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Ytterbium-mediated synthesis of 2, 4-diarylpyrroles from α-halo oxime ethers

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Supporting information

Table of contents:

General details

THF was distilled from sodium benzophenone under nitrogen. All reactions were conducted under a nitrogen atmosphere. Metallic ytterbium and and all other chemicals were purchased from a commercial source without further purification before use. Petroleum ether (PE) used refers to the 60-90^{o}C boiling point fraction of petroleum. The flash column chromatography was carried out on silica gel (200-300 mesh). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a 400 MHz spectrometer. Chemical shifts in ^{1}H NMR spectra are reported in parts per million (ppm, δ) downfield from the internal standard Me_4Si (TMS, δ = 0.00 ppm). Chemical shifts in ^{13}C NMR spectra are reported relative to the central line of the chloroform signal (δ = 77.0 ppm) or DMSO signal (δ = 40.0 ppm). HRMS were obtained with a TOF-Q III instrument.

General procedure for Synthesis of of α-halo oxime ethers [16]

The appropriate α-haloketone (10.0 mmol) and *O*-methyl (or Benzyl) hydroxylamine hydrochloride (15.0 mmol) were dissolved in ethanol (30 mL) containing one drop of concentrated sulphuric acid. The mixture was stirred at room temperature (heating, if necessary) for 2-12 h. The reaction progress was monitored by TLC. When the starting material disappeared, the solvent was evaporated in vacuum to near dryness. Ether (50 mL) was added and the solution was washed with 1 M aqueous $KHSO_4$ (2 × 20 ml), saturated aqueous $NaHCO_3$ (20 ml) and water (20 ml). The organic phase was dried over Na_2SO_4, filtered and the solvent evaporated in vacuum. The residue was purified by column chromatography (PE/dichloromethane) through deactivated silica gel. Finally, solvents were removed in vacuum affording the corresponding α-halo oxime ethers.

General procedure for Synthesis of 2, 4-diarylpyrroles

α-halo oxime ethers (0.5 mmol) and ytterbium powder (0.75 mmol, 130 mg) were suspended in dry THF (5 mL) under a N_2 atmosphere, catalytic amount I_2 was added, the mixture was stirred (the color turned to brown) under a N_2 atmosphere at room

temperature for 12h, then was quenched with 10 mL H_2O, The resulting mixture was extracted with ethyl acetate (3×20 mL) The organic phase was dried over Na_2SO_4, filtered and the solvent evaporated in vacuum. The residue was purified by column chromatography (PE/EA) through silica gel. Finally, solvents were removed in vacuum affording the corresponding pyrroles.

(*Z/E*)-2-bromo-1-phenylethanone *O*-methyl oxime (1a)[15]

Yield 89% (2.03 g); colorless liquid; The *Z/E* ratio was 70:30. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.71 - 7.68 (m, 2H), 7.39 - 7.37 (m, 3H), 4.51 & 4.33 (s, 2H),4.07 & 4.05 (s, 3H) ppm ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.54, 152.47, 133.36, 133.32, 129.62, 129.60, 128.59, 128.27, 126.06, 125.95, 62.72, 62.65, 32.46, 17.94 ppm.

(*Z/E*)-2-bromo-1-(p-tolyl) ethanone *O*-methyl oxime (1b) [15]

Yield 83% (2.01 g); colorless liquid; The *Z/E* ratio was 38:62. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.59 - 7.57 (d, 2H, *J* = 8 Hz), 7.19 - 7.17 (d, 2H, *J* = 8 Hz), 4.50 & 4.31 (s, 2H),4.06 & 4.04 (s, 3H), 2.35(s, 3 H) ppm ; ^{13}C NMR (100 MHz,$CDCl_3$) δ 152.48, 152.41, 139.72, 139.69, 130.45, 130.42, 129.28, 129.26, 125.93, 125.82, 62.60, 62.52, 32.42, 21.24, 17.97 ppm.

(*Z/E*)-2-bromo-1-(m-tolyl)ethanone *O*-methyl oxime (1c)

Yield 86% (2.08 g); colorless liquid; The *Z/E* ratio was 24:76. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.52 - 7.47 (m, 2H), 7.30 - 7.20 (m, 2H), 4.51 & 4.33 (s, 2H), 4.08 & 4.07 (s, 3H), 2.38 (s, 3H) ppm ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.81, 152.73, 138.32, 138.30, 133.33, 133.29, 130.47, 130.45, 128.51, 128.49, 126.67, 126.57, 123.26, 123.14, 62.71, 62.64, 32.63, 21.43, 18.14 ppm; HRMS (ESI) m/z ($M+H^+$) calcd for $C_{10}H_{13}BrNO^+$ 242.0182, found 242.0184.

(*Z/E*)-2-bromo-1-(o-tolyl)ethanone *O*-methyl oxime (1d) [15]

Yield 90% (2.18 g); colorless liquid; The *Z/E* ratio was 31:69. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.31 - 7.24 (m, 2H), 7.23 - 7.19 (m, 2H), 4.46 & 4.25 (s, 2H), 4.04 & 4.01 (s, 3H), 2.38 & 2.37 (s, 3H) ppm ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.36, 154.01, 136.57, 136.50, 134.08, 133.77, 130.73, 130.63, 129.04, 129.02, 128.69, 125.78, 125.73, 62.47, 62.40, 36.18, 21.67, 20.04, 20.00 ppm.

(*Z/E*)-2-bromo-1-(4-pentylphenyl)ethanone *O*-methyl oxime (1e)

Yield 88% (2.62 g); colorless oil; The *Z/E* ratio was 45:55. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.62 - 7.59 (m, 2H), 7.21 - 7.18 (m, 2H), 4.50 & 4.32 (s, 2H), 4.06 & 4.04 (s, 3H), 2.60 (t, 2H,

J=8Hz), 1.64 – 1.55 (m, 2H), 1.37 – 1.26 (m, 4H), 0.88 (t, 3H, *J*=8Hz) ppm ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.54, 152.47, 144.75, 144.73, 130.72, 130.69, 128.65, 128.63, 125.95, 125.83, 62.61, 62.53, 35.65, 32.47, 31.38, 30.89, 22.48, 17.99, 13.97 ppm; HRMS (ESI) m/z ($M+H^+$) calcd for $C_{14}H_{21}BrNO^+$ 300.0788, found 300.0784.

(*Z/E*)-2-bromo-1-(4-chlorophenyl)ethanone *O*-methyl oxime (1f) [15]

Yield 80% (2.1 g); white solid; The *Z/E* ratio was 29:71. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ7.64 - 7.61 (m, 2H), 7.37 - 7.34 (m, 2H), 4.49 & 4.30 (s, 2H),4.07 & 4.06 (s, 3H) ppm ; ^{13}C NMR (100 MHz,$CDCl_3$) δ 151.46, 151.39, 135.62, 135.60, 131.77, 131.73, 128.79, 128.77, 127.34, 127.22 ppm.

(*Z/E*)-2-bromo-1-(4-fluorophenyl)ethanone *O*-methyl oxime (1g) [15]

Yield 77% (1.89 g); white solid; The *Z/E* ratio was 24:76. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.71 - 7.67 (m, 2H), 7.11 - 7.05 (m, 2H), 4.51 & 4.32 (s, 2H),4.07 & 4.06 (s, 3H) ppm ; ^{13}C NMR (100 MHz,$CDCl_3$) δ 164.78, 164.76, 162.30, 162.27, 151.49, 151.41, 129.48, 129.44, 129.40, 128.01, 127.93, 127.89, 127.81, 115.68, 115.66, 115.46, 115.44, 62.69, 62.61, 32.28, 17.72 ppm.

(*Z/E*)-2-bromo-1-(3, 4-dichlorophenyl)ethanone *O*-methyl oxime (1h) [15]

Yield 82% (2.44 g); white solid; The *Z/E* ratio was 37:63. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.82 - 7.81 (m, 1H), 7.55- 7.52 (m, 1H), 7.47 - 7.45 (m, 1H), 4.49 & 4.30 (s, 2H), 4.10 & 4.08 (s, 3H) ppm ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.50, 150.43, 133.77, 133.75, 133.29, 133.25, 133.01, 132.98, 130.54, 130.52, 127.94, 127.82, 125.24, 125.11, 63.12, 63.03, 31.94, 17.22 ppm.

(*Z/E*)-2-bromo-1-(2, 4-dichlorophenyl)ethanone *O*-methyl oxime (1i) [15]

Yield 78% (2.31 g); white solid; The *Z/E* ratio was 45:55. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.46 - 7.43 (m, 1H), 7.36- 7.25 (m, 2H), 4.56 & 4.35 (s, 2H), 4.06 & 4.04 (s, 3H) ppm ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.00, 152.77, 136.04, 135.97, 133.63, 133.48, 132.68, 132.47, 132.01, 131.77, 129.63, 129.56, 127.28, 127.24, 62.80, 62.74, 35.55, 20.90 ppm.

(Z/E)-2-bromo-1-(4-methoxyphenyl)ethan-1-one O-methyl oxime (1j)

Yield 80% (2.05 g); white solid; The *Z/E* ratio was 71:29. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.21 – 7.47 (m, 2H), 7.06 – 6.70 (m, 2H), 4.52 (s, 1H), 4.34 (s, 1H), 4.05 (d, *J* = 6.5 Hz, 3H), 3.83 (s, 3H) ppm**;** ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.94, 160.92, 152.35, 152.27, 127.67, 127.55, 125.99, 125.96, 114.17, 114.16, 77.48, 77.16, 76.84, 62.74, 62.67, 55.45, 32.63, 18.19 . ppm.

methyl (Z/E)-4-(2-bromo-1-(methoxyimino)ethyl)benzoate (1k)

Yield 89% (2.54 g); white solid; The *Z/E* ratio was 79:21. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.06 (d, *J* = 8.6 Hz, 2H), 7.79 (d, *J* = 8.6 Hz, 2H), 4.55 (s, 1H), 4.36 (s, 1H), 4.11 (d, *J* = 6.7 Hz, 3H), 3.93 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.69, 151.82, 137.65, 131.05, 129.95, 126.17, 126.05, 77.48, 77.16, 76.84, 63.15, 52.37, 32.32, 17.67 ppm.

(Z)-2-bromo-1-(4-ethynylphenyl)ethan-1-one O-methyl oxime (1l)

Yield 82% (2.07 g); white solid; The *Z/E* ratio was 58:42. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.83 (dd, *J* = 8.6, 1.7 Hz, 2H), 7.69 (d, *J* = 8.7 Hz, 2H), 4.53 (s, 1H), 4.34 (s, 1H), 4.12 (d, *J* = 6.7 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.07, 151.02, 137.73, 137.69, 132.49, 132.47, 126.78, 126.64, 118.58, 113.18, 77.48, 77.16, 76.84, 63.44, 63.36, 31.99, 17.22 ppm.

(*Z/E*)-2-bromo-1-(3-chlorophenyl)ethanone *O*-methyl oxime (1m) [15]

Yield 92% (2.41 g); colorless oil; The *Z/E* ratio was 27:73. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.72 - 7.70 (m, 1H), 7.57 - 7.54 (m, 2H), 7.36 - 7.28 (m, 2H), 4.48 & 4.29 (s, 2H),4.08 & 4.06 (s, 3H) ppm ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.26, 151.19, 135.10, 135.05, 134.63, 134.61, 129.78, 129.76, 129.56, 129.54, 126.10, 126.00, 124.16, 124.03, 62.93, 62.85, 32.13, 17.49 ppm.

(*Z/E*)-2-bromo-1-(naphthalen-2-yl)ethanone *O*-methyl oxime (1o) [15]

Yield 85% (2.36 g); white solid; The *Z/E* ratio was 62:38. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.07 (s, 1H), 7.92 - 7.85 (m, 2H), 7.82 - 7.80 (m, 2H),7.50 - 7.46(m, 2H),4.62 & 4.44 (s, 2H),4.12 & 4.11(s, 3H) ppm ; ^{13}C NMR (100 MHz,$CDCl_3$) δ152.33, 152.25, 133.71, 133.69, 132.93, 130.52, 128.46, 128.25, 128.23, 127.54, 126.78, 126.36, 125.84, 125.67, 123.09, 123.04, 62.78, 62.70, 32.18, 17.68 ppm.

(*Z/E*)-2-bromo-1-(thiophen-2-yl) ethanone *O*-methyl oxime (1p) [15]

Yield 53% (1.24 g); white solid; The *Z/E* ratio was 68:32. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.32 - 7.29 (m, 2H), 7.05 - 7.02 (m, 1H), 4.48 & 4.31 (s, 2H),4.04 & 4.03(s, 3H) ppm ; ^{13}C NMR (100 MHz,$CDCl_3$) δ149.03, 148.86, 136.95, 136.92, 127.41, 127.39, 127.19, 127.17, 126.75, 126.50, 62.81, 62.74, 32.43, 17.59 ppm.

(*Z/E*)-2-bromo-1-phenylethanone *O*-benzyl oxime (1q) [15]

Yield 88% (2.67 g); colorless liquid; The *Z/E* ratio was 44:56. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.71 - 7.67 (m, 2H), 7.44 - 7.28 (m, 8H), 5.32 & 5.31 (s, 2H), 4.55 & 4.37(s, 2H) ppm ; ^{13}C NMR (100 MHz,$CDCl_3$) δ 152.91, 152.85, 137.38, 137.33, 133.44, 133.37, 129.66, 129.64, 128.58, 128.56, 128.39, 128.38, 128.12, 128.07, 127.95, 127.93, 126.15, 126.03, 76.97, 76.91, 32.69 , 18.19 ppm.

2, 4-diphenyl-1H-pyrrole (2a) [5b]

Yield 58% (31.8 mg); white solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.31 (s, 1H), 7.55 - 7.53 (m, 2H), 7.46 - 7.44 (m, 2H), 7.36 - 7.32 (m, 4H), 7.23 - 7.17 (m, 2H), 7.03 - 7.02 (m, 1H), 6.82 – 6.81 (m, 2H) ppm ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.4, 133.0, 132.4, 128.9, 128.7, 126.4, 125.7, 125.1, 123.8, 115.7, 103.8 ppm; LC-MS(ESI):$[M+H]^+$ m/z= 221.1.

2,4-di-p-tolyl-1H-pyrrole (2b) [5b]

Yield 52% (32.1 mg); white solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.36 (s, 1H), 7.46 - 7.38 (m, 4H), 7.19 - 7.15 (m, 4H), 7.07 (s, 1H), 6.75 (s, 1H), 2.36 (s, 3H), 2.35 (s, 3H) ppm ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.13, 135.18, 133.07, 132.71, 129.80, 129.56, 129.29, 126.46, 125.07, 123.79, 114.81, 103.39, 21.12, 21.09 ppm; LC-MS(ESI):$[M+H]^+$ m/z= 248.1.

2,4-di-m-tolyl-1H-pyrrole (2c)

Yield 55% (34 mg); white solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.32 (s, 1H), 7.37 - 7.34 (m, 2H), 7.30 - 7.29 (m, 1H), 7.26 - 7.20 (m, 3H), 7.04 – 7.00 (m, 3H), 6.80 – 6.79 (m, 1H), 2.365 (s, 3H), 2.359 (s, 3H) ppm ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 138.1, 135.4, 133.0, 132.4 128.8, 128.5, 127.2, 126.4, 126.4, 125.9, 124.5, 122.2, 120.8, 115.5, 103.8, 21.51, 21.48 ppm; HRMS (ESI) m/z ($M+H^+$) calcd for $C_{18}H_{18}N^+$ 248.1434, found 248.1435.

2, 4-di-o-tolyl-1H-pyrrole (2d)

Yield 51% (32 mg); white solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.24 (s, 1H), 7.44 - 7.42 (m, 1H), 7.39 - 7.36 (m, 1H), 7.27 - 7.13 (m, 6H), 6.92 – 6.91 (m, 1H), 6.51 – 6.50 (m, 1H), 2.49 (s, 3H), 2.48 (s, 3H) ppm ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.6, 135.2, 135.0, 132.6, 131.1, 131.0, 130.6, 129.1, 127.7, 126.8, 126.1, 126.0, 125.2, 116.8, 109.9, 21.4, 21.3 ppm; HRMS (ESI) m/z ($M+H^+$) calcd for $C_{18}H_{18}N^+$ 248.1434, found 248.1435.

2,4-bis(4-pentylphenyl)-1H-pyrrole (2e)

Yield 50% (45 mg); white solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.28 (s, 1H), 7.46 - 7.36 (m, 4H), 7.17 - 7.15 (m, 4H), 7.00 – 6.99 (m, 1H), 6.75 – 6.74 (m, 1H), 2.61 – 2.57 (m, 4H), 1.66 – 1.58 (m, 4H), 1.37 – 1.31 (m, 8H), 0.91 – 0.88 (m, 6H) ppm ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 140.3, 133.0, 132.9, 130.0, 128.9, 128.6, 126.4, 125.0, 123.7, 114.9, 103.3, 35.60, 35.58, 31.54, 31.50, 31.23, 31.11, 22.57, 22.54, 14.05, 14.04 ppm; HRMS (ESI) m/z ($M+H^+$) calcd for $C_{26}H_{34}N^+$ 360.2686, found 360.2685.

2,4-bis(4-chlorophenyl)-1H-pyrrole (2f) [5b]

Yield 43% (31 mg); white solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.58 (s, 1H), 7.71 - 7.68 (m,

2H), 7.64 - 7.62 (m, 2H), 7.43 - 7.41 (m, 3H), 7.37 - 7.35 (m, 2H), 7.01 - 7.00 (m, 1H) ; ^{13}C NMR (100 MHz, DMSO-d_6) δ 135.0, 131.9, 131.8, 130.5, 129.8, 129.2, 129.0, 126.5, 125.5, 124.2, 118.1, 104.4 ppm; LC-MS(ESI):$[M+H]^+$ m/z= 288.0.

2,4-bis(4-fluorophenyl)-1H-pyrrole (2g) [5b]

Yield 45% (28.7 mg); white solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.47 (s, 1H), 7.75 - 7.71 (m, 2H), 7.67 - 7.63 (m, 2H), 7.35 - 7.34 (m, 1H), 7.26 - 7.22 (m, 2H), 7.19 - 7.15 (m, 2H), 6.93 – 6.92 (m, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.06 (^1J(C, F)=241 Hz), 160.76 (^1J(C, F)=240 Hz), 132.755 (^4J(C, F)=3 Hz), 131.94, 129.815 (^4J(C, F)=3 Hz), 126.55 (^3J(C, F)=8 Hz), 125.78 (^3J(C, F)=8 Hz), 124.34, 116.97, 116.275 (^2J(C, F)=21 Hz), 115.735 (^2J(C, F)=21 Hz), 103.72 ppm; LC-MS(ESI): $[M+H]^+$ m/z= 256.1.

2,4-bis(3,4-dichlorophenyl)-1H-pyrrole (2h)

Yield 41% (36.6 mg); light yellow solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.76 (s, 1H), 7.98 - 7.97 (m, 1H), 7.90 - 7.89 (m, 1H), 7.67 - 7.57 (m, 5H), 7.25 - 7.23 (m, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 136.8, 133.5, 132.1, 131.9, 131.4, 131.1, 130.7, 128.2, 127.5, 126.4, 125.4, 124.9, 123.9, 123.2, 119.6, 105.7 ppm; HRMS (ESI) m/z ($M+H^+$) calcd for $C_{16}H_{10}Cl_4N^+$ 355.9562, found 355.9560.

