Electronic Supporting Information

Ruthenium(II) / Acetate Catalyzed Intermolecular Dehydrogenative *Ortho* C-H Silylation of 2-Aryl *N*-Containing Heterocycles

Shun liu,[a] Qiao Lin,[a] Chunshu Liao,[a] Jing Chen,[a] Kun Zhang,[a] Qiang Liu,[ab] and Bin Li*[a]

[a]*School of Biotechnology and Health Sciences, Wuyi University, 22 Dongchengcun, Jiangmen 529020, P. R. China*

[b]*Center of Basic Molecular Science (CBMS), Department of Chemistry, Tsinghua University, Beijing, China*

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General remarks

All reagents were obtained from commercial sources and used as received. Technical grade petroleum ether (40-60°C bp.) and ethyl acetate were used for chromatography column.

^{1}H NMR spectra were recorded in $CDCl_3$ at ambient temperature on Bruker AVANCE I 300 or 500 spectrometers at 300.1 or 500.1 MHz, using the solvent as internal standard (7.26 ppm). ^{13}C NMR spectra were obtained at 75 MHz and referenced to the internal solvent signals (central peak is 77.2 ppm). Chemical shift (δ) and coupling constants (*J*) are given in ppm and in Hz, respectively. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, and br. for broad.

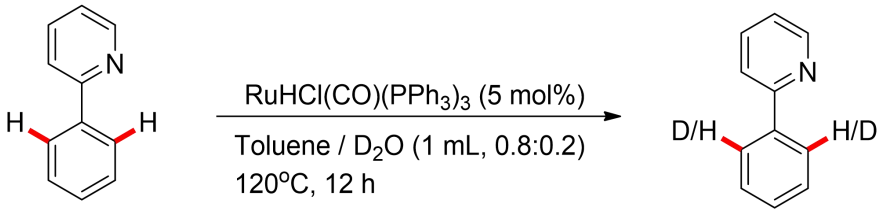
GC analyses were performed with GC-14C (Shimadzu) equipped with a 30-m capillary column (Supelco, SPB-5, fused silica capillary column, 30 M*0.25 mm*0.25 mm film thickness), was used with N_2/air as vector gas. GCMS were measured by GCMS-7890A-5975C (Agilent) with GC-7890A equipped with a 30-m capillary column (HP-5ms, fused silica capillary column, 30 M*0.25 mm*0.25 mm film thickness), was used with helium as vector gas. HRMS were measured by MAT 95XP (Termol) (LCMS-IT-TOF).

The following GC conditions were used: initial temperature 80 °C, for 2 minutes, then rate 20 °C/min. until 260 °C and 260°C for 20 minutes.

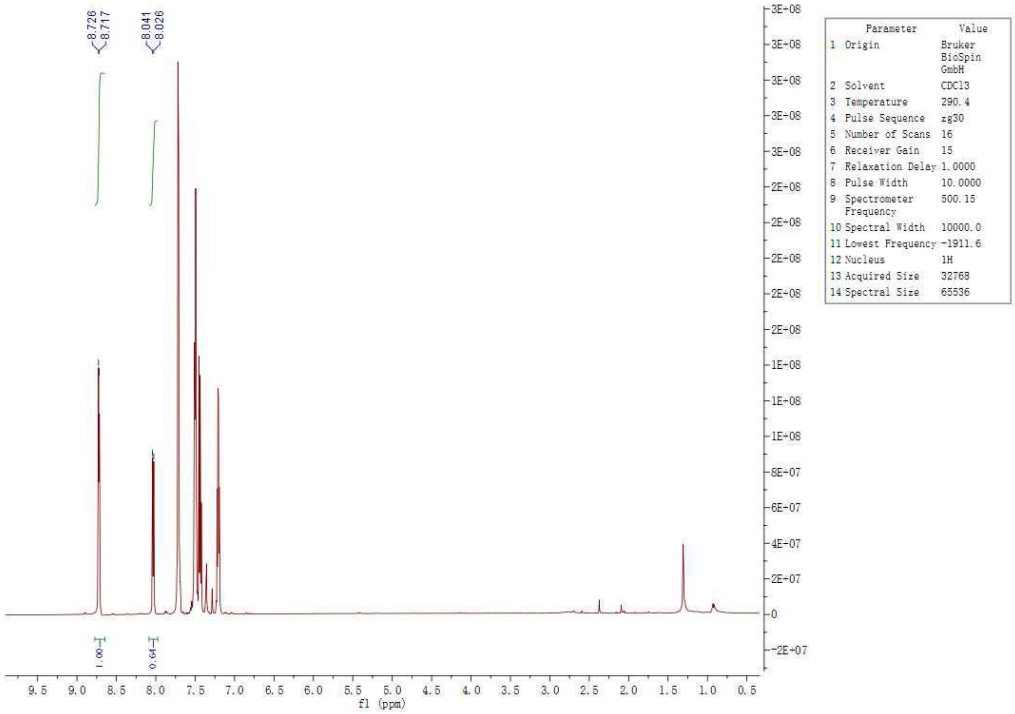
General procedure for$Ru(PPh_3)_3(CO)HCl$ catalyzed selective C-H mono-silylation of pyridine derivatives with hydrosilane

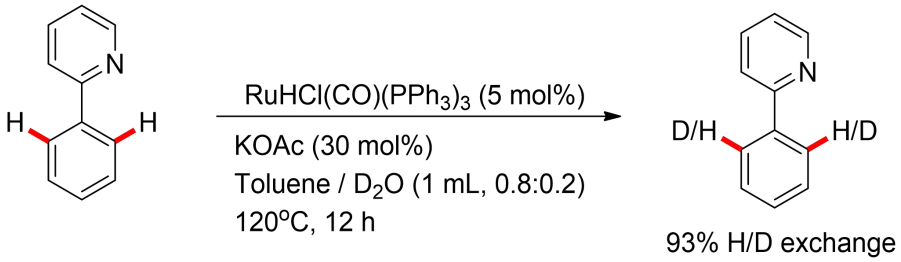
$Ru(PPh_3)_3(CO)HCl$ (0.025 mmol, 23.8 mg), pyridines (0.5 mmol), hydrosilane (2.0 mmol), KOAc (0.15 mmol, 15 mg), norbornylene (2.0 mmol, 197 μL) and toluene (1 mL) were introduced in a tube under N_2, equipped with magnetic stirring bar and was stirred at 120 ^{o}C. After 20 h, the conversion of the reaction was analyzed by gas chromatography. The solvent was then evaporated under vacuum and the desired product was purified by using a silica gel chromatography column and a mixture of petrol ether/ethyl acetate as eluent.

H/D scrambling experiments



68% H/D exchange





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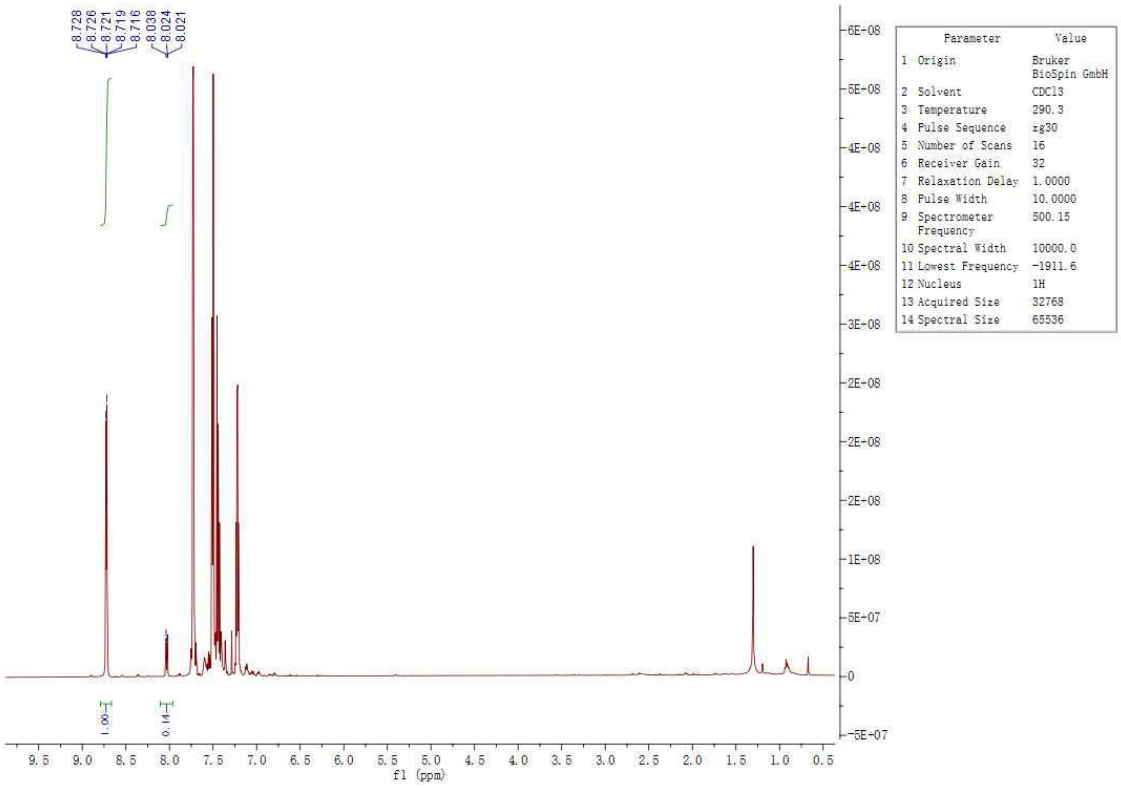
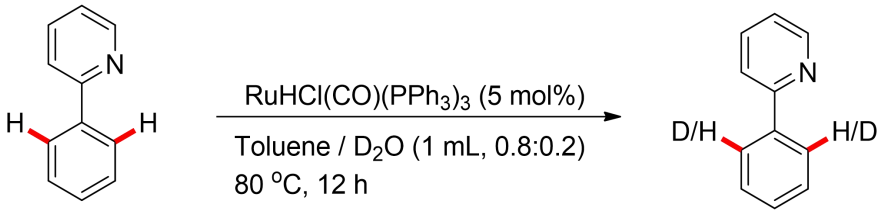
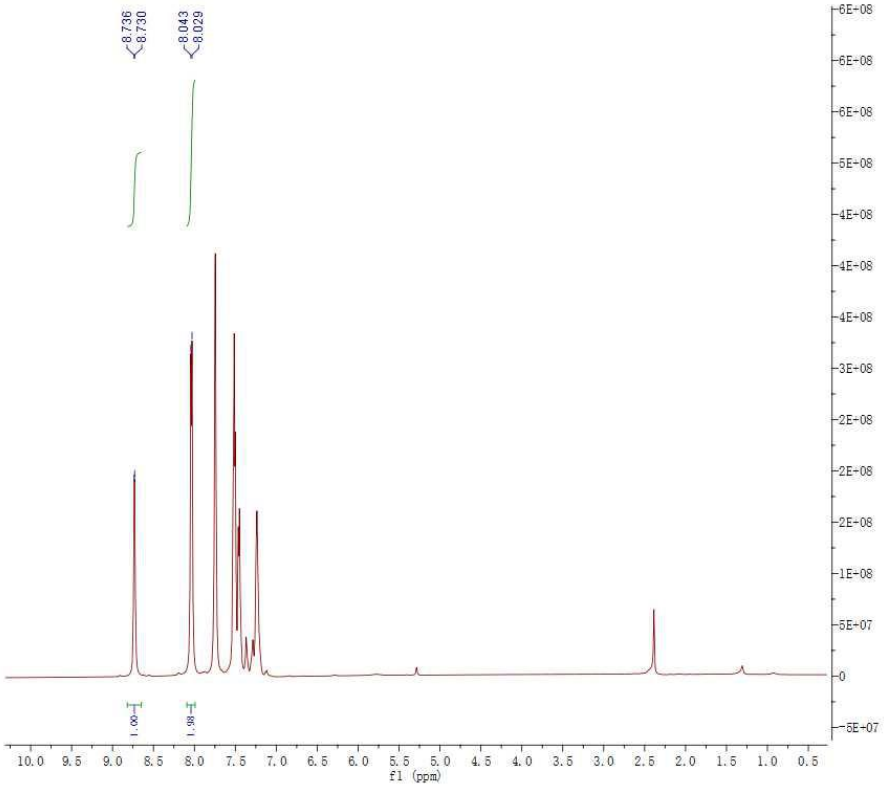
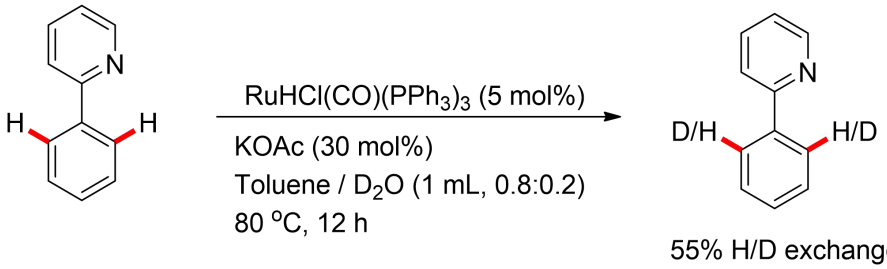




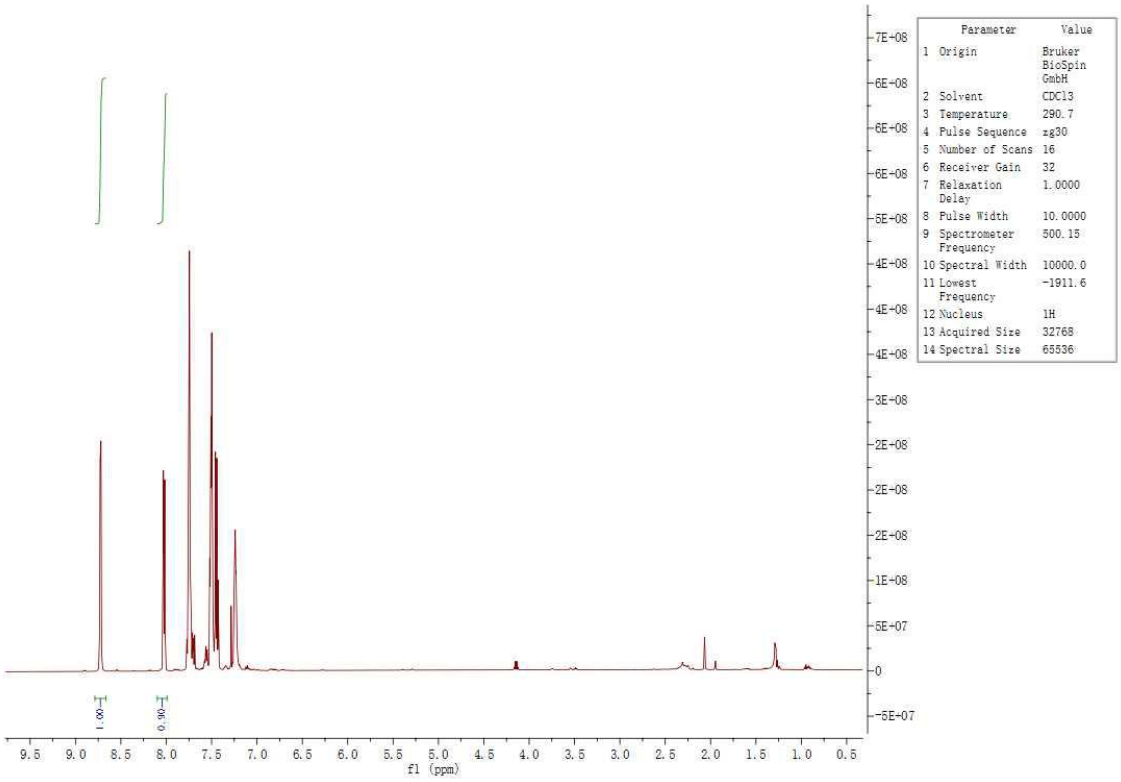
1% H/D exchange



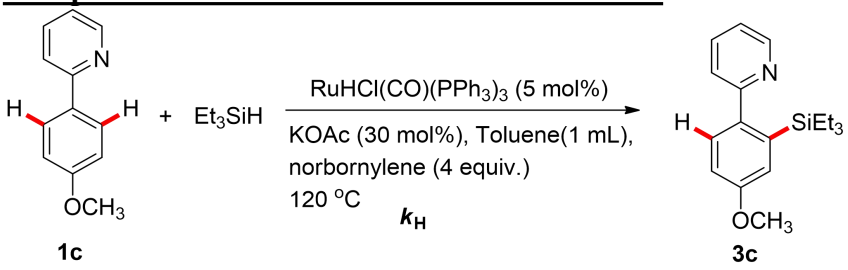
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Solvent	CDCl3
3	Temperature	290.6
4	Pulse Sequence	zg30
5	Number of Scans	16
6	Receiver Gain	32
7	Relaxation Delay	1.0000
8	Pulse Width	10.0000
9	Spectrometer Frequency	500.15
10	Spectral Width	10000.0
11	Lowest Frequency	-1911.6
12	Nucleus	1H
13	Acquired Size	32768
14	Spectral Size	65536



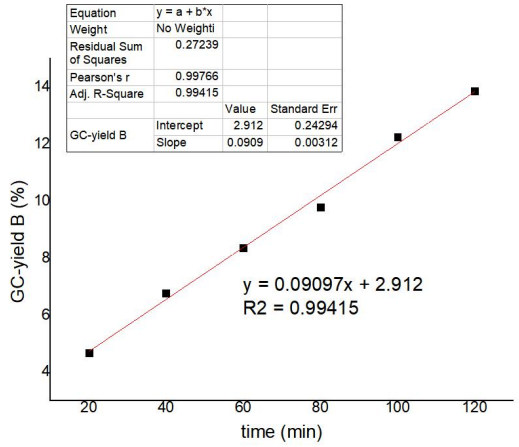
55% H/D exchange

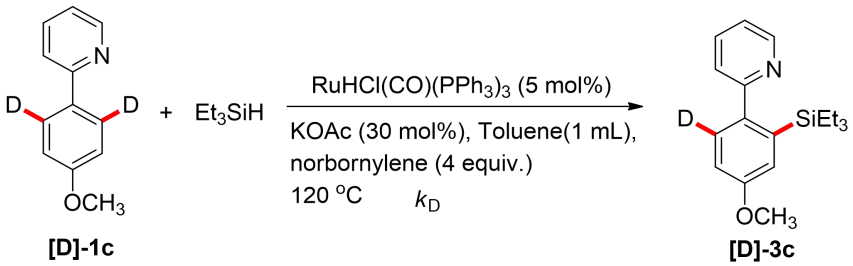


Isotope Effect of Deuterium-Labeled Substrates.

