Photochemical Intramolecular Amination for the Synthesis of Heterocycles.

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SUPPORTING INFORMATION

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General:

All reactions that were carried out under anhydrous conditions were performed under an inert argon or nitrogen atmosphere in glassware that had previously been dried overnight at 120 °C or had been flame dried and cooled under a stream of argon or nitrogen.[1] All chemical products were obtained from Sigma-Aldrich Chemical Company or Alfa Aesar and were reagent quality. The following products were prepared according to their respective literature procedures: Methyl (2*Z*,4*E*)-2-azido-5-phenylpenta-2,4-dienoate Technical solvents were obtained from VWR International Co. Anhydrous solvents (CH_2Cl_2, Et_2O, THF, DMF, toluene, and *n*-hexane) were dried and deoxygenated using a GlassContour system (Irvine, CA). Isolated yields reflect the mass obtained following flash column silica gel chromatography. Organic compounds were purified using the method reported by W. C. Still[2] and using silica gel obtained from Silicycle Chemical division (40-63 nm; 230-240 mesh). Analytical thin-layer chromatography (TLC) was performed on glass-backed silica gel 60 coated with a fluorescence indicator (Silicycle Chemical division, 0.25 mm, F_{254}.). Visualization of TLC plate was performed by UV (254 nm), $KMnO_4$ or *p*-anisaldehyde stains. All mixed solvent eluents are reported as v/v solutions. Concentration refers to removal of volatiles at low pressure on a rotary evaporator. All reported compounds were homogeneous by thin layer chromatography (TLC) and by ^{1}H NMR. NMR spectra were taken in deuterated $CDCl_3$ using Bruker AV-300 and AV-400 instruments unless otherwise noted. Signals due to the solvent served as the internal standard ($CHCl_3$: δ 7.27 for ^{1}H, δ 77.0 for ^{13}C). The acquisition parameters are shown on all spectra. The ^{1}H NMR chemical shifts and coupling constants were determined assuming first-order behavior. Multiplicity is indicated by one or more of the following: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad); the list of couplings constants (*J*) corresponds to the order of the multiplicity assignment. High resolution mass spectroscopy (HRMS) was done by the Centre régional de spectrométrie de masse at the Département de Chimie, Université de Montréal from an Agilent LC-MSD TOF system using ESI mode of ionization unless otherwise noted.

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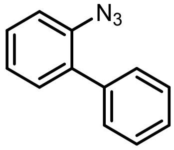
[1] Shriver, D. F.; Drezdon, M. A. in *The Manipulation of Air-Sensitive Compounds*; Wiley-VCH: New York, 1986.

[2] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

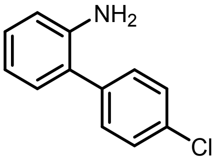
SYNTHESIS OF PRECURSORS

General Procedure for Suzuki Cross-Coupling (C): An oven-dried sealed tube was charged with 2-iodoaniline (1 equiv.), arylboronic acid (1.2 equiv.), K_2CO_3 (4 equiv.), $Pd(PPh_3)_2Cl_2$ (2 mol %) and a mixture of dimethoxyethane/water (1:1 [0.25 M]) under a nitrogen atmosphere. The mixture was stirred at 80 ºC for 18 h under nitrogen. Upon cooling, the biphasic solution was diluted with ethyl acetate (20 mL) and the phases were separated. The aqueous phase was extracted twice with EtOAc (20 mL) and the combined organic phases were washed with brine (50 mL). The organic phases were dried over Na_2SO_4, filtered and concentrated. The crude mixture was purified by silica gel column chromatography (hexanes/ethyl acetate) to afford corresponding product.

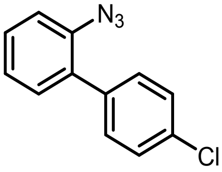
General Procedure for Sandmeyer reaction (D): The corresponding 2-aminobiaryl (1.0 equiv.) was dissolved in a mixture of acetic acid / water (2:1, 0.1 M) and cooled to 0 ºC. $NaNO_2$ (1.4 equiv.) was added and the resulting was stirred at 0 ºC for one hour. NaN_3 (1.5 equiv.) was then added slowly, the resulting mixture was warmed to room temperature and stirred for an additional hour. The solution was diluted with CH_2Cl_2 (20 mL) and made basic by the slow addition of saturated aqueous K_2CO_3 until bubbling ceased. The phases were separated and the aqueous phase was extracted twice with CH_2Cl_2 (20 mL). The combined organic phases were washed with water (50 mL) and brine (50 mL). The organic phases were dried over Na_2SO_4, filtered and concentrated. The crude mixture was purified by silica gel column chromatography (hexanes/ethyl acetate) to afford corresponding product.



2-Azido-1,1'-biphenyl (1): Following the General Procedure D, starting from [1,1'-biphenyl]-2-amine (1.0 g, 5.9 mmol), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a yellow solid (1.08 g, 94 % yield). NMR data was in accordance with what was previously reported.[3]



4'-Chloro-[1,1'-biphenyl]-2-amine (S1): Following the General Procedure C, starting from 4-chlorophenylboronic acid (0.28 g, 1.8 mmol, 1.2 equiv.), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a brown oil (0.25 g, 81 % yield). NMR data was in accordance with what was previously reported.[4]



2-Azido-4'-chloro-1,1'-biphenyl (2): Following the General Procedure D, starting from 4'-chloro-[1,1'-biphenyl]-2-amine **S1** (0.25 g, 1.2 mmol), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a yellow solid (0.20 g, 74 % yield). NMR data was in accordance with what was previously reported.[5]

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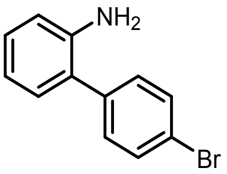
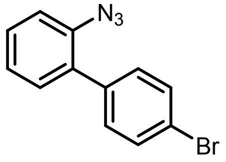
[3] Stokes, B. J.; Jovanović, B.; Dong, H.; Richert, K. J.; Riell, R. D.; Driver, T. G. *J. Org. Chem.* **2009**, *74*, 3225-3228

[4] Liang, Z.; Feng, R.; Yin, H.; Zhang, Y. *Org. Lett.* **2013**, *15*, 4544-4547

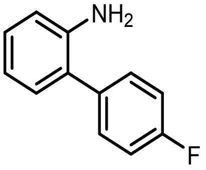
[5] Nagaki, A.; Ichinari, D.; Yoshida, J. *J. Am. Chem. Soc.* **2014**, *136*, 12245-12248



4’-Bromo-[1,1’-biphenyl]-2-amine (S2): Following the General Procedure C, starting from 4-bromophenylboronic acid (0.36 g, 1.8 mmol, 1.2 equiv.), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a yellow solid (0.25 g, 68 % yield). NMR data was in accordance with what was previously reported.[6]



2-Azido-4’-bromo-1,1’-biphenyl (3): Following the General Procedure D, starting from 4’-bromo-[1,1’-biphenyl]-2-amine **S2** (0.25 g, 1.0 mmol), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a yellow solid (0.23 g, 84 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.55 (d, J = 8.5 Hz, 2H,), 7.44-7.38 (m, 1H), 7.34-7.29 (m, 3H), 7.26-7.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 137.1, 137.0, 132.4, 131.3, 131.0, 129.1, 125.0, 121.8, 118.8; HRMS (ESI) m/z calculated for $C_{12}H_7BrN$ $[M-N_2-H]^+$ 243.9751; found 243.9762.



4’-Fluoro-[1,1’-biphenyl]-2-amine (S3): Following the General Procedure C, starting from 4-fluorophenylboronic acid (0.17 g, 1.2 mmol, 1.2 equiv.), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a brown solid (0.15 g, 83 % yield). NMR data was in accordance with what was previously reported.[3]

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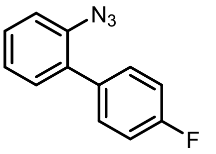
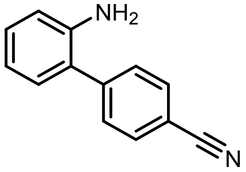
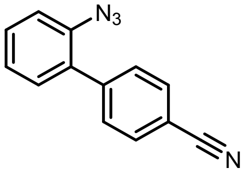
[6] Ohwada, A.; Nara, S.; Sakamoto, T.; Kikugawa, Y. *J. Chem. Soc., Perkin Trans. I*, **2001**, 3064-3068



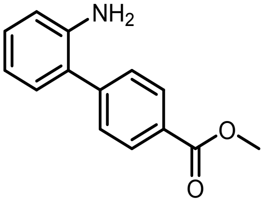
2-Azido-4’-fluoro-1,1’-biphenyl (S4): Following the General Procedure D, starting from 4’-fluoro-[1,1’-biphenyl]-2-amine **S3** (0.15 g, 0.8 mmol), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (0.15 g, 87 % yield). NMR data was in accordance with what was previously reported.[3]



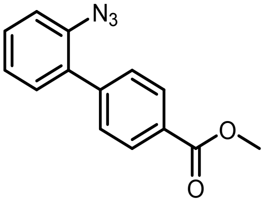
2’-Amino-[1,1’-biphenyl]-4-carbonitrile (S5): Following the General Procedure C, starting from 4-cyanophenylboronic acid (0.18 g, 1.2 mmol, 1.2 equiv.), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 30 % ethyl acetate in hexanes), to afford the desired product as a yellow solid (0.18 g, 92 % yield). NMR data was in accordance with what was previously reported.[3]



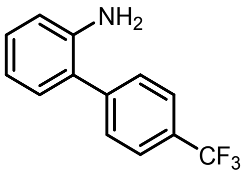
2’-Azido-[1,1’-biphenyl]-4-carbonitrile (S6): Following the General Procedure D, starting from 2’-amino-[1,1’-biphenyl]-4-carbonitrile **S5** (0.18 g, 0.9 mmol), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a yellow solid (0.08 g, 41 % yield). NMR data was in accordance with what was previously reported.[3]



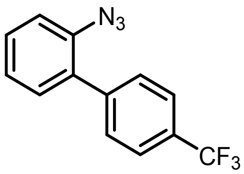
Methyl 2’-amino-[1,1’-biphenyl]-4-carboxylate (S7): Following the General Procedure C, starting from 4-methoxycarbonylphenylboronic acid (0.43 g, 2.4 mmol, 1.2 equiv.), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 15 % ethyl acetate in hexanes), to afford the desired product as a pale yellow solid (0.29 g, 65 % yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 8.12 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H) 7.20 (ddd, *J* = 7.5, 7.5, 1.7 Hz, 1H), 7.14 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.85 (ddd, *J* = 7.5, 7.5, 1.1 Hz, 1H), 6.79 (dd, *J* = 7.9, 0.9 Hz, 1H), 3.96 (s, 3H), 3.76 (brs, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ = 166.7, 144.3, 143.3, 130.2, 129.9, 129.0, 128.9, 128.7, 126.1, 118.6, 115.7, 51.9; HRMS (ESI) m/z calculated for $C_{14}H_{13}NO_2H$ [M+H]$^+$ 228.1015; found 228.1019.



Methyl 2'-azido-[1,1'-biphenyl]-4-carboxylate (S8): Following the General Procedure D, starting from methyl 2'-amino-[1,1'-biphenyl]-4-carboxylate **S7** (0.29 g, 1.3 mmol), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a yellow solid (0.29 g, 88 % yield). ^{1}H NMR (300 MHz, CDCl$_3$) δ = 8.11 (d, *J* = 8.6 Hz, 2H), 7.54 (d, *J* = 8.6 Hz, 2H), 7.47-7.41 (m, 1H), 7.36 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.30-7.21 (m, 2H), 3.95 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ = 166.9, 142.8, 137.2, 132.6, 131.1, 129.5, 129.4, 129.3, 129.1; 125.0, 118.8, 52.1; HRMS (ESI) m/z calculated for $C_{14}H_{11}N_3O_2H$ [M+H]$^+$ 254.0921; found 254.0924.

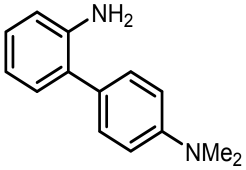


4'-(Trifluoromethyl)-[1,1'-biphenyl]-2-amine (S9): Following the General Procedure C, starting from 4-(trifluoromethyl)phenylboronic acid (0.23 g, 1.2 mmol, 1.2 equiv.), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a tan oil (0.20 g, 83 % yield). NMR data was in accordance with what was previously reported.[3]

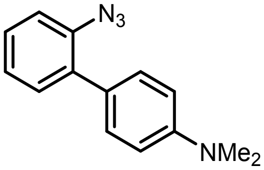


2-Azido-4'-trifluoromethyl-1,1'-biphenyl (S10): Following the General Procedure D, starting from 4'-(trifluoromethyl)-[1,1'-biphenyl]-2-amine **S9** (0.20 g, 0.8 mmol), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10

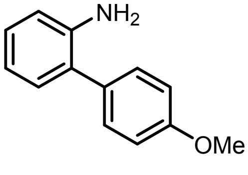
% ethyl acetate in hexanes), to afford the desired product as a clear oil (0.16 g, 78 % yield). NMR data was in accordance with what was previously reported.[3]



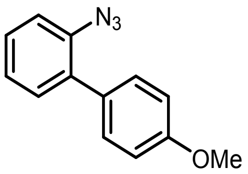
***N*4',*N*4'-Dimethyl-[1,1'-biphenyl]-2,4'-diamine (S11):** Following the General Procedure C, starting from 4-(dimethylamino)phenylboronic acid (0.20 g, 1.2 mmol, 1.2 equiv.), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a red oil (0.19 g, 88 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 (d, *J* = 8.6 Hz, 1H), 7.15-7.10 (m, 2H), 6.84-6.76 (m, 4H), 3.79 (brs, 2H), 3.01 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.5, 143.7, 130.3, 129.6, 127.7, 127.6, 127.2, 118.4, 115.3, 112.6, 40.4; HRMS (ESI) m/z calculated for $C_{14}H_{16}N_2H$ [M+H]$^+$ 213.1377; found 213.1386.



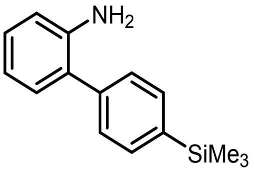
2'-Azido-*N*,*N*-dimethyl-[1,1'-biphenyl]-4-amine (S12): Following the General Procedure D, starting from *N*$^{4'}$,*N*$^{4'}$-dimethyl-[1,1'-biphenyl]-2,4'-diamine **S11** (0.19 g, 0.9 mmol), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a yellow solid (0.19 g, 90 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38-7.32 (m, 4H), 7.25-7.17 (m, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 3.01 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.8, 136.8, 133.9, 190.9, 130.1, 127.6, 125.8, 124.8, 118.6, 111.9, 40.4; HRMS (ESI) m/z calculated for $C_{14}H_{14}N_4H$ [M+H]$^+$ 239.1296; found 239.1291.



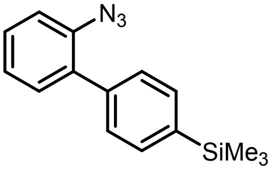
4'-Methoxy-[1,1'-biphenyl]-2-amine (S13): Following the General Procedure C, starting from 4-methoxyphenylboronic acid (0.18g, 1.2 mmol, 1.2 equiv.), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a pale yellow oil (0.19 g, 97 % yield). NMR data was in accordance with what was previously reported.[3]



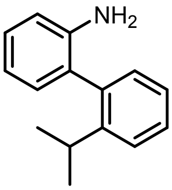
2-Azido-4’-methoxy-1,1’-biphenyl (S14): Following the General Procedure D, starting from 4’-methoxy-[1,1’-biphenyl]-2-amine **S13** (0.19 g, 0.97 mmol), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a yellow solid (0.19 g, 89 % yield). NMR data was in accordance with what was previously reported.[3]



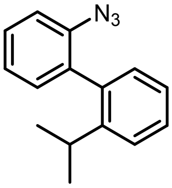
4’-(Trimethylsilyl)-[1,1’-biphenyl]-2-amine (S15): Following the General Procedure C, starting from (4-(trimethylsilyl)phenyl)boronic acid (0.35 g, 1.8 mmol, 1.2 equiv.), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 5 % ethyl acetate in hexanes), to afford the desired product as a yellow oil (0.31 g, 86 % yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.61 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.19-7.14 (m, 2 H), 6.83 (ddd, *J* = 7.4, 7.4, 1.2 Hz, 1H), 6.78 (dd, *J* = 8.0, 0.8 Hz, 1 H), 3.78 (brs, 2H), 0.32 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ = 143.5, 139.9, 139.2, 133.8, 130.4, 128.5, 128.3, 127.6, 118.6, 115.6, -1.1; HRMS (ESI) m/z calculated for $C_{15}H_{19}NSiH$ [M+H]$^+$ 242.1356; found 242.1359.



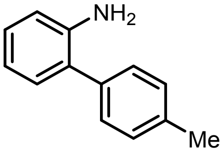
(2’-Azido-[1,1’-biphenyl]-4-yl)trimethylsilane (S16): Following the General Procedure D, starting from 4’-(trimethylsilyl)-[1,1’-biphenyl]-2-amine **S15** (0.31 g, 1.3 mmol), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 5 % ethyl acetate in hexanes), to afford the desired product as a pale yellow solid (0.26 g, 74 % yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.61 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.43-7.39 (m, 1H), 7.36 (dd, J_1 = 7.6 Hz, J_2 = 1.5 Hz, 1H), 7.29-7.27 (m, 1H), 7.25-7.21 (m, 1H), 0.32 (s, 9H) ; ^{13}C NMR (100 MHz, CDCl$_3$) δ = 139.5, 138.5, 137.1, 133.6, 133.1, 131.2, 128.7, 128.6, 124.9, 118.6, -1.1; HRMS (ESI) m/z calculated for $C_{15}H_{17}N_3SiNH_4$ [M+NH$_4$]$^+$ 285.1522; found 285.1530.



2’-Isopropyl-[1,1’-biphenyl]-2-amine (S17): Following the General Procedure C, starting from 1-bromo-2-isopropylbenzene (0.17 mL, 1.1 mmol, 1.1 equiv.) and 2-aminophenylboronic acid hydrochloride (0.17 g, 1.0 mmol, 1.0 equiv.), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a tan oil (0.22 g, 99 % yield). NMR data was in accordance with what was previously reported.[7]



2-Azido-2’-isopropyl-1,1’-biphenyl (S18): Following the General Procedure D, starting from 2’-isopropyl-[1,1’-biphenyl]-2-amine **S17** (0.22 g, 1.0 mmol), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a pale brown solid (0.15 g, 68 % yield). NMR data was in accordance with what was previously reported.[7]



4’-Methyl-[1,1’-biphenyl]-2-amine (S19): Following the General Procedure C, starting from 4-methylphenylboronic acid (0.16 g, 1.2 mmol, 1.2 equiv.), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a clear oil (0.15 g, 83 % yield). NMR data was in accordance with what was previously reported.[3]

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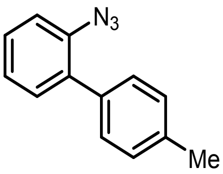
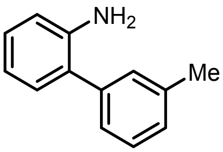
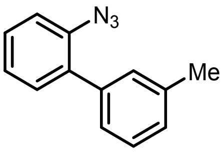
[7] Intrieri, D.; Mariani, M.; Caselli, A.; Ragaini, F.; Gallo, E. *Chem. Eur. J.* **2012**, *18*, 10487-10490



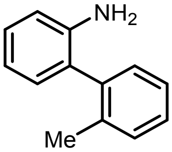
2-Azido-4’-methyl-1,1’-biphenyl (S20): Following the General Procedure D, starting from 4’-methyl-[1,1’-biphenyl]-2-amine **S19** (0.15 g, 0.8 mmol), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a clear oil (0.13 g, 79 % yield). NMR data was in accordance with what was previously reported.[3]



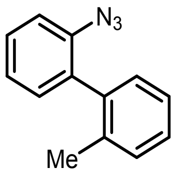
3’-Methyl-[1,1’-biphenyl]-2-amine (S21): Following the General Procedure C, starting from 3-methylphenylboronic acid (0.16 g, 1.2 mmol, 1.2 equiv.), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a tan oil (0.14 g, 76 % yield). NMR data was in accordance with what was previously reported.[3]



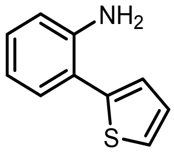
2-Azido-3’-methyl-1,1’-biphenyl (S22): Following the General Procedure D, starting from 3’-methyl-[1,1’-biphenyl]-2-amine **S21** (0.14 g, 0.8 mmol), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a tan oil (0.12 g, 77 % yield). NMR data was in accordance with what was previously reported.[3]



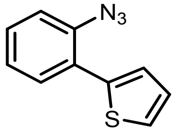
2’-Methyl-[1,1’-biphenyl]-2-amine (S23): Following the General Procedure C, starting from 2-methylphenylboronic acid (0.16 g, 1.2 mmol, 1.2 equiv.), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a tan oil (0.15 g, 84 % yield). NMR data was in accordance with what was previously reported.[3]



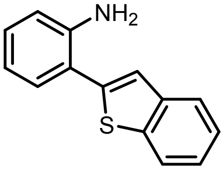
2-Azido-2'-methyl-1,1'-biphenyl (S24): Following the General Procedure D, starting from 2'-methyl-[1,1'-biphenyl]-2-amine **S23** (0.15 g, 0.8 mmol), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a tan oil (0.15 g, 84 % yield). NMR data was in accordance with what was previously reported.[3]



2-(Thiophen-2-yl)aniline (S25): Following the General Procedure C, starting from 2-thienylboronic acid (0.31 g, 2.4 mmol, 1.2 equiv.), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a tan oil (0.30 g, 84 % yield). NMR data was in accordance with what was previously reported.[8]



2-(2-Azidophenyl)thiophene (S26): Following the General Procedure D, starting from 2-(thiophen-2-yl)aniline **S25** (0.30 g, 1.7 mmol), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a tan oil (0.30 g, 89 % yield). NMR data was in accordance with what was previously reported.[9]



2-(Benzo[*b*]thiophen-2-yl)aniline (S27): Following the General Procedure C, starting from benzo[*b*]thien-2-ylboronic acid (0.43 g, 2.4 mmol, 1.2 equiv.), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate

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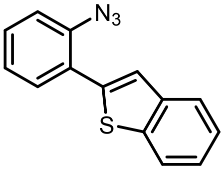
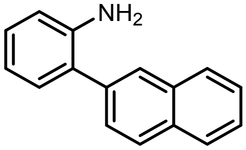
[8] Liang, Z.; Ju, L.; Xie, Y.; Huang, L.; Zhang, Y. *Chem. Eur. J.* **2012**, *18*, 15816-15821

[9] Alt, I. T.; Plietker, B. *Angew. Chem. Int. Ed.* **2016**, *55,* 1519-1522

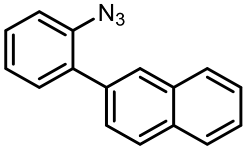
in hexanes), to afford the desired product as a white solid (0.36 g, 79 % yield). NMR data was in accordance with what was previously reported.[10]



2-(2-Azidophenyl)benzo[*b*]thiophene (S28): Following the General Procedure D, starting from 2-(benzo[*b*]thiophen-2-yl)aniline **S27** (0.36 g, 1.6 mmol), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a pale yellow solid (0.14 g, 35 % yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.88-7.82 (m, 2H), 7.72 (s, 1H), 7.68 (dd, J_1 = 7.7, 1.5 Hz, 1H) 7.43-7.33 (m, 3H), 7.30 (dd, J = 8.1, 0.9 Hz, 1H), 7.24-7.20 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ = 140.0, 139.9, 139.2, 136.9, 130.7, 129.2, 125.9, 125.0, 124.5, 124.4, 123.8, 123.7, 121.9, 119.1; HRMS (ESI) m/z calculated for $C_{14}H_8NS$ [M-N$_2$-H]$^+$ 222.0376; found 222.0378.



