Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Rh(III)-catalyzed chemoselective C–H functionalizations of tertiary aniline *N*-oxides with alkynes

Xiaolei Huang, Wenbo Liang, Yang Shi and Jingsong You*

Key Laboratory of Green Chemistry and Technology of Ministry of Education, College of Chemistry, and State Key Laboratory of Biotherapy, West China Medical School, Sichuan University, 29 Wangjiang Road, Chengdu 610064, PR China

Fax: 86-28-85412203; E-mail: jsyou@scu.edu.cn

Table of Contents

I. General remarks

NMR spectra were obtained on an Agilent 400-MR DD2 spectrometer. The ^{1}H NMR (400 MHz) chemical shifts were measured relative to $CDCl_3$ as the internal reference ($CDCl_3$: δ = 7.26). The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$ as the internal standard ($CDCl_3$: δ = 77.16). High-resolution mass spectra (HRMS) were obtained with a Shimadzu LCMS-IT-TOF (ESI). GC-MS spectra were recorded by Shimadzu GCMS-QP2010 SE. Melting points were determined with XRC-1 and are uncorrected. Analytical thin layer chromatography was performed on HG/T2354-92 GF_{254} plates (Qingdao Haiyang Chemical Co., Ltd.).

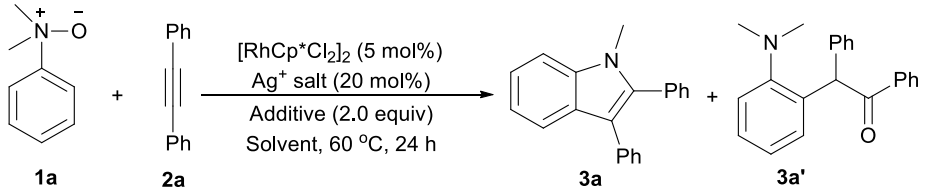
Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. $RhCl_3$ $3H_2O$ were purchased from Shanxi Kaida Chemical Engineering (China) CO., Ltd. Various arylamines and diphenylacetylene were purchased from Adamas-beta Ltd. $[Cp^*RhCl_2]_2$ (Cp* = pentamethyl cyclopentadienyl),[1] tertiary anilines,[2] tertiary aniline *N*−oxides,[3] and *N*,*N*−dimethylaniline−2,3,4,5,6−d_5 *N*−oxide (**1a**-$[D_5]$)[4] were prepared according to the literature procedures. Dichloroethane (DCE) and *N*,*N*-dimethylformamide (DMF) were dried by refluxing over CaH_2. MeOH and 1,4-dioxane were dried by refluxing over Mg and Na, respectively, and freshly distilled prior to use.

II. Optimization of the Rh-catalyzed annulation of *N*,*N*-dimethylaniline *N*-oxide 1a with diphenylacetylene 2a

A sealable tube with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (7.8 mg, 12.5 μmol, 5 mol%), Ag^+ salt (20 mol%), additive (2.0 equiv), *N*,*N*-dimethylaniline *N*-oxide **1a** (68.6 mg, 0.50 mmol, 2.0 equiv), diphenylacetylene **2a** (44.6 mg, 0.25 mmol) and solvent (1.0 mL) under an N_2 atmosphere. The reaction mixture was stirred at 60 ℃ for 24 h. After being cooled to ambient temperature, the resulting solution was diluted with 5 mL of dichloromethane, filtered through a celite pad and washed with 10-20 mL of dichloromethane. The combined organic phases were evaporated, and the resulting residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1 to 50/1, v/v) to provide the desired product

3a and 2-(2-(dimethylamino)phenyl)-1,2-diphenylethanone **3a′** as by-product.

Table S1 Optimization of reaction conditions.[a]



Entry	Ag^+ salt	Additive	Solvent	Yield of **3a** (%)[b]	Yield of **3a′** (%)[b]
1	$AgSbF_6$	PivOH	MeOH	60	25
2	$AgSbF_6$	PivOH	dioxane	0	0
3	$AgSbF_6$	PivOH	DMF	0	0
4	$AgSbF_6$	PivOH	DCE	18	35
5	$AgSbF_6$	PivOH	*t*-AmOH	15	19
6	$AgSbF_6$	HOAc	MeOH	40	28
7	$AgSbF_6$	CF_3COOH	MeOH	0	0
8	$AgSbF_6$	AdCOOH	MeOH	45	27
9	**$AgSbF_6$**	**CyCOOH**	**MeOH**	**70**	**trace**
10	$AgSbF_6$	$Cu(OAc)_2$	MeOH	trace	trace
11	$AgSbF_6$	CsOPiv	MeOH	15	22
12	$AgPF_6$	CyCOOH	MeOH	45	18
13	AgOPiv	CyCOOH	MeOH	62	14
14	AgOAc	CyCOOH	MeOH	0	trace
15	-	CyCOOH	MeOH	44	27
16[c]	$AgSbF_6$	CyCOOH	MeOH	72	trace
17[d]	$AgSbF_6$	CyCOOH	MeOH	61	11
18[e]	$AgSbF_6$	CyCOOH	MeOH	0	0

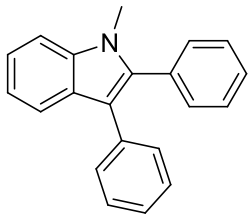
[a] Reaction conditions: **1a** (0.50 mmol, 2.0 equiv), **2a** (0.25 mmol), $[RhCp^*Cl_2]_2$ (5.0 mol%), Ag^+ salt (20 mol%) and additive (2.0 equiv) in solvent (1.0 mL) at 60 ℃ for 24 h under an N_2 atmosphere. [b] Isolated yields. [c] 40 mol% of $AgSbF_6$ was used. [d] **1a** (0.25 mmol), **2a** (0.25 mmol), and $AgSbF_6$ (1.2 equiv). [e] *N*,*N*-Dimethylaniline or *N*-methylaniline instead of **1a** was used as the substrate. DMF = dimethyl formamide, DCE = 1,2-dichloroethane, *t*-AmOH = *tert*-amyl alcohol, AdCOOH = 1-adamantanecarboxylic acid, CyCOOH = cyclohexanecarboxylic acid.

III. General procedure for the Rh-catalyzed functionalization of tertiary aniline *N*-oxides 1 with alkynes 2

A sealable tube with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (7.8 mg, 12.5

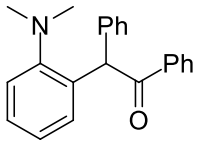
μmol, 5 mol%), $AgSbF_6$ (17.2 mg, 50 μmol, 20 mol%), cyclohexanecarboxylic acid (CyCOOH) (64 mg, 0.5 mmol, 2.0 equiv), tertiary aniline *N*-oxide **1** (0.50 mmol, 2.0 equiv), alkyne **2** (0.25 mmol), and MeOH (1.0 mL) under an N_2 atmosphere. The reaction mixture was stirred at 60 ℃ for 24 h. After being cooled to ambient temperature, the resulting solution was diluted with 5 mL of dichloromethane, filtered through a celite pad and washed with 10-20 mL of dichloromethane. The combined organic phases were evaporated, and the resulting residue was purified by column chromatography on silica gel to provide the desired product.

IV. Experimental data for the described substances



1-Methyl-2,3-diphenyl-1*H*-indole (3a)[5]

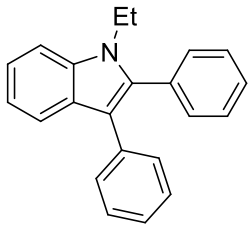
Following the general procedure. *N*,*N*-Dimethylaniline oxide **1a** (68.6 mg, 0.50 mmol) and 1,2-diphenylethyne **2a** (44.6 mg, 0.25 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 100/1, v/v) afforded **3a** as a white solid (50 mg, 70% yield). M.p.: 137-138 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, J = 8.0 Hz, 1H), 7.43-7.37 (m, 4H), 7.35-7.29 (m, 5H), 7.27-7.25 (m, 2H), 7.22-7.16 (m, 2H), 3.69 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.9, 137.5, 135.4, 132.1, 131.3, 130.0, 128.5, 128.3, 128.2, 127.1, 125.6, 122.3, 120.3, 119.8, 115.3, 109.7, 31.1 ppm. HRMS (ESI): calcd for $C_{21}H_{18}N$ $[M+H]^+$ 284.1439, found 284.1433.



2-(2-(Dimethylamino)phenyl)-1,2-diphenylethanone (3a′)

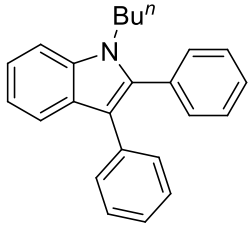
M.p.: 54-56 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, J = 7.6 Hz, 2H), 7.48 (t, J =

7.2 Hz, 1H), 7.41-7.33 (m, 6H), 7.29-7.25 (m, 3H), 7.07-7.02 (m, 2H), 6.48 (s, 1H), 2.51 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.1, 151.8, 138.3, 137.7, 137.3, 132.5, 130.03, 129.95, 128.8, 128.5, 128.4, 128.2, 127.2, 124.8, 121.7, 53.8, 44.8 ppm. HRMS (ESI): calcd for $C_{22}H_{21}NNaO$ $[M+Na]^+$ 338.1521, found 338.1523.



1-Ethyl-2,3-diphenyl-1*H*-indole (3b)[5]

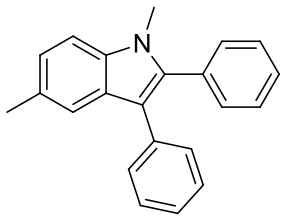
Following the general procedure. *N*,*N*-Diethylaniline oxide **1b** (82.6 mg, 0.50 mmol) and 1,2-diphenylethyne **2a** (44.6 mg, 0.25 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 100/1, v/v) afforded **3b** as a white solid (42 mg, 57% yield). M.p.: 118-120 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.39-7.24 (m, 10H), 7.21-7.15 (m, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.4, 136.1, 135.3, 132.3, 131.2, 129.9, 128.6, 128.23, 128.22, 127.3, 125.5, 122.1, 120.2, 119.9, 115.3, 109.9, 38.8, 15.6 ppm. HRMS (ESI): calcd for $C_{22}H_{19}NNa$ $[M+Na]^+$ 320.1415, found 320.1412.



1-Butyl-2,3-diphenyl-1*H*-indole (3c)

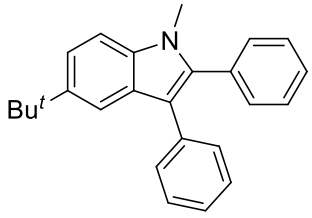
Following the general procedure. *N*,*N*-Dibutylaniline oxide **1c** (110.7 mg, 0.50 mmol), 1,2-diphenylethyne **2a** (44.6 mg, 0.25 mmol), and $AgSbF_6$ (34.4 mg, 0.10 mmol) were used at 110 ℃. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 100/1, v/v) afforded **3c** as a white solid (49 mg, 60% yield). M.p.: 72-74 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.0

Hz, 1H), 7.39-7.24 (m, 10H), 7.20-7.14 (m, 2H), 4.09 (t, J = 7.6 Hz, 2H), 1.71-1.63 (m, 2H), 1.24-1.15 (m, 2H), 0.79 (t, J = 7.6 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.7, 136.5, 135.4, 132.4, 131.3, 130.0, 128.5, 128.21, 128.17, 127.2, 125.5, 122.1, 120.2, 119.8, 115.3, 110.1, 43.8, 32.2, 20.2, 13.8 ppm. HRMS (ESI): calcd for $C_{24}H_{24}N$ $[M+H]^+$ 326.1909, found 326.1910.



1,5-Dimethyl-2,3-diphenyl-1*H*-indole (3d)[5]

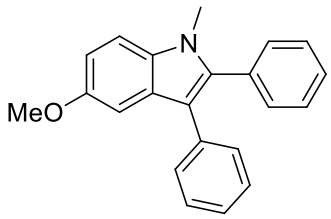
Following the general procedure. *N*,*N*,4-Trimethylaniline oxide **1d** (75.6 mg, 0.50 mmol) and 1,2-diphenylethyne **2a** (44.6 mg, 0.25 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 100/1, v/v) afforded **3d** as a white solid (54 mg, 72% yield). M.p.: 107-108 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (s, 1H), 7.37 (m, 3H), 7.33-7.26 (m, 7H), 7.19-7.18 (m, 1H), 7.14 (d, J = 8.4 Hz, 1H), 3.67 (s, 3H), 2.48 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137. 9, 135.8, 135.5, 132.1, 131.2, 130.0, 129.6, 128.5, 128.3, 128.0, 127.2, 125.5, 123.8, 119.2, 114.6, 109.4, 31.1, 21.7 ppm. HRMS (ESI): calcd for $C_{22}H_{19}NNa$ $[M+Na]^+$ 320.1425, found 320.1425.



5-(*tert*-Butyl)-1-methyl-2,3-diphenyl-1*H*-indole (3e)[6]

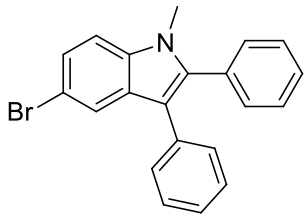
Following the general procedure. 4-*(tert*-Butyl)-*N*,*N*-dimethylaniline oxide **1e** (96.7 mg, 0.50 mmol) and 1,2-diphenylethyne **2a** (44.6 mg, 0.25 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 100/1, v/v) afforded **3e** as a white solid (44 mg, 52% yield). M.p.: 168-169 ℃. ^{1}H

NMR (400 MHz, $CDCl_3$): δ = 7.78 (s, 1H), 7.42-7.39 (m, 1H), 7.37-7.35 (m, 4H), 7.32-7.28 (m, 6H), 7.20-7.16 (m, 1H), 3.66 (s, 3H), 1.40 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.4, 138.1, 135.7, 135.6, 132.2, 131.3, 130.0, 128.5, 128.3, 128.1, 126.7, 125.5, 120.6, 115.4, 115.2, 109.3, 34.9, 32.1, 31.1 ppm. HRMS (ESI): calcd for $C_{25}H_{25}NNa$ $[M+Na]^+$ 362.1885, found 362.1880.



5-Methoxy-1-methyl-2,3-diphenyl-1*H*-indole (3f)[5]

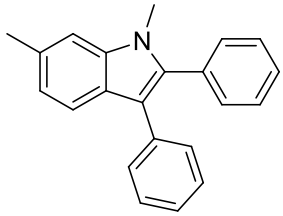
Following the general procedure. 4-Methoxy-*N*,*N*-dimethylaniline oxide **1f** (83.6 mg, 0.50 mmol), 1,2-diphenylethyne **2a** (44.6 mg, 0.25 mmol), and $AgSbF_6$ (34.4 mg, 0.10 mmol) were used at 110 ℃. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 20/1, v/v) afforded **3f** as a white solid (51 mg, 65% yield). M.p.: 132-134 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (m, 3H), 7.33-7.26 (m, 8H), 7.19 (m, 1H), 6.97 (d, J = 8.8 Hz, 1H), 3.86 (s, 3H), 3.67 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.8, 135.5, 132.8, 132.0, 131.2, 129.9, 128.5, 128.4, 128.1, 127.2, 125.5, 114.8, 112.5, 110.5, 110.1, 101.2, 56.2, 31.2 ppm. HRMS (ESI): calcd for $C_{22}H_{19}NNaO$ $[M+Na]^+$ 336.1364, found 336.1360.



5-Bromo-1-methyl-2,3-diphenyl-1*H*-indole (3g)[6]

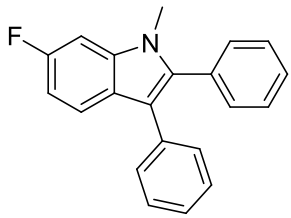
Following the general procedure. 4-Bromo-*N*,*N*-dimethylaniline oxide **1g** (108 mg, 0.50 mmol) and 1,2-diphenylethyne **2a** (44.6 mg, 0.25 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 100/1, v/v) afforded **3g** as a white solid (72 mg, 80% yield). M.p.: 124-126 ℃. ^{1}H NMR (400

MHz, $CDCl_3$): δ = 7.90 (s, 1H), 7.42-7.37 (m, 4H), 7.33-7.25 (m, 7H), 7.21-7.18 (m, 1H), 3.67 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.9, 136.1, 134.6, 131.5, 131.2, 129.9, 128.8, 128.6, 128.5, 128.4, 126.0, 125.1, 122.2, 114.9, 113.7, 111.2, 31.2 ppm. HRMS (ESI): calcd for $C_{21}H_{16}BrKN$ $[M+K]^+$ 400.0103, found 400.0107.



1,6-Dimethyl-2,3-diphenyl-1*H*-indole (3h)[7]

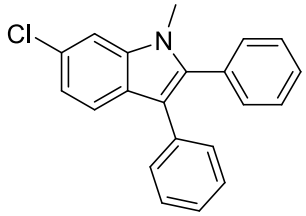
Following the general procedure. *N*,*N*,3-Trimethylaniline oxide **1h** (75.6 mg, 0.50 mmol) and 1,2-diphenylethyne **2a** (44.6 mg, 0.25 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 100/1, v/v) afforded **3h** as a white solid (45 mg, 60% yield). M.p.: 105-106 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.68 (d, J = 8.0 Hz, 1H), 7.38-7.37 (m, 3H), 7.33-7.24 (m, 6H), 7.21 (s, 1H), 7.16 (t, J = 6.8 Hz, 1H), 7.03 (d, J = 8.0 Hz, 1H), 3.65 (s, 3H), 2.55 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.9, 137.2, 135.5, 132.2, 131.3, 129.9, 128.5, 128.3, 128.0, 125.5, 124.9, 122.0, 119.4, 115.0, 109.7, 31.0, 22.1 ppm. HRMS (ESI): calcd for $C_{22}H_{19}NNa$ $[M+Na]^+$ 340.1415, found 340.1416



6-Fluoro-1-methyl-2,3-diphenyl-1*H*-indole (3i)

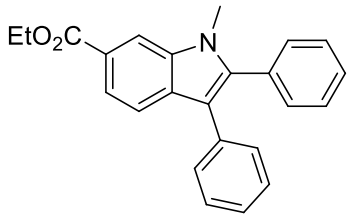
Following the general procedure. 3-Fluoro-*N*,*N*-dimethylaniline oxide **1i** (77.6 mg, 0.50 mmol) and 1,2-diphenylethyne **2a** (44.6 mg, 0.25 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 100/1, v/v) afforded **3i** as a white solid (40 mg, 53% yield). M.p.: 138-140 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36 (m, 3H), 7.28-7.16 (m, 9H), 6.86-6.82 (m, 1H), 3.68 (s, 3H)

ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.3, 155.8, 140.0, 139.9, 138.33, 138.32, 134.91, 134.90, 131.4, 131.3, 131.2, 130.99, 130.96, 129.9, 128.6, 128.5, 128.4, 128.3, 127.6, 125.9, 122.4, 122.3, 115.7, 115.5, 113.7, 113.6, 105.8, 105.7, 105.5, 31.61 ppm. HRMS (ESI): calcd for $C_{21}H_{16}FNNa$ $[M+Na]^+$ 324.1164, found 324.1158.



6-Chloro-1-methyl-2,3-diphenyl-1*H*-indole (3j)[6]

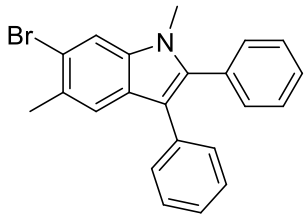
Following the general procedure. 3-Chloro-*N*,*N*-dimethylaniline oxide **1j** (85.8 mg, 0.50 mmol) and 1,2-diphenylethyne **2a** (44.6 mg, 0.25 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 100/1, v/v) afforded **3j** as a white solid (52 mg, 66% yield). M.p.: 140 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (d, J = 8.4 Hz, 1H), 7.40-7.38 (m, 4H), 7.33-7.26 (m, 6H), 7.22-7.17 (m, 1H), 7.14 (d, J = 8.4 Hz, 1H), 3.64 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.4, 137.9, 134.8, 131.6, 131.2, 129.9, 128.6, 128.41, 128.39, 128.1, 125.9, 125.7, 120.9, 120.7, 115.4, 109.7, 31.2 ppm. HRMS (ESI): calcd for $C_{21}H_{16}ClNNa$ $[M+Na]^+$ 340.0869, found 340.0873.



Ethyl 1-methyl-2,3-diphenyl-1*H*-indole-6-carboxylate (3k)

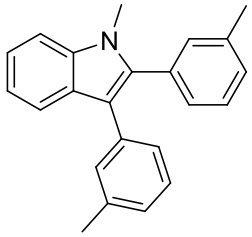
Following the general procedure. 3-(Ethoxycarbonyl)-*N*,*N*-dimethylaniline oxide **1k** (104.6 mg, 0.50 mmol), 1,2-diphenylethyne **2a** (44.6 mg, 0.25 mmol), and $AgSbF_6$ (34.4 mg, 0.10 mmol) were used at 110 ℃. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 20/1, v/v) afforded **3k** as a white solid (55 mg, 62% yield). M.p.: 138-140 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (s, 1H), 7.88 (d,

J = 8.4 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.40 (m, 3H), 7.35-7.32 (m, 2H), 7.29-7.28 (m, 4H), 7.23-7.19 (m, 1H), 4.45 (q, *J* = 7.2 Hz, 2H), 3.76 (s, 3H), 1.46 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.9, 141.0, 136.8, 134.7, 131.4, 131.1, 130.5, 129.9, 128.64, 128.60, 128.4, 126.0, 124.0, 121.3, 119.2, 115.7, 112.1, 110.1, 60.9, 31.3, 14.6 ppm. HRMS (ESI): calcd for $C_{24}H_{21}NNaO_2$ $[M+Na]^+$ 378.1470, found 378.1464.



6-Bromo-1,5-dimethyl-2,3-diphenyl-1*H*-indole (3l)

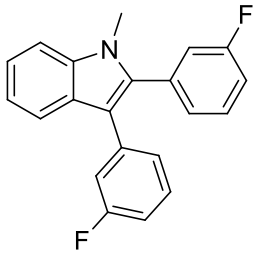
Following the general procedure. 3-Bromo-*N*,*N*,4-trimethylaniline oxide **1l** (115 mg, 0.50 mmol) and 1,2-diphenylethyne **2a** (44.6 mg, 0.25 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 100/1, v/v) afforded **3l** as a white solid (58 mg, 62% yield). M.p.: 176-178 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (s, 2H), 7.38-7.37 (m, 3H), 7.32-7.25 (m, 6H), 7.20-7.17 (m, 1H), 3.63 (s, 3H), 2.50 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.4, 136.9, 135.0, 131.6, 131.2, 129.9, 129.0, 128. 6, 128.4, 128.3, 126.7, 125.8, 120.6, 118.8, 114.8, 113.3, 31.2, 23.3 ppm. HRMS (ESI): calcd for $C_{22}H_{19}BrN$ $[M+H]^+$ 376.0701, found 376.0695.



1-Methyl-2,3-di-*m*-tolyl-1*H*-indole (4a)

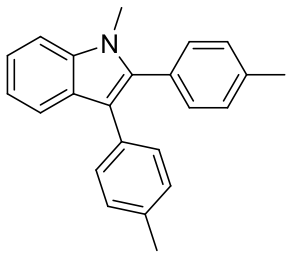
Following the general procedure. *N*,*N*-Dimethylaniline oxide **1a** (68.6 mg, 0.50 mmol) and 1,2-di-*m*-tolylethyne **2b** (51.6 mg, 0.25 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 100/1, v/v) afforded **4a** as a

white solid (53 mg, 68% yield). M.p.: 94 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.26-7.25 (m, 1H), 7.21-7.11 (m, 6H), 7.06 (d, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 7.2 Hz, 1H), 3.67 (s, 3H), 2.36 (s, 3H), 2.30 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.02, 138.00, 137.61, 137.4, 135.3, 132.0, 131.8, 130.6, 128.9, 128.5, 128.3, 128.1, 127.2, 127.1, 126.4, 122.1, 120.2, 119.8, 115.1, 109.6, 31.1, 21.7, 21.6 ppm. HRMS (ESI): calcd for $C_{23}H_{21}NNa$ $[M+Na]^+$ 334.1572, found 334.1570.



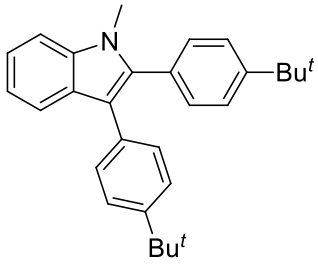
2,3-Bis(3-fluorophenyl)-1-methyl-1*H*-indole (4b)

Following the general procedure. *N*,*N*-Dimethylaniline oxide **1a** (68.6 mg, 0.50 mmol) and 1,2-bis(3-fluorophenyl)ethyne **2c** (53.6 mg, 0.25 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 100/1, v/v) afforded **4b** as a white solid (57 mg, 72% yield). M.p.: 106-108 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.41-7.33 (m, 2H), 7.27-7.21 (m, 2H), 7.13-6.99 (m, 5H), 6.90 (t, *J* = 8.0 Hz, 1H), 3.69 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.2, 164.0, 161.8, 161.5, 137.5, 137.33, 137.25, 136.64, 136.62, 133.9, 133. 8, 130.3, 130.2, 129.83, 129.75, 127.08, 127.05, 126.7, 125.63, 125.60, 122.9, 120.8, 119.7, 118.2, 118.0, 116.6, 116.4, 115.6, 115.4, 114.7, 114.6, 112.9, 112.7, 109.9, 31.1 ppm. HRMS (ESI): calcd for $C_{21}H_{16}F_2N$ $[M+H]^+$ 320.1251, found 320.1247.



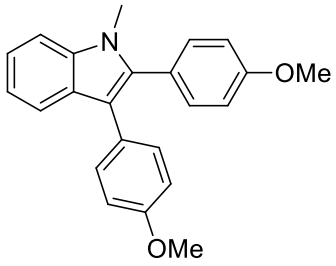
1-Methyl-2,3-di-*p*-tolyl-1*H*-indole (4c)[5]

Following the general procedure. *N*,*N*-Dimethylaniline oxide **1a** (68.6 mg, 0.50 mmol) and 1,2-di-*p*-tolylethyne **2d** (51.6 mg, 0.25 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 100/1, v/v) afforded **4a** as a white solid (40 mg, 52% yield). M.p.: 108-110 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, J = 8.0 Hz, 1H), 7.40 (d, J = 8.4 Hz, 1H), 7.31-7.16 (m, 8H), 7.10 (d, J = 8.0 Hz, 2H), 3.67 (s, 3H), 2.40 (s, 3H), 2.34 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.9, 137.8, 137.4, 135.0, 132.5, 131.1, 129.8, 129.2, 129.13, 129.05, 127.2, 122.1, 120.1, 119.7, 114.9, 109.6, 31.0, 21.5, 21.3 ppm. HRMS (ESI): calcd for $C_{23}H_{21}NNa$ $[M+Na]^+$ 334.1572, found 334.1570.



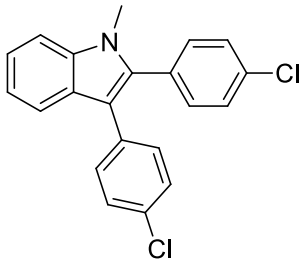
2,3-Bis(4-(*tert*-butyl)phenyl)-1-methyl-1*H*-indole (4d)[5]

Following the general procedure. *N*,*N*-Dimethylaniline oxide **1a** (68.6 mg, 0.50 mmol) and 1,2-bis(4-(*tert*-butyl)phenyl)ethyne **2e** (72.6 mg, 0.25 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 100/1, v/v) afforded **4d** as a white solid (47 mg, 48% yield). M.p.: 180-182 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, J = 7.6 Hz, 1H), 7.40 (d, J = 8.4 Hz, 3H), 7.30-7.24 (m, 7H), 7.17 (t, J = 7.6 Hz, 1H), 3.66 (s, 3H), 1.36 (s, 9H), 1.32 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.0, 148.1, 137.8, 137.4, 132.4, 130.9, 129.5, 129.1, 127.3, 125.3, 125.1, 122.0, 120.0, 119.9, 114.8, 109.6, 34.8, 34.6, 31.6, 31.5, 31.1 ppm. HRMS (ESI): calcd for $C_{29}H_{34}N$ $[M+H]^+$ 396.2691, found 396.2696.



2,3-Bis(4-methoxyphenyl)-1-methyl-1*H*-indole (4e)[5]

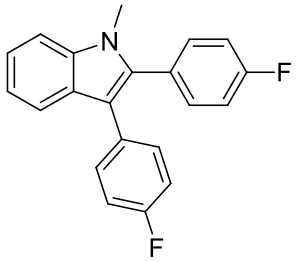
Following the general procedure. *N*,*N*-Dimethylaniline oxide **1a** (68.6 mg, 0.50 mmol) and 1,2-bis(4-methoxyphenyl)ethyne **2f** (59.6 mg, 0.25 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 20/1, v/v) afforded **4e** as a white solid (34 mg, 40% yield). M.p.: 116-118 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, J = 7.6 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.30-7.22 (m, 5H), 7.17 (t, J = 7.6 Hz, 1H), 6.92 (d, J = 8.4 Hz, 2H), 6.84 (d, J = 8.4 Hz, 2H), 3.85 (s, 3H), 3.80 (s, 3H), 3.67 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4, 157.6, 137.4, 137.3, 132.5, 131.0, 127.9, 127.3, 124.4, 122.0, 120.1, 119.6, 114.5, 114.0, 113.8, 109.6, 55.4, 55.3, 31.0 ppm. HRMS (ESI): calcd for $C_{23}H_{22}NO_2$ $[M+H]^+$ 344.1651, found 344.1652.



2,3-Bis(4-chlorophenyl)-1-methyl-1*H*-indole (4f)[7]

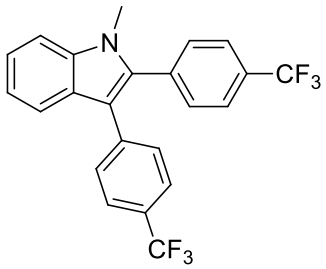
Following the general procedure. *N*,*N*-Dimethylaniline oxide **1a** (68.6 mg, 0.50 mmol) and 1,2-bis(4-chlorophenyl)ethyne **2g** (61.8 mg, 0.25 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 100/1, v/v) afforded **4f** as a white solid (58 mg, 66% yield). M.p.: 142-144 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, J = 8.0 Hz, 1H), 7.41 (d, J = 8.4 Hz, 1H), 7.39-7.37 (m, 2H), 7.32 (t, J = 7.6 Hz, 1H), 7.27-7.19 (m, 7H), 3.67 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.6, 136.6, 134.6, 133.6, 132.5, 131.6, 131.2, 130.2, 129.0,

128.7, 126.8, 122.8, 120.7, 119.5, 114.5, 109.9, 31.1 ppm. HRMS (ESI): calcd for $C_{21}H_{15}Cl_2KN$ $[M+K]^+$ 390.0219, found 390.0252.



2,3-Bis(4-fluorophenyl)-1-methyl-1*H*-indole (4g)

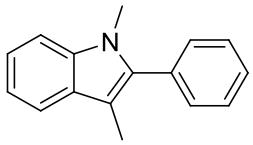
Following the general procedure. *N*,*N*-Dimethylaniline oxide **1a** (68.6 mg, 0.50 mmol) and 1,2-bis(4-fluorophenyl)ethyne **2h** (53.6 mg, 0.25 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 100/1, v/v) afforded **4g** as a white solid (46 mg, 58% yield). M.p.: 133-134 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, J = 8.0 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.34-7.19 (m, 6H), 7.10 (t, J = 8.8 Hz, 2H), 6.98 (t, J = 8.8 Hz, 2H), 3.67 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.0, 162.5, 161.5, 160.34, 160.33, 160.1, 151.5, 137.4, 136.7, 133.0, 132.9, 131.4, 131.3, 131.09, 131.06, 127.9, 127.8, 127.0, 122.6, 120.5, 119.5, 115.9, 115.7, 115.5, 115.2, 114.5, 109.8, 31.0 ppm. HRMS (ESI): calcd for $C_{21}H_{16}F_2N$ $[M+H]^+$ 320.1251, found 320.1254.



1-Methyl-2,3-bis(4-(trifluoromethyl)phenyl)-1*H*-indole (4h)[7]

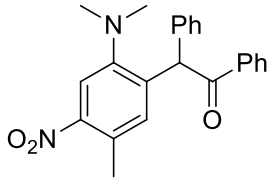
Following the general procedure. *N*,*N*-Dimethylaniline oxide **1a** (68.6 mg, 0.50 mmol), 1,2-bis(4-(trifluoromethyl)phenyl)ethyne **2i** (78.6 mg, 0.25 mmol), and $AgSbF_6$ (34.4 mg, 0.10 mmol) were used at 110 ℃. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 100/1, v/v) afforded **4h** as a

white solid (64 mg, 61% yield). M.p.: 136-138 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 7.6 Hz, 2H), 7.55 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 7.6 Hz, 3H), 7.39-7.35 (m, 3H), 7.25 (t, J = 7.6 Hz, 1H), 3.71 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.8, 137.8, 136.7, 135.8, 135.3, 131.5, 130.7, 130.4, 130.0, 128.1, 127.8, 126.7, 125.8, 125.7, 125.6, 125.52, 125.48, 125.4, 123.2, 122.8, 121.1, 119.6, 114.9, 110.1, 31.3 ppm. HRMS (ESI): calcd for $C_{23}H_{16}F_6N$ $[M+H]^+$ 420.1187, found 420.1192.



