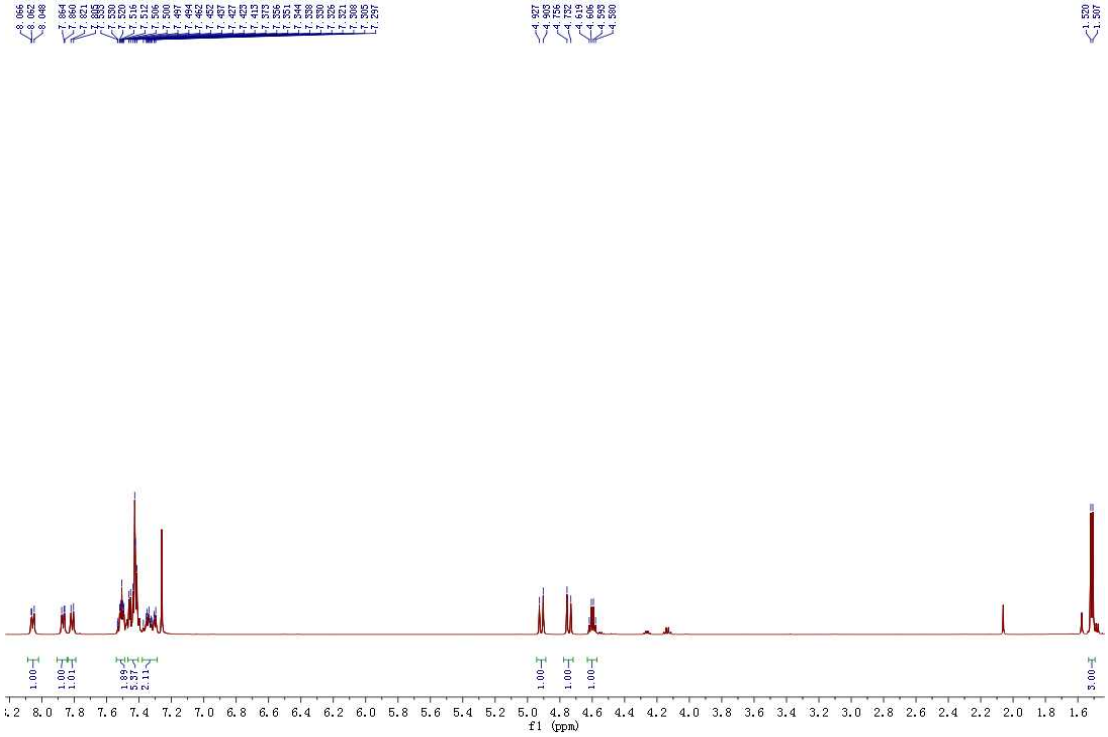
^{13}C NMR



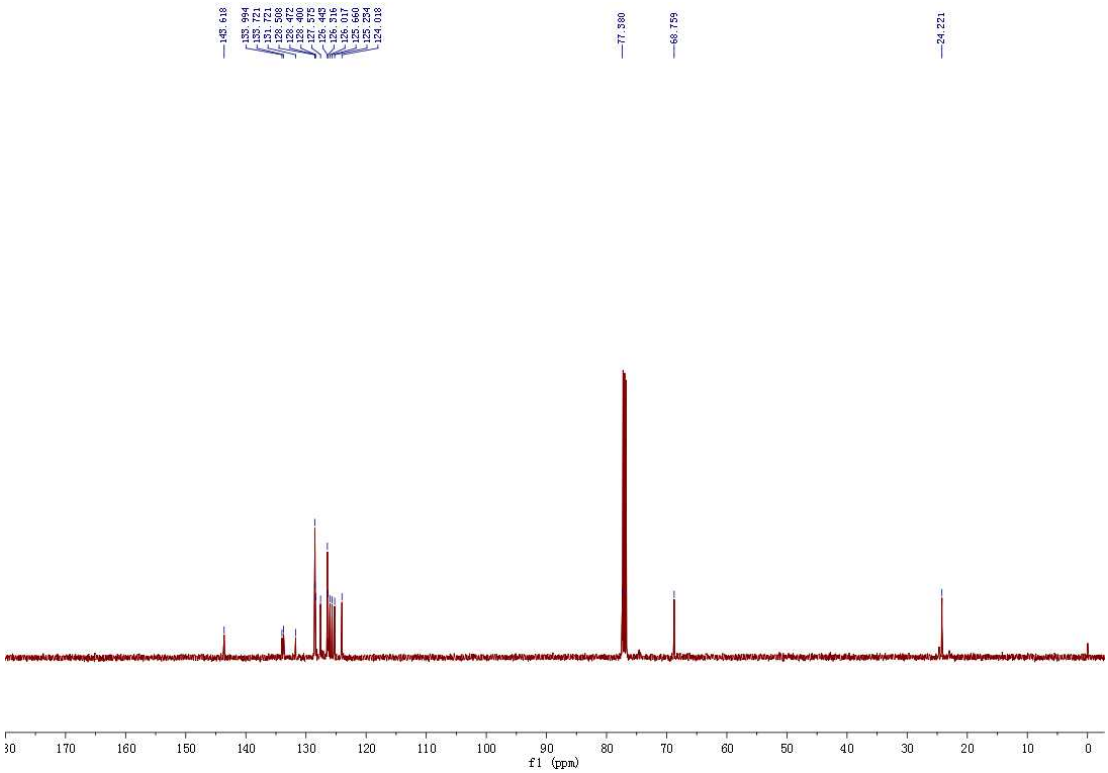


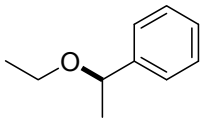
(4f)

^{1}H NMR



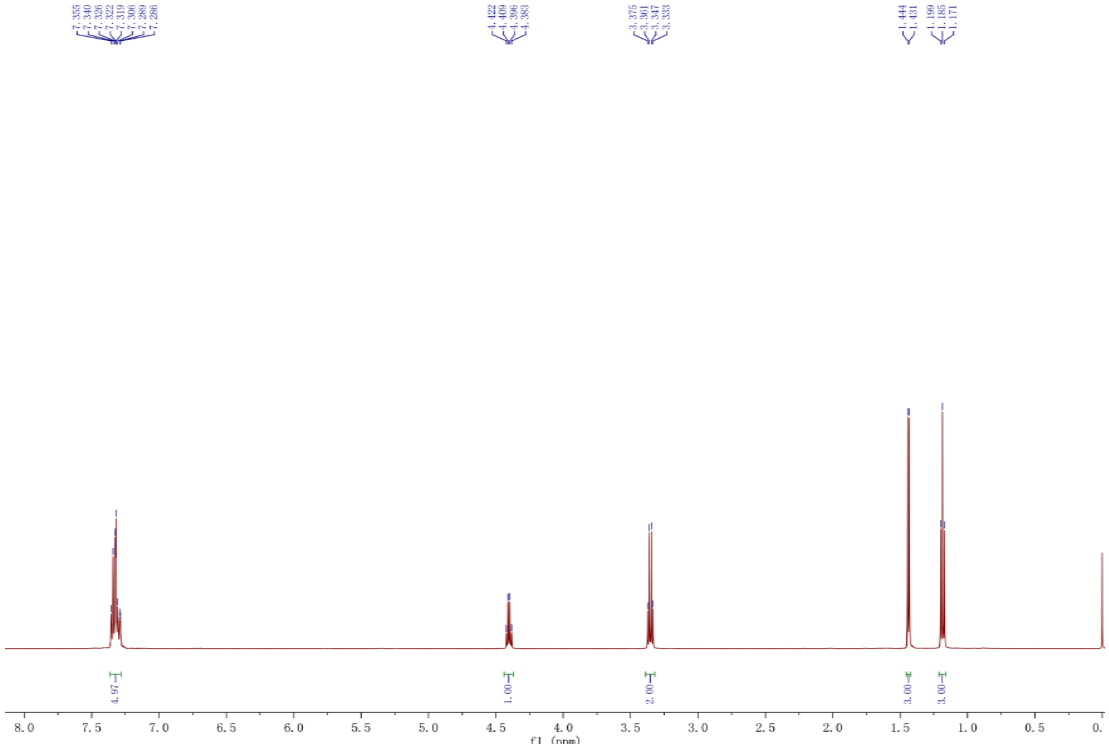
^{13}C NMR





(4g)