2-(Naphthalen-2-yl)aniline (S29): Following the General Procedure C, starting from 2-naphthylboronic acid (0.41 g, 2.4 mmol, 1.2 equiv.), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a yellow oil (0.36 g, 82 % yield). NMR data was in accordance with what was previously reported.[9]



2-(2-Azidophenyl)naphthalene (S30): Following the General Procedure D, starting from 2-(naphthalen-2-yl)aniline **S29** (0.36 g, 1.6 mmol), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a yellow oil (0.34 g, 93 % yield). NMR data was in accordance with what was previously reported.[9]

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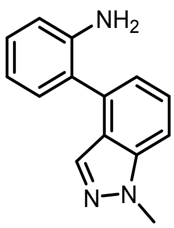
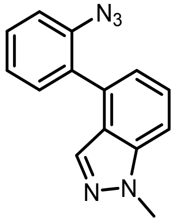
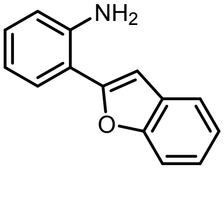
[10] David, E.; Pellet-Rostaing, S.; Lemaire, M. *Tetrahedron*, **2007**, *63*, 8999-9006



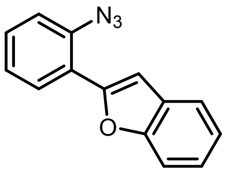
2-(1-Methyl-1*H*-indazol-4-yl)aniline (S31): Following the General Procedure C, starting from 1-methyl-4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-1*H*-indazole (0.57 g, 2.2 mmol, 1.1 equiv.), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 20 % ethyl acetate in hexanes), to afford the desired product as a tan oil (0.39 g, 87 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.90$ (d, $J = 0.7$ Hz, 1H), 7.48 (dd, $J = 8.4, 7.0$ Hz, 1H), 7.40 (d, $J = 8.4$ Hz, 1 H), 7.27-7.19 (m, 3H), 6.90-6.83 (m, 2H), 4.13 (s, 3H), 3.76 (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 143.8$, 140.2, 132.9, 132.8, 130.7, 128.9, 126.6, 124.8, 123.2, 121.1, 118.4, 115.7, 107.9, 35.7; HRMS (ESI) m/z calculated for $C_{14}H_{13}N_3H$ [M+H]$^+$ 224.1186; found 224.1182.



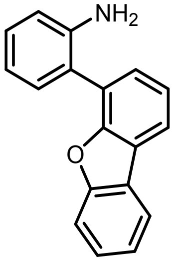
4-(2-Azidophenyl)-1-methyl-1*H*-indazole (S32): Following the General Procedure D, starting from 2-(1-methyl-*1H*-indazol-4-yl)aniline **S31** (0.39 g, 1.7 mmol), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 15 % ethyl acetate in hexanes), to afford the desired product as a tan solid (0.29 g, 71 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.84$ (d, $J = 0.7$ Hz, 1H), 7.51-7.42 (m, 4H), 7.34 (d, $J = 7.7$ Hz, 1H), 7.30-7.26 (m, 1H), 7.16 (dd, $J = 6.8, 0.9$ Hz, 1H), 4.13 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 139.9$, 137.7, 132.6, 131.6, 131.5, 131.4, 129.2, 126.0, 124.9, 123.4, 121.6, 118.9, 108.4, 35.6; HRMS (ESI) m/z calculated for $C_{14}H_{11}N_5H$ [M+H]$^+$ 250.1092; found 250.1087 .



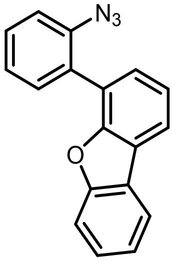
2-(Benzofuran-2-yl)aniline (S33): Following the General Procedure C, starting from 2-benzofuranylboronic acid (0.39 g, 2.4 mmol, 1.2 equiv.), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a brown solid (0.41 g, 99 % yield). NMR data was in accordance with what was previously reported.[11]



2-(2-Azidophenyl)benzofuran (S34): Following the General Procedure D, starting from 2-(benzofuran-2-yl)aniline **S33** (0.41 g, 1.99 mmol), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a yellow solid (0.34 g, 72 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.08 (dd, J = 7.8, 1.2 Hz, 1H), 7.63 (dd, J = 7.3, 1.5 Hz, 1H), 7.54-7.51 (m, 2H), 7.43-7.22 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.0, 151.3, 136.3, 129.3, 129.1, 127.8, 124.9, 124.6, 122.9, 121.9, 121.3, 118.9, 110.9, 106.9; HRMS (ESI) m/z calculated for $C_{14}H_9N_3OH$ $[M+H]^+$ 236.0818; found 236.0822.



2-(Dibenzo[*b,d*]furan-4-yl)aniline (S35): Following the General Procedure C, starting from 4-(dibenzofuranyl)boronic acid (0.35 g, 1.7 mmol, 1.2 equiv.), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (0.26 g, 73 % yield). NMR data was in accordance with what was previously reported.[12]



4-(2-Azidophenyl)dibenzo[*b,d*]furan (S36): Following the General Procedure D, starting from 2-(dibenzo[*b,d*]furan-4-yl)aniline **S35** (0.26 g, 1.0 mmol), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (0.25 g, 89 % yield). NMR data was in accordance with what was previously reported.[13]

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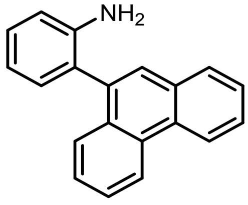
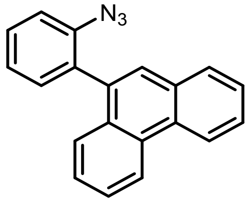
[11] Carril, M.; SanMartin, R.; Tellitu, I.; Dominguez, E. *Org. Lett.* **2006**, *8*, 1467-1470

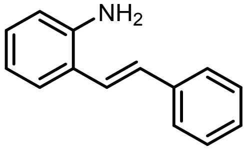
[12] Rong, J.; Deng, L.; Tan, P.; Ni, C.; Gu, Y.; Hu, J. *Angew Chem., Int. Ed.* **2016**, *55*, 2743-2747



2-(Phenanthren-9-yl)aniline (S37): Following the General Procedure C, starting from 9-phenanthracenylboronic acid (0.53 g, 2.4 mmol, 1.2 equiv.), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (0.45 g, 84 % yield). NMR data was in accordance with what was previously reported.[14]



9-(2-Azidophenyl)phenanthrene (S38): Following the General Procedure D, starting from 2-(phenanthren-9-yl)aniline **S37** (0.45 g, 1.7 mmol), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (0.40 g, 81 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.79 (d, *J* = 8.2 Hz, 1H), 8.75 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 7.7 Hz, 1H), 7.72-7.61 (m, 4H), 7.56-7.52 (m, 3H), 7.41 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 1 H), 7.33-7.29 (m, 1H); (100 MHz, $CDCl_3$) δ = 138.9, 134.9, 132.4, 132.2, 131.3, 131.1, 130.3 (2C), 129.2, 128.8, 128.1, 126.8 (2C), 126.7, 126.6, 126.5, 124.8, 122.9, 122.6, 118.4; HRMS (ESI) m/z calculated for $C_{20}H_{13}N_3NH_4$ $[M+NH_4]^+$ 313.1438; found 313.1448.



(***E***)**-2-Styrylaniline (S39):** Following the General Procedure C, starting from trans-2-phenylvinylboronic acid (0.53 g, 3.6 mmol, 1.2 equiv.), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a pale yellow solid (0.49 g, 83 % yield). NMR data was in accordance with what was previously reported.[9]

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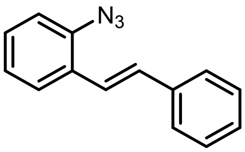
[13] Yang, L.; Li, H.; Zhang, H.; Lu, H. *Eur. J. Org. Chem.* **2016**, 5611-5615

[14] Wu, B.; Yoshikai, N. *Angew Chem., Int. Ed.* **2015**, *54*, 8736-8739



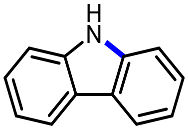
(*E*)-1-Azido-2-styrylbenzene (S40): Following the General Procedure D, starting from (*E*)-2-styrylaniline **S39** (0.20 g, 1.0 mmol), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a yellow solid (0.2 g, 88 % yield). NMR data was in accordance with what was previously reported.[9]

SYNTHESIS OF CARBAZOLES

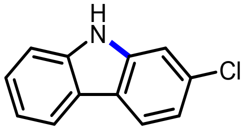
Figure S1. Continuous-flow reactor set-up used for the UV-light-mediated synthesis of heterocycles.

Photodecomposition Procedure at 254 nm under Continuous-Flow (A): A solution of biarylazide (0.15 mmol, 1.0 equiv.) and THF (5 mL, 30 mM) was injected via a syringe into an aluminium foil-covered 5 mL injection loop (6-way valve). The carrier solvent was pumped by a Syrris Asia pumping module. The pump was turned on at a flow rate of 1.6 mL/min. The reaction mixture was pumped through a 16 mL FEP-coiled reactor irradiated with 254 nm light source for a 10 minutes residence time. The collected solution was concentrated under vacuum to provide a crude reaction mixture which was purified by column chromatography on silica-gel (hexanes/ethyl acetate) to afford corresponding product.

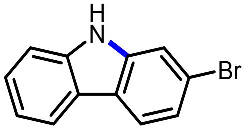
Photodecomposition Procedure at 394 nm under Continuous-Flow (B): A solution of biarylazide (0.15 mmol, 1.0 equiv.) and THF (5 mL, 30 mM) was injected via a syringe into an aluminium foil-covered 5 mL injection loop (6-way valve). The carrier solvent was pumped by a Syrris Asia pumping module. The pump was turned on at a flow rate of 0.0542 mL/min. The reaction mixture was pumped through a 13 mL PFA-coiled reactor irradiated with 394 nm (purple LED light source) for a 4 hours residence time. The collected solution was concentrated under vacuum to provide a crude reaction mixture which was purified by column chromatography on silica-gel (hexanes/ethyl acetate) to afford corresponding product.



9*H*-Carbazole (4): Following the Photodecomposition Procedure A, starting from 2-azido-1,1'-biphenyl **1**, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (20.0 mg, 80 % yield). Following the Photodecomposition Procedure B, starting from 2-azido-1,1'-biphenyl **1**, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (20.0 mg, 80 % yield). NMR data was in accordance with what was previously reported.[3]



2-Chloro-9*H*-carbazole (5): Following the Photodecomposition Procedure A, starting from 2-azido-4'-chloro-1,1'-biphenyl, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (18.5 mg, 61 % yield). Following the Photodecomposition Procedure B, starting from 2-azido-4'-chloro-1,1'-biphenyl, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a yellow solid (22.8 mg, 81 % yield). NMR data was in accordance with what was previously reported.[15]



2-Bromo-9*H*-carbazole (6): Following the Photodecomposition Procedure A, starting from 2-azido-4'-bromo-1,1'-biphenyl, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (16.6 mg, 45 % yield). Following the Photodecomposition Procedure B, starting from 2-azido-4'-bromo-1,1'-biphenyl, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (29.6 mg, 80 % yield). NMR data was in accordance with what was previously reported.[15]

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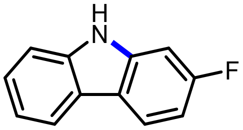
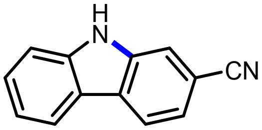
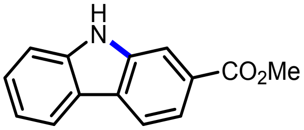
[15] Pan, J.; Wang, X.; Zhang, Y.; Buchwald, S. L. *Org. Lett.* **2011**, *13*, 4974-4976



2-Fluoro-9*H*-carbazole (7): Following the Photodecomposition Procedure A, starting from 2-azido-4’-fluoro-1,1’-biphenyl, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (24.2 mg, 87 % yield). Following the Photodecomposition Procedure B, starting from 2-azido-4’-fluoro-1,1’-biphenyl and using ethyl acetate as the solvent, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (19.7 mg, 71 % yield). NMR data was in accordance with what was previously reported.[3]



2-Cyano-9*H*-carbazole (8): Following the Photodecomposition Procedure A, starting from 2’-azido-[1,1’-biphenyl]-4-carbonitrile, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (22.5 mg, 78 % yield). Following the Photodecomposition Procedure B, starting from 2’-azido-[1,1’-biphenyl]-4-carbonitrile and using ethyl acetate as the solvent, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (19.9 mg, 69 % yield). NMR data was in accordance with what was previously reported.[16]



Methyl 9*H*-carbazole-2-carboxylate (9): Following the Photodecomposition Procedure A, starting from Methyl 2’-azido-[1,1’-biphenyl]-4-carboxylate, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (24.3 mg, 72 % yield). Following the Photodecomposition Procedure B, starting from Methyl 2’-azido-[1,1’-biphenyl]-4-carboxylate, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (27.7 mg, 82 % yield). NMR data was in accordance with what was previously reported.[16]

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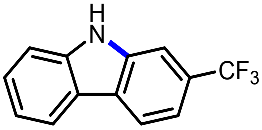
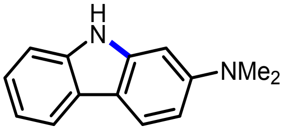
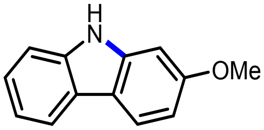
[16] Takamatsu, K.; Hirano, K.; Satoh, T.; Miura, M. *Org. Lett.* **2014**, *16*, 2892-2895



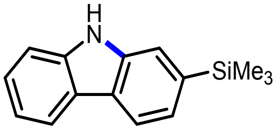
2-(Trifluoromethyl)-9*H*-carbazole (10): Following the Photodecomposition Procedure A, starting from 2-azido-4'-trifluoromethyl-1,1'-biphenyl, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (11.5 mg, 33 % yield). Following the Photodecomposition Procedure B, starting from 2-azido-4'-trifluoromethyl-1,1'-biphenyl and using ethyl acetate as the solvent, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (26.2 g, 74 % yield). NMR data was in accordance with what was previously reported.[3]



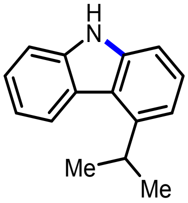
2-(Dimethylamino)-9*H*-carbazole (11): Following the Photodecomposition Procedure A, starting from 2'-azido-*N,N*-dimethyl-[1,1'-biphenyl]-4-amine, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a pale yellow solid (26.5 mg, 84 % yield). Following the Photodecomposition Procedure B, starting from 2'-azido-*N,N*-dimethyl-[1,1'-biphenyl]-4-amine and using ethyl acetate as the solvent, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a pale yellow solid (22.7 mg, 72 % yield). NMR data was in accordance with what was previously reported.[16]



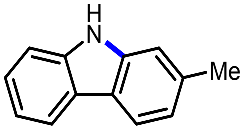
2-Methoxy-9*H*-carbazole (12): Following the Photodecomposition Procedure A, starting from 2-azido-4'-methoxy-1,1'-biphenyl, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (27.5 mg, 93 % yield). Following the Photodecomposition Procedure B, starting from 2-azido-4'-methoxy-1,1'-biphenyl and using ethyl acetate as the solvent, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (19.5 mg, 66 % yield). NMR data was in accordance with what was previously reported.[3]



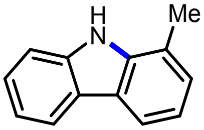
2-Methoxy-9*H*-carbazole (13): Following the Photodecomposition Procedure A, starting from 2-azido-4’-methoxy-1,1’-biphenyl, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a pale yellow solid (25.1 mg, 70 % yield). Following the Photodecomposition Procedure B, starting from 2-azido-4’-methoxy-1,1’-biphenyl, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a pale yellow solid (29.1 mg, 81 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.17 (s, 1H), 8.09 (m, 2H), 7.62 (s, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.40-7.37 (m, 1H), 7.29 (d, J = 7.4 Hz, 1H), 7.16-7.13 (m, 1H), 0.32 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 139.8, 139.5, 136.4, 125.7, 122.9 (2C), 122.2, 120.2, 119.6, 118.4, 115.6, 110.9, -0.8; HRMS (ESI) m/z calculated for $C_{15}H_{17}NSi$ $[M-H]^-$ 238.1052; found 238.1052.



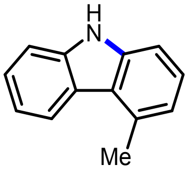
4-Isopropyl-9*H*-carbazole (14): Following the Photodecomposition Procedure A, starting from 2-azido-2’-isopropyl-1,1’-biphenyl, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a yellow solid (16.6 mg, 53 % yield). Following the Photodecomposition Procedure B, starting from 2-azido-2’-isopropyl-1,1’-biphenyl and using ethyl acetate as the solvant, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a yellow solid (16.0 mg, 51 % yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.29 (s, 1H), 8.11 (d, J = 8.1 Hz, 1H), 7.50 (d, J = 8.1 Hz, 1H), 7.39-7.31 (m, 3H), 7.19-7.15 (m, 1H), 7.08-7.03 (m, 1H), 3.92-3.82 (m, 1H), 1.41 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 143.9, 140.3, 140.1, 126.0, 125.2, 122.8, 122.2, 119.9, 119.1, 114.9, 111.2, 108.9, 30.2, 22.8 (2C); HRMS (ESI) m/z calculated for $C_{15}H_{15}N$ $[M-H]^-$ 208.1130; found 208.1126.



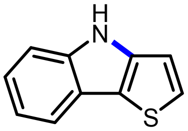
2-Methyl-9*H*-carbazole (15): Following the Photodecomposition Procedure A, starting from 2-azido-4’-methyl-1,1’-biphenyl, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (18.8 mg, 69 % yield). Following the Photodecomposition Procedure B, starting from 2-azido-4’-methyl-1,1’-biphenyl, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (23.9 mg, 88 % yield). NMR data was in accordance with what was previously reported.[3]



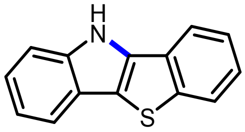
1-Methyl-9*H*-carbazole (16): Following the Photodecomposition Procedure A, starting from 2-azido-3’-methyl-1,1’-biphenyl, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford an inseparable mixture of regioisomers as a pale yellow solid (21.5 mg, 79 % yield, 70:30). Following the Photodecomposition Procedure B, starting from 2-azido-3’-methyl-1,1’-biphenyl, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford an inseparable mixture of regioisomers as a pale yellow solid (25.8 mg, 95 % yield, 53:47). NMR data was in accordance with what was previously reported.[3]



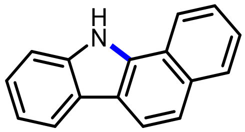
4-Methyl-9*H*-carbazole (17): Following the Photodecomposition Procedure A, starting from 2-azido-2’-methyl-1,1’-biphenyl, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (22.6 mg, 83 % yield). Following the Photodecomposition Procedure B, starting from 2-azido-2’-methyl-1,1’-biphenyl and using ethyl acetate as the solvant, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (24.5 mg, 90 % yield). NMR data was in accordance with what was previously reported.[3]



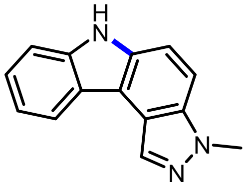
4*H*-Thieno[3,2-b]indole (18): Following the Photodecomposition Procedure A, starting from 2-(2-azidophenyl)thiophene, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (17.9 mg, 69 % yield). Following the Photodecomposition Procedure B, starting from 2-(2-azidophenyl)thiophene, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (19.7 mg, 76 % yield). NMR data was in accordance with what was previously reported.[16]



10*H*-Benzo[4,5]thieno[3,2-*b*]indole (19): Following the Photodecomposition Procedure A, starting from 2-(2-azidophenyl)benzo[*b*]thiophene, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (24.1 mg, 72 % yield). Following the Photodecomposition Procedure B, starting from 2-(2-azidophenyl)benzo[b]thiophene, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (19.1 mg, 57 % yield). NMR data was in accordance with what was previously reported.[16]



11*H*-Benzo[*a*]carbazole (20): Following the Photodecomposition Procedure A, starting from 2-(2-azidophenyl)naphthalene, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (22.5 mg, 69 % yield). Following the Photodecomposition Procedure B, starting from 2-(2-azidophenyl)naphthalene, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (27.4 mg, 84 % yield). NMR data was in accordance with what was previously reported.[17]



3-Methyl-3,6-dihydropyrazolo[3,4-*c*]carbazole (21): Following the Photodecomposition Procedure A, starting from 4-(2-azidophenyl)-1-methyl-1*H*-indazole, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 25 % ethyl acetate in hexanes), to afford the desired product as a yellow solid (23.2 mg, 70 % yield). Following the Photodecomposition Procedure B, starting from 4-(2-azidophenyl)-1-methyl-1*H*-indazole, the crude mixture was purified by silica gel

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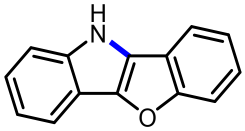
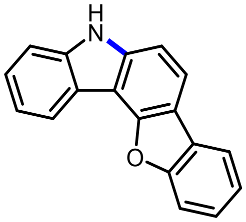
[17] Budén, M. E.; Vaillard, V. A.; Martin, S. E.; Rossi, R. A. *J. Org. Chem.* **2009**, *74*, 4490-4498

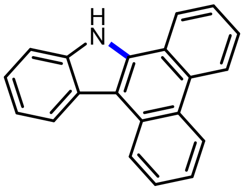
column chromatography (100 % hexanes → 25 % ethyl acetate in hexanes), to afford the desired product as a yellow solid (28.5 mg, 86 % yield). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ = 11.49 (s, 1H) 8.57 (d, *J* = 0.9 Hz, 1H), 8.32 (d, *J* = 8.1 Hz, 1H), 7.67 (dd, *J* =9.0, 0.7 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H) 7.57 (d, *J* = 8.1 Hz, 1H) 7.40-7.37 (m, 1H), 7.24-7.20 (m, 1H), 4.15 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ = 138.8, 135.7, 134.2, 129.7, 124.4, 121.8, 121.1, 118.6, 116.8, 112.2, 111.5, 111.3, 108.1, 35.8; HRMS (ESI) m/z calculated for $C_{14}H_{11}N_3H$ [M+H]$^+$ 222.1036; found 222.1026.



