Supporting Information

Cyano-Borrowing: Titanium-Catalyzed Direct Amination of Cyanohydrins with Amines and Enantioselective Examples

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Contents:

I. General information

^{1}H and **^{13}C NMR** spectra were recorded on a Bruker Avance 600 MHZ instruments. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.0) or tetramethylsilane (TMS δ 0.00) was used as a reference. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), bs (broad singlet). Coupling constants were reported in Hertz (Hz). All high resolution mass spectra (**HRMS**) were obtained on a Bruker Apex-2. For thin layer chromatography (**TLC**), Qingdao Haiyang Chemical were used, and compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with iodine, or potassium permanganate solution followed by heating using a heat gun. Flash chromatography separations were performed on Qingdao Haiyang Chemical 300-400 mesh silica gel. The enantiomeric excess (**ee**) of products were determined by chiral phase HPLC analysis on SHIMAZU HPLC units, including the following instruments: pump, LC-20A; detector, SPD-20A; column, Chiralcel IC. All reactions were carried out under nitrogen atmosphere. All commercially available reagents were used as received for the reactions without any purification. All solvents were dried on alumina columns using a solvent dispensing system.

II. General Procedure for preparation of product from cyanohydrins

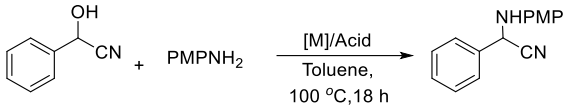
Method A: To a vial equipped with a dried stir bar was added amines (0.2 mmol) cyanohydrins (0.4 mmol), Ti(O^{i}-Pr)$_4$ (10 mol%), toluene (1 mL) in the glovebox. The reaction mixture was taken outside the glovebox. Then, the reaction mixture was allowed to stir at the settle temperature for 18 hours. The reaction mixture was added to water (10 mL), extracted with EtOAc (3 × 5 mL). The organic layer was washed with aqueous $NaHCO_3$ and brine and dried over Na_2SO_4. And the residue was purified by column chromatography with silica gel to give pure products.

Method B: To a vial equipped with a dried stir bar was added Ti(O^{i}-Pr)$_4$ (0.01 mmol), (*S*)-BINOL (0.01 mmol), quinine (0.025 mmol) and toluene (1 mL) in the glovebox. The mixture was taken outside the glovebox. Then, the mixture was allowed to stir at

40 ^{o}C for 2 hours to give a clear solution. After that, $PMPNH_2$ (0.1 mmol), cyanohydrins (0.2 mmol), TBME (2 mL) was added to the mixture in the glovebox. The reaction mixture was taken outside the glovebox. Then, the reaction mixture was allowed to stir at 40 ^{o}C for 36 hours. The reaction mixture was added to water (10 mL), extracted with EtOAc (3 × 5 mL). The organic layer was washed with aqueous $NaHCO_3$ and brine and dried over Na_2SO_4. And the residue was purified by column chromatography with silica gel to give pure products.

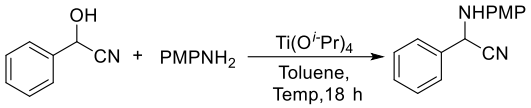
III. Optimization of Reaction Parameters

Table S1. Effect of transition metal



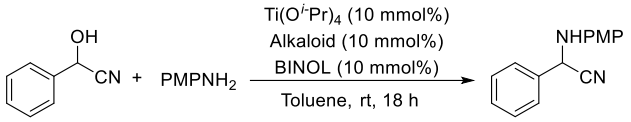
Entry	[M]	Acid	Yield (%)
1	$Ni(OTf)_2$	TsOH	Trace
2	$Pd(TFA)_2$	TsOH	NR
3	AgOTf	TsOH	NR
4	$Sc(OTf)_3$	TsOH	67
5	$Ti(OiPr)_4$	TsOH	90
6	**$Ti(OiPr)_4$**	**--**	**90**

Table S2. Effect of temperature



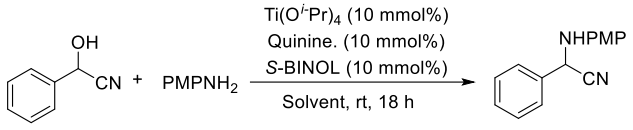
Entry	Temp (^{o}C)	Yield (%)
1	100	90
2	80	87
3	60	88
4	**40**	**89**
5	25	84

Table S3. Effect of chiral ligand's configuration in asymmetric reaction



Entry	Alkaloid	(R/S)BINOL	Yield (%)	ee (%)
1	Cinchonine	*S*	87	0
2	Cinchonidine	*S*	88	0
3	**Quinine**	***S***	**91**	**14**
4	Quinidine	*S*	91	0
5	Quinine	*R*	90	0

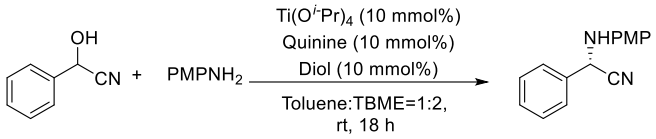
Table S4. Effect of solvent in asymmetric reaction



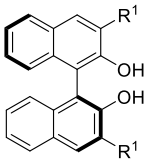
Entry	Solvent	Yield (%)	ee (%)
1	Toluene	91	14
2	THF	10	0
3	DME	82	8
4	TBME	36	30
5[a]	TBME	12	50
6	CPME	trace	
7	DCM	62	3
8	Toluene:TBME=1:1	9	27
9[a,b]	Toluene:TBME=1:1	29	57
10[a,b]	Toluene:TBME=1:2	44	65
11[a,b,c]	**Toluene:TBME=1:2**	**89**	**67**
12[a,b]	Toluene:TBME=1:3	28	60
13[a,b]	Toluene:TBME=2:1	30	45
14[a,b]	Toluene:TBME=3:1	29	48

[a] $PMPNH_2$ 0.1 mmol was used. [b] The mixture was string in toluene, and then $PMPNH_2$ 0.1 mmol, anhydrous cyanohydrin 0.2 mmol,TBME 2 mL was added. [c] The reaction temperature was 40 ºC.

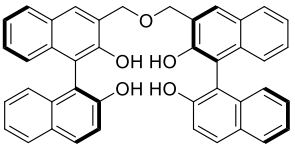
Table S5. Effect of Diols in asymmetric reaction



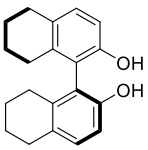
Entry	Diol	Yield (%)	ee (%)
1	**L1**	89	67
2	**L2**	89	13
3	**L3**	90	22
4	**L4**	83	28
5	**L5**	91	26
6	**L6**	87	5
7	**L7**	84	6
8	**L8**	82	5
9	**L9**	89	4
10	**L10**	90	3
11	**L11**	93	2
12	**L12**	90	4
13	**L13**	89	36
14	**L14**	91	19
15	**L15**	87	14
16	**L16**	91	15
17	**L17**	88	15
18	**L18**	87	9
19	**L19**	82	0
20	**L20**	84	0
21	**L21**	89	0



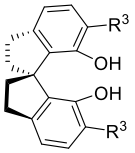
L1: R^1 = H
L2: R^1 = C_6H_5
L3: R^1 = *p*-Et-C_6H_4
L4: R^1 = 2-Naphthyl
L5: R^1 = *p*-Ph-C_6H_4
L6: R^1 = $SiPh_3$
L7: R^1 = 9-Anthracene
L8: R^1 = 3,5-$(CF_3)_2$-C_6H_3
L9: R^1 = 3,5-$(CH_3)_2$-C_6H_3
L10: R^1 = 4-tBu-C_6H_4
L11: R^1 = 2,4,6-$(iPr)_3$-C_6H_2
L12: R^1 = 4-MeO-3,5-(tBu)-C_6H_2
L13: R^1 = Me
L14: R^1 = Br



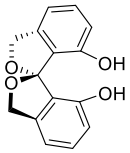
L15



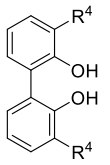
L16



L17: R^3 = H
L18: R^3 = Ph

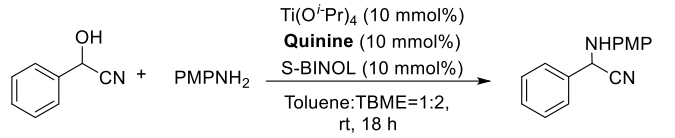


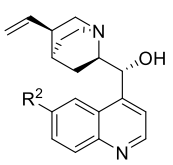
L18



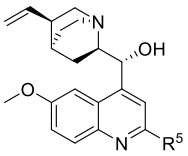
L19: R^4 = H
L20: R^4 = Cl
L21: R^4 = Ph

Table S6. Effect of Quinines in asymmetric reaction

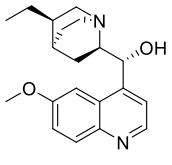




L22: R^2 = *p*-Me-C_6H_4
L23: R^2 = *p*-CF_3-C_6H_4
L24: R^2 = *p*-*i*-Pr-C_6H_4
L25: R^2 = 2-Naphthyl
L26: R^2 = BnO
L27: R^2 = O*i*-Pr
L28: R^2 = OH



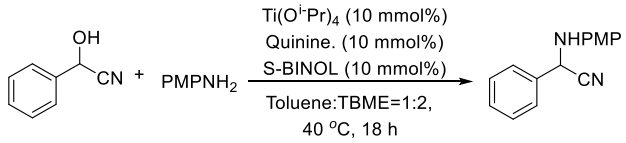
L29: R^5 = *n*-Bu
L30: R^5 = *p*-Me-C_6H_4
L31: R^5 = C_6H_5



L32

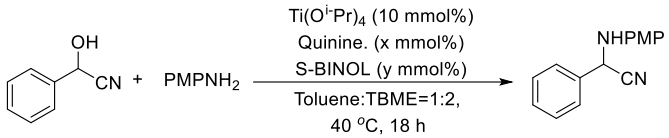
Entry	Quninie	Yield (%)	ee (%)
1	**L22**	54	25
2	**L23**	61	20
3	**L24**	55	15
4	**L25**	86	43
5	**L26**	83	43
6	**L27**	86	37
7	**L28**	84	0
8	**L29**	78	35
9	**L30**	66	15
10	**L31**	60	21
11	**L32**	89	43

Table S7. Effect of temperature in asymmetric reaction



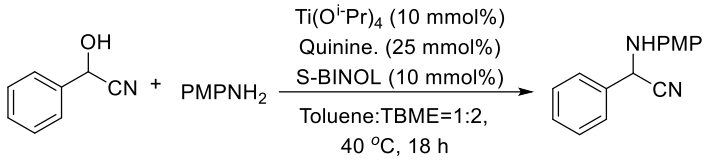
Entry	Temp (^{o}C)	Yield (%)	ee (%)
1	**40**	**89**	**67**
2	20	54	60
3	30	83	65

Table S8. Effect of ligand quantity in asymmetric reaction



Entry	*S*-BINOL(x mmol%)	Quinine (y mmol%)	Yield (%)	ee (%)
1	10	20	90	60
2	20	10	89	41
3	20	20	91	55
4	0	10	42	3
5	10	0	trace	
5	10	15	90	60
6	10	22	90	61
7	**10**	**25**	**91**	**70**
8	10	30	91	66

Table S9. Effect of Concentration in asymmetric reaction



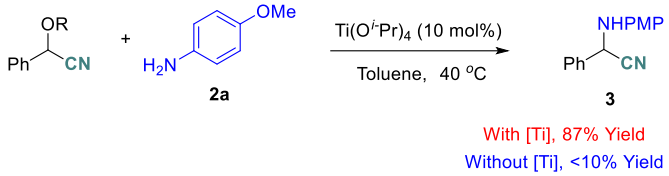
Entry	Concentration (mmol/mL)	Yield (%)	ee (%)
1	0.1	89	67
2	0.067	56	70
3	0.050	45	70
4[a]	**0.033**	**67**	**77**

[a] The reaction time was 36 h.

IV. The mechanism studies.

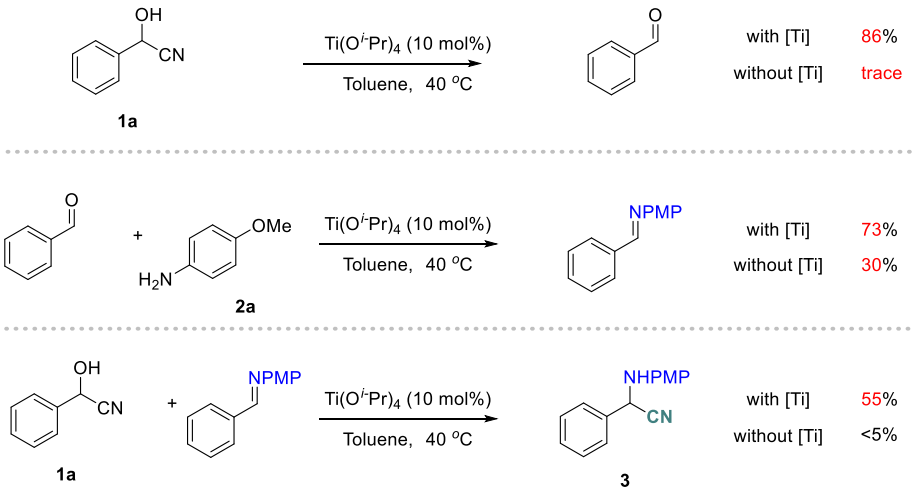
1, The role of titanium catalyst in the cyano-borrowing reaction.

While this cyano borrowing reaction was carried out without titanium catalyst, low reactivity was achieved, and deliver the product was obtained in <10% yield, but we got imine as a byproduct.



Fjgure S1. The importance of Ti(O^{i}-Pr)$_4$.

Additionally, in order to understand the role of titanium catalyst, we have tested every step of the reaction in the presence and absence of the titanium catalyst, respectively, as is shown in Finger S2. We found that the titanium catalyst improves the step of imine intermediate formation, and the titanium catalyst was indispensable for the cleavage of C-CN bond in cyanohydrins and the formation of C-CN in the Stercker reaction under the optimal reaction condition.



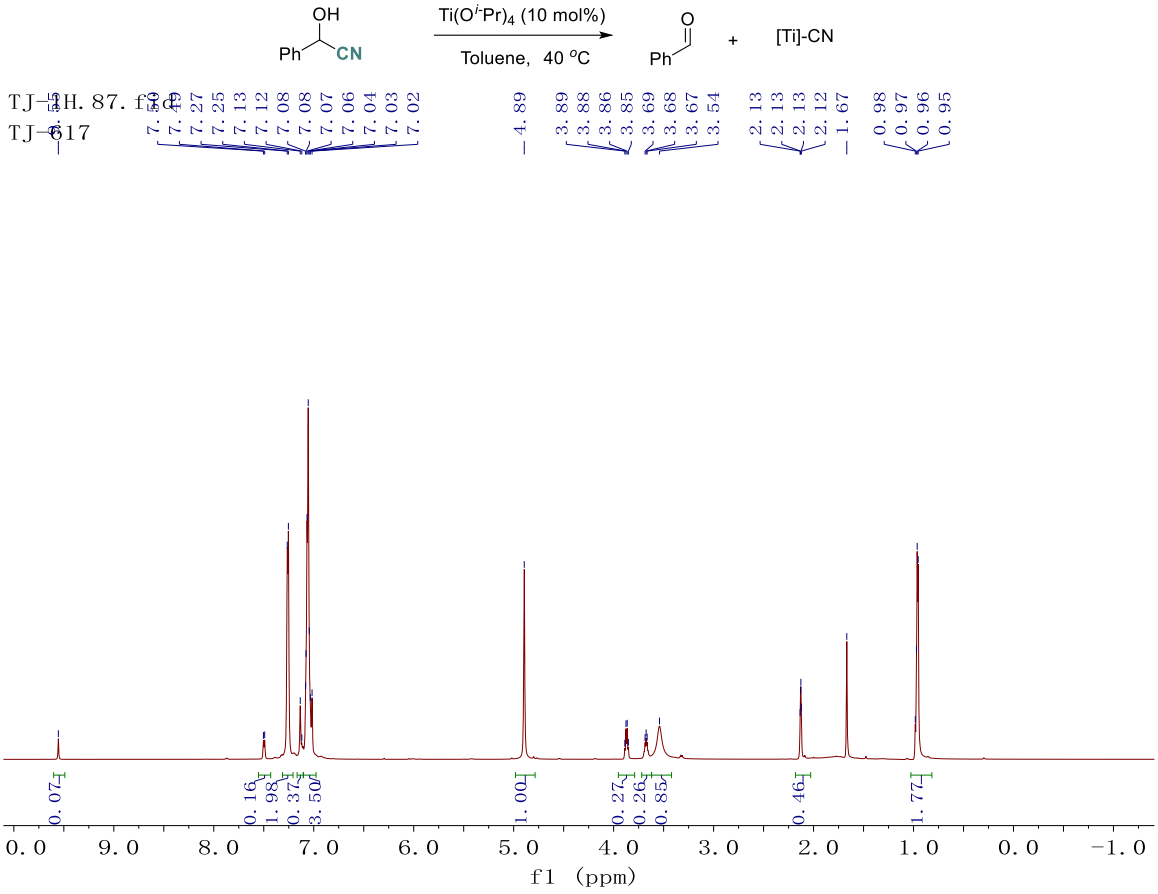
Finger S2. The role of titanium catalyst in the transformation.

2, The evidence for the formation of Ti-CN

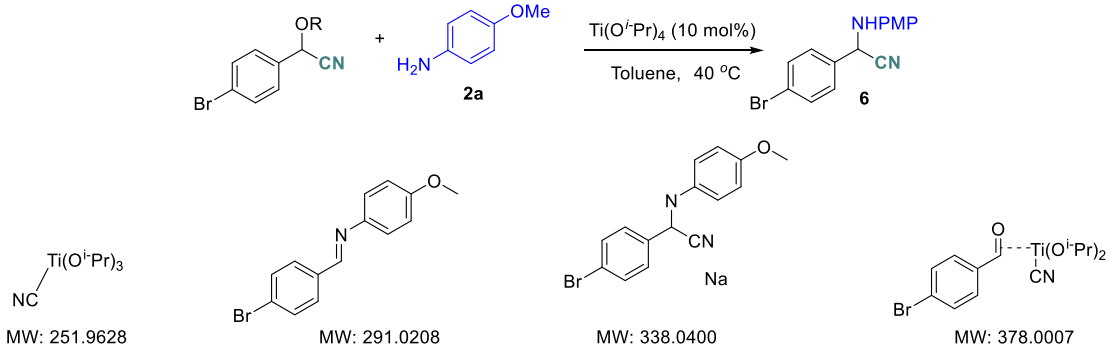
The ^{1}H NMR and HIMS of the reaction mixture were tested. The NMR shows that under the titanium catalyst, cyanohydrin **1a** could cleavage C-CN bond, and led to aldehyde (ppm: 9.55). As it shown below, we found the fragment of [Ti(O^{i}-Pr)$_3$(CN)+H^{+}]

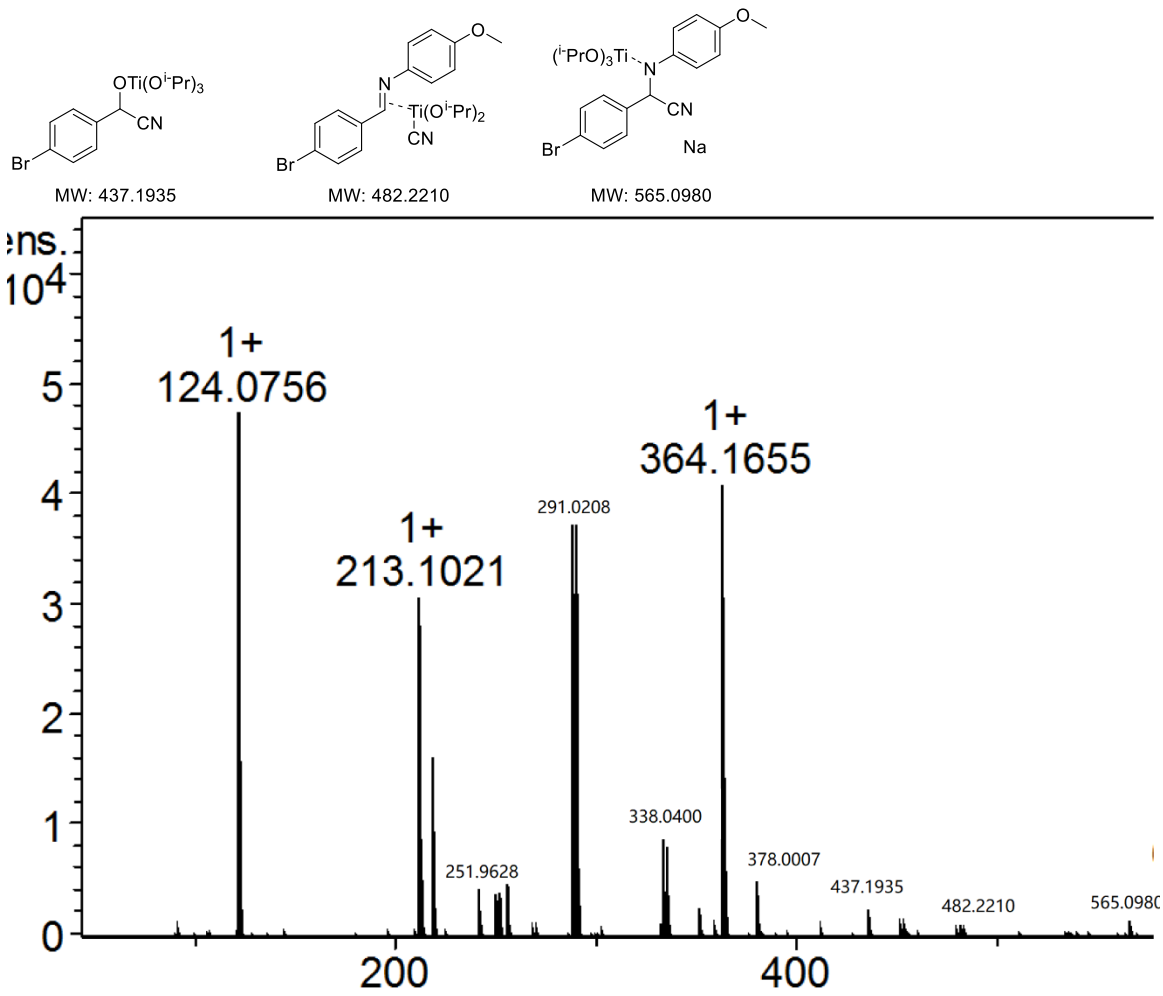
(251.9628), [*p*-BrC$_6$H$_4$CH(CN)O-Ti(O^i-Pr)$_3$] (437.1935), [*p*-BrC$_6$H$_4$CHO-Ti(CN)(O^i-Pr)$_2$] (378.0007) and [imine-Ti(CN)(O^i-Pr)$_2$] (482.2210). All these results could prove the formation of Ti-CN bond.

The ^{1}H NMR of the reaction mixture of Cyanohydrin 1a with Ti(O^i-Pr)$_4$.

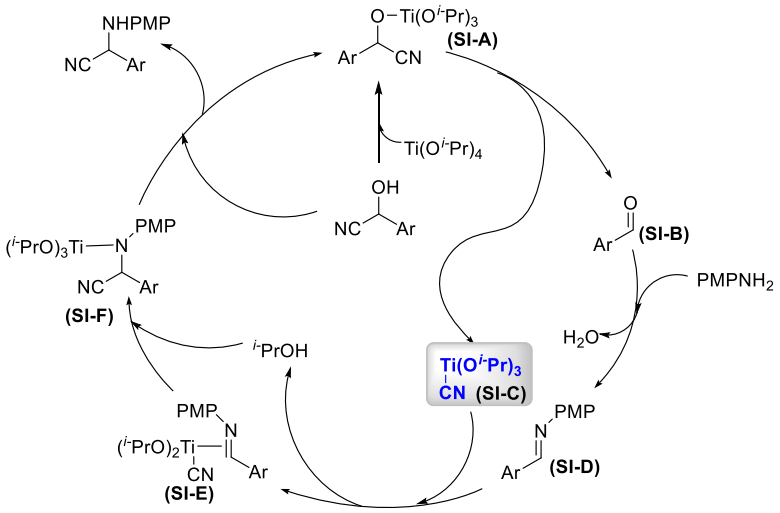


The HIMS for the mixture of *p*-Bromobenzaldehyde cyanohydrin (1d), PMPNH$_2$ (2a) with Ti(O^i-Pr)$_4$ under the standard reaction condition.





