Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supplementary Information

Ni-Catalyzed Cross-Coupling Reactions of *N*-Acylpyrrole-Type Amides with Organoboron Reagents

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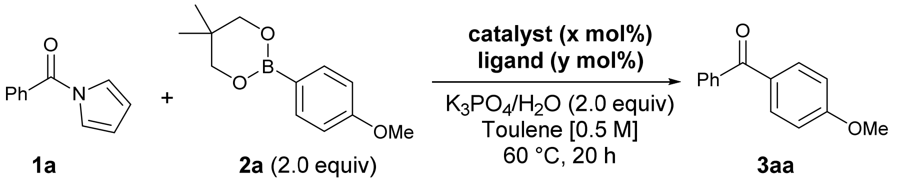
General information

Unless otherwise stated, reactions were run under an Argon atmosphere with rigid exclusion of moisture from reagents and glassware. All glassware was dried in Infrared rapid drying box prior to use. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 or Bruker 500 (^{1}H/400 or 500 MHz, ^{13}C/100 or 125 MHz) spectrometer. Chemical shifts are expressed in parts per million (δ) relative to an internal standard of tetramethylsilane (TMS). ESI-Mass spectra were recorded on a Bruker Dalton ESquire 3000 plus MS apparatus. Optical rotations were measured with an Anton Paar MCP 500 polarimeter. Melting points were uncorrected. Infrared spectra were recorded with a Nicolet Avatar 330 FT-IR spectrometer using film KBr pellet technique. HRMS spectra were recorded on a Bruker En Apex ultra 7.0T FT-MS apparatus. Unless otherwise stated, commercial reagents were purchased from the reagent supplier (Adamas-beta®, Alfa Aesar, Sigma-Aldrich) and used without purification. Silica gel (300–400 mesh) was used for flash column chromatography. THF was distilled over sodium benzophenone ketyl under Argon. Dichloromethane was distilled over calcium hydride under Argon. Toluene was distilled over sodium benzophenone ketyl under Argon. Extra dry 1,4-dioxane was obtained from J&K Scientific Ltd and oxygen-excluded prior to use. Ni(COD)$_2$ was obtained from Strem Chemicals. (Hetero)aryl boric acids were obtained from Ark Pharm. (Hetero)arylboronate neopentylglycol esters **2a**-**n**[1] were synthesized from corresponding (hetero)arylboric acid according to literature procedure.[1a] 2,4,6-Triisopropylaniline was synthesized from 1,3,5-triisopropylbenzene in two steps according to the literature procedure.[2] 1,1'-Carbonyldipyrrole **4** was synthesized from 1,1'-carbonyldiimidazole according to literature procedures[3].

Experimental procedures and characterization data

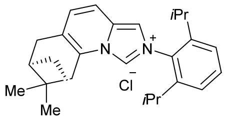
1. Reaction optimization and Control experiments

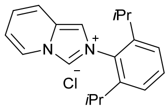
Table S1. Optimization of the catalyst and ligand.[a]



Entry	**cat. (x mol%)**	**ligand (y mol%)**	Yield[a] of **3aa** (%)
1	Pd(dba) (10)	PCy$_3$ (10)	0
2	PdCl$_2$ (10)	PCy$_3$ (10)	0
3	PdCl$_2$ (10)	PPh$_3$ (10)	0
4	Ni(dppf)Cl$_2$ (10)	-	0
5	Ni(COD)$_2$ (10)	P(*t*Bu$_3$) (10)	0

6	Ni(COD)$_2$ (10)	PCy$_3$ (10)	0
7	Ni(COD)$_2$ (10)	PPh$_3$ (10)	0
8	Ni(COD)$_2$ (10)	2,2-bipyridine (10)	0
9	Ni(COD)$_2$ (10)	**L1**·HCl/*t*-BuOK (10)	33 (30[b])
10	Ni(COD)$_2$ (10)	**L1**·HCl (10)	33
11	Ni(COD)$_2$ (10)	**L2**·HCl (10)	Trace
12	Ni(COD)$_2$ (10)	**L3**·HCl (10)	45 (41[b])
13	Ni(COD)$_2$ (10)	**L4**·HCl (10)	13 (9[b])
14	Ni(COD)$_2$ (10)	**L5**·HBF$_4$ (10)	38
15	Ni(COD)$_2$ (10)	**L6**·2HCl (10)	51 (49[b])
16	Ni(COD)$_2$ (10)	**L9**·4HBr (10)	86 (83[b])
17	Ni(COD)$_2$ (10)	**L7**·2HCl (10)	88 (86[b])
18	**Ni(COD)$_2$ (10)**	**L8·2HCl (10)**	**96 (94[b])**
19	Ni(COD)$_2$ (10)	**L8**·2HCl (5)	57
20	Ni(COD)$_2$ (10)	IPr·HCl/*t*-BuOK (20)	89 (87 [b])
21	Ni(COD)$_2$ (10)	IMes·HCl/*t*-BuOK (10)	Trace


L1•HCl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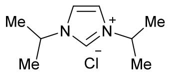
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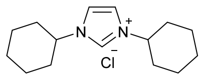
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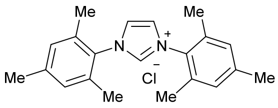
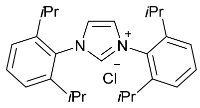

IMes•HCl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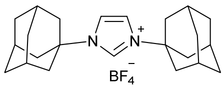
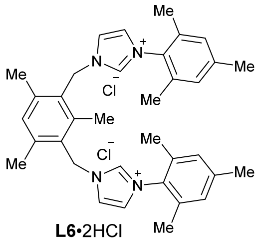
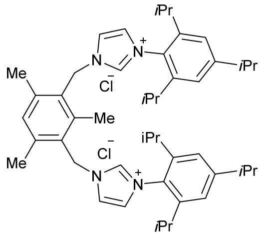
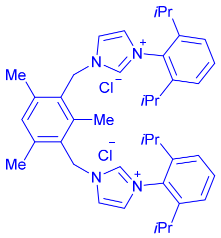
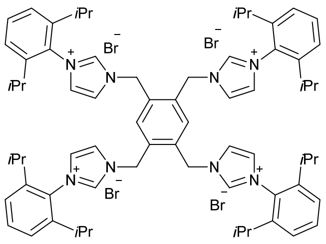

L5•HBF$_4$


L6•2HCl


L7•2HCl

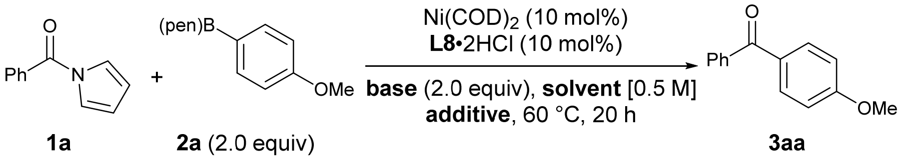

L8•2HCl


L9•4HBr

[a] Yields were determined by ^{1}H NMR analysis of crude mixture by using 1,3,5-trimethoxybenzene as a internal standard. [b] Isolated yields.

A vial packaged with tin foil was charged with powdered K$_3$PO$_4$ (101.9 mg, 0.48 mmol, 2.0 equiv), *N*-acylpyrrole **1a** (41.1 mg, 0.24 mmol, 1.0 equiv), arylboronic acid neopentyl glycol ester **2a** (105.6 mg, 0.48 mmol, 2.0 equiv), **ligand (y mol%)** and a magnetic stir bar. Then the vial was taken into a glove box and charged with **cat. (x mol %)**. After that, toluene (0.48 mL, 0.5 M) and water (8.6 uL, 0.48 mmol, 2.0 equiv) was added. The vial was sealed with screw cap, removed from the glove box, and stirred vigorously at 60 °C for 20 h. After cooling to room temperature, the mixture was diluted with CH_2Cl_2 (1 mL), washed with a saturated aqueous Na_2CO_3 solution (1 mL) and brine (1 mL), and then dried over anhydrous Na_2SO_4. The organic layer was filtered and concentrated under reduced pressure. The residue was analyzed by ^{1}H NMR or purified by flash column chromatography to yield the desired ketone **3aa**.

Table S2. Optimization of the base, solvent and additive.

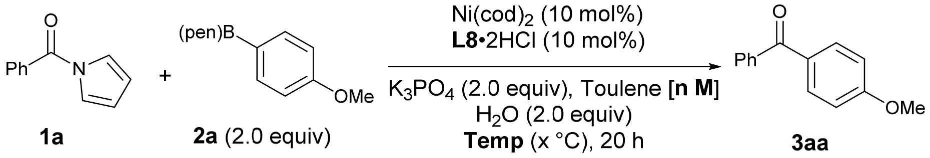


Entry	**base**	**solvent**	**additive** (x equiv)	Yield[a] of **3aa** (%)
1	Et_3N	Toluene	H_2O (2)	20
2	$Ba(OH)_2$	Toluene	H_2O (2)	34
3	LiCl	Toluene	H_2O (2)	36
4	Cs_2CO_3	Toluene	H_2O (2)	25
5	K_2CO_3	Toluene	H_2O (2)	16
6	**K_3PO_4**	**Toluene**	**H_2O (2)**	**96**
7	K_3PO_4	Toluene	H_2O (4)	96
8	K_3PO_4	Toluene	-	43
9	K_3PO_4	THF	H_2O (2)	20
10	K_3PO_4	DMF	H_2O (2)	4
11	K_3PO_4	1,4-dioxane	H_2O (2)	Trace
12	K_3PO_4	Toluene	H_3BO_3 (2)	0
13	K_3PO_4	Toluene	TMSOTf (2)	10
14	K_3PO_4	Toluene	4Å MS (2)	30

[a] Yields were determined by ^{1}H NMR analysis of crude mixture by using 1,3,5-trimethoxybenzene as an internal standard. Nep = neopentylglycol.

A vial packaged with tin foil was charged with **base** (0.48 mmol, equiv), *N*-acylpyrrole **1a** (41.1 mg, 0.24 mmol, 1.0 equiv), arylboronic acid neopentyl glycol ester **2a** (105.6 mg, 0.48 mmol, 2.0 equiv), **L8**·2HCl (16.2 mg, 0.024 mmol, 10 mol%) and a magnetic stir bar. Then the vial was taken into a glove box and charged with $Ni(COD)_2$ (6.6 mg, 0.024 mmol, 10 mol %). After that, **solvent (**0.48 mL, 0.5 M**)** and **additive** was added. The vial was sealed with screw cap, removed from the glove box, and stirred vigorously at 60 °C for 20 h. After cooling to room temperature, the mixture was diluted with CH_2Cl_2 (1 mL), washed with a saturated aqueous Na_2CO_3 solution (1mL) and brine (1 mL), and then dried over anhydrous Na_2SO_4. The combined organic layer was filtered and concentrated under reduced pressure. The residue was analyzed by ^{1}H NMR or purified by flash column chromatography to yield the desired ketone **3aa**.

Table S3. Optimisation of the Temp, concentration.

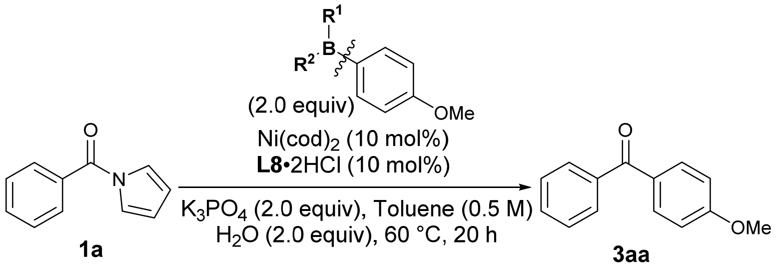


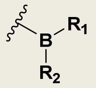
Entry	**Temp**	concentration **[n M]**	Yield[a] of **3aa**
1	**60 °C**	**0.50**	**96**
2	40 °C	0.50	75
3	RT	0.50	45
4	80 °C	0.50	96
5	60 °C	0.25	81
6	60 °C	1.00	65

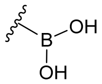
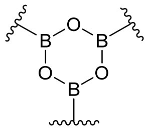
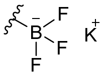
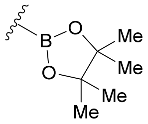
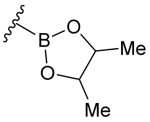
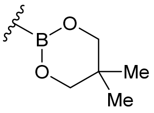
[a] Yields were determined by ^{1}H NMR analysis of crude mixture by using 1,3,5-trimethoxybenzene as an internal standard. RT = room temperature. Temp = temperature

A vial packaged with tin foil was charged with powdered K_3PO_4 (101.9 mg, 0.48 mmol, 2.0 equiv), *N*-acylpyrrole **1a** (41.1 mg, 0.24 mmol, 1.0 equiv), arylboronic acid neopentyl glycol ester **2a** (105.6 mg, 0.48 mmol, 2.0 equiv), **L8**·2HCl (16.2 mg, 0.024 mmol, 10 mol%) and a magnetic stir bar. Then the vial was taken into a glove box and charged with Ni(COD)$_2$ (6.6 mg, 0.024 mmol, 10 mol %). After that, toluene (**n M**) and water (8.6 uL, 0.48 mmol, 2.0 equiv) was added. The vial was sealed with screw cap, removed from the glove box, and stirred vigorously at **x °C** for 20 h. After cooling to room temperature, the mixture was diluted with CH_2Cl_2 (1 mL), washed with a saturated aqueous Na_2CO_3 solution (1 mL) and brine (1 mL), and then dried over anhydrous Na_2SO_4. The combined organic layer was filtered and concentrated under reduced pressure. The residue was analyzed by ^{1}H NMR or purified by flash column chromatography to yield the desired ketone **3aa**.

Table S4. Screening different organoboron compounds in the cross-coupling reactions of *N*-acylpyrrole **1a**.

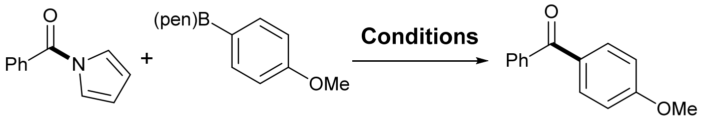


Entry		Yield[a] of **3aa** (%)

1		0
2		0
3		0
4		88
5		0
6		**96 (94[b])**

[a] Yields were determined by ^{1}H NMR analysis of crude mixture by using 1,3,5-trimethoxybenzene as an internal standard. [b] Isolated yields.

Table S5. Control experiments.



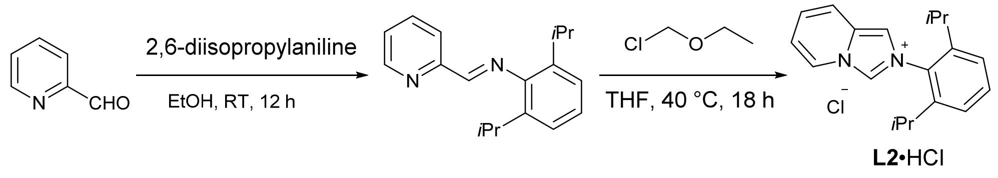
1a **2a** (2.0 equiv) **3aa**

Entry	**Conditions**	Yield[a] of **3aa** (%)
1	**L8**·2HCl (10 mol%), K_3PO_4 (2.0 equiv), H_2O (2.0 equiv) Toluene (0.5 M), 60 °C, 20 h	0
2	Ni(cod)$_2$ (10 mol%), K_3PO_4 (2.0 equiv), H_2O (2.0 equiv) Toluene (0.5 M), 60 °C, 20 h	0
3	Ni(cod)2 (10 mol%), **L8**·2HCl (10 mol%), H_2O (2.0 equiv) Toluene (0.5 M), 60 °C, 20 h	0
4	Ni(cod)2 (10 mol%), **L8**·2HCl (10 mol%), K_3PO_4 (2.0 equiv) Toluene (0.5 M), 60 °C, 20 h	43

[a] Yields were determined by ^{1}H NMR analysis of crude mixture by using 1,3,5-trimethoxybenzene as an internal standard.

2. Synthesis of the precursors of NHC Ligands (L2·HCl, L6–L8·2HCl, L9·4HBr)

(1) Synthesis of the precursor of NHC Ligand **L2**·HCl.



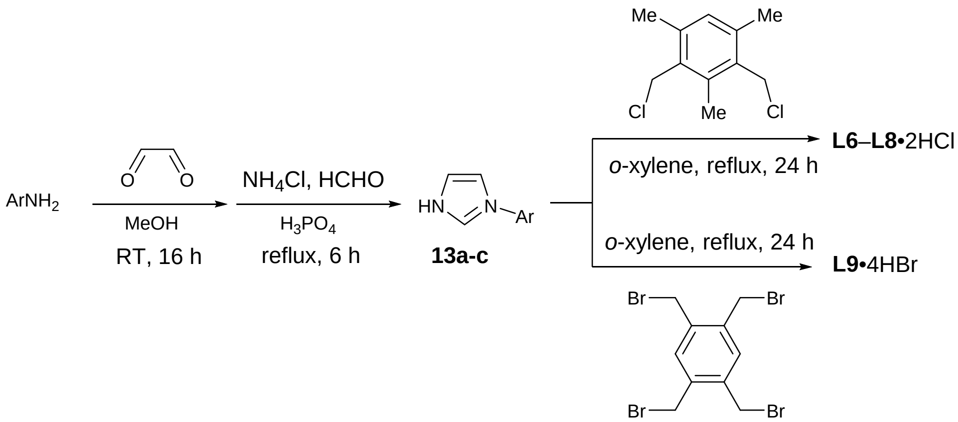
2-(2,6-Diisopropylphenyl)imidazo[1,5-a]pyridin-2-ium chloride (L2·HCl)

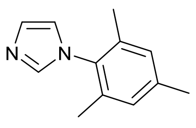
A reported procedure was followed.[4]

(a) A mixture containing 2,6-diisopropylaniline (3.8 mL, 20.0 mmol), picolinaldehyde (1.9 mL, 20.0 mmol) and EtOH (40.0 ml) was stirred at room temperature for 12 h. Then the reaction mixture was filtered, and the precipitate was washed with cold EtOH (10 mL), after dried in vacuum, gave the desired crude imine.

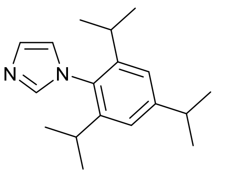
(b) Chloromethyl ethyl ether (2.1 mL, 22 mmol) was added dropwise to the solution of imine (prepared above) in THF (50.0 mL) under Argon. The reaction was stirred at 40 **°**C for 18 h. Then the mixture was dried under vacuum. The residue was purified by flash column chromatography (eluent: MeOH/CH_2Cl_2 = 1/5) and recrystallization from ethyl acetate to afforded desired product **L2**·HCl as a white solid (3.21 g, 51% Yield, over two steps). R_f: 0.4 (MeOH/CH_2Cl_2 = 1/3); mp: 218-220 °C; IR (film): 3054, 2962, 2920, 1651, 1601, 1542, 1467, 1385, 1365, 1325, 1093, 817, 761; ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.3 (s, 1H), 9.83 (s, *J* = 7.0 Hz, 1H), 7.80 (d, *J* = 9.5 Hz, 1H), 7.64 (s, 1H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.38-7.30 (m, 3H), 7.13 (t, *J* = 6.8 Hz, 1H), 2.13 (sept, *J* = 6.8 Hz, 2H), 1.23 (d, *J* = 6.8 Hz, 6H), 1.15 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (500 MHz, $CDCl_3$): δ 145.1 (2C), 132.0, 130.6, 130.1, 129.3, 126.5, 126.3, 124.6 (2C), 117.7, 117.4, 113.8, 28.7 (2C), 24.44 (2C), 24.37 (2C) ; HRMS (ESI) m/z calcd for $[C_{19}H_{23}N_2]^+$ (M-Cl^-): 279.1856; found: 279.1865.

(2) Synthesis of the precursors of NHC Ligands **L6**–**L8·2HCl, L9·4HBr**.

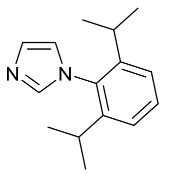




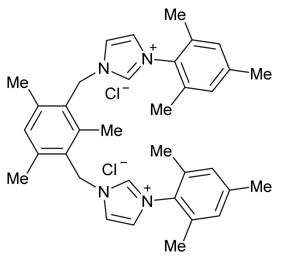
13a



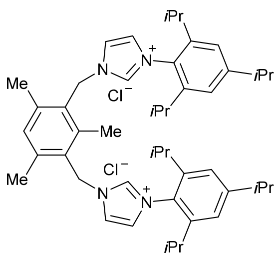
13b



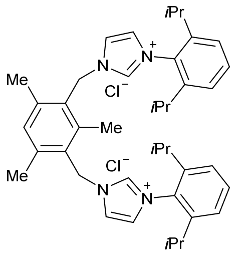
13c



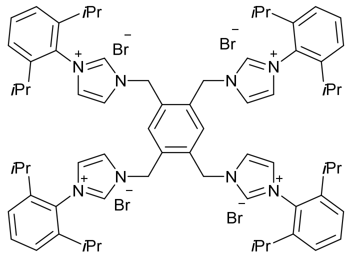
L6•2HCl



L7•2HCl



L8•2HCl



L9•4HBr

General procedure A for synthesis of the precursors of NHC Ligands L6–L8·2HCl, L9·4HBr from aromatic amines.

A reported procedure[5,6] with some modifications was followed.

(a) A solution of aromatic amines (50.0 mmol, 1.0 equiv) in MeOH (100.0 mL, 0.5 M) was added glyoxal (40% aq, 5.5 mL, 50.0 mmol, 1.0 equiv) at 0 °C and the reaction was stirred for 16 h at RT. Then NH_4Cl (5.35 g, 100.0 mmol, 2.0 equiv) was added followed by formaldehyde (37% aq, 7.5 mL, 100.0 mmol, 2.0 equiv). The mixture was diluted with MeOH (200 mL, 0.25 M) and the resulting mixture was refluxed for 1 h. After that, H_3PO_4 (85%, 4.6 mL, 75.0 mmol, 1.5 equiv) was added over a period of 10 mins. The resulting mixture was then reflux for a further 5 h. The reaction was monitored by TLC. After removal of the solvent, the dark residue was poured into ice and neutralized with aq 40% KOH solution until pH 9. The resulting mixture was extracted with Et_2O (5×70 mL). The combined organic layer was washed with H_2O (60 mL) and brine (60 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: EtOAc/Hexane = 1/5) affording the desired 1-arylimidazole **13**.

(b) A mixture containing 1-arylimidazole **13** (20.0 mmol, 1.0 equiv), 2,4-bis(chloromethyl)-1,3,5-trimethylbenzene (2.17 g, 10.0 mmol, 0.5 equiv) or 1,2,4,5-tetrakis(bromomethyl)benzene (2.25 g, 5.0 mmol, 0.25 equiv) and *o*-xylene (100.0 mL, 0.2 M) was refluxed for 24 h. The reaction was monitored by TLC. After removal of the solvent, the residue was purified by flash column chromatography to afford crude product. Then the crude product was recrystallization from ethyl acetate to afford the desired precursor of NHC ligand.

1,1'-((2,4,6-Trimethyl-1,3-phenylene)bis(methylene))bis(3-mesityl-1*H*-imidazol-3-ium) chloride (L6·2HCl)

Following **general procedure A-(a)**, the reaction of 2,4,6-trimethylaniline (7.02 mL, 50.0 mmol) with glyoxal (40% aq, 5.5 mL, 50.0 mmol), NH_4Cl (5.35 g, 100.0 mmol) and formaldehyde (37% aq, 7.5 mL, 100.0 mmol), afforded 1-arylimidazole **13a** as a yellow solid (4.10 g, 44% Yield), Rf: 0.3 (EtOAc/Hexane = 1/5). The spectral data were identical with those reported in the literature.[5]

Following **general procedure A-(b)**, the reaction of 1-Arylimidazole **13a** (3.73 g, 20.0 mmol) with 2,4-bis(chloromethyl)-1,3,5-trimethylbenzene (2.17 g, 10.0 mmol), afforded **L6**·2HCl as a light yellow solid (4.36 g, 74% Yield). R_f: 0.4 ($MeOH/CH_2Cl_2$ = 1/3); mp: the compound decomposed at 275 °C; IR (film): 2969, 1653, 1635, 1607, 1544, 1486, 1456, 1384, 1266, 1195, 1180, 1156, 1142, 1075, 1036, 969, 855, 730 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 10.63 (s, 2H), 8.08 (s, 2H), 7.18 (t, *J* = 1.73 Hz, 2H), 7.00 (br s, 2H), 6.99 (s, 2H), 6.95 (s, 1H), 6.07 (s, 4H), 2.47 (s, 3H), 2.34 (s, 6H), 2.33 (s, 6H), 2.06 (s, 6H), 2.05 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.1 (2C), 140.1 (2C), 138.9, 137.7 (2C), 134.1 (4C), 131.8 (2C), 130.8 (2C), 129. 8 (4C), 128.3, 123.8 (2C), 123.6 (2C), 48.4 (2C), 21.1 (2C), 20.1 (2C), 17.6 (4C), 16.7; HRMS (ESI) *m/z* calcd for $[C_{35}H_{42}ClN_4]^+$ ($M-Cl^-$): 553.3093; found: 553.3096.

1,1'-((2,4,6-Trimethyl-1,3-phenylene)bis(methylene))bis(3-(2,4,6-triisopropylphenyl)-1*H*-imidazol-3-ium) chloride (L8·2HCl)

Following **general procedure A-(a)**, the reaction of 2,4,6-triisopropylaniline (10.97 g, 50.0 mmol) with glyoxal (40% aq, 5.5 mL, 50.0 mmol), NH_4Cl (5.35 g, 100.0 mmol) and formaldehyde (37% aq, 7.5 mL, 100.0 mmol), afforded 1-Arylimidazole **13b** as a light yellow solid (6.76 g, 50% Yield). R_f: 0.3 (EtOAc/Hexane = 1/5); mp: 186-188 °C; IR (film): 3112, 3095, 2919, 2850, 1643, 1608, 1499, 1470, 1313, 1298, 1281, 1238, 1096, 1066, 909, 776 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.45 (s, 1H), 7.22 (s, 1H), 7.08 (s, 2H), 6.93 (s, 1H), 2.95 (sept, *J* = 6.9 Hz, 1H), 2.39 (sept, *J* = 6.9 Hz, 2H), 1.29 (d, *J* = 6.9 Hz, 6 H), 1.13 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (500 MHz, $CDCl_3$): δ 150.4, 146.2 (2C), 138.7, 130.7, 129.3, 121.7 (3C), 34.4, 28.2 (2C), 24.5 (2C), 24.4 (2C), 24.1 (2C); HRMS (ESI) *m/z* calcd for $[C_{18}H_{27}N_2]^+$ ($M+H^+$): 271.2169; found: 271.2177.

Following **general procedure A-(b)**, the reaction of 1-Arylimidazole **13b** (5.41 g, 20.0 mmol) with 2,4-bis(chloromethyl)-1,3,5-trimethylbenzene (2.17 g, 10.0 mmol), afforded **L8**·2HCl as a white solid (5.38 g, 71% Yield). R_f: 0.4 ($MeOH/CH_2Cl_2$ = 1/3); mp: 115-117 °C; IR (film): 2963, 2928, 2870, 1603, 1543, 1462, 1385, 1366, 1265, 1196, 1179, 1142, 1129, 1103, 1075, 1052, 962, 878, 731 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 10.56 (s, 2H), 8.21 (s, 2H), 7.18 (t, *J* = 1.8 Hz, 2H), 7.11 (s, 4H), 6.93 (s, 1H), 6.14 (s, 4H), 2.95 (sept, *J* = 6.8 Hz, 2H), 2.58 (s, 3H), 2.34 (s, 6H), 2.26 (sept, *J* = 6.8 Hz, 4H), 1.28 (d, *J* = 6.8 Hz, 12H), 1.24 (d, *J* = 6.8 Hz, 12H), 1.15 (d, *J* = 6.8 Hz, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.6 (2C), 145.0 (4C), 140.1 (2C), 138.6, 138.2 (2C), 131.8 (2C), 128.5 (2C), 128.0, 125.0 (2C), 123.6 (2C), 122.5 (4C), 48.4 (2C), 34.5 (2C), 28.7 (4C), 24.6 (4C), 24.1 (4C), 23.9 (4C), 20.0 (2C), 16.8; HRMS (ESI) *m/z* calcd for $[C_{47}H_{66}ClN_4]^+$ ($M-Cl^-$): 721.4971; found: 721.4967.

1,1'-((2,4,6-Trimethyl-1,3-phenylene)bis(methylene))bis(3-(2,6-diisopropylphenyl)-1*H*-imidazol-3-ium) chloride (L8·2HCl)

Following **general procedure A-(a)**, the reaction of 2,6-triisopropylaniline (9.43 mL, 50.0

mmol) with glyoxal (40% aq, 5.5 mL, 50.0 mmol), NH_4Cl (5.35 g, 100.0 mmol) and formaldehyde (37% aq, 7.5 mL, 100.0 mmol), afforded 1-Arylimidazole **13c** as a yellow solid (5.14 g, 45% Yield), R_f: 0.3 (EtOAc/Hexane = 1/5). The spectral data were identical with those reported in the literature.[5]

Following **general procedure A-(b)**, the reaction of 1-Arylimidazole **13c** (5.41 g, 20.0 mmol) with 2,4-bis(chloromethyl)-1,3,5-trimethylbenzene (2.17 g, 10.0 mmol), afforded **L8**·2HCl as a white solid (4.85 g, 72% Yield). R_f: 0.4 ($MeOH/CH_2Cl_2$ = 1/3); mp: 174-176 °C. IR (film): 2963, 2927, 2870, 1657, 1640, 1606, 1546, 1460, 1451, 1385, 1242, 1180, 1142, 1113, 1075, 876, 806, 760, 672, 628 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 10.64 (s, 2H), 8.58 (br s, 2H), 7.52 (t, J = 7.7 Hz, 2H), 7.31-7.29 (m, 2H), 7.28 (br s, 2H), 7.21-7.17 (m, 2H), 6.88 (s, 1H), 6.13 (s, 4H), 2.62 (s, 3H), 2.32 (s, 6H), 2.28 (sept, J = 6.6 Hz, 4H), 1.24 (d, J = 6.6 Hz, 12H), 1.15 (d, J = 6.8 Hz, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.3 (4C), 140.1 (2C), 138.6, 138.1 (2C), 131.9 (2C), 131.8, 130.3 (2C), 128.4 (2C), 124.9 (2C), 124.6 (4C), 124.2 (2C), 48.4 (2C), 28.7 (4C), 24.6 (4C), 24.1 (4C), 20.0 (2C), 17.0; HRMS (ESI) *m/z* calcd for $[C_{41}H_{54}ClN_4]^+$ ($M-Cl^-$): 637.4032; found: 637.4030.

1,1',1'',1'''-(Benzene-1,2,4,5-tetrayltetrakis(methylene))tetrakis(3-(2,6-diisopropylphenyl)-1H-imidazol-3-ium) bromide (L9·4HBr)

Following **general procedure A-(b)**, the reaction of 1-Arylimidazole **13c** (5.41 g, 20.0 mmol) with 1,2,4,5-tetrakis(bromomethyl)benzene (2.25 g, 5.0 mmol), afforded **L9**·4HBr as a white solid (4.63 g, 68% Yield). R_f: 0.4 ($MeOH/CH_2Cl_2$ = 1/3); mp: 174-176 °C. IR (film): 2964, 2870, 1591, 1545, 1461, 1385, 1367, 1274, 1180, 1142, 1116, 1074, 958, 937, 805, 758, 731, 672 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 10.69 (s, 4H), 9.06 (t, J = 1.6 Hz, 4H), 8.44 (s, 2H), 7.54 (t, J = 7.8 Hz, 4H), 7.32 (d, J = 7.8 Hz, 8H), 7.18 (t, J = 1.7 Hz, 4H), 6.54 (s, 8H), 2.31 (sept, J = 6.7 Hz, 8H), 1.26 (d, J = 6.8 Hz, 24H), 1.20 (d, J = 6.8 Hz, 24H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.4 (8C), 137.6 (4C), 134.7 (4C), 134.5 (4C), 132.1 (4C), 130.0 (2C), 125.4 (4C), 124.8 (8C), 124.5 (4C), 49.4 (4C), 28.9 (8C), 24.6 (8C), 24.1 (8C); HRMS (ESI) *m/z* calcd for $[C_{70}H_{90}Br_3N_8]^+$ ($M-Br^-$) : 1283.4798; found 1283.4913.

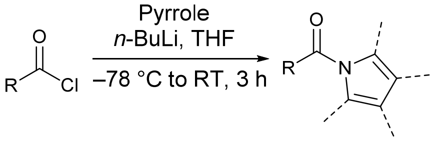
3. Amides 1a–1t, 7–11,

The known amides **1a**[7a], **1b**[7b], **1f**[7c], **1h**[7d], **1i**[7e], **1j**[7b], **1p**[7c], **1t**[7b], **7**[7f], **8**[7f] were synthesized according to **general procedures B**, while **9**[7g] were synthesized according to **general procedures D**. The known amides **10**[7h], **11**[7i] were synthesized according to literature procedure.[7h]

The unknown amides **1c**–**e**, **1g**, **1q**–**s** were synthesized according to **general procedures B**, and the unknown amides **1n**–**o** were synthesized according to **general procedures C**. Meanwhile, the unknown amides **1k**–**m** were synthesized according to specific procedure as follows.

General procedure B for synthesis of *N*-acylpyrroles from acyl chlorides.

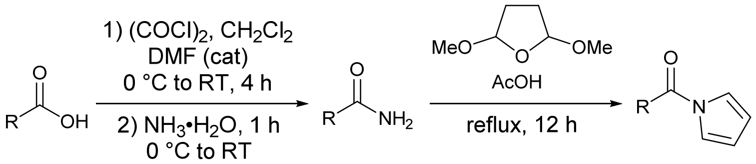
A previously published procedure was followed.[7j]



To a stirred solution of pyrrole (0.38 mL, 7.5 mmol, 1.5 equiv) in THF (10.0 mL) maintained at –78 °C under Argon was added dropwise *n*-BuLi (2.4 M in hexane, 3.1 mL, 1.5 equiv) and the solution was then stirred for 10 mins. After that, a solution of acyl chloride (5.0 mmol, 1.0 equiv) in THF (10.0 mL) was added. Then the reaction was slowly warmed to room temperature and stirred overnight. The reaction was diluted with EtOAc (10 mL), and washed with a saturated aqueous $NaHCO_3$ solution (10 mL) and brine (10 mL), and then dried over anhydrous Na_2SO_4. The organic layer was filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography to afford the desired *N*-acylpyrrole.

General procedure C for synthesis of *N*-acylpyrroles from primary amides.

A previously published procedure was followed.[7k]

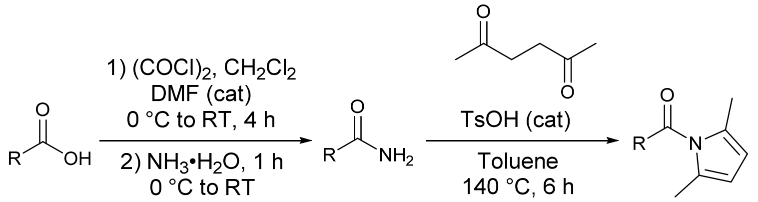


(1) (a): Oxalyl chloride (0.85 mL, 10.0 mmol, 2.0 equiv) and a catalytic amount of DMF were added to a stirred solution of the corresponding carboxylic acid (5.0 mmol, 1.0 equiv) in CH_2Cl_2 (10.0 mL, 0.5 M) at 0 °C. The mixture was allowed to stir at room temperature for 4 h, then the reaction mixture was concentrated to give the acyl chloride. (b): A solution of acyl chloride (prepared above) in anhydrous CH_2Cl_2 (10.0 mL, 0.5 M) was added dropwise to an aqueous ammonia solution (25%, 7.7 mL, 50.0 mmol, 10.0 equiv) at 0 °C. After stirring for 1 h, the precipitate was collected by suction-filtration, washed with water and *n*-hexane, and dried under reduced pressure. The crude solid was recrystallization from ethyl acetate to afford the desired primary amide.

(2) A mixture of primary amide (prepared above), 2,5-dimethoxytetrahydrofuran (1.3 mL, 10.0 mmol, 2.0 equiv) in AcOH (10.0 mL, 0.5 M) was reflux for 12 h. Then the mixture was cooled, poured into ice, neutralized with $NaHCO_3$, and extracted with EtOAc (10 mL×3). The combined organic layer was filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography to yield the desired *N*-acylpyrrole.

General procedure D for synthesis of *N*-benzoyl(2,5-dimethyl)pyrrole from primary amides.

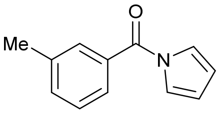
A previously published procedure was followed.[7l]



(1) (a): Oxalyl chloride (0.85 mL, 10.0 mmol, 2.0 equiv) and a catalytic amount of DMF were added to a stirred solution of the corresponding carboxylic acid (5.0 mmol, 1.0 equiv) in CH_2Cl_2 (10.0 mL, 0.5 M) at 0 °C. The mixture was allowed to stir at room temperature for 4 h, then the reaction mixture was concentrated to give the acyl chloride. (b): A solution of acyl chloride (prepared above) in anhydrous CH_2Cl_2 (10.0 mL 0.5 M) was added dropwise to an aqueous ammonia solution (25%, 7.7 mL, 50.0 mmol, 10.0 equiv) at 0 °C. After stirring for 1 h, the precipitate was collected by suction-filtration, washed with water and *n*-hexane, and dried under reduced pressure. The crude solid was recrystallization from ethyl acetate to afford the desired primary amide.

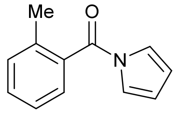
(2) A mixture of primary amide (prepared above), hexane-2,5-dione (1.3 mL, 11.0 mmol, 2.2 equiv) and TsOH·H_2O (95.1 mg, 0.5 mmol, 0.1 equiv) in Toluene (10.0 mL, 0.5 M) was stirred at 140 °C for 12 h. Then the mixture was cooled, poured into ice, neutralized with $NaHCO_3$, and extracted with EtOAc (10 mL×3). The combined organic layer was filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography to yield the desired *N*-benzoyl(2,5-dimethyl)pyrrole.

(1*H*-Pyrrol-1-yl)(*m*-tolyl)methanone (1c)



Following **general procedure B**, the reaction of 3-methylbenzoyl chloride (0.66 mL, 5.0 mmol) with pyrrole (0.38 mL, 7.5 mmol), afforded the *N*-acylpyrrole **1c** as a light yellow oil (759.3 mg, 82% Yield). R$_f$: 0.5 (EtOAc/Hexane = 1/20); IR (film): 2923, 1698, 1605, 1586, 1543, 1466, 1422, 1400, 1331, 1304, 1160, 1087, 1074, 1045, 917, 825, 812, 791, 737, 672 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.56 (s, 1H), 7.52 (dt, *J* = 7.2, 1.8 Hz, 1H), 7.43-7.34 (m, 2H), 7.28 (t, *J* = 2.3 Hz, 2H), 6.34 (t, *J* = 2.3 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 168.0, 138.5, 133.3, 133.1, 130.1, 128.4, 126.7, 121.4 (2C), 113.1 (2C), 21.4; HRMS (ESI) *m/z* calcd for $[C_{12}H_{11}NNaO]^+$ (M+Na$^+$): 208.0733; found: 208.0736.

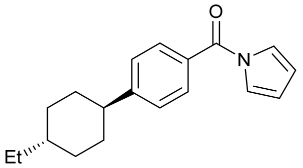
(1*H*-Pyrrol-1-yl)(*o*-tolyl)methanone (1d)



Following **general procedure B**, the reaction of 2-methylbenzoyl chloride (0.65 mL, 5.0 mmol) with pyrrole (0.38 mL, 7.5 mmol), afforded the *N*-acylpyrrole **1d** as a yellow oil (657.5 mg, 71% Yield). R$_f$: 0.5 (EtOAc/Hexane = 1/20); IR (film): 2926, 1706, 1603, 1544, 1467, 1399, 1329, 1305, 1255, 1084, 1073, 882, 796, 777, 738, 664 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.42 (td, *J* = 7.5, 1.2 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.32-7.26 (m, 2H), 7.14 (t, *J* = 2.3 Hz, 2H), 6.31 (t, *J*

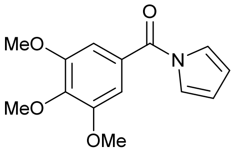
= 2.3 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): *δ* 168.3, 136.5, 133.8, 130.9, 130.8, 127.9, 125.6, 120.7 (2C), 113.5 (2C), 19.4; HRMS (ESI) *m/z* calcd for $[C_{12}H_{11}NNaO]^+$ (M+Na$^+$): 208.0733; found: 208.0736.

