Supporting Information for

Expedient Access to Polysubstituted Acrylamides via Strain-Release-Driven Dual Phosphine and Palladium Catalysis

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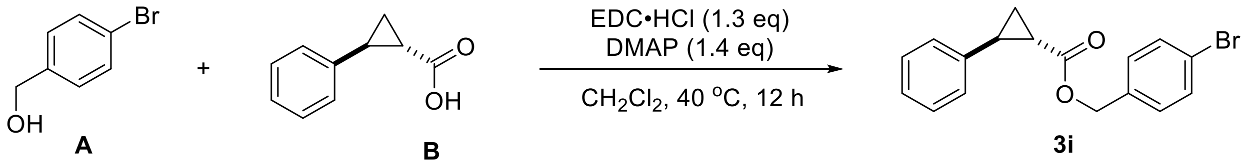
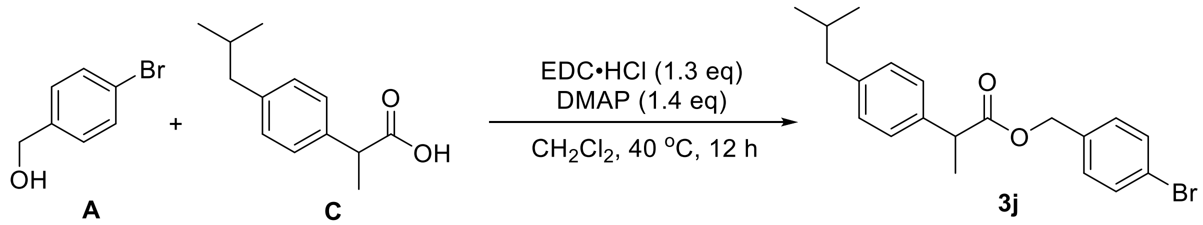
1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. The solvents used were purified by distillation over the drying agents. All reactions were monitored by thin-layer chromatography (TLC) on silica gel plates using UV light as visualizing agent (if applicable). Flash column chromatography was performed using 200-300 mesh silica gel. ^{1}H NMR spectra were recorded on 400 or 600 MHz spectrophotometers. Chemical shifts are reported in delta (δ (ppm)) units in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on 100 or 150 MHz with complete proton-decoupling spectrophotometers ($CDCl_3$: 77.0 ppm, or DMSO-d_6: 39.5 ppm). The high resolution mass spectra (HRMS) were measured on a Shimadzu LCMS-IT-TOF mass spectrometer or DIONEX UltiMate 3000 & Bruker Compact TOF mass spectrometer by ESI and Thermo fisher Q-Exactive mass spectrometer by ACPI. UV/Vis: Measurements were made on a *J*ASCO V-750 Spectrophotometer. Fluorophotometer: Measurements were made on a F-7000 Fluorescence Spectrophotometer.

2. General procedure for the preparation of substrates 3i and 3j[1]

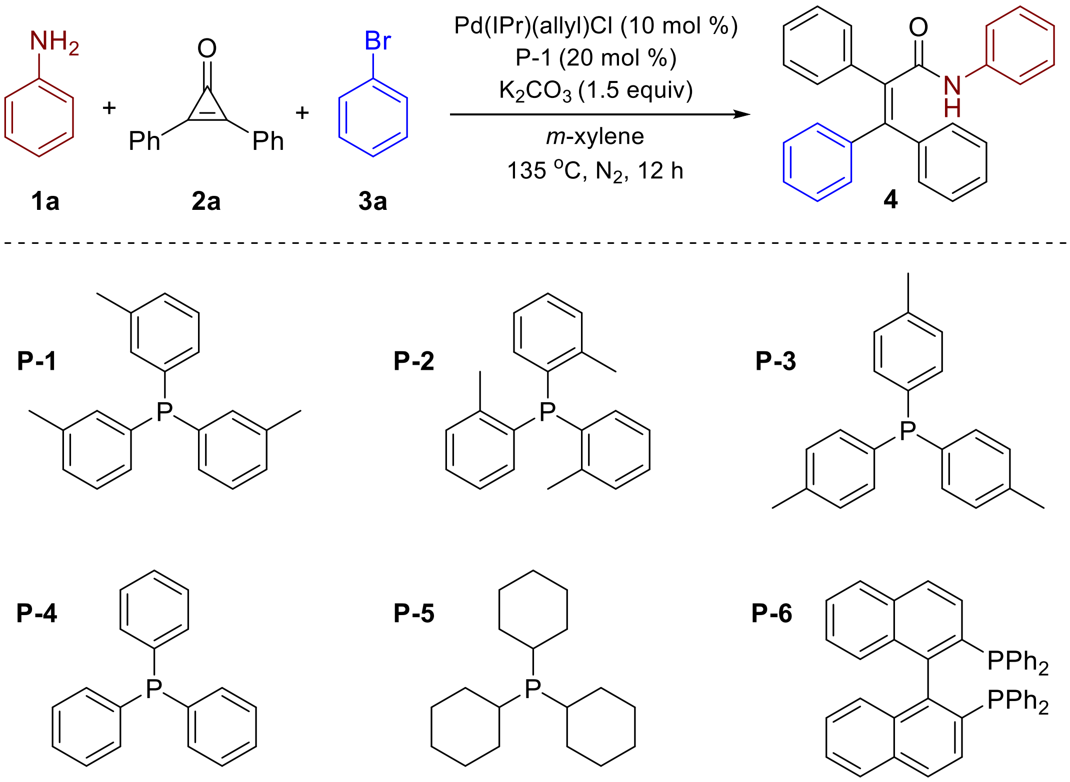


To a dry flask was added **A** (561.1 mg, 3 mmol), **B** (405.5 mg, 2.5 mmol), EDC•HCl (625 mg, 3.25 mmol), and DMAP (427.6 mg, 3.5 mmol). Then, CH_2Cl_2 (30 mL) was added into the flask. Then the mixture was stirred at 40 ^{o}C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 15:1) directly to give the desired product **3i** in (777.0 mg) 94% isolated yield as a colourless liquid.[1]



To a dry flask was added **A** (561.1 mg, 3 mmol), **C** (517 mg, 2.5 mmol), EDC•HCl (625 mg, 3.25 mmol), and DMAP (427.6 mg, 3.5 mmol). Then, CH_2Cl_2 (30 mL) was added into the flask. Then the mixture was stirred at 40 ^{o}C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 15:1) directly to give the desired product **3j** in (932 mg) 99% isolated yield as a colourless liquid. [1]

