Supporting Information

Solvent-Tuned Chemoselective Carboazidation and Diazidation of Alkenes via iron catalysis

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1. General Information.

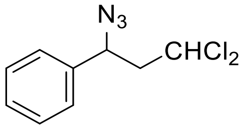
Commercial reagents were purchased from Aldrich, TCI, Energy Chemical and J&K chemical, and were used as received. All reactions were carried out in oven-dried glassware under an atmosphere of nitrogen unless otherwise noted. Chromatographic purification of products was accomplished by flash chromatography using silica gel. Thin-layer chromatography (TLC) was performed on Silicycle 250 mm silica gel F-254 plates.^{1}H and ^{13}C NMR spectra were recorded on Bruker 400 (400 and 100 MHz) and Bruker 600 (600 and 150 MHz), and are internally referenced to residual solvent signals (for $CDCl_3$, δ 7.26 and 77.0 ppm). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration, coupling constant (Hz). ^{13}C spectra were reported as chemical shifts in ppm and multiplicity where appropriate. High resolution mass spectra were obtained at Shanghai Institute of Organic Chemistry mass spectrometry facilities. All alkenes were used from commercial suppliers or prepared using standard literature procedures or the preparation procedures descried in this supporting information.

2. General procedures

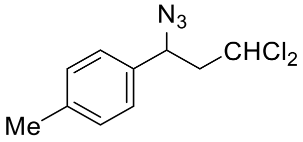
General procedure for the carboazidation reaction: Fe(OTf)$_2$ (0.02 mmol, 10 mol%) were placed in a flame-dried 25 mL sealed tube in glovebox, After DCM (6 mL) was added via a syringe, followed by the addition of DTBP (73.6 ul, 0.4 mmol, 2.0 equiv.) , TMSN$_3$(34.0 ul, 0.26 mmol, 1.3 equiv.) and olefin (0.2 mmol, 1.0 equiv.) under N$_2$ atmosphere. Sealed tube was sealed and the mixture was stirred at 110 ^{o}C (oil bath temperature). After 24 h the reaction mixture was cooled down to room temperature, after evaporation in vacuo, purification by column chromatography on silica gel to afford the product.

General procedure for the diazidation reaction: Fe(OTf)$_2$ (0.01 mmol, 5 mol%) were placed in a flame-dried 25 mL sealed tube in glovebox, After DCM:^{t}BuOH =5:1(1 ml:0.2ml) was added via a syringe, followed by the addition of DTBP (55.0 ul, 0.3 mmol, 1.5 equiv.) , TMSN$_3$(91.8 ul, 0.7mmol, 3.5 equiv.) and olefin (0.2 mmol,1.0 eq). under N$_2$ atmosphere. Sealed tube was sealed and the mixture was stirred at 80 ^{o}C (oil bath temperature). After 24 h the reaction mixture was cooled down to room temperature, after evaporation in vacuo, purification by column chromatography on silica gel to afford the product.

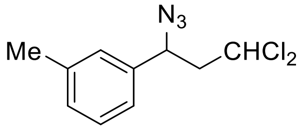
3. Characterizations of products



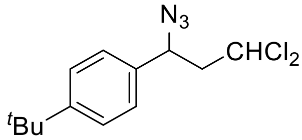
(1-Azido-3,3-dichloropropyl)benzene: According to the general procedure, styrene (23.0 ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN$_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)$_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH$_2$Cl$_2$ (6 mL) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (33.4 mg, 73%);^{1}H NMR (600 MHz, CDCl3) δ 7.45 – 7.40 (m, 2H), 7.39 (dt, J = 9.7, 4.4 Hz, 1H), 7.34 (dd, J = 5.3, 3.3 Hz, 2H), 5.74 (dd, J = 8.4, 4.9 Hz, 1H), 4.75 (dd, J = 9.5, 5.1 Hz, 1H), 2.67 – 2.62 (m, 1H), 2.51 – 2.46 (m, 1H).^{13}C NMR (150 MHz, CDCl$_3$) δ 137.46, 129.21, 129.04, 126.93, 70.03, 63.15, 49.70. HRMS (EI): calcd for C$_9$H$_9$Cl$_2$N$_3$ 229.0174, found 229.0180.



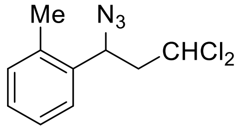
1-(1-Azido-3,3-dichloropropyl)-4-methylbenzene: According to the general procedure,1-methyl-4-vinylbenzene (25.1 ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN$_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)$_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH$_2$Cl$_2$ (6 mL) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (36.1 mg, 74%); ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.22 (s, 4H), 5.71 (dd, J = 8.3, 5.1 Hz, 1H), 4.71 (dd, J = 9.4, 5.3 Hz, 1H), 2.67 – 2.62 (m, 1H), 2.49 – 2.45 (m, 1H), 2.37 (s, 3H). ^{13}C NMR (150 MHz, CDCl$_3$) δ 138.97, 134.33, 129.85, 126.89, 70.11, 62.93, 49.63, 21.17. HRMS (EI): calcd for C$_{10}$H$_{11}$Cl$_2$N$_3$ 243.0330, found 243.0339.



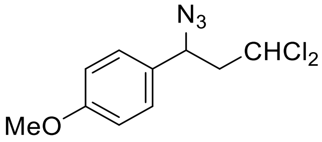
1-(1-Azido-3,3-dichloropropyl)-3-methylbenzene: According to the general procedure, 1-methyl-3-vinylbenzene (26.2 ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN$_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)$_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH$_2$Cl$_2$ (6 mL) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (32.6 mg, 67%);^{1}H NMR (600 MHz, CDCl$_3$) δ 7.30 (t, *J* = 7.9 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 2H), 5.73 (dd, *J* = 8.4, 4.8 Hz, 1H), 4.70 (dd, *J* = 9.5, 5.2 Hz, 1H), 2.66 – 2.61 (m, 1H), 2.49 – 2.45 (m, 1H), 2.39 (s, 3H).^{13}C NMR (150 MHz, CDCl$_3$) δ 139.00, 137.36, 129.78, 129.04, 127.56, 123.96, 70.10, 63.15, 49.68, 21.43. HRMS (EI): calcd for $C_{10}H_{11}Cl_2N_3$ 243.0330, found 243.0336.



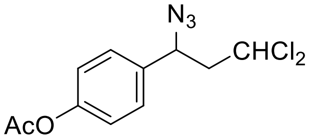
1-(1-Azido-3,3-dichloropropyl)-4-(tert-butyl)benzene: According to the general procedure, 1-(tert-butyl)-4-vinylbenzene (37.0 ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN$_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)$_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH$_2$Cl$_2$ (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=20:1) as a colorless oil liquid (43.9 mg, 77%);^{1}H NMR (600 MHz, CDCl$_3$) δ 7.43 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.3 Hz, 2H), 5.73 (dd, *J* = 8.4, 5.0 Hz, 1H), 4.72 (dd, *J* = 9.4, 5.2 Hz, 1H), 2.67 – 2.62 (m, 1H), 2.50 – 2.45 (m, 1H), 1.33 (s, 9H).^{13}C NMR (150 MHz, CDCl$_3$) δ 152.05, 134.37, 126.61, 126.06, 70.16, 62.86, 49.64, 34.65, 31.24. HRMS (EI): calcd for $C_{13}H_{17}Cl_2N_3$ 285.0800, found 285.0525.



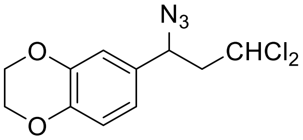
1-(1-Azido-3,3-dichloropropyl)-2-methylbenzene: According to the general procedure, 1-methyl-2-vinyl-benzene (25.9 ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), $TMSN_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and $Fe(OTf)_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH_2Cl_2 (6 mL) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (37.1 mg, 76%).^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.5 Hz, 1H), 7.32 – 7.24 (m, 2H), 7.23 (d, *J* = 7.0 Hz, 1H), 5.84 (dd, *J* = 9.1, 4.1 Hz, 1H), 5.04 (dd, *J* = 10.0, 4.1 Hz, 1H), 2.60 – 2.56 (m, 1H), 2.47 – 2.43 (m, 1H), 2.41 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.72 , 135.46, 131.14, 128.60, 126.88, 126.15, 70.29, 59.47, 49.15, 19.14. HRMS (EI): calcd for $C_{10}H_{11}Cl_2N_3$ 243.0330, found 243.0332.



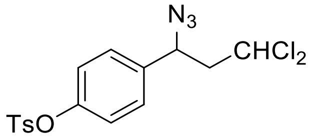
1-(1-Azido-3,3-dichloropropyl)-4-methoxybenzene l: According to the general procedure, 1-methoxy-4-vinylbenzene (26.8 ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), $TMSN_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and $Fe(OTf)_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH_2Cl_2 (6 mL) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (38.4 mg, 74%);^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 5.71 (dd, *J* = 8.2, 5.1 Hz, 1H), 4.70 (dd, *J* = 9.3, 5.4 Hz, 1H), 3.83 (s, 3H), 2.67 – 2.62 (m , 1H), 2.48 – 2.44 (m, 1H).^{13}C NMR (150 MHz, $CDCl_3$) δ 160.03, 129.27, 128.27, 114.50, 70.11, 62.66, 55.31, 49.59. HRMS (EI): calcd for $C_{10}H_{11}Cl_2N_3O$ 259.0279, found 259.0222.



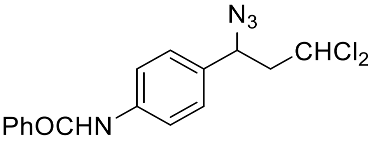
4-(1-Azido-3,3-dichloropropyl)phenyl acetate: According to the general procedure, 4-vinylphenyl acetate (30.6 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), $TMSN_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and $Fe(OTf)_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH_2Cl_2 (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=20:1) as a colorless oil liquid (41.9 mg, 73%);^{1}H NMR (600 MHz, CDCl3) δ 7.38 – 7.34 (m, 2H), 7.18 – 7.14 (m, 2H), 5.75 (dd, J = 8.5, 4.8 Hz, 1H), 4.76 (dd, J = 9.6, 5.0 Hz, 1H), 2.62 (m, 1H), 2.50 – 2.41 (m, 1H), 2.31 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.19, 150.98, 135.09, 128.01, 122.38, 69.89, 62.60, 49.76, 21.11. HRMS (EI): calcd for $C_{11}H_{11}Cl_2N_3O_2$ 287.0228, found 287.0234



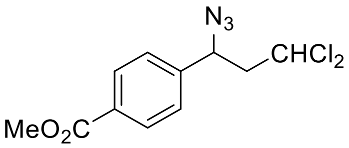
6-(1-Azido-3,3-dichloropropyl)-2,3-dihydrobenzo[b][1,4]dioxine: According to the general procedure, 6-vinyl-2,3-dihydrobenzo[b][1,4]dioxine (32.4 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), $TMSN_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and $Fe(OTf)_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH_2Cl_2 (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=20:1) as a colorless oil liquid (41.6 mg, 72%);^{1}H NMR (600 MHz, $CDCl_3$) δ 6.89 (d, *J* = 8.3 Hz, 1H), 6.85 (d, *J* = 2.1 Hz, 1H), 6.80 (dd, *J* = 8.3, 2.1 Hz, 1H), 5.69 (dd, *J* = 8.1, 5.2 Hz, 1H), 4.63 (dd, *J* = 9.2, 5.5 Hz, 1H), 4.27 (s, 4H), 2.63 – 2.58 (m, 1H), 2.46 – 2.42 (m, 1H).^{13}C NMR (150 MHz, $CDCl_3$) δ 144.10 , 143.91 , 130.46 , 120.02 , 117.86 , 115.87 , 70.06 , 64.31 , 62.64 , 49.57 . HRMS (EI): calcd for $C_{11}H_{11}Cl_2N_3O_2$ 287.0228, found 287.0226.



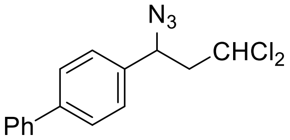
4-(1-Azido-3,3-dichloropropyl)phenyl 4-methylbenzenesulfonate: According to the general procedure, toluene-4-sulfonic acid 4-vinyl-phenyl ester (54.8 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), $TMSN_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and $Fe(OTf)_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH_2Cl_2 (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=10:1) as a colorless oil liquid (62.6 mg, 78%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 8.6 Hz, 2H), 7.08 – 7.03 (m, 2H), 5.73 (dd, J = 8.7, 4.6 Hz, 1H), 4.73 (dd, J = 9.7, 4.8 Hz, 1H), 2.60 – 2.55 (m, 1H), 2.45 (d, J = 5.5 Hz, 3H), 2.45 – 2.38 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.84 , 145.62 , 136.55 , 132.21 , 129.86 , 128.50 , 128.24 , 123.25 , 69.76 , 62.43 , 49.67 , 21.75 . HRMS (EI): calcd for $C_{16}H_{15}Cl_2N_3O_3S$ 399.0211, found 399.0216.



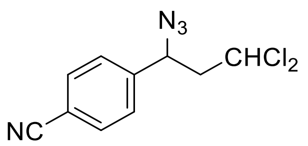
N-(4-(1-Azido-3,3-dichloropropyl)phenyl)benzamide: According to the general procedure, N-(4-vinyl-phenyl)-benzamide (44.6 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), $TMSN_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and $Fe(OTf)_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH_2Cl_2 (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=10:1) as a white solid (49.6 mg, 71%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.87 (d, J = 7.4 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.7 Hz, 2H), 7.35 (d, J = 8.5 Hz, 2H), 5.73 (dd, J = 8.3, 5.0 Hz, 1H), 4.75 (dd, J = 9.4, 5.2 Hz, 1H), 2.67 – 2.62 (m, 1H), 2.49 – 2.45 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.86 , 138.60 , 134.64 , 133.41 , 132.13 , 128.90 , 127.86 , 127.05 , 120.74 , 70.01 , 62.72 , 49.60 . HRMS (EI): calcd for $C_{16}H_{14}Cl_2N_4O$ 348.0545, found 348.0539.



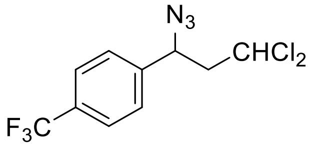
Methyl 4-(1-azido-3,3-dichloropropyl)benzoate: According to the general procedure, 4-vinyl-benzoic acid methyl ester (32.4 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), $TMSN_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and $Fe(OTf)_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH_2Cl_2 (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=5:1) as a colorless oil liquid (40.4 mg, 70%); ^1H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 5.76 (dd, *J* = 8.7, 4.6 Hz, 1H), 4.82 (dd, *J* = 9.7, 4.8 Hz, 1H), 3.94 (s, 3H), 2.65 – 2.60 (m, 1H), 2.49 – 2.45 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.34, 142.46, 130.82, 130.49, 126.91, 69.72, 62.79, 52.29, 49.59. HRMS (EI): calcd for $C_{11}H_{11}Cl_2N_3O_2$ 287.0228, found 287.0231.



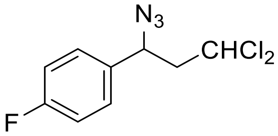
4-(1-Azido-3,3-dichloropropyl)-1,1'-biphenyl: According to the general procedure, 4-vinyl-1,1'-biphenyl (36.0 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), $TMSN_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and $Fe(OTf)_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH_2Cl_2 (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=20:1) as a colorless oil liquid (47.5 mg, 78%); ^1H NMR (600 MHz, $CDCl_3$) δ 7.67 – 7.57 (m, 4H), 7.50 – 7.32 (m, 5H), 5.77 (dd, *J* = 8.4, 4.9 Hz, 1H), 4.80 (dd, *J* = 9.5, 5.2 Hz, 1H), 2.70 – 2.65 (m, 1H), 2.54 – 2.49 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.00, 140.21, 136.36, 128.87, 127.90, 127.68, 127.37, 127.10, 70.03, 62.91, 49.68. HRMS (EI): calcd for $C_{15}H_{13}Cl_2N_3$ 305.0487, found 305.0490.



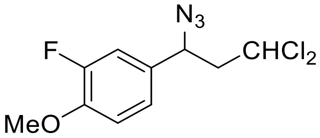
4-(1-Azido-3,3-dichloropropyl)benzonitrile: According to the general procedure, 4-vinylbenzonitrile (16.3 ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), $TMSN_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and $Fe(OTf)_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH_2Cl_2 (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=20:1) as a colorless oil liquid (30.8 mg, 61%);^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 5.78 (dd, *J* = 8.8, 4.4 Hz, 1H), 4.84 (dd, *J* = 9.9, 4.6 Hz, 1H), 2.62 – 2.57 (m, 1H), 2.47 – 2.42 (m, 1H).^{13}C NMR (150 MHz, $CDCl_3$) δ 169.19, 150.98, 135.09, 128.01, 122.38, 69.89, 62.60, 49.76, 21.11.HRMS (EI): calcd for $C_{10}H_8Cl_2N_4$ 254.0126, found 254.0129.



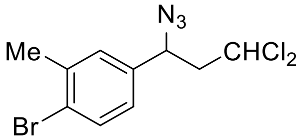
1-(1-Azido-3,3-dichloropropyl)-4-(trifluoromethyl)benzene: According to the general procedure, 1-(trifluoromethyl)-4-vinylbenzene (29.4 ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), $TMSN_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and $Fe(OTf)_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH_2Cl_2 (6 mL) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (24.7 mg, 42%);^{1}H NMR (600 MHz, CDCl3) δ 7.70 (d, J = 8.2 Hz, 2H), 7.48 (d, J = 8.1 Hz, 2H), 5.77 (dd, J = 8.7, 4.6 Hz, 1H), 4.84 (dd, J = 9.7, 4.8 Hz, 1H), 2.65 – 2.60 (m, 1H), 2.49 – 2.44 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.69 (s), 131.28 (q, J = 32.7 Hz), 127.31 (s), 126.28 (q, J = 3.7 Hz), 123.75 (q, J = 272.3 Hz) , 69.64 , 62.68 , 49.72 .HRMS (EI): calcd for $C_{10}H_8F_3Cl_2N_3$ 297.0047, found 296.9949.



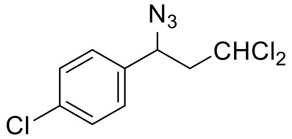
1-(1-Azido-3,3-dichloropropyl)-4-fluorobenzene: According to the general procedure, 1-fluoro-4-vinylbenzene (23.8 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), $TMSN_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and $Fe(OTf)_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH_2Cl_2 (6 mL) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (30.8 mg, 62%);^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (dd, J = 8.5, 5.3 Hz, 2H), 7.12 (t, J = 8.5 Hz, 2H), 5.73 (dd, J = 8.5, 4.8 Hz, 1H), 4.75 (dd, J = 9.5, 5.1 Hz, 1H), 2.65 – 2.60 (m, 1H), 2.47 – 2.43 (m, 1H).^{13}C NMR (150 MHz, $CDCl_3$) δ 162.88 (d, J = 248.5 Hz), 133.35 (d, J = 3.3 Hz), 128.73 (d, J = 8.3 Hz), 116.23 (d, J = 21.7 Hz) ,69.85, 62.46, 49.74. HRMS (EI): calcd for $C_9H_8Cl_2FN_3$ 247.0079, found 247.0081.



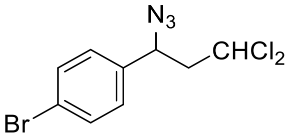
4-(1-Azido-3,3-dichloropropyl)-2-fluoro-1-methoxybenzene: According to the general procedure, 2-fluoro-1-methoxy-4-vinyl-benzene (30.4 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), $TMSN_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and $Fe(OTf)_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH_2Cl_2 (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=20:1) as a colorless oil liquid (41.3 mg, 74%);^{1}H NMR (600 MHz, $CDCl_3$) δ 7.08 (dd, J = 17.3, 5.6 Hz, 2H), 6.99 (t, J = 8.3 Hz, 1H), 5.71 (dd, J = 8.4, 5.0 Hz, 1H), 4.69 (dd, J = 9.4, 5.2 Hz, 1H), 3.91 (d, J = 9.2 Hz, 3H), 2.62 – 2.58 (m, 1H), 2.46 – 2.41 (m, 1H).^{13}C NMR (150 MHz, $CDCl_3$) δ 152.50 (d, J = 248.1 Hz), 148.16 (d, J = 10.6 Hz), 130.16 (d, J = 5.6 Hz), 123.08 (d, J = 3.5 Hz), 114.61 (d, J = 19.2 Hz), 113.58 (d, J = 2.0 Hz), 69.83 , 62.30 , 56.26 , 49.53 . HRMS (EI): calcd for $C_{10}H_{10}Cl_2FN_3O$ 277.0185, found 277.0178.



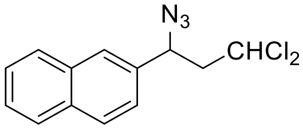
4-(1-Azido-3,3-dichloropropyl)-1-bromo-2-methylbenzene: According to the general procedure, 1-bromo-2-methyl-4-vinyl-benzene (39.4 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), $TMSN_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and $Fe(OTf)_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH_2Cl_2 (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=20:1) as a colorless oil liquid (43.9 mg, 68%);^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 1H), 7.20 (d, *J* = 1.9 Hz, 1H), 7.03 (dd, *J* = 8.2, 2.1 Hz, 1H), 5.73 (dd, *J* = 8.5, 4.9 Hz, 1H), 4.69 (dd, *J* = 9.5, 5.1 Hz, 1H), 2.63 – 2.58 (m, 1H), 2.46 – 2.41 (m, 4H).^{13}C NMR (150 MHz, $CDCl_3$) δ 139.05 , 136.79 , 133.17 , 129.27 , 125.76 , 125.50 , 69.85 , 62.61 , 49.63 , 23.05 . HRMS (EI): calcd for $C_{10}H_{10}BrCl_2N_3$ 320.9435, found $[M-N_2]^+$292.9387.



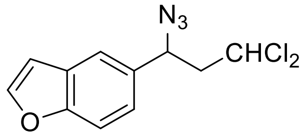
1-(1-Azido-3,3-dichloropropyl)-4-chlorobenzene: According to the general procedure, 1-chloro-4-vinylbenzene (24.0 ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), $TMSN_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and $Fe(OTf)_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH_2Cl_2 (6 mL) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (31.2 mg, 59%);^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 5.73 (dd, *J* = 8.5, 4.8 Hz, 1H), 4.74 (dd, *J* = 9.6, 5.0 Hz, 1H), 2.63 – 2.58 (m, 1H), 2.46 – 2.42 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 136.07, 134.97, 129.48, 128.30, 69.79, 62.53, 49.67. HRMS (EI): calcd for $C_9H_8Cl_3N_3$ 262.9784, found 262.9787.



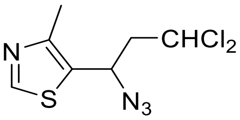
1-(1-Azido-3,3-dichloropropyl)-4-bromobenzene: According to the general procedure, 1- bromo -4-vinylbenzene (26.2 ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), $TMSN_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and $Fe(OTf)_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH_2Cl_2 (6 mL) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (31.9 mg, 52%);^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 5.73 (dd, *J* = 8.5, 4.8 Hz, 1H), 4.73 (dd, *J* = 9.6, 5.0 Hz, 1H), 2.63 – 2.58 (m, 1H), 2.46 – 2.41 (m, 1H).^{13}C NMR (150 MHz, $CDCl_3$) δ 136.61, 132.44, 128.59, 123.09, 69.76, 62.59, 49.63. HRMS (EI): calcd for $C_9H_8BrCl_2N_3$ 306.9279, found 306.9282.



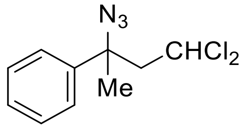
2-(1-Azido-3,3-dichloropropyl)naphthalene : According to the general procedure, 2-vinyl-naphthalene (30.8 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), $TMSN_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and $Fe(OTf)_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH_2Cl_2 (6 mL) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (26.0 mg, 47%);^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.5 Hz, 1H), 7.86 (dd, *J* = 5.4, 2.8 Hz, 2H), 7.80 (s, 1H), 7.53 (dd, *J* = 6.3, 3.0 Hz, 2H), 7.43 (dd, *J* = 8.5, 1.6 Hz, 1H), 5.76 (dd, *J* = 8.3, 5.0 Hz, 1H), 4.92 (dd, *J* = 9.4, 5.3 Hz, 1H), 2.76 – 2.71 (m, 1H), 2.59 – 2.54 (m, 1H).^{13}C NMR (150 MHz, $CDCl_3$) δ 134.77 , 133.47 , 133.18 , 129.44 , 128.09 , 127.83 , 126.82, 126.79 , 126.60 , 123.94 , 70.08 , 63.43 , 49.65 . HRMS (EI): calcd for $C_{13}H_{11}Cl_2N_3$ 279.0330, found 279.0333.



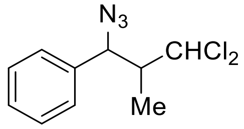
5-(1-Azido-3,3-dichloropropyl)benzofuran: According to the general procedure, 5-vinyl-benzofuran (26.5 ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), $TMSN_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and $Fe(OTf)_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH_2Cl_2 (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=5:1) as a colorless oil liquid (35.2 mg, 65%);^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 2.1 Hz, 1H), 7.59 (d, *J* = 1.5 Hz, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.27 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.79 (t, *J* = 7.6 Hz, 1H), 5.72 (dd, *J* = 8.2, 5.2 Hz, 1H), 4.86 (dd, *J* = 9.3, 5.4 Hz, 1H), 2.73 – 2.68 (m, 1H), 2.54 – 2.50 (m, 1H).^{13}C NMR (150 MHz, $CDCl_3$) δ 155.00 , 146.15 , 132.07 , 128.06 , 123.10 , 119.98 , 112.24 , 106.66 , 70.11 , 63.33 , 50.08 . HRMS (EI): calcd for $C_{11}H_9Cl_2N_3O$ 269.0123, found 269.0125.



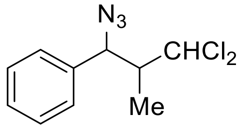
5-(1-Azido-3,3-dichloropropyl)-4-methylthiazole: According to the general procedure, 4-methyl-5-vinylthiazole (22.9 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), $TMSN_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and $Fe(OTf)_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH_2Cl_2 (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=5:1) as a colorless oil liquid (25.4 mg, 51%);^{1}H NMR (600 MHz, $CDCl_3$) δ 8.77 (s, 1H), 5.75 (dd, *J* = 8.4, 4.9 Hz, 1H), 5.15 (dd, *J* = 9.3, 5.2 Hz, 1H), 2.69 – 2.64 (m, 1H), 2.53 (s, 3H), 2.51 – 2.44 (m, 1H).^{13}C NMR (150 MHz, $CDCl_3$) δ 152.28 , 151.63 , 128.52 , 69.29 , 55.74 , 50.15 , 15.48 . HRMS (EI): calcd for $C_7H_9Cl_2N_4S$ 250.9925, found 250.9920.



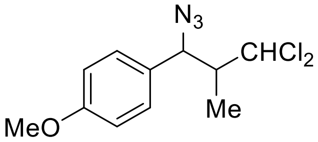
(2-Azido-4,4-dichlorobutan-2-yl)benzene: According to the general procedure, prop-1-en-2-ylbenzene (26.0 ul , 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), $TMSN_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and $Fe(OTf)_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH_2Cl_2 (6 mL) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (37.3 mg, 77%);^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 4.1 Hz, 4H), 7.33 (dt, *J* = 8.7, 4.2 Hz, 1H), 5.55 (t, *J* = 5.7 Hz, 1H), 2.84 – 2.74 (m, 2H), 1.82 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 141.53, 128.95 , 128.08 , 125.45 , 68.84 , 65.33 , 55.25 , 25.71 . HRMS (EI): calcd for $C_{10}H_{11}Cl_2N_3$ 243.0330, found 243.0272.



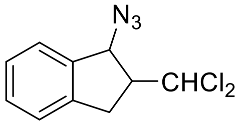
(1-Azido-3,3-dichloro-2-methylpropyl)benzene: According to the general procedure, (Z)-prop-1-en-1-ylbenzene (23.6 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), $TMSN_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and $Fe(OTf)_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH_2Cl_2 (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=20:1) as a colorless oil liquid (32.8 mg, 67%), dr = 1.25:1 (determined by crude ^{1}H NMR). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 – 7.37 (m, 3H), 7.36 – 7.28 (m, 2H), 6.37 (d, *J* = 2.3 Hz, 0.54H), 5.39 (d, *J* = 3.8 Hz, 0.43H), 4.52 (d, *J* = 8.6 Hz, 0.44H), 4.34 (d, *J* = 10.6 Hz, 0.55H), 2.48 – 2.37 (m, 1H), 1.34 (d, *J* = 6.5 Hz, 1.43H), 0.92 (d, *J* = 6.7 Hz, 1.72H).^{13}C NMR (150 MHz, $CDCl_3$) δ 136.83 (137.02), 129.25 (129.025), 129.11 (129.080), 127.84 (127.31), 75.86 (75.58), 68.65 (68.46), 48.37 (49.59), 10.28 (10.79). HRMS (EI): calcd for $C_{10}H_{11}Cl_2N_3$ 243.0330, found 243.0336.



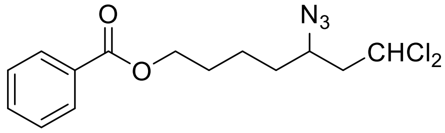
(1-Azido-3,3-dichloro-2-methylpropyl)benzene: According to the general procedure, (E)-prop-1-en-1-ylbenzene (23.6 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN$_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)$_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH$_2$Cl$_2$ (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=20:1) as a colorless oil liquid (34.7 mg, 71%), dr = 1.16:1 (determined by crude ^{1}H NMR). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.46 – 7.37 (m, 3H), 7.35 – 7.28 (m, 2H), 6.37 (d, *J* = 2.3 Hz, 0.51H), 5.39 (d, *J* = 3.8 Hz, 0.44H), 4.52 (d, *J* = 8.6 Hz, 0.44H), 4.34 (d, *J* = 10.6 Hz, 0.52H), 2.43 – 2.42 (m , 1H), 1.34 (d, *J* = 6.5 Hz, 1.51H), 0.92 (d, *J* = 6.7 Hz, 1.64H).^{13}C NMR (150 MHz, CDCl$_3$) δ 136.83 (137.02), 129.25 (129.03), 129.11 (129.08), 127.84 (127.31), 75.87 (75.58), 68.65 (68.46), 48.37 (49.59), 10.28 (10.79).HRMS (EI): calcd for $C_{10}H_{11}Cl_2N_3$ 243.0330, found 243.0334.



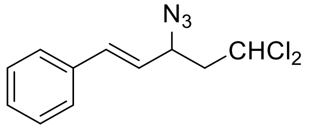
1-(1-Azido-3,3-dichloro-2-methylpropyl)-4-methoxybenzene: According to the general procedure, (E)-1-methoxy-4-(prop-1-en-1-yl)benzene (29.6 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), TMSN$_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and Fe(OTf)$_2$ (14.0 mg, 0.04 mmol, 20 mol%) in CH$_2$Cl$_2$ (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=20:1) as a colorless oil liquid (48.3 mg, 89%), dr = 1.32:1 (determined by crude ^{1}H NMR).^{1}H NMR (600 MHz, CDCl3) δ 7.25 – 7.19 (m, 2H), 6.94 (m, 2H), 6.35 (d, J = 2.3 Hz, 0.5H), 5.37 (d, J = 3.4 Hz, 0.38H), 4.41 (d, J = 9.1 Hz, 0.39H), 4.29 (d, J = 10.6 Hz, 0.52H), 3.84 (s, 1.13H), 3.83 (s, 1.48H), 2.39 (m, 1H), 1.35 (d, J = 6.5 Hz, 1.29H), 0.92 (d, J = 6.6 Hz, 1.64H). ^{13}C NMR (150 MHz, CDCl3) δ 160.02 (160.00), 129.04 (128.61), 128.79(128.76), 114.60 (114.42), 75.95 (75.64), 68.17 (68.22) , 55.32 (55.35), 48.46 (49.48), 29.10, 10.32 (10.78) .HRMS (EI): calcd for $C_{11}H_{13}Cl_2N_3O$ 273.0436, found 273.0434.



Azido-2-(dichloromethyl)-2,3-dihydro-1H-indene: According to the general procedure, 1H-indene (23.3ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), $TMSN_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and $Fe(OTf)_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH_2Cl_2 (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=20:1) as a colorless oil liquid (41.5 mg, 86%);^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.0 Hz, 1H), 7.32 (dd, *J* = 7.2, 5.9 Hz, 2H), 7.27 (s, 1H), 6.03 (d, *J* = 4.1 Hz, 1H), 4.94 (d, *J* = 6.0 Hz, 1H), 3.32 (dd, *J* = 14.3, 6.6 Hz, 1H), 3.19 – 3.07 (m, 2H).^{13}C NMR (150 MHz, $CDCl_3$) δ 140.37 , 139.25 , 129.29 , 127.56 , 125.06 , 124.54 , 73.96 , 67.79 , 57.02 , 33.20 . HRMS (EI): calcd for $C_{10}H_9Cl_2N_3$ 241.0174, found $[M-N_2]^+$ 213.0118



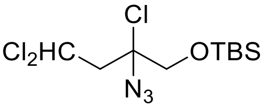
5-Azido-7,7-dichloroheptyl benzoate: According to the general procedure, benzoic acid hex-5-enyl ester (40.8 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), $TMSN_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and $Fe(OTf)_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH_2Cl_2 (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=20:1) as a colorless oil liquid (30.4 mg, 46%);^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 5.88 – 5.77 (m, 1H), 5.04 (d, *J* = 17.1 Hz, 1H), 4.98 (d, *J* = 10.1 Hz, 1H), 4.33 (t, *J* = 6.5 Hz, 2H), 2.14 (d, *J* = 7.0 Hz, 2H), 1.84 – 1.74 (m, 2H), 1.63 – 1.51 (m, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 166.64, 132.85, 130.40, 129.51, 128.33, 73.52, 64.83, 43.46, 28.54, 28.20, 25.83, 25.79. HRMS (EI): calcd for $C_{14}H_{17}Cl_2N_3O_2$ 329.0698, found 329.0692.



(E)-Buta-1,3-dien-1-ylbenzene was prepared through a known procedure[1]

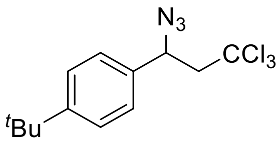
(E)-(3-azido-5,5-dichloropent-1-en-1-yl)benzene: According to the general procedure, (E)-buta-1,3-dien-1-ylbenzene (28.0 ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), $TMSN_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and $Fe(OTf)_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH_2Cl_2 (6 mL) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (27.4 mg, 54%);

^1H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.3 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.31 (dd, *J* = 8.4, 6.1 Hz, 1H), 6.73 (d, *J* = 15.8 Hz, 1H), 6.09 (dd, *J* = 15.8, 8.4 Hz, 1H), 5.82 (dd, *J* = 8.3, 5.0 Hz, 1H), 4.35 (td, *J* = 8.7, 5.3 Hz, 1H), 2.48 – 2.45 (m, 1H), 2.43 – 2.37 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.24, 135.20, 128.75, 128.66, 126.80, 124.31, 69.84, 61.90, 48.07.. HRMS (EI): calcd for $C_{11}H_{11}Cl_2N_3$ 255.0330, found 255.0323.

