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An expedient one-pot synthesis of benzophenone Schiff bases from benzene

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Contents

General experimental procedure and equipment

All reagents used were purchased from ordinary suppliers and were dried over anhydrous $CaCl_2$. All samples were weighted and introduced into the reactions in the air. The reactions were monitored by GC on a Focus GC Thermo Scientific instrument. All products were characterized by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy and MS spectrometry. NMR spectra were recorded on a Bruker Avance (400 and in a special case, 500 MHz; ^{13}C NMR 100.61 MHz in $CDCl_3$, δ from Me_4Si), ^{19}F 376.49 MHz, δ from $CFCl_3$, *J*, Hz).).^{19}F NMR spectra were recorded with full ^{1}H–^{19}F decoupling. The GC–MS spectra were recorded on a Finnigan Polaris GCO Plus instrument. Melting points were measured using a melting point apparatus and were uncorrected. IR spectra were recorded on a Tensor-37 Fourier spectrometer.

Atom numbering in the structures is given for assignment and differs from systematic.

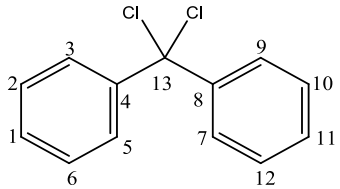
Synthesis of dichloro(diphenyl)methane (1)

a) in CH_2Cl_2

A mixture of dried C_6H_6 (0.505 g, 6.47 mmol), CCl_4 (0.490 g, 3.19 mmol), $AlCl_3$ (0.429 g, 3.22 mmol) (a molar ratio ca 2:1:1) in CH_2Cl_2 (1.0 ml) was stirred at 20 °C for 1 h. Then at 0 °C, the mixture was carefully hydrolyzed with cold water. The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (10 ml). The combined organic extracts were washed with cold H_2O until neutral and dried over Na_2SO_4. The volatile products were removed in vacuum. Yield 0.491g, 65%.

b) without CH_2Cl_2

Under the similar conditions, Ph_2CCl_2 was obtained from C_6H_6 (0.501 g, 6.41 mmol), CCl_4 (1.500 g, 9.75 mmol), $AlCl_3$ (0.425 g, 3.19 mmol) (a molar ratio = 1:1.5:0.5). The yield was 0.675 g, 89%.



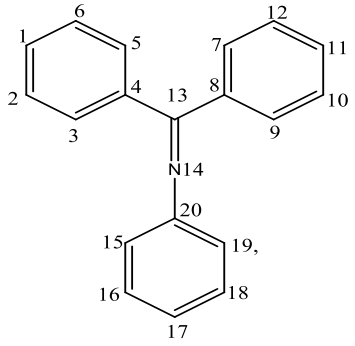
^{1}H NMR (400.13 MHz, $CDCl_3$): 7.46–7.48 (m, 4H, $^{3,5.7,9}C\mathbf{H}$); 7.76–7.78 (m. 6H, $^{1,2,,6,10,\ 11,12}C\mathbf{H}$). ^{13}C NMR (100.61 MHz, $CDCl_3$): 92.0 ($^{13}\mathbf{C}$); 127.4 ($^{3,5,7,9}\mathbf{C}H$); 128.1 ($^{2,6,10,12}\mathbf{C}H$); 129.1 ($^{1,11}\mathbf{C}H$); 144.1 ($^{4,8}\mathbf{C}$). MS (EI, ion trap, m/z, I, %):: 236, 240, M^+ (0.5), 201, M^+ – Cl (100); 203, M^+ – Cl (33); 167 (7); 166 (32); 165 (92); 164 (10); 139 (7); 115 (4); 89 (3); 87 (3); 83 (10); 82 (19); 81 (5); 77 (3); 74 (3); 69 (5); 63 (6); 62 (3); 51 (4). (Cf. Ref. [S1]).

General procedure for the synthesis of Schiff bases 2a─k

A mixture of dried C_6H_6, CCl_4, and $AlCl_3$ in a ratio [1]:[1 or 1.5]:[0.5] was stirred at room temperature for 1 h. To the mixture containing *in situ* generated Ph_2CCl_2 (**1**), an aromatic amine was added as a CH_2Cl_2 solution (at a molar ratio [C_6H_6] : [$ArNH_2$] = 1:0.5). The reactions with 1,5-$Me_2C_6H_3NH_2$ was carried out at room temperature for 1.5, the reactions with the rest anilines were performed at 55-60 °C for 1–3 h. Next, H_2O (10 ml) and $CHCl_3$ or CH_2Cl_2 (30 ml) were carefully added to the mixture. The organic layer was separated and the aqueous one was extracted with $CHCl_3$ or CH_2Cl_2 (10 ml). The combined organic extracts were washed with H_2O until neutral, and dried over Na_2SO_4. After removal the solvent in vacuum, the products were purified by recrystallization. Melting points, NMR, MS and IR spectra of products **1**, **2a─i** were identical to the literature. The structures of new compounds 2**j** and 2**k** were proved by elemental analyses, NMR, MS and IR spectra.

Synthesis of *N*-(diphenylmethylidene)aniline (2a)

A mixture of C_6H_6 (0.562 g, 7.20 mmol), CCl_4 (1.107 g, 7.20 mmol) and $AlCl_3$ (0.480 g, 3.60 mmol) was stirred at room temperature for 1 h. Then $C_6H_5NH_2$ (0.3354 g, 3.60 mmol) in CH_2Cl_2 (1 ml) was added, and the mixture was heated at 55 °C for 3 h and was left overnight at room temperature. Water H_2O (10 ml) and $CHCl_3$ (30 ml) were carefully added. The organic layer was separated and the remaining aqueous one was extracted with $CHCl_3$ (10 ml). The combined organic extracts were washed with H_2O until neutral, and dried over Na_2SO_4. The solvents were removed under vacuum. The product was recrystallized from light petroleum. Yield 0.680 g, 73.3%, mp 103–105 °C (lit. [S2] mp 104–106 °C).

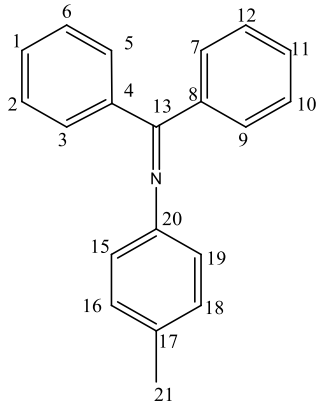


^{1}H NMR (400.13 MHz, $CDCl_3$): 7.81 (d, 2H, ^{7,9}CH, $^3J_{HH}$ = 7.3), 7.53 (t, 1H, ^{1}C**H**, $^3J_{HH}$ = 7.3), 7.45 (t, 2H, ^{10,12}C**H**, $^3J_{HH}$ = 7.6), 7.35–7.25 (m, 3H, ^{3,5,11}C**H**), 7.22–7.12 (m, 4H, ^{2,6,16,18}C**H**), 6.97 (t, 1H, ^{17}C**H**, $^3J_{HH}$ = 7.2), 6.78 (d, 2H, ^{15,19}C**H**, $^3J_{HH}$ = 7.2). ^{13}C NMR (100.61 MHz, $CDCl_3$): 168.2 (^{13}**C**); 151.1 (^{20}**C**); 139.6 (^{4,8}**C**), 136.1 (^{2}**C**); 130.6 (^{1,11}**C**H); 129.4 (^{3,9}**C**H); 129.2 (^{15,19}**C**H);

128.5 (^{7}**C**H); 128.4 (^{2,10}**C**H); 128.1 (^{5}**C**H); 127.8 (^{6,12}**C**H); 123.1 (^{17}**C**H), 120.8 (^{16,18}**C**H). MS (EI, ion trap, m/z, I, %): 257, M^+ (67), 180, M^+–C_6H_5 (100); 179 (3); 178 (7); 166, M^+–NC_6H_5 (19); M^+–NC_6H_4, 165 (96); 164 (3); 163 (3); 153 (5); 152 (9); 151 (6); 127 (7); 78 (4); 77 (49). IR (KBr pellet, ν, cm^{-1}): 3054 (aromatic C–H stretchings), 1611, 1593 (C=N), 1293, 1072, 697 (aromatic C–H deformations) (Cf. Ref. [S3]).

Synthesis of *N*-(diphenylmethylidene)-4-methylaniline (2b)

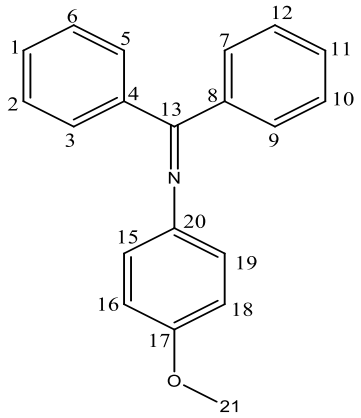
A mixture of C_6H_6 (0.516 g, 6.60 mmol), CCl_4 (1.523 g, 9.90 mmol) and $AlCl_3$ (O.440 g, 3.30 mmol) was stirred at room temperature for 1 h. Then 4-methylaniline (0.354 g, 3.30 mmol) in CH_2Cl_2 (2 ml) was added, and the mixture was heated at 55–60 °C for 3 h. Water (10 ml) was then carefully added. The organic layer was separated and the aqueous one was extracted with $CHCl_3$ (10 ml). The combined organic extracts were washed with H_2O until neutral, and dried over Na_2SO_4. The solvents were removed under vacuum. The product was recrystallized from hexane. Yield 0.651 g, 72.7 %, mp 47 °C (lit. [S4] mp 48–50 °C).



^{1}H NMR (400.13 MHz, $CDCl_3$): 7.78 (d, 2H, ^{7,9}C**H**, $^{3}J_{HH}$ = 7.3), 7.50 (t, 1H, ^{1}CH, $^{3}J_{HH}$ = 7.6), 7.43 (t, 2H, ^{12,10}C**H**, $^{3}J_{HH}$ = 7.6), 7.35–7.25 (m, 3H, ^{3,5,11}C**H**), 7.22–7.12 (m, 2H, ^{2,6}C**H**), 6.98 (d, 2H, ^{15,19}C**H**, $^{3}J_{HH}$ = 8.0), 6.68 (d, 2H, ^{16,18}C**H**, $^{3}J_{HH}$ = 8.2), 2.27 (s, 3H, ^{21}CH). ^{13}C NMR (100.61 MHz, $CDCl_3$): 168.1 (^{13}**C**); 151.2 (^{20}**C**); 139.5 (^{8}**C**), 136.1 (^{4}**C**); 132.3 (^{17}**C**H), 130.6 (^{1,11}**C**H); 129.4 (^{3,9}**C**H); 129.2 (^{15,19}**C**H); 129.0 (^{7}**C**H); 128.5 (^{2,10}**C**H); 128.1 (^{5}**C**H); 127.0 (^{6,12}**C**H); 121.0 (^{16,18}**C**H), 20.7 (^{21}**C**H_3). MS (EI, ion trap, m/z, I, %): 271, M^+ (94); 270, M^+–1, (48); 256 (7); 254 (3); 195, M^+–C_6H_4 (13); 194, M^+–C_6H_5 (100); 193 (4); 179, M^+–C_6H_5Me (4); 178 (5); 167 (5); 166, M^+–NC_6H_4Me (5); 165, M^+–NC_6H_5Me (84); 164 (4); 152 (5); 134 (6); 127 (4); 91, $C_6H_5CH_2^+$ (26); 89 (4); 77 (6); 65 (16). IR (KBr pellet, ν, cm^{-1}): 3057 (aromatic C–H deformations, 2923, 2854 (aliphatic C–H stretchings). 1638, 1610 (C=N), 1444, 1317 (aliphatic C–H deformations), 1010, 939. 703 (aromatic C–H deformations) (Cf. Ref. [S3]).

Synthesis of *N*-(diphenylmethylidene)-4-methoxyaniline (2c)

A mixture of C_6H_6 (0.586 g, 7.50 mmol), CCl_4 (1.730 g, 11.250 mmol) and $AlCl_3$ (0.50 g, 3.75 mmol) was stirred at room temperature for 1.5 h. Then 4-methoxyaniline (1.461 g, 3.75 mmol) in CH_2Cl_2 (2 ml) was added, and the mixture was heated at 55-60 °C for 2.5 h. Water (10 ml) and $CHCl_3$ (30 ml) were carefully added. The organic layer was separated and the aqueous one was extracted with $CHCl_3$ (10 ml). The combined organic extracts were washed with H_2O until neutral, and dried over Na_2SO_4. The solvents were removed under vacuum. The product was recrystallized from heptane. Yield 0.802 g, 88%, mp 71–72 °C (lit. [S2,S4] mp 70–72 °C).

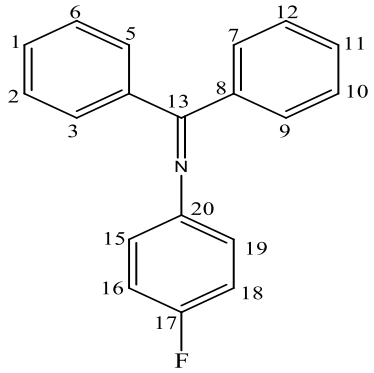


^{1}H NMR (400.13 MHz, $CDCl_3$): 7.81 (d, 2H, ^{7,9}C**H**, $^3J_{HH}$ = 7.2), 7.50 (t, 1H, ^{1}C**H**, $^3J_{HH}$ = 7.6), 7.44 (t, 2H, ^{10,12}C**H)** $^3J_{HH}$ = 7.6), 7.38–7.28 (m, 3H, ^{3,5,11}C**H**), 7.22–7.15 (m, 2H, ^{2,6}C**H**), 6.80–6.72 (m, 4H, ^{15,16,18,19}C**H**), 3.75 (s, 3H, ^{21}C**H**$_3$). ^{13}C NMR (100.61 MHz, $CDCl_3$): 167.7 (^{13}**C**); 155.8 (^{20}**C**); 144.2 (^{17}**C**), 139.9 (^{8}**C**), 136.5 (^{4}**C**); 130.5 (^{1,11}**C**H); 129.5 (^{3,9}**C**H); 129.1 (^{15,19}**C**H); 128.4 (^{7}**C**H); 128.1 (^{2,10}**C**H); 128.0 (^{5}**C**H); 122.6 (^{6,12}**C**H); 113.7 (^{16,18}**C**H), 55.2 (^{21}**C**H$_3$). MS (EI, ion trap, m/z, I, %): 287, M^+ (100), 286 (26), 273 (10); 272, M^+–Me (46); 243 (3); 242 (4); 241 (4); 211 (7); 210, M^+–C_6H_5 (62); 195 (11) 179 (4); 170 (5); 169 (43); 168 (4); 167 (20); 166 (13); 165, M^+–NC_6H_5OMe (66); 164 (3); 142 (10); 141 (79); 140 (4); 139 (6); 136 (3); 123 (3); 122 (35); 121 (3); 116 (3); 115 (28); 108 (3); 107, $^+C_6H_4OMe$ (3); 103 (3); 95 (3); 77 (20). IR (KBr pellet, ν, cm^{-1}): 3057 (aromatic C–H stretchings), 2998, 2834 (aliphatic C–H stretchings), 1660; 1608, 1570 (C=N), 1466, 1443, 1317 (aliphatic C–H deformations), 1031 (C–O stretchings), 697 (aromatic C–H deformations) (Cf. Refs. [S3,S4]).

Synthesis of *N*-(diphenylmethylidene)-4-fluoroaniline (2d)

A mixture of C_6H_6 (0.515 g, 6.60 mmol), CCl_4 (1.522 g, 9.90 mmol) and $AlCl_3$ (0.440 g, 3.30 mmol) was stirred at room temperature for 1 h. Then 4-fluoroaniline (0.366 g, 3.30 mmol) in CH_2Cl_2 (1 ml) was added and the mixture was stirred at 18-20 °C for 2 h. Water (10 ml) and $CHCl_3$ (30 ml) were carefully added. The organic layer was separated and the aqueous one was extracted with CH_2Cl_2 (10 ml). The combined organic extracts were washed with H_2O until

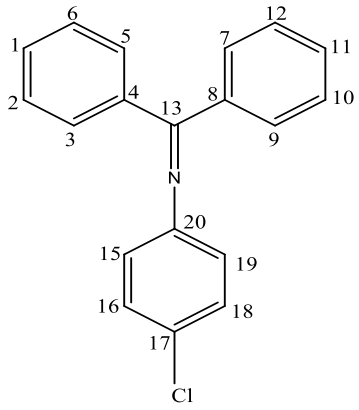
neutral, and dried over Na_2SO_4. The solvents were removed under vacuum. The product was recrystallized from heptane. Yield 0.560g, 62%, mp 106–108 °C (lit. [S2] mp 102–104 °C).