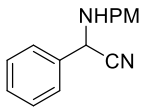
The proposed catalytic cycle is shown as Finger S3: the cyanohydrin replaced one of the iPrO in Ti(O^{i}-Pr)$_4$ and deliver the intermediate **SI-A**, then aldehyde (**SI-B**) and the fragment [Ti(O^{i}-Pr)$_3$(CN)] (**SI-C**) were formed via the β-carbon elimination of **SI-A**. Condensation of the aldehyde with the amine to form imine (Shift base, **SI-D**), connation of **SI-C** with imine gave **SI-E**, then transfer the cyano group from titanium to imine and led to the intermediate **SI-F**, protonation of **SI-F** with cyanohydrin and deliver the product and **SI-A** for a new catalyst cycle.



Finger S3. The proposed catalytic cycle.

V. The analytical and spectral characterization data

2-((4-methoxyphenyl)amino)-2-phenylacetonitrile (3)[1]



3

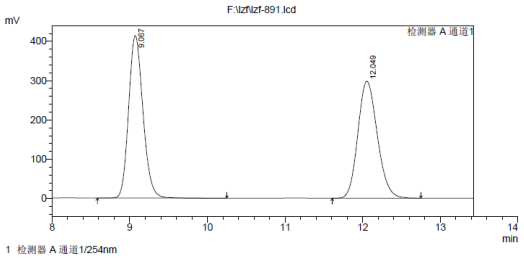
The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.5 in hexane:ethyl acetate = 5:1) resulting in a yellow solid in 89% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 6.7 Hz, 2H), 7.40-7.31 (m, 3H), 6.77 (d, *J* = 8.8 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 5.26 (d, *J* = 8.1 Hz, 1H), 3.69 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 154.25, 138.65, 134.27, 129.43, 129.26, 127.25, 118.46, 116.43, 115.08, 55.68, 51.68.

HPLC condition: Dalcel IC column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 13.2 min for minor isomer, t_R = 9.6 min for major isomer, 78% ee.

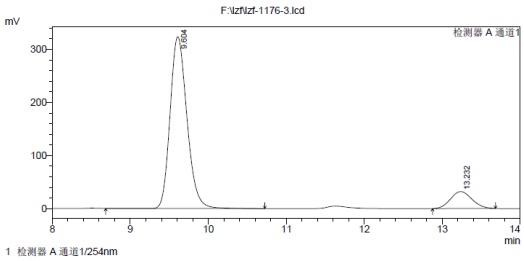
$[\alpha]_D^{20}$ = -7.5 (c = 0.01, CH_2Cl_2).



峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	9.067	5301684	413028	50.636	58.142
2	12.049	5168567	297353	49.364	41.858
总计		10470250	710380	100.000	100.000

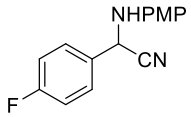


峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	9.604	4860350	323746	88.866	91.023
2	13.232	608927	31930	11.134	8.977
总计		5469277	355676	100.000	100.000

2-(4-fluorophenyl)-2-((4-methoxyphenyl)amino)acetonitrile (4)



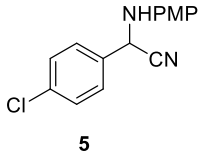
4

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.4 in hexane:ethyl acetate = 5:1) resulting in a yellow solid in 91% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 8.3 Hz, 5.2 Hz, 2H), 7.05 (t, *J* = 8.5 Hz, 2H), 6.76 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 5.24 (s, 1H), 3.68 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 164.04, 162.38, 154.39, 138.37, 129.15 (d, *J* = 8.5 Hz), 118.30, 116.62, 116.25 (d, *J* = 22.0 Hz), 115.07, 55.66, 51.06.

2-(4-chlorophenyl)-2-((4-methoxyphenyl)amino)acetonitrile (5)



5

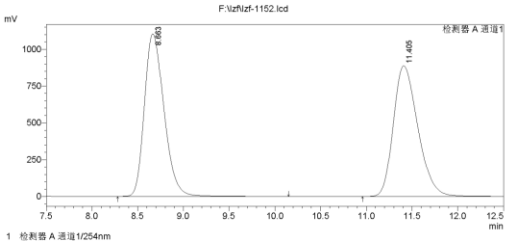
The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.4 in hexane:ethyl acetate = 5:1) resulting in a yellow solid in 92% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 6.76 (d, *J* = 8.8 Hz, 2H), 6.66 (d, *J* = 8.8 Hz, 2H), 5.24 (s, 1H), 3.68 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 154.44, 138.27, 135.49, 132.76, 129.44, 128.60, 118.10, 116.70, 115.08, 55.66, 51.14.

HRMS (ESI): m/z Calcd. for $[C_{15}H_{13}ClN_2O, M+H]^+$: 273.0789; Found: 273.0790.

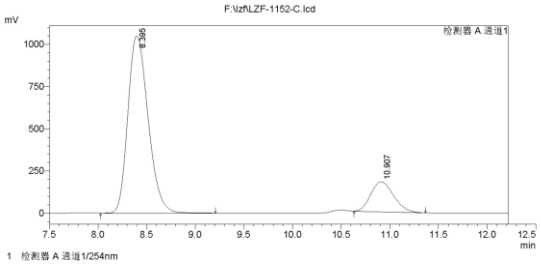
HPLC condition: Dalcel IC column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 11.4 min for minor isomer, t_R = 8.6 min for major isomer, 68% ee. $[\alpha]_D^{20}$ = -41.1 (c = 0.08, CH_2Cl_2).



峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	8.663	16427130	1104403	49.758	55.461
2	11.405	16587223	886902	50.242	44.539
总计		33014353	1991306	100.000	100.000

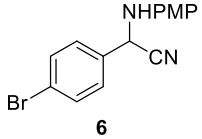


峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	8.395	15079560	1049871	83.804	85.530
2	10.907	2914311	177622	16.196	14.470
总计		17993872	1227493	100.000	100.000

2-(4-bromophenyl)-2-((4-methoxyphenyl)amino)acetonitrile (6)[2]



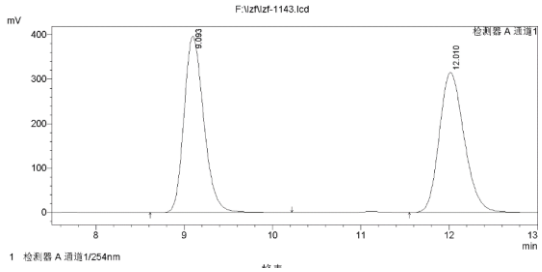
6

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.4 in hexane:ethyl acetate = 5:1) resulting in a yellow solid in 90% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 6.75 (d, *J* = 8.9 Hz, 2H), 6.65 (d, *J* = 8.8 Hz, 2H), 5.22 (s, 1H), 3.68 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 154.43, 138.25, 133.27, 132.41, 128.88, 123.60, 118.05, 116.68, 115.08, 55.67, 51.19.

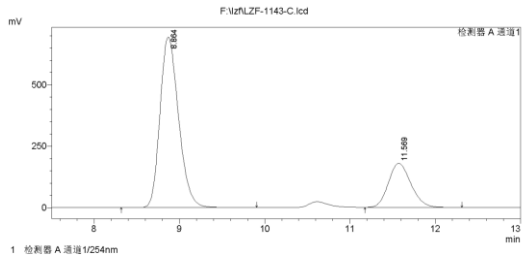
HPLC condition: Dalcel IC column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 12.0 min for minor isomer, t_R = 9.0 min for major isomer, 52% ee. $[\alpha]_D^{20}$ = -116.9 (c = 0.24, CH_2Cl_2).



峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	9.093	6166298	396585	49.980	55.741
2	12.010	6171261	314899	50.020	44.259
总计		12337558	711483	100.000	100.000

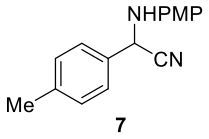


峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	8.864	10504775	693537	76.112	79.489
2	11.569	3296903	178959	23.888	20.511
总计		13801678	872497	100.000	100.000

2-((4-methoxyphenyl)amino)-2-(p-tolyl)acetonitrile (7)[3]



7

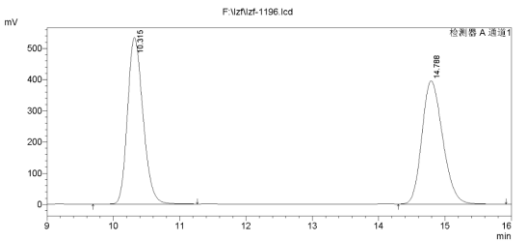
The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.4 in hexane:ethyl acetate = 5:1) resulting in a yellow solid in 90% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.7 Hz, 2H), 6.77 (d, *J* = 8.9 Hz, 2H), 6.67 (d, *J* = 8.9 Hz, 2H), 5.22 (s, 1H), 3.69 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 154.16, 139.46, 138.72, 131.32, 129.90, 127.16, 118.61, 116.32, 115.05, 55.69, 51.39, 21.16.

HPLC condition: Dalcel IC column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 14.7 min for minor isomer, t_R = 10.3 min for major isomer, 64% ee.

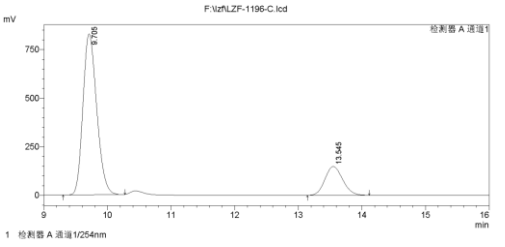
$[\alpha]_D^{20}$ = -29.75 (c = 0.4, CH_2Cl_2).



峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	10.315	8659444	533907	50.191	57.500
2	14.788	8593483	394628	49.809	42.500
总计		17252926	928536	100.000	100.000

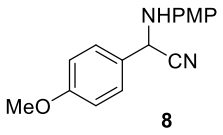


峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	9.705	12444469	827833	81.261	84.826
2	13.545	2869791	148082	18.739	15.174
总计		15314261	975915	100.000	100.000

2-(4-methoxyphenyl)-2-((4-methoxyphenyl)amino)acetonitrile (8)[3]



8

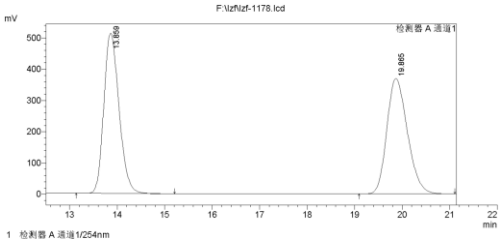
The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.4 in hexane:ethyl acetate = 5:1) resulting in a yellow solid in 90% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.9 Hz, 2H), 6.68 (d, *J* = 8.9 Hz, 2H), 3.77 (s, 3H), 3.70 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 160.43, 154.19, 138.70, 128.58, 126.28, 118.65, 116.36, 115.05, 114.60, 55.68, 55.42, 51.12.

HPLC condition: Dalcel IC column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 19.8 min for minor isomer, t_R = 13.8 min for major isomer, 48% ee.

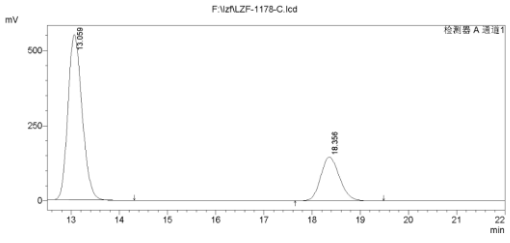
$[\alpha]_D^{20}$ = -47.8 (c = 0.28, CH_2Cl_2).



峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	13.859	11371543	512354	50.587	58.171
2	19.865	11107596	368424	49.413	41.829
总计		22479138	880778	100.000	100.000

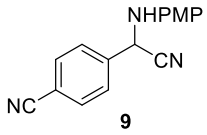


峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	13.059	11279686	549904	74.205	79.124
2	18.356	3920949	145085	25.795	20.876
总计		15200635	694989	100.000	100.000

4-(cyano((4-methoxyphenyl)amino)methyl)benzonitrile (9)



9

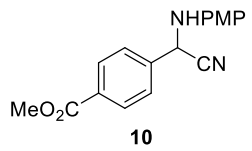
The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.2 in hexane:ethyl acetate = 5:1) resulting in a yellow solid in 49% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (s, 4H), 6.77 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 5.36 (d, *J* = 9.4 Hz, 1H), 3.82 (d, *J* = 9.3 Hz, 1H), 3.70 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 154.75, 139.19, 137.77, 132.98, 127.99, 117.93, 117.44, 117.02, 115.12, 113.58, 55.65, 51.49.

HRMS (ESI): m/z Calcd. for $[C_{16}H_{13}N_3O, M^+H]^+$: 286.0651; Found: 286.0650.

Methyl 4-(cyano((4-methoxyphenyl)amino)methyl)benzoate (10) [3]



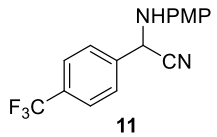
10

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.3 in hexane:ethyl acetate = 5:1) resulting in a yellow solid in 41% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 6.77 (d, *J* = 8.9 Hz, 2H), 6.68 (d, *J* = 8.9 Hz, 2H), 5.34 (d, *J* = 9.1 Hz, 1H), 3.87 (s, 3H), 3.79 (d, *J* = 8.9 Hz, 1H), 3.69 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 166.26, 154.50, 138.84, 138.19, 131.28, 130.46, 127.26, 117.93, 116.76, 115.08, 55.66, 52.34, 51.53.

2-((4-methoxyphenyl)amino)-2-(4-(trifluoromethyl)phenyl)acetonitrile (11)[4]



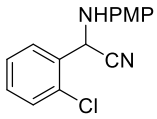
11

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.3 in hexane:ethyl acetate = 5:1) resulting in a yellow solid in 85% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 7.9 Hz, 5.3 Hz, 2H), 7.04 (t, *J* = 8.4 Hz, 2H), 6.76 (d, *J* = 8.7 Hz, 2H), 6.66 (d, *J* = 8.7 Hz, 2H), 5.24 (s, 1H), 3.68 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 164.03, 162.38, 154.38, 138.39, 130.12 (d, *J* = 3.1 Hz), 129.15 (d, *J* = 8.4 Hz), 118.32, 116.62, 116.25 (q, *J* = 22.0 Hz), 115.08, 55.66, 51.05.

2-(2-chlorophenyl)-2-((4-methoxyphenyl)amino)acetonitrile (12) [3]



12

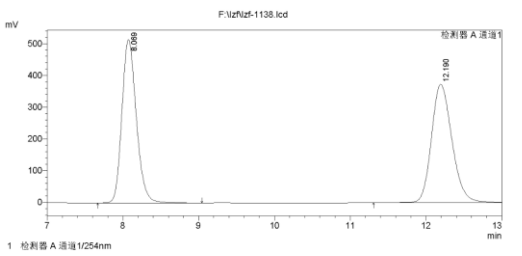
The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.3 in hexane:ethyl acetate = 5:1) resulting in a yellow solid in 92% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66-7.62 (m, 1H), 7.42-7.38 (m, 1H), 7.33-7.29 (m, 2H), 6.82-6.75 (m, 2H), 6.72 (d, *J* = 8.9 Hz, 2H), 5.55 (d, *J* = 8.4 Hz, 1H), 3.69 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 154.52, 138.43, 133.52, 132.08, 130.89, 130.44, 129.06, 127.73, 118.00, 116.95, 115.05, 55.65, 49.69.

HPLC condition: Dalcel IC column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 12.1 min for minor isomer, t_R = 8.0 min for major isomer, 87% ee.

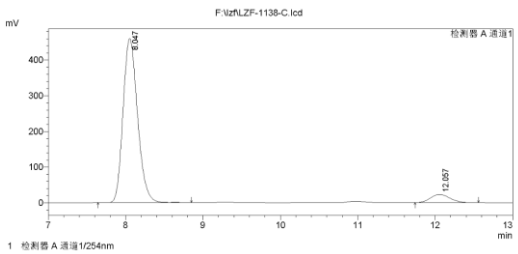
$[\alpha]_D^{20}$ = -62.4 (c = 0.25, CH_2Cl_2).



峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	8.069	6820617	514701	49.067	57.956
2	12.190	7079907	373390	50.933	42.044
总计		13900525	888090	100.000	100.000

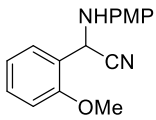


峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	8.047	5983480	460357	93.698	95.236
2	12.057	402461	23031	6.302	4.764
总计		6385941	483388	100.000	100.000

2-(2-methoxyphenyl)-2-((4-methoxyphenyl)amino)acetonitrile (13)



13

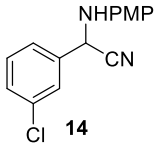
The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.3 in hexane:ethyl acetate = 5:1) resulting in a yellow oil in 69% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40-7.37 (m, 1H), 7.30 (dd, *J* = 12.5 Hz, 4.6 Hz, 2H), 6.92 (dd, *J* = 9.5 Hz, 5.4 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.75 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 8.9 Hz, 2H), 5.38 (s, 1H), 3.83 (s, 3H), 3.66 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.82, 154.14, 139.00, 130.92, 128.76, 122.79, 121.18, 118.87, 116.77, 114.98, 111.48, 55.84, 55.67, 47.45.

HRMS (ESI): m/z Calcd. for $[C_{16}H_{16}N_2O_2, M+H]^+$: 269.1285; Found: 269.1283.

2-(3-chlorophenyl)-2-((4-methoxyphenyl)amino)acetonitrile (14)



14

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.5 in hexane:ethyl acetate = 5:1) resulting in a white solid in 81% yield.

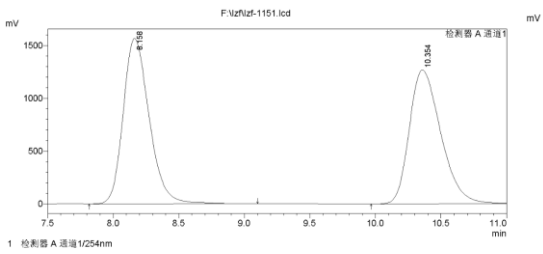
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.33-7.28 (m, 2H), 6.76 (d, *J* = 8.9 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 5.25 (s, 1H), 3.69 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 154.50, 138.16, 136.13, 135.27, 130.50, 129.67, 127.46, 125.35, 116.75, 115.10, 55.67, 51.25.

HRMS (ESI): m/z Calcd. for $[C_{15}H_{13}ClN_2O, M+Na]^+$: 295.0609; Found: 295.0608.

HPLC condition: Dalcel IC column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 10.3 min for minor isomer, t_R = 8.1 min for major isomer, 51% ee.

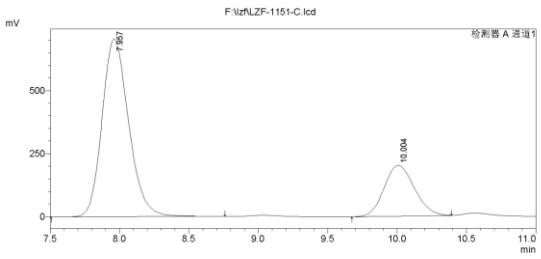
$[\alpha]_D^{20}$ = -60.8 (c = 0.12, CH_2Cl_2).



峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	8.158	21643186	1567147	50.520	55.275
2	10.354	21197348	1268051	49.480	44.725
总计		42840534	2835198	100.000	100.000

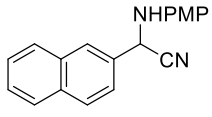


峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	7.957	9393747	703582	75.544	77.773
2	10.004	3041094	201074	24.456	22.227
总计		12434841	904656	100.000	100.000

2-((4-methoxyphenyl)amino)-2-(naphthalen-2-yl)acetonitrile (15)[3]



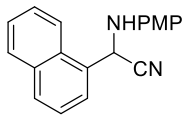
15

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.5 in hexane:ethyl acetate = 5:1) resulting in a yellow solid in 93% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.82-7.74 (m, 3H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.47-7.42 (m, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 5.38 (s, 1H), 3.66 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 154.28, 138.68, 133.53, 133.16, 131.52, 129.32, 128.26, 127.80, 127.10, 126.95, 126.57, 124.50, 118.53, 116.53, 115.10, 55.69, 51.82.

2-((4-methoxyphenyl)amino)-2-(naphthalen-1-yl)acetonitrile (16)



16

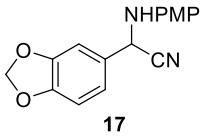
The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.5 in hexane:ethyl acetate = 5:1) resulting in a yellow solid in 89% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93-7.81 (m, 4H), 7.52-7.41 (m, 3H), 6.81 (d, *J* = 8.9 Hz, 2H), 6.76 (d, *J* = 8.9 Hz, 2H), 5.88 (s, 1H), 3.71 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 154.47, 134.07, 130.71, 130.26, 129.11, 127.44, 126.56, 126.42, 125.26, 122.84, 118.37, 116.35, 115.18, 55.72, 49.87.

HRMS (ESI): m/z Calcd. for $[C_{19}H_{16}N_2O, M+Na]^+$: 311.1155; Found: 311.1154.

2-(benzo[d][1,3]dioxol-5-yl)-2-((4-methoxyphenyl)amino)acetonitrile (17)



17

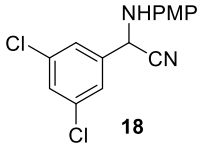
The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.3 in hexane:ethyl acetate = 5:1) resulting in a yellow solid in 80% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.99 (d, *J* = 8.0 Hz, 1H), 6.95 (s, 1H), 6.77-6.74 (m, 3H), 6.66 (d, *J* = 8.8 Hz, 2H), 5.91 (s, 2H), 5.15 (s, 1H), 3.68 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 154.23, 148.55, 148.47, 138.56, 128.01, 120.92, 118.52, 116.45, 115.05, 108.64, 107.69, 101.63, 55.67, 51.36.

HRMS (ESI): m/z Calcd. for $[C_{16}H_{14}N_2O_3, M+Na]^+$: 305.0897; Found: 305.0896.

2-(3,5-dichlorophenyl)-2-((4-methoxyphenyl)amino)acetonitrile (18)



18

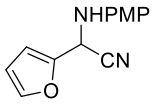
The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.4 in hexane:ethyl acetate = 5:1) resulting in a yellow solid in 68% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 1.1 Hz, 2H), 7.34 (s, 1H), 6.77 (d, *J* = 8.9 Hz, 2H), 6.66 (d, *J* = 8.9 Hz, 2H), 5.24 (s, 1H), 3.69 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 154.70, 137.77, 137.45, 135.98, 129.70, 125.75, 117.40, 116.94, 115.11, 55.65, 50.93.

HRMS (ESI): m/z Calcd. for $[C_{15}H_{12}Cl_2N_2O, M+Na]^+$: 329.0219; Found: 329.0217.

2-(furan-2-yl)-2-((4-methoxyphenyl)amino)acetonitrile (19) [1]



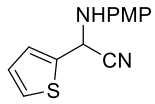
19

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.3 in hexane:ethyl acetate = 5:1) resulting in a yellow solid in 79% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 0.9 Hz, 1H), 6.83-6.76 (m, 2H), 6.71 (d, *J* = 8.9 Hz, 2H), 6.49 (d, *J* = 3.2 Hz, 1H), 6.35 (dd, *J* = 3.1 Hz, 1.8 Hz, 1H), 5.31 (d, *J* = 9.4 Hz, 1H), 3.83 (d, *J* = 9.3 Hz, 1H), 3.70 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 154.66, 146.47, 143.88, 137.83, 117.19, 116.70, 115.04, 110.87, 109.51, 55.63, 46.03.

2-((4-methoxyphenyl)amino)-2-(thiophen-2-yl)acetonitrile (20)



20

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.3 in hexane:ethyl acetate = 5:1) resulting in a yellow oil in 56% yield.