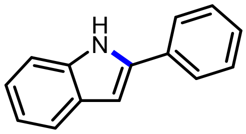
10*H*-Benzofuro[3,2-*b*]indole (22): Following the Photodecomposition Procedure A, starting from 2-(2-azidophenyl)benzofuran, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (23.6 g, 76 % yield). Following the Photodecomposition Procedure B, starting from 2-(2-azidophenyl)benzofuran, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (14.6 mg, 47 % yield). NMR data was in accordance with what was previously reported.[16]



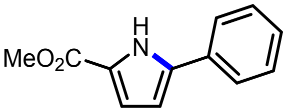
5*H*-Benzofuro[3,2-*c*]carbazole (23): Following the Photodecomposition Procedure A, starting from 4-(2-azidophenyl)dibenzo[*b,d*]furan, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a yellow crystalline solid (22.0 mg, 57 % yield). Following the Photodecomposition Procedure B, starting from 4-(2-azidophenyl)dibenzo[b,d]furan, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a yellow crystalline solid (35.9 mg, 93 % yield). NMR data was in accordance with what was previously reported.[13]



9*H*-Dibenzo[*a,c*]carbazole (24): Following the Photodecomposition Procedure A, starting from 9-(2-Azidophenyl)phenanthrene, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a yellow solid (30.5 mg, 76 % yield). Following the Photodecomposition Procedure B, starting from 2-azido-1,1'-biphenyl, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a yellow solid (22.1 mg, 55 % yield). NMR data was in accordance with what was previously reported.[17]



2-Phenyl-1*H*-indole (25): Following the Photodecomposition Procedure A, starting from (*E*)-1-Azido-2-styrylbenzene, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (19.6 mg, 66 % yield). Following the Photodecomposition Procedure B, starting from 2-azido-1,1'-biphenyl, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (22.9 mg, 79 % yield). NMR data was in accordance with what was previously reported.[18]



Methyl 5-phenyl-1*H*-pyrrole-2-carboxylate (26): Following the Photodecomposition Procedure A, starting from 2-azido-1,1'-biphenyl, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (15.1 mg, 50 % yield). Following the Photodecomposition Procedure B, starting from 2-azido-1,1'-biphenyl, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (25.1 mg, 83 % yield). NMR data was in accordance with what was previously reported.[19]

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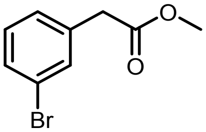
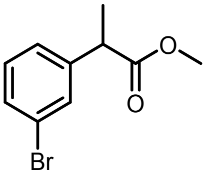
[18] Shen, M.; Leslie, B. E.; Driver, T. G. *Angew. Chem., Int. Ed.* **2008**, *47*, 5056-5059

[19] Dong, H.; Shen, M.; Redford, J. E.; Stokes, B. J.; Pumphrey, A. L.; Driver, T. G. *Org. Lett.* **2007**, *9*, 5191-5194

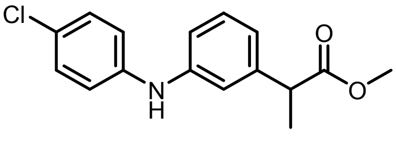
SYNTHESIS OF METHYL CARPROFEN



Methyl 2-(3-bromophenyl)aceteta (S41): An oven-dried sealed tube was charge with 3-bromophenyl acetic acid (2.15 g, 10 mmol, 1 equiv.), sulfuric acid (catalytic amount) and methanol (20 mL, 0.5 M). The mixture was stirred at 65 ºC for 16 h. Upon cooling, the reaction mixture was diluted with ethyl acetate (50 mL) and water (50 mL), the phases were separated. The aqueous phase was extracted twice with EtOAc (20 mL) and the combined organic phases were washed with brine (50 mL). The organic phases were dried over Na_2SO_4, filtered and concentrated. The crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a clear oil (2.07 g, 90 % yield). NMR data was in accordance with what was previously reported.[20]



Methyl 2-(3-bromophenyl)propanoate (S42): Methyl 2-(3-bromophenyl)acetate **S41** (1.77 g, 7.7 mmol) in dry THF (15 mL) was added dropwise to a stirred solution of lithium diisopropylamide (LDA) (8.9 mmol, 1.15 equiv.) in THF (20 mL) at -78 ºC under nitrogen (N_2), and after 30 min, iodomethane (0.5 mL, 8.1 mmol) was added slowly. The resulting solution was stirred for 2 h with the temperature changed from -78 to 0 ºC, then evaporated to dryness, and extracted with CH_2Cl_2 (50 mL). The organic phases were dried over Na_2SO_4, filtered and concentrated. The crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a clear oil (1.28 g, 68 % yield). NMR data was in accordance with what was previously reported.[21]



Methyl 2-(3-((4-chlorophenyl)amino)phenyl)propanoate (27): An oven-dried sealed tube was charged with 4-chloroaniline (0.42 g, 3.3 mmol, 1.1 equiv.), Cs_2CO_3 (1.47 g, 4.5 mmol, 1.5 equiv.), xPhos (0.11 mg, 0.24 mmol, 8 mol %), $Pd_2(dba)_3$ (27.0 mg, 0.12

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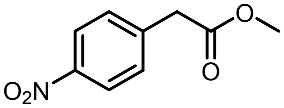
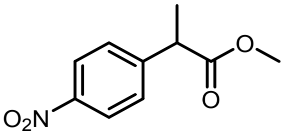
[20] Hutchby, M.; Houlden, C. E.; Haddow, M. F.; Tyler, S. N. G.; Lloyd-Jones, G. C.; Booker-Milburn, K. I. *Angew. Chem., Int. Ed.* **2012**, *51*, 548-551

[21] Dang, T.T.; Seayad A. M. *Adv. Synth. Catal.* **2016**, *358*, 3373 –3380

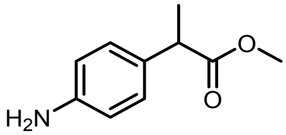
mmol, 4 mol %), anhydrous toluene (15 mL, 0.20 M) and methyl 2-(3-bromophenyl)propanoate **S42** (0.73 g, 3.0 mmol, 1.0 equiv.) under a nitrogen atmosphere. The mixture was stirred at 100 °C for 24 h under nitrogen. Upon cooling, the reaction mixture was diluted with dichloromethane (30 mL), filtered on Celite® and then dried over Na_2SO_4. Concentration under reduced pressure afforded the crude product that was purified by silica gel column chromatography (5% ethyl acetate in hexanes) to afford the desired product as yellow oil (0.67 g, 77 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.25-7.21 (m, 3H), 7.01-6.95 (m, 4H), 6.89-6.87 (m, 1H), 5.61 (brs, 1H), 3.71-3.66 (m, 4H), 1.49 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 174.9, 142.9, 141.7, 141.5, 129.5, 129.1, 125.3, 120.2, 118.7, 116.8, 116.2, 51.9, 45.2, 18.3; HRMS (ESI) m/z calculated for $C_{16}H_{16}ClNO_2H$ $[M+H]^+$ 290.0929; found 290.0942.



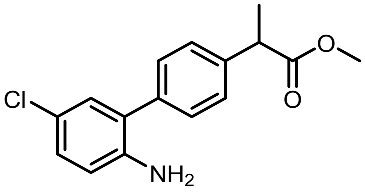
Methyl 2-(4-nitrophenyl)acetate (S43): An oven-dried sealed tube was charged with 4-nitrophenyl acetic acid (5.44 g, 30 mmol, 1 equiv.), sulfuric acid (catalytic amount) and methanol (30 mL, 1 M). The mixture was stirred at 65 ºC for 16 h. Upon cooling, the reaction mixture was diluted with ethyl acetate (60 mL) and water (60ml), the phases were separated. The aqueous phase was extracted twice with EtOAc (30 mL) and the combined organic phases were washed with brine (60 mL). The organic phases were dried over Na_2SO_4, filtered and concentrated. The crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a yellow solid (5.6 g, 96 % yield). NMR data was in accordance with what was previously reported NMR data was in accordance with what was previously reported.[20]



Methyl 2-(4-nitrophenyl)propanoate (S44): An oven-dried round-bottom flask, was charged with methyl 2-(4-nitrophenyl)acetate **S43** (1.01 g, 5.17 mmol, 1.0 equiv.), sodium hydride (0.20 g, 4.92 mmol, 0.95 equiv.) and anhydrous THF (10 mL, 0.52 M). The mixture was stirred at 0 ºC and iodomethane (0.48 mL, 7.76 mmol, 1.5 equiv.) was added dropwise. The mixture was warmed to room temperature and the reaction was followed by TLC until completion. The reaction mixture was diluted with ethyl acetate (50 mL) and water (50 mL), the phases were separated. The aqueous phase was extracted twice with EtOAc (20 mL) and the combined organic phases were washed with brine (50 mL). The organic phases were dried over Na_2SO_4, filtered and concentrated. The crude mixture was purified by silica gel column chromatography (100 % hexanes → 20 % ethyl acetate in hexanes), to afford the desired product as a yellow oil (1.08 g, 94 % yield). NMR data was in accordance with what was previously reported.[22]



Methyl 2-(4-aminophenyl)propanoate (S45): An oven-dried round-bottom flask, was charged with methyl 2-(4-nitrophenyl)propanoate **S44** (0.30 g, 1.4 mmol, 1.0 equiv.), palladium on charcoal (10% Pd, 0.15 g) and methanol (14 mL, 0.125 M). The mixture was hydrogenated (1 atm of H_2) until complete disappearance (4-5h) of the starting material (TLC). After filtration on a pad of Celite, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 20 % ethyl acetate in hexanes), to afford the desired product as a yellow solid (0.22 g, 89 % yield). NMR data was in accordance with what was previously reported.[23]



Methyl 2-(2'-amino-5'-chloro-[1,1'-biphenyl]-4-yl)propanoate (S46): A round-bottom flask was charged with methyl 2-(4-aminophenyl)propanoate **S45** (0.11 g, 0.6 mmol, 1.0 equiv.), sodium nitrite (46 mg, 0.66 mmol, 1.1 equiv.) and a mixture of methanol/HCl [6M] (0.33 M, 2:1). The mixture was cooled to 0 ºC and stirred for 1 hour. Bis(pinacolato)diboron (0.17 g, 0.66 mmol, 1.1 equiv.) was added to the mixture and stirred for an additional 2 hours at room temperature. The solution was diluted with CH_2Cl_2 (20 mL) and basified by the slow addition of saturated aqueous K_2CO_3 until bubbling ceased. The phases were separated and the aqueous phase was extracted twice with CH_2Cl_2 (20 mL). The combined organic phases were washed with water (50 mL) and brine (50 mL). The organic phases were dried over Na_2SO_4, filtered and concentrated. The crude mixture was submitted to General Procedure C, starting from methyl 2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propanoate (0.25 g, 1.1 mmol, 1.1 equiv.), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 20 % ethyl acetate in hexanes), to afford the desired product as a pale yellow oil (0.14 g, 62 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39 (s, 4H), 7.11-7.09 (m, 2H), 6.69-6.67 (m, 1H), 3.81-3.76 (m, 3H), 3.71 (s, 3H), 1.55 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 174.8, 142.2, 139.9, 137.1, 129.9, 129.1, 128.4, 128.1, 128.0, 123.1, 116.6, 52.1, 45.1, 18.5; HRMS (ESI) m/z calculated for $C_{16}H_{16}ClNO_2H$ $[M+H]^+$ 290.0930; found 290.0942.

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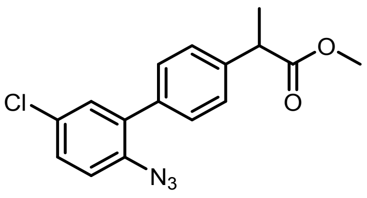
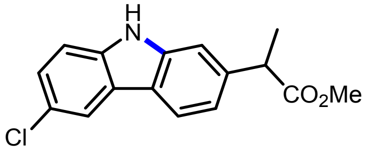
[22] Hama, T.; Ge, S.; Hartwig, J. F. *J. Org. Chem.* **2013**, *78*, 8250-8266

[23] Verma, A.; Patel, S.; Meenakshi; Kumar, A.; Yadav, A.; Kumar, S.; Jana, S.; Sharma, S.; Prasad, C. D.; Kumar, S. *Chem. Commun.* **2015,** *51*, 1371-1374



Methyl 2-(2’-azido-5’-chloro-[1,1’-biphenyl]-4-yl)propanoate (28): Following the General Procedure D, starting from methyl 2-(2’-amino-5’-chloro-[1,1’-biphenyl]-4-yl)propanoate **S46** (0.25 g, 0.87 mmol), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % diethyl ether in hexanes), to afford the desired product as a clear oil (0.22 g, 79 % yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.42-7.32 (m, 6H), 7.18 (d, *J* = 8.4 Hz, 1H), 3.79 (q, *J* = 7.2 Hz, 1H), 3.70 (s, 3H), 1.55 (d, *J* = 7.2 Hz, 3H); (100 MHz, CDCl$_3$) δ = 174.8, 140.3, 135.7, 135.6, 134.7, 131.0, 130.2, 129.5, 128.5, 127.4, 120.0, 52.1, 45.1, 18.5; HRMS (ESI) m/z calculated for $C_{16}H_{14}ClN_3O_2NH_4$ [M+NH$_4$]$^+$ 333.1123; found 333.1113.



Methyl 2-(6-chloro-9*H*-carbazol-2-yl)propanoate (29): Following the Photodecomposition Procedure A, starting from methyl 2-(2’-azido-5’-chloro-[1,1’-biphenyl]-4-yl)propanoate **28**, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 15 % ethyl acetate in hexanes), to afford the desired product as a white solid (21.6 mg, 50 % yield). Following the Photodecomposition Procedure B, starting from methyl 2-(2’-azido-5’-chloro-[1,1’-biphenyl]-4-yl)propanoate **28**, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 15 % ethyl acetate in hexanes), to afford the desired product as a whtie solid (27.6 mg, 64 % yield). NMR data was in accordance with what was previously reported.[24]

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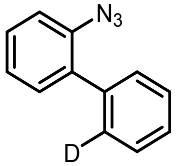
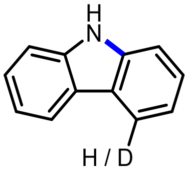
[24] Louillat, M.-L.; Biafora, A.; Legros, F.;Patureau, F. W. *Angew. Chem. Int. Ed.* **2014**, *53*, 3505-3509

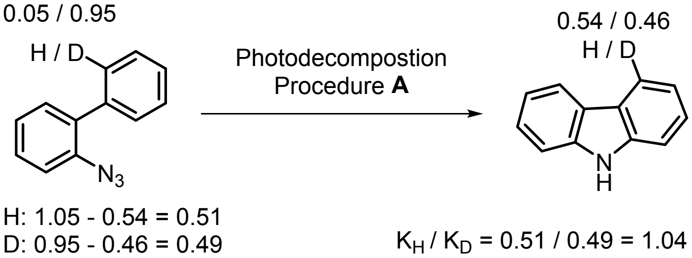
KINETIC ISOTOPE EFFECTS

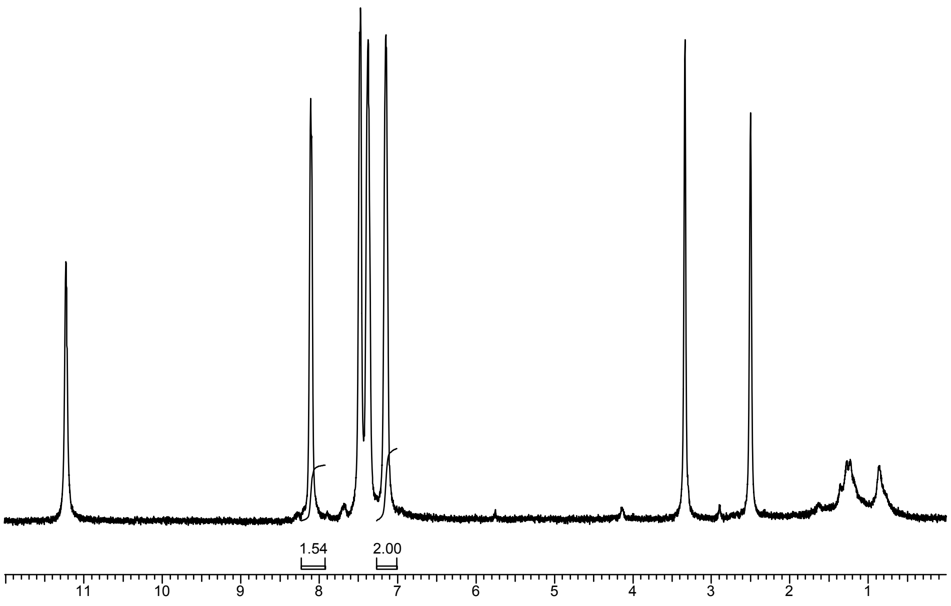


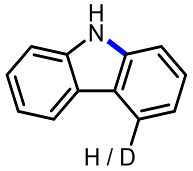
2-Azido-1,1’-biphenyl-2’-*d* (30): Following the General Procedure D, starting from [1,1'-biphenyl]-2'-*d*-2-amine [9] (0.27 g, 1.6 mmol), the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a tan oil (0.23 g, 74 % yield), ^{1}H NMR showed 95 % deuterium incorporation. NMR data was in accordance with what was previously reported.[9]



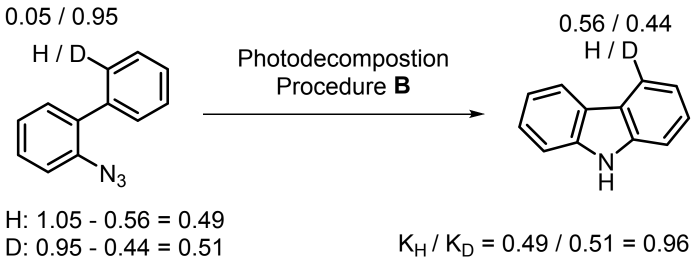
9*H*-Carbazole-4-*d* (*d*-31 or 31): Following the Photodecomposition Procedure A, starting from 2-azido-1,1’-biphenyl-2’-d **30**, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (20.1 mg, 80 % yield, K_H / K_D = 1.04). NMR data was in accordance with what was previously reported.[3]

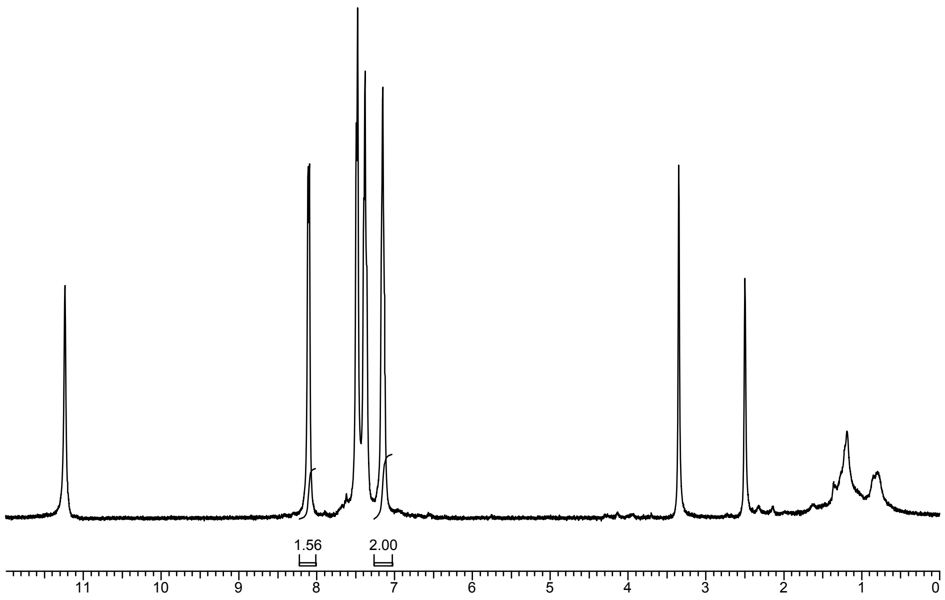






9*H*-Carbazole-4-*d* (*d*-31 or 31): Following the Photodecomposition Procedure B for 2 hours (0.108 mL/min), starting from 2-azido-1,1'-biphenyl-2'-d **30** and using ethyl acetate as the solvent, the crude mixture was purified by silica gel column chromatography (100 % hexanes → 10 % ethyl acetate in hexanes), to afford the desired product as a white solid (20.1 mg, 80 % yield, K_H / K_D = 0.96). NMR data was in accordance with what was previously reported.[3]

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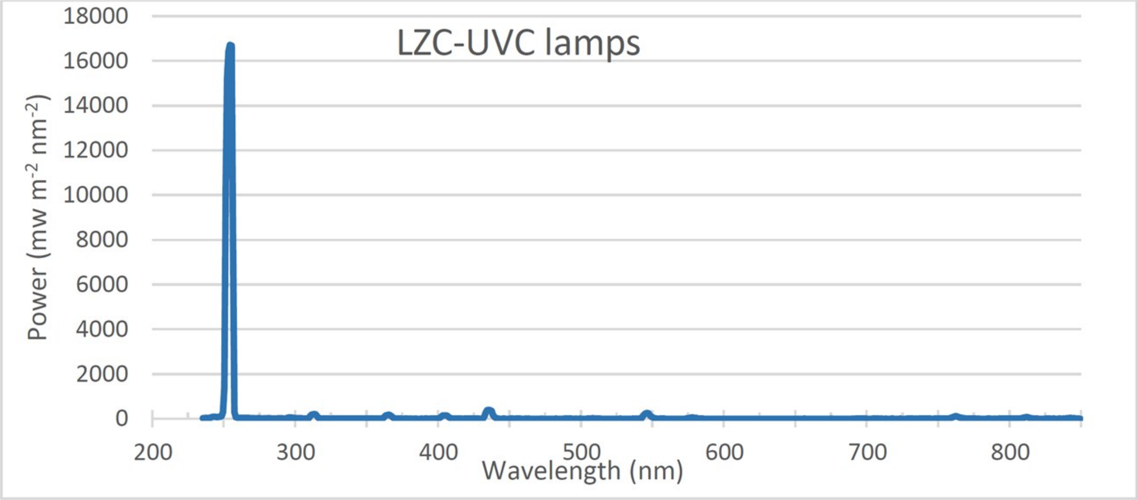
11
10
9
8
7
6
5
4
3
2
1
0