1,3-Dimethyl-2-phenyl-1*H*-indole (4i)[7]

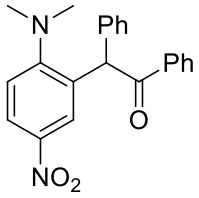
Following the general procedure. *N*,*N*-Dimethylaniline oxide **1a** (68.6 mg, 0.50 mmol), prop-1-yn-1-ylbenzene **2j** (31.3 μL, 0.25 mmol), and $AgSbF_6$ (34.4 mg, 0.10 mmol) were used at 110 ℃. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 100/1, v/v) afforded **4i** as a white solid (29 mg, 52% yield). M.p.: 62-64 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, J = 7.6 Hz, 1H), 7.53-7.50 (m, 2H), 7.45-7.42 (m, 3H), 7.36 (d, J = 8.0 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.19 (t, J = 7.6 Hz, 1H), 3.64 (s, 3H), 2.32 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.8, 137.3, 132.2, 130.8, 128.51, 128.45, 127.9, 121.8, 119.2, 118.9, 109.4, 108.6, 31.1, 9.5 ppm. HRMS (ESI): calcd for $C_{16}H_{16}N$ $[M+H]^+$ 222.1283, found 222.1276.



2-(2-(Dimethylamino)-5-methyl-4-nitrophenyl)-1,2-diphenylethanone (5a)

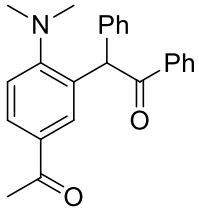
Following the general procedure. *N*,*N*,4-Trimethyl-3-nitroaniline oxide **1o** (98.1 mg, 0.50 mmol) and 1,2-diphenylethyne **2a** (44.6 mg, 0.25 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 30/1, v/v) afforded **5a** as a yellow solid (60 mg, 64% yield). M.p.: 128-130 ℃. ^{1}H NMR (400

MHz, $CDCl_3$): δ = 8.02 (d, J = 8.0 Hz, 2H), 7.87 (s, 1H), 7.52 (t, J = 7.2 Hz, 1H), 7.44-7.36 (m, 4H), 7.33-7.29 (m, 3H), 6.97 (s, 1H), 6.49 (s, 1H), 2.54 (s, 6H), 2.47 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.5, 150.8, 148.3, 143.0, 137.2, 137.1, 134.5, 133.0, 130.0, 129.7, 129.2, 128.7, 128.5, 127.8, 118.2, 53.7, 44.8, 20.7 ppm. HRMS (ESI): calcd for $C_{23}H_{22}N_2NaO_3$ $[M+Na]^+$ 397.1528, found 397.1527.



2-(2-(Dimethylamino)-5-nitrophenyl)-1,2-diphenylethanone (5b)

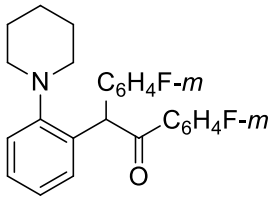
Following the general procedure. *N*,*N*-Dimethyl-4-nitroaniline oxide **1p** (91.1 mg, 0.50 mmol) and 1,2-diphenylethyne **2a** (44.6 mg, 0.25 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 30/1, v/v) afforded **5b** as a yellow solid (56 mg, 62% yield). M.p.: 162-164 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (s, 1H), 8.02 (d, J = 7.6 Hz, 2H), 7.90 (d, J = 8.4 Hz, 1H), 7.52 (t, J = 7.2 Hz, 1H), 7.44-7.29 (m, 7H), 7.17 (d, J = 8.4 Hz, 1H), 6.50 (s, 1H), 2.57 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.4, 153.1, 147.9, 144.9, 137.10, 137.08, 133.1, 131.3, 129.7, 129.3, 128.8, 128.4, 127.9, 119.6, 116.9, 54.1, 44.7 ppm. HRMS (ESI): calcd for $C_{22}H_{20}N_2NaO_3$ $[M+Na]^+$ 383.1372, found 383.1366.



2-(5-Acetyl-2-(dimethylamino)phenyl)-1,2-diphenylethanone (5c)

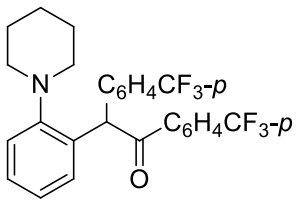
Following the general procedure. 4-Acetyl-*N*,*N*-dimethylaniline oxide **1q** (89.6 mg, 0.50 mmol) and 1,2-diphenylethyne **2a** (44.6 mg, 0.25 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded

5c as greenish yellow oil (64 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, J = 7.6 Hz, 2H), 7.86 (d, J = 8.4 Hz, 1H), 7.67 (s, 1H), 7.49 (t, J = 7.2 Hz, 1H), 7.41-7.29 (m, 7H), 7.26-7.24 (m, 1H), 6.47 (s, 1H), 2.61 (s, 6H), 2.45 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.2, 197.4, 156.7, 138.0, 137.2, 135.7, 133.0, 132.9, 131.2, 129.7, 129.0, 128.6, 128.5, 127.5, 120.9, 53.9, 44.6, 26.6 ppm. HRMS (ESI): calcd for $C_{24}H_{23}NNaO_2$ $[M+Na]^+$ 380.1626, found 380.1622.



1,2-Bis(3-fluorophenyl)-2-(2-(piperidin-1-yl)phenyl)ethanone (5d)

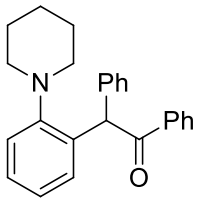
Following the general procedure. 1-Phenylpiperidine 1-oxide **1r** (88.6 mg, 0.50 mmol) and 1,2-bis(3-fluorophenyl)ethyne **2c** (53.6 mg, 0.25 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 50/1, v/v) afforded **5d** as a white solid (73 mg, 75% yield). M.p.: 100-102 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 10 Hz, 1H), 7.39-7.17 (m, 5H), 7.11-6.95 (m, 5H), 6.56 (s, 1H), 2.84-2.65 (m, 4H), 1.63-1.44 (m, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.72, 196.70, 164.3, 164.1, 161.9, 161.7, 152.1, 140.93, 140.86, 138.94, 138.88, 134.6, 130.19, 130.18, 130.12, 130.09, 129.8, 128.7, 125.34, 125.31, 124.7, 124.57, 124.54, 122.2, 120.1, 119.9, 116.8, 116.5, 115.9, 115.7, 114.4, 114.2, 53.28, 53.26, 26.6, 24.2 ppm. HRMS (ESI): calcd for $C_{25}H_{23}F_2NNaO$ $[M+Na]^+$ 414.1645, found 414.1640.



2-(2-(Piperidin-1-yl)phenyl)-1,2-bis(4-(trifluoromethyl)phenyl)ethanone (5e)

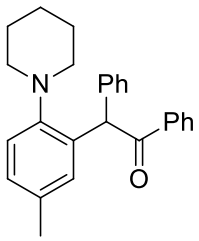
Following the general procedure. 1-Phenylpiperidine 1-oxide **1r** (88.6 mg, 0.50 mmol) and 1,2-bis(4-(trifluoromethyl)phenyl)ethyne **2i** (78.6 mg, 0.25 mmol) were used.

Purification via column chromatography on silica gel (petroleum ether/EtOAc = 40/1, v/v) afforded **5e** as a white solid (91 mg, 74% yield). M.p.: 128-130 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 7.6 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.29-7.25 (m, 2H), 7.08-7.07 (m, 2H), 6.67 (s, 1H), 2.83-2.49 (m, 4H), 1.65-1.42 (m, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.9, 152.3, 142.4, 139.4, 135.0, 134.6, 134.3, 134.0, 130.10, 130.09, 129.90, 129.89, 129.87, 129.86, 129.6, 129.4, 129.3, 129.1, 125.83, 125.80, 125.77, 125.2, 125.0, 123.0, 122.6, 122.4, 53.7, 26.8, 24.3 ppm. HRMS (ESI): calcd for $C_{27}H_{23}F_6NNaO$ $[M+Na]^+$ 514.1582, found 514.1577.



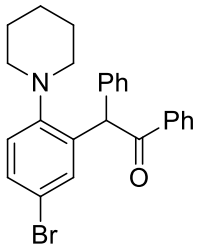
1,2-Diphenyl-2-(2-(piperidin-1-yl)phenyl)ethanone (5f)

Following the general procedure. 1-Phenylpiperidine 1-oxide **1r** (88.6 mg, 0.50 mmol) and 1,2-diphenylethyne **2a** (44.6 mg, 0.25 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 50/1, v/v) afforded **5f** as a white solid (74 mg, 83% yield). M.p.: 102-104 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, J = 7.6 Hz, 2H), 7.48 (t, J = 7.6 Hz, 1H), 7.39 (t, J = 7.6 Hz, 2H), 7.34-7.33 (m, 4H), 7.29-7.21 (m, 3H), 7.11-7.03 (m, 2H), 6.62 (s, 1H), 2.86-2.68 (m, 4H), 1.57-1.51 (m, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.5, 152.2, 138.6, 137.2, 136.3, 132.8, 130.1, 129.7, 129.0, 128.8, 128.5, 128.2, 127.1, 124.6, 122.0, 53.6, 26.5, 24.3 ppm. HRMS (ESI): calcd for $C_{25}H_{25}NNaO$ $[M+Na]^+$ 378.1834, found 378.1829.



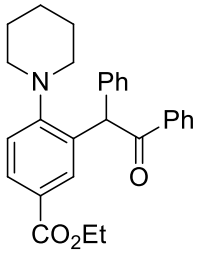
2-(5-Methyl-2-(piperidin-1-yl)phenyl)-1,2-diphenylethanone (5g)

Following the general procedure. 1-(*p*-Tolyl)piperidine 1-oxide **1s** (95.7 mg, 0.50 mmol) and 1,2-diphenylethyne **2a** (44.6 mg, 0.25 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 50/1, v/v) afforded **5g** as a white solid (75 mg, 81% yield). M.p.: 132-134 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 8.0 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.33 (m, 4H), 7.26 (m, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.90 (s, 1H), 6.61 (s, 1H), 2.80-2.61 (m, 4H), 2.22 (s, 3H), 1.56-1.49 (m, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.6, 149.7, 138.7, 137.2, 136.0, 134.1, 132.8, 130.5, 129.7, 129.0, 128.9, 128.7, 128.5, 127.1, 121.9, 53.5, 26.6, 24.3, 21.2 ppm. HRMS (ESI): calcd for $C_{26}H_{27}NNaO$ $[M+Na]^+$ 392.1990, found 392.1986.



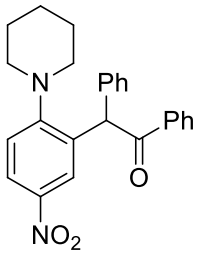
2-(5-Bromo-2-(piperidin-1-yl)phenyl)-1,2-diphenylethanone (5h)

Following the general procedure. 1-(4-Bromophenyl)piperidine 1-oxide **1t** (128 mg, 0.50 mmol) and 1,2-diphenylethyne **2a** (44.6 mg, 0.25 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 50/1, v/v) afforded **5h** as a white solid (100 mg, 92% yield). M.p.: 108-110 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.42-7.28 (m, 8H), 7.14 (s, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 6.52 (s, 1H), 2.79-2.63 (m, 4H), 1.56-1.43 (m, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.8, 151.3, 139.1, 137.6, 137.0, 133.00, 132.95, 131.2, 129.6, 129.1, 129.0, 128.6, 127.5, 123.9, 118.1, 53.5, 26.4, 24.1 ppm. HRMS (ESI): calcd for $C_{25}H_{24}BrNNaO$ $[M+Na]^+$ 456.0939, found 456.0942



Ethyl 3-(2-oxo-1,2-diphenylethyl)-4-(piperidin-1-yl)benzoate (5i)

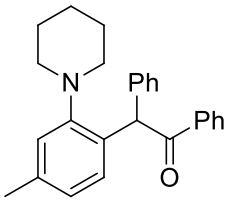
Following the general procedure. 1-(4-(Ethoxycarbonyl)phenyl)piperidine 1-oxide **1u** (125 mg, 0.50 mmol) and 1,2-diphenylethyne **2a** (44.6 mg, 0.25 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 20/1, v/v) afforded **5i** as a white solid (90 mg, 84% yield). M.p.: 132 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, J = 7.6 Hz, 2H), 7.92 (d, J = 8.4 Hz, 1H), 7.81 (s, 1H), 7.48 (t, J = 7.2 Hz, 1H), 7.40-7.31 (m, 6H), 7.29-7.26 (m, 1H), 7.21 (d, J = 8.4 Hz, 1H), 6.54 (s, 1H), 4.28 (q, J = 7.2 Hz, 2H), 2.91-2.88 (m, 2H), 2.70 (m, 2H), 1.60-1.51 (m, 6H), 1.31 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.0, 166.5, 156.5, 138.2, 137.0, 135.5, 133.0, 131.7, 129.9, 129.5, 129.0, 128.6, 127.4, 126.2, 121.3, 60.9, 54.1, 53.6, 26.5, 24.2, 14.5 ppm. HRMS (ESI): calcd for $C_{28}H_{29}NNaO_3$ $[M+Na]^+$ 450.2045, found 450.2045.



2-(5-Nitro-2-(piperidin-1-yl)phenyl)-1,2-diphenylethanone (5j)

Following the general procedure. 1-(4-Nitrophenyl)piperidine 1-oxide **1v** (111 mg, 0.50 mmol) and 1,2-diphenylethyne **2a** (44.6 mg, 0.25 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 30/1, v/v) afforded **5j** as a yellow solid (65 mg, 65% yield). M.p.: 192-194 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, J = 8.8 Hz, 1H), 8.06 (d, J = 8.0 Hz, 2H), 7.96 (s, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.43-7.36 (m, 4H), 7.33-7.29 (m, 3H), 7.26-7.23 (m, 1H),

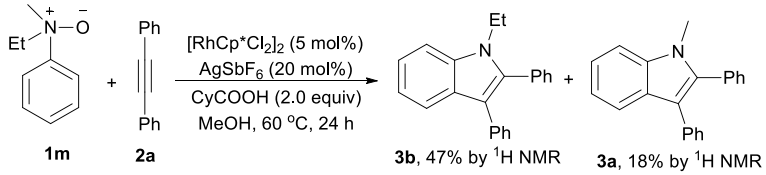
6.50 (s, 1H), 2.94-2.91 (m, 2H), 2.75-2.73 (m, 2H), 1.55-1.50 (m, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.5, 158.3, 144.1, 137.4, 137.2, 136.7, 133.3, 129.4, 129.3, 128.9, 128.7, 127.9, 126.3, 123.8, 121.6, 54.0, 53.8, 26.3, 24.0 ppm. HRMS (ESI): calcd for $C_{25}H_{24}N_2NaO_3$ $[M+Na]^+$ 423.1685, found 423.1683.



2-(4-Methyl-2-(piperidin-1-yl)phenyl)-1,2-diphenylethanone (5k)

Following the general procedure. 1-(*m*-Tolyl)piperidine 1-oxide **1w** (95.6 mg, 0.50 mmol) and 1,2-diphenylethyne **2a** (44.6 mg, 0.25 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 50/1, v/v) afforded **5k** as a white solid (79 mg, 85% yield). M.p.: 112-114 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, J = 7.6 Hz, 2H), 7.47 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.33-7.32 (m, 4H), 7.26-7.25 (m, 1H), 7.02-6.98 (m, 2H), 6.86 (d, J = 7.6 Hz, 1H), 6.57 (s, 1H), 2.83-2.66 (m, 4H), 2.29 (s, 3H), 1.56-1.51 (m, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.7, 152.0, 138.9, 137.9, 137.2, 133.0, 132.7, 129.9, 129.7, 129.0, 128.7, 128.5, 127.0, 125.3, 122.8, 53.3, 26.6, 24.3, 21.4 ppm. HRMS (ESI): calcd for $C_{26}H_{27}NNaO$ $[M+Na]^+$ 392.1990, found 392.1986.

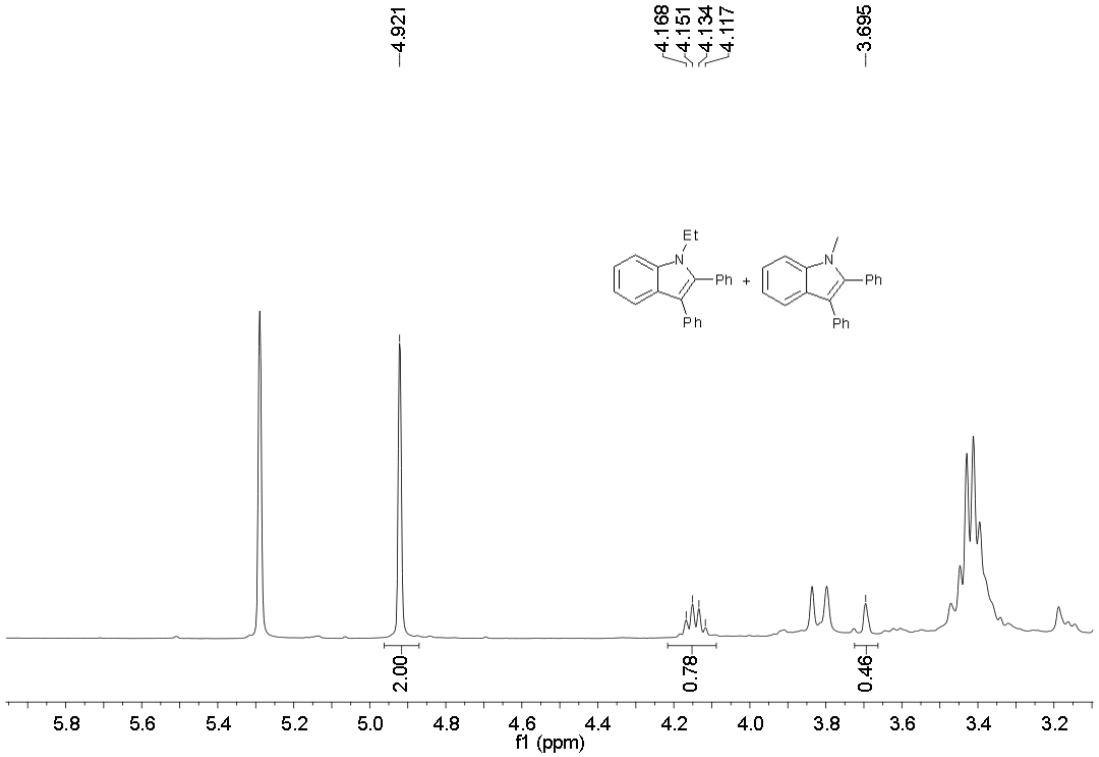
V. Rh(III)-catalyzed annulation of *N*-ethyl-*N*-methylaniline *N*-oxide and *N*-benzyl-*N*-methylaniline *N*-oxide with diphenylacetylene

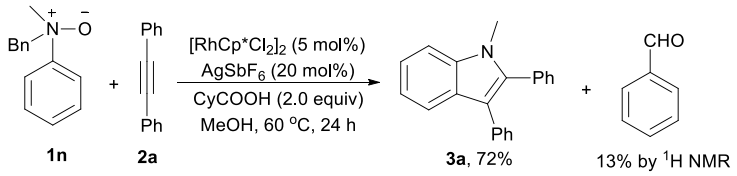


1m **2a** **3b**, 47% by ^{1}H NMR **3a**, 18% by ^{1}H NMR

Following the general procedure in **III**. *N*-Ethyl-*N*-methylaniline *N*-oxide **1m** (75.6 mg, 0.50 mmol) and diphenylacetylene **2a** (44.6 mg, 0.25 mmol) were used. The resulting solution was subsequently diluted with 5 mL of dichloromethane, filtered through a celite pad and washed with 10-20 mL of dichloromethane. The combined

organic phases were evaporated, and the resulting residue was analyzed by ^{1}H NMR using CH_2Br_2 (21 μL, 0.30 mmol) as an internal standard. As a result, *N*-ethyl and *N*-methyl substituted indoles **3b** and **3a** were observed in 47% and 18% yields, respectively.

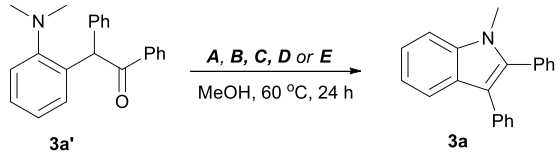




Following the general procedure in **III**. *N*-Benzyl-*N*-methylaniline *N*-oxide **1n** (106.7 mg, 0.50 mmol) and diphenylacetylene **2a** (44.6 mg, 0.25 mmol) were used. The resulting solution was subsequently diluted with 5 mL of dichloromethane, filtered through a celite pad and washed with 10-20 mL of dichloromethane. The combined organic phases were evaporated, and the resulting residue was analyzed by ^{1}H NMR using CH_2Br_2 (14 μL, 0.20 mmol) as an internal standard. As a result, benzaldehyd*e* was observed in 13% yield. Then, the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1, v/v) to afford the product **3a** in 72% yield.

VI. Mechanism study

1. The investigation of transformation of 3a′ to 3a.



3a' **3a**

A: $[RhCp^*Cl_2]_2$ (5 mol%), 0% yield
B: CyCOOH (2.0 equiv), 0% yield
C: $AgSbF_6$ (20 mol%), 14% yield
D: $[RhCp^*Cl_2]_2$ (5 mol%) and CyCOOH (2.0 equiv), 0% yield
E: $[RhCp^*Cl_2]_2$ (5 mol%), $AgSbF_6$ (20 mol%) and CyCOOH (2.0 equiv), 10% yield

A) A Schlenk tube with a magnetic stir bar was charged with **3a′** (25 mg, 0.08 mmol), $[RhCp^*Cl_2]_2$ (2.5 mg, 0.004 mmol), and MeOH (0.5 mL) under an N_2 atmosphere. The resulting mixture was stirred at 60 ℃ for 24 h. TLC showed that no **3a** was produced.

B) A Schlenk tube with a magnetic stir bar was charged with **3a′** (25 mg, 0.08 mmol), CyCOOH (20.5 mg, 0.16 mmol), and MeOH (0.5 mL) under an N_2 atmosphere. The resulting mixture was stirred at 60 ℃ for 24 h. TLC showed that no **3a** was produced.

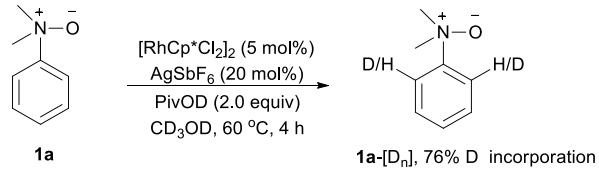
C) A Schlenk tube with a magnetic stir bar was charged with **3a′** (50 mg, 0.16 mmol), $AgSbF_6$ (11 mg, 0.032 mmol), and MeOH (1.0 mL) under an N_2 atmosphere. The resulting mixture was stirred at 60 ℃ for 24 h. After being cooled to ambient temperature, the resulting solution was concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1, v/v) to provide **3a** (6.3 mg, 14% yield).

D) A Schlenk tube with a magnetic stir bar was charged with **3a′** (25 mg, 0.08 mmol), $[RhCp^*Cl_2]_2$ (2.5 mg, 0.004 mmol), CyCOOH (20.5 mg, 0.16 mmol), and MeOH (0.5 mL) under an N_2 atmosphere. The resulting mixture was stirred at 60 ℃ for 24 h. TLC showed that no **3a** was produced.

E) A Schlenk tube with a magnetic stir bar was charged with **3a′** (50 mg, 0.16 mmol), $[RhCp^*Cl_2]_2$ (5.0 mg, 0.008 mmol), CyCOOH (41 mg, 0.32 mmol), $AgSbF_6$ (11 mg, 0.032 mmol), and MeOH (1.0 mL) under an N_2 atmosphere. The resulting mixture was stirred at 60 ℃ for 24 h. After being cooled to ambient temperature, the resulting

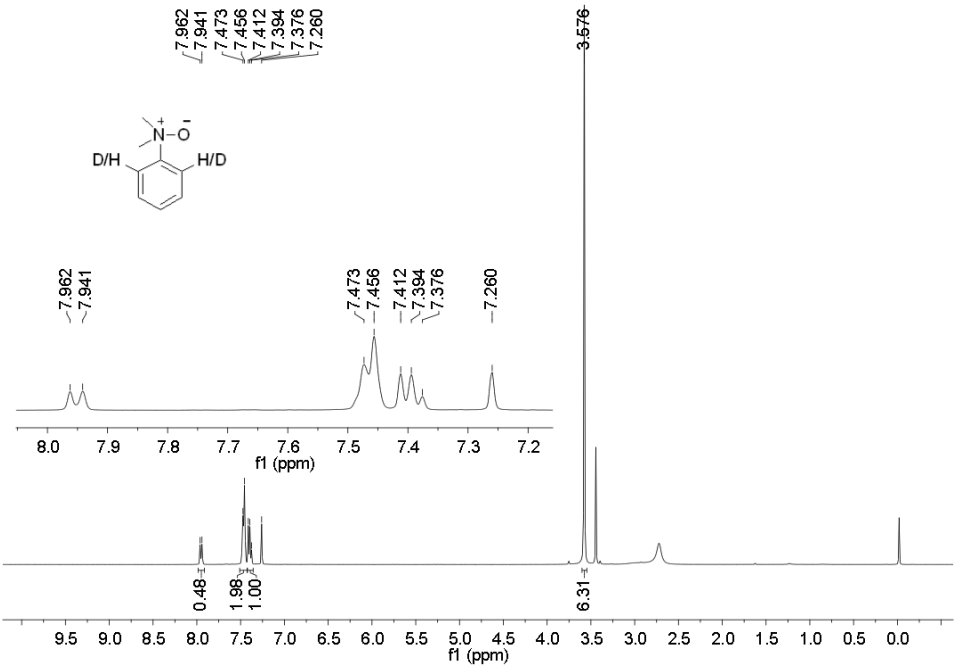
solution was concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 100/1, v/v) to provide **3a** (4.5 mg, 10% yield).

2. Hydrogen-deuterium exchange experiment

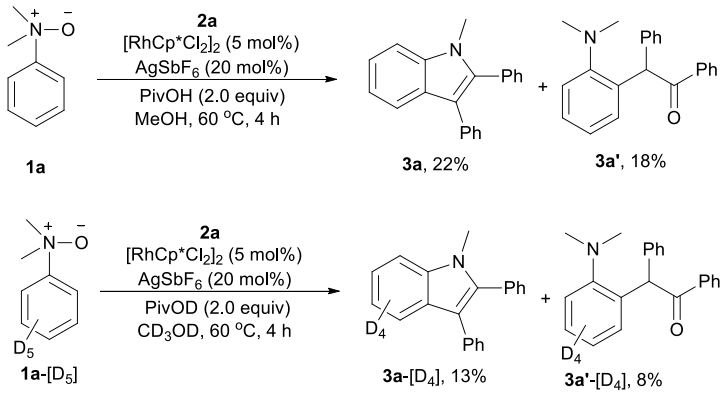


1a **1a**-[D_n], 76% D incorporation

A sealable tube with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (7.8 mg, 12.5 μmol, 5 mol%), $AgSbF_6$ (17.2 mg, 50 μmol, 20 mol%), PivOD (51.5 mg, 0.5 mmol, 2.0 equiv), **1a** (34.3 mg, 0.25 mmol), and CD_3OD (1.0 mL) under an N_2 atmosphere. The reaction mixture was stirred at 60 ℃ for 4 h. After being cooled to ambient temperature, the resulting solution was diluted with 5 mL of dichloromethane, filtered through a celite pad and washed with 10-20 mL of dichloromethane. The combined organic phases were evaporated, and the resulting residue was purified by column chromatography on silica gel to provide the desired product **1a**-[D_n]. ^{1}H NMR analysis showed that 76% hydrogen at the *ortho* position of phenyl ring of *N*,*N*-dimethylaniline *N*-oxide was deuterated



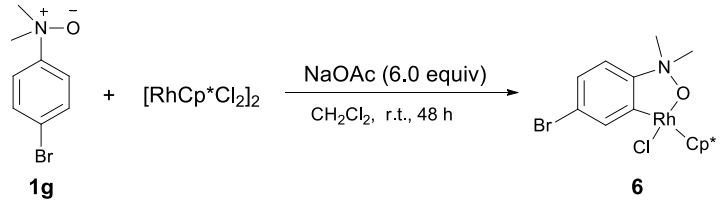
3. Kinetic isotope effect



A sealable tube with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (7.8 mg, 12.5 μmol, 5 mol%), $AgSbF_6$ (17.2 mg, 50 μmol, 20 mol%), PivOH or PivOD (0.5 mmol, 2.0 equiv), **1a** or **1a**-[D_5] (0.50 mmol, 2.0 equiv), **2a** (44.6 mg, 0.25 mmol) and MeOH or CD_3OD (1.0 mL) under an N_2 atmosphere. The reaction mixture was stirred at 60 ℃ for 4 h. After being cooled to ambient temperature, the resulting solution was diluted with 5 mL of dichloromethane, filtered through a celite pad and washed with 10-20 mL of dichloromethane. The combined organic phases were evaporated, and the resulting residue was purified by column chromatography on silica gel to provide **3a**/**3a′** or **3a**-[D_4]/**3a′**-[D_4]. A KIE value of 1.9 [(22% + 18%)/(13% + 8%)] was observed.

4. The synthesis and reaction of cyclometalated Rh(III) complex 6

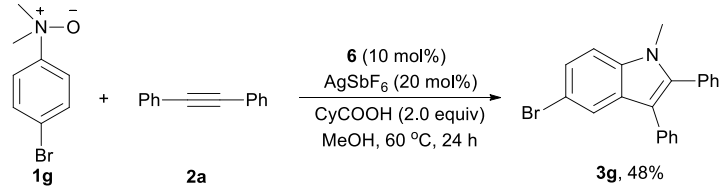
1). Synthesis of cyclometalated Rh(III) complex 6[4]



A Schlenk tube with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (100 mg, 0.162 mmol), NaOAc (80 mg, 0.972 mmol), 4-bromo-*N*,*N*-dimethylaniline *N*-oxide **1g** (87.5 mg, 0.405 mmol), and CH_2Cl_2 (1.0 mL) under an N_2 atmosphere. The resulting mixture was stirred at room temperature for 48 h and then diluted with 3 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on alumina (CH_2Cl_2/acetone = 3/1, v/v) to

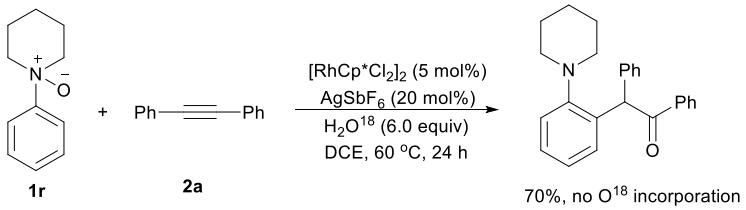
provide the complex **6** as a red orange solid (128 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.62 (s, 15H), 3.28 (s, 3H), 3.45 (s, 3H), 6.59 (d, J = 8.4 Hz, 1H), 7.06 (d, J = 8.4 Hz, 1H), 7.82 (s, 1H) ppm.

2). Complex 6-catalyzed annulation of aniline *N*-oxide 1g



A Schlenk tube with a magnetic stir bar was charged with complex **6** (12.2 mg, 25 μmol), $AgSbF_6$ (17.2 mg, 50 μmol), CyCOOH (64 mg, 0.50 mmol), **1g** (108 mg, 0.50 mmol), **2a** (44.6 mg, 0.25 mmol), and MeOH (1.0 mL) under an N_2 atmosphere. The reaction mixture was stirred at 60 ℃ for 24 h. After being cooled to ambient temperature, the resulting solution was diluted with 5 mL of dichloromethane, filtered through a celite pad and washed with 10-20 mL of dichloromethane. The combined organic phases were evaporated, and the resulting residue was purified by column chromatography on silica gel to provide 43 mg of **3g** in 48% yield.

5. O^{18} labeling experiment



A Schlenk tube with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (7.8 mg, 12.5 μmol, 5 mol%), $AgSbF_6$ (17.2 mg, 50 μmol, 20 mol%), H_2O^{18} (27 μL, 1.5 mmol, 6.0 equiv), **1r** (88.6 mg, 0.50 mmol, 2.0 equiv), **2a** (44.6 mg, 0.25 mmol) and DCE (1.0 mL) under an N_2 atmosphere. The reaction mixture was stirred at 60 ℃ for 24 h. After being cooled to ambient temperature, the resulting solution was diluted with 5 mL of dichloromethane, filtered through a celite pad and washed with 10-20 mL of dichloromethane. The combined organic phases were evaporated, and the resulting residue was purified by column chromatography on silica. GC-MS and HRMS

analysis showed no O^{18} incorporation in the isolated product.

VII. References

1 J. W. Kang, K. Moseley and P. M. Maitlis, *J. Am. Chem. Soc.*, 1969, **91**, 5970.

2 (a) K. Kinashi, K.-P. Lee, S. Matsumoto, K. Ishida and Y. Ueda, *Dyes Pigm.*, 2011, **92**, 783; (b) A. G. Giumanini, G. Chiavari, M. M. Musiani and P. Rossi, *Synthesis*, 1980, 743; (c) L. Zhang, C. Peng, D. Zhao, Y. Wang, H.-J. Fu, Q. Shen and J.-X. Li, *Chem. Commun.*, 2012, **48**, 5928; (d) X.-F. Xia, X.-Z. Shu, K.-G. Ji, A. Shaukat, X.-Y. Liu and Y.-M. Liang, *J. Org. Chem.*, 2011, **76**, 342; (e) T. Kubo, C. Katoh, K. Yamada, K. Okano, H. Tokuyama and T. Fukuyama, *Tetrahedron*, 2008, **64**, 11230.