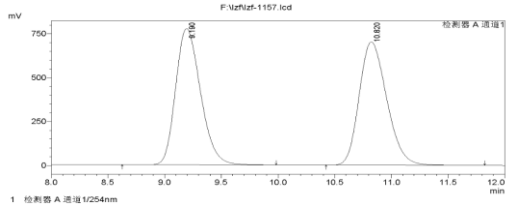
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32-7.29 (m, 1H), 7.28-7.25 (m, 1H), 6.96 (dd, *J* = 5.0 Hz, 3.7 Hz, 1H), 6.81-6.75 (m, 2H), 6.71 (d, *J* = 8.9 Hz, 2H), 5.47 (d, *J* = 9.0 Hz, 1H), 3.85 (d, *J* = 9.0 Hz, 1H), 3.70 (s, 3H).

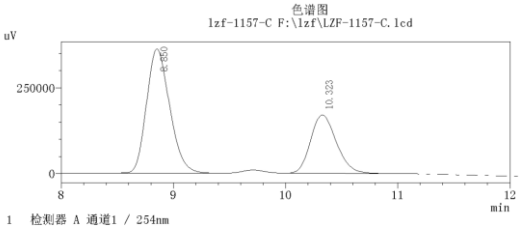
^{13}C NMR (150 MHz, $CDCl_3$) δ 154.66, 137.97, 137.25, 127.12, 127.09, 126.94, 117.78, 117.14, 115.06, 55.65, 47.86.

HRMS (ESI): m/z Calcd. for $[C_{13}H_{12}N_2OS, M+Na]^+$: 267.0563; Found: 267.0561.

HPLC condition: Dalcel IC column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 10.8 min for minor isomer, t_R = 9.1 min for major isomer, 31% ee.

$[\alpha]_D^{20}$ = -116.9 (c = 0.12, CH_2Cl_2).





峰表

检测器 A Ch1 254nm

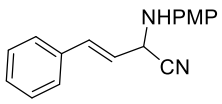
峰#	保留时间	面积	高度	面积 %	高度 %
1	9.190	11848125	775999	49.968	52.513
2	10.820	11863148	701715	50.032	47.487
总计		23711272	1477714	100.000	100.000

峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	8.850	5178924	361031	65.546	67.954
2	10.323	2722340	170256	34.454	32.046
总计		7901264	531288	100.000	100.000

2-((4-methoxyphenyl)amino)-4-phenylbut-3-enenitrile (21) [5]



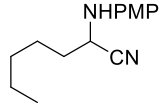
21

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.3 in hexane:ethyl acetate = 5:1) resulting in a white solid in 81% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 15.9 Hz, 1H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 6.32 (dd, *J* = 15.9 Hz, 5.0 Hz, 1H), 5.00 (dd, *J* = 8.9 Hz, 4.9 Hz, 1H), 3.80 (s, 3H), 3.68 (d, *J* = 9.5 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 154.38, 138.31, 135.07, 134.89, 128.88, 128.84, 126.94, 121.45, 117.94, 116.78, 115.10, 55.67, 49.36.

2-((4-methoxyphenyl)amino)heptanenitrile (22)



22

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed

using hexanes and ethyl acetate (10:1) (R*f* = 0.5 in hexane:ethyl acetate = 7:1) resulting in a white solid in 63% yield.

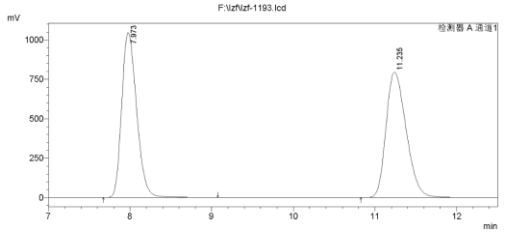
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.76 (d, *J* = 8.9 Hz, 2H), 6.65 (d, *J* = 8.8 Hz, 2H), 4.04 (t, *J* = 7.1 Hz, 1H), 3.69 (s, 3H), 1.85 (dd, *J* = 15.2 Hz, 7.7 Hz, 2H), 1.52 (dd, *J* = 14.0 Hz, 6.7 Hz, 2H), 1.29 (dd, *J* = 7.0 Hz, 3.3 Hz, 4H), 0.84 (t, *J* = 9.7 Hz, 3H).

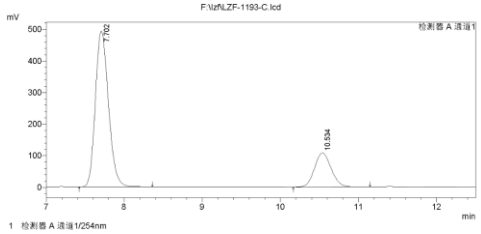
^{13}C NMR (150 MHz, $CDCl_3$) δ 154.13, 138.71, 119.82, 116.34, 115.06, 55.67, 47.54, 33.54, 31.11, 25.31, 22.36, 13.87.

HRMS (ESI): m/z Calcd. for $[C_{14}H_{20}N_2O, M+Na]^+$: 255.1468; Found: 255.1466.

HPLC condition: Dalcel IC column, *n*-hexane/*i*-PrOH = 80:20, flow rate = 1 mL/min, wavelength = 254 nm, t_R = 11.2 min for minor isomer, t_R = 7.9 min for major isomer, 57% ee.

$[\alpha]_D^{20}$ = -206.5 (c = 0.06, CH_2Cl_2).





峰表

检测器 A Ch1 254nm

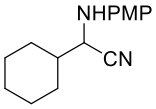
峰#	保留时间	面积	高度	面积 %	高度 %
1	7.973	13347777	1045322	49.433	56.821
2	11.235	13653798	794351	50.567	43.179
总计		27001575	1839673	100.000	100.000

峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	7.702	5737660	492744	78.277	82.058
2	10.534	1592242	107740	21.723	17.942
总计		7329901	600485	100.000	100.000

2-cyclohexyl-2-((4-methoxyphenyl)amino)acetonitrile (23) [6]



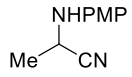
23

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.3 in hexane:ethyl acetate = 5:1) resulting in a white solid in 48% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.76 (d, *J* = 8.8 Hz, 2H), 6.63 (d, *J* = 8.8 Hz, 2H), 3.88 (dd, *J* = 10.0 Hz, 6.4 Hz, 1H), 3.69 (s, 3H), 3.42 (d, *J* = 10.0 Hz, 1H), 1.89 (d, *J* = 11.5 Hz, 2H), 1.84-1.71 (m, 3H), 1.66 (d, *J* = 12.1 Hz, 1H), 1.26-1.13 (m, 5H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 153.98, 139.13, 119.10, 116.21, 115.06, 55.70, 53.37, 40.87, 29.71, 28.92, 25.97, 25.68, 25.60.

2-((4-methoxyphenyl)amino)propanenitrile (24) [7]



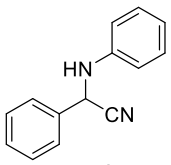
24

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.3 in hexane:ethyl acetate = 5:1) resulting in a yellow solid in 56% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.77 (d, *J* = 8.8 Hz, 2H), 6.63 (d, *J* = 8.8 Hz, 2H), 4.14 (s, 1H), 3.69 (s, 3H), 3.40 (s, 1H), 1.59 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 154.17, 138.69, 120.31, 116.34, 115.08, 55.67, 42.38, 19.83.

2-phenyl-2-(phenylamino)acetonitrile (25)[8]



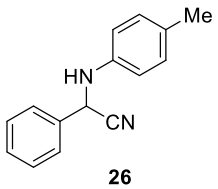
25

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.5 in hexane:ethyl acetate = 7:1) resulting in a white solid in 86% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55-7.46 (m, 2H), 7.36 (q, *J* = 6.2 Hz, 3H), 7.19 (t, *J* = 7.9 Hz, 2H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.69 (d, *J* = 7.9 Hz, 2H), 5.33 (s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 144.71, 134.03, 129.60, 129.55, 129.36, 127.28, 120.36, 118.22, 114.28, 50.31.

2-phenyl-2-(p-tolylamino)acetonitrile (26)[8]



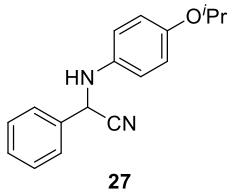
26

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.5 in hexane:ethyl acetate = 7:1) resulting in a white solid in 87% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 6.7 Hz, 2H), 7.39-7.32 (m, 3H), 6.99 (d, *J* = 8.2 Hz, 2H), 6.61 (d, *J* = 8.3 Hz, 2H), 5.30 (s, 1H), 2.20 (s, 3H).

^{13}C NMR (150 Hz, $CDCl_3$) δ 142.45, 134.22, 130.07, 129.79, 129.45, 129.30, 127.26, 118.36, 114.58, 50.76, 20.50.

2-((4-isopropoxyphenyl)amino)-2-phenylacetonitrile (27)



27

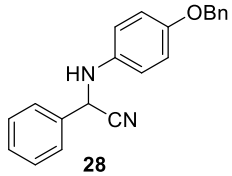
The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.5 in hexane:ethyl acetate = 7:1) resulting in a yellow solid in 92% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 6.9 Hz, 2H), 7.42-7.30 (m, 3H), 6.76 (d, *J* = 8.8 Hz, 2H), 6.66 (d, *J* = 8.8 Hz, 2H), 5.26 (s, 1H), 4.34 (dt, *J* = 12.1 Hz, 6.1 Hz, 1H), 1.23 (d, *J* = 6.1 Hz, 6H).

^{13}C NMR (150MHz, $CDCl_3$) δ 152.34, 138.69, 134.27, 129.43, 129.26, 127.26, 118.49, 117.73, 116.26, 70.88, 51.57, 29.71, 22.15.

HRMS (ESI): m/z Calcd. for $[C_{17}H_{18}N_2O, M+Na]^+$: 289.1311; Found: 289.1310.

2-((4-(benzyloxy)phenyl)amino)-2-phenylacetonitrile (28)



28

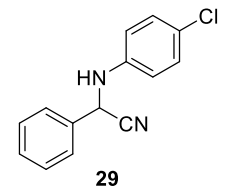
The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.3 in hexane:ethyl acetate = 7:1) resulting in a yellow solid in 72% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 6.8 Hz, 2H), 7.35 (dd, *J* = 11.5 Hz, 8.2 Hz, 5H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 5.26 (s, 1H), 4.94 (s, 2H).

^{13}C NMR (150 z, $CDCl_3$) δ 153.40, 138.88, 137.30, 134.21, 129.46, 129.29, 128.57, 127.91, 127.49, 127.26, 118.44, 116.24, 70.69, 51.55.

HRMS (ESI): m/z Calcd. for $[C_{21}H_{18}N_2O, M+Na]^+$: 337.1311; Found: 337.1310.

2-((4-chlorophenyl)amino)-2-phenylacetonitrile (29) [9]



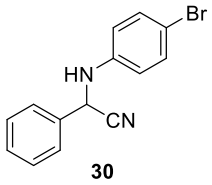
29

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.4 in hexane:ethyl acetate = 7:1) resulting in a white solid in 59% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53-7.48 (m, 2H), 7.41-7.35 (m, 3H), 7.15 (d, *J* = 8.8 Hz, 2H), 6.63 (d, *J* = 8.8 Hz, 2H), 5.31 (s, 1H).

^{13}C NMR (150 Hz, $CDCl_3$) δ 143.19, 133.56, 129.71, 129.50, 129.43, 127.23, 125.29, 117.84, 115.48, 50.39.

2-((4-bromophenyl)amino)-2-phenylacetonitrile (30)



30

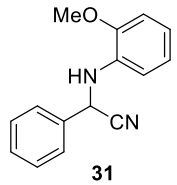
The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.4 in hexane:ethyl acetate = 7:1) resulting in a yellow solid in 61% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54-7.47 (m, 2H), 7.42-7.35 (m, 3H), 7.28 (d, *J* = 8.8 Hz, 2H), 6.57 (d, *J* = 8.8 Hz, 2H), 5.30 (s, 1H).

^{13}C NMR (150 Hz, $CDCl_3$) δ 143.68, 133.53, 132.39, 129.72, 129.44, 127.22, 117.81, 115.87, 112.39, 50.23.

HRMS (ESI): m/z Calcd. for $[C_{14}H_{11}BrN_2, M+Na]^+$: 308.9998; Found: 308.9997.

2-((2-methoxyphenyl)amino)-2-phenylacetonitrile (31) [10]

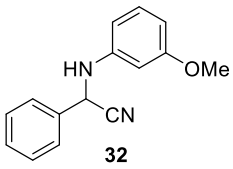


31

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.4 in hexane:ethyl acetate = 7:1) resulting in a yellow solid in 47% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.0 Hz, 2H), 7.41-7.31 (m, 3H), 6.86 (dd, *J* = 10.2 Hz, 4.4 Hz, 1H), 6.77 (dt, *J* = 11.7 Hz, 7.9 Hz, 3H), 5.37 (s, 1H), 3.75 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 147.57, 134.66, 134.24, 129.42, 129.30, 127.31, 121.28, 119.68, 118.26, 111.83, 110.15, 55.54, 50.02.



32

2-((2-methoxyphenyl)amino)-2-phenylacetonitrile (32)

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography

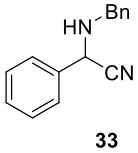
was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.4 in hexane:ethyl acetate = 7:1) resulting in a white solid in 84% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54-7.46 (m, 2H), 7.37 (dt, *J* = 14.5, 4.8 Hz, 3H), 7.09 (t, *J* = 8.1 Hz, 1H), 6.38 (dd, *J* = 8.2 Hz, 2.1 Hz, 1H), 6.30 (dd, *J* = 8.0 Hz, 1.8 Hz, 1H), 6.24 (t, *J* = 2.0 Hz, 1H), 5.33 (s, 1H), 3.69 (s, 3H).

^{13}C NMR (150 Hz, $CDCl_3$) δ 160.92, 146.11, 146.08, 133.99, 130.43, 129.55, 129.36, 127.26, 118.17, 118.15, 106.88, 105.53, 100.60, 55.22, 50.24.

HRMS (ESI): m/z Calcd. for $[C_{15}H_{14}N_2O, M+Na]^+$: 261.0998; Found: 261.0998.

2-(benzylamino)-2-phenylacetonitrile (33) [10]



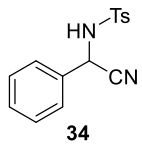
33

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.5 in hexane:ethyl acetate = 9:1) resulting in a white solid in 51% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.3 Hz, 2H), 7.35-7.30 (m, 4H), 7.28 (dd, *J* = 12.7 Hz, 5.2 Hz, 3H), 7.22 (t, *J* = 7.2 Hz, 1H), 4.68 (s, 1H), 3.99 (d, *J* = 13.0 Hz, 1H), 3.88 (d, *J* = 13.0 Hz, 1H).

^{13}C NMR (150 Hz, $CDCl_3$) δ 138.14, 134.80, 129.05, 128.98, 128.66, 128.43, 127.67, 127.32, 118.74, 53.49, 51.31.

N-(cyano(phenyl)methyl)-4-methylbenzenesulfonamide (34) [10]



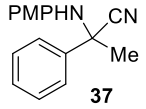
34

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.4 in hexane:ethyl acetate = 7:1) resulting in a white solid in 47% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.37 (dd, *J* = 6.4 Hz, 2.8 Hz, 2H), 7.35-7.31 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.40 (s, 1H), 5.10 (s, 1H), 2.39 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 144.72, 136.12, 132.17, 130.08, 129.92, 129.43, 127.36, 127.09, 116.28, 48.25, 21.65.

2-((4-methoxyphenyl)amino)-2-phenylpropanenitrile (37) [11]



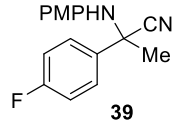
37

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.5 in hexane:ethyl acetate = 7:1) resulting in a white solid in 62% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 8.9 Hz, 2H), 6.47 (d, *J* = 8.9 Hz, 2H), 3.62 (s, 3H), 1.83 (s, 3H).

^{13}C NMR (150 Hz, $CDCl_3$) δ 154.22, 140.20, 137.23, 129.14, 128.59, 125.16, 121.00, 118.58, 114.50, 58.27, 55.51, 32.91.

2-(4-fluorophenyl)-2-((4-methoxyphenyl)amino)propanenitrile (39)[12]



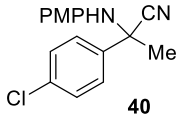
39

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.5 in hexane:ethyl acetate = 7:1) resulting in a yellow solid in 52% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 8.6 Hz, 5.1 Hz, 2H), 7.02 (t, *J* = 8.5 Hz, 2H), 6.64 (d, *J* = 8.9 Hz, 2H), 6.47 (d, *J* = 8.9 Hz, 2H), 3.91 (s, 1H), 3.64 (s, 3H), 1.82 (s, 3H).

^{13}C NMR (150 Hz, $CDCl_3$) δ 163.52, 161.87, 154.42, 136.93, 135.94, 127.08 (d, *J* = 8.3 Hz), 120.78, 118.78, 116.08 (d, *J* = 21.8 Hz), 114.54, 57.78, 55.50, 32.97.

2-(4-chlorophenyl)-2-((4-methoxyphenyl)amino)propanenitrile (40)[12]



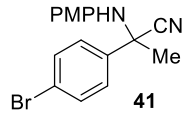
40

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.5 in hexane:ethyl acetate = 7:1) resulting in a yellow solid in 59% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 6.63 (d, *J* = 8.9 Hz, 2H), 6.47 (d, *J* = 8.7 Hz, 2H), 3.63 (s, 3H), 1.82 (s, 3H).

^{13}C NMR (150 Hz, $CDCl_3$) δ 154.46, 138.78, 136.80, 134.57, 129.35, 126.71, 120.57, 118.71, 114.58, 57.87, 55.51, 32.79.

2-(4-bromophenyl)-2-((4-methoxyphenyl)amino)propanenitrile (41)[12]



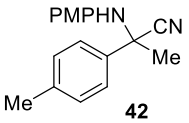
41

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.5 in hexane:ethyl acetate = 7:1) resulting in a yellow solid in 64% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54-7.35 (m, 4H), 6.63 (d, *J* = 8.9 Hz, 2H), 6.45 (d, *J* = 8.9 Hz, 2H), 3.94 (s, 1H), 3.63 (s, 3H), 1.80 (s, 3H).

^{13}C NMR (150 Hz, $CDCl_3$) δ 154.39, 139.39, 136.85, 132.32, 127.00, 122.66, 120.54, 118.59, 114.57, 57.86, 55.51, 32.83.

2-((4-methoxyphenyl)amino)-2-(p-tolyl)propanenitrile (42)[12]



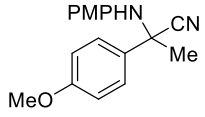
42

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.5 in hexane:ethyl acetate = 7:1) resulting in a yellow solid in 57% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.62 (d, *J* = 8.9 Hz, 2H), 6.48 (d, *J* = 8.9 Hz, 2H), 3.91 (s, 1H), 3.62 (s, 3H), 2.28 (s, 3H), 1.81 (s, 3H).

^{13}C NMR (150 Hz, $CDCl_3$) δ 154.16, 138.43, 137.36, 137.26, 129.79, 125.07, 121.13, 118.57, 114.49, 58.05, 55.51, 32.92, 21.05.

2-(4-methoxyphenyl)-2-((4-methoxyphenyl)amino)propanenitrile (43)



43

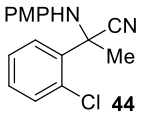
The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.5 in hexane:ethyl acetate = 7:1) resulting in a yellow solid in 55% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 9.0 Hz, 2H), 6.63 (d, *J* = 9.0 Hz, 2H), 6.50 (d, *J* = 7.6 Hz, 2H), 3.74 (s, 3H), 3.63 (s, 3H), 1.82 (s, 3H).

^{13}C NMR (150 Hz, $CDCl_3$) δ 159.74, 154.30, 137.29, 132.11, 126.47, 121.13, 118.86, 114.49, 114.42, 57.87, 55.50, 55.34, 32.83.

HRMS (ESI): m/z Calcd. for $[C_{17}H_{18}N_2O_2, M+Na]^+$: 305.1260; Found: 305.1260.

2-(2-chlorophenyl)-2-((4-methoxyphenyl)amino)propanenitrile (44)



44

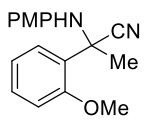
The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.5 in hexane:ethyl acetate = 7:1) resulting in a yellow solid in 51% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76-7.62 (m, 1H), 7.41-7.30 (m, 1H), 7.27-7.13 (m, 2H), 6.65 (d, *J* = 8.9 Hz, 2H), 6.53 (d, *J* = 8.9 Hz, 2H), 4.11 (s, 1H), 3.63 (s, 3H), 2.01 (s, 3H).

^{13}C NMR (150 Hz, $CDCl_3$) δ 154.08, 136.91, 135.16, 132.06, 131.47, 129.94, 128.91, 127.41, 120.08, 118.21, 114.47, 57.33, 55.51, 28.41.

HRMS (ESI): m/z Calcd. for $[C_{16}H_{15}ClN_2O, M+Na]^+$: 309.0765; Found: 309.0764.

2-(2-methoxyphenyl)-2-((4-methoxyphenyl)amino)propanenitrile (45)[12]



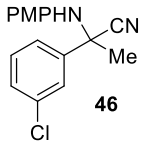
45

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.4 in hexane:ethyl acetate = 5:1) resulting in a yellow solid in 52% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.7 Hz, 1.4 Hz, 1H), 7.41-7.36 (m, 1H), 7.05-6.97 (m, 1H), 6.79 (d, *J* = 9.0 Hz, 1H), 6.77-6.72 (m, 2H), 4.02 (s, 2H), 3.78 (s, 3H), 2.04 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.39, 154.20, 137.59, 129.90, 127.50, 126.56, 121.16, 120.99, 119.37, 114.32, 112.15, 55.68, 55.50, 28.25.

2-(3-chlorophenyl)-2-((4-methoxyphenyl)amino)propanenitrile (46)[12]



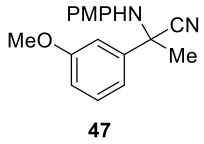
46

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.5 in hexane:ethyl acetate = 7:1) resulting in a yellow solid in 56% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.46 (dd, *J* = 6.9 Hz, 3.3 Hz, 1H), 7.30-7.22 (m, 2H), 6.64 (d, *J* = 8.9 Hz, 2H), 6.46 (d, *J* = 8.9 Hz, 2H), 3.92 (s, 1H), 3.63 (s, 3H), 1.82 (s, 3H).

^{13}C NMR (150 Hz, $CDCl_3$) δ 154.44, 142.45, 136.82, 135.25, 130.46, 128.94, 125.47, 123.44, 120.43, 118.63, 114.59, 57.92, 55.51, 32.82.

2-(3-methoxyphenyl)-2-((4-methoxyphenyl)amino)propanenitrile (47)[13]



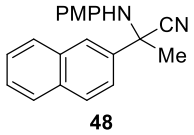
47

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.3 in hexane:ethyl acetate = 7:1) resulting in a yellow solid in 48% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (t, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 7.11 (s, 1H), 6.81 (dd, *J* = 8.1 Hz, 1.8 Hz, 1H), 6.63 (d, *J* = 8.9 Hz, 2H), 6.51 (d, *J* = 8.2 Hz, 2H), 3.73 (s, 3H), 3.63 (s, 3H), 1.85 (s, 3H).

^{13}C NMR (150 Hz, $CDCl_3$) δ 160.28, 154.25, 141.92, 137.24, 130.21, 120.93, 118.53, 117.42, 114.51, 113.97, 110.98, 58.25, 55.51, 55.34, 32.83.

2-((4-methoxyphenyl)amino)-2-(naphthalen-2-yl)propanenitrile (48)[12]



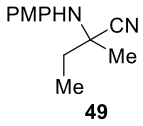
48

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.5 in hexane:ethyl acetate = 7:1) resulting in a white solid in 67% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.82-7.71 (m, 3H), 7.63 (dd, *J* = 8.6 Hz, 1.7 Hz, 1H), 7.49-7.39 (m, 2H), 6.59 (d, *J* = 8.9 Hz, 2H), 6.50 (d, *J* = 8.9 Hz, 2H), 4.01 (s, 1H), 3.58 (s, 3H), 1.89 (s, 3H).

^{13}C NMR (150 Hz, $CDCl_3$) δ 154.28, 137.67, 137.32, 133.28, 133.26, 129.31, 128.31, 127.70, 126.70, 124.63, 122.48, 121.05, 118.66, 114.55, 58.54, 55.48, 32.85.