2,4-bis(2,4-dichlorophenyl)-1H-pyrrole (2i)

Yield 45% (40 mg); white solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.71 (s, 1H), 7.72 - 7.64 (m, 4H), 7.55 - 7.52 (m, 1H), 7.47 - 7.42 (m, 2H), 7.07 - 7.06 (m, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 133.5, 131.7, 131.6, 131.5, 131.1, 130.8, 130.4, 130.3, 130.0, 128.0, 127.9, 127.5, 120.8, 120.7, 111.1 ppm; HRMS (ESI) m/z ($M+H^+$) calcd for $C_{16}H_{10}Cl_4N^+$ 355.9562, found 355.9560.

2,4-bis(3-chlorophenyl)-1H-pyrrole(2j)

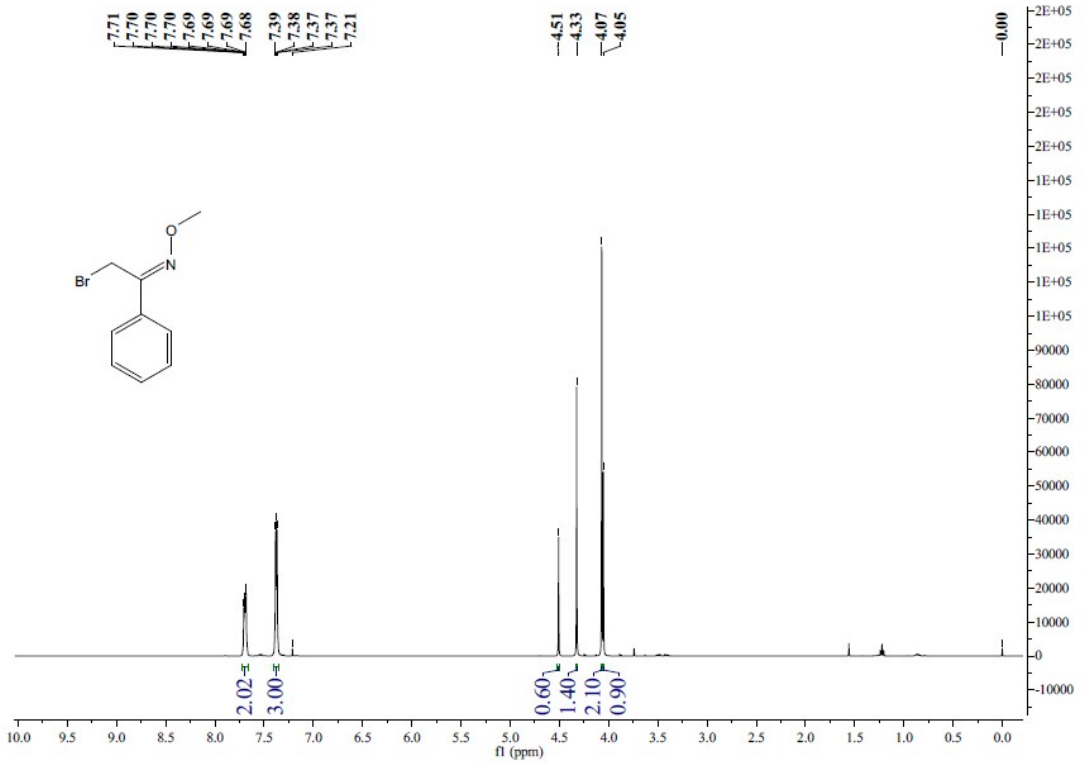
Yield 57% (41 mg); white solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.38 (s, 1H), 7.50 - 7.49 (m, 1H), 7.42 - 7.36 (m, 2H), 7.30 - 7.21 (m, 3H), 7.18 - 7.14 (m, 2H), 7.05 - 7.03 (m, 1H), 6.76 – 6.75 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 134.8, 134.5, 133.8, 131.8, 130.2, 129.9, 126.4, 125.7, 125.3, 125.0, 123.8, 123.1, 121.7, 116.6, 104.6 ppm; HRMS (ESI) m/z ($M+H^+$) calcd for $C_{16}H_{12}Cl_2N^+$ 288.0341, found 288.0339.

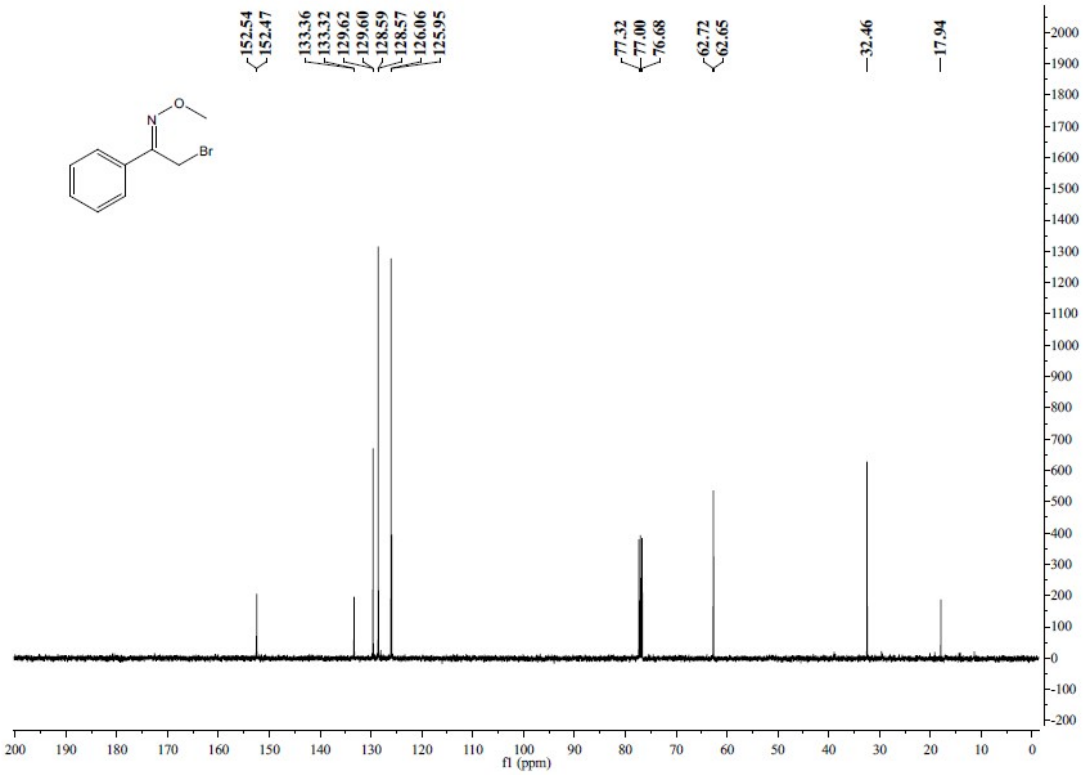
2,4-bis(2-fluorophenyl)-1H-pyrrole (2k)

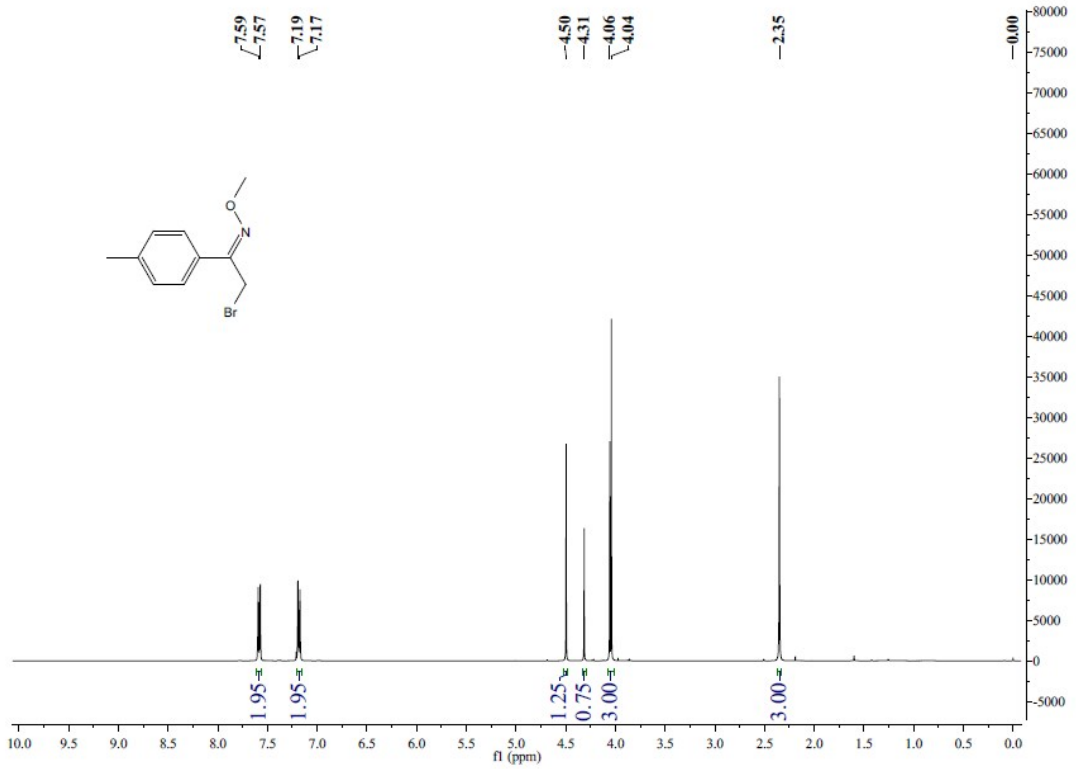
Yield 56% (35.7 mg); white solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 9.07 (s, 1H), 7.68 - 7.58 (m, 2H), 7.34 - 7.33 (m, 2H), 7.19 - 7.07 (m, 6H), 7.02 - 7.00 (m, 1H) ppm; ^{13}C NMR (100 MHz,

$CDCl_3$) δ 159.65 (^1J(C, F)=245 Hz), 158.66 (^1J(C, F)=243 Hz), 127.73, 127.69, 127.39, 127.30, 127.26, 126.73, 126.65, 126.60, 124.71, 124.68, 124.16, 124.13, 123.00, 122.87, 119.81, 119.70, 119.19, 118.99, 118.96, 118.89, 118.86, 116.25 (^2J(C, F)=23 Hz), 115.94 (^2J(C, F)=23 Hz), 106.35(t, ^4J(C, F)=2.5 Hz) ppm; HRMS (ESI) m/z ($M+H^+$) calcd for $C_{16}H_{12}F_2N^+$ 256.0932, found 256.0930.

