Supporting Information for

Metal-free Aminoamidiniumation Employing N-iodosuccinimide: Facile Syntheses of Bicyclic Imidazolidiniums and cyclic vicinal diamines

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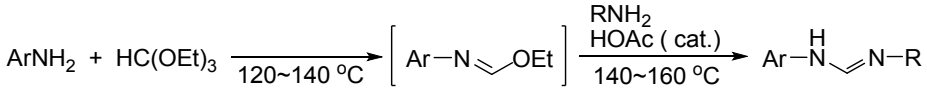
Experimental Section

General Information:

Unless otherwise stated, all reactions and manipulations were performed using standard Schlenk techniques. All solvents were purified by distillation using standard methods. Commercially available reagents were used without further purification. NMR spectra were recorded by using a Bruker 400 MHz spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (^{1}H NMR $CDCl_3$: 7.26 ppm ; ^{13}C NMR $CDCl_3$: 77.0 ppm). Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer 341 MC digital polarimeter with a 10 cm cell (c given in g per 100 mL) and $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. Mass spectra were recorded on the HP-5989 instrument by EI/ESI methods. X-ray diffraction analysis was performed by using a Bruker Smart-1000X-ray diffractometer.

Preparation and characterization

Synthesis of various formamidines:



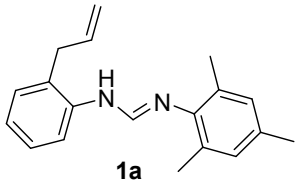
Scheme S1: Synthesis of various formamidines **1a~1e, 1l~1o**

General procedure A:

The mixture of aromatic amines (1.0 eq.) and triethylorthoformate (1.0 eq.) was heated at 120~140 °C. After 3 h, the mixture was allowed to cool to room temperature. Second amine (1.0 eq.) and glacial acetic acid (0.05 eq.) was added. The mixture was stirred at 140~160 °C

for 5 h, and was purified by column chromatography (PE/EtOAc) to afford the desired product.

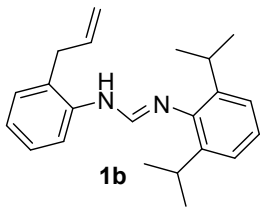
N-(2-allylphenyl)-N'-mesitylformimidamide (1a)



1a

Following the general procedure A, 2,4,6-trimethylaniline (1.5 g, 11.09 mmol, 1.0 eq.), triethylorthoformate (1.7 g, 11.09 mmol, 1.0 eq.), 2-allylaniline (1.5 g, 11.09 mmol, 1.0 eq.) and glacial acetic acid (34 mg, 0.56 mmol, 0.05 eq.) afforded the product **1a** as pale white solid (1.5 g, 49%). The product was obtained as a mixture of isomers. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.85 (d, J = 11.6 Hz, 0.5H), 7.64 (s, 0.5H), 7.23 (d, J = 7.2 Hz, 1H), 7.17 (d, J = 7.6 Hz, 1H), 7.10 (d, J = 6.4 Hz, 0.5H), 7.04-7.00 (m, 1H), 6.89 (s, 2H), 6.50 (d, J = 11.2 Hz, 0.5H), 6.04-5.94 (m, 0.5H), 5.59-5.49 (m, 0.5H), 5.10 (d, J = 9.6 Hz, 0.5H), 5.05 (d, J = 17.6 Hz, 0.5H), 4.66 (d, J = 10.0 Hz, 1H), 4.36 (d, J = 16.8 Hz, 1H), 3.44 (d, J = 5.6 Hz, 1H), 3.05 (d, J = 6.4 Hz, 1H), 2.27 (s, 3H), 2.23 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.3, 142.6, 138.2, 134.9, 132.4, 130.7, 129.0, 128.9, 127.9, 127.8, 127.3, 127.2, 123.2, 116.6, 115.9, 37.3, 35.9, 20.7, 18.6, 17.7; HRMS (EI): m/z $[M]^+$ calcd. for $C_{19}H_{22}N_2^+$: 278.1783, found: 278.1784.

N-(2-allylphenyl)-N'-(2,6-diisopropylphenyl)formimidamide (1b)

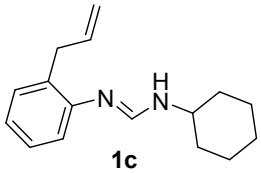


1b

Following the general procedure A, 2,6-diisopropylaniline (1.0 g, 5.65 mmol, 1.0 eq.), triethylorthoformate (836 mg, 5.65 mmol, 1.0 eq.), 2-allylaniline (746 mg, 5.65 mmol, 1.0 eq.) and glacial acetic acid (17 mg, 0.28 mmol, 0.05 eq.) afforded the product **1b** as brown solid (900 mg, 63%). The product was obtained as a mixture of isomers. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 (d, J = 11.2 Hz, 0.5H), 7.67(s, 0.5H), 7.25-6.98 (m, 7H), 6.05-5.97(m, 0.5H), 5.53-5.43 (m, 0.5H), 5.17-5.06 (m, 1H), 4.57 (dd, J = 10.4 Hz, 0.8 Hz,

0.5H), 4.21 (dd, J = 17.6 Hz, 1.2 Hz, 0.5H), 3.46 (d, J = 6.0 Hz, 1H), 3.24-3.17 (m, 1H), 3.08-3.02 (m, 2H), 1.22-1.16 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.4, 142.9, 138.6, 138.2, 134.8, 130.8, 128.0, 127.5, 127.0, 123.9, 123.5, 123.1, 116.7, 115.6, 37.2, 36.0, 27.9, 23.6, 23.5; HRMS (EI): m/z $[M]^+$ calcd. for $C_{22}H_{28}N_2^+$: 320.2252, found: 320.2249.

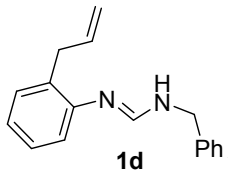
N'-(2-allylphenyl)-N-cyclohexylformimidamide (1c)



1c

Following the general procedure A, 2-allylaniline (1.0 g, 7.51 mmol, 1.0 eq.), triethylorthoformate (1.2 g, 7.51 mmol, 1.0 eq.), cyclohexanamine (745 mg, 7.51 mmol, 1.0 eq.) and glacial acetic acid (23 mg, 0.38 mmol, 0.05 eq.) afforded the product **1c** as pale brown solid (950 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 (s, 1H), 7.13 (t, J = 7.6 Hz, 2H), 6.98 (t, J = 7.6 Hz, 1H), 6.77 (d, J = 7.6 Hz, 1H), 6.03-5.93 (m, 1H), 5.05-4.99 (m, 2H), 4.51-4.29 (m, 1H), 3.82 (br, 1H), 3.45 (d, J = 6.4 Hz, 2H), 2.05-2.03 (m, 2H), 1.78-1.73 (m, 2H), 1.65-1.61 (m, 1H), 1.40-1.34 (m, 2H), 1.24-1.22 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.9, 129.1, 126.9, 122.7, 119.3, 114.8, 36.0, 33.3, 25.5, 24.8; HRMS (EI): m/z $[M]^+$ calcd. for $C_{16}H_{22}N_2^+$: 242.1783, found: 242.1784.

N'-(2-allylphenyl)-N-benzylformimidamide (1d)

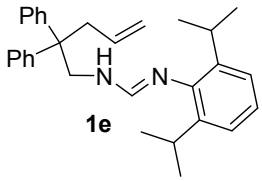


1d

Following the general procedure A, 2-allylaniline (1.0 g, 7.51 mmol, 1.0 eq.), triethylorthoformate (1.2 g, 7.51 mmol, 1.0 eq.), benzylamine (805 mg, 7.51 mmol, 1.0 eq.) and glacial acetic acid (23 mg, 0.38 mmol, 0.05 eq.) afforded the product **1d** as brown oil (756 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58 (s, 1H), 7.37-7.35 (m, 4H), 7.29-7.27 (m, 1H), 7.15-7.12 (m, 2H), 7.01-6.98 (m, 1H), 6.79 (d, J = 7.6 Hz, 1H), 5.99-5.93 (m, 1H), 4.99 (d, J = 13.2 Hz, 2H), 4.56 (s, 2H), 3.43 (d, J = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.8, 137.8, 135.3, 130.7, 130.1, 129.1, 128.4, 127.6, 127.2, 126.9, 122.9, 119.2, 116.8, 114.8, 36.1, 35.8; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{17}H_{19}N_2^+$: 251.1548; found:

251.1549.

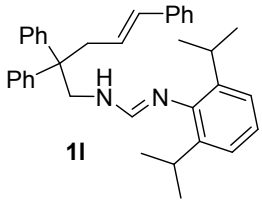
N'-(2,6-diisopropylphenyl)-N-(2,2-diphenylpent-4-en-1-yl)formimidamide (1e)



1e

Following the general procedure A, 2,6-diisopropylaniline (1.0 g, 5.65 mmol, 1.0 eq.), triethylorthoformate (836 mg, 5.65 mmol, 1.0 eq.), 2,2-diphenylpent-4-en-1-amine (1.3 g, 5.65 mmol, 1.0 eq.) and glacial acetic acid (17 mg, 0.28 mmol, 0.05 eq.) afforded the product **1e** as pale white solid (1.3 g, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35-7.31 (m, 4H), 7.26-7.19 (m, 6H), 7.08-6.99 (m, 4H), 5.49-5.44 (m, 1H), 5.05 (d, J = 17.2 Hz, 1H), 4.99 (d, J = 10.0 Hz, 1H), 4.19-4.04 (m, 2H), 3.10-3.08 (m, 2H), 2.99 (d, J = 6.8 Hz, 2H), 1.14 (d, J = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.2, 145.4, 144.9, 140.2, 138.7, 133.9, 128.3, 128.2, 128.0, 127.6, 126.5, 123.2, 123.0, 122.8, 122.7, 118.5,118.3, 51.0, 49.9, 49.8, 40.8, 27.7, 27.5, 23.7, 23.6, 23.2; HRMS (EI): m/z $[M]^+$ calcd. for $C_{30}H_{36}N_2$: 424.2878, found: 424.2877.

N'-(2,6-diisopropylphenyl)-N-((E)-2,2,5-triphenylpent-4-en-1-yl)formimidamide (1l)

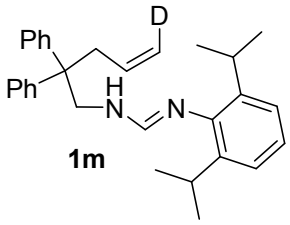


1l

Following the general procedure A, 2,6-diisopropylaniline (565 mg, 3.19 mmol, 1.0 eq.), triethylorthoformate (475 mg, 3.19 mmol, 1.0 eq.), (E)-2,2,5-triphenylpent-4-en-1-amine (1.0 g, 3.19 mmol, 1.0 eq.) and glacial acetic acid (10 mg, 0.16 mmol, 0.05 eq.) afforded the product **1l** as pale white solid (830 mg, 52%). The product was obtained as a mixture of isomers. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36-7.14 (m, 15H), 7.06-6.97 (m, 4H), 6.34 (d, J = 15.6 Hz, 0.8H), 6.25 (d, J = 15.6 Hz, 0.2H), 5.88-5.86 (m, 0.8H), 5.70-5.63 (m, 0.2H), 4.21-4.19 (m, 2H), 3.12 (d, J = 6.8 Hz, 1.6H), 3.06-3.03 (m, 1.6H), 2.93 (d, J = 6.8 Hz, 0.8H), 1.11 (d, J = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.3, 140.3, 138.7, 133.3, 128.5, 128.3, 128.1, 127.6, 127.1, 126.6, 126.1, 126.0, 125.7, 123.0,

122.8, 122.7, 50.7, 50.4, 40.0, 27.7, 27.6, 23.7, 23.2; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{36}H_{41}N_2^+$: 501.3270; found: 501.3271.

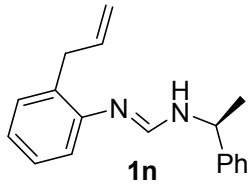
N'-(2,6-diisopropylphenyl)-N-((Z)-2,2-diphenylpent-4-en-1-yl-5-d)formimidamide (1m)



1m

Following the general procedure A, 2,6-diisopropylaniline (500 mg, 2.82 mmol, 1.0 eq.), triethylorthoformate (418 mg, 2.82 mmol, 1.0 eq.), (Z)-2,2-diphenylpent-4-en-5-d-1-amine (671 mg, 5.65 mmol, 1.0 eq.) and glacial acetic acid (9 mg, 0.14 mmol, 0.05 eq.) afforded the product **1m** as pale white solid (620 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35-7.31 (m, 4H), 7.27-7.20 (m, 6H), 7.08-7.00 (m, 4H), 5.49-5.45 (m, 1H), 4.98 (d, J = 10.4 Hz, 1H), 4.18-4.09 (m, 2H), 3.09-3.06 (m, 2H), 2.99 (d, J = 6.8 Hz, 2H), 1.14 (d, J = 7.2 Hz, 12H); HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{30}H_{36}DN_2^+$: 426.3020; found: 426.3018.

(S)-N'-(2-allylphenyl)-N-(1-phenylethyl)formimidamide (1n)

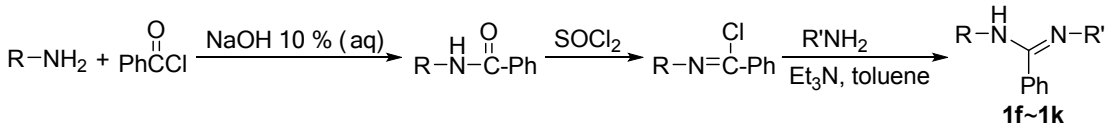


1n

Following the general procedure A, 2-allylaniline (1.0 g, 7.51 mmol, 1.0 eq.), triethylorthoformate (1.2 g, 7.51 mmol, 1.0 eq.), (S)-1-phenylethan-1-amine (910 mg, 7.51 mmol, 1.0 eq.) and glacial acetic acid (23 mg, 0.38 mmol, 0.05 eq.) afforded the product **1n** as brown oil (634 mg, 32%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50 (s, 1H), 7.36-7.35 (m, 4H), 7.28-7.22 (m, 1H), 7.12-7.09 (m, 2H), 6.97 (t, J = 7.2 Hz, 1H), 6.75 (d, J = 8.4 Hz, 1H), 5.93-5.86 (m, 1H), 5.19-5.04 (m, 1H), 4.95-4.90 (m, 2H), 3.32 (d, J = 5.6 Hz, 2H), 1.56 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.2, 137.8, 129.2, 128.5, 127.1, 126.9, 126.1, 122.9, 119.1, 114.7, 35.8, 22.5; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{18}H_{21}N_2^+$: 265.1705; found: 265.1702.

Preparation of various benzimidamides:

The benzimidamides were prepared following the literature method.[1]

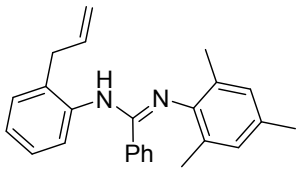


Scheme S-2: Synthesis of various benzimidamides **1f~1k.**

General procedure B:

The corresponding benzimidamide (1.0 eq.) was refluxed in $SOCl_2$ (2 mL) for 1 h at 80 °C, and then the reaction mixture was cooled to room temperature. Excess $SOCl_2$ was evaporated off under vacuum. Into the resulting residue, a mixture of amine (1.0 eq.) and triethylamine (4.0 eq.) in toluene (10 mL) was added. The mixture was refluxed for 20 h and then cooled to room temperature, washed with water, dried over $MgSO_4$ and concentrated. The crude product was purified by column chromatography using silica gel (PE/EtOAc) to give the product benzimidamide.

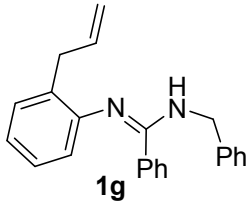
N-(2-allylphenyl)-N'-mesitylbenzimidamide (1f)



1f

Following the general procedure B, N-mesitylbenzamide (600 mg, 2.51 mmol, 1.0 eq.), $SOCl_2$ (2 mL), 2-allylaniline (334 mg, 2.51 mmol, 1.0 eq.), toluene (10 mL) and triethylamine (1.0 g, 10.04 mmol, 4.0 eq.) afford **1f** as brown oil (650 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61 (d, J = 6.8 Hz, 1H), 7.38-7.30 (m, 4H), 7.10-7.05 (m, 1H), 6.92-6.85 (m, 3H), 6.43 (d, J = 8.0 Hz, 1H), 6.23 (s, 1H), 5.73-5.63 (m, 1H), 5.17-5.04 (m, 1H), 4.74 (d, J = 4.0 Hz, 1H), 3.32 (d, J = 6.0 Hz, 2H), 2.40 (s, 3H), 2.27 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.2, 143.4, 139.0, 135.1, 135.0, 132.1, 130.5, 129.8, 128.9, 128.1, 128.0, 126.7, 124.2, 123.7, 116.0, 36.9, 20.7, 18.7, 17.8; HRMS (EI): m/z $[M]^+$ calcd. for $C_{25}H_{26}N_2^+$: 354.2096, found: 354.2099.

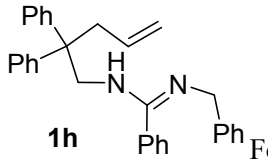
N'-(2-allylphenyl)-N-benzylbenzimidamide (1g)



1g

Following the general procedure B, N-benzylbenzamide (788 mg, 3.75 mmol, 1.0 eq.), $SOCl_2$ (2 mL), 2-allylaniline (500 mg, 3.75 mmol, 1.0 eq.), toluene (10 mL) and triethylamine (1.5 g, 15.00 mmol, 4.0 eq.) afford **1g** as a pale yellow solid (530 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45 (d, J = 6.8 Hz, 2H), 7.38 (t, J = 6.8 Hz, 2H), 7.32-7.23 (m, 6H), 7.07 (d, J = 6.4 Hz, 1H), 6.84-6.80 (m, 2H), 6.32 (d, J = 5.2 Hz, 2H), 6.02-5.95 (m, 1H), 5.10-5.03 (m, 2H), 4.85 (br, 1H), 4.73 (s, 2H), 3.40 (d, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.8, 148.6, 139.3, 137.7, 135.0, 132.2, 129.1, 128.8, 128.6, 128.2, 128.1, 128.0, 127.9, 127.2, 126.1, 122.5, 121.6, 115.2, 45.9, 36.2; HRMS (EI): m/z $[M]^+$ calcd. for $C_{23}H_{22}N_2^+$: 326.1783, found: 326.1781.

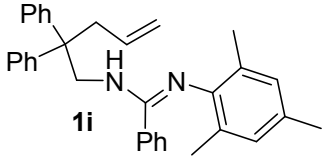
N'-benzyl-N-(2,2-diphenylpent-4-en-1-yl)benzimidamide (1h)



1h

Following the general procedure B, N-benzylbenzamide (445 mg, 2.11 mmol, 1.0 eq.), $SOCl_2$ (2 mL), 2,2-diphenylpent-4-en-1-amine (500 mg, 2.11 mmol, 1.0 eq.), toluene (10 mL) and triethylamine (853 mg, 8.44 mmol, 4.0 eq.) afford **1h** as brown oil (450 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30-6.87 (m, 20H), 5.46-5.36 (m, 1H), 5.00 (d, J = 17.6 Hz, 1H), 4.93 (s, 1H), 4.36 (s, 2H), 4.21 (br, 1H), 3.75 (br, 1H), 2.99 (d, J = 3.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.1, 134.5, 128.8, 128.2, 128.1, 128.0, 127.4, 126.0, 117.6, 51.2, 48.3, 41.0, 29.5; HRMS (EI): m/z $[M]^+$ calcd. for $C_{31}H_{30}N_2^+$: 430.2409, found: 430.2408.

N-(2,2-diphenylpent-4-en-1-yl)-N'-mesitylbenzimidamide (1i)

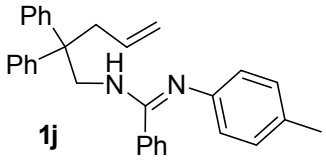


1i

Following the general procedure B, N-mesitylbenzamide (1.0 g,

4.18 mmol, 1.0 eq.), $SOCl_2$ (2 mL), 2,2-diphenylpent-4-en-1-amine (990 mg, 4.18 mmol, 1.0 eq.), toluene (10 mL) and triethylamine (1.7 g, 16.72 mmol, 4.0 eq.) afford **1i** as brown oil (1.6 mg, 84%). The product was obtained as a mixture of isomers. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54-7.09 (m, 12.2H), 6.97-6.94 (m, 1.4H), 6.87 (s, 1.4H), 6.78 (s, 0.6H), 6.65 (s, 1.4H), 5.61-5.51 (m, 0.7H), 5.15-4.83 (m, 2.3H), 4.28 (s, 1.4H), 3.57 (s, 0.6H), 3.05 (d, J = 6.8 Hz, 1.4H), 2.69 (d, J = 6.4 Hz, 0.6H), 2.31 (s, 0.7H), 2.29 (s, 0.3H), 2.15 (s, 1.4H), 2.09 (s, 0.6H), 1.99 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.7, 144.8, 136.1, 134.1, 133.5, 129.1, 128.7, 128.2, 128.2, 128.1, 127.9, 127.5, 126.9, 126.3, 121.7, 118.2, 50.5, 50.3, 50.1, 47.7, 42.6, 40.9, 20.8, 20.6, 18.7, 17.7, 17.5; HRMS (EI): m/z $[M]^+$ calcd. for $C_{33}H_{34}N_2^+$: 458.2722, found: 458.2724.

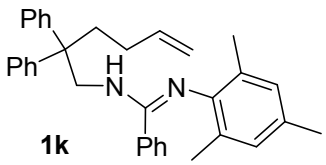
N-(2,2-diphenylpent-4-en-1-yl)-N'-(p-tolyl)benzimidamide (1j)



1j

Following the general procedure B, N-(p-tolyl)benzamide (1.0 g, 5.05 mmol, 1.0 eq.), $SOCl_2$ (2 mL), 2,2-diphenylpent-4-en-1-amine (1.2 g, 5.05 mmol, 1.0 eq.), toluene (10 mL) and triethylamine (2.0 g, 20.20 mmol, 4.0 eq.) afford **1j** as brown oil (1.5 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28 -7.08 (m, 13H), 6.98 (d, J = 6.8 Hz, 2H), 6.82 (d, J = 8.0 Hz, 2H), 6.48 (d, J = 6.8 Hz, 2H), 5.56-5.49 (m, 1H), 5.04 (d, J = 16.8 Hz, 1H), 4.96 (d, J = 10.4 Hz, 1H), 4.28 (s, 2H), 4.20 (br, 1H), 3.01 (d, J = 7.2 Hz, 2H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.0, 145.5, 134.0, 128.8, 128.1, 128.0 126.3, 122.6, 118.4, 50.6, 47.3, 42.6, 20.6; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{31}H_{31}N_2^+$: 431.2487; found: 431.2480.

N-(2,2-diphenylhex-5-en-1-yl)-N'-mesitylbenzimidamide (1k)

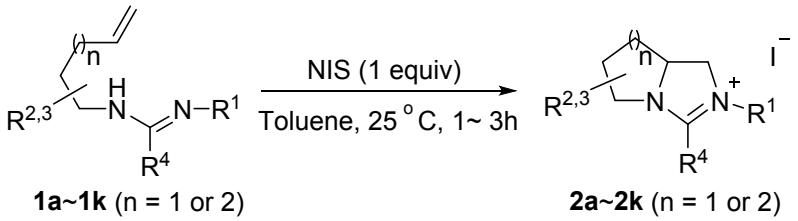


1k

Following the general procedure B, N-mesitylbenzamide (478 mg, 2.0 mmol, 1.0 eq.), $SOCl_2$ (2 mL), 2,2-diphenylhex-5-en-1-amine (500 mg, 2.0 mmol, 1.0 eq.), toluene (10 mL) and triethylamine(808 mg, 8.0 mmol, 4.0 eq.) afford **1k** as brown solid (735

mg, 77%). The product was obtained as a mixture of isomers. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.59-7.09 (m, 12.6H), 6.95 (d, J = 5.2 Hz, 1.2H), 6.85 (s, 1.2H), 6.78 (s, 0.8H), 6.65 (s, 1.2H), 5.82-5.72 (m, 0.6H), 5.69-5.61 (m, 0.3H), 4.98-4.85 (m, 2H), 4.32 (s, 1.2H), 4.13-4.04 (m, 0.8H), 3.58 (s, 0.8), 2.36-2.28 (m, 2.4H), 2.21-2.09 (m, 3.8H), 1.99 (s, 6H), 1.91-1.90 (m, 1.2H), 1.45-1.42 (m, 0.8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.2, 146.0, 138.7, 136.1, 130.2, 129.1, 128.8, 128.7, 128.4, 128.2, 128.1, 128.0, 127.7, 127.6, 127.0, 126.3, 114.4, 50.5, 47.5, 37.4, 28.8, 20.7, 20.6, 18.7, 17.8, 17.6; HRMS (EI): m/z $[M]^+$ calcd. for $C_{34}H_{36}N_2^+$: 472.2878, found: 472.2874.