2-((4-methoxyphenyl)amino)-2-methylbutanenitrile (49)



49

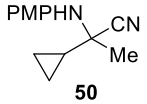
The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.5 in hexane:ethyl acetate = 7:1) resulting in a yellow solid in 72% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.94 (d, *J* = 8.8 Hz, 2H), 6.82-6.73 (m, 2H), 3.71 (s, 3H), 1.89-1.81 (m, 1H), 1.80-1.75 (m, 1H), 1.47 (s, 3H), 1.06 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (150 Hz, $CDCl_3$) δ 155.84, 136.64, 123.16, 121.94, 114.55, 55.53, 33.62, 29.68, 24.98, 8.48 .

HRMS (ESI): m/z Calcd. for $[C_{12}H_{16}N_2O, M+Na]^+$: 227.1155; Found: 227.1155.

2-cyclopropyl-2-((4-methoxyphenyl)amino)propanenitrile (50)



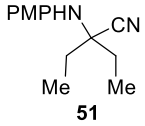
50

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.5 in hexane:ethyl acetate = 7:1) resulting in a yellow solid in 24% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.89 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 9.0 Hz, 2H), 3.70 (s, 3H), 3.44 (dd, *J* = 14.6 Hz, 7.6 Hz, 1H), 3.31 (dt, *J* = 12.7, 6.3 Hz, 1H), 2.56-2.47 (m, 1H), 2.07-1.98 (m, 2H), 1.97-1.91 (m, 1H), 1.54 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 152.07, 136.44, 119.78, 117.12, 112.56, 56.15, 53.62, 49.10, 39.77, 22.31, 19.99.

2-ethyl-2-((4-methoxyphenyl)amino)butanenitrile (51)[14]

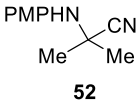


51

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.5 in hexane:ethyl acetate = 7:1) resulting in a yellow oil in 52% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.89 (d, *J* = 8.8 Hz, 4H), 6.75 (d, *J* = 8.8 Hz, 3H), 3.70 (s, 1H), 1.82 (dt, *J* = 15.3 Hz, 7.6 Hz, 2H), 1.79-1.72 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 6H).
^{13}C NMR (150 Hz, $CDCl_3$) δ 155.38, 136.86, 122.26, 121.56, 114.58, 59.45, 55.54, 29.54, 7.92.

2-((4-methoxyphenyl)amino)-2-methylpropanenitrile (52)[15].



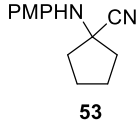
52

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.5 in hexane:ethyl acetate = 5:1) resulting in a yellow oil in 42% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.92 (d, *J* = 8.8 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 3.71 (s, 3H), 1.54 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.04, 136.63, 123.45, 122.58, 114.55, 55.52, 51.07, 28.16.

1-((4-methoxyphenyl)amino)cyclopentane-1-carbonitrile (53)[14].



53

The title compound was prepared according to the general procedure as described, silica gel flash column chromatography was performed using hexanes and ethyl acetate (10:1) (R*f* = 0.5 in hexane:ethyl acetate = 7:1) resulting in a yellow oil in 57% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.86-6.72 (m, 2H), 3.69 (s, 2H), 2.21 (dd, *J* = 12.6 Hz, 6.5 Hz, 3H), 1.85-1.81 (m, 2H), 1.80-1.73 (m, 2H), 1.01-0.98 (m, 4H).

^{13}C NMR (150 Hz, $CDCl_3$) δ 154.52, 137.69, 122.65, 119.29, 114.75, 59.02, 55.63, 40.94, 39.97, 23.63, 23.17.

VI. References

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VII. NMR spectra of the products

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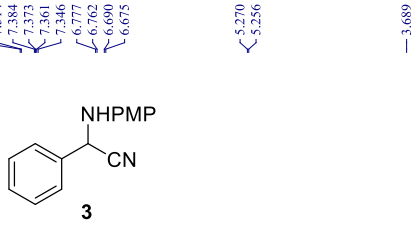
LZF-1138-2



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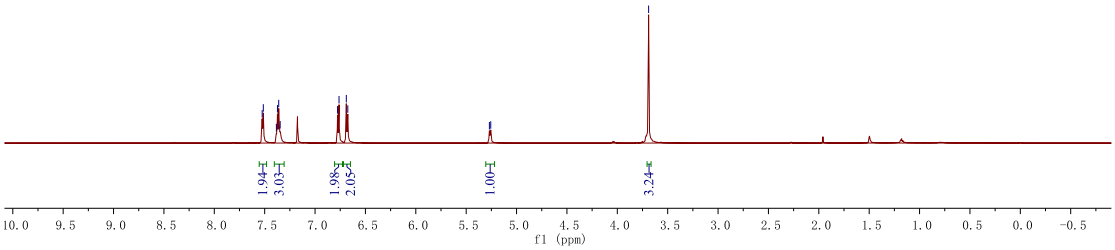

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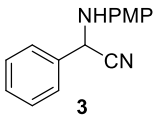

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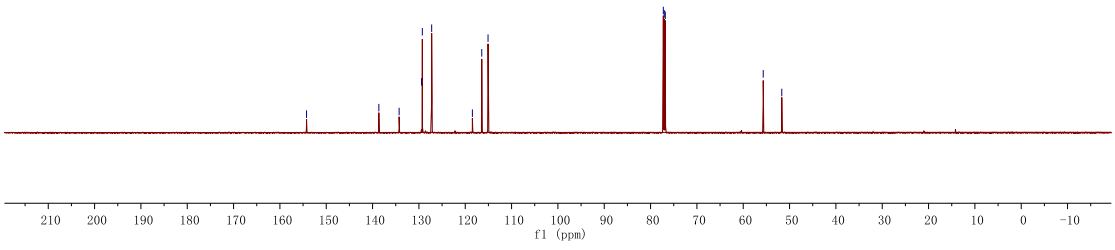

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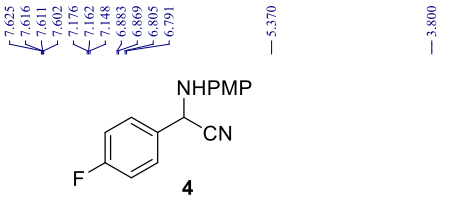
LZF-1245



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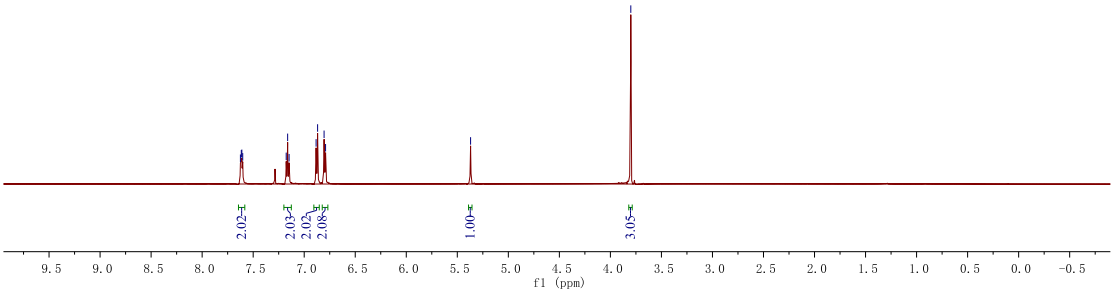

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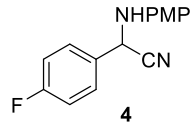
LZF-1145



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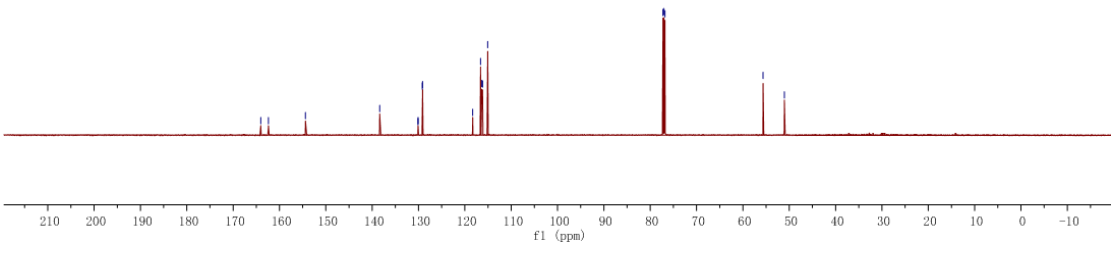

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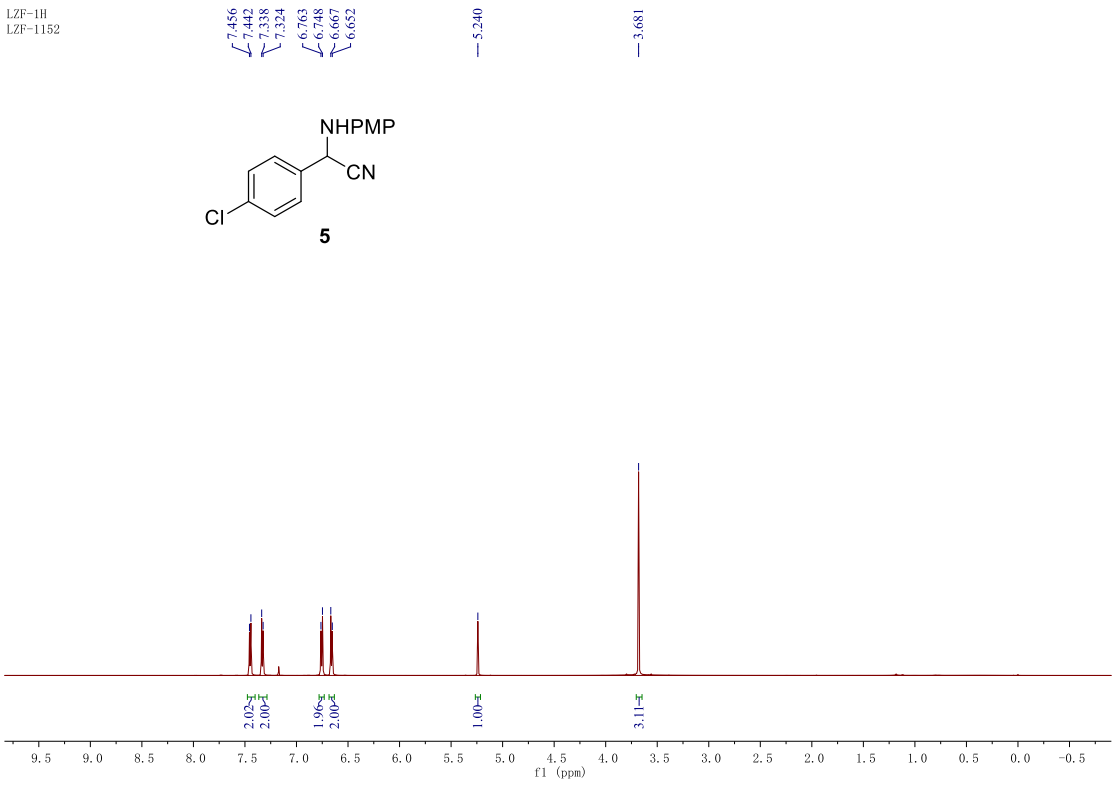
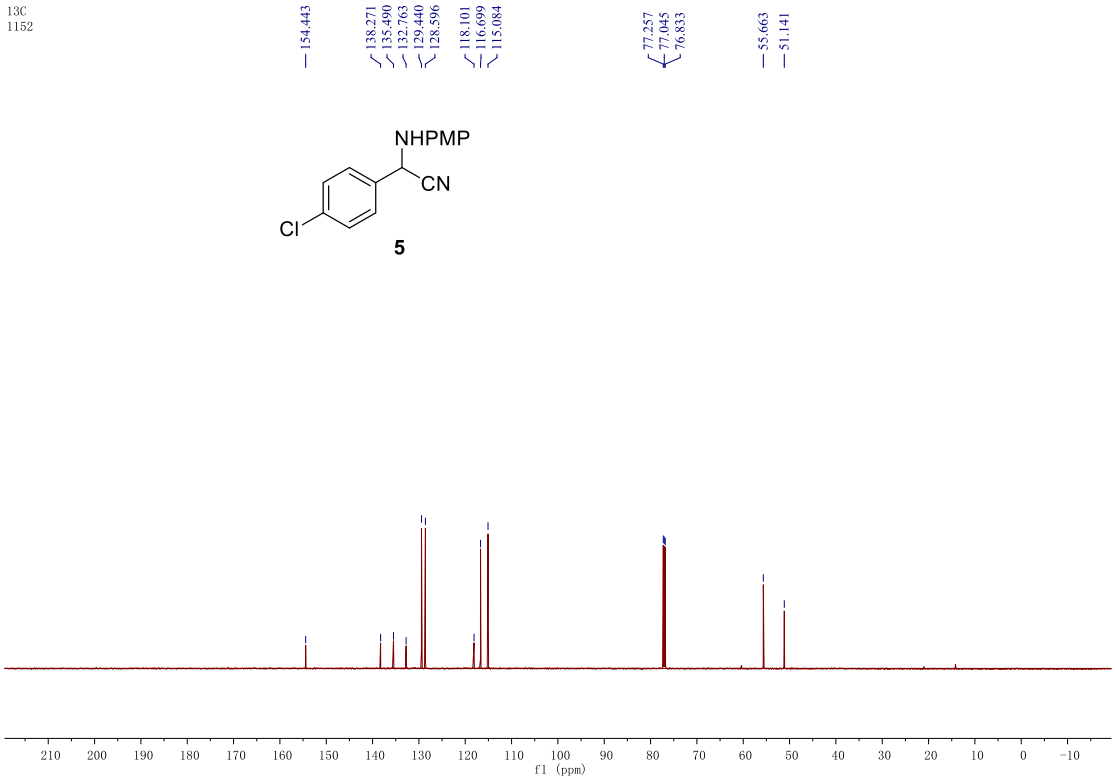
LZF-1152



13C
1152



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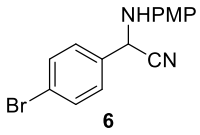
LZF-1143



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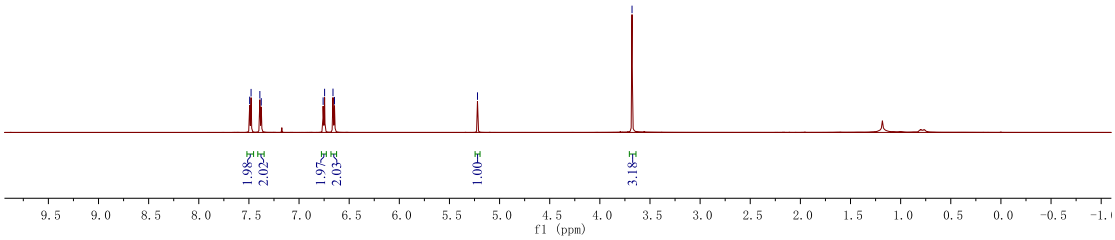
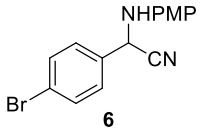


LZF-13C
LZF-1143



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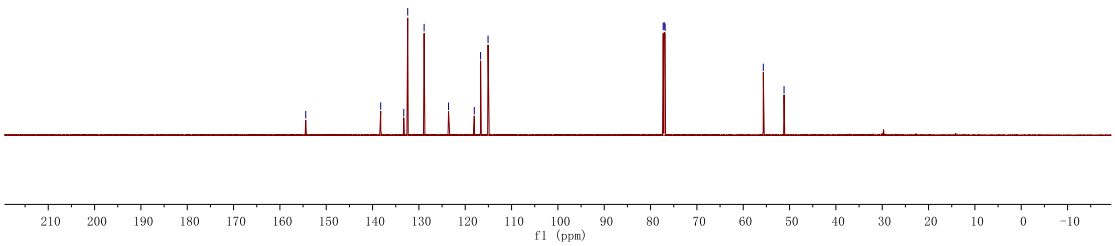

LZF-1H
LZF-1196

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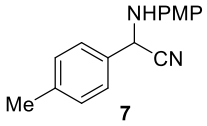
7.388
7.179
7.166
6.775
6.760
6.682
6.667
5.216
3.691
2.311



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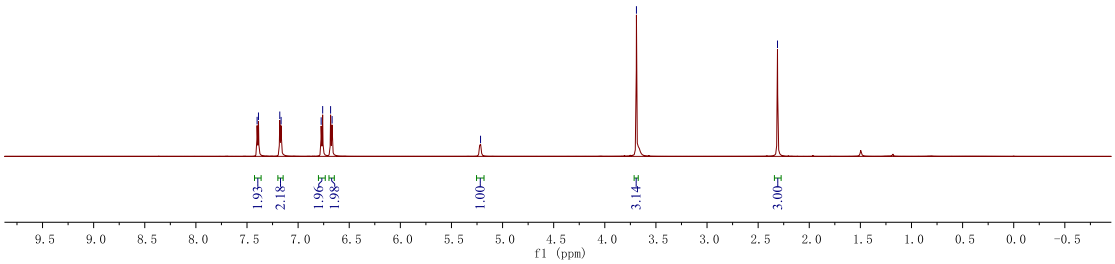
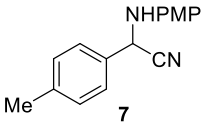


LZF-13C
LZF-1196

154.159
139.464
138.718
131.315
129.904
127.159
118.612
116.323
115.051
77.244
77.032
76.821
55.685
51.390
21.161



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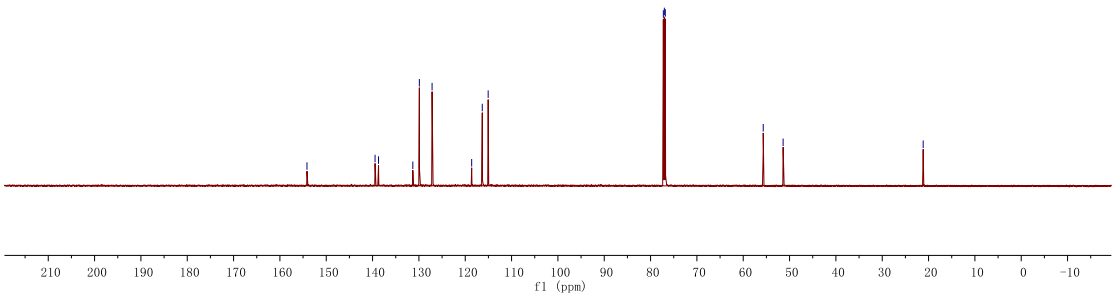

LZF-1H
LZF-1178

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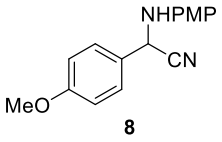
7.427
6.894
6.879
6.783
6.769
6.692
6.677

3.766
3.700



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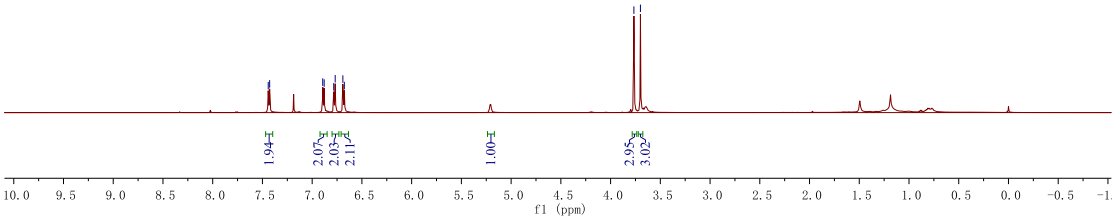

LZF-13C
LZF-1178

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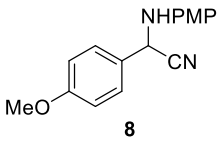
154.188
138.698
128.584
126.278
118.649
116.363
115.054
114.605

77.215
77.004
76.792

55.684
55.419
51.122



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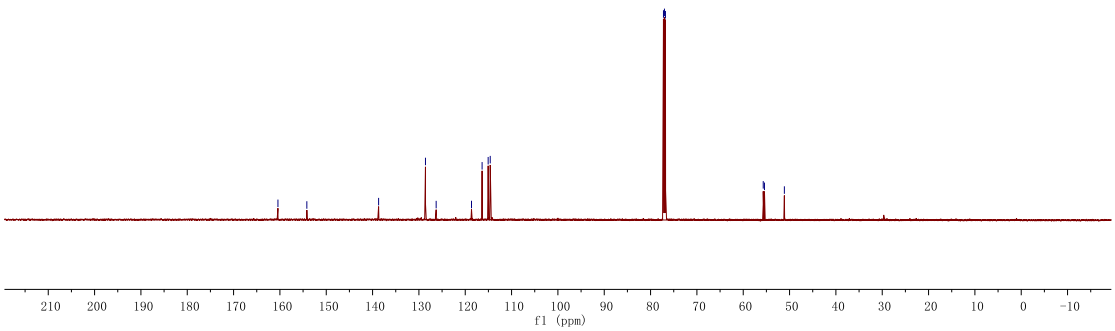

LZF-1H
LZF-1144

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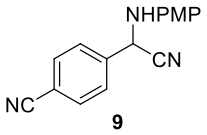
6.779
6.764
6.677
6.662
5.366
5.350
3.825
3.809
3.697



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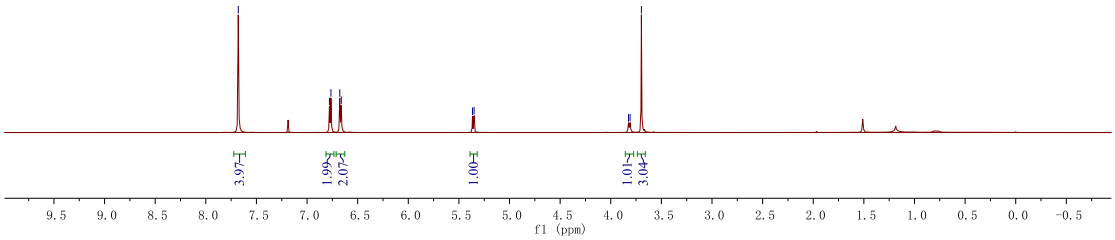

LZF-13C
LZF-1144

154.749
139.191
137.769
132.978
127.987
117.929
117.437
117.021
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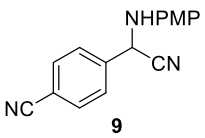
113.584
77.230
77.019
76.807
55.649
51.487



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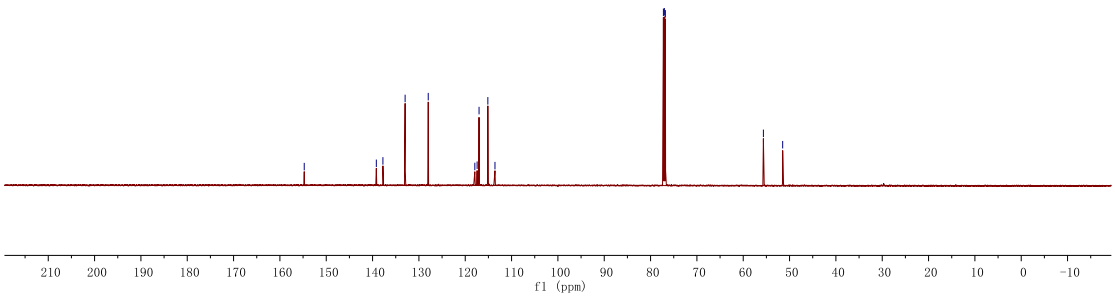
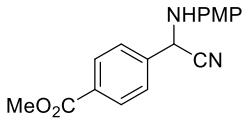


LZF-1H
LZF-1202

8.040
8.026
7.621
7.607
6.777
6.763
6.691
6.676
5.345
5.330
3.867
3.794
3.780
3.694



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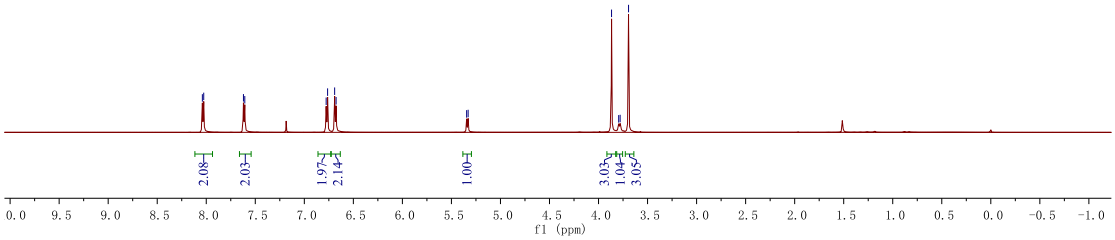
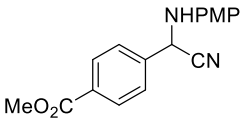


