

Supplementary information

Waste PVC upcycling enables oxidant-free C-H and C-C bond editing

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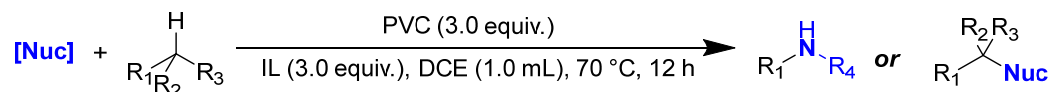
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1. General Information

All commercially available compounds were purchased from Sigma-Aldrich, Alfa-Aesar, Aladdin, J&K Scientific, Bide Pharmatech Ltd. and Leyan. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Analysis of crude reaction mixture was done on Bruker AVANCE III-400 spectrometers. Products were purified by flash chromatography on silica gel. ^1H NMR spectra were recorded on Bruker AVANCE III-400 spectrometers. Chemical shifts were referenced tetramethylsilane (TMS) added to CDCl_3 ($\delta = 0$ ppm) or as the residual peak of the solvent (CDCl_3 7.26 ppm; $\text{DMSO}-d_6$ 2.50 ppm). ^{13}C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl_3 ($\delta = 77.00$ ppm), $\text{DMSO}-d_6$ ($\delta = 39.50$ ppm). Coupling constants are reported in Hertz (Hz). Data for ^1H NMR and ^{13}C NMR spectra are reported as follows: chemical shift (ppm, referenced to protium: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet, coupling constant (Hz), and integration). ^{19}F NMR and ^{27}Al NMR spectra were obtained by using the same NMR spectrometers. Gel permeation chromatography (GPC) measurements were performed in stabilized, HPLC grade THF using an Agilent 1260 Infinity II system equipped with a refractive index (RI) detector. The instrument was calibrated with narrow-dispersity polystyrene standards. All runs were performed at 1.0 mL/min flow rate and 30 °C. Molecular weights (MW) were calculated using Chemstation GPC data analysis software based on the refractive index signals. Infrared Spectroscopy (IR) spectra were recorded on a Nicolet iS50 spectrometer equipped with an ATR accessory, using powder samples. High resolution mass spectra were obtained with a Waters Xevo G2 Q-TOF mass spectrometer. Unless otherwise specified, the reagents used are commercially available Analytical Reagent (AR).

2. General Procedure

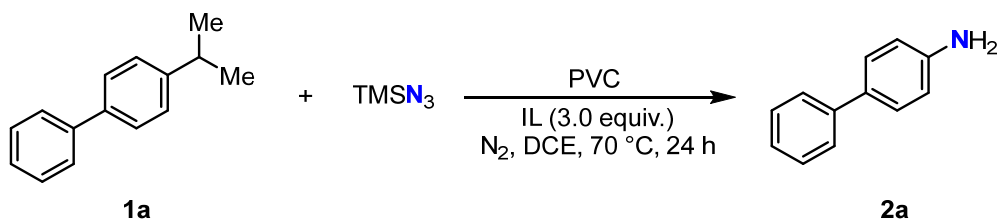


General Procedure: To a 25 mL Schlenk tube equipped with a rubber septum cap and Tefloncoated magnetic stir bar were charged with Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer) and 1-Butylpyridinium chloride (257.5 mg, 1.5 mmol, 3.0 equiv.). The tube was evacuated and backfilled with N₂ for 3 times. Subsequently, Aluminum (III) chloride (400.0 mg, 3 mmol, 6.0 equiv.) was added to the mixture and the vial was quickly resealed with the septum cap. The mixture was stirred until converted to a dark yellow suspension. Then a solution of **cumene derivatives** or **alkanes** (0.5 mmol, 1.0 equiv.) and **nucleophiles** (1.0 mmol, 2.0 equiv.) in 1 mL of 1,2-dichloroethane were added respectively with syringe under N₂. The mixture was then stirred at 70 °C for 12 h. After cooling to room temperature, the resulting mixture was quenched by a saturated solution of potassium sodium tartrate in 2.5 mol/L aqueous sodium hydroxide (5 mL) and extracted with ethyl acetate (3 × 5 mL). The organic layers were combined and the solvent was removed under reduced pressure. Flash chromatography affords the desired products.

3. Condition Optimization of the Ionic Liquid-based PVC Degradation System

3.1 Condition optimization

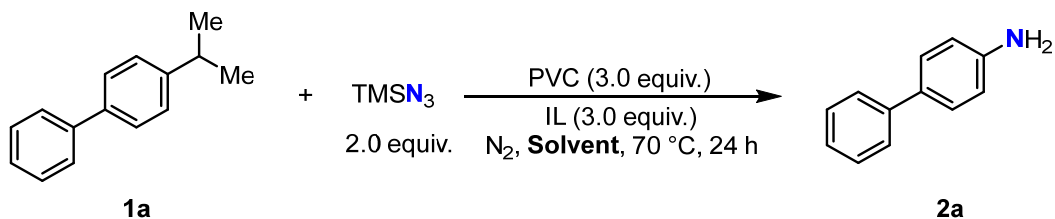
Table S1. Optimization details for effects of the equivalents of PVC and TMSN₃ on the ionic liquid-based PVC degradation system ^a



Entry	equiv. of PVC	equiv. TMSN ₃	of Yield (%)	SM (%)	Remain
1	1.5	1.5	50	27	
2	1.5	2.0	52	33	
3	3.0	3.0	57	34	
4	6.0	3.0	59	29	
5	4.0	4.0	57	25	
6	6.0	4.0	60	32	

^a Reaction conditions: **1a** (0.5 mmol, 1.0 equiv.), Polyvinyl chloride (equiv. calculated by corresponding monomer), azidotrimethylsilane in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL), under N₂, 70 °C, 12 h. Isolated yields are reported.

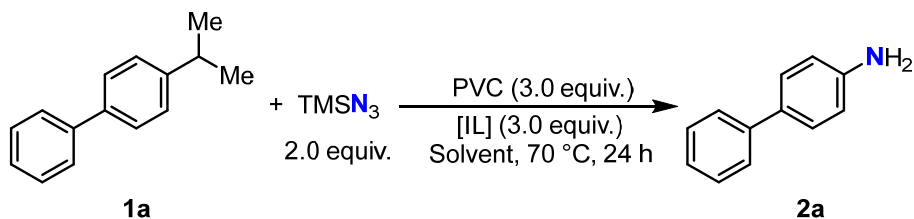
Table S2. Optimization details for effects of the solvent on the ionic liquid-based PVC degradation system ^a



Entry	Solvent	Yield (%)	SM (%)	Remain
1	DMF	n.d.	60	
2	PhNO ₂	n.d.	34	
3	MeNO ₂	n.d.	22	
4	THF	n.d.	29	
5	1,4-dioxane	n.d.	75	
6	DCM	53	25	
7	1,1,2-TCE	55	29	
8	TeCA	58	33	
9	MeCN	n.d.	55	
10	Toluene	n.d.	n.d.	
11	PhCl	n.d.	n.d.	
12	None	49	33	

^a Reaction conditions: **1a** (0.5 mmol, 1.0 equiv.), Polyvinyl chloride (3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (1.0 mmol, 2.0 equiv.), in ionic liquid (3.0 equiv. calculated by corresponding cation) and solvent (1.0 mL), under N₂, 70 °C, 12 h. Isolated yields are reported.

Table S3. Optimization details for effects of the ionic liquid on the ionic liquid-based PVC degradation system ^a



Entry	[IL]	Yield (%)	SM (%)	Remain
1	IL-2	45	47	
2	IL-3	55	28	
3	IL-4	n.d.	90	
4	IL-5	44	50	
5	IL-6	54	30	
6	AlCl ₃	18	72	
7	none	n.d.	95	

^a Reaction conditions: **1a** (0.5 mmol, 1.0 equiv.), Polyvinyl chloride (3.0 equiv. calculated by corresponding monomer), azidotrimethylsiane (1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL), under N₂, 70 °C, 12 h. Isolated yields are reported.

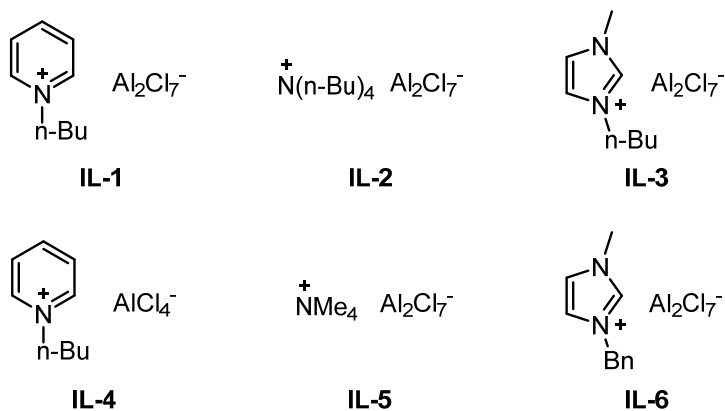
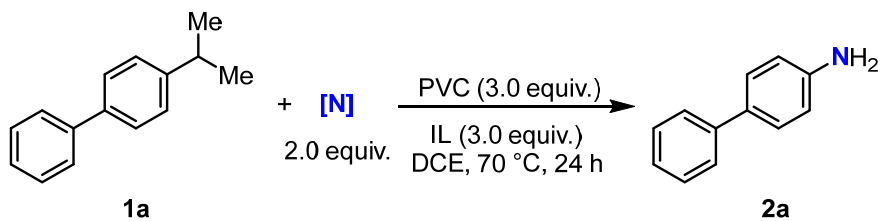
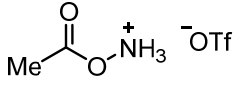
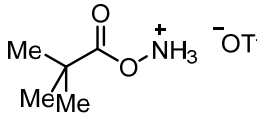
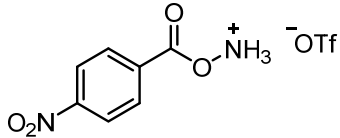


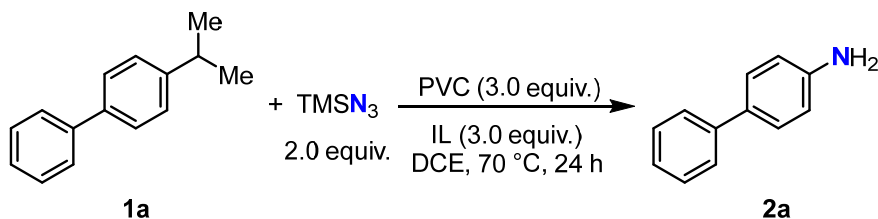
Table S4. Optimization details for effects of aminating reagents of the ionic liquid-based PVC degradation system ^a



Entry	[N]	Yield (%)	SM (%)	Remain
1	NaN ₃	58	33	
2		42	n.d.	
3		48	n.d.	
4		n.d.	n.d.	

^a Reaction conditions: **1a** (0.5 mmol, 1.0 equiv.), Polyvinyl chloride (3.0 equiv. calculated by corresponding monomer), [N] reagents (1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL), 12 h. Isolated yields are reported.

Table S5. Optimization details for effects of temperature and control experiments of the ionic liquid-based PVC degradation system ^a



Entry	Variations from standard conditions	Yield (%)	SM (%)	Remain
1	Under -20 °C	Trace	75	
2	Under 0 °C	Trace	60	
3	Under r.t.	31	57	
4	Under 40 °C	46	55	
5	Without PVC	8	79	
6	i-PrCl instead of PVC	30	n.d.	
7	t-BuCl instead of PVC	24	n.d.	
8	Under O ₂	50	n.d.	
9	Under Air	45	20	

^a Reaction conditions: **1a** (0.5 mmol, 1.0 equiv.), additive (3.0 equiv.; for PVC, calculated by corresponding monomer), azidotrimethylsilane (1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL), 12 h. Isolated yields are reported.

3.2 Tracking the time course of the ionic liquid-based PVC degradation system

To a 25 mL Schlenk tube equipped with a rubber septum cap and Tefloncoated magnetic stir bar were charged with Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer) and 1-Butylpyridinium chloride (257.5 mg, 1.5 mmol, 3.0 equiv.). The tube was evacuated and backfilled with N₂ for 3 times. Subsequently, Aluminum (III) chloride (400.0 mg, 3 mmol, 6.0 equiv.) was added to the suspension and the vial was quickly resealed with the septum cap. Then a solution of **1a** (98.1 mg, 0.5 mmol, 1.0 equiv.) and azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in 1 mL of 1,2-dichloroethane were added respectively with syringe under N₂. The mixture was then stirred at 70 °C for 0, 1, 2, 3, 6, 9 and 12 hours. After cooling to room temperature, the resulting mixture was quenched by a saturated solution of potassium sodium tartrate in 2.5 mol/L aqueous sodium hydroxide (5 mL) and extracted with tetrahydrofuran (5 mL). The organic layer was directly used for GPC tests. Isolated yields are reported.

Table S6. Time course of the ionic liquid-based PVC degradation system

Entry	Time (h)	Yield of 2a (%)	M _n (kDa)	PDI
1	0	0	107.83	1.61
2	1	4	97.99	1.77
3	2	8	87.88	1.80
4	3	18	67.11	1.79
5	6	35	30.15	2.50
6	9	49	<1	-
7	12	60	-	-

3.3 Ionic liquid recycling experiments of the ionic liquid-based PVC degradation system

To a 25 mL Schlenk tube equipped with a rubber septum cap and Tefloncoated magnetic stir bar were charged with Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer) and 1-Butylpyridinium chloride (257.5 mg, 1.5 mmol, 3.0 equiv.). The tube was evacuated and backfilled with N₂ for 3 times. Subsequently, Aluminum (III) chloride (400.0 mg, 3 mmol, 6.0 equiv.) was added to the suspension and the vial was quickly resealed with the septum cap. Then a solution of **1a** (98.1 mg, 0.5 mmol, 1.0 equiv.) and azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in 1 mL of 1,2-dichloroethane were added respectively with syringe under N₂. The mixture was then stirred at 70 °C for 12 hours. After cooling to room temperature, the resulting mixture was extracted with toluene (5 × 3 mL). The organic layer was combined and extracted with saturated Sodium bicarbonate aqueous. The solvent was removed under reduced pressure. Flash chromatography affords the desired products. The ionic liquid layer was added Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), Aluminum (III) chloride (200.0 mg, 1.5 mmol, 3.0 equiv.) and a solution of **1a** (98.1 mg, 0.5 mmol, 1.0 equiv.) and azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in 1 mL of 1,2-dichloroethane for another catalytic cycle. Isolated yields are reported.

Table S7. Ionic liquid recycling experiments of the ionic liquid-based PVC degradation system

Cycle	Yield of 2a (%)
1	51
2	61
3	55
4	53

4. Characterization of the Ionic Liquid-based PVC Degradation System

4.1 GPC Analysis of degraded polyvinyl chloride

Table S8. GPC Analysis of degraded polyvinyl chloride after 0 h

Peak	Time (min)	M_p (Da)	M_n (Da)	M_w (Da)	M_z (Da)	M_{z+1} (Da)	$\bar{D}$
1	11.612	161897	107834	173915	252448	330964	1.612803

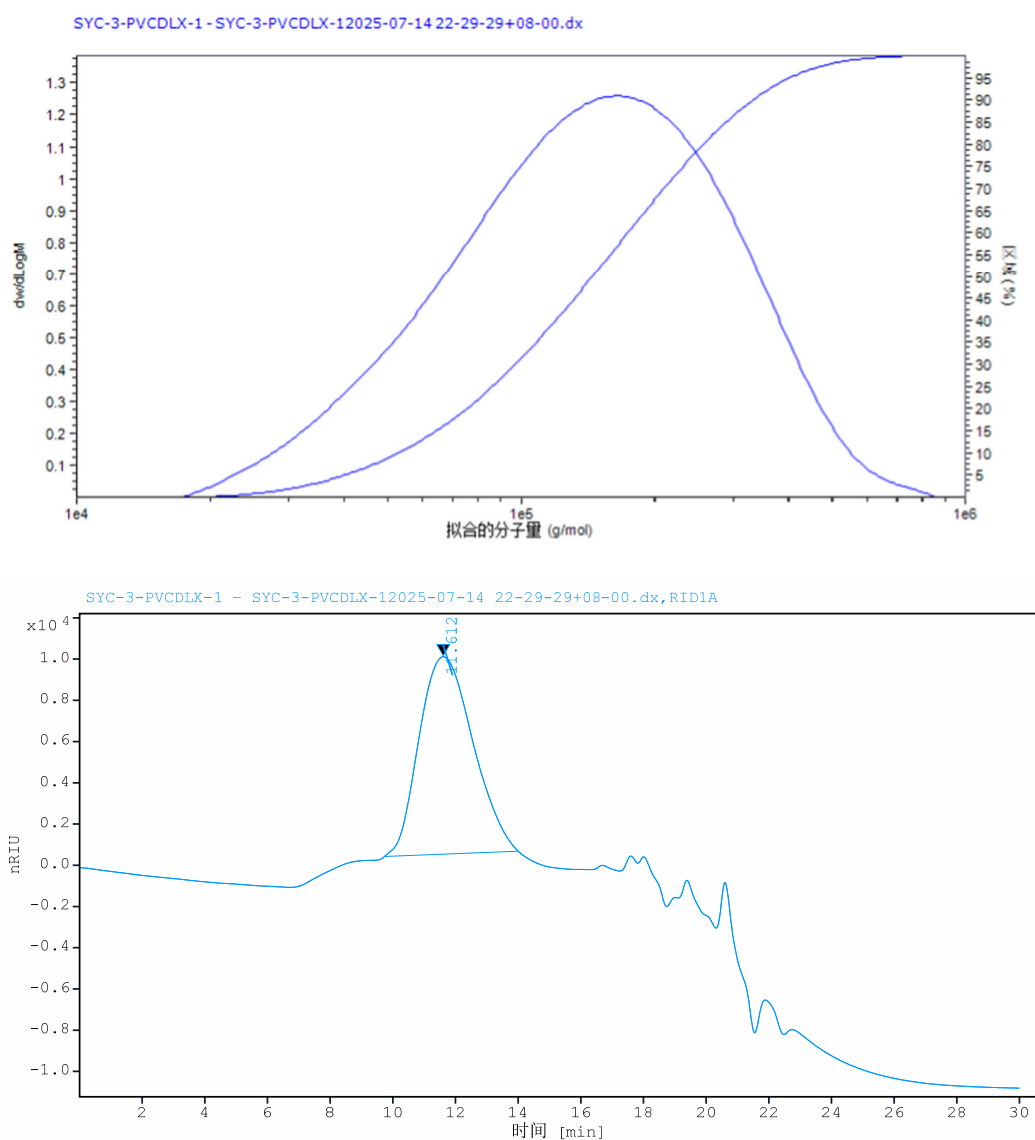


Table S9. GPC Analysis of degraded polyvinyl chloride after 1 h

Peak	Time (min)	M _p (Da)	M _n (Da)	M _w (Da)	M _z (Da)	M _{z+1} (Da)	Đ
1	11.581	167968	97989	173840	262467	350120	1.774077
2	19.404	150	182	207	253	329	1.137363

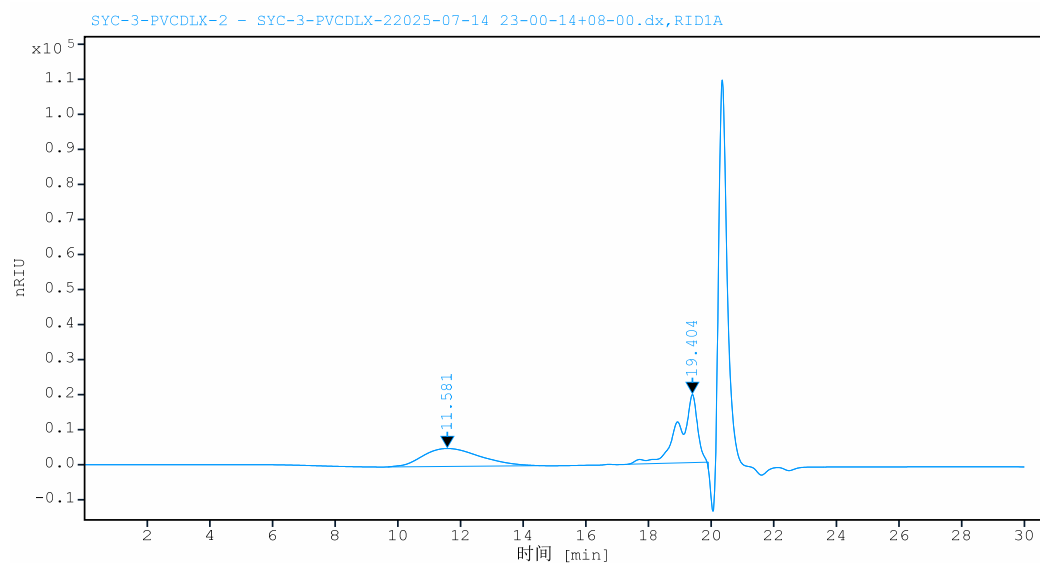
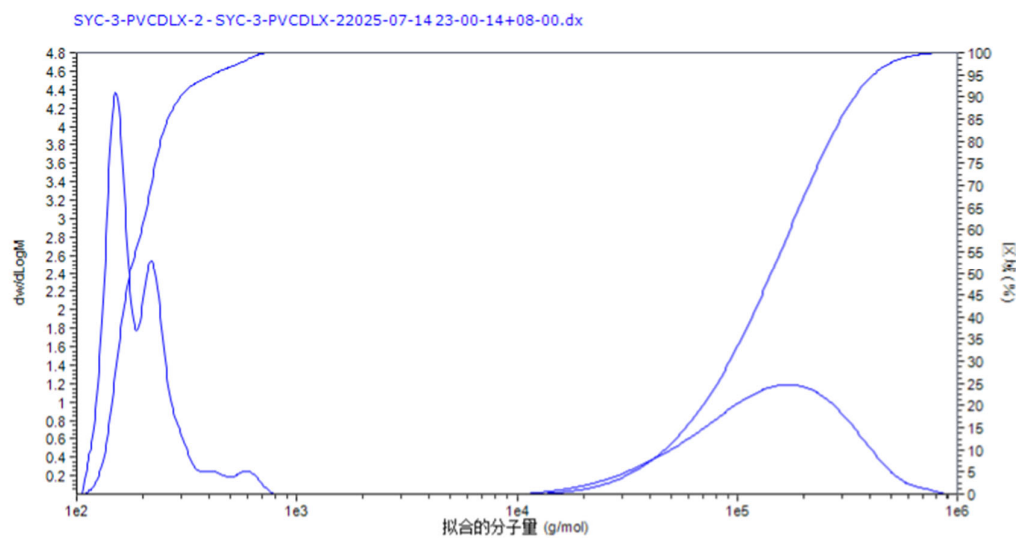


Table S10. GPC Analysis of degraded polyvinyl chloride after 2 h

Peak	Time (min)	M _p (Da)	M _n (Da)	M _w (Da)	M _z (Da)	M _{z+1} (Da)	Đ
1	11.688	151672	87878	158617	241377	321991	1.804968
2	19.440	146	149	167	225	382	1.120805

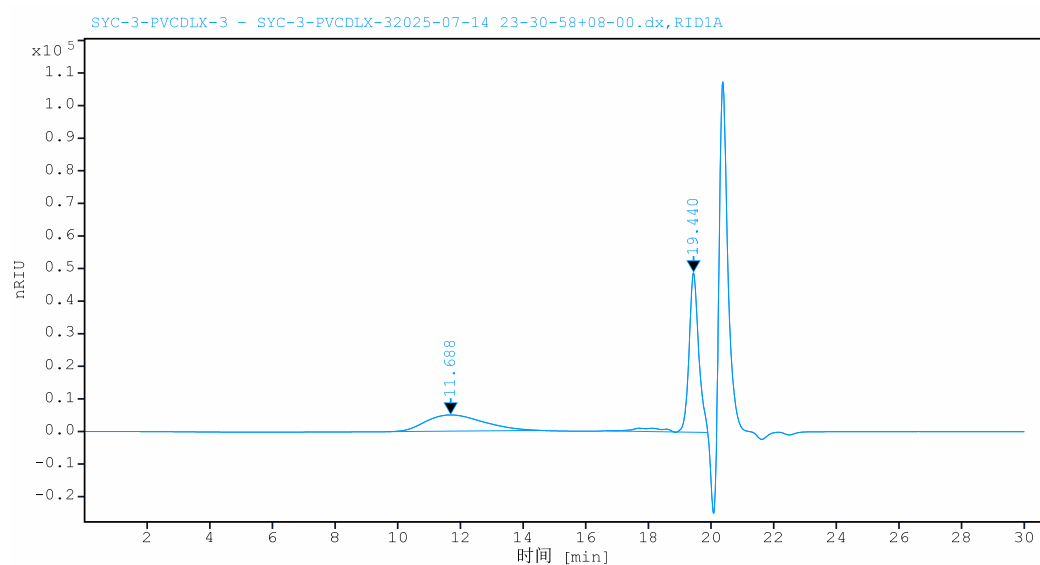
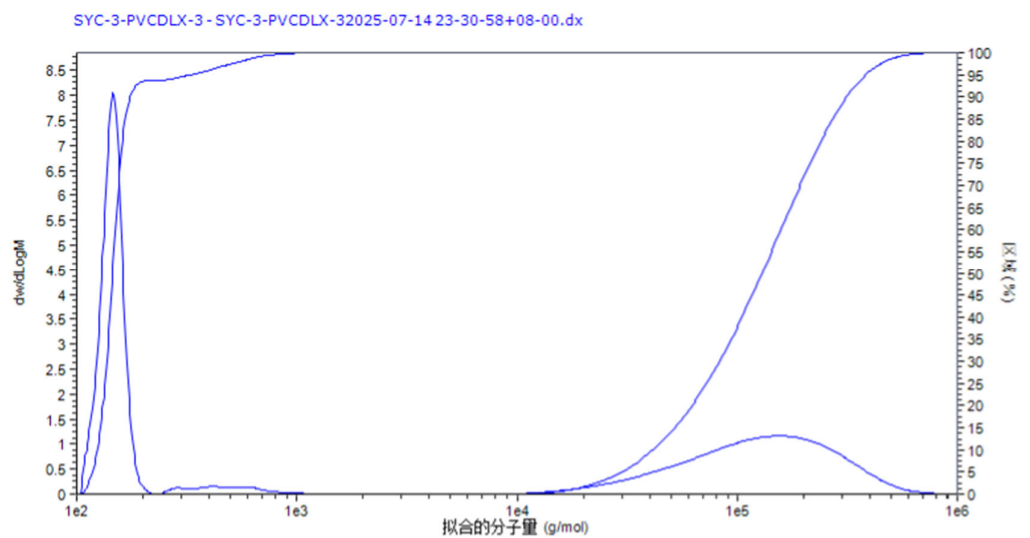


Table S11. GPC Analysis of degraded polyvinyl chloride after 3 h

Peak	Time (min)	M _p (Da)	M _n (Da)	M _w (Da)	M _z (Da)	M _{z+1} (Da)	Đ
1	12.027	111460	67113	119842	181975	239192	1.785675
2	19.300	162	165	177	206	274	1.072727

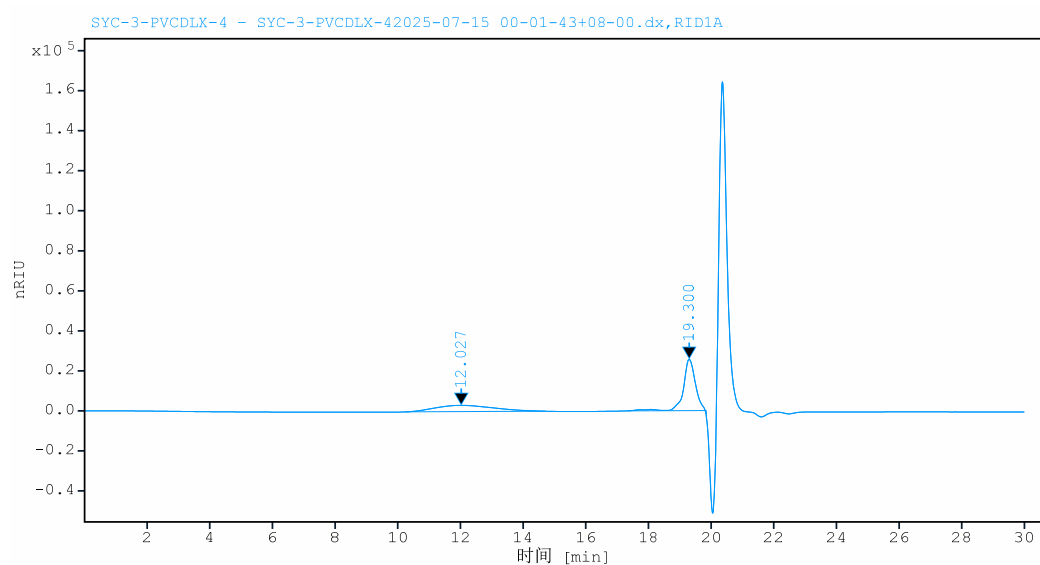
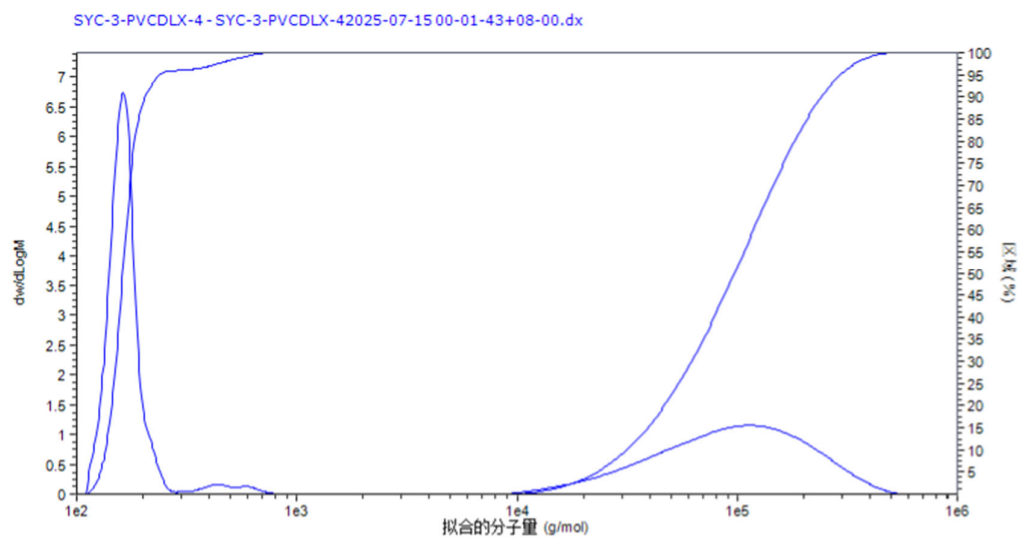


Table S12. GPC Analysis of degraded polyvinyl chloride after 6 h

Peak	Time (min)	M _p (Da)	M _n (Da)	M _w (Da)	M _z (Da)	M _{z+1} (Da)	Đ
1	13.062	44854	30150	75369	170150	283149	2.499801
2	18.395	333	223	253	285	319	1.134529

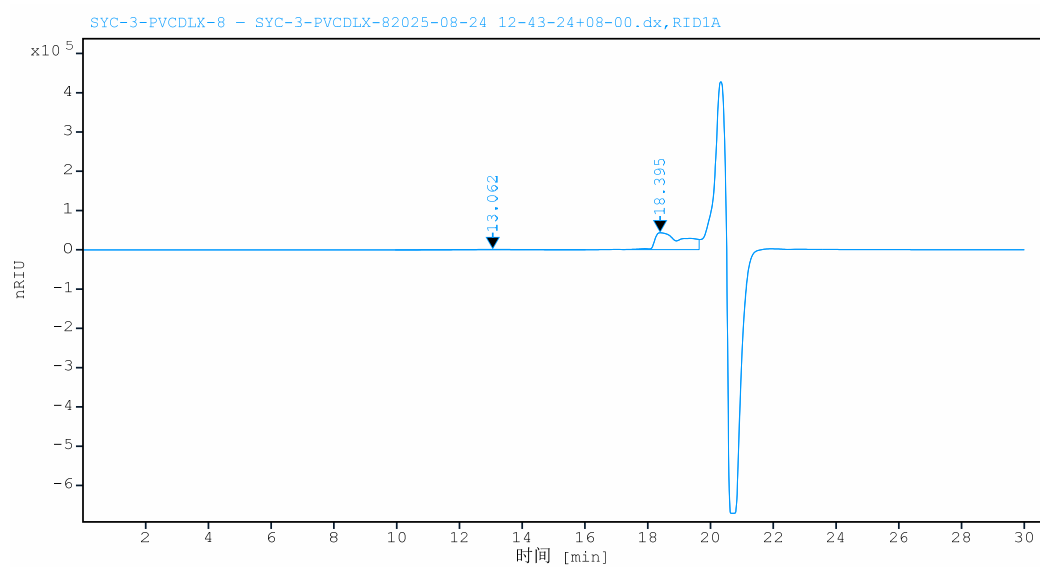
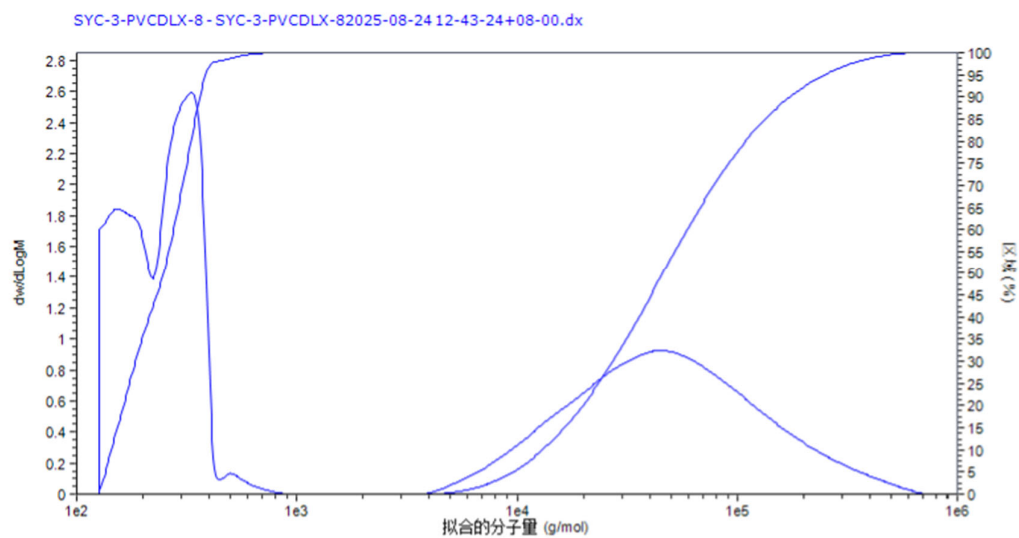
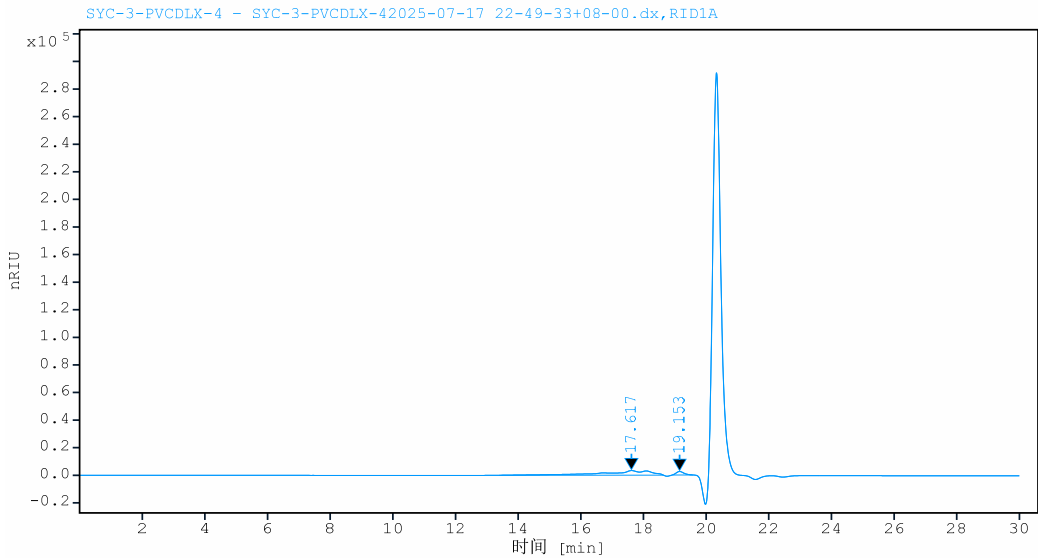
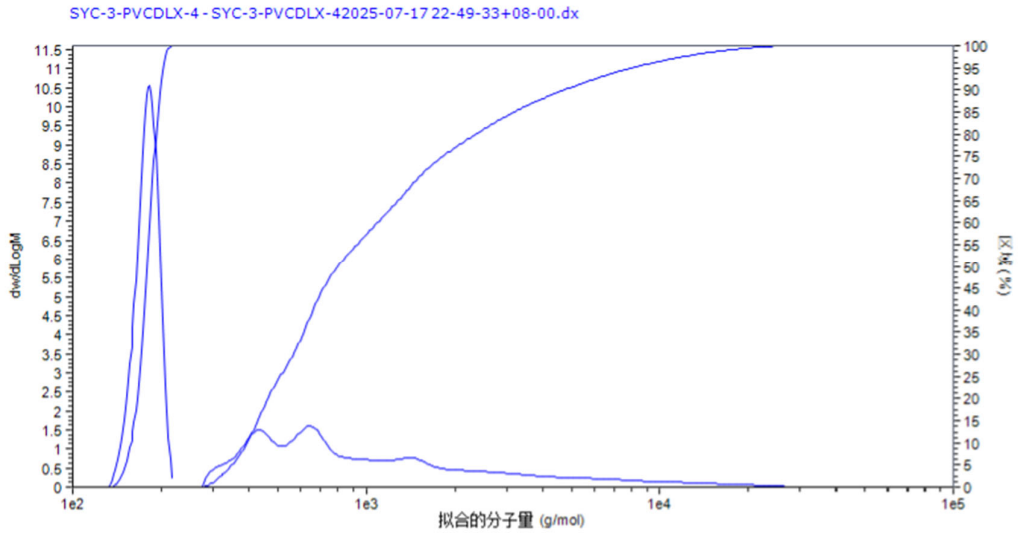


Table S13. GPC Analysis of degraded polyvinyl chloride after 9 h

Peak	Time (min)	M _p (Da)	M _n (Da)	M _w (Da)	M _z (Da)	M _{z+1} (Da)	Đ
1	17.617	639	764	1978	6978	13315	2.589005
2	19.153	182	178	179	181	182	1.005618



4.2 IR spectra of degraded polyvinyl chloride

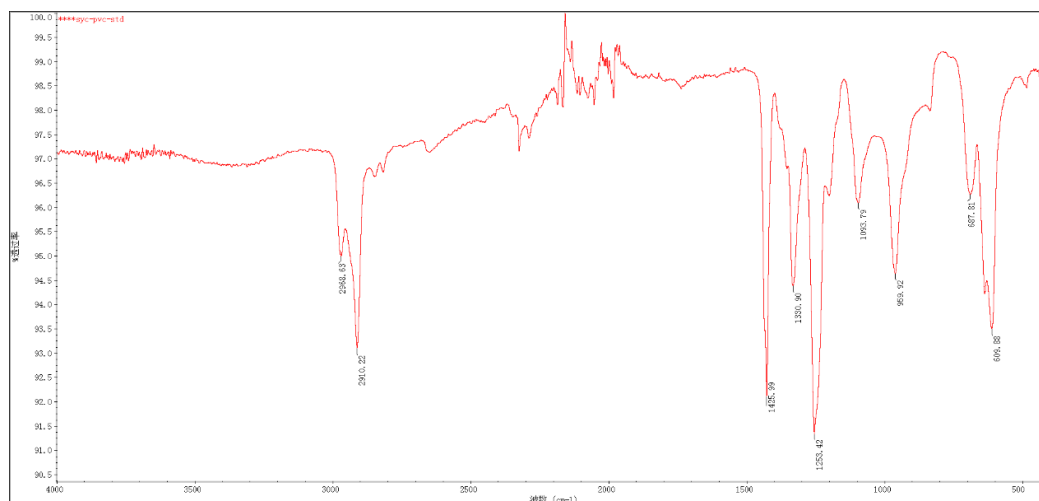


Figure S1. IR spectra of polyvinyl chloride

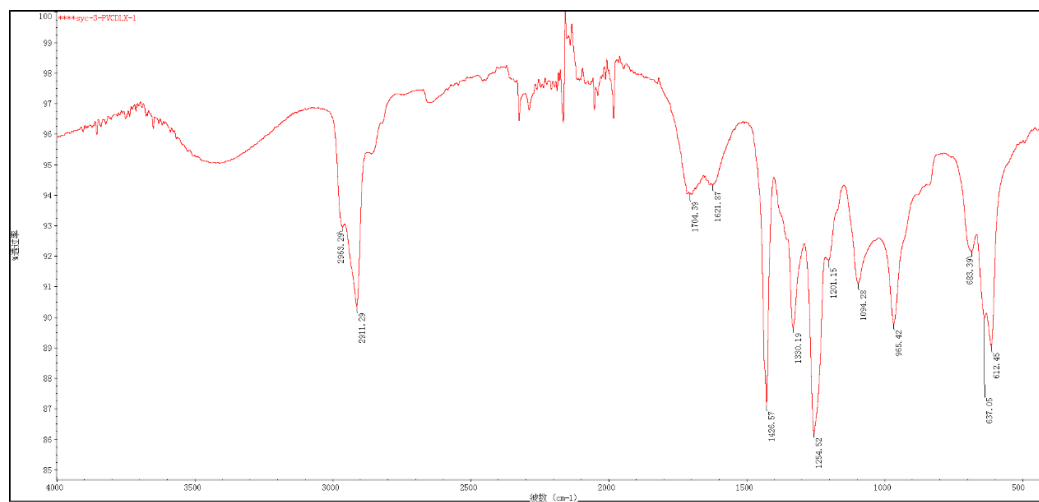


Figure S2. IR spectra of degraded polyvinyl chloride at 6 h

4.3 ^1H NMR spectra of degraded polyvinyl chloride

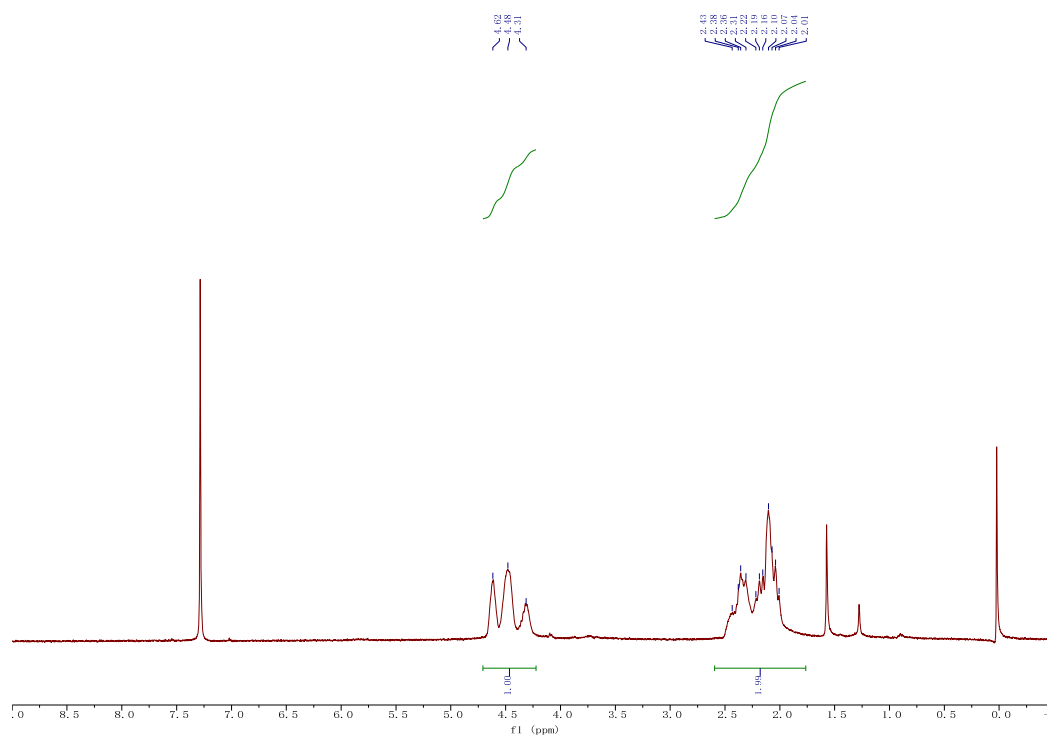


Figure S3. ^1H NMR spectrum of polyvinyl chloride

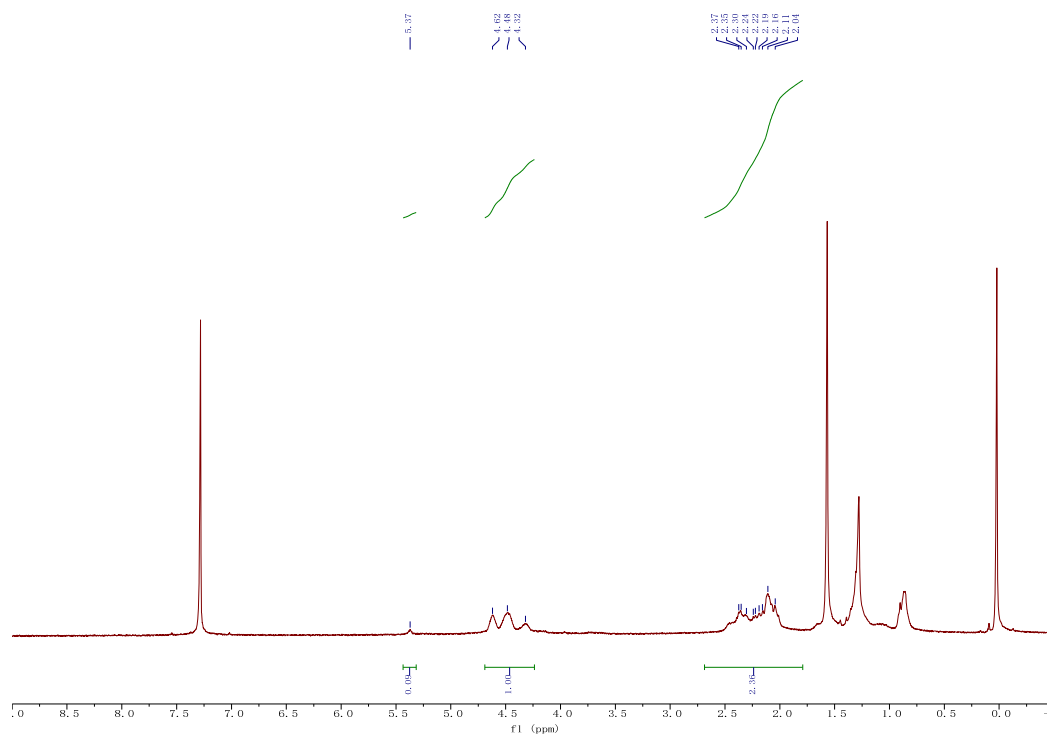


Figure S4. ^1H NMR spectrum of degraded polyvinyl chloride at 6 h

To a 25 mL Schlenk tube equipped with a rubber septum cap and Tefloncoated magnetic stir bar were charged with Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer) and 1-Butylpyridinium chloride (257.5 mg, 1.5 mmol, 3.0 equiv.). The tube was evacuated and backfilled with N₂ for 3 times. Subsequently, Aluminum (III) chloride (400.0 mg, 1.5 mmol, 3.0 equiv.) was added to the suspension and the vial was quickly resealed with the septum cap. Then a solution of **1a** (98.1 mg, 0.5 mmol, 1.0 equiv.) and azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in 1 mL of 1,2-dichloroethane were added respectively with syringe under N₂. The mixture was then stirred at 70 °C for 0, 1, 2, 3, 6, 9 and 12 hours. After cooling to room temperature, the resulting mixture quenched by a saturated solution of potassium sodium tartrate in 2.5 mol/L aqueous sodium hydroxide (5 mL) and extracted with tetrahydrofuran (5 mL). The organic layer was directly used for GPC tests. The organic layer of the 6 h group was dropped into MeOH and got the desired degraded PVC at 6 h for ¹H NMR and IR tests.