(4-((1*R*,4*R*)-4-Ethylcyclohexyl)phenyl)(1*H*-pyrrol-1-yl)methanone (1e)



Following **general procedure C**, the reaction of 4-((1*R*,4*R*)-4-ethylcyclohexyl) benzoic acid (1.16 g, 5.0 mmol), with an aqueous ammonia solution (25%, 7.7 mL, 50.0 mmol) and pyrrole (0.38 mL, 7.5 mmol), afforded the *N*-acylpyrrole **1e** as a white solid (872.3 mg, 62% Yield, over two steps). R$_f$: 0.5 (EtOAc/Hexane = 1/20); mp: 51-53 °C; IR (film): 2959, 2921, 2851, 1697, 1608, 1466, 1448, 1415, 1400, 1331, 1299, 1255, 1180, 1088, 1073, 884, 846, 766, 741, 720, 680 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): *δ* 7.68 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.30 (t, *J* = 2.3 Hz, 2H), 6.34 (t, *J* = 2.4 Hz, 2H), 2.56 (tt, *J* = 12.1, 3.3 Hz, 1H), 1.96-1.88 (m, 4H), 1.48 (qd, *J* = 12.7, 3.3 Hz, 2H), 1.32-1.24 (m, 2H), 1.24-1.18 (m, 1H), 1.12-1.02 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): *δ* 167.8, 152.9, 130.7, 129.9 (2C), 127.1 (2C), 121.4 (2C), 112.9 (2C), 44.8, 39.1, 34.1 (2C), 33.1 (2C), 30.0, 11.6; HRMS (ESI) *m/z* calcd for $[C_{19}H_{23}NNaO]^+$ (M+Na$^+$): 304.1672; found: 304.1674; $[\alpha]_D^{20}$ −0.36 (*c* 1.0, CHCl$_3$).

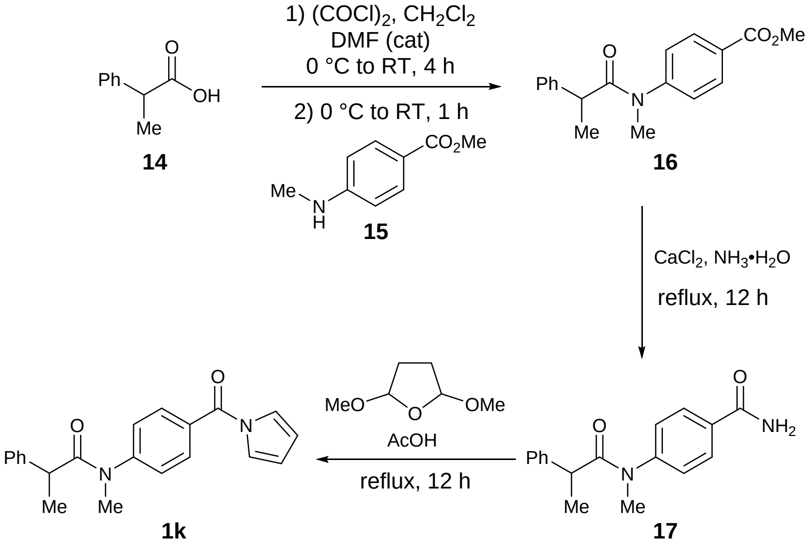
(1*H*-Pyrrol-1-yl)(3,4,5-trimethoxyphenyl)methanone (1g)



Following **general procedure B**, the reaction of 3,4,5-trimethoxybenzoyl chloride (1.15 g, 5.0 mmol) with pyrrole (0.38 mL, 7.5 mmol), afforded the *N*-acylpyrrole **1g** as a white solid (914.6 mg, 70% Yield). R$_f$: 0.4 (EtOAc/Hexane = 1/10); mp: 89-91 °C; IR (film): 3138, 3112, 2944, 2829, 1681, 1586, 1503, 1466, 1454, 1417, 1404, 1351, 1311, 1292, 1240, 1155, 1126, 1102, 995, 935, 812, 761, 742 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): *δ* 7.32 (t, *J* = 2.2 Hz, 2H), 7.00 (s, 2H), 6.36 (t, *J* = 2.2 Hz, 2H), 3.94 (s, 3H), 3.90 (s, 6H); ^{13}C NMR (125 MHz, CDCl$_3$): *δ* 167.2, 153.1 (2C), 141.6, 128.1, 121.4 (2C), 113.1 (2C), 107.2 (2C), 61.0, 56.4 (2C); HRMS (ESI) *m/z* calcd for $[C_{14}H_{15}NNaO_4]^+$ (M+Na$^+$): 284.0893; found: 284.0894.

Synthesis of *N*-acylpyrrole **1m** from 2-phenylpropanoic acid **14**.

***N*-(4-(1*H*-Pyrrole-1-carbonyl)phenyl)-*N*-methyl-2-phenylpropanamide (1k)**



(1) (a) Oxalyl chloride (0.34 mL, 4.0 mmol) and a catalytic amount of DMF were added to a stirred solution of the corresponding carboxylic acid **14** (300.0 mg, 2.0 mmol) in CH_2Cl_2 (4.0 mL) at 0 °C. The mixture was allowed to stir at room temperature for 4 h, then the reaction mixture was concentrated to give the acyl chloride. (b): A solution of acyl chloride prepared above in anhydrous CH_2Cl_2 (4.0 mL) was added dropwise to a solution of Methyl 4-(methylamino)benzoate (496.0 mg, 3.0 mmol) in CH_2Cl_2 (4.0 mL) at 0 °C. After stirring for 1 h, the precipitate was collected by suctionfiltration, washed with water (5 mL) and *n*-hexane (4×2 mL), and dried under reduced pressure. The crude product was purified by flash column chromatography (eluent: EtOAc/Hexane = 1/5) to yield the desired amide **16** as a light yellow oil (481.6 mg, 81% Yiled). R_f: 0.4 (EtOAc/Hexane = 1/5); IR (film): 3027, 2930, 1724, 1663, 1603, 1507, 1492, 1452, 1435, 1376, 1331, 1279, 1114, 1101, 1021, 747, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.01 (d, J = 8.1 Hz, 2H), 7.25-7.15 (m, 3H), 7.06 (d, J = 7.1 Hz, 2H), 7.01 (d, J = 7.1 Hz, 2H), 3.94 (s, 3H), 3.63 (s, 1H), 3.25 (s, 3H), 1.40 (d, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.8, 166.3, 148.0, 141.6, 131.0 (2C), 128.6 (2C), 127.8 (2C), 127.5 (2C), 126.9 (2C), 52.4, 43.6, 37.7, 20.5; HRMS (ESI) *m/z* calcd for $[C_{18}H_{19}NNaO_3]^+$ ($M+Na^+$): 320.1257; found: 320.1258.

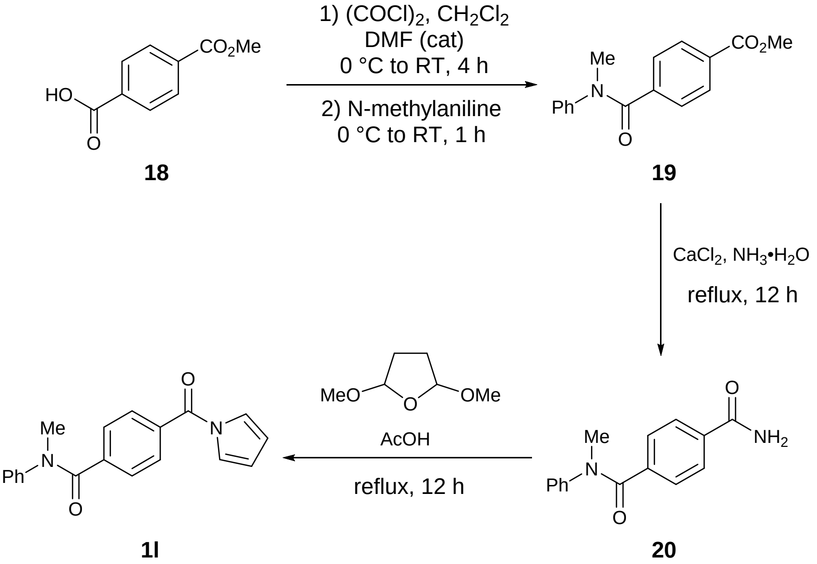
(2) To a reaction vessel equipped with a magnetic stir bar under Argon were added the substrate amide **16** (prepared above), $CaCl_2$ (179.8 mg, 1.62 mmol), and NH_3 (7 N in MeOH, 2.3 mL). The reaction vessel is sealed and heated at 80 °C for 24 h. Then the reaction mixture is concentrated and the residue is treated with saturated NH_4Cl solution (2.4 mL) and H_2O (2.4 mL). The resulting mixture is adjusted to pH 5 with 2N HCl and the mixture is stirred for 20 min to dissolve Ca salts, after which the precipitated amide is filtered, washed with H_2O (4 mL), and dried. The resulting crude primary amide was used in the next step without further purification.

(3) A mixture of primary amide **17** (prepared above), 2,5-dimethoxytetrahydrofuran (0.42 mL, 3.24 mmol) in AcOH (3.2 mL) was reflux for 12 h. The mixture was cooled, poured into ice, neutralized with $NaHCO_3$, and extracted with EtOAc (4 mL×2). The combined

organic layer was filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (eluent: EtOAc/Hexane = 1/5) to yield the desired *N*-acylpyrrole **1k** as a light oil (251.4 mg, 51% Yield, over two steps). R_f: 0.5 (EtOAc/Hexane = 1/5); IR (film): 2970, 2930, 2870, 1698, 1663, 1603, 1509, 1492, 1467, 1401, 1375, 1331, 1123, 1090, 1074, 1022, 976, 881, 857, 804, 771, 746, 701 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, *J* = 7.7 Hz, 2H), 7.28 (t, *J* = 2.3 Hz, 2H), 7.25-7.17 (m, 3H), 7.12 (d, *J* = 7.3 Hz, 2H), 7.02 (d, *J* = 7.3 Hz, 2H), 6.39 (t, *J* = 2.3 Hz, 2H), 3.29 (s, 3H), 1.66-1.57 (m, 1H), 1.43 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.6, 166.7, 147.3, 141.6 (2C), 130.7 (2C), 128.6 (2C), 127.8 (2C), 127.4 (2C), 126.9, 121.2 (2C), 113.5 (2C), 43.8, 37.7, 20.5; HRMS (ESI) *m/z* calcd for $[C_{21}H_{20}N_2NaO_2]^+$ (M+Na$^+$): 355.1417; found: 355.1421.

Synthesis of *N*-acylpyrrole **1n** from 4-(methoxycarbonyl)benzoic acid **18**:

N-Methyl-*N*-phenyl-4-(1*H*-pyrrole-1-carbonyl)benzamide (1l)



(1) (a) Oxalyl chloride (0.34 mL, 4.0 mmol) and a catalytic amount of DMF were added to a stirred solution of the corresponding carboxylic acid **18** (360.4 mg, 2.0 mmol) in CH_2Cl_2 (4.0 mL) at 0 °C. The mixture was allowed to stir at room temperature for 4 h, then the reaction mixture was concentrated to give the acyl chloride. (b): A solution of acyl chloride prepared above in anhydrous CH_2Cl_2 (4.0 mL) was added dropwise to a solution of *N*-methylaniline (0.33 mL, 3.0 mmol) in CH_2Cl_2 (4.0 mL) at 0 °C. After stirring for 1 h, the precipitate was collected by suctionfiltration, washed with water (5 mL) and *n*-hexane (4×2 mL), and dried under reduced pressure. The crude solid was recrystallization from ethyl acetate to afford the desired amide **19** as a white solid (447.0 mg, 83% Yield). R_f: 0.5 (EtOAc/Hexane = 1/5); mp: 113-115 °C; IR (film): 3061, 2951, 1723, 1644, 1595, 1496, 1435, 1371, 1279, 1108, 1020, 865, 771, 736, 723, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.22 (t, *J* = 7.7 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 7.7 Hz, 2H), 3.86 (s, 3H), 3.51 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$): δ 169.8, 166.4, 144.3, 140.3, 130.9, 129.4 (2C), 129.1 (2C), 128.6 (2C), 127.0

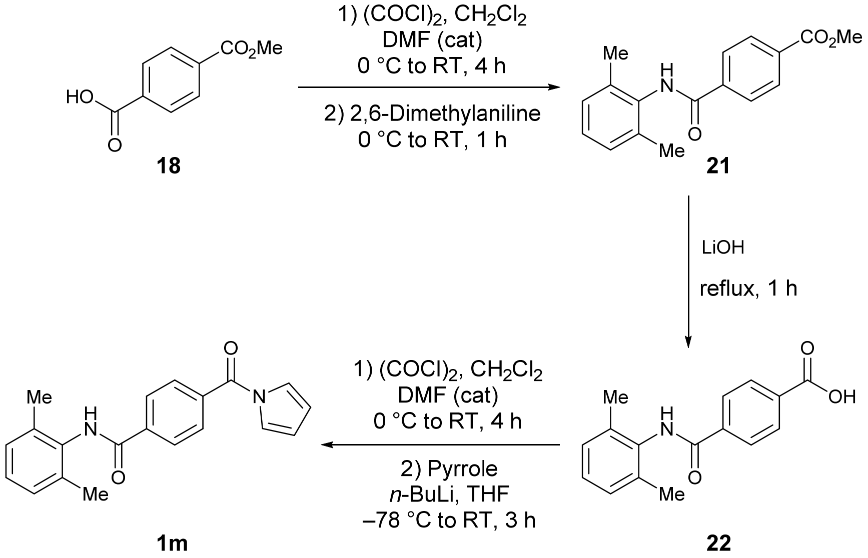
(3C), 52.3, 38.4; MS (ESI) *m/z* 270 ($M+H^+$, 100%).

(2) To a reaction vessel equipped with a magnetic stir bar under Argon were added the amide **19** (prepared above), $CaCl_2$ (184.0 mg, 1.66 mmol) and NH_3 (7 N in MeOH, 2.4 mL). The reaction vessel is sealed and heated at 80 °C for 24 h. Then the reaction mixture is concentrated and the residue is treated with saturated NH_4Cl (2.5 mL) solution and H_2O (2.5 mL). The resulting mixture is adjusted to pH 5 with 2N HCl and the mixture is stirred for 20 min to dissolve Ca salts, after which the precipitated amide is filtered, washed with H_2O (4 mL), and dried. The resulting crude primary amide was used in the next step without further purification.

(3) A mixture of primary amide **20** (prepared above), 2,5-dimethoxytetrahydrofuran (0.4 mL, 3.32 mmol) in AcOH (3.3 mL) was reflux for 12 h. The mixture was cooled, poured into ice, neutralized with $NaHCO_3$, and extracted with EtOAc (4 mL×2). The combined organic layer was filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (eluent: EtOAc/Hexane = 1/5) to yield the desired *N*-acylpyrrole **1l** as a white solid (252.6 mg, 50% Yield, over two steps). R_f: 0.5 (EtOAc/Hexane = 1/5); mp: 112-114 °C; IR (film): 3060, 2927, 1697, 1644, 1595, 1564, 1495, 1467, 1403, 1371, 1331, 1301, 1196, 1176, 1090, 1075, 1030, 975, 886, 871, 856, 743, 700, 574 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.25 (t, *J* = 7.6 Hz, 2H), 7.20-7.12 (m, 3H), 7.05 (d, *J* = 7.6 Hz, 2H), 6.31 (d, *J* = 2.3 Hz, 2H), 3.53 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.4, 167.0, 144.3, 139.8, 134.0, 129.5 (2C), 129.0 (2C), 128.7 (2C), 127.2, 127.0 (2C), 121.2 (2C), 113.4 (2C), 38.4; HRMS (ESI) *m/z* calcd for $[C_{19}H_{16}N_2NaO_2]^+$ ($M+Na^+$): 327.1104; found: 327.1103.

Synthesis of *N*-acylpyrrole **1o** from 4-(methoxycarbonyl)benzoic acid **18**.

N-(2,6-Dimethylphenyl)-4-(1*H*-pyrrole-1-carbonyl)benzamide (1m)

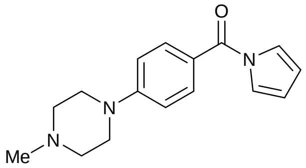


(a) Oxalyl chloride (0.34 mL, 4.0 mmol) and a catalytic amount of DMF were added to a stirred solution of the corresponding carboxylic acid **18** (360.4 mg, 2.0 mmol) in CH_2Cl_2 (4.0 mL) at 0 °C. The mixture was allowed to stir at room temperature for 4 h, then the reaction mixture was concentrated to give the acyl chloride. (b): A solution of acyl chloride prepared above in anhydrous CH_2Cl_2 (4.0 mL) was added dropwise to a solution of 2,6-Dimethylaniline (0.37 mL, 3.0 mmol) in CH_2Cl_2 (4.0 mL) at 0 °C. After stirring for 1 h, the precipitate was collected by suctionfiltration, washed with water (5 mL) and *n*-hexane (5 mL), and dried under reduced pressure. The crude solid was recrystallization from ethyl acetate to afford the desired amide **21** as a light yellow solid (425.0 mg, 75% Yield). R_f: 0.5 (EtOAH c/Hexane = 1/5); mp: 192-194 °C; IR (film): 3097, 2953, 2919, 1721, 1645, 1613, 1572, 1529, 1497, 1439, 1283, 1193, 1123, 1110, 1016, 821, 777, 730 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.2 Hz, 2H), 7.95 (d, *J* = 8.2 Hz, 2H), 7.59 (s, 1H), 7.18-7.09 (m, 3H), 3.96 (s, 3H), 2.26 (s, 6H); ^{13}C NMR (500 MHz, $CDCl_3$): δ 166.3, 165.2, 138.4, 135.6 (2C), 133.6, 133.0, 130.1 (2C), 128.4 (2C), 127.7, 127.3 (2C), 52.5, 18.5 (2C); HRMS (ESI) *m/z* calcd for $[C_{17}H_{17}NNaO_3]^+$ (M+Na$^+$): 306.1101; found: 306.1100.

(2) A solution of LiOH (96 mg, 3.0 mmol) in water (15.0 mL) was added to the solution of amide **21** (prepared above) in THF (15.0 mL). After refluxing for 1 h, the reaction mixture was adjusted to acidic by 2N HCl, and then extracted with EtOAc (15 mL×3). The organic phase was concentrated under reduced pressure. The resulting crude carboxylic acid **22** was used in the next step without further purification.

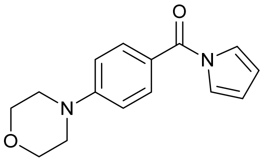
(3) (a) Oxalyl chloride (0.34 mL, 3.0 mmol) and a catalytic amount of DMF were added to a stirred solution of the corresponding carboxylic acid **22** (prepared above) in CH_2Cl_2 (4.0 mL) at 0 °C. The mixture was allowed to stir at room temperature for 4 h, then the reaction mixture was concentrated to give the acyl chloride. b): To a stirred solution of pyrrole (0.16 mL, 2.3 mmol) in THF (3.0 mL) maintained at –78 °C under Argon was added dropwise *n*-BuLi (2.4 M in hexane, 1.0 mL) and the solution was then stirred for 10 mins. After that, a solution of acyl chloride (prepared above) in THF (3.0 mL) was added. Then the reaction was slowly warmed to room temperature, and stirred overnight. The reaction was diluted with EtOAc (5 mL), and washed with a saturated aqueous $NaHCO_3$ solution (5 mL) and brine (5 mL), and then dried over anhydrous Na_2SO_4. The organic layer was filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: EtOAc/Hexanes = 1/5) to yield the desired *N*-acylpyrrole **1m** as a white solid (195.8 mg, 41% Yield, over two steps). R_f: 0.5 (EtOAc/Hexane = 1/5); mp: The compound decomposed at 194 °C; IR (film): 2923, 2853, 1698, 1648, 1522, 1495, 1467, 1403, 1332, 1301, 1196, 1132, 1088, 1076, 1019, 881, 771, 730 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.03 (d, *J* = 7.9 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.62 (s, 1H), 7.27 (t, *J* = 2.3 Hz, 2H), 7.20-7.09 (m, 3H), 6.39 (t, *J* = 2.3 Hz, 2H), 2.29 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.9, 164.9, 137.8, 136.3, 135.6, 133.6, 129.8 (2C), 128.5 (2C), 127.8 (2C), 127.5 (2C), 121.2 (2C), 113.8 (2C), 18.5 (2C); HRMS (ESI) *m/z* calcd for $[C_{20}H_{18}N_2NaO_2]^+$ (M+Na$^+$): 341.1261; found: 341.1265.

(4-(4-Methylpiperazin-1-yl)phenyl)(1*H*-pyrrol-1-yl)methanone (1n)



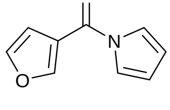
Following **general procedure C**, the reaction of 4-(4-methylpiperazin-1-yl)benzoic acid (1.16 g, 5.0 mmol) with an aqueous ammonia solution (25%, 7.7 mL, 50 mmol) and 2,5-dimethoxytetrahydrofuran (1.3 mL, 10 mmol), afforded the *N*-acylpyrrole **1n** as a yellow solid (686.7 mg, 51% Yield, over two steps). R$_f$: 0.3 (EtOAc/Hexane = 1/2); mp: 91-93 °C; IR (film): 2936, 2796, 1681, 1604, 1518, 1464, 1398, 1382, 1330, 1296, 1246, 1182, 1142, 1008, 924, 882, 764, 774 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.72 (d, *J* = 8.8 Hz, 2H), 7.31 (t, *J* = 2.3 Hz, 2H), 6.92 (t, *J* = 8.9 Hz, 2H), 6.32 (t, *J* = 2.3 Hz, 2H), 3.39 (t, *J* = 5.0 Hz, 4H), 2.58 (t, *J* = 5.0 Hz, 4H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 167.3, 153.9, 132.1 (2C), 122.2, 121.5 (2C), 113.7 (2C), 112.4 (2C), 54.8 (2C), 47.4 (2C), 46.2; HRMS (ESI) *m/z* calcd for $[C_{16}H_{19}N_3NaO]^+$ (M+Na$^+$): 292.1420; found: 292.1420.

(4-Morpholinophenyl)(1*H*-pyrrol-1-yl)methanone (1o)



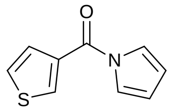
Following **general procedure C**, the reaction of 4-morpholinobenzoic acid (1.04 g, 5.0 mmol) with an aqueous ammonia solution (25%, 7.7 mL, 50 mmol) and 2,5-dimethoxytetrahydrofuran (1.3 mL, 10 mmol), afforded the *N*-acylpyrrole **1o** as a yellow solid (692.0 mg, yield: 54%). Mp: 112-114 °C; IR (film): 2960, 2921, 2852, 1682, 1603, 1517, 1465, 1449, 1398, 1383, 1330, 1296, 1242, 1182, 1123, 1088, 1073, 928, 882, 831, 764, 743, 659 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.74 (d, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 2.2 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.33 (t, *J* = 2.2 Hz, 2H), 3.87 (t, *J* = 4.8 Hz, 4H), 3.32 (t, *J* = 4.8 Hz, 4H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 167.3, 154.0, 132.1 (2C), 122.7, 121.4 (2C), 113.5 (2C), 112.5 (2C), 66.6 (2C), 47.7 (2C); HRMS (ESI) *m/z* calcd for $[C_{15}H_{16}N_2NaO_2]^+$: 279.1104; found: 279.1105.

Furan-3-yl(1*H*-pyrrol-1-yl)methanone (1q)



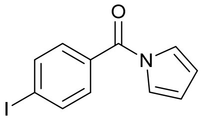
Following **general procedure B**, the reaction of furan-3-carbonyl chloride (0.49 mL, 5.0 mmol) with pyrrole (0.38 mL, 7.5 mmol), afforded the *N*-acylpyrrole **1q** as a light yellow solid (523.9 mg, 65% Yield). R$_f$: 0.5 (EtOAc/Hexane = 1/20); mp: 33-36 °C; IR (film): 3149, 2920, 1693, 1642, 1565, 1504, 1467, 1405, 1381, 1343, 1259, 1238, 1180, 1162, 1142, 1103, 1075, 1020, 876, 838, 739, 600 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.02 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.53 (t, *J* = 1.7 Hz, 1H), 7.40 (t, *J* = 2.3 Hz, 2H), 6.85 (dd, *J* = 1.9, 0.8 Hz, 1H), 6.36 (t, *J* = 2.3 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 161.2, 147.3, 144.0, 120.7, 120.5 (2C), 113.4 (2C), 110.9; HRMS (ESI) *m/z* calcd for $[C_9H_7NNaO_2]^+$ (M+Na$^+$): 184.0369; found: 184.0370.

(1*H*-Pyrrol-1-yl)(thiophen-3-yl)methanone (1r)



Following **general procedure B**, the reaction of thiophene-3-carbonyl chloride (733.0 mg, 5.0 mmol) with pyrrole (0.38 mL, 7.5 mmol), afforded the *N*-acylpyrrole **1r** as a yellow oil (487.4 mg, yield: 55%). IR (film): 3106, 2924, 2863, 1686, 1605, 1584, 1534, 1516, 1466, 1451, 1412, 1325, 1297, 1247, 1200, 1151, 1075, 1044, 881, 844, 815, 750, 737 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 (dd, *J* = 1.5, 0.8 Hz, 1H), 7.53 (t, *J* = 1.7 Hz, 1H), 7.40 (t, *J* =2.3 Hz, 2H), 6.85 (dd, *J* = 1.9, 0.8 Hz, 1H), 6.36 (t, *J* = 2.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.2, 147.3, 144.0, 120.7, 120.5 (2C), 113.4 (2C), 110.9; HRMS (ESI) *m/z* calcd for $[C_9H_7NNaOS]^+$: 200.0141; found: 200.0146.

(4-Iodophenyl)(1*H*-pyrrol-1-yl)methanone (1s)



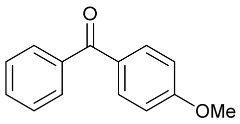
Following **general procedure B**, the reaction of 4-iodobenzoyl chloride (1.33 g, 5.0 mmol) with pyrrole (0.38 mL, 7.5 mmol), afforded the *N*-acylpyrrole **1s** as a white solid (1.23 g, 83% Yield). R_f: 0.5 (EtOAc/Hexane = 1/20); mp: 73-74 °C; IR (film): 3031, 2917, 2849, 1694, 1584, 1467, 1401, 1392, 1331, 1298, 1090, 1075, 1008, 878, 838, 740, 681 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.8 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.25 (t, *J* = 2.2 Hz, 2H), 6.36 (t, *J* = 2.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.0, 137.9 (2C), 132.7, 131.0 (2C), 121.2 (2C), 113.6 (2C), 99.7; HRMS (ESI) *m/z* calcd for $[C_{11}H_8INNaO]^+$ (M+Na$^+$): 319.9543; found: 319.9544.

4. The scope of amides and neopentyl glycol esters

General procedure E for coupling of *N*-acylpyrrole 1 and (hetero)arylboronic acid neopentyl glycol esters 2 to yield ketones 3.

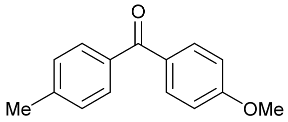
A vial packaged with tin foil was charged with powdered K_3PO_4 (101.9 mg, 0.48 mmol, 2.0 equiv), *N*-acylpyrrole **1** (0.24 mmol, 1.0 equiv), (hetero)arylboronic acid neopentyl glycol ester **2** (0.48 mmol, 2.0 equiv), **L8**·2HCl (16.2 mg, 0.024 mmol, 10 mol%) and a magnetic stir bar. Then, the vial was taken into a glove box and charged with $Ni(COD)_2$ (6.6mg, 0.024 mmol, 10 mol%). After that, toluene (0.5 mL, 0.5 M) and water (8.6 uL, 0.48 mmol, 2.0 equiv) was added. The vial was sealed with screw cap, removed from the glove box, and stirred vigorously at 60 °C for 20 h. After cooling to room temperature, the mixture was diluted with CH_2Cl_2 (1 mL), washed with a saturated aqueous Na_2CO_3 solution (1 mL) and brine (1.0 mL), and then dried over anhydrous Na_2SO_4. The combined organic layer was filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography to yield the desired ketone **3**.

(4-Methoxyphenyl)(phenyl)methanone (3aa)



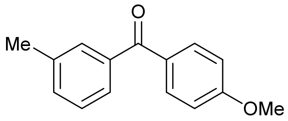
Following **general procedure E**, the reaction of *N*-acylpyrrole **1a** (41.1 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2a** (105.6 mg, 0.48 mmol), afforded the ketone **3aa**[8a] as a white solid (47.9 mg, 94% Yield). R_f: 0.4 (EtOAc/Hexane = 1/10); mp: 60-62 °C; IR (film): 2933, 2839, 1653, 1599, 1577, 1508, 1445, 1419, 1317, 1281, 1257, 1172, 1148, 1029, 938, 923, 844, 793, 741 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, J = 8.8 Hz, 2H), 7.75 (d, J = 7.8 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.6, 163.3, 138.3, 132.6 (2C), 131.9, 130.2, 129.8 (2C), 128.2 (2C), 113.6 (2C), 55.5; MS (ESI) *m/z* 213 ($M+H^+$, 100%).

4-Methoxyphenyl)(*p*-tolyl)methanone (3ba)



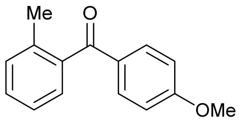
Following **general procedure E**, the reaction of *N*-acylpyrrole **1b** (44.4 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2a** (105.6 mg, 0.48 mmol), afforded the ketone **3ba**[8b] as a light yellow solid (50.0 mg, 92% Yield). R_f: 0.4 (EtOAc/Hexane = 1/10); mp: 89-90 °C; IR (film): 3148, 2920, 2850, 1697, 1609, 1543, 1509, 1466, 1401, 1329, 1303, 1089, 1074, 882, 832, 740 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (d, J =8.8 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.4, 163.1, 142.7, 135.6, 132.5 (2C), 130.6, 130.1 (2C), 128.9 (2C), 113.6 (2C), 55.5, 21.7; MS (ESI) *m/z* 186 ($M+H^+$, 100%).

(4-Methoxyphenyl)(*m*-tolyl)methanone (3ca)



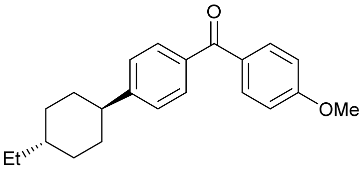
Following **general procedure E**, the reaction of *N*-acylpyrrole **1c** (44.4 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2a** (105.6 mg, 0.48 mmol), afforded the ketone **3ca**[8b] as a white solid (50.5 mg, 93% Yield). R_f: 0.4 (EtOAc/Hexane = 1/10); mp 53-54 °C; IR (film): 2920, 1651, 1598, 1572, 1508, 1460, 1420, 1313, 1286, 1258, 1170, 1030, 960, 846, 755, 712 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.82 (d, J = 8.8 Hz, 2H), 7.57 (s, 1H), 7.53 (d, J = 7.2 Hz, 1H), 7.39-7.32 (m, 2H), 6.96 (d, J = 8.7 Hz, 2H), 3.88 (s, 3H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 195.9, 163.2, 138.4, 138.1, 132.7, 132.6 (2C), 130.4, 130.2, 128.1, 127.0, 113.6 (2C), 55.5, 21.4; MS (ESI) *m/z* 227 ($M+H^+$, 100%).

(4-Methoxyphenyl)(*o*-tolyl)methanone (3da)



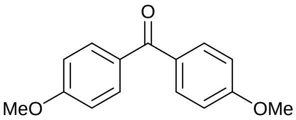
Following **general procedure E**, the reaction of *N*-acylpyrrole **1d** (44.4 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2a** (105.6 mg, 0.48 mmol), afforded the ketone **3da**[8c] as a colorless oil (28.8 mg, 53% Yield). R_f: 0.4 (EtOAc/Hexane = 1/10); IR (film): 2924, 1656, 1599, 1574, 1508, 1456, 1314, 1292, 1258, 1179, 1149, 1028, 926, 846, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.79 (d, J = 8.7 Hz, 2H), 7.34 (t, J = 7.4 Hz, 1H), 7.30-7.26 (m, 2H), 7.24 (t, J = 7.4 Hz, 1H), 6.93 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H), 2.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 197.5, 163.8, 139.3, 136.2, 132.6 (2C), 130.9, 130.6, 129.9, 128.0, 125.2, 113.8 (2C), 55.6, 19.9; MS (ESI) *m/z* 227 (M+H$^+$, 100%).

(4-((1*R*,4*R*)-4-Ethylcyclohexyl)phenyl)(4-methoxyphenyl)methanone (3ea)



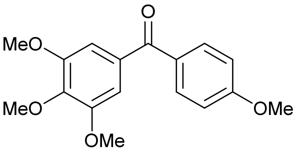
Following **general procedure E**, the reaction of *N*-acylpyrrole **1e** (67.5 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2a** (105.6 mg, 0.48 mmol), afforded the ketone **3ea** as a white solid (63.4 mg, 82% Yield). R_f: 0.4 (EtOAc/Hexane = 1/10); mp:71-72 °C; IR (film): 2919, 2849, 1650, 1603, 1509, 1446, 1416, 1312, 1281, 1256, 1180, 1171, 1142, 1076, 1029, 929, 852, 769 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, J = 8.9 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H), 2.51-2.59 (m, 1H), 1.87-1.96 (m, 4H), 1.44-1.54 (m, 2H), 124-1.32 (m, 2H), 1.17-1.24 (m, 1H), 1.12-1.02 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.4, 163.0, 152.4, 135.9, 132.5 (2C), 130.5, 130.1 (2C), 126.7 (2C), 113.5 (2C), 55.5, 44.8, 39.0, 34.1 (2C), 33.1 (2C), 30.0, 11.5; HRMS (ESI) *m/z* calcd for $[C_{22}H_{26}NaO_2]^+$ (M+Na$^+$): 345.1825; found: 345.1826. $[\alpha]_D^{20}$ −0.24 (*c* 0.5, $CHCl_3$).

Bis(4-methoxyphenyl)methanone (3fa)



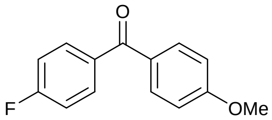
Following **general procedure E**, the reaction of *N*-acylpyrrole **1f** (48.3 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2a** (105.6 mg, 0.48 mmol), afforded **3fa**[8d] as a pale yellow solid (48.3 mg, 83% Yield). R_f: 0.4 (EtOAc/PE = 1/10); mp: 129-135°C; IR (film): 2965, 2917, 2843, 1636, 1605, 1503, 1417, 1314, 1255, 1181, 1150, 1076, 1026, 851, 765, 687 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 8.6 Hz, 4H), 6.96 (d, J = 8.7 Hz, 4H), 3.89 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.6, 162.9 (2C), 132.3 (4C), 130.8 (2C), 113.5 (4C), 55.5 (2C); MS (ESI) *m/z* 243 (M+H$^+$, 100%).

(4-Methoxyphenyl)(3,4,5-trimethoxyphenyl)methanone (3ga)



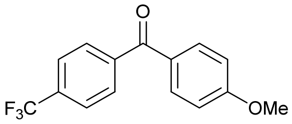
Following **general procedure E**, the reaction of *N*-acylpyrrole **1g** (62.7 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2a** (105.6 mg, 0.48 mmol), afforded the ketone **3ga**[8d] as a colorless oil (58.0 mg, 80% Yield). R_f: 0.4 (EtOAc/Hexane = 1/5); IR (film): 3052, 2936, 2838, 1648, 1600, 1581, 1508, 1459, 1412, 1333, 1254, 1232, 1169, 1125, 1027, 998, 845, 765 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.83 (d, *J* = 8.6 Hz, 2H), 7.03 (s, 2H), 6.98 (d, *J* = 8.6 Hz, 2H), 3.94 (s, 3H), 3.90 (s, 3H), 3.88 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 194.7, 163.2, 152.9 (2C), 141.7, 133.4, 132.5 (2C), 130.3, 113.6 (2C), 107.5 (2C), 61.0, 56.4 (2C), 55.6; MS (ESI) *m/z* 325 ($M+Na^+$, 100%).

(4-Fluorophenyl)(4-methoxyphenyl)methanone (3ha)



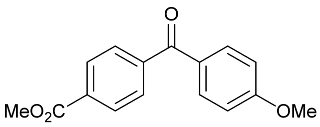
Following **general procedure E**, the reaction of *N*-acylpyrrole **1h** (45.4 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2a** (105.6 mg, 0.48 mmol), afforded the ketone **3ha**[8a] as a white solid (47.5 mg, 86% Yield). R_f: 0.4 (EtOAc/Hexane = 1/10); mp: 91-92 °C; IR (film): 2917, 2847, 1641, 1603, 1501, 1384, 1261, 1180, 1148, 1076, 1030, 857, 842, 765, 682 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (t, *J* = 2.5 Hz, 2H), 7.79 (t, *J* = 2.5 Hz, 2H), 7.15 (t, *J* = 8.6 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.2, 165.1 (d, *J* = 253.3 Hz), 163.3, 134.5 (d, *J* = 3.6 Hz), 132.5 (2C), 132.4 (d, *J* = 9.1 Hz, 2C), 130.1, 115.4 (d, *J* = 22.1 Hz, 2C), 113.7 (2C), 55.6; MS (ESI) *m/z* 253 ($M+Na^+$, 100%).

(4-Methoxyphenyl)(4-(trifluoromethyl)phenyl)methanone (3ia)



Following **general procedure E**, the reaction of *N*-acylpyrrole **1i** (57.4 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2a** (105.6 mg, 0.48 mmol), afforded the ketone **3ia**[8d] as a white solid (59.9 mg, 89% Yield). R_f: 0.4 (eluent: EtOAc/Hexane = 1/10); mp: 123-124 °C. IR (film): 2969, 1727, 1644, 1602, 1574, 1509, 1460, 1407, 1328, 1265, 1168, 1131, 1068, 1030, 1017, 862, 844, 771, 686 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.86-7.79 (m, 4H), 7.74 (d, *J* = 8.2 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 194.4, 163.8, 141.6, 133.3 (q, *J* = 32.6 Hz), 132.7 (2C), 129.9 (2C), 129.4, 125.3 (q, *J* = 3.7 Hz, 2C), 123.8 (q, *J* = 272.7 Hz), 113.9 (2C), 55.6; MS (ESI) *m/z* 281 ($M+H^+$, 100%).

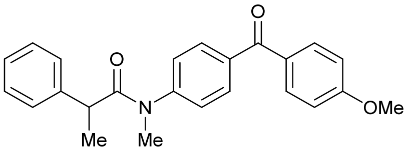
Methyl 4-(4-methoxybenzoyl)benzoate (3ja)



Following **general procedure E**, the reaction of *N*-acylpyrrole **1j** (55.0 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2a** (105.6 mg, 0.48 mmol), afforded the ketone **3ja**[8f] (30.5 mg, 47% Yield) as a white solid. Mp: 160-162 °C. IR (film): 3011, 2918, 2848, 1716, 1641, 1602, 1433, 1405, 1284, 1255, 1146, 1107, 1026, 873, 844, 745, 709 cm^{-1}; ^1H NMR (500 MHz,

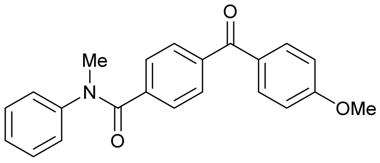
$CDCl_3$): δ 8.14 (d, *J* = 8.3 Hz, 2H), 7.82 (d, *J* = 8.8 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.97 (s, 3H), 3.90 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 194.8, 166.4, 163.7, 142.2, 132.8, 132.6 (2C), 129.6, 129.5 (4C), 113.8 (2C), 55.6, 52.4; MS (ESI) *m/z* 271 ($M+H^+$, 100%).

***N*-(4-(4-Methoxybenzoyl)phenyl)-*N*-methyl-2-phenylpropanamide (3ka)**



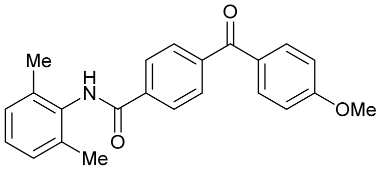
Following **general procedure E**, the reaction of *N*-acylpyrrole **1k** (79.8 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2a** (105.6 mg, 0.48 mmol), afforded ketone **3ka** as a light yellow oil (78.9 mg, 88% Yield). R_f: 0.4 (EtOAc/Hexane = 1/5); IR (film): 2970, 2931, 2839, 1656, 1600, 1509, 1454, 1419, 1377, 1314, 1279, 1257, 1171, 1149, 1122, 1025, 929, 860, 843, 775, 700, 688 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.8 Hz, 2H), 7.73 (d, *J* = 7.9 Hz, 2H), 7.26-7.16 (m, 3H), 7.10 (d, *J* = 7.3 Hz, 2H), 7.05 (d, *J* = 7.3 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.91 (s, 3H), 3.29 (s, 3H), 1.42 (d, *J* = 6.9 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 194.4, 173.8, 163.6, 147.0, 141.8, 132.6 (2C), 131.0 (2C), 129.8, 128.6 (2C), 127.5 (4C), 126.8 (2C), 113.8 (2C), 55.6, 43.7, 37.8, 20.5; HRMS (ESI) *m/z* calcd for $[C_{24}H_{23}NNaO_3]^+$ ($M+Na^+$): 396.1570; found: 396.1572.

4-(4-Methoxybenzoyl)-*N*-methyl-*N*-phenylbenzamide (3la)



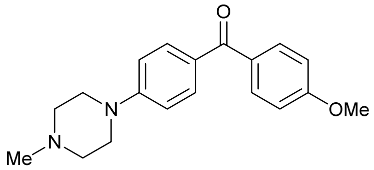
Following **general procedure E**, the reaction of *N*-acylpyrrole **1l** (73.0 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2a** (105.6 mg, 0.48 mmol), afforded ketone **3la** as a light yellow oil (64.7 mg, 78% Yield). R_f: 0.4 (EtOAc/Hexane = 1/5); IR (film): 2919, 2850, 1650, 1596, 1495, 1418, 1383, 1315, 1258, 1180, 1143, 1076, 1029, 930, 876, 860, 748, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 2H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 7.6 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H), 3.53 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 194.9, 169.9, 163.5, 144.4, 139.3, 139.0, 132.6 (2C), 129.8, 129.4 (2C), 129.2 (2C), 128.5 (2C), 127.0 (3C), 113.7 (2C), 55.6, 38.5; HRMS (ESI) *m/z* calcd for $[C_{22}H_{19}NNaO_3]^+$ ($M+Na^+$): 368.1257; found: 368.1260.

