Supporting Information

Metal-Free C-3 Selective C(sp^2)-C(sp^3) Heteroarylation of Anilines with Imidazo[1,2-*a*]pyridine Derivatives *via* Cross-Dehydrogenative Coupling

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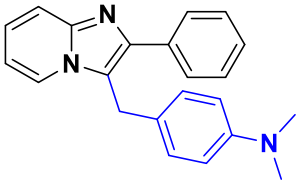
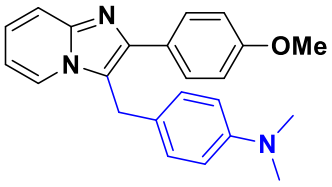
***N,N*-dimethyl-4-((2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (3a)**



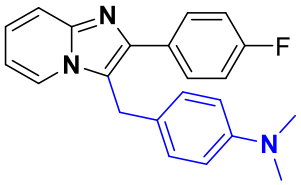
Obtained as a white solid in 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 6.7 Hz, 2H), 7.74 (d, J = 6.1 Hz, 1H), 7.68 (d, J = 8.9 Hz, 1H), 7.43 (t, J = 6.6 Hz, 2H), 7.35 (d, J = 7.3 Hz, 1H), 7.17 (t, J = 7.4 Hz, 1H), 7.01 (d, J = 7.7 Hz, 2H), 6.69 (dd, J = 8.9, 7.1 Hz, 3H), 4.40 (s, 2H), 2.92 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.63, 144.75, 143.71, 134.58, 128.63, 128.39, 128.27, 127.66, 124.13, 123.67, 118.54, 117.40, 113.15, 112.12, 40.66, 28.89. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{22}H_{22}N_3$: 328.1808, Found: 328.1801.

4-((2-(4-methoxyphenyl)imidazo[1,2-*a*]pyridin-3-yl)methyl)-*N,N*-dimethylaniline (3b)



Obtained as a white solid in 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (t, J = 9.0 Hz, 3H), 7.66 (d, J = 9.0 Hz, 1H), 7.14 (t, J = 7.8 Hz, 1H), 7.01-6.95 (m, 4H), 6.69-6.65 (m, 3H), 4.37 (s, 2H), 3.83 (s, 3H), 2.90 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.28, 149.58, 144.60, 143.53, 129.38, 128.35, 127.16, 124.22, 123.90, 123.50, 117.79, 117.15, 114.05, 113.11, 111.94, 55.27, 40.63, 28.86. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{23}H_{24}N_3O$: 358.1914, Found: 358.1918.

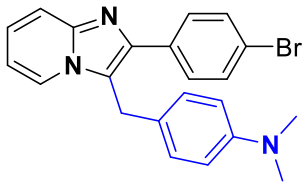
4-((2-(4-fluorophenyl)imidazo[1,2-*a*]pyridin-3-yl)methyl)-*N,N*-dimethylaniline (3c)



Obtained as a white solid in 54% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.75 (m, 3H), 7.70 (d, J = 9.1 Hz, 1H), 7.23-7.19 (m, 1H), 7.16-7.11 (m, 2H), 7.01 (d, J = 8.7 Hz, 2H), 6.76-6.72 (m, 1H), 6.69 (d, J = 8.7 Hz, 2H), 4.39 (s, 2H), 2.94 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.82 (d, $J_{C\text{-}F}$ = 246.0 Hz), 149.67, 144.59, 142.62, 130.50 (d, $J_{C\text{-}F}$ = 3.0 Hz), 129.94 (d, $J_{C\text{-}F}$ = 8.0 Hz), 128.31, 124.43, 123.82, 123.68, 118.36, 117.29, 115.70 (d, $J_{C\text{-}F}$ = 21.0 Hz), 113.14, 112.32, 40.64, 28.79. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.73. HRMS (ESI) ($[M+H]^+$)

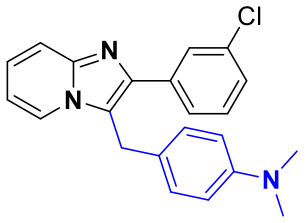
Calcd. for $C_{22}H_{21}N_3F$: 346.1714. Found: 346.1718.

4-((2-(4-bromophenyl)imidazo[1,2-*a*]pyridin-3-yl)methyl)-*N*,*N*-dimethylaniline (3d)



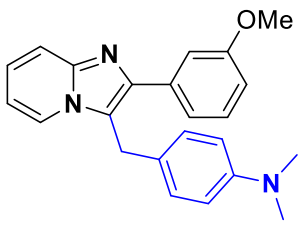
Obtained as a white solid in 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 6.8 Hz, 1H), 7.69 (t, J = 7.2 Hz, 3H), 7.56 (d, J = 8.3 Hz, 2H), 7.23-7.15 (m, 1H), 7.00 (d, J = 8.3 Hz, 2H), 6.76-6.65 (m, 3H), 4.38 (s, 2H), 2.93 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.64, 144.75, 142.49, 133.54, 131.71, 129.69, 128.27, 124.36, 123.70, 123.62, 121.78, 118.72, 117.39, 113.10, 112.26, 40.59, 28.80. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{22}H_{21}BrN_3$: 406.0913, Found: 406.0919.

4-((2-(3-chlorophenyl)imidazo[1,2-*a*]pyridin-3-yl)methyl)-*N*,*N*-dimethylaniline (3e)



Obtained as a white solid in 55% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.77 (d, J = 6.8 Hz, 1H), 7.73-7.64 (m, 2H), 7.39-7.31 (m, 2H), 7.21 (t, J = 7.5 Hz, 1H), 7.00 (d, J = 7.7 Hz, 2H), 6.73 (t, J = 6.8 Hz, 1H), 6.69 (d, J = 7.4 Hz, 2H), 4.40 (s, 2H), 2.93 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.65, 144.70, 142.10, 136.35, 134.61, 129.81, 128.33, 128.26, 127.69, 126.18, 124.53, 123.72, 123.70, 119.09, 117.43, 113.14, 112.38, 40.61, 28.81. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{22}H_{21}ClN_3$: 362.1419, Found: 362.1411.

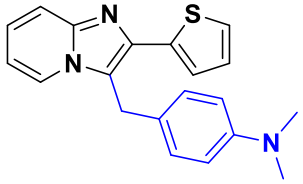
4-((2-(3-methoxyphenyl)imidazo[1,2-a]pyridin-3-yl)methyl)-*N*,*N*-dimethylaniline (3f)



Obtained as a white solid in 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 6.9 Hz, 1H), 7.70 (d, J = 9.1 Hz, 1H), 7.44 (d, J = 2.0 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1H),

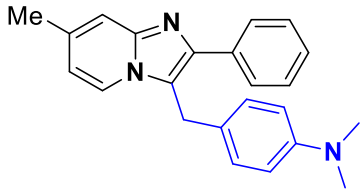
7.33 (t, *J* = 7.8 Hz, 1H), 7.21-7.14 (m, 1H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.95-6.90 (m, 1H), 6.69 (dd, *J* = 10.1, 7.8 Hz, 3H), 4.42 (s, 2H), 3.83 (s, 3H), 2.92 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.88, 149.61, 144.69, 143.63, 136.04, 129.57, 128.38, 124.18, 124.09, 123.64, 120.60, 118.75, 117.42, 114.04, 113.15, 112.11, 55.32, 40.66, 28.91. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{23}H_{24}N_3O$: 358.1914, Found: 358.1918.

_N,N_-dimethyl-4-((2-(thiophen-2-yl)imidazo[1,2-a]pyridin-3-yl)methyl)aniline (3g)



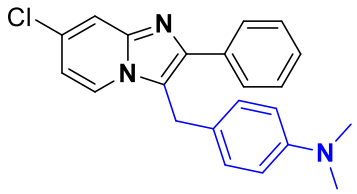
Obtained as a white solid in 52% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.74 (m, 1H), 7.66 (d, *J* = 9.1 Hz, 1H), 7.46-7.43 (m, 1H), 7.35 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.18-7.14 (m, 1H), 7.10 (dd, *J* = 5.1, 3.6 Hz, 1H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.71-6.65 (m, 3H), 4.45 (s, 2H), 2.91 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.65, 144.66, 138.21, 137.76, 128.48, 127.74, 125.43, 124.51, 124.33, 123.74, 123.40, 118.26, 117.24, 113.09, 112.25, 40.65, 28.90. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{20}H_{20}N_3S$: 334.1372, Found: 334.1377.

_N,N_-dimethyl-4-((7-methyl-2-phenylimidazo[1,2-a]pyridin-3-yl)methyl)aniline (3h)



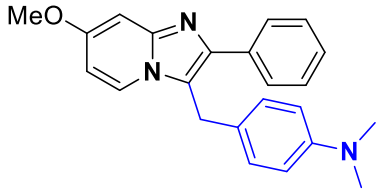
Obtained as a white solid in 50% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.76 (m, 2H), 7.61 (d, *J* = 7.0 Hz, 1H), 7.42 (dd, *J* = 12.8, 5.3 Hz, 3H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.67 (d, *J* = 8.7 Hz, 2H), 6.53 (dd, *J* = 7.0, 1.5 Hz, 1H), 4.37 (s, 2H), 2.91 (s, 6H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.59, 145.07, 143.12, 135.21, 134.58, 128.60, 128.38, 128.17, 127.55, 124.35, 122.91, 117.91, 115.74, 114.81, 113.13, 40.68, 28.85, 21.37. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{23}H_{24}N_3$: 342.1965, Found: 342.1970.

4-((7-chloro-2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)-*N*,*N*-dimethylaniline (3i)



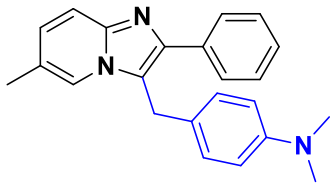
Obtained as a white solid in 38% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.75 (m, 2H), 7.69-7.62 (m, 2H), 7.47-7.36 (m, 3H), 7.02-6.96 (m, 2H), 6.71-6.63 (m, 3H), 4.40 (s, 2H), 2.94 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.68, 144.52, 144.39, 134.08, 130.68, 128.68, 128.32, 128.19, 127.91, 123.98, 123.55, 118.86, 116.19, 113.70, 113.14, 40.61, 28.82. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{22}H_{21}ClN_3$: 362.1419, Found: 362.1410.

4-((7-methoxy-2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)-*N*,*N*-dimethylaniline (3j)



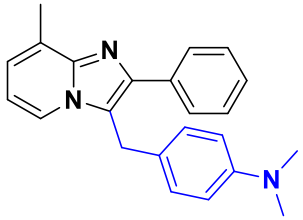
Obtained as a white solid in 55% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.78 (m, 2H), 7.57 (d, J = 7.5 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 7.34 (t, J = 7.3 Hz, 1H), 7.04-7.00 (m, 3H), 6.69 (d, J = 8.6 Hz, 2H), 6.44 (dd, J = 7.4, 2.3 Hz, 1H), 4.37 (s, 2H), 3.88 (s, 3H), 2.93 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.80, 149.62, 146.02, 142.77, 134.58, 128.58, 128.38, 127.98, 127.46, 124.41, 124.19, 117.32, 113.15, 107.14, 94.62, 55.52, 40.67, 28.82. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{23}H_{24}N_3O$: 358.1914, Found: 358.1910.

***N*,*N*-dimethyl-4-((6-methyl-2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (3k)**



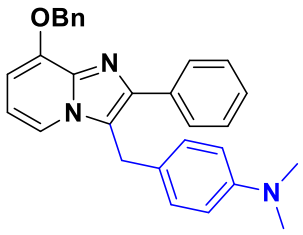
Obtained as a white solid in 48% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 7.3 Hz, 2H), 7.60 (d, J = 9.1 Hz, 1H), 7.55 (s, 1H), 7.43 (t, J = 7.4 Hz, 2H), 7.39-7.32 (m, 1H), 7.04 (d, J = 8.5 Hz, 3H), 6.71 (d, J = 8.5 Hz, 2H), 4.39 (s, 2H), 2.94 (s, 6H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.54, 143.77, 143.40, 134.66, 128.55, 128.34, 128.07, 127.47, 127.30, 124.35, 121.71, 121.16, 118.21, 116.68, 113.11, 40.64, 28.81, 18.42. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{23}H_{24}N_3$: 342.1965, Found: 342.1960.

***N*,*N*-dimethyl-4-((8-methyl-2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (3m)**



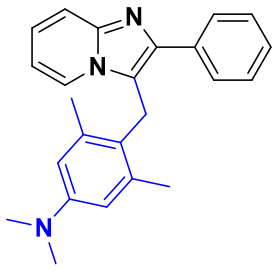
Obtained as a white solid in 47% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 7.2 Hz, 2H), 7.64 (d, J = 6.8 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.36 (t, J = 7.4 Hz, 1H), 7.03 (d, J = 8.6 Hz, 2H), 6.98 (d, J = 6.8 Hz, 1H), 6.70 (d, J = 8.6 Hz, 2H), 6.63 (t, J = 6.8 Hz, 1H), 4.39 (s, 2H), 2.93 (s, 6H), 2.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.53, 145.16, 143.34, 134.89, 128.54, 128.41, 128.38, 127.44, 127.31, 124.50, 122.83, 121.50, 118.83, 113.09, 112.02, 40.65, 28.95, 17.19. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{23}H_{24}N_3$: 342.1965, Found: 342.1970.

4-((8-(benzyloxy)-2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)-*N*,*N*-dimethylaniline (3n)



Obtained as a white solid in 51% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, J = 5.2, 3.3 Hz, 2H), 7.54 (d, J = 7.2 Hz, 2H), 7.46-7.32 (m, 7H), 7.03 (d, J = 8.7 Hz, 2H), 6.69 (dd, J = 9.2, 2.3 Hz, 2H), 6.55-6.50 (m, 1H), 6.46 (d, J = 7.0 Hz, 1H), 5.43 (s, 2H), 4.39 (s, 2H), 2.93 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.52, 147.85, 143.04, 139.26, 136.51, 134.59, 128.58, 128.45, 128.40, 128.38, 127.93, 127.45, 127.21, 124.40, 119.52, 116.80, 113.08, 111.82, 102.77, 70.67, 40.64, 29.05. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{29}H_{28}N_3O$: 434.2227, Found: 434.2222.

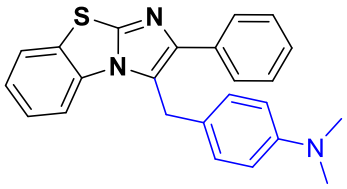
***N*,*N*,3,5-tetramethyl-4-((2-phenylimidazo[1,2-*a*]pyridin-3-yl)methyl)aniline (3o)**



Obtained as a white solid in 45% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.74 (m, 2H), 7.64-7.61 (m, 1H), 7.55-7.53 (m, 1H), 7.48-7.45 (m, 2H), 7.40 – 7.34 (m, 1H), 7.10-7.06 (m, 1H), 6.58 (td, J = 6.9, 1.2 Hz, 1H), 6.40 (s, 2H), 4.47 (s, 2H), 2.91 (s, 6H), 2.10 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.31, 144.33, 143.32, 137.59, 135.00, 128.94, 128.29, 127.37, 123.99, 123.27, 120.96, 118.98, 117.36, 113.26, 111.89, 40.57, 25.00, 21.19.