The ¹H NMR spectrum of the oxidatively degraded polystyrene was compared with that of a standard PVC sample. Signals corresponding to protons of C=C double bonds were observed in the ¹H NMR spectrum. Additionally, the increased integral ratio of the signal related to hydrogen atoms in -CH₂- and -CHCl- groups indicates that chlorine atoms in PVC were replaced by hydrogen atoms during degradation.

4.4 ^{27}Al NMR spectra of the ionic liquid-based PVC degradation system

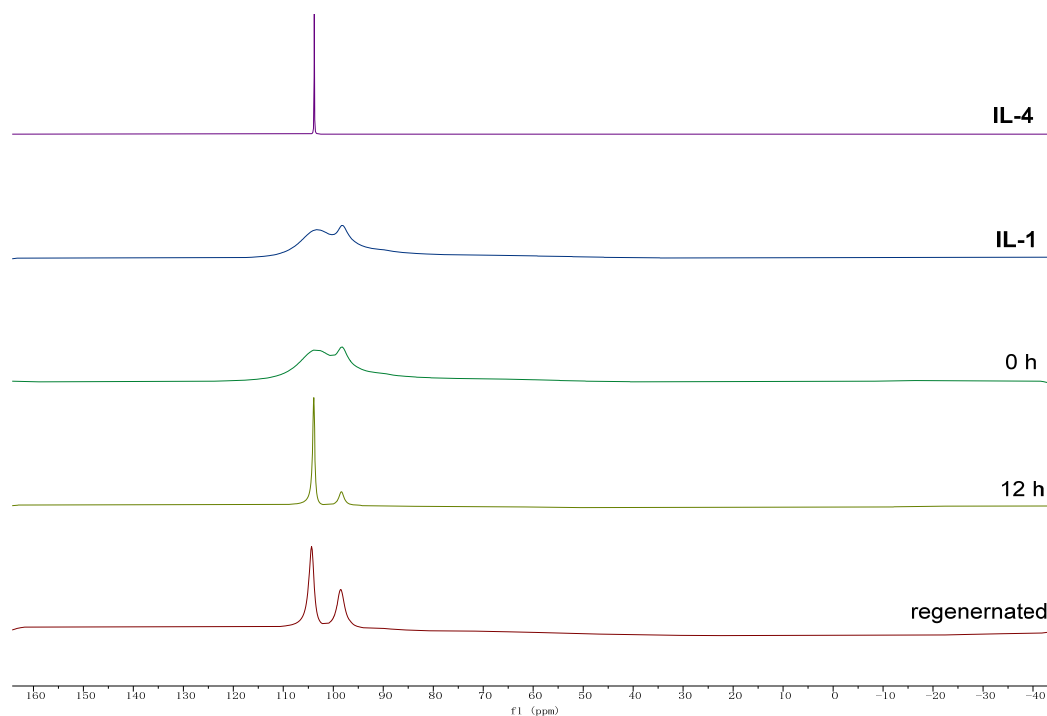
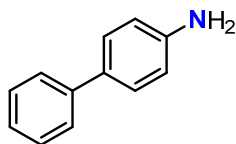


Figure S5. ^{27}Al NMR spectra of ionic liquid and ionic liquid-based PVC degradation system

Following General Procedure, the solution was directly diluted with CDCl_3 without quenching for ^{27}Al NMR tests.

5. Experimental Procedure and Characterization Data of Products



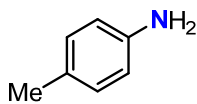
2a

[1,1'-biphenyl]-4-amine (2a): Following the general procedure, the reaction was performed with 4-isopropyl-1,1'-biphenyl **1a** (98.1 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **2a** as a yellow solid (49.7 mg, 59%; 91% after deduction of recovered raw material, recovery of starting material 34.4 mg). Spectral data was found in agreement with the literature¹.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, J = 7.4 Hz, 2H), 7.53 – 7.42 (m, 4H), 7.34 (t, J = 7.4 Hz, 1H), 6.81 (d, J = 8.3 Hz, 2H), 3.75 (s, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 145.92, 141.22, 131.60, 128.73, 128.06, 126.46, 126.32, 115.45.

HRMS (ESI) m/z calcd. for C₁₂H₁₂N⁺ (M)⁺: 170.0964, found: 170.0963

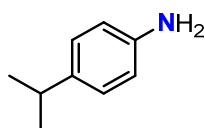


2b

***p*-toluidine (2b):** Following the general procedure, the reaction was performed with *p*-cymene **1b** (67.1 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **2b** as a yellow solid (30.6 mg, 57%). Spectral data was found in agreement with the literature¹.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.00 (d, J = 7.7 Hz, 2H), 6.65 (d, J = 7.3 Hz, 2H), 3.56 (s, 2H), 2.28 (d, J = 3.8 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 143.83, 129.78, 127.82, 115.29, 20.47.

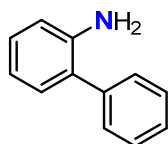


2c

4-isopropylaniline (2c): Following the general procedure, the reaction was performed with 1,4-diisopropylbenzene **1c** (81.1 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **2c** as a yellow solid (35.6 mg, 57%). Spectral data was found in agreement with the literature¹.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.08 (d, J = 8.3 Hz, 2H), 6.69 (d, J = 8.4 Hz, 2H), 3.56 (s, 2H), 2.92 – 2.81 (m, 1H), 1.27 (d, J = 6.9, 6H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 144.21, 139.18, 127.19, 115.26, 33.28, 24.31.

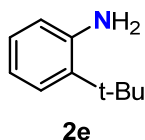


2d

[1,1'-biphenyl]-2-amine (2d): Following the general procedure, the reaction was performed with 2-isopropyl-1,1'-biphenyl **1d** (98.1 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **2d** as a yellow solid (47.0 mg, 56%; 87% after deduction of recovered raw material, recovery of starting material 35.5 mg). Spectral data was found in agreement with the literature².

¹H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.54 (m, 4H), 7.47 (td, J = 6.9, 1.9 Hz, 1H), 7.31 – 7.27 (m, J = 7.6, 1.9 Hz, 2H), 6.97 (t, J = 7.5 Hz, 1H), 6.87 (d, J = 7.9 Hz, 1H), 3.80 (s, 2H).

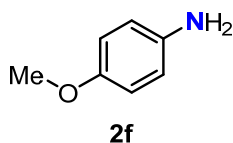
¹³C NMR (101 MHz, Chloroform-*d*) δ 143.69, 139.72, 130.61, 129.25, 128.97, 128.66, 127.74, 127.31, 118.77, 115.76.



2-(*tert*-butyl)aniline (2e): Following the general procedure, the reaction was performed with 1-(*tert*-butyl)-2-isopropylbenzene **1e** (88.2 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **2e** as a yellow oil (33.2 mg, 40%). Spectral data was found in agreement with the literature³.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.33 (d, J = 7.7 Hz, 1H), 7.21 – 7.05 (m, 1H), 6.91 – 6.79 (m, 1H), 6.72 (d, J = 7.8 Hz, 1H), 3.87 (s, 2H), 1.51 (s, 9H).

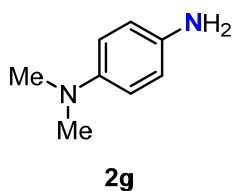
¹³C NMR (101 MHz, Chloroform-*d*) δ 144.69, 133.78, 127.05, 126.61, 118.72, 117.86, 34.34, 29.68.



4-methoxyaniline (2f): Following the general procedure, the reaction was performed with 1-isopropyl-4-methoxybenzene **1f** (75.1 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **2f** as a yellow solid (34.7 mg, 56%). Spectral data was found in agreement with the literature¹.

¹H NMR (400 MHz, Chloroform-*d*) δ 6.78 (d, J = 8.8 Hz, 2H), 6.67 (d, J = 8.9 Hz, 2H), 3.77 (s, 3H), 3.46 (s, 2H).

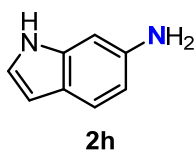
¹³C NMR (101 MHz, Chloroform-*d*) δ 152.79, 139.99, 116.45, 114.81, 55.75.



***N,N*-dimethylbenzene-1,4-diamine (2g):** Following the general procedure, the reaction was performed with 4-isopropyl-*N,N*-dimethylaniline **1g** (81.6 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **2g** as a yellow solid (36.7 mg, 54%). Spectral data was found in agreement with the literature⁴.

¹H NMR (400 MHz, Chloroform-*d*) δ 6.83 – 6.59 (m, 4H), 3.38 (s, 2H), 2.86 (s, 6H).

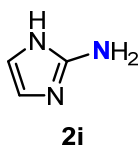
¹³C NMR (101 MHz, Chloroform-*d*) δ 144.88, 137.95, 116.61, 115.60, 42.14.



1*H*-indol-6-amine (2h): Following the general procedure, the reaction was performed with 6-isopropyl-1*H*-indole **1h** (79.6 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **2h** as a yellow solid (27.1 mg, 41%). Spectral data was found in agreement with the literature².

¹H NMR (400 MHz, Chloroform-*d*) δ 8.11 – 7.93 (br-s, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 7.15 (t, *J* = 2.9 Hz, 1H), 6.98 (d, *J* = 2.2 Hz, 1H), 6.70 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.40 (t, *J* = 2.6 Hz, 1H), 3.32 – 3.04 (br-s, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 139.51, 130.70, 128.80, 124.72, 112.99, 111.52, 105.59, 101.59.



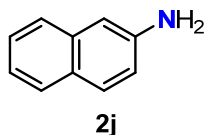
1*H*-imidazol-2-amine (2i): Following the general procedure, the reaction was performed with 2-isopropyl-1*H*-imidazole **1i** (55.1 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-

dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **2i** as a yellow oil (16.6 mg, 40%).

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.30 – 5.24 (m, 5H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 150.33, 117.54, 48.98.

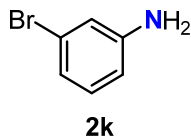
HRMS (ESI) *m/z* calcd. for C₃H₆N₃⁺ (M)⁺: 84.0556, found: 84.0554



naphthalen-2-amine (2j): Following the general procedure, the reaction was performed with 2-isopropyl-naphthalene **1j** (85.1 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **2j** as a yellow solid (49.3 mg, 69%). Spectral data was found in agreement with the literature⁵.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.71 (dd, *J* = 13.8, 8.6 Hz, 2H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.40 (t, *J* = 6.5 Hz, 1H), 7.27 (d, *J* = 9.1 Hz, 1H), 7.11 – 6.89 (m, 2H), 3.86 (s, 2H).

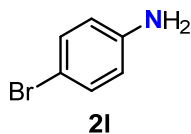
¹³C NMR (101 MHz, Chloroform-*d*) δ 144.12, 134.93, 129.23, 127.99, 127.73, 126.36, 125.81, 122.49, 118.25, 108.61.



3-bromoaniline (2k): Following the general procedure, the reaction was performed with 1-bromo-3-isopropylbenzene **1k** (99.5 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **2k** as a yellow solid (50.1 mg, 58%; 78% after deduction of recovered raw material, recovery of starting material 25.2 mg). Spectral data was found in agreement with the literature⁶.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.12 – 6.97 (m, 1H), 6.97 – 6.88 (m, 1H), 6.85 (t, J = 2.1 Hz, 1H), 6.62 – 6.59 (m, 1H), 3.69 (s, 2H).

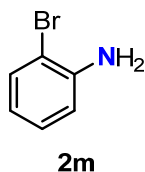
¹³C NMR (101 MHz, Chloroform-*d*) δ 148.63, 134.73, 122.44, 121.32, 117.85, 113.80.



4-bromoaniline (2l): Following the general procedure, the reaction was performed with 1-bromo-4-isopropylbenzene **1l** (99.5 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **2l** as a yellow solid (45.4 mg, 53 %; 75% after deduction of recovered raw material, recovery of starting material 29.5 mg). Spectral data was found in agreement with the literature¹.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.26 (d, J = 8.7 Hz, 2H), 6.59 (d, J = 8.7 Hz, 2H), 3.69 (s, 2H).

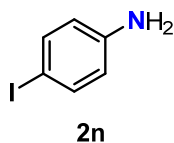
¹³C NMR (101 MHz, Chloroform-*d*) δ 145.42, 132.03, 116.72, 110.22.



2-bromoaniline (2m): Following the general procedure, the reaction was performed with 1-bromo-2-isopropylbenzene **1m** (99.5 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **2m** as a yellow solid (44.2 mg, 51%; 71% after deduction of recovered raw material, recovery of starting material 27.2 mg). Spectral data was found in agreement with the literature¹.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.43 (dd, J = 8.0, 1.4 Hz, 1H), 7.13 (td, J = 7.6, 1.4 Hz, 1H), 6.79 (dd, J = 8.0, 1.5 Hz, 1H), 6.65 (td, J = 7.6, 1.5 Hz, 1H), 4.10 (s, 2H).

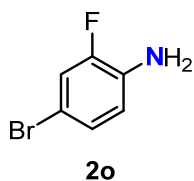
^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.08, 132.60, 128.36, 119.43, 115.77, 109.35.



4-iodoaniline (2n): Following the general procedure, the reaction was performed with 1-iodo-4-isopropylbenzene **1n** (123.0 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **2n** as a yellow solid (62.6 mg, 57%; 80% after deduction of recovered raw material, recovery of starting material 35.2 mg). Spectral data was found in agreement with the literature¹.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, J = 8.6 Hz, 2H), 6.49 (d, J = 8.6 Hz, 2H), 3.66 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.10, 137.93, 117.34, 79.42.

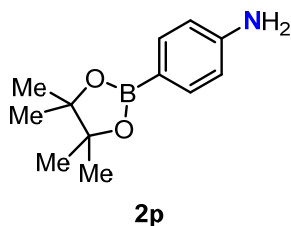


4-bromo-2-fluoroaniline (2o): Following the general procedure, the reaction was performed with 4-bromo-2-fluoro-1-isopropylbenzene **1o** (108.5 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **2o** as a yellow solid (36.1 mg, 38%; 89% after deduction of recovered raw material, recovery of starting material 62.4 mg). Spectral data was found in agreement with the literature⁷.

^1H NMR (400 MHz, Chloroform-*d*) δ 6.92 (dd, J = 8.0, 2.3 Hz, 1H), 6.87 (dd, J = 10.7, 8.6 Hz, 1H), 6.80 (ddd, J = 8.6, 4.3, 2.3 Hz, 1H), 3.92 – 3.71 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.66 (d, J = 240.1 Hz), 136.02 (d, J = 14.0 Hz), 121.05 (d, J = 7.0 Hz), 119.31 (d, J = 3.7 Hz), 116.74 (d, J = 3.3 Hz), 116.59 (d, J = 20.3 Hz).

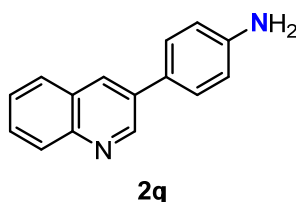
¹⁹F NMR (376 MHz, Chloroform-*d*) δ -137.51.



4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (2p): Following the general procedure, the reaction was performed with 2-(4-isopropylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **1p** (123.1 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **2p** as a yellow solid (82.4 mg, 75%). Spectral data was found in agreement with the literature².

¹H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.4 Hz, 2H), 6.68 (d, *J* = 8.4 Hz, 2H), 3.85 (s, 2H), 1.34 (d, *J* = 1.3 Hz, 12H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 149.30, 136.43, 114.09, 114.09, 83.31, 24.86.

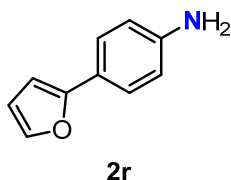


4-(quinolin-3-yl)aniline (2q): Following the general procedure, the reaction was performed with 3-(4-isopropylphenyl)quinoline **1q** (123.7 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **2q** as a yellow solid (31.8 mg, 29%; 89% after deduction of recovered raw material, recovery of starting material 83.5 mg). Spectral data was found in agreement with the literature⁸.

¹H NMR (400 MHz, Chloroform-*d*) δ 9.18 (s, 1H), 8.25 (d, *J* = 2.3 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.87 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.73 – 7.68 (m, 1H), 7.63 – 7.54 (m, 3H), 6.89 – 6.82

(m, 2H), 4.13 – 3.65 (br-s, 2H).

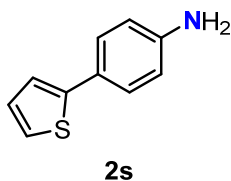
¹³C NMR (101 MHz, Chloroform-*d*) δ 149.88, 146.86, 146.70, 133.83, 131.69, 129.17, 128.79, 128.36, 128.26, 127.87, 127.82, 126.84, 115.62.



4-(furan-2-yl)aniline (2r): Following the general procedure, the reaction was performed with 2-(4-isopropylphenyl)furan **1r** (93.1 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **2r** as a yellow solid (37.4 mg, 47%). Spectral data was found in agreement with the literature⁹.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.49 (m, 2H), 7.45 – 7.42 (m, 1H), 6.76 – 6.69 (m, 2H), 6.52 – 6.44 (m, 2H), 3.73 (s, 2H).

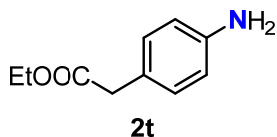
¹³C NMR (101 MHz, Chloroform-*d*) δ 154.63, 145.87, 140.91, 125.24, 122.02, 115.17, 111.47, 102.42.



4-(thiophen-2-yl)aniline (2s): Following the general procedure, the reaction was performed with 2-(4-isopropylphenyl)thiophene **1s** (101.2 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **2s** as a yellow solid (48.3 mg, 55%). Spectral data was found in agreement with the literature¹⁰.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, J = 8.1 Hz, 2H), 7.19 (t, J = 4.5 Hz, 2H), 7.06 (dd, J = 5.1, 3.6 Hz, 1H), 6.72 (d, J = 8.2 Hz, 2H), 4.22 – 3.44 (br-s, 2H).

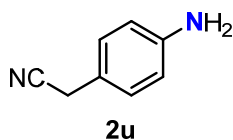
¹³C NMR (101 MHz, Chloroform-*d*) δ 146.05, 145.06, 127.88, 127.19, 125.18, 123.12, 121.31, 115.34.



ethyl 2-(4-aminophenyl)acetate (2t): Following the general procedure, the reaction was performed with ethyl 2-(4-isopropylphenyl)acetate **1t** (103.1 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **2t** as a yellow solid (44.6 mg, 50%; 89% after deduction of recovered raw material, recovery of starting material 45.5 mg). Spectral data was found in agreement with the literature⁷.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.09 (d, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 8.4 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.77 – 3.29 (m, 4H), 1.27 (t, *J* = 7.1 Hz, 3H).

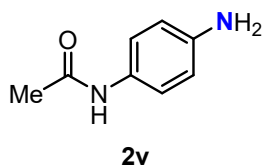
¹³C NMR (101 MHz, Chloroform-*d*) δ 172.22, 145.35, 130.10, 124.08, 115.26, 60.69, 40.60, 14.21.



2-(4-aminophenyl)acetonitrile (2u): Following the general procedure, the reaction was performed with 2-(4-isopropylphenyl)acetonitrile **1u** (79.6 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **2u** as a yellow solid (26.2 mg, 40%; 70% after deduction of recovered raw material, recovery of starting material 34.8 mg). Spectral data was found in agreement with the literature¹¹.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.11 (d, *J* = 8.1 Hz, 2H), 6.69 (d, *J* = 8.5 Hz, 2H), 3.74 (s, 2H), 3.65 (s, 2H).

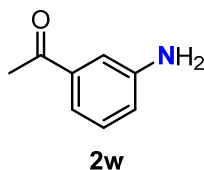
¹³C NMR (101 MHz, Chloroform-*d*) δ 146.24, 128.95, 119.35, 118.52, 115.47, 22.83.



***N*-(4-aminophenyl)acetamide (2v):** Following the general procedure, the reaction was performed with *N*-(4-isopropylphenyl)acetamide **1v** (88.6 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **2v** as a yellow solid (18.3 mg, 24%). Spectral data was found in agreement with the literature¹.

¹H NMR (400 MHz, DMSO-*d*₆) δ 9.47 (s, 1H), 7.18 (d, *J* = 8.2 Hz, 2H), 6.48 (d, *J* = 8.4 Hz, 2H), 4.82 (s, 2H), 1.95 (s, 3H).

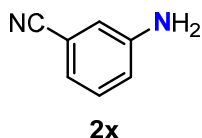
¹³C NMR (101 MHz, DMSO-*d*₆) δ 172.42, 149.80, 133.82, 126.06, 119.02, 28.90.



1-(3-aminophenyl)ethan-1-one (2w): Following the general procedure, the reaction was performed with 1-(3-isopropylphenyl)ethan-1-one **1w** (81.1 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **2w** as a yellow solid (25.7 mg, 38%; 96% after deduction of recovered raw material, recovery of starting material 48.9 mg). Spectral data was found in agreement with the literature⁴.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 7.7 Hz, 1H), 7.30 – 7.23 (m, 2H), 6.89 (dd, *J* = 7.9, 2.9 Hz, 1H), 4.14 – 3.39 (br-s, 2H), 2.58 (s, 3H).

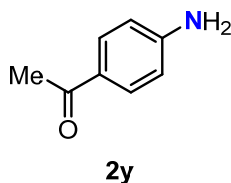
¹³C NMR (101 MHz, Chloroform-*d*) δ 198.45, 146.69, 138.26, 129.46, 119.67, 118.92, 114.03, 26.72.



3-aminobenzonitrile (2x): Following the general procedure, the reaction was performed with 3-isopropylbenzonitrile **1x** (72.6 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **2x** as a yellow solid (21.4 mg, 36%; 94% after deduction of recovered raw material, recovery of starting material 44.6 mg). Spectral data was found in agreement with the literature⁶.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.24 (t, J = 7.9 Hz, 1H), 7.04 (d, J = 7.6 Hz, 1H), 6.92 (s, 1H), 6.89 (d, J = 8.6 Hz, 1H), 3.90 (s, 2H).

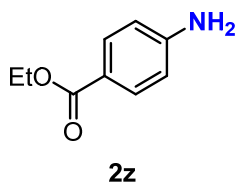
¹³C NMR (101 MHz, Chloroform-*d*) δ 146.92, 130.07, 122.03, 119.19, 119.16, 117.46, 112.98.



1-(4-aminophenyl)ethan-1-one (2y): Following the general procedure, the reaction was performed with 1-(4-isopropylphenyl)ethan-1-one **1y** (81.1 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **2y** as a yellow solid (16.2 mg, 24%; 91% after deduction of recovered raw material, recovery of starting material 59.7 mg). Spectral data was found in agreement with the literature⁴.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, J = 8.5 Hz, 2H), 6.67 (d, J = 8.4 Hz, 2H), 4.15 (s, 2H), 2.53 (s, 3H).

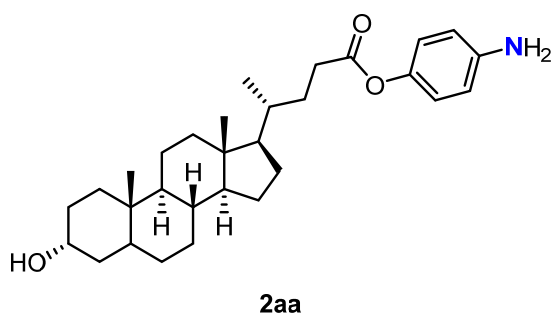
¹³C NMR (101 MHz, Chloroform-*d*) δ 196.46, 151.08, 130.81, 127.95, 113.74, 26.10.



benzocaine (2z): Following the general procedure, the reaction was performed with ethyl 4-isopropylbenzoate **1z** (96.1 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **2z** as a yellow solid (28.3 mg, 34%; 76% after deduction of recovered raw material, recovery of starting material 52.6 mg). Spectral data was found in agreement with the literature⁷.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.6 Hz, 2H), 6.66 (d, *J* = 8.7 Hz, 2H), 4.34 (q, *J* = 7.2 Hz, 2H), 4.10 (s, 2H), 1.38 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 166.73, 150.76, 131.56, 120.11, 113.79, 60.32, 14.44.



4-aminophenyl (4R)-4-((3R,8R,9S,10S,13R,14S,17R)-3-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate (2aa):

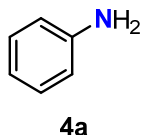
Following the general procedure, the reaction was performed with 4-isopropylphenyl (4R)-4-((3R,8R,9S,10S,13R,14S,17R)-3-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate **1aa** (247.4 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **2aa** as a yellow solid (83.3 mg, 36%).

¹H NMR (400 MHz, Chloroform-*d*) δ 6.87 (d, *J* = 8.4 Hz, 2H), 6.68 (d, *J* = 8.4 Hz, 2H), 3.82

– 3.45 (m, 3H), 2.62 – 2.55 (m, 2H), 2.49 – 2.41 (m, 2H), 2.04 – 0.84 (m, 28H), 0.68 (s, 6H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 173.35, 144.07, 142.98, 122.16, 115.64, 71.88, 56.52, 56.00, 42.79, 42.11, 40.45, 40.20, 36.47, 35.87, 35.41, 35.37, 34.59, 31.37, 31.04, 30.57, 28.25, 27.21, 26.43, 24.23, 23.39, 20.85, 18.34, 12.08.

HRMS (ESI) m/z calcd. for $C_{30}H_{46}NO_3^+$ (M+H)⁺: 468.3458, found: 468.3472



aniline (4a): Following the general procedure, the reaction was performed with cumene **3a** (60.1 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **4a** as a yellow oil (25.8 mg, 55%).

Following the general procedure, the reaction was performed with ethylbenzene **3b** (53.1 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **4a** as a yellow oil (20.9 mg, 45%).

Following the general procedure, the reaction was performed with cyclohexylbenzene **3c** (80.1 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **4a** as a yellow oil (23.2 mg, 50%).

Following the general procedure, the reaction was performed with butylbenzene **3d** (67.1 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **4a** as a yellow oil (23.8 mg, 51%).

Following the general procedure, the reaction was performed with *tert*-pentylbenzene **3e** (74.1

mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **4a** as a yellow oil (5.1 mg, 11%).

Following the general procedure, the reaction was performed with diphenylmethane **3f** (84.1 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **4a** as a yellow oil (27.7 mg, 60%).

Following the general procedure, the reaction was performed with 4-phenylcyclohexan-1-one **3g** (87.1 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **4a** as a yellow oil (21.4 mg, 46%; 80% after deduction of recovered raw material, recovery of starting material 36.9 mg).

Following the general procedure, the reaction was performed with 3-phenylcyclobutan-1-one **3h** (73.1 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **4a** as a yellow oil (18.2 mg, 39%).

Following the general procedure, the reaction was performed with (4-bromobutyl)benzene **3i** (106.6 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **4a** as a yellow oil (30.8 mg, 66%).

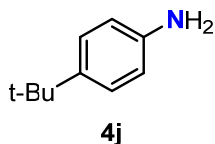
Following the general procedure, the reaction was performed with 3-phenylbutanoic acid **3k** (82.1 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **4a** as a yellow oil (24.3 mg, 52%). Spectral data was found in

agreement with the literature².

¹H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.17 (m, 2H), 6.82 (tt, J = 7.4, 1.1 Hz, 1H), 6.78 – 6.70 (m, 2H), 3.68 (s, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 146.46, 129.35, 118.58, 115.15.

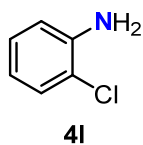
HRMS (ESI) m/z calcd. for C₆H₇N⁺ (M)⁺: 97.0573, found: 97.0573



4-(*tert*-butyl)aniline (4j): Following the general procedure, the reaction was performed with bis(4-(*tert*-butyl)phenyl)methane **3j** (140.2 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **4k** as a yellow solid (28.7 mg, 38%). Spectral data was found in agreement with the literature⁴.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.25 (d, J = 8.6 Hz, 2H), 6.70 (d, J = 8.6 Hz, 2H), 3.57 (s, 2H), 1.34 (s, 9H).

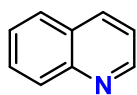
¹³C NMR (101 MHz, Chloroform-*d*) δ 143.86, 141.44, 126.11, 114.97, 33.96, 31.60.



2-chloroaniline (4l): Following the general procedure, the reaction was performed with amlodipine **3l** (204.4 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **4l** as a yellow solid (25.5 mg, 40%). Spectral data was found in agreement with the literature³.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.27 (dd, J = 8.0, 1.5 Hz, 1H), 7.09 (td, J = 7.7, 1.5 Hz, 1H), 6.79 (td, J = 8.0, 1.4 Hz, 1H), 6.72 (td, J = 7.6, 1.5 Hz, 1H), 4.04 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.93, 129.44, 127.65, 119.32, 119.05, 115.89.

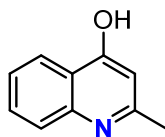


4m

quinoline (4m): Following the general procedure, the reaction was performed with 1*H*-indene **3m** (58.1 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **4m** as a yellow oil (38.3 mg, 59%). Spectral data was found in agreement with the literature¹².

^1H NMR (400 MHz, Chloroform-*d*) δ 8.90 (dd, J = 4.2, 1.7 Hz, 1H), 8.19 – 8.06 (m, 2H), 7.77 (dd, J = 8.2, 1.5 Hz, 1H), 7.79 – 7.76 (m, 1H), 7.71 – 7.67 (m, 1H), 7.35 (dd, J = 8.3, 4.2 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.41, 148.27, 136.05, 129.46, 129.44, 128.27, 127.80, 126.54, 121.07.

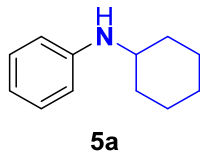


4n

2-methylquinolin-4-ol (4n): Following the general procedure, the reaction was performed with 3-methyl-2,3-dihydro-1*H*-inden-1-one **3n** (73.1 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), azidotrimethylsilane (115.2 mg, 1.0 mmol, 2.0 equiv.) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **4n** as a yellow solid (37.3 mg, 47%). Spectral data was found in agreement with the literature¹³.

^1H NMR (400 MHz, DMSO-*d*₆) δ 11.55 (s, 1H), 8.04 (d, J = 8.2 Hz, 1H), 7.61 (t, J = 7.8 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.27 (t, J = 7.7 Hz, 1H), 5.91 (s, 1H), 2.34 (s, 3H).

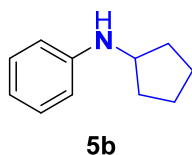
^{13}C NMR (101 MHz, DMSO-*d*₆) δ 177.19, 150.08, 140.57, 131.90, 125.26, 124.97, 123.15, 118.19, 108.86, 19.92.



N-cyclohexylaniline (5a): Following the general procedure, the reaction was performed with cumene **3a** (60.1 mg, 0.5 mmol, 1.0 equiv.), azidocyclohexane (125.2 mg, 1.0 mmol, 2.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **5a** as a yellow oil (40.4 mg, 46%). Spectral data was found in agreement with the literature¹⁴.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.19 (t, J = 7.4 Hz, 2H), 6.72 – 6.65 (m, 1H), 6.62 (d, J = 8.0 Hz, 2H), 3.54 (s, 1H), 3.29 (tt, J = 10.0, 3.8 Hz, 1H), 2.12 – 2.07 (m, 2H), 1.86 – 1.74 (m, 2H), 1.71 – 1.66 (m, 1H), 1.48 – 1.34 (m, 2H), 1.32 – 1.12 (m, 3H).

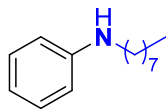
¹³C NMR (101 MHz, Chloroform-*d*) δ 147.43, 129.28, 116.83, 113.15, 51.70, 33.52, 25.97, 25.05.



N-cyclopentylaniline (5b): Following the general procedure, the reaction was performed with cumene **3a** (60.1 mg, 0.5 mmol, 1.0 equiv.), azidocyclopentane (111.1 mg, 1.0 mmol, 2.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **5b** as a yellow oil (41.1 mg, 51%). Spectral data was found in agreement with the literature¹⁵.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.23 (t, J = 7.7 Hz, 2H), 6.75 (t, J = 7.3 Hz, 1H), 6.67 (d, J = 7.9 Hz, 2H), 3.85 (p, J = 6.1 Hz, 1H), 3.68 (s, 1H), 2.13 – 2.04 (m, 2H), 1.90 – 1.75 (m, 2H), 1.73 – 1.65 (m, 2H), 1.60 – 1.46 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 148.10, 129.24, 116.93, 113.20, 54.68, 33.65, 24.14.

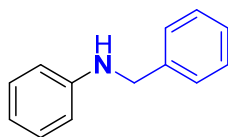


5c

N-octylaniline (5c): Following the general procedure, the reaction was performed with cumene **3a** (60.1 mg, 0.5 mmol, 1.0 equiv.), 1-azidooctane (155.2 mg, 1.0 mmol, 2.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **5c** as a yellow oil (62.5 mg, 57%). Spectral data was found in agreement with the literature¹⁶.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.25 (t, J = 7.7 Hz, 2H), 6.76 (t, J = 7.3 Hz, 1H), 6.68 (s, 2H), 3.63 (s, 1H), 3.17 (t, J = 7.1 Hz, 2H), 1.69 (p, J = 7.1 Hz, 2H), 1.54 – 1.30 (m, 10H), 0.98 (t, J = 6.7 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 148.62, 129.27, 117.11, 112.74, 44.06, 31.92, 29.66, 29.51, 29.36, 27.27, 22.75, 14.18.

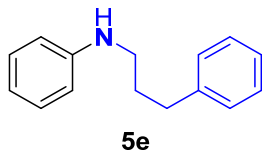


5d

N-benzylaniline (5d): Following the general procedure, the reaction was performed with cumene **3a** (60.1 mg, 0.5 mmol, 1.0 equiv.), (azidomethyl)benzene (133.2 mg, 1.0 mmol, 2.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **5d** as a yellow oil (41.3 mg, 45%). Spectral data was found in agreement with the literature¹⁴.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.34 (m, 4H), 7.34 – 7.29 (m, 1H), 7.24 – 7.18 (m, 2H), 6.75 (t, J = 7.3 Hz, 1H), 6.67 (d, J = 7.4 Hz, 2H), 4.37 (s, 2H), 4.06 (s, 1H).

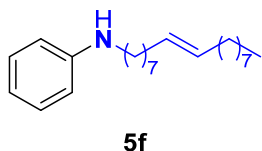
¹³C NMR (101 MHz, Chloroform-*d*) δ 148.17, 139.44, 129.29, 128.66, 127.54, 127.26, 117.58, 112.85, 48.33.



***N*-(3-phenylpropyl)aniline (5e):** Following the general procedure, the reaction was performed with cumene **3a** (60.1 mg, 0.5 mmol, 1.0 equiv.), (3-azidopropyl)benzene (161.2 mg, 1.0 mmol, 2.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **5e** as a yellow oil (52.6 mg, 50%). Spectral data was found in agreement with the literature¹⁷.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.37 (t, J = 7.6 Hz, 2H), 7.30 – 7.22 (m, 5H), 6.77 (t, J = 7.3 Hz, 1H), 6.65 (d, J = 7.9 Hz, 2H), 3.61 (s, 1H), 3.22 (t, J = 7.0 Hz, 2H), 2.81 (t, J = 7.6 Hz, 2H), 2.02 (p, J = 7.3 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 148.42, 141.75, 129.30, 128.51, 128.48, 126.03, 117.28, 112.82, 43.47, 33.47, 31.13.

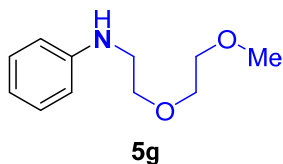


***(E)*-N-(heptadec-8-en-1-yl)aniline (5f):** Following the general procedure, the reaction was performed with cumene **3a** (60.1 mg, 0.5 mmol, 1.0 equiv.), (*E*)-1-azidoheptadec-8-ene (279.5 mg, 1.0 mmol, 2.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **5f** as a yellow oil (68.6 mg, 42%).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.21 (t, J = 7.8 Hz, 2H), 6.73 (t, J = 7.3 Hz, 1H), 6.64 (d, J = 7.9 Hz, 2H), 5.50 – 5.37 (m, 2H), 3.61 (s, 1H), 3.14 (t, J = 7.1 Hz, 2H), 2.02 (q, J = 5.1 Hz, 4H), 1.65 (p, J = 7.2 Hz, 2H), 1.49 – 1.24 (m, 20H), 0.93 (t, J = 6.7 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 148.55, 130.53, 130.24, 129.24, 117.09, 112.70, 44.01, 32.66, 32.61, 31.95, 29.70, 29.61, 29.61, 29.54, 29.37, 29.35, 29.23, 29.12, 27.19, 22.73, 14.17.