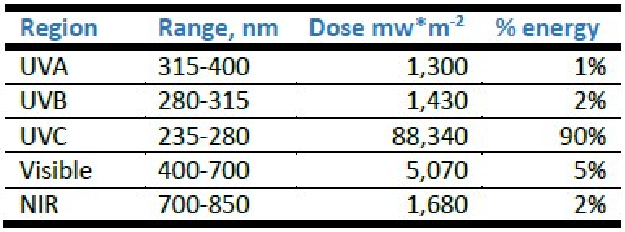
BACKGROUND ON LIGHT SOURCES

For reactions using irradiation at 254 nm, a previously published experimental set up was used: A. Caron, A. C. Hernandez-Perez and S. K. Collins *Org. Process Res. Dev.* 2014, **18**, 1571. The UV light sources was purchased from Luzchem (http://www.luzchem.com/). The following data is available online for the UVC lamp used:

Chamber Temp. 25 ˚C
Photoreactor model LZC-ICH2
Monitored range 235 to 850 nm
Resolved peaks : 254, 313, 365, 405, 435, 546, 762 nm

The follwoing data was reproduced from the Luzchem website :
(http://www.luzchem.com/ExposureStandards.php)

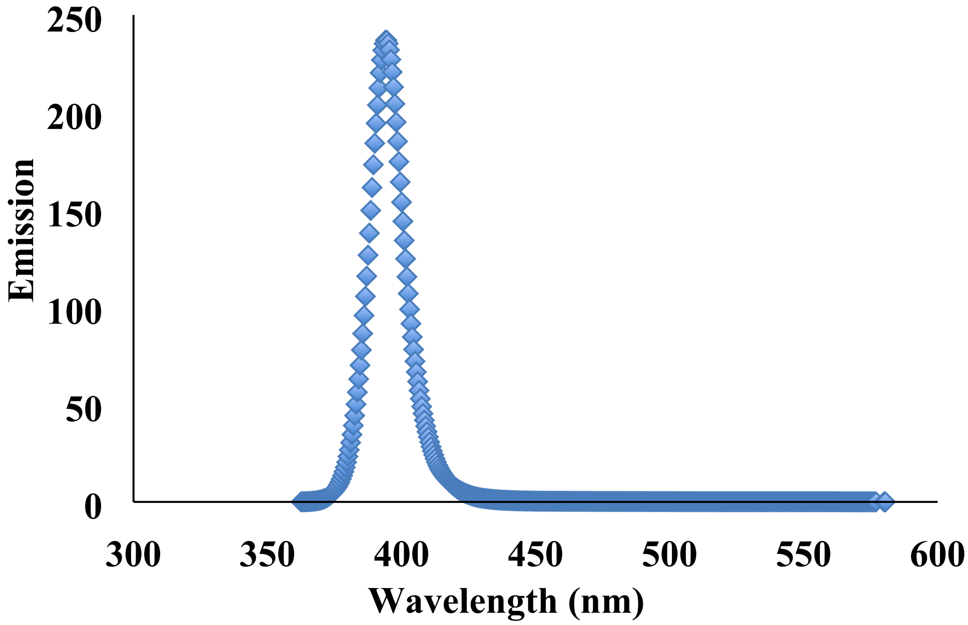




Region	Range, nm	Dose mw*m^{-2}	% energy
UVA	315-400	1,300	1%
UVB	280-315	1,430	2%
UVC	235-280	88,340	90%
Visible	400-700	5,070	5%
NIR	700-850	1,680	2%

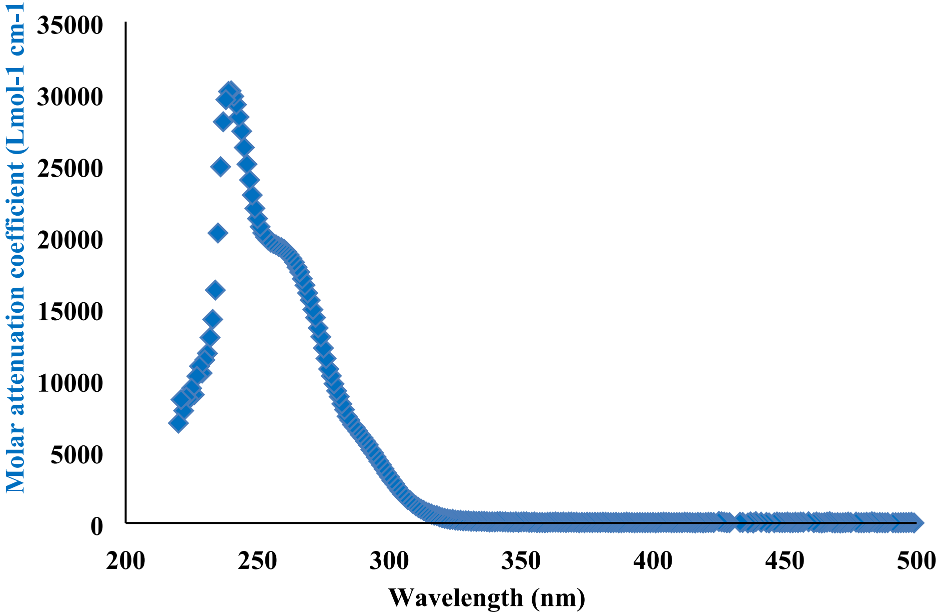
For reactions using irradiation at 394 nm, the light sources was purchased from Creative Lighting (https://www.creativelightings.com/). The LED strips used were: http://www.creativelightings.com/Purple-UV-LED-Flex-Strips-12vdc-WP-300-Meter-p/cl-frs5050wpdd-5m-12v-uv.htm. The following data was reproduced from the Creative Lightings website :

Purple/UV Water Resistant LED Flexible Ribbon Spool - 5050 Series - 300 Purple/UV LEDs 400-410nm
Standard length: 5 meters (16.4ft)/reel
Strip width: single color 10mm, (3/8in)
Color of PCB: Black, Silicone PVC encapsulated, super flexible
Color: Purple **Ultra Violet / Purple** (1/2 the normal brightness - MORE UV REACTIVE) 400-410nm
Working voltage: 12 Volt DC (24v Optional)
LED quantity of entire strip: single color **300pcs**, RGB 150pcs or 300pcs
LED Density: Double Density = .75" LED spacing - Provides high output and more even light output
Lifespan (approx. 100,000 hours)
Wattage: 72 Watts per 5 Meter Spool
Water resistant/Rustproof IP-66 rated

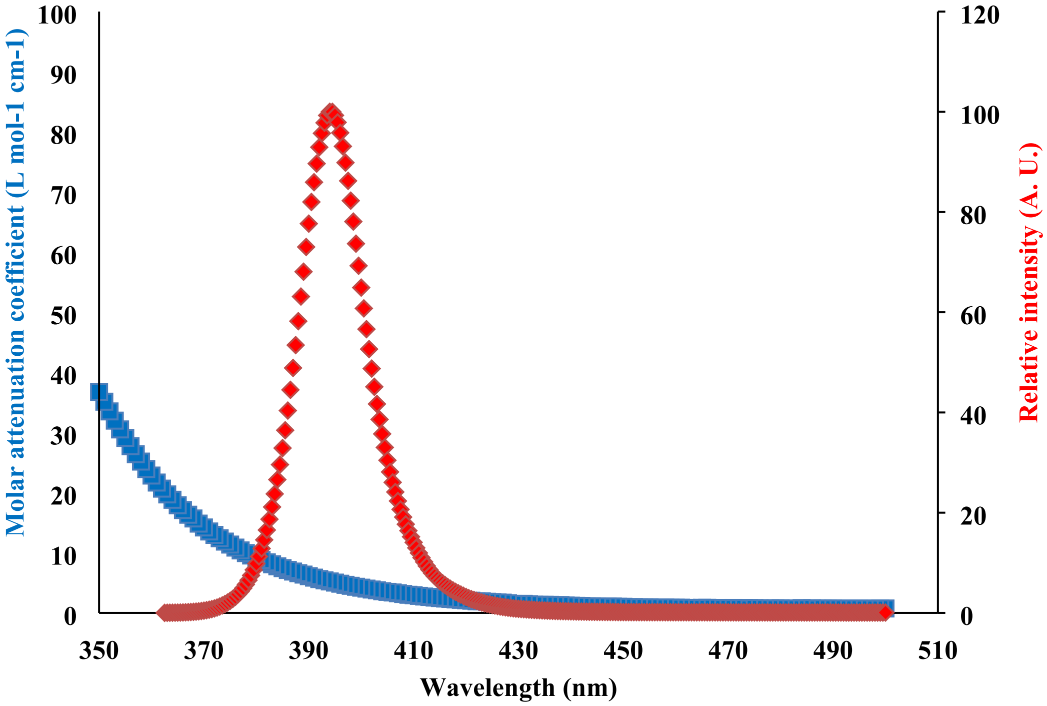


ABSORPTION/EMISSION DATA

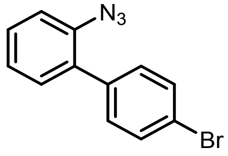
Absorption spectrum for 2-azido-1,1’-biphenyl (**1**) (25 µM in THF)



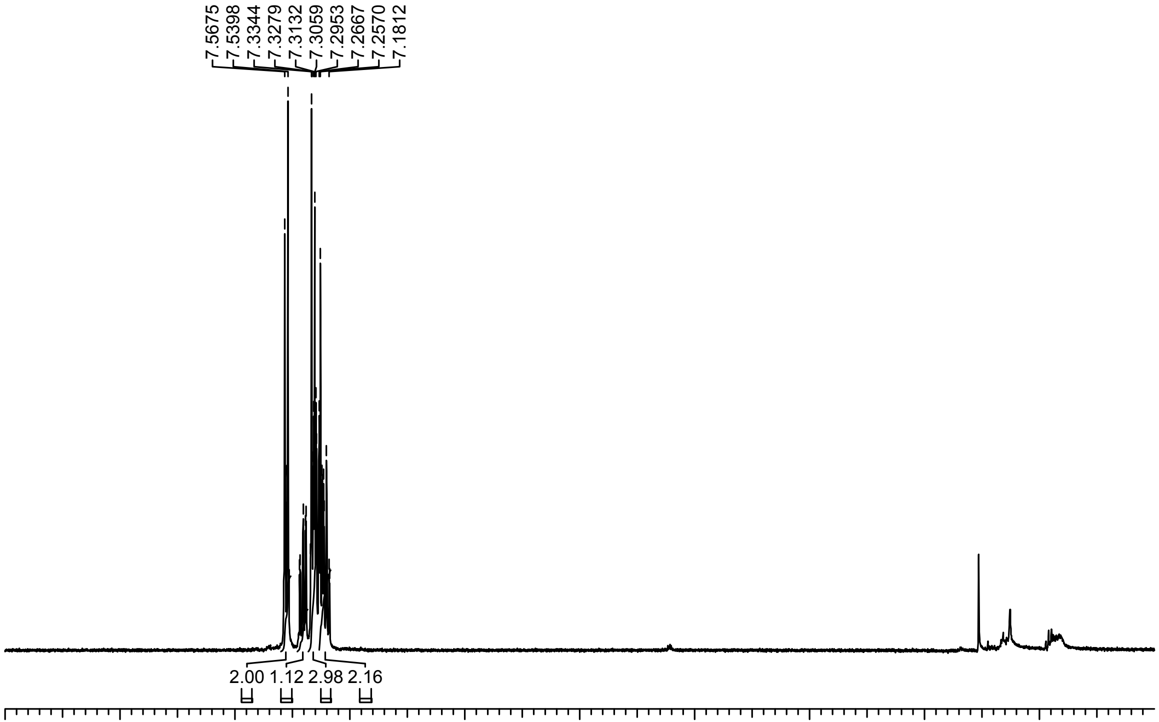
Overlapping the absorption spectrum for 2-azido-1,1’-biphenyl (**1**) with the emission spectrum of the purple LED at the concentration used for the photochemical decomposition of the azide (30 mM in THF)

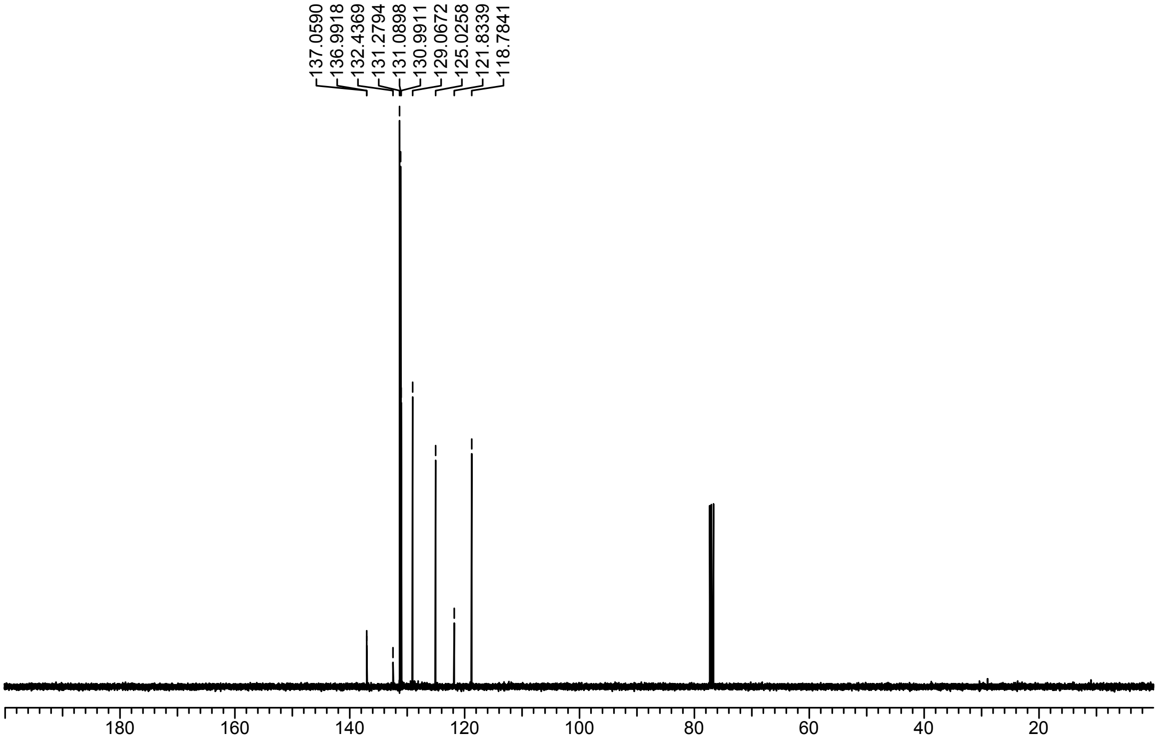


NMR DATA FOR ALL NEW COMPOUNDS



3

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131.2794
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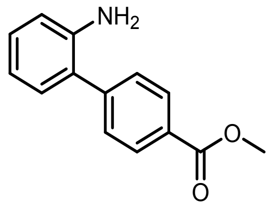
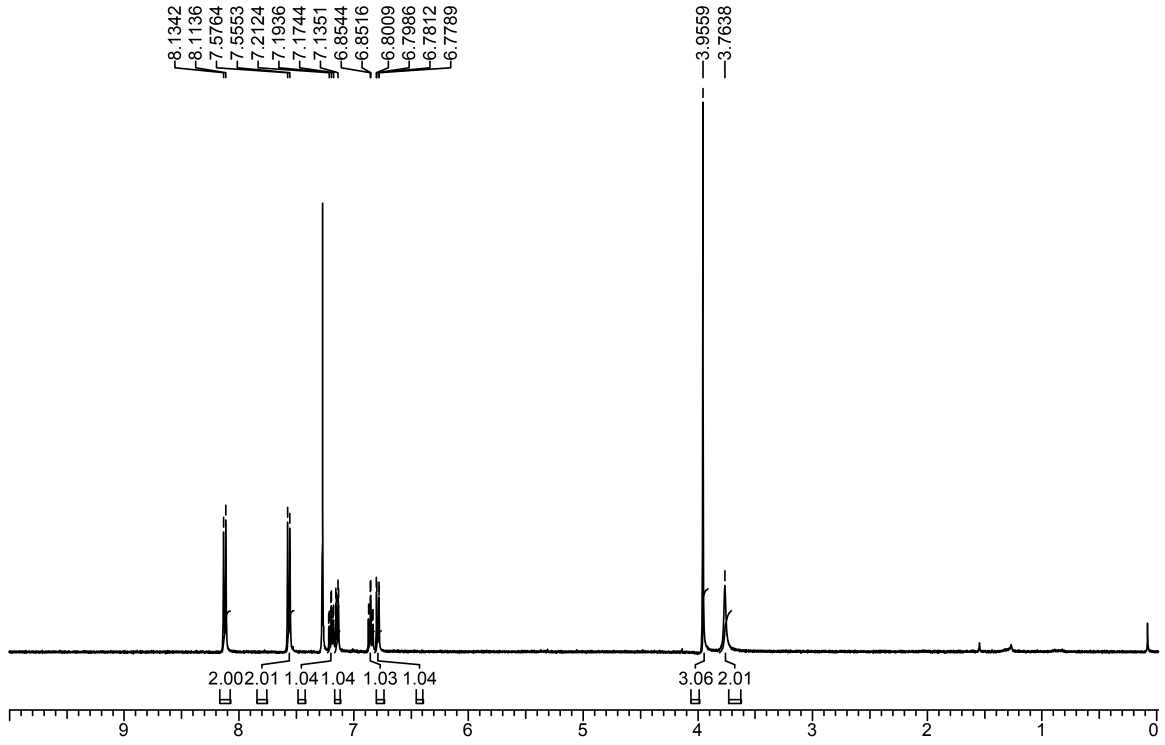
160
140
120
100
80
60
40
20



S7



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6.8516
6.8009
6.7986
6.7812
6.7789
3.9559
3.7638
2.00
2.01
1.04
1.04
1.03
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2.01
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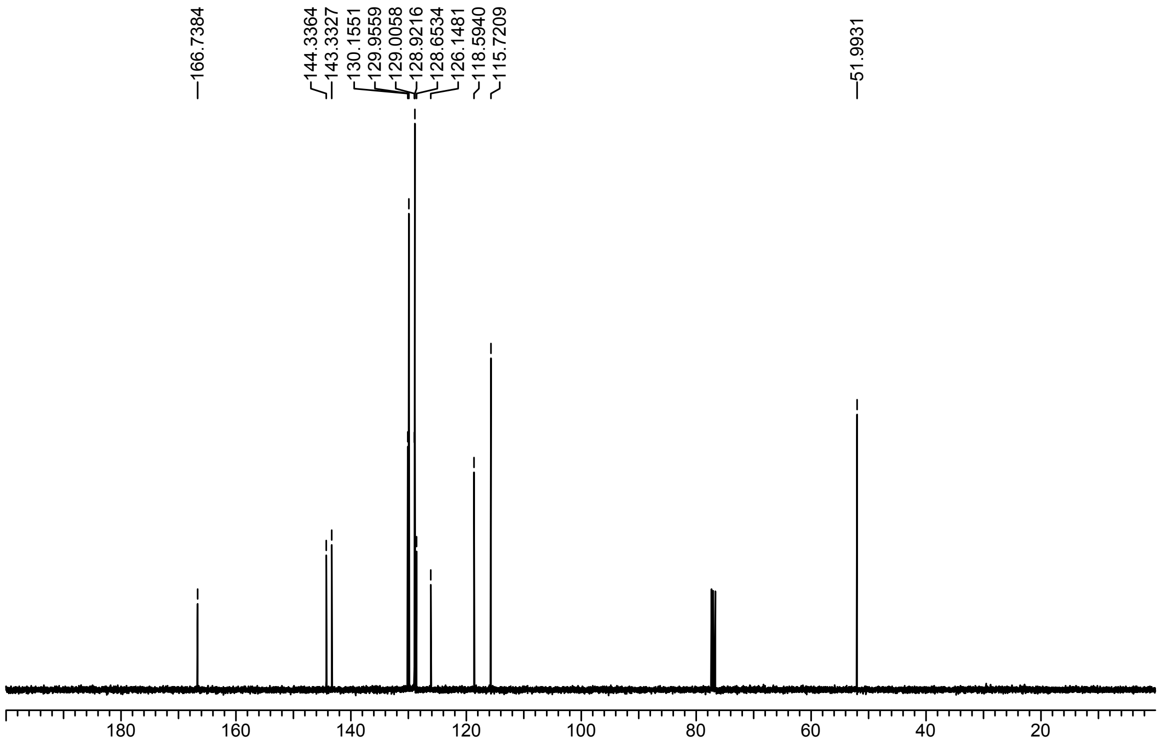
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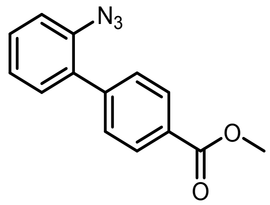
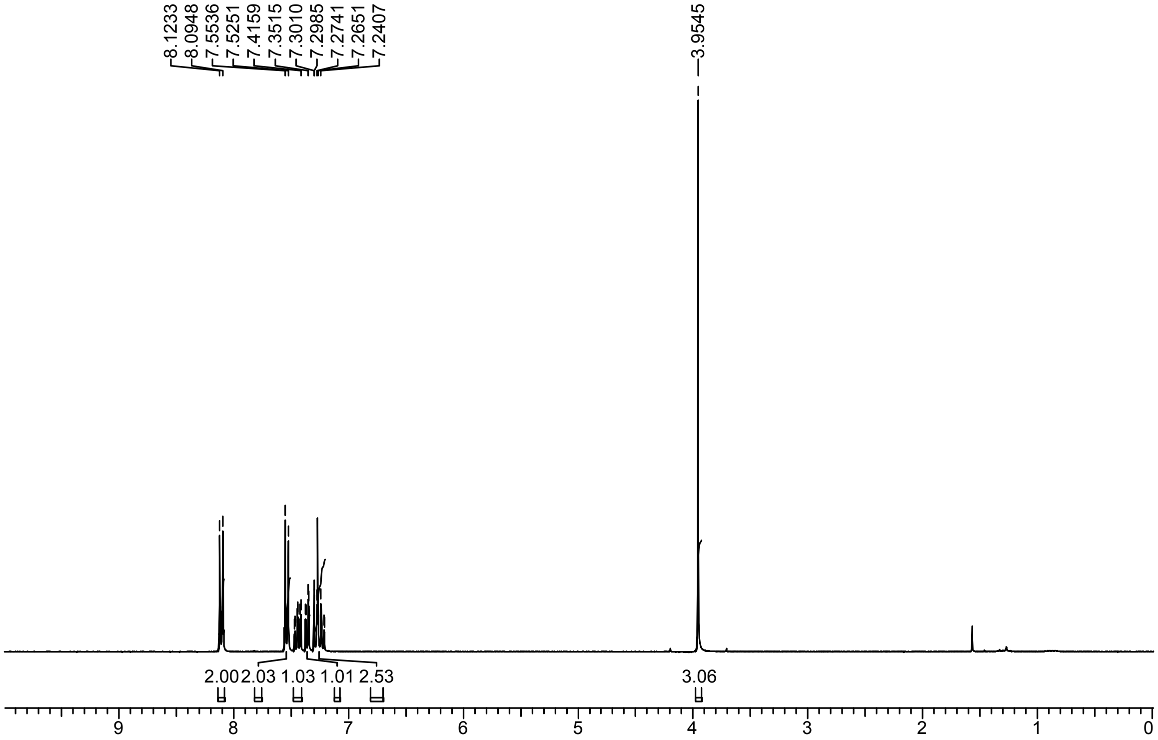