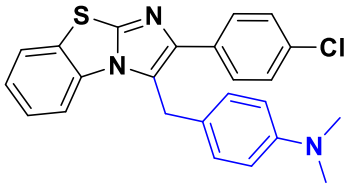
HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{24}H_{26}N_3$: 356.2121, Found: 356.2127.

_N,N_-dimethyl-4-((2-phenylbenzo[_d_]imidazo[2,1-_b_]thiazol-3-yl)methyl)aniline (3p)



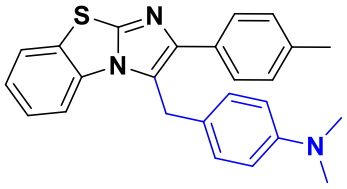
Obtained as a white solid in 54% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.00-7.95 (m, 1H), 7.67-7.61 (m, 2H), 7.55-7.51 (m, 1H), 7.42-7.38 (m, 2H), 7.35-7.29 (m, 3H), 7.01 (d, J = 8.7 Hz, 2H), 6.66 (d, J = 8.8 Hz, 2H), 4.53 (s, 2H), 2.81 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.69, 146.46, 144.30, 134.77, 132.78, 129.85, 129.08, 128.43, 127.61, 127.30, 126.86, 125.36, 125.11, 124.97, 123.40, 113.90, 113.47, 29.42. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{24}H_{22}N_3S$: 384.1529, Found: 384.1533.

4-((2-(4-chlorophenyl)benzo[_d_]imidazo[2,1-_b_]thiazol-3-yl)methyl)-_N,N_-dimethylanili_ne_ (3q)



Obtained as a white solid in 48% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.59 (m, 3H), 7.43-7.41 (m, 1H), 7.33 (d, J = 8.3 Hz, 2H), 7.25-7.21 (m, 2H), 7.10 (d, J = 8.4 Hz, 2H), 6.72 (d, J = 8.5 Hz, 2H), 4.49 (s, 2H), 2.92 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.49, 147.14, 144.01, 133.05, 132.91, 130.36, 129.62, 128.73, 128.62, 128.29, 126.14, 124.38, 124.12, 122.71, 113.52, 113.36, 40.66, 29.90. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{24}H_{21}ClN_3S$: 418.1139, Found: 418.1130.

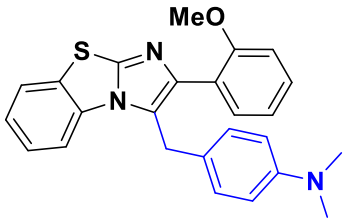
_N,N_-dimethyl-4-((2-(_p_-tolyl)benzo[_d_]imidazo[2,1-_b_]thiazol-3-yl)methyl)aniline (3r)



Obtained as a white solid in 59% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.65 (m, 3H), 7.52-7.49 (m, 1H),7.34-7.29 (m, 4H), 7.22 (d, J = 7.1 Hz, 2H), 6.81 (d, J = 6.8 Hz, 2H), 4.60 (s, 2H), 3.01 (s, 6H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 144.76, 142.10, 140.50, 132.22, 128.35, 126.88, 125.63, 124.55, 123.64, 122.62, 121.30, 120.58, 119.41, 119.32,

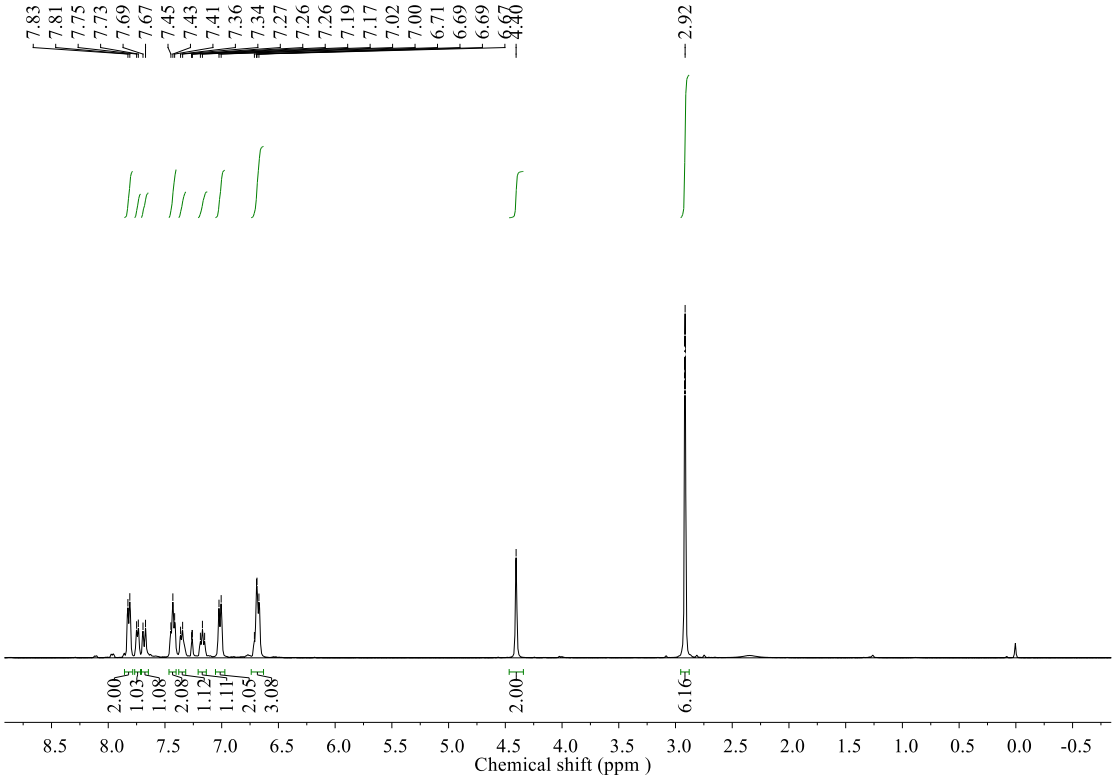
117.46, 108.74, 108.55, 35.93, 25.24, 16.53. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{25}H_{24}N_3S$: 398.1685, Found: 398.1691.

4-((2-(2-methoxyphenyl)benzo[*d*]imidazo[2,1-*b*]thiazol-3-yl)methyl)-*N*,*N*-dimethylaniline (3s)

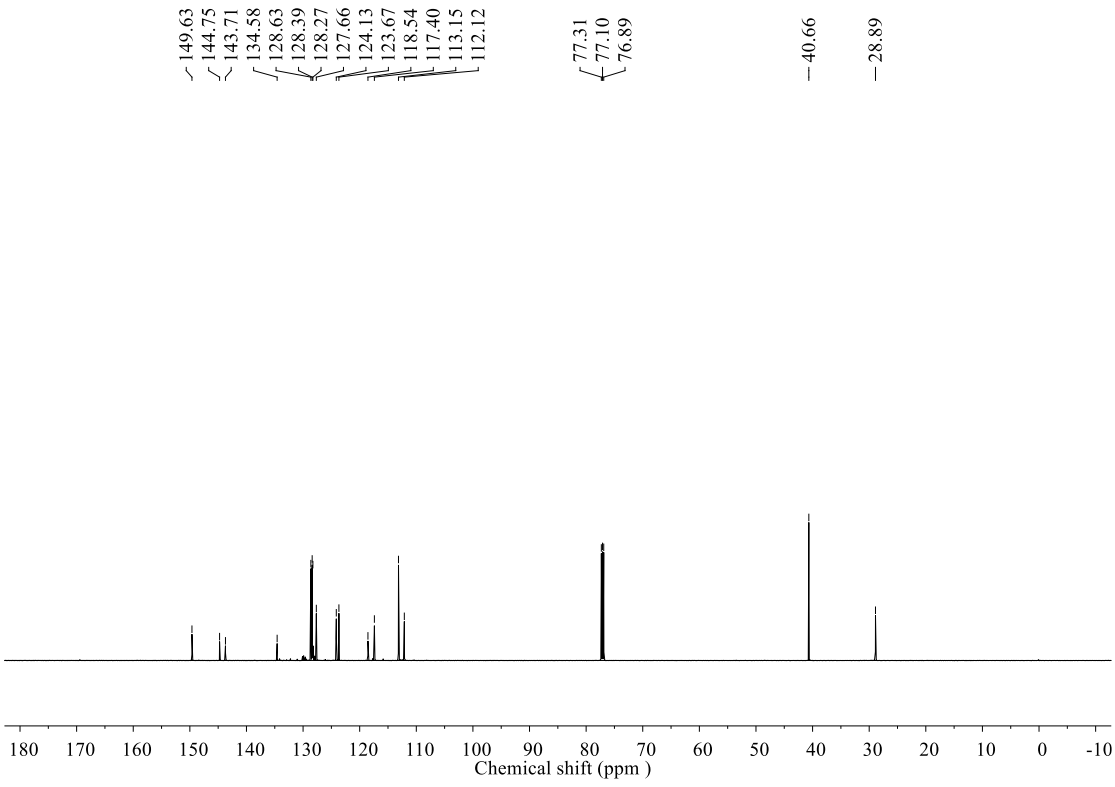


Obtained as a white solid in 40% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.63 (m, 1H),7.65-7.54 (m, 1H), 7.42-7.38 (m, 1H), 7.36-7.31 (m, 1H), 7.20-7.15 (m, 2H), 7.08 (d, J = 8.5 Hz, 2H), 7.02 (t, J = 7.4 Hz, 1H), 6.97 (d, J = 8.3 Hz, 1H), 6.69 (d, J = 8.6 Hz, 2H), 4.34 (s, 2H), 3.67 (s, 3H), 2.91 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.15, 149.27, 146.69, 142.17, 133.16, 131.90, 130.33, 129.18, 128.43, 126.12, 125.89, 124.25, 124.00, 123.92, 123.46, 120.57, 113.80, 113.13, 110.89, 55.28, 40.76, 30.01. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{25}H_{24}N_3OS$: 414.1635, Found: 414.1631.