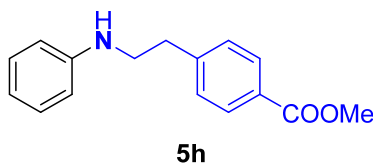
HRMS (ESI) m/z calcd. for $C_{23}H_{40}N^+$ ($M+H$) $^+$: 330.3155, found: 330.3143



***N*-(2-(2-methoxyethoxy)ethyl)aniline (5g):** Following the general procedure, the reaction was performed with cumene **3a** (60.1 mg, 0.5 mmol, 1.0 equiv.), 1-azido-2-(2-methoxyethoxy)ethane (145.2 mg, 1.0 mmol, 2.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **5g** as a yellow oil (53.4 mg, 51%). Spectral data was found in agreement with the literature¹⁴.

1H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.16 (m, 2H), 6.74 (tt, J = 7.3, 1.1 Hz, 1H), 6.70 – 6.62 (m, 2H), 4.61 – 3.81 (br-s, 2H), 3.74 (t, J = 5.3 Hz, 2H), 3.69 – 3.64 (m, 2H), 3.62 – 3.56 (m, 2H), 3.43 (s, 3H), 3.34 (t, J = 5.3 Hz, 2H).

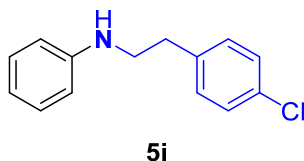
^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.27, 129.22, 117.53, 113.12, 71.93, 70.27, 69.71, 59.10, 43.49.



methyl 4-(2-(phenylamino)ethyl)benzoate (5h): Following the general procedure, the reaction was performed with cumene **3a** (60.1 mg, 0.5 mmol, 1.0 equiv.), methyl 4-(2-azidoethyl)benzoate (205.2 mg, 1.0 mmol, 2.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **5h** as a yellow oil (65.1 mg, 51%). Spectral data was found in agreement with the literature¹⁸.

1H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.22 (t, J = 7.7 Hz, 2H), 6.75 (t, J = 7.3 Hz, 1H), 6.64 (d, J = 8.0 Hz, 2H), 3.94 (s, 3H), 3.81 – 3.57 (br-s, 1H), 3.46 (t, J = 7.0 Hz, 2H), 3.00 (t, J = 6.9 Hz, 2H).

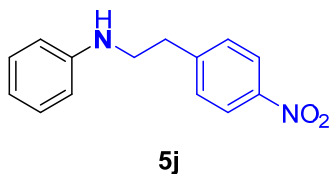
¹³C NMR (101 MHz, Chloroform-*d*) δ 167.03, 147.75, 144.86, 129.93, 129.36, 128.86, 128.46, 117.68, 113.01, 52.08, 44.70, 35.56.



***N*-(4-chlorophenethyl)aniline (5i):** Following the general procedure, the reaction was performed with cumene **3a** (60.1 mg, 0.5 mmol, 1.0 equiv.), 1-(2-azidoethyl)-4-chlorobenzene (181.6 mg, 1.0 mmol, 2.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **5i** as a yellow oil (77.3 mg, 67%). Spectral data was found in agreement with the literature¹⁹.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.89 (t, *J* = 7.3 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 2H), 3.64 (s, 1H), 3.48 (t, *J* = 7.0 Hz, 2H), 2.98 (t, *J* = 7.0 Hz, 2H).

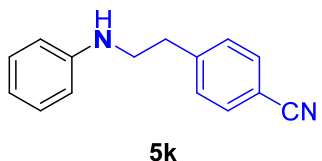
¹³C NMR (101 MHz, Chloroform-*d*) δ 147.99, 138.01, 132.31, 130.33, 129.51, 128.84, 117.74, 113.15, 45.01, 34.95.



***N*-(4-nitrophenethyl)aniline (5j):** Following the general procedure, the reaction was performed with cumene **3a** (60.1 mg, 0.5 mmol, 1.0 equiv.), 1-(2-azidoethyl)-4-nitrobenzene (192.2 mg, 1.0 mmol, 2.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **5j** as a yellow oil (64.2 mg, 53%). Spectral data was found in agreement with the literature²⁰.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.23 (t, *J* = 8.5 Hz, 2H), 6.78 (t, *J* = 7.2 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 2H), 3.70 (s, 1H), 3.50 (t, *J* = 7.0 Hz, 2H), 3.06 (t, *J* = 6.9 Hz, 2H).

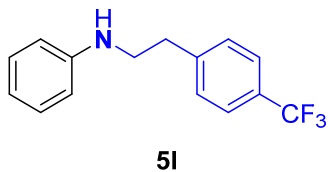
^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.45, 147.31, 146.78, 129.67, 129.44, 123.83, 117.91, 112.99, 44.55, 35.46.



4-(2-(phenylamino)ethyl)benzonitrile (5k): Following the general procedure, the reaction was performed with cumene **3a** (60.1 mg, 0.5 mmol, 1.0 equiv.), 4-(2-azidoethyl)benzonitrile (172.2 mg, 1.0 mmol, 2.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **5k** as a yellow oil (66.9 mg, 60%). Spectral data was found in agreement with the literature²⁰.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 7.27 – 7.16 (m, 2H), 6.76 (t, J = 7.3 Hz, 1H), 6.68 – 6.61 (m, 2H), 3.68 (s, 1H), 3.46 (t, J = 6.9 Hz, 2H), 3.00 (t, J = 6.9 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.51, 145.12, 132.39, 129.63, 129.42, 118.93, 117.86, 112.98, 110.39, 44.54, 35.69.

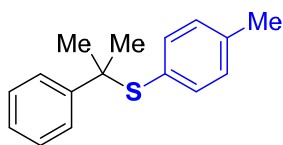


N-(4-(trifluoromethyl)phenethyl)aniline (5l): Following the general procedure, the reaction was performed with cumene **3a** (60.1 mg, 0.5 mmol, 1.0 equiv.), 1-(2-azidoethyl)-4-(trifluoromethyl)benzene (215.2 mg, 1.0 mmol, 2.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **5l** as a yellow solid (54.9 mg, 41%). Spectral data was found in agreement with the literature²⁰.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, J = 7.9 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.26 – 7.20 (m, 2H), 6.82 – 6.73 (m, 1H), 6.73 – 6.60 (m, 2H), 3.70 (s, 1H), 3.47 (t, J = 6.9 Hz, 2H), 3.02 (d, J = 6.9 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.68, 143.54, 129.39, 129.15, 128.84 (q, J = 32.6 Hz), 125.52 (q, J = 3.67 Hz), 124.28 (q, J = 272.8 Hz), 117.75, 113.00, 44.74, 35.37.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.36.

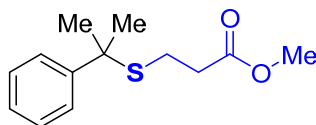


6a

(2-phenylpropan-2-yl)(*p*-tolyl)sulfane (6a): Following the general procedure, the reaction was performed with cumene **3a** (60.1 mg, 0.5 mmol, 1.0 equiv.), 4-methylbenzenethiol (124.2 mg, 1.0 mmol, 2.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **6a** as a yellow oil (48.6 mg, 40%). Spectral data was found in agreement with the literature²¹.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.52 (m, 2H), 7.42 – 7.35 (m, 2H), 7.34 – 7.27 (m, 1H), 7.21 – 7.15 (m, 2H), 7.09 (d, J = 7.9 Hz, 2H), 2.40 (s, 3H), 1.80 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.60, 138.71, 136.73, 129.47, 129.19, 127.99, 126.69, 126.59, 50.83, 29.77, 21.33.

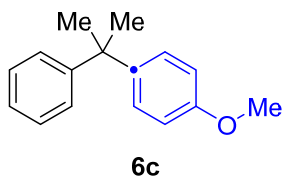


6b

methyl 3-((2-phenylpropan-2-yl)thio)propanoate (6b): Following the general procedure, the reaction was performed with cumene **3a** (60.1 mg, 0.5 mmol, 1.0 equiv.), methyl 3-mercaptopropanoate (120.2 mg, 1.0 mmol, 2.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **6b** as a yellow oil (49.3 mg, 41%). Spectral data was found in agreement with the literature²².

^1H NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, J = 7.3 Hz, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.23 (t, J = 7.1 Hz, 1H), 3.65 (s, 3H), 2.52 (t, J = 7.5 Hz, 2H), 2.34 (t, J = 7.5 Hz, 2H), 1.74 (s, 6H).

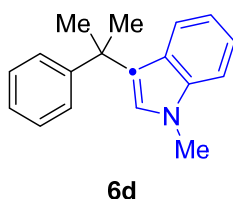
¹³C NMR (101 MHz, Chloroform-*d*) δ 172.42, 146.29, 128.15, 126.58, 126.48, 51.68, 47.84, 34.13, 30.16, 24.47.



1-methoxy-4-(2-phenylpropan-2-yl)benzene (6c): Following the general procedure, the reaction was performed with cumene **3a** (60.1 mg, 0.5 mmol, 1.0 equiv.), anisole (108.1 mg, 1.0 mmol, 2.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **6c** as a colorless oil (50.1 mg, 44%). Spectral data was found in agreement with the literature²³.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.45 (m, 4H), 7.41 – 7.37 (m, 3H), 7.04 (dd, *J* = 8.7, 2.1 Hz, 2H), 3.96 (s, 3H), 1.91 (s, 6H).

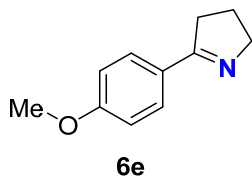
¹³C NMR (101 MHz, Chloroform-*d*) δ 157.69, 151.14, 143.06, 128.22, 128.01, 126.96, 125.79, 113.54, 55.30, 42.51, 31.16.



1-methyl-3-(2-phenylpropan-2-yl)-1H-indole (6d): Following the general procedure, the reaction was performed with cumene **3a** (60.1 mg, 0.5 mmol, 1.0 equiv.), 1-methyl-1H-indole (131.2 mg, 1.0 mmol, 2.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer) in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **6d** as a yellow oil (58.4 mg, 47%). Spectral data was found in agreement with the literature²⁴.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.50 (m, 2H), 7.44 – 7.37 (m, 3H), 7.33 – 7.27 (m, 2H), 7.24 – 7.20 (m, 1H), 7.10 – 7.07 (m, 1H), 7.05 – 7.00 (m, 1H), 3.87 (t, *J* = 1.3 Hz, 3H), 1.93 (t, *J* = 1.3 Hz, 6H).

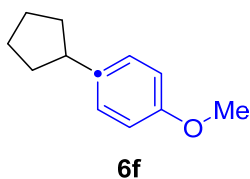
^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.20, 137.90, 128.12, 126.55, 126.52, 125.66, 125.64, 124.68, 121.51, 121.31, 118.46, 109.24, 39.03, 32.73, 30.93.



5-(4-methoxyphenyl)-3,4-dihydro-2H-pyrrole (6e): Following the general procedure, the reaction was performed with 1-(4-azidobutyl)-4-methoxybenzene (102.6 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer), in ionic liquid (3.0 equiv. calculated by corresponding cation) and 1,2-dichloroethane (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **6e** as a yellow oil (48.4 mg, 55%). Spectral data was found in agreement with the literature²⁵.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, J = 8.7 Hz, 2H), 6.94 (d, J = 8.9 Hz, 2H), 4.06 (tt, J = 7.4, 2.0 Hz, 2H), 3.86 (s, 3H), 2.94 (tt, J = 8.7, 1.9 Hz, 2H), 2.09 – 1.99 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.65, 161.32, 129.21, 127.48, 113.73, 61.32, 55.33, 34.87, 22.74.

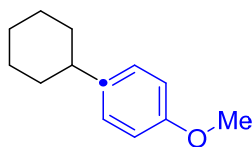


1-cyclopentyl-4-methoxybenzene (6f): Following the general procedure, the reaction was performed with anisole (54.1 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer) in ionic liquid (3.0 equiv. calculated by corresponding cation) and cyclopentane (0.5 mL) under nitrogen atmosphere at room temperature for 12 hours. The mixture was purified by column chromatography to obtain **6f** as a colorless oil (33.5 mg, 38%). Spectral data was found in agreement with the literature²⁶.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.17 (m, 2H), 6.94 – 6.83 (m, 2H), 3.83 (s, 3H), 2.99 (tt, J = 9.8, 7.4 Hz, 1H), 2.18 – 2.02 (m, 2H), 1.90 – 1.79 (m, 2H), 1.78 – 1.66 (m, 2H), 1.65 – 1.54 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.68, 138.58, 127.95, 113.67, 55.28, 45.19, 34.76,

25.45.

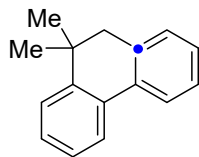


6g

1-cyclohexyl-4-methoxybenzene (6g): Following the general procedure, the reaction was performed with anisole (54.1 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer) in ionic liquid (3.0 equiv. calculated by corresponding cation) and cyclohexane (0.5 mL) under nitrogen atmosphere at room temperature for 12 hours. The mixture was purified by column chromatography to obtain **6g** as a white solid (28.4 mg, 30%). Spectral data was found in agreement with the literature²⁶.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.24 (d, J = 8.6 Hz, 2H), 6.95 (d, J = 8.6 Hz, 2H), 3.88 (s, 3H), 2.60 – 2.53 (m, 1H), 2.02 – 1.90 (m, 4H), 1.89 – 1.82 (m, 1H), 1.58 – 1.43 (m, 4H), 1.42 – 1.30 (m, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 157.78, 140.42, 127.70, 113.75, 55.25, 43.81, 34.85, 27.08, 26.30.



6h

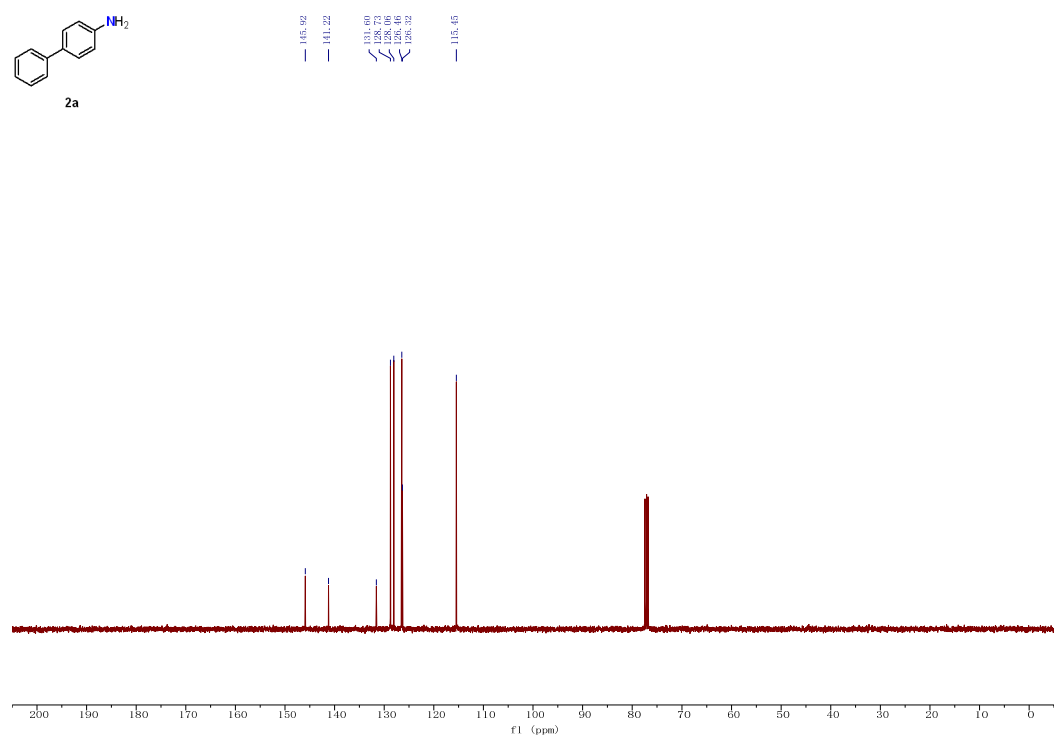
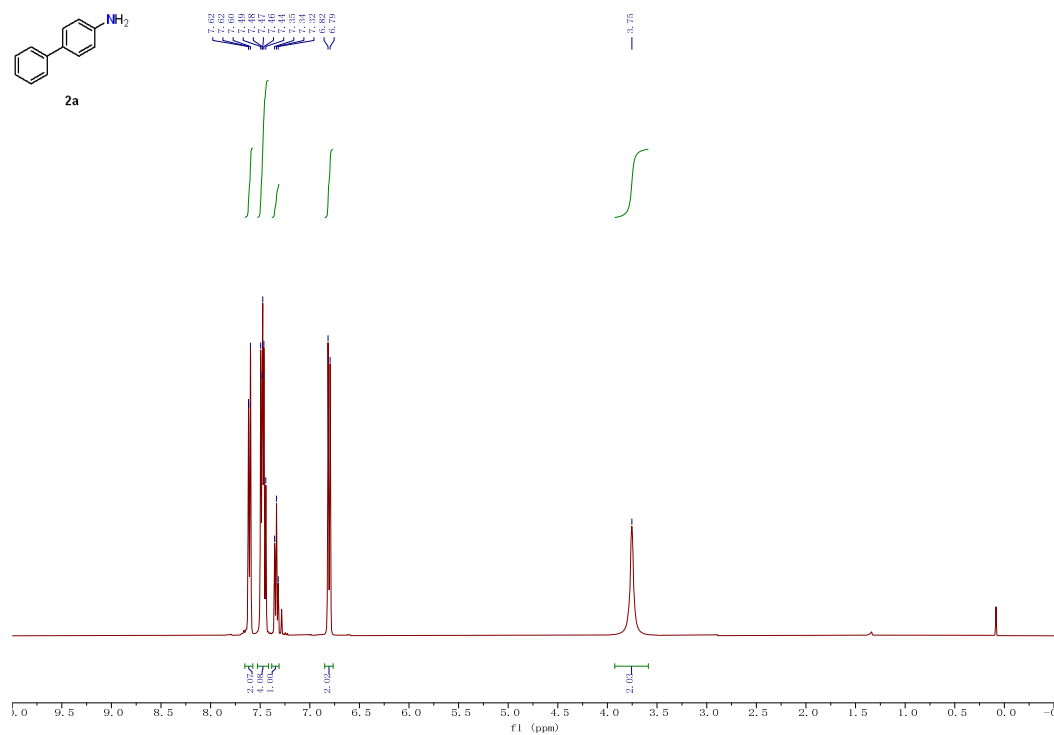
9,9-dimethyl-9,10-dihydrophenanthrene (6h): Following the general procedure, the reaction was performed with 2-(*tert*-butyl)-1,1'-biphenyl (105.2 mg, 0.5 mmol, 1.0 equiv.), Polyvinyl chloride (93.8 mg, 1.5 mmol, 3.0 equiv. calculated by corresponding monomer) in ionic liquid (3.0 equiv. calculated by corresponding cation) and DCE (1.0 mL) under nitrogen atmosphere at 70 °C for 12 hours. The mixture was purified by column chromatography to obtain **6h** as a white solid (30.4 mg, 29%). Spectral data was found in agreement with the literature²⁷.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.80 (m, 2H), 7.51 – 7.45 (m, 1H), 7.40 – 7.34 (m, 3H), 7.32 – 7.24 (m, 2H), 2.85 (s, 2H), 1.33 (s, 6H).

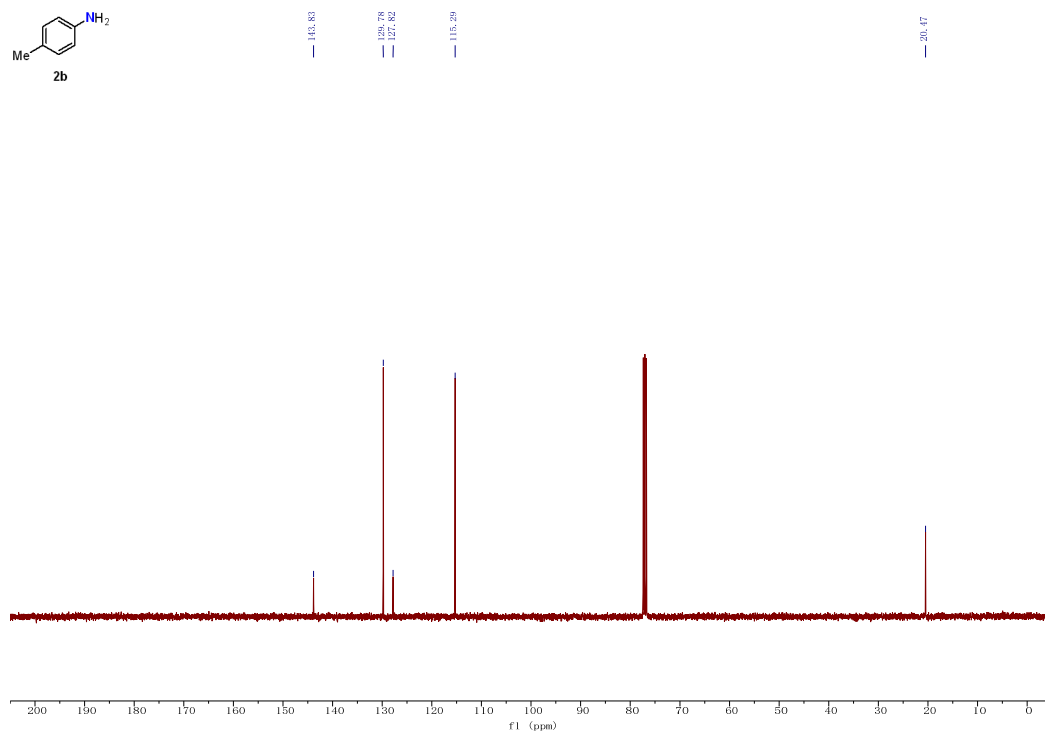
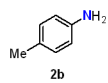
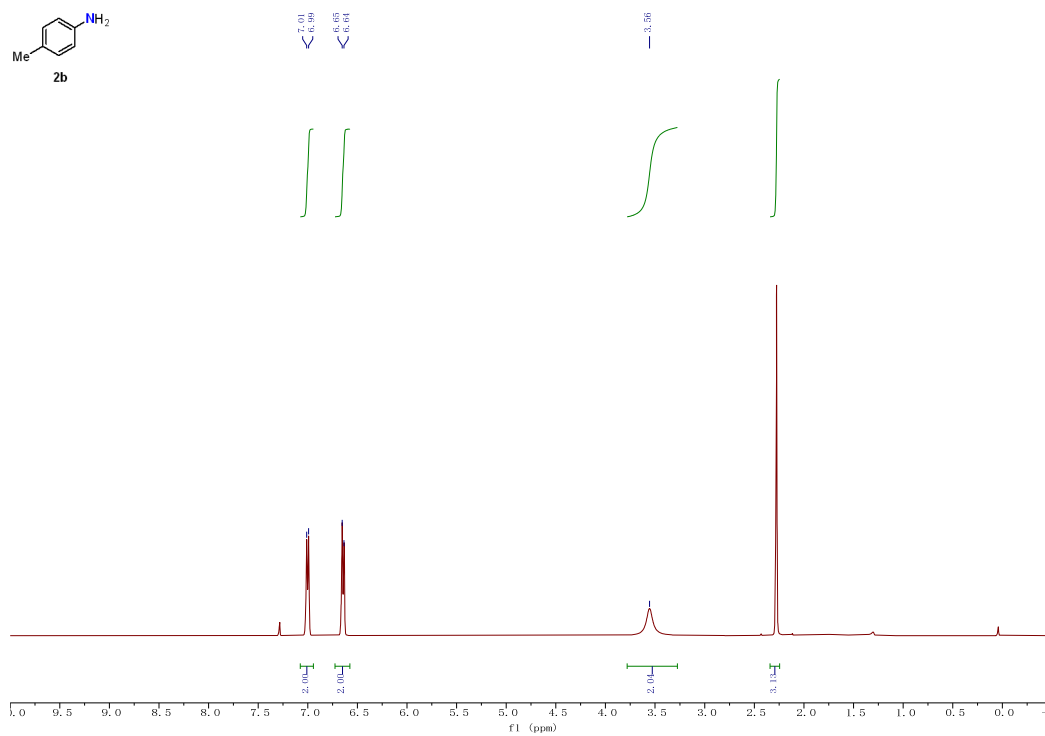
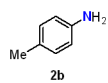
¹³C NMR (101 MHz, Chloroform-*d*) δ 145.46, 136.06, 134.23, 133.30, 128.69, 127.99, 127.47, 126.90, 126.60, 124.30, 124.13, 123.55, 44.10, 34.19, 27.98.