^{1}H and ^{13}C of all compounds



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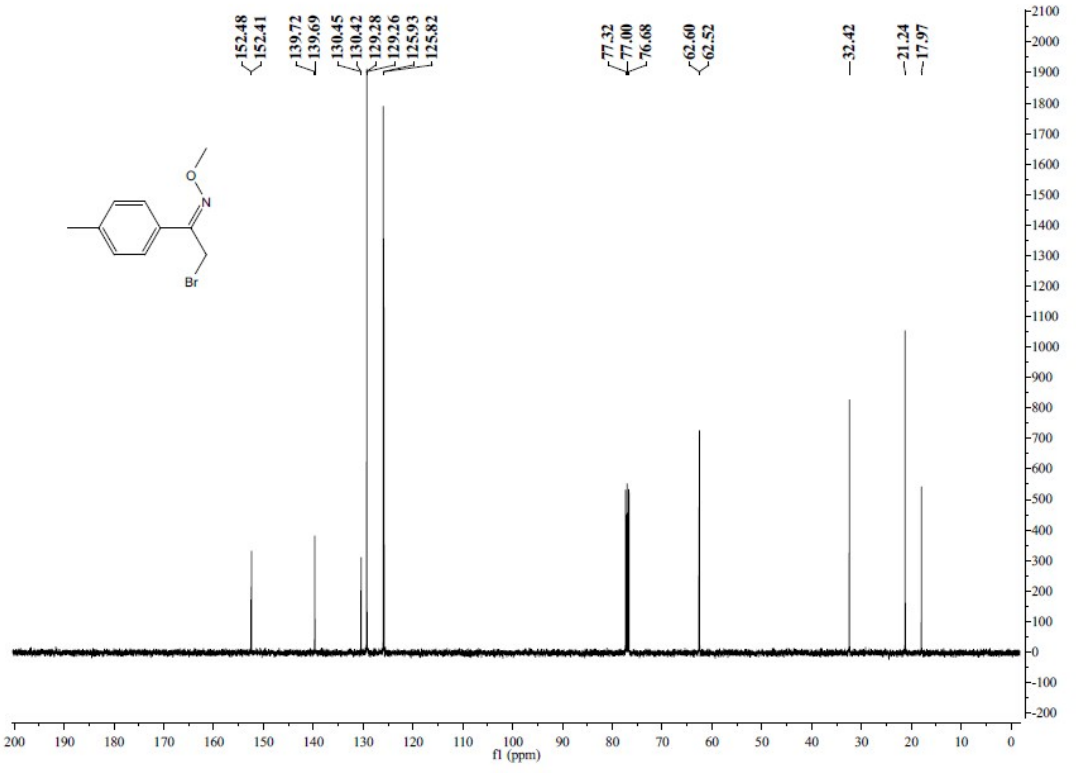
3.00
f1 (ppm)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129.26
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76.68
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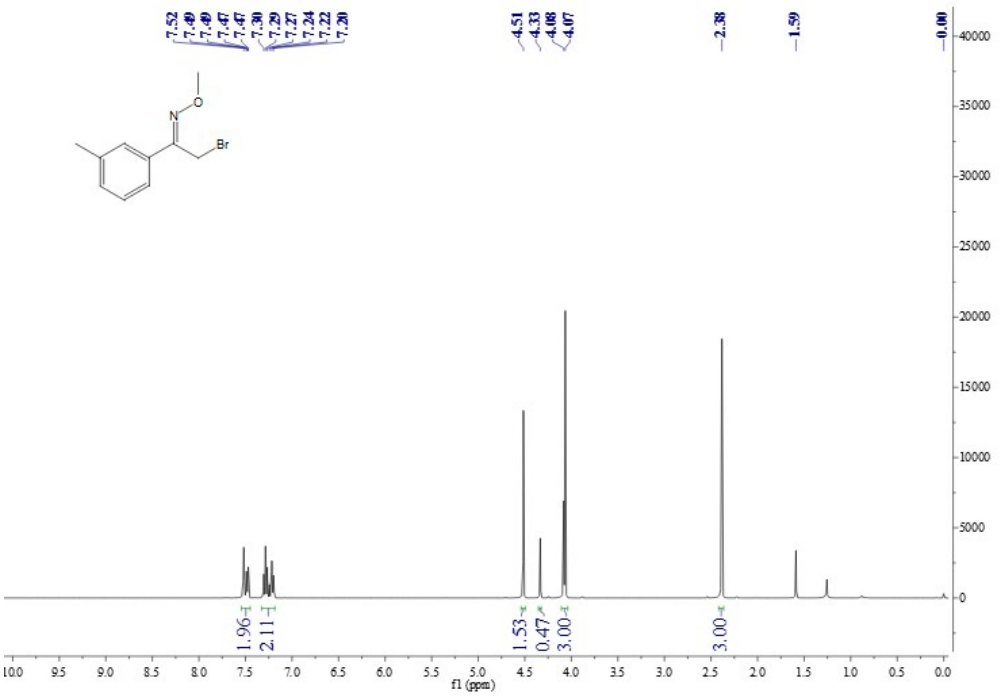
62.52
32.42
21.24
17.97
O
N
Br
f1 (ppm)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7.20
4.51
4.33
4.08
4.07
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2.11
1.53
0.47
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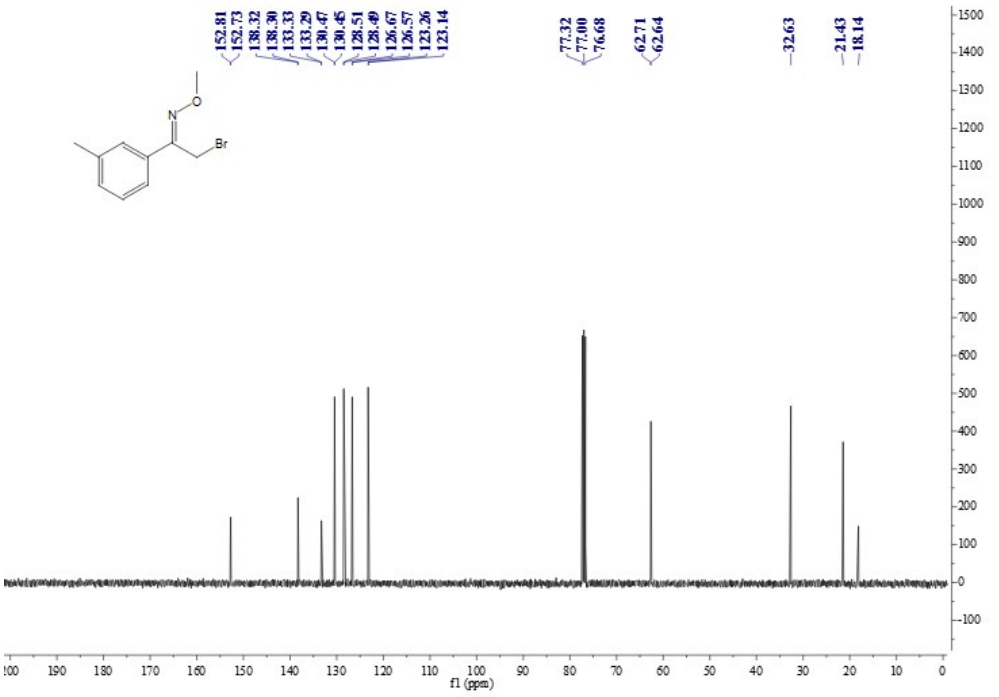
3.00
f1 (ppm)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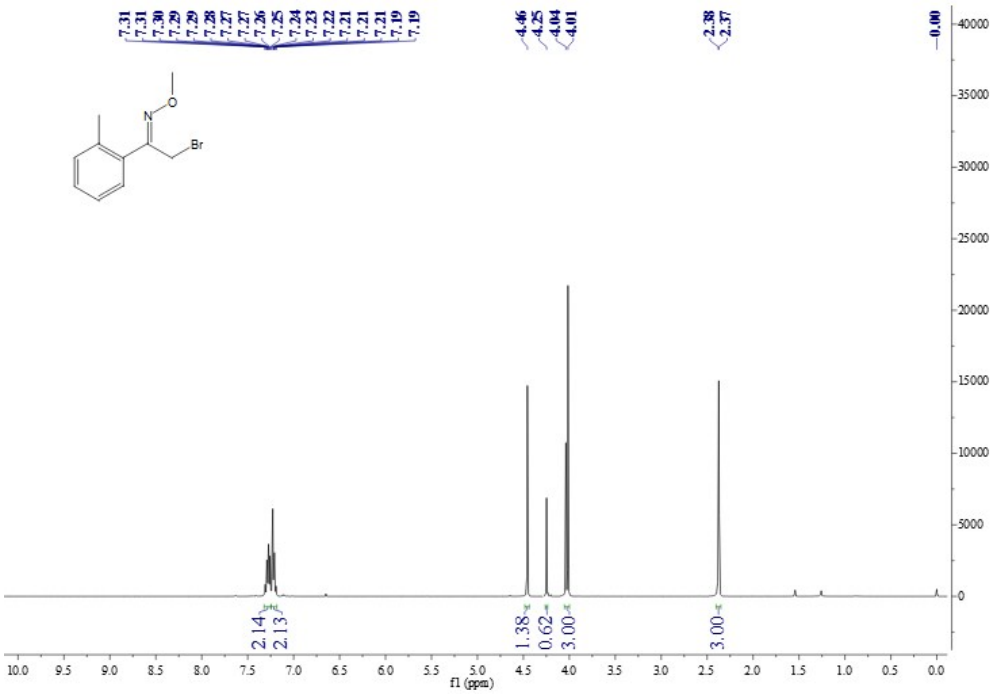
O
Br
f1 (ppm)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7.22
7.21
7.21
7.21
7.19
7.19
4.46
4.25
4.04
4.01
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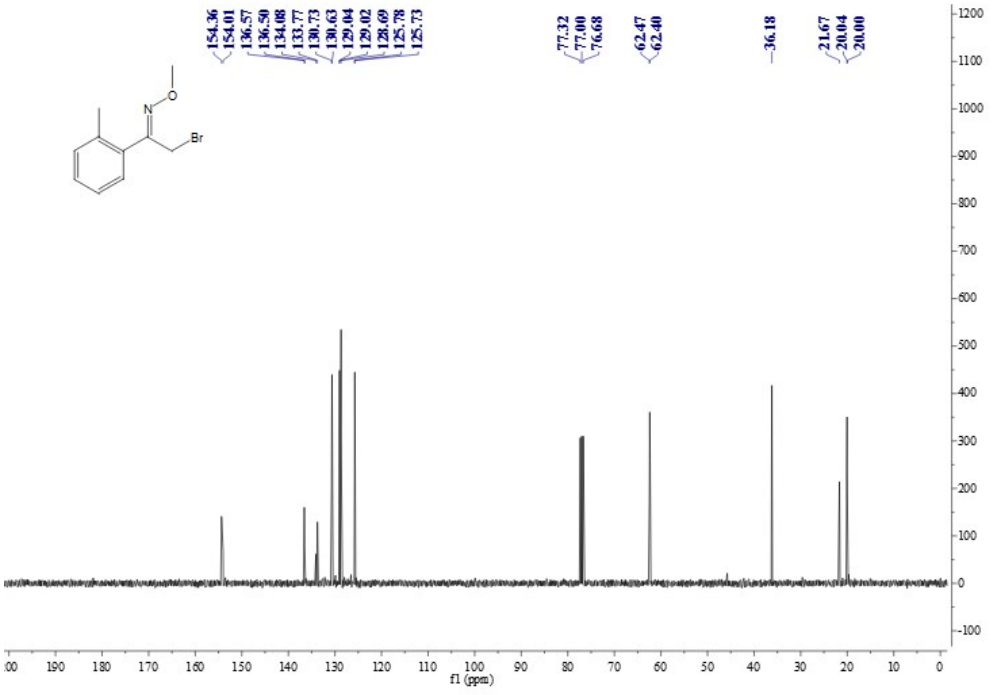
N
O
Br
2.14
2.13
1.38
0.62
3.00
3.00
f1 (ppm)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125.73
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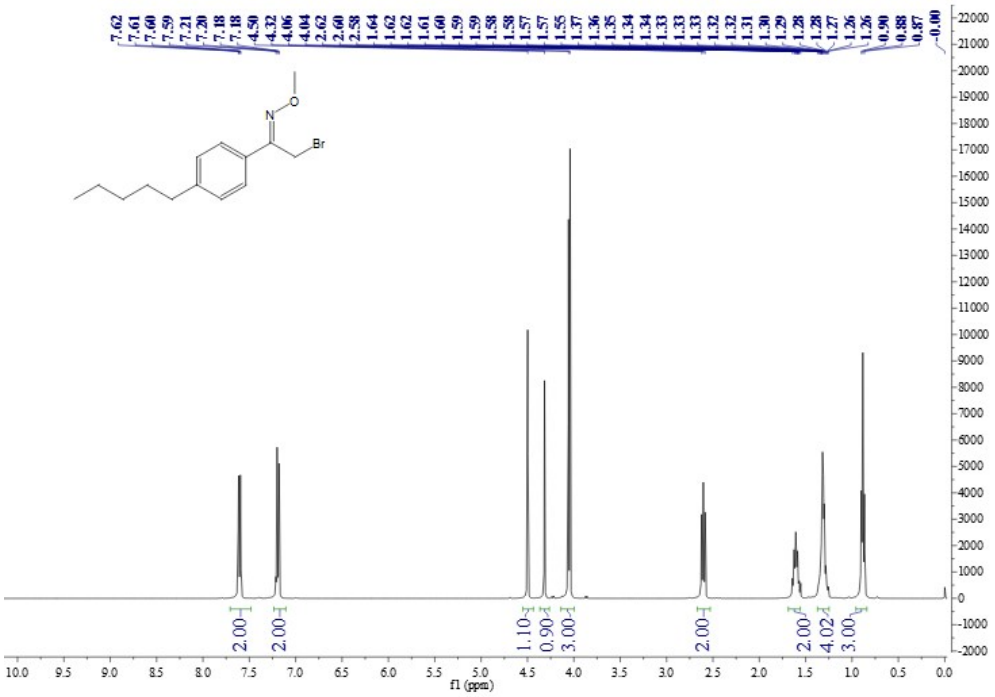
20.04
20.00
N
O
Br
f1 (ppm)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7.18
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4.06
4.04
2.62
2.60
2.58
1.64
1.62
1.62
1.61
1.60
1.59
1.59
1.58
1.58
1.57
1.57
1.55
1.37
1.36
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1.33
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1.32
1.32
1.31
1.30
1.29
1.28
1.28
1.27
1.26
1.26
0.90
0.88
0.87
0.00
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2.00
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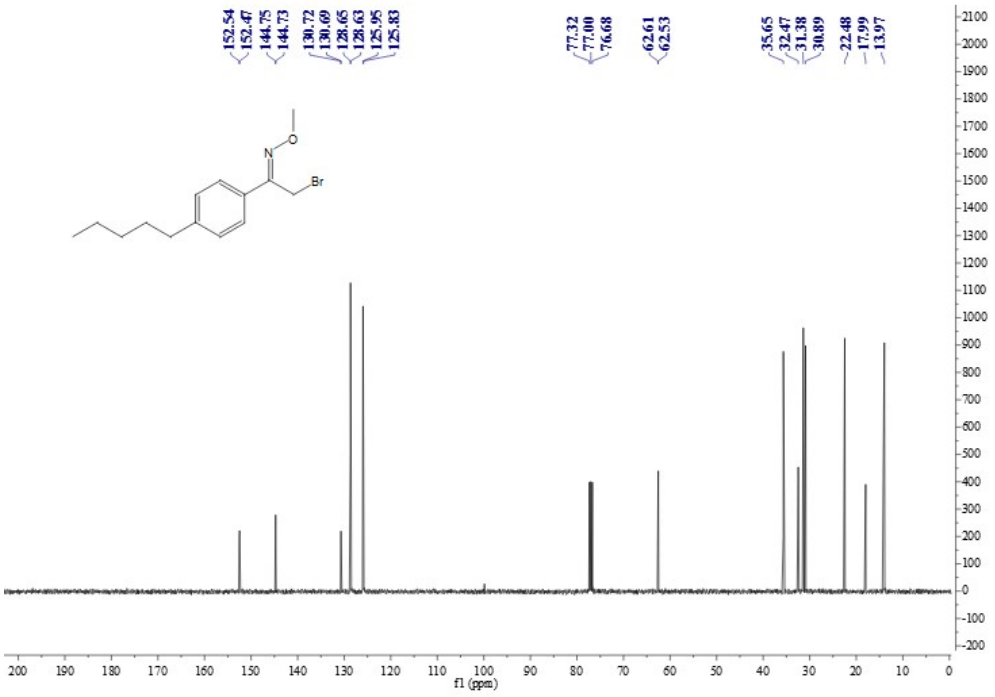
0.90
3.00
2.00
2.00
4.02
3.00
f1 (ppm)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77.00
76.68
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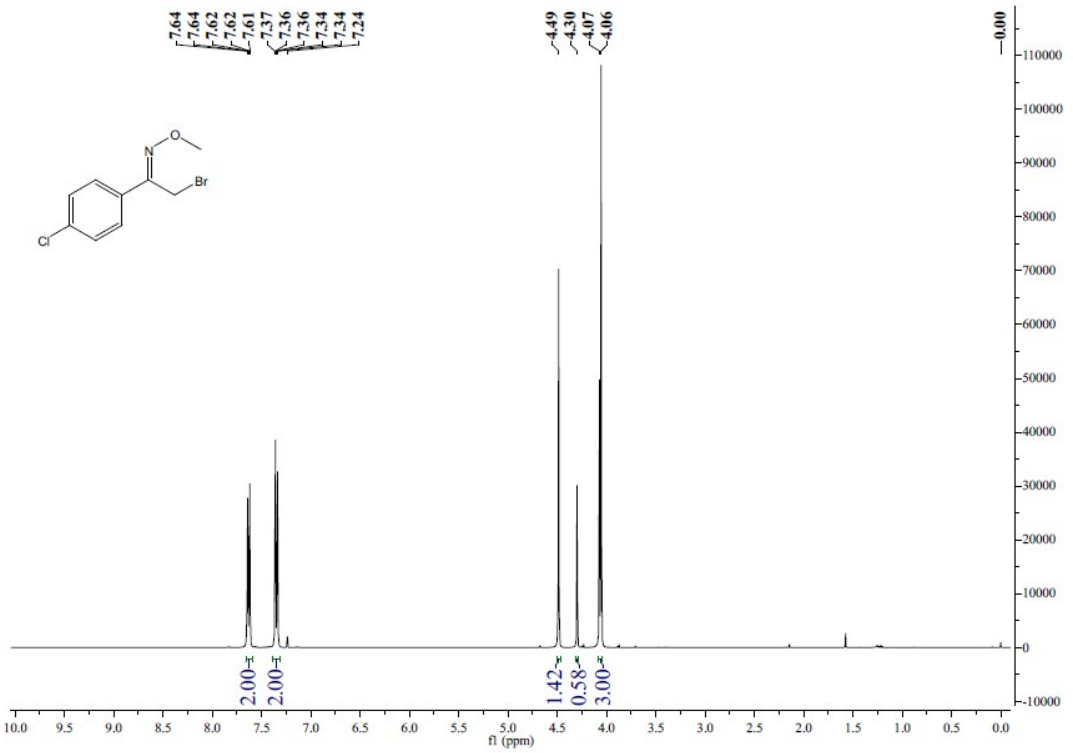
32.47
31.38
30.89
22.48
17.99
13.97
N
O
Br
f1 (ppm)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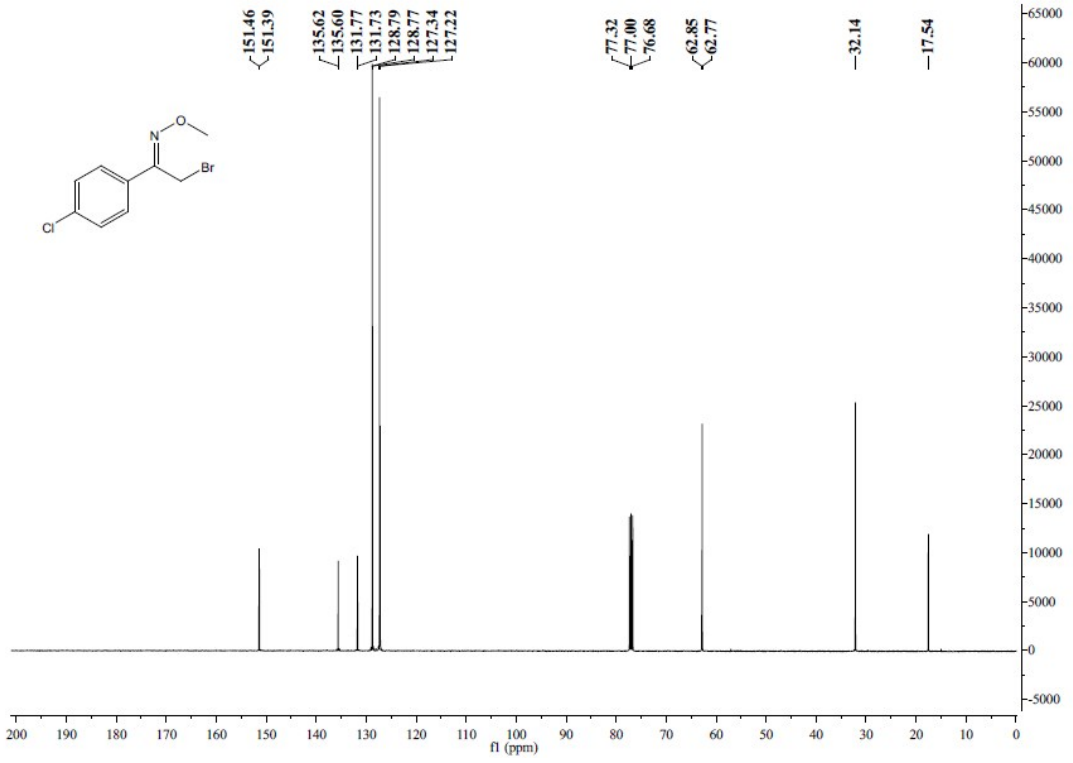
7.62
7.61
7.37
7.36
7.36
7.34
7.34
7.24
4.49
4.30
4.07
4.06
0.00
N
O
Br
Cl
2.00
2.00
1.42
0.58
3.00
f1 (ppm)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128.77
127.34
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62.85
62.77
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17.54
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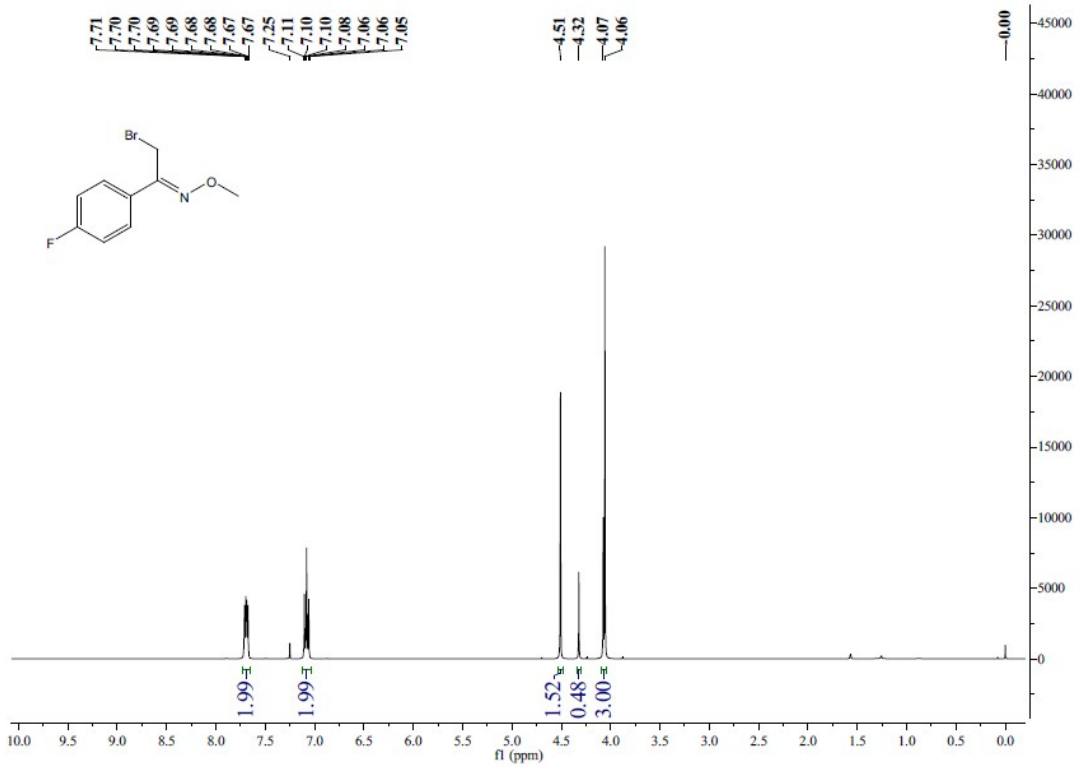
O
Br
Cl
f1 (ppm)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7.68
7.68
7.67
7.67
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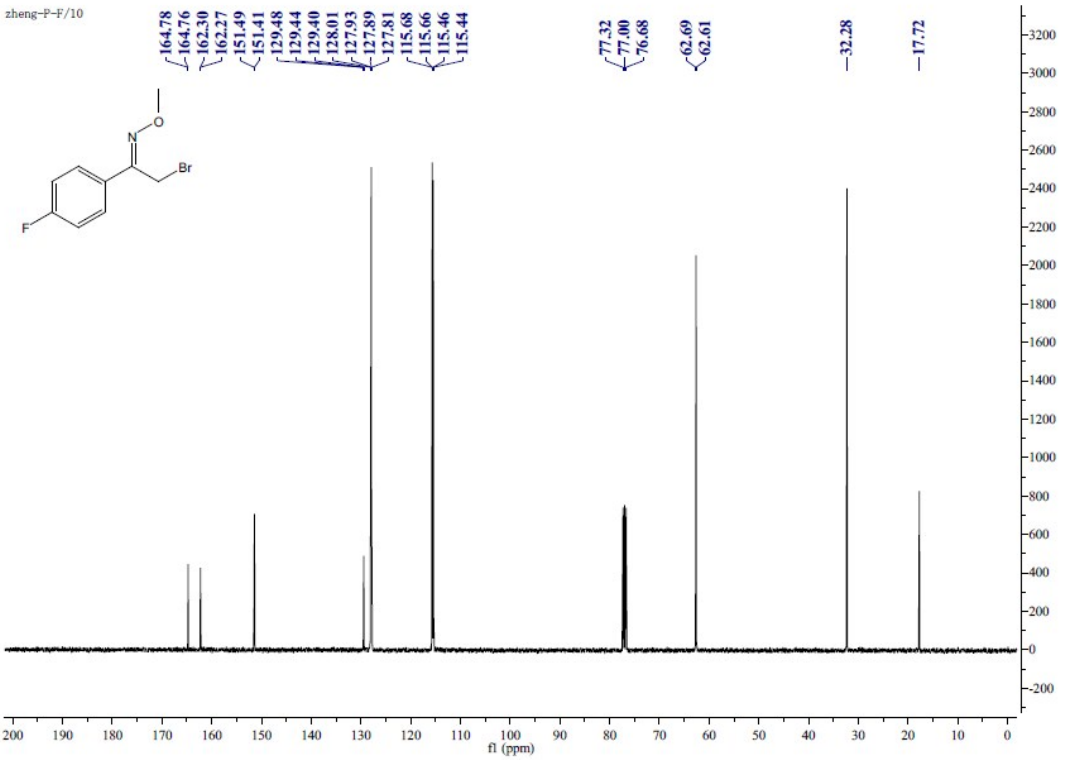
7.11
7.10
7.10
7.08
7.06
7.06
7.05
4.51
4.32
4.07
4.06
0.00
Br
N
O
F
1.99
1.99
1.52
0.48
3.00
f1 (ppm)