3. Table S1. Optimization of reaction conditions.



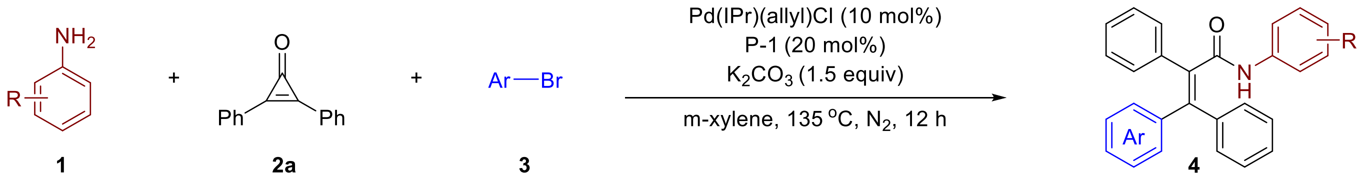
entry	variation of standard condition	yield of **4** (%)[b]
1	none	80
2	$[Rh(COD)Cl]_2$ instead of Pd(IPr)(allyl)Cl	15
3	[Pd]-2 instead of Pd(IPr)(allyl)Cl	50
4	[Pd]-3 instead of Pd(IPr)(allyl)Cl	trace
5	P-2 instead of P-1	31
6	P-3 instead of P-1	59
7	P-4 instead of P-1	60
8	P-5 instead of P-1	51
9	P-6 instead of P-1	trace
10	CH_3CN instead of m-xylene	15
11	THF instead of m-xylene	22
12	toluene instead of m-xylene	77
13	without P-1	24
14	without Pd(IPr)(allyl)Cl	trace

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), **3a** (1 mmol), Pd(IPr)(allyl)Cl (0.02 mmol, 10 mol %), phosphine (0.04 mmol, 20 mol %), base (0.3 mmol), solvent (1.5 mL) at 135 °C for 12 h. [b] Isolated yields based on **1a**. [Pd]-2: $[Pd(cinnamyl)Cl]_2$. [Pd]-3: $Pd_2(dba)_3$.

To test the feasibility of the proposed three-component reaction, we conducted the coupling reaction of readily available aniline **1a**, cyclopropenone **2a** and bromobenzene **3a** in the presence of phosphine and palladium catalysts. After a brief survey of parameters, we established the optimal condition by a synergistic combination of nucleophilic phosphine catalyst P-1 (20 mol%) and Pd(IPr)(allyl)Cl (10 mol%), K_2CO_3 as the base in *m*-xylene at 135 °C for 12 h, delivering the desired triphenyl acrylamide **4** in 80% yield (entry 1). $[Rh(COD)Cl]_2$ that is an effective catalyst for the three-component reaction of cyclopropenone, water and bromobenzene in our previous work, proved to be unsuitable for this reaction (entry 2, 15%). $[Pd(cinnamyl)Cl]_2$ can promote this reaction in relatively lower efficiency, while $Pd_2(dba)_3$ was not effective (entries 3 and 4). Further screening of phosphine catalysts demonstrated phosphine catalyst P-1 is the optimal catalyst (entries 5-9). A significant solvent effect was observed, and inferior yields were obtained when CH_3CN or THF was used as the solvent (entries 10-12). The reaction can be also performed in toluene to give product **4** with 77% yield. Control experiments demonstrated the important role of phosphine and palladium catalysts in this transformation (entries 13 and 14).

4. General Procedure and Spectral Data of Polysubstituted Acrylamides

4.1 General procedure for the synthesis of products 4-17 and 18-34

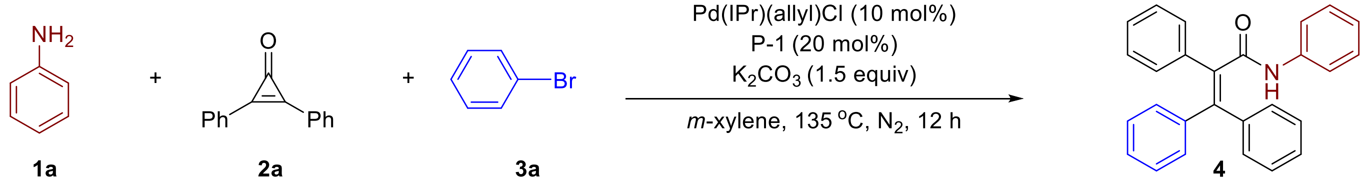


To an over dried bottle equipped with a magnetic stir bar, **1** (1 equiv, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3** (5 equiv, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) were added. Then, *m*-xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 °C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) directly to give the desired product **4** in 80% isolated yield as a white solid.

Products **4-17** and **18-34** were prepared according to the above procedures.

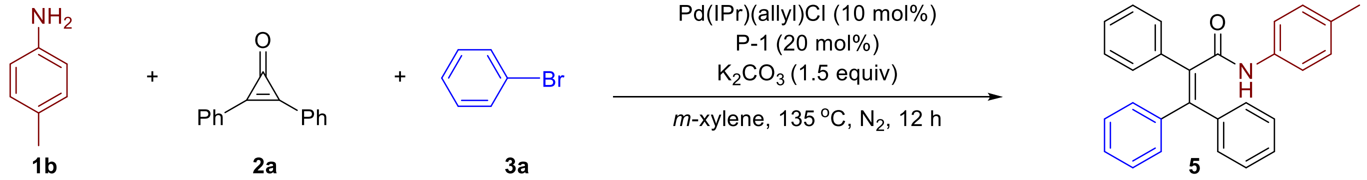
4.2 Spectral data of the products 4-35 and 35-D

Product 4 (known compound, CAS: 96069-37-3)[4]