6. NMR spectra

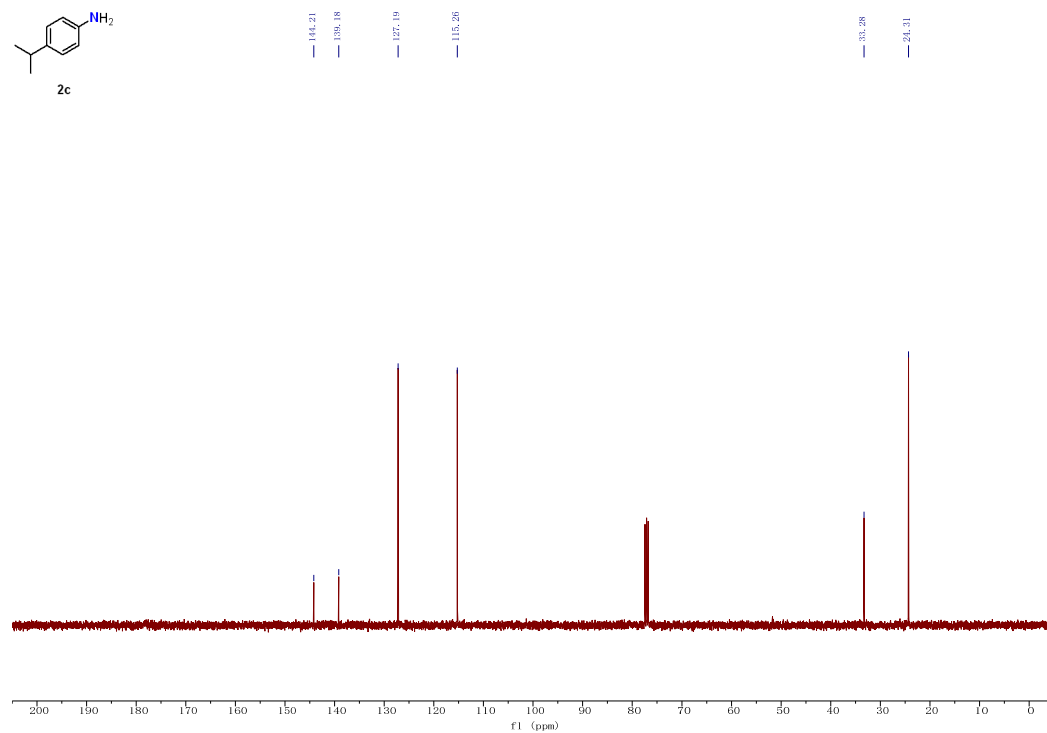
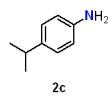
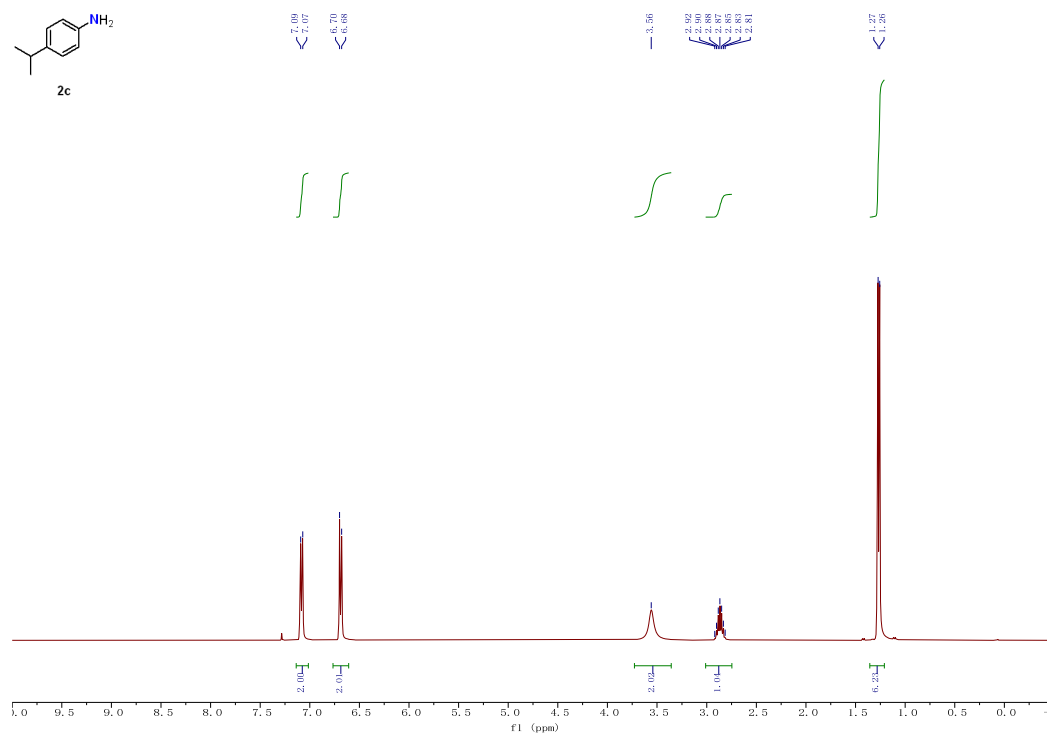
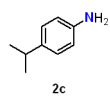
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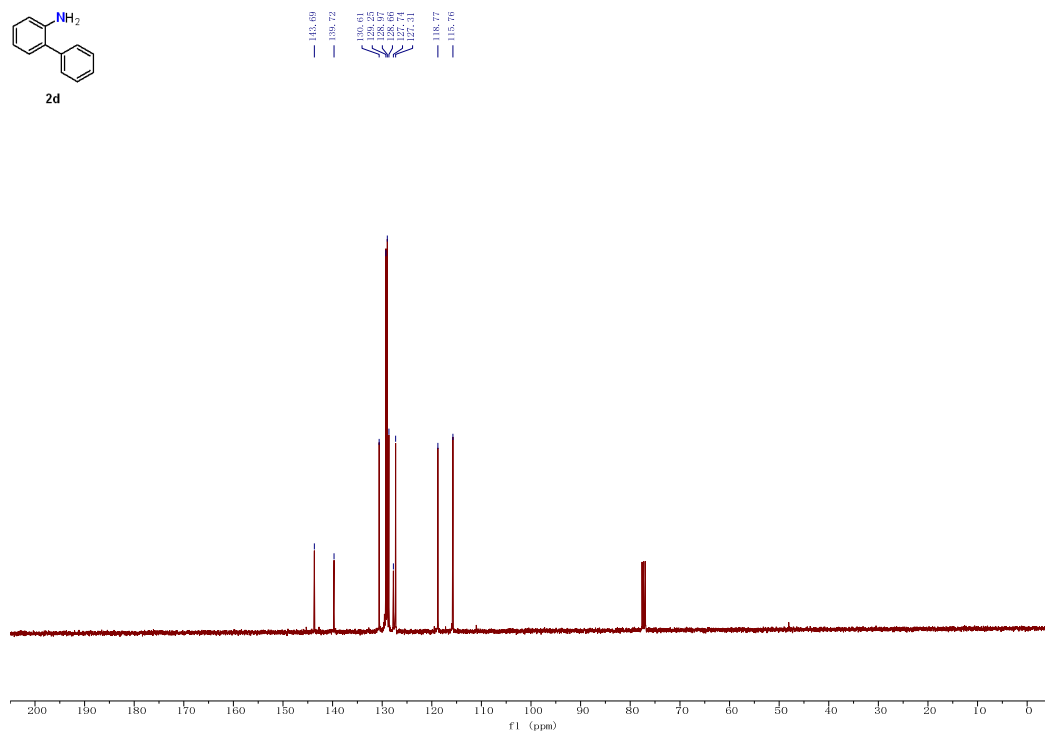
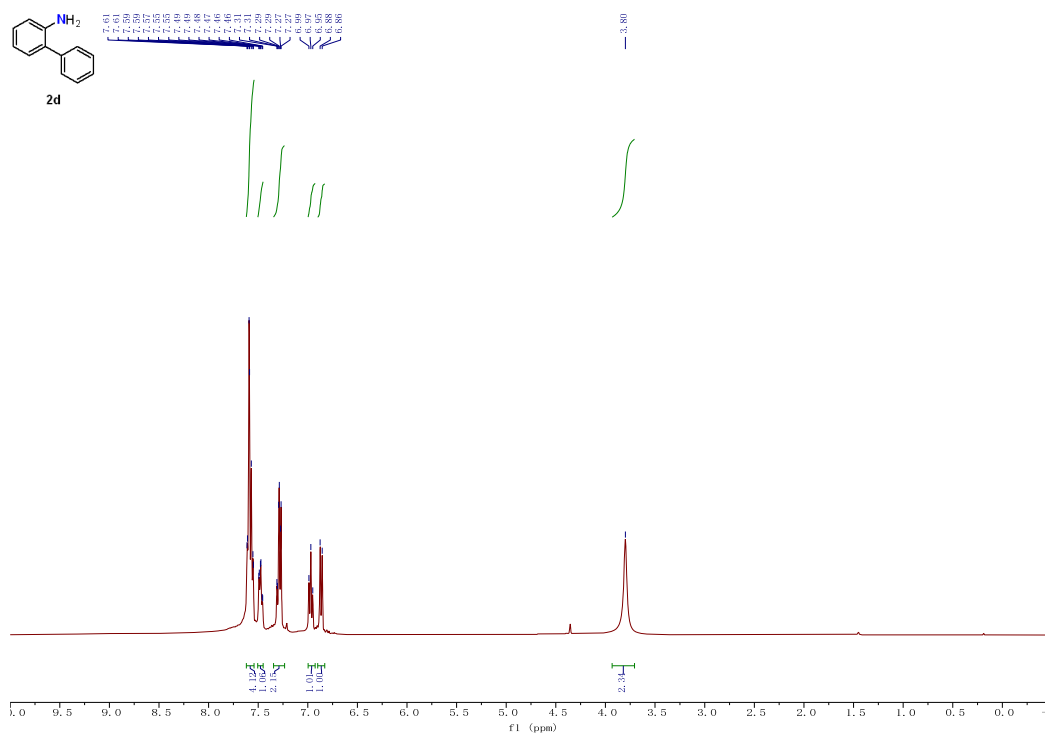
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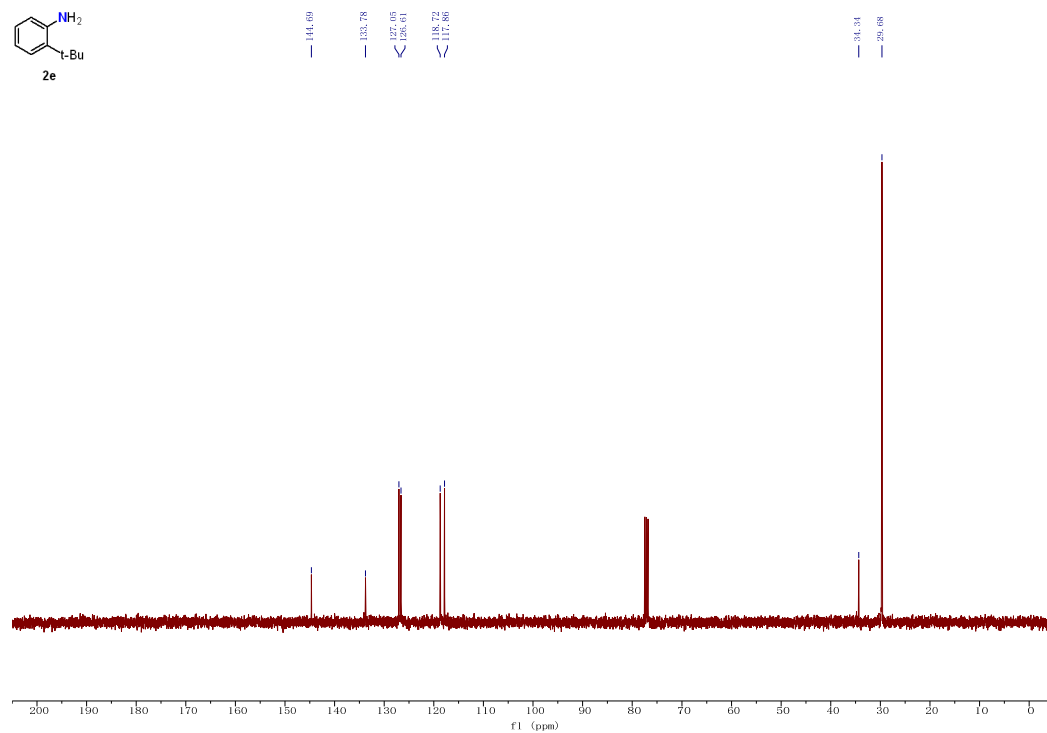
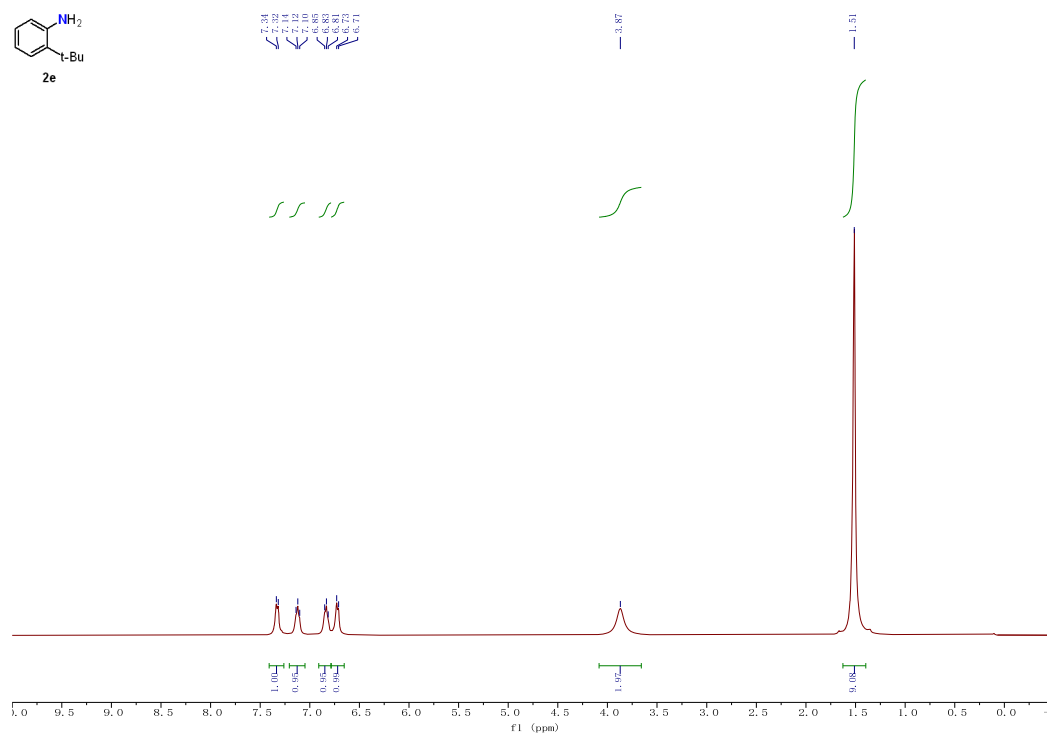
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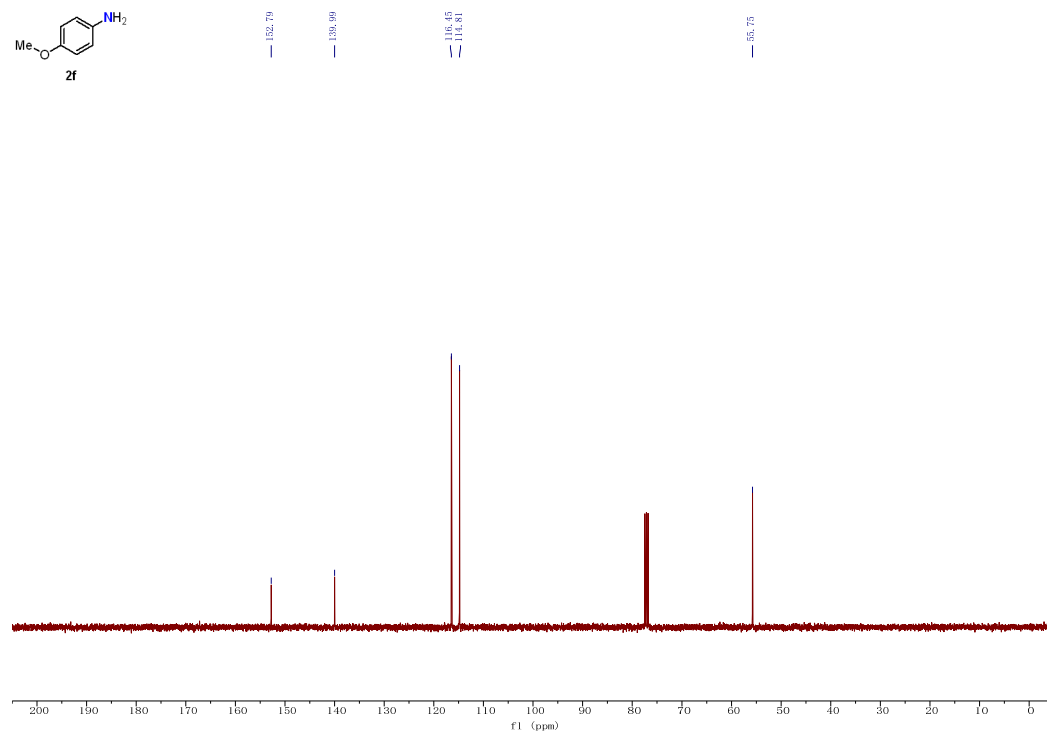
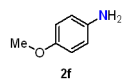
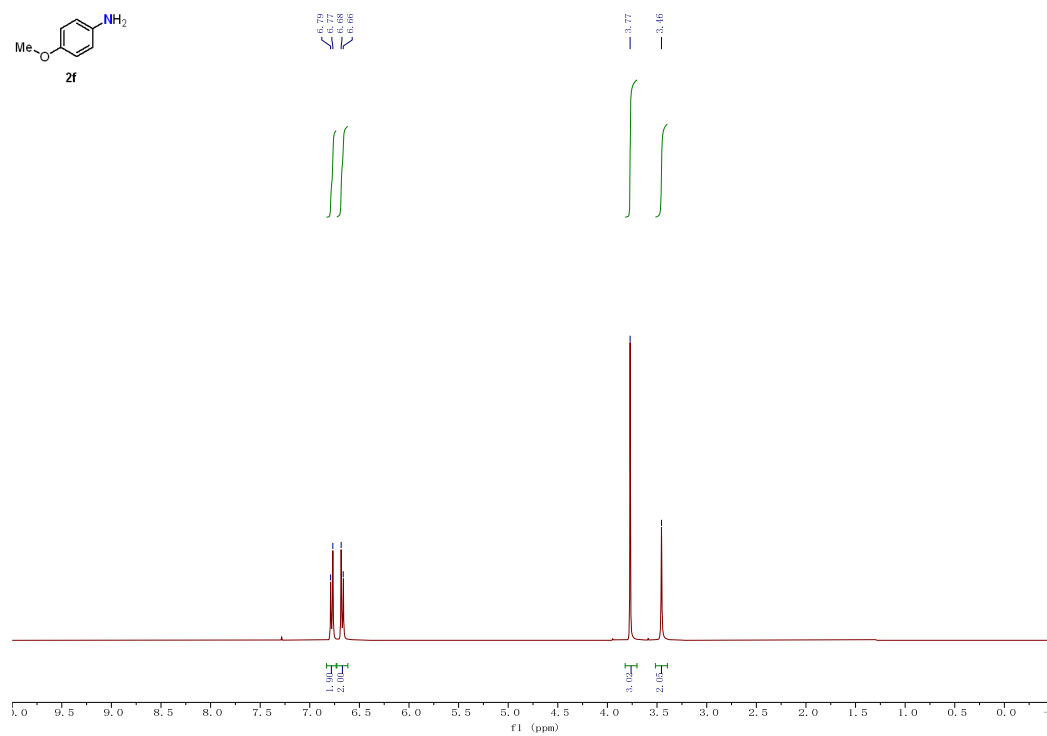
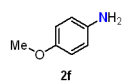
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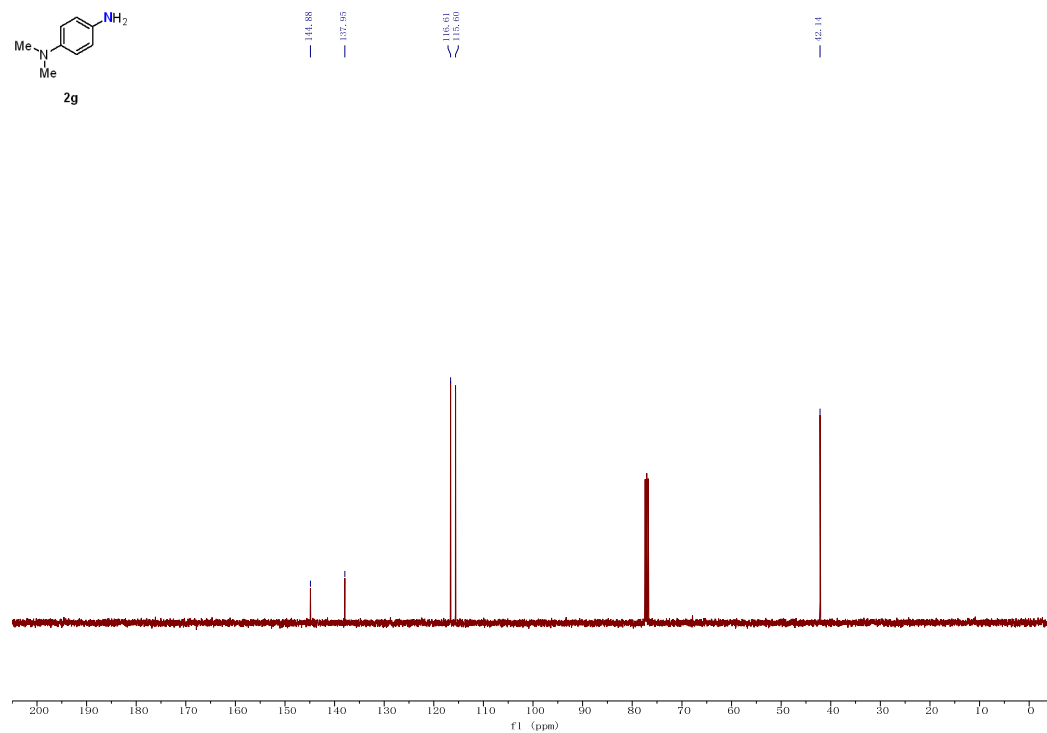
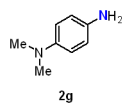
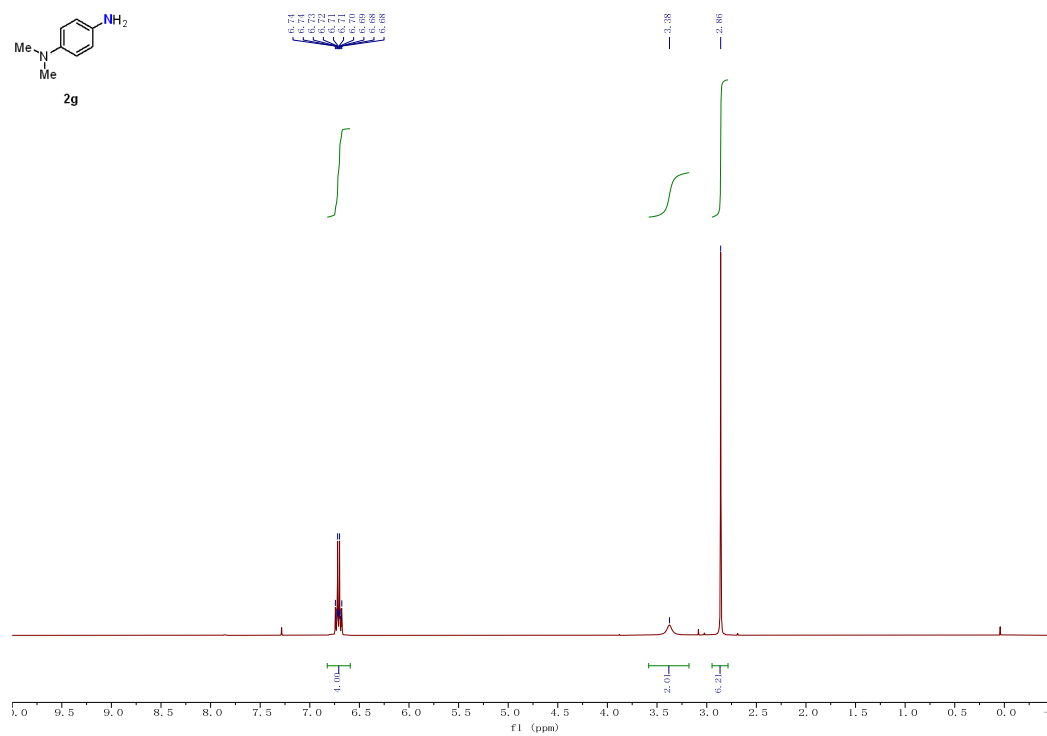
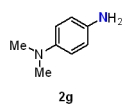
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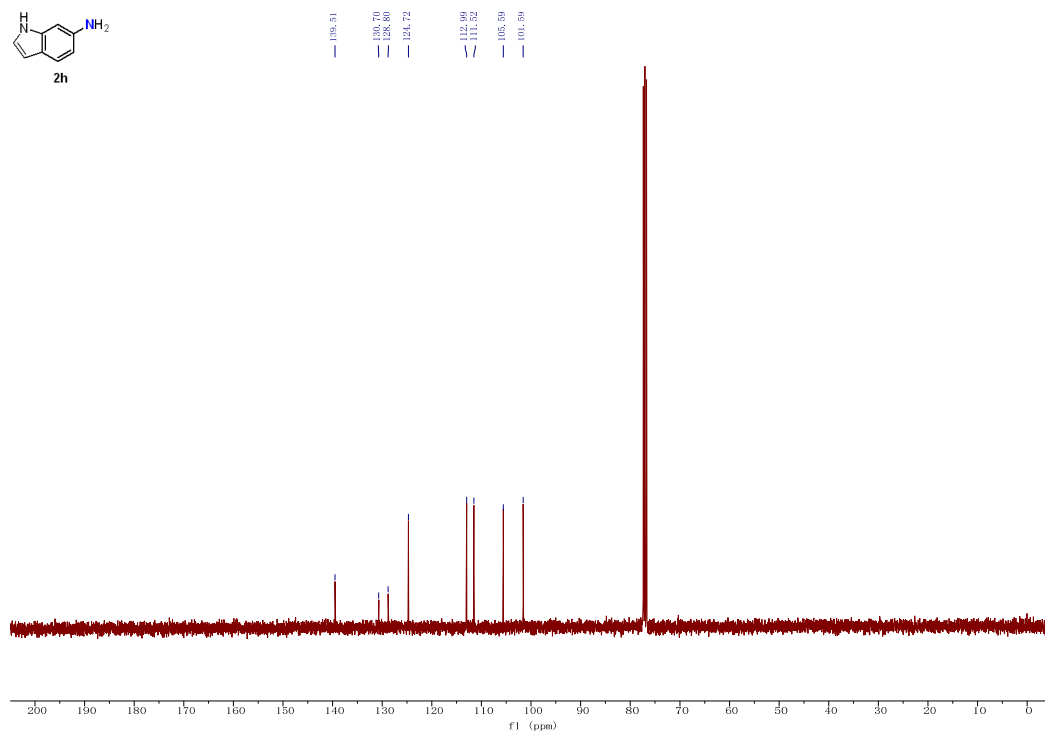
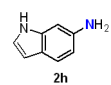
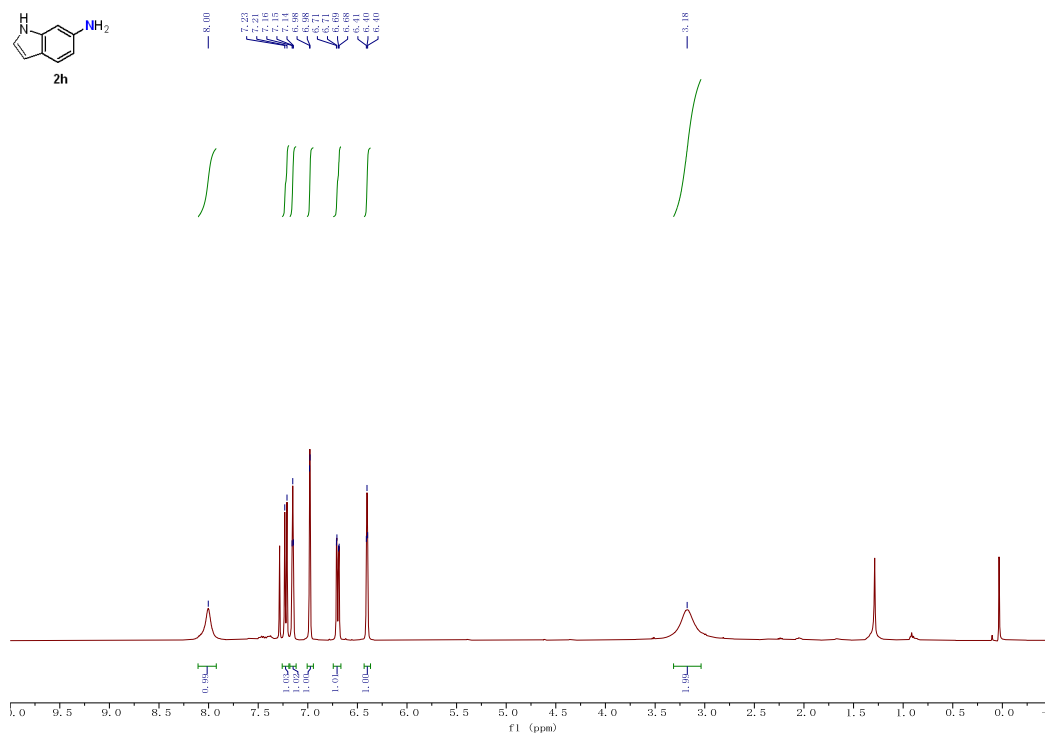
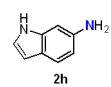
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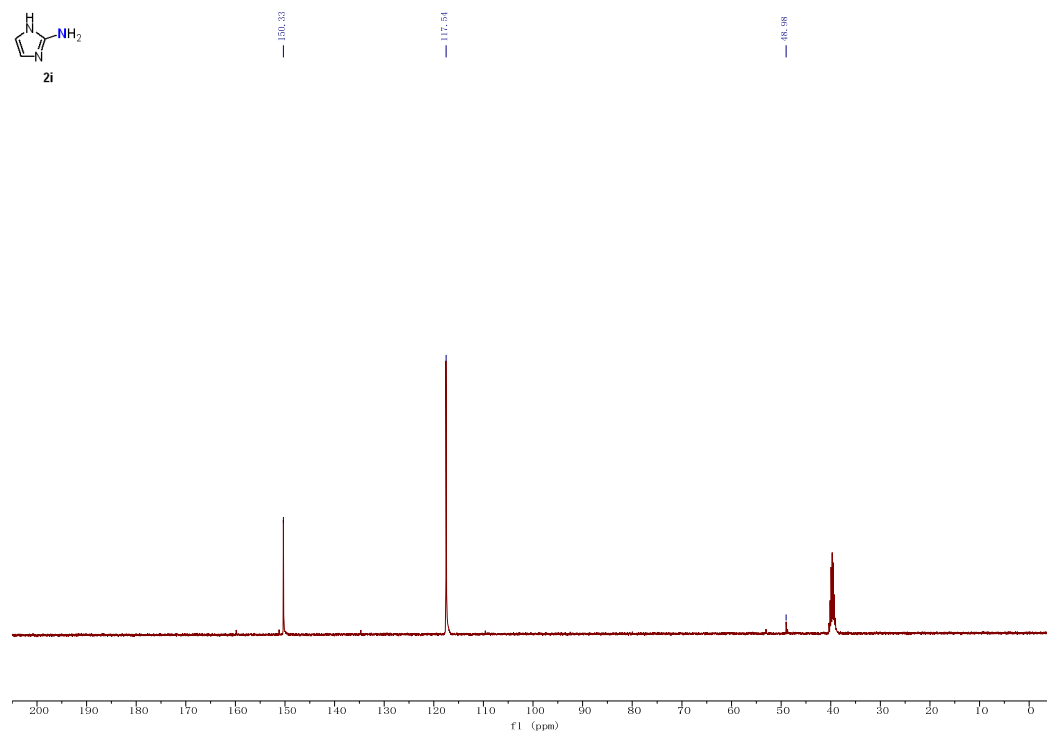
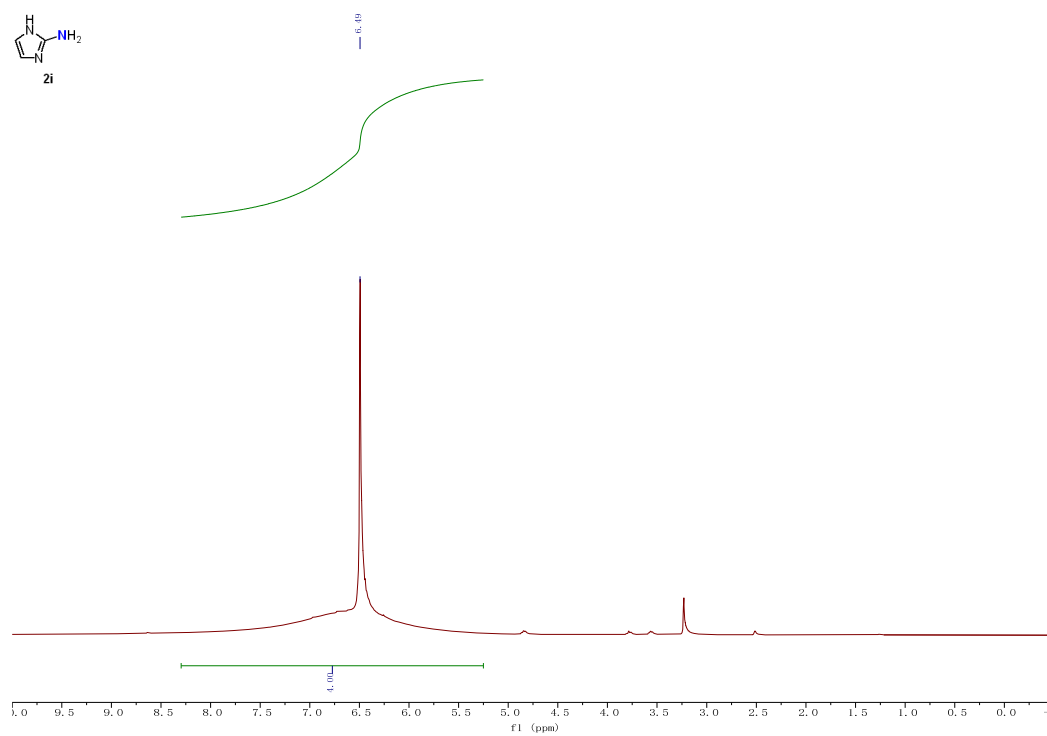
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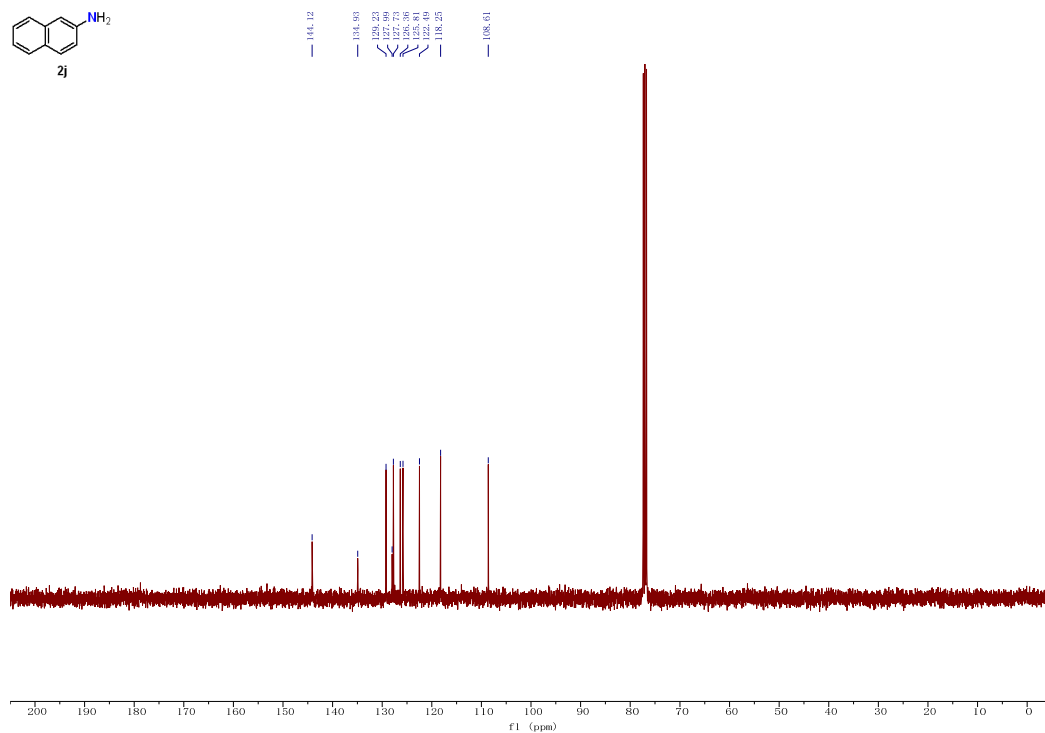
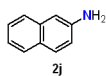
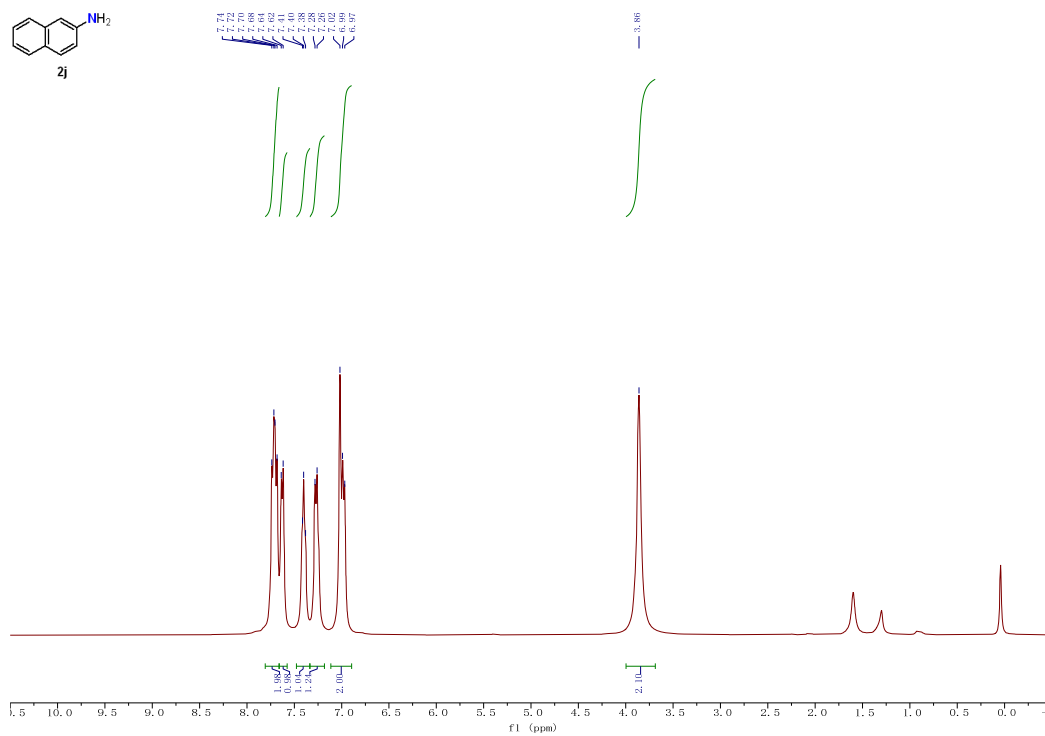
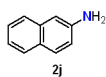
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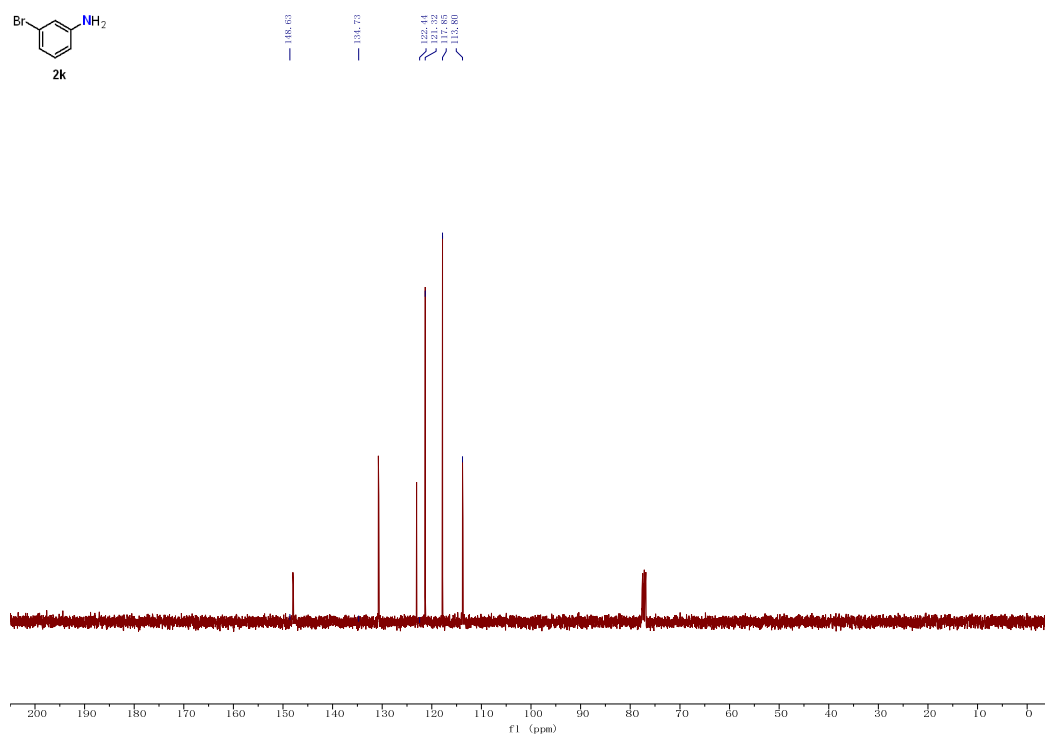
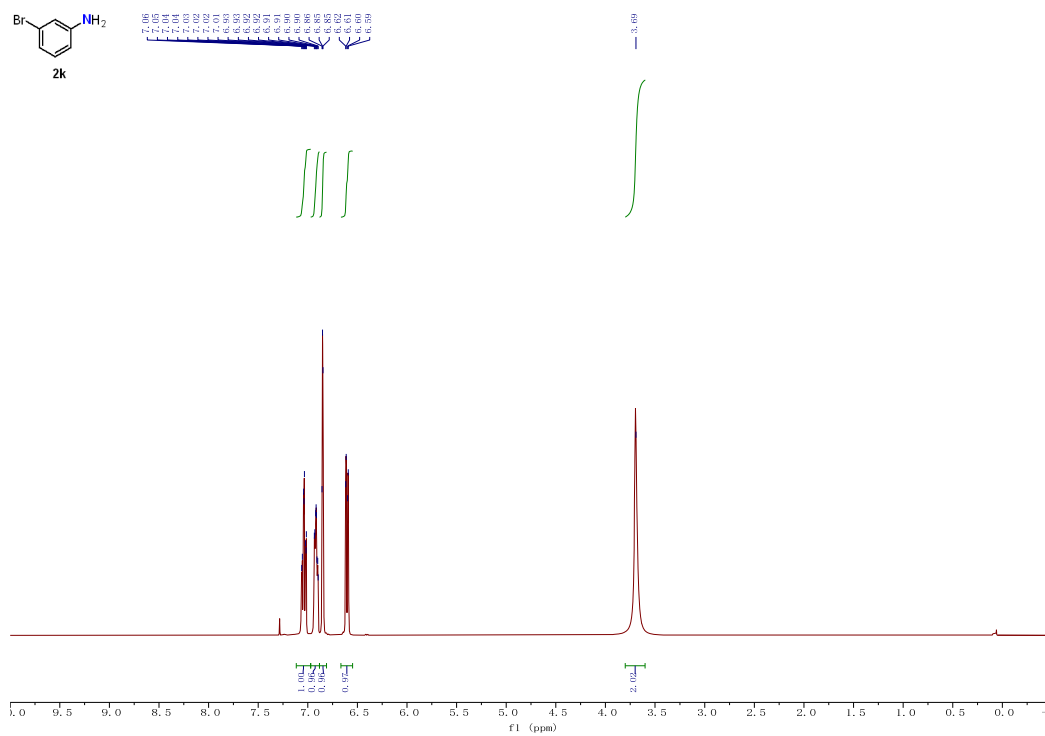
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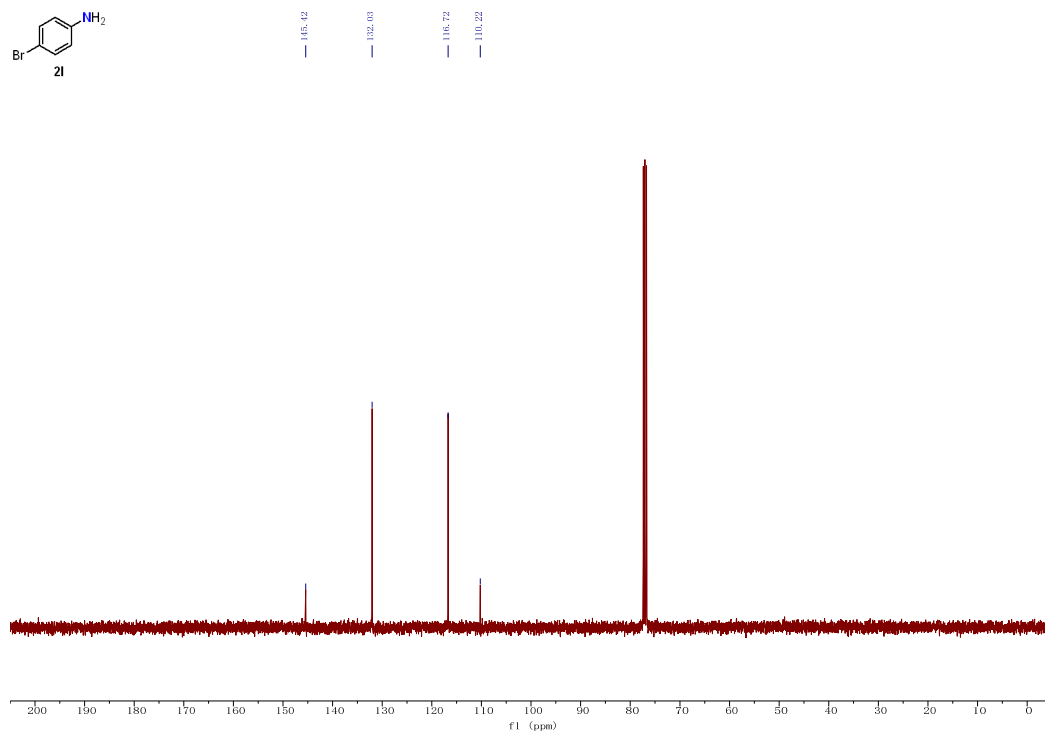
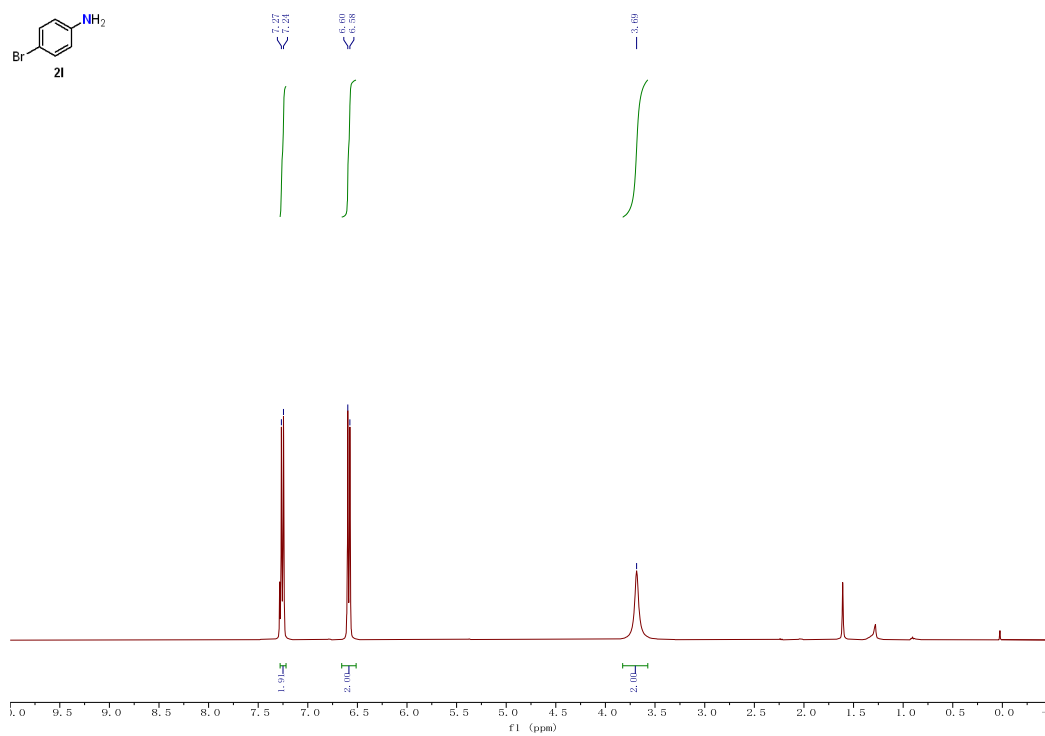
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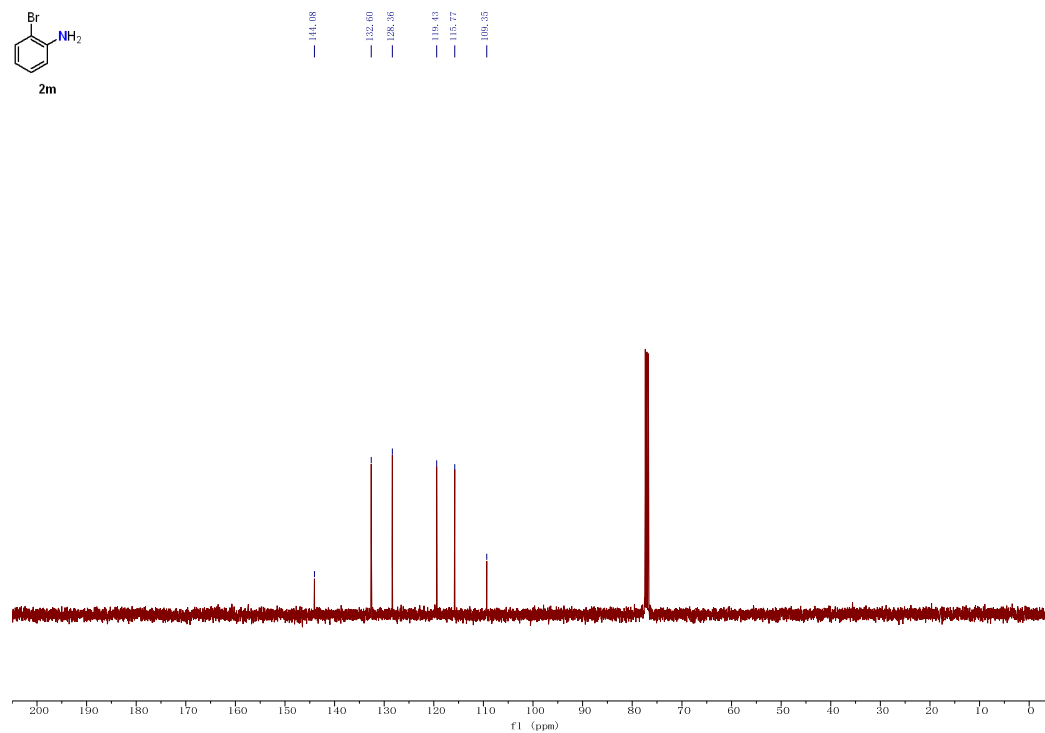
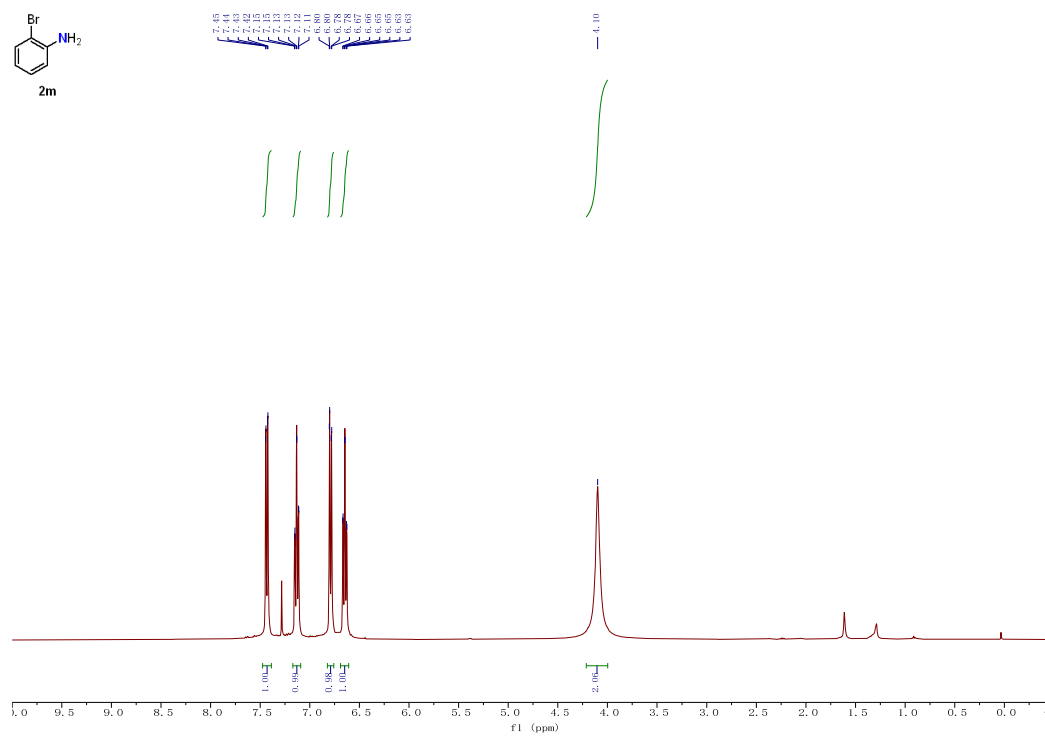
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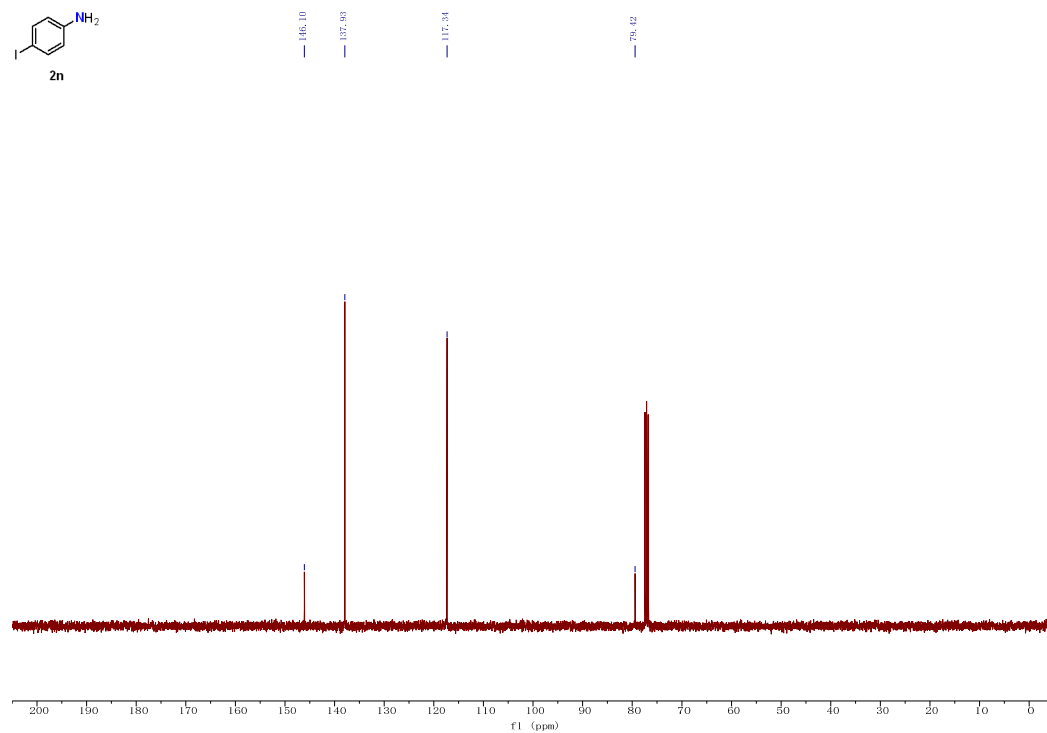
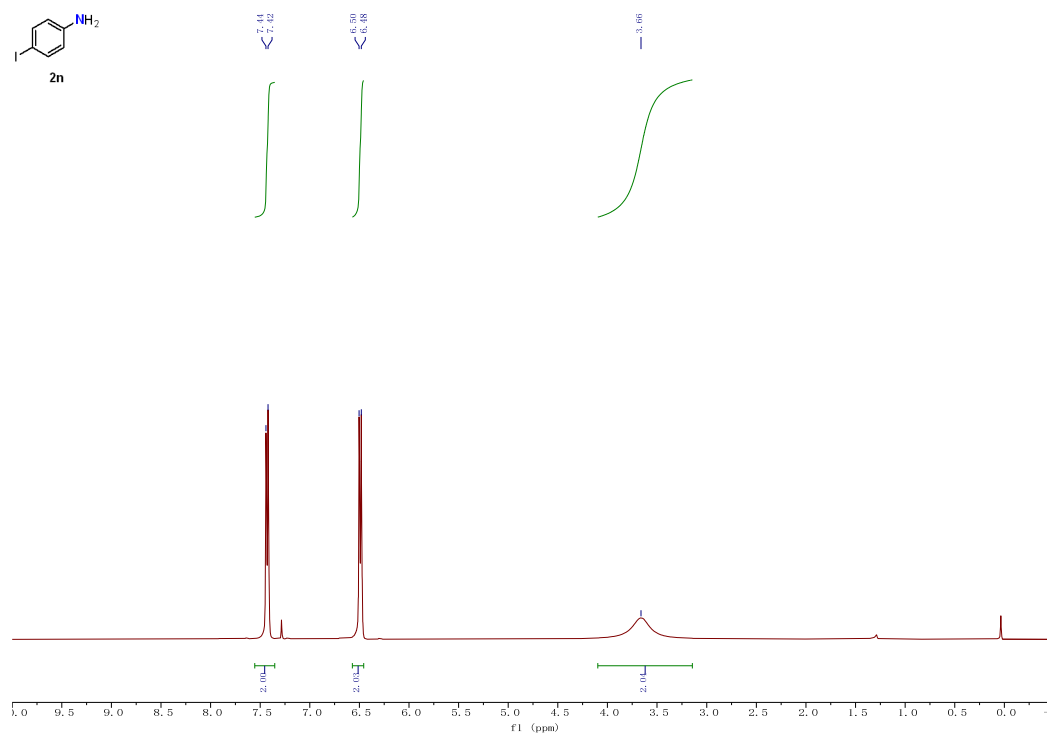
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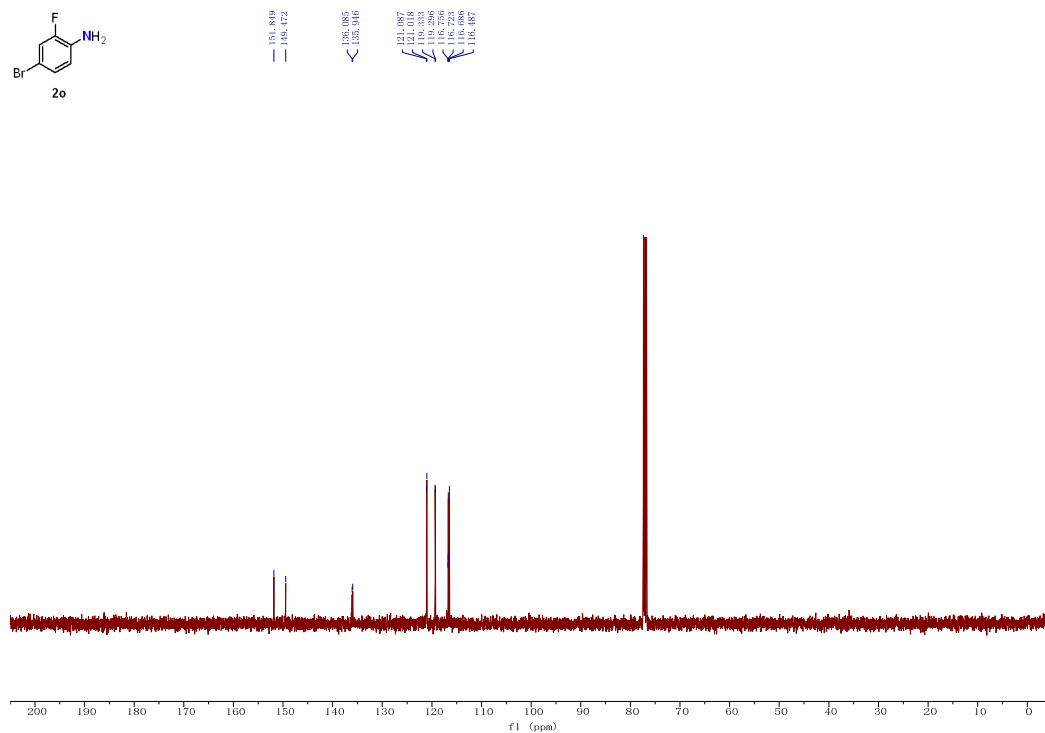
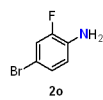
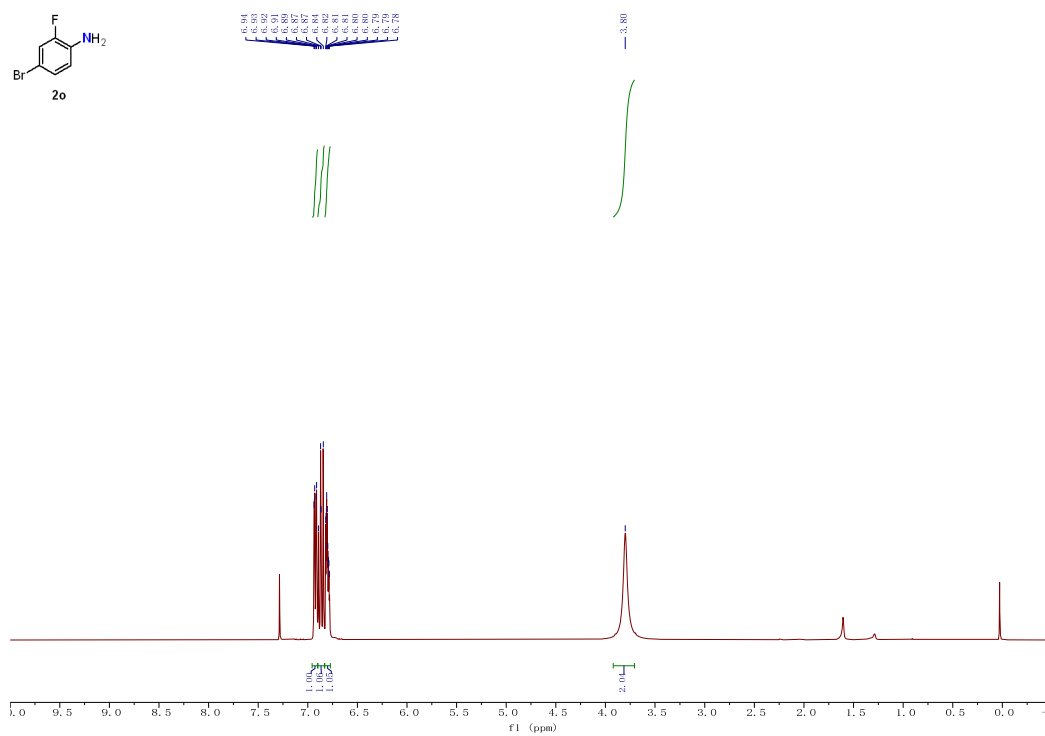
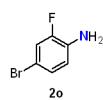
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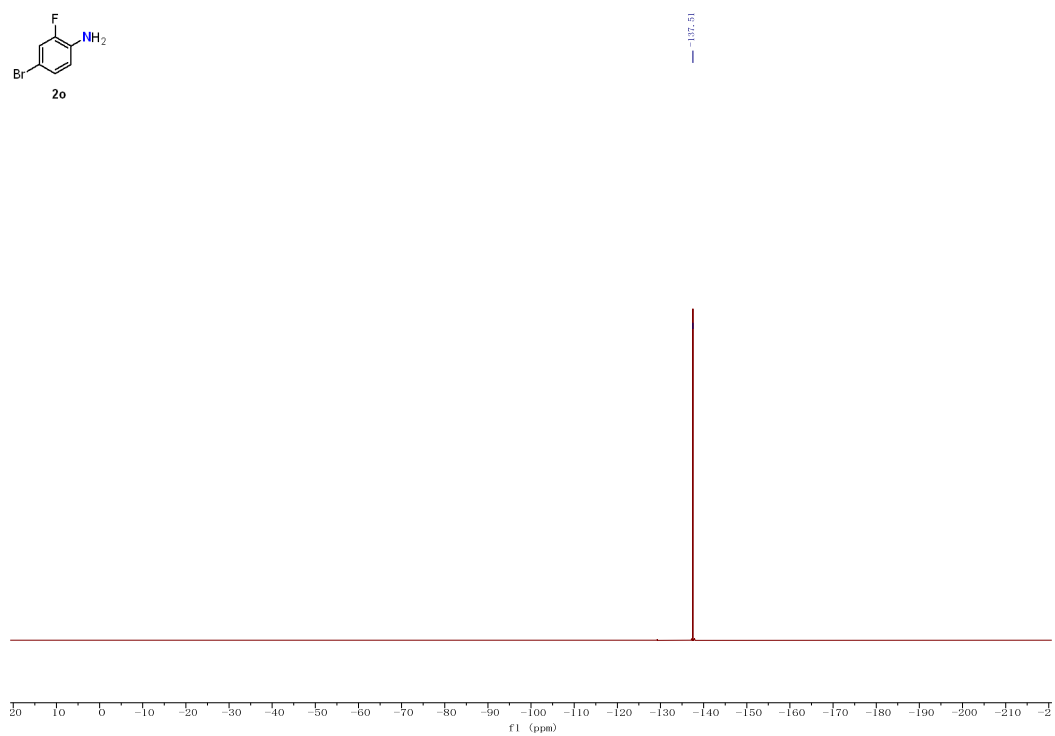


