Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Homocoupling of Benzyl Pyridyl Ethers via Visible Light-Mediated Deoxygenation

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1. General information

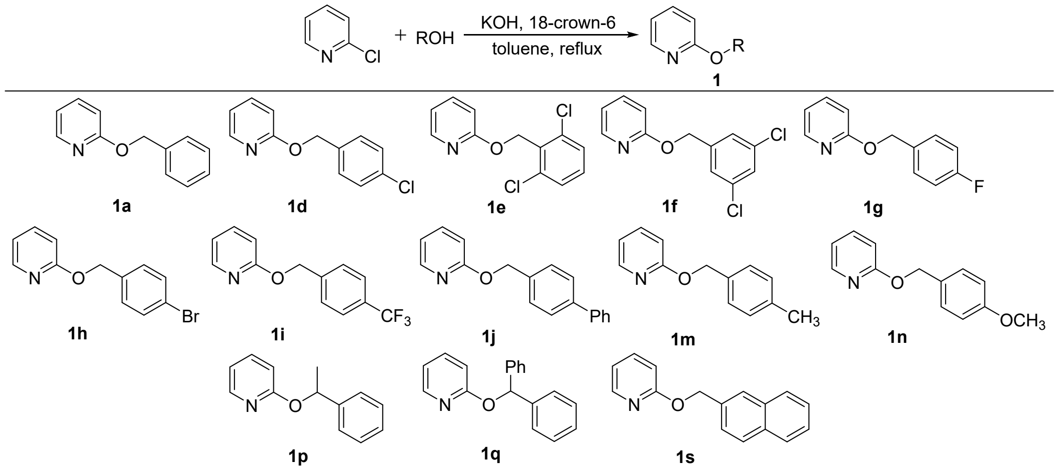
All solvents and commercially available reagents were purchased as reagent grade and were used without further purification, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) and visualized using UV-light or $KMnO_4$ stain as a developing agent. Column chromatography was performed using silica gel (200-300 mesh). Solvent removal was carried out by RE-52AA rotary evaporator under reduced pressure. The ^1H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker Avance III using $CDCl_3$ as the deuterated solvent. The chemical shifts (δ) were reported in parts per million (ppm), referenced relative to TMS (0 ppm for ^1H NMR), $CDCl_3$ (7.26 ppm for ^1H NMR), $CDCl_3$ (77.0 ppm for ^{13}C NMR). Coupling constants (J) are reported in hertz (Hz). The following abbreviations are used for spin multiplicity: s, singlet; d, doublet; t, triplet; dt, doublet of triplets; td, triplet of doublets; dd, doublet of doublets; ddd, doublet of doublet of doublets; m, multiplet; app, apparent. IR spectra were recorded on an FT-IR NICOLET iS10 spectrometer. HRMS were recorded on a Thermo Scientific LTQ Orbitrap Discovery spectrometer (ESI). LC-MS were recorded on a Agilent 1290II-6460 spectrometer (ESI). GC-MS analyses were performed using Agilent 7890B-5977A spectrometer gas chromatograph with FID detector and Zebron ZB 5MSi column.

2. Photoreaction setup

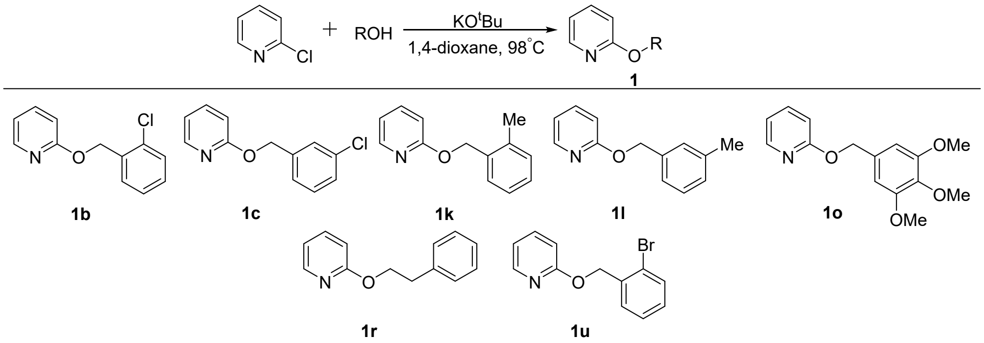
Photoredox reactions were carried out in the YM-GHX-V type photochemical reactor purchased from Shanghai YuMing Instrument CO.LTD. The reactor used the 50 mL round quartz tube matched with the instrument. The distance between the light source and the reaction tube is about 3 cm. Blue light – λ_{max} = 450-455 nm, 30W*1.

3. General synthetic procedures

3.1 Preparation of Pyridyl Ethers

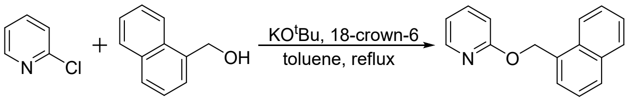


The above pyridyl ethers were obtained using the literature procedure by Dudley[1] and Yang[2]. A 50 mL, round-bottomed flask equipped with a magnetic stirring bar with reflux condenser was charged with 2-chloropyridine (0.95 ml, 10 mmol, 1.0 equiv), alcohol (15 mmol, 1.5 equiv), potassium hydroxide (1.85 g, 33 mmol, 3.3 equiv), 18-crown-6 (135 mg, 0.5 mmol, 0.05 equiv) and toluene (20 mL). The reaction mixture was heated to reflux with a heating mantle. The reaction was monitored by TLC until completion or no obvious progress observed then allowed to cool to room temperature. The resulting mixture was diluted with H_2O and extracted with EtOAc. The combined organic extract was then washed with brine, dried (Na_2SO_4), filtered, concentrated under vacuum, and purified on silica gel to provide the above pyridyl ethers.



The above pyridyl ethers were obtained using the literature procedure by Anderson.[3] A 150mL, round-bottomed flask equipped with a magnetic stirring bar with reflux condenser was charged with 2-

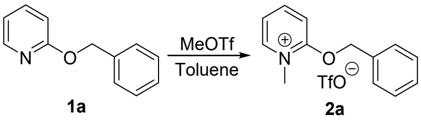
chloropyridine (0.95 ml, 10 mmol, 1.0 equiv), alcohol (15 mmol, 1.5 equiv), potassium tert-butoxide (1.68 g, 15 mmol, 1.5 equiv) and 1,4-dioxane (40 mL). The reaction mixture was heated to reflux with a heating mantle. The reaction was monitored by TLC until completion or no obvious progress observed then allowed to cool to room temperature. The resulting mixture was diluted with H_2O and extracted with EtOAc. The combined organic extract was then washed with brine, dried (Na_2SO_4), filtered, concentrated under vacuum, and purified on silica gel to provide the above pyridyl ethers.



1t

2-(1-Naphthalenylmethoxy)pyridine **1t** was obtained using the literature procedure by Tobisu and Chatani.[4] 1-Naphthalenemethanol (1.39 g, 8.8 mmol, 1.1 equiv) was added to a 50 ml round-bottomed flask followed by 18-crown-6 (0.11g, 0.4 mmol, 0.05 equiv) and potassium t-butoxide (1.08 g, 9.6 mmol, 1.2 equiv). The mixture was dissolved in 16 mL of toluene. After 2-chloropyridine (0.76 ml, 8 mmol, 1.0 equiv) was added, the mixture was heated to reflux for 12 h. The resulting mixture was allowed to cool to room temperature and then diluted with H_2O and extracted with EtOAc. The combined organic extract was then washed with brine, dried (Na_2SO_4), filtered, concentrated under vacuum, and purified on silica gel to provide the 2-(1-naphthalenylmethoxy)pyridine **1t** as colorless oil (1.36 g, 72%).

3.2 Preparation of Pyridinium Salts 2a

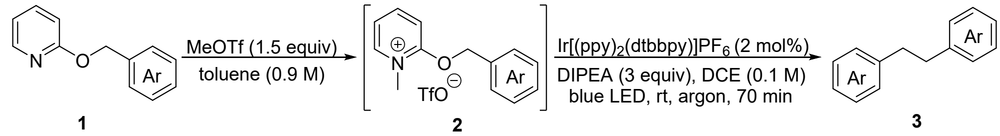


1a 2a

Pyridinium salt **2a** was obtained using the literature procedure by Dudley.[1] A round-bottomed flask equipped with a magnetic stirrer was charged with pyridyl ether **1a** (0.28 g, 1.5 mmol, 1.0 equiv) then degassed and backfilled with argon for three times. Toluene (1.7 mL, 0.9 M) was added to the flask via syringe. The resulting solution was cooled to 0°C in an ice bath. Methyl trifluoromethanesulfonate (0.2 mL, 1.6 mmol, 1.1 equiv) was added dropwise via syringe over 15 min. The ice bath was removed and the viscous slurry was allowed to warm to ambient temperature. After 1 h, the heterogeneous reaction mixture was diluted with 10 mL of petroleum ether and the solids were isolated by filtration, washed with one additional portion of petroleum ether or toluene (10 mL) and dried to provide pyridinium salt

2a as white solid (0.5 g, 94%).

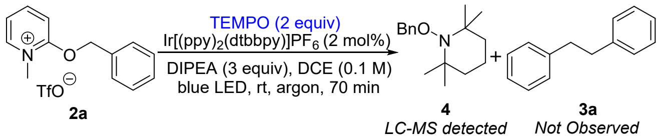
3.3 Homocoupling of Benzyl Pyridyl Ethers via Visible Light-Mediated Deoxygenation



A 50 mL quartz reaction tube equipped with a stirring bar and sealed with septum was charged with benzyl pyridyl ether **1** (0.4 mmol, 1.0 equiv), then degassed and backfilled with argon for three times. Toluene (0.44 mL, 0.9 M) was added via syringe and the resulting mixture was cooled to 0°C, then the MeOTf (68 μL, 0.6 mmol, 1.5 equiv) was added dropwise while stirring, followed by stirring at room temperature for another 1 h. After the reaction was completed, the toluene was removed in vacuo. Ir[(ppy)$_2$(dtbbpy)]PF$_6$ (8 mg, 8 μmol, 2.0 mol%) was added, then the resulting mixture was degassed and backfilled with argon for three times. Subsequently, DIPEA (0.21 mL, 1.2 mmol, 3 equiv) and DCE (4 mL, 0.1 M) were added with syringe under the protection of argon, placed in a photoreactor and irradiated with a 30 W blue LED (see section 2) for 70 min. After this time, the mixture was diluted with EtOAc, transferred to a round-botted flask, and concentrated in vacuo. The crude product was purified by thin layer chromatography to afford product **3**.

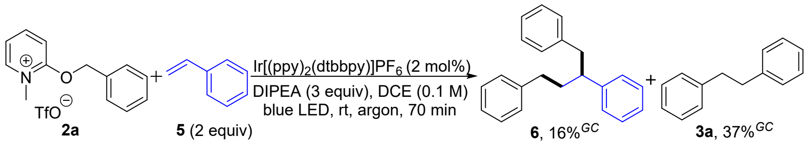
4. Mechanistic considerations

4.1 Radical trap experiment



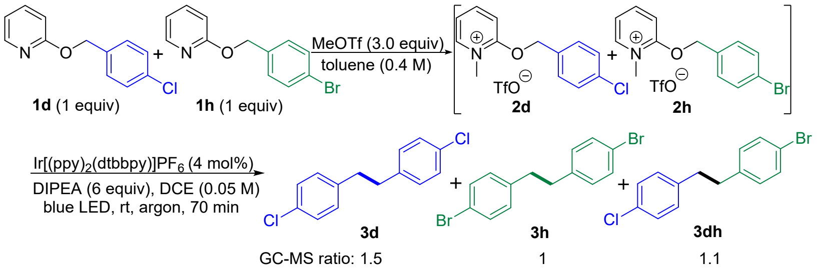
The reaction was set up according to standard conditions using pyridium salt **2a** as the starting material on 0.1 mmol scale. Subsequently, 2.0 equivalents of TEMPO [2,2,6,6-tetramethylpiperidinooxy] were added. After 70 min of blue LED irradiation, the reaction mixture was examined using LC-MS indicating a presence of benzylated TEMPO **4**. The coupling product **3a** was not observed.

4.2 Radical addition experiment with styrene



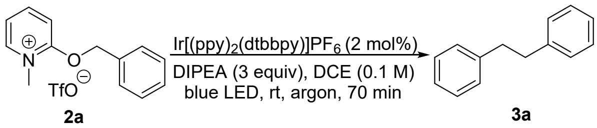
The reaction was set up according to standard conditions using pyridium salt **2a** as the starting material on 0.4 mmol scale. Subsequently, 2.0 equivalents of styrene **5** were added. After 70 min of blue LED irradiation, 20 µL tetradecane was added as an internal standard. The reaction mixture was examined using GC-MS indicating the cross-coupling product **6** was produced in 16% yield and the homocoupling product **3a** was produced in 37% yield.

4.3 The radical cross-coupling experiment



The radical cross-coupling experiment was performed with 0.1 mmol pyridyl ethers **1d** and 0.1 mmol pyridyl ethers **1h** as reaction materials. After 70 min of blue LED irradiation, 20 µL tetradecane was added as an internal standard and the reaction mixture was examined using GC-MS. The reaction yielded three coupling products, including homocoupling product **3d**, homocoupling product **3h** and the cross-coupling product **3dh**, with a GC-MS ratio of 1.5:1:1.1.

4.4 Light on-off experiment



The reaction was set up according to standard condition on 0.1 mmol scale with addition of tetradecane (20 µl) as an internal standard. The reaction was conducted for 1 h under alternating periods of irradiation (blue LED) and darkness meanwhile monitored by GC-MS.

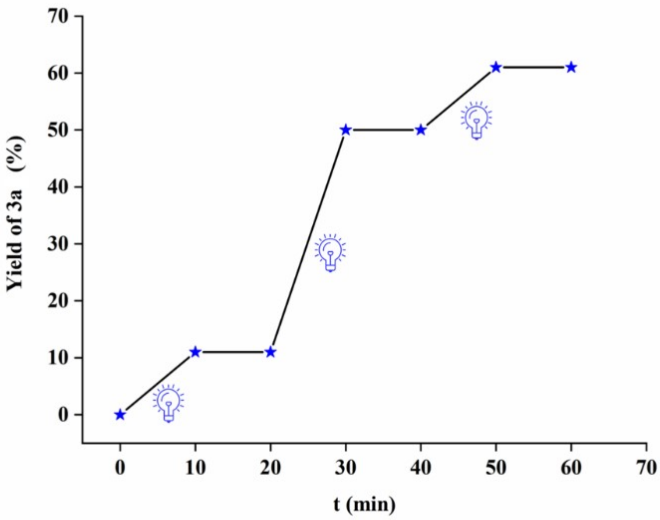
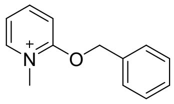


Figure S1. Light on-off experiment.