Synthesis of various imidazolinium salts



1a~1k (n = 1 or 2) **2a~2k** (n = 1 or 2)

Scheme S3: Synthesis of various imidazolinium salts **2a~2k.**

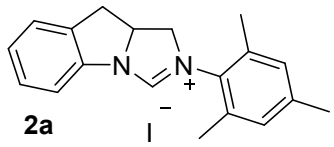
General procedure C:

A Schlenk tube was chareged with formamidines (1.0 eq.) and NIS (1.0 eq.), evacuated and filled with N_2. Dry toluene was added, the mixture was stirred at room temperature for 1~3 h, and yellow precipitate formed slowly. Filtered the precipitate, and washed with hot toluene. The filtrate was concentrated by distillation, and a second precipitate formed. Combine it with the first precipitate to obtain the desired product.

General procedure D:

A Schlenk tube was chareged with benzimidamides (1.0 eq.) and NIS (2.0 eq.), evacuated and filled with N_2. Dry toluene was added. The reaction mixture was stirred at room temperature for 3 h, and monitored by TLC. After the reaction is completed, the mixture was quenched with saturated $Na_2S_2O_3$ aqueous solution, and extracted by DCM three times. The organic layer was dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (DCM/EtOH) on silica gel to provide the desired product.

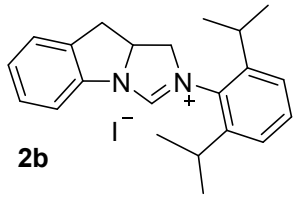
2-mesityl-9,9a-dihydro-1H-imidazo[1,5-a]indol-2-ium iodide (2a)



2a

Following general procedure C, formamidine **1a** (300 mg, 1.08 mmol, 1.0 eq.), NIS (243 mg, 1.08 mmol, 1.0 eq.) and toluene 30 mL afford **2a** as pale yellow powder (320 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.27 (s, 1H), 8.19 (d, J = 7.6 Hz, 1H), 7.38-7.33 (m, 2H), 7.31-7.27 (m, 1H), 6.94 (d, J = 7.6 Hz, 2H), 5.47-5.36 (m, 1H), 4.59 (t, J = 11.6 Hz, 1H), 4.16 (t, J = 12.0 Hz, 1H), 3.62 (dd, J = 15.6 Hz, 8.4 Hz, 1H), 3.27 (dd, J = 15.6 Hz, 10.4 Hz, 1H), 2.41 (s, 3H), 2.29 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ = 155.2, 139.6, 136.8, 135.3, 131.4, 129.4, 128.2, 127.2, 126.7, 114.8, 64.4, 56.3, 34.2, 20.6, 18.0, 17.5; HRMS (ESI): m/z [M – I]$^+$ calcd. for $C_{19}H_{21}N_2^+$: 277.1705, found: 277.1705.

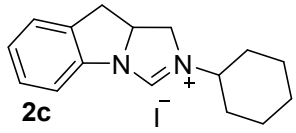
2-(2,6-diisopropylphenyl)-9,9a-dihydro-1H-imidazo[1,5-a]indol-2-ium (2b)



2b

Following general procedure C, formamidine **1b** (200 mg, 0.63 mmol, 1.0 eq.), NIS (142 mg, 0.63 mmol, 1.0 eq.) and toluene 20 mL afford **2b** as pale brown powder (98 mg, 36%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.46 (s, 1H), 8.30 (d, J = 7.6 Hz, 1H), 7.47-7.44 (m, 1H), 7.40-7.28 (m, 4H), 7.25-7.23 (m, 1H), 5.43-5.36 (m, 1H), 4.61 (t, J = 12.0 Hz, 1H), 4.12 (t, J = 12.4 Hz, 1H), 3.69 (dd, J = 15.6 Hz, 8.0 Hz, 1H), 3.27 (dd, J = 15.2 Hz, 10.0 Hz, 1H), 3.07-3.00 (m, 1H), 2.72-2.66 (m, 1H), 1.33 (d, J = 6.8 Hz, 3H), 1.30 (d, J = 6.8 Hz, 3H), 1.27 (d, J = 6.8 Hz, 3H), 1.23 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.8, 146.5, 145.4, 135.9, 134.0, 131.4, 129.8, 129.0, 128.1, 126.4, 124.9, 124.8, 117.0, 65.2, 60.0, 35.7, 29.0, 28.9, 25.3, 25.0, 24.5, 24.0; HRMS (ESI): m/z [M – I]$^+$ calcd. for $C_{22}H_{27}N_2^+$: 319.2174, found: 319.2180.

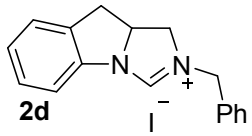
2-cyclohexyl-9,9a-dihydro-1H-imidazo[1,5-a]indol-2-ium iodide (2c)



2c

Following general procedure C, formamidine **1c** (200 mg, 0.83 mmol, 1.0 eq.), NIS (187 mg, 0.83 mmol, 1.0 eq.) and toluene 20 mL afford **2c** as pale yellow powder (196 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.09 (s, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.30-7.26 (m, 2H), 7.20-7.14 (m, 1H), 5.14-5.06 (m, 1H), 4.46 (t, J = 11.6 Hz, 1H), 4.00-3.88 (m, 2H), 3.43 (dd, J = 15.2 Hz, 8.0 Hz, 1H), 3.25 (dd, J = 15.2 Hz, 10.0 Hz, 1H), 2.21-2.19 (m, 2H), 1.87-1.84 (m, 2H), 1.70-1.60 (m, 3H), 1.43-1.33 (m, 2H), 1.24-1.14 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.6, 136.8, 133.1, 128.8, 128.7, 128.4, 128.0, 126.9, 126.1, 125.0, 115.4, 63.4, 58.9, 53.4, 35.2, 31.3, 31.2, 24.5, 24.4 21.2; HRMS (ESI): m/z $[M - I]^+$ calcd. for $C_{16}H_{21}N_2^+$: 241.1705, found: 241.1706.

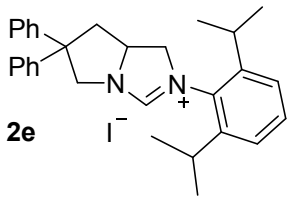
2-benzyl-9,9a-dihydro-1H-imidazo[1,5-a]indol-2-ium iodide (2d)



2d

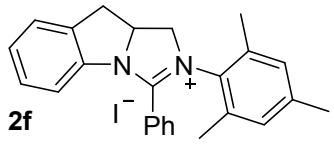
Following general procedure C, formamidine **1d** (200 mg, 0.80 mmol, 1.0 eq.), NIS (180 mg, 0.80 mmol, 1.0 eq.) and toluene 20 mL afford **2d** as pale yellow powder (127 mg, 42%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.47 (s, 1H), 7.65 (d, J = 7.6 Hz, 1H), 7.50-7.49 (m, 2H), 7.42-7.41 (m, 3H), 7.31-7.29 (m, 2H), 7.23-7.19 (m, 1H), 5.17 (d, J = 11.4 Hz, 1H), 5.05-4.97 (m, 1H), 4.99 (d, J = 11.4 Hz, 1H), 4.19 (t, J = 11.2 Hz, 1H), 3.89 (t, J = 11.2 Hz, 1H), 3.39-3.24 (m, 2H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ = 160.8, 155.4, 134.0, 137.6, 134.2, 133.1, 131.7, 129.9, 129.8, 129.0, 128.8, 128.7, 128.6, 128.0, 127.6, 126.6, 126.4, 125.9, 124.4, 114.3, 111.0, 63.8, 54.3, 53.4, 51.9, 50.8, 45.0, 34.6, 31.8; HRMS (ESI): m/z $[M - I]^+$ calcd. for $C_{17}H_{17}N_2^+$: 249.1392, found: 249.1382.

2-(2,6-diisopropylphenyl)-6,6-diphenyl-5,6,7,7a-tetrahydro-1H-pyrrolo[1,2-c]imidazol-2-ium (2e)



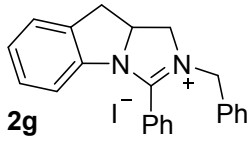
Following general procedure C, formamidine **1e** (300 mg, 0.71 mmol, 1.0 eq.), NIS (160 mg, 0.71 mmol, 1.0 eq.) and toluene 30 mL afford **2e** as pale white powder (202 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.99 (s, 1H), 7.54 (d, J = 8.0 Hz, 2H), 7.43-7.39 (m, 3H), 7.36-7.24 (m, 5H), 7.22-7.16 (m, 3H), 5.55 (d, J = 12.8 Hz, 1H), 5.03-4.94 (m, 1H), 4.45 (d, J = 12.8 Hz, 1H), 4.18 (t, J = 11.6 Hz, 1H), 3.96 (t, J = 10.8 Hz, 1H), 3.10 (dd, J = 13.2 Hz, 7.2 Hz, 1H), 2.91 (dd, J = 12.8 Hz, 7.6 Hz, 1H), 2.82-2.76 (m, 1H), 2.21-2.14 (m, 1H), 1.28 (d, J = 6.8 Hz, 3H), 1.26 (d, J = 6.8 Hz, 3H), 1.16 (d, J = 6.8 Hz, 3H) 1.06 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.7, 146.2, 145.4, 144.1, 142.9, 130.9, 129.2, 129.1, 128.8, 128.7, 128.0, 127.2, 126.9, 126.7, 126.4, 125.1, 124.7, 124.6, 62.3, 60.1, 57.5, 56.6, 42.5, 28.5, 28.1, 25.1, 24.9, 24.3, 23.7; HRMS (ESI): m/z $[M - I]^+$ calcd. for $C_{30}H_{35}N_2^+$: 423.2800, found: 423.2813.

2-mesityl-3-phenyl-9,9a-dihydro-1H-imidazo[1,5-a]indol-2-ium iodide (2f)



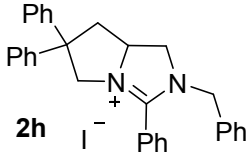
Following general procedure D, formamidine **1f** (300 mg, 0.85 mmol, 1.0 eq.), NIS (382 mg, 1.70 mmol, 2.0 eq.) and toluene 15 mL afford **2f** as pale yellow powder (280 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.71-7.67 (m, 1H), 7.55-7.54 (m, 3H), 7.43-7.41 (m, 1H), 7.27-7.24 (m, 2H), 7.08 (t, J = 16.0 Hz, 1H), 6.94 (s, 1H), 6.78-6.76 (m, 2H), 6.19-6.10 (m, 1H), 4.97 (t, J = 12.0 Hz, 1H), 4.65 (t, J = 16.0 Hz, 1H), 3.89 (dd, J = 16.4 Hz, 8.8 Hz, 1H), 3.52 (dd, J = 16.0 Hz, 10.0 Hz, 1H), 2.48 (s, 3H), 2.24 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.1, 140.3, 137.3, 135.2, 134.8, 134.5, 134.3, 130.7, 130.0, 129.8, 129.3, 128.1, 128.0, 126.8, 121.1, 114.5, 65.1, 57.8, 35.6, 20.8, 18.7, 18.6; HRMS (ESI): m/z $[M - I]^+$ calcd. for $C_{25}H_{25}N_2^+$:353.2018, found: 353.2028.

2-benzyl-3-phenyl-9,9a-dihydro-1H-imidazo[1,5-a]indol-2-ium iodide (2g)



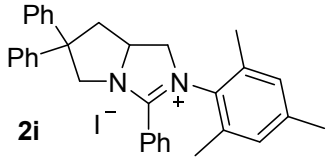
2g Following general procedure D, formamidine **1g** (100 mg, 0.31 mmol, 1.0 eq.), NIS (140 mg, 0.62 mmol, 2.0 eq.) and toluene 15 mL afford **2g** as pale yellow powder (55 mg, 39%).^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.12 (d, J = 7.2 Hz, 1H), 8.01 (d, J = 7.6 Hz, 1H), 7.82-7.76 (m, 2H), 7.67-7.63 (m, 1H), 7.41-7.39 (m, 3H), 7.32-7.26 (m, 3H), 7.18-7.14 (m, 1H), 7.01-6.97 (m, 1H), 6.40 (d, J = 8.0 Hz, 1H), 5.50-5.40 (m, 1H), 4.94 (d, J = 15.2 Hz, 1H), 4.86 (d, J = 15.2 Hz, 1H), 4.56 (t, J = 11.6 Hz, 1H), 4.40 (t, J = 11.6 Hz, 1H), 3.66 (dd, J = 15.6 Hz, 10.0 Hz, 1H), 3.40 (dd, J = 15.6 Hz, 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.7, 137.6, 134.4, 133.9, 132.1, 130.6, 129.6, 129.3, 129.2, 128.9, 128.3, 127.8, 127.4, 126.5, 121.4, 114.3, 63.7, 54.3, 52.7, 34.8; HRMS (ESI): m/z $[M - I]^+$ calcd. for $C_{23}H_{21}N_2^+$:325.1705, found: 325.1709.

2-benzyl-3,6,6-triphenyl-1,2,5,6,7,7a-hexahydropyrrolo[1,2-c]imidazol-4-ium iodide (2h)



2h Following general procedure D, formamidine **1h**(400 mg, 0.93 mmol, 1.0 eq.), NIS (419 mg, 1.86 mmol, 2.0 eq.) and toluene 25 mL afford **2h** as pale yellow powder (400mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.90 (d, J = 7.2 Hz, 2H), 7.71 (t, J = 7.6 Hz, 1H), 7.62 (t, J = 7.2 Hz, 2H), 7.35-7.28 (m, 6H), 7.25-7.17 (m, 7H), 7.07-7.05 (m, 2H), 4.90 (d, J = 15.6 Hz, 1H), 4.81 (d, J = 15.6 Hz, 1H), 4.78-4.69 (m, 1H), 4.56 (t, J = 11.2 Hz, 1H), 4.27 (d, J = 11.2 Hz, 1H), 4.09 (t, J = 12.0 Hz, 1H), 3.85 (d, J = 11.2 Hz, 1H), 3.58 (dd, J = 12.4 Hz, 8.4 Hz, 1H), 2.69 (dd, J = 15.6 Hz, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.6, 144.1, 142.9, 134.2, 132.3, 130.2, 129.8, 129.1, 128.9, 128.8, 128.7, 128.6, 128.0, 127.9, 127.2, 127.0; 126.5, 122.0, 60.2, 58.1, 57.2, 54.5, 52.2, 41.4; HRMS (ESI): m/z $[M - I]^+$ calcd. for $C_{31}H_{29}N_2^+$: 429.2331, found: 429.2332; Anal. Calcd for $C_{31}H_{29}IN_2$: C, 66.91; H, 5.25; N, 5.03. Found: C, 66.61; H, 5.37; N, 4.48.

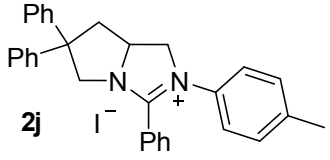
2-mesityl-3,6,6-triphenyl-5,6,7,7a-tetrahydro-1H-pyrrolo[1,2-c]imidazol-2-ium iodide (2i)



2i

Following general procedure D, formamidine **1i** (500 mg, 1.09 mmol, 1.0 eq.), NIS (491 mg, 2.18 mmol, 2.0 eq.) and toluene 25 mL afford **2i** as pale yellow powder (485mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65-7.61 (m, 1H), 7.47-7.39 (m, 4H), 7.29-7.27 (m, 5H), 7.23-7.18 (m, 5H), 6.86 (s, 1H), 6.68 (s, 1H), 5.77-5.71 (m, 1H), 4.57 (d, *J* = 12.4 Hz, 1H), 4.43-4.35 (m, 3H), 3.35-3.21 (m, 2H), 2.20 (s, 3H), 2.00 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.5, 143.6, 142.3, 140.0, 135.0, 134.4, 134.0, 131.0, 130.2, 130.1, 129.8, 129.5, 129.1, 128.7, 127.4, 126.9, 126.8, 126.5, 121.6, 60.8, 58.9, 58.1, 57.1, 41.6, 20.8, 18.1, 17.9; HRMS (ESI): m/z $[M - I]^+$ calcd. for $C_{33}H_{33}N_2^+$:457.2644, found: 457.2646; Anal. Calcd for $C_{33}H_{33}IN_2$: C, 67.81; H, 5.69; N, 4.79. Found: C, 66.53; H, 6.04; N, 4.53.

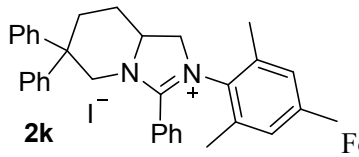
3,6,6-triphenyl-2-(p-tolyl)-5,6,7,7a-tetrahydro-1H-pyrrolo[1,2-c]imidazol-2-ium iodide (2j)



2j

Following general procedure D, formamidine **1j** (200 mg, 0.47 mmol, 1.0 eq.), NIS (212 mg, 0.94 mmol, 2.0 eq.) and toluene 15 mL afford **2j** as pale yellow powder (164mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.39 (dd, *J* = 14.8 Hz, 7.6 Hz, 4H), 7.31-7.26 (m, 7H), 7.24-7.17 (m, 3H), 7.07 (d, *J* = 8.0 Hz, 2H), 5.45 (t, *J* = 11.2 Hz, 1H), 4.99-4.90 (m, 1H), 4.48 (d, *J* = 11.2 Hz, 1H), 4.37 (t, *J* = 11.2 Hz, 1H), 4.02 (d, *J* = 11.6 Hz, 1H), 3.94 (dd, *J* = 12.4 Hz, 9.2 Hz, 1H), 2.77 (dd, *J* = 12.8 Hz, 9.2 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.4, 144.2, 142.8, 138.9, 134.1, 133.8, 131.2, 130.1, 130.0, 129.2, 129.0, 128.9, 128.8, 128.7, 128.6, 127.7, 127.3, 127.2, 127.1, 126.7, 126.6, 126.4, 124.7, 122.0, 60.5, 59.3, 58.3, 57.9, 41.0, 21.0; HRMS (ESI): m/z $[M - I]^+$ calcd. for $C_{31}H_{29}N_2^+$: 429.2331, found: 429.2332.

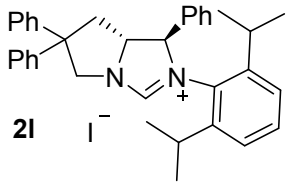
2-mesityl-3,6,6-triphenyl-1,5,6,7,8,8a-hexahydroimidazo[1,5-a]pyridin-2-ium iodide (2k)



2k

Following general procedure D, formamidine **1k** (100 mg, 0.21 mmol, 1.0 eq.), NIS (95 mg, 0.42 mmol, 2.0 eq.) and toluene 10 mL afford **2k** as pale yellow powder (70 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57-7.45 (m, 2H), 7.43-7.41 (m, 2H), 7.35-7.29 (m, 1H), 7.25-7.15 (m, 6H), 7.07-7.05 (m, 2H), 6.95-6.93 (m, 2H), 6.86 (s, 1H), 6.71 (s, 1H), 5.84-5.75 (m, 1H), 4.83 (d, *J* = 13.6 Hz, 1H), 4.53-4.41 (m, 2H), 3.64 (dd, *J* = 11.2 Hz, 8.0Hz 1H), 2.86-2.82 (m, 1H), 2.69-2.61 (m, 1H), 2.34-2.29 (m, 2H), 2.20 (s, 3H), 2.13 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ =163.2, 145.1, 140.9, 139.9, 135.9, 134.9, 133.1, 130.1, 130.0, 129.4, 128.7, 127.8, 126.9, 126.8, 126.7, 126.4, 121.1, 58.7, 56.4, 53.7, 47.5, 33.2, 28.3, 20.8, 19.1, 17.3; HRMS (ESI): m/z $[M - I]^+$ calcd. for $C_{34}H_{35}N_2^+$: 471.2800, found: 471.2795.

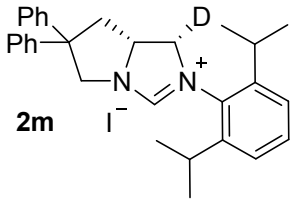
2-(2,6-diisopropylphenyl)-1,6,6-triphenyl-5,6,7,7a-tetrahydro-1H-pyrrolo[1,2-c]imidazol-2-ium iodide (2l)



2l

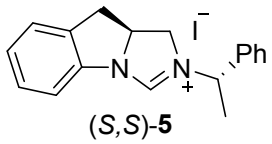
Following general procedure C, formamidine **1l** (300 mg, 0.60 mmol, 1.0 eq.), NIS (135 mg, 0.60mmol, 1.0 eq.) and toluene 30 mL afford brown powder, and then quenched with saturated $Na_2S_2O_3$, and extracted by DCM three times. The organic layer was dried over Na_2SO_4, and concentrated in vacuo afford **2l** as a pale white power (165 mg, 44%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.32 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.37-7.28 (m, 10H), 7.16-7.13 (m, 3H), 6.95 (d, *J* = 7.6 Hz, 1H), 5.70 (d, *J* = 12.4 Hz, 1H), 5.21 (d, *J* = 8.8 Hz, 1H), 5.13-5.07 (m, 1H), 4.62 (d, *J* = 13.2 Hz, 1H), 3.17 (dd, *J* = 12.8 Hz, 6.8 Hz, 1H), 2.87 (dd, *J* = 12.4 Hz, 8.4 Hz, 1H), 2.50-2.41 (m, 2H), 1.29 (d, *J* = 6.8 Hz, 3H), 1.18 (d, *J* = 6.4 Hz, 3H), 1.16 (d, *J* = 6.4 Hz, 3H), 0.43 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.8, 147.5, 145.2, 143.9, 143.5, 131.6, 131.4, 130.6, 129.7, 129.5, 129.3, 129.2, 127.8, 127.5, 127.3, 126.7, 126.6, 125.1, 125.0, 68.8, 57.7, 57.4, 42.9, 29.1, 28.9, 27.0, 25.9, 24.3, 22.6; HRMS (ESI): m/z $[M - I]^+$ calcd. for $C_{36}H_{39}N_2^+$: 499.3113, found: 499.3116.

2-(2,6-diisopropylphenyl)-6,6-diphenyl-5,6,7,7a-tetrahydro-1H-pyrrolo[1,2-c]imidazol-2-ium-1-d (2m)



Following general procedure C, formamidine **1m** (200 mg, 0.36 mmol, 1.0 eq.), NIS (135 mg, 0.36mmol, 1.0 eq.) and toluene 30 mL afford **2m** as a pale white power (105 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.32 (s, 1H), 7.50 (d, J = 7.2 Hz, 2H), 7.45-7.41(m, 3H), 7.38-7.28 (m, 5H), 7.24-7.22(m, 2H), 7.19 (dd, J = 7.6 Hz, 0.8 Hz, 1H) 5.27 (d, J = 12.8 Hz, 1H), 5.08-5.02 (m, 1H), 4.55 (d, J = 12.4Hz, 1H), 4.22 (d, J = 11.2 Hz, 1H), 3.11 (dd, J = 12.8 Hz, 7.2 Hz, 1H), 2.99 (dd, J = 13.2 Hz, 7.6 Hz, 1H), 2.88-2.81 (m, 1H), 2.27-2.20(m, 1H), 1.30 (d, J = 6.0 Hz, 6H), 1.28 (d, J = 6.4 Hz, 3H), 1.15 (d, J = 6.4 Hz, 3H) 1.11 (d, J = 6.8 Hz, 3H); HRMS (ESI): m/z [M – I]$^+$ calcd. for $C_{30}H_{34}DN_2^+$: 424.2863, found: 424.2861.

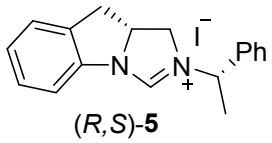
(S)-2-((S)-1-phenylethyl)-9,9a-dihydro-1H-imidazo[1,5-a]indol-2-ium (*(S,S)*-5)



(*S,S*)-**5**

Following general procedure C, formamidine **1n** (200 mg, 0.76 mmol, 1.0 eq.), NIS (171 mg, 0.76 mmol, 1.0 eq.) and toluene 20 mL afford a mixture of **(***S,S***)-5** and **(***R,S***)-5** as pale yellow powder. The mixture was recrystallized from CH_2Cl_2/Hexane to only obtain **(***S,S***)-5** (106 mg, 36%). The filtrate was concentrated by distillation, and the residue was purified by column chromatography (DCM/EtOH) on silica gel to provide **(***R,S***)-5** (91 mg, 31%). **(***S,S***)-5**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.26 (s, 1H), 7.91 (d, J = 7.6 Hz, 1H), 7.45-7.36 (m, 5H), 7.31-7.28 (m, 2H), 7.20 (t, J = 7.6 Hz, 1H), 5.20 (q, J = 6.4 Hz, 13.6 Hz, 1H), 5.02-4.92 (m, 1H), 4.05 (t, J = 11.6 Hz, 1H), 3.87 (t, J = 12.0Hz, 1H), 3.31 (d, J = 8.8 Hz, 2H), 1.91 (d, J = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.1, 137.3, 136.9, 133.2, 129.4, 129.2, 128.8, 127.4, 127.1, 126.2, 116.0, 63.9, 59.8, 53.6, 35.0, 20.9; HRMS (ESI): m/z [M – I]$^+$ calcd. for $C_{18}H_{19}N_2^+$:263.1548, found: 263.1548. $[\alpha]^{25}_D$ –260 (c = 0.100, CH_2Cl_2).