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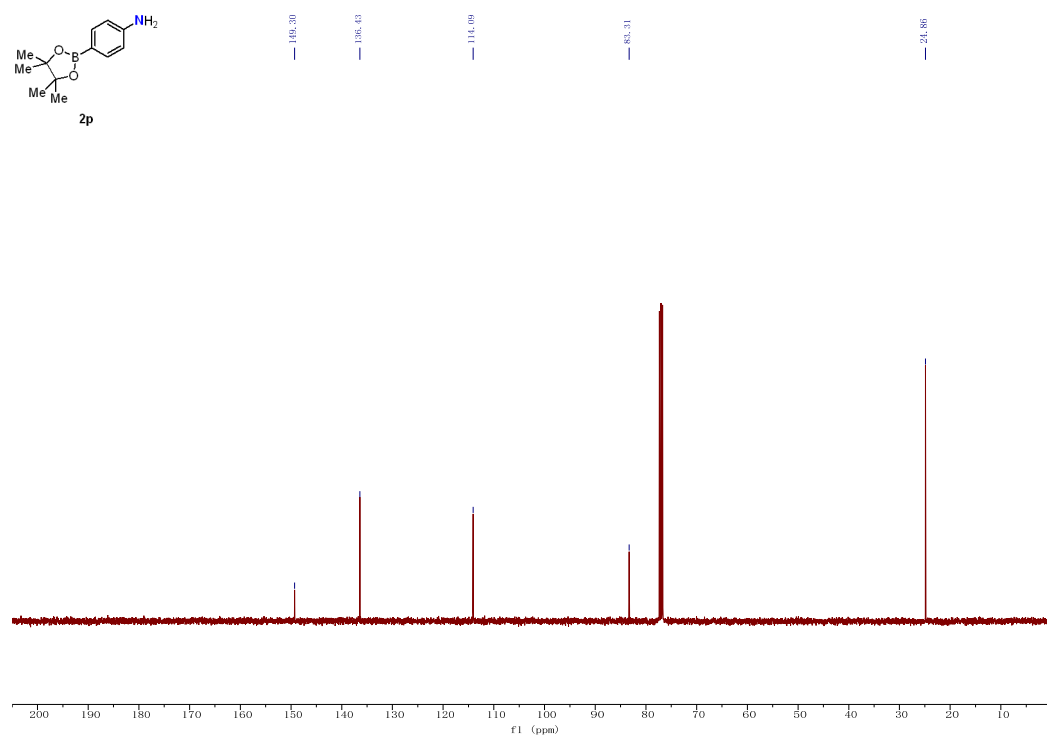
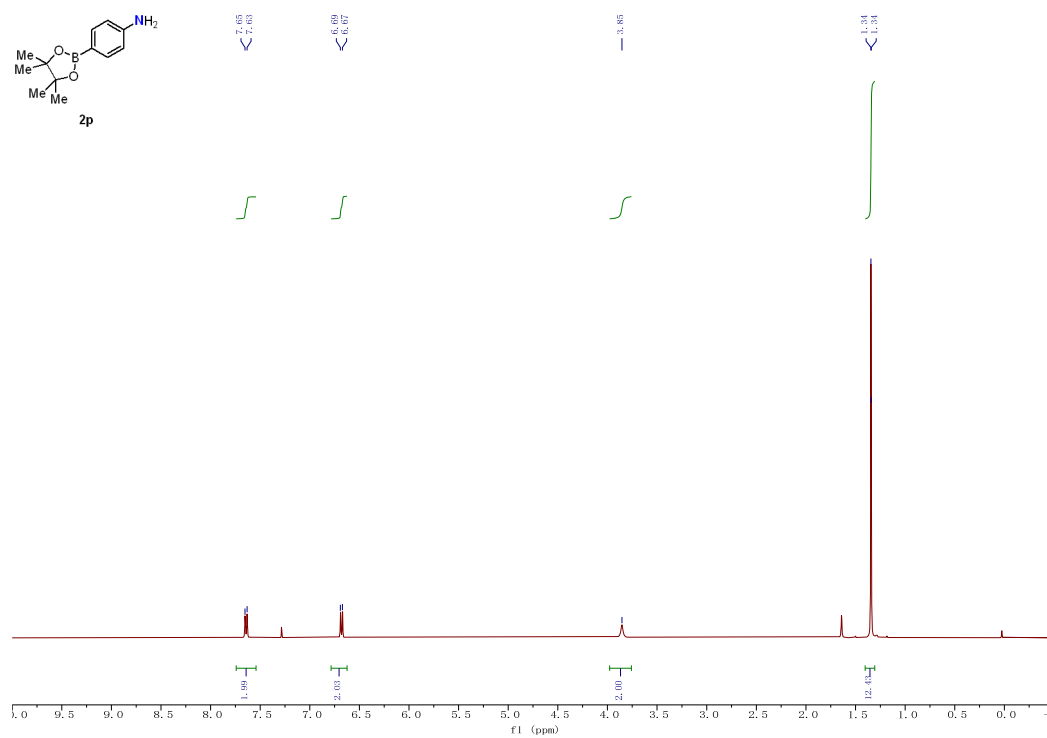


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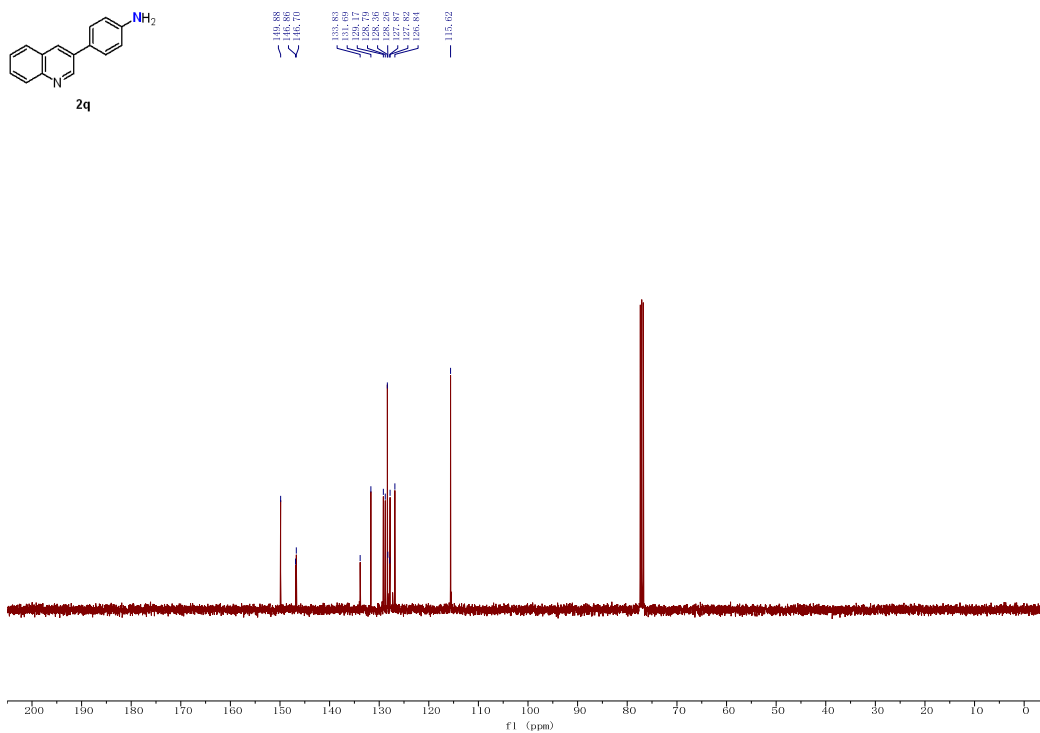
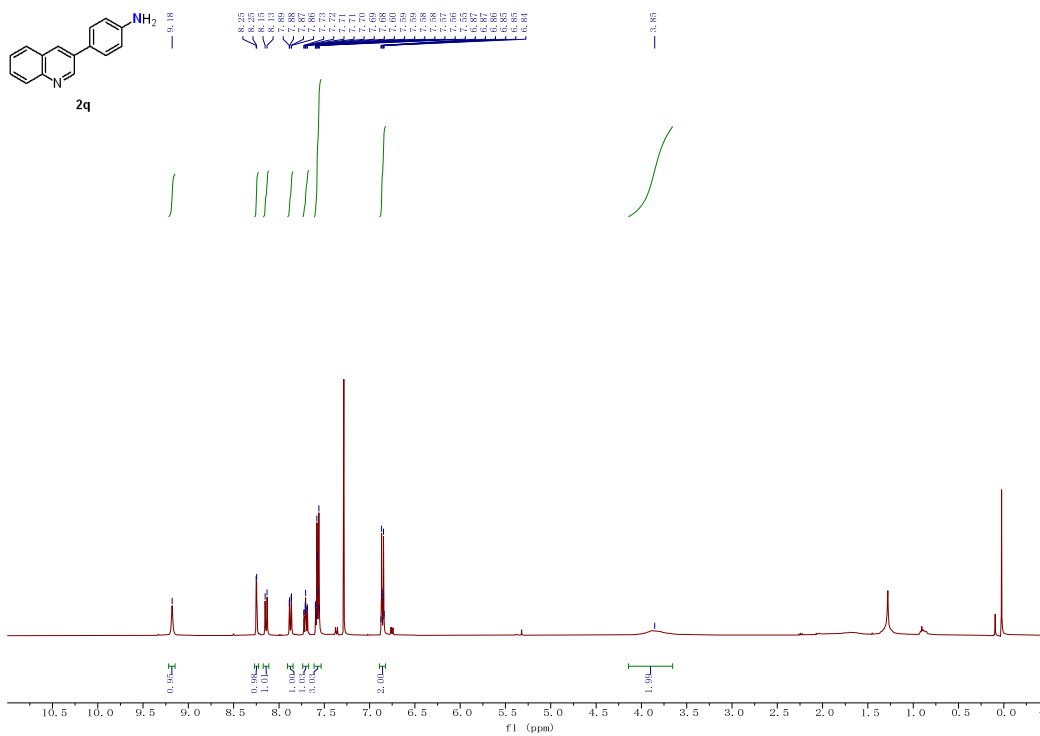