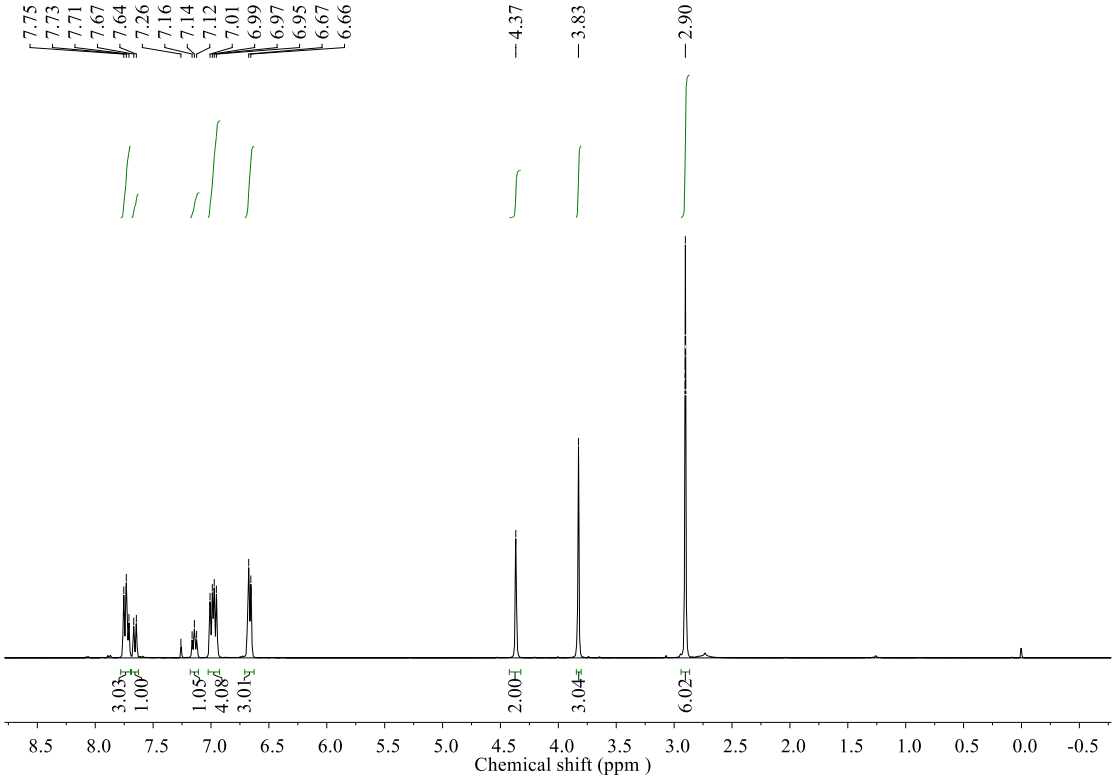
3a ^{1}H NMR



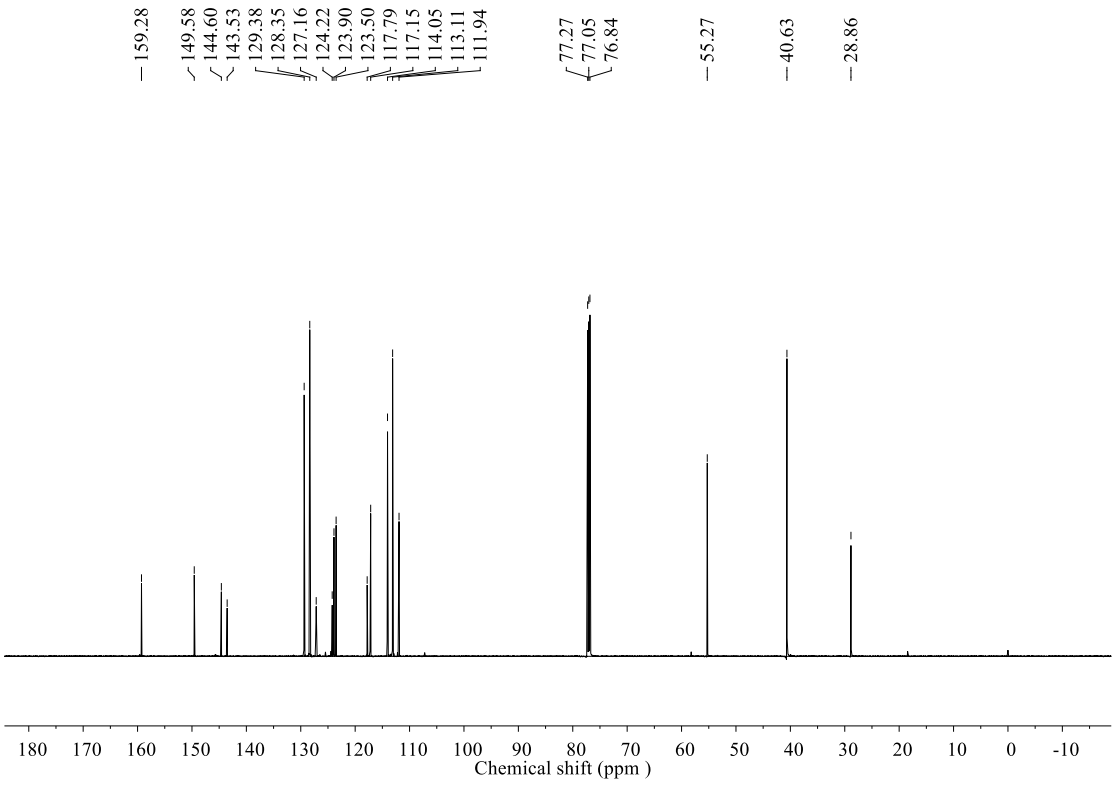
3a ^{13}C NMR



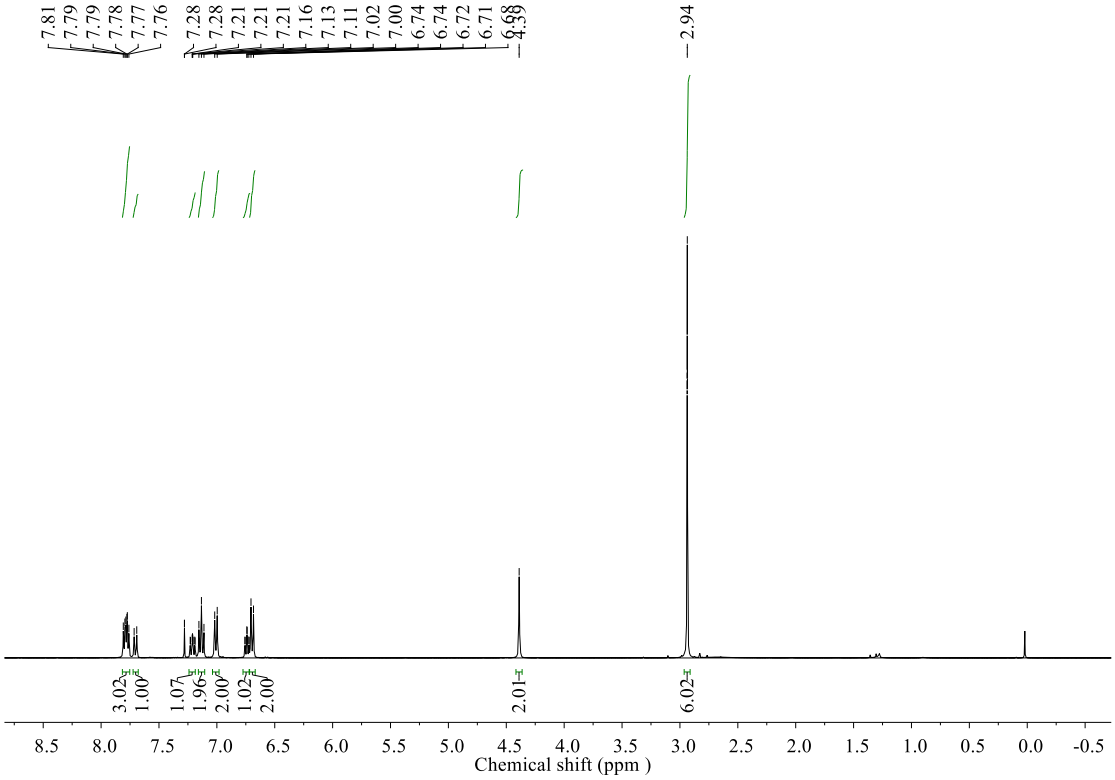
3b ^{1}H NMR



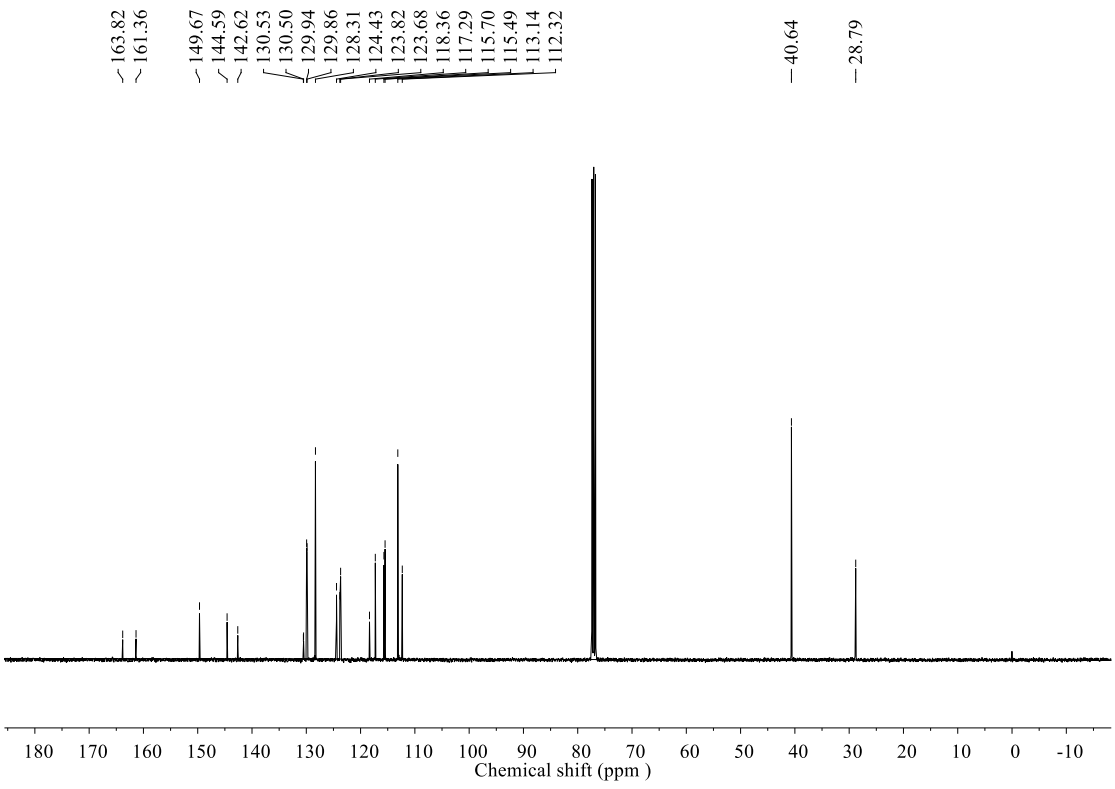
3b ^{13}C NMR



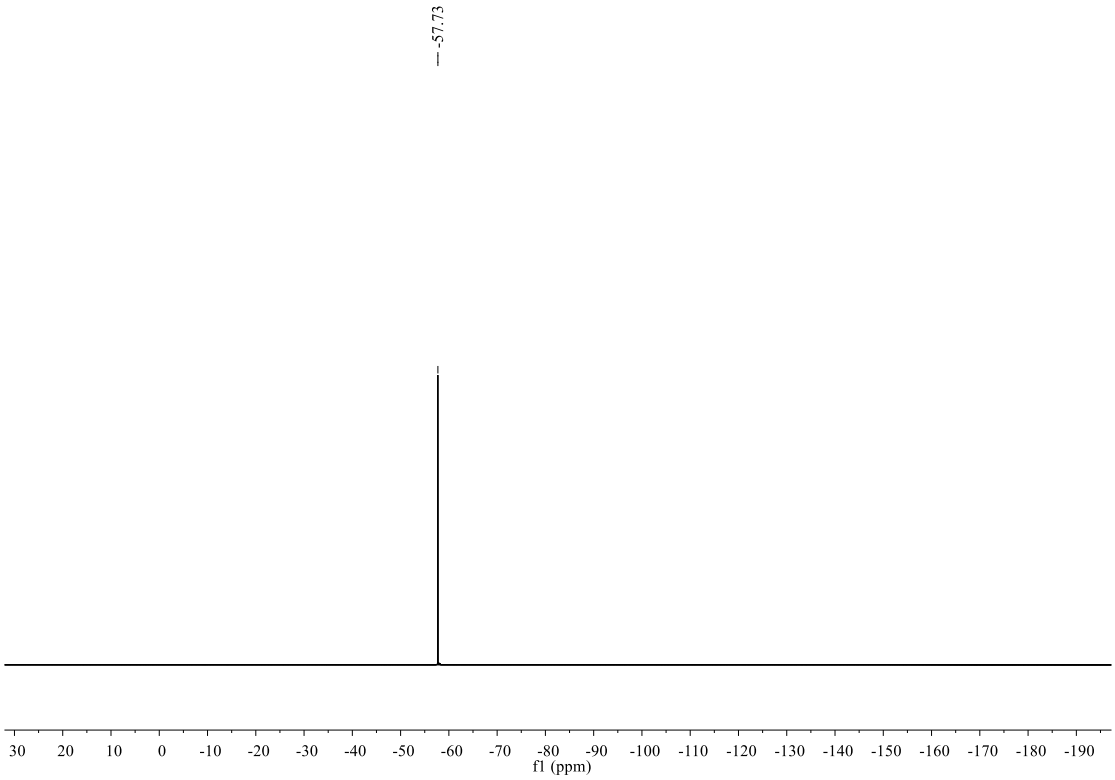
3c ^{1}H NMR



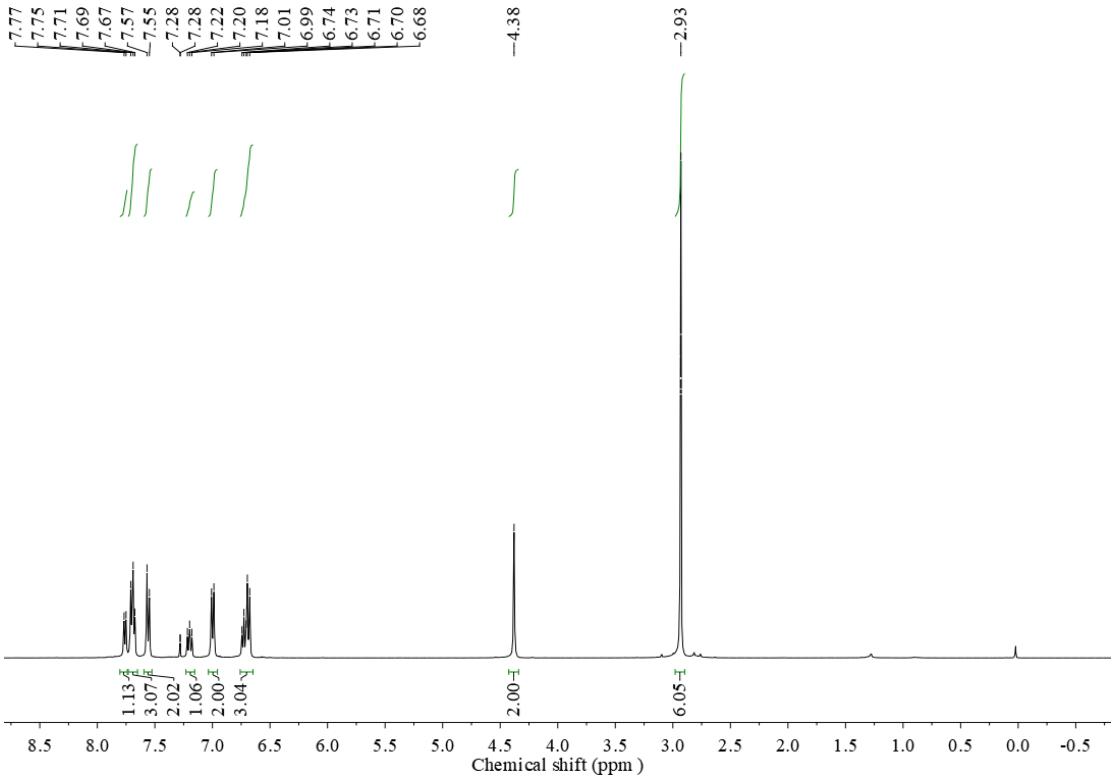
3c ^{13}C NMR



