Supporting Information

Dehydroxylation of alcohols for nucleophilic substitution

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Content

1. General information

Solvents and reagents were purchased from commercial sources and used as received unless otherwise noted. ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were detected on a 500 MHz, 400MHz or 300 MHz NMR spectrometer. Data for ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and ^{31}P NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, coupling constant (*J*) in Hz). Mass spectra were obtained on a GC-MS or LC-MS. High resolution mass data were recorded on a high resolution mass spectrometer in the EI, ESI or DART mode.

2. Evidence for the proposed mechanism

Usually, Ph_3P would readily undergo alkylation with alkyl iodides to give alkylphosphonium salts. Surprisingly, Ph_3P was almost completely transformed into $Ph_3P{=}O$, and neither monophosphonium salt ($Ph_3P^+CH_2CH_2I$ I^-) nor diphosphonium salt ($Ph_3P^+CH_2CH_2P^+Ph_3$ $2I^-$) was observed in the dehydroxy-functionalization reaction. Furthermore, diphosphonium salt ($Ph_3P^+CH_2CH_2P^+Ph_3$ $2I^-$) could not promote dehydroxy-functionlization, suggesting that the alkylation process did not occur. NMR spectroscopy was then used to monitor the reaction of Ph_3P with ICH_2CH_2I. Mixing Ph_3P (0.2 mmol) and ICH_2CH_2I (0.2 mmol) in DMF (2 mL) at room temperature would immediately led to the rapid evolution of gas and the complete conversion of both ICH_2CH_2I and Ph_3P. ^{1}H NMR analysis of the reaction mixture revealed that ICH_2CH_2I was converted into ethylene ($CH_2{=}CH_2$) (Figure S1). Ph_3P was transformed into two new species (**A** and **B**), the signals of which detected by ^{31}P NMR spectroscopy appeared at 25.5 ppm and 11.9 ppm, respectively. The signal at 25.5 ppm was assigned to $Ph_3P{=}O$, as the intensity of this signal in ^{31}P NMR spectrum was increased by external addition of $Ph_3P{=}O$ into the system. Intermediate **B** is so fragile that the attempts at its isolation or further characterization were unsuccessful. Its structure is proposed to be a pentacoordinate species (Figure S1). $Ph_3P{=}O$ should be formed from this species with the simultaneous formation of Vilsmeier–Haack type intermediate **C**. After intermediates **A** and **B** were generated, the subsequent addition of phenylbutanol and sodium phenolate gave the desired product in 28% yield, indicating that both species **B** and **C** are key intermediates of the reaction. This low yield is because these two species are unstable and would readily undergo side reactions in the absence of substrates. If substrates are added before intermediates **B** and **C** are formed, high yields would be obtained, as shown in Tables 1 and 2.

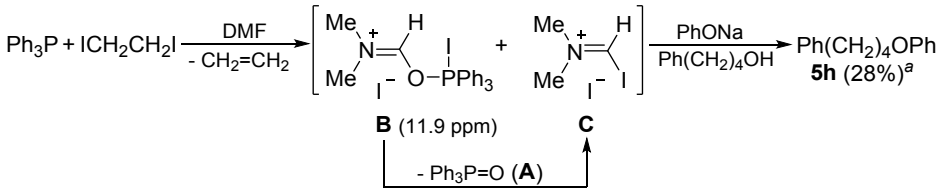


Figure S1. The reaction of Ph_3P with ICH_2CH_2I in DMF. [a]The yield was determined by ^1H NMR spectroscopy.

The reaction of Ph_3P with ICH_2CH_2I to furnish intermediate **B** occurs so fast that no direct evidence could be collected to elucidate this process. Fortunately, we found that the conversion in chloroform proceeded slowly. Therefore, the reaction in $CDCl_3$ in a NMR tube was monitored by ^{31}P NMR spectroscopy. New phosphorus species **D** and **E** were detected immediately after mixing Ph_3P and ICH_2CH_2I (Figure S2-A). They were too unstable to be isolated for characterization, and thus their structures were determined based on their ^{31}P NMR signals. The formation of intermediates **D** and **E** should be because of a strong P-I halogen bond.[1] In intermediate **D**, the phosphorus atom carries slightly positive charge, therefore a downfield shift was observed in ^{31}P NMR spectroscopy. Intermediate **E** is close to a pentacoordinate phosphorus species, thus its signal would move upfield.[2] This intermediate could be either a linear or a cyclic structure, depending on the interaction of terminal *Ph*$_3$P and *CH*$_2$I moiety. Intermediates **D** and **E** were slowly transformed into two new species **F** and **G**, with ^{31}P NMR signals appearing at +45.8 ppm and -18.7 ppm, respectively (Figure S2-B). **F** and **G** were determined to be Ph_3PI_2 and $[Ph_3P^+I\ I^-]$, respectively, based on the reported phosphorus signals of Ph_3PI_2[3] and $[Ph_3P^+I\ I^-]$[3-4].

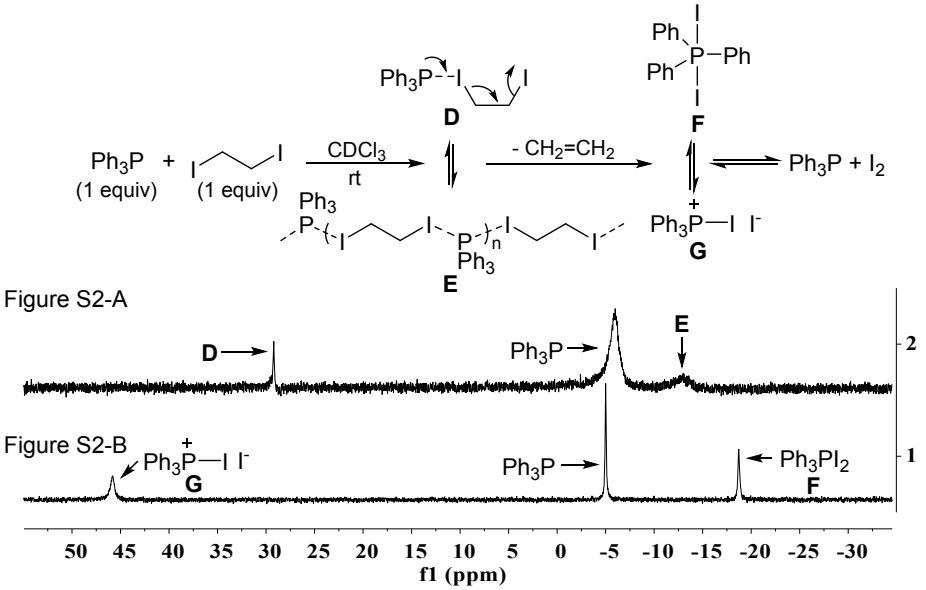
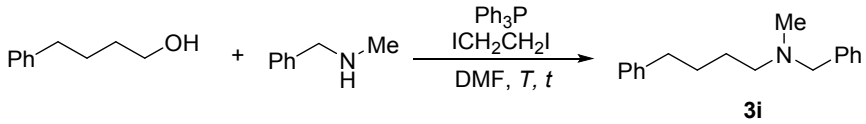


Figure S2. The reaction of Ph_3P with ICH_2CH_2I in $CDCl_3$.

3. Screening reaction conditions of dehydroxy-amination of alcohols



3i

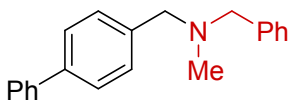
Entry	Ratio[a]	T (°C)	t (hour)	Yield (%)[b]
1	1:3:1.2:1.2	r.t.	10 h	66
2	1:3:1.2:1.2	50	10 h	63
3	1:3:1.2:1.2	80	10 h	62
4	1:3.5:1.2:1.2	r.t.	10 h	68
5	1:4:1.2:1.2	r.t.	10 h	75
6	1:4:1.1:1.1	r.t.	10 h	55
7	1:4:1.3:1.3	r.t.	10 h	70
8	1:4:1.5:1.5	r.t.	10 h	72
9	1:4:1.2:1.2	r.t.	2	44
10	1:4:1.2:1.2	r.t.	4	45
11	1:4:1.2:1.2	r.t.	6	56

Reaction conditions: **1** (0.5 mmol), **2**, Ph_3P and ICH_2CH_2I in DMF (5 mL). [a]Molar ratio of 1:2:Ph_3P:ICH_2CH_2I. [b]Determined by ^1H NMR with the use of anisole as an internal standard.

4. General procedure for dehydroxy-functionalization of alcohols

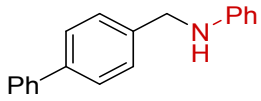
4.1. General procedure for dehydroxylation of alcohols to form C-N and C-S bonds

Alcohol **1a** (1.0 equiv, 0.5 mmol, 92.1 mg), triphenylphosphine (1.2 equiv, 0.6 mmol, 157.4 mg) and anhydrous DMF (5.0 mL) were added into a 10 mL sealed tube under a N_2 atmosphere. 1,2-Diiodoethane (1.2 equiv, 0.6 mmol, 169.1 mg) was then added and the resulting mixture was stirred for around 1 min until the 1,2-diiodoethane was completely dissolved. Amine **2a** (3.0 equiv, 1.5 mmol, 181.8 mg) was added subsequently and the mixture was stirred at room temperature for 10-12 h. Dichloromethane (20 mL) was added and the resulting solution was washed with water (20 mL x 3). The organic layer was dried over Na_2SO_4. After filtration, the solvent was removed by concentration under reduced pressure. The residue was subjected to flash column chromatography to afford the pure product **3a**.

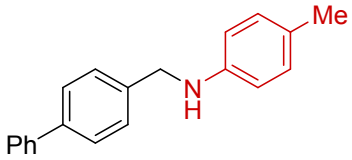


1-([1,1'-biphenyl]-4-yl)-*N*-benzyl-*N*-methylmethanamine (**3a**):[5] 96%; white solid. ^1H NMR (400 MHz, chloroform-*d*) δ 7.64 – 7.55 (m, 4H), 7.49 – 7.38 (m, 6H), 7.38 –

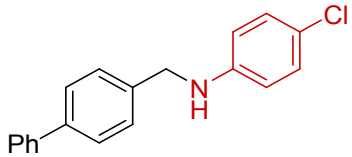
7.31 (m, 3H), 7.30 – 7.23 (m, 1H), 3.58 (s, 2H), 3.57 (s, 2H), 2.24 (s, 3H). LC-MS (ESI) Calcd. for $C_{21}H_{22}N$ $[M+H]^+$ 288.2; found 288.2.



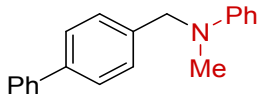
N-([1,1'-biphenyl]-4-ylmethyl)aniline (**3b**).[5] 4 equiv of N-nucleophile was used as the nucleophile; the reaction temperature was 50 °C. 90%; white solid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.57 (t, *J* = 7.0 Hz, 4H), 7.46 – 7.39 (m, 4H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 7.9 Hz, 2H), 4.36 (s, 2H), 4.05 (s, 1H).



N-([1,1'-biphenyl]-4-ylmethyl)-4-methylaniline (**3c**). 4 equiv of N-nucleophile was used as the nucleophile; the reaction temperature was 50 °C. 94%; white solid. m.p. 122 – 123 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.62 – 7.52 (m, 4H), 7.49 – 7.39 (m, 4H), 7.39 – 7.29 (tt, *J* = 7.4, 1.6 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.59 (d, *J* = 8.4 Hz, 2H), 4.35 (s, 2H), 3.94 (s, 1H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 145.9, 140.9, 140.1, 138.8, 129.8, 128.8, 127.9, 127.4, 127.2, 127.1, 126.8, 113.0, 48.3, 20.4. IR (neat) ν = 3392, 2924, 2852, 1612, 1520, 1406, 1928, 1156, 1080, 826, 815, 771, 727, 697, 512 cm^{-1}. HRMS (EI) Calcd. for $C_{20}H_{19}N$ $[M]^+$: 273.1517; found 273.1517.

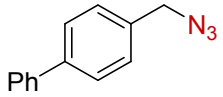


N-([1,1'-biphenyl]-4-ylmethyl)-4-chloroaniline (**3d**). 4 equiv of N-nucleophile was used as the nucleophile; the reaction temperature was 50 °C. 82%; white solid. m.p. 124 – 125 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.68 – 7.51 (m, 4H), 7.50 – 7.38 (m, 4H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.12 (d, *J* = 8.7 Hz, 2H), 6.57 (d, *J* = 8.7 Hz, 2H), 4.34 (s, 2H), 4.09 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 146.6, 140.8, 140.4, 138.0, 129.1, 128.8, 127.8, 127.45, 127.35, 127.1, 122.2, 114.0, 48.1. IR (neat) ν = 3383, 3026, 2843, 1594, 1494, 1400, 1339, 1157, 1077, 1006, 815, 762, 689, 669, 505 cm^{-1}. HRMS (EI) Calcd. for $C_{19}H_{16}NCl$ $[M]^+$: 293.0971; found 293.0963.

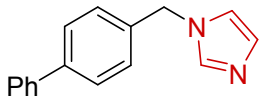


N-([1,1'-biphenyl]-4-ylmethyl)-*N*-methylaniline (**3e**).[6] 4 equiv of N-nucleophile was used as the nucleophile; the reaction temperature was 50 °C. quantitative; white solid.

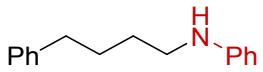
^{1}H NMR (400 MHz, chloroform-*d*) δ 7.63 – 7.52 (m, 4H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.39 – 7.28 (m, 3H), 7.29 – 7.17 (m, 2H), 6.80 (d, *J* = 8.0 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 4.59 (s, 2H), 3.06 (s, 3H).



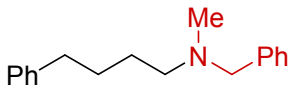
4-(azidomethyl)-1,1'-biphenyl (**3f**).[7] NaN_3 was used as the nucleophile. quantitative; white solid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.65 – 7.52 (m, 4H), 7.49 – 7.42 (m, 2H), 7.41 – 7.31 (m, 3H), 4.38 (s, 2H).



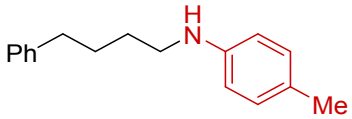
1-([1,1'-biphenyl]-4-ylmethyl)-1H-imidazole (**3g**).[8] 4 equiv of N-nucleophile was used as the nucleophile; the reaction temperature was 50 °C. 78%; white solid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.61 – 7.50 (m, 5H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.10 (s, 1H), 6.92 (s, 1H), 5.14 (s, 2H).



N-(4-phenylbutyl)aniline (**3h**).[9] 4 equiv of N-nucleophile was used as the nucleophile; the reaction temperature was 50 °C. 71%; yellow liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.32 – 7.25 (m, 2H), 7.25 – 7.12 (m, 5H), 6.68 (t, *J* = 7.1 Hz, 1H), 6.58 (d, *J* = 8.1 Hz, 2H), 3.57 (s, 1H), 3.12 (t, *J* = 6.9 Hz, 2H), 2.66 (t, *J* = 7.4 Hz, 2H), 1.80 – 1.59 (m, 4H).

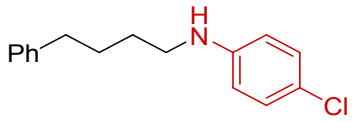


N-benzyl-*N*-methyl-4-phenylbutan-1-amine (**3i**).[10] 4 equiv of N-nucleophile was used as the nucleophile. 59%; colorless liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.34 – 7.28 (m, 4H), 7.28 – 7.21 (m, 3H), 7.20 – 7.13 (m, 3H), 3.47 (s, 2H), 2.61 (t, *J* = 7.5 Hz, 2H), 2.38 (t, *J* = 7.2 Hz, 2H), 2.17 (s, 3H), 1.73 – 1.48 (m, 4H).

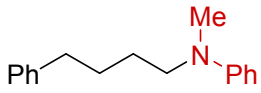


4-methyl-*N*-(4-phenylbutyl)aniline (**3j**). 4 equiv of N-nucleophile was used as the nucleophile; the reaction temperature was 50 °C. 74%; white solid. m.p. 32 – 33 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.32 – 7.25 (m, 2H), 7.22 – 7.11 (m, 3H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.52 (d, *J* = 8.3 Hz, 2H), 3.44 (s, 1H), 3.10 (t, *J* = 6.9 Hz, 2H), 2.65 (t, *J* = 7.4 Hz, 2H), 2.23 (s, 3H), 1.79 – 1.58 (m, 4H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 146.2, 142.2, 129.7, 128.4, 128.3, 126.4, 125.8, 112.9, 44.2, 35.7,

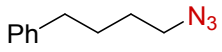
29.2, 29.0, 20.4. IR (neat) ν = 3406, 3061, 3024, 2932, 2857, 1619, 1495, 1478, 1453, 1373, 1317, 1250, 1181, 1125, 806, 747, 698, 508 cm^{-1}. HRMS (EI) Calcd. for $C_{17}H_{21}N$ $[M]^+$: 239.1674; found 239.1681.



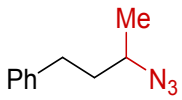
4-chloro-*N*-(4-phenylbutyl)aniline (**3k**). 4 equiv of N-nucleophile was used as the nucleophile; the reaction temperature was 50 °C. 53%; yellow liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.29 (t, *J* = 7.4 Hz, 2H), 7.23 – 7.15 (m, 3H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.49 (d, *J* = 8.4 Hz, 2H), 3.57 (s, 1H), 3.09 (t, *J* = 7.0 Hz, 2H), 2.66 (t, *J* = 7.5 Hz, 2H), 1.81 – 1.57 (m, 4H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 147.0, 142.1, 129.0, 128.4, 128.4, 125.9, 121.6, 113.7, 44.0, 35.6, 29.0, 28.9. IR (neat) ν = 3415, 3261, 3061, 3025, 2935, 2857, 1600, 1502, 1475, 1401, 1320, 1248, 1177, 1090, 814, 748, 699, 669, 504 cm^{-1}. HRMS (EI) Calcd. for $C_{16}H_{18}NCl$ $[M]^+$: 259.1128; found 259.1123.



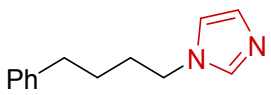
N-methyl-*N*-(4-phenylbutyl)aniline (**3l**).[11] 4 equiv of N-nucleophile was used as the nucleophile; the reaction temperature was 50 °C. 80%; yellow liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.32 – 7.26 (m, 2H), 7.26 – 7.13 (m, 5H), 6.72 – 6.64 (m, 3H), 3.33 (t, *J* = 6.9 Hz, 2H), 2.91 (s, 3H), 2.64 (t, *J* = 7.3 Hz, 2H), 1.73 – 1.56 (m, 4H).



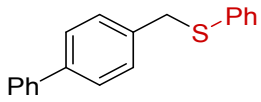
(4-azidobutyl)benzene (**3m**).[12] NaN_3 was used as the nucleophile. Irrespective of whether a base (2 equiv of 2,6-lutidine) was used or not, a quantitative yield was obtained. If the base is used, it should be added after NaN_3. colorless liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.28 (t, *J* = 7.4 Hz, 2H), 7.22 – 7.14 (m, 3H), 3.27 (t, *J* = 6.6 Hz, 2H), 2.64 (t, *J* = 7.4 Hz, 2H), 1.77 – 1.57 (m, 4H).



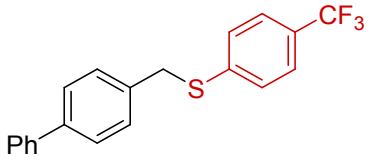
(3-azidobutyl)benzene (**3n**).[13] NaN_3 was used as the nucleophile. 98%; colorless liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.28 (t, *J* = 7.4 Hz, 2H), 7.22 – 7.15 (m, 3H), 3.43 (h, *J* = 6.6 Hz, 1H), 2.80 – 2.59 (m, 2H), 1.88 – 1.69 (m, 2H), 1.28 (d, *J* = 6.5 Hz, 3H).



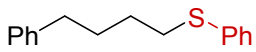
1-(4-phenylbutyl)-1H-imidazole (**3o**).[14] 4 equiv of N-nucleophile was used as the nucleophile; the reaction temperature was 50 °C. 82%; yellow liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.92 (s, 1H), 7.34 – 7.25 (m, 2H), 7.20 (tt, *J* = 7.3, 1.5 Hz, 1H), 7.17 – 7.10 (m, 3H), 6.92 (s, 1H), 3.96 (t, *J* = 7.2 Hz, 2H), 2.64 (t, *J* = 7.2 Hz, 2H), 1.82 (p, *J* = 7.3 Hz, 2H), 1.63 (p, *J* = 7.5 Hz, 2H).



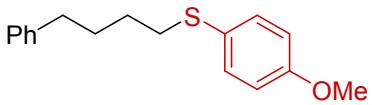
([1,1'-biphenyl]-4-ylmethyl)(phenyl)sulfane (**3p**).[5] PhS^-Na^+ was used as the nucleophile. 93%; white solid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.56 (d, *J* = 7.5 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.38 – 7.29 (m, 5H), 7.29 – 7.22 (m, 3H), 7.21 – 7.14 (m, 1H), 4.15 (s, 2H). GC-MS (EI) Calcd. for $C_{19}H_{16}S$ $[M]^+$ 276.1; found 276.1.



([1,1'-biphenyl]-4-ylmethyl)(4-(trifluoromethyl)phenyl)sulfane (**3q**): 85%; white solid. m.p. 161 – 162 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.63 – 7.52 (m, 4H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.47 – 7.31 (m, 7H), 4.22 (s, 2H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -62.45 (s, 3F). ^{13}C NMR (101 MHz, chloroform-*d*) δ 142.0, 142.0, 140.55, 140.48, 135.4, 129.2, 128.8, 128.0, 127.8 (q, *J* = 33.3 Hz), 127.4, 127.0, 125.7 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272.7 Hz), 37.4. IR (neat) ν = 1654, 1403, 1322, 1176, 1157, 1118, 845, 823, 773, 745, 689, 590, 495 cm^{-1}. HRMS (EI) Calcd. for $C_{20}H_{15}F_3S$ $[M]^+$: 344.0847; found 344.0835.