LZF-13C
LZF-1202

166.259
154.500
138.840
138.190
131.277
130.458
127.260
117.930
116.761
115.081
77.231
77.019
76.807
55.655
52.339
51.528



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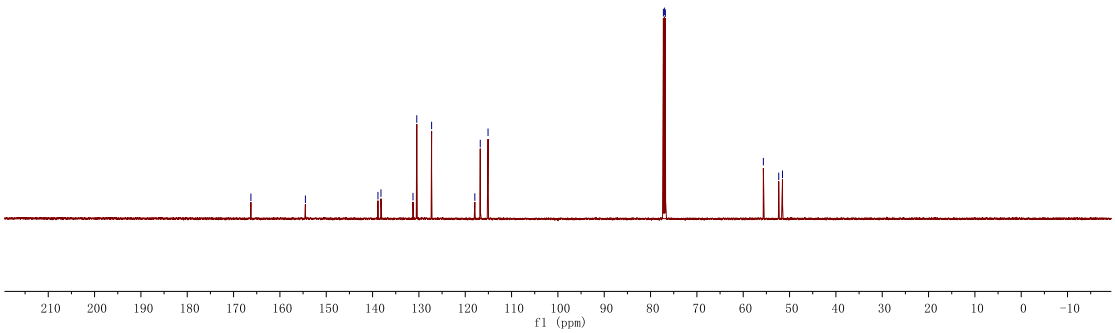

LZF-1H
LZF-1140

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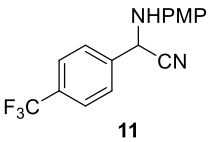
7.491
7.486
7.478
7.055
7.041
7.027
6.763
6.749
6.672
6.657

3.678



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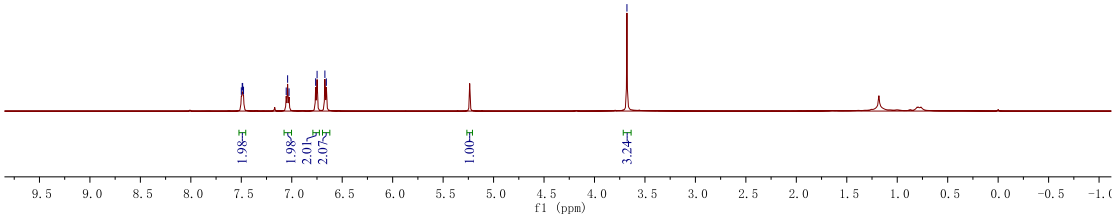

LZF-13C
LZF-1140

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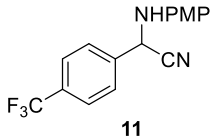
162.379
154.379
138.392
130.114
129.179
129.123
118.324
116.624
116.318
116.172
115.076

77.266
77.055
76.843

55.658
51.046



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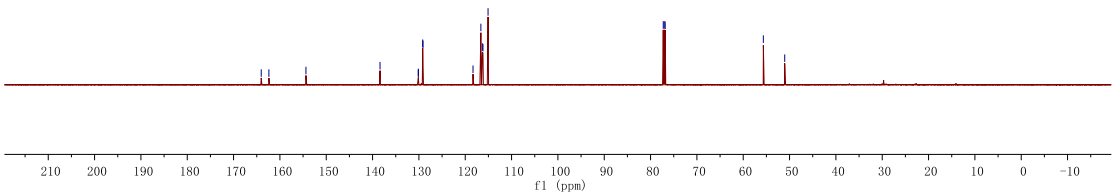


LZF-1H
LZF-1138
7.646
7.644
7.637
7.636
7.631
7.408
7.404
7.398
7.395
7.392
7.313
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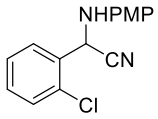
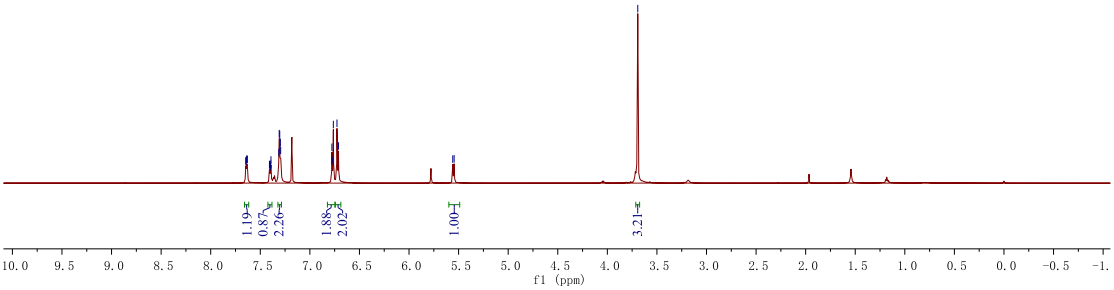
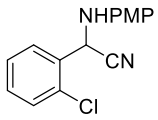
6.763
6.727
6.712
5.559
5.545
3.693


NHPMP
CN
Cl

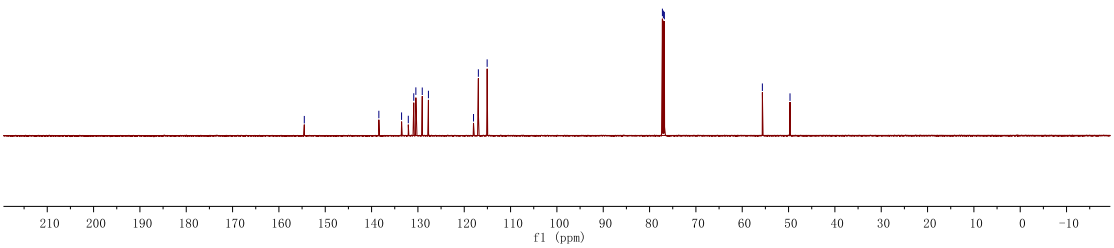
12


1.19
0.87
2.26
1.88
2.02
1.00
3.21
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)

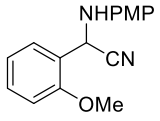

LZF-13C
LZF-1138
154.522
138.430
133.523
132.076
130.895
130.442
129.062
127.732
117.998
116.953
115.055
77.232
77.020
76.808
55.652
49.688


NHPMP
CN
Cl

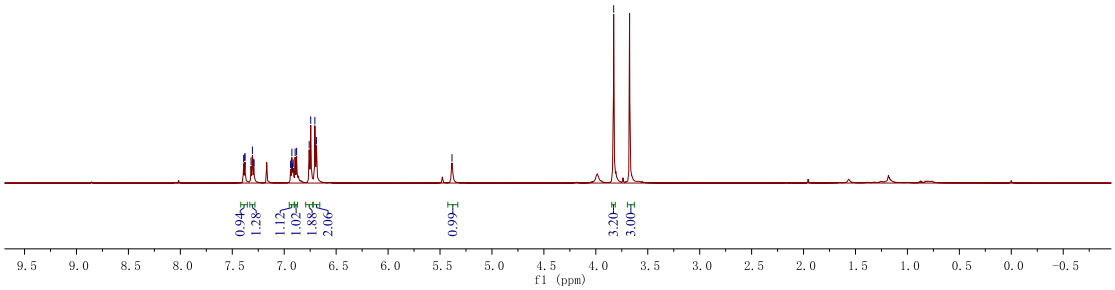
12


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

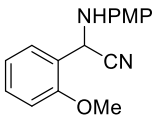
LZF-1H
LZF-1141



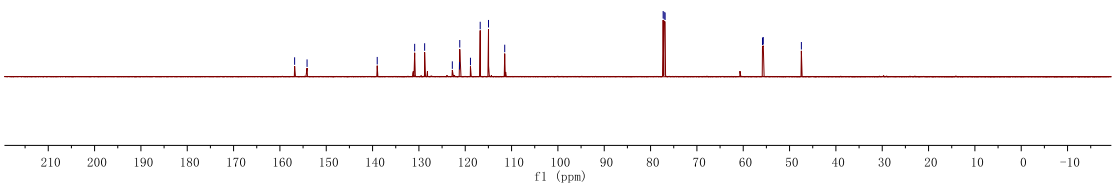
13



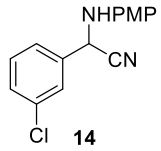
LZF-13C
LZF-1141



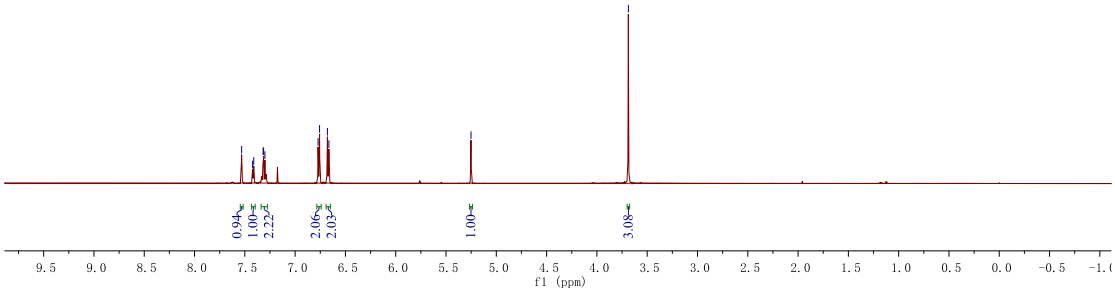
13



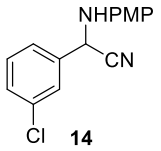
LZF-1H
LZF-1151



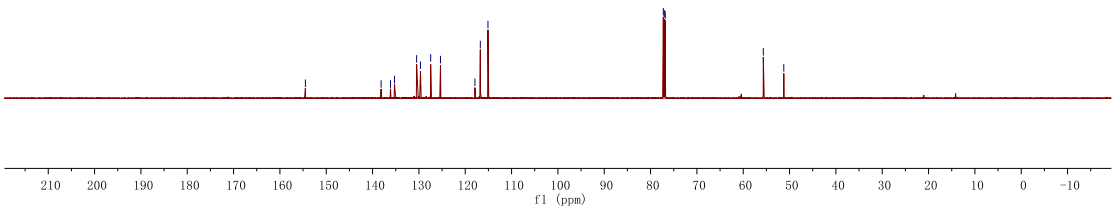
14



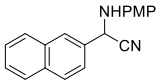
13C
1151



14



LZF-1H
LZF-1139



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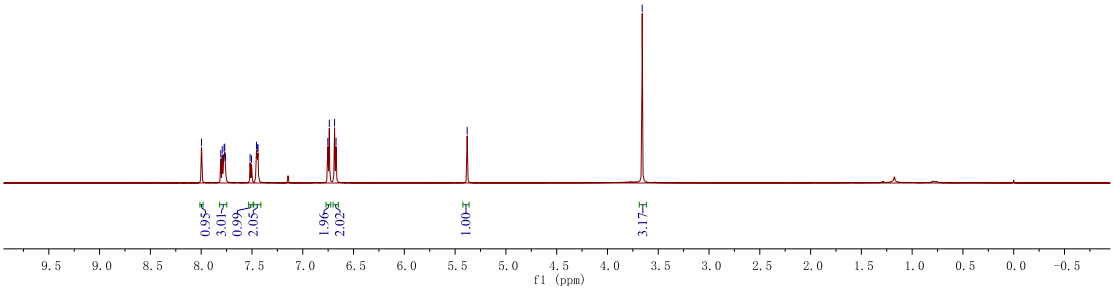
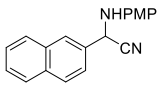
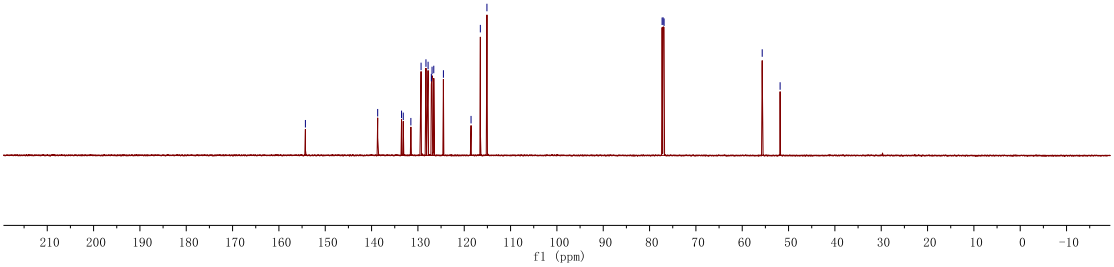


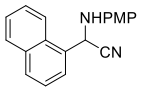
LZF-13C
LZF-1139



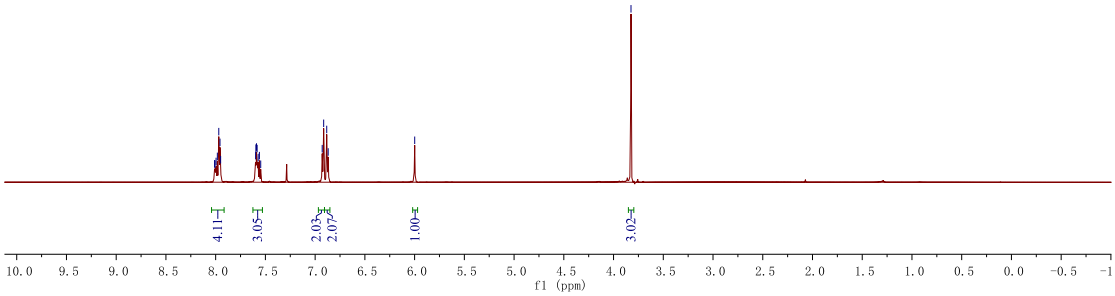
15



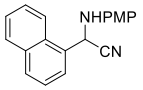
LZF-1H
LZF-1254



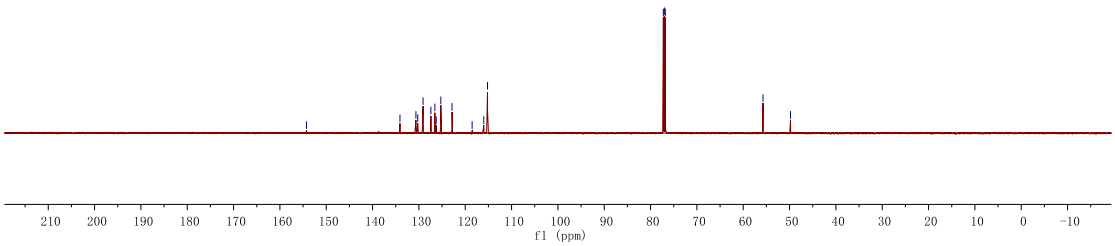
16



LZF-13C
1154

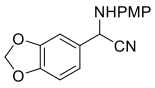


16

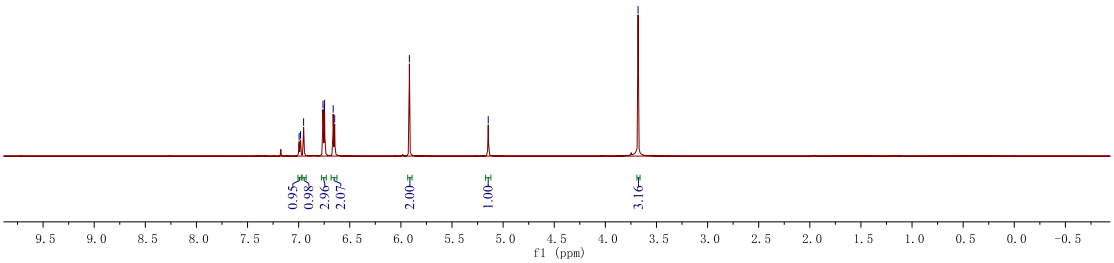


LZF-1H
LZF-1153

6.996
6.982
6.952
6.762
6.749
6.747
6.662
6.648
5.917
5.146
3.680

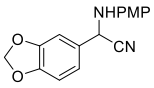


17

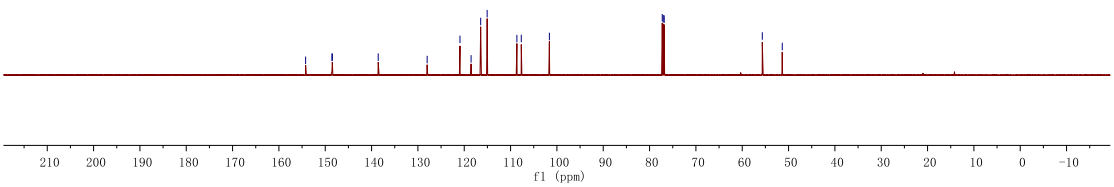


13C
1153

154.235
148.546
148.474
138.564
128.007
120.922
118.521
116.453
115.054
108.637
107.690
101.625
77.262
77.050
76.839
55.669
51.364

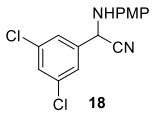


17

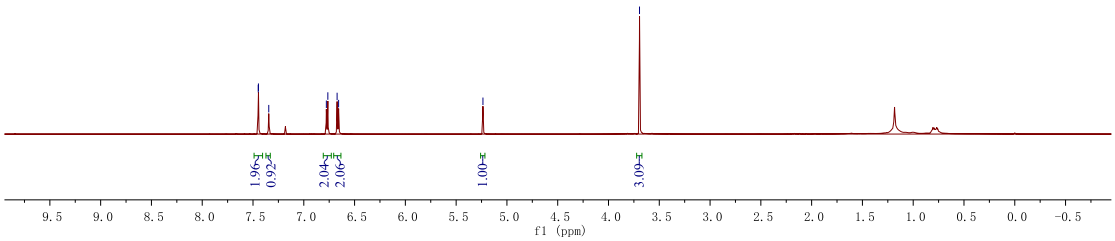


LZF-1H
LZF-1180

7.448
7.446
7.345
6.778
6.763
6.672
6.657
5.236
3.695

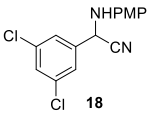


18

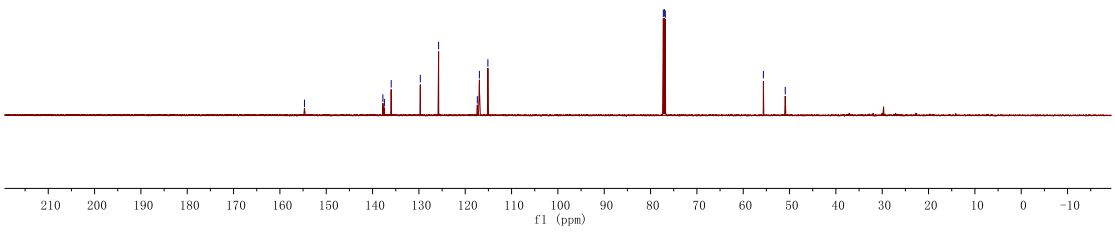


LZF-13C
LZF-1180

154.700
137.774
137.449
135.985
129.698
125.749
117.398
116.944
115.113
77.244
77.032
76.821
55.647
50.933

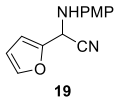


18

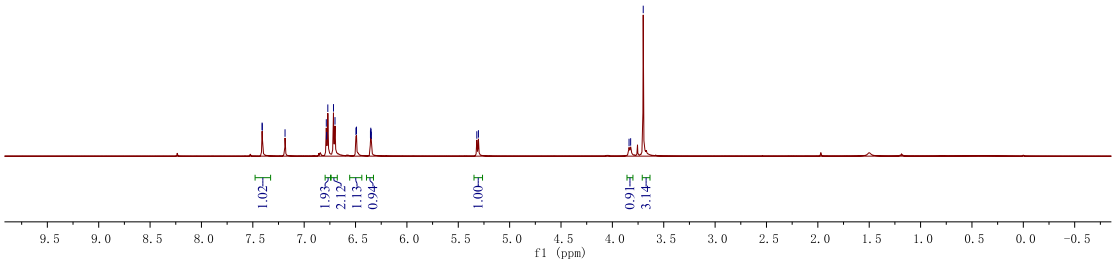


LZF-1H
LZF-1155

7.409
7.408
7.186
6.785
6.770
6.715
6.700
6.496
6.491
6.355
6.352
6.350
6.347
5.326
5.304
3.838
3.822
3.700

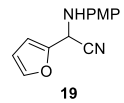


19

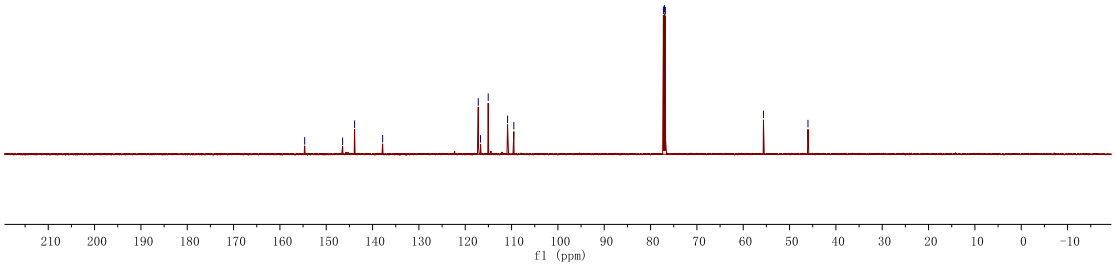


LZF-13C
LZF-1155

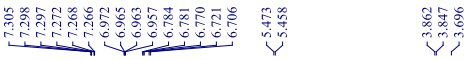
154.657
146.467
143.884
137.828
117.191
116.697
115.042
110.867
109.510
77.226
77.015
76.803
55.634
46.025

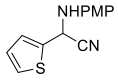


19

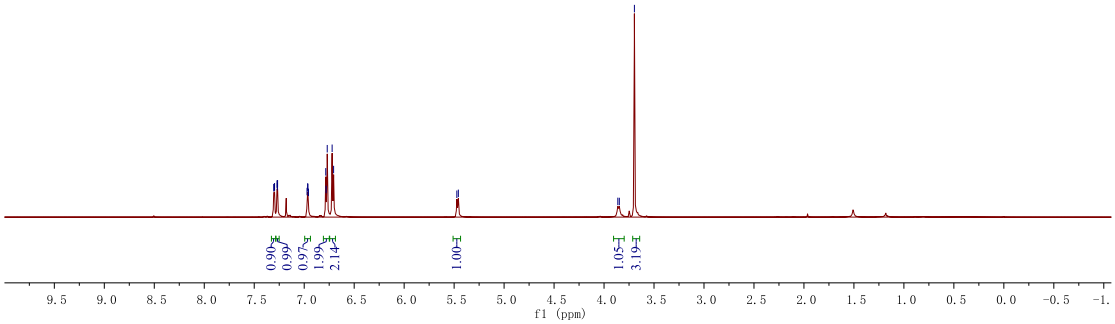


LZF-1H
LZF-1157

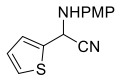




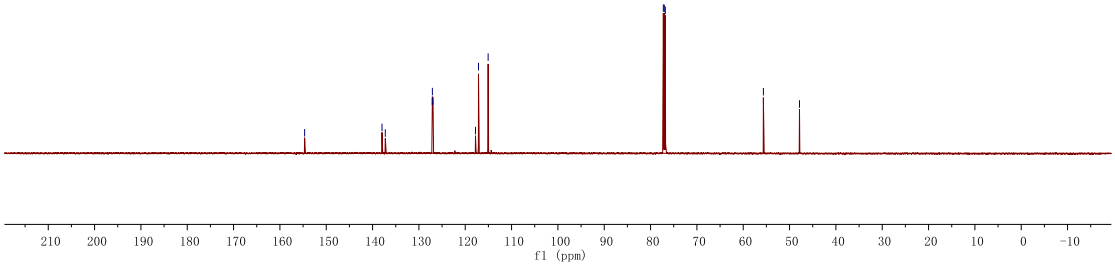
20



LZF-13C
LZF-1157



20

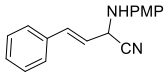


LZF-1H
LZF-1181

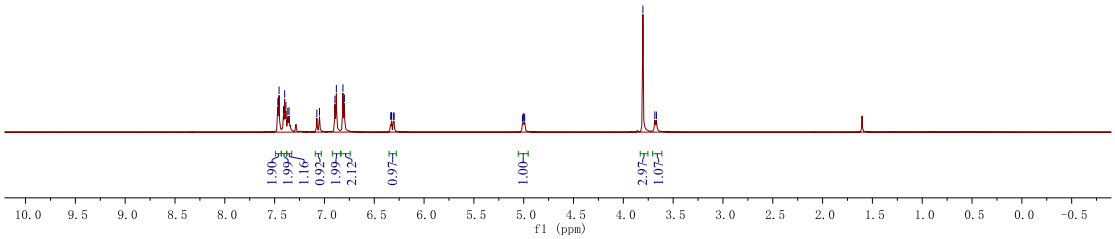
7.468
7.455
7.411
7.399
7.387
7.367
7.355
7.076
7.050
6.895
6.880
6.814
6.800
6.335
6.327
6.309
6.300