***N*-(2,6-Dimethylphenyl)-4-(4-methoxybenzoyl)benzamide (3ma)**



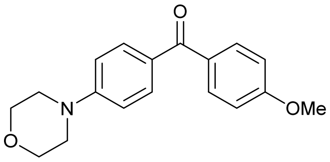
Following **general procedure E**, the reaction of *N*-acylpyrrole **1m** (76.4 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2a** (105.6 mg, 0.48 mmol), afforded the ketone **3ma** as a light yellow solid (65.6 mg, 76% Yield). R_f: 0.4 (EtOAc/Hexane = 1/5); mp: The compound decomposed at 189 °C; IR (film): 2923, 2852, 1650, 1599, 1511, 1493, 1316, 1282, 1259, 1195, 1173, 1149, 1132, 1077, 1027, 930, 843 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.2 Hz, 2H), 7.86 (d, *J* = 6.3 Hz, 2H), 7.84 (d, *J* = 6.9 Hz, 2H), 7.46 (s, 1H), 7.19-7.12 (m, 3H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.91 (s, 3H), 2.31 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 194.7, 165.2, 163.7, 141.4, 137.3, 135.6 (2C), 133.7, 132.7 (2C), 130.0 (2C), 129.7, 128.5 (2C), 127.8, 127.2 (2C), 113.9 (2C), 55.7, 18.6 (2C); HRMS (ESI) *m/z* calcd for $[C_{23}H_{21}NNaO_3]^+$ (M+Na$^+$): 382.1414; found: 382.1414.

(4-Methoxyphenyl)(4-(4-methylpiperazin-1-yl)phenyl)methanone (3na)



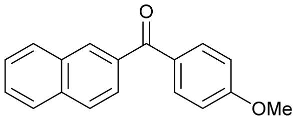
Following **general procedure E** (except the T = 80 °C), the reaction of *N*-acylpyrrole **1n** (64.6 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2a** (105.6 mg, 0.48 mmol), afforded ketone **3na** as a light yellow oil (36.5 mg, 49% Yield). R_f: 0.4 (EtOAc); IR (film): 2934, 2846, 2797, 1636, 1601, 1559, 1541, 1516, 1456, 1381, 1291, 1241, 1180, 1170, 1142, 1076, 1029, 1009, 924, 770, 685 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.80-7.74 (m, 4H), 6.95 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* =8.8 Hz, 2H), 3.88 (s, 3H), 3.95 (t, *J* = 5.1 Hz, 4H), 2.60 (t, *J* = 5.0 Hz, 4H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 194.3, 162.6, 153.7, 132.3 (2C), 132.1 (2C), 131.3, 128.1, 113.6 (2C), 113.4 (2C), 55.5, 54.8 (2C), 47.5 (2C), 46.1. HRMS (ESI) *m/z* calcd for $[C_{19}H_{23}N_2O_2]^+$ (M+Na$^+$): 311.1754; found: 311.1755.

(4-Methoxyphenyl)(4-morpholinophenyl)methanone (**3oa**)



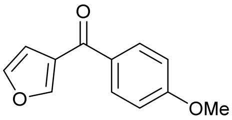
Following the **general procedure E** (except the T = 80 °C), the reaction of *N*-acylpyrrole **1o** (61.5 mg, 0.24 mmol) and arylboronic acid neopentyl glycol ester **2a** (105.6 mg, 0.48 mmol), afforded ketone **3oa** as a light yellow solid (31.4 mg, 44% Yield). R_f: 0.5 (EtOAc); mp: 144-146 °C; IR (film): 2921, 2851, 1640, 1600, 1510, 1448, 1318, 1257, 1237, 1170, 1123, 1027, 926, 768 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.80-7.75 (m, 4H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 3.88 (s, 3H), 3.87 (t*, J* =5.0 Hz, 4H), 3.32 (t*, J* =5.0 Hz, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 194.3, 162.7, 153.9, 132.2 (2C), 132.1 (2C), 131.2, 128.6, 113.5 (2C), 113.4 (2C), 66.7 (2C), 55.5, 47.8 (2C); HRMS (ESI) *m/z* calcd for $[C_{18}H_{19}NNaO_3]^+$: 320.1257; found: 320.1258.

(4-Methoxyphenyl)(naphthalen-2-yl)methanone (3pa)



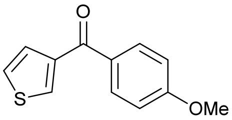
Following **general procedure E**, the reaction of *N*-acylpyrrole **1p** (53.1 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2a** (105.6 mg, 0.48 mmol), afforded ketone **3pa**[8d] as a white solid (43.4 mg, 69% Yield). R_f: 0.4 (EtOAc/Hexane = 1/10); mp: 90-92 °C; IR (film): 2918, 2849, 1650, 1601, 1537, 1442, 1384, 1258, 1180, 1142, 1076, 877, 764, 637 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.23 (s, 1H), 7.95-7.86 (m, 6H), 7.62-7.52 (m, 2H), 7.00 (d, J = 8.8 Hz, 2H), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 195.6, 163.3, 135.6, 135.1, 132.7 (2C), 132.3, 131.2, 130.5, 129.3, 128.2, 128.1, 127.9, 126.8, 125.9, 113.7 (2C), 55.6; MS (ESI) *m/z* 263 ($M+H^+$, 100%).

Furan-3-yl(4-methoxyphenyl)methanone (3qa)



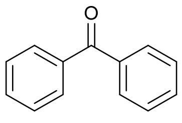
Following **general procedure E** (except the T = 80 °C), the reaction of *N*-acylpyrrole **1q** (38.7 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2a** (105.6 mg, 0.48 mmol), afforded ketone **3qa** as a white solid (26.2 mg, 54% Yield). R_f: 0.4 (EtOAc/Hexane = 1/10); mp: 74-76 °C; IR (film): 2979, 2919, 1644, 1607, 1559, 1507, 1455, 1329, 1157, 1112, 1016, 872, 842, 762, 707 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.91 (s, 1H), 7.89 (d, J = 8.4 Hz, 2H), 7.50 (t, J = 1.6 Hz, 1H), 6.98 (d, J = 8.6 Hz, 2H), 6.88 (s, 1H), 3.89 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 188.1, 163.3, 147.8, 143.8, 131.6, 131.3 (2C), 126.6, 113.9 (2C), 110.5, 55.6; HRMS (ESI) *m/z* calcd for $[C_{12}H_{10}NaO_3]^+$ ($M+Na^+$): 225.0522; found: 225.0526.

(4-Methoxyphenyl)(thiophen-3-yl)methanone (3ra)



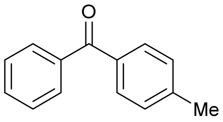
Following **general procedure E** (except the T = 80 °C), the reaction of *N*-acylpyrrole **1r** (42.5 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2a** (105.6 mg, 0.48 mmol), afforded ketone **3ra**[8b] (24.5 mg, 43% Yield) a as a white solid. Mp: 67-69 °C. IR (film): 3112, 2918, 2848, 1639, 1598, 1573, 1507, 1419, 1386, 1310, 1277, 1256, 1170, 1138, 1026, 859, 843, 754, 702 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.95-7.83 (m, 3H), 7.56 (d, J = 5.0 Hz, 1H), 7.38 (dd, J = 5.1, 2.9 Hz, 1H), 6.98 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 188.9, 163.2, 141.6, 132.8, 131.9 (2C), 131.2, 128.7, 126.0, 113.7 (2C), 55.5; MS (ESI) *m/z* 241 ($M+Na^+$, 100%).

Benzophenone (3ab)



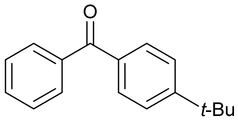
Following **general procedure E**, the reaction of *N*-acylpyrrole **1a** (41.1 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2b** (91.2 mg, 0.48 mmol), afforded ketone **3ab**[8a] as a white solid (39.4 mg, 90% Yield). R_f: 0.4 (EtOAc/Hexane = 1/20); mp: 47-48 °C; IR (film): 3059, 2918, 1659, 1598, 1577, 1447, 1317, 1277, 1179, 1142, 1075, 1028, 1000, 941, 919, 763, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): *δ* 7.45-7.50 (m, 4H), 7.56-7.62 (m, 2H), 7.77-7.83 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 196.8, 137.7 (2C), 132.5 (2C), 128.3 (4C), 130.1 (4C); MS (ESI) *m/z* 205 ($M+Na^+$, 100%).

Phenyl(*p*-tolyl)methanone (3ac)



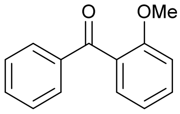
Following **general procedure E**, the reaction of *N*-acylpyrrole **1a** (41.1 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2c** (98.0 mg, 0.48 mmol), afforded ketone **3ac**[8a] as a white solid (42.9 mg, 91% Yield). R_f: 0.4 (EtOAc/Hexane = 1/20); mp: 51-53 °C; IR (film): 2919, 1656, 1605, 1446, 1385, 1276, 1180, 1142, 1076, 922, 730, 699 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): *δ* 7.80-7.77 (m, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.58 (td, *J* = 7.4, 1.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 8.1 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 196.6, 143.3, 138.0, 135.0, 132.2, 130.4 (2C), 130.0 (2C), 129.1 (2C), 128.3 (2C), 21.7; MS (ESI) *m/z* 197 ($M+H^+$, 100%)..

(4-(*tert*-Butyl)phenyl)(phenyl)methanone (3ad)



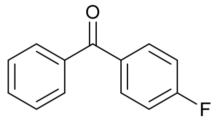
Following **general procedure E**, the reaction of *N*-acylpyrrole **1a** (41.1 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2d** (118.2 mg, 0.48 mmol), afforded ketone **3ad**[8h] as a white solid (53.2 mg, 93% Yield). R_f: 0.4 (EtOAc/Hexane = 1/20); mp: 38-39 °C; IR (film): 3060, 2963, 1659, 1605, 1447, 1406, 1364, 1316, 1278, 1105, 939, 850, 702, 668 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): *δ* 7.80 (d, *J* = 7.6 Hz, 2H), 7.76 (t, *J* = 8.3 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.52-7.44 (m, 4H), 1.36 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 196.5, 156.2, 137.9, 134.8, 132.2, 130.2 (2C), 130.0 (2C), 128.2 (2C), 125.3 (2C), 35.1, 31.2 (3C); MS (ESI) *m/z* 239 ($M+H^+$, 100%).

(2-Methoxyphenyl)(phenyl)methanone (3ae)



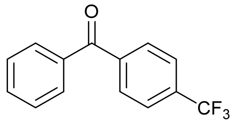
Following **General procedure E**, the reaction of *N*-acylpyrrole **1a** (41.1 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2e** (105.6 mg, 0.48 mmol), afforded ketone **3ae**[8d] (36.7 mg, 36% Yield; recover SM: 68.5 mg) after FC (eluent: EtOAc/PE = 1/10) as a white solid. Mp: 30-32 °C; IR (film): 2941, 1666, 1599, 1581, 1487, 1462, 1449, 1435, 1316, 1259, 1180, 1023, 925, 755, 702, 636 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): 7.83-7.78 (m, 2H), 7.57-7.52 (m, 1H), 7.49-7.44 (m, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.36 (dd, *J* = 7.4, 1.8 Hz, 1H,), 7.04 (td, *J* = 7.5, 0.8 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 3.72 (s, 3H); ^{13}C NMR (CDCl$_3$, 125 MHz): 196.5, 157.4, 137.9, 133.0, 131.9, 129.9 (2C), 129.6, 128.9, 128.3 (2C), 120.6, 111.5, 55.7; MS (ESI) *m/z* 235 (M+Na$^+$, 100%).

(4-Fluorophenyl)(phenyl)methanone (3af)



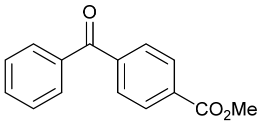
Following **general procedure E**, the reaction of *N*-acylpyrrole **1a** (41.1 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2f** (99.8 mg, 0.48 mmol), afforded ketone **3af**[8a] as a white solid (38.0 mg, 79% Yield). R$_f$: 0.4 (EtOAc/Hexane = 1/20); mp: 48-49 °C; IR (film): 3061, 2919, 1647, 1598, 1504, 1446, 1407, 1298, 1230, 1149, 1097, 940, 851, 735, 700 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.85 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.16 (t, *J* = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 115.5 (d, *J* = 22.0 Hz), 128.4 (2C), 129.9 (2C), 132.5 (2C), 132.7 (d, *J* = 9.2 Hz, 2C), 133.8 (d, *J* = 3.4 Hz), 137.5, 165.4 (d, *J* = 255.1 Hz), 195.3; MS (ESI) *m/z*: 201 (M+H$^+$, 100%).

Phenyl(4-(trifluoromethyl)phenyl)methanone (3ag)



Following **general procedure E**, the reaction of *N*-acylpyrrole **1a** (41.1 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2g** (123.8 mg, 0.48 mmol), afforded ketone **3ag**[8d] as a white solid (42.6 mg, 71% Yield). R$_f$: 0.4 (EtOAc/Hexane = 1/20); mp: 115-116 °C; IR (film): 3052, 2919, 1651, 1598, 1447, 1408, 1335, 1276, 1169, 1134, 1117, 1068, 857, 750, 696 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.89 (d, *J* = 8.1 Hz, 2H), 7.83-7.79 (m, 2H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.63 (td, *J* = 7.6, 1.3 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 194.6, 139.8, 135.8, 132.8 (q, *J* = 33.0 Hz), 132.2, 129.2 (2C), 129.1 (2C), 127.6 (2C), 124.4 (q, *J* = 3.8 Hz, 2C), 122.8 (q, *J* = 272.3 Hz); MS (ESI) *m/z*: 251 (M+H$^+$, 100%).

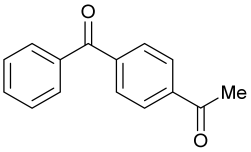
Methyl 4-benzoylbenzoate (3ah)



Following **general procedure E**, the reaction of *N*-acylpyrrole **1a** (41.1 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2h** (119.1 mg, 0.48 mmol), afforded ketone **3ah**[8e] as a white solid (35.2 mg, 61% Yield). R$_f$: 0.4 (EtOAc/Hexane = 1/10); mp: 107-108 °C; IR (film): 2920, 2850, 1720, 1647, 1596, 1437, 1399, 1361, 1283, 1194, 1180, 1142, 1109, 1076, 1020, 711, 698 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.15 (d, *J* = 8.2 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 7.9 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 3.97 (s, 3H); ^{13}C NMR

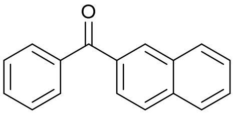
(125 MHz, $CDCl_3$): δ 196.1, 166.4, 141.4, 137.0, 133.3, 133.0, 130.2 (2C), 129.9 (2C), 129.6 (2C), 128.6 (2C), 52.6; MS (ESI) *m/z* 241 ($M+H^+$, 100%).

1-(4-Benzoylphenyl)ethanone (3ai)



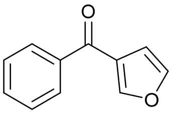
Following **general procedure E**, the reaction of *N*-acylpyrrole **1a** (41.1 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2i** (111.4 mg, 0.48 mmol), afforded ketone **3ai**[8i] as a white solid (32.3 mg, 60% Yield). R_f: 0.4 (EtOAc/Hexane = 1/10); mp: 83-84 °C; IR (film): 2917, 1688, 1660, 1597, 1499, 1447, 1403, 1317, 1277, 1180, 1142, 1076, 925, 742, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.1 Hz, 2H), 7.89 (d, *J* = 8.2 Hz, 2H), 7.83 (d, *J* = 7.6 Hz, 2H), 7.65 (t, *J* =7.3 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 2.69 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.6, 196.0, 141.4, 139.7, 137.0, 133.1, 130.2 (2C), 130.1 (2C), 128.6 (2C), 128.2 (2C), 26.9; MS (ESI) *m/z* 247 ($M+Na^+$, 100%).

Naphthalen-2-yl(phenyl)methanone (3aj)



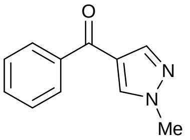
Following **general procedure E**, the reaction of *N*-acylpyrrole **1a** (41.1 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2j** (115.2 mg, 0.48 mmol), afforded ketone **3aj**[8d] as a white solid (45.7 mg, 82% Yield). R_f: 0.4 (EtOAc/Hexane = 1/20); mp: 76-77 °C. IR (film): 3058, 2962, 1657, 1598, 1577, 1467, 1446, 1353, 1287, 1235, 1143, 1076, 920, 795, 750, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.26 (s, 1 H), 7.96-7.93 (m, 2H), 7.91 (dd, *J* = 8.2, 3.6 Hz, 2H), 7.86 (d, *J* = 7.8 Hz, 2H), 7.64-7.58 (m, 2H), 7.57-7.48 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.8, 137.0, 134.3, 133.9, 131.5, 131.3, 131.0, 129.2 (2C), 128.5, 127.4 (3C), 127.3, 126.9, 125.9, 124.9; MS (ESI) *m/z* 255 ($M+Na^+$, 100%).

Furan-3-yl(phenyl)methanone (3ak)



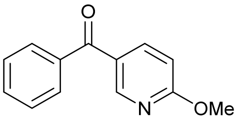
Following **general procedure E**, the reaction of *N*-acylpyrrole **1a** (41.1 mg, 0.24 mmol) with heteroarylboronic acid neopentyl glycol ester **2k** (86.4 mg, 0.48 mmol), afforded ketone **3ak**[8j] as a light yellow oil (21.1 mg, 51% Yield). R_f: 0.4 (EtOAc/Hexane = 1/20); IR (film): 3132, 3060, 1649, 1599, 1577, 1560, 1509, 1446, 1384, 1323, 1195, 1178, 1151, 1079, 1016, 872, 721 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): 7.92 (s, 1H), 7.85 (d, 7.8 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.52-7.46 (m, 3H), 6.91 (d, *J* = 1.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.5, 148.6, 144.0, 138.9, 132.5, 128.9 (2C), 128.6 (2C), 126.6, 110.3; MS (ESI) *m/z* 195 ($M+Na^+$, 100%).

(1-Methyl-1*H*-pyrazol-4-yl)(phenyl)methanone (3al)



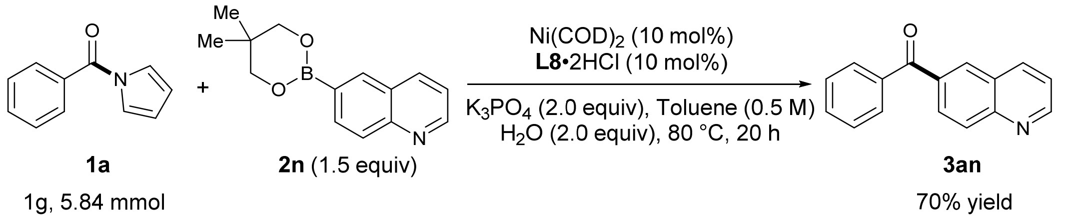
Following **general procedure E**, the reaction of *N*-acylpyrrole **1a** (41.1 mg, 0.24 mmol) with heteroarylboronic acid neopentyl glycol ester **2l** (93.1 mg, 0.48 mmol), afforded ketone **3al**[8k] as a light yellow solid (32.6 mg, 73% Yield). R_f: 0.4 (EtOAc/Hexane = 1/5); mp: 81-82 °C; IR (film): 2919, 1642, 1599, 1576, 1542, 1445, 1385, 1238, 1180, 1142, 1076, 893, 726, 713, 670 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.94 (d, *J* = 4.1 Hz, 2H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 3.98 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): 188.9, 141.9, 139.2, 134.3, 132.3, 128.9 (2C), 128.6 (2C), 122.9, 39.5; MS (ESI) *m/z* 187 ($M+H^+$, 100%).

(6-Methoxypyridin-3-yl)(phenyl)methanone (3am)



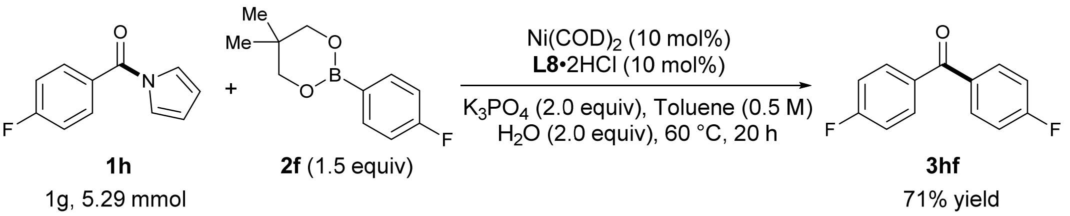
Following **general procedure E** (except the T = 80 °C), the reaction of *N*-acylpyrrole **1a** (41.1 mg, 0.24 mmol) with heteroarylboronic acid neopentyl glycol ester **2m** (106.1 mg, 0.48 mmol), afforded ketone **3am**[8l] as a light yellow solid (43.0 mg, 84% Yield). R_f: 0.4 (EtOAc/Hexane = 1/5); mp: 59-60 °C; IR (film): 2920, 1655, 1599, 1493, 1446, 1370, 1281, 1196, 1131, 1021, 921, 840, 709 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.62 (dd, *J* = 2.4, 0.7 Hz, 1H), 8.11 (dd, *J* = 8.7, 2.5, 1H), 7.80-7.77 (m, 2H), 7.60 (td, *J* = 7.4, 1.7 Hz, 1H), 7.52-7.47 (m, 2H), 6.84 (dd, *J* = 8.6 Hz, 0.6 Hz, 1H), 4.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 194.3, 166.5, 150.9, 140.1, 137.6, 132.6, 129.8 (2C), 128.5 (2C), 127.0, 111.1, 54.1; MS (ESI) *m/z* 214 ($M+H^+$, 100%).

5. Gram-scale synthesis and a synthetic application



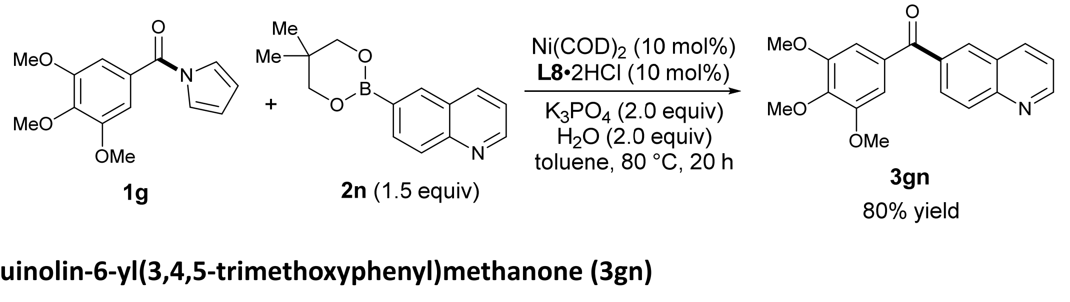
Phenyl(quinolin-6-yl)methanone (3an)

A sealed tube packaged with tin foil paper was charged with powdered K_3PO_4 (2.48 g, 11.68 mmol), *N*-acylpyrrole **1a** (1.00 g, 5.84 mmol), heteroarylboronic acid neopentyl glycol ester **2n** (2.11 g, 8.76 mmol), **L8**·2HCl (393.5 mg, 0.58 mmol) and a magnetic stir bar. Then the sealed tube was taken into a glove box and charged with $Ni(COD)_2$ (160.7 mg, 0.58 mmol). After that, toluene (11.7 mL) and water (210.2 uL, 11.7 mmol) was added. The sealed tube was sealed with screw cap, removed from the glove box, and stirred vigorously at 80 °C for 20 h. After cooling to room temperature, the mixture was diluted with CH_2Cl_2 (20 mL), washed with a saturated aqueous Na_2CO_3 solution (20 mL) and brine (20 mL), and then dried over anhydrous Na_2SO_4. The organic layer was filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: EtOAc/Hexane = 1/5) to yield the desired ketone **3an** as a colorless oil (953.8 mg, 70% Yield). R_f: 0.4 (EtOAc/Hexane = 1/5); IR (film): 3062, 2962, 2929, 1658, 1620, 1597, 1571, 1477, 1458, 1426, 1378, 1327, 1292, 1252, 1185, 1124, 1114, 1076, 861, 845, 801, 770, 718, 700 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.03 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.29-8.14 (m, 4H), 7.86 (d, *J* = 7.8 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.56-7.46 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.1, 152.6, 149.9, 137.5, 137.4, 135.6, 132.8, 131.4, 130.2 (2C), 130.0, 129.6, 128.5 (2C), 127.4, 122.1; HRMS (ESI) *m/z* calcd for $[C_{16}H_{11}NNaO]^+$ (M+Na$^+$): 256.0733; found: 256.0729.



Bis(4-fluorophenyl)methanone (3hf)

A sealed tube packaged with tin foil paper was charged with powdered K_3PO_4 (2.25 g, 10.58 mmol), *N*-acylpyrrole **1h** (1.00 g, 5.29 mmol), arylboronic acid neopentyl glycol ester **2f** (1.65 g, 7.94 mmol), **L8**·2HCl (356.4 mg, 0.53 mmol) and a magnetic stir bar. Then the sealed tube was taken into a glove box and charged with $Ni(COD)_2$ (145.5 mg, 0.53 mmol). After that, toluene (10.6 mL) and water (190.4 uL, 10.58 mmol) was added. The sealed tube was sealed with screw cap, removed from the glove box, and stirred vigorously at 60 °C for 20 h. After cooling to room temperature, the mixture was diluted with CH_2Cl_2 (20 mL), washed with a saturated aqueous Na_2CO_3 solution (20 mL) and brine (20 mL), and then dried over anhydrous Na_2SO_4. The organic layer was filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: EtOAc/Hexane = 1/20) to yield the desired ketone **7hf**[8m] as a colorless oil (819.5 mg, 71% Yield). R_f: 0.4 (EtOAc/Hexane = 1/20); mp: 107-109 °C; IR (film): 2918, 1649, 1598, 1501, 1409, 1298, 1280, 1229, 1145, 1076, 856, 846, 764 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85-7.79 (m, 4H), 7.20-7.14 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.9, 166.5 (d, *J* = 254.2 Hz, 2C), 133.8 (d, *J* = 3.5 Hz, 2C), 132.6 (d, *J* = 9.2 Hz, 4C), 115.6 (d, *J* = 21.9 Hz, 4C); MS (ESI) *m/z* 214 (M+H$^+$, 100%).



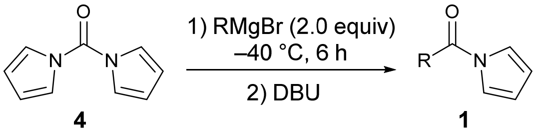
Quinolin-6-yl(3,4,5-trimethoxyphenyl)methanone (3gn)

A vial packaged with tin foil was charged with powdered K_3PO_4 (101.9 mg, 0.48 mmol), *N*-acylpyrrole **1g** (62.7 mg, 0.24 mmol), heteroarylboronic acid neopentyl glycol ester **2n**

(86.8 mg, 0.36 mmol), **L8**·2HCl (16.2 mg, 0.024 mmol) and a magnetic stir bar. Then the vial was taken into a glove box and charged with Ni(COD)$_2$ (6.6mg, 0.024 mmol). After that, toluene (0.5 mL) and water (8.6 uL, 0.48 mmol) was added. The vial was sealed with screw cap, removed from the glove box, and stirred vigorously at 80 °C for 20 h. After cooling to room temperature, the mixture was diluted with CH_2Cl_2 (1 mL), washed with a saturated aqueous Na_2CO_3 solution (1 mL), brine (1 mL) and then dried over anhydrous Na_2SO_4. The organic layer was filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (eluent: EtOAc/Hexane = 1/3) to yield the desired ketone **3gn** as a light yellow solid (62.1 mg, 80% Yield). R_f: 0.5 (EtOAc/Hexane = 1/5); mp: 122-124 °C; IR (film): 2937, 1652, 1619, 1581, 1502, 1460, 1413, 1357, 1332, 1232, 1180, 1127, 1076, 1002, 785, 743 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.04 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.30-8.25 (m, 2H), 8.22 (d, *J* = 8.8 Hz, 1H), 8.14 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.51 (dd, *J* =8.4, 4.2 Hz, 1H), 7.12 (s, 2H), 3.97 (s, 3H), 3.88 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.1, 153.0 (2C), 152.5, 149.7, 142.4, 137.3, 135.8, 132.4, 130.9, 129.8, 129.5, 127.4, 122.1, 107.9 (2C), 61.0, 56.4 (2C); HRMS (ESI) *m*/*z* calcd for $[C_{19}H_{17}NNaO_4]^+$ (M+Na$^+$): 346.1050; found: 346.1053.

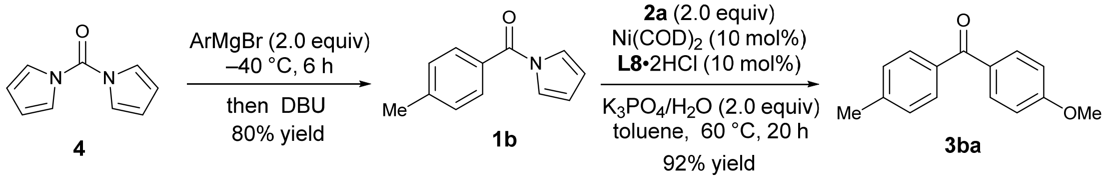
6. Convergent synthesis of diarylketones

General procedure F for synthesis of *N*-acylpyrroles (1b, 1f) from 1,1′-carbonyldipyrrole 4.



A previously reported procedure was followed.[7j]

To a solution of **4** (80.1 mg, 0.50 mmol, 1.0 equiv) in CH_2Cl_2 (4.0 mL, 0.13 M) at –40 °C was added Grignard reagent (1.00 mmol, 2.0 equiv) dropwise. Then the mixture was stirred at –40 °C for 6 h. When complete, the reaction was quenched with saturated aqueous NH_4Cl (4 mL), diluted with EtOAc (4 mL) and warmed to room temperature. The organic layer was washed with saturated aqueous NH_4Cl (2 mL×2), dried over Na_2SO_4, filtered and concentrated. The residue remaining after concentration was dissolved in THF (4.0 mL), cooled to 0 °C, and treated with DBU (4.5 uL, 0.03 mmol). After stirring for 45 min, the reaction was diluted with EtOAc (4 mL), washed with brine (4 mL), dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography to yield the desired *N*-acylpyrrole **1**.

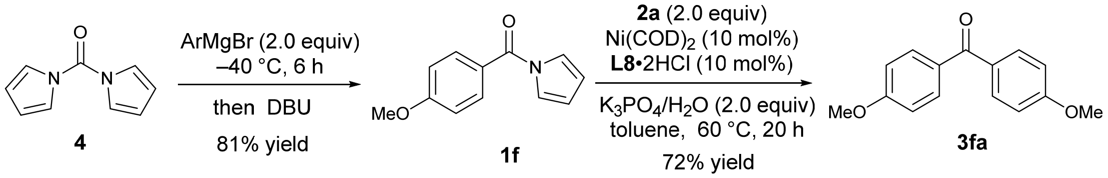


(1*H*-Pyrrol-1-yl)(*p*-tolyl)methanone (1b)

Following **general procedure F**, the reaction of 1,1′-carbonyldipyrrole **4** (80.1 mg, 0.5 mmol) with *p*-tolylmagnesium bromide (1M in 2-MeTHF, 1.0 mL, 1.0 mmol), afforded the desired *N*-acylpyrrole **1b**[7b] as a light yellow oil (74.1 mg, 80% Yield). R_f: 0.5 (EtOAc/Hexane = 1/20); IR (film): 3148, 2920, 2850, 1697, 1609, 1543, 1509, 1466, 1401, 1329, 1303, 1089, 1074, 882, 832, 740 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, J = 7.8 Hz, 2H), 7.33-7.26 (m, 4H), 6.33 (t, J = 2.2 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.8, 143.1, 130.4, 129.8 (2C), 129.2 (2C), 121.4 (2C), 113.0 (2C), 21.7; MS (ESI) *m/z* 186 (M+H$^+$, 100%).

(4-Methoxyphenyl)(*p*-tolyl)methanone (3ba)

Following **general procedure E**, the reaction of *N*-acylpyrrole **1b** (44.4 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2a** (105.6 mg, 0.48 mmol), afforded the desired ketone **3ba**[8b] as a white solid (50.0 mg, 92%). The spectral data are identical with those described above for **3ba**.



(4-Methoxyphenyl)(1H-pyrrol-1-yl)methanone (1f)

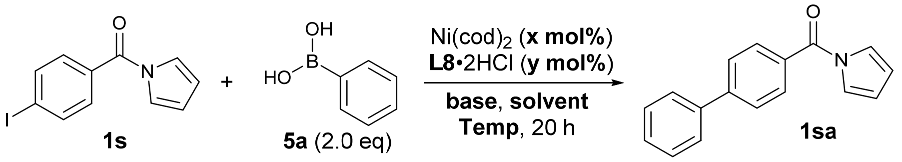
Following **general procedure E**, the reaction of 1,1'-carbonyldipyrrole **4** (80.1 mg, 0.50 mmol) with (4-methoxyphenyl)magnesium bromide (1.0 M in THF, 1.0 mL, 0.50 mmol), afforded the desired *N*-acylpyrrole **1f**[7c] as a light yellow oil (81.5 mg, 81% Yield). R$_f$: 0.5 (EtOAc/Hexane = 1/20); IR (film): 3147, 2932, 2840, 1690, 1604, 1575, 1512, 1465, 1421, 1400, 1330, 1299, 1258, 1172, 1089, 1074, 1027, 883, 843, 764, 742, 645, 623 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, J = 8.7 Hz, 2H), 7.29 (t, J = 2.2 Hz, 2H), 6.99 (d, J = 8.5 Hz, 2H), 6.33 (t, J = 2.2 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.2, 163.0, 132.1 (2C), 125.3, 121.4 (2C), 113.9 (2C), 112.8 (2C), 55.6; MS (ESI) *m/z* 224 (M+Na$^+$, 100%).

Bis(4-methoxyphenyl)methanone (3fa)

Following **general procedure E**, the reaction of *N*-acylpyrrole **1f** (48.3 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2a** (105.6 mg, 0.48 mmol), afforded the desired ketone **3fa**[8d] as a pale yellow solid (41.9 mg, 72%). The spectral data are identical with those described above for **3fa**.

7. Chemoselective Suzuki-coupling of *N*-(*p*-iodo/bromo)benzoylpyrrole with functionalized boronic acids

Table S6. Reaction optimization

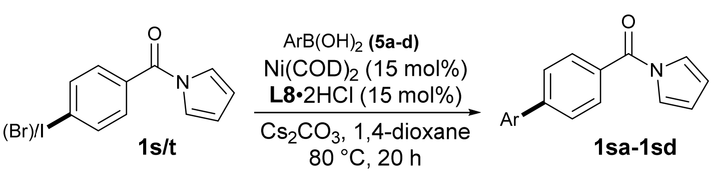


Entry	Ni(COD)$_2$ (x mol%)	**L8**·2HCl (y mol%)	base (equiv)	Temp	solvent	Yield[a] of 1sa (%)
1	10	10	K_3PO_4 (2.0)	80 °C	Toluene	15
2	10	10	Cs_2CO_3 (2.0)	80 °C	Toluene	30
3	**10**	**10**	**Cs_2CO_3 (2.0)**	**80 °C**	**1,4-dioxane**	**98 (92[b])**
4	5	5	Cs_2CO_3 (2.0)	80 °C	1,4-dioxane	45
5	10	10	Cs_2CO_3 (2.0)	70 °C	1,4-dioxane	88
6	10	10	Cs_2CO_3 (2.0)	90 °C	1,4-dioxane	98

[a] Yields were determined by ^{1}H NMR analysis of crude mixture by using 1,3,5-trimethoxybenzene as an internal standard. [b] Isolated yields.

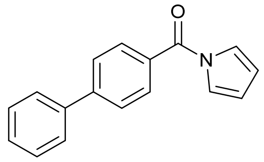
A vial packaged with tin foil was charged with anhydrous **base** (0.48 mmol, 2.0 equiv), *N*-(*p*-iodo)pyrrole **1s** (71.3 mg, 0.24 mmol, 1.0 equiv), phenylboronic acid **5a** (58.5 mg, 0.48 mmol, 2.0 equiv) and a magnetic stir bar. Then the vial was taken into a glove box, charged with Ni(COD)$_2$ (**x mol%**) and **L8**·2HCl (**y mol%**). After that, **solvent** (0.5 M) was added. The vial was sealed with screw cap, removed from the glove box, and stirred vigorously at **T** °C for 20 h. After cooling to room temperature, the mixture was diluted with CH_2Cl_2 (1 mL), washed with a saturated aqueous Na_2CO_3 solution (1 mL) and brine (1 mL), and then dried over anhydrous Na_2SO_4. The organic layer was filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography to yield the desired *N*-acylpyrrole **1sa**.

General procedure G for Suzuki-Miyaura coupling of *N*-(*p*-iodo/bromobenzoyl)pyrrole 1s/t and arylboronic acids 5a-d to yield *N*-acylpyrroles 1sa-1sd.



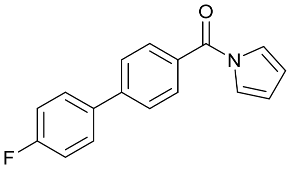
A vial packaged with tin foil was charged with anhydrous Cs_2CO_3 (156.4 mg, 0.48 mmol, 2.0 equiv), *N*-(*p*-iodo/bromobenzoyl)pyrrole **1s/t** (71.3 mg, 0.24 mmol, 1.0 equiv), arylboronic acid **5** (0.48 mmol, 2.0 equiv) and a magnetic stir bar. Then the vial was taken into a glove box, charged with Ni(COD)$_2$ (9.9 mg, 0.036 mmol, 15 mol%) and **L8**·2HCl (24.3 mg, 0.036 mmol, 15 mol%). After that, 1,4-dioxane (0.5 mL, 0.5 M) was added. The vial was sealed with screw cap, removed from the glove box, and stirred vigorously at 80 °C for 20 h. After cooling to room temperature, the mixture was diluted with CH_2Cl_2 (1 mL), washed with a saturated aqueous Na_2CO_3 solution (1 mL) and brine (1 mL), and then dried over anhydrous Na_2SO_4. The combined organic layer was filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography to yield the desired *N*-acylpyrrole.

(1,1'-Biphenyl-4-yl)(1*H*-pyrrol-1-yl)methanone (1sa)



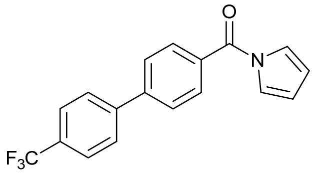
Following **general procedure G** [except Ni(COD)$_2$ (6.6 mg, 0.024 mmol), **L8**·2HCl (16.2 mg, 0.024 mmol)], the reaction of *N*-(*p*-iodo/bromobenzoyl)pyrrole **1s/1t** (0.24 mmol) with phenylboronic acid **5a** (58.5 mg, 0.48 mmol), afforded the desired *N*-acylpyrrole **1sa** as a white solid (for **1s**: 54.6 mg, 92% Yield; for **1t**: 49.9 mg, 84% Yield). R_f: 0.4 (EtOAc/Hexane = 1/20); mp: 109-111 °C; IR (film): 3121, 1681, 1606, 1467, 1404, 1334, 1302, 1192, 1132, 1095, 1076, 882, 851, 741, 704 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.66-7.62 (m, 2H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 1H), 7.33 (t, *J* = 2.1 Hz, 2H), 6.37 (t, *J* = 2.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.6, 145.3, 139.8, 131.9, 130.3 (2C), 129.1 (2C), 128.4, 127.3 (2C), 127.2 (2C), 121.4 (2C), 113.2 (2C); HRMS (ESI) *m/z* calcd for $[C_{17}H_{13}NNaO]^+$ (M+Na$^+$): 270.0889; found: 270.0891.

[4'-Fluoro-(1,1'-biphenyl)-4-yl](1*H*-pyrrol-1-yl)methanone (1sb)



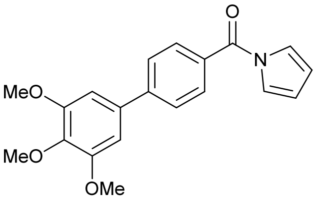
Following **general procedure G**, the reaction of *N*-(*p*-iodobenzoyl)pyrrole **1s** (71.3 mg, 0.24 mmol) with arylboronic acid **5b** (67.2 mg, 0.48 mmol), afforded the desired *N*-acylpyrrole **1sb** as a white solid (45.8 mg, 72% Yield). R_f: 0.4 (EtOAc/Hexane = 1/20); mp: 90-92 °C; IR (film): 2922, 1691, 1604, 1523, 1496, 1466, 1399, 1329, 1300, 1256, 1196, 1182, 1159, 1132, 1088, 1075, 882, 828, 741, 716, 632; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.63-7.58 (m, 2H), 7.33 (t, *J* = 2.3 Hz, 2H), 7.37 (t, *J* = 2.3 Hz, 2H), 6.37 (t, *J* = 2.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.5, 163.1 (d, *J* = 248.6 Hz), 144.3, 135.9 (d, *J* = 2.9 Hz), 132.0, 130.3 (2C), 129.0 (d, *J* = 8.2 Hz, 2C), 127.1 (2C), 121.4 (2C), 116.1 (d, *J* = 21.8 Hz, 2C), 113.3 (2C); HRMS (ESI) *m/z* calcd for $[C_{17}H_{12}FNNaO]^+$ (M+Na$^+$): 288.0795; found: 288.0794.