^{1}H NMR



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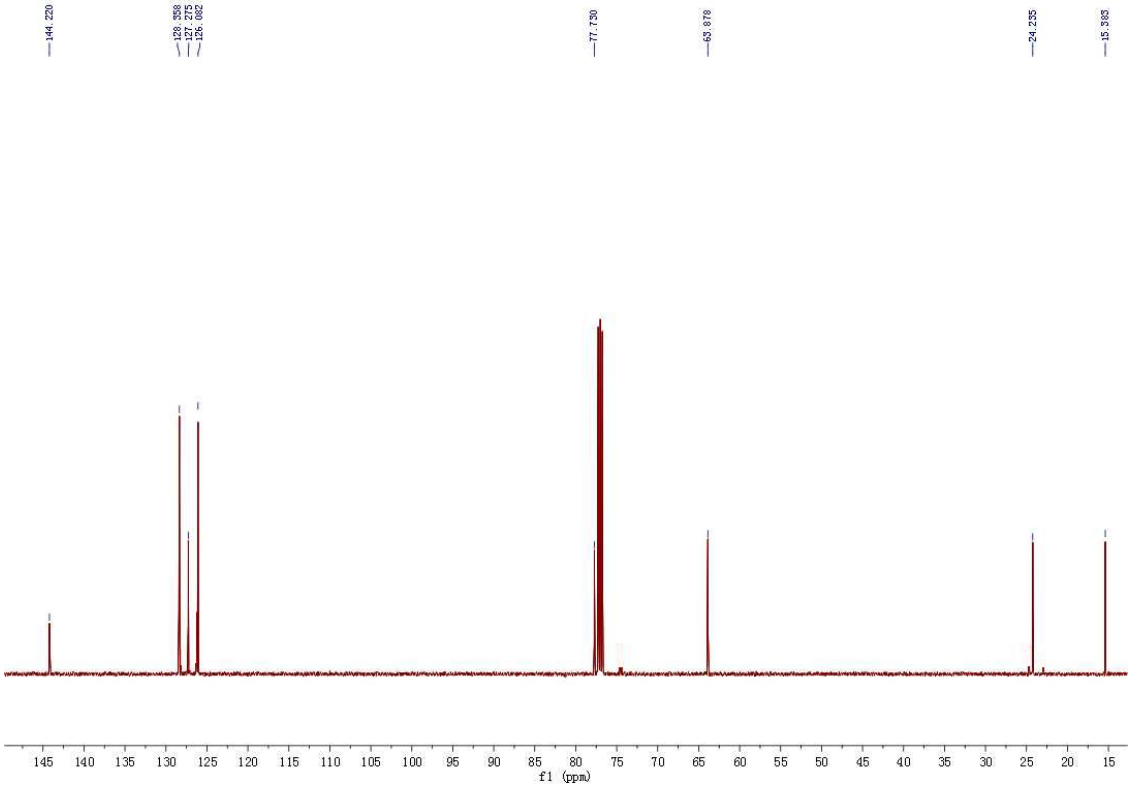
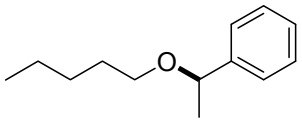
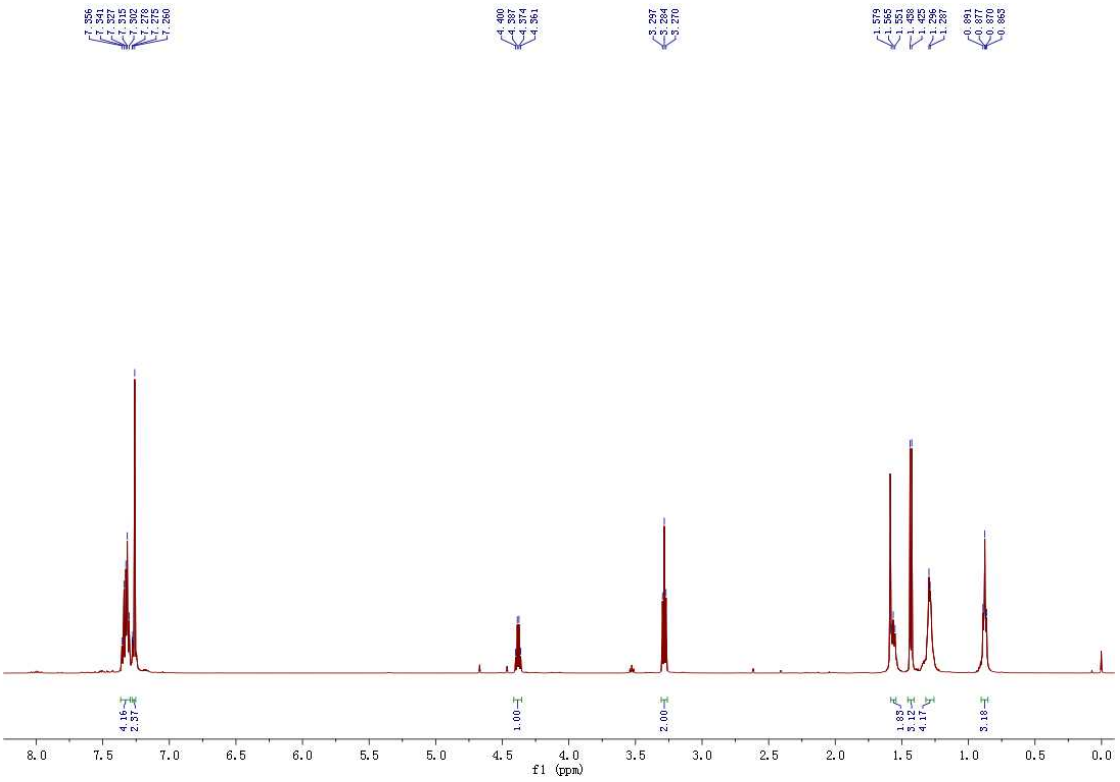




(4h)

^{1}H NMR



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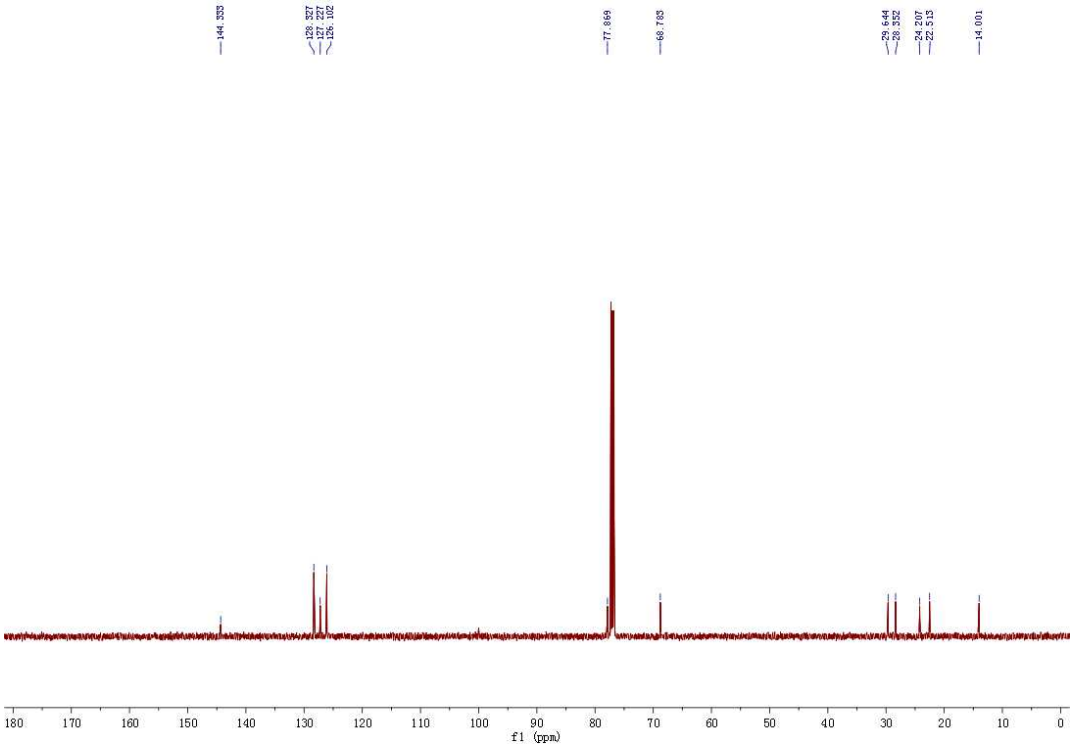
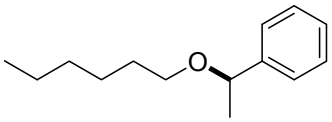
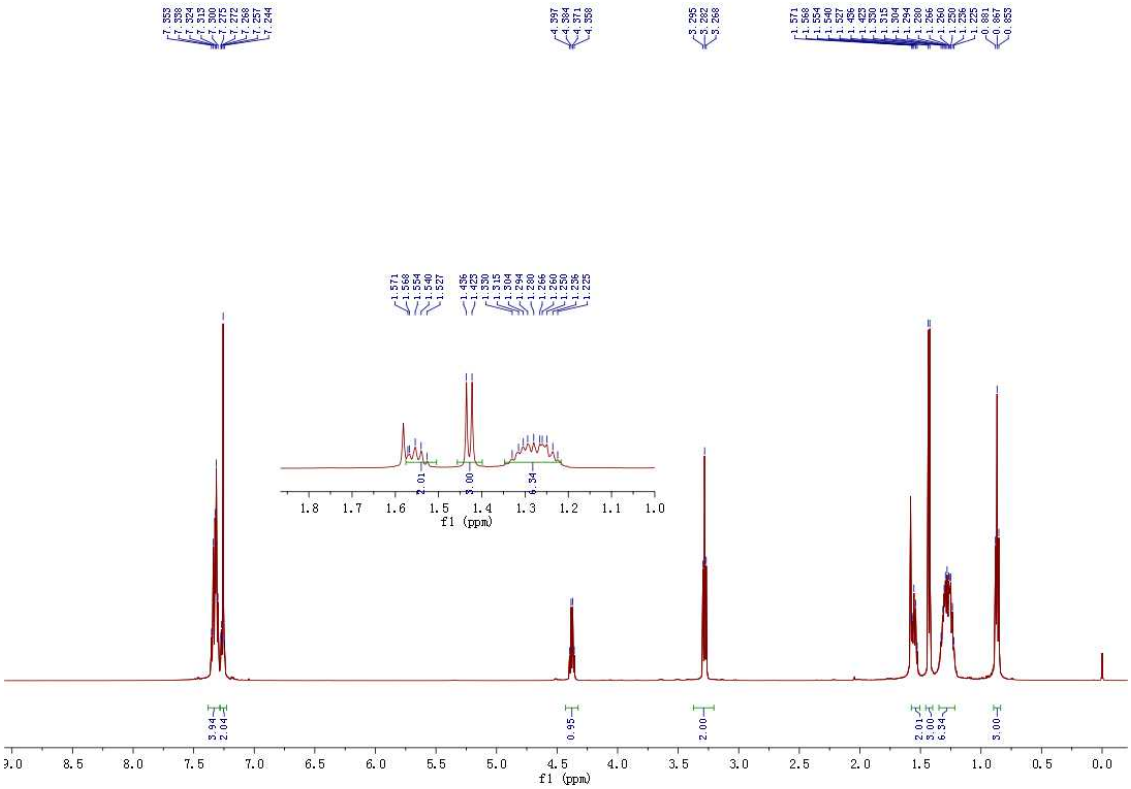


