Electrochemical four-component aminochlorination tuned by benzimidazoles

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Supporting Information

Table of Contents

1. General Information

^{1}H NMR and ^{13}C NMR were recorded on a Bruker 400 MHz and 600 MHz spectrometer (^{1}H NMR: 400MHz, ^{13}C NMR: 100MHz, 150MHz). The chemical shifts (δ) and coupling constants (*J*) were expressed in ppm and Hz respectively. ^{1}H NMR spectra were referenced to the solvent residual peak (TMS, δ 0 ppm) and ^{13}C{^{1}H} NMR spectra were referenced to the solvent residual peak ($CDCl_3$, δ 77.0 ppm). High Resolution mass spectra were obtained using ThermoFisher LTQ Orbitrap XL mass spectrometer. Cyclic voltammograms were recorded on electrochemical workstation CHI660E (Shanghai CH Instruments Co., Ltd.). All solvents were purified and dried according to the standard procedures unless otherwise noted. Commercially substrates were purchased and used directly. Alkene substrates[1], cinnamates[2], **INT-1**[3] were prepared according to the literature procedures.

2. Cyclic voltammetric experiments

The electrochemical analysis was demonstrated with Ag wire as a reference electrode, which is not a stable reference electrode. CVs can be calibrated using ferrocene as an external reference. (Fig. S1) $E_0(Fc/Fc^+)$ = (0.09-0.02)/2 = 0.035V.

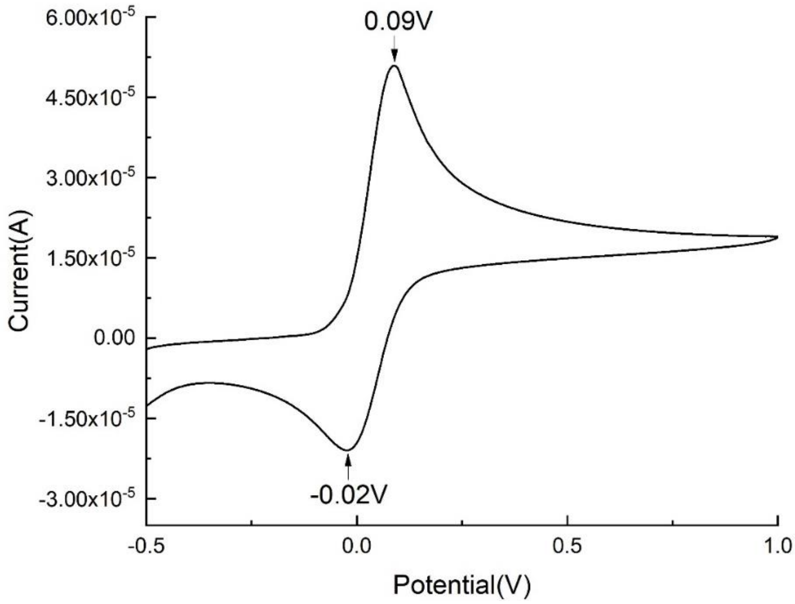


Fig. S1. Cyclic voltammograms of ferrocene (0.02 M) in 0.1 M $LiClO_4$ (CH_3CN), using a glassy carbon working electrode and Pt wire, Ag/$AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 mV/s scan rate.

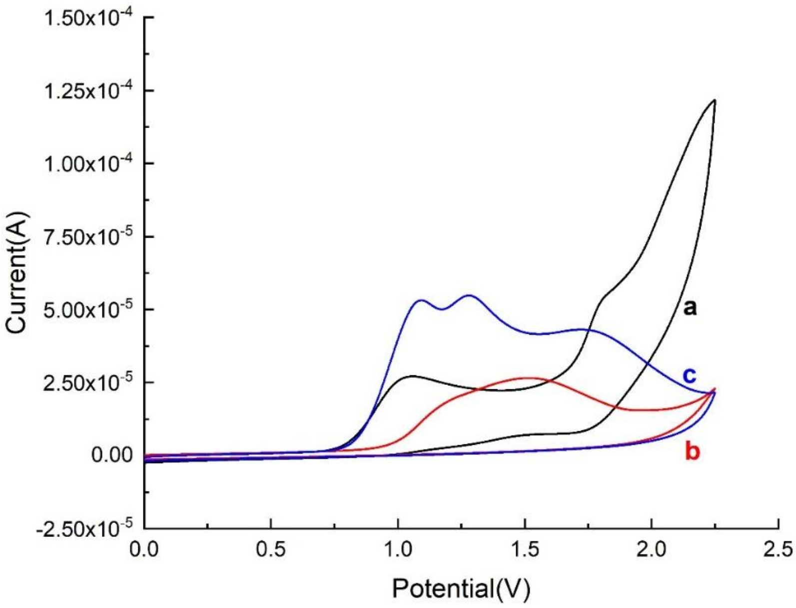
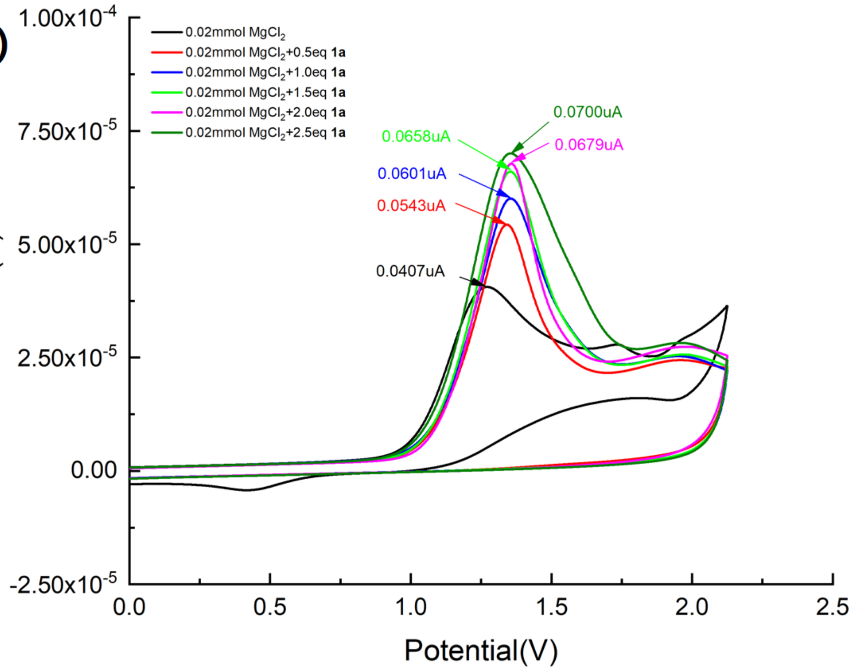


Fig. S2. Cyclic voltammograms of benzimidazole and $MgCl_2$ in 0.1 M $LiClO_4$ (CH_3CN), using a glassy carbon working electrode and Pt wire, $Ag/AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 mV/s scan rate: a. $MgCl_2$ (0.02 M); b. Benzimidazole (0.02 M); c. Mixture of $MgCl_2$ (0.02 M) and benzimidazole (0.04 M).

As shown above, $MgCl_2$ has two oxidation peaks at 1.04 V and 1.80 V, which were assigned to the process Cl^-/Cl and $Cl\cdot/Cl^+$, respectively. Benzimidazole has a broad oxidation wave ranging from 1.0 V to 1.80 V. Upon treating $MgCl_2$ with 2 equivalents of benzimidazole, significant increase of the first oxidation peak (that is, catalytic current) of $MgCl_2$ was observed, suggesting that benzimidazole could rapidly react with chlorine radical to accelerate the process of $Cl^-/Cl\cdot$.

a)



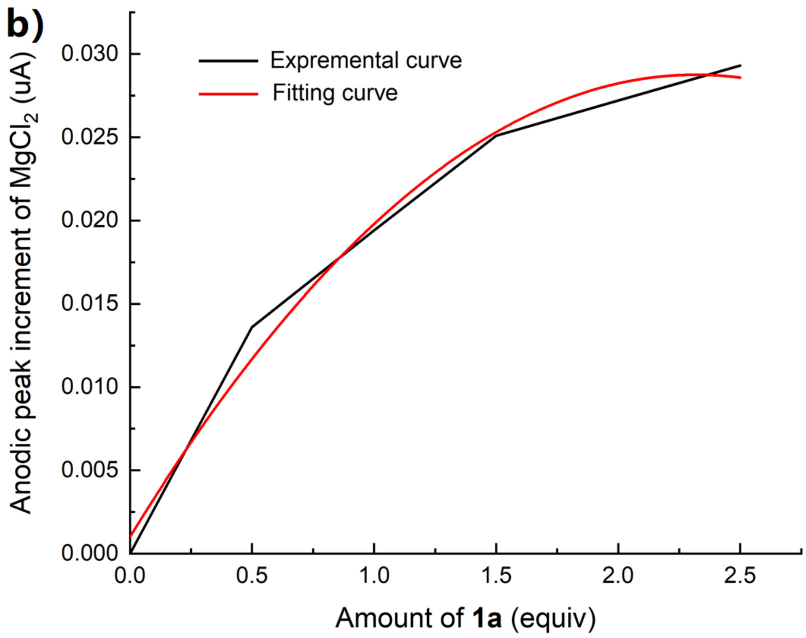


Fig. S3. a) Cyclic voltammograms of benzimidazole and $MgCl_2$ in 0.1 M $LiClO_4$ (CH_3CN), using a glassy carbon working electrode and Pt wire, $Ag/AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 mV/s scan rate; b) The reactionship of the anodic peak increment of $MgCl_2$ with the amount of benzimidazole.

To clarify the catalytic current arising from the mixture of $MgCl_2$ and benzimidazole (**1a**), titration experiment of $MgCl_2$ and **1a** was conducted in the cyclic voltammograms (Figure S3a). We noticed the increment of anodic peak is not linear relationship with the amount of **1a**. When the amount of **1a** was increased to 2 equivalents, the increase the anodic peak of $MgCl_2$ is sluggish. This relationship was concluded in the Figure S3b. It clearly suggested that the increment of anodic peak is not arising from the plus effect of $MgCl_2$ and benzimidazole, and supported the catalytic current in the reaction.

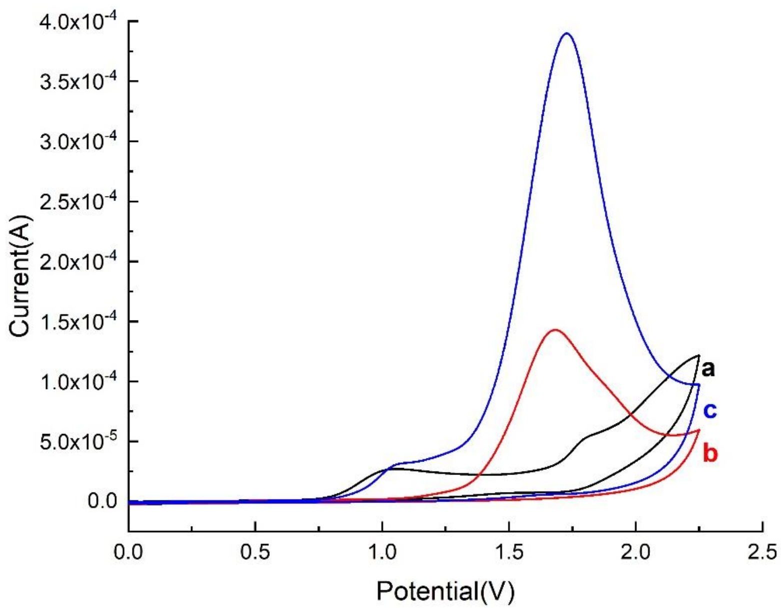


Fig. S4. Cyclic voltammograms of substrates in 0.1 M $LiClO_4$ (CH_3CN), using a glassy carbon working electrode and Pt wire, Ag/$AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 mV/s scan rate: a) $MgCl_2$ (0.02 M); b) Styrene (0.02 M); c) Mixture of $MgCl_2$ (0.02 M) and styrene (0.04 M).

In the contrast, treating $MgCl_2$ with excessive styrene led to no significant change in the oxidation peak of $MgCl_2$. This result suggests that chlorine radical cannot rapidly be intercepted by styrene. The direct addition between chlorine radical and styrene might be unlikely in the aminochlorination.

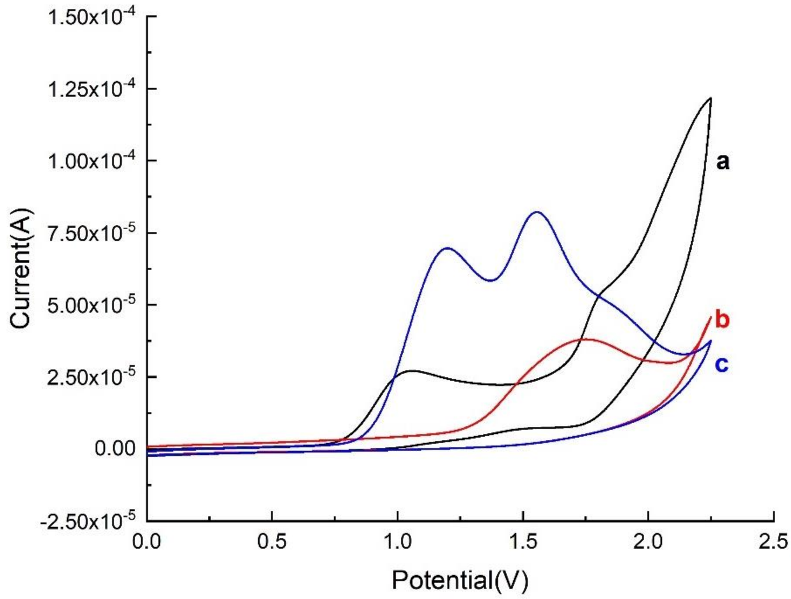


Fig. S5. Cyclic voltammograms of benzimidazole and $MgCl_2$ in 0.1 M $LiClO_4$ (CH_3CN), using a glassy carbon working electrode and Pt wire, Ag/$AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 mV/s scan rate: a. $MgCl_2$ (0.02 M); b. 5,6-chloro-1*H*-benzo[d]imidazole (0.02 M); c. Mixture of $MgCl_2$ (0.02 M) and 5,6-chloro-1*H*-benzo[d]imidazole (0.04 M).

As shown above, mixing $MgCl_2$ with 5,6-chloro-1*H*-benzo[*d*]imidazole also resulted in an obvious catalytic current. This result supports the reaction between chlorine radical and **1e**.

To better understand redox behavior of benzimidazole derivatives, a broad range of CV experiments of benzimidazole derivatives are listed below.

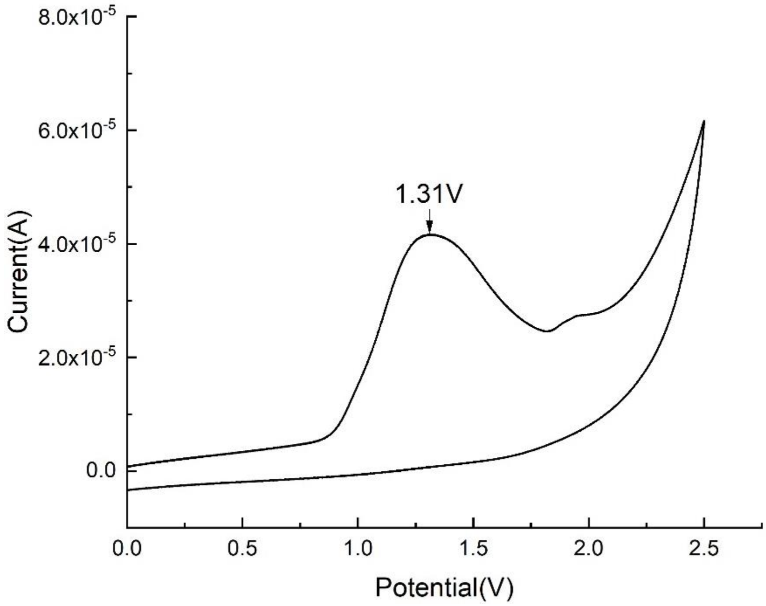


Fig. S6. Cyclic voltammograms of 5,6-dimethyl-1*H*-benzo[*d*]imidazole (**1b**) (0.02 M) in 0.1 M $LiClO_4$ (CH_3CN), using a glassy carbon working electrode and Pt wire, Ag/$AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 mV/s scan rate.

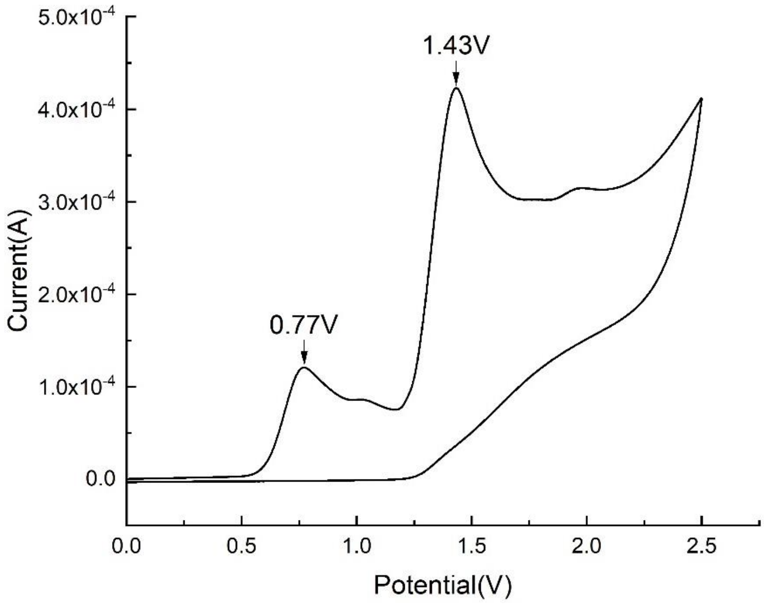


Fig. S7. Cyclic voltammograms of 5,6-dimethoxy-1*H*-benzo[*d*]imidazole (**1c**) (0.02 M) in 0.1 M $LiClO_4$ (CH_3CN), using a glassy carbon working electrode and Pt wire, Ag/$AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 mV/s scan rate.

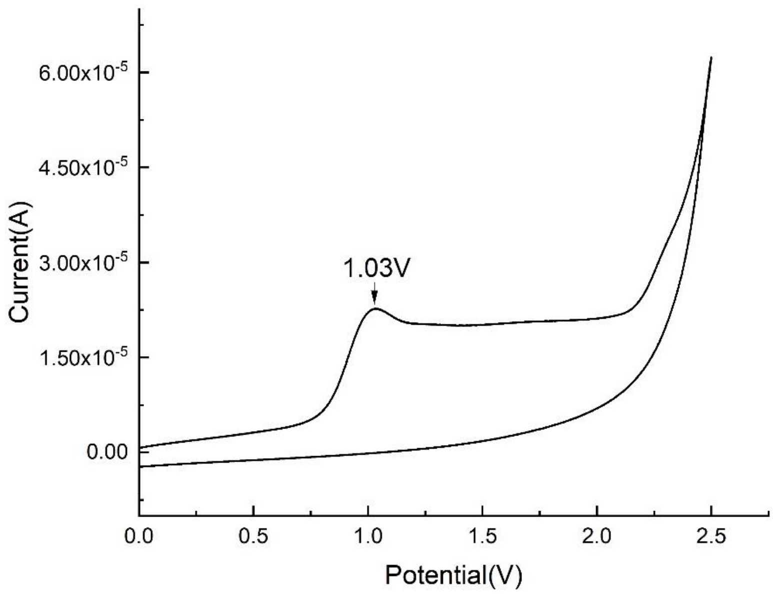


Fig. S8. Cyclic voltammograms of 1*H*-imidazole (**1d**) (0.02 M) in 0.1 M $LiClO_4$ (CH_3CN), using a glassy carbon working electrode and Pt wire, Ag/$AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 mV/s scan rate.

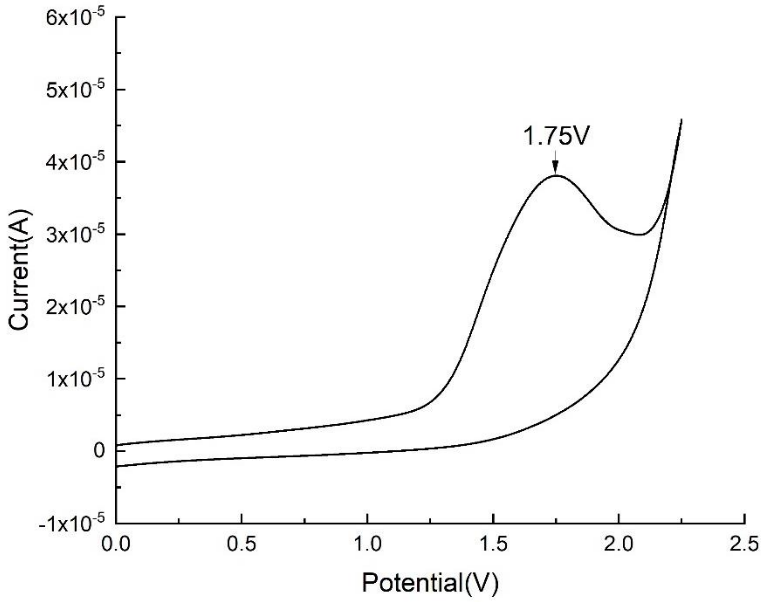


Fig. S9. Cyclic voltammograms of 5,6-chloro-1*H*-benzo[*d*]imidazole (**1e**) (0.02 M) in 0.1 M $LiClO_4$ (CH_3CN), using a glassy carbon working electrode and Pt wire, Ag/$AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 mV/s scan rate.

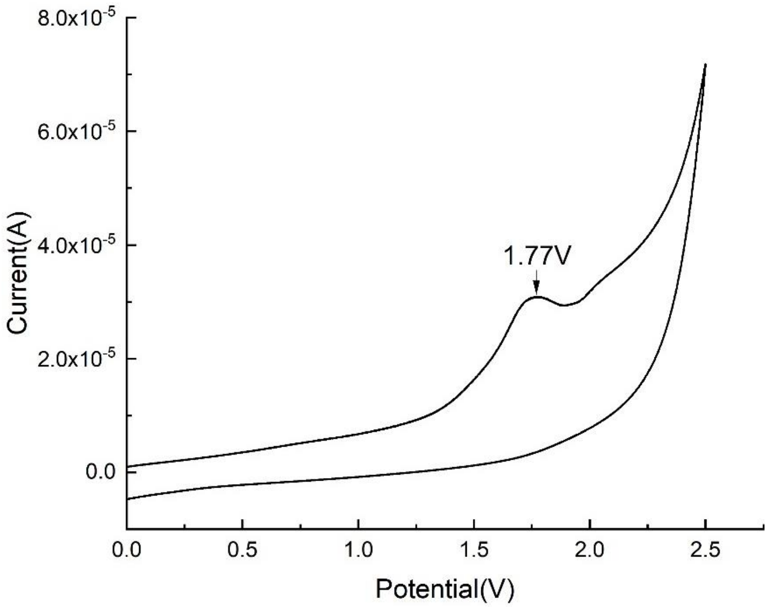


Fig. S10. Cyclic voltammograms of benzotriazole (**1f**) (0.02 M) in 0.1 M $LiClO_4$ (CH_3CN), using a glassy carbon working electrode and Pt wire, Ag/$AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 mV/s scan rate.

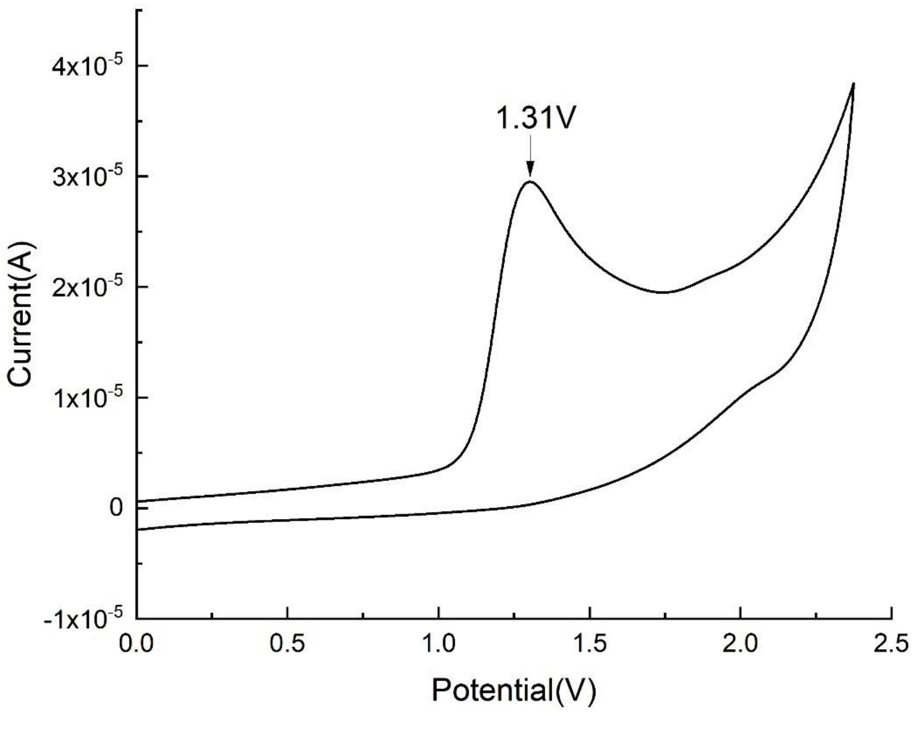


Fig. S11. Cyclic voltammograms of 2-isopropyl-1*H*-benzo[*d*]imidazole (**1g**) (0.02 M) in 0.1 M $LiClO_4$ (CH_3CN), using a glassy carbon working electrode and Pt wire, Ag/$AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 mV/s scan rate.

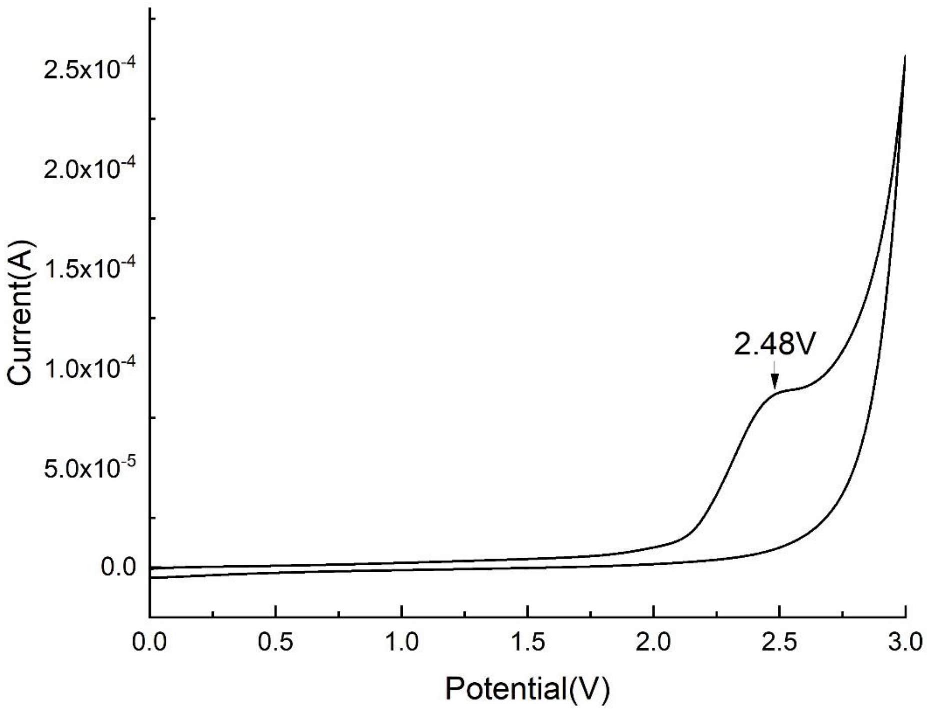


Fig. S12. Cyclic voltammograms of *p*-toluenesulfonamide (**1h)** (0.02 M) in 0.1 M $LiClO_4$ (CH_3CN), using a glassy carbon working electrode and Pt wire, Ag/$AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 mV/s scan rate.

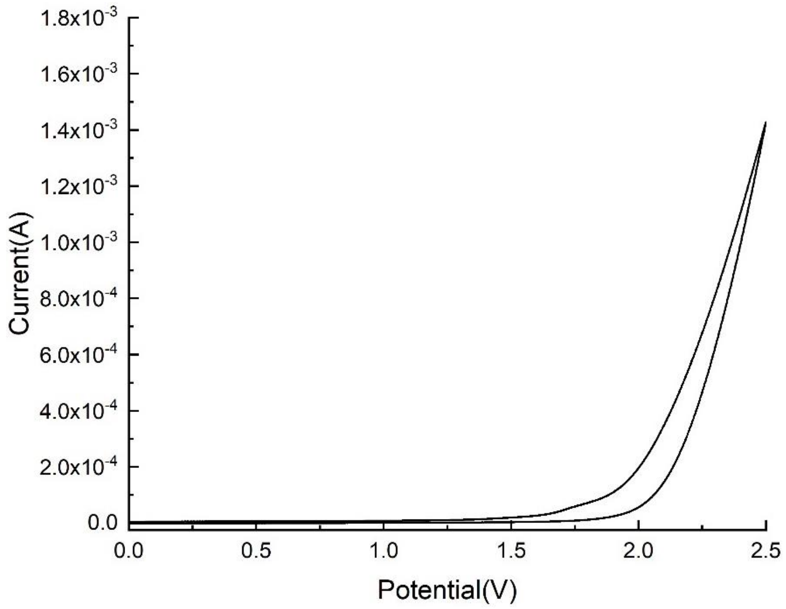


Fig. S13. Cyclic voltammograms of benzoic acid (**1i)** (0.02 M) in 0.1 M $LiClO_4$ (CH_3CN), using a glassy carbon working electrode and Pt wire, Ag/$AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 mV/s scan rate.

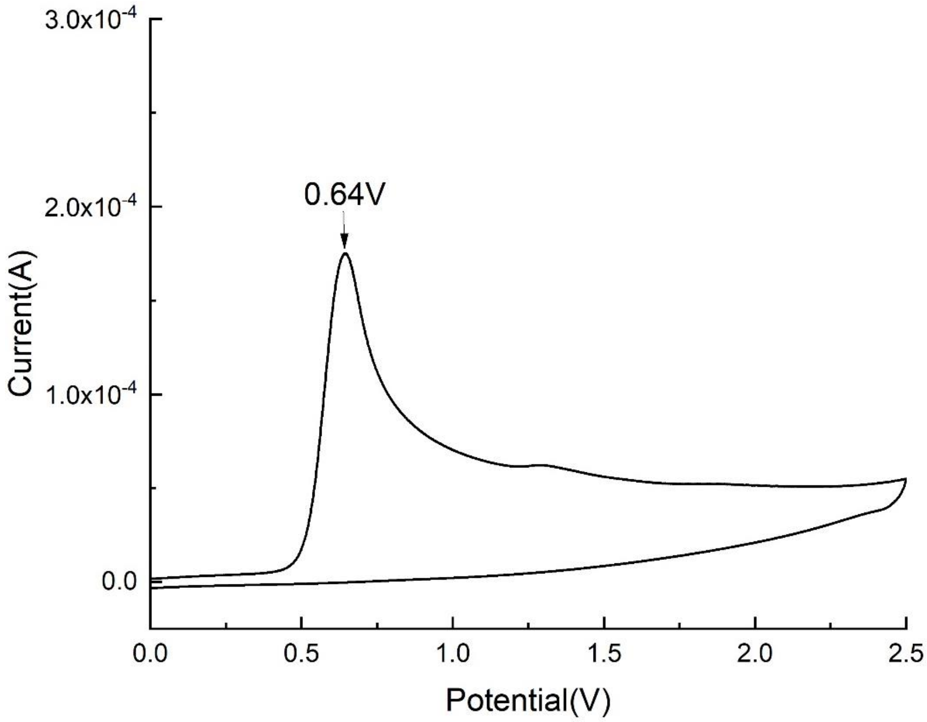


Fig. S14. Cyclic voltammograms of aniline (**1j**) (0.02 M) in 0.1 M $LiClO_4$ (CH_3CN), using a glassy carbon working electrode and Pt wire, Ag/$AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 mV/s scan rate.

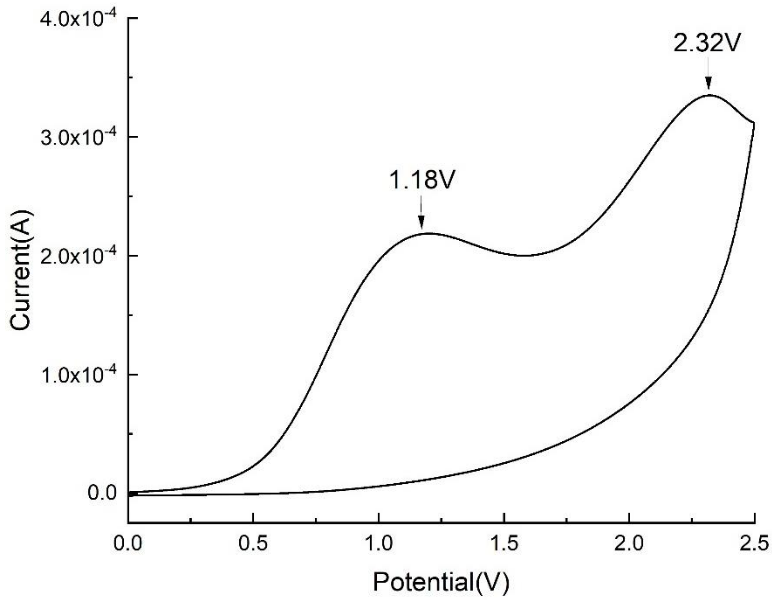


Fig. S15. Cyclic voltammograms of pyrrolidine (**1k**) (0.02 M) in 0.1 M $LiClO_4$ (CH_3CN), using a glassy carbon working electrode and Pt wire, Ag/$AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 mV/s scan rate.

Next, a range of alkene substrates were studied, and their CV spectra were shown below.

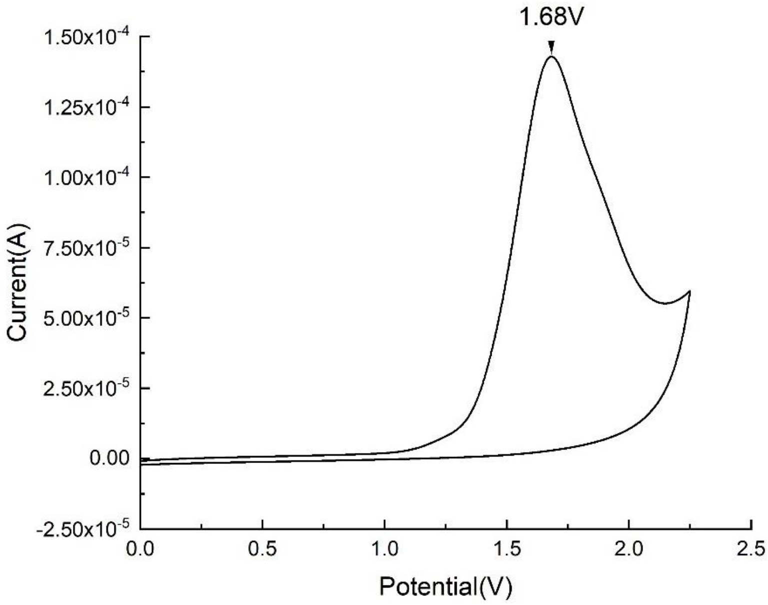


Fig. S16. Cyclic voltammograms of styrene (**2a**) (0.02 M) in 0.1 M $LiClO_4$ (CH_3CN), using a glassy carbon working electrode and Pt wire, Ag/$AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 mV/s scan rate.

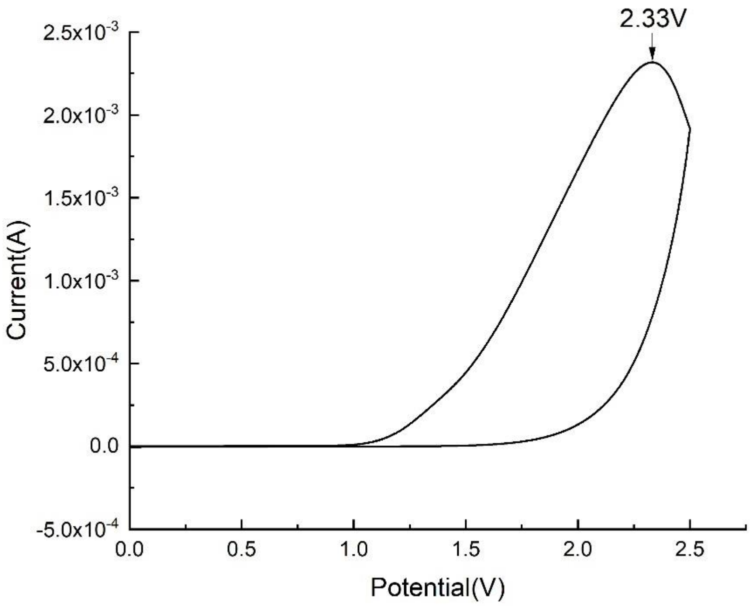


Fig. S17. Cyclic voltammograms of α-methyl styrene (0.02 M) in 0.1 M $LiClO_4$ (CH_3CN), using a glassy carbon working electrode and Pt wire, Ag/$AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 mV/s scan rate.

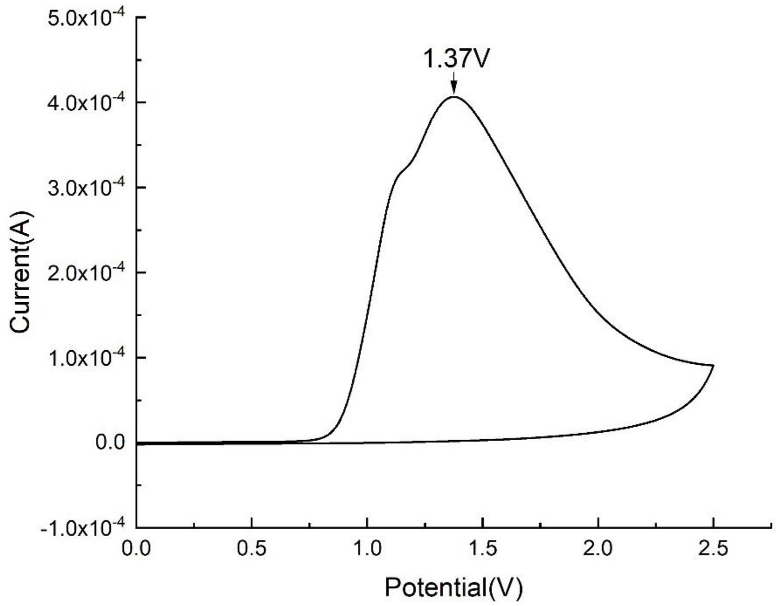


Fig. S18. Cyclic voltammograms of 4-methoxystyrene (0.02 M) in 0.1 M $LiClO_4$ (CH_3CN), using a glassy carbon working electrode and Pt wire, Ag/$AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 mV/s scan rate.

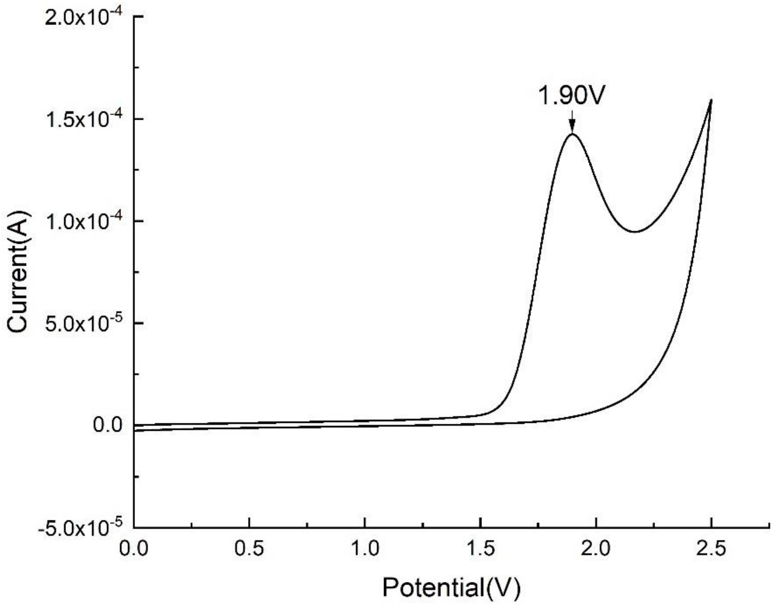


Fig. S19. Cyclic voltammograms of methyl cinnamate (0.02 M) in 0.1 M $LiClO_4$ (CH_3CN), using a glassy carbon working electrode and Pt wire, Ag/$AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 mV/s scan rate.

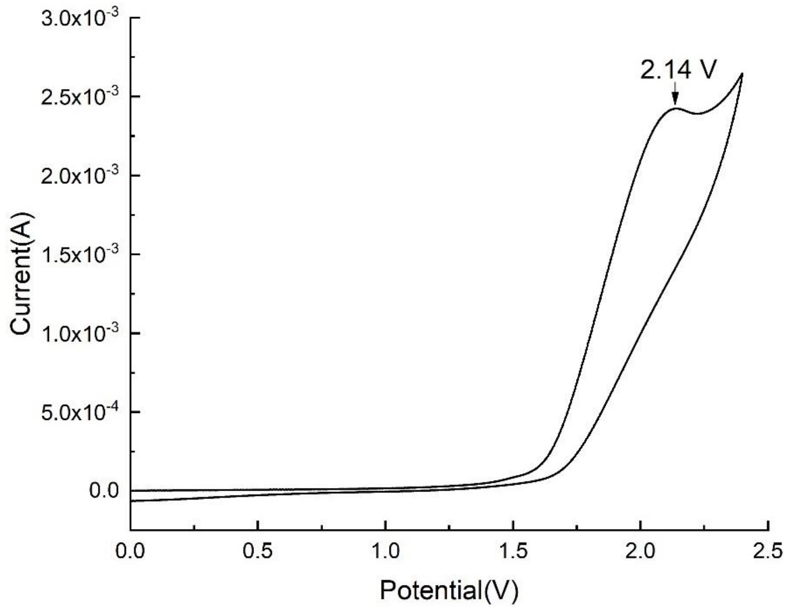
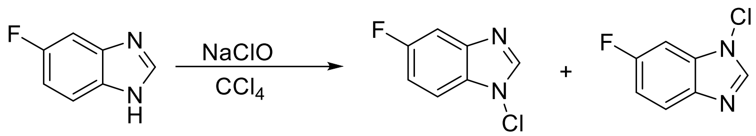


Fig. S20. Cyclic voltammograms of phenylacetylene (0.02 M) in 0.1 M $LiClO_4$ (CH_3CN), using a glassy carbon working electrode and Pt wire, Ag/$AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrodes at a 100 mV/s scan rate.

3. ^{19}F NMR monitoring for *N*-chlorobenzimidazole

To better understand the instability of *N*-chlorobenzimidazole, fluorine-containing variant was synthesized and ^{19}F NMR monitoring was conducted.



As shown in the ^{19}F NMR (Figure S21), the *N*-chlorobenzimidazole is sensitive to both heat and light. Specifically, *N*-chlorobenzimidazole decomposes completly in the half hour under sunlight.

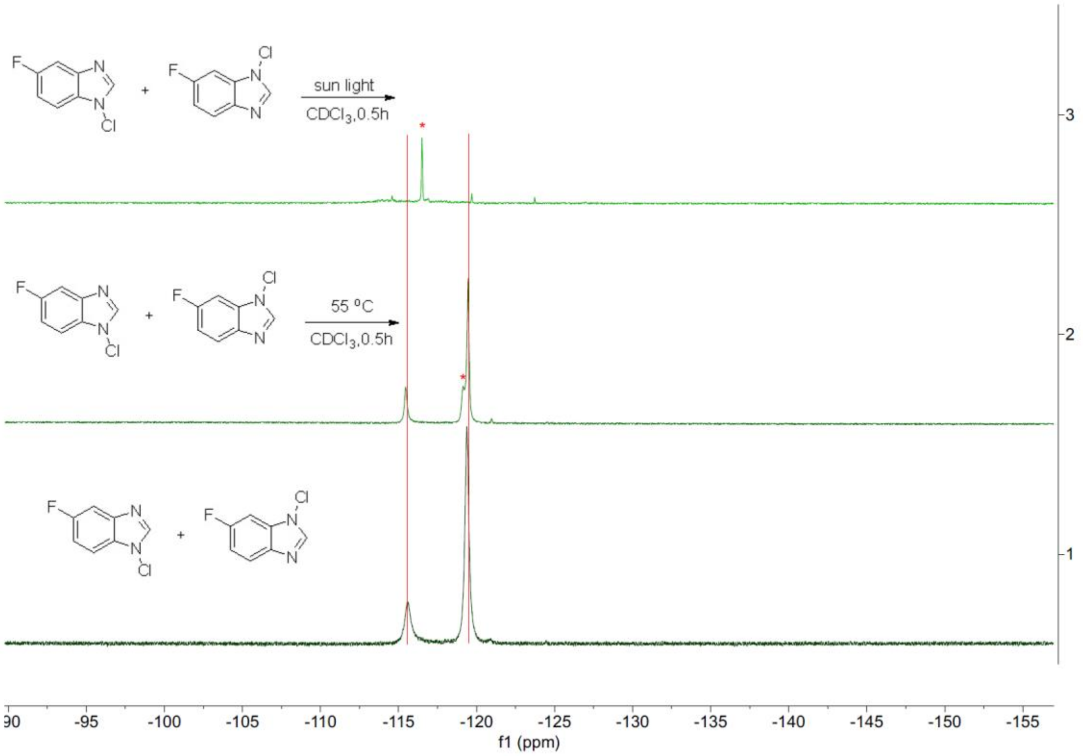
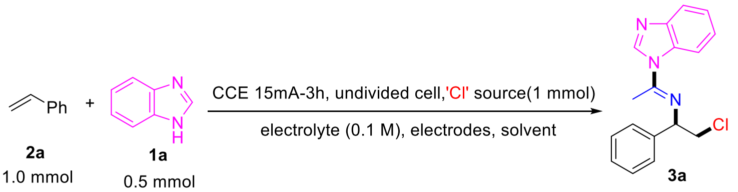


Fig. S21. ^{19}F NMR monitoring for *N*-chlorobenzimidazole

4. Optimization of reaction conditions

Table S1. Optimization of electrochemical aminochlorination[a]



MgCl$_2$

E_{ox} = 1.04 V (Cl$^-$/Cl·)
1.80 V (Cl·/Cl$^+$)

E_{ox} = 1.68 V

E_{ox} = 1.51 V

Entry	Electrolyte	Electrodes	Solvent	'Cl' source	Yield (%)[b]
1	Et_4NClO_4	Pt(+)-Pt(-)	CH_3CN/HFIP (9/1)	$MgCl_2$	93
2	Et_4NClO_4	Pt(+)-Pt(-)	CH_3CN	$MgCl_2$	23
3	Bu_4NClO_4	Pt(+)-Pt(-)	CH_3CN/HFIP (9/1)	$MgCl_2$	81
4	Bu_4NPF_6	Pt(+)-Pt(-)	CH_3CN/HFIP (9/1)	$MgCl_2$	69
5	Bu_4NBF_4	Pt(+)-Pt(-)	CH_3CN/HFIP (9/1)	$MgCl_2$	60
6	Bu_4NOAc	Pt(+)-Pt(-)	CH_3CN/HFIP (9/1)	$MgCl_2$	trace
7	Bu_4NCl	Pt(+)-Pt(-)	CH_3CN/HFIP (9/1)	-	53
8	Et_4NClO_4	Pt(+)-Pt(-)	CH_3CN/HFIP (9/1)	NaCl	trace
9	Et_4NClO_4	Pt(+)-Pt(-)	CH_3CN/HFIP (9/1)	LiCl	trace
10	Et_4NClO_4	Pt(+)-Pt(-)	CH_3CN/HFIP (9/1)	TMSCl	51
11	Et_4NClO_4	Pt(+)-C(-)	CH_3CN/HFIP (9/1)	$MgCl_2$	53
12	Et_4NClO_4	C(+)-Pt(-)	CH_3CN/HFIP (9/1)	$MgCl_2$	69
13	Et_4NClO_4	C(+)-C(-)	CH_3CN/HFIP (9/1)	$MgCl_2$	59

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), 'Cl' source (1 mmol), electrolyte (1 mmol), solvent (10 mL), electrodes, 15 mA, 3h (3.7 F/mol), room temperature. [b] Isolated yield.

We commenced our studies using benzimidazole (**1a**) and styrene (**2a**) as pilot substrates in a mixed solvent of acetonitrile and hexafluoroisopropanol (HFIP) under constant current electrolysis (Table S1). After screening of reaction conditions, the optimal result (entry 1) was achieved with $MgCl_2$ as chloride source, Et_4NClO_4 as supporting electrolyte, and platinum plate as electrodes. Interestingly, the desired Ritter-type product **3a** was exclusively produced in high Markovnikov selectivity and 93% yield. Removal of HFIP led to diminished yield (entry 2), which is presumably attributed to the key role of HFIP in the process of proton-coupled electron transfer (PECT). Replacing Et_4NClO_4 with other electrolytes failed to give better yields (entry 3-7). Variation of chlorine source was also explored (entry 8-10), and organic chloride (TMSCl) proved to be better than inorganic salts (NaCl, LiCl). This result can be understood by the poor solubility of the inorganic salts in the reaction solvent. Additionally, effect of electrodes was also studied. It was found that platinum electrode is essential for high yield.

5. General procedure for the electrochemical aminochlorination

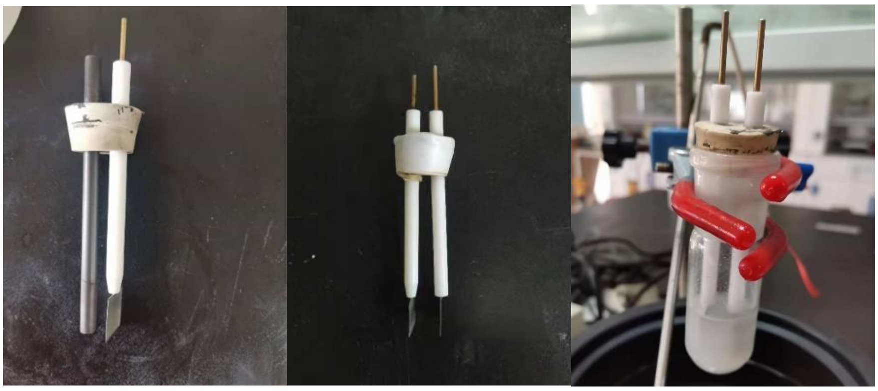
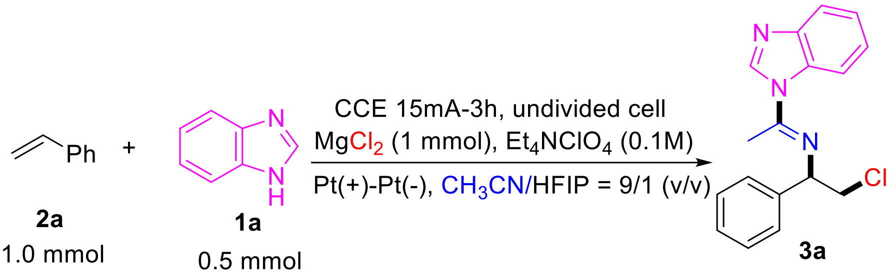


Fig. S22. Electrolysis setup (graphite rod: diameter 0.6 cm, length 10 cm; platinum plate: 1.5 cm *1.5 cm)

3a as example



An undivided cell was equipped with a magnet stirrer, platinum plates (1.5 *1.5 cm^2) as electrodes (the electrolysis setup is shown in Fig. S22). Substrates styrene **2a** (115 μL, 1 mmol), benzoimidazole **1a** (59 mg, 0.5 mmol), $MgCl_2$ (95 mg, 1 mmol) and Et_4NClO_4 (229 mg, 1 mmol) were added to the solvent MeCN/HFIP (9/1 mL). The resulting mixture was allowed to stir and electrolyze under constant current condition (15 mA) at room temperature for 3 hours. The reaction mixture was condensed with a rotary evaporator, the resulting mixture was purified with column chromatography (PE/EA/Et_3N = 80/40/1.2 - 60/60/1.2), and the desired product **3a** (138 mg) was observed in 93 % yield.

6. Procedure for gram scale reaction and the derivatization

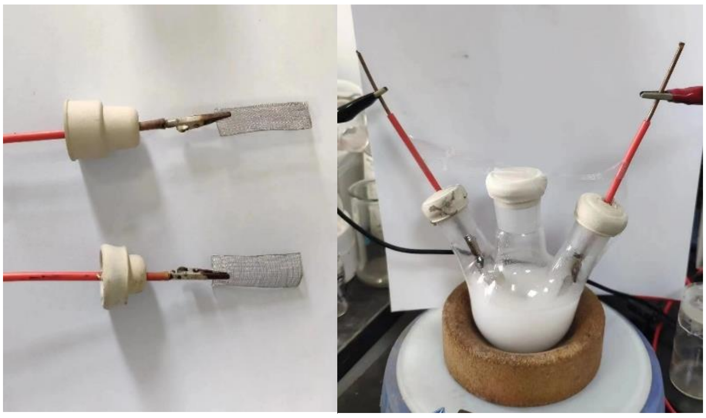
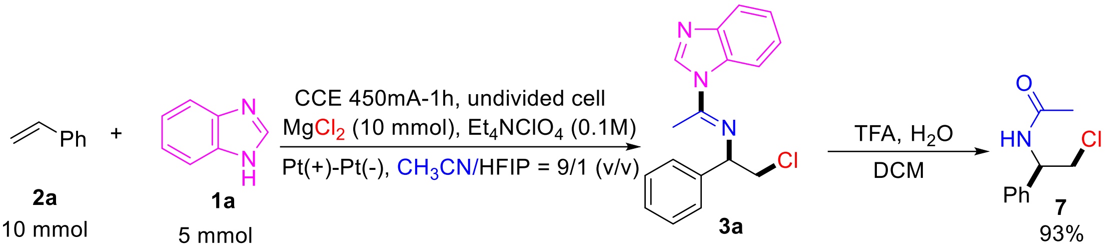


Fig. S23. Gram electrolysis device (platinum mesh: length 5.0 cm, width 2.0 cm, immersion depth 2.0 cm)

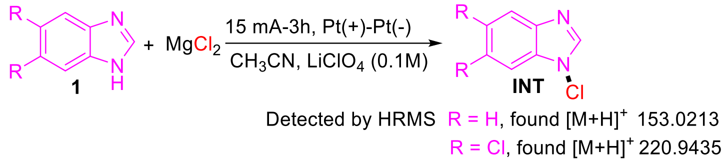


An undivided cell was equipped with a magnet stirrer, platinum mesh (2.0 *2.0 cm^2) as electrodes (the electrolysis setup is shown in Fig. S23). Substrates styrene **2a** (1.15 mL, 10 mmol), benzoimidazole **1a** (0.59 g, 5 mmol), $MgCl_2$ (0.95 g, 10 mmol) and Et_4NClO_4 (1.60 g, 7 mmol) were added to the solvent MeCN/HFIP (63/7 mL). The resulting mixture was allowed to stir and electrolyze under constant current condition (450 mA) at room temperature for 1 hours. The reaction mixture was condensed with a rotary evaporator, the resulting mixture was purified with column chromatography (PE/EA/Et_3N = 80/40/1.2 - 60/60/1.2), and the desired product **3a** (1.35 g) was observed in 91 % yield.

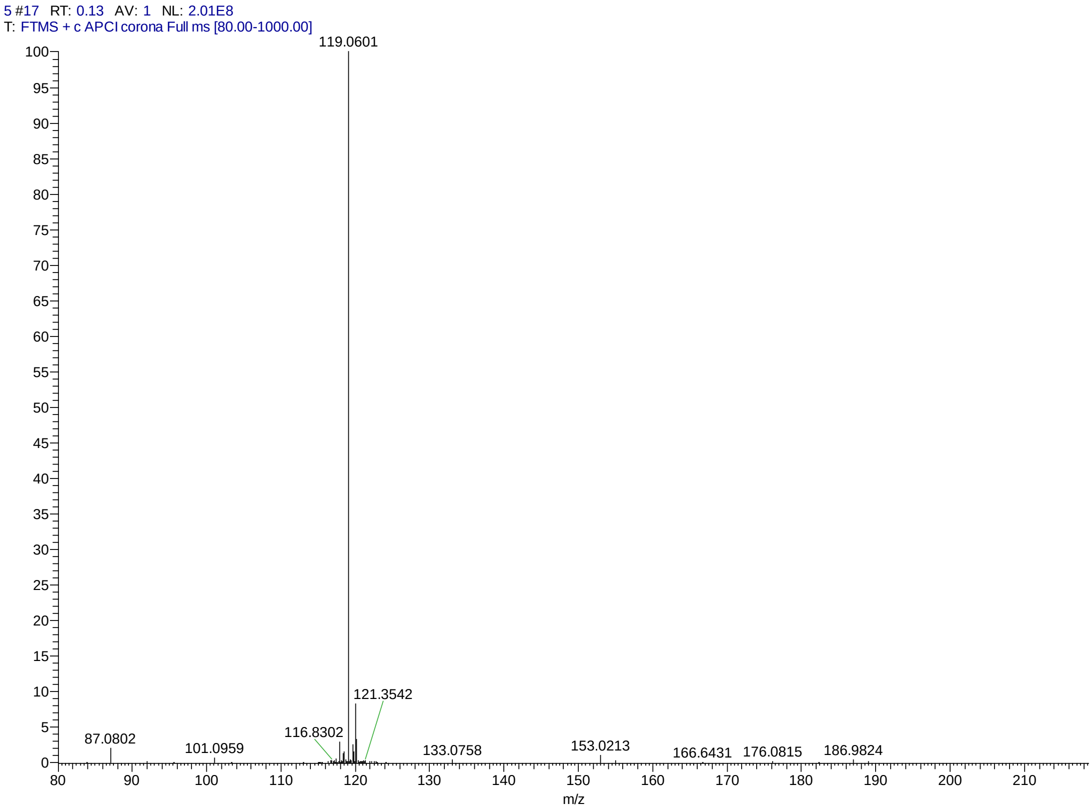
The sequential hydrolysis of **3a** (1.35 g) was conducted in the DCM (50 mL) and water (5 mL). By treating with TFA (18 mmol, 4 equiv), the reaction mixture was allowed to be stirred at room temperature for 6 hours. the reaction mixture was poured into dilute HCl (150 mL, 2M) and extracted with ethyl ether (50 mL*3). The combined organic phase was dried over anhydrous Na_2SO4 and condensed with a rotary evaporator. The residue was purified by column chromatography (PE/ EA= 1/1-1/1.5) on silica gel to afford the desired product **7** (837 mg) in 93 % yield.

7. Control experiments

Detection of *N*-chloro species



An undivided cell was equipped with a magnet stirrer, platinum plates (1.5 *1.5 cm^2) as electrodes (the electrolysis setup is shown in Fig. S22). Substrates benzoimidazole **1a** (59 mg, 0.5 mmol), $MgCl_2$ (95 mg, 1 mmol) and $LiClO_4$ (106 mg, 1 mmol) were added to the solvent MeCN/HFIP (9/1 mL). The resulting mixture was allowed to stir and electrolyze under constant current condition (15 mA) at room temperature for 3 hours. The reaction mixture was condensed with a rotary evaporator, and the resulting mixture was tested with high resolution mass spectrometry (Fig. S24-S25).



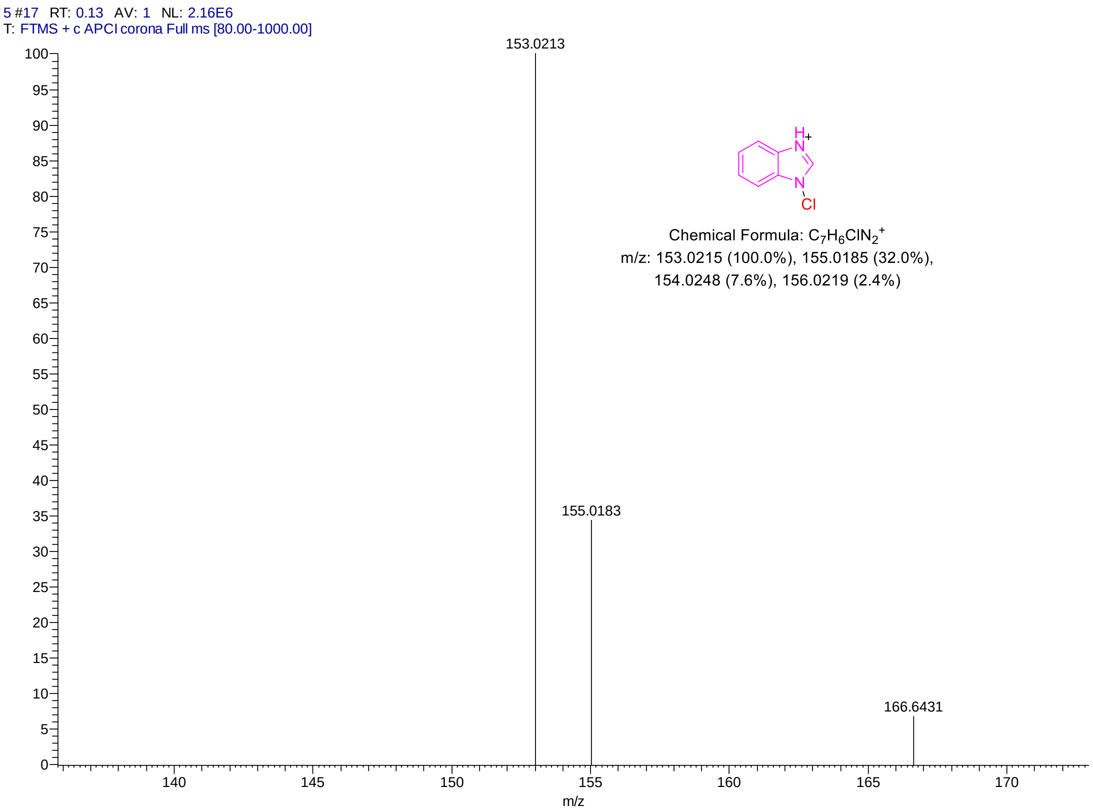
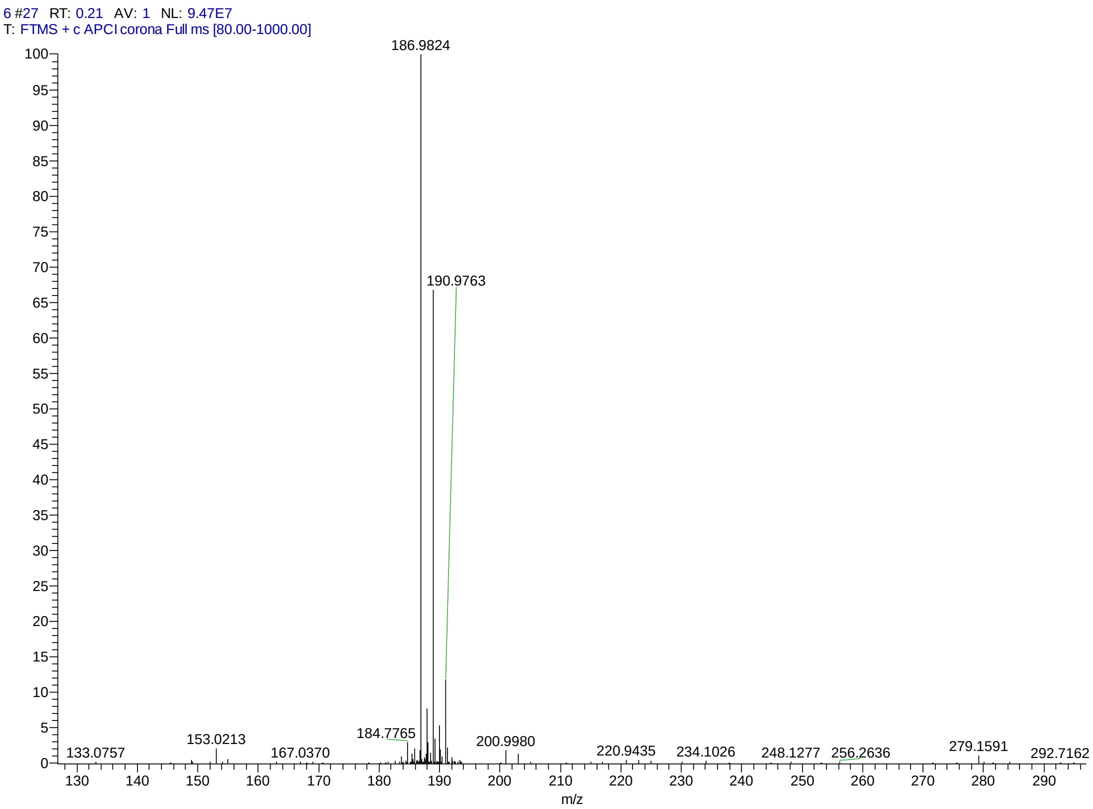


Fig. S24. HRMS spectra of reaction mixture 1a and $MgCl_2$ (INT-1)



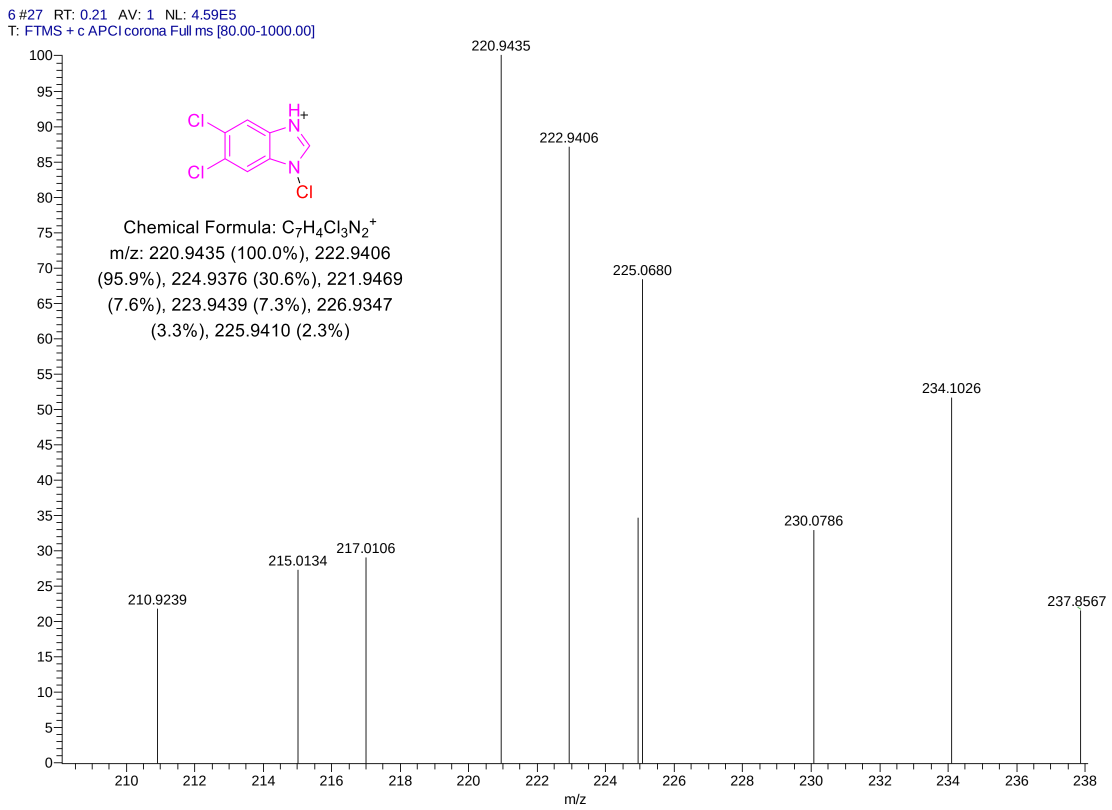
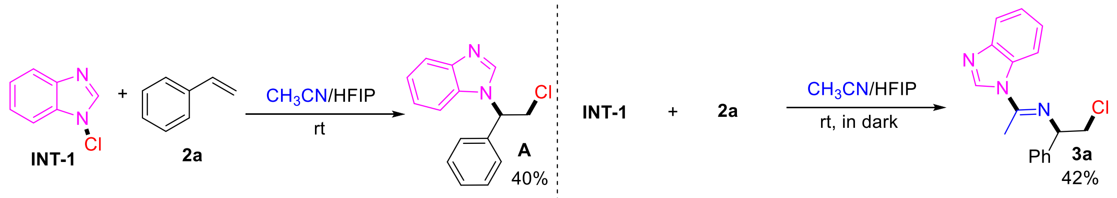


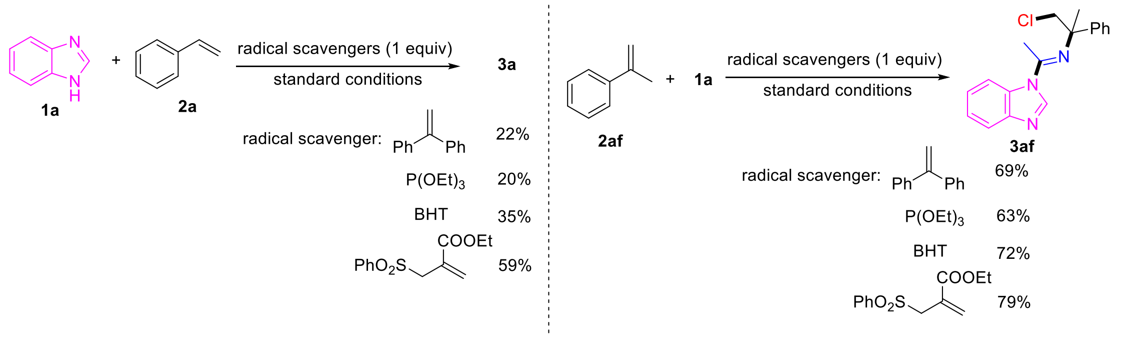
Fig. S25. HRMS spectra of reaction mixture 1e and $MgCl_2$ (INT-2)

Aminochlorination of alkenes with *N*-chlorobenzimidazole



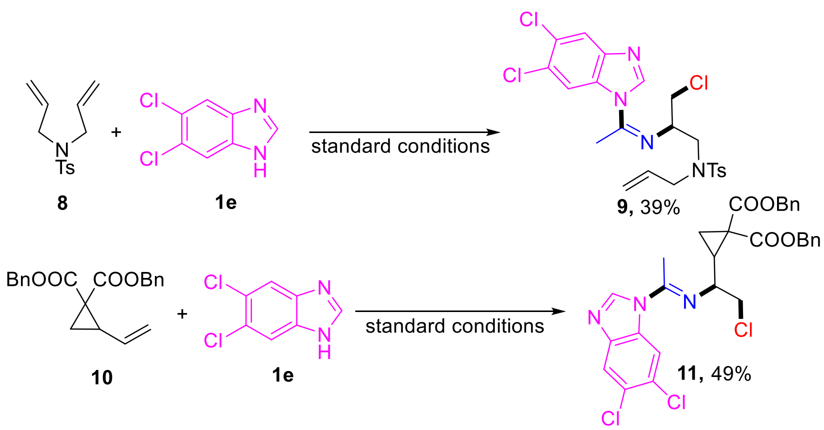
To the solution of **2a** (115 μL, 1 mmol) in CH_3CN/HFIP (9/1 mL), *N*-chlorobenzimidazole (76 mg, 0.5 mmol) was added. After stirring at room temperature for 3 hours, the reaction mixture was condensed with a rotary evaporator, and purified with column chromatography (PE/EA/Et_3N = 80/40/1.2 - 60/60/1.2) to afford product A (51 mg, 40% yield). When we conducted the reaction in dark, product **3a** was observed in 42% yield.