5. Computational calculation

All calculations were performed using density functional theory (DFT) by *Gaussian16* software package, with B3LYP exchange-correlation functional. The basis set of 6-31+G (d, p) for all atoms was used for structural optimizations and frequency calculations. The polarizable continuum model (PCM) with dichloroethane as solvent was used. The Gibbs free energy was calculated for each structure. Gibbs free energy in Hartree and Cartesian coordinates in Å are given for each structure as the following.

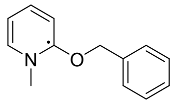


Gibbs free energy = -633.466045 Hartree

Cartesian coordinates:

C	-2.2684	-1.4084	-0.0004
C	-3.6546	-1.4465	-0.0008
C	-4.3934	-0.2547	-0.0006
C	-3.7135	0.9417	0.0001
H	-1.6882	-2.3206	-0.0006
H	-4.1623	-2.4049	-0.0012
H	-5.4757	-0.2537	-0.0009
H	-4.2129	1.9017	0.0004
C	-1.6481	2.2864	0.0014
H	-2.3954	3.0760	0.0024
H	-1.0228	2.3587	0.8913
H	-1.0235	2.3603	-0.8889
C	-1.6178	-0.1674	0.0002
C	0.6086	-1.1121	-0.0000
H	0.3995	-1.7022	-0.8955
H	0.3998	-1.7026	0.8952
C	2.0089	-0.5738	-0.0001

C	2.6673	-0.3157	-1.2110
C	2.6684	-0.3180	1.2106
C	3.9659	0.1986	-1.2116
H	2.1650	-0.5210	-2.1527
C	3.9670	0.1963	1.2111
H	2.1669	-0.5252	2.1523
C	4.6163	0.4559	-0.0003
H	4.4702	0.3928	-2.1533
H	4.4721	0.3886	2.1527
H	5.6277	0.8513	-0.0004
N	-2.3532	0.9839	0.0006
O	-0.3109	0.0400	0.0005

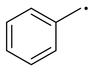


Gibbs free energy = -633.458284 Hartree

Cartesian coordinates:

C	2.2324	-1.3991	0.0990
C	3.6661	-1.4944	0.1242
C	4.4018	-0.2998	0.0313
C	3.7661	0.9131	-0.1044
H	1.6280	-2.2931	0.1789
H	4.1506	-2.4562	0.2418
H	5.4873	-0.3081	0.0657
H	4.2876	1.8568	-0.1955
C	1.6226	-0.1800	-0.0374
C	-0.6059	-1.0700	0.0741
H	-0.3903	-1.5721	1.0242
H	-0.4234	-1.7725	-0.7470
N	2.3588	0.9964	-0.2026

C	1.7313	2.3038	-0.0255
H	2.3757	3.0573	-0.4828
H	0.7593	2.3277	-0.5149
H	1.6012	2.5510	1.0386
C	-2.0200	-0.5538	0.0420
C	-2.7163	-0.4610	-1.1714
C	-2.6548	-0.1478	1.2245
C	-4.0230	0.0338	-1.2045
H	-2.2346	-0.7797	-2.0923
C	-3.9610	0.3479	1.1951
H	-2.1251	-0.2222	2.1708
C	-4.6470	0.4400	-0.0205
H	-4.5531	0.0985	-2.1502
H	-4.4432	0.6572	2.1178
H	-5.6638	0.8213	-0.0442
O	0.2847	0.0579	-0.0690

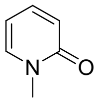


Gibbs free energy = -270.834703 Hartree

Cartesian coordinates:

C	1.8519	0.0000	0.0000
C	1.1473	1.2077	-0.0000
C	-0.2508	1.2075	-0.0000
C	-0.2508	-1.2075	0.0000
C	1.1473	-1.2077	0.0000
H	2.9382	0.0000	0.0000
H	1.6846	2.1522	-0.0000
H	-0.7904	2.1507	-0.0000
H	-0.7904	-2.1507	0.0000

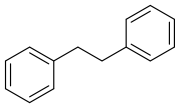
H	1.6846	-2.1522	0.0000
C	-0.9745	0.0000	-0.0000
C	-2.4538	0.0000	0.0000
H	-3.0131	0.0000	0.9316
H	-3.0131	-0.0000	-0.9316



Gibbs free energy = -362.776320 Hartree

Cartesian coordinates:

C	1.9817	-0.4219	0.0002
C	1.7355	0.9765	-0.0001
C	0.4358	1.4059	-0.0002
C	0.9377	-1.3106	0.0002
H	0.1701	2.4564	0.0002
H	2.5422	1.6986	0.0001
H	3.0044	-0.7885	-0.0004
H	1.0981	-2.3828	-0.0000
C	-1.9953	1.0221	0.0001
H	-2.5198	0.6574	-0.8855
H	-2.5197	0.6577	0.8858
H	-1.9813	2.1113	-0.0002
C	-0.4351	-0.8686	-0.0000
O	-1.4330	-1.6164	-0.0002
N	-0.6130	0.5289	0.0001

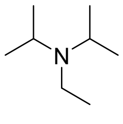


Gibbs free energy = -541.777920 Hartree

Cartesian coordinates:

C	-2.6211	-1.2048	-0.2145

C	-2.6212	1.2049	-0.2137
C	-3.9886	1.2078	0.0789
C	-4.6777	-0.0002	0.2267
C	-3.9884	-1.2081	0.0781
H	-2.0952	-2.1494	-0.3337
H	-2.0955	2.1497	-0.3322
H	-4.5152	2.1521	0.1866
H	-5.7405	-0.0004	0.4510
H	-4.5150	-2.1525	0.1851
C	-1.9161	0.0002	-0.3639
C	-0.4290	0.0003	-0.6467
H	-0.1651	0.8810	-1.2437
H	-0.1650	-0.8800	-1.2443
C	0.4290	-0.0001	0.6467
H	0.1650	-0.8807	1.2437
H	0.1650	0.8803	1.2442
C	1.9162	-0.0000	0.3639
C	2.6213	-1.2049	0.2144
C	2.6211	1.2048	0.2138
C	3.9885	-1.2080	-0.0782
H	2.0955	-2.1495	0.3335
C	3.9884	1.2080	-0.0789
H	2.0952	2.1495	0.3323
C	4.6777	-0.0000	-0.2267
H	4.5152	-2.1523	-0.1853
H	4.5149	2.1523	-0.1864
H	5.7405	-0.0000	-0.4510

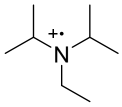


Gibbs free energy = -370.853088 Hartree

Cartesian coordinates:

N	0.0014	0.2670	0.2004
C	0.2928	1.4717	-0.5839
C	-0.2830	2.7537	0.0298
H	-0.0539	1.3819	-1.6300
H	1.3791	1.5863	-0.6372
H	-0.0125	3.6193	-0.5865
H	-1.3755	2.7289	0.0971
H	0.1139	2.9085	1.0386
C	-1.3924	-0.2102	0.0748
C	-1.8571	-0.9305	1.3506
C	-1.7047	-1.0584	-1.1776
H	-1.9982	0.6993	-0.0031
H	-1.6996	-0.2975	2.2293
H	-2.9242	-1.1706	1.2825
H	-1.3213	-1.8733	1.5093
H	-1.3838	-0.5557	-2.0960
H	-1.2185	-2.0392	-1.1342
H	-2.7847	-1.2295	-1.2531
C	1.0606	-0.7671	0.1939
C	2.1650	-0.4061	1.2023
C	1.6829	-1.0940	-1.1831
H	0.5872	-1.6853	0.5568
H	1.7447	-0.2795	2.2046
H	2.9282	-1.1921	1.2402
H	2.6671	0.5285	0.9250
H	0.9245	-1.3454	-1.9284
H	2.2745	-0.2570	-1.5701

H	2.3582	-1.9521	-1.0880



Gibbs free energy = -370.660633 Hartree

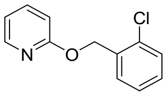
Cartesian coordinates:

N	0.0007	0.1249	-0.2321
C	0.5547	1.2367	-0.9969
C	0.3775	2.5926	-0.2821
H	0.0240	1.2562	-1.9566
H	1.6090	1.0415	-1.1869
H	0.7993	3.3634	-0.9318
H	-0.6747	2.8289	-0.1103
H	0.9099	2.6075	0.6710
C	-1.4646	0.0288	-0.0954
C	-1.8877	0.1101	1.3839
C	-1.9863	-1.2472	-0.7881
H	-1.8652	0.8961	-0.6242
H	-1.5301	1.0297	1.8525
H	-2.9805	0.1106	1.4161
H	-1.5335	-0.7471	1.9615
H	-1.6872	-1.2819	-1.8384
H	-1.6479	-2.1566	-0.2855
H	-3.0782	-1.2218	-0.7432
C	0.8822	-0.8995	0.3522
C	1.8901	-0.2666	1.3309
C	1.5823	-1.7025	-0.7662
H	0.2315	-1.5747	0.9089
H	1.3849	0.3011	2.1153
H	2.4479	-1.0807	1.8009

H	2.6078	0.3816	0.8218
H	0.8599	-2.1465	-1.4540
H	2.2843	-1.0867	-1.3335
H	2.1451	-2.5092	-0.2888

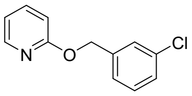
6. Scope and characterization of key compounds

The specific synthesis and structural characterization of pyridyl ethers **1a**, **1d**, **1e**, **1f**, **1g**, **1h**, **1i**, **1j**, **1m**, **1n**, **1p**, **1q**, **1r**, **1s** and pyridinium salt **2a** are described in detail in previous report.[5]



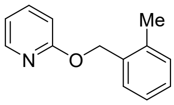
2-[(2-Chlorophenyl)methoxy]pyridine (1b)

The compound **1b** was obtained from 2-chloropyridine (0.95 mL, 10.0 mmol) and 2-chlorobenzyl alcohol (2.10 g, 15.0 mmol) as a colorless oil (2.00 g, 91%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.17 (ddd, *J* = 4.7, 2.4, 0.9 Hz, 1H), 7.61 – 7.50 (m, 2H), 7.41 – 7.35 (m, 1H), 7.28 – 7.19 (m, 2H), 6.87 (ddd, *J* = 6.6, 5.5, 1.0 Hz, 1H), 6.82 (dt, *J* = 8.3, 1.0 Hz, 1H), 5.49 (s, 2H). ^{1}H NMR spectrum is consistent with data reported in literature.[3]



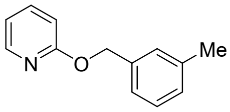
2-[(3-Chlorophenyl)methoxy]pyridine (1c)

The compound **1c** was obtained from 2-chloropyridine (0.95 mL, 10.0 mmol) and 3-chlorobenzyl alcohol (2.10 g, 15.0 mmol) as a pale yellow oil (2.15 g, 98 %). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.15 (ddd, *J* = 4.6, 2.4, 0.9 Hz, 1H), 7.56 (ddd, *J* = 8.2, 7.3, 1.9 Hz, 1H), 7.45 (app d, *J* = 1.0 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.28 – 7.22 (m, 2H), 6.89 – 6.83 (m, 1H), 6.80 (dt, *J* = 8.3, 1.0 Hz, 1H), 5.35 (s, 2H). ^{1}H NMR spectrum is consistent with data reported in literature.[3]



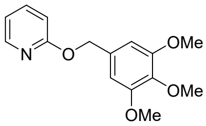
2-[(2-Methylphenyl)methoxy]pyridine (1k)

The compound **1k** was obtained from 2-chloropyridine (0.76 mL, 8.0 mmol) and 2-methylbenzyl alcohol (1.47 g, 12.0 mmol) as a pale yellow oil (1.35 g, 85 %). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.18 (ddd, *J* = 4.6, 2.4, 0.8 Hz, 1H), 7.58 – 7.49 (m, 1H), 7.46 – 7.40 (m, 1H), 7.25 – 7.15 (m, 3H), 6.85 (ddd, *J* = 6.7, 5.6, 1.0 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 5.36 (s, 2H), 2.38 (s, 3H). ^{1}H NMR spectrum is consistent with data reported in literature.[3]



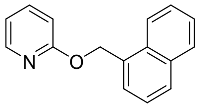
2-[(3-Methylphenyl)methoxy]pyridine (1l)

The compound **1l** was obtained from 2-chloropyridine (0.76 mL, 8.0 mmol) and 3-methylbenzyl alcohol (1.47 g, 12.0 mmol) as a pale yellow oil (1.28 g, 80 %). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.16 (ddd, *J* = 4.7, 2.4, 0.8 Hz, 1H), 7.53 (ddd, *J* = 8.0, 7.2, 2.0 Hz, 1H), 7.30 – 7.20 (m, 3H), 7.14 – 7.07 (m, 1H), 6.83 (ddd, *J* = 6.6, 5.5, 1.0 Hz, 1H), 6.78 (dt, *J* = 8.4, 1.0 Hz, 1H), 5.34 (s, 2H), 2.34 (s, 3H). ^{1}H NMR spectrum is consistent with data reported in literature.[3]



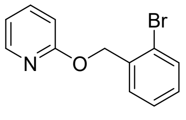
2-((3,4,5-Trimethoxybenzyl)oxy)pyridine (1o)

The compound **1o** was obtained from 2-chloropyridine (0.95 mL, 10.0 mmol) and 3,4,5-trimethoxybenzyl alcohol (1.93 ml, 12.0 mmol) as a colorless oil (2.00 g, 73 %). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.22 – 8.13 (m, 1H), 7.62 – 7.52 (m, 1H), 6.92 – 6.85 (m, 1H), 6.81 (app d, *J* = 8.4 Hz, 1H), 6.70 (s, 2H), 5.31 (s, 2H), 3.86 (s, 6H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 163.5, 153.3, 146.8, 138.6, 137.6, 132.9, 117.0, 111.2, 105.2, 67.7, 60.7, 56.0. IR 2937, 2838, 1592, 1569, 1506, 1461, 1431, 1419, 1366, 1330, 1310, 1272, 1233, 1123, 1042, 1003 cm^{-1}. HRMS (ESI) [M+H]$^+$ calcd for $C_{15}H_{18}NO_4^+$: 276.1230, found: 276.1225.