(*R*)-2-((*S*)-1-phenylethyl)-9,9a-dihydro-1H-imidazo[1,5-a]indol-2-ium iodide (*(R,S)*-5)

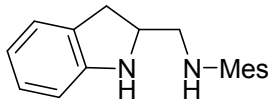


(*R,S*)-**5**

^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.29 (s, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.48-7.36 (m, 6H), 7.33-7.28 (m, 2H), 5.39 (q, *J* = 6.8 Hz, 13.6 Hz, 1H), 5.13-5.02 (m, 1H), 4.22 (t, *J* = 11.6 Hz, 1H), 3.74 (t, *J* = 11.6 Hz, 1H), 3.37 (dd, *J* = 15.6 Hz, 8.4 Hz, 1H), 3.15 (dd, *J* = 15.6 Hz, 10.4 Hz, 1H), 1.94 (d, *J* = 6.8Hz, 3H);

Synthesis of various vicinal diamine:

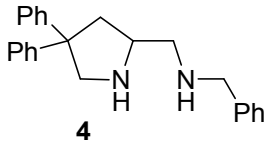
***N*-(indolin-2-ylmethyl)-2,4,6-trimethylaniline (3)**



3

Imidazolinium salt **2a** (200 mg, 0.49 mmol, 1.0 eq.) and KO^{t}Bu(66 mg, 0.59 mmol, 1.2eq.) was dissolved in 15 mL THF. The mixture was refluxed for 4 h, then added water and extracted with EtOAc for three times. The organic layer was dried over Na_2SO_4, and concentrated in vacuo. The residue was directly used for next step without further purified. The residue was dissolved in a 5:1 (v:v), MeOH:HCl solution, the mixture was refluxed for 3 h, and then 10% NaOH solution was added to make the pH = 10 and extracted with EtOAc for three times. The organic layer was dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (PE/EtOAc = 4:1) on silica gel to provide **3** as brown oil (61 mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.10 (d, *J* = 7.2 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.83 (s, 2H), 6.72 (t, *J* = 7.2 Hz, 1H), 6.67 (d, *J* = 7.6 Hz, 1H), 4.11-4.07 (m, 1H), 3.18 (dd, *J* = 15.6 Hz, 8.8 Hz, 1H), 3.04 (d, *J* = 5.2 Hz, 2H), 2.89 (dd, *J* = 15.6 Hz, 7.6 Hz, 1H), 2.27 (s, 6H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.7, 143.1, 131.6, 130.0, 129.4, 128.6, 127.3, 124.7, 118.7, 109.6, 59.7, 53.2, 33.6, 20.5, 18.2; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{18}H_{23}N_2^+$: 267.1861; found: 267.1873.

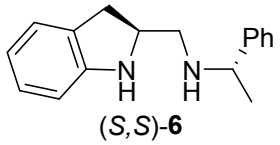
N-benzyl-1-(4,4-diphenylpyrrolidin-2-yl)methanamine (4)



4

Imidazolinium salt **2h** (200 mg, 0.36 mmol, 1.0 eq.) and KOH (24 mg, 0.43 mmol, 1.2eq.) was dissolved in 15 mL MeOH. The mixture was refluxed for 4 h, then added water and extracted with EtOAc for three times. The organic layer was dried over Na_2SO_4, and concentrated in vacuo. The residue was directly used for next step without further purified. The residue was dissolved in a 5:1 (v:v), MeOH:HCl solution, the mixture was refluxed for 24 h, and then 10% NaOH solution was added to make the pH= 10 and extracted with EtOAc for three times. The organic layer was dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (PE/EtOAc = 4:1) on silica gel to provide **4** as brown oil (76 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31-7.16 (m, 15H), 3.81 (d, J = 4.0 Hz, 1H), 3.64 (d, J = 11.6 Hz, 1H), 3.51-3.46 (m, 1H), 3.34 (d, J = 11.6 Hz, 1H), 2.84 (dd, J = 12.8 Hz, 7.2 Hz, 1H), 2.67-2.57 (m, 2H), 2.00 (dd, J = 12.8 Hz, 8.8 Hz, 1H), 1.80 (br, 2H). The data were agreement with previously reported[3].

(S)-N-(((S)-indolin-2-yl)methyl)-1-phenylethan-1-amine (*(S,S)*-6)

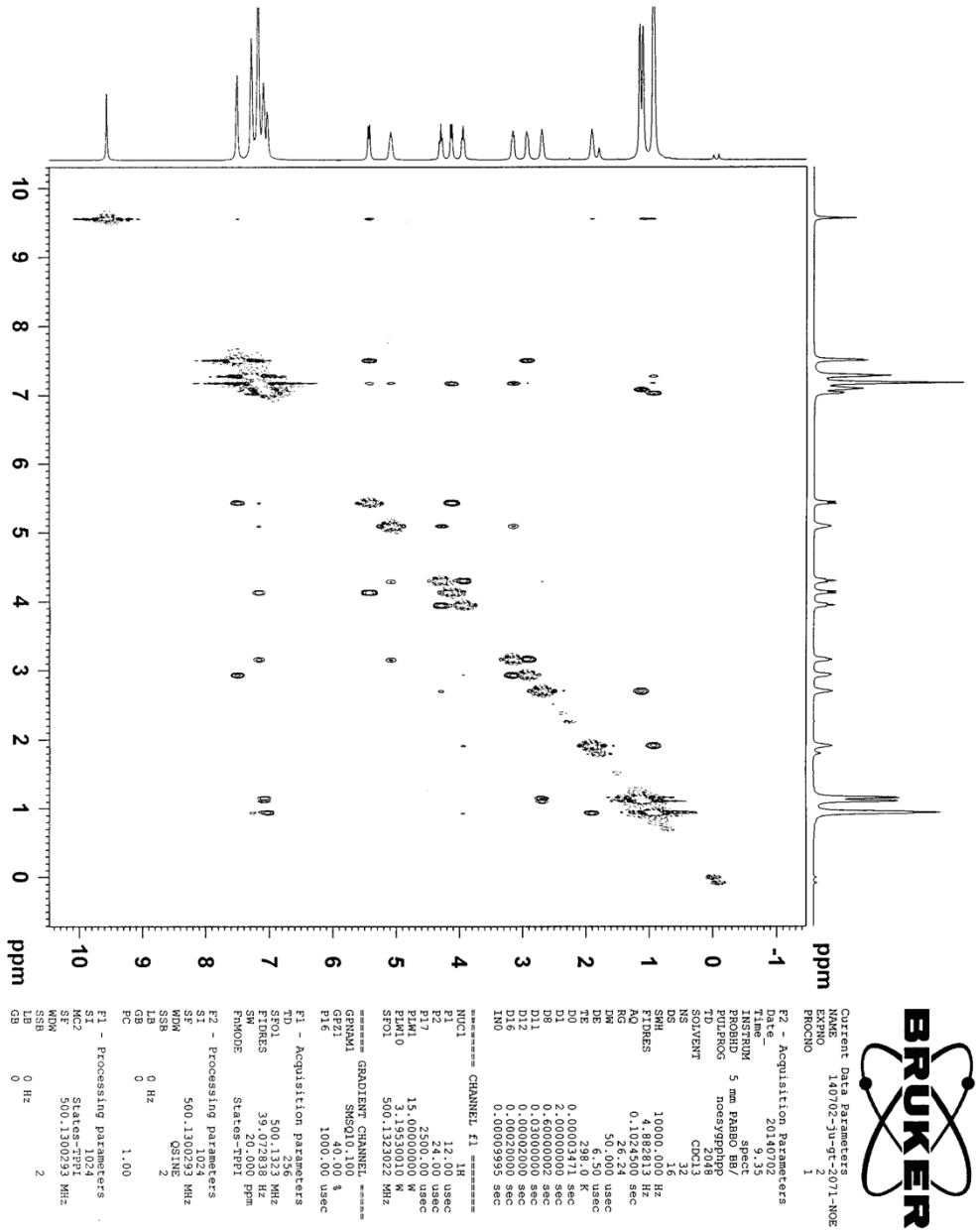


(*S,S*)-**6**

Imidazolinium salt *(S,S)*-**5** (200 mg, 0.51 mmol, 1.0 eq.) and KO^{t}Bu (68 mg, 0.61 mmol, 1.2eq.) was dissolved in 15 mL THF. The mixture was refluxed for 4 h, then added water and extracted with EtOAc for three times. The organic layer was dried over Na_2SO_4, and concentrated in vacuo. The residue was directly used for next step without further purified. The residue was dissolved in a 5:1 (v:v), MeOH:HCl solution, the mixture was refluxed for 3 h, and then 10% NaOH solution was added to make the pH = 10 and extracted with EtOAc for three times. The organic layer was dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (PE/EtOAc = 4:1) on silica gel to provide *(S,S)*-**6** as brown oil (90 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35-7.29 (m, 4H), 7.24-7.23 (m, 1H), 7.05 (d, J = 7.2 Hz, 1H), 7.01 (t, J = 7.6 Hz, 1H), 6.68 (t, J = 7.6 Hz, 1H), 6.63 (d, J = 8.0 Hz, 1H), 3.86-3.79 (m, 1H), 3.75 (q, J = 6.4 Hz, 12.8 Hz, 1H), 3.08 (dd, J = 16.0 Hz, 9.2 Hz, 1H), 2.66 (dd, J = 15.6 Hz, 7.2 Hz, 1H), 2.60-2.54 (m,

2H), 1.58 (br, 2H), 1.36 (d, J = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.7, 145.7, 128.6, 128.4, 127.2, 126.9, 126.4, 126.3, 124.7, 118.6, 109.6, 59.1, 58.6, 53.2 33.9, 24.3; HRMS (ESI): m/z [M + H]$^+$calcd for $C_{17}H_{21}N_2^+$: 253.1704; found: 253.1705. $[\alpha]^{25}_D$ –35 (c = 0.100, CH_2Cl_2).

NOE Spectra of 2e:



Reference:

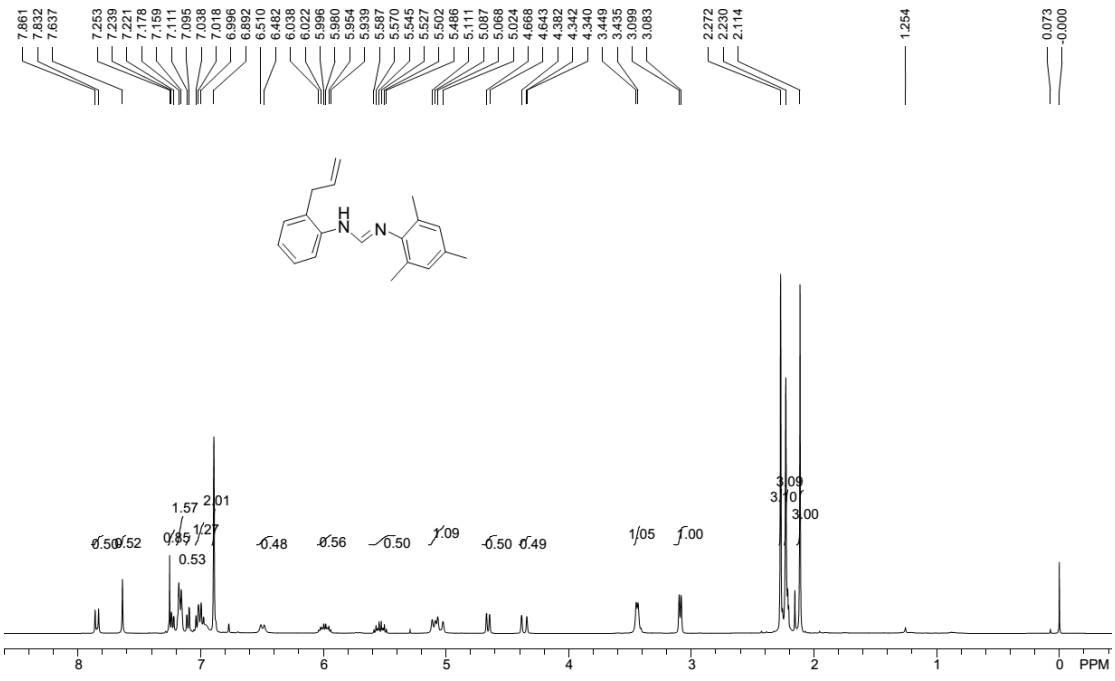
1. F. Qian, K. Liu, H. Ma, *Dalton Trans*. **2010**, *39*, 8071;

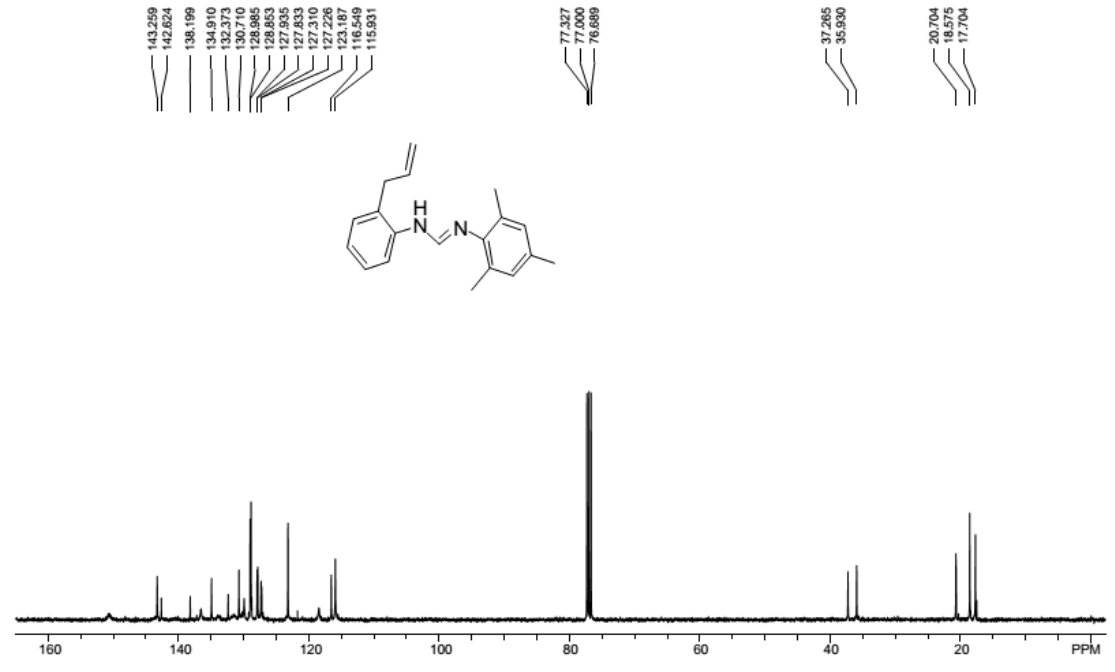
2. G. Zhang, Y. Luo, Y. Wang, L. Zhang, *Angew. Chem. Int. Ed*. **2011**, *50*, 4450;

3. Y. Wang, X. Zhu, S. Chiba. *J*. Am. Chem. Soc. **2012**, *134*, 3679.

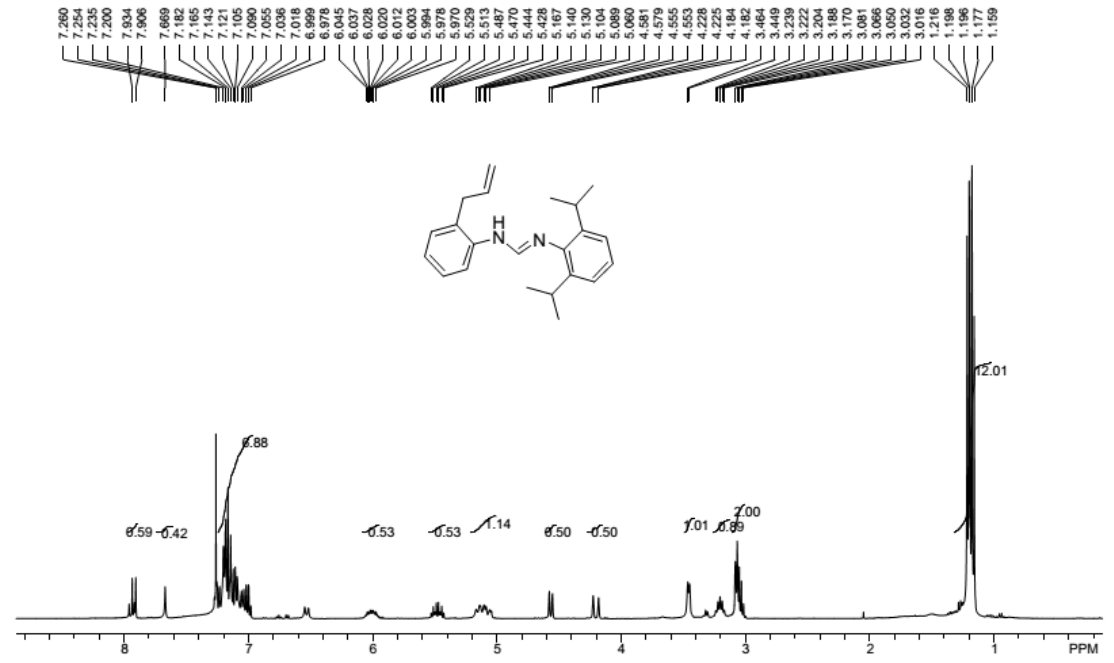
NMR Spectra:

1a





1b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6.999
6.978
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H
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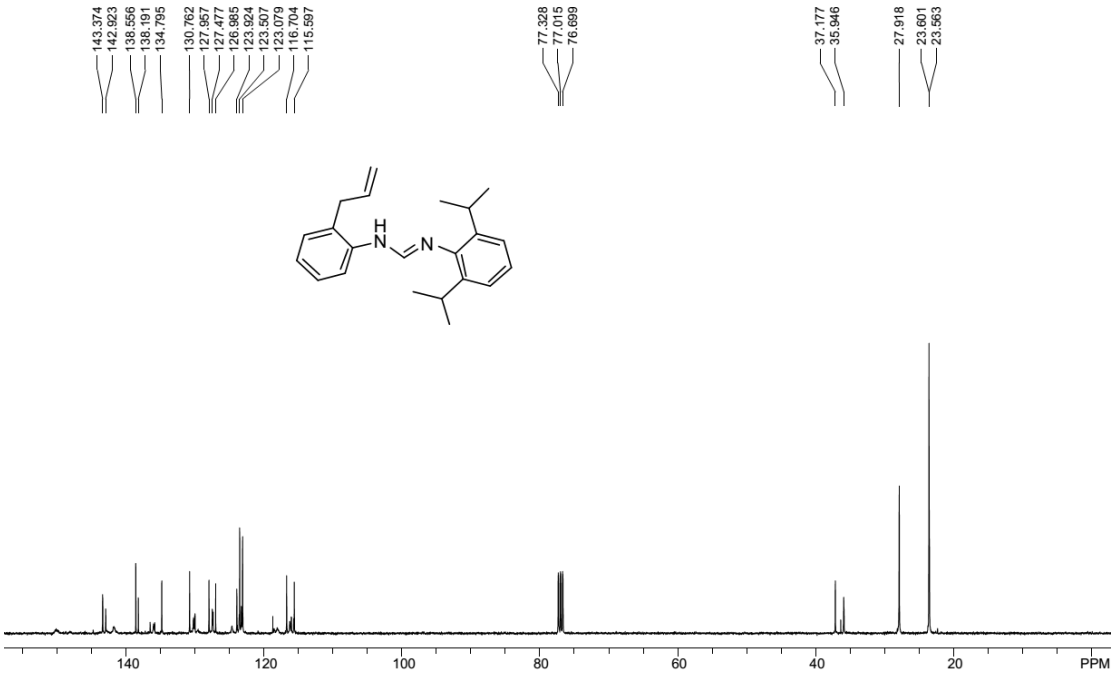
PPM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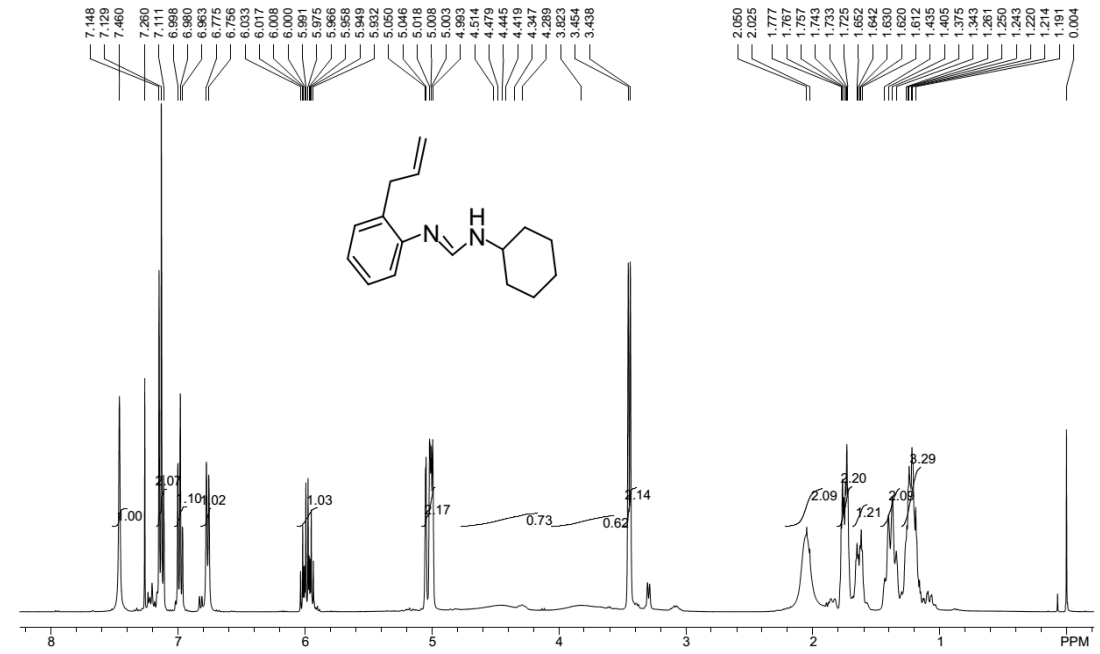
1c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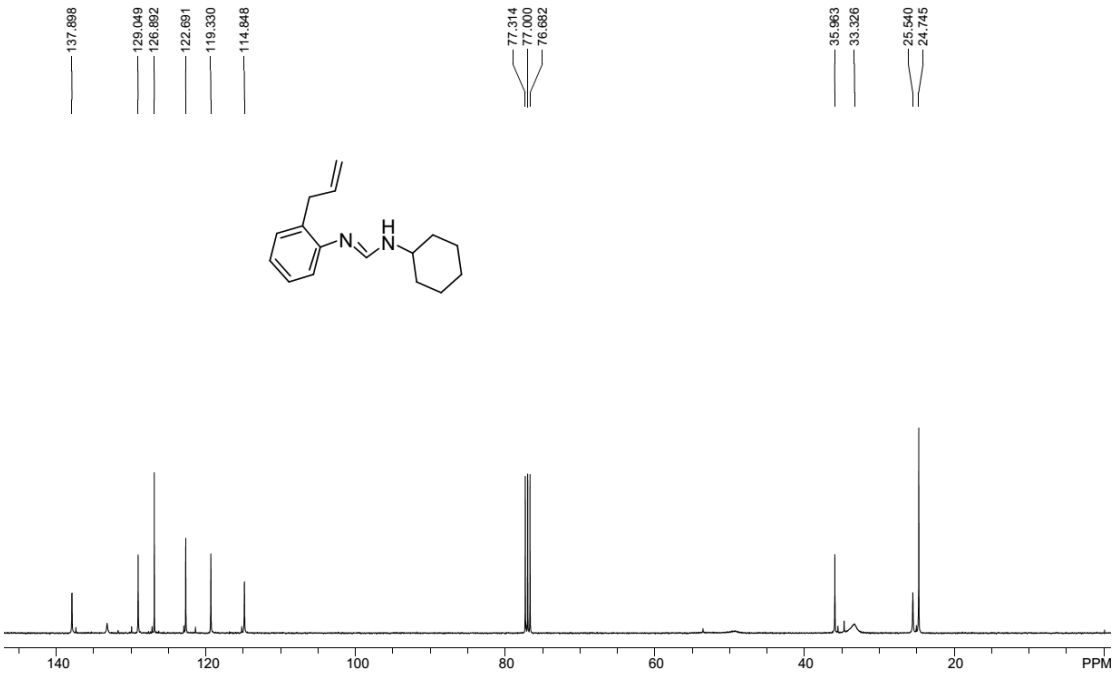
7
6
5
4
3
2
1
PPM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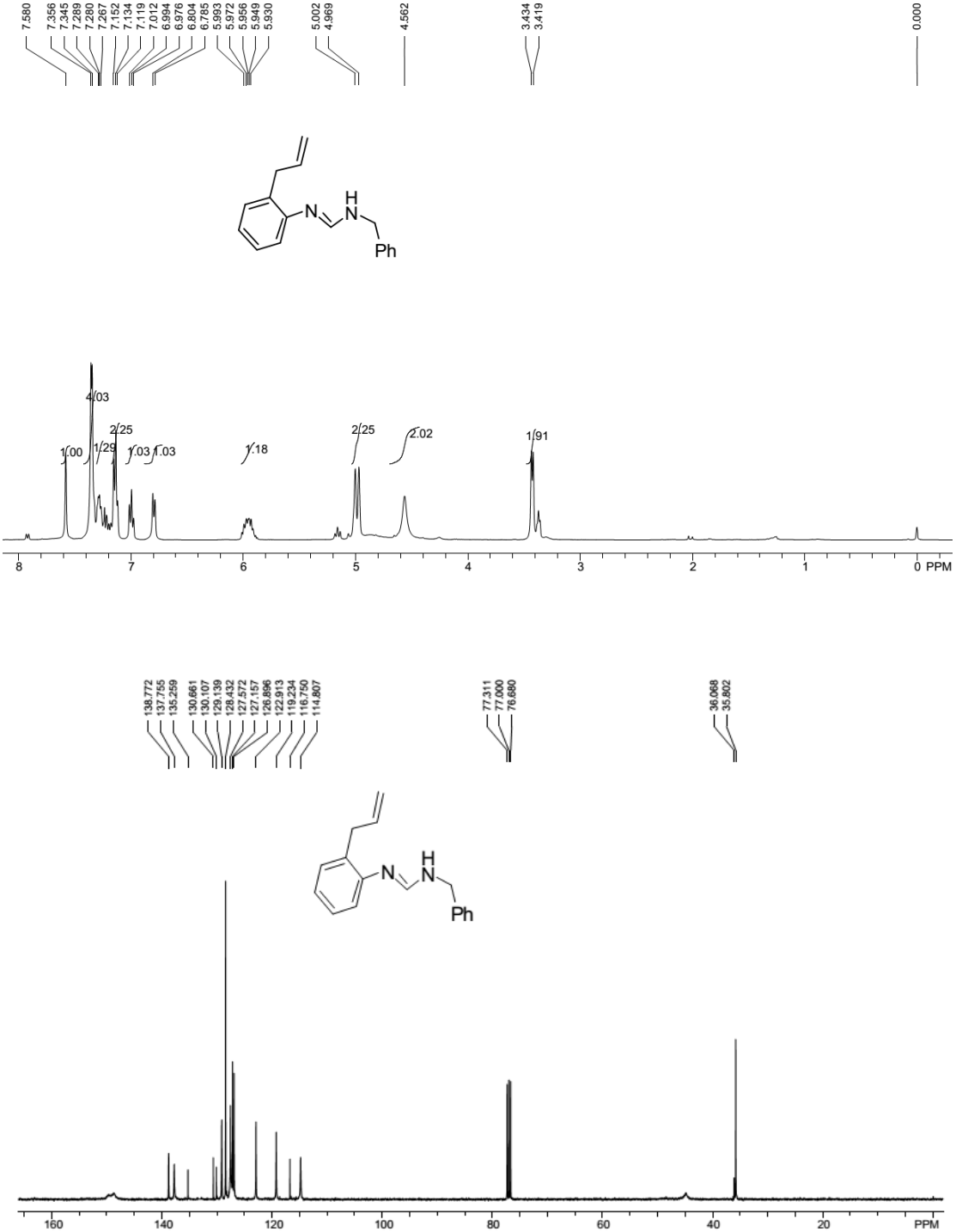
20
PPM