zheng-P-F/10
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162.30
162.27
151.49
151.41
129.48
129.44
129.40
128.01
127.93
127.89
127.81
115.68
115.66
115.46
115.44
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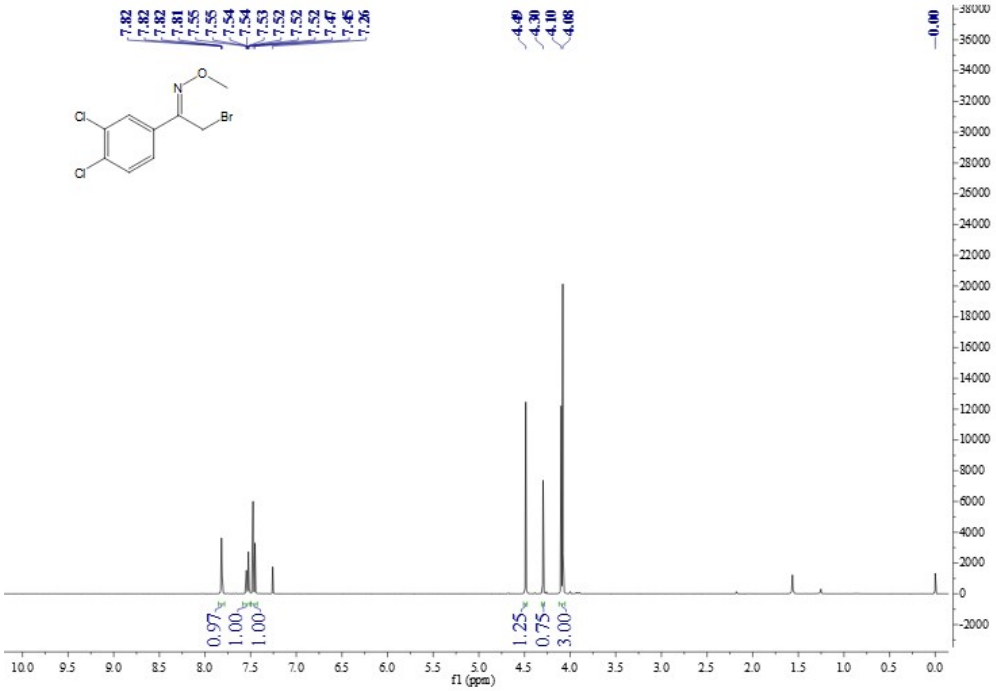
77.00
76.68
62.69
62.61
32.28
17.72
N
O
Br
F
f1 (ppm)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7.82
7.82
7.81
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7.55
7.54
7.54
7.53
7.52
7.52
7.52
7.47
7.45
7.26
4.49
4.30
4.10
4.08
0.00
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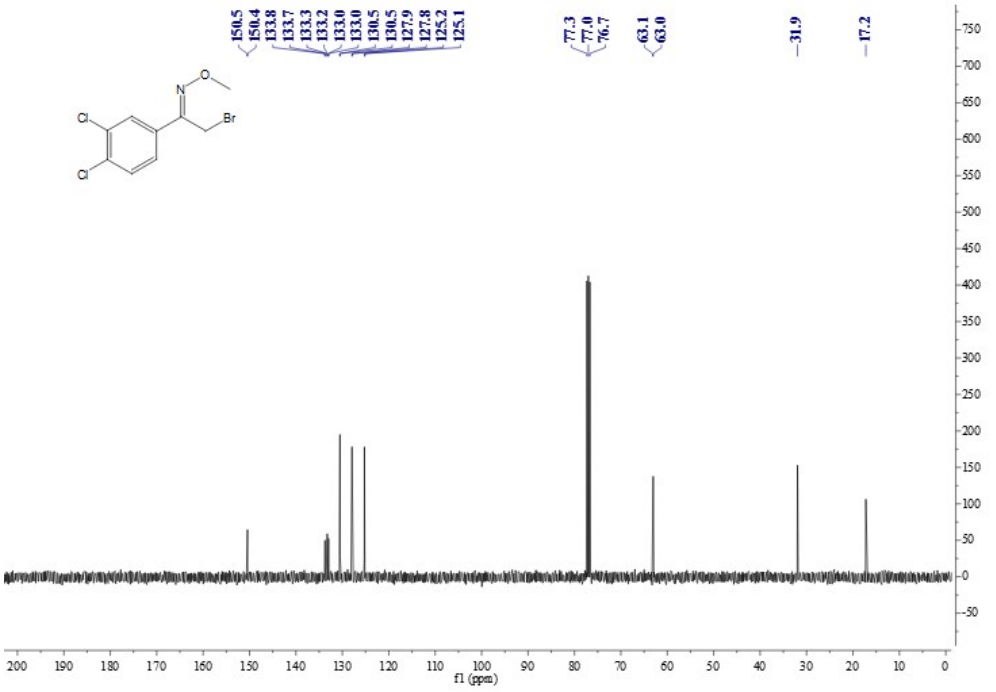
O
Br
Cl
Cl
0.97
1.00
1.00
1.25
0.75
3.00
f1 (ppm)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133.2
133.0
133.0
130.5
130.5
127.9
127.8
125.2
125.1
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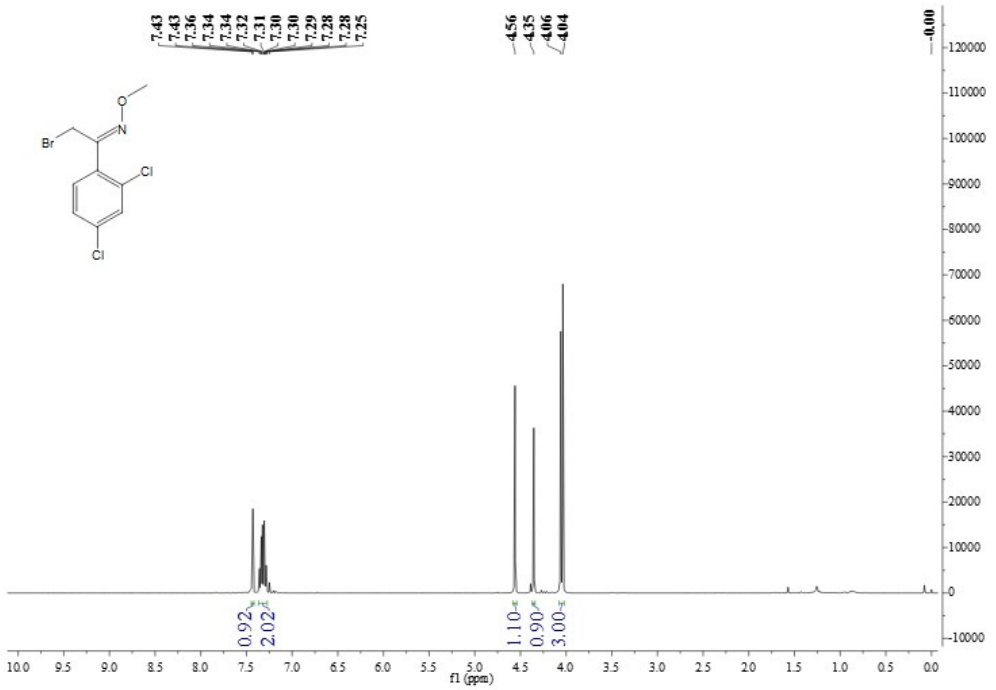
77.0
76.7
63.1
63.0
31.9
17.2
N
O
Br
Cl
Cl
f1 (ppm)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7.34
7.32
7.31
7.30
7.30
7.29
7.28
7.28
7.25
4.56
4.35
4.06
4.04
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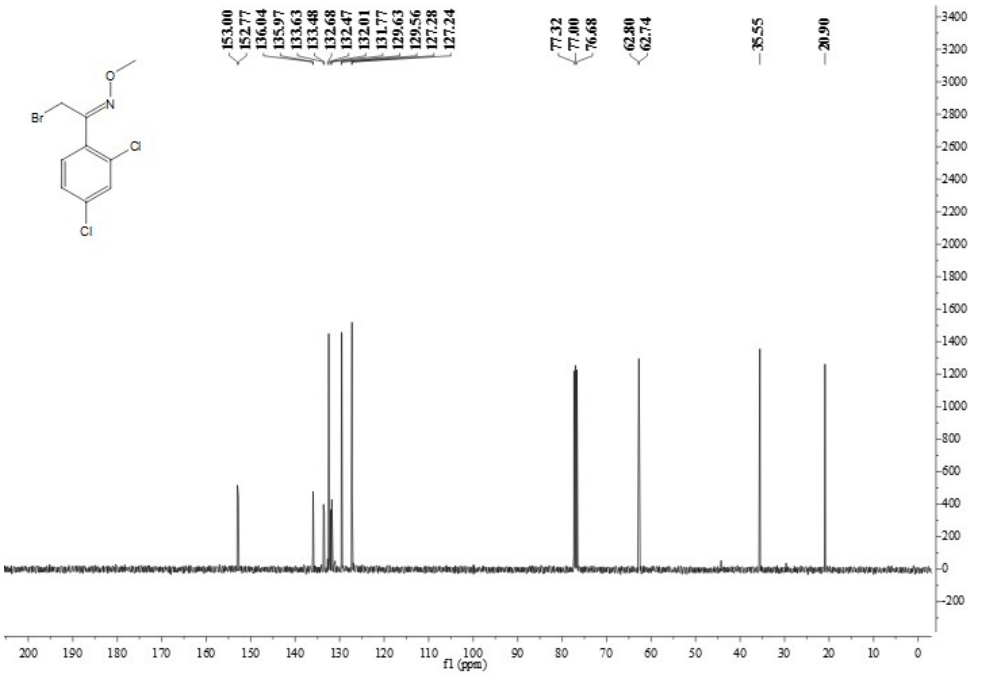
Br
O
N
Cl
Cl
0.92
2.02
1.10
0.90
3.00
f1 (ppm)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133.48
132.68
132.47
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131.77
129.63
129.56
127.28
127.24
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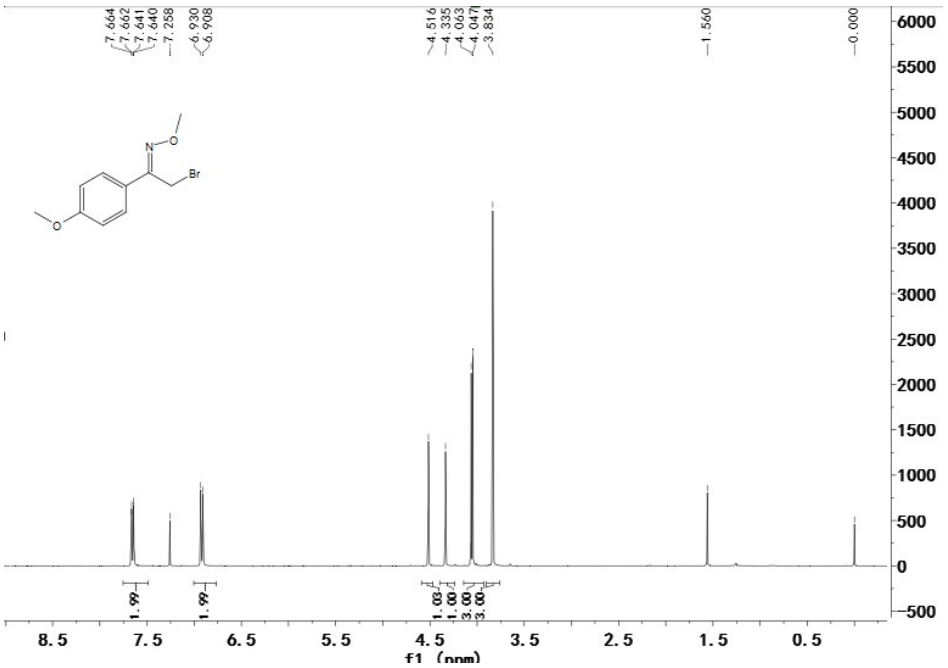
77.00
76.68
62.80
62.74
35.55
20.90
Br
O
N
Cl
Cl
f1 (ppm)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7.640
7.258
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6.908
4.516
4.335
4.063
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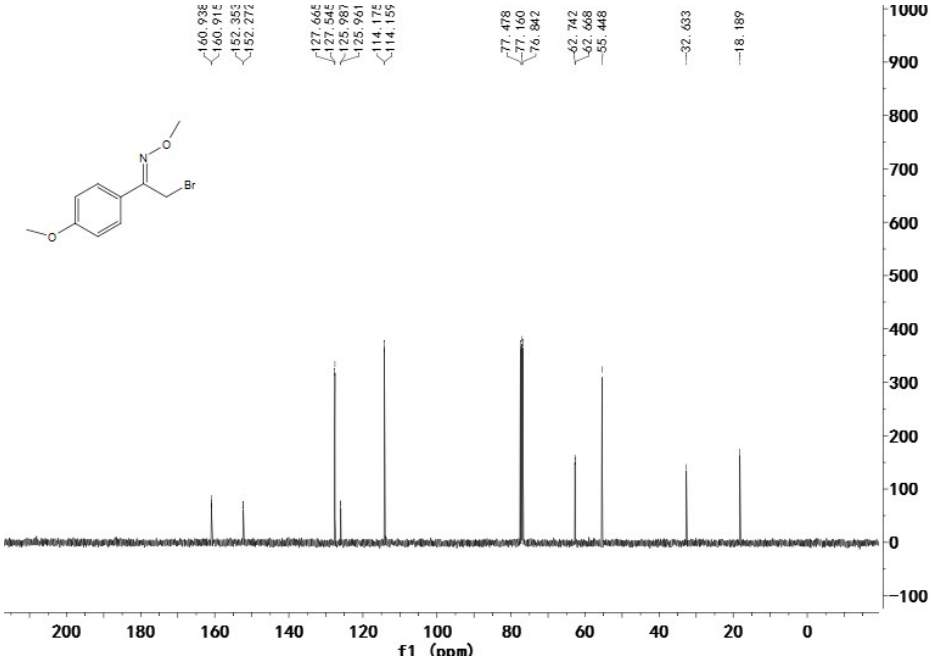
1.560
0.000
1.99
1.99
1.00
1.00
3.00
3.00
f1 (ppm)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152.353
152.272
127.665
127.545
125.987
125.961
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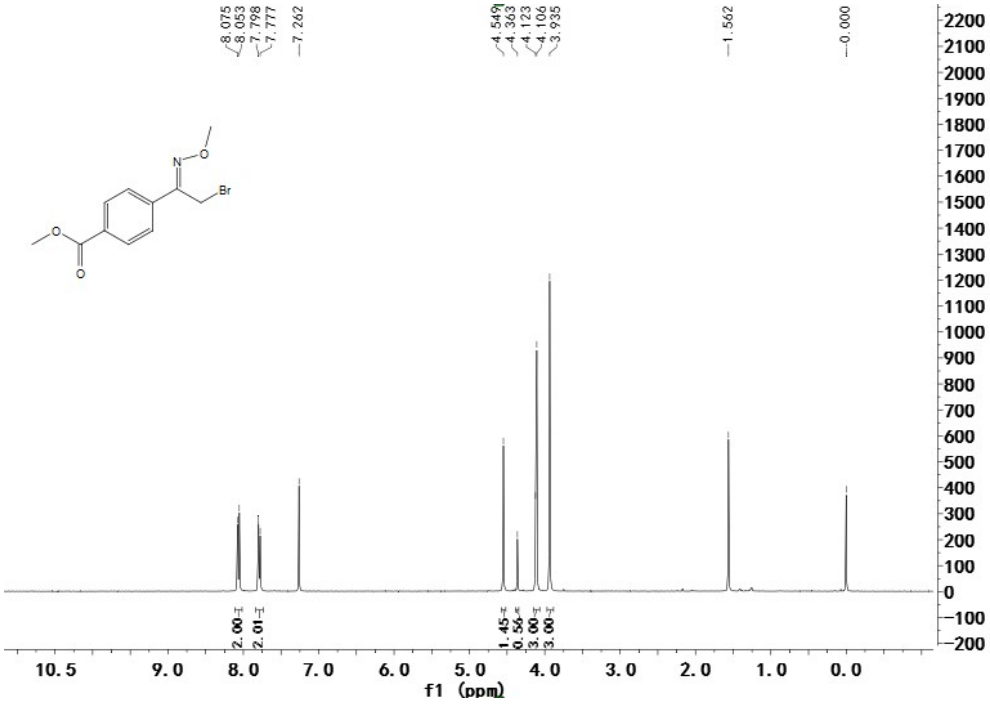
77.478
77.160
76.842
62.742
62.668
55.448
32.633
18.189
f1 (ppm)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7.798
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7.262
4.549
4.363
4.123
4.106
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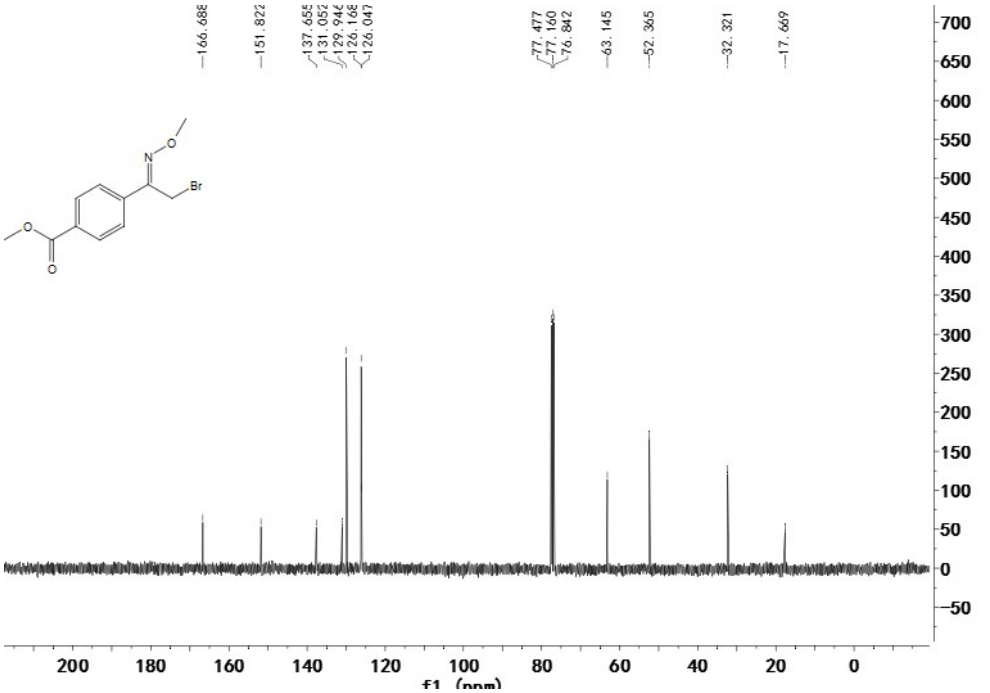
1.562
0.000
2.00
2.01
1.45
0.56
3.00
3.00
f1 (ppm)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131.052
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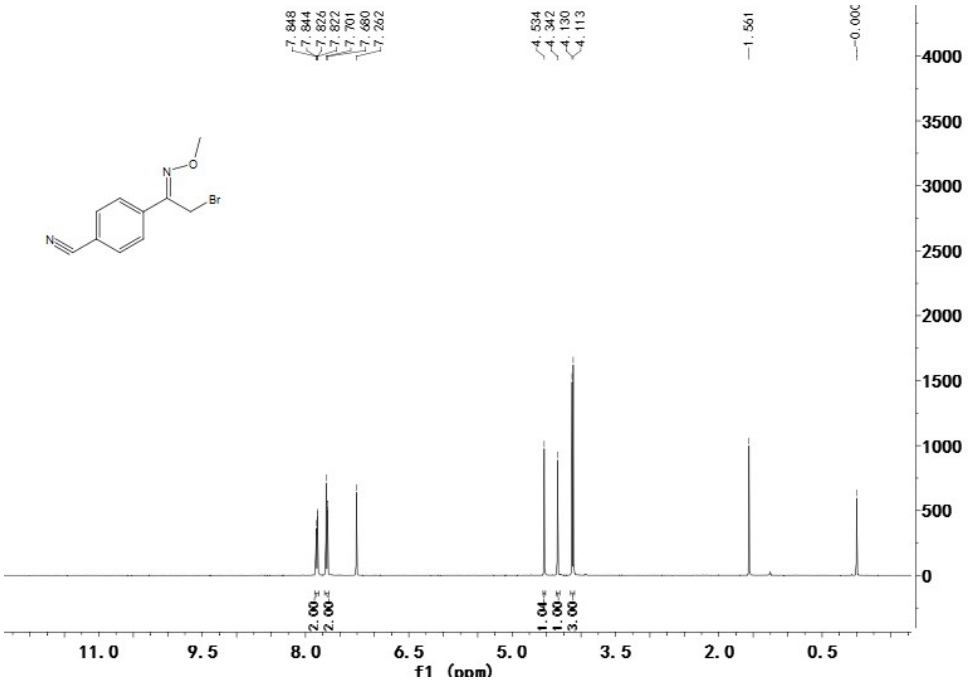
126.047
77.477
77.160
76.842
63.145
52.365
32.321
17.669
f1 (ppm)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7.844
7.826
7.822
7.701
7.660
7.262
4.534
4.342
4.130
4.113
1.561
0.000
N
O
Br
N
2.00
2.00
1.04
1.00
3.00
11.0
9.5
8.0
6.5
5.0
3.5
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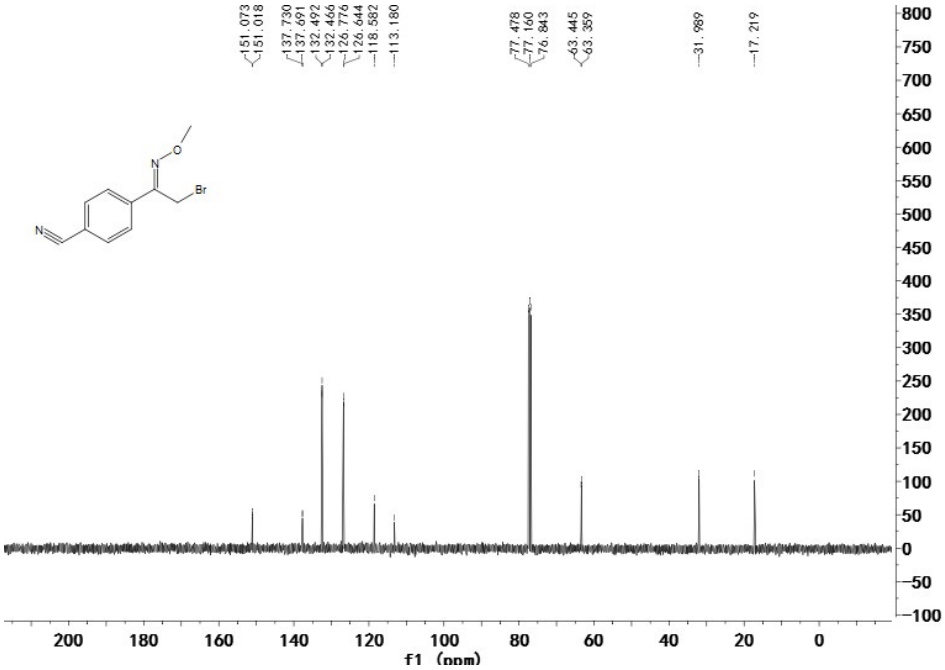
0.5
f1 (ppm)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126.644
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76.843
63.445
63.359
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O
Br
N
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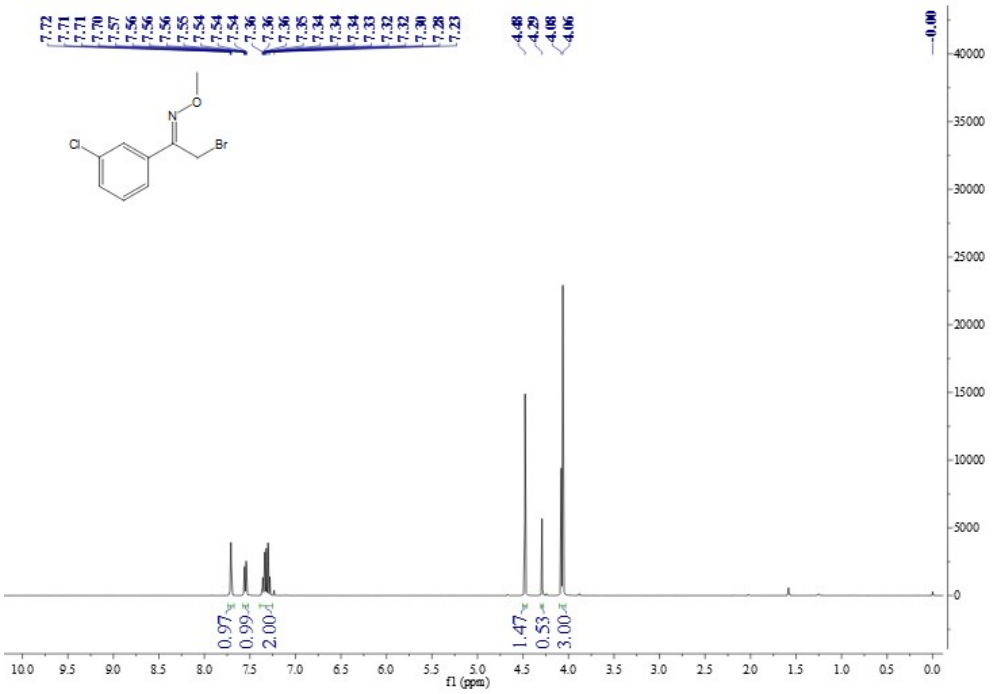
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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7.56
7.56
7.55
7.54
7.54
7.54
7.36
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7.36
7.35
7.34
7.34
7.34
7.33
7.32
7.32
7.30
7.28
7.23
4.48
4.29
4.08
4.06
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N
O
Cl
Br
0.97
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1.47
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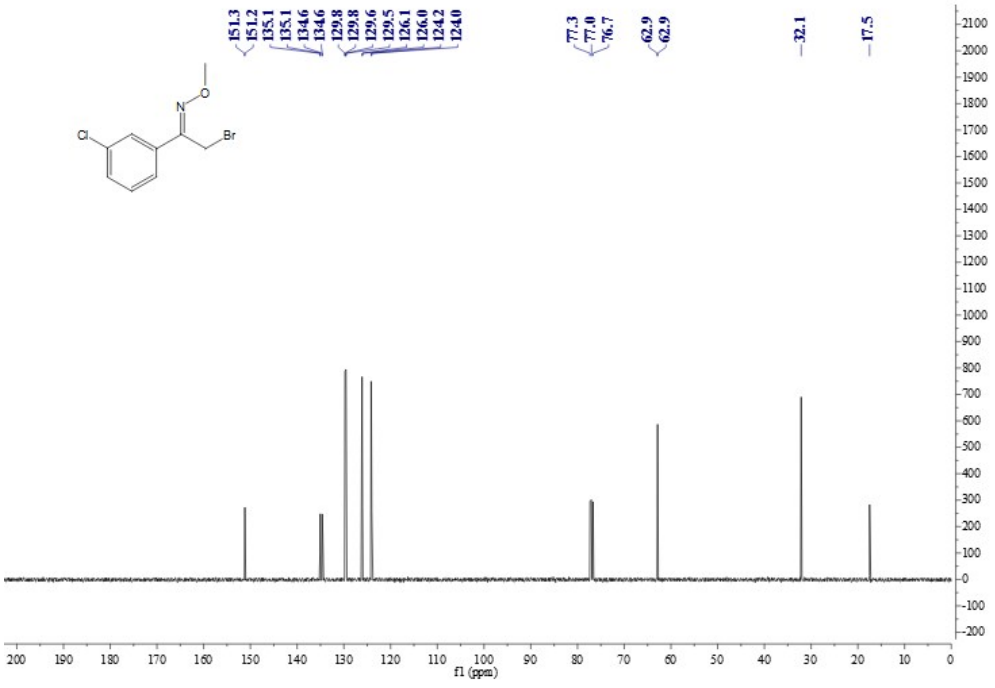
3.00
f1 (ppm)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135.1
134.6
134.6
129.8
129.8
129.6
129.5
126.1
126.0
124.2
124.0
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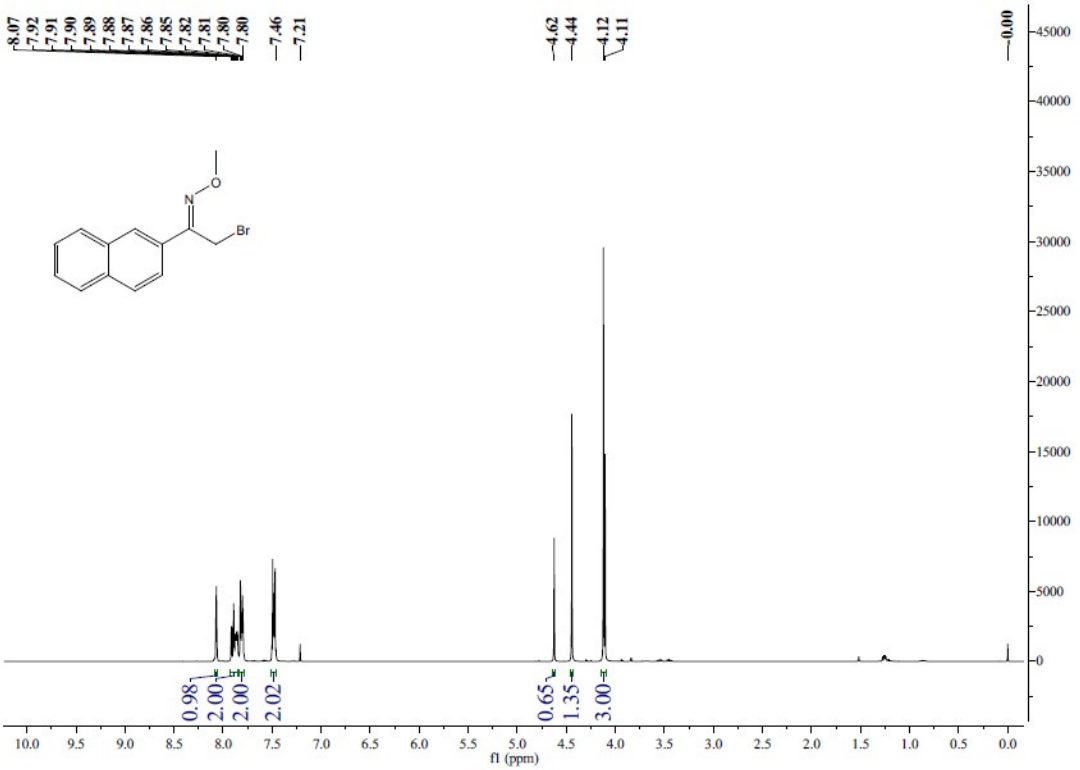
77.0
76.7
62.9
62.9
32.1
17.5
N
O
Cl
Br
f1 (ppm)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7.86
7.85
7.82
7.81
7.80
7.80
7.46
7.21
4.62
4.44
4.12
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O
Br
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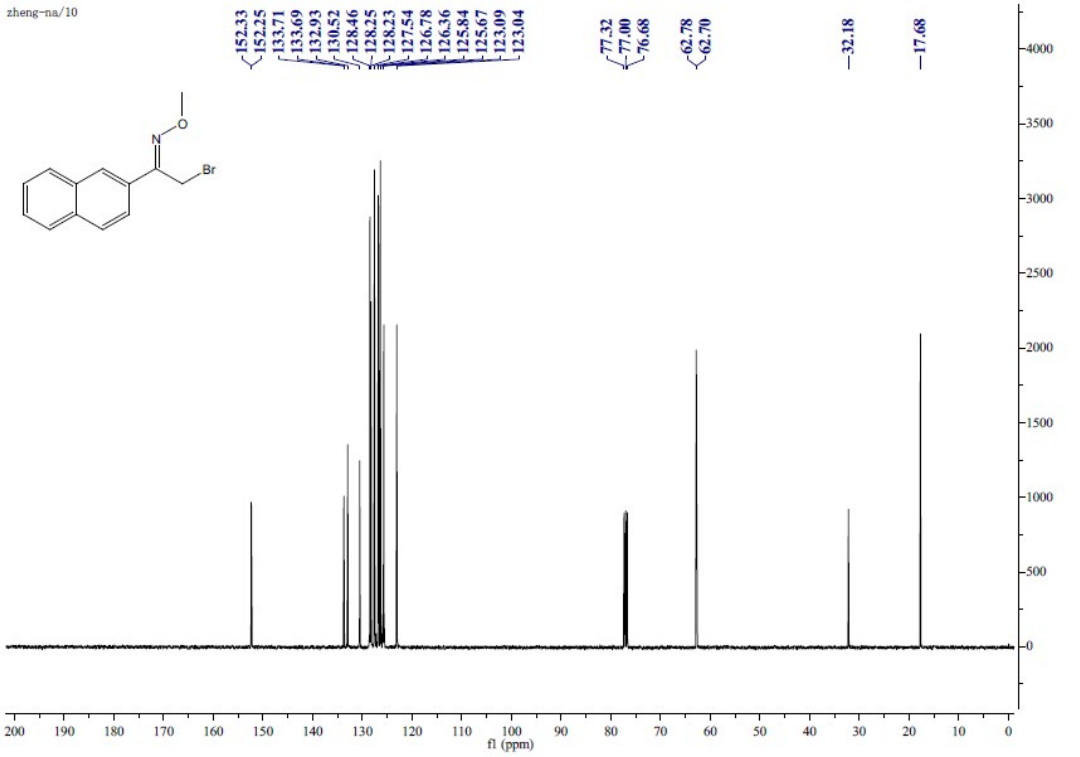
2.00
2.02
0.65
1.35
3.00
f1 (ppm)