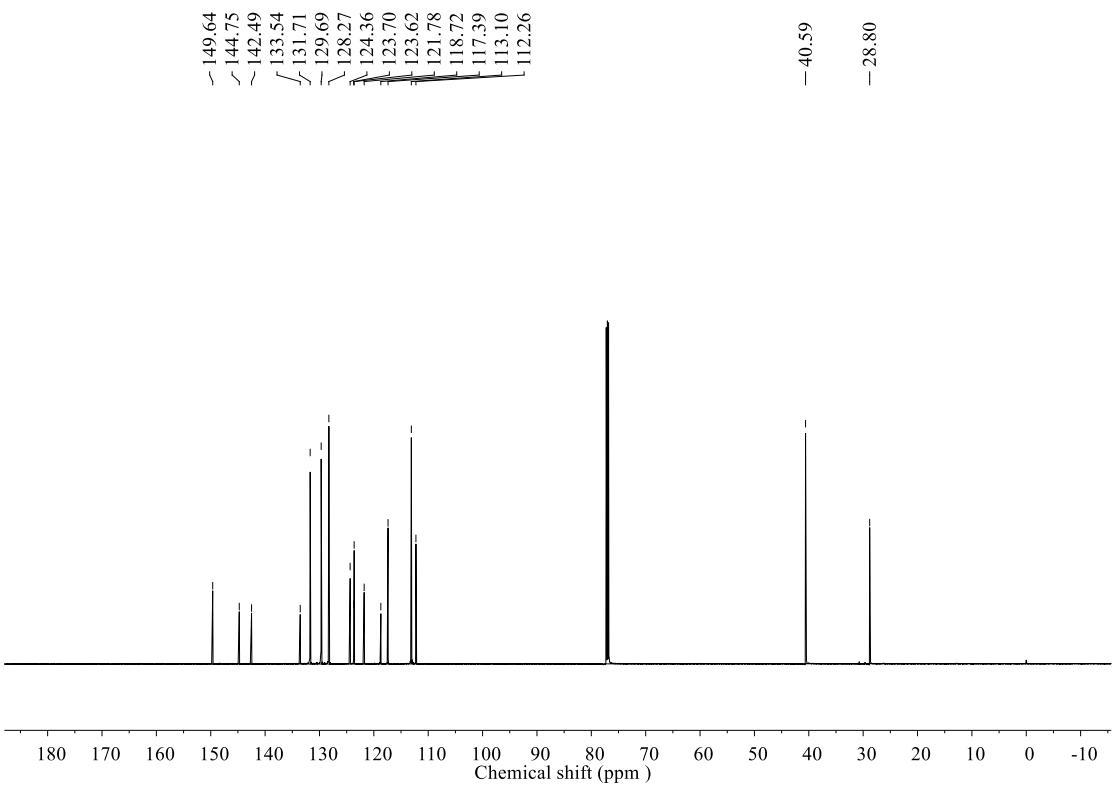
3c ^{19}F NMR


-57.73
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

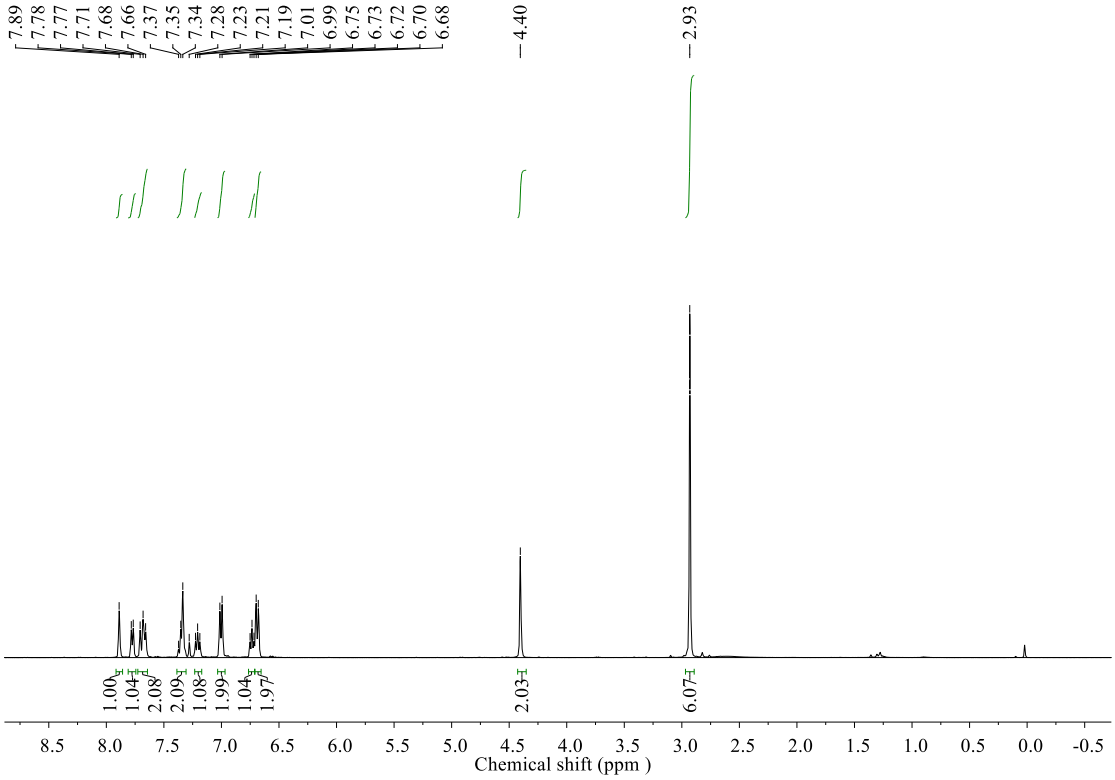
3d ^{1}H NMR



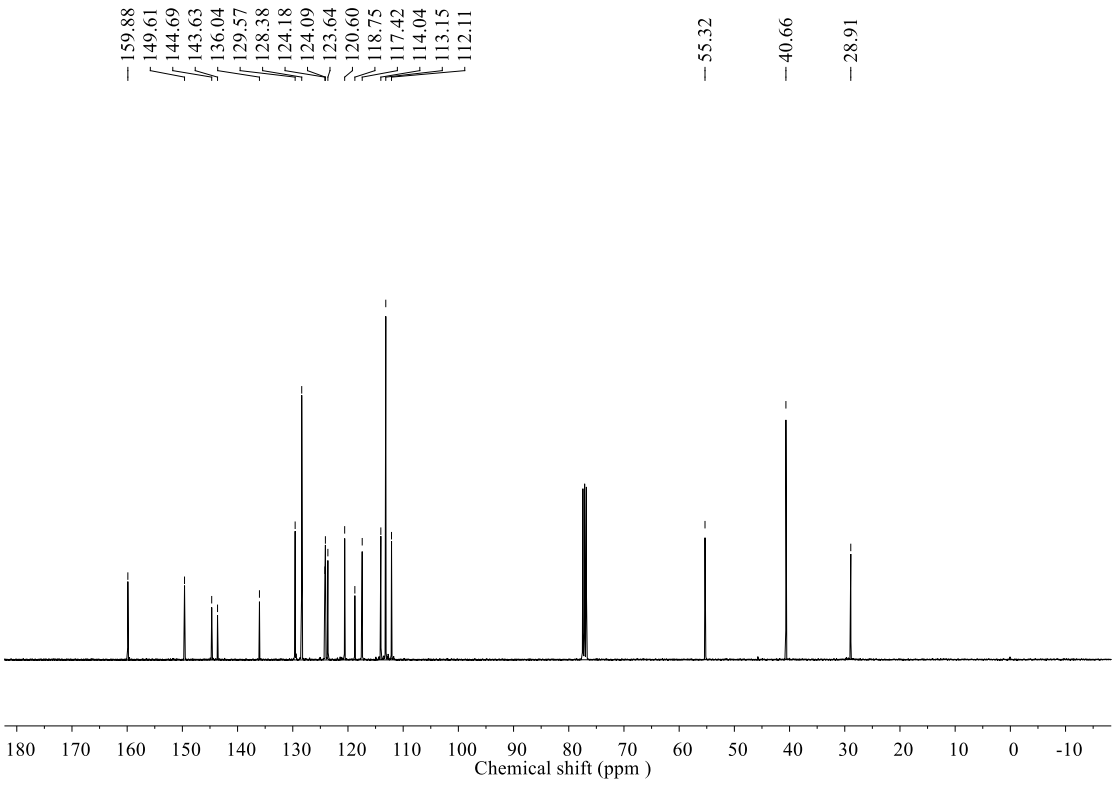
3d ^{13}C NMR



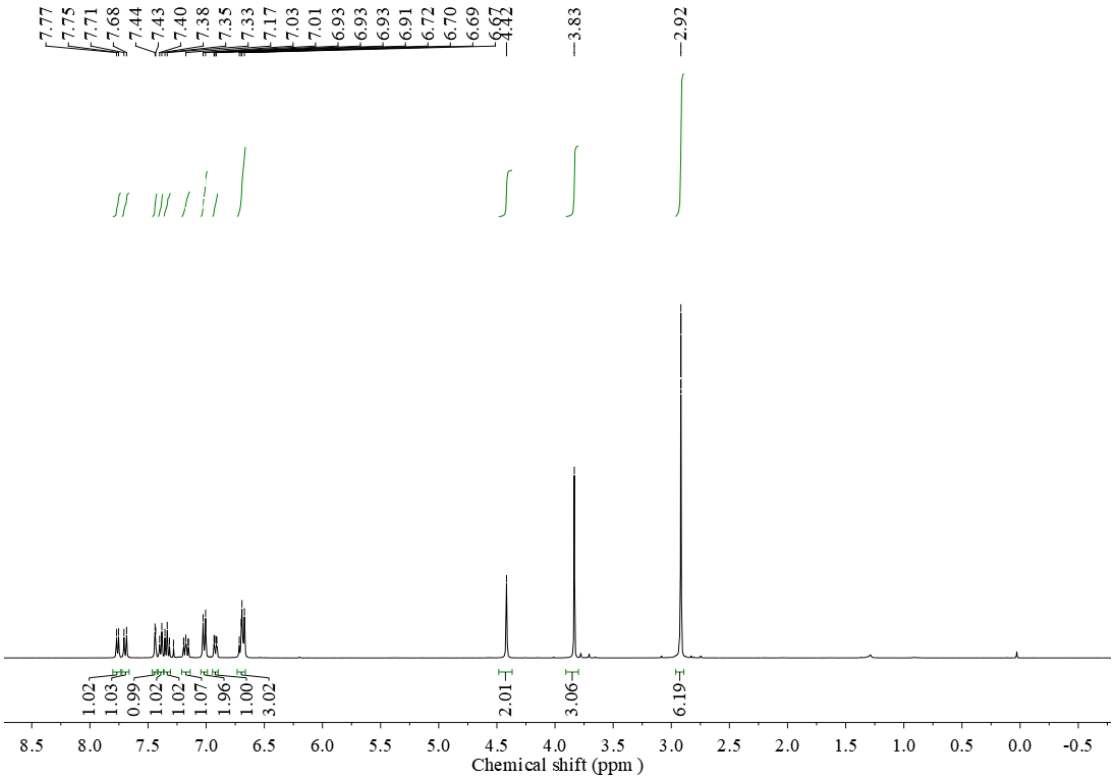
3e ^{1}H NMR



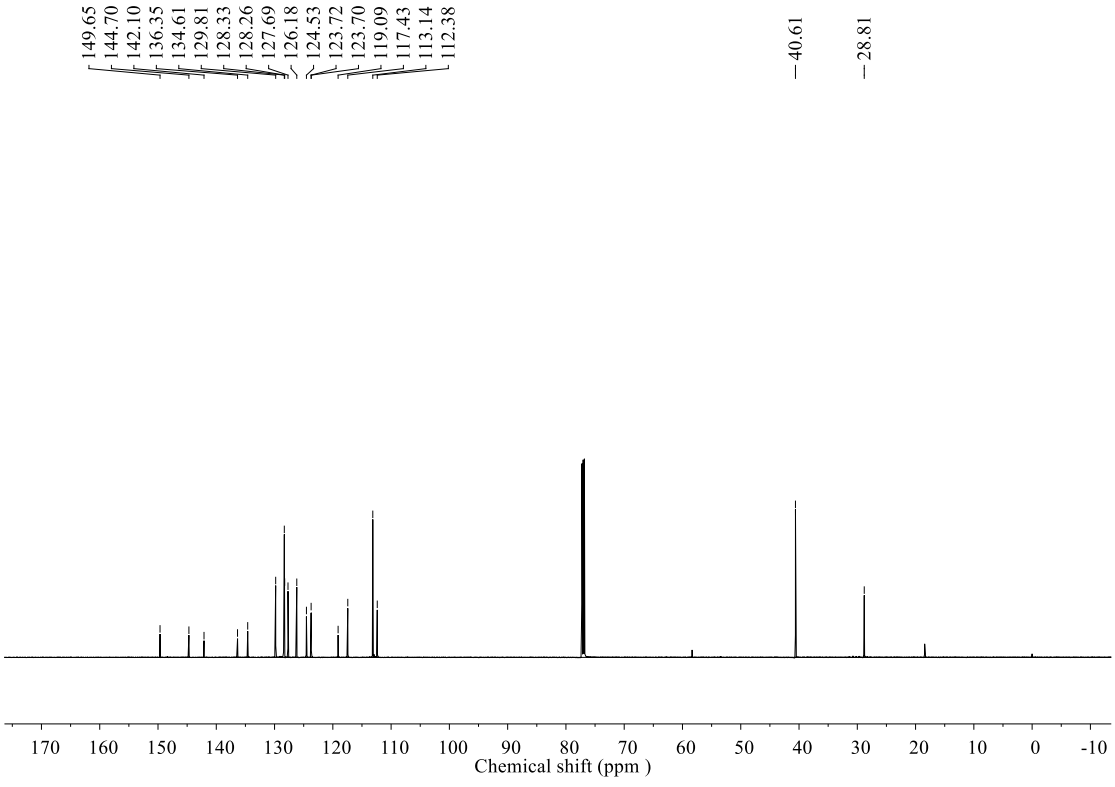
3e ^{13}C NMR