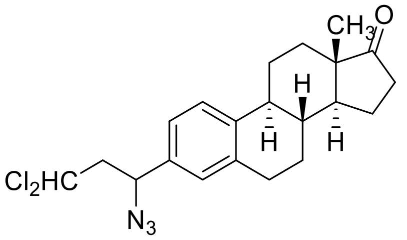


(2-Azido-2,4,4-trichlorobutoxy)(tert-butyl)dimethylsilane: According to the general procedure, tert-Butyl-(2-chloro-allyloxy)-dimethyl-silane (38.9 ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), $TMSN_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and $Fe(OTf)_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH_2Cl_2 (6 mL) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (29.1 mg, 44%);^1H NMR (600 MHz, $CDCl_3$) δ 6.07 (t, *J* = 5.6 Hz, 1H), 4.00 (s, 2H), 3.22 (d, *J* = 5.6 Hz, 2H), 0.94 – 0.91 (m, 9H), 0.12 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$)

δ 87.93 , 72.00 , 68.17 , 55.18 , 25.70 , 18.27 , -5.35 . HRMS (EI): calcd for $C_{10}H_{20}Cl_3N_3OSi$ 331.0441, found 331.0446.

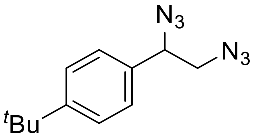


1-(1-Azido-3,3,3-trichloropropyl)-4-(tert-butyl)benzene: According to the general procedure, 1-(tert-butyl)-4-vinylbenzene (37.0 ul, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), $TMSN_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and $Fe(OTf)_2$ (14.0 mg, 0.04 mmol, 10 mol%) in $CHCl_3$ (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=20:1) as a colorless oil liquid (45.0 mg, 46%);^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.3 Hz, 2H), 4.92 (dd, J = 7.6, 3.5 Hz, 1H), 3.22 (dd, J = 15.2, 7.6 Hz, 1H), 3.11 (dd, J = 15.2, 3.5 Hz, 1H), 1.34 (s, 9H).^{13}C NMR (150 MHz, $CDCl_3$) δ 151.92, 135.70, 126.51, 126.08, 63.15, 60.11, 34.68, 31.29. HRMS (EI): calcd for $C_{13}H_{16}Cl_3N_3$ 319.0410, found 319.0413.

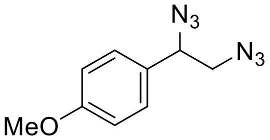


3-(1-Azido-3,3-dichloropropyl)-13-methyl 6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one: According to the general procedure, 13-Methyl-3-vinyl 6,7,8,9,11,12,13,14,15,16-decahydro-cyclopenta[a]phenanthren-17-one (56.0 mg, 0.2 mmol, 1.0 equiv.), DTBP (73.4 ul, 0.4 mmol, 2.0 equiv.), $TMSN_3$ (34.0 ul, 0.26 mmol, 1.3 equiv.) and $Fe(OTf)_2$ (14.0 mg, 0.04 mmol, 10 mol%) in CH_2Cl_2 (6 mL) were used. After 24h, the product was isolated by flash chromatography (PE:EA=10:1) as a colorless oil liquid (45.4 mg, 56%);^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (d, J = 8.0 Hz, 1H), 7.11 (d, J = 8.0 Hz, 1H), 7.05 (s, 1H), 5.73 (dd, J = 8.3, 5.0

Hz, 1H), 4.68 (dd, *J* = 9.4, 5.2 Hz, 1H), 2.97 – 2.90 (m, 2H), 2.65 – 2.61 (m, 1H), 2.58 – 2.39 (m, 3H), 2.31 (td, *J* = 10.9, 3.7 Hz, 1H), 2.16 (dt, *J* = 18.6, 9.1 Hz, 1H), 2.10 – 2.04 (m, 2H), 1.98 (dd, *J* = 12.5, 3.3 Hz, 1H), 1.69 – 1.61 (m, 2H), 1.58 – 1.42 (m, 4H), 0.92 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 220.67 , 140.74 , 137.49 , 134.83 , 127.53 , 126.18 , 124.29 , 70.14 , 62.90 , 50.48 , 49.64 , 47.93 , 44.36 , 37.96 , 35.82 , 31.55 , 29.39 , 26.34 , 25.64 , 21.57 , 13.83 .HRMS (ESI): calcd for $C_{21}H_{25}Cl_2N_3O$ 405.1375, found [M+H] 406.1447.

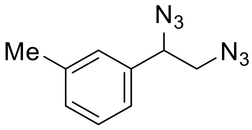


1-(*tert*-Butyl)-4-(1,2-diazidoethyl)benzene: ^{2}According to the general procedure, 1-(tert-butyl)-4-vinylbenzene (37.0 ul, 0.2 mmol, 1.0 equiv.), DTBP (55.0 ul, 0.3 mmol, 1.5 equiv.), $TMSN_3$ (91.8 ul, 0.7mmol, 3.5eq.) and $Fe(OTf)_2$ (0.01 mmol, 5 mol%) in DCM:^{t}BuOH =5:1(1 ml:0.2ml) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (38.0 mg, 78%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 7.5 Hz, 2H), 4.65 (dd, *J* = 8.6, 4.7 Hz, 1H), 3.50 (dd, *J* = 12.8, 8.6 Hz, 1H), 3.43 (dd, *J* = 12.8, 4.7 Hz, 1H),1.32(s, 9H).

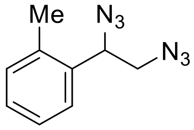


1-(1,2-Diazidoethyl)-4-methoxybenzene: ^{2}According to the general procedure, 1-methoxy-4-vinylbenzene (20.8 ul, 0.2 mmol, 1.0 equiv.), DTBP (55.0 ul, 0.3 mmol, 1.5 equiv.), $TMSN_3$ (91.8 ul, 0.7mmol, 3.5eq.) and $Fe(OTf)_2$ (0.01 mmol, 5 mol%) in DCM:^{t}BuOH =5:1(1 ml:0.2ml) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (33.1 mg, 76%);^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 4.62 (dd, *J* =

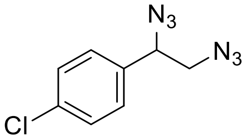
8.3, 5.0 Hz, 1H), 3.82 (s, 3H), 3.49 (dd, *J* = 12.7, 8.4 Hz, 1H), 3.41 (dd, *J* = 12.7, 5.0 Hz, 1H).



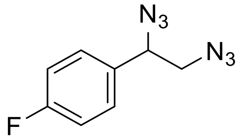
1-(1,2-Diazidoethyl)-3-methylbenzene: [2] According to the general procedure, 1-methyl-3-vinylbenzene (23.6 mg, 0.2 mmol, 1.0 equiv.), DTBP (55.0 ul, 0.3 mmol, 1.5 equiv.), $TMSN_3$ (91.8 ul, 0.7mmol, 3.5eq.) and $Fe(OTf)_2$ (0.01 mmol, 5 mol%) in DCM:^{t}BuOH =5:1(1 ml:0.2ml) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (28.3 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 7.7 Hz, 2H), 4.63 (dd, *J* = 8.4, 4.9 Hz, 1H), 3.46 (dd, *J* = 17.6, 12.7, 6.7 Hz, 2H), 2.39 (s, 3H).



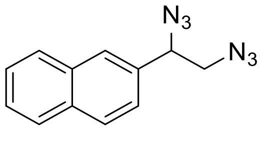
1-(1,2-Diazidoethyl)-2-methylbenzene: [2] According to the general procedure, 1-methyl-2-vinylbenzene (23.6 mg, 0.2 mmol, 1.0 equiv.), DTBP (55.0 ul, 0.3 mmol, 1.5 equiv.), $TMSN_3$ (91.8 ul, 0.7mmol, 3.5eq.) and $Fe(OTf)_2$ (0.01 mmol, 5 mol%) in DCM:^{t}BuOH =5:1(1 ml:0.2ml) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (33.9 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 1H), 7.27 (dd, *J* = 6.1, 3.2 Hz, 2H), 7.24 – 7.20 (m, 1H), 4.93 (dd, *J* = 8.7, 4.5 Hz, 1H), 3.50 (dd, *J* = 12.8, 8.7 Hz, 1H), 3.41 (dd, *J* = 12.8, 4.5 Hz, 1H), 2.39 (s, 3H).



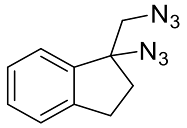
1-Chloro-4-(1,2-diazidoethyl)benzene: [2] According to the general procedure, 1-chloro-4-vinylbenzene (24.0 ul, 0.2 mmol, 1.0 equiv.), DTBP (55.0 ul, 0.3 mmol, 1.5 equiv.), $TMSN_3$ (91.8 ul, 0.7mmol, 3.5 eq.) and $Fe(OTf)_2$ (0.01 mmol, 5 mol%) in DCM:^{t}BuOH =5:1(1 ml:0.2ml) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (30.2 mg, 68%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 4.65 (dd, *J* = 8.1, 5.0 Hz, 1H), 3.48 (dd, *J* = 12.8, 8.1 Hz, 1H), 3.43 (dd, *J* = 12.8, 5.0 Hz, 1H).



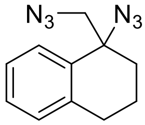
1-(1,2-Diazidoethyl)-4-fluorobenzene: [2] According to the general procedure, 1-fluoro-4-vinylbenzene (23.8 ul, 0.2 mmol, 1.0 equiv.), DTBP (55.0 ul, 0.3 mmol, 1.5 equiv.), $TMSN_3$ (91.8 ul, 0.7mmol, 3.5eq.) and $Fe(OTf)_2$ (0.01 mmol, 5 mol%) in DCM:^{t}BuOH =5:1(1 ml:0.2ml) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (35.4 mg, 86%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 2H), 7.11 (dd, *J* = 11.7, 5.2 Hz, 2H), 4.66 (dd, *J* = 8.0, 5.1 Hz, 1H), 3.49 (dd, *J* = 12.7, 8.2 Hz, 1H), 3.43 (dd, *J* = 12.7, 5.0 Hz, 1H).



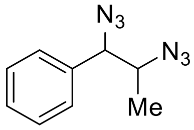
2-(1,2-Diazidoethyl)naphthalene: [2] According to the general procedure, 2-vinylnaphthalene (30.8 mg, 0.2 mmol, 1.0 equiv.), DTBP (55.0 ul, 0.3 mmol, 1.5 equiv.), $TMSN_3$ (91.8 ul, 0.7mmol, 3.5eq.) and $Fe(OTf)_2$ (0.01 mmol, 5 mol%) in DCM:^{t}BuOH =5:1(1 ml:0.2ml) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (20.2 mg, 48%);^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 – 7.73 (m, 4H), 7.56 – 7.51 (m, 2H), 7.40(d, *J* = 8.5 Hz, 1H) 4.85 (dd, *J* = 8.4, 4.9 Hz, 1H), 3.60 (dd, *J* = 12.8, 8.5 Hz, 1H), 3.53 (dd, *J* = 12.8, 4.8 Hz, 1H).



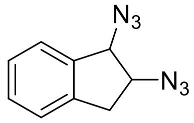
1-azido-1-(azidomethyl)-2,3-dihydro-1H-indene: According to the general procedure, 1-methylene-2,3-dihydro-1H-indene (26.0 mg, 0.2 mmol, 1.0 equiv.), DTBP (55.0 ul, 0.3 mmol, 1.5 equiv.), TMSN$_3$ (91.8 ul, 0.7mmol, 3.5eq.) and Fe(OTf)$_2$ (0.01 mmol, 5 mol%) in DCM:^{t}BuOH =5:1(1 ml:0.2ml) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (27.1 mg, 63%);^{1}H NMR (600 MHz, CDCl$_3$) δ 7.32 – 7.31 (m, 4H), 4.16 (t, *J* = 6.8 Hz, 2H), 3.33 – 3.31 (m , 2H), 2.92 – 2.88 (m, 2H).^{13}C NMR (150 MHz, CDCl$_3$) δ 142.55, 138.05, 129.27 , 127.83, 125.22 , 122.99 , 73.42 , 70.11 , 35.46 , 19.78 . HRMS (EI): calcd for $C_{10}H_{10}N_6$ 214.0967, found 214.0970.



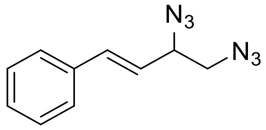
1-Azido-1-(azidomethyl)-1,2,3,4-tetrahydronaphthalene: According to the general procedure, 1-methylene-1,2,3,4-tetrahydronaphthalene (26.0 mg, 0.2 mmol, 1.0 equiv.), DTBP (55.0 ul, 0.3 mmol, 1.5 equiv.), TMSN$_3$ (91.8 ul, 0.7mmol, 3.5eq.) and Fe(OTf)$_2$ (0.01 mmol, 5 mol%) in DCM:^{t}BuOH =5:1(1 ml:0.2ml) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (29.8 mg, 65%);^{1}H NMR (600 MHz, CDCl$_3$) δ 7.48 – 7.42 (m, 1H), 7.26 (dt, *J* = 3.2, 2.1 Hz, 2H), 7.16 (dd, *J* = 5.6, 3.2 Hz, 1H), 3.56 (d, *J* = 12.8 Hz, 1H), 3.46 (d, *J* = 12.8 Hz, 1H), 2.88 – 2.81 (m, 1H), 2.81 (dt, *J* = 16.9, 5.9 Hz, 1H), 2.31 – 2.23 (m, 1H), 2.05 (m, *J* = 12.2, 7.7, 2.7 Hz, 1H), 2.01 – 1.93 (m, 1H), 1.88 – 1.79 (m, 1H).^{13}C NMR (150 MHz, CDCl$_3$) δ 137.79 , 134.38 , 129.65 , 128.51 , 126.96 , 126.65 , 65.50 , 59.02 , 31.23 , 29.38 , 19.56 . HRMS (EI): calcd for $C_{11}H_{12}N_6$ 228.1123, found 228.1126.



(1,2-Diazidopropyl)benzene: [2] According to the general procedure, (E)-prop-1-en-1-ylbenzene (26.0 mg, 0.2 mmol, 1.0 equiv.), DTBP (55.0 ul, 0.3 mmol, 1.5 equiv.), $TMSN_3$ (91.8 ul, 0.7mmol, 3.5eq.) and $Fe(OTf)_2$ (0.01 mmol, 5 mol%) in DCM:^{t}BuOH =5:1(1 ml:0.2ml) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (28.5 mg, 71%), dr = 1:1.09 (determined by crude ^{1}H NMR); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 3H), 7.32 (dd, J = 18.9, 7.6 Hz, 2H), 4.53 (d, J = 5.8 Hz, 0.49H), 4.37 (d, J = 7.7 Hz, 0.51H), 3.74 – 3.63 (m, 1H), 1.26 (d, J = 6.6 Hz, 1.47H), 1.11 (d, J = 6.7 Hz, 1.59H).

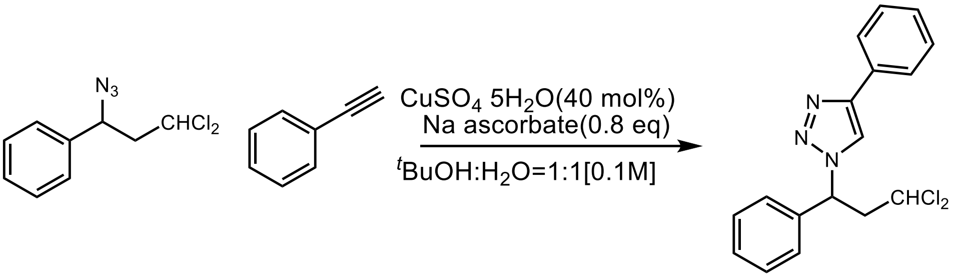


1,2-diazido-2,3-dihydro-1H-indene: [3] According to the general procedure, 1H-indene (23.2 mg, 0.2 mmol, 1.0 equiv.), DTBP (55.0 ul, 0.3 mmol, 1.5 equiv.), $TMSN_3$ (91.8 ul, 0.7mmol, 3.5eq.) and $Fe(OTf)_2$ (0.01 mmol, 5 mol%) in DCM:^{t}BuOH =5:1(1 ml:0.2ml) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (25.9 mg, 65%)**;** ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.23 (m, 4H) , 4.77 (d, J = 5.6 Hz, 1H), 4.17 (d, J =12.7, 6.2 Hz, 1H), 3.35 (dd, J = 15.9, 7.3 Hz, 1H), 2.95 (dd, J = 15.9, 6.5 Hz, 1H).

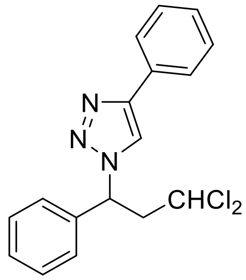


(E)-(3,4-Diazidobut-1-en-1-yl)benzene:[4] According to the general procedure, (E)-Buta-1,3-dien-1-ylbenzene (26.0 mg, 0.2 mmol, 1.0 equiv.), DTBP (55.0 ul, 0.3 mmol, 1.5 equiv.), $TMSN_3$ (91.8 ul, 0.7mmol, 3.5eq.) and $Fe(OTf)_2$ (0.01 mmol, 5 mol%) in DCM:^{t}BuOH =5:1(1 ml:0.2ml) were used. After 24h, the product was isolated by flash chromatography (pure PE) as a colorless oil liquid (28.5 mg, 71%);^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 7.36 (m, 2H), 7.33 – 7.29 (m, 1H), 6.74 (d, *J* = 15.8 Hz, 1H), 6.13 (dd, *J* = 15.8, 8.0 Hz, 1H), 4.30 – 4.23 (m, 1H), 3.40 (m, 2H).

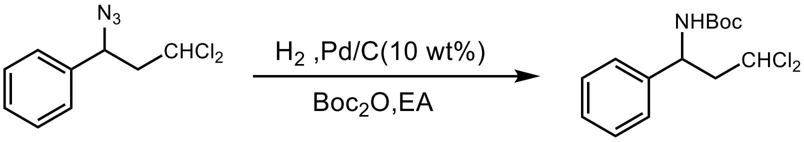
4. Synthetic transformations of products



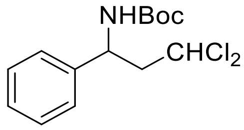
To a mixture of (1-azido-3,3-dichloropropyl)benzene (22.9 mg, 0.1 mmol,1.0 equiv.), phenyl acetylene (11 ul, 0.11 mmol , 1.1 equiv.) in $H_2O/^tBuOH$ (1 mL/1 mL) was added $CuSO_4 \cdot 5H_2O$ (10 mg, 0.4 equiv.) and sodium ascorbate (16 mg, 0.8 equiv.). The resulting mixture was stirred at room temperature for 17 h before diluted with ethyl acetate (5 mL) and water (5 mL). The aqueous layer was extracted with ethyl acetate (5 mL×3). The combined organic layers were dried over Na_2SO_4, filtered through a short silica gel plug, and concentrated in vacuo to afford 1-(3,3-dichloro-1-phenylpropyl)-4-phenyl-1H-1,2,3-triazole as white solid (32.3 mg, 98% yield).



1-(3,3-Dichloro-1-phenylpropyl)-4-phenyl-1H-1,2,3-triazole: ^1H NMR (600 MHz, $CDCl_3$) δ 7.86 – 7.76 (m, 2H), 7.69 (s, 1H), 7.43 – 7.38 (m, 5H), 7.38 – 7.35 (m, 2H), 7.33 (ddd, J = 6.9, 2.3, 1.2 Hz, 1H), 5.82 (dd, J = 9.2, 5.7 Hz, 1H), 5.66 (dd, J = 8.1, 5.3 Hz, 1H), 3.64 – 3.6 (m, 1H), 3.11 – 3.07 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.05, 137.29, 130.14, 129.42, 129.29, 128.83, 128.36, 126.81, 125.68, 119.85, 69.75, 62.54, 48.48 . HRMS (EI): calcd for $C_{17}H_{15}Cl_2N_3$ 331.0643, found 331.0646.



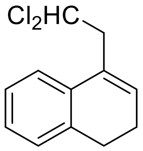
To an oven-dried three neck round bottom flask (10 mL) was added Pd/C (10.0 mg, 5 wt%). After the flask was evacuated and back filled with H_2. A solution of the (1-azido-3,3-dichloropropyl) benzene (45.8 mg, 0.2 mmol, 1.0 equiv.) and Boc_2O (52.0 mg, 0.2 mmol, 1.0 equiv.) in ethyl acetate (3.0 mL) was added to the flask via syringe. Then, the reaction mixture was vigorously stirred under H_2 (1 atm, hydrogen-filled balloon) at room temperature until the reduction completed. After that, the balloon was removed and the reaction mixture was further stirred for 10 h. The mixture was then concentrated in vacuo and the residue was subsequently purified through a silica gel column to afford tert-butyl (3,3-dichloro-1-phenylpropyl) carbamate as white solid (52.1 mg, 86% yield).



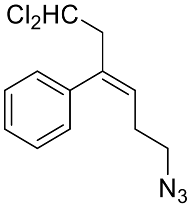
***tert*-Butyl (3,3-dichloro-1-phenylpropyl)carbamate:** ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.4 Hz, 2H), 7.30 (dd, *J* = 15.4, 7.7 Hz, 3H), 5.52 (s, 1H), 4.94 (s, 1H), 2.79 (dd, *J* = 13.9, 7.1 Hz, 1H), 2.59 (s, 1H), 1.42 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.90, 140.21, 129.05, 128.07, 126.35, 70.25, 52.63, 50.20, 28.29. HRMS (EI): calcd for $C_{14}H_{19}Cl_2NO_2$ 303.0793, found 303.0796.

5. Mechanistic Investigations.

According to the general procedure, $Fe(OTf)_2$ (0.02 mmol, 10 mol%) were placed in a flame-dried 25 mL sealed tube in glovebox, After DCM (6 mL) was added via a syringe, followed by the addition of DTBP (73.6 ul, 0.4 mmol, 2.0 equiv.) , $TMSN_3$(34.0 ul, 0.26mmol, 1.3 eq.) and (1-cyclopropylvinyl)benzene (0.2 mmol, 1.0 eq). and the mixture was stirred 24h at 110 ^{o}C. After 24 h the reaction mixture was cooled down to room temperature, after evaporation in vacuo, purification by column chromatography on silica gel to afford the product.



4-(2,2-Dichloroethyl)-1,2-dihydronaphthalene： ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (m, *J* = 7.6, 5.7, 3.3 Hz, 1H), 7.19 – 7.16 (m, 2H), 7.14 (d, *J* = 7.6 Hz, 1H), 6.06 (t, *J* = 4.6 Hz, 1H), 5.85 (t, *J* = 6.6 Hz, 1H), 3.34 (dd, *J* = 6.6, 1.0 Hz, 2H), 2.81 – 2.73 (m, 2H), 2.34 – 2.26 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 136.84, 133.26 , 131.02 , 130.61 , 128.08 , 127.28 , 126.60 , 121.87 , 71.63 , 47.42 , 27.99 , 23.09 . HRMS (EI): calcd for $C_{12}H_{12}Cl_2$ 226.0316, found 226.0319.



(Z)-(6-Azido-1,1-dichlorohex-3-en-3-yl)benzene： ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.33 (d, *J* = 6.9 Hz, 3H) , 5.87 (t, *J* = 7.2 Hz, 1H), 5.57 (t, *J* = 6.8 Hz, 1H), 3.67 (t, *J* = 6.8 Hz, 2H), 3.47 (d, *J* = 6.8 Hz, 2H), 2.80 (q, *J* = 7.1 Hz, 2H).^{13}C

NMR (150 MHz, $CDCl_3$) δ 140.48, 137.21, 129.17, 128.74 , 127.83, 126.66, 71.29, 44.29, 43.79, 32.09 . HRMS (EI): calcd for $C_{11}H_{13}Cl_2N_3$ 269.0487, found 269.0490.

6 References

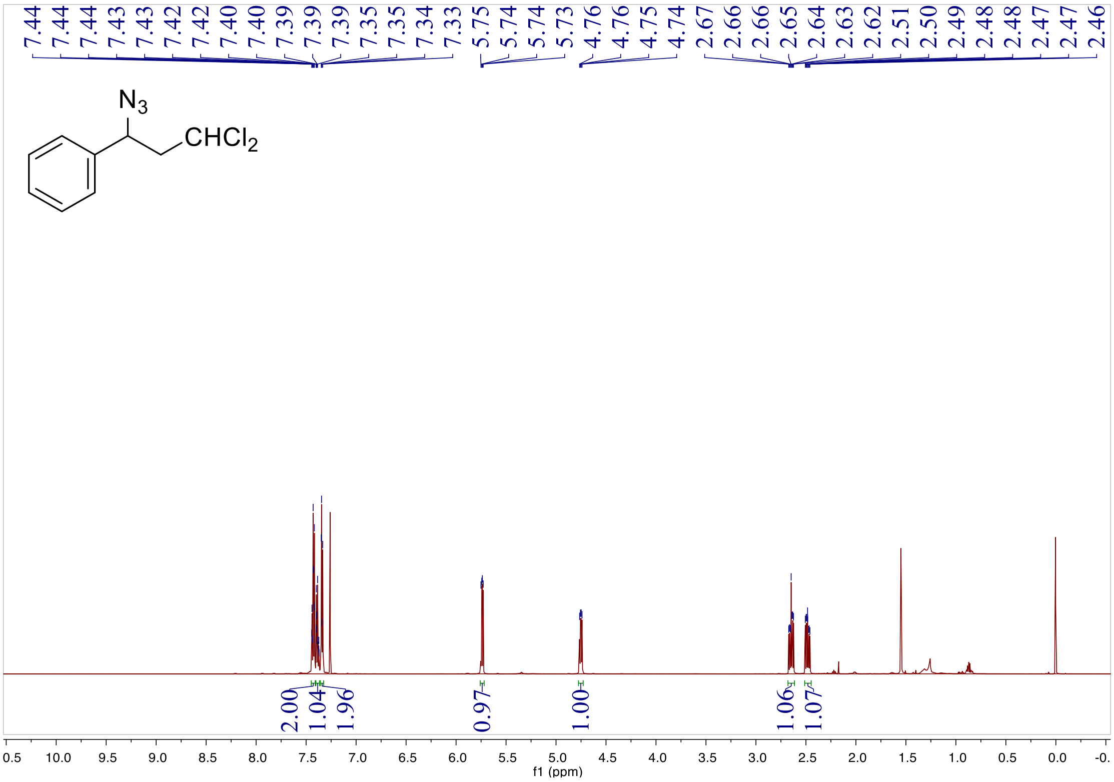
1. Lu, D.-F.; Zhu, C.-L.; Jia, Z.-X.; Xu, H., *J. Am. Chem. Soc.* **2014,** *136* (38), 13186-13189.

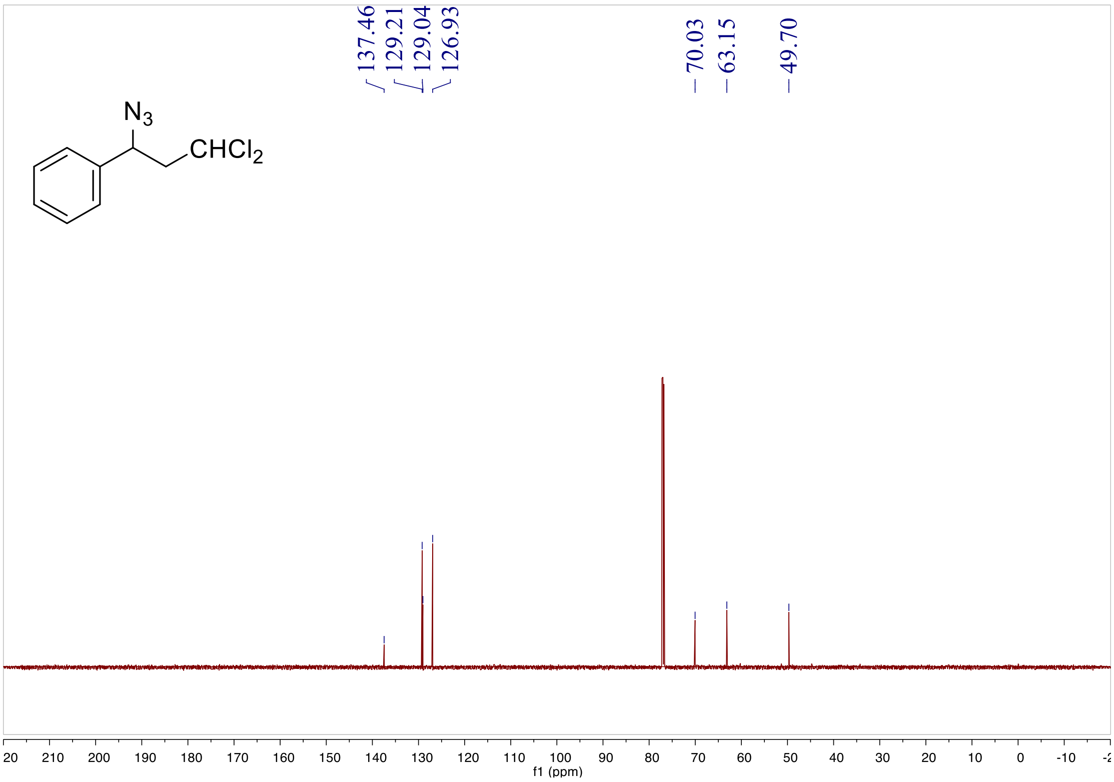
2. Zhou, H.; Jian, W.; Qian, B.; Ye, C.; Li, D.; Zhou, J.; Bao, H., *Org. lett.* **2017,** *19* (22), 6120-6123.

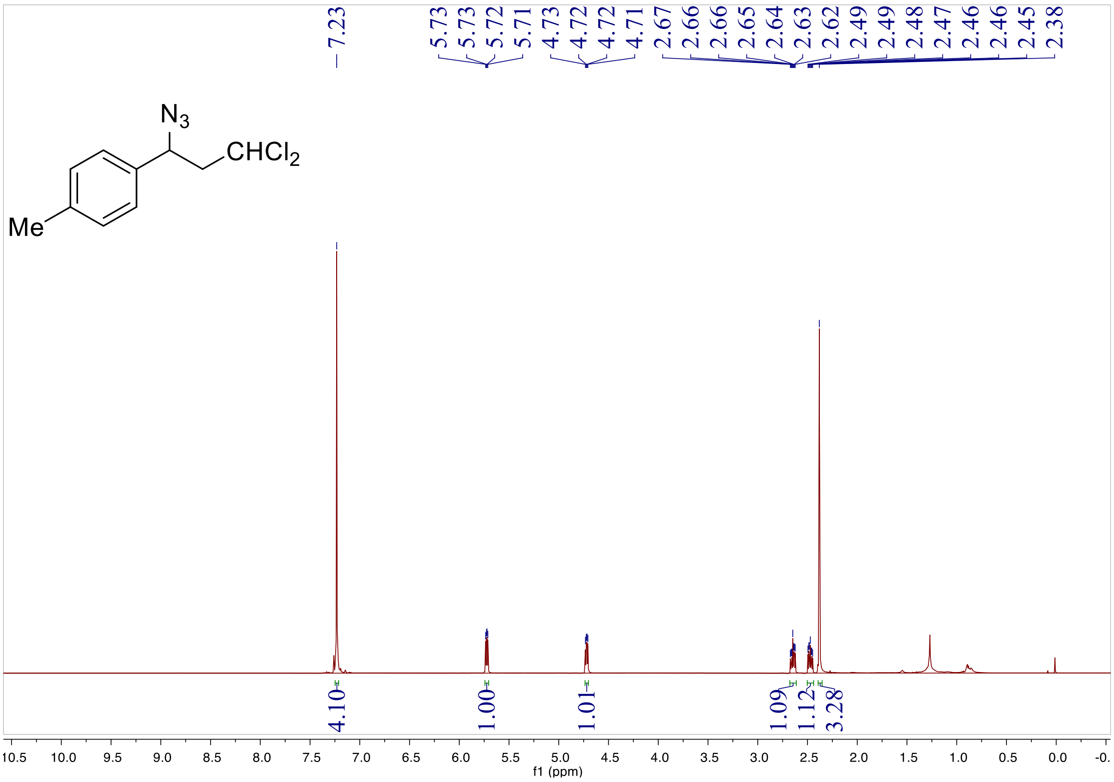
3. Song, L., Metal-catalyzed electrochemical diazidation of alkenes. *Science* **2017,** *357*.

4. Shen, S.-J.; Zhu, C.-L.; Lu, D.-F.; Xu, H., Iron-Catalyzed Direct Olefin Diazidation via Peroxyester Activation Promoted by Nitrogen-Based Ligands. *ACS Catal.* **2018,** *8* (5), 4473-4482.