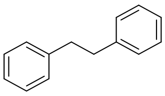
2-(1-Naphthalenylmethoxy)pyridine (1t)

The compound **1t** was obtained from 2-chloropyridine (0.76 mL, 8.0 mmol) and 1-naphthalenemethanol (1.39 g, 8.8 mmol) as a colorless oil (1.36 g, 72%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.21 (ddd, *J* = 4.7, 2.4, 0.9 Hz, 1H), 8.13 – 8.05 (m, 1H), 7.89 – 7.76 (m, 2H), 7.62 (d, *J* = 7.0 Hz, 1H), 7.57 – 7.38 (m, 4H), 6.85 (ddd, *J* = 6.6, 5.5, 1.0 Hz, 1H), 6.78 (dt, *J* = 8.4, 1.0 Hz, 1H), 5.82 (s, 2H). ^{1}H NMR spectrum is consistent with data reported in literature.[4]



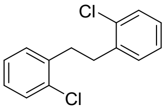
2-[(2-Bromophenyl)methoxy]pyridine (1u)

The compound **1u** was obtained from 2-chloropyridine (0.95 mL, 10.0 mmol) and 2-bromobenzyl alcohol (2.83 g, 15.0 mmol) as a pale yellow solid (2.31 g, 88 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (ddd, *J* = 4.6, 2.5, 0.8 Hz, 1H), 7.62 – 7.55 (m, 2H), 7.55 – 7.50 (m, 1H), 7.30 (td, *J* = 7.4, 1.2 Hz, 1H), 7.16 (td, *J* = 7.8, 1.8 Hz, 1H), 6.88 (ddd, *J* = 6.6, 5.5, 1.0 Hz, 1H), 6.84 (dt, *J* = 8.4, 1.0 Hz, 1H), 5.46 (s, 2H). ^{1}H NMR spectrum is consistent with data reported in literature.[6]



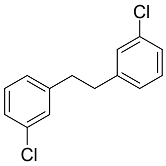
Dibenzyl (3a)

The compound **3a** was obtained from **1a** (37 mg, 0.2 mmol) as a white soild (15 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (app t, *J* = 7.7 Hz, 4H), 7.18 (t, *J* = 7.0 Hz, 6H), 2.91 (s, 4H). ^{1}H NMR spectrum is consistent with data reported in literature.[7]



2,2′-Dichlorobibenzyl (3b)

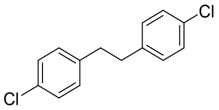
The compound **3b** was obtained from **1b** (88 mg, 0.4 mmol) as a white soild (41 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 2H), 7.18 – 7.09 (m, 6H), 3.03 (s, 4H). ^{1}H NMR spectrum is consistent with data reported in literature.[7]



1,2-Bis(3-chlorophenyl)ethane (3c)

The compound **3c** was obtained from **1c** (88 mg, 0.4 mmol) as a white soild (29 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.12 (m, 6H), 7.01 (dt, *J* = 6.2, 2.3 Hz, 2H), 2.87 (s, 4H).

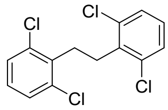
^{1}H NMR spectrum is consistent with data reported in literature.[8]



1,2-Bis(4-chlorophenyl)ethane (3d)

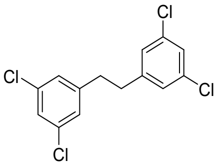
The compound **3d** was obtained from **1d** (88 mg, 0.4 mmol) as a white soild (41 mg, 81%). ^{1}H NMR

(400 MHz, $CDCl_3$) δ 7.26 – 7.17 (m, 4H), 7.07 – 7.00 (m, 4H), 2.85 (s, 4H). ^{1}H NMR spectrum is consistent with data reported in literature.[7]



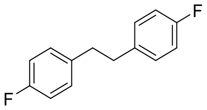
1,1′-(1,2-Ethanediyl)bis[2,6-dichlorobenzene] (3e)

The compound **3e** was obtained from **1e** (102 mg, 0.4 mmol) as a white soild (42 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 8.1 Hz, 4H), 7.06 (t, J = 8.2 Hz, 2H), 3.24 (s, 4H). ^{1}H NMR spectrum is consistent with data reported in literature.[9]



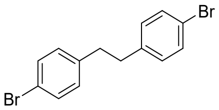
1,1′-(1,2-Ethanediyl)bis[3,5-dichlorobenzene] (3f)

The compound **3f** was obtained from **1f** (102 mg, 0.4 mmol) as a white soild (43 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, J = 2.0 Hz, 2H), 7.04 (d, J = 1.9 Hz, 4H), 2.84 (s, 4H). ^{1}H NMR spectrum is consistent with data reported in literature.[10]



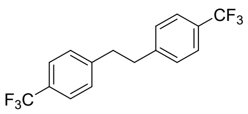
1,2-Bis(4-fluorophenyl)ethane (3g)

The compound **3g** was obtained from **1g** (81 mg, 0.4 mmol) as a white soild (42 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 – 7.02 (m, 4H), 6.98 – 6.89 (m, 4H), 2.86 (s, 4H). ^{1}H NMR spectrum is consistent with data reported in literature.[8]



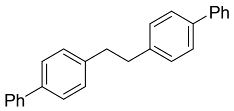
1,2-Bis(4-bromophenyl)ethane (3h)

The compound **3h** was obtained from **1h** (106 mg, 0.4 mmol) as a white soild (49 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 4H), 7.01 – 6.95 (m, 4H), 2.83 (s, 4H). ^{1}H NMR spectrum is consistent with data reported in literature.[8]



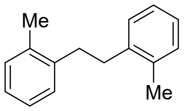
1,1′-(1,2-Ethanediyl)bis[4-(trifluoromethyl)benzene] (3i)

The compound **3i** was obtained from **1i** (38 mg, 0.15 mmol) as a white soild (15 mg, 61%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.53 (d, *J* = 8.0 Hz, 4H), 7.28 – 7.22 (m, 4H), 2.99 (s, 4H). ^{1}H NMR spectrum is consistent with data reported in literature.[7]



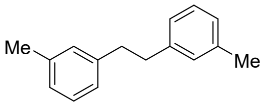
4-(2-[1,1′-Biphenyl]-4-ylethyl)-1,1′-biphenyl (3j)

The compound **3j** was obtained from **1j** (105 mg, 0.4 mmol) as a white soild (65 mg, 54%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.59 (d, *J* = 8.0 Hz, 4H), 7.53 (d, *J* = 7.8 Hz, 4H), 7.43 (t, *J* = 7.6 Hz, 4H), 7.36 – 7.26 (m, 6H), 3.00 (s, 4H). ^{1}H NMR spectrum is consistent with data reported in literature.[7]



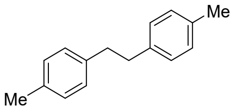
1,2-Bis(2-methylphenyl)ethane (3k)

The compound **3k** was obtained from **1k** (80 mg, 0.4 mmol) as a white soild (62 mg, 74%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.18 – 7.08 (m, 8H), 2.85 (s, 4H), 2.31 (s, 6H). ^{1}H NMR spectrum is consistent with data reported in literature.[7]



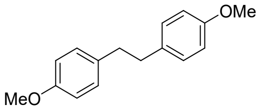
1,2-Bis(3-methylphenyl)ethane (3l)

The compound **3l** was obtained from **1l** (80 mg, 0.4 mmol) as a white soild (63 mg, 75%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.17 (t, *J* = 7.6 Hz, 2H), 7.06 – 6.94 (m, 6H), 2.86 (s, 4H), 2.33 (s, 6H). ^{1}H NMR spectrum is consistent with data reported in literature.[7]



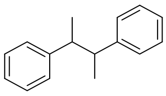
1,2-Bis(4-methylphenyl)ethane (3m)

The compound **3m** was obtained from **1m** (80 mg, 0.4 mmol) as a white soild (20 mg, 47%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.08 (s, 8H), 2.85 (s, 4H), 2.32 (s, 6H). ^{1}H NMR spectrum is consistent with data reported in literature.[8]



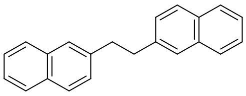
1,2-Bis(4-methoxyphenyl)ethane (3n)

The compound **3n** was obtained from **1n** (86 mg, 0.4 mmol) as a white soild (17 mg, 34%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.11 – 7.05 (m, 4H), 6.85 – 6.79 (m, 4H), 3.79 (s, 6H), 2.83 (s, 4H). ^{1}H NMR spectrum is consistent with data reported in literature.[7]



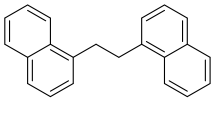
2,3-Diphenylbutane (3p)

The compound **3p** was obtained from **1p** (80 mg, 0.4 mmol) as a white soild (35 mg, 82%). The isolated as a mixture of dl and meso compounds (about 1:1). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36 – 7.26 (m, 2H), 7.26 – 7.13 (m, 5H), 7.12 – 6.96 (m, 3H), 3.00 – 2.88 (m, 1H), 2.86 – 2.73 (m, 1H), 1.30 – 1.24 (m, 3H), 1.08 – 0.96 (m, 3H). ^{1}H NMR spectrum is consistent with data reported in literature.[11]



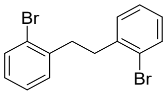
2,2′-(1,2-Ethanediyl)bis[naphthalene] (3s)

The compound **3s** was obtained from **1s** (94 mg, 0.4 mmol) as a white soild (57 mg, 51%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.84 – 7.73 (m, 6H), 7.65 (app s, 2H), 7.48 – 7.39 (m, 4H), 7.36 (dd, J = 8.4, 1.8 Hz, 2H), 3.18 (s, 4H). ^{1}H NMR spectrum is consistent with data reported in literature.[7]



1,1′-(1,2-Ethanediyl)bis[naphthalene] (3t)

The compound **3t** was obtained from **1t** (94 mg, 0.4 mmol) as a white soild (44 mg, 39%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.12 (d, J = 8.2 Hz, 2H), 7.92 – 7.82 (m, 2H), 7.74 (d, J = 8.1 Hz, 2H), 7.56 – 7.45 (m, 4H), 7.39 (t, J = 7.0 Hz, 2H), 7.36 – 7.30 (m, 2H), 3.51 (s, 4H). ^{1}H NMR spectrum is consistent with data reported in literature.[12]



1,2-Bis(2-bromophenyl)ethane (3u)

The compound **3u** was obtained from **1u** (117 mg, 0.4 mmol) as a white soild (49 mg, 71%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.54 (dd, *J* = 8.0, 1.3 Hz, 2H), 7.25 – 7.14 (m, 4H), 7.06 (ddd, *J* = 7.9, 6.8, 2.4 Hz, 2H), 3.03 (s, 4H). ^{1}H NMR spectrum is consistent with data reported in literature.[8]

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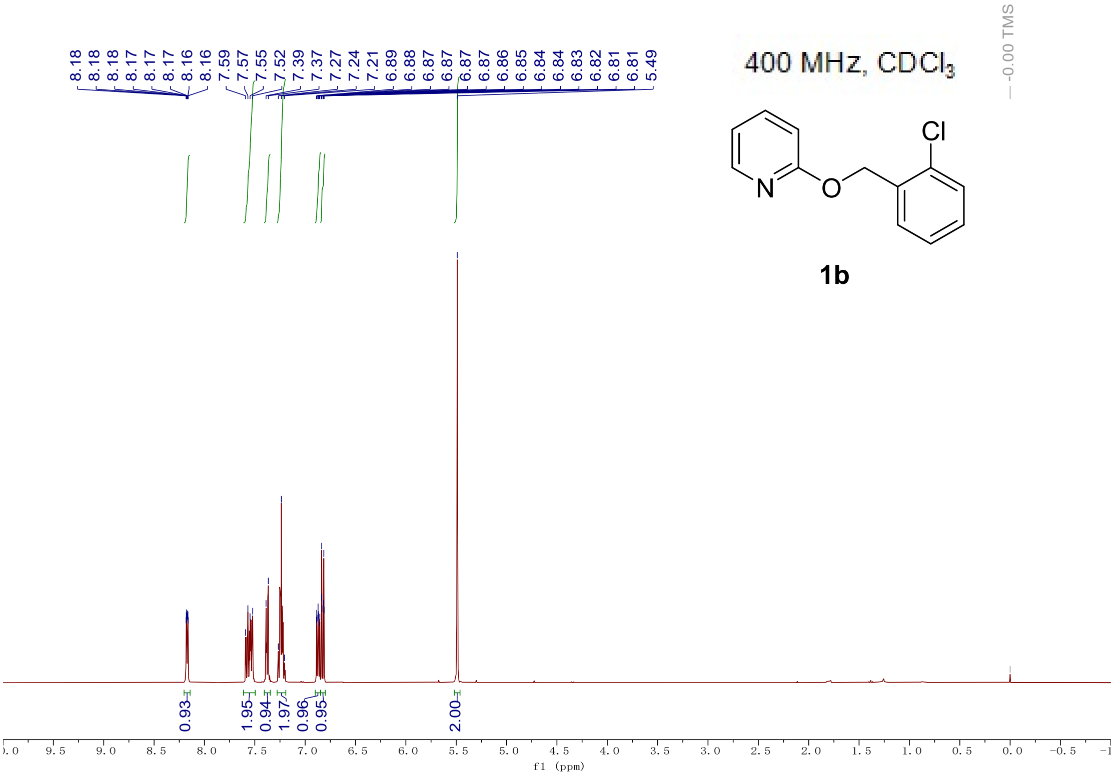
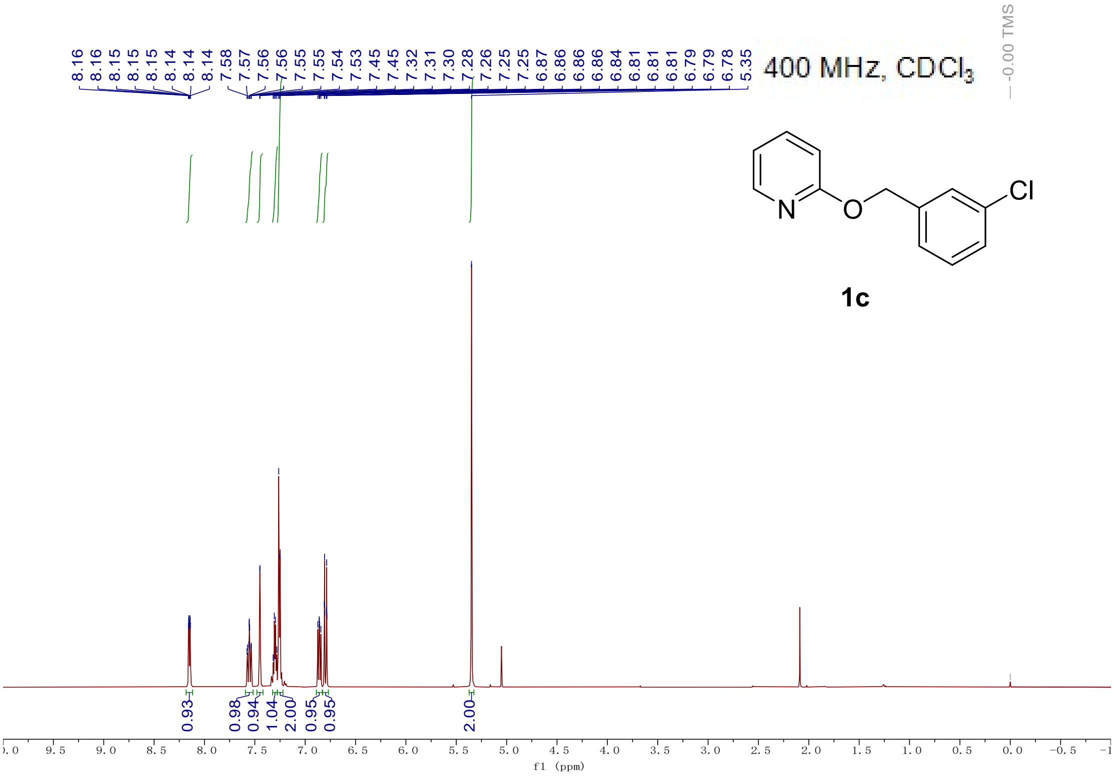
NMR SPECTR



