Supplementary Information

Selective *N*-Demethylation of Aryl Tertiary Amines via a Photoinduced COF Catalytic Strategy.

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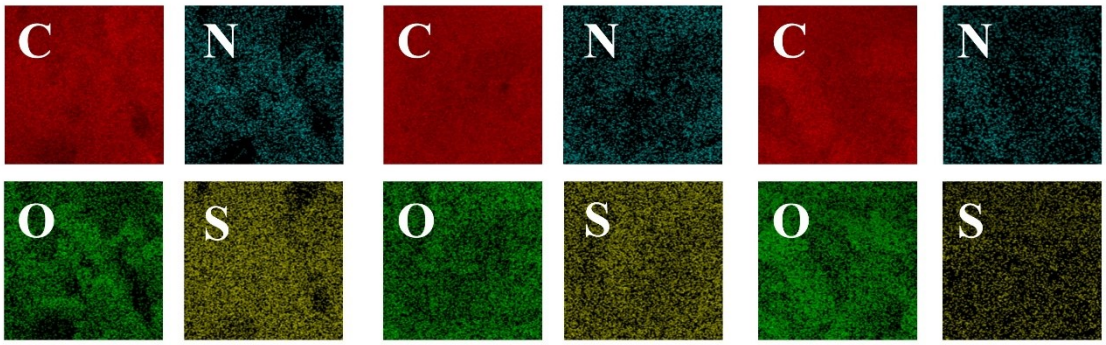


Fig. S1 EDX images of Py-BSZ-COF(C=N), Py-BSZ-COF(C=C), Py-TB-COF(C=C).

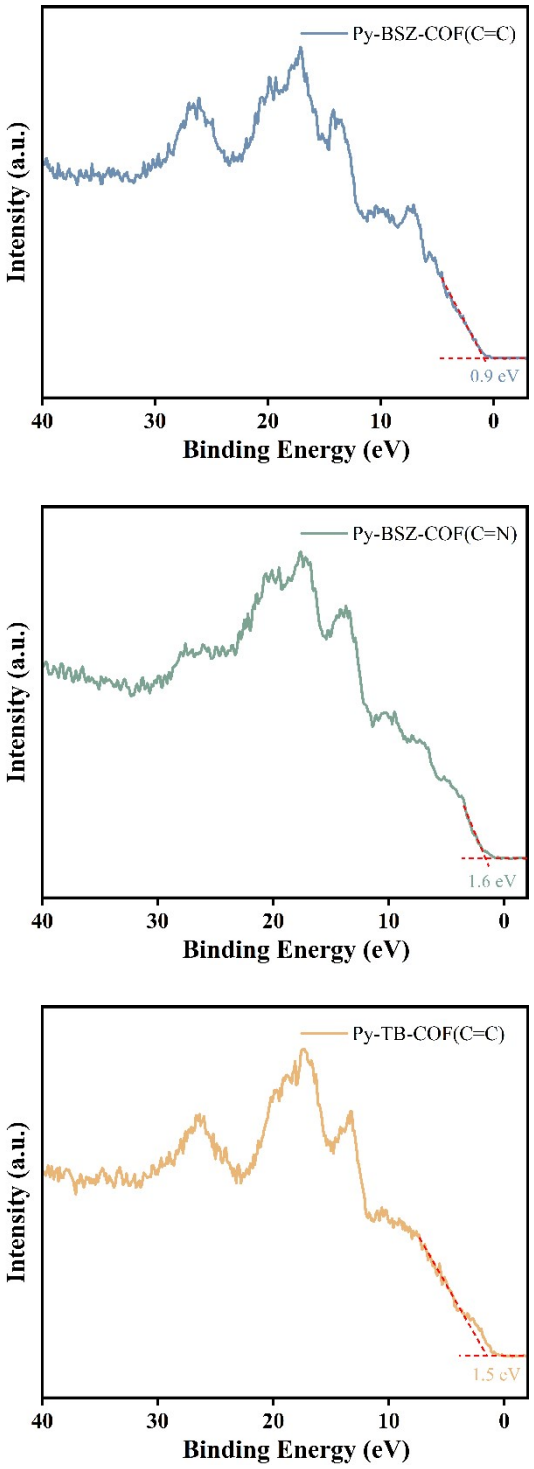


Fig. S2 The XPS valence band spectra of three COFs.

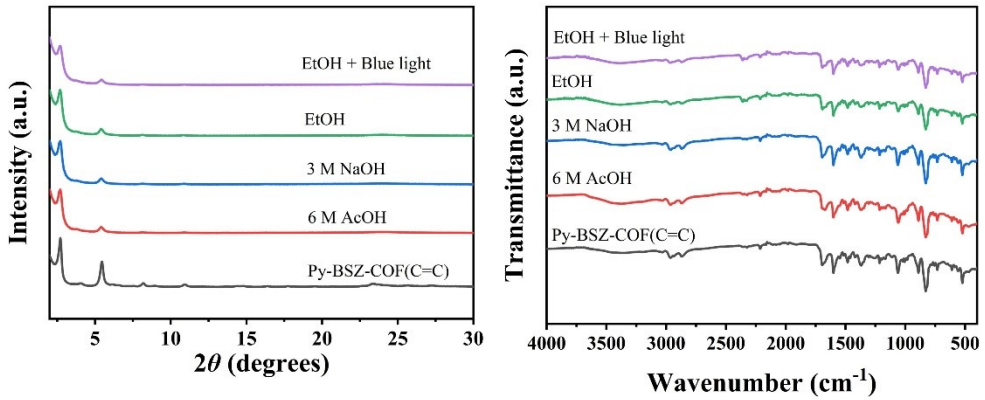


Fig. S3 PXRD patterns (left) and FTIR spectra (right) of the treated Py-BSZ-COF(C=C) under different conditions (6 M HCl, 3 M NaOH, EtOH and EtOH + 30 W Blue light irradiation).

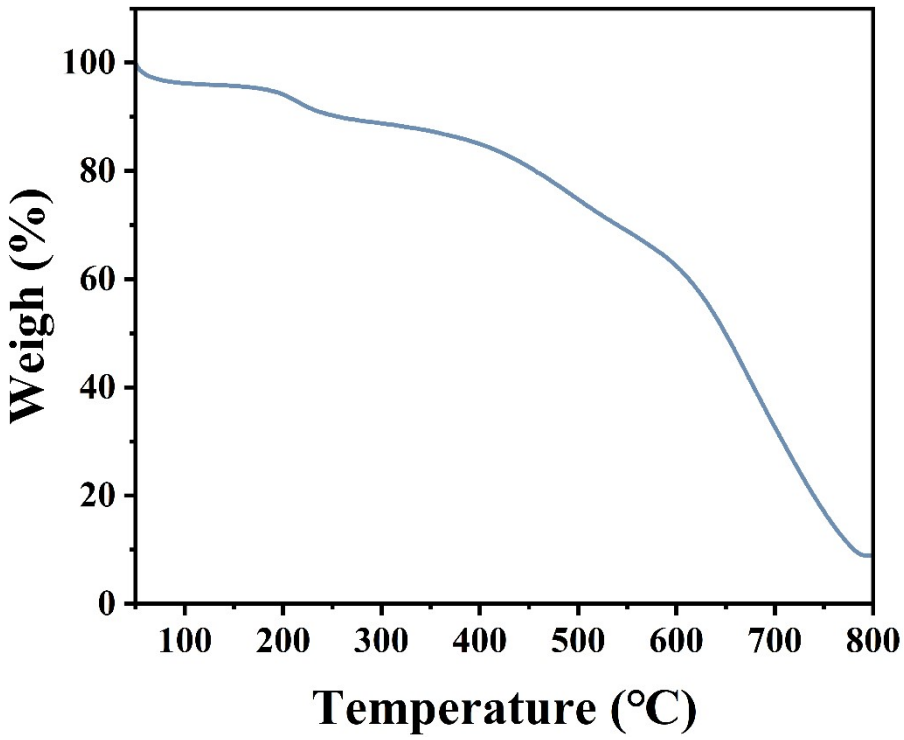


Fig. S4 TGA of Py-BSZ-COF(C=C).

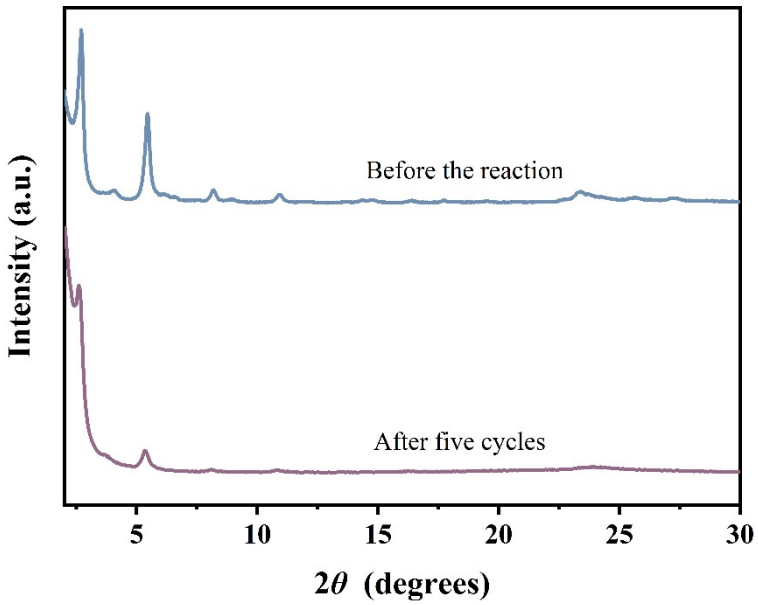


Fig. S5 Comparison of XRD patterns of Py-BSZ-COF (C=C) before and after reaction.

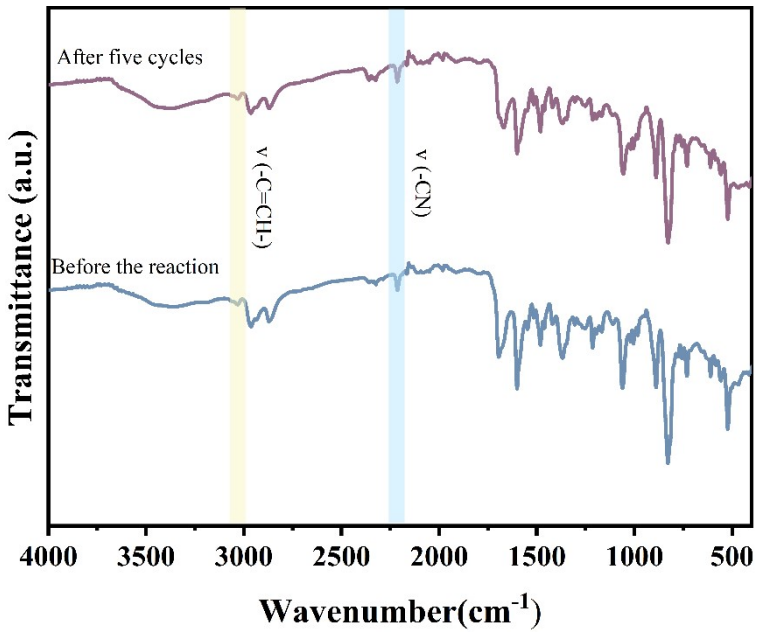


Fig. S6 Comparison of FT-IR patterns of Py-BSZ-COF (C=C) before and after reaction.

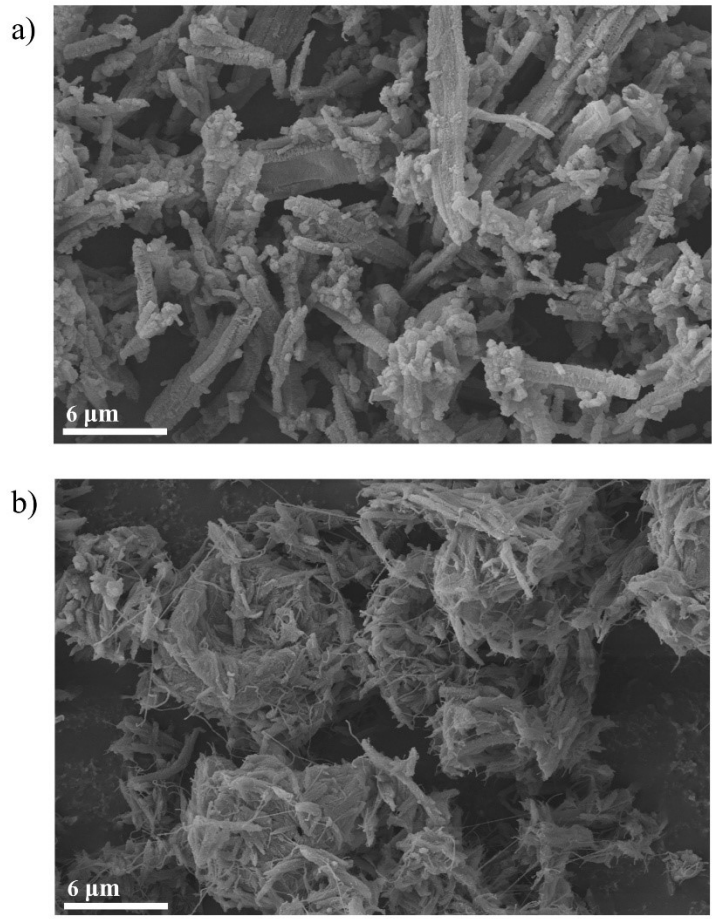


Fig. S7 Comparison of SEM patterns of Py-BSZ-COF (C=C) before (a) and after reaction (b).