7. Spectral Data.



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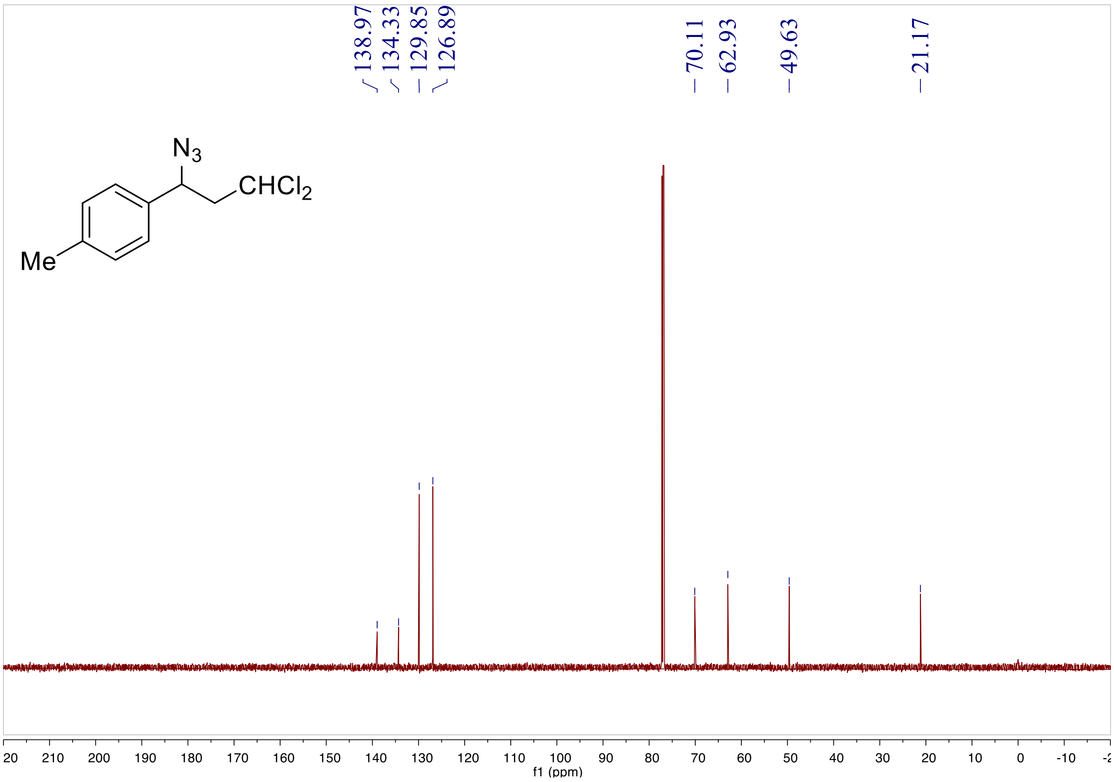
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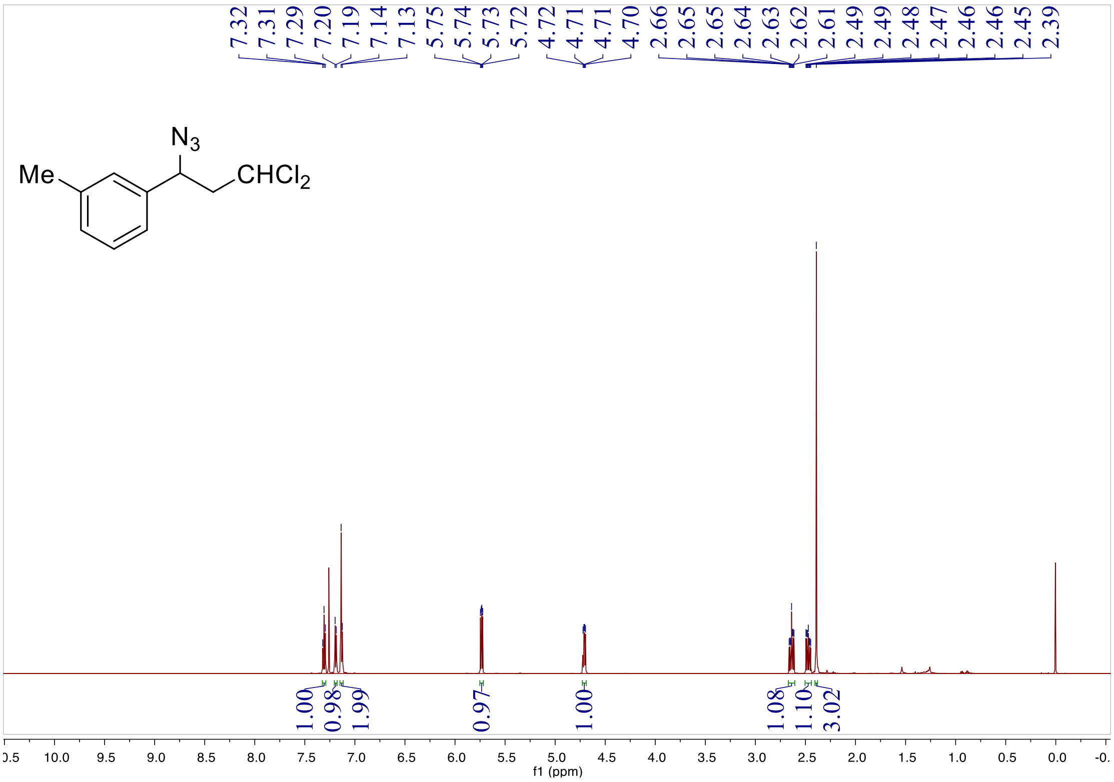
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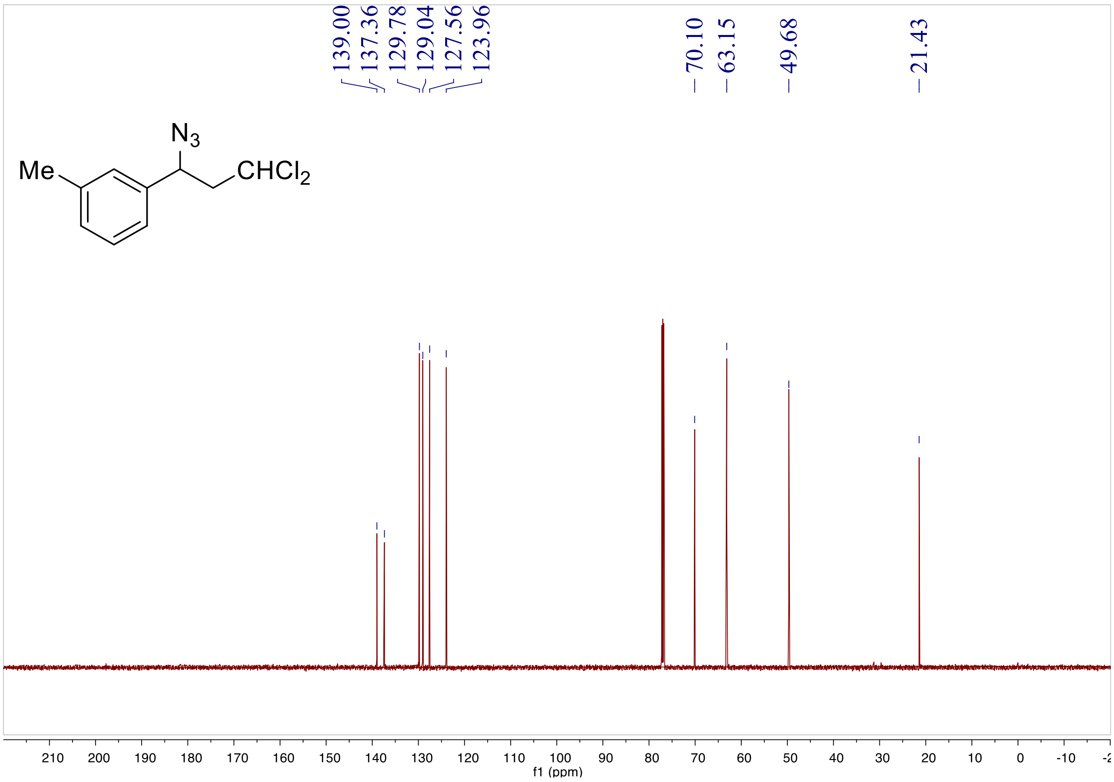
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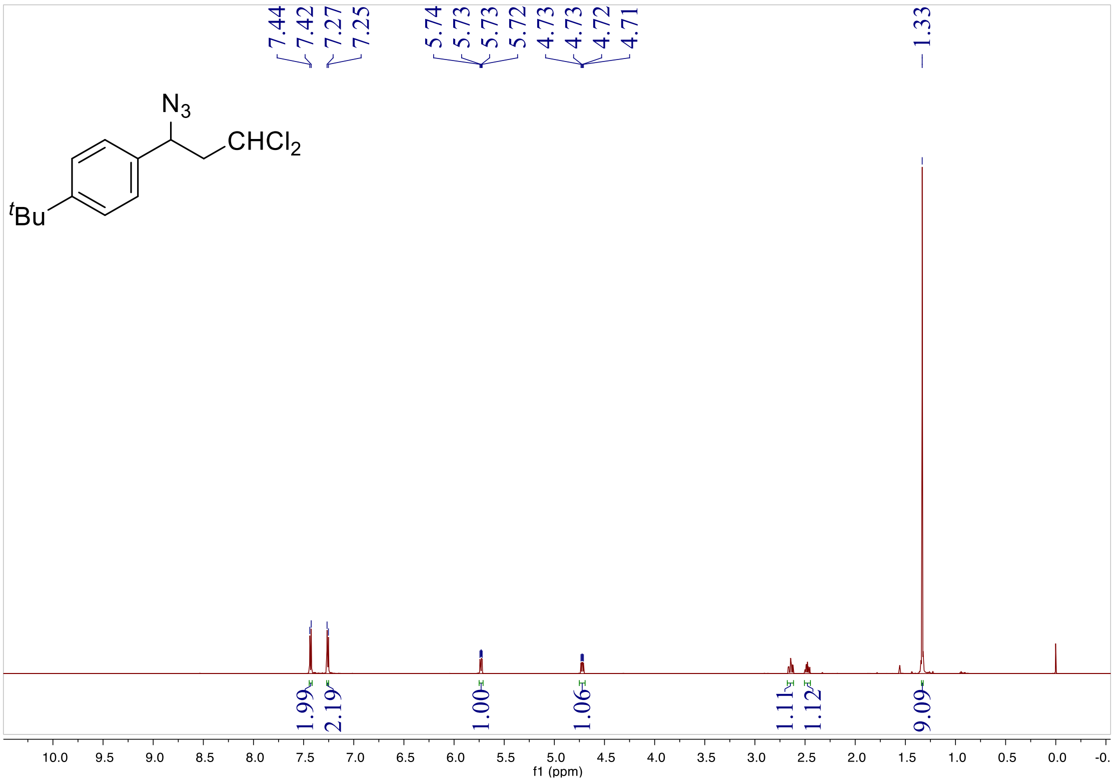
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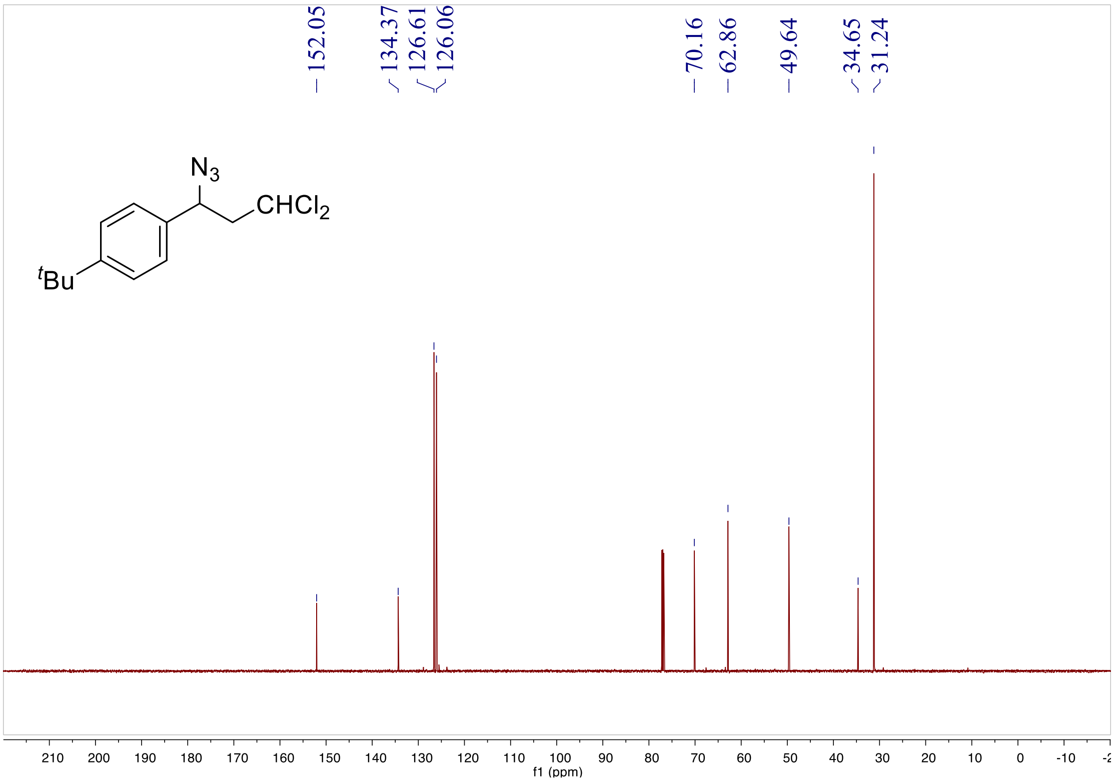
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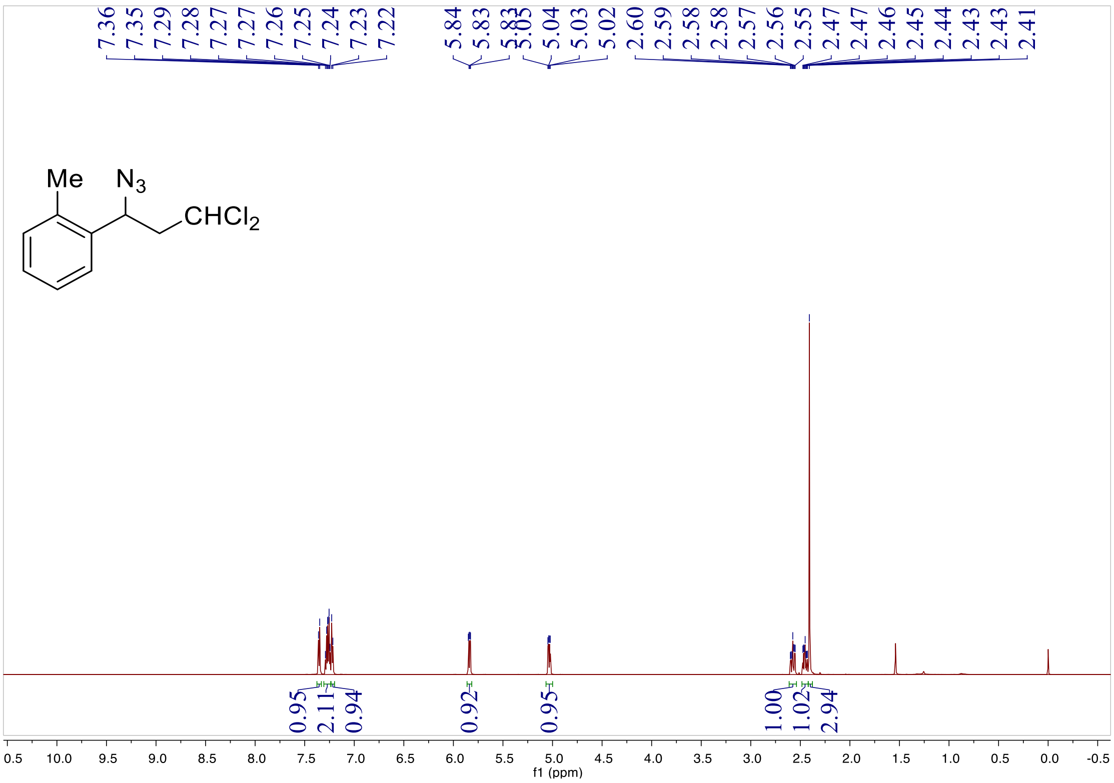
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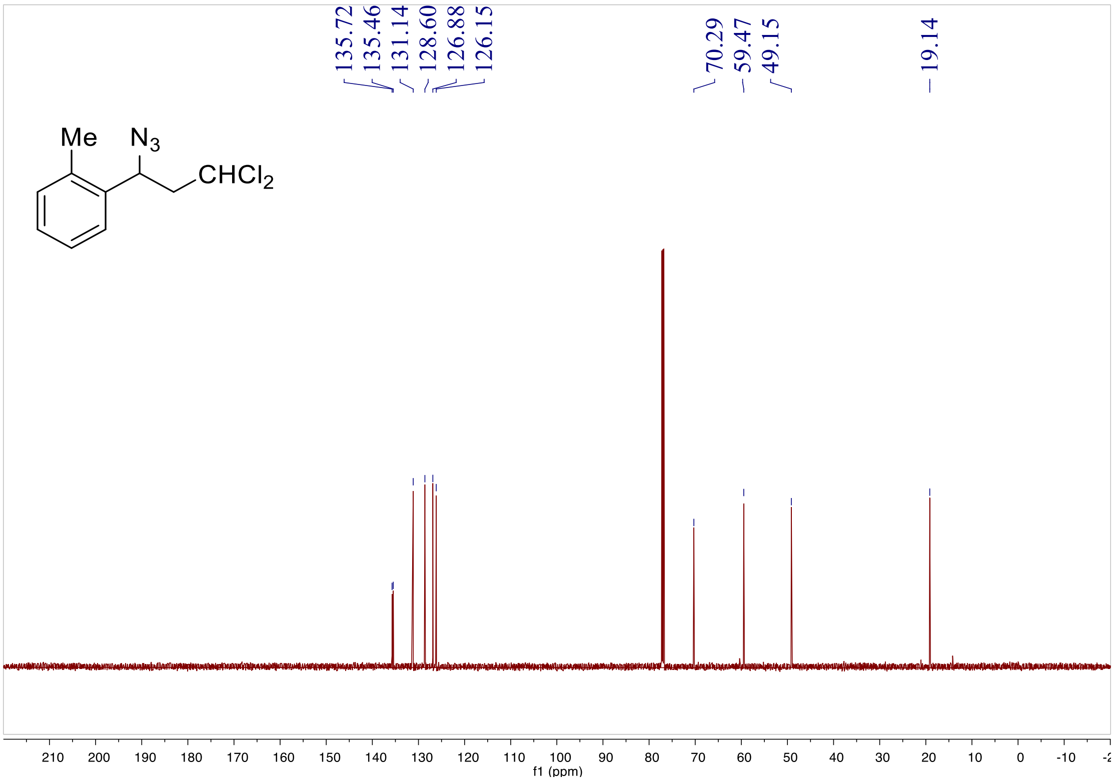
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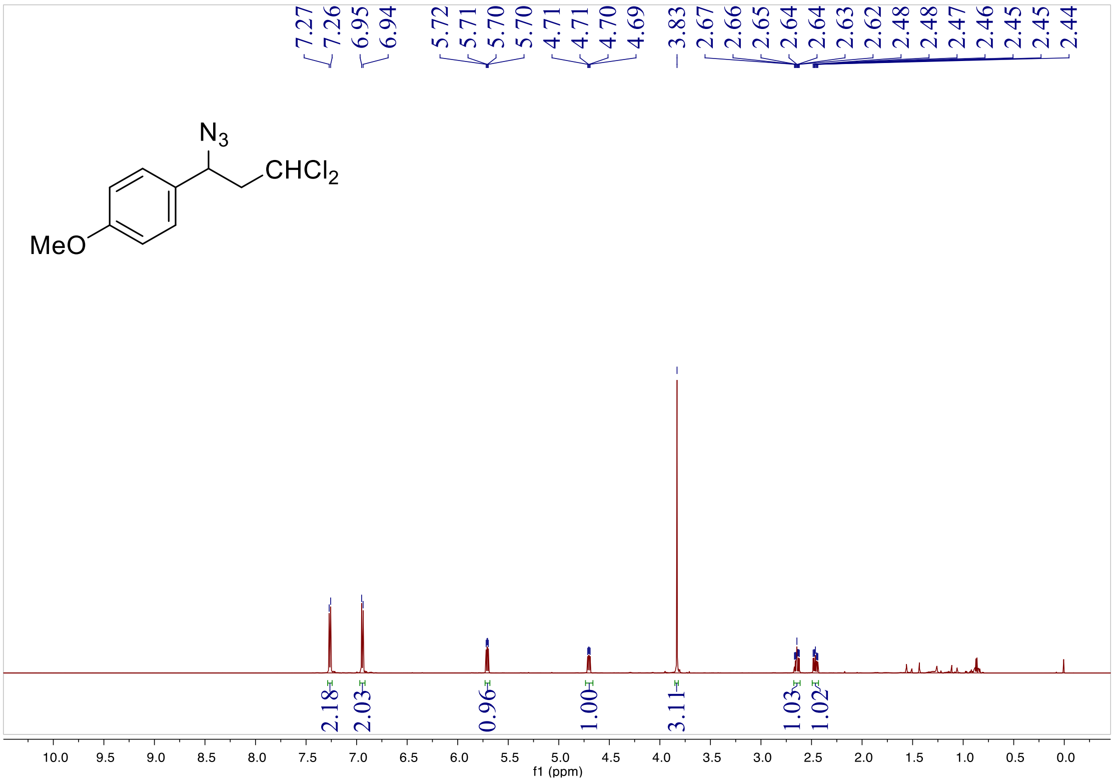
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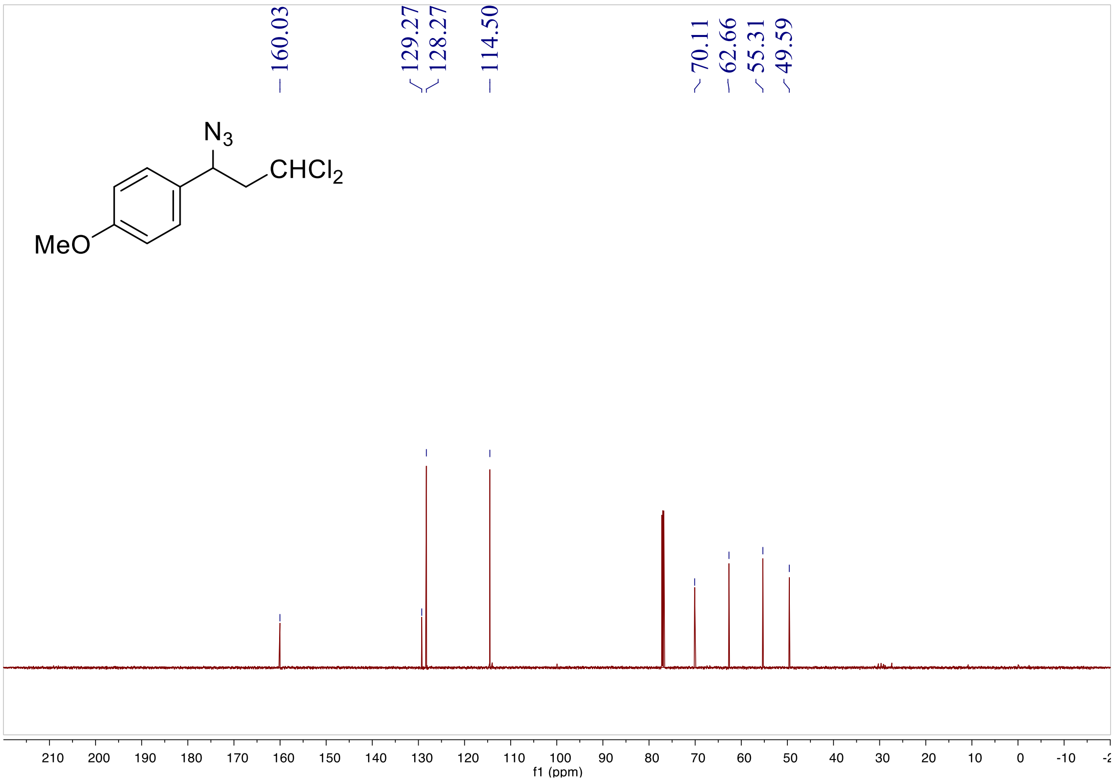
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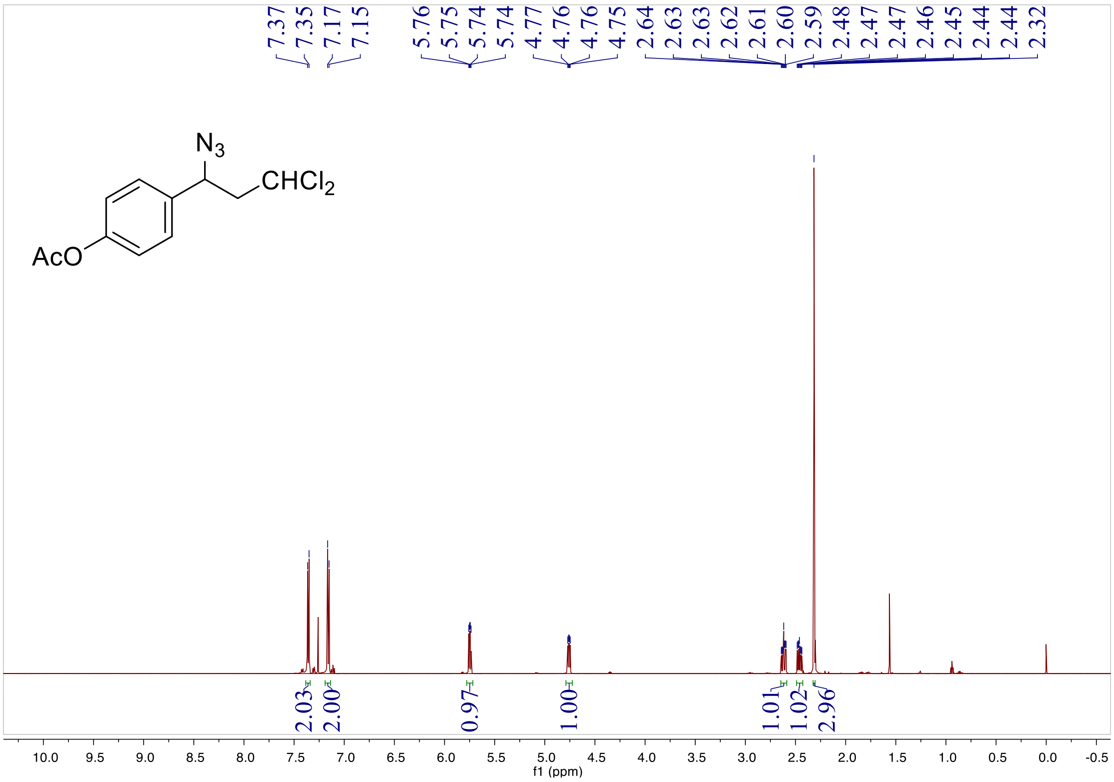
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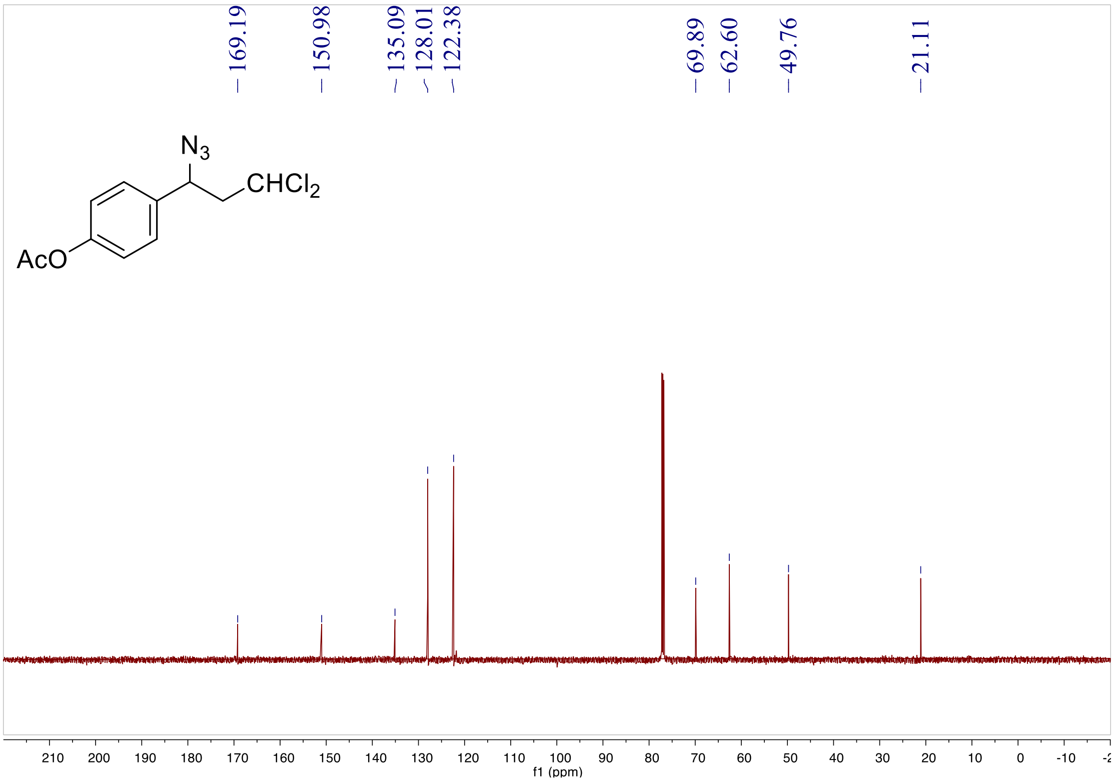
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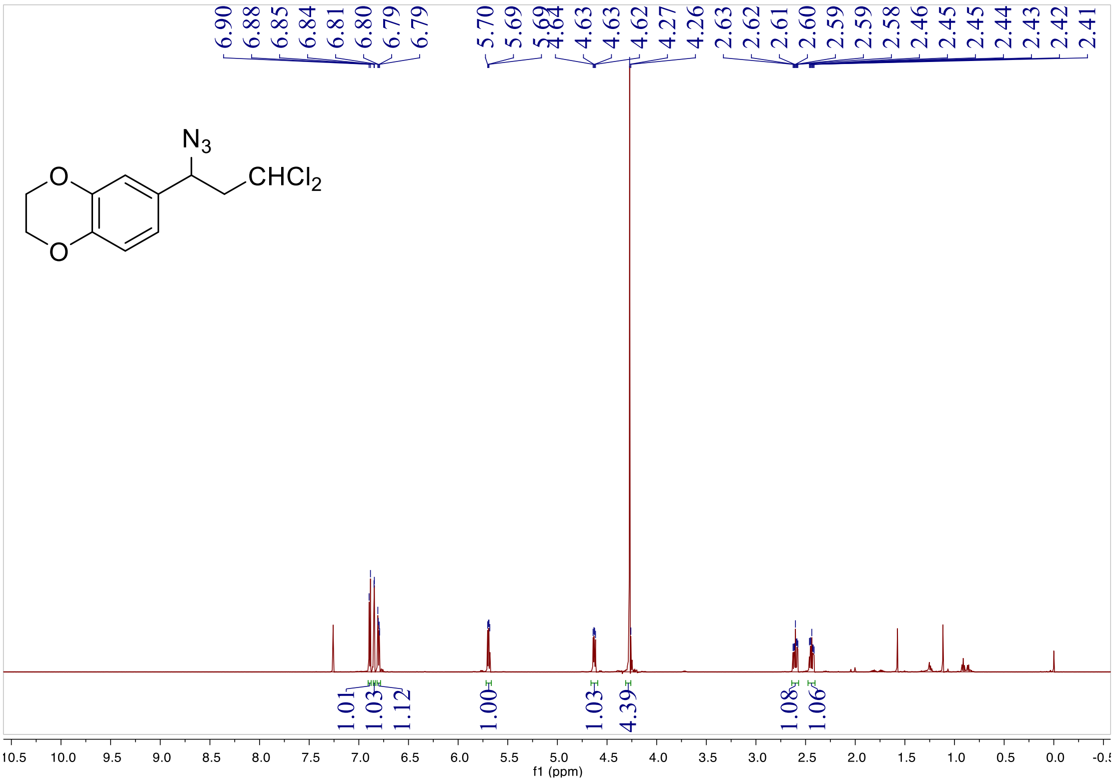
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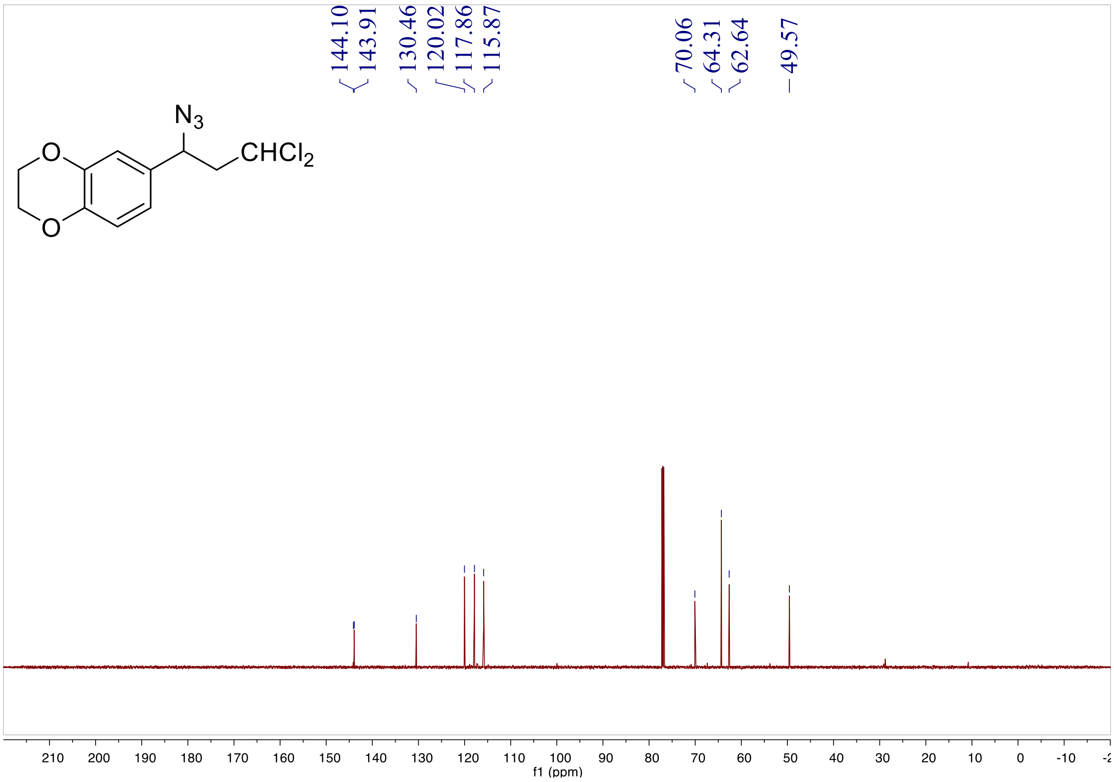
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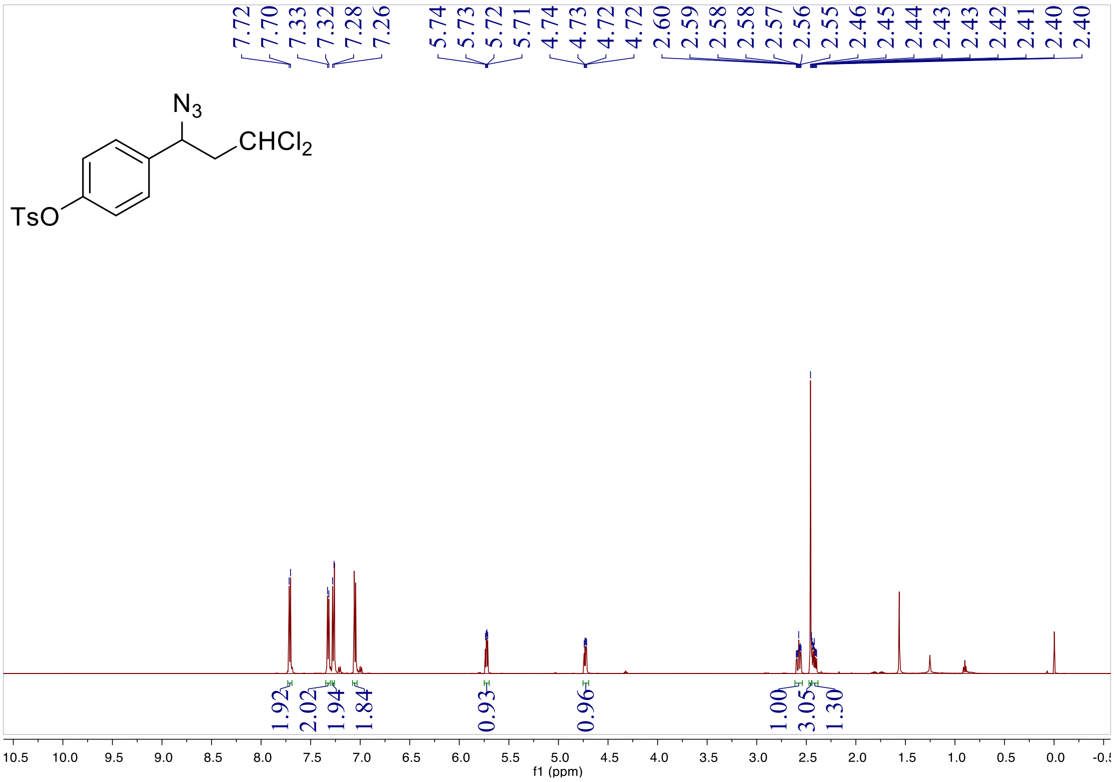