zheng-na/10
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133.69
132.93
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128.25
128.23
127.54
126.78
126.36
125.84
125.67
123.09
123.04
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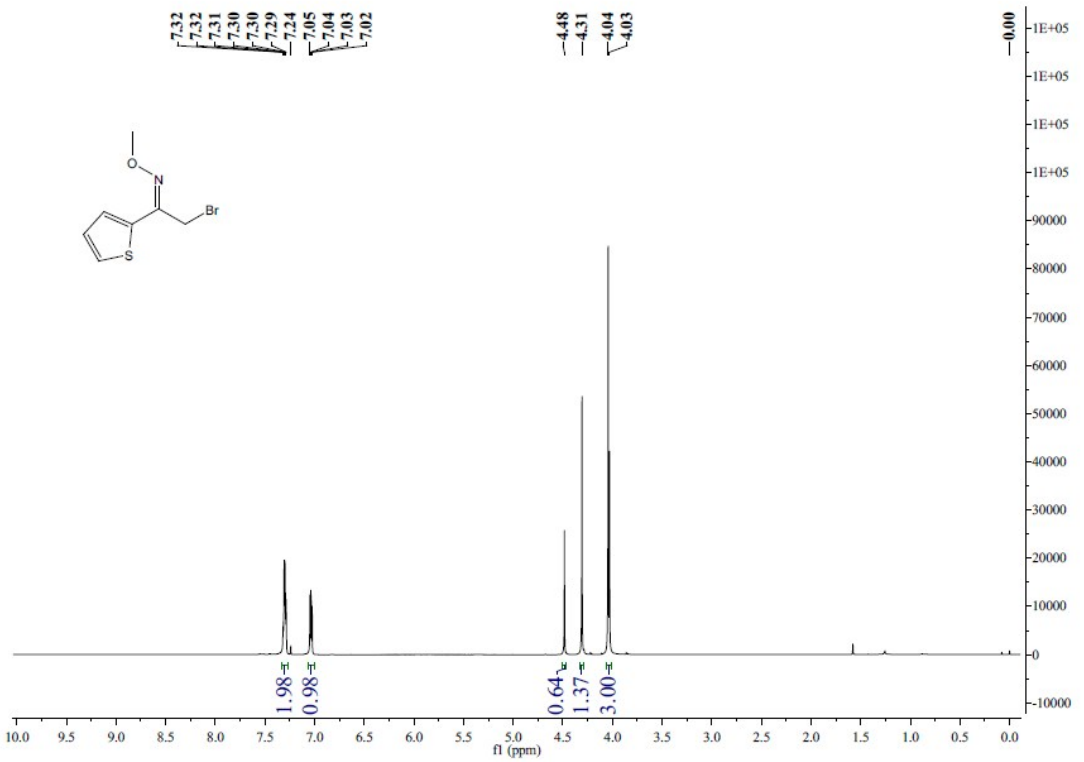
77.00
76.68
62.78
62.70
32.18
17.68
N
O
Br
f1 (ppm)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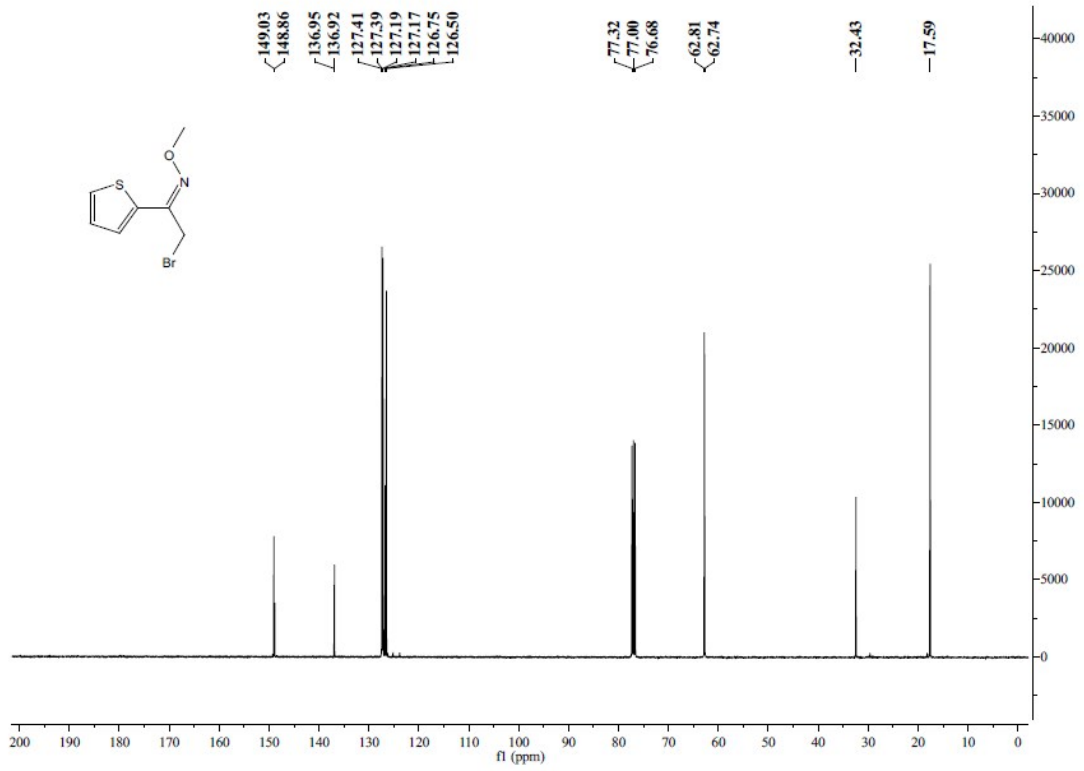
7.31
7.30
7.30
7.29
7.24
7.05
7.04
7.03
7.02
4.48
4.31
4.04
4.03
0.00
1.98
0.98
0.64
1.37
3.00
f1 (ppm)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77.00
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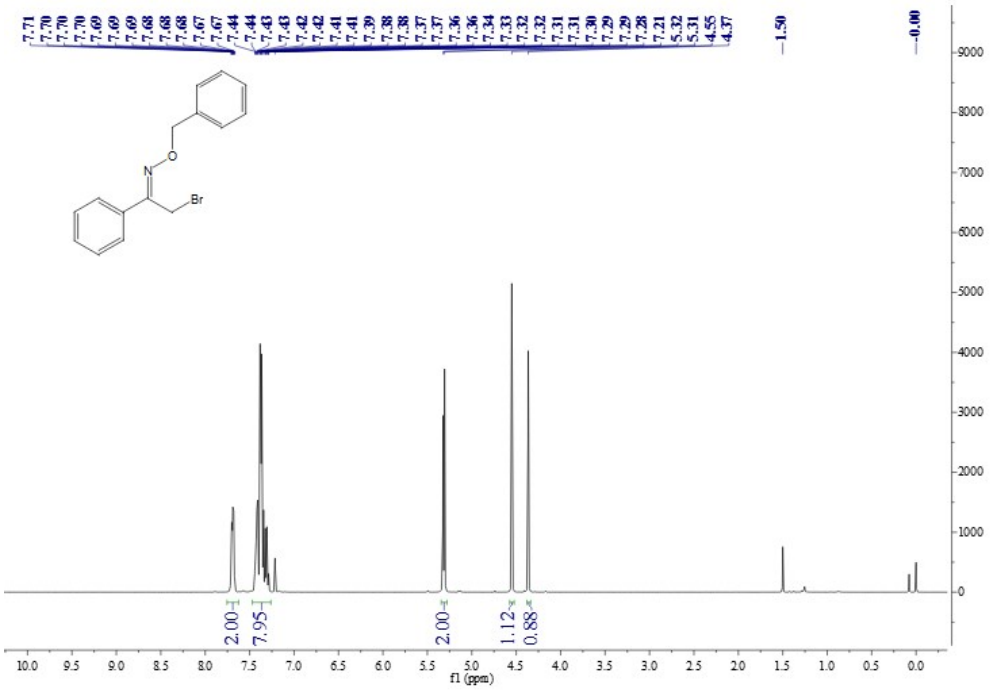
62.81
62.74
32.43
17.59
f1 (ppm)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7.70
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7.69
7.68
7.68
7.68
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7.43
7.43
7.42
7.42
7.41
7.41
7.39
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7.31
7.30
7.29
7.29
7.28
7.21
5.32
5.31
4.55
4.37
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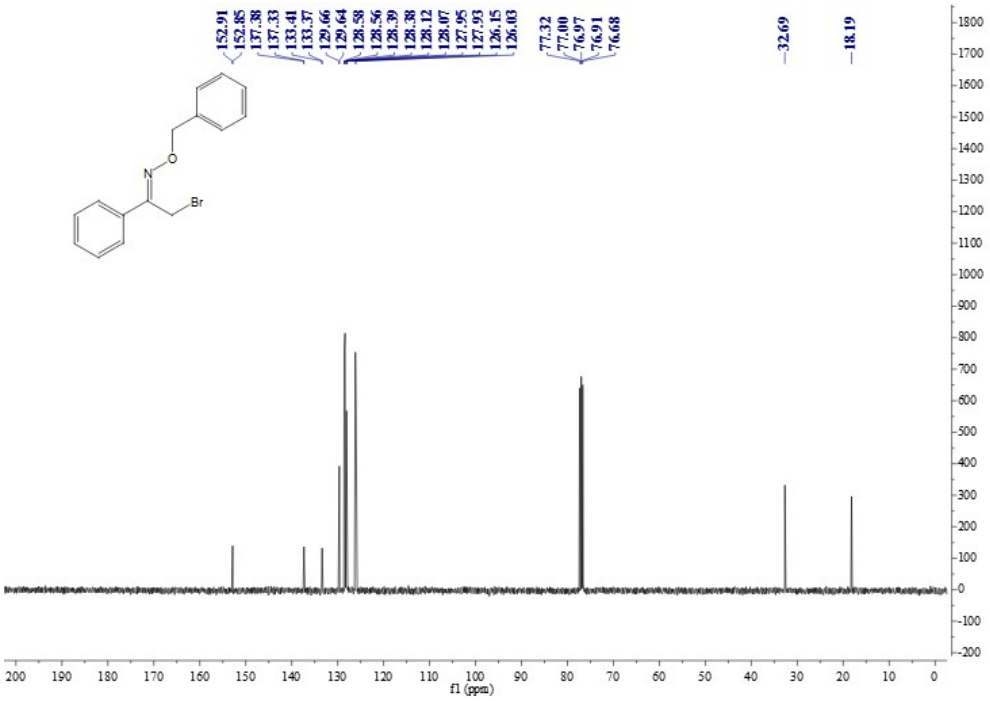
0.00
N
O
Br
2.00
7.95
2.00
1.12
0.88
f1 (ppm)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128.38
128.12
128.07
127.95
127.93
126.15
126.03
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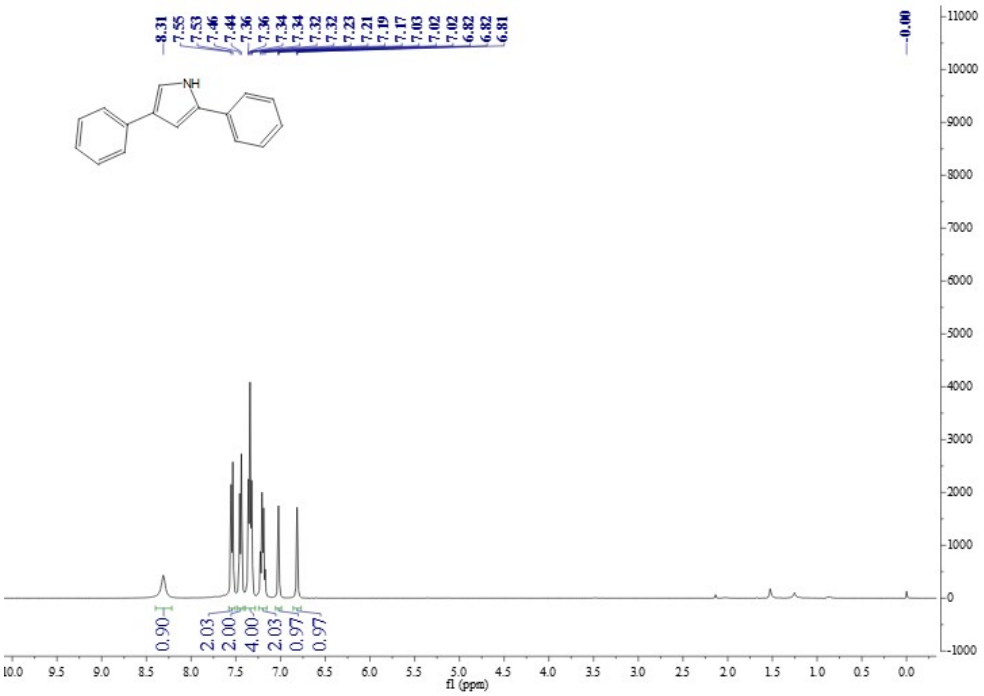
77.00
76.97
76.91
76.68
32.69
18.19
N
O
Br
f1 (ppm)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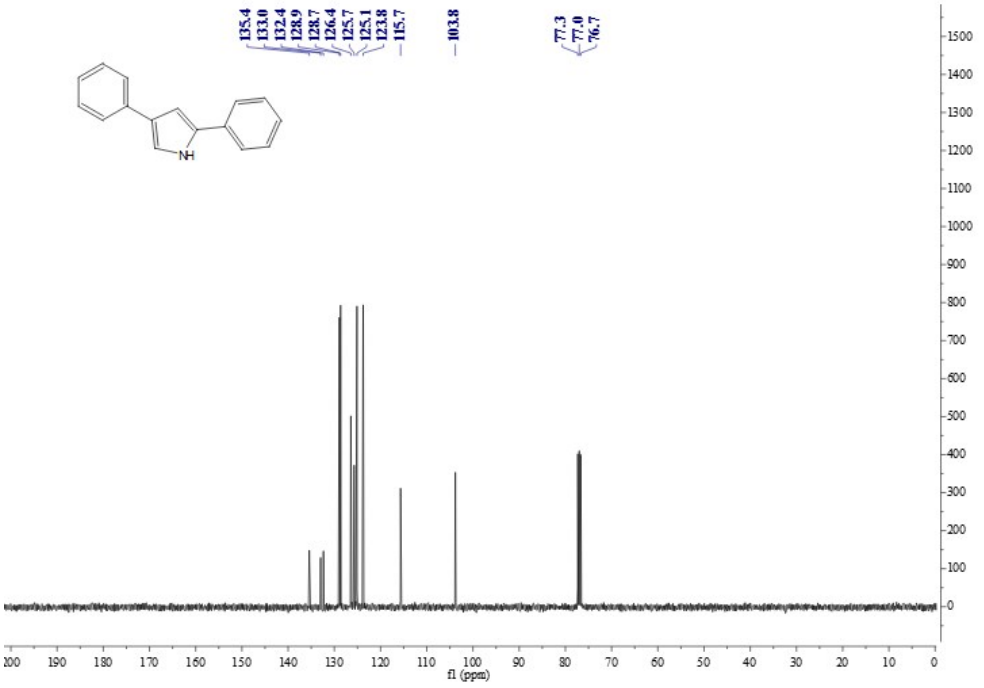
7.32
7.23
7.21
7.19
7.17
7.03
7.02
7.02
6.82
6.81
0.00
NH
0.90
2.03
2.00
4.00
2.03
0.97
0.97
f1 (ppm)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133.0
132.4
128.9
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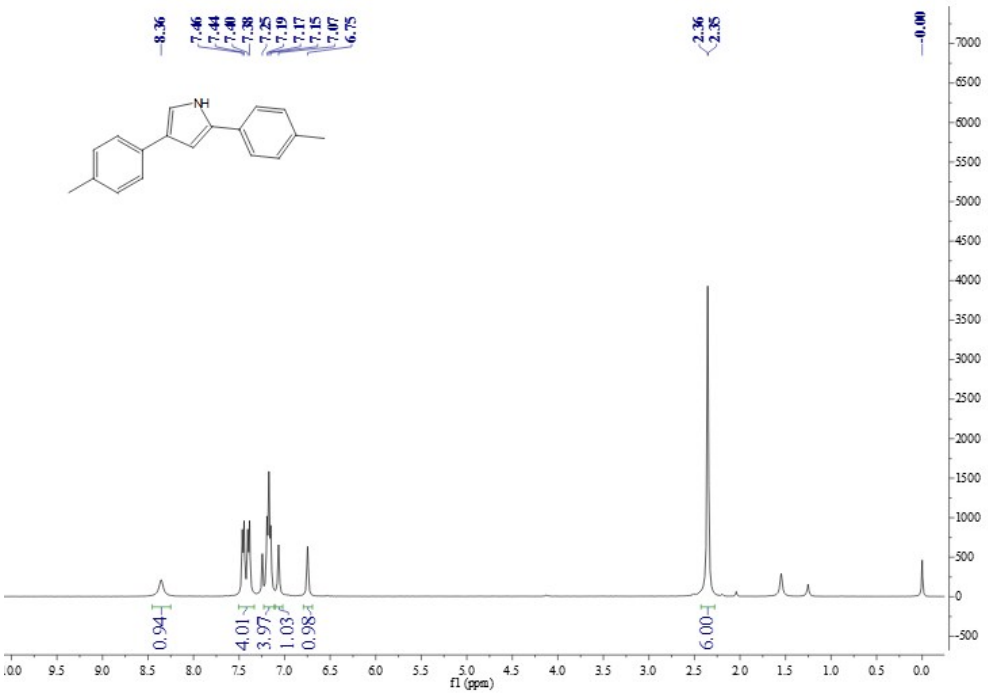
126.4
125.7
125.1
123.8
115.7
103.8
77.3
77.0
76.7
NH
f1 (ppm)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7.46
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7.17
7.15
7.07
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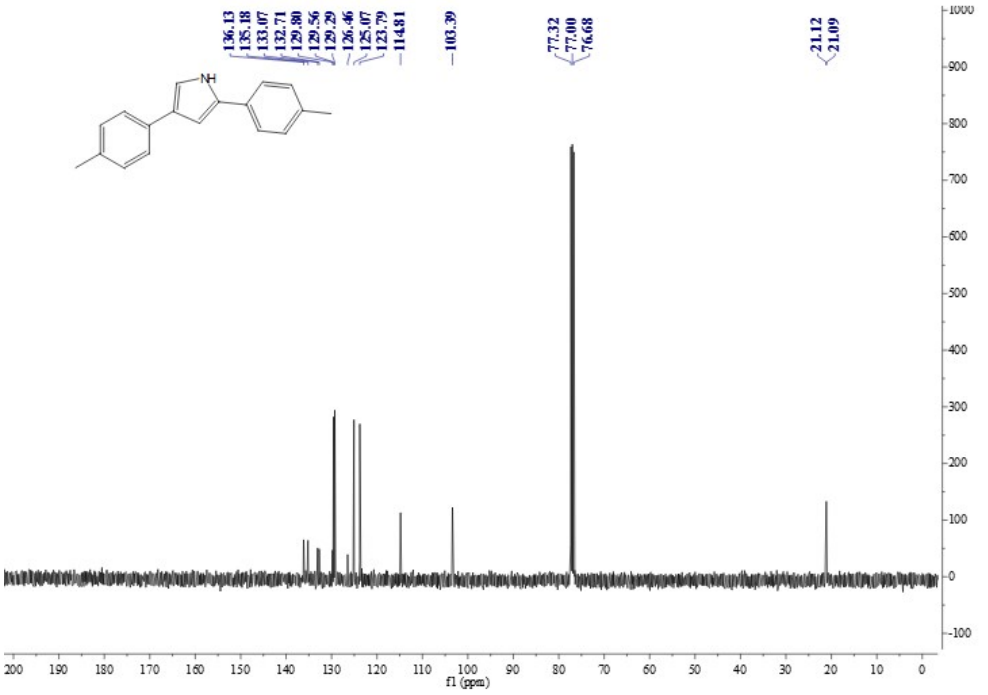
2.35
0.00
NH
0.94
4.01
3.97
1.03
0.98
6.00
f1 (ppm)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129.29
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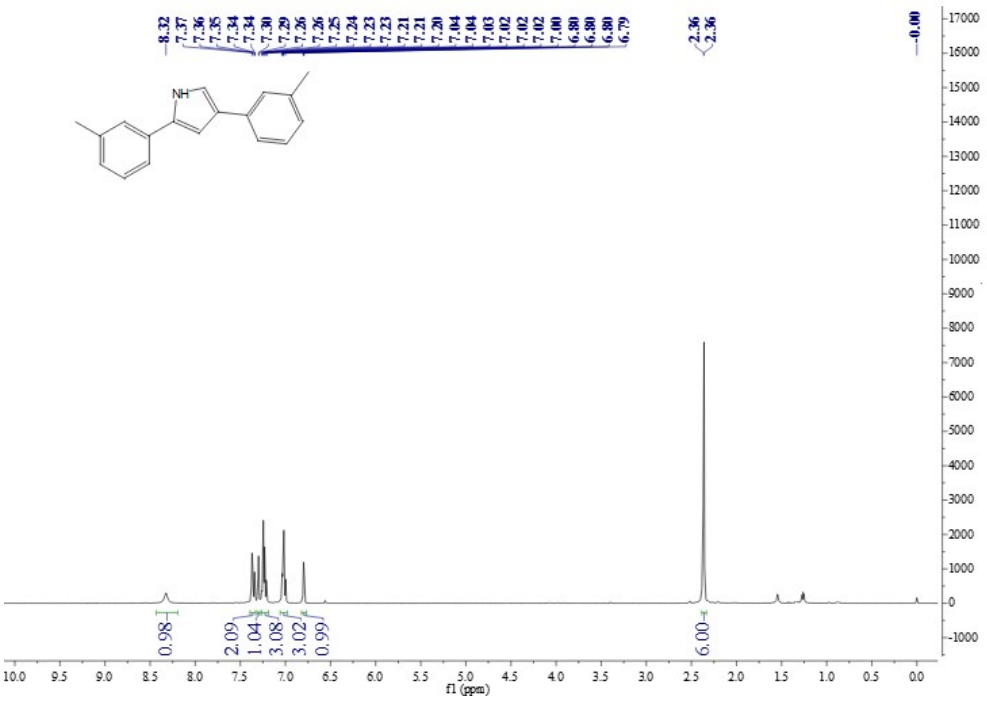
123.79
114.81
103.39
77.32
77.00
76.68
21.12
21.09
NH
f1 (ppm)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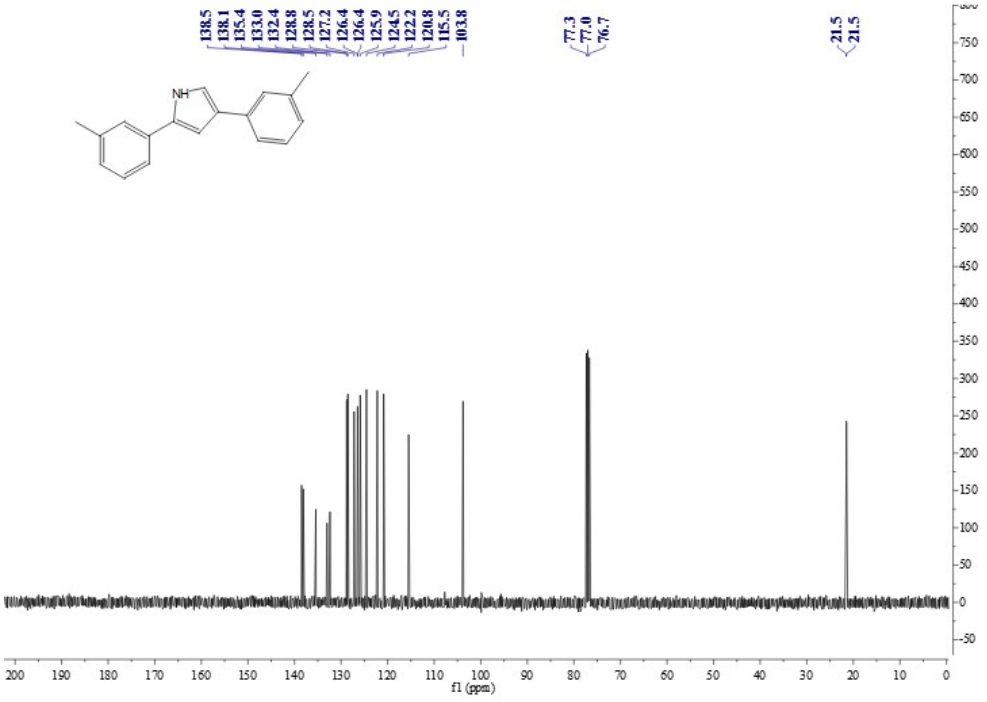
7.24
7.23
7.23
7.21
7.21
7.20
7.04
7.04
7.03
7.02