Radical suppression experiment



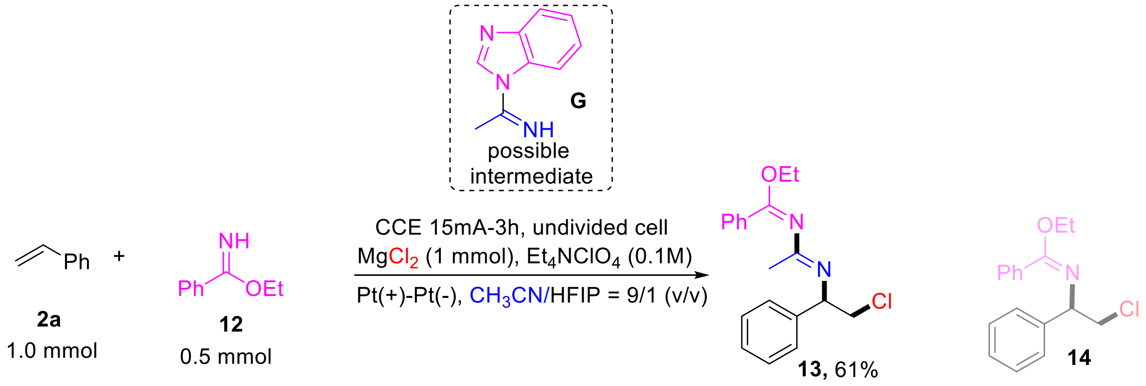
An undivided cell was equipped with a magnet stirrer, platinum plates (1.5*1.5 cm^2) as electrodes (the electrolysis setup is shown in Fig. S22). Substrates styrene **2a** (115 μL, 1 mmol), benzoimidazole **1a** (59 mg, 0.5 mmol), $MgCl_2$ (95 mg, 1 mmol) Et_4NClO_4 (229 mg, 1 mmol) and radical scavengers (0.5 mmol) were added to the solvent MeCN/HFIP (9/1 mL). The resulting mixture was allowed to stir and electrolyze under constant current condition (15 mA) at room temperature for 3 hours. The reaction mixture was condensed with a rotary evaporator, the resulting mixture was purified with column chromatography (PE/EA/Et_3N = 80/40/1.2 - 60/60/1.2).

Radical clock experiment



The radical clock experiment was carried out using **7** and **9** as substrates. As shown above, neither radical-initiated cyclization nor ring-opening product was observed in both cases. These results hinted that ionic pathway might be more feasible in the transformation.

Control experiment to ruling out possible pathway



To exclude a possible pathway involving *in-situ* generation of **G**, an analog **11** was tested in the transformation. Surprisingly, no desired product **13** was detected. Instead, product **12** arising from four component reaction was obtained in 61% yield. This result indicates that stepwise Ritter-type pathway might be more likely.

Anode potential monitoring

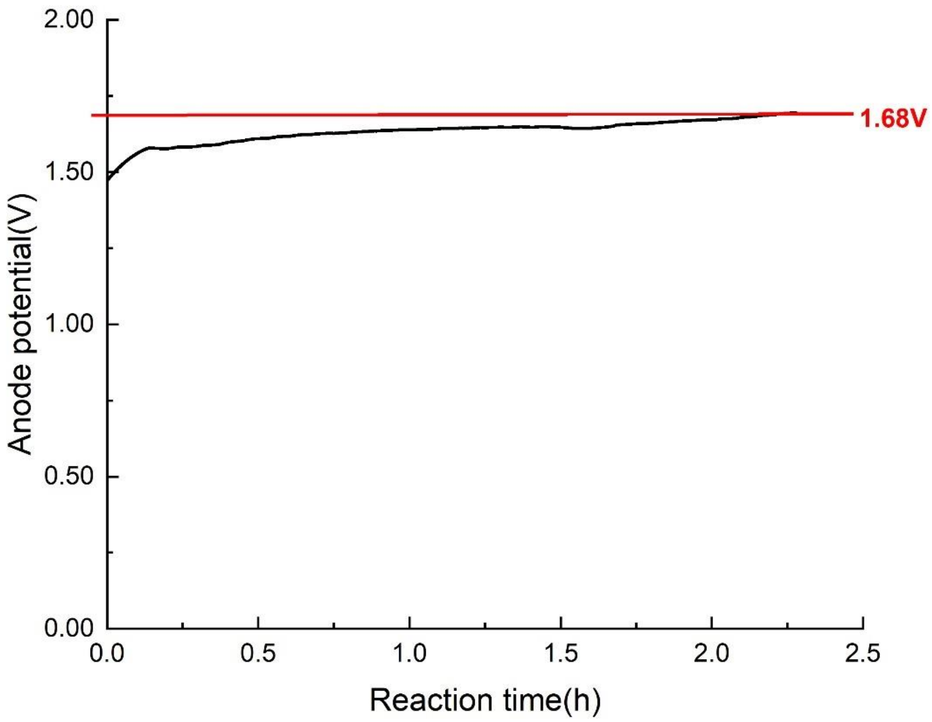
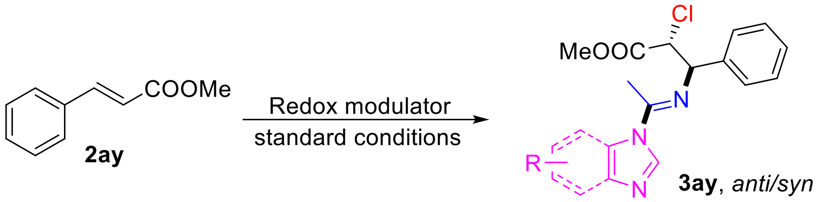


Fig. S26. Anode potential monitoring of the model reaction

We monitored the anode potential of the model reaction between **1a** and **2a**, it showed that the anode potential is below to 1.68V (the anodic peak of styrene) in the first 2 hours. This result clearly suggested that the reaction is initiated by the oxidation of both $MgCl_2$ and benzimidazole.

8. Tunable selectivity exploration

Tunable stereoselectivity investigation



Redox modulator:	1a	1b	1d	1e	1f	1g
anti/syn:	**2.8/1**	**12/1**	**-**	**>20/1**	**-**	**-**
Yield:	45%	8%	trace	64%	trace	trace

Using **1a** as a reactivity modulator in the reaction with cinnamate give isomers of products (*dr* 2.8/1) and low yield 45%. The spectra of mixture of products were shown below.

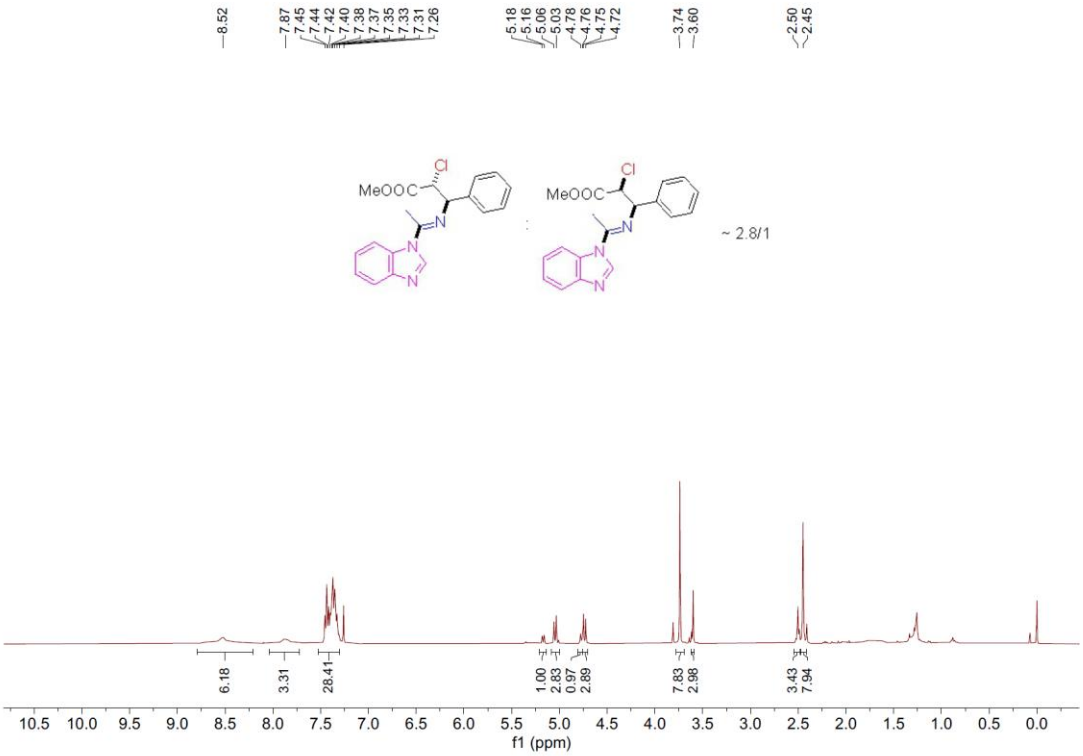


Fig. S27. ^{1}H NMR spectra of products using 1a as a reactivity modulator

Using **1b** as a reactivity modulator in the reaction with cinnamate give isomers of products (*dr* ~ 12/1) and low yield 8%. The spectra of mixture of products were shown below.

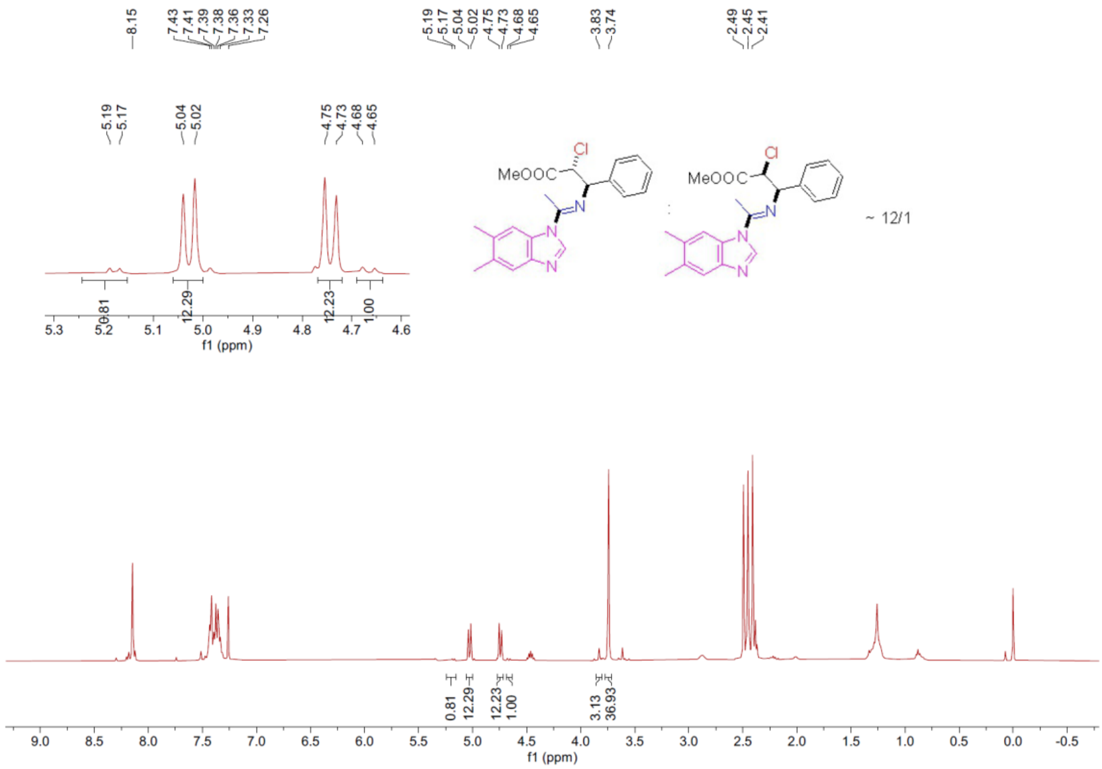


Fig. S28. ^{1}H NMR spectra of products using 1b as a reactivity modulator

Using **1e** as a reactivity modulator in the reaction with cinnamate give isomers of products (*dr* > *20*/1) and low yield 8%. The spectra of mixture of products were shown below.

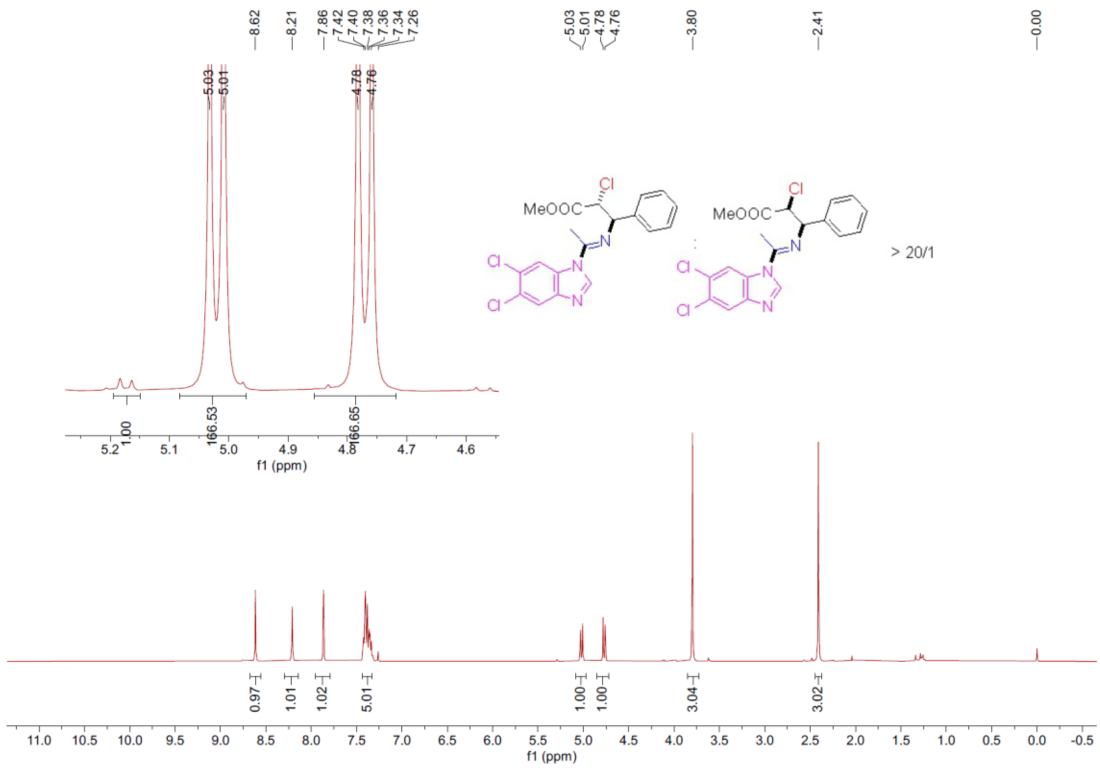
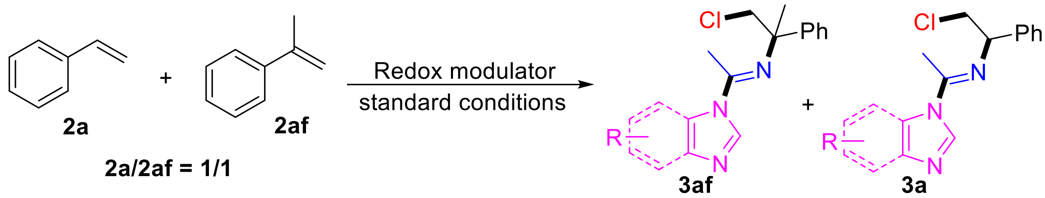


Fig. S29. ^{1}H NMR spectra of products using 1e as a reactivity modulator

Tunable chemoselectivity investigation



Redox modulator:	1a	1b	1d	1e	1f	1g
3af/3a:	15/1	14/1	6/1	6/1	5/1	1/5

The above reaction was performed to understand reaction chemoselectivity. Ratio of products was determined by ^{1}H NMR spectra of the crude product. Corresponding spectra are listed below.

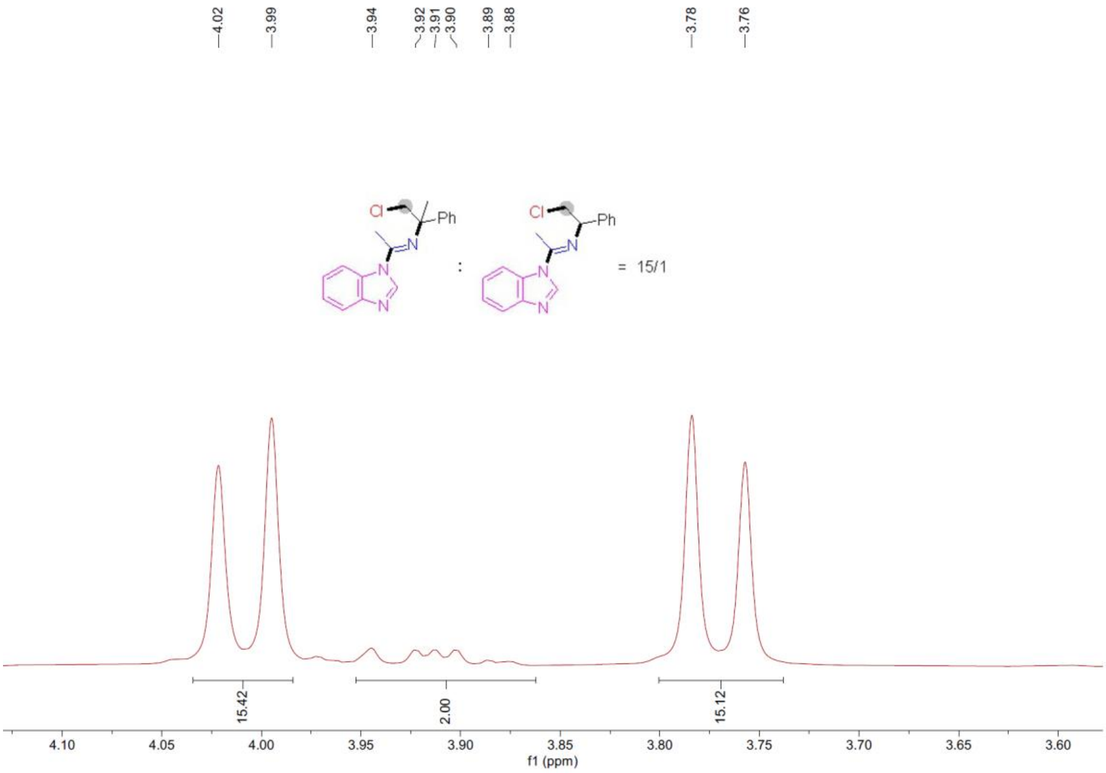


Fig. S30. ^{1}H NMR spectra of products using 1a as a reactivity modulator

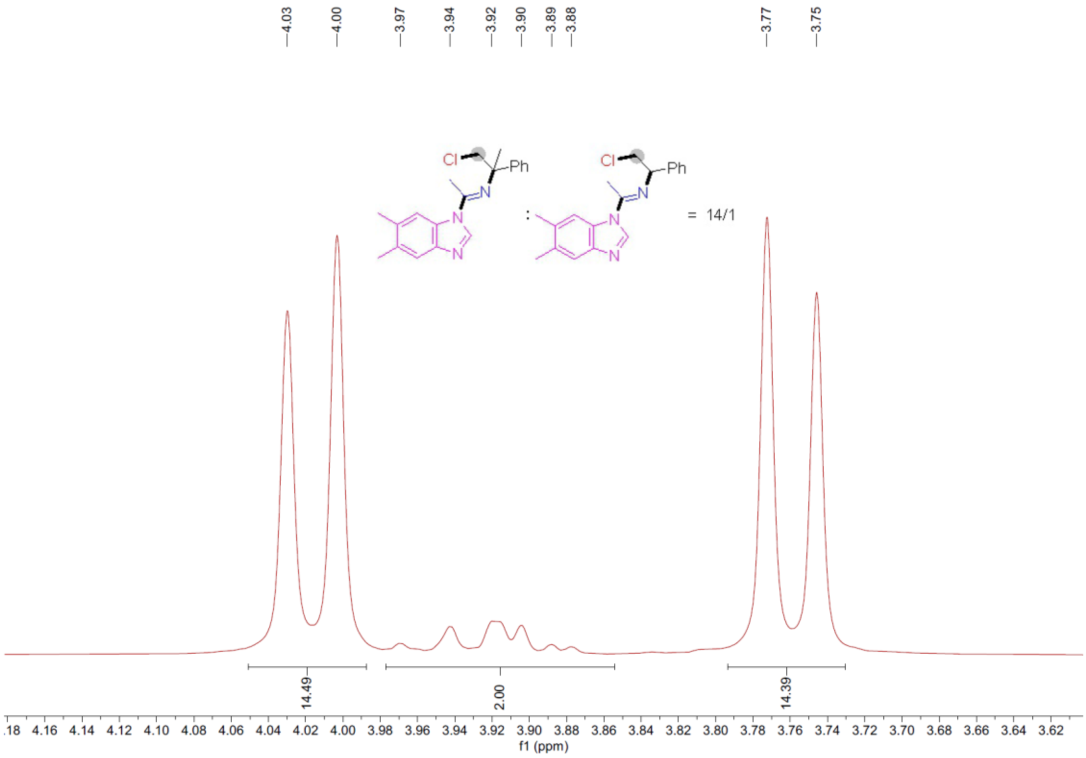


Fig. S31. ¹H NMR spectra of products using 1b as a reactivity modulator

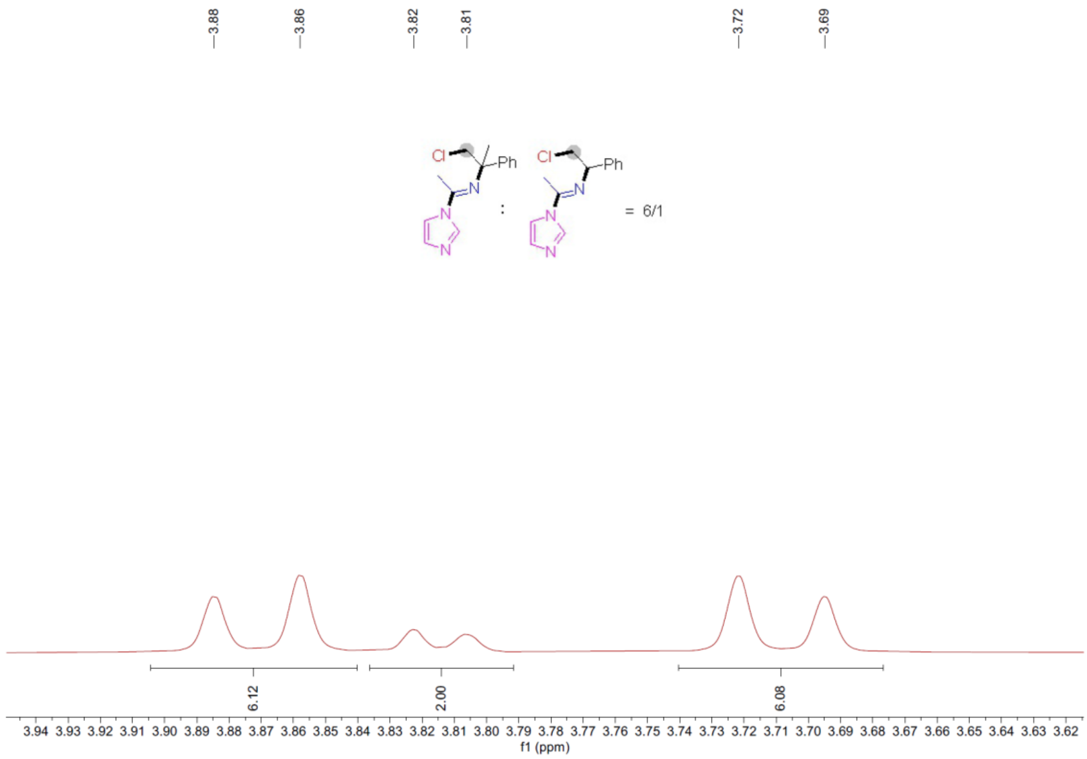


Fig. S32. ¹H NMR spectra of products using 1d as a reactivity modulator

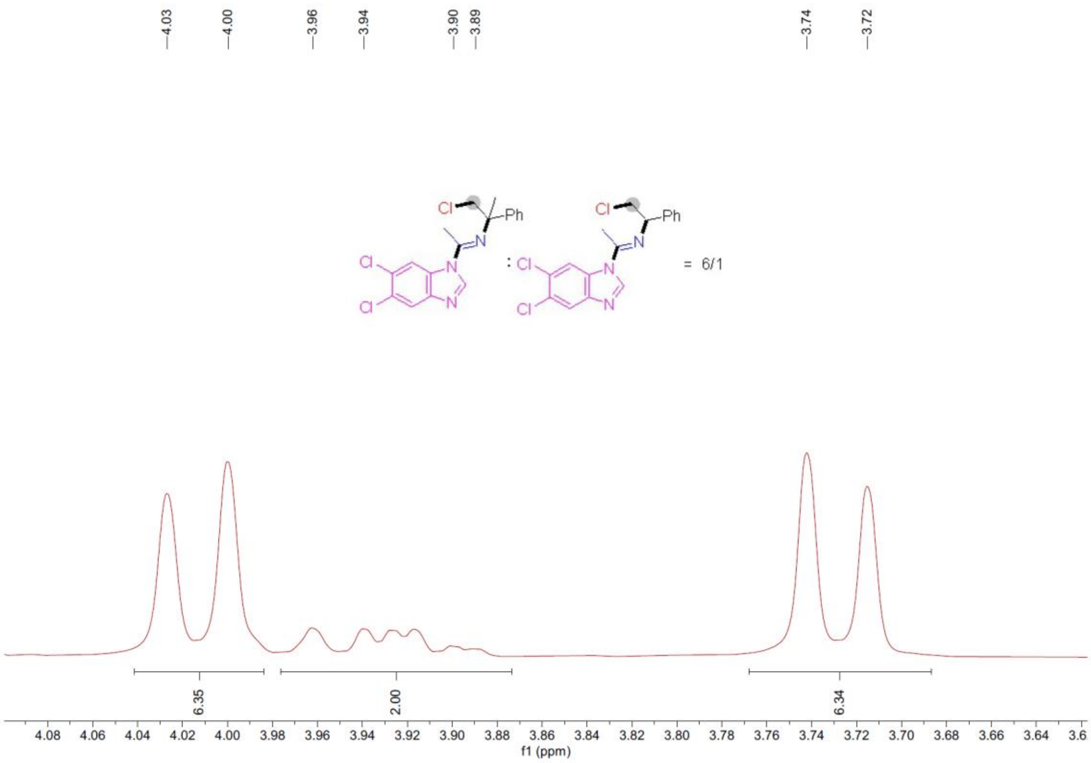


Fig. S33. ^{1}H NMR spectra of products using 1e as a reactivity modulator

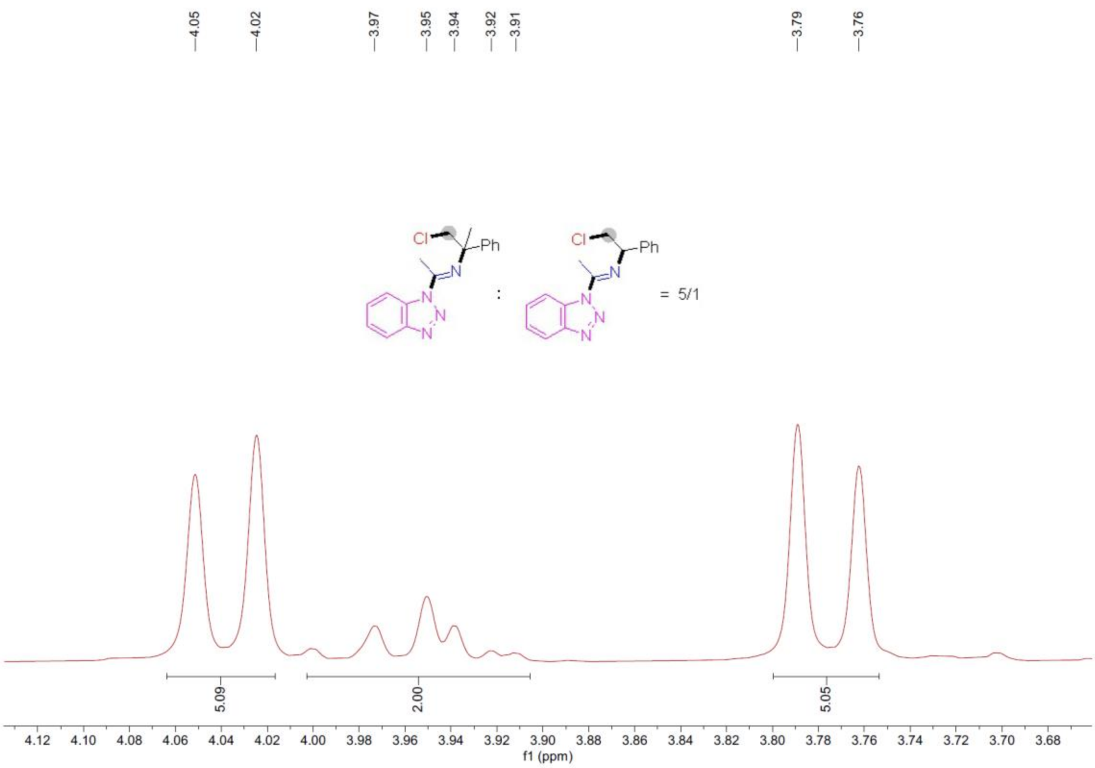


Fig. S34. ^{1}H NMR spectra of products using 1f as a reactivity modulator

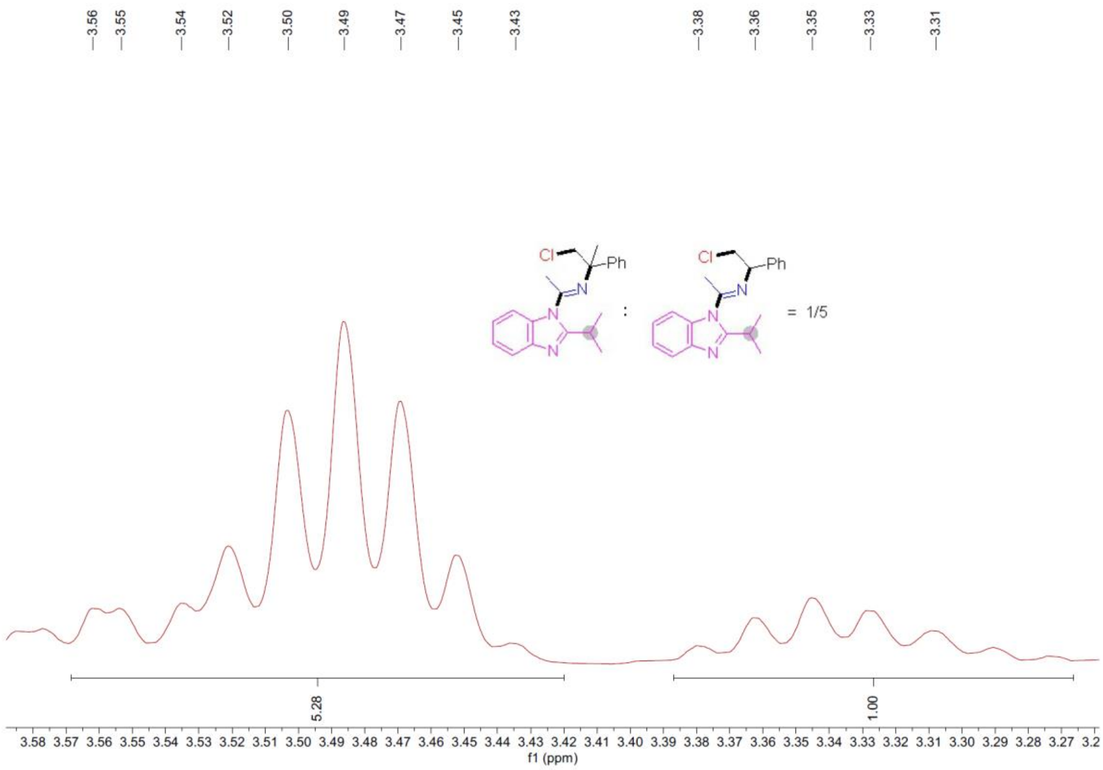
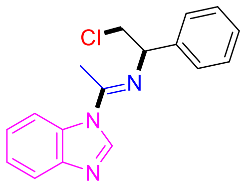
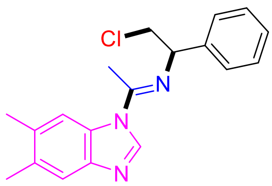


Fig. S35. ^{1}H NMR spectra of products using 1g as a reactivity modulator

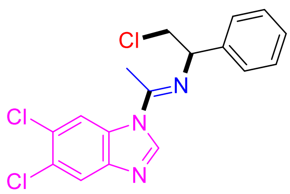
9. Experimental data



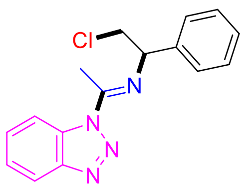
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2-chloro-1-phenylethyl)ethan-1-imine **(3a)**: 138 mg, 93% yield; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (d, *J* = 8.0 Hz, 1H), 8.32 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.39 (m, 7H), 4.92 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 3.92 (m, 2H), 2.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.3, 144.3, 141.0, 140.2, 132.3, 128.9, 128.1, 127.2, 124.7, 123.7, 120.1, 116.3, 65.4, 50.5, 15.7; HRMS (ESI): cacld for $C_{17}H_{16}ClN_3$ $[M+H]^+$: 298.1106, found 298.1107.



N-(2-chloro-1-phenylethyl)-1-(5,6-dimethyl-1*H*-benzo[*d*]imidazol-1-yl)ethan-1-imine **(3b)**: 140 mg, 86% yield; pale yellow solid, m.p. 124-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 1H), 8.21 (s, 1H), 7.55 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 1H), 4.90 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 3.92 (m, 2H), 2.45 (s, 3H), 2.42 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.3, 142.8, 140.4, 140.2, 133.6, 132.6, 130.8, 128.8, 128.1, 127.2, 120.1, 116.5, 65.3, 50.6, 20.8, 20.1, 15.6; HRMS (ESI): cacld. for $C_{19}H_{20}ClN_3$ $[M+H]^+$: 326.1419, found 346.1423.

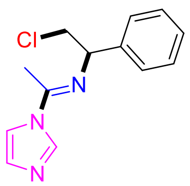


N-(2-chloro-1-phenylethyl)-1-(5,6-dichloro-1*H*-benzo[*d*]imidazol-1-yl)ethan-1-imine **(3c)**: 142 mg, 78% yield; pale yellow solid, m.p. 129-131 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (s, 1H), 8.29 (s, 1H), 7.87 (s, 1H), 7.38 (m, 5H), 4.92 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 3.94 (m, 2H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.0, 143.6, 142.4, 139.9, 131.4, 129.1, 128.7, 128.4, 127.9, 127.1, 121.2, 118.1, 65.6, 50.4, 15.6; HRMS (ESI): cacld. for $C_{17}H_{14}Cl_3N_3$ $[M+H]^+$: 366.0326, found 366.0327.

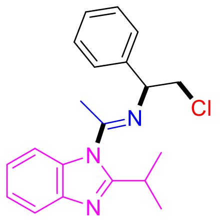


1-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-*N*-(2-chloro-1-phenylethyl)ethan-1-imine **(3d)**: 52 mg, 35% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (d, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 12.0 Hz, 1H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 3H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 5.03

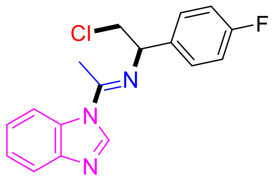
(dd, J = 4.0 Hz, J = 8.0 Hz, 1H), 3.96 (m, 2H), 2.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.7, 146.7, 139.9, 131.5, 129.1, 128.9, 128.2, 127.2, 125.2, 119.7, 115.8, 65.3, 50.4, 15.3; HRMS (ESI): cacld. for $C_{16}H_{15}ClN_4$ $[M+H]^+$: 299.1058, found 299.1052.



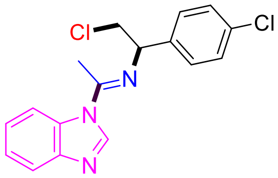
N-(2-chloro-1-phenylethyl)-1-(1*H*-imidazol-1-yl)ethan-1-imine **(3e)**: 63 mg, 51% yield; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.70 (s, 1H), 7.36 (m, 5H), 7.12 (s, 1H), 4.82 (t, J = 8.0 Hz, 1H), 3.81 (d, J = 8.0 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.6, 140.1, 130.1, 128.8, 128.2, 127.1, 65.1, 50.2, 14.9; HRMS (ESI): cacld. for $C_{13}H_{14}ClN_3$ $[M+H]^+$: 248.0949, found 248.0950.



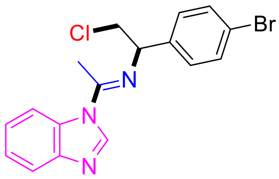
N-(2-chloro-1-phenylethyl)-1-(2-isopropyl-1*H*-benzo[*d*]imidazol-1-yl)ethan-1-imine **(3f)**: 100 mg, 59% yield; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): 7.76 (d, J = 8.0 Hz, 1H), 7.36 (m, 6H), 7.22 (m, 2H), 4.94 (q, J = 4.0 Hz, 1H), 3.89 (m, 2H),3.49 (m, 1H), 2.48 (s, 3H), 1.40 (q, J = 8.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.6, 154.6, 142.4, 139.2, 133.6, 129.0, 128.4, 127.2, 122.7, 122.4, 119.5, 110.6, 66.7, 49.8, 27.1, 21.7, 19.0. HRMS (ESI): cacld. for $C_{20}H_{22}ClN_3$ $[M+H]^+$: 340.1575, found 340.1576.



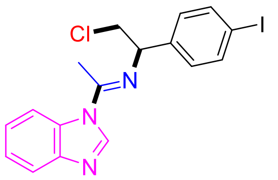
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2-chloro-1-(4-fluorophenyl)ethyl)ethan-1-imine **(3g)**: 148 mg, 94% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (d, J = 8.0 Hz, 1H), 8.32 (s, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.40 (m, 4H), 7.07 (t, J = 8.0 Hz, 2H), 4.92 (dd, J = 4.0 Hz, J = 8.0 Hz, 1H), 3.89 (m, 2H), 2.52 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 162.4 (d, $J_{F\text{-}C}$ = 247.6 Hz), 152.4, 144.3, 140.9, 136.0, 132.3, 128.8 (d, $J_{F\text{-}C}$ = 7.6 Hz), 124.8, 123.9, 120.3, 116.3, 115.8 (d, $J_{F\text{-}C}$ = 21.1 Hz), 64.7, 50.4, 15.7; HRMS (ESI): cacld. for $C_{17}H_{15}ClFN_3$ $[M+H]^+$: 316.1011, found 316.1020.



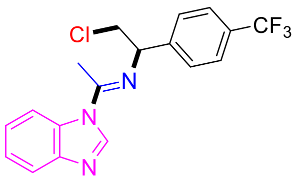
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2-chloro-1-(4-chlorophenyl)ethyl)ethan-1-imine **(3h)**: 164 mg, 99% yield; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, *J* = 8.0 Hz, 1H), 8.31 (s, 1H), 7.81 (d, *J* = 8.0 Hz,1H), 7.38 (m, 6H), 4.90 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 3.88 (m, 2H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.6, 144.4, 140.9, 138.7, 134.0, 132.3, 129.1, 128.6, 124.7, 123.9, 120.3, 116.3, 64.7, 50.2, 15.7; HRMS (ESI): cacld. for $C_{17}H_{15}Cl_2N_3$ $[M+H]^+$: 332.0716, found 332.0716.



1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(1-(4-bromophenyl)-2-chloroethyl)ethan-1-imine **(3i)**: 186 mg, 99% yield; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 8.0 Hz, 1H), 8.31 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.39 (m, 2H), 7.33 (d, *J* = 12.0 Hz, 2H), 4.88 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 3.87 (m, 2H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.6, 144.4, 140.9, 139.2, 132.3, 132.0, 128.9, 124.8, 123.9, 122.1, 120.3, 116.3, 64.8, 50.1, 15.7; HRMS (ESI): cacld. for $C_{17}H_{15}BrClN_3$ $[M+H]^+$: 376.0211, found 376.0212.

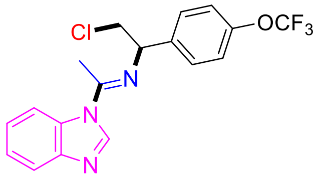


1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2-chloro-1-(4-iodophenyl)ethyl)ethan-1-imine **(3j)**: 197 mg, 93% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, *J* = 8.0 Hz, 1H), 8.32 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.39 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 4.87 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 3.87 (m, 2H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.7, 144.4, 140.9, 139.9 138.0, 132.3, 129.1, 124.8, 123.9, 120.3, 116.3, 93.7, 64.9, 50.1, 15.7; HRMS (ESI): cacld. for $C_{17}H_{15}ClIN_3$ $[M+H]^+$: 424.0072, found 424.0072.

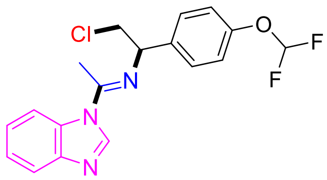


1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2-chloro-1-(4-(trifluoromethyl)phenyl)ethyl)ethan-1-imine **(3k)**: 172 mg, 94% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, *J* = 8.0 Hz, 1H), 8.34 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.41 (m, 2H), 5.01 (dd, *J* =

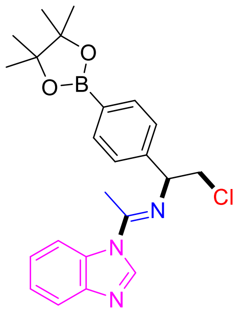
4.0 Hz, J = 8.0 Hz, 1H), 3.92 (m, 2H), 2.53 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.9, 144.3, 144.1, 140.9, 132.3, 130.5 (q, $J_{F\text{-}C}$ = 32.3 Hz), 127.7, 125.9 (q, $J_{F\text{-}C}$ = 4.0 Hz), 124.9, 124.0, 123.9 (q, $J_{F\text{-}C}$ = 273.7 Hz), 120.3, 116.3, 65.0, 50.0, 15.7; HRMS (ESI): cacld. for $C_{18}H_{15}ClF_3N_3$ $[M+H]^+$: 366.0979, found 366.0977.



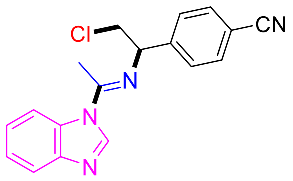
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2-chloro-1-(4-(trifluoromethoxy)phenyl)ethyl)ethan-1-imine **(3l)**: 149 mg, 78% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (d, J = 8.0 Hz, 1H), 8.35 (s, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.40 (m, 2H), 7.24 (d, J = 8.0 Hz, 2H), 4.96 (dd, J = 4.0 Hz, J = 8.0 Hz, 1H), 3.89 (m, 2H), 2.53 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.7, 148.9, 144.3, 141.0, 138.8, 132.3, 128.7, 124.8, 123.9, 121.3, 120.4 (q, $J_{F\text{-}C}$ = 256.0 Hz), 120.2, 116.3, 64.6, 50.2, 15.7; HRMS (ESI): cacld. for $C_{18}H_{15}ClF_3N_3O$ $[M+H]^+$: 382.0929, found 382.0930.



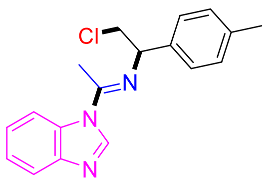
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2-chloro-1-(4-(difluoromethoxy)phenyl)ethyl)ethan-1-imine **(3m)**: 85 mg, 47% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (d, J = 8.0 Hz, 1H), 8.34 (s, 1H), 7.81 (d, J = 4.0 Hz, 1H), 7.46 (d, J = 8.0 Hz, 2H), 7.38 (m, 2H), 7.13 (d, J = 8.0 Hz, 2H), 6.50 (t, J = 72.0 Hz, 1H), 4.93 (dd, J = 4.0 Hz, J = 8.0 Hz, 1H), 3.90 (m, 2H), 2.51 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.6, 150.8, 144.3, 141.0, 137.4, 132.3, 128.7, 124.8, 123.9, 120.2, 120.0, 116.3, 115.7 (t, $J_{F\text{-}C}$ = 259.0 Hz), 64.7, 50.3, 15.7; HRMS (ESI): cacld. for $C_{18}H_{16}ClF_2N_3O$ $[M+H]^+$: 364.1023, found 364.1023.



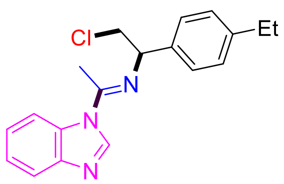
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2-chloro-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl)ethyl)ethan-1-imine **(3n)**: 156 mg, 74% yield; white solid; m.p. 174-176°C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.51 (d, J = 8.0 Hz, 1H), 8.31 (s, 1H), 7.81 (t, J = 8.0 Hz, 3H), 7.45 (d, J = 4.0 Hz, 2H), 7.37 (m, 2H), 4.92 (q, J = 4.0 Hz, 1H), 3.92 (m, 2H), 2.47 (s, 3H), 1.33 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.5, 144.3, 143.1, 140.9, 135.3, 132.3, 126.6, 124.6, 123.7, 120.1, 116.3, 83.8, 65.5, 50.3, 24.8, 15.7. HRMS (ESI): cacld. for $C_{23}H_{27}BClN_3O_2$ $[M+H]^+$: 424.1958, found 424.1966.



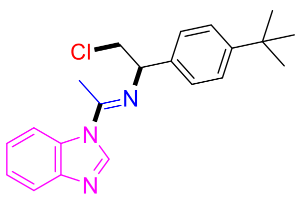
4-(1-((1-(1*H*-benzo[*d*]imidazol-1-yl)ethylidene)amino)-2-chloroethyl)benzonitrile **(3o)**: 129 mg, 80% yield; pale yellow solid, m.p. 209-211 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (d, *J* = 8.0 Hz, 1H), 8.35 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.40 (m, 2H), 5.00 (t, *J* = 8.0 Hz, 1H), 3.89 (d, *J* = 8.0 Hz, 2H), 2.54 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.1, 145.3, 144.3, 141.0, 132.7, 132.2, 128.1, 124.9, 124.0, 120.3, 118.3, 116.2, 112.1, 64.8, 49.7, 15.7; HRMS (ESI): cacld. for $C_{18}H_{15}ClN_4$ $[M+H]^+$: 323.1058, found 323.1062.



1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2-chloro-1-(p-tolyl)ethyl)ethan-1-imine **(3p)**: 115 mg, 74% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (d, *J* = 8.0 Hz, 1H), 8.31 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.39 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 4.89 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 3.91 (m, 2H), 2.49 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.2, 144.4, 140.9, 138.0, 137.3, 132.4, 129.6, 127.1, 124.7, 123.7, 120.2, 116.4, 65.2, 50.6, 21.1, 15.7; HRMS (ESI): cacld. for $C_{18}H_{18}ClN_3$ $[M+H]^+$: 312.1262, found 312.1265.

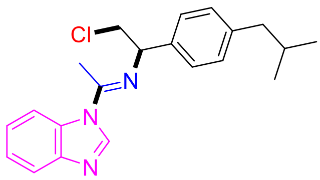


1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2-chloro-1-(4-ethylphenyl)ethyl)ethan-1-imine **(3q)**: 146 mg, 90% yield; white solid, m.p. 105-107 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (d, *J* = 8.0 Hz, 1H), 8.31 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.39 (m, 4H), 7.20 (d, *J* = 8.0 Hz, 2H), 4.90 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 3.91 (m, 2H), 2.64 (q, *J* = 8.0 Hz, 2H), 2.50 (s, 3H), 1.22 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 152.2, 144.3, 144.3, 140.9, 137.4, 132.4, 128.4, 127.1, 124.7, 123.8, 120.1, 116.4, 65.3, 50.6, 28.5, 15.7, 15.4; HRMS (ESI): cacld. for $C_{19}H_{20}ClN_3$ $[M+H]^+$: 326.1419, found 326.1416.

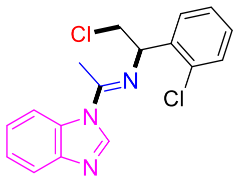


1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(1-(4-(tert-butyl)phenyl)-2-chloroethyl)ethan-1-imine **(3r)**: 147 mg, 83% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, *J* = 8.0 Hz, 1H), 8.31 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.38 (m, 6H), 4.91 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 3.92 (m, 2H), 2.50 (s, 3H), 1.30

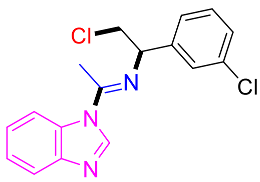
(s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.8, 150.5, 144.2, 140.8, 140.7, 132.4, 126.0, 125.7, 124.8, 123.7, 120.0, 116.8, 62.9, 58.1, 34.4, 31.2, 22.2, 19.3; HRMS (ESI): cacld. for $C_{21}H_{24}ClN_3$ $[M+H]^+$: 354.1732, found 354.1732.



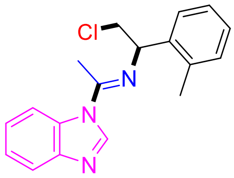
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2-chloro-1-(4-isobutylphenyl)ethyl)ethan-1-imine **(3s)**: 138 mg,78% yield; pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, *J* = 8.0 Hz, 1H), 8.32 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.38 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 4.90 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 3.91 (m, 2H), 2.50 (s, 3H), 2.46 (d, *J* = 4.0 Hz, 2H), 1.84 (m, 1H), 0.90 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.2, 144.4, 141.8, 141.0, 137.4, 132.4, 129.6, 126.9, 124.6, 123.7, 120.2, 116.4, 65.3, 50.7, 45.0, 30.1, 22.3, 15.7; HRMS (ESI): cacld. for $C_{21}H_{24}ClN_3$ $[M+H]^+$: 354.1732, found 354.1738.



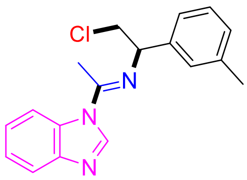
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2-chloro-1-(2-chlorophenyl)ethyl)ethan-1-imine **(3t)**: 113 mg, 68% yield; yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, *J* = 8.0 Hz, 1H), 8.33 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.61 (m, 1H), 7.40 (m, 3H), 7.29 (m, 1H), 7.24 (m, 1H), 5.46 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 3.93 (m, 2H), 2.52 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.2, 144.3, 141.0, 137.6, 132.5, 132.3, 129.7, 129.2, 129.1, 127.5, 124.8, 123.9, 120.2, 116.4, 61.2, 49.0, 16.1; HRMS (ESI): cacld. for $C_{17}H_{15}Cl_2N_3$ $[M+H]^+$: 332.0716, found 332.0722.



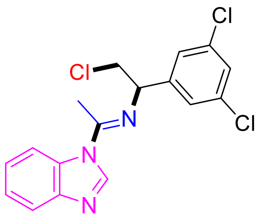
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2-chloro-1-(3-chlorophenyl)ethyl)ethan-1-imine **(3u)**: 157 mg, 95% yield; pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, *J* = 8.0 Hz, 1H), 8.33 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.37 (m, 6H), 4.90 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 3.89 (m, 2H), 2.51 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.8, 144.3, 142.1, 140.9, 134.7, 132.2, 130.2, 128.4, 127.4, 125.4, 124.8, 123.9, 120.2, 116.3, 64.9, 50.2, 15.7; HRMS (ESI): cacld. for $C_{17}H_{15}Cl_2N_3$ $[M+H]^+$: 332.0716, found 332.0713.



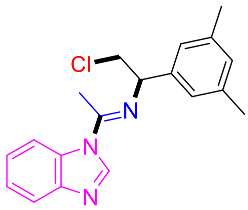
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2-chloro-1-(o-tolyl)ethyl)ethan-1-imine **(3v)**: 151 mg, 97% yield; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, *J* = 8.0 Hz, 1H), 8.30 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.51 (q, *J* = 4.0 Hz, 1H), 7.39 (m, 2H), 7.20 (d, *J* = 4.0 Hz, 3H), 5.12 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 3.94 (m, 1H), 3.83 (m, 1H), 2.49 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.1, 144.2, 140.9, 138.5, 134.6, 132.3, 130.8, 127.8, 127.3, 126.7, 124.7, 123.8, 120.1, 116.3, 61.7, 49.6, 19.5, 16.0; HRMS (ESI): cacld. for $C_{18}H_{18}ClN_3$ $[M+H]^+$: 312.1262, found 312.1265.



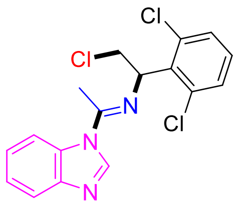
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2-chloro-1-(m-tolyl)ethyl)ethan-1-imine **(3w)**: 146 mg, 94% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, *J* = 8.0 Hz, 1H), 8.33 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.39 (m, 2H), 7.24 (m, 3H), 7.12 (d, *J* = 8.0 Hz, 1H), 4.89 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 3.92 (m, 2H), 2.49 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 152.3, 144.3, 141.0, 140.1, 138.6, 132.4, 128.9, 128.8, 127.8, 124.6, 124.2, 123.7, 120.2, 116.3, 65.5, 50.6, 21.4, 15.7; HRMS (ESI): cacld. for $C_{18}H_{18}ClN_3$ $[M+H]^+$: 312.1262, found 312.1267.



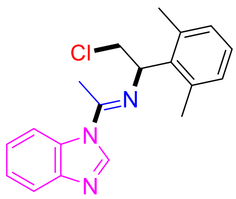
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2-chloro-1-(3,5-dichlorophenyl)ethyl)ethan-1-imine **(3x)**: 179 mg, 98% yield; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, *J* = 8.0 Hz, 1H), 8.34(s, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.41 (m, 2H), 7.35 (d, *J* =4.0 Hz, 2H), 7.32 (t, *J* = 4.0 Hz, 1H), 4.87 (t, *J* = 8.0 Hz, 1H), 3.87 (d, *J* = 8.0 Hz, 2H), 2.53 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.2, 144.3, 143.4, 141.0, 135.4, 132.2, 128.4, 125.8, 124.9, 124.0, 120.2, 116.2, 64.4, 49.8, 15.8; HRMS (ESI): cacld. for $C_{17}H_{14}Cl_3N_3$ $[M+H]^+$: 366.0326, found 366.0332.



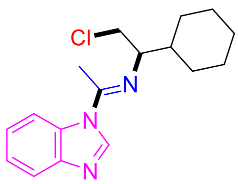
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2-chloro-1-(3,5-dimethylphenyl)ethyl)ethan-1-imine **(3y)**: 120 mg, 74% yield; pale yellow solid, m.p.130-132 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (d, *J* = 8.0 Hz, 1H), 8.32 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.38 (m, 2H), 7.02 (s, 2H), 6.93 (s, 1H), 4.83 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 3.91 (m, 2H), 2.48 (s, 3H), 2.30 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.2, 144.3, 141.0, 140.1, 138.4, 132.4, 129.8, 124.9, 124.6, 123.7, 120.1, 116.3, 65.5, 50.6, 21.3, 15.7; HRMS (ESI): cacld. for $C_{19}H_{20}ClN_3$ $[M+H]^+$: 326.1419, found 326.1416.



1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2-chloro-1-(2,6-dichlorophenyl)ethyl)ethan-1-imine **(3z)**: 181 mg, 99% yield; white solid, m.p. 183-185 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (d, *J* = 8.0 Hz, 1H), 8.32 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.36 (m, 4H), 7.19 (t, *J* = 8.0 Hz, 1H), 5.79 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 4.43 (dd, *J* = 8.0 Hz, *J* = 12.0 Hz, 1H), 4.16 (dd, *J* = 8.0 Hz, *J* = 12.0 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.1, 144.3, 141.0, 135.2, 134.9, 132.3, 129.7, 124.7, 123.8, 120.1, 116.6, 61.9, 46.1, 16.3; HRMS (ESI): cacld. for $C_{17}H_{14}Cl_3N_3$ $[M+H]^+$: 366.0326, found 366.0322.

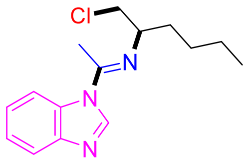


1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2-chloro-1-(2,6-dimethylphenyl)ethyl)ethan-1-imine **(3aa)**: 109 mg, 67% yield; white solid, m.p. 165-167 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, *J* = 8.0 Hz, 1H), 8.27 (s, 1H), 7.80 (d, *J* = 4.0 Hz, 1H), 7.37 (m, 2H), 7.09 (t, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 2H), 5.25 (m, 1H), 4.26 (t, *J* = 8.0 Hz, 1H), 3.85 (m, 1H), 2.46 (s, 6H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.9, 144.4, 140.9, 136.5, 136.2, 132.4, 127.8, 124.6, 123.7, 120.1, 116.2, 62.2, 47.4, 21.7, 16.2; HRMS (ESI): cacld. for $C_{19}H_{20}ClN_3$ $[M+H]^+$: 326.1419, found 326.1415.

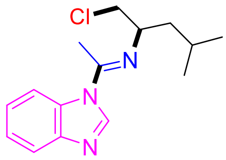


1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2-chloro-1-cyclohexylethyl)ethan-1-imine **(3ab)**: 65 mg, 43%

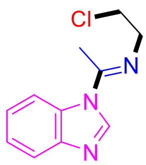
yield; yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 8.39 (m, 1H), 8.35 (s, 1H), 7.80 (m, 1H), 7.36 (m, 2H), 3.87 (d, *J* = 8.0 Hz, 1H), 3.69 (m, 2H), 2.52 (s, 3H), 1.76 (m, 4H), 1.68 (m, 1H), 1.24 (m, 3H), 1.12 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 151.1, 144.1, 141.0, 132.4, 124.5, 123.7, 120.0, 116.4, 66.1, 47.9, 42.0, 30.1, 28.7, 26.24, 26.16, 26.1, 15.2. HRMS (ESI): cacld. for $C_{17}H_{22}ClN_3$ $[M+H]^+$: 304.1575, found 304.1577.



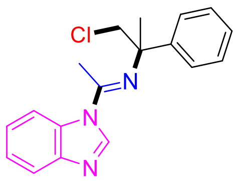
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(1-chlorohexan-2-yl)ethan-1-imine **(3ac)**: 35 mg, 25% yield; pale yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 8.37 (m, 1H), 8.35 (s, 1H), 7.80 (m, 1H), 7.35 (m, 2H), 3.85 (m, 1H), 3.76 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 3.65 (dd, *J* = 8.0 Hz, *J* = 12.0 Hz, 1H), 2.54 (s, 3H), 1.76 (m, 1H), 1.66 (m, 1H), 1.33 (m, 4H), 0.90 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.1, 144.3, 141.0, 132.4, 124.5, 123.7, 120.1, 116.3, 61.2, 49.1, 34.2, 28.3, 22.6, 15.3, 13.9; HRMS (ESI): cacld. for $C_{15}H_{20}ClN_3$ $[M+H]^+$: 278.1419, found 278.1420.



1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(1-chloro-4-methylpentan-2-yl)ethan-1-imine **(3ad)**: 85 mg, 61% yield; yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 8.37 (m, 1H), 8.34 (s, 1H), 7.79 (m, 1H), 7.34 (m, 2H), 3.94 (m, 1H), 3.73 (m, 1H), 3.62 (m, 1H), 2.55 (s, 3H), 1.63 (m, 2H), 1.54 (m, 1H), 0.96 (d, *J* = 4.0 Hz, 3H), 0.92 (d, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.1, 144.3, 141.0, 132.4, 124.5, 123.6, 120.1, 116.3, 59.2, 49.4, 43.6, 25.0, 23.4, 22.0, 15.3; HRMS (ESI): cacld. for $C_{15}H_{20}ClN_3$ $[M+H]^+$: 278.1419, found 278.1422.

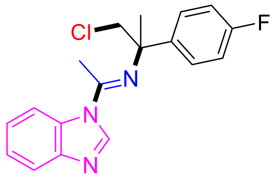


1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2-chloroethyl)ethan-1-imine **(3ae)**: 69 mg, 62% yield; white oil; ^1H NMR (400 MHz, $CDCl_3$): δ 8.38 (m, 1H), 8.31 (s, 1H), 7.79 (m, 1H), 7.35 (m, 2H), 3.90 (t, *J* = 4.0 Hz, 2H), 3.86 (t, *J* = 4.0 Hz, 2H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.3, 144.3, 140.8, 132.2, 124.6, 123.7, 120.1, 116.1, 51.8, 44.8, 15.3; HRMS (ESI): cacld. for $C_{11}H_{12}ClN_3$ $[M+H]^+$: 222.0793, found 222.0797.

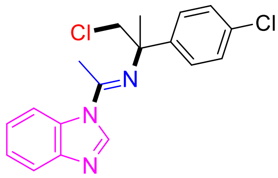


1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(1-chloro-2-phenylpropan-2-yl)ethan-1-imine **(3af)**: 134 mg, 86%

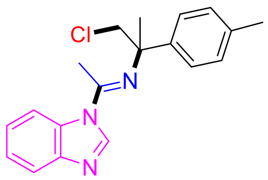
yield; pale yellow solid, m.p. 117-119 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, *J* = 8.0 Hz, 1H), 8.24 (s, 1H), 7.81 (s, 1H), 7.37 (m, 7H), 4.02 (d, *J* = 12.0 Hz, 1H), 3.79 (d, *J* = 12.0 Hz, 1H), 2.05 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 151.9, 144.0, 132.5, 128.8, 127.6, 126.4, 124.8, 123.8, 120.1, 116.8, 63.1, 58.0, 22.2, 19.3; HRMS (ESI): cacld. for $C_{18}H_{18}ClN_3$ [M+H]$^+$: 312.1262, found 312.1259.



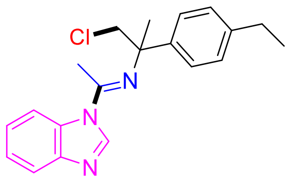
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(1-chloro-2-(4-fluorophenyl)propan-2-yl)ethan-1-imine **(3ag)**: 123 mg, 75% yield; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (d, *J* = 8.0 Hz, 1H), 8.23 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.39 (m, 4H), 7.07 (t, *J* = 8.0 Hz, 2H), 3.98 (d, *J* = 8.0 Hz, 1H), 3.78 (d, *J* = 8.0 Hz, 1H), 2.07 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.0 (d, $J_{F\text{-}C}$ = 248.5 Hz), 152.0, 144.2, 140.6, 139.8 (d, $J_{F\text{-}C}$ = 4.0 Hz), 132.3, 128.2 (d, $J_{F\text{-}C}$ = 8.1 Hz), 124.9, 123.9, 120.1, 116.7, 115.7 (d, $J_{F\text{-}C}$ = 21.2 Hz), 62.7, 57.9, 22.3, 19.3; HRMS (ESI): cacld. for $C_{18}H_{17}ClFN_3$ [M+H]$^+$: 330.1168, found 330.1173.



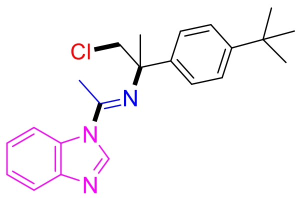
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(1-chloro-2-(4-chlorophenyl)propan-2-yl)ethan-1-imine **(3ah)**: 135 mg, 78% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (d, *J* = 8.0 Hz, 1H), 8.23 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.37 (m, 6H), 3.97 (d, *J* = 12.0 Hz, 1H), 3.79 (d, *J* = 12.0 Hz, 1H), 2.07 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 152.1, 144.3, 142.5, 140.7, 133.6, 132.3, 129.0, 127.9, 124.8, 123.9, 120.2, 116.7, 62.8, 57.7, 22.2, 19.4; HRMS (ESI): cacld. for $C_{18}H_{17}Cl_2N_3$ [M+H]$^+$: 346.0872, found 346.0870.



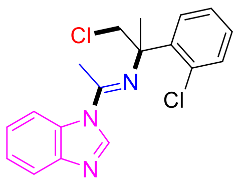
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(1-chloro-2-(*p*-tolyl)propan-2-yl)ethan-1-imine **(3ai)**: 91 mg, 56% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (d, *J* = 8.0 Hz, 1H), 8.22 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.39 (m, 3H), 7.27 (s, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 4.00 (d, *J* = 12.0 Hz, 1H), 3.76 (d, *J* = 12.0 Hz, 1H), 2.35 (s, 3H), 2.05 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.7, 144.1 140.9, 140.7, 137.3, 132.3, 129.5, 126.2, 124.8, 123.8, 120.0, 116.8, 62.9, 58.0, 22.2, 21.0, 19.2; HRMS (ESI): cacld. for $C_{19}H_{20}ClN_3$ [M+H]$^+$: 326.1419, found 326.1416.



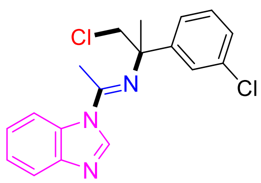
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(1-chloro-2-(4-ethylphenyl)propan-2-yl)ethan-1-imine **(3aj)**: 136 mg, 80% yield; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, *J* = 8.0 Hz, 1H), 8.22 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.39 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 4.01 (d, *J* = 12.0 Hz, 1H), 3.75 (d, *J* = 8.0 Hz, 1H), 2.66 (q, *J* = 8.0 Hz, 2H), 2.06 (s, 3H), 1.83 (s, 3H), 1.24 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.7, 143.9, 143.6, 141.1, 140.6, 132.3, 128.3, 126.3, 124.9, 123.9, 119.9, 116.8, 63.0, 58.0, 28.3, 22.2, 19.3, 15.3; HRMS (ESI): cacld. for $C_{20}H_{22}ClN_3$ $[M+H]^+$: 340.1575, found 340.1571.



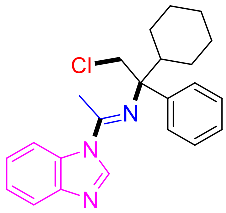
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2-(4-(*tert*-butyl)phenyl)-1-chloropropan-2-yl)ethan-1-imine **(3ak)**: 129 mg, 70% yield; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (d, *J* = 8.0 Hz, 1H), 8.23 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.39 (m, 4H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.02 (d, *J* = 12.0 Hz, 1H), 3.75 (d, *J* = 8.0 Hz, 1H), 2.06 (s, 3H), 1.84 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.8, 150.5, 144.2, 140.8, 140.7, 132.4, 126.0, 125.7, 124.8, 123.7, 120.0, 116.8, 62.9, 58.1, 34.4, 31.2, 22.2, 19.3; HRMS (ESI): cacld. for $C_{22}H_{26}ClN_3$ $[M+H]^+$: 368.1888, found 368.1888.



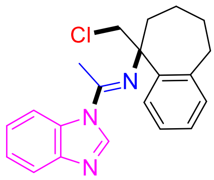
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(1-chloro-2-(3-chlorophenyl)propan-2-yl)ethan-1-imine **(3al)**: 131 mg, 76% yield; white solid, m.p. 148-150 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (d, *J* = 8.0 Hz, 1H), 8.23 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.36 (m, 5H), 4.30 (d, *J* = 12.0 Hz, 1H), 4.19 (d, *J* = 12.0 Hz, 1H), 2.02 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.9, 144.3, 140.8, 140.2, 132.5, 132.4, 132.1, 129.5, 129.4, 127.1, 124.6, 123.7, 120.1, 116.7, 63.8, 53.0, 23.8, 18.1; HRMS (ESI): cacld. for $C_{18}H_{17}Cl_2N_3$ $[M+H]^+$: 346.0872, found 346.0885.



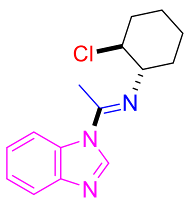
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(1-chloro-2-(3-chlorophenyl)propan-2-yl)ethan-1-imine **(3am)**: 148 mg, 86% yield; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (d, *J* = 8.0 Hz, 1H), 8.24 (s, 1H), 7.81 (d, *J* = 4.0 Hz, 1H), 7.39 (m, 3H), 7.30 (m, 3H), 3.98 (d, *J* = 12.0 Hz, 1H), 3.79 (d, *J* = 8.0 Hz, 1H), 2.08 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.2, 146.1, 144.3, 140.7, 134.8, 132.3, 130.1, 127.9, 126.6, 124.9, 124.7, 123.9, 120.2, 116.7, 62.9, 57.6, 22.2, 19.4; HRMS (ESI): cacld. for $C_{18}H_{17}Cl_2N_3$ $[M+H]^+$: 346.0872, found 346.0876.