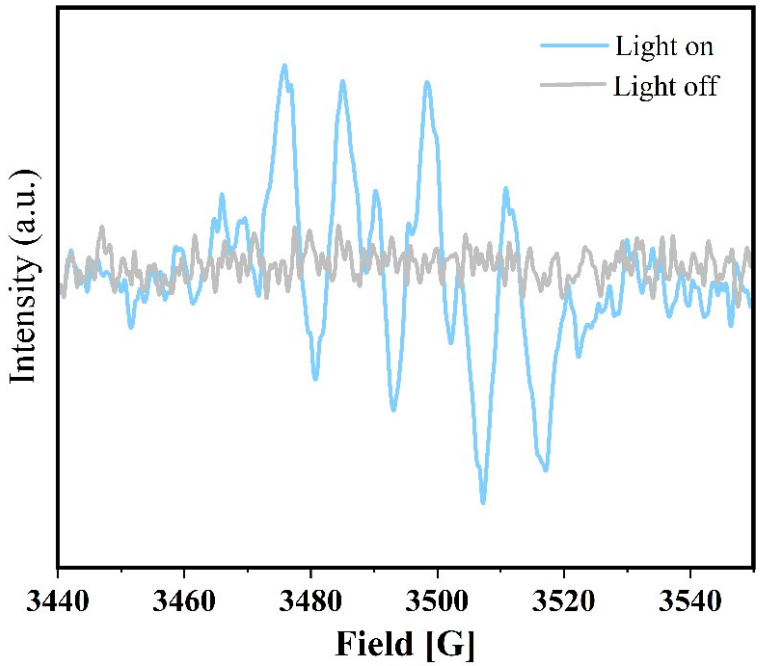


Fig. S8 EPR spectra of 2,2,6,6-tetramethylpiperidine (TEMP) treated by Py-BSZ-COF(C=C) under blue light (427m).

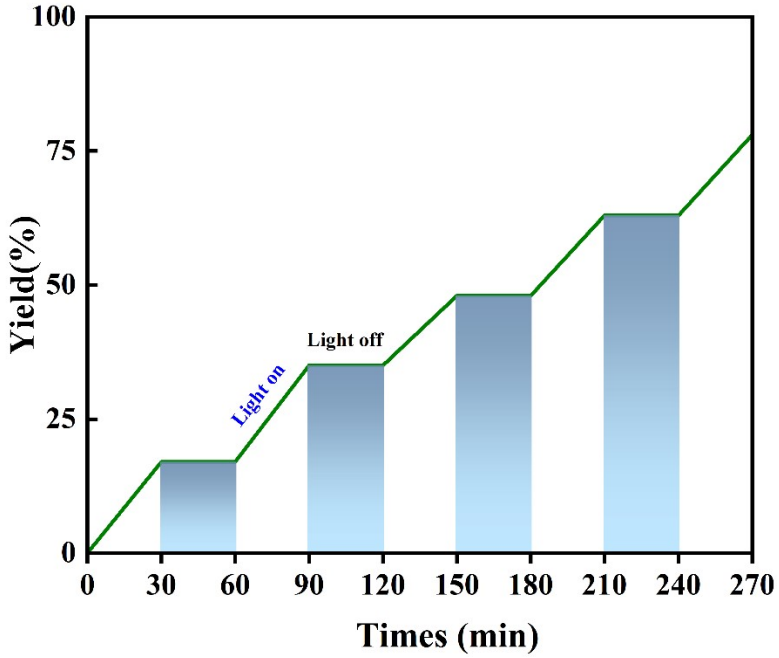


Fig. S9 Light on-off cycling experiment for the *N*-demethylation mediated by Py-BSZ-COF(C=C).

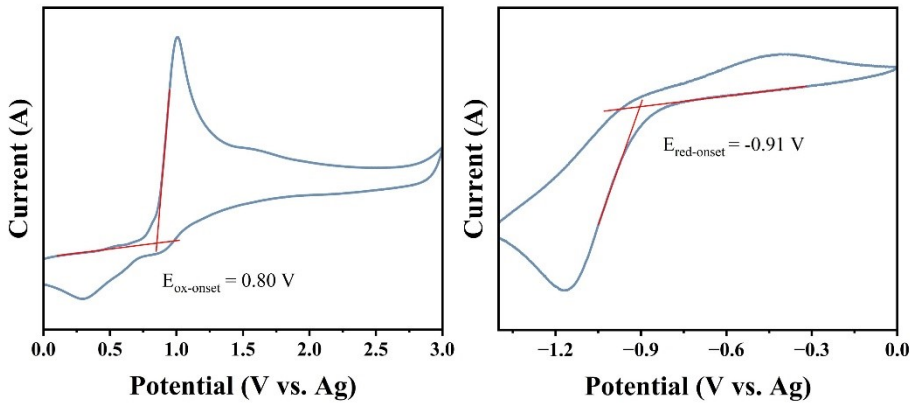


Fig. S10 Cyclic voltammetry (CV) measurements of *N*,*N*-dimethyl-*p*-bromoaniline.

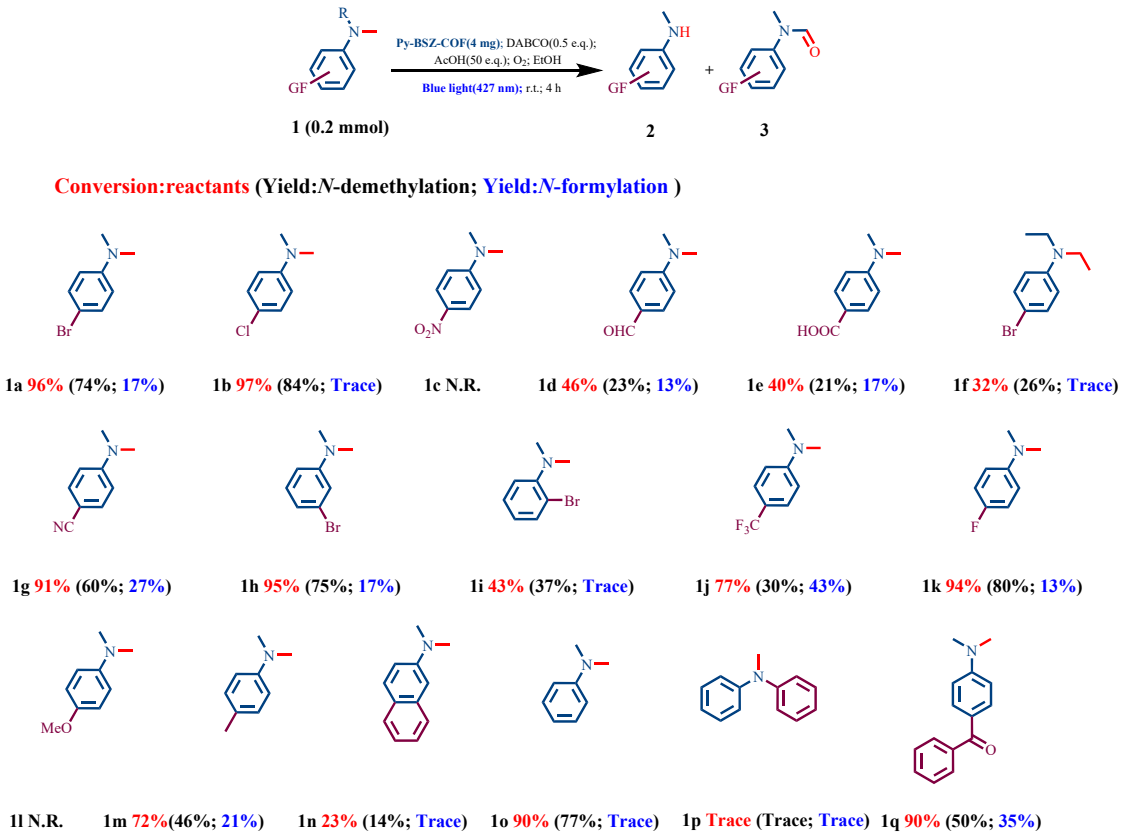
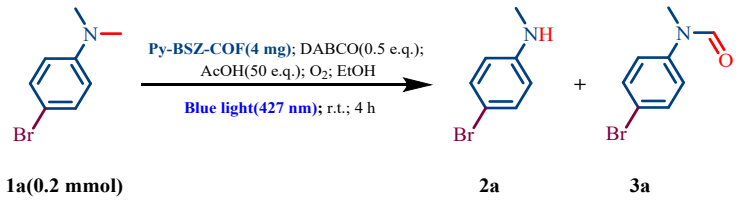


Fig. S11 Expansion of light reaction substrates (*N*-demethylation; *N*-formylation).



1a(0.2 mmol) **2a** **3a**

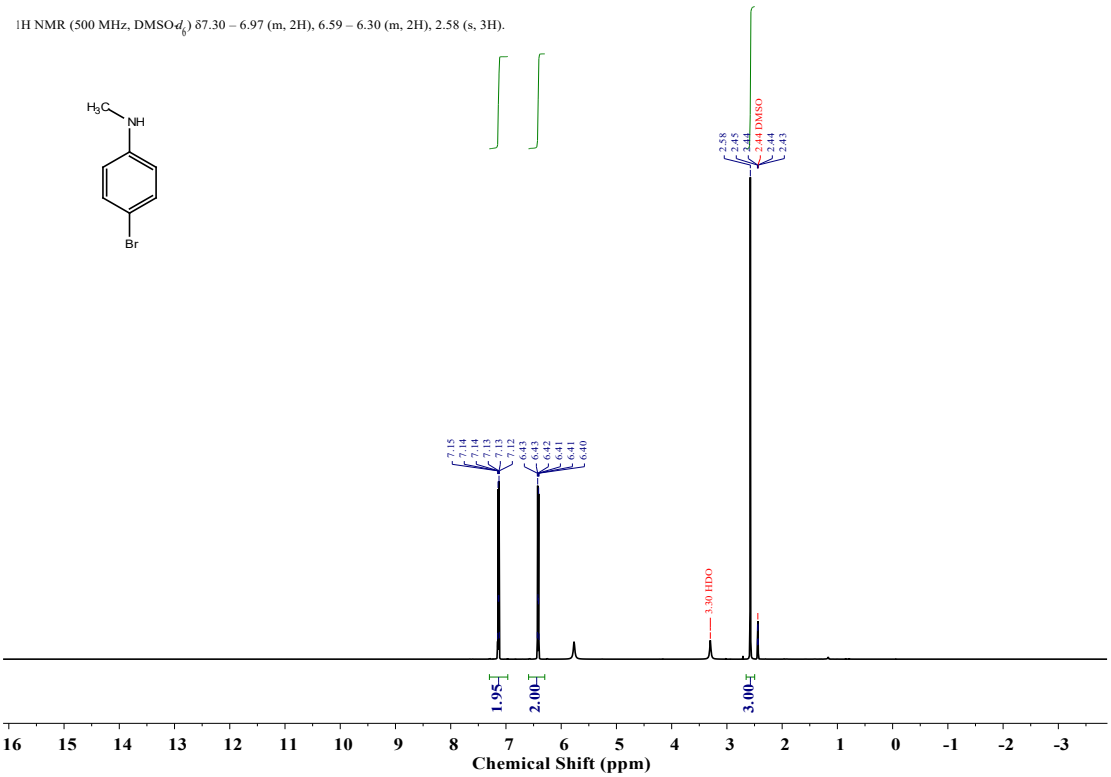
Table S1. Optimization of reaction conditons.