3 J. C. Craig and K. K. Purushothaman, *J. Org. Chem.*, 1970, **35**, 1721.

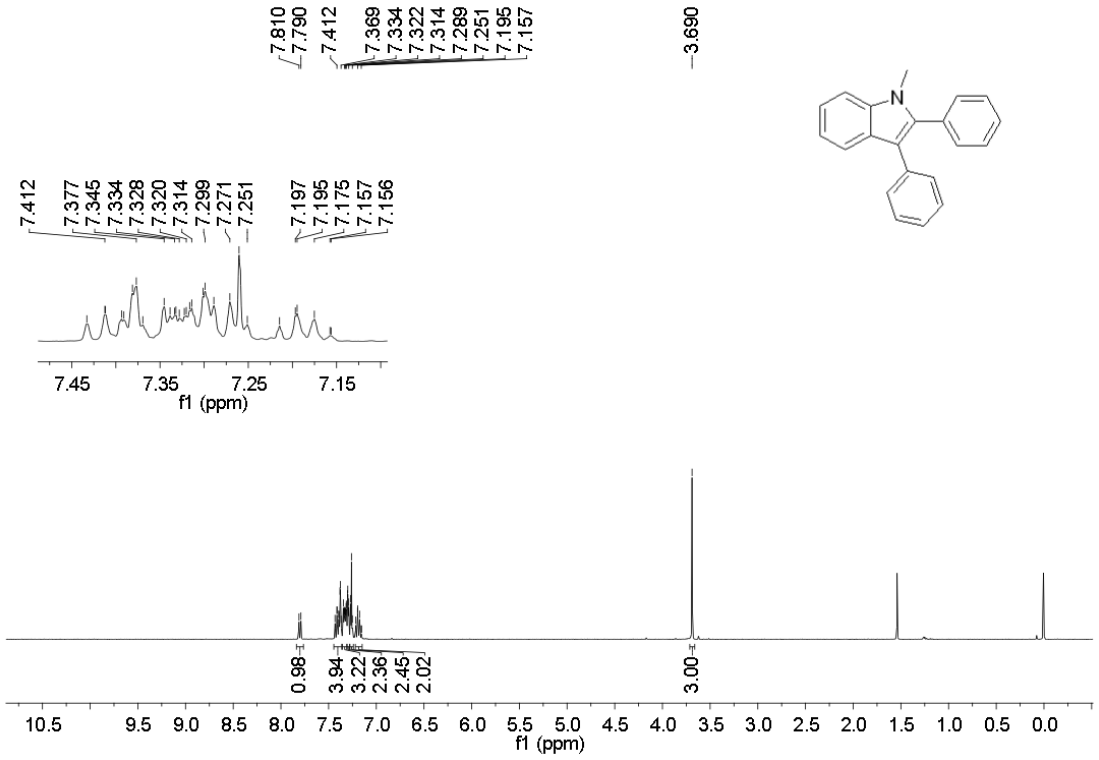
4 X. Huang, J. Huang, C. Du, X. Zhang, F. Song and J. You, *Angew. Chem. Int. Ed.*, 2013, **52**, 12970.

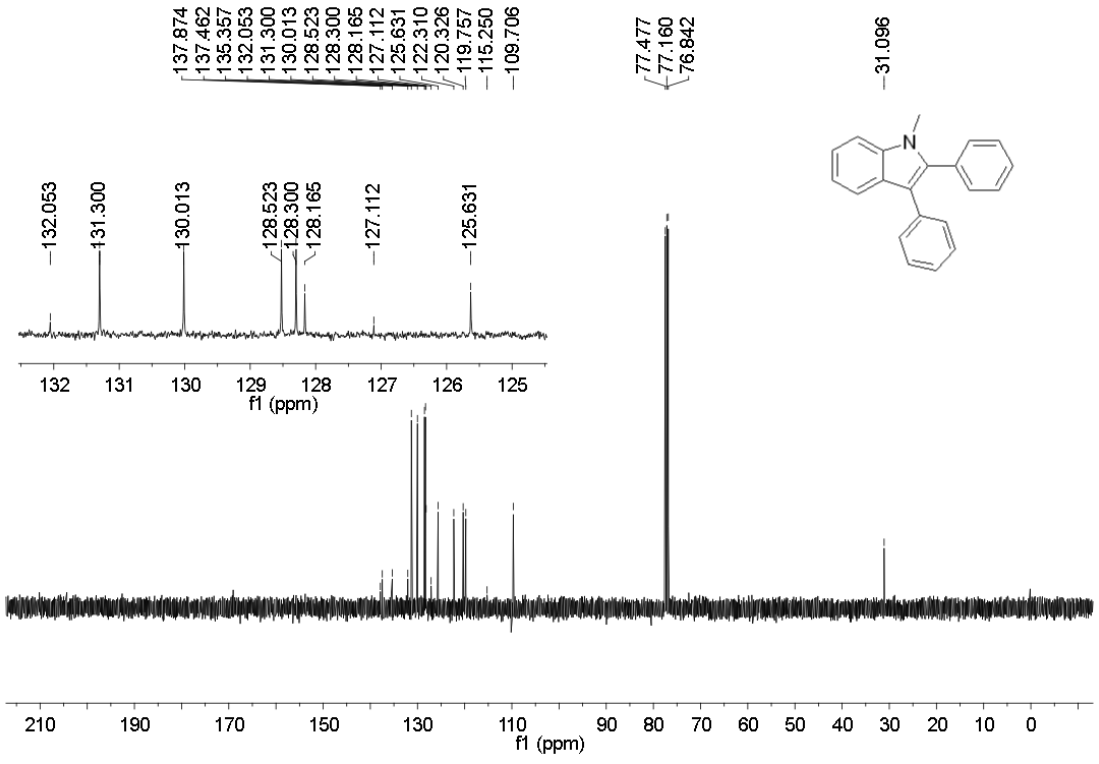
5 C. Wang and Y. Huang, *Org. Lett.*, 2013, **15**, 5294.

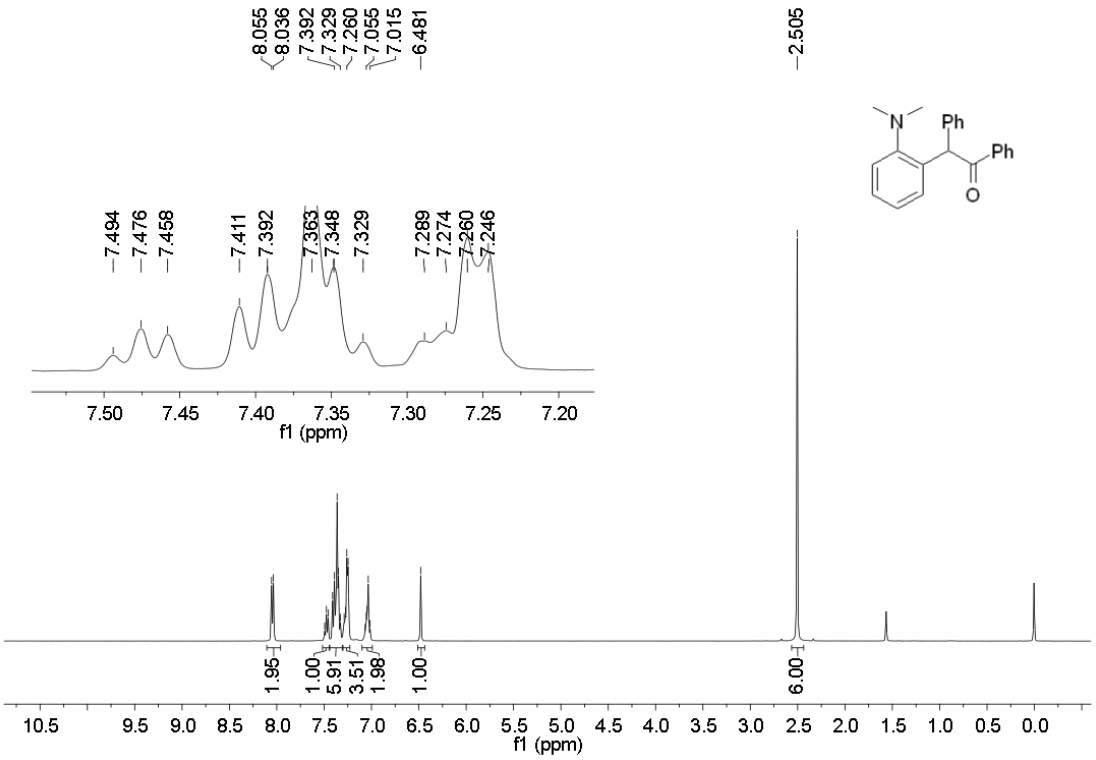
6 Y. Liang and N. Jiao, *Angew. Chem. Int. Ed.*, 2016, DOI: 10.1002/anie.201511002.

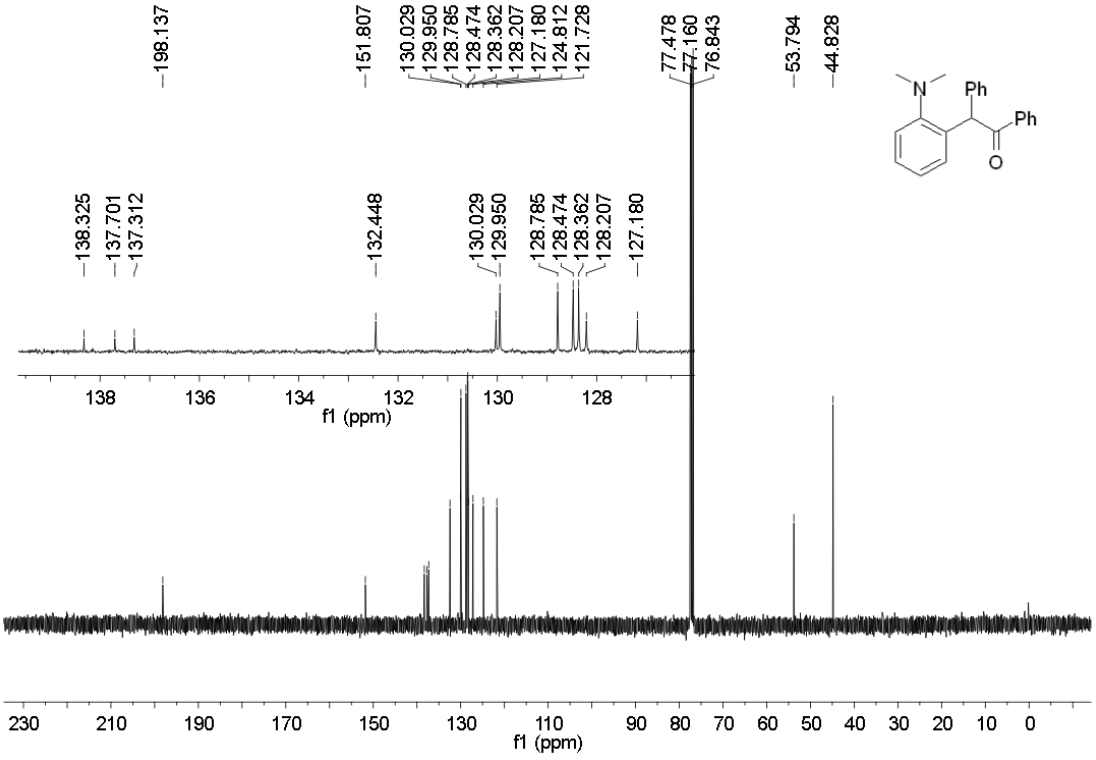
7 M. Takanori and T. YuKi, *Tetrahedron Lett.*, 2014, **55**, 3302.

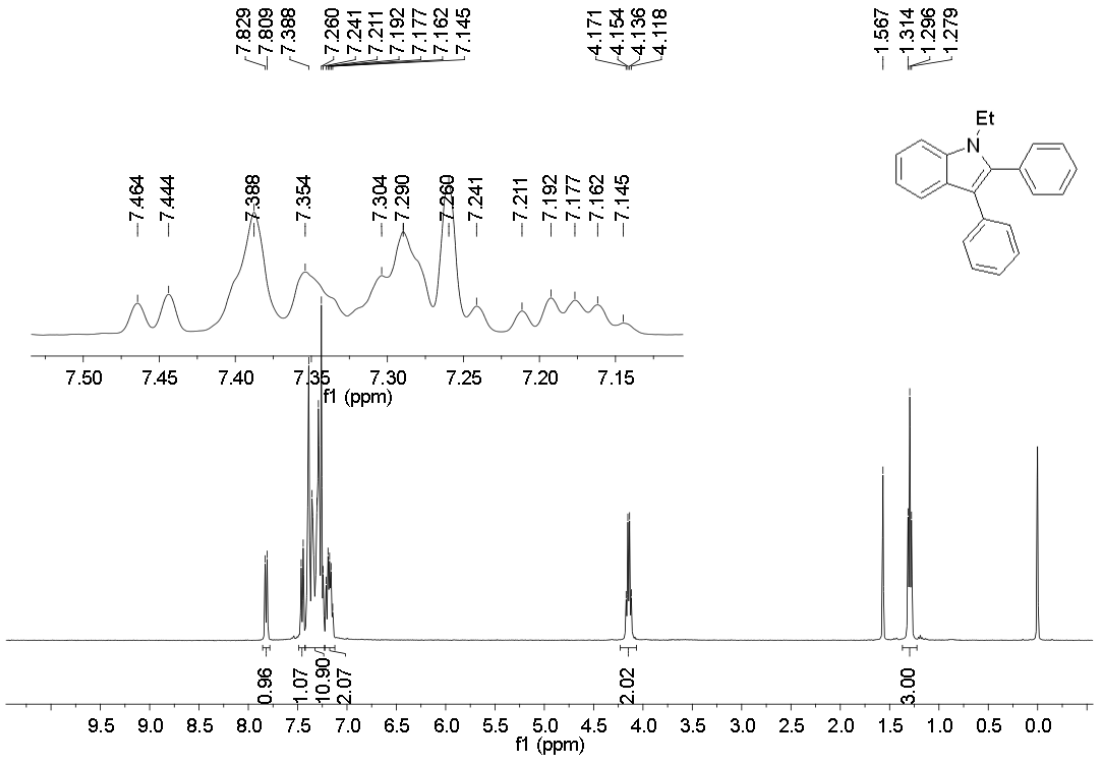
VIII. Copies of ^{1}H and ^{13}C NMR spectra

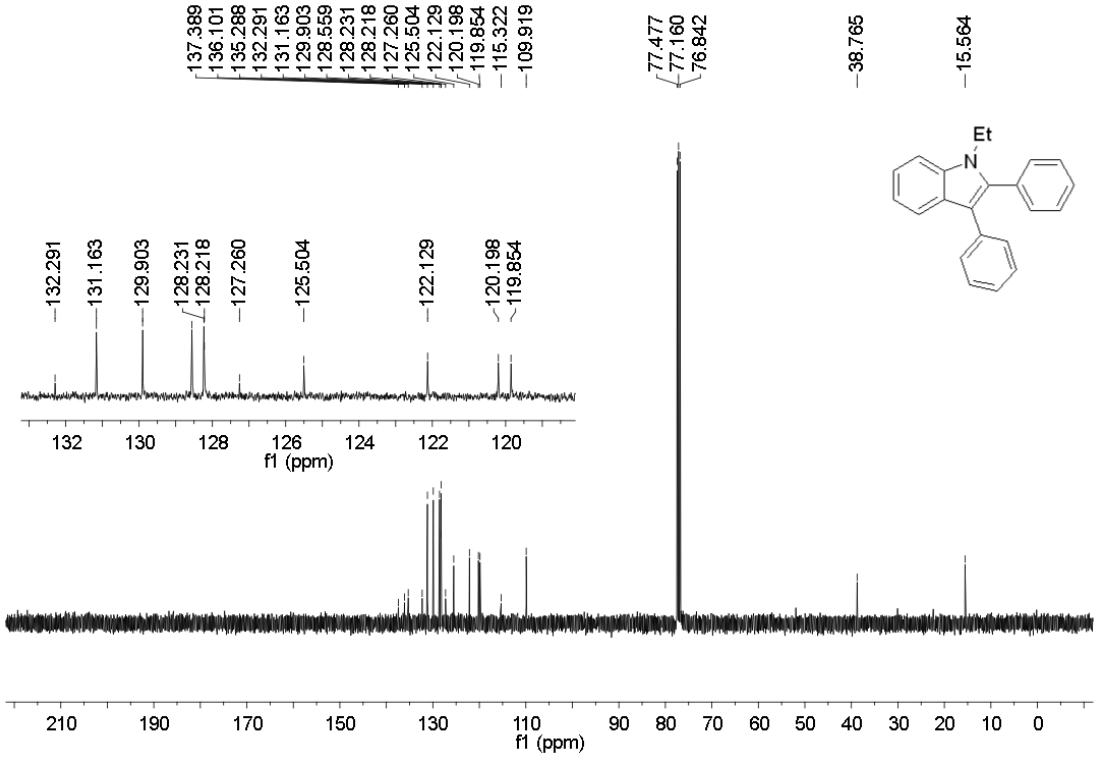


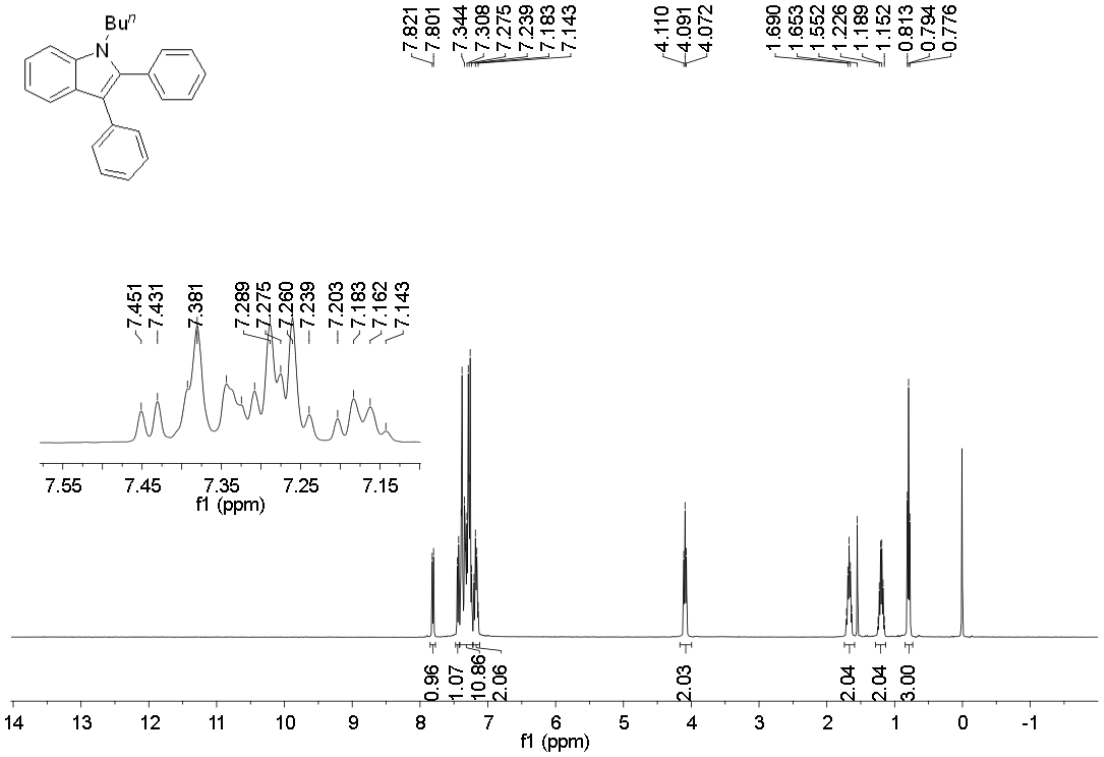


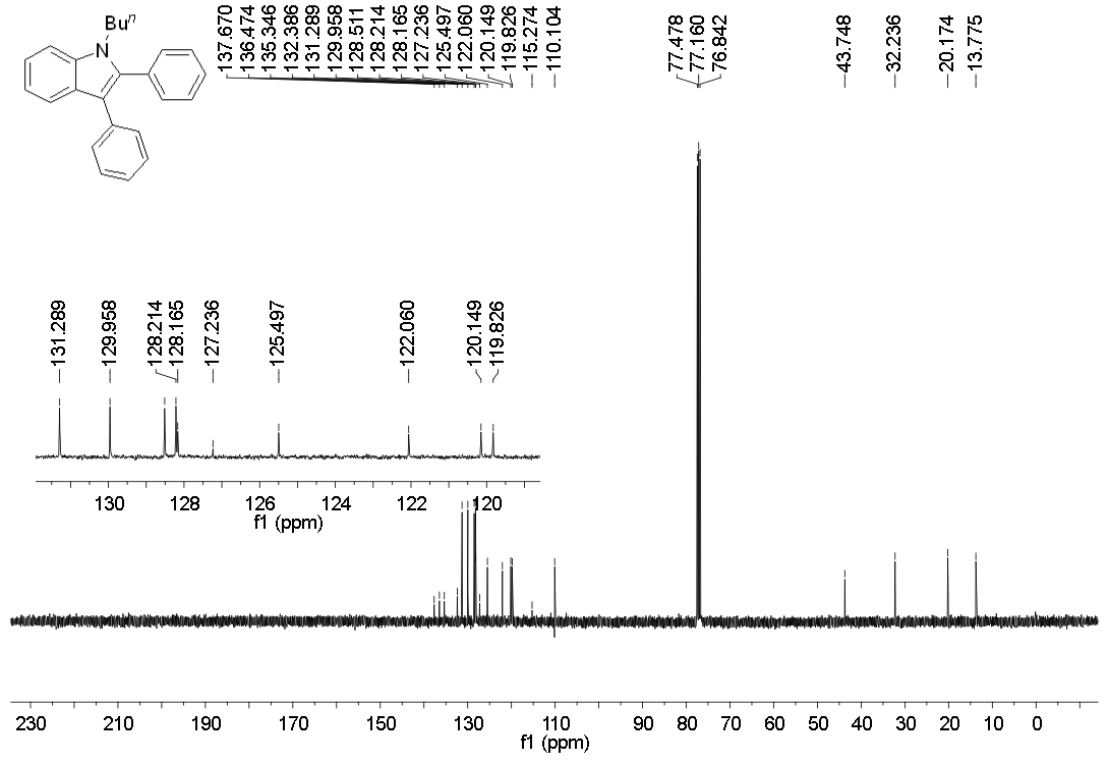

8.055
8.036
7.392
7.329
7.260
7.055
7.015
6.481
2.505
N
Ph
Ph
O
7.494
7.476
7.458
7.411
7.392
7.363
7.348
7.329
7.289
7.274
7.260
7.246
7.50 7.45 7.40 7.35 7.30 7.25 7.20
f1 (ppm)
1.95
1.00
5.91
3.51
1.98
1.00
6.00
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

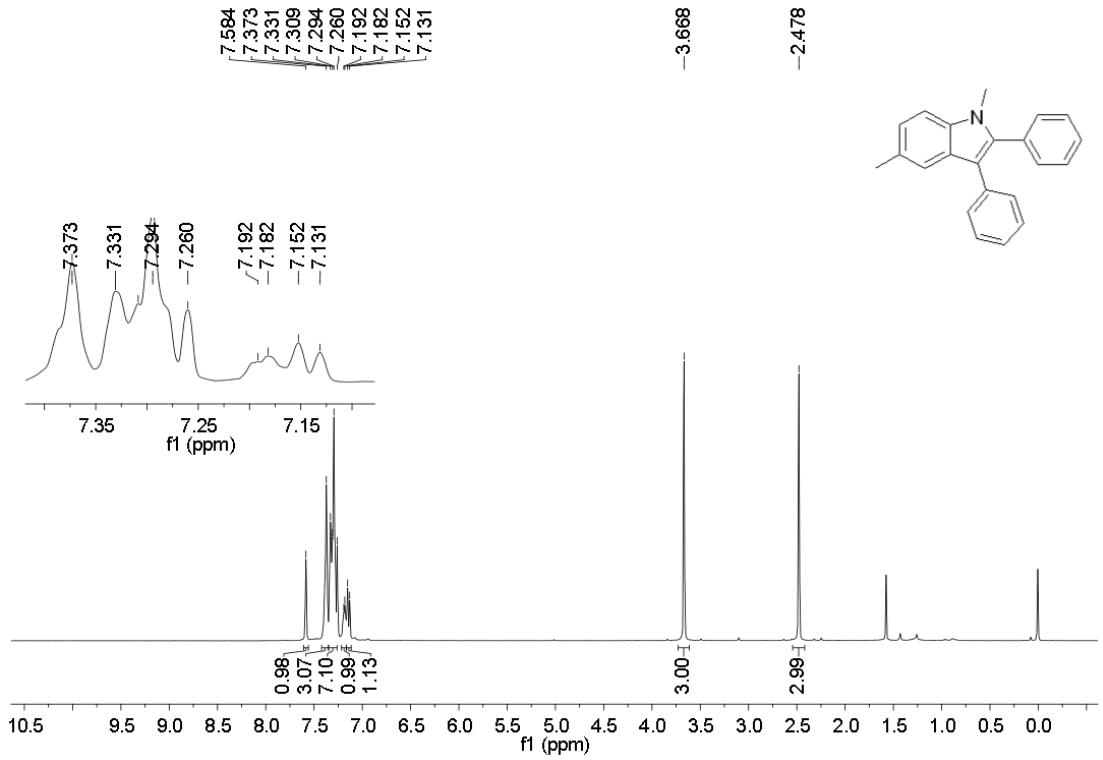

198.137
151.807
130.029
129.950
128.785
128.474
128.362
128.207
127.180
124.812
121.728
77.478
77.160
76.843
53.794
44.828
N
Ph
Ph
O
138.325
137.701
137.312
132.448
130.029
129.950
128.785
128.474
128.362
128.207
127.180
138 136 134 132 130 128
f1 (ppm)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

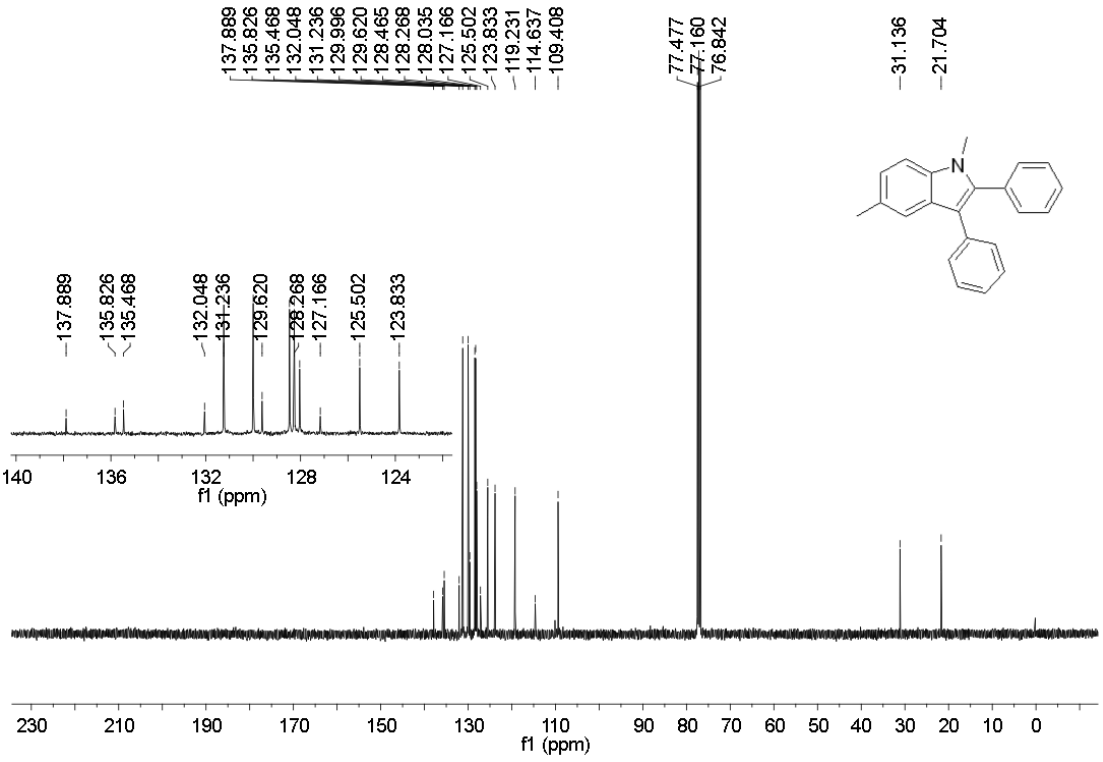

7.829
7.809
7.388
7.260
7.241
7.211
7.192
7.177
7.162
7.145
4.171
4.154
4.136
4.118
1.567
1.314
1.296
1.279
Et
N
7.464
7.444
7.388
7.354
7.304
7.290
7.260
7.241
7.211
7.192
7.177
7.162
7.145
7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15
f1 (ppm)
0.96
1.07
10.90
2.07
2.02
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

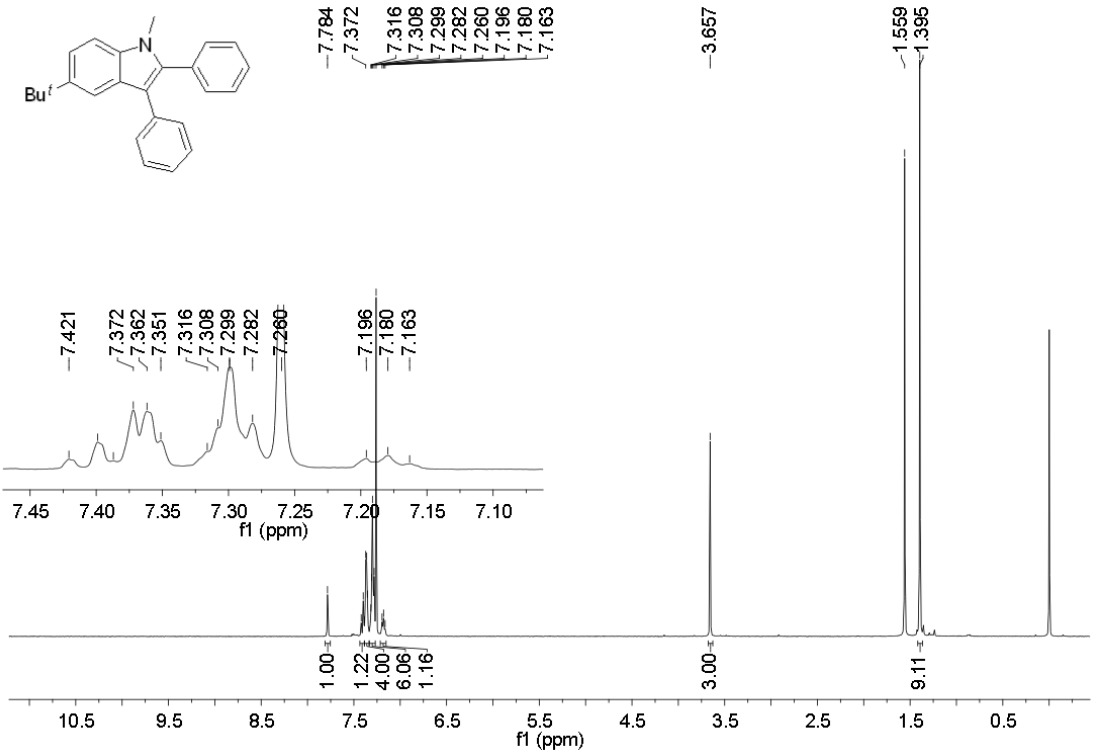

137.389
136.101
135.288
132.291
131.163
129.903
128.559
128.231
128.218
127.260
125.504
122.129
120.198
119.854
115.322
109.919
77.477
77.160
76.842
38.765
15.564
Et
N
132.291
131.163
129.903
128.231
128.218
127.260
125.504
122.129
120.198
119.854
132 130 128 126 124 122 120
f1 (ppm)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

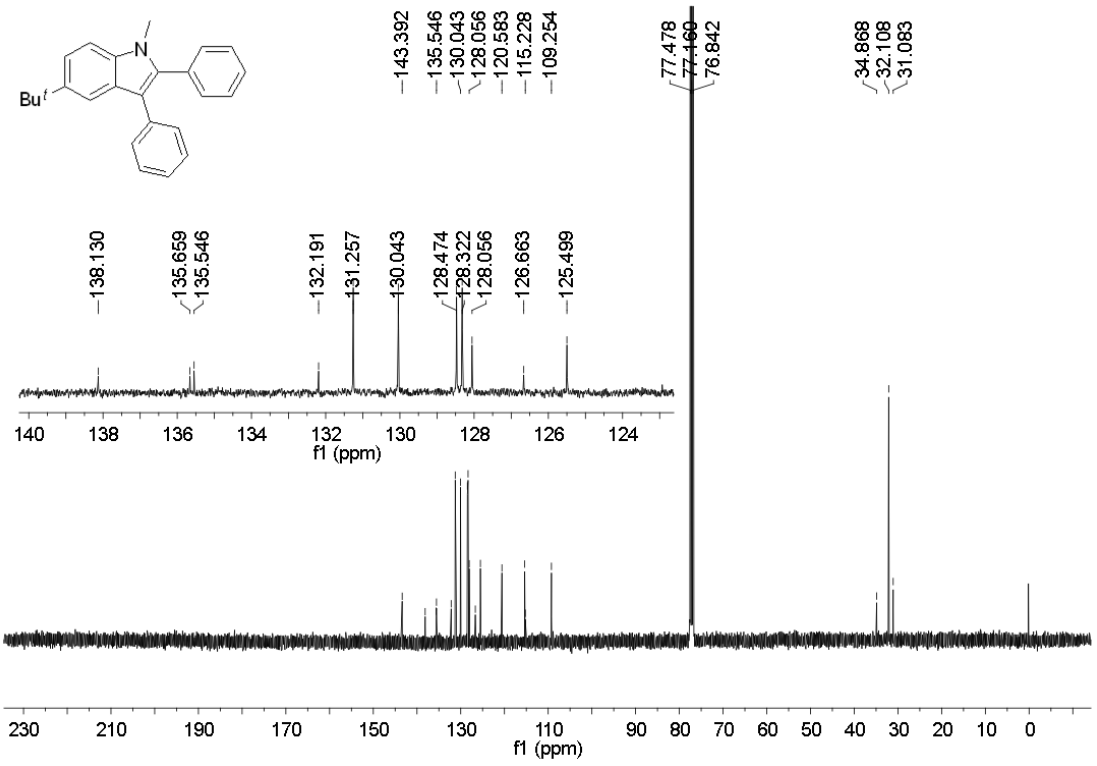

Bu^n
N
7.821
7.801
7.344
7.308
7.275
7.239
7.183
7.143
4.110
4.091
4.072
1.690
1.653
1.552
1.226
1.189
1.152
0.813
0.794
0.776
7.451
7.431
7.381
7.289
7.275
7.260
7.239
7.203
7.183
7.162
7.143
7.55
7.45
7.35
7.25
7.15
f1 (ppm)
0.96
1.07
10.86
2.06
2.03
2.04
2.04
3.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