5.013
5.005
4.998
4.990

3.803
3.684
3.668



21



LZF-13C
LZF-1181

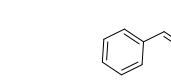
154.377

138.308
135.068
134.888
128.883
128.843
126.945
121.450
117.941
116.782
115.098

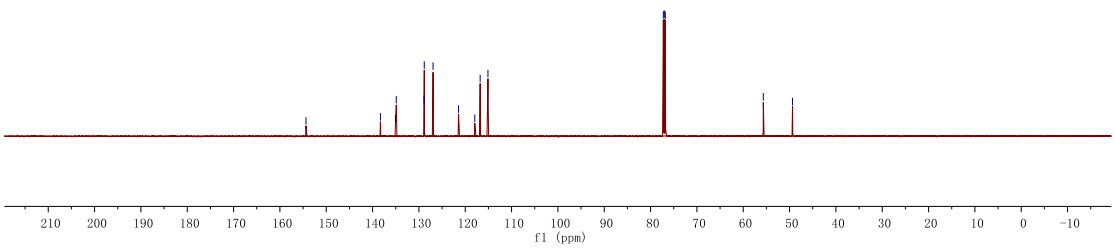
77.245
77.033
76.821

55.672

49.364

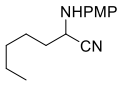


21

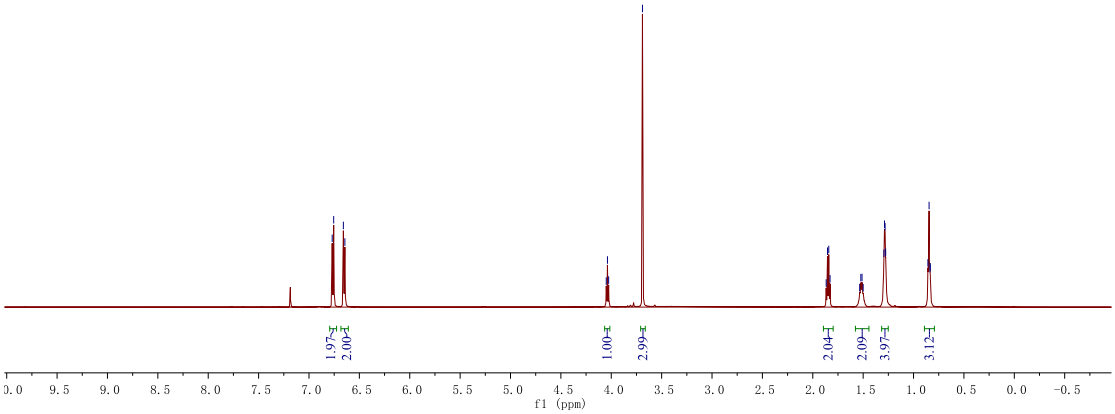


LZF-1H
LZF-1193

6.770
6.755
6.659
6.644
4.050
4.038
4.026
3.690
1.867
1.854
1.841
1.829
1.535
1.523
1.511
1.500
1.294
1.288
1.282
1.277
0.857
0.846
0.837
0.834

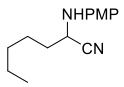


22

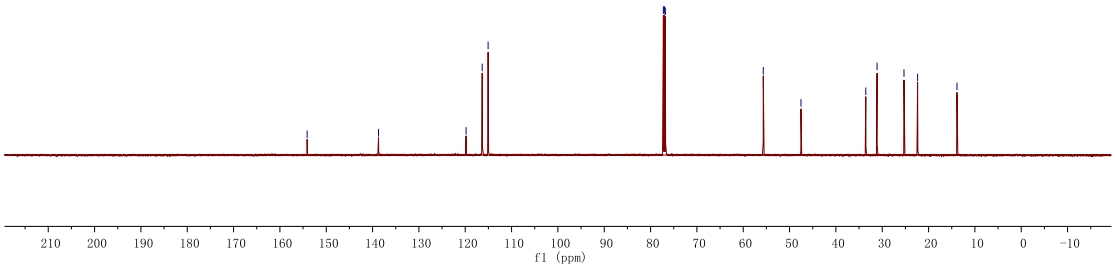


LZF-13C
LZF-1193

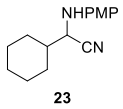
154.126
138.713
119.823
116.340
115.063
77.233
77.022
76.810
55.675
47.539
33.544
31.114
25.505
22.365
13.870



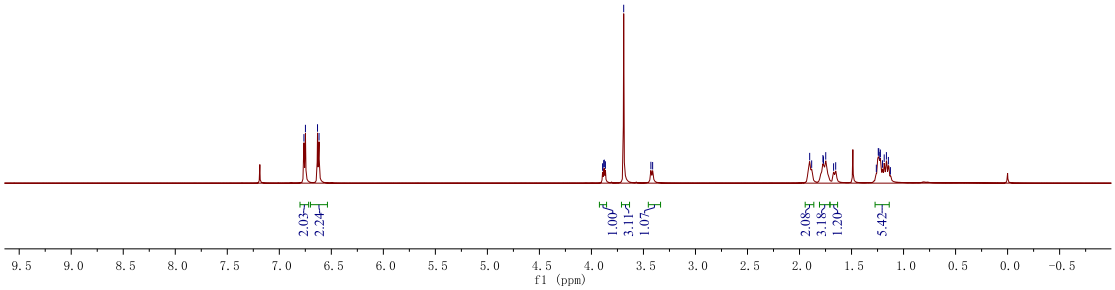
22



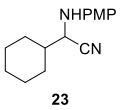
LZF-1H
LZF-1179



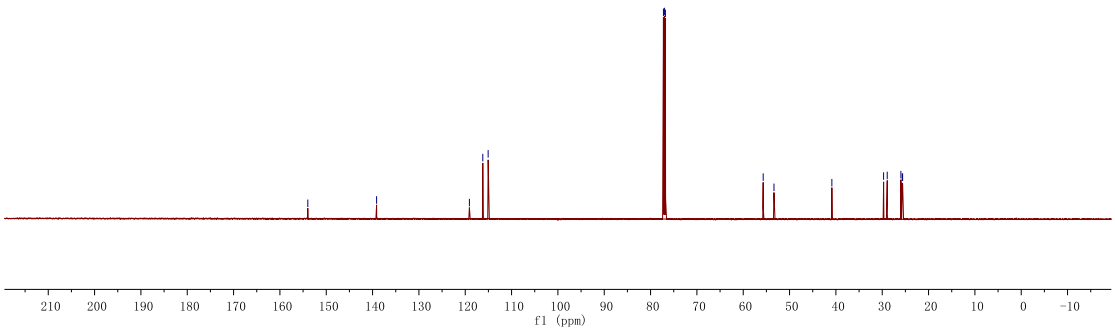
23



LZF-13C
LZF-1179

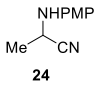


23

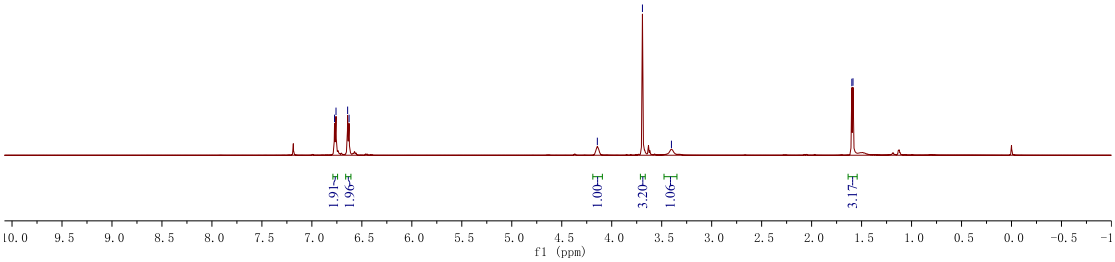


LZF-1H
LZF-1201

6.773
6.759
6.642
6.628
4.144
3.693
3.402
1.598
1.586

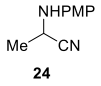


24

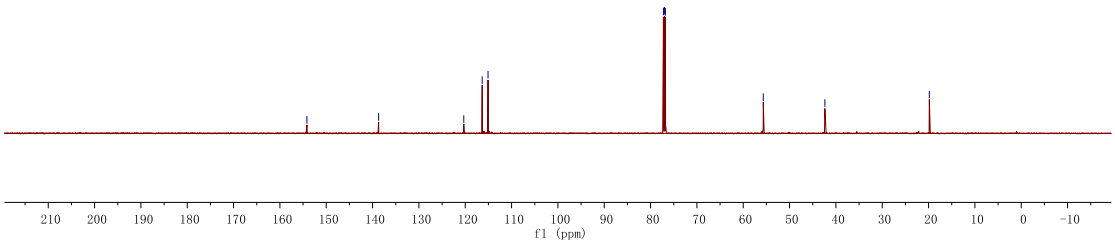


LZF-13C
LZF-1201

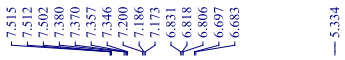
154.169
138.694
120.315
116.341
115.079
77.224
77.012
76.800
55.674
42.380
19.834

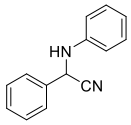


24



LZF-1H
LZF-1164





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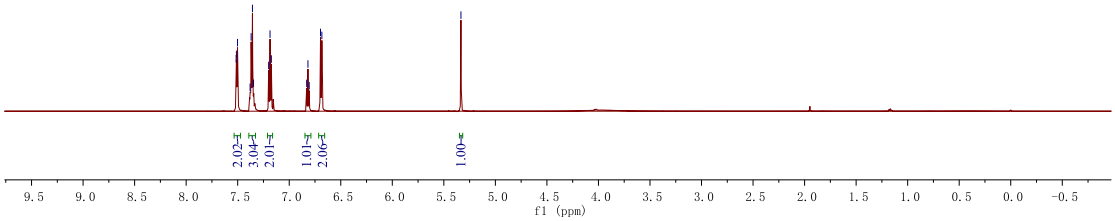
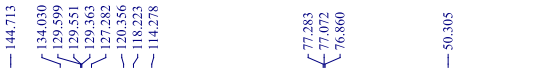
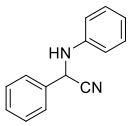


LZF-13C
LZF-1164





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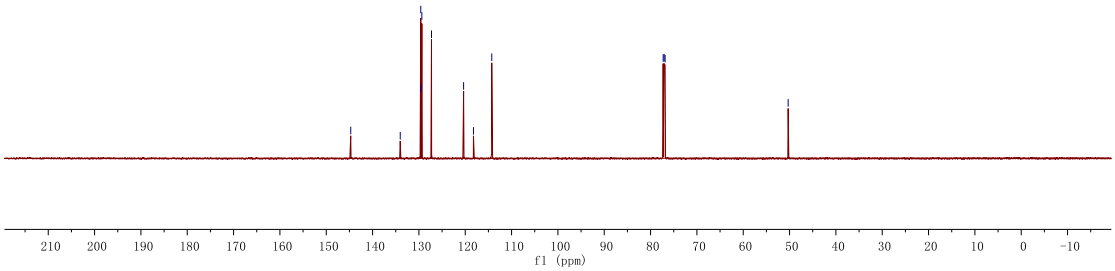
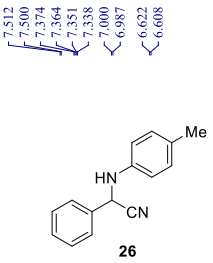
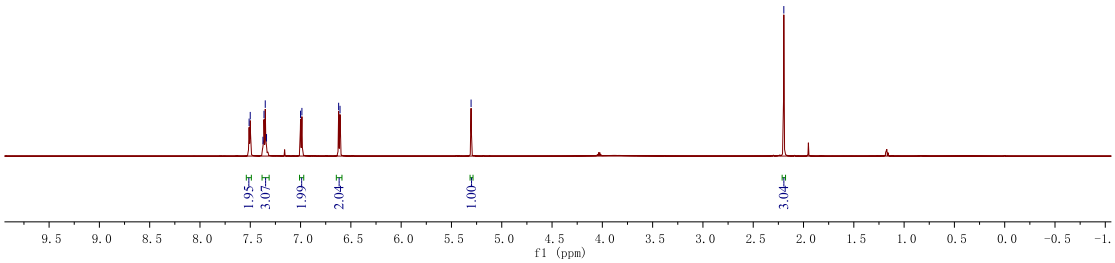


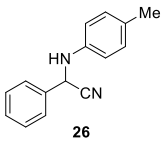
LZF-1H
LZF-1165



26



LZF-13C
LZF-1165



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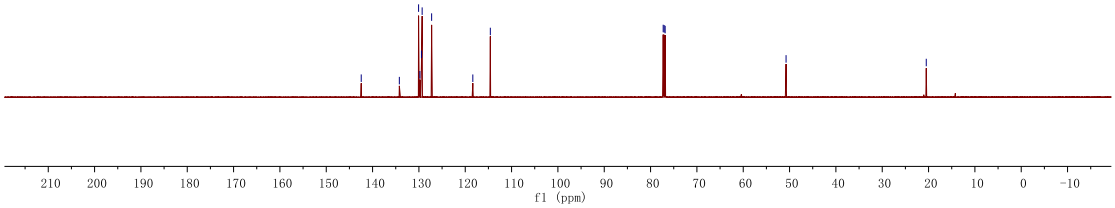
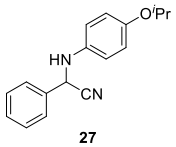


LZF-1H
LZF-1166

7.523
7.511
7.385
7.381
7.371
7.358
7.355
7.344
6.769
6.754
6.668
6.653
5.259
4.365
4.355
4.345
4.335
4.325
1.235
1.225



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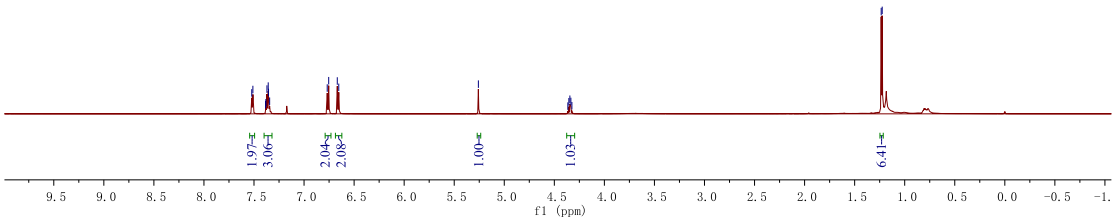
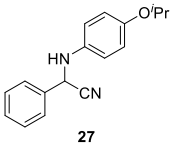


LZF-13C
LZF-1166

152.341
138.695
134.273
129.431
129.265
127.265
118.486
117.731
116.264
77.255
77.043
76.831
70.881
51.572
22.155



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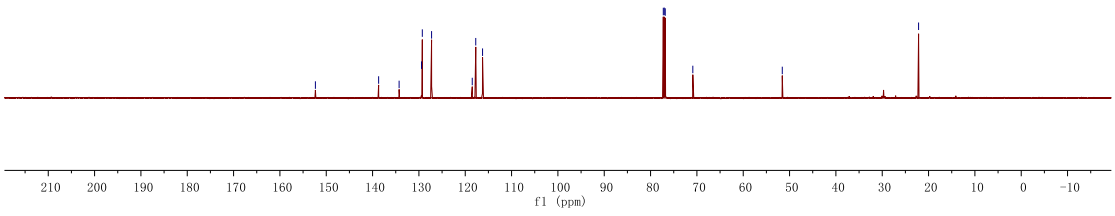
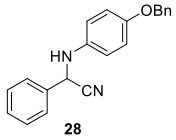
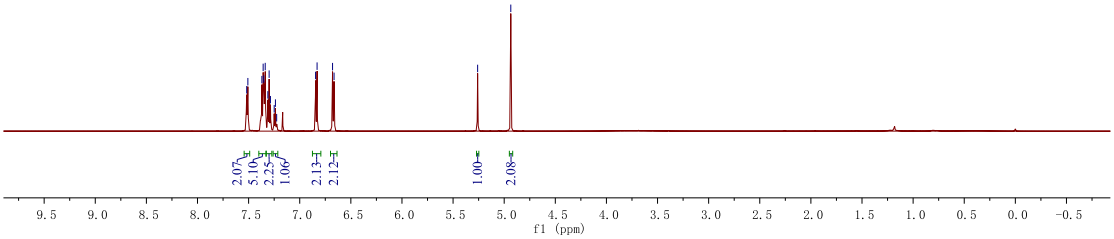


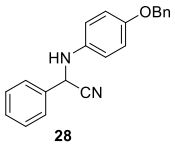
LZF-1H
LZF-1167



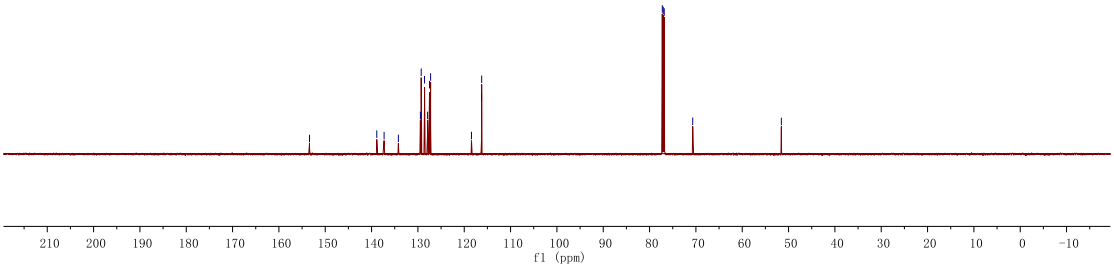
28



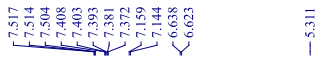
LZF-13C
LZF-1167

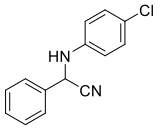


28



LZF-1H
LZF-1168





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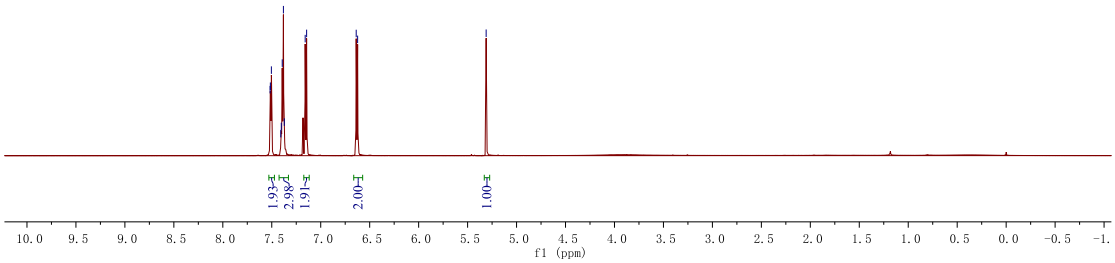
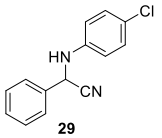


LZF-13C
LZF-1168



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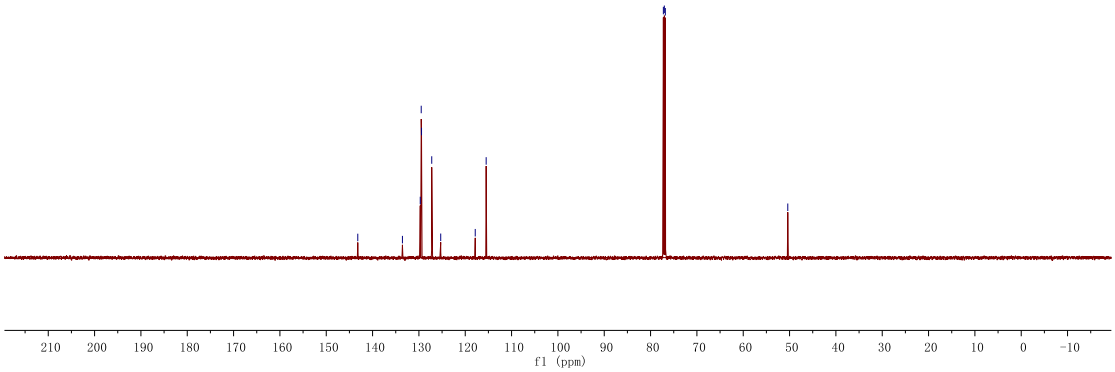
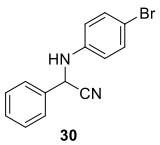
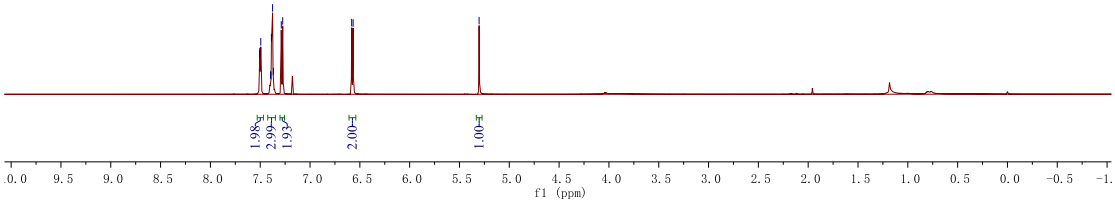


LZF-1H
LZF-1169

7.507
7.505
7.494
7.397
7.393
7.388
7.376
7.368
7.289
7.274
6.582
6.568
5.303

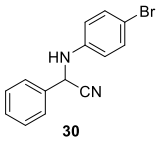


30

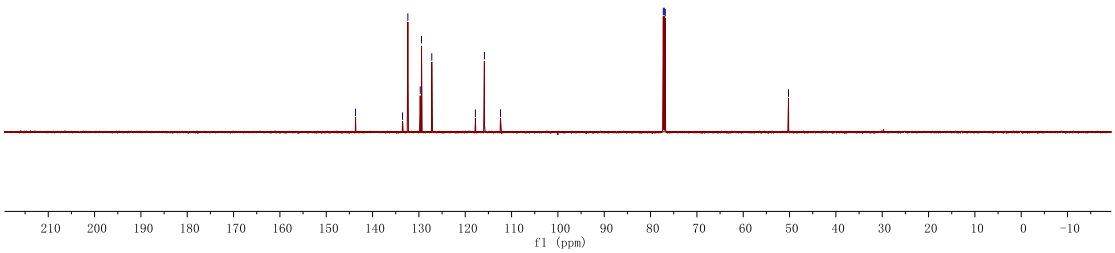


LZF-13C
LZF-1169

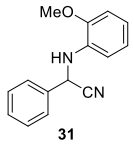
143.679
133.527
132.387
129.716
129.442
127.220
117.810
115.866
112.392
77.252
77.040
76.828
50.231