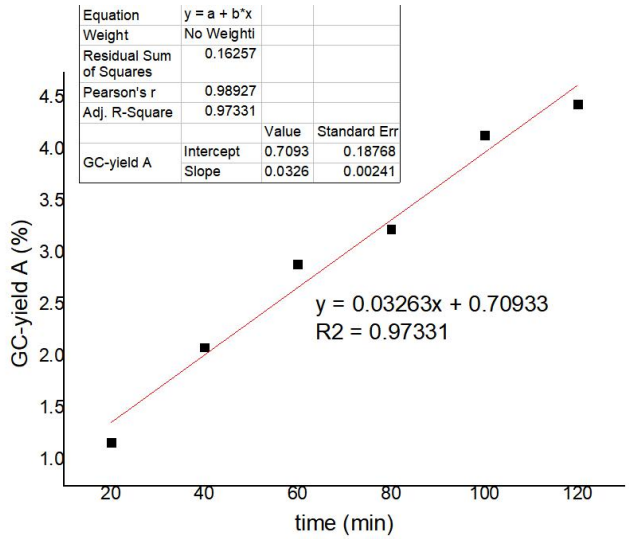


1c **3c**



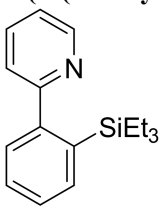


[D]-1c **[D]-3c**



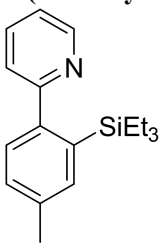
Characterization data of substrates

2-(2-(triethylsilyl)phenyl)pyridine[1] (3a)



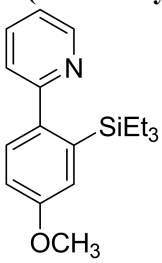
Light yellow oil, yield = 85%, 114 mg, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.69-8.67 (m, 1H), 7.78-7.69 (m, 2H), 7.50-7.41 (m, 4H), 7.31-7.27 (m, 1H), 0.88 (t, 9H, J = 8.1 Hz), 0.65-0.57 (m, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 162.0, 148.6, 148.0, 136.5, 136.2, 136.0, 129.2, 128.7, 127.3, 123.4, 122.1, 7.8, 4.6. HRMS (EI): *m/z* calcd for $C_{17}H_{24}NSi$ $[M+H]^+$ 270.1678, found 270.1650.

2-(4-methyl-2-(triethylsilyl)phenyl)pyridine[1] (3b)



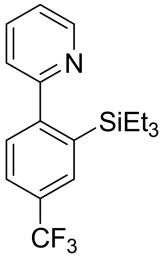
Light yellow oil, yield = 84%, 119 mg, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.67-8.66 (m, 1H), 7.76-7.71 (m, 1H), 7.49-7.46 (m, 2H), 7.40-7.37 (m, 1H), 7.29-7.24 (m, 2H), 2.46 (s, 3H), 0.89 (t, 9H, J = 8.1 Hz), 0.66-0.58 (m, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 162.0, 148.6, 145.2, 137.3, 136.6, 136.2, 135.9, 129.4, 129.1, 123.3, 121.9, 21.6, 7.9, 4.7. HRMS (EI): *m/z* calcd for $C_{18}H_{26}NSi$ $[M+H]^+$ 284.1835, found 284.1805.

2-(4-methoxy-2-(triethylsilyl)phenyl)pyridine[1] (3c)



Brown oil, yield = 73%, 109 mg, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.64-8.62 (m, 1H), 7.75-7.69 (m, 1H), 7.47-7.41 (m, 2H), 7.26-7.22 (m, 2H), 6.98-6.95 (m, 1H), 3.88 (s, 3H), 0.87 (t, 9H, J = 8.1 Hz), 0.65-0.57 (m, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 161.5, 158.8, 148.5, 140.5, 138.0, 136.3, 130.4, 123.1, 122.9, 121.7, 113.0, 55.3, 7.87, 4.77. HRMS (EI): *m/z* calcd for $C_{18}H_{26}NOSi$ $[M+H]^+$ 300.1784, found 300.1759.

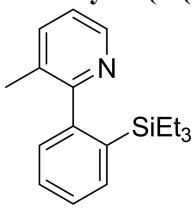
2-(2-(triethylsilyl)-4-(trifluoromethyl)phenyl)pyridine[1] (3d)



Light yellow oil, yield = 52%, 88 mg, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.69 (s, 1H), 7.89-7.28 (m, 6H), 0.85 (d, 9H, J = 8.1 Hz), 0.60-0.58 (m, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ =

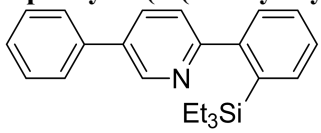
160.6, 151.2, 148.8, 137.8, 136.7, 132.9, 129.4, 125.6, 123.4, 122.8, 7.7, 4.5. ^{19}F NMR (470 MHz, $CDCl_3$): δ = -62.4 ppm. HRMS (EI): *m/z* calcd for $C_{18}H_{23}F_3NSi$ $[M+H]^+$ 338.1552, found 338.1530.

3-methyl-2-(2-(triethylsilyl)phenyl)pyridine[1] (3e)



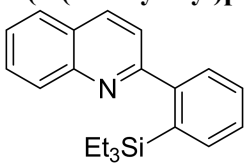
Light yellow oil, yield = 81%, 115 mg, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.50-8.48 (m, 1H), 7.69-7.66 (m, 1H), 7.59-7.56 (m, 1H), 7.43-7.36 (m, 2H), 7.24-7.20 (m, 2H), 2.19 (s, 3H), 0.85 (t, 9H, *J* = 7.8 Hz), 0.50-0.42 (m, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 161.4, 147.3, 146.1, 137.8, 136.1, 135.9, 131.6, 128.9, 128.3, 126.8, 122.6, 19.9, 7.6, 3.7. HRMS (EI): *m/z* calcd for $C_{18}H_{26}NSi$ $[M+H]^+$ 284.1835, found 284.1805.

5-phenyl-2-(2-(triethylsilyl)phenyl)pyridine (3f)



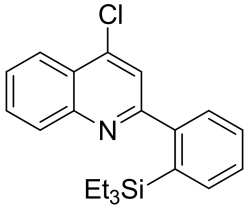
Light yellow solid, yield = 72%, 124 mg, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.95 (s, 1H), 8.01-7.98 (m, 1H), 7.72-7.71 (m, 3H), 7.56-7.47 (m, 7H), 0.91 (t, 9H, *J* = 7.8 Hz), 0.66-0.68 (m, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 160.7, 147.5, 146.9, 137.9, 136.6, 136.2, 134.9, 134.7, 129.3, 129.2, 128.8, 128.2, 127.4, 127.2, 123.1, 7.9, 4.8. HRMS (EI): *m/z* calcd for $C_{23}H_{28}NSi$ $[M+H]^+$ 346.1991, found 346.1950.

2-(2-(triethylsilyl)phenyl)quinoline (3g)



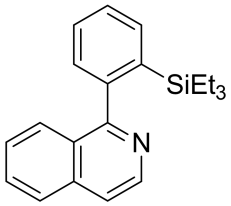
Light yellow solid, yield = 77%, 123 mg, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.26-8.18 (m, 2H), 7.92-7.89 (m, 1H), 7.81-7.74 (m, 2H), 7.67-7.66 (m, 5H), 0.89-0.84 (m, 9H), 0.68-0.60 (m, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 161.9, 148.3, 147.5, 136.7, 136.5, 129.9, 129.7, 129.6, 128.8, 127.8, 127.6, 127.5, 127.0, 126.5, 121.9, 7.8, 4.7. HRMS (EI): *m/z* calcd for $C_{21}H_{26}NSi$ $[M+H]^+$ 320.1835, found 320.1799.

4-chloro-2-(2-(triethylsilyl)phenyl)quinoline (3h)



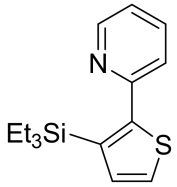
Brown oil, yield = 75%, 133 mg, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.34-8.31 (m, 1H), 8.23-8.20 (m, 1H), 7.86-7.66 (m, 4H), 7.59-7.46 (m, 3H), 0.91-0.86 (m, 9H), 0.71-0.63 (m, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 161.7, 148.4, 147.1, 142.7, 136.8, 136.6, 130.8, 129.9, 129.5, 128.9, 127.9, 127.4, 125.2, 124.2, 121.8, 7.8, 4.9. HRMS (EI): *m/z* calcd for $C_{21}H_{25}ClNSi$ $[M+H]^+$ 354.1445, found 354.1409.

1-(2-(triethylsilyl)phenyl)isoquinoline (3i)



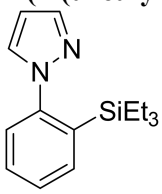
Light yellow solid, yield = 81%, 129 mg, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.61 (d, 1H, J = 2.7 Hz), 7.90-7.66 (m, 5H), 7.51-7.39 (m, 4H), 0.77 (t, 9H, J = 7.8 Hz), 0.39-0.31 (m, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 163.1, 146.0, 141.7, 137.0, 136.4, 136.2, 130.1, 129.9, 128.1, 128.0, 127.2, 126.9, 126.8, 120.2, 7.5, 3.8. HRMS (EI): *m/z* calcd for $C_{21}H_{26}NSi$ $[M+H]^+$ 320.1835, found 320.1798.

2-(3-(triethylsilyl)thiophen-2-yl)pyridine[2] (3j)



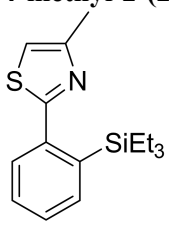
Brown oil, yield = 74%, 102 mg, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.64-8.62 (m, 1H), 7.71-7.58 (m, 2H), 7.41 (d, 1H, J = 5.1 Hz), 7.25-7.17 (m, 2H), 0.96-0.84 (m, 15H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 154.3, 150.2, 148.8, 137.0, 136.3, 135.7, 125.5, 122.2, 122.0, 7.9, 4.9. HRMS (EI): *m/z* calcd for $C_{15}H_{22}NSSi$ $[M+H]^+$ 276.1242, found 276.1240.

1-(2-(triethylsilyl)phenyl)-1H-pyrazole[1] (3k)



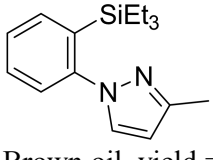
Brown oil, yield = 57%, 74 mg, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70-7.62 (m, 3H), 7.46-7.43 (m, 2H), 7.30-7.28 (m, 1H), 6.45 (t, 1H, J = 2.0 Hz), 0.89 (t, 9H, J = 7.6 Hz), 0.61-0.55 (m, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 146.6, 140.0, 136.8, 133.9, 130.5, 129.7, 126.3, 106.7, 7.7, 3.6. HRMS (EI): *m/z* calcd for $C_{15}H_{23}N_2Si$ $[M+H]^+$ 259.1631, found 259.1626.

4-methyl-2-(2-(triethylsilyl)phenyl)thiazole (3l)



Colorless oil, yield = 43%, 62 mg, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68-7.57 (m, 2H), 7.43-7.40 (m, 2H), 6.93 (d, 1H, J = 0.9 Hz), 2.52 (s, 3H), 0.89 (t, 9H, J = 8.1 Hz), 0.78-0.72 (m, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 169.2, 153.0, 140.7, 136.8, 129.9, 128.8, 128.4, 114.5, 17.2, 7.9, 4.6. HRMS (EI): *m/z* calcd for $C_{16}H_{24}NSSi$ $[M+H]^+$ 290.1399, found 290.1394.

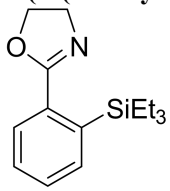
3-methyl-1-(2-(triethylsilyl)phenyl)-1H-pyrazole (3m)



Brown oil, yield = 70%, 95 mg, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65-7.62 (m, 1H), 7.52-7.27 (m, 4H), 6.22 (d, 1H, J = 2.1 Hz), 2.39 (s, 3H), 0.91 (t, 9H, J = 8.1 Hz), 0.67-0.59 (m, 6H).

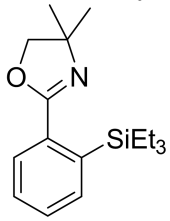
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ = 149.1, 146.6, 136.8, 133.5, 130.8, 129.6, 127.3, 125.6, 106.4, 13.6, 7.7, 3.7. HRMS (EI): *m/z* calcd for $C_{16}H_{25}N_2Si$ $[M+H]^+$ 273.1787, found 273.1787.

2-(2-(triethylsilyl)phenyl)-4,5-dihydrooxazole[3] (3n)



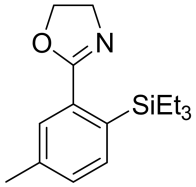
Light yellow oil, yield = 65%, 85 mg, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84-7.80 (m, 1H), 7.62-7.59 (m, 1H), 7.45-7.37 (m, 2H), 4.41 (t, 2H, *J* = 9.6 Hz), 4.06 (t, 2H, *J* = 9.6 Hz), 1.00-0.84 (m, 15H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ = 166.6, 137.1, 136.1, 134.4, 129.5, 129.4, 128.5, 67.5, 55.0, 7.7, 4.2. HRMS (EI): *m/z* calcd for $C_{15}H_{24}NOSi$ $[M+H]^+$ 262.1627, found 262.1614.

4,4-dimethyl-2-(2-(triethylsilyl)phenyl)-4,5-dihydrooxazole[4] (3o)



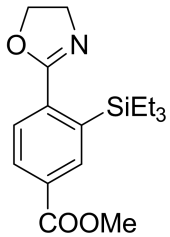
Light yellow oil, yield = 53%, 77 mg, ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.86-7.85 (m, 1H), 7.60-7.58 (m, 1H), 7.44-7.38 (m, 2H), 4.12 (s, 2H), 1.41 (s, 6H), 0.96-0.85 (m, 15H). $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$): δ = 164.3, 137.0, 136.3, 134.7, 130.0, 129.7, 128.7, 79.3, 67.9, 28.7, 8.0, 4.5. HRMS (EI): *m/z* calcd for $C_{17}H_{28}NOSi$ $[M+H]^+$ 290.1940, found 290.1912.

2-(5-methyl-2-(triethylsilyl)phenyl)-4,5-dihydrooxazole[3] (3p)



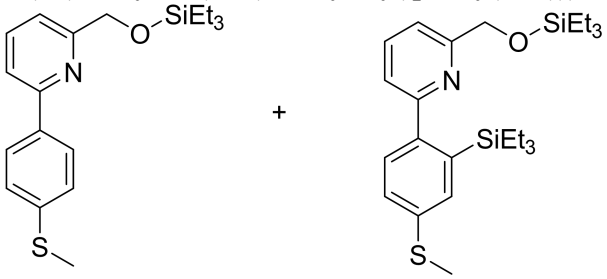
Colorless oil, yield = 45%, 62 mg, ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.67 (s, 1H), 7.49 (d, 1H, *J* = 8.0 Hz), 7.28-7.25 (m, 1H), 4.43 (t, 2H, *J* = 9.5 Hz), 4.07 (t, 2H, *J* = 9.5 Hz), 2.38 (s, 3H), 0.95-0.82 (m, 15H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ = 166.9, 138.6, 136.4, 134.4, 133.5, 130.6, 130.4, 67.6, 55.2, 21.2, 7.9, 4.4. HRMS (EI): *m/z* calcd for $C_{16}H_{26}NOSi$ $[M+H]^+$ 276.1784, found 276.1782.

methyl 4-(4,5-dihydrooxazol-2-yl)-3-(triethylsilyl)benzoate[3] (3q)



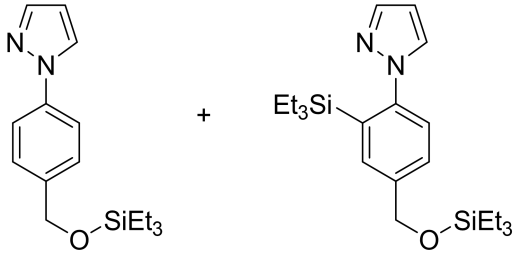
Brown oil, yield = 60%, 96 mg, ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.26 (d, 1H, *J* = 1.5 Hz,), 8.05-8.03 (m, 1H), 7.87 (d, 1H, *J* = 8.0 Hz), 4.45 (t, 2H, *J* = 9.5 Hz), 4.09 (t, 2H, *J* = 9.5 Hz), 3.94 (s, 3H), 0.95-0.87 (m, 15H). ^{13}C NMR (125.8 MHz, $CDCl_3$) δ = 167.1, 165.8, 138.7, 138.0, 137.3, 130.7, 129.8, 129.6, 67.8, 55.3, 52.4, 7.8, 4.3. HRMS (EI): *m/z* calcd for $C_{17}H_{26}NO_3Si$ $[M+H]^+$ 320.1682, found 320.1679.

Mixture of 2-(4-(methylthio)phenyl)-6-(((triethylsilyl)oxy)methyl)pyridine (4a) and 2-(4-(methylthio)-2-(triethylsilyl)phenyl)-6-(((triethylsilyl)oxy)methyl)pyridine (5a) (65:35)



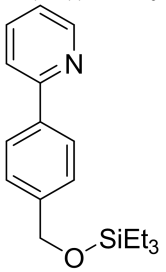
Yellow oil, yield = 75%, 127 mg, with ratio of mono : di = 65:35. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.99-7.93 (m, 1.34H), 7.79-7.72 (m, 1.19H), 7.57-7.48 (m, 2.02H), 7.37-7.28 (m, 2.31H), 4.94 (s, 1.02H), 4.92 (s, 0.48H), 2.54 (s, 0.88H), 2.53 (s, 1.97H), 1.04 (t, 7.67H, J = 8.1 Hz), 0.86 (t, 2.64H, J = 7.8 Hz), 0.77-0.69 (m, 5.12H), 0.60-0.57 (m, 1.78H). HRMS (EI): *m/z* calcd for $C_{19}H_{27}NOSSiNa$ $[M+Na]^+$ 366.1682, found 366.1681. HRMS (EI): *m/z* calcd for $C_{25}H_{41}NOSSi_2Na$ $[M+Na]^+$ 480.2547, found 480.2552.

Mixture of 1-(4-(((triethylsilyl)oxy)methyl)phenyl)-1H-pyrazole (4b) and 1-(2-(triethylsilyl)-4-(((triethylsilyl)oxy)methyl)phenyl)-1H-pyrazole (5b) (30:70)



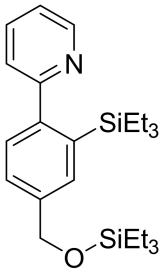
Brown oil, yield = 72%, 133 mg, with ratio of mono : di = 30:70. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68-7.55 (m, 4H), 7.43-7.38 (m, 1.35H), 7.26-7.21 (m, 1.40H), 6.44-6.42 (m, 1.29H), 4.83 (s, 2H), 4.70 (s, 0.77H), 1.02 (t, 9H, J = 8.1 Hz), 0.88 (t, 13.2H, J = 7.8 Hz), 0.74-0.66 (m, 6H), 0.61-0.53 (m, 8.37H). HRMS (EI): *m/z* calcd for $C_{16}H_{25}N_2OSi$ $[M+H]^+$ 289.1730, found 289.1742. HRMS (EI): *m/z* calcd for $C_{22}H_{39}N_2OSi_2$ $[M+H]^+$ 403.2595, found 403.2602.