7.02
7.02
7.00
6.80
6.80
6.80
6.79
2.36
2.36
0.00
NH
0.98
2.09
1.04
3.08
3.02
0.99
6.00
f1 (ppm)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128.5
127.2
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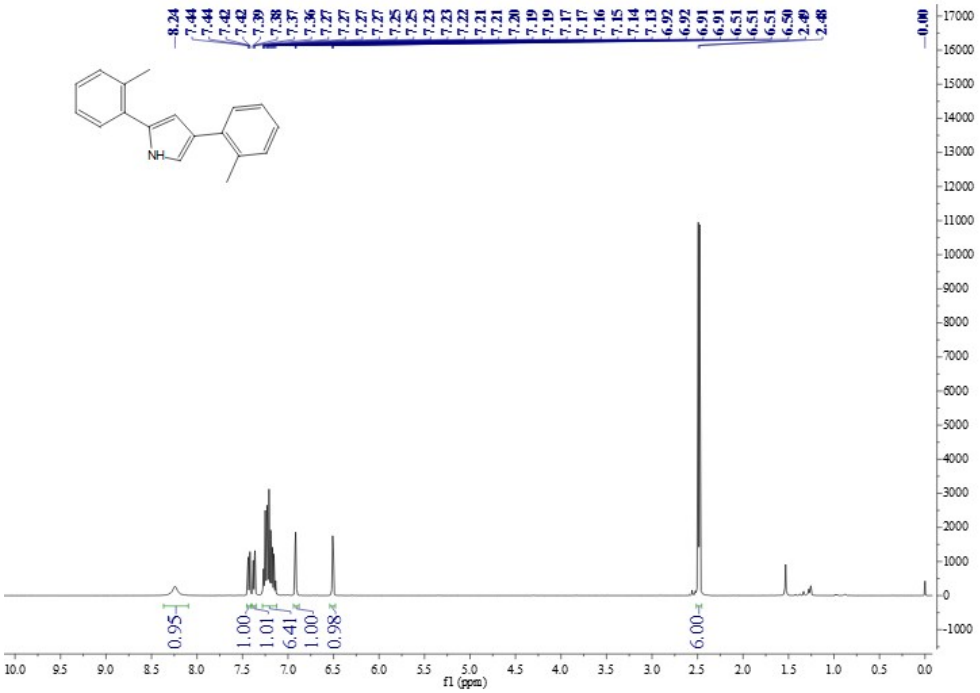
126.4
125.9
124.5
122.2
120.8
115.5
103.8
77.3
77.0
76.7
21.5
21.5
NH
f1 (ppm)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7.37
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7.27
7.27
7.27
7.25
7.23
7.23
7.22
7.21
7.21
7.20
7.19
7.19
7.17
7.17
7.16
7.15
7.14
7.13
6.92
6.92
6.91
6.91
6.51
6.51
6.51
6.50
2.49
2.48
0.00
NH
0.95
1.00
1.01
6.41
1.00
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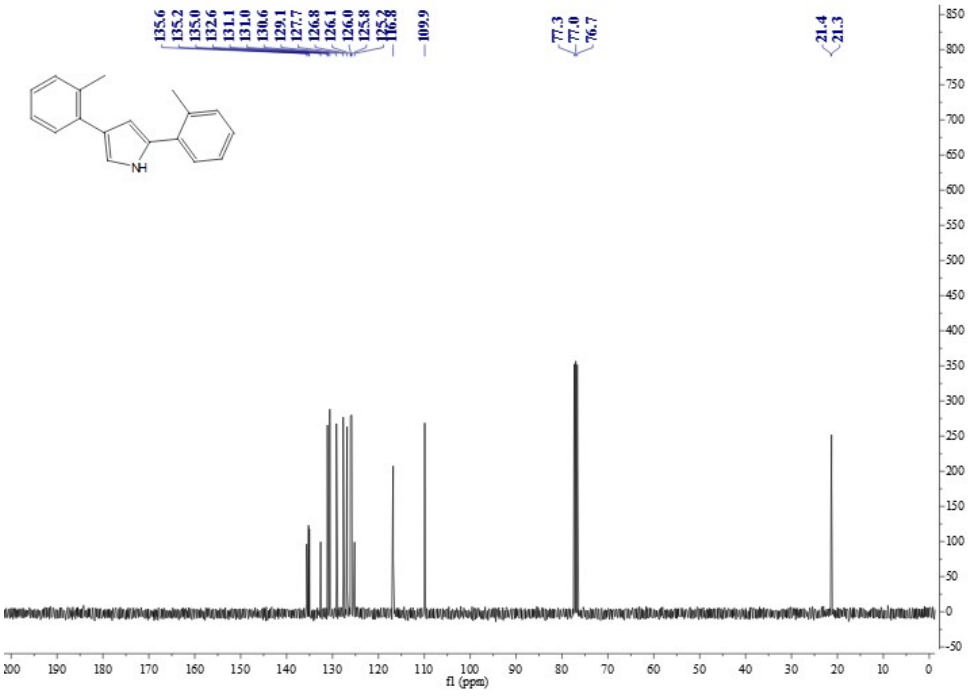
6.00
f1 (ppm)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131.1
131.0
130.6
129.1
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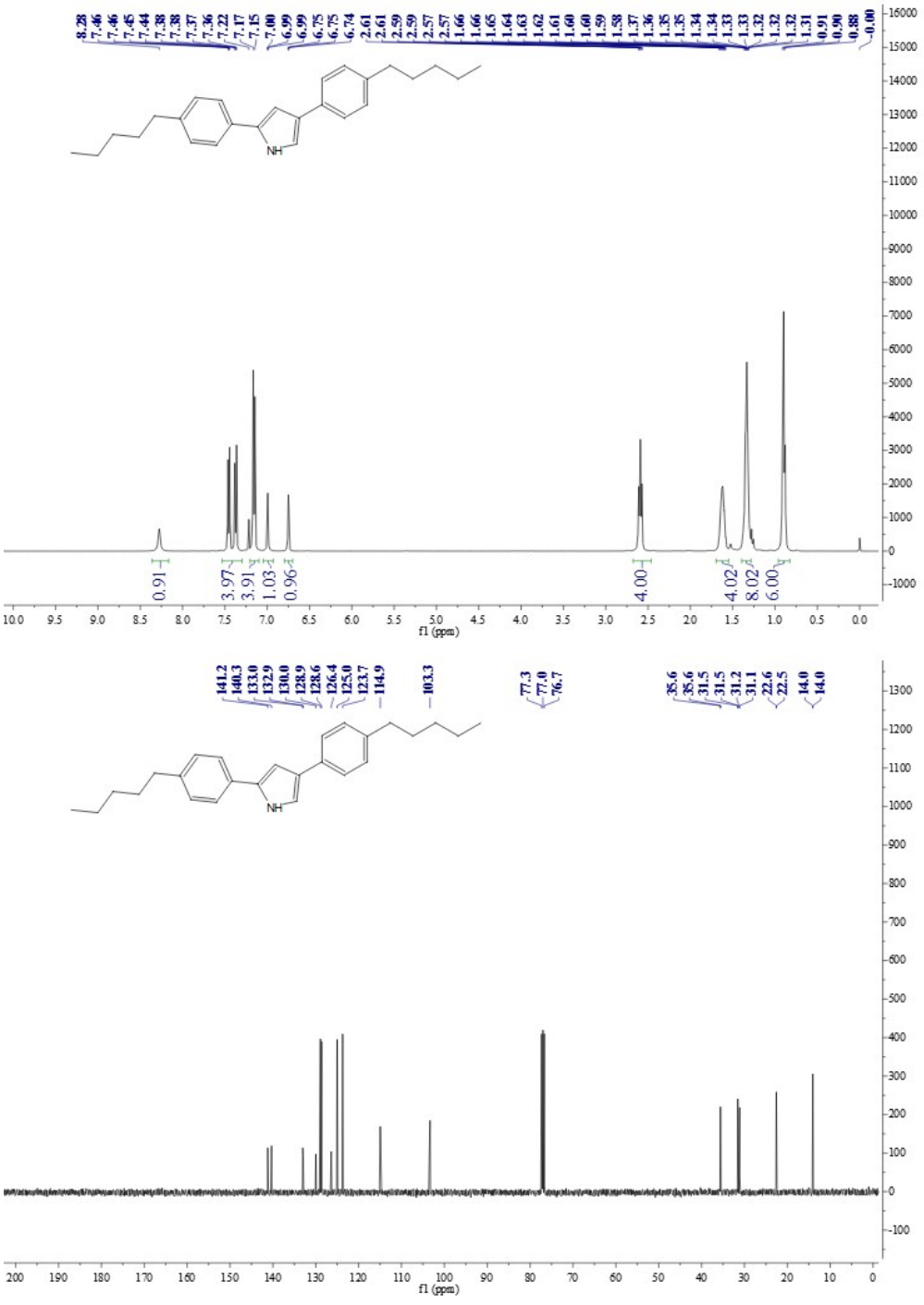
126.8
126.1
126.0
125.8
125.2
116.8
109.9
77.3
77.0
76.7
21.4
21.3
NH
f1 (ppm)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7.36
7.22
7.17
7.15
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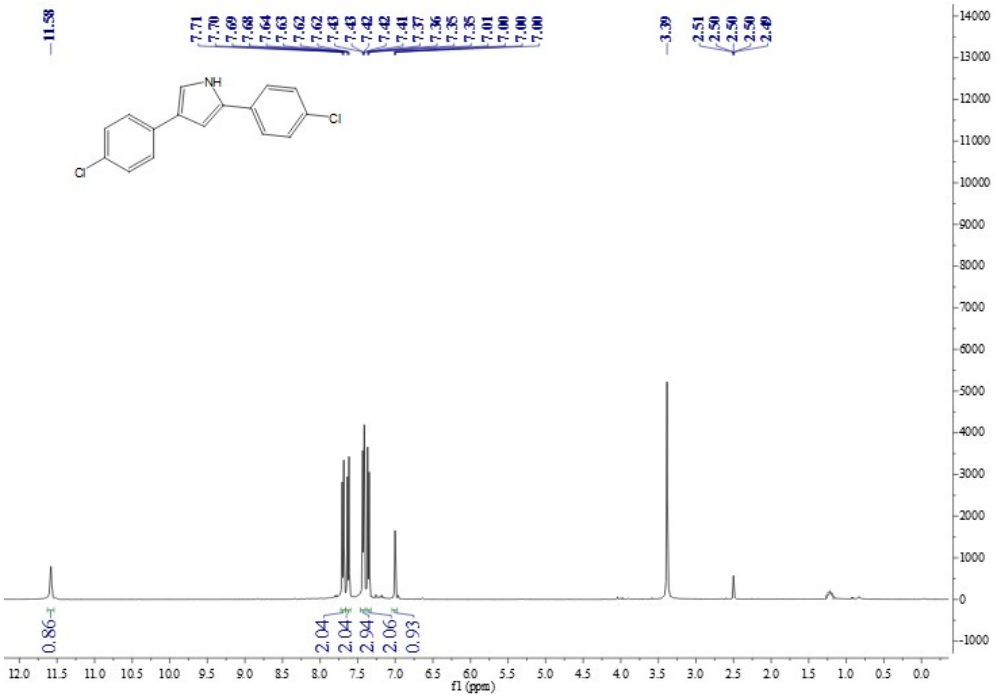
6.99
6.99
6.75
6.75
6.74
2.61
2.61
2.59
2.59
2.57
2.57
1.66
1.65
1.64
1.63
1.62
1.61
1.60
1.60
1.59
1.58
1.37
1.36
1.35
1.35
1.34
1.34
1.33
1.32
1.32
1.32
1.31
0.91
0.90
0.88
0.00
NH
0.91
3.97
3.91
1.03
0.96
4.00
4.02
8.02
6.00
f1 (ppm)
141.2
140.3
133.0
132.9
130.0
128.9
128.6
126.4
125.0
123.7
114.9
103.3
77.3
77.0
76.7
35.6
35.6
31.5
31.5
31.2
31.1
22.6
22.5
14.0
14.0
NH
f1 (ppm)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7.64
7.63
7.62
7.62
7.43
7.43
7.42
7.42
7.41
7.37
7.36
7.35
7.01
7.00
7.00
7.00
3.39
2.51
2.50
2.50
2.50
2.49
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Cl
Cl
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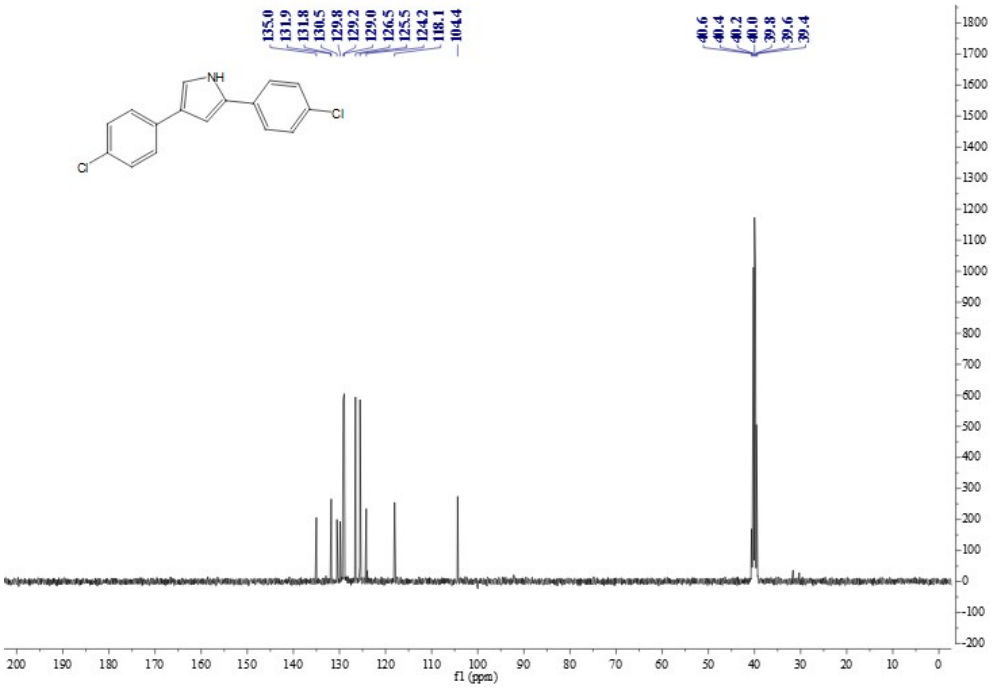
2.04
2.94
2.06
0.93
f1 (ppm)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129.8
129.2
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126.5
125.5
124.2
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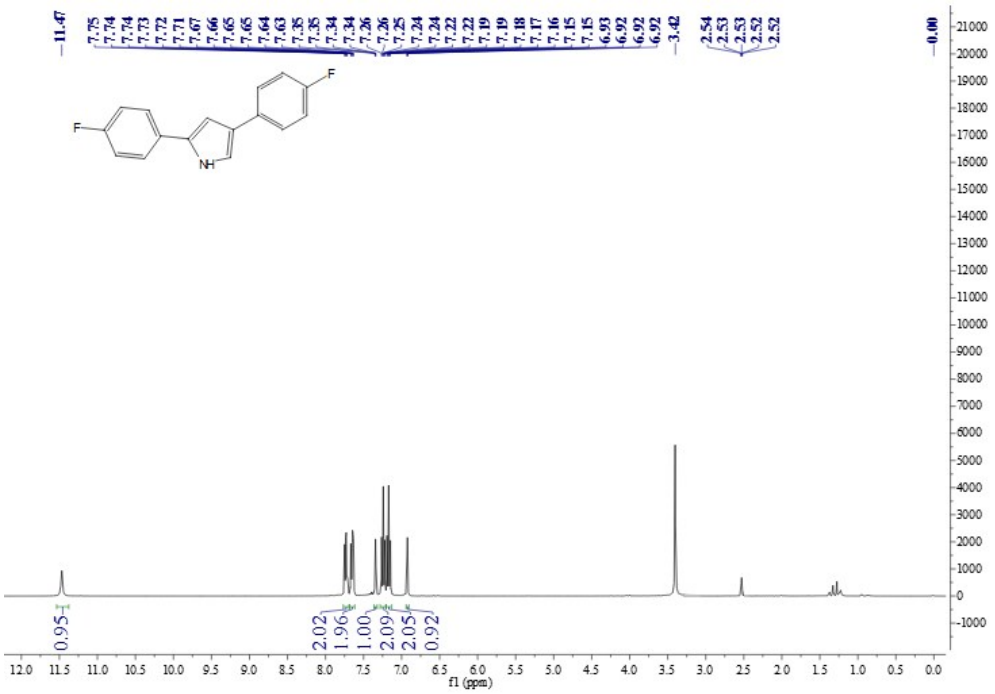
40.4
40.2
40.0
39.8
39.6
39.4
NH
Cl
Cl
f1 (ppm)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7.72
7.71
7.67
7.66
7.65
7.65
7.64
7.63
7.35
7.35
7.34
7.34
7.26
7.26
7.25
7.24
7.24
7.22
7.19
7.19
7.18
7.17
7.16
7.15
7.15
6.93
6.92
6.92
6.92
3.42
2.54
2.53
2.53
2.52
2.52
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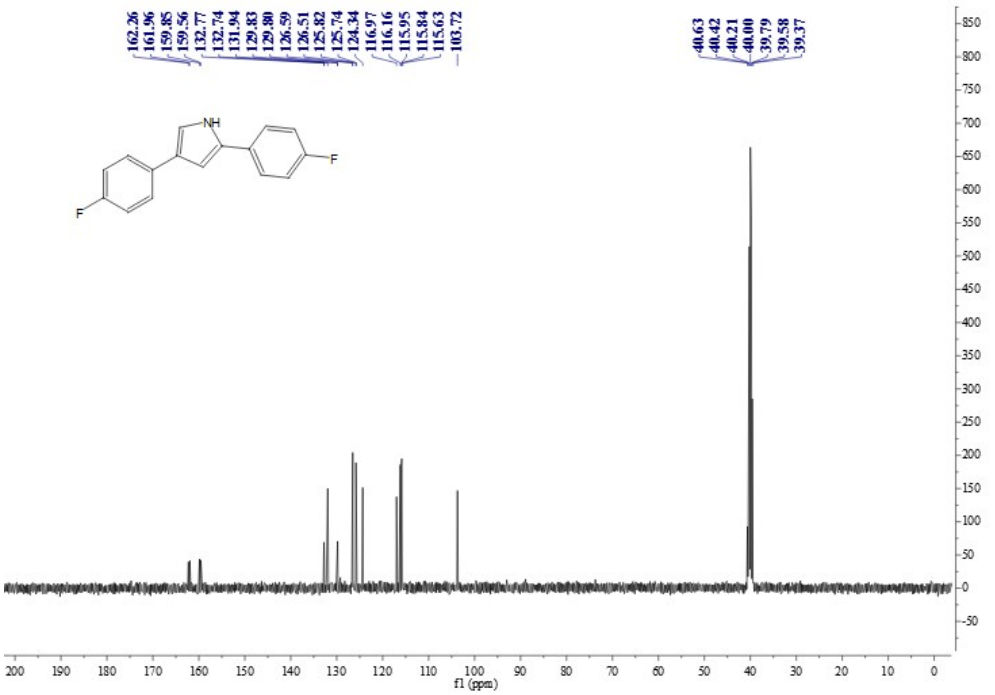
F
NH
F
0.95
2.02