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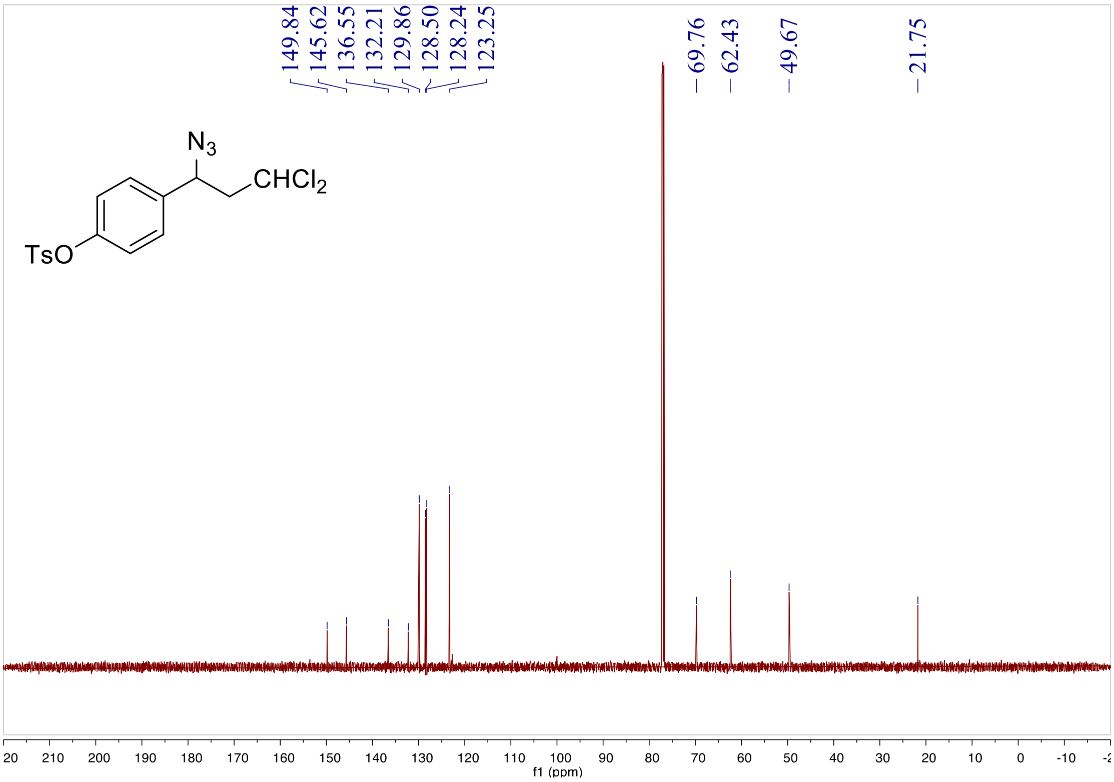