1d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N
Ph
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2.25
1.00
1.29
1.03
1.03
1.18
2.25
2.02
1.91
8
7
6
5
4
3
2
1
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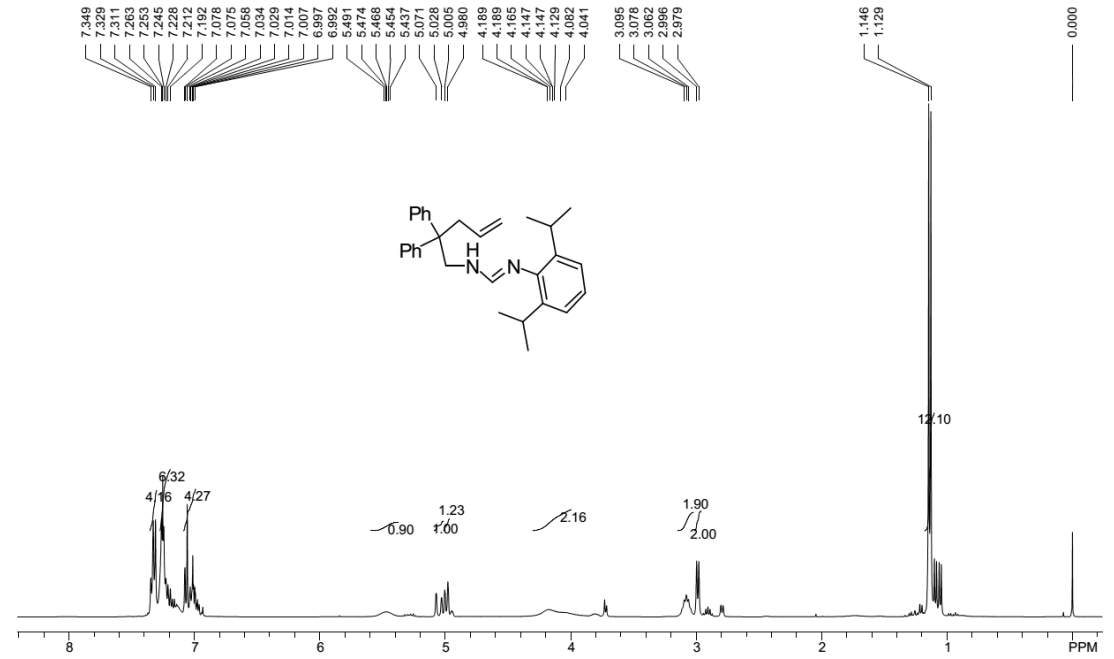
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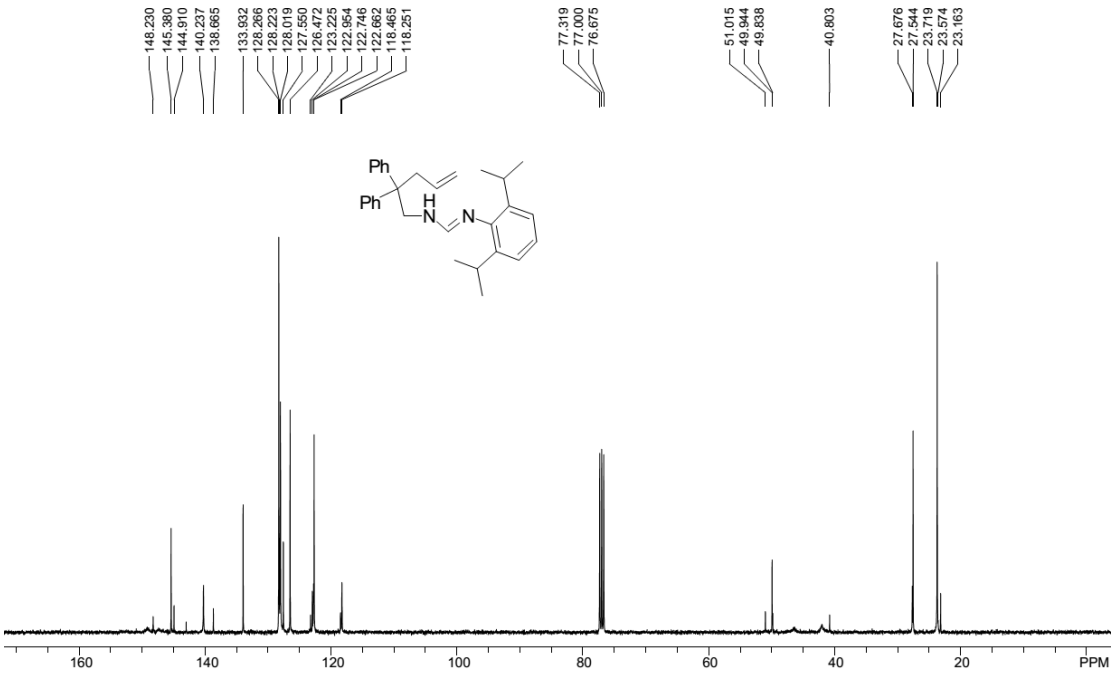
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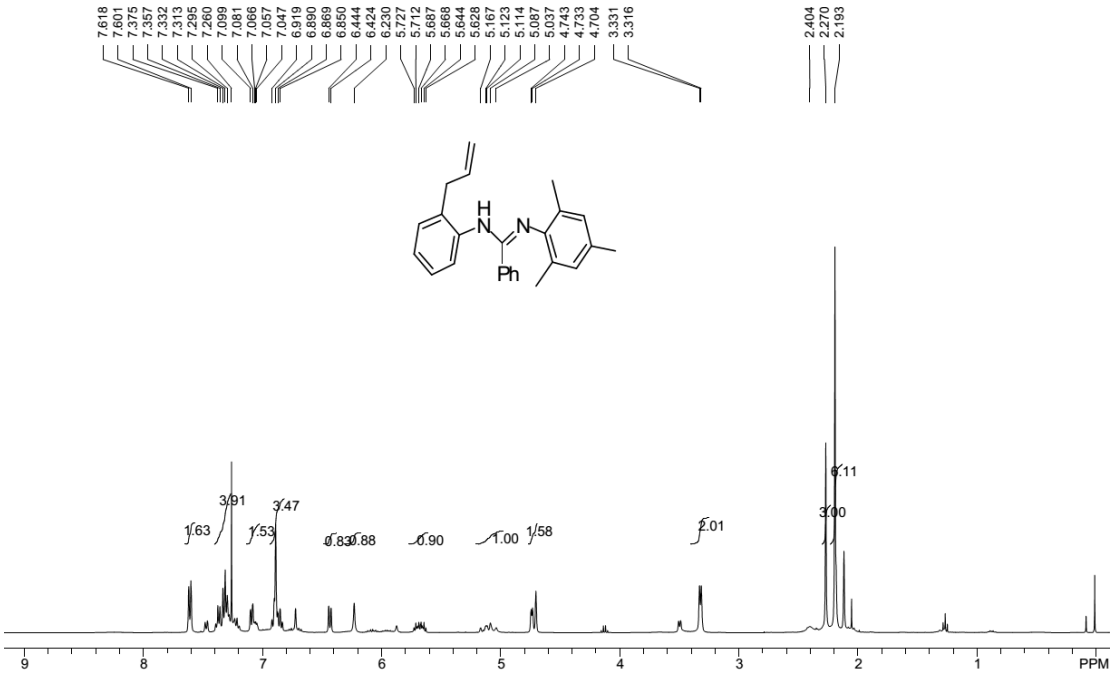
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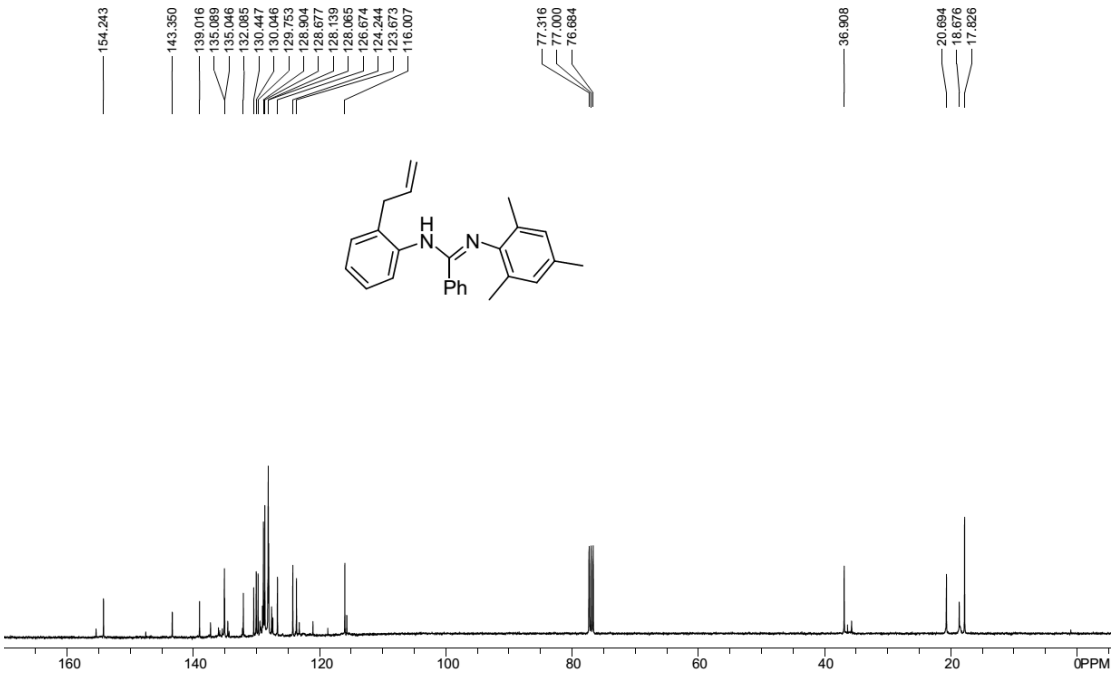
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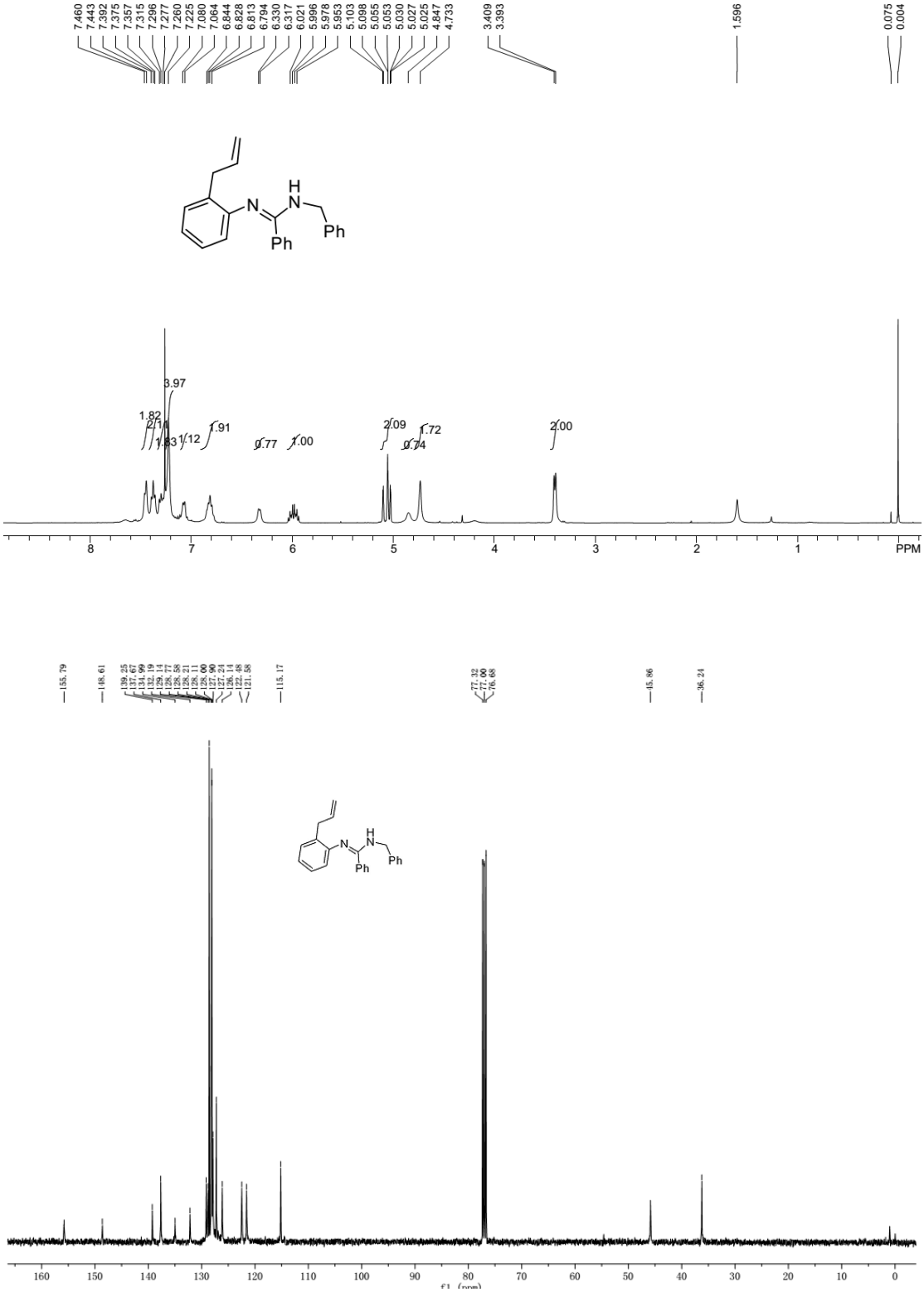
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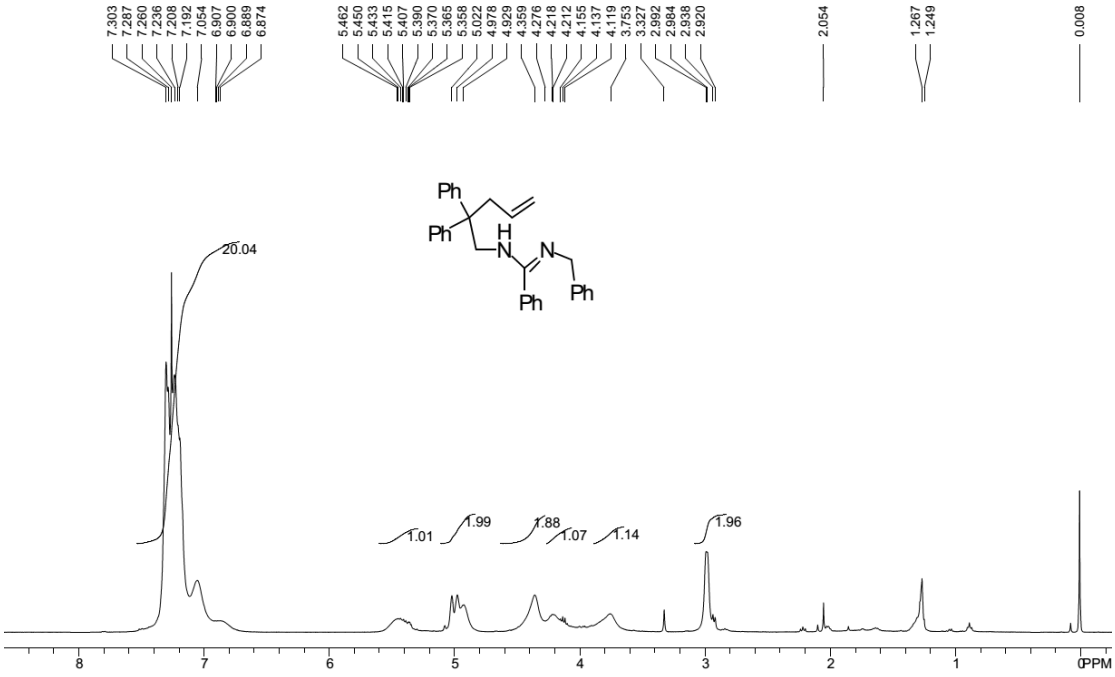
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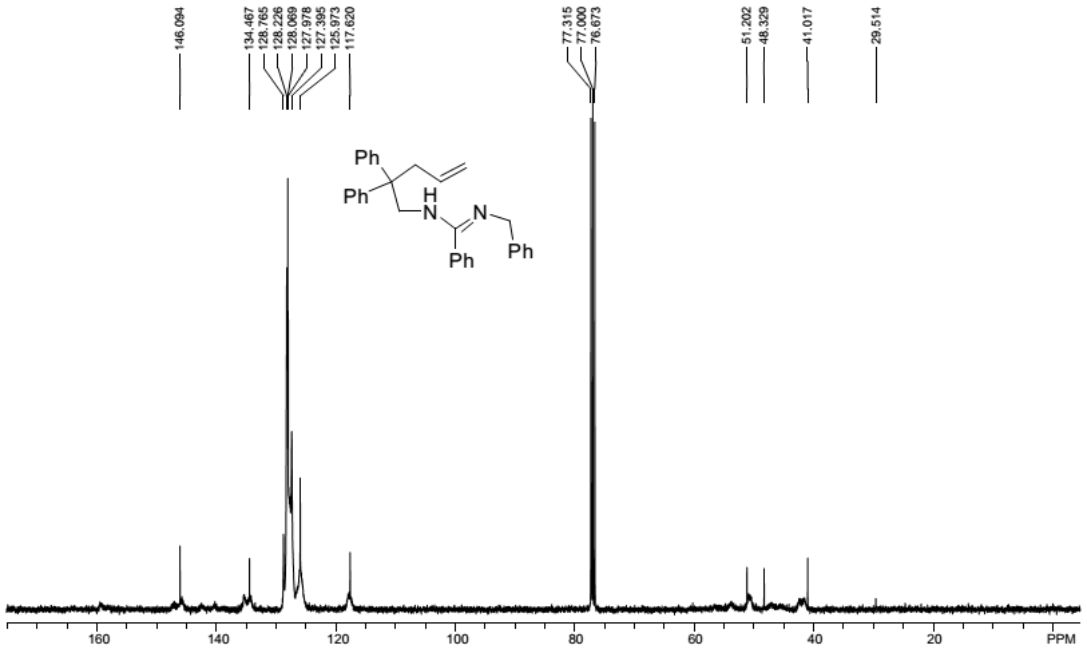
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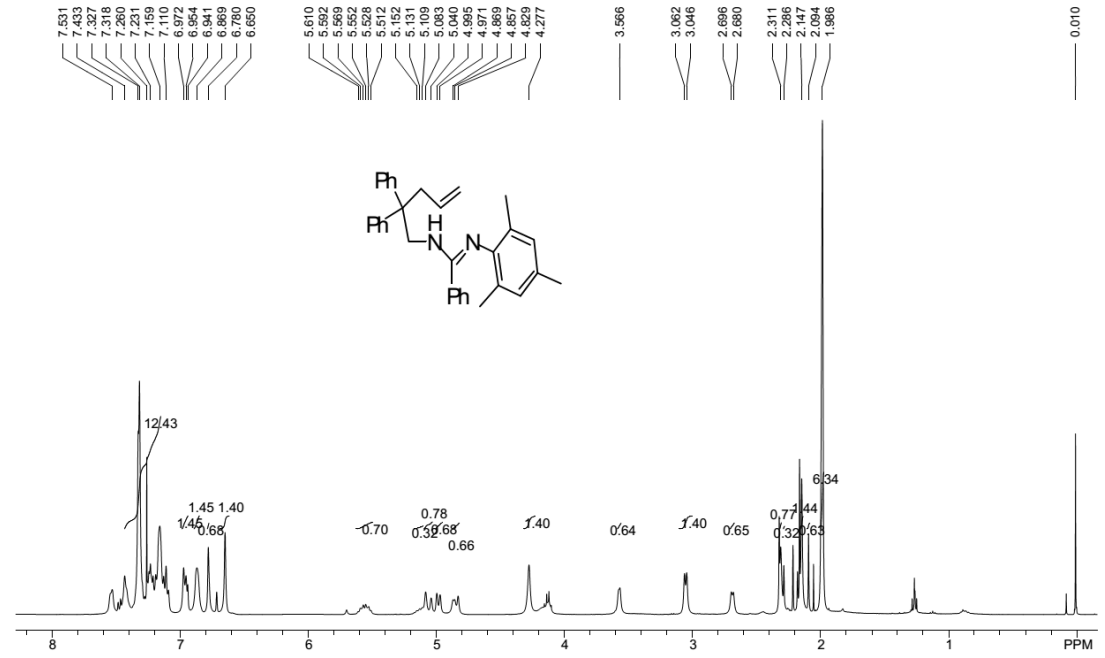
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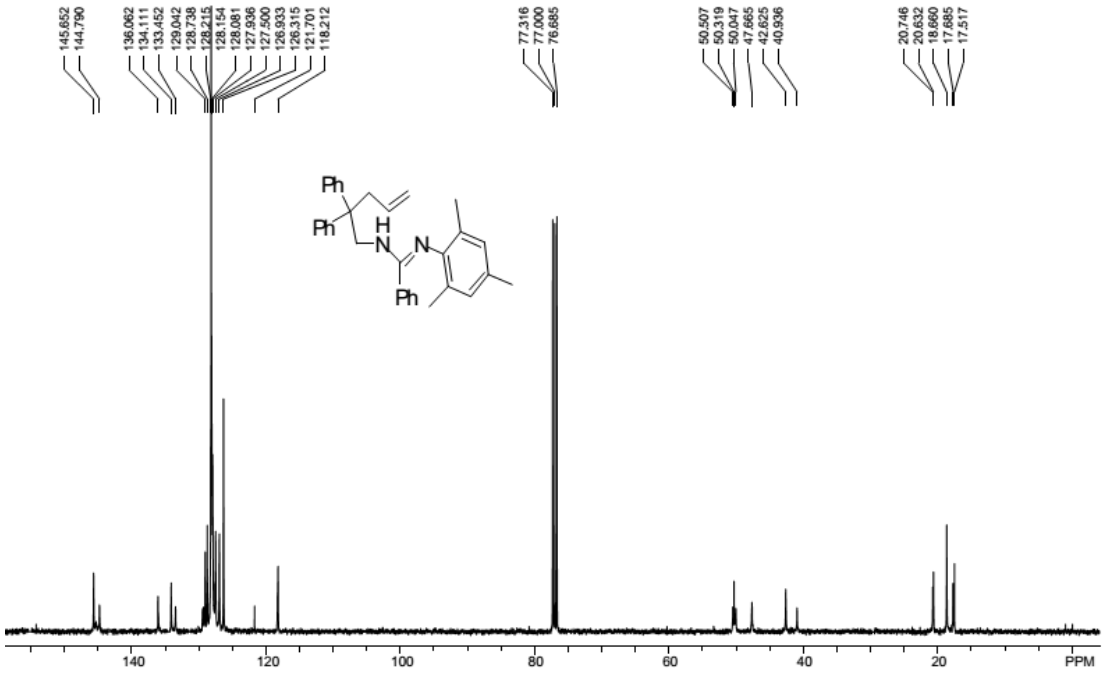
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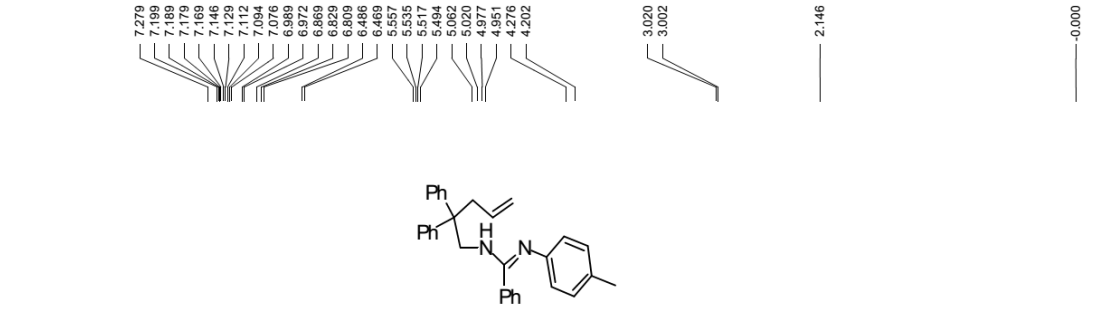
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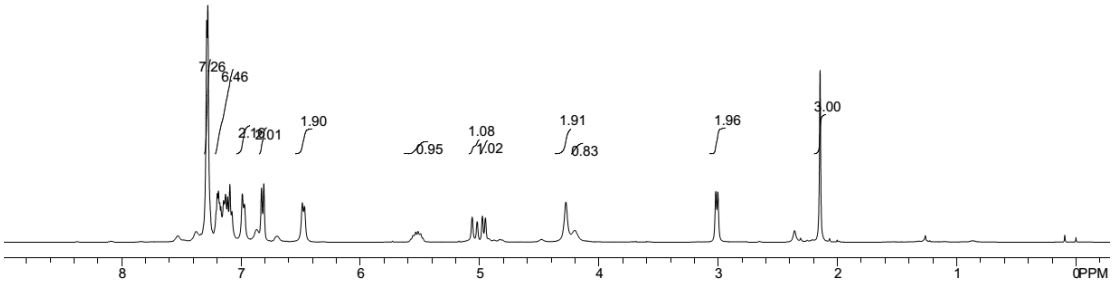
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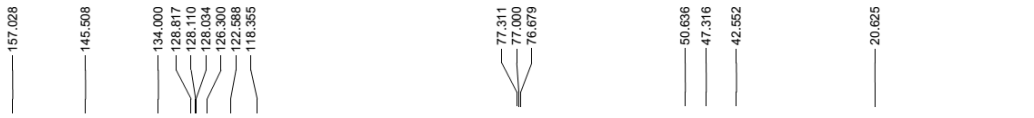
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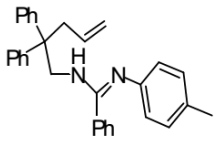
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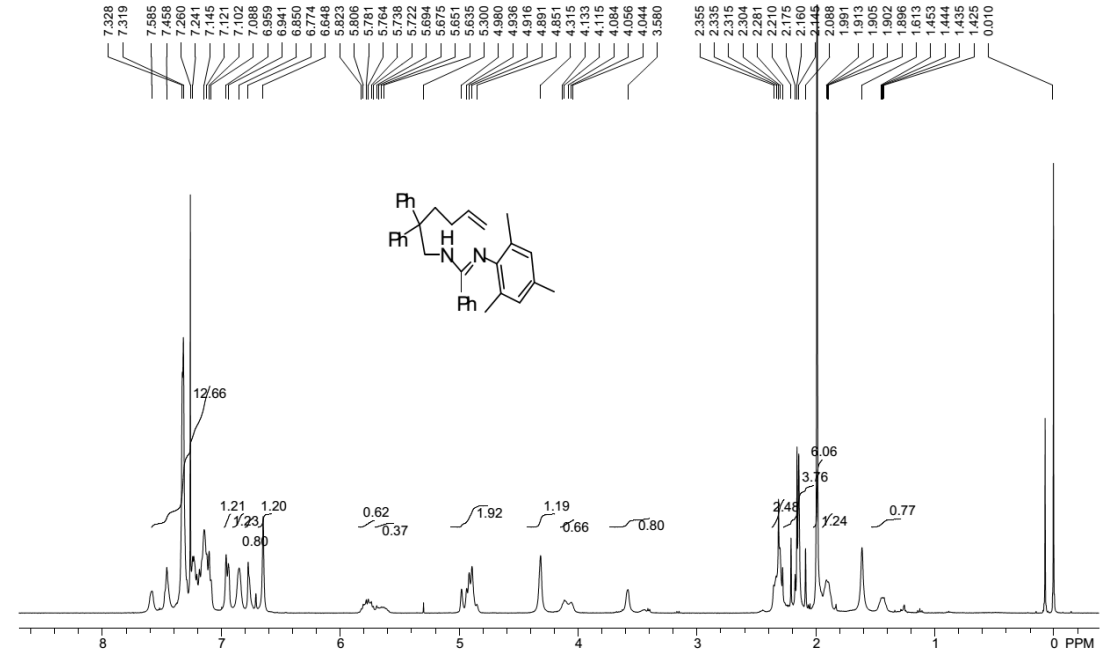
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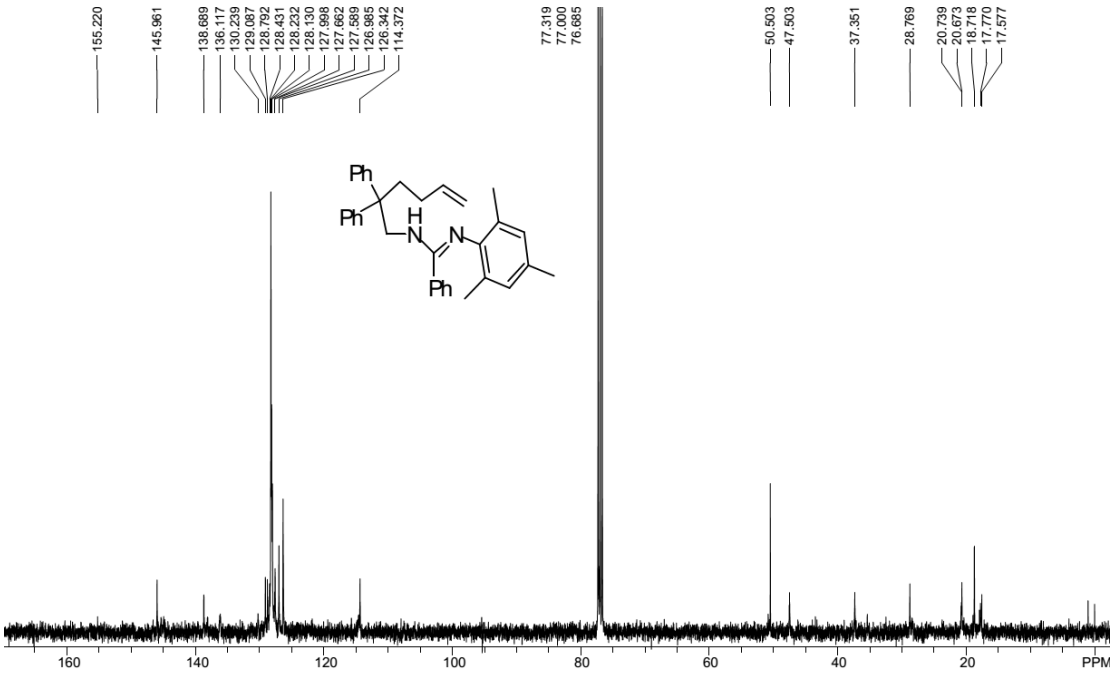
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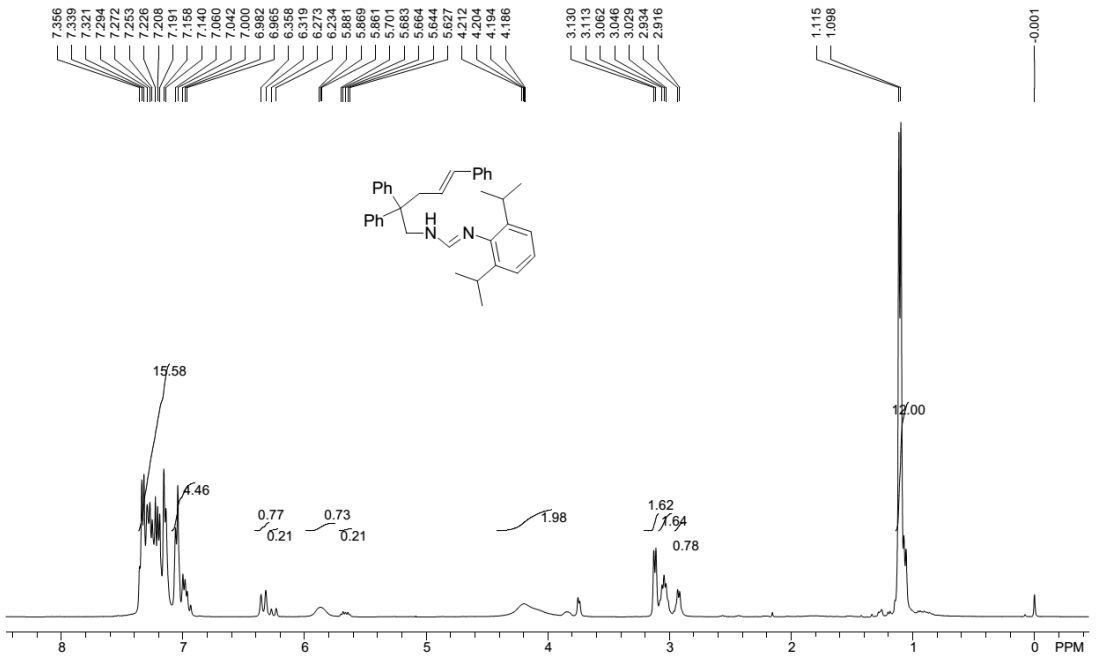
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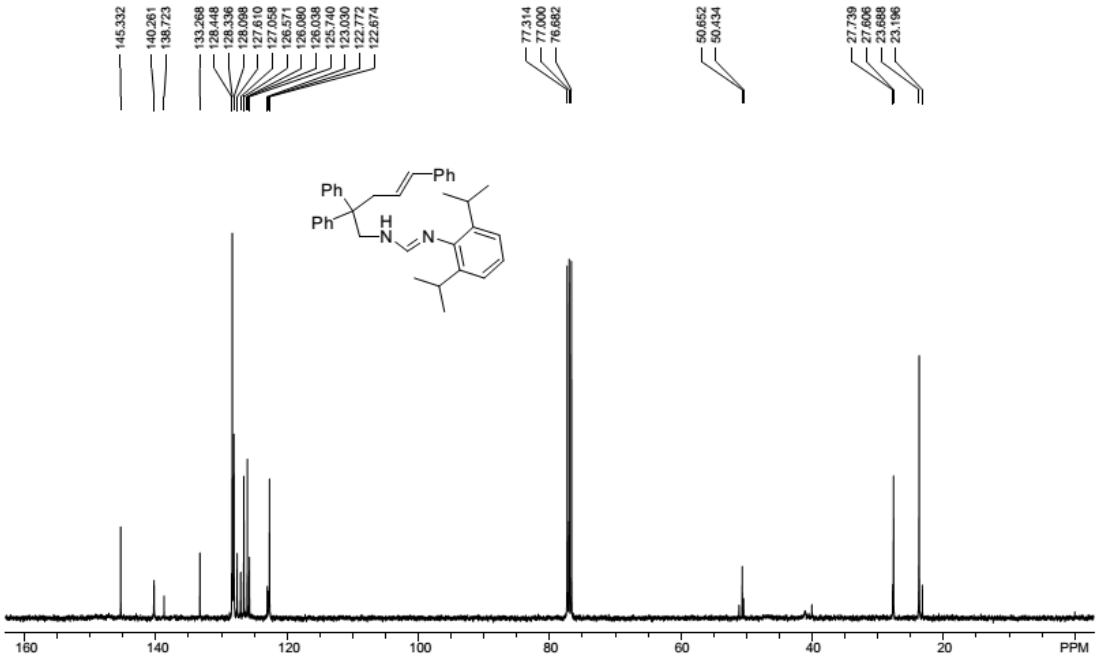
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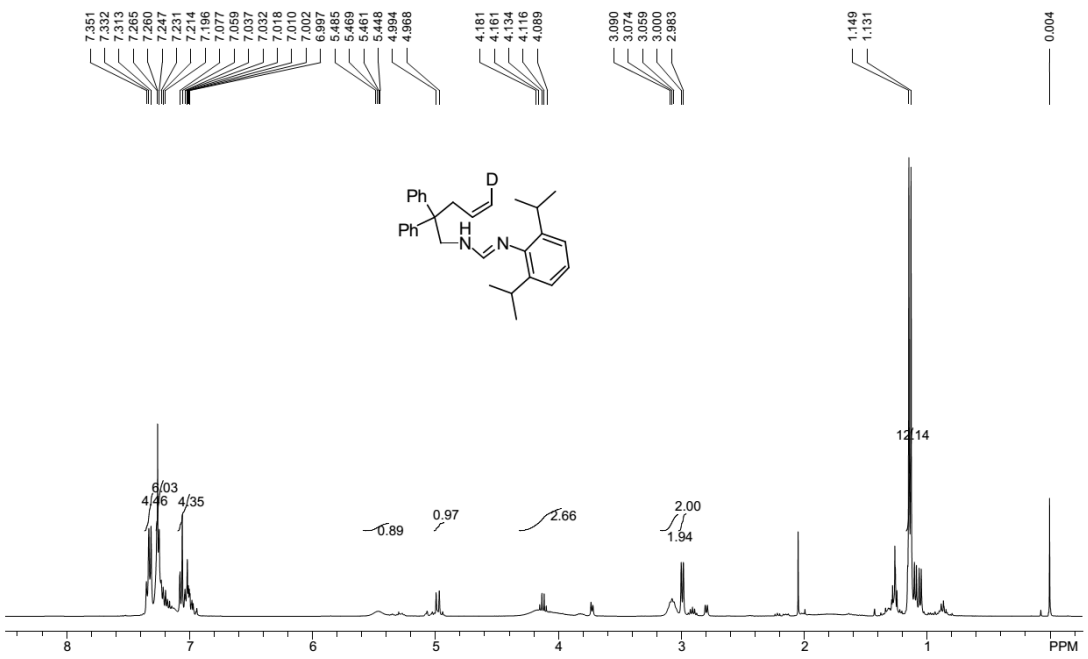
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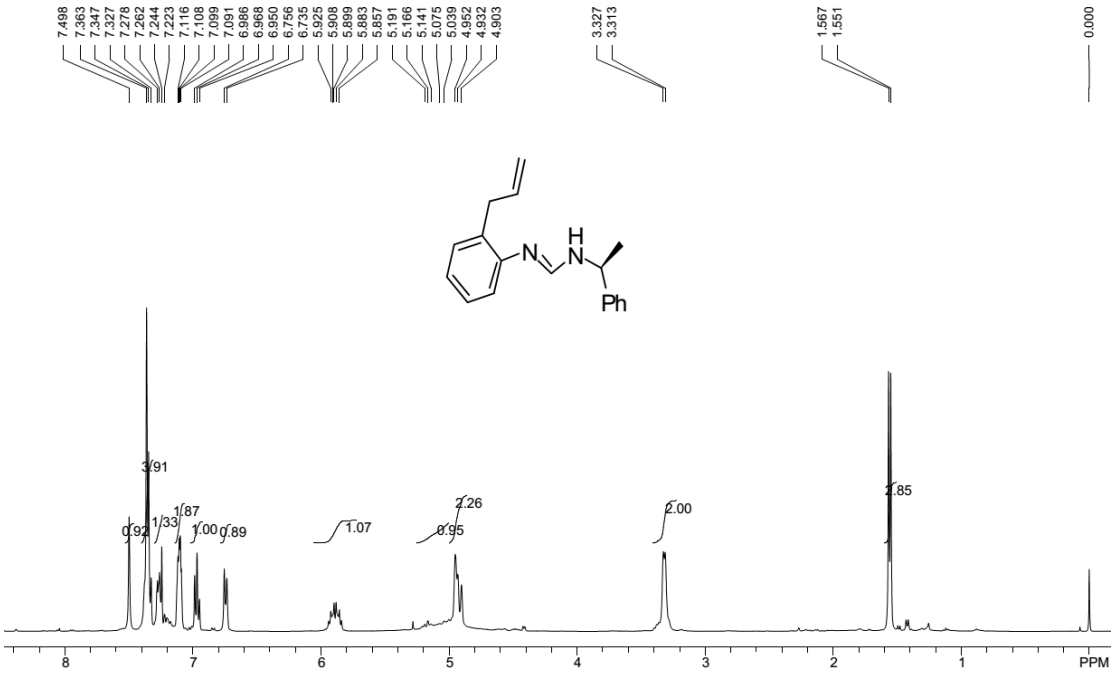
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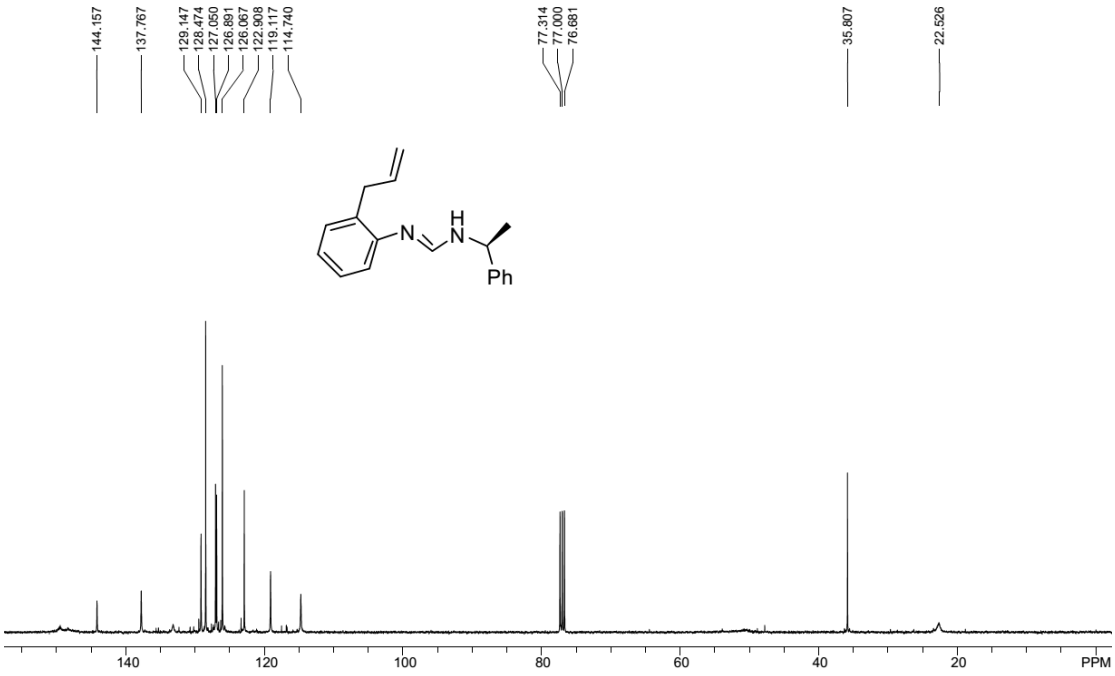
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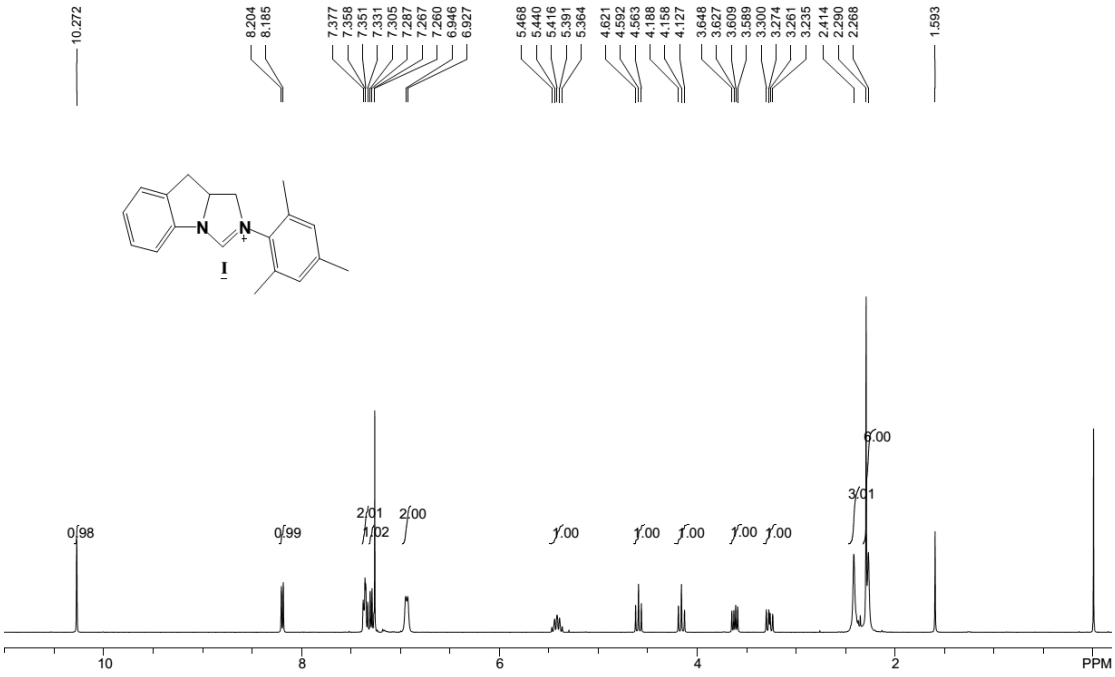
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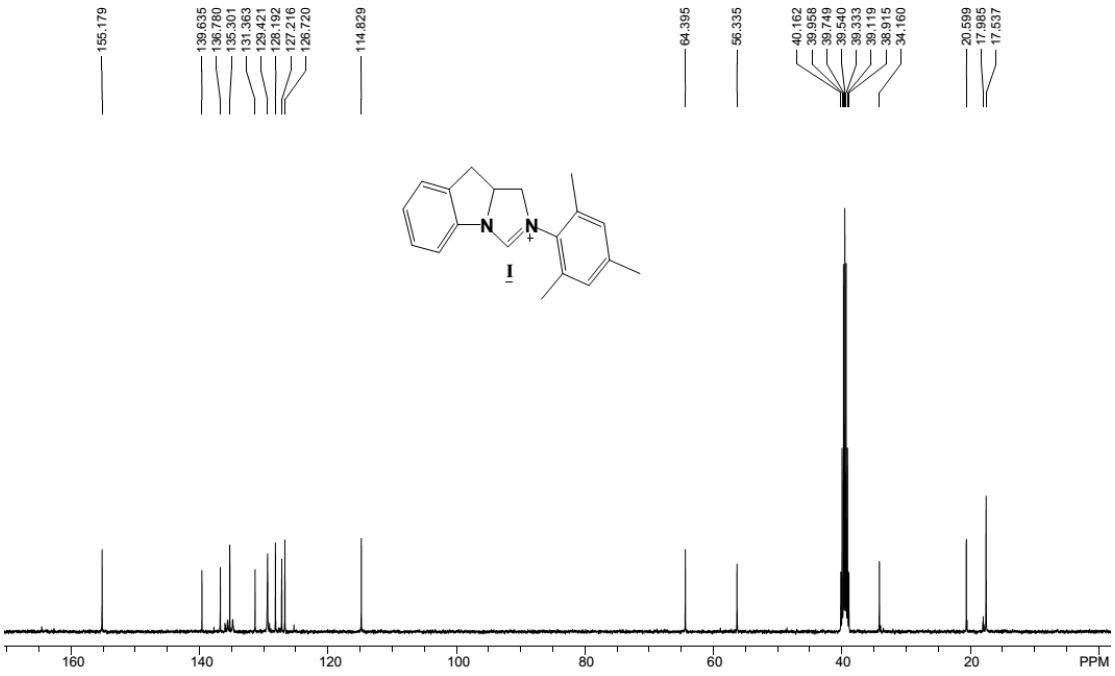
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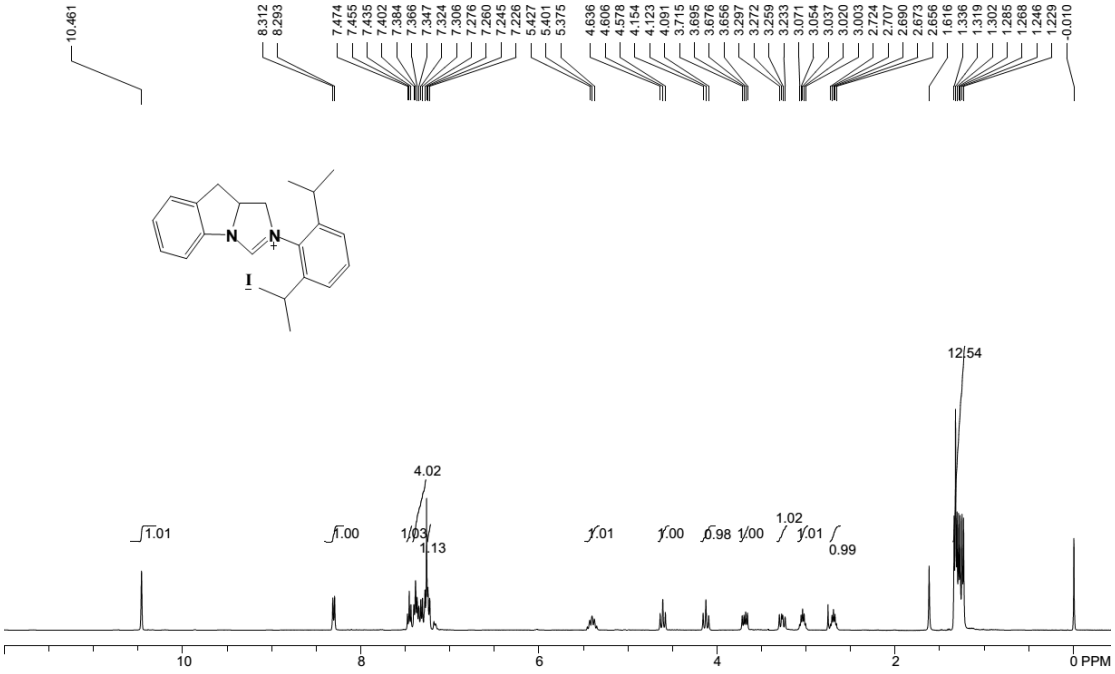
2b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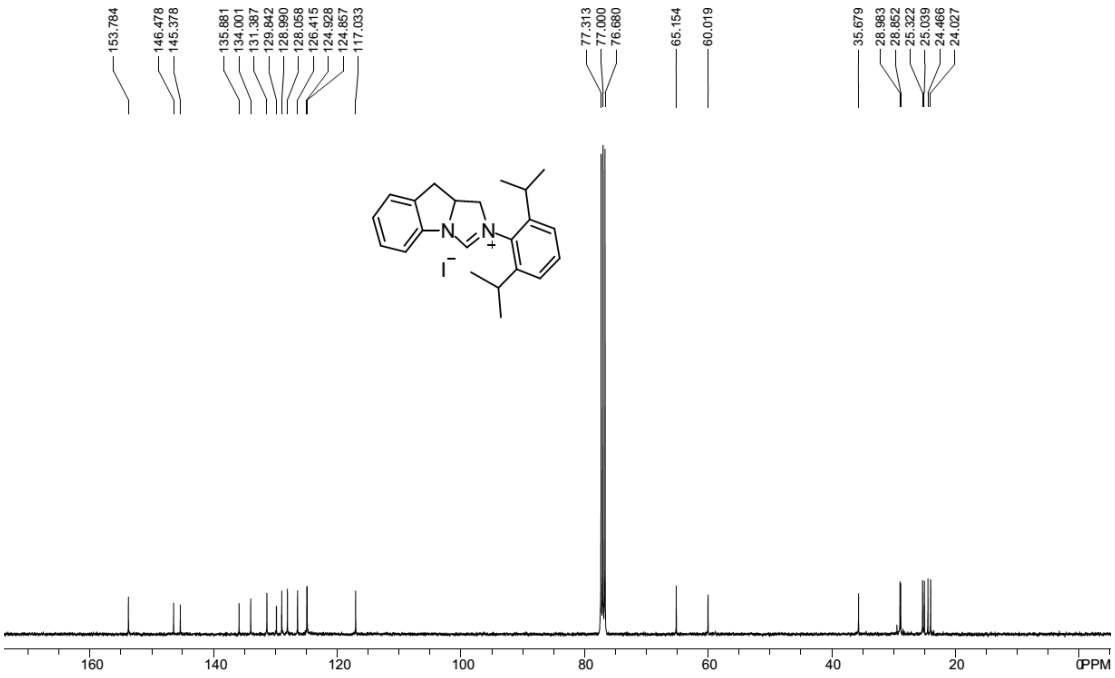
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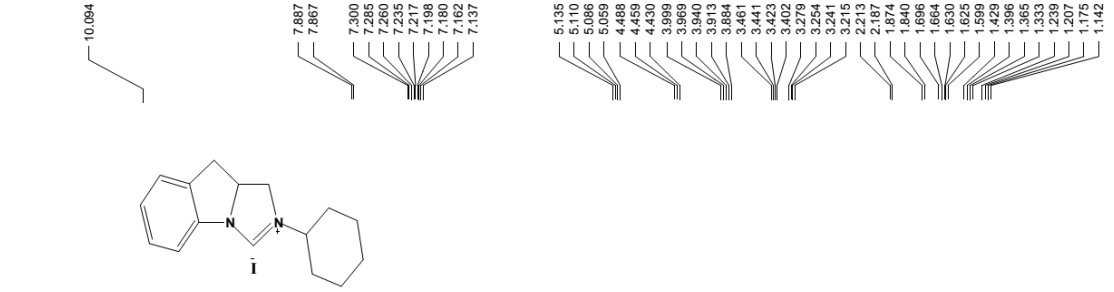
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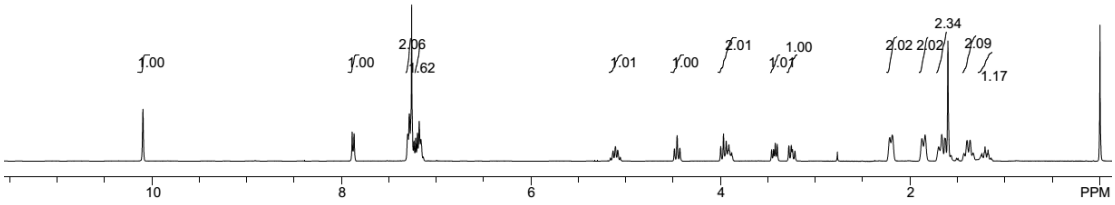
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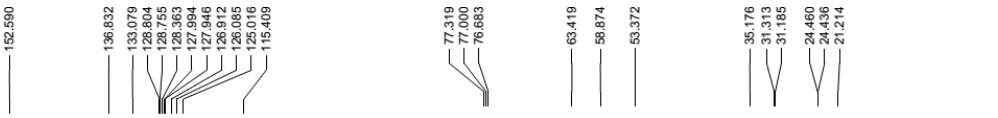
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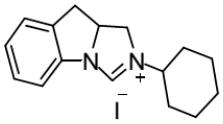
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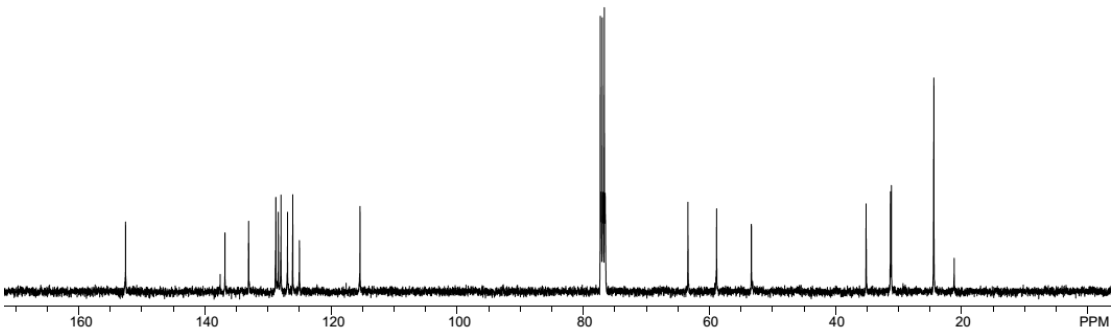
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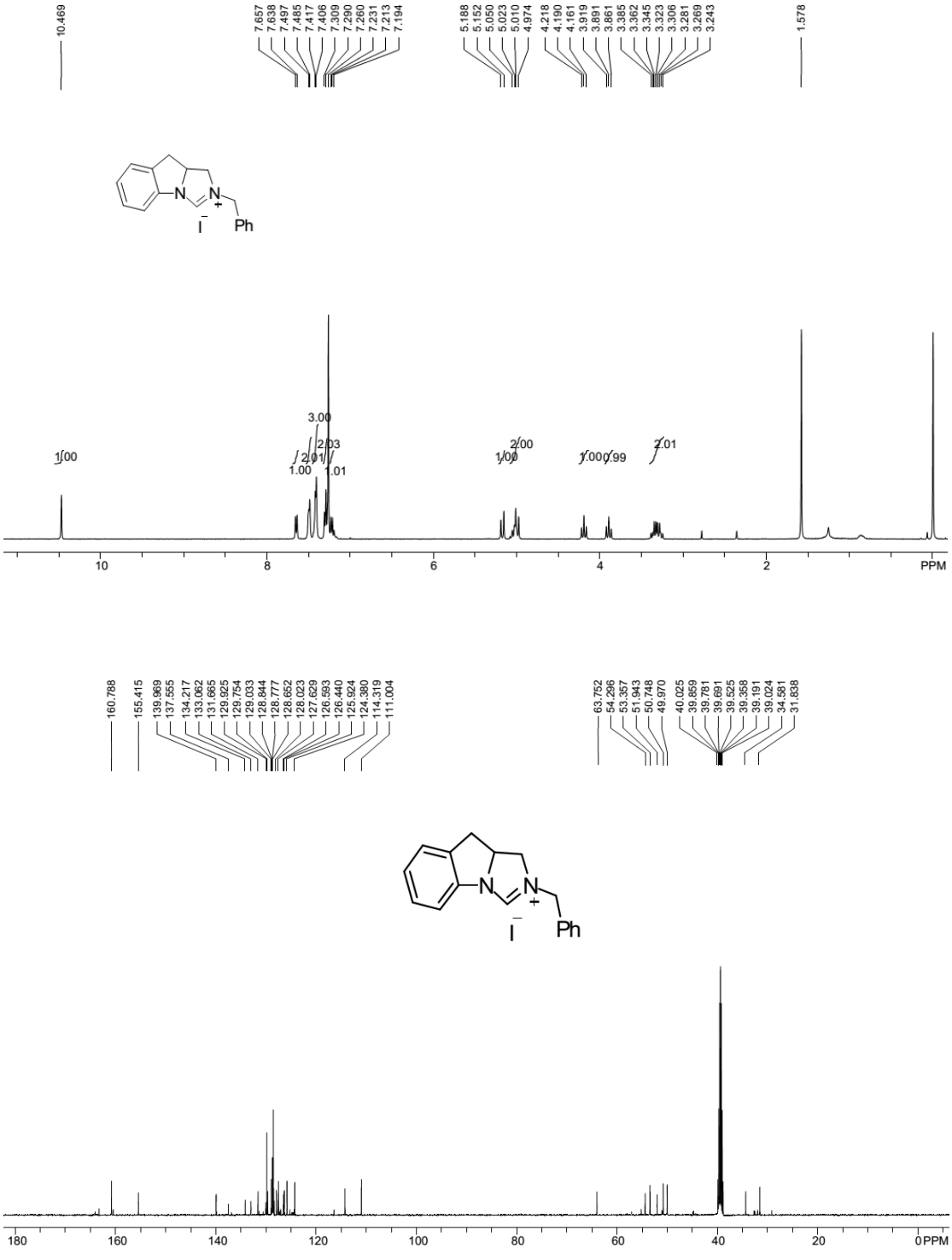
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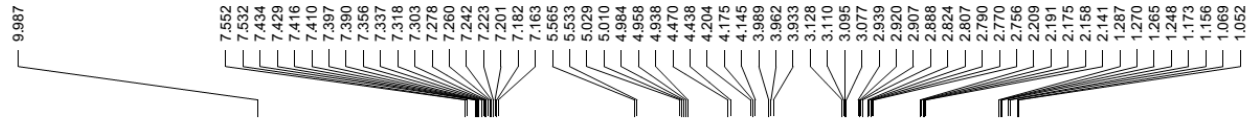
2e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7.260
7.242
7.223
7.201
7.182
7.163
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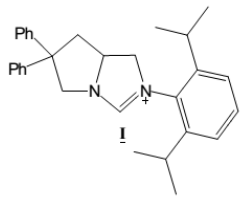
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Ph
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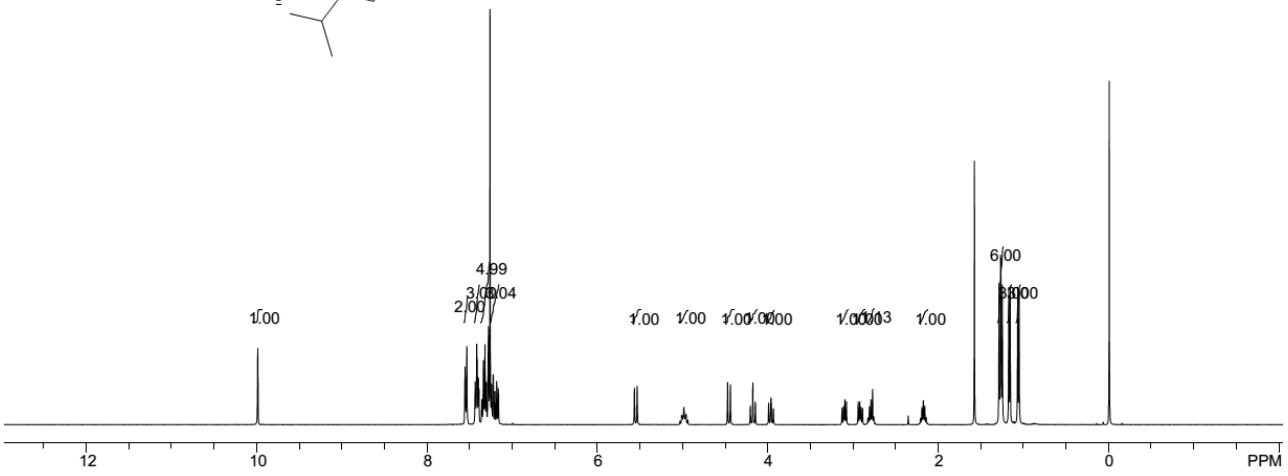
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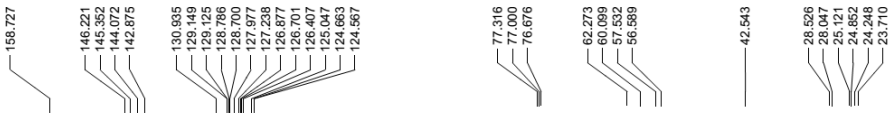
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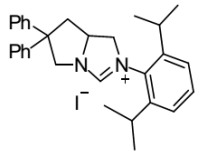
23.710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Ph
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I
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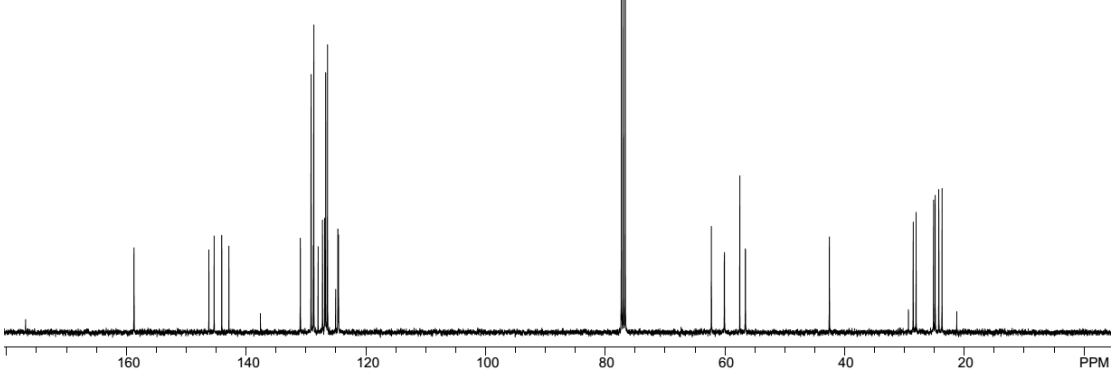
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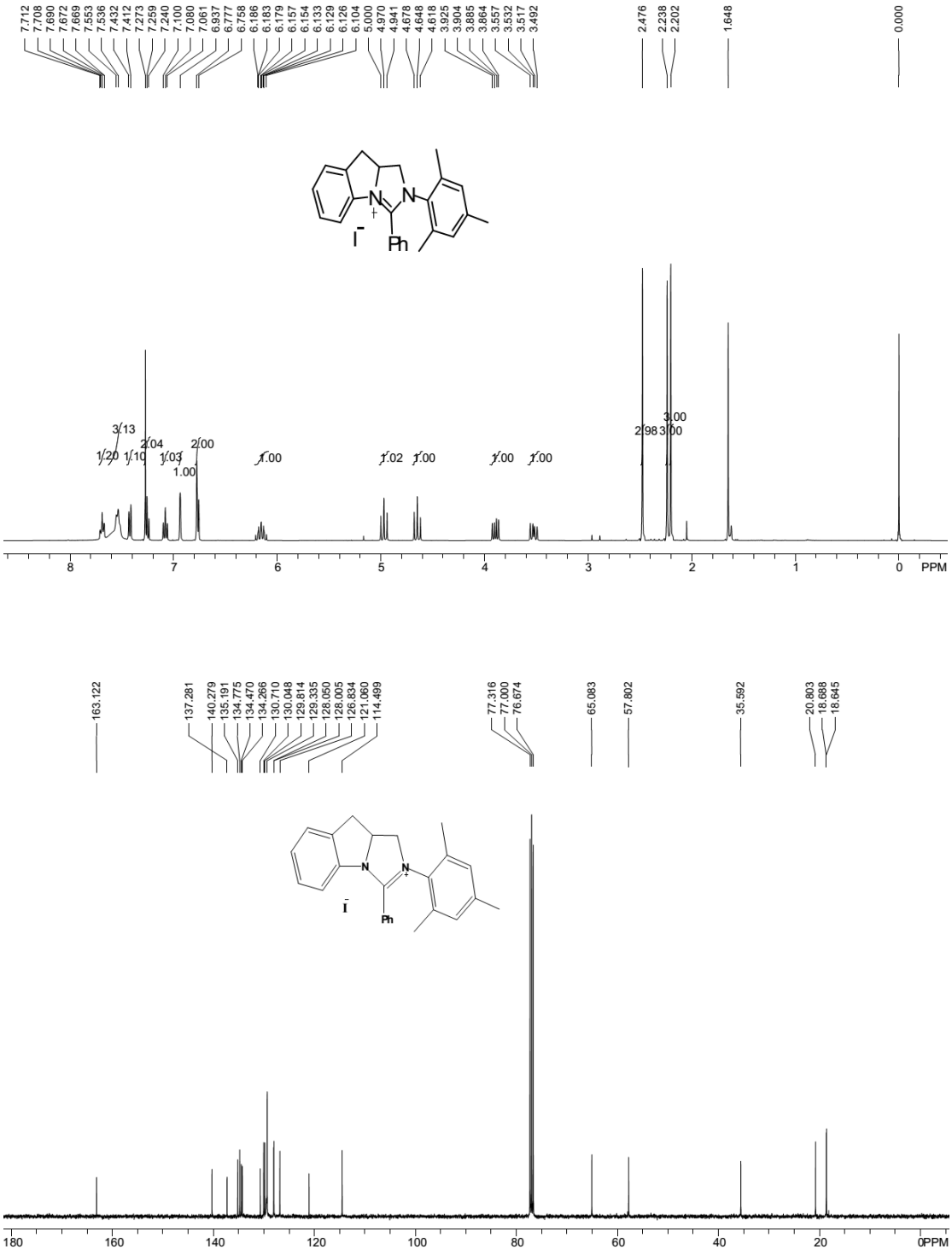
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7.240
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7.080
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6.179
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3.925
3.904
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I⁻
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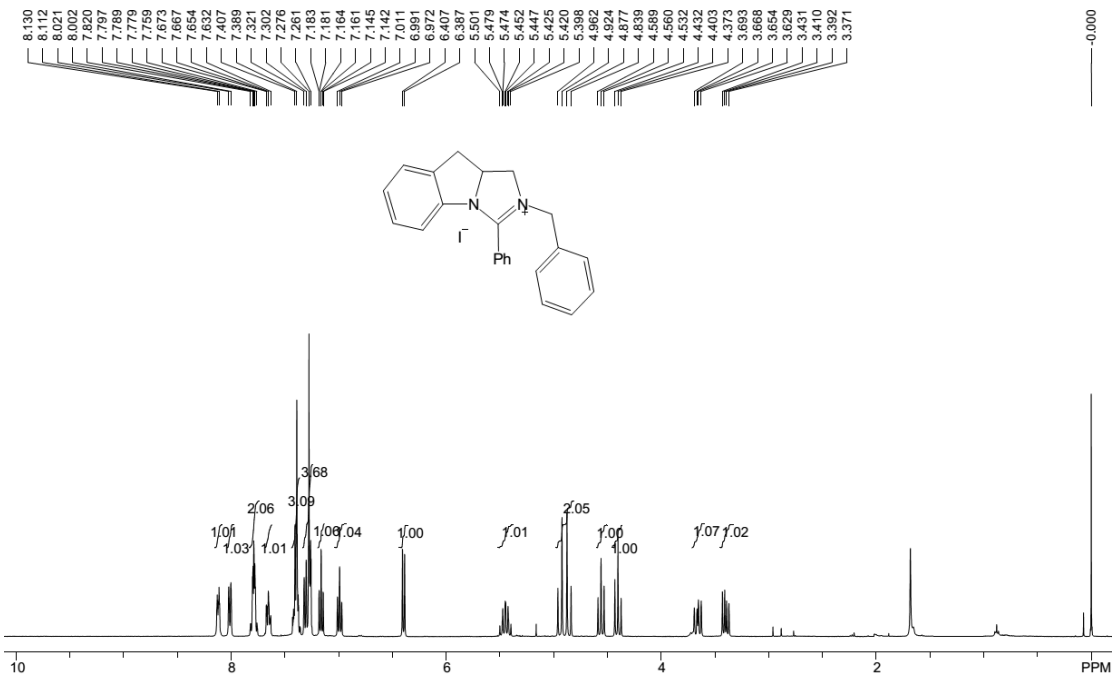
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I⁻
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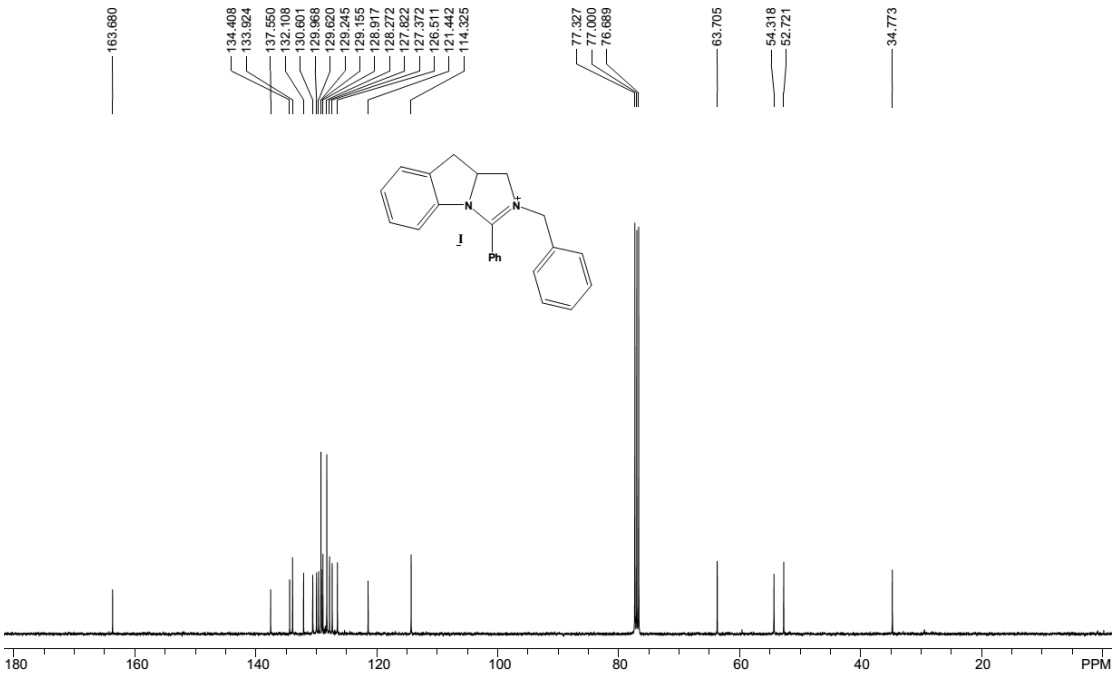
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N
I⁻
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20
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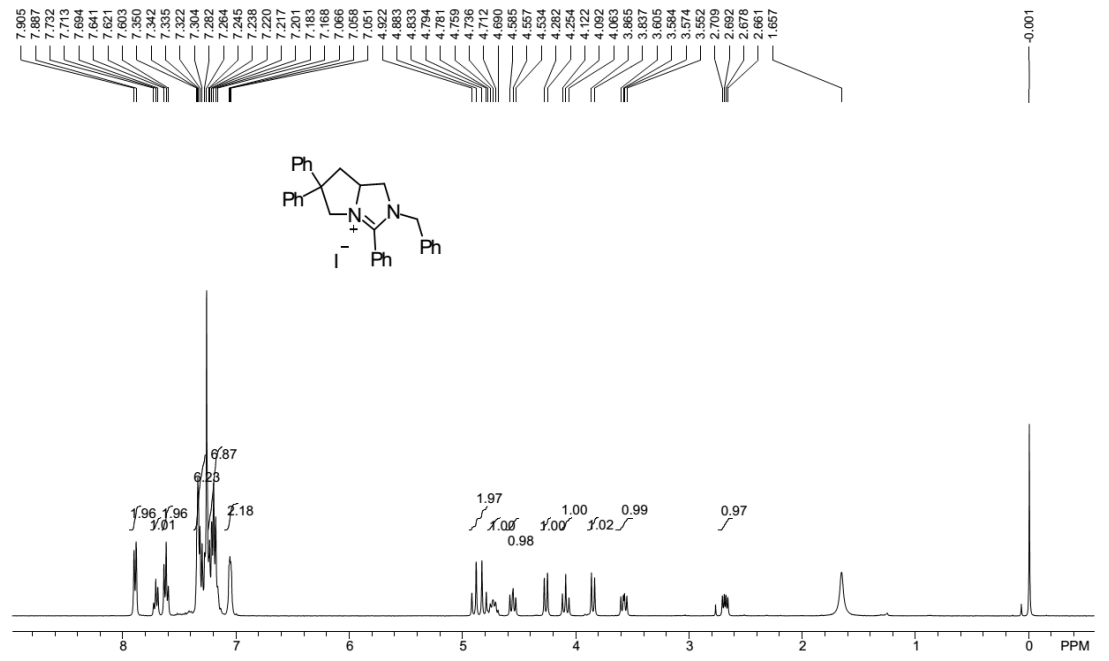
2h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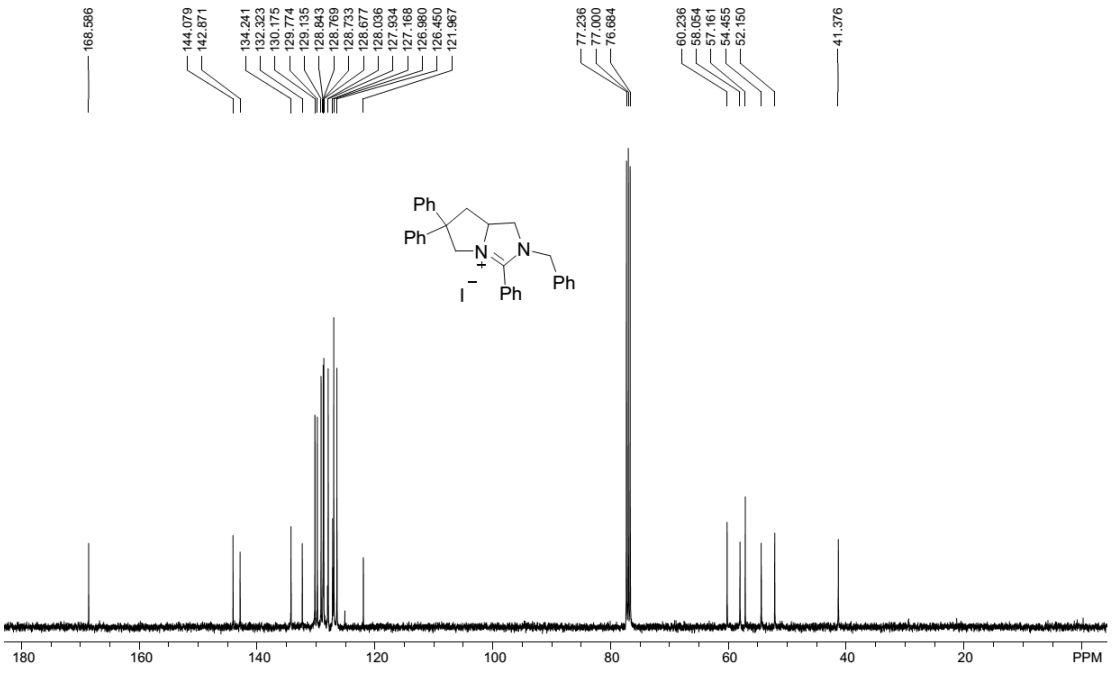
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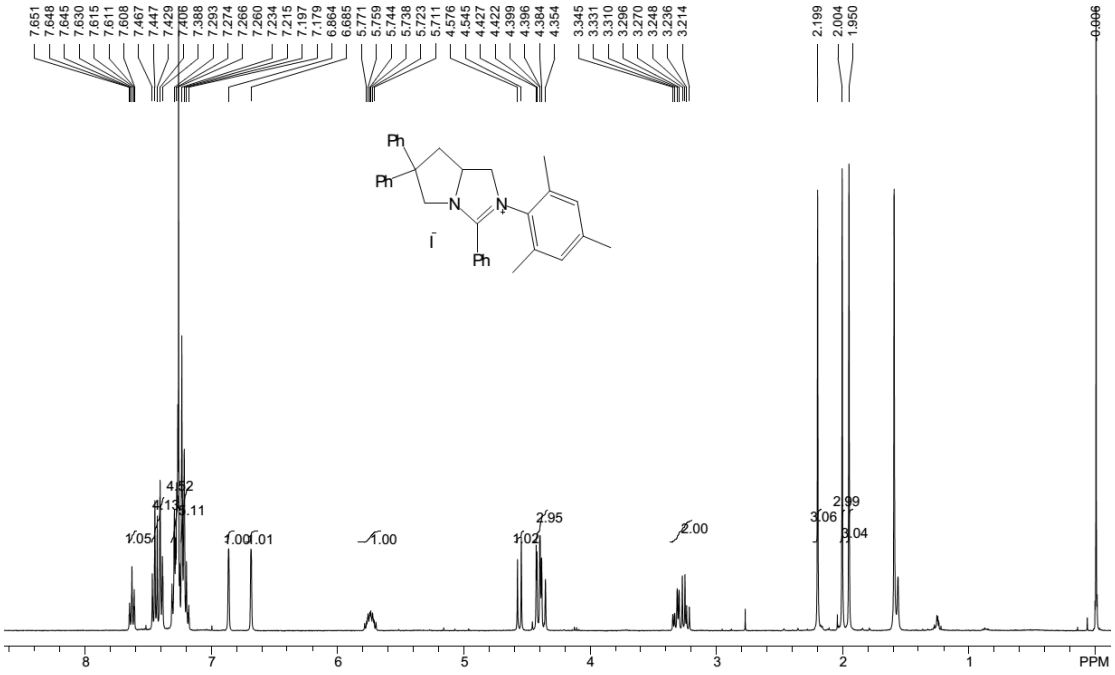
PPM