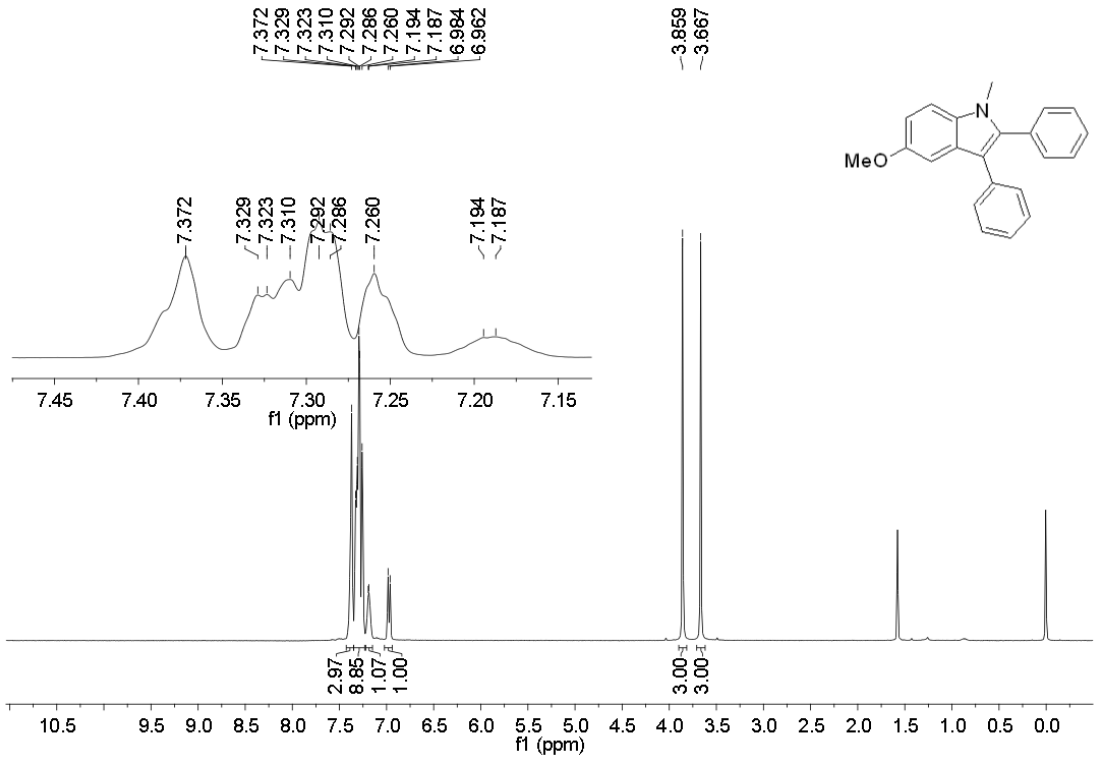

Bu^n
N
137.670
136.474
135.346
132.386
131.289
129.958
128.511
128.214
128.165
127.236
125.497
122.060
120.149
119.826
115.274
110.104
77.478
77.160
76.842
43.748
32.236
20.174
13.775
131.289
129.958
128.214
128.165
127.236
125.497
122.060
120.149
119.826
130
128
126
124
122
120
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

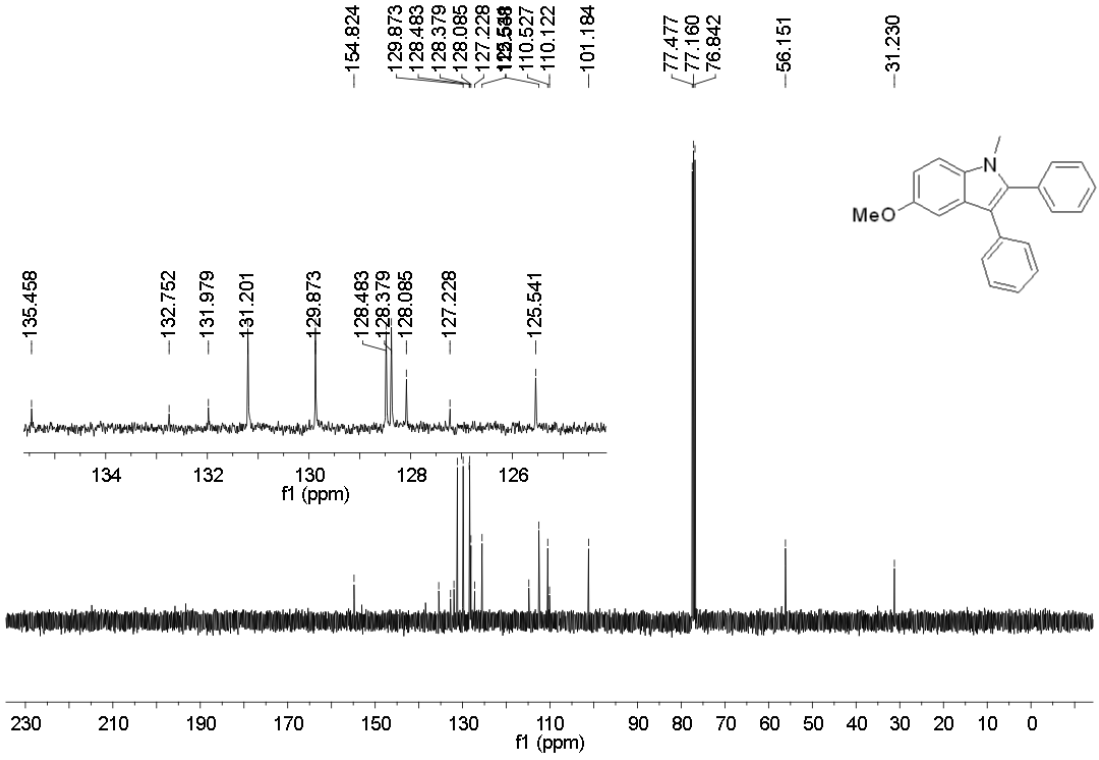

7.584
7.373
7.331
7.309
7.294
7.260
7.192
7.182
7.152
7.131
3.668
2.478
N
7.373
7.331
7.294
7.260
7.192
7.182
7.152
7.131
7.35
7.25
7.15
f1 (ppm)
0.98
3.07
7.10
0.99
1.13
3.00
2.99
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

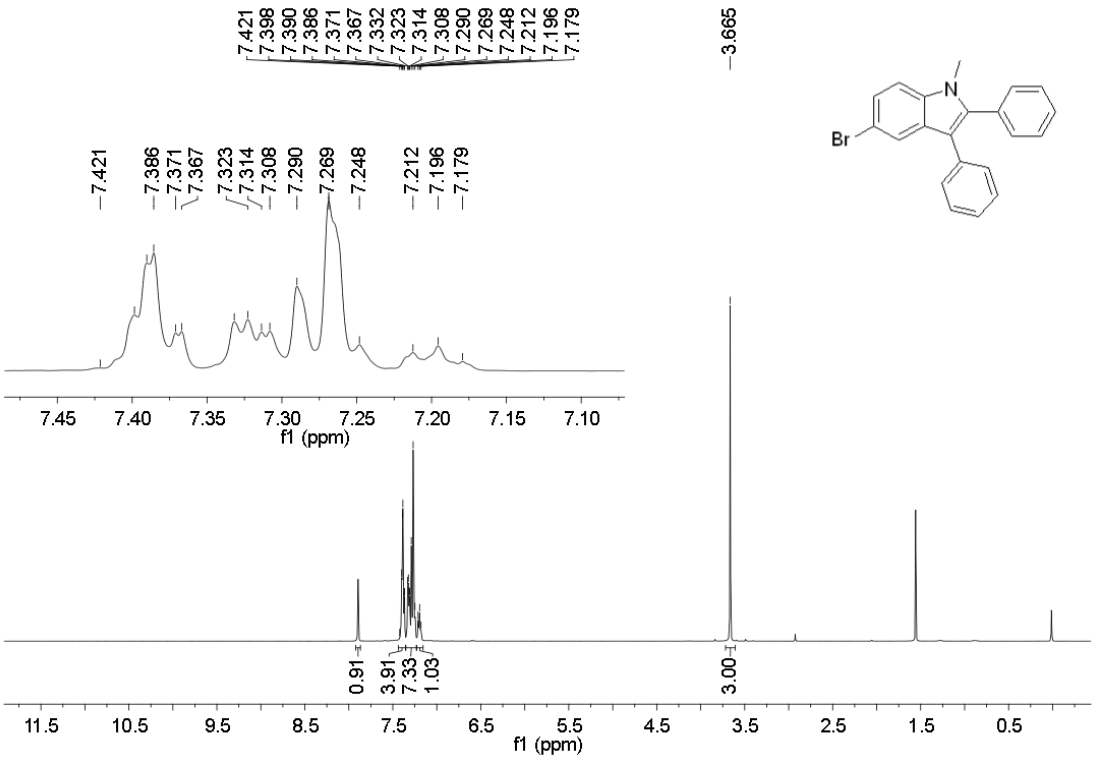

137.889
135.826
135.468
132.048
131.236
129.996
129.620
128.465
128.268
128.035
127.166
125.502
123.833
119.231
114.637
109.408
77.477
77.160
76.842
31.136
21.704
N
137.889
135.826
135.468
132.048
131.236
129.620
128.268
127.166
125.502
123.833
140
136
132
128
124
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

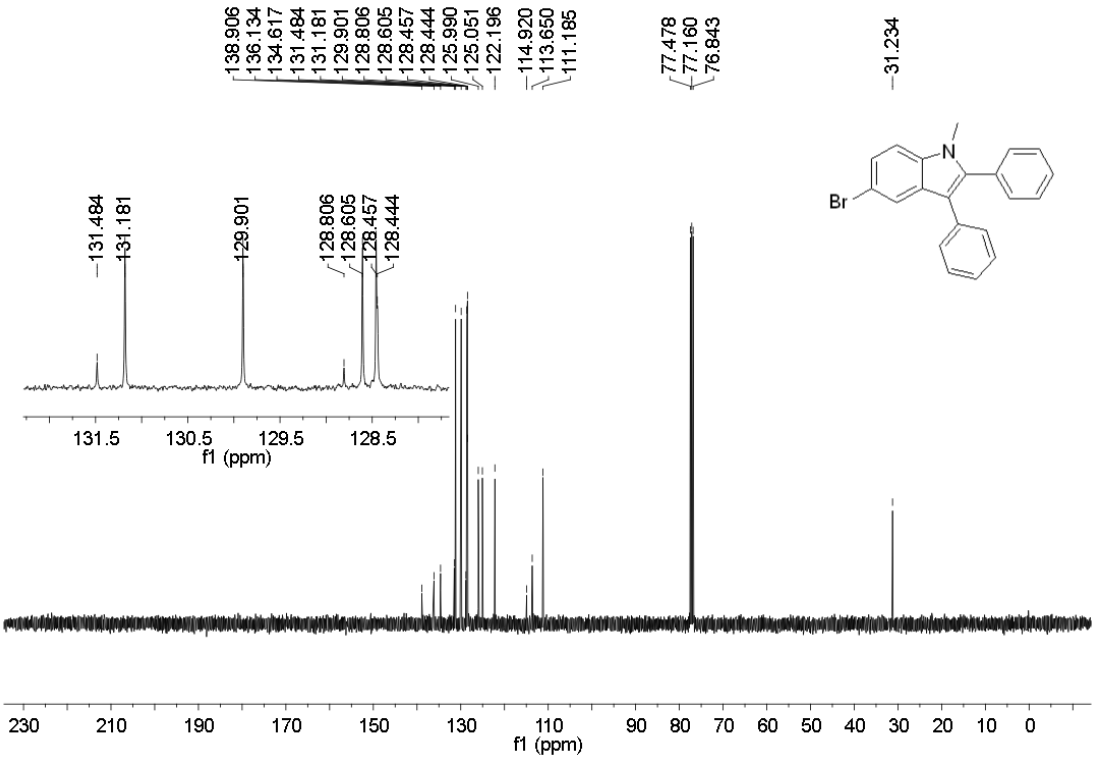

Bu^t
7.784
7.372
7.316
7.308
7.299
7.282
7.260
7.196
7.180
7.163
3.657
1.559
1.395
7.421
7.372
7.362
7.351
7.316
7.308
7.299
7.282
7.260
7.196
7.180
7.163
7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10
f1 (ppm)
1.00
1.22
4.00
6.06
1.16
3.00
9.11
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)

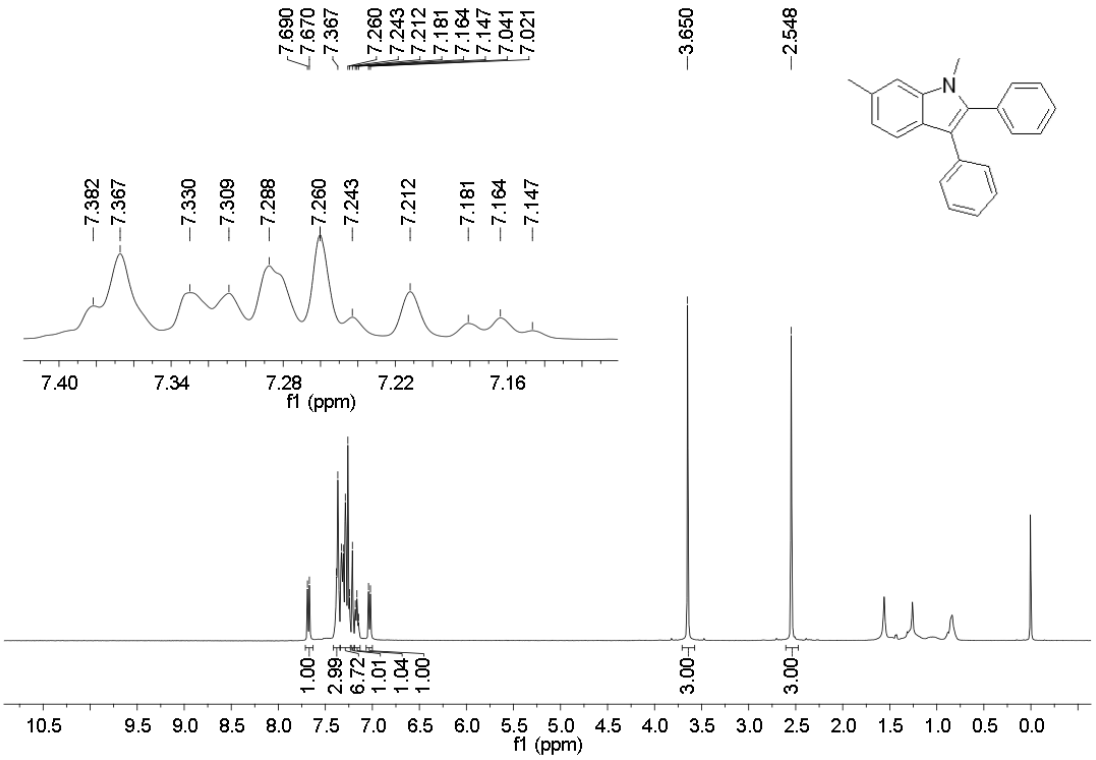

Bu^t
143.392
135.546
130.043
128.056
120.583
115.228
109.254
77.478
77.160
76.842
34.868
32.108
31.083
138.130
135.659
135.546
132.191
131.257
130.043
128.474
128.322
128.056
126.663
125.499
140 138 136 134 132 130 128 126 124
f1 (ppm)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

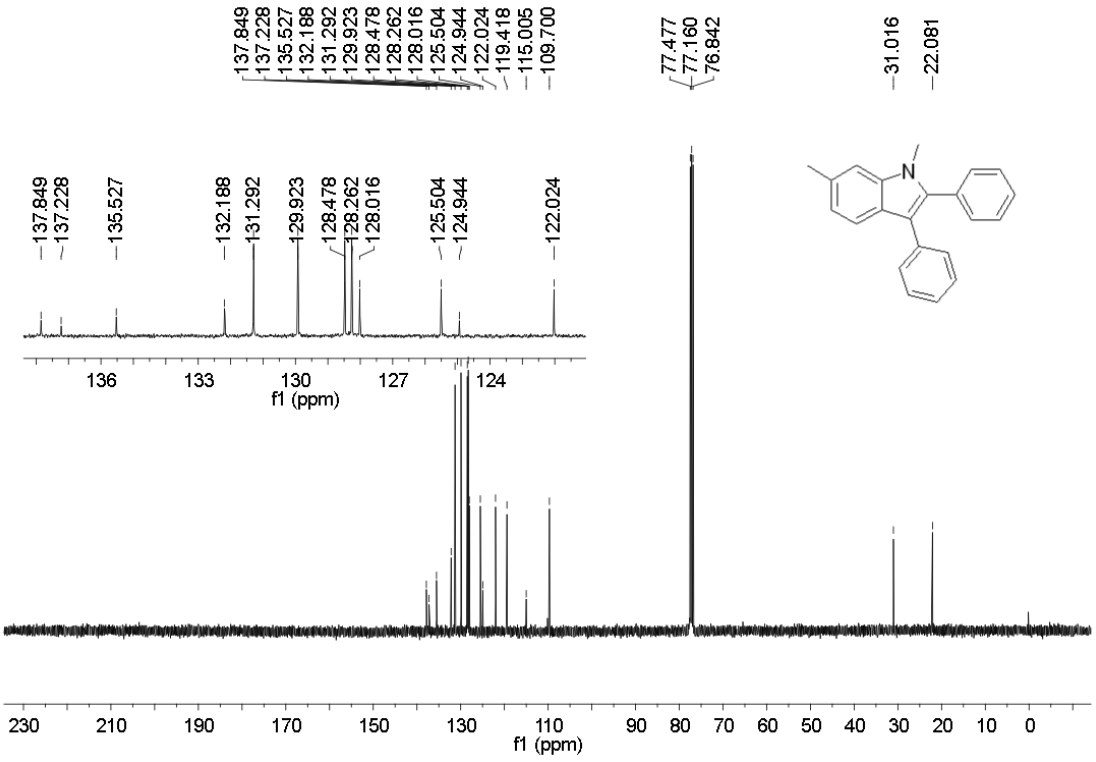

7.372
7.329
7.323
7.310
7.292
7.286
7.260
7.194
7.187
6.984
6.962
3.859
3.667
MeO
N
7.45
7.40
7.35
7.30
7.25
7.20
7.15
f1 (ppm)
2.97
8.85
1.07
1.00
3.00
3.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

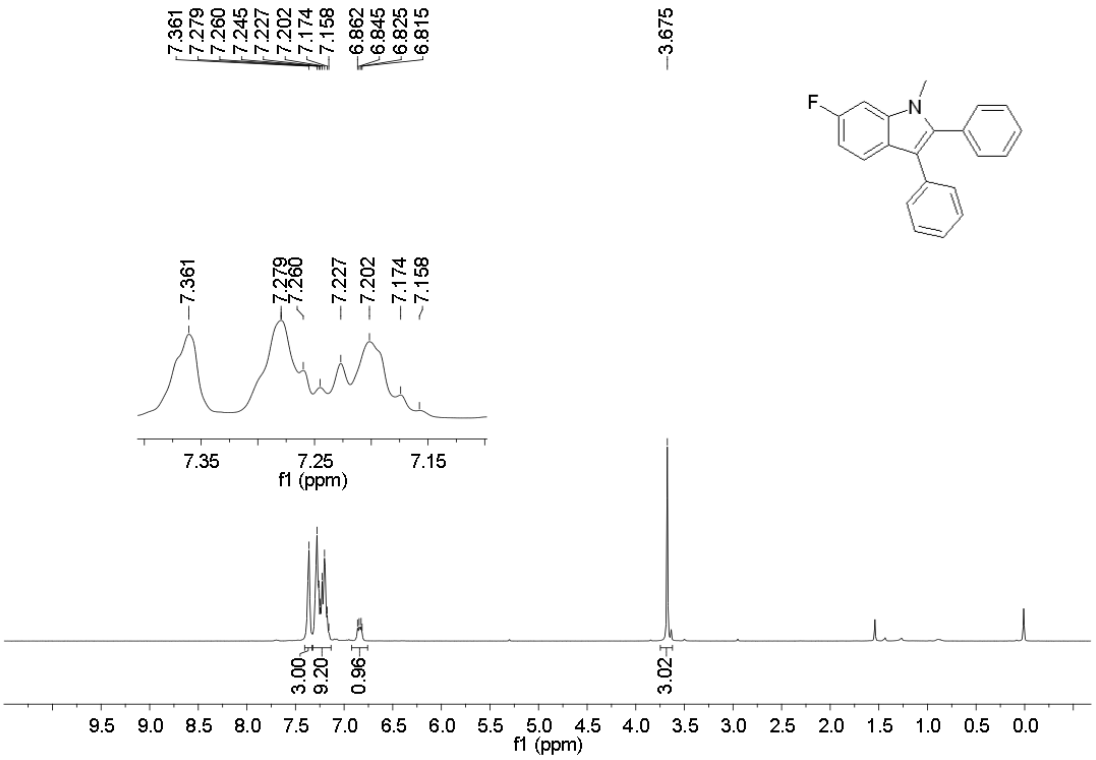

154.824
129.873
128.483
128.379
128.085
127.228
110.527
110.122
101.184
77.477
77.160
76.842
56.151
31.230
MeO
N
135.458
132.752
131.979
131.201
129.873
128.483
128.379
128.085
127.228
125.541
134
132
130
128
126
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

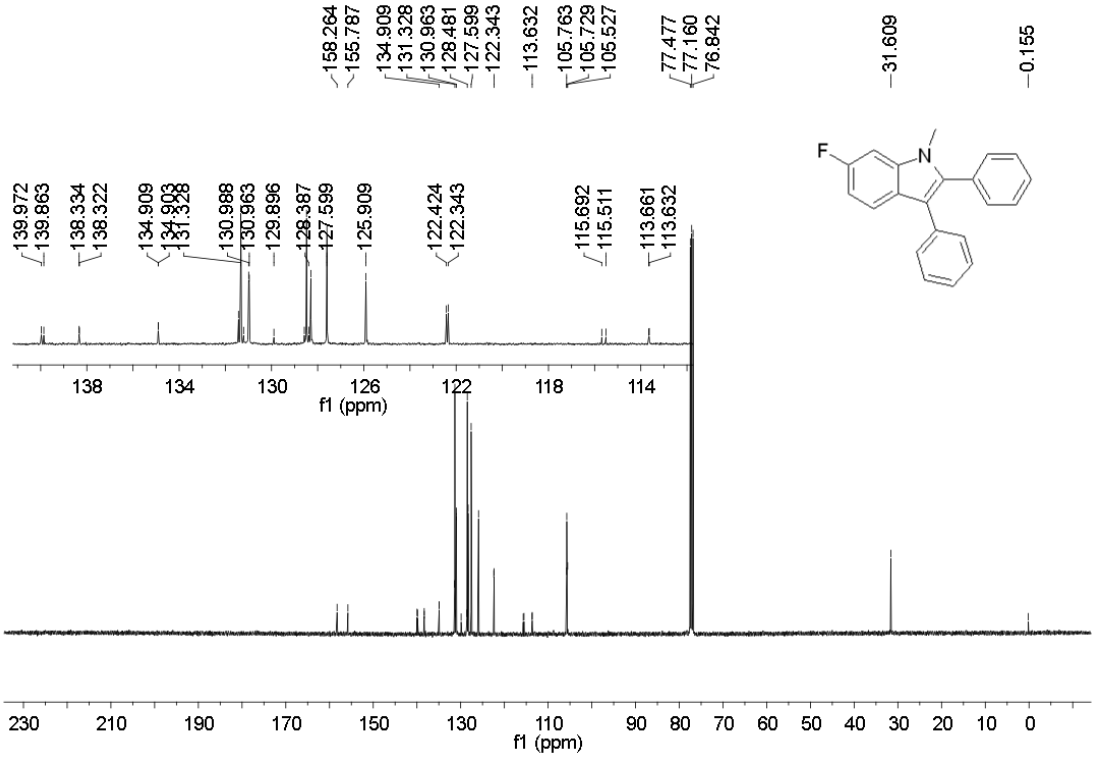

7.421
7.398
7.390
7.386
7.371
7.367
7.332
7.323
7.314
7.308
7.290
7.269
7.248
7.212
7.196
7.179
3.665
Br
N
f1 (ppm)
0.91
3.91
7.33
1.03
3.00

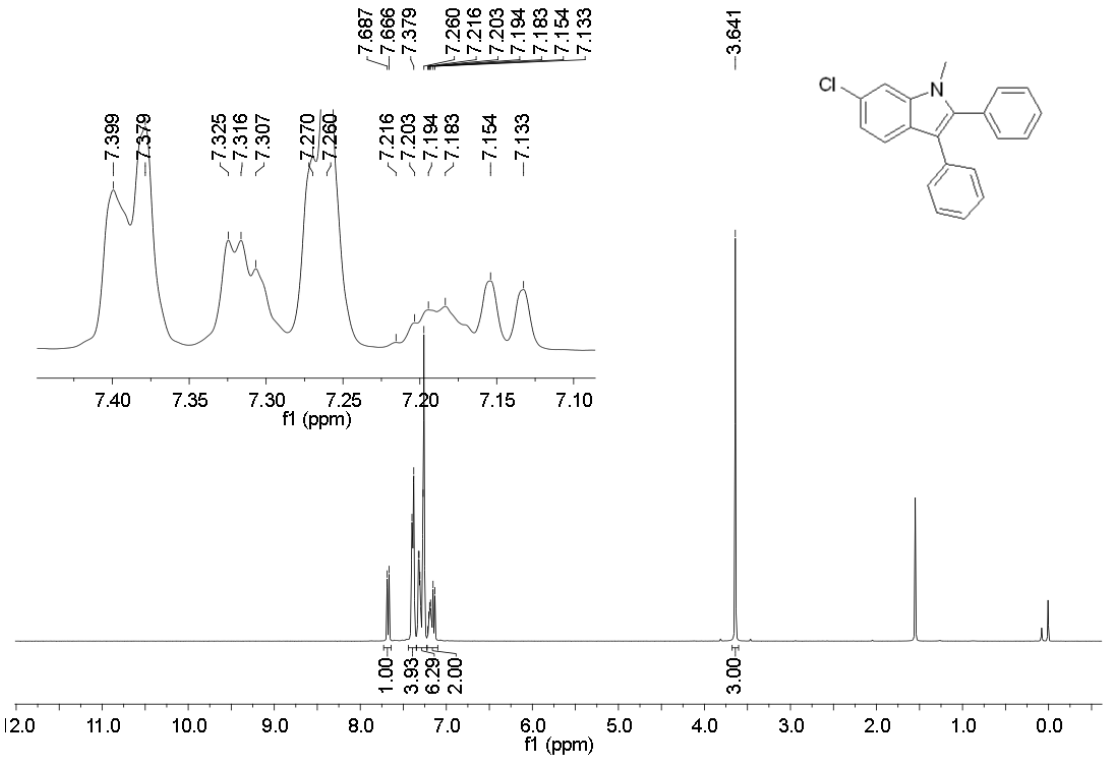

138.906
136.134
134.617
131.484
131.181
129.901
128.806
128.605
128.457
128.444
125.990
125.051
122.196
114.920
113.650
111.185
77.478
77.160
76.843
31.234
Br
N
f1 (ppm)

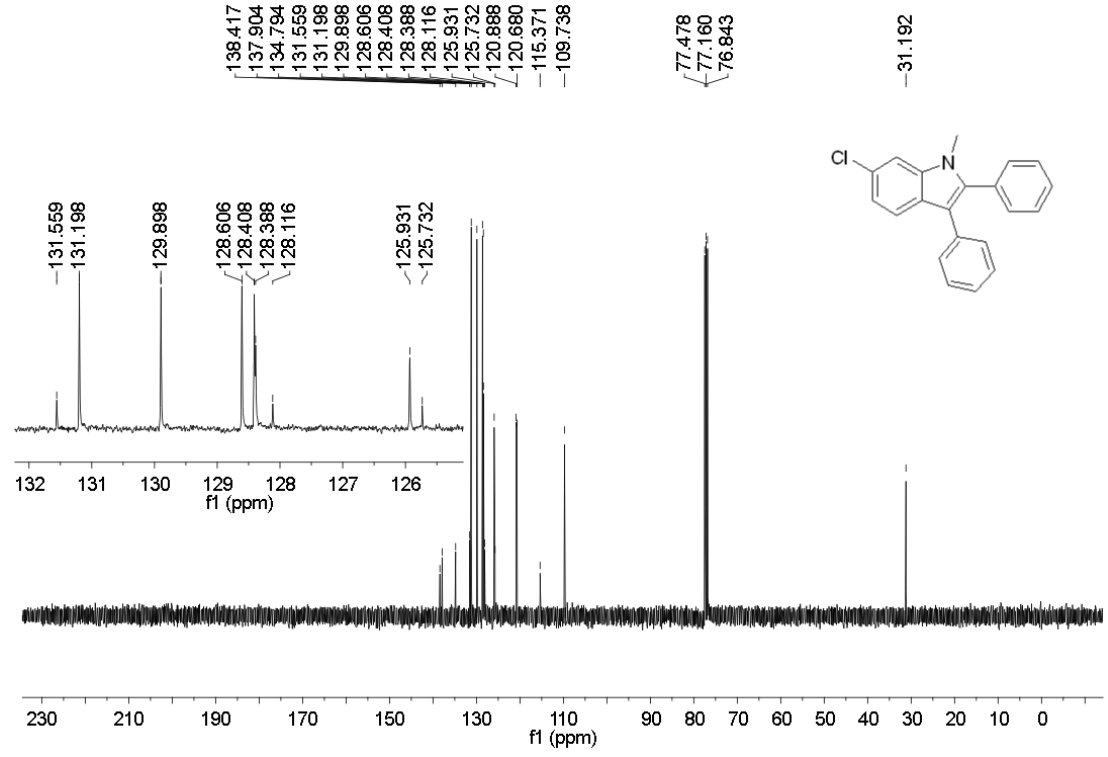

7.690
7.670
7.367
7.260
7.243
7.212
7.181
7.164
7.147
7.041
7.021
3.650
2.548
7.382
7.367
7.330
7.309
7.288
7.260
7.243
7.212
7.181
7.164
7.147
7.40
7.34
7.28
7.22
7.16
f1 (ppm)
1.00
2.99
6.72
1.01
1.04
1.00
3.00
3.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

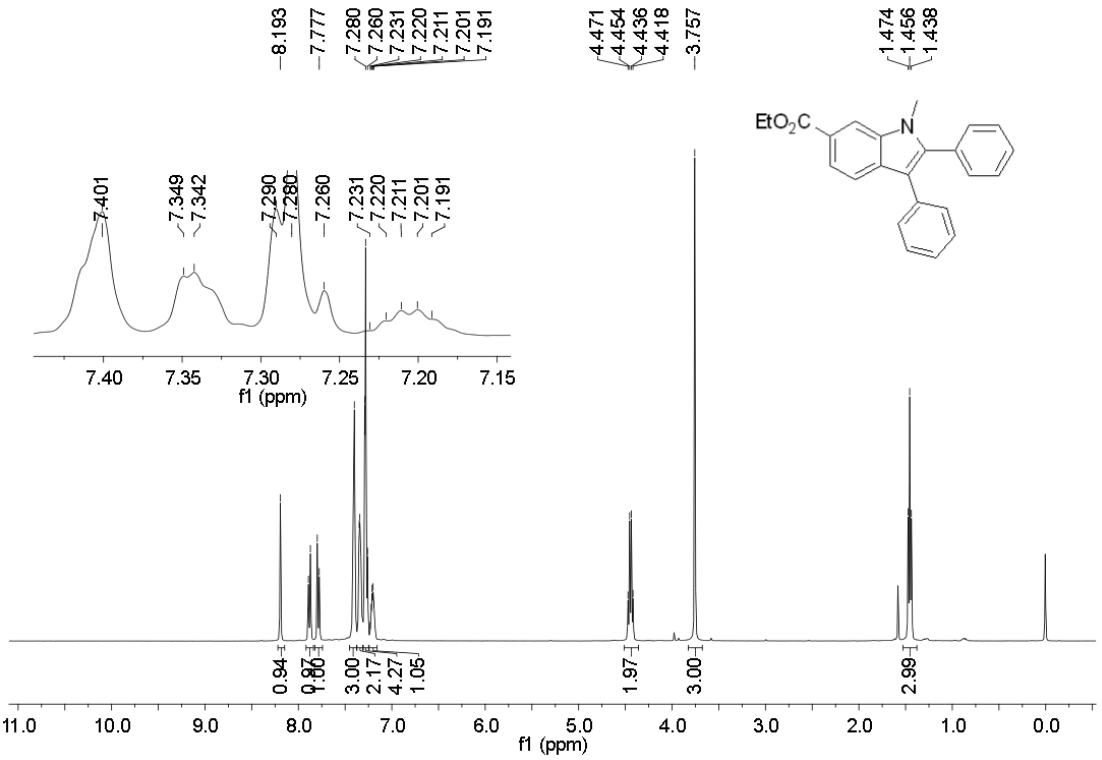

137.849
137.228
135.527
132.188
131.292
129.923
128.478
128.262
128.016
125.504
124.944
122.024
119.418
115.005
109.700
77.477
77.160
76.842
31.016
22.081
137.849
137.228
135.527
132.188
131.292
129.923
128.478
128.262
128.016
125.504
124.944
122.024
136
133
130
127
124
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