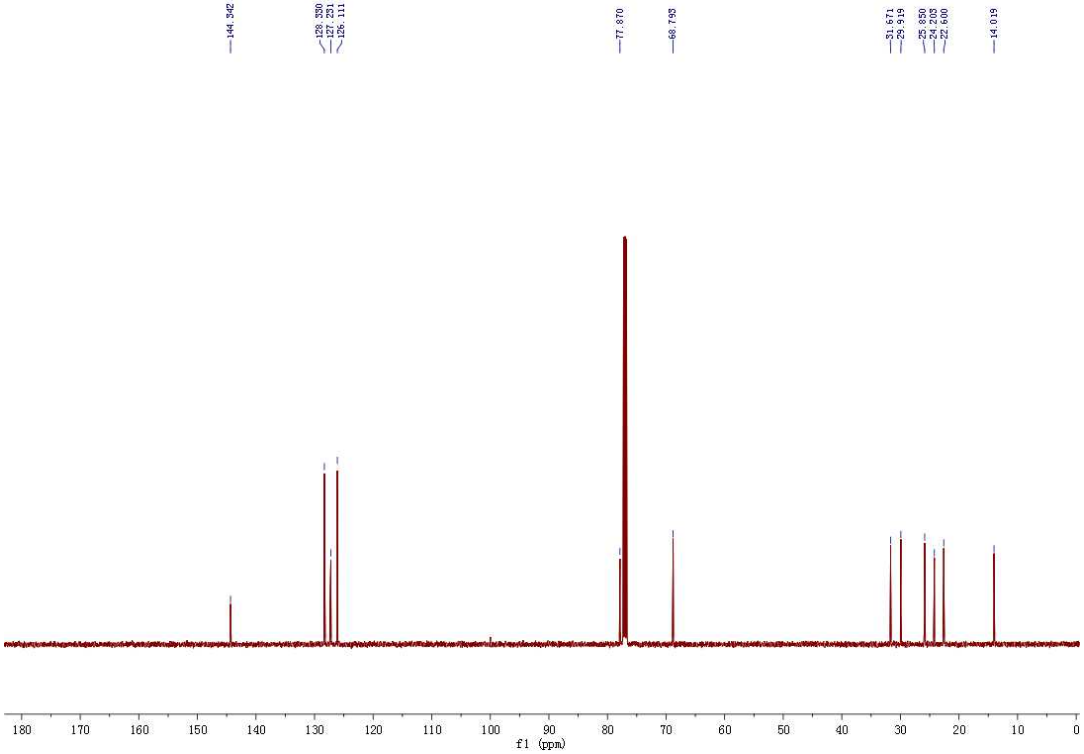


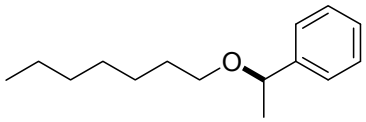
(4i)

^{1}H NMR



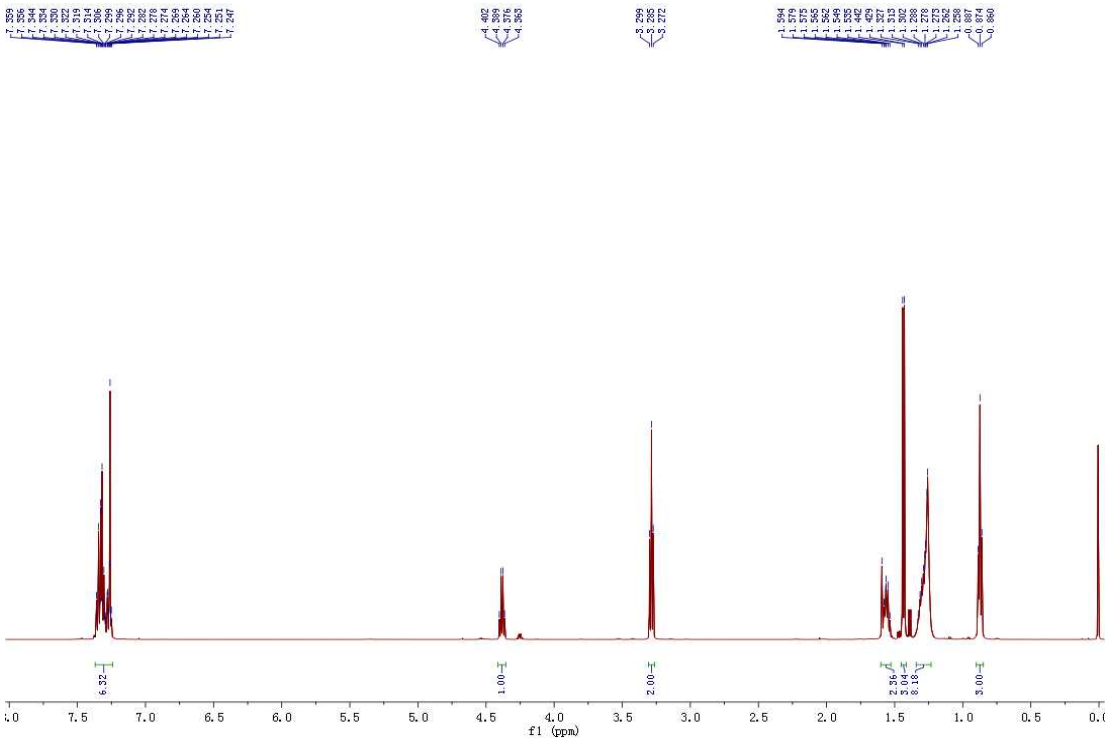
^{13}C NMR





(4j)

^{1}H NMR



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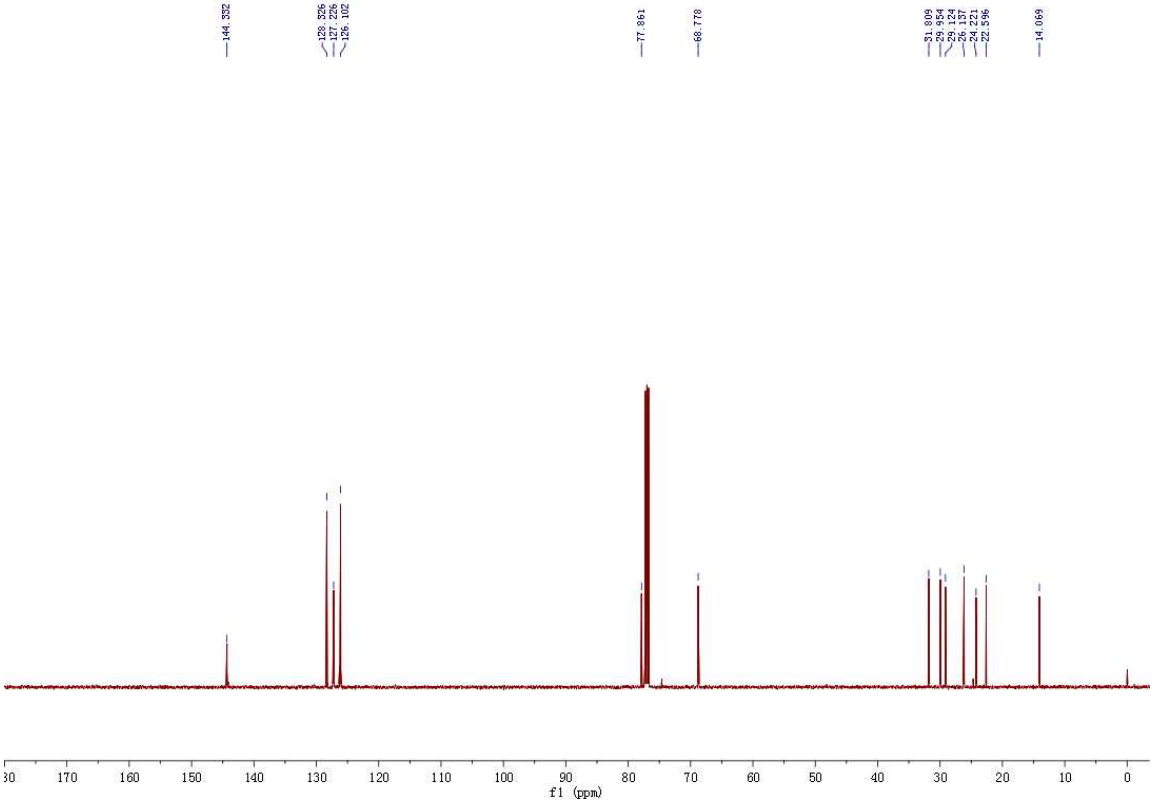
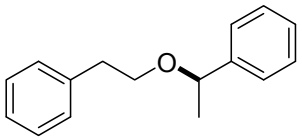
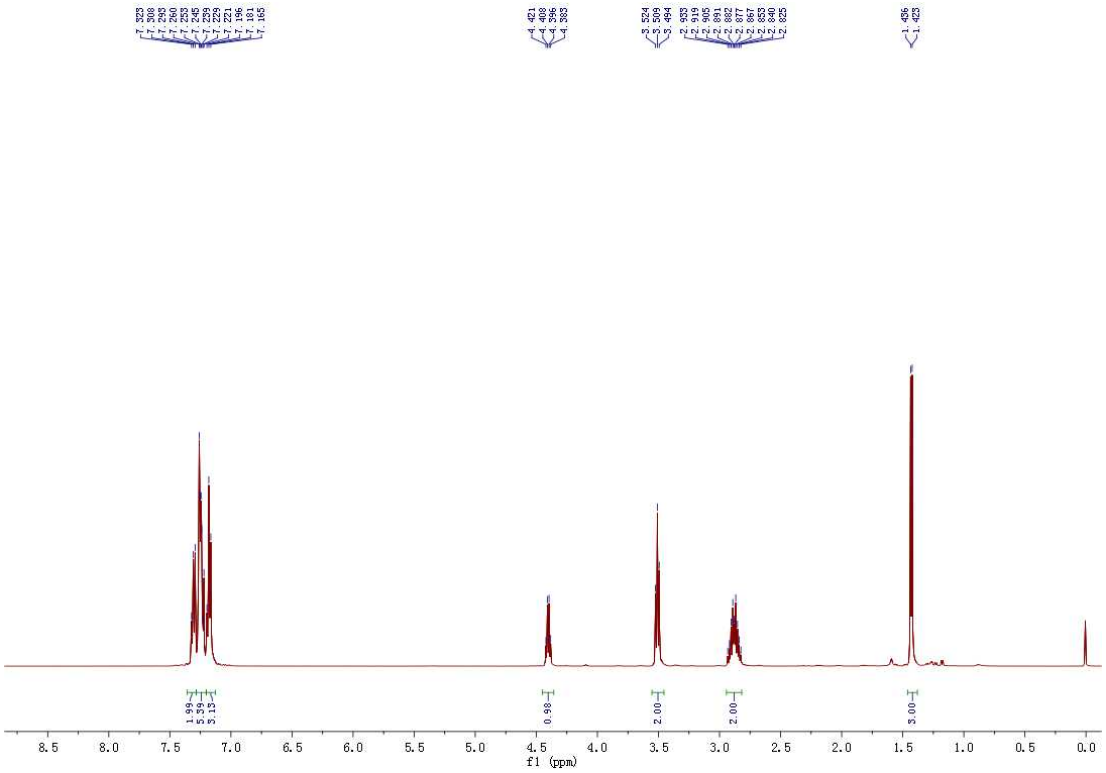