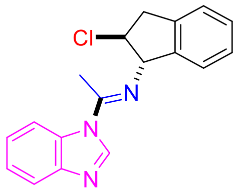
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2-chloro-1-cyclohexyl-1-phenylethyl)ethan-1-imine **(3an)**: 74 mg, 39% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, *J* = 8.0 Hz, 1H), 8.32 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.35 (m, 6H), 7.25 (s, 1H), 4.28 (d, *J* = 12.0 Hz, 1H), 4.23 (d, *J* = 12.0 Hz, 1H), 2.30 (t, *J* = 12.0 Hz, 1H), 2.05 (s, 3H), 1.97 (m, 2H), 1.79 (m, 2H), 1.67 (d, *J* = 12.0 Hz, 1H), 1.35 (m, 2H), 1.00 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.4, 144.2, 141.6, 141.0, 132.4, 128.2, 127.13, 127.10, 124.6, 123.6, 120.1, 116.3, 68.3, 49.4, 47.9, 28.0, 27.9, 26.9, 26.8, 26.4, 21.4, 14.1; HRMS (ESI): cacld. for $C_{23}H_{26}ClN_3$ $[M+H]^+$: 380.1888, found 380.1885.



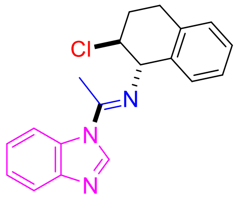
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(5-(chloromethyl)-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-yl)ethan-1-imine **(3ao)**: 74 mg, 42% yield; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (d, *J* = 8.0 Hz, 1H), 8.23 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.37 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 3H), 4.14 (d, *J* = 12.0 Hz, 1H), 3.97 (d, *J* = 8.0 Hz, 1H), 3.04 (m, 1H), 2.76 (m, 1H), 2.36 (m, 1H), 2.16 (m, 1H), 2.01 (m, 6H), 1.70 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.1, 144.1, 142.3, 141.9, 140.8, 132.4, 131.7, 128.7, 127.6, 126.6, 124.8, 123.7, 119.9, 117.0, 67.0, 53.8, 35.3, 34.3, 26.7, 24.0, 19.6; HRMS (ESI): cacld. for $C_{21}H_{22}ClN_3$ $[M+H]^+$: 352.1575, found 352.1568.



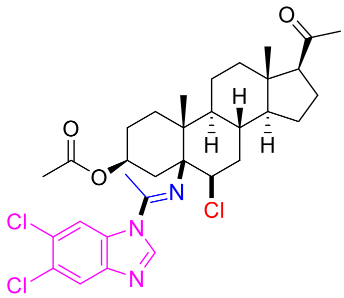
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2-chlorocyclohexyl)ethan-1-imine **(3ap)**: 85 mg, 62% yield; pale yellow solid, m.p. 86-88 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (m, 1H), 8.31 (s, 1H), 7.78 (m, 1H), 7.33 (m, 2H), 4.06 (m, 1H), 3.60 (m, 1H), 2.51 (s, 3H), 2.36 (m, 1H),1.82 (m, 4H), 1.63 (m, 1H), 1.44 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.4, 144.2, 140.9, 132.4, 124.3, 123.5, 120.0, 116.2, 65.1, 35.4, 33.3, 25.6, 23.7, 15.2; HRMS (ESI): cacld. for $C_{15}H_{18}ClN_3$ $[M+H]^+$: 276.1262, found 276.1259.



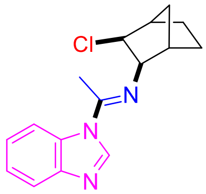
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2-chloro-2,3-dihydro-1*H*-inden-1-yl)ethan-1-imine **(3aq)**: 138 mg, 89% yield; pale yellow solid, m.p. 103-105 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (s, 1H), 8.33 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.31 (m, 4H), 7.25 (m, 1H), 7.09 (d, *J* = 4.0 Hz, 1H), 5.28 (d, *J* = 8.0 Hz, 1H), 4.61 (q, *J* = 8.0 Hz, 1H), 3.62 (dd, *J* = 4.0 Hz, *J* = 16.0 Hz, 1H), 3.30 (dd, *J* = 12.0 Hz, *J* = 16.0 Hz, 1H), 2.73 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.1, 144.3, 141.6, 140.99, 140.96, 139.3, 132.3, 128.4, 127.5, 124.6, 123.8, 123.6, 120.1, 116.5, 71.8, 64.2, 40.9, 15.5; HRMS (ESI): cacld. for $C_{18}H_{16}ClN_3$ $[M+H]^+$: 310.1106, found 310.1105.



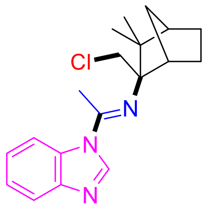
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2-chloro-1,2,3,4-tetrahydronaphthalen-1-yl)ethan-1-imine **(3ar)**: 150 mg, 93% yield; yellow solid, m.p. 119-121 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (s, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.29 (m, 2H), 7.19 (m, 3H), 6.98 (d, *J* = 8.0 Hz, 1H), 4.94 (d, *J* = 8.0 Hz, 1H), 4.39 (m, 1H), 3.07 (m, 2H), 2.71 (s, 3H), 2.59 (m, 1H), 2.32 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.9, 144.1, 141.0, 135.3, 134.8, 132.3, 128.8, 127.6, 127.4, 126.4, 124.5, 123.7, 120.0, 116.4, 65.5, 62.6, 31.3, 28.4, 15.4; HRMS (ESI): cacld. for $C_{19}H_{18}ClN_3$ $[M+H]^+$: 324.1262, found 324.1258.



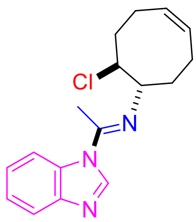
(3*S*,5*S*,6*R*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-17-acetyl-6-chloro-5-((1-(5,6-dichloro-1*H*-benzo[*d*]imidazol-1-yl)ethylidene)amino)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate **(3as)**: 149 mg, 48% yield; pale yellow solid, m.p. 228-230 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (s, 1H), 8.35 (s, 1H), 7.87 (s, 1H), 5.40 (m, 1H), 4.05 (s, 1H), 2.58 (t, *J* = 8.0 Hz, 1H), 2.51 (s, 3H), 2.26 (m, 2H), 2.14 (s, 3H), 2.08 (m, 3H), 2.00 (s, 3H), 1.95 (m, 2H), 1.80 (m, 4H), 1.61 (m, 5H), 1.47 (m, 3H), 1.38 (s, 3H), 0.71 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.4, 149.7, 142.6, 130.9, 128.5, 127.7, 126.1, 121.3, 116.7, 85.2, 70.6, 66.0, 63.5, 55.8, 45.9, 44.2, 40.5, 38.7, 38.5, 34.6, 33.5, 31.7, 31.4, 26.1, 24.4, 23.4, 22.7, 21.3, 21.1, 18.7, 15.0, 13.6; HRMS (ESI): cacld. for $C_{32}H_{40}Cl_3N_3O_3$ $[M+H]^+$: 620.2208, found 620.2210.



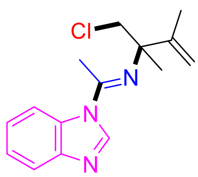
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(3-chlorobicyclo[2.2.1]heptan-2-yl)ethan-1-imine **(3at)**: 52 mg, 36% yield; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 8.0 Hz,1H), 8.27 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.36 (m, 2H), 4.51 (s, 1H), 3.69 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 2.44 (s, 3H), 2.41 (s, 1H), 2.35 (s, 1H), 2.08 (m, 2H), 1.95f (m, 1H), 1.56 (m, 1H), 1.37 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.4, 144.3, 140.8, 132.2, 124.6, 123.7, 120.2, 116.0, 64.6, 60.6, 50.2, 42.1, 38.9, 26.2, 24.0, 15.2; HRMS (ESI): cacld. for $C_{16}H_{18}ClN_3$ $[M+H]^+$: 288.1262, found 288.1261.



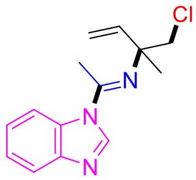
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2-(chloromethyl)-3,3 dimethylbicyclo[2.2.1]heptan-2-yl)ethan-1-imine **(3au)**: 79 mg, 48% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (s, 1H), 8.26 (m, 1H), 7.79 (m, 1H), 7.33 (m, 2H), 4.01 (d, *J* = 12.0 Hz, 1H), 3.82 (m, 1H), 3.57 (d, *J* = 12.0 Hz, 1H), 2.52 (s, 3H), 1.90 (m, 4H), 1.73 (m, 2H), 1.61 (m, 1H), 1.25 (s, 3H), 1.00 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.1, 144.3, 141.2, 132.2, 124.3, 123.4, 120.2, 115.4, 64.0, 53.8, 48.8, 46.7, 46.7, 39.4, 32.7, 26.9, 21.1, 20.5, 15.4; HRMS (ESI): cacld. for $C_{19}H_{24}ClN_3$ $[M+H]^+$: 330.1732, found 330.1729.



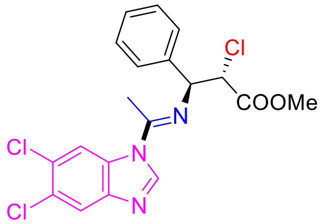
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(8-chlorocyclooct-4-en-1-yl)ethan-1-imine **(3av)**: 74 mg, 49% yield; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (m, 1H), 8.32 (s, 1H), 7.79 (m, 1H), 7.34 (m, 2H), 5.69 (t, *J* = 4.0 Hz, 2H), 4.62 (m, 1H), 4.12 (m, 1H), 2.74 (m, 3H), 2.49 (s, 3H), 2.32 (m, 1H), 2.19 (m, 2H), 2.09 (m, 1H), 1.85 (m, 1H) ; ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.7, 144.3, 141.0, 132.4, 128.9, 128.2, 124.3, 123.5, 120.0, 116.1, 67.6, 63.9, 33.9, 32.3, 25.0, 24.2, 15.3; HRMS (ESI): cacld. for $C_{17}H_{20}ClN_3$ $[M+H]^+$: 302.1419, found 302.1437.



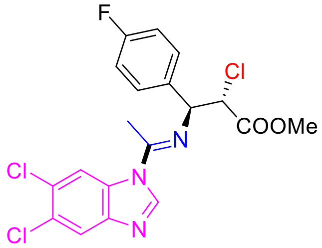
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(1-chloro-2,3-dimethylbut-3-en-2-yl)ethan-1-imine **(3aw)**: 98 mg, 71% yield; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (d, J = 8.0 Hz, 1H), 8.32 (s, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.35 (m, 2H), 5.17 (d, J = 20.0 Hz, 2H), 3.85 (d, J = 8.0 Hz, 1H), 3.77 (d, J = 12.0 Hz, 1H), 2.52 (s, 3H), 1.77 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.0, 145.6, 144.2, 140.7, 132.3, 124.6, 123.7, 120.0, 116.5, 115.2, 64.3, 54.3, 21.8, 19.4, 18.0; HRMS (ESI): cacld. for $C_{15}H_{18}ClN_3$ $[M+H]^+$: 276.1262, found 276.1258.



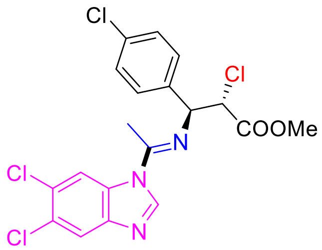
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(1-chloro-3-methylbut-3-en-2-yl)ethan-1-imine **(3ax)**: 93 mg, 71% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, J = 8.0 Hz, 1H), 8.29 (s, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.35 (m, 2H), 6.04 (dd, J = 12.0 Hz, J = 16.0 Hz, 1H), 5.36 (m, 2H), 3.76 (d, J = 12.0 Hz, 1H), 3.68 (d, J = 12.0 Hz, 1H), 2.53 (s, 3H), 1.56 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.4, 144.2, 140.7, 132.3, 124.7, 123.7, 120.0, 117.5, 116.7, 116.4, 61.8, 56.2, 21.4, 18.8; HRMS (ESI): cacld. for $C_{14}H_{16}ClN_3$ $[M+H]^+$: 262.1106, found 262.1110.



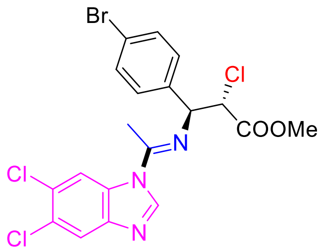
Methyl-2-chloro-3-((1-(5,6-dichloro-1*H*-benzo[*d*]imidazol-1-yl)ethylidene)amino)-3-phenylpropanoate **(3ay)**: 135 mg, 64% yield; pale yellow solid, m.p. 186-188 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (s, 1H), 8.21 (s, 1H), 7.86 (s, 1H), 7.38 (m, 5H), 5.02 (d, J = 12.0 Hz, 1H), 4.77 (d, J = 8.0 Hz, 1H), 3.80 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.7, 153.1, 143.6, 142.3, 138.3, 131.1, 128.8, 128.6, 128.1, 121.4, 1178, 67.3, 60.3, 53.0, 16.0; HRMS (ESI): cacld. for $C_{19}H_{16}Cl_3N_3O_2$ $[M+H]^+$: 424.0381, found 424.0383.



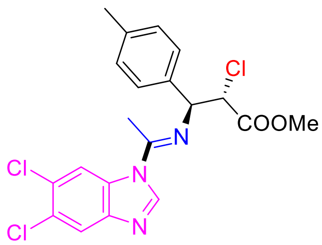
Methyl-2-chloro-3-((1-(5,6-dichloro-1*H*-benzo[*d*]imidazol-1-yl)ethylidene)amino)-3-(4-fluorophenyl)propanoate **(3az)**: 143 mg, 65% yield; white solid, m.p. 224-226 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (s, 1H), 8.23 (s, 1H), 7.87 (s, 1H), 7.40 (m, 2H), 7.08 (t, J = 8.0 Hz, 2H), 5.02 (d, J = 12.0 Hz, 1H), 4.72 (d, J = 12.0 Hz, 1H), 3.80 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.6, 162.6 (d, J_{F-C} = 248.5 Hz), 153.3, 143.6, 142.3, 134.1 (d, J_{F-C} = 3.0 Hz), 131.1, 129.7 (d, J_{F-C} = 8.1 Hz), 128.9, 128.2, 121.4, 117.7, 115.8 (d, J_{F-C} = 22.2 Hz), 66.5, 60.3, 53.1, 16.0; HRMS (ESI): cacld. for $C_{19}H_{15}Cl_3FN_3O_2$ $[M+H]^+$: 442.0287, found 442.0284.



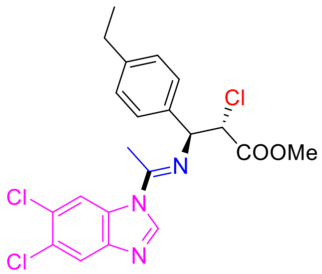
Methyl-2-chloro-3-(4-chlorophenyl)-3-((1-(5,6-dichloro-1*H*-benzo[*d*]imidazol-1-yl)ethylidene)amino)propanoate **(3ba)**: 133 mg, 58% yield; white solid, m.p. 163-165 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (s, 1H), 8.22 (s, 1H), 7.88 (s, 1H), 7.36 (s, 4H), 5.01 (d, *J* = 8.0 Hz, 1H), 4.71 (d, *J* = 8.0 Hz, 1H), 3.80 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.5, 153.5, 142.3, 136.8, 134.6, 129.4, 129.1, 129.0, 128.3, 121.5, 117.7, 66.6, 60.2, 53.2, 16.1; HRMS (ESI): cacld. for $C_{19}H_{15}Cl_4N_3O_2$ [M+H]$^+$: 457.9991, found 457.9990.



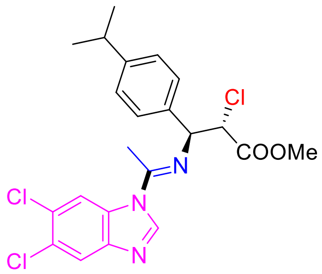
Methyl-3-(4-bromophenyl)-3-chloro-2-((1-(5,6-dichloro-1*H*-benzo[*d*]imidazol-1-yl)ethylidene)amino)propanoate **(3bb)**: 143 mg, 57% yield; white solid, m.p. 182-184 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (s, 1H), 8.22 (s, 1H), 7.87 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.00 (d, *J* = 8.0 Hz,1H), 4.71 (d, *J* = 8.0 Hz, 1H), 3.80 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.4, 153.5, 143.6, 142.4, 137.3, 132.0, 131.1, 129.7, 128.9, 128.2, 122.6, 121.4, 117.7, 66.6, 60.1, 53.1, 16.0; HRMS (ESI): cacld. for $C_{19}H_{15}BrCl_3N_3O_2$ [M+H]$^+$: 501.9486, found 501.9484.



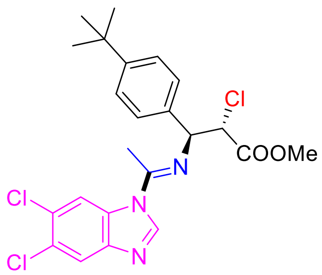
Methyl-3-chloro-2-((1-(5,6-dichloro-1*H*-benzo[*d*]imidazol-1-yl)ethylidene)amino)-3-(*p*-tolyl)propanoate **(3bc)**: 153 mg, 70% yield; white solid, m.p. 174-176 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (s, 1H), 8.22 (s, 1H), 7.88 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.00 (d, *J* = 12.0 Hz, 1H), 4.71 (d, *J* = 8.0 Hz, 1H), 3.80 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.5, 152.1, 144.5, 137.3, 132.1, 129.8, 129.0, 128.3, 122.7, 121.5, 116.9, 66.7, 60.1, 53.2, 16.1; HRMS (ESI): cacld. for $C_{20}H_{18}Cl_3N_3O_2$ [M+H]$^+$: 438.0537, found 438.0537.



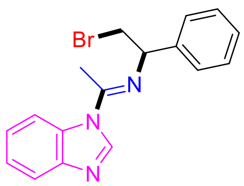
Methyl-3-chloro-2-((1-(5,6-dichloro-1*H*-benzo[*d*]imidazol-1-yl)ethylidene)amino)-3-(4-ethylphenyl)propanoate **(3bd)**: 126 mg, 56% yield; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (s, 1H), 8.21 (s, 1H), 7.87 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 4.99 (d, *J* = 8.0 Hz, 1H), 4.76 (d, *J* = 12.0 Hz, 1H), 3.80 (s, 3H), 2.65 (q, *J* = 8.0 Hz, 2H), 2.41 (s, 3H), 1.23 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.8, 152.9, 144.7, 143.6, 142.3, 135.5, 128.9, 128.3, 128.1, 128.0, 121.4, 117.8, 67.2, 60.4, 53.0, 28.5, 16.0, 15.3; HRMS (ESI): cacld. for $C_{21}H_{20}Cl_3N_3O_2$ $[M+H]^+$: 452.0694, found 452.0690.



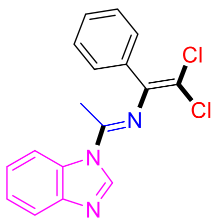
Methyl-3-chloro-2-((1-(5,6-dichloro-1*H*-benzo[*d*]imidazol-1-yl)ethylidene)amino)-3-(4-isopropylphenyl)propanoate **(3be)**: 144 mg, 62% yield; pale yellow solid, m.p. 171-173 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (s, 1H), 8.21 (s, 1H), 7.87 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 4.99 (d, *J* = 8.0 Hz, 1H), 4.75 (d, *J* = 8.0 Hz, 1H), 3.79 (s, 3H), 2.88 (m, 1H), 2.41 (s, 3H), 1.25 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.4, 153.5, 143.6, 142.3, 137.3, 132.0, 131.0, 129.7, 128.9, 128.2, 122.6, 121.4, 117.7, 66.6, 60.1, 53.1, 16.0; HRMS (ESI): cacld. for $C_{22}H_{22}Cl_3N_3O_2$ $[M+H]^+$: 466.0850, found 466.0848.



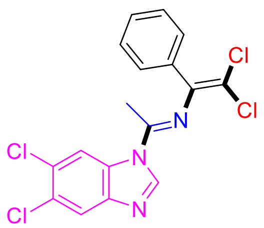
Methyl-3-(4-(*tert*-butyl)phenyl)-2-chloro-3-((1-(5,6-dichloro-1*H*-benzo[*d*]imidazol-1-yl)ethylidene)amino)propanoate **(3bf)**: 129 mg, 54% yield; white solid, m.p. 189-191 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (s, 1H), 8.21 (s, 1H), 7.87 (s, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.00 (d, *J* = 8.0 Hz, 1H), 4.76 (d, *J* = 8.0 Hz, 1H), 3.79 (s, 3H), 2.42 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.8, 152.9, 151.6, 143.6, 142.3, 135.1, 131.1, 128.8, 128.1, 127.7, 125.7, 121.4, 117.8, 67.1, 60.3, 53.0, 34.6, 31.2, 16.0; HRMS (ESI): cacld. for $C_{23}H_{24}Cl_3N_3O_2$ $[M+H]^+$: 480.1007, found 480.0998.



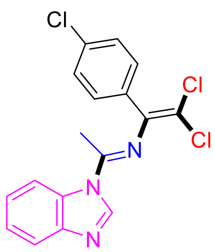
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2-bromo-1-phenylethyl)ethan-1-imine **(3bg)**: 99 mg, 58% yield; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, *J* = 8.0 Hz, 1H), 8.37 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 3H), 7.34 (m, 4H), 4.99 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 3.82 (m, 2H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.3, 144.1, 141.1, 140.8, 132.3, 128.9, 128.2, 127.1, 124.8, 123.8, 120.0, 116.5, 65.3, 39.3, 15.7; HRMS (ESI): cacld. for $C_{17}H_{16}BrN_3$ $[M+H]^+$: 342.0600, found 342.0601.



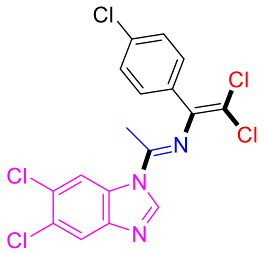
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2,2-dichloro-1-phenylvinyl)ethan-1-imine **(5a)**: 73 mg, 44% yield; Pale yellow solid; m.p. 157-159 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.48 (d, *J* = 8.0 Hz, 1H), 8.32 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.39 (m, 5H), 2.56 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.5, 144.4, 142.6, 141.0, 135.2, 132.0, 129.0, 128.5, 128.4, 125.3, 124.4, 120.5, 116.5, 106.3, 17.8. HRMS (ESI): cacld. for $C_{17}H_{13}Cl_2N_3$ $[M+H]^+$: 330.0559, found 330.0569.



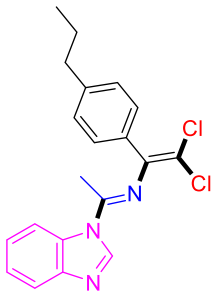
N-(2,2-dichloro-1-phenylvinyl)-1-(5,6-dichloro-1*H*-benzo[*d*]imidazol-1-yl)ethan-1-imine **(5b)**: 115 mg, 58% yield; white solid; m.p. 153-155°C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.65 (s, 1H), 8.29 (s, 1H), 7.89 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.40 (m, 3H), 2.54 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.3, 143.6, 142.4, 142.2, 134.9, 131.0, 129.4, 129.2, 128.7, 128.6, 128.4, 121.5, 118.0, 107.0, 17.6. HRMS (ESI): cacld. for $C_{17}H_{11}Cl_4N_3$ $[M+H]^+$: 397.9780, found 397.9785.



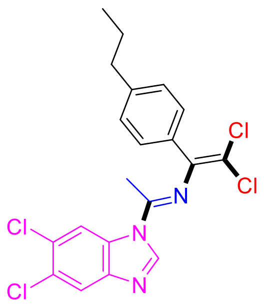
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2,2-dichloro-1-(4-chlorophenyl)vinyl)ethan-1-imine **(5c)**: 87 mg, 48% yield; white solid; m.p. 163-165 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.45 (d, *J* = 8.0 Hz, 1H), 8.32 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 2.54 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.8, 144.4, 141.5, 141.0, 134.9, 133.6, 132.0, 129.8, 128.7, 125.3, 124.5, 120.6, 116.4, 106.8, 17.8. HRMS (ESI): cacld. for $C_{17}H_{12}Cl_3N_3$ $[M+H]^+$: 364.0170, found 364.0171.



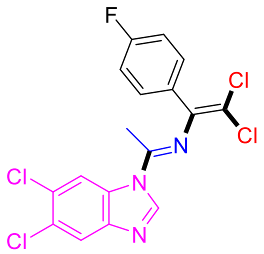
N-(2,2-dichloro-1-(4-chlorophenyl)vinyl)-1-(5,6-dichloro-1*H*-benzo[*d*]imidazol-1-yl)ethan-1-imine **(5d)**: 109 mg, 51% yield; white solid; m.p. 163-165°C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.61 (s, 1H), 8.29 (s, 1H), 7.89 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 2.53 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.6, 143.6, 142.4, 141.1, 135.1, 133.2, 130.9, 129.8, 129.4, 128.8, 128.7, 121.6, 117.9, 107.4, 17.6. HRMS (ESI): cacld. for $C_{17}H_{10}Cl_5N_3$ $[M+H]^+$: 431.9390, found 431.9380.



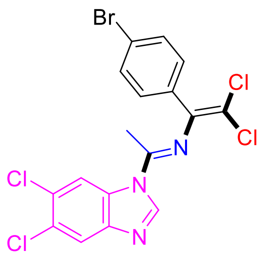
1-(1*H*-benzo[*d*]imidazol-1-yl)-*N*-(2,2-dichloro-1-(4-propylphenyl)vinyl)ethan-1-imine **(5e)**: 47 mg, 25% yield; white solid; m.p. 141-143 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.48 (d, *J* = 8.0 Hz, 1H), 8.32 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.41 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 2.59 (t, *J* = 8.0 Hz, 2H), 2.54 (s, 3H); 1.64 (q, *J* = 8.0 Hz, 2H), 0.94 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.4, 143.8, 142.6, 141.0, 132.5, 128.5, 128.3, 125.2, 124.4, 120.4, 116.5, 105.8, 37.8, 24.3, 17.7, 13.8. HRMS (ESI): cacld. for $C_{20}H_{19}Cl_2N_3$ $[M+H]^+$: 372.1029, found 372.1034.



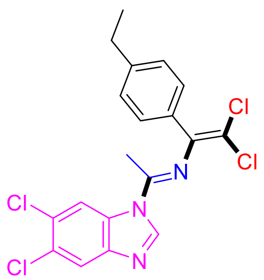
N-(2,2-dichloro-1-(4-propylphenyl)vinyl)-1-(5,6-dichloro-1*H*-benzo[*d*]imidazol-1-yl)ethan-1-imine **(5f)**: 79 mg, 36% yield; Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): 8.66 (s, 1H), 8.27 (s, 1H), 7.89 (s, 1H), 7.48 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 2.60 (t, J = 8.0 Hz, 2H), 2.53 (s, 3H), 1.65 (q, J = 8.0 Hz, 2H), 0.95 (t, J = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.12, 144.1, 143.5, 142.4, 142.2, 132.1, 131.0, 129.4, 128.6, 128.3, 121.5, 118.1, 106.4, 37.8,24.3, 17.6, 13.8. HRMS (ESI): cacld. for $C_{20}H_{17}Cl_4N_3$ $[M+H]^+$: 440.0249, found 440.0243.



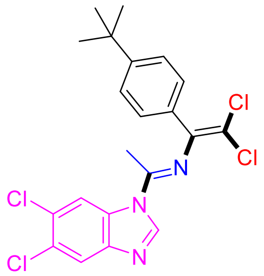
N-(2,2-dichloro-1-(4-fluorophenyl)vinyl)-1-(5,6-dichloro-1*H*-benzo[*d*]imidazol-1-yl)ethan-1-imine **(5g)**: 89 mg, 43% yield; white solid; m.p. 135-137°C; ^{1}H NMR (400 MHz, CD_2Cl_2): 8.65 (s, 1H), 8.32 (s, 1H), 7.86 (s, 1H), 7.60 (t, J = 8.0 Hz, 2H), 7.12 (t, J = 8.0 Hz, 2H), 2.53 (s, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2): δ 164.6, 162.1, 153.6, 144.4, 143.5, 142.0, 131.6 (t, $J_{F\text{-}C}$ = 10.1 Hz), 131.2 (d, $J_{F\text{-}C}$ = 10.1 Hz), 129.5, 128.9, 122.0, 118.6, 116.1 (d, $J_{F\text{-}C}$ = 20.2 Hz), 107.4, 18.1. HRMS (ESI): cacld. for $C_{17}H_{10}Cl_4FN_3$ $[M+H]^+$: 415.9686, found 415.9679.



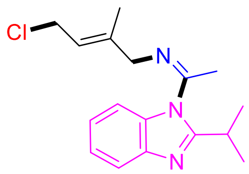
N-(1-(4-bromophenyl)-2,2-dichlorovinyl)-1-(5,6-dichloro-1*H*-benzo[*d*]imidazol-1-yl)ethan-1-imine **(5h)**: 62 mg, 43% yield; white solid; m.p. 171-173°C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.61 (s, 1H), 8.29 (s, 1H), 7.89 (s, 1H), 7.55 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 2.53 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.6, 143.6, 142.4, 141.2, 133.7, 131.8, 130.9, 130.0, 129.4, 128.8, 123.4, 121.6, 117.9, 107.5, 17.6. HRMS (ESI): cacld. for $C_{17}H_{10}BrCl_4N_3$ $[M+H]^+$: 475.8885, found 475.8876.



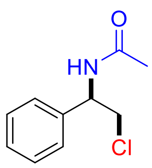
N-(2,2-dichloro-1-(4-ethylphenyl)vinyl)-1-(5,6-dichloro-1*H*-benzo[*d*]imidazol-1-yl)ethan-1-imine **(5i)**: 74 mg, 35% yield; white solid; m.p. 171-173°C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.66 (s, 1H), 8.29 (s, 1H), 7.89 (s, 1H), 7.49 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 2.67 (q, J = 8.0 Hz, 2H), 2.53 (s, 3H), 1.24 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.2, 145.6, 143.5, 142.4, 142.2, 132.1, 131.0 129.4, 128.7, 128.4, 128.0, 121.5, 118.1, 106.5, 28.6, 17.6, 15.2. HRMS (ESI): cacld. for $C_{19}H_{15}Cl_4N_3$ $[M+H]^+$: 426.0093, found 426.0095.



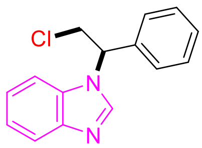
N-(1-(4-(tert-butyl)phenyl)-2,2-dichlorovinyl)-1-(5,6-dichloro-1*H*-benzo[*d*]imidazol-1-yl)ethan-1-imine **(5j)**: 109 mg, 48% yield; white solid; m.p. 184-186°C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.67 (s, 1H), 8.29 (s, 1H), 7.89 (s, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 2.53 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.4, 152.2, 143.6, 142.4, 142.2, 131.8, 131.0, 129.4, 128.6, 128.1, 125.5, 121.5, 118.1, 106.4, 34.8, 31.2, 17.6. HRMS (ESI): cacld. for $C_{21}H_{19}Cl_4N_3$ $[M+H]^+$: 454.0406, found 454.0408.



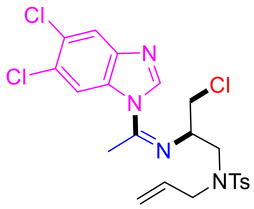
1-*N*-((*E*)-4-chloro-2-methylbut-2-en-1-yl)-1-(2-isopropyl-1*H*-benzo[*d*]imidazol-1-yl)ethan-1-imine **(6)**: 71 mg, 47% yield; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): 7.74 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 4.0 Hz, 2H), 5.82 (t, *J* = 8.0 Hz, 1H), 4.26 (d, *J* = 4.0 Hz, 2H), 4.08 (s, 2H), 3.44 (m, 1H), 2.47 (s, 3H), 1.90 (s, 3H), 1.41 (d, *J* = 8.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.5, 153.8, 142.3, 134.4, 131.8, 126.6, 122.8, 122.5, 119.6, 110.5, 51.3, 49.3, 27.2, 21.6, 18.4, 14.7. HRMS (ESI): cacld. for $C_{17}H_{22}ClN_3$ $[M+H]^+$: 304.1575, found 304.1577.



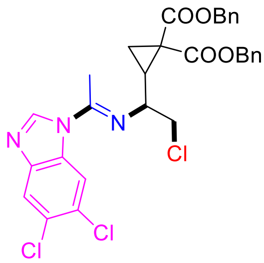
N-(2-chloro-1-phenylethyl)acetamide **(7)**: 92 mg, 93% yield; white solid, m.p. 205-207 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (m, 5H), 6.66 (d, *J* = 4.0 Hz, 1H), 5.31 (m, 1H), 3.81 (d, *J* = 4.0 Hz, 2H), 2.01 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.7, 138.4, 128.7, 128.1, 126.7, 53.6, 47.5, 23.2; These data are in accordance with the literature.[4]



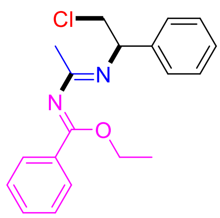
1-(2-Chloro-1-phenylethyl)-1*H*-benzo[*d*]imidazole **(A)**: 51mg, 40% yield; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.34 (m, 5H), 7.23 (m, 3H), 5.74 (t, *J* = 8.0 Hz, 12H), 4.28 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.9, 141.5, 136.1, 133.5, 129.4, 129.2, 126.7, 123.4, 122.7, 120.7, 110.3, 61.4, 44.7; HRMS (ESI): cacld. for $C_{15}H_{13}ClN_2$ $[M+H]^+$: 257.0840, found 257.0841.



N-allyl-*N*-(3-chloro-2-((1-(5,6-dichloro-1*H*-benzo[*d*]imidazol-1-yl)ethylidene)amino)propyl)-4-methylbenzenesulfonamide**(9)**: 100 mg, 39% yield; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (s, 1H), 8.31 (s, 1H), 7.88 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.59 (m, 1H), 5.16 (m, 2H), 4.54 (m, 1H), 3.96 (m, 3H), 3.78 (m, 2H), 3.32 (dd, *J* = 8.0 Hz, *J* = 12.0 Hz, 1H), 2.52 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.3, 143.9, 143.5, 142.3, 135.8, 132.3, 131.3, 129.9, 128.6, 127.8, 127.3, 121.2, 120.2, 118.0, 59.2, 53.2, 52.8, 51.5, 21.5, 15.4; HRMS (ESI): cacld. for $C_{22}H_{23}Cl_3N_4O_2S$ $[M+H]^+$: 513.0680, found 513.0669.



Dibenzyl 2-(2-chloro-1-((1-(5,6-dichloro-1*H*-benzo[*d*]imidazol-1-yl)ethylidene)amino)ethyl) cyclopropane-1,1-dicarboxylate (**11**): 147 mg, 49% yield, *dr* ≈ 1.4/1; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (s, 0.55H) (major isomer), 8.45 (s, 0.39H) (minor isomer), 8.28 (s, 0.56H) (major isomer), 8.01 (s, 0.39H) (minor isomer), 7.85 (s, 1H), 7.30 (m, 7H), 7.07 (m, 3H), 5.06 (m, 4H), 3.76 (m, 3H), 2.40 (m, 3H), 2.10 (s, 1.2H) (minor isomer), 1.70 (m, 1H), 1.55 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.9, 168.6, 168.1, 167.7, 152.5, 152.1, 143.5, 143.4, 142.4, 142.3, 135.2, 135.1, 134.7, 131.2, 128.7, 128.63, 128.57, 128.5, 128.4, 128.3, 128.21, 128.18, 128.02, 127.96, 127.7, 127.3, 121.2, 121.02 118.0, 117.9, 67.8, 67.64, 67.61, 67.4, 59.9, 59.5, 47.94, 47.85, 33.6, 32.8, 32.7, 30.8, 19.4, 18.6, 15.34, 15.29; HRMS (ESI): cacld. for $C_{30}H_{26}Cl_3N_3O_4$ $[M+H]^+$: 598.1062, found 598.1053.



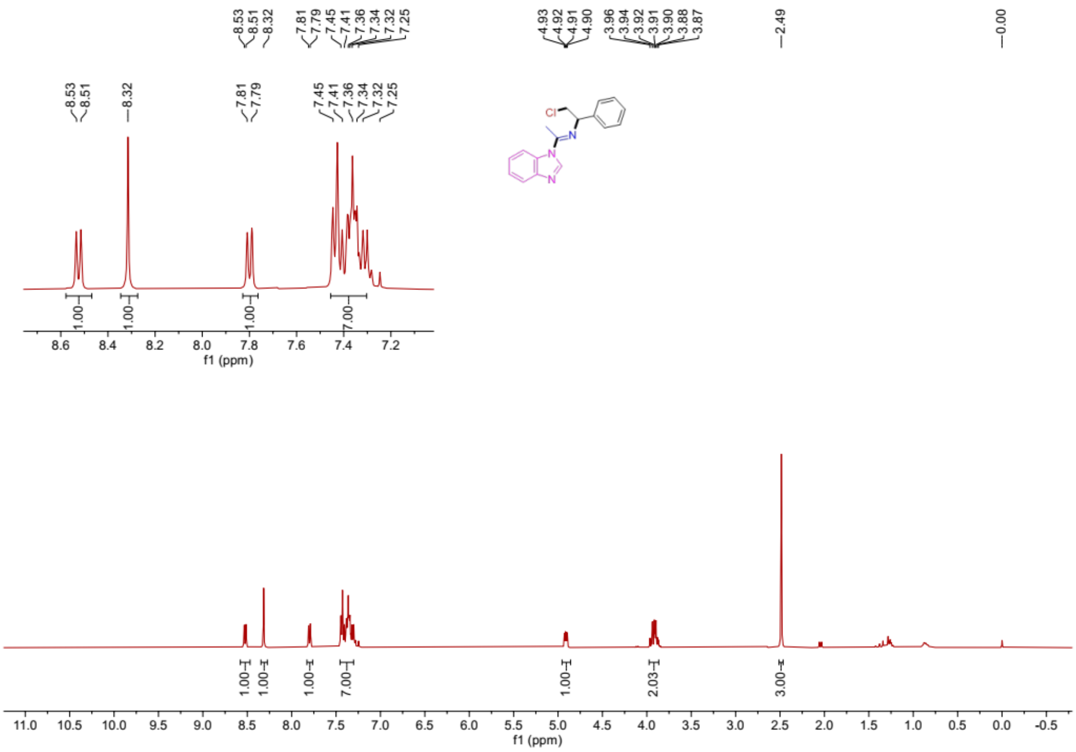
Ethyl-*N*-(1-((2-chloro-1-phenylethyl)imino)ethyl)benzimidate **(13)**: 100 mg, 61% yield; pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (m, 6H), 7.21 (m, 4H), 4.79 (t, *J* = 8.0 Hz, 1H), 4.25 (m, 2H), 3.88 (t, *J* = 8.0 Hz, 1H), 3.77 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 1.89 (s, 3H), 1.40 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.7, 155.8, 141.0, 131.2, 130.9, 128.4, 128.3, 127.9, 127.7, 127.4, 64.3, 62.7, 49.6, 24.1, 14.2. HRMS (ESI): cacld. for $C_{19}H_{21}ClN_2O$ $[M+H]^+$: 329.1415, found 329.1409.

10. References

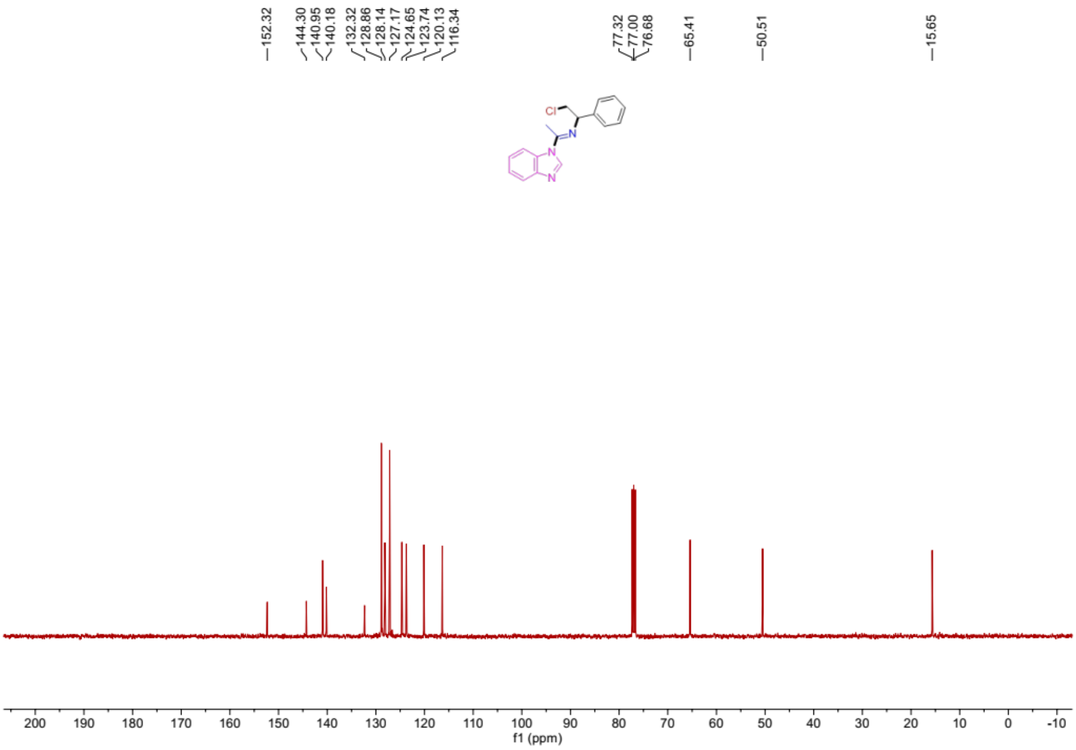
1. S. Zhang, D. Bedi, L. Cheng, D. K. Unruh, G. Li and M. Findlater, *J. Am. Chem. Soc.,* 2020, **142**, 8910–8917.
2. J. Sim, B. Ryou, M. Choi, C. Lee and C.-M. Park, *Org. Lett.,* 2022, **24**, 4264–4269.
3. M. D. Rosa, N. Canudas, D. Arnold and H. Yennawar, *J. Org. Chem.,* 2013, **78**, 7264–7267.
4. D. W. Tay, I. T. Tsoi, J. C. Er, G. Y. Leung and Y.-Y. Yeung, *Org. Lett.* 2013, **15**, 1310–1313

NMR spectra

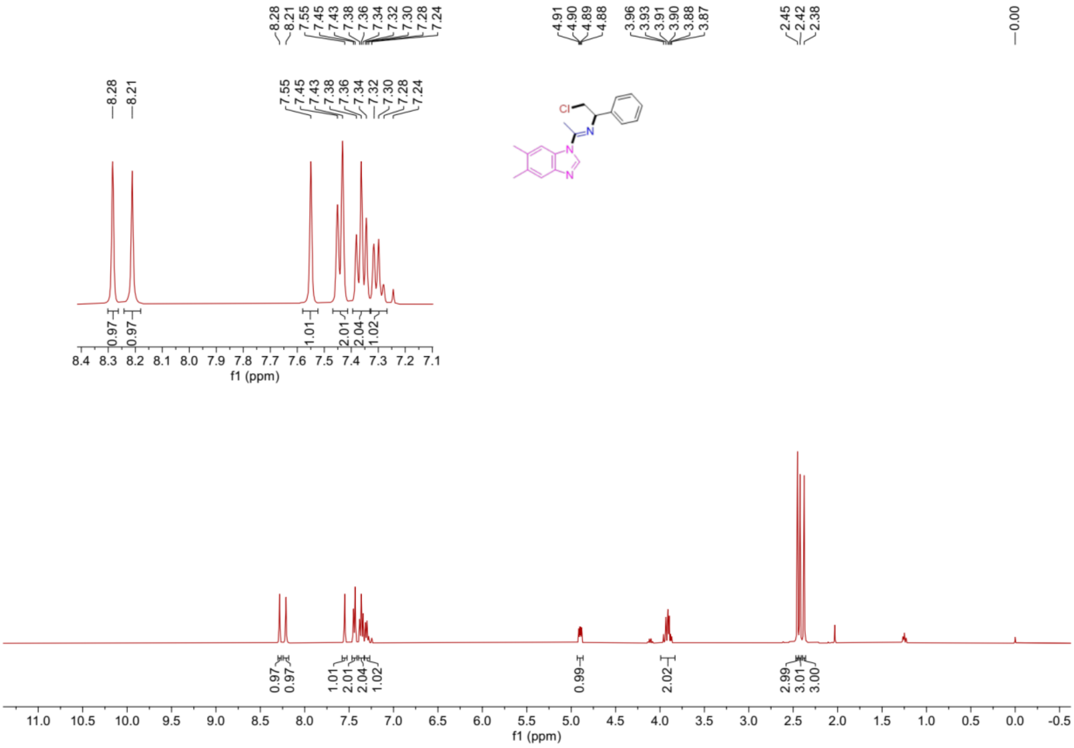
3a ^{1}H NMR



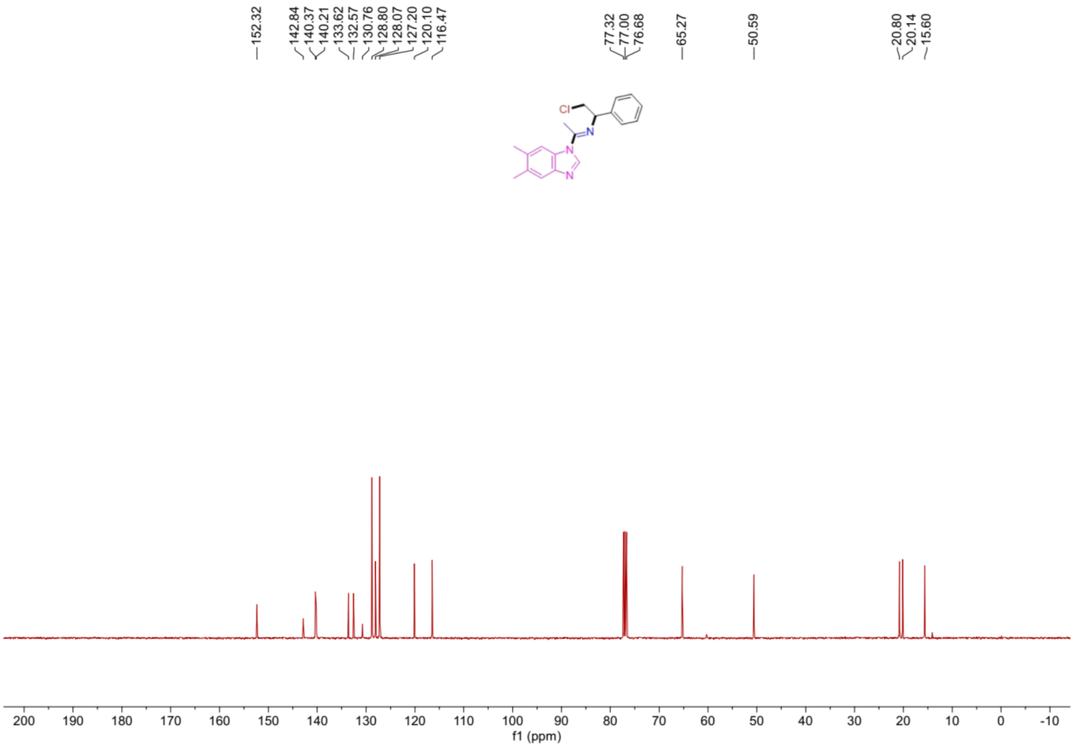
3a ^{13}C NMR



3b ¹H NMR



3b ¹³C NMR



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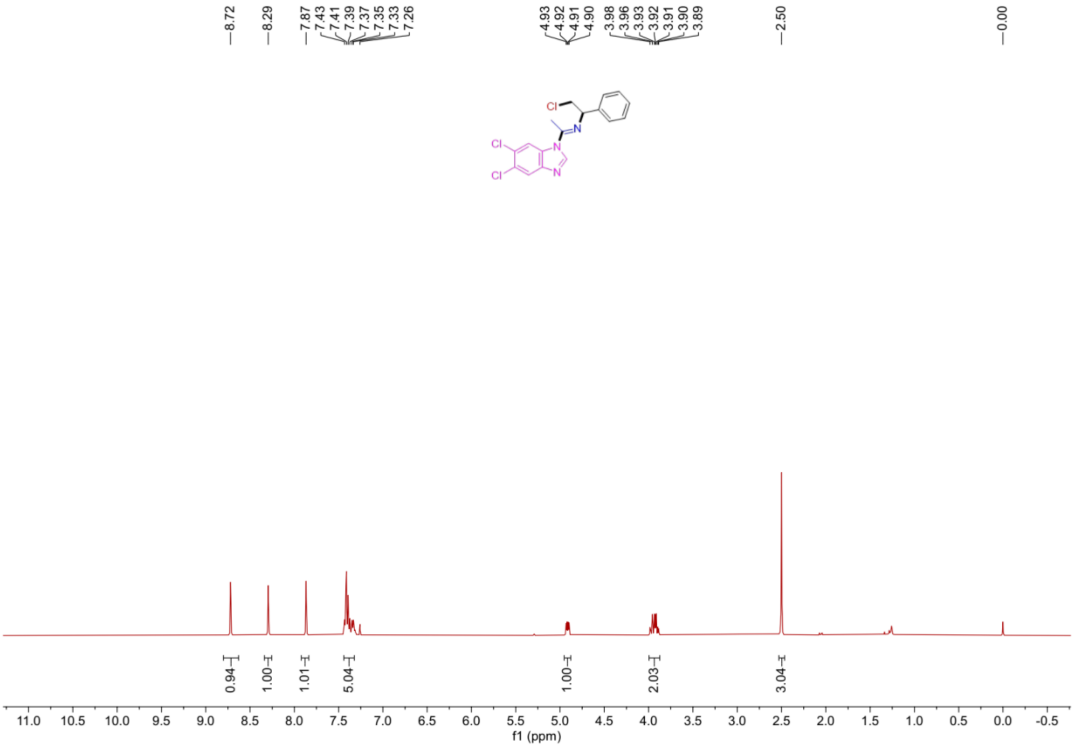

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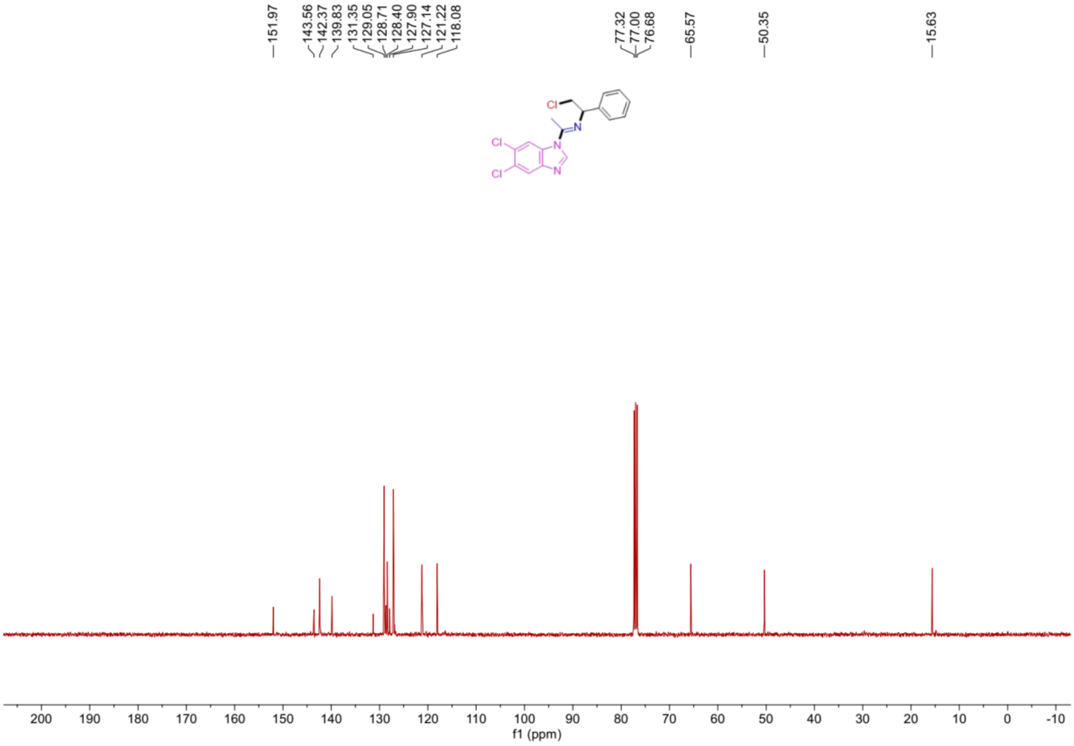

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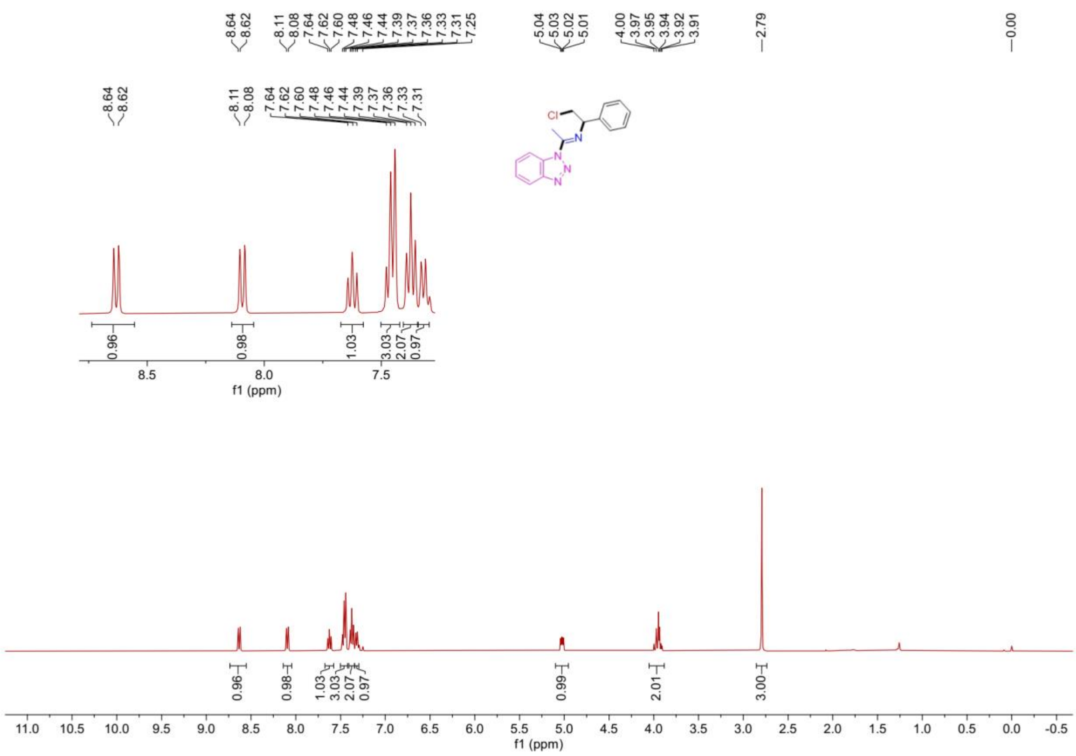

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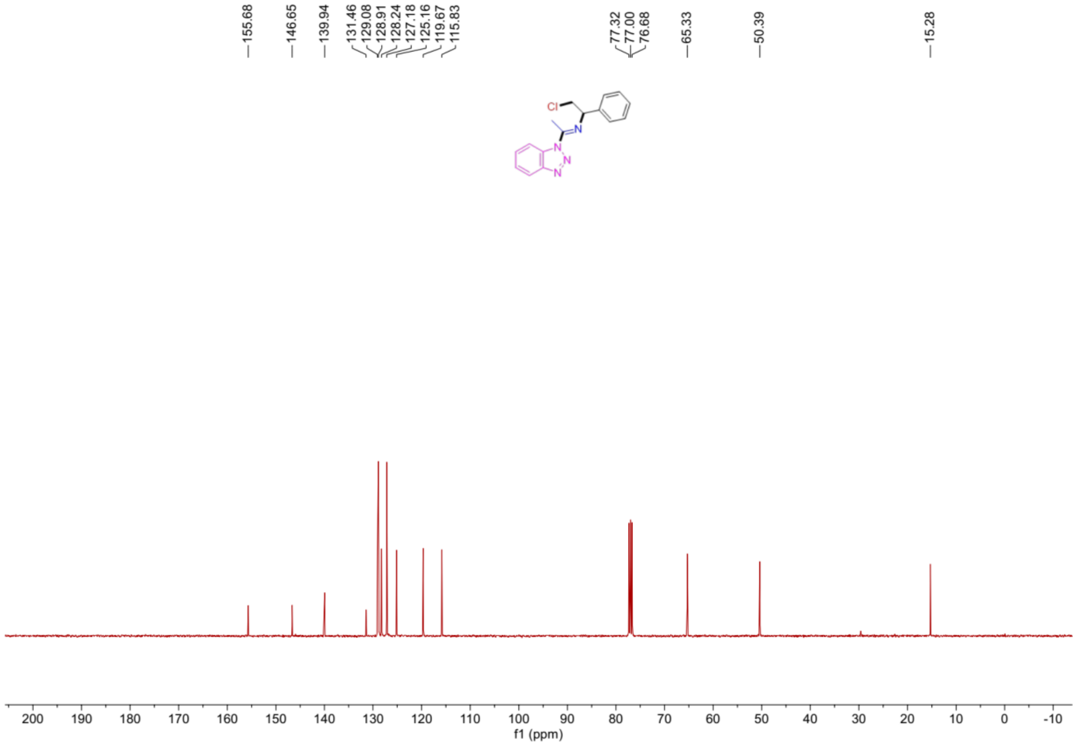
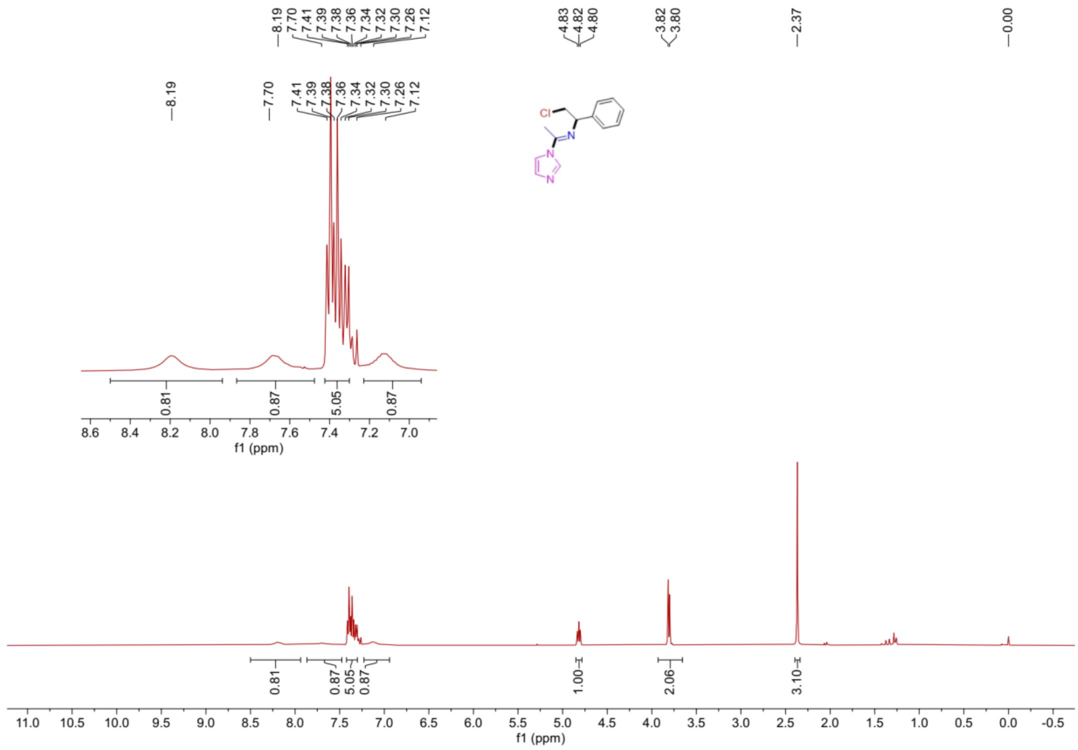
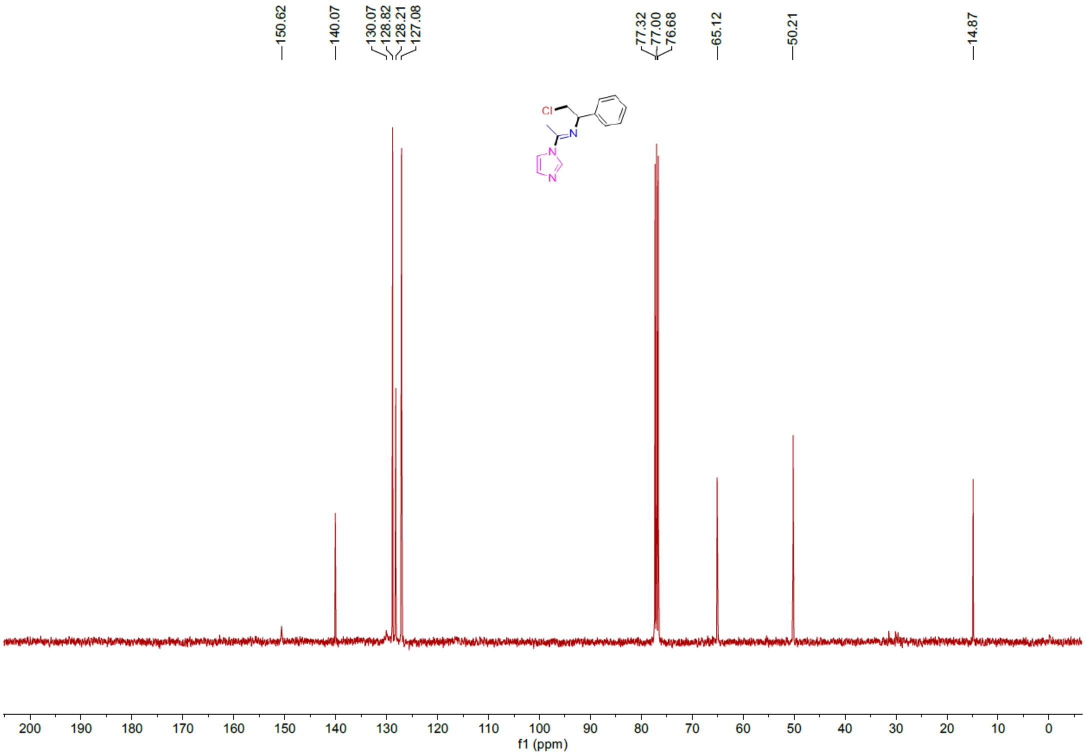