(1*H*-Pyrrol-1-yl)[(4'-(trifluoromethyl)-1,1'-biphenyl-4-yl)methanone (1sc)



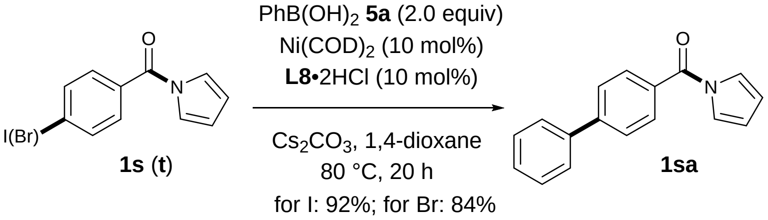
Following **general procedure G**, the reaction of *N*-(*p*-iodobenzoyl)pyrrole **1s** (71.3 mg, 0.24 mmol) with arylboronic acid **5c** (45.6 mg, 0.48 mmol), affording the desired *N*-acylpyrrole **1sc** as a white solid (51.5 mg, 68% Yield). R_f: 0.4 (EtOAc/Hexane = 1/20); mp: 132-134 °C; IR (film): 2922, 1684, 1606, 1648, 1421, 1397, 1330, 1259, 1161, 1122, 1096, 1073, 1017, 1005, 977, 882, 883, 769, 746, 720, 670; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (d, J = 8.2 Hz, 2H), 7.75 (s, 4H), 7.73 (d, J = 8.4 Hz, 2H), 7.33 (t, J = 2.3 Hz, 2H), 6.38 (t, J = 2.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.3, 143.7, 143.3, 132.9, 130.5 (q, J = 261.0 Hz), 130.4 (2C), 127.7 (2C), 127.4 (2C), 126.1 (q, J = 3.7 Hz, 2C), 124.2 (q, J = 272.4 Hz), 121.4 (2C), 113.4 (2C); HRMS (ESI) *m/z* calcd for $[C_{18}H_{12}F_3NNaO]^+$ (M+Na$^+$): 338.0763; found: 338.0764.

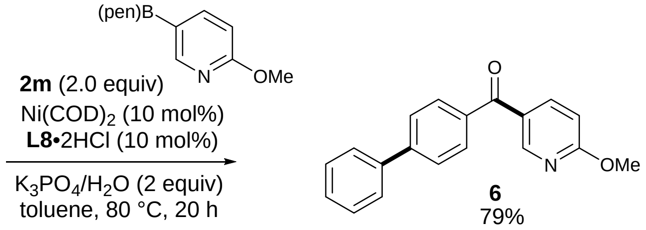
(1*H*-Pyrrol-1-yl) [(3',4',5'-trimethoxy-(1,1'-biphenyl)-4-yl]methanone (1sd)



Following **general procedure G** [except Ni(COD)$_2$ (9.9 mg, 0.036 mmol), **L8**·2HCl (24.3 mg, 0.036 mmol)], the reaction of *N*-(*p*-iodobenzoyl)pyrrole **1s** (71.3 mg, 0.24 mmol) with arylboronic acid **5d** (101.8 mg, 0.48 mmol), afforded the desired *N*-acylpyrrole **1sd** as a white solid (62.4 mg, 77% Yield). R_f: 0.4 (EtOAc/Hexane = 1/20); mp: 146-148 °C; IR (film): 3145, 2963, 2936, 2839, 1090, 1606, 1586, 1559, 1497, 1465, 1421, 1399, 1330, 1302, 1257, 1184, 1171, 1126, 1090, 1008, 888, 870, 825, 744, 688; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, J = 7.9 Hz, 2H), 7.69 (d, J = 8.2 Hz, 2H), 7.33 (t, J = 2.3 Hz, 2H), 6.83 (s, 2H), 6.37 (t, J = 2.4 Hz, 2H), 3.95 (s, 6H), 3.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.5, 153.8 (2C), 145.4, 138.6, 135.7, 131.9, 130.2 (2C), 127.1 (2C), 121.4 (2C), 113.2 (2C), 104.7 (2C), 61.1, 56.4 (2C); HRMS (ESI) *m/z* calcd for $[C_{20}H_{19}NNaO_4]^+$ (M+Na$^+$): 360.1206; found: 360.1205.

8. Sequential C-X and C-N coupling reactions





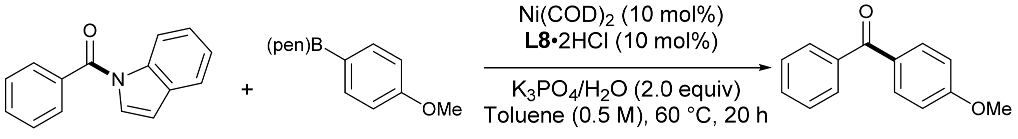
[1,1'-Biphenyl]-4-yl(1*H*-pyrrol-1-yl)methanone (1sa)

Following **General procedure G**, the reaction of *N*-(*p*-iodobenzoyl)pyrrole **1s** (71.3 mg, 0.24 mmol) or *N*-(*p*-bromobenzoyl)pyrrole **1t** (60.0 mg, 0.24 mmol) with phenylboronic acid **5a (**58.5 mg, 0.48 mmol**)**, afforded the desired *N*-acylpyrrole **1sa** as a white solid (for **1s**: 54.6 mg, 92% Yield; for **1t**: 49.9 mg, 84% Yield). R_f: 0.4 (EtOAc/Hexane = 1/20). The spectral data are identical with those described above for **1sa**.

[1,1'-Biphenyl]-4-yl(6-methoxypyridin-3-yl)methanone (6)

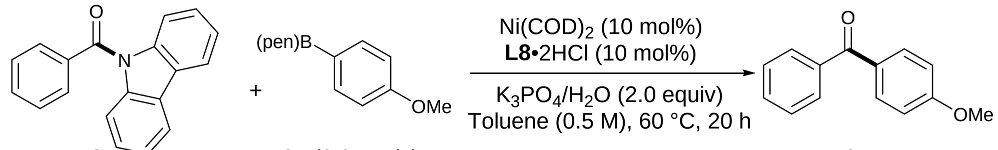
Following **general procedure E** (except T = 80 °C), the reaction of *N*-acylpyrrole **1sa** (54.6 mg, 0.22 mmol) with heteroarylboronic acid neopentyl glycol ester **2m** (97.3 mg, 0.44 mmol), afforded the desired ketone **6** as a white solid (54.9 mg, 79% Yield). R_f: 0.4 (EtOAc/PE = 1/5); mp: 112-113 °C; IR (film): 2921, 1636, 1601, 1558, 1493, 1448, 1403, 1371, 1293, 1264, 1155, 1131, 1017, 853, 835, 738, 698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (d, J = 2.3 Hz, 1H), 8.12 (dd, J = 8.7, 2.5 Hz, 1H), 7.87 (d, J = 8.1 Hz, 2H), 7.71 (d, J = 8.2 Hz, 2H), 7.65 (d, J = 7.7 Hz, 2H), 7.48 (t, J = 7.5 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H), 6.86 (d, J = 8.6 Hz, 1H), 4.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.8, 166.5, 150.7, 145.4, 140.1, 139.9, 136.2, 130.5 (2C), 129.1 (2C), 128.3, 127.4 (2C), 127.2 (2C), 127.1, 111.1, 54.1; HRMS (ESI) *m/z* calcd for $[C_{19}H_{15}NNaO_2]^+$ (M+Na$^+$): 312.0995; found 312.0996.

9. The coupling reactions of amides 7–11 with arylboronic acid neopentyl glycol ester 2a



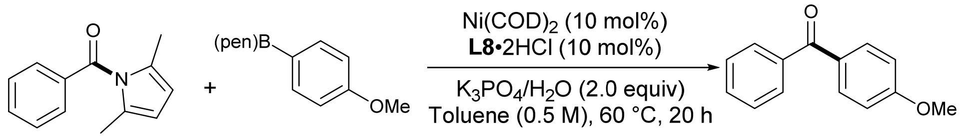
7 **2a** (2.0 equiv) **3aa**

Following **general procedure E**, the reaction of *N*-acylindole **7** (53.1 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2a** (105.6 mg, 0.48 mmol), afforded the desired ketone **3aa** as a white solid (48.4 mg, 95% Yield). R_f: 0.4 (EtOAc/Hexane = 1/10). The spectral data are identical with those described above for **3aa**.



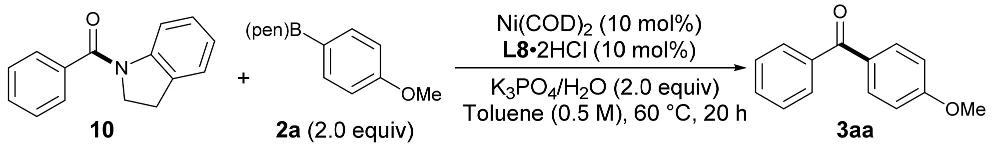
8 **2a** (2.0 equiv) **3aa**

Following **general procedure E**, the reaction of *N*-acylcarbazole **8** (65.1 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2a** (105.6 mg, 0.48 mmol), afforded the desired ketone **3aa** as a white solid (47.9 mg, 94% Yield). R_f: 0.4 (EtOAc/Hexane = 1/10). The spectral data are identical with those described above for **3aa**.



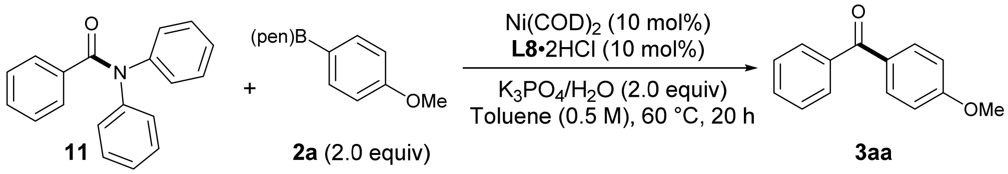
9 **2a** (2.0 equiv) **3aa**

Following **general procedure E**, the reaction of *N*-benzoyl(2,5-dimethyl)pyrrole **9** (47.8 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2a** (105.6 mg, 0.48 mmol), afforded the desired ketone **3aa** as a white solid (40.2 mg, 79% Yield). R_f: 0.4 (EtOAc/Hexane = 1/10). The spectral data are identical with those described above for **3aa**.



10 **2a** (2.0 equiv) **3aa**

Following **general procedure E**, the reaction of *N*-benzoylindoline **10** (53.6 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2a** (105.6 mg, 0.48 mmol), afforded the desired ketone **3aa** as a white solid (12.2 mg, 24% Yield). R_f: 0.4 (EtOAc/Hexane = 1/10). The spectral data are identical with those described above for **3aa**.



Following **general procedure E**, the reaction of *N*,*N*-diphenylbenzamide **11** (65.6 mg, 0.24 mmol) with arylboronic acid neopentyl glycol ester **2a** (105.6 mg, 0.48 mmol), afforded the desired ketone **3aa** as a white solid (7.6 mg, 15% Yield). R$_f$: 0.4 (EtOAc/Hexane = 1/10). The spectral data are identical with those described above for **3aa**.

References

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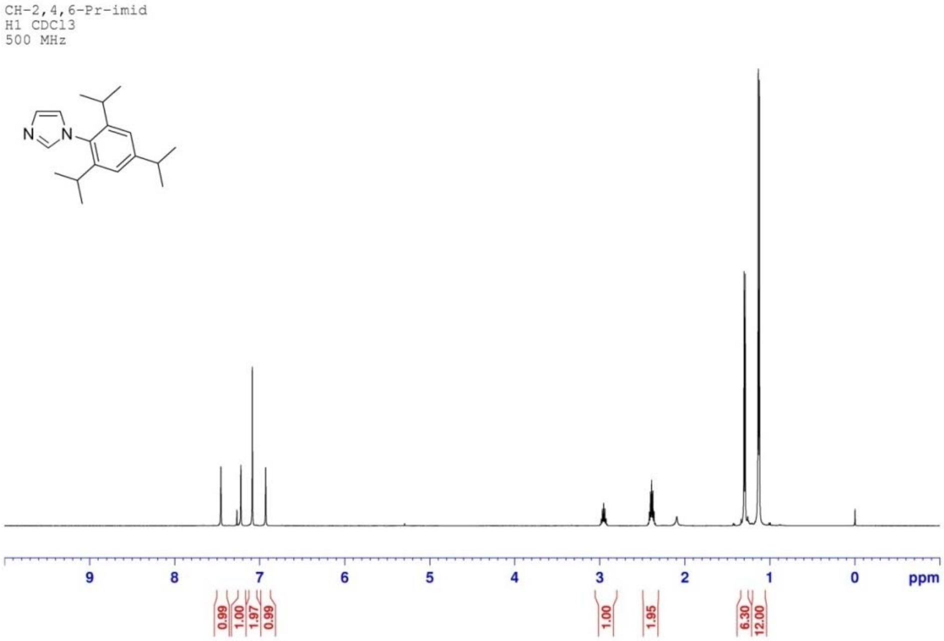
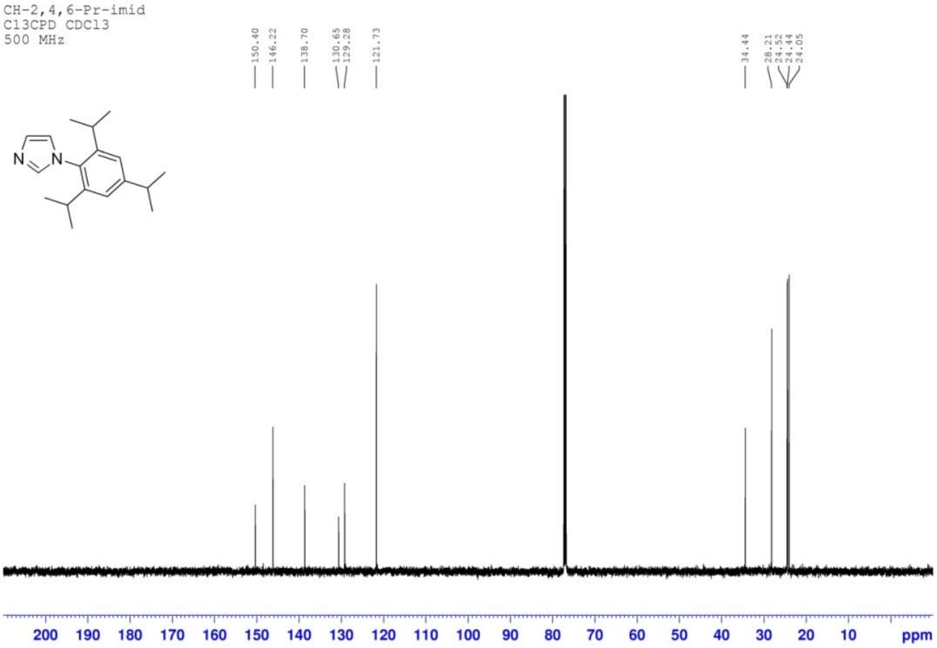
NMR Spectra

^{1}H and ^{13}C NMR spectra of compound 13b





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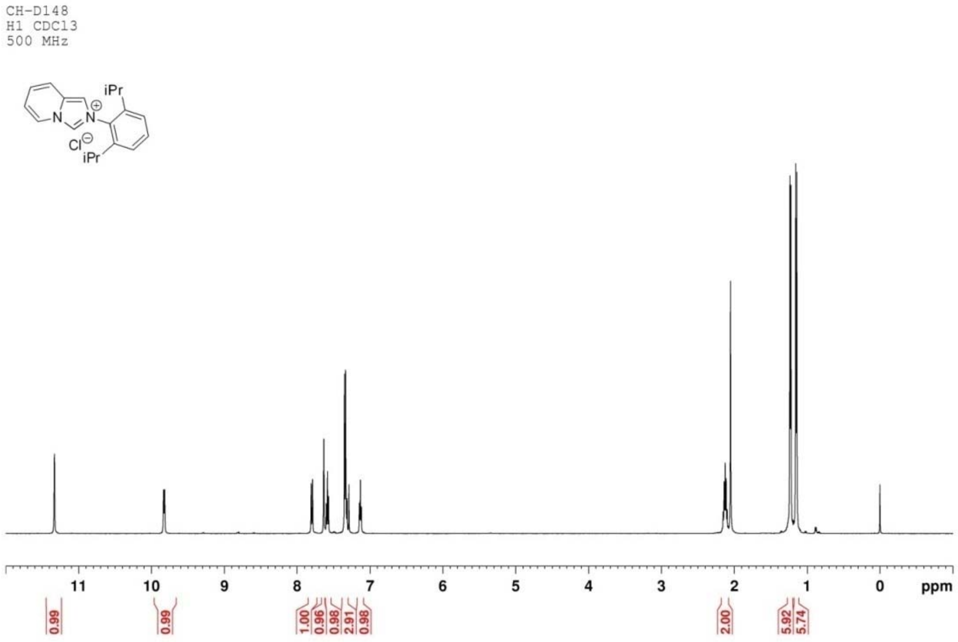

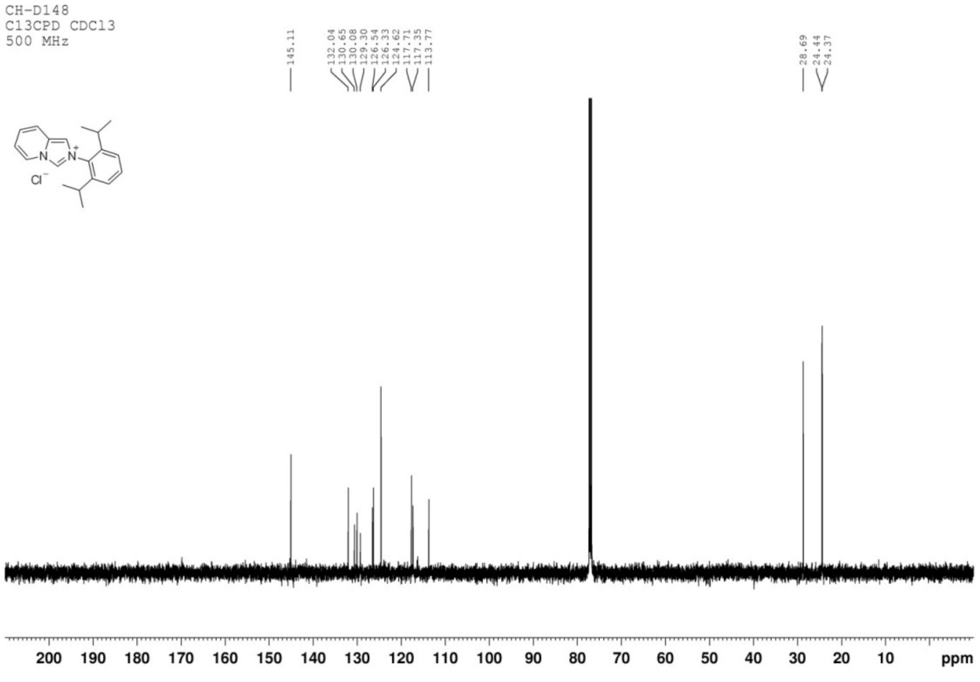

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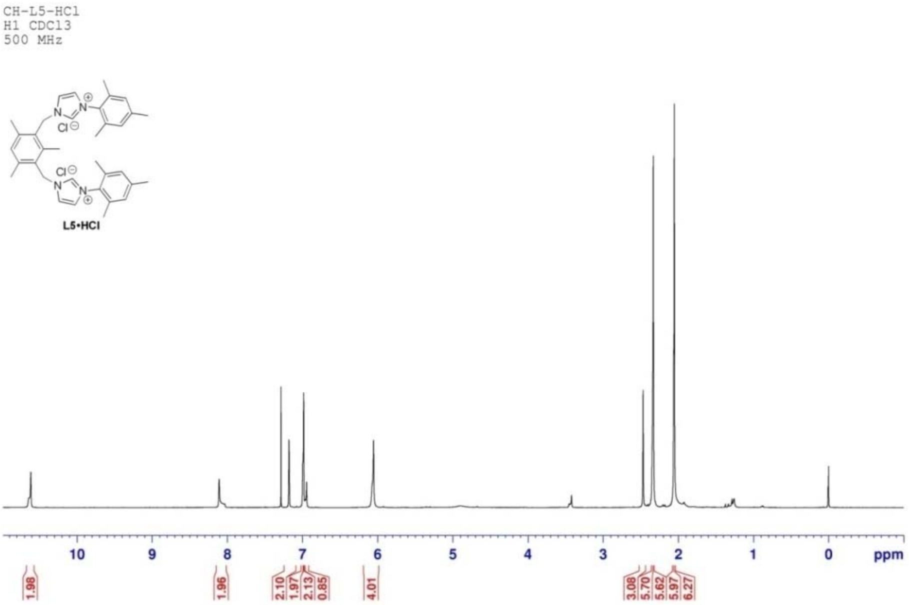

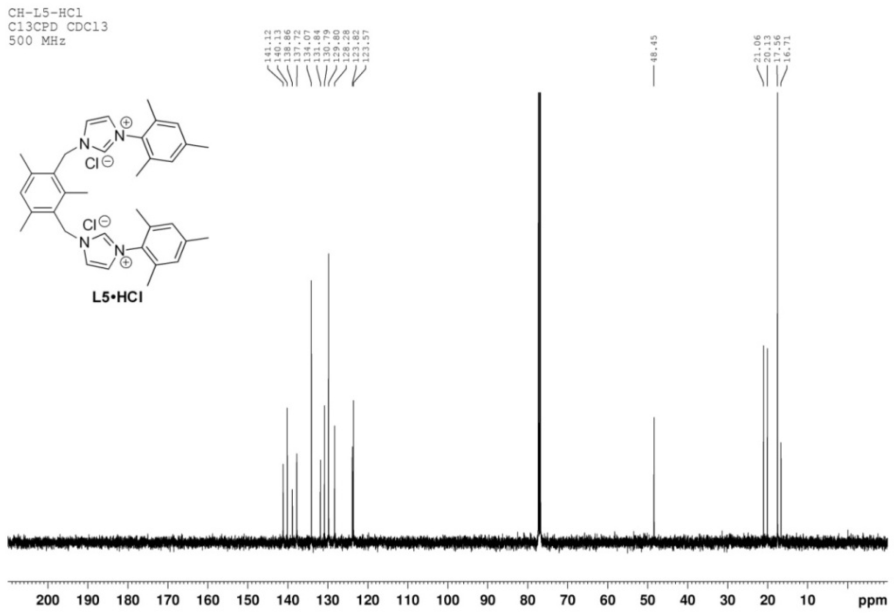

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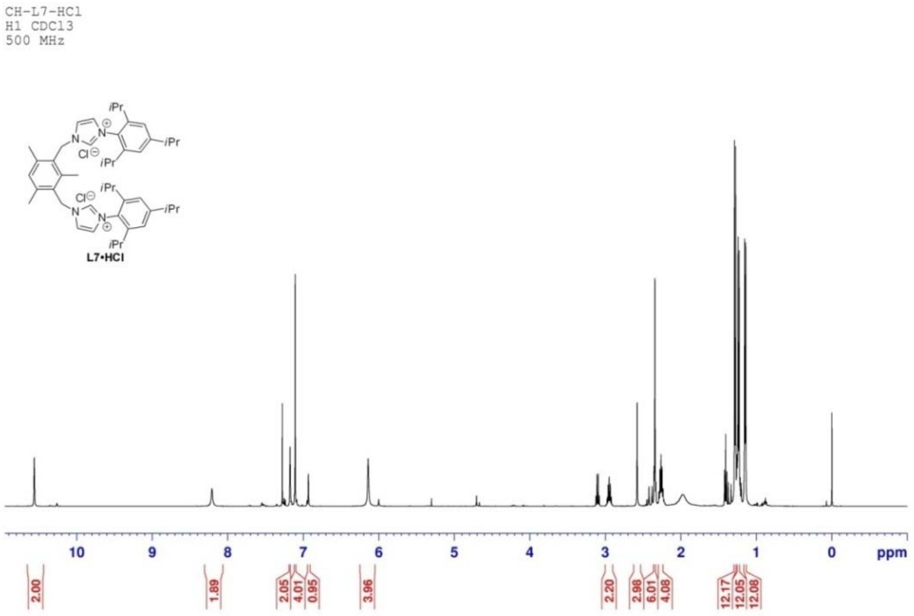

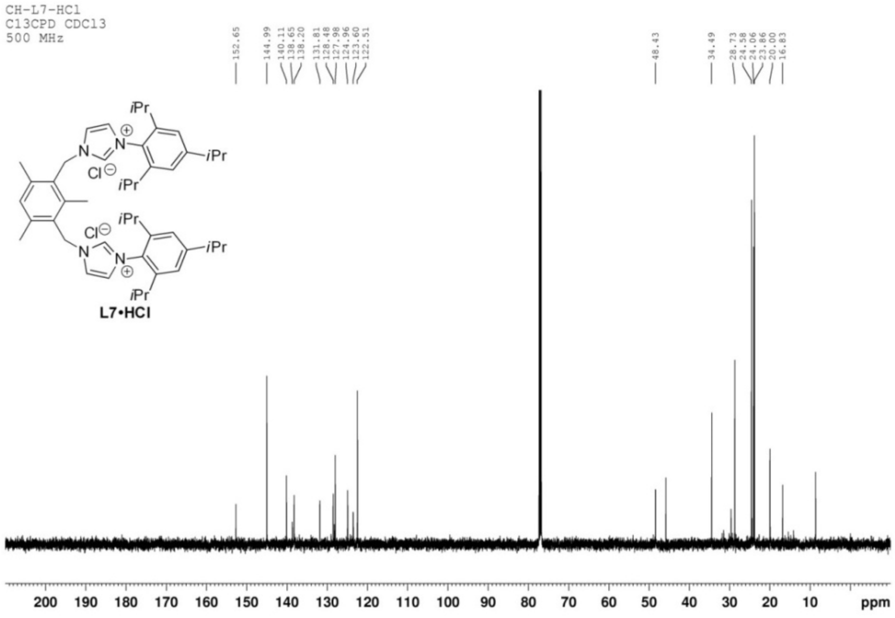

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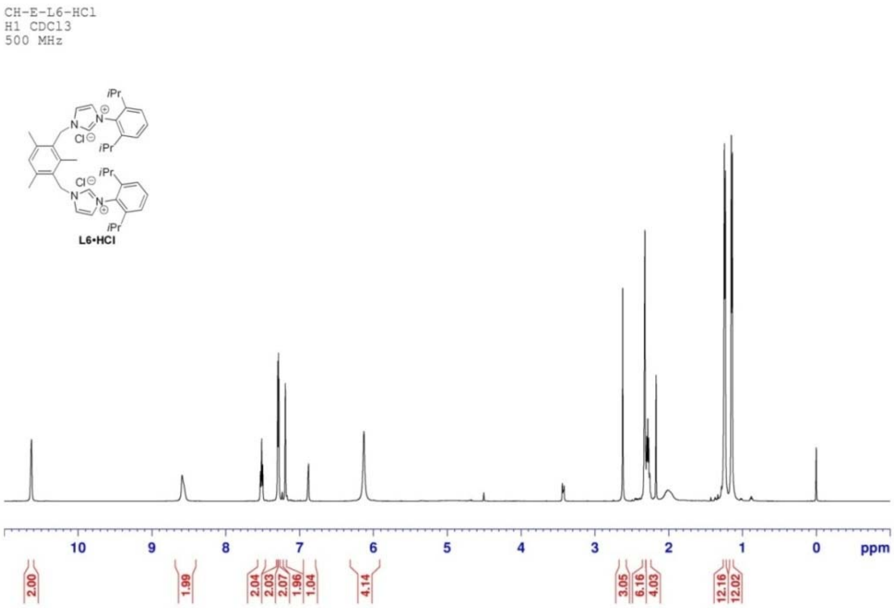

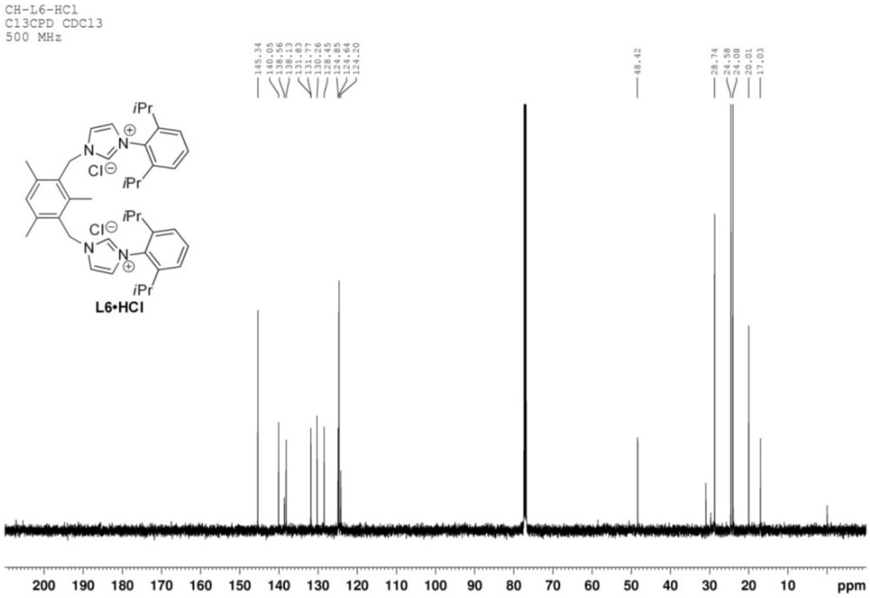

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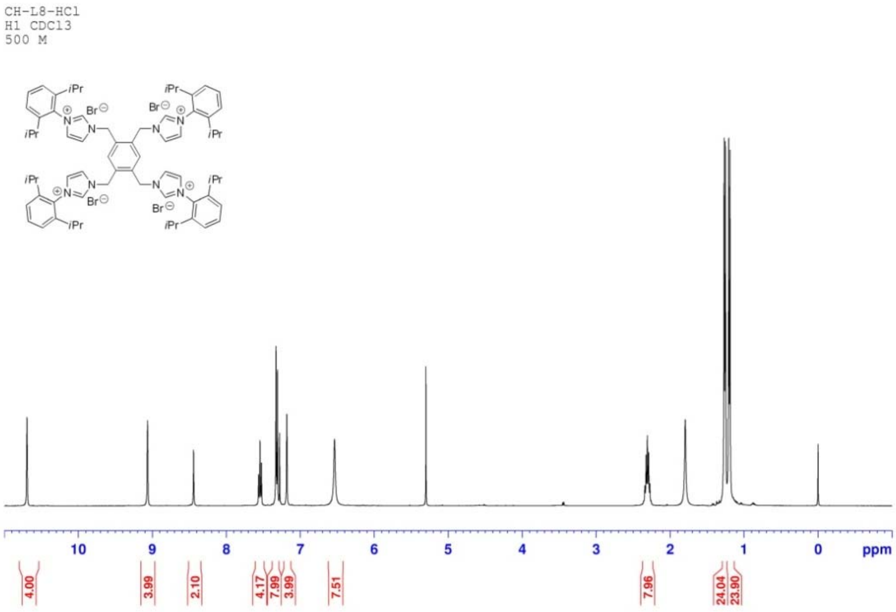
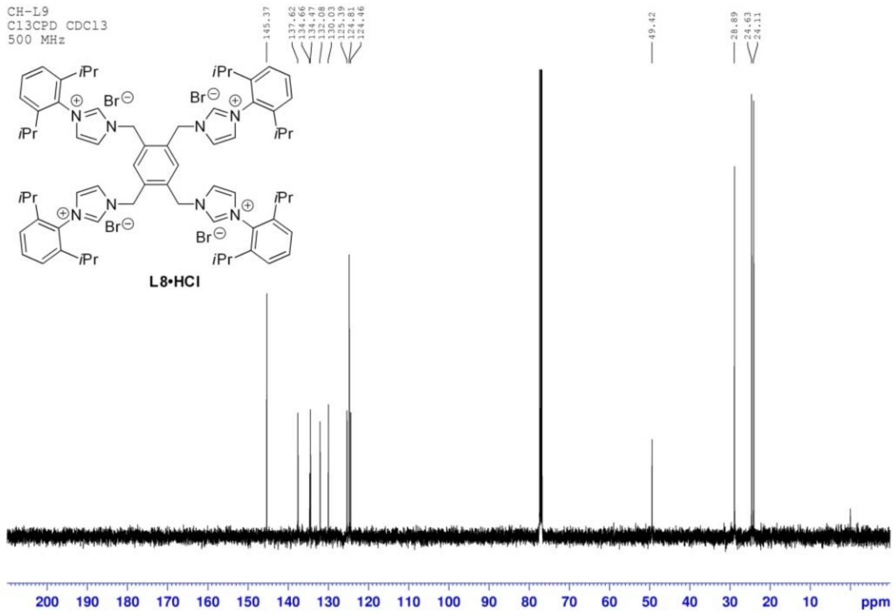
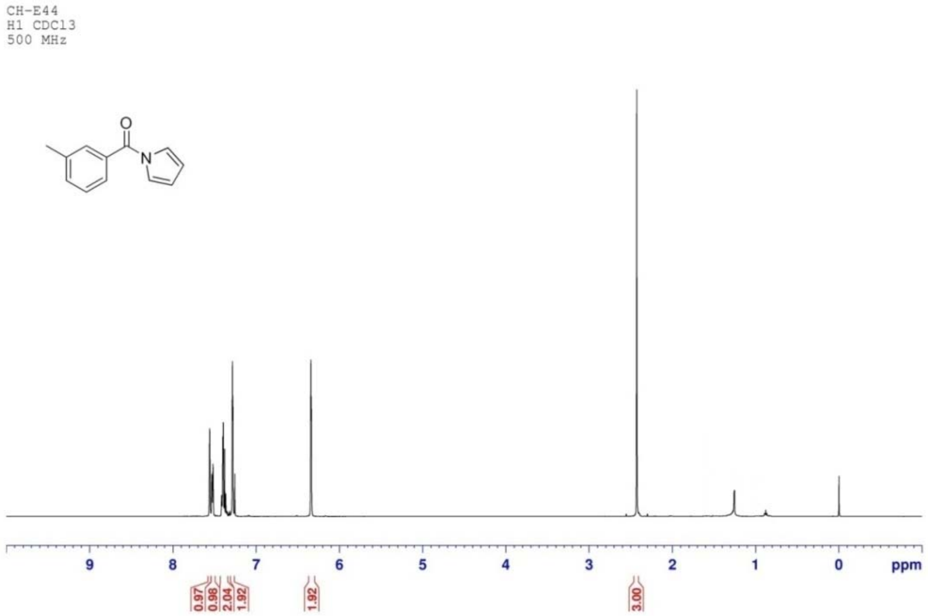
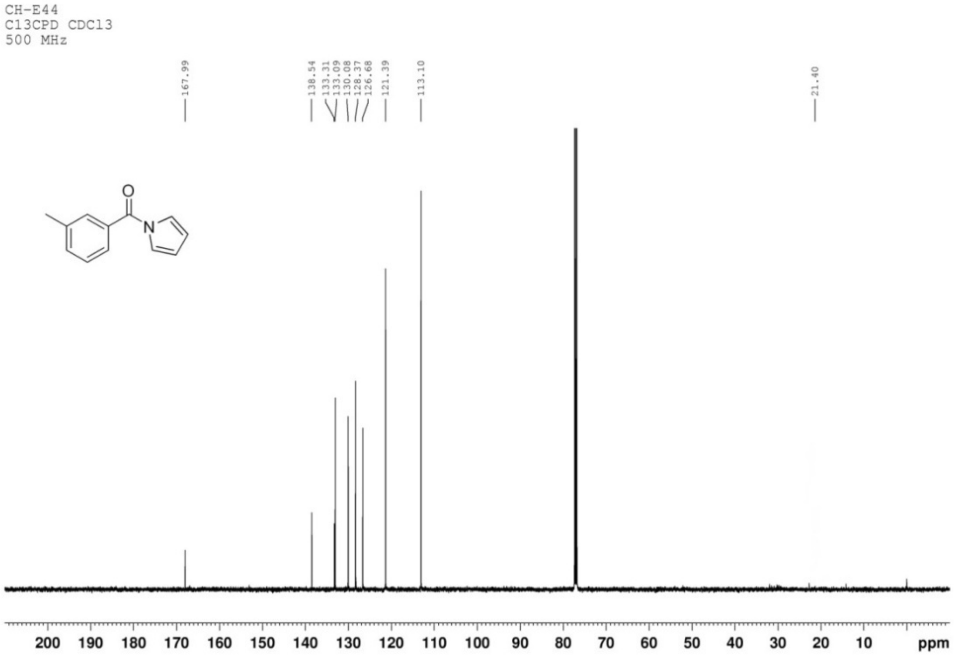




^{1}H and ^{13}C NMR spectra of compound 1c





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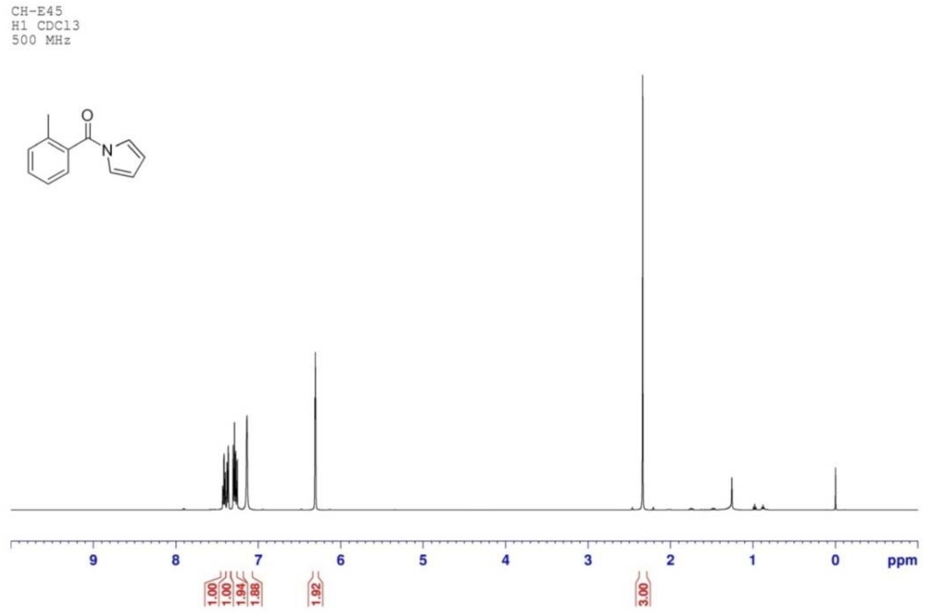

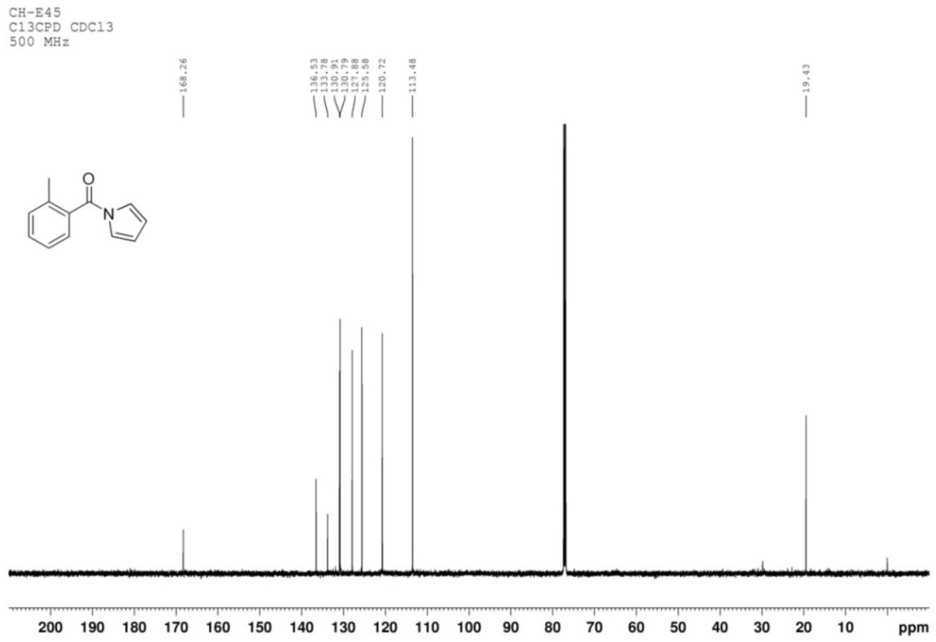

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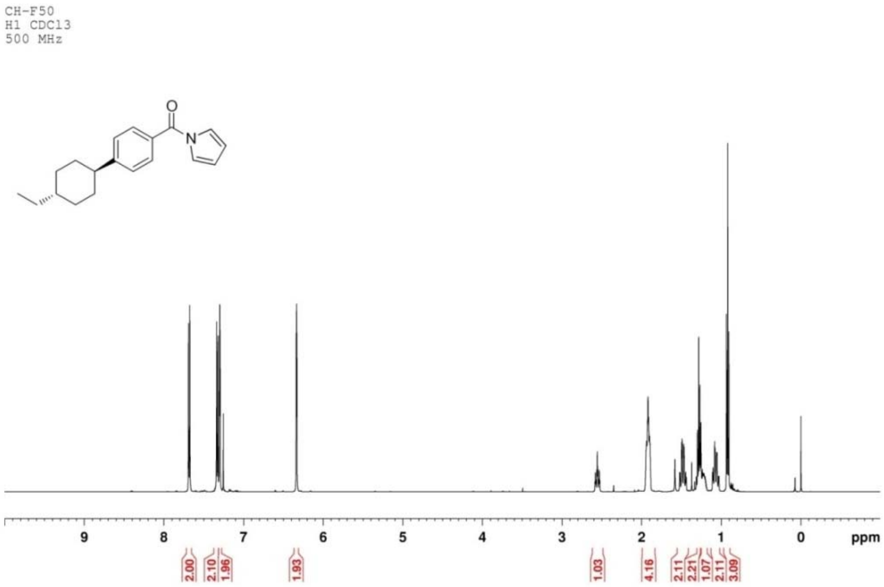