1.96
1.00
2.09
2.05
0.92
f1 (ppm)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159.85
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132.74
131.94
129.83
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126.59
126.51
125.82
125.74
124.34
116.97
116.16
115.95
115.84
115.63
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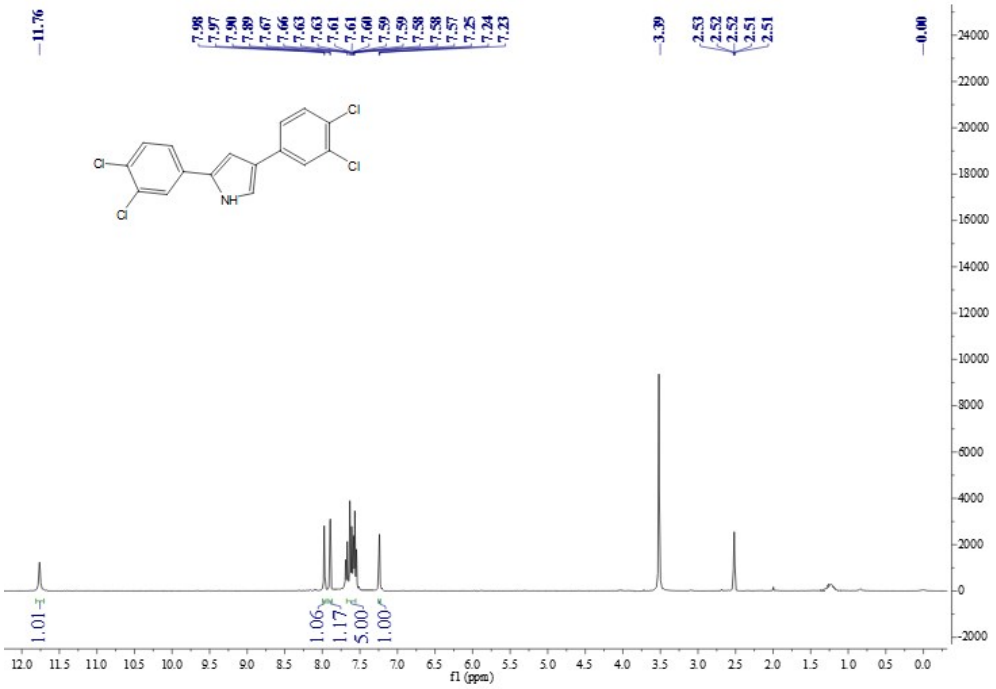
40.42
40.21
40.00
39.79
39.58
39.37
NH
F
F
f1 (ppm)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7.61
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7.58
7.58
7.57
7.25
7.24
7.23
3.39
2.53
2.52
2.52
2.51
2.51
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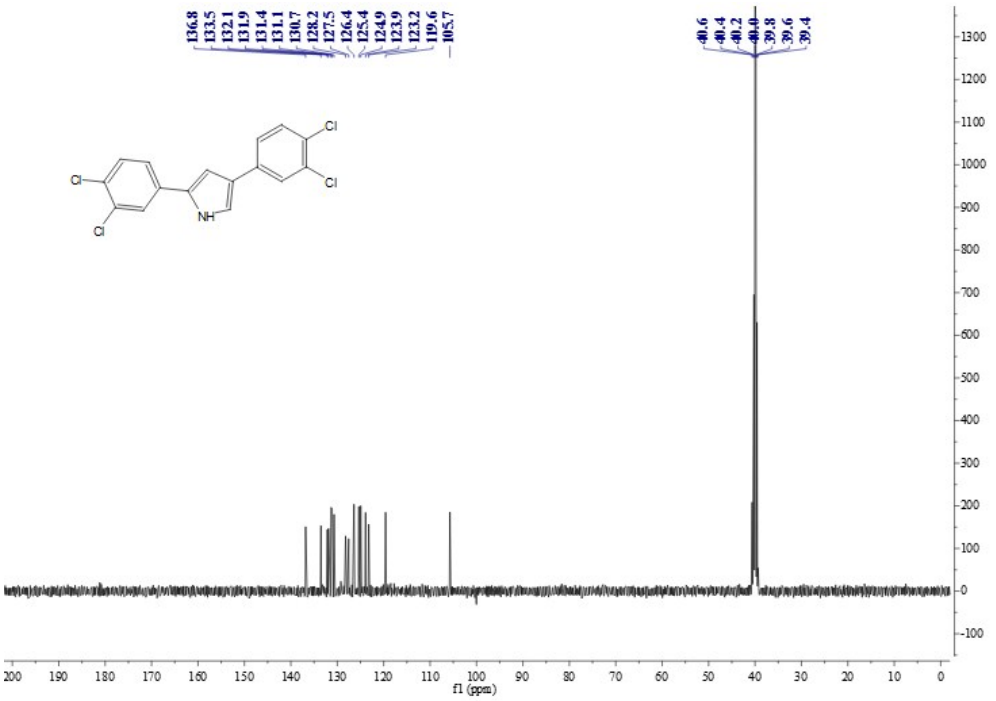
Cl
Cl
Cl
Cl
NH
1.01
1.06
1.17
5.00
1.00
f1 (ppm)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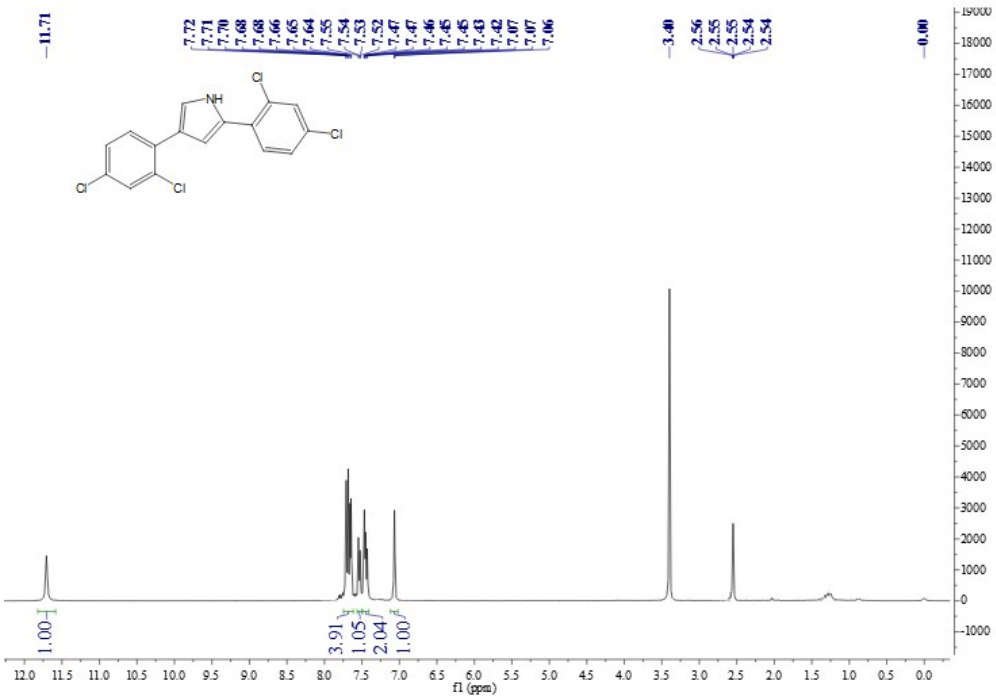
130.7
128.2
127.5
126.4
125.4
124.9
123.9
123.2
119.6
105.7
40.6
40.4
40.2
40.0
39.8
39.6
39.4
Cl
Cl
Cl
Cl
NH
f1 (ppm)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7.65
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7.54
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7.52
7.47
7.47
7.46
7.45
7.45
7.43
7.42
7.07
7.07
7.06
3.40
2.56
2.55
2.55
2.54
2.54
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NH
Cl
Cl
Cl
Cl
1.00
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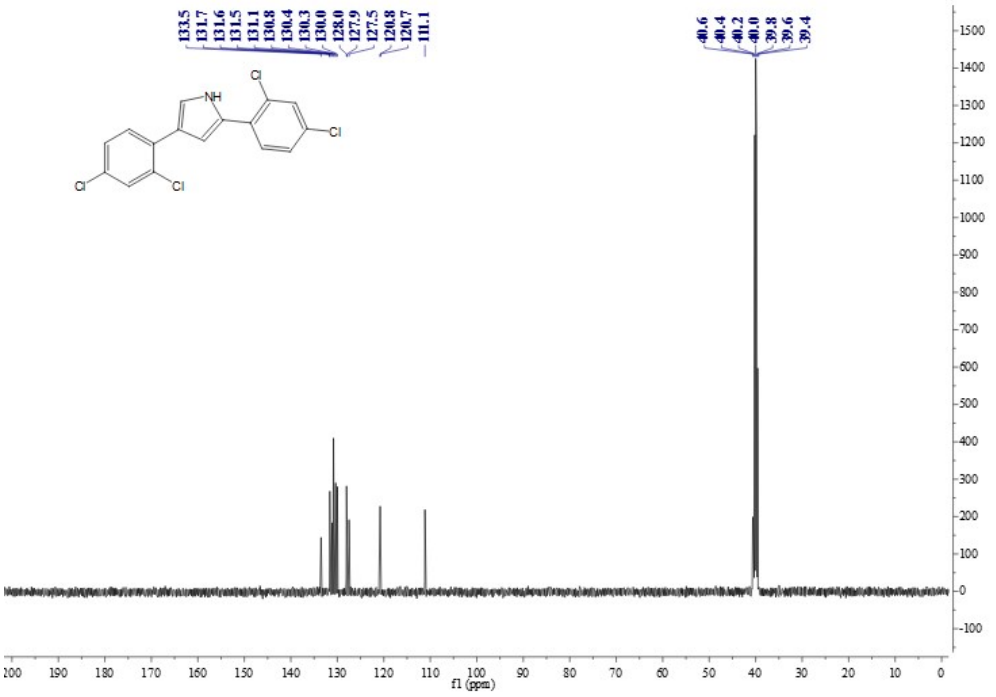
1.05
2.04
1.00
f1 (ppm)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130.3
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127.5
120.8
120.7
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39.8
39.6
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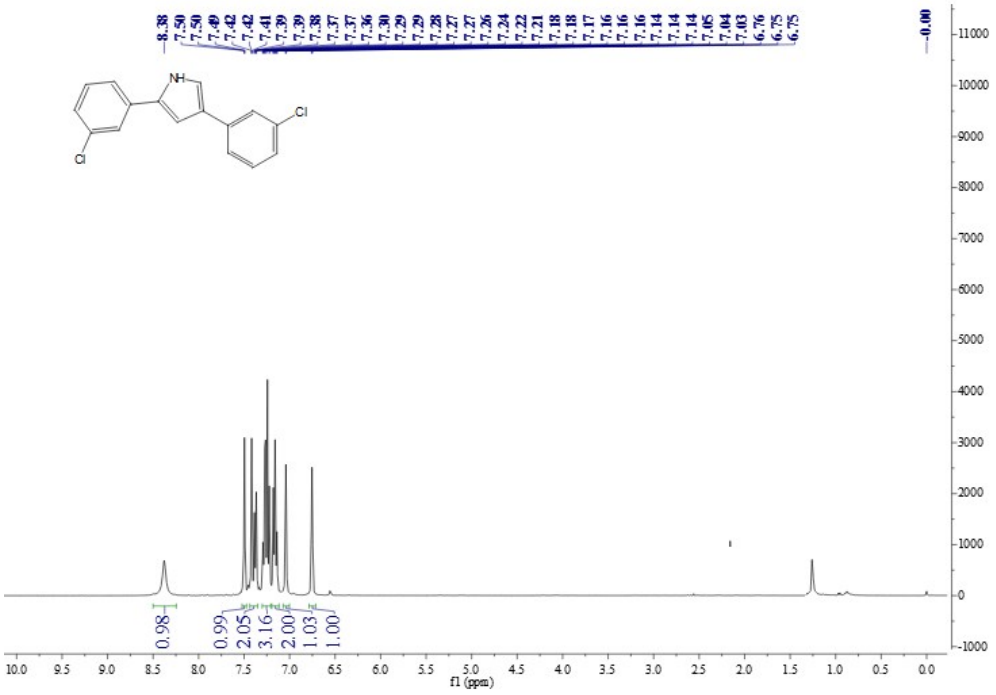
NH
Cl
Cl
Cl
Cl
f1 (ppm)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7.29
7.28
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7.27
7.26
7.24
7.22
7.21
7.18
7.18
7.17
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7.16
7.14
7.14
7.14
7.05
7.04
7.03
6.76
6.75
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Cl
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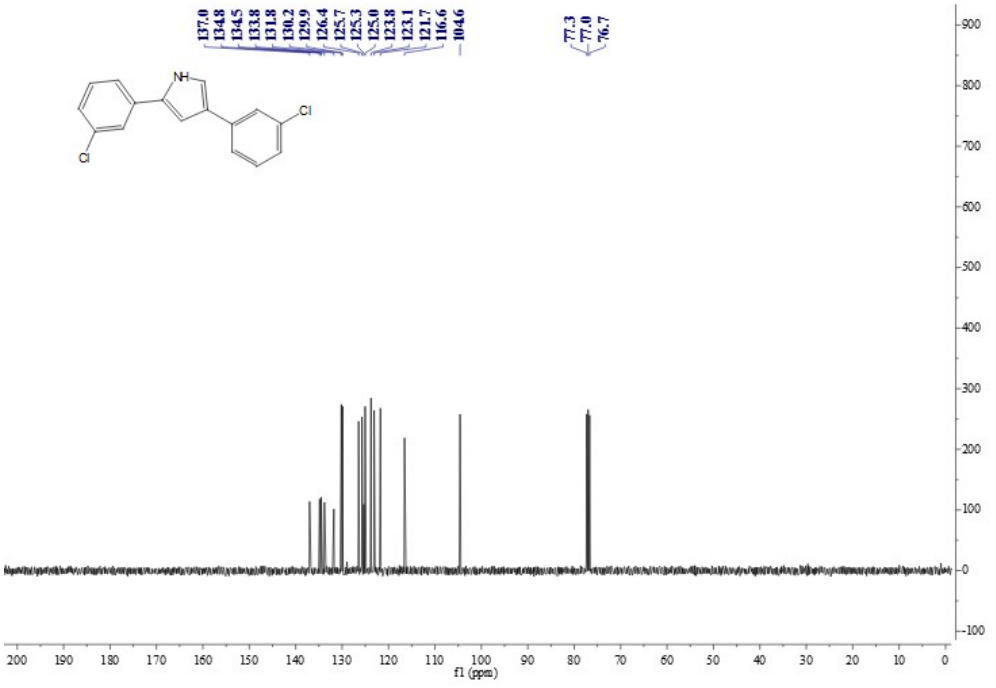
1.00
f1 (ppm)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134.8
134.5
133.8
131.8
130.2
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125.7
125.3
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123.8
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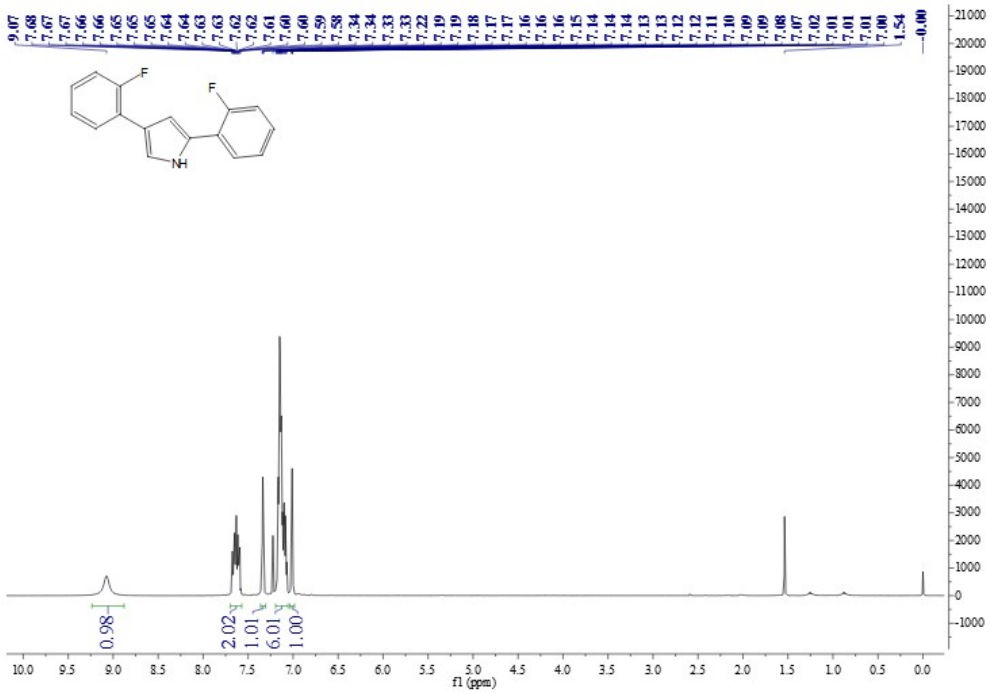
121.7
116.6
104.6
77.3
77.0
76.7
NH
Cl
Cl
f1 (ppm)