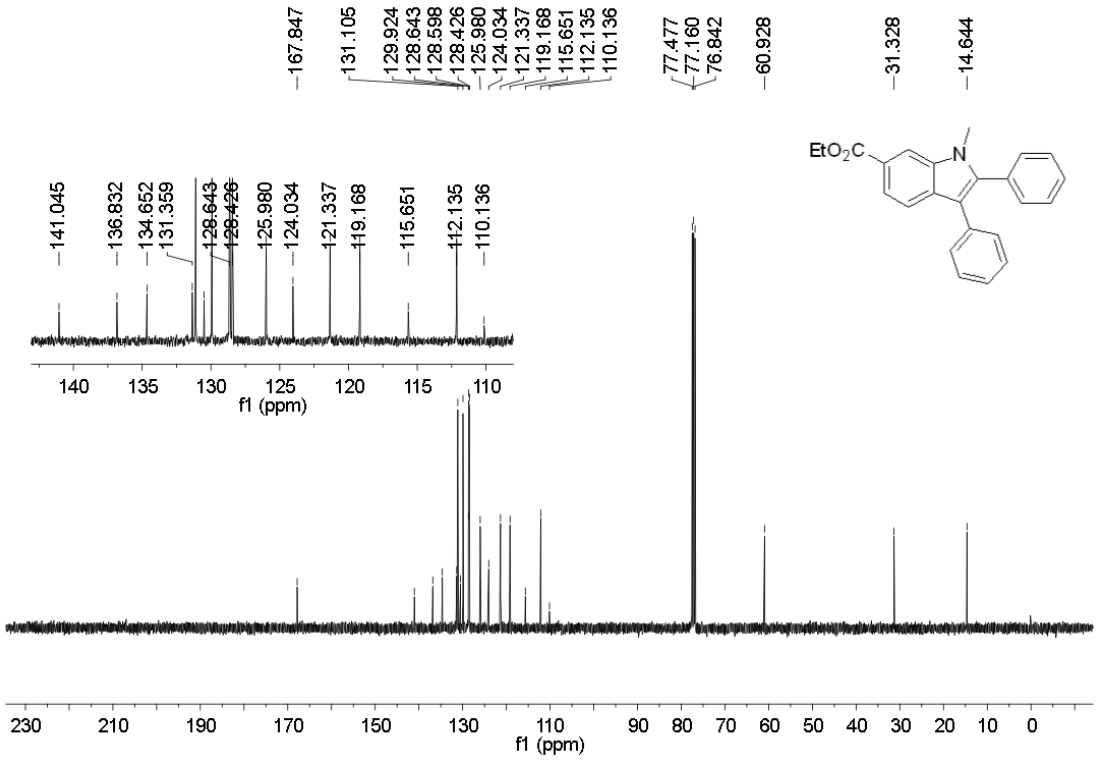

7.361
7.279
7.260
7.245
7.227
7.202
7.174
7.158
6.862
6.845
6.825
6.815
3.675
F
N
7.35
7.25
7.15
f1 (ppm)
3.00
9.20
0.96
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

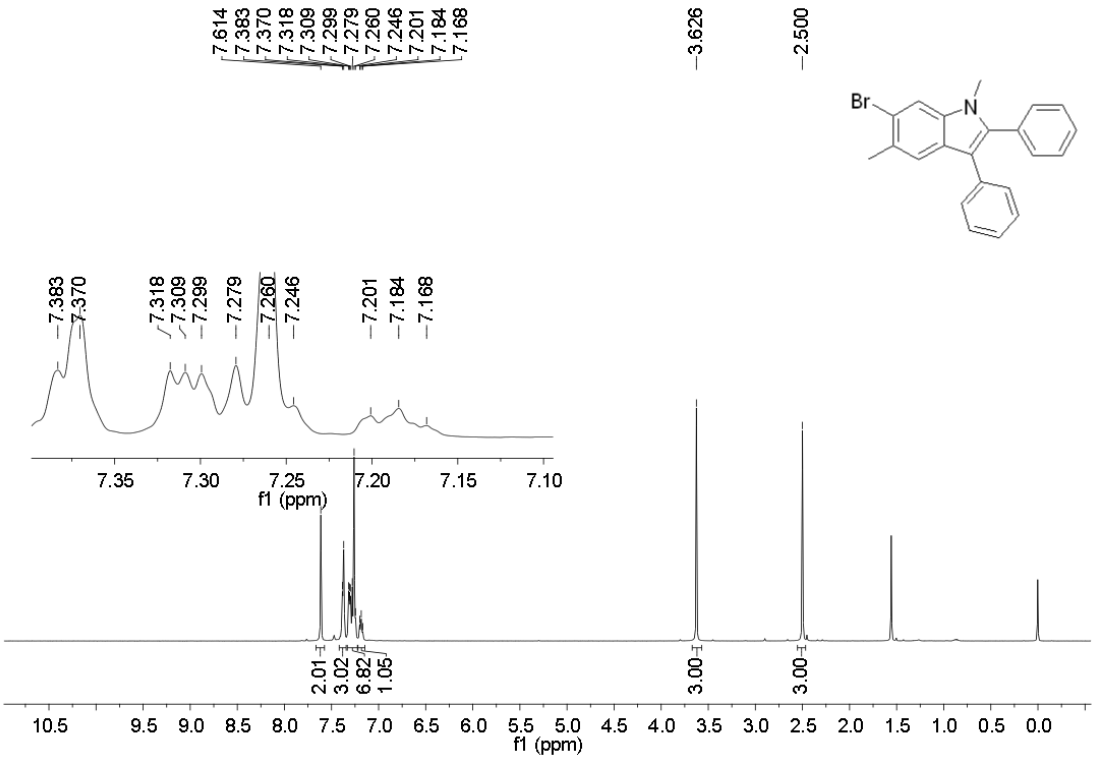

158.264
155.787
134.909
131.328
130.963
128.481
127.599
122.343
113.632
105.763
105.729
105.527
77.477
77.160
76.842
31.609
0.155
F
N
139.972
139.863
138.334
138.322
134.909
134.903
131.328
130.988
130.963
129.896
128.387
127.599
125.909
122.424
122.343
115.692
115.511
113.661
113.632
138
134
130
126
122
118
114
f1 (ppm)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

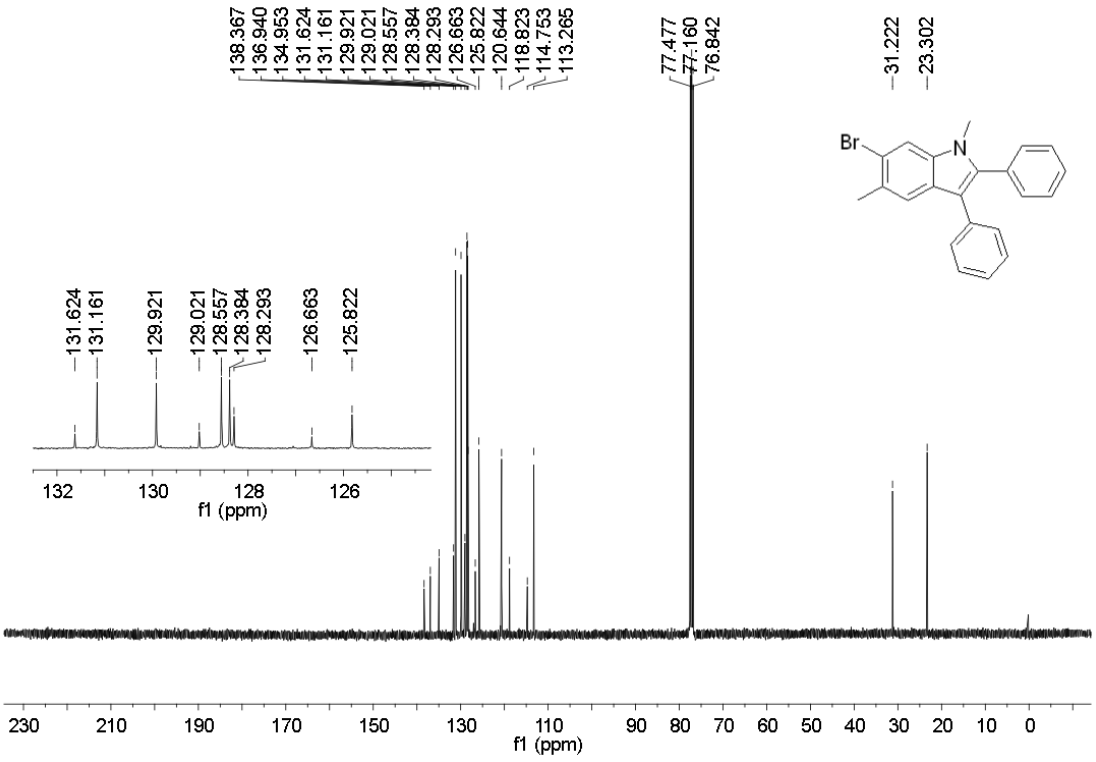

7.687
7.666
7.379
7.260
7.216
7.203
7.194
7.183
7.154
7.133
3.641
7.399
7.379
7.325
7.316
7.307
7.270
7.260
7.216
7.203
7.194
7.183
7.154
7.133
Cl
N
7.40 7.35 7.30 7.25 7.20 7.15 7.10
f1 (ppm)
1.00
3.93
6.29
2.00
3.00
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

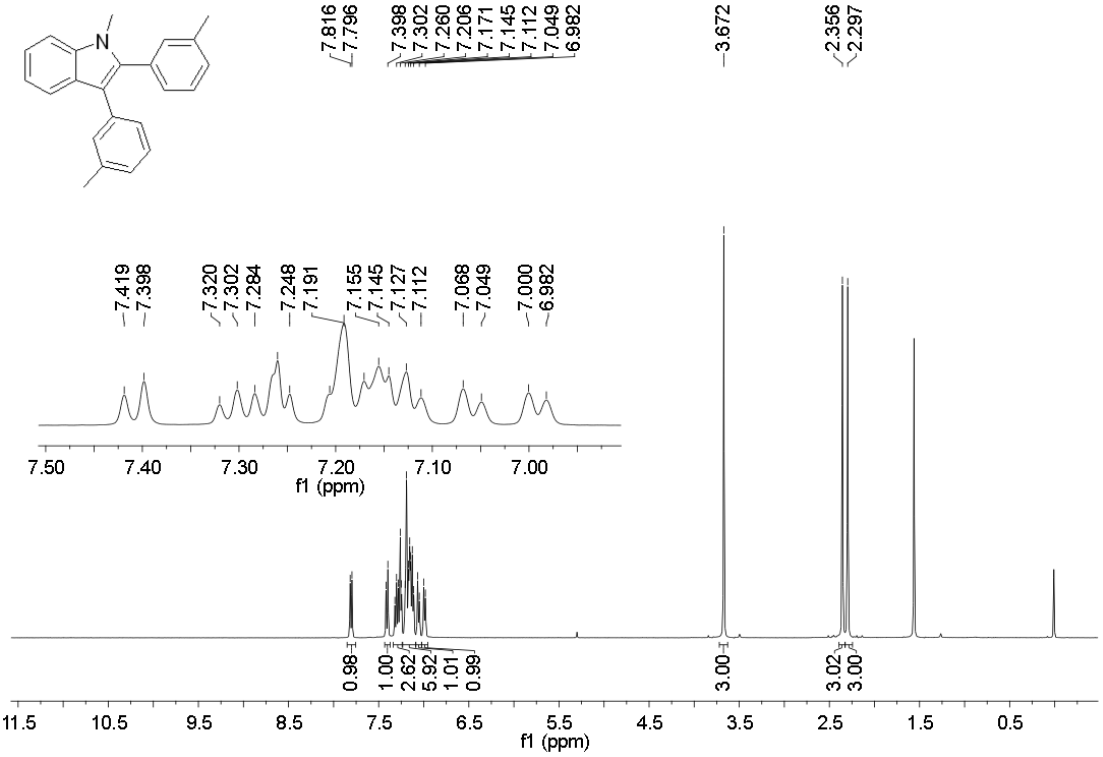

138.417
137.904
134.794
131.559
131.198
129.898
128.606
128.408
128.388
128.116
125.931
125.732
120.888
120.680
115.371
109.738
77.478
77.160
76.843
31.192
Cl
N
131.559
131.198
129.898
128.606
128.408
128.388
128.116
125.931
125.732
132 131 130 129 128 127 126
f1 (ppm)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

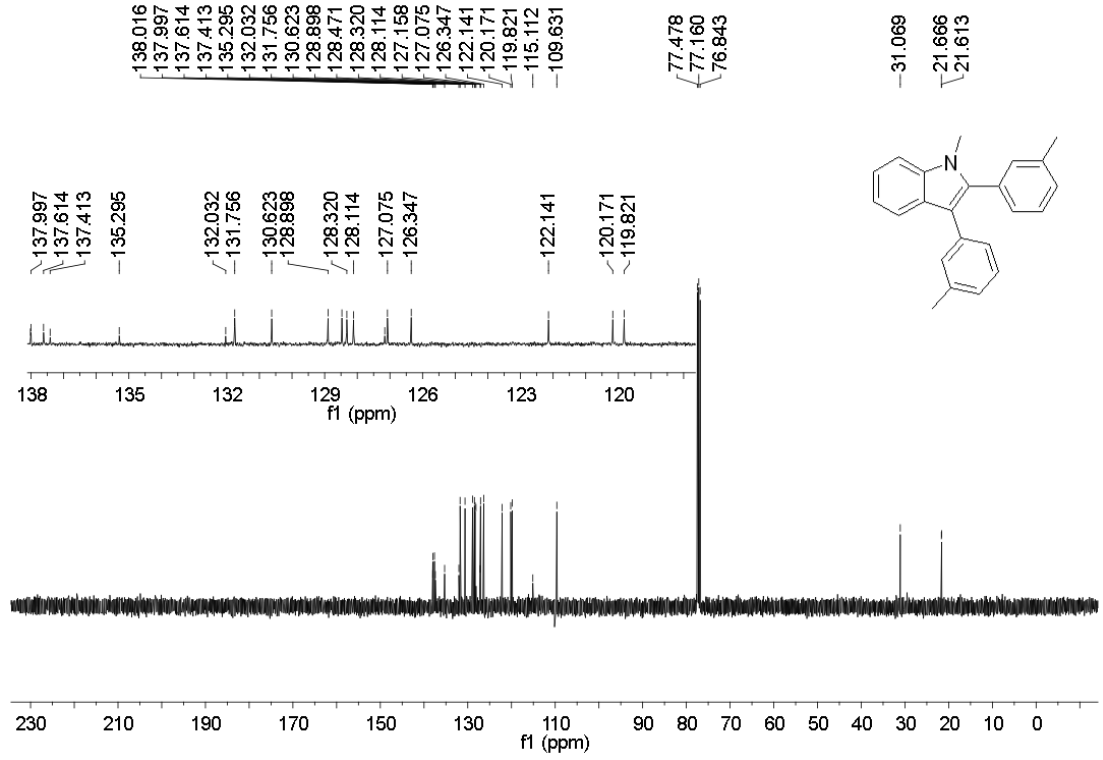

8.193
7.777
7.280
7.260
7.231
7.220
7.211
7.201
7.191
4.471
4.454
4.436
4.418
3.757
1.474
1.456
1.438
EtO2C
N
7.401
7.349
7.342
7.290
7.280
7.260
7.231
7.220
7.211
7.201
7.191
7.40 7.35 7.30 7.25 7.20 7.15
f1 (ppm)
0.94
0.97
1.00
3.00
2.17
4.27
1.05
1.97
3.00
2.99
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

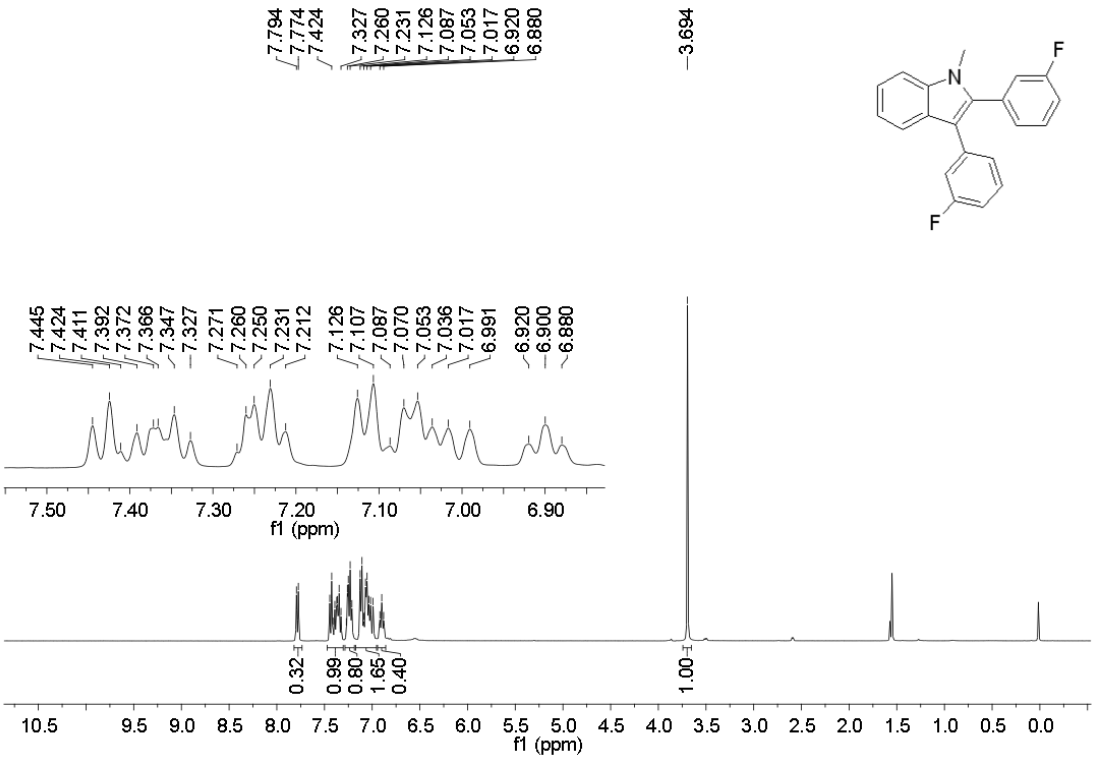

167.847
131.105
129.924
128.643
128.598
128.426
125.980
124.034
121.337
119.168
115.651
112.135
110.136
77.477
77.160
76.842
60.928
31.328
14.644
EtO2C
N
141.045
136.832
134.652
131.359
125.980
124.034
121.337
119.168
115.651
112.135
110.136
140 135 130 125 120 115 110
f1 (ppm)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

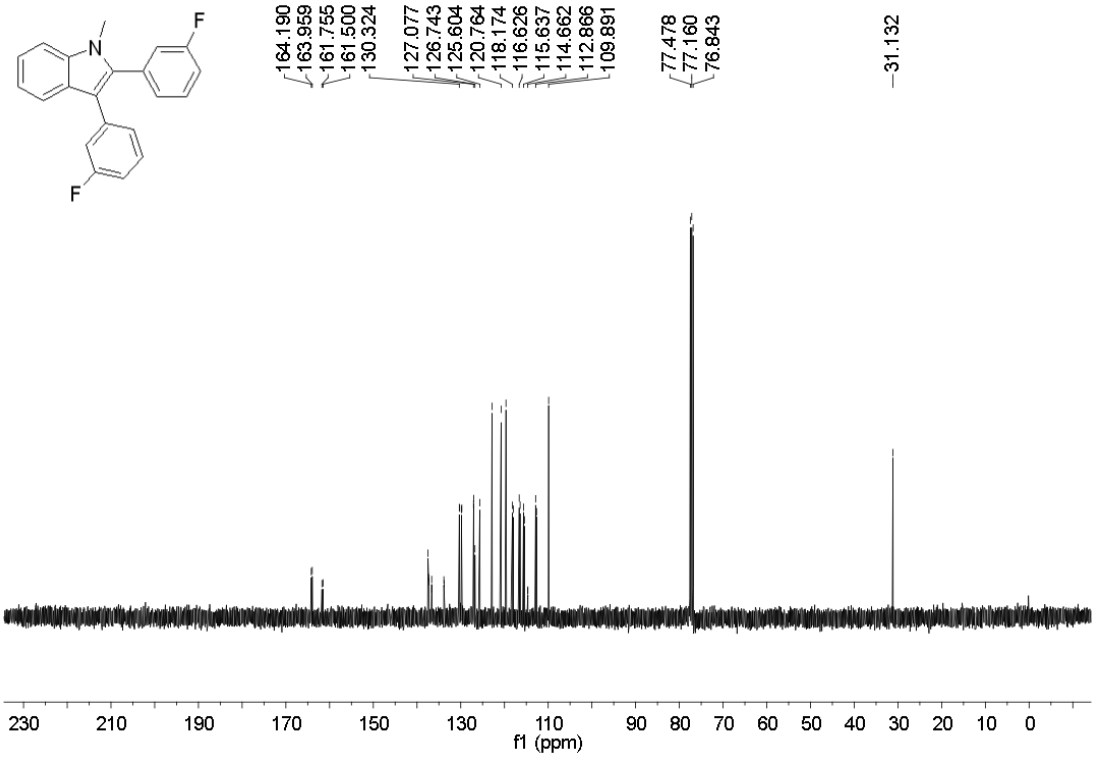

7.614
7.383
7.370
7.318
7.309
7.299
7.279
7.260
7.246
7.201
7.184
7.168
3.626
2.500
Br
N
7.35
7.30
7.25
7.20
7.15
7.10
f1 (ppm)
2.01
3.02
6.82
1.05
3.00
3.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

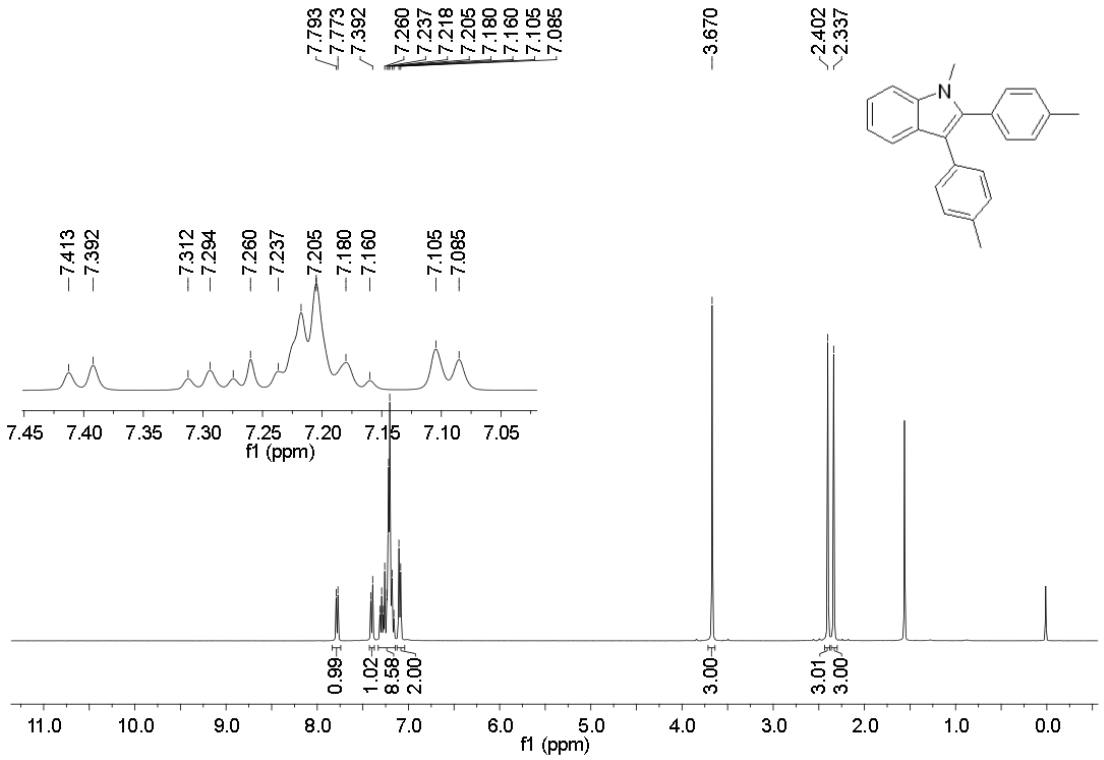

138.367
136.940
134.953
131.624
131.161
129.921
129.021
128.557
128.384
128.293
126.663
125.822
120.644
118.823
114.753
113.265
77.477
77.160
76.842
31.222
23.302
Br
N
132
130
128
126
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

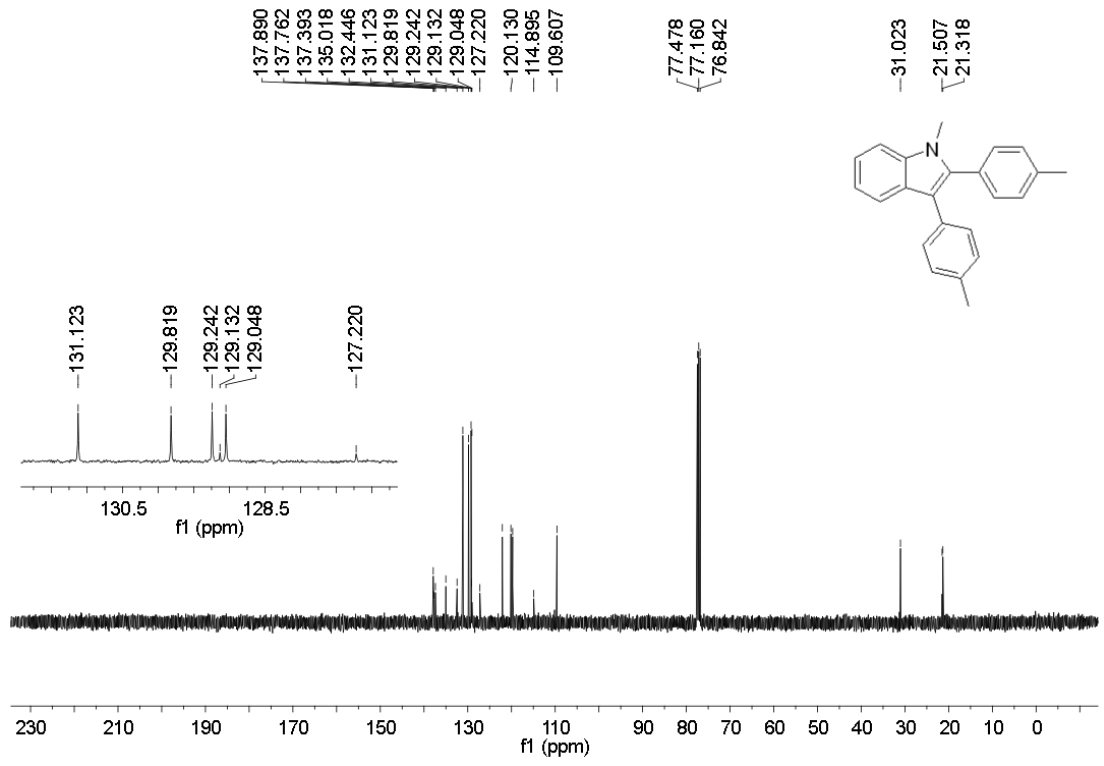

7.816
7.796
7.398
7.302
7.260
7.206
7.171
7.145
7.112
7.049
6.982
3.672
2.356
2.297
7.419
7.398
7.320
7.302
7.284
7.248
7.191
7.155
7.145
7.127
7.112
7.068
7.049
7.000
6.982
7.50
7.40
7.30
7.20
7.10
7.00
f1 (ppm)
0.98
1.00
2.62
5.92
1.01
0.99
3.00
3.02
3.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

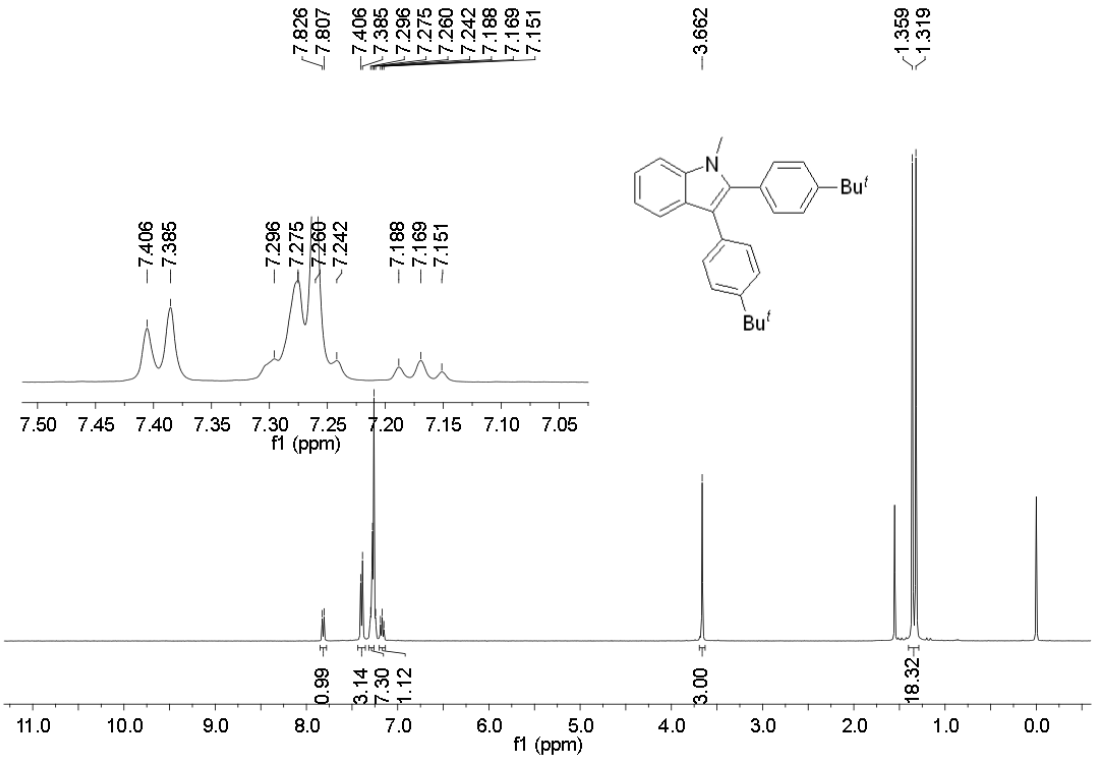

138.016
137.997
137.614
137.413
135.295
132.032
131.756
130.623
128.898
128.471
128.320
128.114
127.158
127.075
126.347
122.141
120.171
119.821
115.112
109.631
77.478
77.160
76.843
31.069
21.666
21.613
137.997
137.614
137.413
135.295
132.032
131.756
130.623
128.898
128.320
128.114
127.075
126.347
122.141
120.171
119.821
138
135
132
129
126
123
120
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

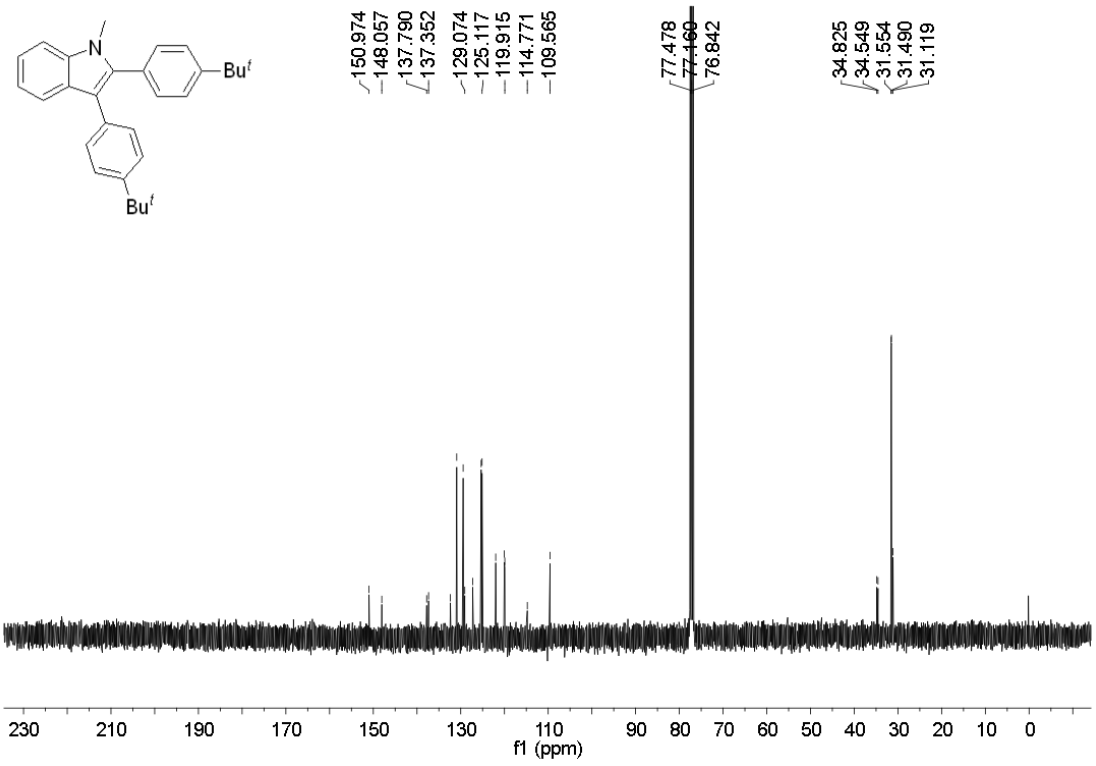

7.794
7.774
7.424
7.327
7.260
7.231
7.126
7.087
7.053
7.017
6.920
6.880
3.694
F
N
F
7.445
7.424
7.411
7.392
7.372
7.366
7.347
7.327
7.271
7.260
7.250
7.231
7.212
7.126
7.107
7.087
7.070
7.053
7.036
7.017
6.991
6.920
6.900
6.880
7.50
7.40
7.30
7.20
7.10
7.00
6.90
f1 (ppm)
0.32
0.99
0.80
1.65
0.40
1.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