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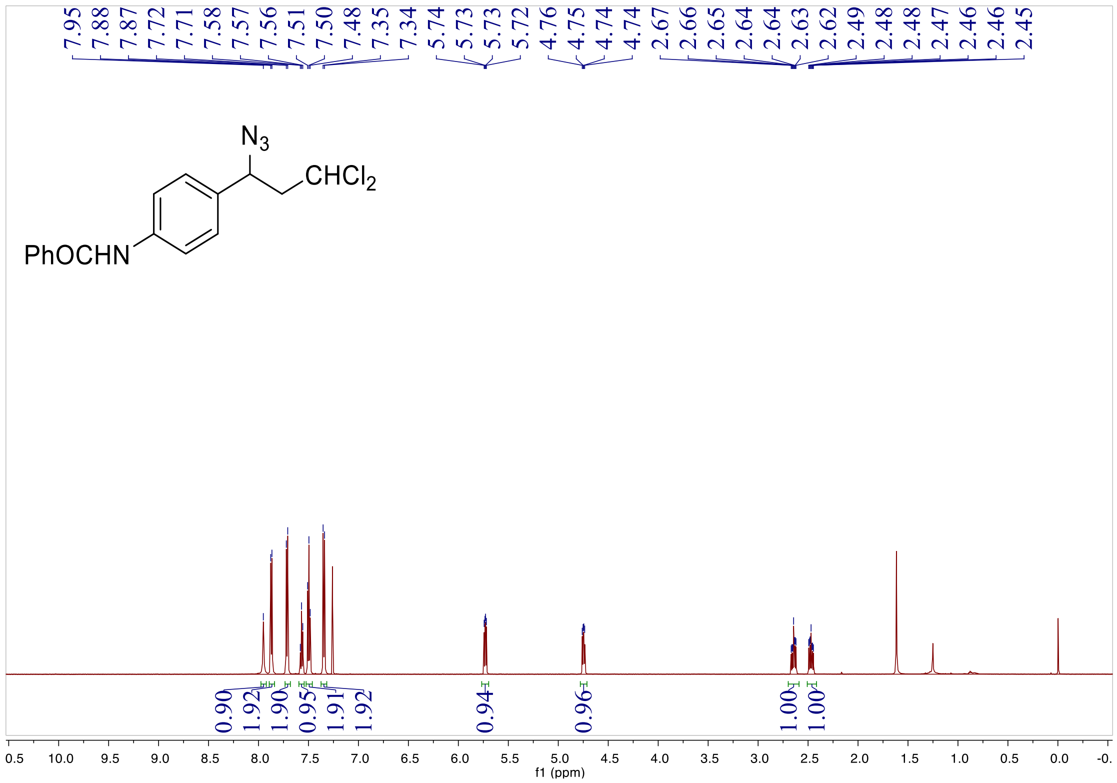
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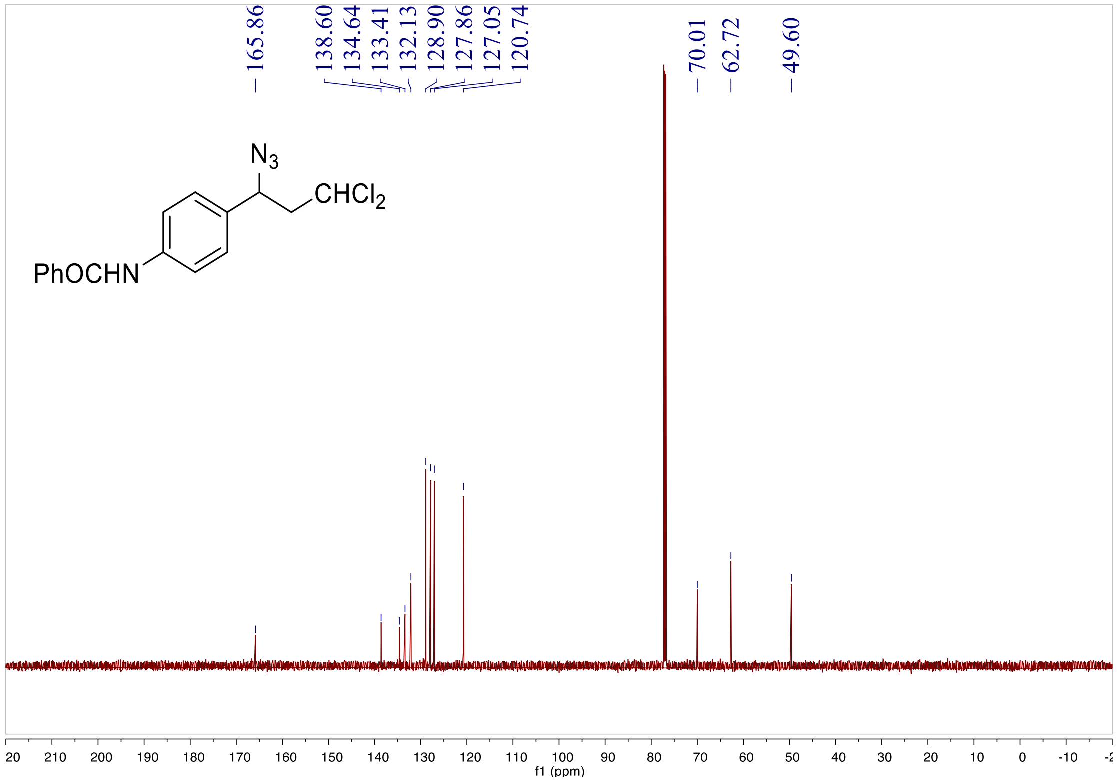
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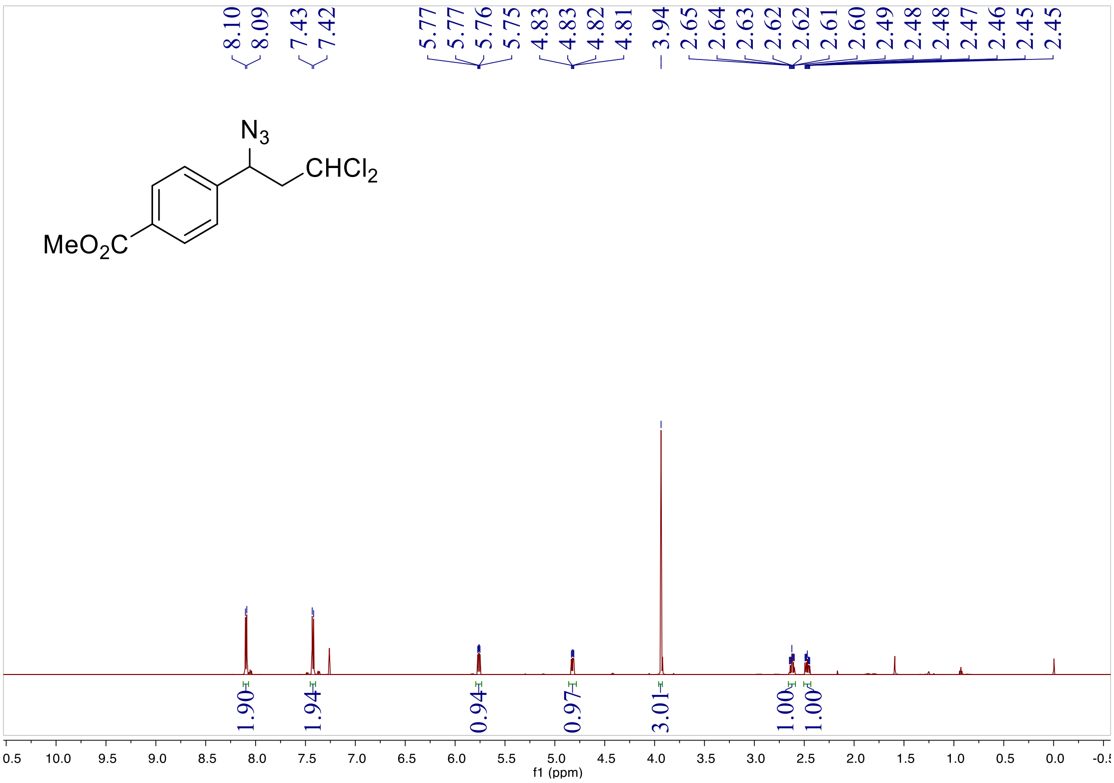
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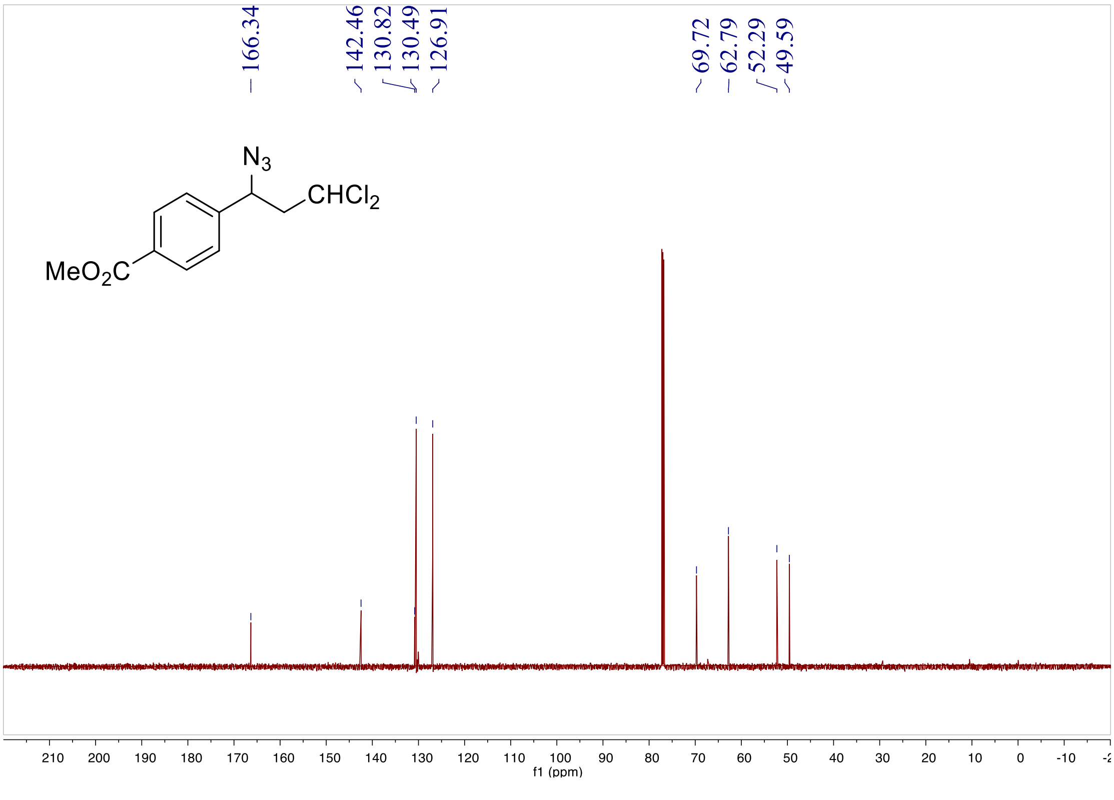
0.0
f1 (ppm)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69.72
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52.29
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N3
CHCl2
MeO2C
210
200
190
180
170
160
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120
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100
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80
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40
30
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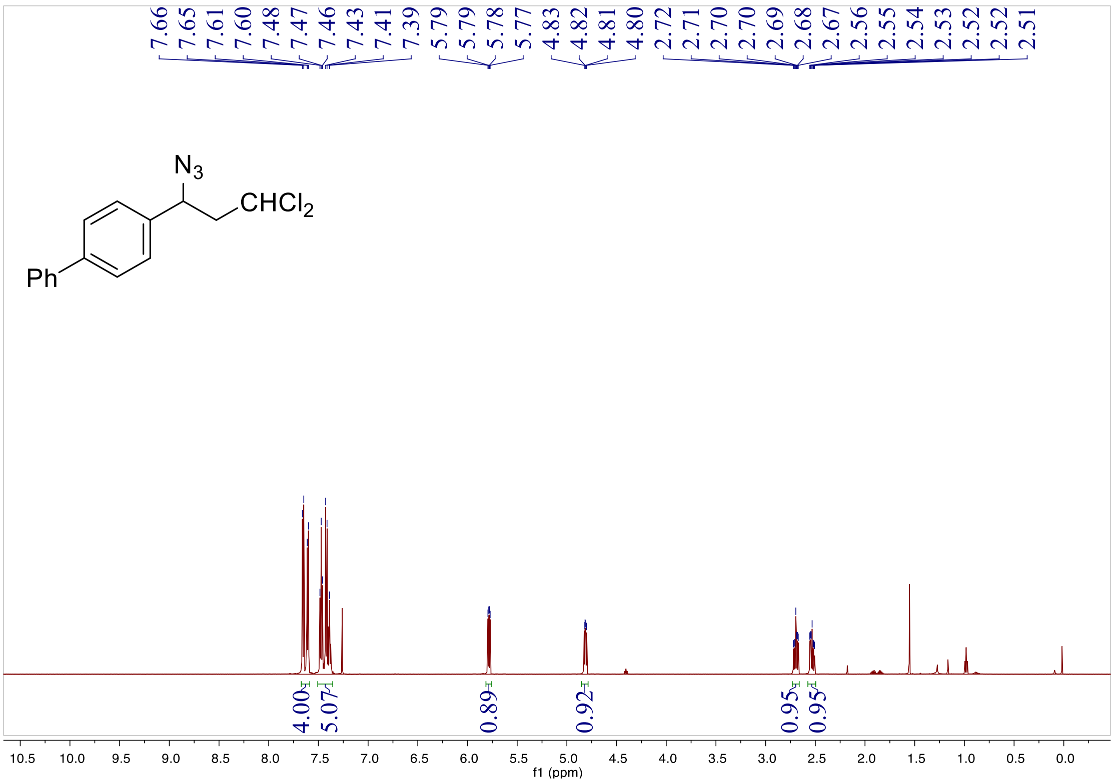
-10
f1 (ppm)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5.78
5.77
4.83
4.82
4.81
4.80
2.72
2.71
2.70
2.70
2.69
2.68
2.67
2.56
2.55
2.54
2.53
2.52
2.52
2.51
N3
CHCl2
Ph
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0.95
0.95
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9.0
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8.0
7.5
7.0
6.5
6.0
5.5
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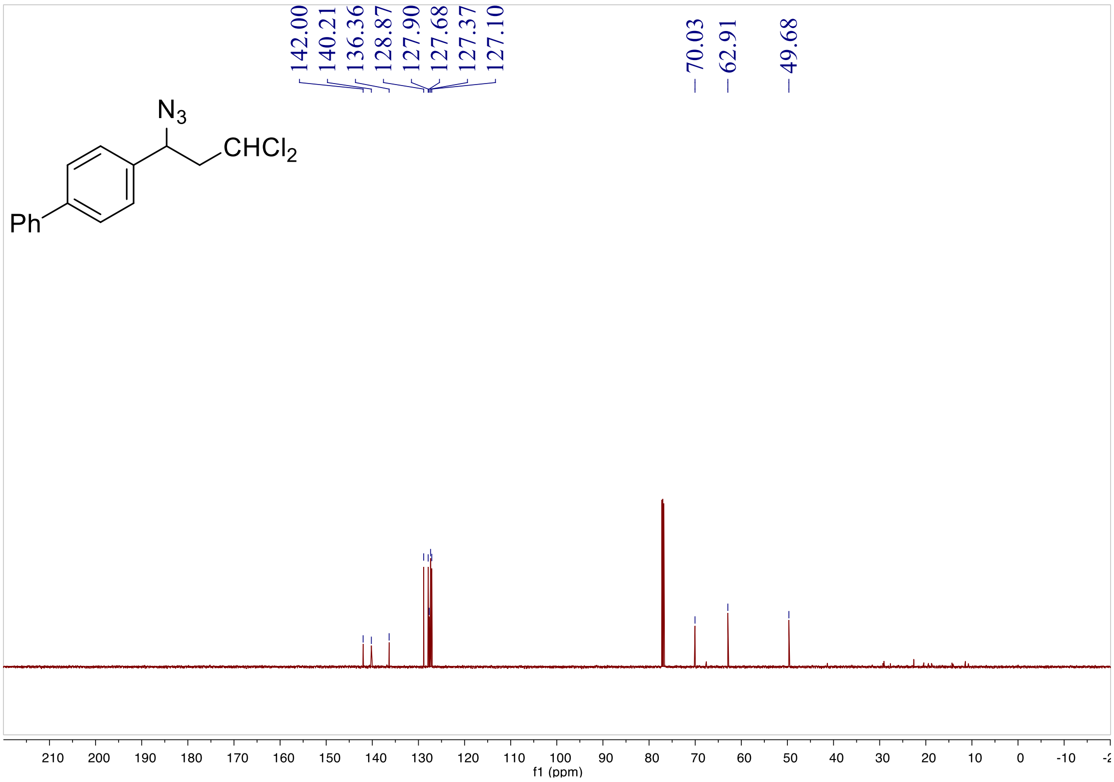
0.0
f1 (ppm)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N3
CHCl2
Ph
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200
190
180
170
160
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100
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80
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30
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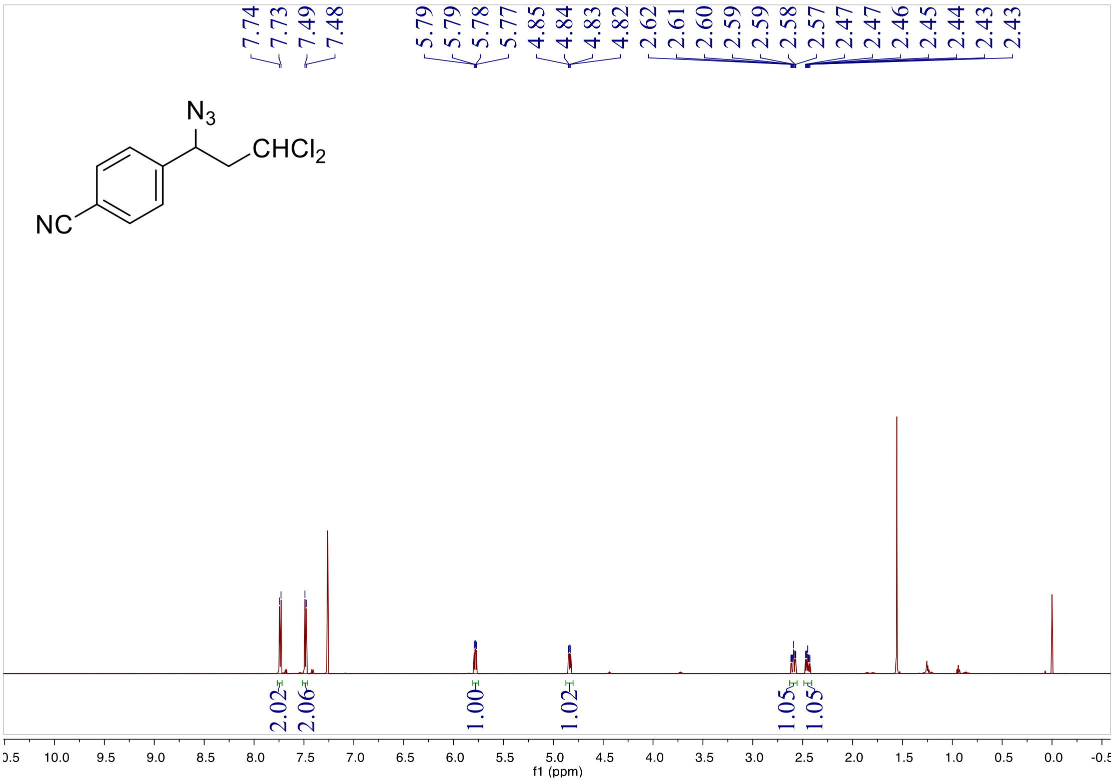
-10
f1 (ppm)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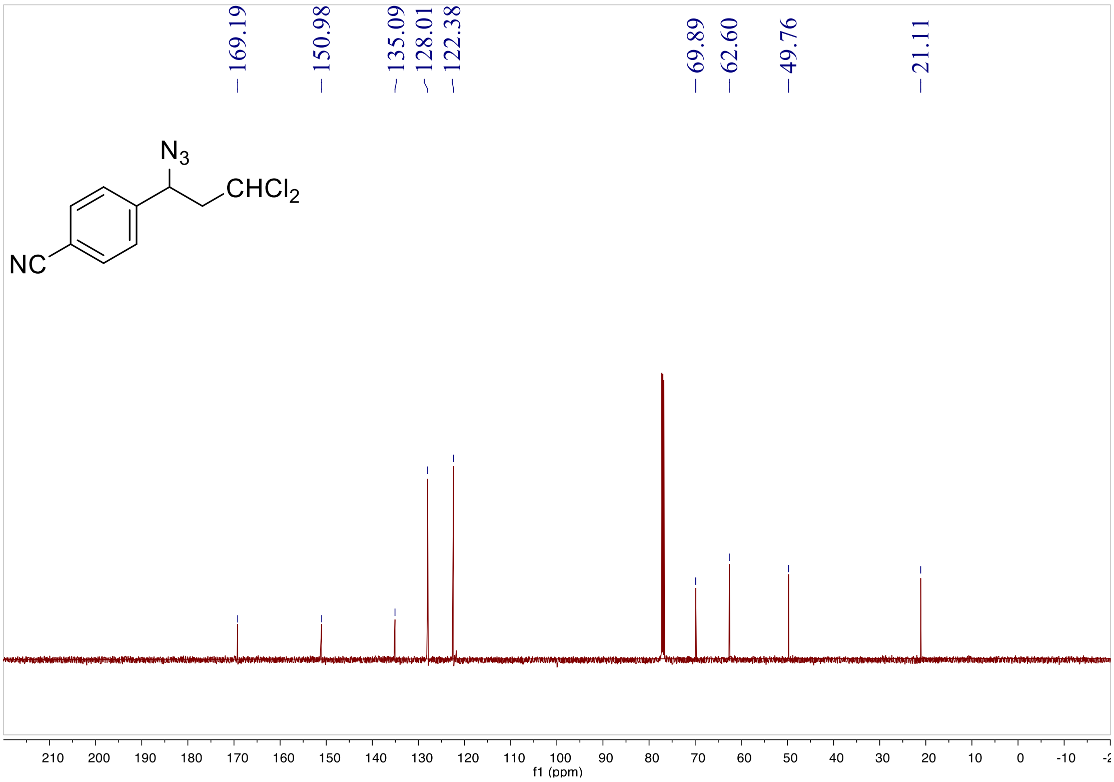
4.83
4.82
2.62
2.61
2.60
2.59
2.59
2.58
2.57
2.47
2.47
2.46
2.45
2.44
2.43
2.43
N3
CHCl2
NC
2.02
2.06
1.00
1.02
1.05
1.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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21.11
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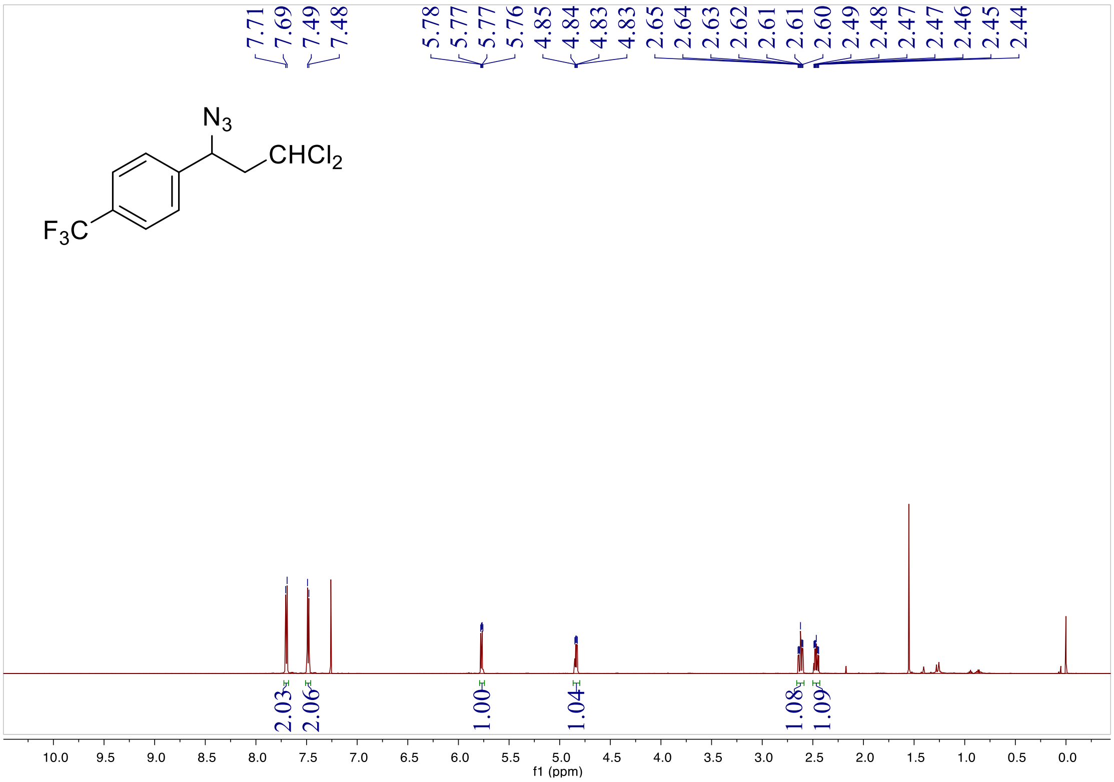
CHCl2
NC
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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4.84
4.83
4.83
2.65
2.64
2.63
2.62
2.61
2.61
2.60
2.49
2.48
2.47
2.47
2.46
2.45
2.44
N3
CHCl2
F3C
2.03
2.06
1.00
1.04
1.08
1.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
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1.0
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0.0
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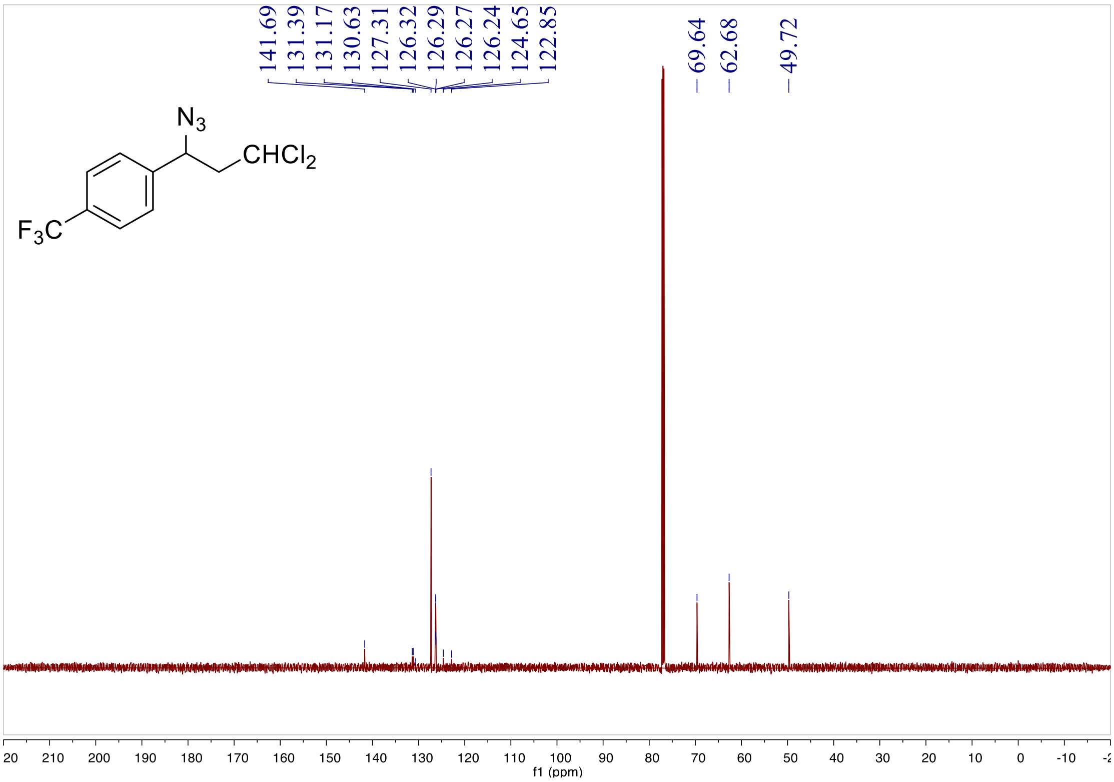
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122.85
69.64
62.68
49.72
N3
CHCl2
F3C
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200
190
180
170
160
150
140
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120
110
100
90
80
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60
50
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30
20
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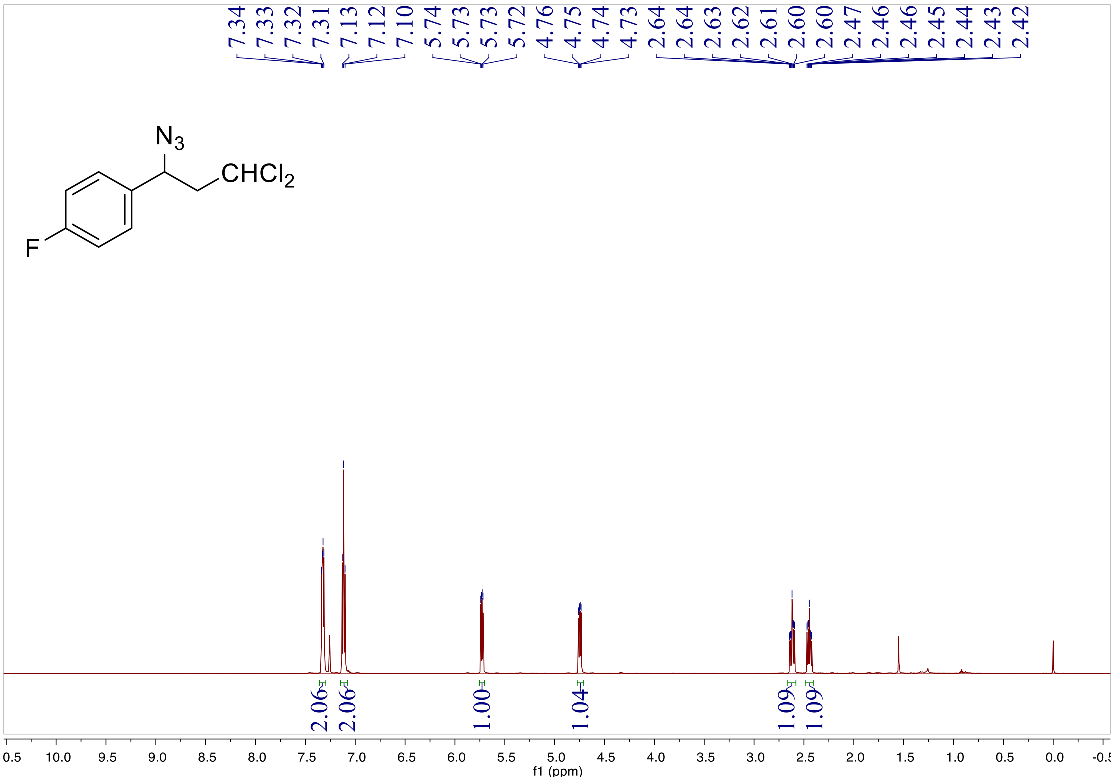
0
-10
f1 (ppm)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5.73
5.72
4.76
4.75
4.74
4.73
2.64
2.64
2.63
2.62
2.61
2.60
2.60
2.47
2.46
2.46
2.45
2.44
2.43
2.42
N3
CHCl2
F
2.06
2.06
1.00
1.04
1.09
1.09
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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3.0
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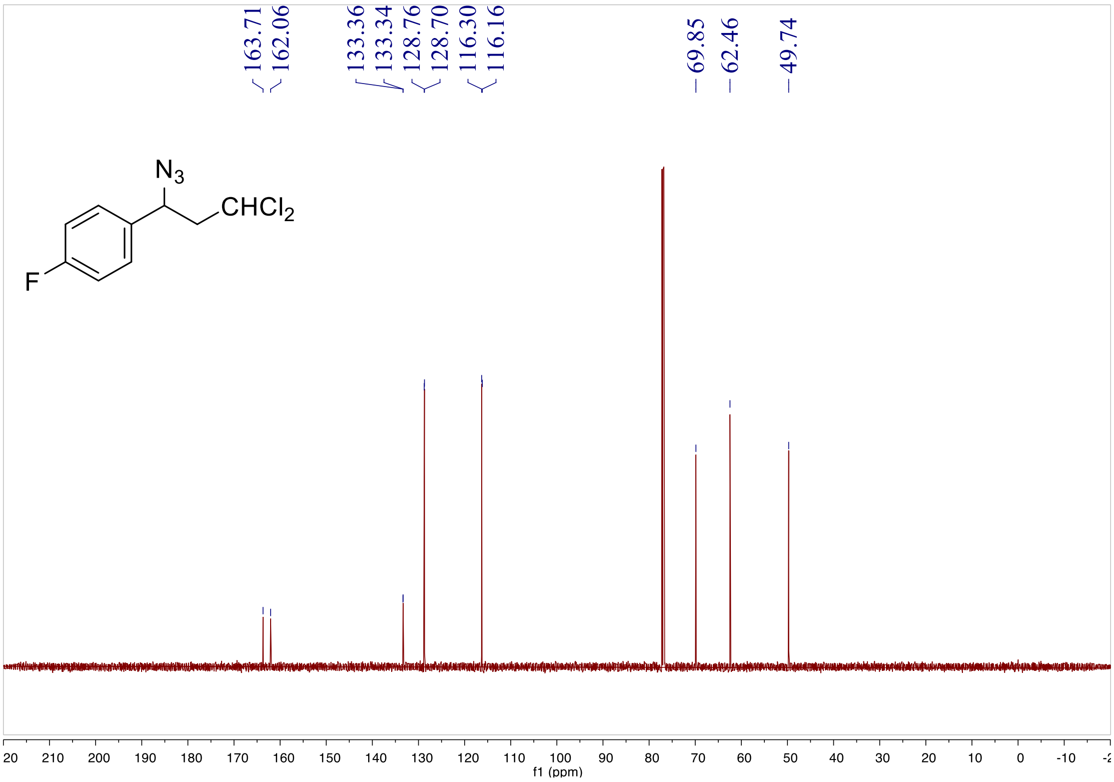
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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162.06
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128.70
116.30
116.16
69.85
62.46
49.74
N3
CHCl2
F
20
210
200
190
180
170
160
150
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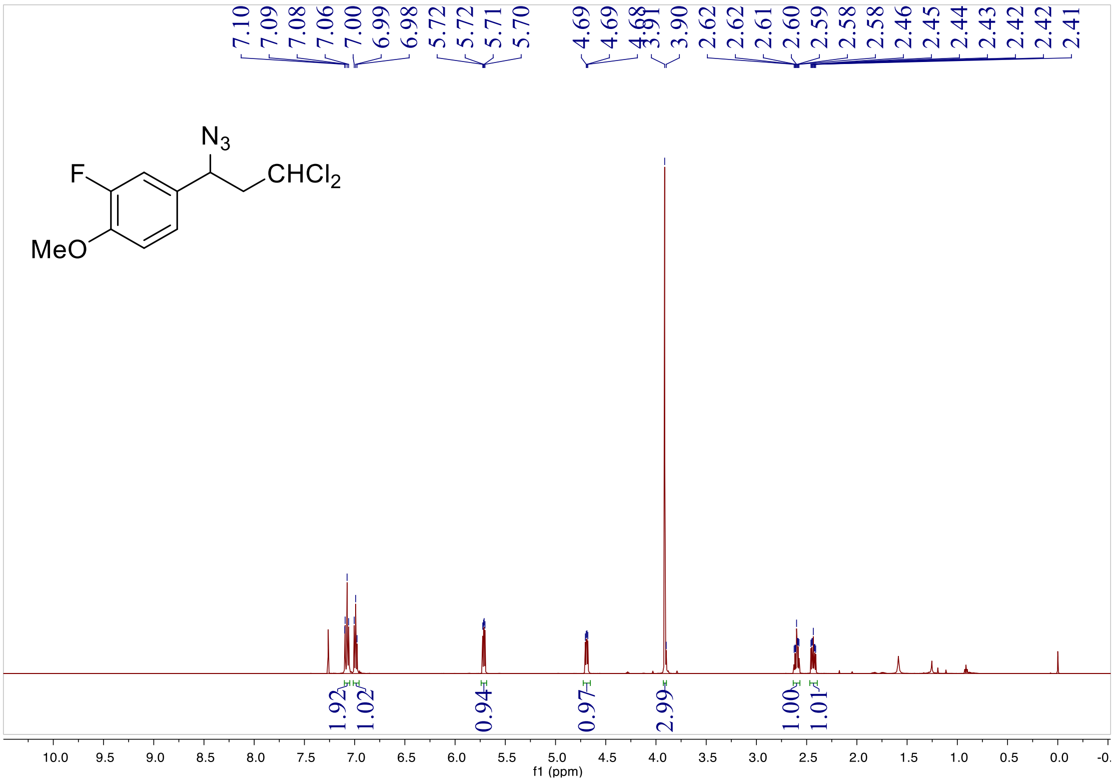
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)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5.71
5.70
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4.69
4.68
3.91
3.90
2.62
2.62
2.61
2.60
2.59
2.58
2.58
2.46
2.45
2.44
2.43
2.42
2.42
2.41
N3
F
CHCl2
MeO
1.92
1.02
0.94
0.97
2.99
1.00
1.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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3.0
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2.0
1.5
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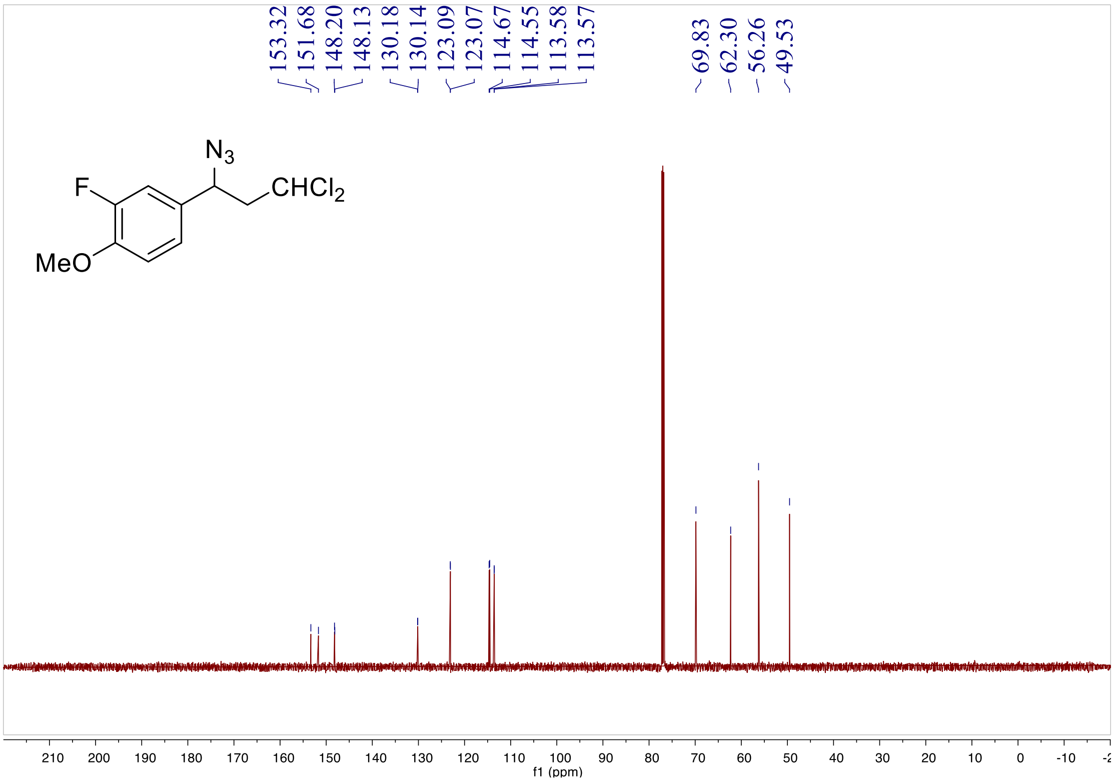
-0.
f1 (ppm)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123.07
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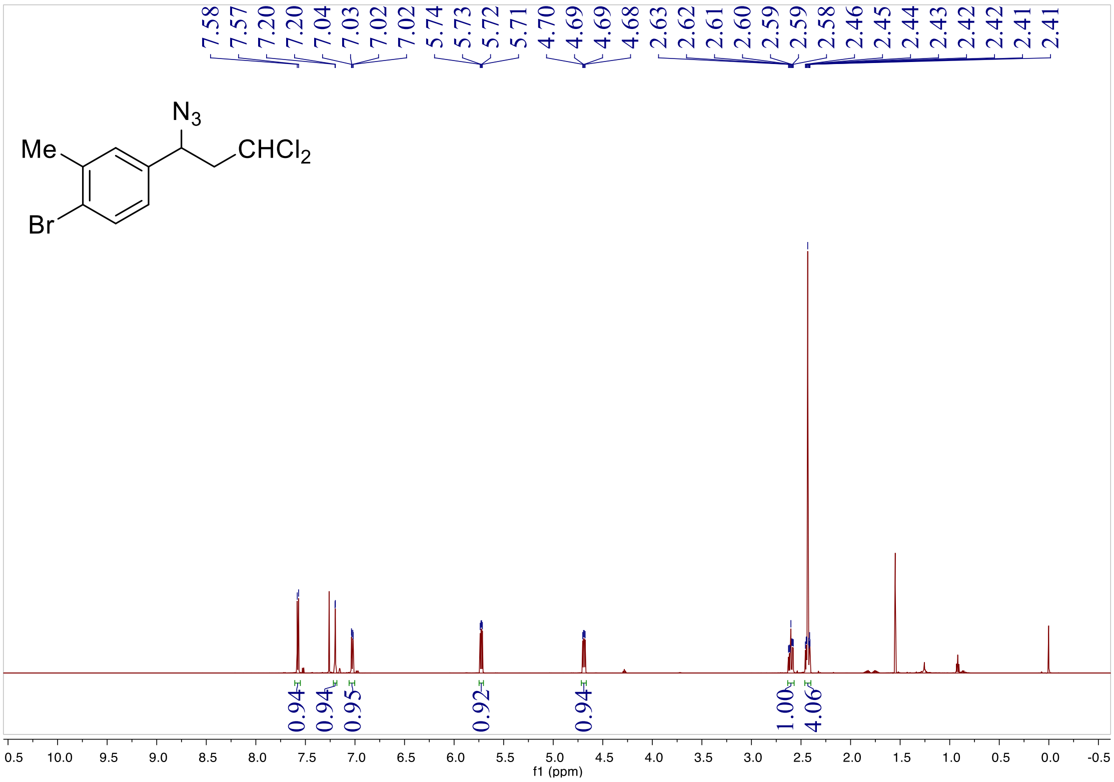
114.55
113.58
113.57
69.83
62.30
56.26
49.53
N3
F
CHCl2
MeO
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)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7.02
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4.69
4.68
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2.62
2.61
2.60
2.59
2.59
2.58
2.46
2.45
2.44
2.43
2.42
2.42
2.41
2.41
N3
Me
CHCl2
Br
0.94
0.94
0.95
0.92
0.94
1.00
4.06
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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2.0
1.5
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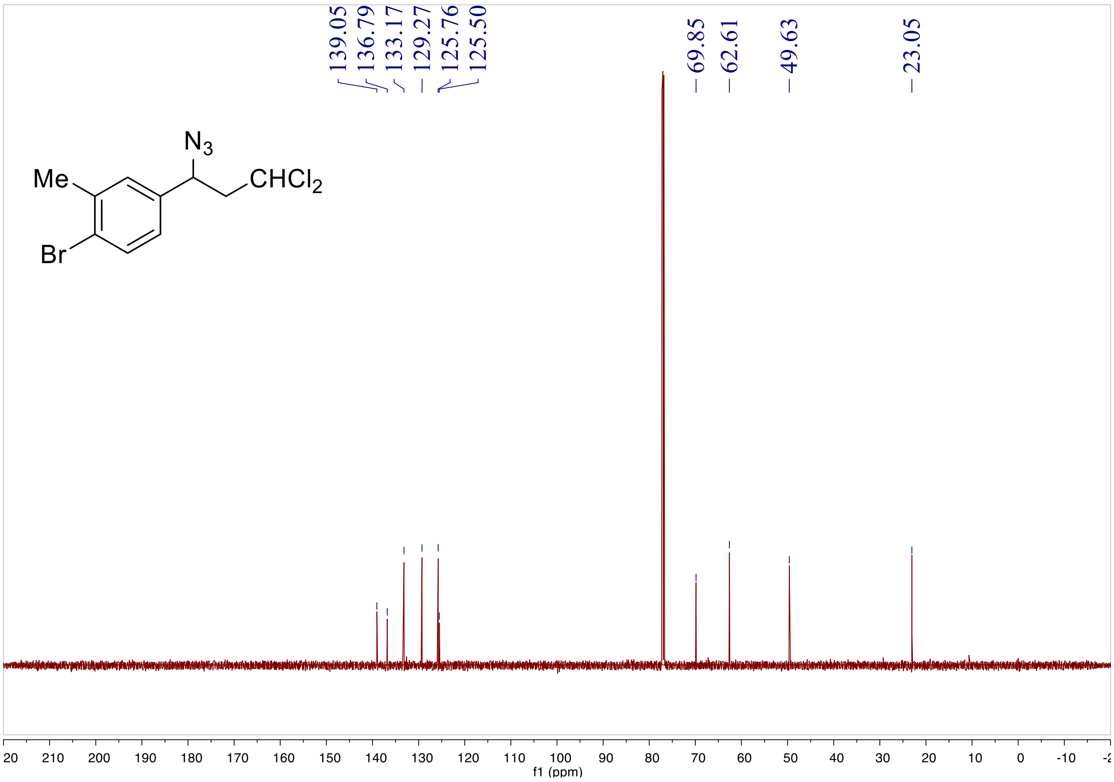
0.5
0.0
-0.5
f1 (ppm)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23.05
N3
Me
CHCl2
Br
20
210
200
190
180
170
160
150
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100
90
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60
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40
30
20
10
0
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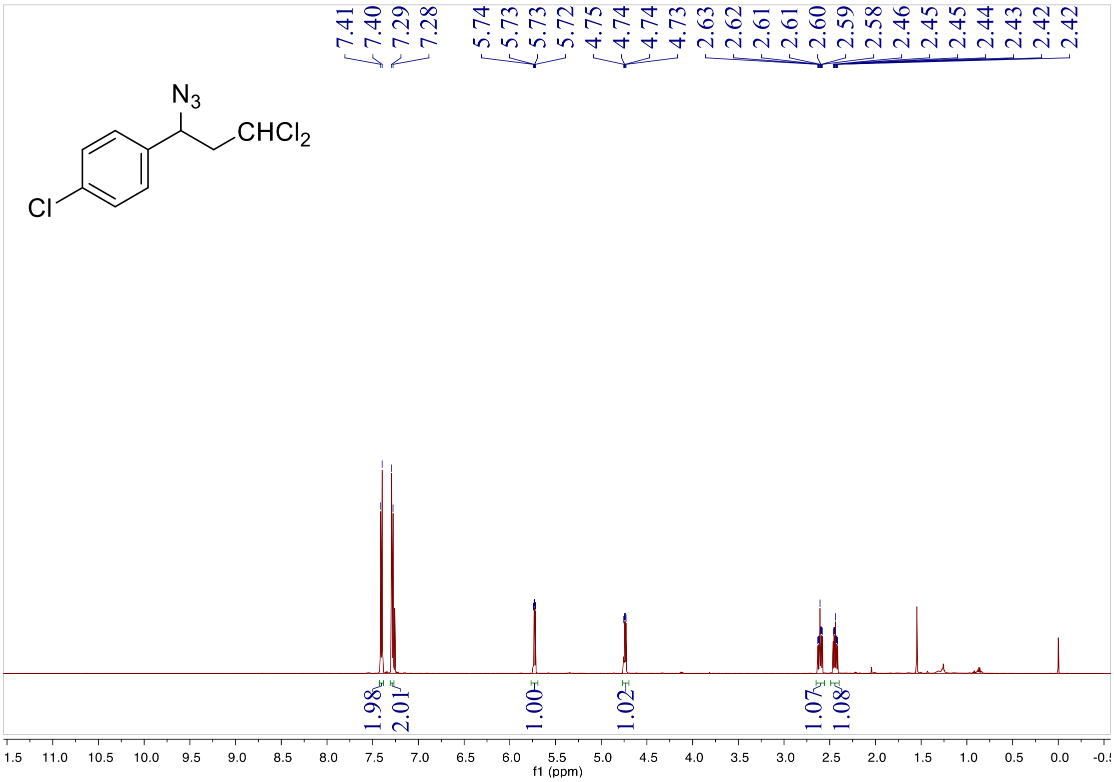
-2
f1 (ppm)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2.61
2.61
2.60
2.59
2.58
2.46
2.45
2.45
2.44
2.43
2.42
2.42
N3
CHCl2
Cl
1.98
2.01
1.00
1.02
1.07
1.08
1.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.0
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1.0
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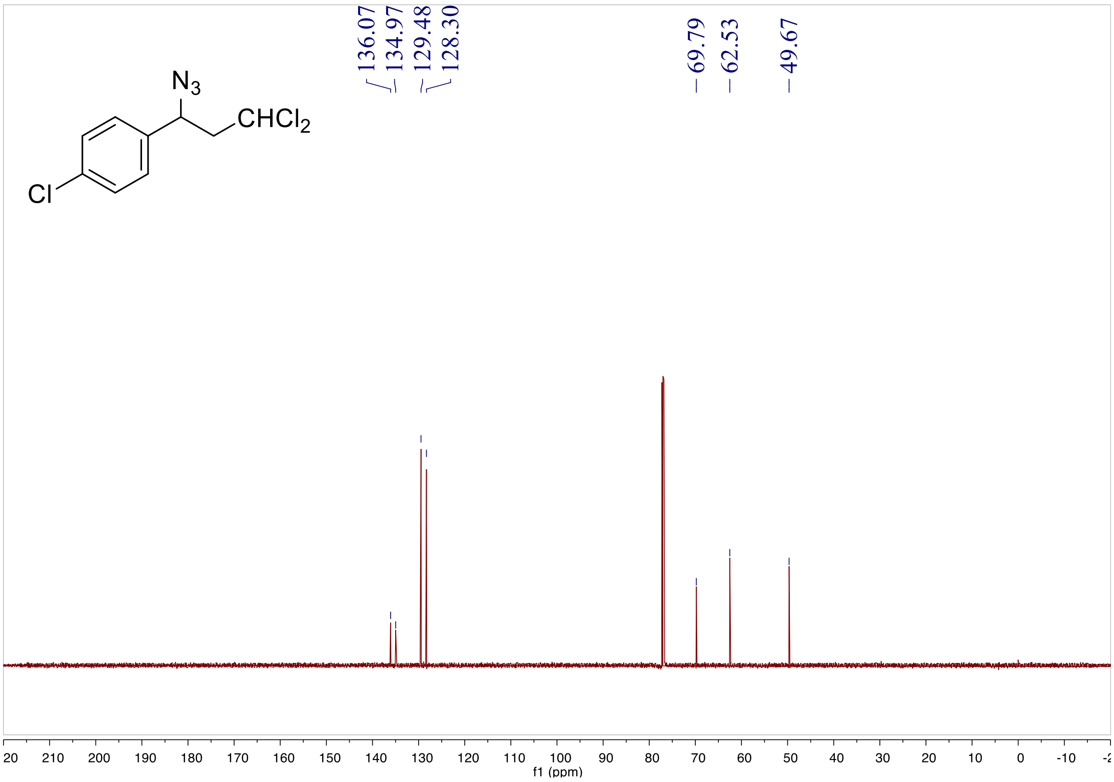
-0.
f1 (ppm)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Cl
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180
170
160
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90
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70
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50
40
30
20
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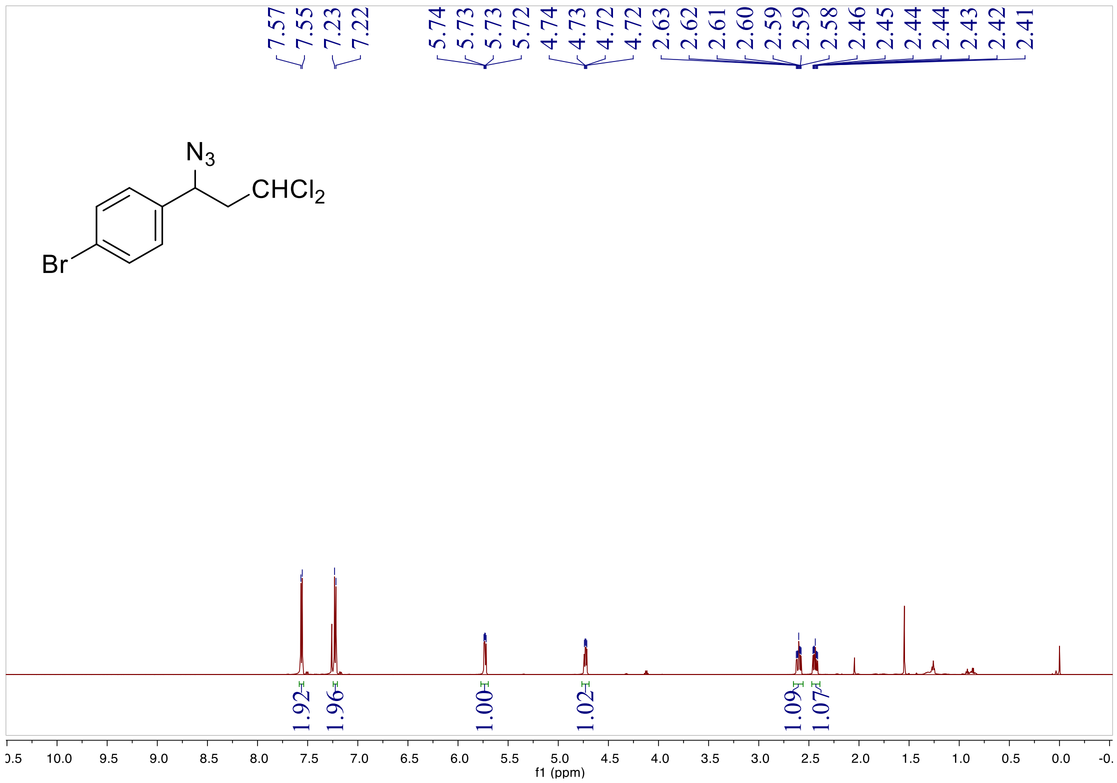
-10
-
f1 (ppm)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4.72
4.72
2.63
2.62
2.61
2.60
2.59
2.59
2.58
2.46
2.45
2.44
2.44
2.43
2.42
2.41
N3
CHCl2
Br
1.92
1.96
1.00
1.02
1.09
1.07
0.5
10.0
9.5
9.0
8.5
8.0
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7.0
6.5
6.0
5.5
5.0
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2.0
1.5
1.0
0.5
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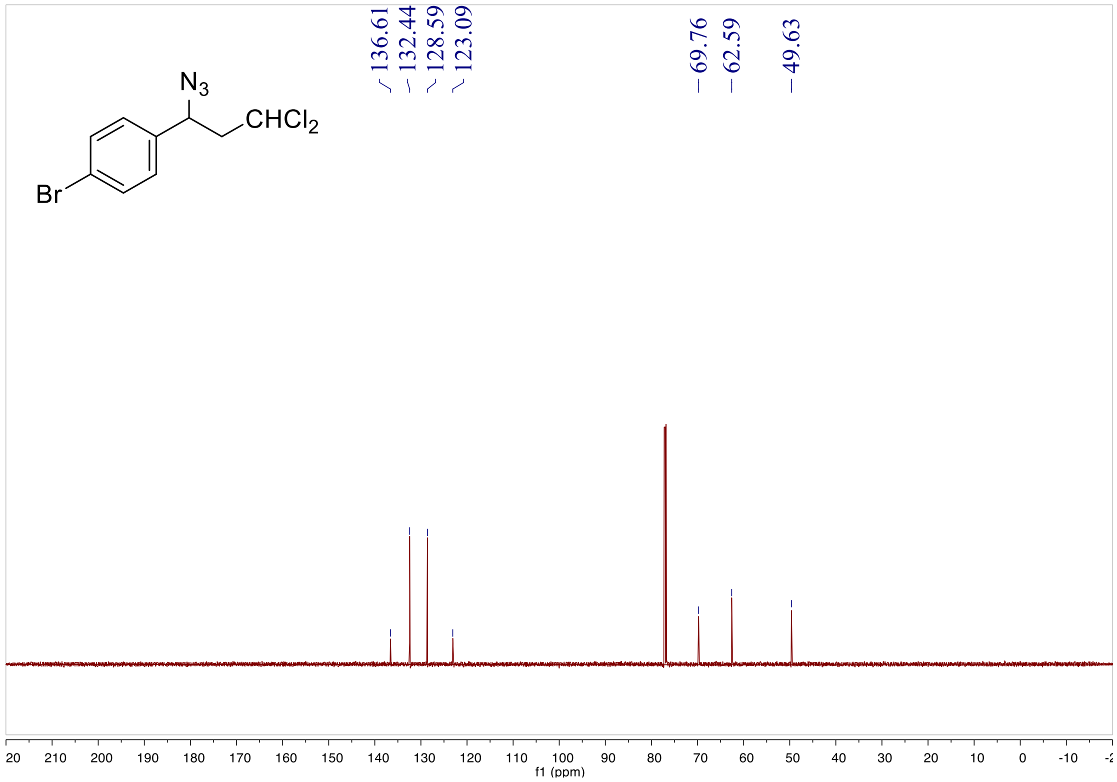
-0.
f1 (ppm)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N3
CHCl2
Br
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170
160
150
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100
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80
70
60
50
40
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20
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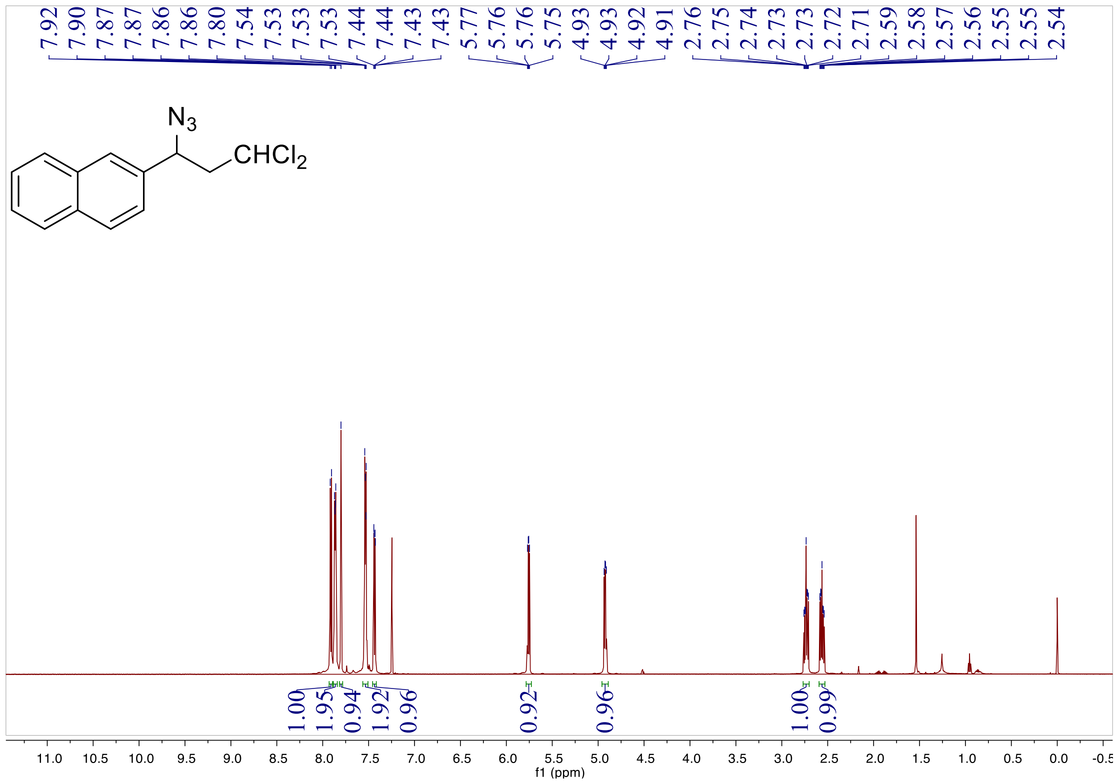
-2
f1 (ppm)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7.43
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5.75
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4.93
4.92
4.91
2.76
2.75
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2.73
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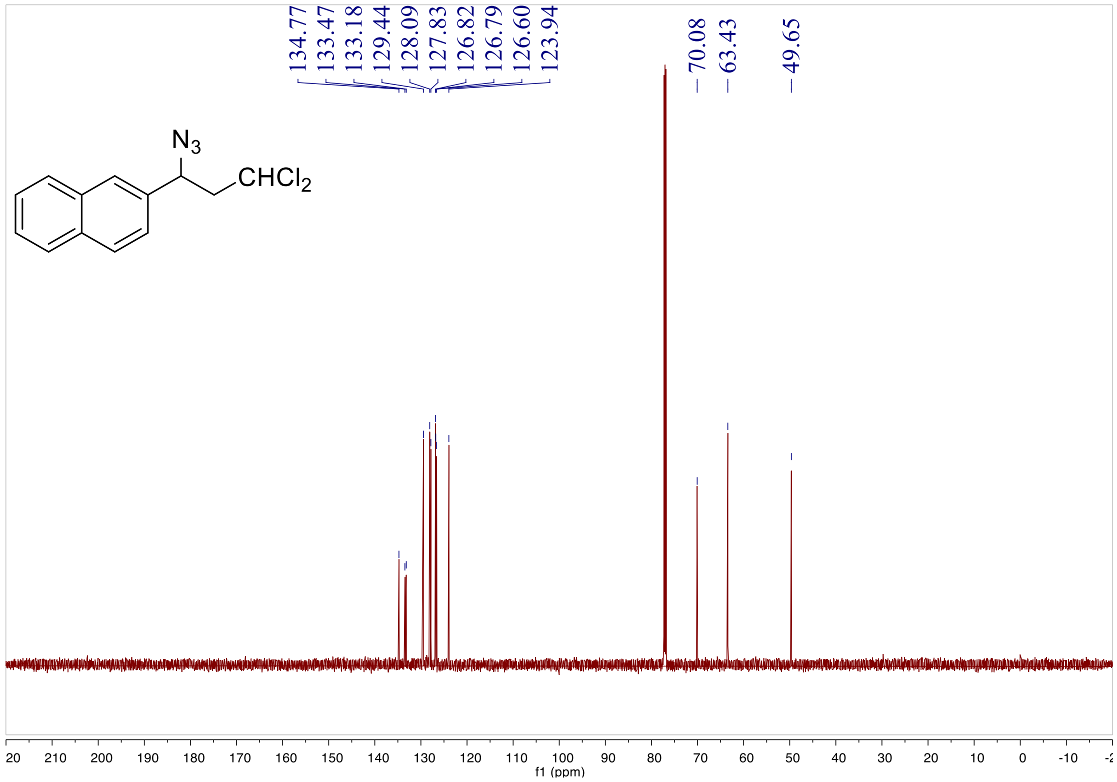
2.72
2.71
2.59
2.58
2.57
2.56
2.55
2.55
2.54
N3
CHCl2
1.00
1.95
0.94
1.92
0.96
0.92
0.96
1.00
0.99
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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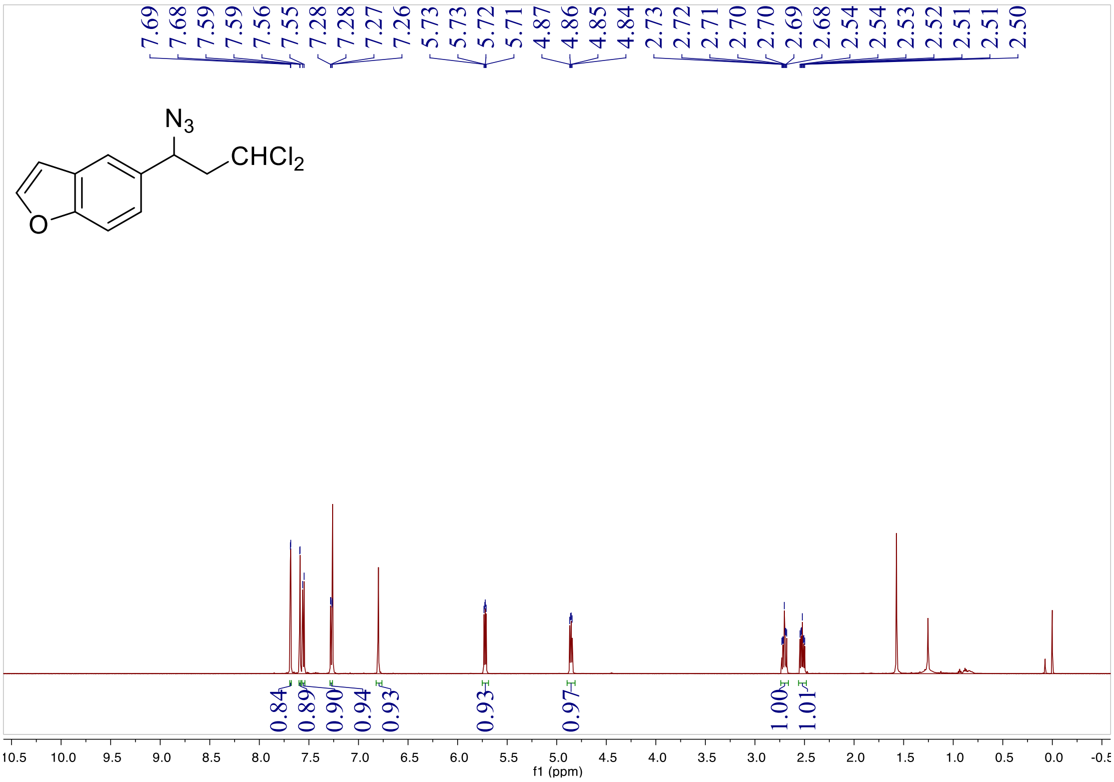
126.60
123.94
70.08
63.43
49.65
N3
CHCl2
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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7.28
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5.73
5.72
5.71
4.87
4.86
4.85
4.84
2.73
2.72
2.71
2.70
2.70
2.69
2.68
2.54
2.54
2.53
2.52
2.51
2.51
2.50
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O
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0.90
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0.93
0.93
0.97
1.00
1.01
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10.0
9.5
9.0
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8.0
7.5
7.0
6.5
6.0
5.5
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2.5
2.0
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1.0
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0.0
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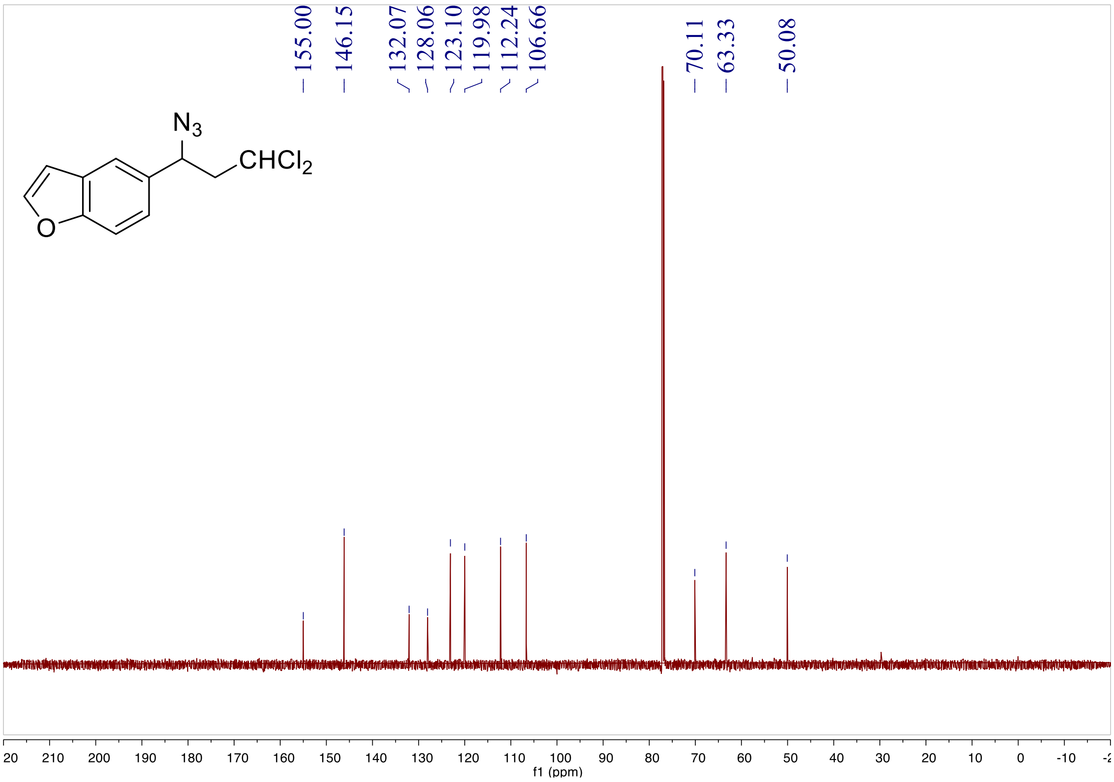
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63.33
50.08
N3
CHCl2
O
210
200
190
180
170
160
150
140
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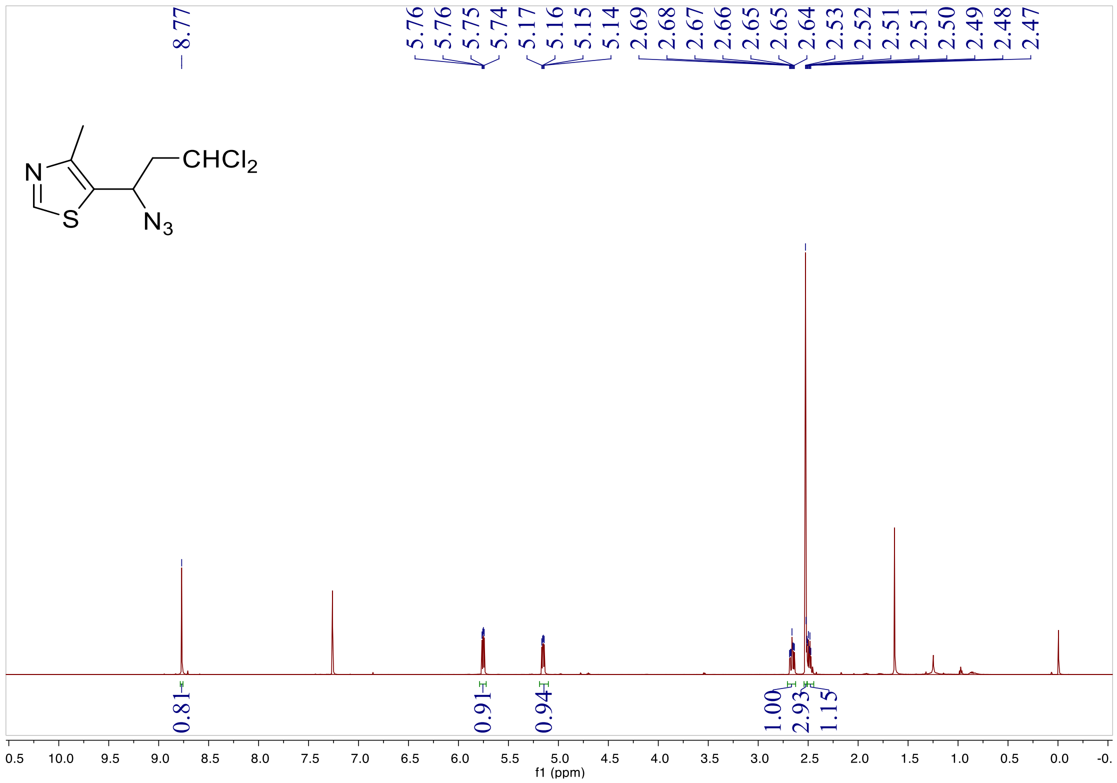
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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2.68
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2.53
2.52
2.51
2.51
2.50
2.49
2.48
2.47
CHCl2
N
S
N3
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0.91
0.94
1.00
2.93
1.15
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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3.0
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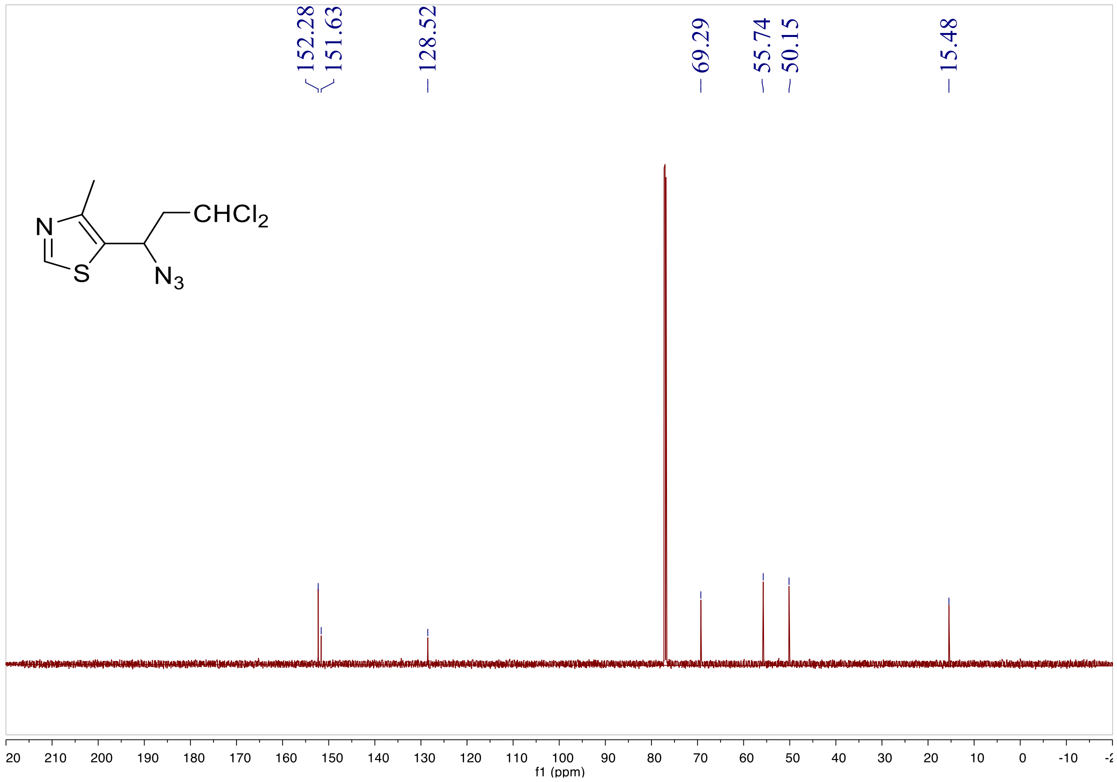
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)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CHCl2
N
S
N3
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210
200
190
180
170
160
150
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130
120
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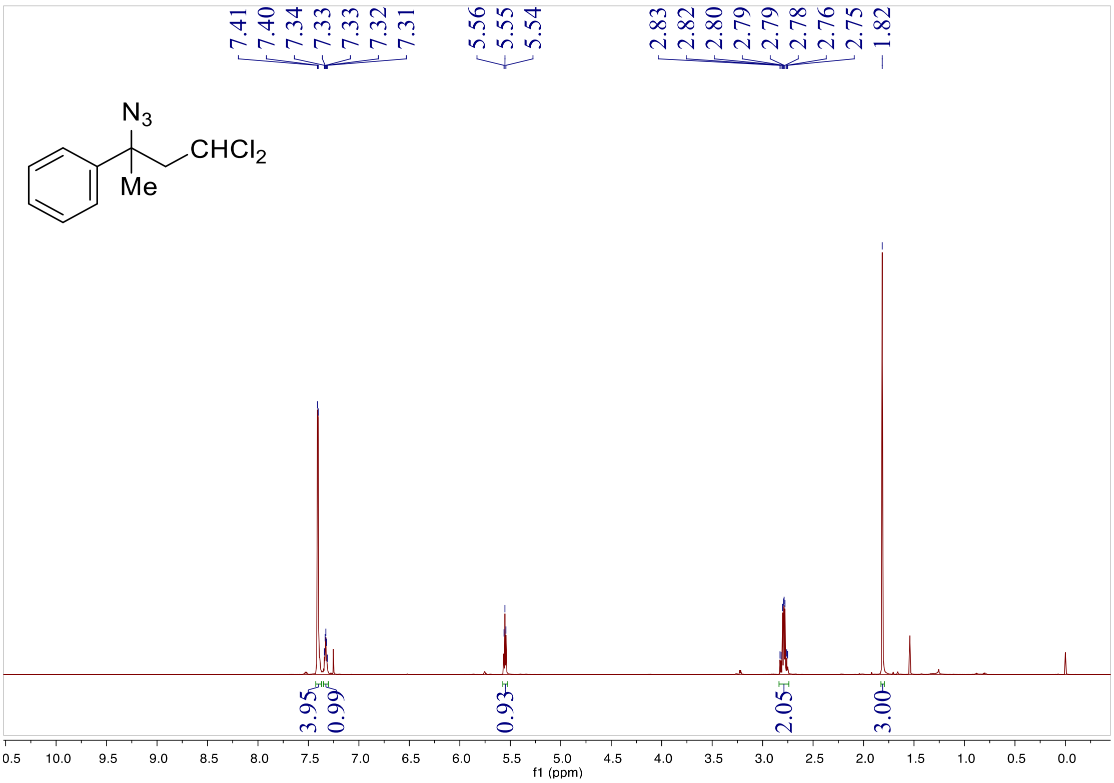
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)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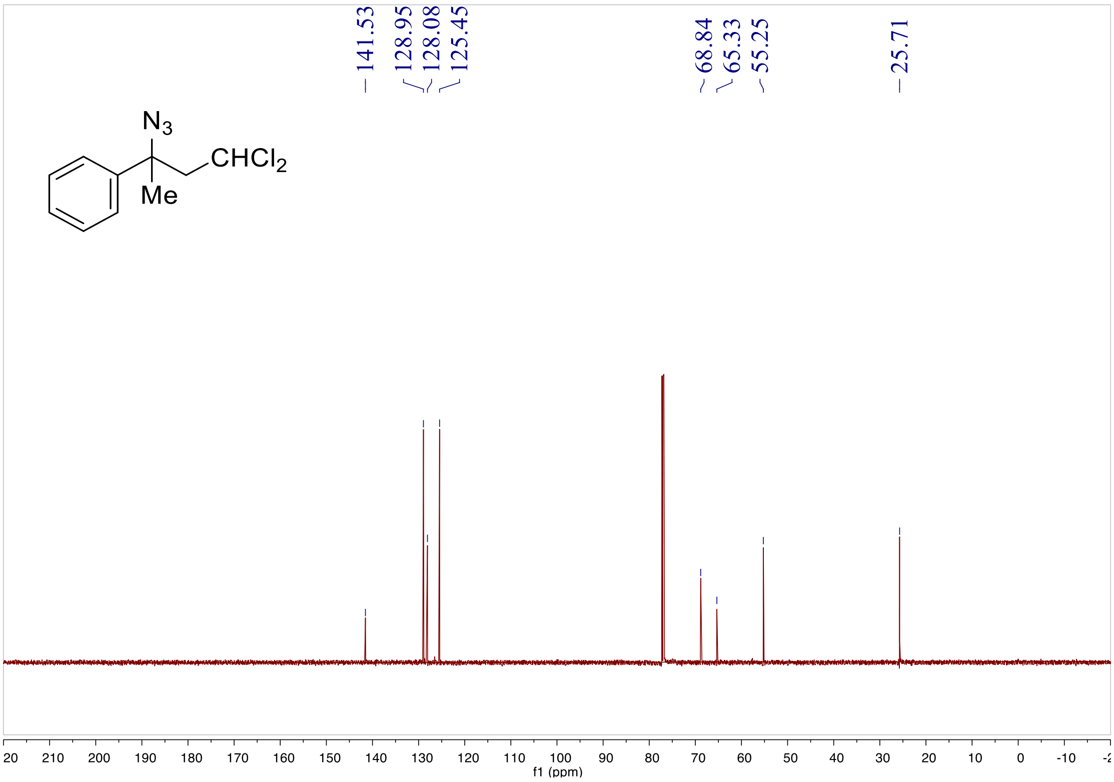
7.33
7.32
7.31
5.56
5.55
5.54
2.83
2.82
2.80
2.79
2.79
2.78
2.76
2.75
1.82
N_3
$CHCl_2$
Me
3.95
0.99
0.93
2.05
3.00
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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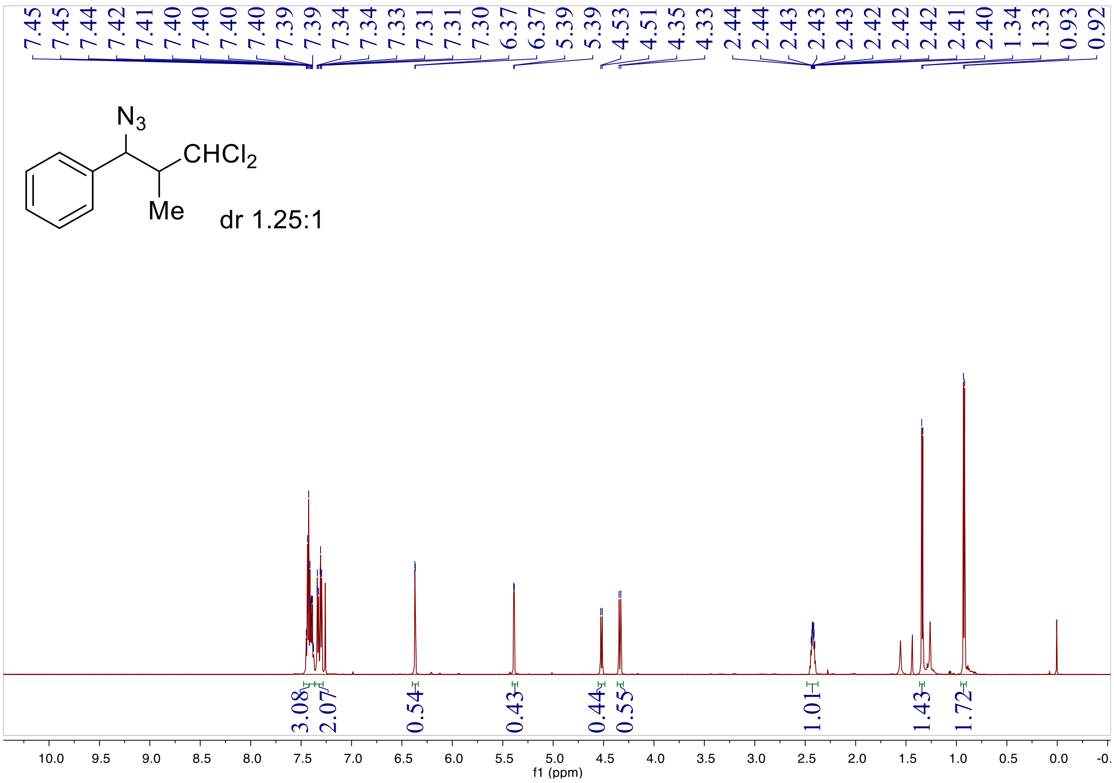
128.08
125.45
68.84
65.33
55.25
25.71
N_3
$CHCl_2$
Me
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)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7.42
7.41
7.40
7.40
7.40
7.40
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7.31
7.30
6.37
6.37
5.39
5.39
4.53
4.51
4.35
4.33
2.44
2.44
2.43
2.43
2.43
2.42
2.42
2.42
2.41
2.40
1.34
1.33
0.93
0.92
N_3
$CHCl_2$
Me
dr 1.25:1
3.08
2.07
0.54
0.43
0.44
0.55
1.01
1.43
1.72
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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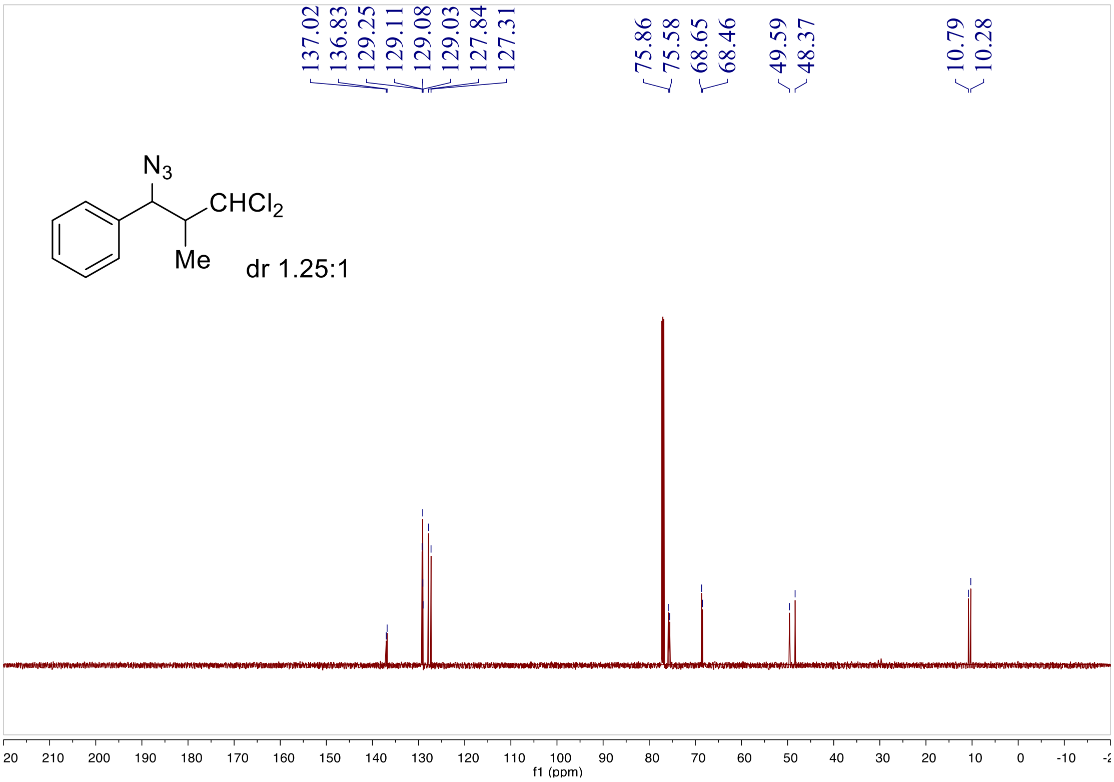
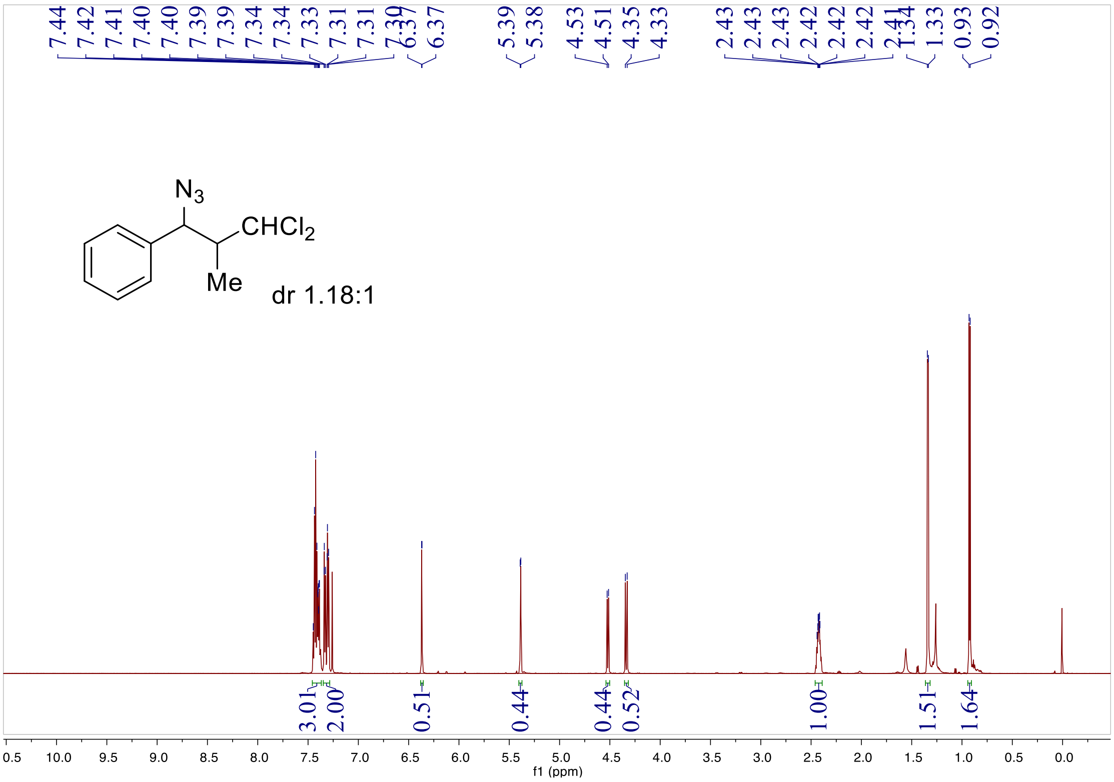
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)