F
F
NH
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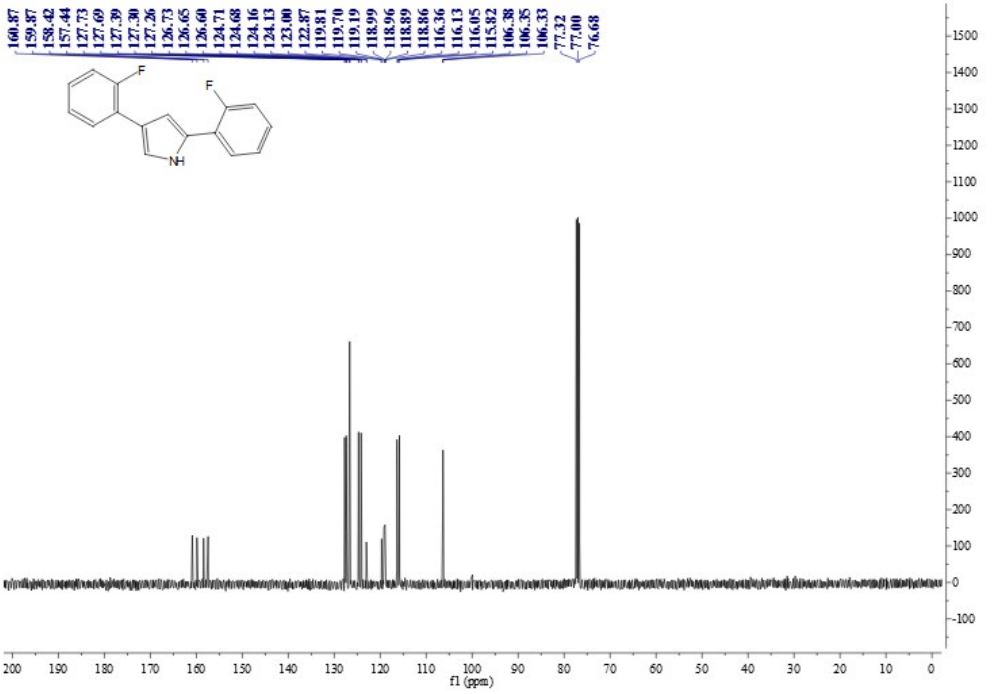
6.01
1.00
f1 (ppm)


F
F
NH
f1 (ppm)