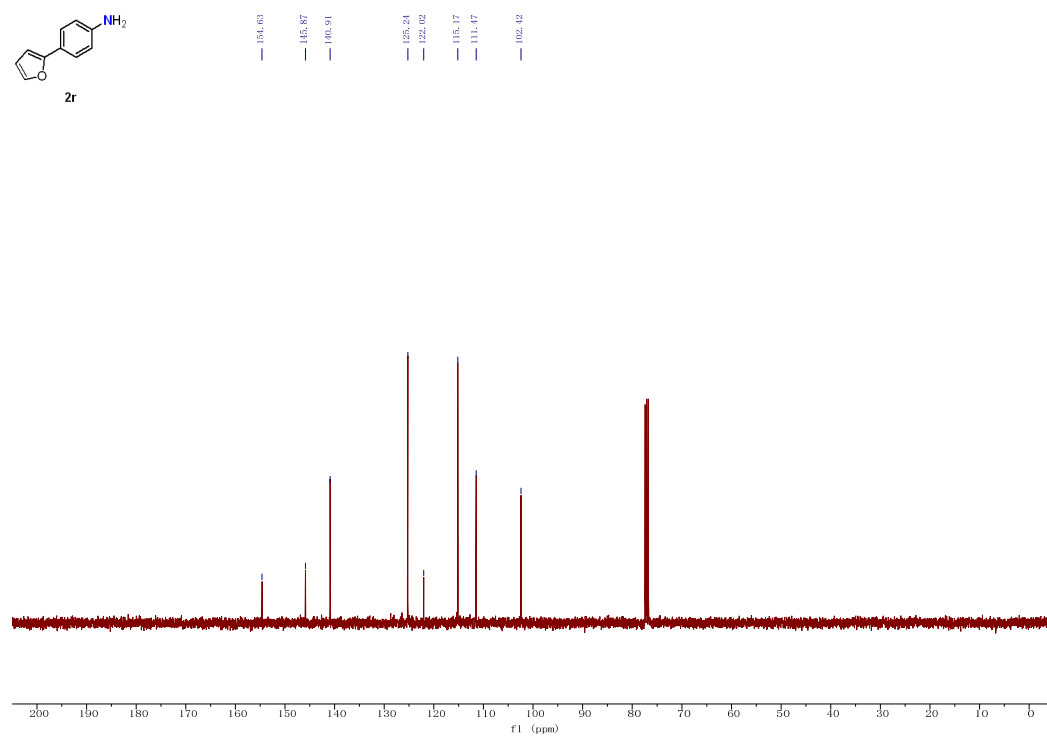
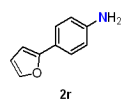
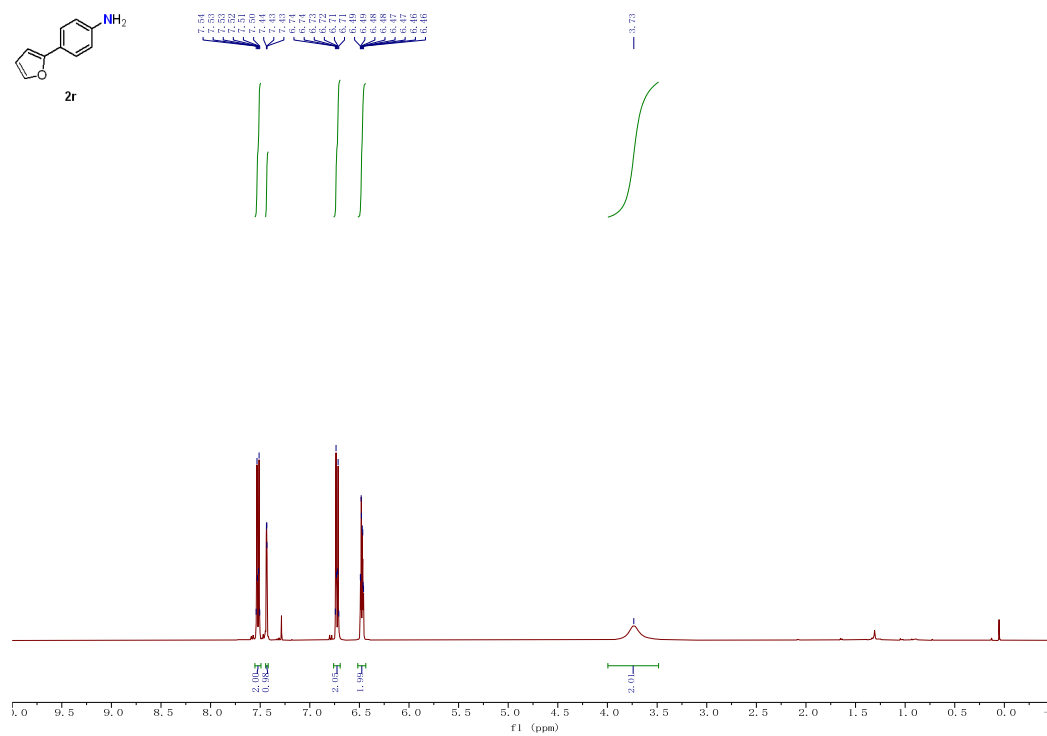
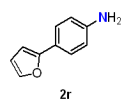
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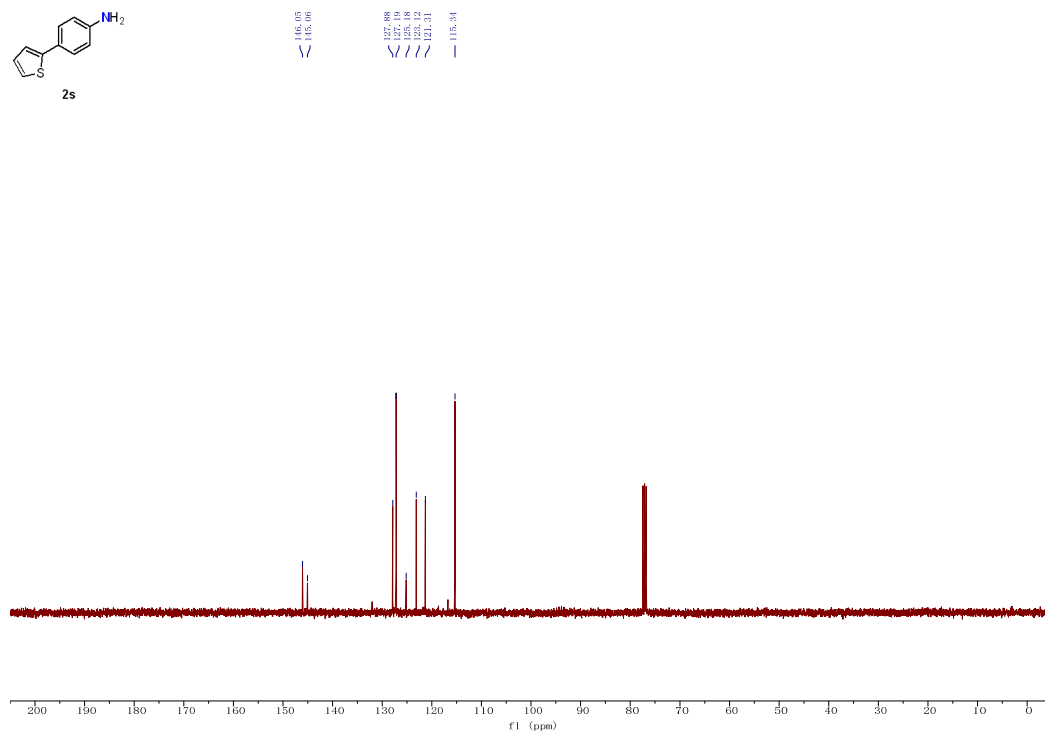
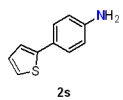
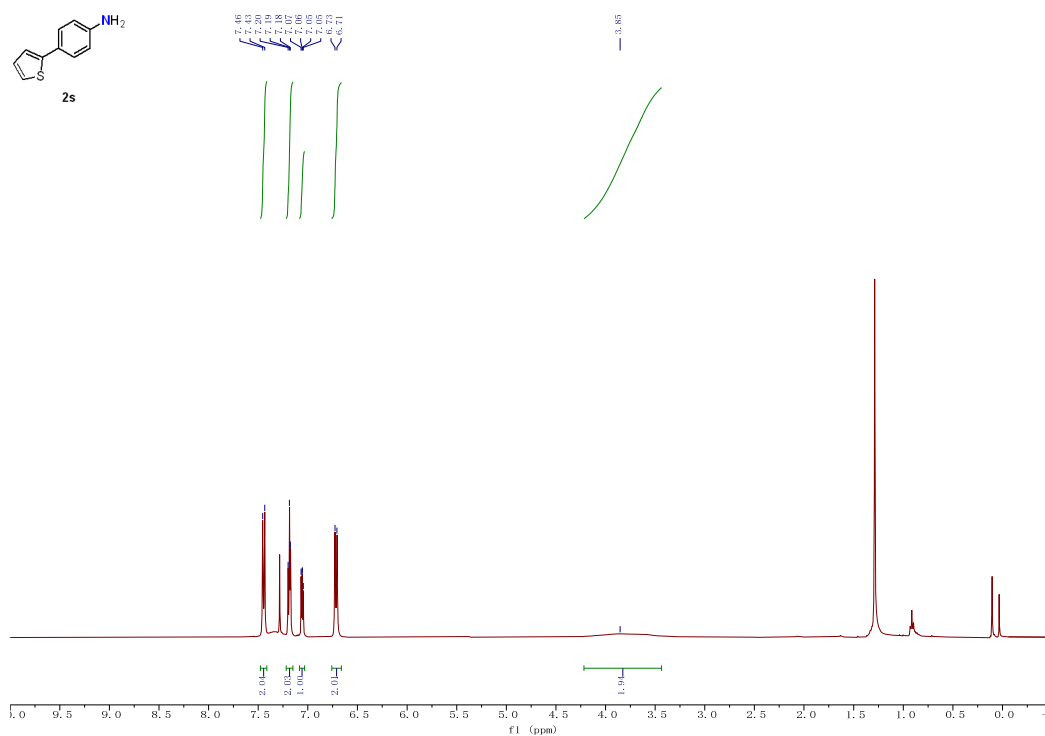
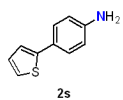
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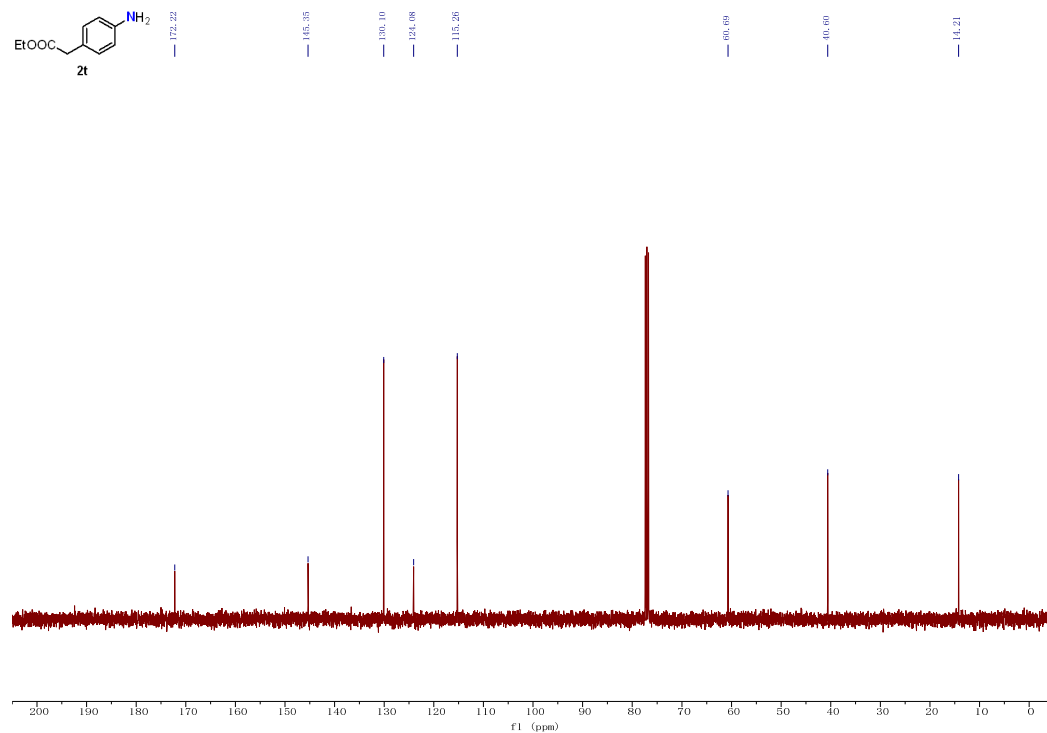
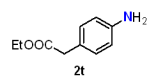
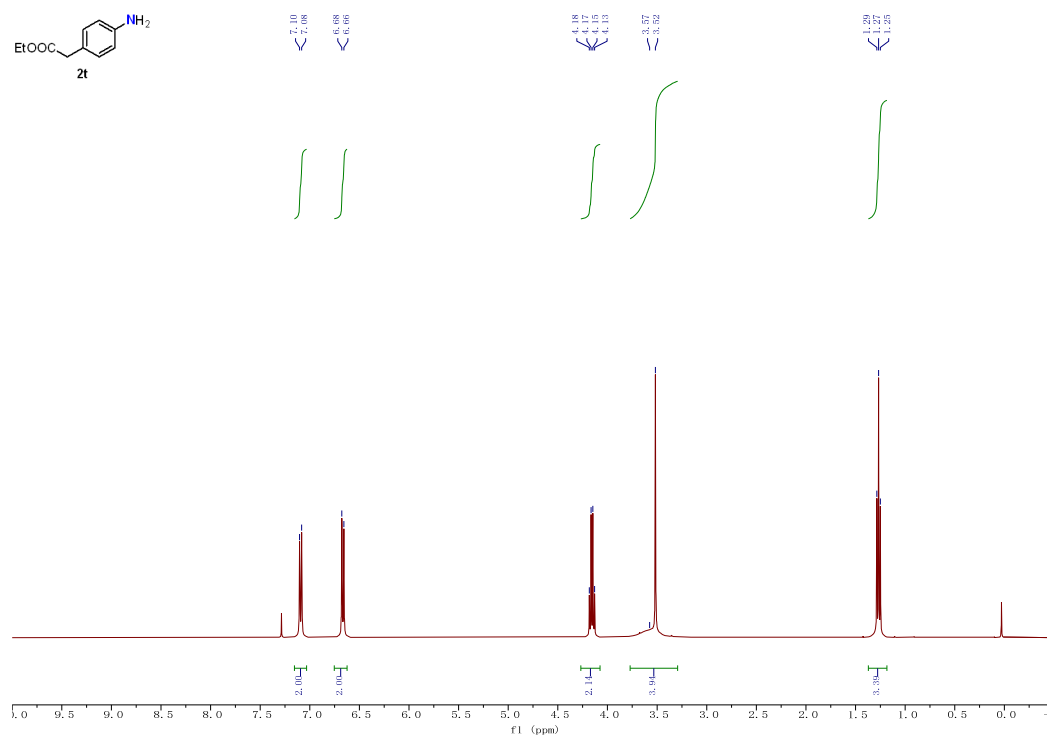
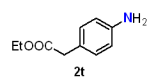
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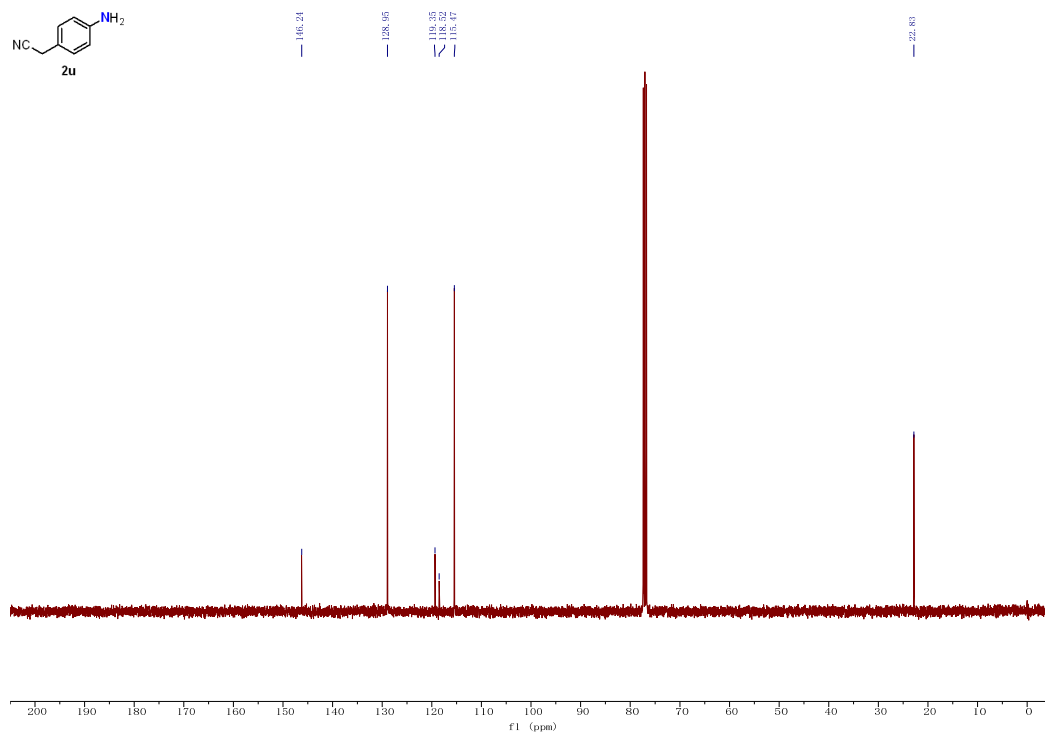
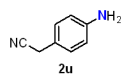
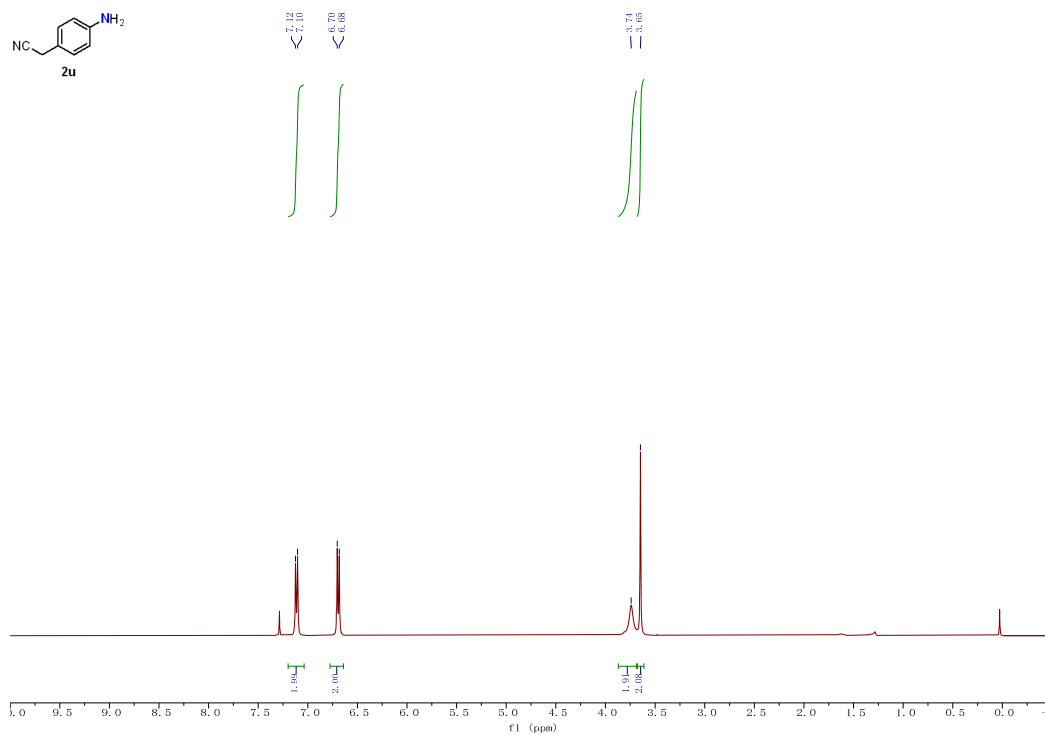
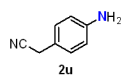
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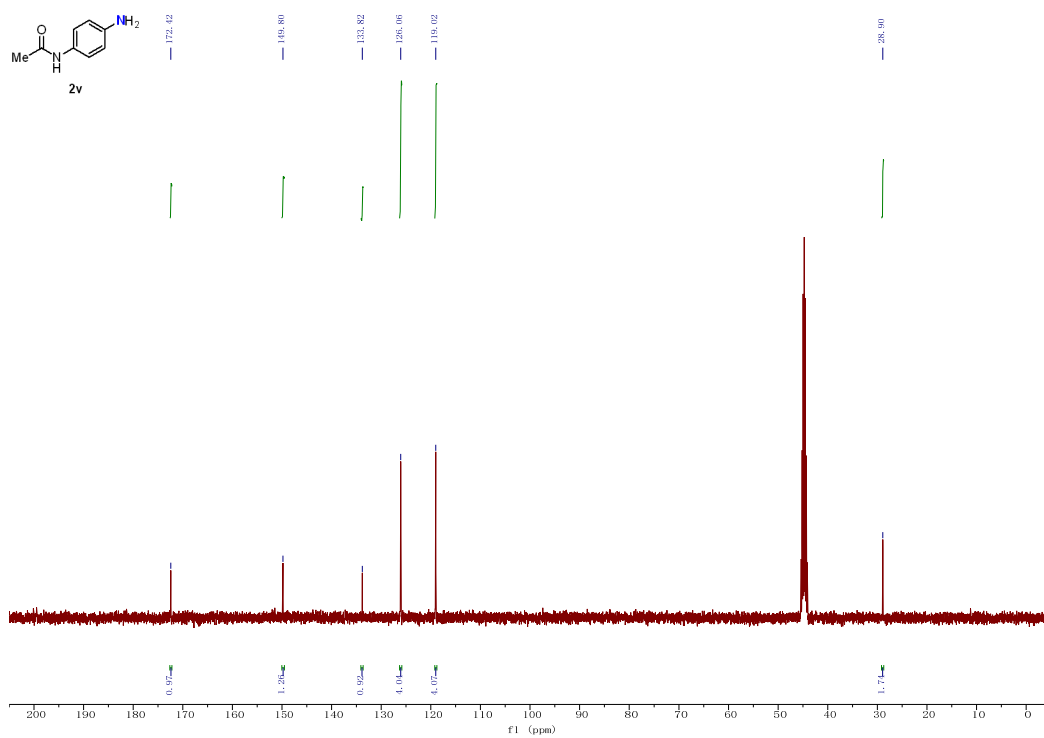
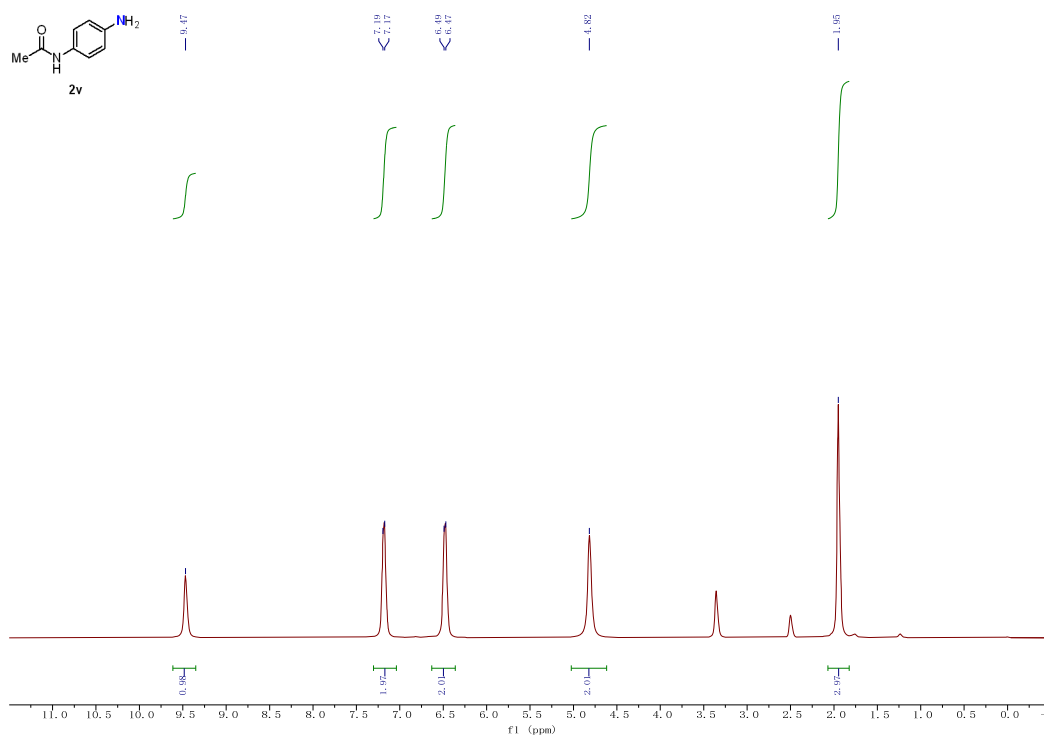
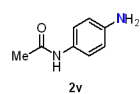
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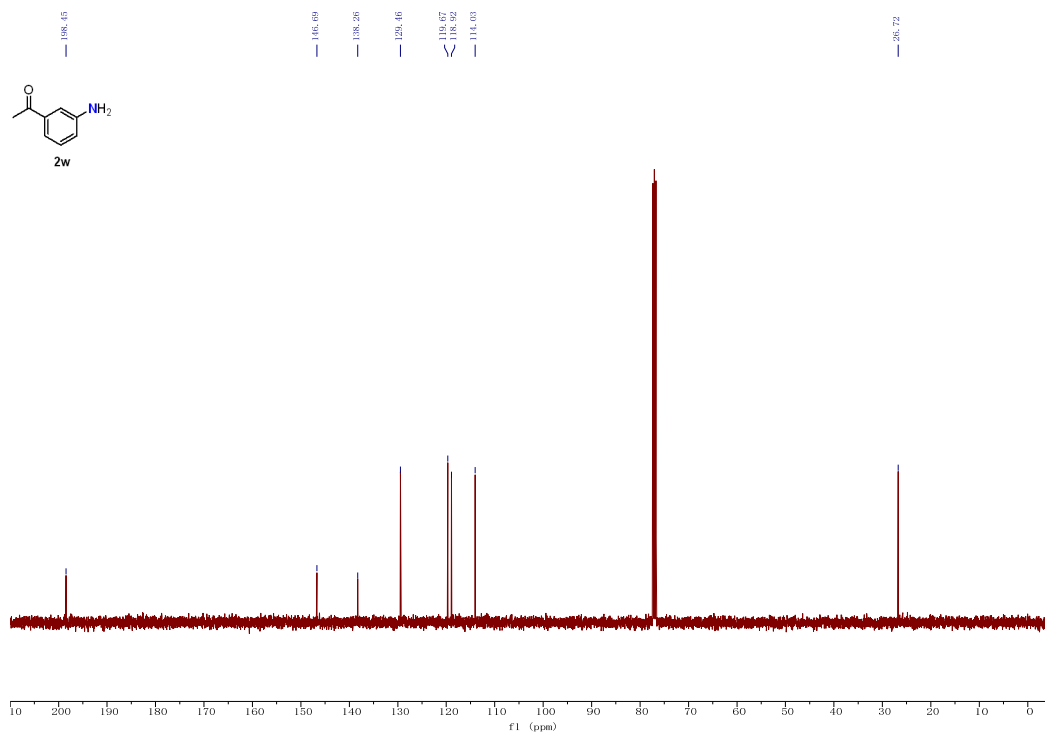
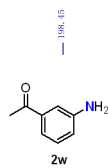
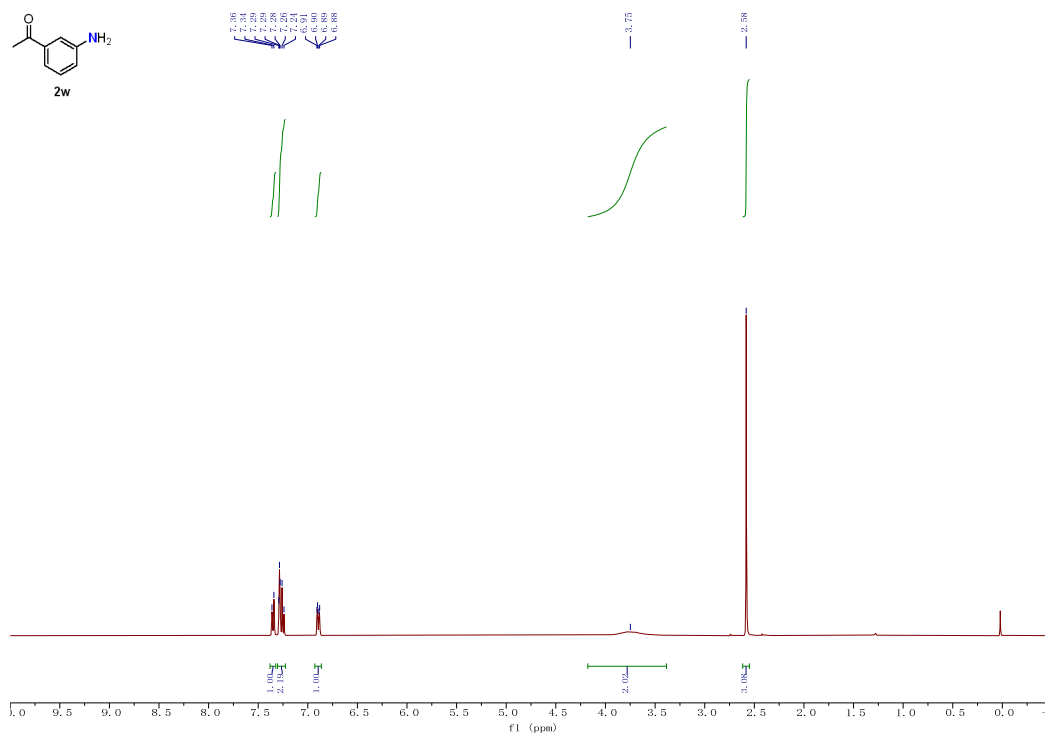
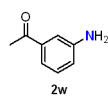
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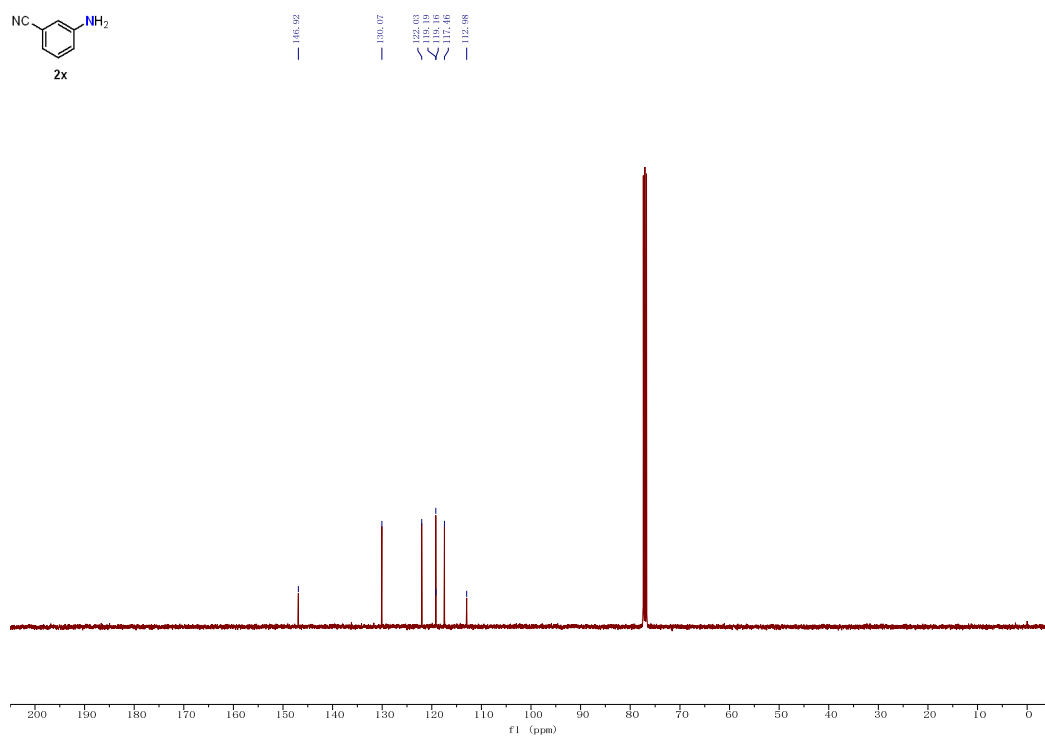
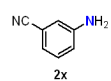
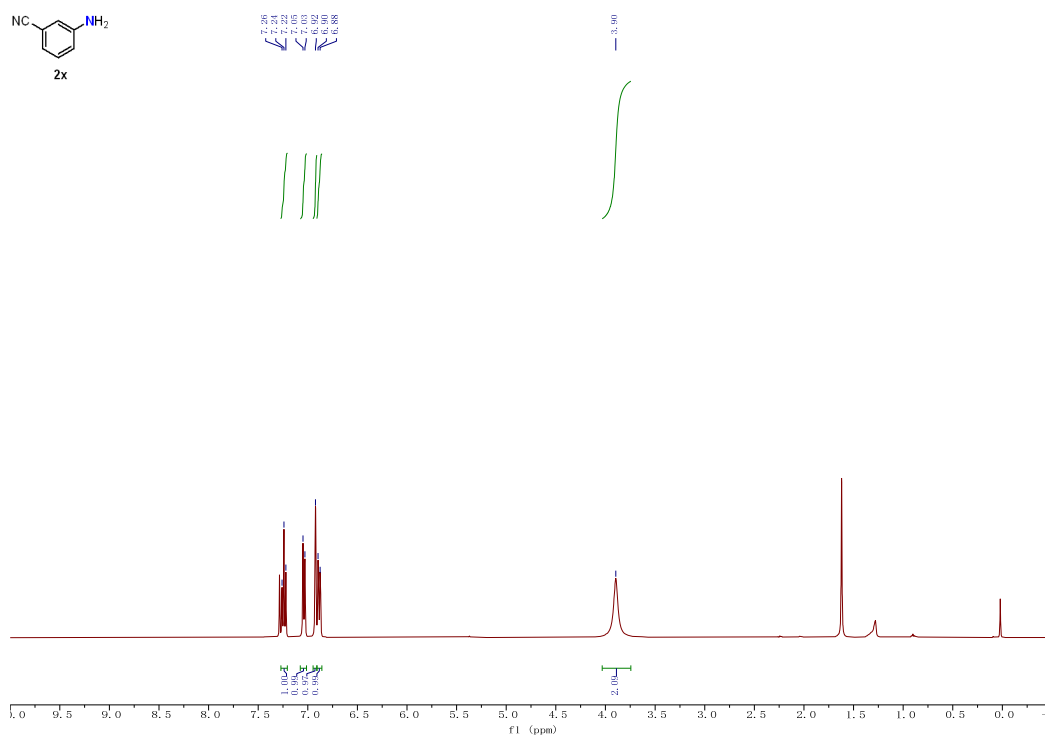
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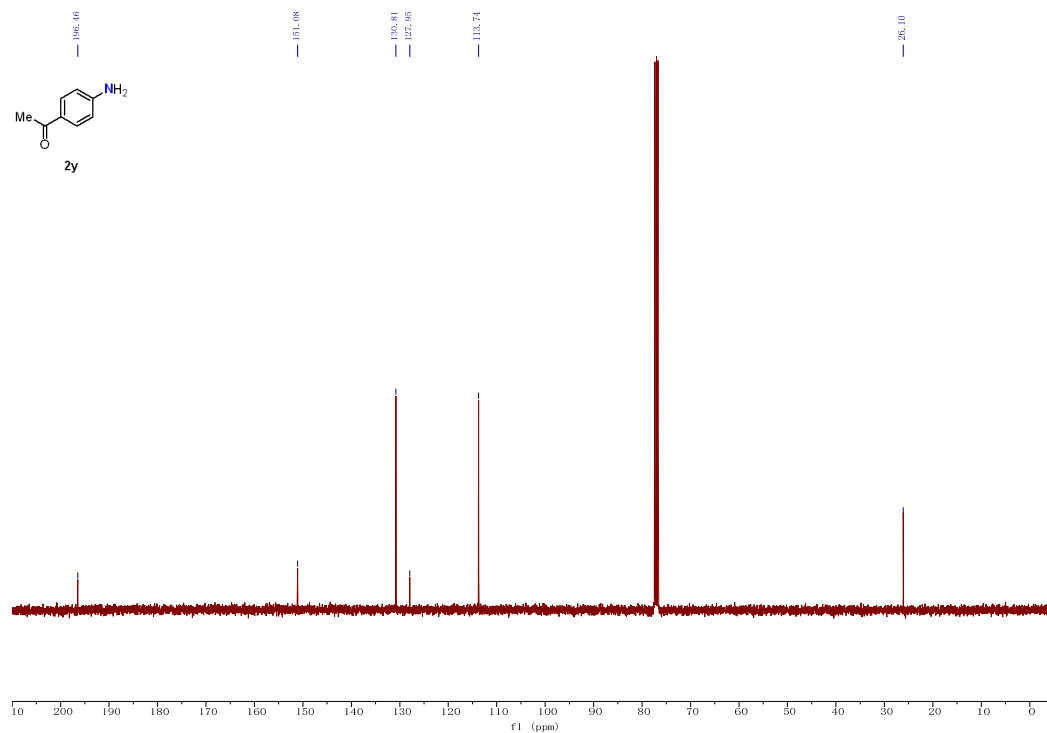
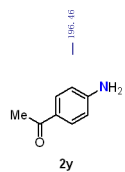
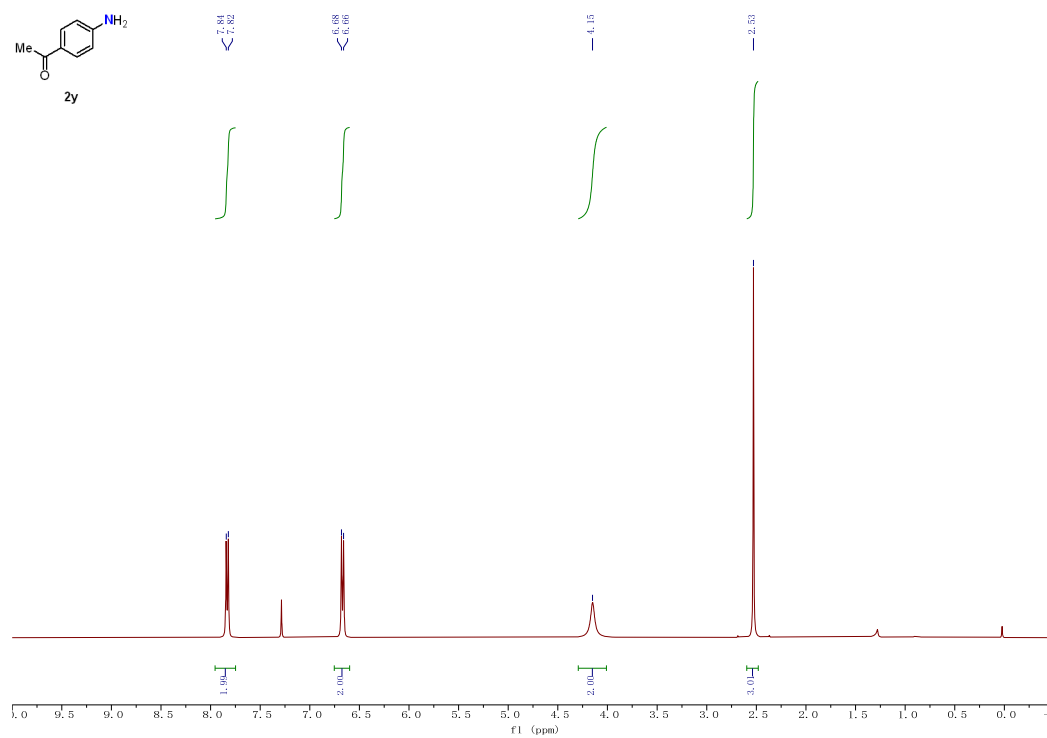
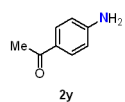
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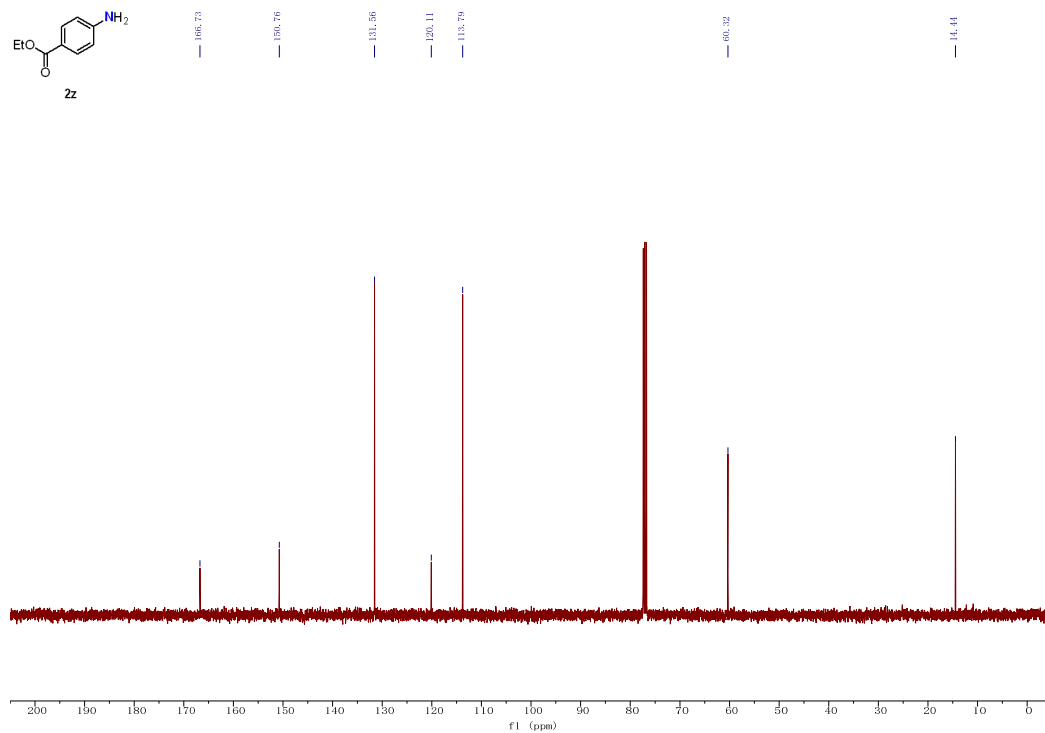
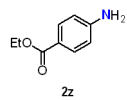
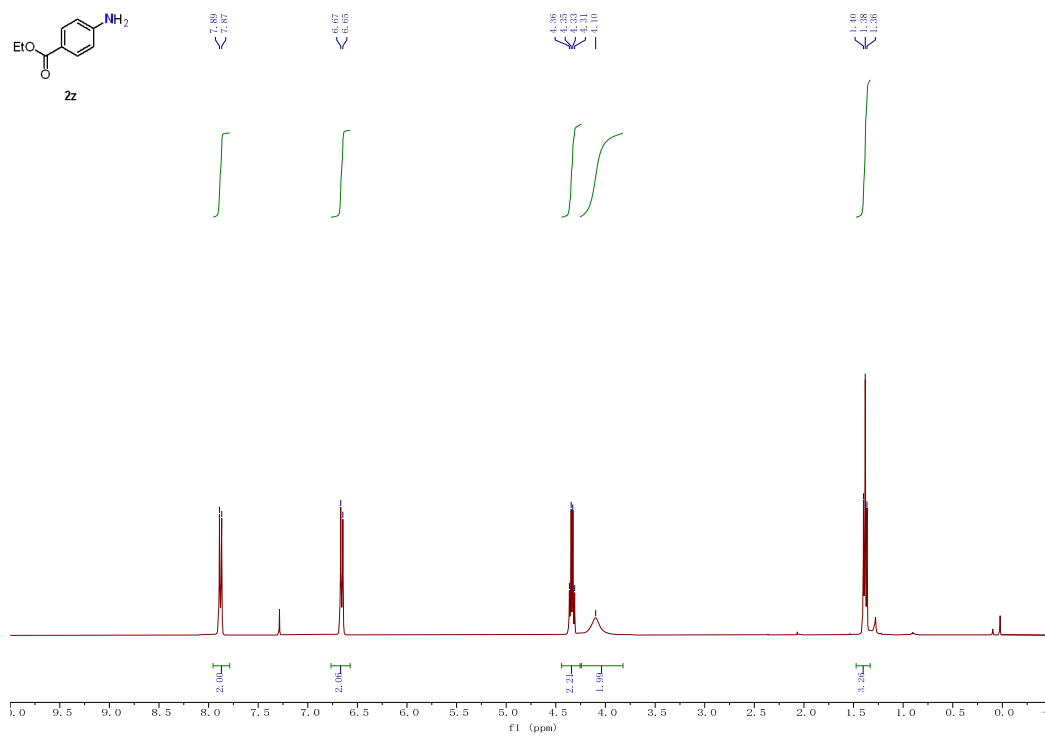
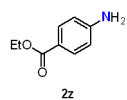
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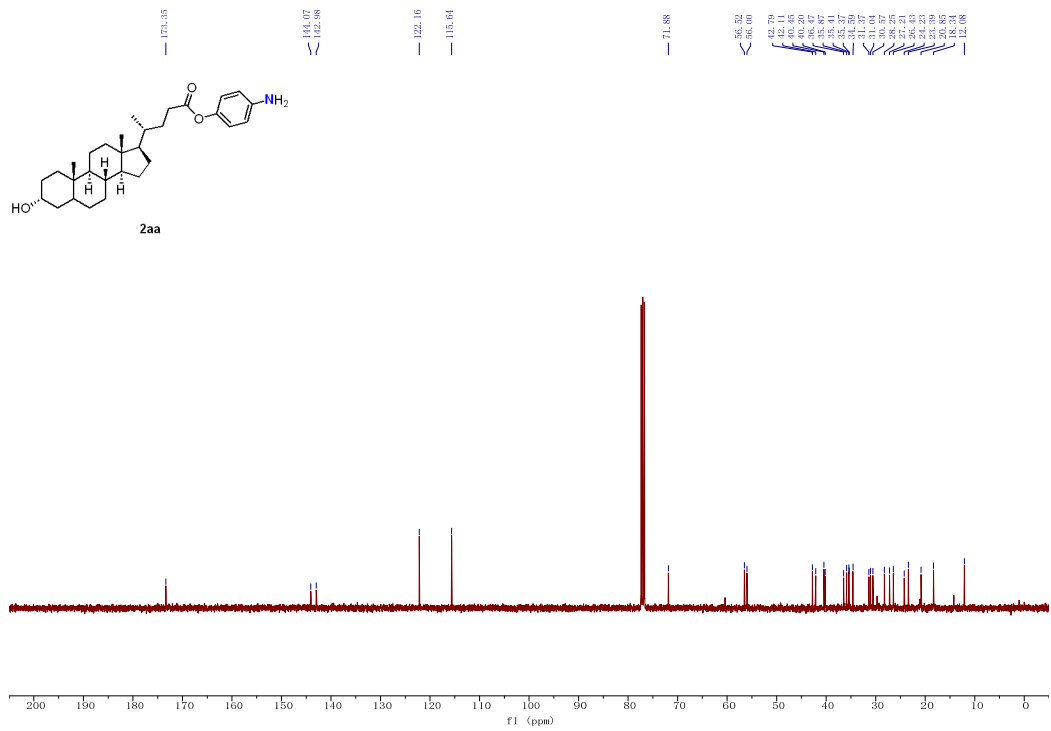
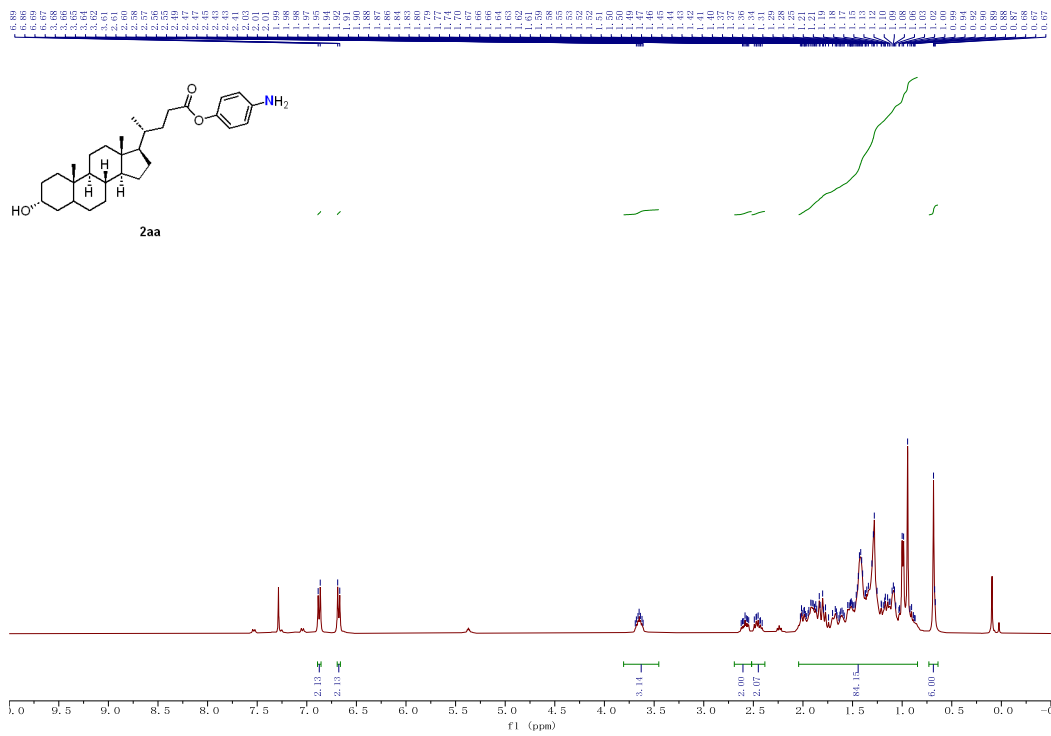
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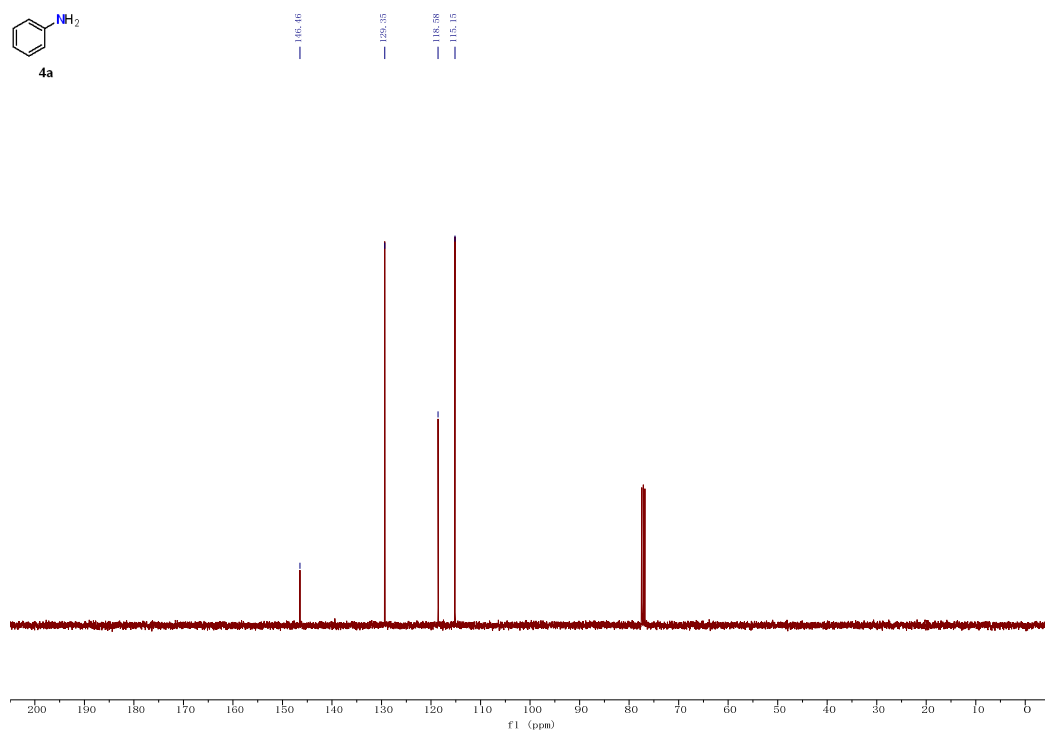
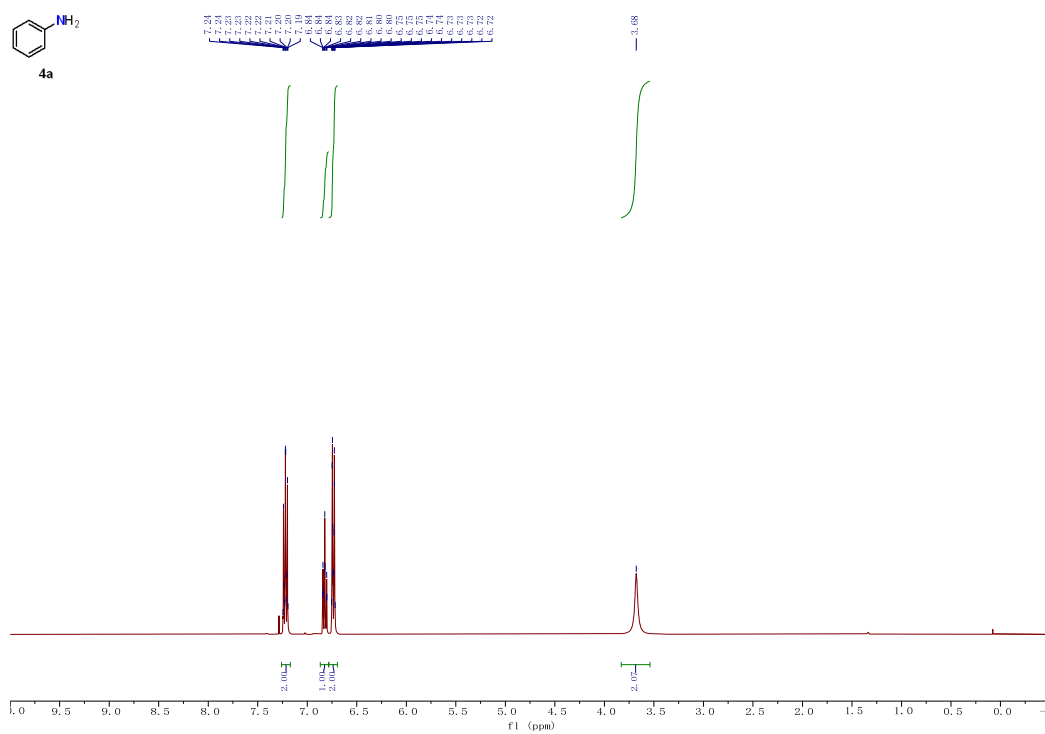
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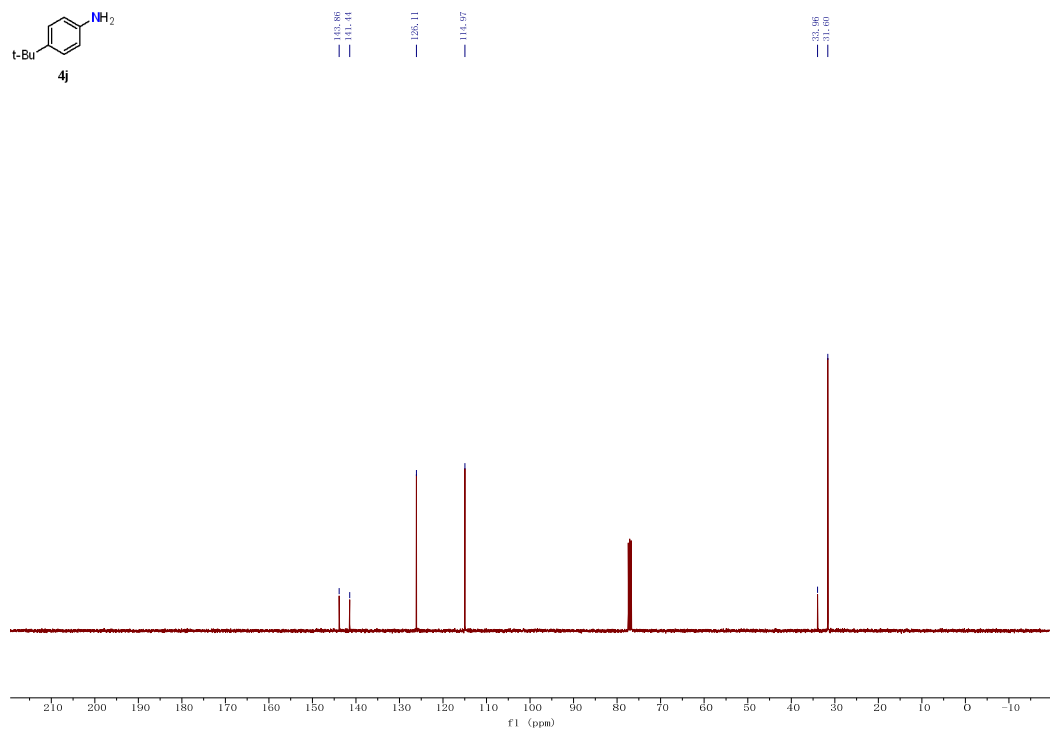
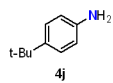
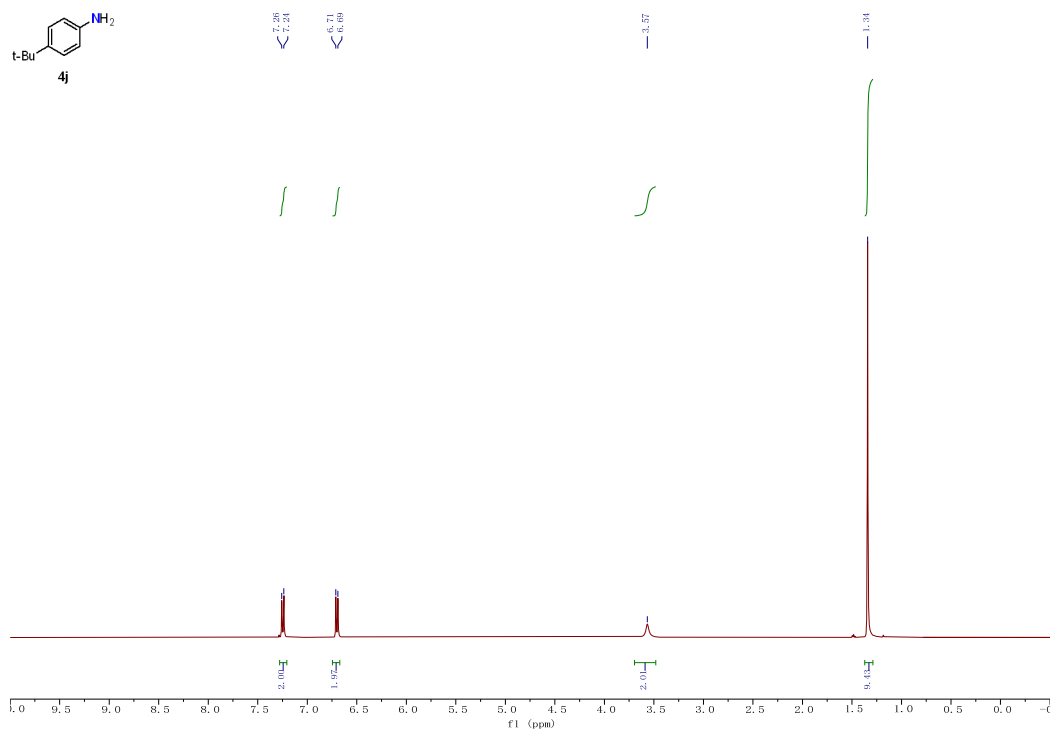
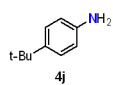
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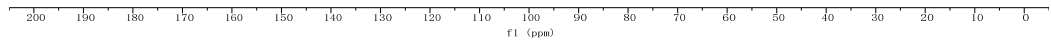
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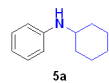
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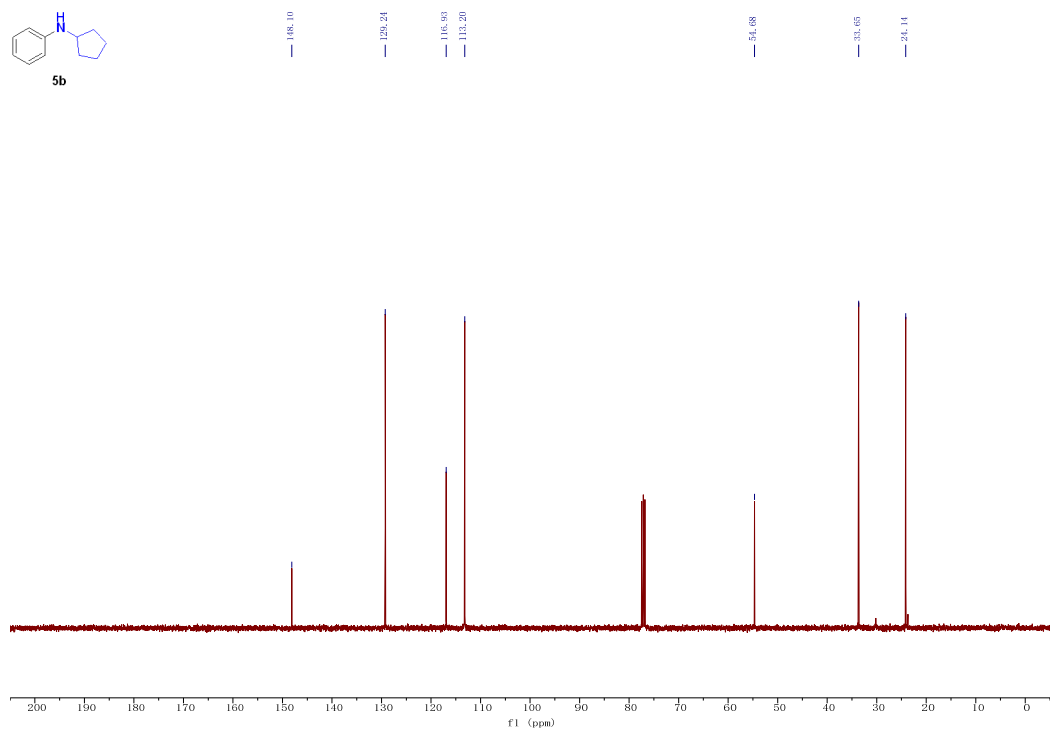
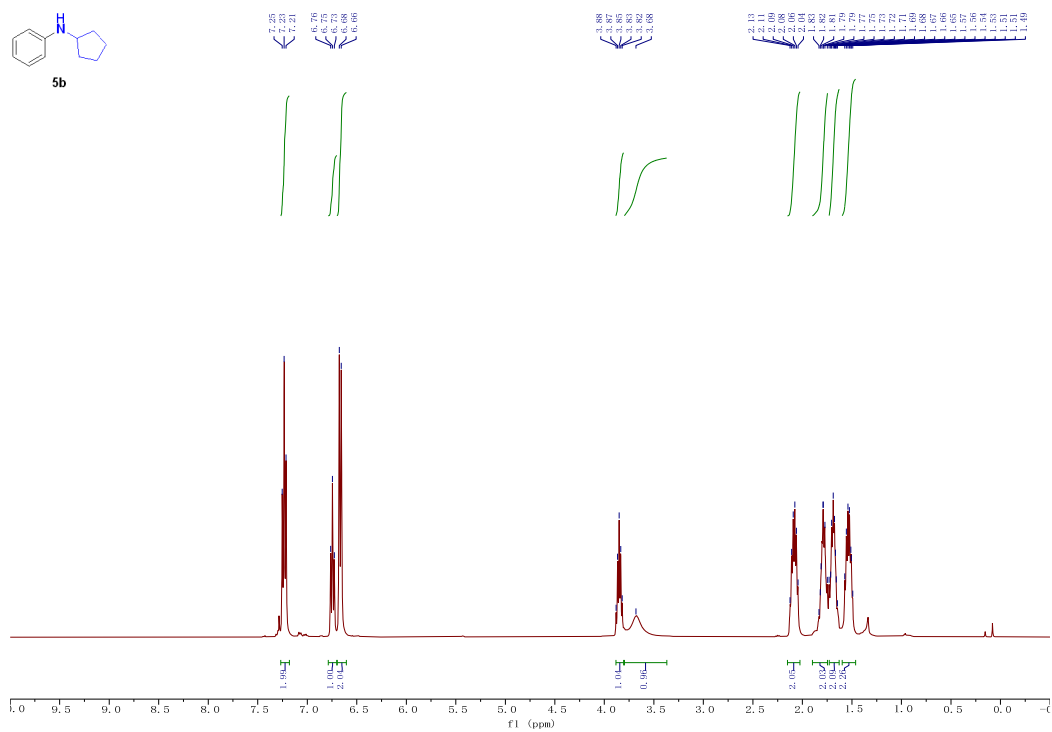