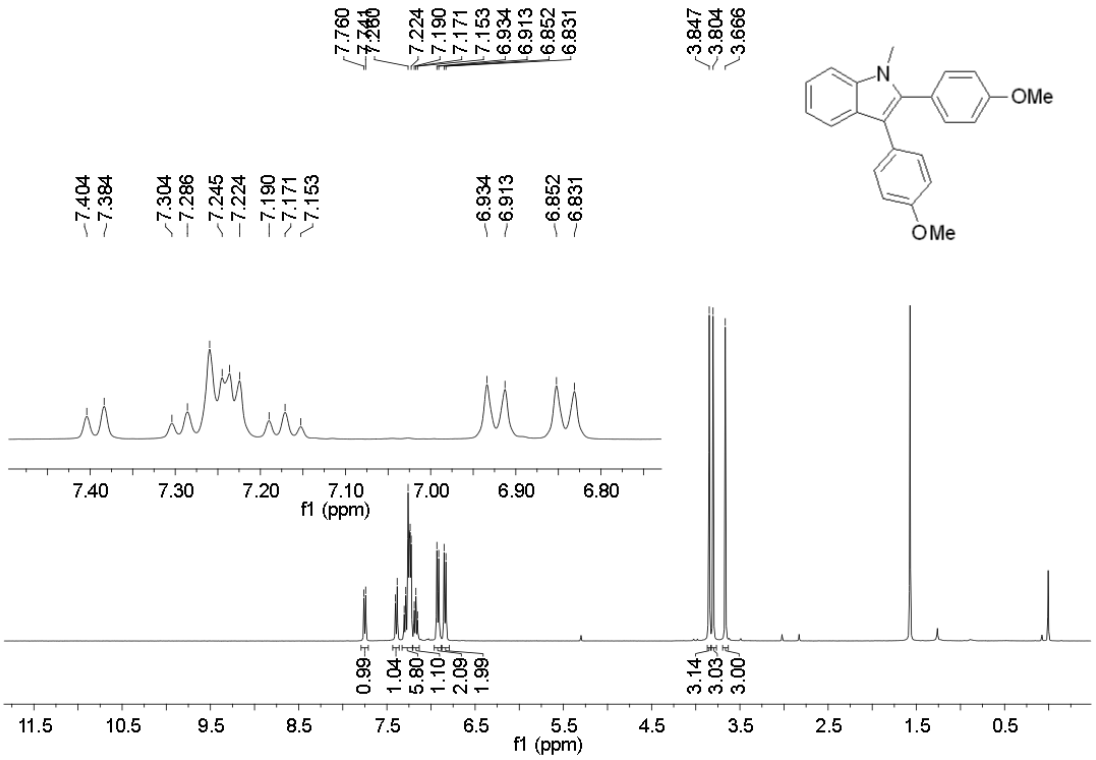

F
N
F
164.190
163.959
161.755
161.500
130.324
127.077
126.743
125.604
120.764
118.174
116.626
115.637
114.662
112.866
109.891
77.478
77.160
76.843
31.132
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

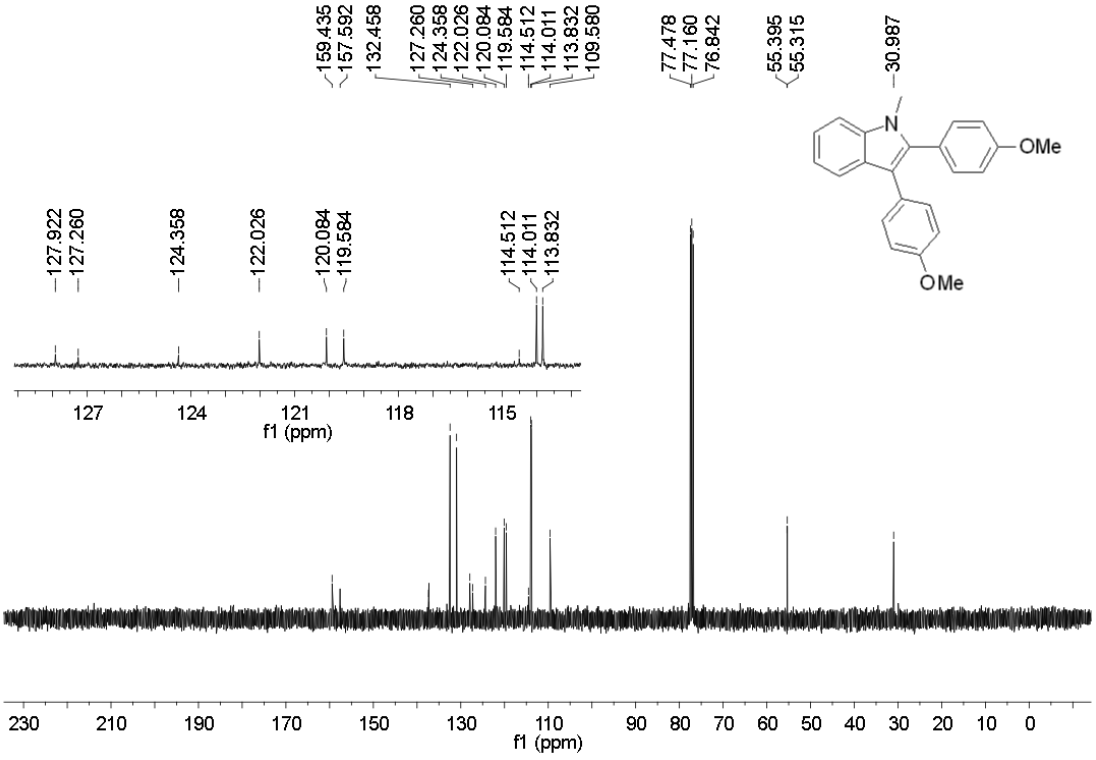

7.793
7.773
7.392
7.260
7.237
7.218
7.205
7.180
7.160
7.105
7.085
3.670
2.402
2.337
7.413
7.392
7.312
7.294
7.260
7.237
7.205
7.180
7.160
7.105
7.085
7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05
f1 (ppm)
0.99
1.02
8.58
2.00
3.00
3.01
3.00
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

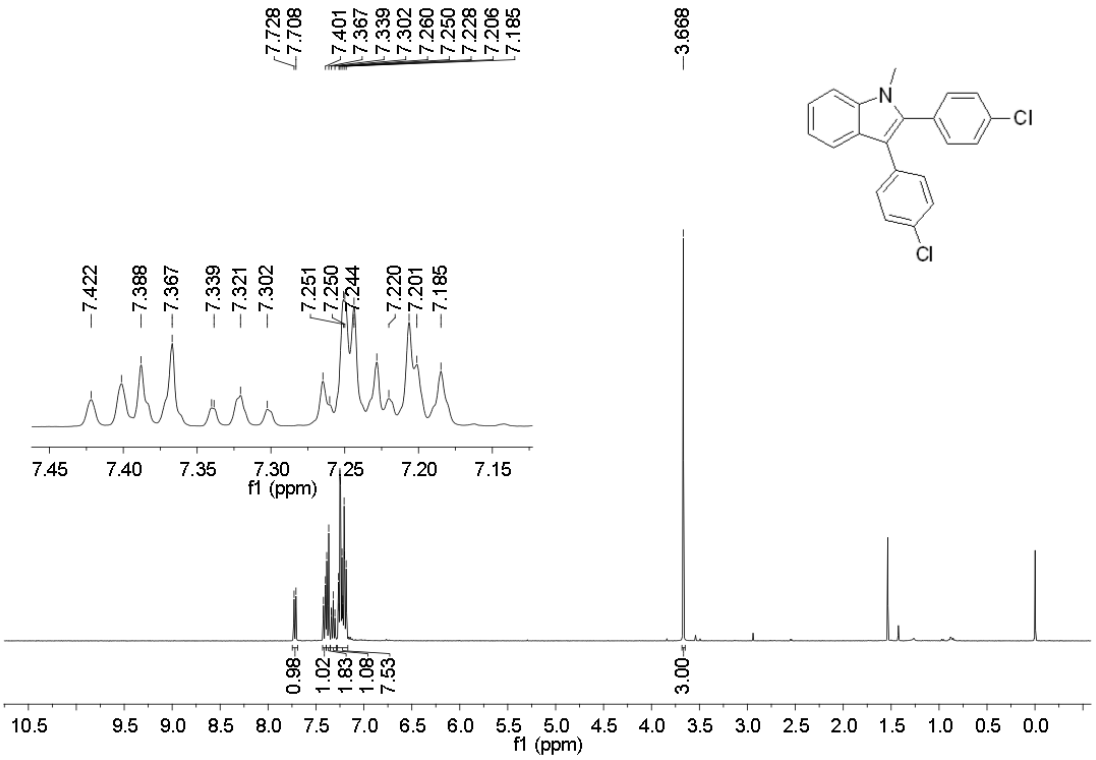

137.890
137.762
137.393
135.018
132.446
131.123
129.819
129.242
129.132
129.048
127.220
120.130
114.895
109.607
77.478
77.160
76.842
31.023
21.507
21.318
131.123
129.819
129.242
129.132
129.048
127.220
130.5
128.5
f1 (ppm)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

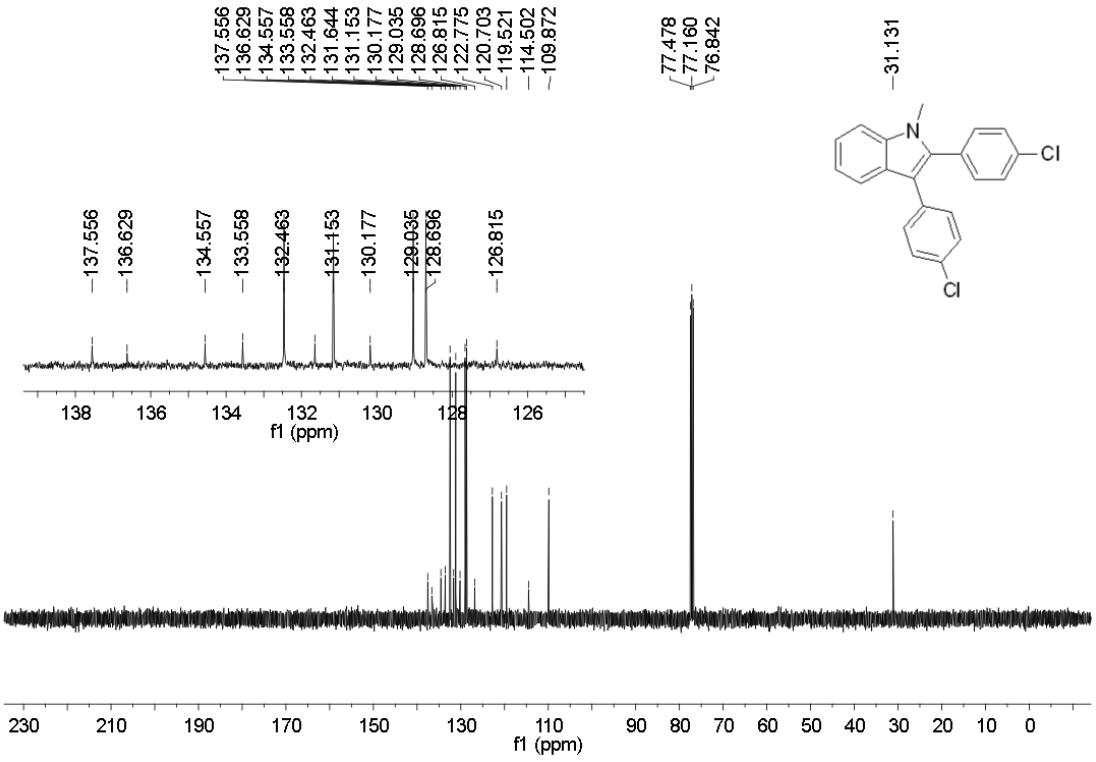

7.826
7.807
7.406
7.385
7.296
7.275
7.260
7.242
7.188
7.169
7.151
3.662
1.359
1.319
Bu^t
Bu^t
f1 (ppm)
0.99
3.14
7.30
1.12
3.00
18.32
f1 (ppm)

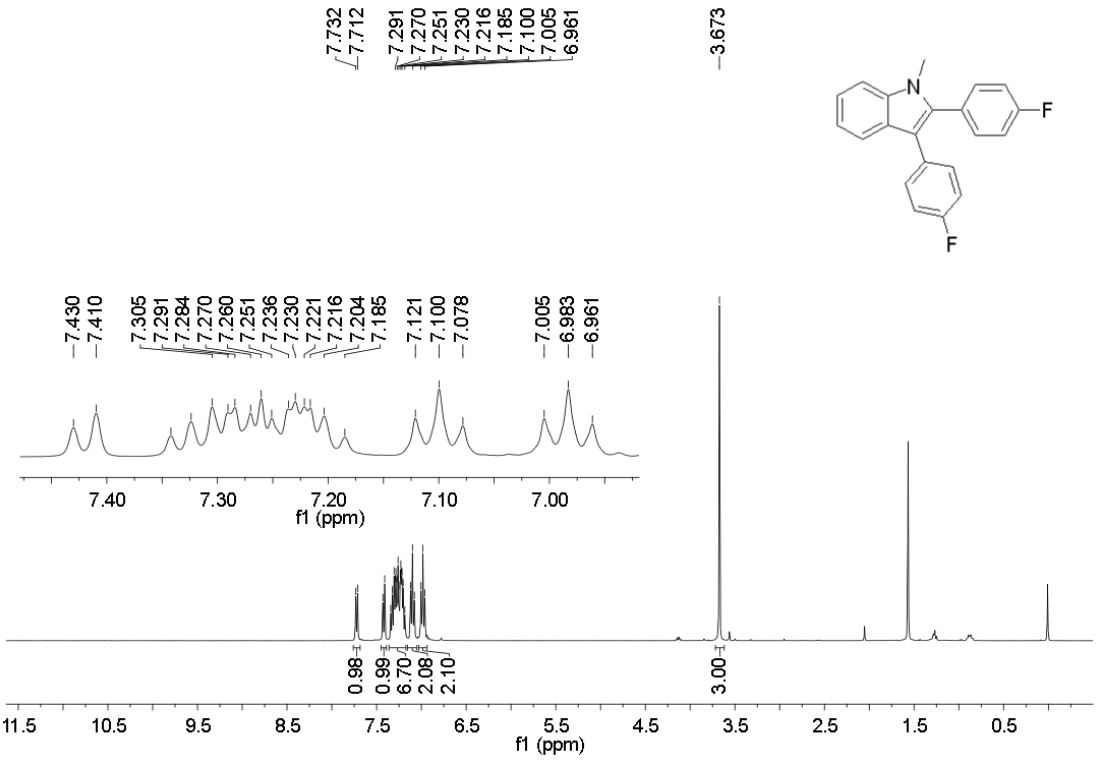

150.974
148.057
137.790
137.352
129.074
125.117
119.915
114.771
109.565
77.478
77.160
76.842
34.825
34.549
31.554
31.490
31.119
Bu^t
Bu^t
f1 (ppm)

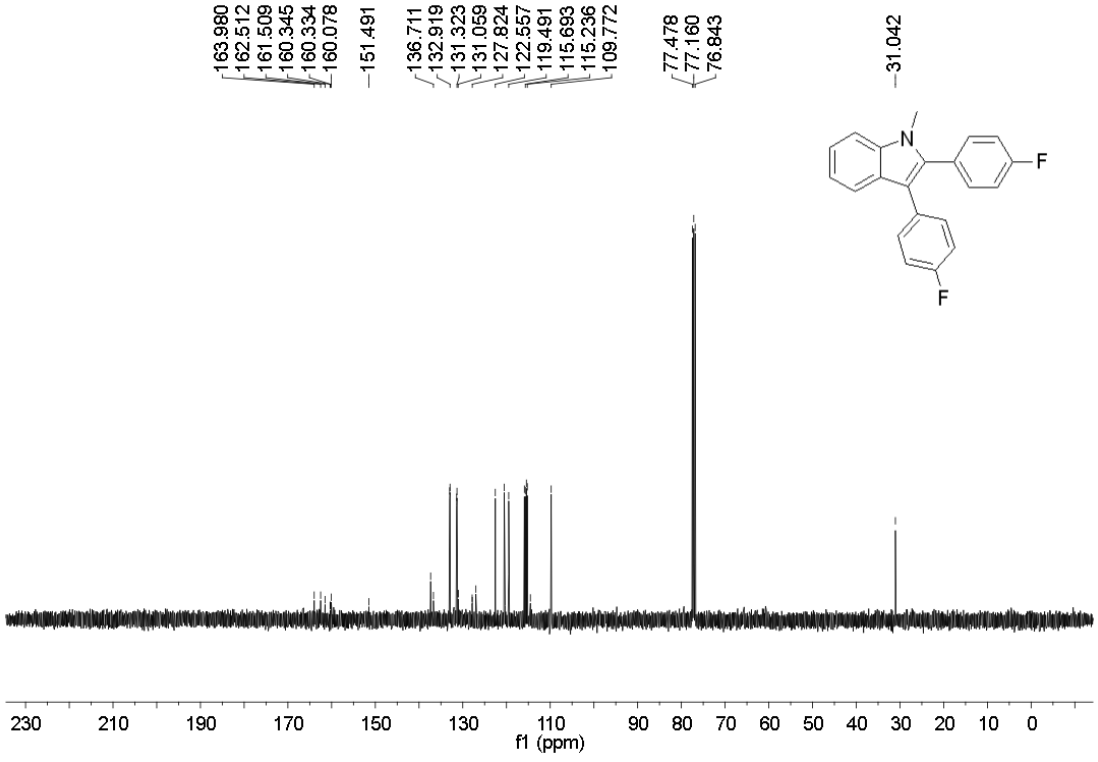

7.760
7.224
7.190
7.171
7.153
6.934
6.913
6.852
6.831
3.847
3.804
3.666
OMe
OMe
7.404
7.384
7.304
7.286
7.245
7.224
7.190
7.171
7.153
6.934
6.913
6.852
6.831
7.40
7.30
7.20
7.10
7.00
6.90
6.80
f1 (ppm)
0.99
1.04
5.80
1.10
2.09
1.99
3.14
3.03
3.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

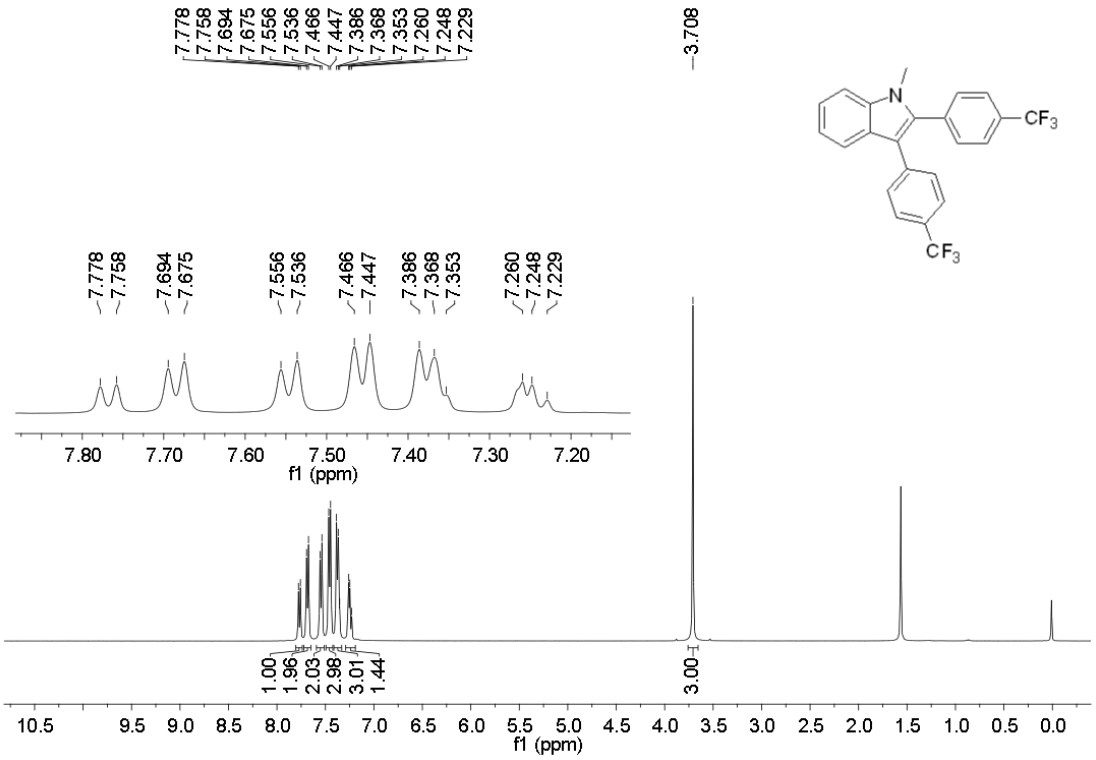

159.435
157.592
132.458
127.260
124.358
122.026
120.084
119.584
114.512
114.011
113.832
109.580
77.478
77.160
76.842
55.395
55.315
30.987
OMe
OMe
127.922
127.260
124.358
122.026
120.084
119.584
114.512
114.011
113.832
127
124
121
118
115
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

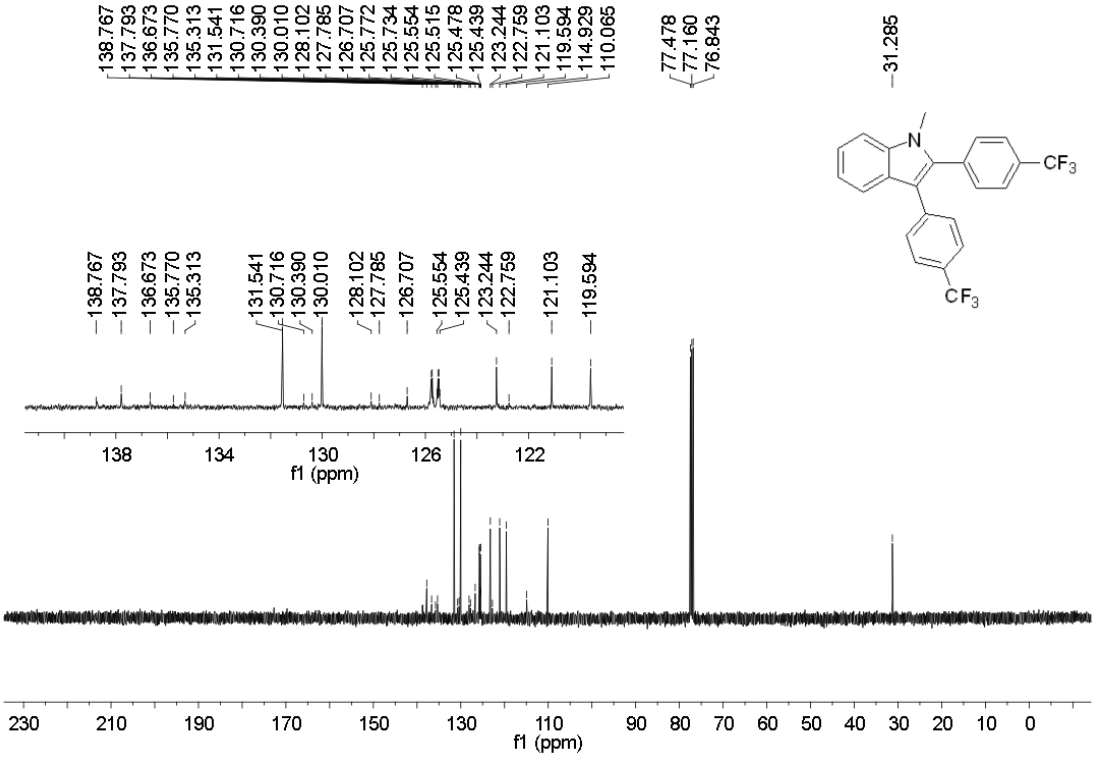

7.728
7.708
7.401
7.367
7.339
7.302
7.260
7.250
7.228
7.206
7.185
3.668
Cl
Cl
7.422
7.388
7.367
7.339
7.321
7.302
7.251
7.250
7.244
7.220
7.201
7.185
7.45 7.40 7.35 7.30 7.25 7.20 7.15
f1 (ppm)
0.98
1.02
1.83
1.08
7.53
3.00
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

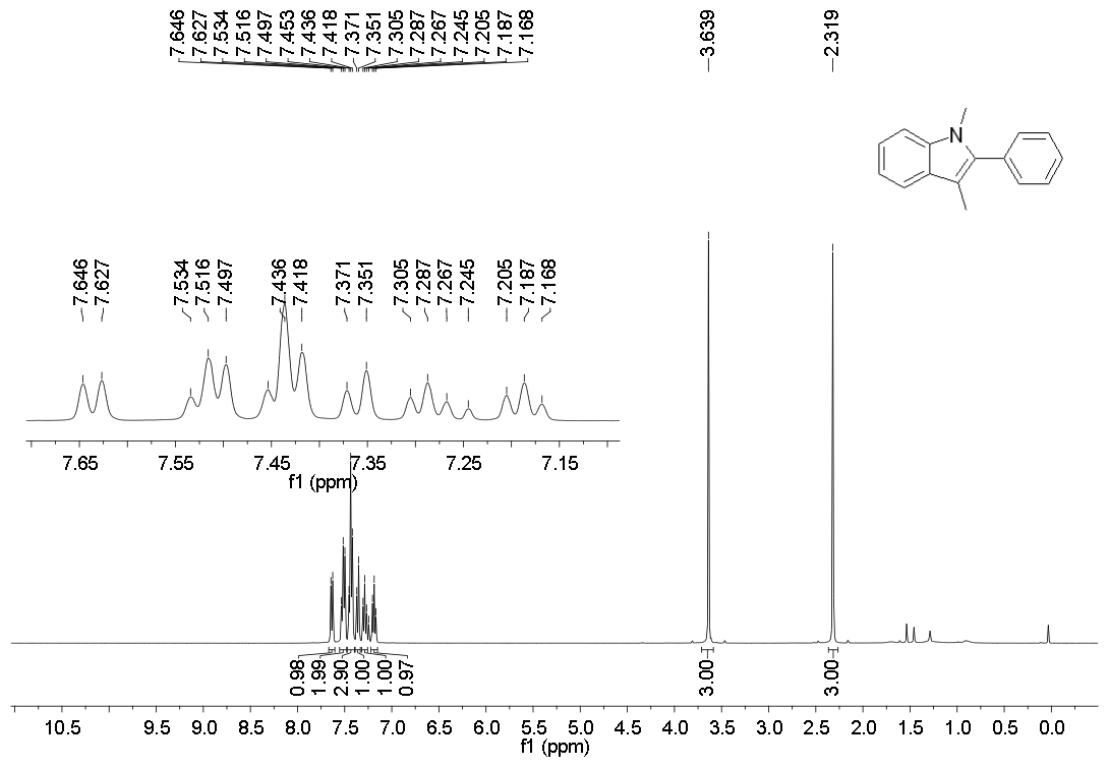

137.556
136.629
134.557
133.558
132.463
131.644
131.153
130.177
129.035
128.696
126.815
122.775
120.703
119.521
114.502
109.872
77.478
77.160
76.842
31.131
Cl
Cl
137.556
136.629
134.557
133.558
132.463
131.153
130.177
129.035
128.696
126.815
138 136 134 132 130 128 126
f1 (ppm)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

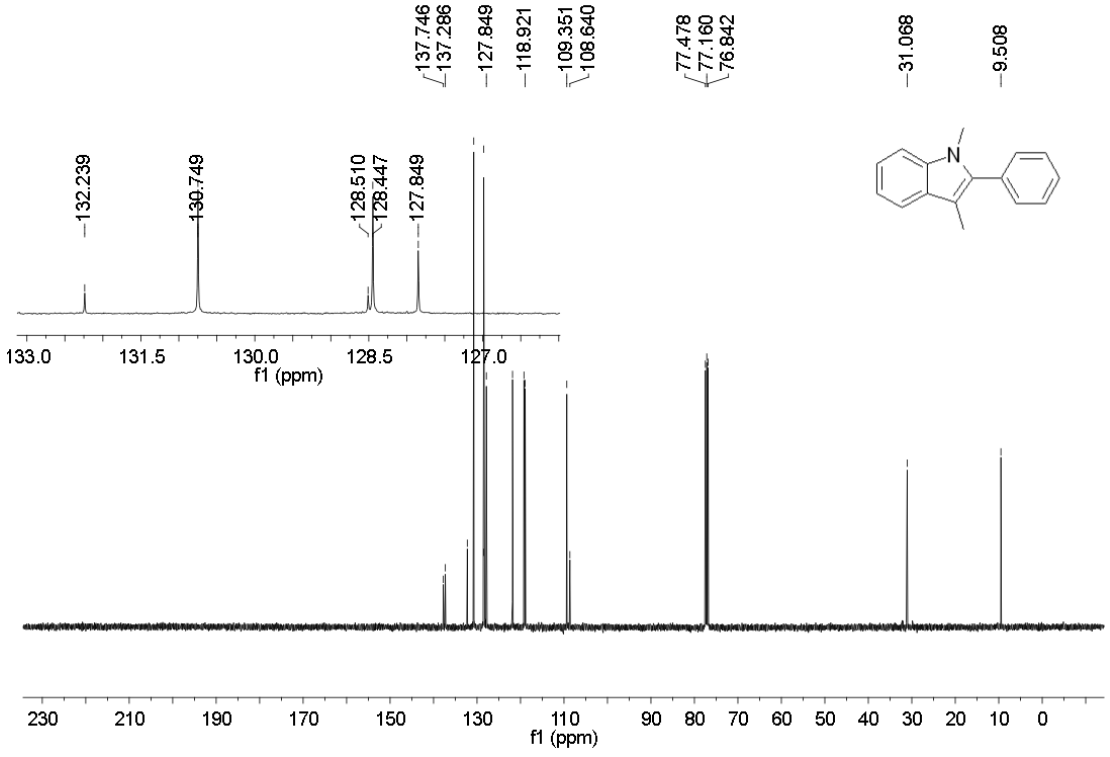

7.732
7.712
7.291
7.270
7.251
7.230
7.216
7.185
7.100
7.005
6.961
3.673
N
F
F
7.430
7.410
7.305
7.291
7.284
7.270
7.260
7.251
7.236
7.230
7.221
7.216
7.204
7.185
7.121
7.100
7.078
7.005
6.983
6.961
7.40
7.30
7.20
7.10
7.00
f1 (ppm)
0.98
0.99
6.70
2.08
2.10
3.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

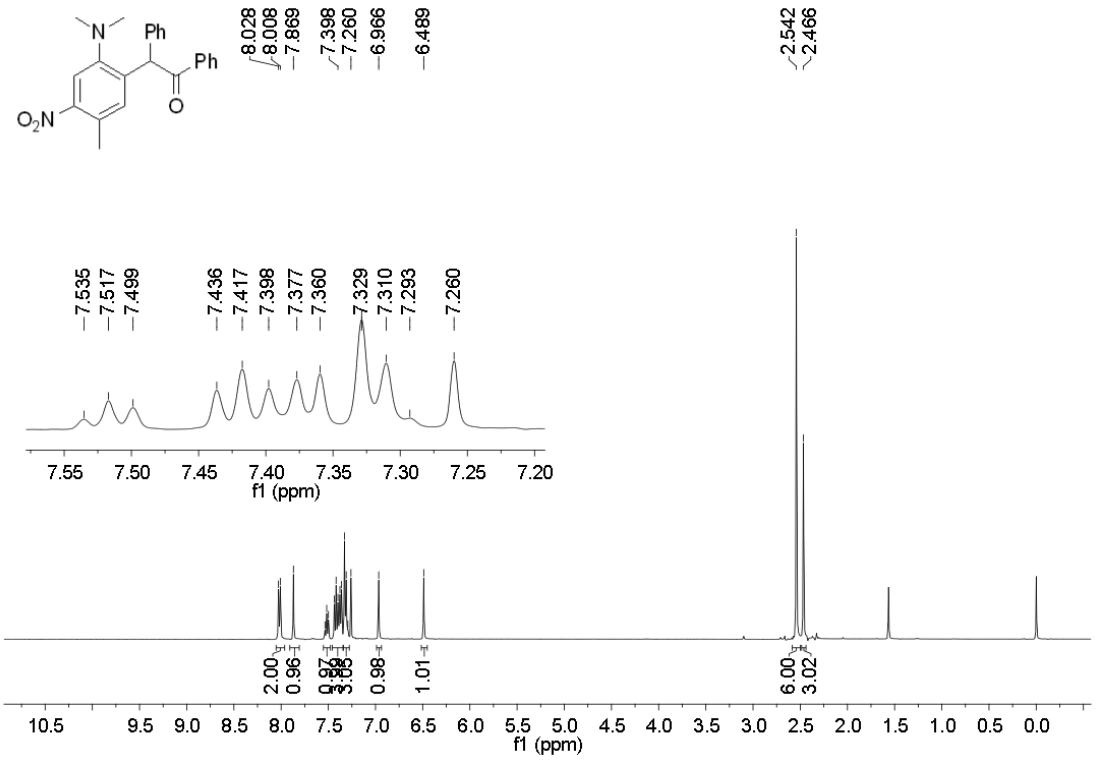

163.980
162.512
161.509
160.345
160.334
160.078
151.491
136.711
132.919
131.323
131.059
127.824
122.557
119.491
115.693
115.236
109.772
77.478
77.160
76.843
31.042
N
F
F
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