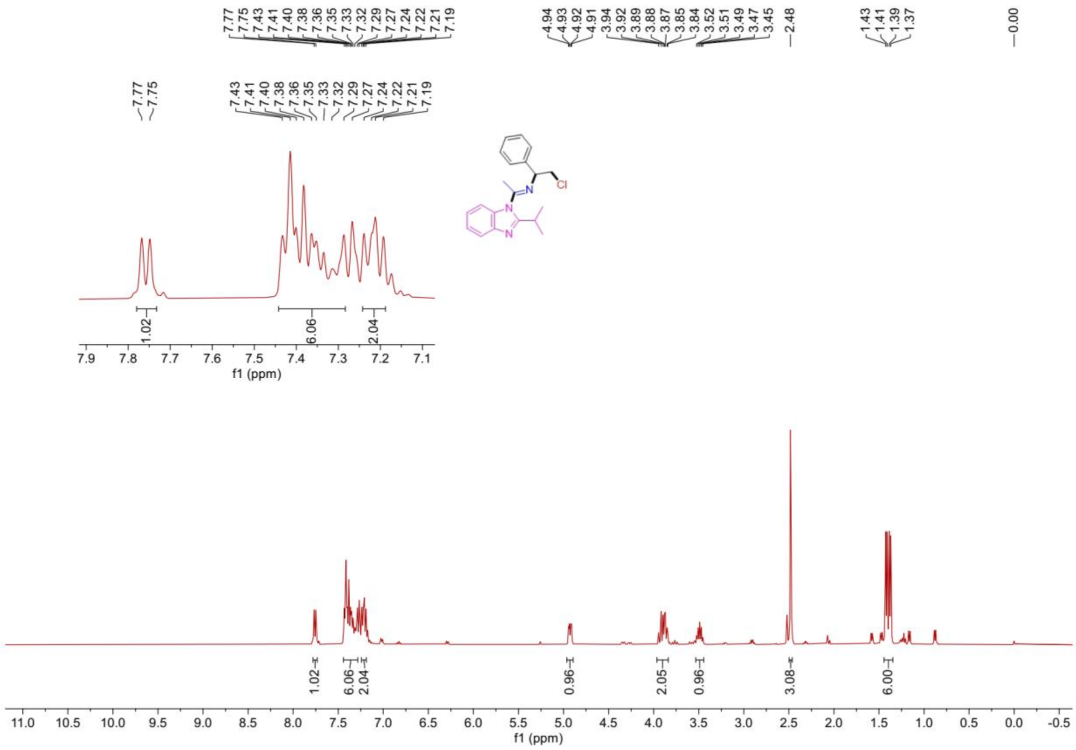
3e ^{1}H NMR



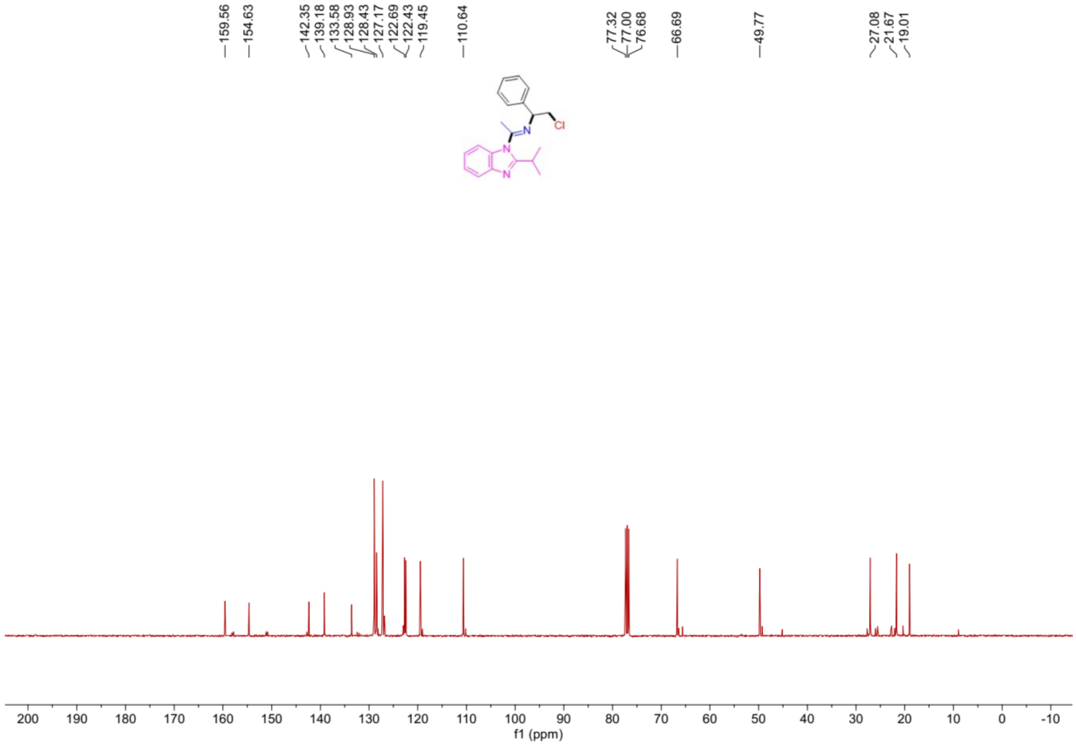
3e ^{13}C NMR



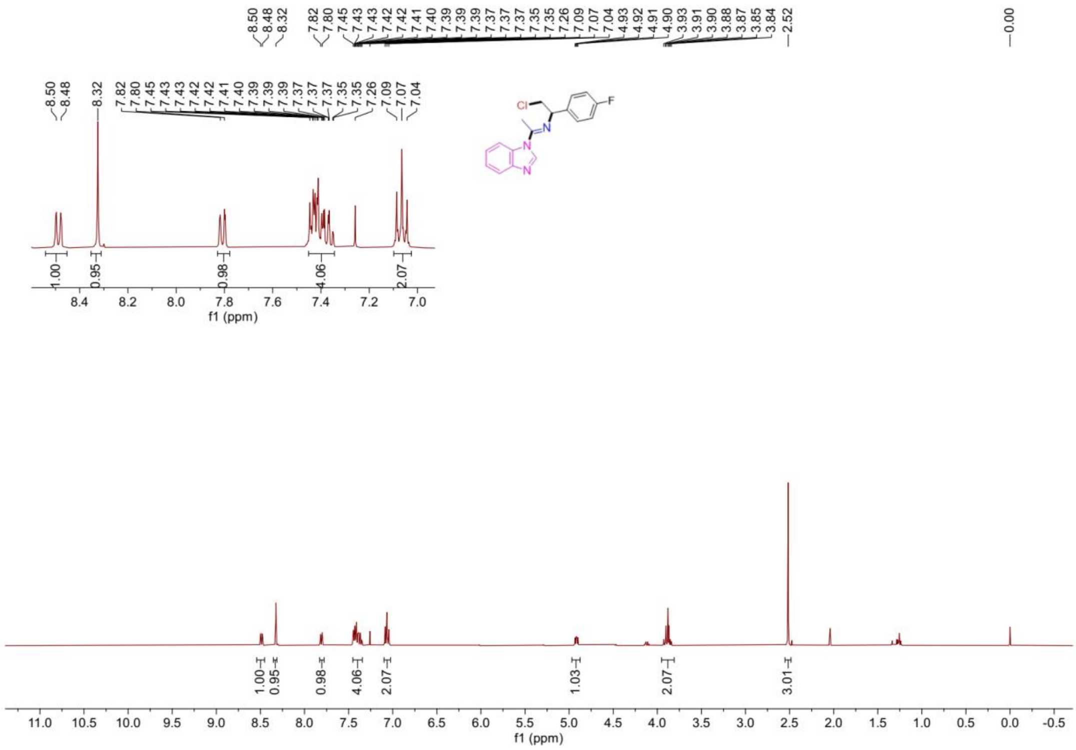
3f ¹H NMR



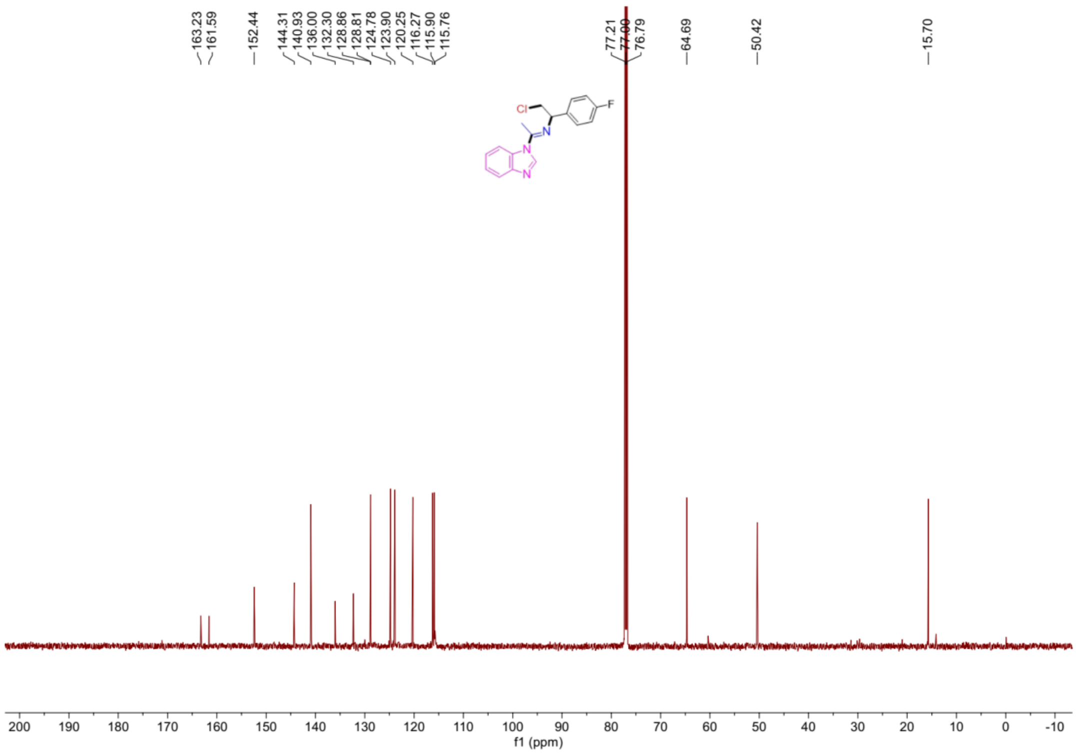
3f ¹³C NMR



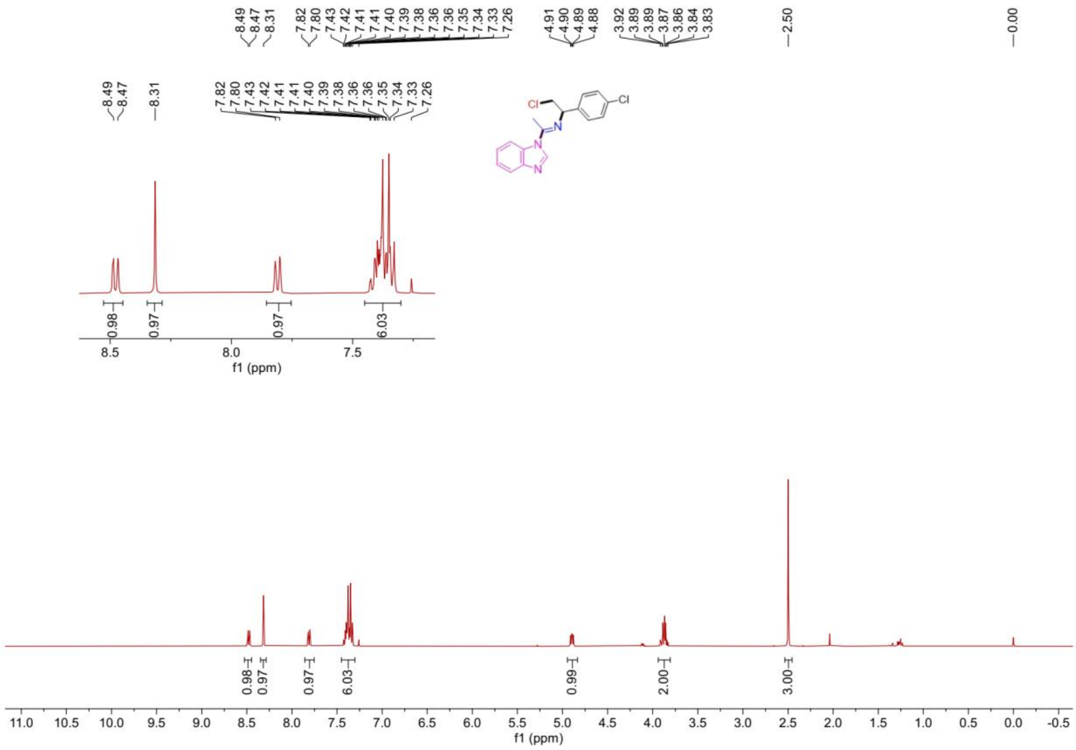
3g [1]H NMR



3g [13]C NMR



3h ^{1}H NMR



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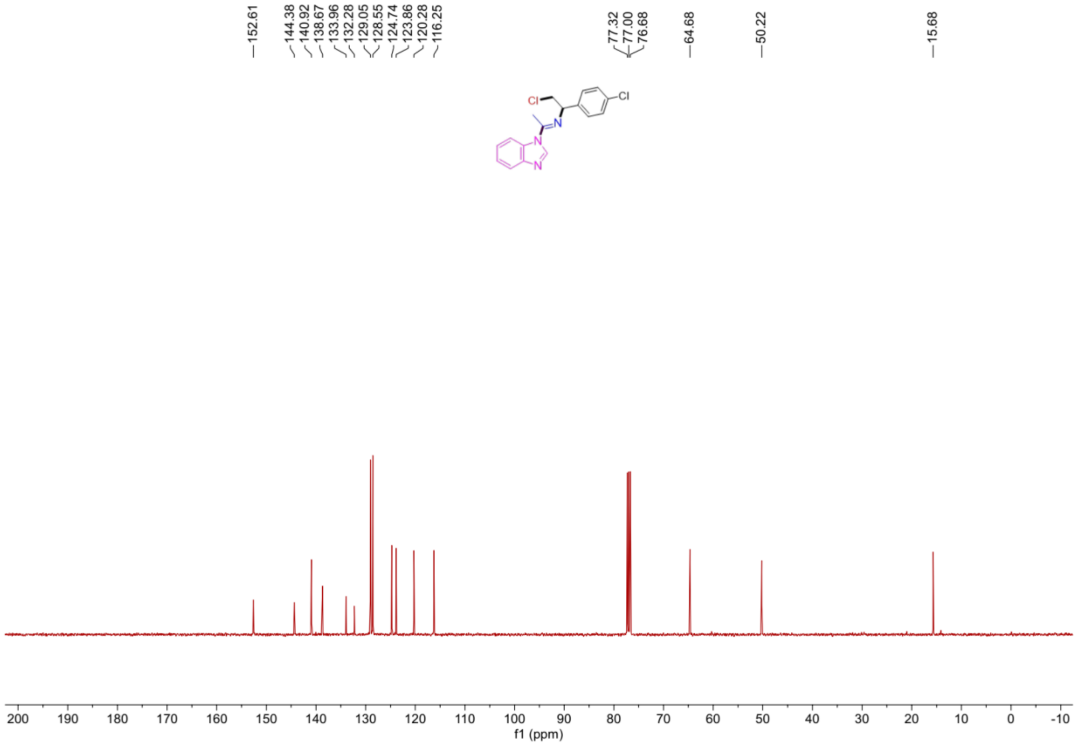

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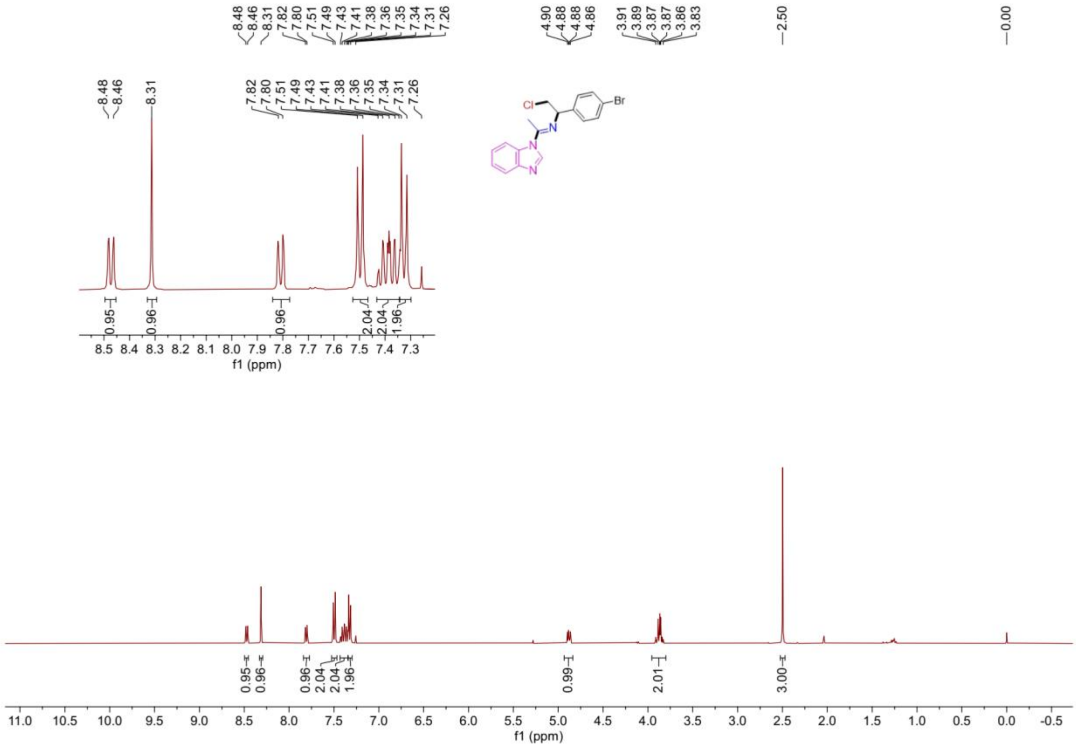

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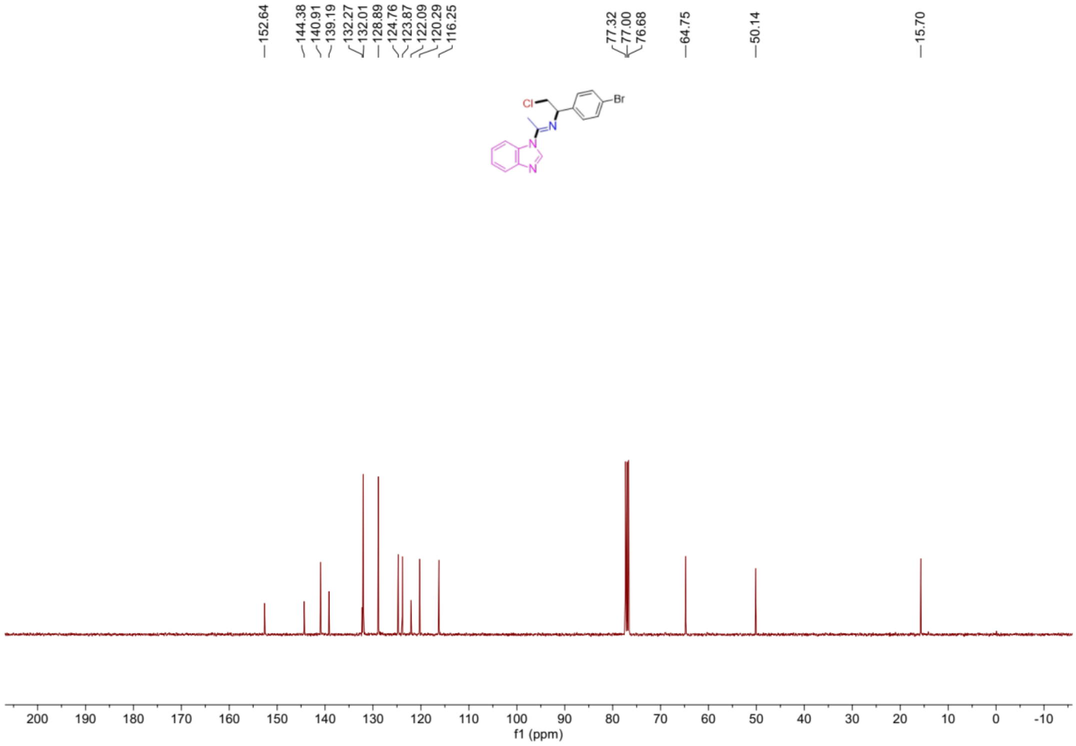

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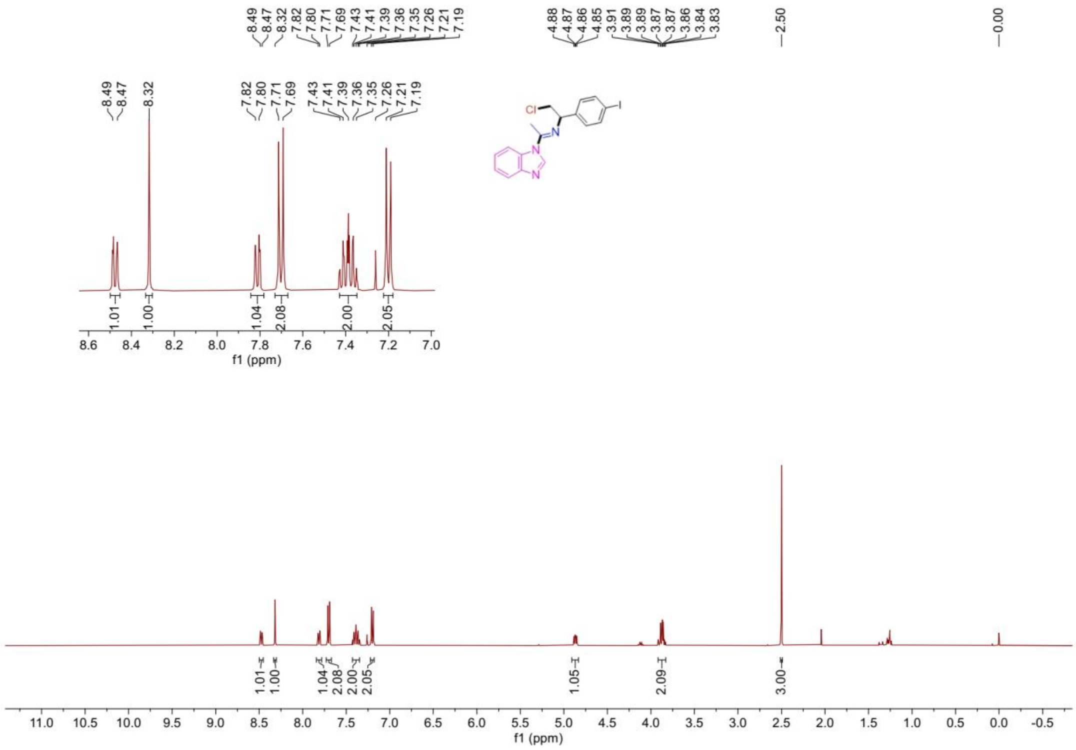

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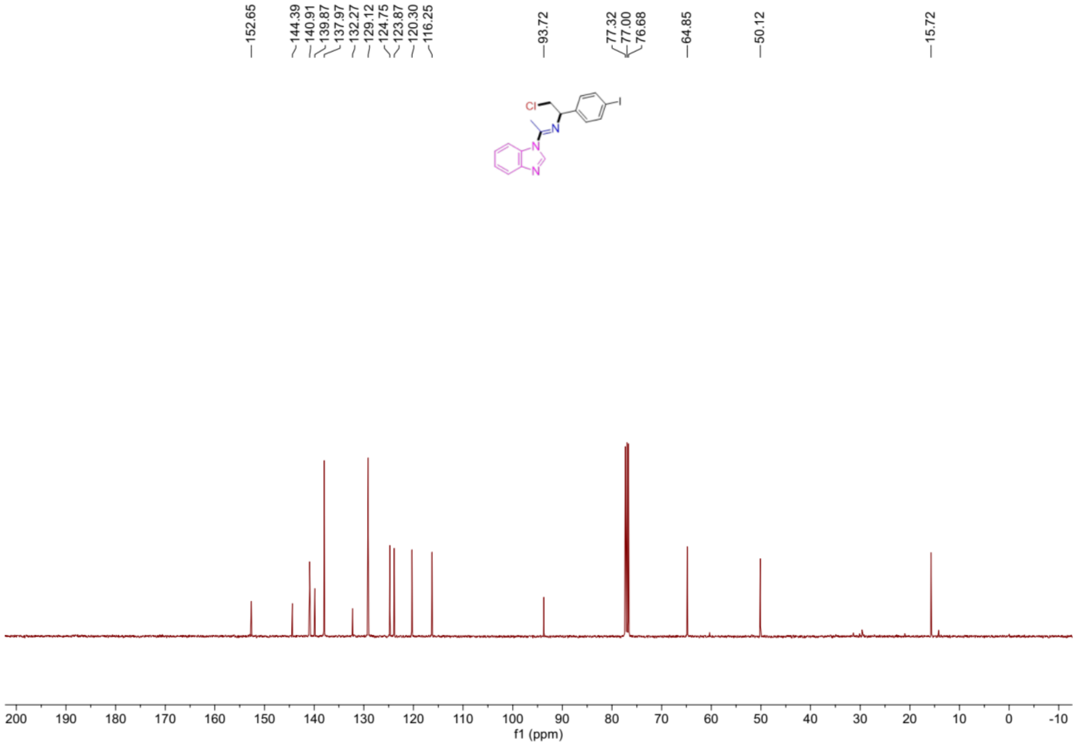

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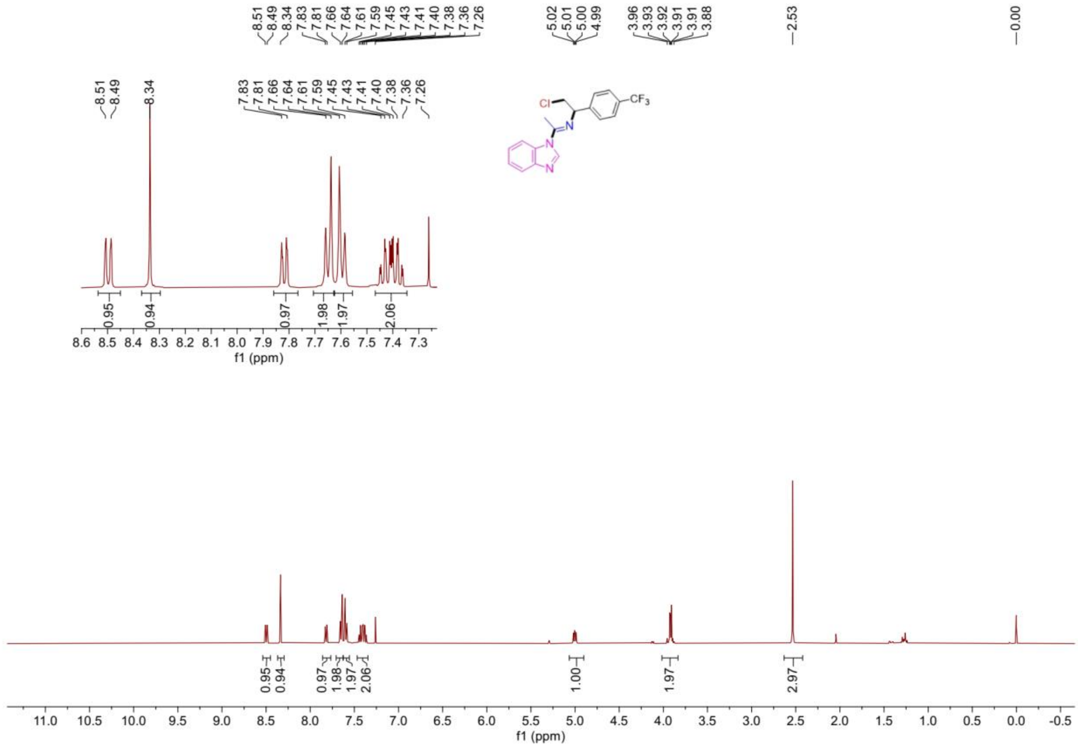

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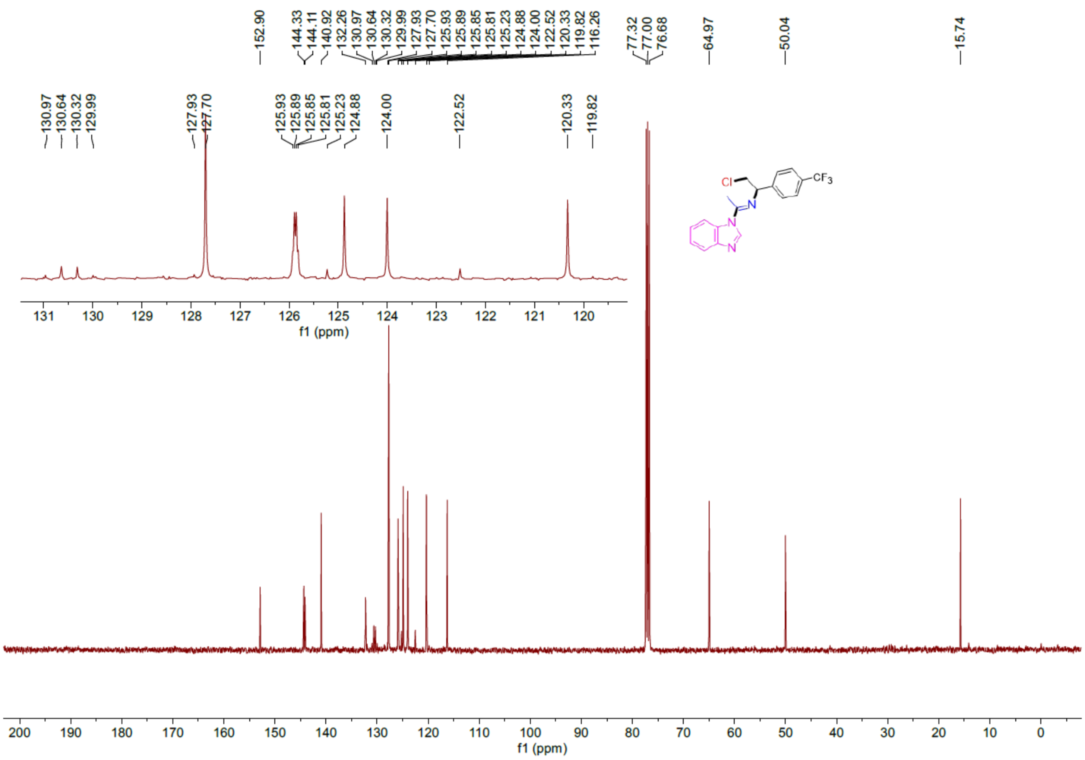

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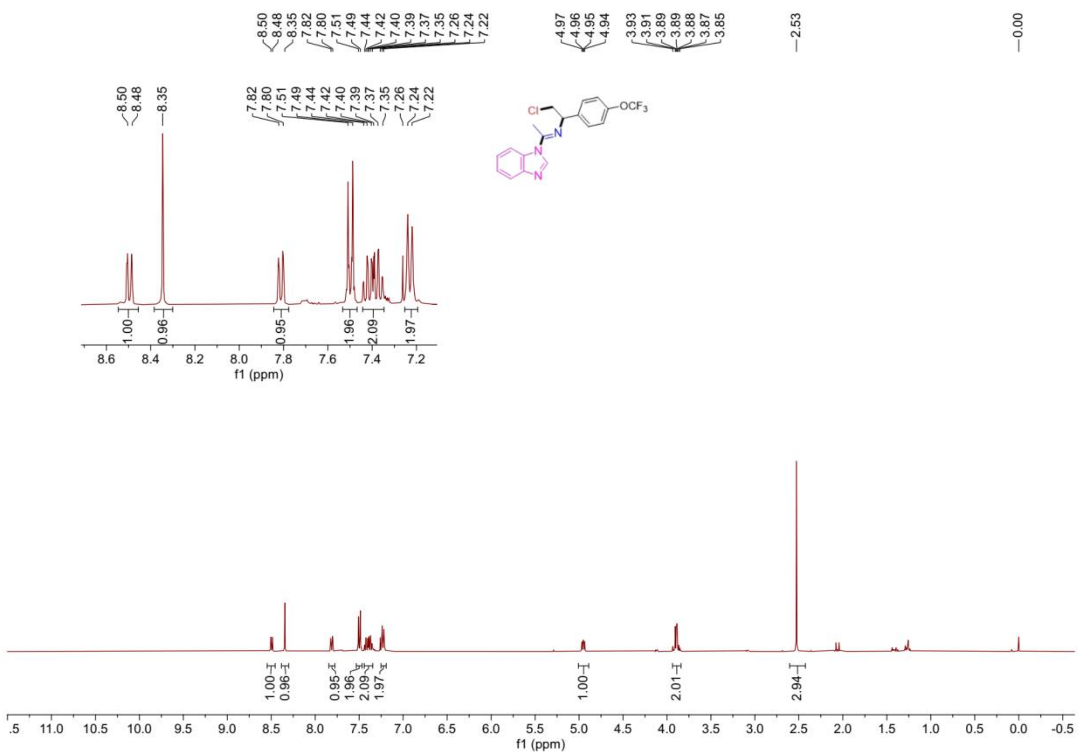

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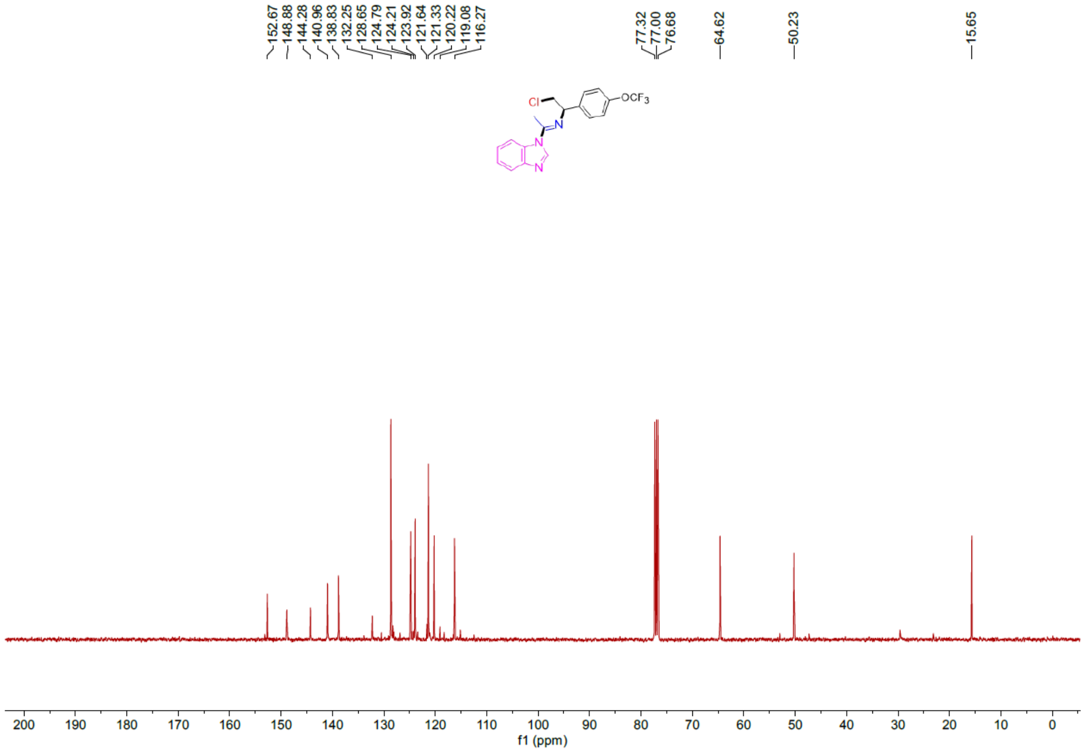

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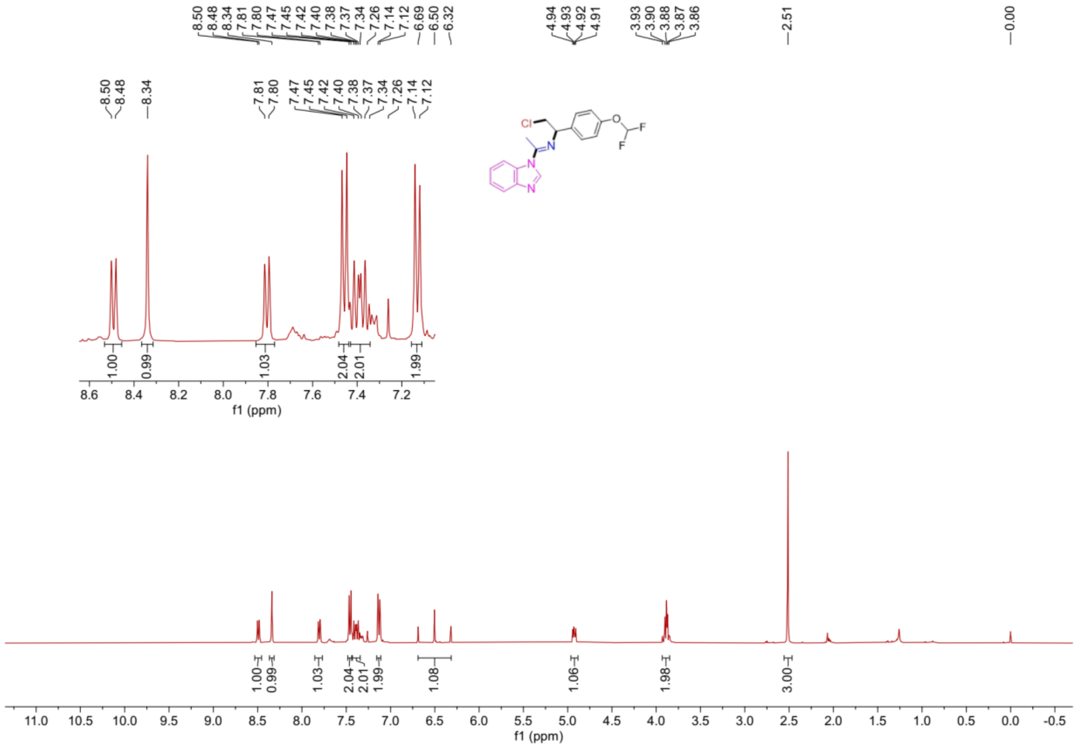

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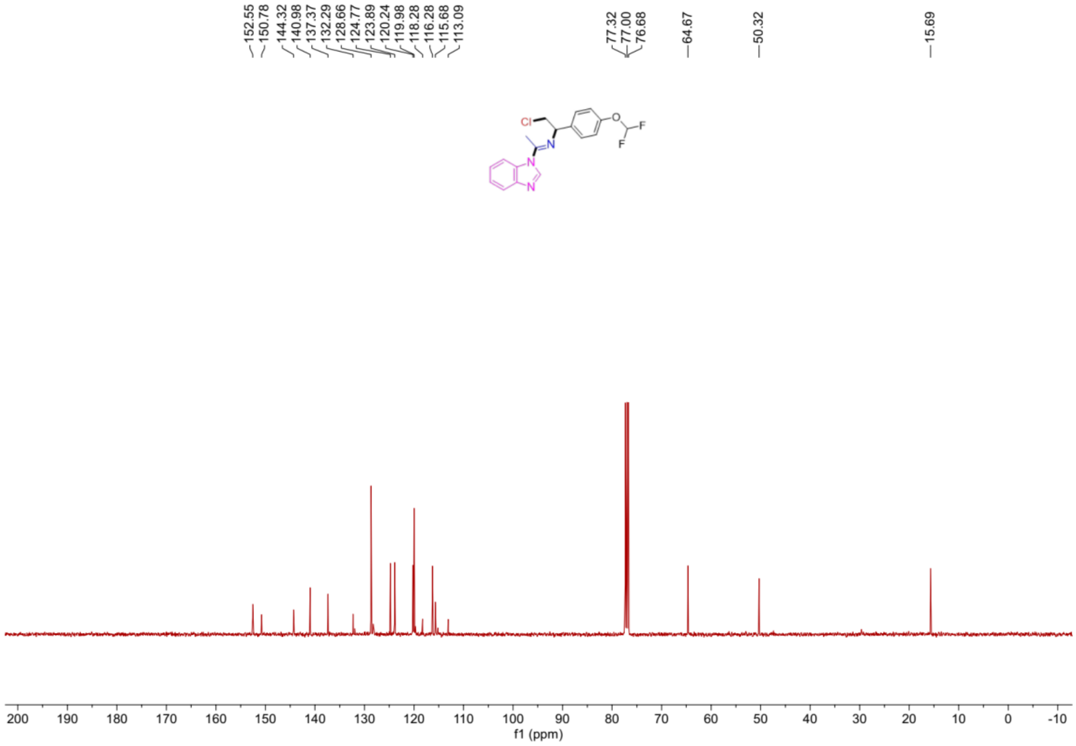

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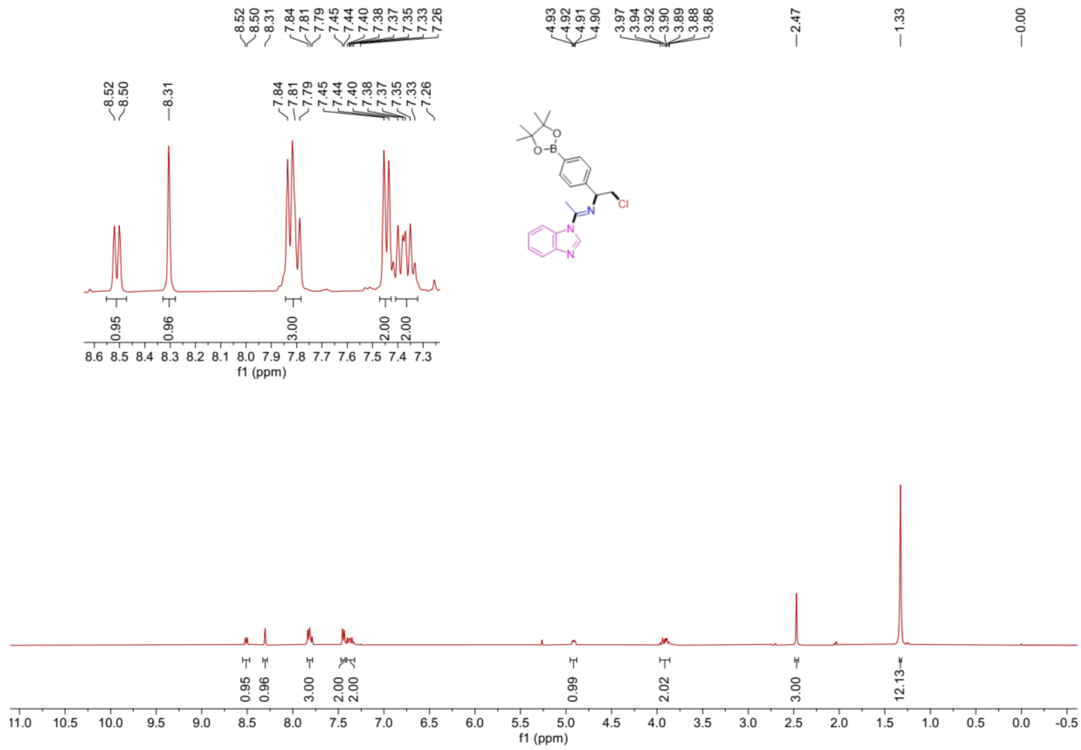

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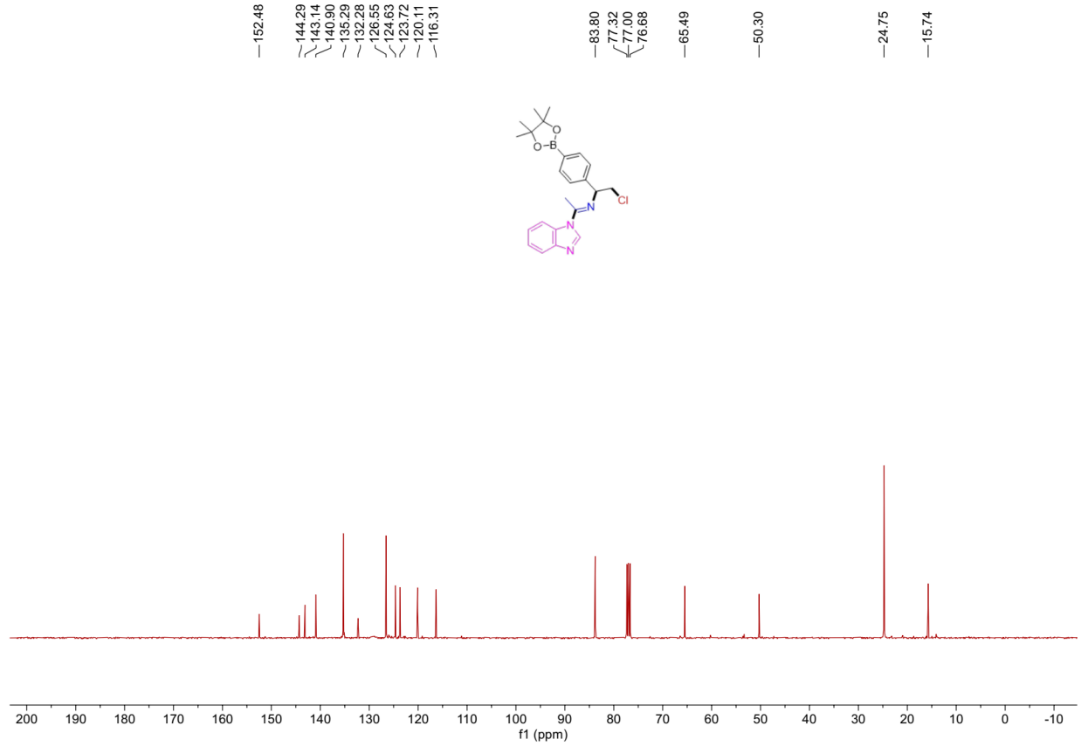

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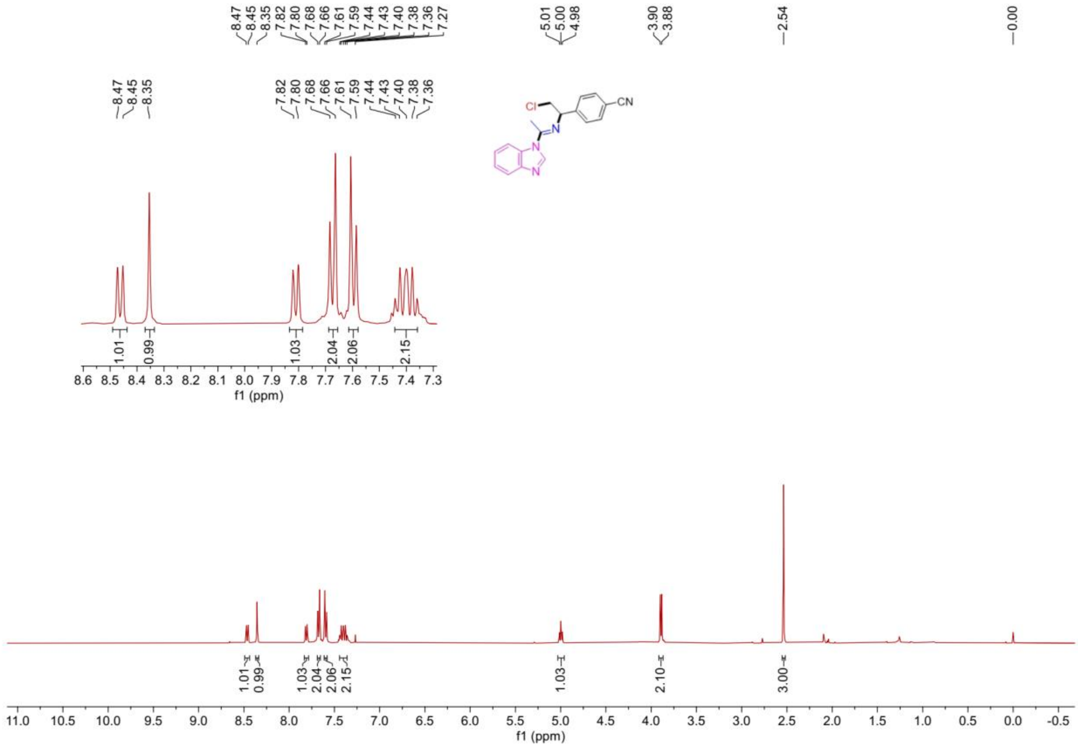

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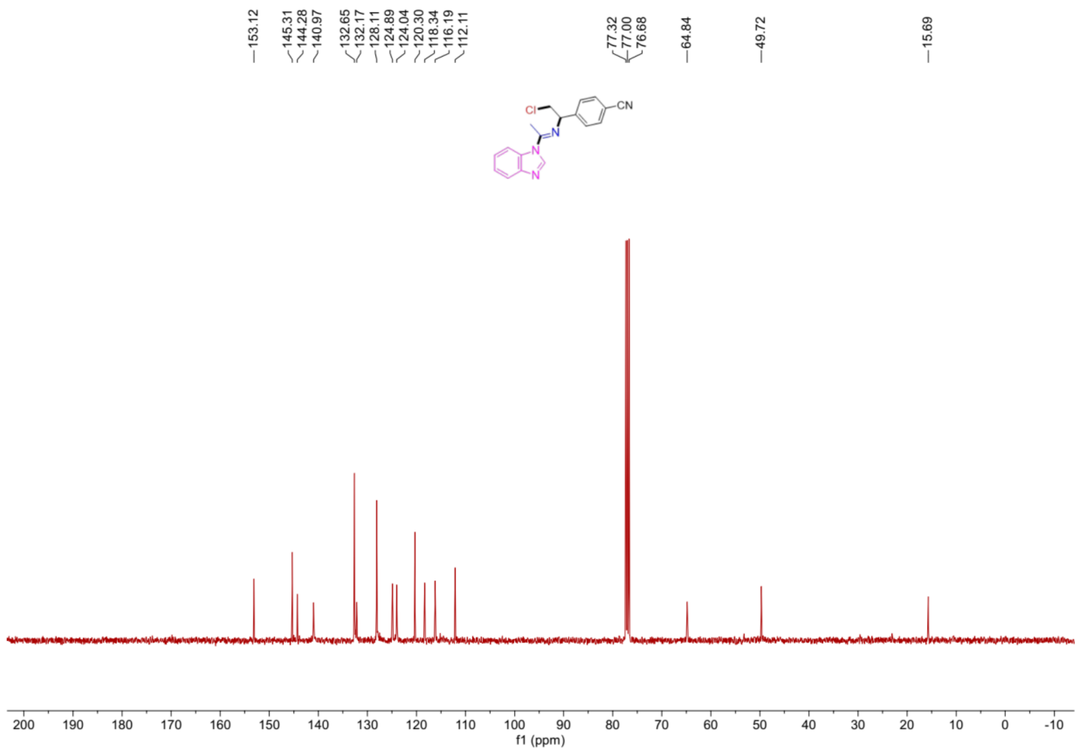

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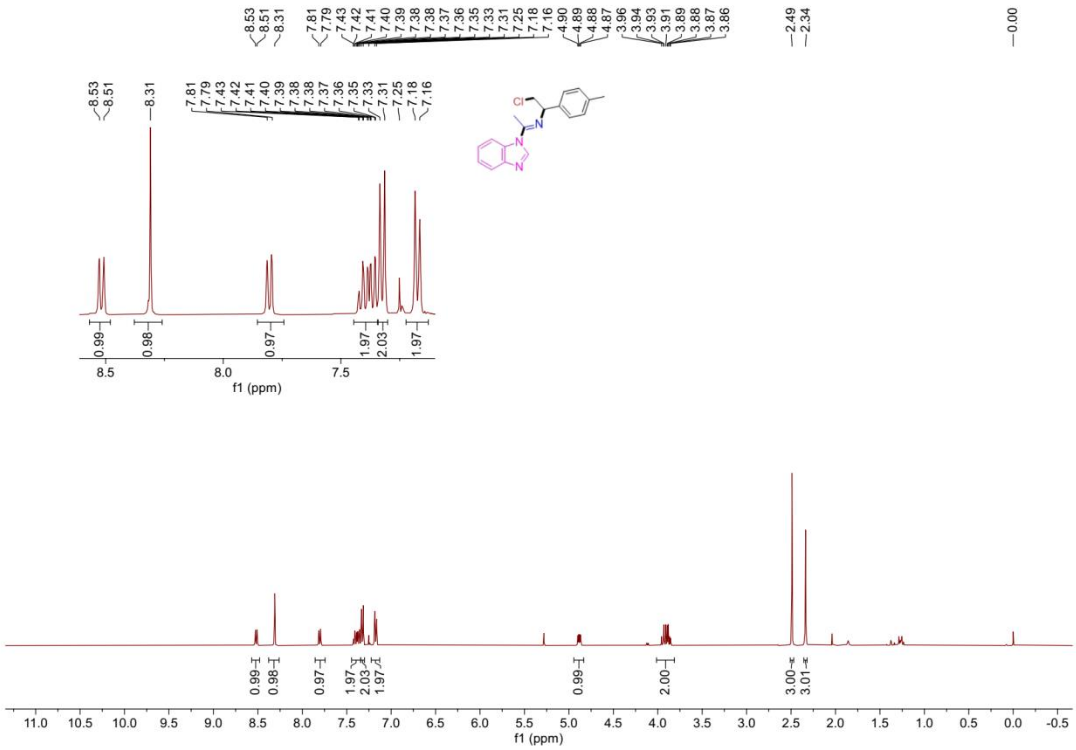

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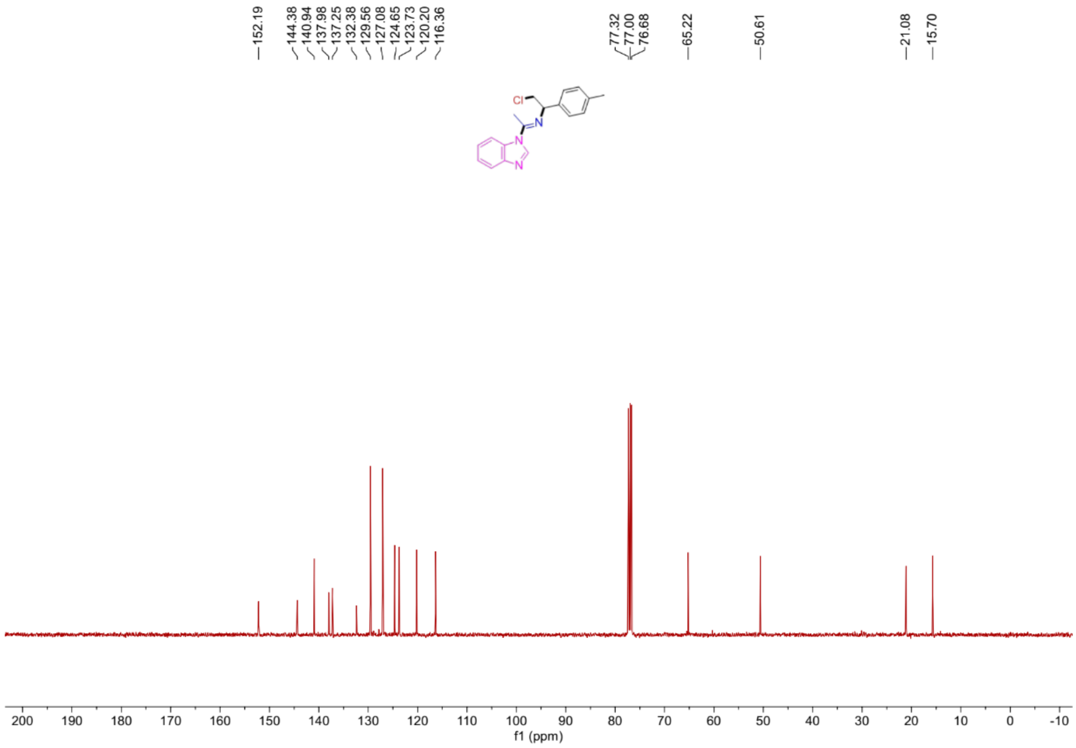

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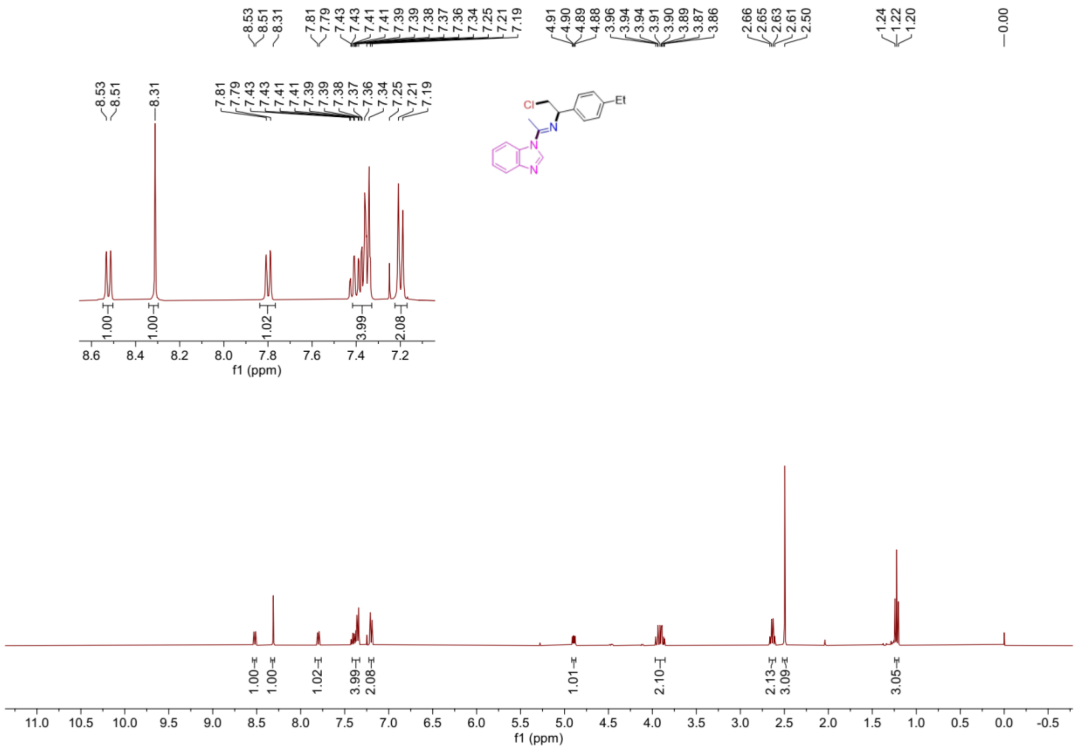
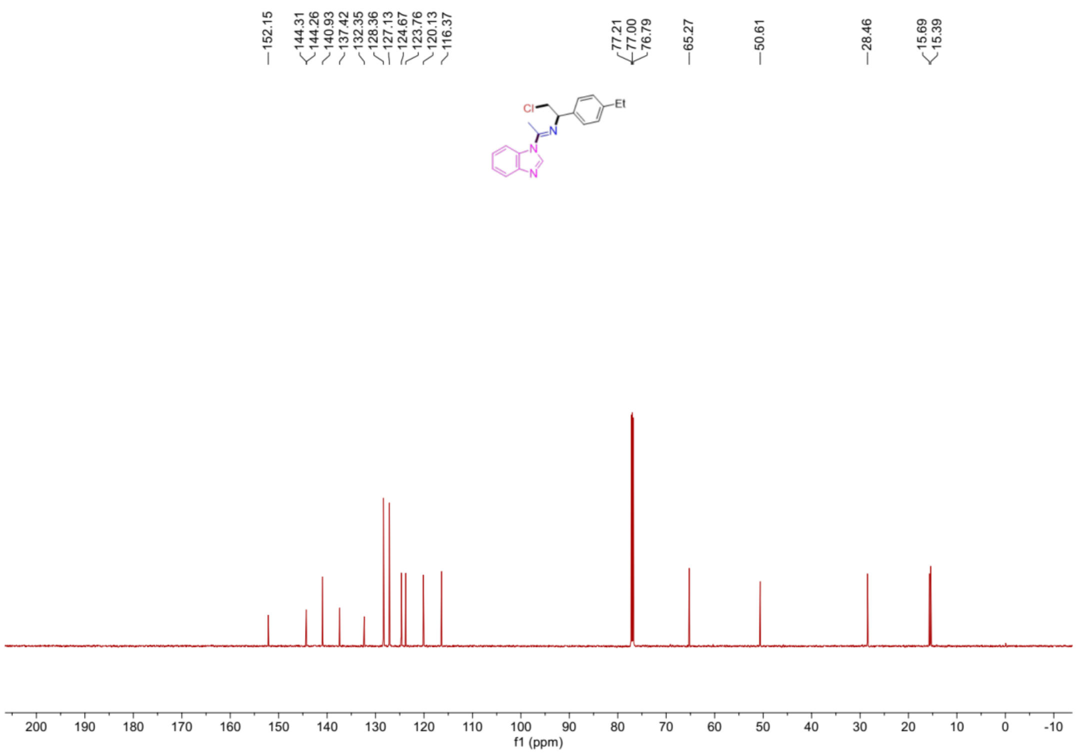


3q ¹³C NMR



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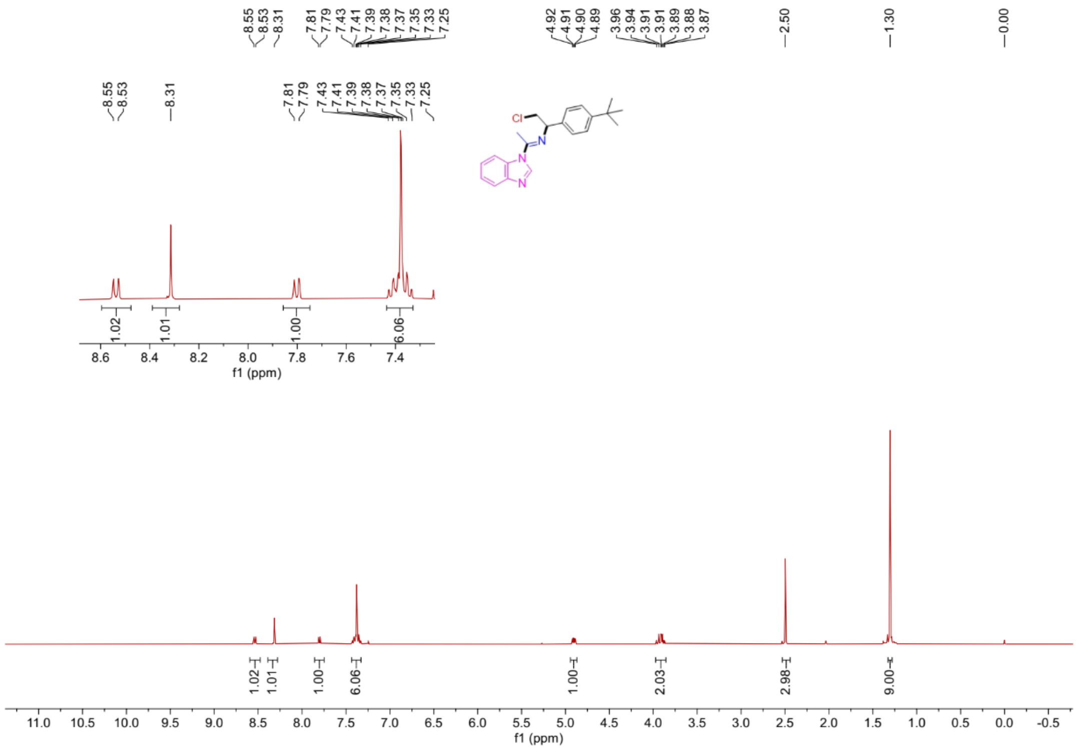

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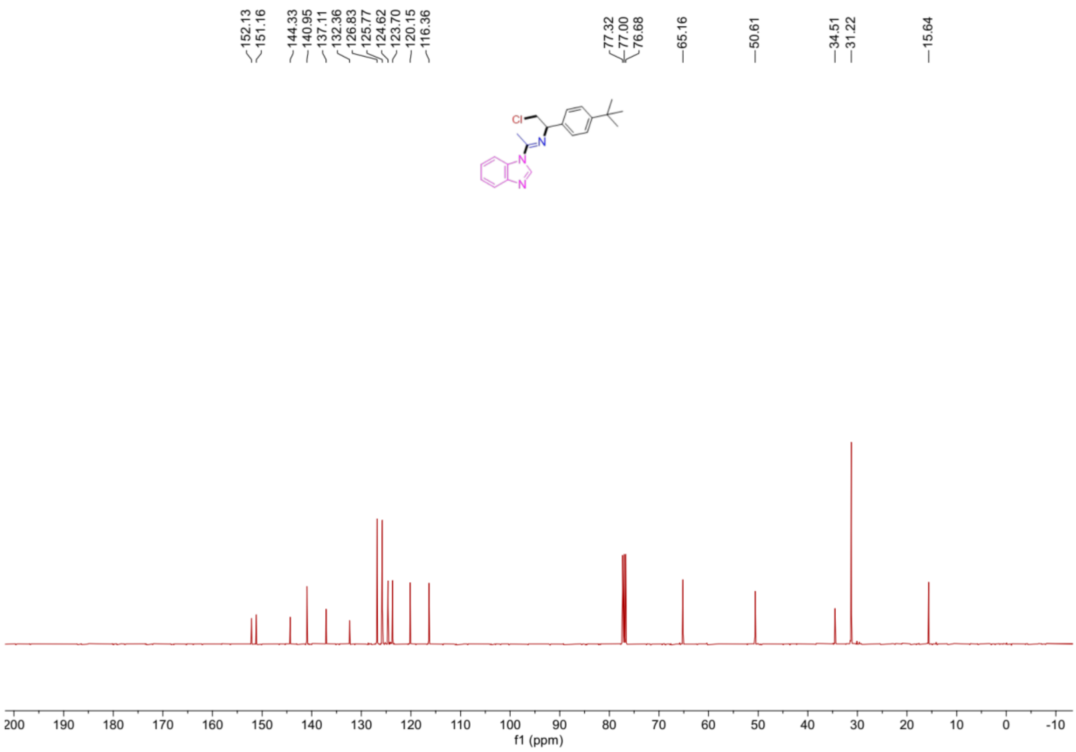
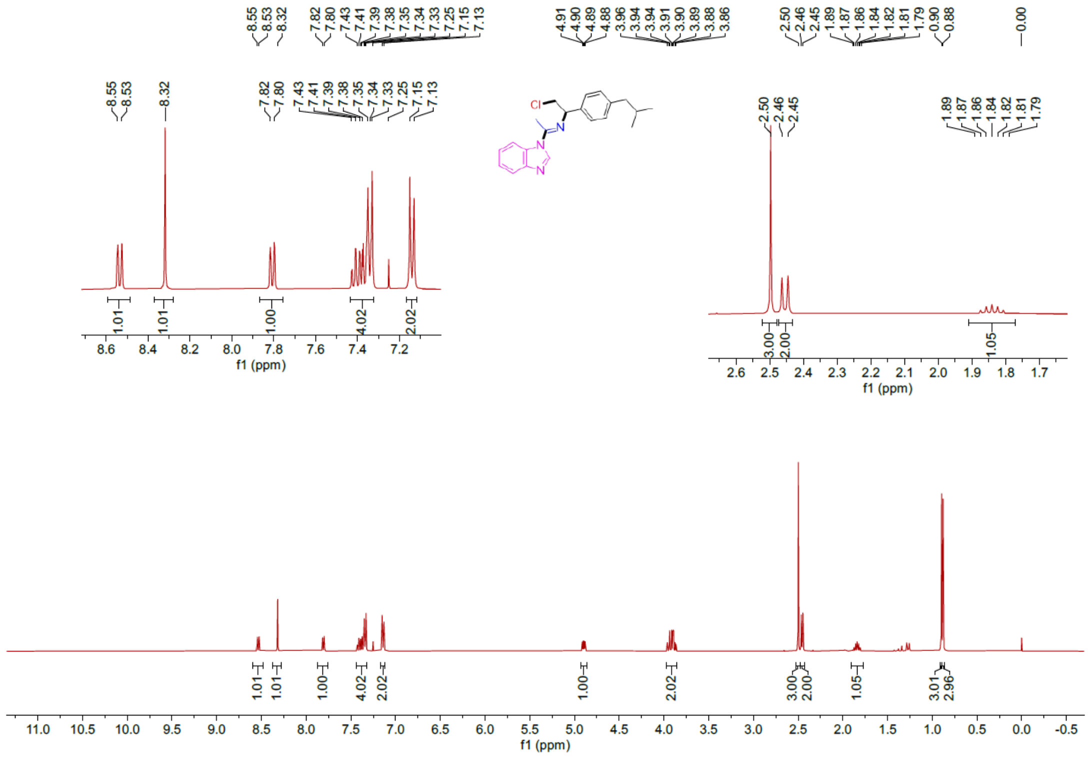


3s ¹H NMR



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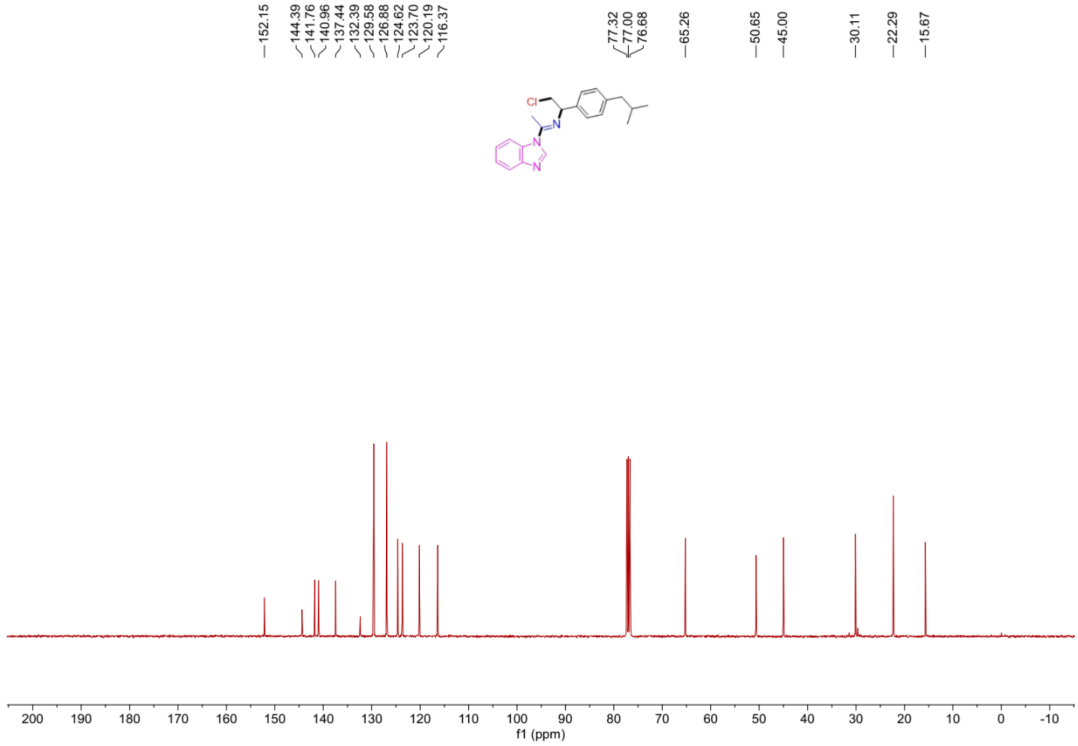

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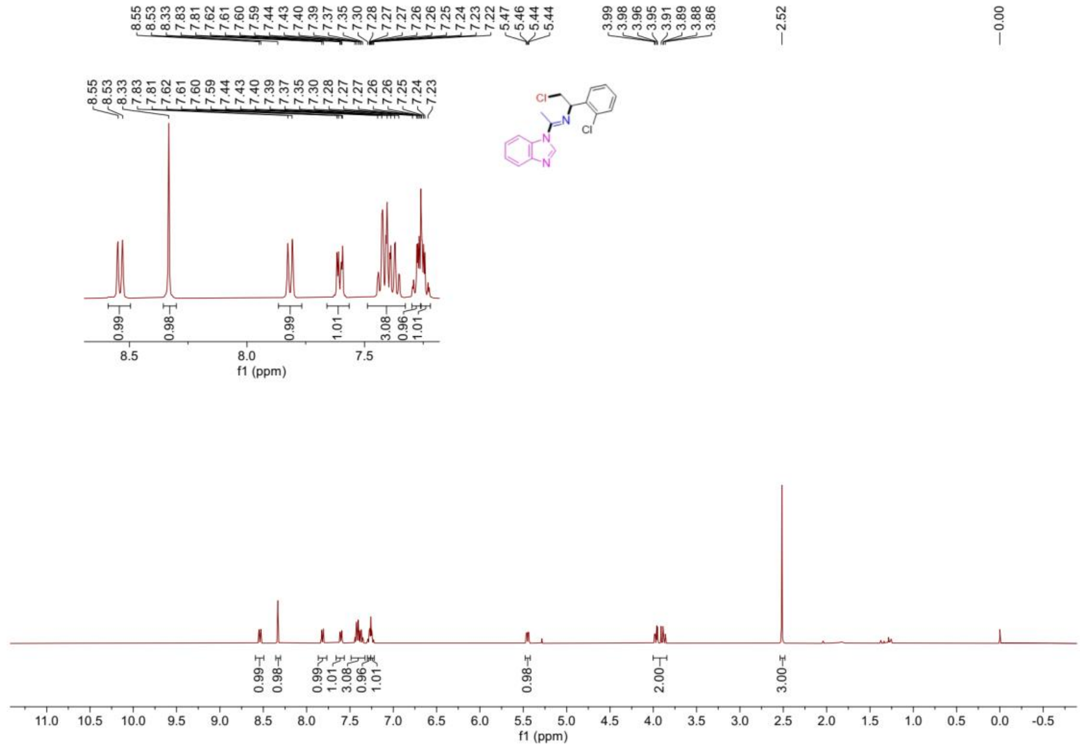

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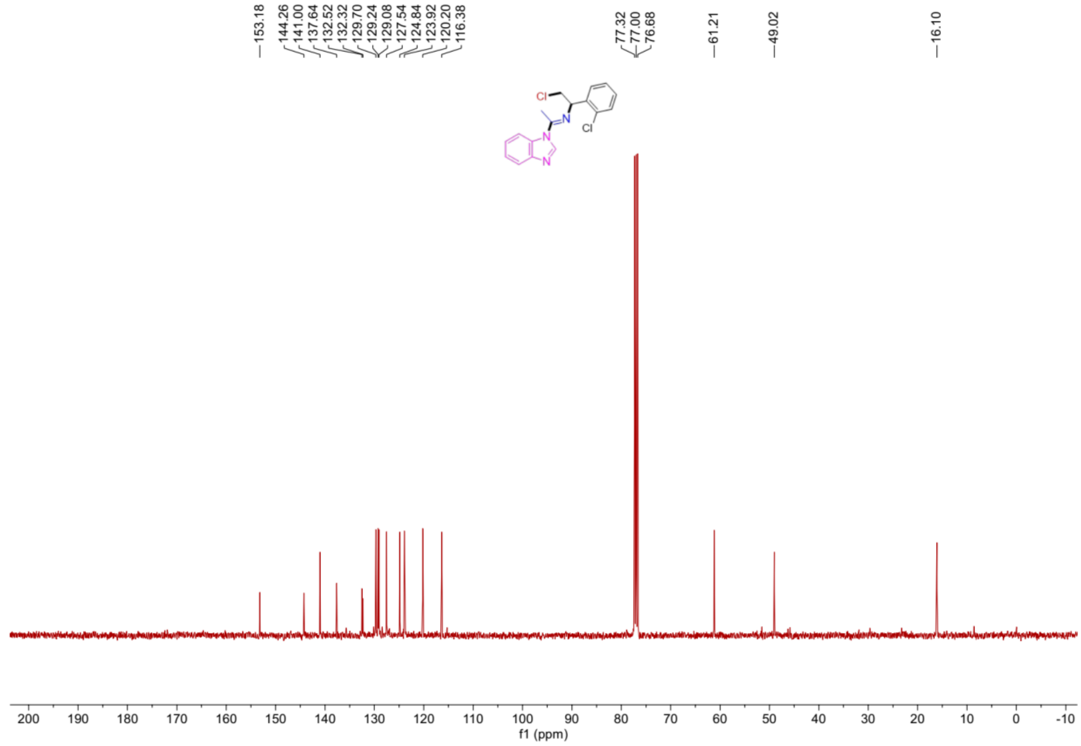