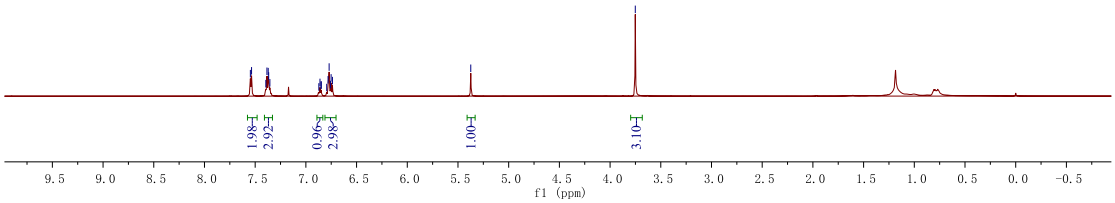
30



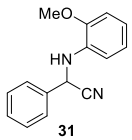
LZF-1H
LZF-1137



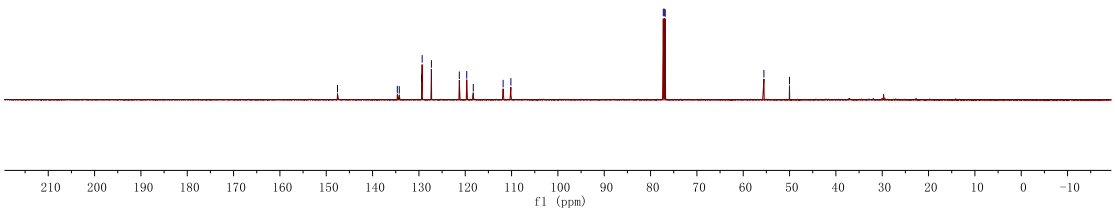
31



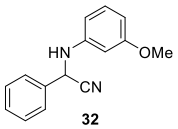
LZF-13C
LZF-1137



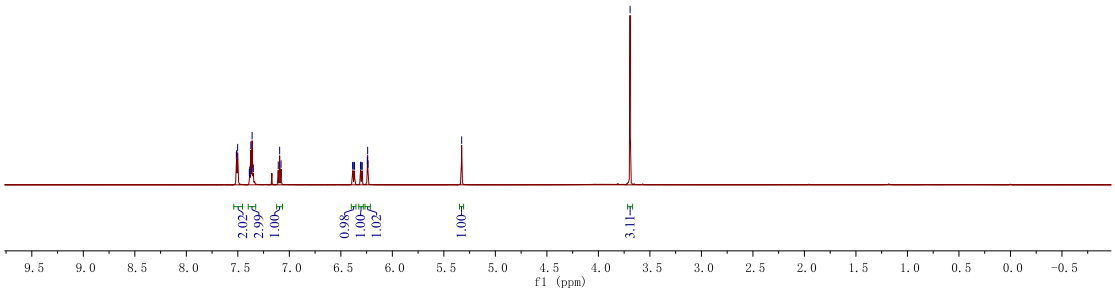
31



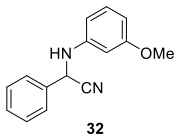
LZF-1H
LZF-1170



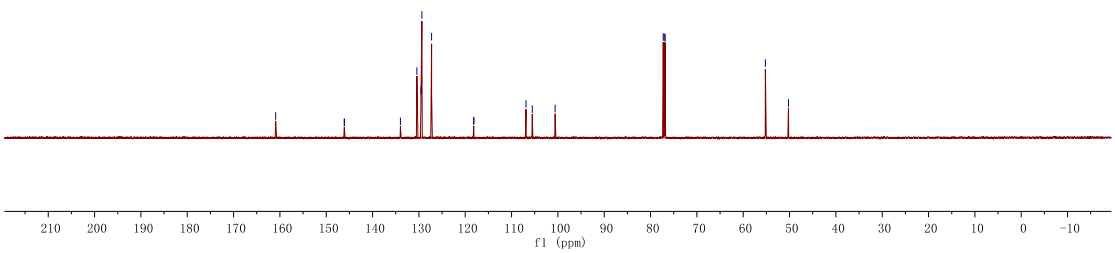
32



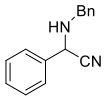
LZF-13C
LZF-1170



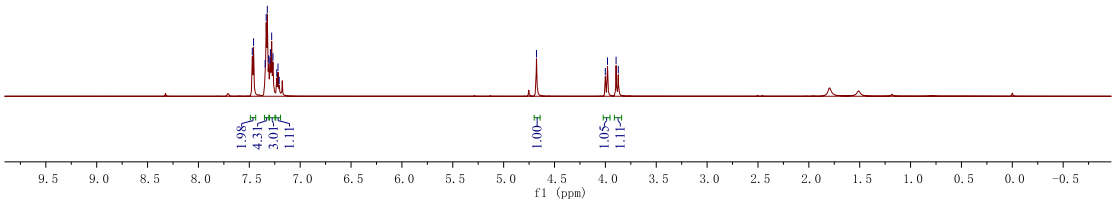
32



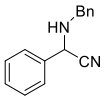
LZF-1H
LZF-1171



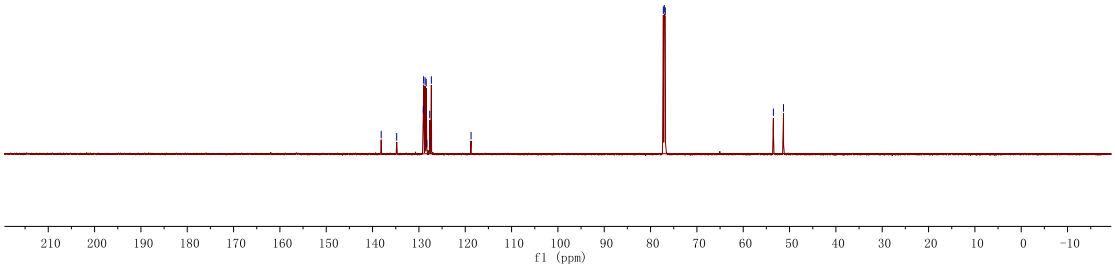
33



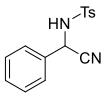
LZF-13C
LZF-1171



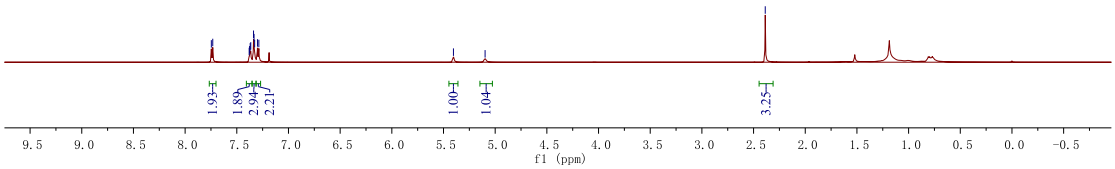
33



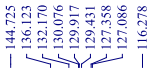
LZF-1H
LZF-1175

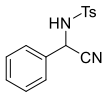


34

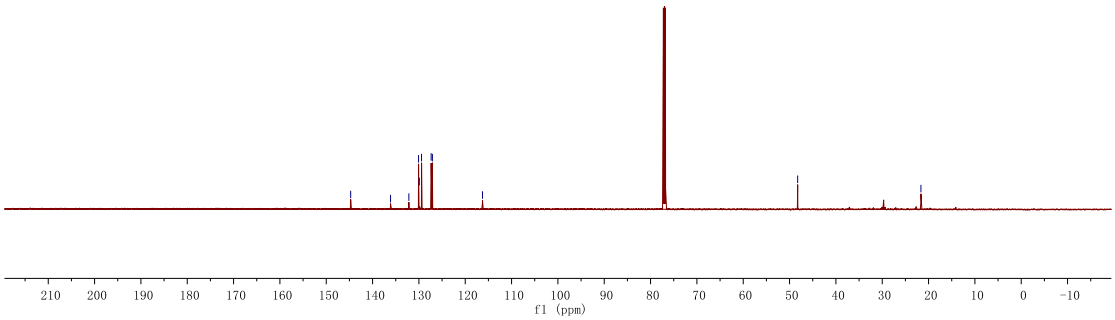


LZF-13C
LZF-1175

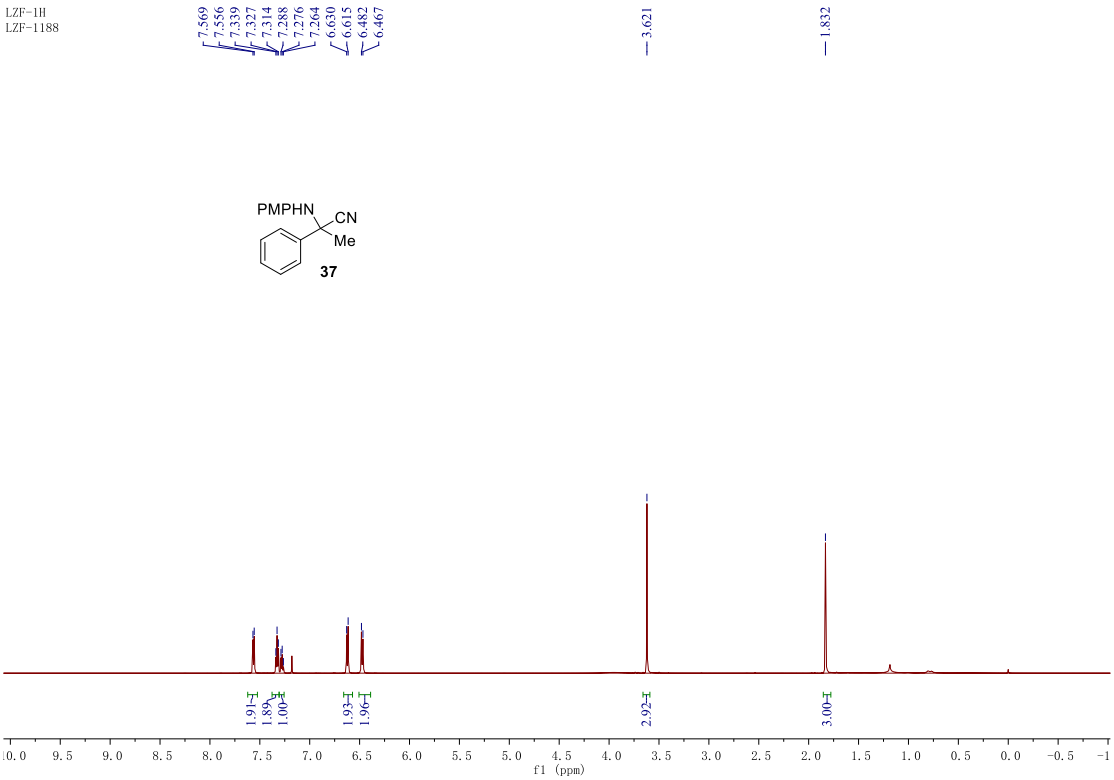




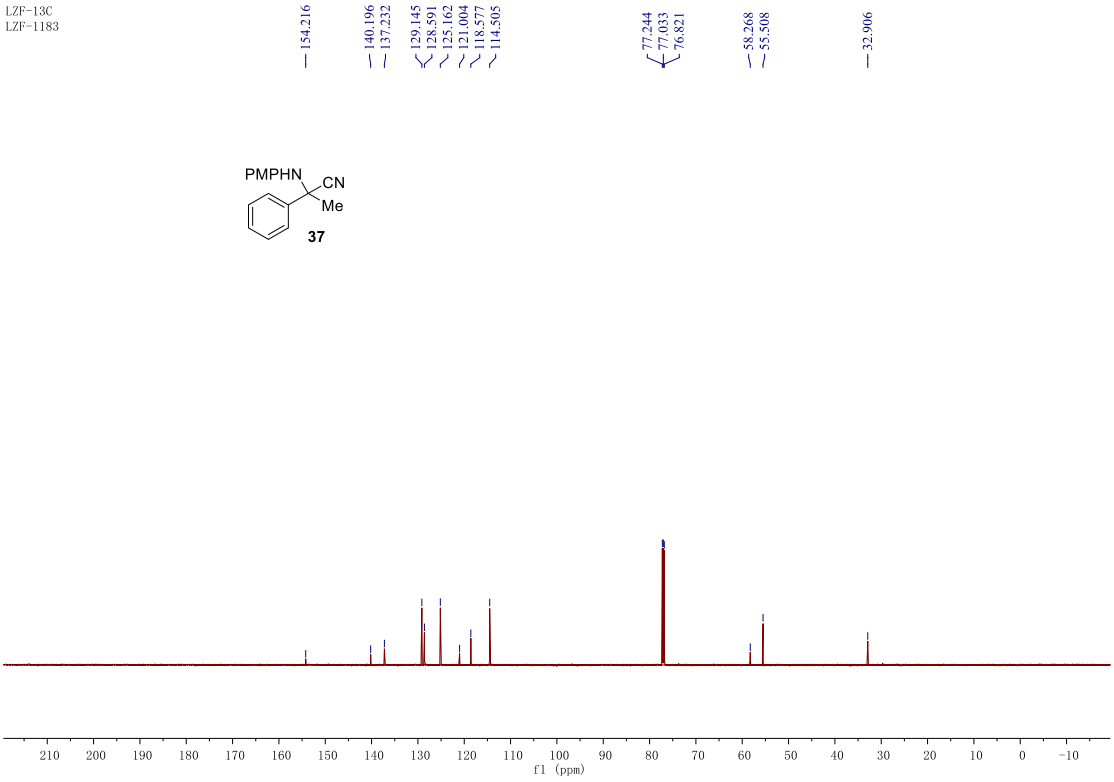
34



LZF-1H
LZF-1188

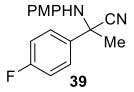


LZF-13C
LZF-1183

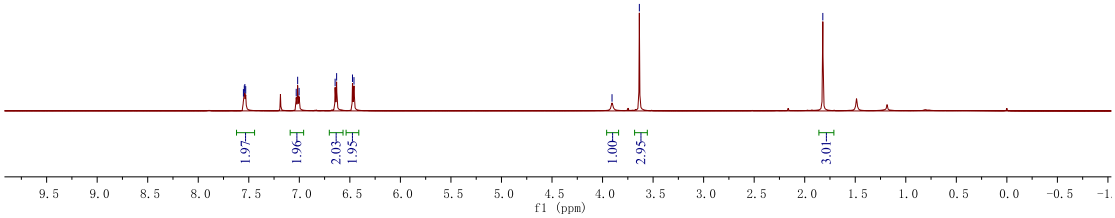


LZF-1H
LZF-1199

7.553
7.545
7.539
7.530
7.016
7.002
6.646
6.631
6.474
6.459
3.906
3.636
1.821

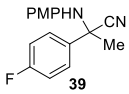


39

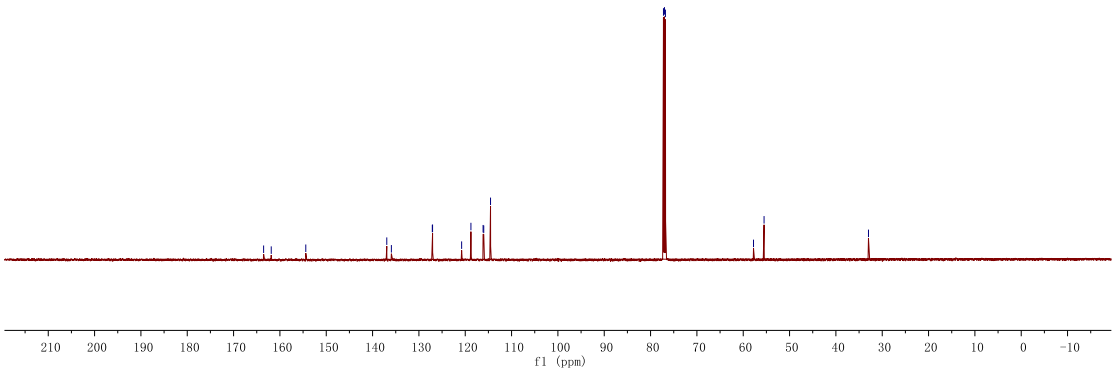


LZF-13C
LZF-1199

163.516
161.872
154.417
136.934
135.943
127.107
127.052
120.780
118.775
116.149
116.005
114.540
77.215
77.003
76.791
57.781
55.504
32.966

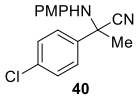


39

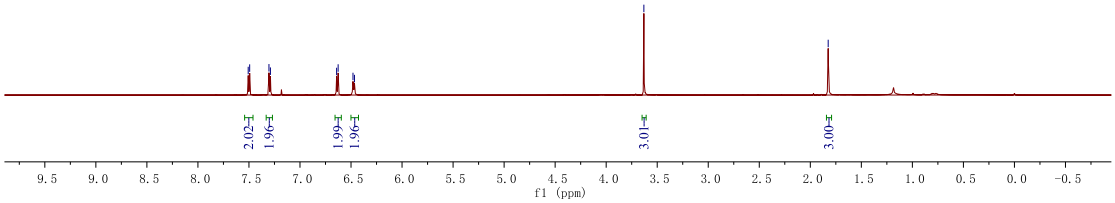


TJ-1H
TJ-94

7.507
7.493
7.304
7.290
6.641
6.626
6.481
6.466
3.631
1.825

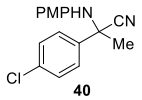


40

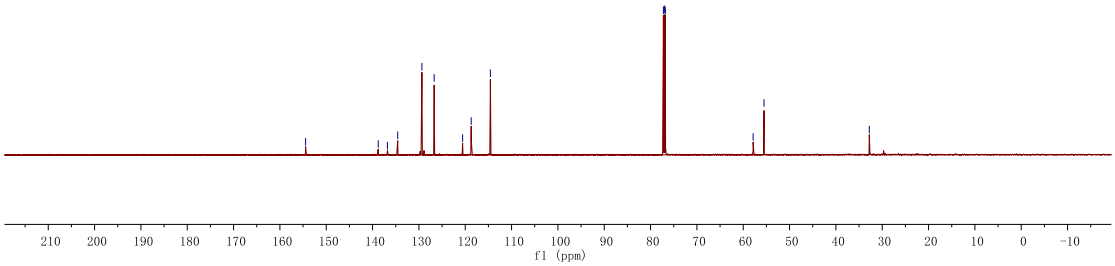


TJ-13C
LJ-095

154.457
138.781
136.796
134.573
129.351
126.709
120.567
118.712
114.577
77.230
77.019
76.807
57.867
55.509
32.795

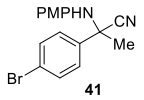


40

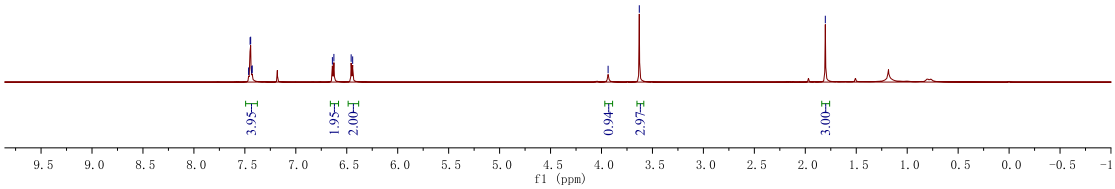


TJ-1H
TJ-086

7.463
7.449
7.443
7.432
7.428
6.641
6.626
6.457
6.442
3.935
3.629
1.804

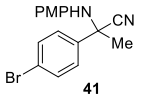


41

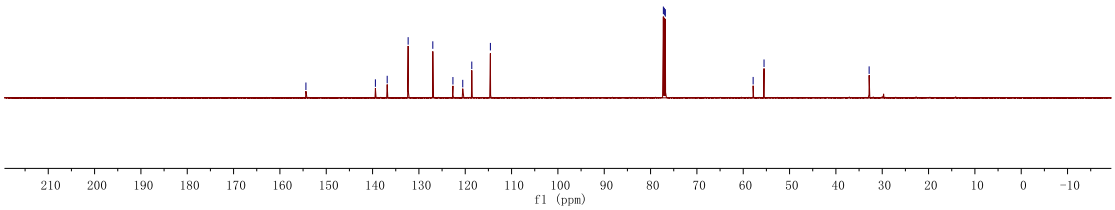


TJ-13C
TJ-086

154.387
139.393
136.846
132.325
127.000
122.657
120.536
118.586
114.574
77.239
77.028
76.816
57.865
55.511
32.826

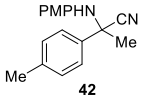


41

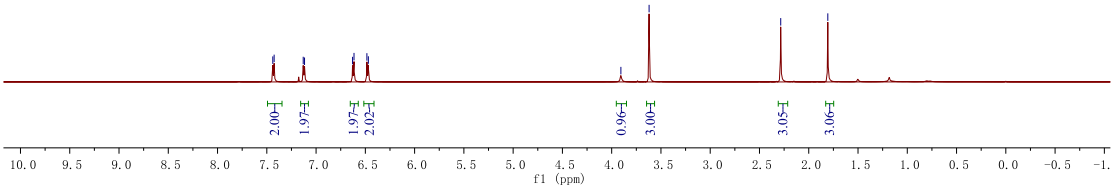


TJ-1H
TJ-94

7.439
7.426
7.131
7.117
6.630
6.615
6.484
6.469
3.907
3.620
2.284
1.807

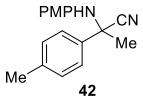


42

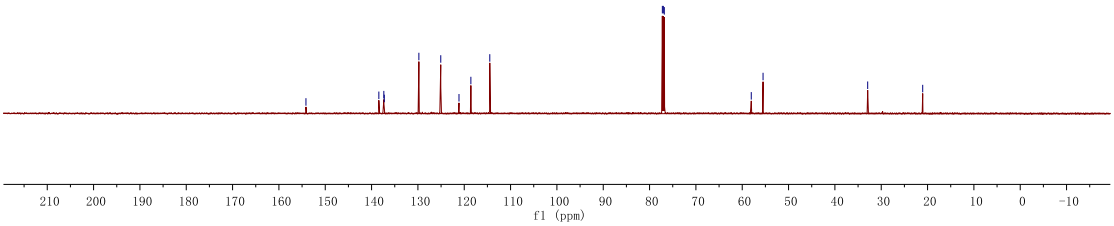


TJ-13C
TJ-94

154.163
138.432
137.357
137.263
129.792
125.068
121.134
118.568
114.485
77.243
77.031
76.820
58.051
55.506
32.924
21.048

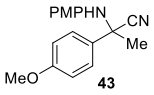


42

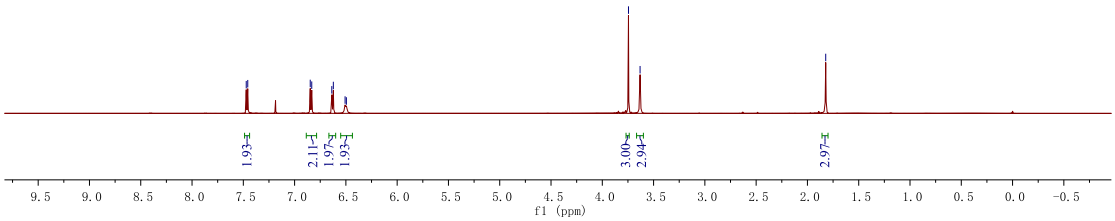


TJ-1H
TJ-087

7.471
7.457
6.848
6.833
6.637
6.622
6.508
6.495
3.745
3.632
1.822

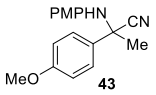


43

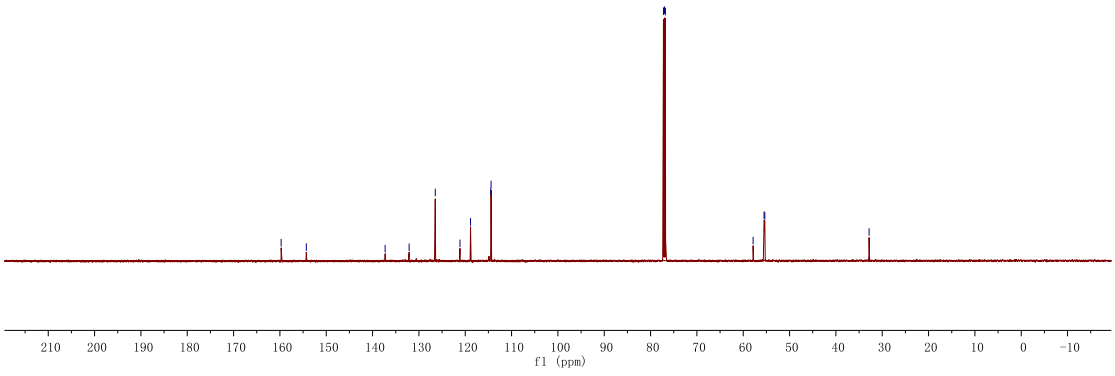


TJ-13C
LJ-087

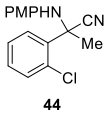
159.737
154.296
137.288
132.109
126.471
121.135
118.860
114.485
114.424
77.217
77.005
76.794
57.869
55.503
55.339
32.834