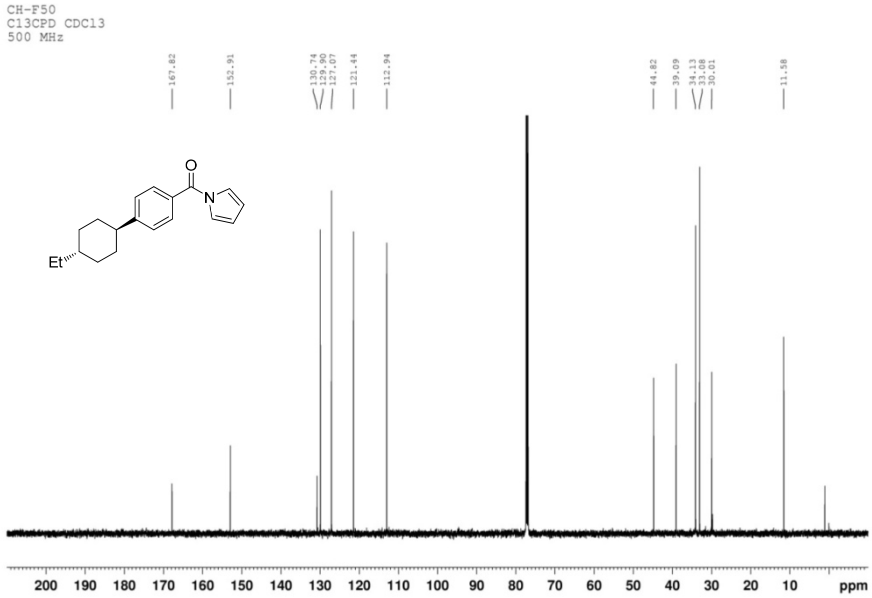

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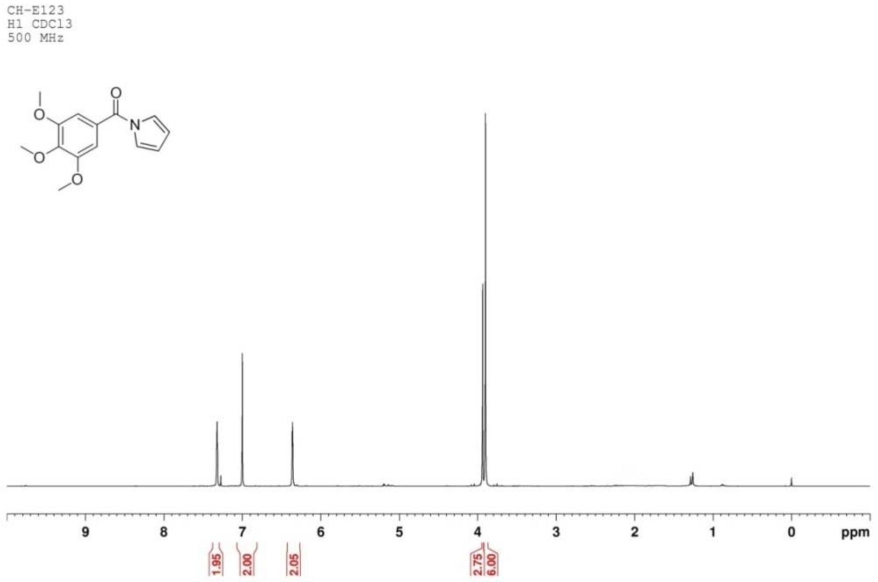
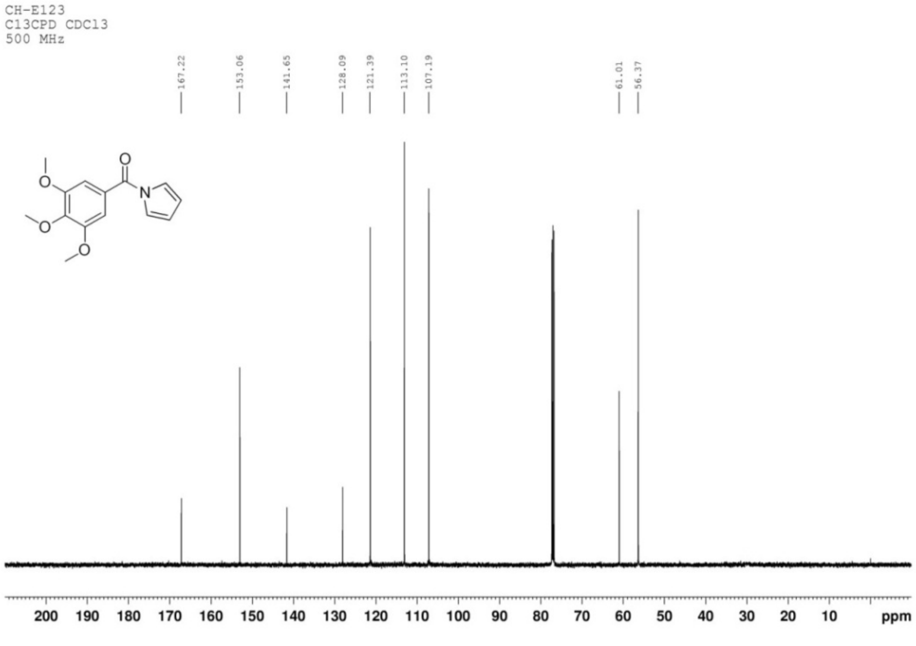
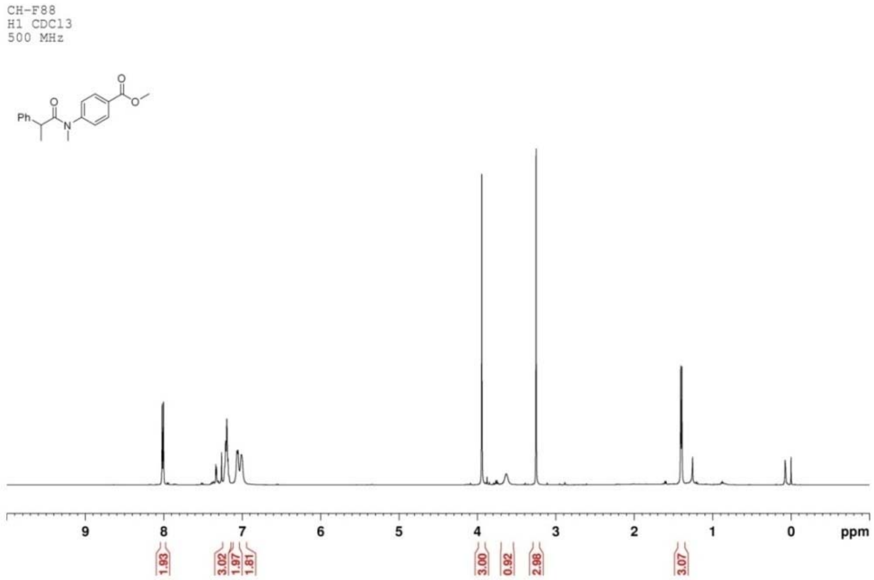
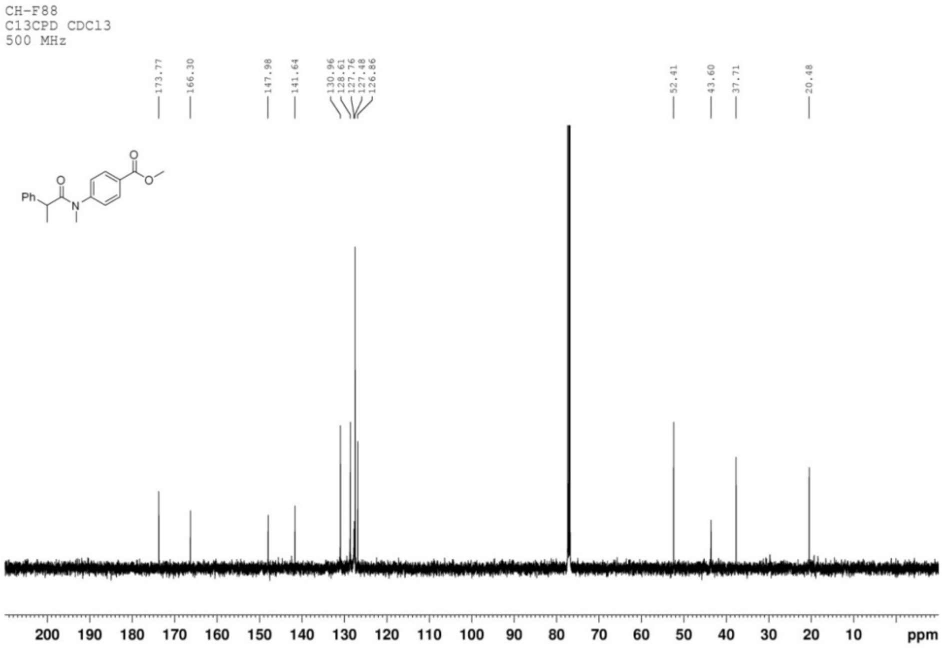




^{1}H and ^{13}C NMR spectra of compound 16





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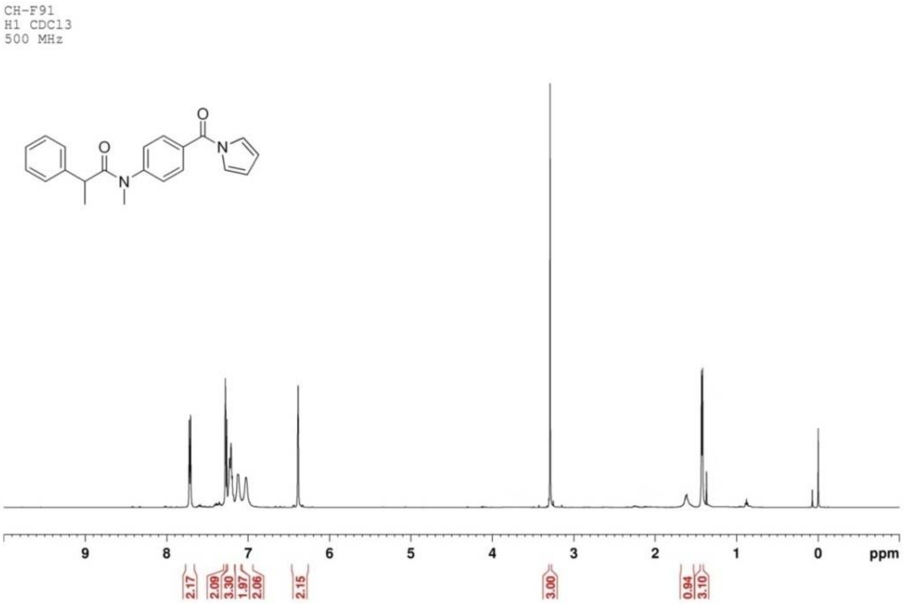

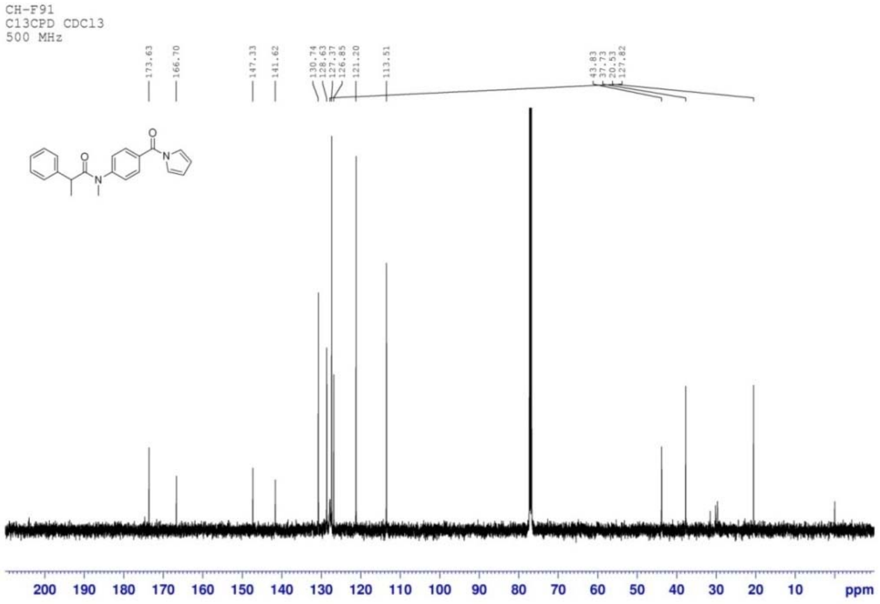

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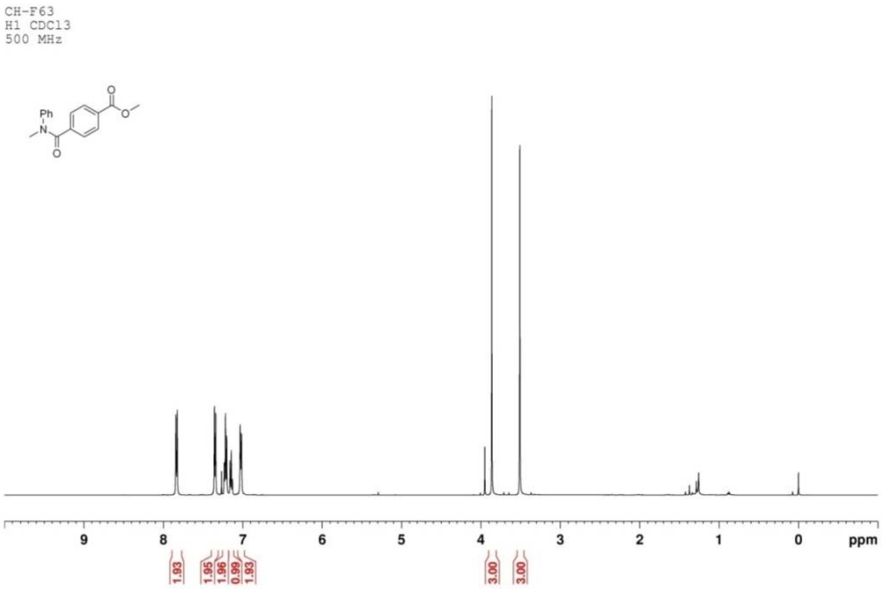

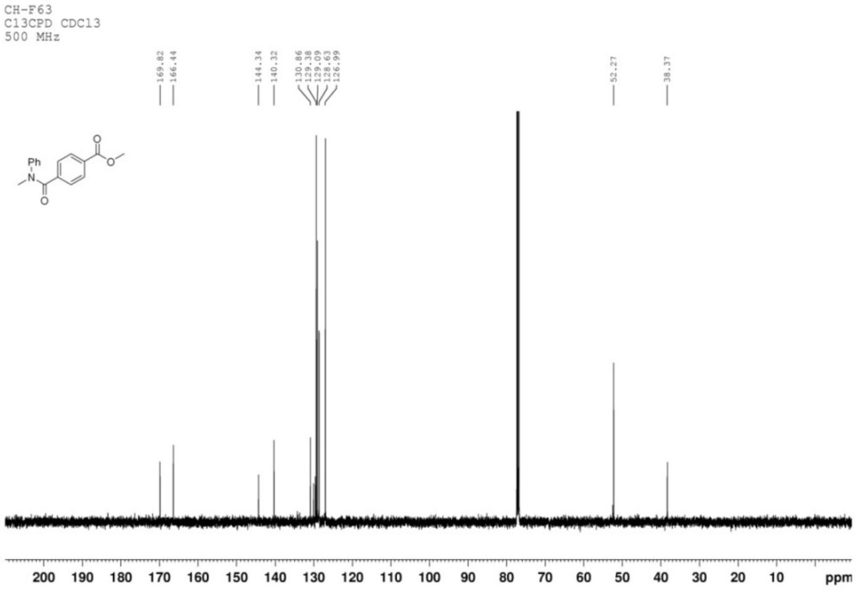

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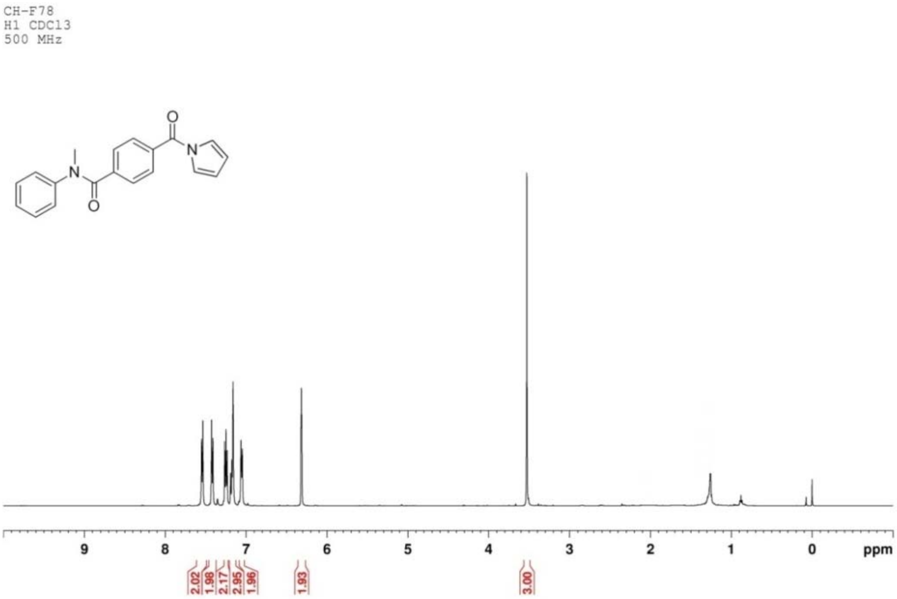
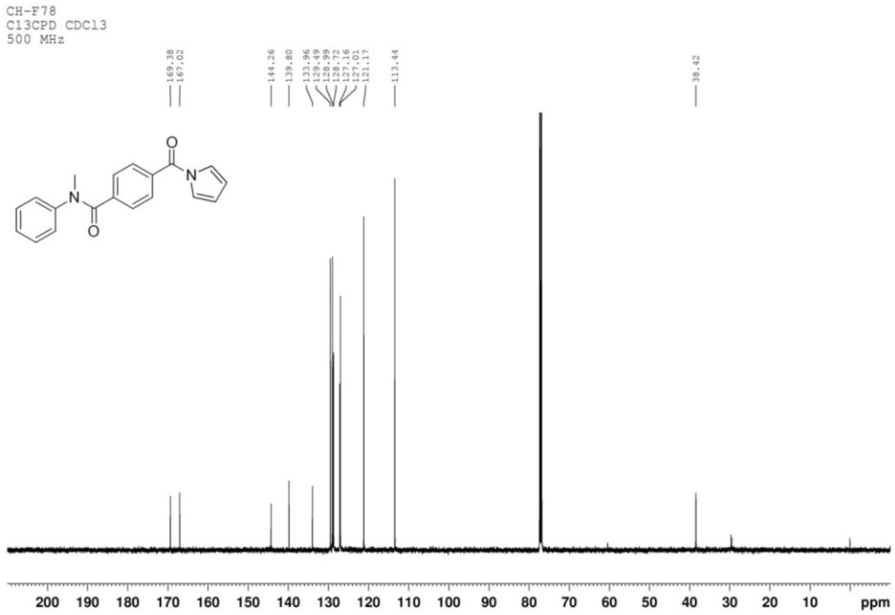
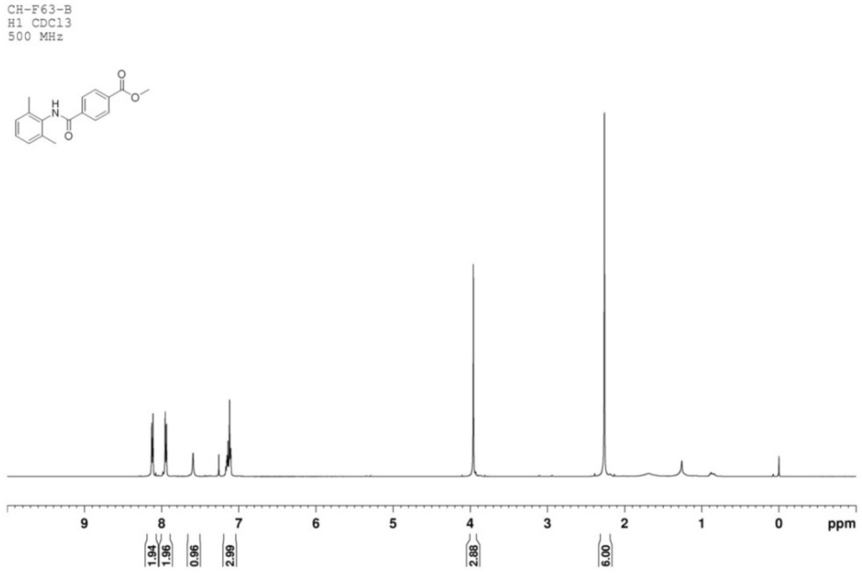
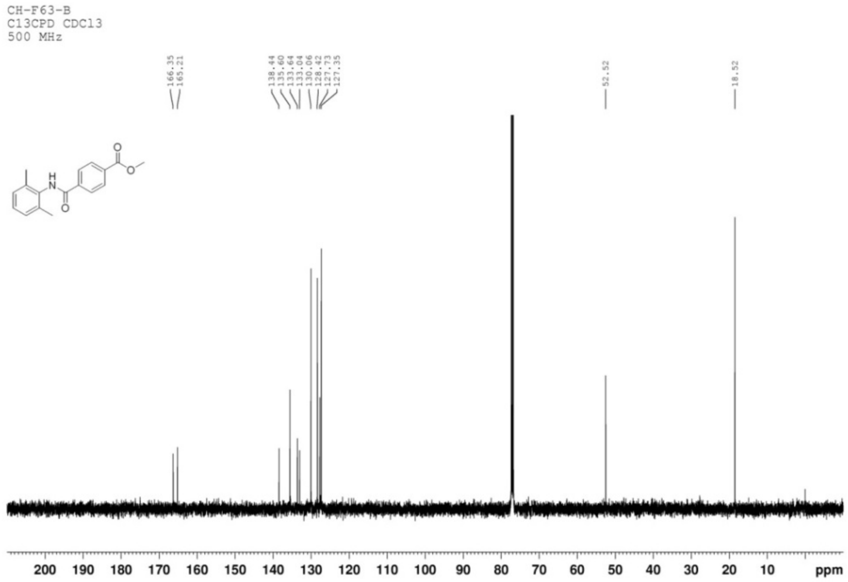




^{1}H and ^{13}C NMR spectra of compound 21





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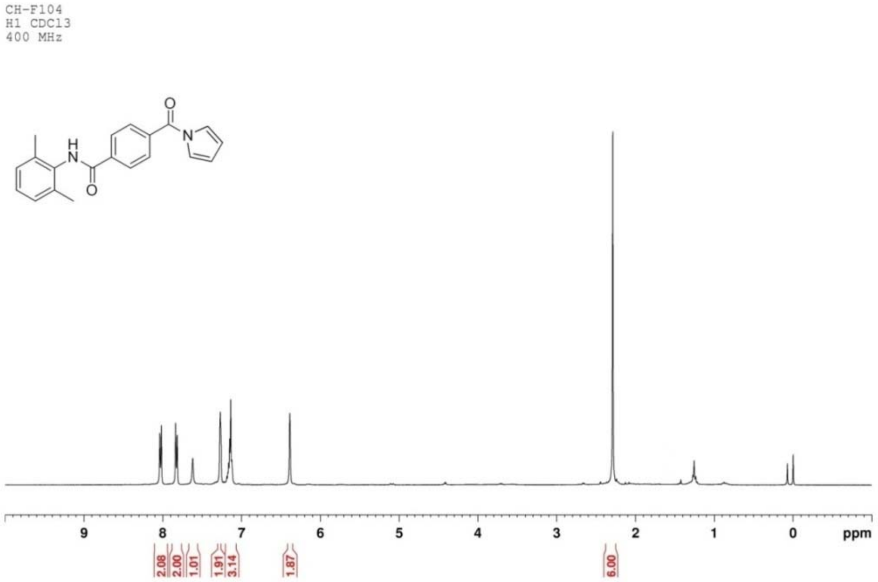

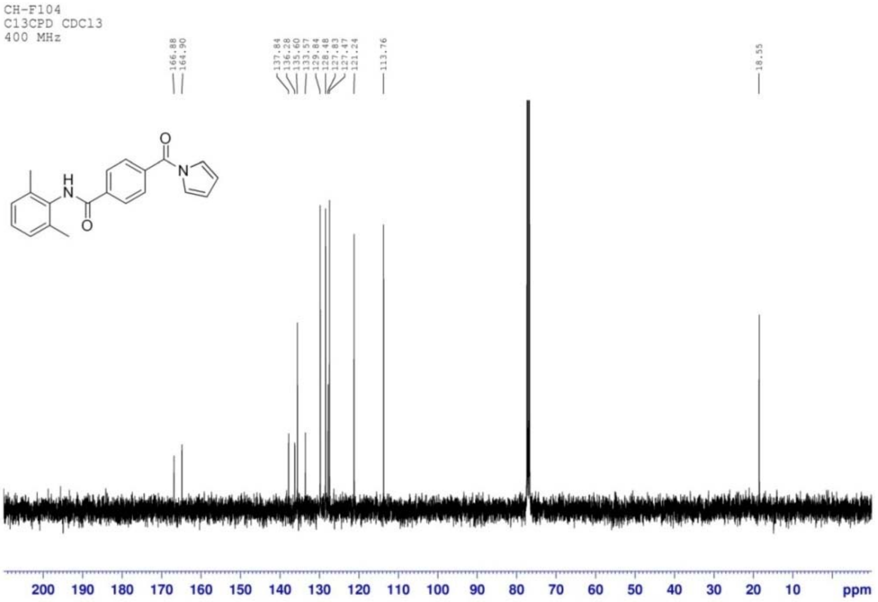

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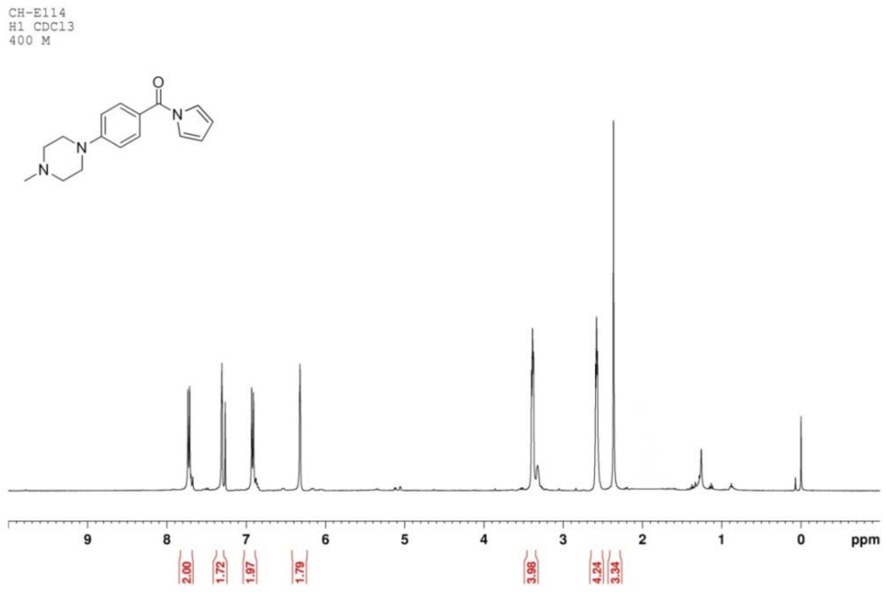

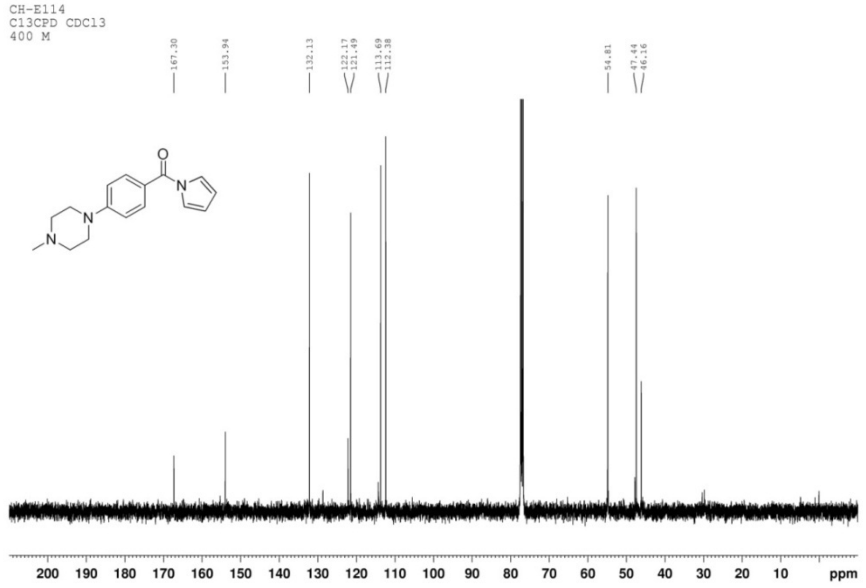

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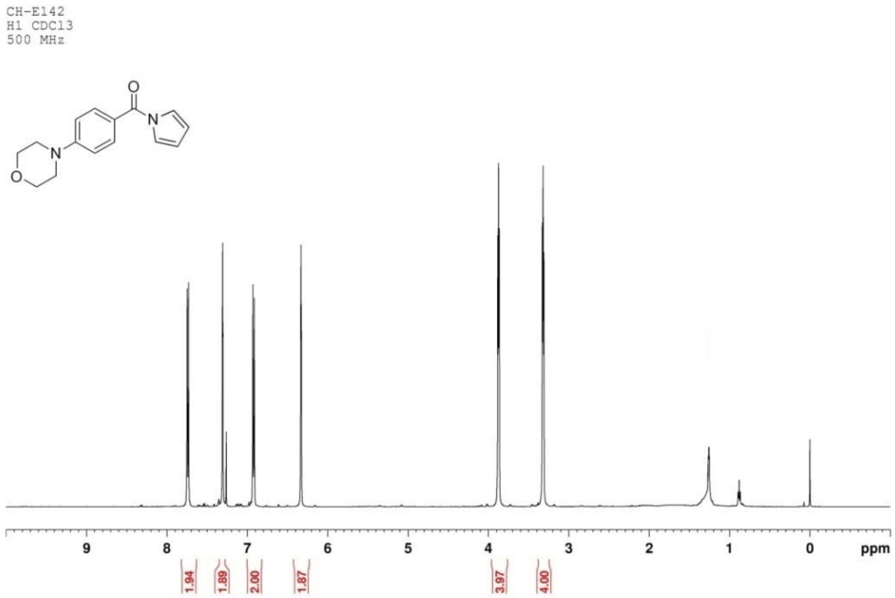

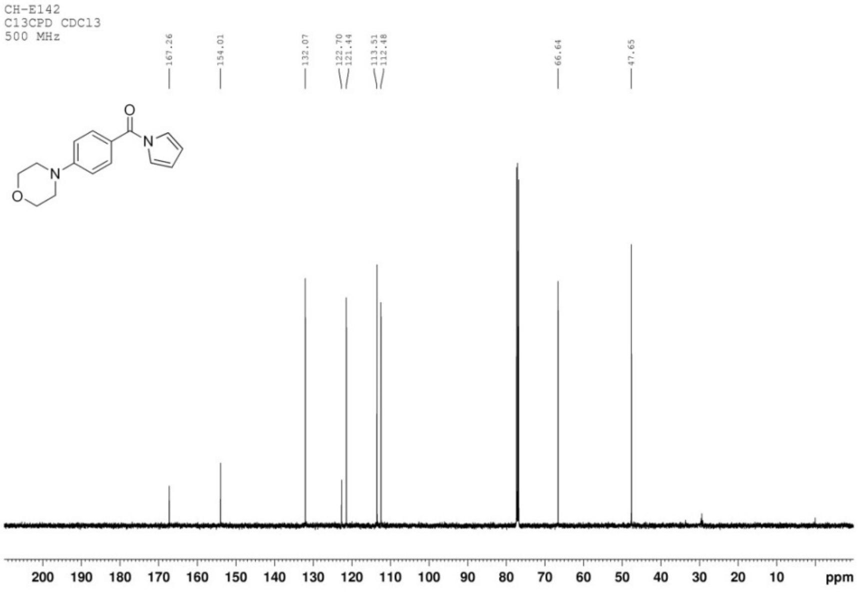

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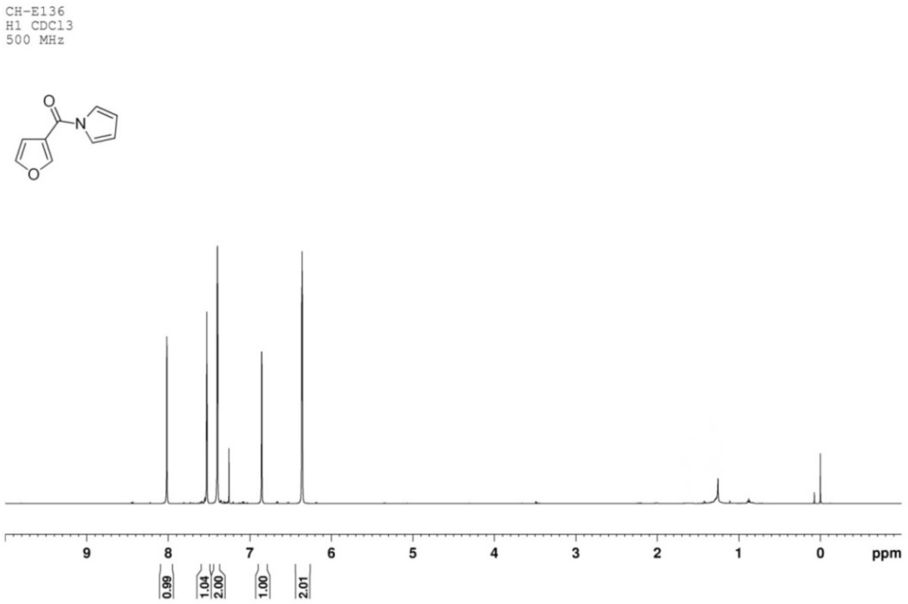

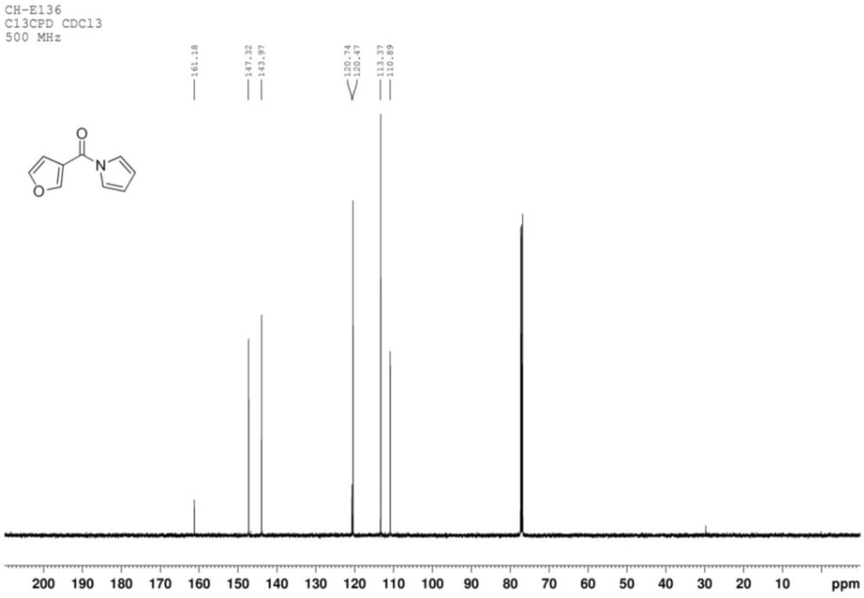

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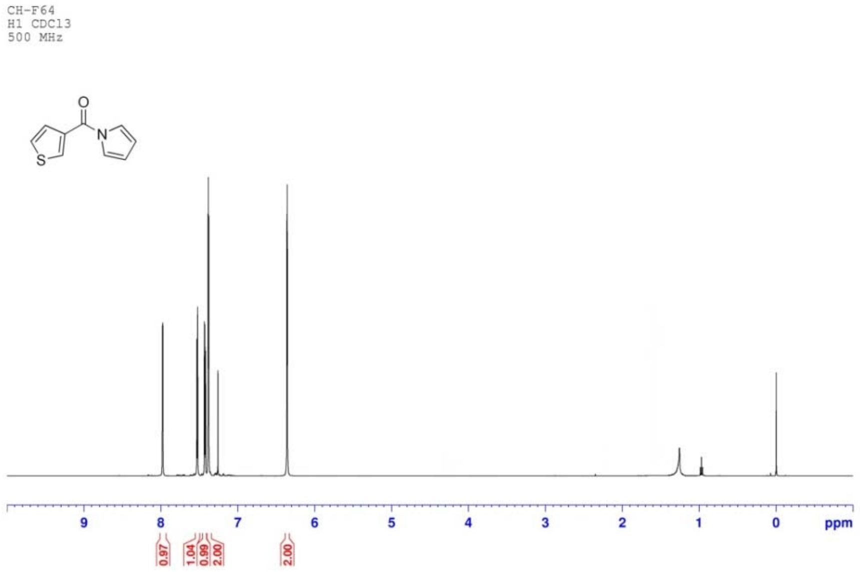

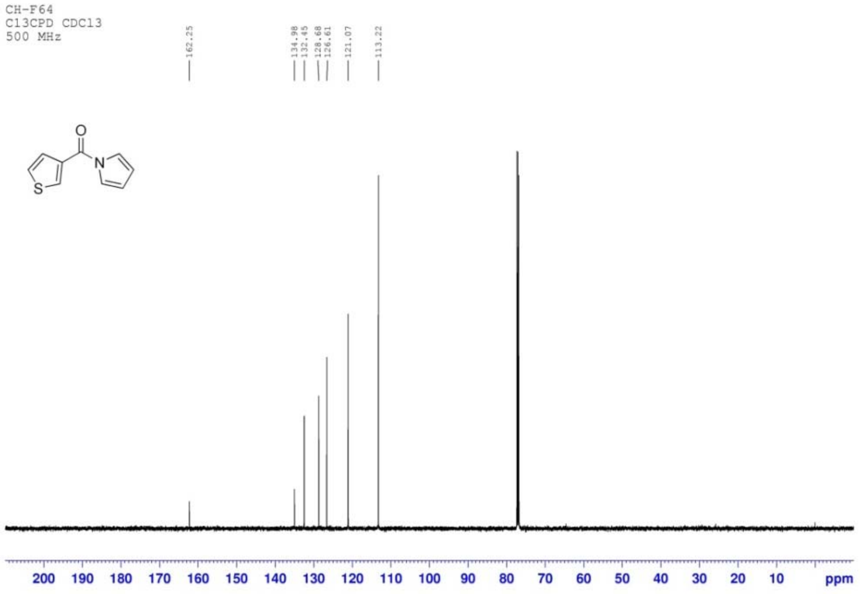

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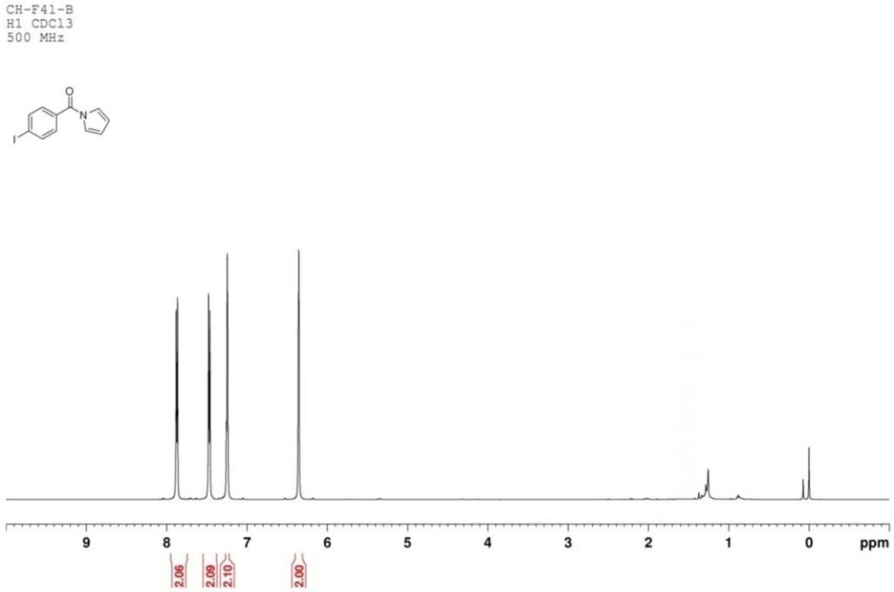