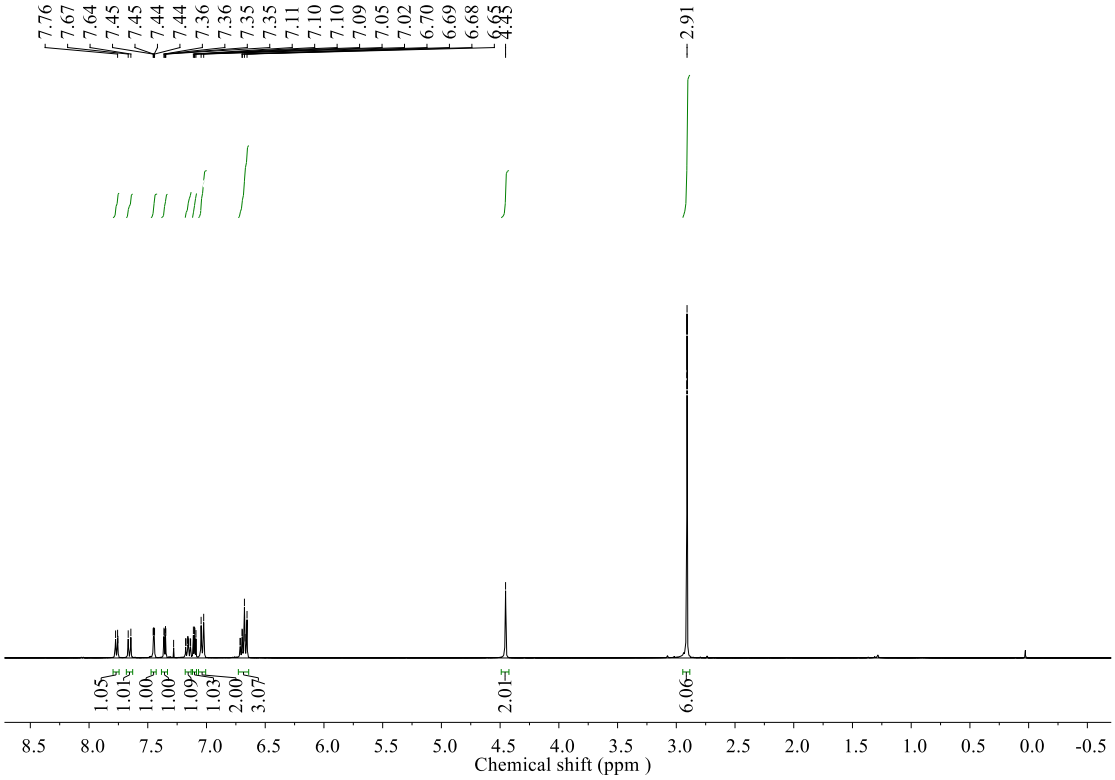
3f ^{1}H NMR



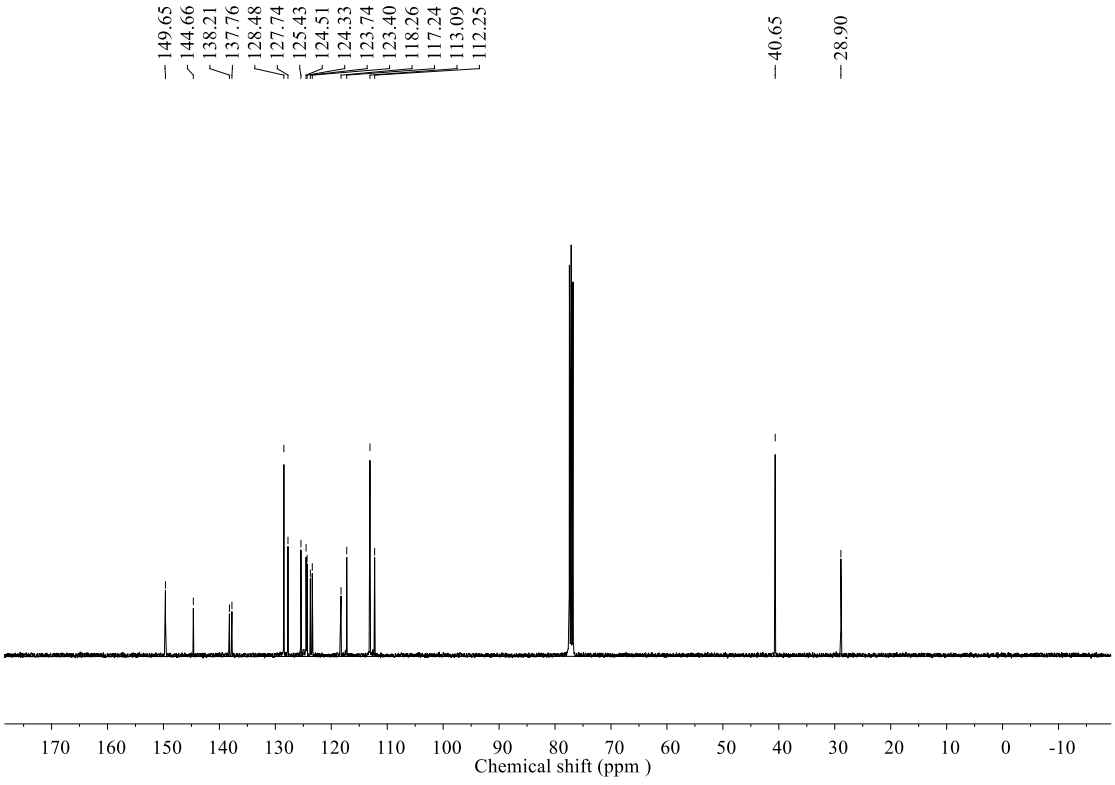
3f ^{13}C NMR



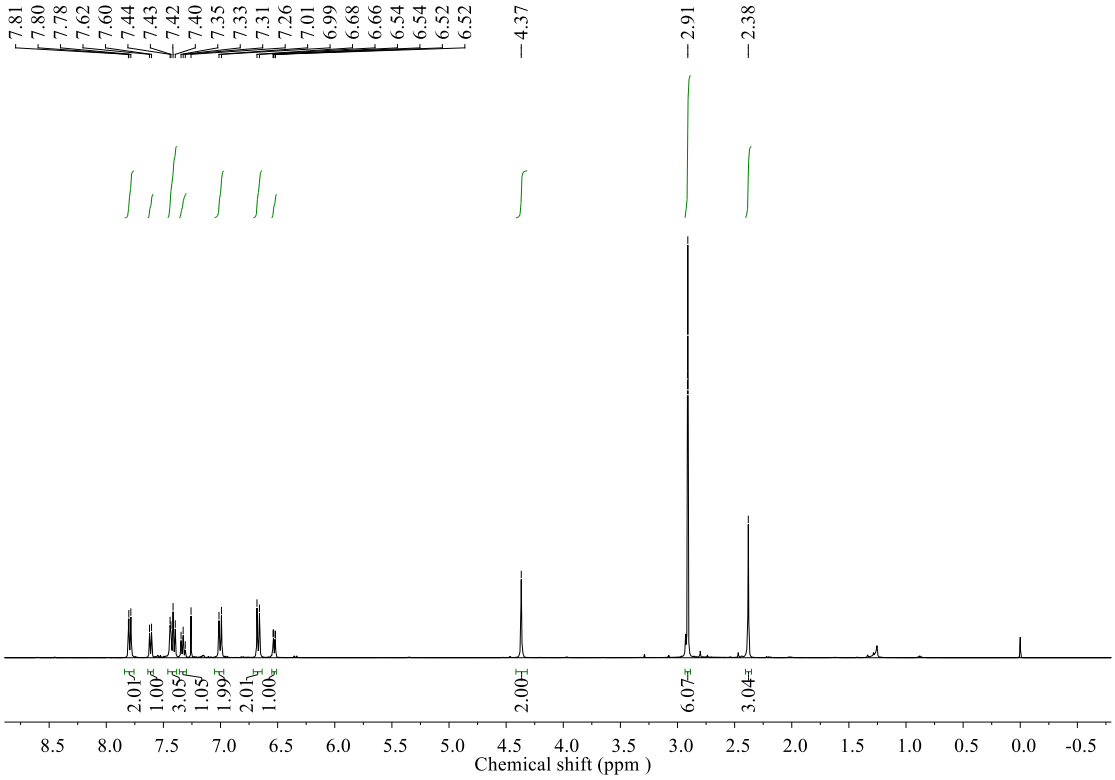
3g ^{1}H NMR



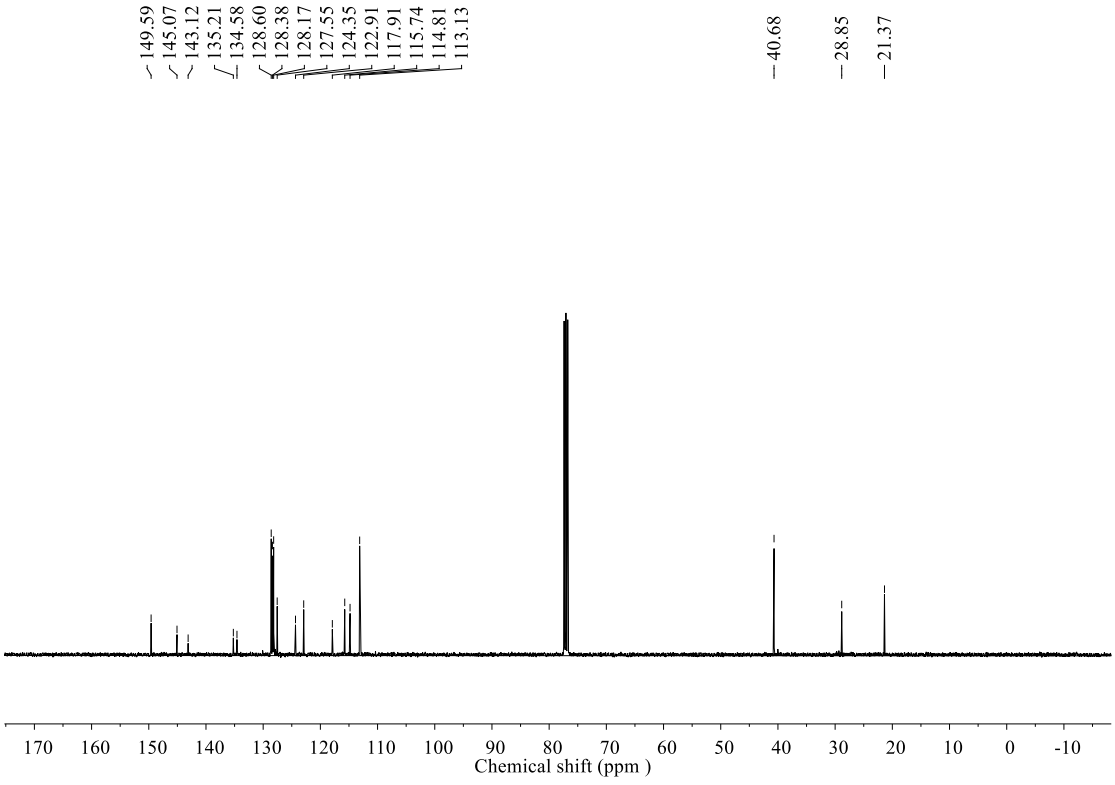
3g ^{13}C NMR



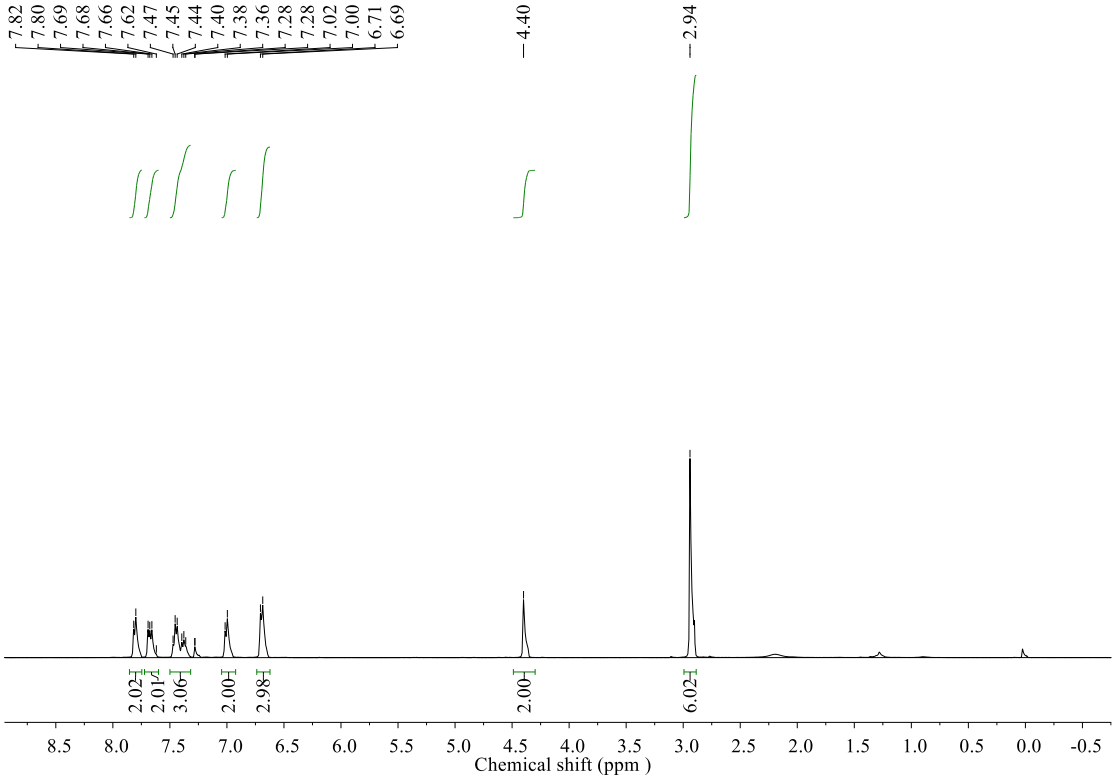
3h ^{1}H NMR



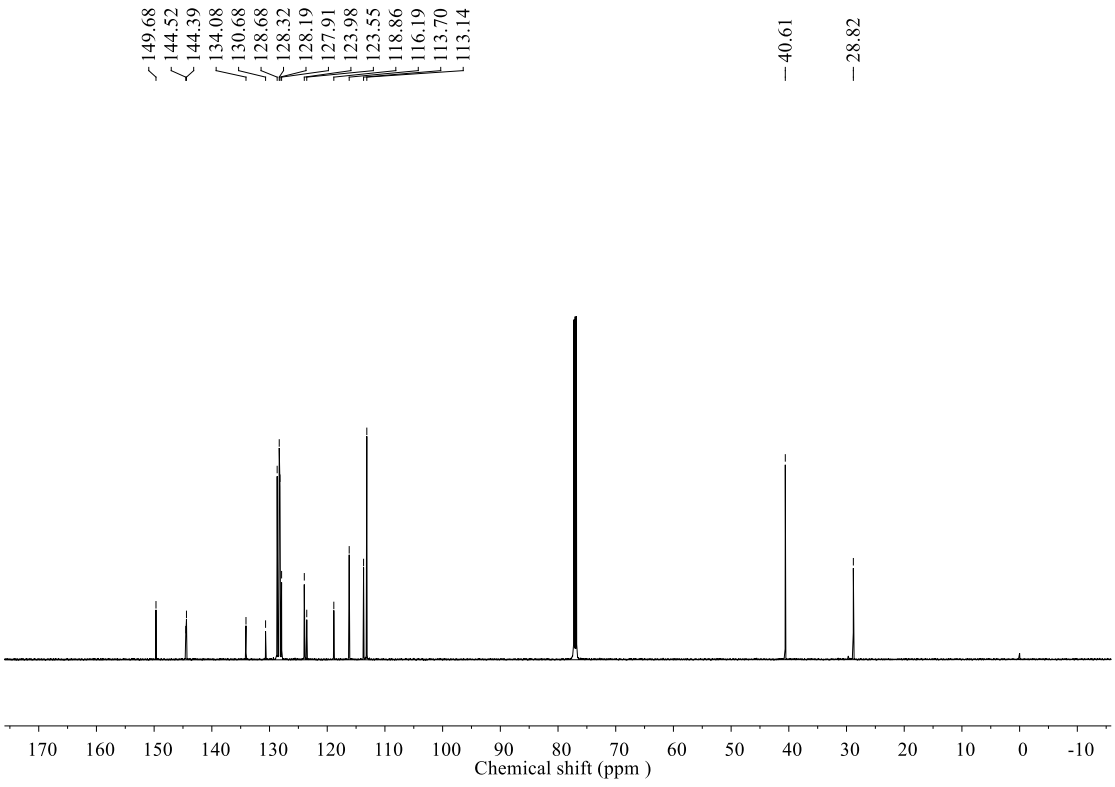
3h ^{13}C NMR