N3
O
O

S8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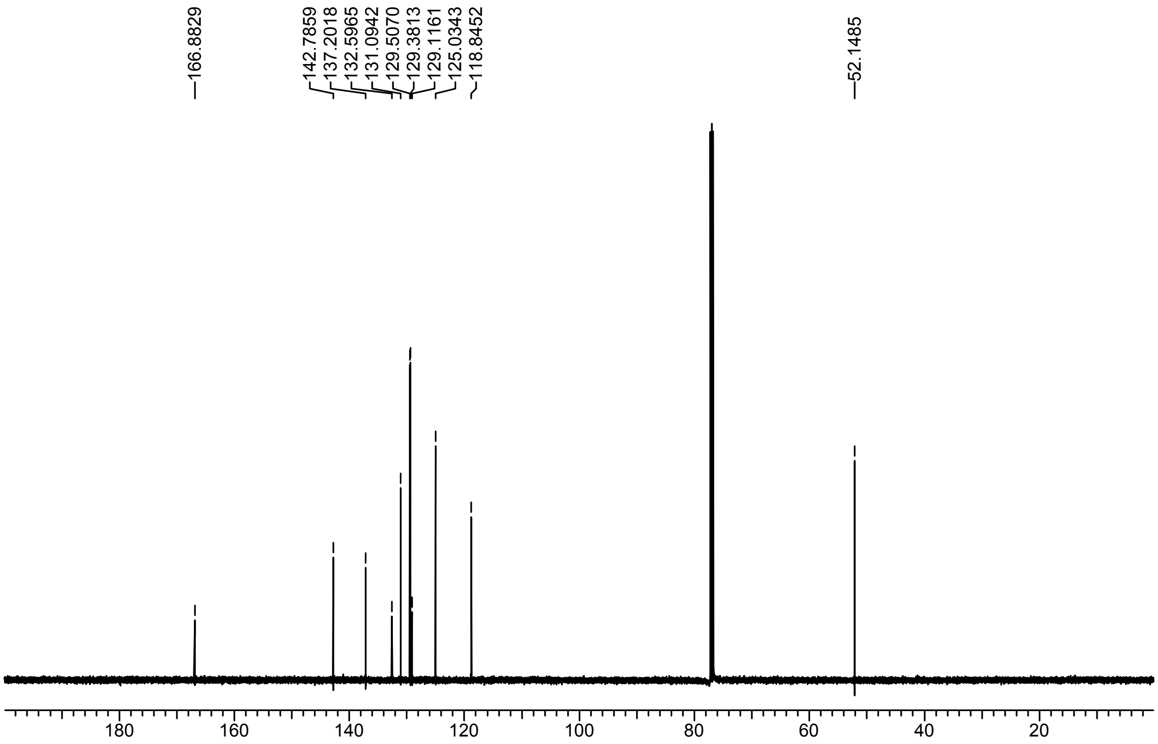
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40
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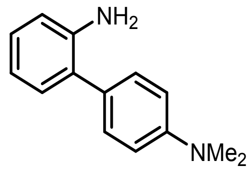
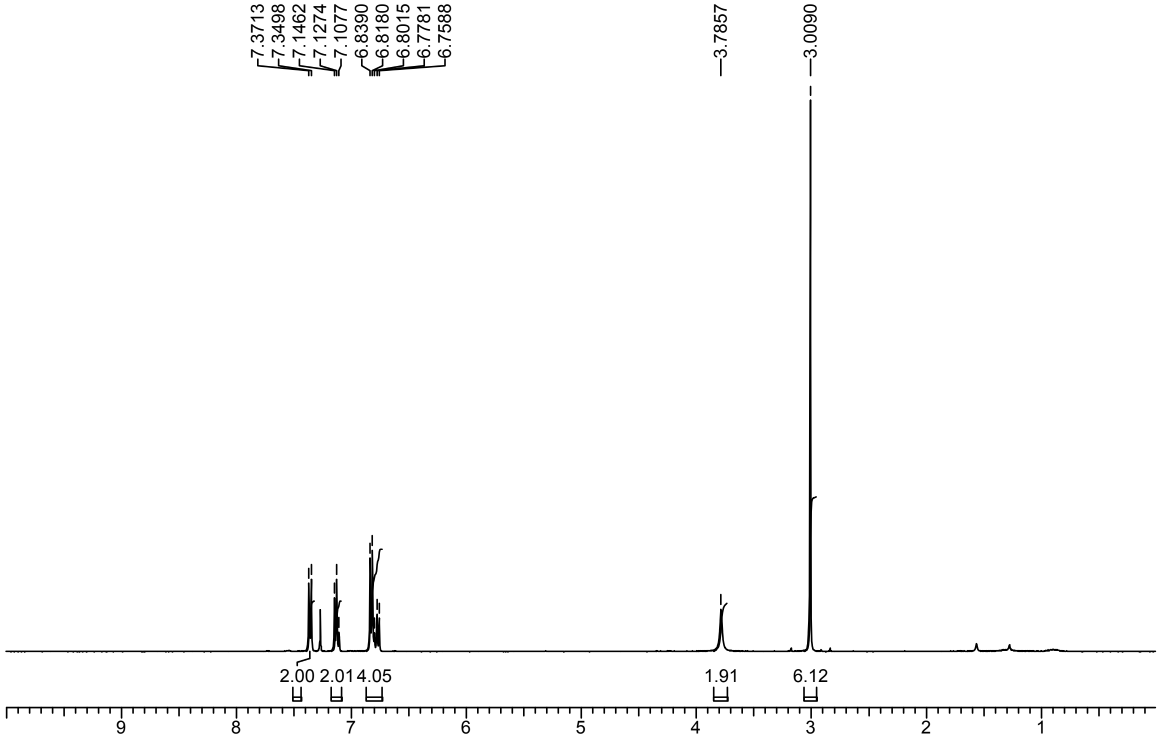

NH2
NMe2

S11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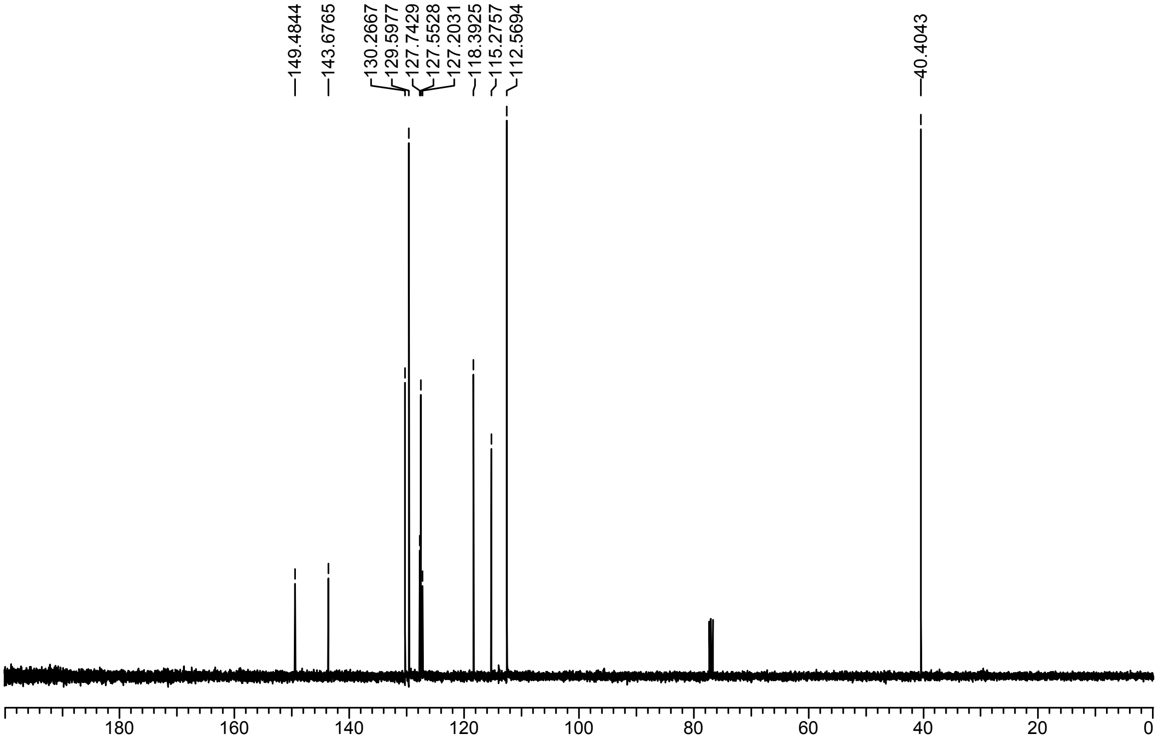
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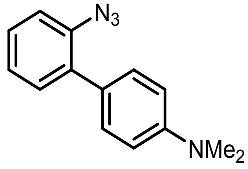
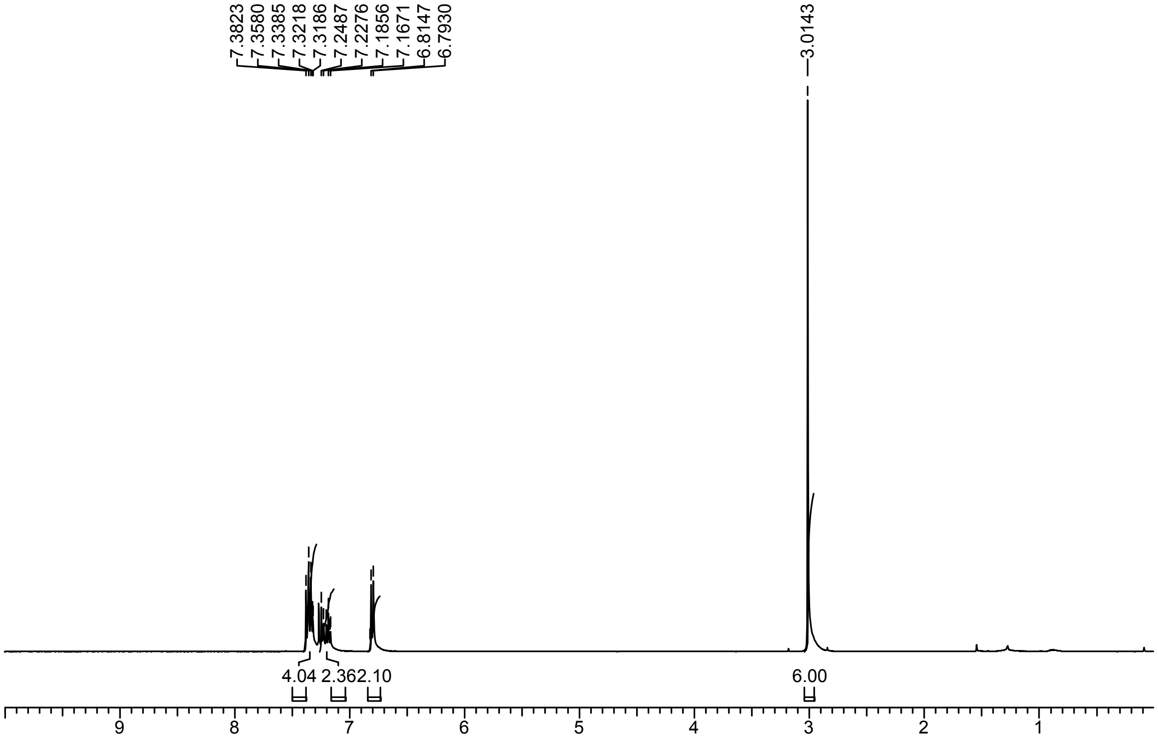

N3
NMe2

S12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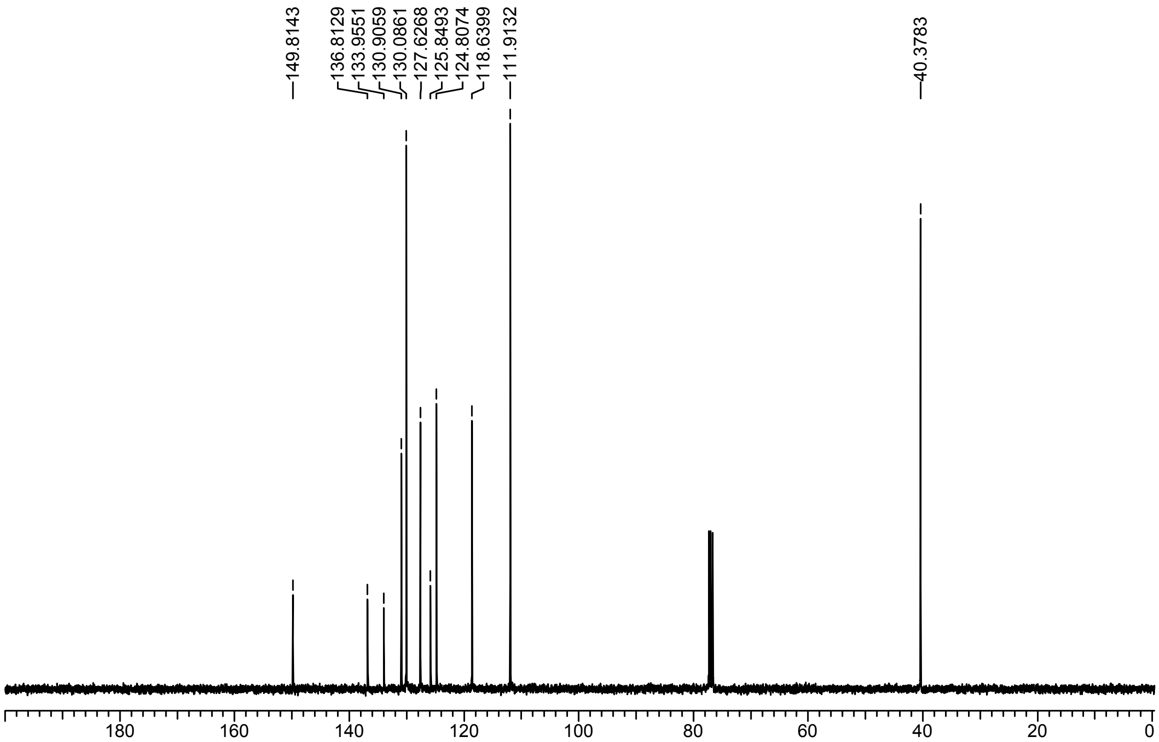
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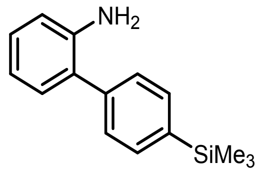
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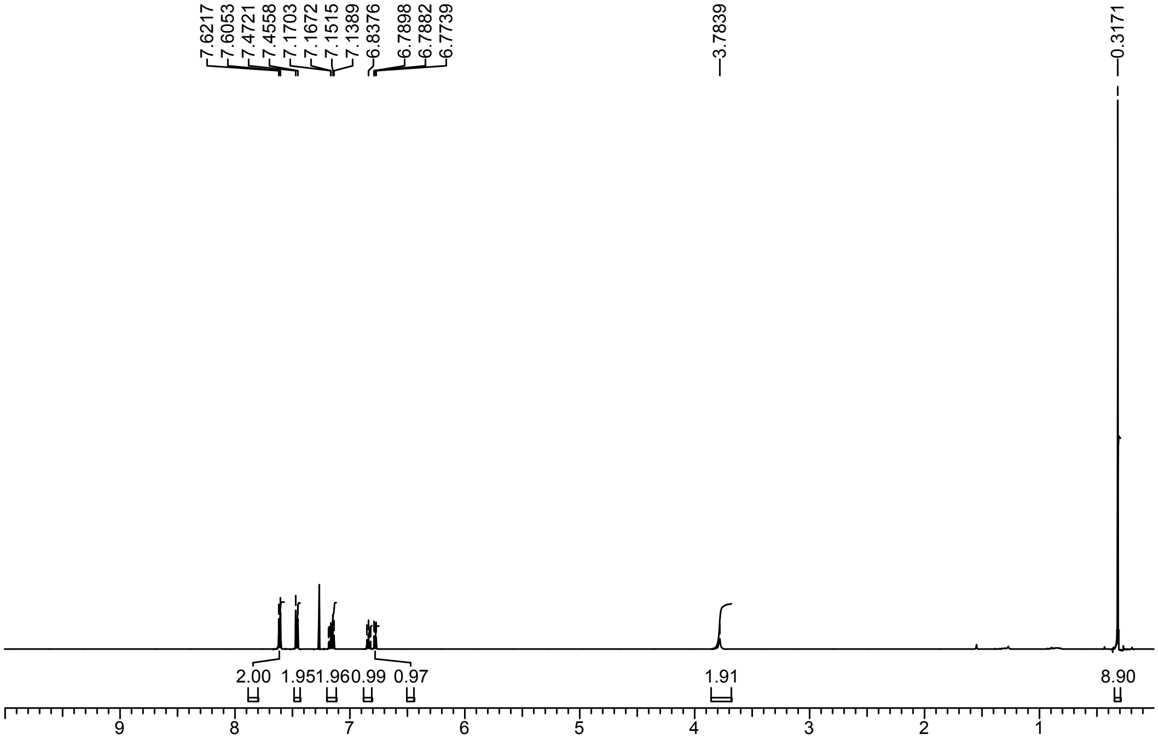
SiMe3

S15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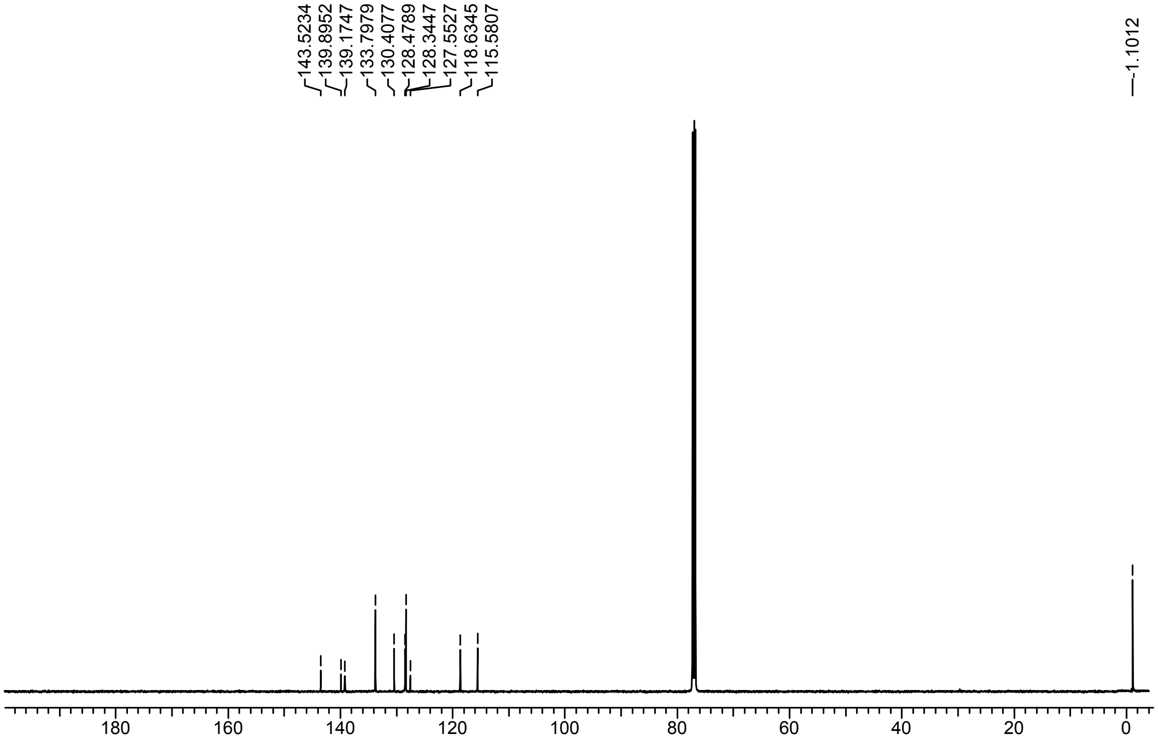
3
2
1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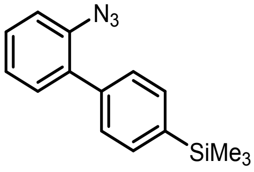
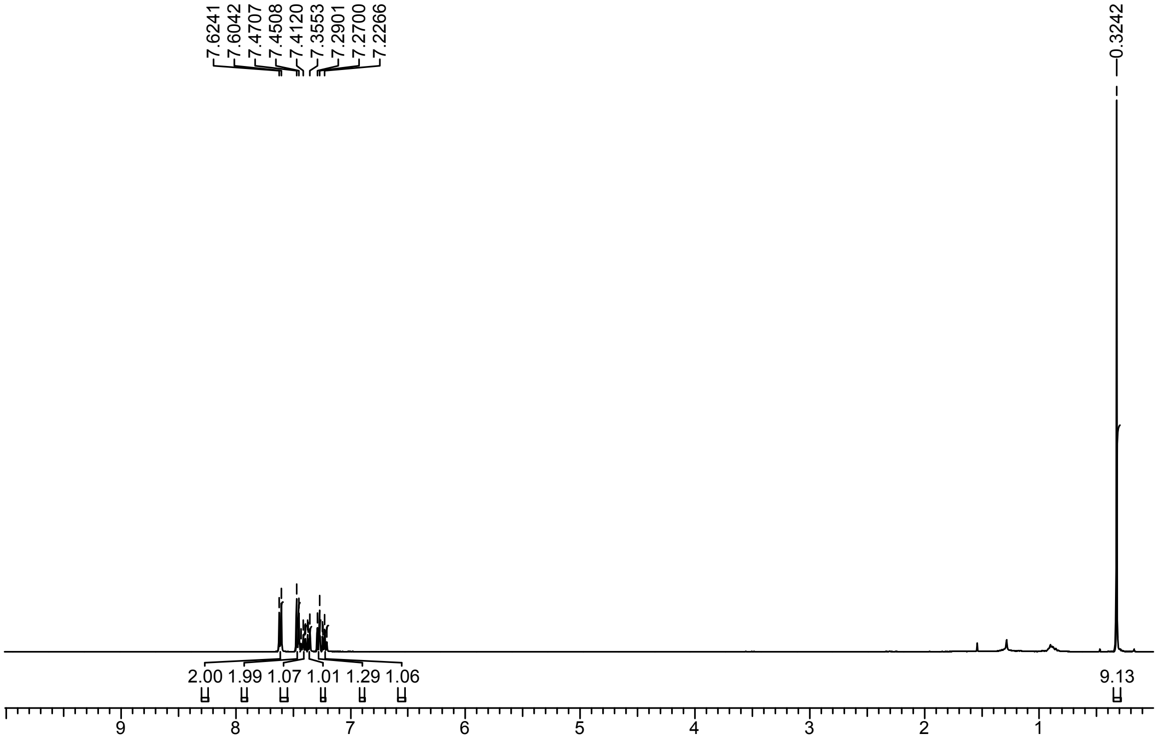