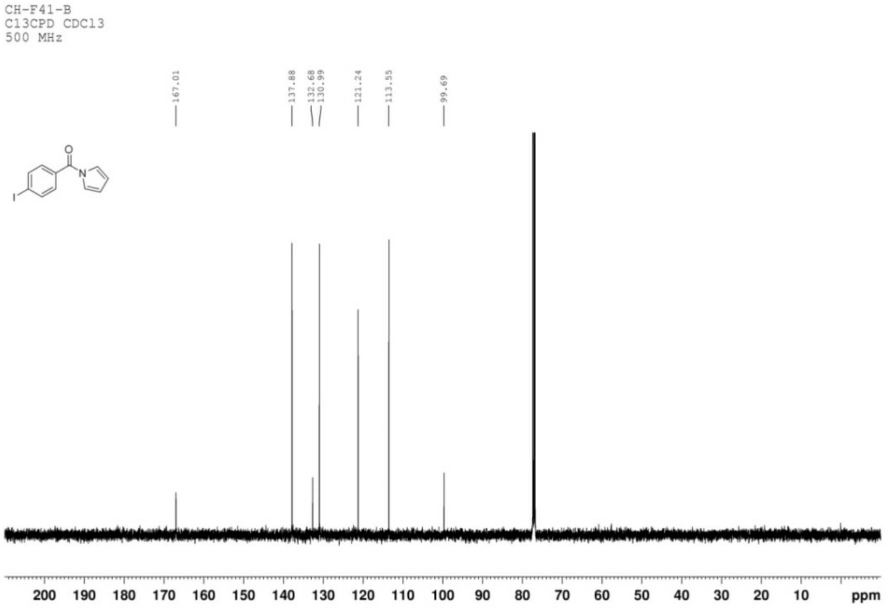

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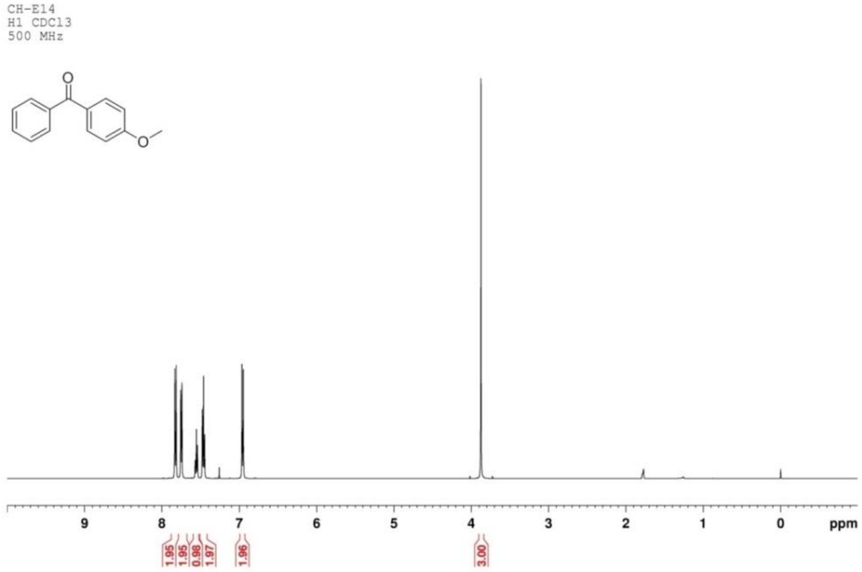

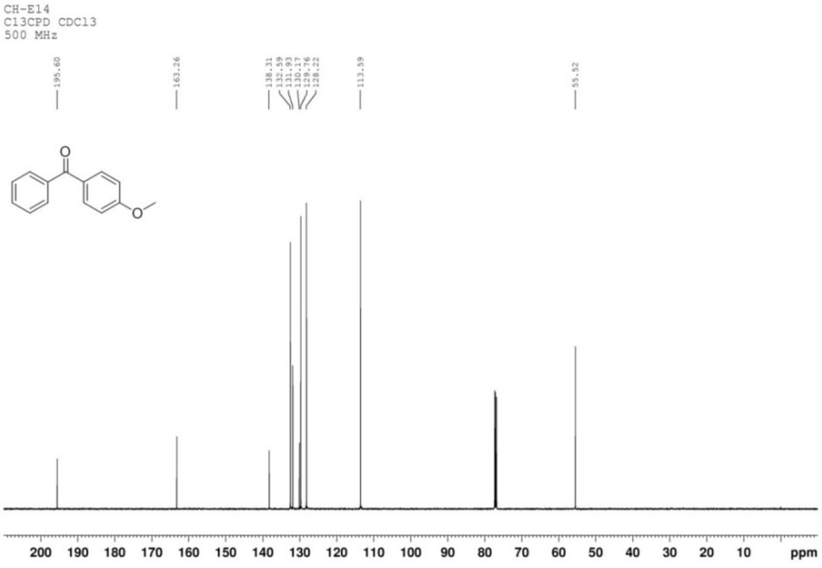

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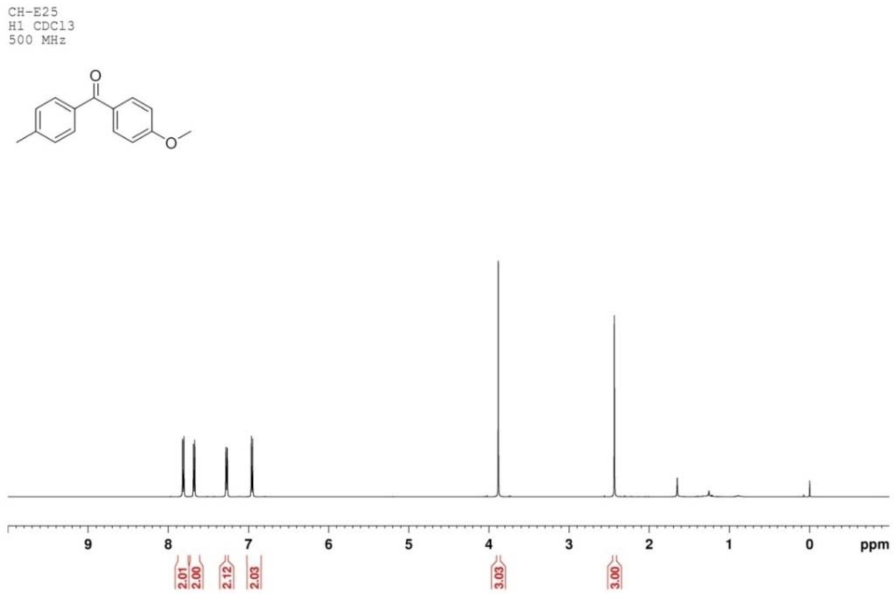

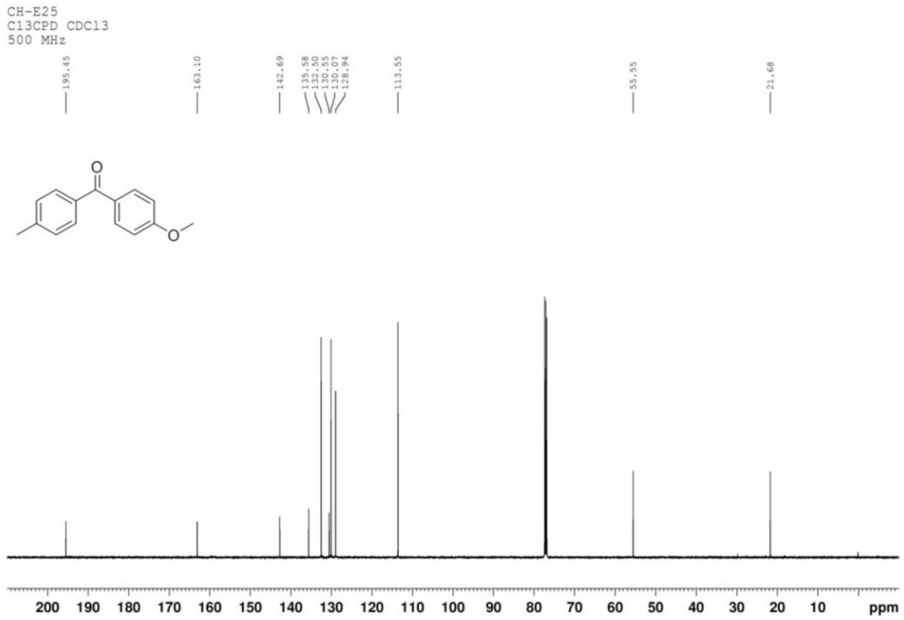

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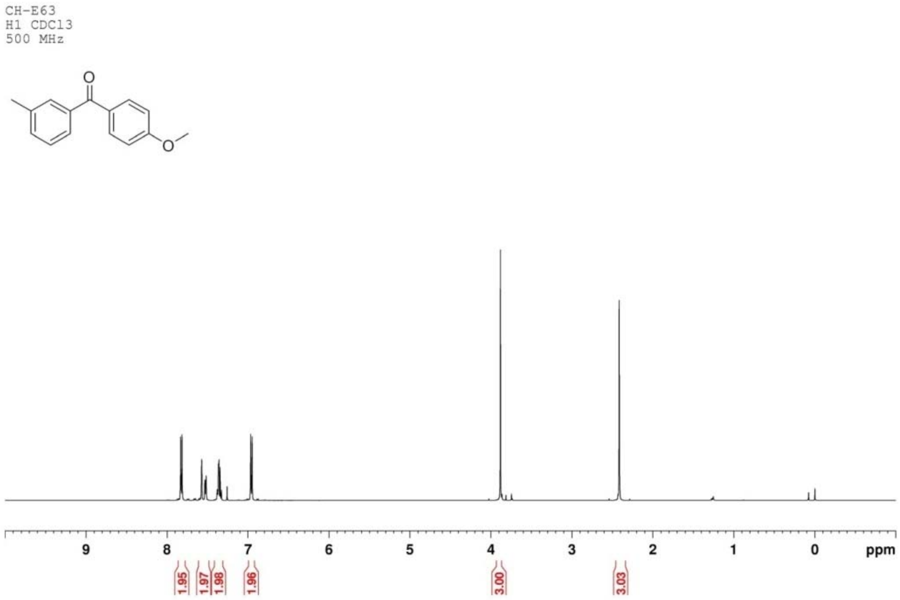

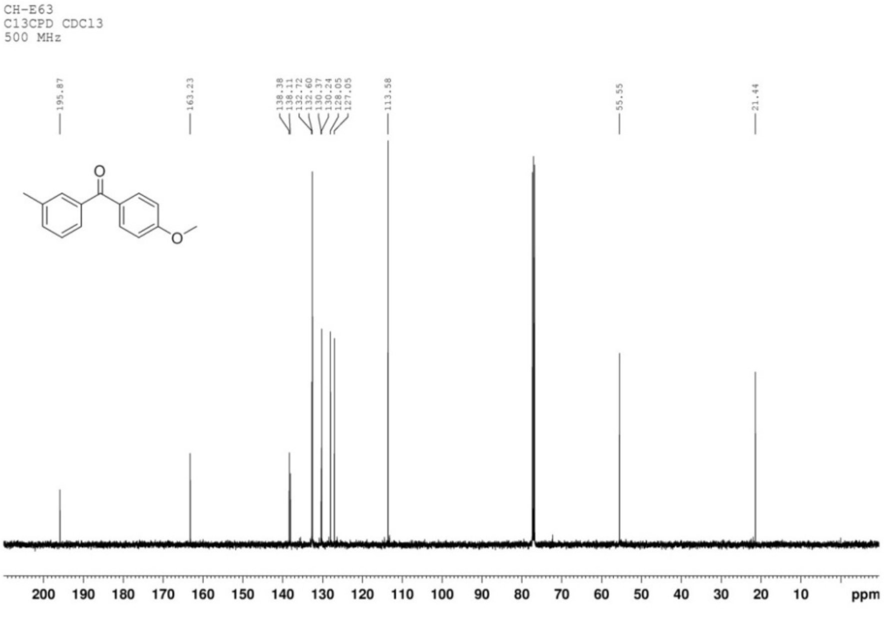

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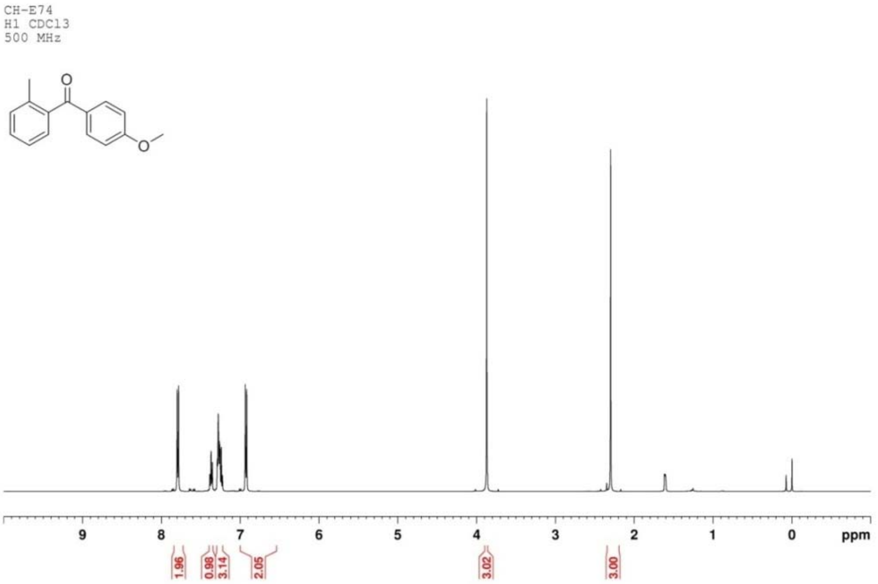

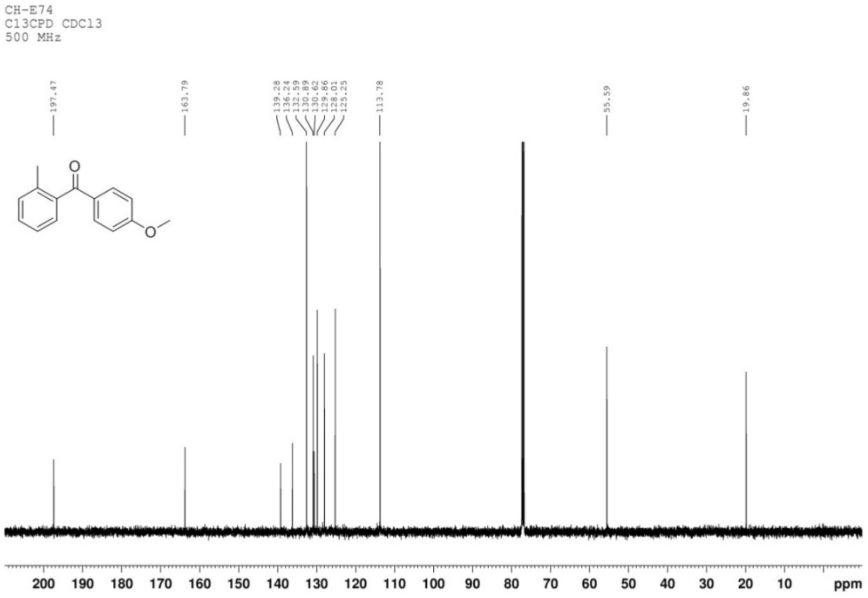

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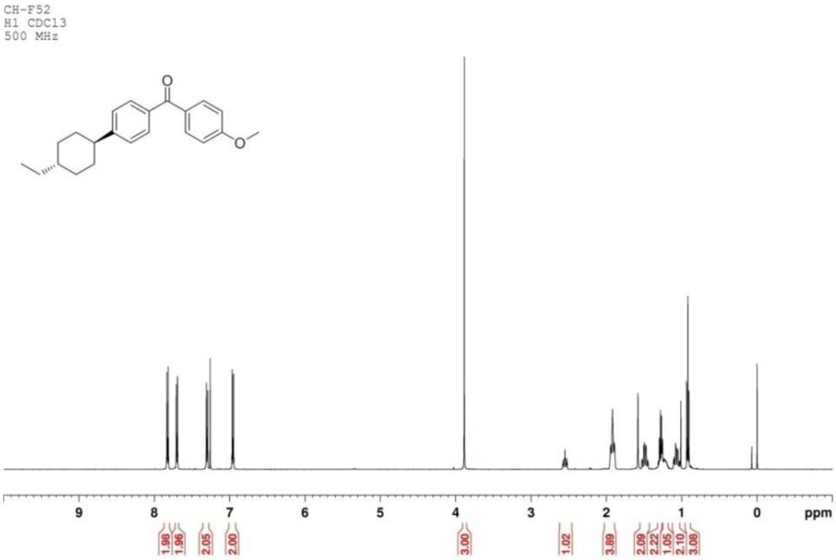

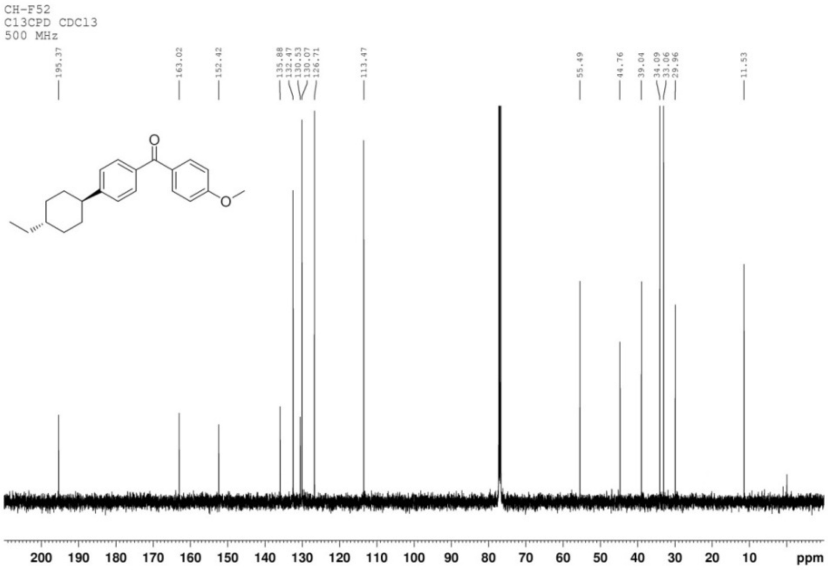

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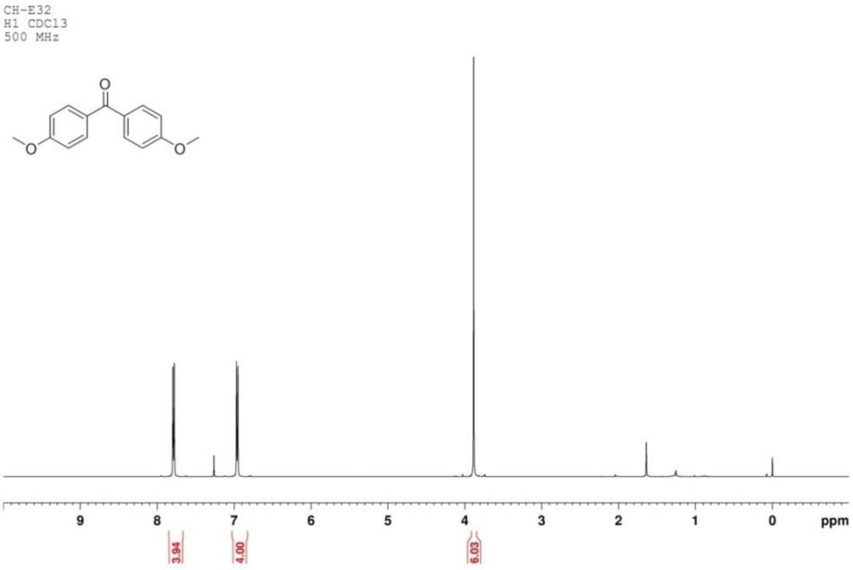

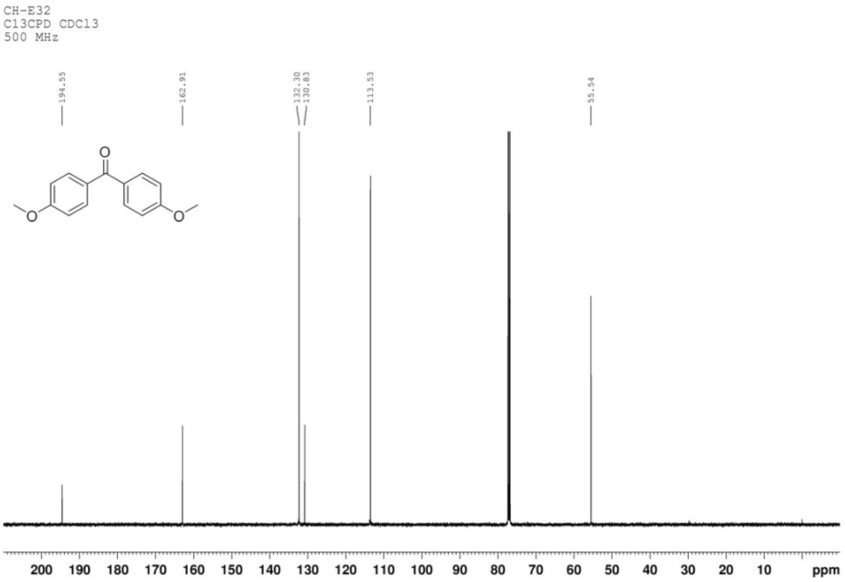

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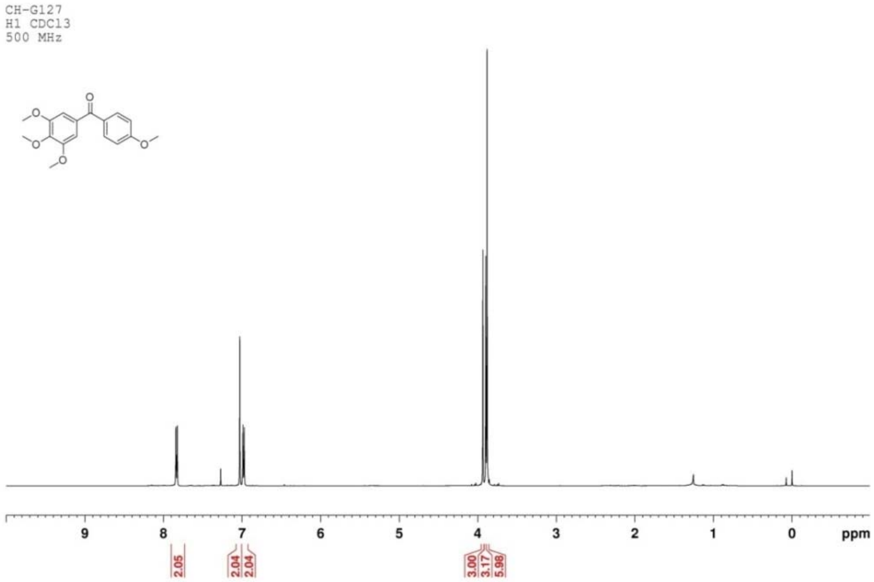

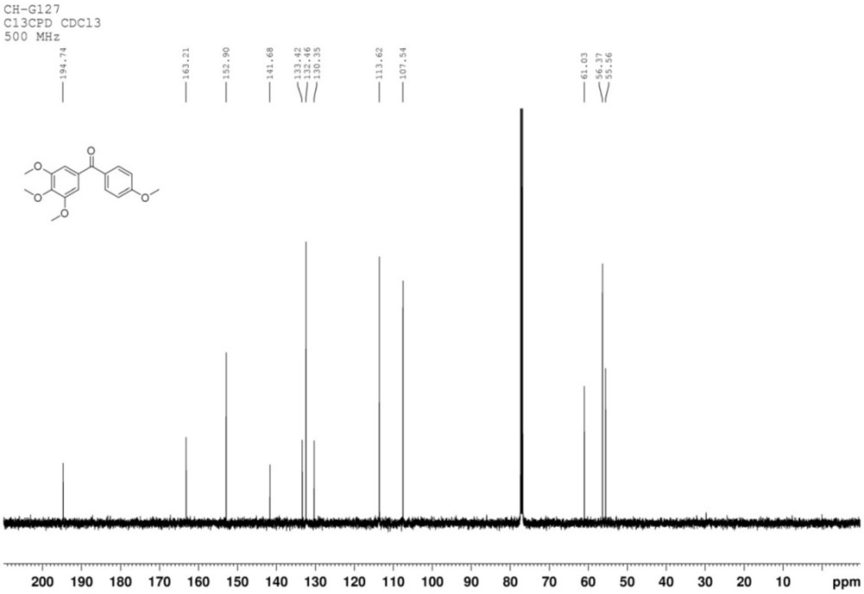

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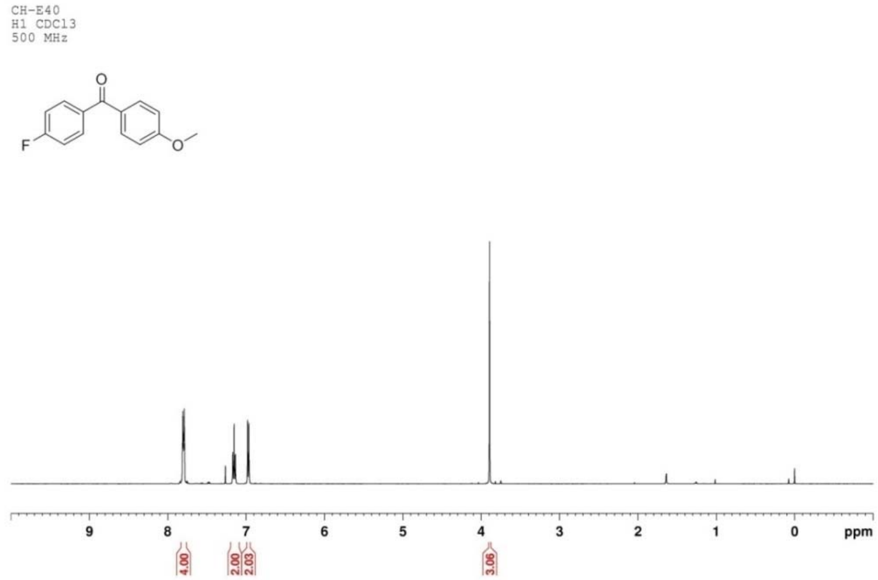
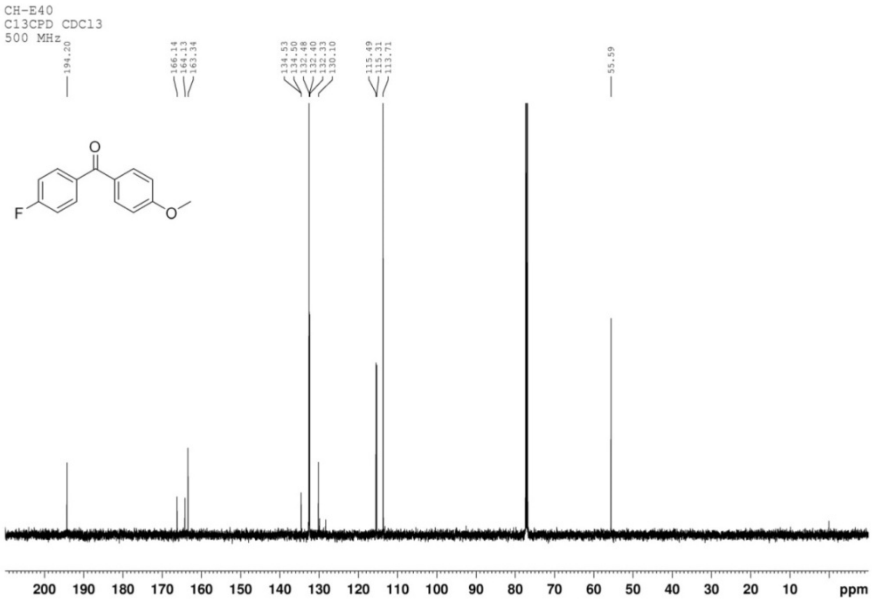
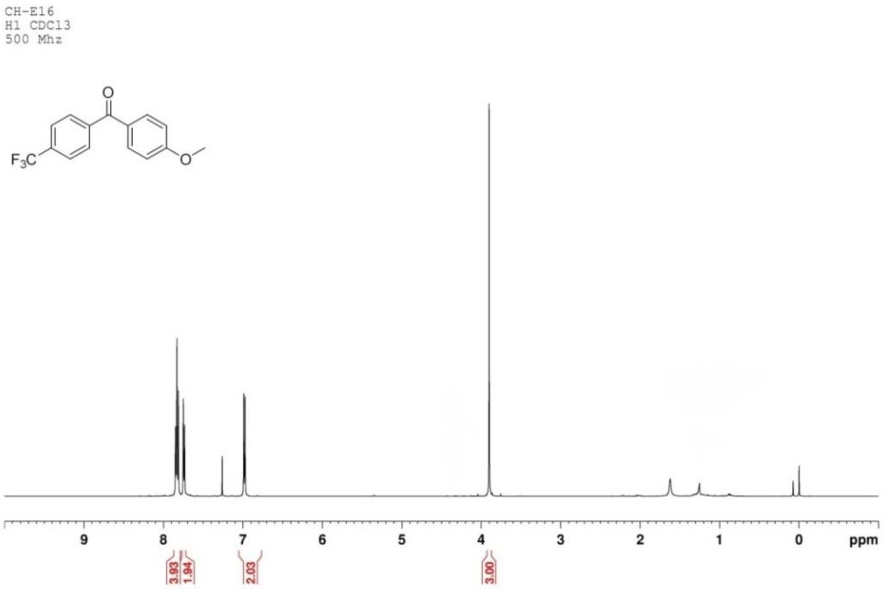
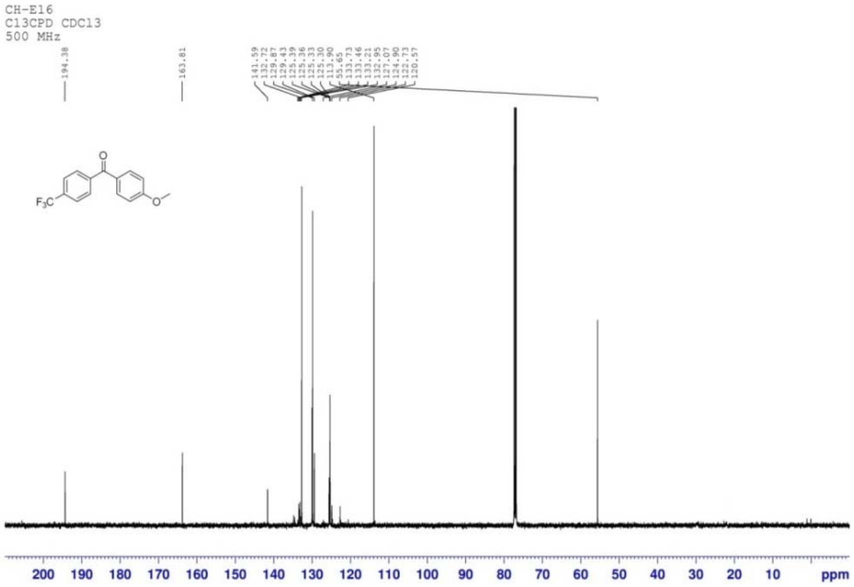


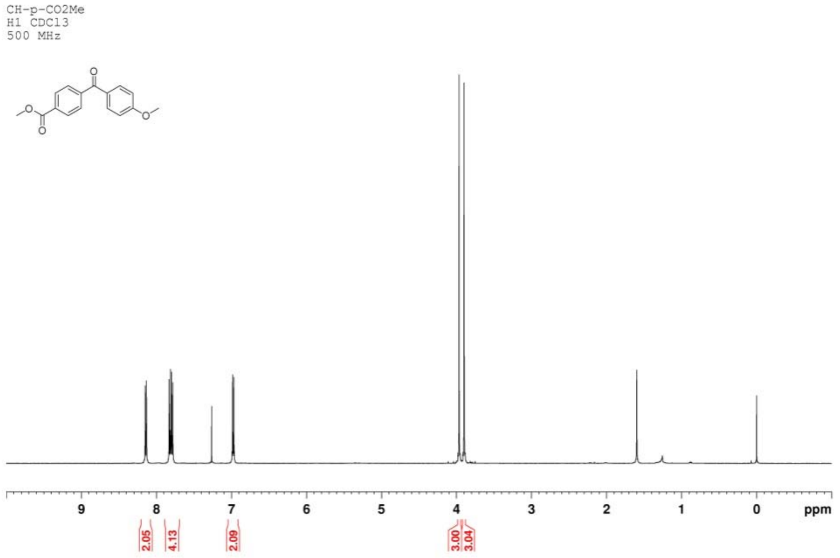


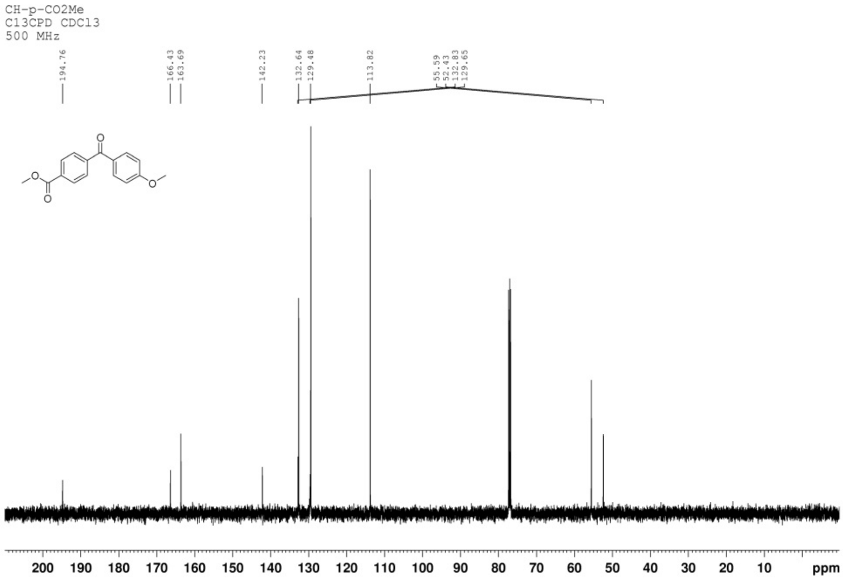
^1H and ^{13}C NMR spectra of compound 3ia



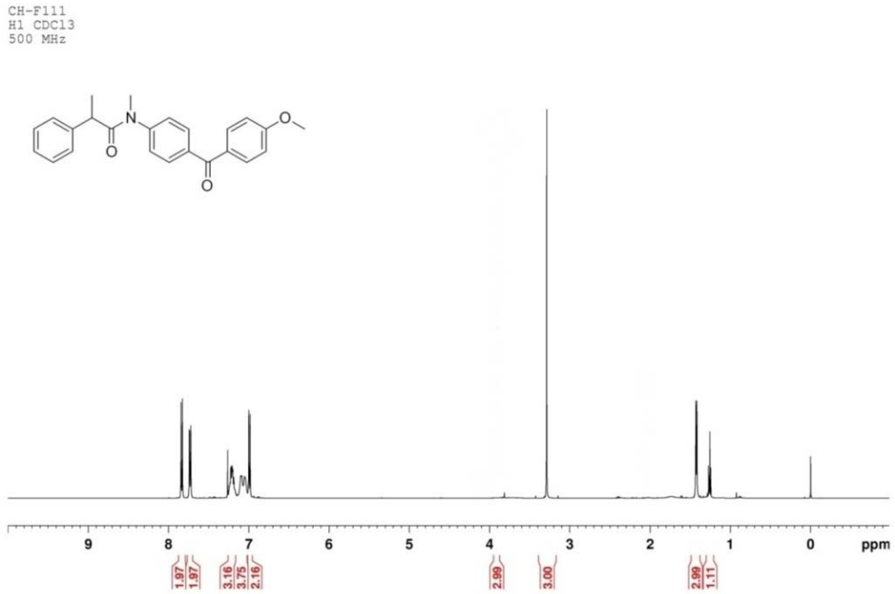


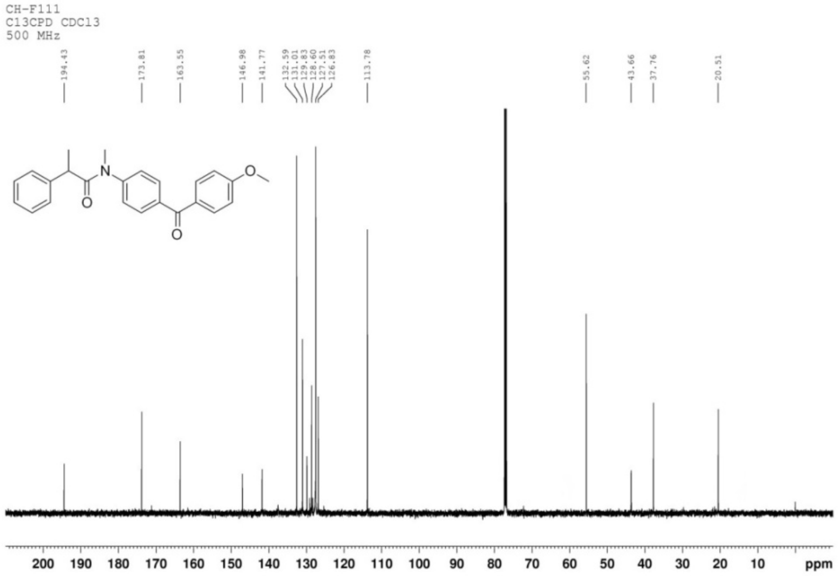
^{1}H and ^{13}C NMR spectra of compound 3ja



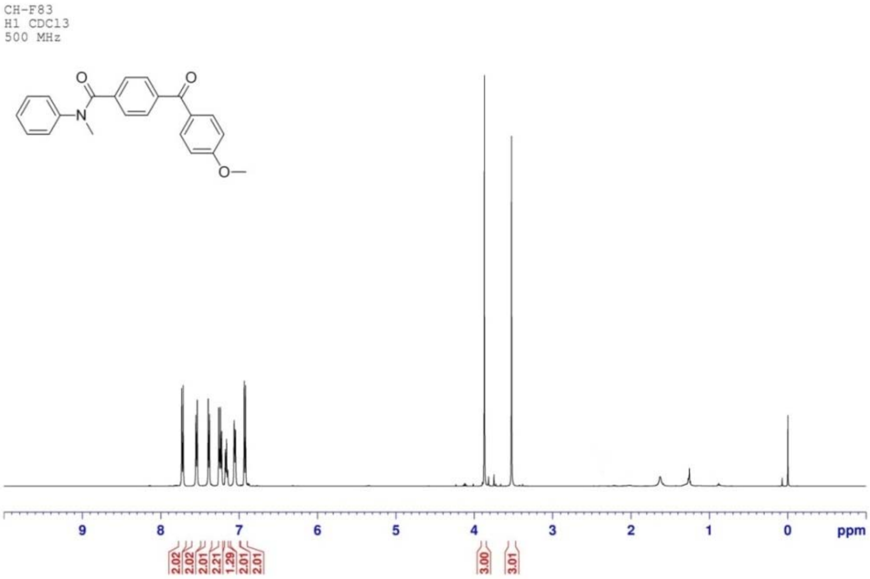


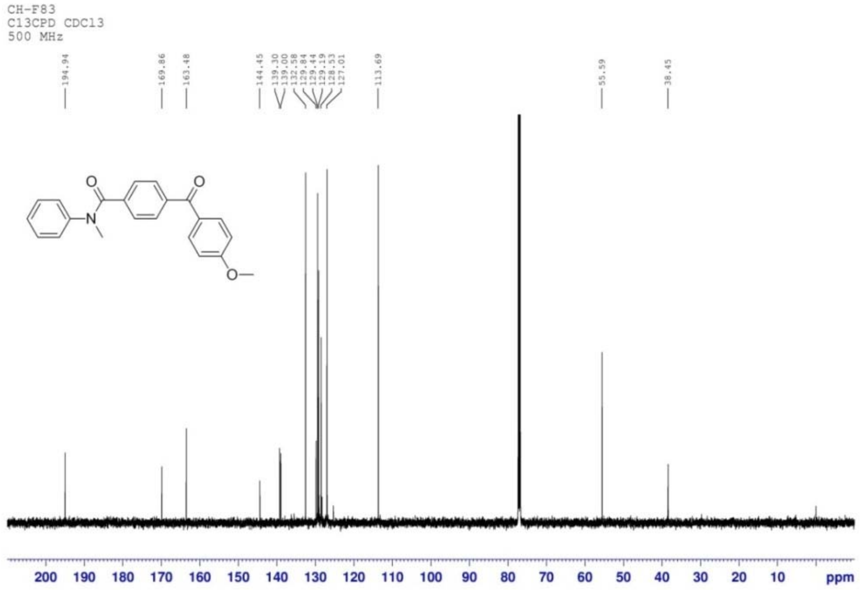
^{1}H and ^{13}C NMR spectra of compound 3ka