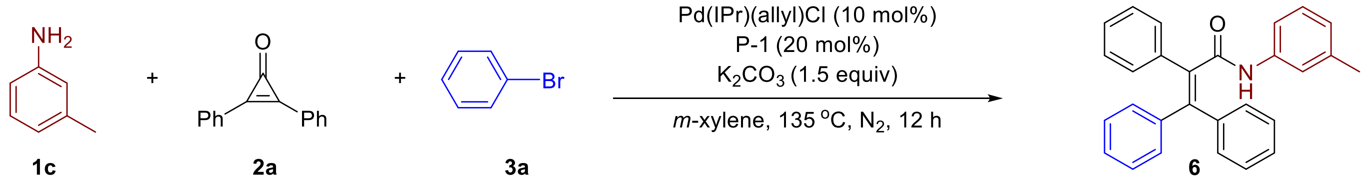
To an over dried bottle equipped with a magnetic stir bar, **1a** (18.6 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3a** (156 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) were added. Then, *m*-xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 °C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 8:1) directly to give the desired product **4** in 80% isolated yield (60.2 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.37 (d, *J* = 7.2 Hz, 2H), 7.31 (d, *J* = 6.7 Hz, 3H), 7.24 – 7.12 (m, 12H), 7.11 – 6.98 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 168.5, 144.7, 141.8, 140.9, 138.0, 137.6, 137.3, 130.9, 130.2, 129.2, 128.8, 128.6, 128.4, 128.3, 127.9, 127.6, 127.6, 124.4, 120.0. M P: 211.5-212.5 °C. HRMS (ACPI): m/z $[M + H]^+$ calcd for $C_{27}H_{21}NO$: 376.1696; found: 376.1700.

Product 5 (unknown compound)



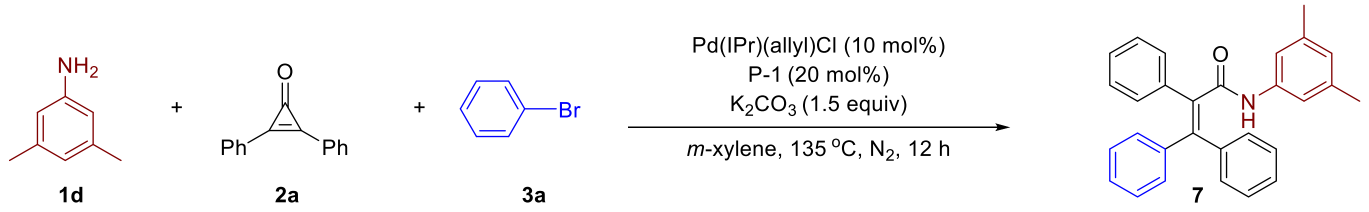
To an over dried bottle equipped with a magnetic stir bar, **1b** (21.4 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3a** (156 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) were added. Then, *m*-xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 °C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 8:1) directly to give the desired product **5** in 81% isolated yield (63.2 mg) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 7.36 (dd, *J* = 7.9, 1.8 Hz, 2H), 7.32 – 7.26 (m, 3H), 7.20 – 7.12 (m, 8H), 7.10 (s, 1H), 7.02 (q, *J* = 8.4 Hz, 6H), 2.26 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) = 168.5, 144.4, 141.8, 140.9, 138.0, 137.3, 134.9, 134.1, 130.9, 130.2, 129.2, 129.2, 128.5, 128.3, 128.2, 127.9, 127.6, 127.5, 120.1, 20.8. M P: 197.5-198.5 ^{o}C. HRMS (ACPI): m/z $[M + H]^+$ calcd for $C_{28}H_{23}NO$: 390.1852; found: 390.1850.

Product 6 (unknown compound)



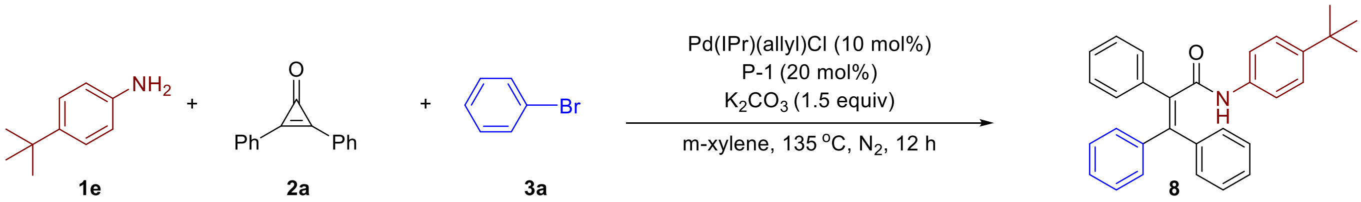
To an over dried bottle equipped with a magnetic stir bar, **1c** (21.4 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3a** (156 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) were added. Then, *m*-xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 ^{o}C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 6:1) directly to give the desired product **6** in 83% isolated yield (65.0 mg) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.36 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.34 – 7.28 (m, 3H), 7.20 – 7.13 (m, 8H), 7.11 – 7.04 (m, 3H), 7.02 (dd, *J* = 8.0, 1.7 Hz, 2H), 6.87 (d, *J* = 8.1 Hz, 2H), 2.26 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 168.5, 144.6, 141.8, 140.9, 138.7, 138.0, 137.4, 137.3, 130.9, 130.2, 129.2, 128.6, 128.6, 128.4, 128.3, 127.9, 127.6, 127.6, 125.2, 120.7, 117.0, 21.4. M P: 215.5-216.5 ^{o}C. HRMS (ACPI): m/z $[M + H]^+$ calcd for $C_{28}H_{23}NO$: 390.1852; found: 390.1857.

Product 7 (unknown compound)



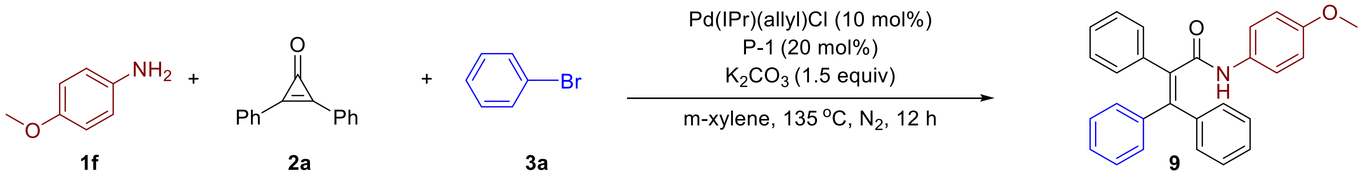
To an over dried bottle equipped with a magnetic stir bar, **1d** (24.2 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3a** (156 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) were added. Then, *m*-xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 ^{o}C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 6:1) directly to give the desired product **7** in 68% isolated yield (54.7 mg) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.36 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.34 – 7.29 (m, 3H), 7.20 – 7.13 (m, 8H), 7.04 – 6.99 (m, 3H), 6.81 (s, 2H), 6.70 (s, 1H), 2.22 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 168.5, 144.5, 141.8, 141.0, 138.5, 138.0, 137.3, 130.9, 130.2, 129.2, 128.6, 128.3, 128.3, 127.9, 127.8, 127.6, 127.5, 126.2, 117.7, 21.3. M P: 247.5-248.5 °C. HRMS (ACPI): m/z $[M + H]^+$ calcd for $C_{29}H_{25}NO$: 404.2009; found: 404.2014.