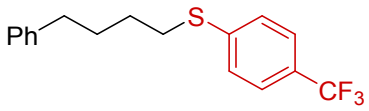


phenyl(4-phenylbutyl)sulfane (**3r**).[15] PhS^-Na^+ was used as the nucleophile. 95%; colorless liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.34 – 7.23 (m, 6H), 7.21 – 7.13 (m, 4H), 2.93 (t, *J* = 7.1 Hz, 2H), 2.62 (t, *J* = 7.4 Hz, 2H), 1.85 – 1.62 (m, 4H). GC-MS (EI) Calcd. for $C_{16}H_{18}S$ $[M]^+$ 242.1; found 242.1.

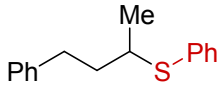


(4-methoxyphenyl)(4-phenylbutyl)sulfane (**3s**): 96%; colorless liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.36 – 7.22 (m, 4H), 7.21 – 7.09 (m, 3H), 6.83 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 2.83 (t, *J* = 7.2 Hz, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 1.73 (p, *J* = 7.0 Hz, 2H), 1.62 (p, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 158.8, 142.2, 133.2, 128.4, 128.3, 126.7, 125.8, 114.5, 55.3, 35.8, 35.4, 30.4, 28.8. IR (neat) ν = 3061, 3025, 3001, 2934, 2855, 2835, 1592, 1570, 1493, 1461, 1440, 1284, 1245, 1179,

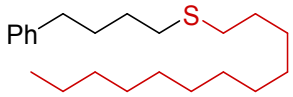
1103, 1032, 826, 747, 699, 638, 625, 526 cm^{-1}. HRMS (EI) Calcd. for $C_{17}H_{20}OS$ $[M]^+$: 272.1235; found 272.1229.



(4-phenylbutyl)(4-(trifluoromethyl)phenyl)sulfane (**3t**): quantitative; colorless liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.49 (d, *J* = 8.2 Hz, 2H), 7.36 – 7.22 (m, 4H), 7.23 – 7.10 (m, 3H), 2.97 (t, *J* = 7.0 Hz, 2H), 2.64 (t, *J* = 7.3 Hz, 2H), 1.90 – 1.62 (m, 4H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -62.41 (s, 3F). ^{13}C NMR (101 MHz, chloroform-*d*) δ 142.5, 142.5, 141.8, 128.4, 127.3, 127.2 (q, *J* = 33.3 Hz), 125.9, 125.6 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 272.7 Hz), 35.3, 32.4, 30.4, 28.3. IR (neat) ν = 3086, 3063, 3027, 2934, 2858, 1607, 1497, 1454, 1402, 1328, 1166, 1126, 1095, 1030, 1013, 824, 745, 699, 590, 494 cm^{-1}. HRMS (EI) Calcd. for $C_{17}H_{20}OS$ $[M]^+$: 310.1003; found 310.1004.



phenyl(4-phenylbutan-2-yl)sulfane (**3u**).[16] PhS^-Na^+ was used as the nucleophile. 40%; colorless liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.39 – 7.33 (m, 2H), 7.31 – 7.24 (m, 4H), 7.24 – 7.14 (m, 4H), 3.20 (h, *J* = 6.7 Hz, 1H), 2.87 – 2.70 (m, 2H), 1.99 – 1.87 (m, 1H), 1.87 – 1.76 (m, 1H), 1.32 (d, *J* = 6.7 Hz, 3H).

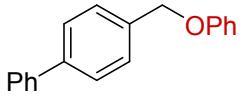


dodecyl(4-phenylbutyl)sulfane (**3v**): 80%; colorless liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.30 – 7.23 (m, 2H), 7.20 – 7.12 (m, 3H), 2.62 (t, *J* = 7.5 Hz, 2H), 2.51 (t, *J* = 7.3 Hz, 2H), 2.47 (t, *J* = 7.4 Hz, 2H), 1.77 – 1.66 (m, 2H), 1.66 – 1.58 (m, 2H), 1.58 – 1.50 (m, 2H), 1.40 – 1.19 (m, 18H), 0.87 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.3, 128.4, 128.3, 125.7, 35.5, 32.2, 32.0, 31.9, 30.6, 29.7, 29.68, 29.65, 29.63, 29.56, 29.4, 29.28, 29.26, 29.0, 22.7, 14.1. IR (neat) ν = 3085, 3062, 3026, 2925, 2853, 1604, 1496, 1454, 1377, 1261, 1030, 743, 698 cm^{-1}. HRMS (EI) Calcd. for $C_{22}H_{38}S$ $[M]^+$: 334.2694; found 334.2699.

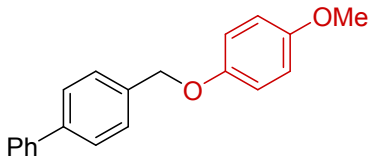
4.2. General procedure for dehydroxylation of alcohols to form C-O and C-X (X = Cl, Br, I) bonds

Alcohol **1a** (1.0 equiv, 0.5 mmol, 92.1 mg), triphenylphosphine (1.2 equiv, 0.6 mmol, 157.4 mg) and anhydrous DMF (5.0 mL) were added into a 10 mL sealed tube under a N_2 atmosphere. 1,2-Diiodoethane (1.2 equiv, 0.6 mmol, 169.1 mg) was then added and the resulting mixture was stirred for around 1 min until the 1,2-diiodoethane was completely dissolved. Sodium phenolate **4a** (3.0 equiv, 1.5 mmol, 174.1 mg) was added subsequently and the mixture was stirred at room temperature for 10-12 h.

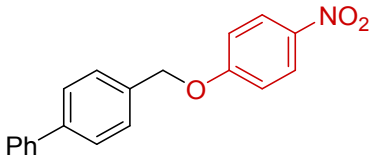
Dichloromethane (20 mL) was added and the resulting solution was washed with water (20 mL x 3). The organic layer was dried over Na_2SO_4. After filtration, the solvent was removed by concentration under reduced pressure. The residue was subjected to flash column chromatography to afford the pure product **5a**.



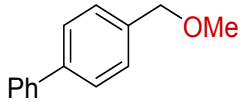
4-(phenoxymethyl)-1,1'-biphenyl (**5a**):[17] 98%; white solid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.60 (t, *J* = 7.4 Hz, 4H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.38 – 7.26 (m, 3H), 7.04 – 6.93 (m, 3H), 5.10 (s, 2H). GC-MS (EI) Calcd. for $C_{19}H_{16}O$ $[M]^+$ 260.1; found 260.1.



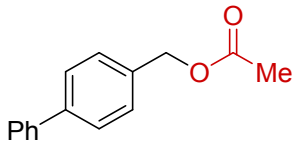
4-((4-methoxyphenoxy)methyl)-1,1'-biphenyl (**5b**): 83%; white solid. m.p. 162 – 163 ^{o}C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.64 – 7.57 (m, 4H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 6.94 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 9.1 Hz, 2H), 5.05 (s, 2H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 154.0, 153.0, 140.9, 140.8, 136.3, 128.8, 128.0, 127.37, 127.35, 127.2, 115.9, 114.7, 70.5, 55.7. IR (neat) ν = 2995, 2958, 2927, 2833, 1506, 1488, 1438, 1407, 1388, 1290, 1232, 1220, 1178, 1127, 1112, 1039, 1016, 877, 824, 767, 745, 717, 688, 524 cm^{-1}. HRMS (EI) Calcd. for $C_{20}H_{18}O_2$ $[M]^+$: 290.1307; found 290.1310.



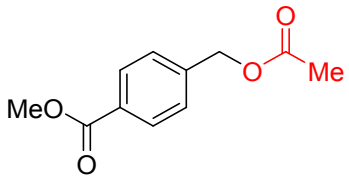
4-((4-nitrophenoxy)methyl)-1,1'-biphenyl (**5c**):[18] 76%; yellow solid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.21 (d, *J* = 9.1 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.52 – 7.41 (m, 4H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.04 (d, *J* = 9.1 Hz, 2H), 5.19 (s, 2H).



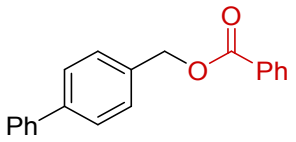
4-(methoxymethyl)-1,1'-biphenyl (**5d**):[19] 92%; colorless liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.62 – 7.54 (m, 4H), 7.47 – 7.38 (m, 4H), 7.34 (tt, *J* = 7.3, 1.5 Hz, 1H), 4.50 (s, 2H), 3.42 (s, 3H).



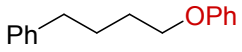
[1,1'-biphenyl]-4-ylmethyl acetate (**5e**).[20] $CH_3CO_2^-K^+$ was used as the nucleophile. 99%; colorless liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.62 – 7.55 (m, 4H), 7.48 – 7.40 (m, 4H), 7.38 – 7.32 (m, 1H), 5.15 (s, 2H), 2.12 (s, 3H).



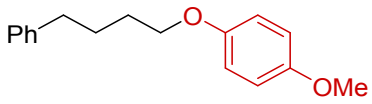
methyl 4-(acetoxymethyl)benzoate (**5f**).[21] $CH_3CO_2^-K^+$ was used as the nucleophile. 96%; colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 5.13 (s, 2H), 3.90 (s, 3H), 2.11 (s, 3H).



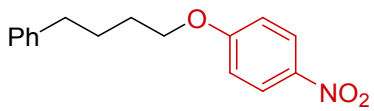
[1,1'-biphenyl]-4-ylmethyl benzoate (**5g**):[22] quantitative; white solid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.14 – 8.06 (m, 2H), 7.64 – 7.57 (m, 4H), 7.57 – 7.50 (m, 3H), 7.48 – 7.41 (m, 4H), 7.35 (tt, *J* = 7.3, 1.6 Hz, 1H), 5.41 (s, 2H).



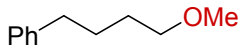
(4-phenoxybutyl)benzene (**5h**):[23] quantitative; white solid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.32 – 7.23 (m, 4H), 7.23 – 7.15 (m, 3H), 6.96 – 6.86 (m, 3H), 3.96 (t, *J* = 5.9 Hz, 2H), 2.69 (t, *J* = 7.0 Hz, 2H), 1.96 – 1.67 (m, 4H).



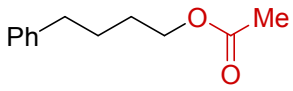
1-methoxy-4-(4-phenylbutoxy)benzene (**5i**): quantitative; colorless liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.28 (t, *J* = 7.5 Hz, 2H), 7.22 – 7.15 (m, 3H), 6.84 – 6.80 (m, 4H), 3.92 (t, *J* = 4.9 Hz, 2H), 3.76 (s, 3H), 2.68 (t, *J* = 6.5 Hz, 2H), 1.85 – 1.76 (m, 4H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 153.7, 153.2, 142.3, 128.4, 128.3, 125.8, 115.4, 114.6, 68.4, 55.8, 35.6, 29.0, 27.9. IR (neat) ν = 3025, 2999, 2939, 2861, 2832, 1508, 1465, 1389, 1288, 1232, 1180, 1107, 1040, 825, 745, 699, 524 cm^{-1}. HRMS (EI) Calcd. for $C_{17}H_{20}O_2$ $[M]^+$: 256.1463; found 256.1470.



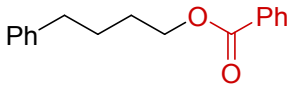
1-nitro-4-(4-phenylbutoxy)benzene (**5j**):[24] 46%; yellow liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.17 (d, *J* = 9.3 Hz, 2H), 7.32 – 7.25 (m, 2H), 7.22 – 7.16 (m, 3H), 6.91 (d, *J* = 9.2 Hz, 2H), 4.04 (t, *J* = 5.8 Hz, 2H), 2.69 (t, *J* = 7.0 Hz, 2H), 1.92 – 1.74 (m, 4H).



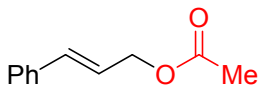
(4-methoxybutyl)benzene (**5k**):[25] 40%; colorless liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.30 – 7.23 (m, 2H), 7.19 – 7.13 (m, 3H), 3.37 (t, *J* = 6.3 Hz, 2H), 3.31 (s, 3H), 2.62 (t, *J* = 7.5 Hz, 2H), 1.73 – 1.57 (m, 4H).



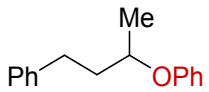
4-phenylbutyl acetate (**5l**).[26] $CH_3CO_2^-K^+$ was used as the nucleophile. quantitative; colorless liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.30 – 7.25 (m, 2H), 7.21 – 7.14 (m, 3H), 4.07 (t, *J* = 6.2 Hz, 2H), 2.63 (t, *J* = 7.1 Hz, 2H), 2.03 (s, 3H), 1.73 – 1.62 (m, 4H).



4-phenylbutyl benzoate (**5m**):[27] 60%; colorless liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.06 – 8.00 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.31 – 7.25 (m, 2H), 7.22 – 7.15 (m, 3H), 4.33 (t, *J* = 6.0 Hz, 2H), 2.68 (t, *J* = 7.0 Hz, 2H), 1.88 – 1.73 (m, 4H).

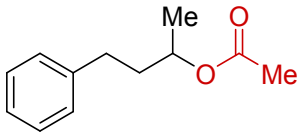


cinnamyl acetate (**5n**).[21] $CH_3CO_2^-K^+$ was used as the nucleophile. 99%; colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.35 (m, 2H), 7.35 – 7.28 (m, 2H), 7.28 – 7.20 (m, 1H), 6.64 (d, *J* = 15.9 Hz, 1H), 6.27 (dt, *J* = 15.9, 6.5 Hz, 1H), 4.71 (dd, *J* = 6.5, 1.1 Hz, 2H), 2.09 (s, 3H).

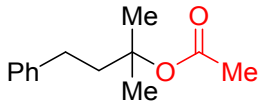


(3-phenoxybutyl)benzene (**5o**):[28] 32%; colorless liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.30 – 7.25 (m, 4H), 7.21 – 7.14 (m, 3H), 6.92 (t, *J* = 7.3 Hz, 1H), 6.86 (d, *J* = 7.9 Hz, 2H), 4.36 (h, *J* = 6.0 Hz, 1H), 2.87 – 2.66 (m, 2H), 2.14 – 2.01 (m,

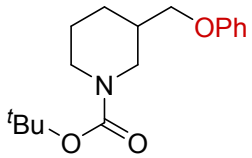
1H), 1.96 – 1.82 (m, 1H), 1.32 (d, J = 6.1 Hz, 3H).



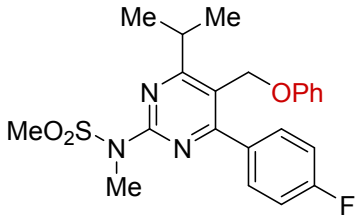
4-phenylbutan-2-yl acetate (**5p**).[16] $CH_3CO_2^-K^+$ was used as the nucleophile. 40%; colorless liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.30 – 7.23 (m, 2H), 7.20 – 7.13 (m, 3H), 4.92 (h, J = 6.3 Hz, 1H), 2.73 – 2.53 (m, 2H), 2.01 (s, 3H), 1.98 – 1.86 (m, 1H), 1.86 – 1.73 (m, 1H), 1.23 (d, J = 6.3 Hz, 3H).



2-methyl-4-phenylbutan-2-yl acetate (**5q**).[16] $CH_3CO_2^-K^+$ was used as the nucleophile; 60 °C of reaction temperature and 5 h of reaction time were used. 44%; colorless liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.23 (m, 2H), 7.21 – 7.13 (m, 3H), 2.67 – 2.59 (m, 2H), 2.10 – 2.01 (m, 2H), 1.96 (s, 3H), 1.49 (s, 6H).

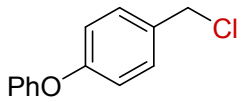


tert-butyl 3-(phenoxymethyl)piperidine-1-carboxylate (**5r**): 55%; white solid. m.p. 57 – 58 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.29 (t, J = 7.8 Hz, 2H), 6.98 – 6.88 (m, 3H), 4.21 – 3.53 (m, 4H), 2.89 (br, 2H), 1.95 – 1.73 (m, 2H), 1.72 – 1.56 (m, 1H), 1.56 – 1.05 (m, 11H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 158.9, 155.0, 129.4, 120.7, 114.5, 79.4, 69.9, 47.2, 44.5, 35.9, 28.4, 27.4, 24.5. IR (neat) ν = 3447, 2975, 2930, 2857, 1692, 1599, 1587, 1497, 1469, 1421, 1365, 1266, 1242, 1175, 1148, 1041, 753, 691, 668 cm^{-1}. HRMS (EI) Calcd. for $C_{17}H_{25}NO_3$ $[M]^+$: 291.1834; found 291.1842.

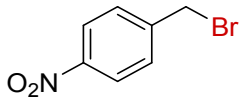


N-(4-(4-fluorophenyl)-6-isopropyl-5-(phenoxymethyl)pyrimidin-2-yl)-*N* methylmethanesulfonamide (**5s**): 77%; white solid. m.p. 129 – 130 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.77 – 7.69 (m, 2H), 7.37 – 7.29 (m, 2H), 7.08 (t, J = 8.7 Hz, 2H), 7.03 (t, J = 7.4 Hz, 1H), 6.94 (d, J = 8.6 Hz, 2H), 4.89 (s, 2H), 3.59 (s, 3H), 3.52 (s, 3H), 3.40 – 3.26 (m, 1H), 1.32 (d, J = 6.7 Hz, 6H). ^{19}F NMR (376 MHz, chloroform-*d*) δ -110.85 – -110.98 (m, 1F). ^{13}C NMR (101 MHz, chloroform-*d*) δ

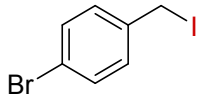
178.4, 166.6, 163.8 (d, J = 250.3 Hz), 158.4, 158.0, 133.8 (d, J = 3.1 Hz), 131.4 (d, J = 8.5 Hz), 129.7, 121.6, 117.5, 115.6 (d, J = 21.7 Hz), 114.7, 63.3, 42.5, 33.1, 31.8, 22.1. IR (neat) ν = 2974, 2931, 1872, 1605, 1594, 1553, 1480, 1339, 1231, 1155, 1069, 1029, 957, 896, 848, 820, 772, 756, 691, 600, 575, 521, 495 cm^{-1}. HRMS (EI) Calcd. for $C_{22}H_{24}N_3O_3FS$ $[M]^+$: 429.1522; found 429.1528.



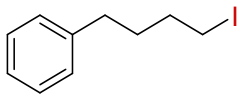
1-(chloromethyl)-4-phenoxybenzene (**5t**).[29] $^nBu_4N^+Cl^-$ was used as the nucleophile. 55%; colorless liquid. ^1H NMR (400 MHz, chloroform-*d*) δ 7.40 – 7.30 (m, 4H), 7.12 (t, J = 7.4 Hz, 1H), 7.02 (d, J = 7.7 Hz, 2H), 6.97 (d, J = 8.6 Hz, 2H), 4.58 (s, 2H).



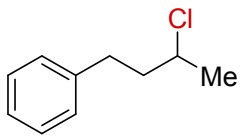
1-(bromomethyl)-4-nitrobenzene (**5u**).[30] $^nBu_4N^+Br^-$ was used as the nucleophile. quantitative; white solid. ^1H NMR (400 MHz, chloroform-*d*) δ 8.14 (d, J = 8.7 Hz, 2H), 7.51 (d, J = 8.7 Hz, 2H), 4.46 (s, 2H).



1-bromo-4-(iodomethyl)benzene (**5v**).[31] NaI was not required as the iodide anion was generated from ICH_2CH_2I; 60 °C of reaction temperature and 2 h of reaction time in CH_3CN were used. 92%; white solid. ^1H NMR (500 MHz, chloroform-*d*) δ 7.44 – 7.40 (m, 2H), 7.26 – 7.23 (m, 2H), 4.40 (s, 2H).

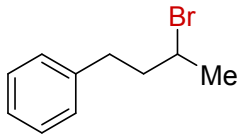


(4-iodobutyl)benzene (**5w**).[12] NaI was not required as the iodide anion was generated from ICH_2CH_2I; 60 °C of reaction temperature and 2 h of reaction time in CH_3CN were used. 85%; yellow liquid. ^1H NMR (400 MHz, chloroform-*d*) δ 7.28 (t, J = 7.4 Hz, 2H), 7.23 – 7.15 (m, 3H), 3.20 (t, J = 6.9 Hz, 2H), 2.63 (t, J = 7.5 Hz, 2H), 1.92 – 1.80 (m, 2H), 1.80 – 1.68 (m, 2H).

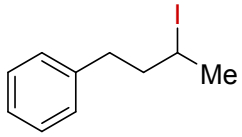


(3-chlorobutyl)benzene (**5x**).[32] $^nBu_4N^+Cl^-$ was used as the nucleophile. 79%; colorless liquid. ^1H NMR (400 MHz, chloroform-*d*) δ 7.33 – 7.25 (m, 2H), 7.23 – 7.16 (m, 3H), 3.99 (h, J = 6.5 Hz, 1H), 2.90 – 2.80 (m, 1H), 2.79 – 2.69 (m, 1H), 2.05 – 1.97 (m,

2H), 1.53 (d, J = 6.5 Hz, 3H).



(3-bromobutyl)benzene (**5y**).[33] $^{n}Bu_4N^+Br^-$ was used as the nucleophile. 62%; colorless liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.32 – 7.26 (m, 2H), 7.23 – 7.16 (m, 3H), 4.13 – 4.02 (m, 1H), 2.91 – 2.81 (m, 1H), 2.79 – 2.69 (m, 1H), 2.19 – 1.98 (m, 2H), 1.72 (d, J = 6.7 Hz, 3H).