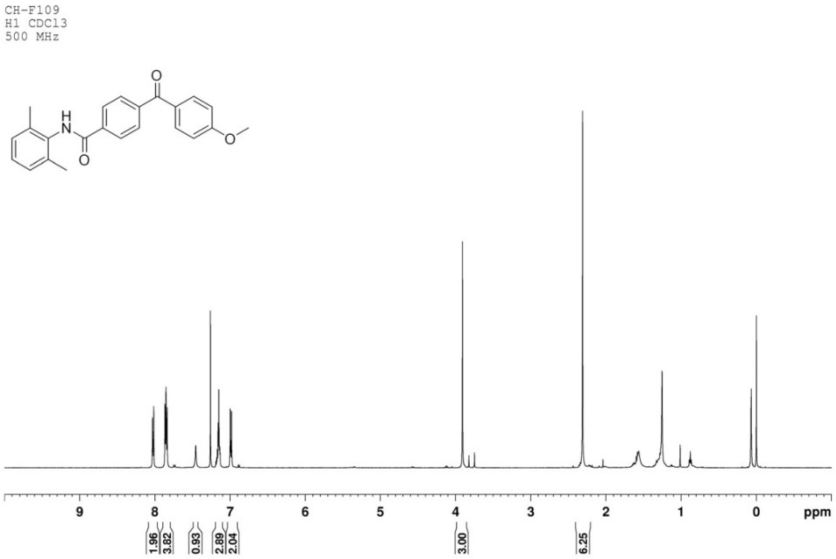


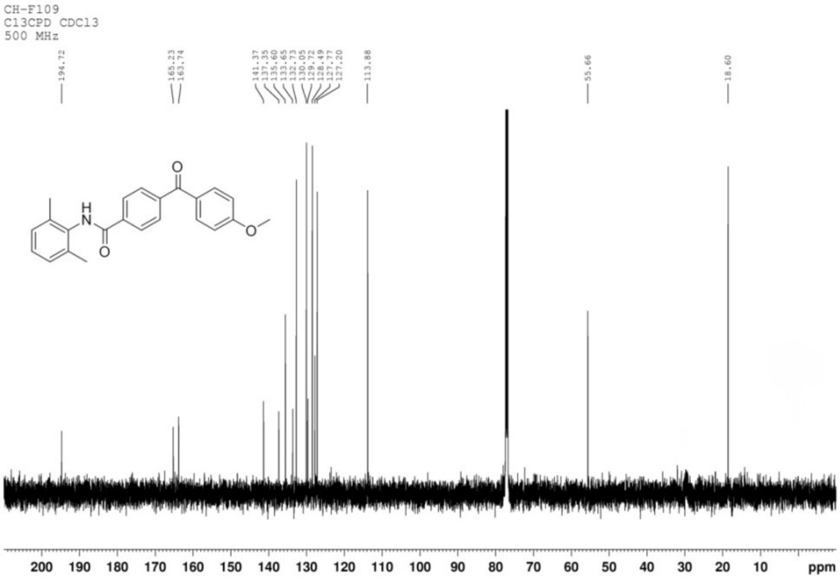
^{1}H and ^{13}C NMR spectra of compound 3la



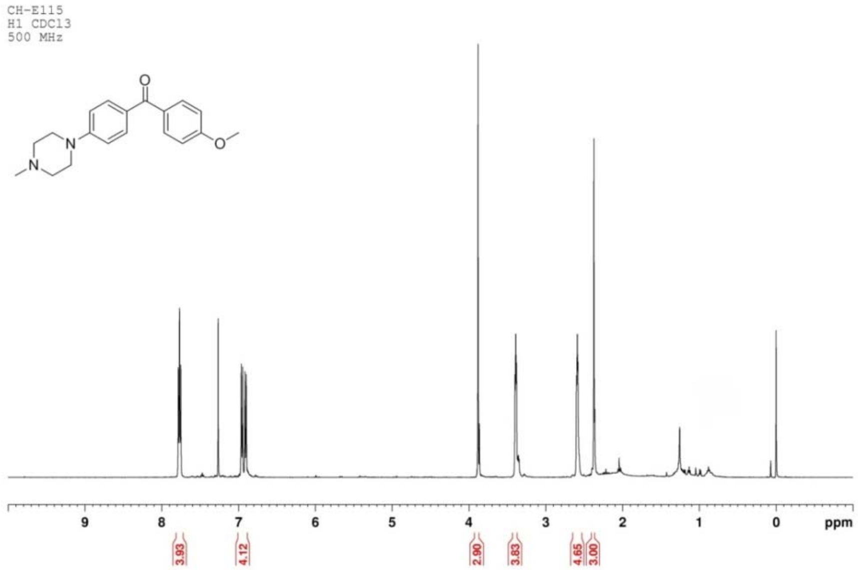


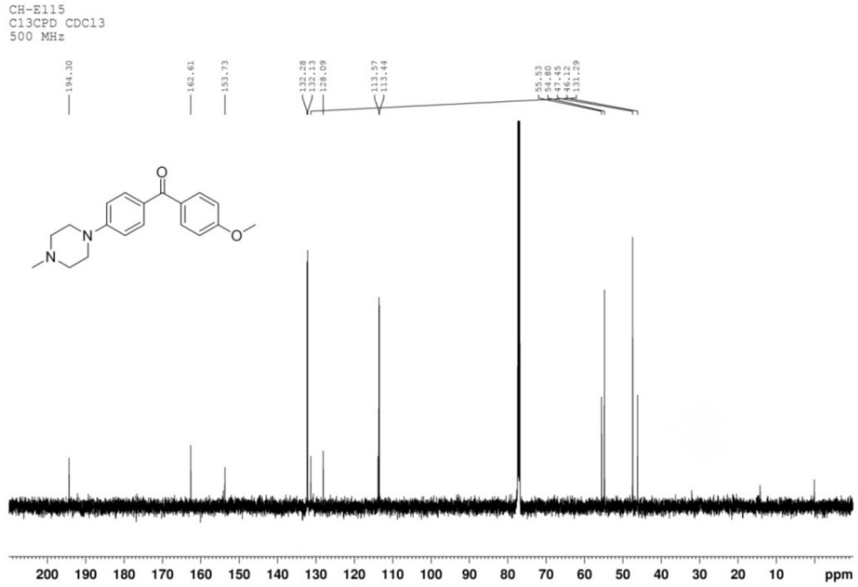
^{1}H and ^{13}C NMR spectra of compound 3ma



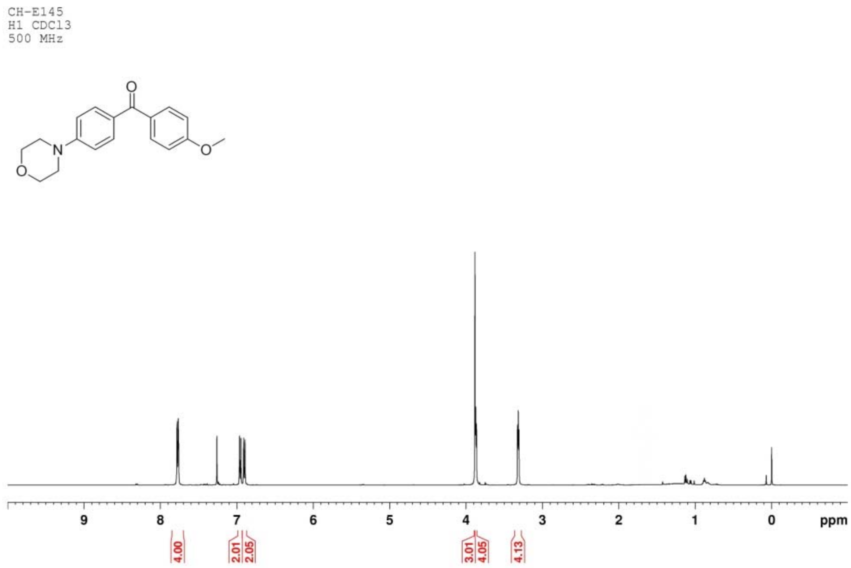


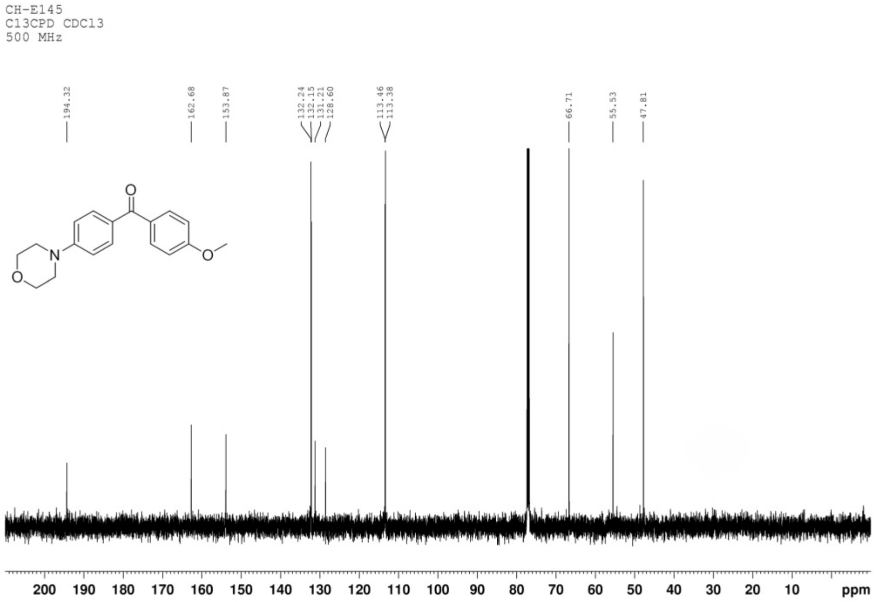
^{1}H and ^{13}C NMR spectra of compound 3na



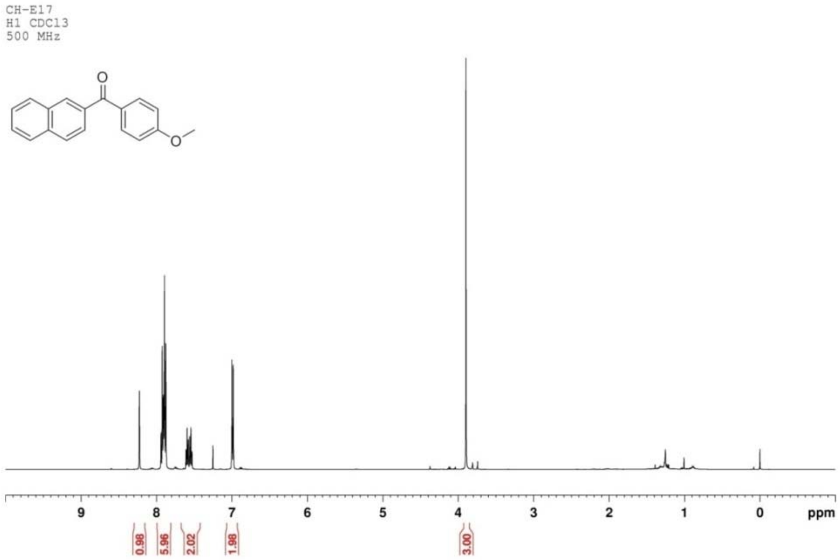


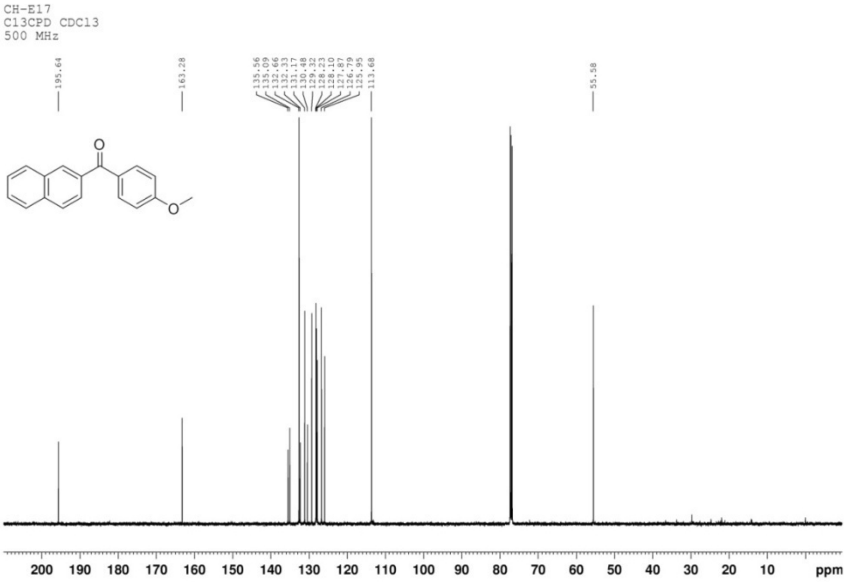
^{1}H and ^{13}C NMR spectra of compound 3oa



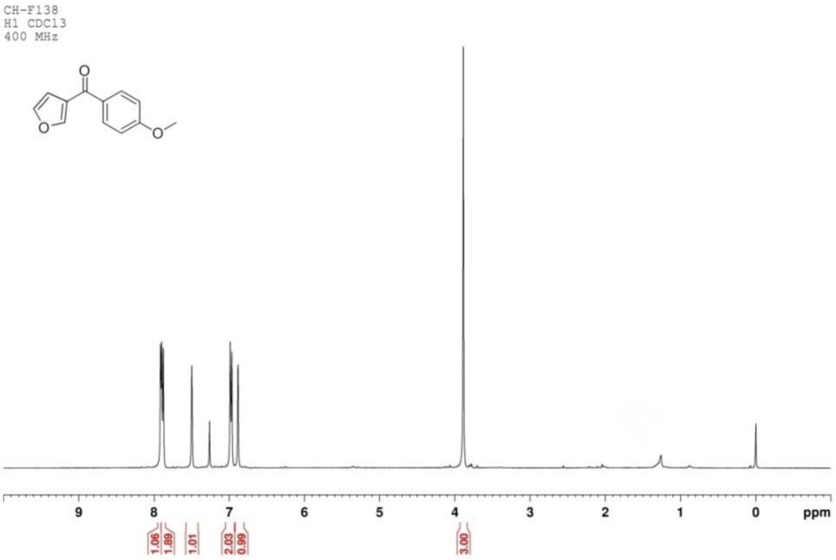


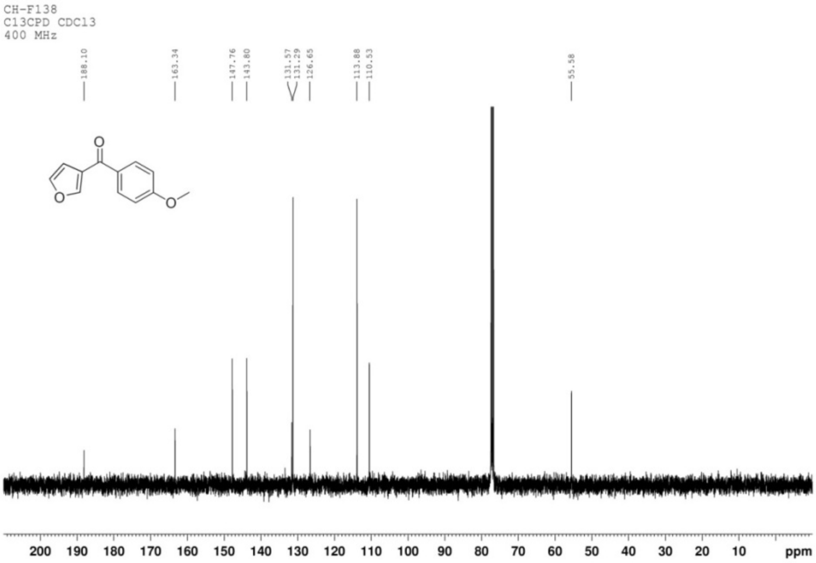
^{1}H and ^{13}C NMR spectra of compound 3pa



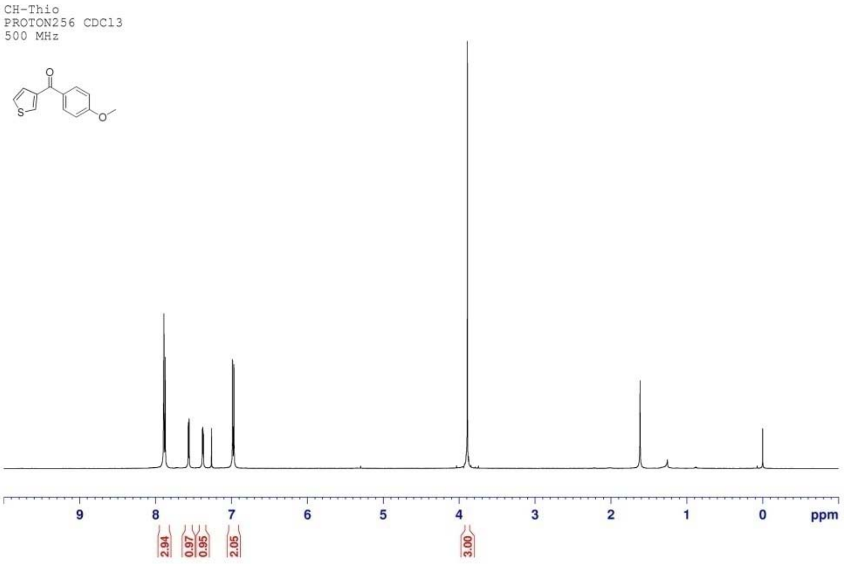


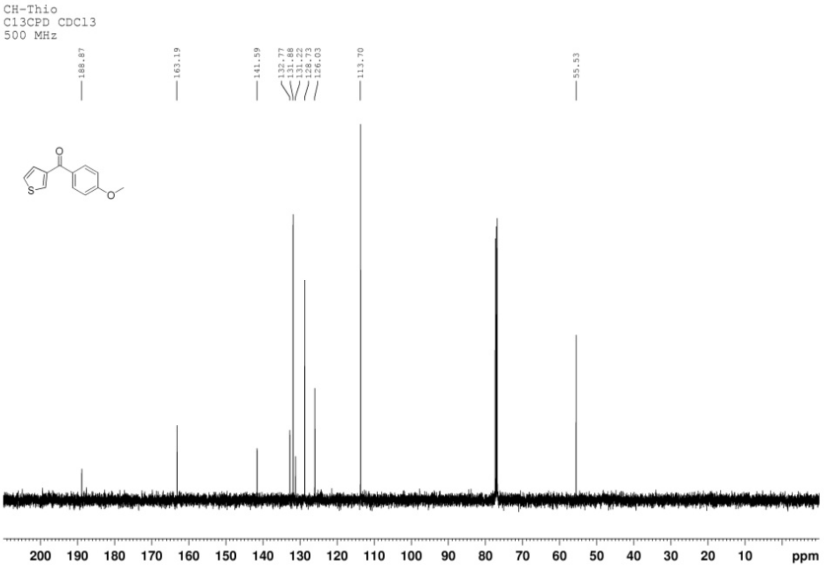
^{1}H and ^{13}C NMR spectra of compound 3qa



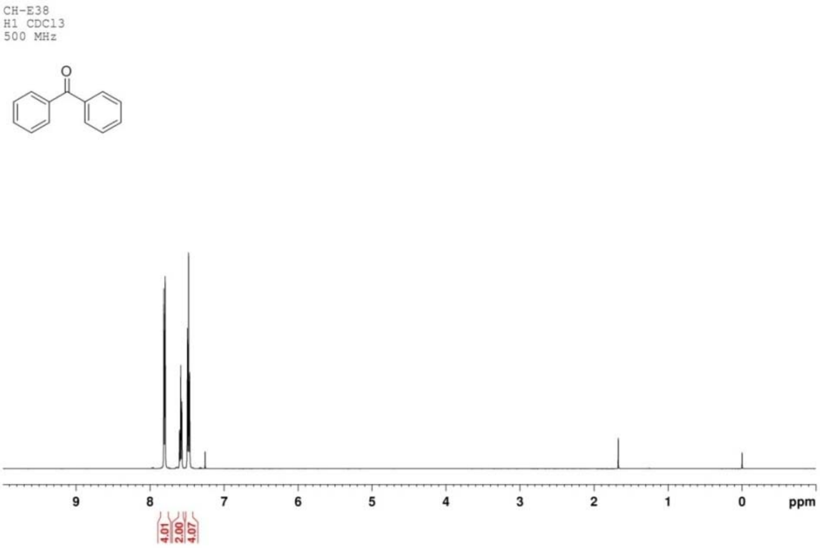


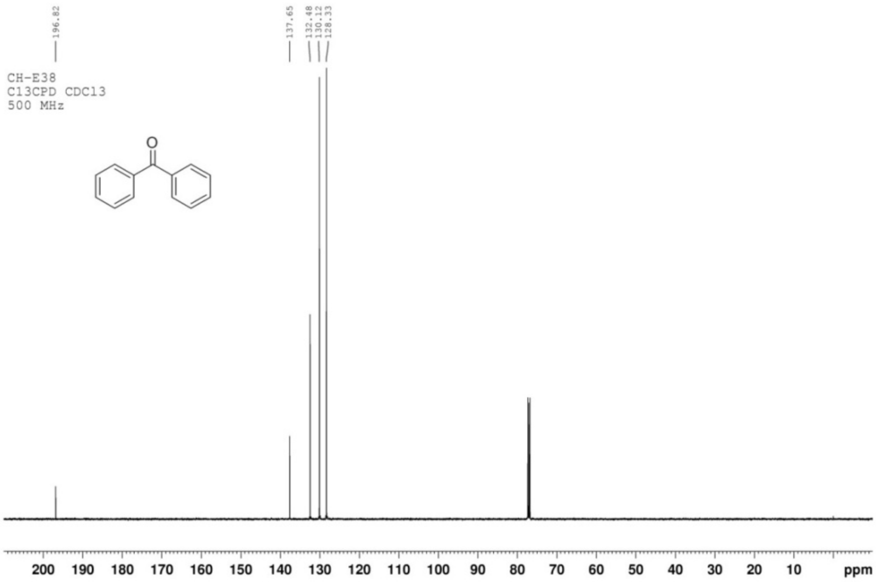
^{1}H and ^{13}C NMR spectra of compound 3ra



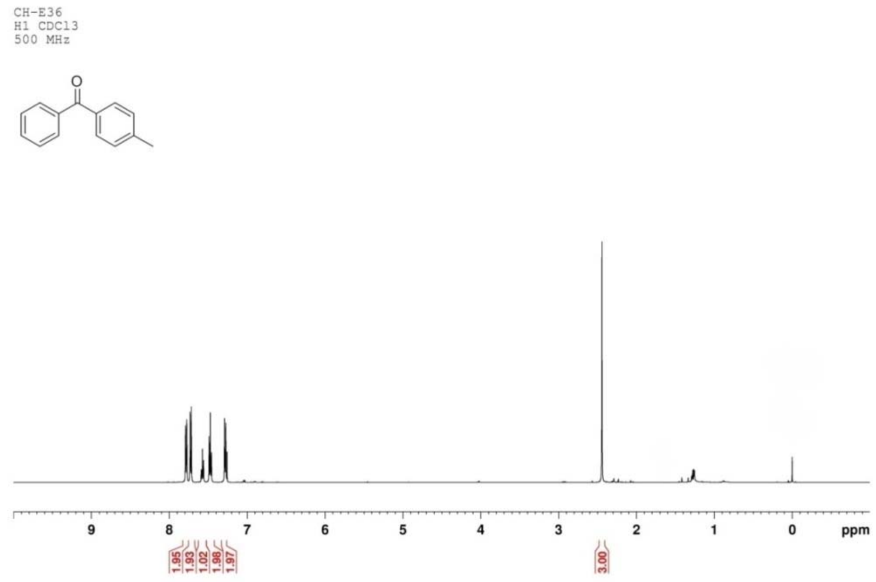


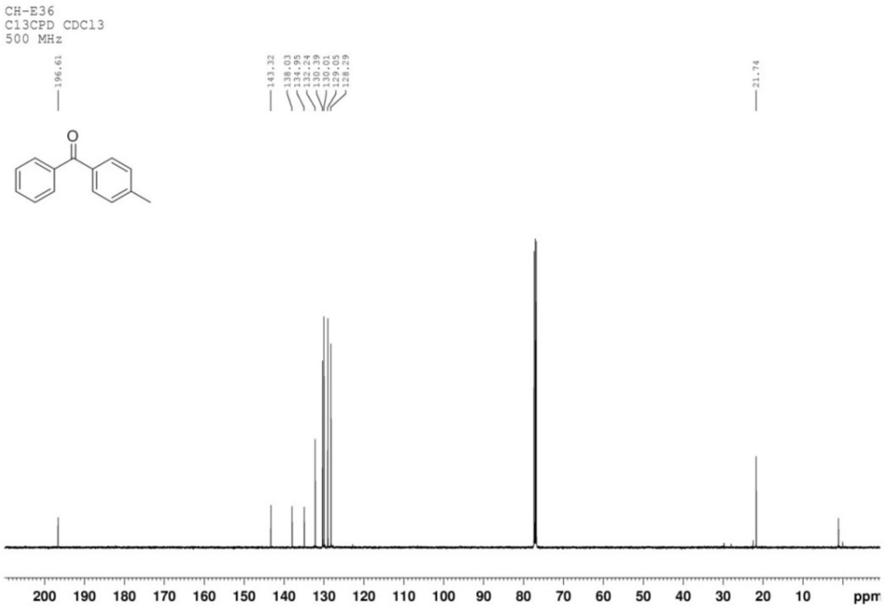
^{1}H and ^{13}C NMR spectra of compound 3ab



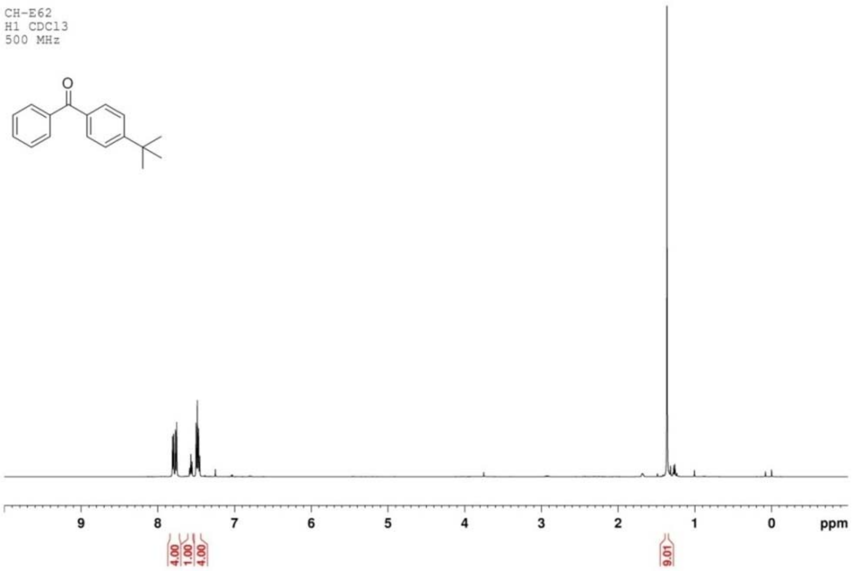


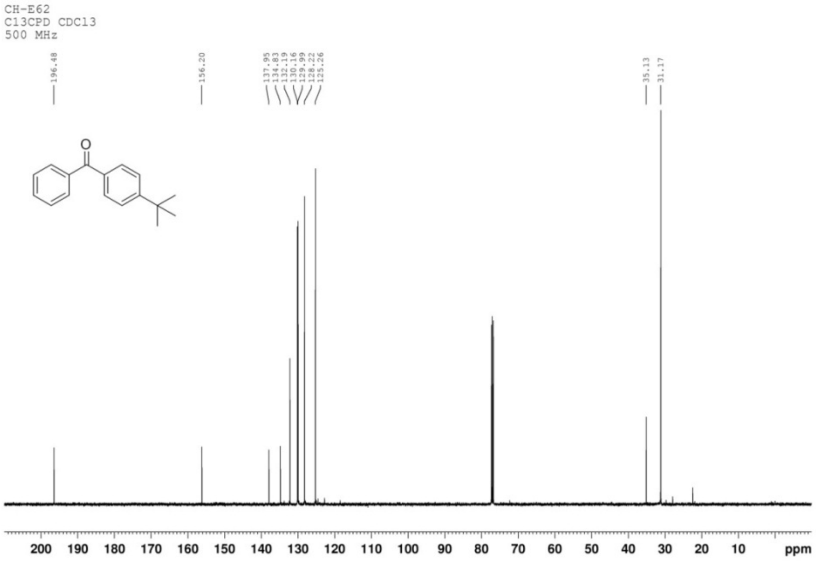
^{1}H and ^{13}C NMR spectra of compound 3ac



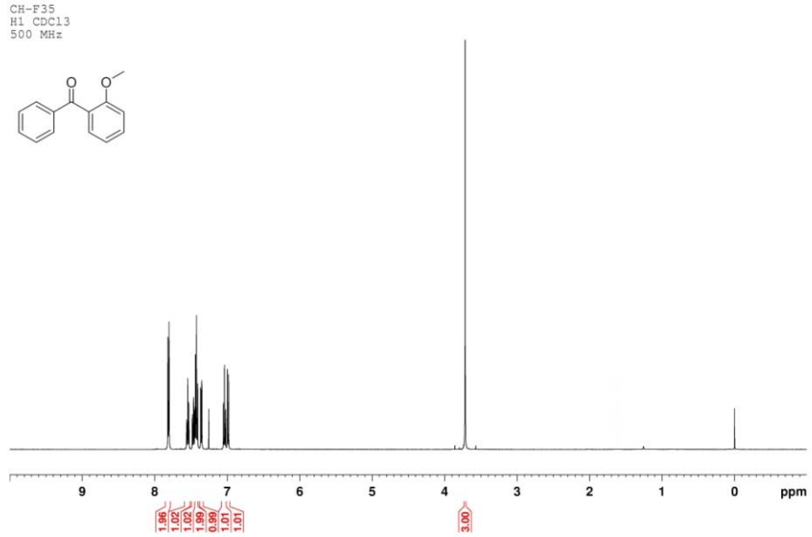


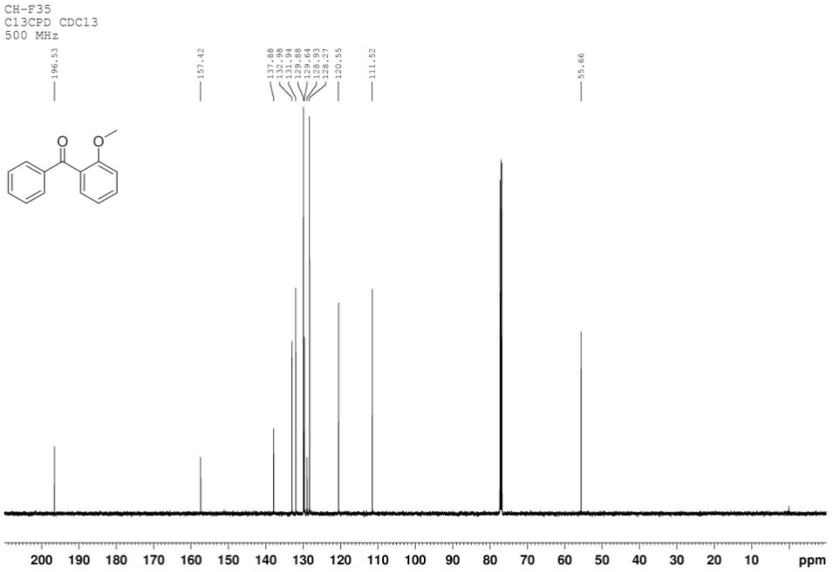
^{1}H and ^{13}C NMR spectra of compound 3ad



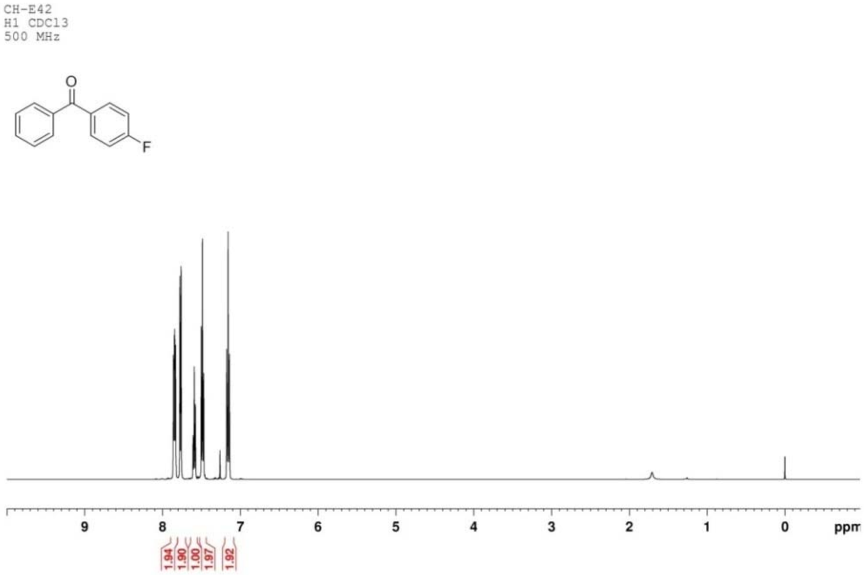


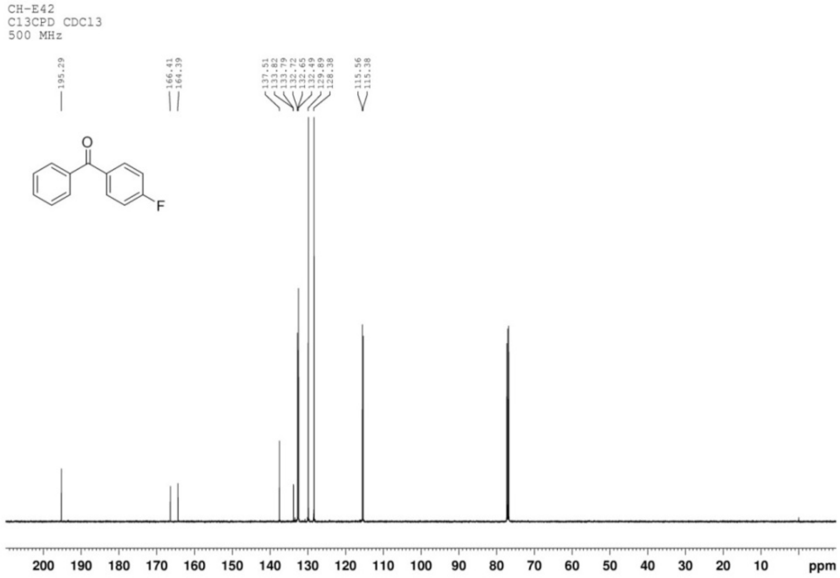
^{1}H and ^{13}C NMR spectra of compound 3ae



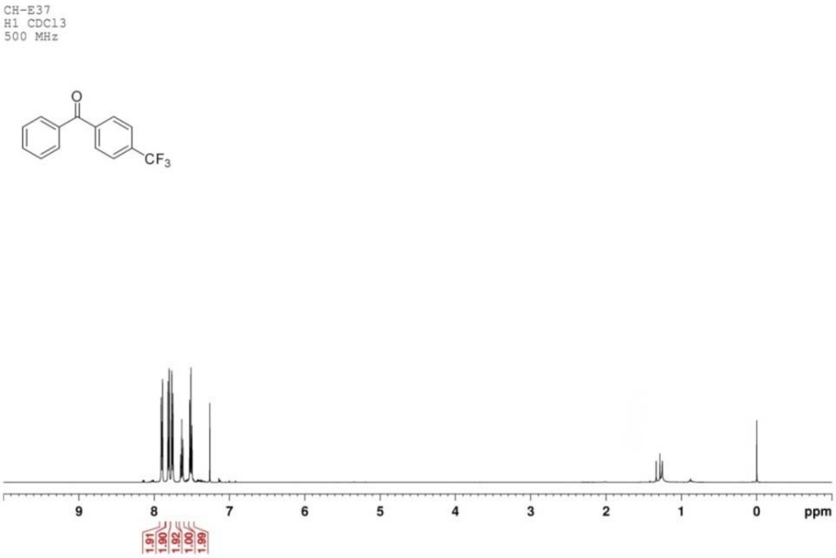


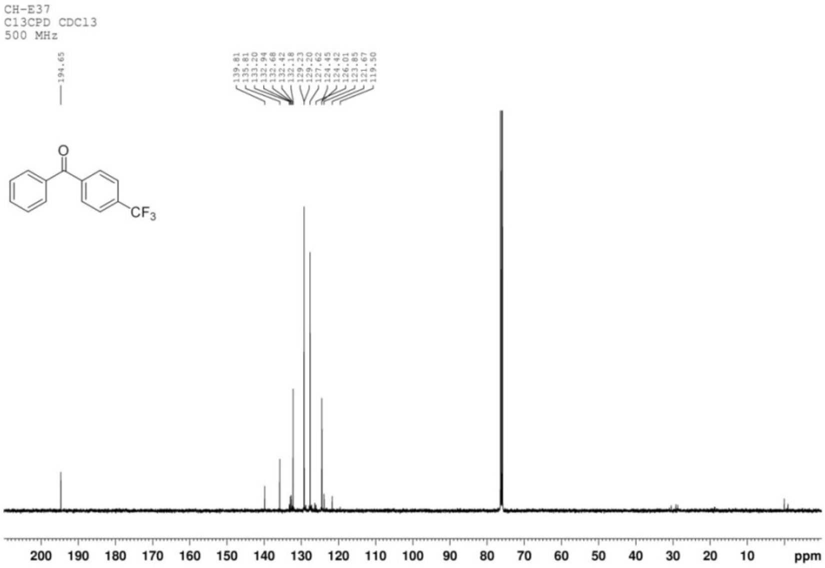
^{1}H and ^{13}C NMR spectra of compound 3af



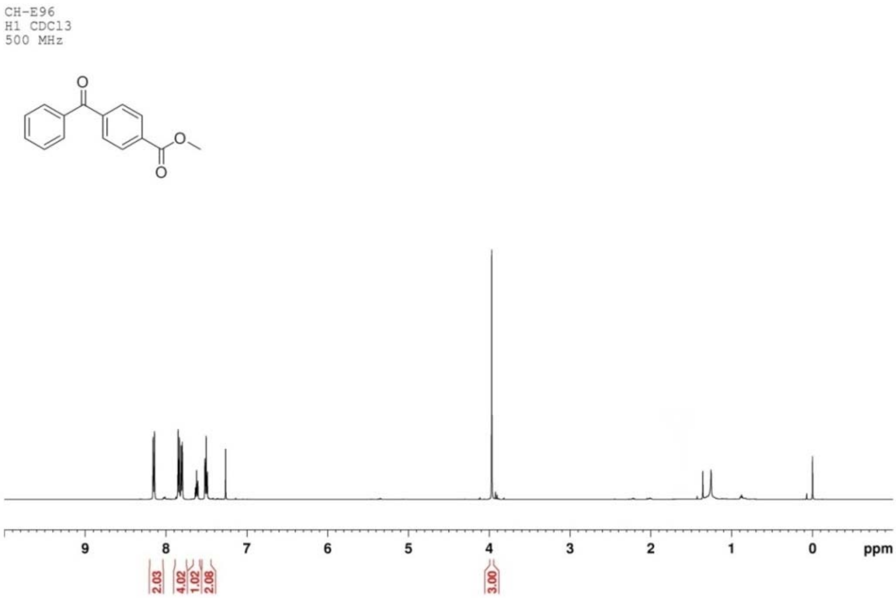


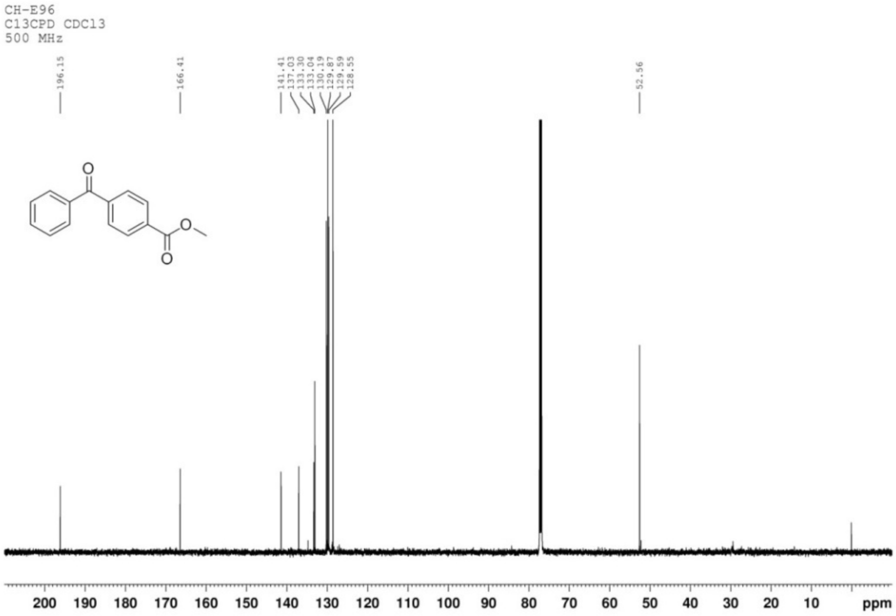
^{1}H and ^{13}C NMR spectra of compound 3ag