(4k)

^{1}H NMR



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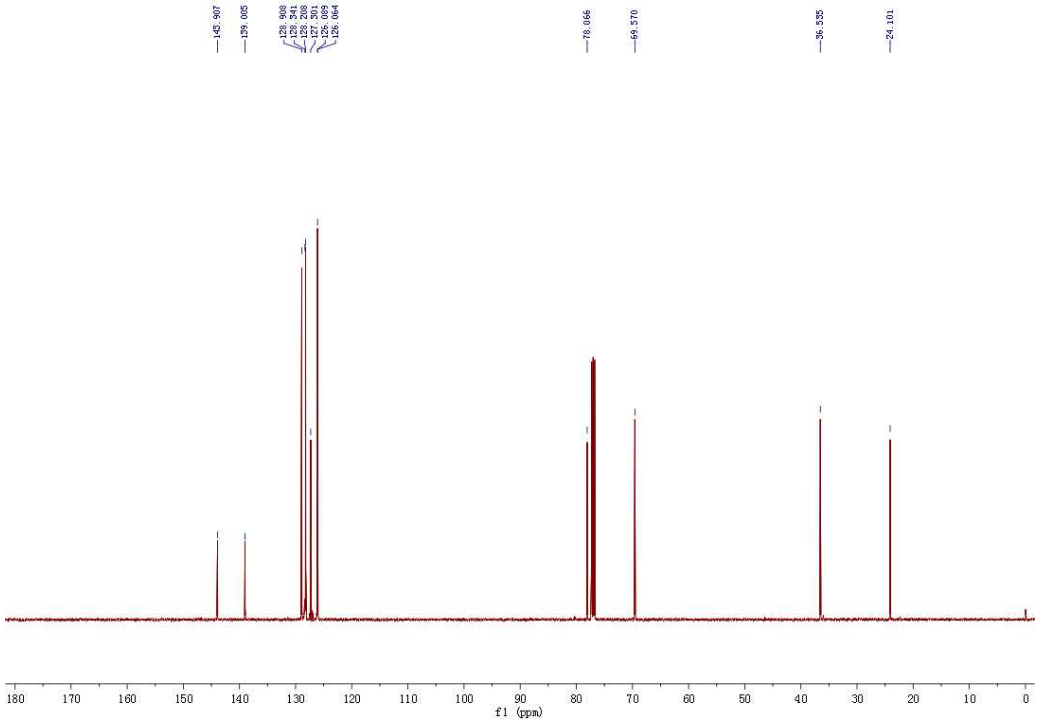
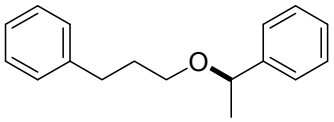
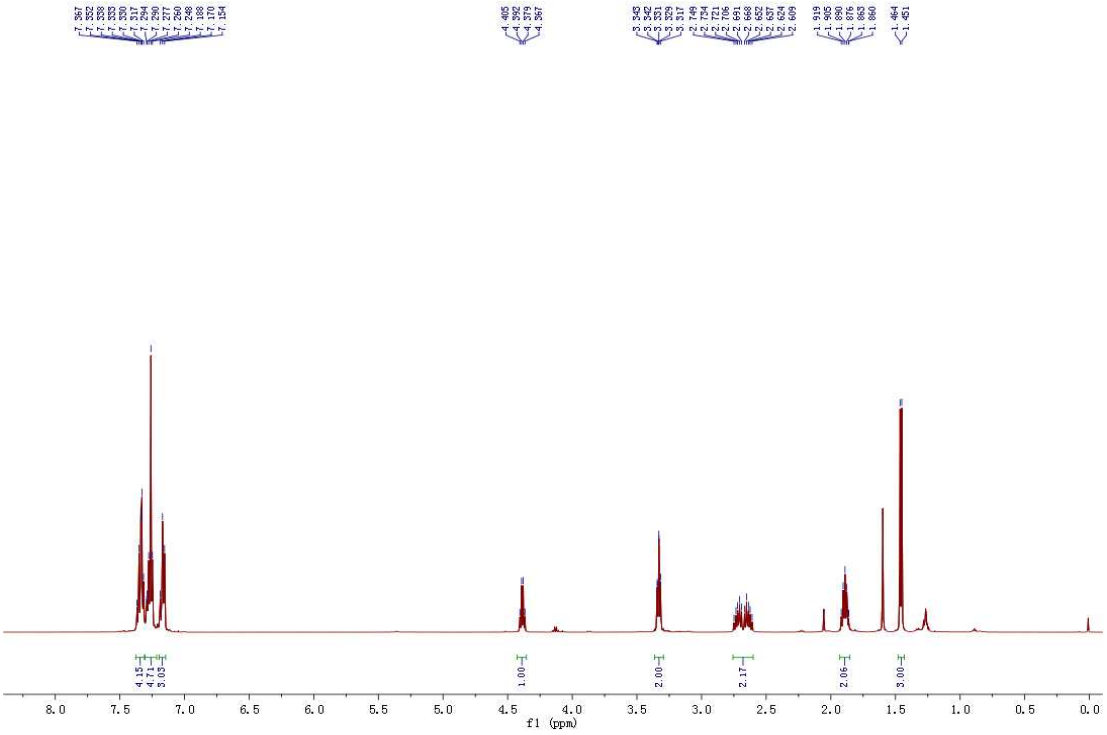


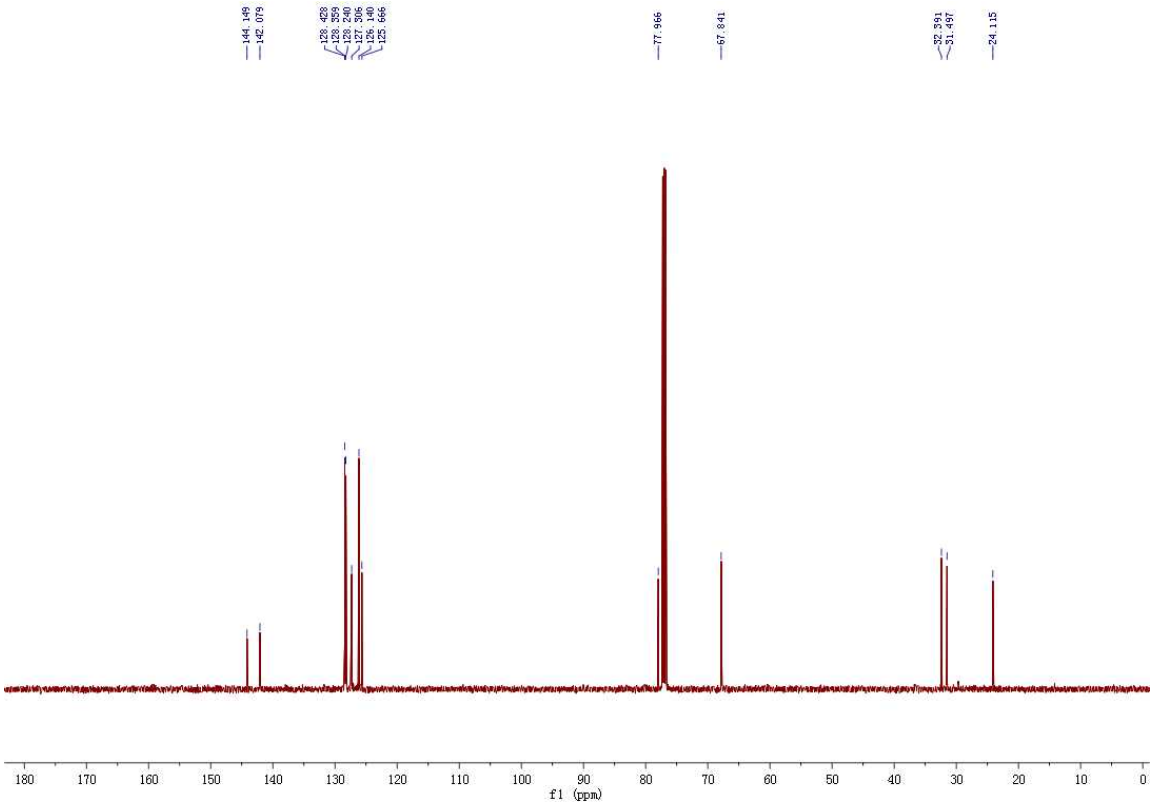


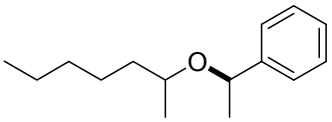
(4l)