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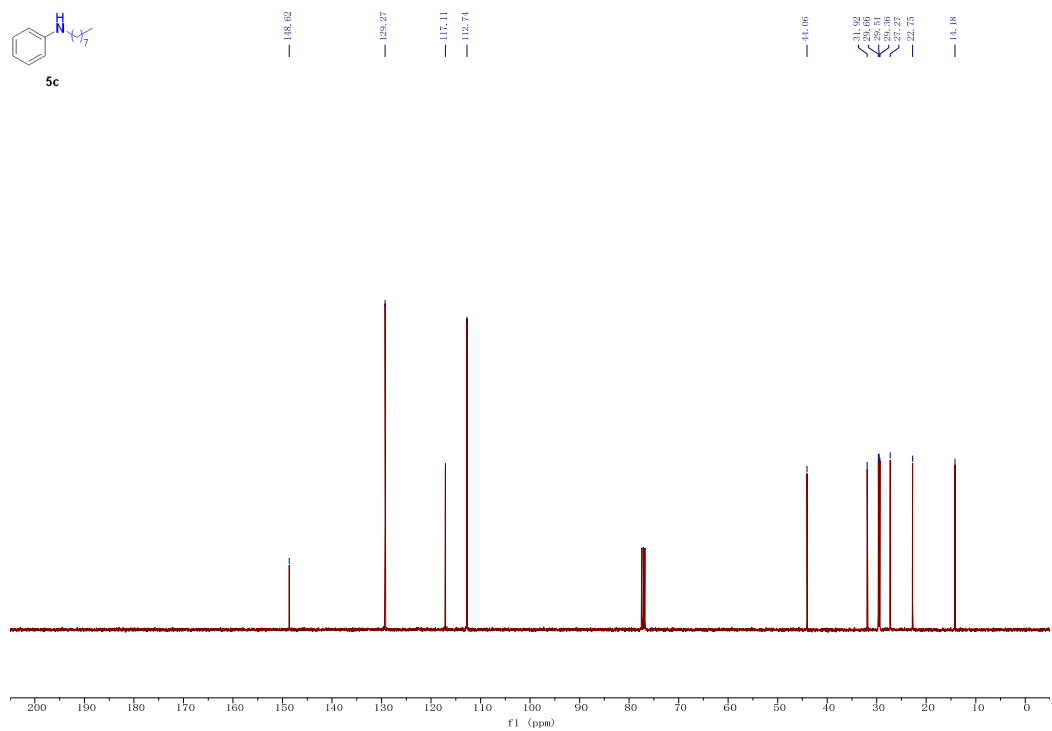
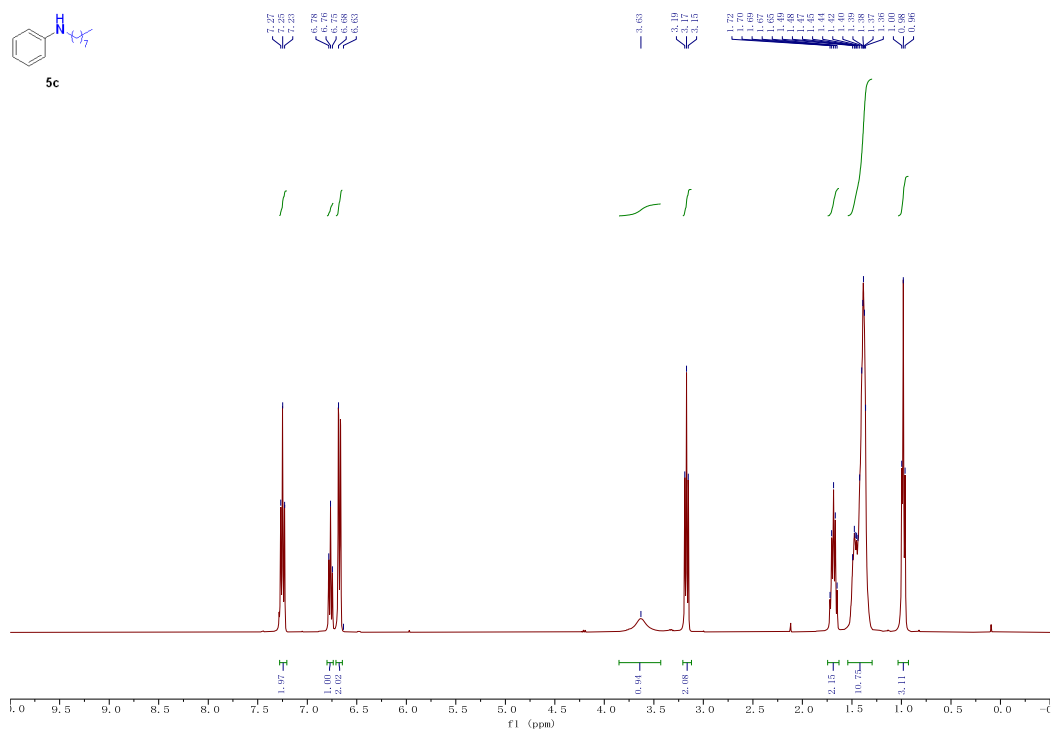
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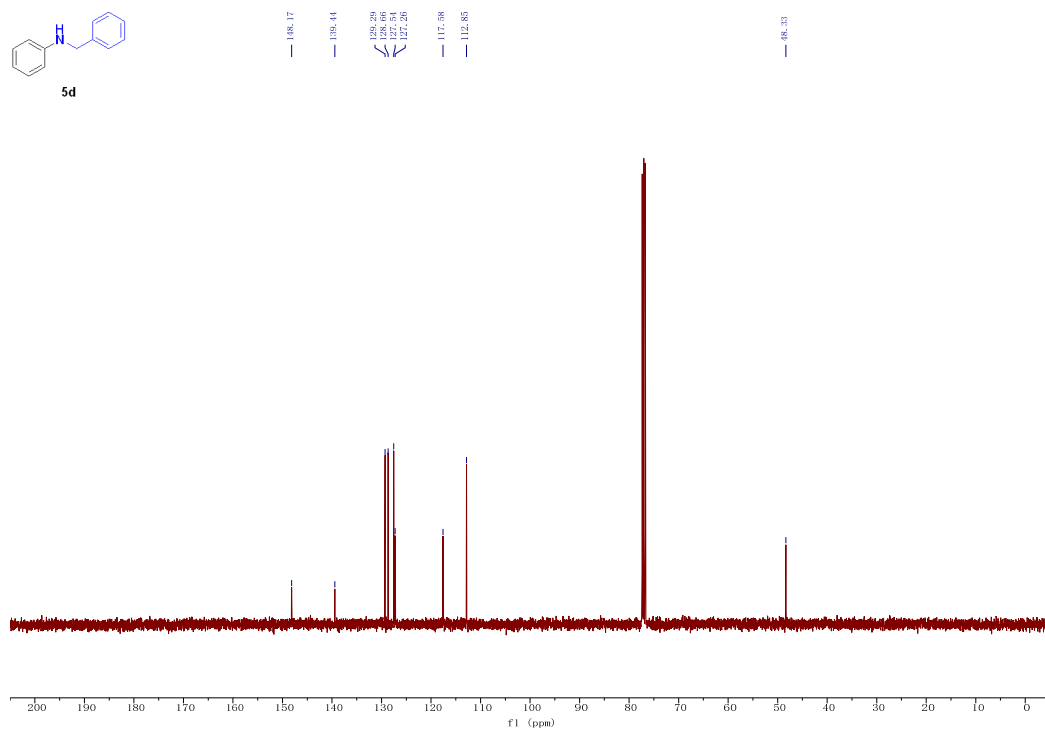
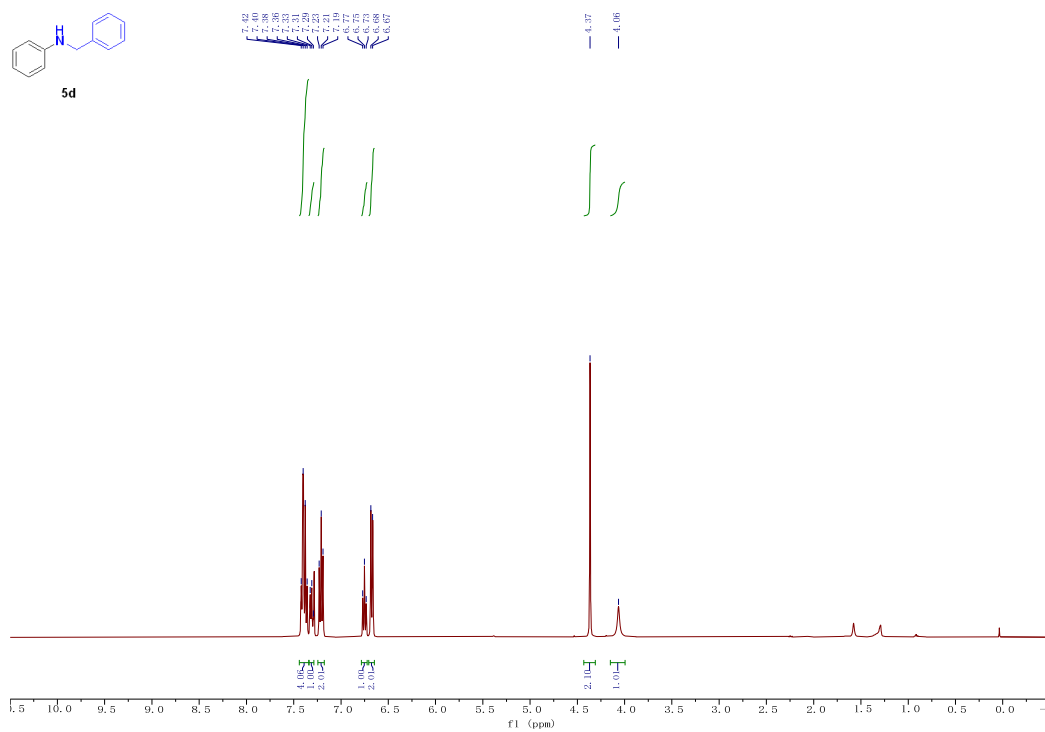
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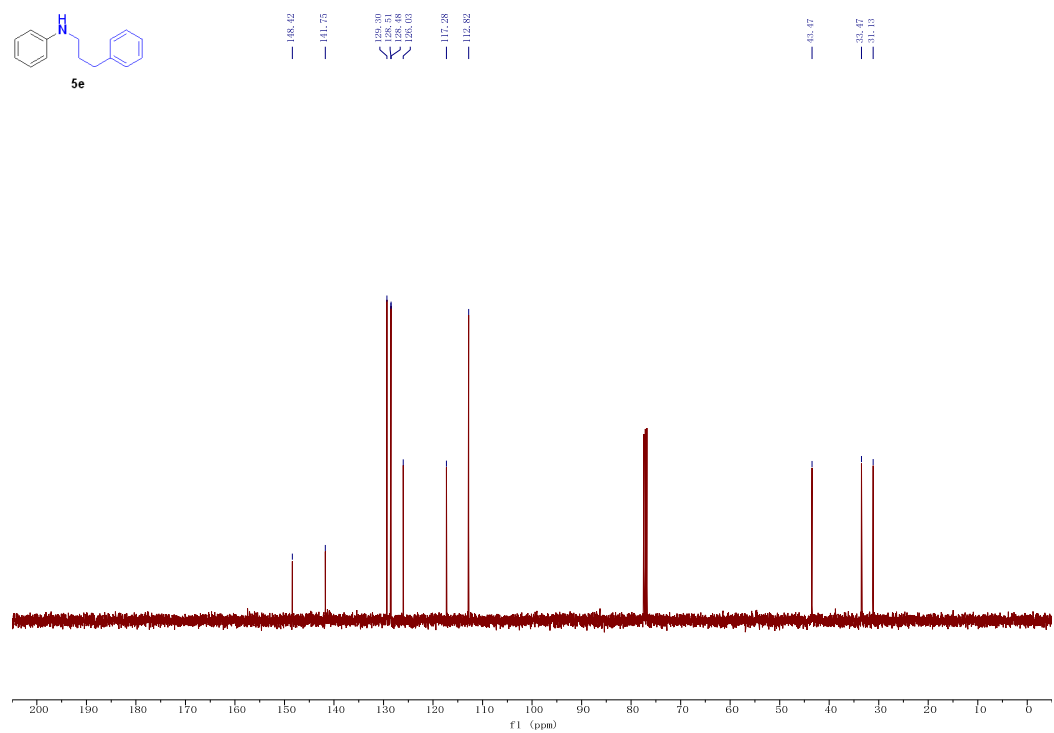
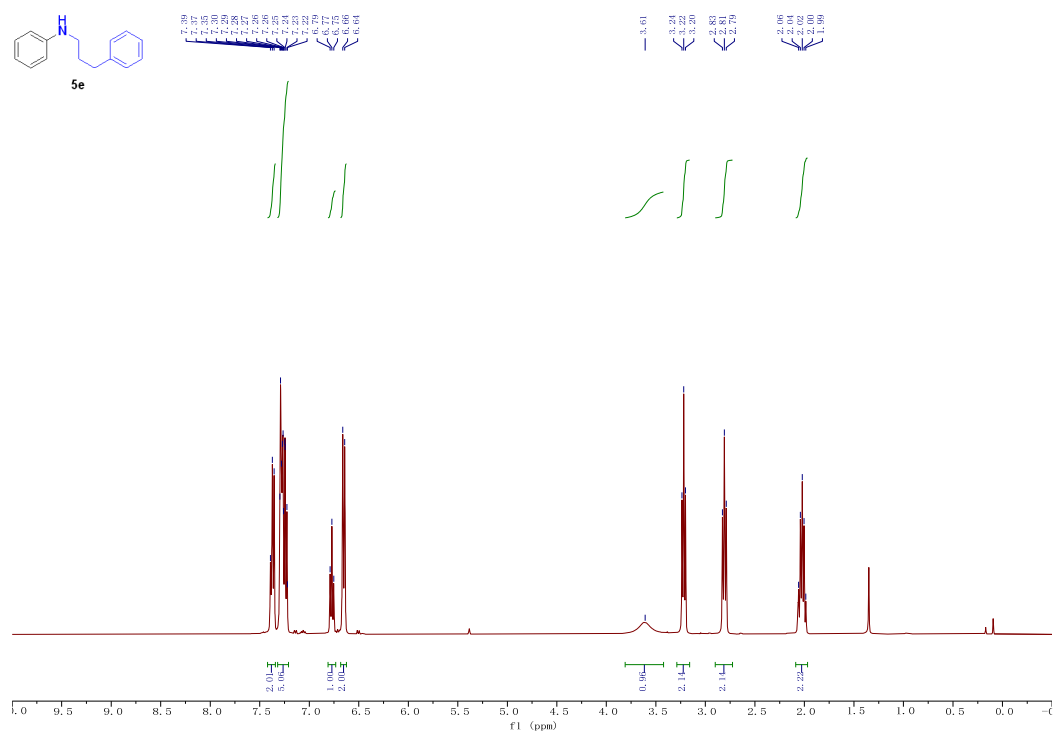
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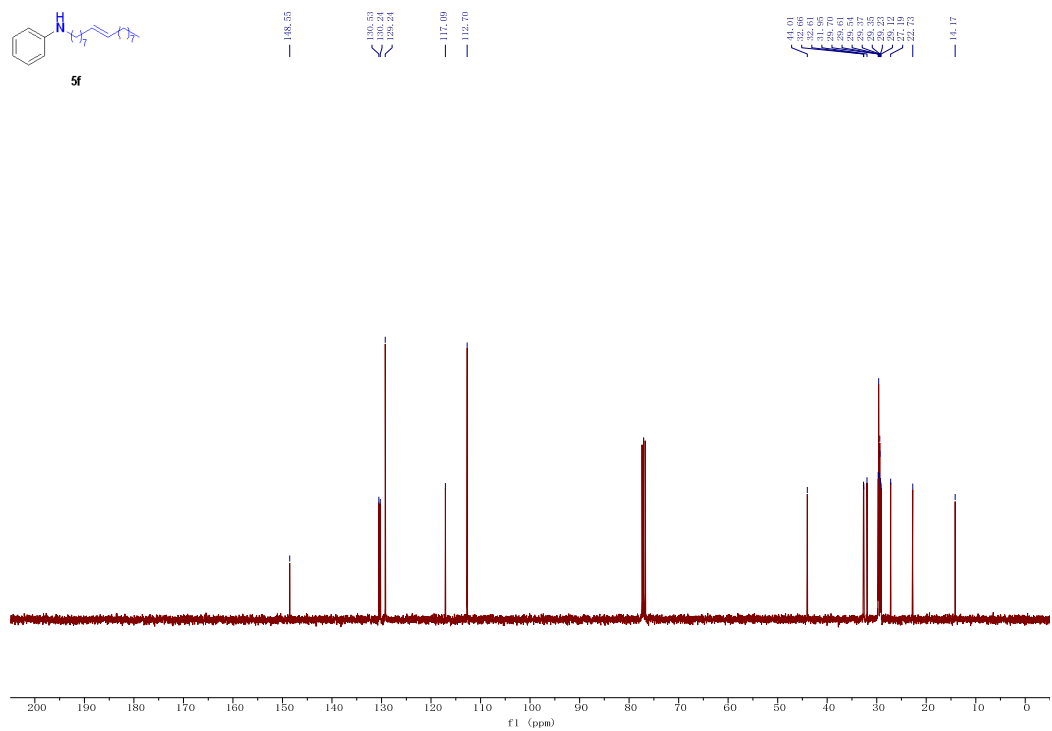
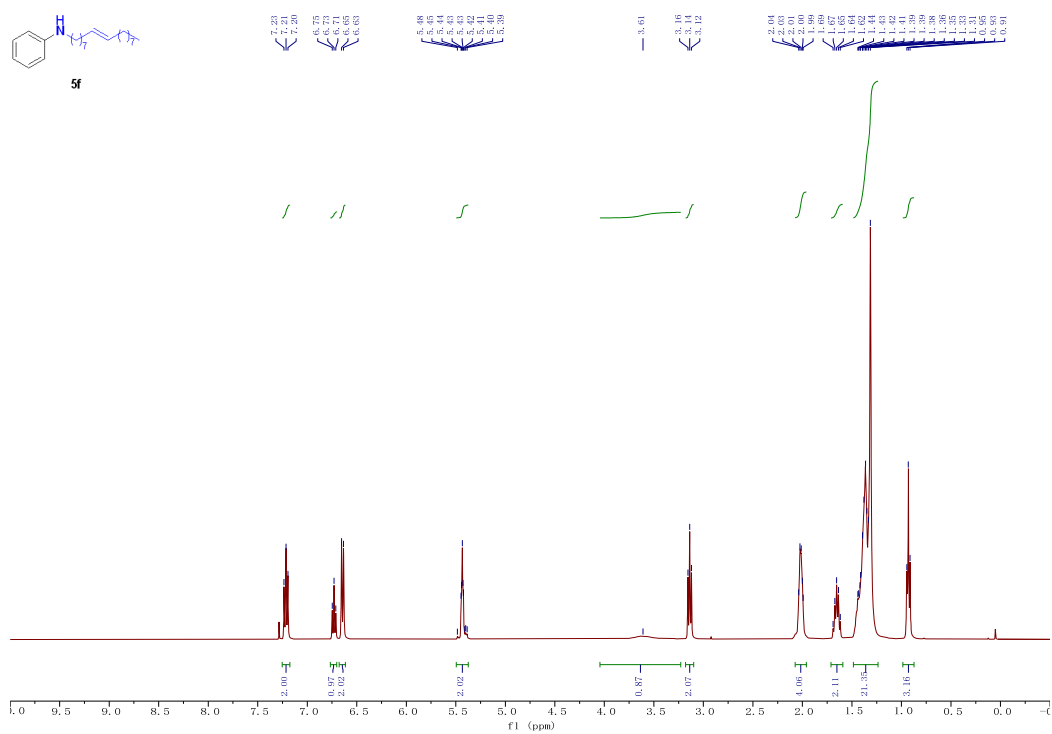
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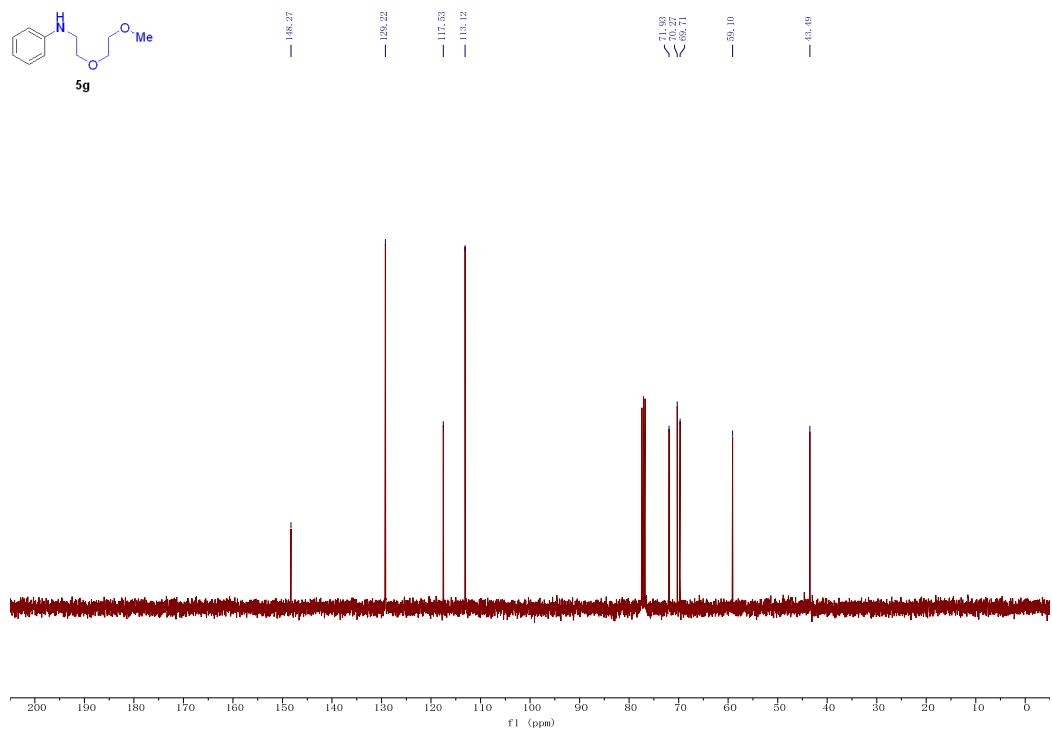
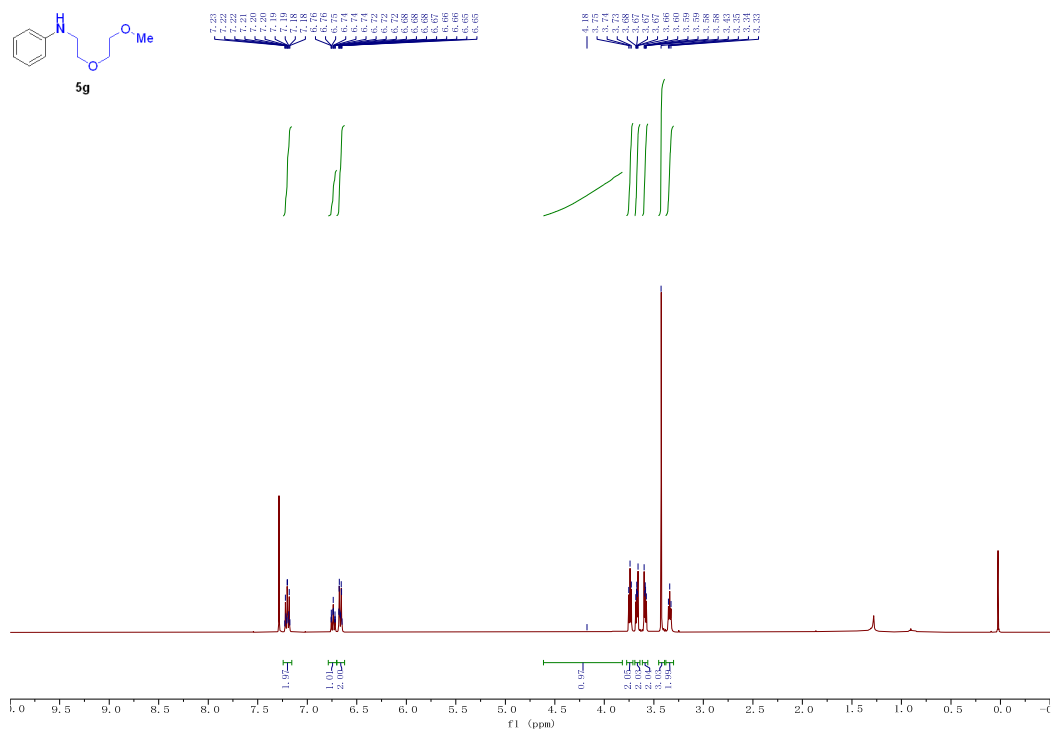
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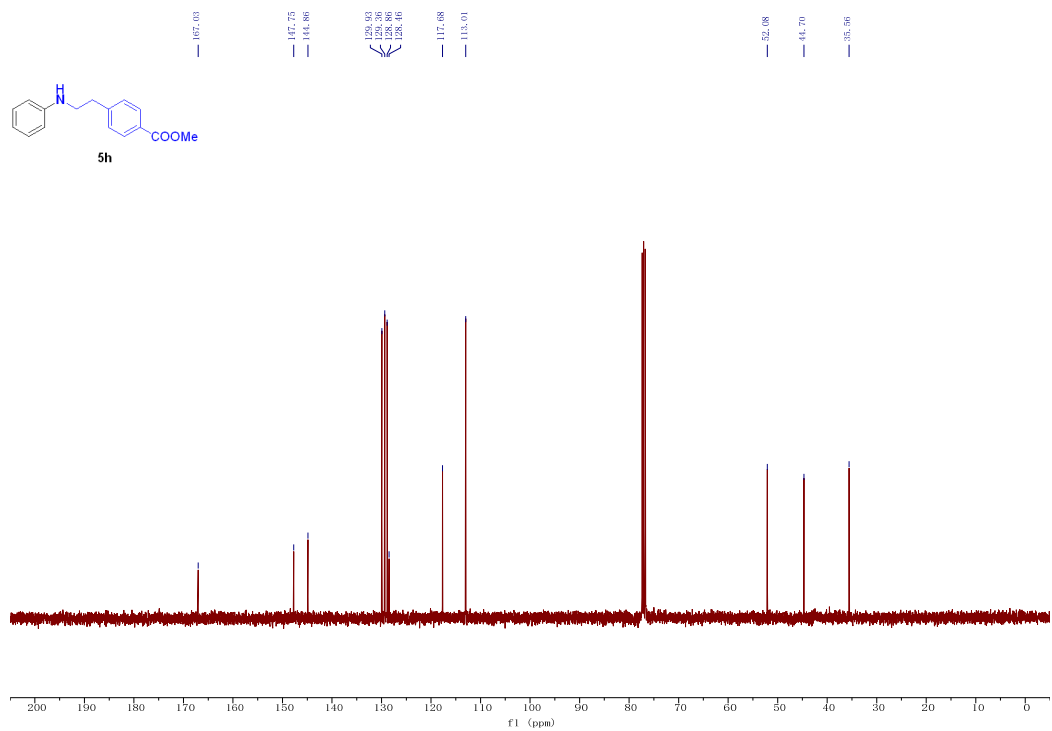
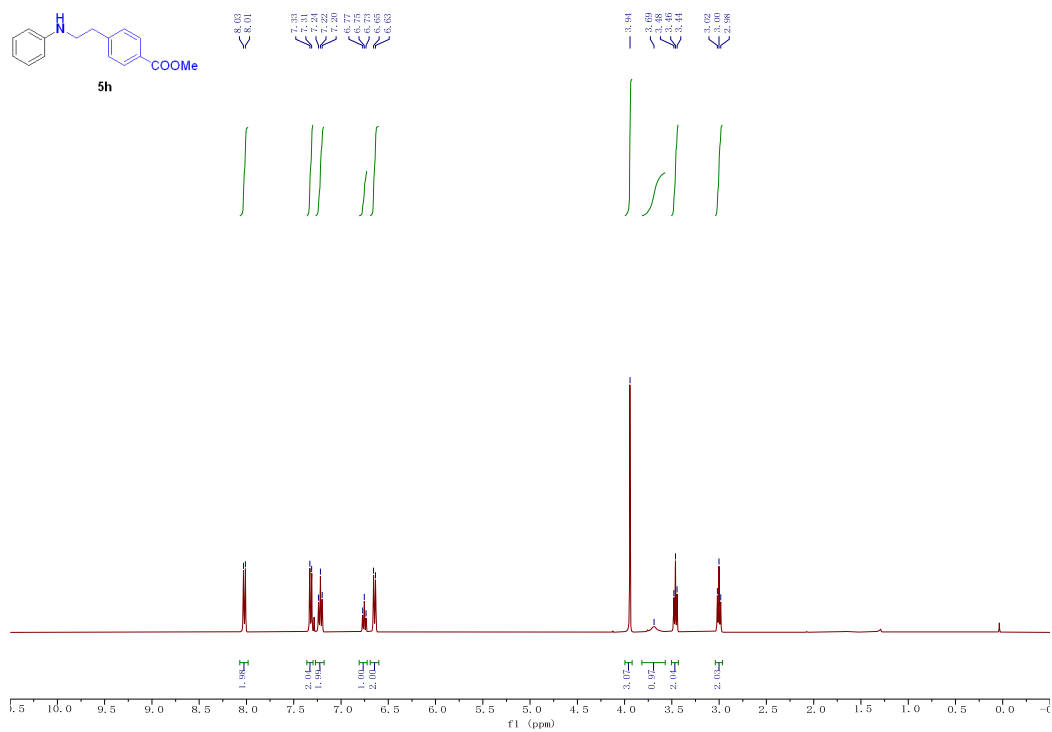
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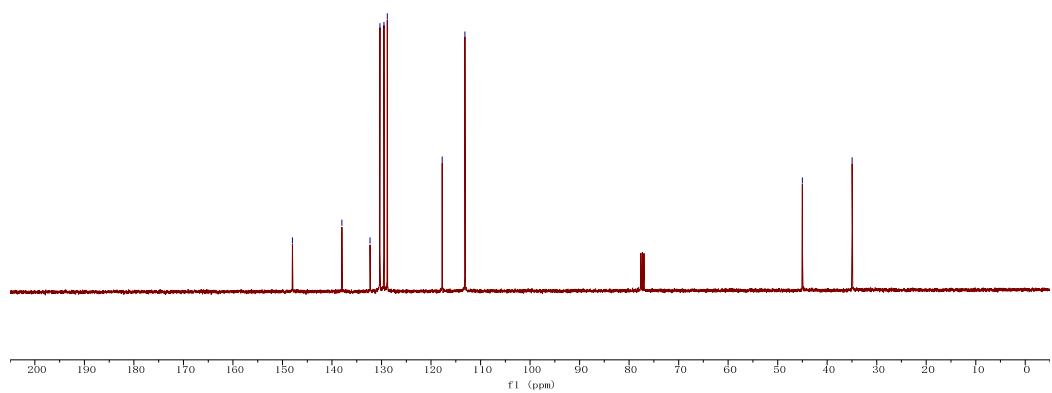
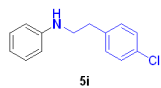
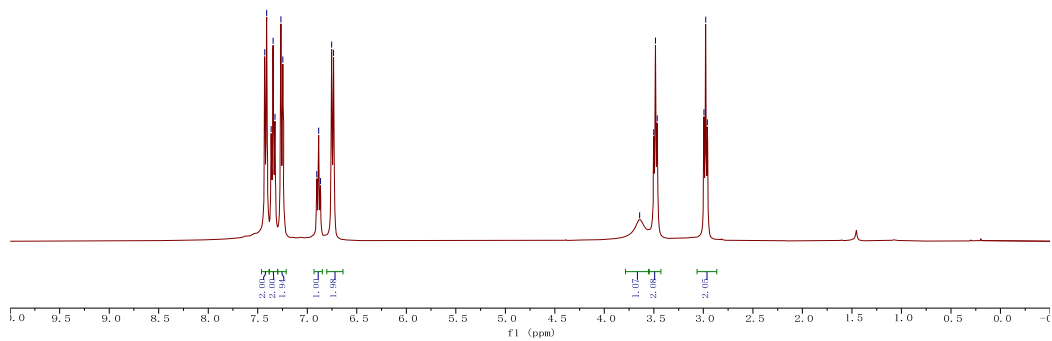
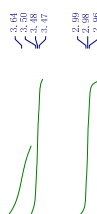
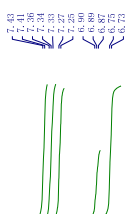
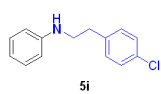
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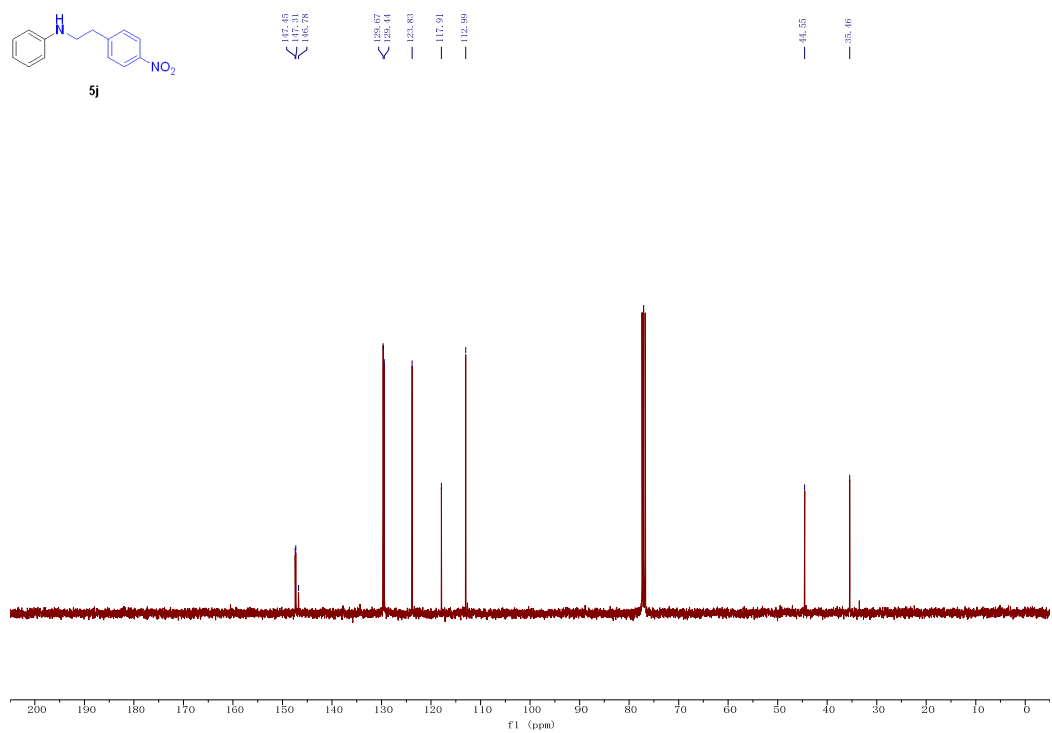
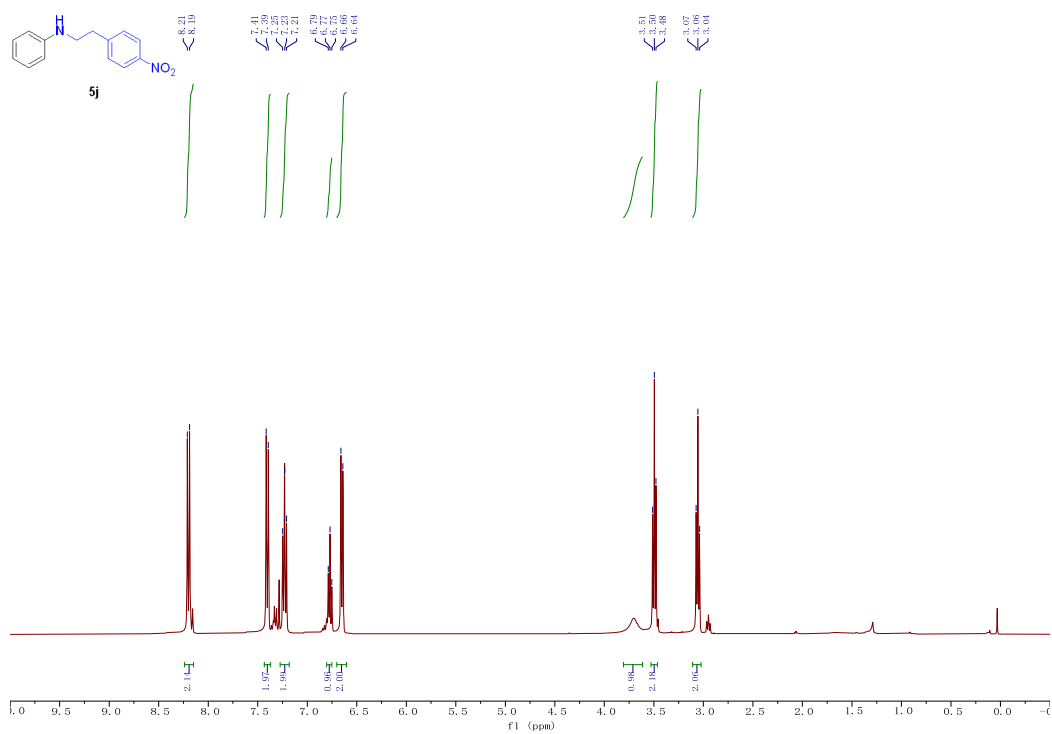
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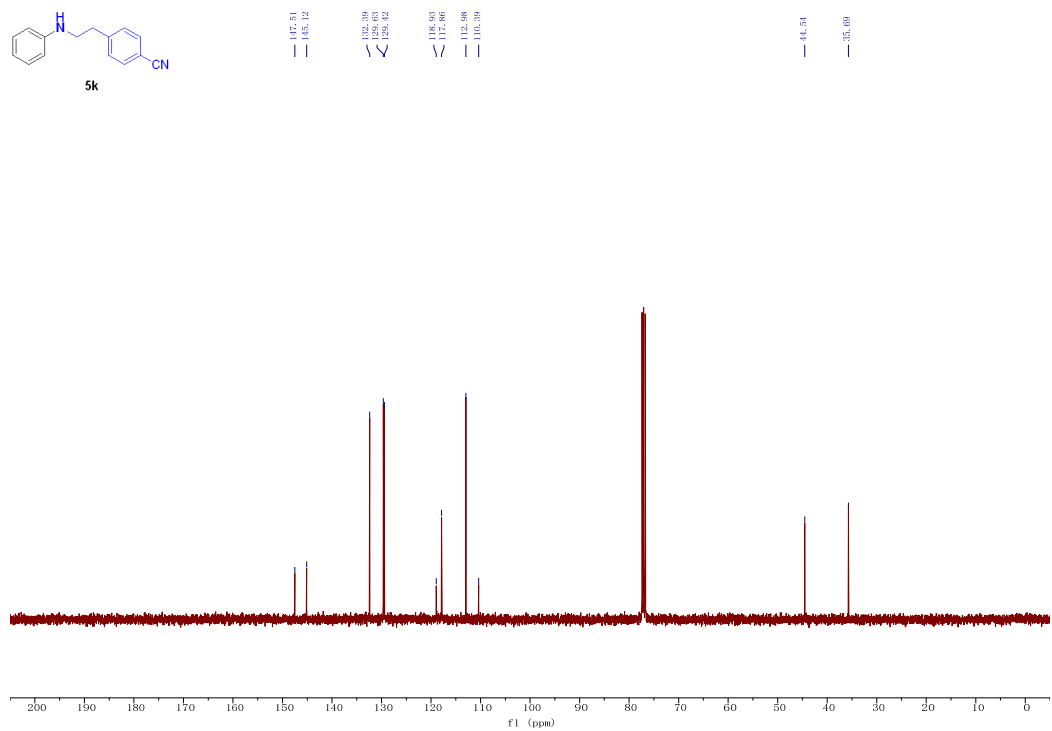
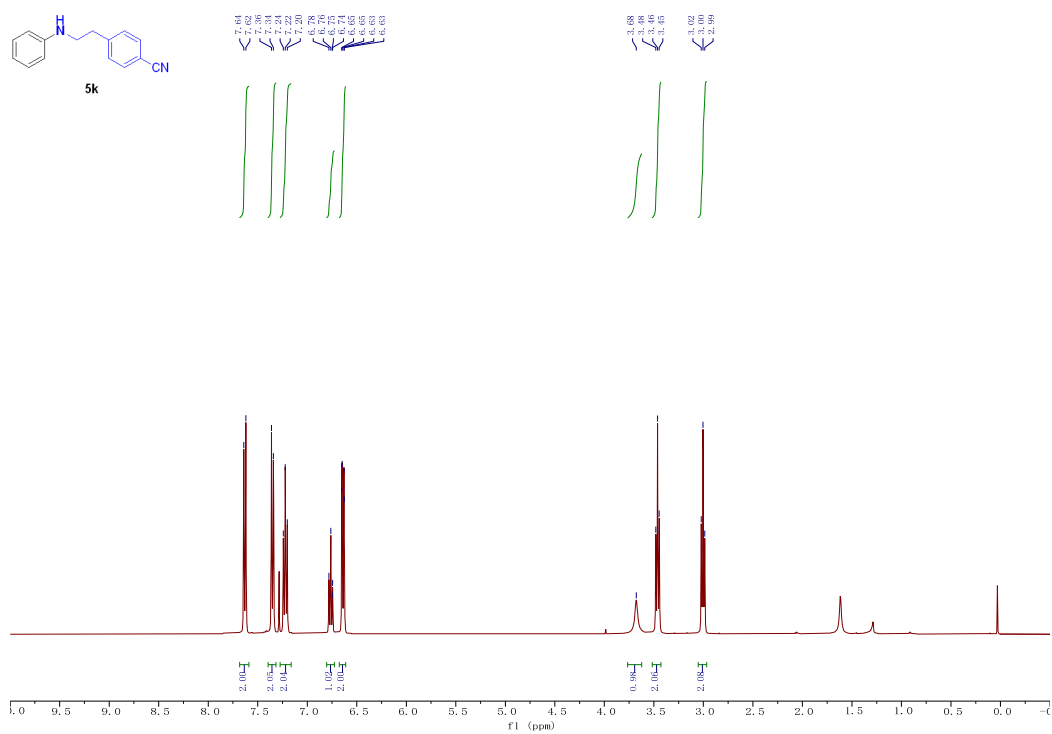
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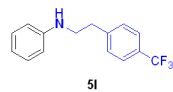