^{1}H NMR (400.13 MHz, $CDCl_3$): 7.78 (d, 2H, ^{7,9}C**H**, $^3J_{HH}$ = 7.2), 7.52 (t, 1H, ^{1}C**H**, $^3J_{HH}$ = 7.6), 7.44 (t, ^{2}C**H**, ^{10,12}C**H**, $^3J_{HH}$ = 7.6), 7.38–7.28 (m, 3H, ^{3,5,11}C**H**), 7.18–7.10 (m, 2H, ^{2,6}C**H**), 6.87 (dd, 2H, ^{16,18}C**H**, $^3J_{HH}$ = $^4J_{F-H}$= 8.2), 6.73 (dd, 2H, ^{15,19}C**H**, $^3J_{HH}$ = $^3J_{FH}$=8.4). ^{13}C NMR (100.61 MHz, $CDCl_3$): 169.5 (^{13}**C**); 158.5 (d, ^{17}**C**, $^1J_{CF}$= 242.12); 146.2 (^{20}**C**), 139.2 (^{8}**C**), 135.7 (^{4}**C**); 130.8 (^{11}**C**H); 129.3 (^{3,9}**C**H); 129.2 (^{6,12}**C**H); 128.6 (^{7}**C**H); 128.1 (**^{2,10}C**H); 127.9 (^{2}**C**H); 122.2 (d, $^3J_{CF}$=8.0, ^{15,19}**C**H); 115.0 (d, $^2J_{CF}$=22,3, ^{16,18} **C**H). ^{19} F NMR (376.49 MHz, $CDCl_3$): -120.27. MS (EI, ion trap, m/z, I, %): 275, M^+ (89), 274, M^+–H (69), 199 (15); 198 (78); 196 (4); 178 (6), 170 (4); 166 (41); 165, M^+–NC_6H_5F (100), 151 (11); 127 (4); 95 (19), 77 (25); 75 (25); 74 (16). IR (KBr pellet, ν, cm^{-1}): 3065, 3037 (aromatic C–H stretchings), 1598, 1569 (C=N), 1210 (C–F), 1073, 838, 693, 674 (aromatic C–H deformations) (Cf. Ref. [S2]).

Synthesis of 4-chloro-*N*-(diphenylmethylidene)aniline (2e)

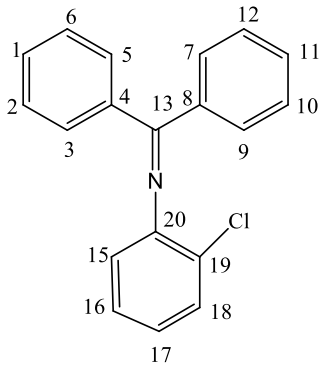
A mixture of C_6H_6 (0.538 g, 6.90 mmol), CCl_4 (1.591g, 10.35 mmol) and $AlCl_3$ (0.460 g, 3.45 mmol) was stirred at room temperature for 1 h. Then 4-chloroaniline (0.440 g, 3.45 mmol) in CH_2Cl_2 (2 ml) was added, and the mixture was stirred at 18-20 °C for 2 h. Water (10 ml) and $CHCl_3$ (30 ml) were carefully added. The organic layer was separated and the aqueous one was extracted with $CHCl_3$ (10 ml). The combined organic extracts were washed with H_2O until neutral, and dried over Na_2SO_4. The solvents were removed under vacuum. The product was recrystallized from heptane. Yield 0.811 g, 77%, mp 88–89 °C. (lit. [S4] mp 88–89 °C).



^{1}H NMR (400.13 MHz, $CDCl_3$): 7.77 (d, 2H, ^{7,9}C**H**, $^{3}J_{HH}$ = 7.6), 7.51 (t, 1H, ^{1}C**H**, $^{3}J_{HH}$ = 7.2), 7.44 (t, 2CH, ^{10,12}C**H**, $^{3}J_{HH}$ = 7.6), 7.38–7.28 (m, 3H, ^{3,5,11}C**H)**, 7.18–7.10 (m, 4H, ^{2,6,15,19}C**H**), 6.72 (d, 2H, ^{16,18}C**H**, $^{3}J_{HH}$ = 8.2). ^{13}C NMR (100.61 MHz, $CDCl_3$): 166.1 (^{13}**C**); 151.5 (^{20}**C**); 138.9 (^{8}**C**), 135.6 (^{4}**C**); 132.5 (^{17}**C**), 130.1 (^{1,11}**C**H); 129.7 (^{3,9}**C**H); 129.6 (^{15,19}**C**H); 129.2 (^{7}**C**H); 128.7 (^{2,10}**C**H); 128.3 (^{5}**C**H); 128.2 (^{6,12}**C**H); 122.6 (^{16,18}**C**H). MS (EI, ion trap, m/z, I, %): 291, 293, M^+ (52, 18), 255, M^+–HCl (3), 254 (5); 215, 217, M^+–C_6H_4 (11, 3); 214, 216, M^+–C_6H_5 (65, 22); 179 (4); 178 (6); 177 (5) 166 (15); 165, M^+–NC_6H_5Cl (100); 164 (3); 152 (5); 151 (11); 127 (6); 113 (5); 111 (12); 77 (18); 75 (16). IR (ν, cm^{-1}): 3046 (aromatic C–H stretchings), 1610, 1596, 1570 (C=N), 1294, 1109, 958, 863, 707 (aromatic C–H deformations), 693 (C–Cl stretchings) (Cf. Ref. [S4]).

Synthesis of 2-chloro-*N*-(diphenylmethylidene)aniline (2f)

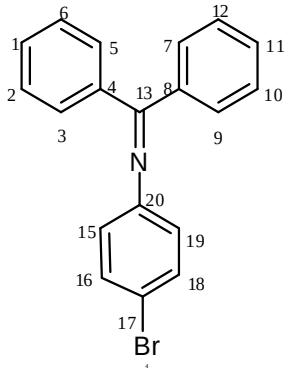
A mixture of C_6H_6 (0.538 g, 6.90 mmol), CCl_4 (1.591 g, 10.35 mmol) and $AlCl_3$ (0.460 g, 3.45 mmol) was stirred at room temperature for 1 h. Then 2-chloroaniline (0.440 g, 3.450 mmol) in CH_2Cl_2 (2 ml) was added, and the mixture was stirred at 18-20 °CC for 2 h. Water (10 ml) and $CHCl_3$ (30 ml) were carefully added. The organic layer was separated and the aqueous one was extracted with $CHCl_3$ (10 ml). The combined organic extracts were washed with H_2O until neutral and dried over Na_2SO_4. The solvents were removed under vacuum. Yield 0.691 g, 69%, mp 100–102 °C (from pentane, lit. [S2] mp 93–95 °C).



^{1}H NMR(400.13 MHz, $CDCl_3$): 7.87 (d, 2H, ^{7,9}C**H**, $^{3}J_{HH}$ = 8.0), 7.55 (t, 1H, ^{1}C**H**, $^{3}J_{HH}$ = 7.2), 7.47 (t, 2H, ^{10,12}C**H**, $^{3}J_{HH}$ =7.6), 7.38–7.28 (m, 5H, ^{2,3,5,6,11}C**H**), 7.22 (d, 1H, ^{18}C**H**, $^{3}J_{HH}$ = 7.4), 7.05 (t, 1H, ^{17}C**H**, $^{3}J_{HH}$ = 7.8), 6.90 (t, 1H, ^{16}C**H**, $^{3}J_{HH}$ = 7.8), 6.65 (d, 1H, ^{15}C**H**, $^{3}J_{HH}$ = 7.8). ^{13}C NMR (100.61 MHz, $CDCl_3$): 170.0 (^{13}**C**); 148.7 (^{20}**C**); 138.7 (^{8}**C**), 136.0 (^{4}**C**); 131.1 (^{1,11}**C**H); 129.5 (^{2,10}**C**H); 129.3 (^{3,9}**C**H); 128.9 (^{16,18}**C**H); 128.6 (^{7}**C**H); 128.2 (^{5}**C**H); 127.8 (^{6}**C**H), 126.8 (^{12}**C**H), 124.8 (^{19}**C**H), 124.05 (^{17}**C**H), 121.3 (^{15}**C**H). MS (EI, ion trap, m/z, I, %): 291, M^+ (57); 292 (23); 256 , M^+–Cl (15); 255 (5); 254 (16); 253 (5); 217 (4); 216 (34); 215 (16); 214, M^+–C_6H_5 (100); 182 (4); 181 (5); 179 (4); 178 (8); 177 (5); 166 (33); 165, M^+–NC_6H_5Cl (95); 164 (4); 152 (9); 151 (10); 128 (6); 127 (9); 113 (7); 112 (6); 111 (13); 105 (6); 77 (28); 75 (25). IR (KBr pellet, ν, cm^{-1}): 3056 (aromatic C-H stretchings), 1615, 1577 (C=N), 767 (aromatic C–H deformations), 699 (C–Cl stretchings) (Cf. Ref. [S2]).

Synthesis of 4-bromo-*N*-(diphenylmethylidene)aniline (2g)

A mixture of C_6H_6 (0.538 g, 6.91 mmol), CCl_4 (1.591 g, 10.35 mmol) and $AlCl_3$ (0.460 g, 3.45 mmol) was stirred at room temperature for 1 h. Then 4-bromoaniline (0.593 g, 3.45 mmol) in CH_2Cl_2 (2 ml) was added, and the mixture was heated at 55-60 °C for 1 h. Water (10 ml) and $CHCl_3$ (30 ml) were carefully added. The organic layer was separated and the aqueous one was extracted with CH_2Cl_3 (10 ml). The combined organic extracts were washed with H_2O until neutral, and dried over Na_2SO_4. The solvents were removed under vacuum. The product was recrystallized from hexane. Yield 0.72 g, 62%, mp 80–82 °C (lit. [S2] mp 82–83 °C).

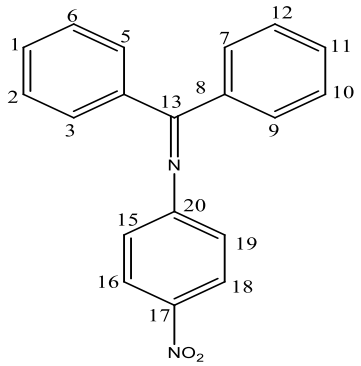


^{1}H NMR (400.13 MHz, $CDCl_3$): 7.78 (d, 2H, ^{7,9}C**H**, $^{3}J_{HH}$ = 8.0), 7.52 (t, 1H, ^{1}C**H**, $^{3}J_{HH}$ = 7.2), 7.45 (t, ^{2}C**H**^{2}, ^{10,12}CH, $^{3}J_{HH}$=7.6), 7.38–7.25 (m, 5H, ^{2,3,5,6,11}C**H**), 7.14 (d, 2H, ^{15,19}C**H**, $^{3}J_{HH}$=7.4), 6.65 (d, 2H,^{16,18}C**H**, $^{3}J_{HH}$ = 8.4). ^{13}C NMR (100.61 MHz, $CDCl_3$): 168.9 (^{13}**C**); 150.0 (^{20}**C**); 139.2 (^{8}**C**), 135.7 (^{4}**C**); 131.5 (^{2,10}CH); 131.0 (^{1,11}**C**H); 129.4 (^{16,18}**C**H); 129.3 (^{7}**C**H); 128.8 (^{5}**C**H); 128.2 (^{6}**C**H); 128.0 (^{12}**C**H); 122.7 (^{16,18}**C**H), 116.2 (^{17}**C**H). MS (EI, ion trap, m/z, I, %): 337, 335, M^+ (66, 65), 336, 334, M^+–H (47, 37), 261, 259, M^+–C_6H_4 (10); 260, 258, M^+–C_6H_5 (46); 256 (6); 255 (8); 254 (13); 180 (5); 179 (11); 167 (8); 166 (52); 165, M^+–NC_6H_5Br (100); 164 (4); 158 (4); 155 (9); 153 (5); 152 (8); 157 (9); 151 (6); 129 (10); 128 (9); 127 (5); 77 (18);

76 (12); 75 (13); 74 (6). IR (KBr pellet, ν, cm^{-1}): 3053 (aromatic C–H stretchings), 1611, 1594, 1575 (C=N), 781 (aromatic C–H deformations), 688 (C–Br stretchings) (Cf. Ref. [S5]).

Synthesis of *N*-(diphenylmethylidene)-4-nitroaniline (2h)

A mixture of C_6H_6 (0.492 g, 6.30 mmol), CCl_4 (1.450 g, 9.45 mmol) and $AlCl_3$ (0.42 g, 3.15 mmol) was stirred at room temperature for 1 h. Then 4-$O_2NC_6H_4NH_2$ (0.440 g, 3.15 mmol) in CH_2Cl_2 (2 ml) was added and the mixture was heated at 55-60 °C for 3 h. Water (10 ml) and $CHCl_3$ (30 ml) were carefully added. The organic layer was separated and the aqueous one was extracted with $CHCl_3$ (10 ml). The combined organic extracts were washed with H_2O until neutral, and dried over Na_2SO_4. The solvents were removed under vacuum. The product was recrystallized from ethanol. Yield 0.79 g, 83%, mp 156–157 °C (lit. [S2] mp 152–153 °C).

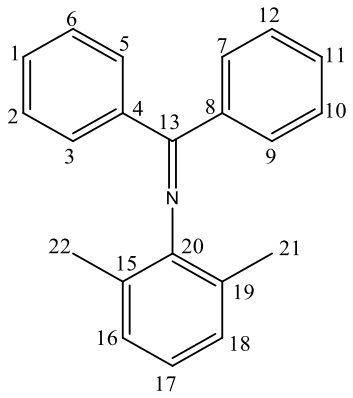


^{1}H NMR (400.13 MHz, $CDCl_3$): 8.06 (d, 2H, ^{7,9}C**H**, $^3J_{HH}$ = 8.0), 7.85–7.70 (m, 2H, ^{10,12}C**H**), 7.65–7.25 (m, 6H, $^{1\text{-}3,5,6,11}$C**H**), 7.14 (br. s, 2H, ^{15,19}C**H**), 6.83 (d, 2H, ^{16,18}C**H**, $^3J_{HH}$ = 8.4). ^{13}C NMR (100.61 MHz, $CDCl_3$): 169.7 (^{13}**C**); 157.5 (^{20}**C**); 143.4 (^{17}**C**), 139.6 (^{8}**C**), 135.1 (^{4}**C**); 131.7 (^{2,10}**C**H); 130.1 (^{1,11}**C**H); 129.3 (^{16,18}**C**H); 128.4 (^{7}**C**H, ^{5}**C**H, ^{6}**C**H), 124.7 (^{12}**C**H); 121.0 (^{16,18}**C**H). MS (EI, ion trap, m/z, I, %): 302, M^+ (33), 256, $M^+–NO_2$ (4); 255 (13); 254 (7); 226 (6); 225, $M^+–C_6H_5$ (31); 179 (3); 180 (6); 179, $M^+–C_6H_5NO_2$ (34); 178 (6); 167 (7); 166 (17); 165, $M^+–NHC_6H_4NO_2$ (100); 164 (3); 153 (3); 152 (7); 151 (4); 126 (3); 115 (4); 77 (4); 76 (15). IR (KBr pellet, ν, cm^{-1}): 3056, 3018 (aromatic C–H stretchings), 1610, 1586 (C=N), 1510, 1340 (NO_2), 1109, 958, 850, 787, 707, 693 (aromatic C–H deformations) (**S6**, page **S38**).

Synthesis of *N*-(diphenylmethylidene)-2,6-dimethylaniline (2i)

A mixture of C_6H_6 (0.867 g, 11.10 mmol), CCl_4 (2.5614 g, 16.65 mmol) and $AlCl_3$ (0.740 g, 5.55 mmol) was stirred at room temperature for 1h. Then 1,6-dimethylaniline (0.672 g, 5.55 mmol) in CH_2Cl_2 (2 ml) was added, and the mixture was kept at 20-25 °C for 1.5 h. Water (10 ml) and $CHCl_3$ (30 ml) were carefully added. The organic layer was separated and the aqueous one was extracted with $CHCl_3$ (10 ml). The combined organic extracts were washed with H_2O until

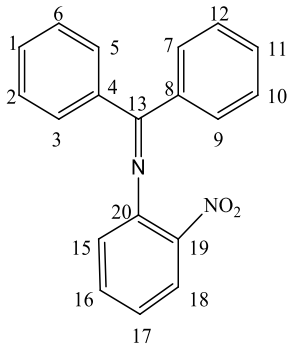
neutral, and dried over Na_2SO_4. The solvents were removed under vacuum. The product was recrystallized from cyclohexane. Yield 1.100 g, 75 %, mp 90–92 °C (lit. [S2] mp 90–92 °C).



^{1}H NMR (400.13 MHz, $CDCl_3$): 7.87 (d, 2H, ^{7,9}C**H**, $^3J_{HH}$ = 7.6), 7.56 (t, 1H, ^{1}C**H**, $^3J_{HH}$ = 7.2), 7.48 (t, 2H, ^{10,12}C**H**, $^3J_{HH}$ = 7.6), 7.35–7.22 (m, 3H, ^{3,5,11}C**H**), 7.22–7.12 (m, 2H, ^{2,6}C**H**), 6.95 (d, 2H, ^{16,18}C**H**, $^3J_{HH}$ = 7.6), 6.86 (t, 1H, ^{17}C**H**, $^3J_{HH}$ = 8.0), 2.12 (s, 6H, ^{21,22}C**H**$_3$). ^{13}C NMR (100.61 MHz, $CDCl_3$): 167.2 (^{13}**C**); 148.9 (^{20}**C**); 139.8 (^{8}**C**), 136.8 (^{4}**C**); (^{17}**C**H, 130.6 (^{1,11}**C**H); 129.4 (^{3,9}**C**H); 129.1 (^{7}**C**H); 128.5 (^{2,10}**C**H); 128.2 (^{5}**C**H); 127.8 (^{6}**C**H); 127.7 (^{12}**C**H), 125.8 (^{15,19}**C**H), 122.8 (^{16,18}**C**H), 18.6 (^{21,22}**C**H$_3$). MS (EI, ion trap, m/z, I, %): 285, M^+ (38), 284 (9); 209, M^+–C_6H_4 (17); 208, M^+–C_6H_5 (100); 207 (6); 206 (4); 194 (7); 193 (35); 192 (3); 166 (6); 165, M^+–$NHC_6H_3Me_2$ (25); 130 (3); 105 (3); 103 (6); 91 (3); 79 (6); 77 (12). IR (KBr pellet, ν, cm^{-1}): 3065, 3018 (aromatic C–H stretchings), 2917, 2858 (aliphatic C–H stretchings); 1660, 1608, 1570 (C=N), 1466, 1443, 1317 (aliphatic C–H deformations)), 1619, 1591, 1577, (C=N), 1489, 1443, 1373 (aliphatic C–H deformations), 1074, 787, 701, 678 (aromatic C–H deformations) (Cf. Ref. [S7]).