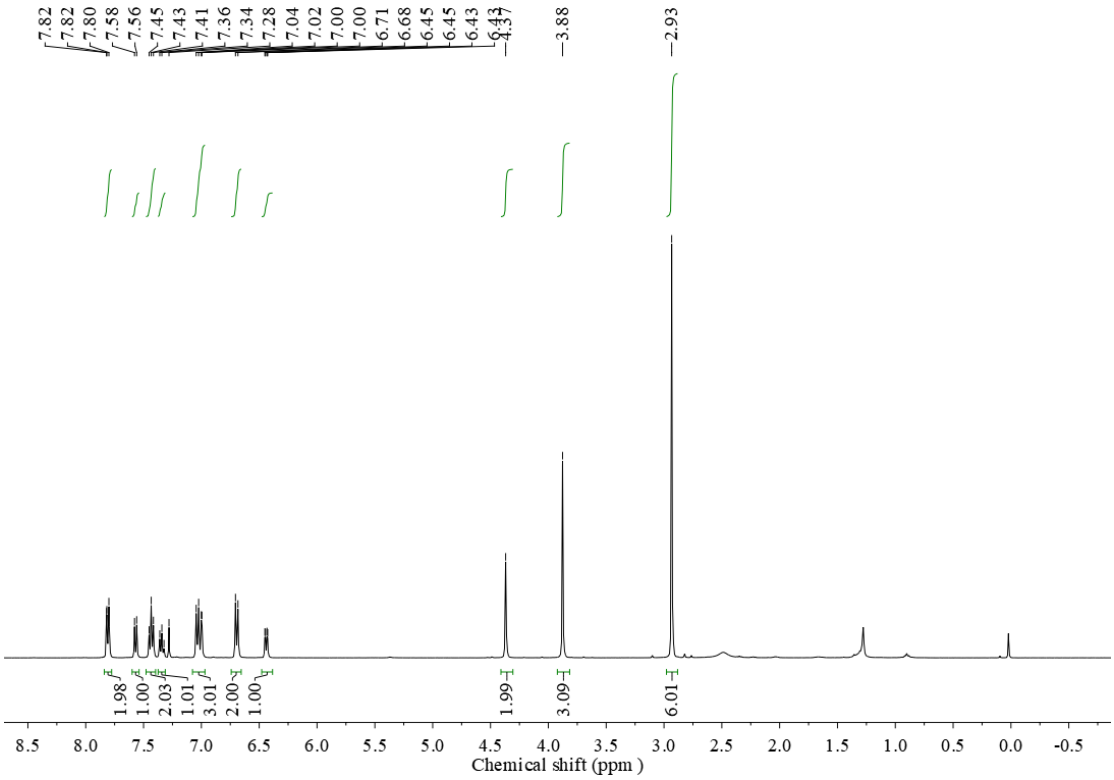
3i ^{1}H NMR



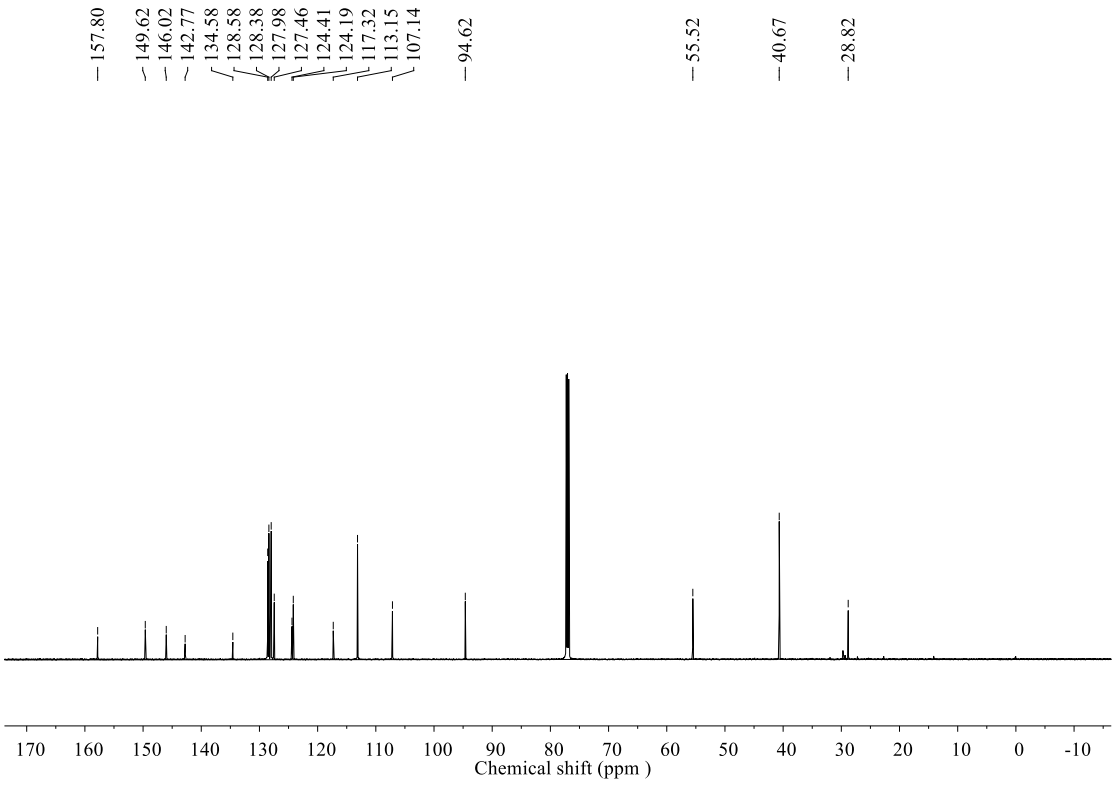
3i ^{13}C NMR



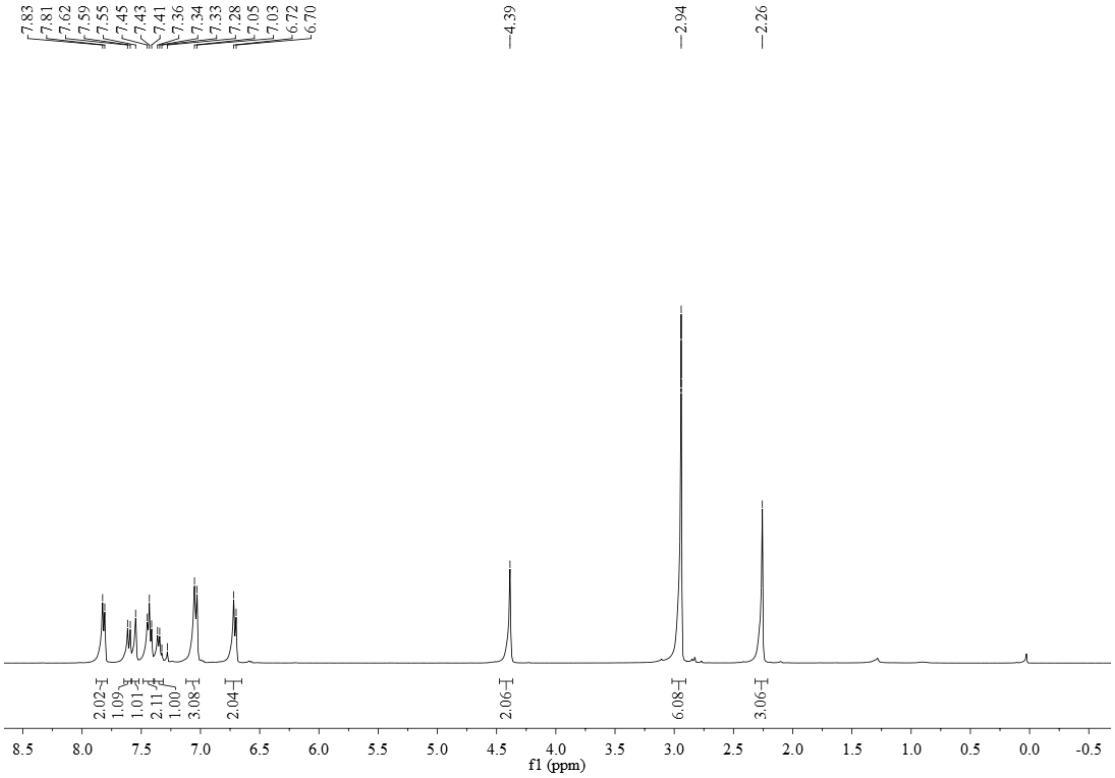
3j ^{1}H NMR



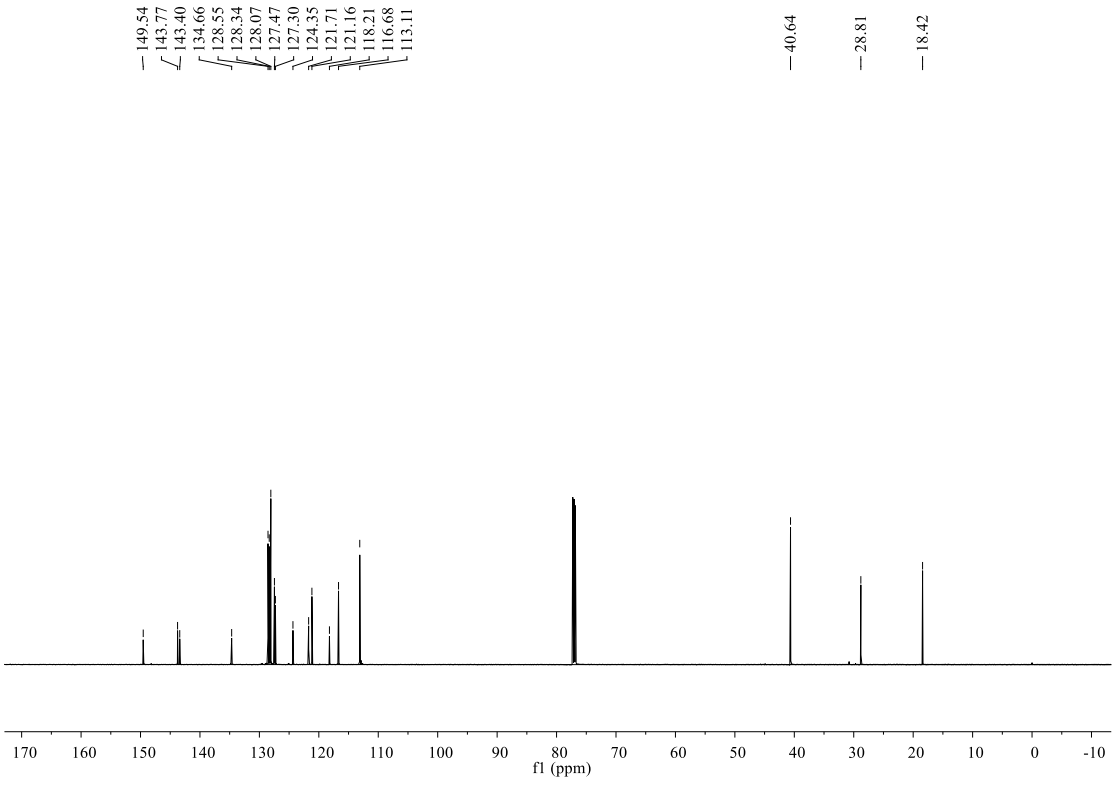
3j ^{13}C NMR



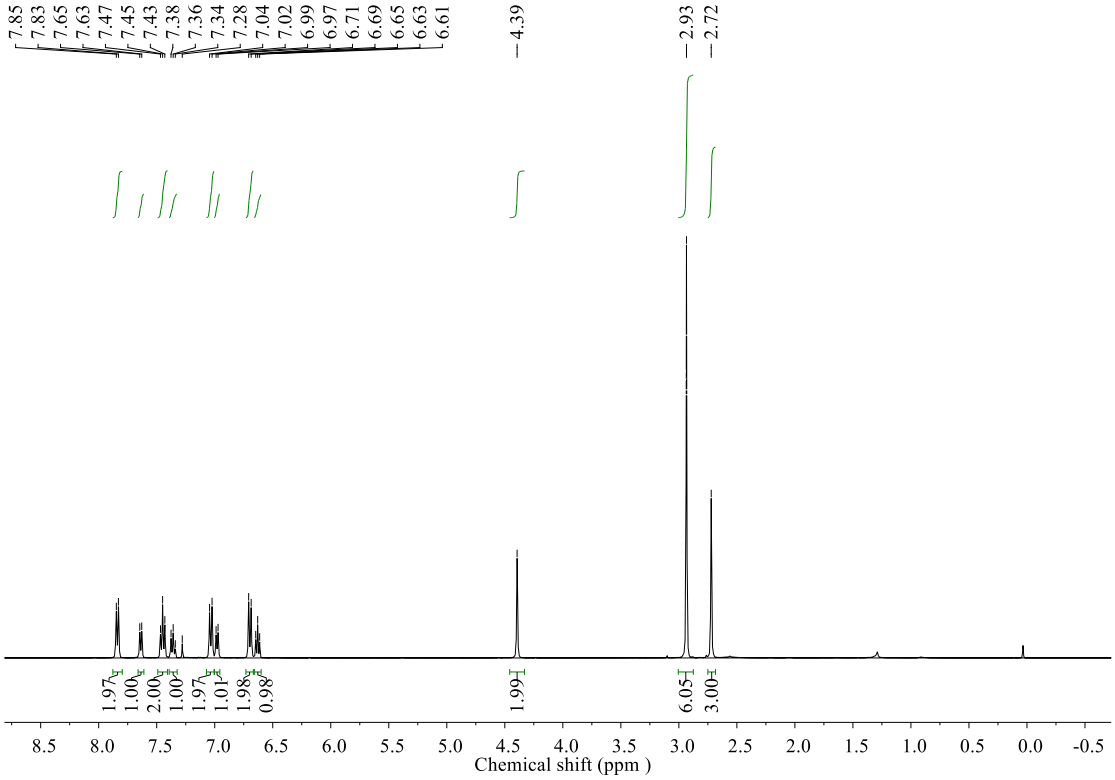
3k ^{1}H NMR



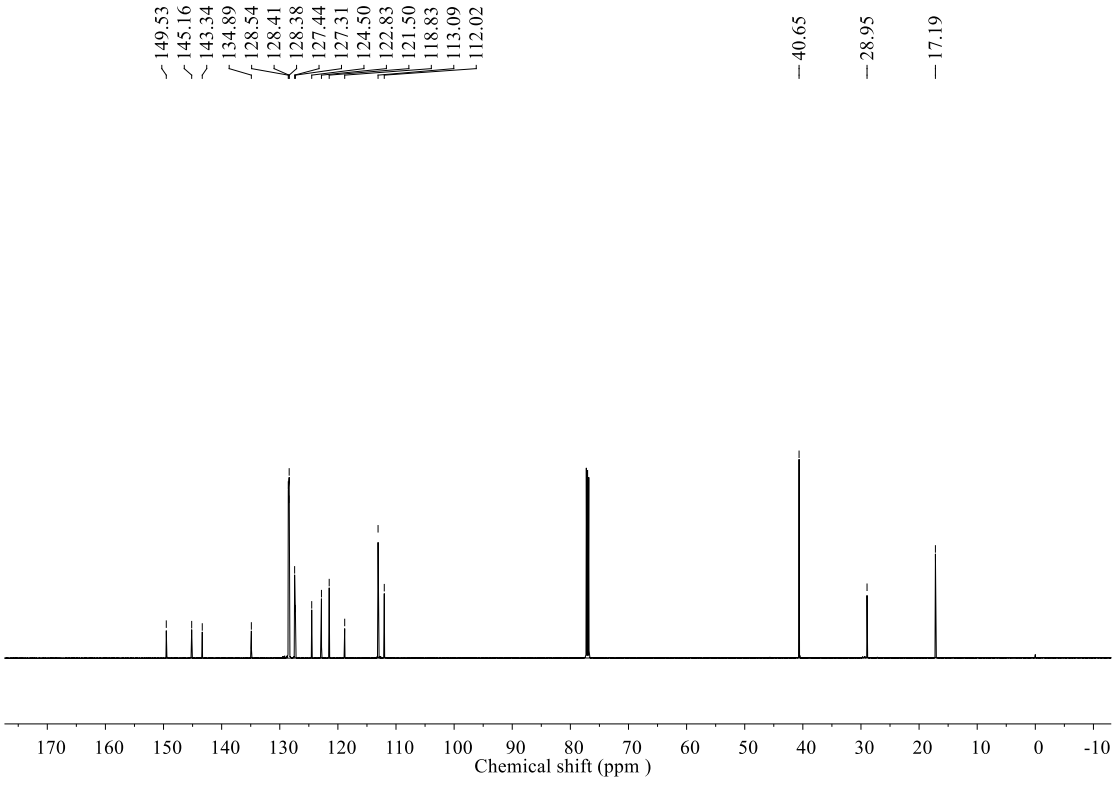