2-(4-((triethylsilyl)oxy)phenyl)pyridine (4c)



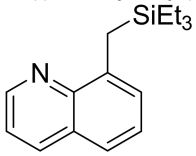
Colorless oil, yield = 88%, 132 mg, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.70 (d, 1H, J = 4.8 Hz), 8.00 (d, 2H, J = 8.4 Hz), 7.73 (d, 2H, J = 3.3 Hz), 7.47 (d, 2H, J = 8.4 Hz), 7.24-7.19 (m, 1H), 4.83 (s, 2H), 1.02 (t, 9H, J = 7.8 Hz), 0.74-0.66 (m, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 157.4, 149.7, 142.4, 138.2, 136.8, 126.9, 126.6, 122.0, 120.5, 64.6, 6.9, 4.6. HRMS (EI): *m/z* calcd for $C_{18}H_{26}NOSi$ $[M+H]^+$ 300.1784, found 300.1751.

2-(2-(triethylsilyl)-4-((triethylsilyl)oxy)phenyl)pyridine (5c)



Brown oil, yield = 68%, 140 mg, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.66 (d, 1H, J = 4.2 Hz), 7.75-7.68 (m, 2H), 7.48-7.44 (m, 3H), 7.28-7.24 (m, 1H), 4.86 (s, 2H), 1.05 (t, 9H, J = 8.1 Hz), 0.88 (t, 9H, J = 7.8 Hz), 0.76-0.57 (m, 12H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 161.9, 148.6, 146.8, 139.9, 136.2, 135.9, 134.4, 129.1, 126.7, 123.4, 122.0, 64.9, 7.8, 6.9, 4.7, 4.6. HRMS (EI): *m/z* calcd for $C_{24}H_{40}NOSi_2$ $[M+H]^+$ 414.2648, found 414.2649.

8-((triethylsilyl)methyl)quinoline[5] (6)



Colorless oil, yield = 81%, 104 mg, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.93-8.91 (m, 1H), 8.12-8.09 (m, 1H), 7.58-7.35 (m, 4H), 2.90 (s, 2H), 0.92 (t, 9H, J = 7.8 Hz), 0.57-0.49 (m, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 148.7, 146.8, 141.0, 136.2, 128.6, 128.0, 126.3, 123.9, 120.8, 17.1, 7.5, 3.7. HRMS (EI): *m/z* calcd for $C_{16}H_{24}NSi$ $[M+H]^+$ 258.1678, found 258.1652.

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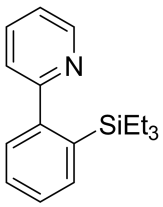
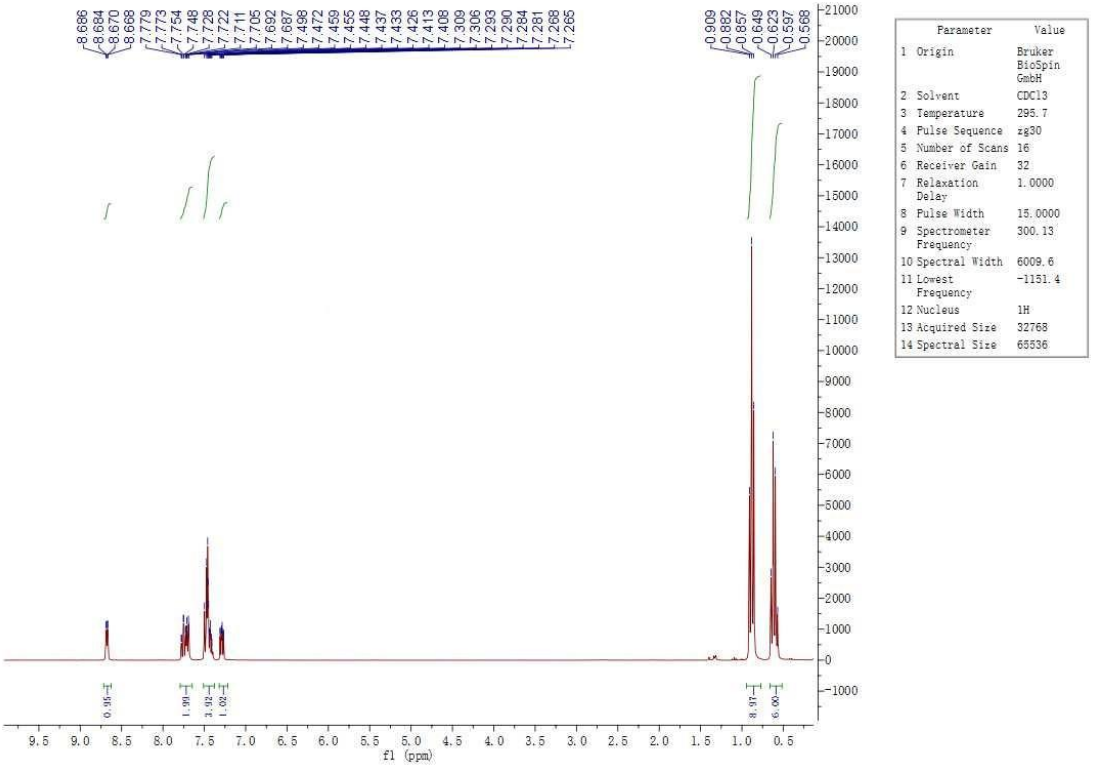
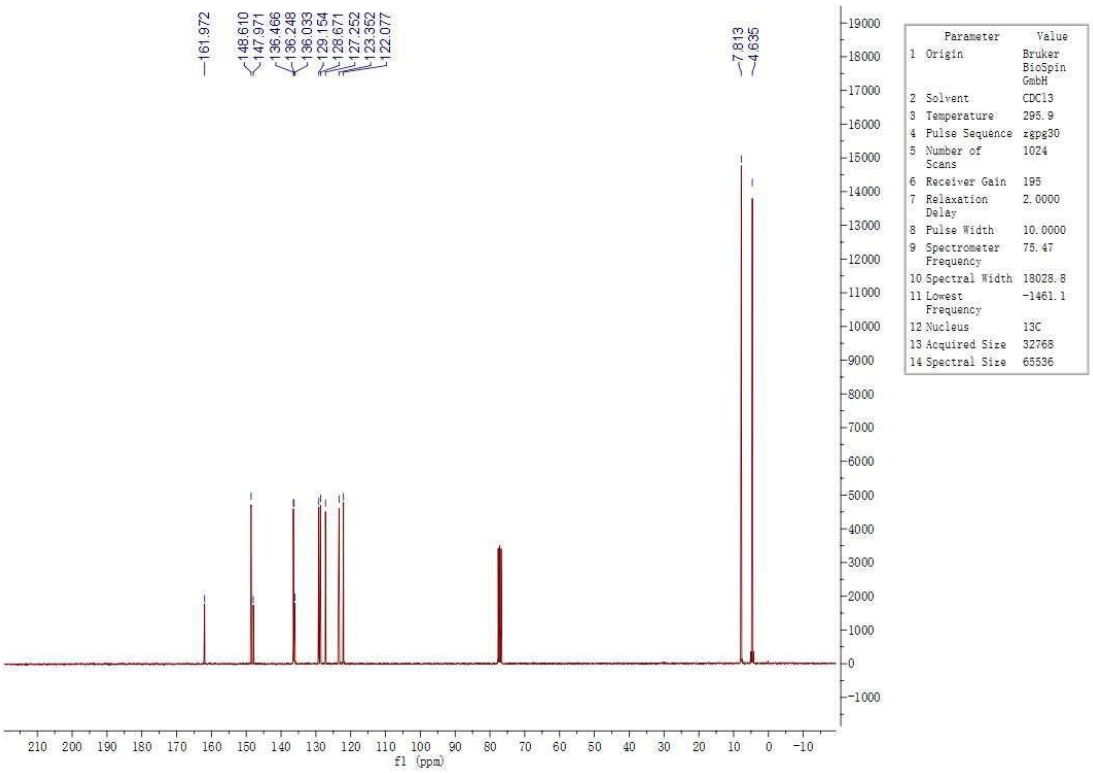
[1] Choi, G.; Tsurugi, H.; Mashima, K. *J. Am. Chem. Soc.*, **2013**, *135*, 13149.
[2] Rubio-Pérez, L.; Iglesias, M.; Munárriz, J.; Polo, V.; Passarelli, V.; Pérez-Torrente, J. J.; Oro, L. A. *Chem. Sci.*, **2017**, *8*, 4811.
[3] Liu, S.; Zhang, S.; Lin, Q.; Huang, Y.; Li, B. *Org. Lett.* **2019**, *21*, 1134.
[4] Kakiuchi, F.; Matsumoto, M.; Tsuchiya, K.; Igi, K.; Hayamizu, T.; Chatani, N.; Murai, S. *J. Organom. Chem.*, **2003**, *686*, 134.
[5] Mita, T.; Michigami, K.; Sato, Y. *Org. Lett.*, **2012**, *14*, 3462.

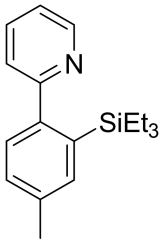
2-(2-(triethylsilyl)phenyl)pyridine (3a)

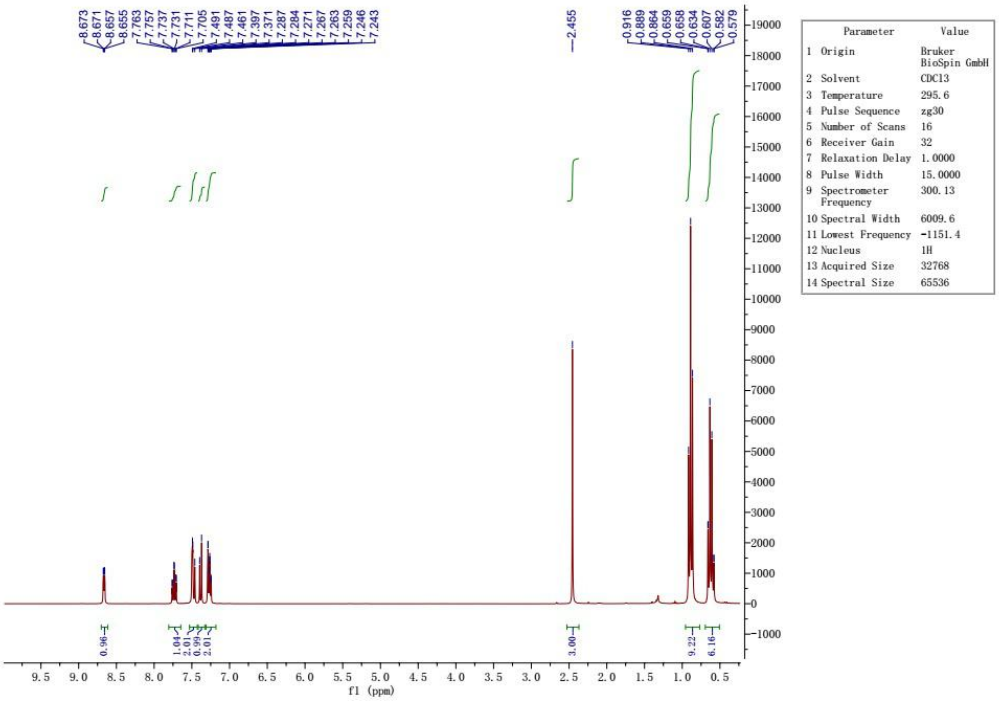






2-(4-methyl-2-(triethylsilyl)phenyl)pyridine (3b)





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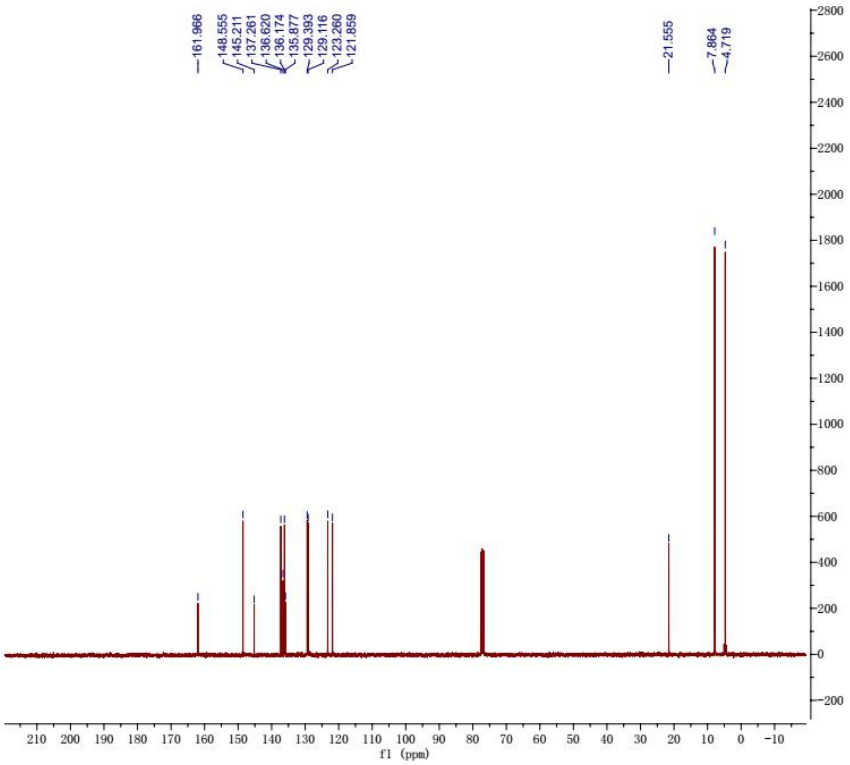
9	Spectrometer Frequency	300.13
10	Spectral Width	6009.6
11	Lowest Frequency	-1151.4
12	Nucleus	1H
13	Acquired Size	32768
14	Spectral Size	65536



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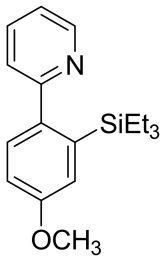
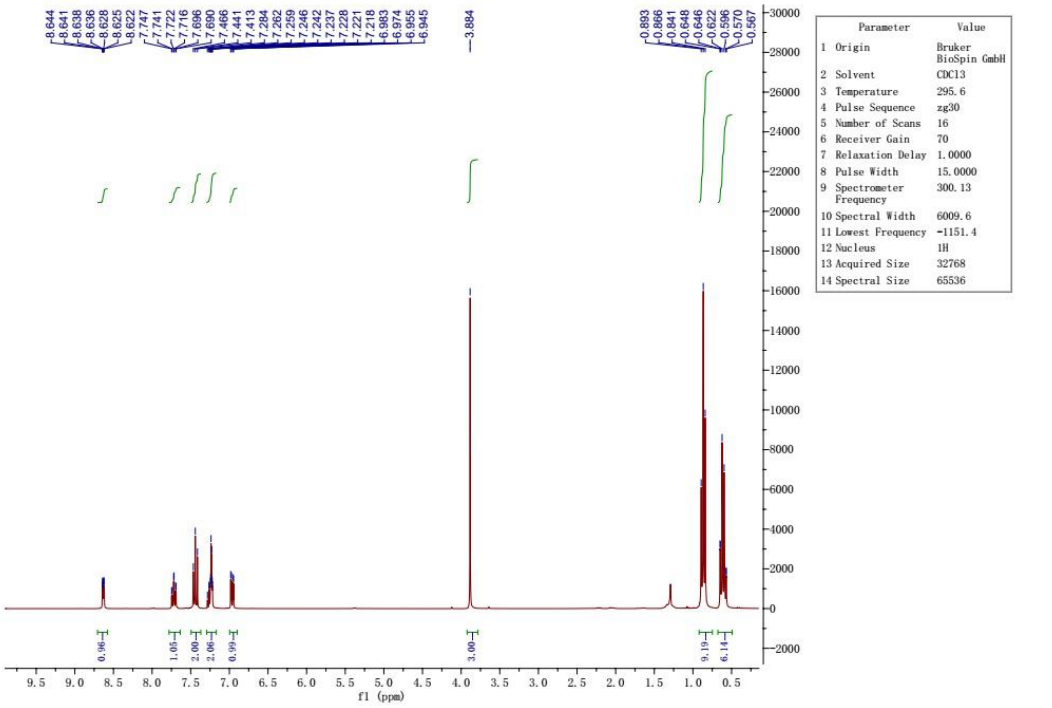
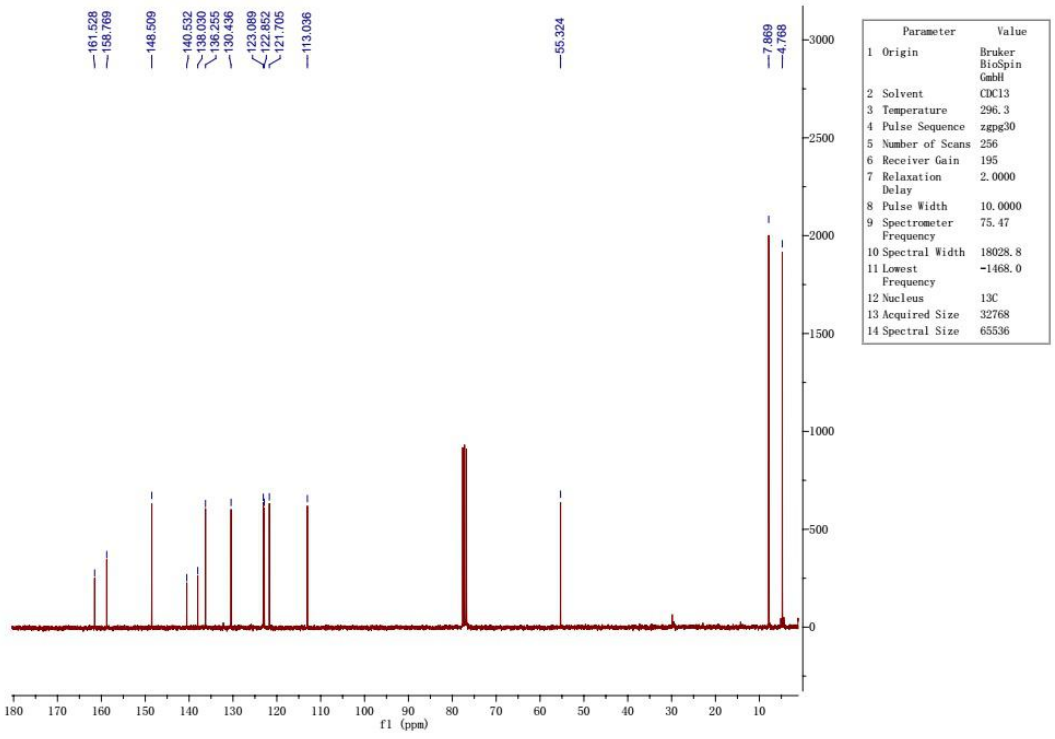
10	Spectral Width	18028.8
11	Lowest Frequency	-1460.8
12	Nucleus	13C
13	Acquired Size	32768
14	Spectral Size	65536