Entry	Change from standard conditions	1a Conversion(%)	2a Yield(%)	3a Yield(%)
1	Standard conditions	96	74	18
2	No COF	N.R[a].	0	0
3	No light	N.R[a].	0	0
4	No DABCO and AcOH	15	trace	Trace
5	No DABCO	30	17	Trace
6	No AcOH	90	40	34
7	25 e.q. AcOH	97	68	21
8	100 e.q. AcOH	66	55	Trace
9	0.25 e.q. DABCO	94	63	22
10	1 e.q. DABCO	97	72	20
11	Air,instead of O_2	74	54	13
12	N_2,instead of O_2	Trace	Trace	Trace
13	2 mg COF	84	59	20
14	12 mg COF	98	40	28
15	THF as the solvent	99	36	47
16	ACN as the solvent	22	17	Trace
17	DBU as the base	99	59	22
18	KOH as the base	98	73	14
19	$NaHCO_3$ as the base	64	42	15
20	12.5 e.q. AcOH	97	52	22
21	75 e.q. AcOH	99	50	40
22	EA as the solvent	97	50	38

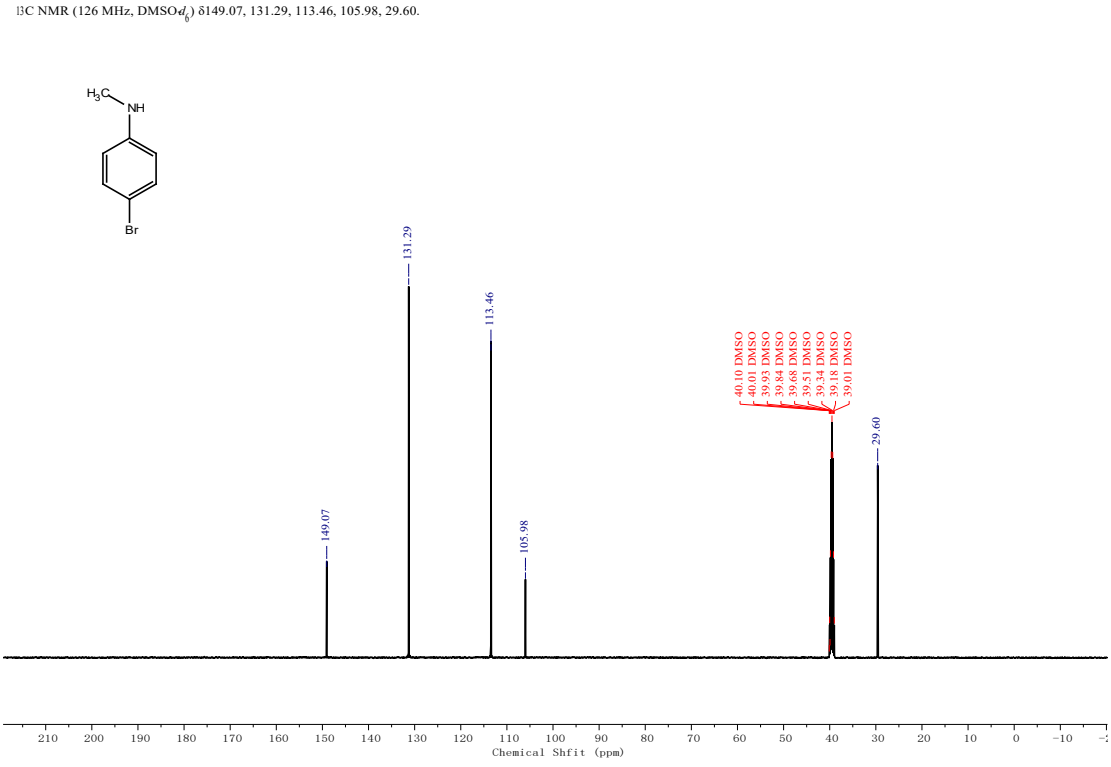
23	DMSO as the solvent	97	37	43
24	8 mg COF	98	46	32
25	2 e.q. DABCO	97	67	13
26	Reaction time: 2 h	43	33	Trace
27	Reaction time: 2.5 h	54	42	Trace
28	Reaction time:3 h	78	68	Trace
29	Reaction time:3.5 h	93	72	14
30	Reaction time:4.5 h	98	63	17
31	Reaction time:5 h	97	48	37
32	Additional 2 mg MnO_2	71	64	Trace
33	Additional 20 mg MnO_2	70	65	Trace

Standard Conditions: Raw Material(0.2 mmol); 4 mg Py-BSZ-COF(C=C); 0.5 e.q. DABCO; 50 e.q. AcOH; 4 mL EtOH; 30 W 427 nm Blue Light; O_2; r.t.; 4 h; N.R.[a]=No reaction

^{1}H NMR and ^{13}C NMR spectra for products.

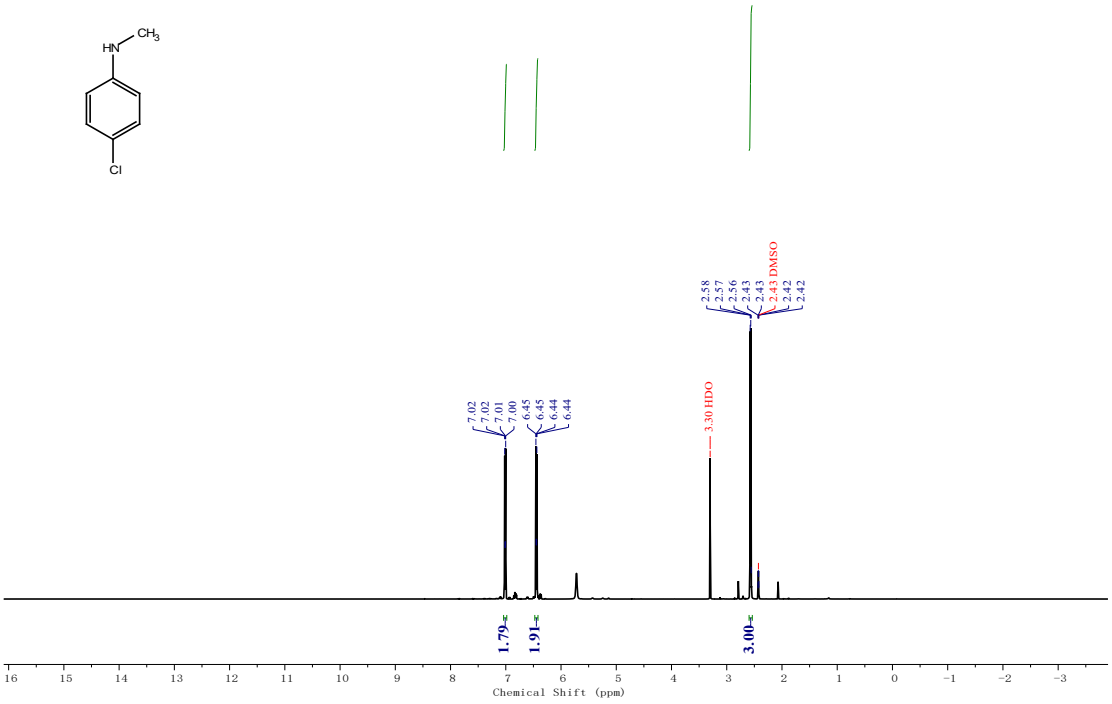


2a-^{1}H NMR



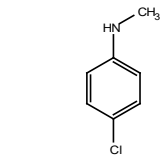
2a-^{13}C NMR

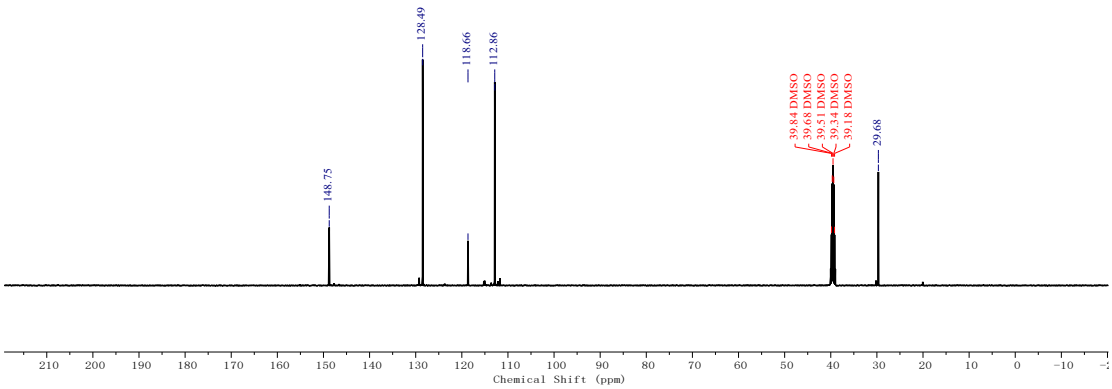
^{1}H NMR (500 MHz, DMSO-d_6) δ7.06 – 6.96 (m, 2H), 6.49 – 6.40 (m, 2H), 2.57 (d, *J*= 5.1 Hz, 3H).



2b-^{1}H NMR

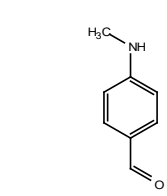
^{13}C NMR (126 MHz, DMSO-d_6) δ148.75, 128.49, 118.66, 112.86, 29.68.



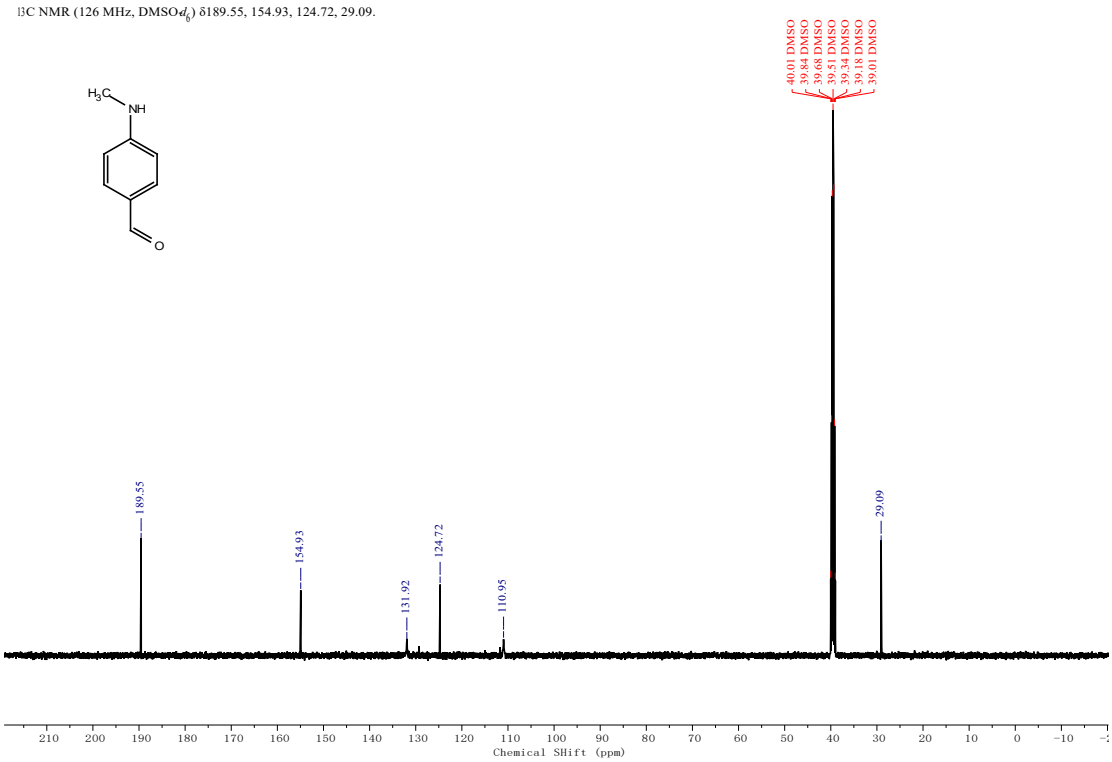


2b-^{13}C NMR

^{1}H NMR (500 MHz, DMSO-d_6) δ9.54 (s, 1H), 7.67 – 7.43 (m, 2H), 6.56 (d, *J*= 8.8 Hz, 2H), 2.70 (d, *J*= 3.5 Hz, 3H).