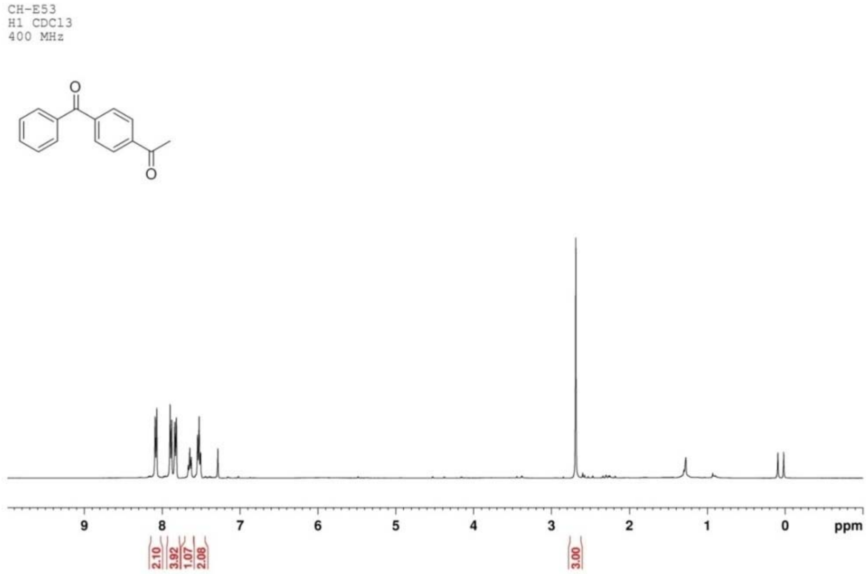


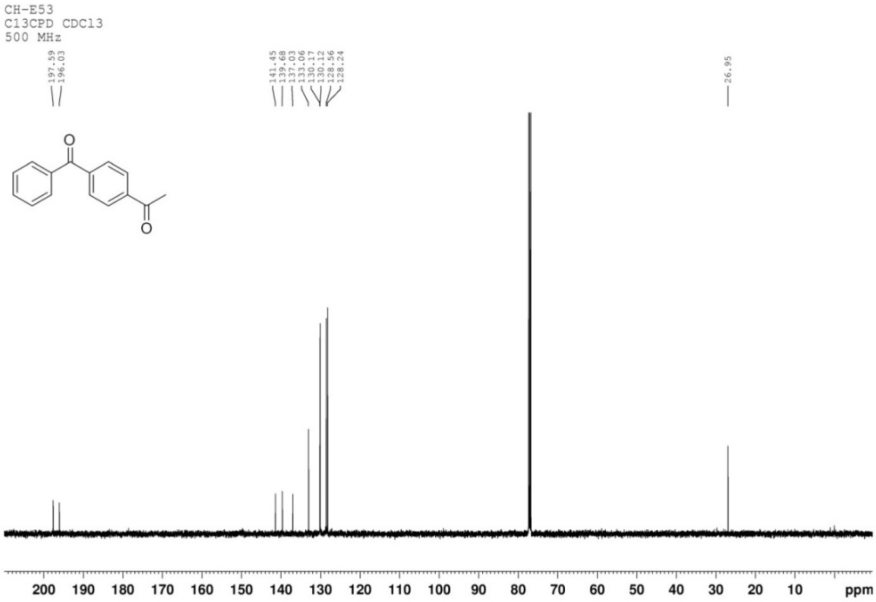
^{1}H and ^{13}C NMR spectra of compound 3ah



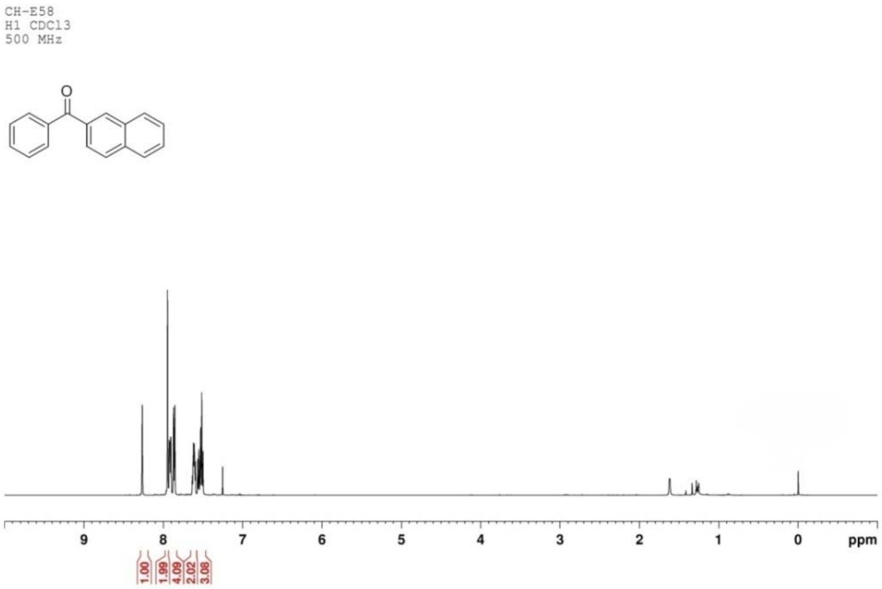


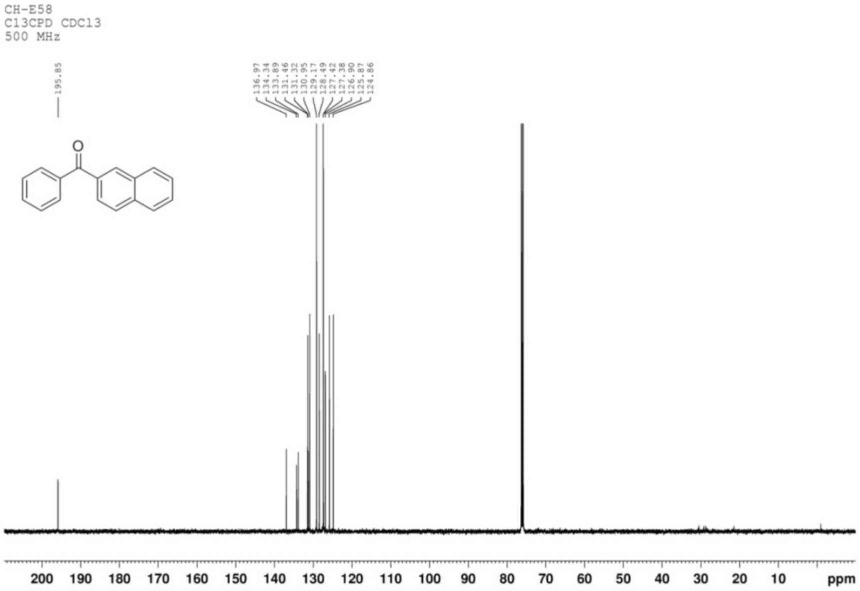
^{1}H and ^{13}C NMR spectra of compound 3ai



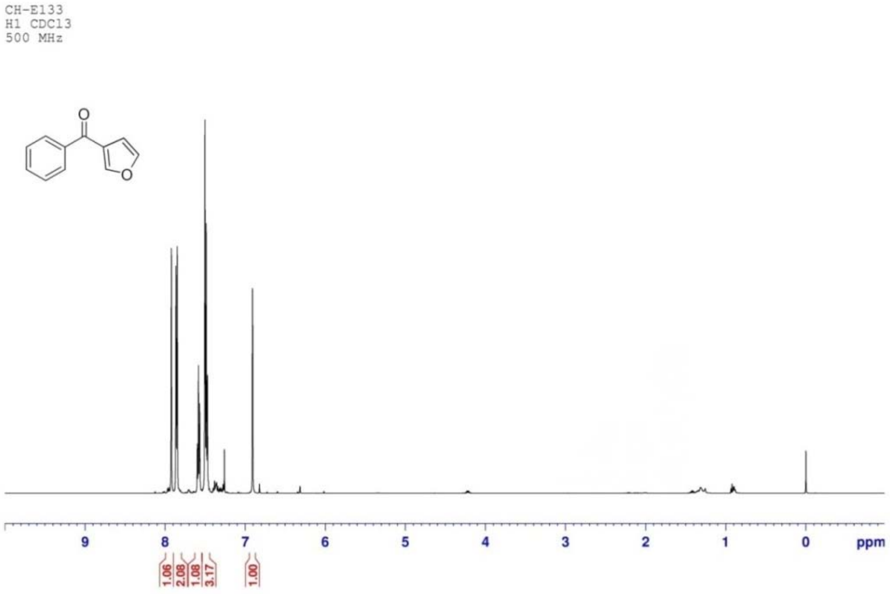


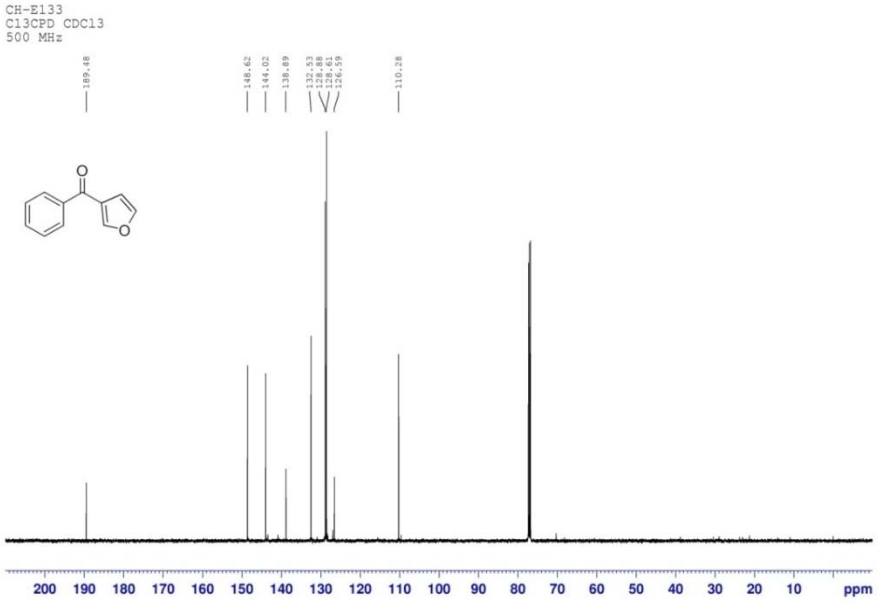
^{1}H and ^{13}C NMR spectra of compound 3aj



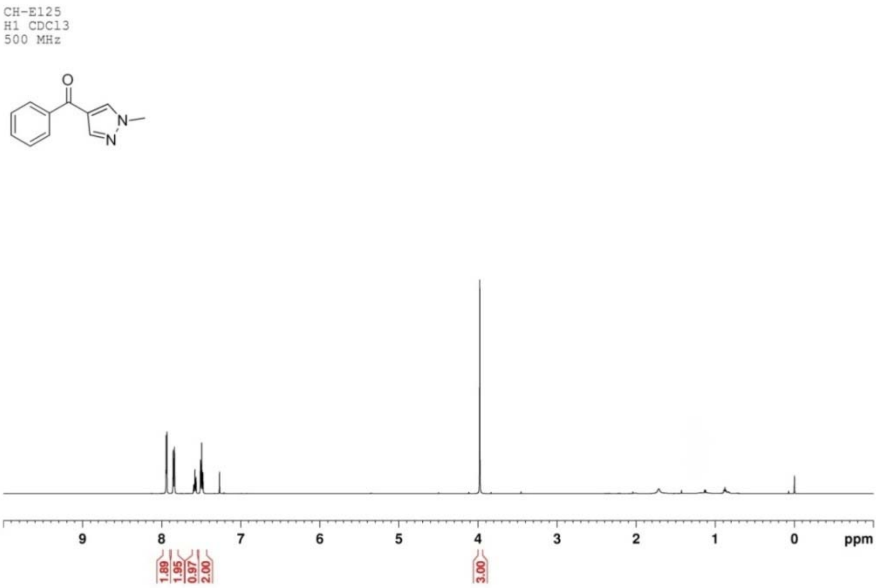


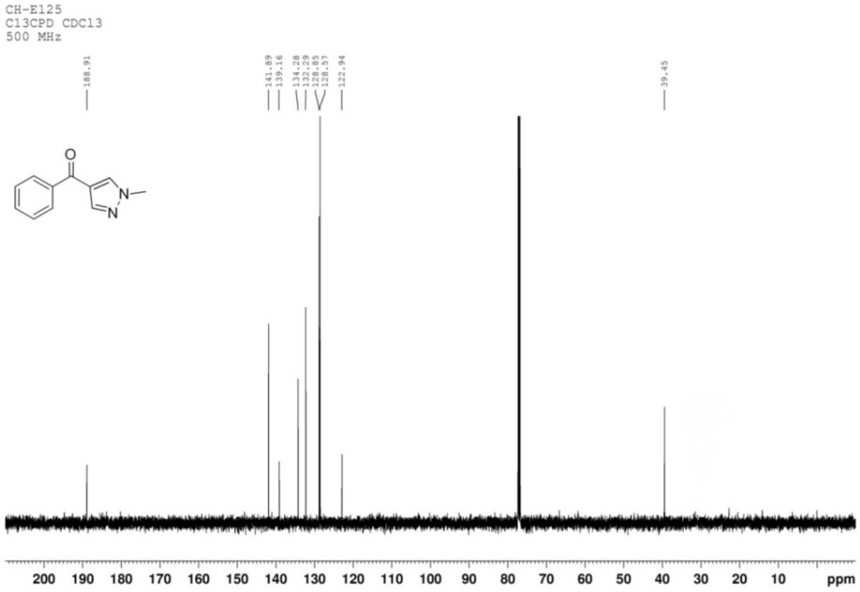
^{1}H and ^{13}C NMR spectra of compound 3ak



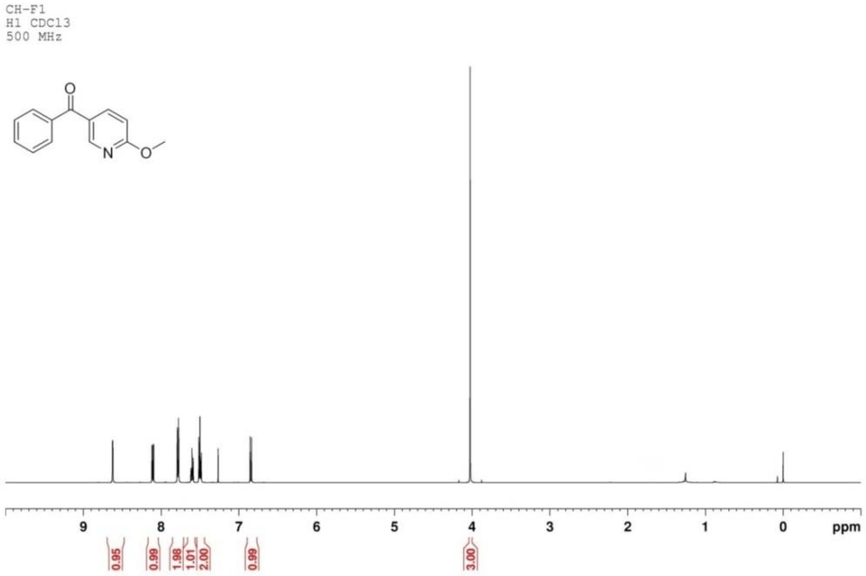


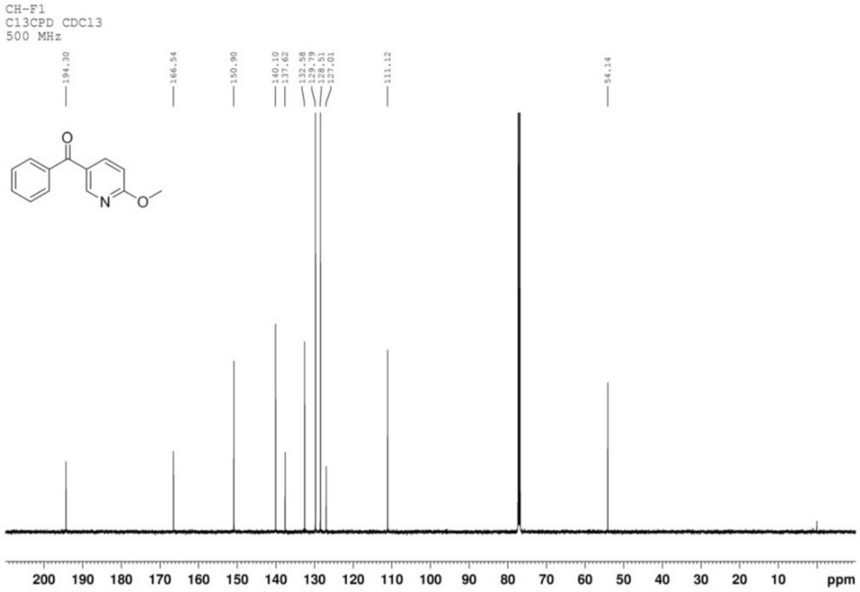
^{1}H and ^{13}C NMR spectra of compound 3al



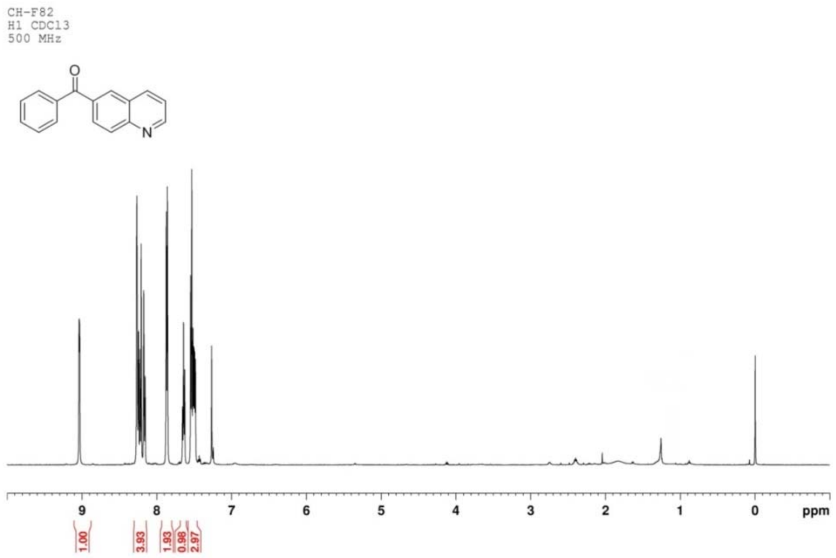


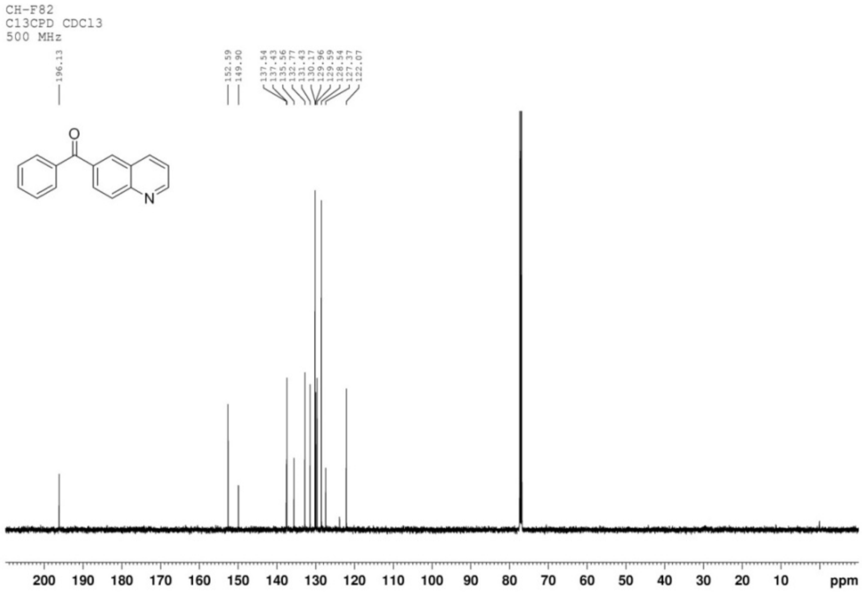
^{1}H and ^{13}C NMR spectra of compound 3am



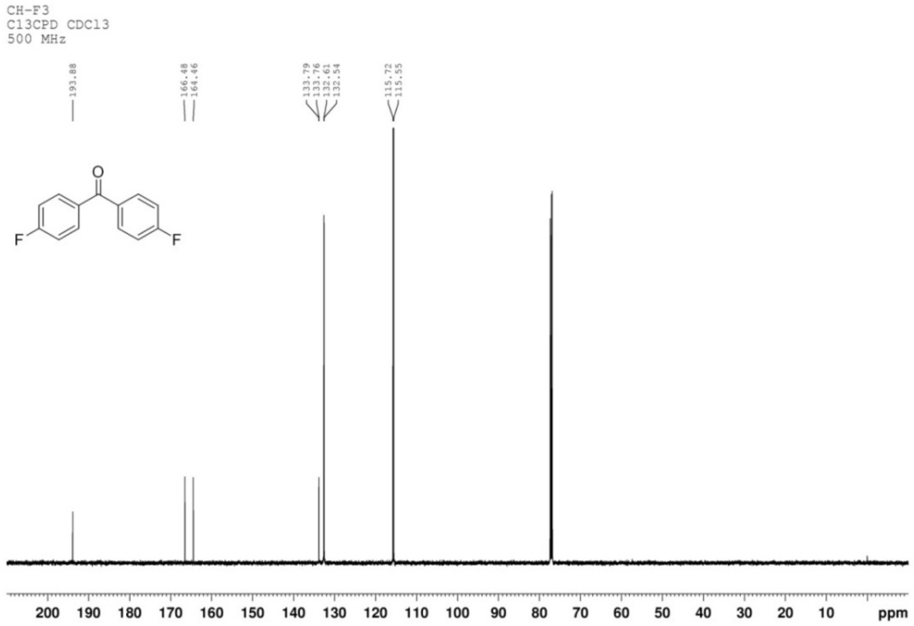


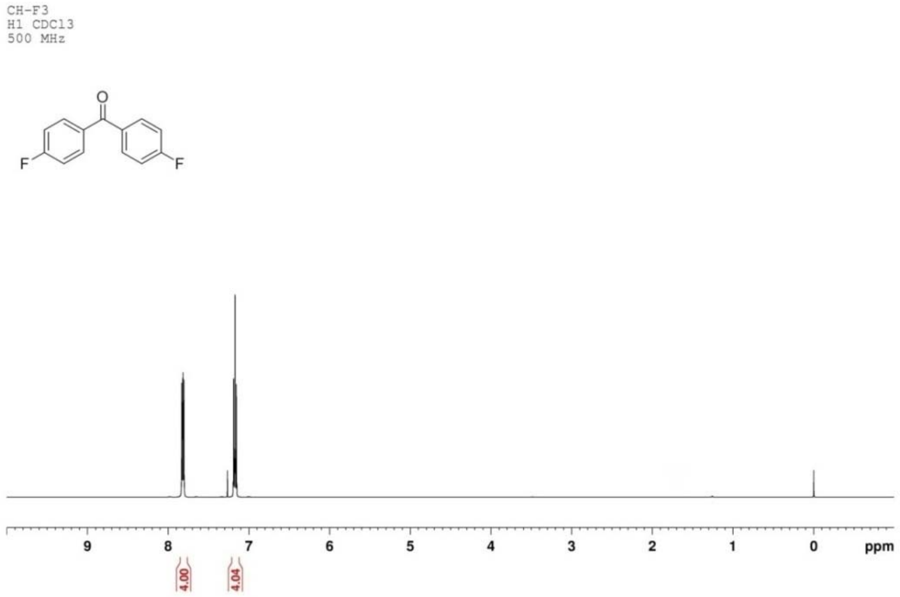
^{1}H and ^{13}C NMR spectra of compound 3an



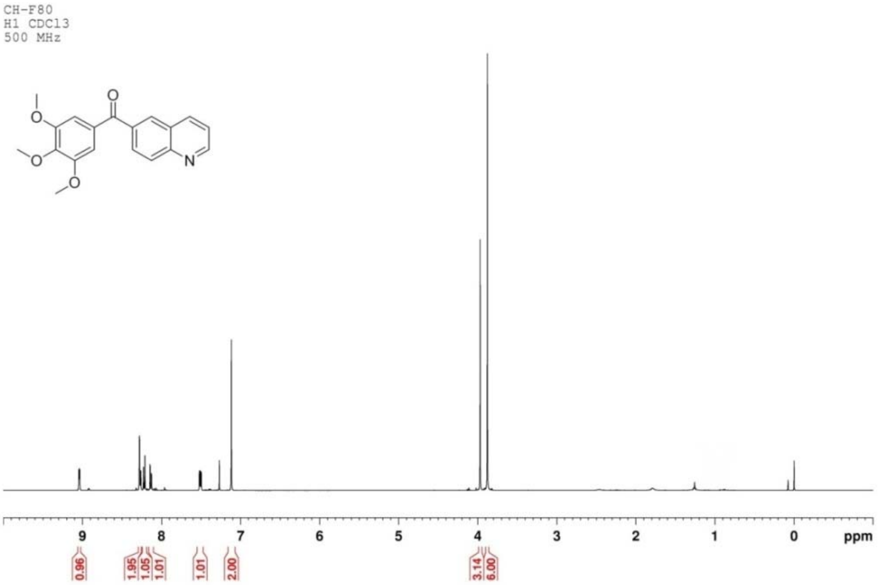


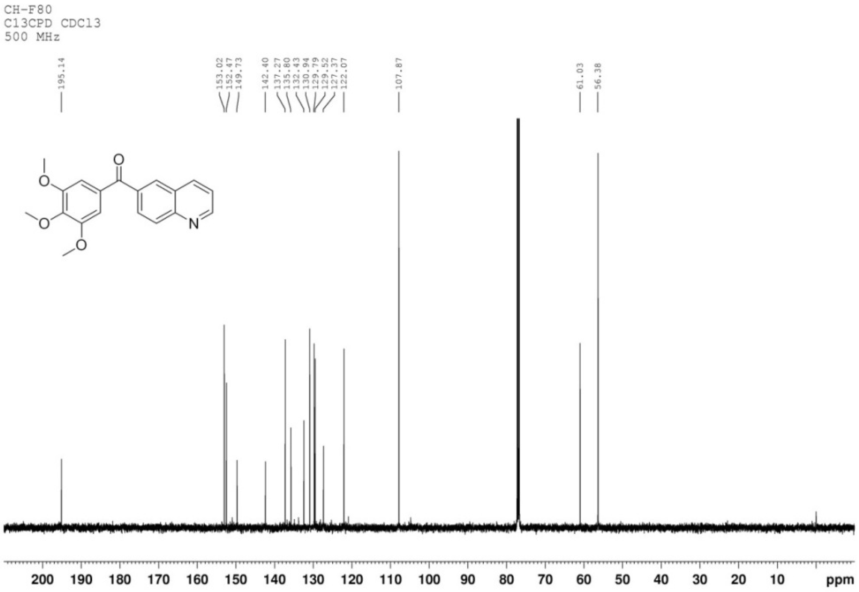
^{1}H and ^{13}C NMR spectra of compound 3hf



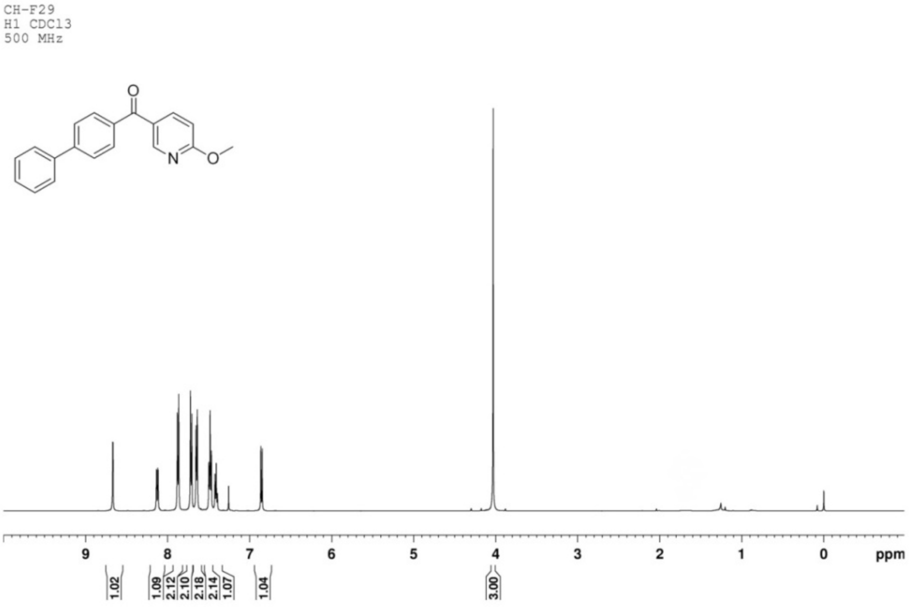


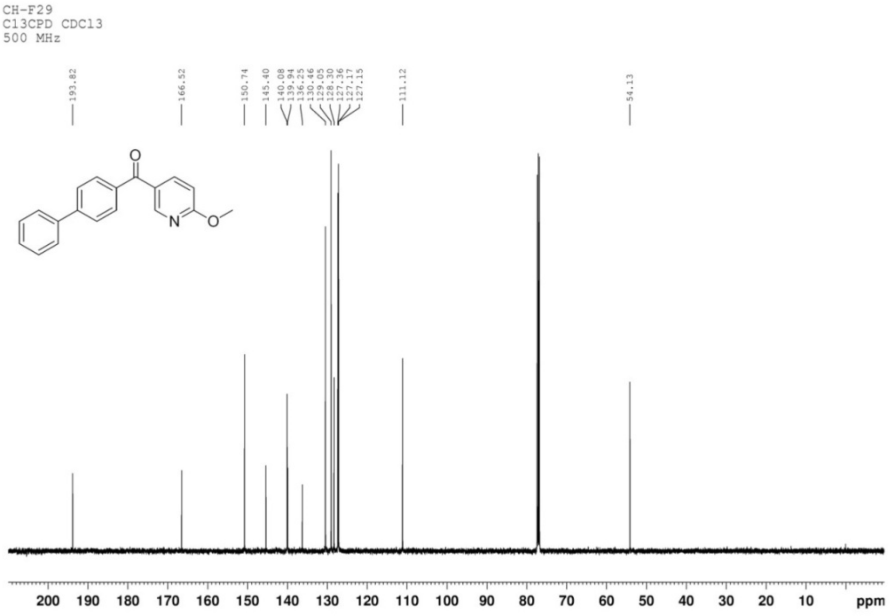
^{1}H and ^{13}C NMR spectra of compound 3gn



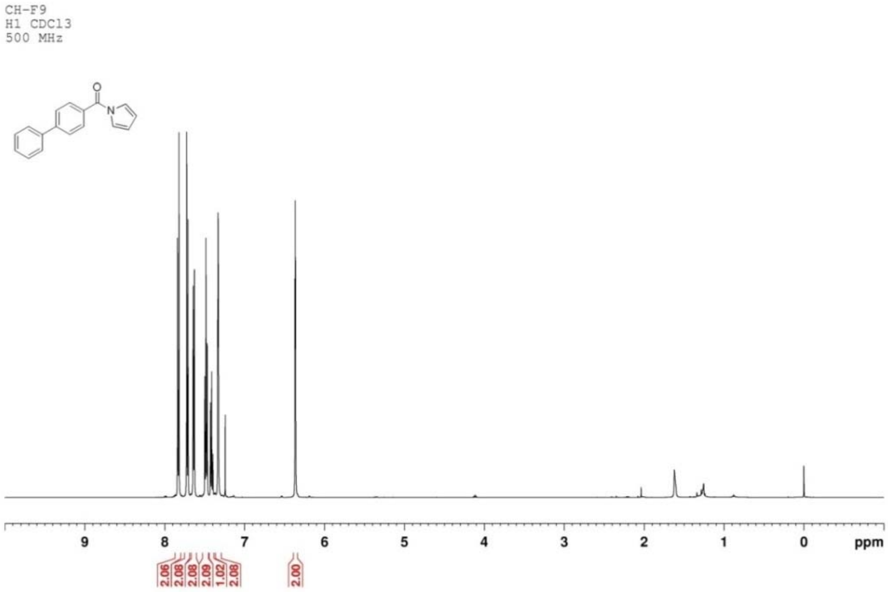


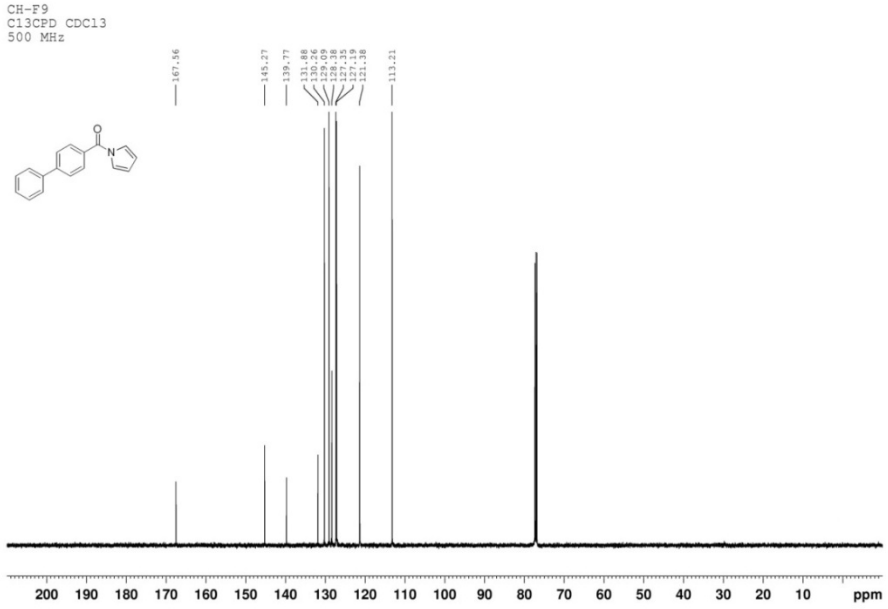
^{1}H and ^{13}C NMR spectra of compound 6



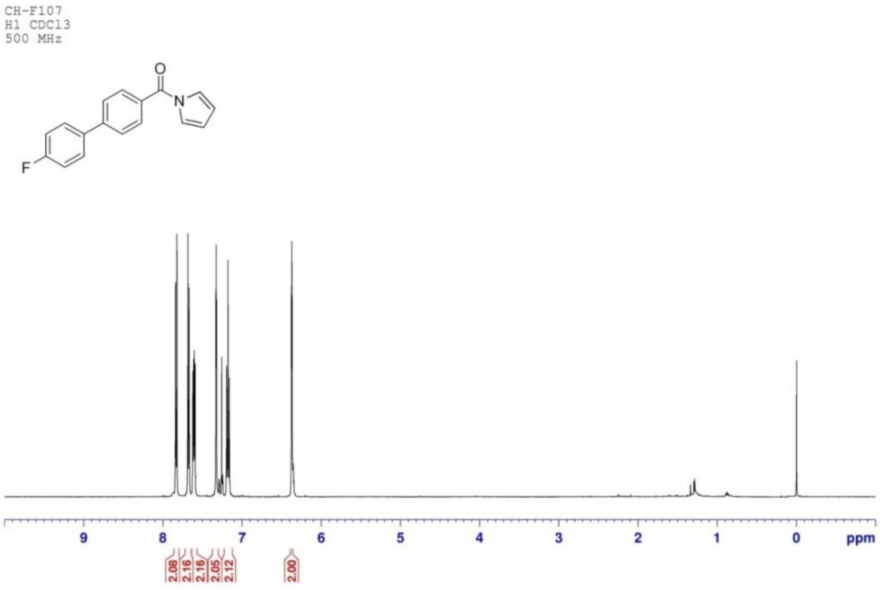


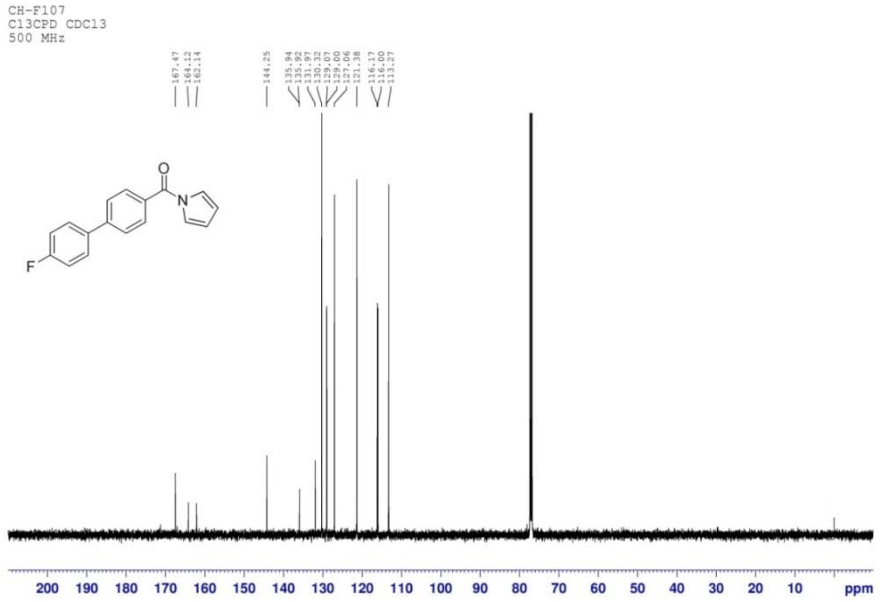
^{1}H and ^{13}C NMR spectra of compound 1sa



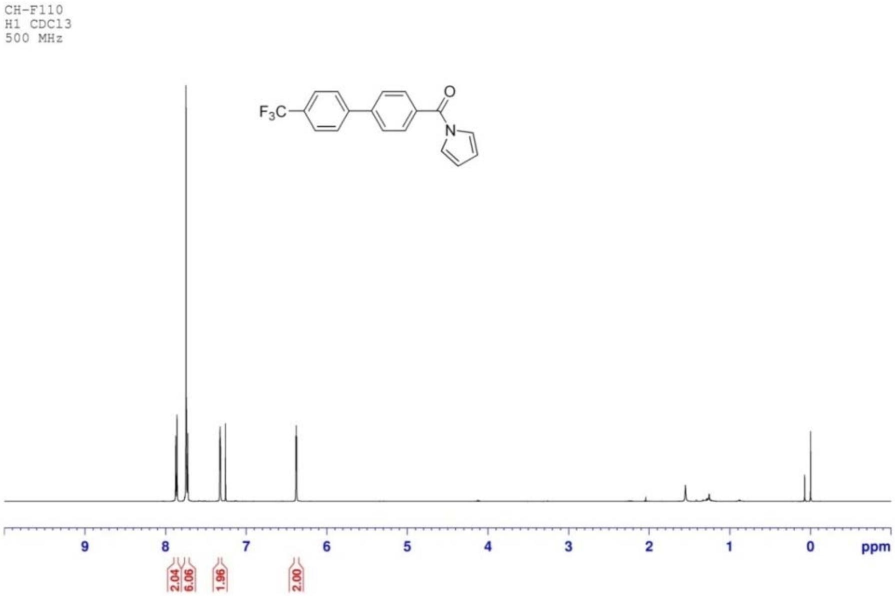


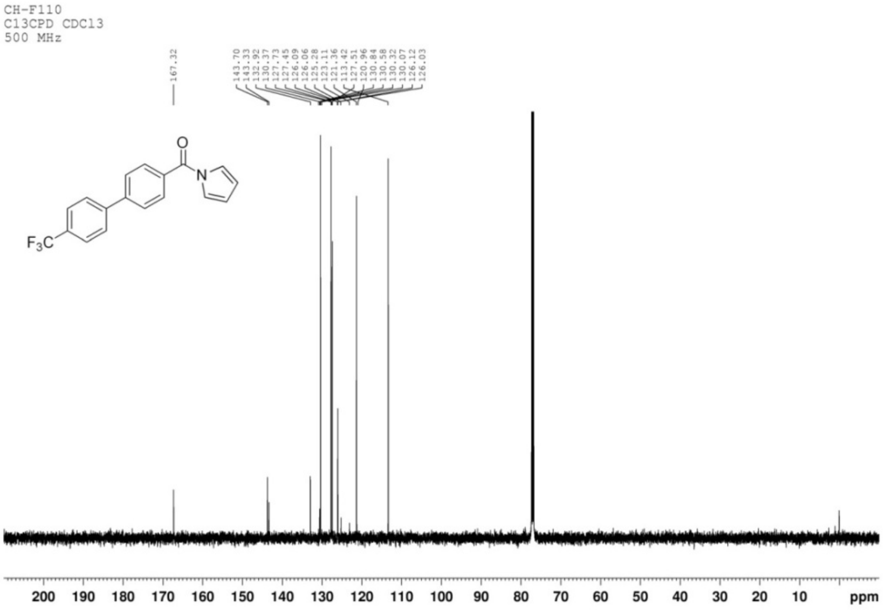
^{1}H and ^{13}C NMR spectra of compound 1sb





^{1}H and ^{13}C NMR spectra of compound 1sc





^{1}H and ^{13}C NMR spectra of compound 1sd