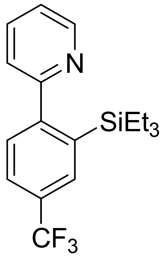
2-(4-methoxy-2-(triethylsilyl)phenyl)pyridine (3c)

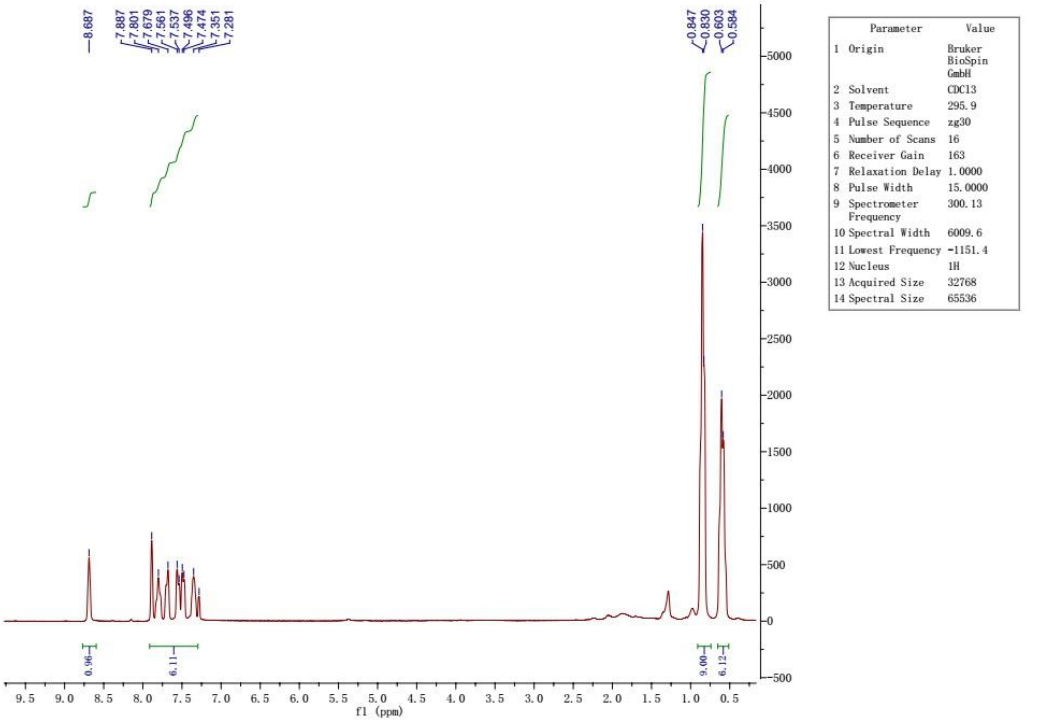


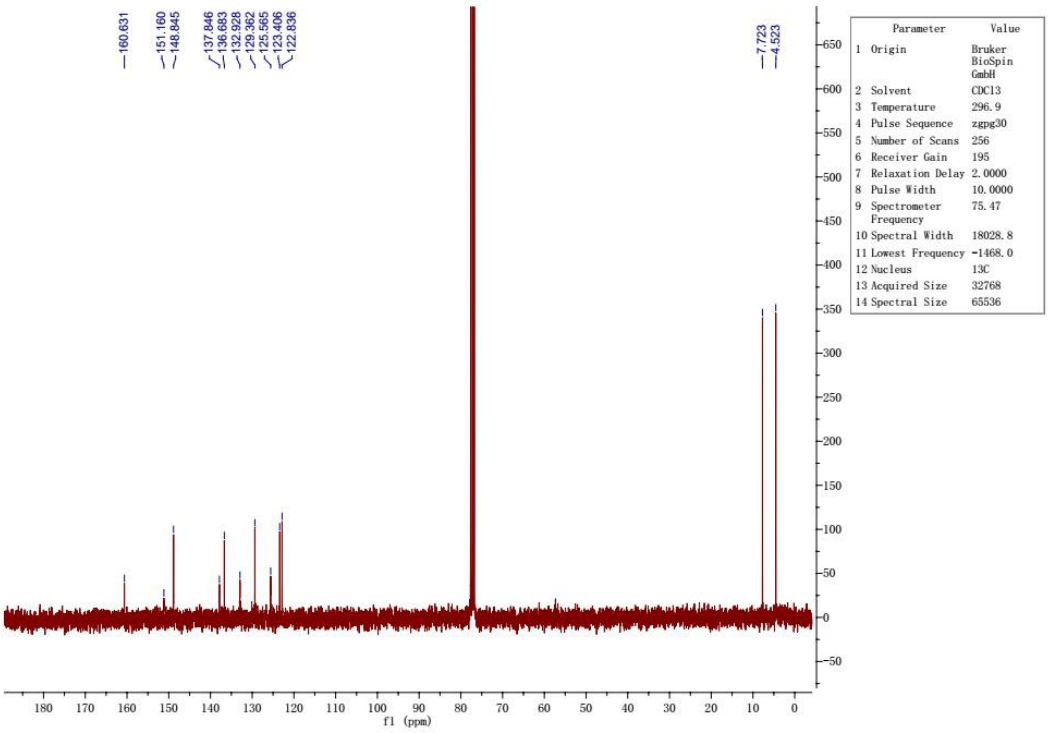




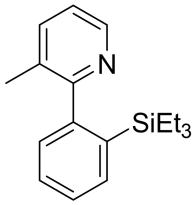
2-(2-(triethylsilyl)-4-(trifluoromethyl)phenyl)pyridine (3d)

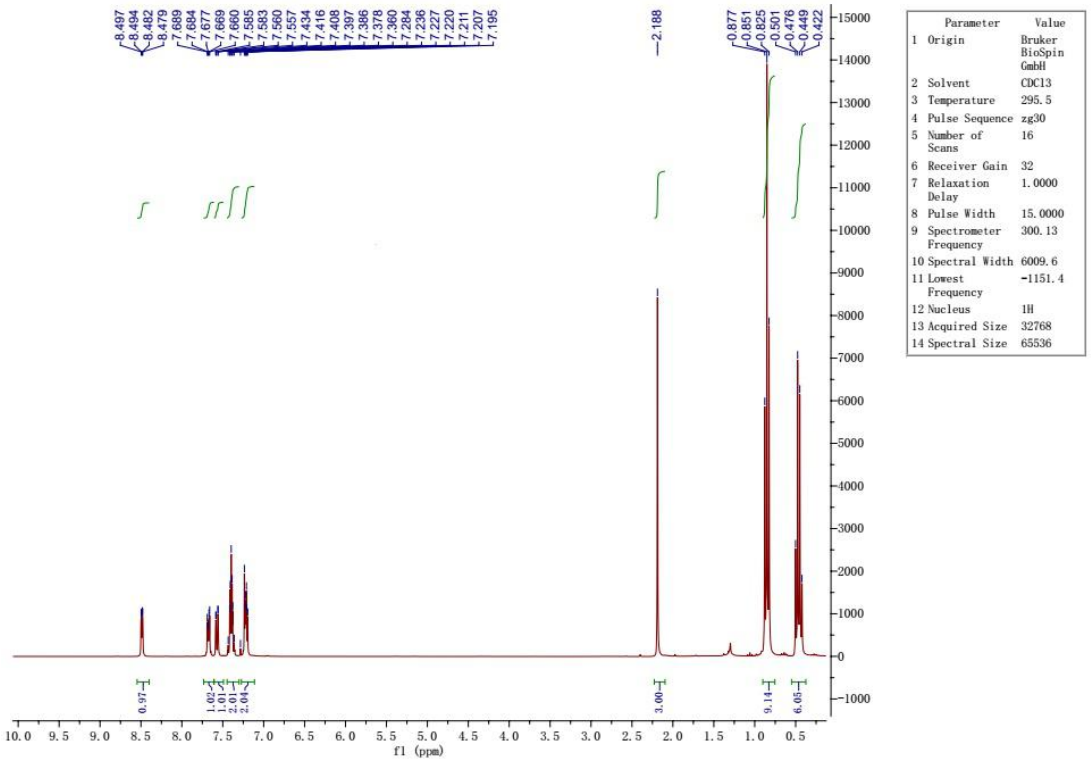






3-methyl-2-(2-(triethylsilyl)phenyl)pyridine (3e)





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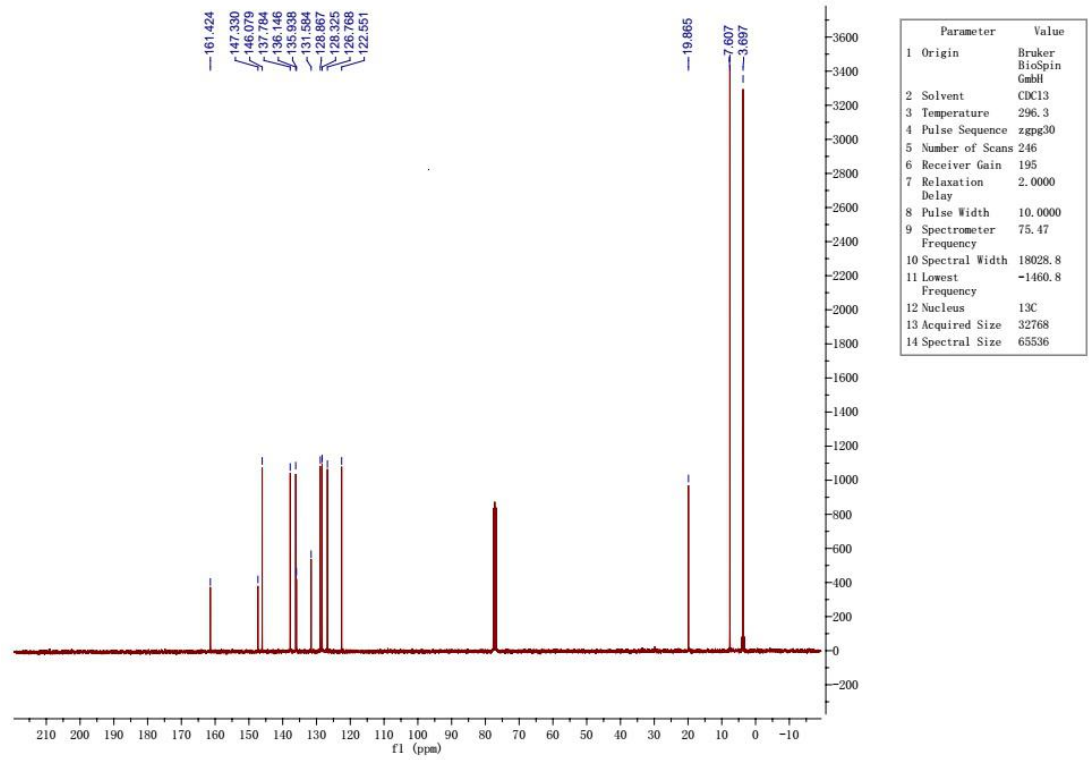
5	Number of Scans	16
6	Receiver Gain	32
7	Relaxation Delay	1.0000
8	Pulse Width	15.0000
9	Spectrometer Frequency	300.13
10	Spectral Width	6009.6
11	Lowest Frequency	-1151.4
12	Nucleus	1H
13	Acquired Size	32768
14	Spectral Size	65536



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4	Pulse Sequence	zgpg30
5	Number of Scans	246
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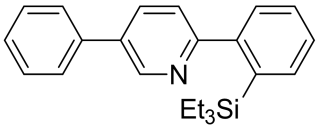
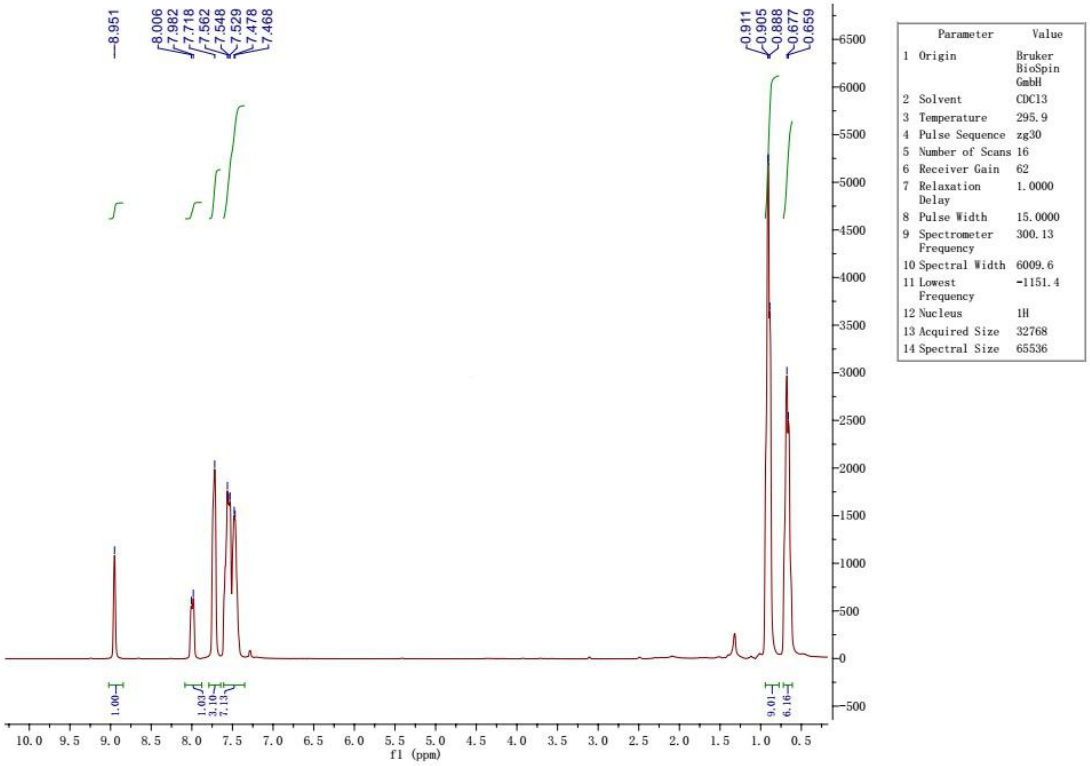
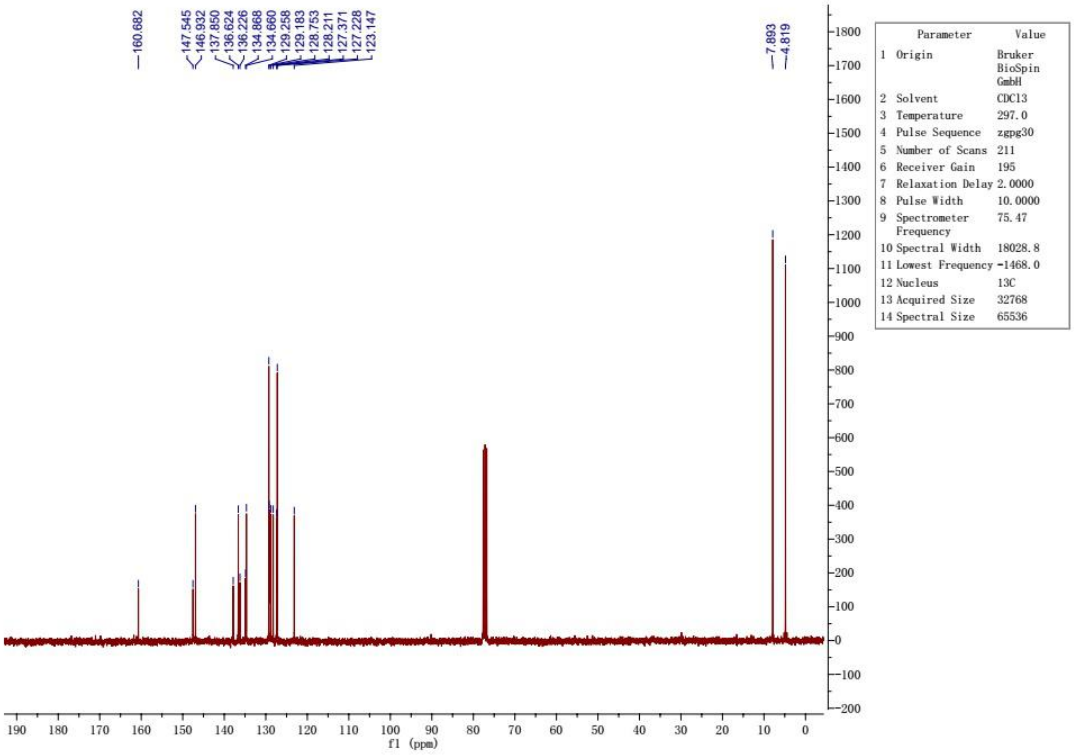
7	Relaxation Delay	2.0000
8	Pulse Width	10.0000
9	Spectrometer Frequency	75.47
10	Spectral Width	18028.8
11	Lowest Frequency	-1460.8
12	Nucleus	13C
13	Acquired Size	32768
14	Spectral Size	65536

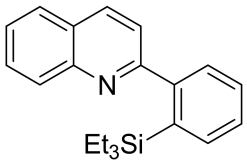
5-phenyl-2-(2-(triethylsilyl)phenyl)pyridine (3f)