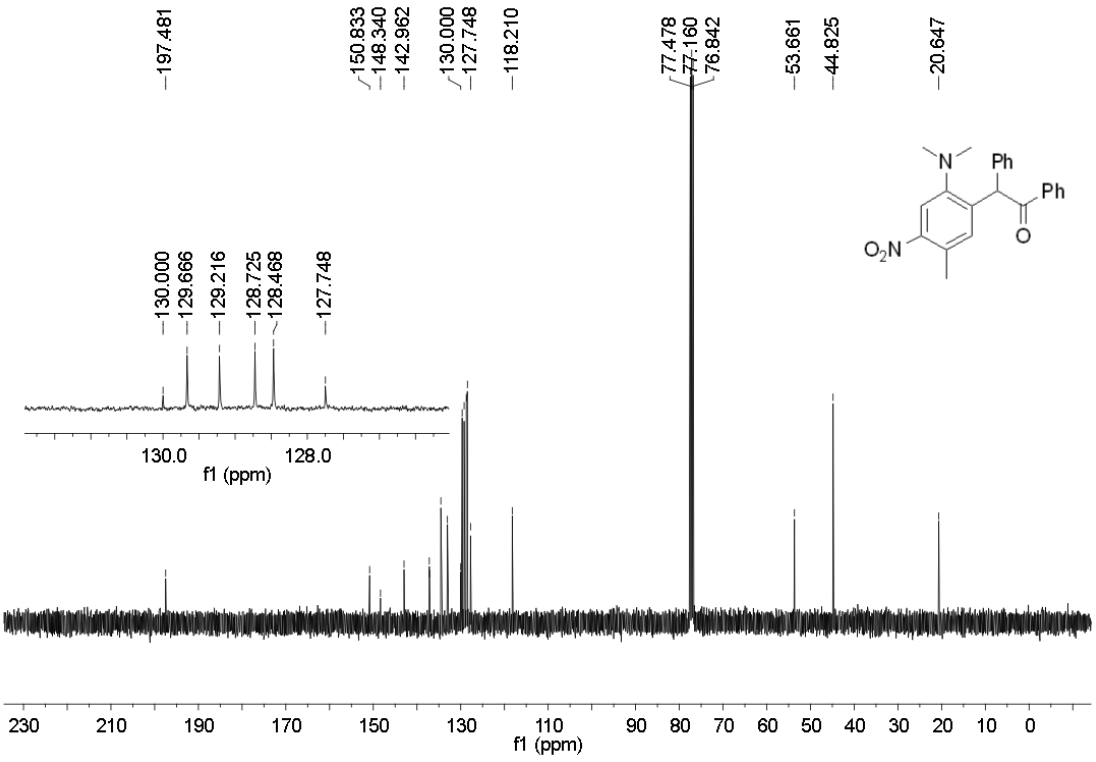

7.778
7.758
7.694
7.675
7.556
7.536
7.466
7.447
7.386
7.368
7.353
7.260
7.248
7.229
3.708
N
CF3
CF3
f1 (ppm)
1.00
1.96
2.03
2.98
3.01
1.44
3.00
f1 (ppm)

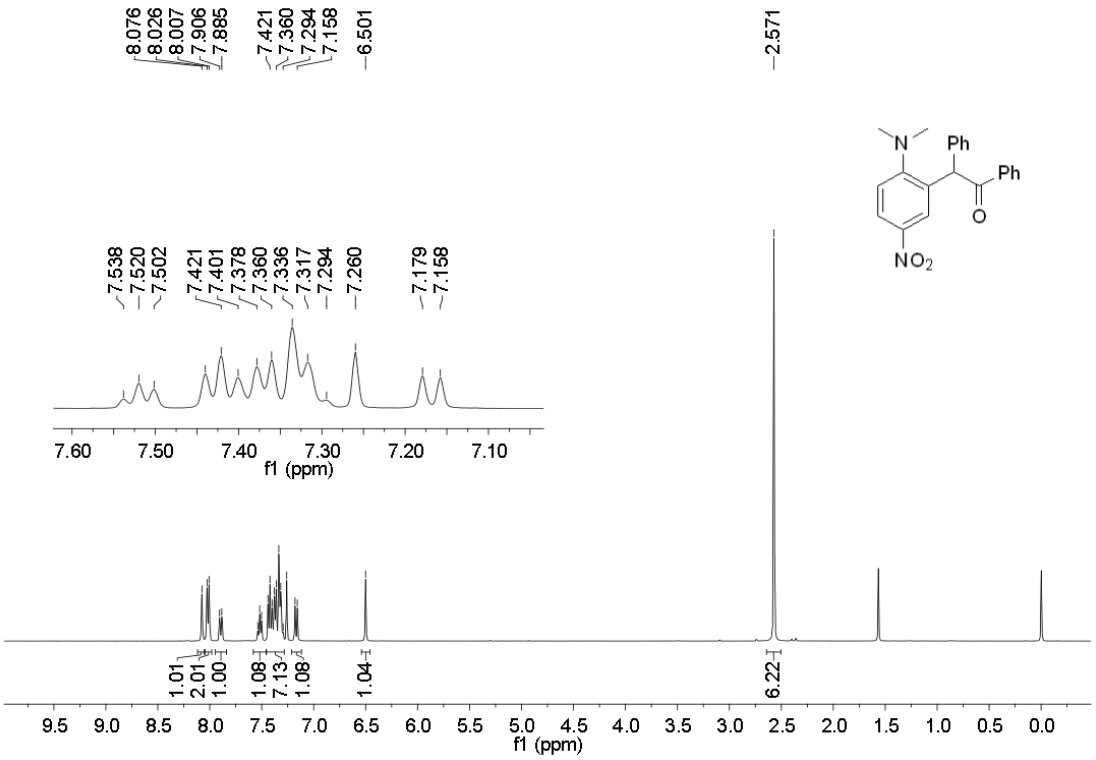

138.767
137.793
136.673
135.770
135.313
131.541
130.716
130.390
130.010
128.102
127.785
126.707
125.772
125.734
125.554
125.515
125.478
125.439
123.244
122.759
121.103
119.594
114.929
110.065
77.478
77.160
76.843
31.285
N
CF3
CF3
f1 (ppm)
f1 (ppm)

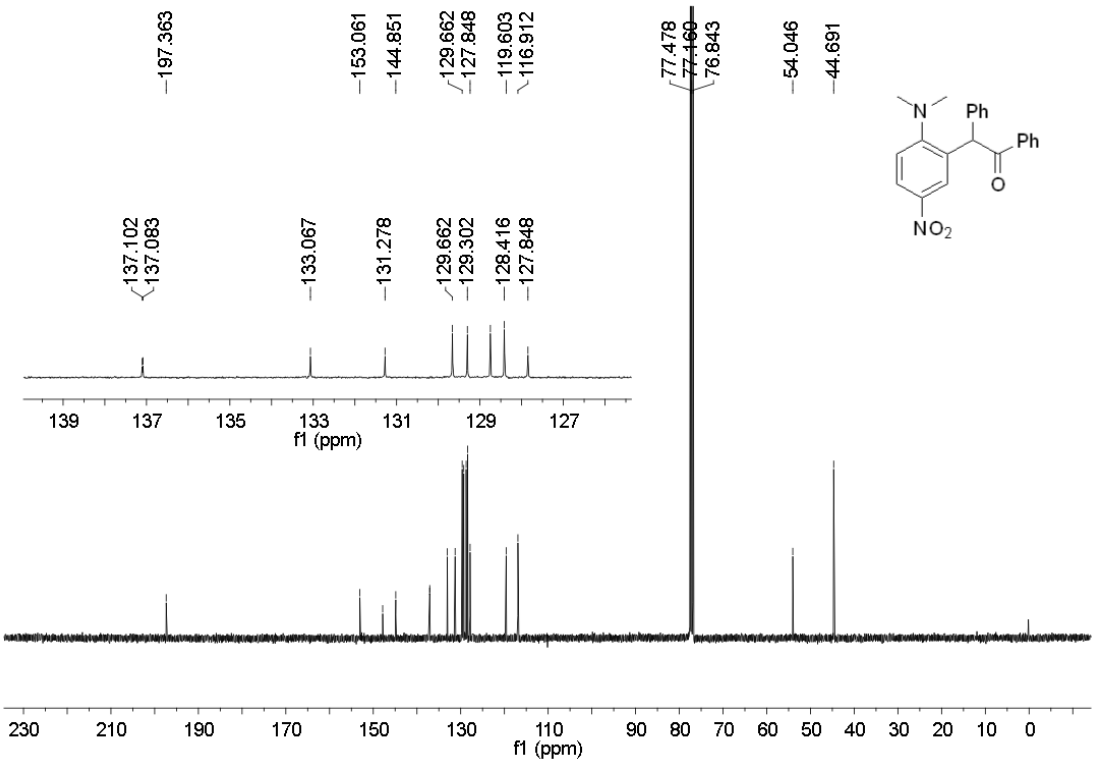

7.646
7.627
7.534
7.516
7.497
7.453
7.436
7.418
7.371
7.351
7.305
7.287
7.267
7.245
7.205
7.187
7.168
3.639
2.319
N
f1 (ppm)
0.98
1.99
2.90
1.00
1.00
0.97
3.00
3.00

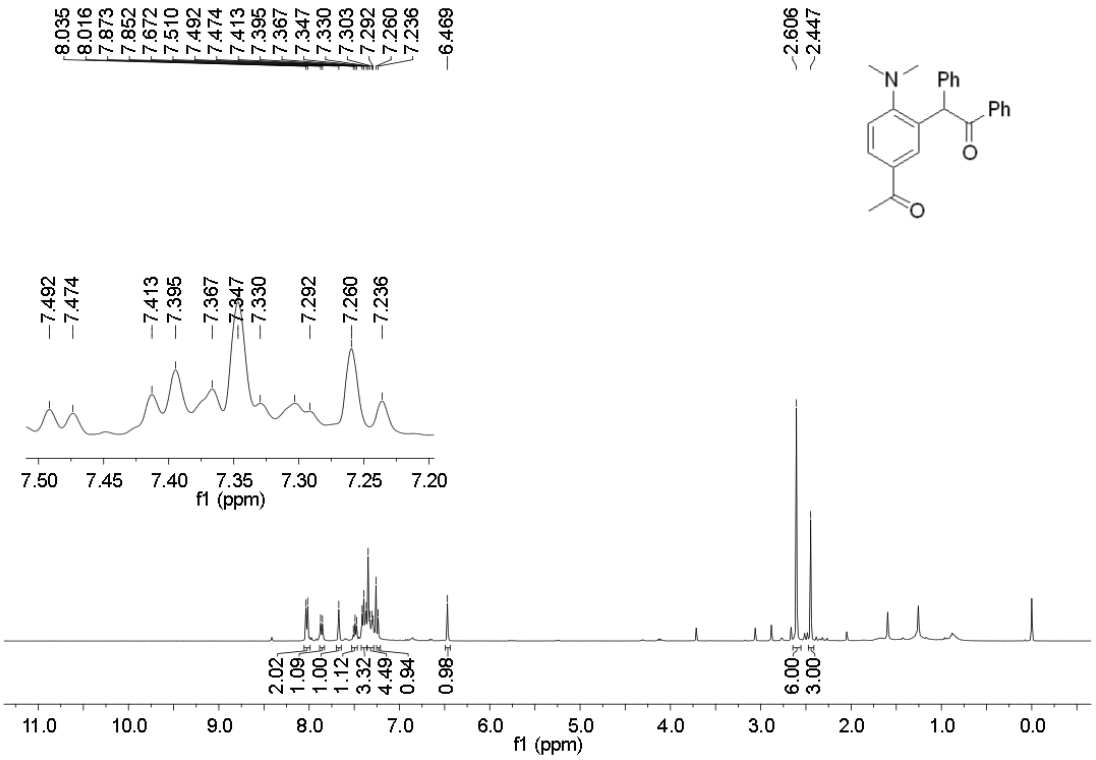

137.746
137.286
127.849
118.921
109.351
108.640
77.478
77.160
76.842
31.068
9.508
132.239
130.749
128.510
128.447
127.849
N
f1 (ppm)

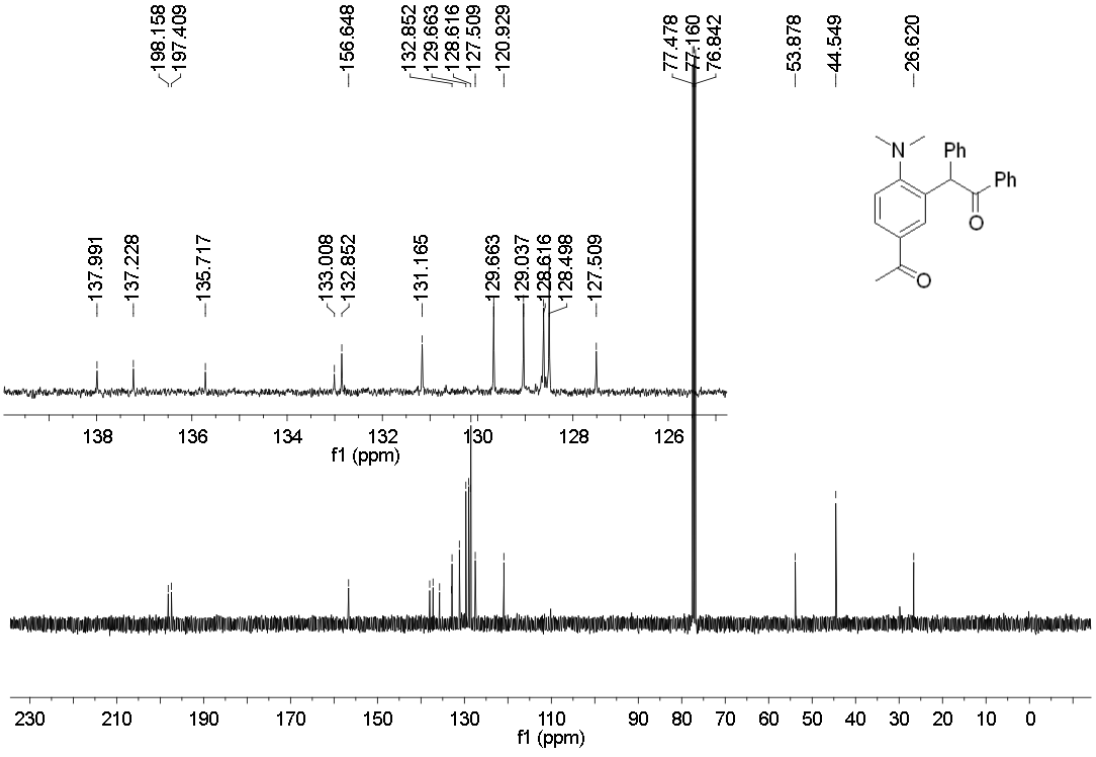

8.028
8.008
7.869
7.398
7.260
6.966
6.489
2.542
2.466
7.535
7.517
7.499
7.436
7.417
7.398
7.377
7.360
7.329
7.310
7.293
7.260
f1 (ppm)
2.00
0.96
0.98
1.01
6.00
3.02
f1 (ppm)

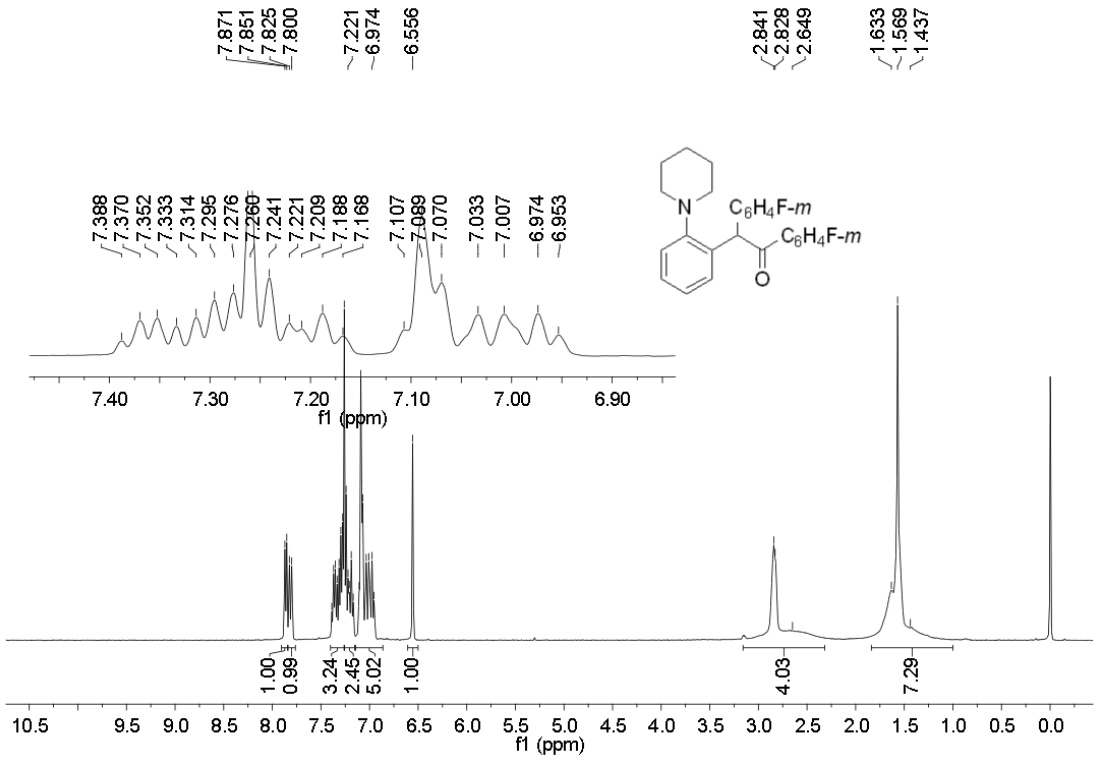

197.481
150.833
148.340
142.962
130.000
127.748
118.210
77.478
77.160
76.842
53.661
44.825
20.647
130.000
129.666
129.216
128.725
128.468
127.748
f1 (ppm)
f1 (ppm)

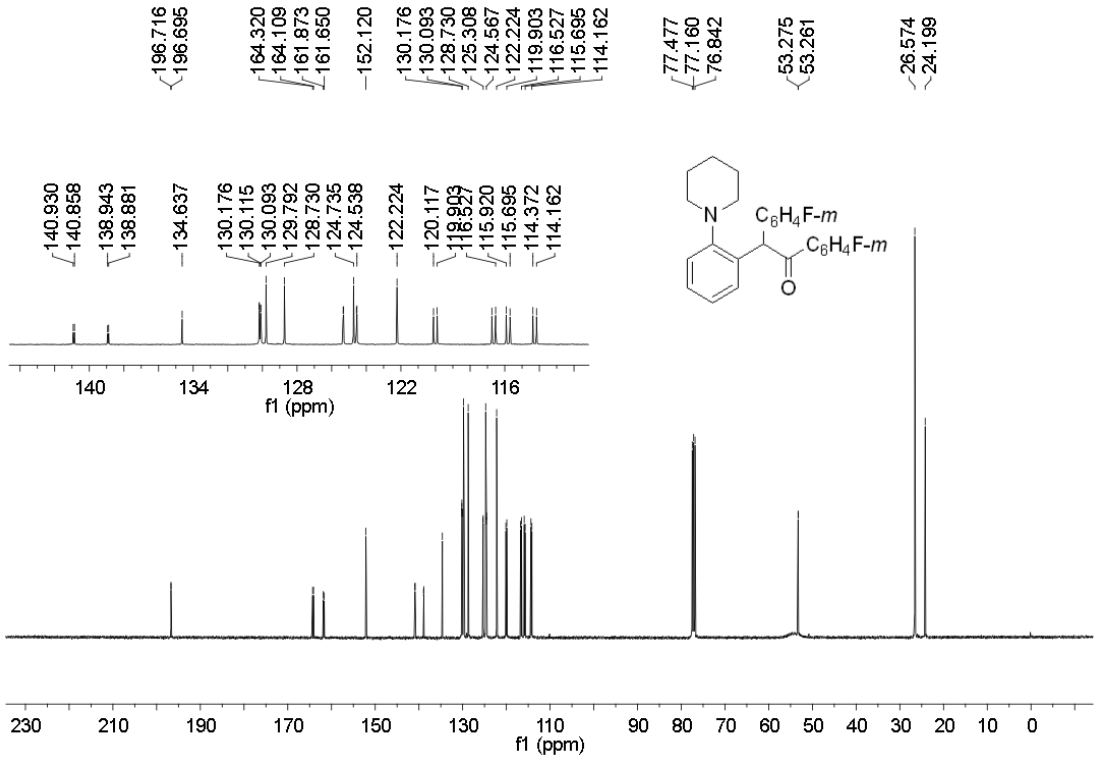

8.076
8.026
8.007
7.906
7.885
7.421
7.360
7.294
7.158
6.501
2.571
N
Ph
Ph
O
NO2
7.538
7.520
7.502
7.421
7.401
7.378
7.360
7.336
7.317
7.294
7.260
7.179
7.158
7.60 7.50 7.40 7.30 7.20 7.10
f1 (ppm)
1.01
2.01
1.00
1.08
7.13
1.08
1.04
6.22
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

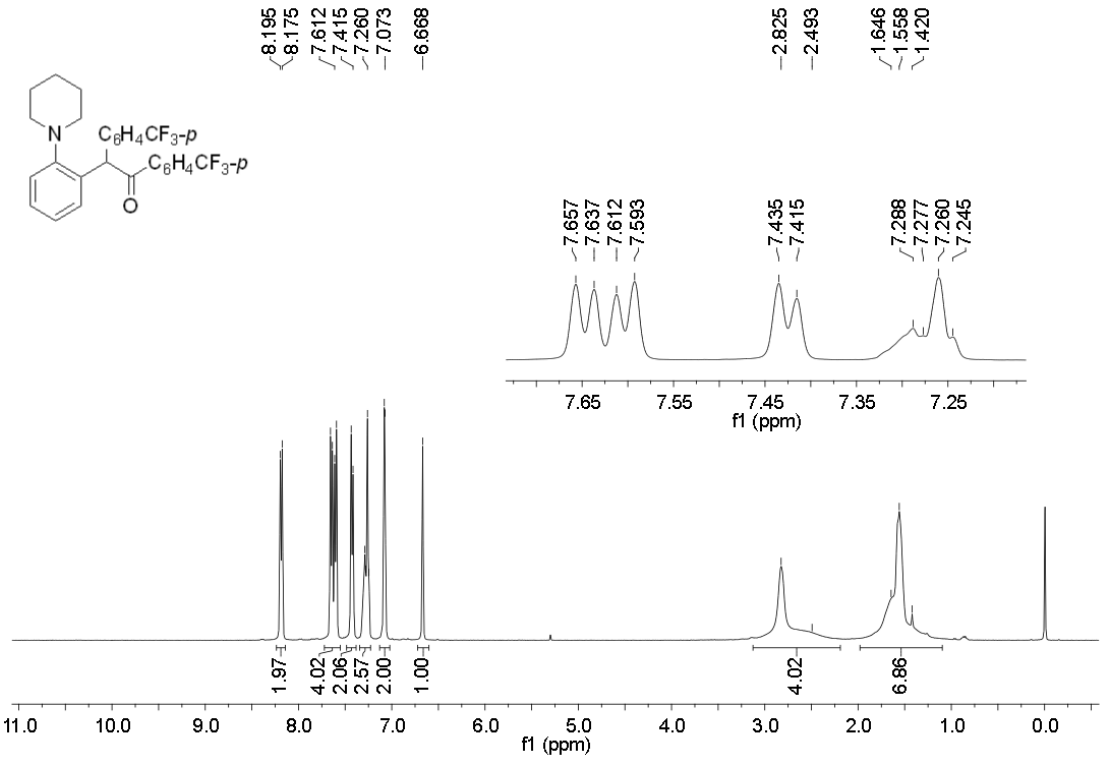

197.363
153.061
144.851
129.662
127.848
119.603
116.912
77.478
77.160
76.843
54.046
44.691
N
Ph
Ph
O
NO2
137.102
137.083
133.067
131.278
129.662
129.302
128.416
127.848
139 137 135 133 131 129 127
f1 (ppm)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

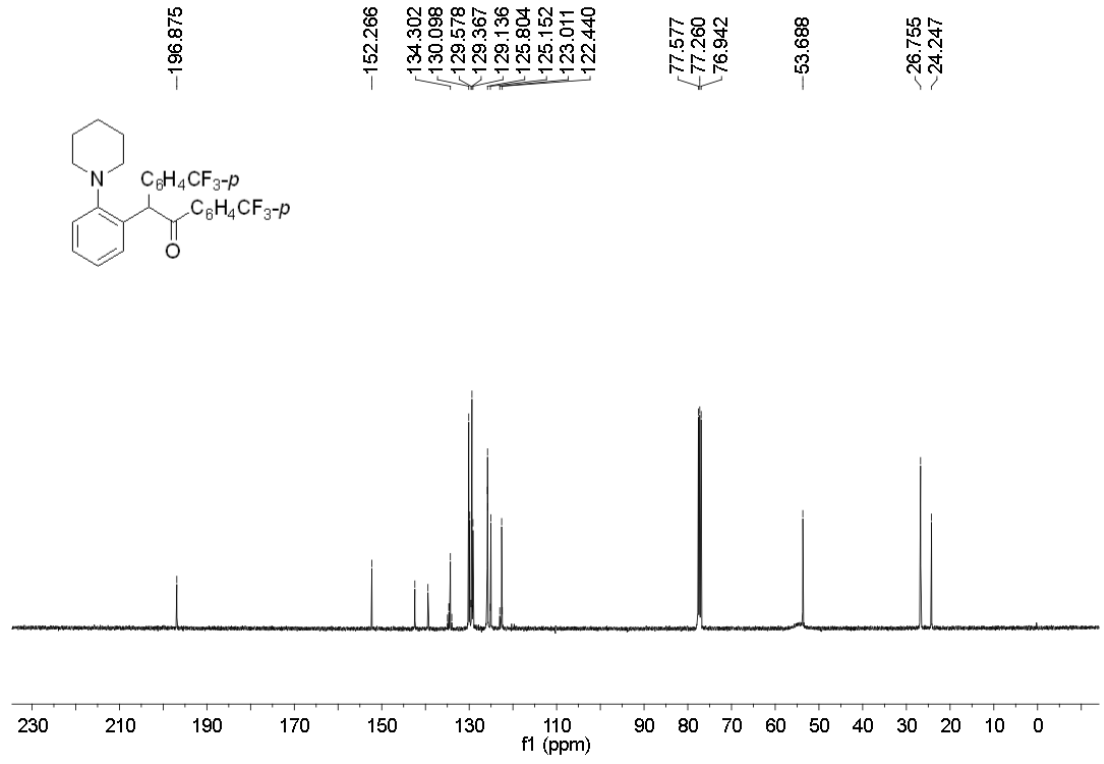

8.035
8.016
7.873
7.852
7.672
7.510
7.492
7.474
7.413
7.395
7.367
7.347
7.330
7.303
7.292
7.260
7.236
6.469
2.606
2.447
N
Ph
Ph
O
O
7.492
7.474
7.413
7.395
7.367
7.347
7.330
7.292
7.260
7.236
7.50 7.45 7.40 7.35 7.30 7.25 7.20
f1 (ppm)
2.02
1.09
1.00
1.12
3.32
4.49
0.94
0.98
6.00
3.00
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

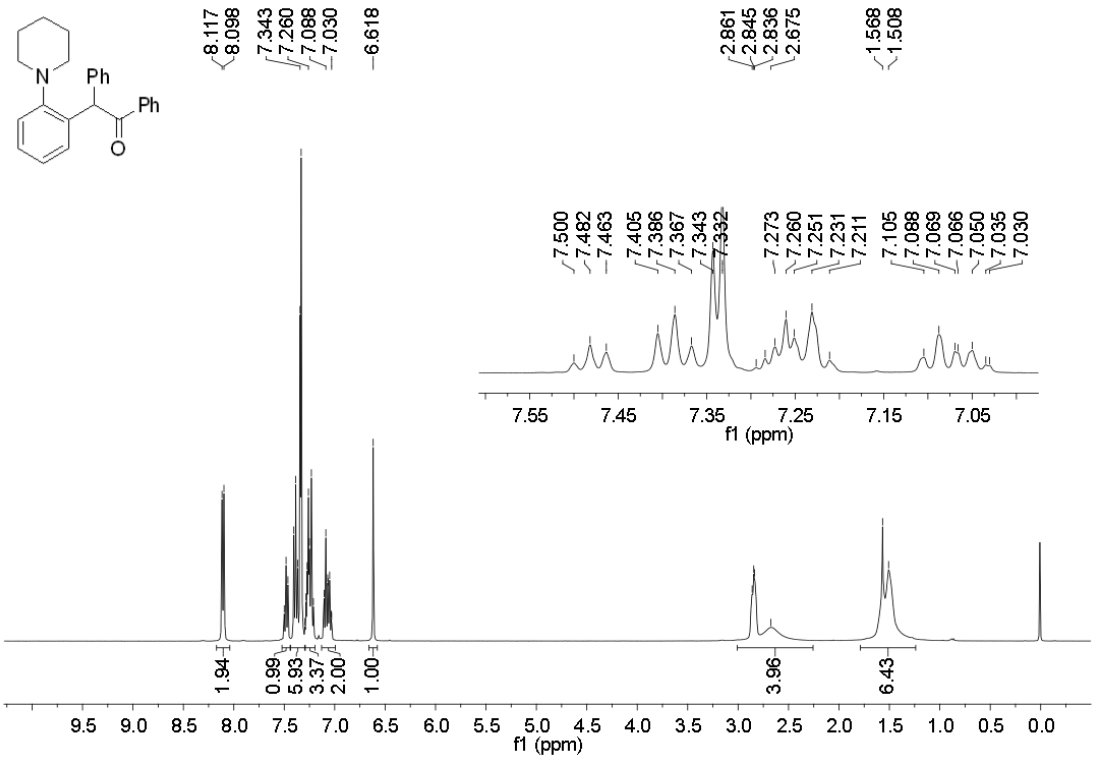

198.158
197.409
156.648
132.852
129.663
128.616
127.509
120.929
77.478
77.160
76.842
53.878
44.549
26.620
N
Ph
Ph
O
O
137.991
137.228
135.717
133.008
132.852
131.165
129.663
129.037
128.616
128.498
127.509
138 136 134 132 130 128 126
f1 (ppm)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

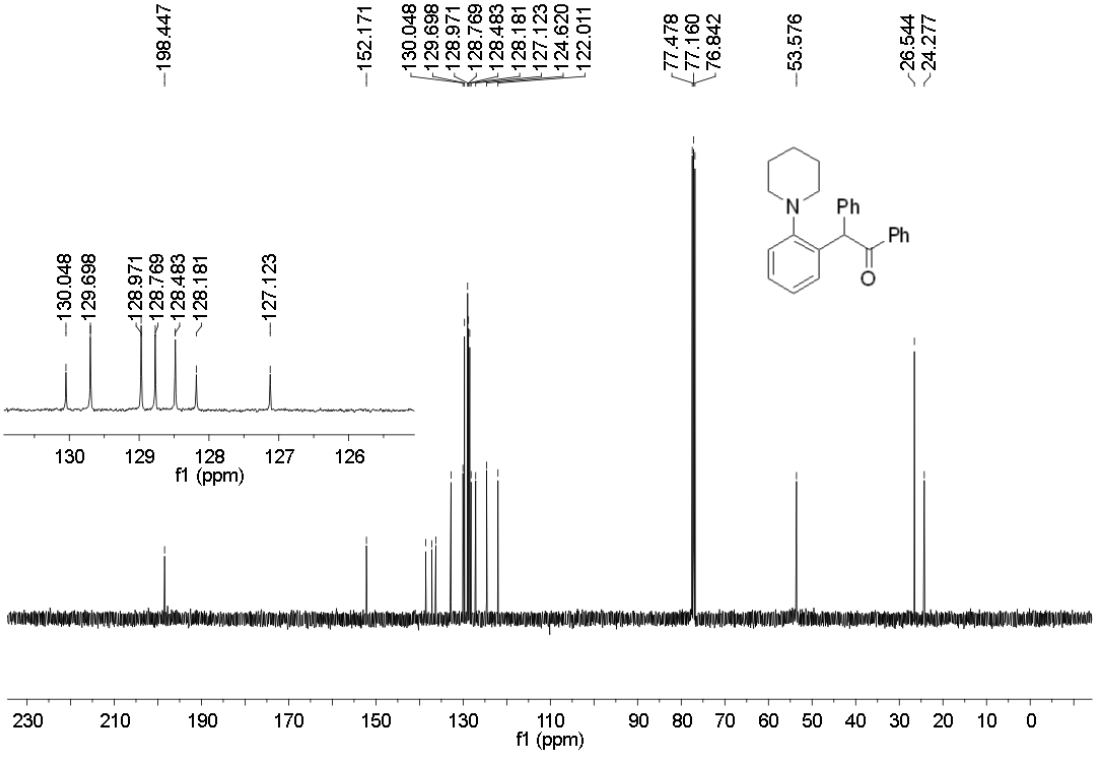

7.871
7.851
7.825
7.800
7.221
6.974
6.556
2.841
2.828
2.649
1.633
1.569
1.437
7.388
7.370
7.352
7.333
7.314
7.295
7.276
7.260
7.241
7.221
7.209
7.188
7.168
7.107
7.089
7.070
7.033
7.007
6.974
6.953
C6H4F-m
C6H4F-m
O
f1 (ppm)
1.00
0.99
3.24
2.45
5.02
1.00
4.03
7.29
f1 (ppm)