1b



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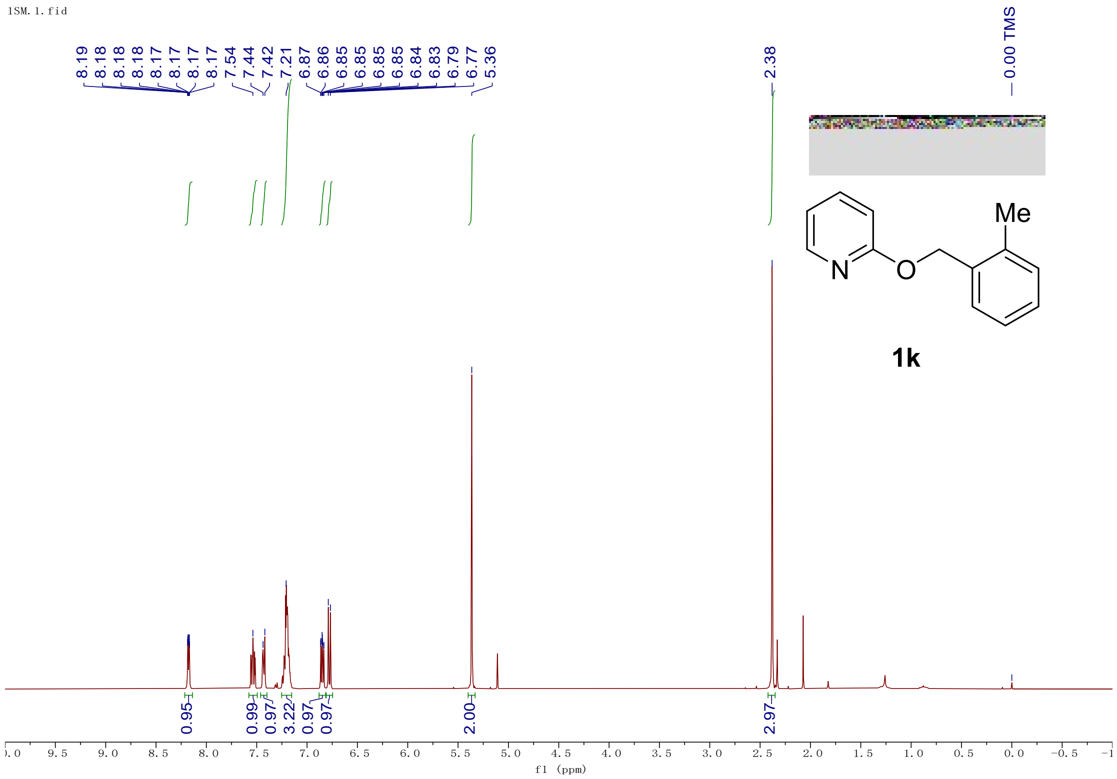
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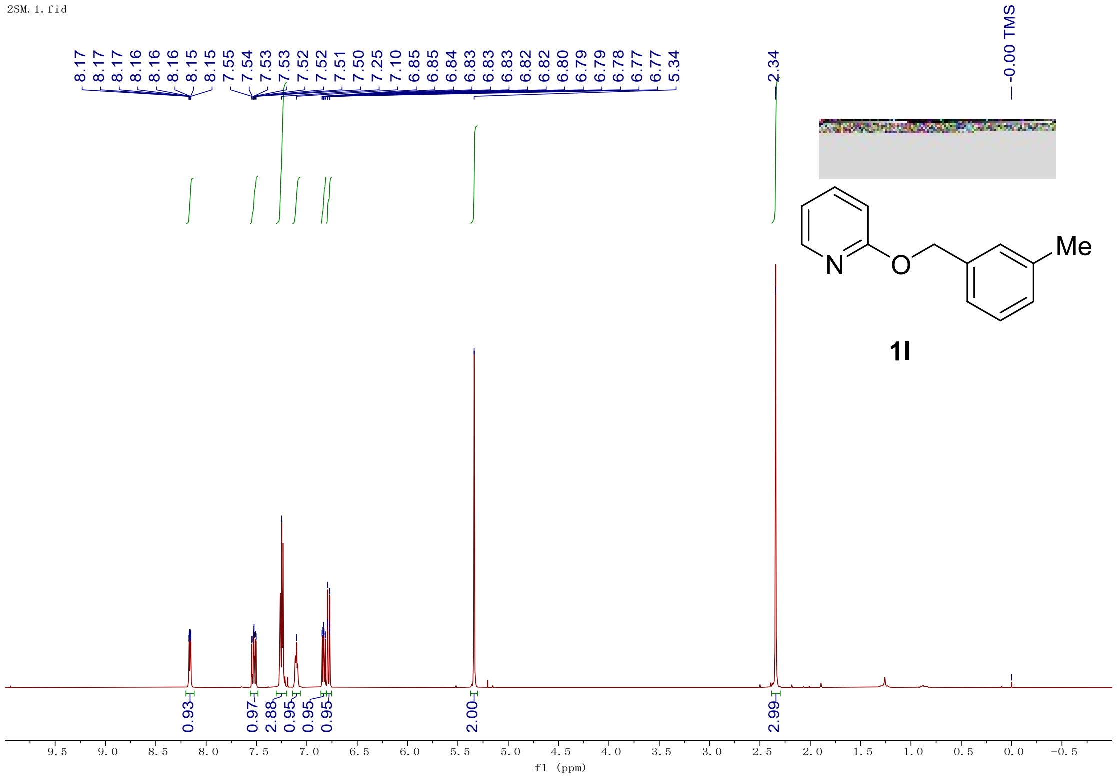
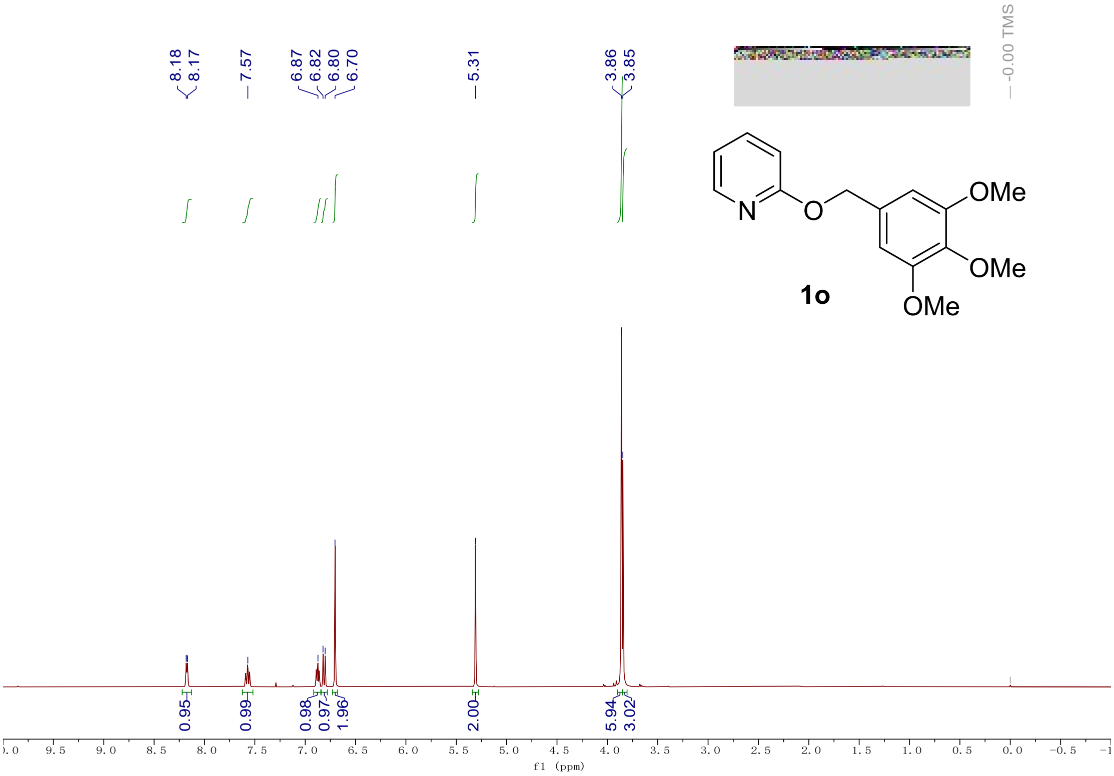
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

1k

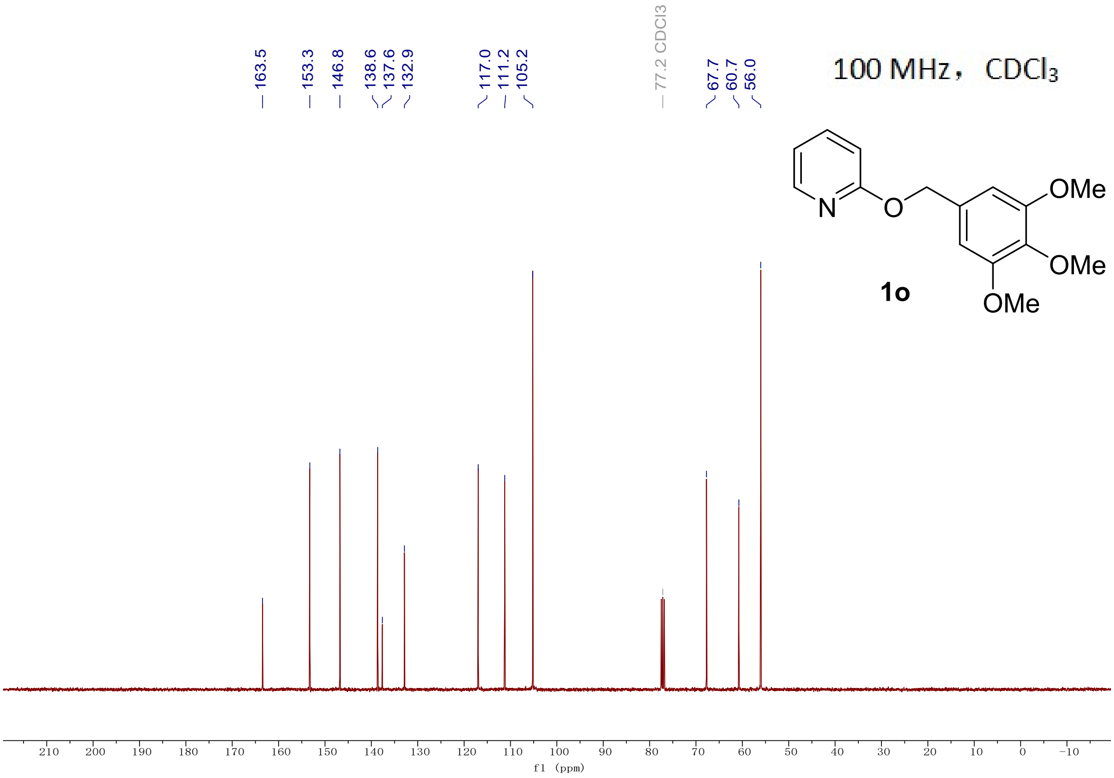

2SM.1.fid
8.17
8.17
8.17
8.16
8.16
8.15
8.15
7.55
7.54
7.53
7.53
7.52
7.52
7.51
7.50
7.25
7.10
6.85
6.85
6.84
6.83
6.83
6.83
6.82
6.82
6.80
6.79
6.78
6.77
5.34
2.34
0.00 TMS
Me
N
O
0.93
0.97
2.88
0.95
0.95
0.95
2.00
2.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