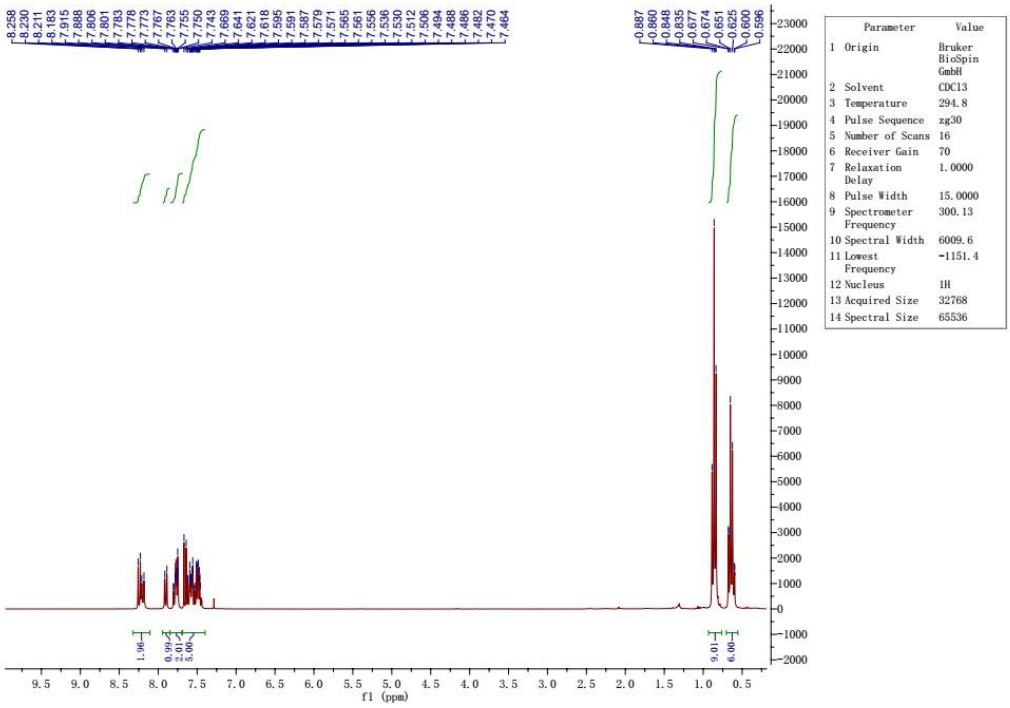


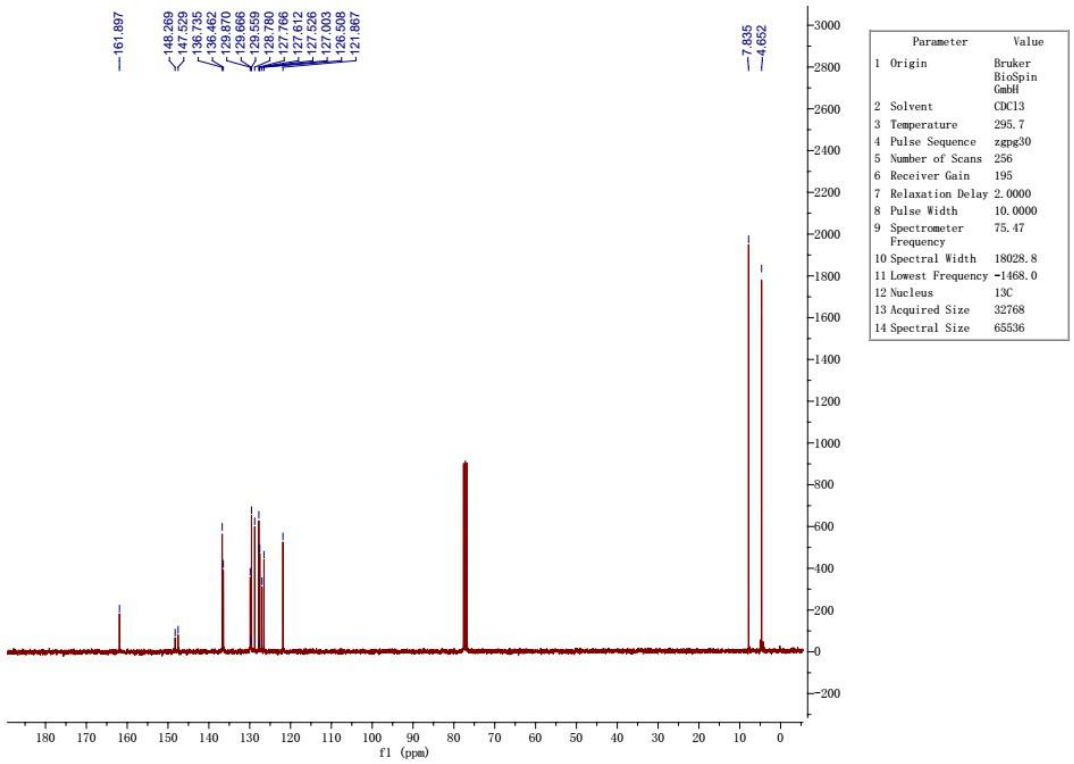




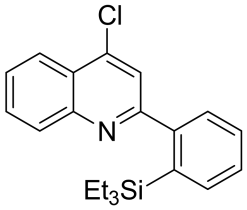
2-(2-(triethylsilyl)phenyl)quinoline (3g)

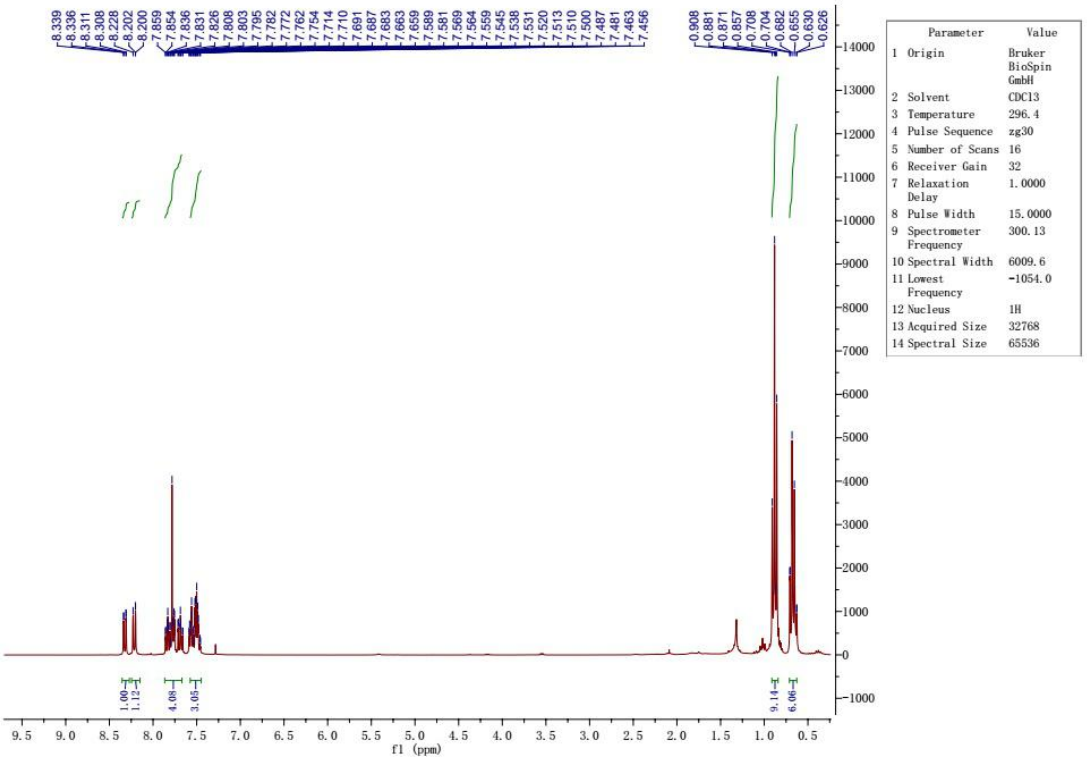


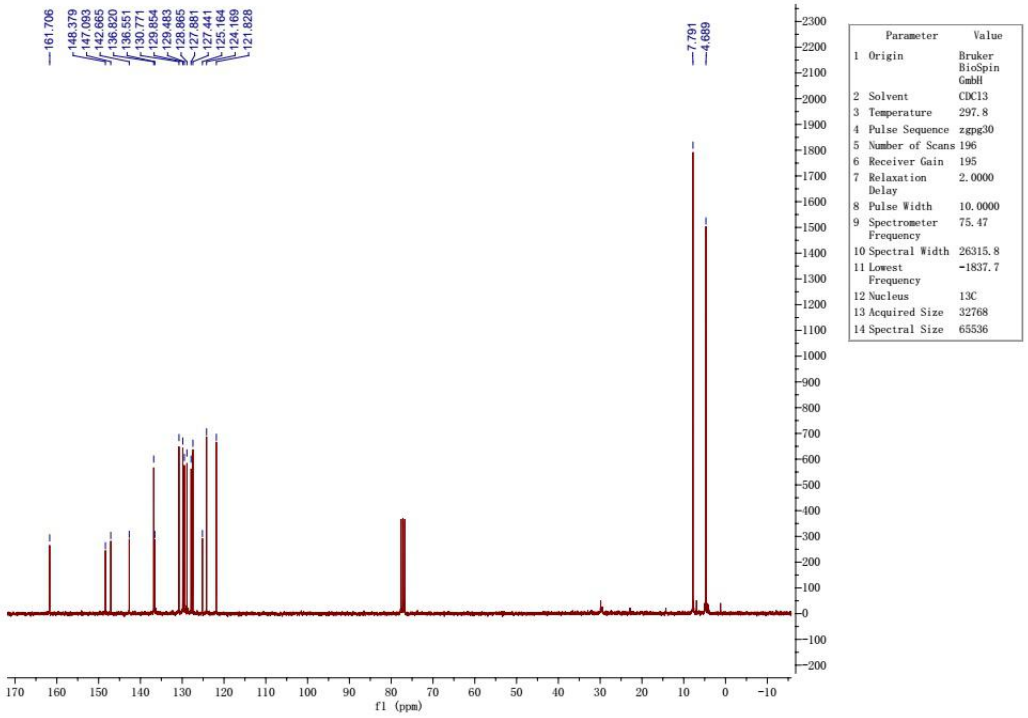




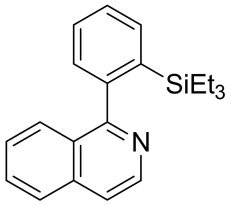
4-chloro-2-(2-(triethylsilyl)phenyl)quinoline (3h)

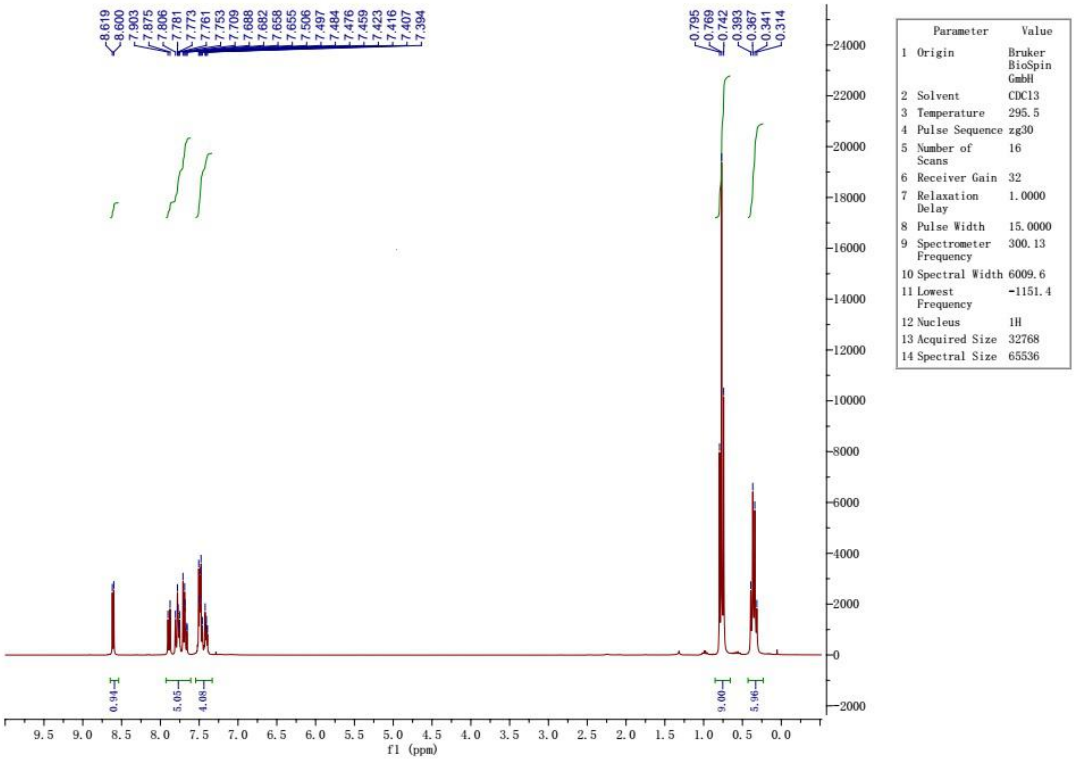


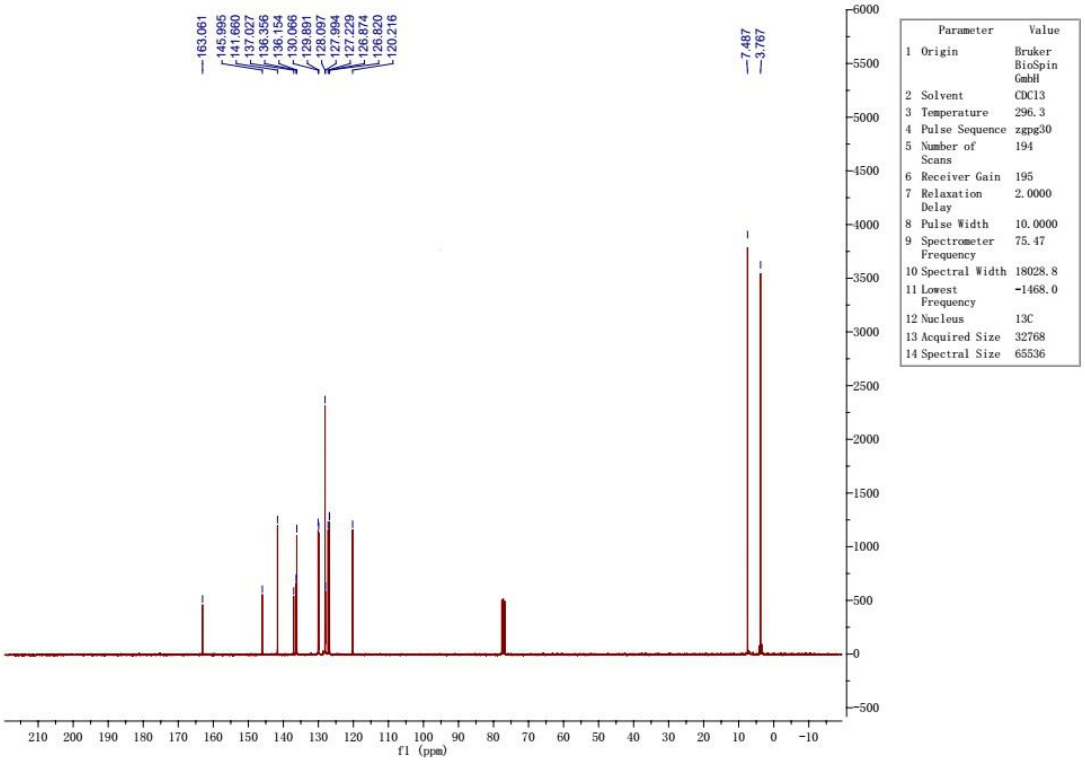




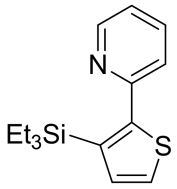
1-(2-(triethylsilyl)phenyl)isoquinoline (3i)

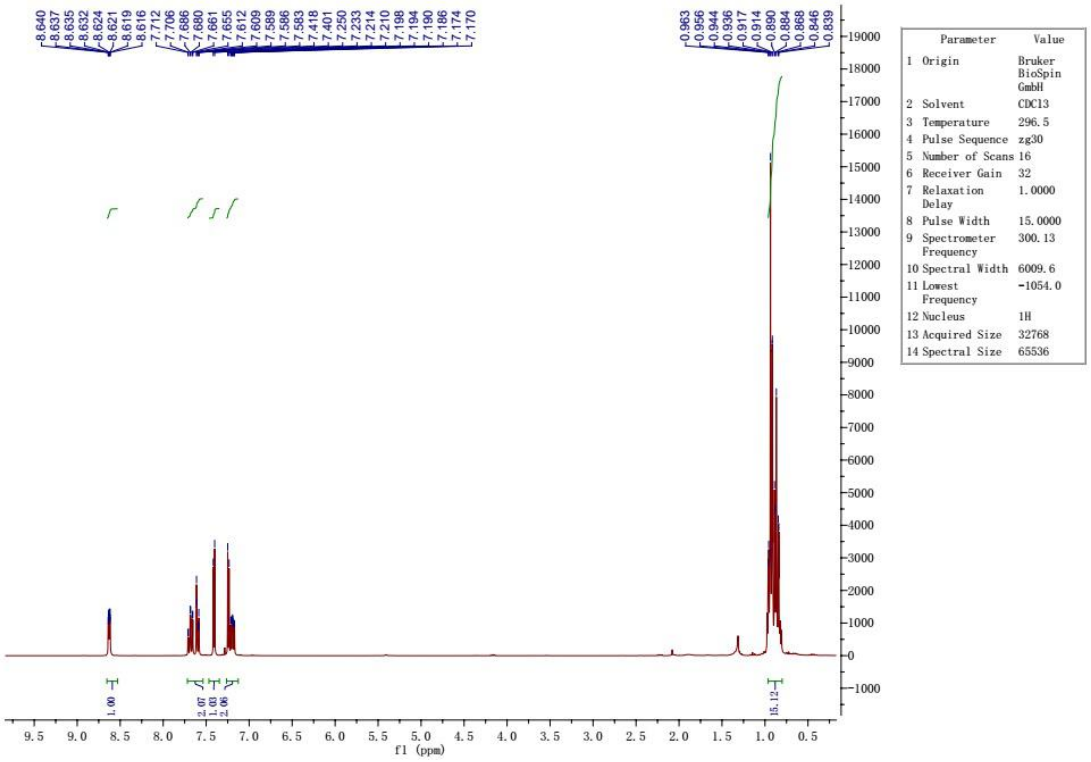


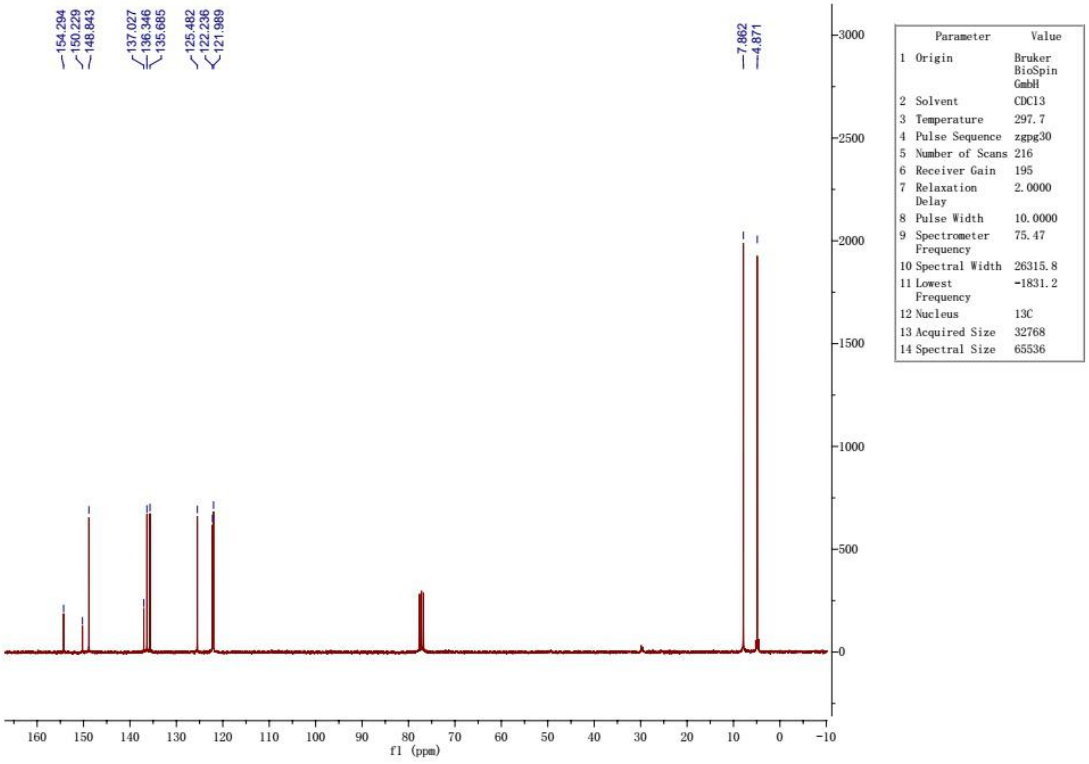




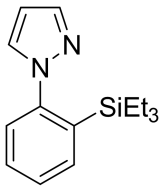
2-(3-(triethylsilyl)thiophen-2-yl)pyridine (3j)