Product 8 (unknown compound)



To an over dried bottle equipped with a magnetic stir bar, **1e** (29.8 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3a** (156 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) were added. Then, *m*-xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 °C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 6:1) directly to give the desired product **8** in 81% isolated yield (70.0 mg) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.38 – 7.36 (m, 2H), 7.33 – 7.29 (m, 3H), 7.25 (s, 1H), 7.23 (s, 1H), 7.19 – 7.12 (m, 8H), 7.09 (d, *J* = 8.7 Hz, 3H), 7.03 – 7.01 (m, 2H), 1.26 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 168.5, 147.4, 144.4, 141.8, 141.0, 138.0, 137.2, 134.8, 130.9, 130.2, 129.2, 128.6, 128.3, 128.27, 127.9, 127.6, 127.5, 125.6, 119.9, 34.3, 31.3. M P: 221.6-222.8 °C. HRMS (ACPI): m/z $[M + H]^+$ calcd for $C_{31}H_{29}NO$: 432.2322; found: 432.2326.

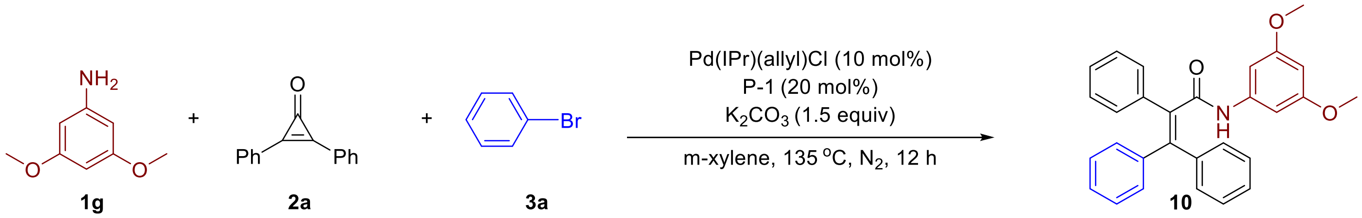
Product 9 (unknown compound)



To an over dried bottle equipped with a magnetic stir bar, **1f** (24.6 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3a** (156 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) were added. Then, m-xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 °C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 6:1) directly to give the desired product **9** in 67% isolated yield (54.2 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.40 – 7.35 (m, 2H), 7.34 – 7.28

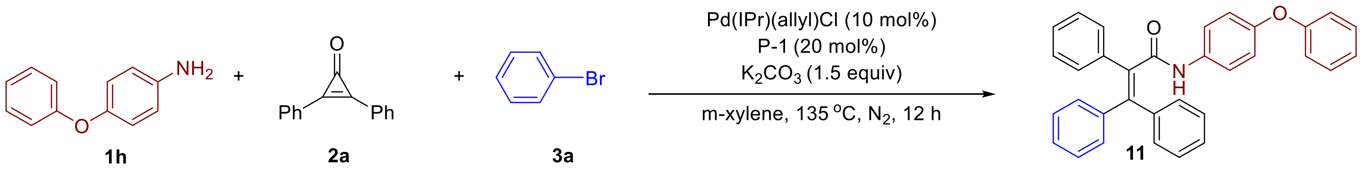
(m, 3H), 7.21 – 7.13 (m, 8H), 7.05 – 7.05 (m, 5H), 6.75 (d, *J* = 8.7 Hz, 2H), 3.75 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 168.5, 156.6, 144.3, 141.9, 140.9, 138.0, 137.3, 130.9, 130.5, 130.2, 129.2, 128.6, 128.3, 128.3, 127.9, 127.6, 127.5, 122.0, 113.9, 55.4. M P: 173.2-174.2 ^{o}C. HRMS (ACPI): m/z $[M + H]^+$ calcd for $C_{28}H_{23}NO_2$: 406.1802; found: 406.1808.

Product 10 (unknown compound)



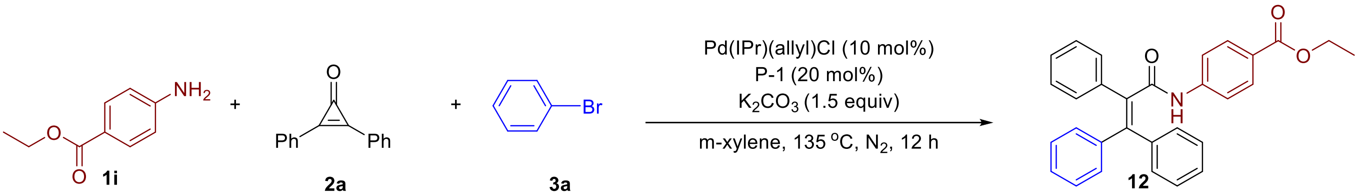
To an over dried bottle equipped with a magnetic stir bar, **1g** (30.6 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3a** (156 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) were added. Then, m-xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 ^{o}C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 6:1) directly to give the desired product **10** in 76% isolated yield (66.1 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.38 – 7.29 (m, 5H), 7.21 – 7.12 (m, 8H), 7.07 – 6.98 (m, 3H), 6.38 (d, *J* = 2.2 Hz, 2H), 6.18 (t, *J* = 2.3 Hz, 1H), 3.70 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 168.5, 160.8, 144.8, 141.7, 140.8, 139.3, 138.0, 137.4, 130.9, 130.2, 129.2, 128.7, 128.4, 128.3, 127.9, 127.6, 127.6, 98.1, 97.1, 55.3. M P: 197.5-198.5 ^{o}C. HRMS (ACPI): m/z $[M + H]^+$ calcd for $C_{29}H_{25}NO_3$: 436.1907; found: 436.1935.