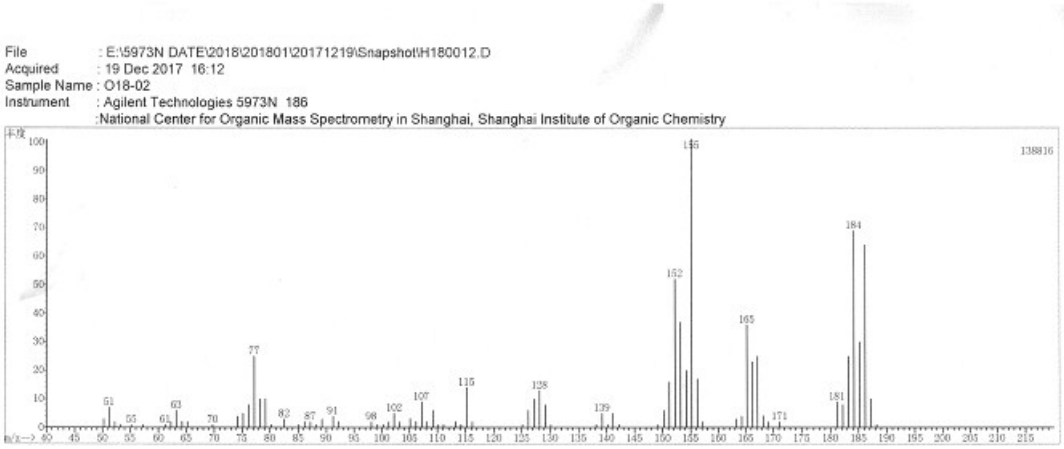
(3-iodobutyl)benzene (**5z**).[34] NaI was not required as the iodide anion was generated from ICH_2CH_2I; 60 °C of reaction temperature and 2 h of reaction time in CH_3CN were used. 35%; colorless liquid. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.32 – 7.26 (m, 2H), 7.24 – 7.16 (m, 3H), 4.19 – 4.05 (m, 1H), 2.90 – 2.80 (m, 1H), 2.75 – 2.64 (m, 1H), 2.22 – 2.10 (m, 1H), 1.95 (d, J = 6.8 Hz, 3H), 1.93 – 1.82 (m, 1H).

5 The synthesis of ^{18}O-1a

NaH (0.6 mmol, 14.4 mg) was added into a solution of $H_2{}^{18}O$ (^{18}O content: 95%, 0.6 mmol, 12.0 mg) in anhydrous DMF (1.0 mL) under N_2 atmosphere. The mixture was stirred for around 3 min to afford the suspension of $Na^{18}OH$ in anhydrous DMF.

Alcohol **1a** (1.0 equiv, 0.2 mmol, 36.8 mg), triphenylphsophine (1.2 equiv, 0.24 mmol, 62.9 mg) and anhydrous DMF (1.0 mL) were added into a 10 mL sealed tube under a N_2 atmosphere. 1,2-Diiodoethane (1.2 equiv, 0.24 mmol, 67.6 mg) was then added and the resulting mixture was stirred for around 1 min until the 1,2-diiodoethane was completely dissolved. The above $Na^{18}OH$ suspension was added subsequently and the mixture was stirred at 50 °C for 5 h. Dichloromethane (20 mL) was added and the resulting solution was washed with water (20 mL x 3). The organic layer was dried over Na_2SO_4. After filtration, the solvent was removed by concentration under reduced pressure. The residue was subjected to flash column chromatography to afford product **^{18}O-1a** (25.0 mg, 67%). MS-EI analysis of the product showed that ^{18}O:^{16}O = 50:50.

MS-EI spectrum of the ^{18}O-product:

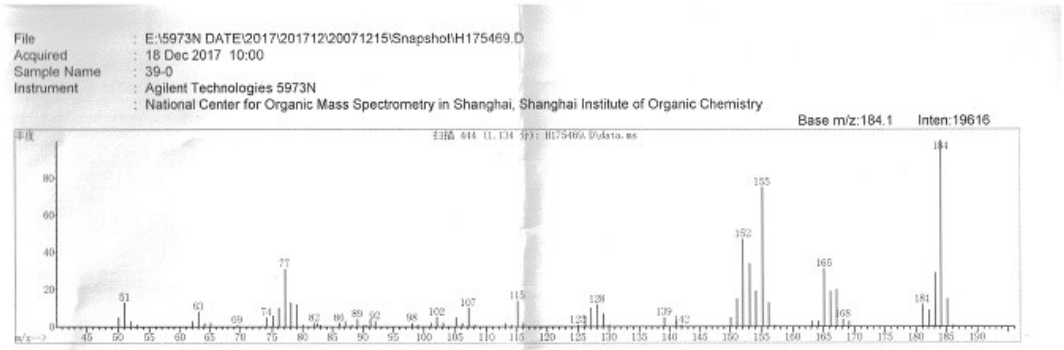


m/z	%RA	m/z	%RA	m/z	%RA	m/z	%RA	m/z	%RA	m/z	%RA	m/z	%RA	m/z	%RA
45	0.11	65	1.59	85	0.59	103	1.59	117	0.22	132	0.14	151	16.08	167	24.87
49	0.12	66	0.18	86	1.59	104	0.26	118	0.22	135	0.12	152	51.50	168	4.17
50	2.97	67	0.19	87	2.47	105	2.83	120	0.25	137	0.49	153	36.99	169	2.20
51	7.27	68	0.16	88	1.08	106	1.54	121	0.17	138	0.55	154	19.92	170	0.49
52	1.64	70	1.11	89	3.28	107	8.71	122	0.41	139	5.22	155	100.00	171	1.73
53	0.92	73	0.27	91	3.73	108	2.06	123	0.24	140	1.00	156	17.02	172	0.23
54	0.12	74	3.71	92	2.43	109	6.06	124	0.15	141	4.48	157	1.59	181	8.85
55	0.50	75	4.66	95	0.15	110	1.00	125	1.02	142	1.06	158	0.30	182	7.89
56	0.19	76	8.41	97	0.29	111	0.63	126	6.13	143	0.27	159	0.18	183	24.61
57	0.50	77	24.54	98	1.71	112	0.19	127	10.30	144	0.14	162	0.36	184	68.11
61	0.53	78	10.08	99	1.23	113	1.81	128	12.44	145	0.26	163	2.79	185	30.00
62	2.19	79	9.90	100	0.67	114	0.94	129	7.96	146	0.18	164	4.07	186	63.13
63	5.90	80	0.78	101	2.02	115	13.91	130	1.04	149	0.56	165	35.87	187	9.65
64	1.56	82	2.55	102	4.54	116	2.16	131	0.17	150	5.68	166	22.64	188	0.69

8 Peak Value:

155	100.00	184	68.11	186	63.13	152	51.50	153	36.99	165	35.87	185	30.00	167	24.87

MS-EI spectrum of the substrate **1a**:

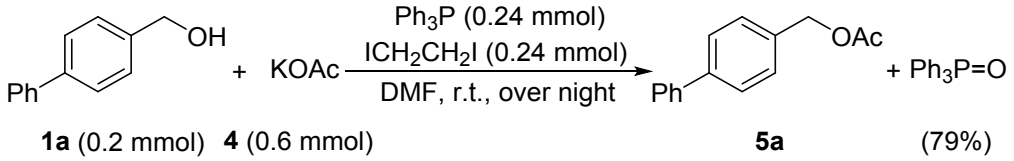


m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%
50	5.07	51	12.62	52	2.8	53	1.48	62	3.03	63	8.35	64	2.11	65	2.36	70	1.22
74	4.67	75	6.27	76	9.53	77	30.98	78	12.5	79	11.58	80	0.92	82	2.09	82	2.11
83	1.48	86	1.85	87	3.11	88	1.05	89	4.39	90	0.86	91	0.83	91	4.14	92	2.92
98	2.07	99	0.92	101	2.2	102	4.95	103	1.75	105	4.97	106	2.26	107	9.8	108	0.83
113	1.86	114	1.09	115	14.19	116	1.81	125	0.81	126	6.08	127	10.02	128	12.36	129	7.18
130	0.83	139	4.95	141	3.92	142	1.03	150	5.29	151	14.67	152	47.11	153	33.54	154	19.08
155	75.06	156	12.57	157	1.47	163	2.5	164	3.38	165	30.83	166	18.72	167	20.49	168	3.5
169	2.92	181	12.22	182	9.29	183	29.44	184	100	185	15.19	186	1.27				

8 Peak Value:

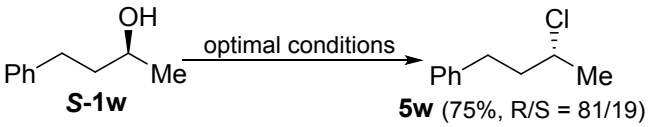
184	100	155	75.06	152	47.11	153	33.54	77	30.98	165	30.83	183	29.44	167	20.49

6. Isolation of $Ph_3P=O$



Esterification of alcohol **1a** (0.2 mmol) with KOAc occurred well under the optimal conditions. After the reaction was completed, 53.0 mg of $Ph_3P=O$ was isolated in 79% yield (based on Ph_3P). ^1H NMR (400 MHz, chloroform-*d*) δ 7.72 – 7.60 (m, 6H), 7.58 – 7.48 (m, 3H), 7.49 – 7.37 (m, 6H). ^{31}P NMR (162 MHz, chloroform-*d*) δ 29.86 (s, 1P).

7. Inversion of configuration



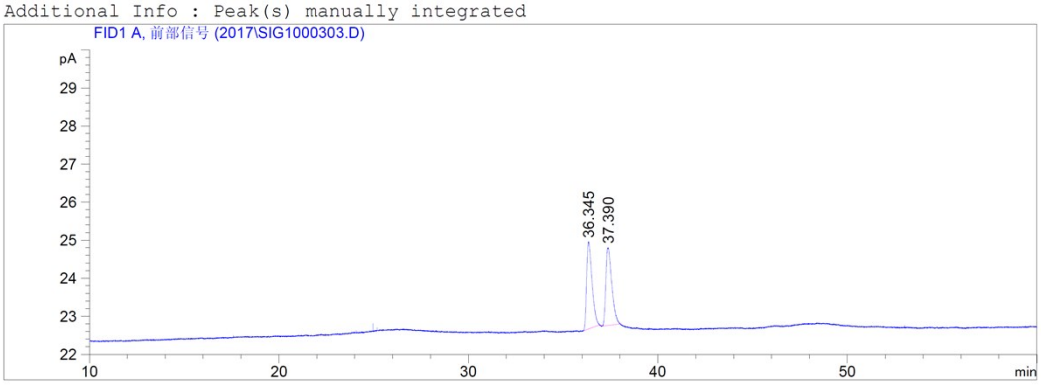
***S*-1w** (0.5 mmol) was converted into ***R*-5w** under the optimized conditions. Enantiomeric excess was determined by chiral GC with a CP-chirasil-DEX CB column (length 25 m, diameter 0.25 mm, 0.25 μm layer thickness) and nitrogen as carrier gas. Injector temperature was 100 °C. Major enantiomer rt = 36.417 min, minor enantiomeric rt = 37.465 min. GC analysis from the isolated product showed an *er* of 81:19.

$[\alpha]_D^{25}$ = -37.4 (c = 1.15 g/100 mL, $CHCl_3$, *er* 81:19).

Lit. $[\alpha]_D^{25}$ = -36.4 (c = 1.00 g/100 mL, $CHCl_3$, *R*-ent, no enantiopurity given).[32]

Gas chromatogram of a racemic sample:

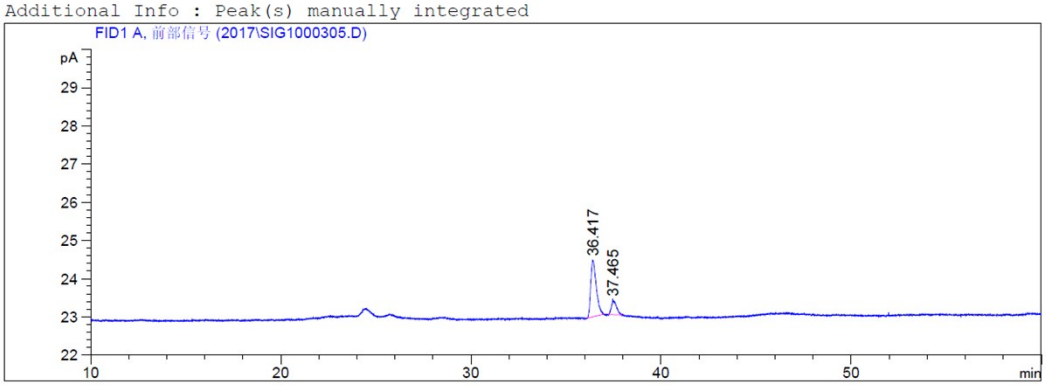
```
Data File C:\CHEM32\1\DATA\2017\SIG1000303.D
Sample Name: 08-90 R/S

    ========================================================================
    Acq. Operator   : YZR
    Acq. Instrument : 仪器 1                          Location : Vial 1
    Injection Date  : 9/25/2017 12:32:29 PM
                                                     Inj Volume : Manually
    Acq. Method     : C:\CHEM32\1\METHODS\TEST2-1.M
    Last changed    : 9/25/2017 1:41:10 PM by YZR
                      (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\TEST2-1.M
    Last changed    : 4/20/2018 3:20:34 PM by lxl
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ========================================================================
                              Area Percent Report
    ========================================================================

    Sorted By             :      Signal
    Multiplier:                   :      1.0000
    Dilution:                     :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID1 A, 前部信号

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [pA*s]      [pA]        %
    ----|-------|----|-------|----------|----------|--------|
       1  36.345 BB    0.2435   45.28983    2.28254 50.45764
       2  37.390 BB    0.2907   44.46829    2.03692 49.54236

    Totals :                    89.75812    4.31946


    ========================================================================
                               *** End of Report ***
```