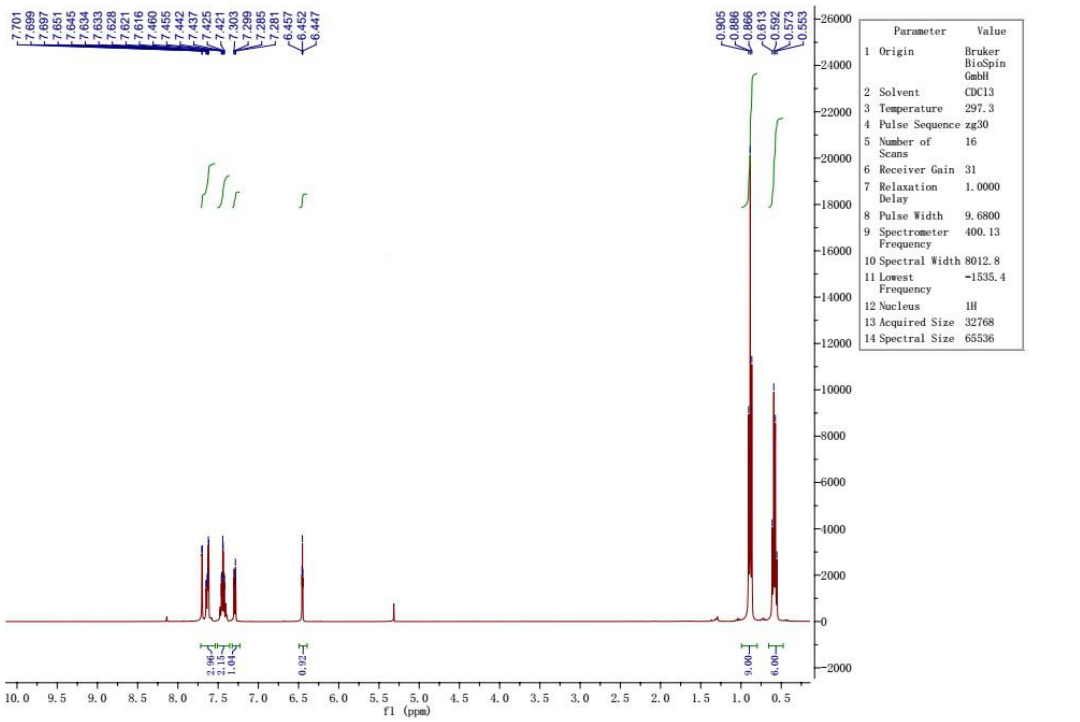


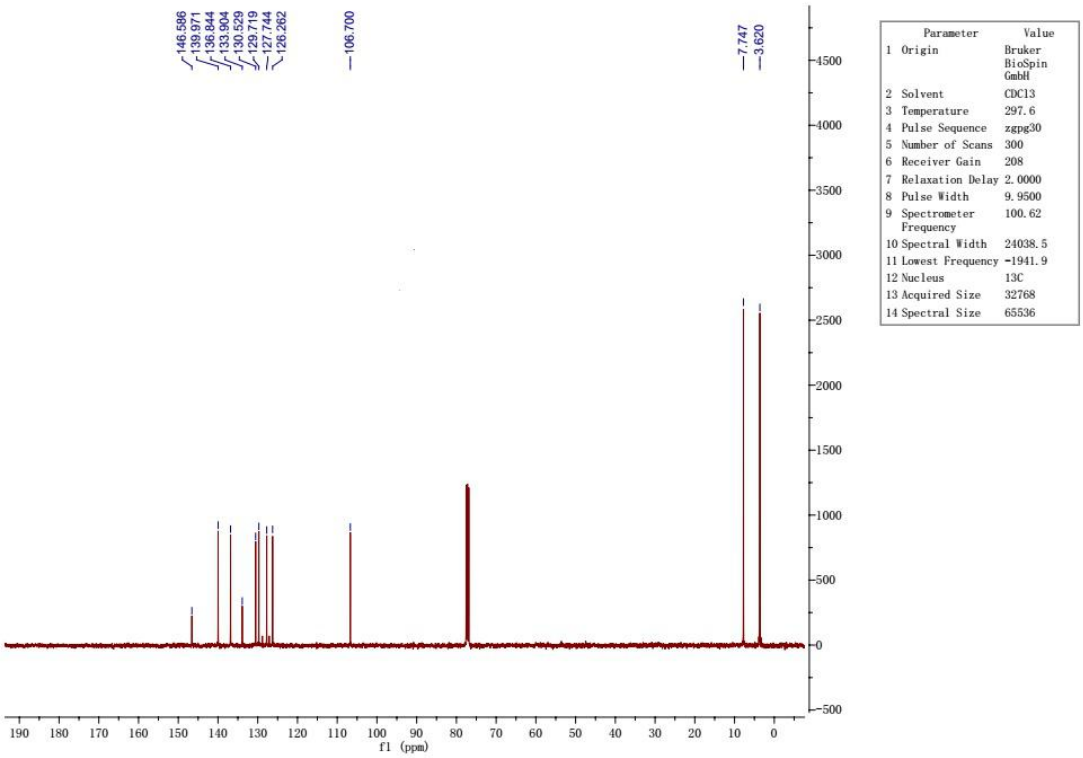




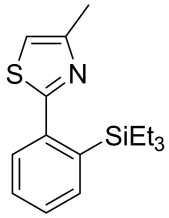
1-(2-(triethylsilyl)phenyl)-1H-pyrazole (3k)

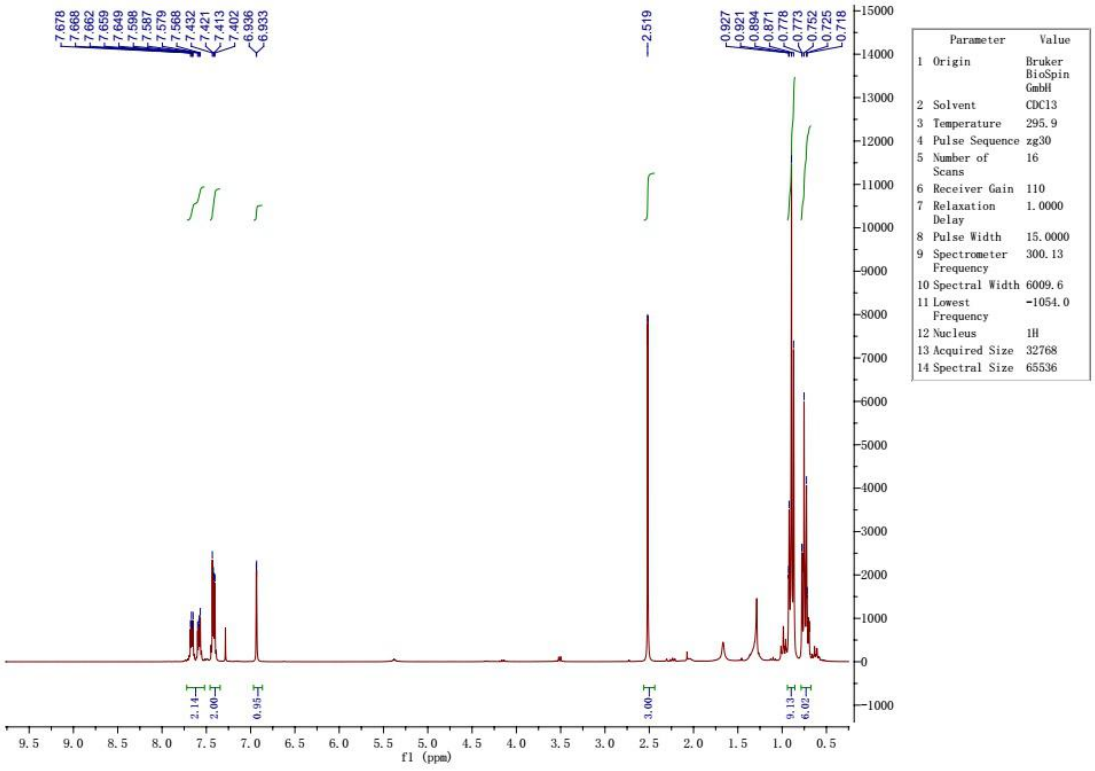


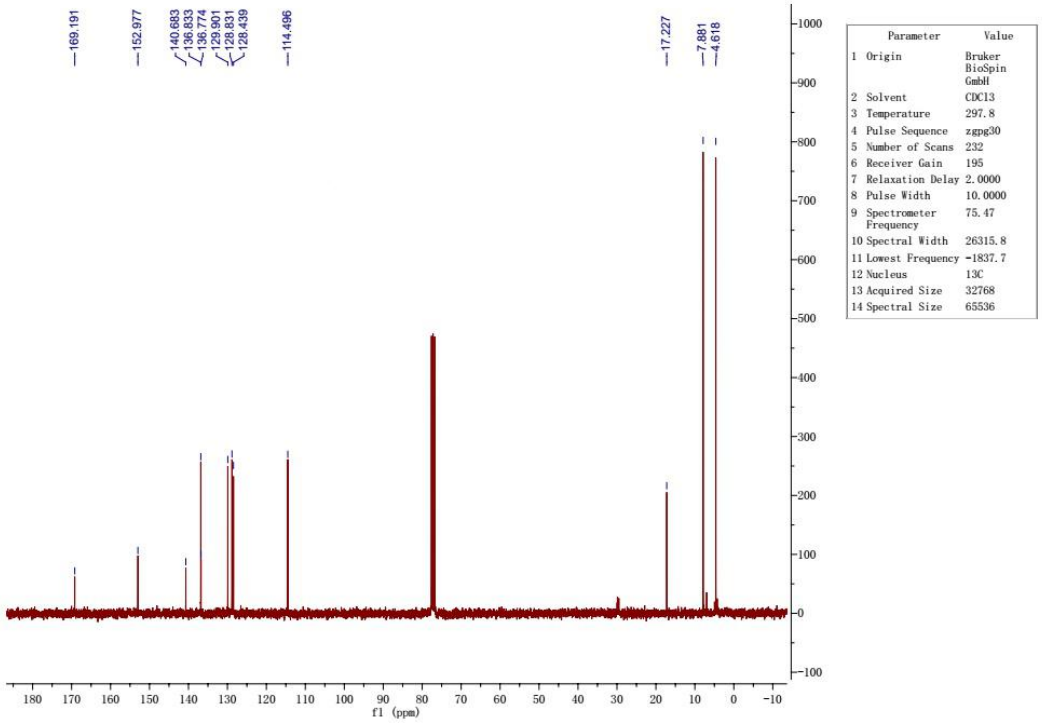




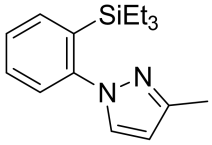
4-methyl-2-(2-(triethylsilyl)phenyl)thiazole (3l)

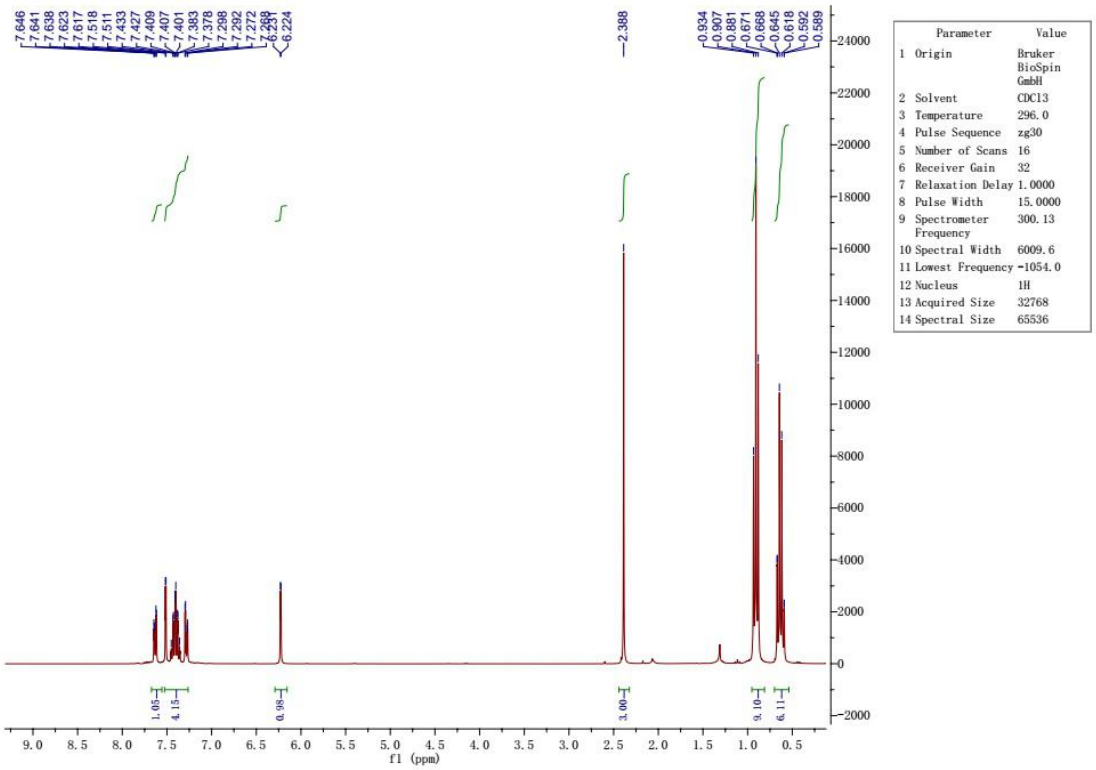


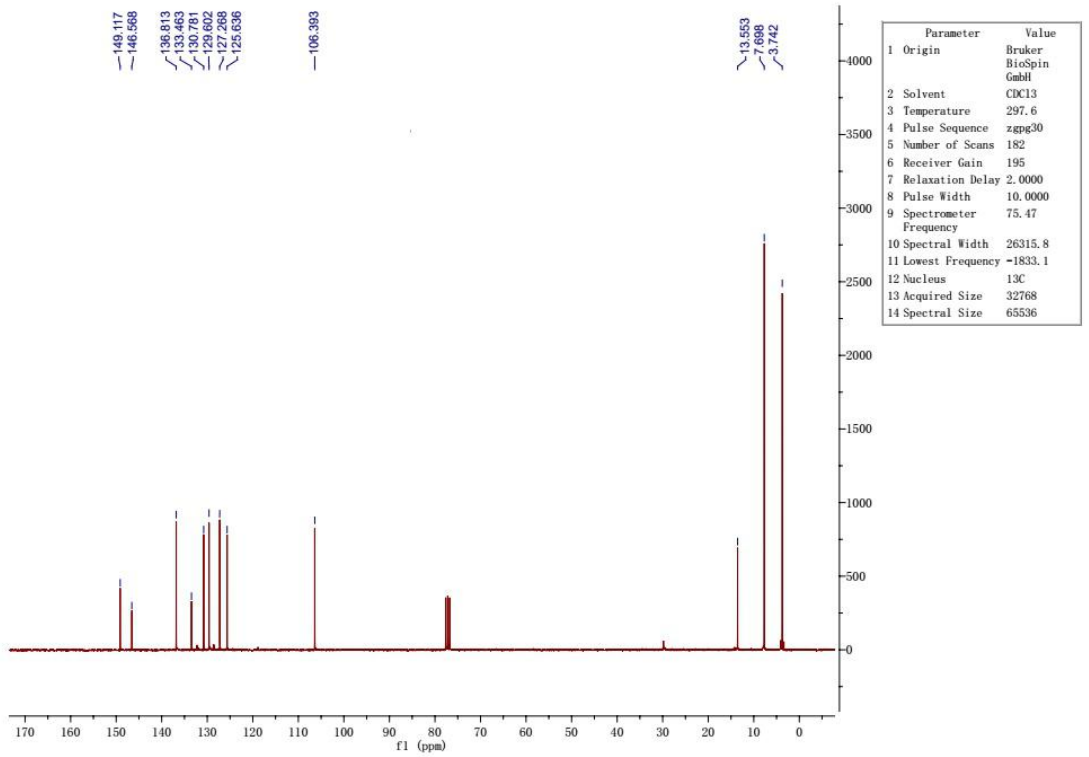




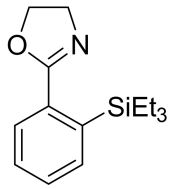
3-methyl-1-(2-(triethylsilyl)phenyl)-1H-pyrazole (3m)