Product 11 (unknown compound)



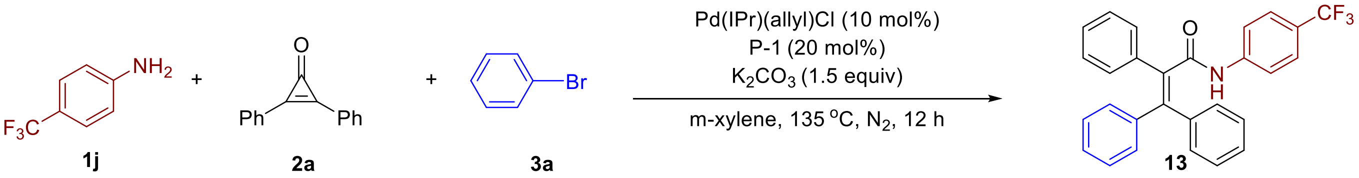
To an over dried bottle equipped with a magnetic stir bar, **1h** (37.0 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3a** (156 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) were added. Then, m-xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 ^{o}C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 6:1) directly to give the desired product **11** in 76% isolated yield (71.3 mg) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.38 – 7.36 (m, 2H), 7.35 – 7.28 (m, 5H), 7.21 – 7.12 (m, 8H), 7.12 – 7.04 (m, 4H), 7.03 – 7.01 (m, 2H), 6.95 (d, *J* = 8.8, 2H), 6.87 (d, *J* = 8.9 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 168.6, 156.4, 153.7, 144.6, 141.8, 140.8, 137.9, 137.2, 132.9, 130.9, 130.2, 129.7, 129.2, 128.6, 128.4, 128.3, 127.9, 127.7, 127.6, 123.1, 121.9, 119.3, 118.5. M P: 199.5-200.5 ^{o}C. HRMS (ACPI): m/z $[M + H]^+$ calcd for $C_{33}H_{25}NO_2$: 468.1958; found: 468.1967.

Product 12 (unknown compound)



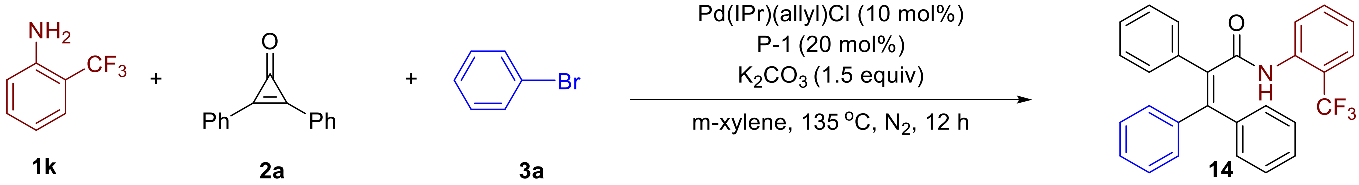
To an over dried bottle equipped with a magnetic stir bar, **1i** (33.0 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3a** (156 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) were added. Then, m-Xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 ^{o}C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 6:1) directly to give the desired product **12** in 65% isolated yield (58.1 mg) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.89 (d, *J* = 8.4 Hz, 2H), 7.34 (s, 2H), 7.27 – 7.25 (m, 5H), 7.19 – 7.15 (m, 8H), 7.01 (d, *J* = 7.0 Hz, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 168.7, 166.1, 145.6, 141.7, 141.6, 140.7, 137.8, 136.9, 130.9, 130.5, 130.2, 129.2, 128.7, 128.6, 128.4, 127.9, 127.8, 127.7, 126.0, 118.8, 60.8, 14.3. M P: 177.8-178.5 ^{o}C. HRMS (ACPI): m/z $[M + H]^+$ calcd for $C_{30}H_{25}NO_3$: 448.1907; found: 448.1912.

Product 13 (unknown compound)



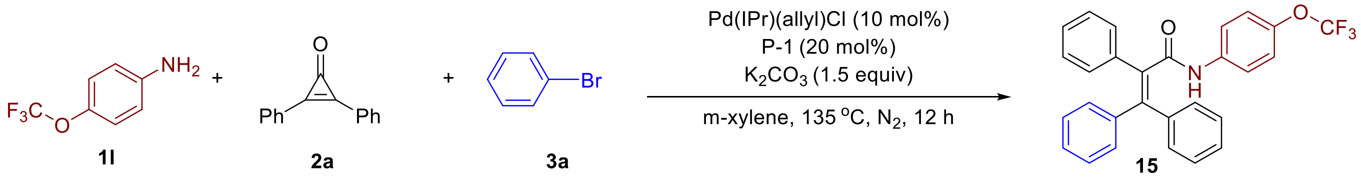
To an over dried bottle equipped with a magnetic stir bar, **1j** (32.2 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3a** (156 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) were added. Then, m-Xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 ^{o}C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) directly to give the desired product **13** in (75.4 mg) 85% isolated yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.46 (d, *J* = 8.4 Hz, 2H), 7.36 – 7.34 (m, 2H), 7.33 – 7.27 (m, 5H), 7.23 – 7.13 (m, 9H), 7.01 (d, *J* = 8.1, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 168.8, 145.6, 141.6, 140.60, 140.59, 137.8, 136.8, 130.9, 130.2, 129.2, 128.7, 128.7, 128.4, 128.0, 127.9, 127.8, 126.1 (q, *J* = 32.5 Hz), 126.05 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 270.0 Hz), 119.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -62.1. M P: 199.7-200.7 °C. HRMS (ACPI): m/z $[M + H]^+$ calcd for $C_{28}H_{20}F_3NO$: 444.1560; found: 444.1563.

Product 14 (unknown compound)



To an over dried bottle equipped with a magnetic stir bar, **1k** (32.2 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3a** (156 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) were added. Then, m-xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 °C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) directly to give the desired product **14** in 62% isolated yield (55.5 mg) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 8.11 (d, *J* = 8.3 Hz, 1H), 7.52 – 7.45 (m, 3H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.34 – 7.27 (m, 3H), 7.21 (s, 5H), 7.18 – 7.11 (m, 4H), 7.02 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 168.6, 146.1, 141.6, 140.8, 137.5, 136.6, 135.2, 132.8, 130.9, 130.1, 129.3, 128.5, 128.4, 128.4, 127.9, 127.8, 127.7, 125.9 (q, *J* = 5.2 Hz), 123.8 (q, *J* = 271.2 Hz), 124.2, 123.6, 119.7 (q, *J* = 30.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -60.8. M P: 197.5-198.5 °C. HRMS (ACPI): m/z $[M + H]^+$ calcd for $C_{28}H_{20}F_3NO$: 444.1560; found: 444.1566.