1l



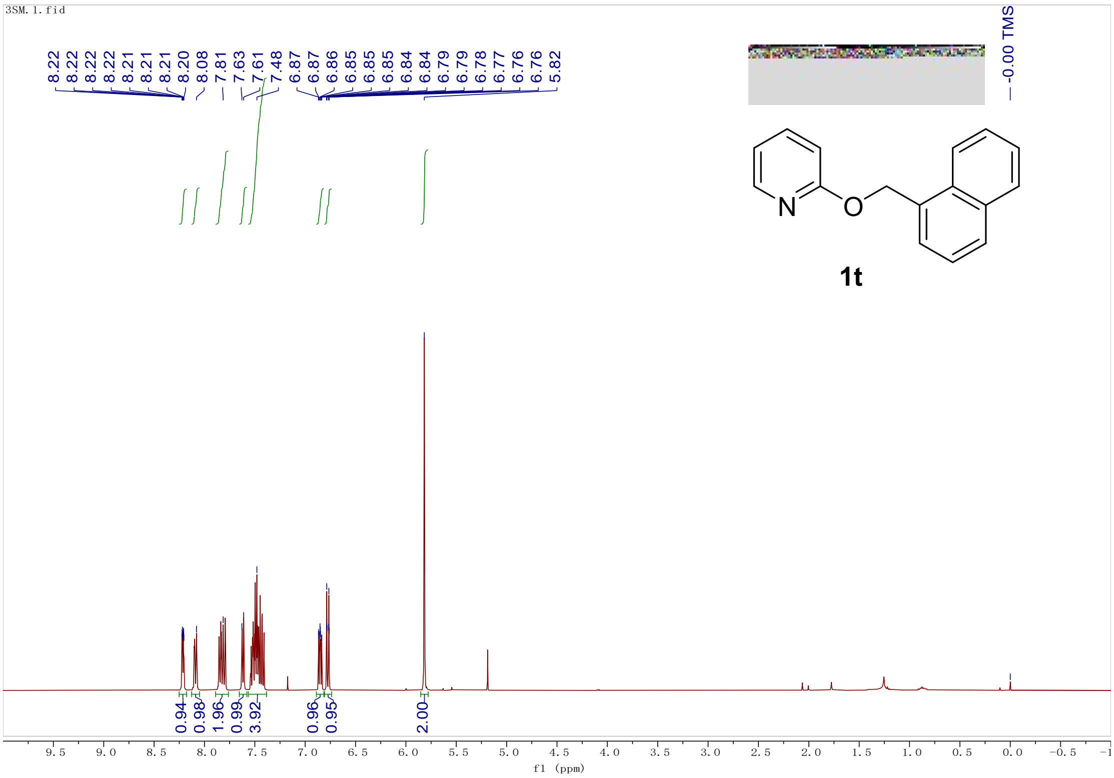
1o

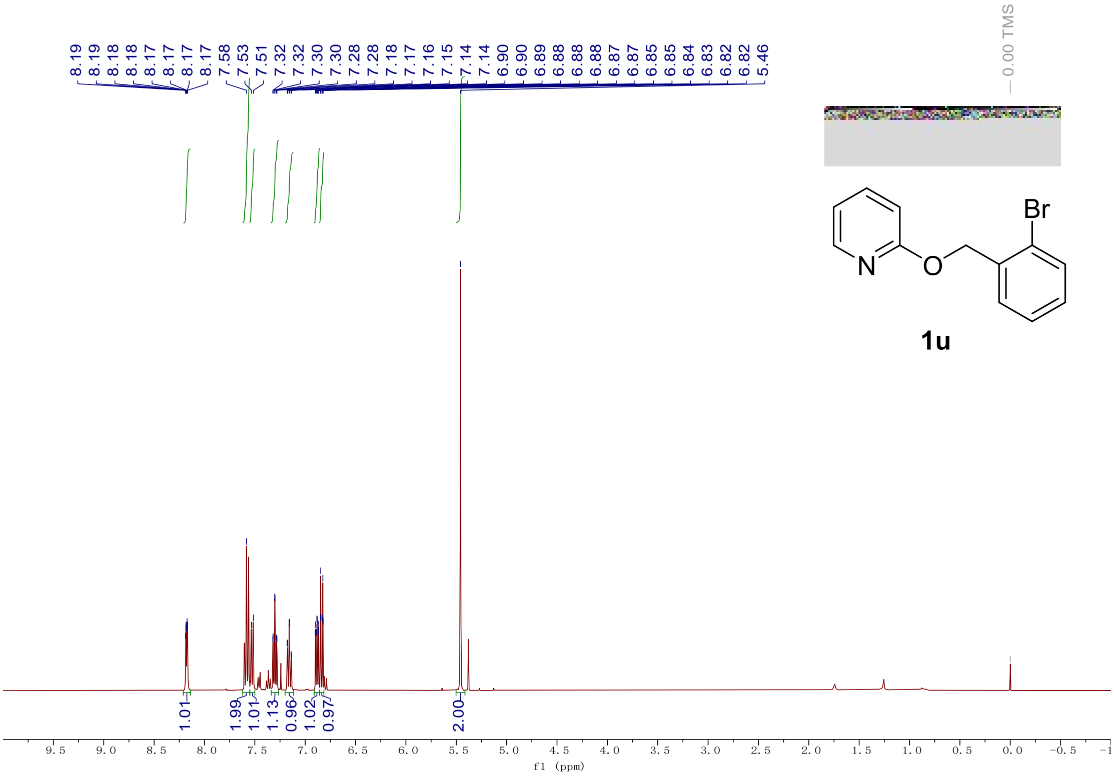
8.18
8.17
7.57
6.87
6.82
6.80
6.70
5.31
3.86
3.85
-0.00 TMS
OMe
OMe
OMe
N
O
0.95
0.99
0.98
0.97
1.96
2.00
5.94
3.02
f1 (ppm)

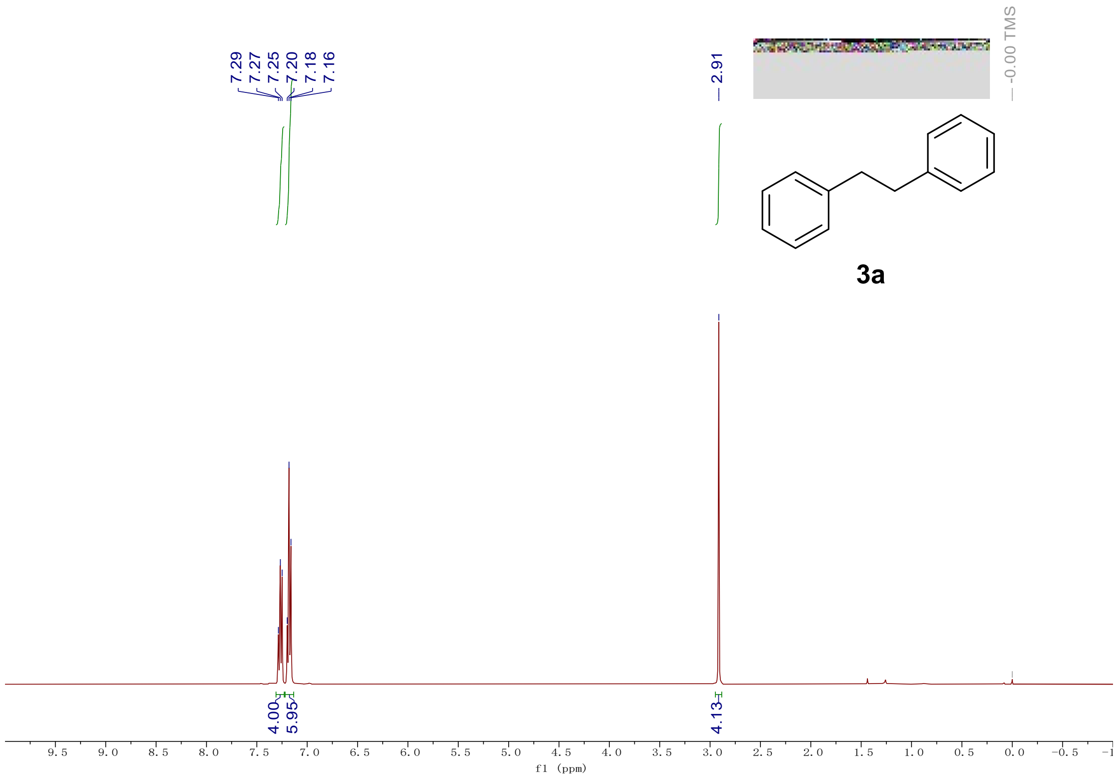


1o

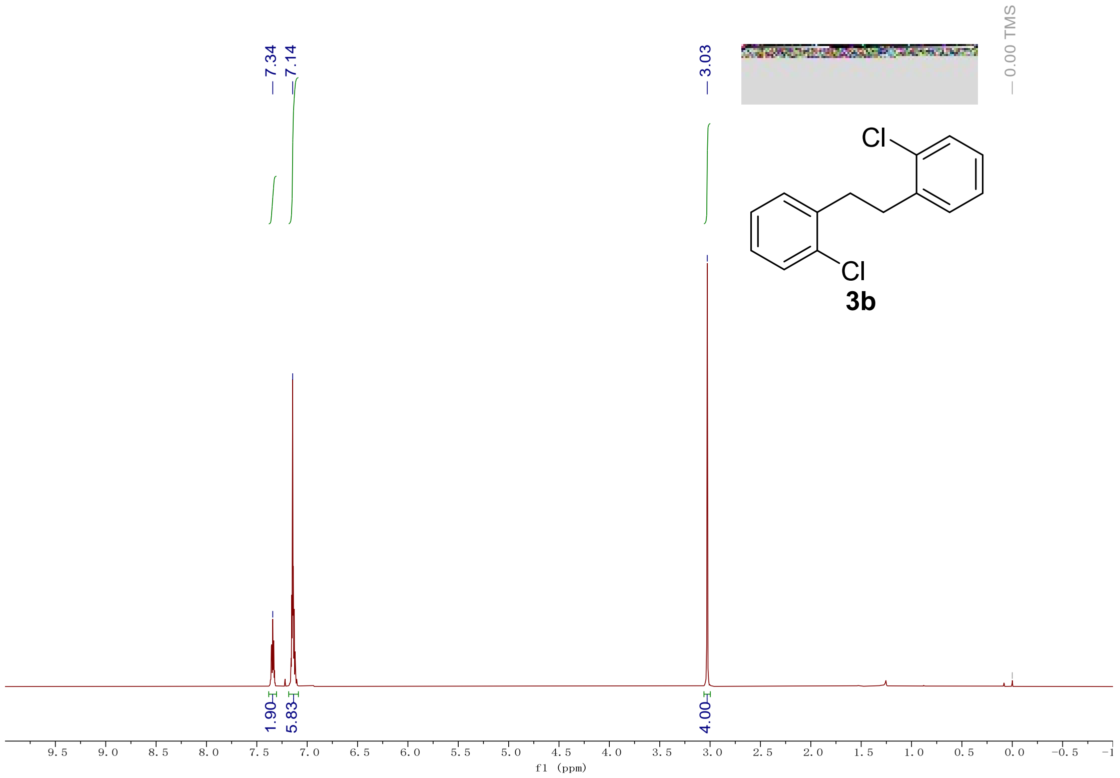
163.5
153.3
146.8
138.6
137.6
132.9
117.0
111.2
105.2
77.2 CDCl3
67.7
60.7
56.0
100 MHz， CDCl3
OMe
OMe
OMe
N
O
f1 (ppm)


3SM.1.fid
8.22
8.22
8.22
8.22
8.21
8.21
8.21
8.20
8.08
7.81
7.63
7.61
7.48
6.87
6.87
6.86
6.85
6.85
6.84
6.84
6.79
6.79
6.78
6.77
6.76
6.76
5.82
-0.00 TMS
N
O
1t
0.94
0.98
1.96
0.99
3.92
0.96
0.95
2.00
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
-1
f1 (ppm)

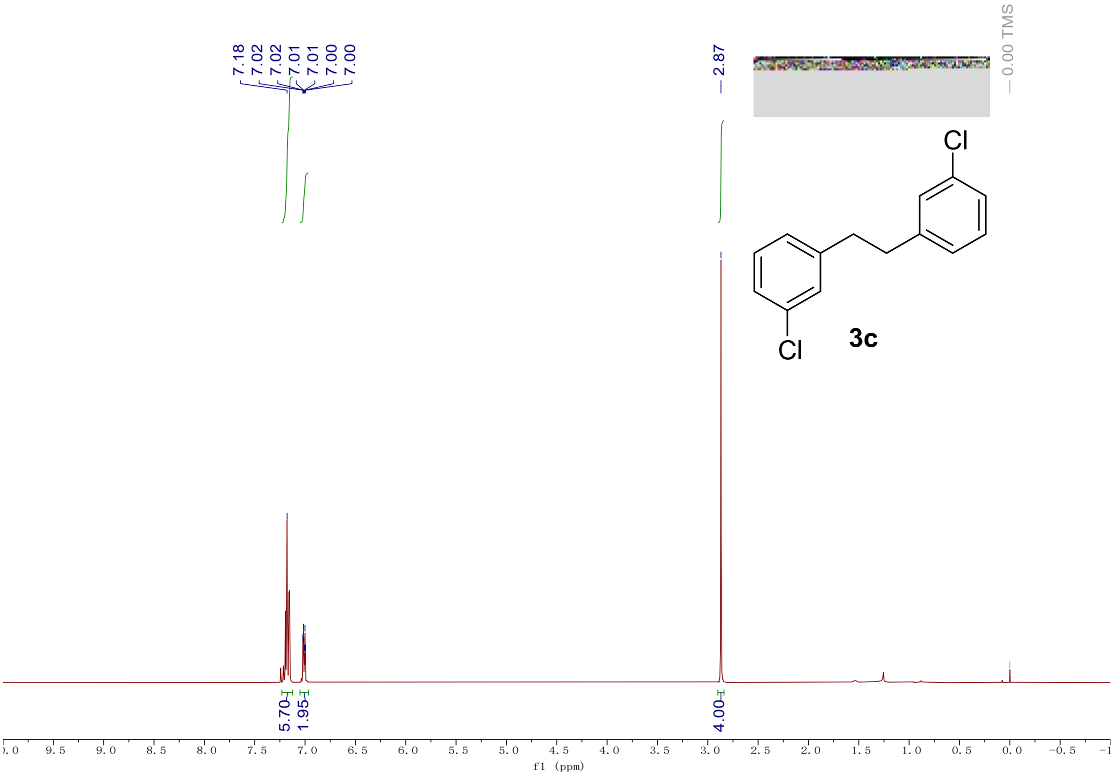

8.19
8.19
8.18
8.18
8.17
8.17
8.17
8.17
7.58
7.53
7.51
7.32
7.32
7.30
7.30
7.28
7.28
7.18
7.17
7.16
7.15
7.14
7.14
6.90
6.89
6.88
6.88
6.88
6.87
6.85
6.85
6.84
6.83
6.82
6.82
5.46
0.00 TMS
Br
N
O
1u
1.01
1.99
1.01
1.13
0.96
1.02
0.97
2.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


7.29
7.27
7.25
7.20
7.18
7.16
2.91
-0.00 TMS
4.00
5.95
4.13
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 -1
f1 (ppm)