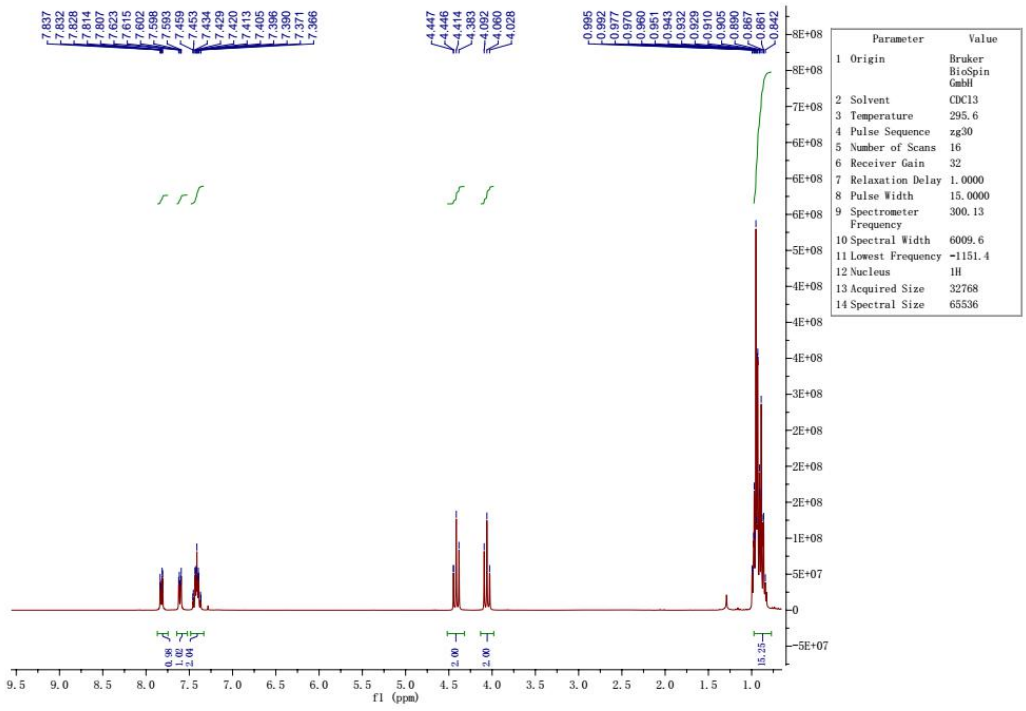


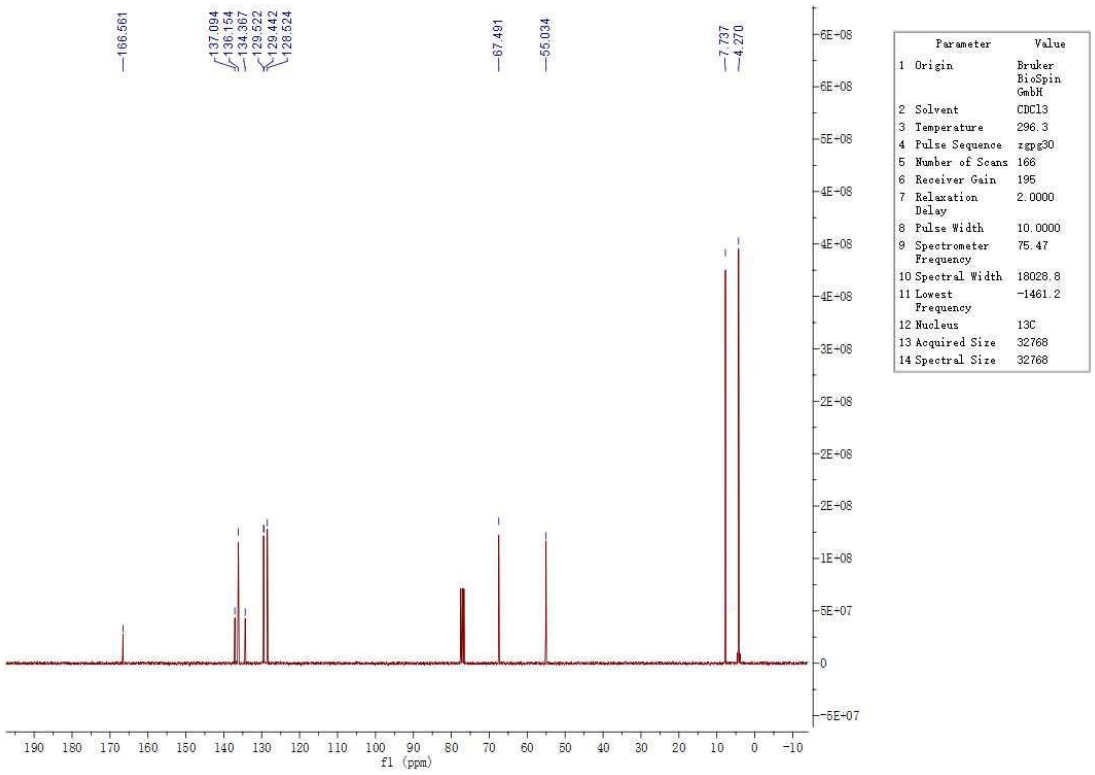




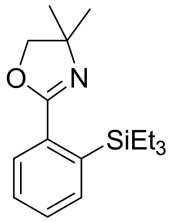
2-(2-(triethylsilyl)phenyl)-4,5-dihydrooxazole (3n)

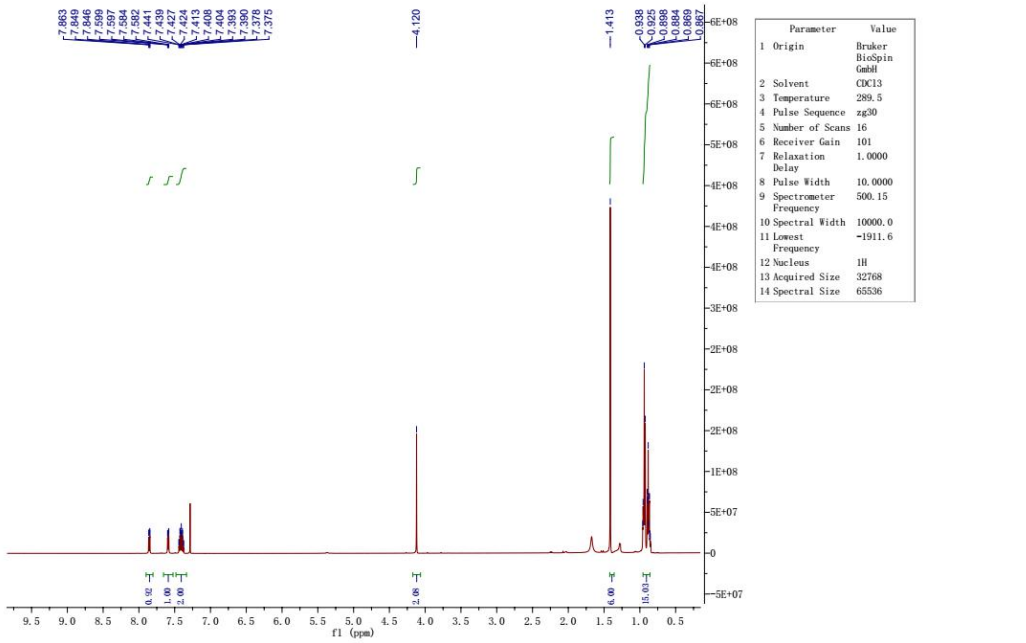


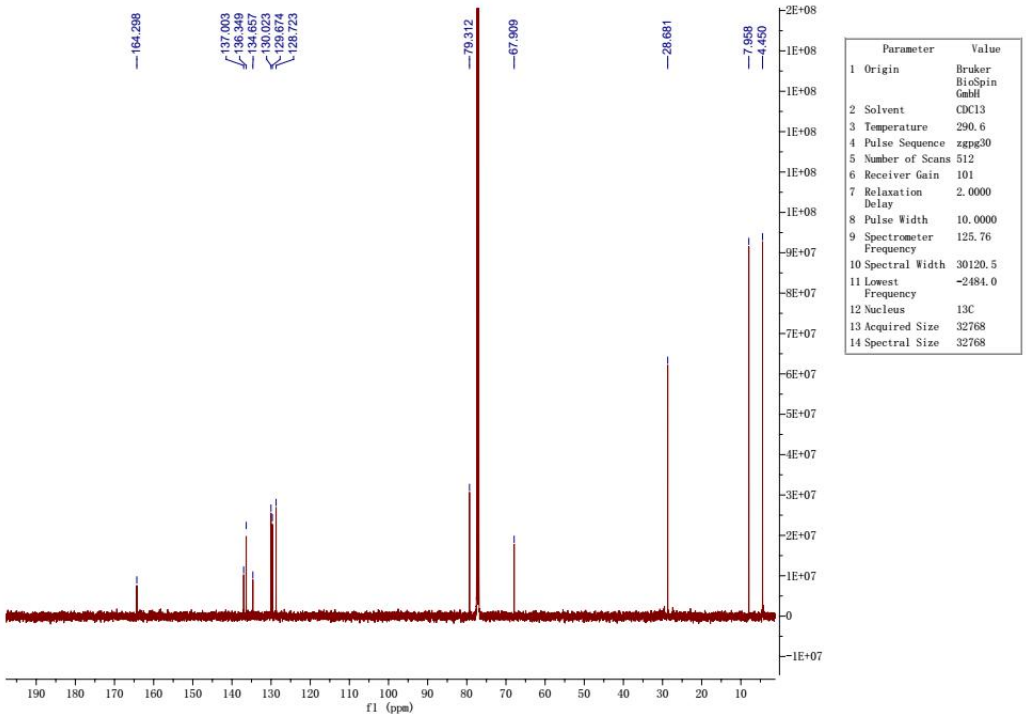




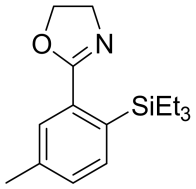
4,4-dimethyl-2-(2-(triethylsilyl)phenyl)-4,5-dihydrooxazole (3o)

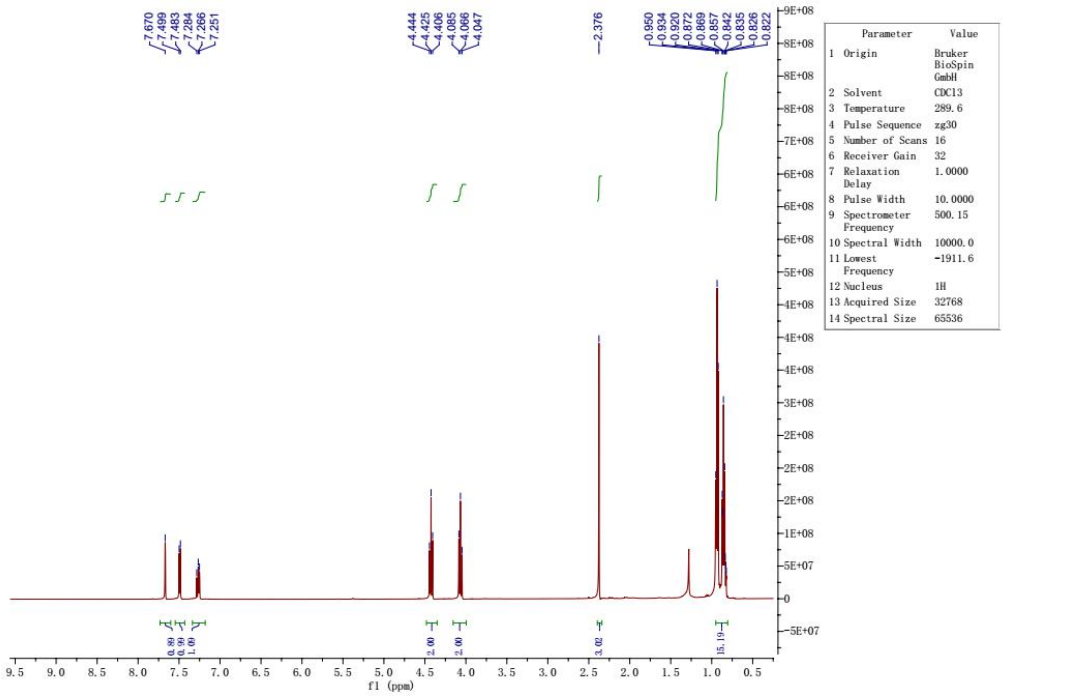




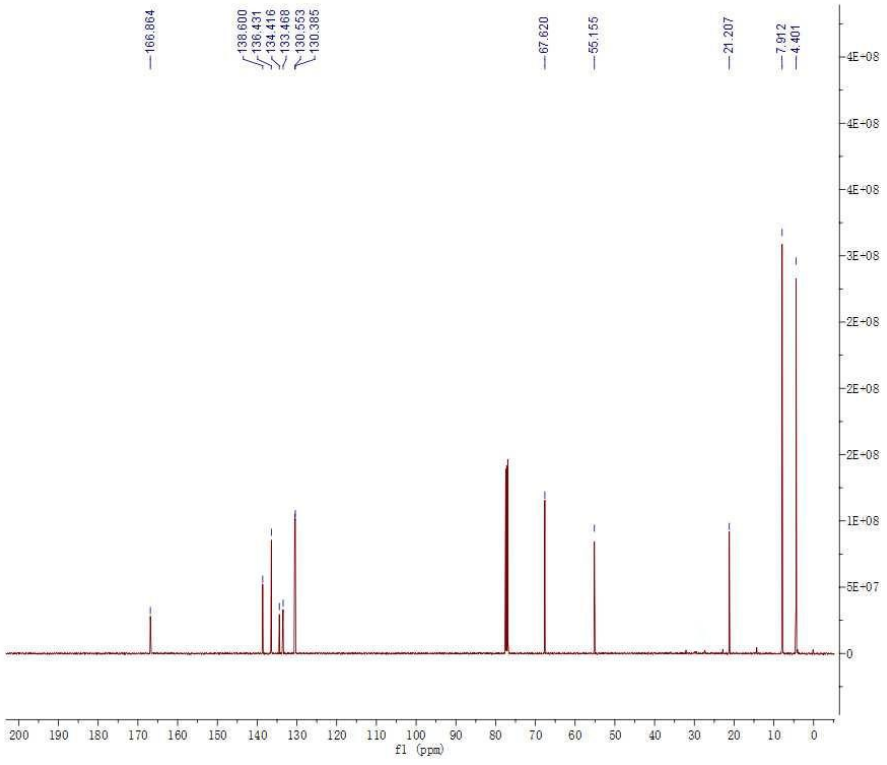


2-(2-(triethylsilyl)-5-methylphenyl)-4,5-dihydrooxazole (3o)



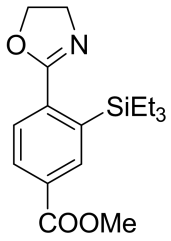


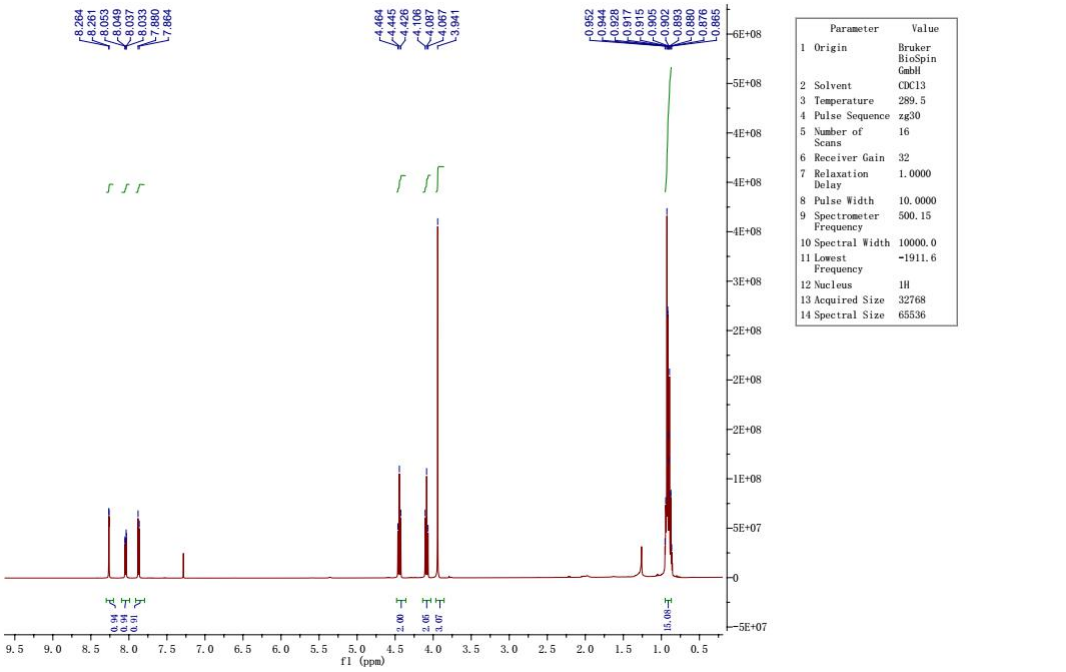
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Solvent	CDCl3
3	Temperature	289.6
4	Pulse Sequence	zg30
5	Number of Scans	16
6	Receiver Gain	32
7	Relaxation Delay	1.0000
8	Pulse Width	10.0000
9	Spectrometer Frequency	500.15
10	Spectral Width	10000.0
11	Lowest Frequency	-1911.6
12	Nucleus	1H
13	Acquired Size	32768
14	Spectral Size	65536

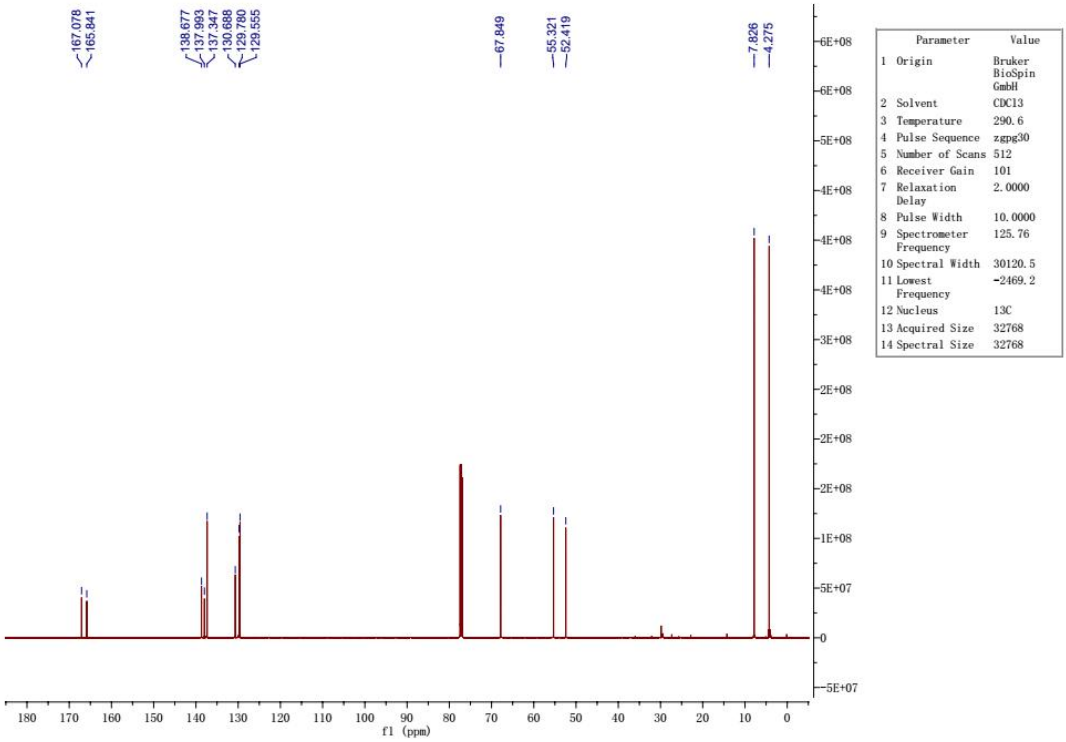


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Solvent	CDCl3
3	Temperature	290.7
4	Pulse Sequence	zgpg30
5	Number of Scans	512
6	Receiver Gain	101
7	Relaxation Delay	2.0000
8	Pulse Width	10.0000
9	Spectrometer Frequency	125.76
10	Spectral Width	30120.5
11	Lowest Frequency	-2484.0
12	Nucleus	13C
13	Acquired Size	32768
14	Spectral Size	32768