Synthesis of *N*-(diphenylmethylidene)-2-nitroaniline (2j)

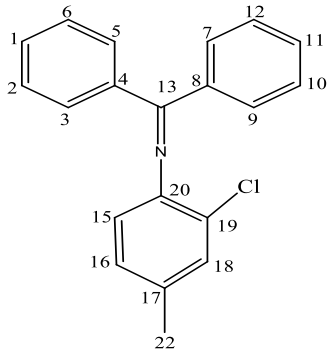
A mixture of C_6H_6 (0.503 g, 6.45 mmol), CCl_4 (1.498 g, 9.68 mmol) and $AlCl_3$ (0.430 g, 3.22 mmol) was stirred at room temperature for 1 h. Then 2-nitroaniline (0.450 g, 3.22 mmol) in CH_2Cl_2 (1 ml) was added, and the mixture heated at 55-60 °C for 2.5 h. Water (10 ml) and $CHCl_3$ (30 ml) were carefully added. The organic layer was separated and the aqueous one was extracted with $CHCl_3$ (10 ml). The combined organic extracts were washed with H_2O until neutral, and dried over Na_2SO_4. The solvents were removed under vacuum. The product was recrystallized from methanol. Yield 0.401g, 40%, mp 106–108 °C. Calculated for $C_{19}H_{14}N_2O_2$, %: C 75.51; H 4.66; N 9.27. Found, %: C 75 52; H 4.78; N 9.31.



^{1}H NMR (400.13 MHz, DMSO-d_6): 7.95 (d, 2H, ^{7,9}C**H**, $^{3}J_{HH}$ = 8.4), 7.85–7.20 (m, 8H, $^{1\text{-}3,5,6,10\text{-}12}$C**H**), 7.12 (t, 2H, ^{16,17}C**H**, $^{3}J_{HH}$ = 8.0), 6.8 (d, 2H, ^{15,18}C**H**, $^{3}J_{HH}$ = 8.0). ^{13}C NMR (100.61 MHz, DMSO-d_6): 169.0 (^{13}**C**); 161.1 (^{20}**C**); 146.5 (^{19}**C**), 140.6 (^{8}**C**), 134.8 (^{4}**C**); 132–128 (br. s, $^{1,2,5,7.10,11}$**C**H); 125.1 (^{12}**C**H); 124.2 (^{16}**C**H), 123.0 (^{18}**C**H). MS (EI, ion trap, m/z, I, %): 303, M^++H (20); 302, M^+ (92), 301 (17); 285 (28); 284 (30); 283 (75); 271 (5); 270 (27); 269 (61); 238 (30); 267 (7); 258 (4); 257 (15); 256, M^+–NO_2 (53); 255 (79); 254 (100); 253 (23); 252 (9); 251 (4); 243 (4); 242 (5); 241 (5); 226 (5); 182 (13); 181 (24); 180 (12); 179 (6); 178 (11); 177 (5); 167 (6); 166 (18); 165 (43); 164 (10); 163 (8); 154 (6); 153 (21); 152 (35); 151 (19); 150 (7); 128 (5); 127 (11); 126 (7); 115 (6); 113 (5); 107 (6); 105 (67); 77 (61). IR (KBr pellet, ν, cm^{-1}): 3059 (aromatic C-H stretchings), 1635, 1599, 1569 (C=N), 1511, 1340 (NO_2), 1077, 956, 862, 778, 693 (aromatic C–H deformations**)**.

Synthesis of 2-chloro-*N*-(diphenylmethylidene)-4-methylaniline (2k)

A mixture of C_6H_6 (0.538 g, 6.90 mmol), CCl_4 (1.591 g, 10.35 mmol) and $AlCl_3$ (0.460 g, 3.45 mmol) was stirred at room temperature for 1 h. Then 2-chloro-4-methylaniline (0.482 g, 3.450 mmol) in CH_2Cl_2 (2 ml) was added, and the mixture was stirred at 18–20 °C for 2 h. Water (10 ml) and $CHCl_3$ (30 ml) were carefully added. The organic layer was separated, and the aqueous one was extracted with $CHCl_3$ (10 ml). The combined organic extracts were washed with H_2O until neutral, and dried over Na_2SO_4. The solvents were removed under vacuum. The product was recrystallized from methanol. Yield 0.801 g, 75.8 %, mp 72–74 °C (from pentane). Calculated for $C_{20}H_{16}NCl$, %: C 78.55; H 5.27; Cl 11.59. Found, %: C 77.67; H 5.10; Cl 11.75.



^{1}H NMR (400.13 MHz, $CDCl_3$): 7.82 (d, 2H, ^{7,9}C**H**, $^{3}J_{HH}$ = 8.0), 7.53 (t, 1H, ^{1}C**H**, $^{3}J_{HH}$ = 7.2), 7.45 (t, 2H, ^{10,12}C**H**, $^{3}J_{HH}$ = 7.6), 7.38–7.28 (m, 5H, ^{2,3,5,6,11}C**H**), 7.11 (s, 1H, ^{18}C**H**), 6.82 (d, 1H, ^{15}C**H**, $^{3}J_{HH}$ = 7.8), 6.54 (d, 1H, ^{16}C**H**, $^{3}J_{HH}$ = 7.8), 2.23 (s, 3H, ^{22}C**H**$_3$). ^{13}C NMR (100.61 MHz, $CDCl_3$): 169.9 (^{13}**C**); 146.1 (^{20}**C**); 138.9 (^{8}**C**), 136.2 (^{4}**C**); 133.7 (^{19}**C**), 130.9 (^{1,11}**C**H); 129.6 (^{2,10}**C**H); 129.5 (^{3,9}**C**H); 128.6 (^{16,18}**C**H); 128.1 (^{7}**C**H); 127.8 (^{5}**C**H); 127.5 (^{6,12}**C**H), 124.5 (^{17}**C**), 124.0 (^{15,19}**C**H), 20.4 (^{22}**C**H$_3$). MS (EI, ion trap, m/z, I, %): 307 (15); 306, M^++H (18); 305, M^+ (45), 304, M–H (22); 270 (12); 268 (8); 231 (5); 230, M^+–C_6H_5 (33); 229 (17); 228, M^+–C_6H_5 (100); 193 (4); 192 (4); 191 (4); 190 (4); 167 (5); 166 (33); 165, M^+–NC_6H_4ClMe (92); 164 (4); 163 (4); 152 (4); 134 (4); 127 (5); 126 (5); 125 (6); 99 (8); 90 (5); 89 (24); 77 (18). IR (KBr pellet, ν, cm^{-1}): 3057 (aromatic C–H stretchings), 2917, 2923 (aliphatic C–H deformations), 1615, 1577 (C=N), 1264, 1073, 955, 782 (aromatic C–H deformations), 1481, 1442, 1315 (aliphatic C–H stretchings), 698 (C–Cl stretchings).

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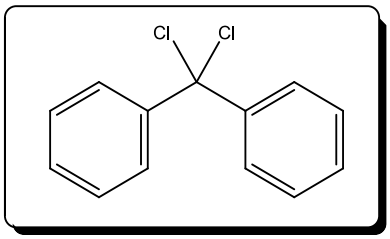

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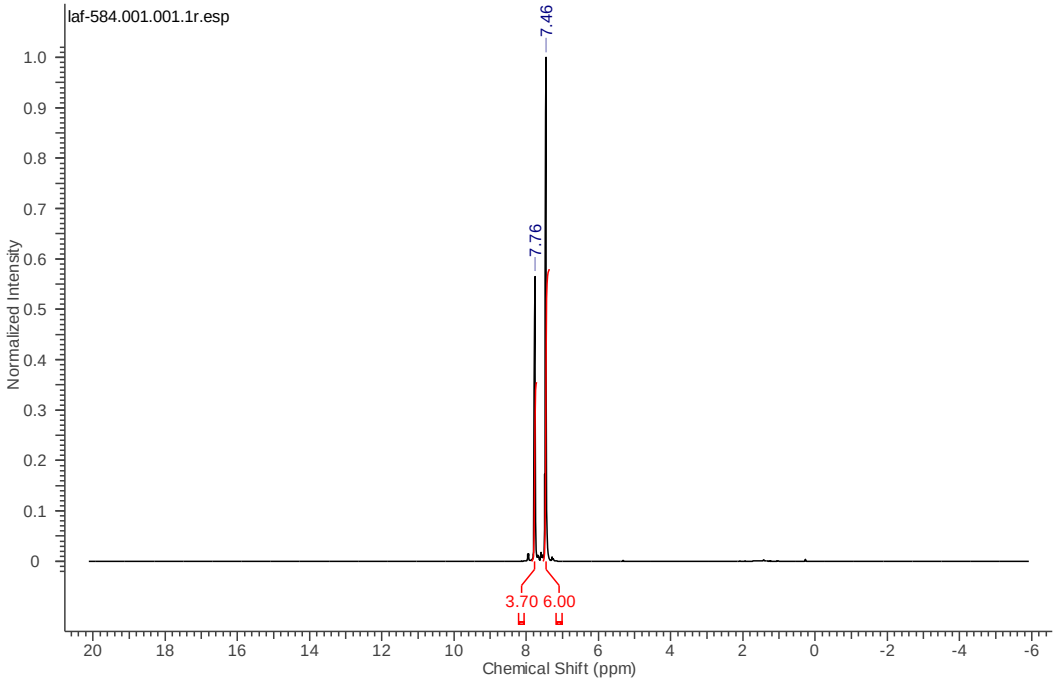


Figure S1: ^{1}H NMR spectrum of compound **1** recorded in $CDCl_3$

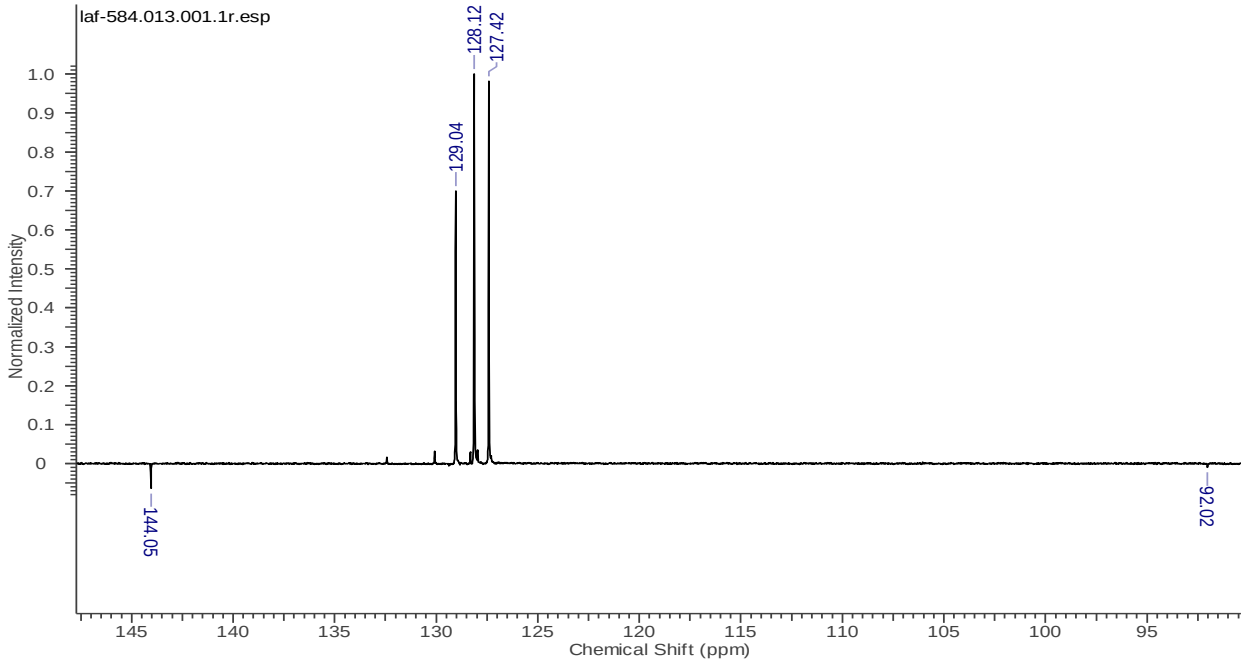
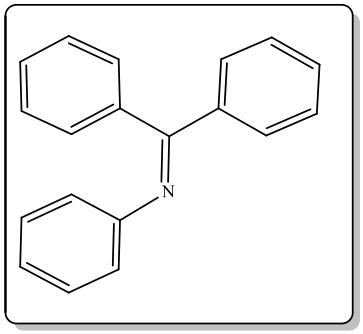