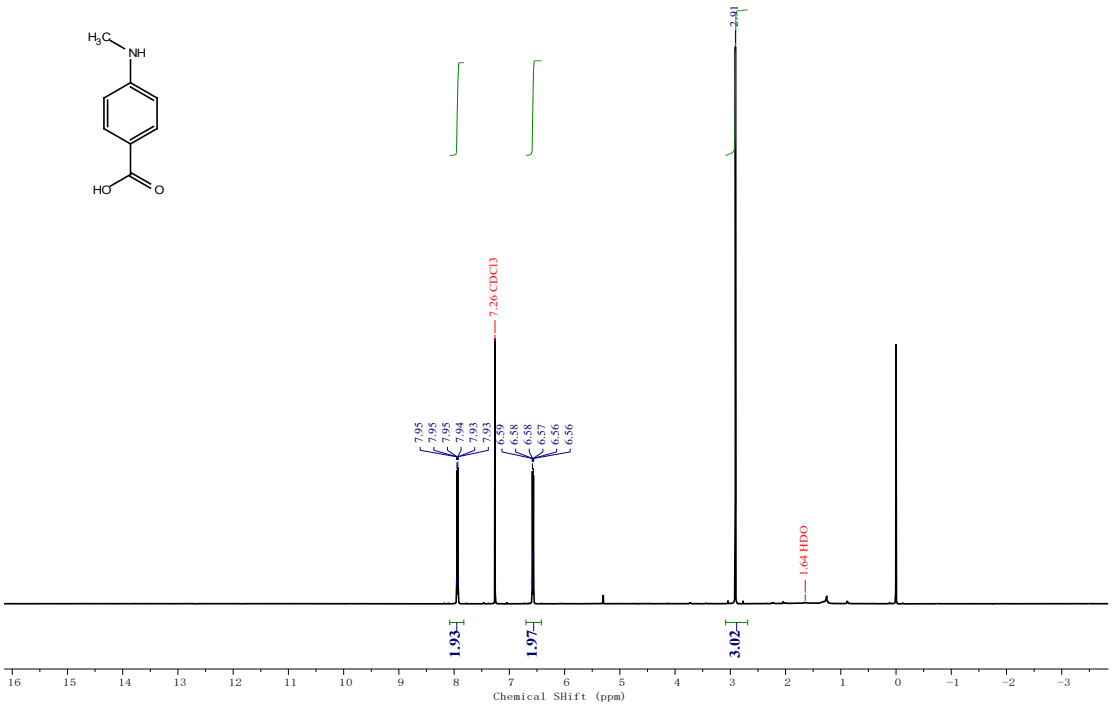


2d-^{1}H NMR


13C NMR (126 MHz, DMSO-d_6) δ189.55, 154.93, 124.72, 29.09.
H_3C
NH
O
40.01 DMSO
39.84 DMSO
39.68 DMSO
39.51 DMSO
39.34 DMSO
39.18 DMSO
39.01 DMSO
189.55
154.93
131.92
124.72
110.95
29.09
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
Chemical SHift (ppm)

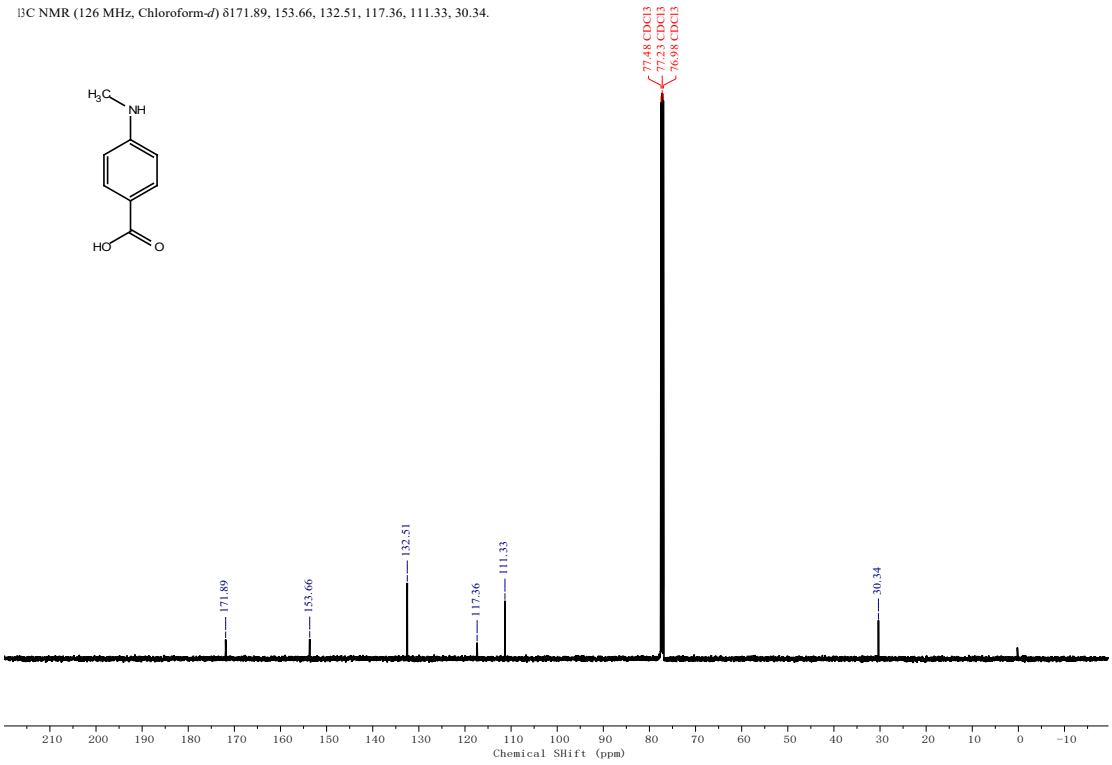
2d-^{13}C NMR

¹H NMR (500 MHz, Chloroform-*d*) δ7.94 (d, *J*= 8.8 Hz, 2H), 6.57 (d, *J*= 8.8 Hz, 2H), 2.91 (s, 3H).



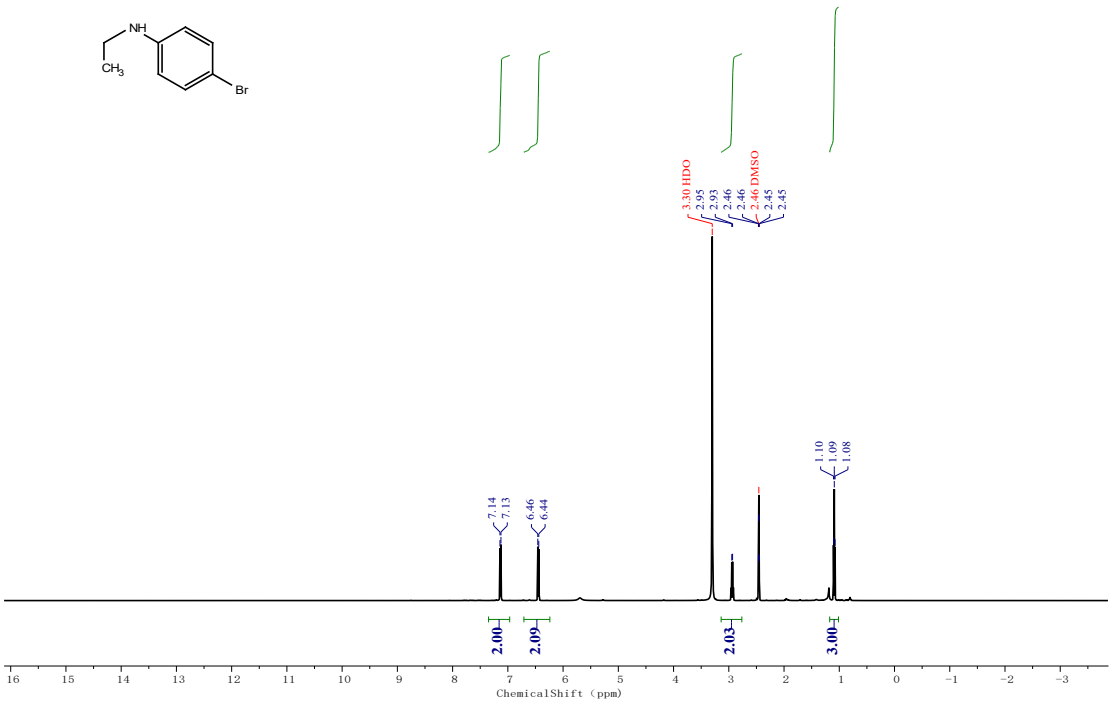
2e-^{1}H NMR

¹³C NMR (126 MHz, Chloroform-*d*) δ171.89, 153.66, 132.51, 117.36, 111.33, 30.34.



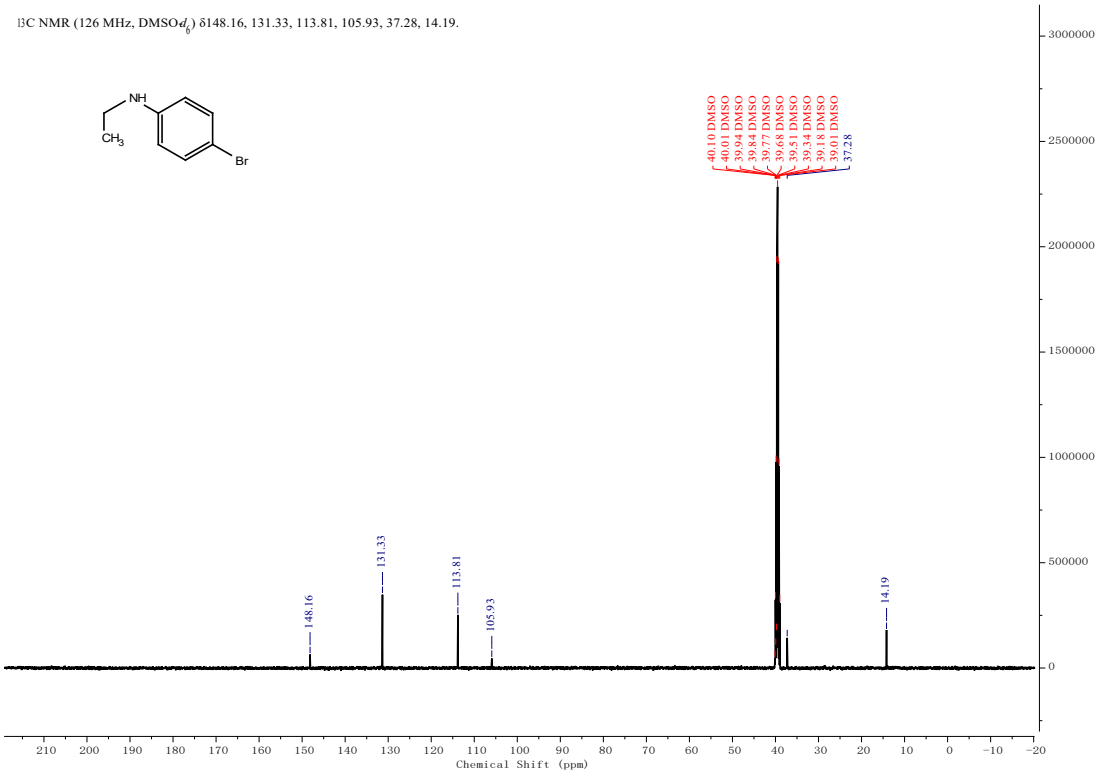
2e-^{13}C NMR

^{1}H NMR (500 MHz, DMSO-d_6) δ7.13 (d, J= 8.8 Hz, 2H), 6.45 (d, J= 8.9 Hz, 2H), 2.94 (d, J = 7.1 Hz, 2H), 1.09 (t, J= 7.1 Hz, 3H).