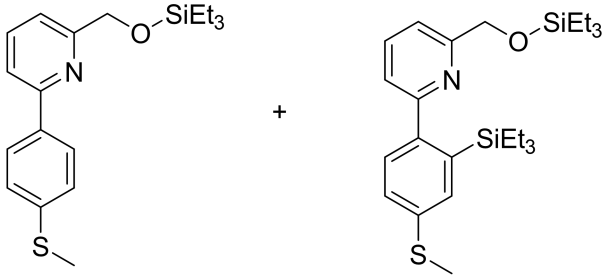
methyl 3-(triethylsilyl)-4-(4,5-dihydrooxazol-2-yl)benzoate (3q)

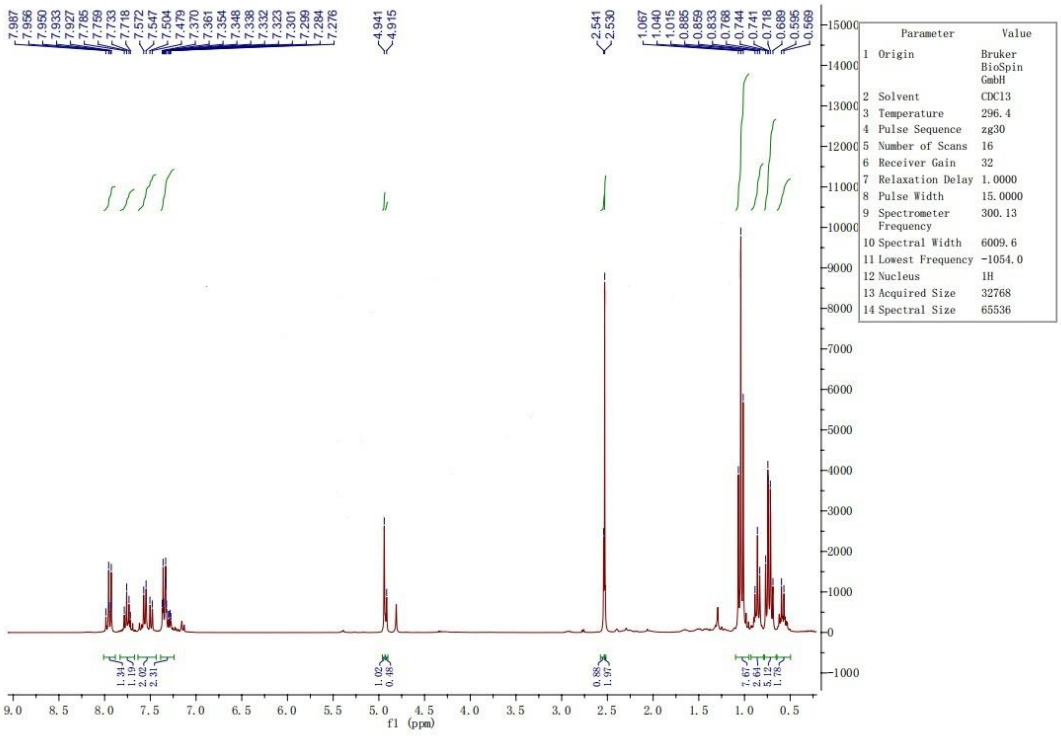




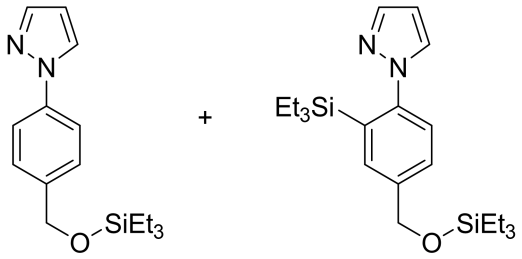


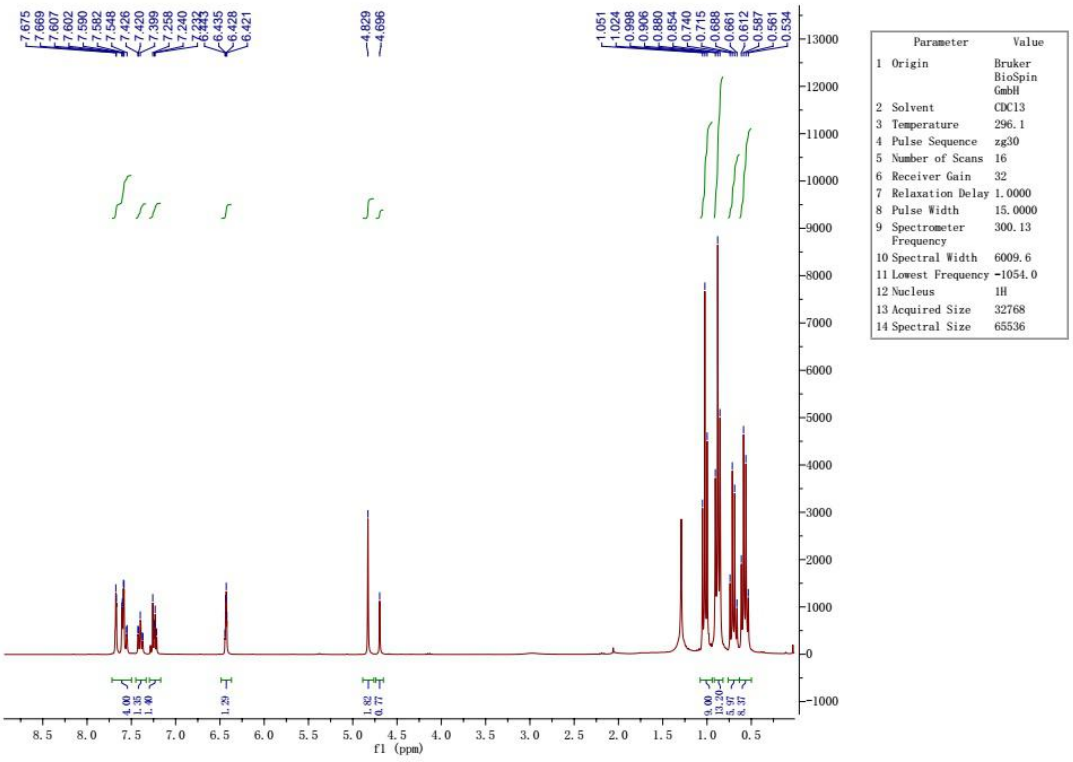
Mixture of 2-(4-(methylthio)phenyl)-6-(((triethylsilyl)oxy)methyl)pyridine (4a) and 2-(4-(methylthio)-2-(triethylsilyl)phenyl)-6-(((triethylsilyl)oxy)methyl)pyridine (5a) (65:35)





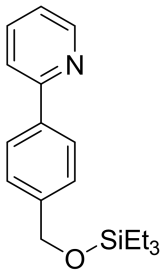
Mixture of 1-(4-(((triethylsilyl)oxy)methyl)phenyl)-1H-pyrazole (4b) and 1-(2-(triethylsilyl)-4-(((triethylsilyl)oxy)methyl)phenyl)-1H-pyrazole (5b) (30:70)

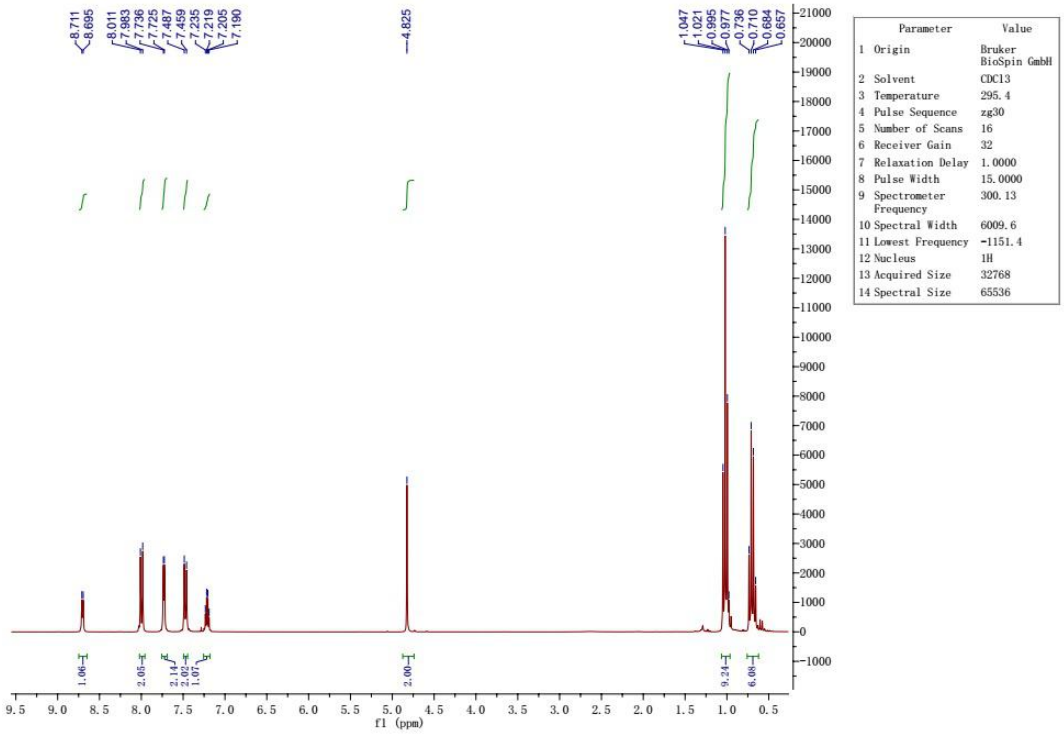




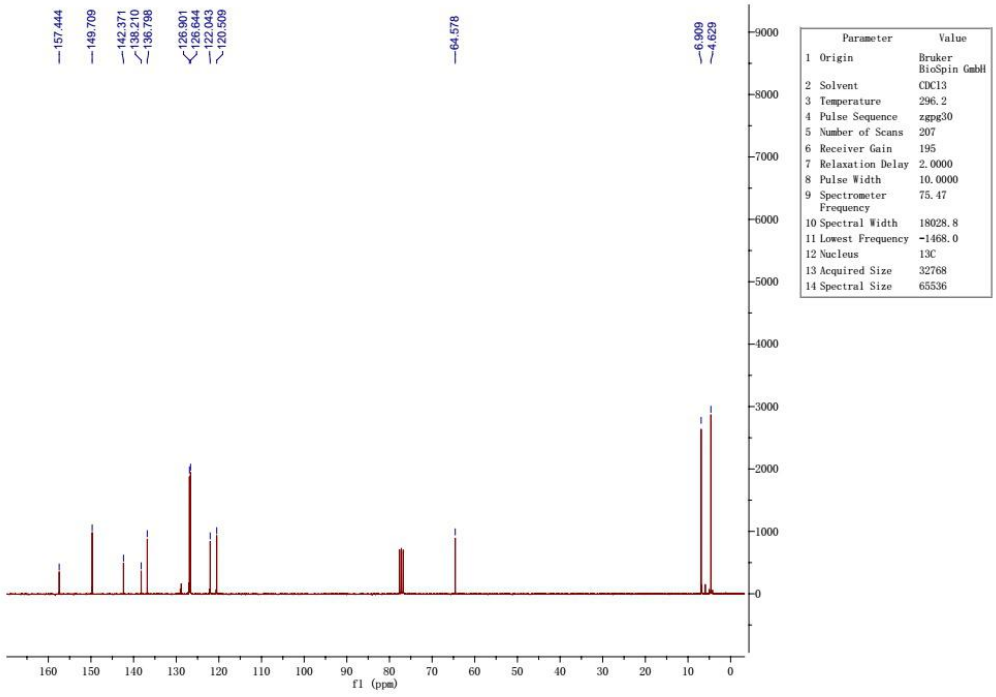
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Solvent	CDCl3
3	Temperature	296.1
4	Pulse Sequence	zg30
5	Number of Scans	16
6	Receiver Gain	32
7	Relaxation Delay	1.0000
8	Pulse Width	15.0000
9	Spectrometer Frequency	300.13
10	Spectral Width	6009.6
11	Lowest Frequency	-1054.0
12	Nucleus	1H
13	Acquired Size	32768
14	Spectral Size	65536

2-(4-((triethylsilyl)oxy)phenyl)pyridine (4c)



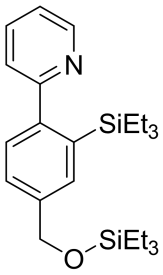


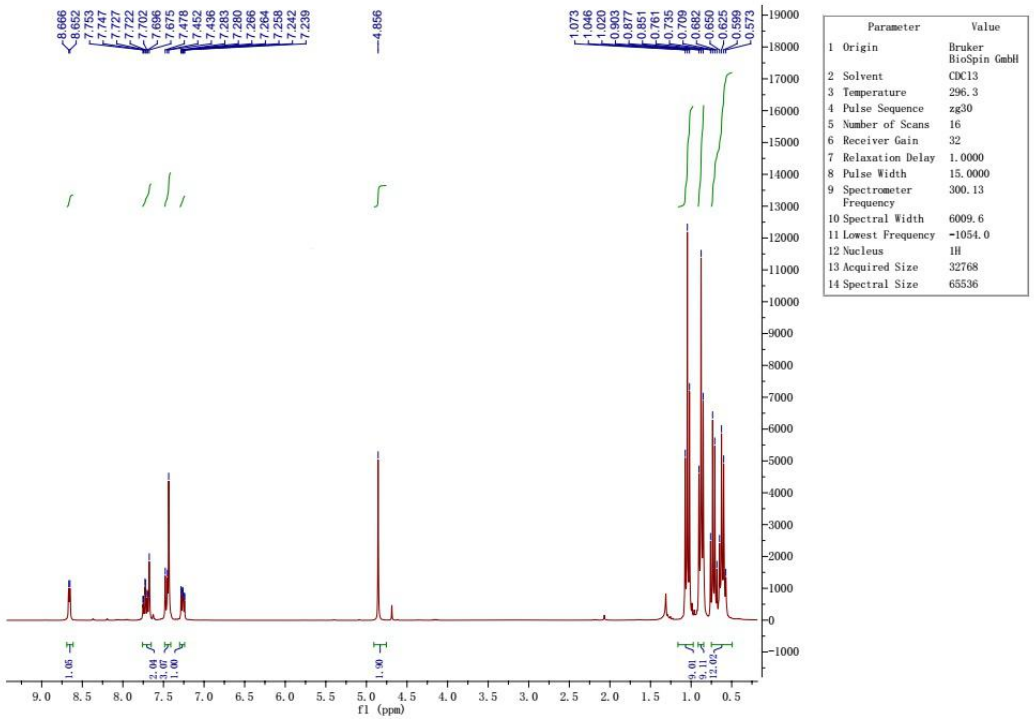
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Solvent	CDCl3
3	Temperature	295.4
4	Pulse Sequence	zg30
5	Number of Scans	16
6	Receiver Gain	32
7	Relaxation Delay	1.0000
8	Pulse Width	15.0000
9	Spectrometer Frequency	300.13
10	Spectral Width	6009.6
11	Lowest Frequency	-1151.4
12	Nucleus	1H
13	Acquired Size	32768
14	Spectral Size	65536



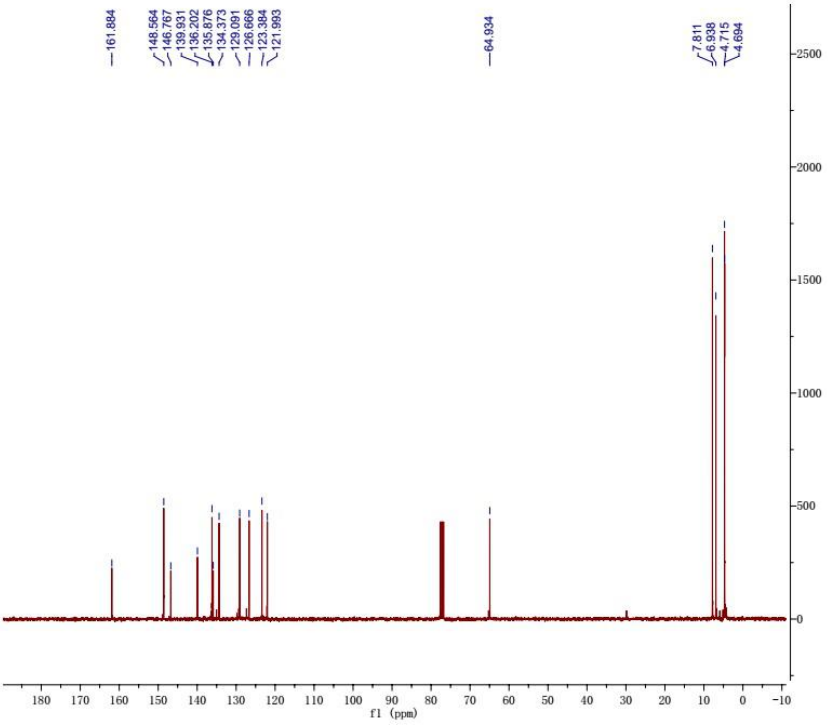
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Solvent	CDCl3
3	Temperature	296.2
4	Pulse Sequence	zgpg30
5	Number of Scans	207
6	Receiver Gain	195
7	Relaxation Delay	2.0000
8	Pulse Width	10.0000
9	Spectrometer Frequency	75.47
10	Spectral Width	18028.8
11	Lowest Frequency	-1468.0
12	Nucleus	13C
13	Acquired Size	32768
14	Spectral Size	65536

2-(2-(triethylsilyl)-4-((triethylsilyl)oxy)phenyl)pyridine (5c)





	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Solvent	CDCl3
3	Temperature	296.3
4	Pulse Sequence	zg30
5	Number of Scans	16
6	Receiver Gain	32
7	Relaxation Delay	1.0000
8	Pulse Width	15.0000
9	Spectrometer Frequency	300.13
10	Spectral Width	6009.6
11	Lowest Frequency	-1054.0
12	Nucleus	1H
13	Acquired Size	32768
14	Spectral Size	65536



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Solvent	CDCl3
3	Temperature	297.2
4	Pulse Sequence	zgpg30
5	Number of Scans	204
6	Receiver Gain	195
7	Relaxation Delay	2.0000
8	Pulse Width	10.0000
9	Spectrometer Frequency	75.47
10	Spectral Width	26315.8
11	Lowest Frequency	-1829.4
12	Nucleus	13C
13	Acquired Size	32768
14	Spectral Size	65536

8-((triethylsilyl)methyl)quinoline (6)