137.02
136.83
129.25
129.11
129.08
129.03
127.84
127.31
75.86
75.58
68.65
68.46
49.59
48.37
10.79
10.28
N_3
$CHCl_2$
Me
dr 1.25:1
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)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7.42
7.41
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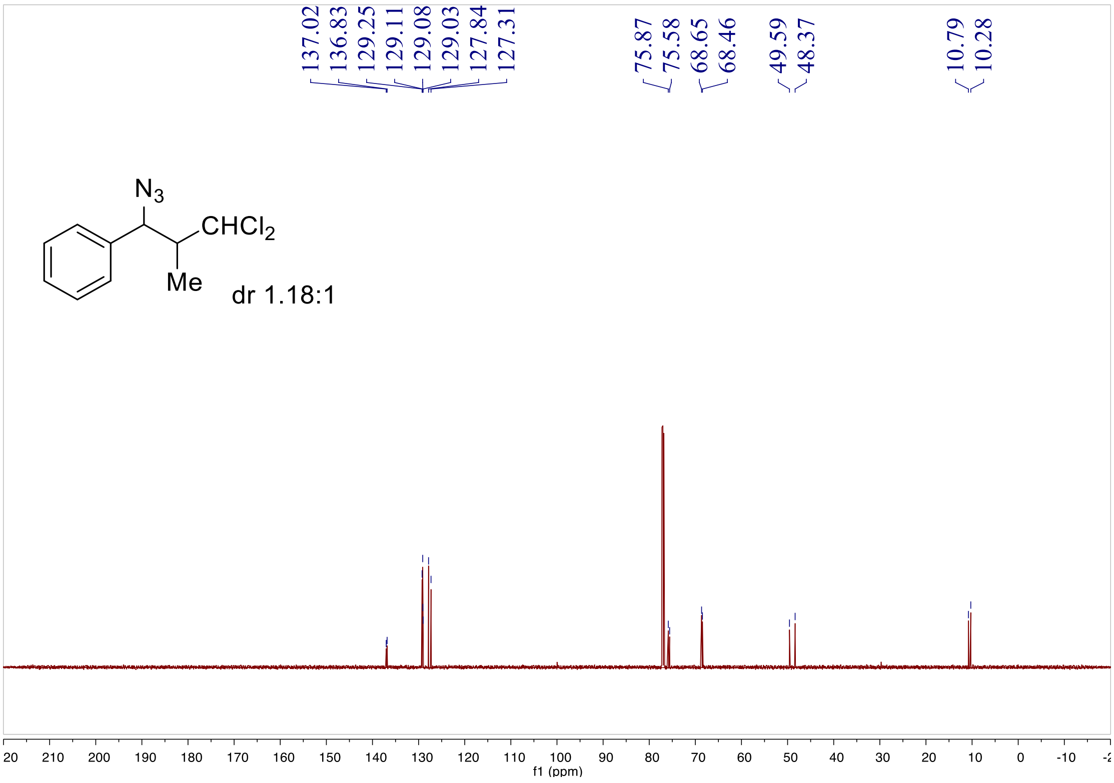
7.40
7.39
7.39
7.34
7.34
7.33
7.31
7.31
7.30
6.37
6.37
5.39
5.38
4.53
4.51
4.35
4.33
2.43
2.43
2.43
2.42
2.42
2.42
2.41
1.34
1.33
0.93
0.92
N3
CHCl2
Me
dr 1.18:1
3.01
2.00
0.51
0.44
0.44
0.52
1.00
1.51
1.64
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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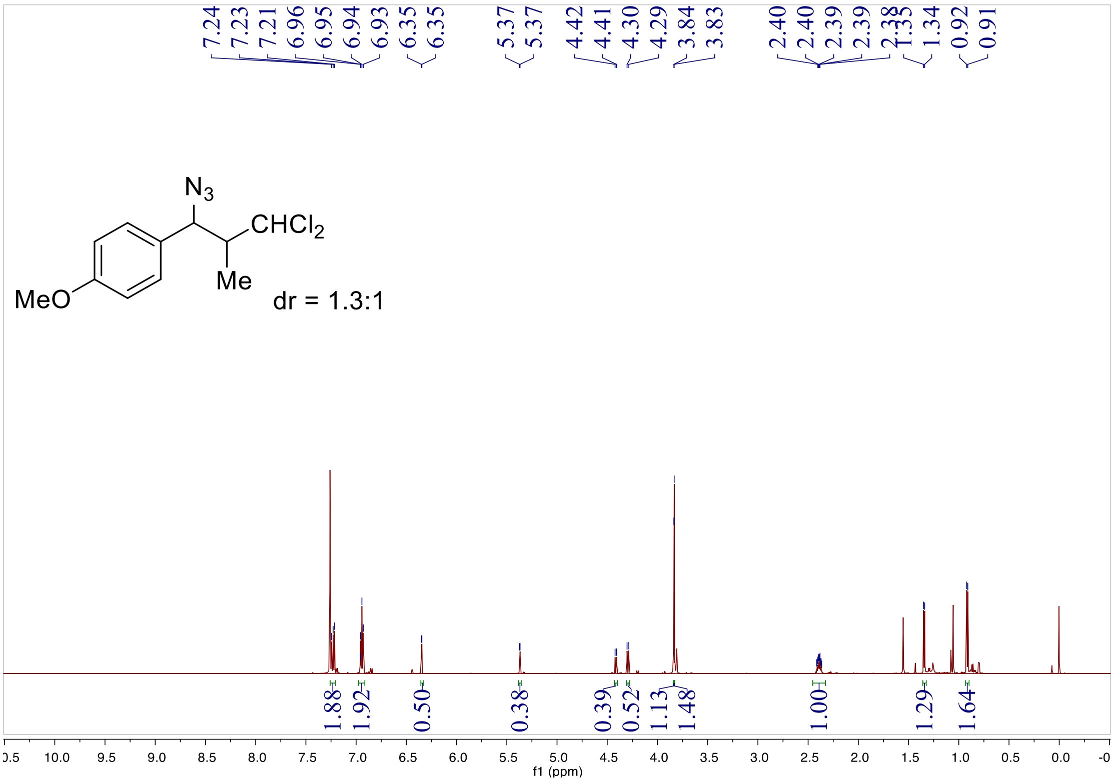
136.83
129.25
129.11
129.08
129.03
127.84
127.31
75.87
75.58
68.65
68.46
49.59
48.37
10.79
10.28
N3
CHCl2
Me
dr 1.18:1
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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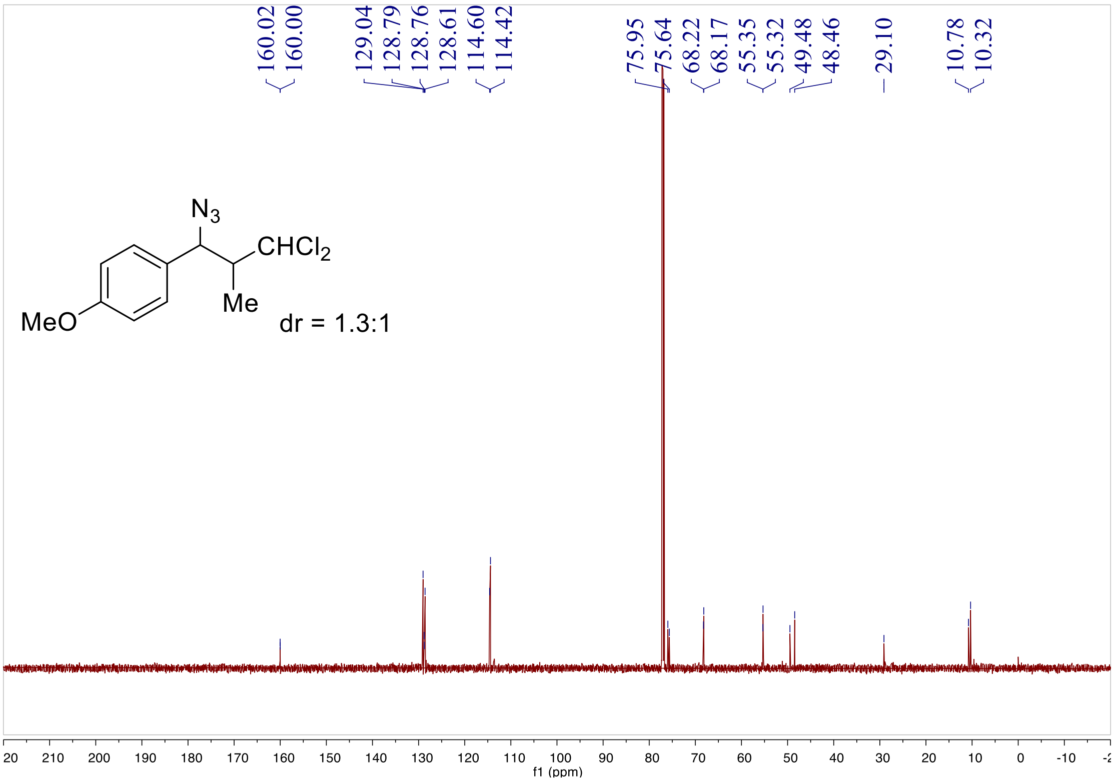
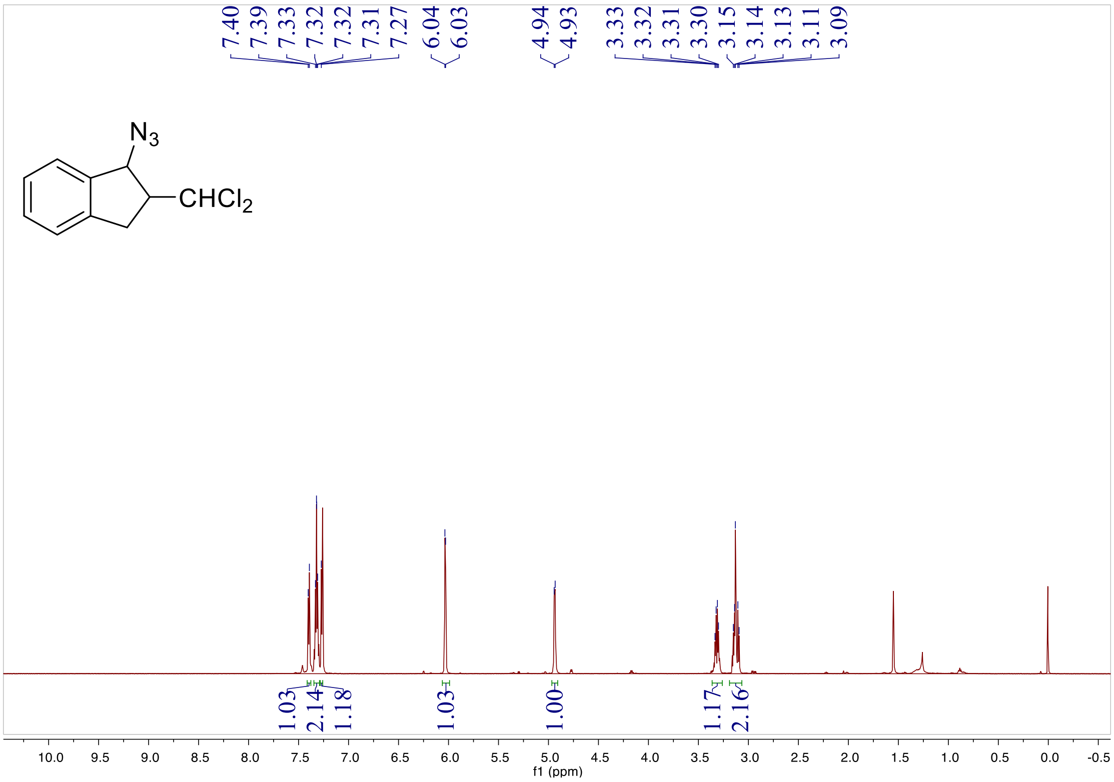
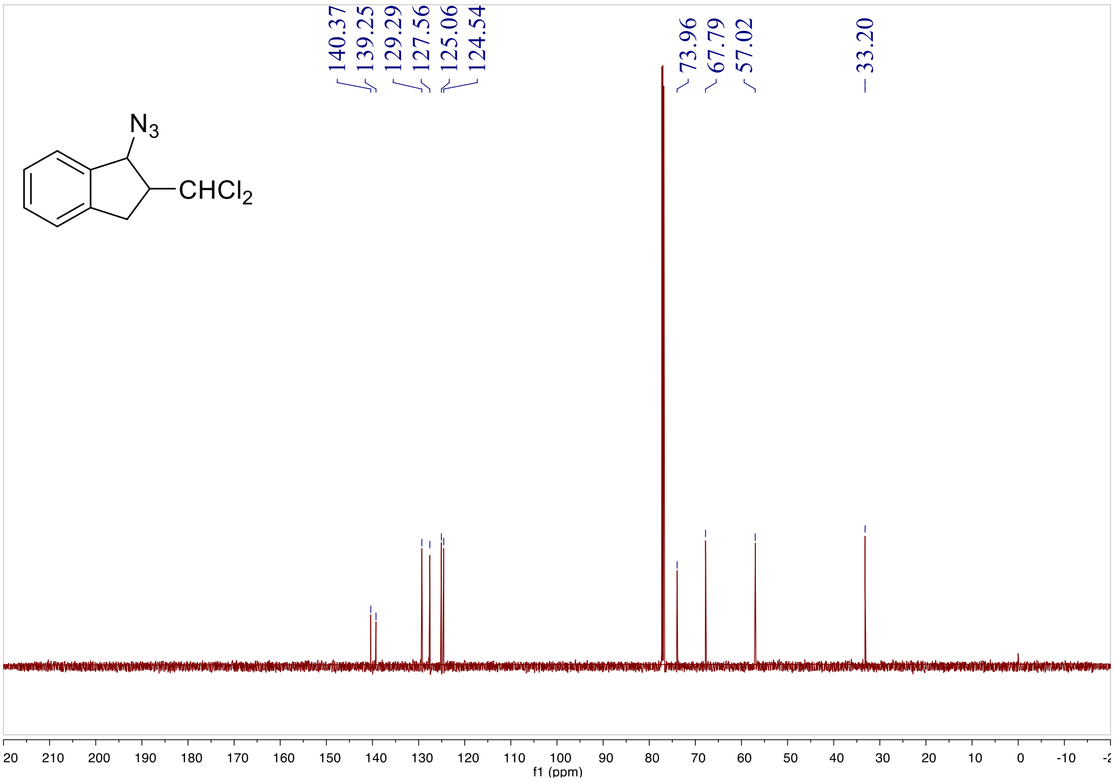
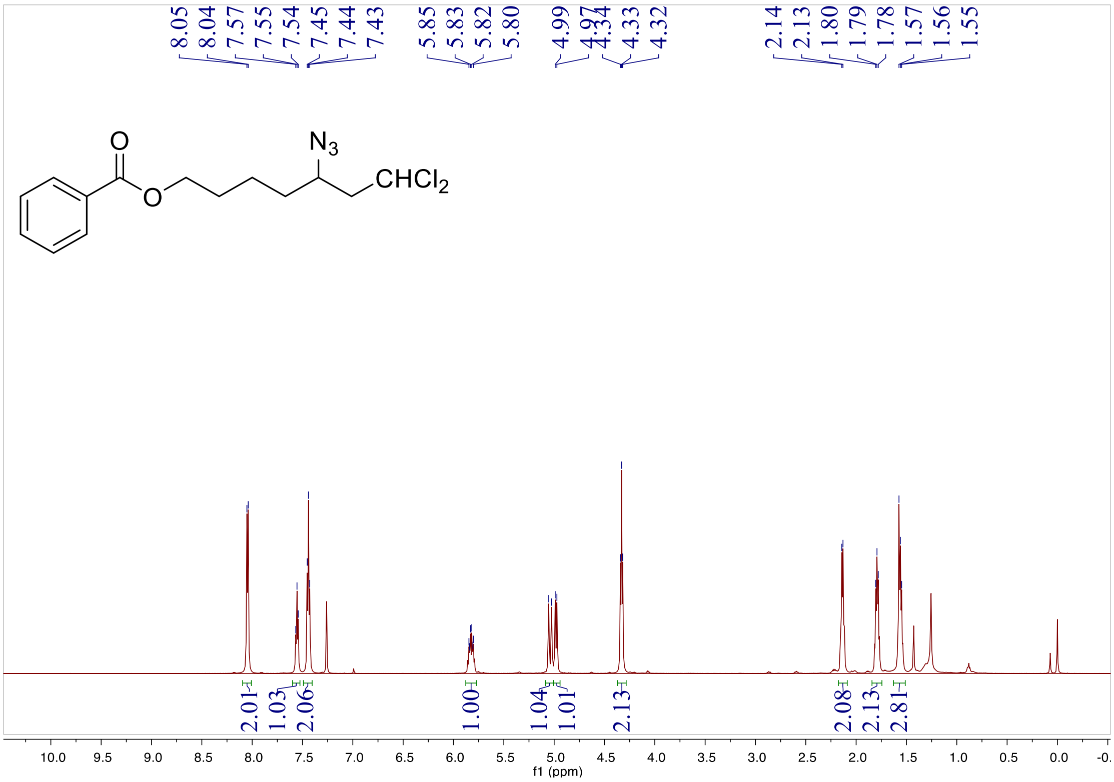
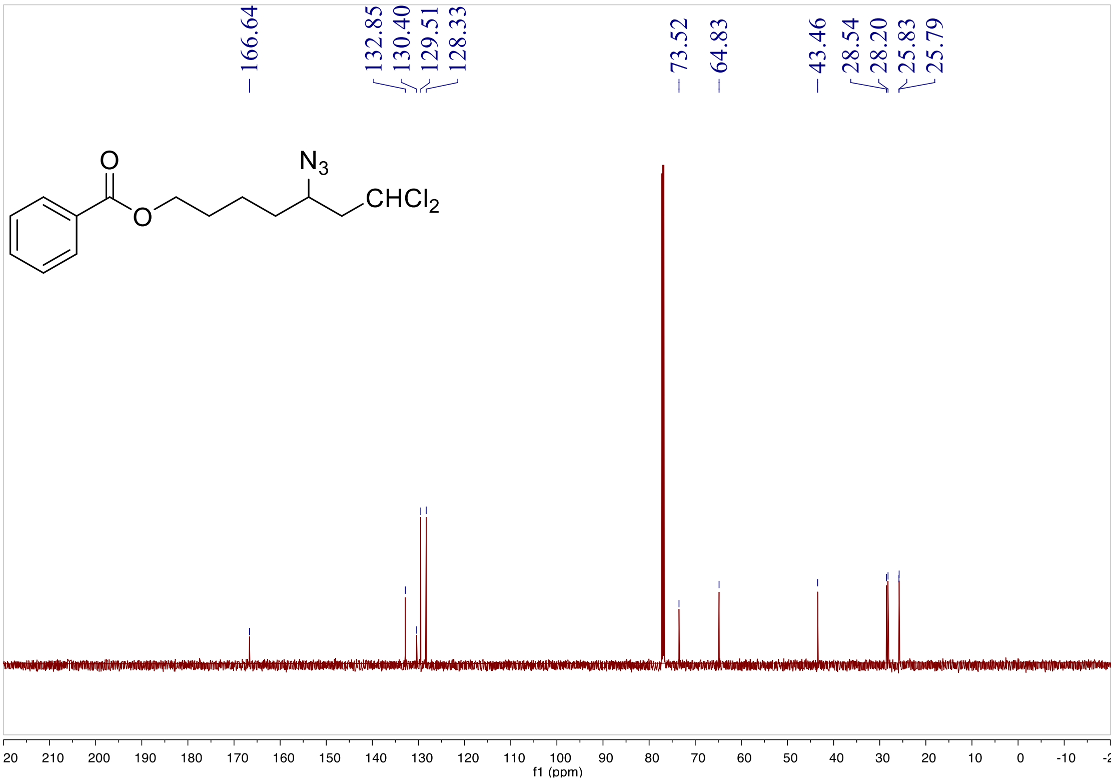
7.23
7.21
6.96
6.95
6.94
6.93
6.35
6.35
5.37
5.37
4.42
4.41
4.30
4.29
3.84
3.83
2.40
2.40
2.39
2.39
2.38
1.35
1.34
0.92
0.91
N3
CHCl2
Me
MeO
dr = 1.3:1
1.88
1.92
0.50
0.38
0.39
0.52
1.13
1.48
1.00
1.29
1.64
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