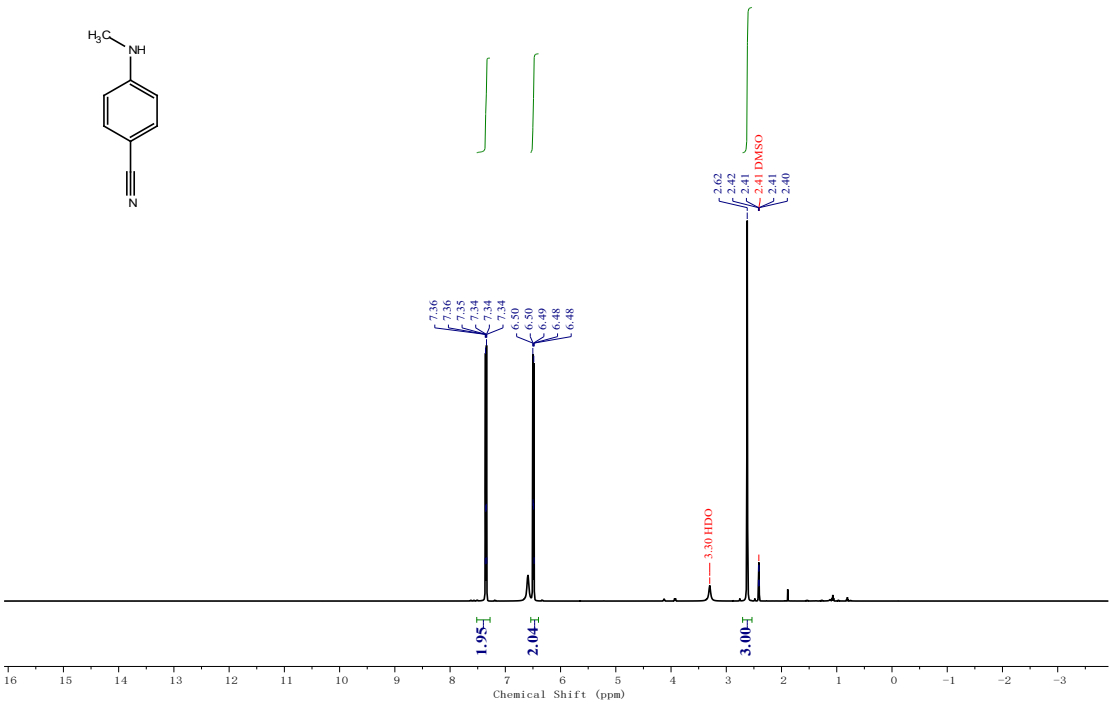
2f-^{1}H NMR

^{13}C NMR (126 MHz, DMSO-d_6) δ148.16, 131.33, 113.81, 105.93, 37.28, 14.19.



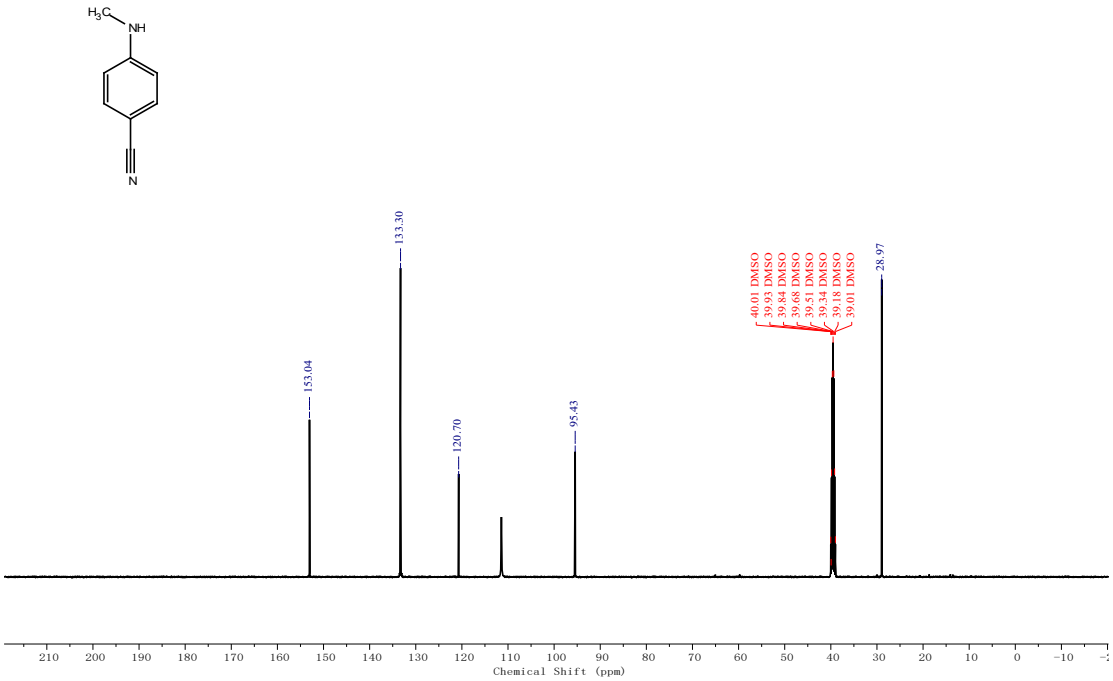
2f-^{13}C NMR

^{1}H NMR (500 MHz, DMSO-d_6) δ7.52 – 7.28 (m, 2H), 6.54 – 6.40 (m, 2H), 2.62 (s, 3H).



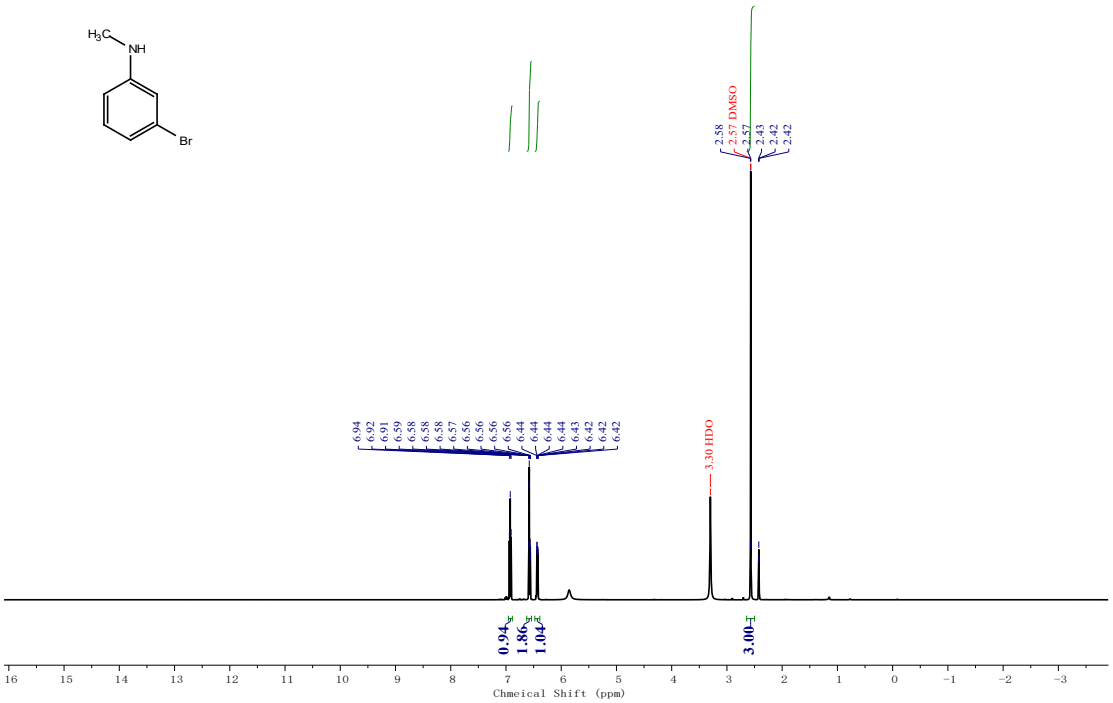
2g-^{1}H NMR

^{13}C NMR (126 MHz, DMSO-d_6) δ153.04, 133.30, 120.70, 95.43, 28.97.



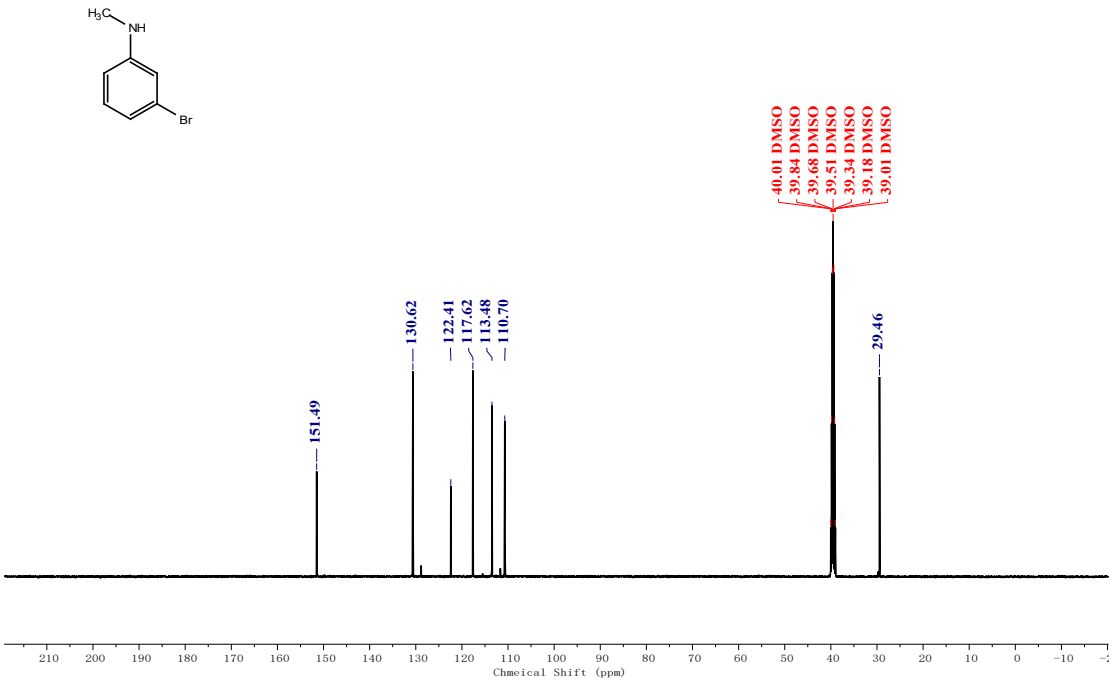
2g-^{13}C NMR

^{1}H NMR (500 MHz, DMSO-d_6) δ6.92 (t, *J*= 7.9 Hz, 1H), 6.62 – 6.54 (m, 2H), 6.43 (ddd, *J*= 8.2, 2.3, 1.0 Hz, 1H), 2.57 (s, 3H).



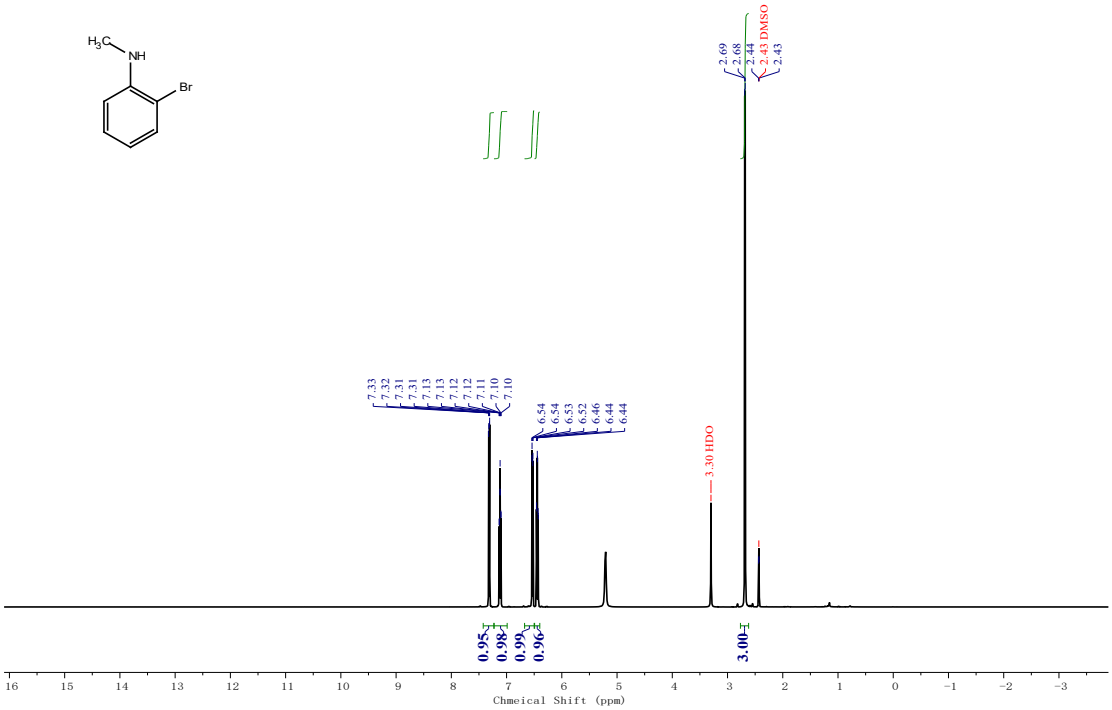
2h-^{1}H NMR

^{13}C NMR (126 MHz, DMSO-d_6) δ151.49, 130.62, 122.41, 117.62, 113.48, 110.70, 29.46.