^{1}H NMR



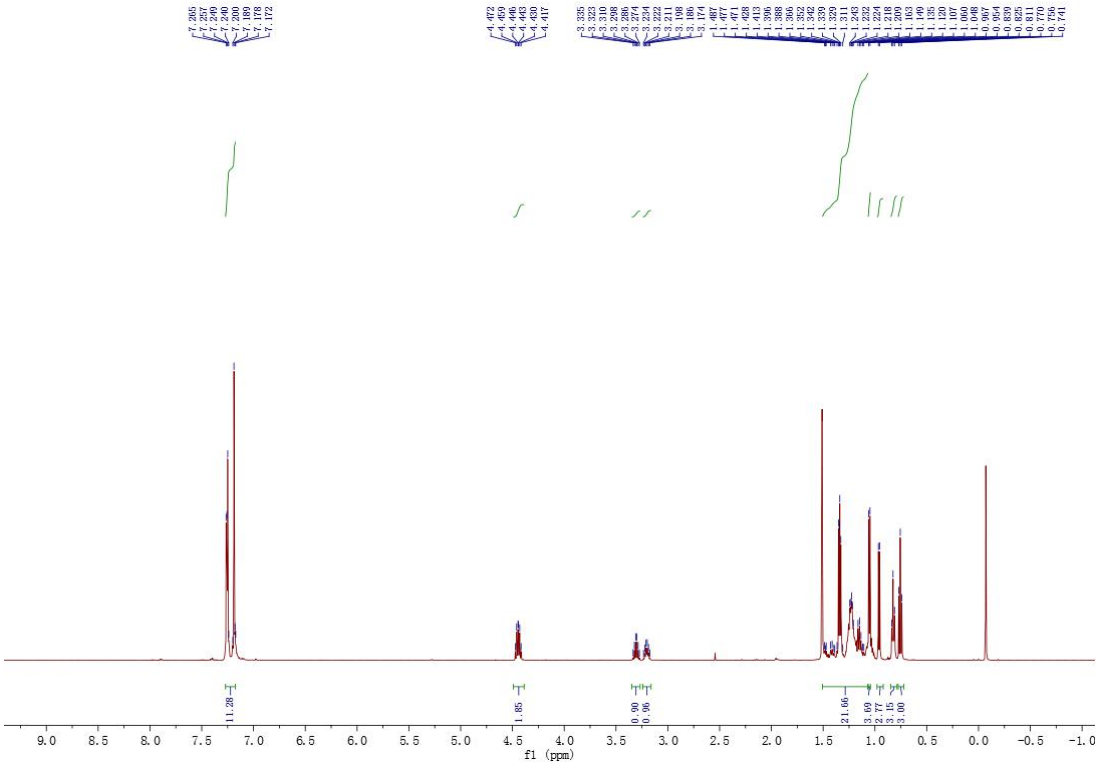
^{13}C NMR





(4m)

^{1}H NMR



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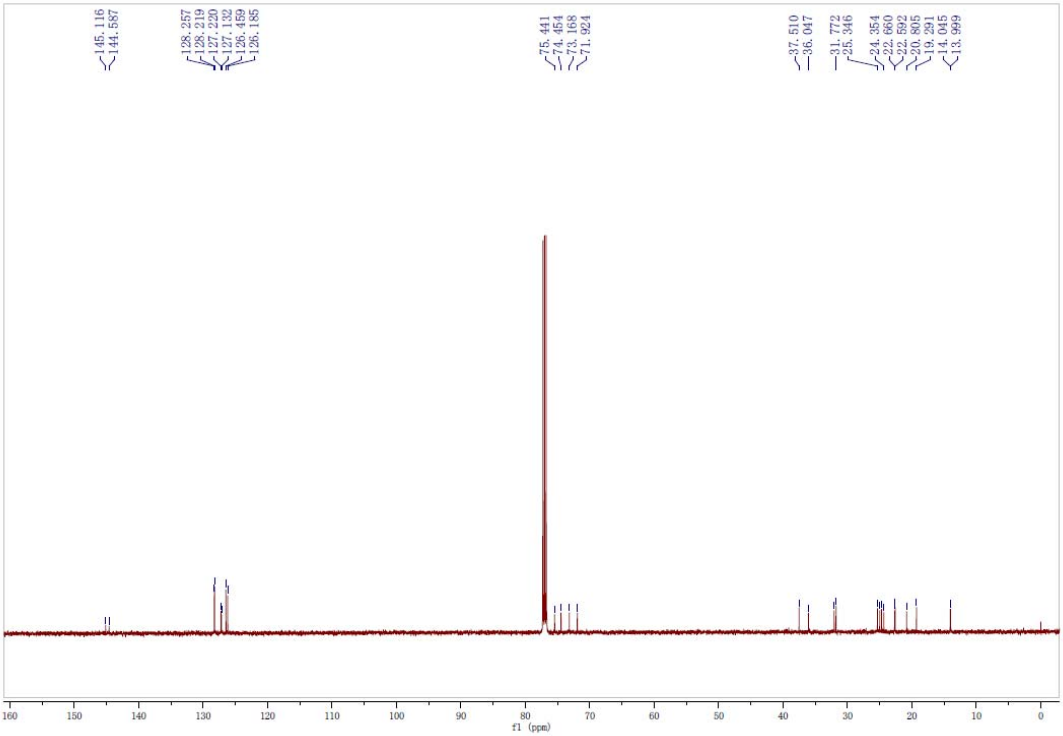
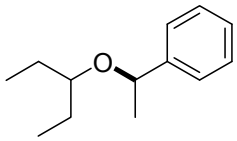
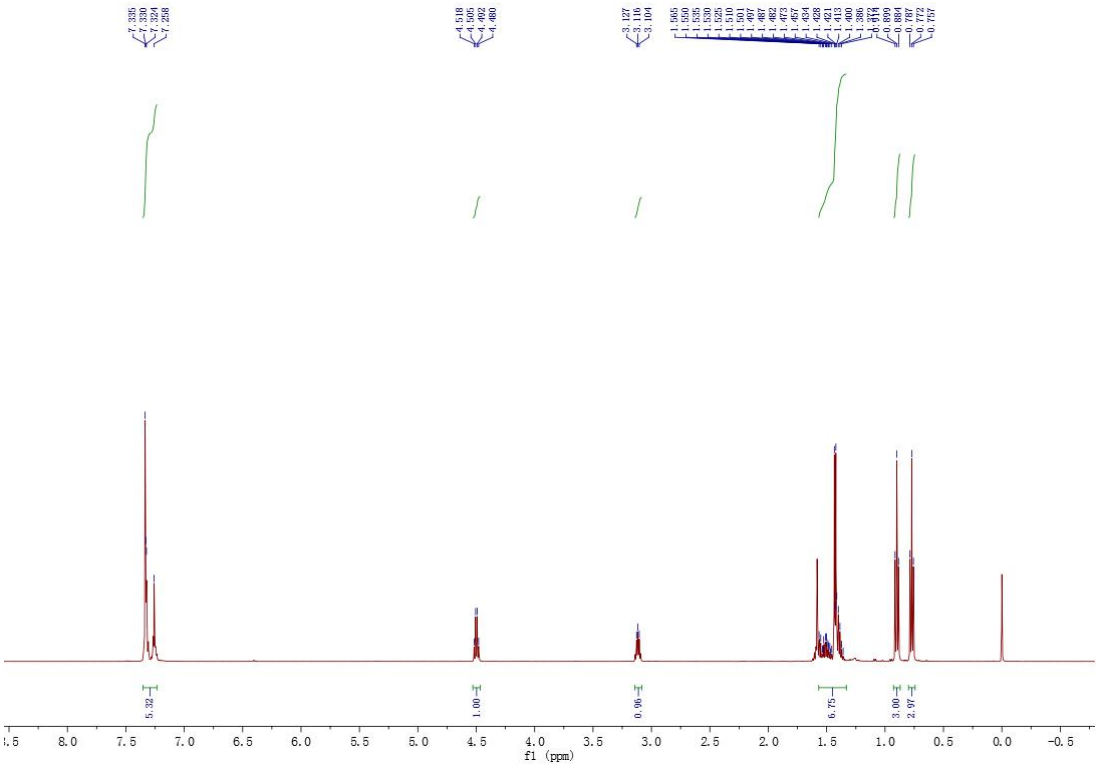




(4n)