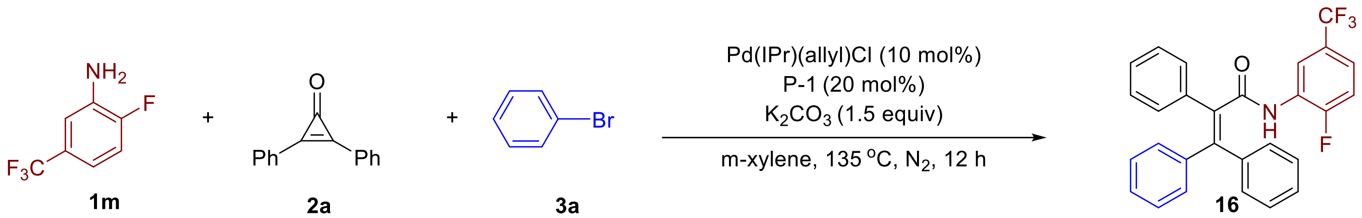
Product 15 (unknown compound)



To an over dried bottle equipped with a magnetic stir bar, **1l** (32.2 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3a** (156 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and

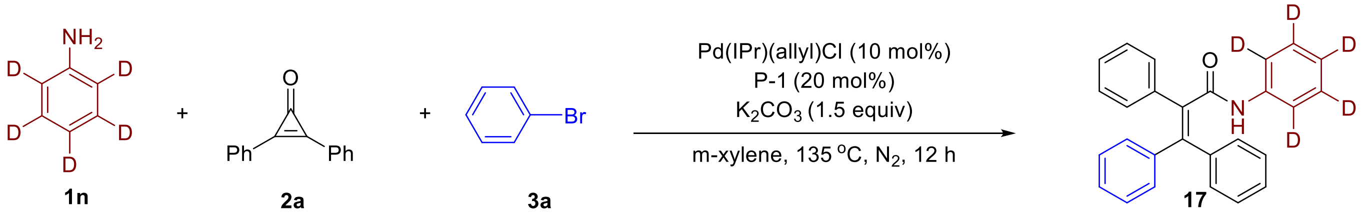
K_2CO_3 (41.5 mg, 0.3 mmol) were added. Then, m-xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 °C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) directly to give the desired product **15** in 92% isolated yield (84.5 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.38 – 7.30 (m, 5H), 7.22 – 7.11 (m, 11H), 7.06 (d, *J* = 8.6 Hz, 2H), 7.01 (d, *J* = 6.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 168.6, 145.4 (q, *J* = 2.0 Hz), 145.2, 141.7, 140.7, 137.8, 137.0, 136.2, 130.9, 130.2, 129.2, 128.7, 128.6, 128.4, 127.8 (d, *J* = 6.2 Hz), 127.7, 121.5, 121.2, 120.4 (d, *J* = 255 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -58.1. M P: 209.5-210.5 °C. HRMS (ACPI): m/z $[M + H]^+$ calcd for $C_{28}H_{20}F_3NO_2$: 460.1519; found: 460.1526.

Product 16 (unknown compound)



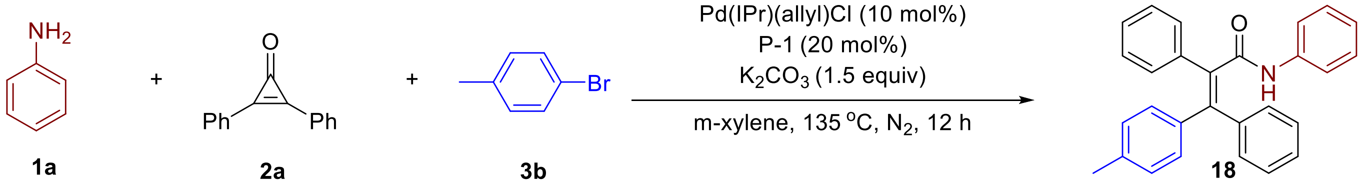
To an over dried bottle equipped with a magnetic stir bar, **1m** (35.8 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3a** (156 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) were added. Then, m-xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 °C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) directly to give the desired product **16** in 68% isolated yield (62.9 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.58 (d, *J* = 8.6 Hz, 1H), 7.38 – 7.29 (m, 6H), 7.23 – 7.12 (m, 8H), 7.07 – 6.99 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) = 168.8, 153.6 (d, *J* = 247.5 Hz), 146.2, 141.4, 140.5, 137.7, 136.4, 130.9, 130.2, 129.2, 128.7, 128.7, 128.4, 127.9, 127.9, 127.8, 127.1 (d, *J* = 33.0 Hz), 126.7 (d, *J* = 10.5 Hz), 123.5 (d, *J* = 270.0 Hz), 121.4 (q, *J* = 4.5 Hz), 118.9 (q, *J* = 15.0 Hz), 115.0 (d, *J* = 19.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -62.1, -126.7. M P: 187.7-188.6 °C. HRMS (ACPI): m/z $[M + H]^+$ calcd for $C_{28}H_{19}F_4NO$: 462.1476; found: 462.1474.

Product 17 (unknown compound)



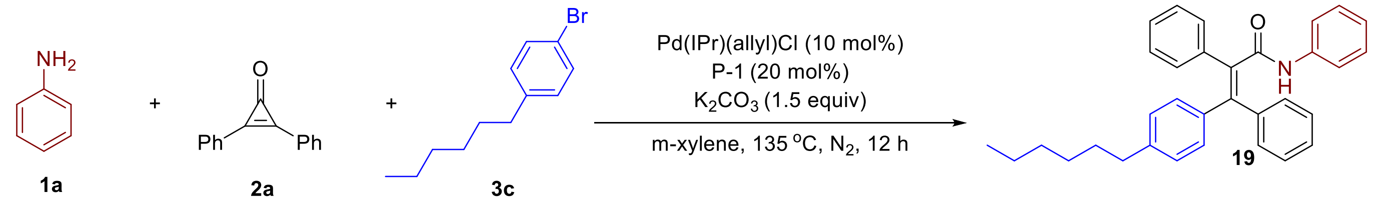
To an over dried bottle equipped with a magnetic stir bar, **1n** (19.6 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3a** (156 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) were added. Then, m-xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 ^{o}C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 6:1) directly to give the desired product **17** in 66% isolated yield (50.3 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.36 (d, *J* = 6.1 Hz, 2H), 7.30 (d, *J* = 6.6 Hz, 3H), 7.21 – 7.10 (m, 9H), 7.02 (d, *J* = 5.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 168.5, 144.7, 141.8, 140.9, 138.0, 137.4, 137.30, 130.9, 130.2, 129.2, 128.6, 128.4, 128.3, 127.9, 127.6, 127.6, 119.8, 119.6, 119.4. M P: 205.5-206.5 ^{o}C. HRMS (ACPI): m/z $[M + H]^+$ calcd for $C_{27}H_{16}D_5NO$: 381.2010; found: 381.2014.