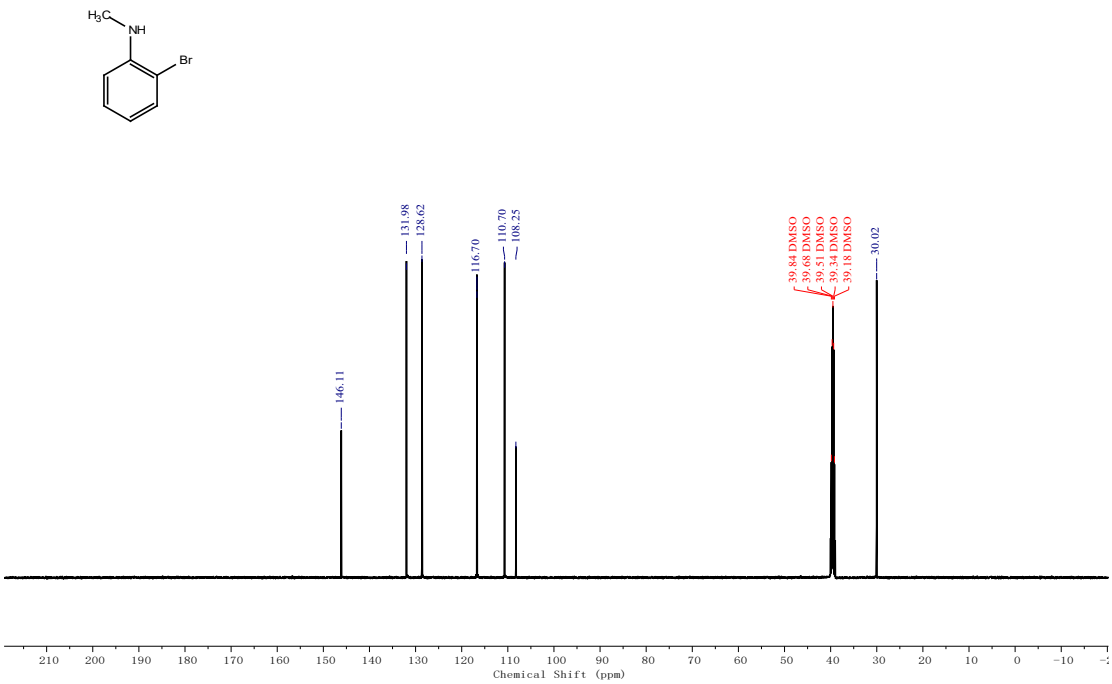
2h-^{13}C NMR

^{1}H NMR (500 MHz, DMSO-d_6) δ7.32 (dd, *J*= 7.9, 1.5 Hz, 1H), 7.12 (ddd, *J*= 8.4, 7.3, 1.5 Hz, 1H), 6.53 (dd, *J*= 8.2, 1.5 Hz, 1H), 6.44 (td, *J*= 7.5, 1.5 Hz, 1H), 5.21 (d, *J*= 5.4 Hz, 1H), 2.68 (d, *J*= 4.8 Hz, 3H).



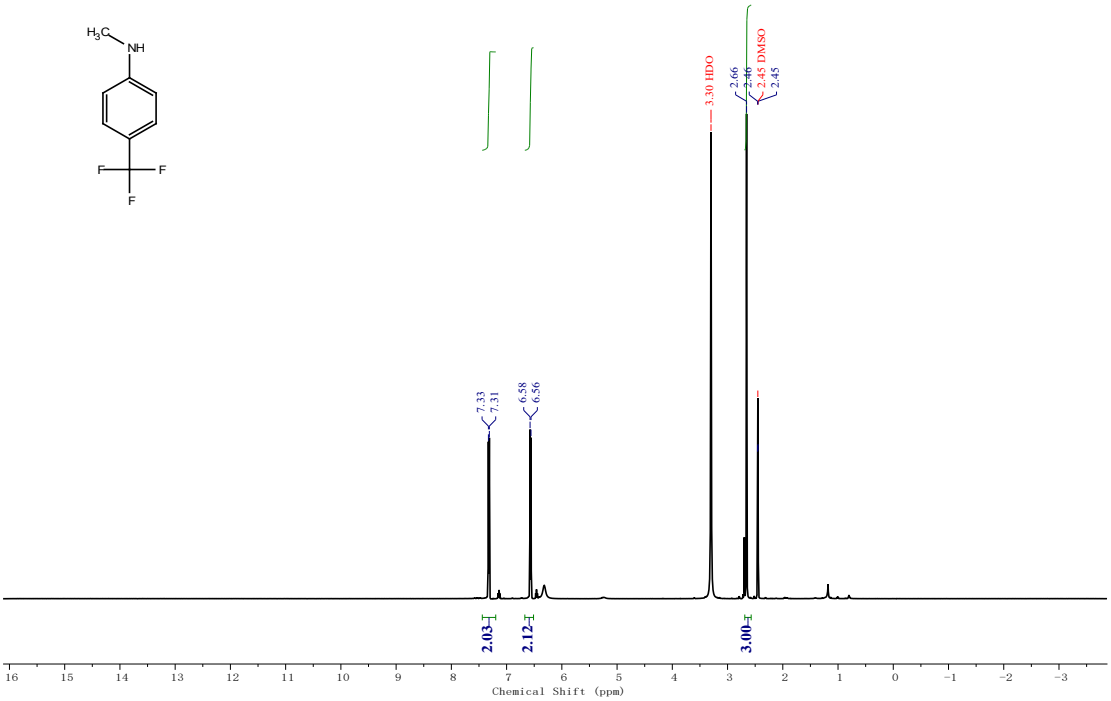
2i-^{1}H NMR

^{13}C NMR (126 MHz, DMSO-d_6) δ146.11, 131.98, 128.62, 116.70, 110.70, 108.25, 30.02.



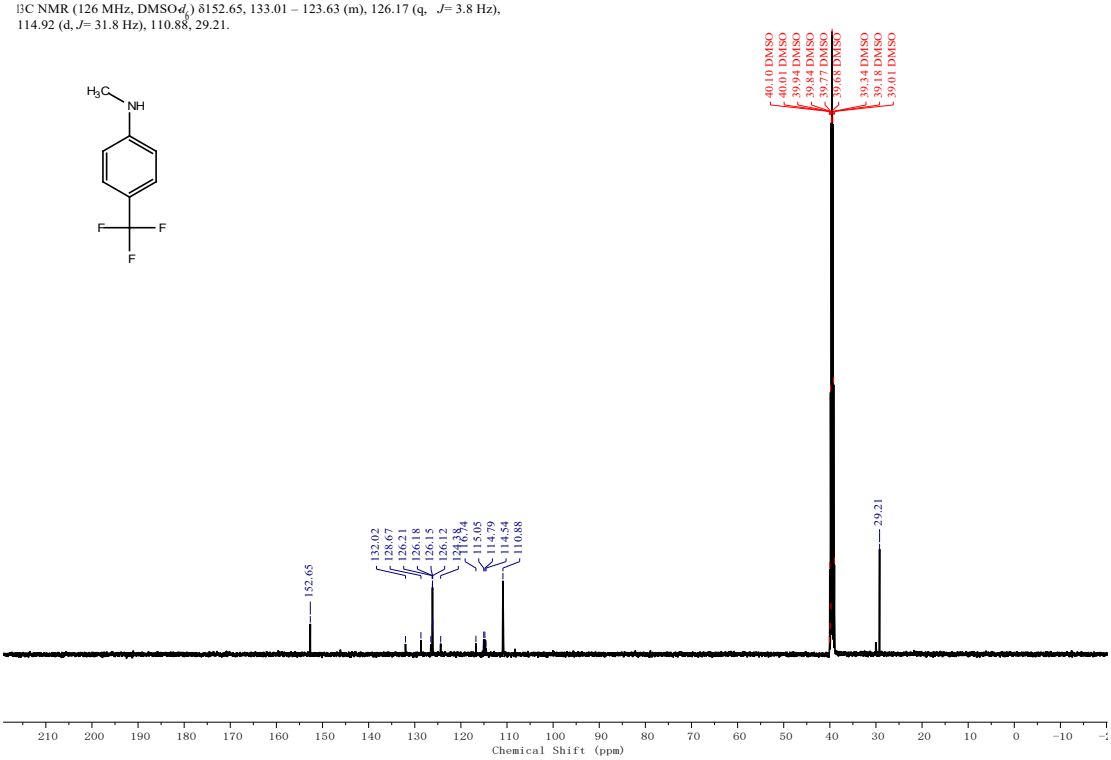
2i-^{13}C NMR

^{1}H NMR (500 MHz, DMSO-d_6) δ7.32 (d, J= 8.5 Hz, 2H), 6.57 (d, J= 8.5 Hz, 2H), 2.66 (s, 3H).



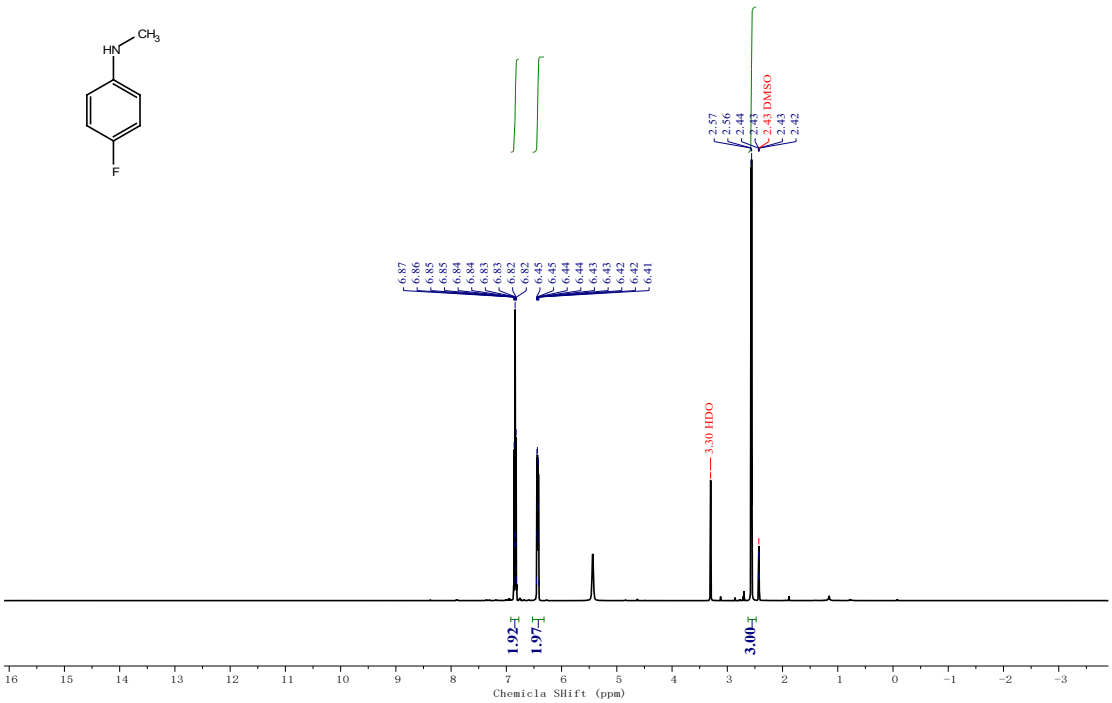
2j-^{1}H NMR

^{13}C NMR (126 MHz, DMSO-d_6) δ152.65, 133.01 – 123.63 (m), 126.17 (q, J= 3.8 Hz), 114.92 (d, J= 31.8 Hz), 110.88, 29.21.