Gas chromatogram of the enantioenriched sample:

```
Data File C:\CHEM32\1\DATA\2017\SIG1000305.D
Sample Name: 0899

=====================================================================
Acq. Operator    : YZR
Acq. Instrument : 仪器 1                          Location : Vial 1
Injection Date  : 9/25/2017 2:50:23 PM
                                                  Inj Volume : Manually
Acq. Method     : C:\CHEM32\1\METHODS\TEST2-1.M
Last changed    : 9/25/2017 2:49:20 PM by YZR
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\TEST2-1.M
Last changed    : 4/20/2018 3:20:34 PM by lxl
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A, 前部信号

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  36.417 BB    0.2578   29.82327    1.47542 81.04265
   2  37.465 BB    0.2300    6.97621 3.60126e-1 18.95735

Totals :                    36.79947    1.83555


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                        *** End of Report ***
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8. References and notes

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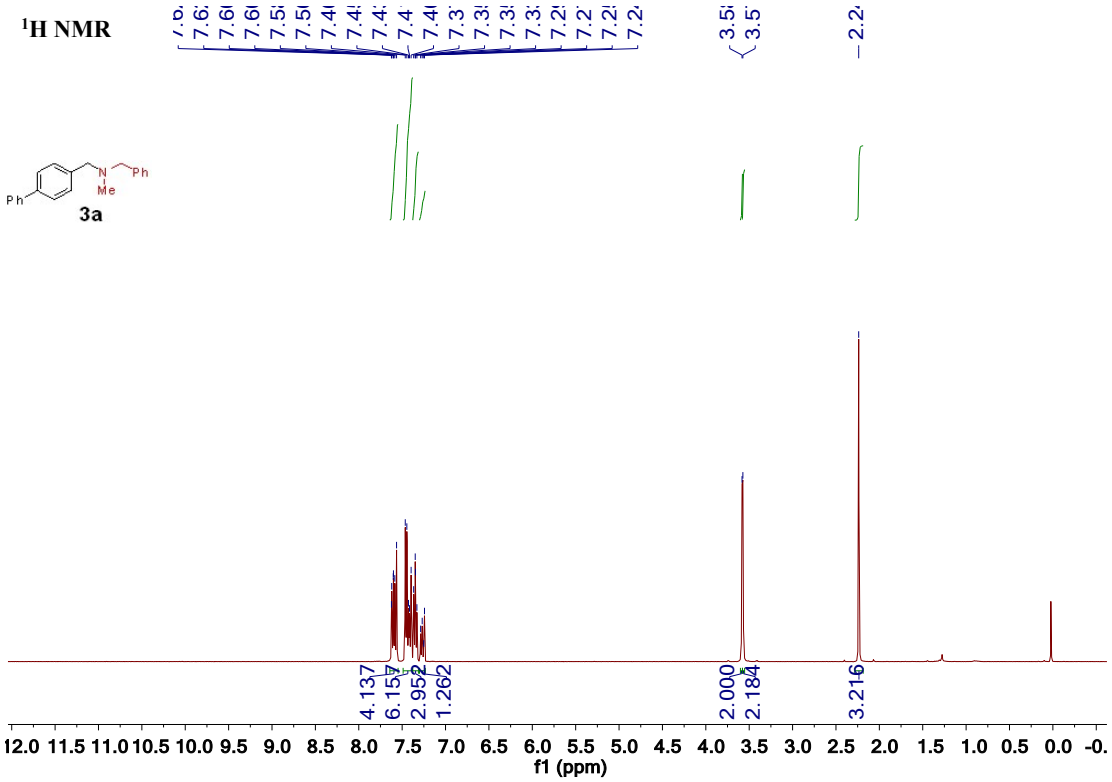
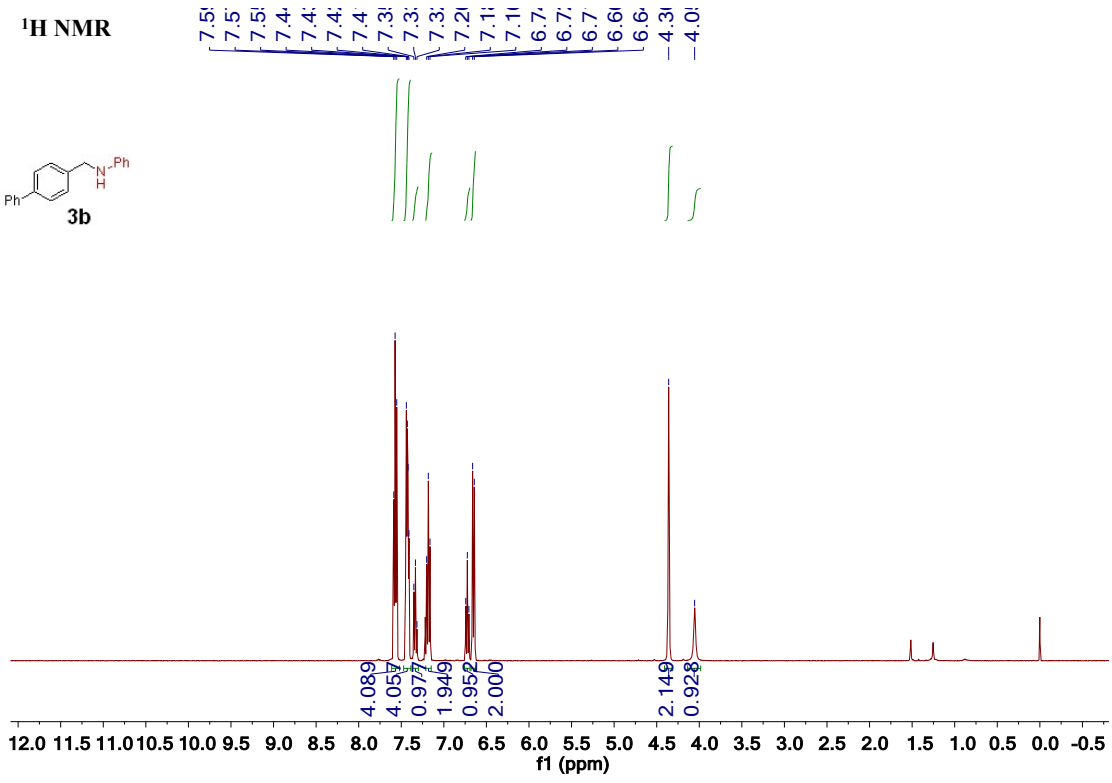
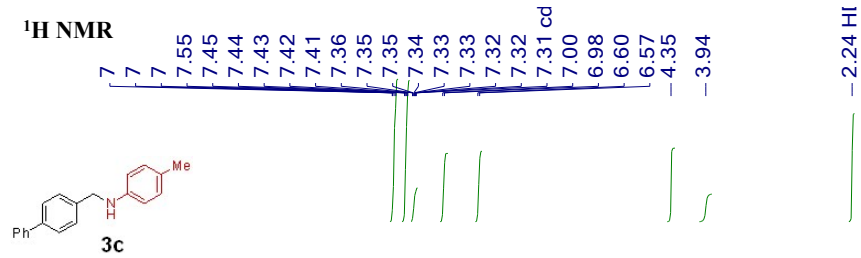
9. Copies of ^{1}H NMR, ^{19}F NMR, ^{13}C NMR and ^{31}P NMR spectra