3k ^{13}C NMR



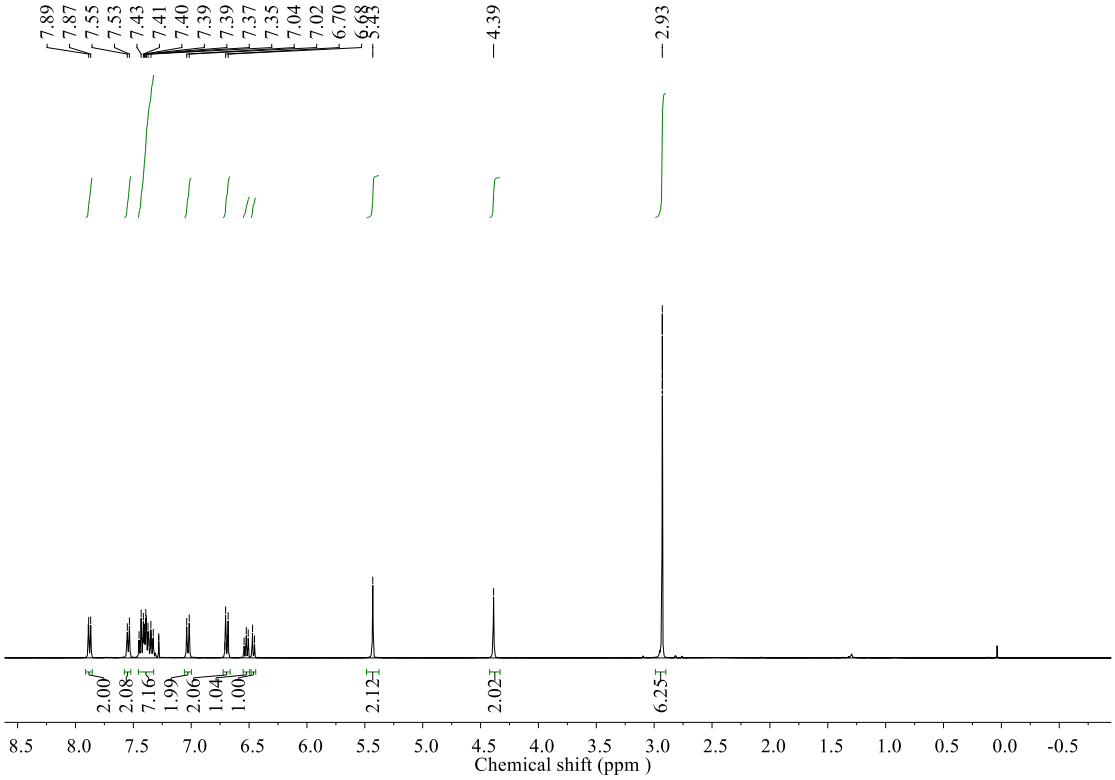
3m ^{1}H NMR



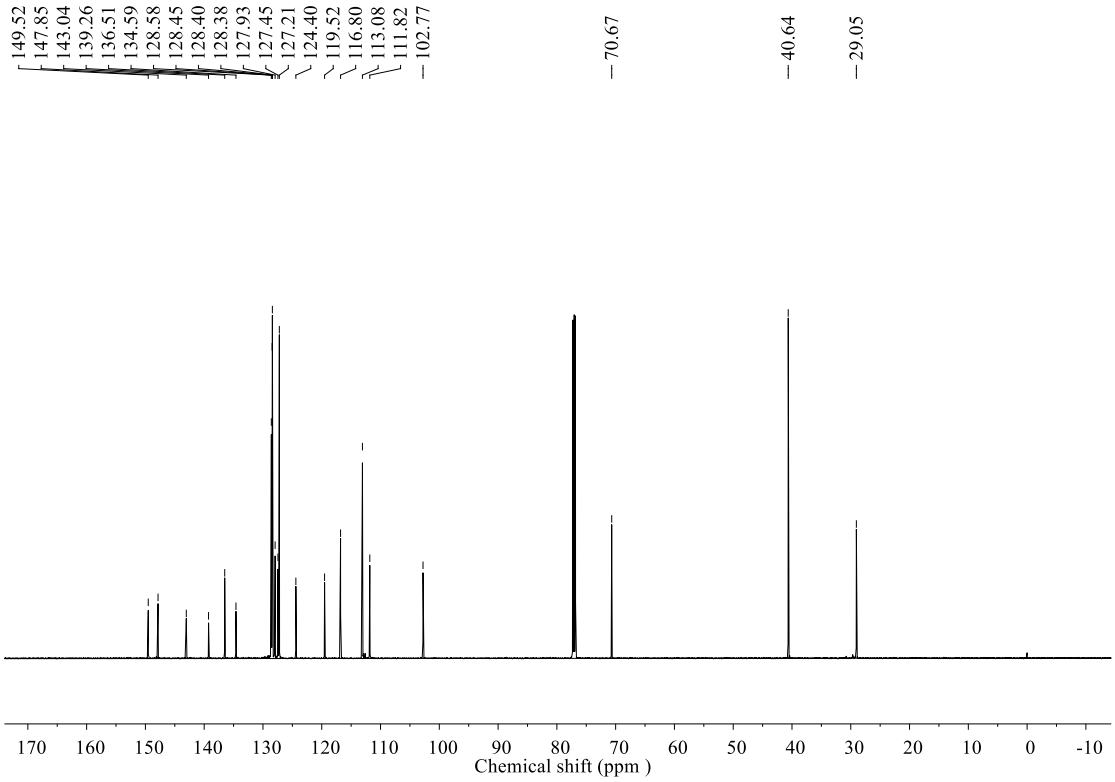
3m ^{13}C NMR



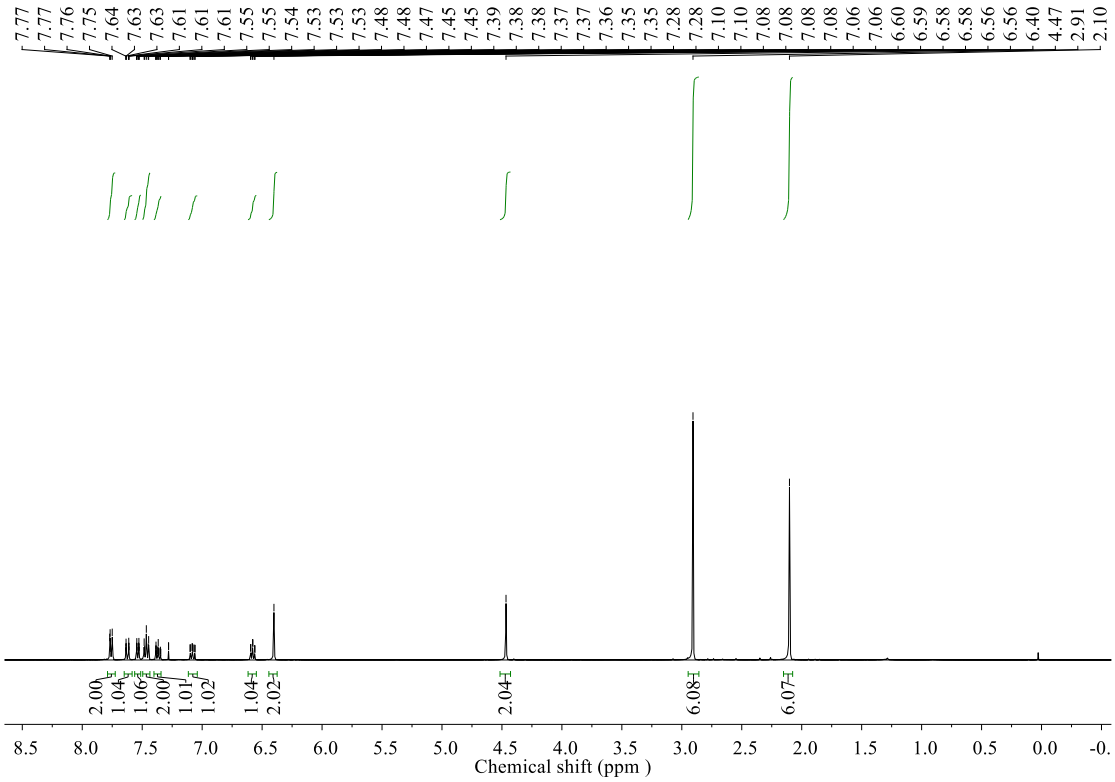
3n ^{1}H NMR



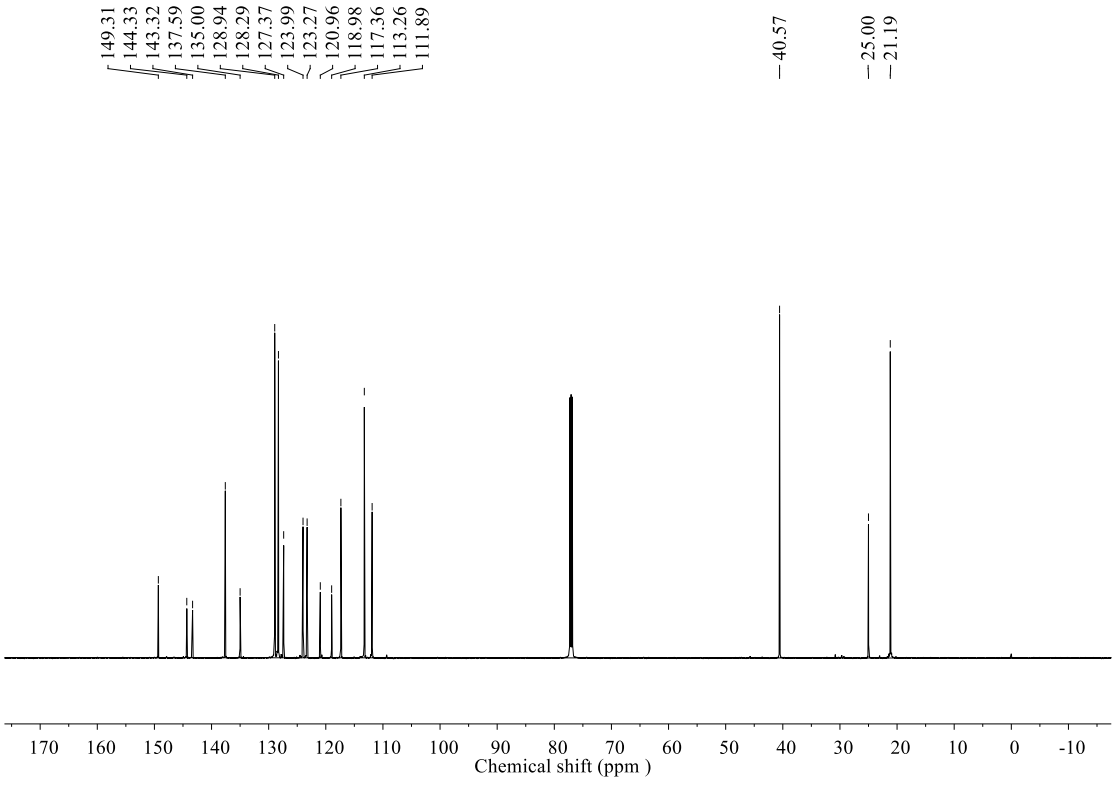
3n ^{13}C NMR



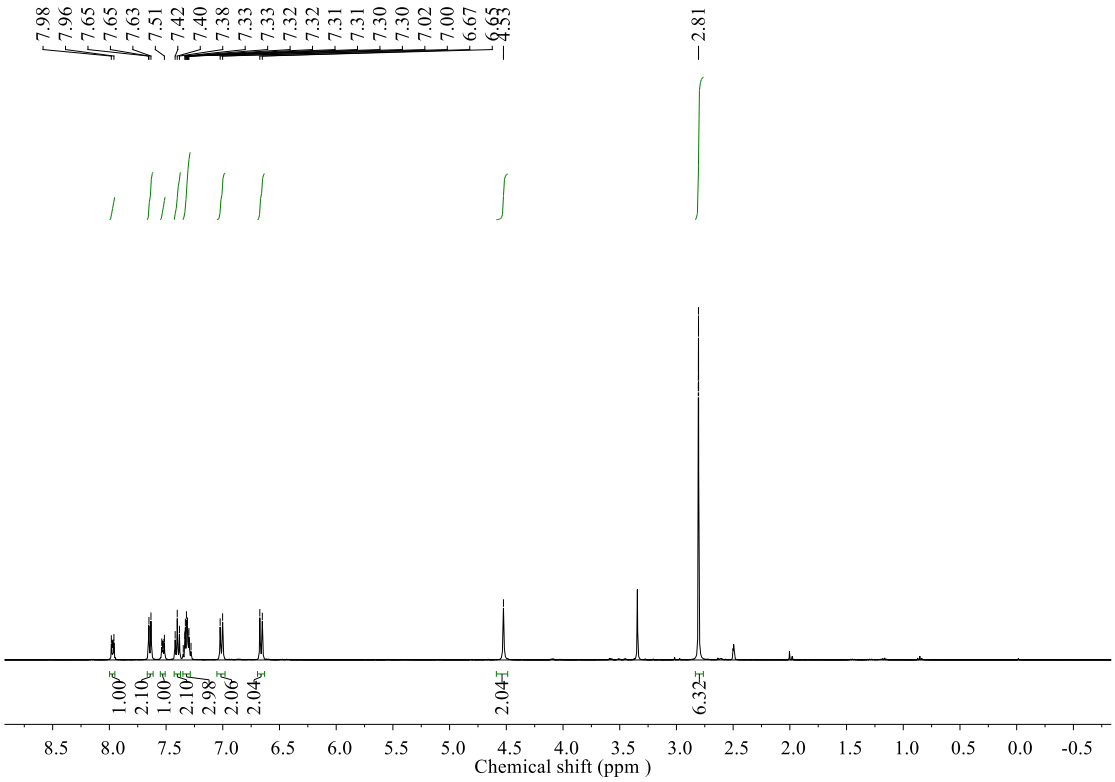
3o ^{1}H NMR



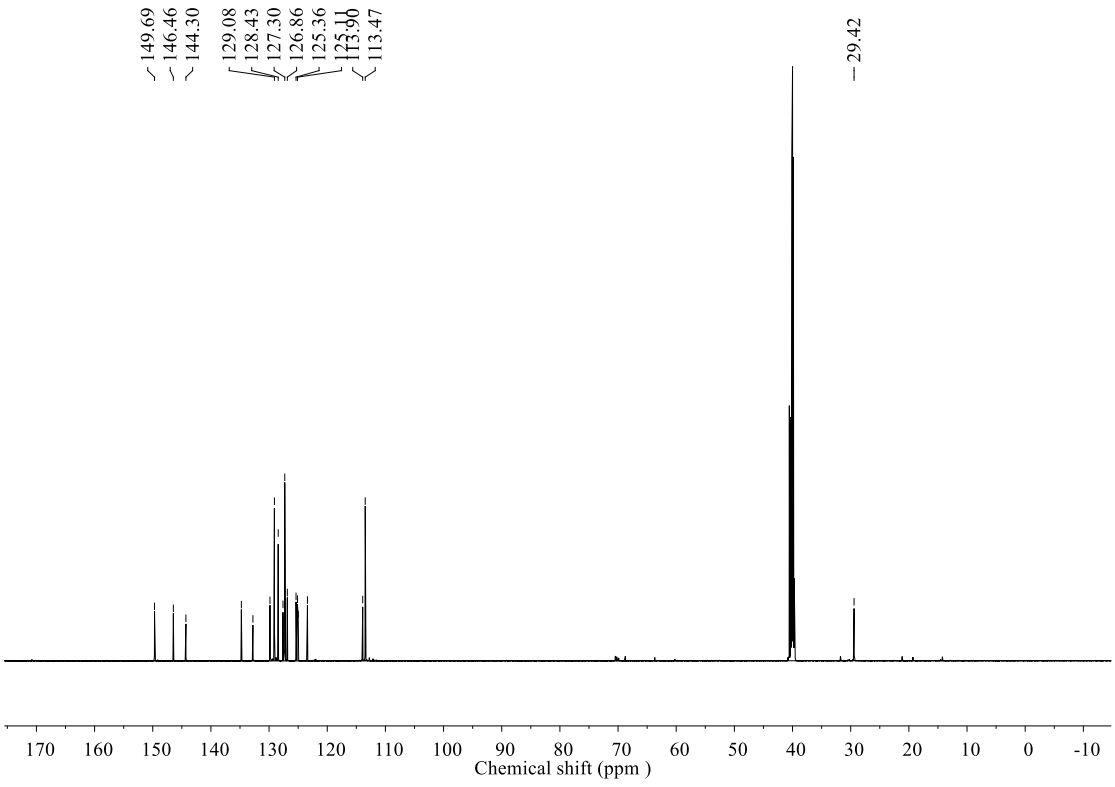