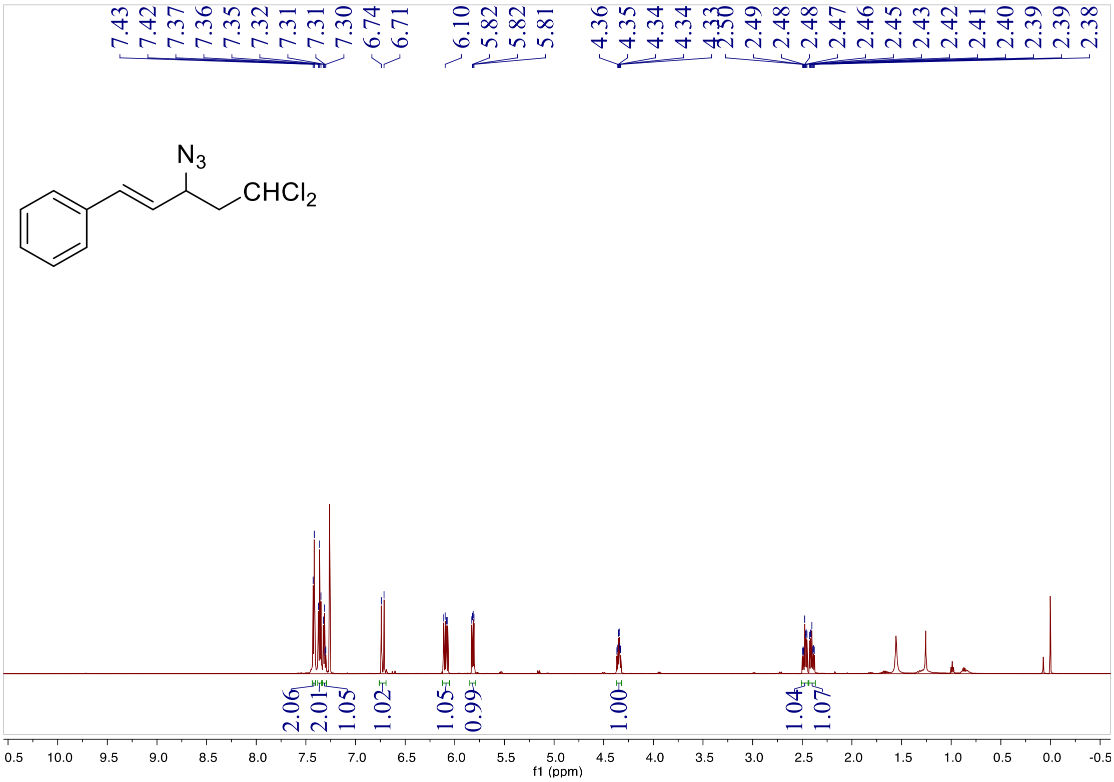

160.02
160.00
129.04
128.79
128.76
128.61
114.60
114.42
75.95
75.64
68.22
68.17
55.35
55.32
49.48
48.46
29.10
10.78
10.32
N3
CHCl2
Me
MeO
dr = 1.3:1
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

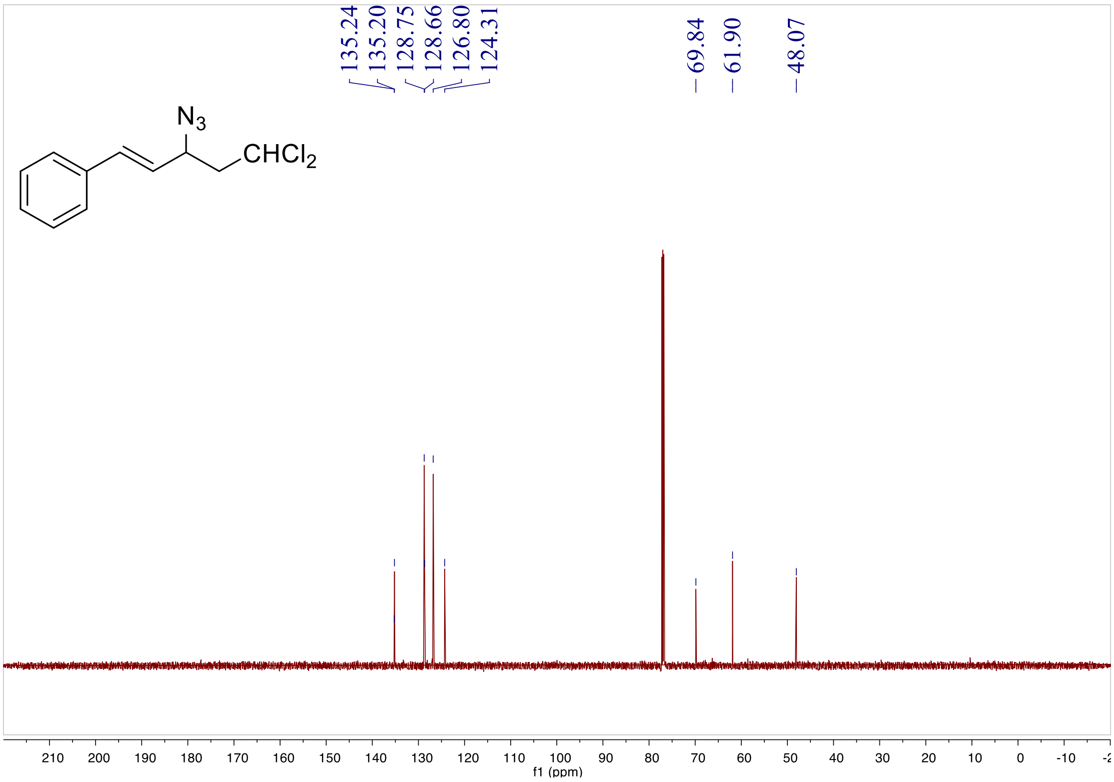

7.40
7.39
7.33
7.32
7.32
7.31
7.27
6.04
6.03
4.94
4.93
3.33
3.32
3.31
3.30
3.15
3.14
3.13
3.11
3.09
N3
CHCl2
1.03
2.14
1.18
1.03
1.00
1.17
2.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

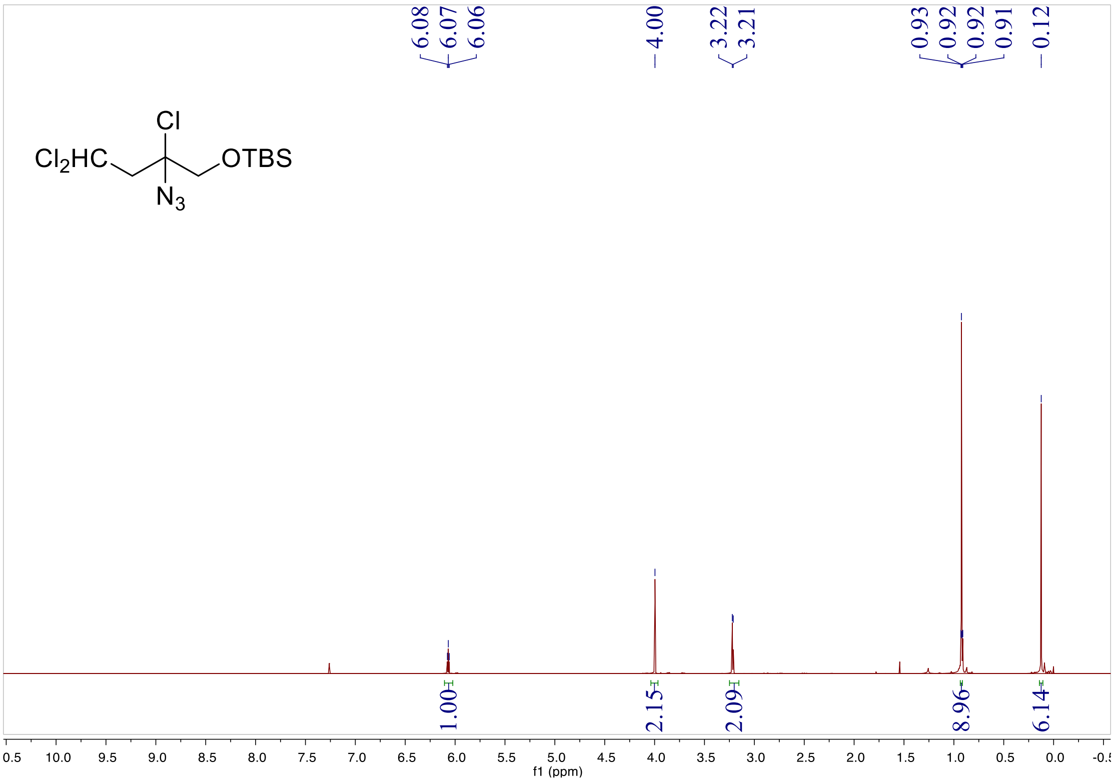

140.37
139.25
129.29
127.56
125.06
124.54
73.96
67.79
57.02
33.20
N3
CHCl2
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

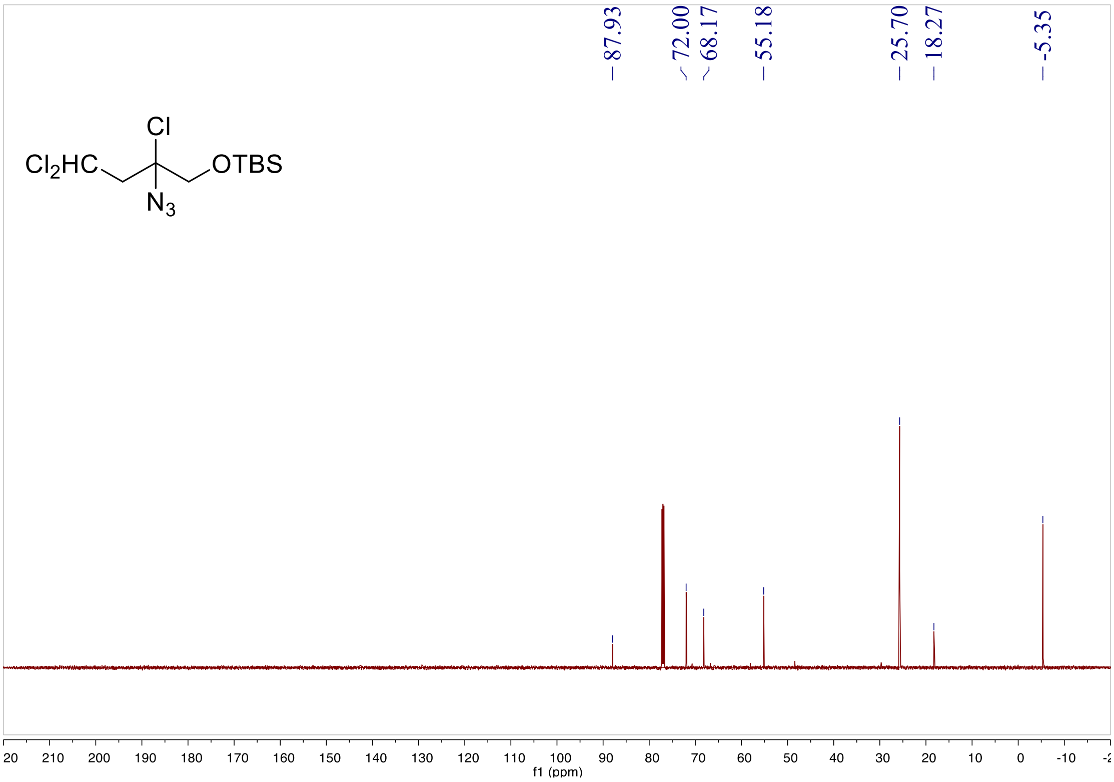

8.05
8.04
7.57
7.55
7.54
7.45
7.44
7.43
5.85
5.83
5.82
5.80
4.99
4.97
4.34
4.33
4.32
2.14
2.13
1.80
1.79
1.78
1.57
1.56
1.55
O
O
N3
CHCl2
2.01
1.03
2.06
1.00
1.04
1.01
2.13
2.08
2.13
2.81
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

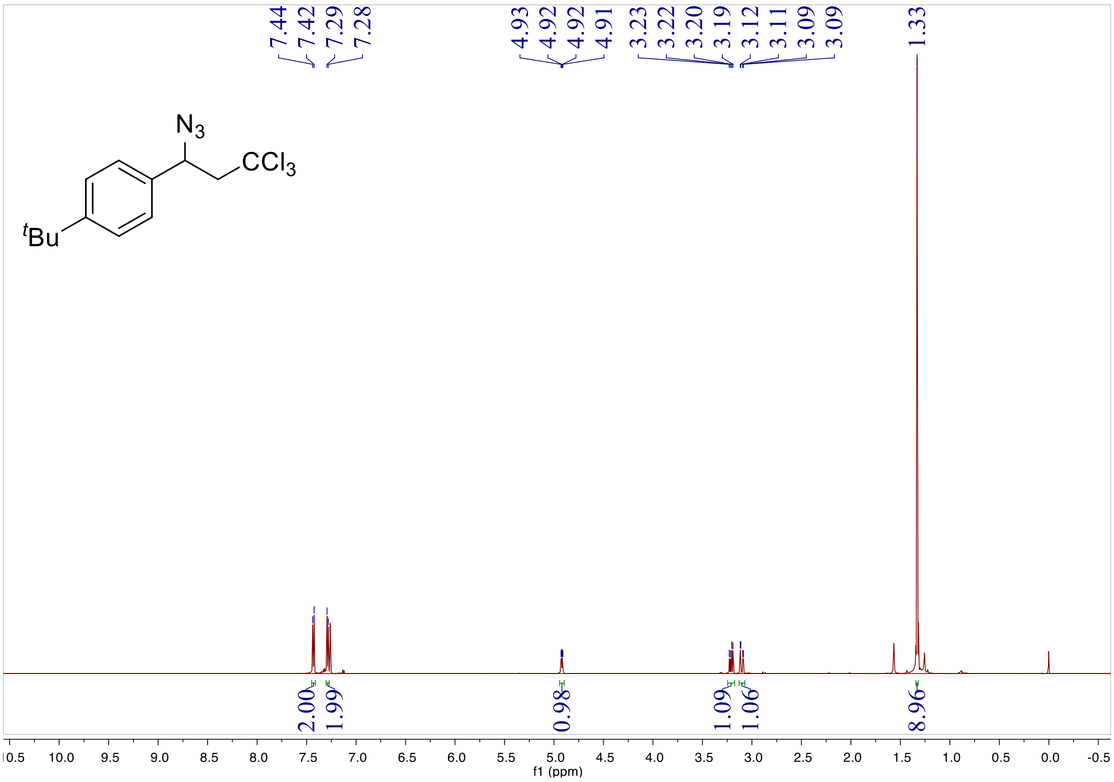

166.64
132.85
130.40
129.51
128.33
73.52
64.83
43.46
28.54
28.20
25.83
25.79
O
O
N3
CHCl2
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)

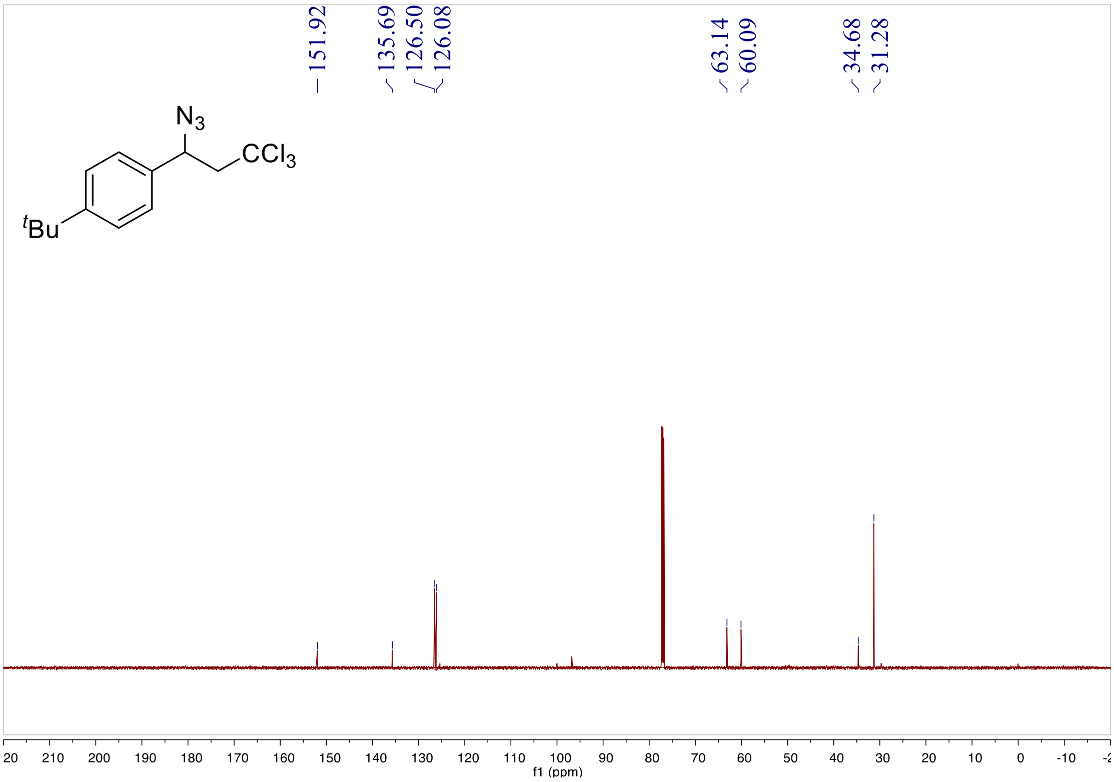

7.43
7.42
7.37
7.36
7.35
7.32
7.31
7.31
7.30
6.74
6.71
6.10
5.82
5.82
5.81
4.36
4.35
4.34
4.34
4.33
2.50
2.49
2.48
2.48
2.47
2.46
2.45
2.43
2.42
2.41
2.40
2.39
2.39
2.38
N_3
$CHCl_2$
2.06
2.01
1.05
1.02
1.05
0.99
1.00
1.04
1.07
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

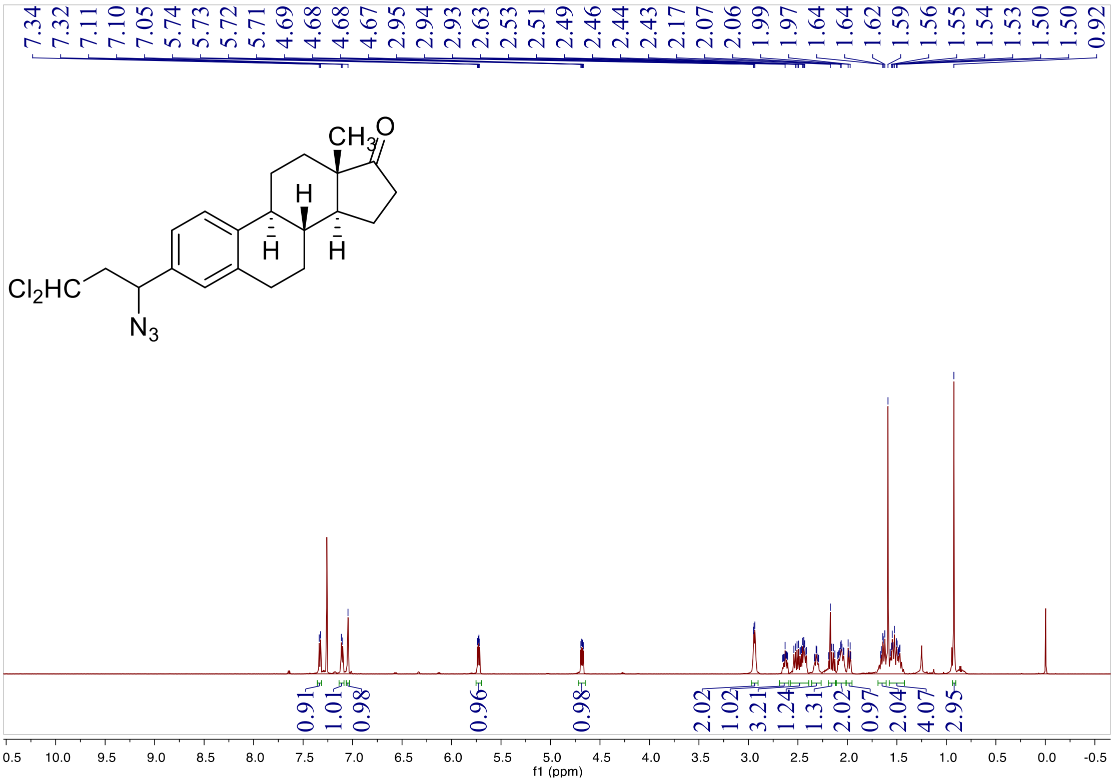

135.24
135.20
128.75
128.66
126.80
124.31
69.84
61.90
48.07
N_3
$CHCl_2$
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

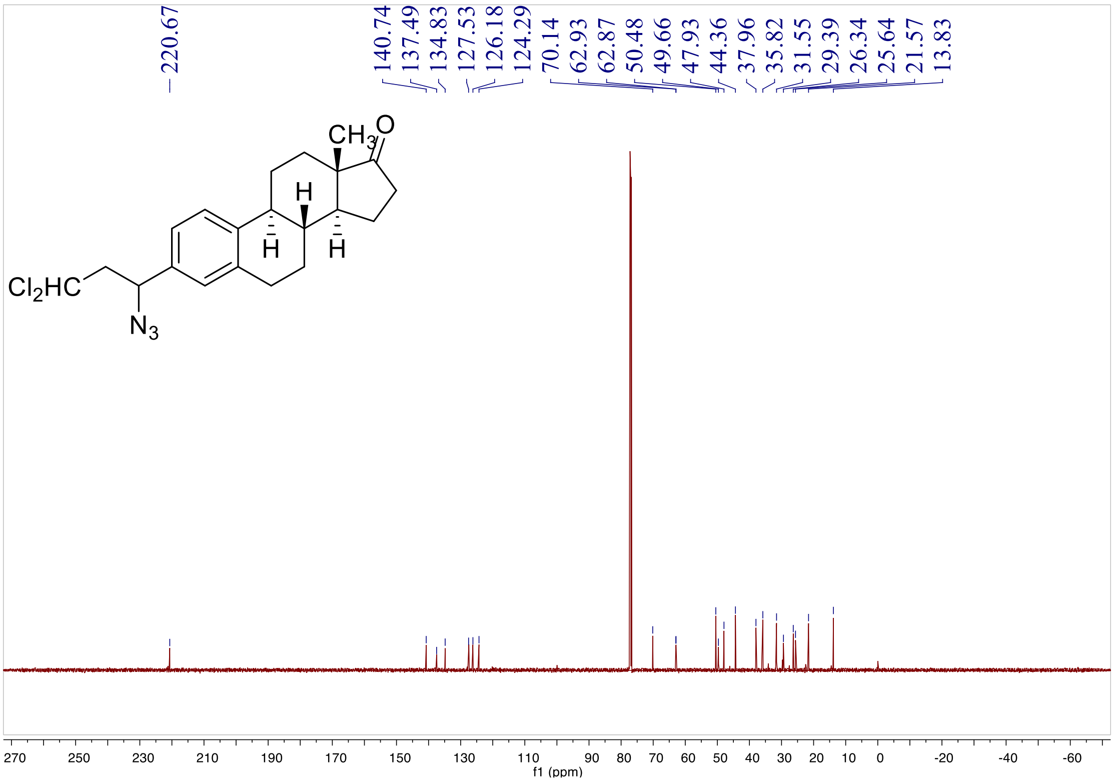

Cl
Cl2HC
OTBS
N3
6.08
6.07
6.06
4.00
3.22
3.21
0.93
0.92
0.92
0.91
0.12
1.00
2.15
2.09
8.96
6.14
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


Cl
Cl2HC
OTBS
N3
87.93
72.00
68.17
55.18
25.70
18.27
-5.35
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)


7.44
7.42
7.29
7.28
4.93
4.92
4.92
4.91
3.23
3.22
3.20
3.19
3.12
3.11
3.09
3.09
1.33
N3
CCl3
tBu
2.00
1.99
0.98
1.09
1.06
8.96
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


151.92
135.69
126.50
126.08
63.14
60.09
34.68
31.28
N3
CCl3
tBu
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