^{1}H NMR



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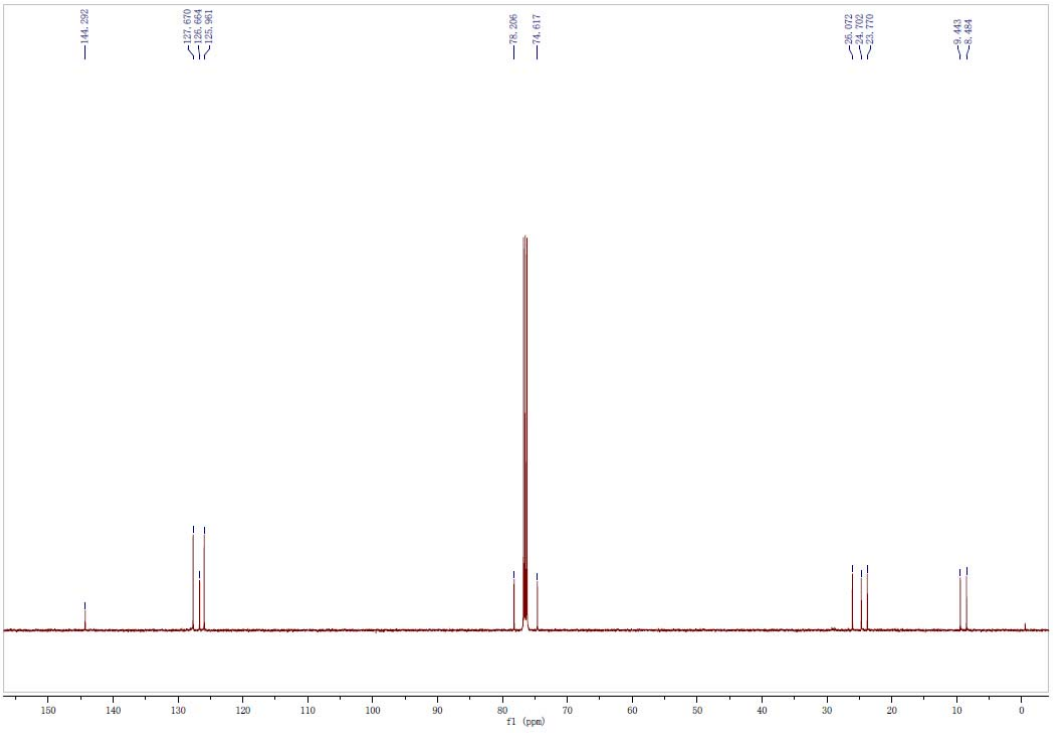
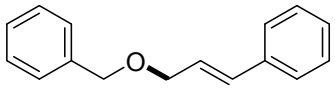
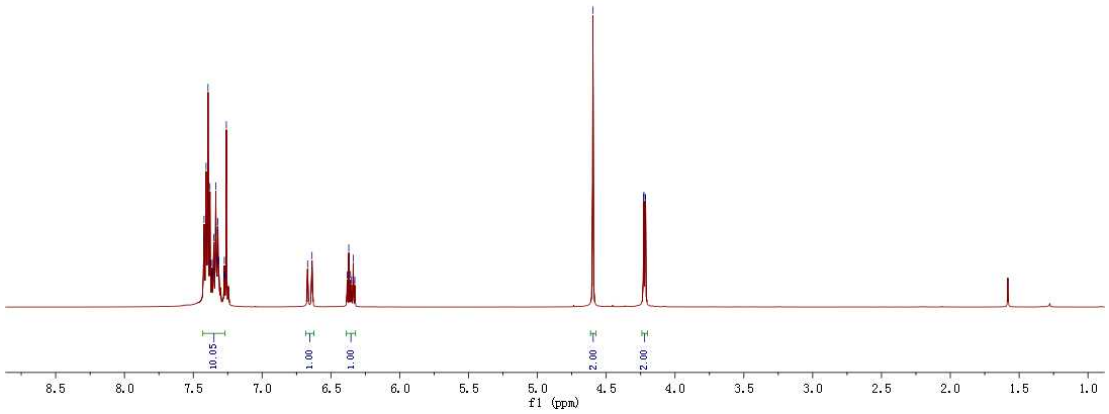


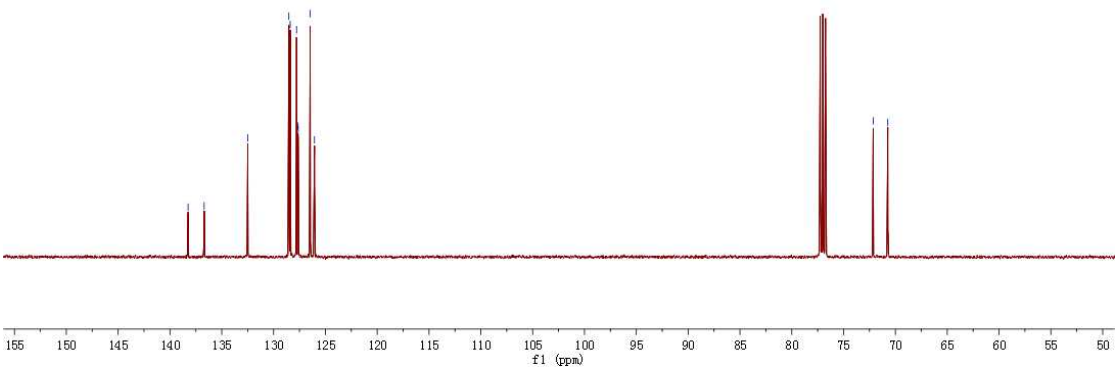


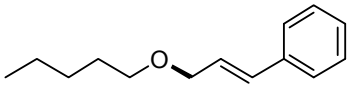
(5a)

^{1}H NMR



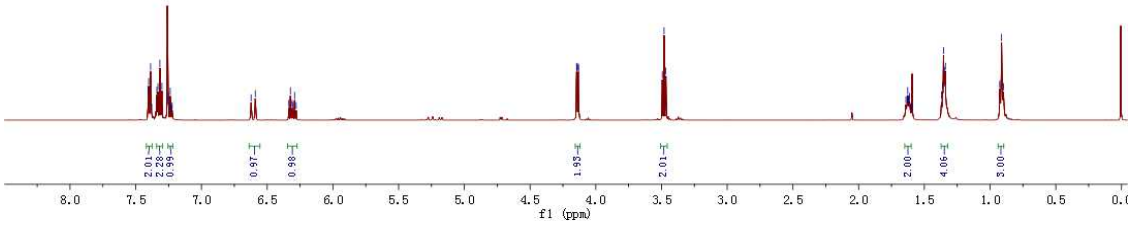
^{13}C NMR



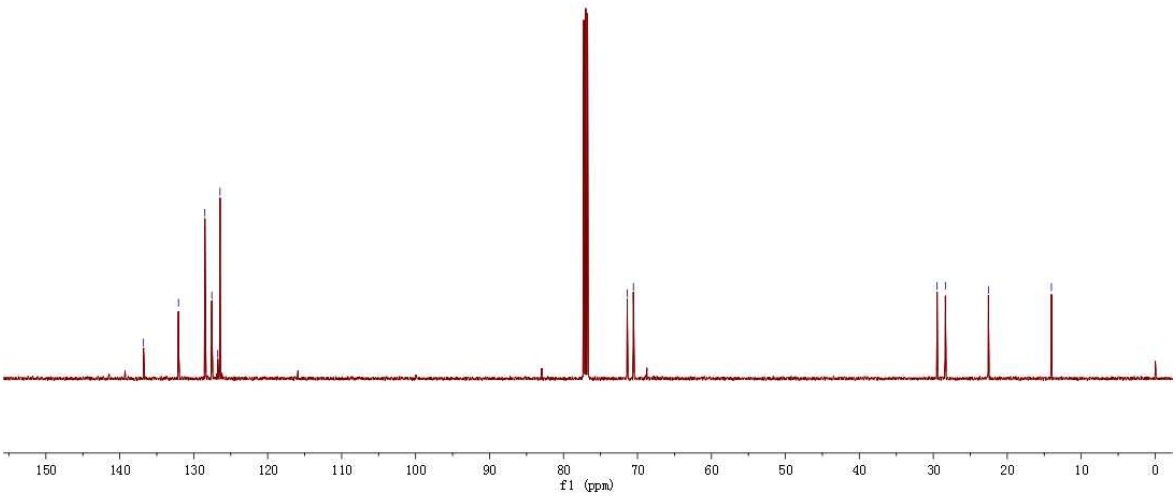


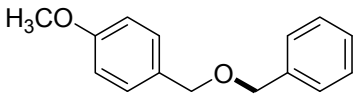
(5b)