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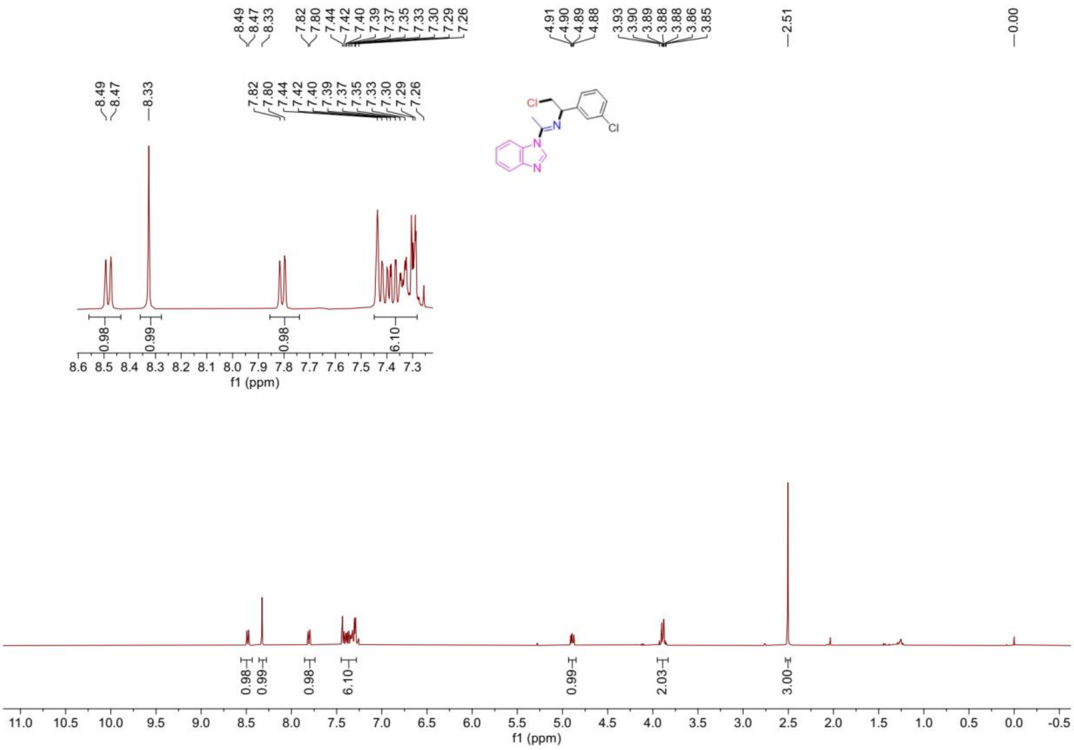

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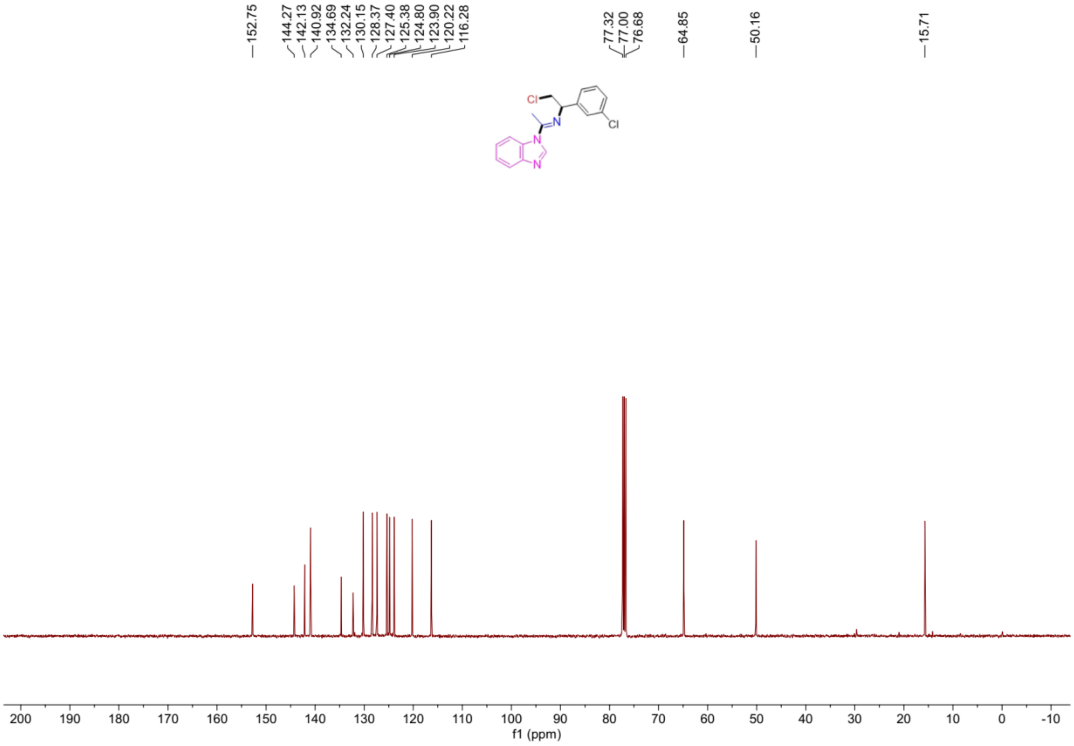

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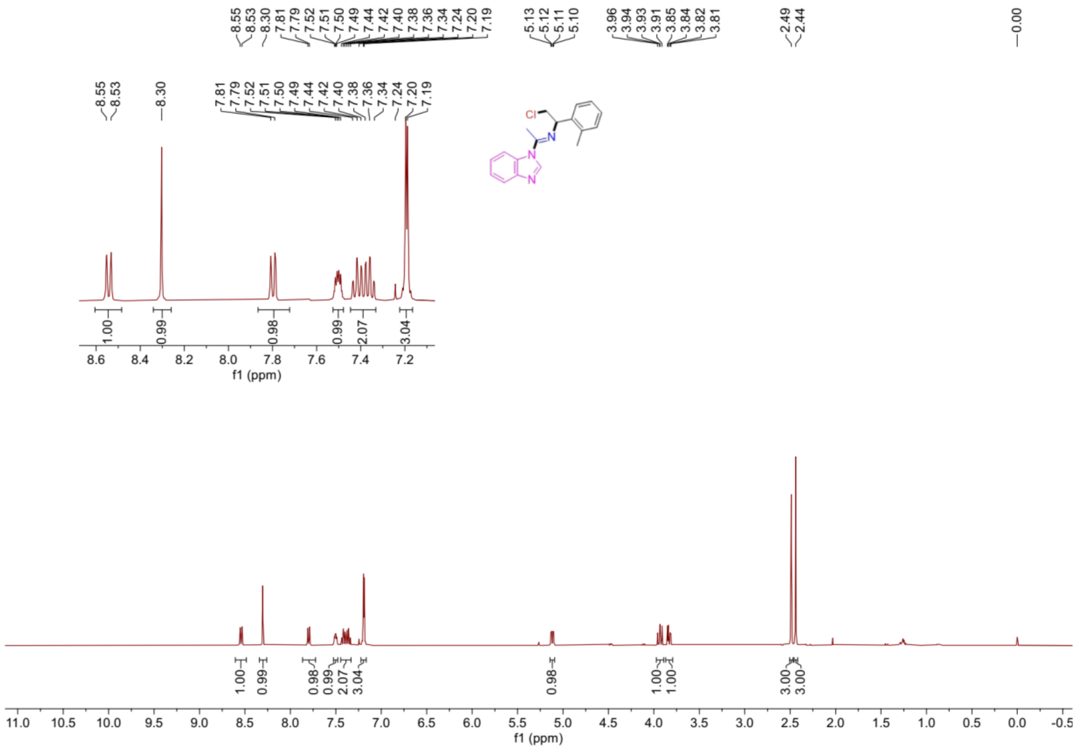

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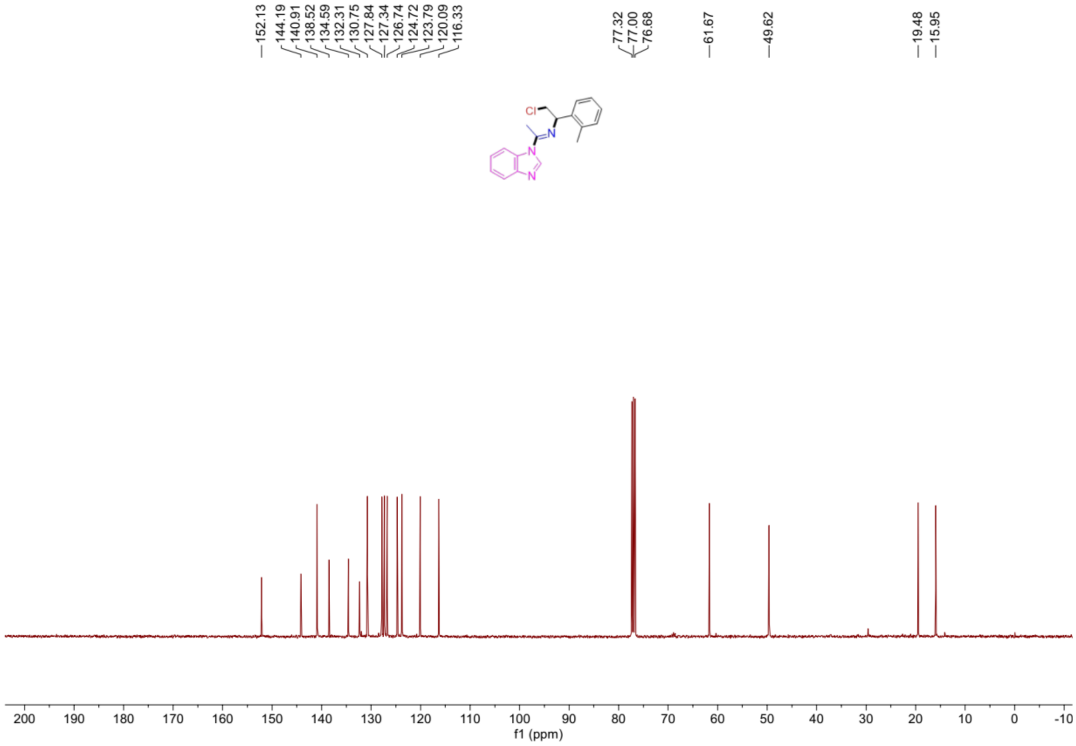

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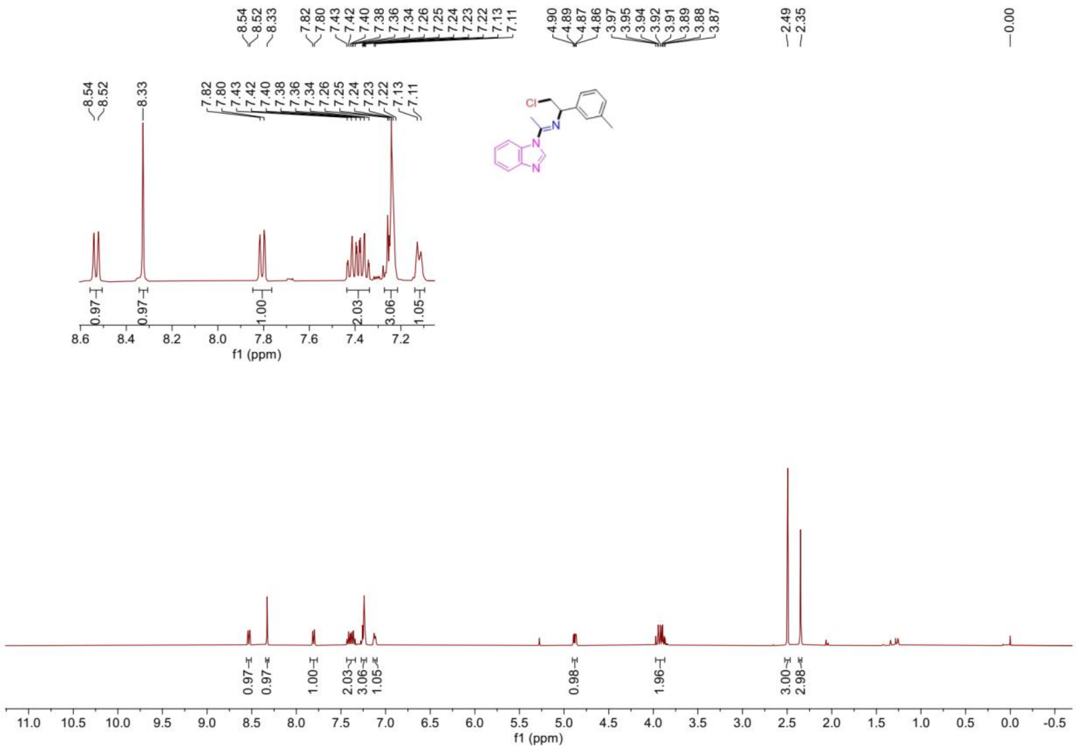

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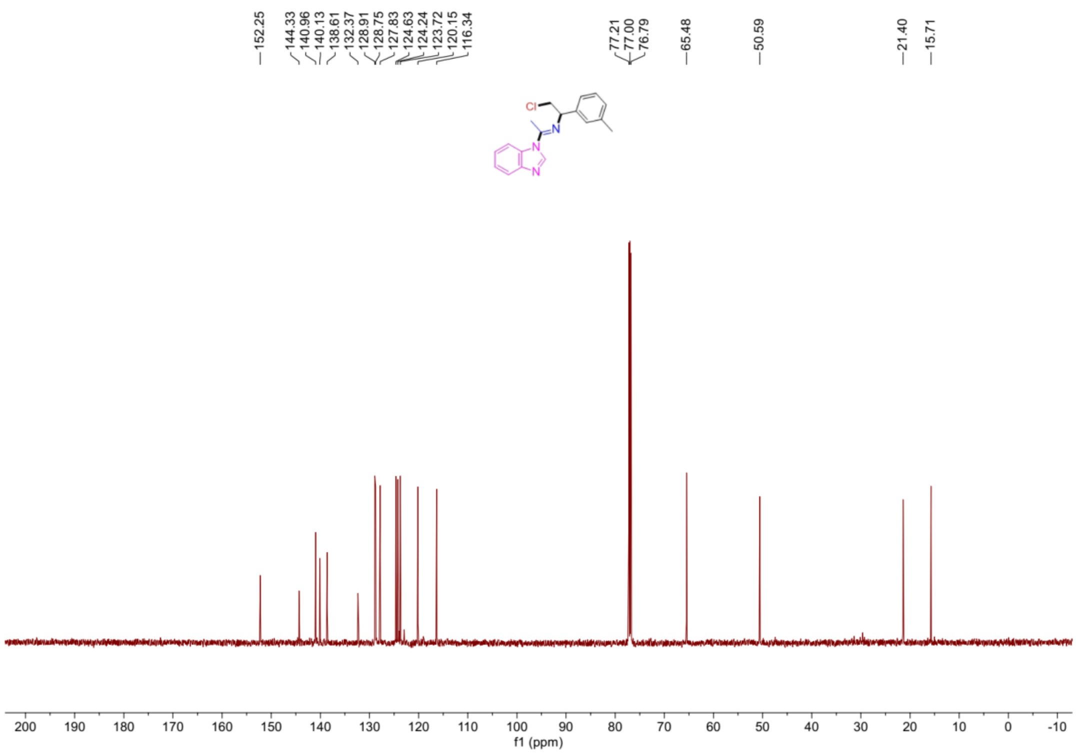

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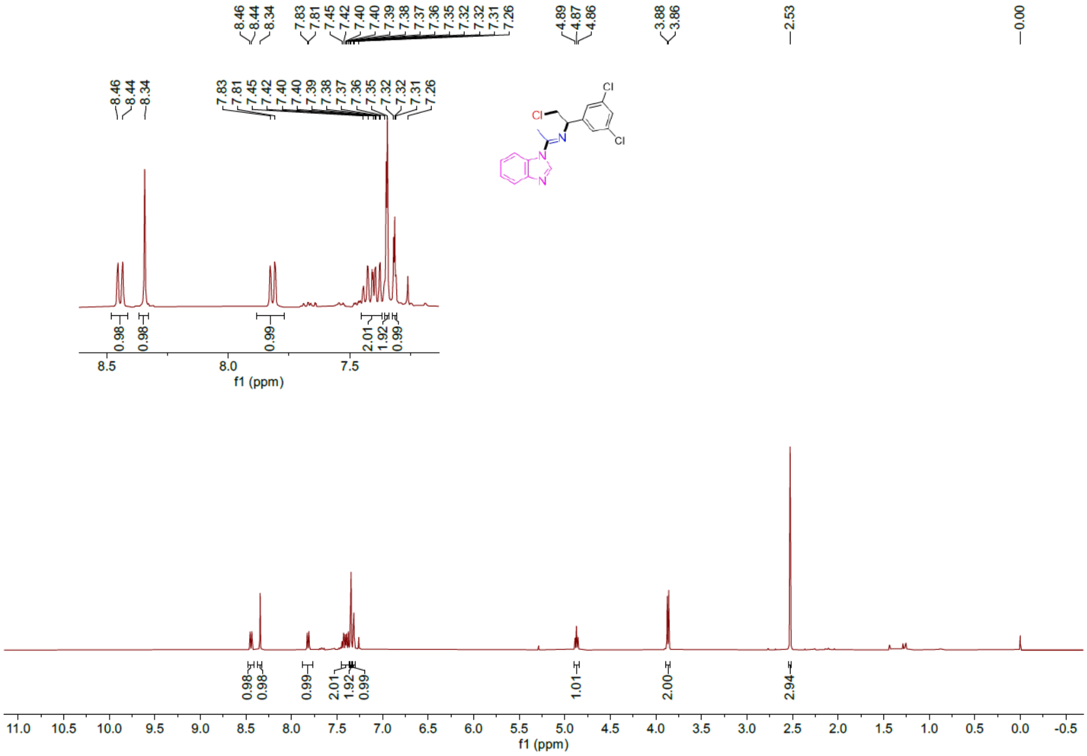

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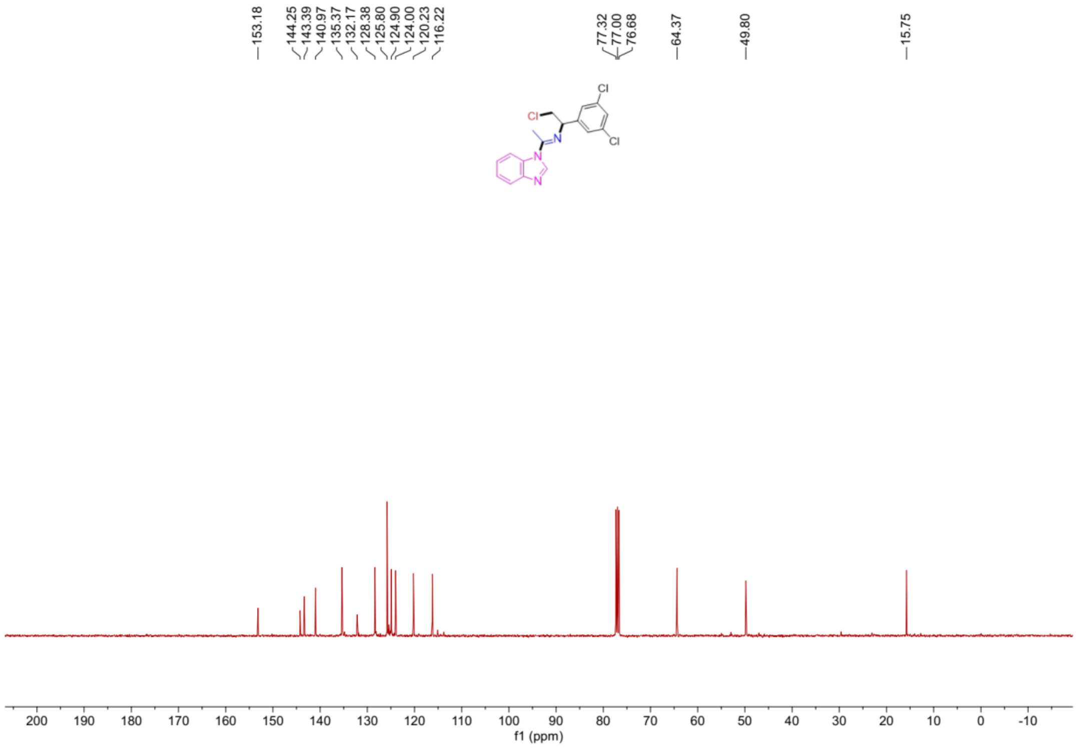

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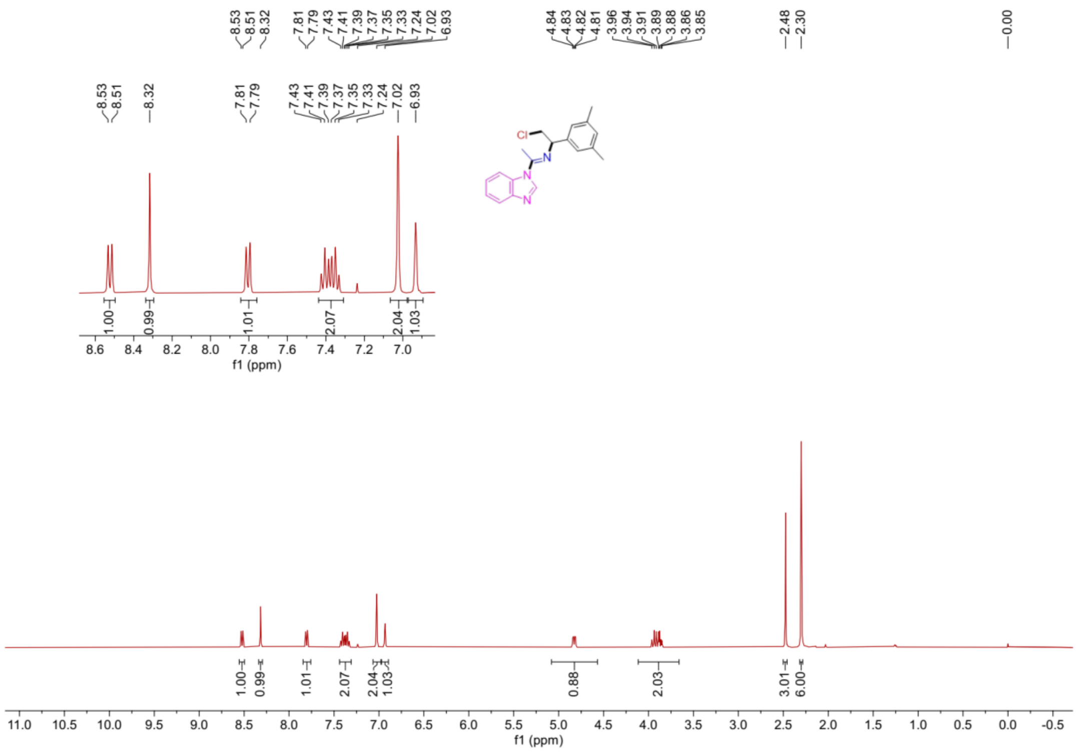

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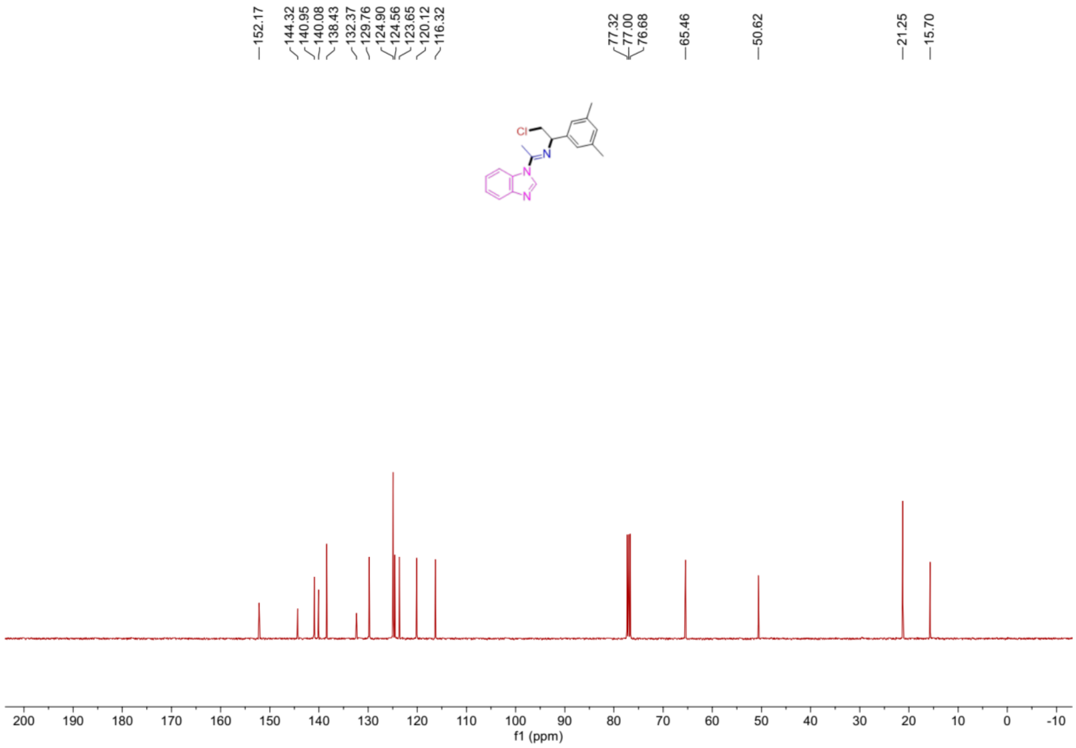

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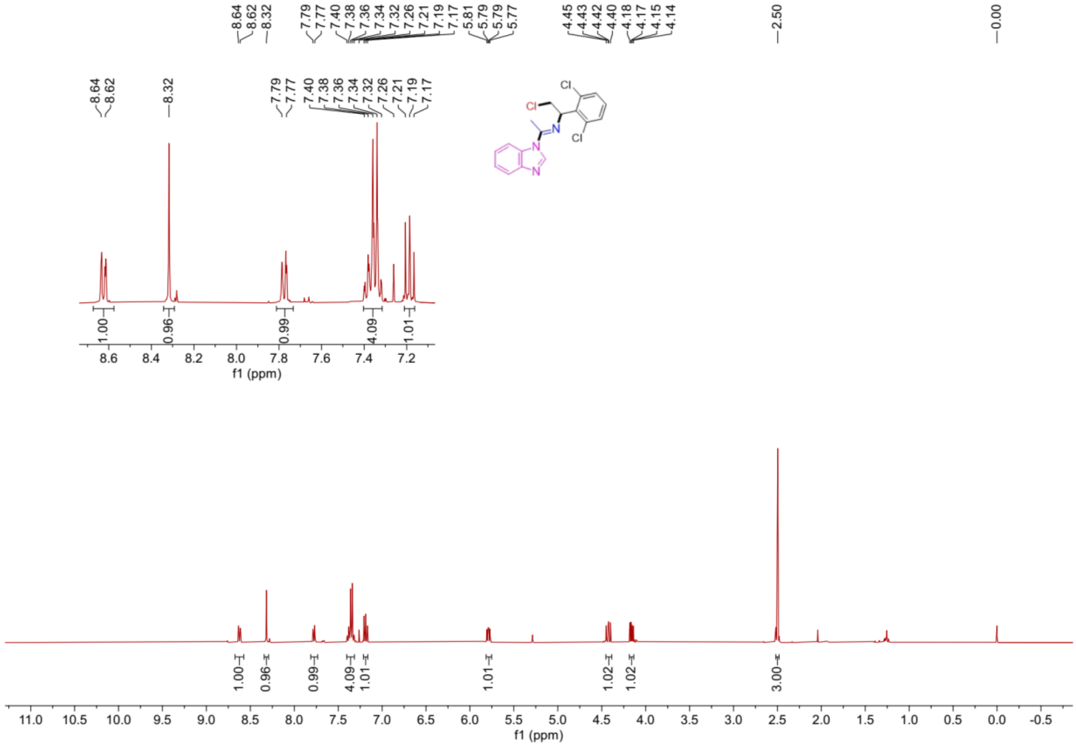

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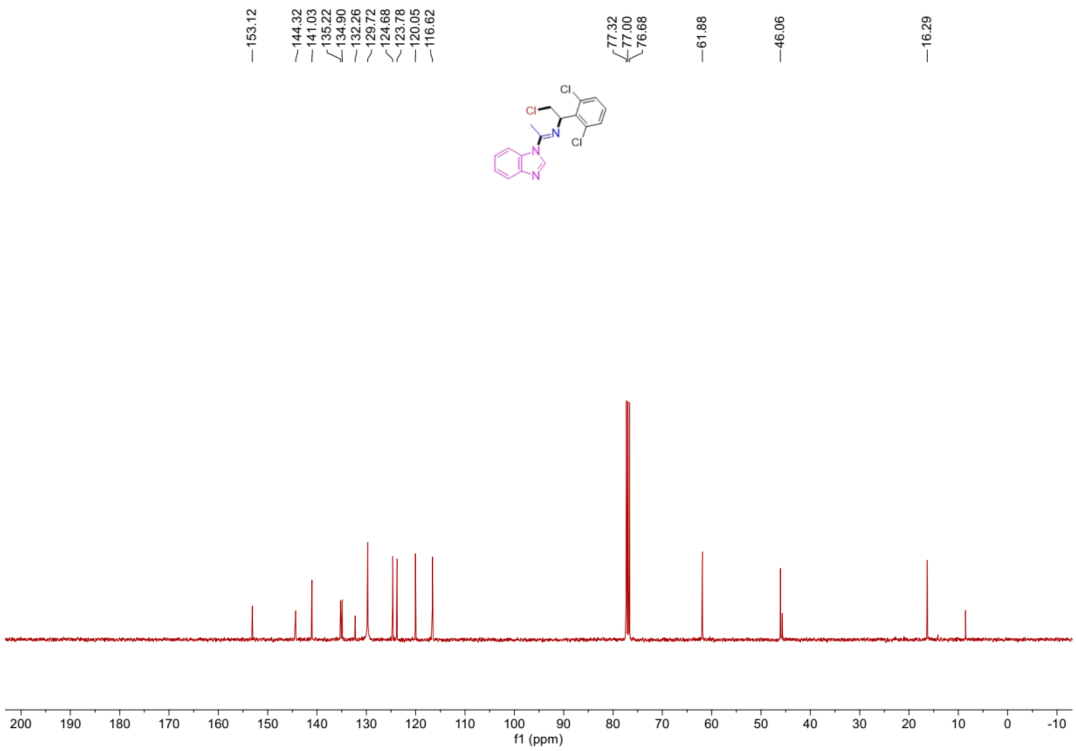

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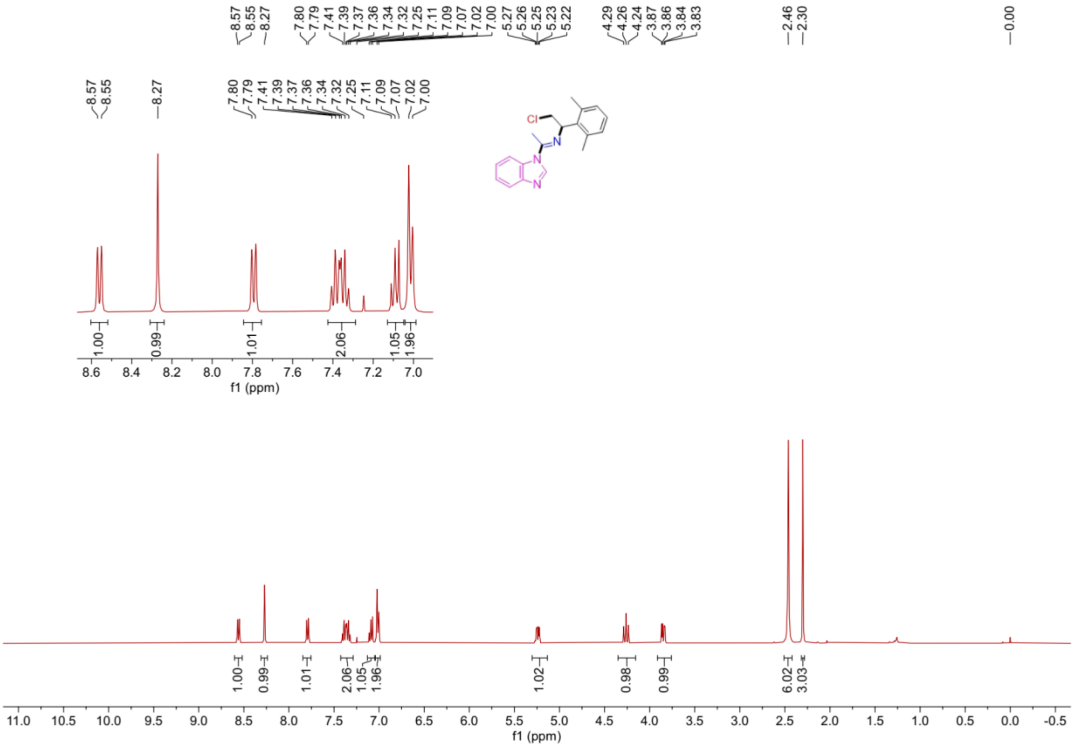

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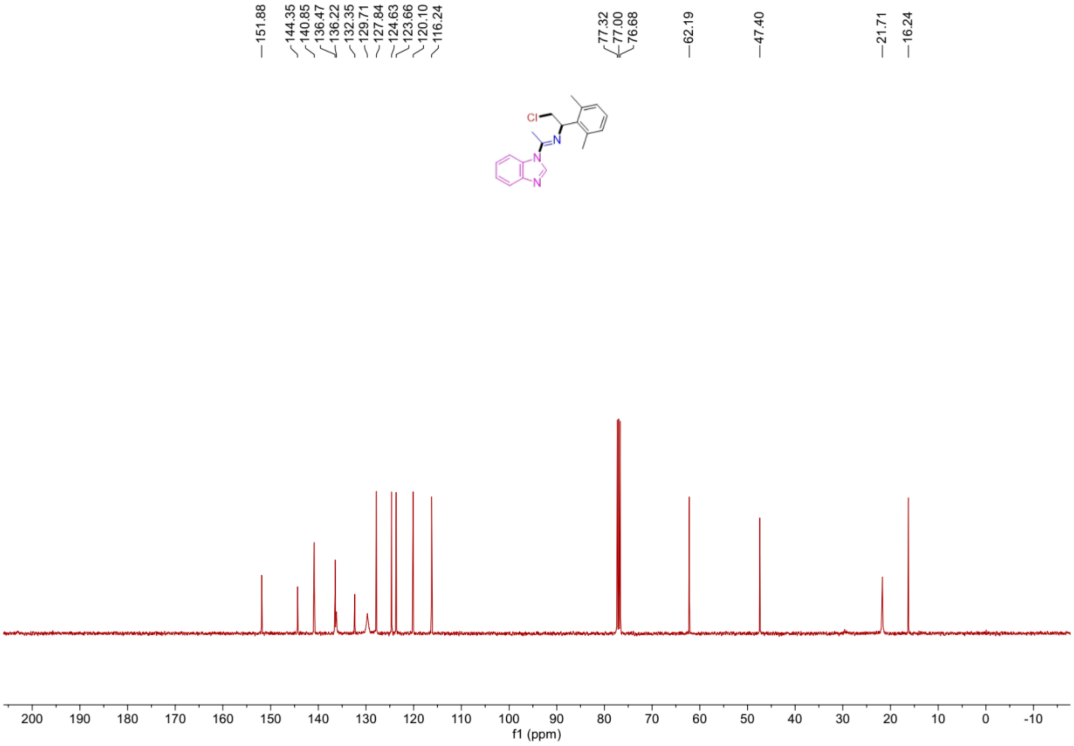

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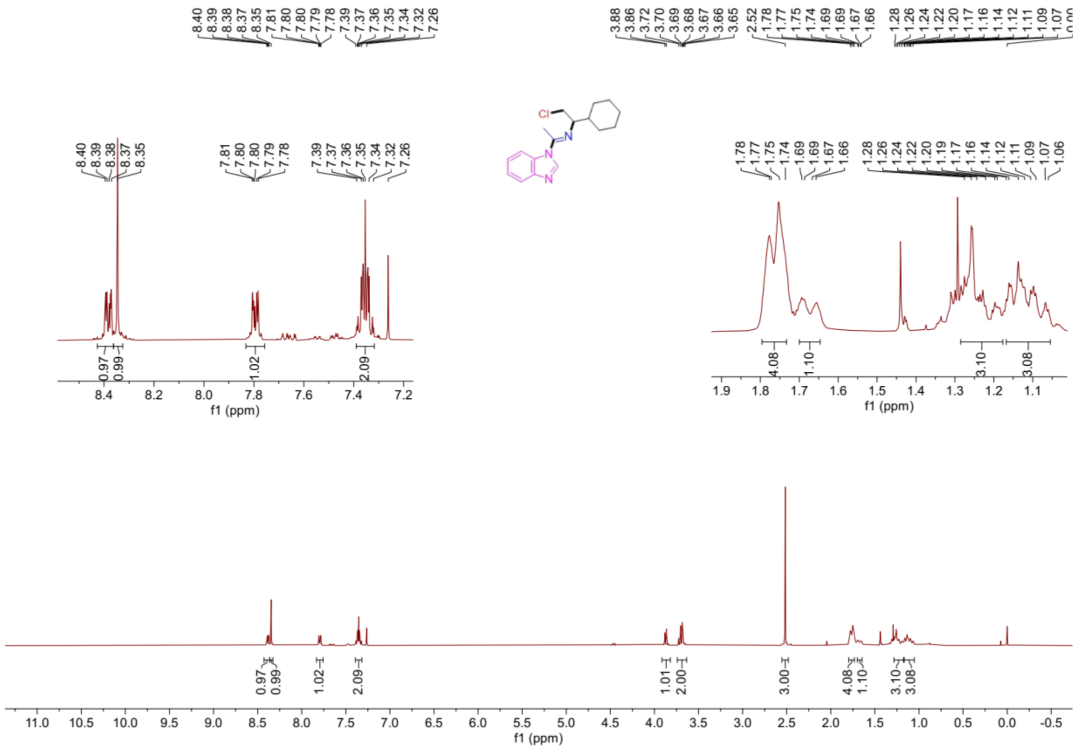

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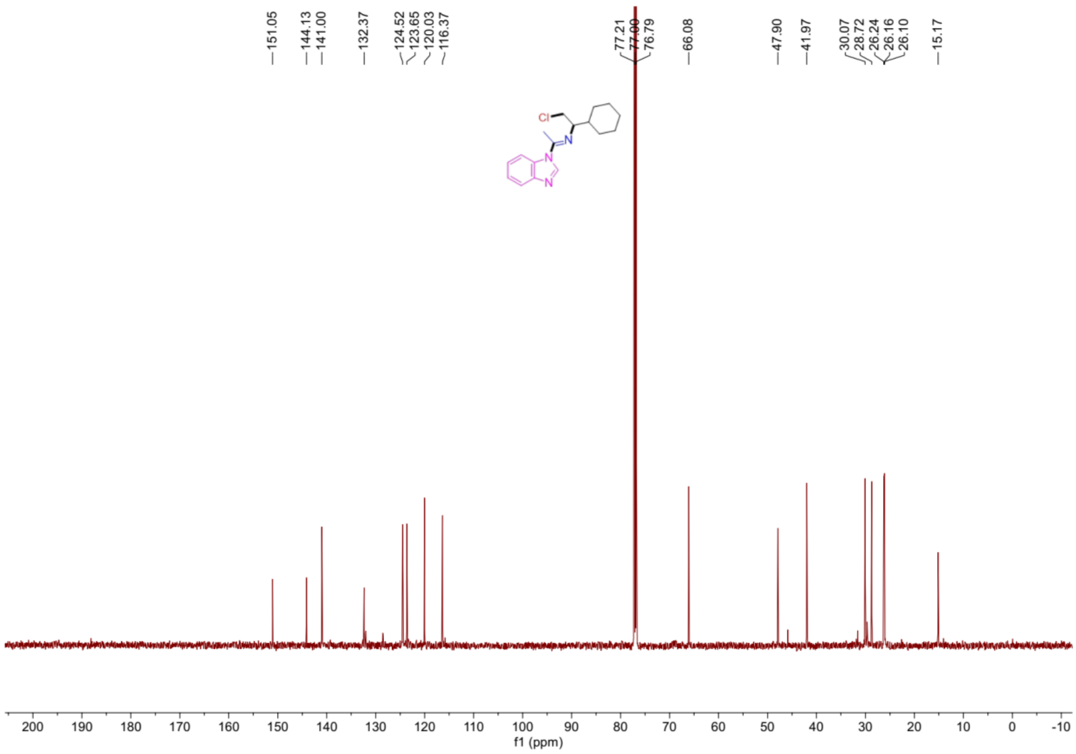

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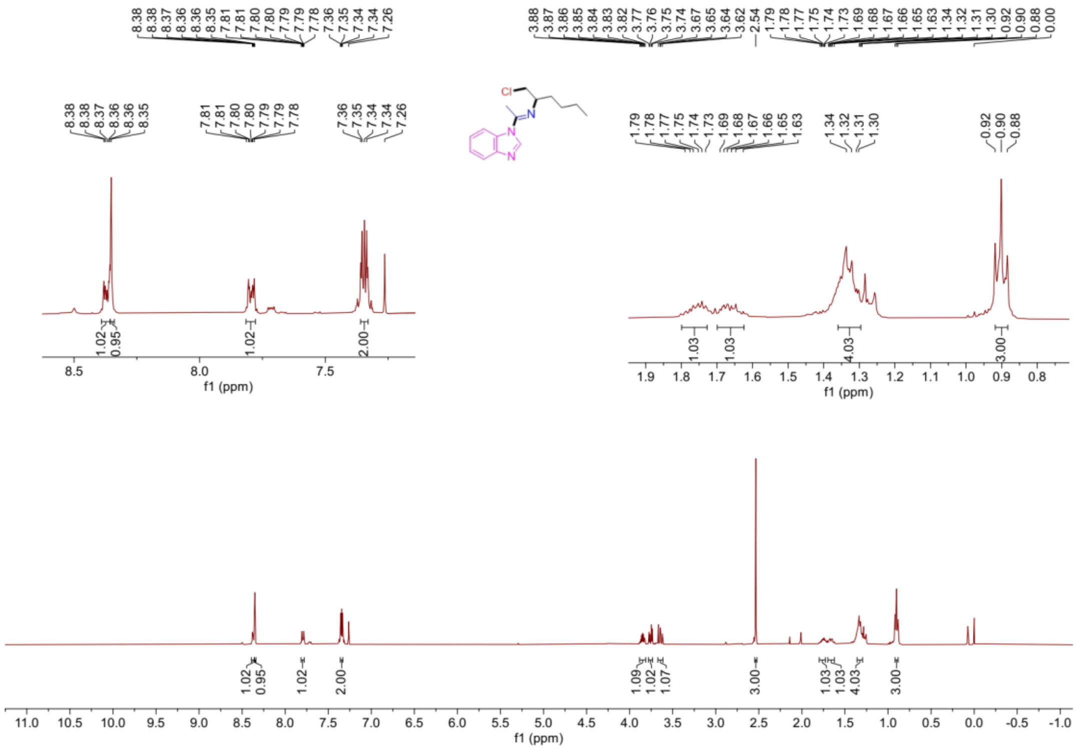

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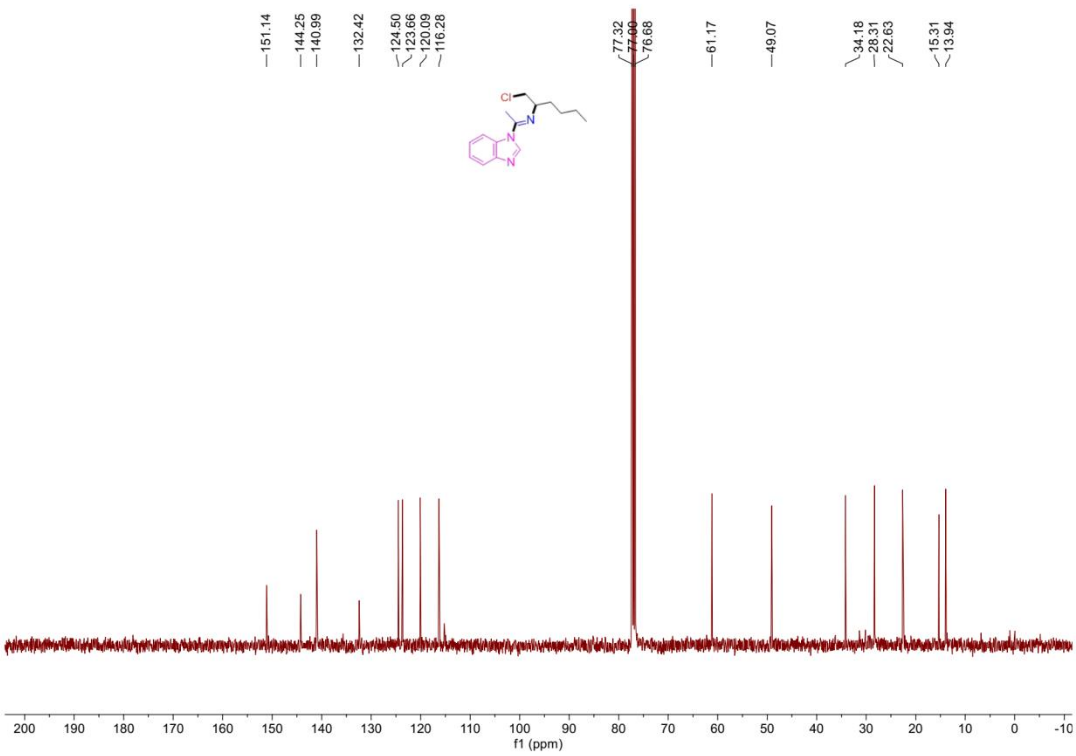

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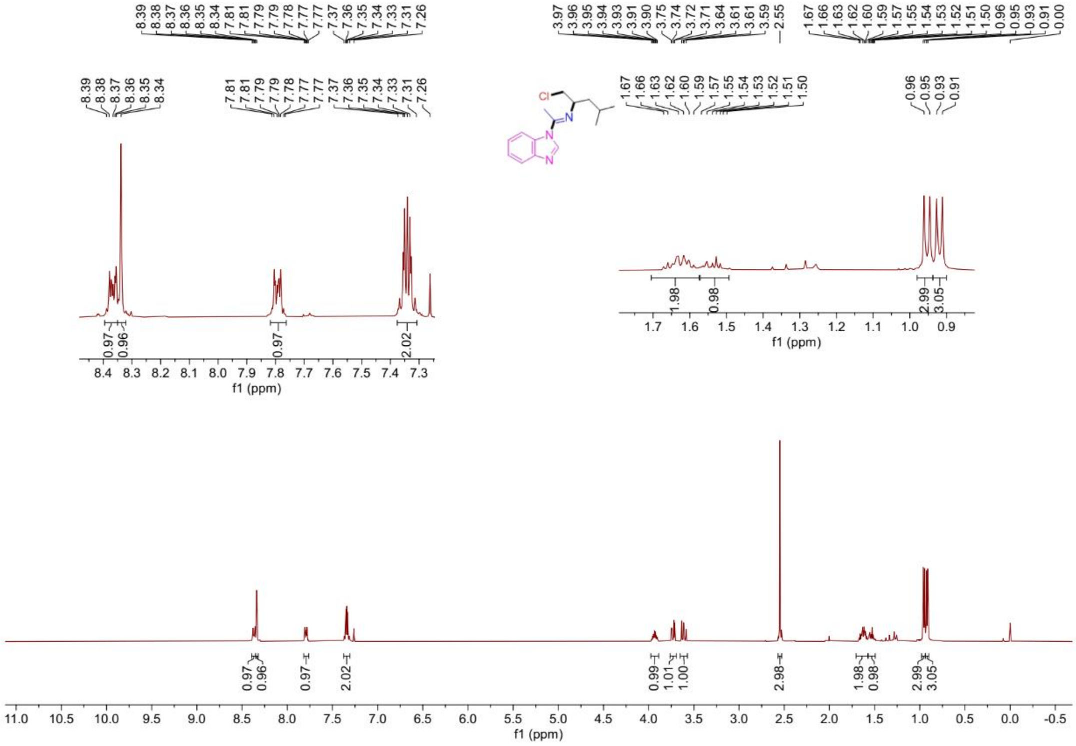

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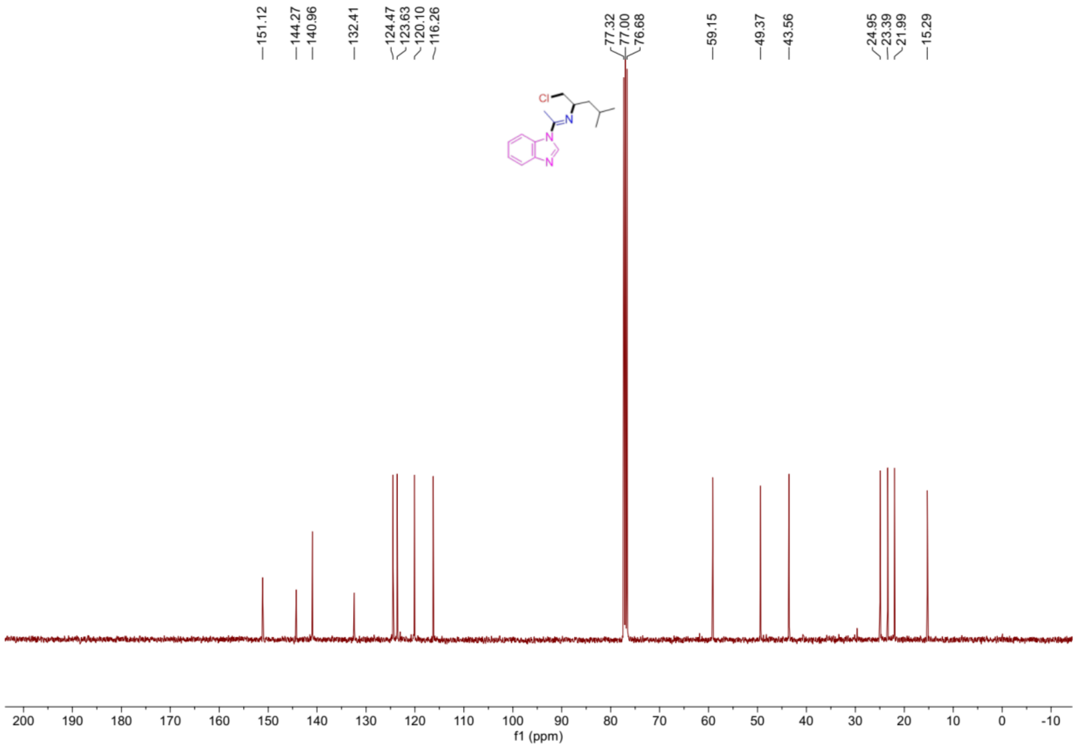

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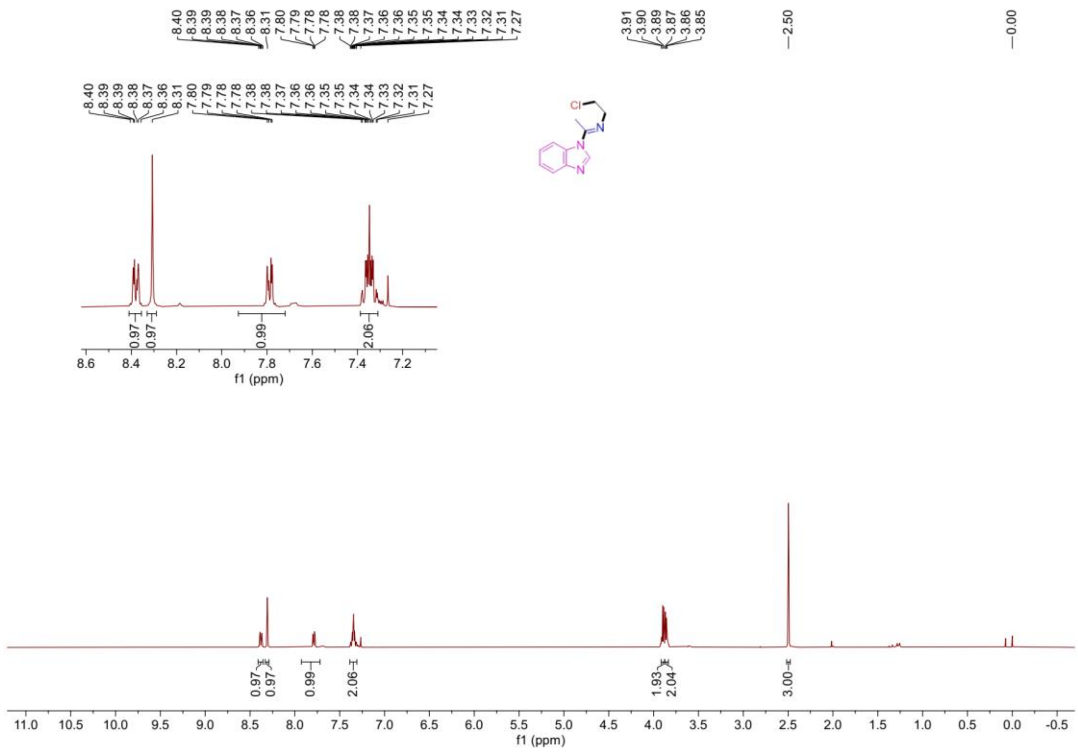

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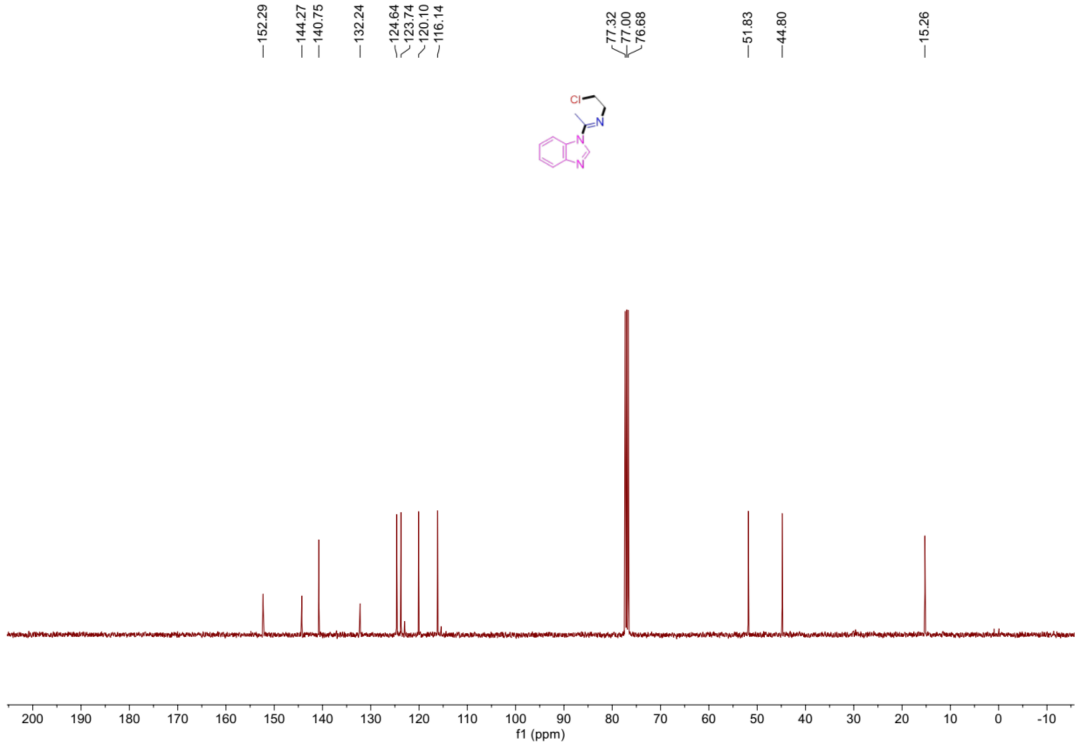

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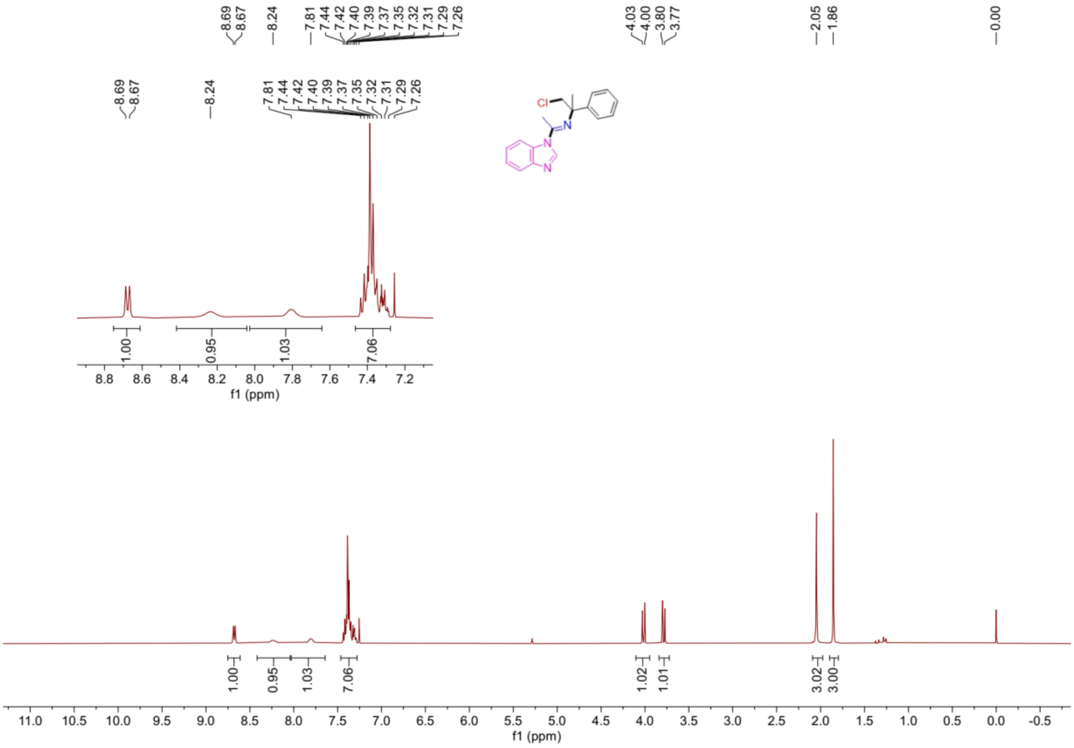

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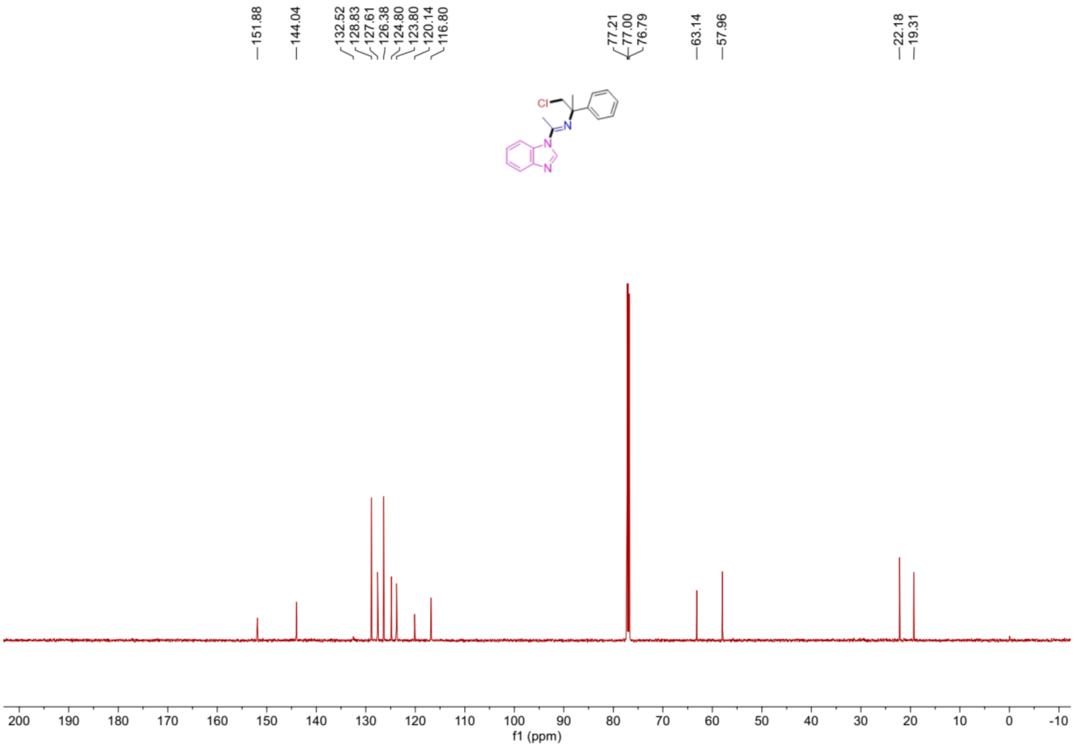

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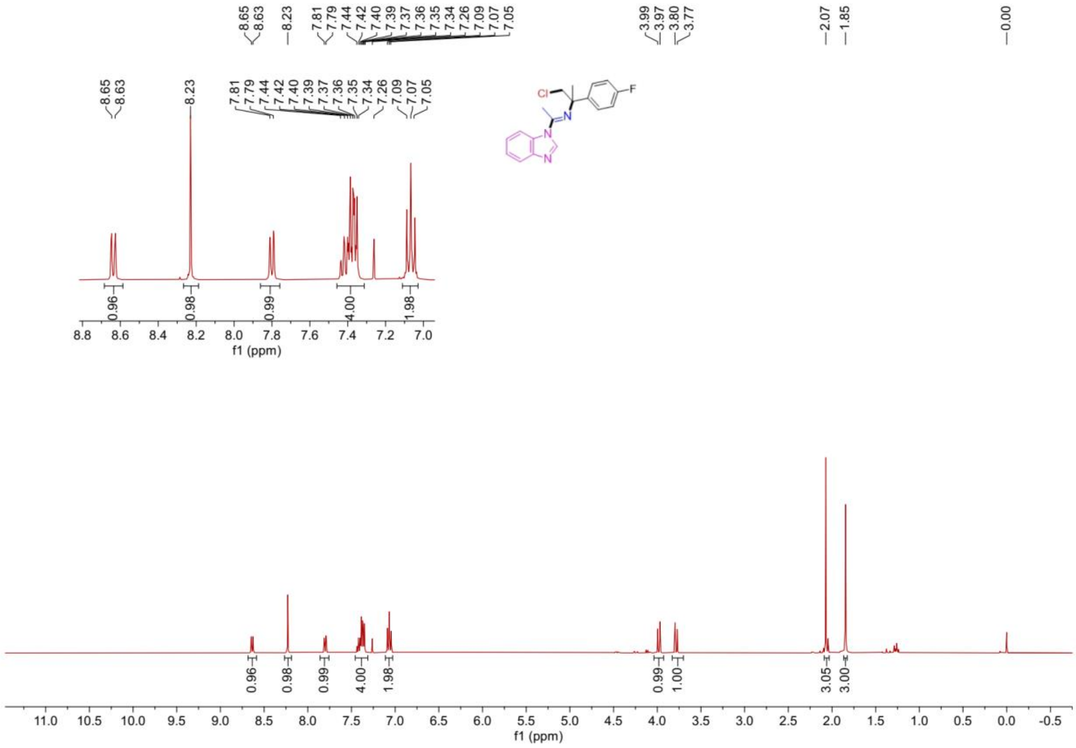

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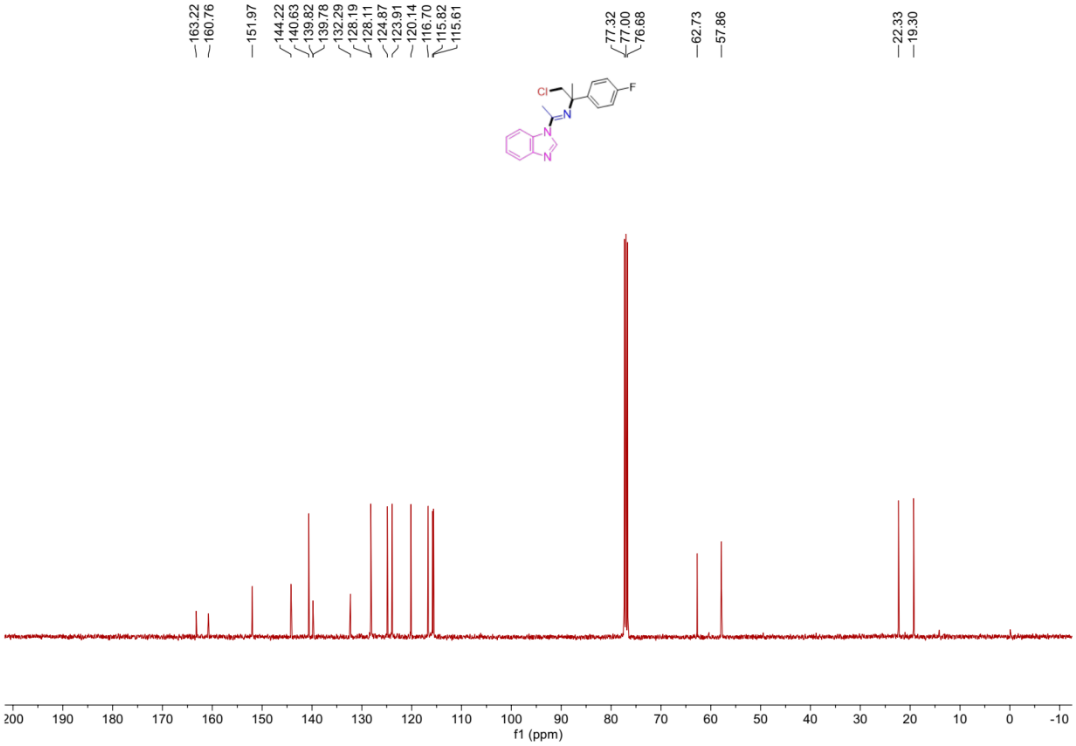

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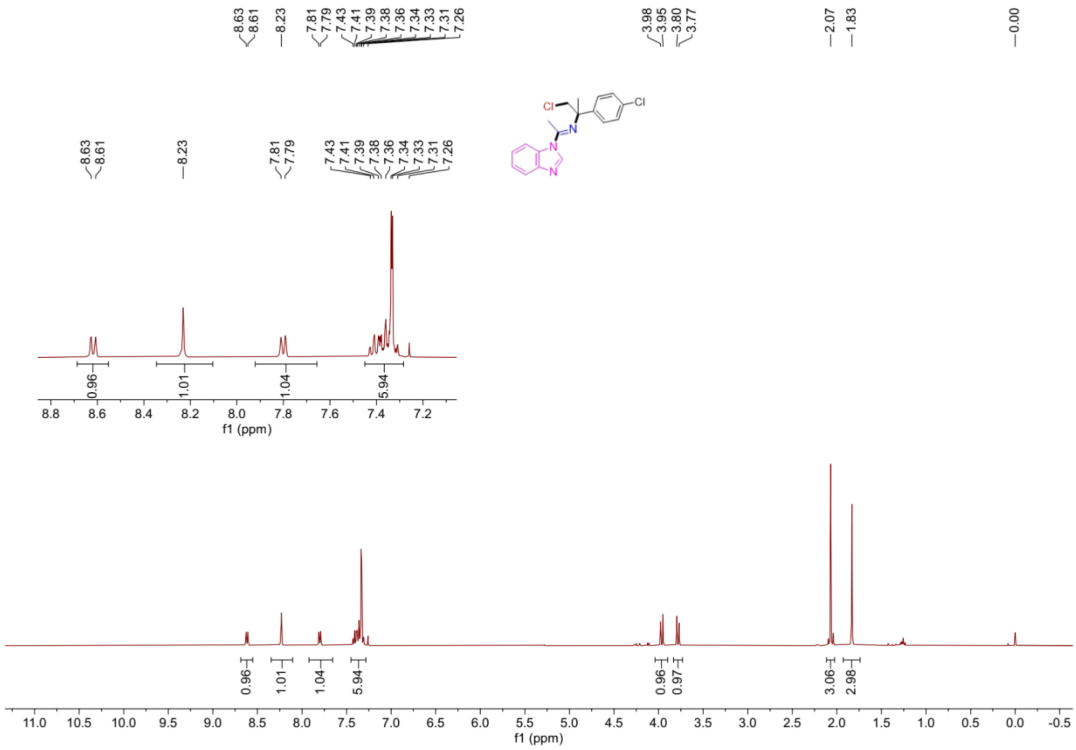

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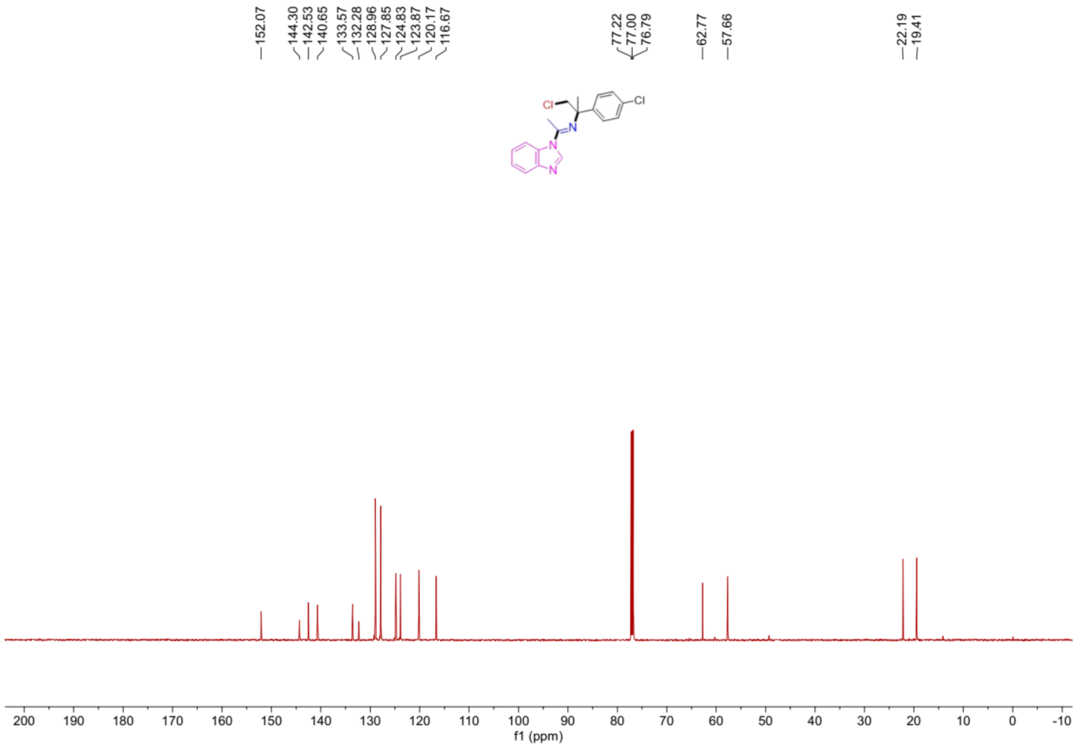