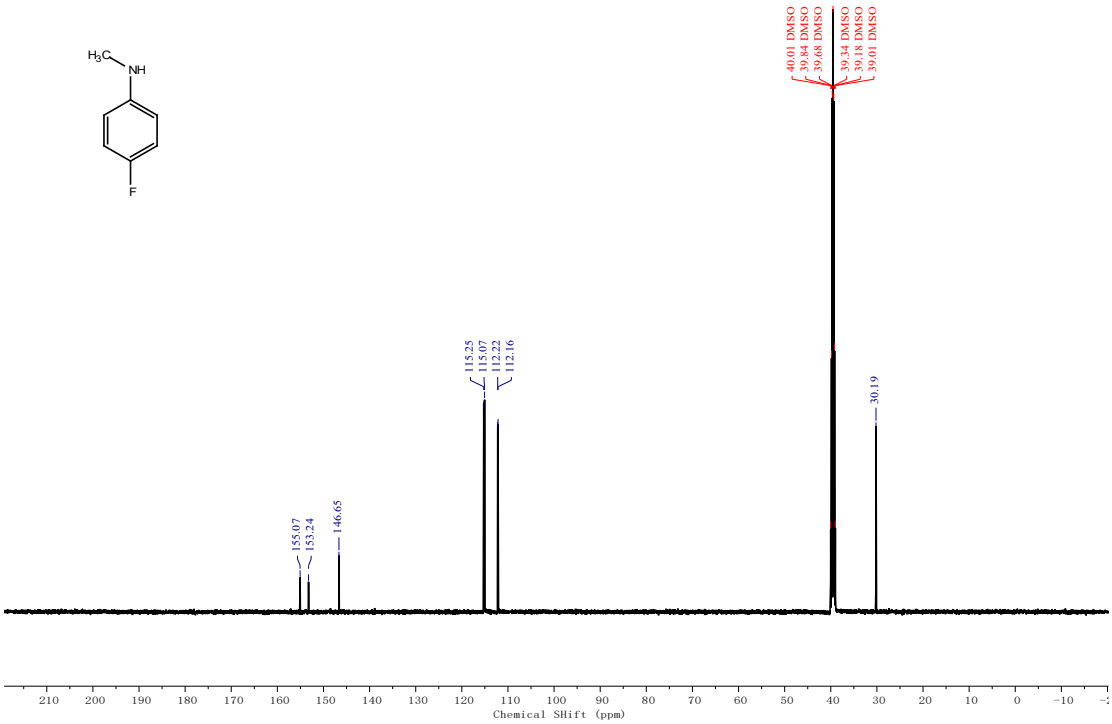
2j-^{13}C NMR

¹H NMR (500 MHz, DMSO-d_6) δ6.92 – 6.77 (m, 2H), 6.53 – 6.32 (m, 2H), 5.44 (q, *J*= 5.2 Hz, 1H), 2.56 (d, *J*= 5.1 Hz, 3H).

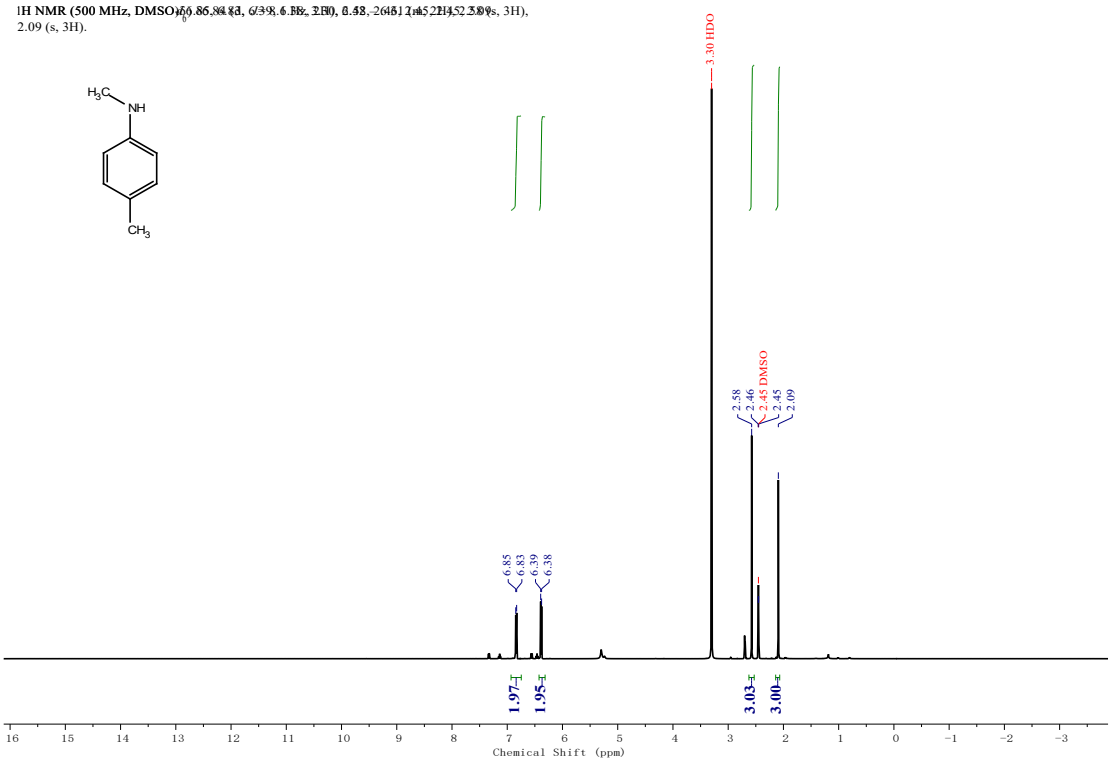


2k-^{1}H NMR

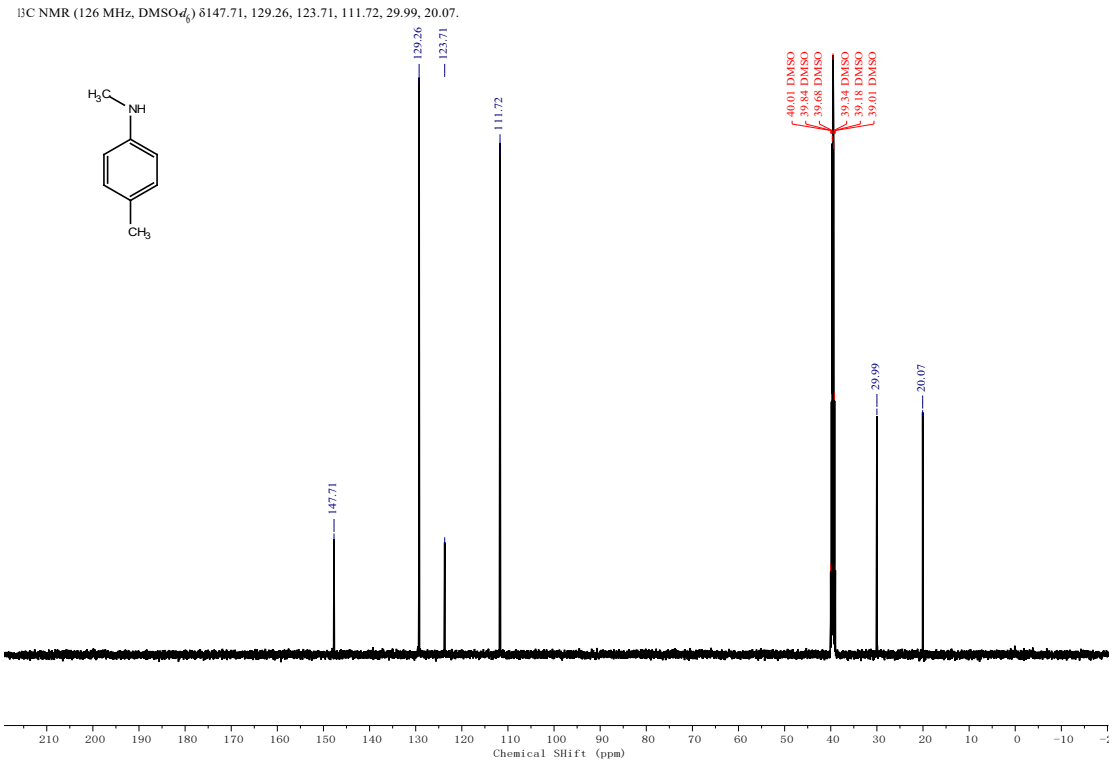
^{13}C NMR (126 MHz, DMSO-d_6) δ154.15 (d, *J*= 230.3 Hz)., 146.65, 115.16 (d, *J*= 22.0 Hz)., 112.19 (d, *J*= 7.3 Hz), 30.19.



2k-^{13}C NMR

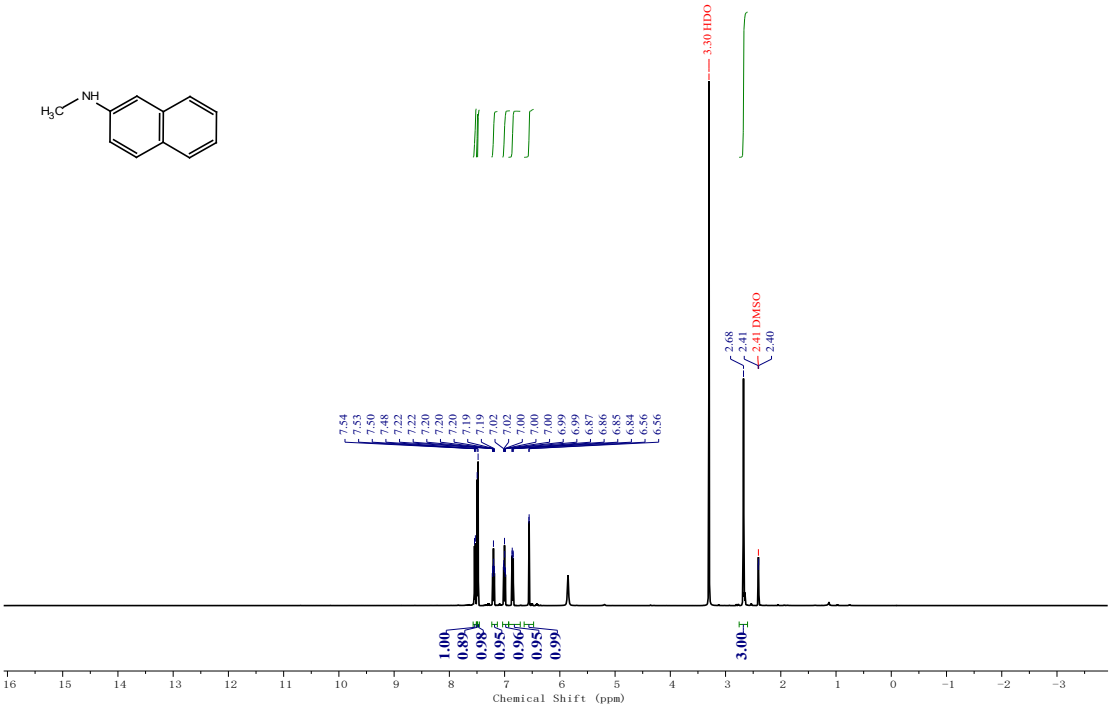


2m-^{1}H NMR



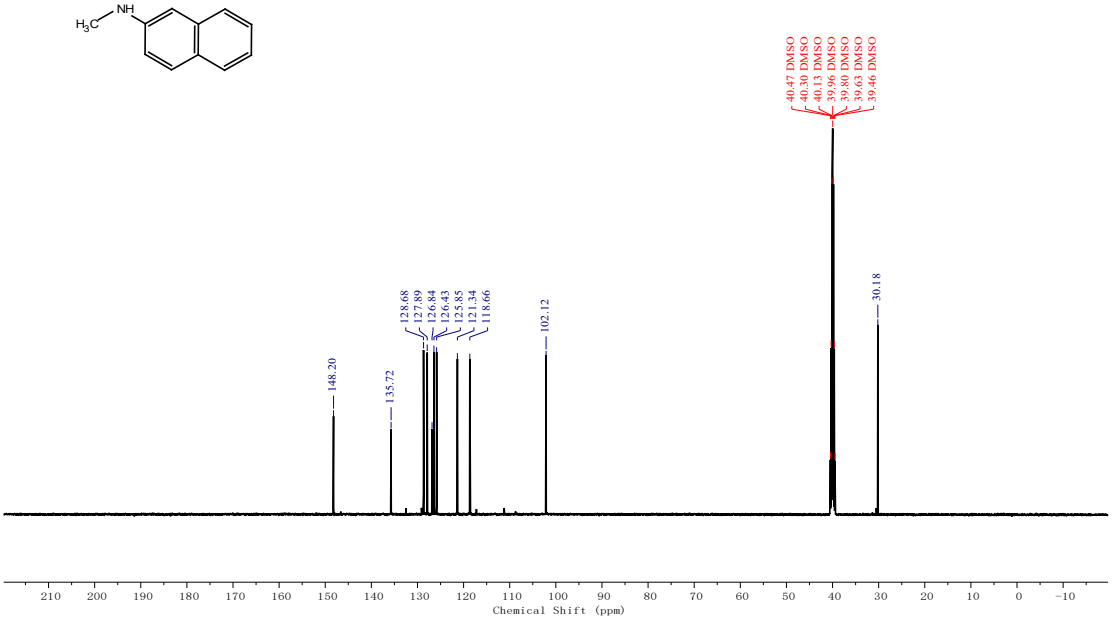
2m-^{13}C NMR

¹H NMR (500 MHz, DMSO-d_6) δ7.54 (d, *J*= 8.1 Hz, 1H), 7.50 (s, 1H), 7.48 (s, 1H), 7.20 (ddd, *J*= 8.2, 6.7, 1.3 Hz, 1H), 7.00 (ddd, *J*= 8.1, 6.7, 1.1 Hz, 1H), 6.86 (dd, *J*= 8.8, 2.3 Hz, 1H), 6.56 (d, *J*= 2.2 Hz, 1H), 2.68 (s, 3H).