Figure S2: ^{13}C NMR spectrum of compound **1** recorded in $CDCl_3$



2a

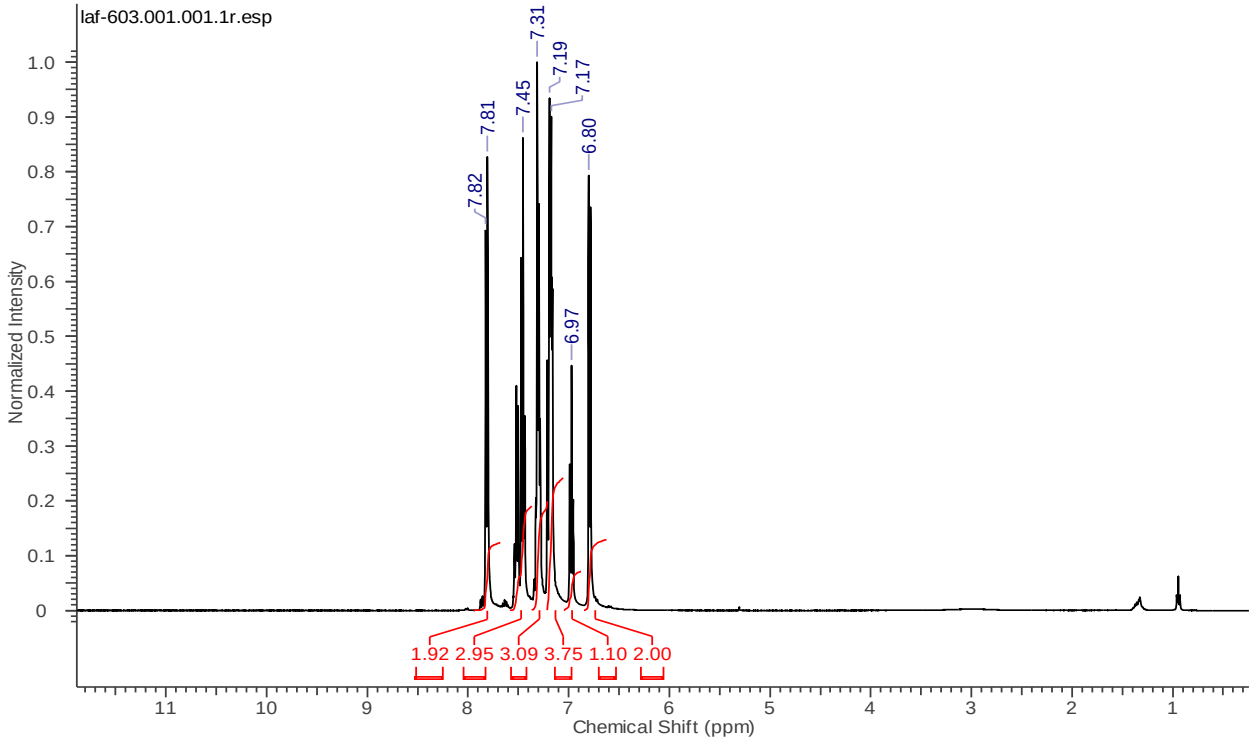


Figure S3: ^{1}H NMR spectrum of compound **2a** recorded in $CDCl_3$

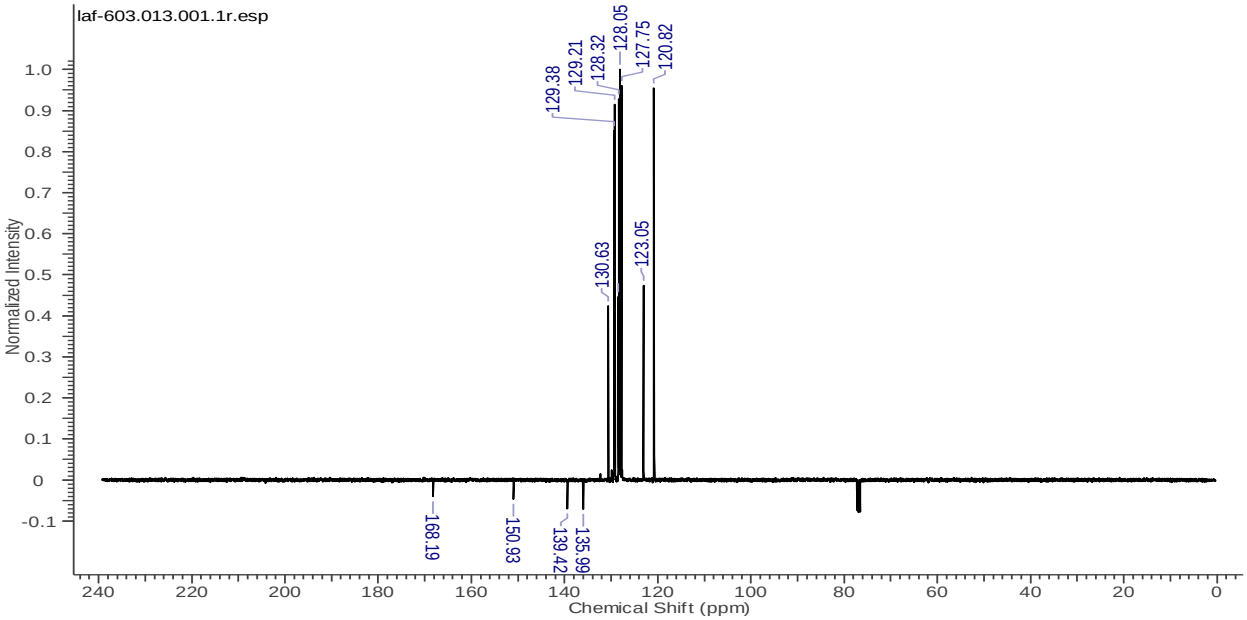


Figure S4: ^{13}C NMR spectrum of compound **2a** recorded in $CDCl_3$

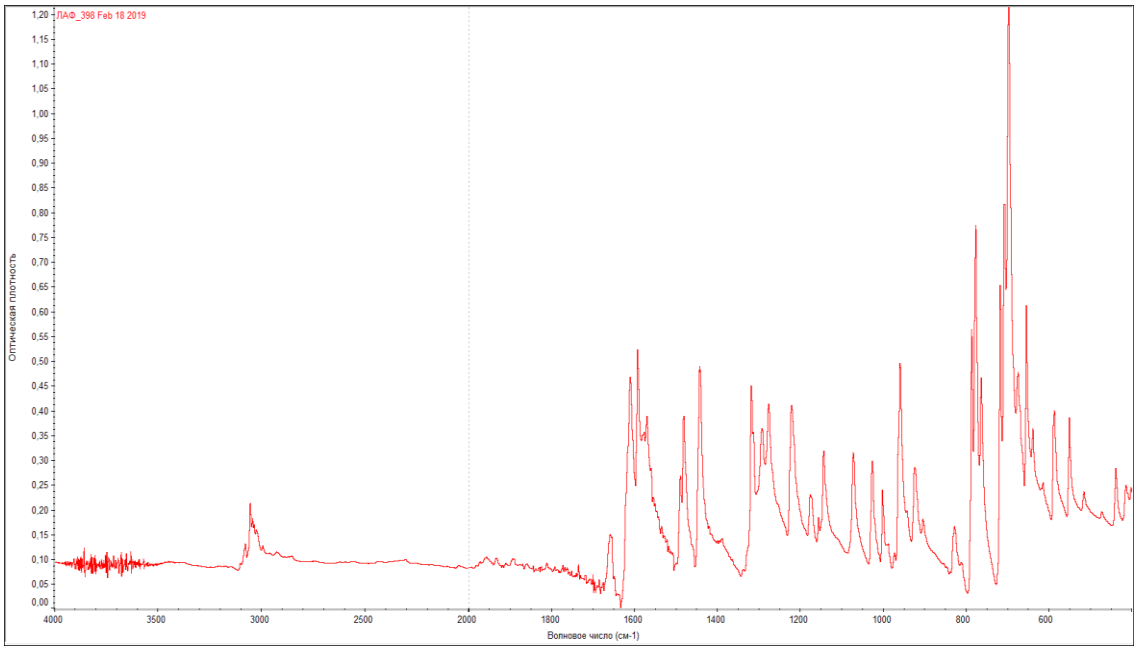
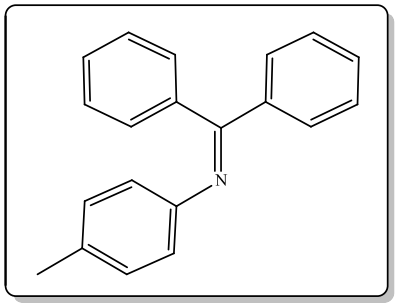


Figure S5: IR spectrum of compound **2a** (KBr pellet, ν, cm^{-1})



2b

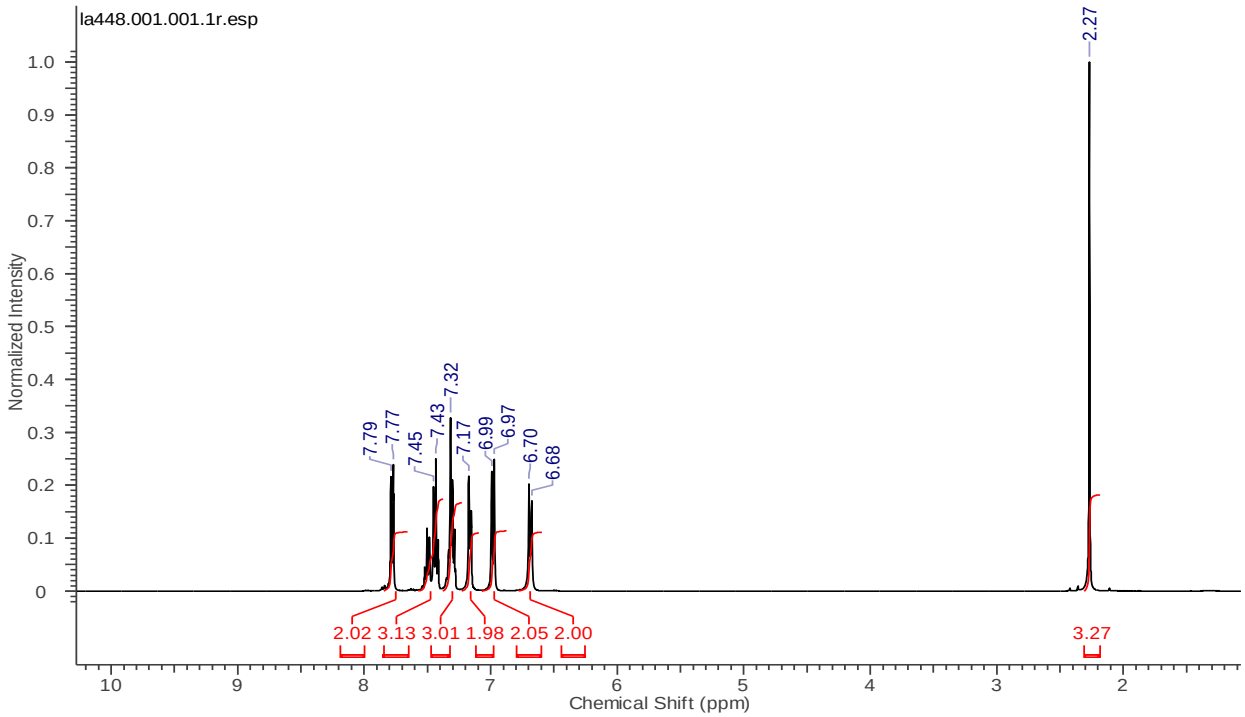


Figure S6: ^{1}H NMR spectrum of compound **2b** recorded in $CDCl_3$

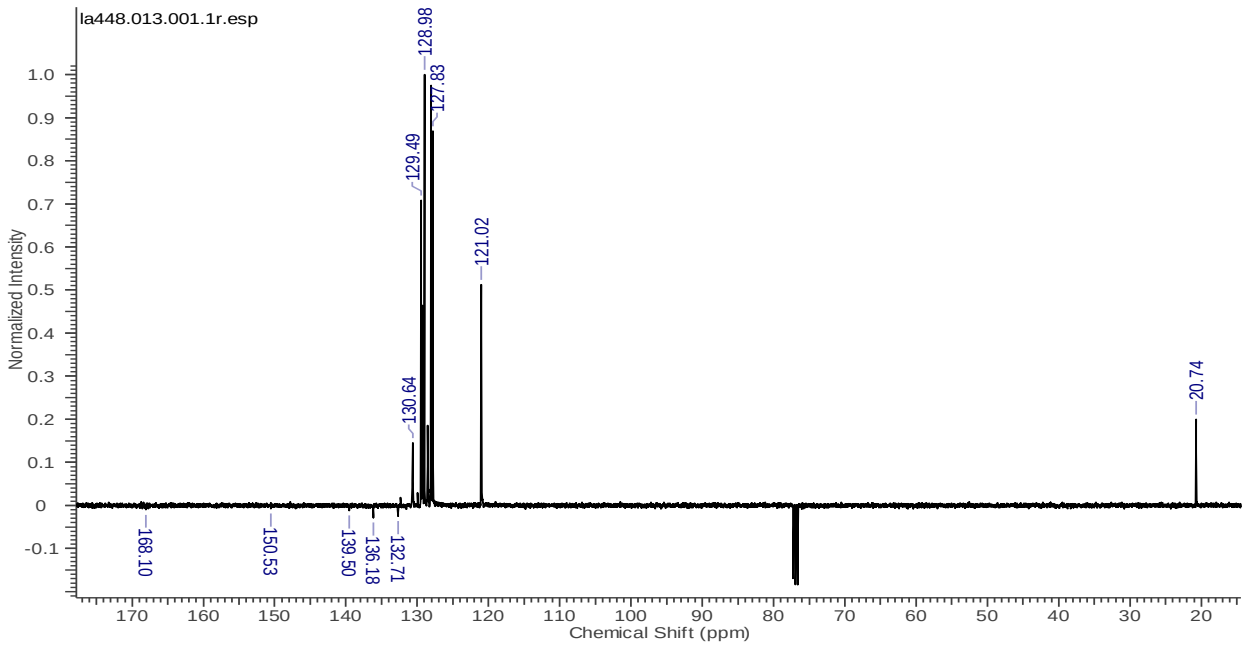


Figure S7: ^{13}C NMR spectrum of compound **2b** recorded in $CDCl_3$

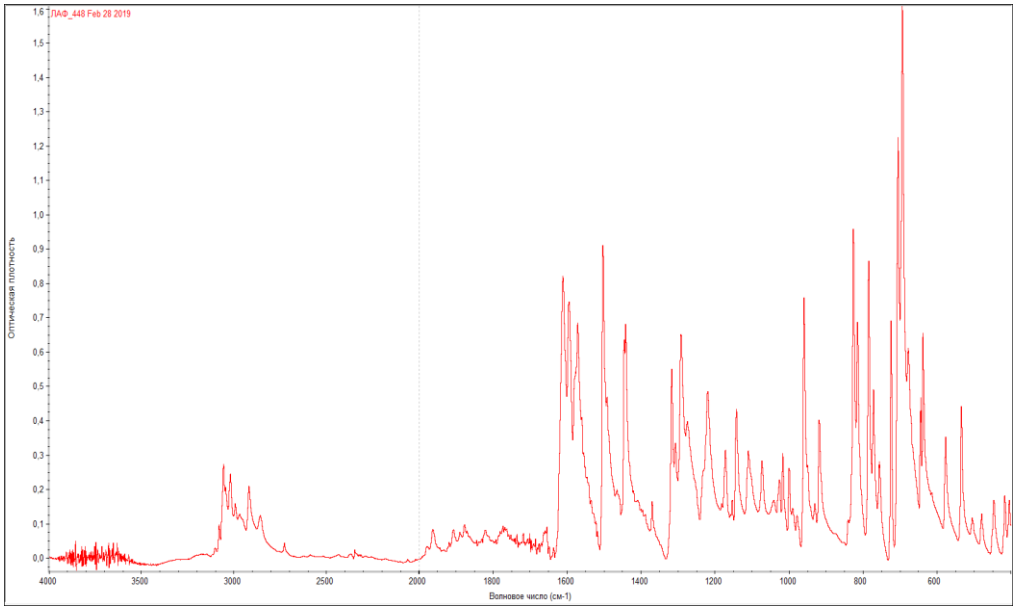
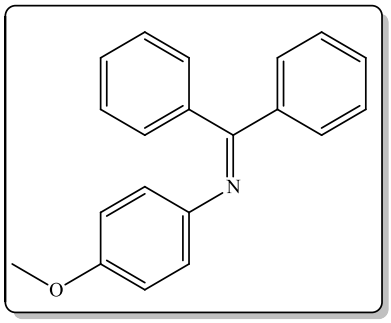


Figure S8: IR spectrum of compound **2b** (KBr pellet, ν, cm^{-1})



2c

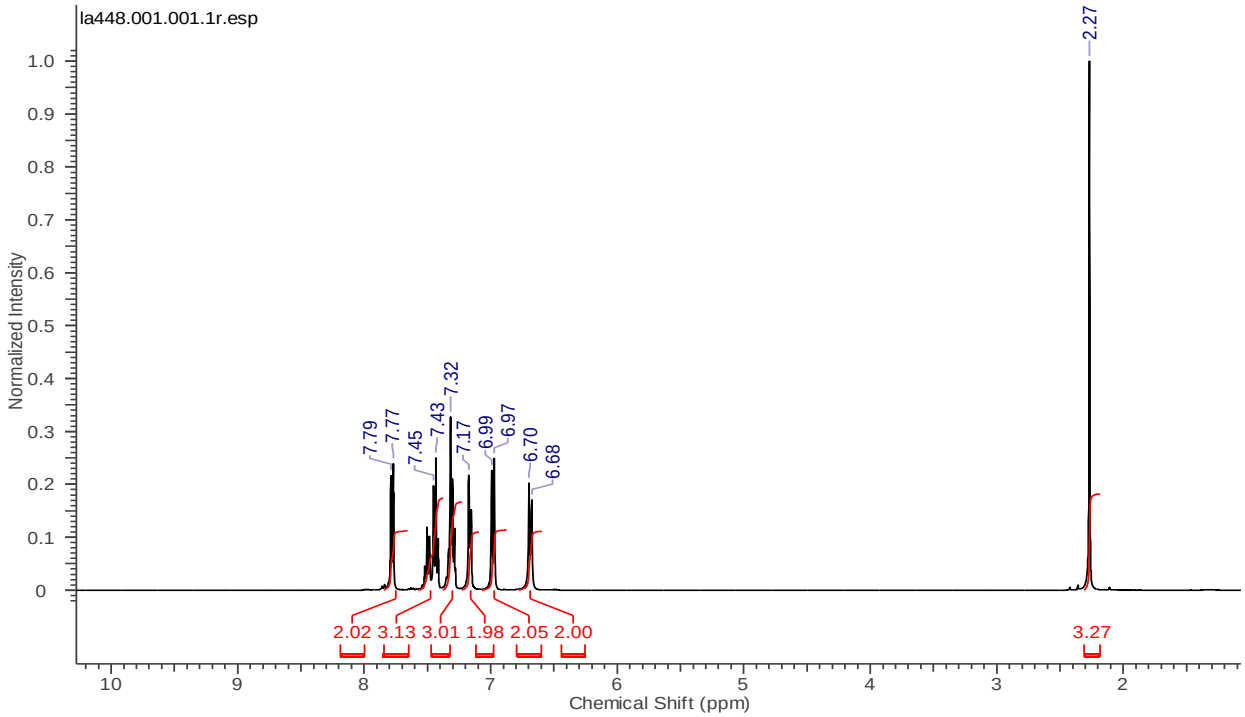


Figure S9: ^{1}H NMR spectrum of compound **2c** recorded in $CDCl_3$

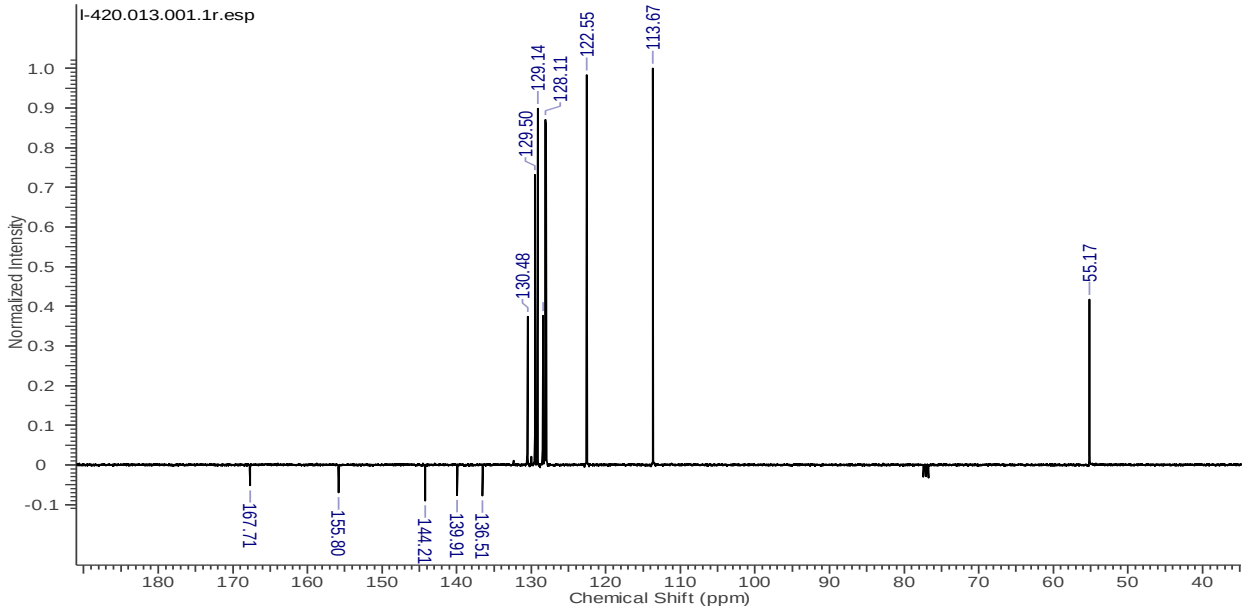


Figure S10: ^{13}C NMR spectrum of compound **2c** recorded in $CDCl_3$

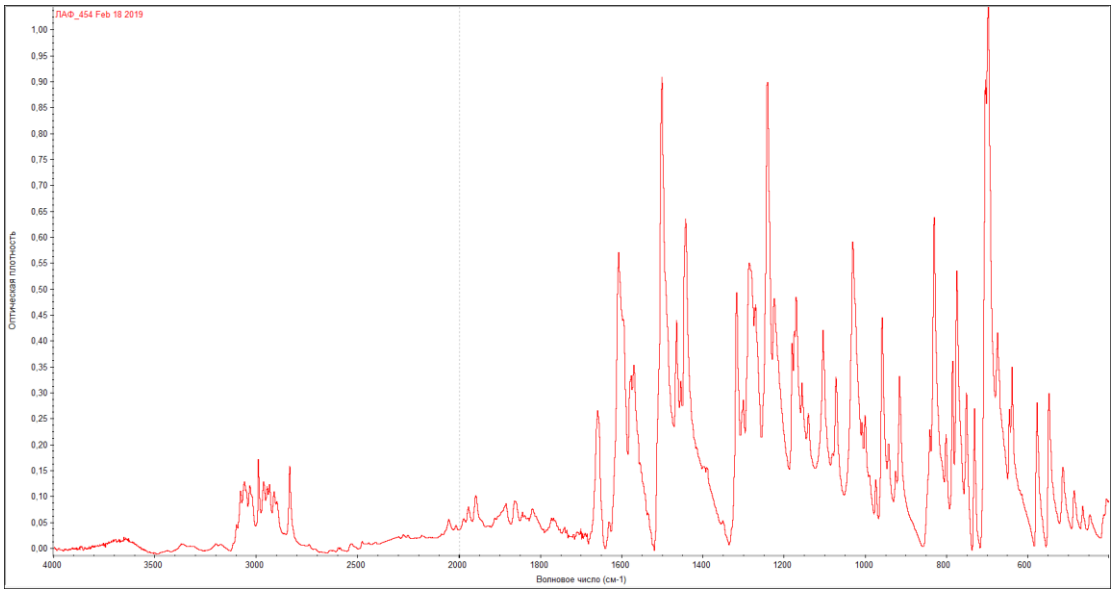
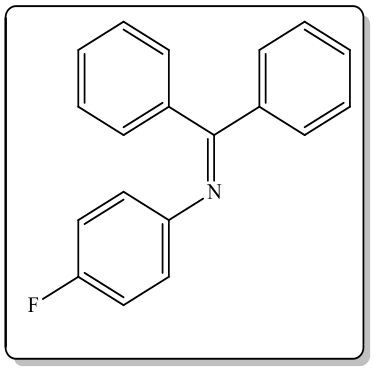