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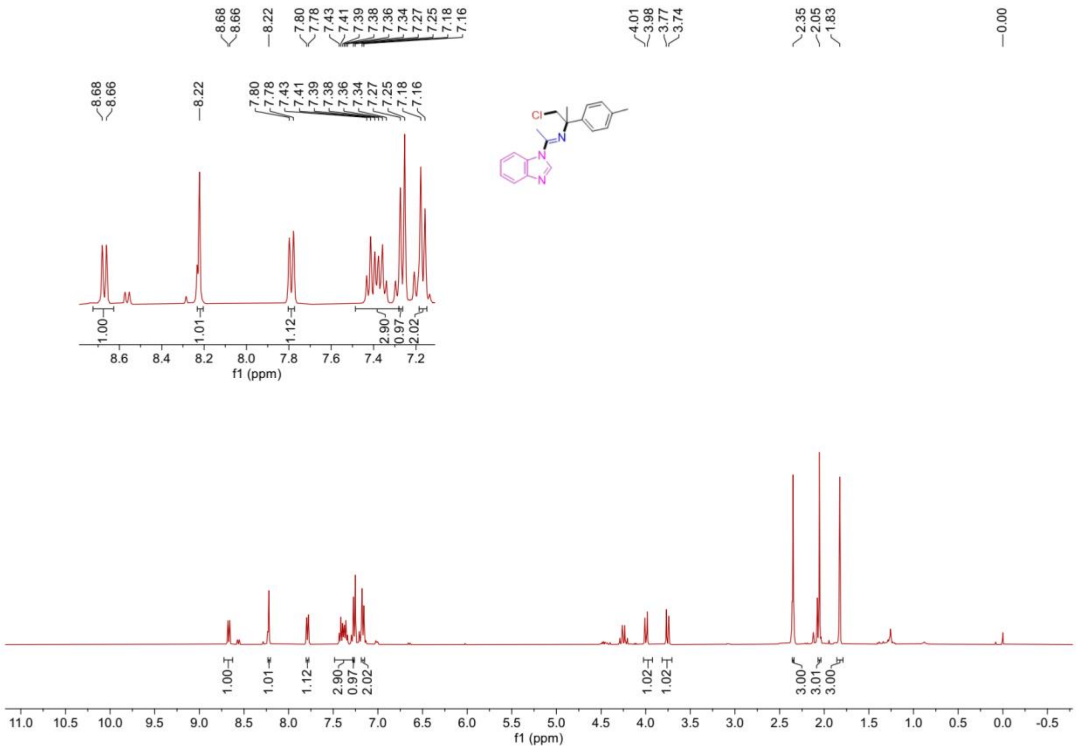

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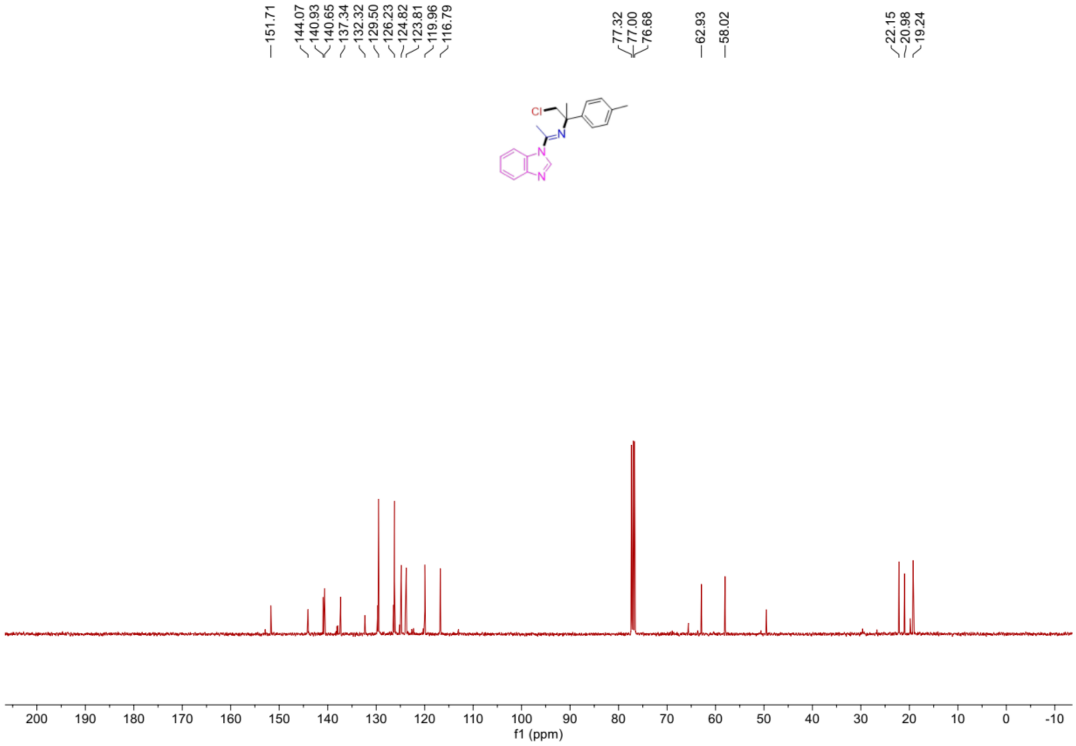

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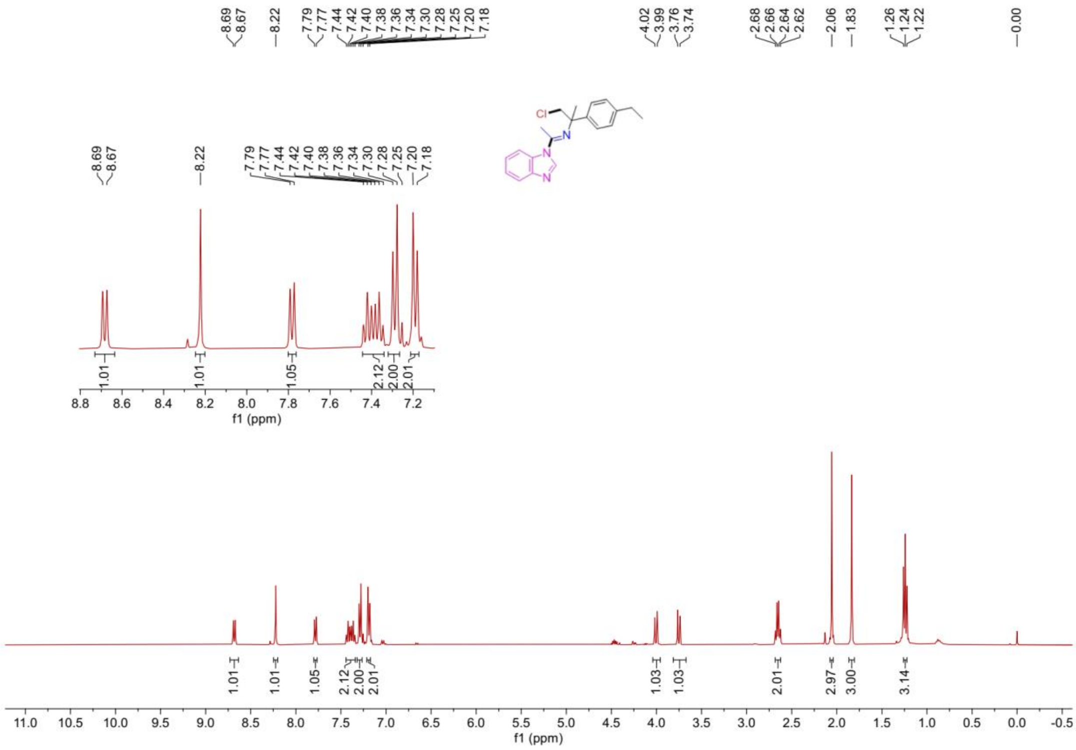

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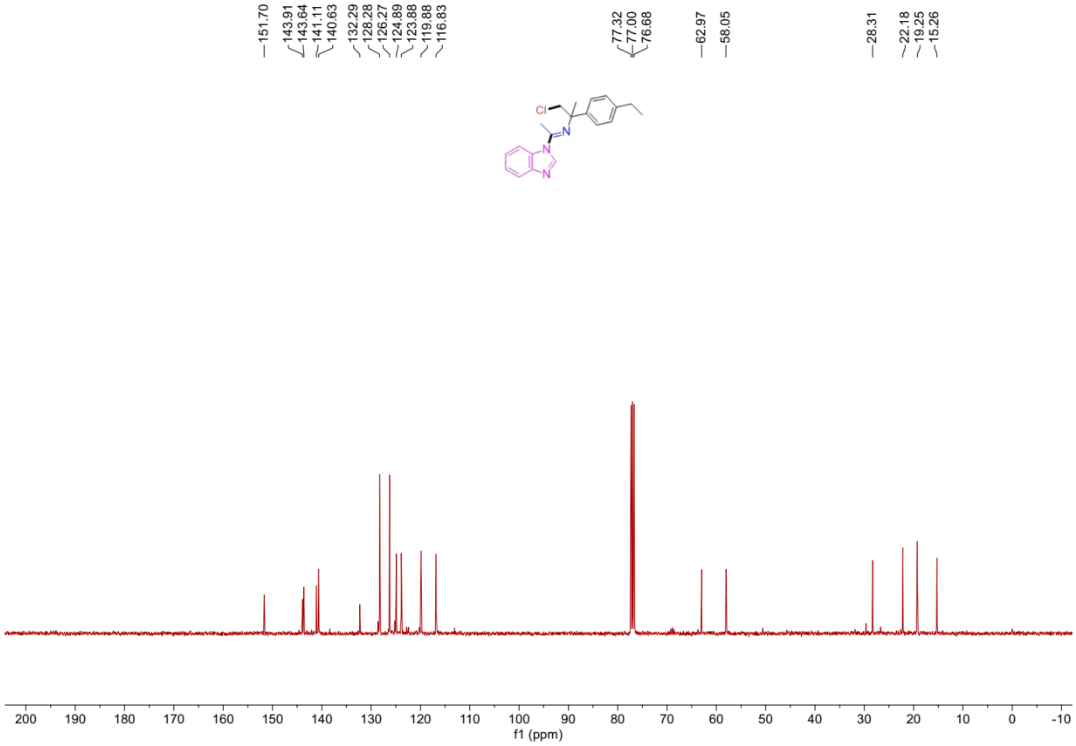

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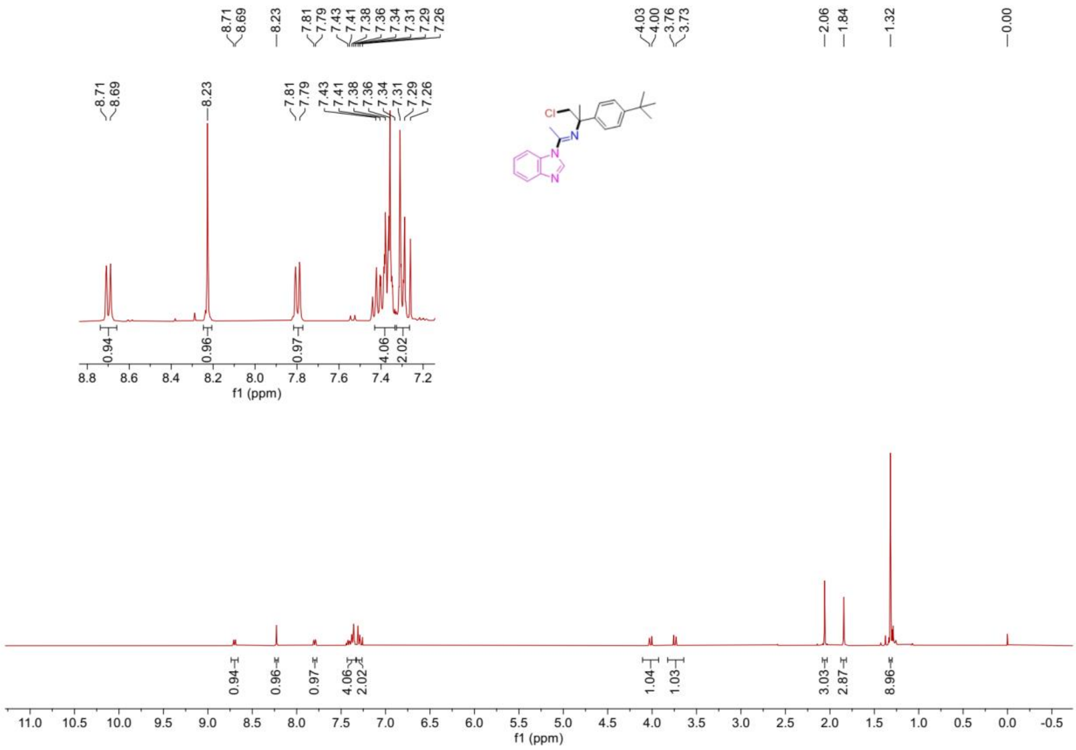

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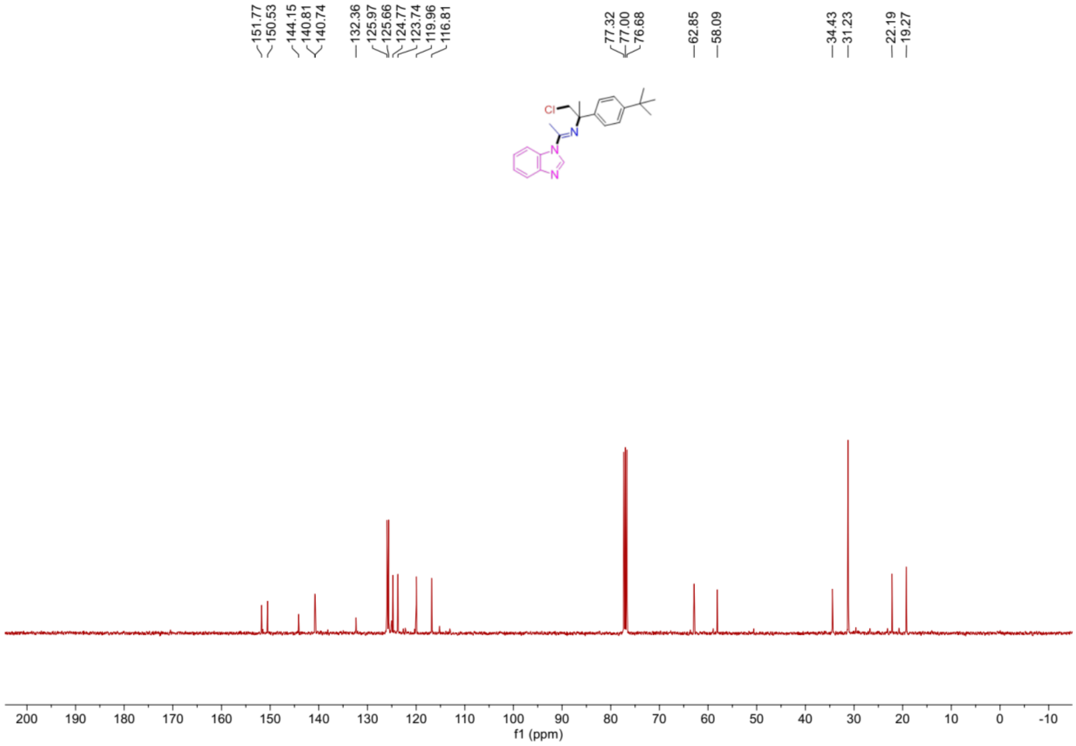
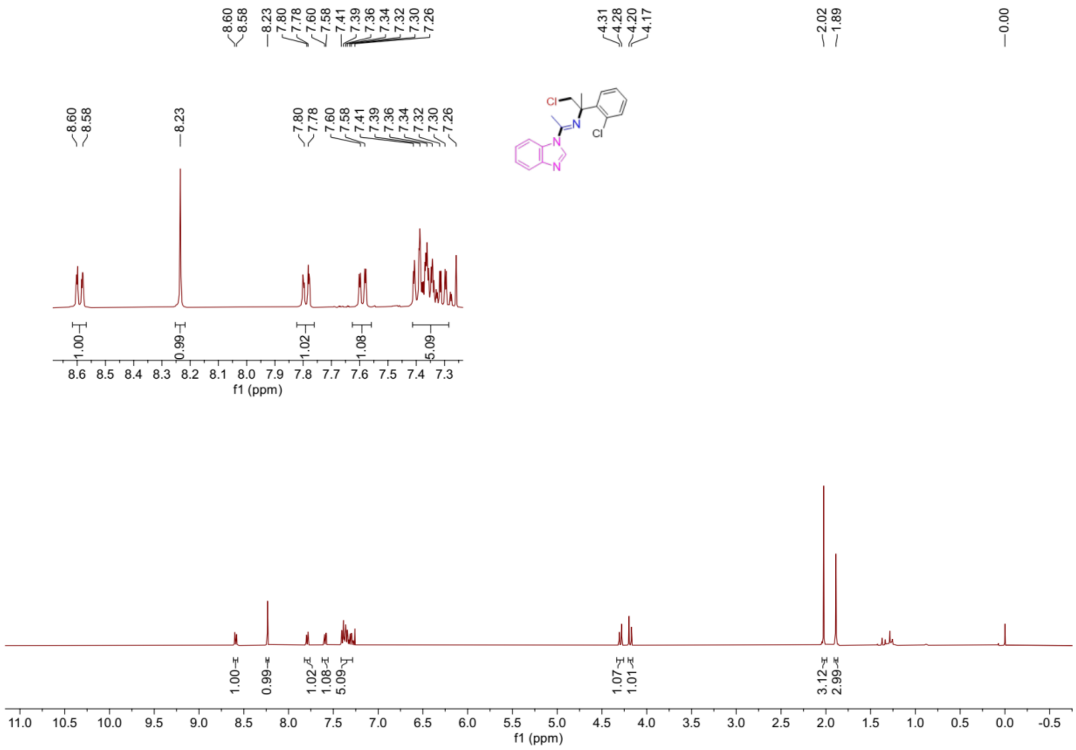


3al ^{1}H NMR



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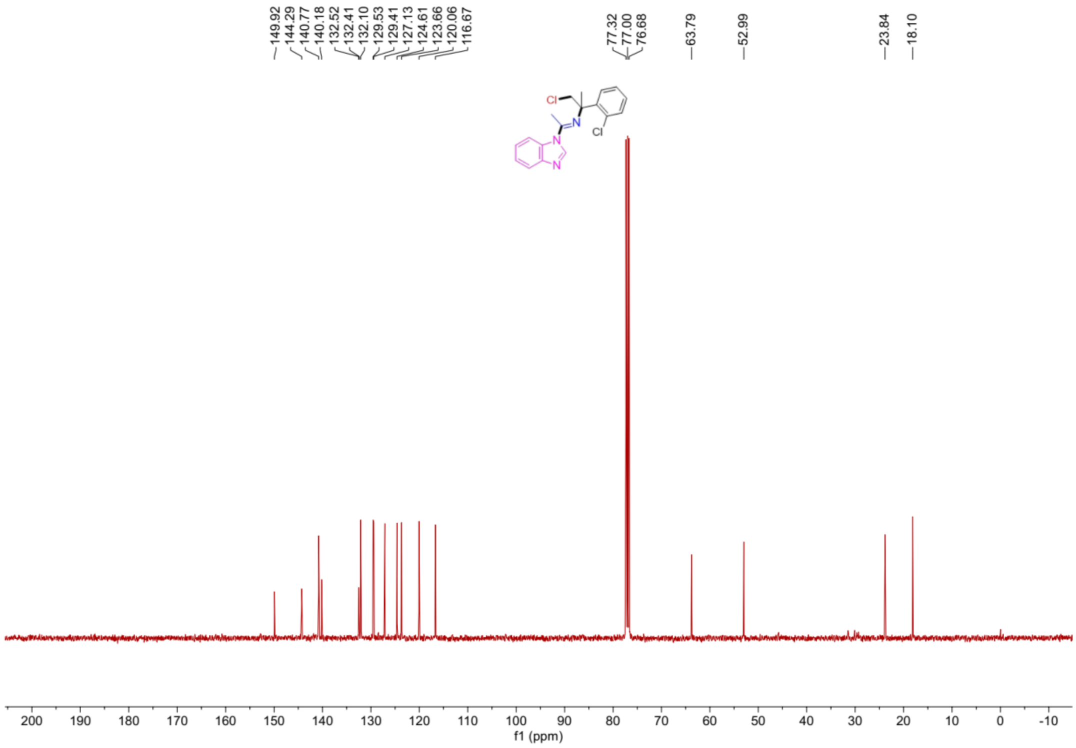

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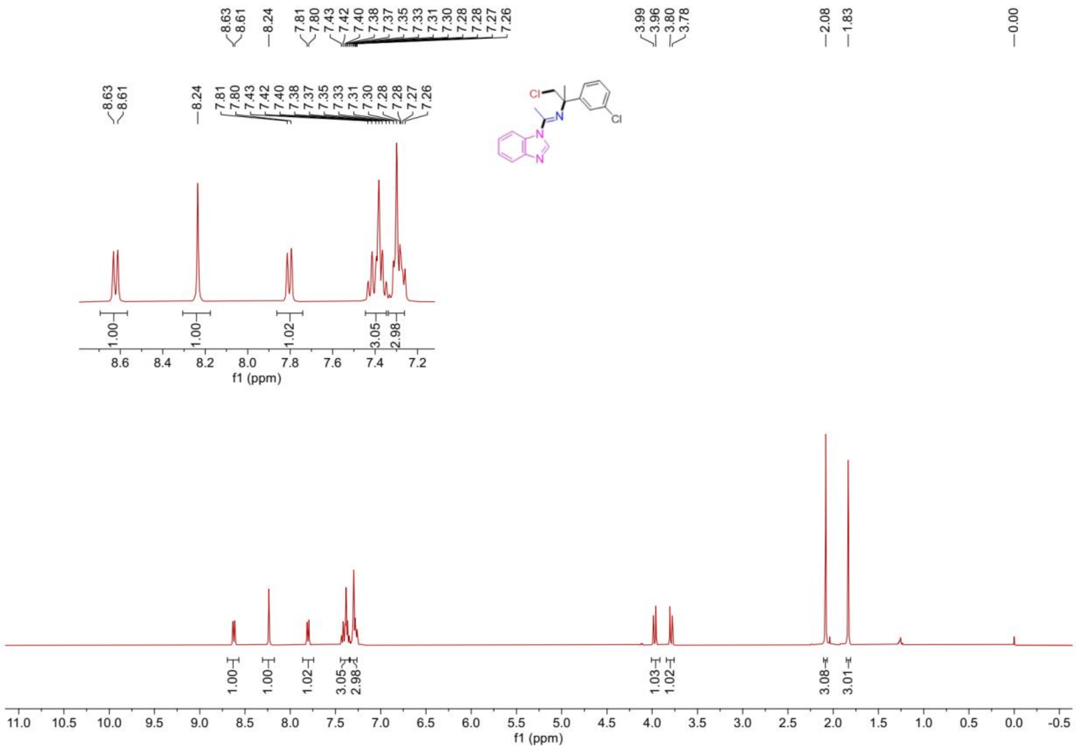

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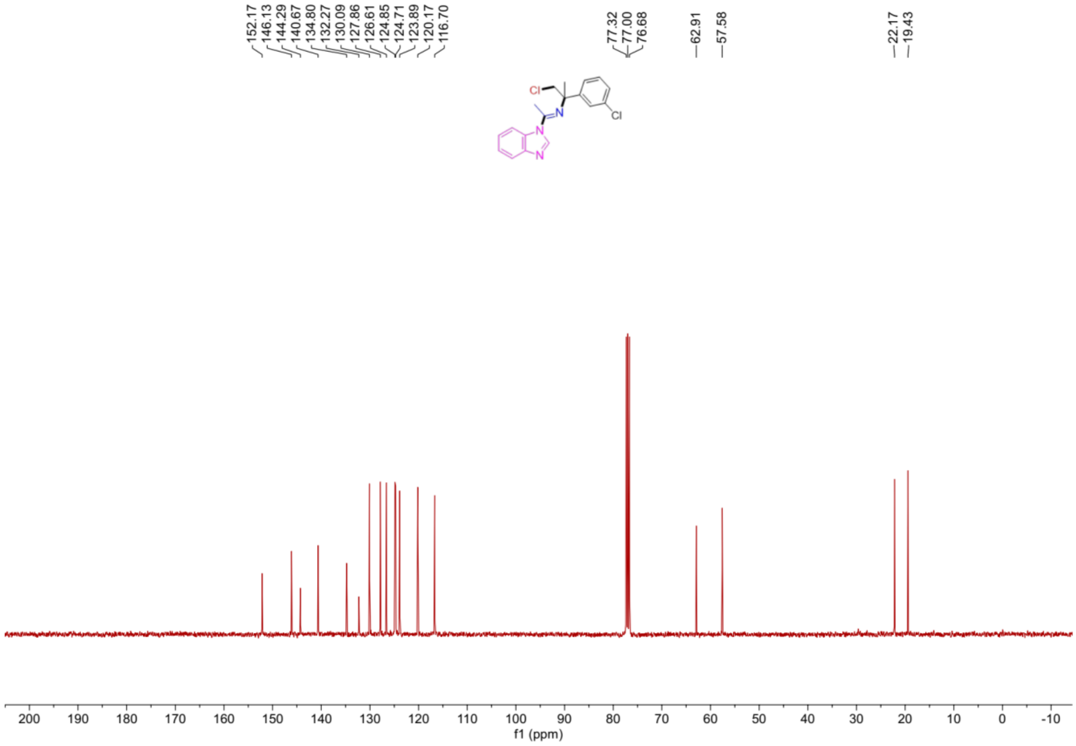

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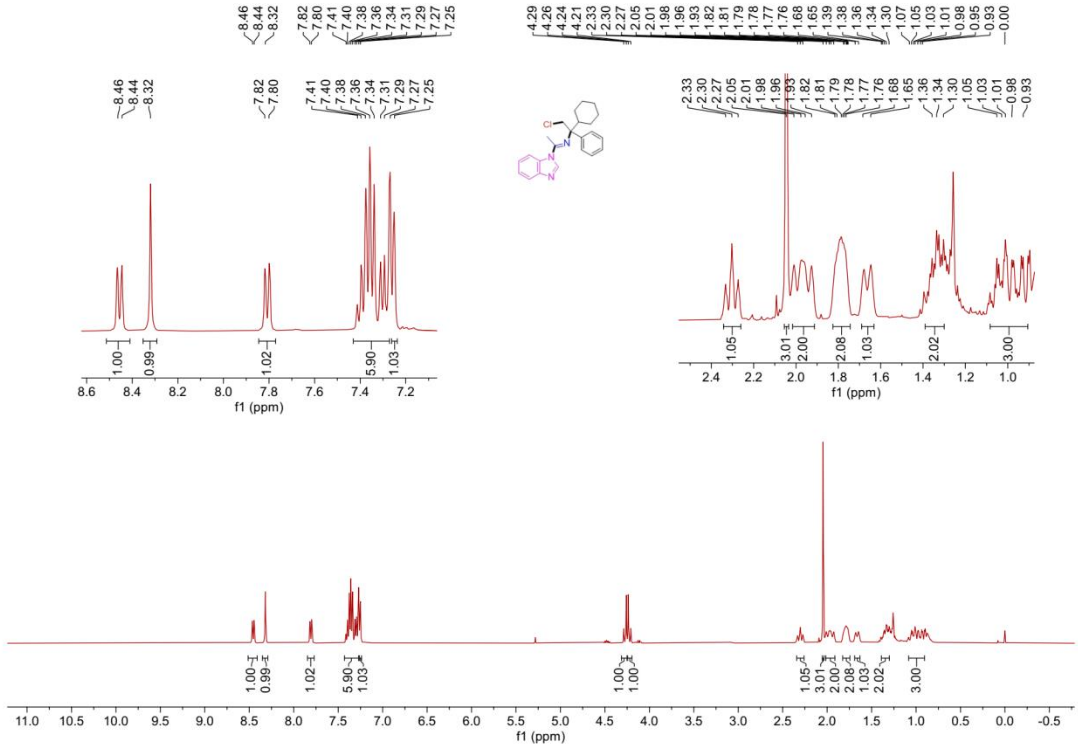

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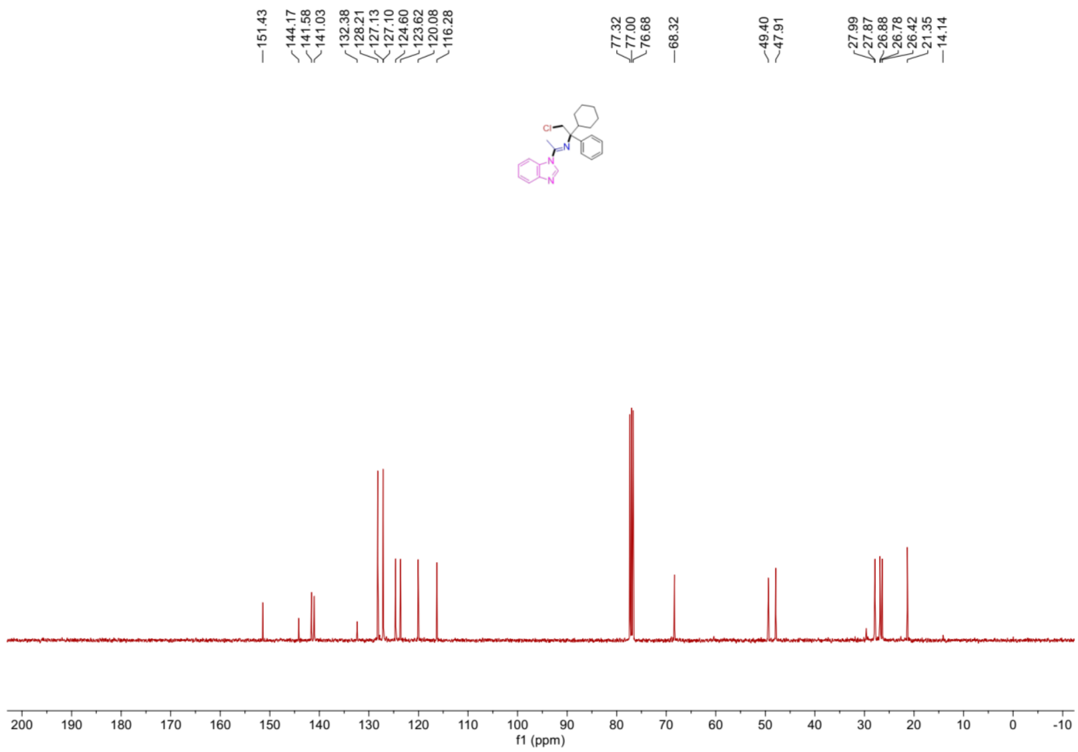

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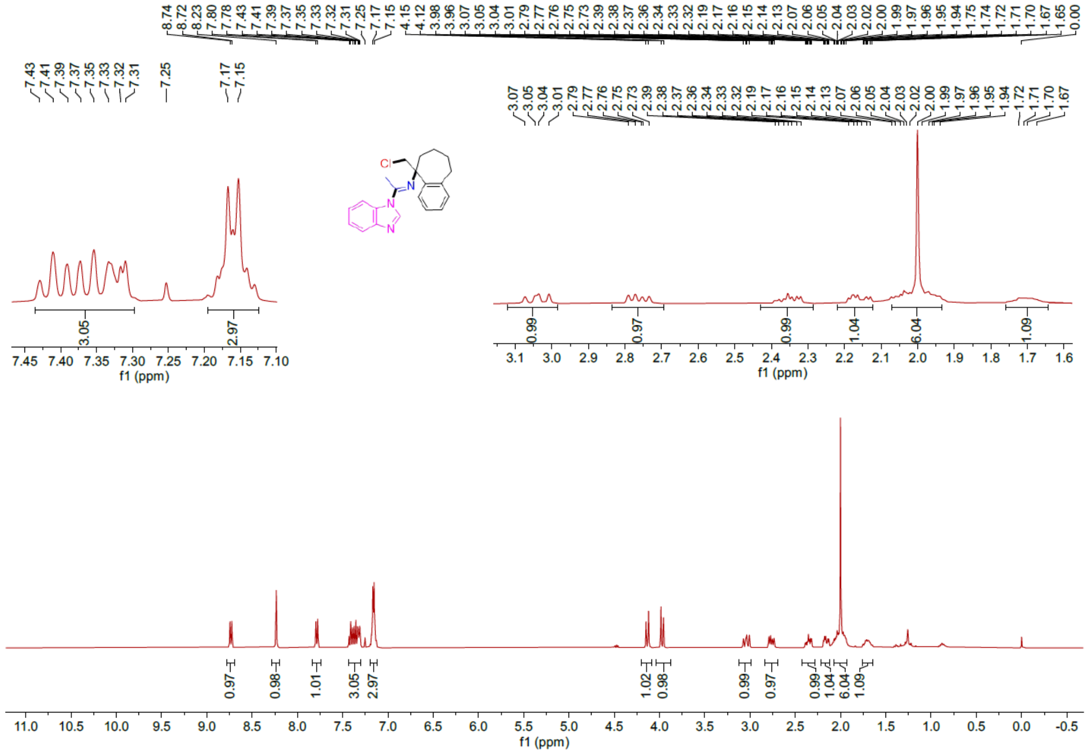

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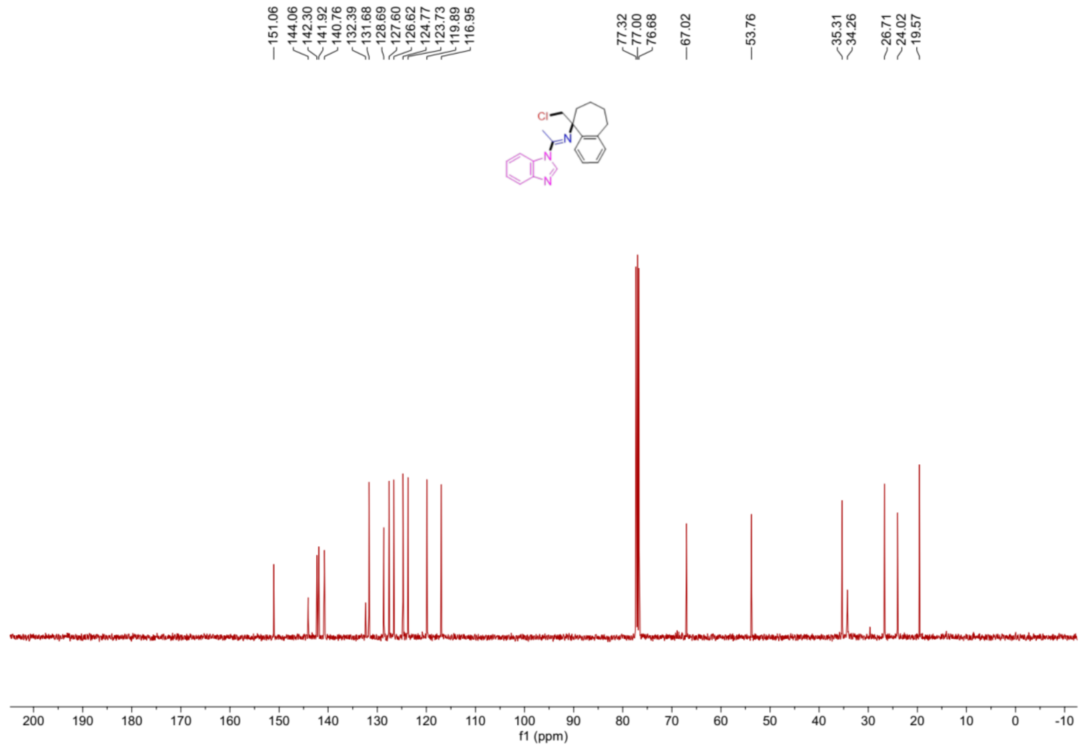

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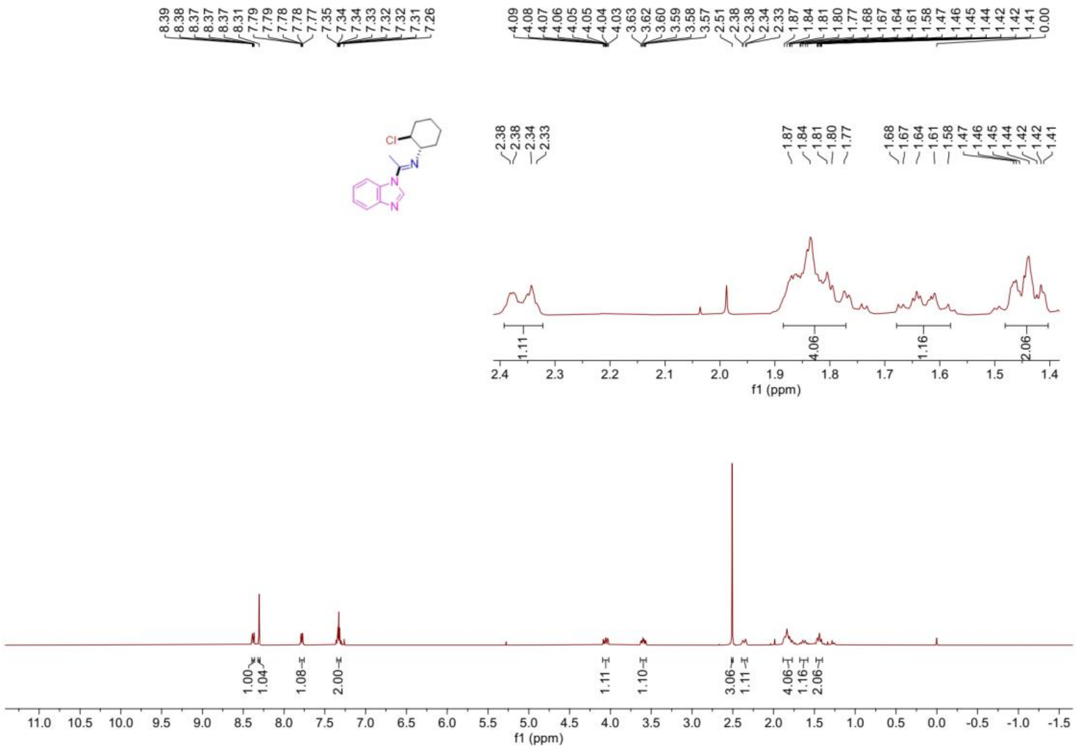

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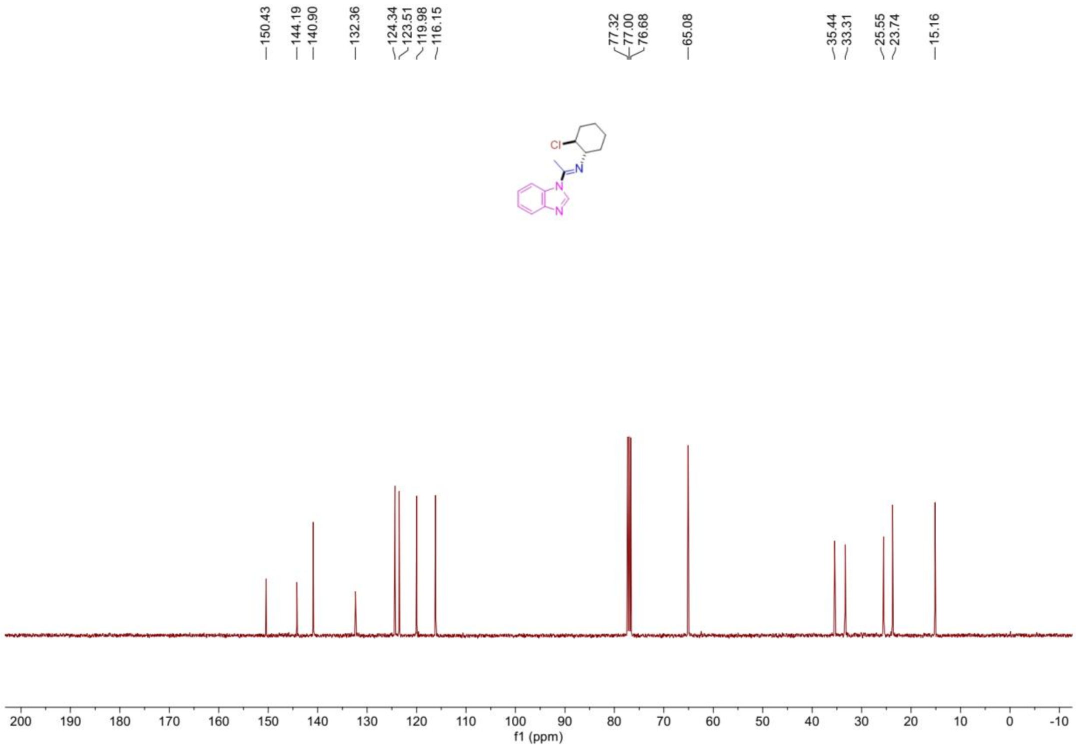
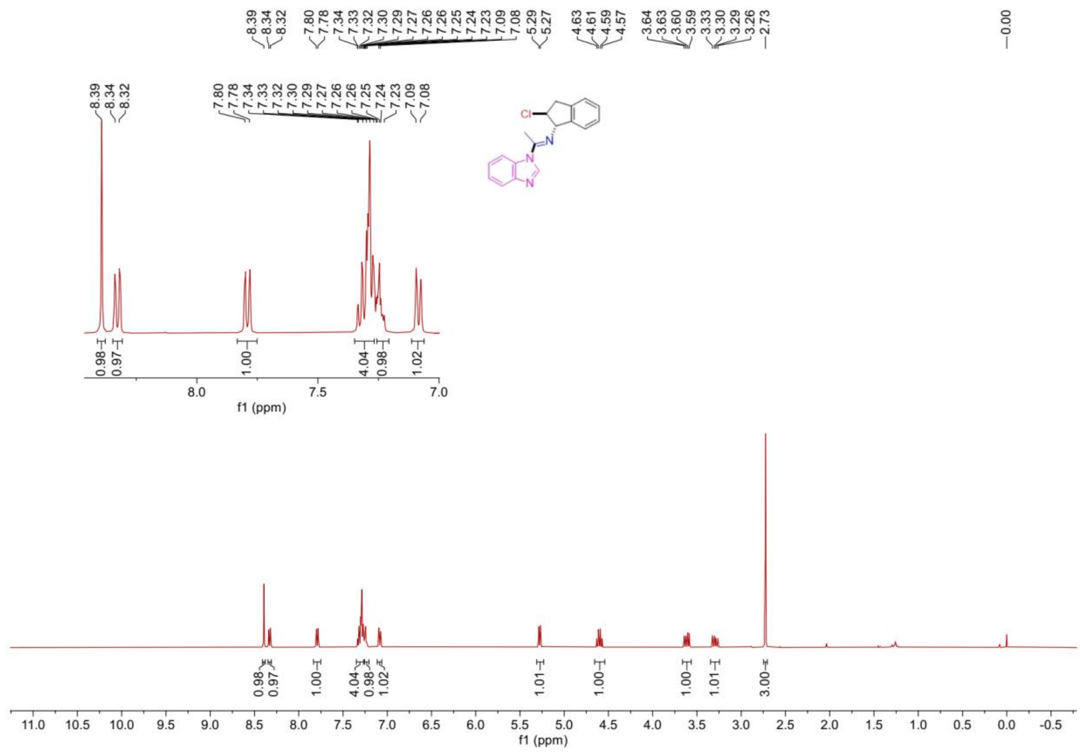
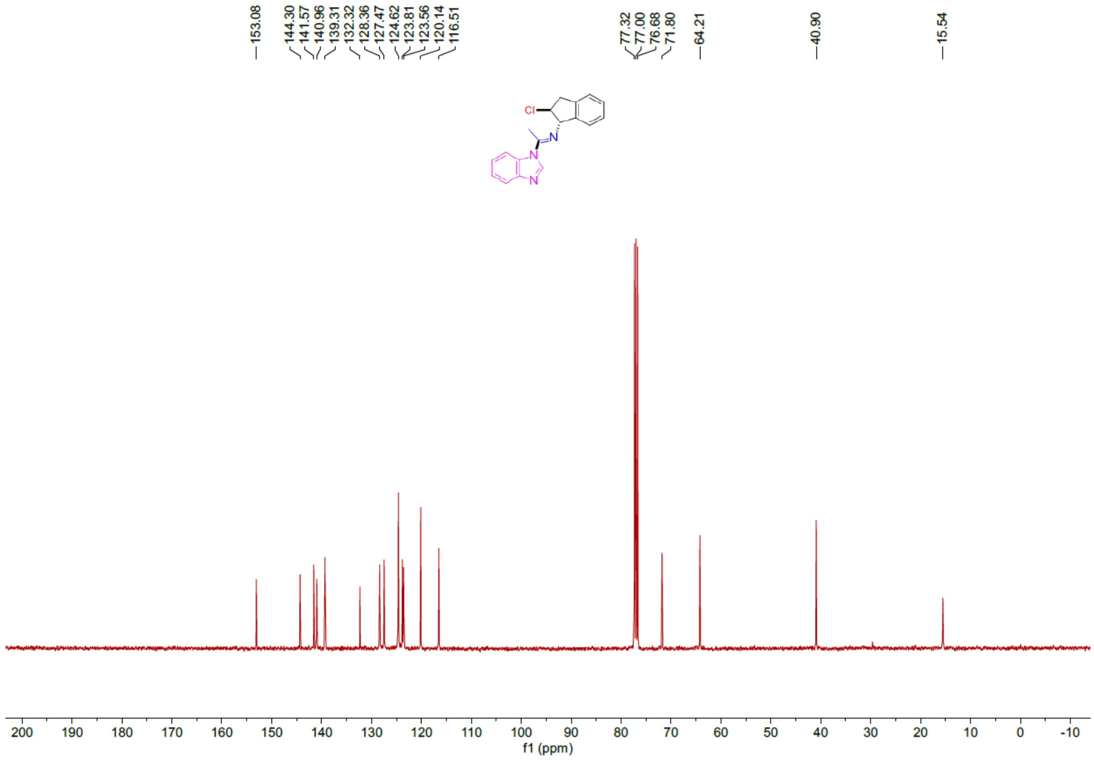


3aq ^{1}H NMR



3aq ^{13}C NMR



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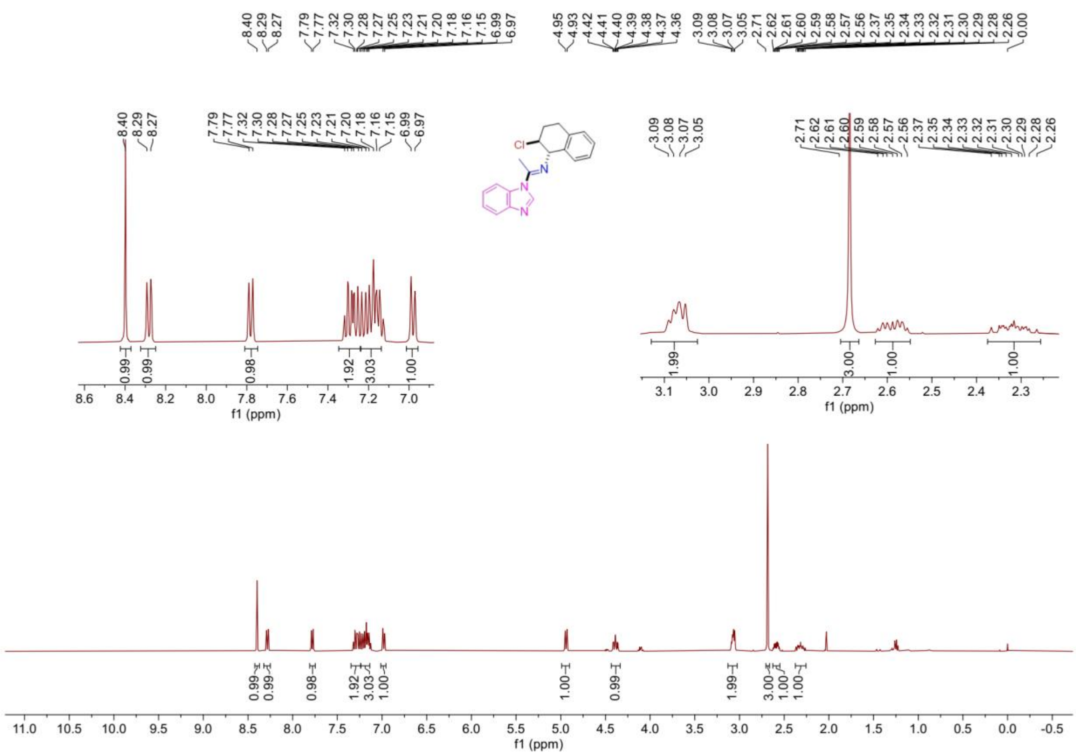

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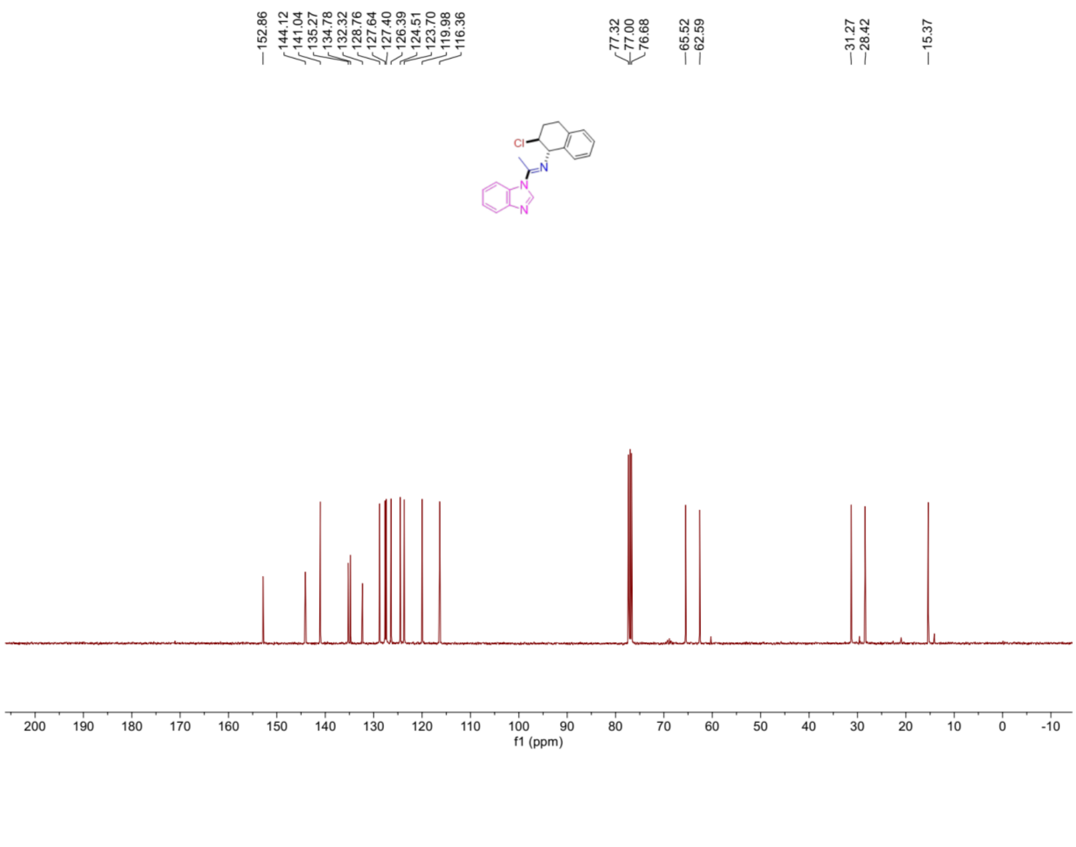

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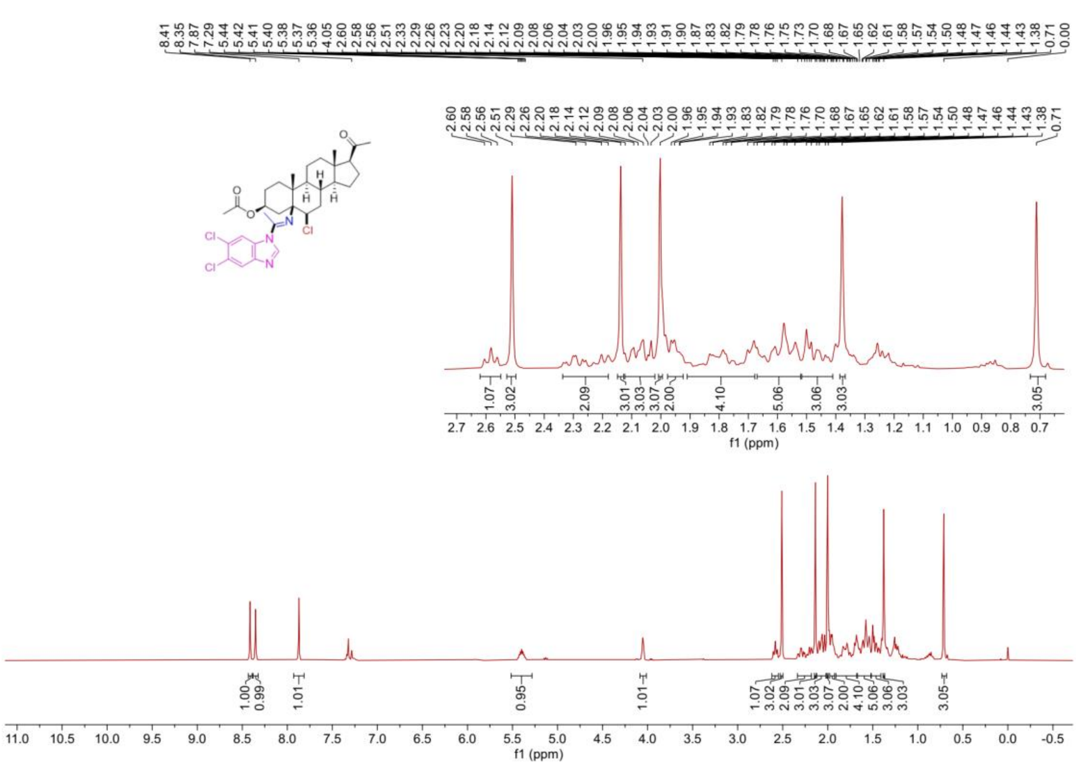

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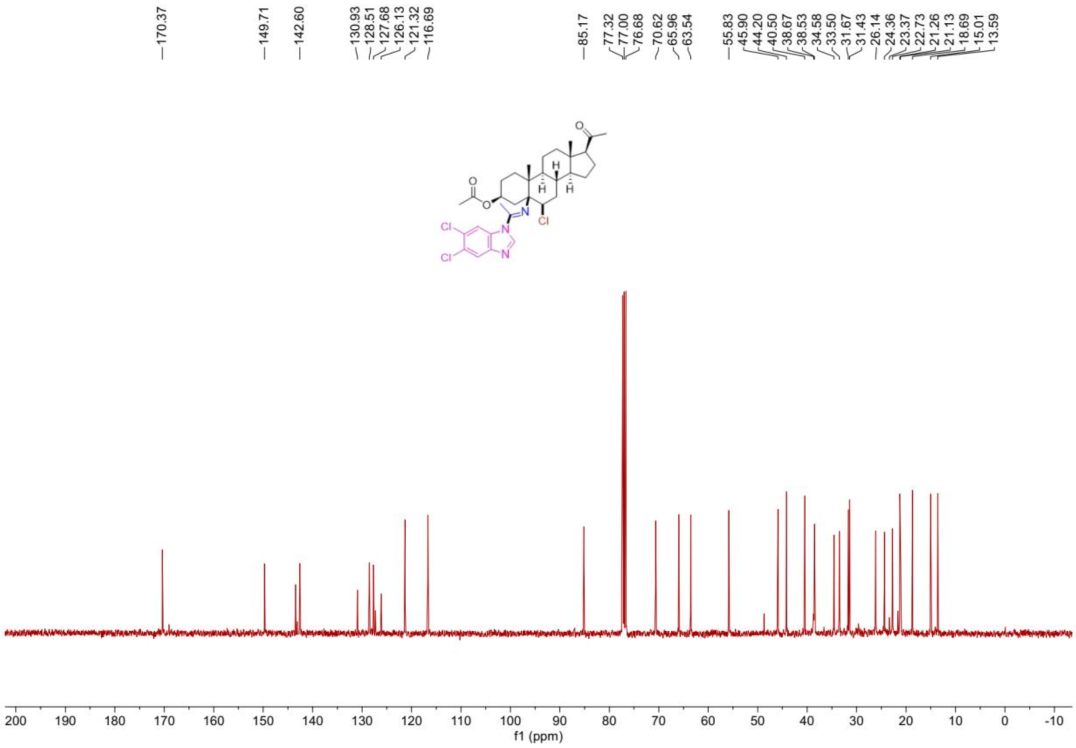

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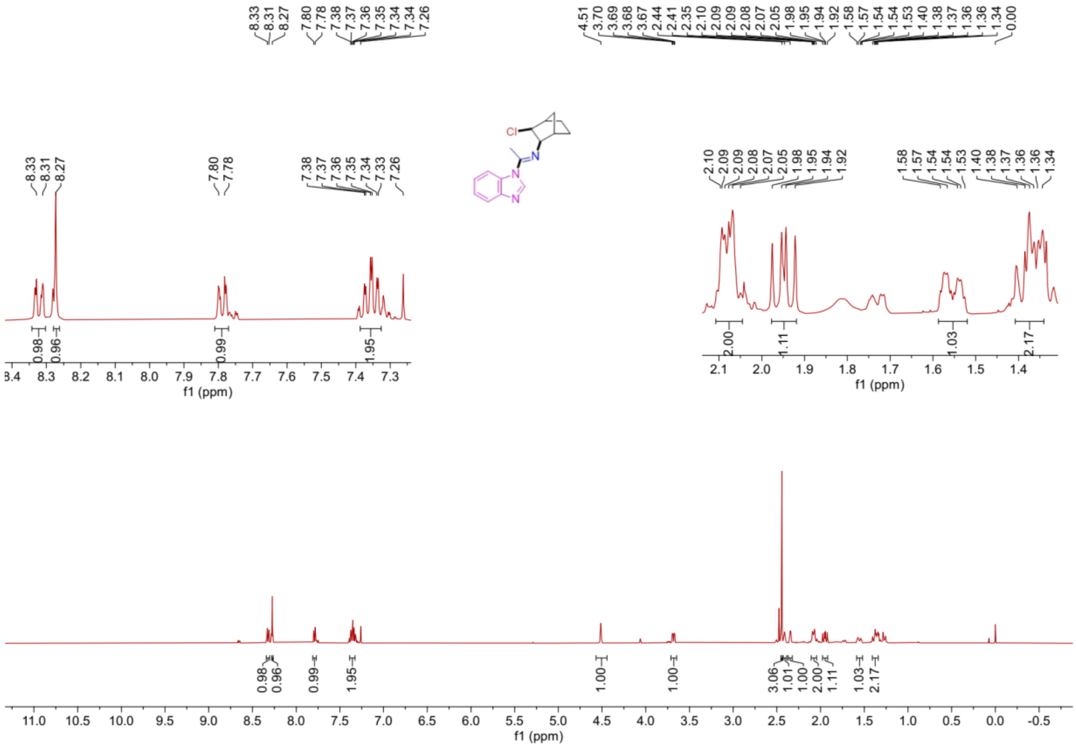

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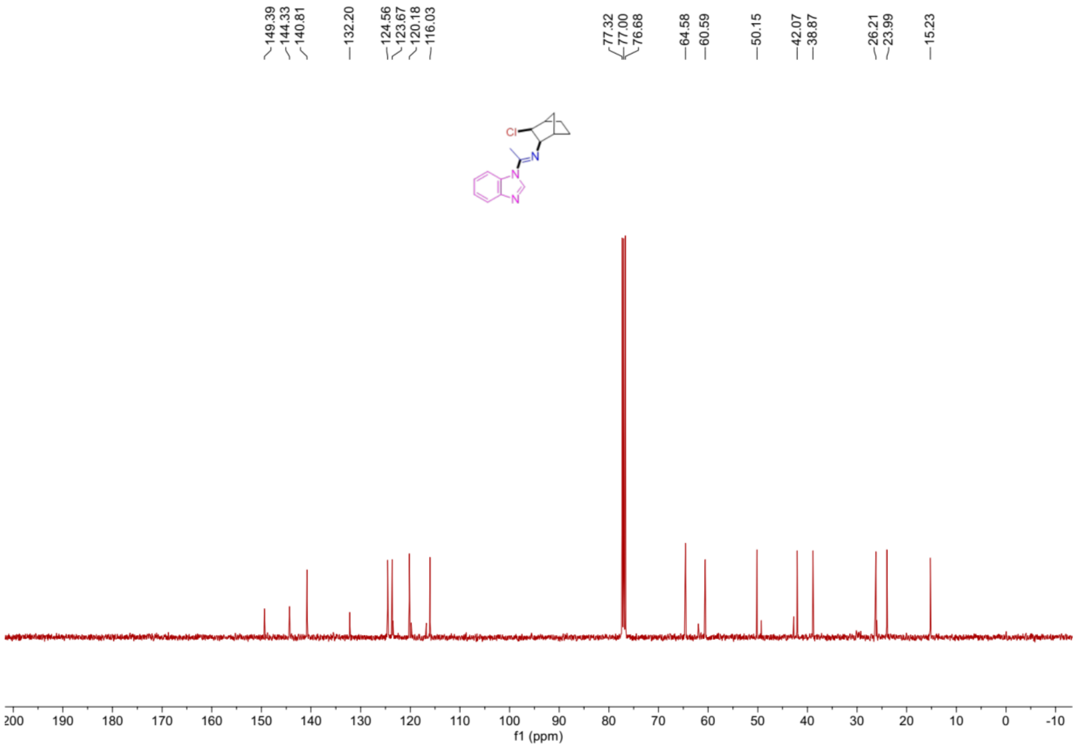

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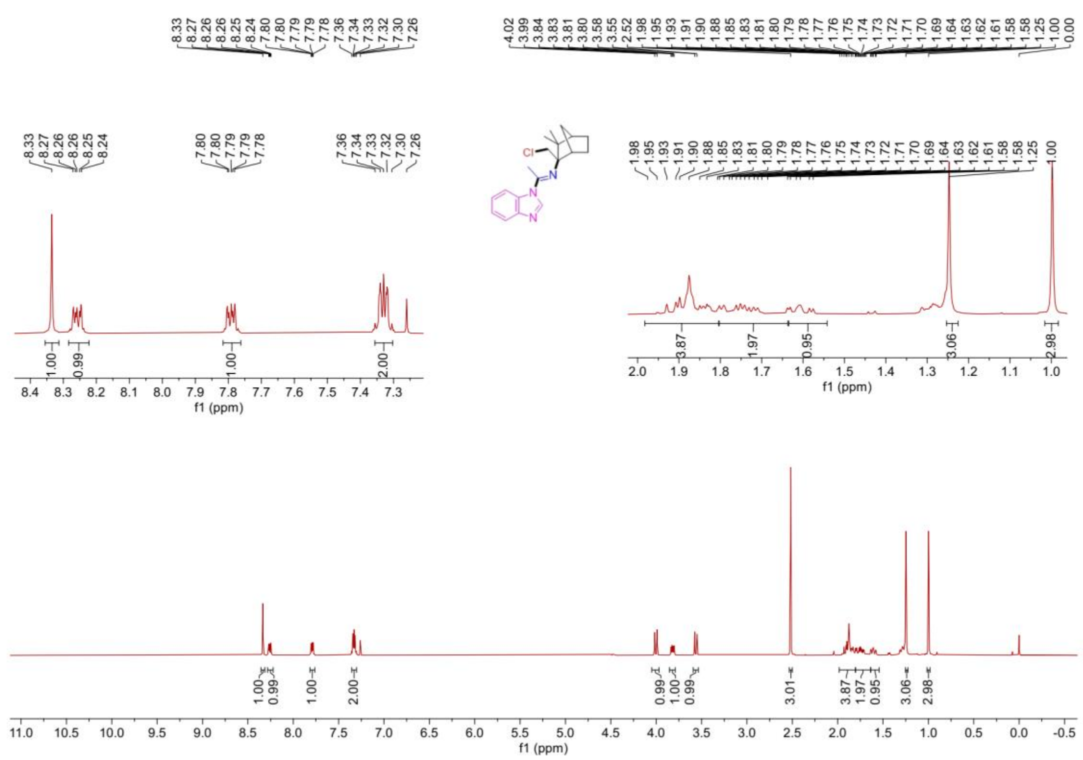

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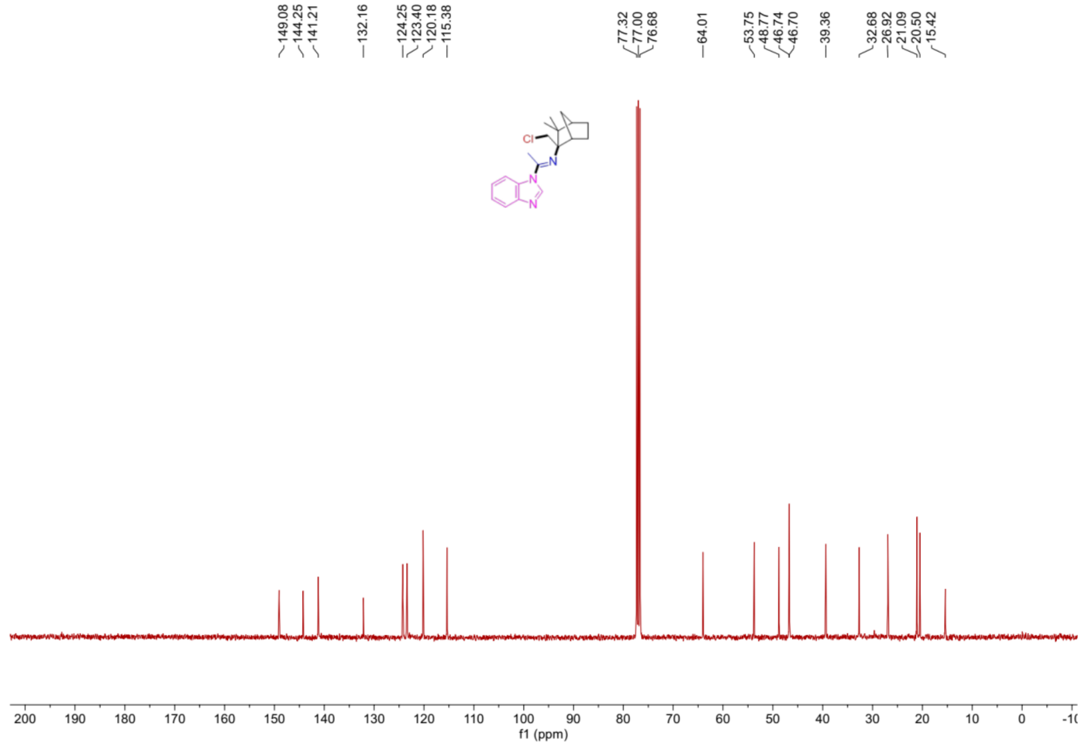

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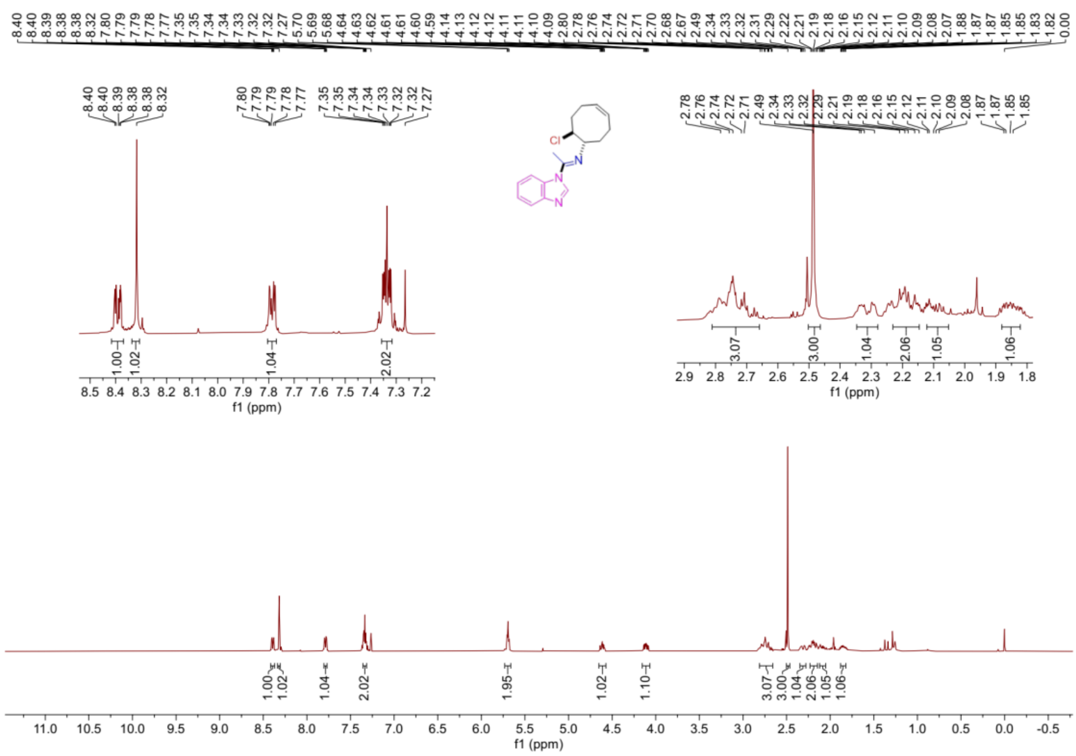