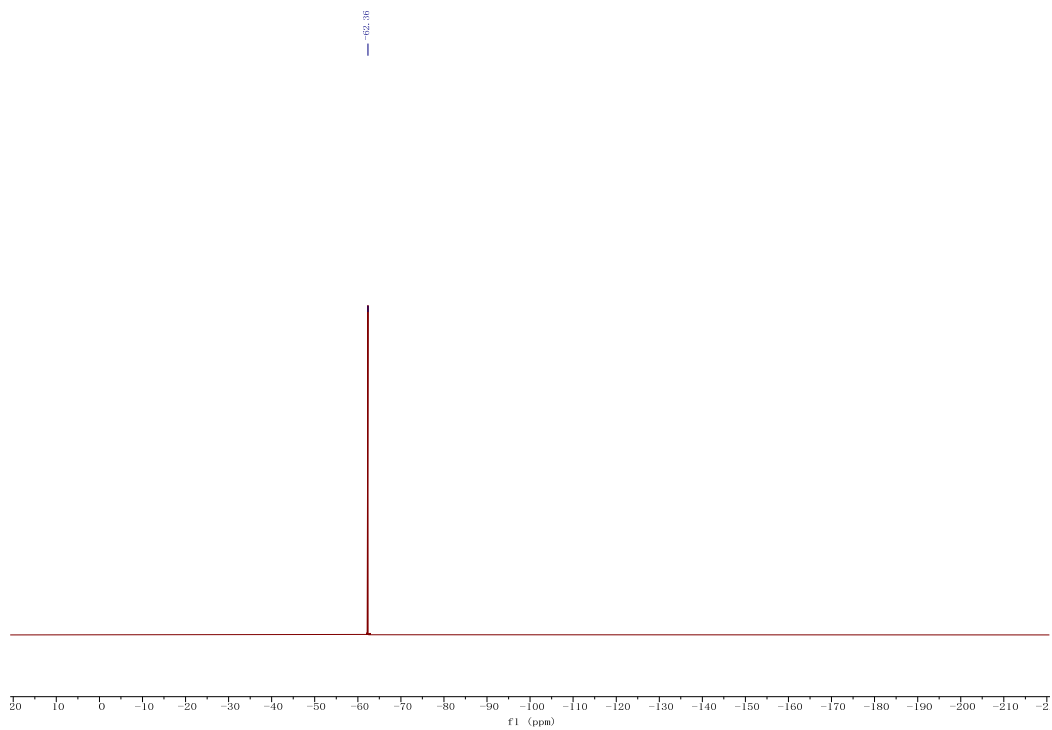
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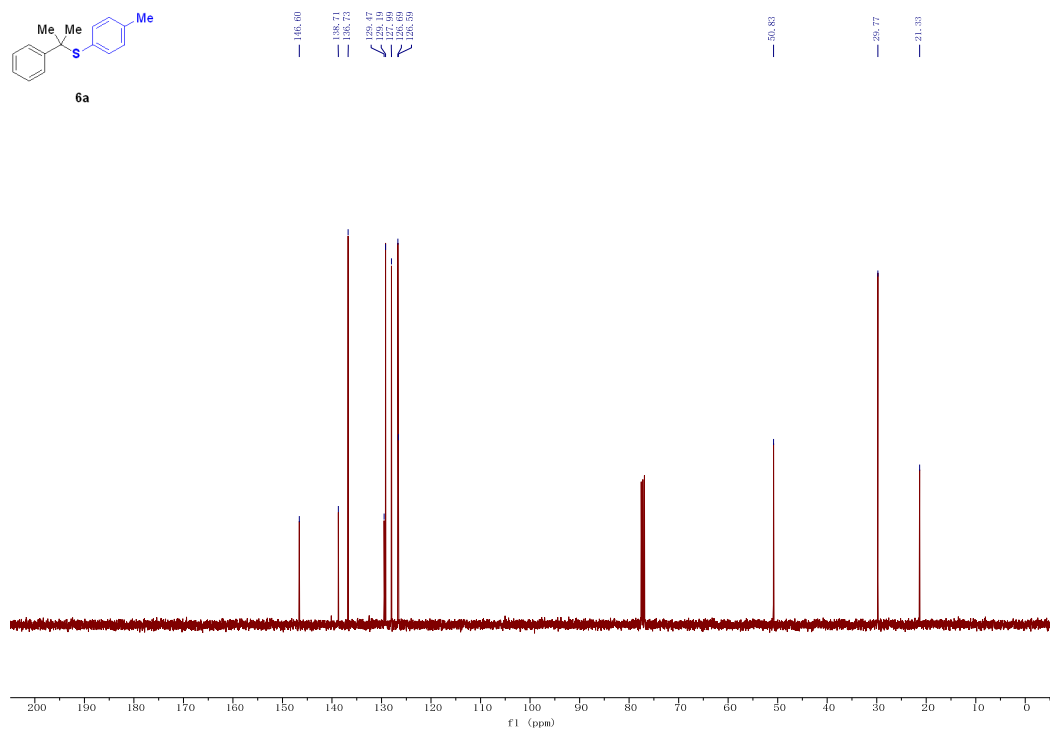
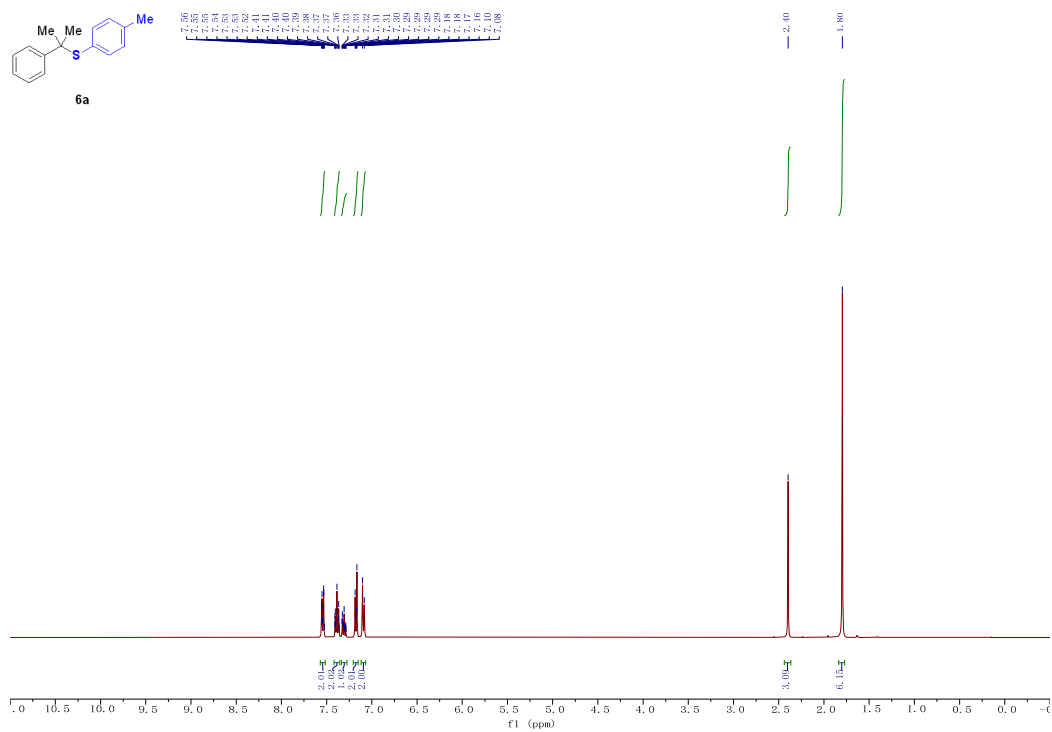
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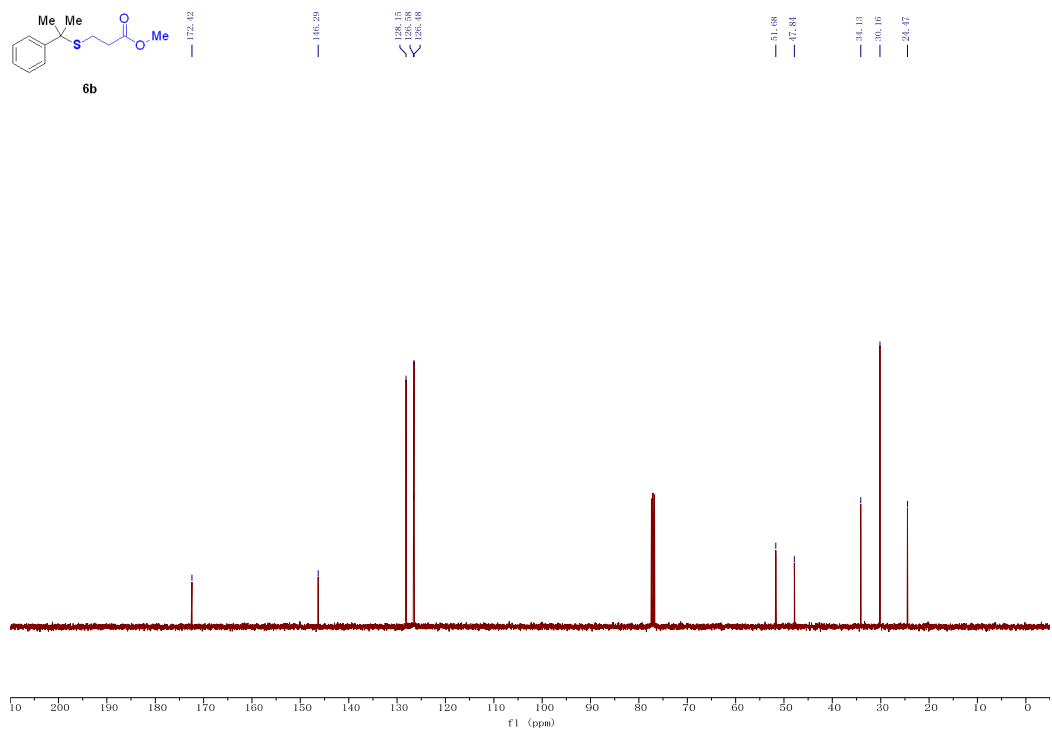
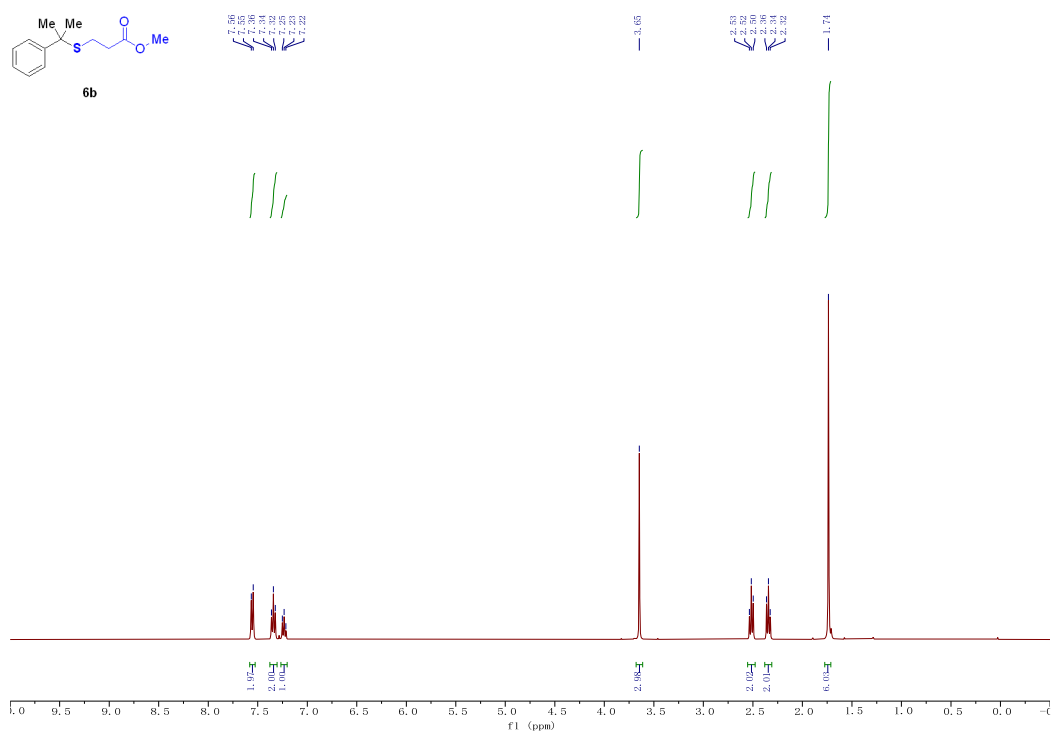




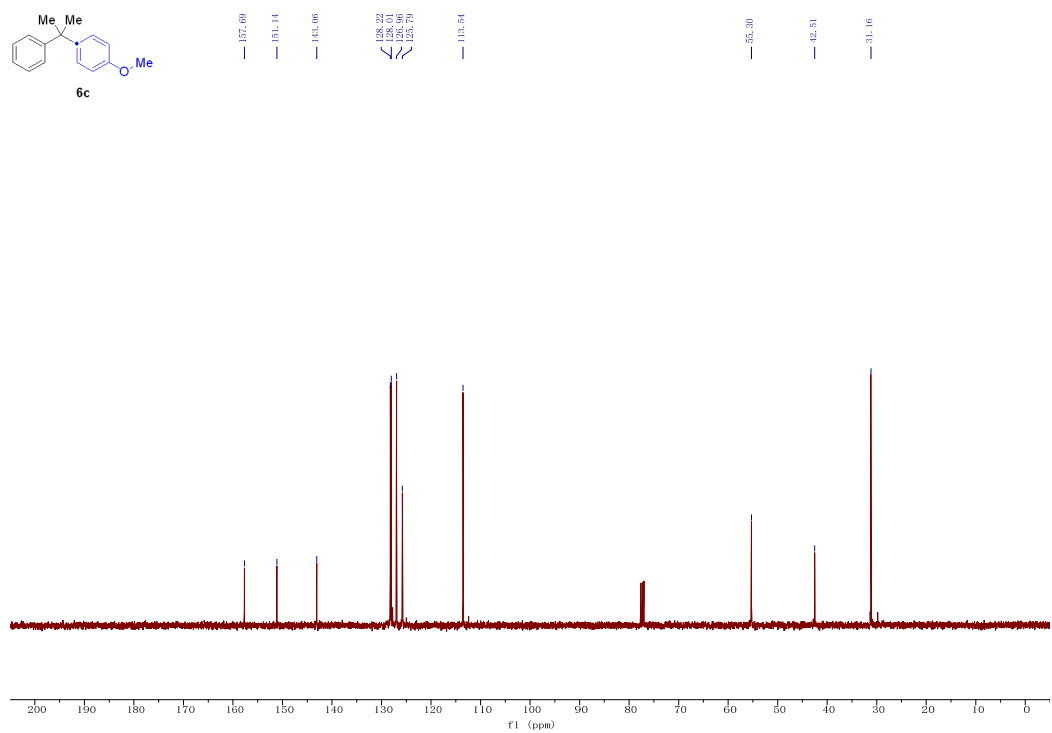
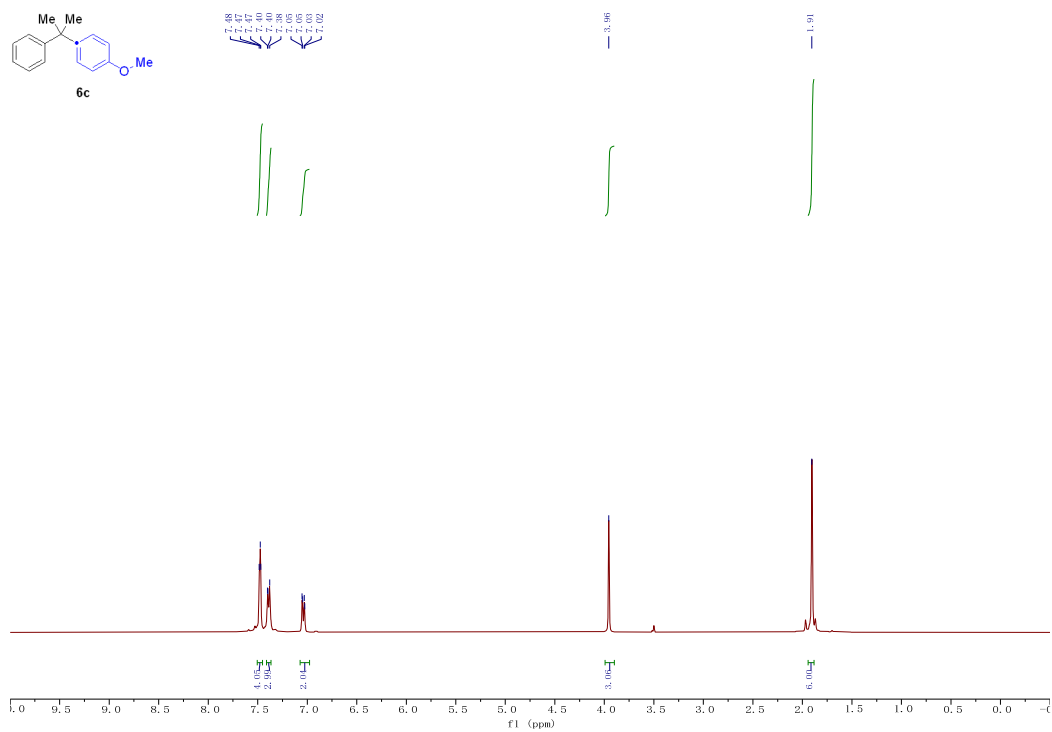
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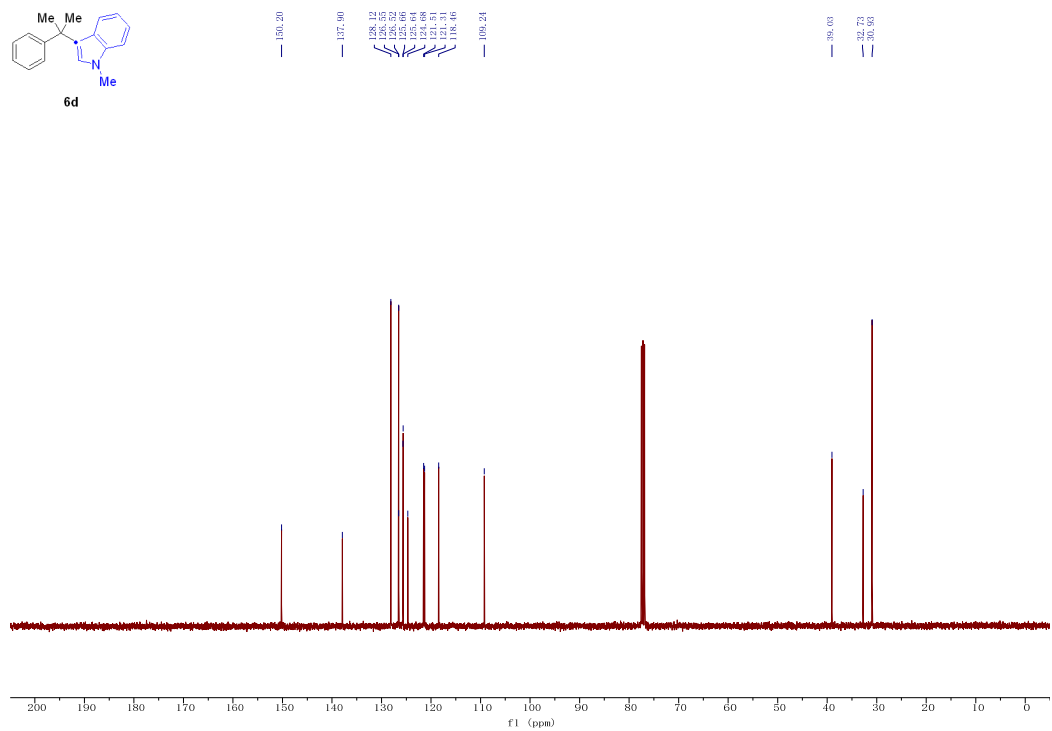
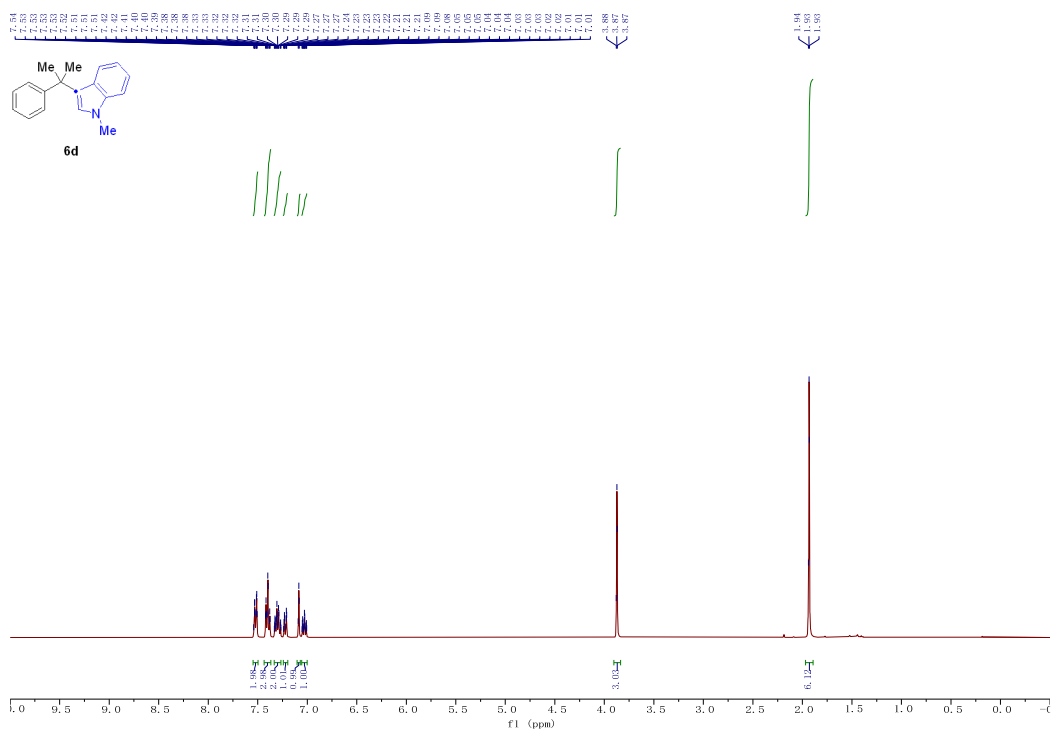
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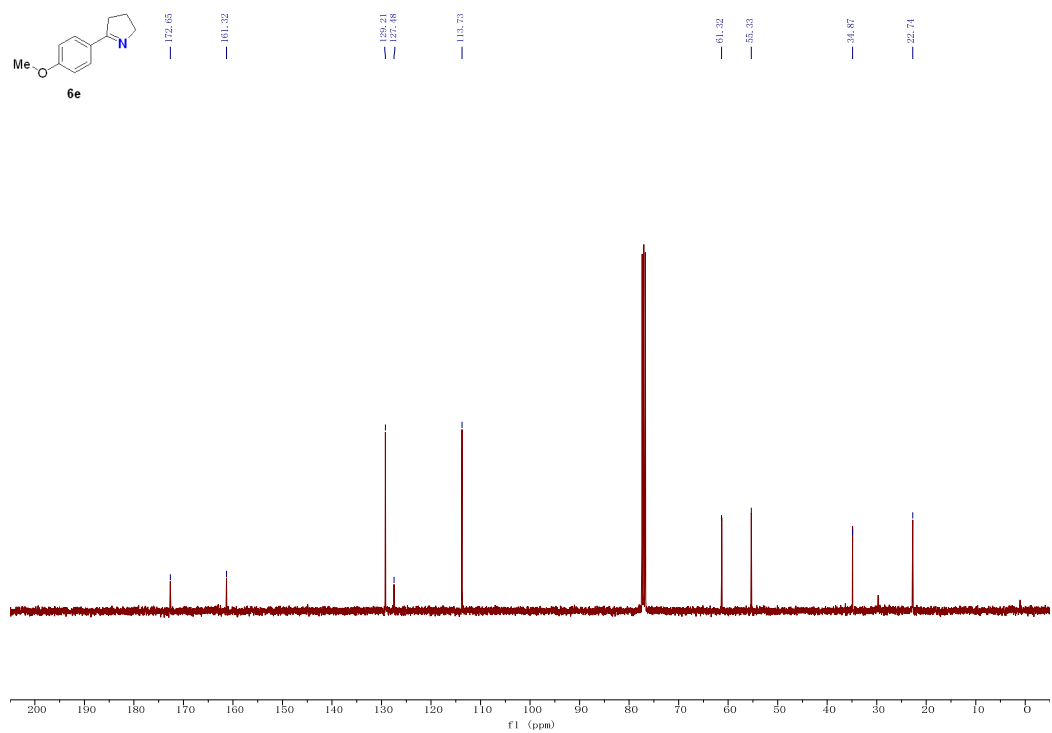
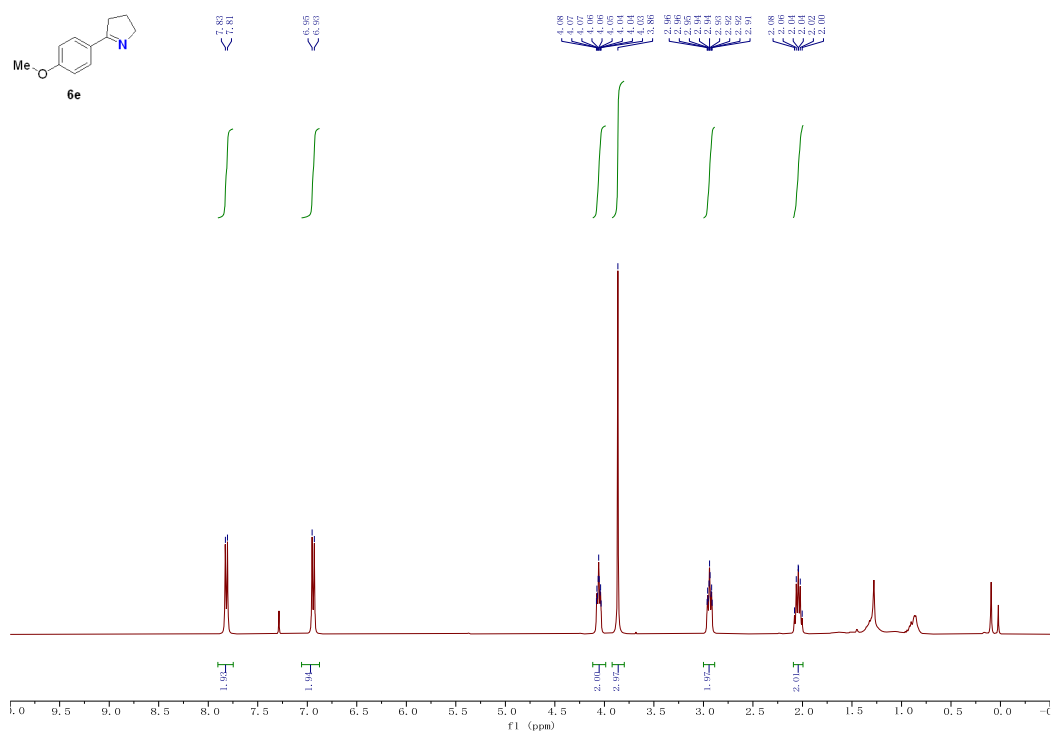
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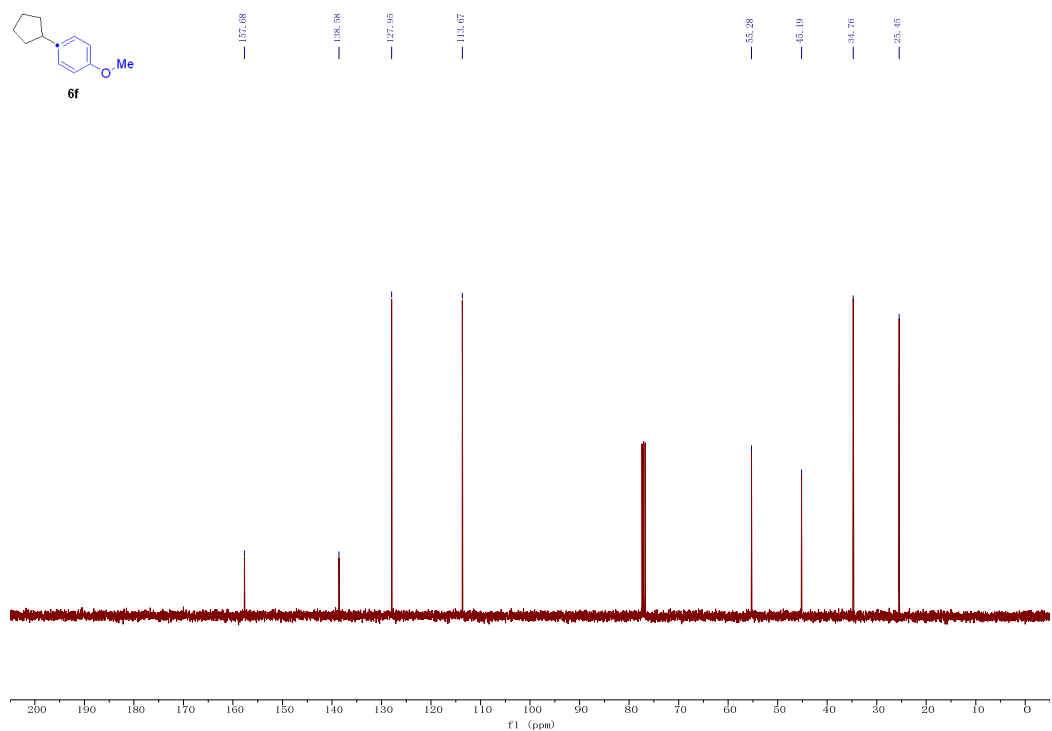
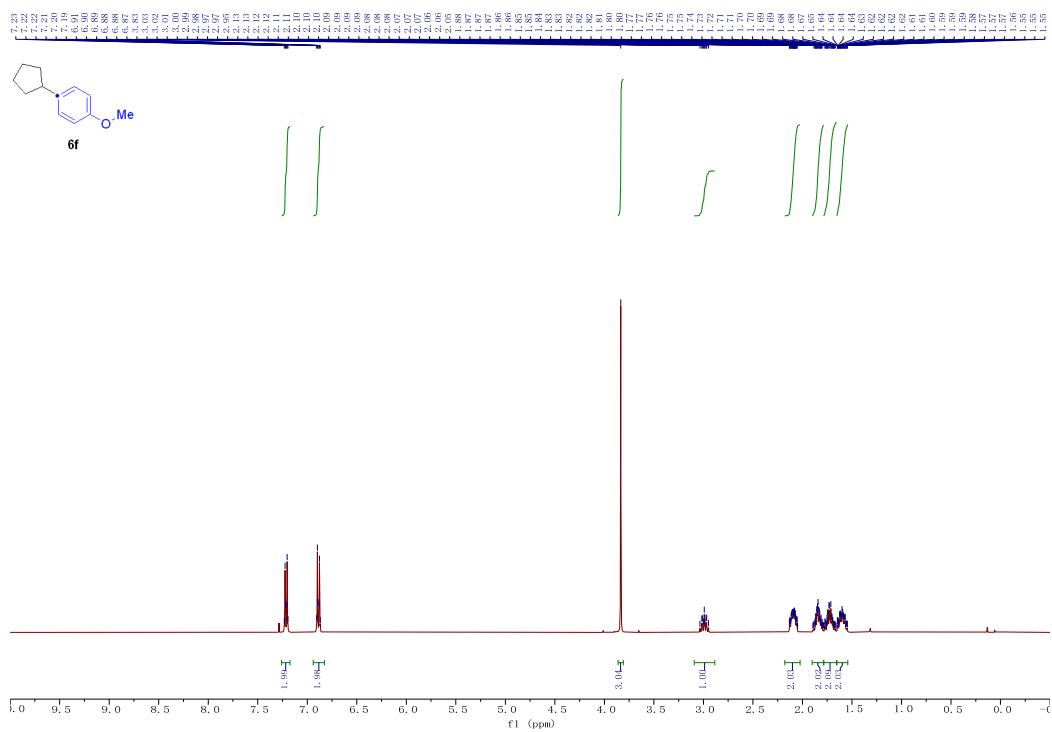
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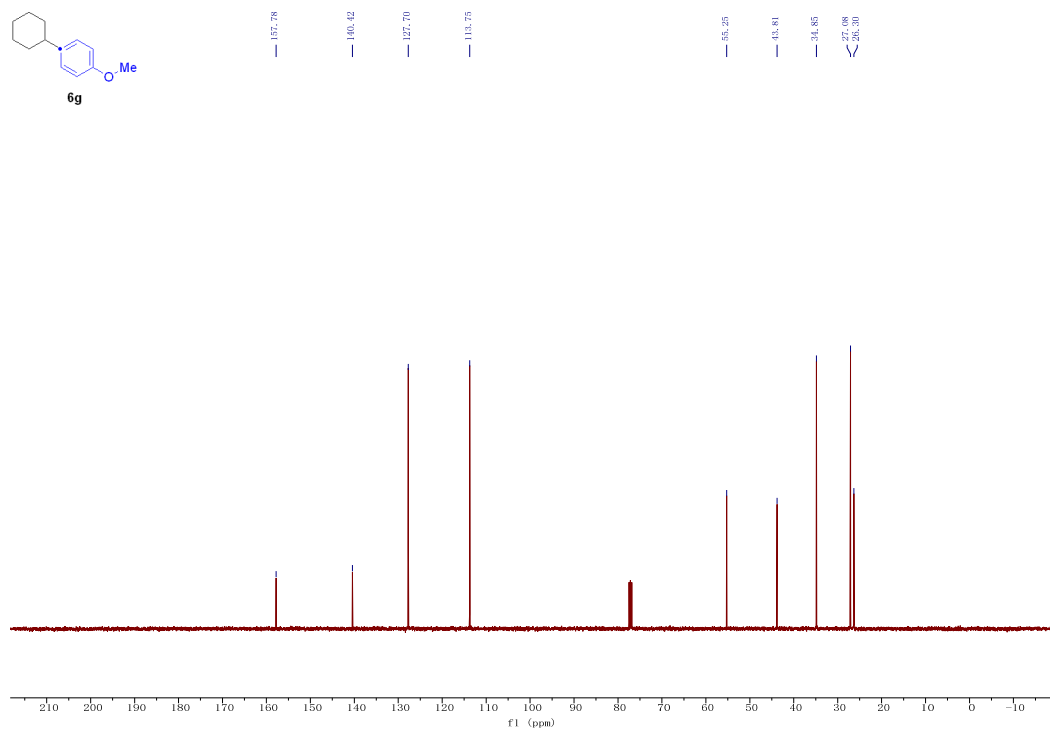
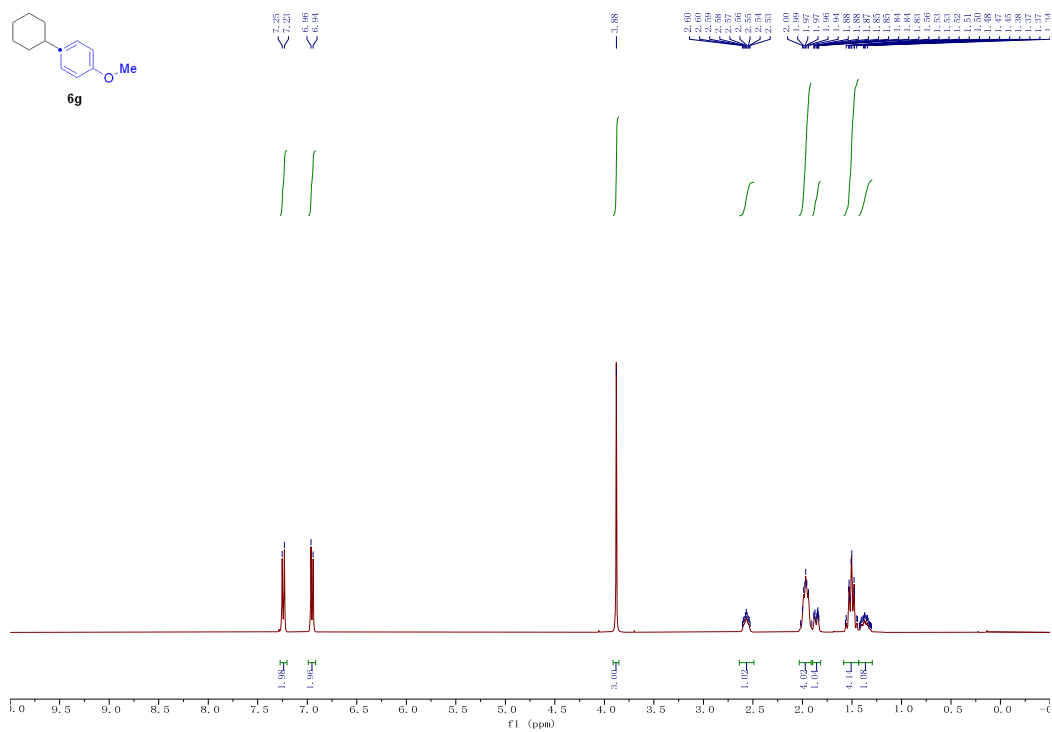
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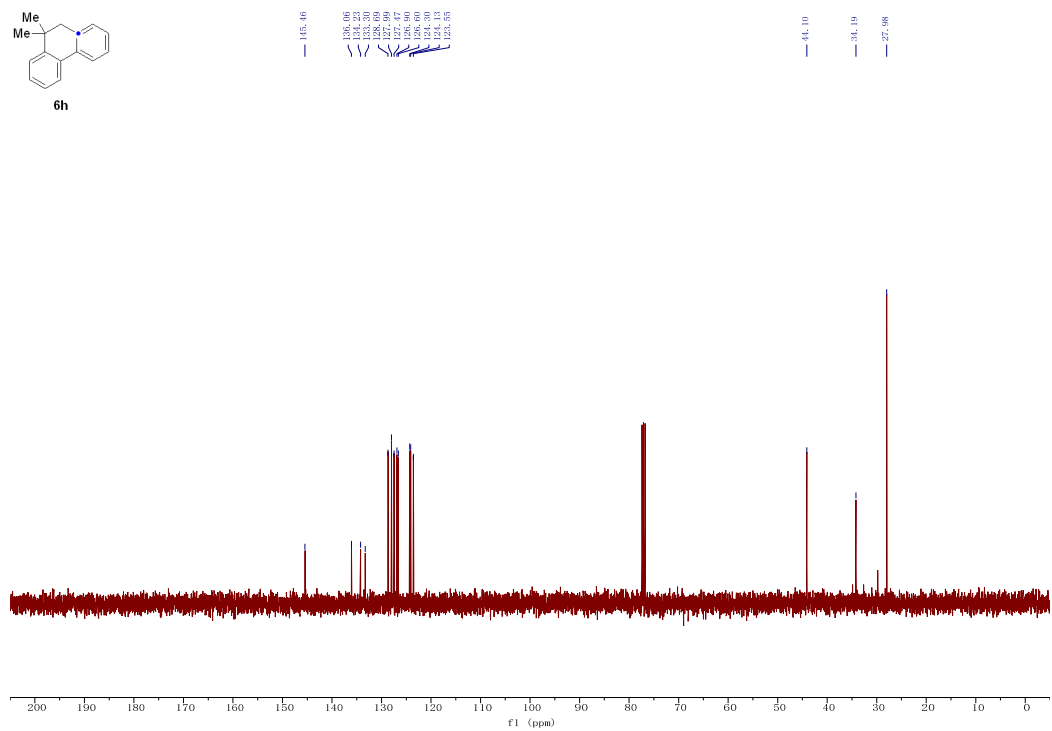
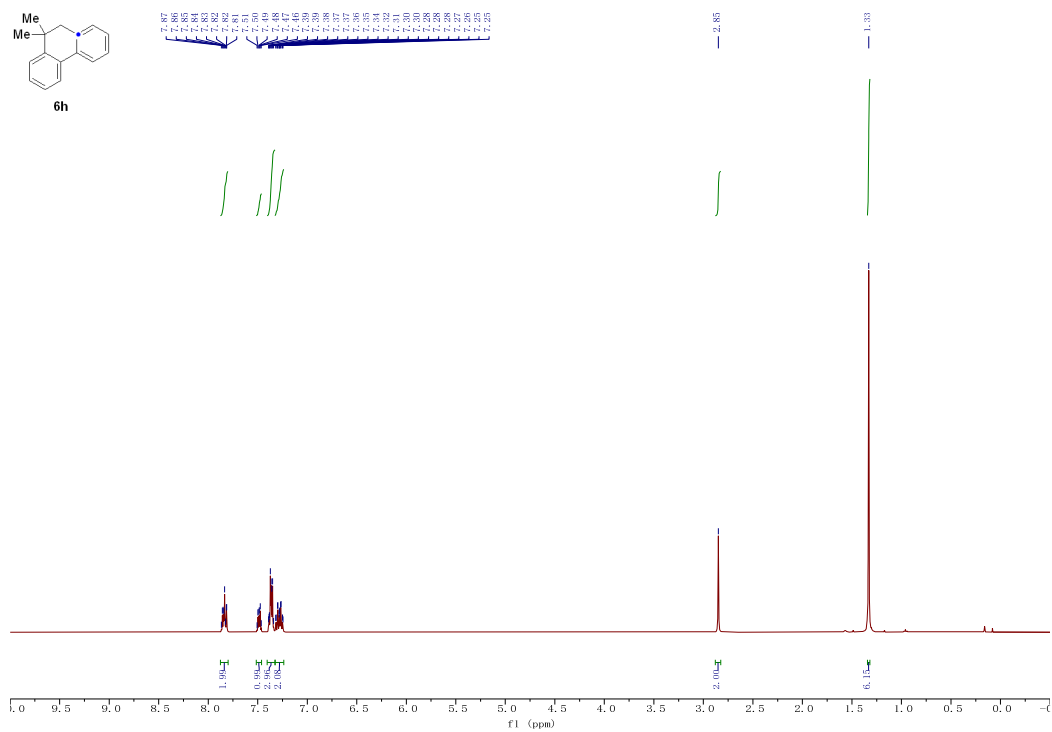
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6h



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