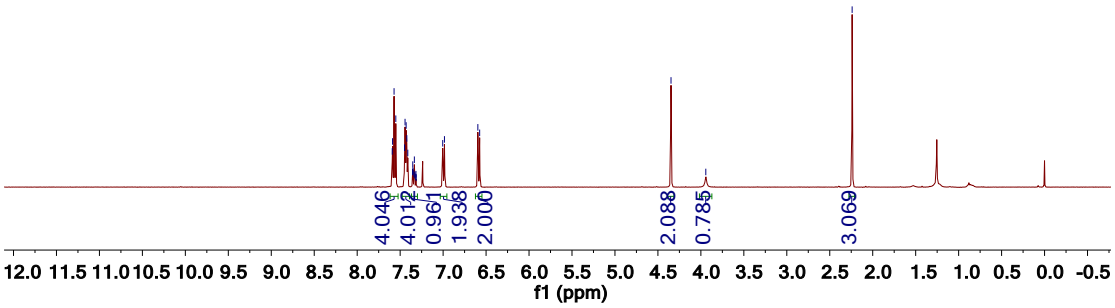




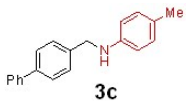
^{1}H NMR



3c



^{13}C NMR



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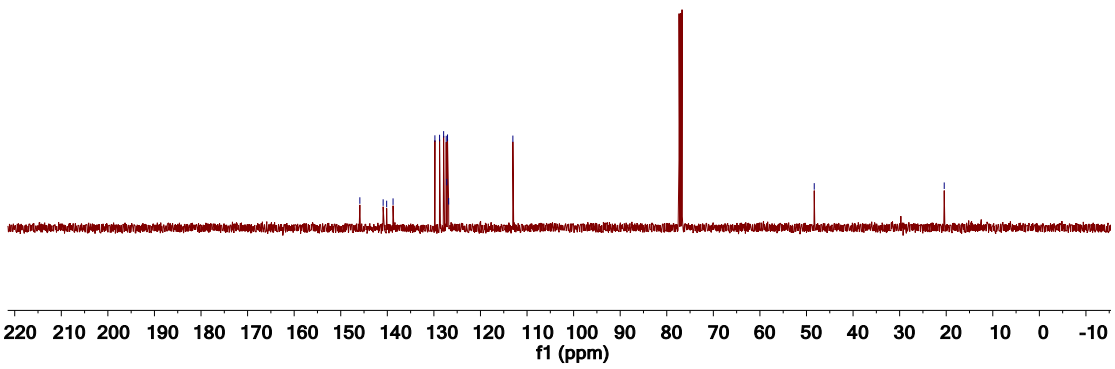

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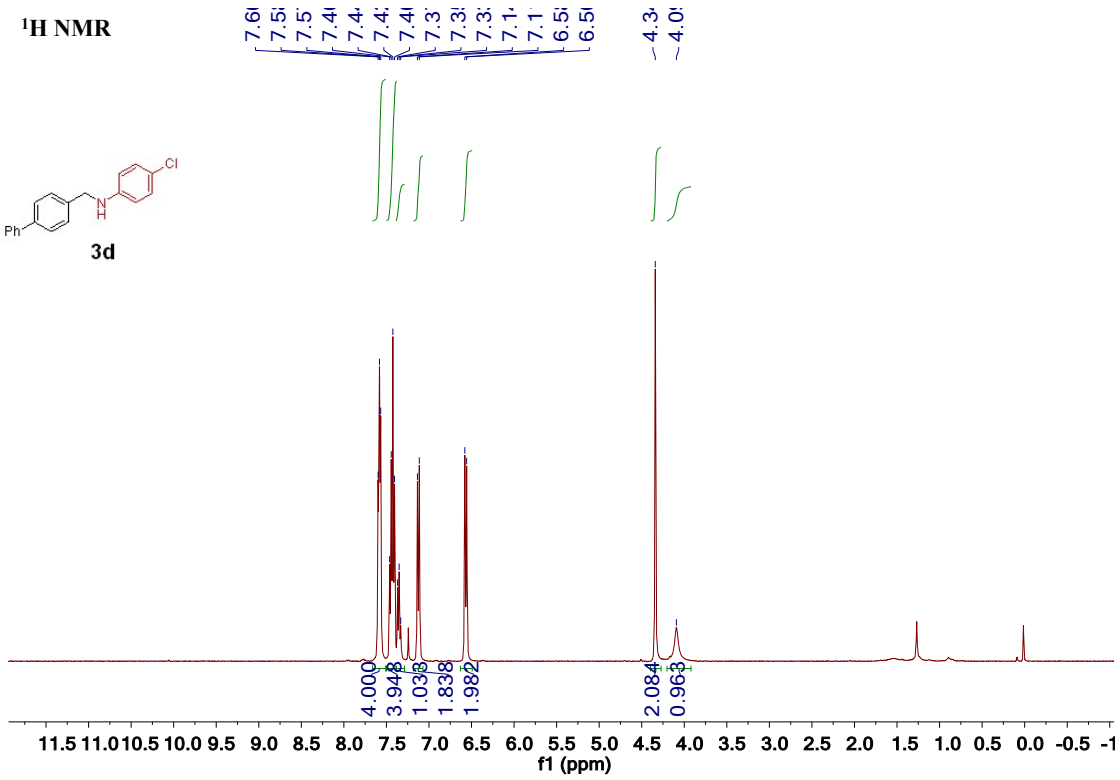

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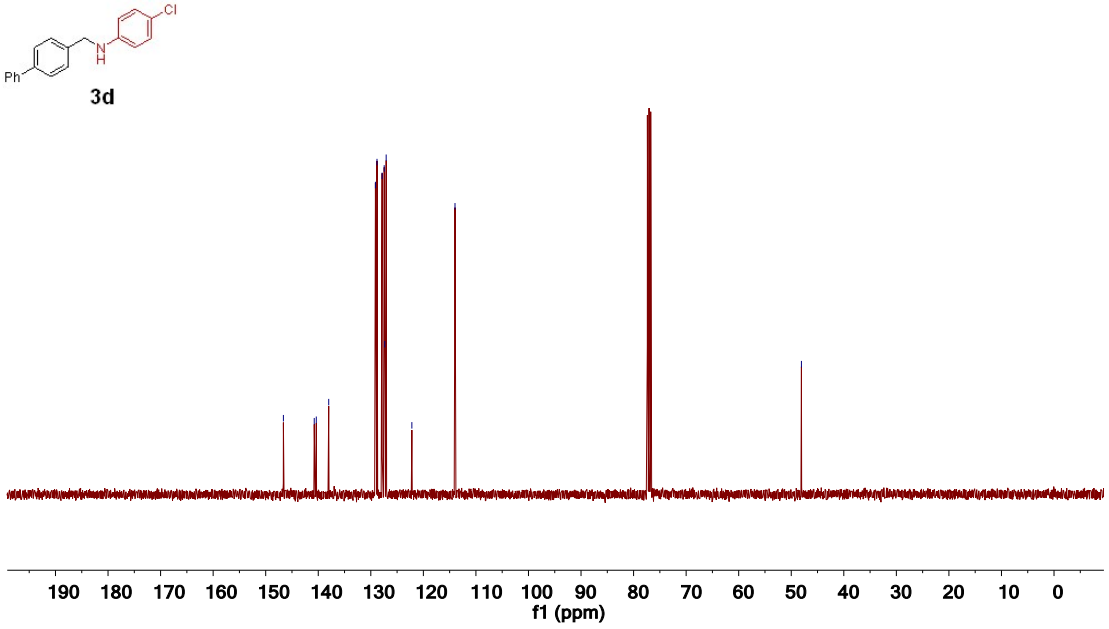
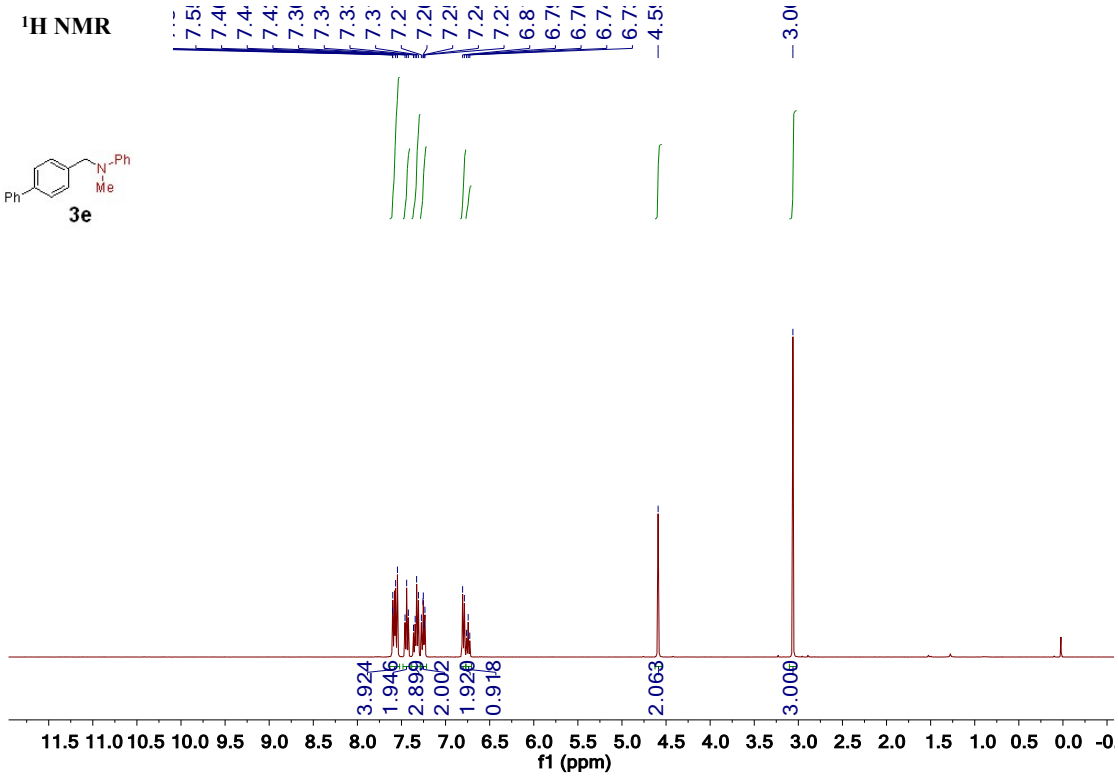
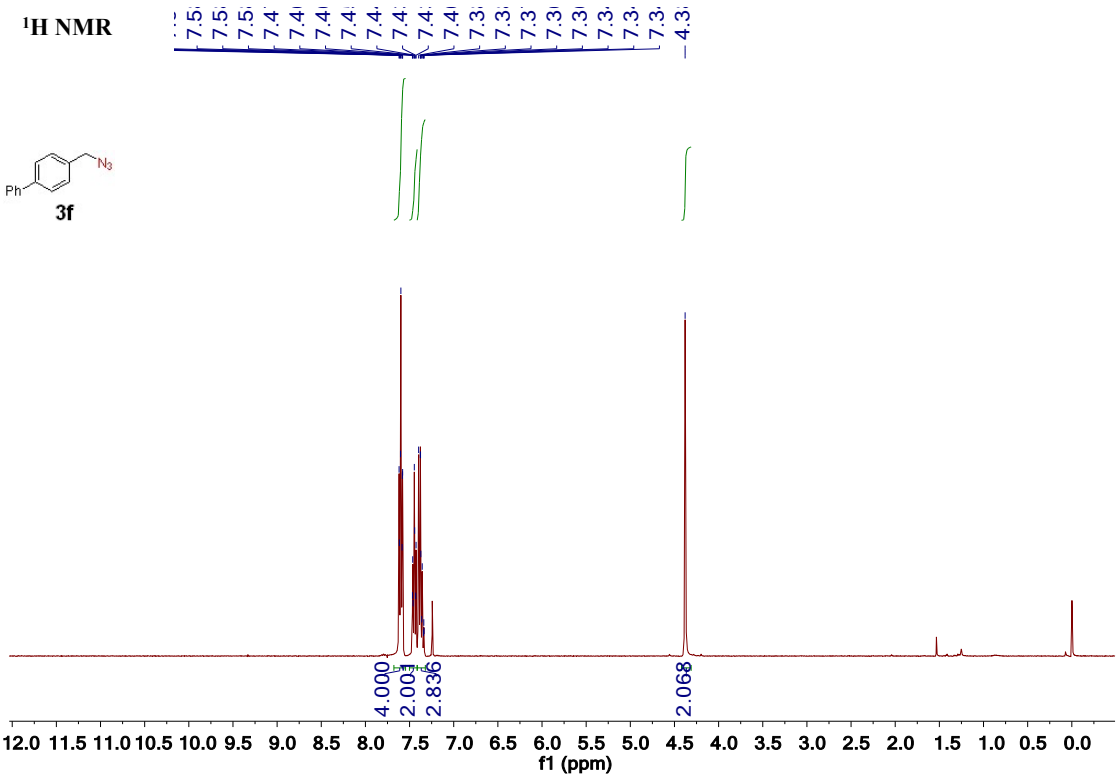


^{1}H NMR


Ph
N
Ph
Me
3e
3.924
1.946
2.899
2.002
1.928
0.918
2.063
3.000
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

^{1}H NMR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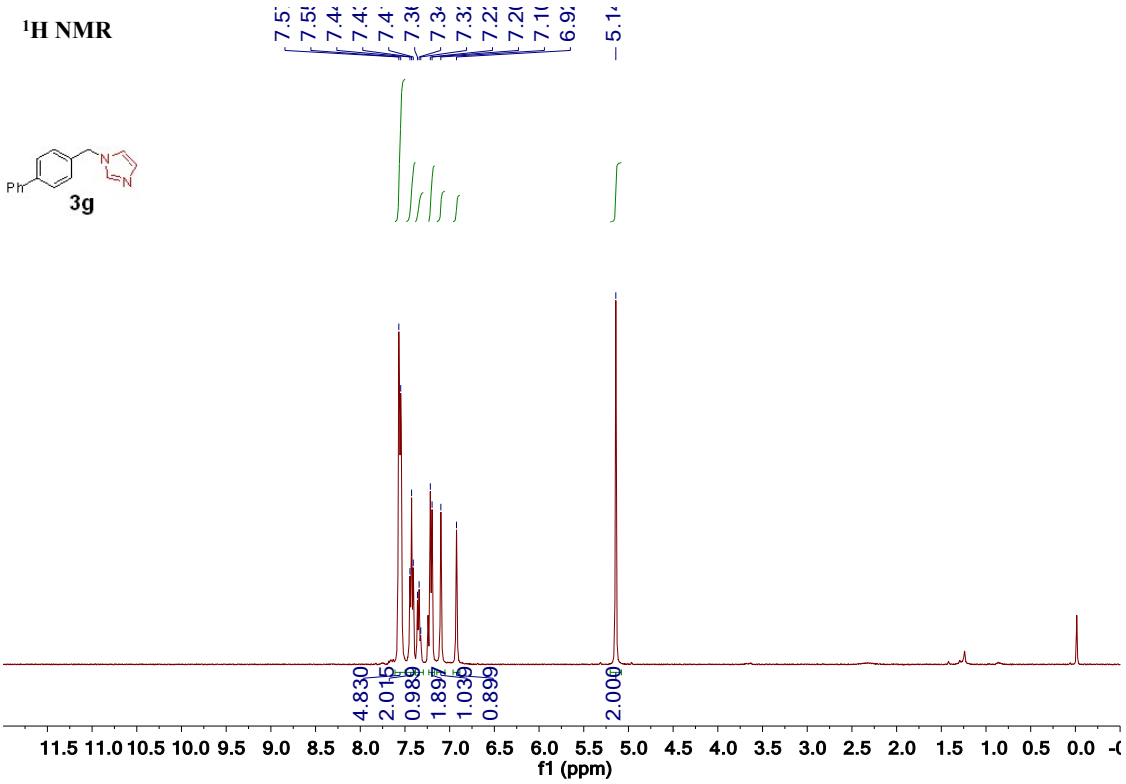
N3
3f
4.000
2.005
2.836
2.068
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

^{1}H NMR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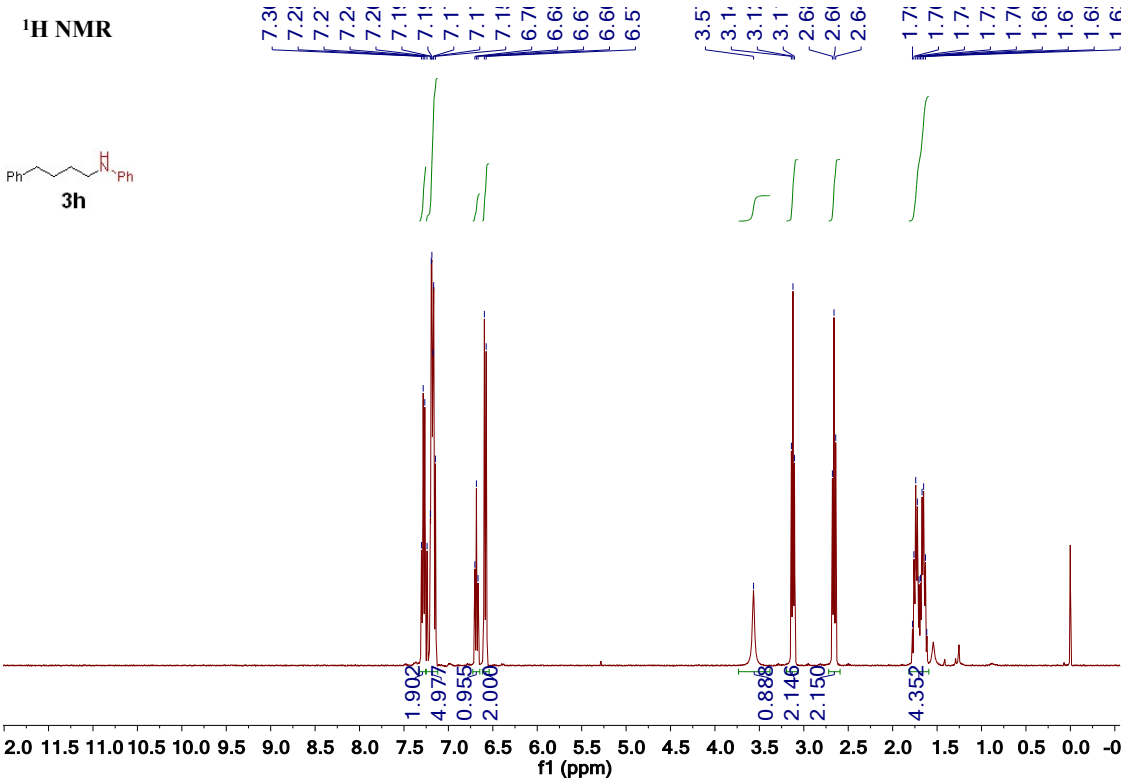
1.897
1.039
0.899
2.000
f1 (ppm)

^{1}H NMR


Ph
Ph
3h
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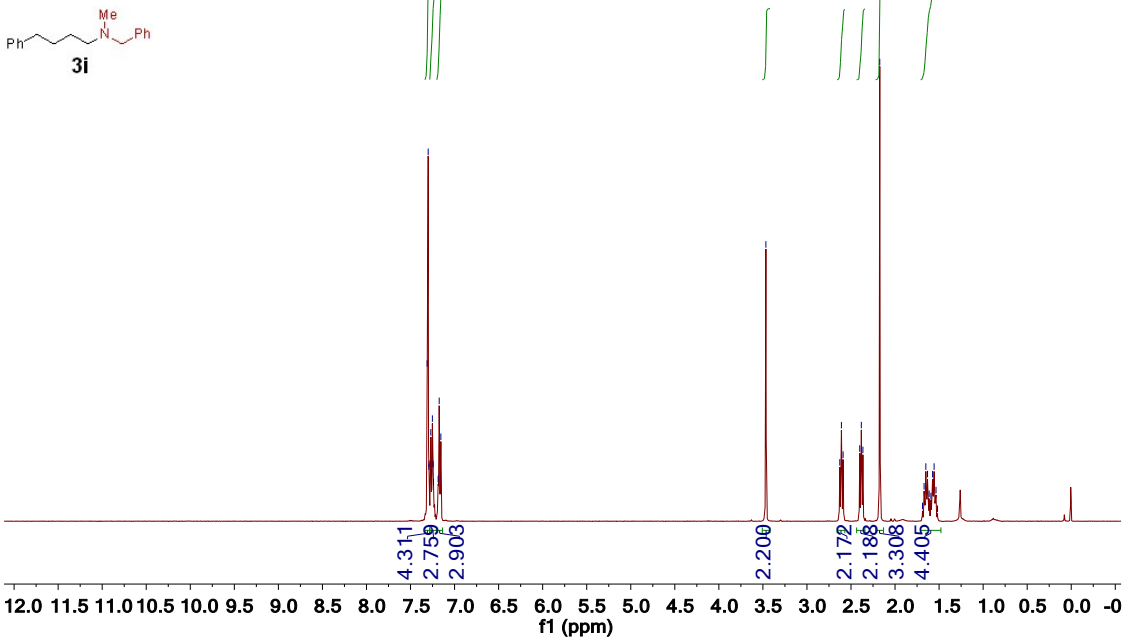
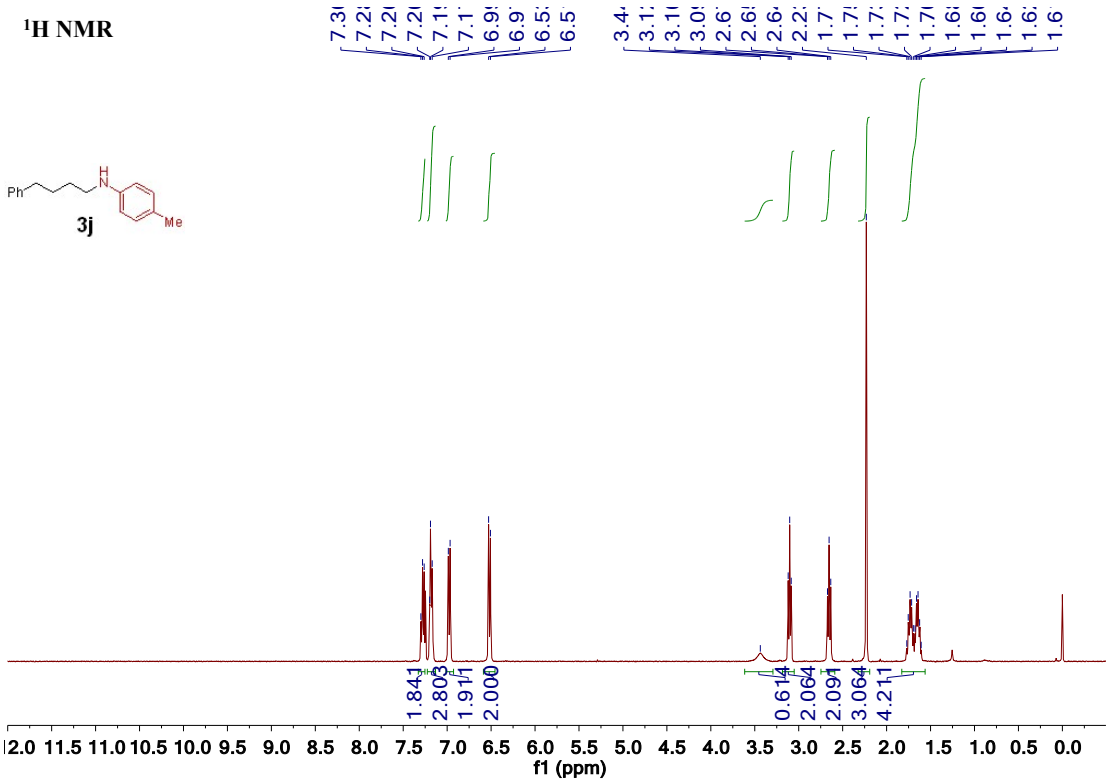
0.955
2.000
0.888
2.146
2.150
4.352
f1 (ppm)

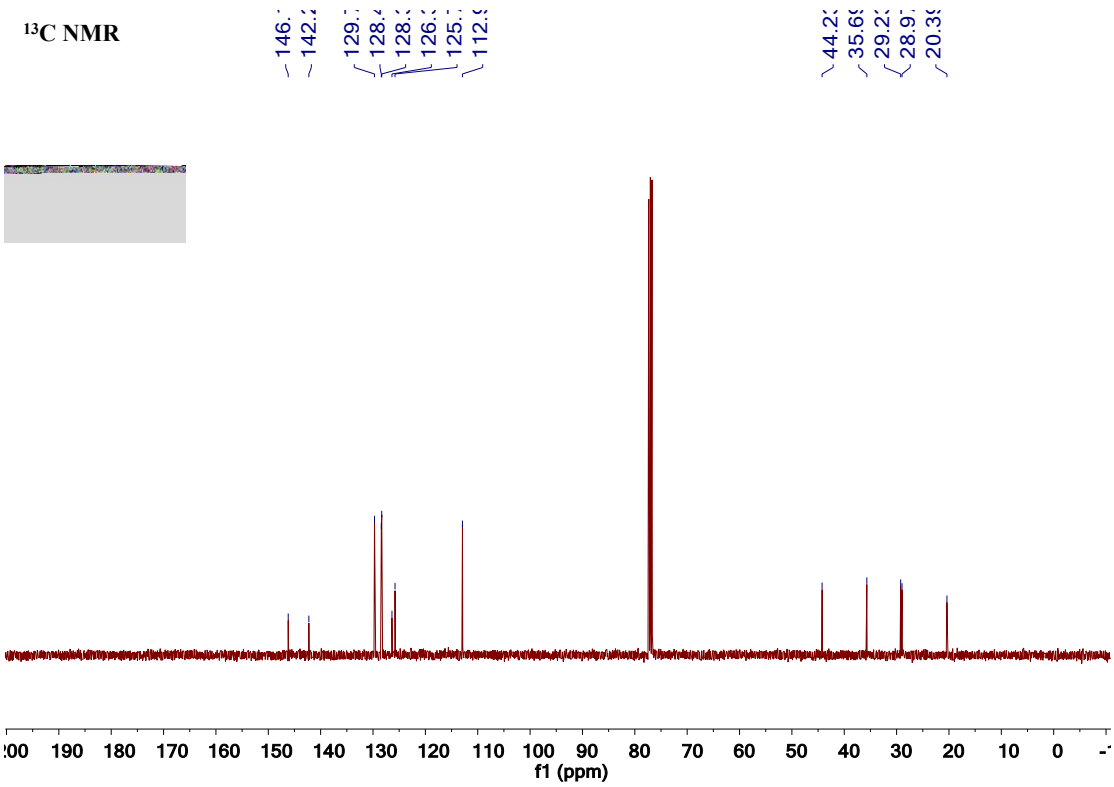
^{1}H NMR



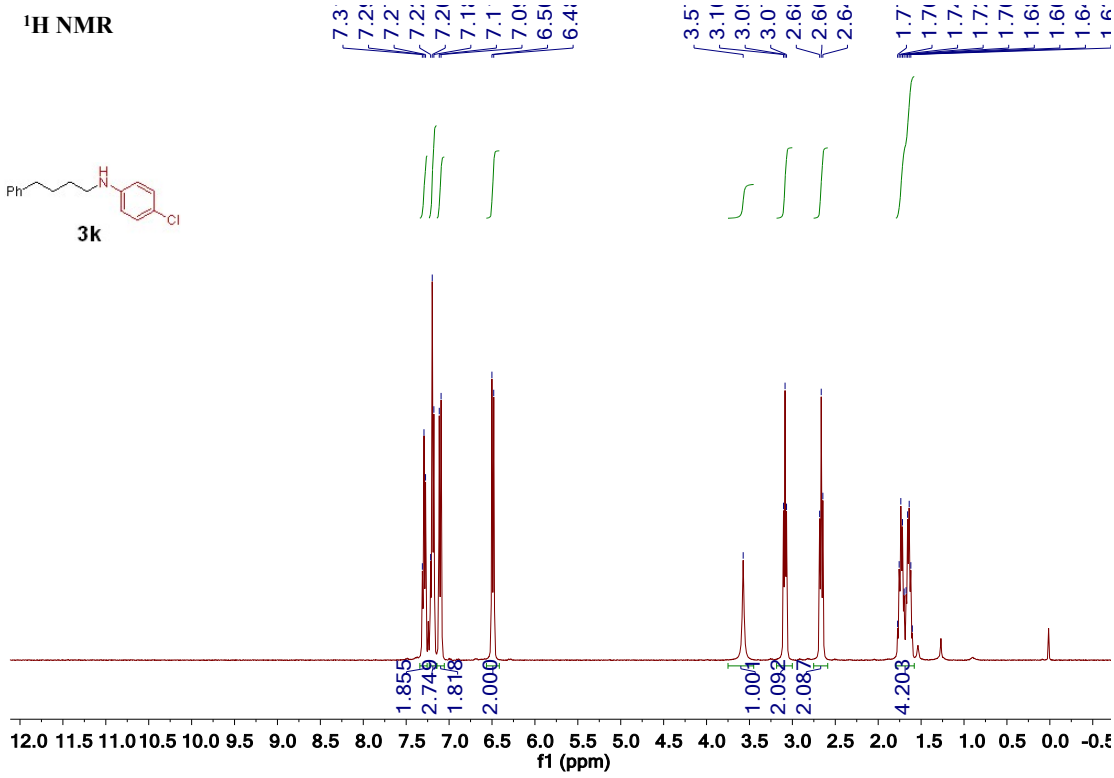
^{1}H NMR



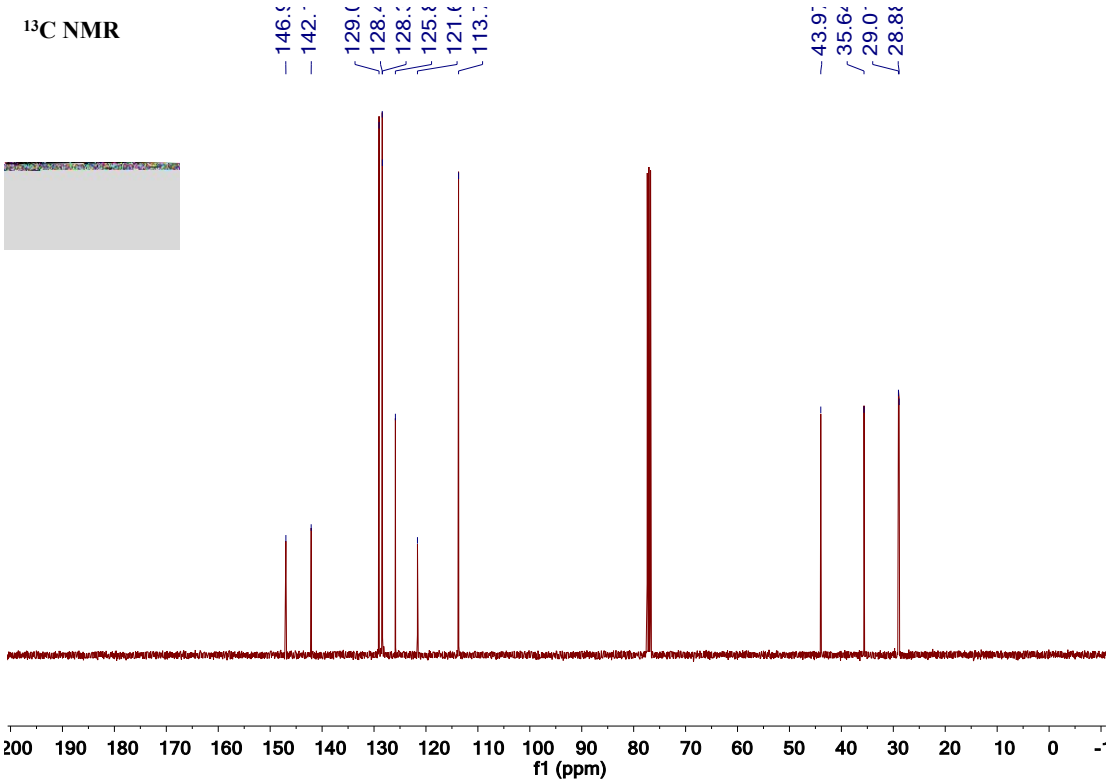