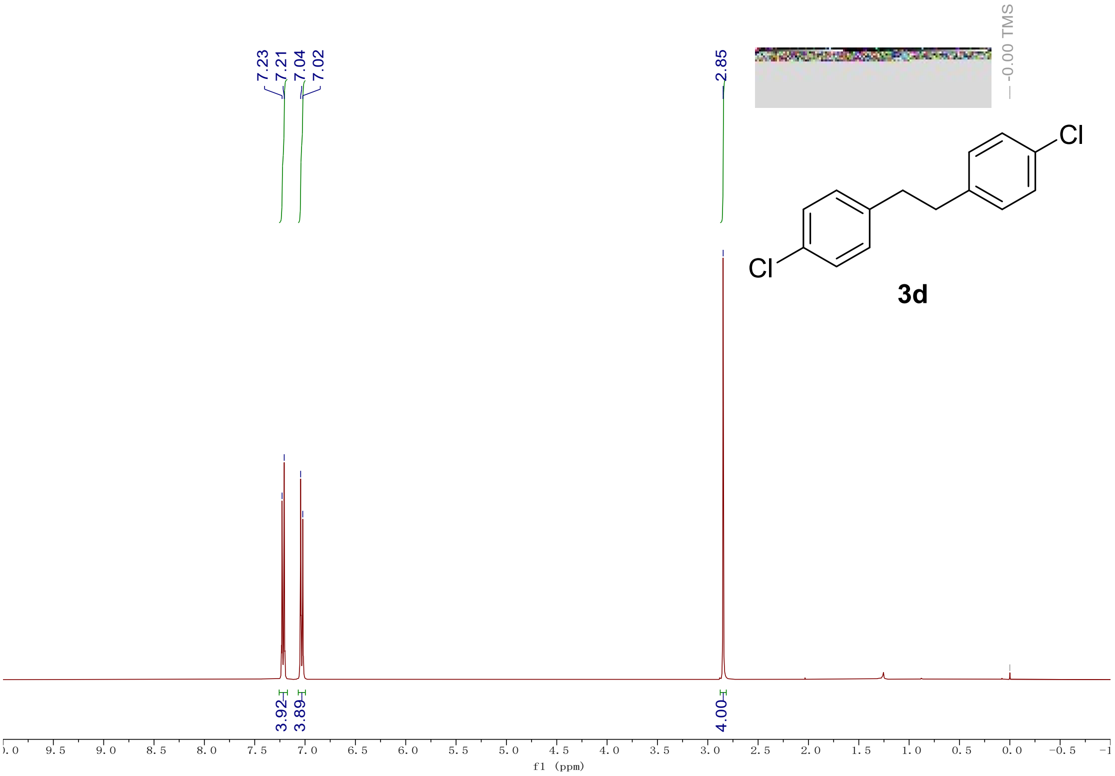
3a


7.34
7.14
3.03
-0.00 TMS
Cl
Cl
1.90
5.83
4.00
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 -1
f1 (ppm)

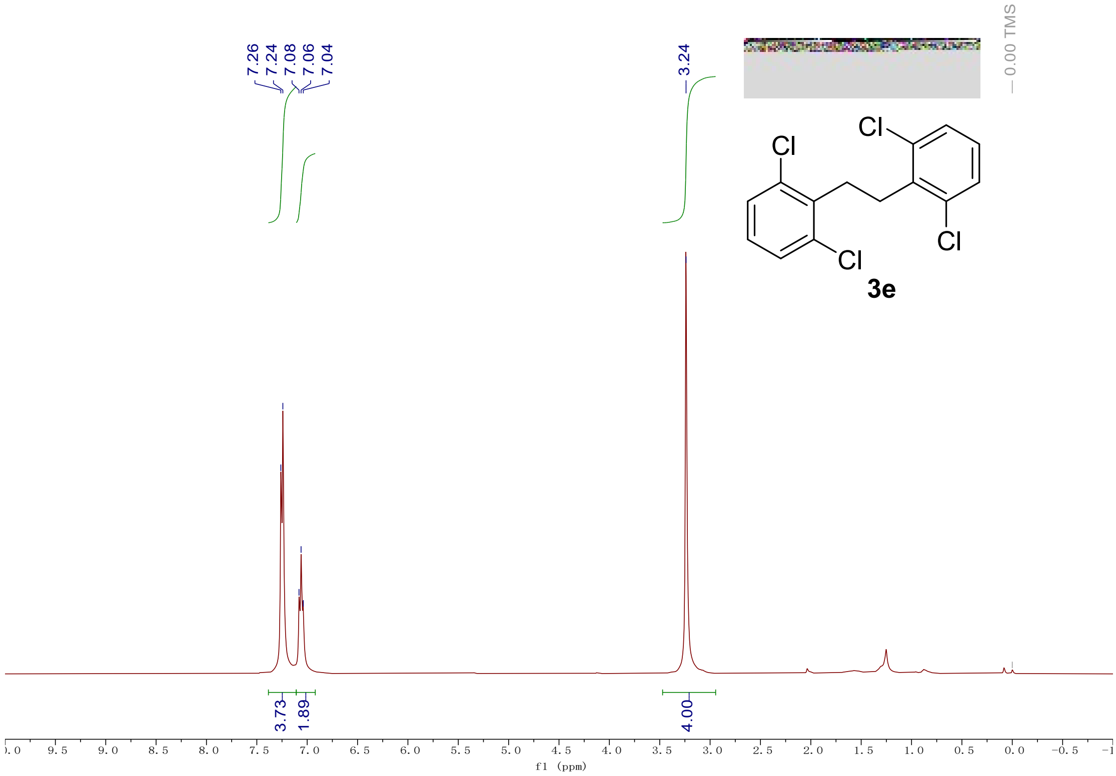
3b


7.18
7.02
7.02
7.01
7.01
7.00
7.00
2.87
0.00 TMS
Cl
Cl
5.70
1.95
4.00
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)

3c

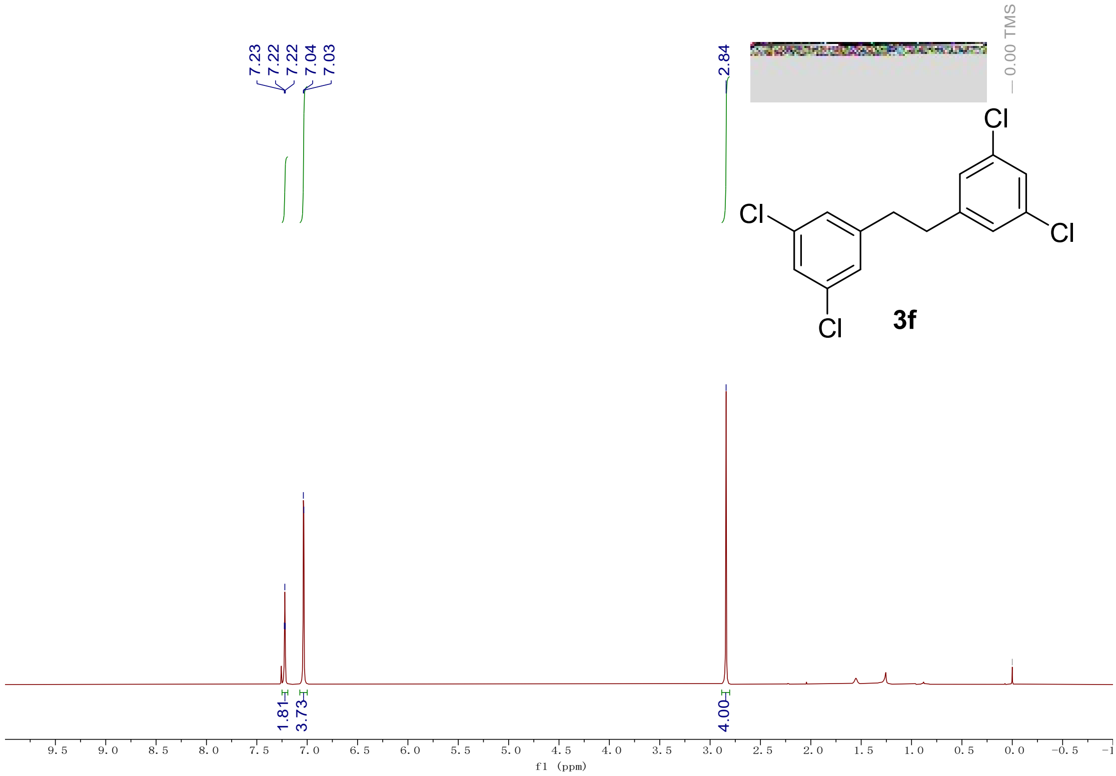

7.23
7.21
7.04
7.02
2.85
-0.00 TMS
Cl
Cl
3.92
3.89
4.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

3d



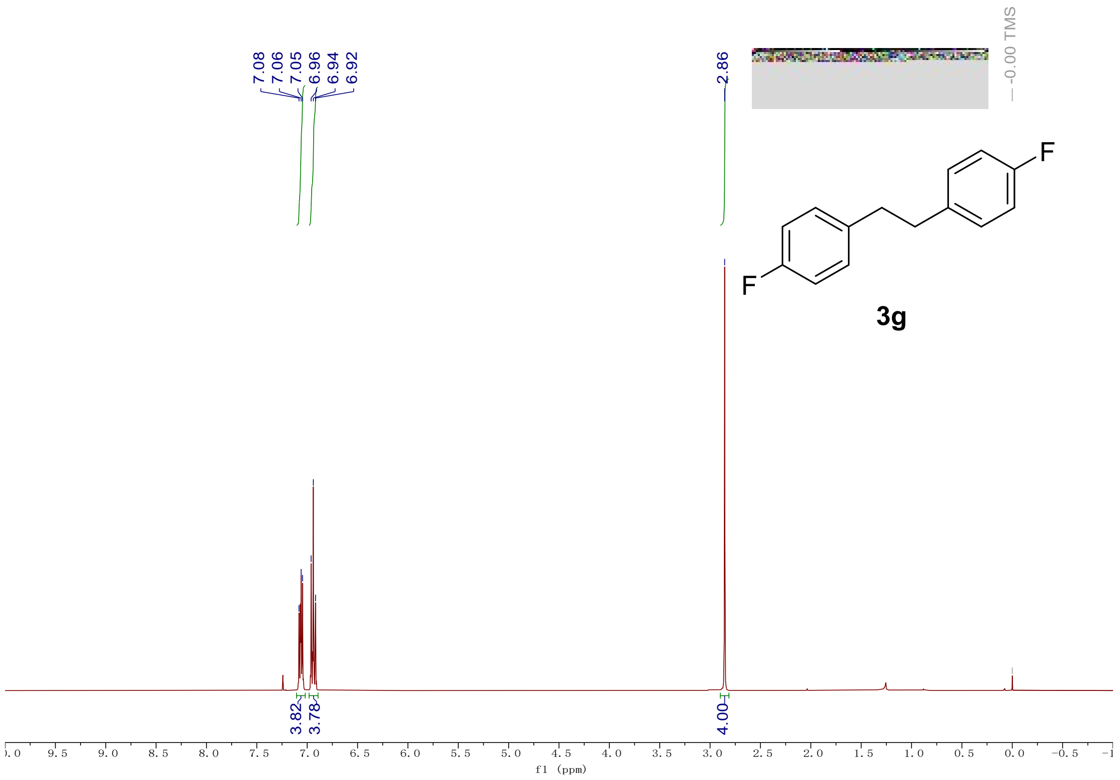
3e

7.26
7.24
7.08
7.06
7.04
3.24
0.00 TMS
Cl
Cl
Cl
Cl
3.73
1.89
4.00
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
-1
f1 (ppm)