Figure S11: IR spectrum of compound **2c** (KBr pellet, ν, cm^{-1})



2d

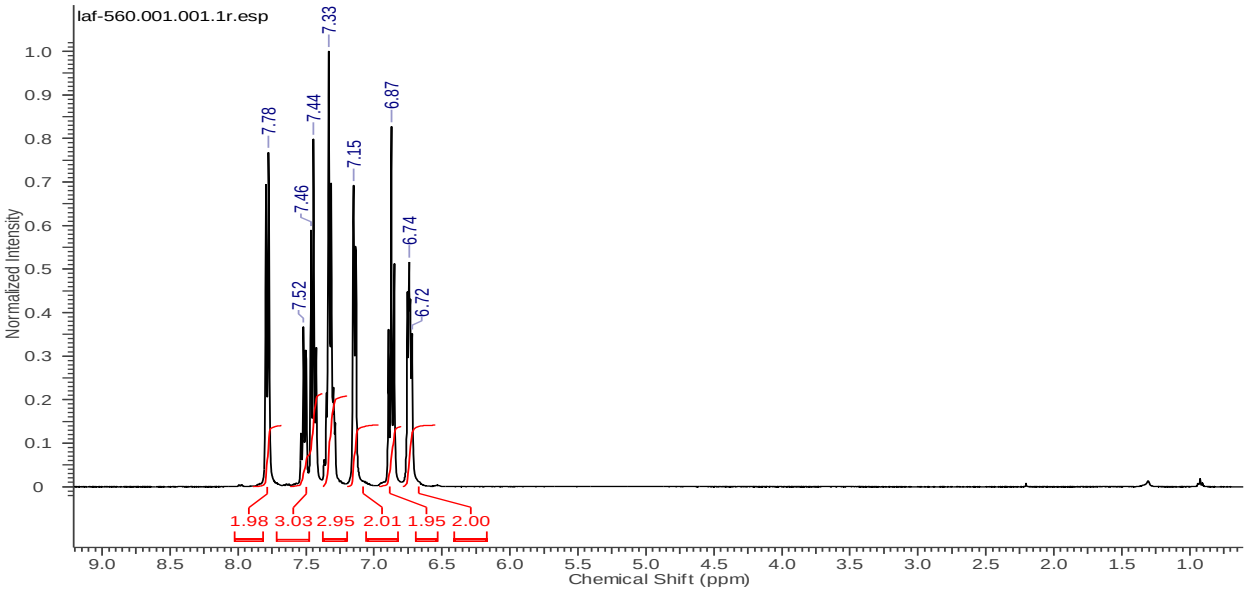


Figure S12: ^{1}H NMR spectrum of compound **2d** recorded in $CDCl_3$

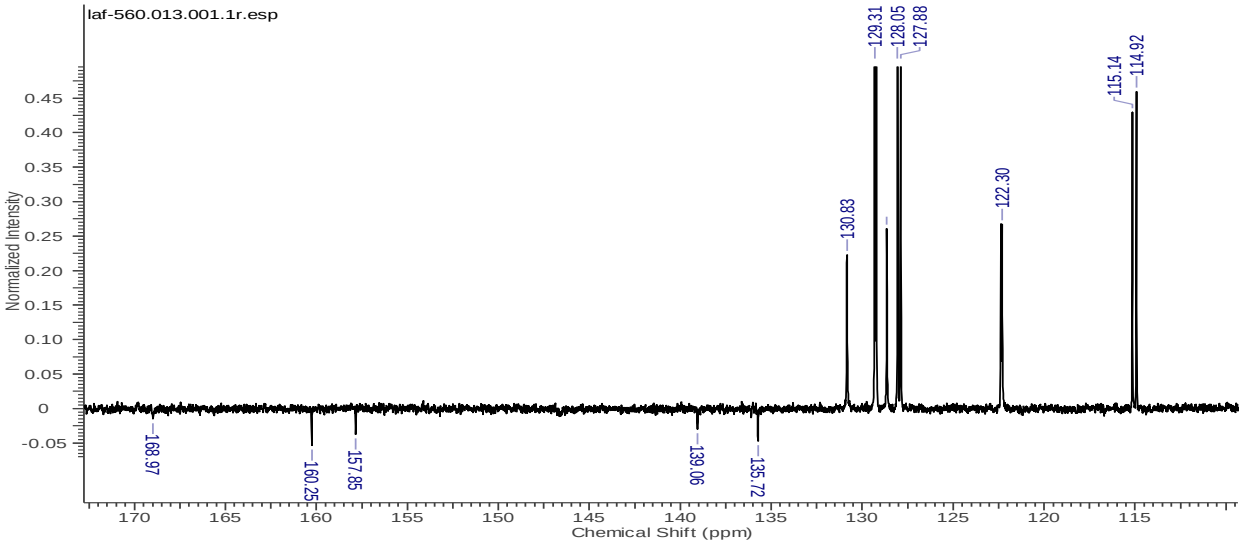


Figure S13: ^{13}C NMR spectrum of compound **2d** recorded in $CDCl_3$

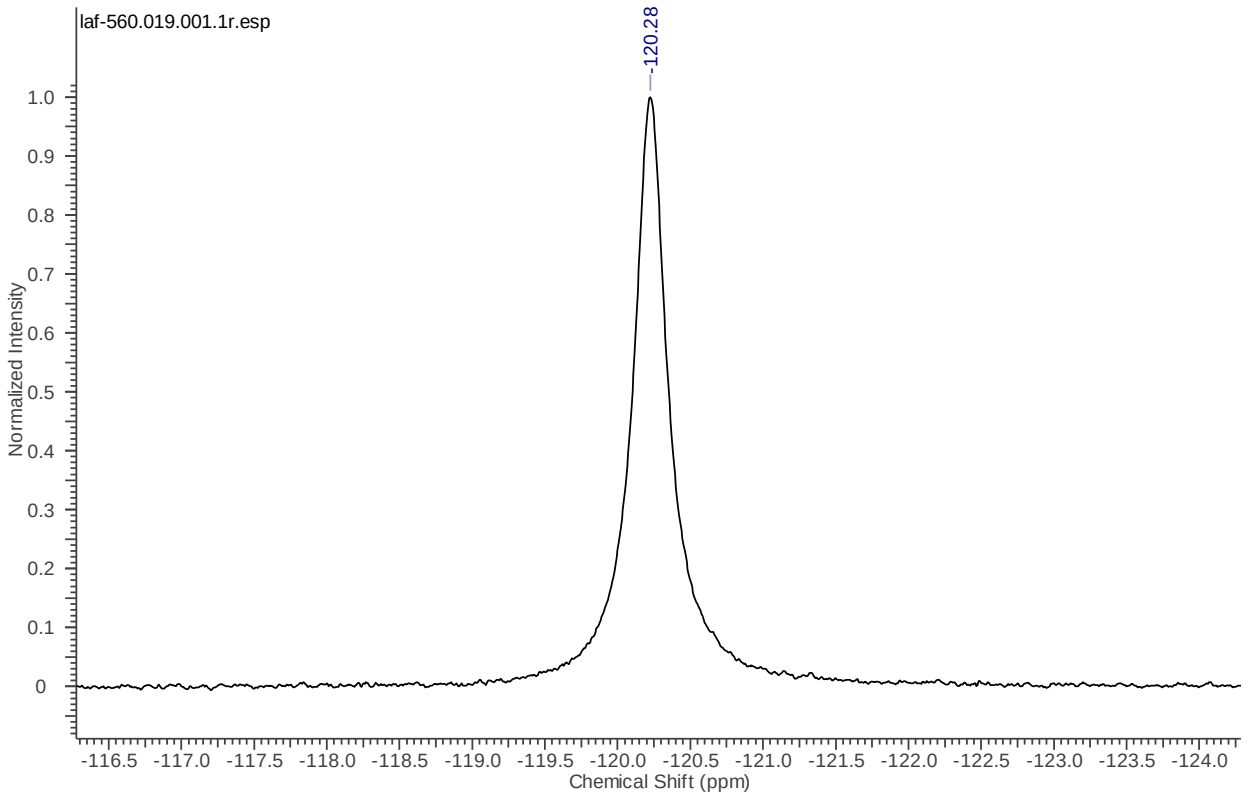


Figure S14: ^{19}F NMR spectrum of compound **2d** recorded in $CDCl_3$

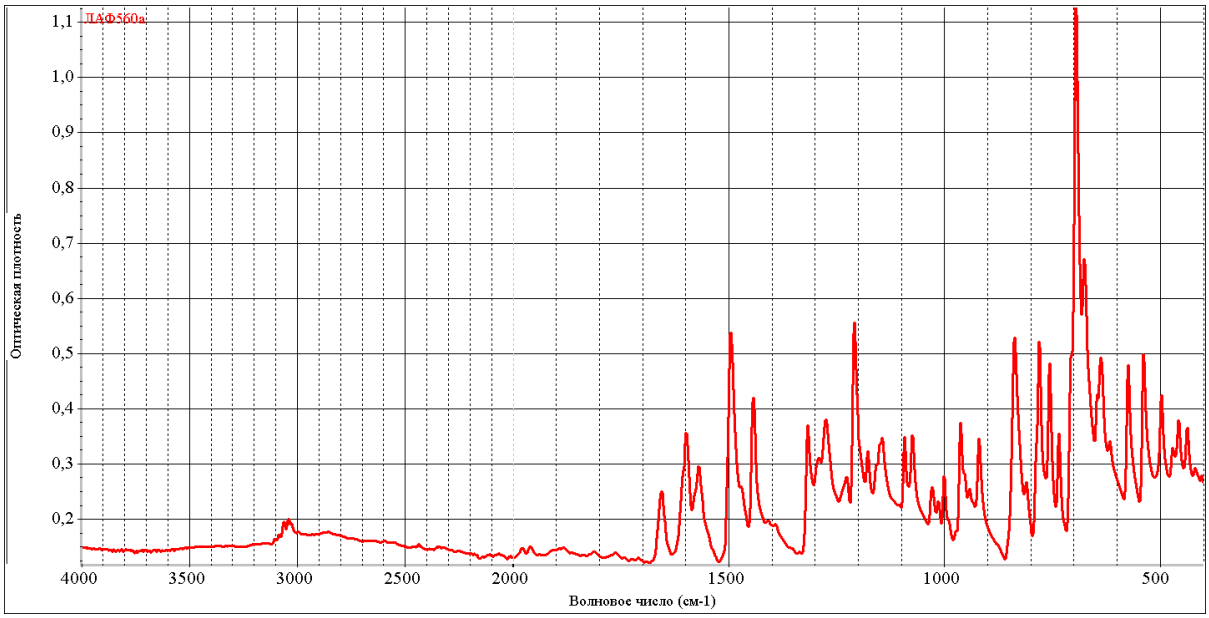
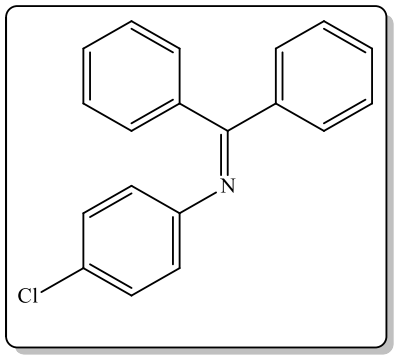


Figure S15: IR spectrum of compound **2d** (KBr pellet, ν, cm^{-1})