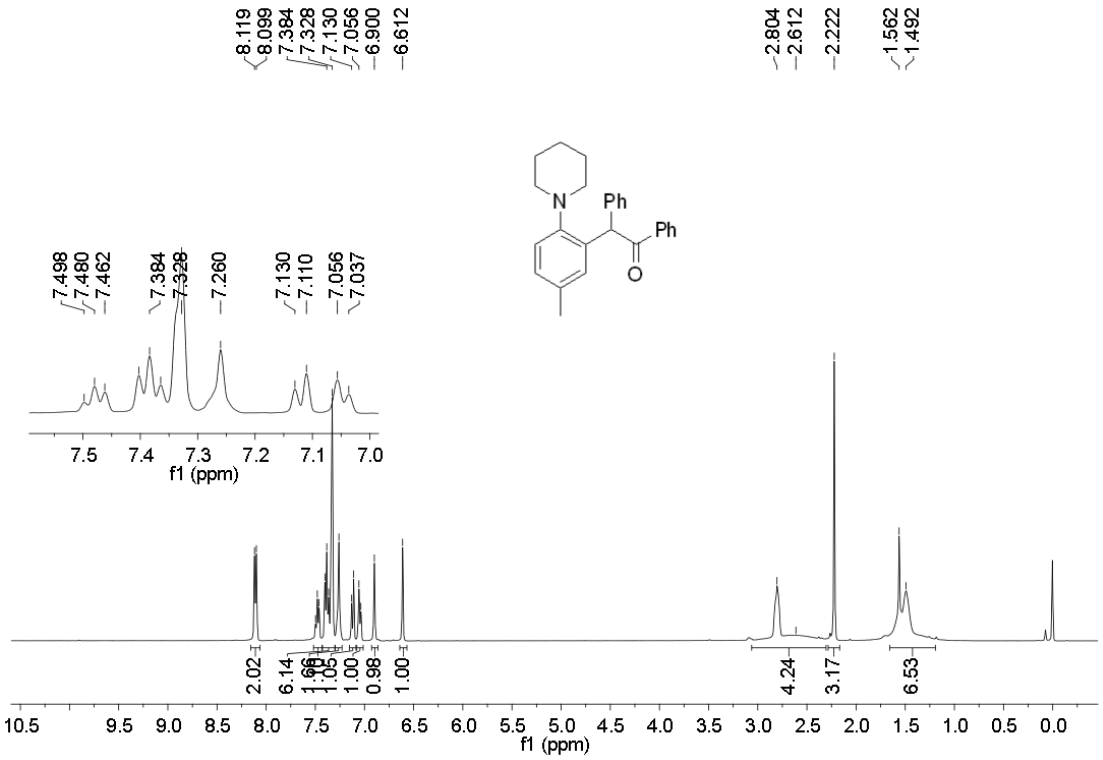

196.716
196.695
164.320
164.109
161.873
161.650
152.120
130.176
130.093
128.730
125.308
124.567
122.224
119.903
116.527
115.695
114.162
77.477
77.160
76.842
53.275
53.261
26.574
24.199
140.930
140.858
138.943
138.881
134.637
130.176
130.115
130.093
129.792
128.730
124.735
124.538
122.224
120.117
115.920
115.695
114.372
114.162
C6H4F-m
C6H4F-m
O
f1 (ppm)
f1 (ppm)

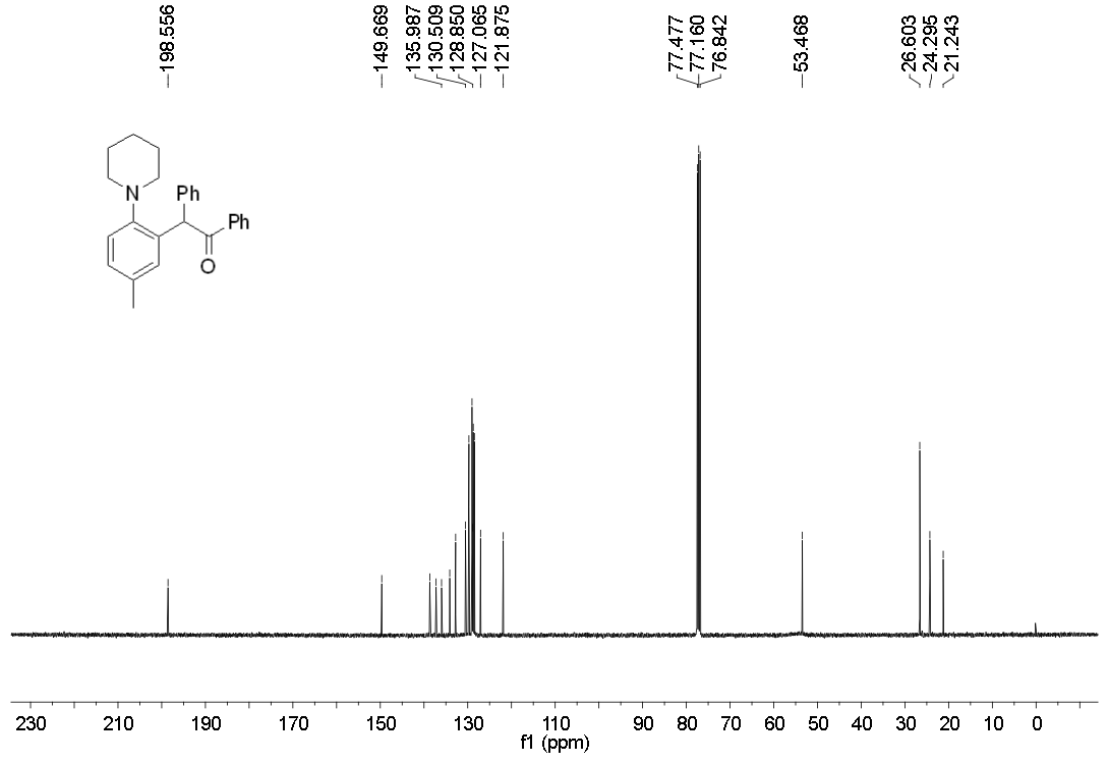

8.195
8.175
7.612
7.415
7.260
7.073
6.668
2.825
2.493
1.646
1.558
1.420
N
C6H4CF3-p
C6H4CF3-p
O
7.657
7.637
7.612
7.593
7.435
7.415
7.288
7.277
7.260
7.245
7.65
7.55
7.45
7.35
7.25
f1 (ppm)
1.97
4.02
2.06
2.57
2.00
1.00
4.02
6.86
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

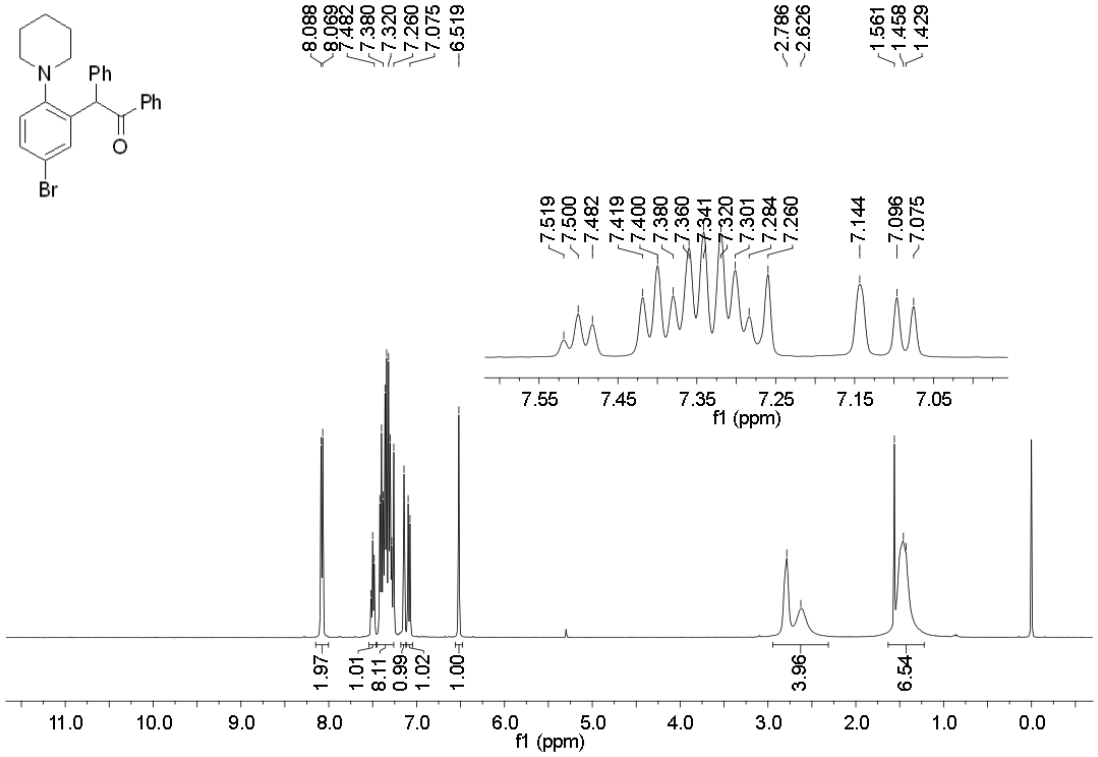

196.875
152.266
134.302
130.098
129.578
129.367
129.136
125.804
125.152
123.011
122.440
77.577
77.260
76.942
53.688
26.755
24.247
N
C6H4CF3-p
C6H4CF3-p
O
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

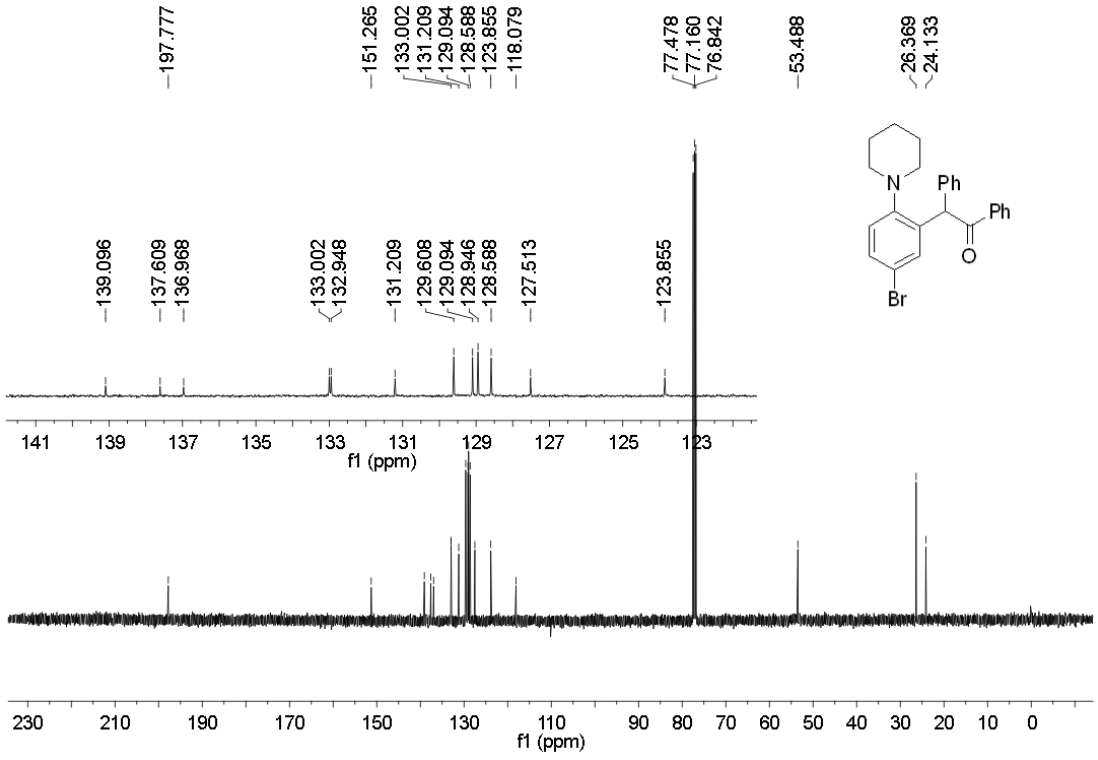

8.117
8.098
7.343
7.260
7.088
7.030
6.618
2.861
2.845
2.836
2.675
1.568
1.508
Ph
Ph
O
N
7.500
7.482
7.463
7.405
7.386
7.367
7.343
7.332
7.273
7.260
7.251
7.231
7.211
7.105
7.088
7.069
7.066
7.050
7.035
7.030
7.55
7.45
7.35
7.25
7.15
7.05
f1 (ppm)
1.94
0.99
5.93
3.37
2.00
1.00
3.96
6.43
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

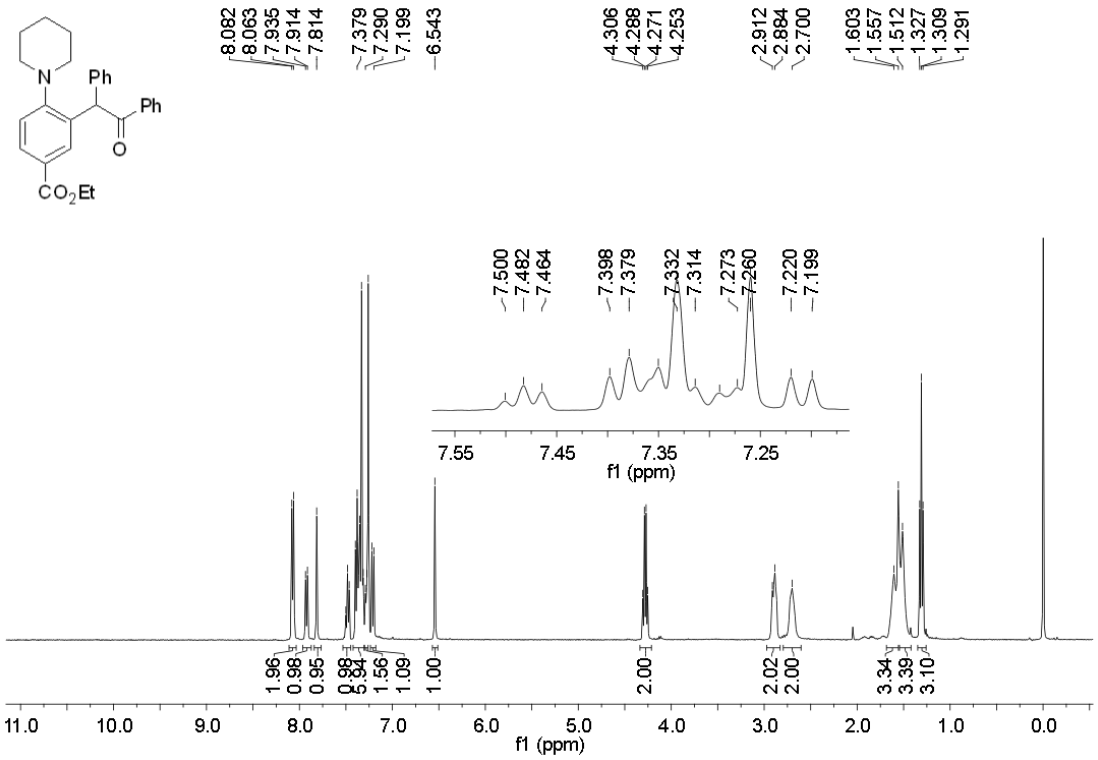

198.447
152.171
130.048
129.698
128.971
128.769
128.483
128.181
127.123
124.620
122.011
77.478
77.160
76.842
53.576
26.544
24.277
Ph
Ph
O
N
130.048
129.698
128.971
128.769
128.483
128.181
127.123
130
129
128
127
126
f1 (ppm)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

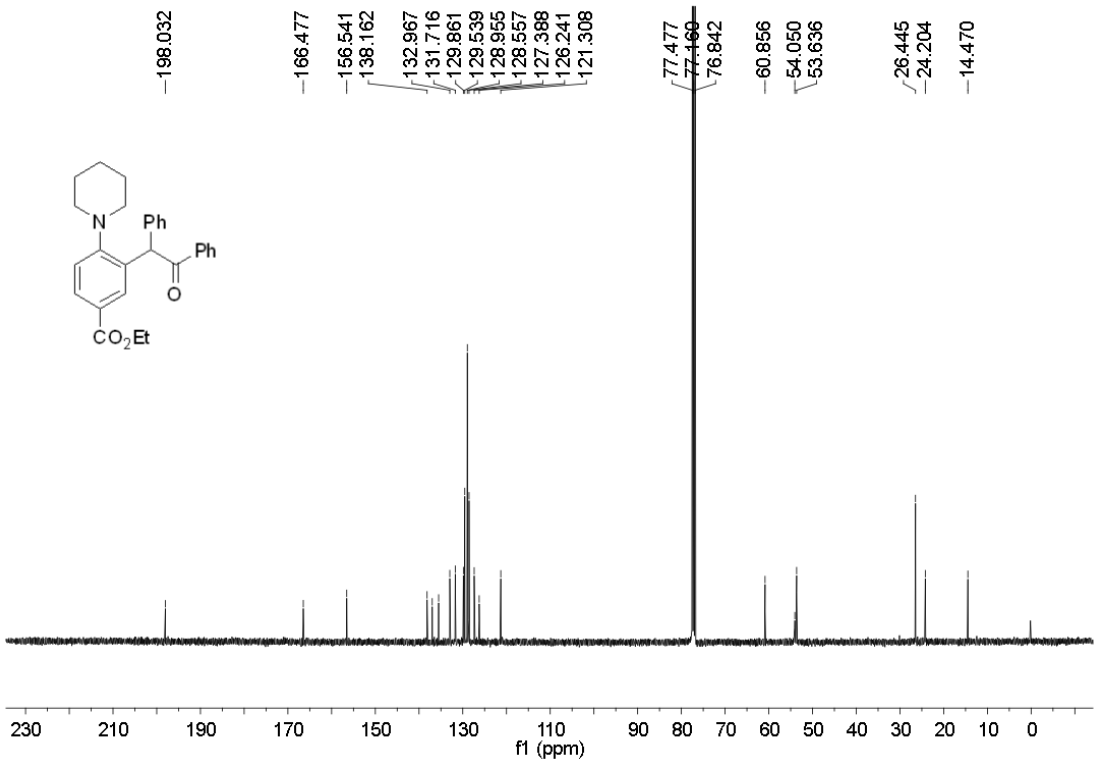

8.119
8.099
7.384
7.328
7.130
7.056
6.900
6.612
2.804
2.612
2.222
1.562
1.492
N
Ph
Ph
O
7.498
7.480
7.462
7.384
7.328
7.260
7.130
7.110
7.056
7.037
7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
2.02
6.14
1.00
0.98
1.00
4.24
3.17
6.53
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

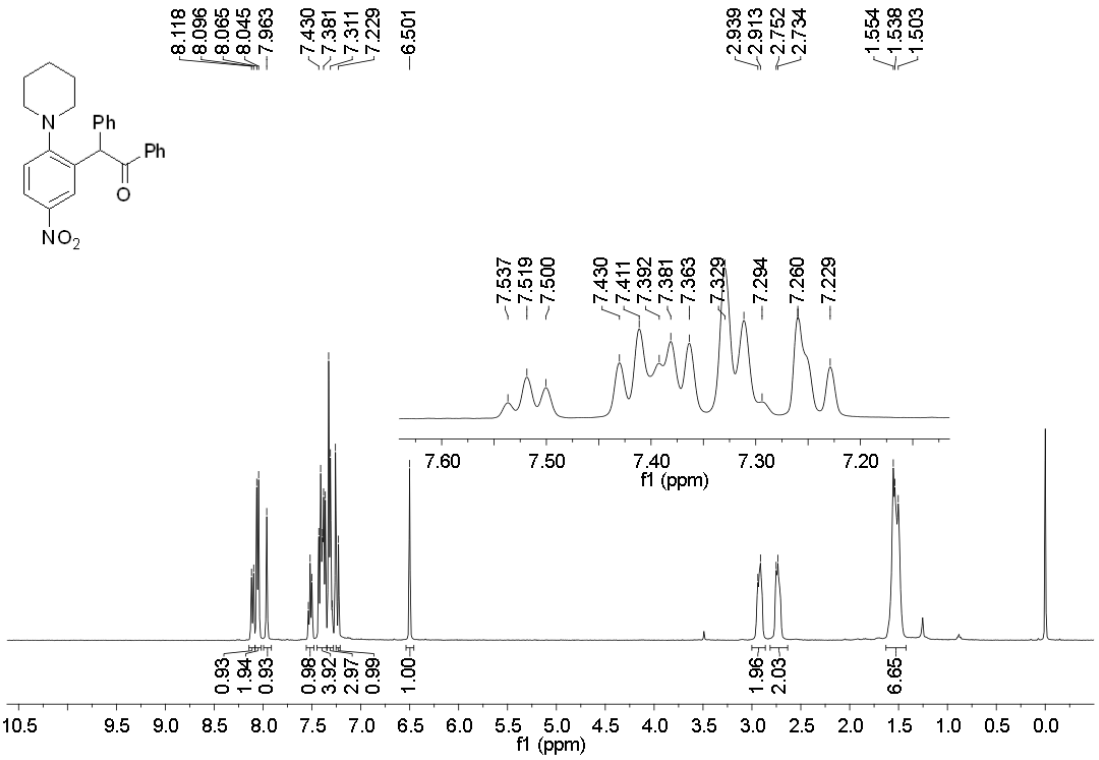

198.556
149.669
135.987
130.509
128.850
127.065
121.875
77.477
77.160
76.842
53.468
26.603
24.295
21.243
N
Ph
Ph
O
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

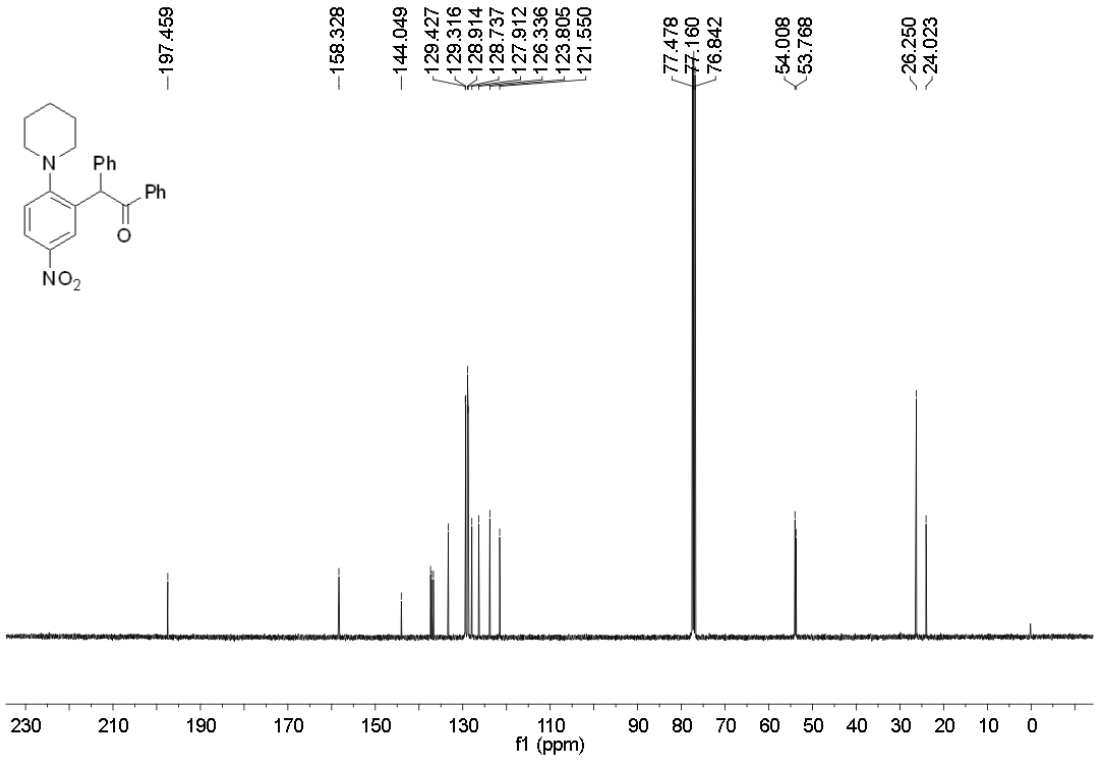

8.088
8.069
7.482
7.380
7.320
7.260
7.075
6.519
2.786
2.626
1.561
1.458
1.429
7.519
7.500
7.482
7.419
7.400
7.380
7.360
7.341
7.320
7.301
7.284
7.260
7.144
7.096
7.075
1.97
1.01
8.11
0.99
1.02
1.00
3.96
6.54
f1 (ppm)
Ph
Ph
O
N
Br

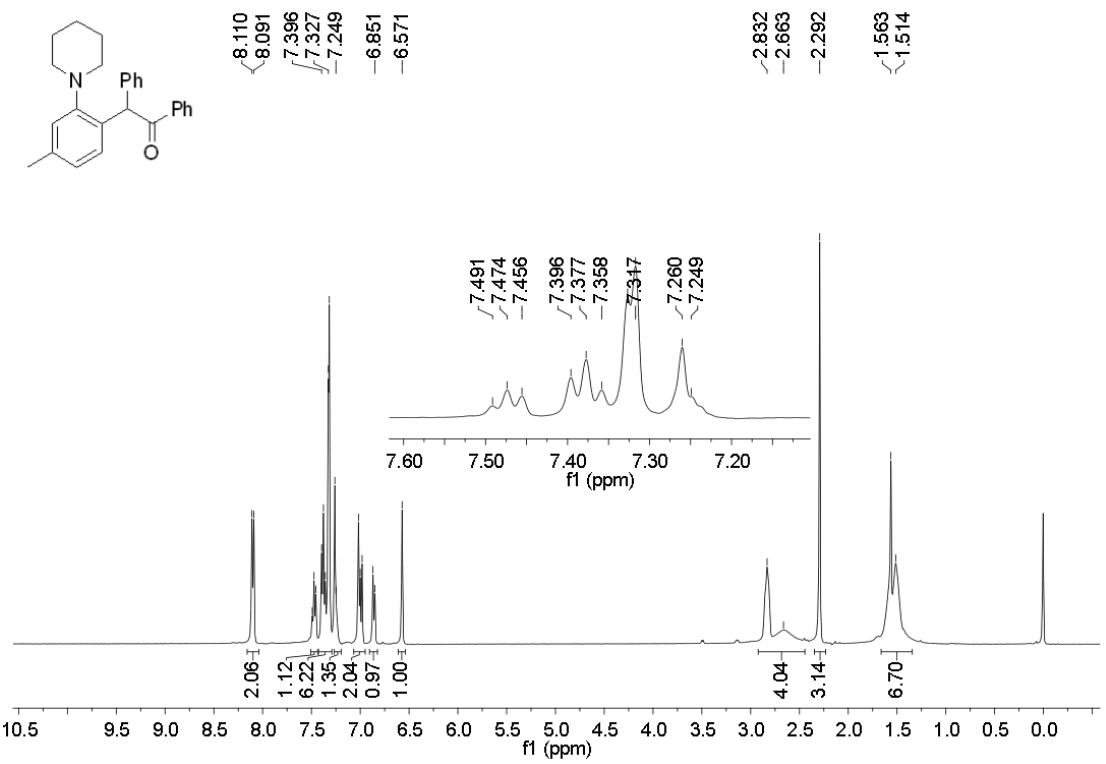

197.777
151.265
133.002
131.209
129.094
128.588
123.855
118.079
77.478
77.160
76.842
53.488
26.369
24.133
139.096
137.609
136.968
133.002
132.948
131.209
129.608
129.094
128.946
128.588
127.513
123.855
f1 (ppm)
Ph
Ph
O
N
Br

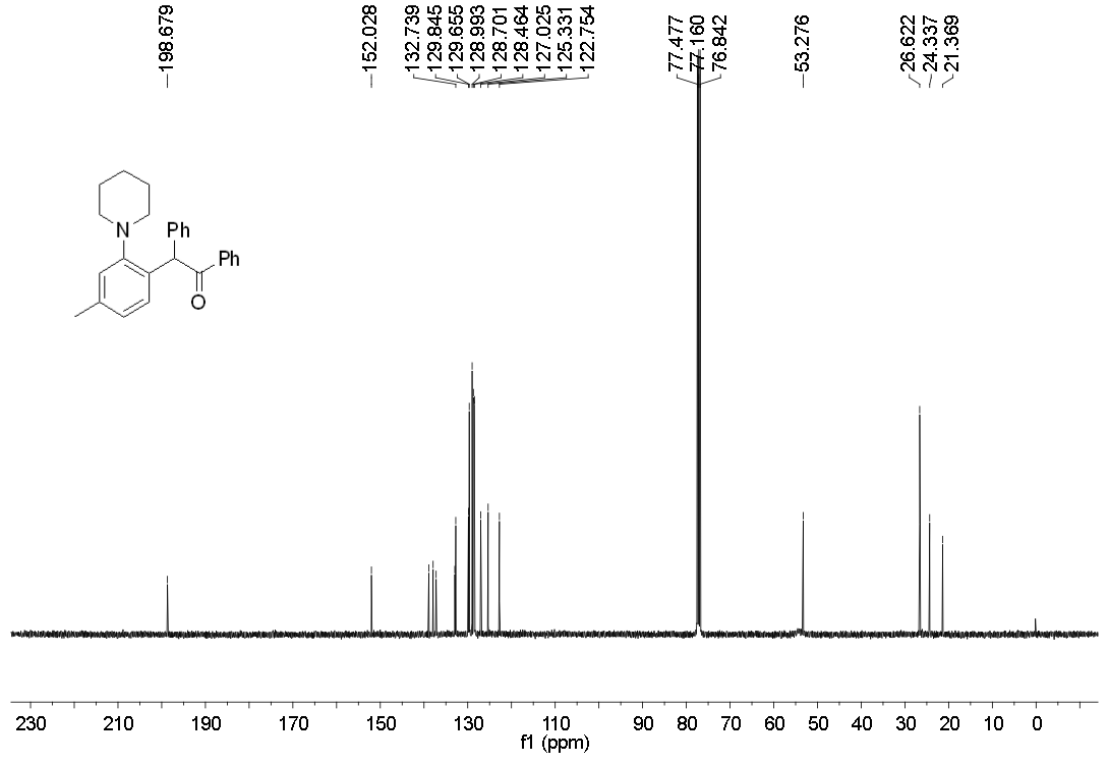

8.082
8.063
7.935
7.914
7.814
7.379
7.290
7.199
6.543
4.306
4.288
4.271
4.253
2.912
2.884
2.700
1.603
1.557
1.512
1.327
1.309
1.291
7.500
7.482
7.464
7.398
7.379
7.332
7.314
7.273
7.260
7.220
7.199
7.55
7.45
7.35
7.25
f1 (ppm)
1.96
0.98
0.95
1.56
1.09
1.00
2.00
2.02
2.00
3.34
3.39
3.10
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
Ph
Ph
O
N
CO2Et


198.032
166.477
156.541
138.162
132.967
131.716
129.861
129.539
128.955
128.557
127.388
126.241
121.308
77.477
77.160
76.842
60.856
54.050
53.636
26.445
24.204
14.470
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
Ph
Ph
O
N
CO2Et


8.118
8.096
8.065
8.045
7.963
7.430
7.381
7.311
7.229
6.501
2.939
2.913
2.752
2.734
1.554
1.538
1.503
N
Ph
Ph
O
NO2
7.537
7.519
7.500
7.430
7.411
7.392
7.381
7.363
7.329
7.294
7.260
7.229
7.60
7.50
7.40
7.30
7.20
f1 (ppm)
0.93
1.94
0.93
0.98
3.92
2.97
0.99
1.00
1.96
2.03
6.65
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


197.459
158.328
144.049
129.427
129.316
128.914
128.737
127.912
126.336
123.805
121.550
77.478
77.160
76.842
54.008
53.768
26.250
24.023
N
Ph
Ph
O
NO2
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.110
8.091
7.396
7.327
7.249
6.851
6.571
2.832
2.663
2.292
1.563
1.514
N
Ph
Ph
O
7.491
7.474
7.456
7.396
7.377
7.358
7.317
7.260
7.249
7.60
7.50
7.40
7.30
7.20
f1 (ppm)
2.06
1.12
6.22
1.35
2.04
0.97
1.00
4.04
3.14
6.70
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


198.679
152.028
132.739
129.845
129.655
128.993
128.701
128.464
127.025
125.331
122.754
77.477
77.160
76.842
53.276
26.622
24.337
21.369
N
Ph
Ph
O
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)