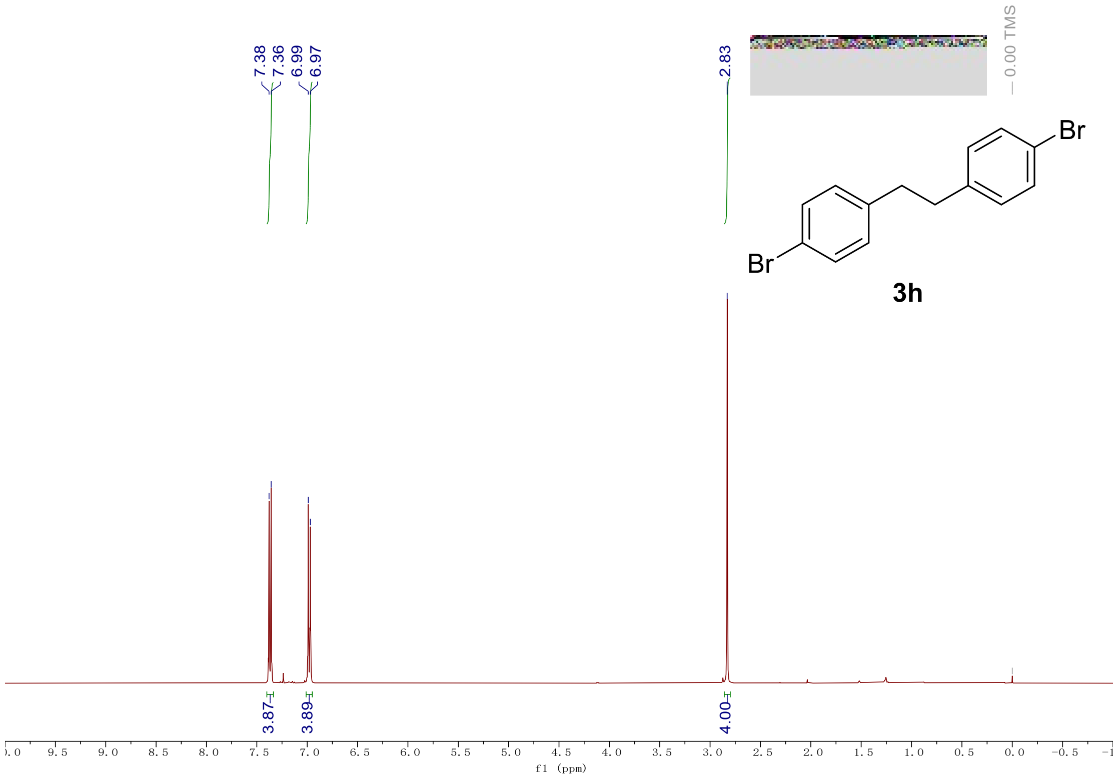


3f

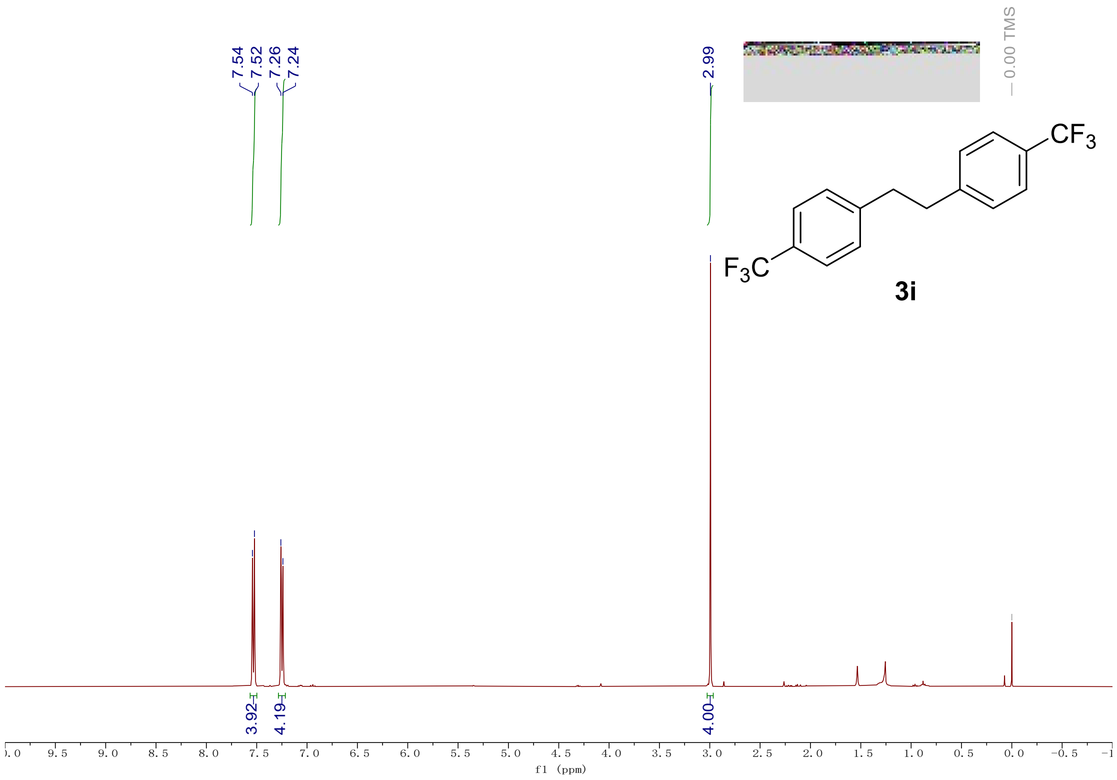
7.23
7.22
7.22
7.04
7.03
2.84
0.00 TMS
Cl
Cl
Cl
Cl
1.81
3.73
4.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


7.08
7.06
7.05
6.96
6.94
6.92
2.86
—0.00 TMS
F
F
3.82
3.78
4.00
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 −1
f1 (ppm)

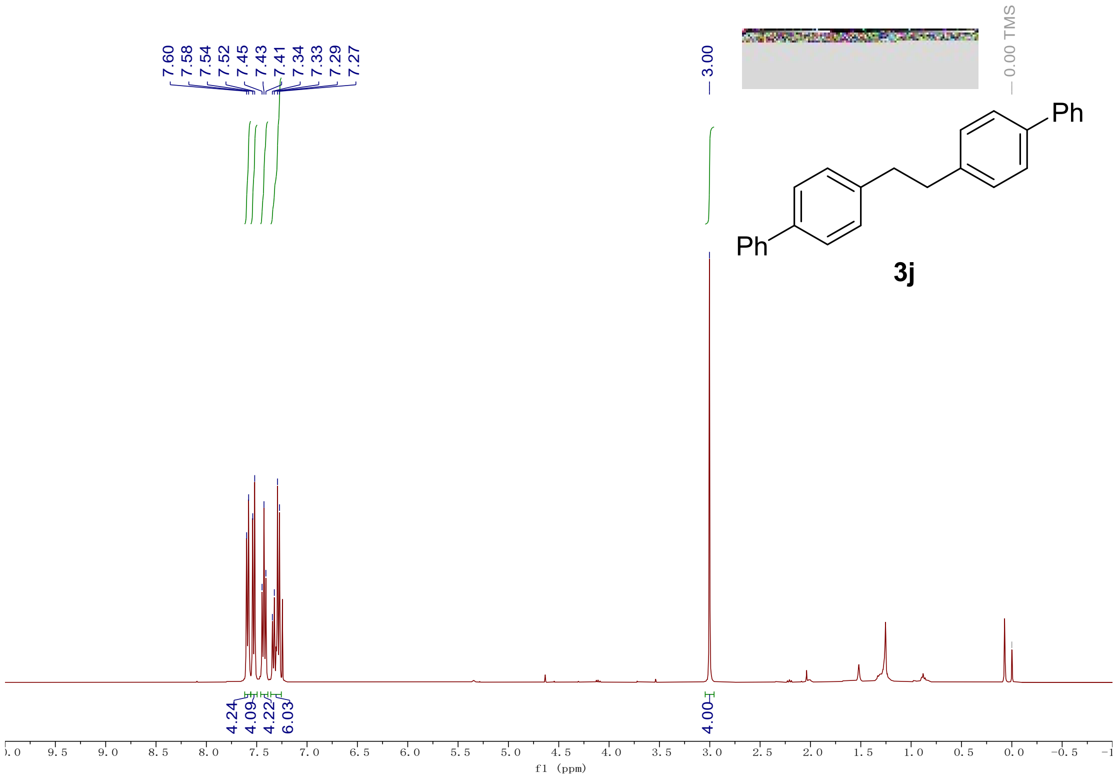
3g


7.38
7.36
6.99
6.97
2.83
—0.00 TMS
Br
Br
3.87
3.89
4.00
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 −1
f1 (ppm)

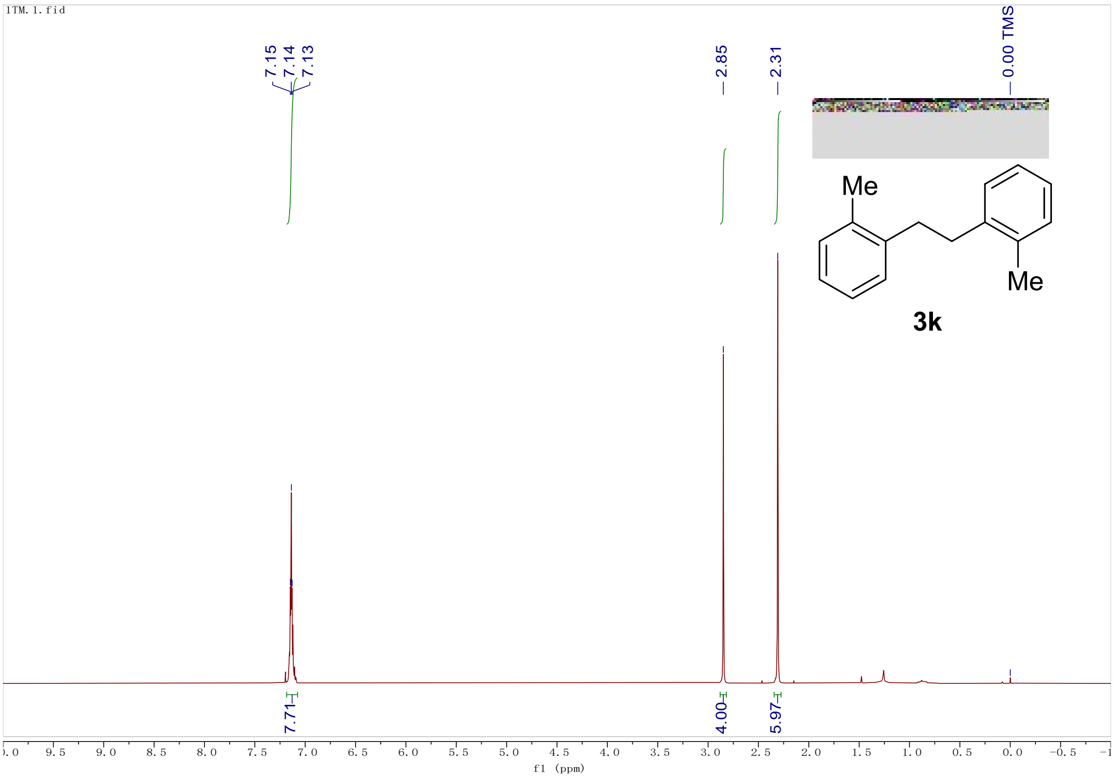
3h

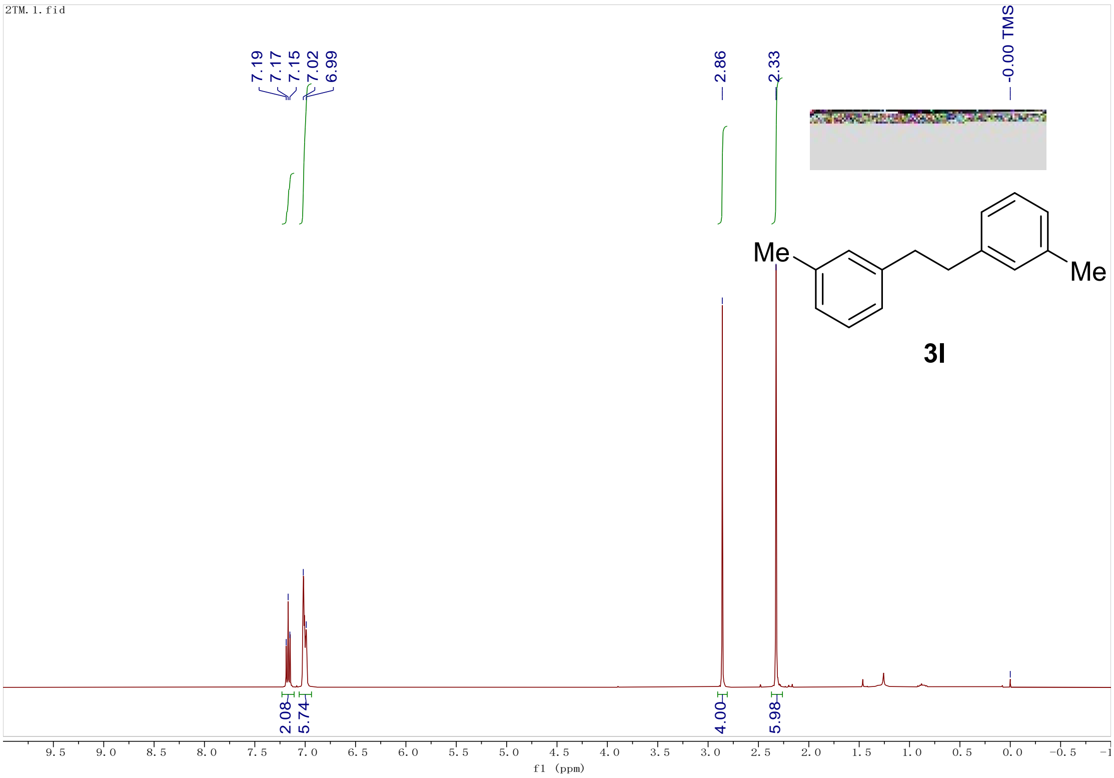


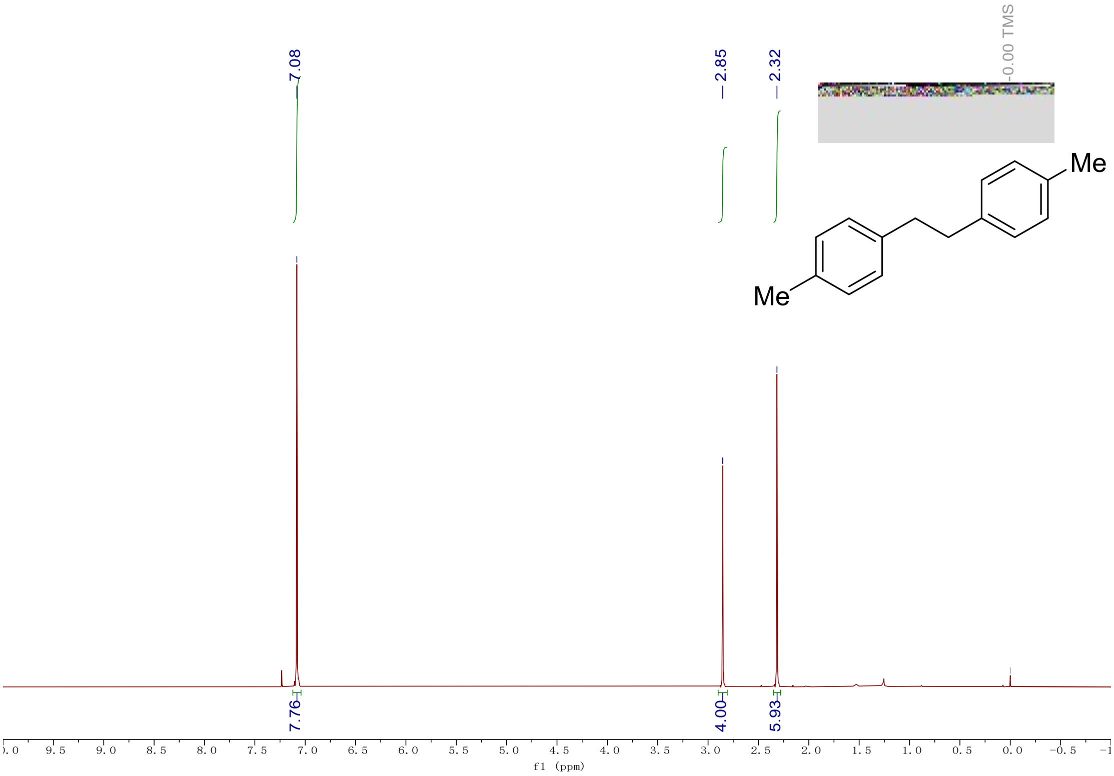
[redacted]