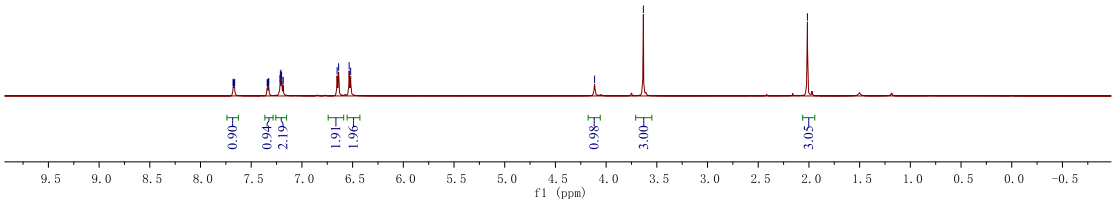
43



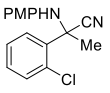
TJ-1H
TJ-077



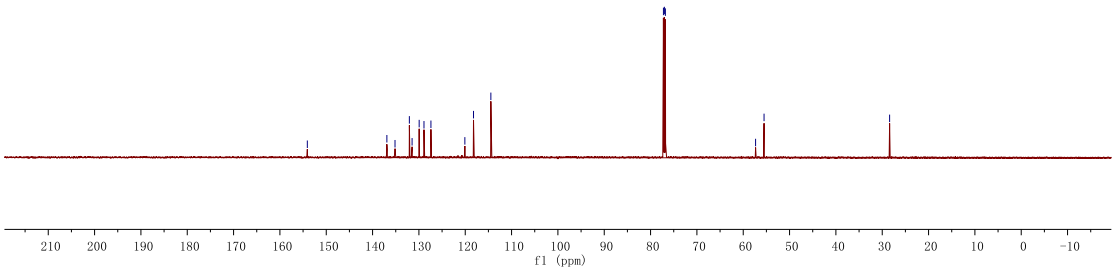
44



TJ-13C
TJ-077



44

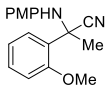


LZF-1H
LZF-1329

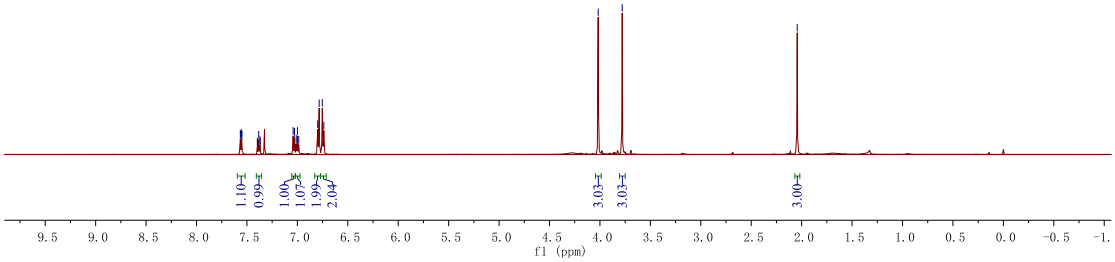
7.565
7.563
7.552
7.550
7.397
7.394
7.383
7.371
7.368
7.042
7.028
7.012
6.999
6.986
6.799
6.784
6.753
6.741
6.738

4.017
3.779

2.044



45



LZF-13C
LZF-1329

156.392
154.202

137.594

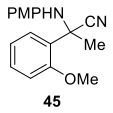
129.901

121.157
120.986
119.367
114.320
112.152

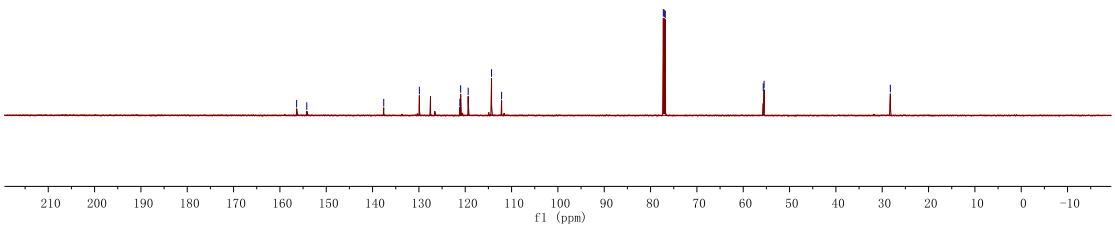
77.245
77.034
76.822

55.683
55.500

28.250

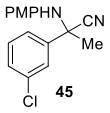


45

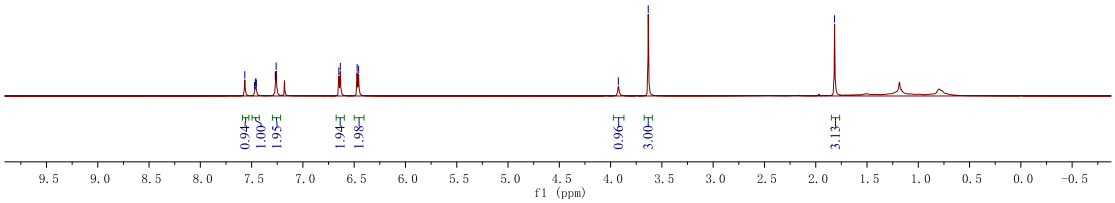


TJ-1H
TJ-076

7.567
7.471
7.464
7.457
7.454
7.269
7.266
7.261
6.650
6.635
6.472
6.457
3.924
3.633
1.817

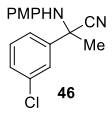


45

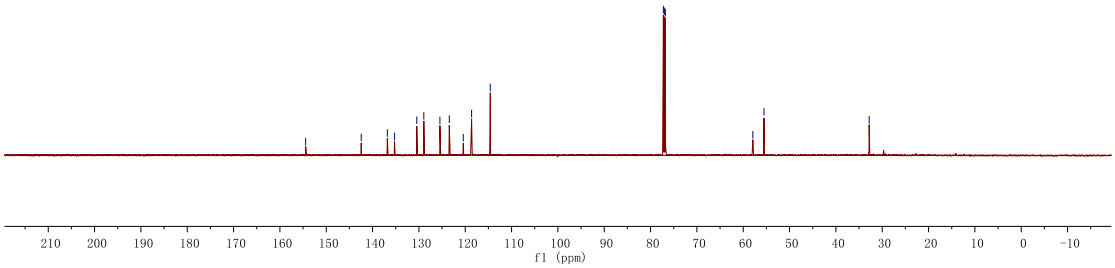


TJ-13C
TJ-076

154.441
142.448
136.819
135.252
130.460
128.937
125.466
123.442
120.426
118.629
114.594
77.234
77.023
76.811
57.924
55.512
32.818



46

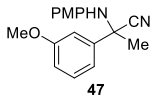


TJ-1H
TJ-075

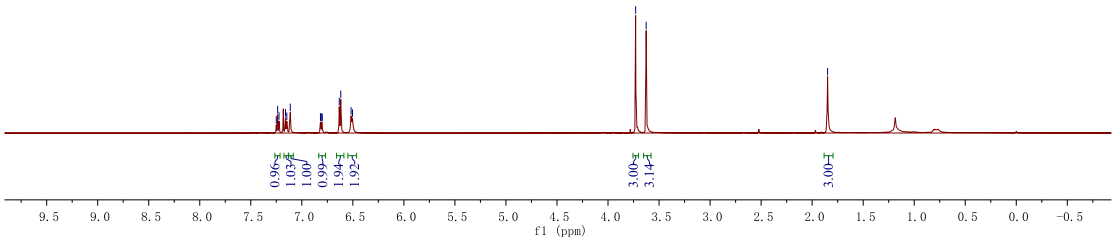
7.250
7.237
7.224
7.160
7.147
7.113
6.817
6.814
6.804
6.801
6.633
6.618
6.517
6.504

3.729
3.626

1.849



47



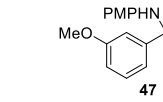
TJ-13C
LJ-075

160.276
154.250
141.921
137.239
130.213
120.931
118.531
117.417
114.514
113.974
110.980

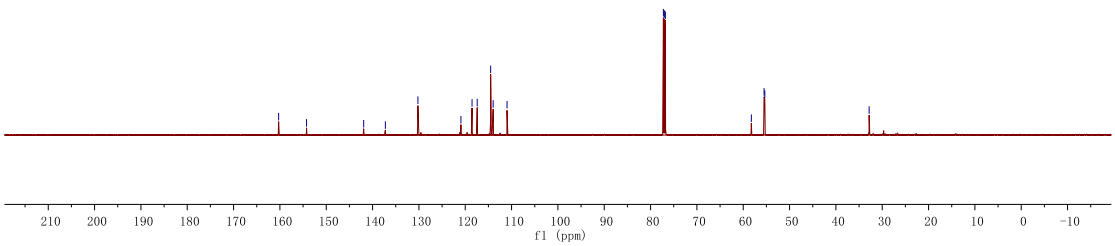
77.230
77.019
76.807

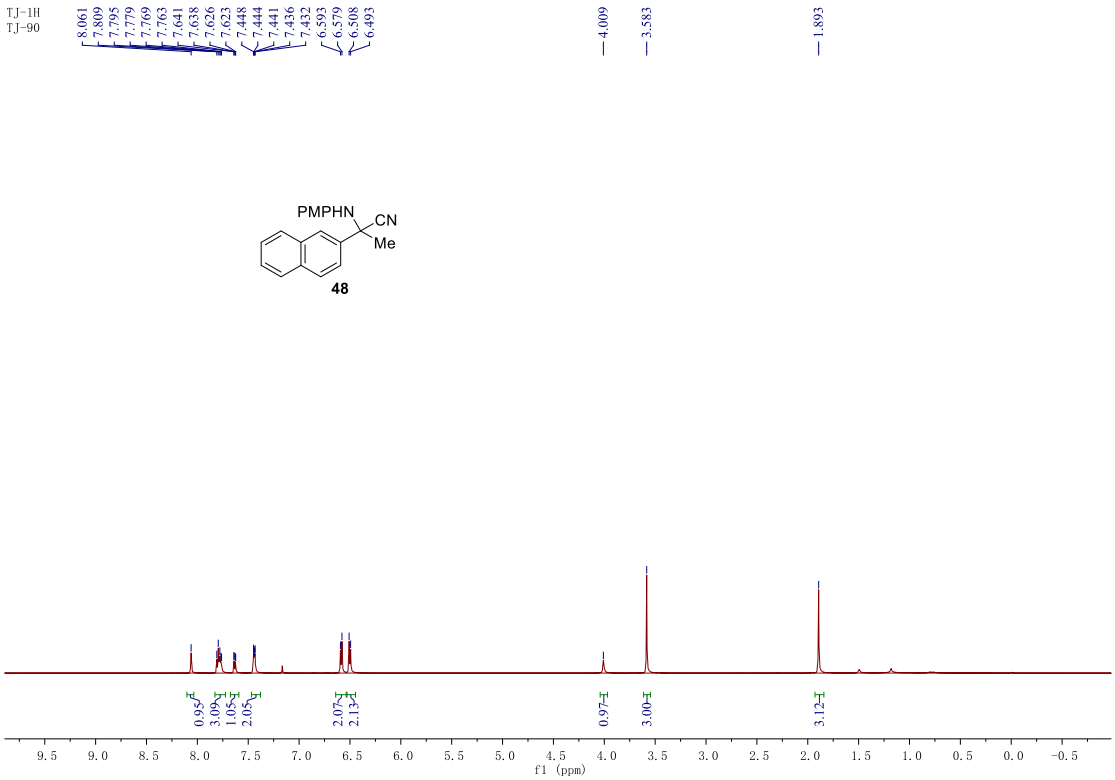
58.249
55.507
55.343

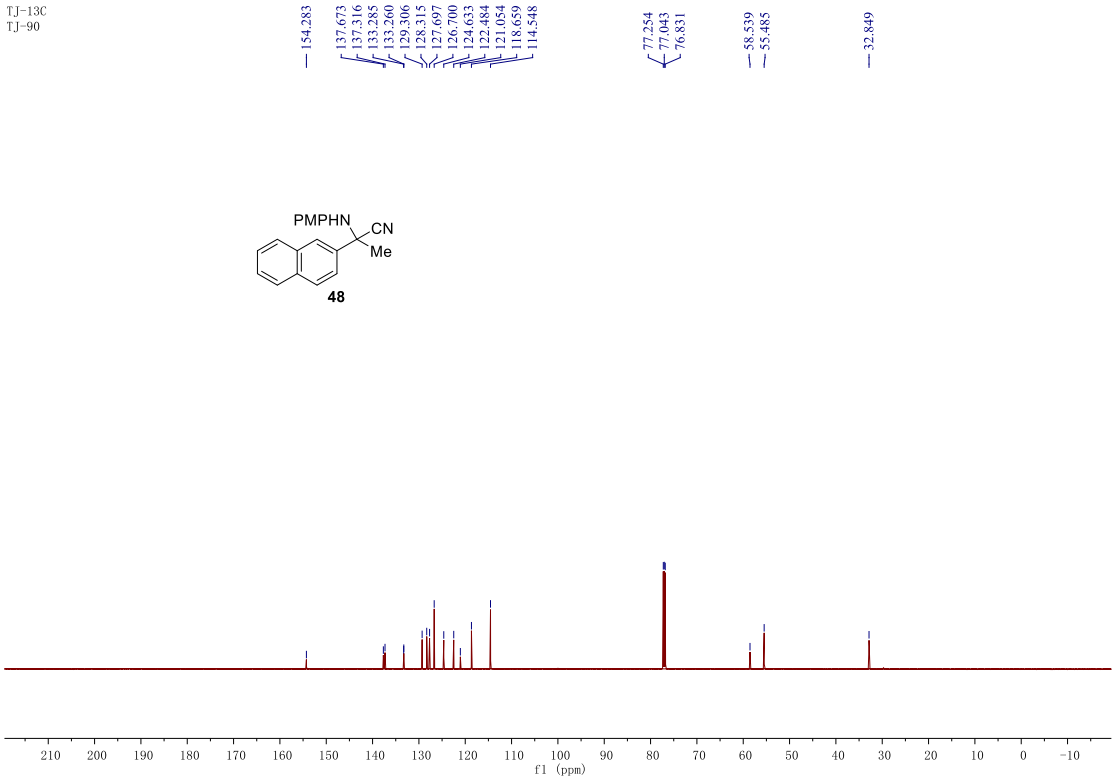
32.826



47

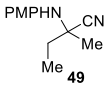



TJ-1H
TJ-90
8.061
7.809
7.795
7.779
7.769
7.763
7.641
7.638
7.626
7.623
7.448
7.444
7.441
7.436
7.432
6.593
6.579
6.508
6.493
4.009
3.583
1.893
PMPHN
CN
Me
48
0.95
3.09
1.05
2.05
2.07
2.13
0.97
3.00
3.12
f1 (ppm)

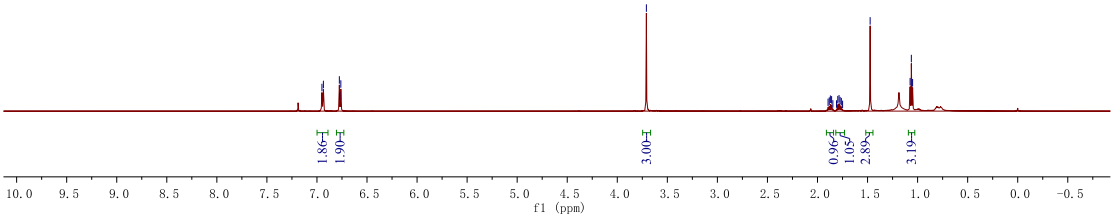

TJ-13C
TJ-90
154.283
137.673
137.316
133.285
133.260
129.306
128.315
127.697
126.700
124.633
122.484
121.054
118.659
114.548
77.254
77.043
76.831
58.539
55.485
32.849
PMPHN
CN
Me
48
f1 (ppm)

TJ-1H
TJ-91

6.950
6.936
6.776
6.773
6.762
3.709
1.894
1.882
1.871
1.859
1.847
1.810
1.797
1.785
1.774
1.762
1.749
1.474
1.075
1.062
1.050

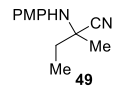


49

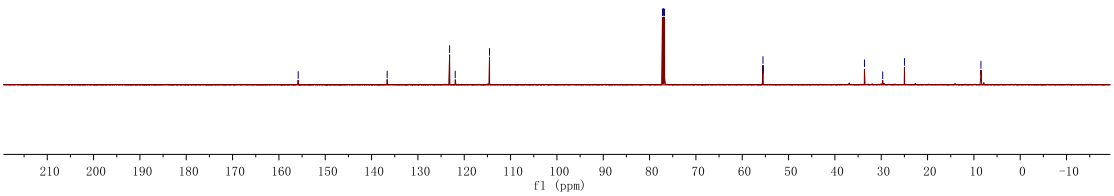


TJ-13C
LJ-091

155.838
136.638
123.158
121.943
114.551
77.216
77.004
76.792
55.540
55.526
33.618
29.683
24.985
8.477



49



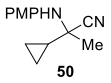
LZF-1H
LZF-1200

6.896
6.882
6.808
6.793

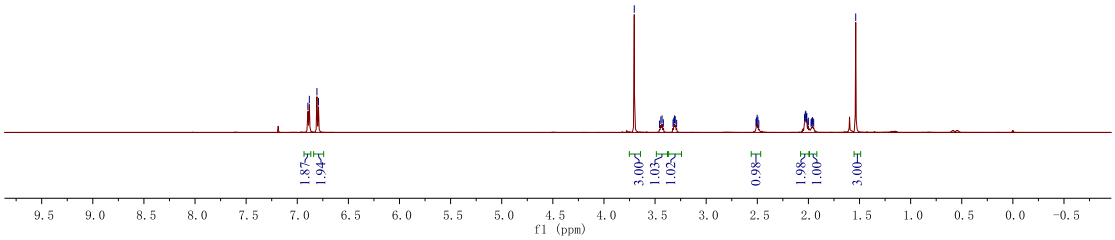
3.703
3.456
3.443
3.432
3.419
3.324
3.317
3.310
3.303
3.289

2.513
2.508
2.502
2.494

2.031
2.025
2.019
2.016
1.537



50



LZF-13C
LZF-1200

152.068
136.435
119.781
117.122
112.556

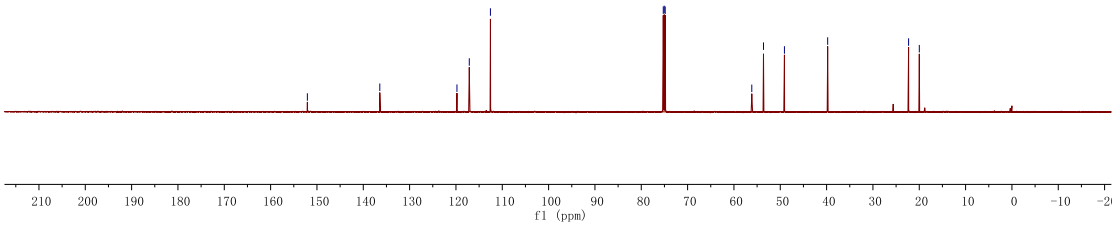
75.253
75.042
74.830

56.145
53.622
49.099

39.769

22.305
19.993

50

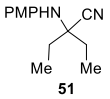


LZF-1H
LZF-1213

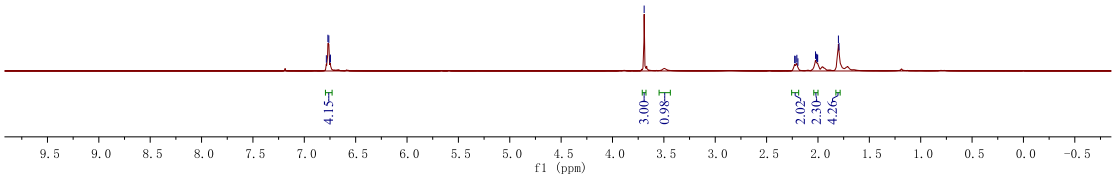
6.785
6.770
6.761
6.750
6.746

3.692

2.227
2.216
2.205
2.195
2.024
2.013
2.007
2.003
1.801
1.795

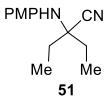


51

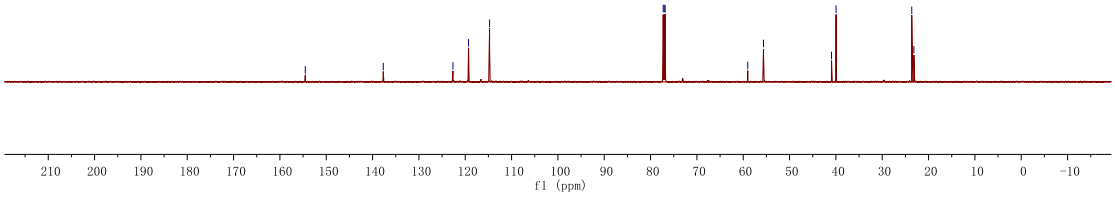


LZF-13C
LZF-1213

154.523
137.693
122.654
119.288
114.747
77.272
77.060
76.848
59.023
55.633
40.940
39.967
23.626
23.171

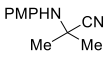


51

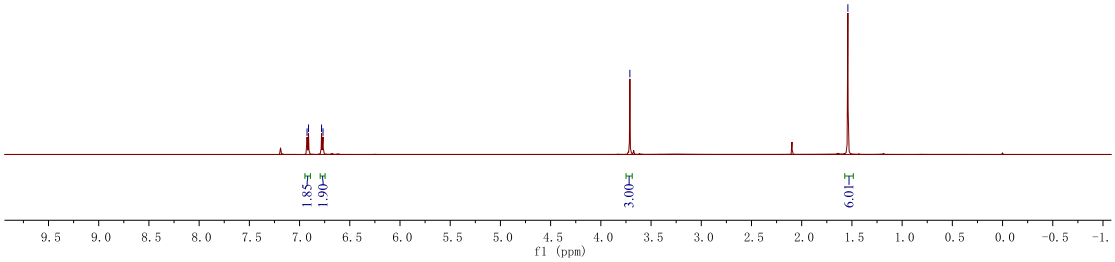


LZF-1H
LZF-1205

6.926
6.911
6.781
6.767
3.711
1.540

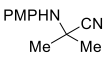


52

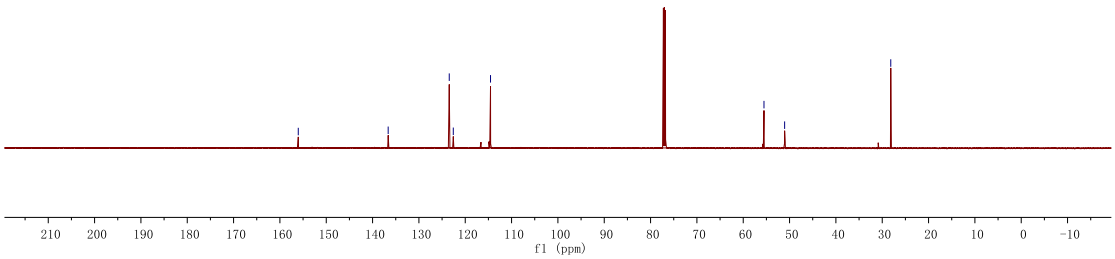


LZF-13C
LZF-1205

156.037
136.632
123.452
122.578
114.545
55.523
51.067
28.158



52



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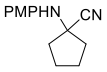
LZF-1219



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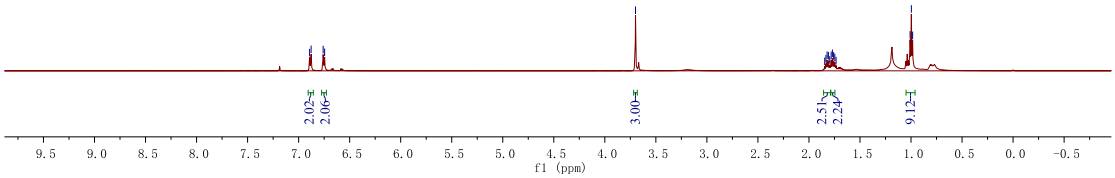

LZF-13C
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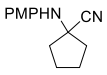

53