^{13}C NMR



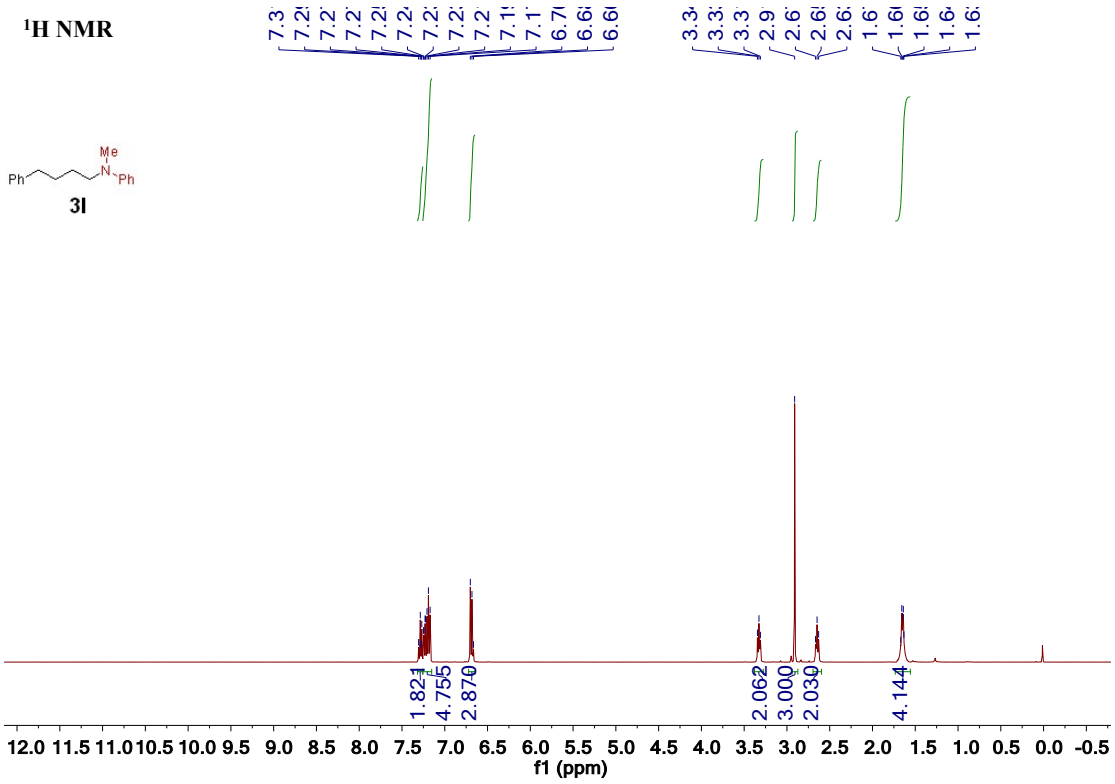
^{1}H NMR



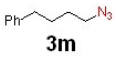
^{13}C NMR



^{1}H NMR

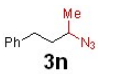


^{1}H NMR



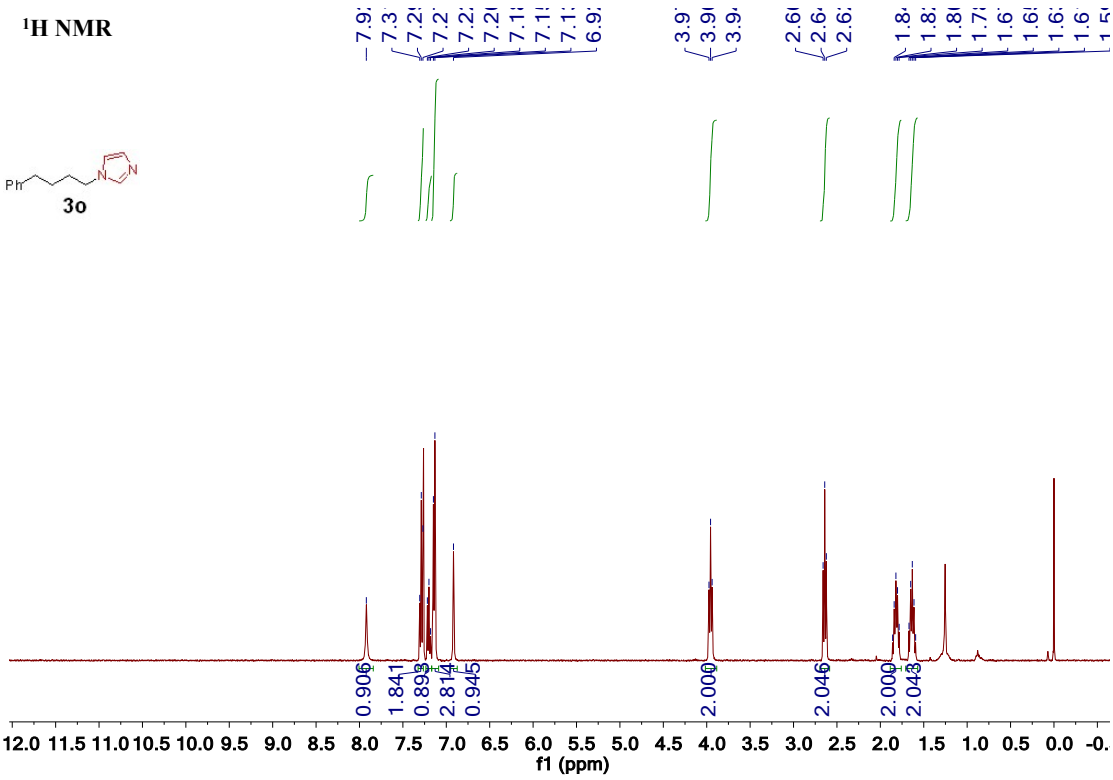
3m

^{1}H NMR



3n

^{1}H NMR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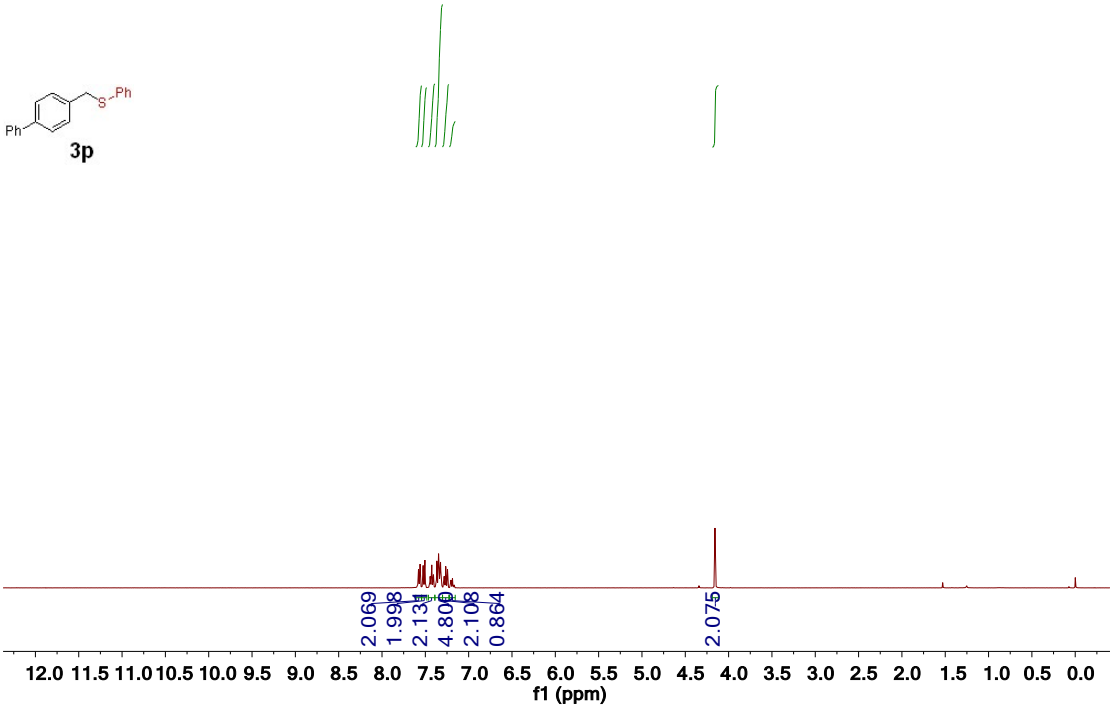
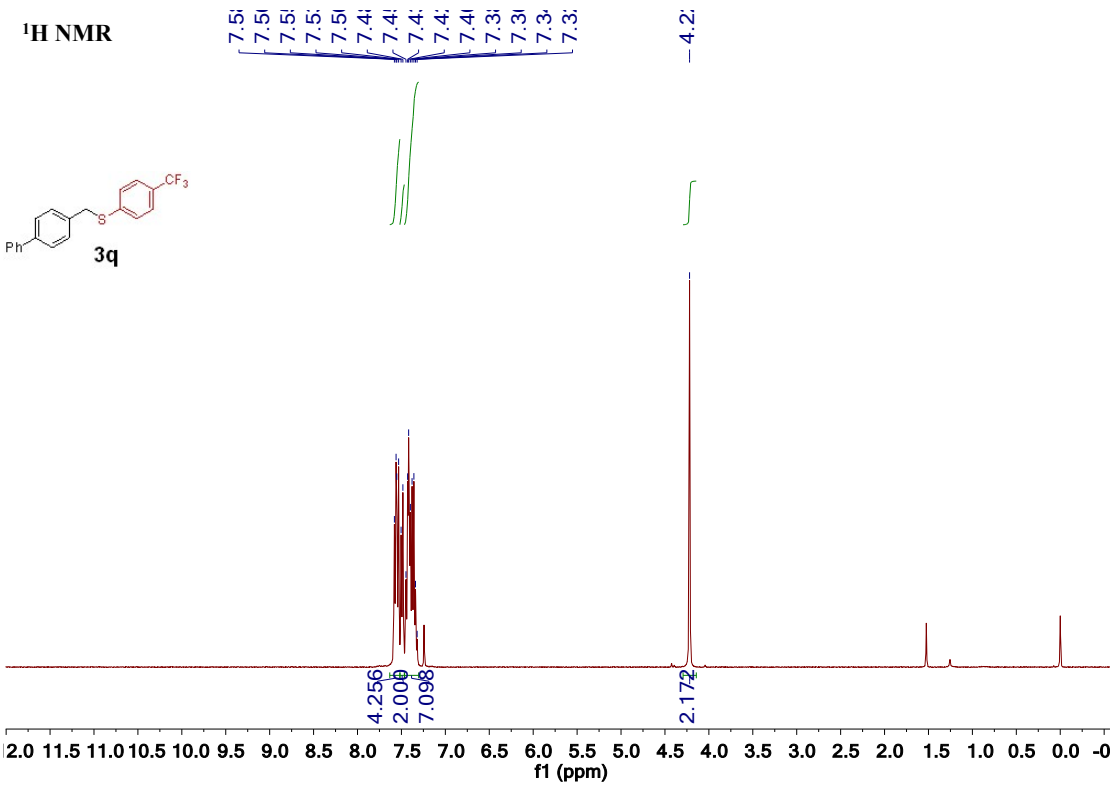
N
N
3o
7.9
7.3
7.2
7.2
7.2
7.2
7.1
7.1
7.1
6.9
3.9
3.9
3.9
2.6
2.6
2.6
1.8
1.8
1.8
1.7
1.6
1.6
1.6
1.6
0.90
1.84
0.89
2.81
0.94
2.00
2.04
2.00
2.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

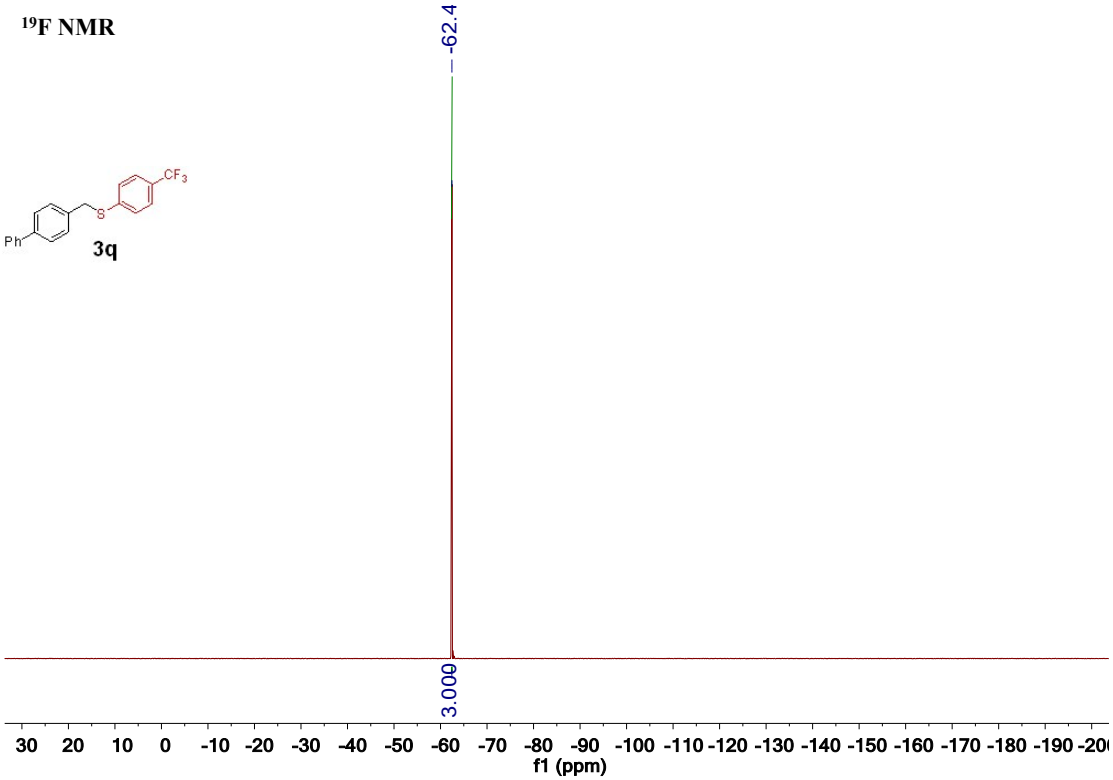
^{1}H NMR


Ph
S
Ph
3p
2.06
1.99
2.13
4.80
2.10
0.86
2.07
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

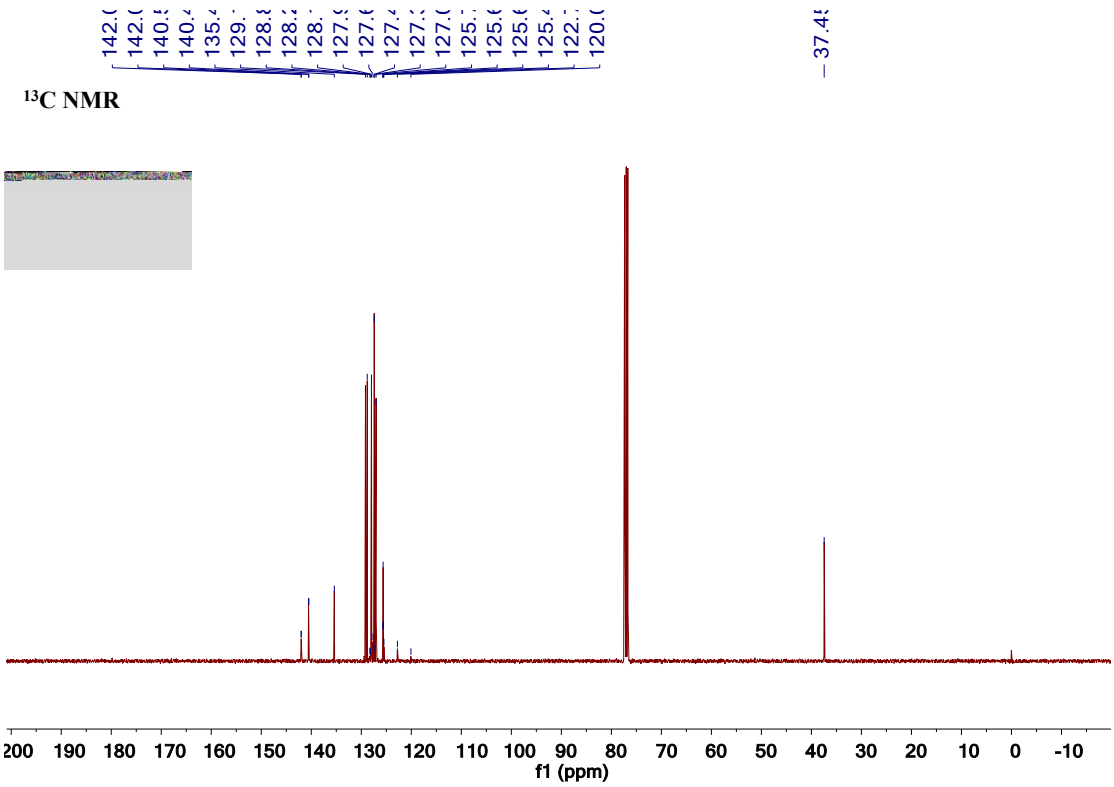
^{1}H NMR



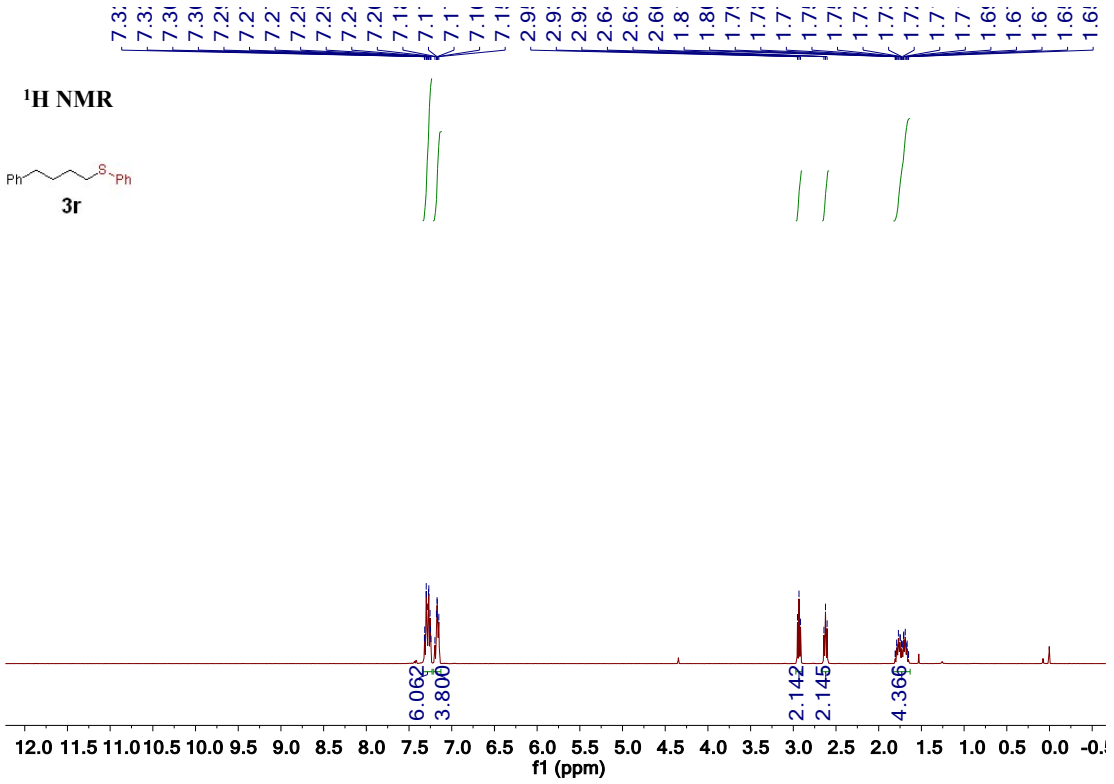
^{19}F NMR



^{13}C NMR

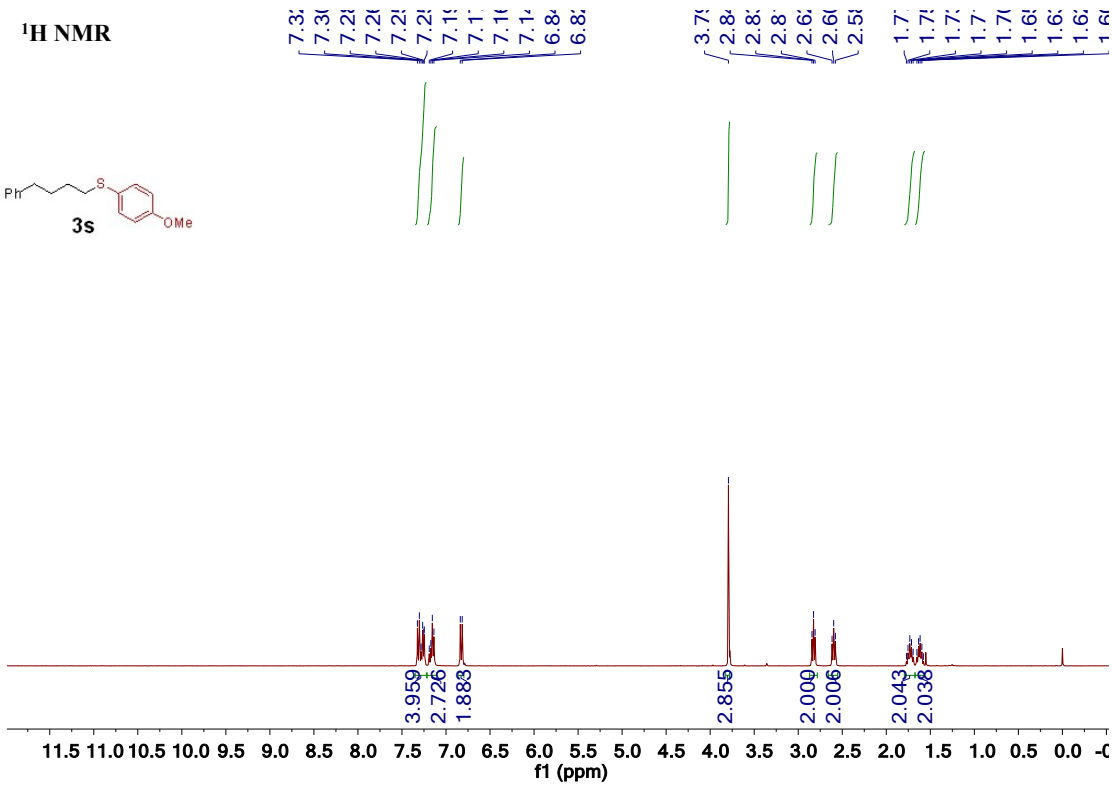


^{1}H NMR

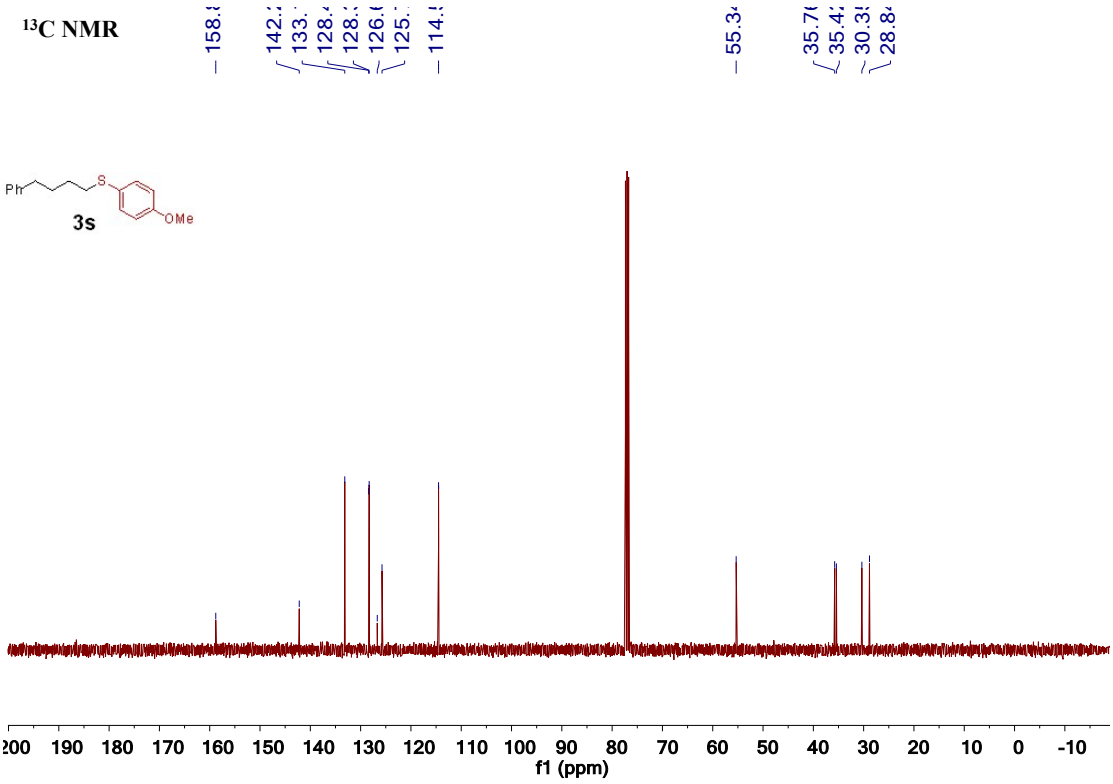


3r

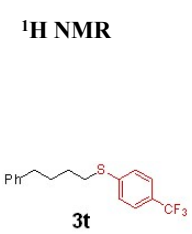
^{1}H NMR



^{13}C NMR

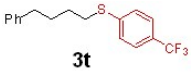


^{1}H NMR



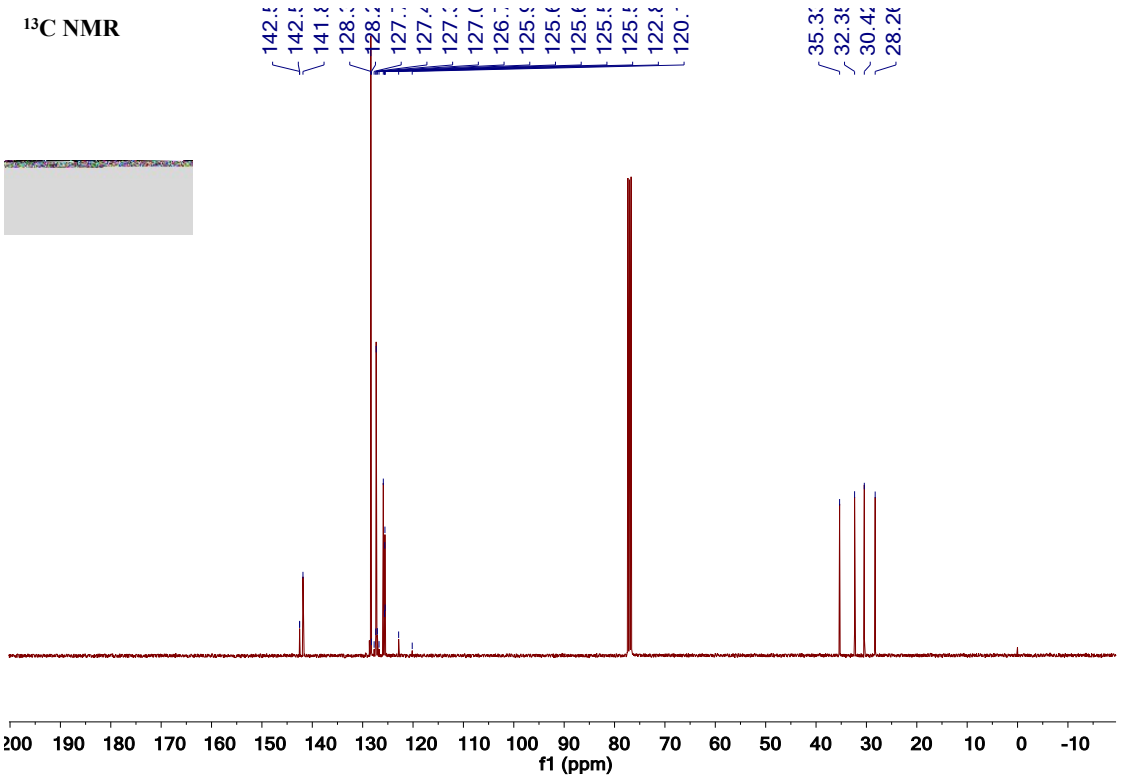
3t

^{19}F NMR

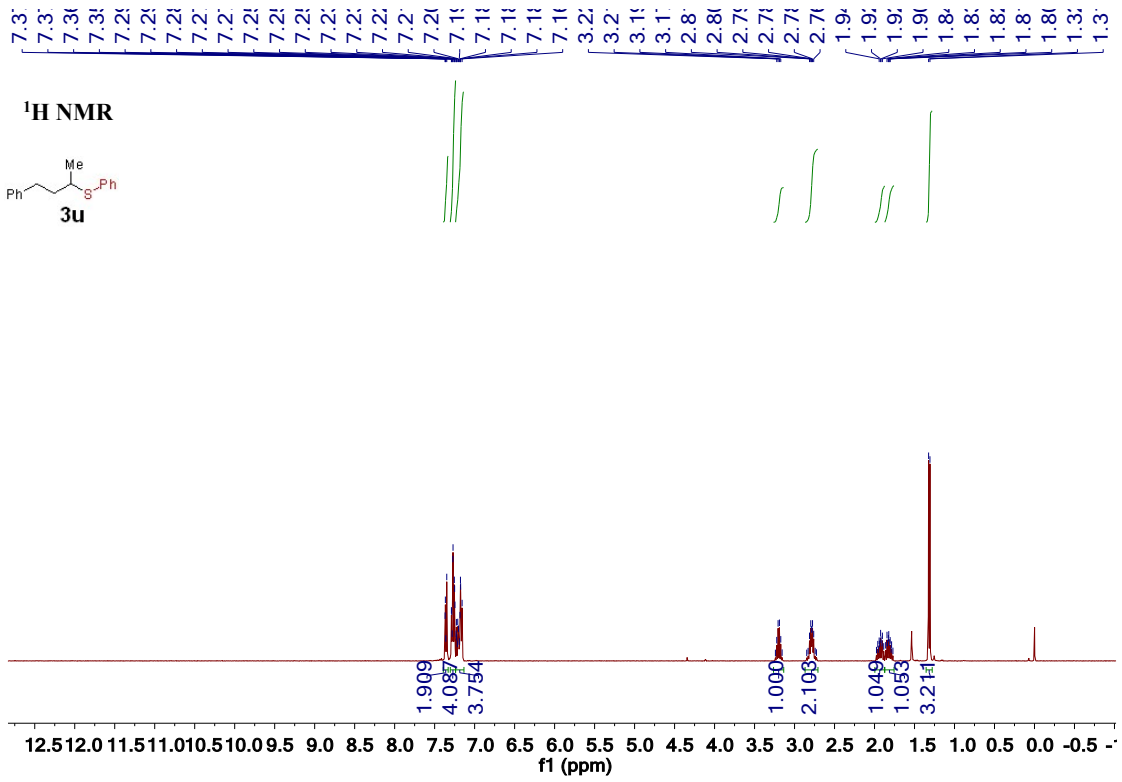


3t

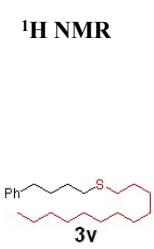
^{13}C NMR



^{1}H NMR