7.34
7.32
7.11
7.10
7.05
5.74
5.73
5.72
5.71
4.69
4.68
4.68
4.67
2.95
2.94
2.93
2.63
2.53
2.51
2.49
2.46
2.44
2.43
2.17
2.07
2.06
1.99
1.97
1.64
1.64
1.62
1.59
1.56
1.55
1.54
1.53
1.50
1.50
0.92
CH3
O
H
H
H
Cl2HC
N3
0.91
1.01
0.98
0.96
0.98
2.02
1.02
3.21
1.24
1.31
2.02
0.97
2.04
4.07
2.95
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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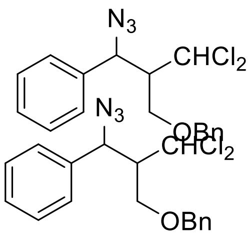
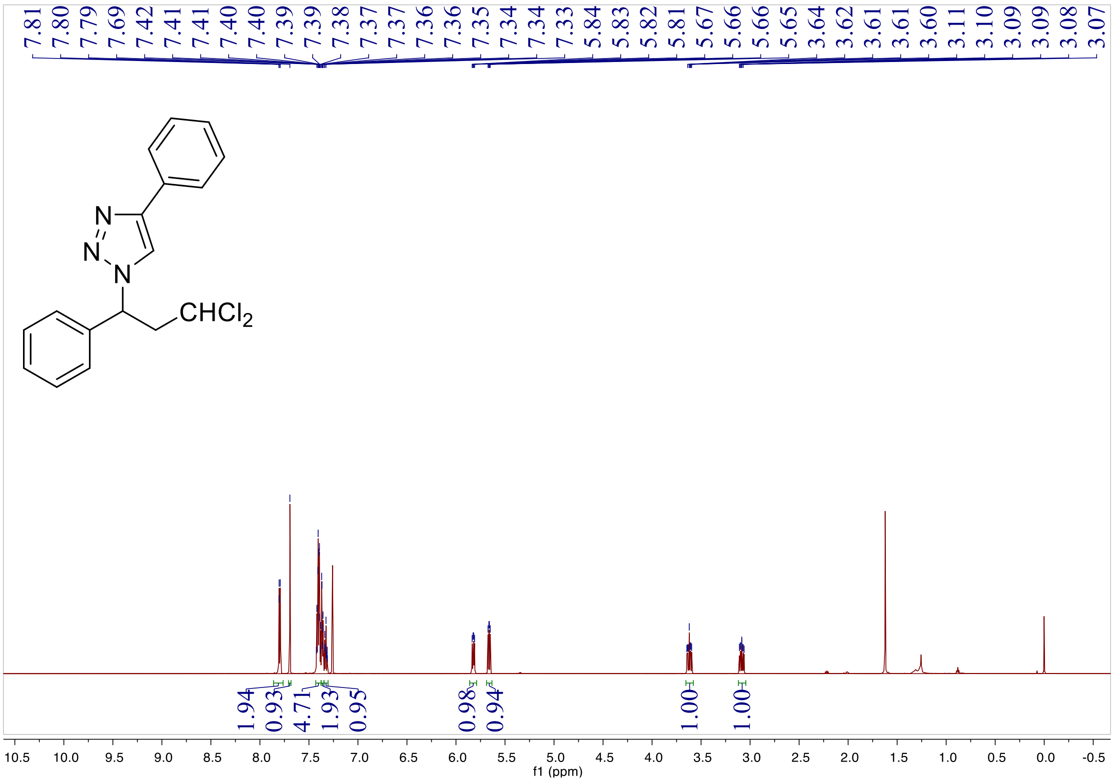
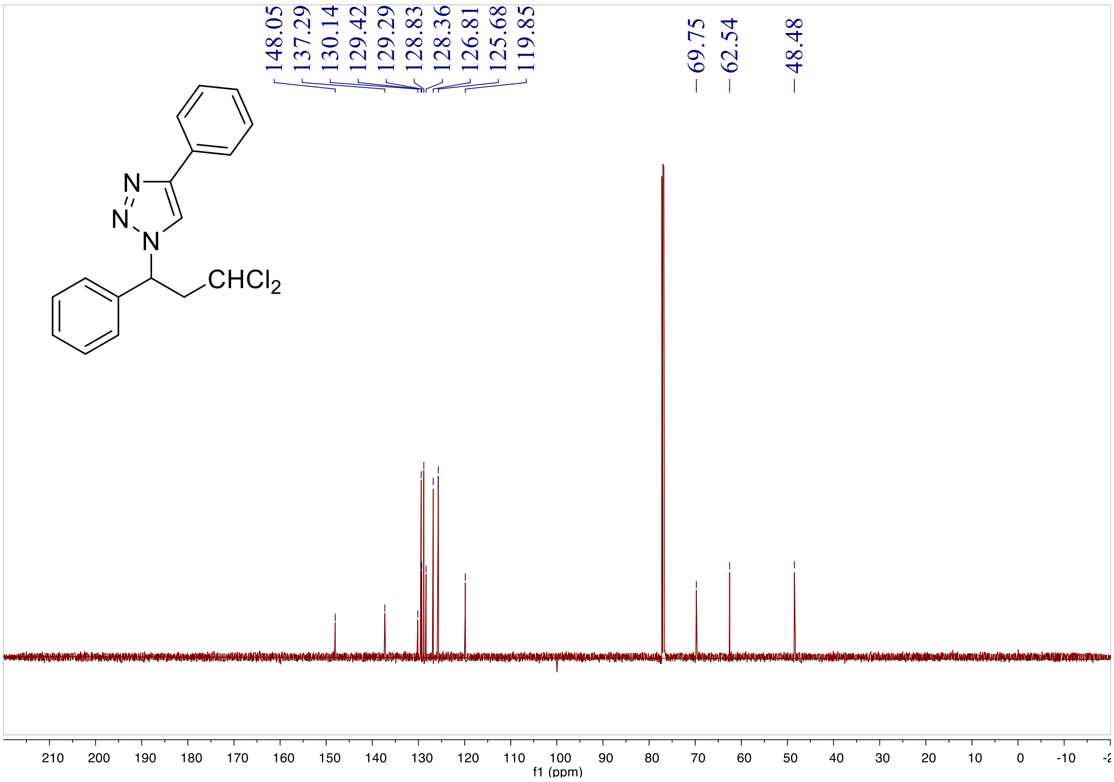
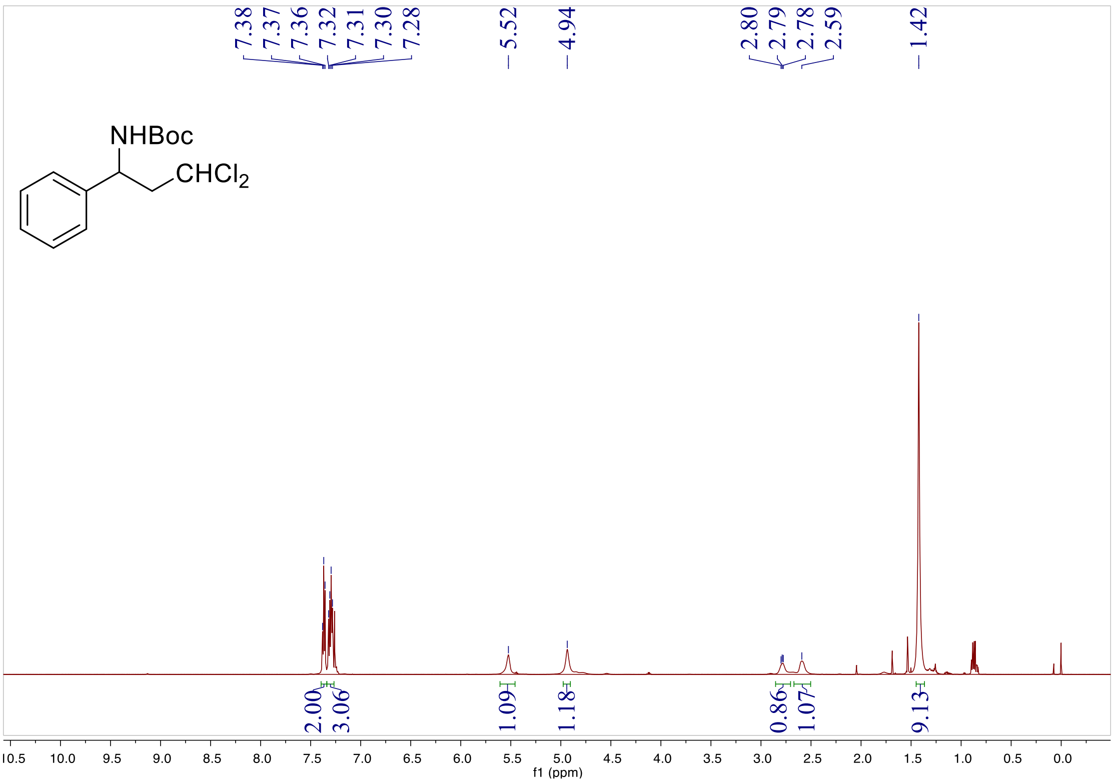
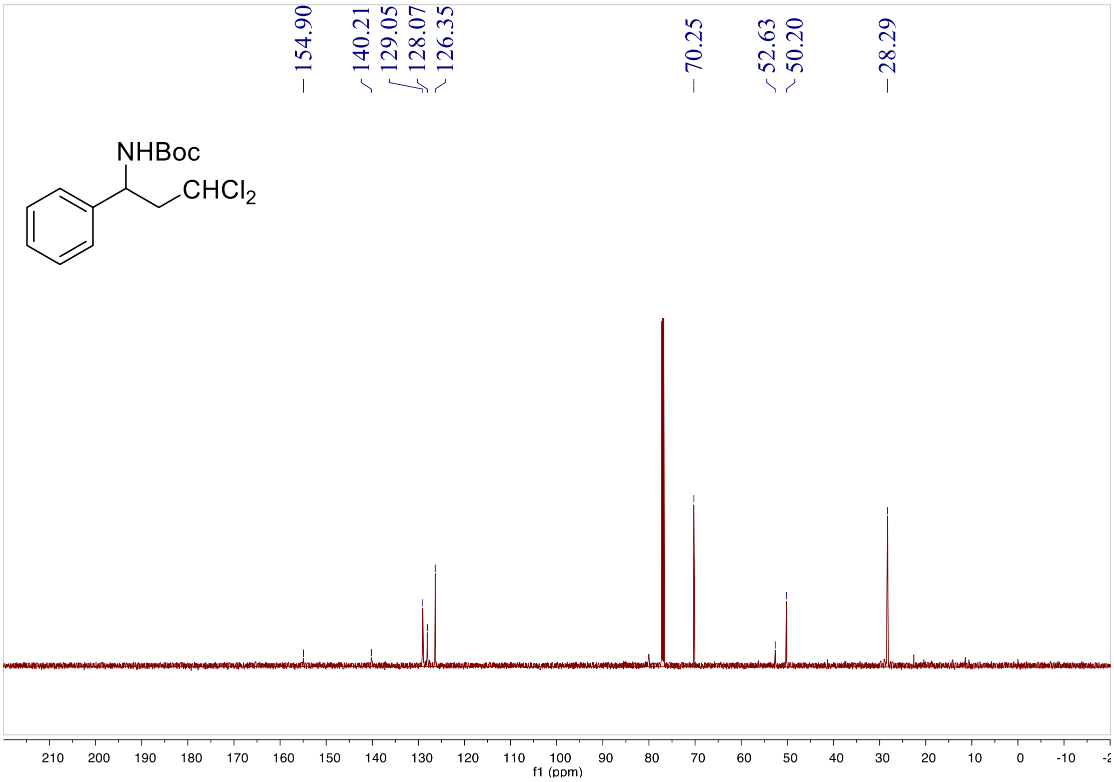
140.74
137.49
134.83
127.53
126.18
124.29
70.14
62.93
62.87
50.48
49.66
47.93
44.36
37.96
35.82
31.55
29.39
26.34
25.64
21.57
13.83
CH3
O
H
H
H
Cl2HC
N3
270
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-20
-40
-60
f1 (ppm)

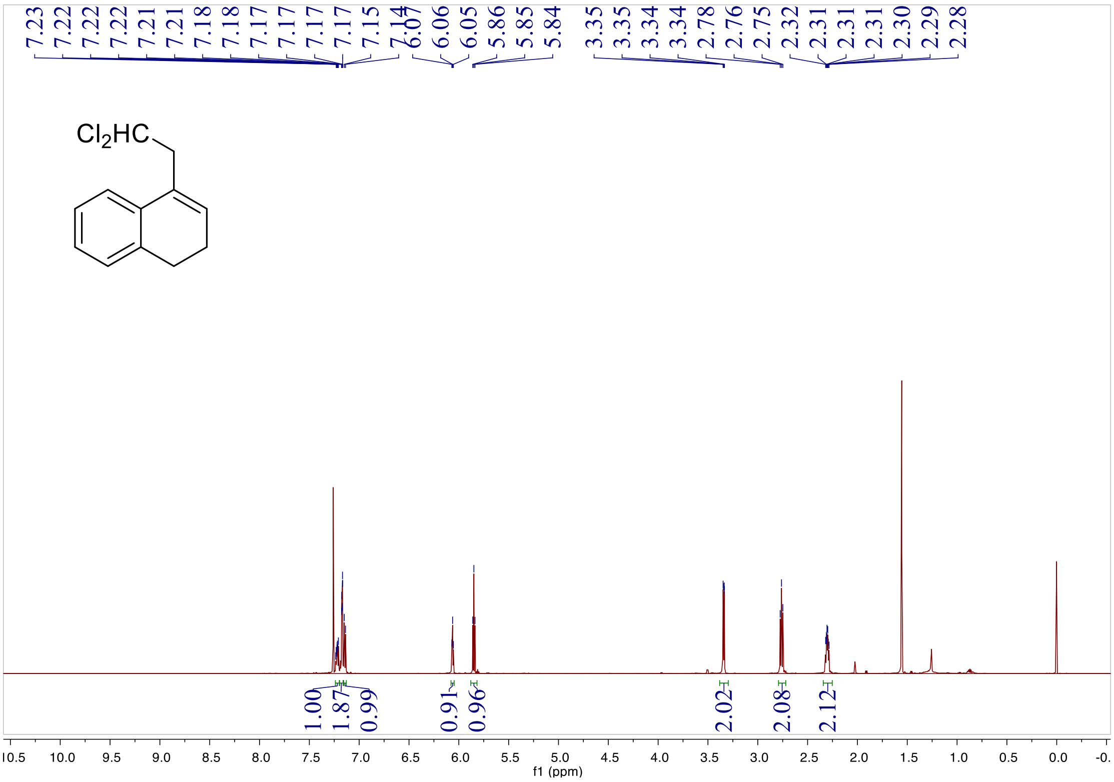

N3
CHCl2
OBn
N3
CHCl2
OBn

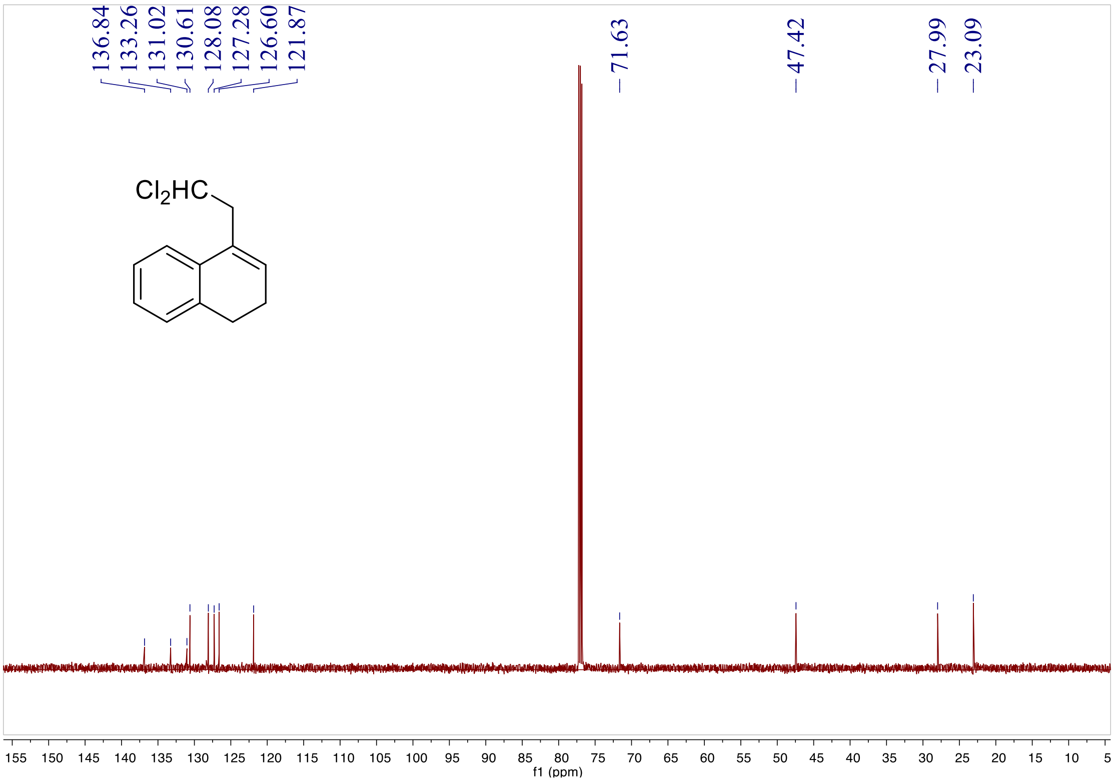

7.81
7.80
7.79
7.69
7.42
7.41
7.41
7.40
7.40
7.39
7.39
7.38
7.37
7.37
7.36
7.36
7.35
7.34
7.34
7.33
5.84
5.83
5.82
5.81
5.67
5.66
5.66
5.65
3.64
3.62
3.61
3.61
3.60
3.11
3.10
3.09
3.09
3.08
3.07
N
N
N
CHCl2
1.94
0.93
4.71
1.93
0.95
0.98
0.94
1.00
1.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

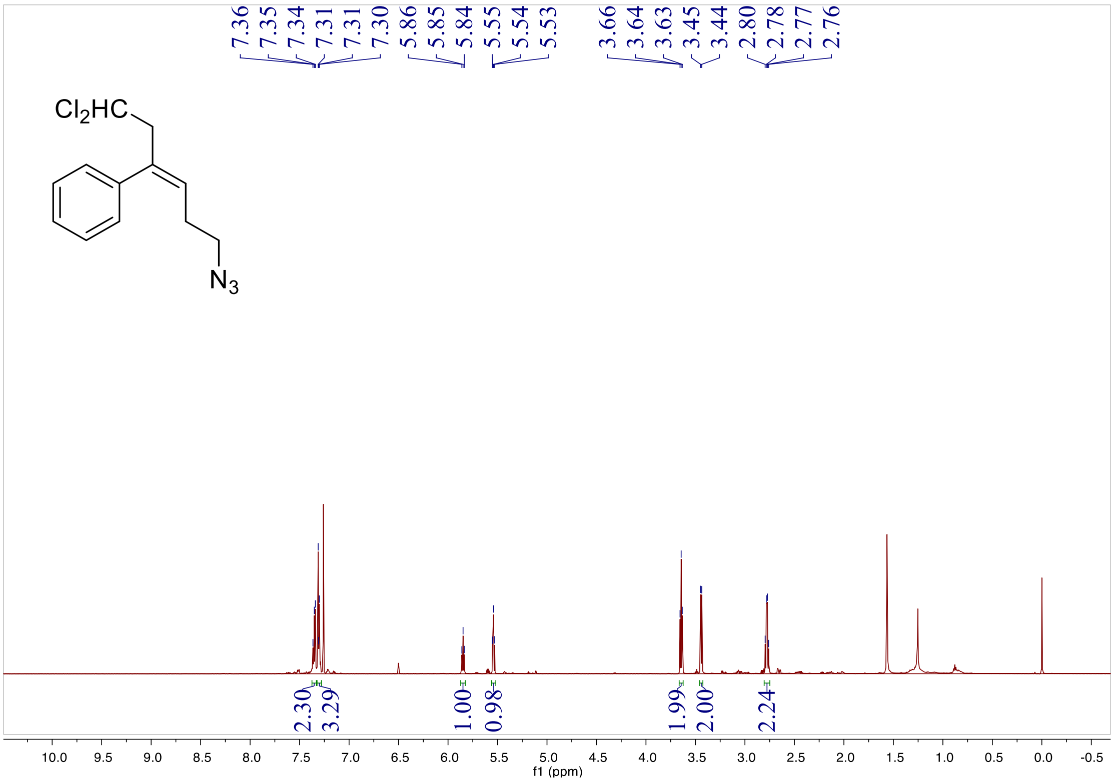

148.05
137.29
130.14
129.42
129.29
128.83
128.36
126.81
125.68
119.85
69.75
62.54
48.48
N
N
N
CHCl2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

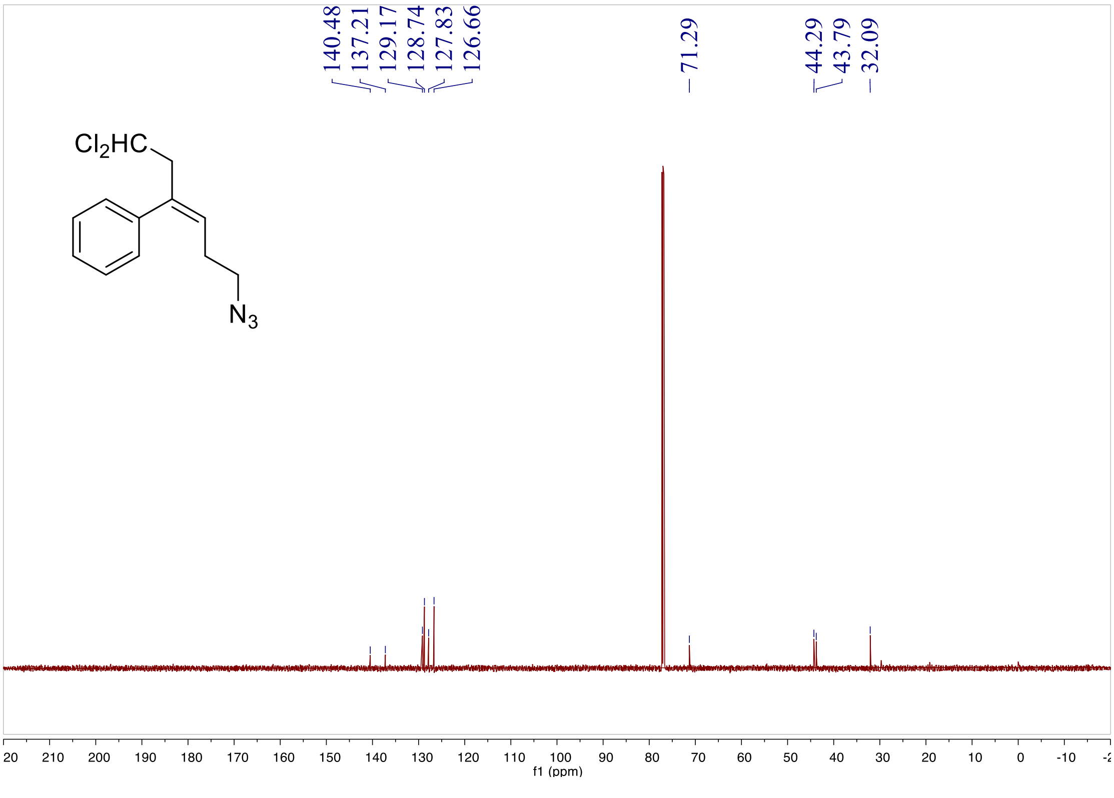

7.38
7.37
7.36
7.32
7.31
7.30
7.28
5.52
4.94
2.80
2.79
2.78
2.59
1.42
NHBoc
CHCl2
2.00
3.06
1.09
1.18
0.86
1.07
9.13
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

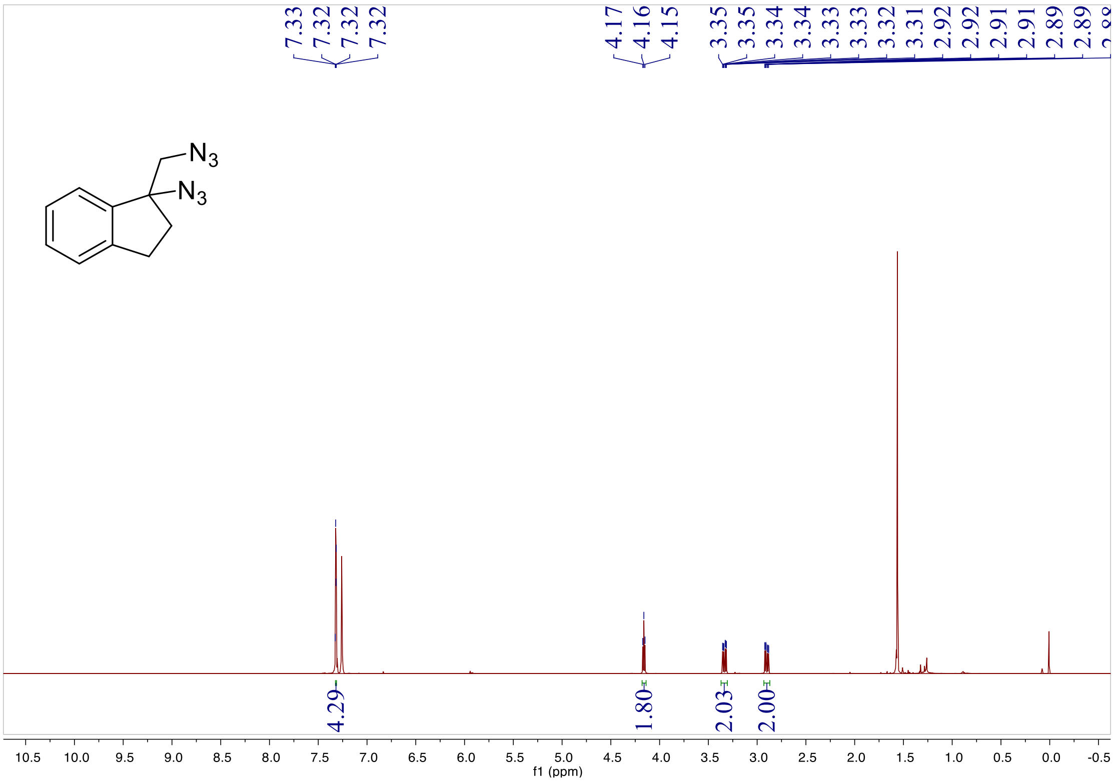

154.90
140.21
129.05
128.07
126.35
70.25
52.63
50.20
28.29
NHBoc
CHCl2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

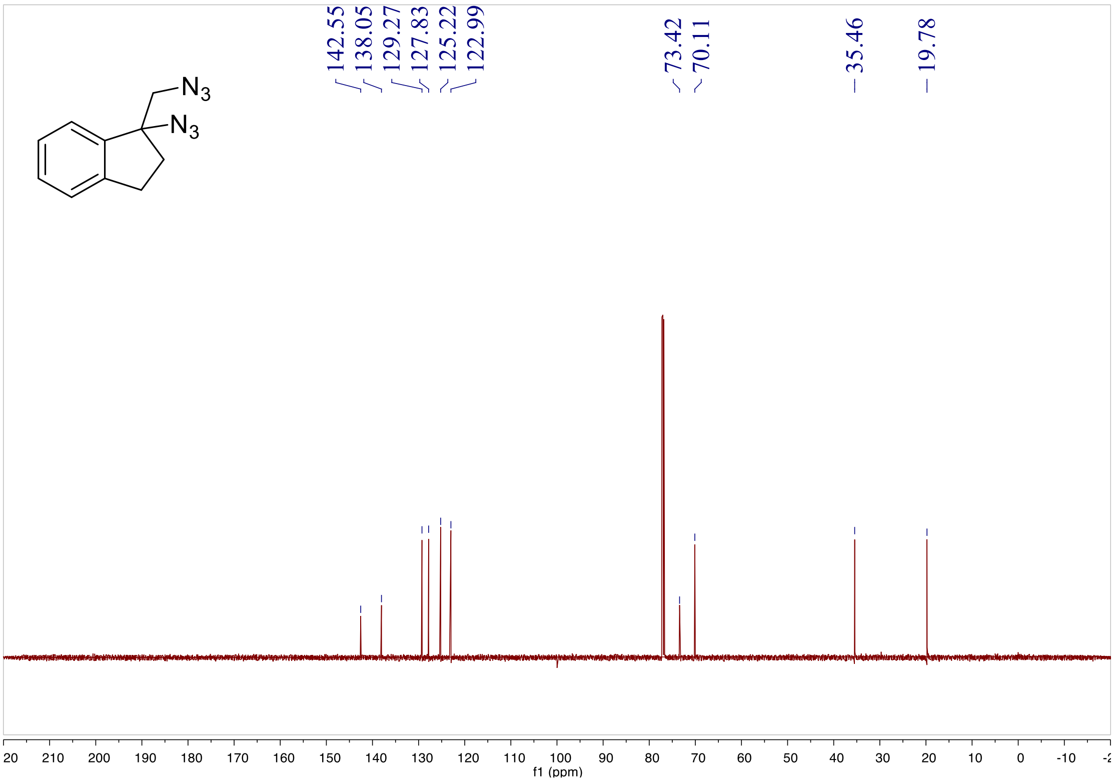

7.23
7.22
7.22
7.22
7.21
7.21
7.18
7.18
7.17
7.17
7.17
7.17
7.15
7.14
6.07
6.06
6.05
5.86
5.85
5.84
3.35
3.35
3.34
3.34
2.78
2.76
2.75
2.32
2.31
2.31
2.31
2.30
2.29
2.28
Cl2HC
1.00
1.87
0.99
0.91
0.96
2.02
2.08
2.12
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

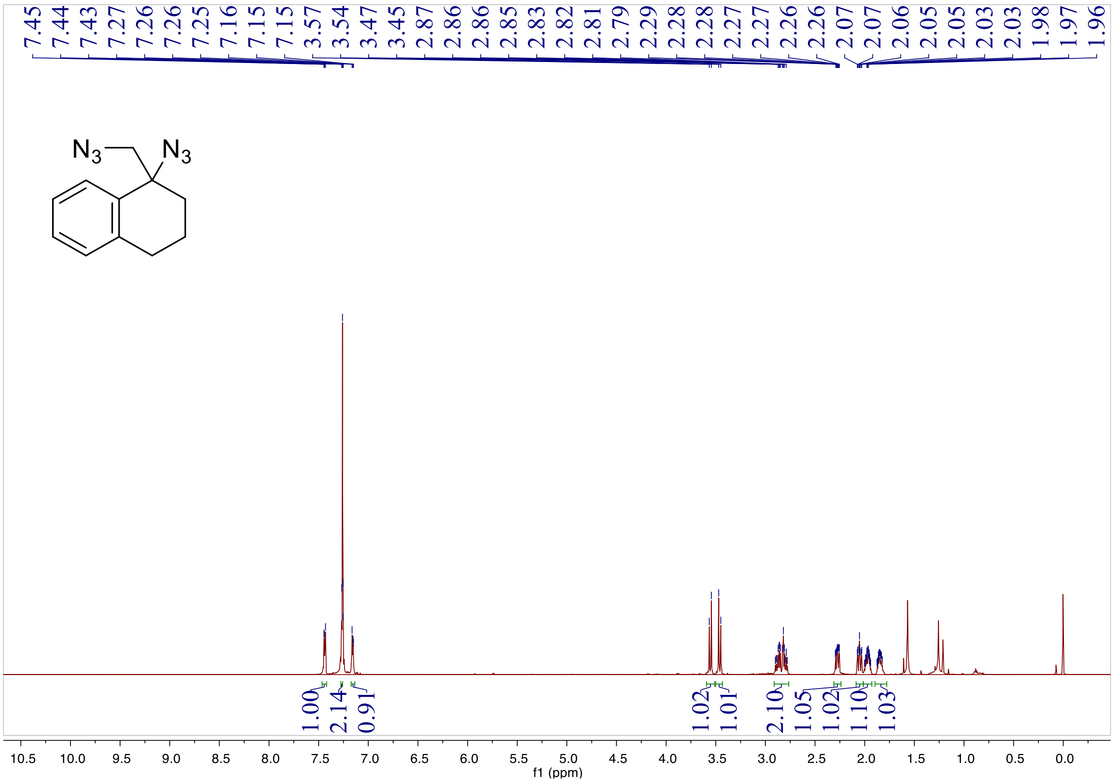

136.84
133.26
131.02
130.61
128.08
127.28
126.60
121.87
71.63
47.42
27.99
23.09
Cl2HC
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)

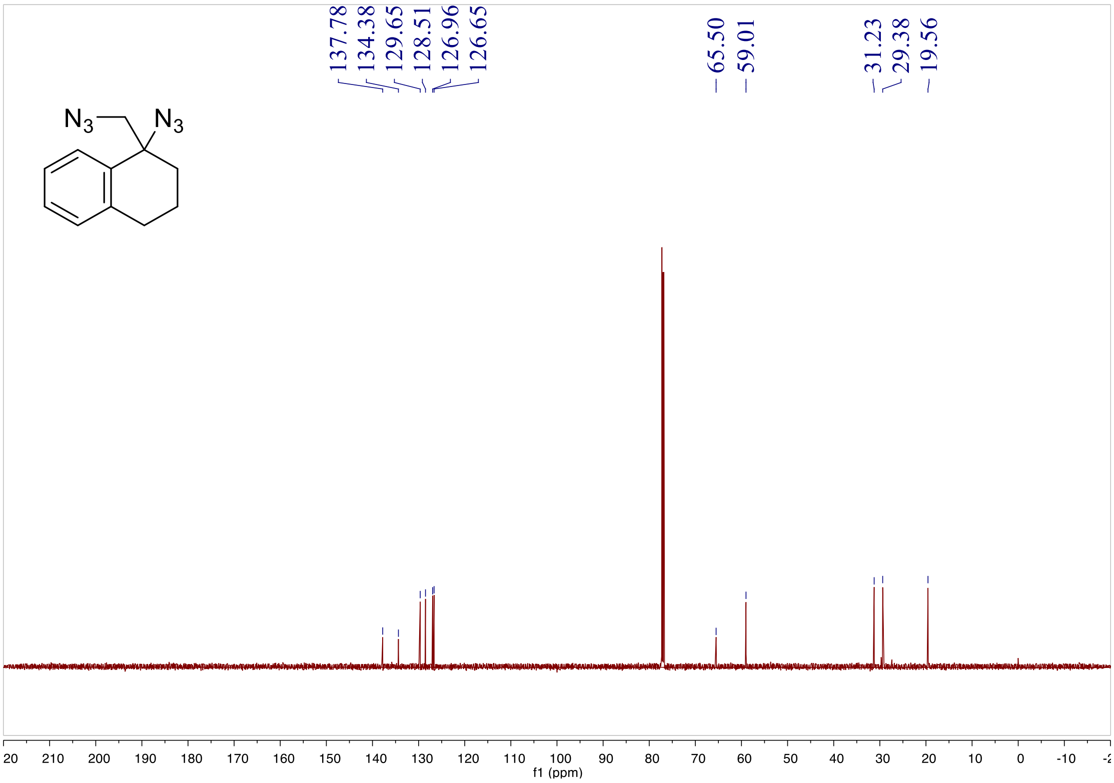

7.36
7.35
7.34
7.31
7.31
7.30
5.86
5.85
5.84
5.55
5.54
5.53
3.66
3.64
3.63
3.45
3.44
2.80
2.78
2.77
2.76
Cl_2HC
N_3
2.30
3.29
1.00
0.98
1.99
2.00
2.24
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


140.48
137.21
129.17
128.74
127.83
126.66
71.29
44.29
43.79
32.09
Cl_2HC
N_3
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)


7.33
7.32
7.32
7.32
4.17
4.16
4.15
3.35
3.35
3.34
3.34
3.33
3.33
3.32
3.31
2.92
2.92
2.91
2.91
2.89
2.89
N3
N3
4.29
1.80
2.03
2.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


142.55
138.05
129.27
127.83
125.22
122.99
73.42
70.11
35.46
19.78
N3
N3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.45
7.44
7.43
7.27
7.26
7.26
7.25
7.16
7.15
7.15
3.57
3.54
3.47
3.45
2.87
2.86
2.86
2.85
2.83
2.82
2.81
2.79
2.29
2.28
2.28
2.27
2.27
2.26
2.26
2.07
2.07
2.06
2.05
2.05
2.03
2.03
1.98
1.97
1.96
N3
N3
1.00
2.14
0.91
1.02
1.01
2.10
1.05
1.02
1.10
1.03
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


137.78
134.38
129.65
128.51
126.96
126.65
65.50
59.01
31.23
29.38
19.56
N3
N3
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)