2e

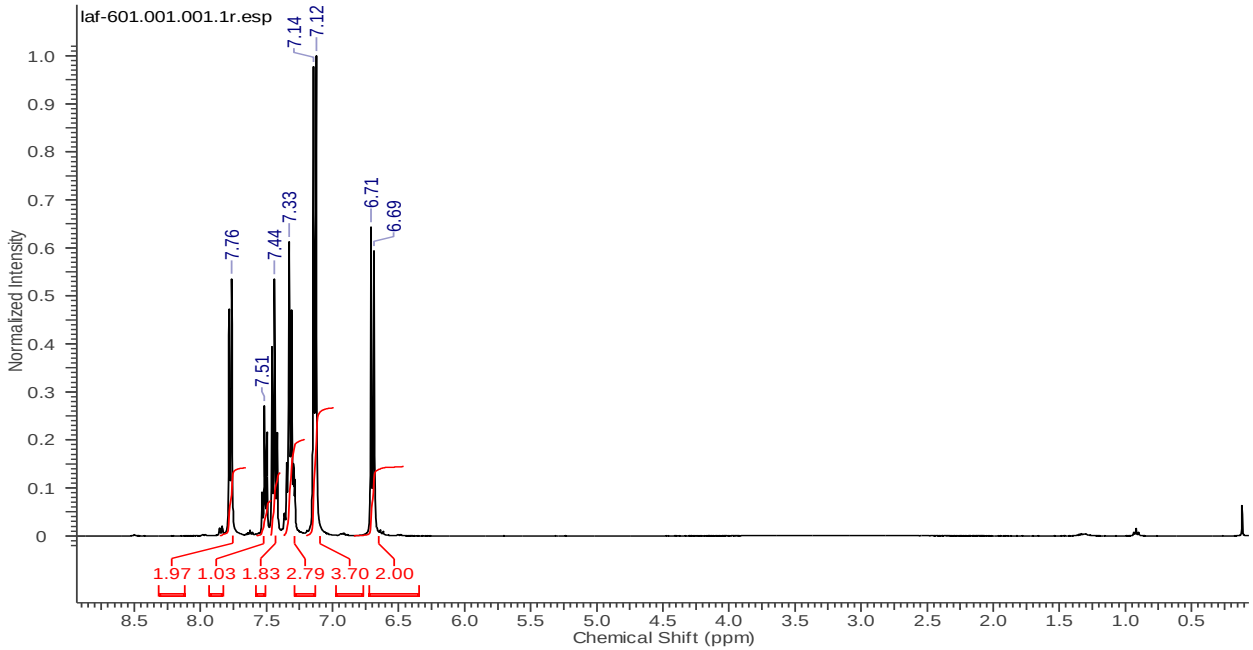


Figure S16: ^{1}H NMR spectrum of compound **2e** recorded in $CDCl_3$

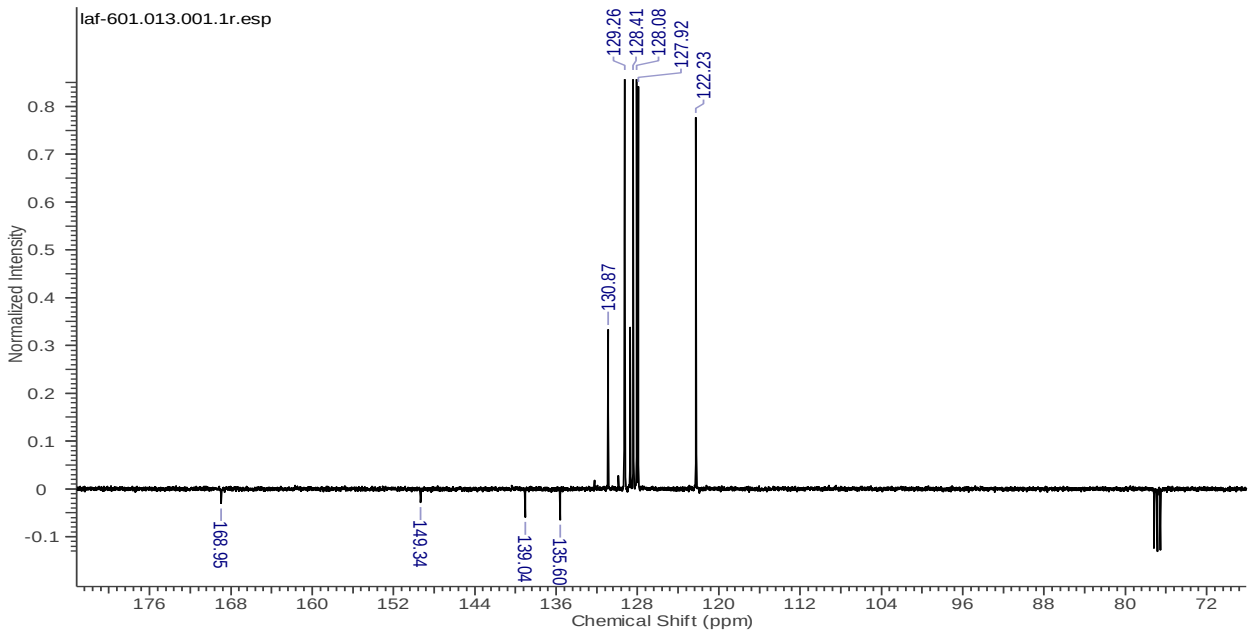


Figure S17: ^{13}C NMR spectrum of compound **2e** recorded in $CDCl_3$

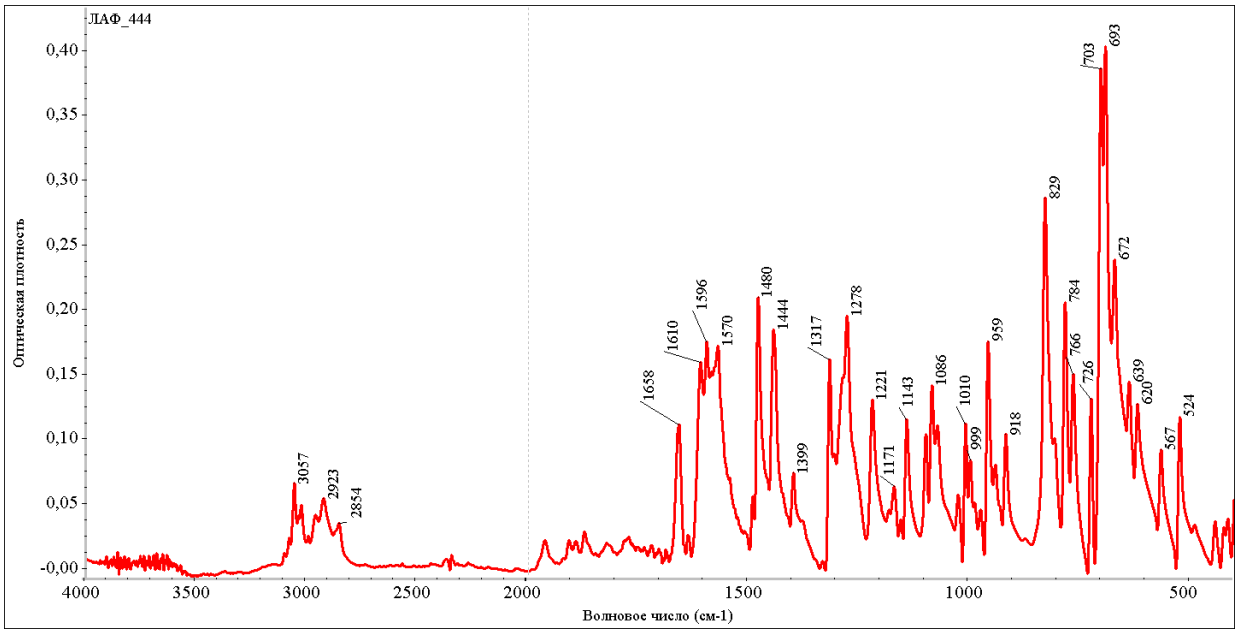
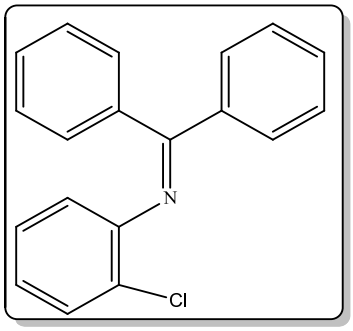


Figure S18: IR spectrum of compound **2e** (KBr pellet, ν, cm^{-1})



2f

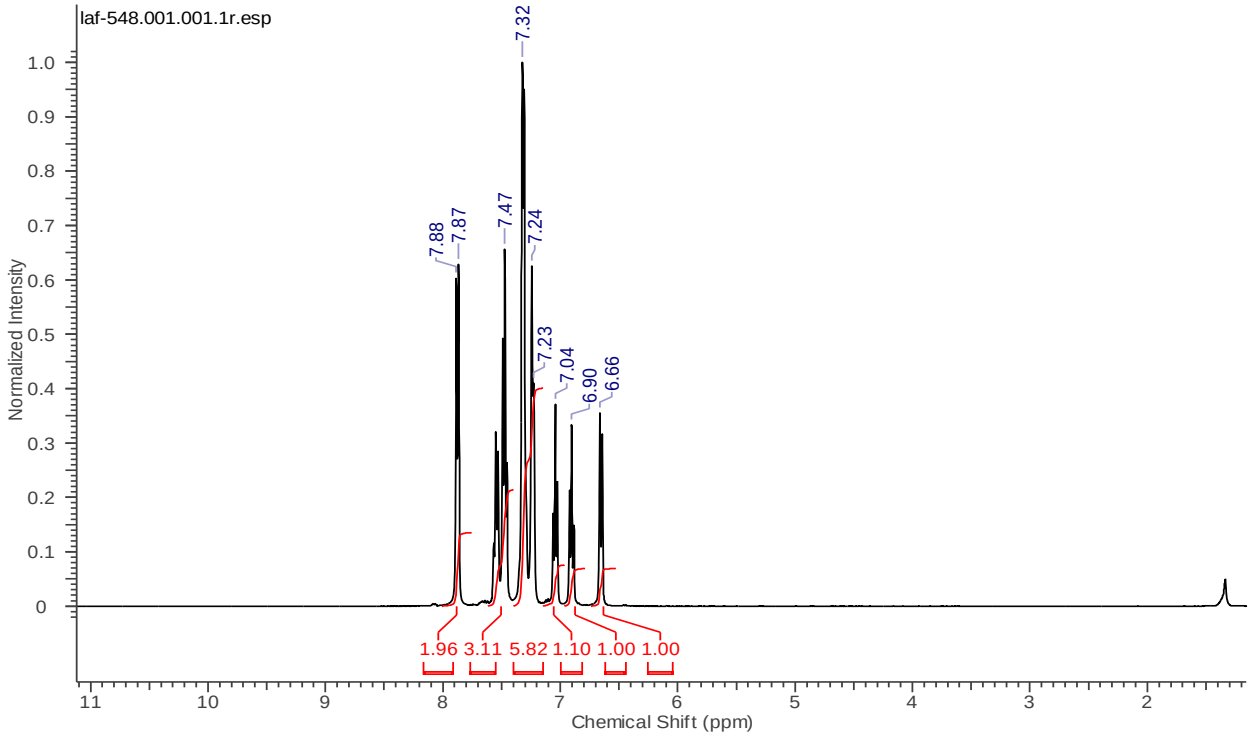


Figure S19: ^{1}H NMR spectrum of compound **2f** recorded in $CDCl_3$

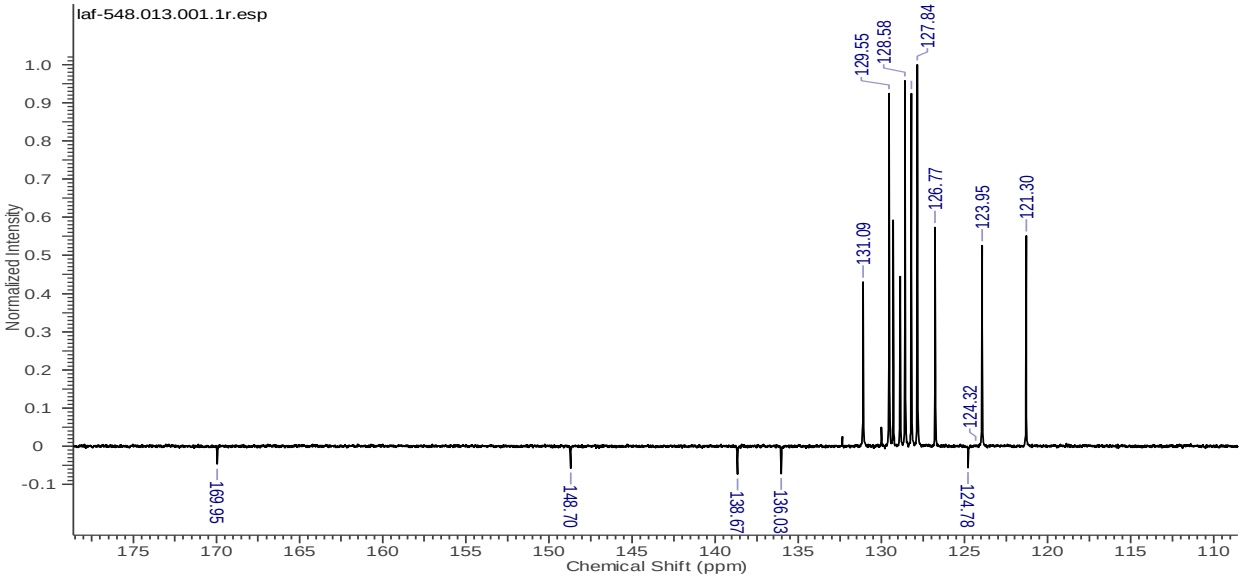


Figure S20: ^{13}C NMR spectrum of compound **2f** recorded in $CDCl_3$

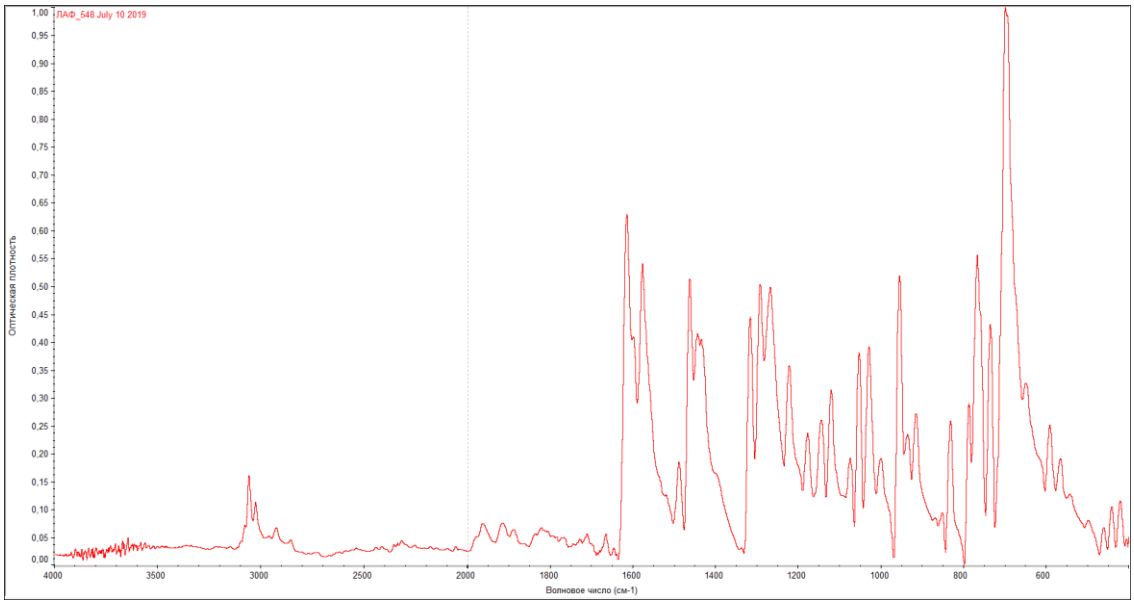
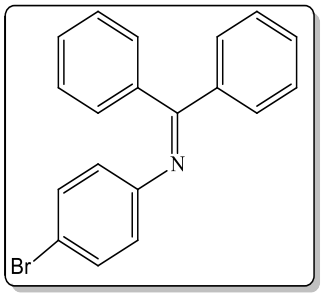


Figure S21: IR spectrum of compound **2f** (KBr pellet)