3o ^{13}C NMR



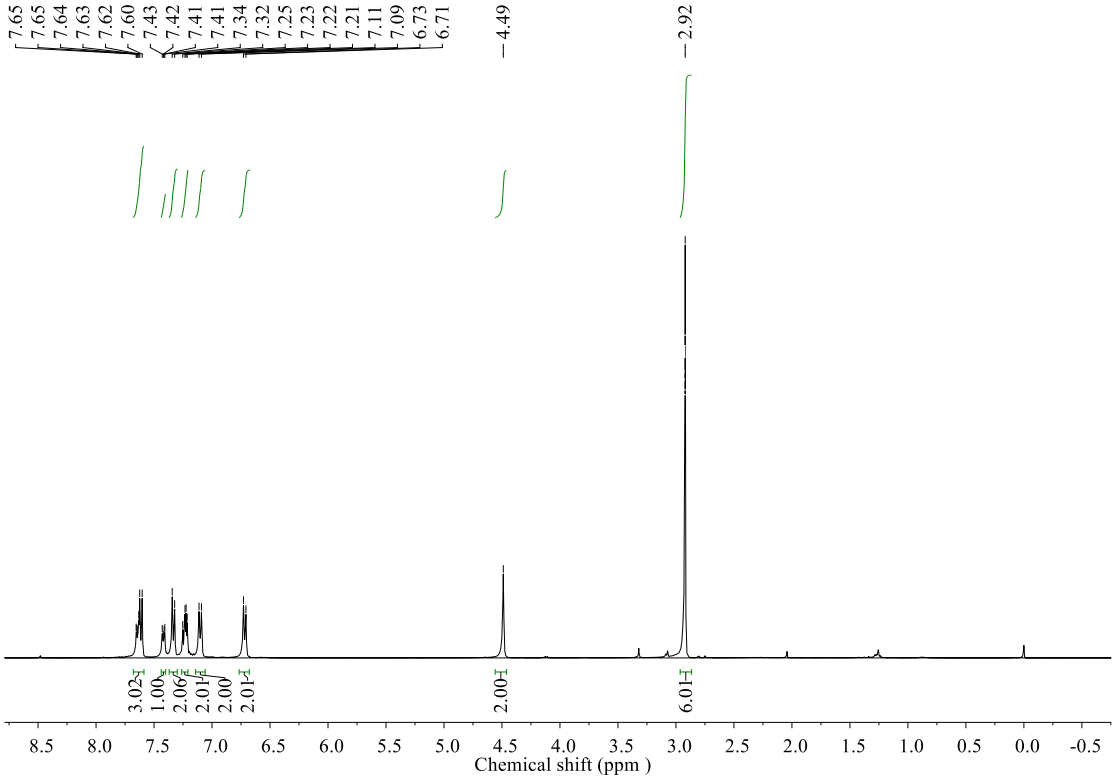
3p ^{1}H NMR



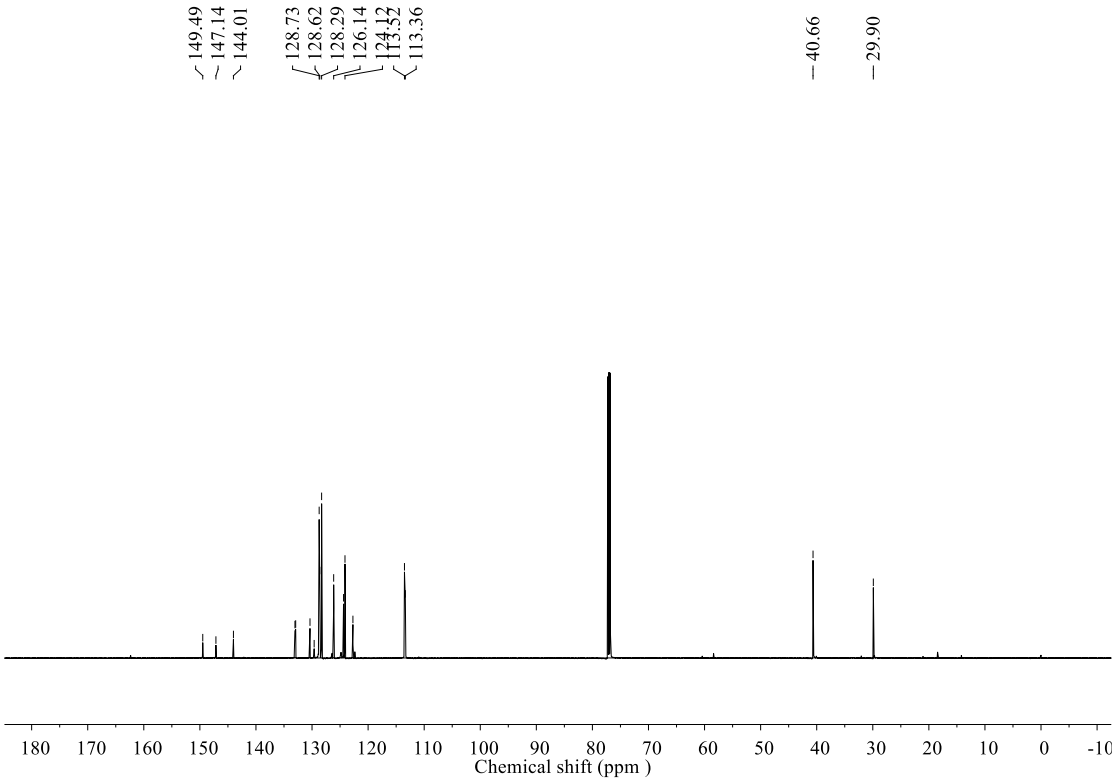
3p ^{13}C NMR



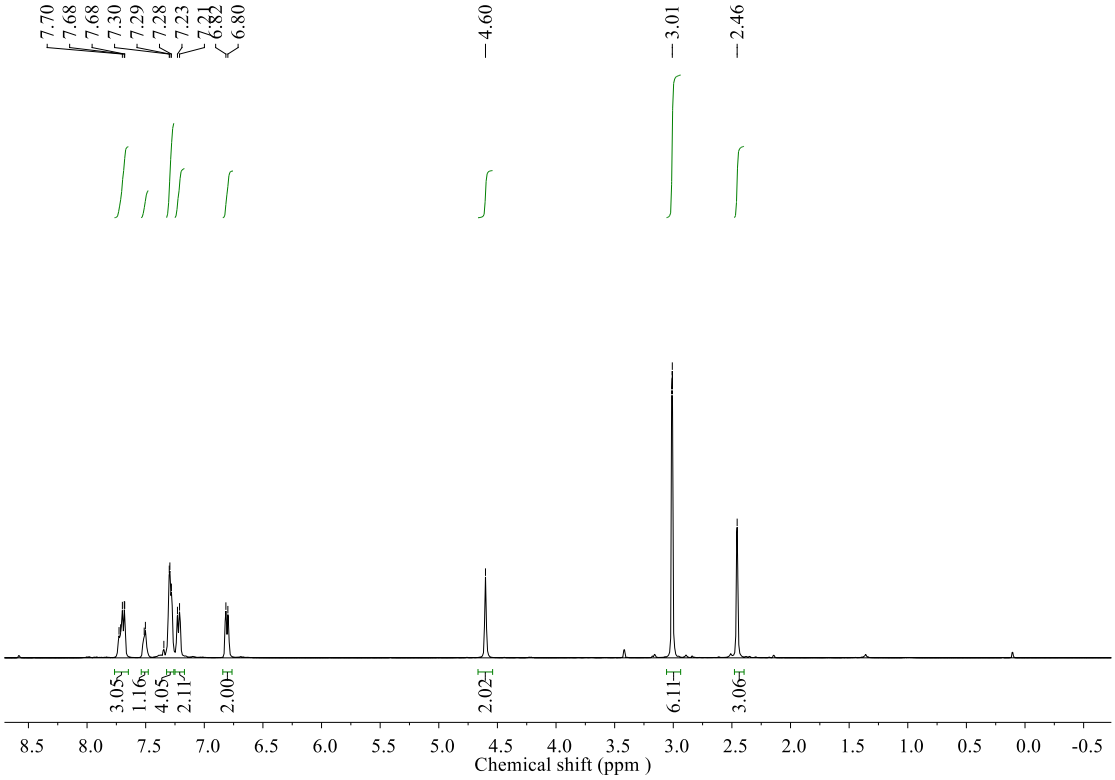
3q ^{1}H NMR



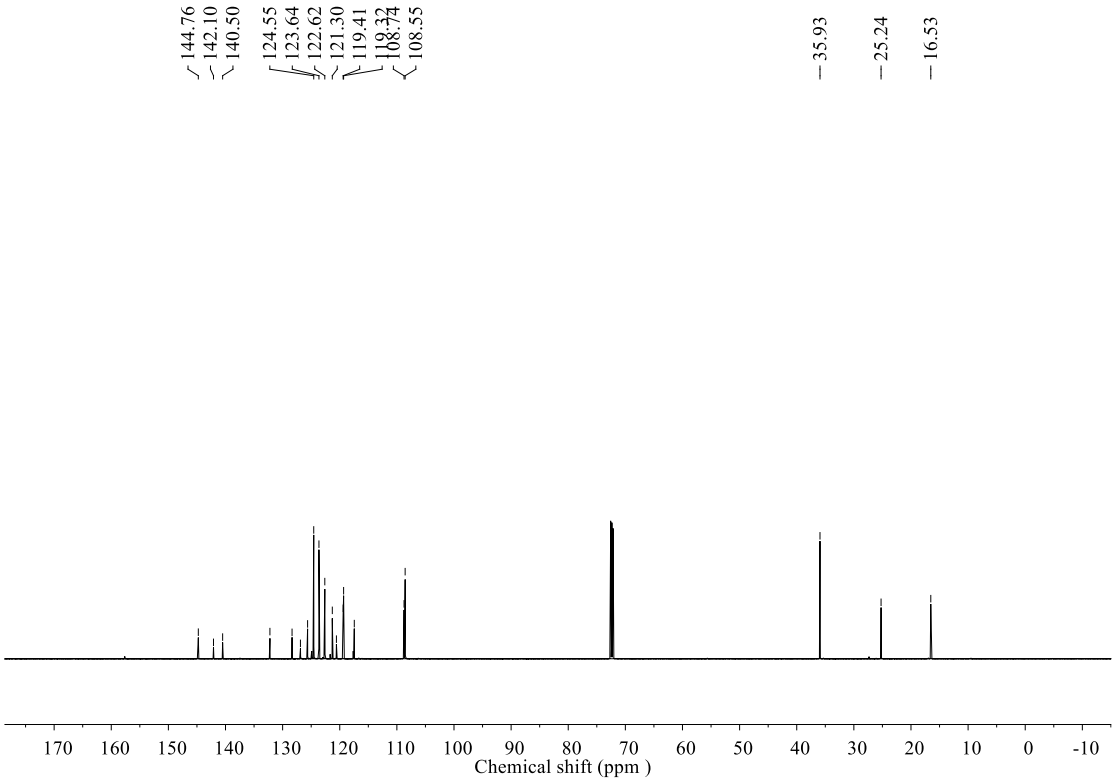
3q ^{13}C NMR



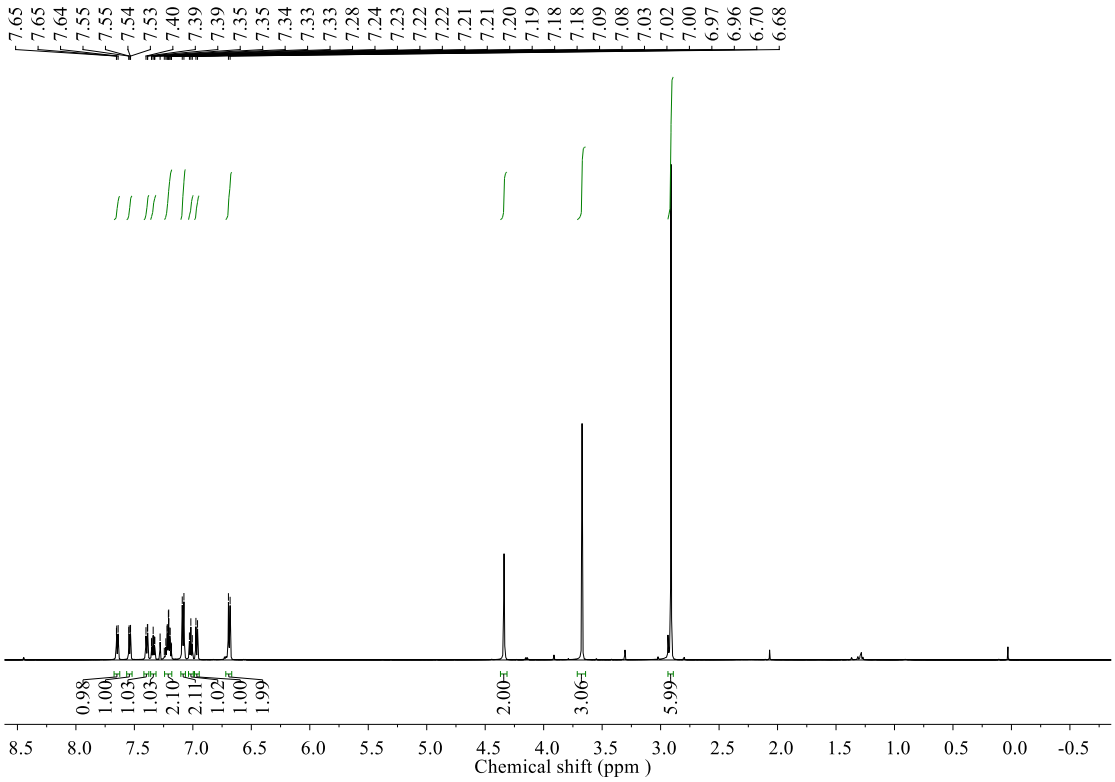
3r ^{1}H NMR



3r ^{13}C NMR



3s ^{1}H NMR



3s ^{13}C NMR