Product 18 (unknown compound)



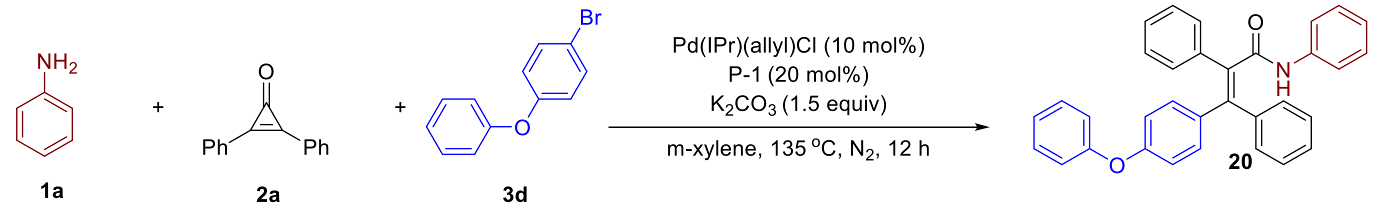
To an over dried bottle equipped with a magnetic stir bar, **1a** (18.6 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3b** (170 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) were added. Then, m-xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 ^{o}C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) directly to give the desired product **18** in (62.7 mg) 80% isolated yield as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.36 (d, *J* = 7.9 Hz, 2H), 7.32 – 7.26 (m, 3H), 7.22 – 7.16 (m, 7H), 7.16 – 7.13 (m, 2H), 7.10 (s, 1H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 8.2 Hz, 2H), 2.27 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 168.7, 144.7, 142.0, 138.2, 137.9, 137.6, 137.5, 136.8, 130.9, 130.2, 129.2, 128.7, 128.6, 128.5, 128.3, 128.3, 127.4, 124.4, 120.0, 21.2. M P: 199.7-200.7 °C. HRMS (ACPI): m/z $[M + H]^+$ calcd for $C_{28}H_{23}NO$: 390.1852; found: 390.1850.

Product 19 (unknown compound)



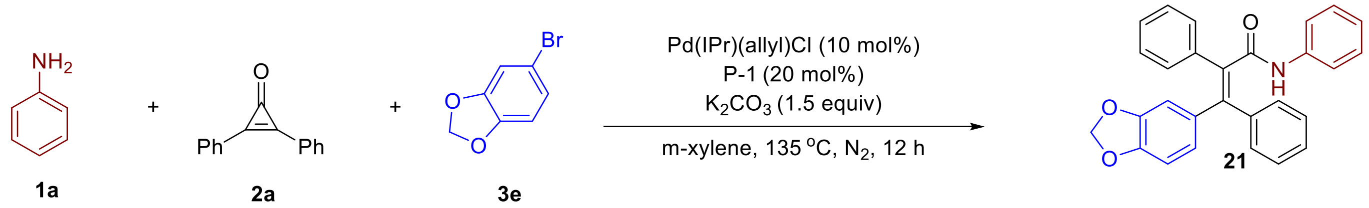
To an over dried bottle equipped with a magnetic stir bar, **1a** (18.6 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3c** (240 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) were added. Then, m-xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 °C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) directly to give the desired product **19** in 78% isolated yield (71.9 mg) as a white solid. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.37 (d, *J* = 7.7 Hz, 2H), 7.36 – 7.29 (m, 3H), 7.22 – 7.14 (m, 9H), 7.11 (s, 1H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.94 (d, *J* = 8.1 Hz, 2H), 6.90 (d, *J* = 8.1 Hz, 2H), 2.55 – 2.48 (t, *J* = 7.6 Hz, 2H), 1.55 (t, *J* = 7.7 Hz, 2H), 1.29 (d, *J* = 9.8 Hz, 6H), 0.87 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 168.8, 144.8, 142.6, 142.0, 138.2, 138.0, 137.6, 136.8, 130.8, 130.2, 129.2, 128.7, 128.5, 128.3, 128.2, 127.9, 127.4, 124.4, 120.0, 35.6, 31.6, 31.0, 28.8, 22.6, 14.0. M P: 139.5-140.5 °C. HRMS (ACPI): m/z $[M + H]^+$ calcd for $C_{33}H_{33}NO$: 460.2635; found: 460.2638.

Product 20 (unknown compound)



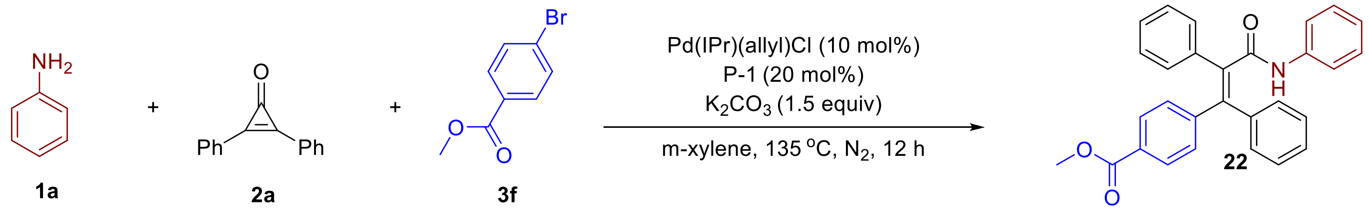
To an over dried bottle equipped with a magnetic stir bar, **1a** (18.6 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3d** (248 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) were added. Then, m-xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 °C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) directly to give the desired product **20** in 49% isolated yield (46.0 mg) as a white solid. ^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm) = 7.39 (d, *J* = 8.1 Hz, 2H), 7.35 – 7.30 (m, 5H), 7.24 – 7.19 (m, 7H), 7.17 – 7.15 (m, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.07 – 7.03 (m, 2H), 7.00 – 6.94 (m, 4H), 6.77 (d, *J* = 2.1 Hz, 1H), 6.76 (d, *J* = 2.1 Hz, 1H). ^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm) = 168.6, 156.9, 156.4, 144.2, 141.8, 138.1, 137.5, 136.9, 135.5, 132.5, 130.2, 129.8, 129.3, 128.8, 128.6, 128.5, 128.4, 127.6, 124.4, 123.6, 120.0, 119.2, 117.7. M P: 171.8-172.5 ^{o}C. HRMS (ACPI): m/z [M + H]$^+$ calcd for $C_{33}H_{25}NO_2$: 468.1958; found: 468.1957.