2i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N
I⁻
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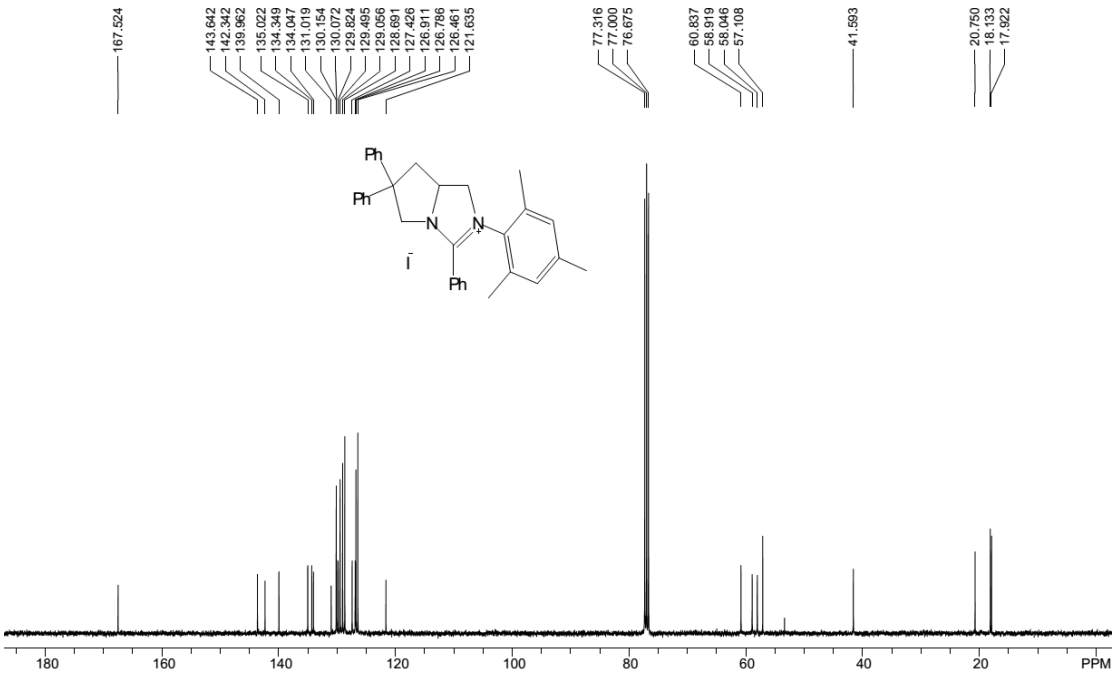
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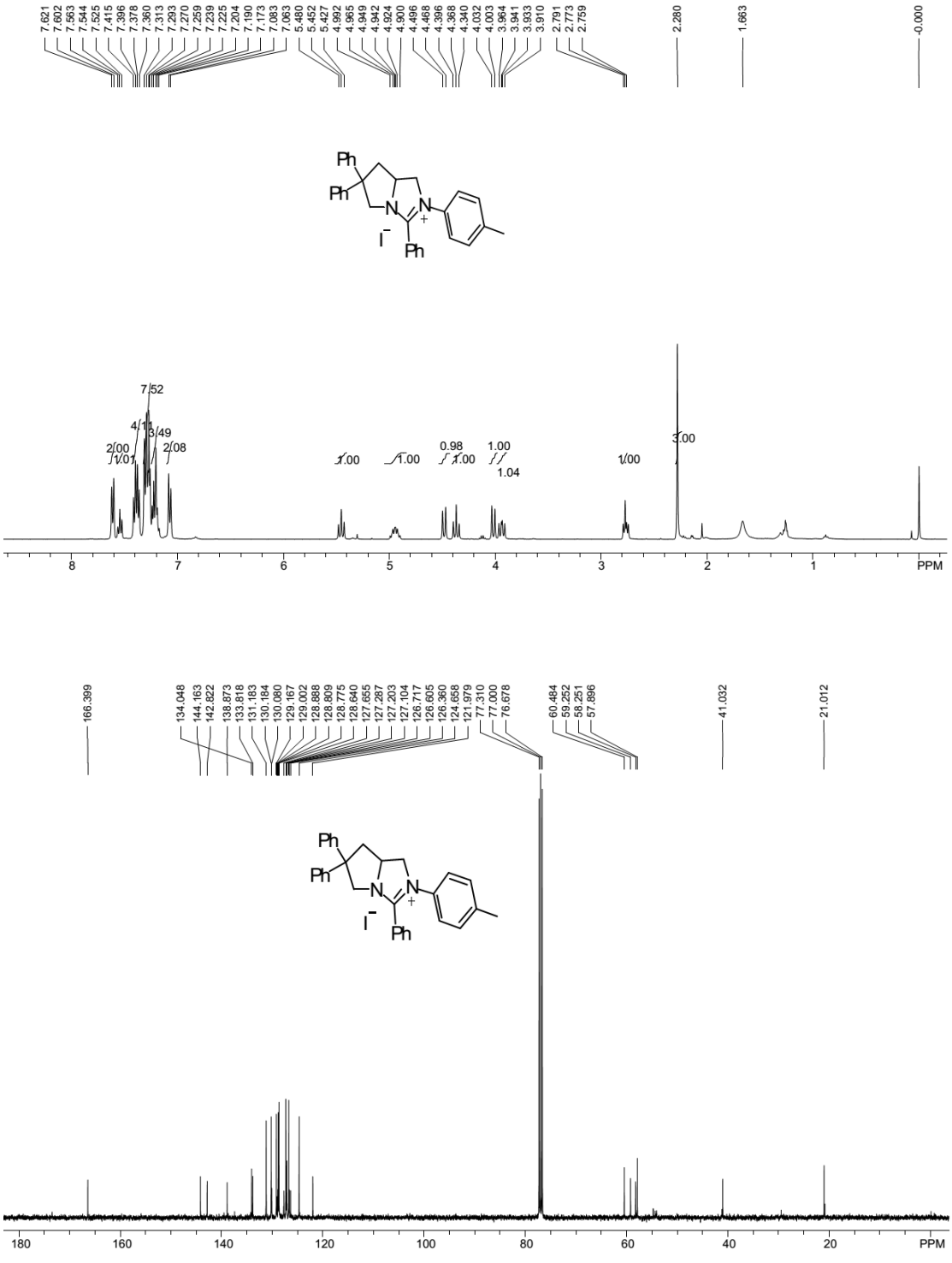
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20
PPM