^{1}H NMR



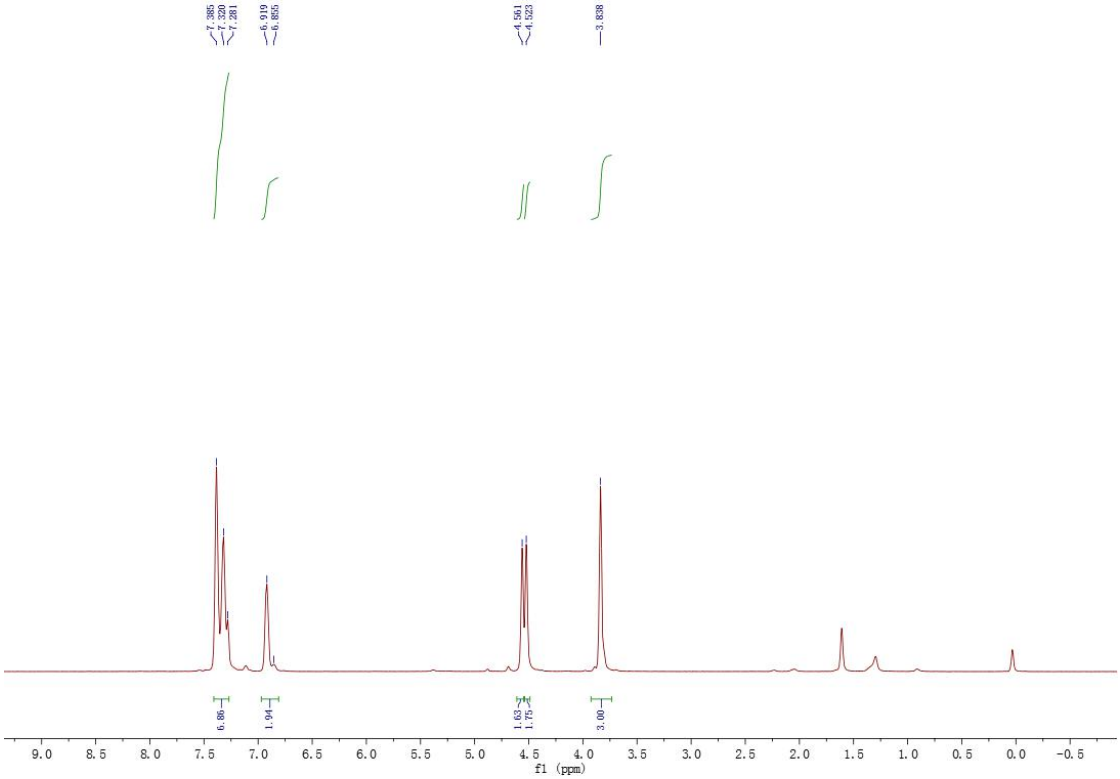
^{13}C NMR



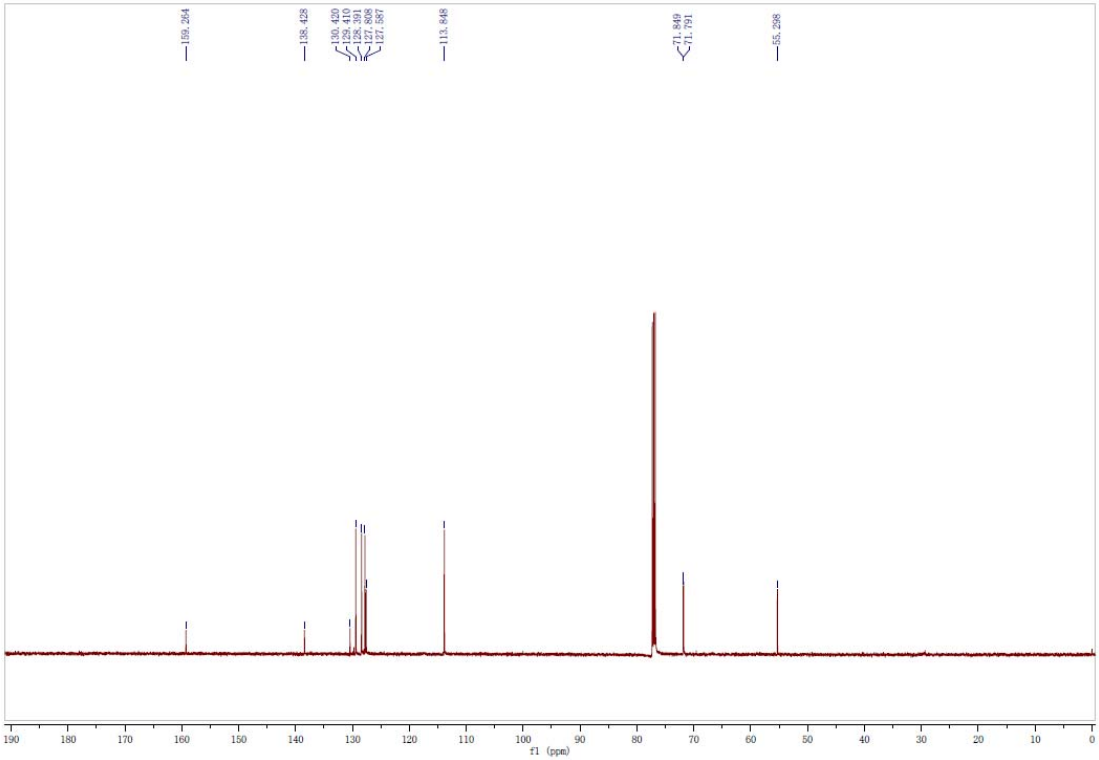


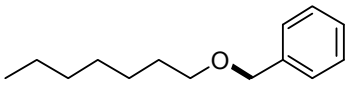
(6a)

^{1}H NMR



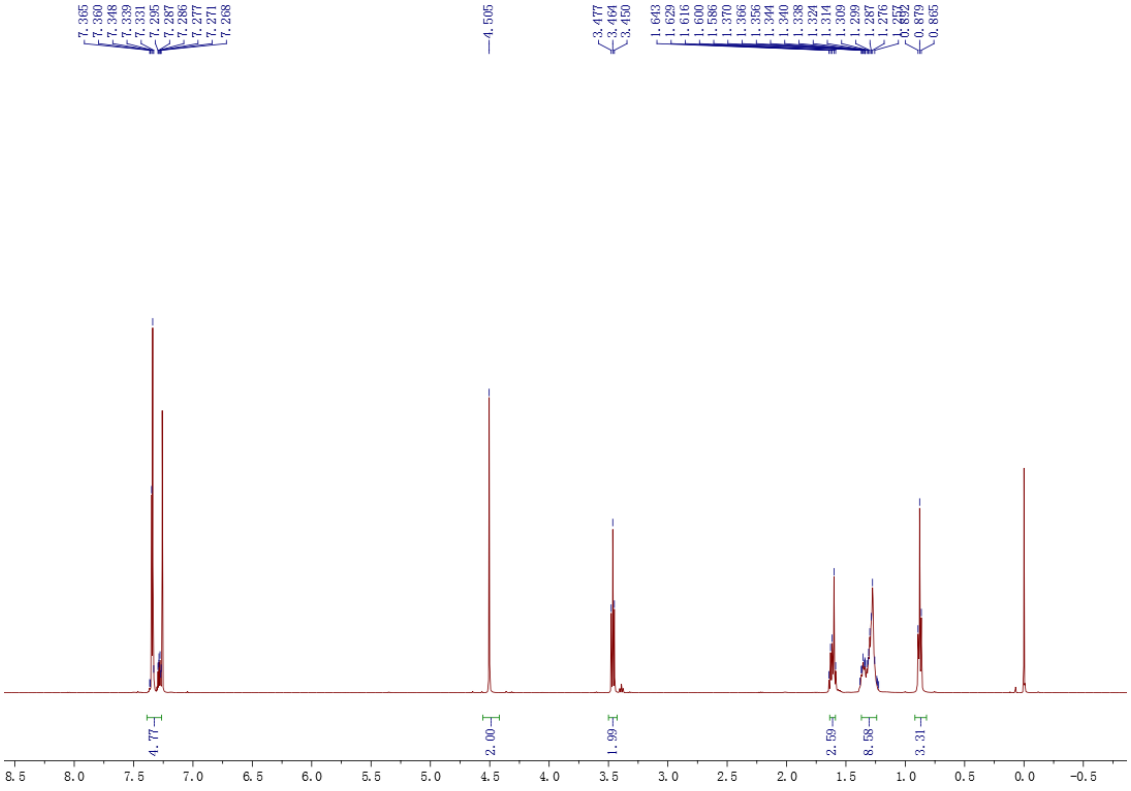
^{13}C NMR



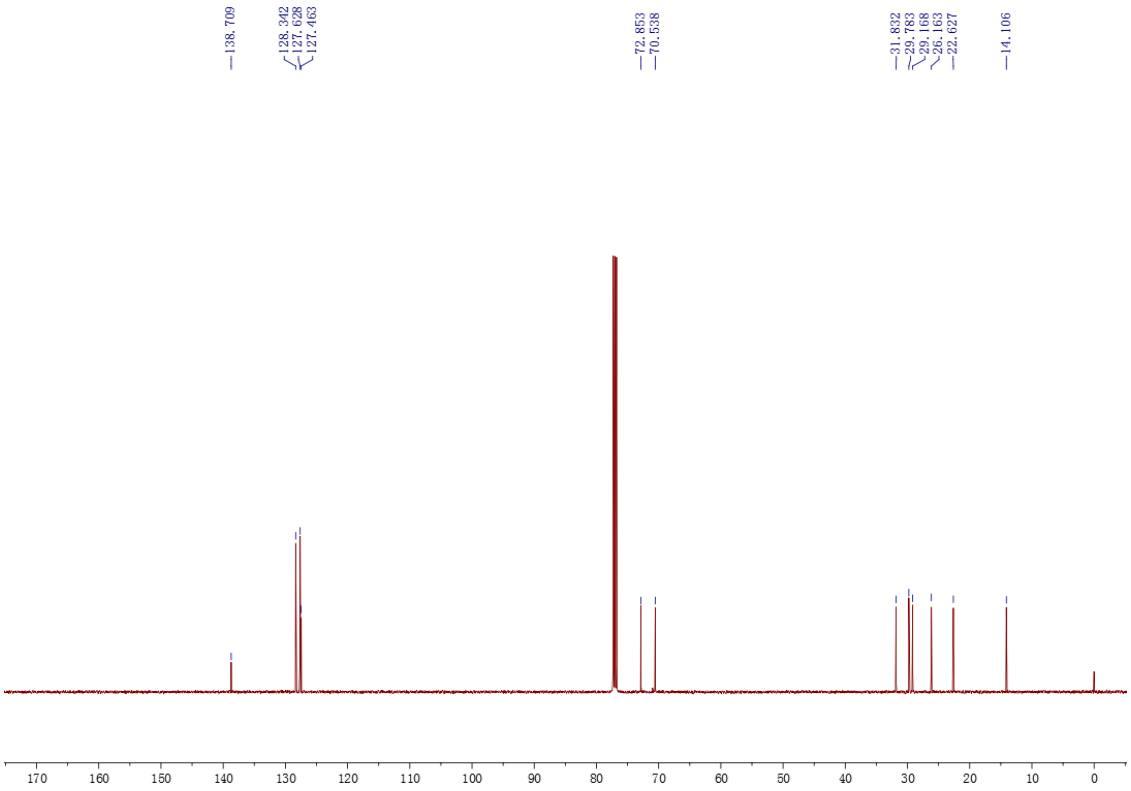


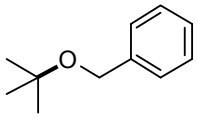
(6b)