N3
SiMe3

S16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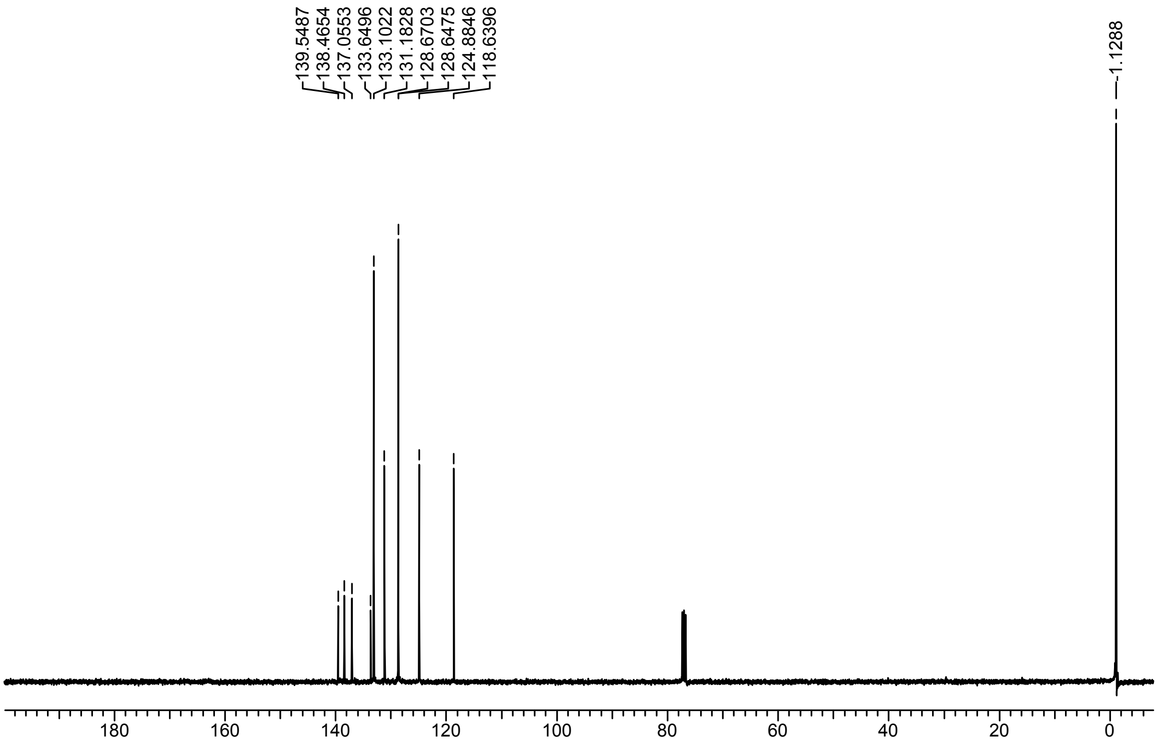
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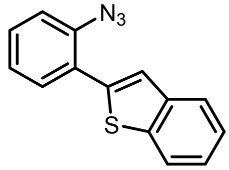
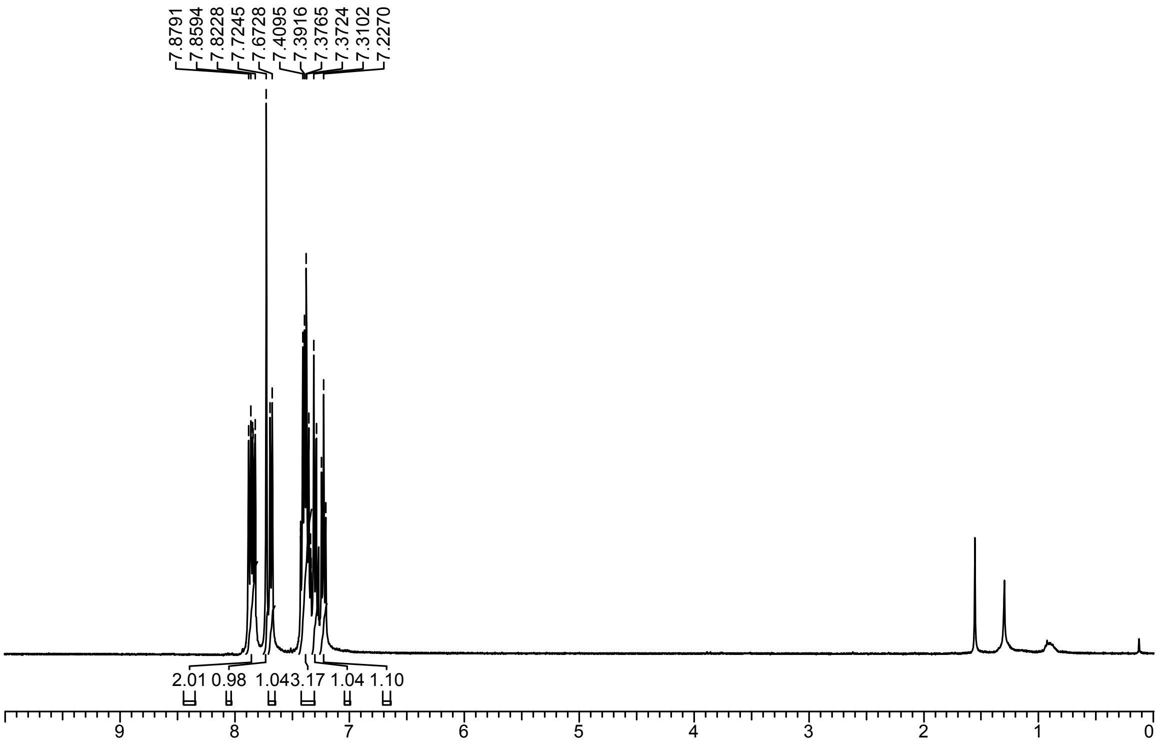

N3
S

S28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7.3916
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7.3724
7.3102
7.2270
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0.98
1.04
3.17
1.04
1.10
9
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7
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5
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1
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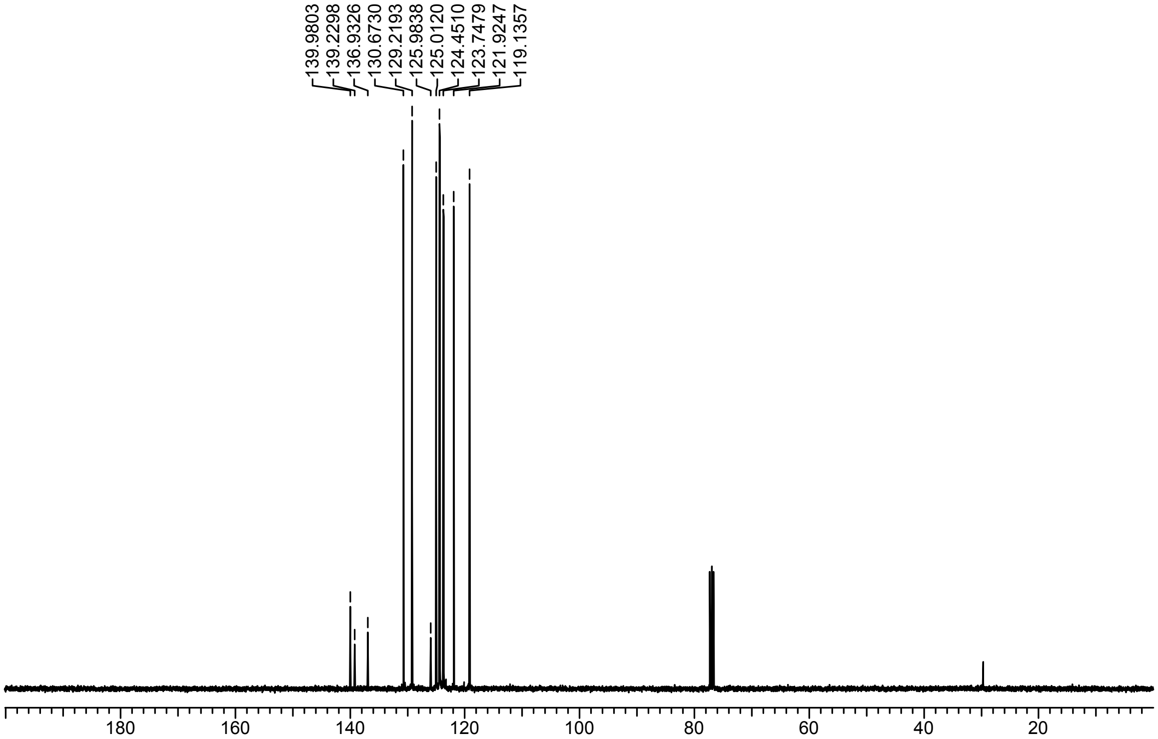

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136.9326
130.6730
129.2193
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125.0120
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123.7479
121.9247
119.1357
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160
140
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100
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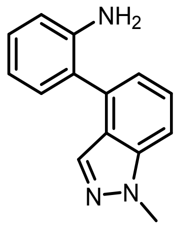
60
40
20


NH2
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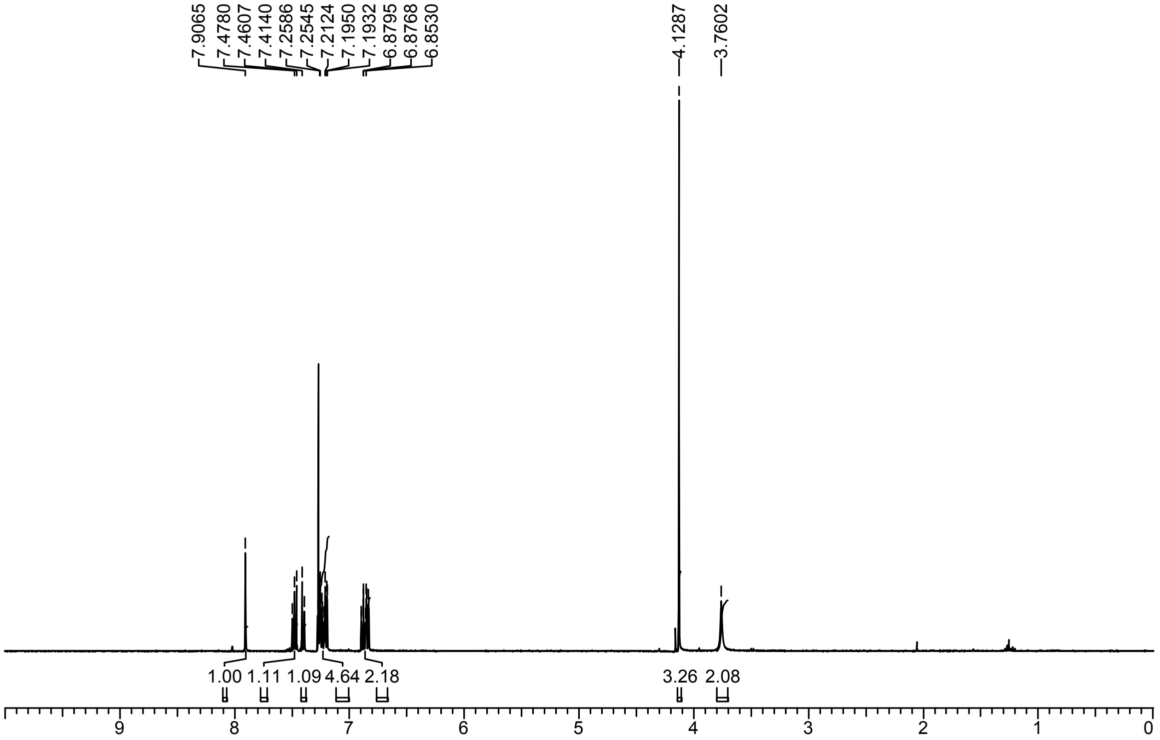
S31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7.4607
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7.2586
7.2545
7.2124
7.1950
7.1932
6.8795
6.8768
6.8530
4.1287
3.7602
1.00
1.11
1.09
4.64
2.18
3.26
2.08
9
8
7
6
5
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3
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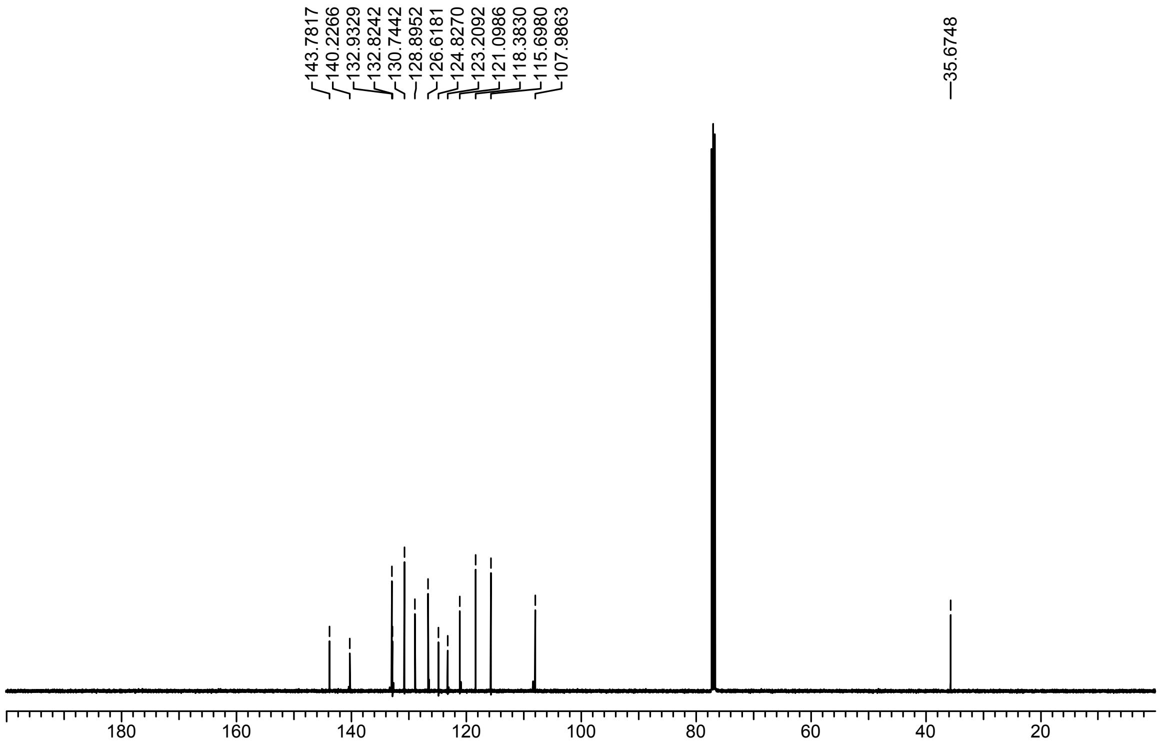
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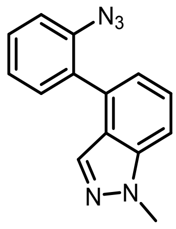
100
80
60
40
20


N3
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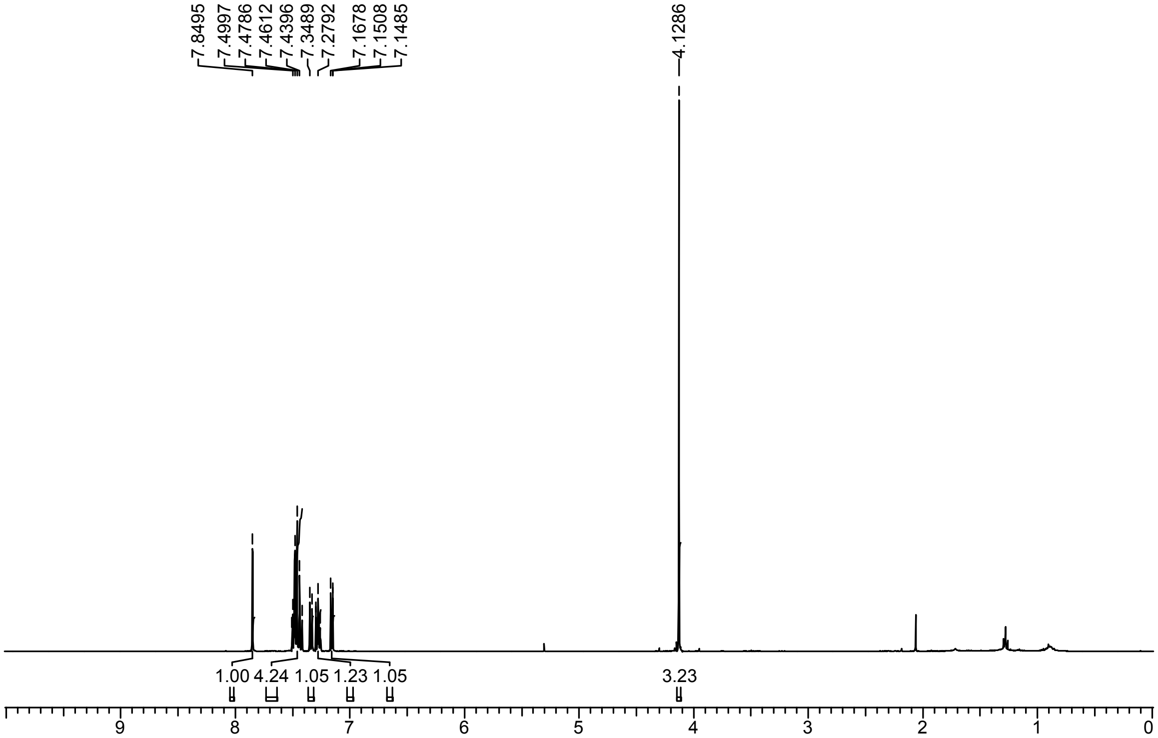
N

S32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7.4396
7.3489
7.2792
7.1678
7.1508
7.1485
4.1286
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1.23
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3.23
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8
7
6
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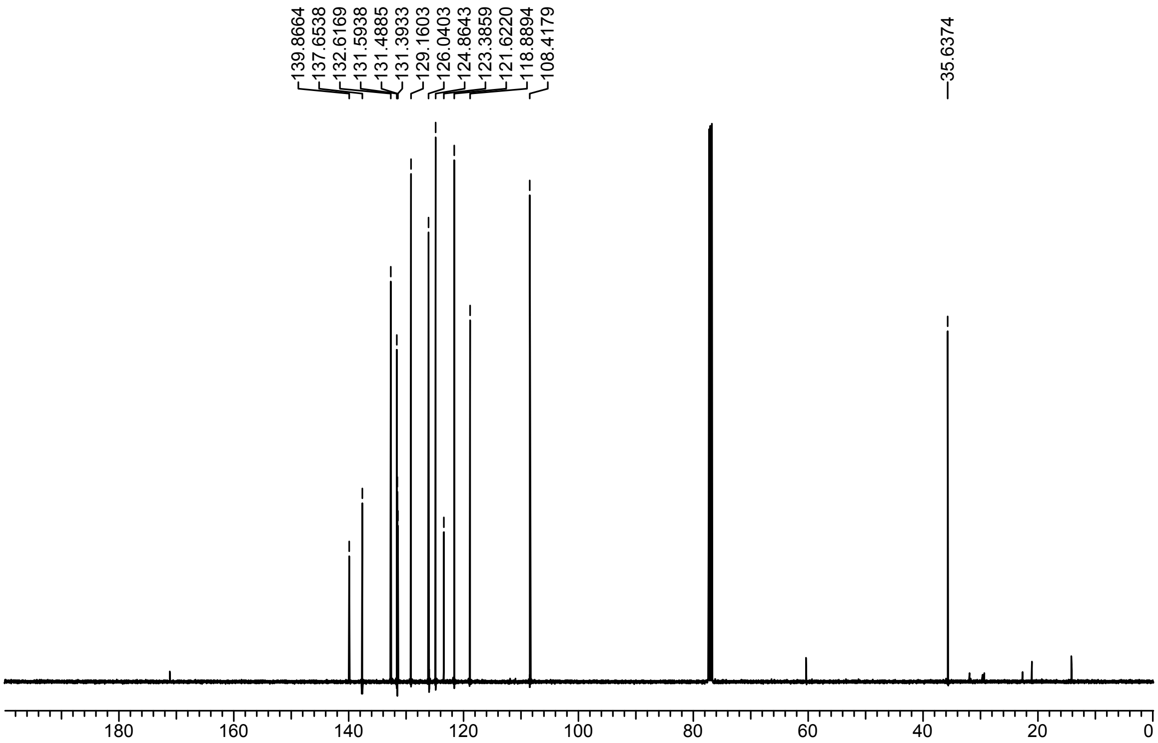