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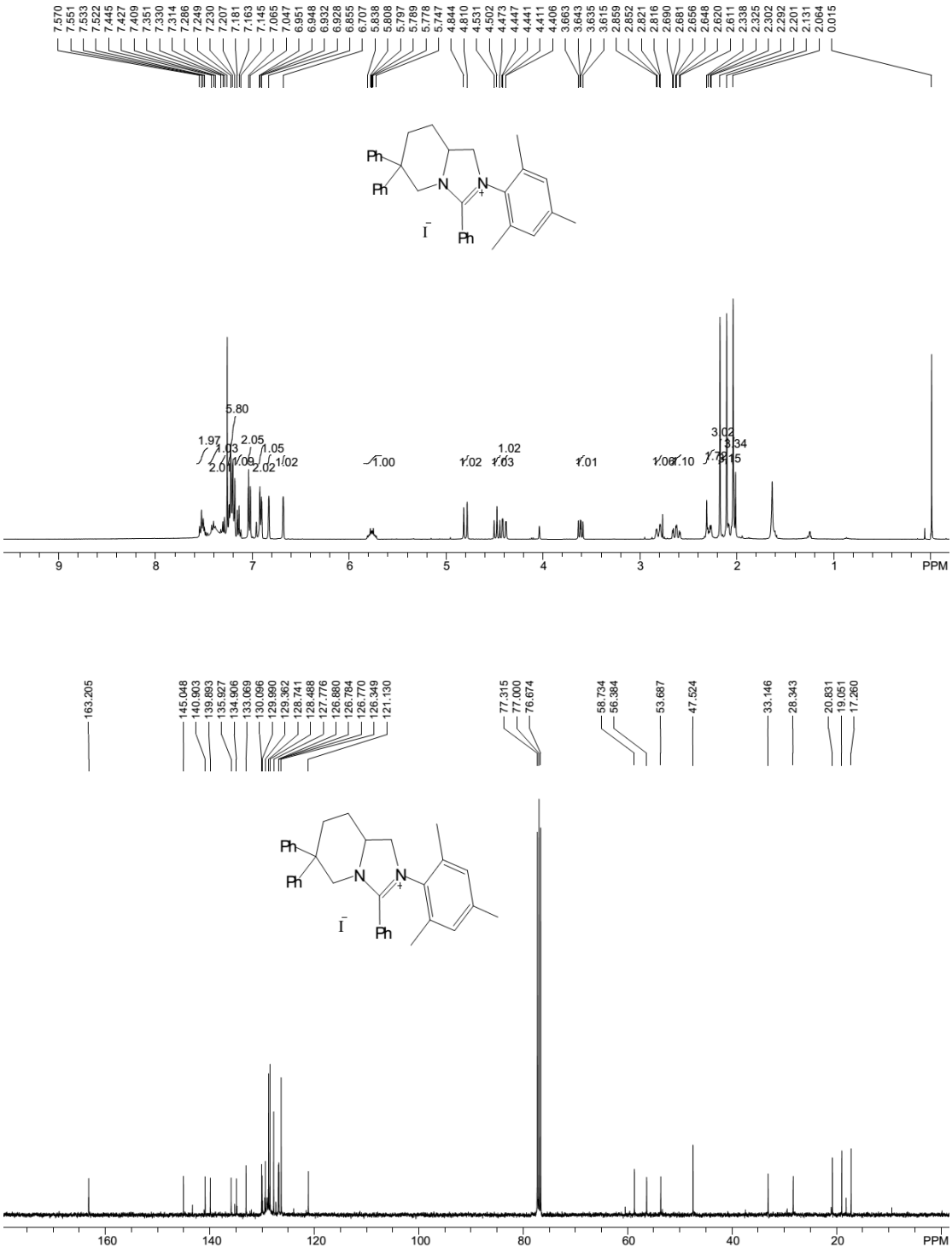
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1.09
2.02
1.02
1.00
1.02
1.03
1.02
1.01
1.06
1.10
3.02
3.34
1.78
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9
8
7
6
5
4
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139.893
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Ph
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I⁻
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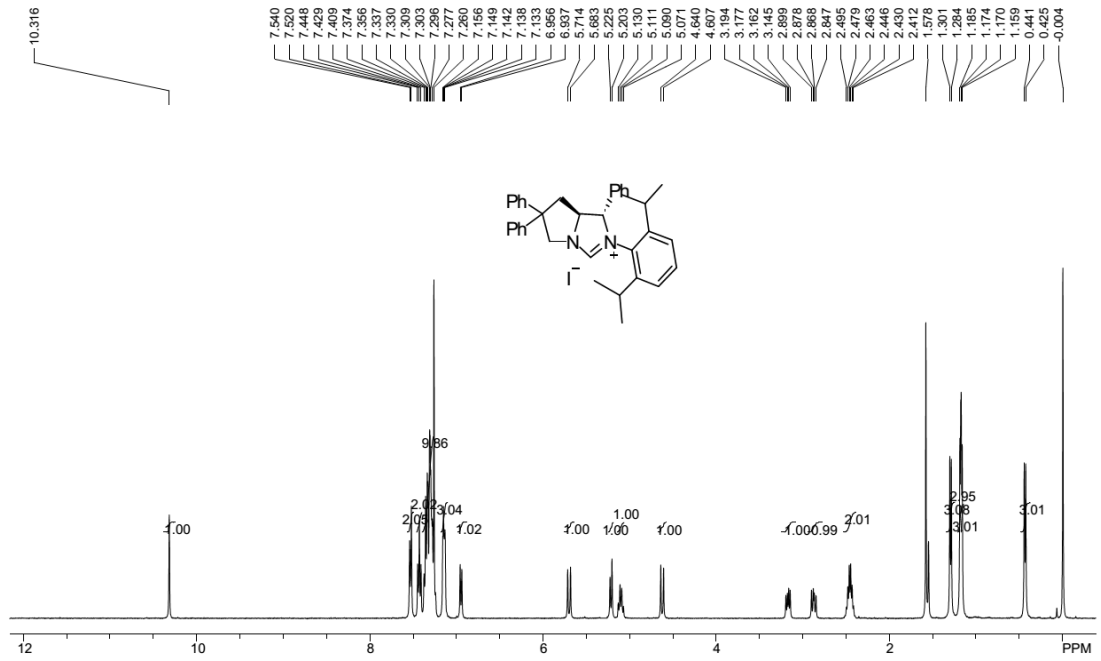
2l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7.149
7.142
7.138
7.133
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5.225
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5.130
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2.446
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1.185
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1.170
1.159
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Ph
Ph
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N
I
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1.00
1.00
1.00
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3.01
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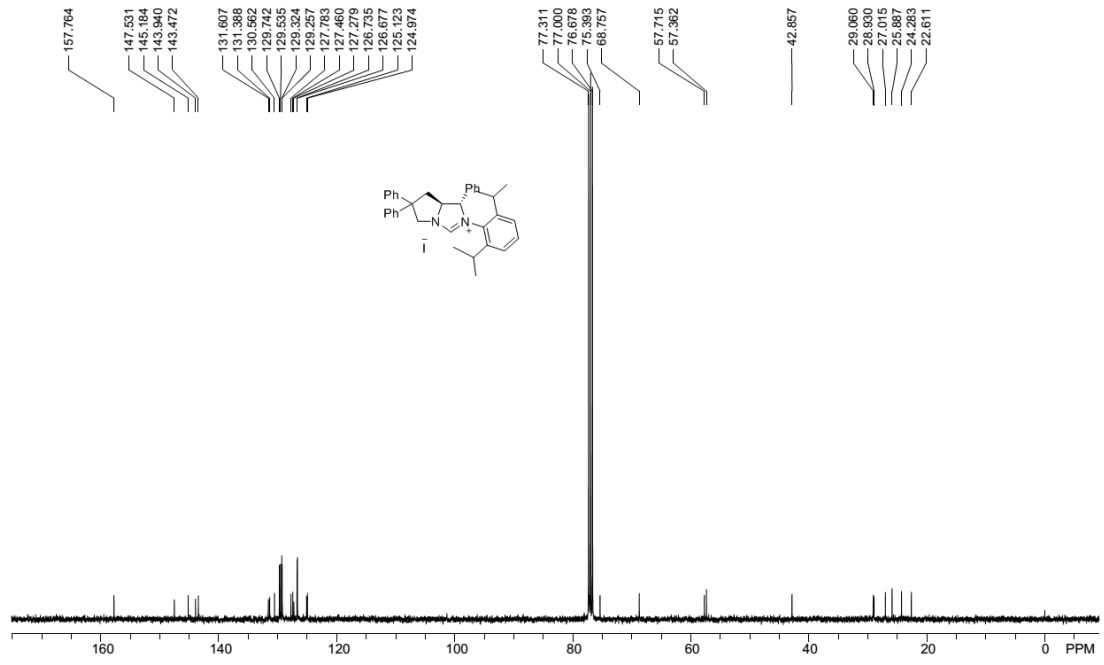
4
2
PPM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0
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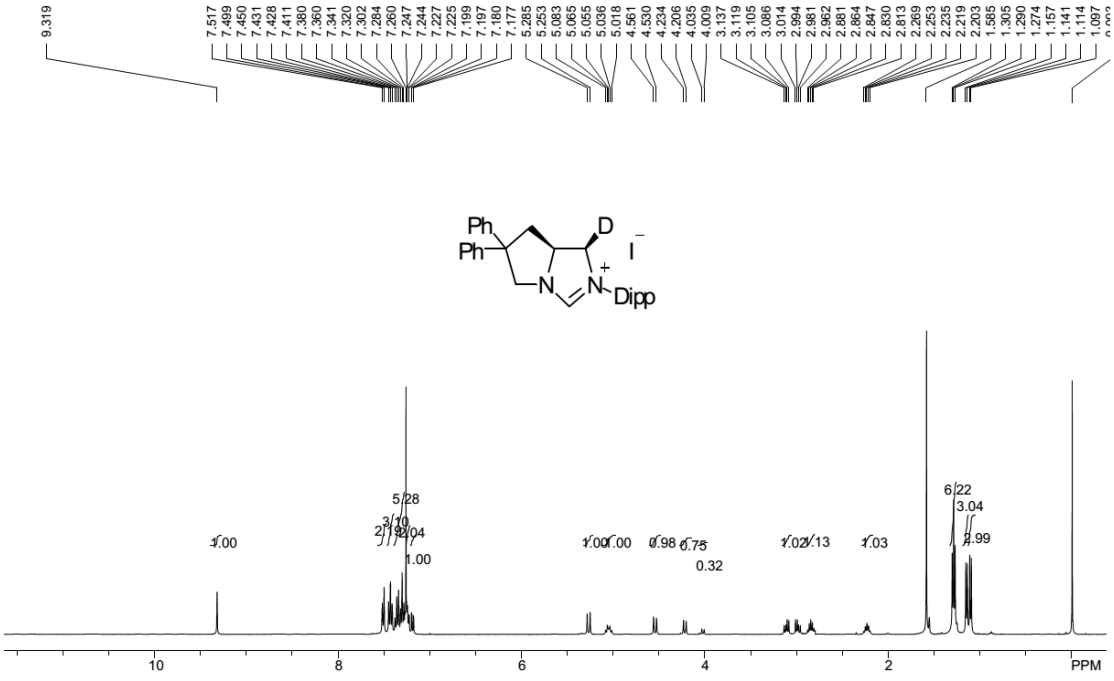
2m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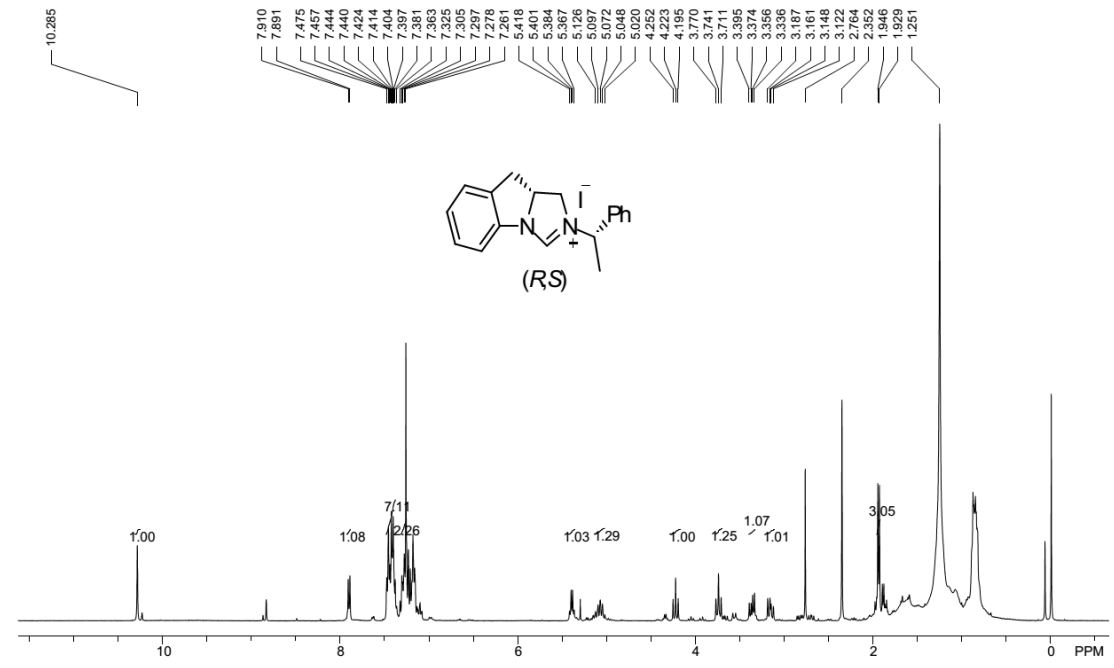
6
4
2
PPM