^{1}H NMR



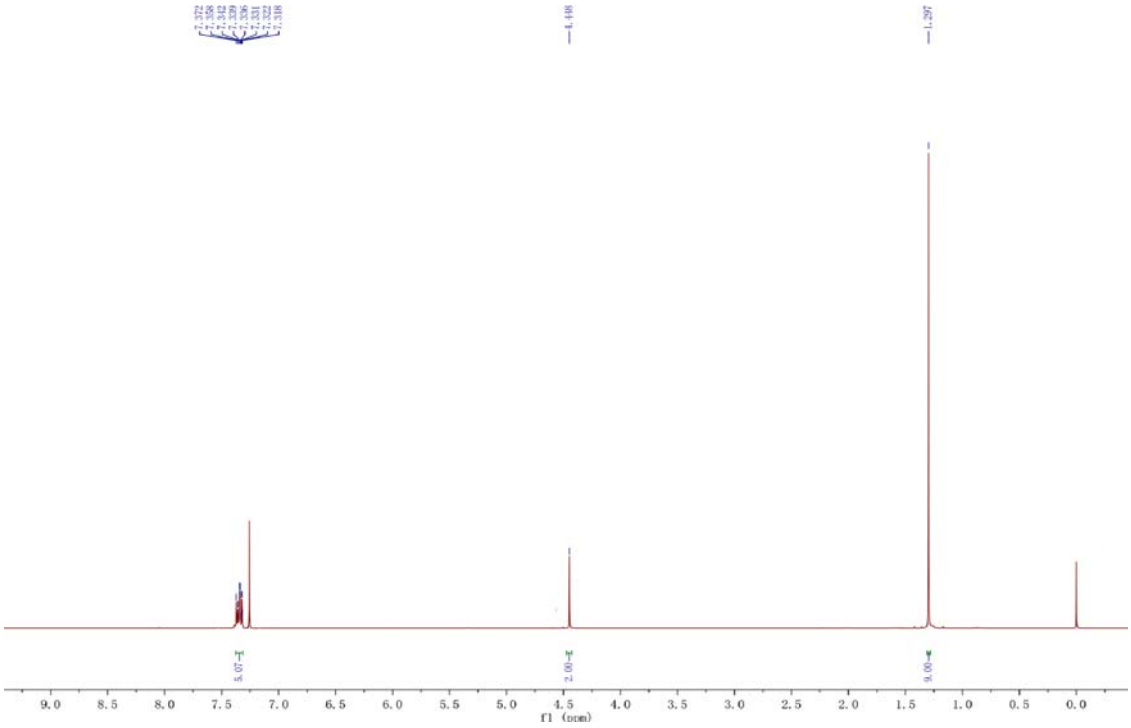
^{13}C NMR



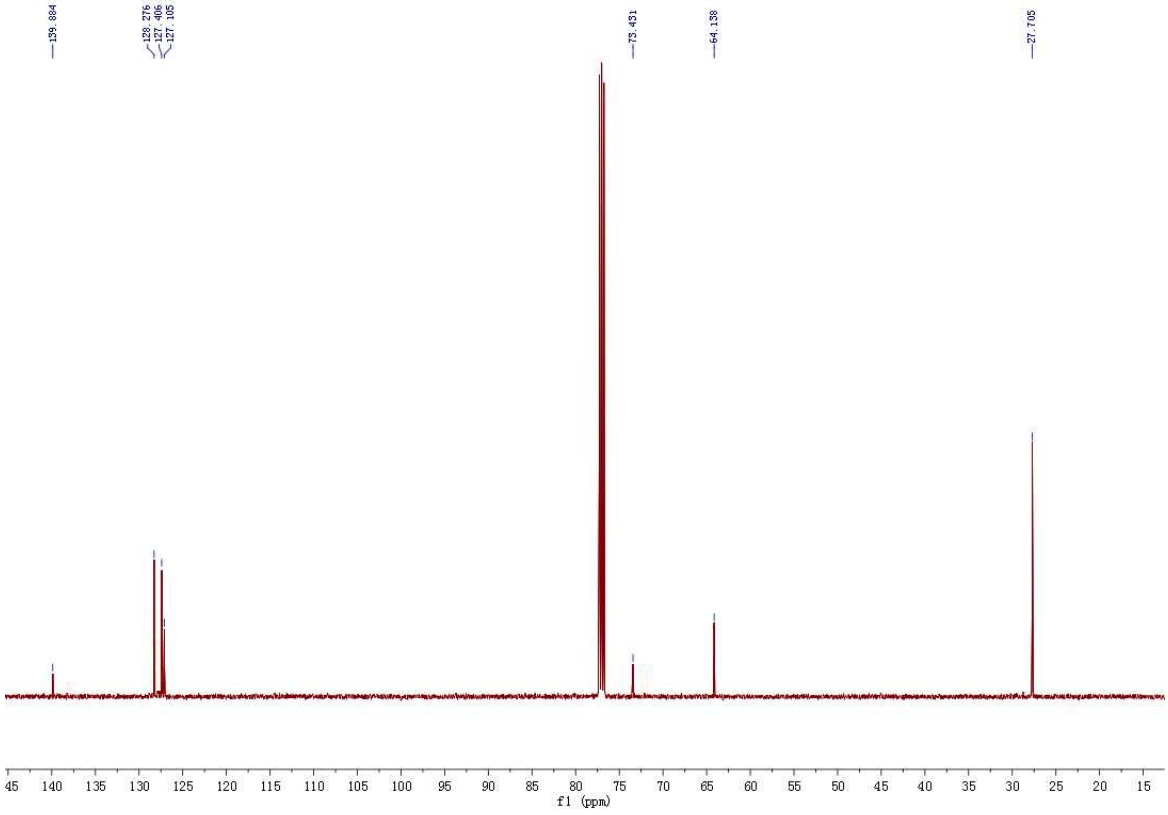


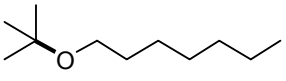
(7a)

^{1}H NMR



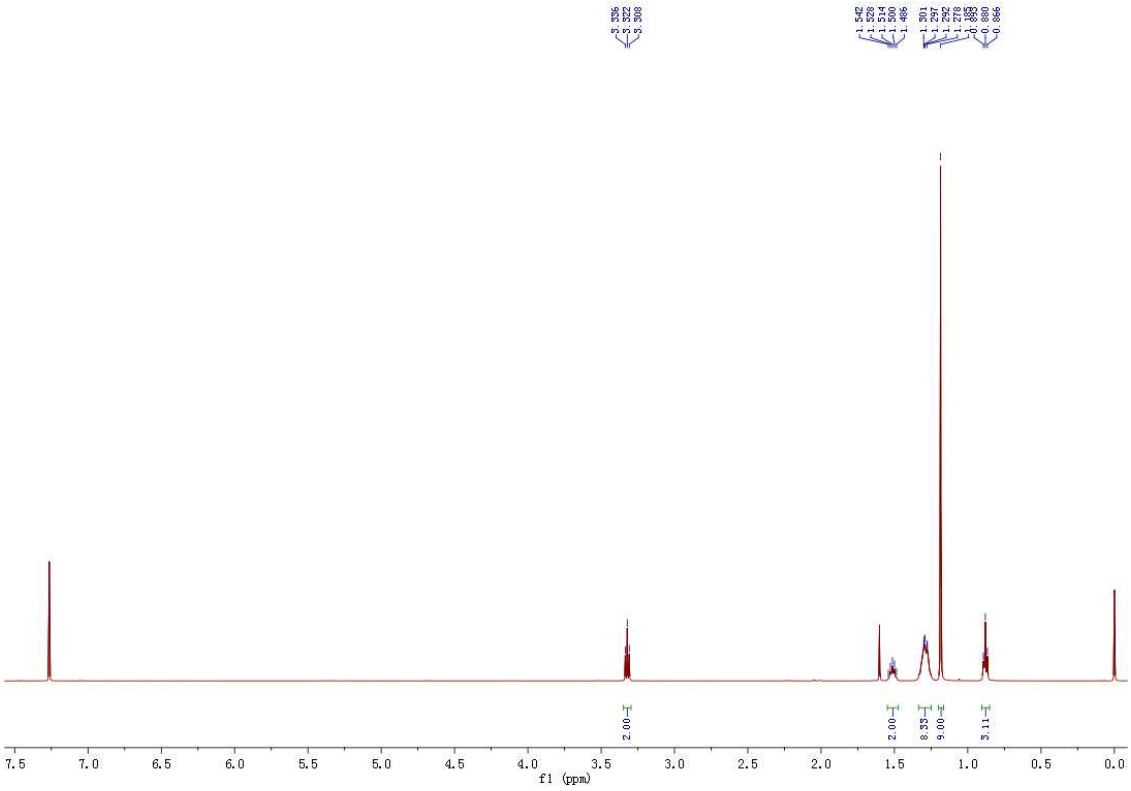
^{13}C NMR





(7b)

^{1}H NMR



^{13}C NMR