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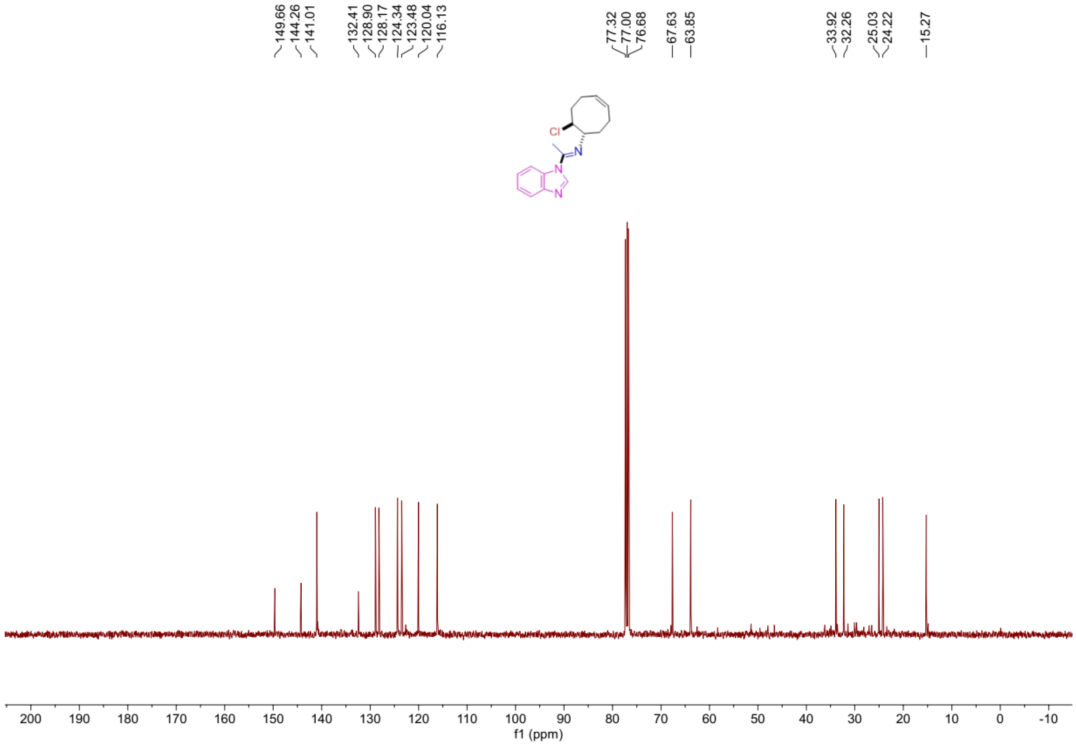

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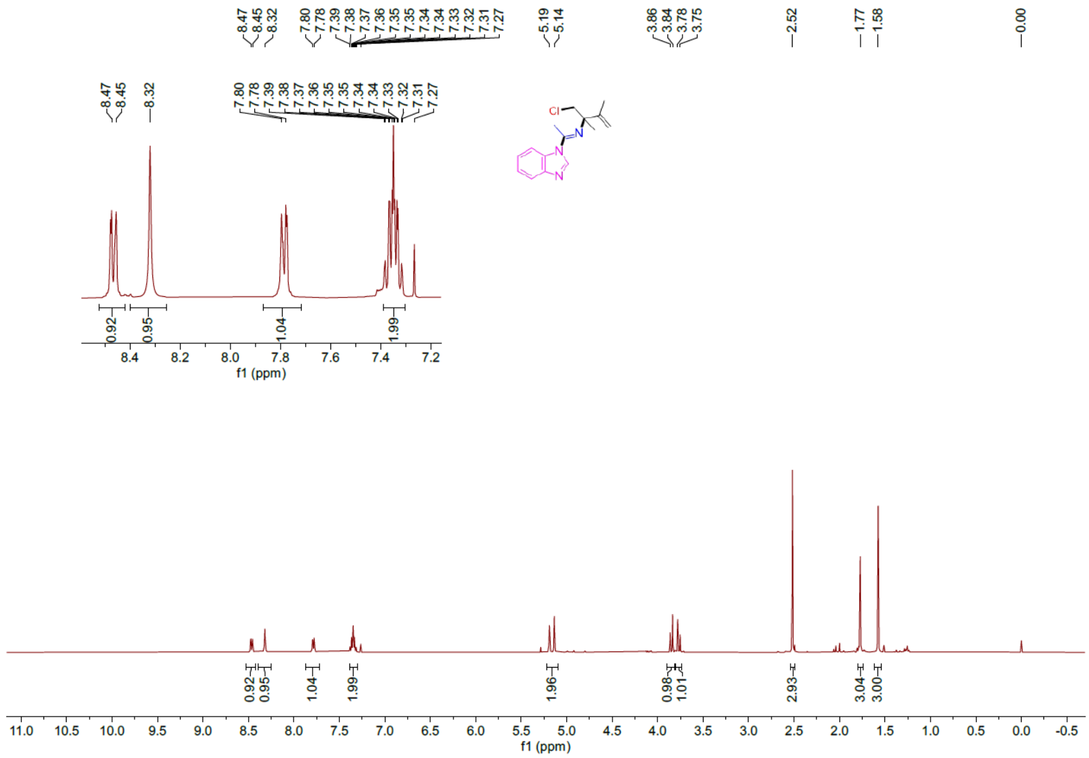

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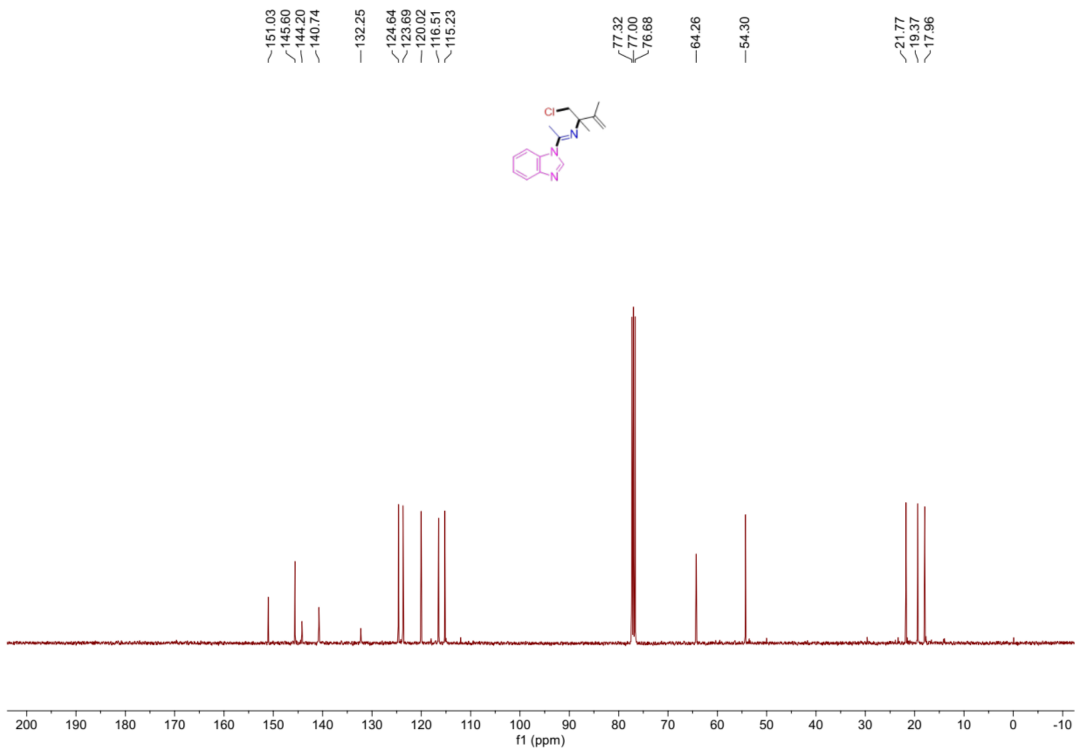

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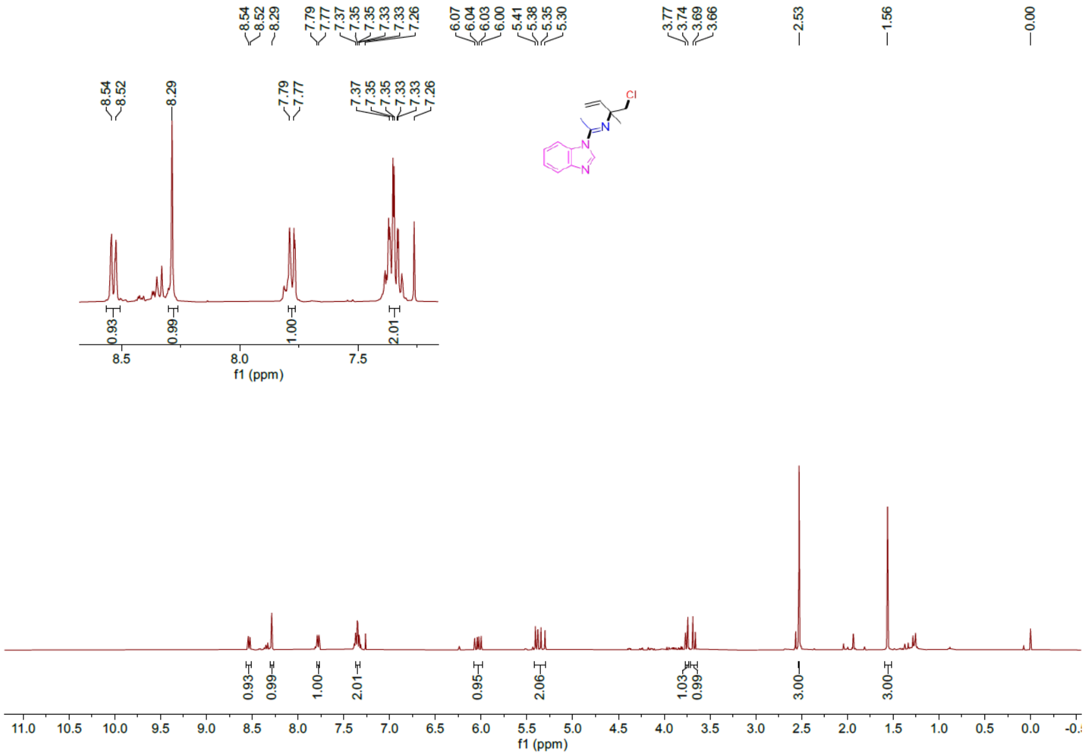

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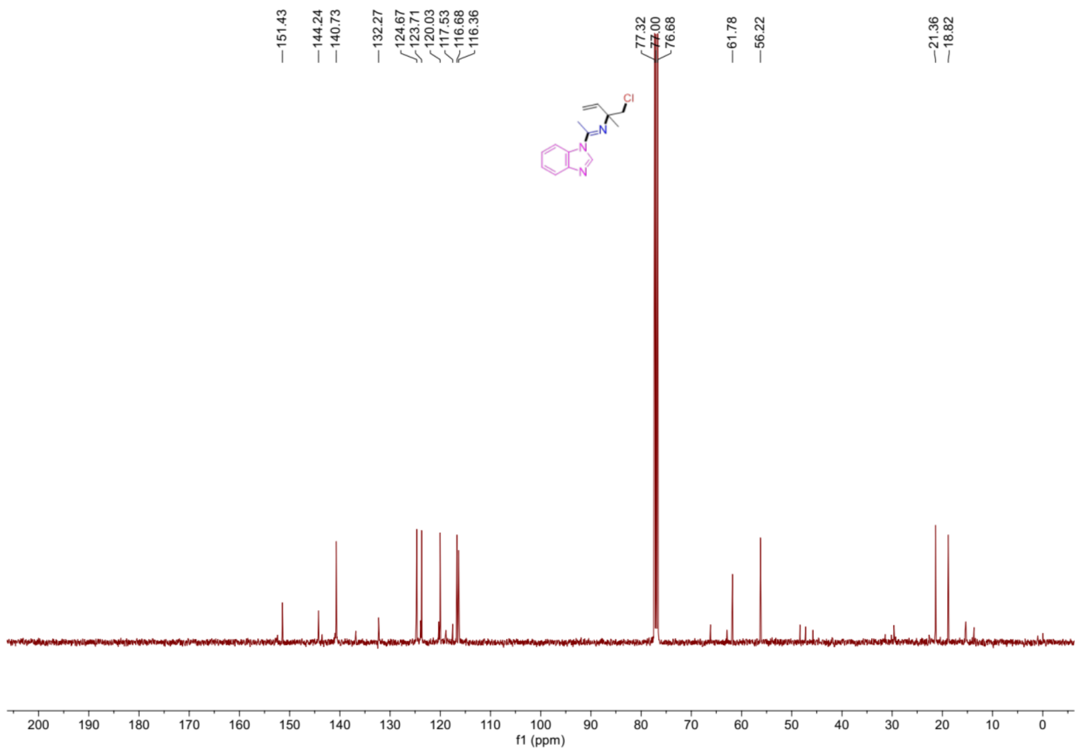

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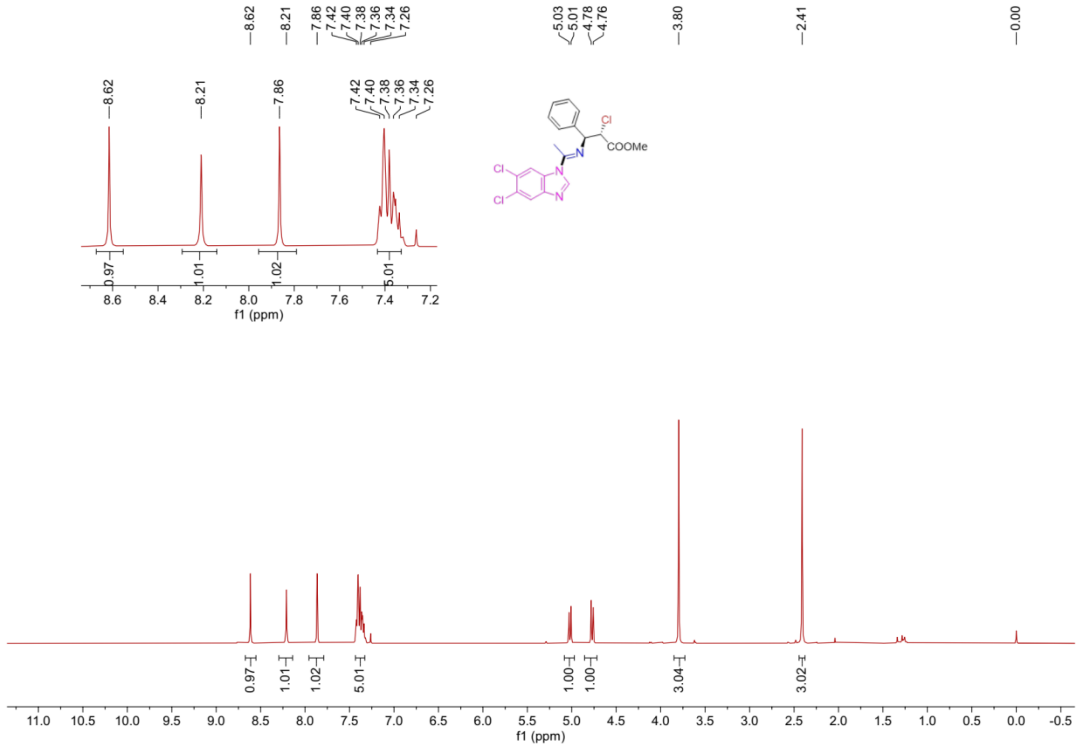

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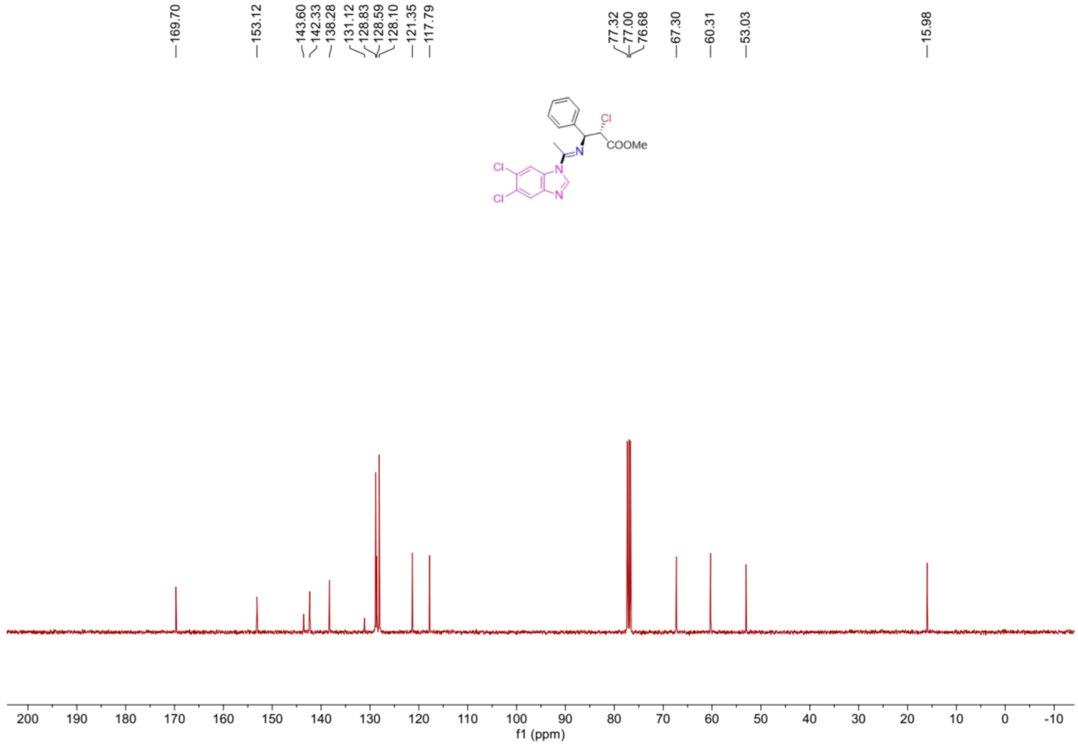

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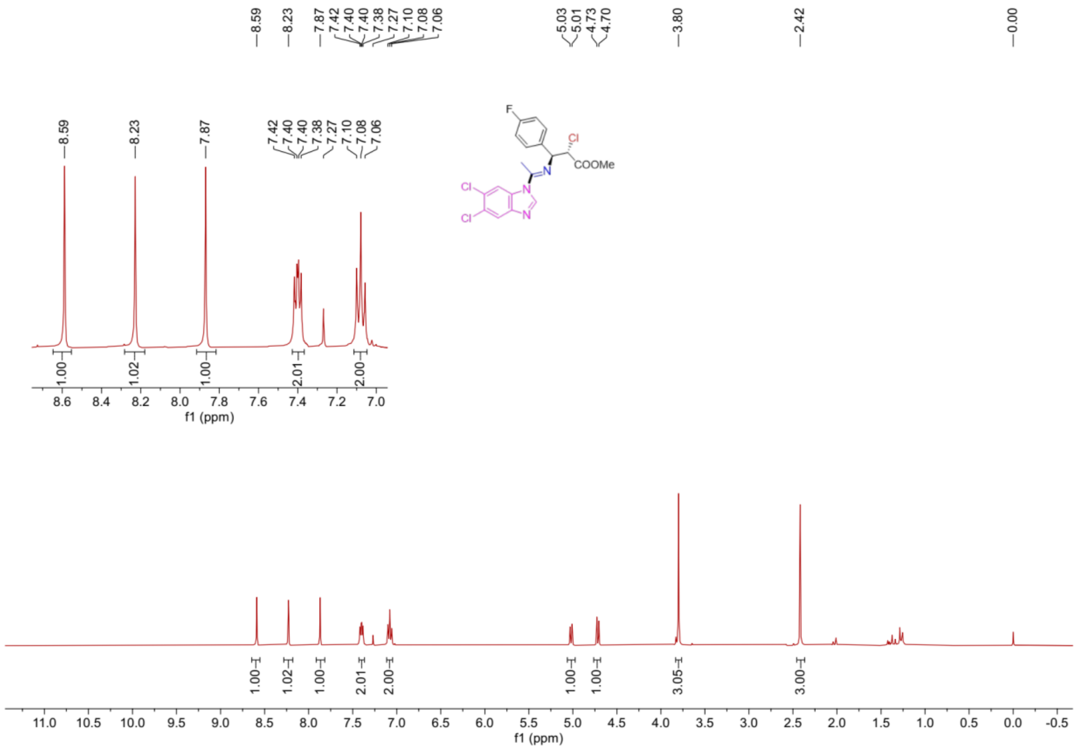

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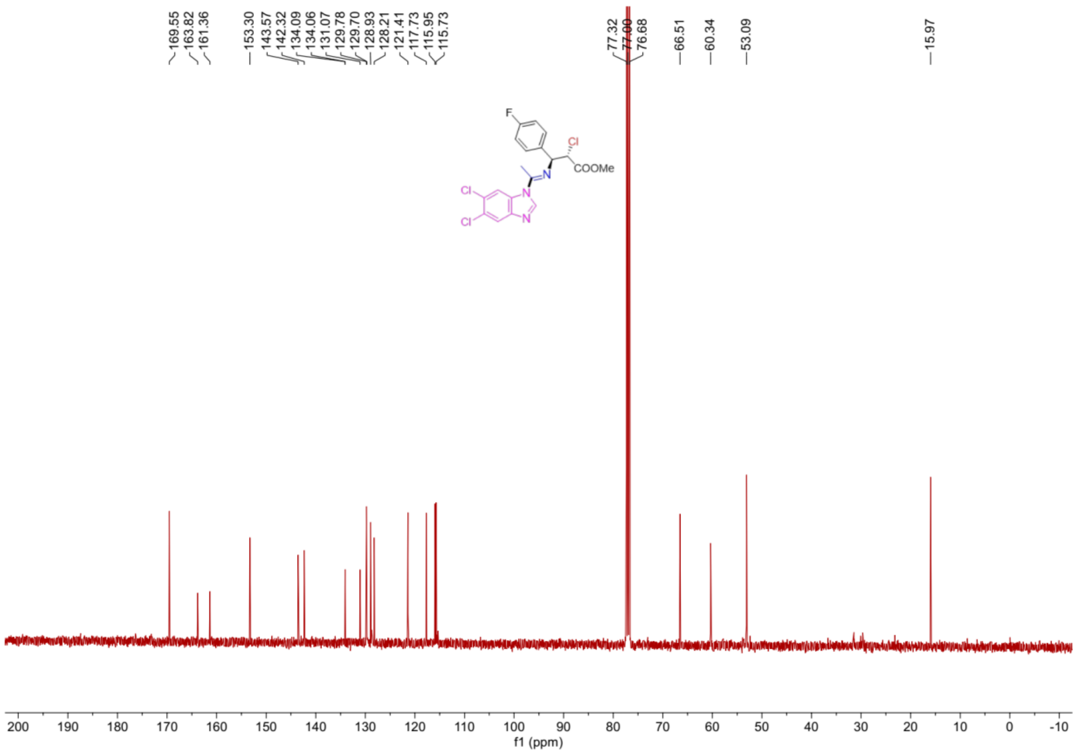
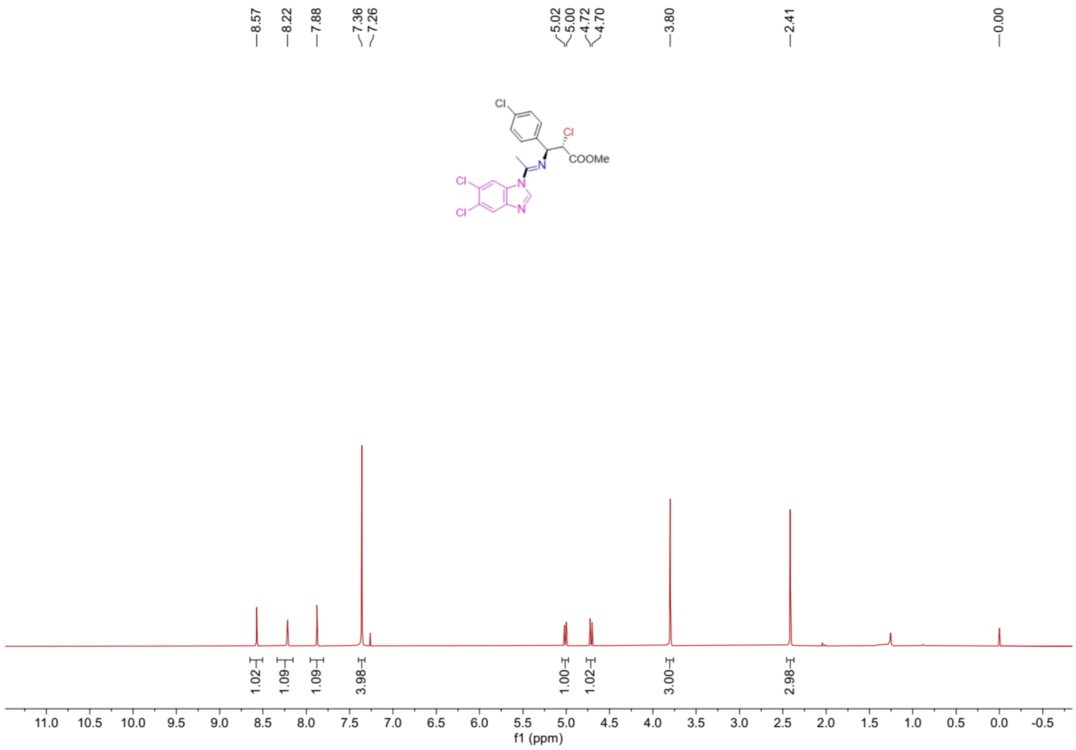


3ba ^{1}H NMR



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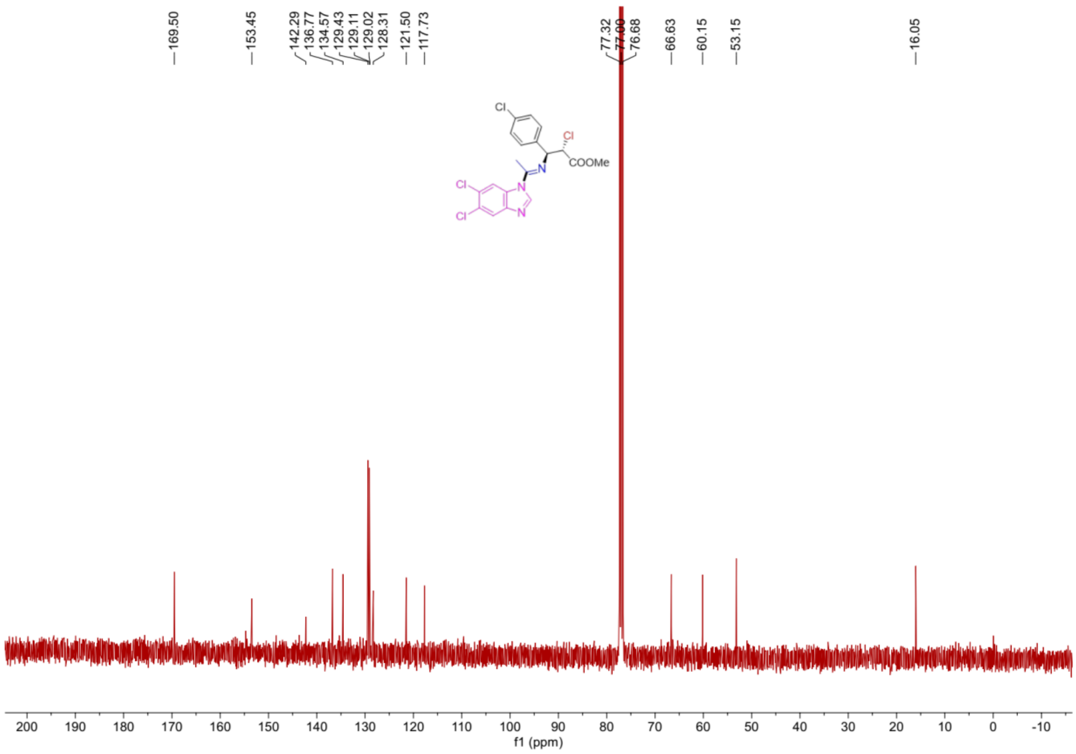

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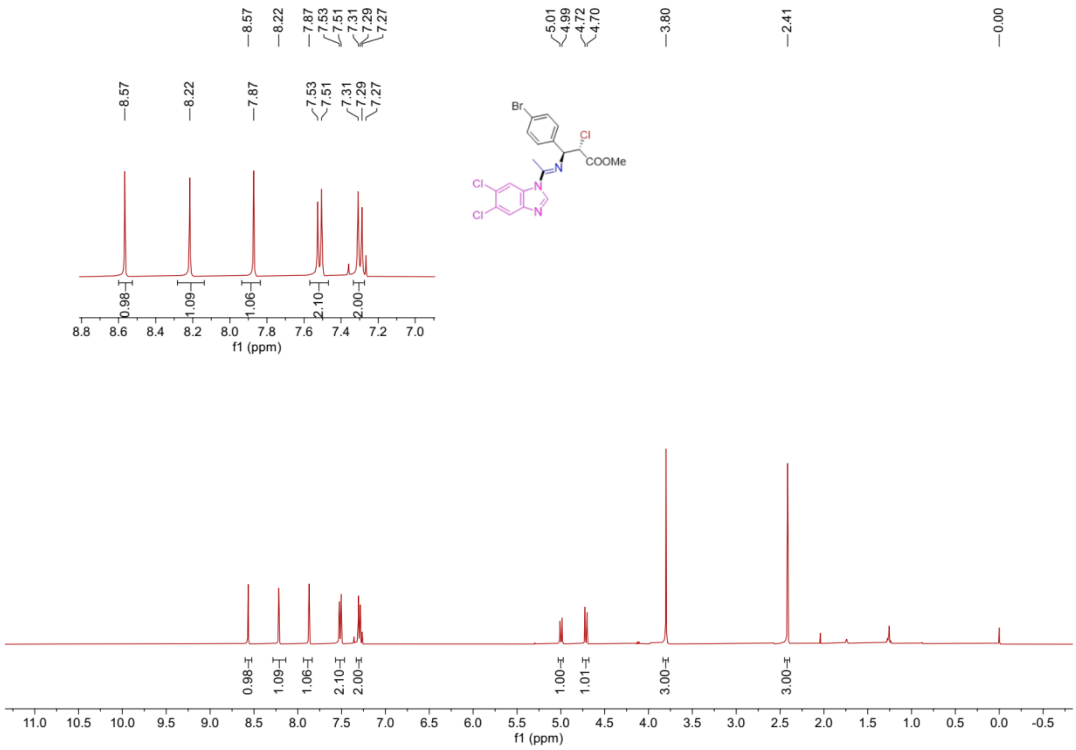

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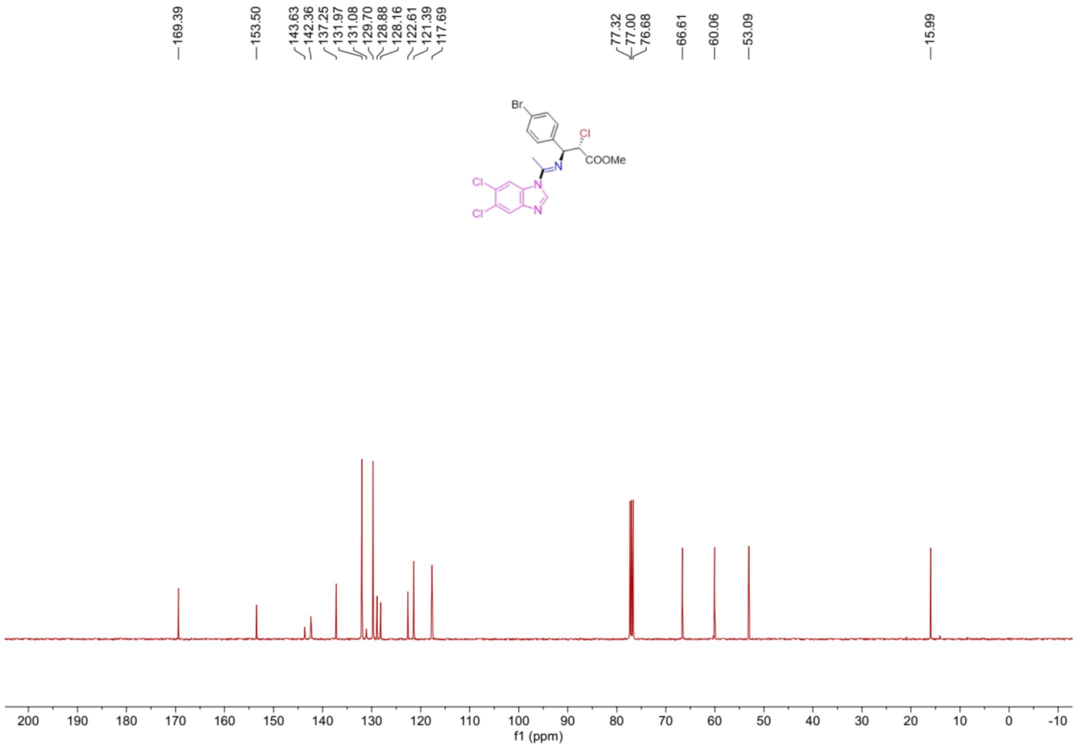

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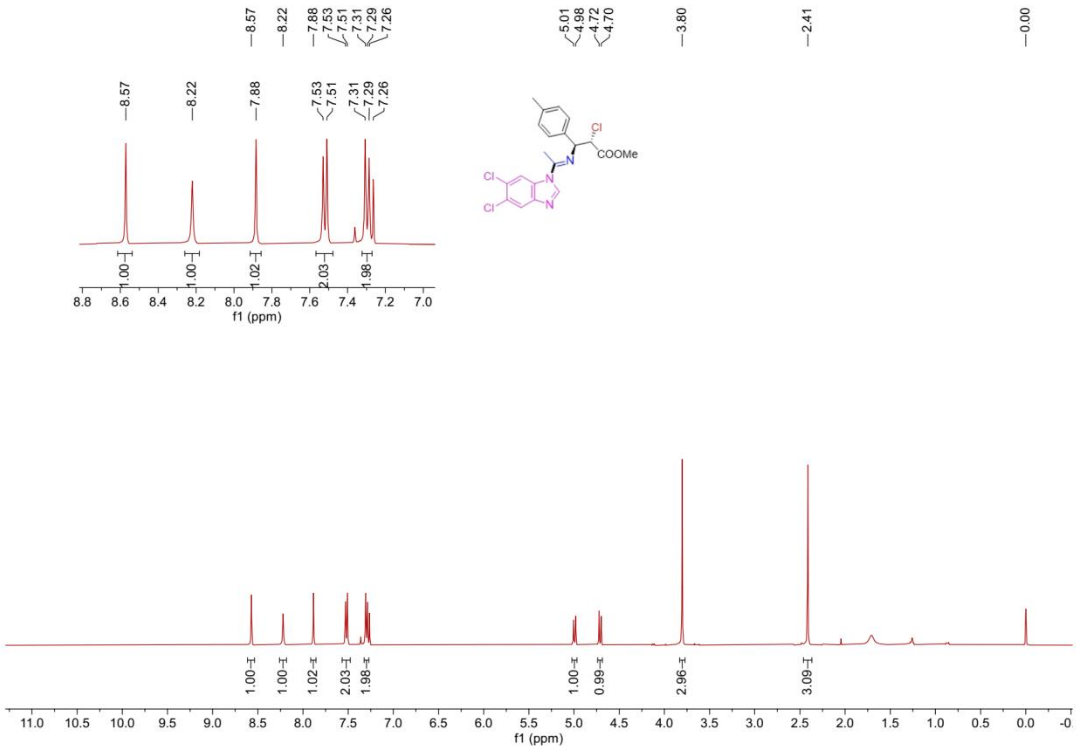

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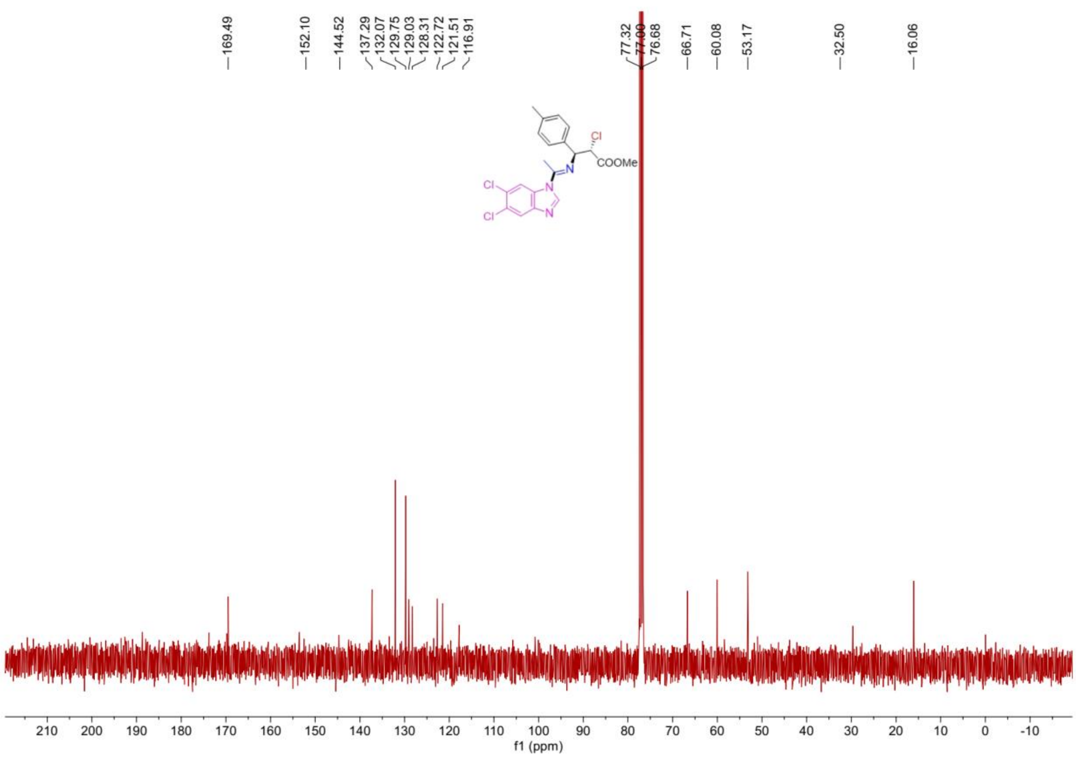

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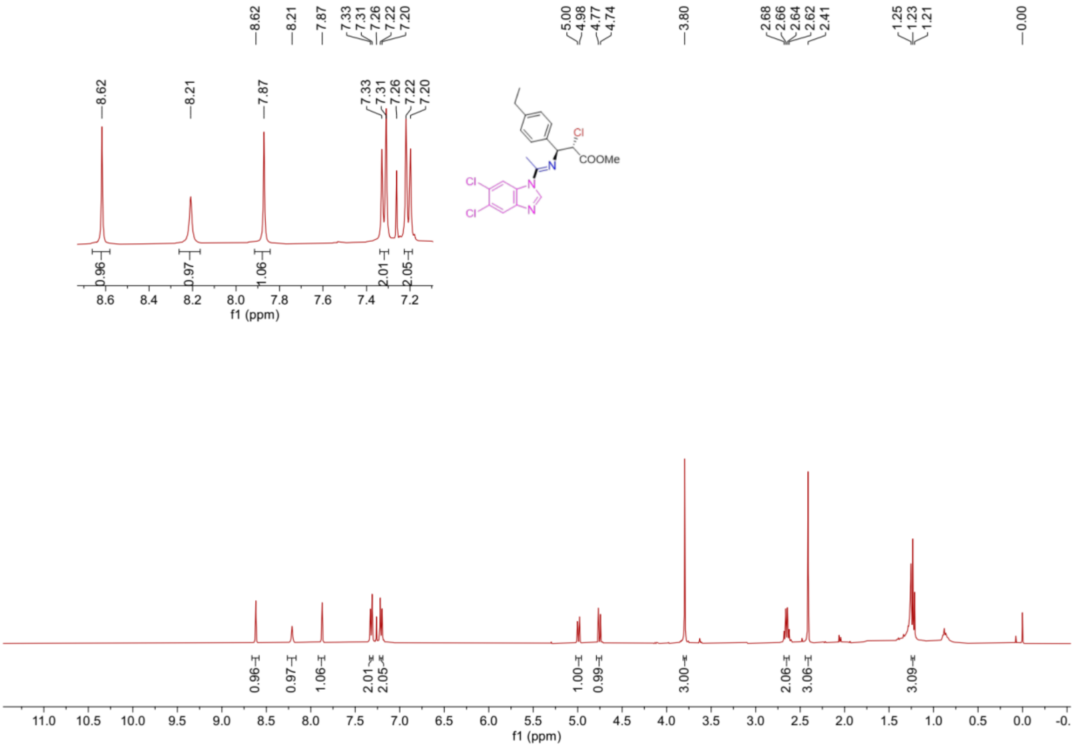

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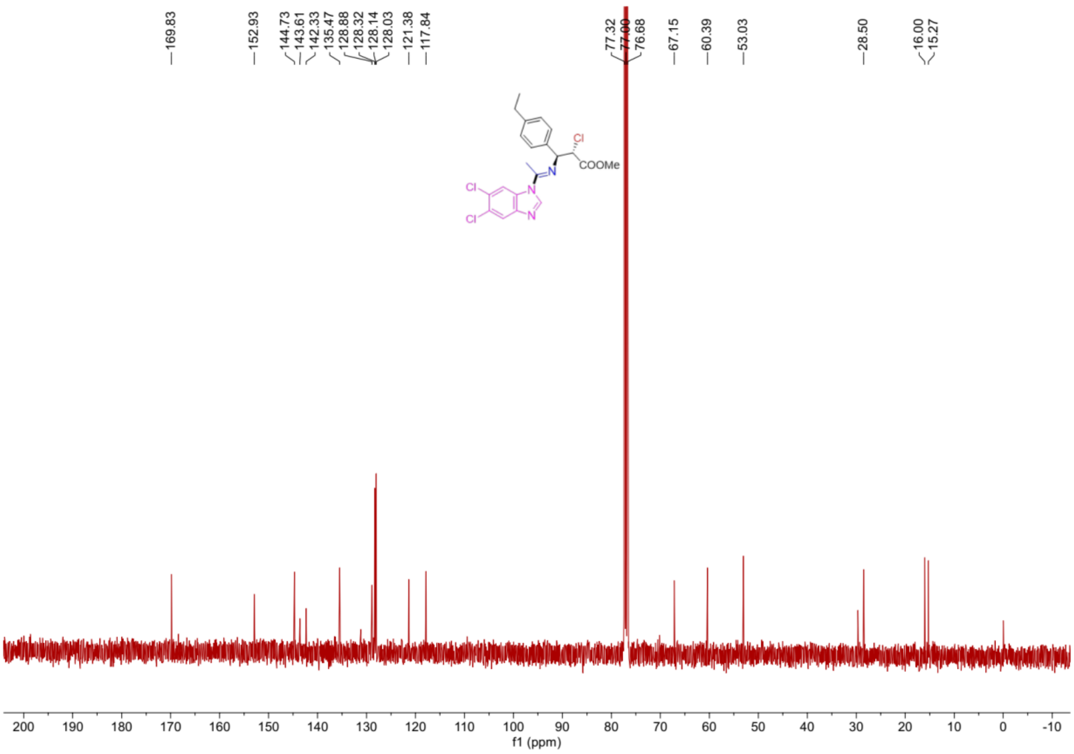

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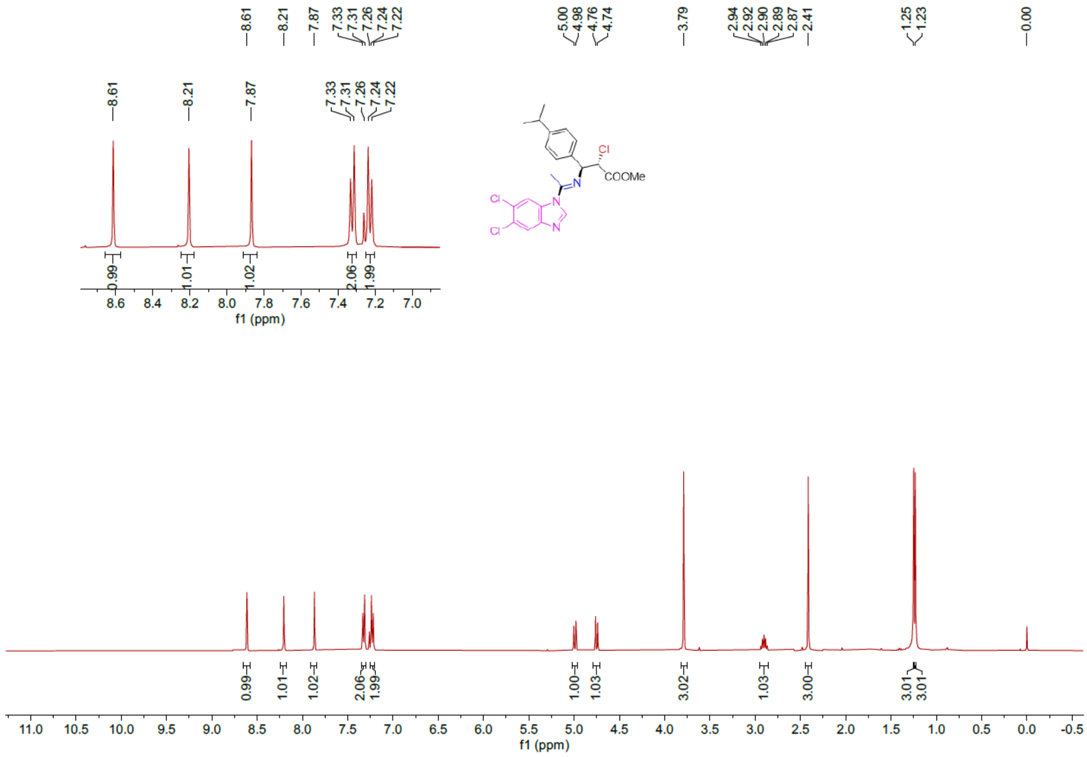

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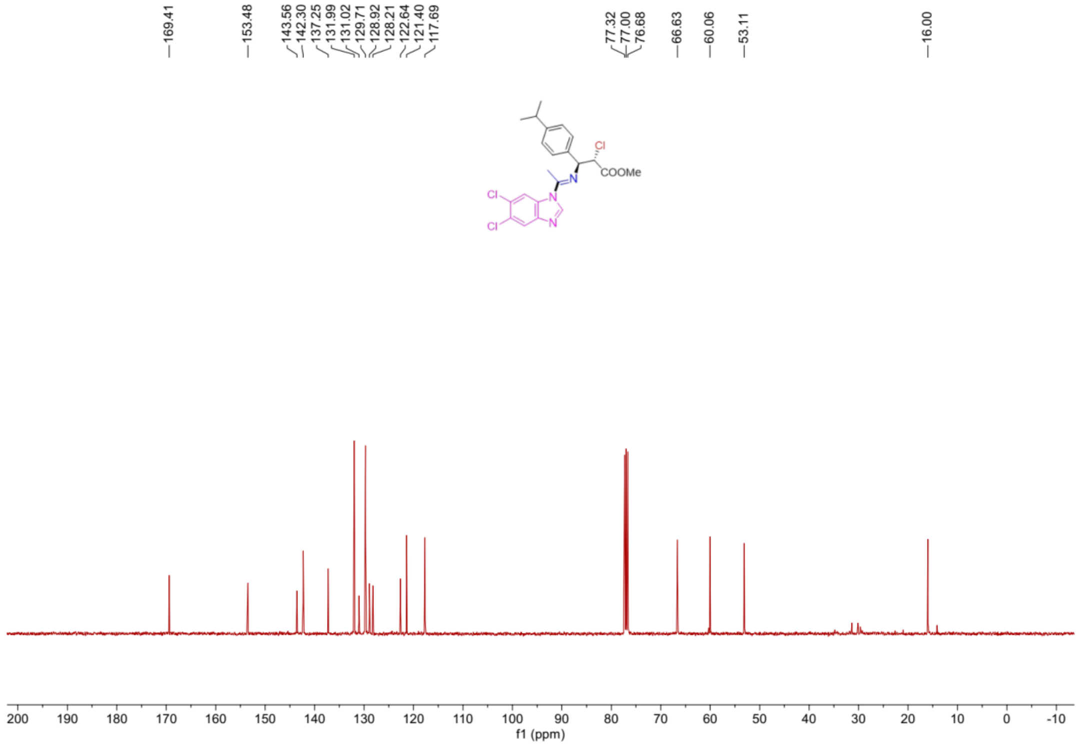

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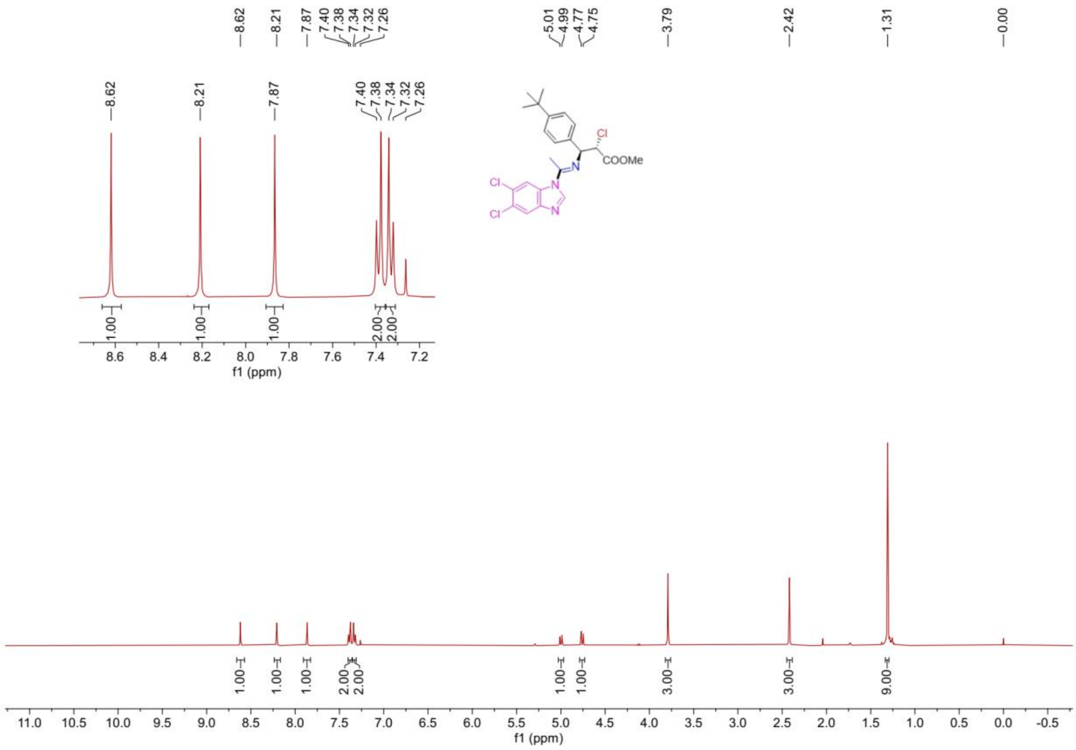

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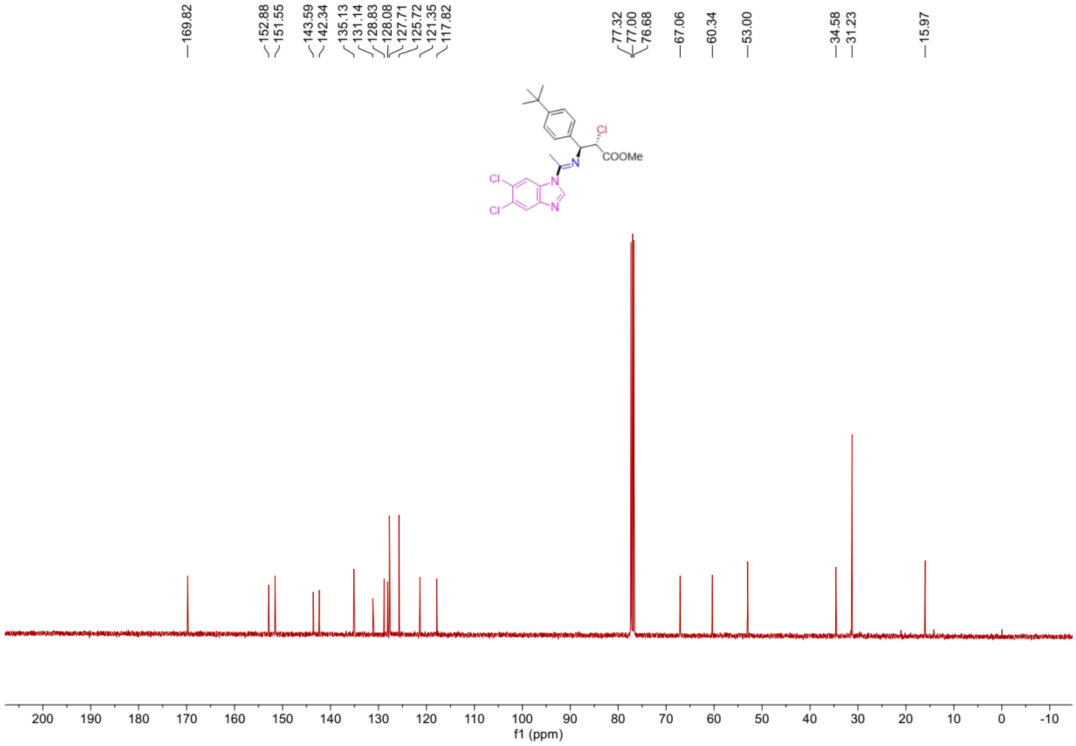

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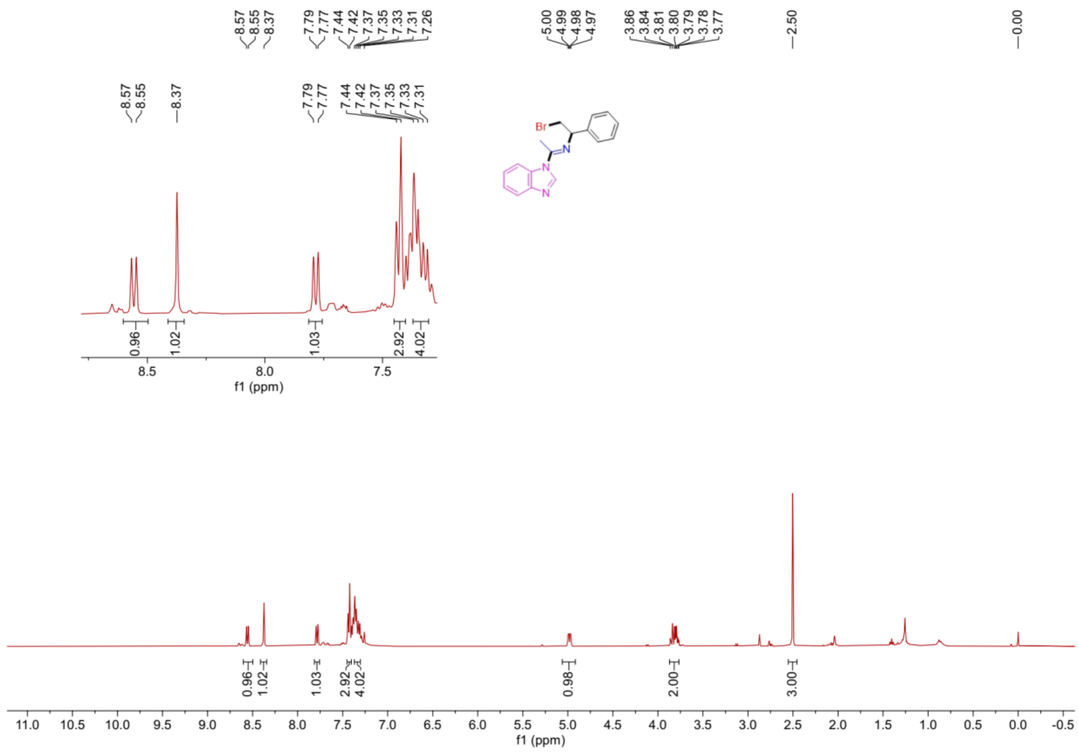

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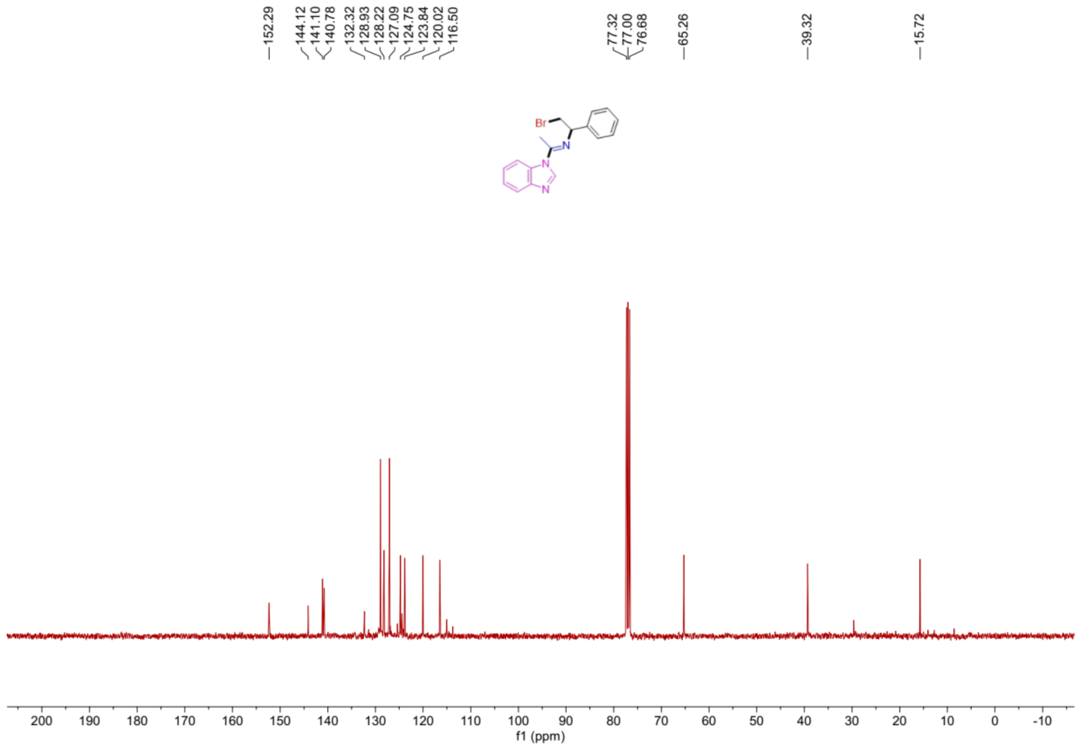

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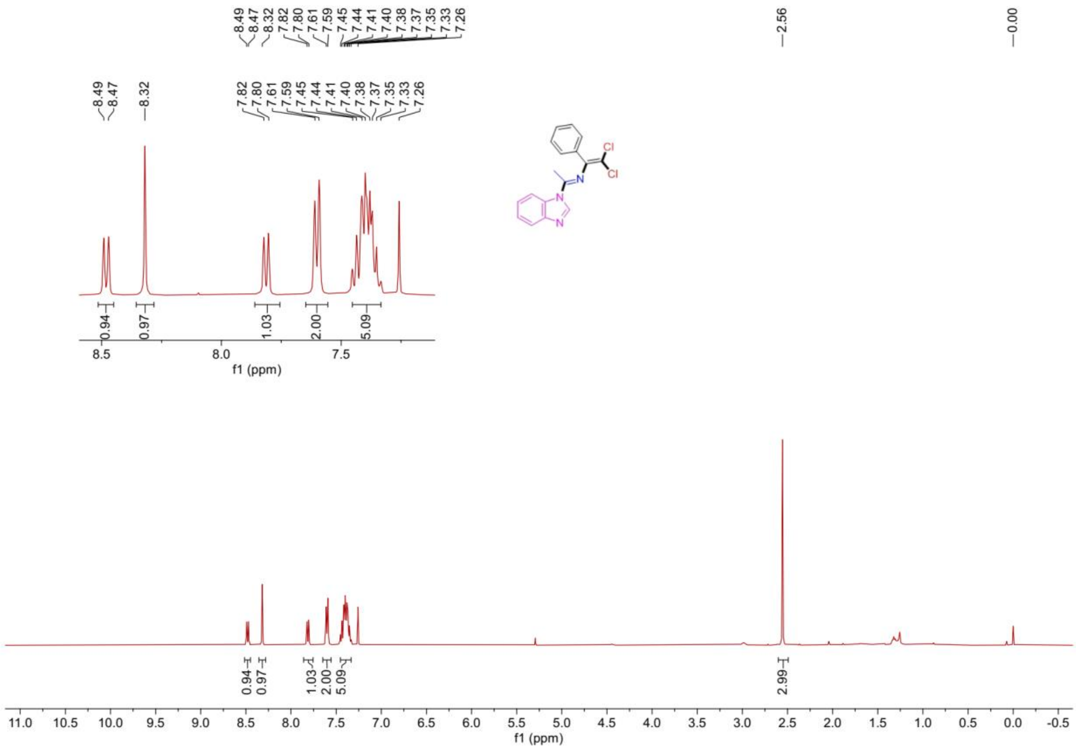

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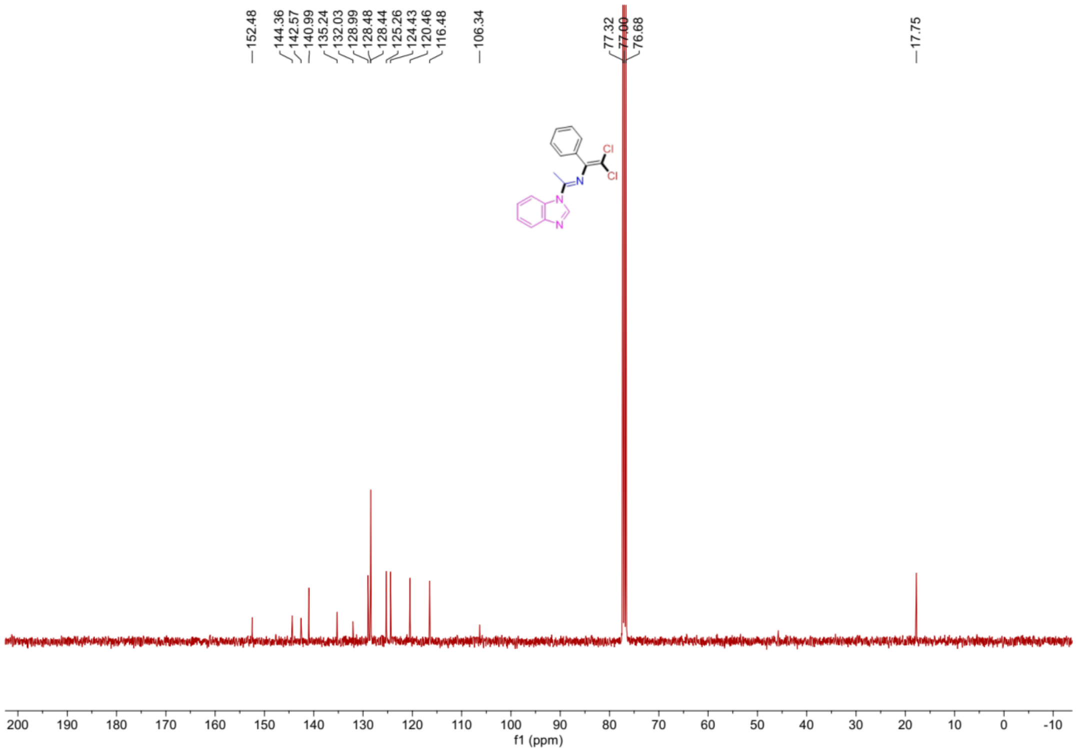

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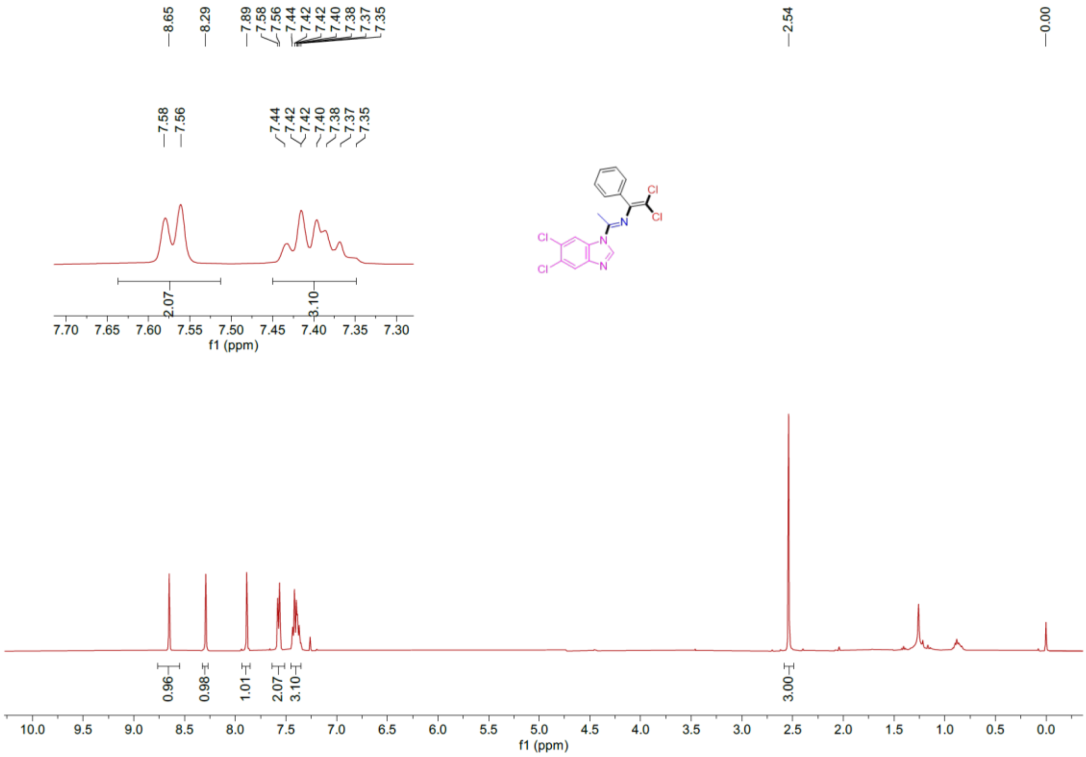

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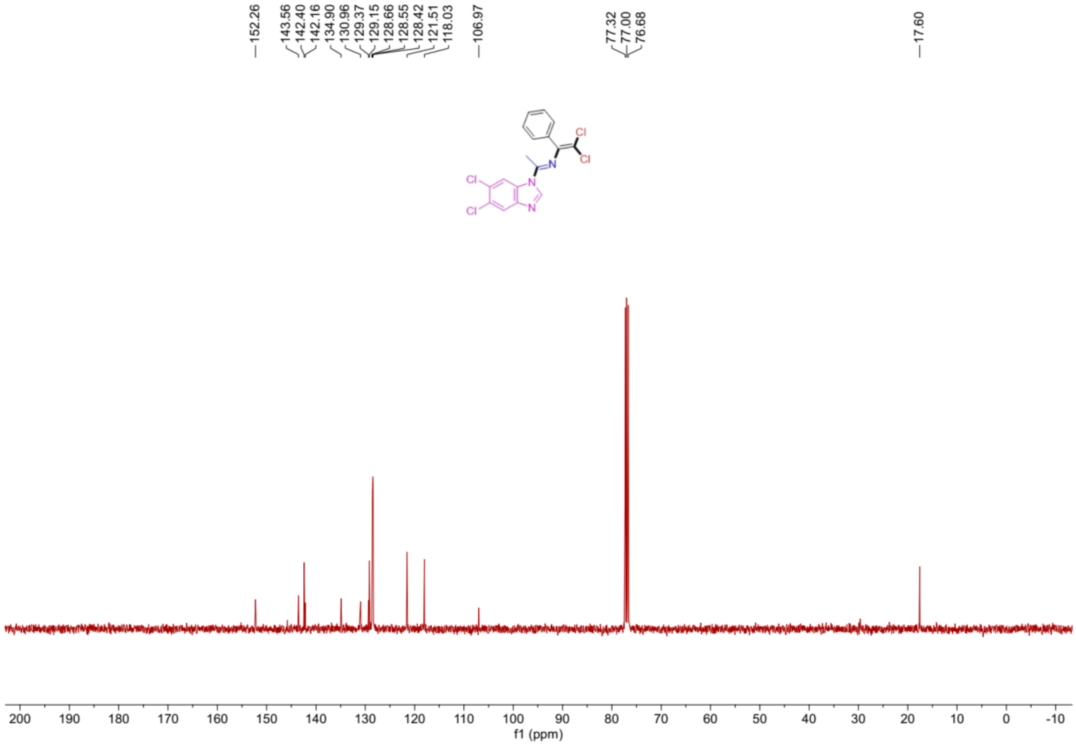

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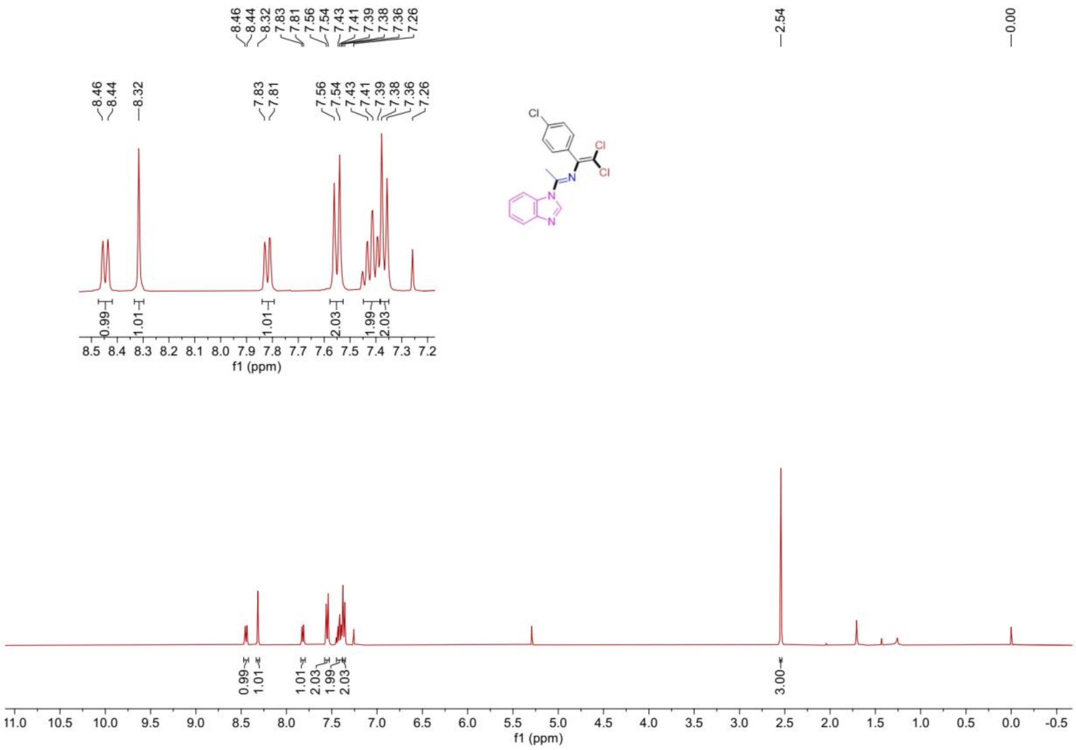