(R,S)-**5**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N
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(R,S)
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3.05
10
8
6
4
2
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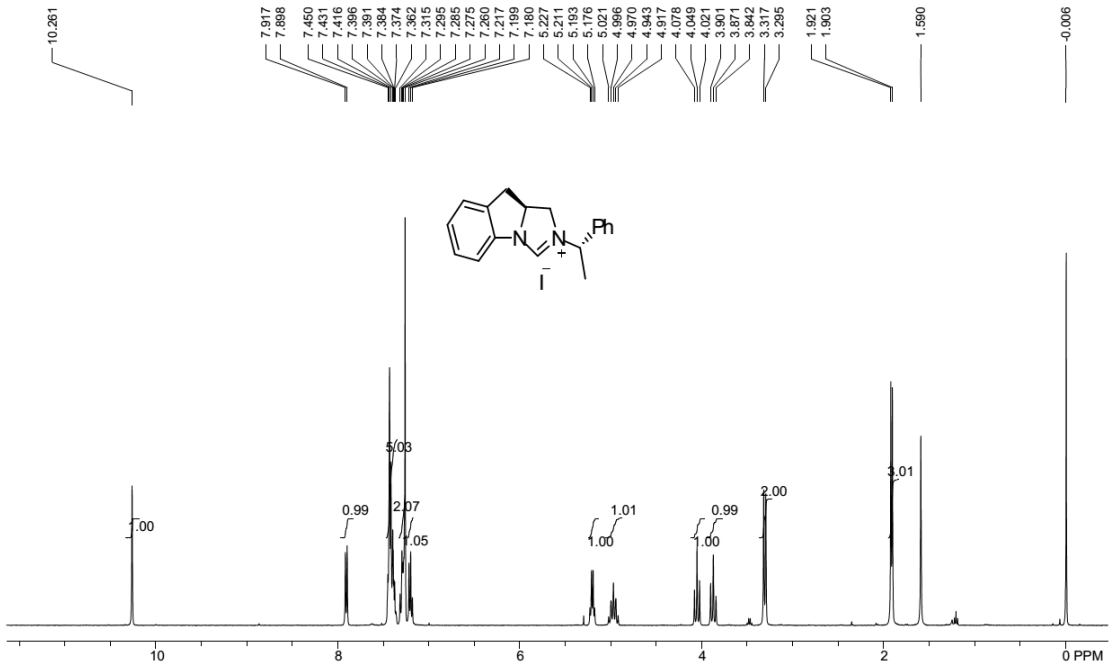
PPM