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132.6169
131.5938
131.4885
131.3933
129.1603
126.0403
124.8643
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121.6220
118.8894
108.4179
35.6374
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120
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60
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20
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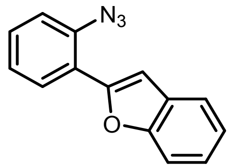
N3
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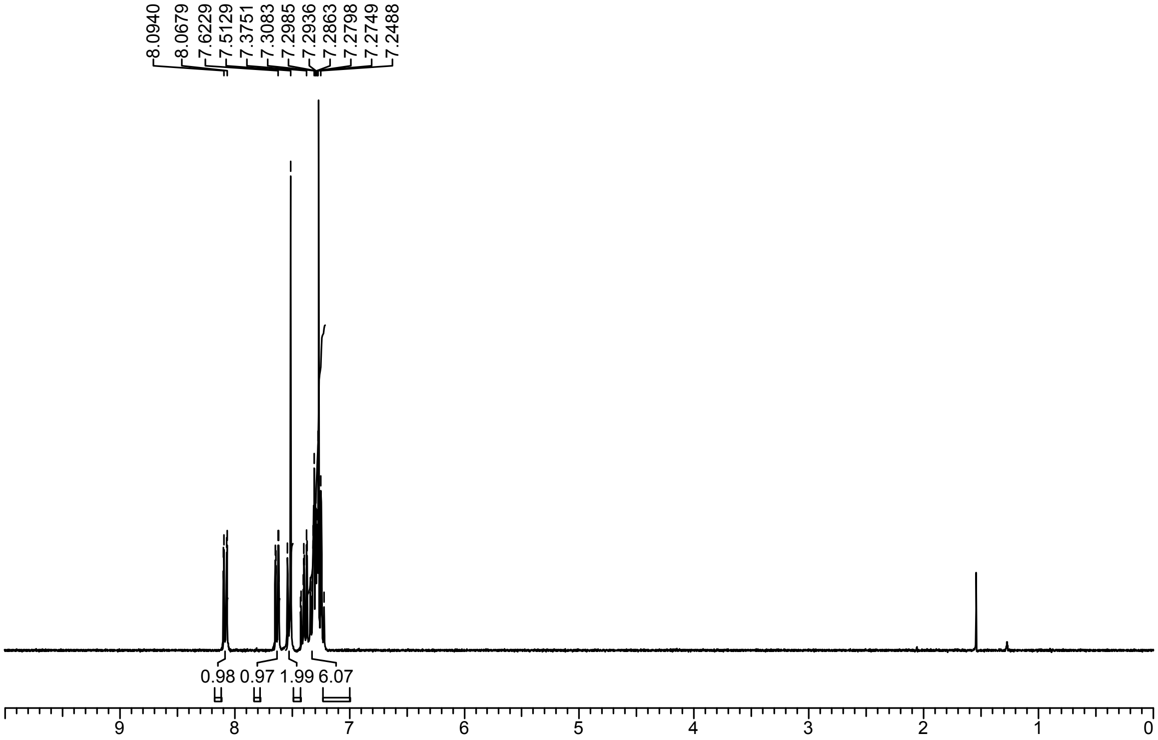
S34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7.6229
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7.3751
7.3083
7.2985
7.2936
7.2863
7.2798
7.2749
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0.98
0.97
1.99
6.07
9
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7
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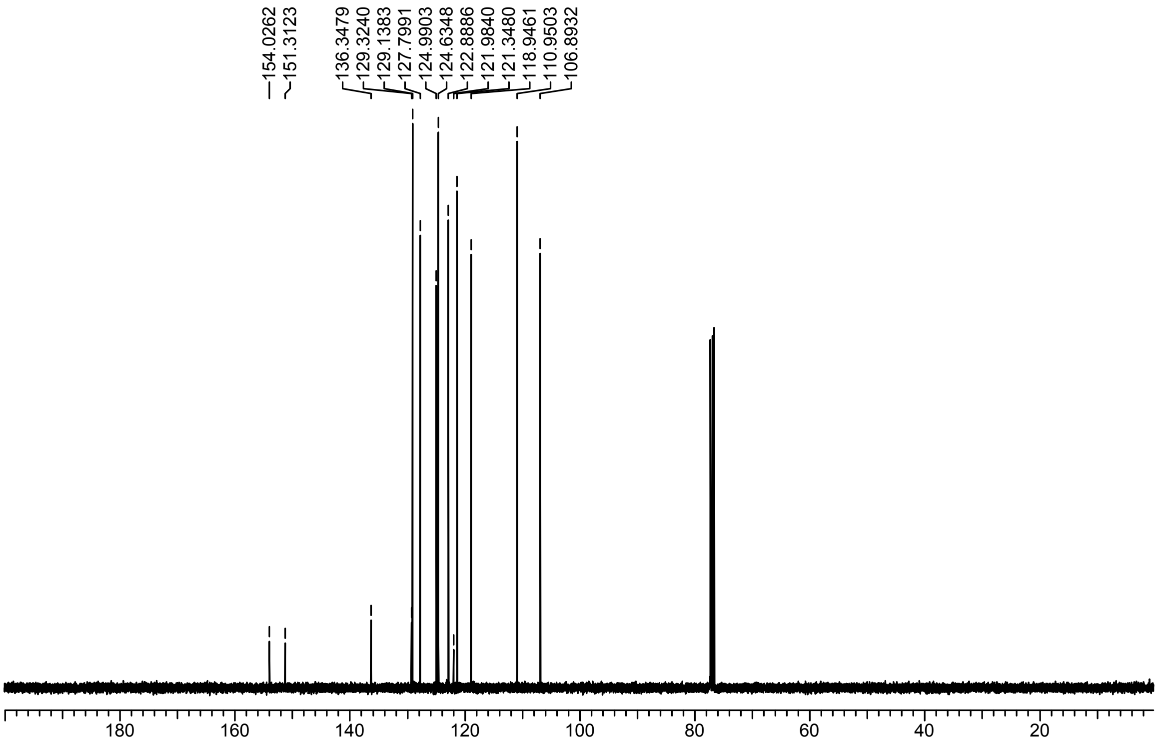
0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136.3479
129.3240
129.1383
127.7991
124.9903
124.6348
122.8886
121.9840
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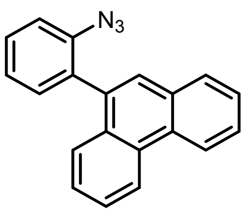
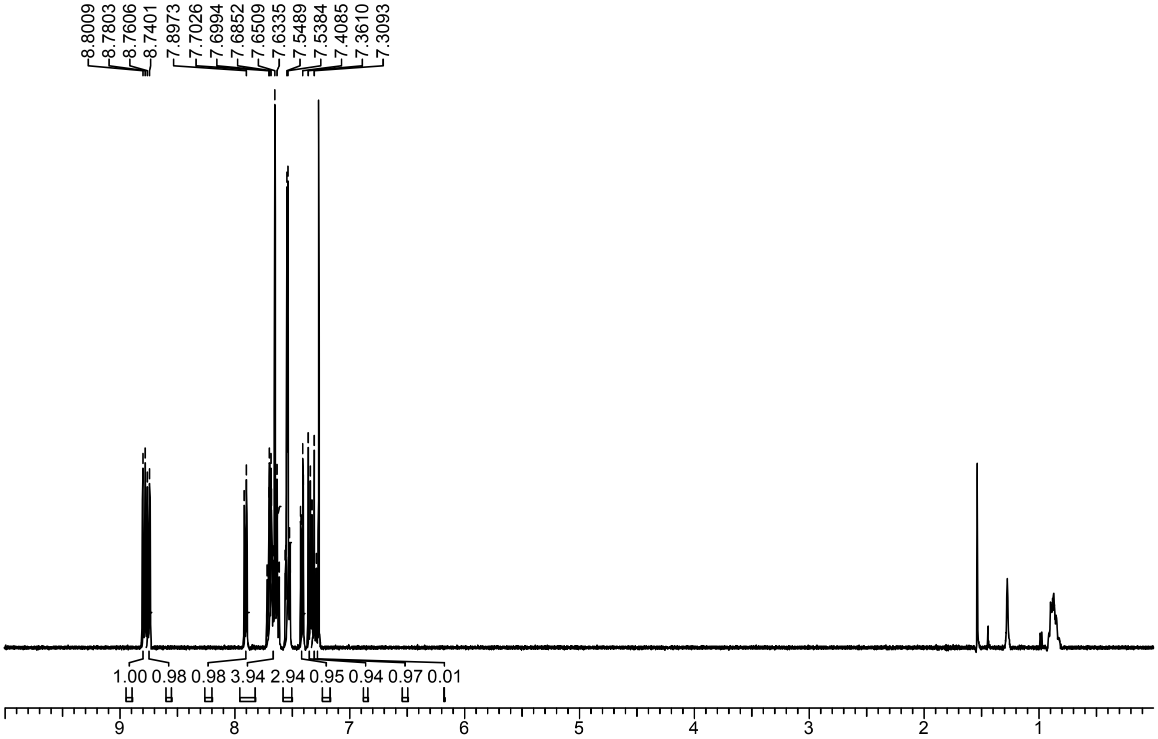
118.9461
110.9503
106.8932
180
160
140
120
100
80
60
40
20



S38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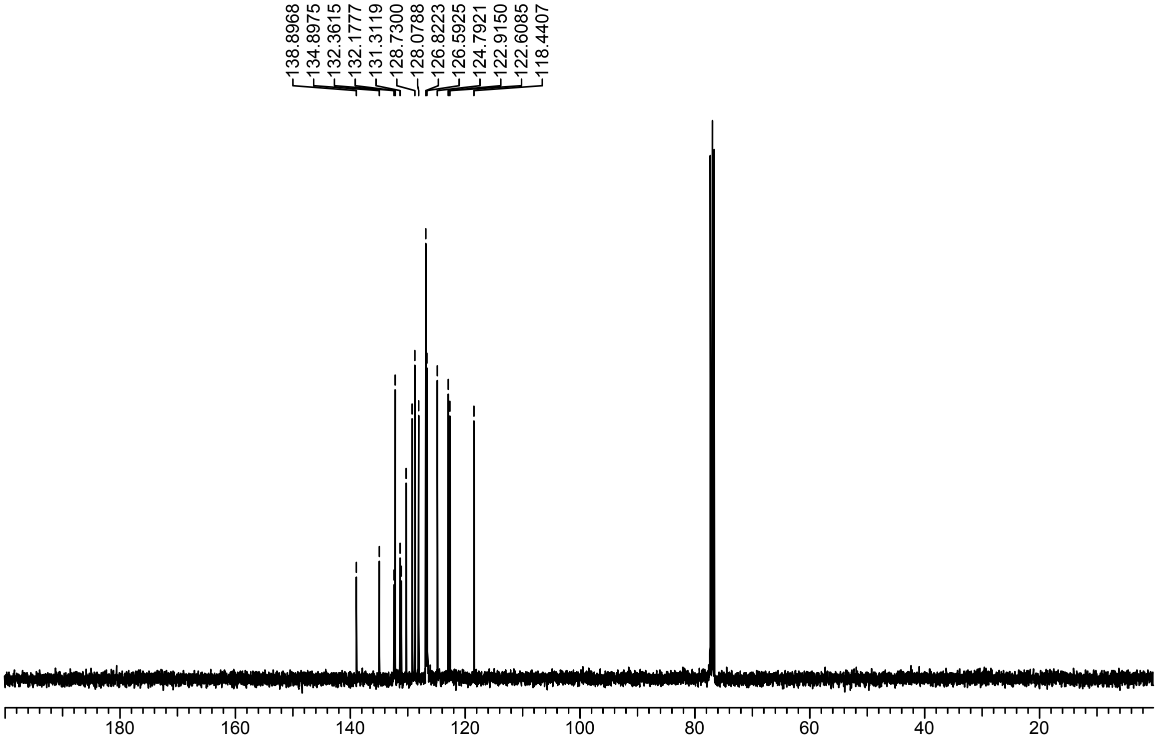
7.8973
7.7026
7.6994
7.6852
7.6509
7.6335
7.5489
7.5384
7.4085
7.3610
7.3093
1.00
0.98
0.98
3.94
2.94
0.95
0.94
0.97
0.01
9
8
7
6
5
4
3
2
1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134.8975
132.3615
132.1777
131.3119
128.7300
128.0788
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124.7921
122.9150
122.6085
118.4407
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160
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100
80
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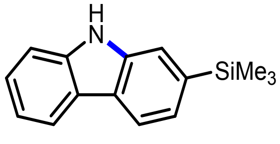
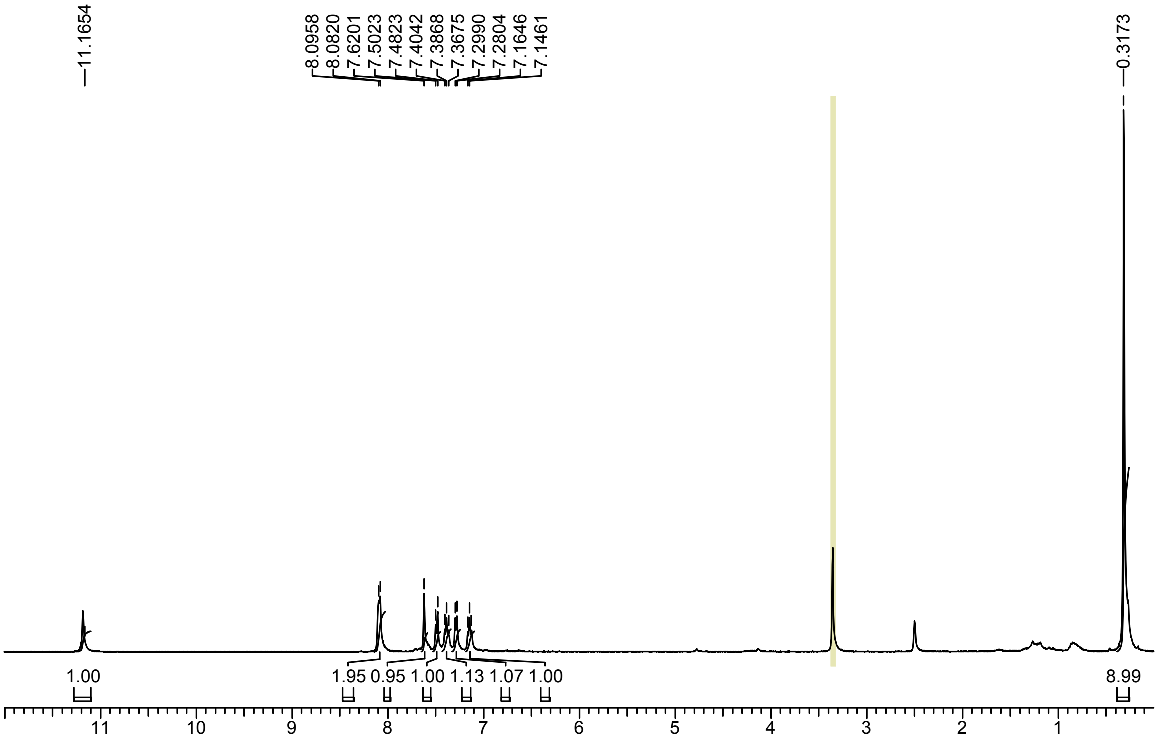
40
20


H
N
SiMe$_3$

13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8.0820
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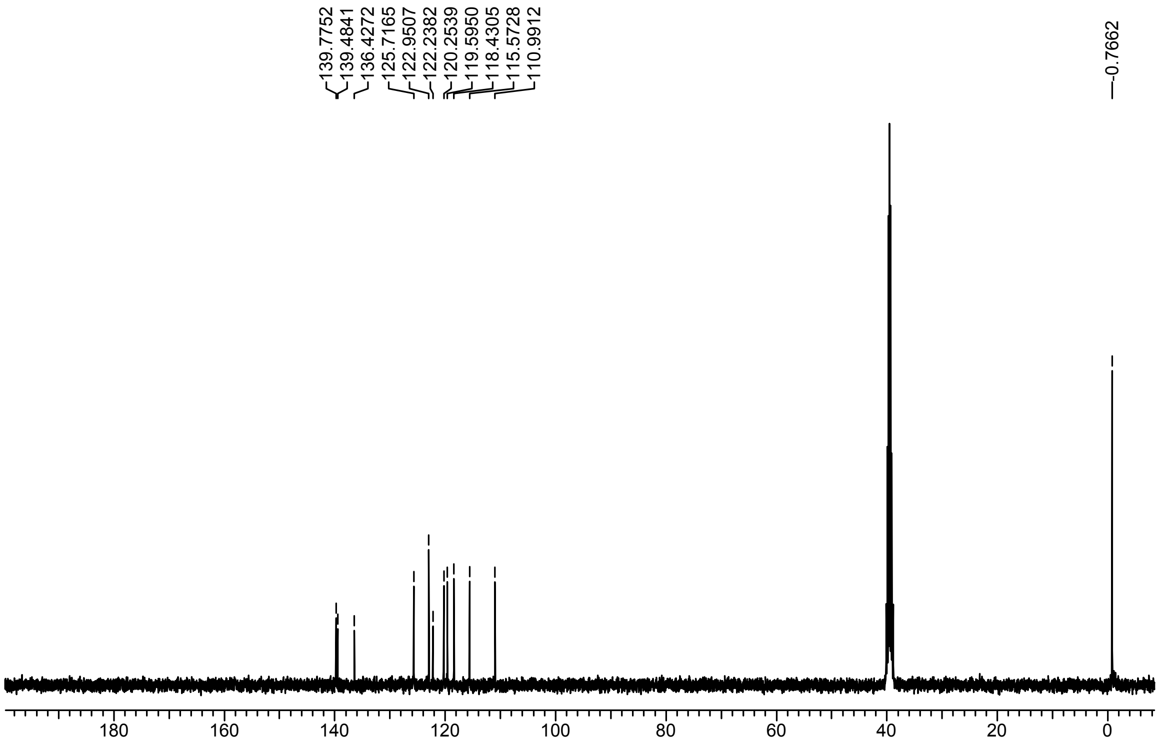
7.5023
7.4823
7.4042
7.3868
7.3675
7.2990
7.2804
7.1646
7.1461
0.3173
1.00
1.95
0.95
1.00
1.13
1.07
1.00
8.99
11
10
9
8
7
6
5
4
3
2
1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110.9912
0.7662
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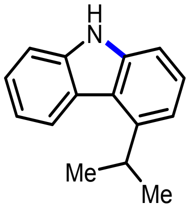
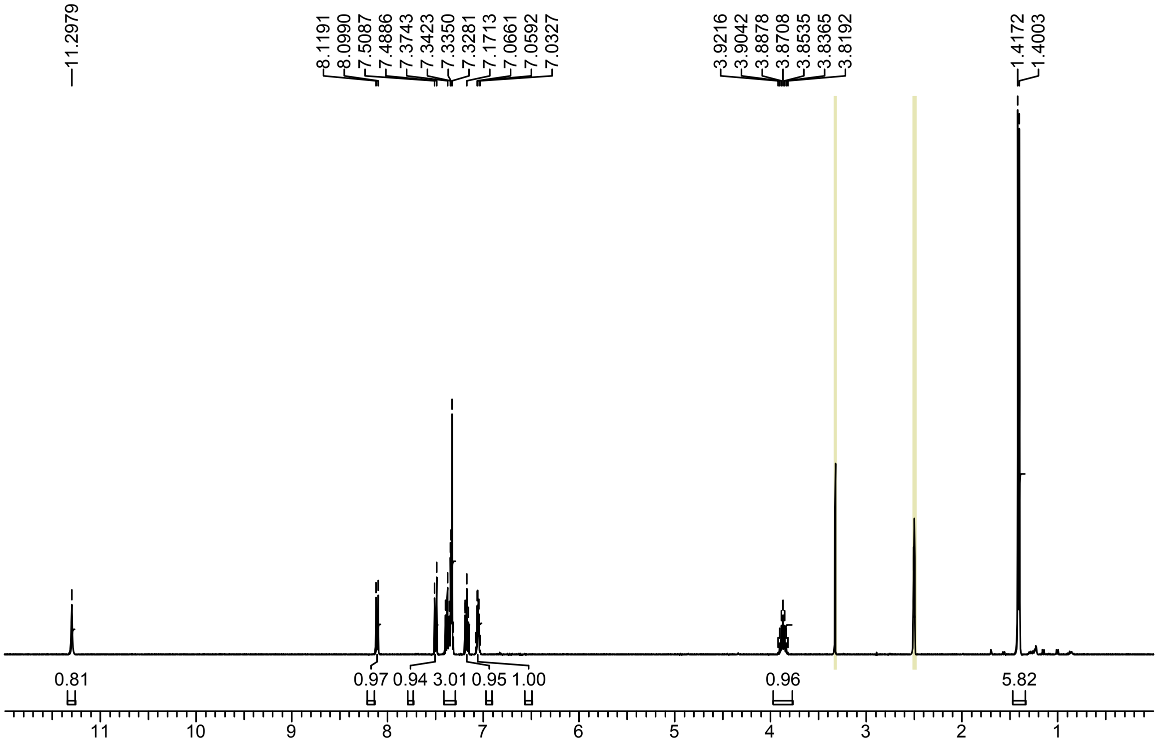

H
N
Me
Me

14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8.0990
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7.4886
7.3743
7.3423
7.3350
7.3281
7.1713
7.0661
7.0592
7.0327
3.9216
3.9042
3.8878
3.8708
3.8535
3.8365
3.8192
1.4172
1.4003
0.81
0.97
0.94
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1.00
0.96
5.82
11
10
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8
7
6
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4
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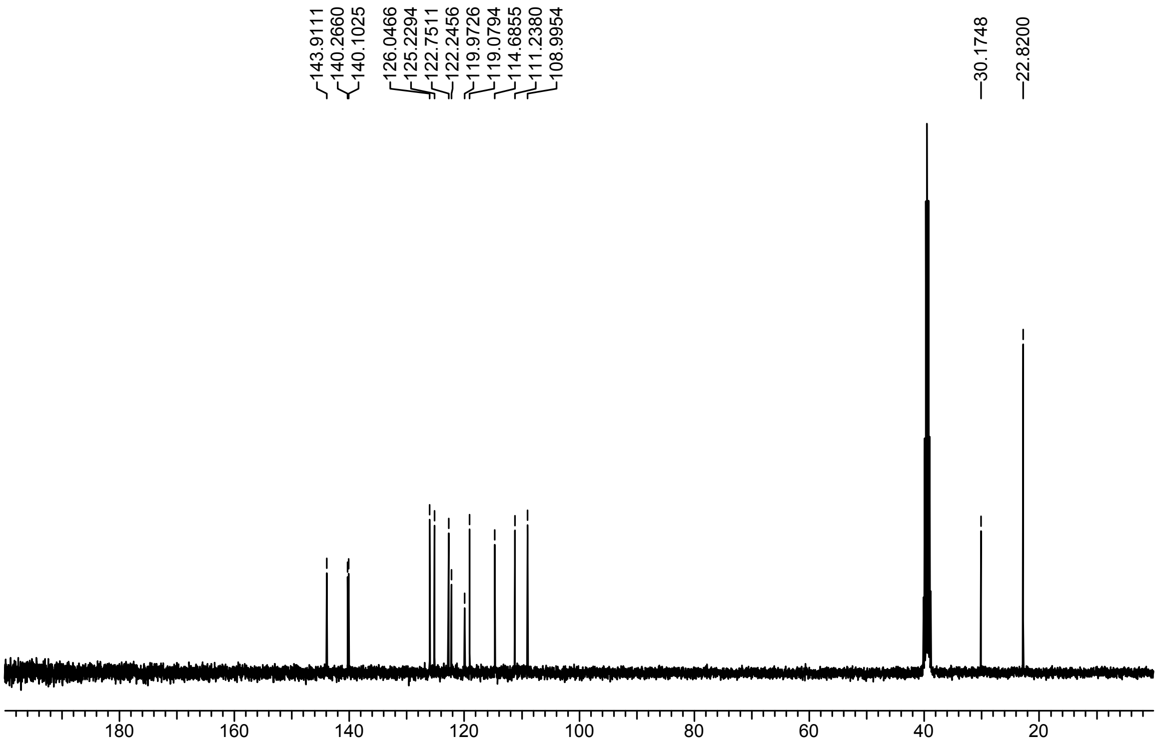
2
1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125.2294
122.7511
122.2456
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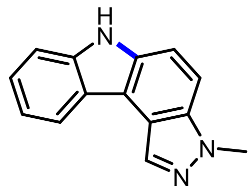
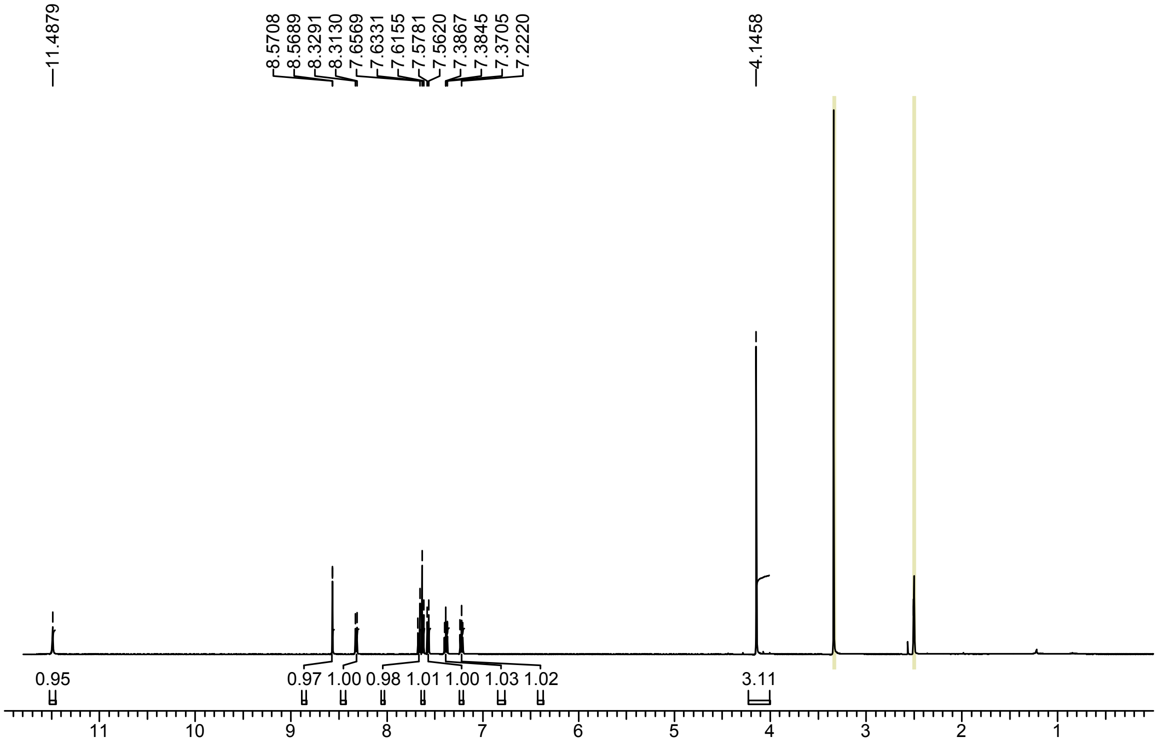
40
20