2g

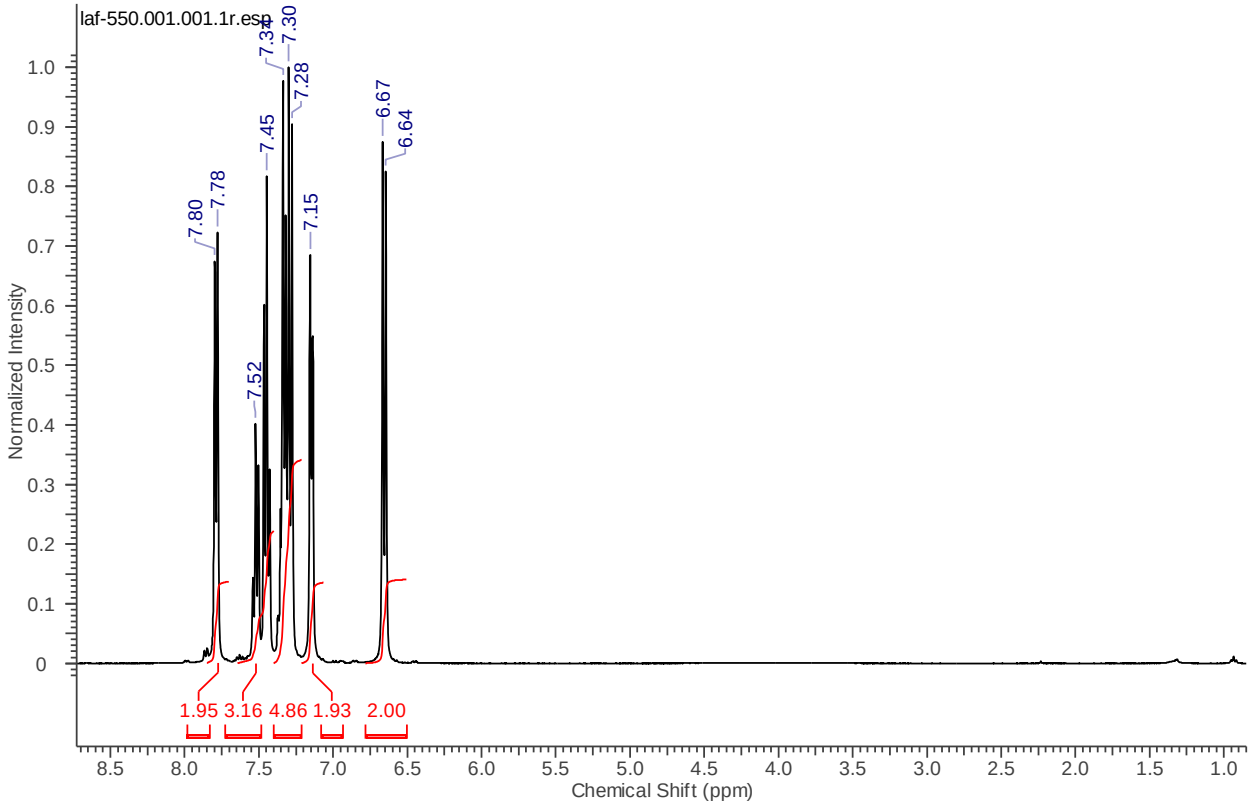


Figure 22 ^{1}H NMR spectrum of compound **2g** recorded in $CDCl_3$

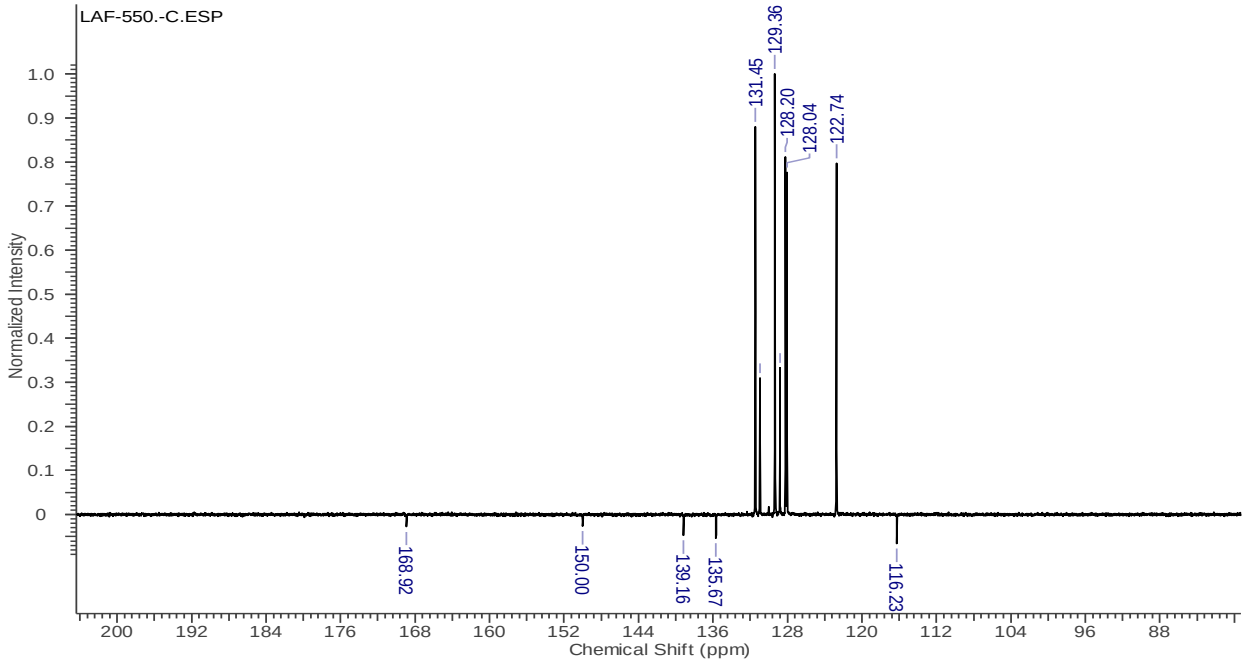


Figure S23: ^{13}C NMR spectrum of compound **2g** recorded in $CDCl_3$

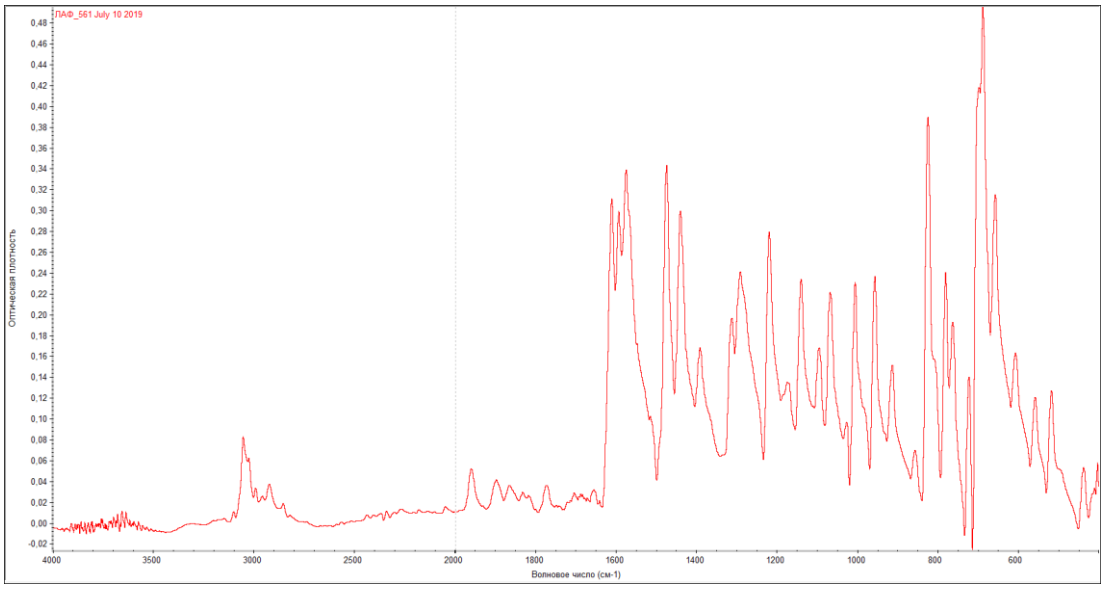
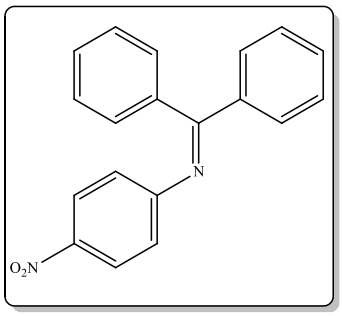


Figure S24: IR spectrum of compound **2g** (KBr pellet, ν, cm^{-1})



2h

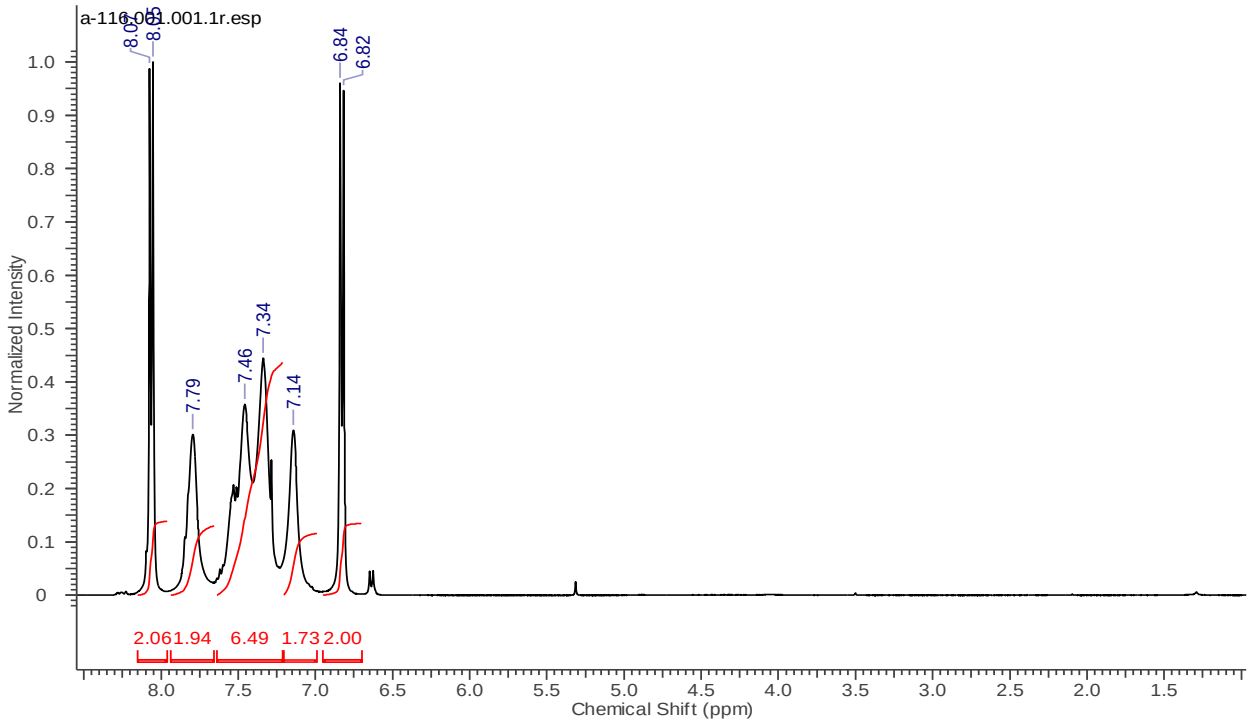


Figure S25: ^{1}H NMR spectrum of compound **2h** recorded in $CDCl_3$

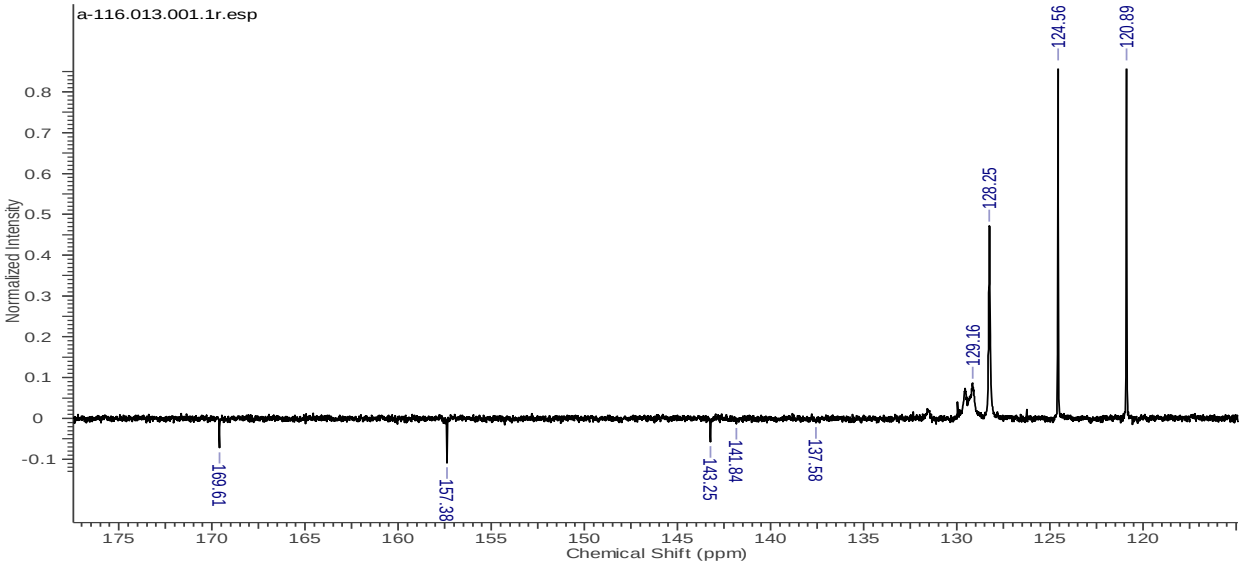


Figure S26: ^{13}C NMR spectrum of compound **2h** recorded in $CDCl_3$

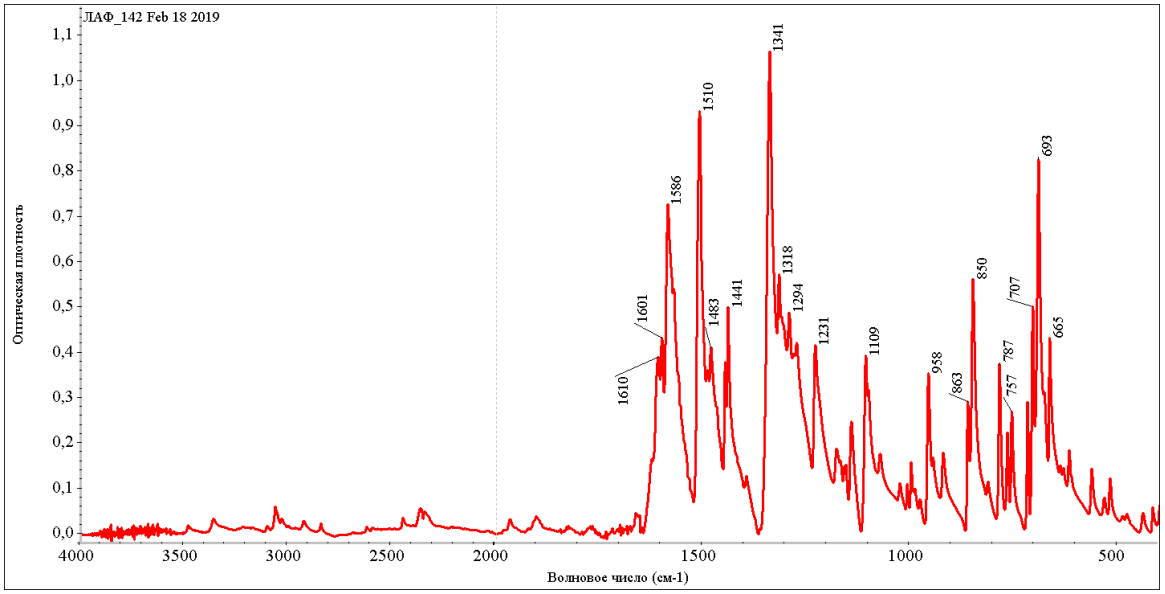
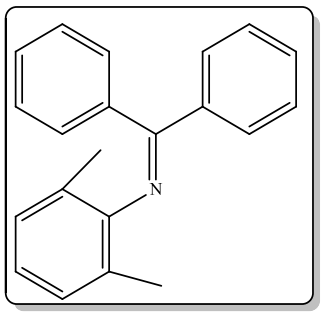


Figure S27: IR spectrum of compound **2h** (KBr pellet, ν, cm^{-1})



2i

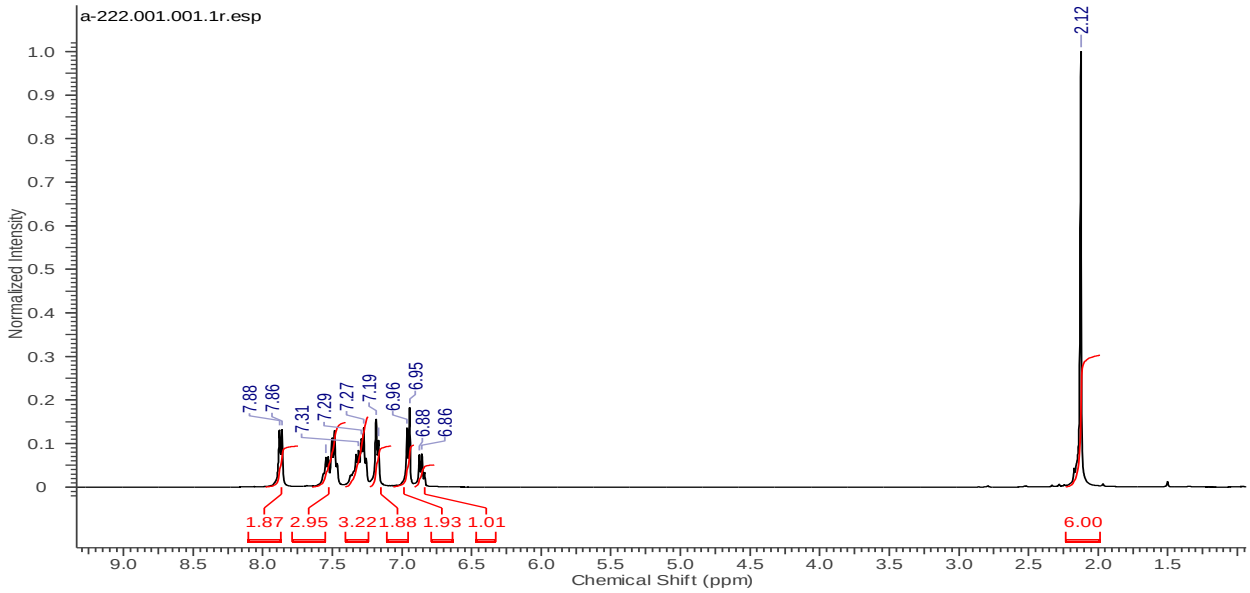


Figure S28: ^{1}H NMR spectrum of compound **2i** recorded in $CDCl_3$

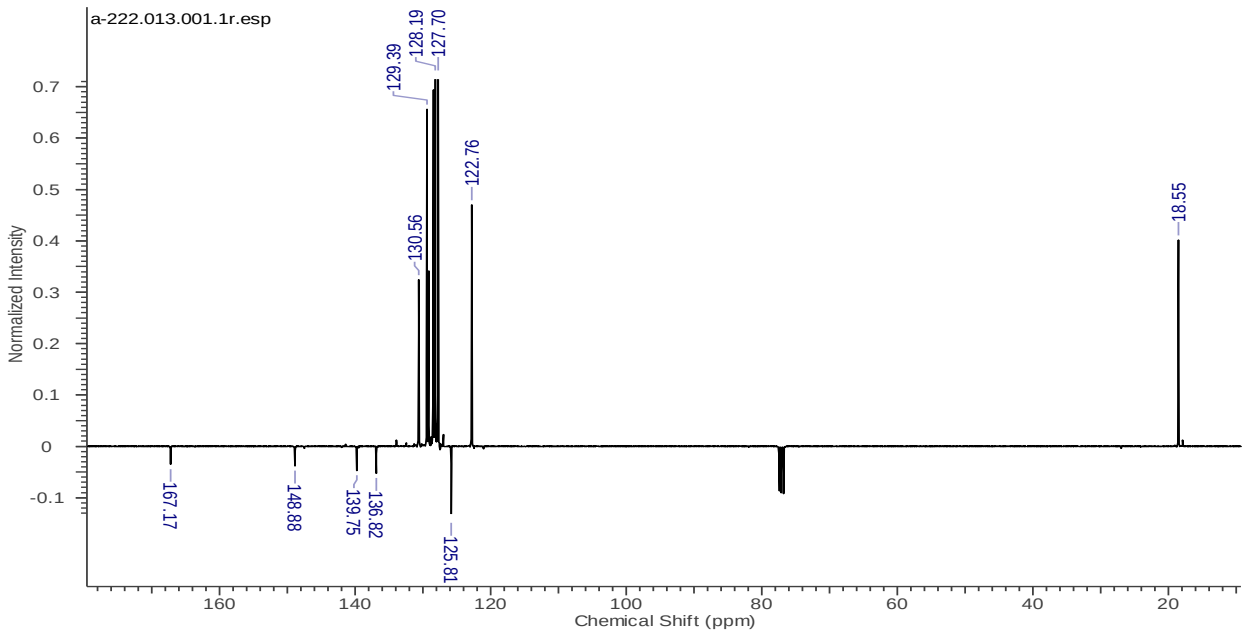


Figure S29: ^{13}C NMR spectrum of compound **2i** recorded in $CDCl_3$

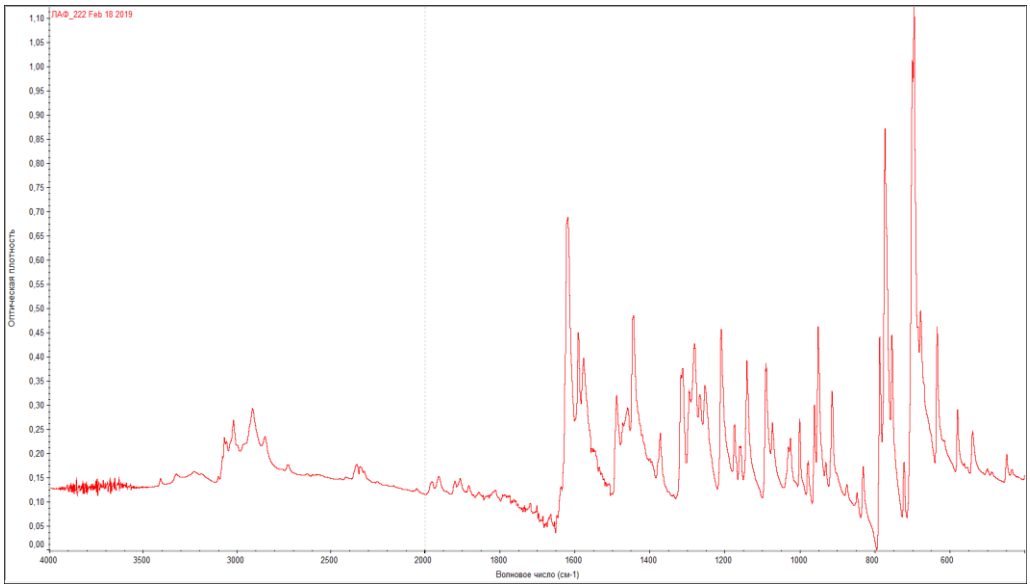
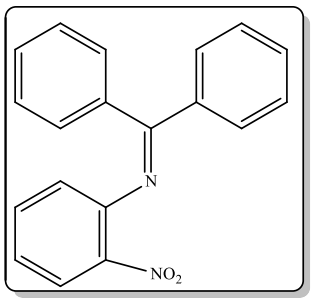