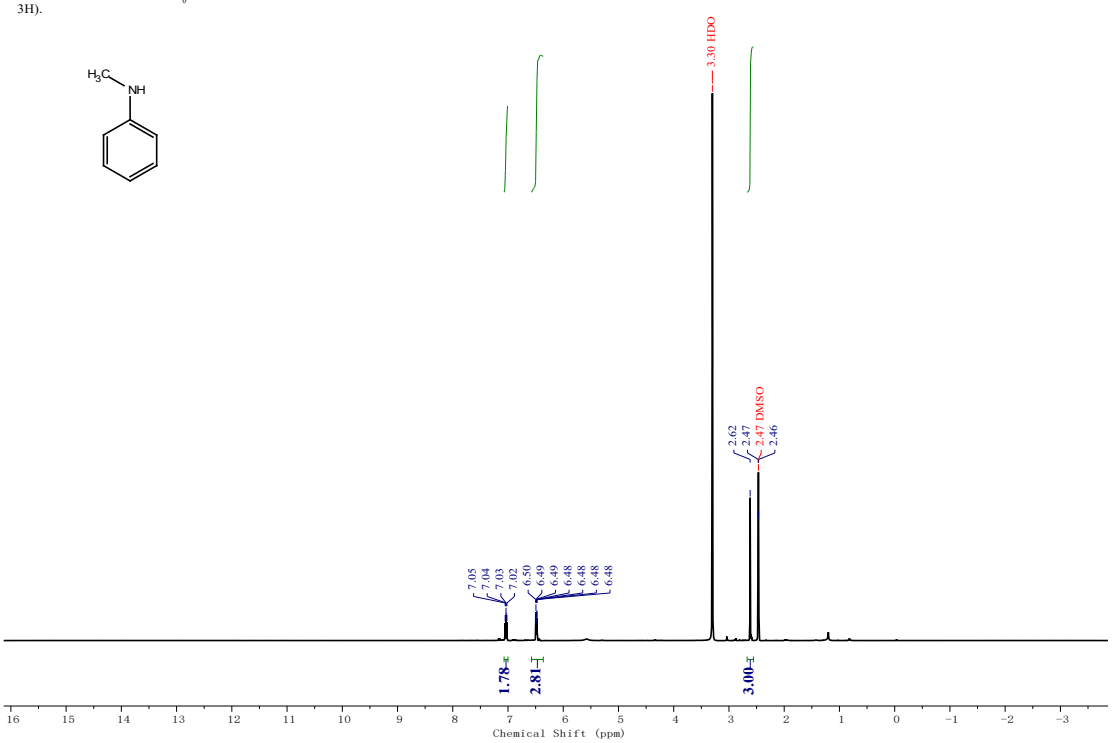
2n-^{1}H NMR

¹³C NMR (126 MHz, DMSO-d_6) δ148.20, 135.72, 128.68, 127.89, 126.84, 126.43, 125.85, 121.34, 118.66, 102.12, 30.18.



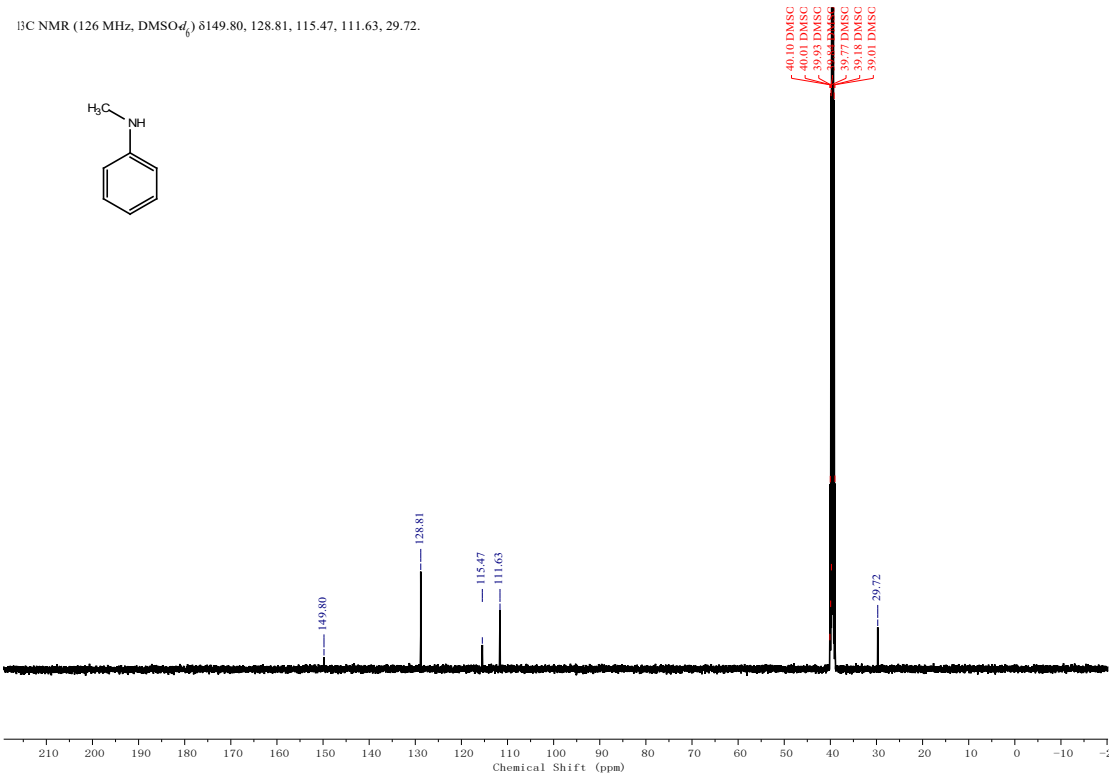
2n-^{13}C NMR

^{1}H NMR (500 MHz, DMSO-d_6) δ7.04 (dd, J= 8.4, 7.3 Hz, 2H), 6.58 – 6.36 (m, 3H), 2.62 (s, 3H).

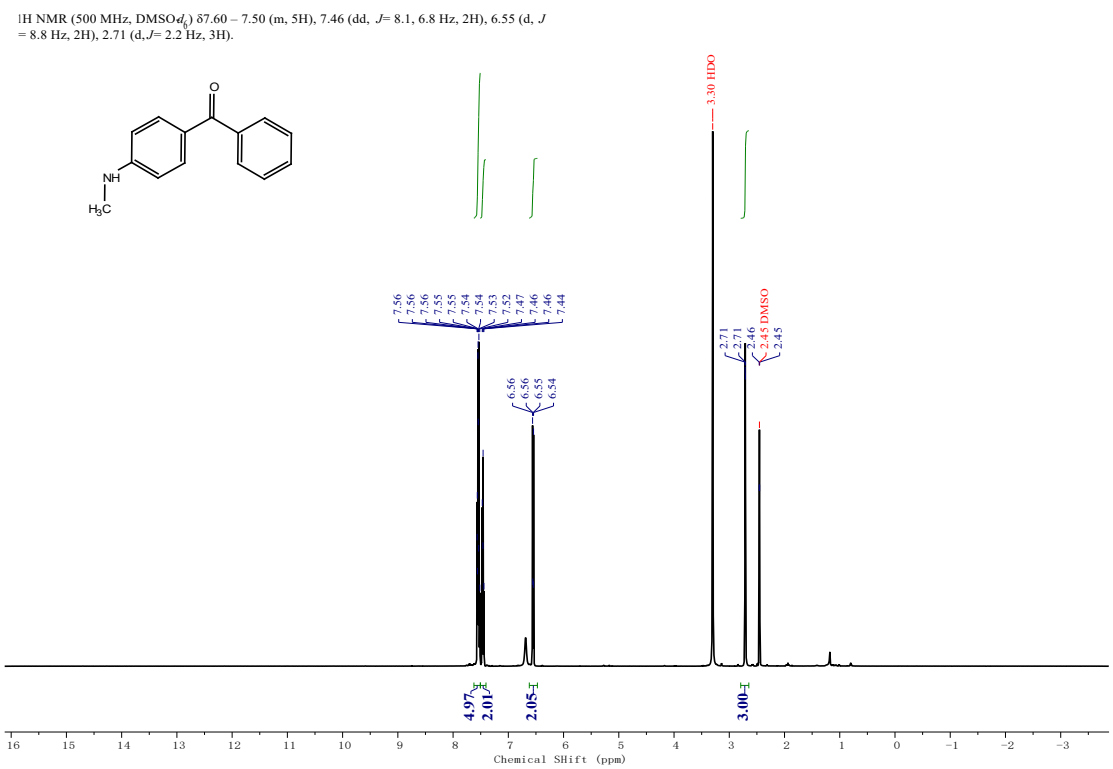


2o-^{1}H NMR

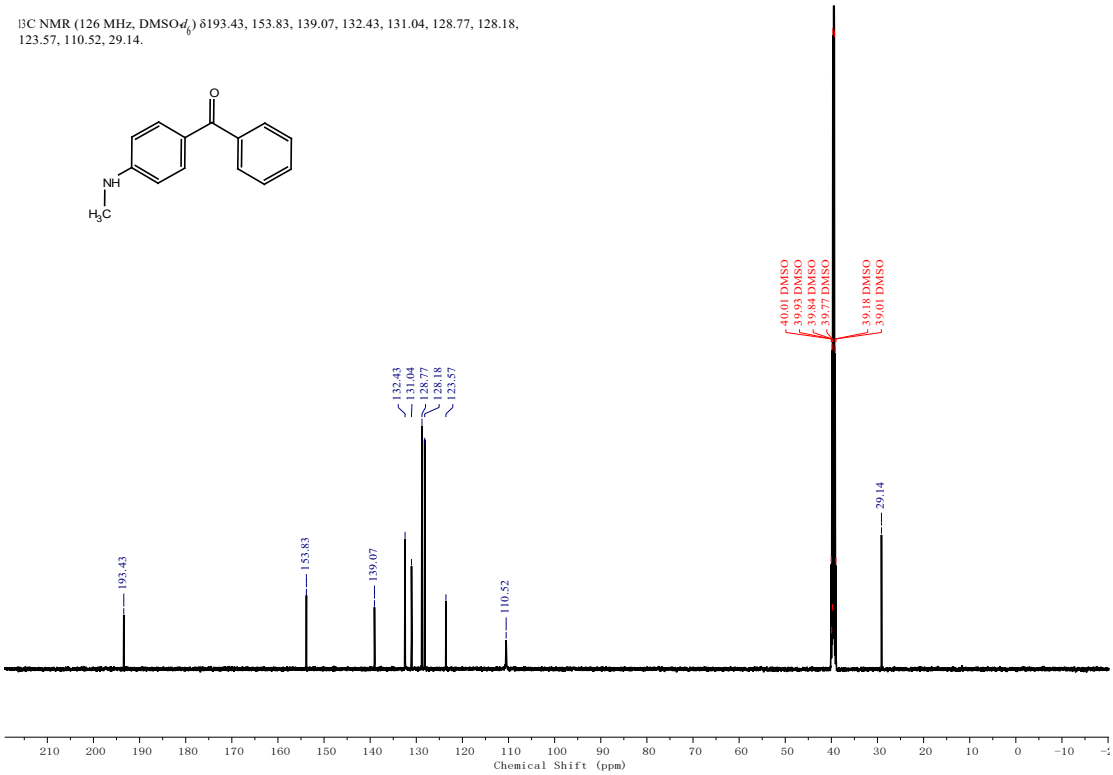
^{13}C NMR (126 MHz, DMSO-d_6) δ149.80, 128.81, 115.47, 111.63, 29.72.



2o-^{13}C NMR



2q-^{1}H NMR



2q-^{13}C NMR