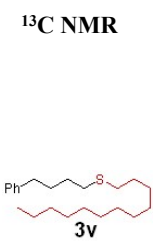


^{1}H NMR



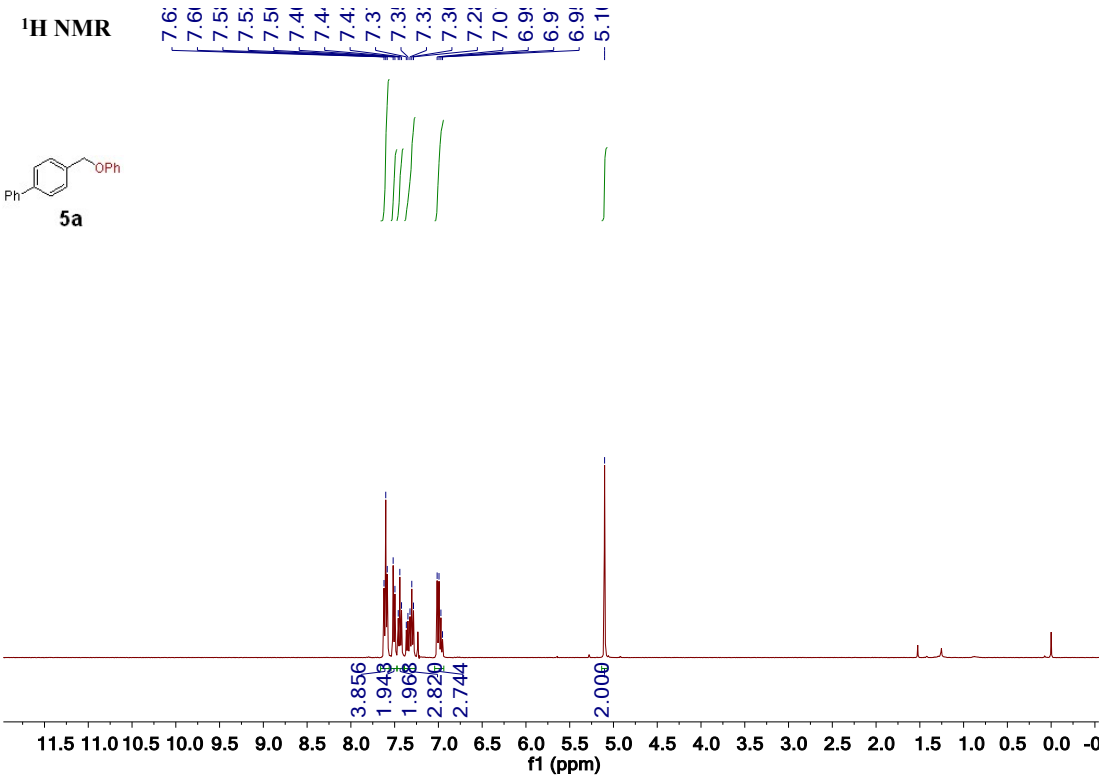
3v

^{13}C NMR



3v

^{1}H NMR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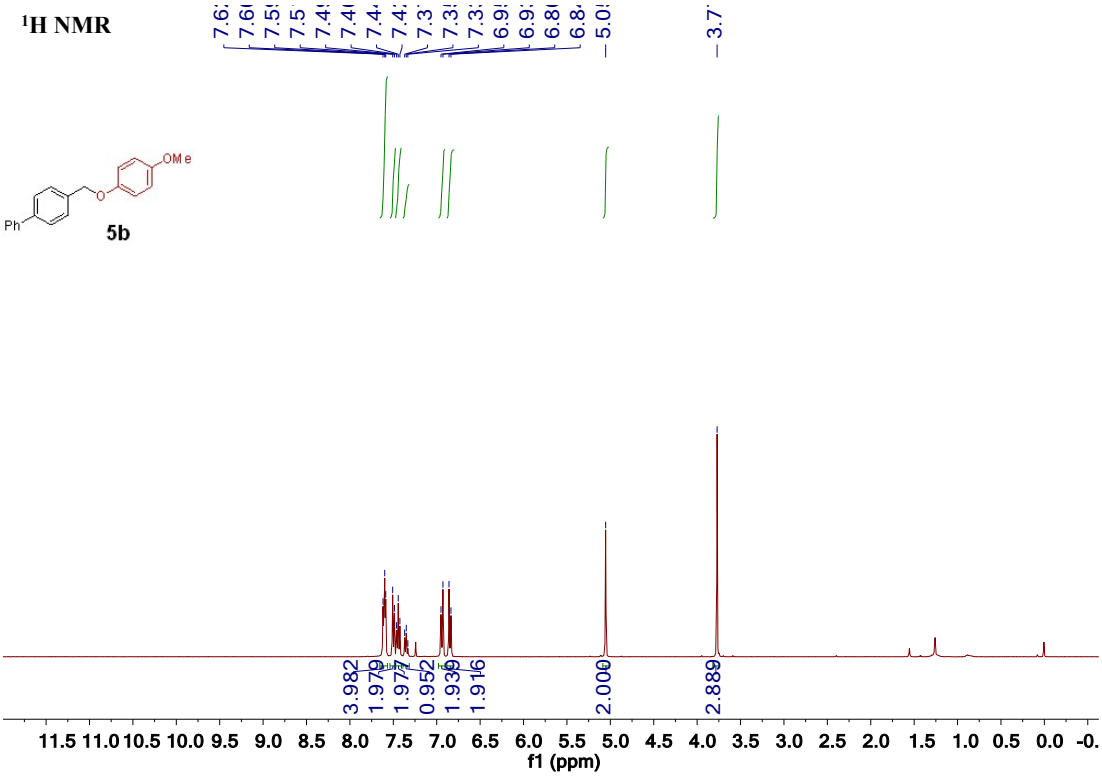
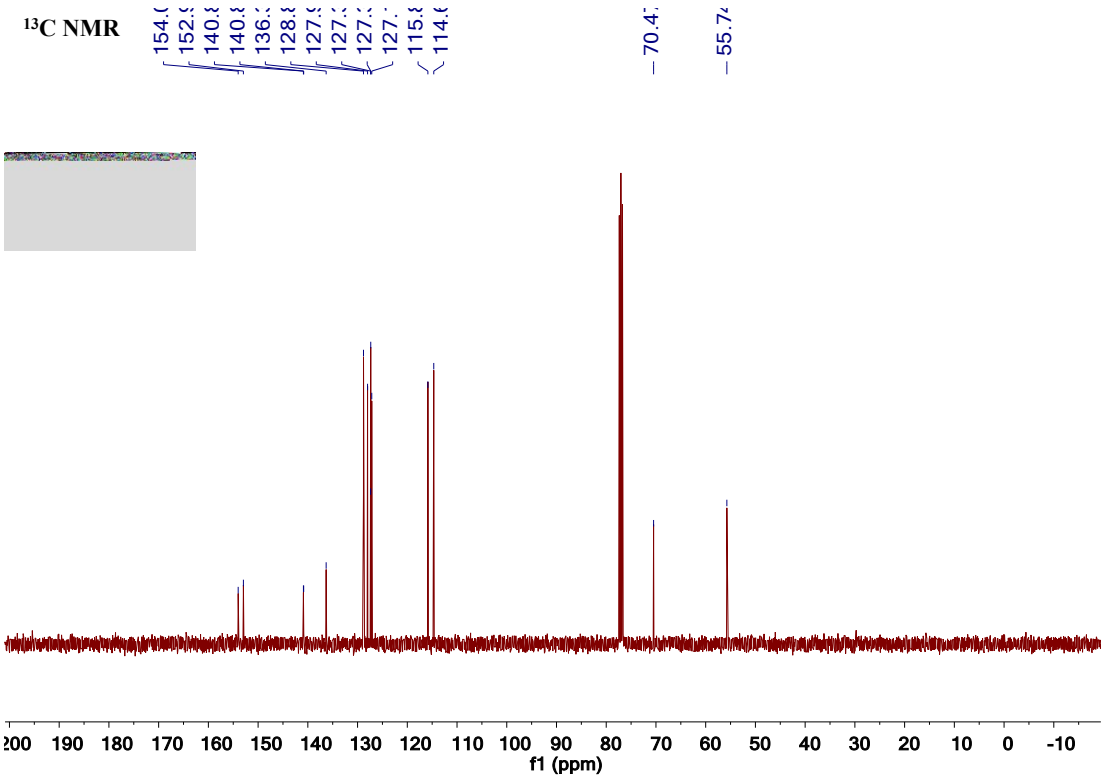
1.968
2.820
2.744
2.000
f1 (ppm)

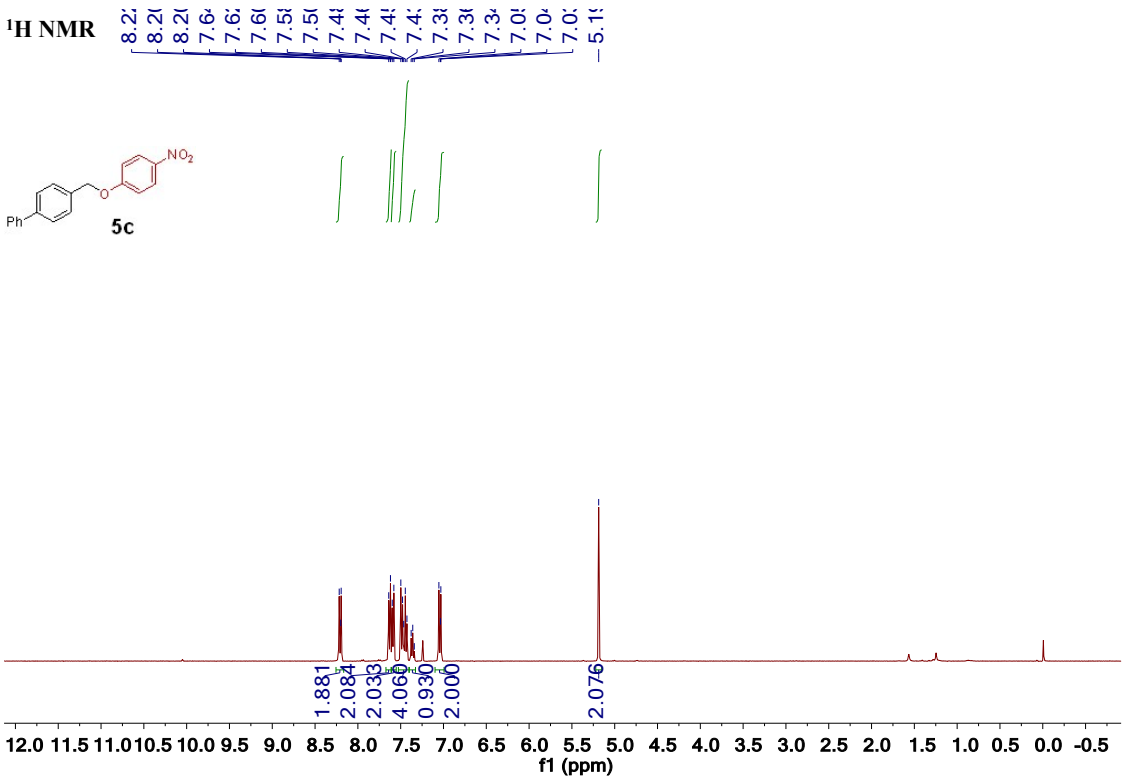
^{1}H NMR


OMe
O
Ph
5b
3.982
1.979
1.977
0.952
1.939
1.916
2.000
2.889
f1 (ppm)

^{13}C NMR

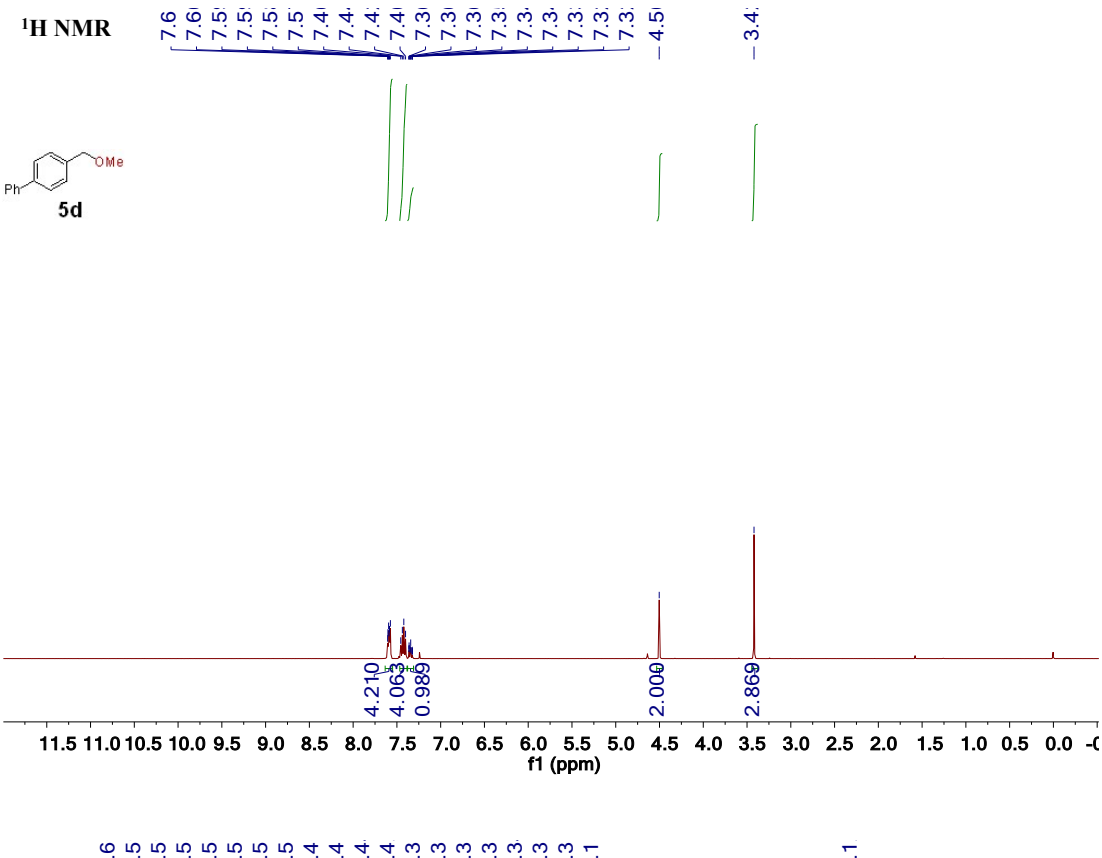


^{1}H NMR



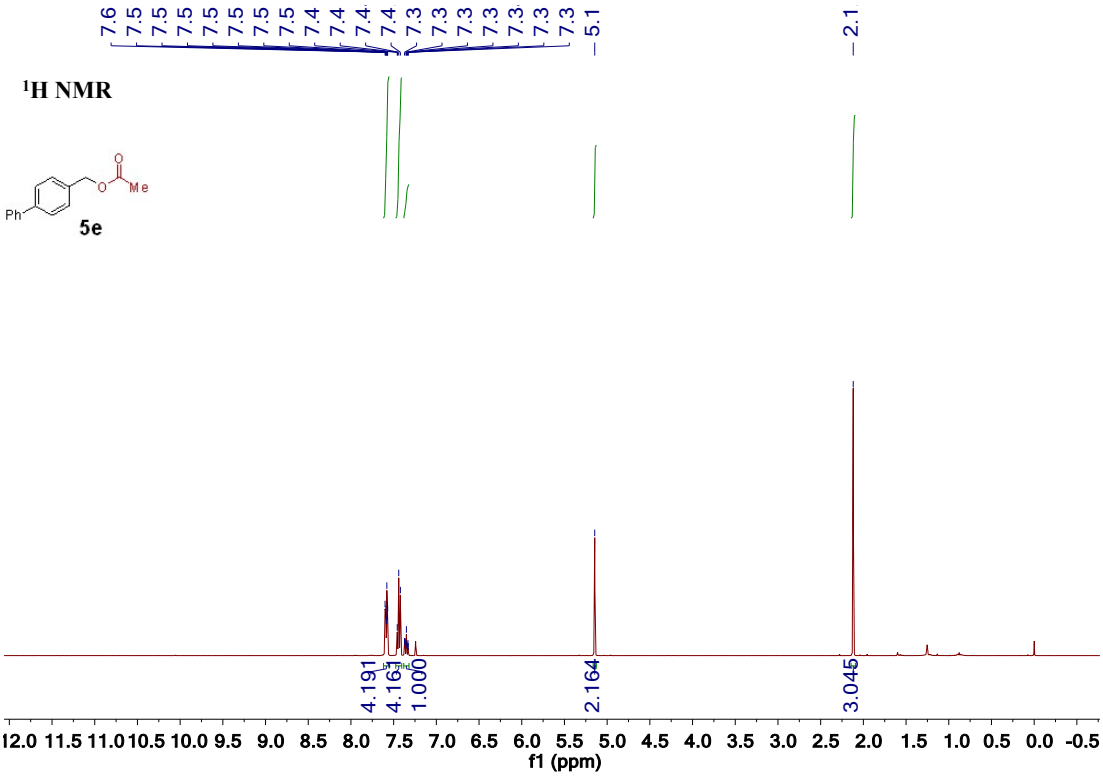
5c

^{1}H NMR



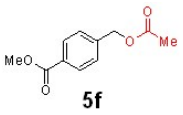
5d

^{1}H NMR



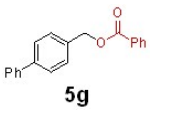
5e

^{1}H NMR



5f

^{1}H NMR



5g

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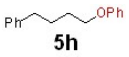

5h

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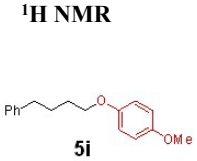

5i

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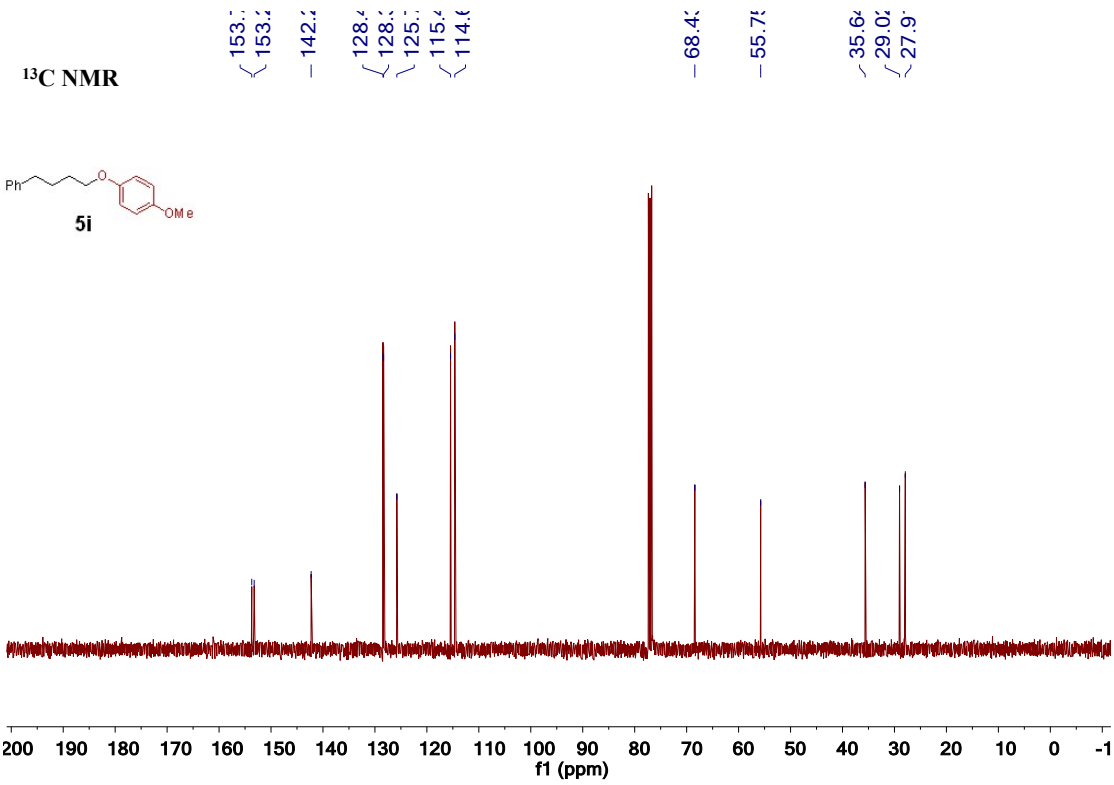
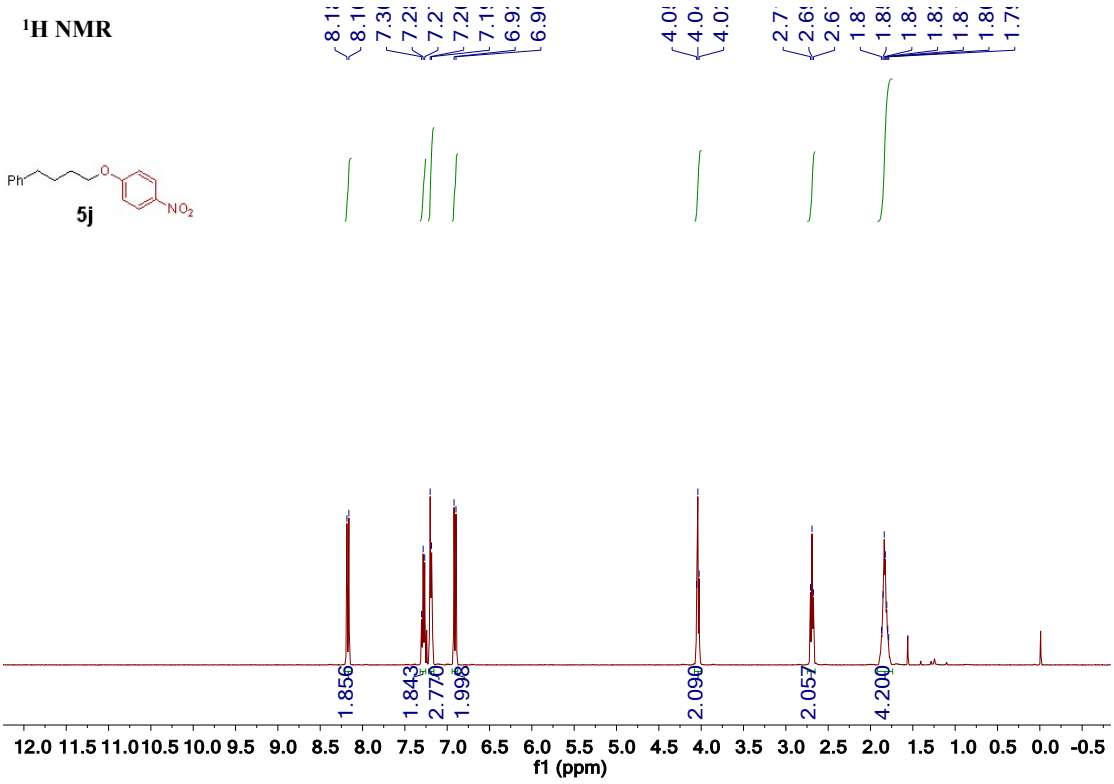
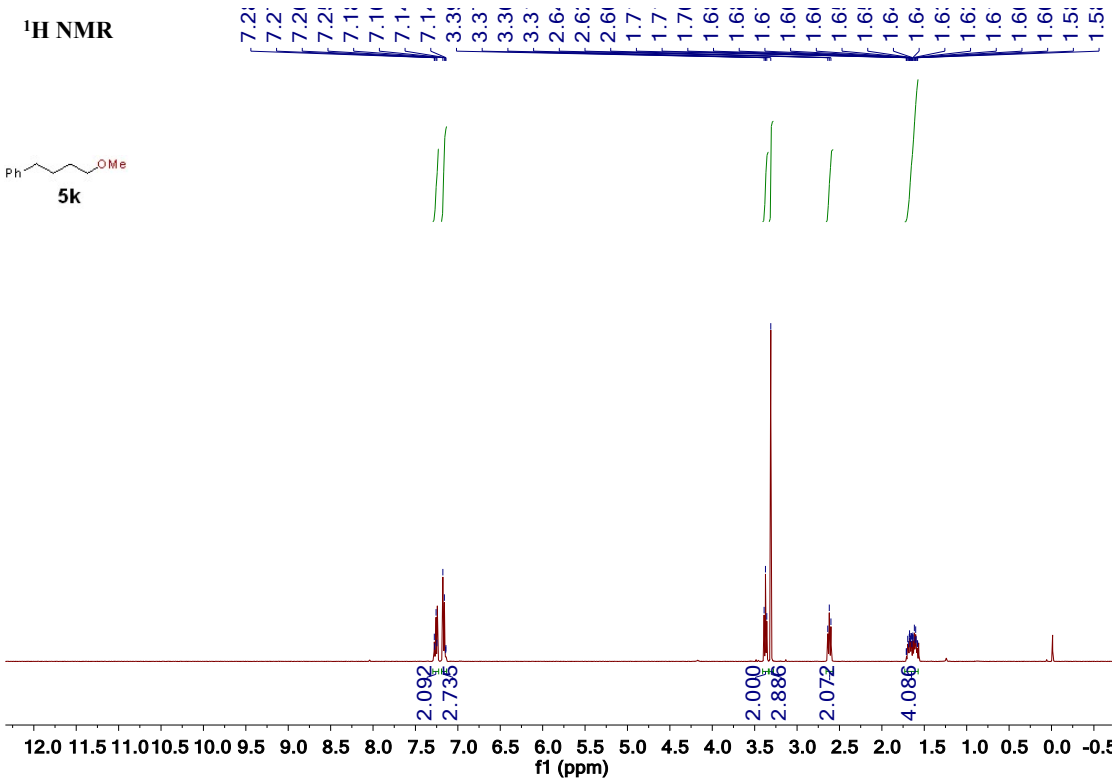


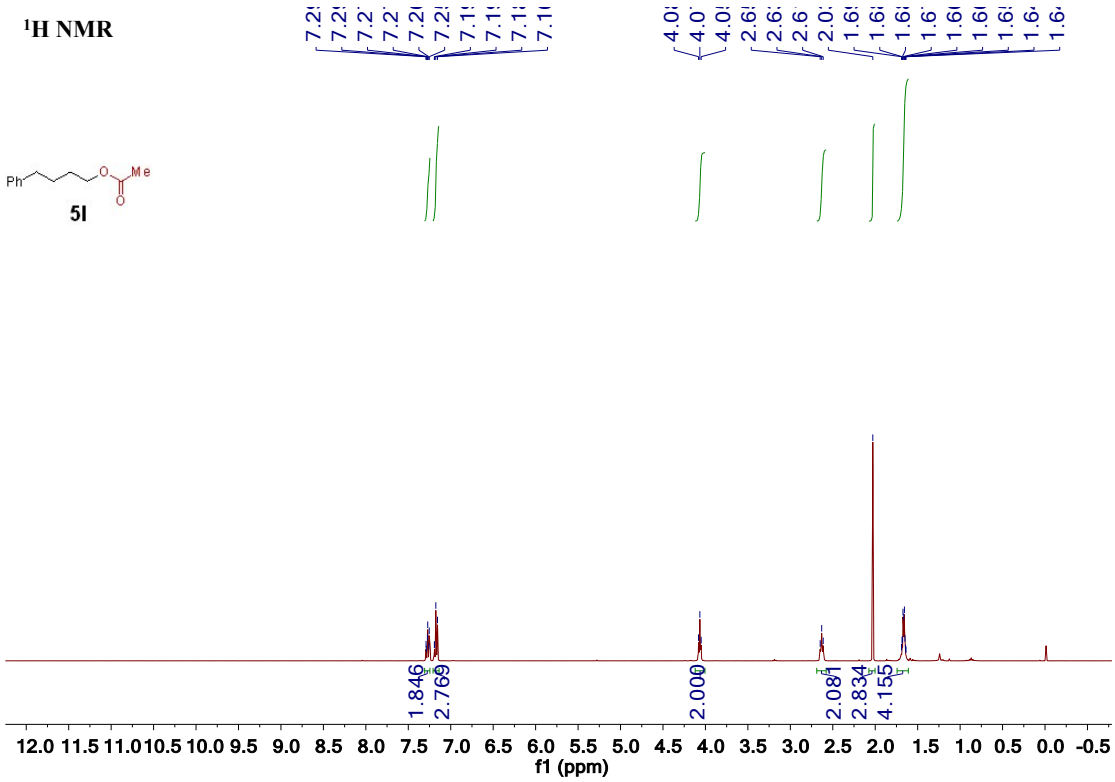
^{1}H NMR



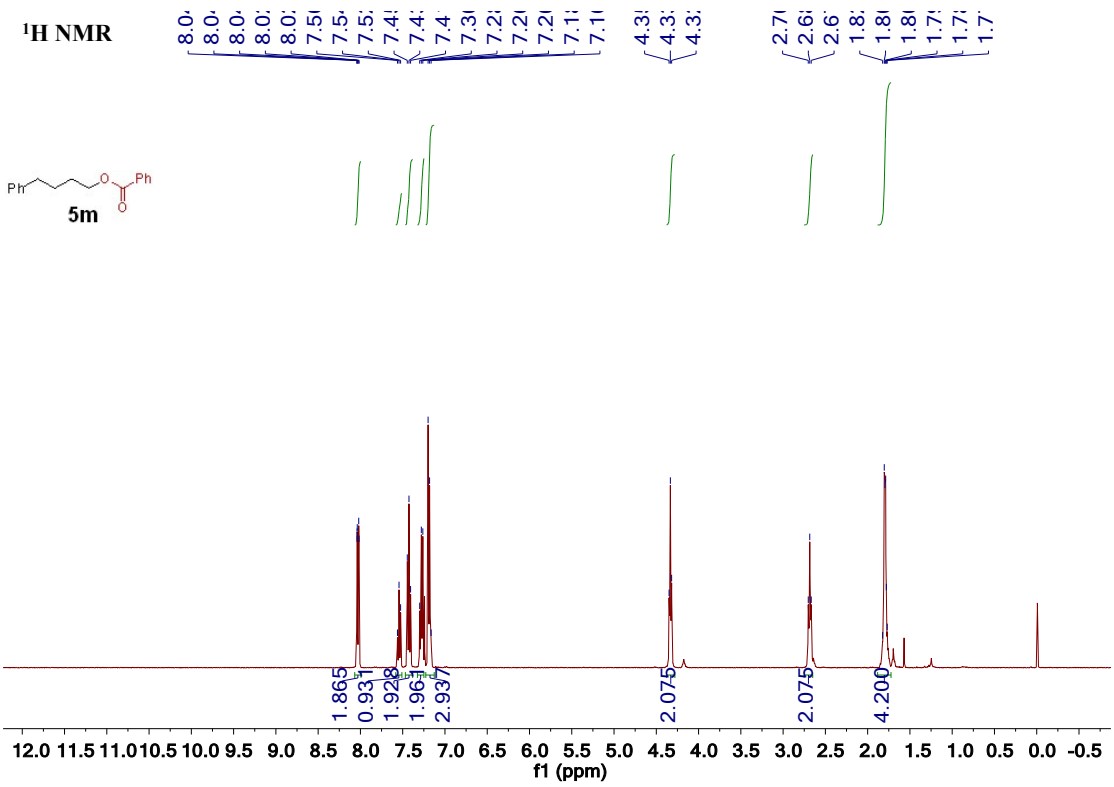
^{1}H NMR


Ph
OMe
5k
2.092
2.735
2.000
2.886
2.072
4.086
f1 (ppm)

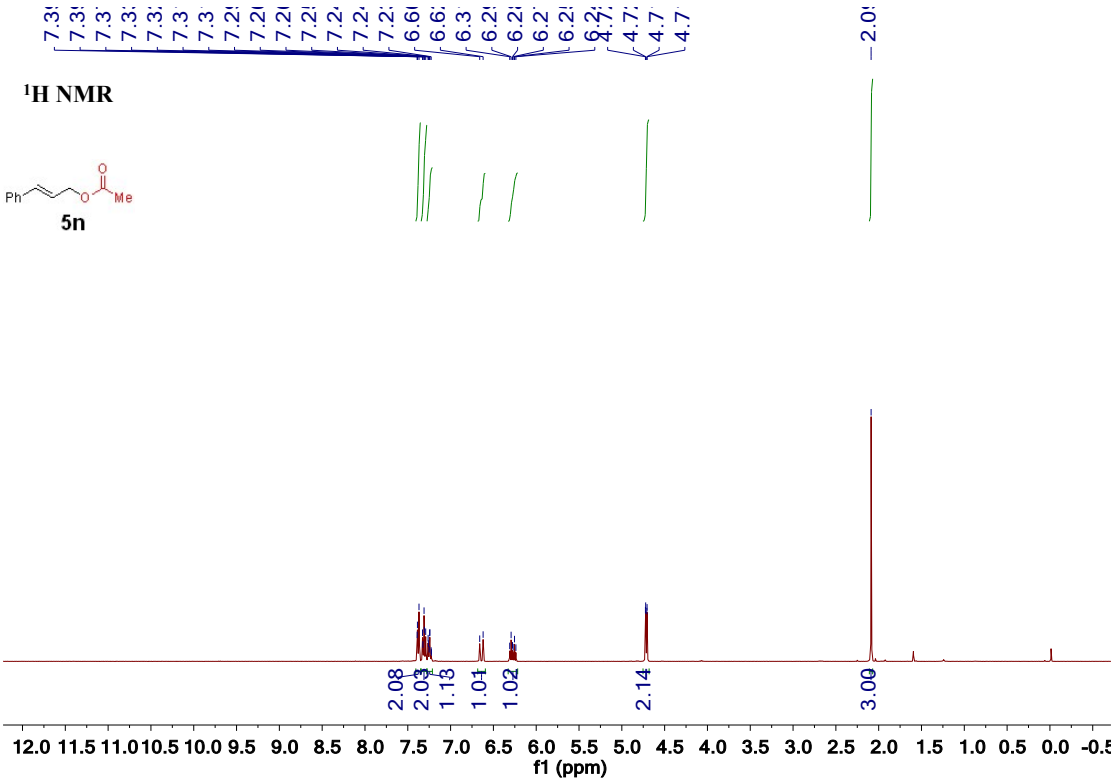
^{1}H NMR


Ph
O