Figure S30: IR spectrum of compound **2i** (KBr pellet, ν, cm^{-1})



2j

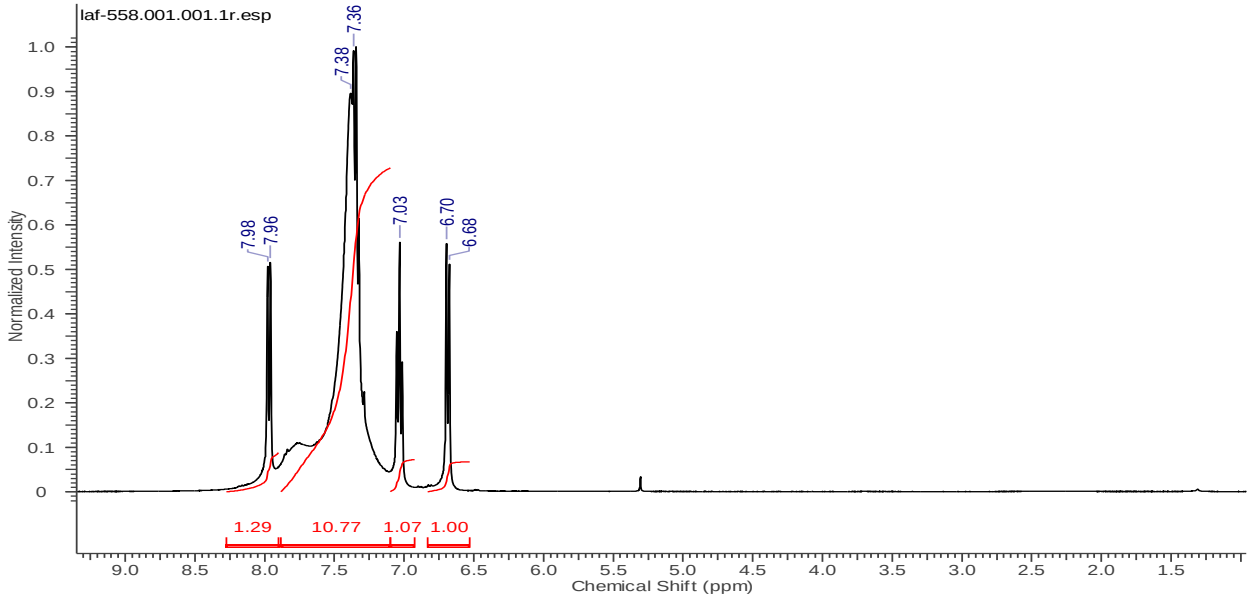


Figure S31: ^{1}H NMR spectrum of compound **2j** recorded in $CDCl_3$

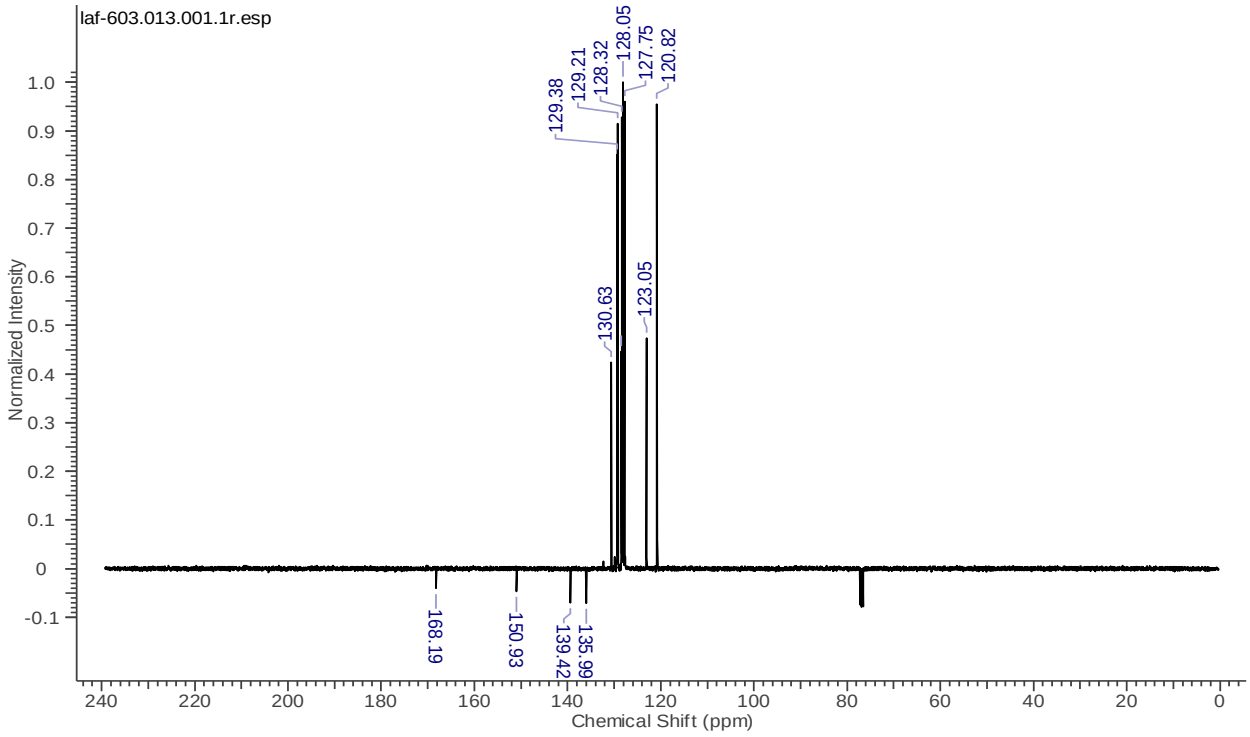


Figure S32: ^{13}C NMR spectrum of compound **2j** recorded in $CDCl_3$

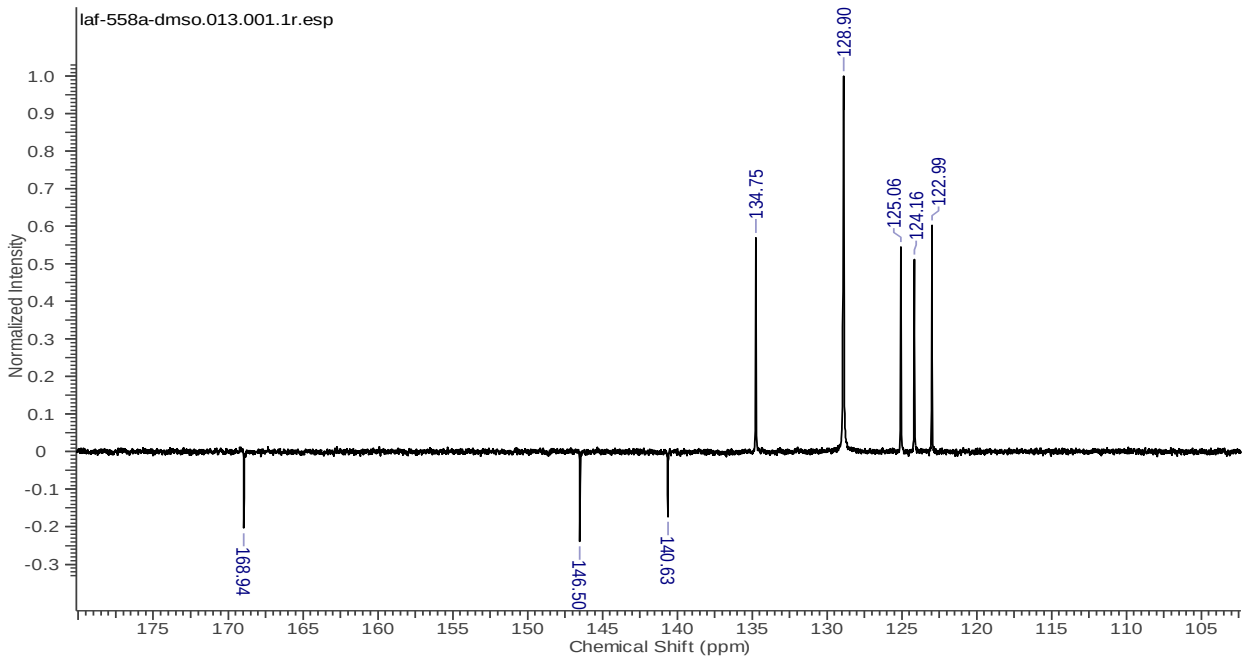


Figure S33 ^{13}C NMR spectrum of compound **2j** recorded in DMSO

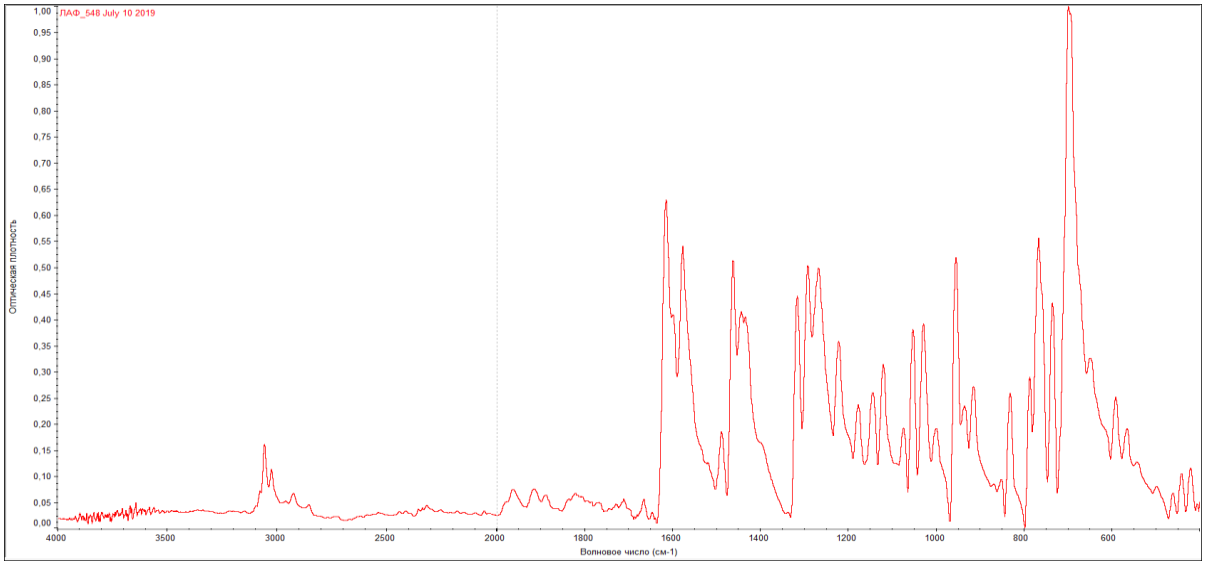
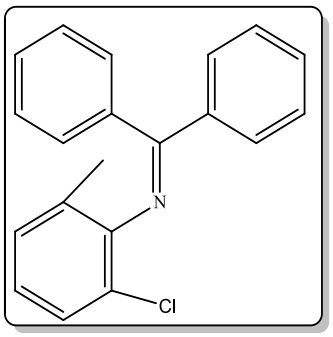


Figure S34: IR spectrum of compound **2j** (KBr pellet):



2k

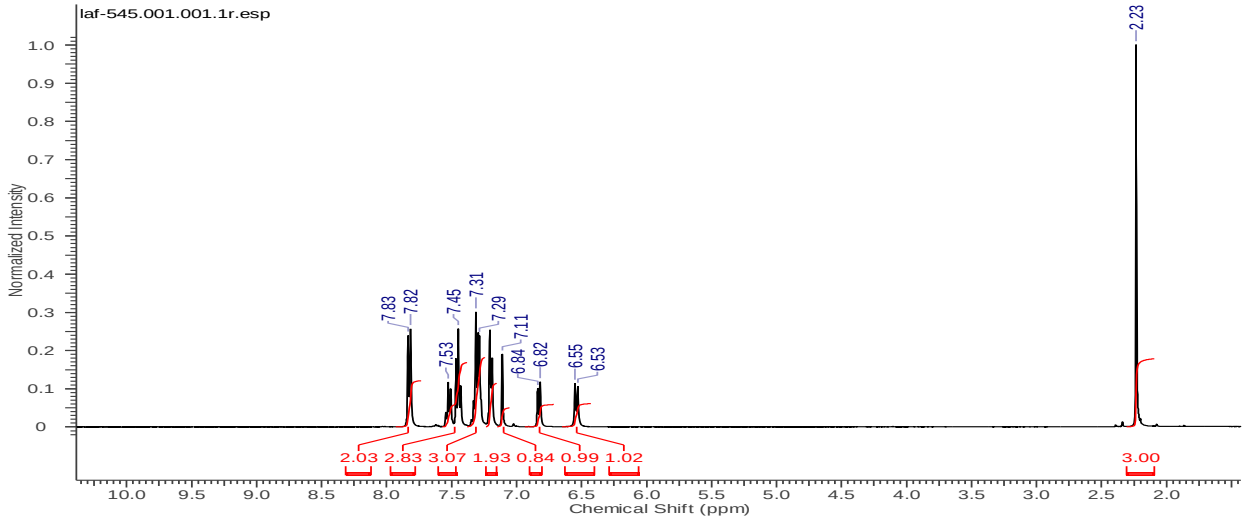


Figure S35: ^{1}H NMR spectrum of compound **2k** recorded in $CDCl_3$

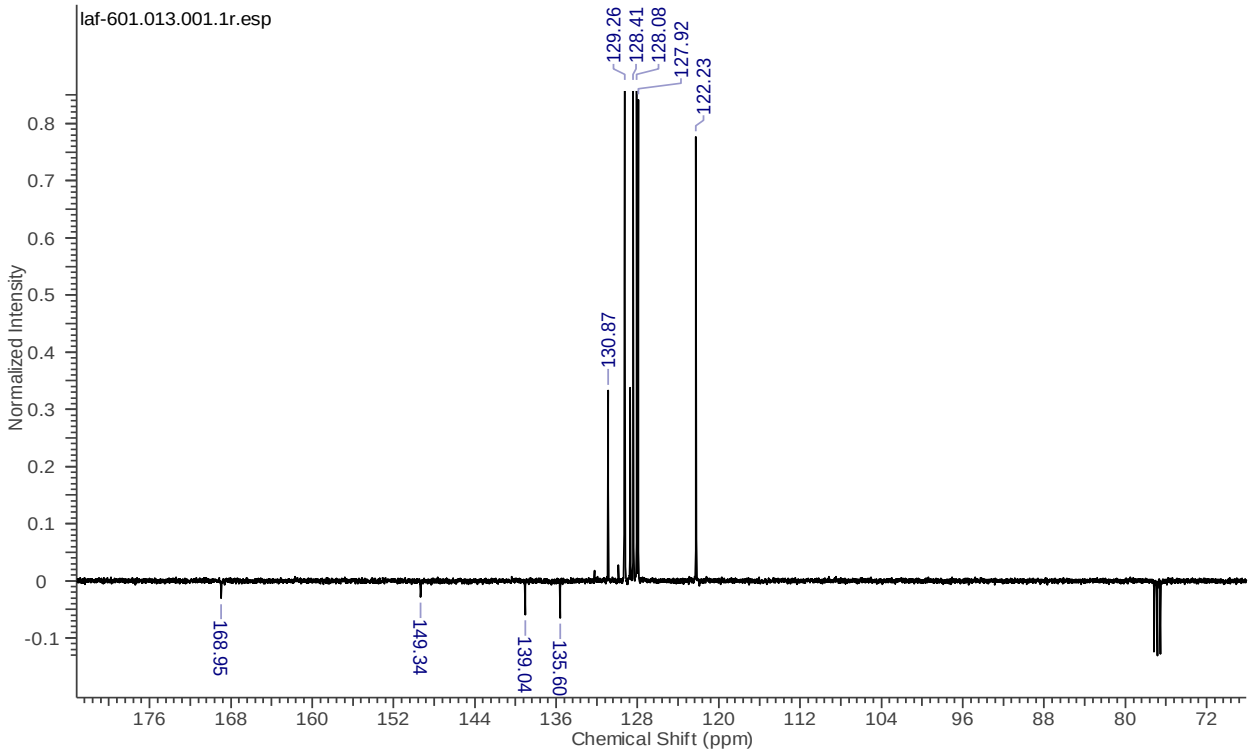


Figure S36: ^{13}C NMR spectrum of compound **2k** recorded in $CDCl_3$

Figure S37: IR spectrum of compound **2k** (KBr pellet)