(S,S)-**5**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5.227
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5.193
5.176
5.021
4.996
4.970
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I
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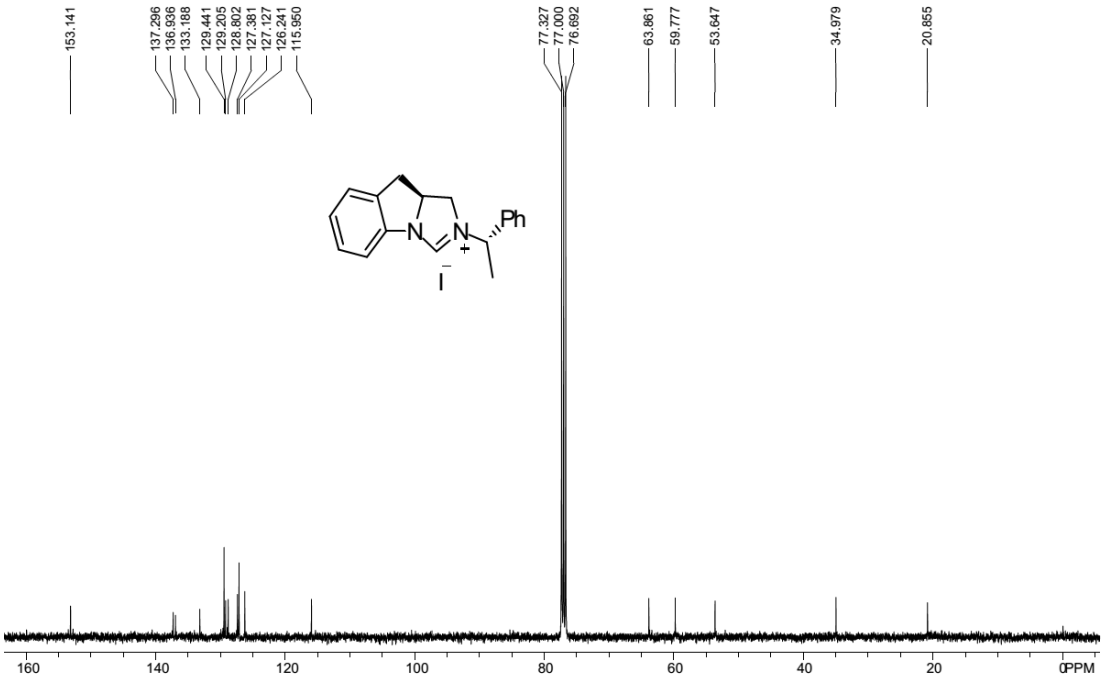
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77.000
76.692
63.861
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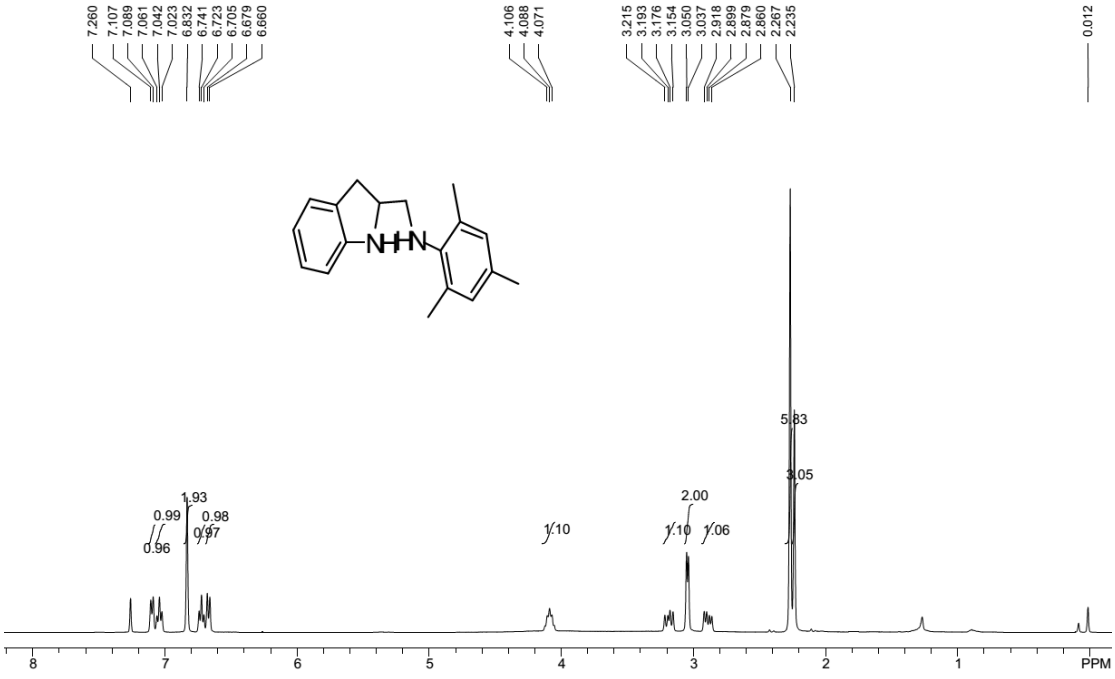
100
80
60
40
20
0PPM

3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6.741
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6.705
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2.879
2.860
2.267
2.235
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NH
HN
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3.05
2.00
1.93
0.99
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0.96
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1.10
1.06
8
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6
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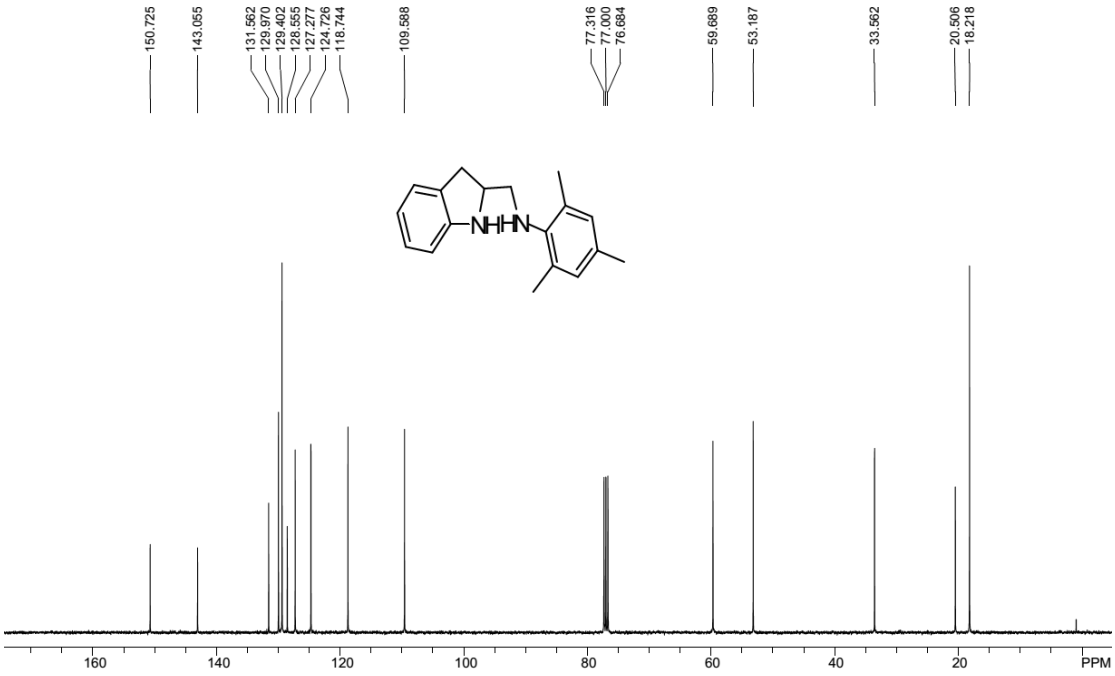
3
2
1
PPM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77.000
76.684
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20.506
18.218
NH
HN
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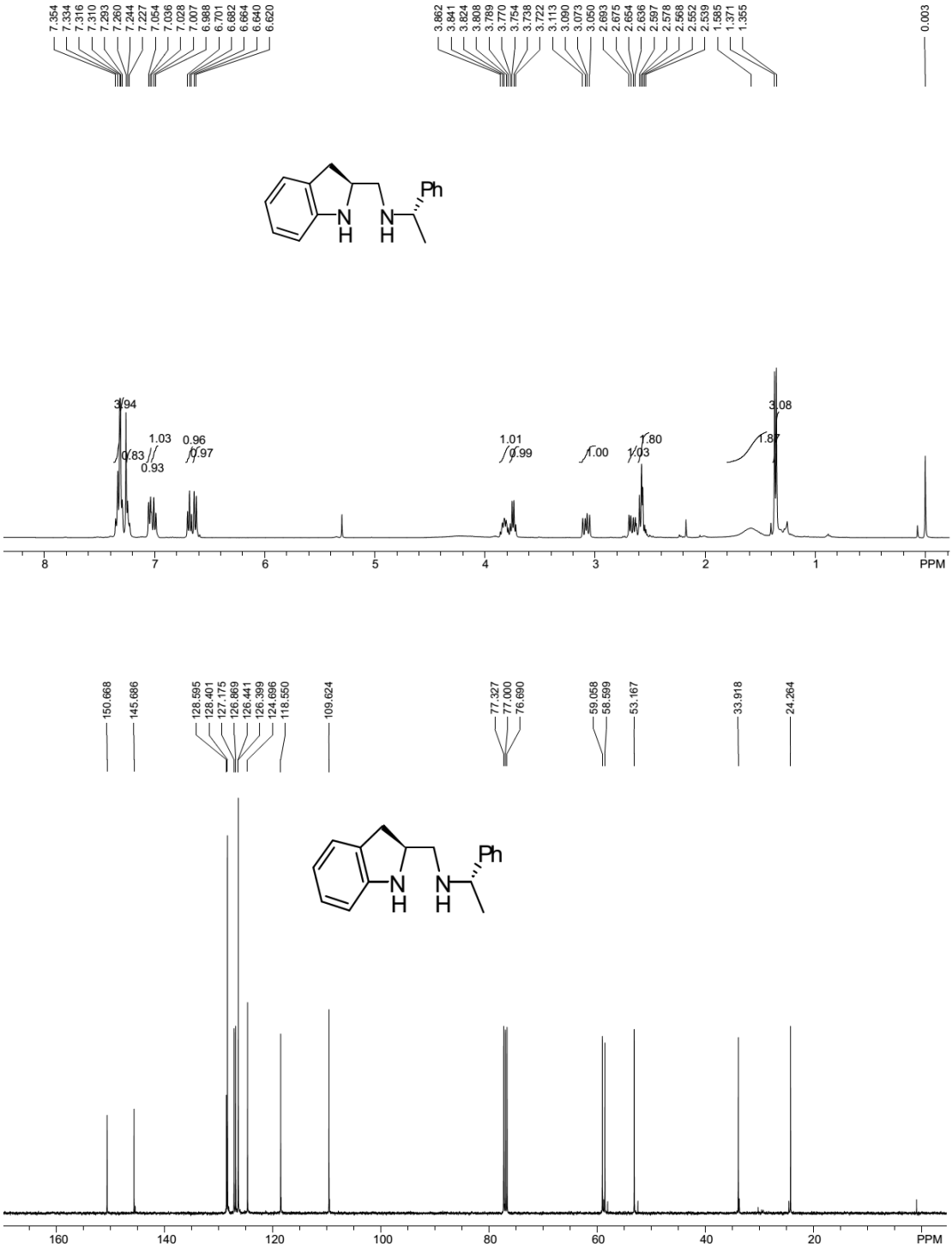
120
100
80
60
40
20
PPM

6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6.701
6.682
6.664
6.640
6.620
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3.841
3.824
3.808
3.789
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3.754
3.738
3.722
3.113
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3.073
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58.599
53.167
33.918
24.264
Ph
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H
N
H
160
140
120
100
80
60
40
20
PPM

X-Ray Crystallography.

Crystallographic measurements were made on a Bruker Smart Apex 100 CCD area detector using graphite monochromated Mo-Kα radiation ($\lambda_{\text{Mo-K}\alpha}$ = 0.71073 Å). The structures were solved by directed methods (SHELXS-97) and refined on F^2 by full-matrix least squares (SHELX-97) using all unique data. All the calculations were carried out with the SHELXTL18 program.[4]

CCDC 1017139 (**2a**), CCDC 1017140 (**2c**), CCDC 1016877 (**2i**), CCDC 1017141 (**2l**), and CCDC 1017397 ((*S,S*)-**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Key details of the crystal and structure refinement data are summarized in Table S1.

Reference:

4. G. M. Sheldrick, SHELL-97, Program for crystal structure refinement, University of Göttingen: Göttingen, Germany, 1997.

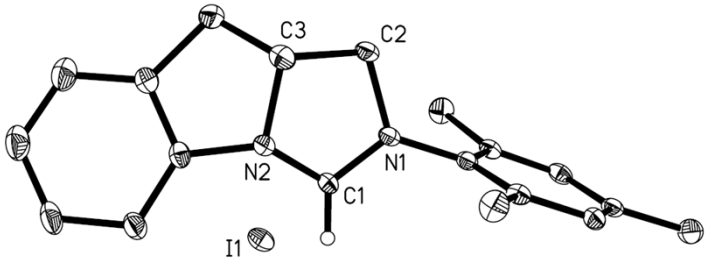

Figure S1 Views of the single-crystal structure of imidazolinium salt **2a**.

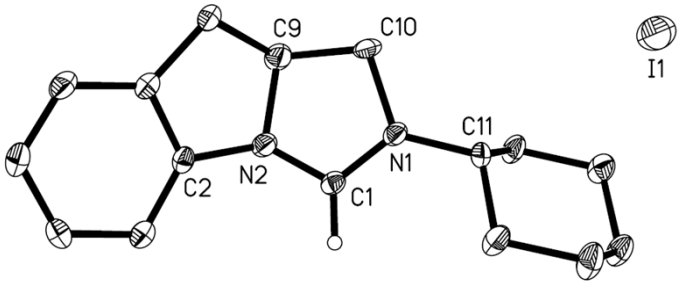

Figure S2 Views of the single-crystal structure of imidazolinium salt **2c**.

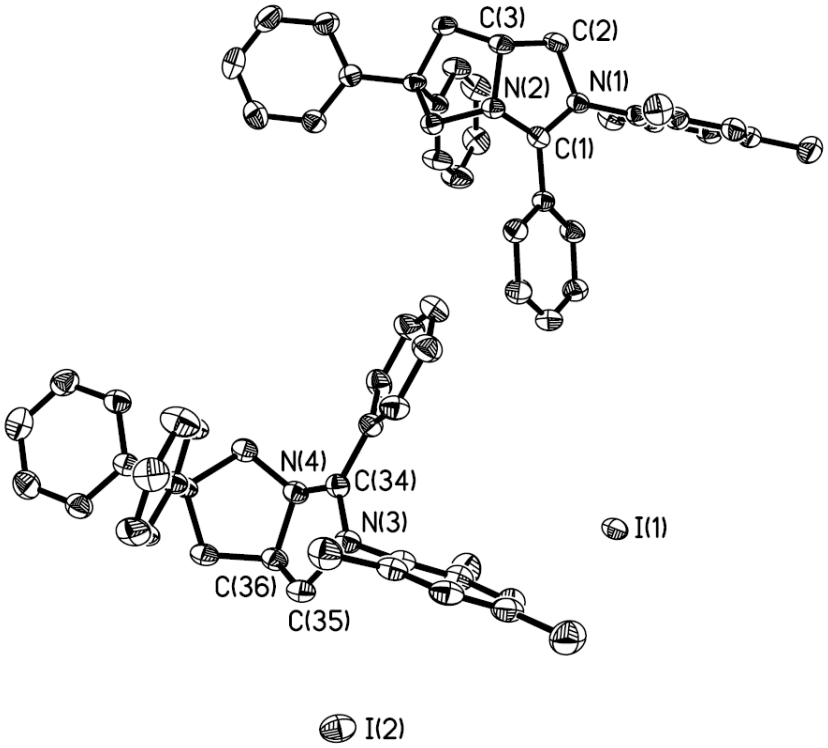

Figure S3 Views of the single-crystal structure of imidazolinium salt **2i₂**·CH_2Cl_2.

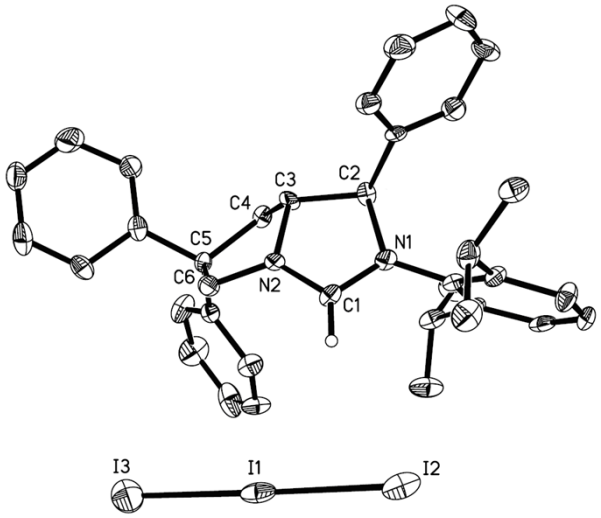

Figure S4 Views of the single-crystal structure of imidazolinium salt **2l**·I_2.

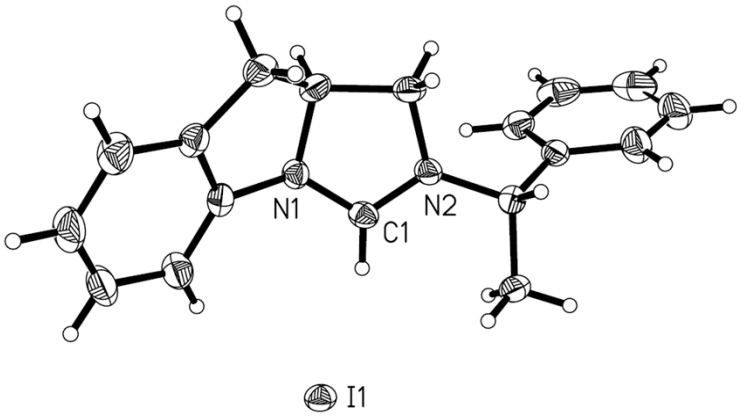

Figure S5 Views of the single-crystal structure of imidazolinium salt *(S,S)*-**5**.

Table S1. Crystal Data, Data Collection, and Structure Refinement for **2a**, **2c**, **2i**$_2$·CH_2Cl_2·H_2O, *(S,S)*-**5**, and **2l**·I_2

	2a	**2c**	**2i**$_2$·CH_2Cl_2·H_2O	*(S,S)*-**10**	**2l**·I_2
Identification code	mo_40106a	mo_40107b	a31202a	a40411a	mo_40708a
Formula	$C_{19}H_{21}IN_2$	$C_{16}H_{21}IN_2$	$C_{67}H_{70}Cl_2I_2N_4O$	$C_{18}H_{19}IN_2$	$C_{36}H_{39}I_3N_2$
Formula weight	404.28	368.25	1271.97	390.25	880.39
T, K	173(2)	173(2)	293(2)	293(2)	173(2
crystal system	Triclinic	Orthorhombic	Triclinic	Orthorhombic	Monoclinic
space group	P -1	P b c a	P -1	P 21 21 21	P 21
a, Å	8.668(3)	11.3435(19)	13.894(7)	6.6862(13)	9.621(2)
b, Å	10.397(3)	12.737(2)	15.126(7)	10.542(2)	14.084(4)
c, Å	10.757(3)	24.224(4)	17.283(8)	23.520(5)	12.671(3)
α, deg	108.642(4)	90	108.209(5)	90	90
β, deg	99.276(4)	90	97.011(6)	90	91.151(5)
γ, deg	101.841(5)	90	114.943(5)	90	90
Volume, Å^3	871.6(5)	3499.9(10)	2990(2)	1657.9(6)	1716.7(8)
Z	2	8	2	4	2
D_{calc}, Mg / m^3	1.540	1.398	1.413	1.564	1.703
absorption coefficient, mm^{-1}	1.836	1.821	1.187	1.927	2.757
F(000)	404	1472	1296	776	856
crystal size, mm	0.240 x 0.120 x 0.090	0.120 x 0.110 x 0.020	0.350 x 0.300 x 0.100	0.200 x 0.100 x 0.050	0.500 x 0.080 x 0.060
2θ range, deg	2.061 to 27.934	2.460 to 27.537	1.617 to 25.009	1.732 to 25.783	2.633 to 25.999
reflections collected /unique	6305/4081 [R(int) = 0.0260]	24480/4030 [R(int) = 0.0785]	12435/10298 [R(int) = 0.0315]	8490/3086 [R(int) = 0.0211]	9133/6215 [R(int) = 0.0275]
data / restraints/ parameters	4081 / 0 / 206	4030 / 0 / 176	10298 / 9 / 698	3086 / 0 / 196	6215 / 1 / 374
goodness of fit on F^2	1.215	0.994	0.990	1.048	1.048
final R indices [I >2σ(I)][a]	R1 = 0.0365, wR2 = 0.1143	R1 = 0.0437, wR2 = 0.0899	R1 = 0.0449, wR2 = 0.1228	R1 = 0.0243, wR2 = 0.0519	R1 = 0.0775, wR2 = 0.2372
R indices (all data)	R1 = 0.0431, wR2 = 0.1341	R1 = 0.0895, wR2 = 0.1006	R1 = 0.0594, wR2 = 0.1305	R1 = 0.0278, wR2 = 0.0530	R1 = 0.0852, wR2 = 0.2449
lgst diff peak and hole, e/Å^3	1.129 and -1.223	0.499 and -0.623	0.773 and -1.067	0.291 and -0.320	2.348 and -1.524