Me
O
5l
1.846
2.769
2.000
2.081
2.834
4.155
f1 (ppm)

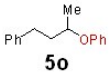
^{1}H NMR


Ph
O
Ph
O
5m
1.865
0.931
1.928
1.963
2.937
2.075
2.075
4.200
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

^{1}H NMR

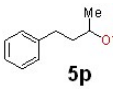

Ph
O
O
Me
5n
2.08
2.03
1.13
1.01
1.02
2.14
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

^{1}H NMR



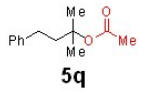
5o

^{1}H NMR



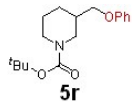
5p

^{1}H NMR



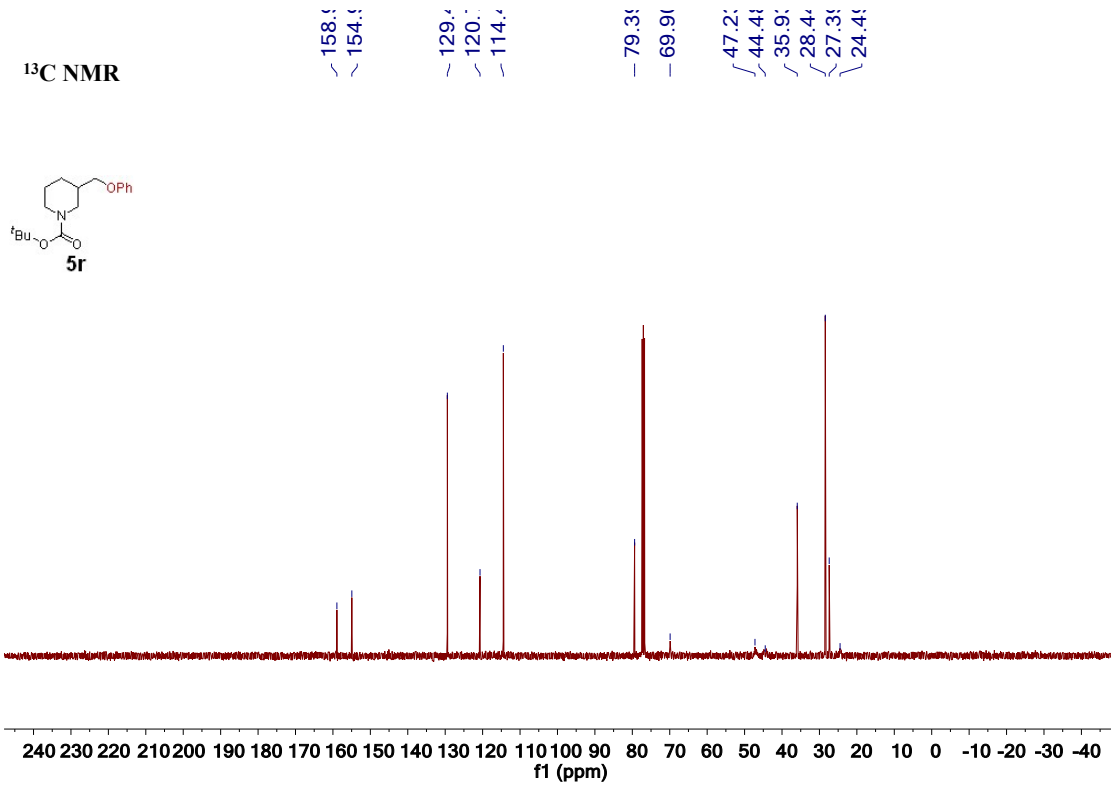
5q

^{1}H NMR

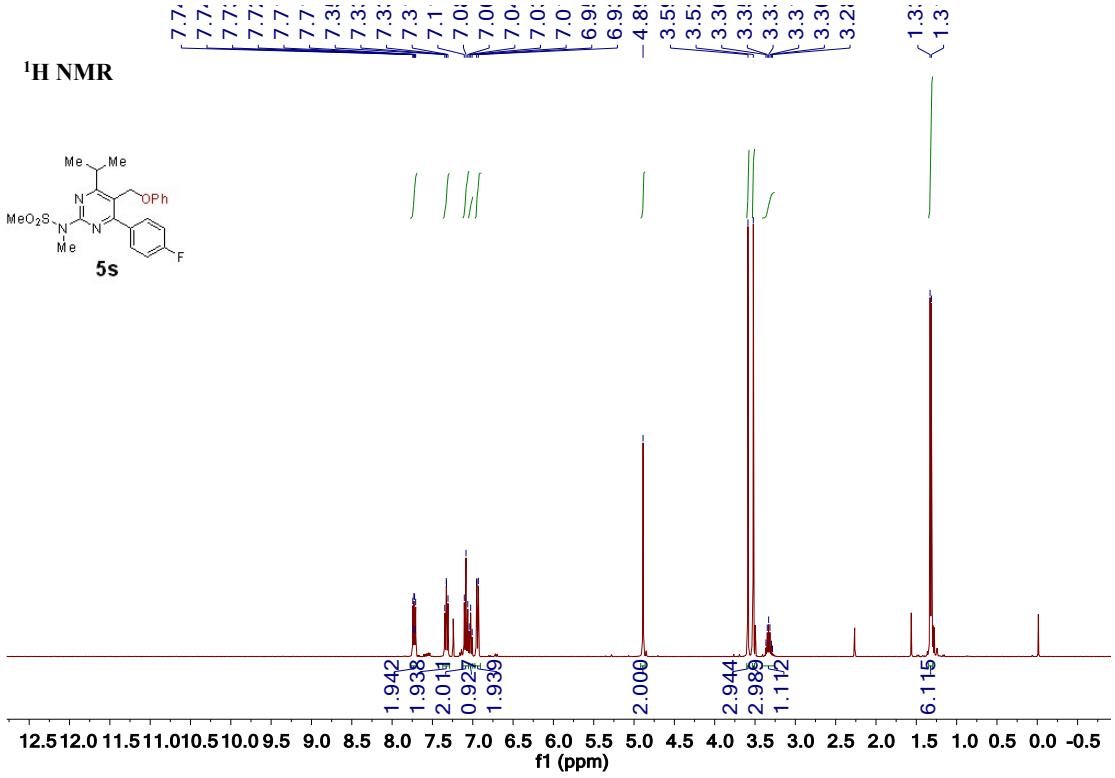


5r

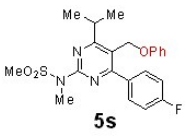
^{13}C NMR



^{1}H NMR

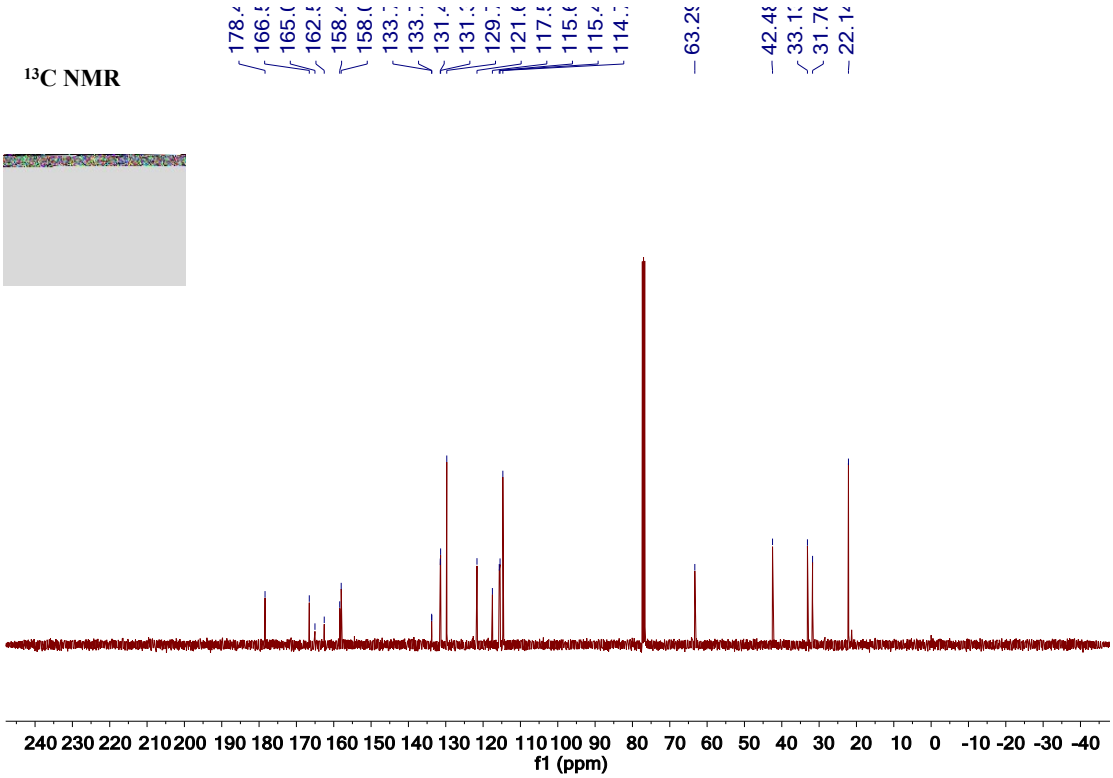


^{19}F NMR

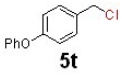


5s

^{13}C NMR

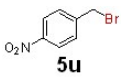


^{1}H NMR



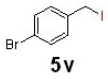
5t

^{1}H NMR



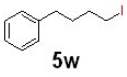
5u

^{1}H NMR



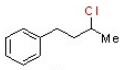
5v

^{1}H NMR



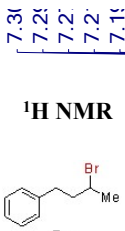
5w

^{1}H NMR



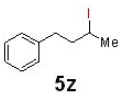
5x

^{1}H NMR



5y

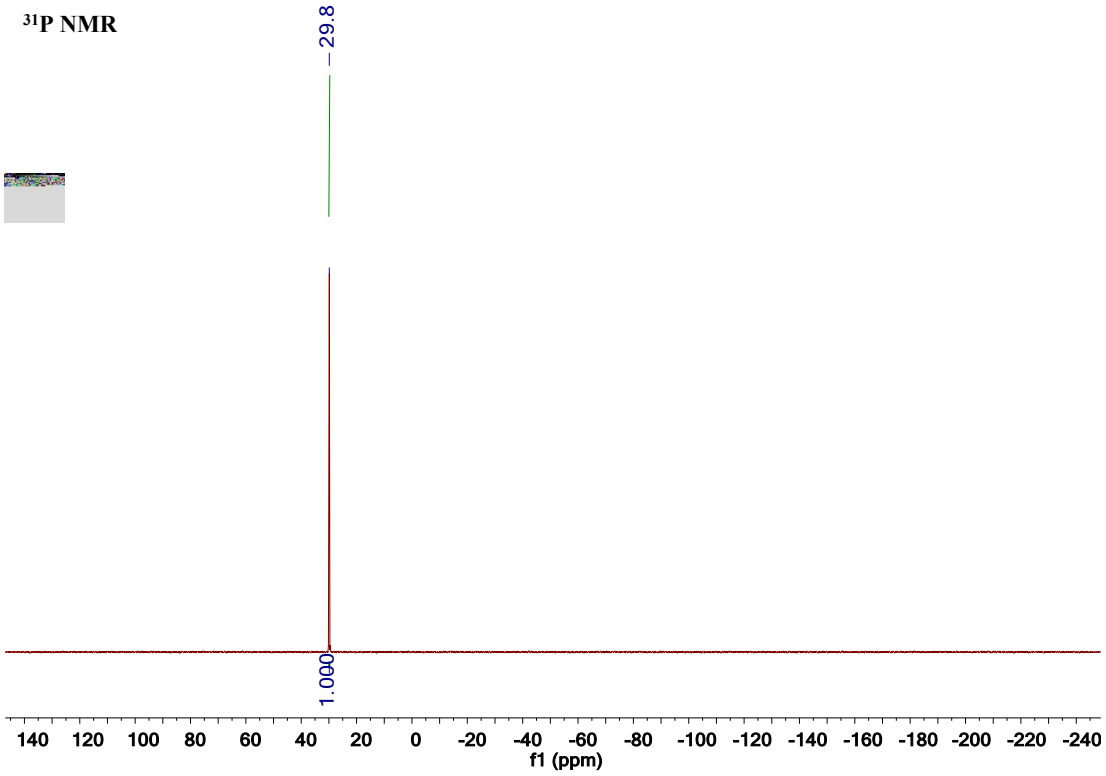
^{1}H NMR



5z

^{1}H NMR

^{31}P NMR


29.8
1.000
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)