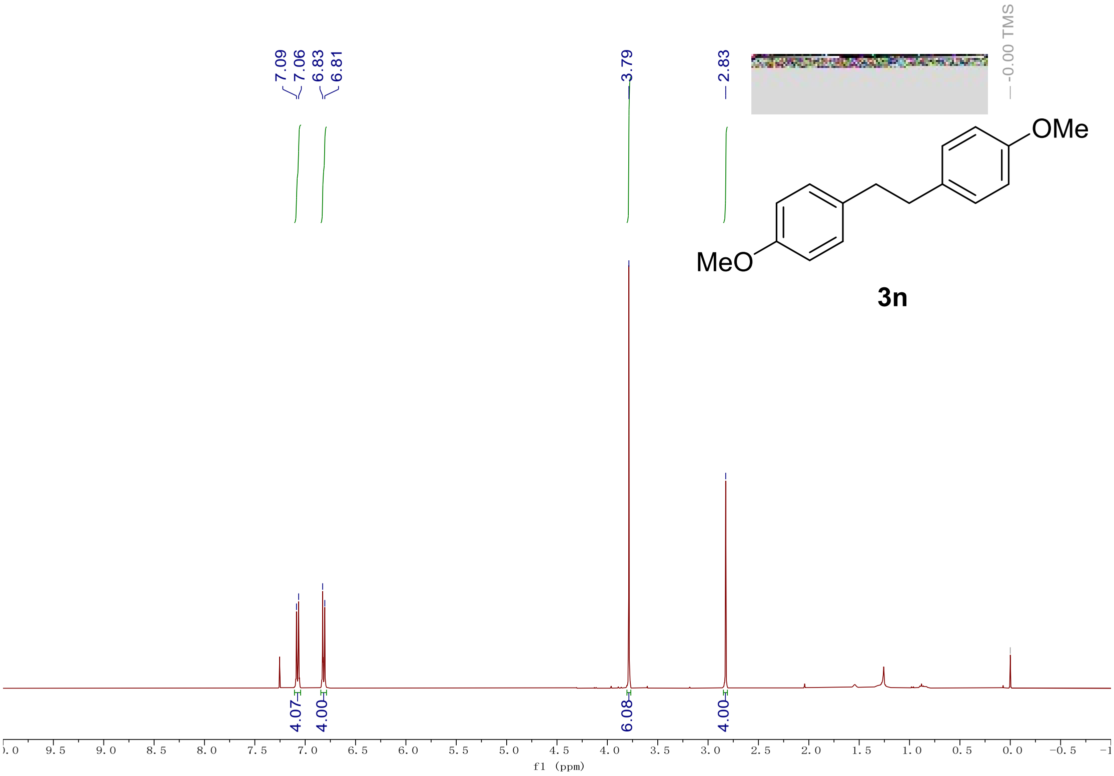


[redacted]

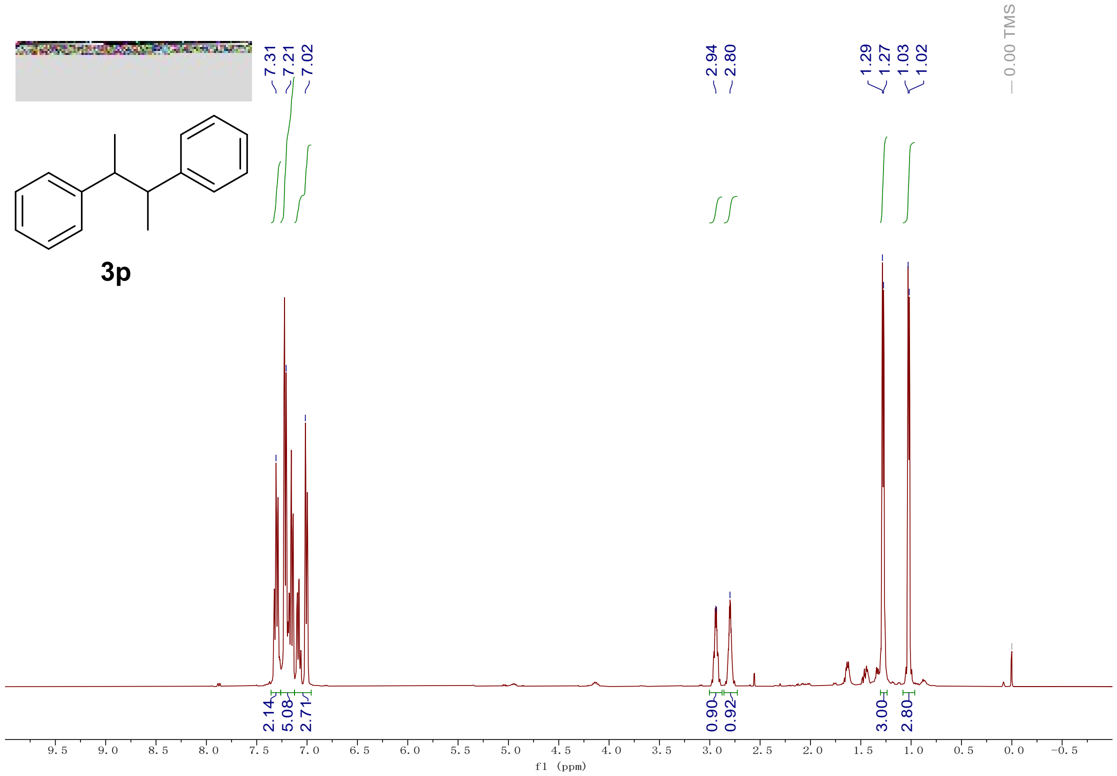

1TM.1.fid
7.15
7.14
7.13
2.85
2.31
0.00 TMS
Me
Me
3k
7.71
4.00
5.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)


2TM.1.fid
7.19
7.17
7.15
7.02
6.99
2.86
2.33
-0.00 TMS
Me
Me
3l
2.08
5.74
4.00
5.98
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 −1
f1 (ppm)


7.08
2.85
2.32
0.00 TMS
Me
Me
7.76
4.00
5.93
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 -1
f1 (ppm)

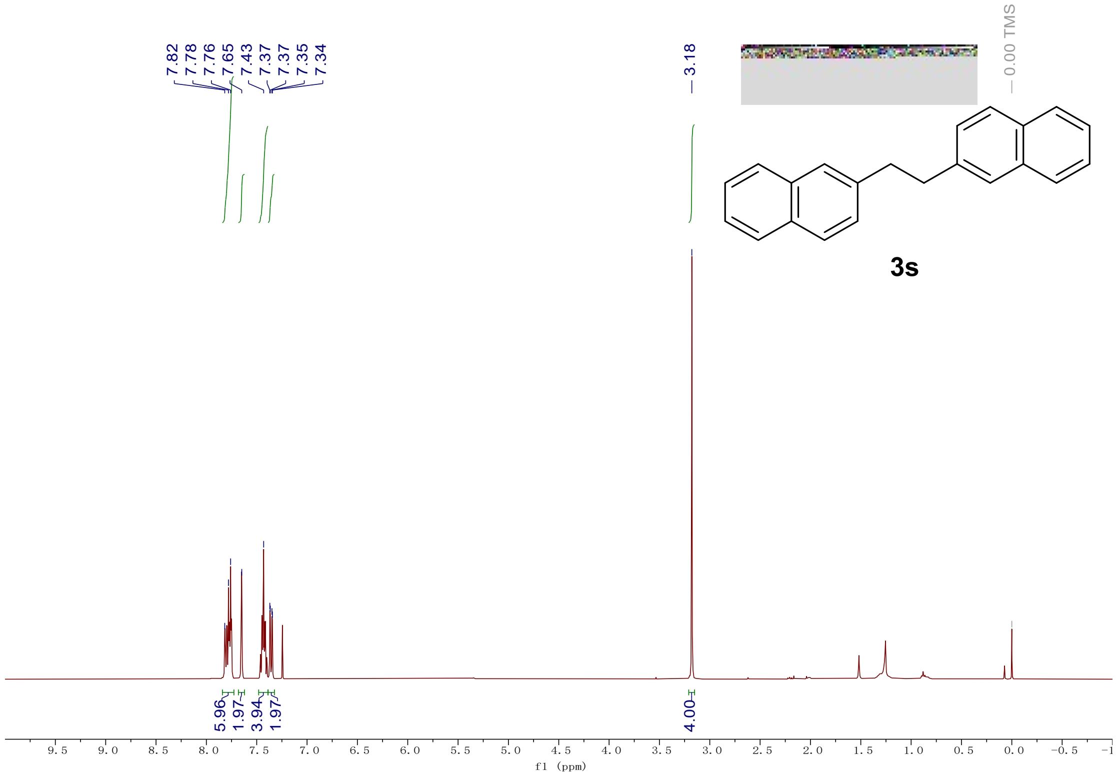

7.09
7.06
6.83
6.81
3.79
2.83
0.00 TMS
OMe
MeO
4.07
4.00
6.08
4.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

3n



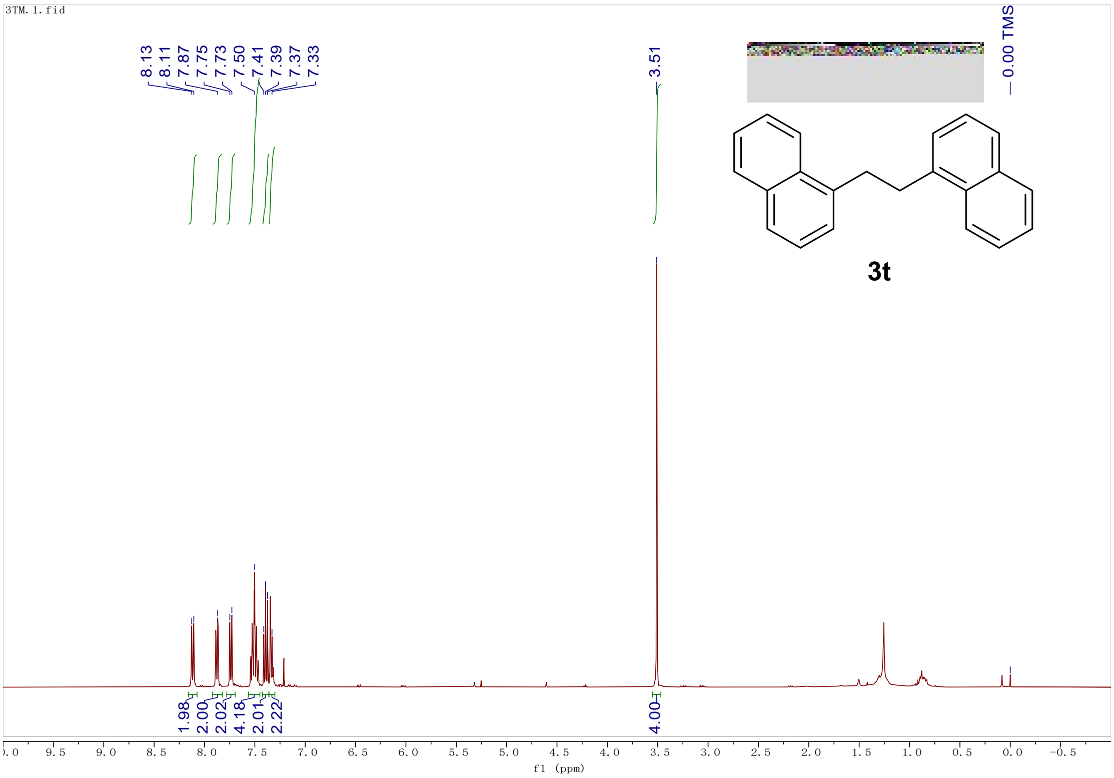
7.31
7.21
7.02
2.94
2.80
1.29
1.27
1.03
1.02
0.00 TMS
2.14
5.08
2.71
0.90
0.92
3.00
2.80
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

3p

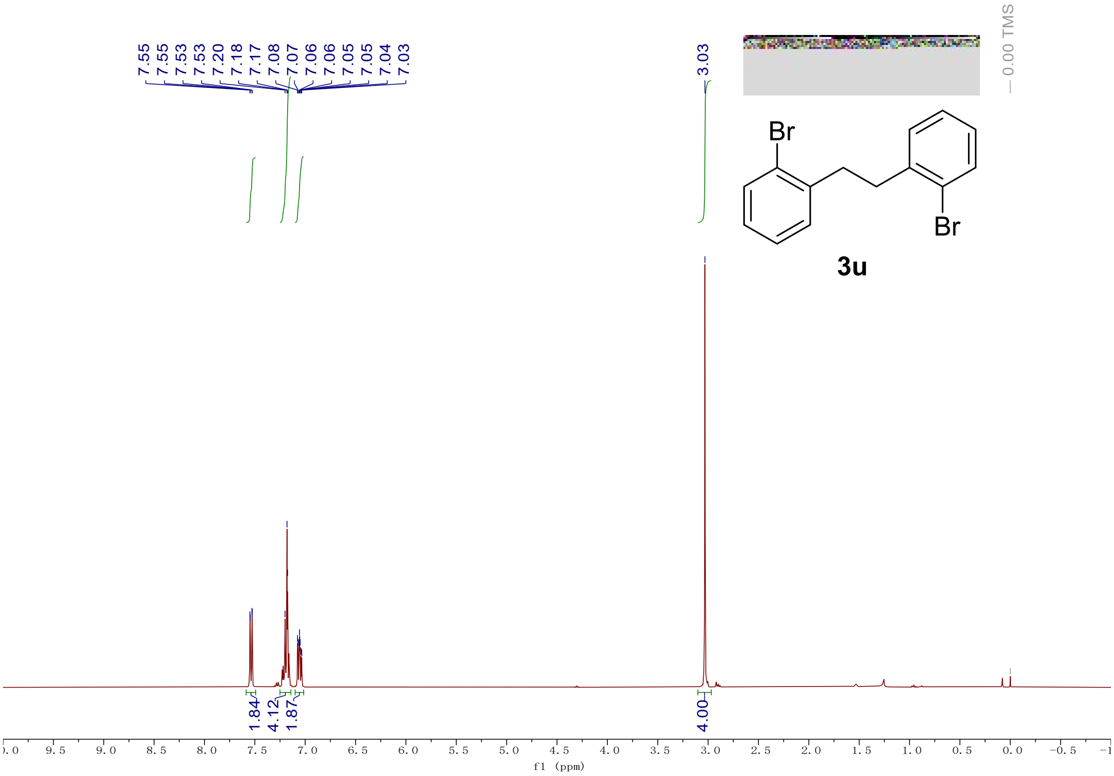


7.82
7.78
7.76
7.65
7.43
7.37
7.37
7.35
7.34
3.18
0.00 TMS
5.96
1.97
3.94
1.97
4.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm)

3s


3TM.1.fid
8.13
8.11
7.87
7.75
7.73
7.50
7.41
7.39
7.37
7.33
3.51
0.00 TMS
1.98
2.00
2.02
4.18
2.01
2.22
4.00
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)

3t


7.55
7.55
7.53
7.20
7.18
7.17
7.08
7.07
7.06
7.05
7.05
7.04
7.03
3.03
0.00 TMS
Br
Br
1.84
4.12
1.87
4.00
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
-1
f1 (ppm)

3u