21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7.6331
7.6155
7.5781
7.5620
7.3867
7.3845
7.3705
7.2220
4.1458
0.95
0.97
1.00
0.98
1.01
1.00
1.03
1.02
3.11
11
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8
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4
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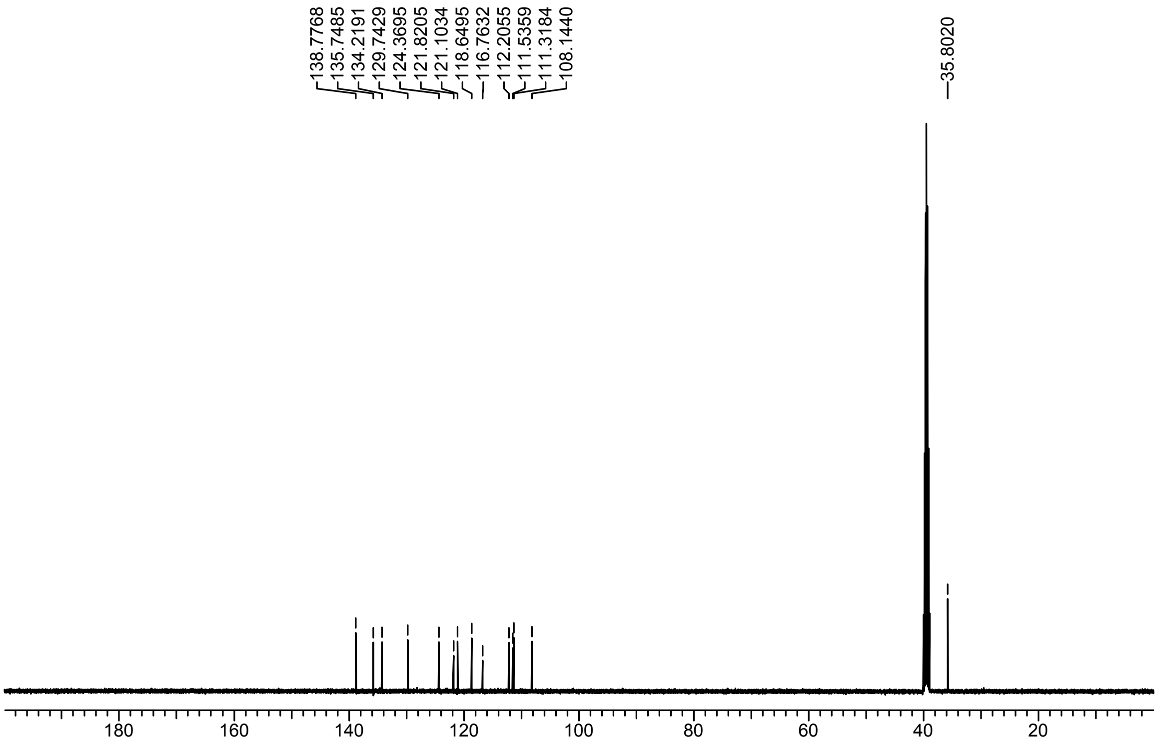
2
1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111.3184
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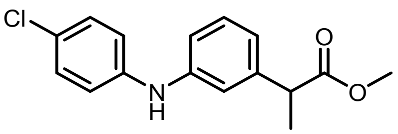
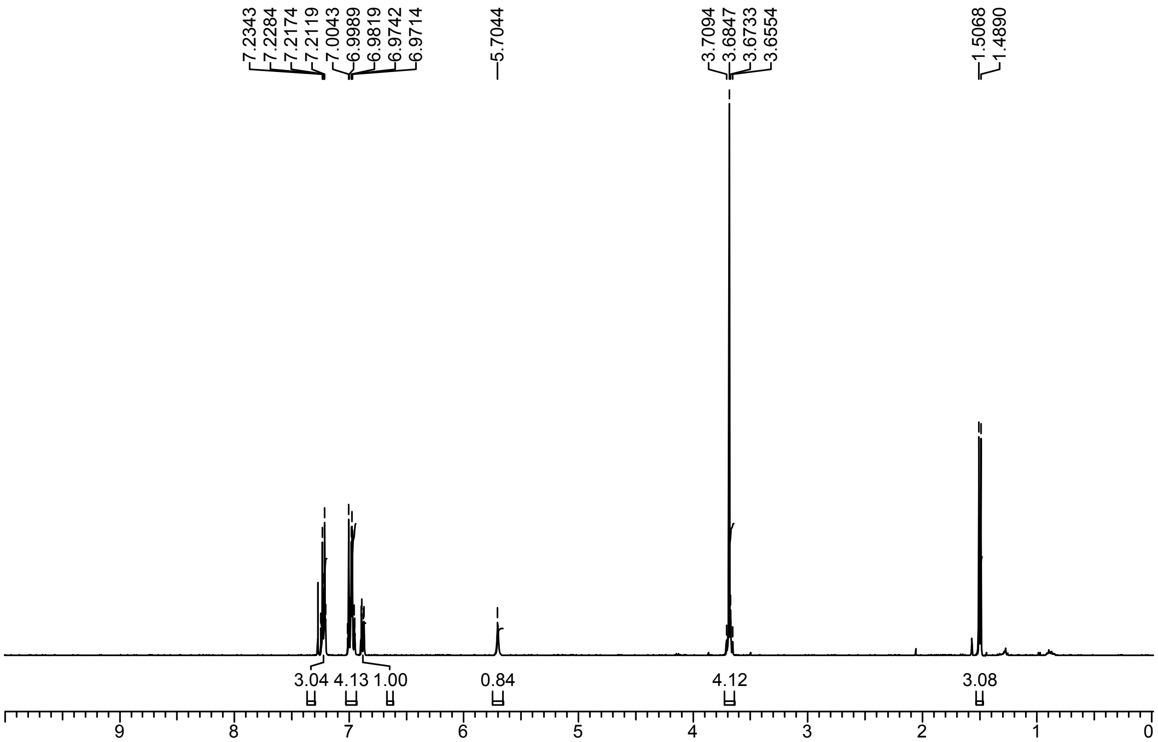


Cl
N
H
O
O

27



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7.2174
7.2119
7.0043
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6.9819
6.9742
6.9714
5.7044
3.7094
3.6847
3.6733
3.6554
1.5068
1.4890
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0.84
4.12
3.08
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7
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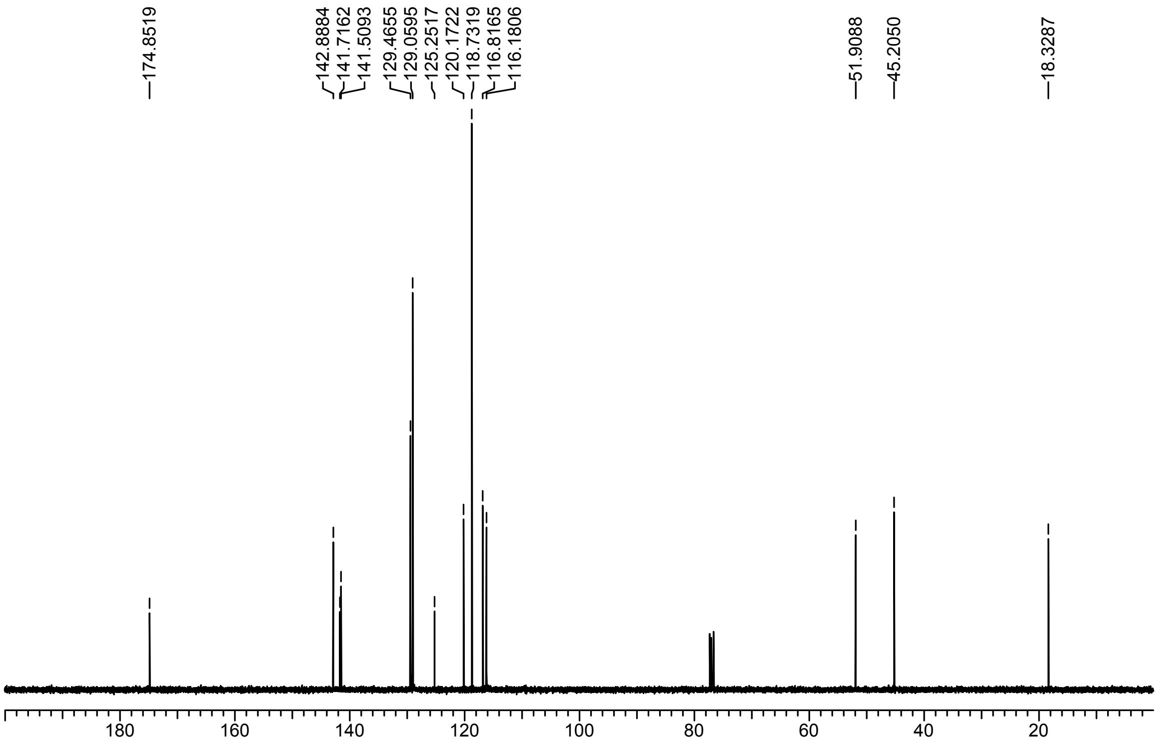

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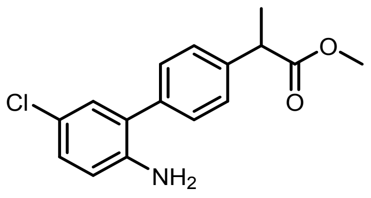
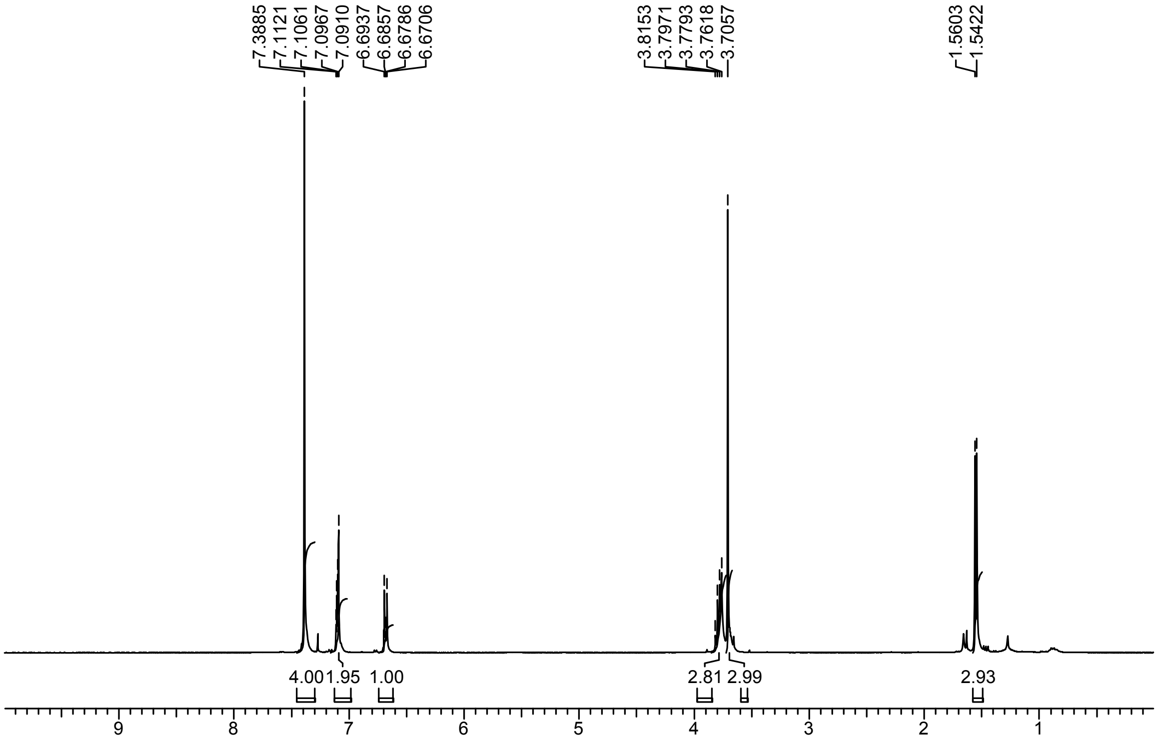

Cl
O
O
NH2

S46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6.6857
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6.6706
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3.7971
3.7793
3.7618
3.7057
1.5603
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2.99
2.93
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8
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6
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4
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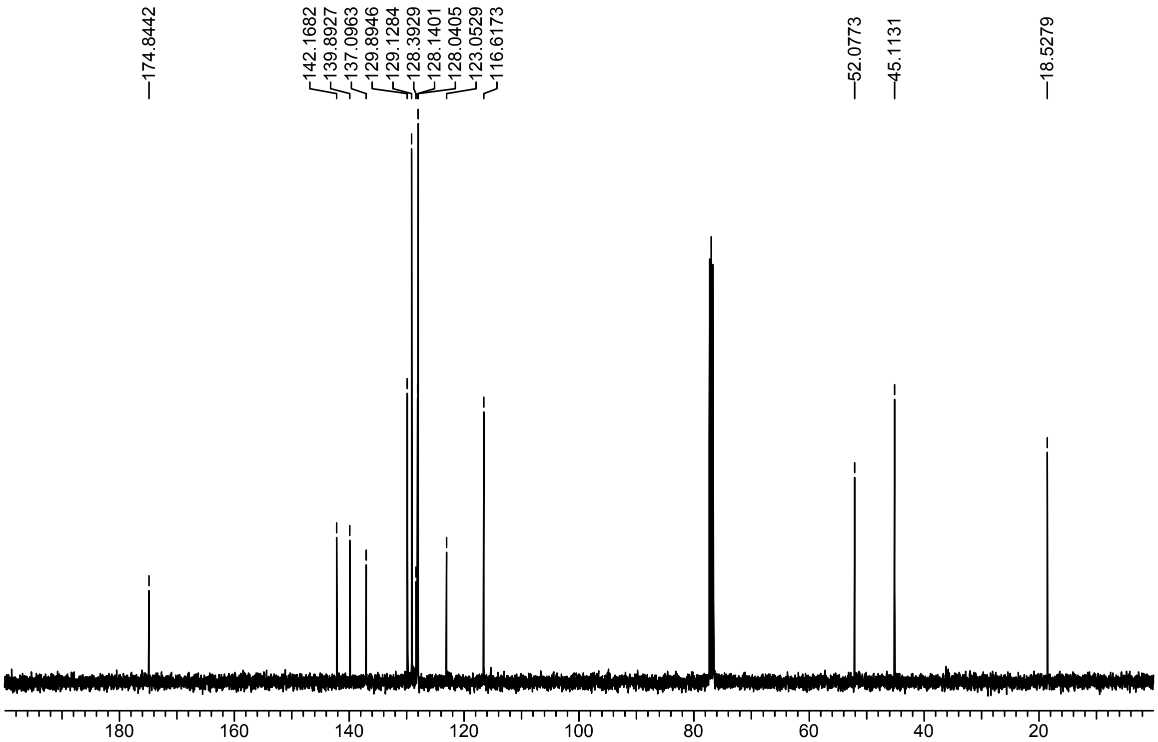
2
1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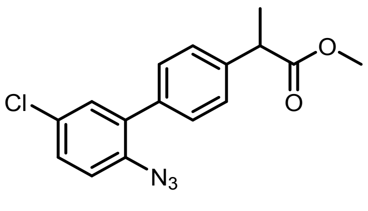
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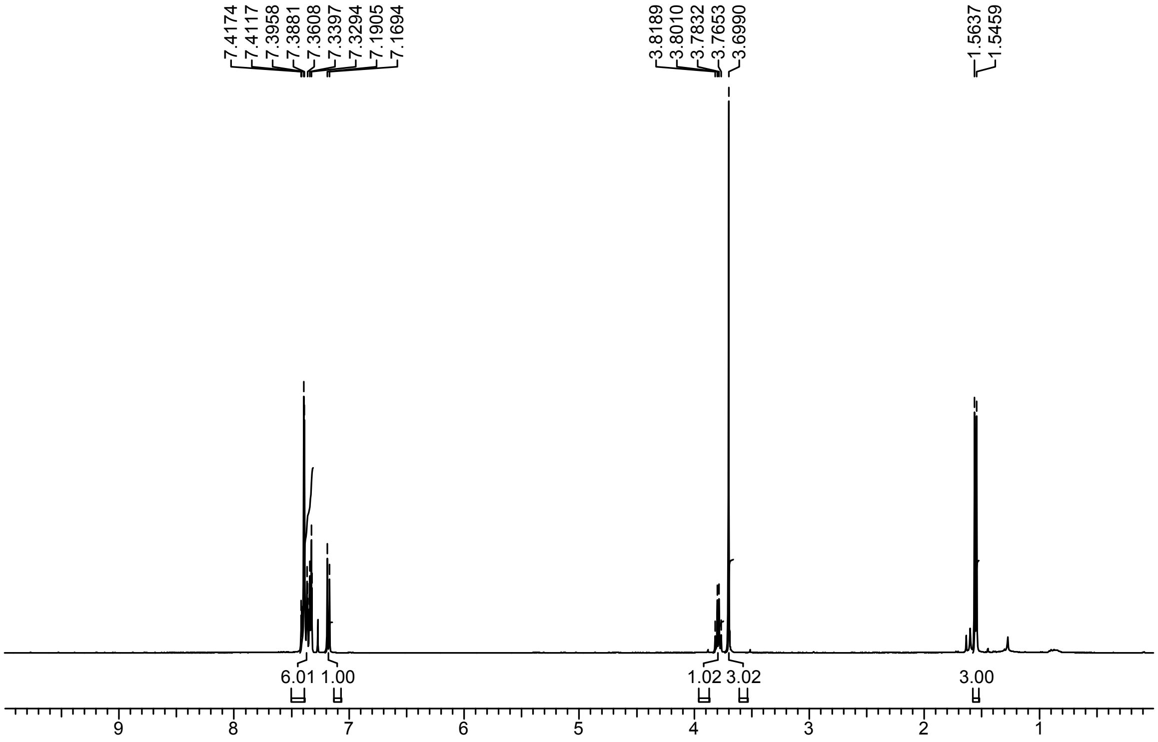
O
O
N3

28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7.1694
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3.8010
3.7832
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3.6990
1.5637
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1.02
3.02
3.00
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8
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2
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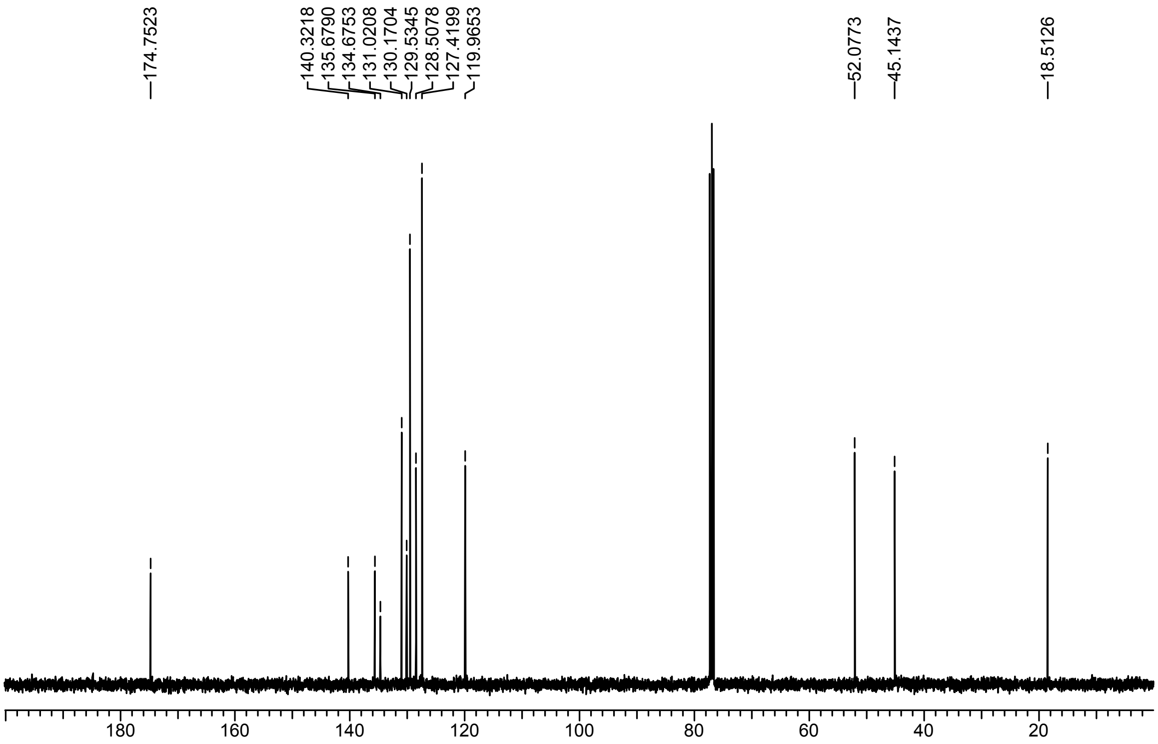
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127.4199
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80
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40
20