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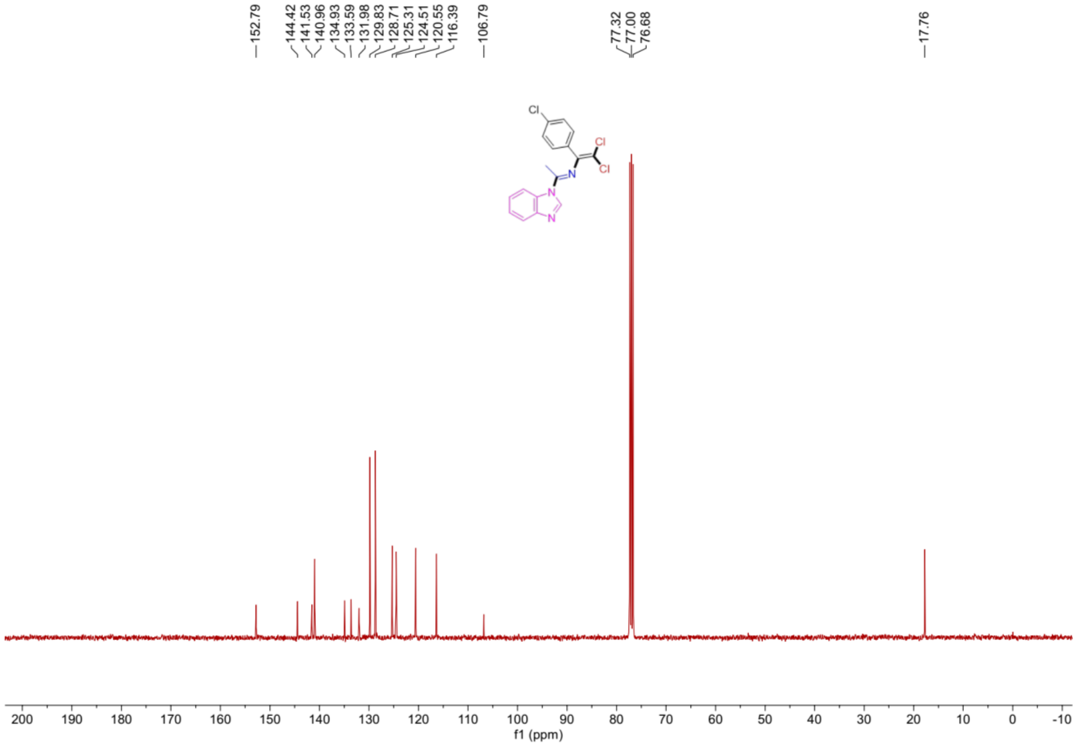

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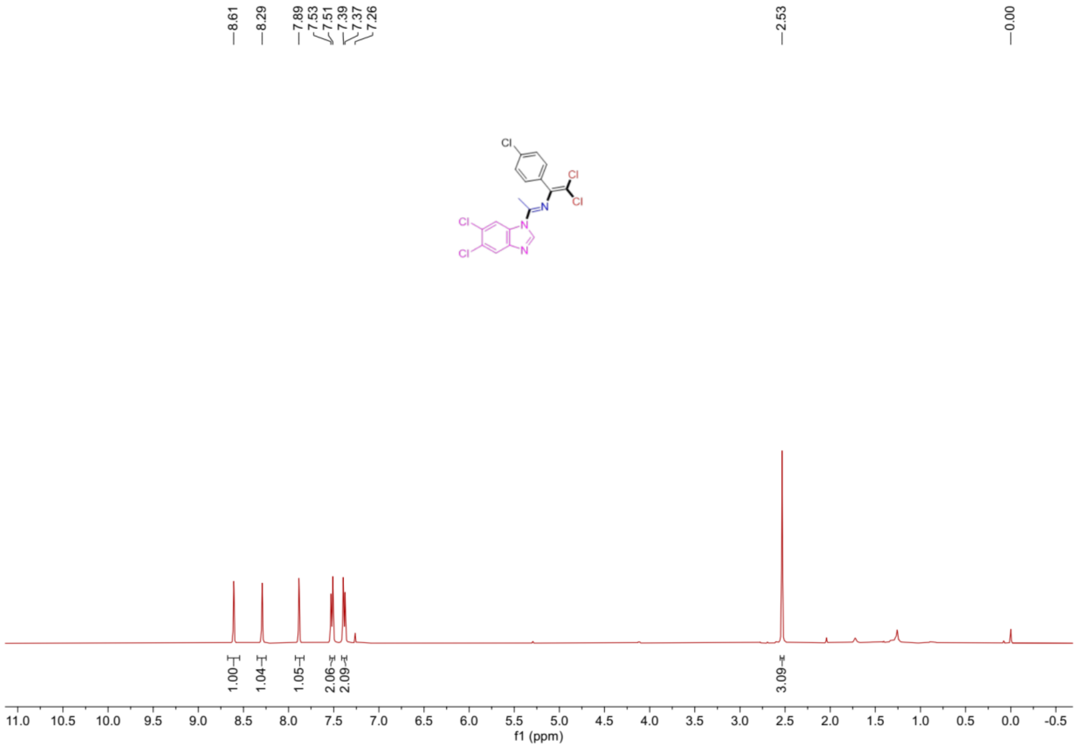

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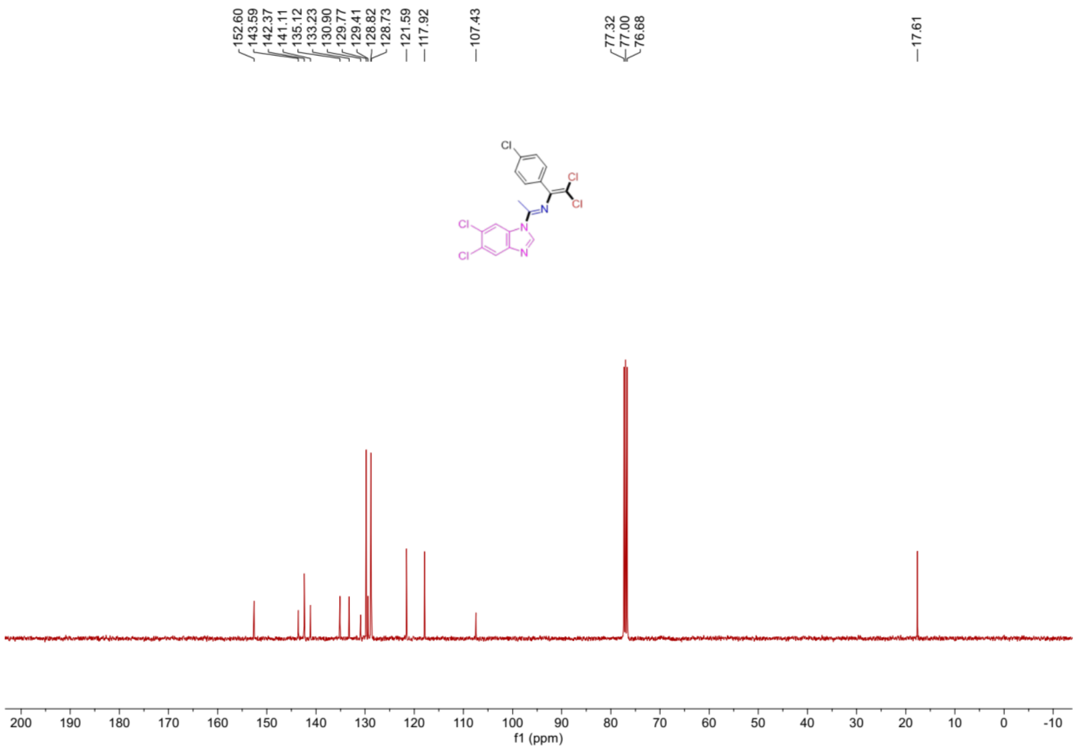

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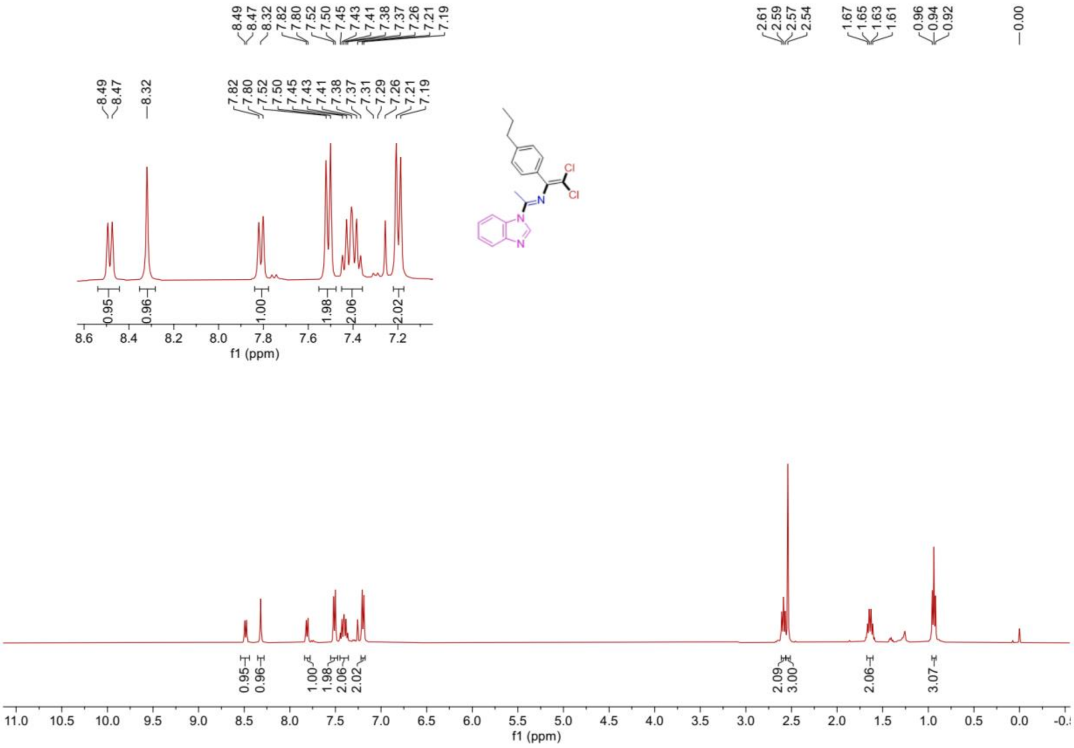

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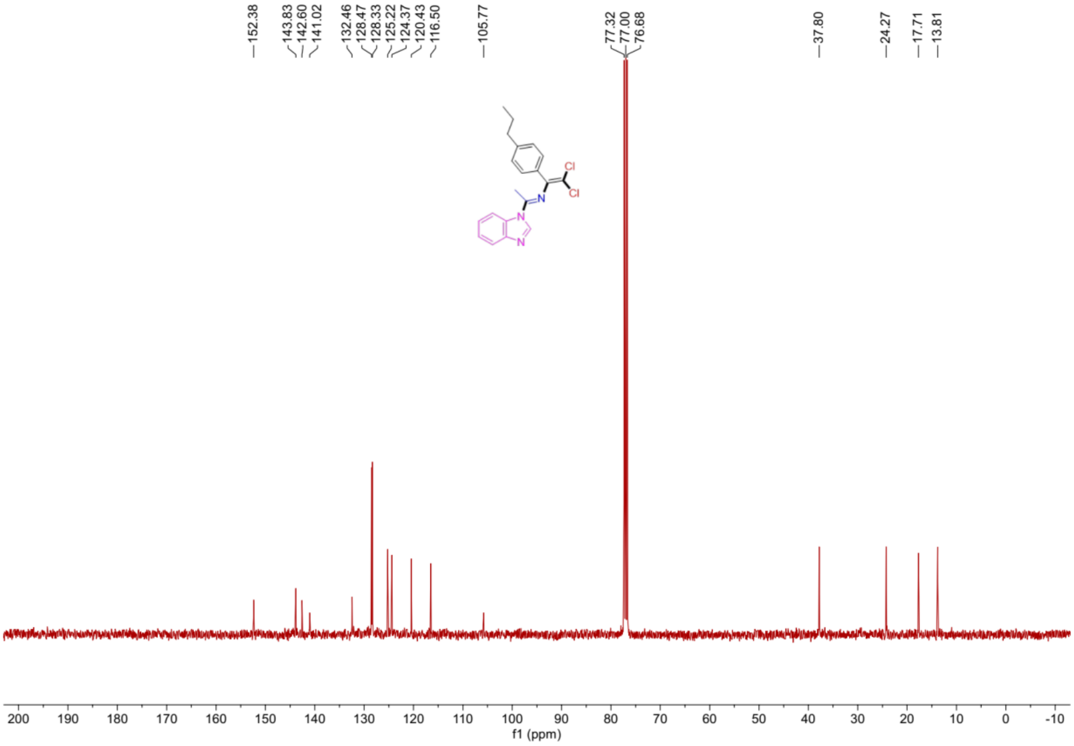

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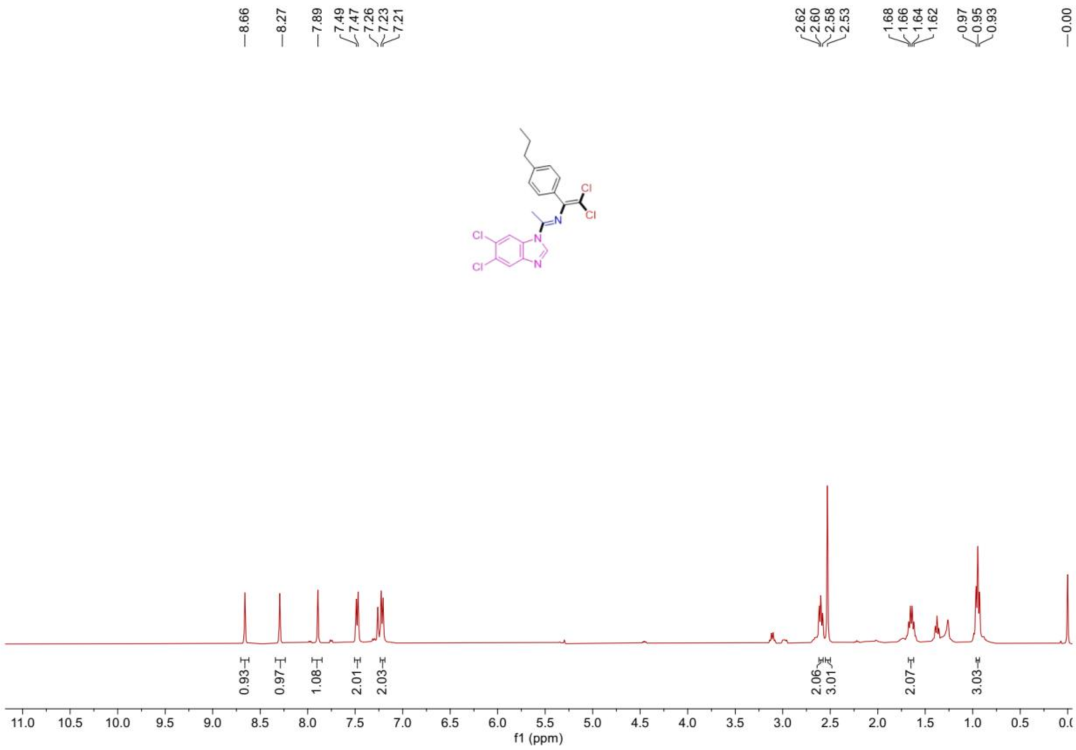

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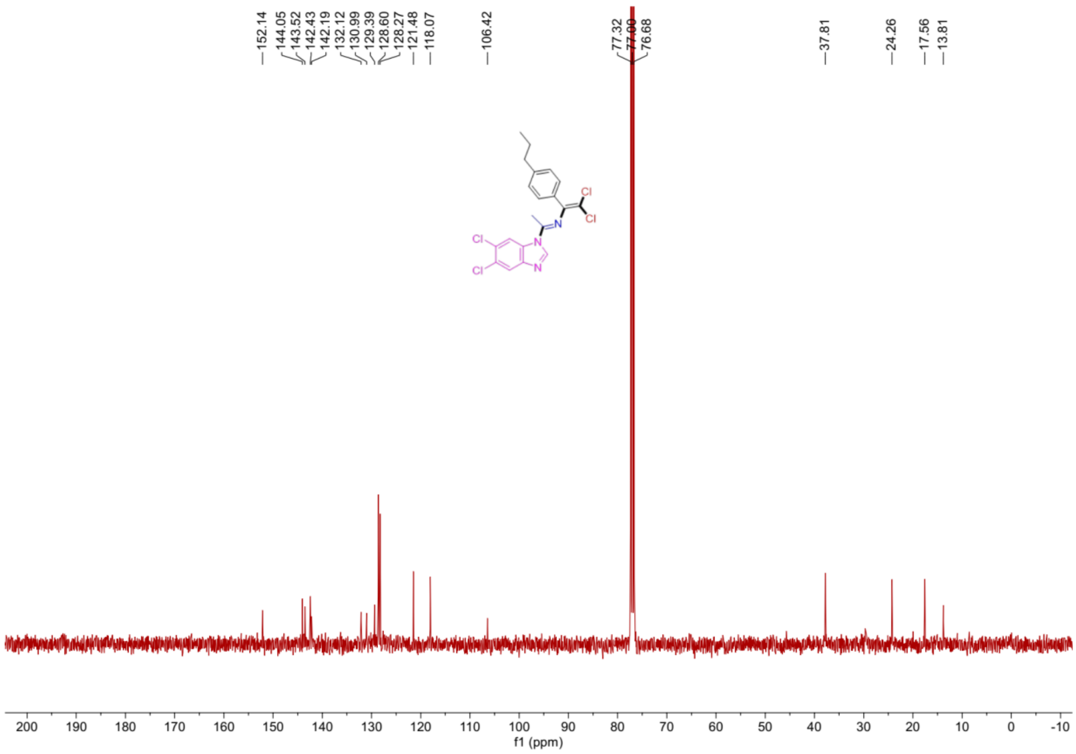

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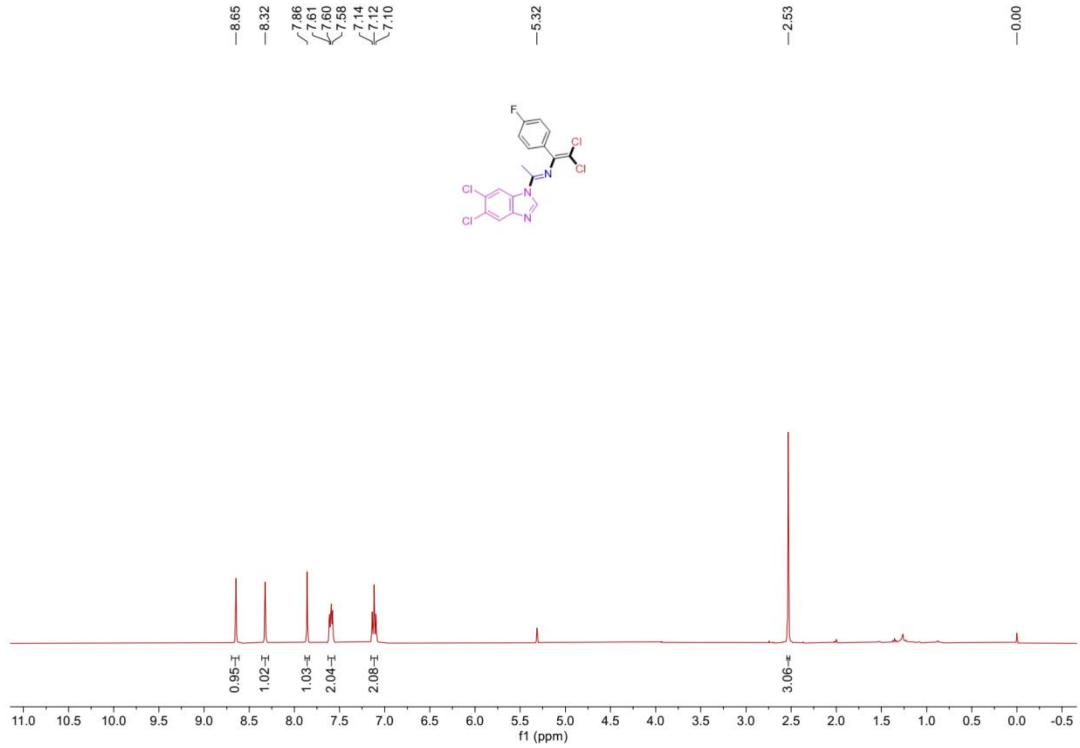

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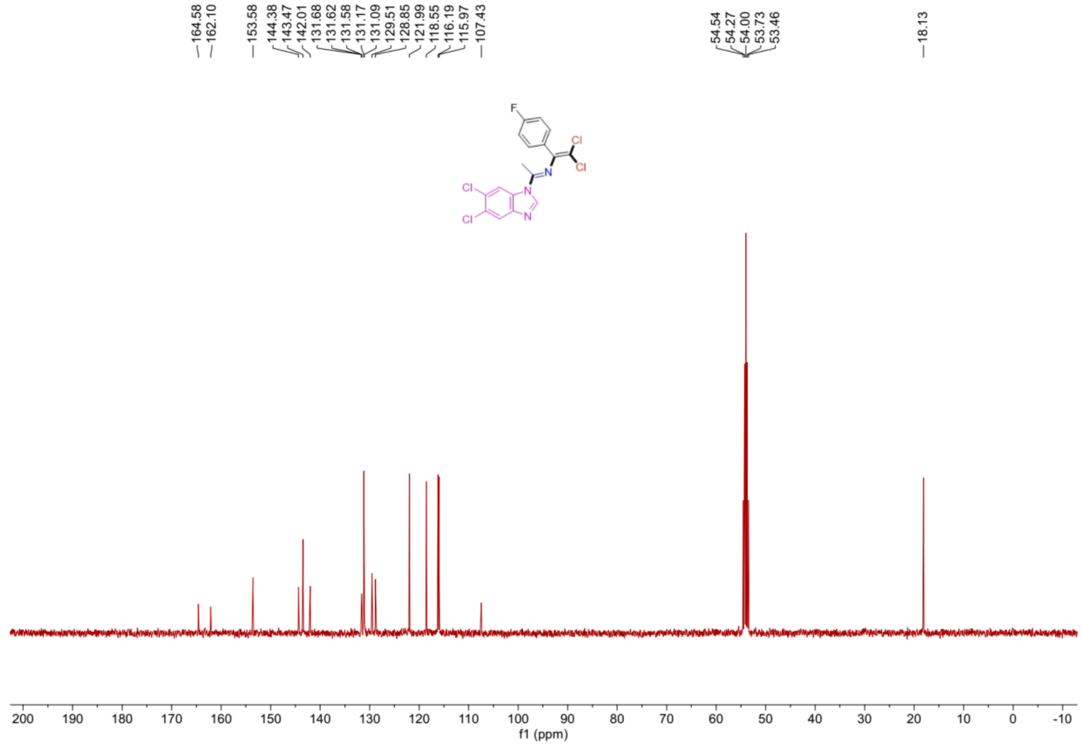

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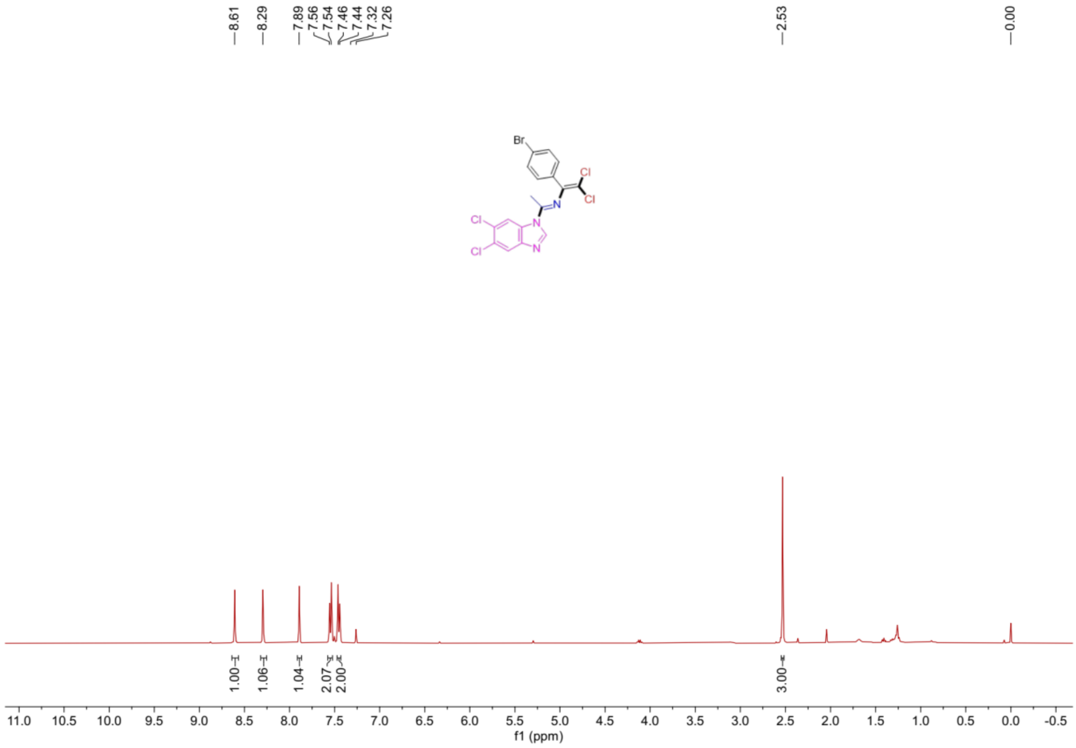

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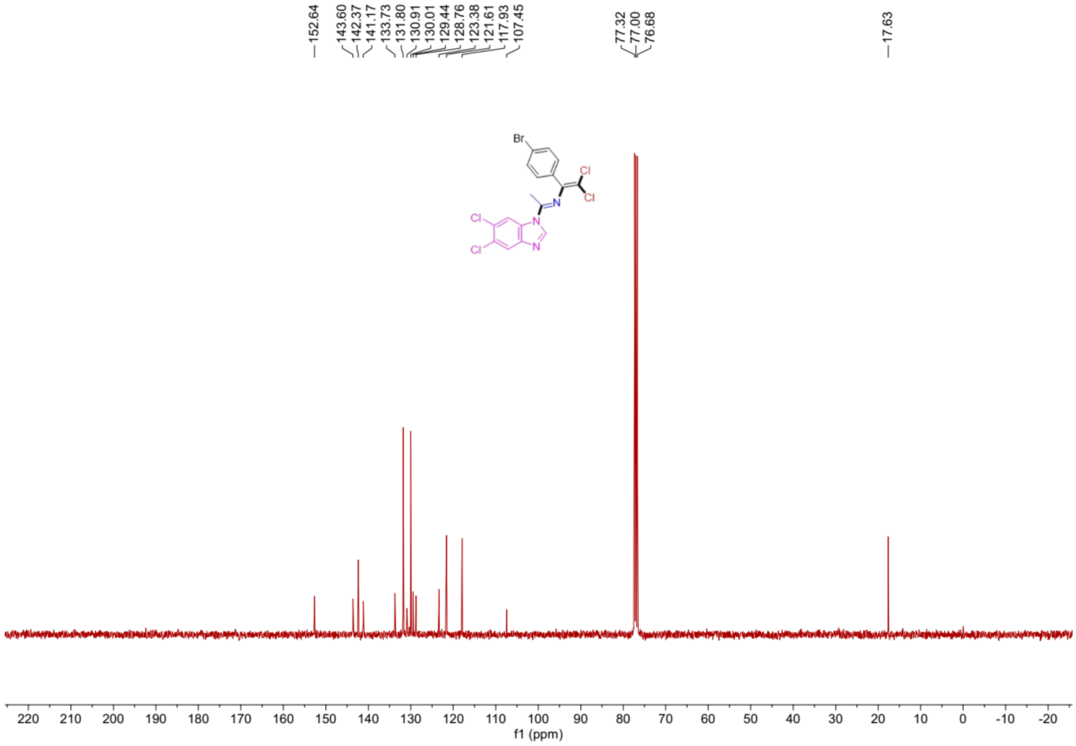

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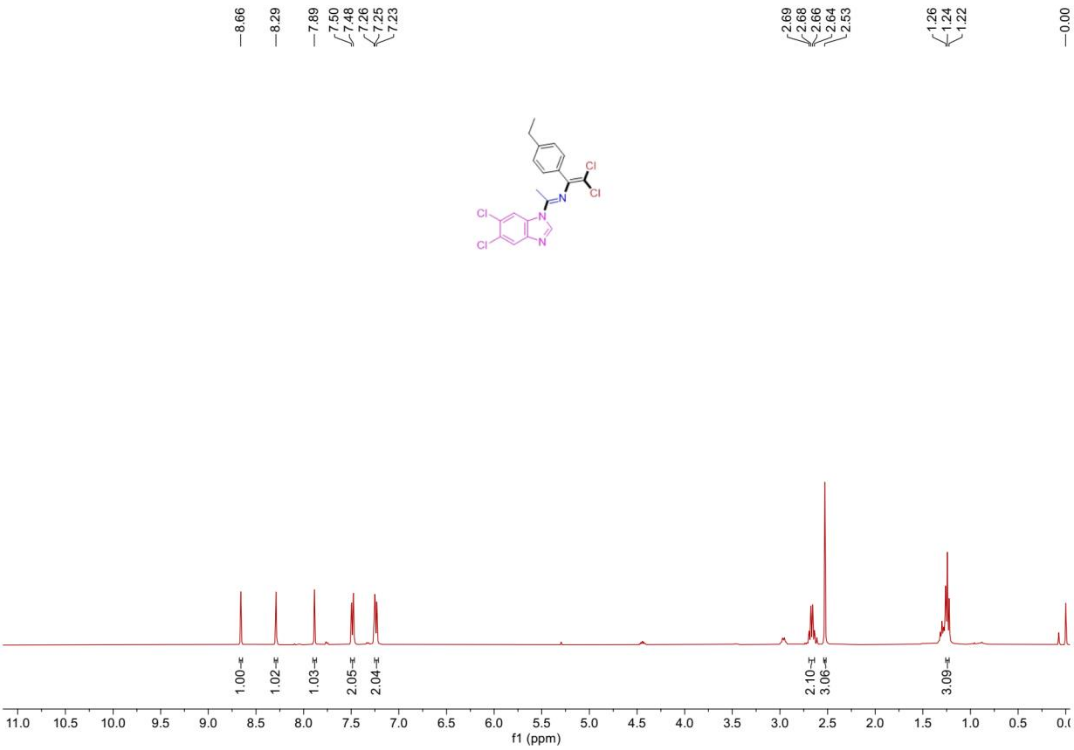

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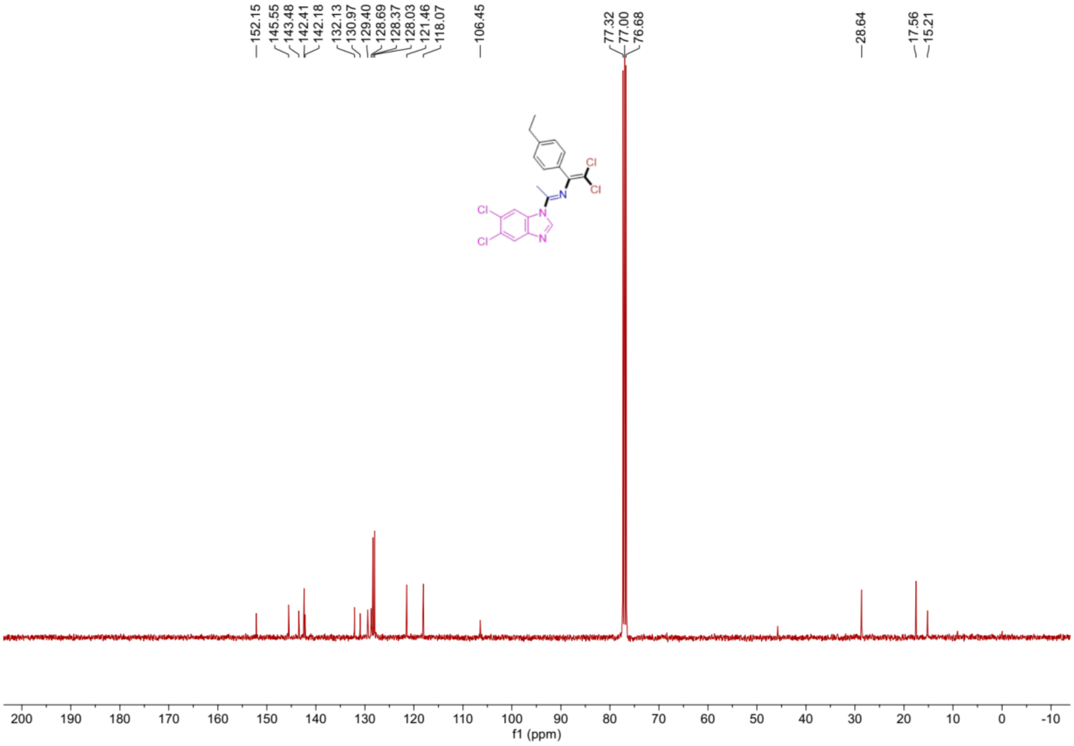

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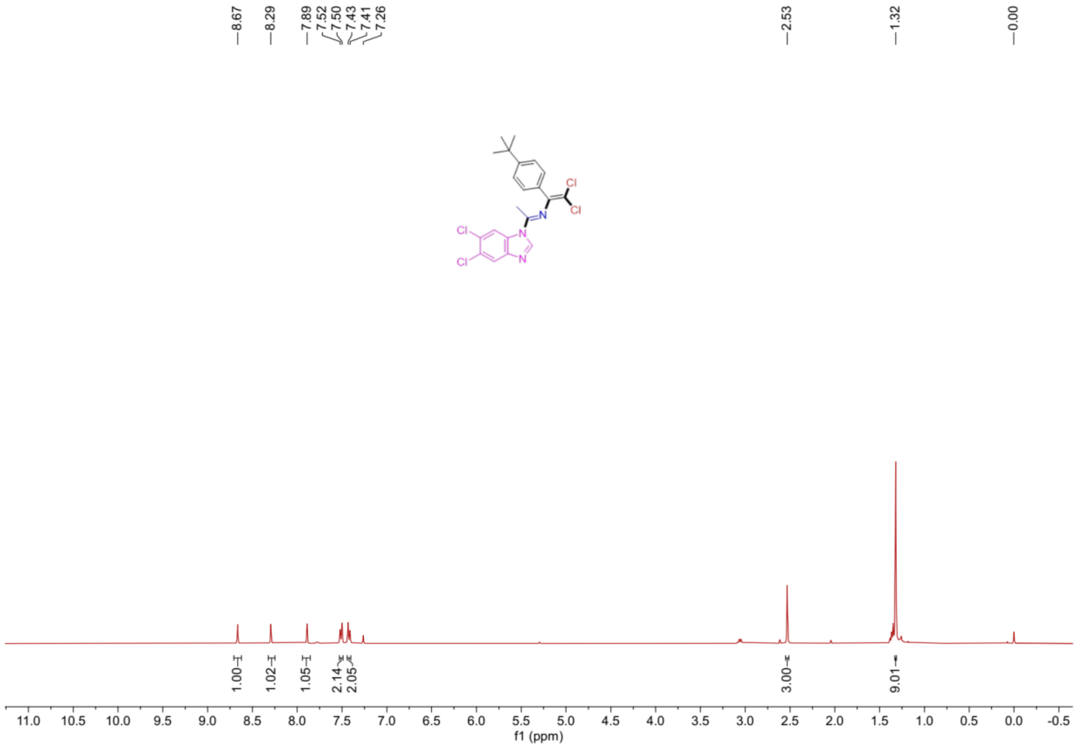

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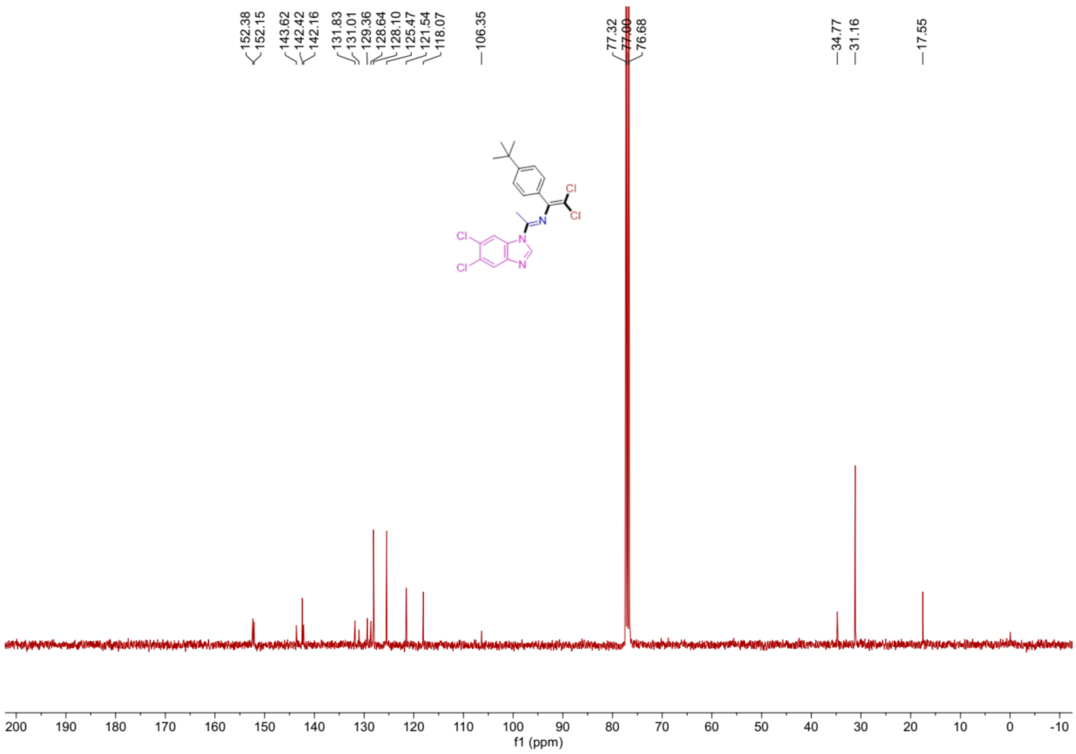

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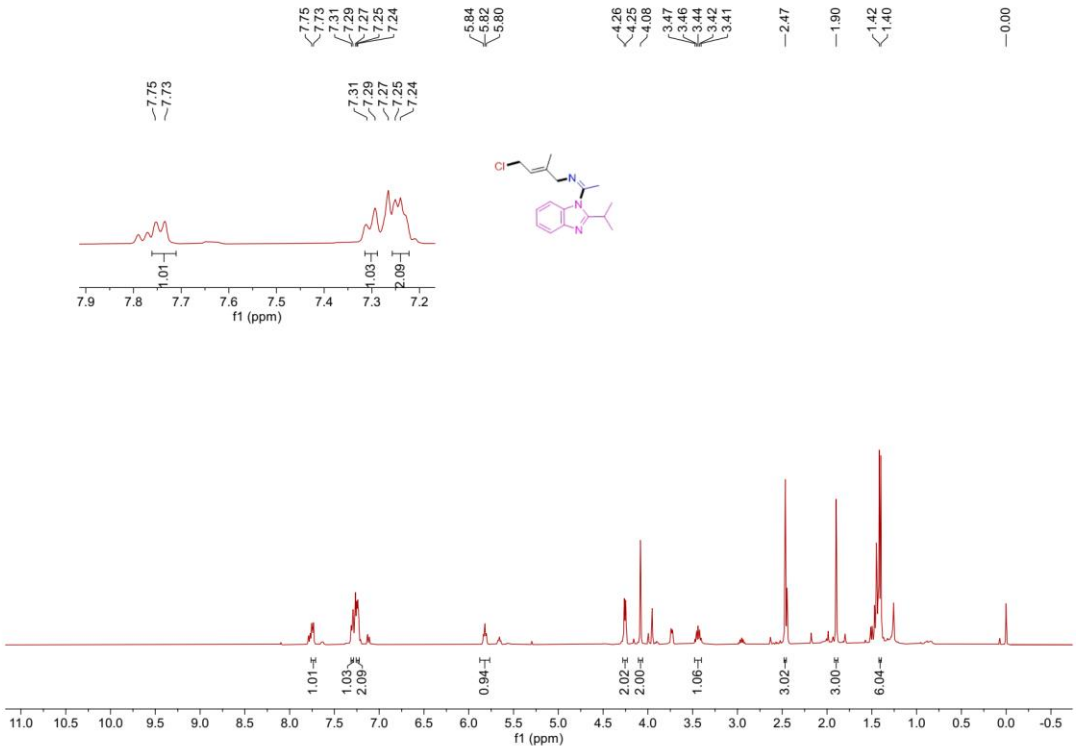
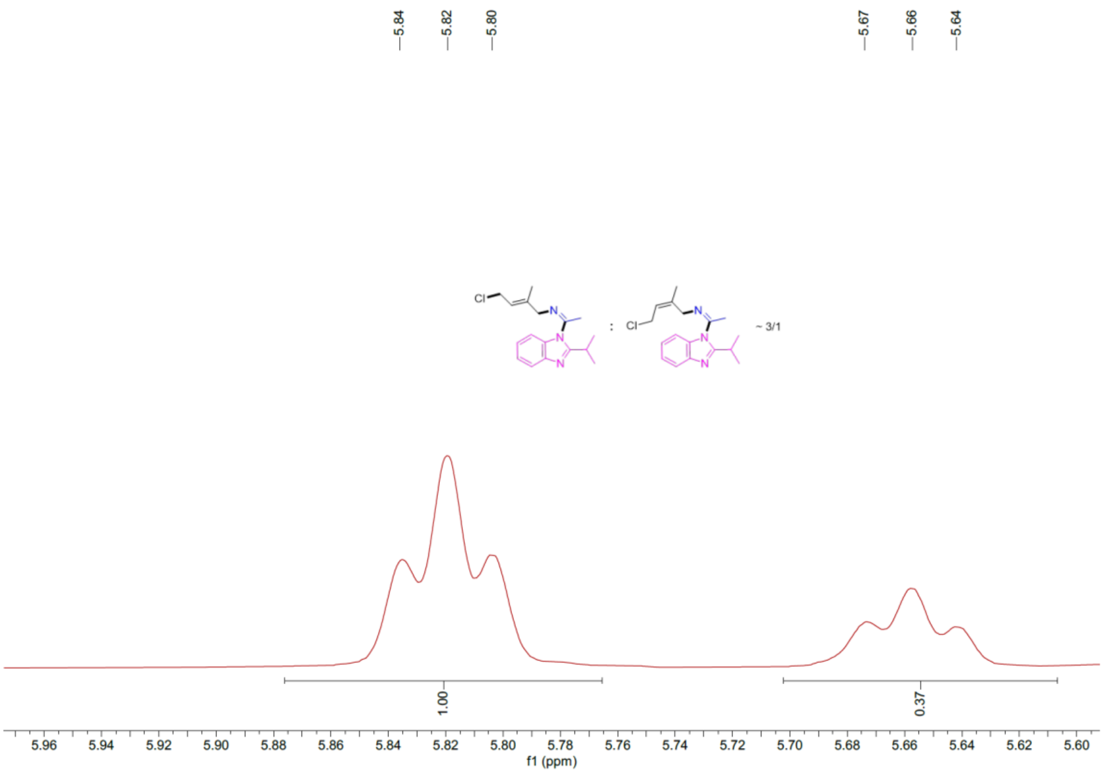


6 E/Z



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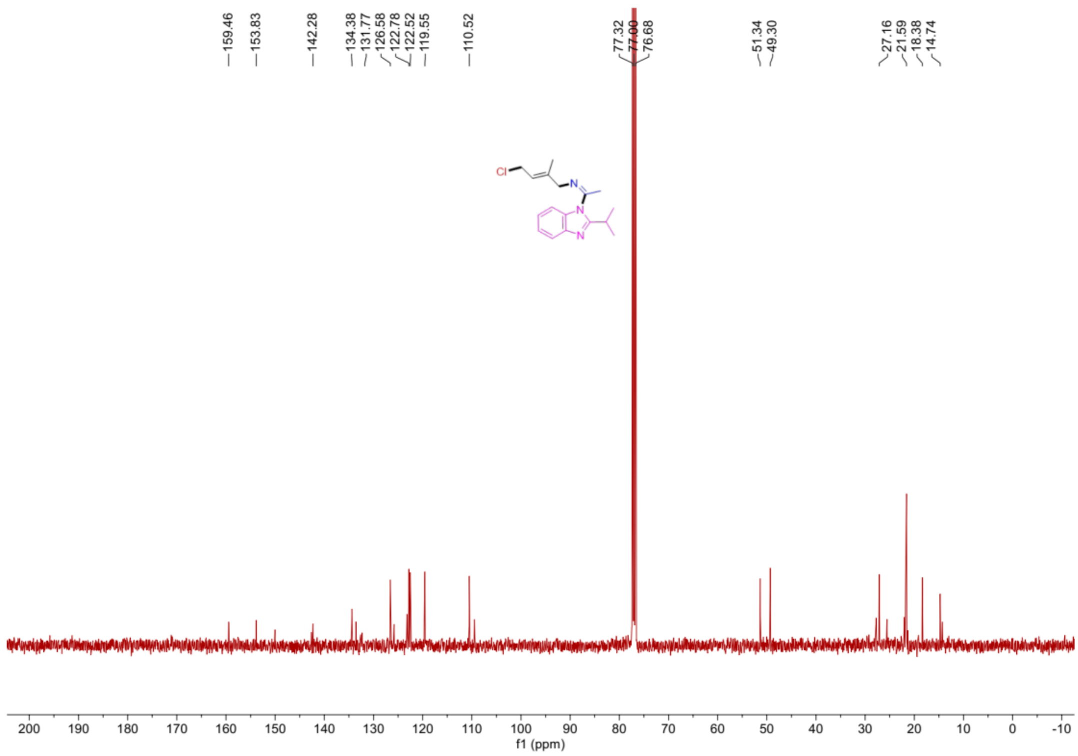

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51.34
49.30
27.16
21.59
18.38
14.74
Cl
N
N
N
200
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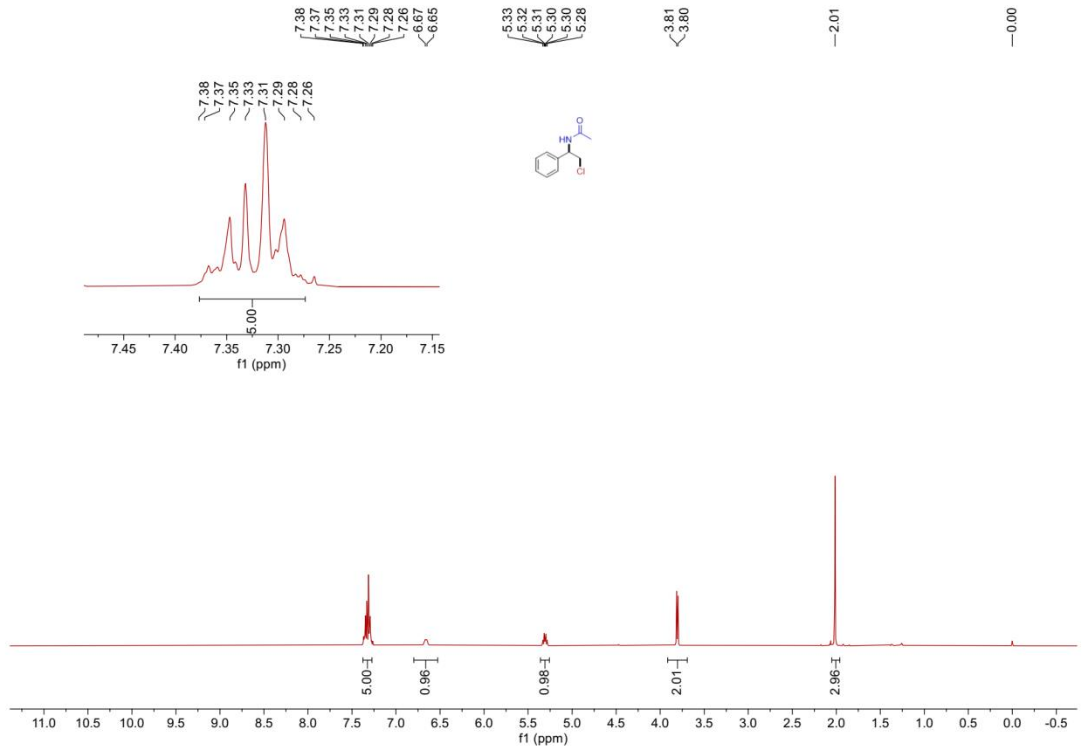
-10
f1 (ppm)

7 ^{1}H NMR



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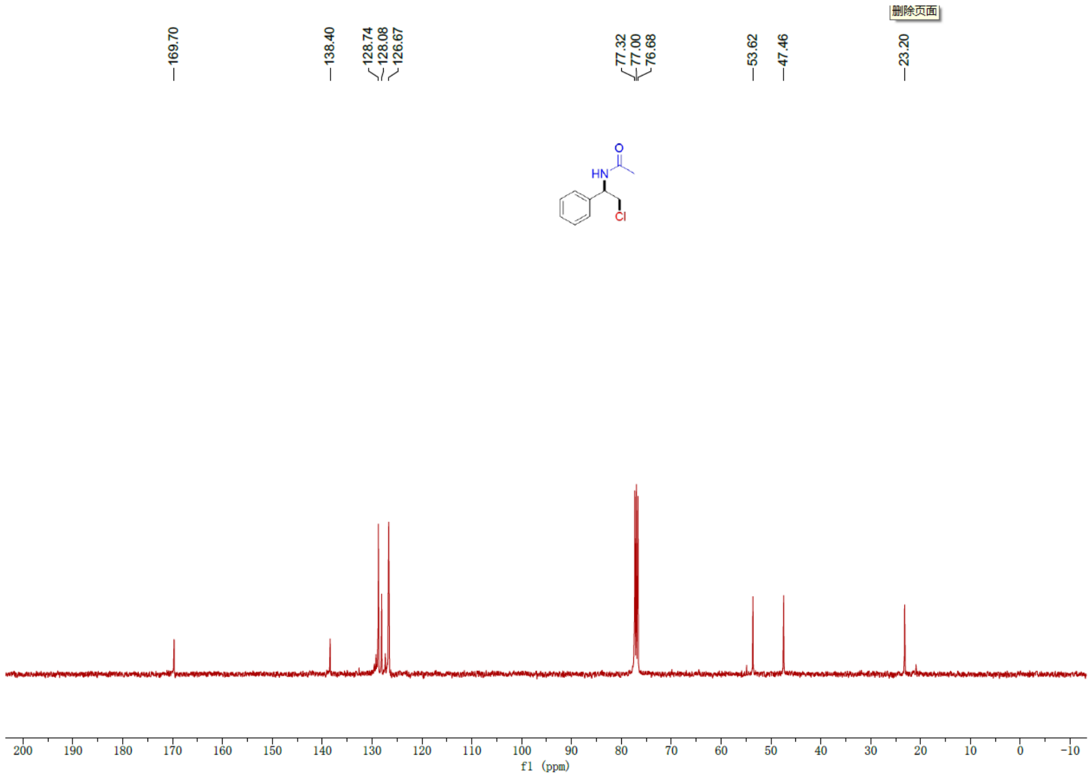

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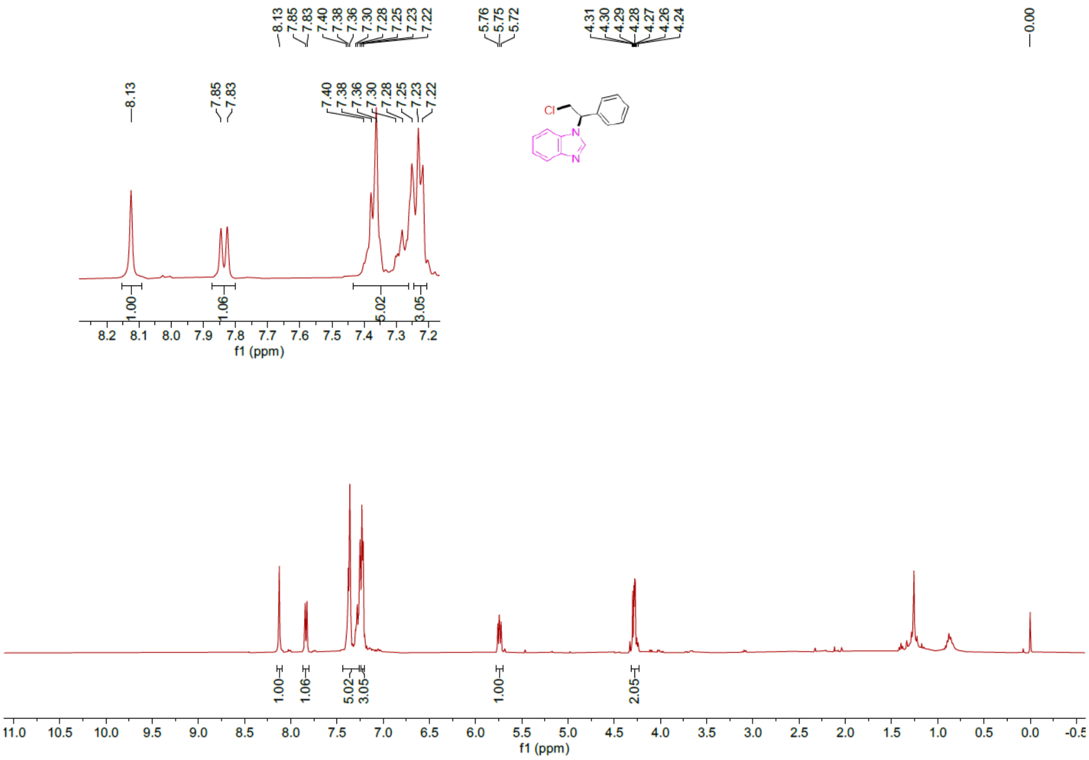

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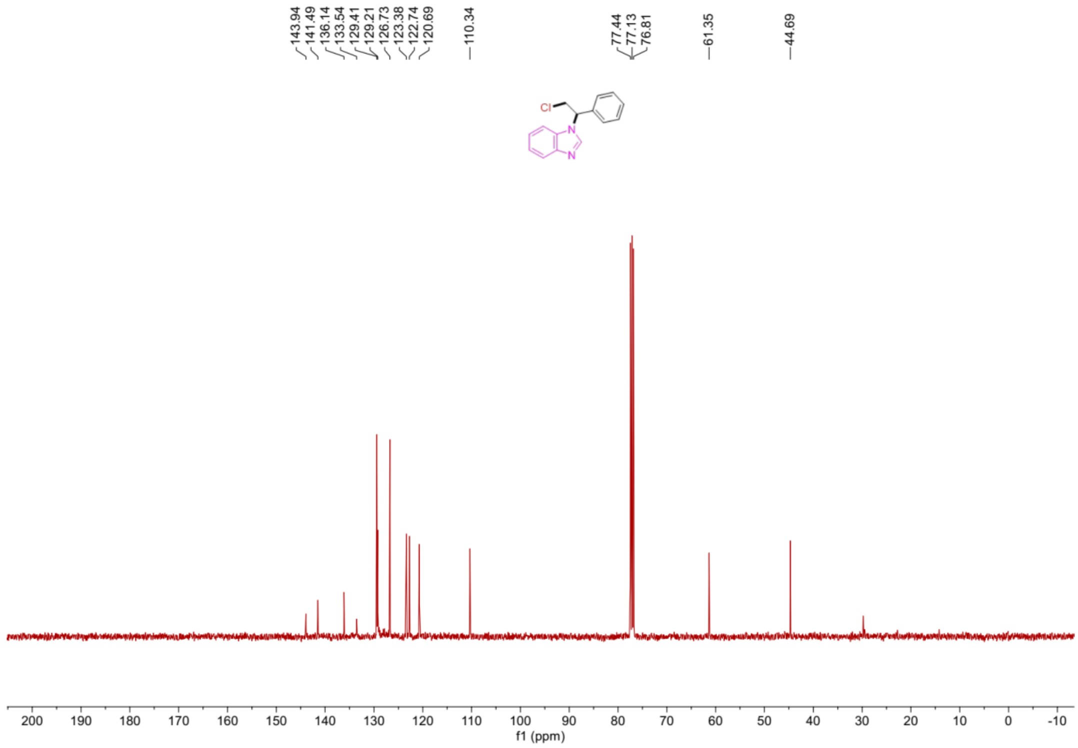

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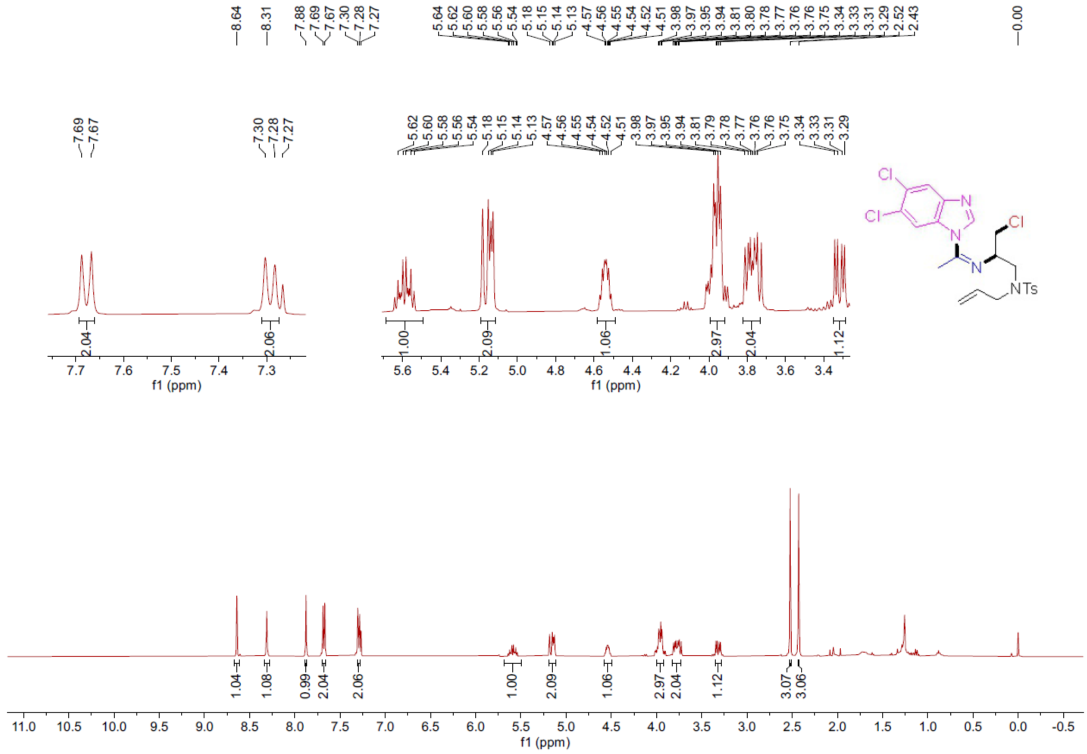

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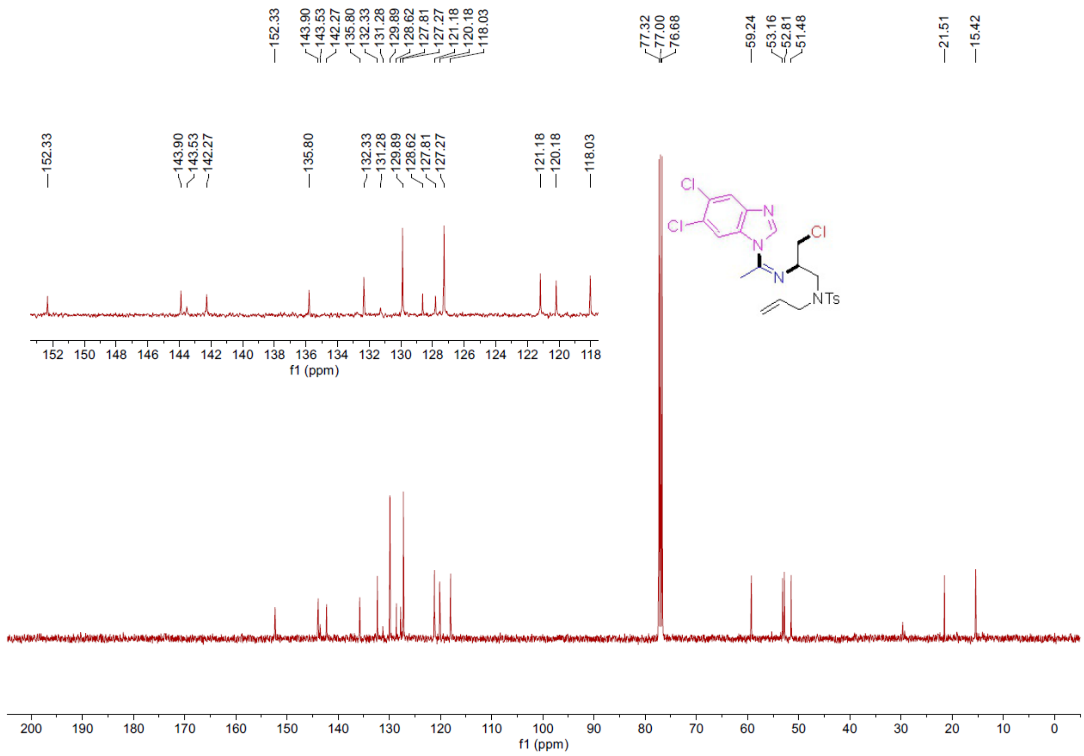

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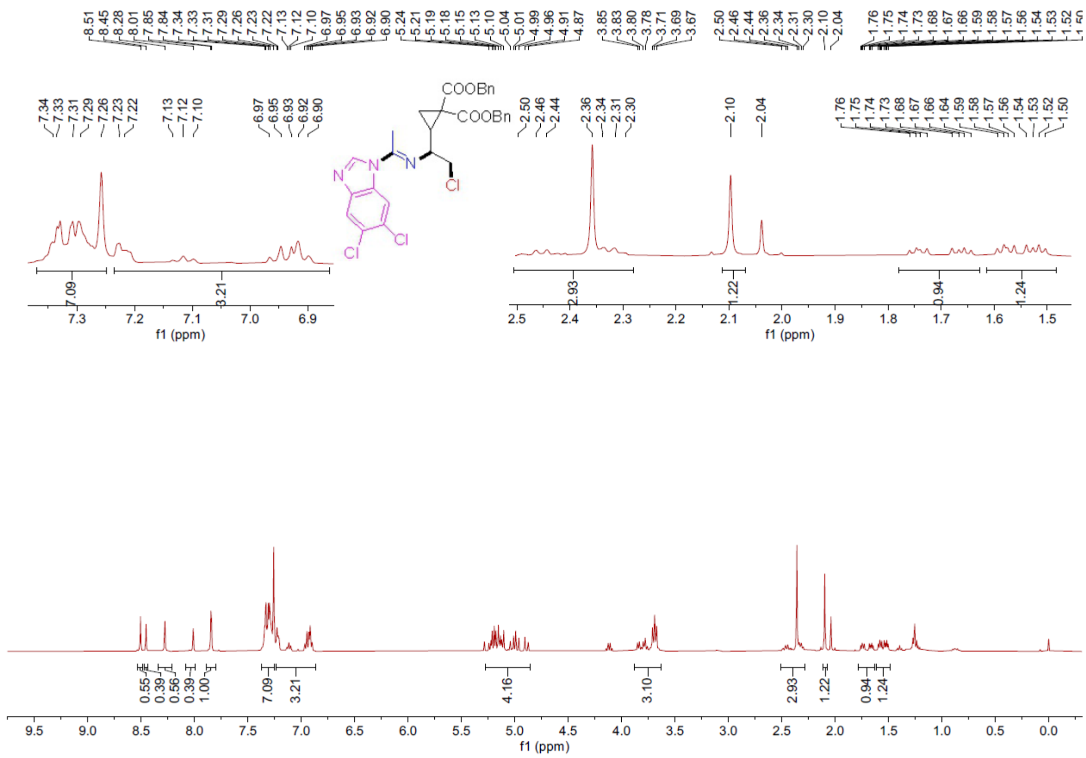

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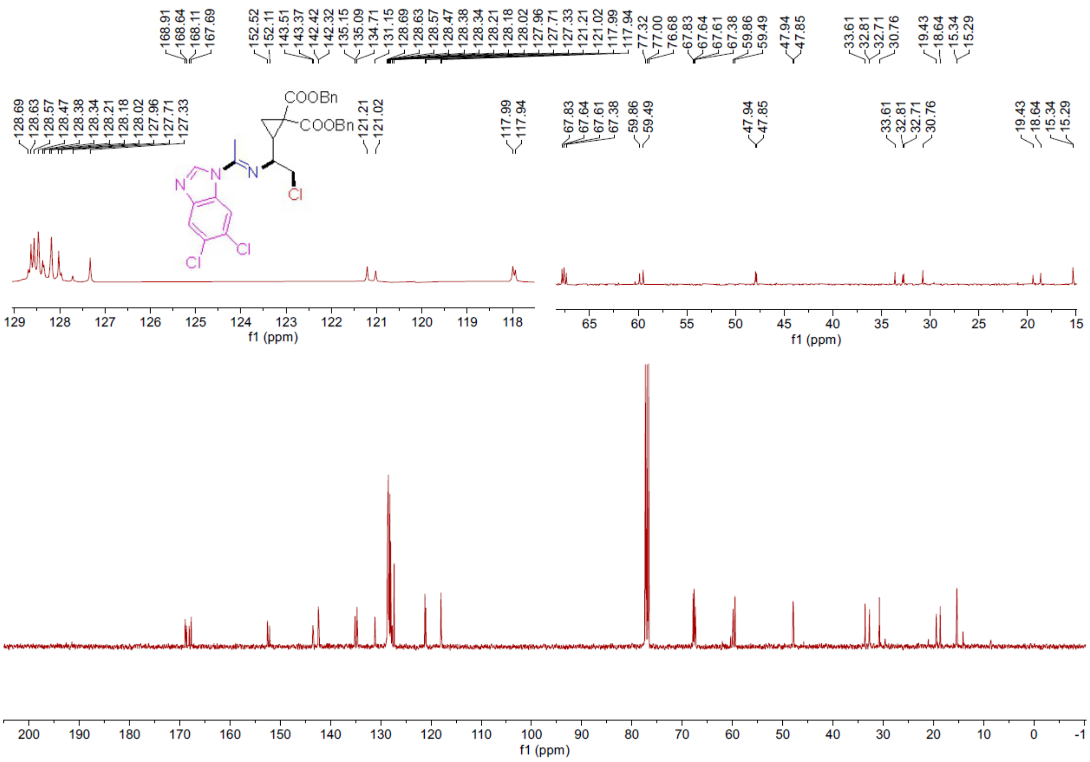

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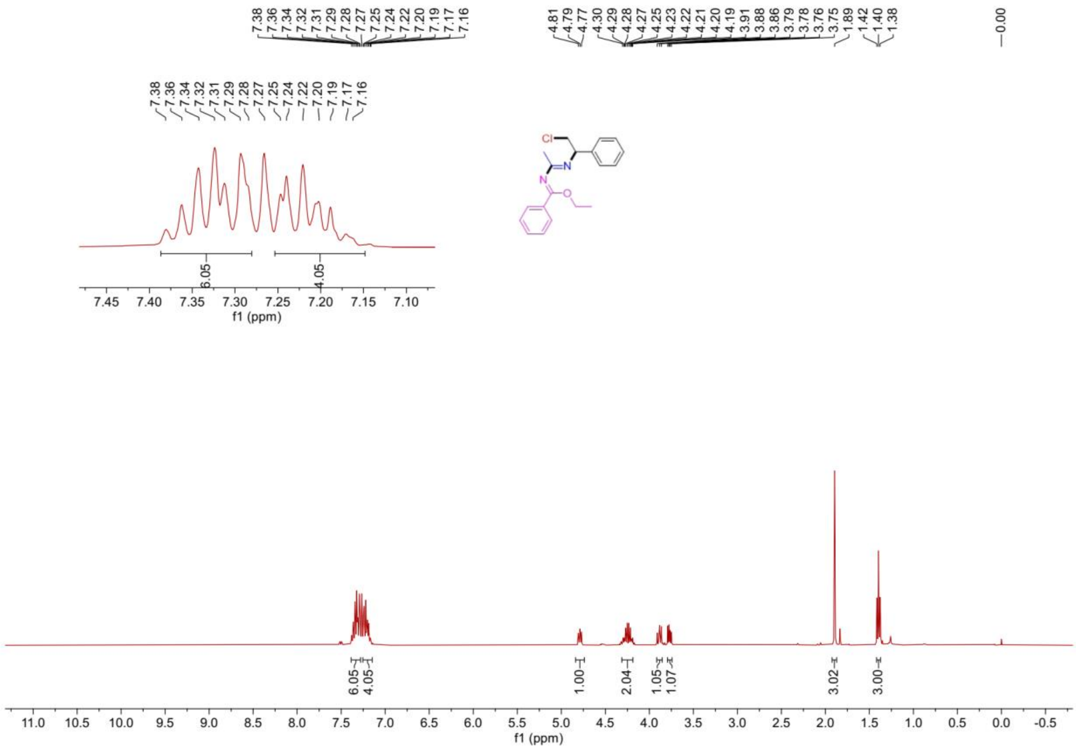

13 ^{13}C NMR