Product 21 (unknown compound)



To an over dried bottle equipped with a magnetic stir bar, **1a** (18.6 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3e** (200 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) were added. Then, m-xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 ^{o}C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) directly to give the desired product **21** in (34.6 mg) 41% isolated yield as a yellow solid. ^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm) = 7.37 – 7.35 (m, 2H), 7.33 – 7.27 (m, 3H), 7.24 – 7.17 (m, 7H), 7.14 (d, *J* = 7.3 Hz, 2H), 7.07 – 7.02 (m, 2H), 6.58 (d, *J* = 8.1 Hz, 1H), 6.53 – 6.42 (m, 2H), 5.90 (s, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm) = 168.6, 147.2, 147.1, 144.4, 141.8, 138.1, 137.5, 136.7, 134.7, 130.1, 129.2, 128.8, 128.6, 128.4, 128.4, 127.6, 125.3, 124.4, 120.0, 111.2, 107.8, 101.1. M P: 201.5-202.5 ^{o}C. HRMS (ACPI): m/z [M + H]$^+$ calcd for $C_{28}H_{21}NO_3$: 420.1594; found: 420.1592.

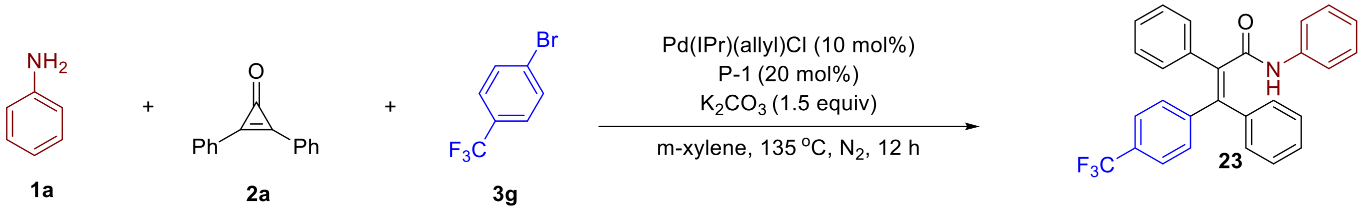
Product 22 (unknown compound)



To an over dried bottle equipped with a magnetic stir bar, **1a** (18.6 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3f** (214 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and

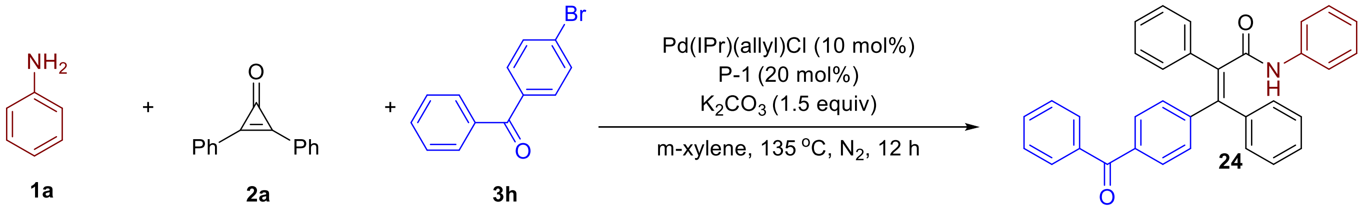
K_2CO_3 (41.5 mg, 0.3 mmol) were added. Then, m-xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 °C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) directly to give the desired product **22** in 59% isolated yield (51.1 mg) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.81 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.29 (m, 5H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.20 – 7.15 (m, 8H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.05 (t, *J* = 7.2 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 168.1, 166.7, 145.8, 143.4, 141.0, 138.4, 137.5, 137.3, 130.9, 130.1, 129.2, 129.2, 129.0, 128.8, 128.7, 128.6, 128.5, 127.96, 124.5, 120.1, 52.1. M P: 201.3-202.8 °C. HRMS (ACPI): m/z $[M + H]^+$ calcd for $C_{29}H_{23}NO_3$: 434.1751; found: 434.1750.

Product 23 (unknown compound)



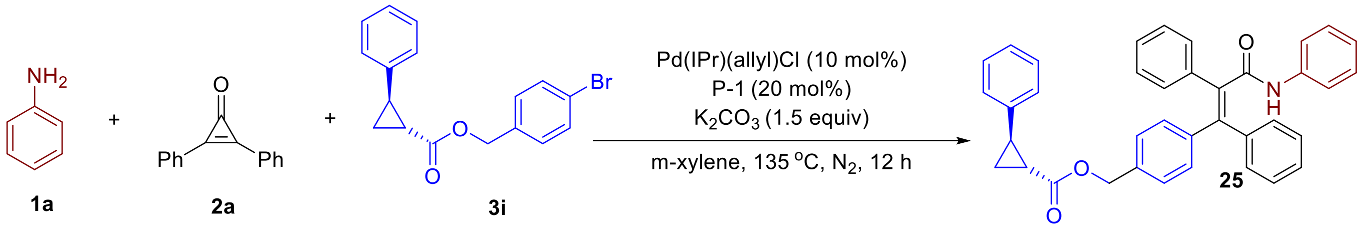
To an over dried bottle equipped with a magnetic stir bar, **1a** (18.6 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3g** (224 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) were added. Then, m-xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 °C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) directly to give the desired product **23** in 44% isolated yield (38.7 mg) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.40 (d, *J* = 8.1 Hz, 2H), 7.34 – 7.32 (m, 5H), 7.26 – 7.20 (m, 5H), 7.20 – 7.10 (m, 7H), 7.07 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 168.0, 144.6, 143.1, 141.0, 138.5, 137.3, 137.2, 131.2, 130.1, 129.5 (d, *J* = 31.2 Hz), 129.2, 128.8, 128.8, 128.7, 128.6, 128.1, 124.9 (q, *J* = 3.6 Hz), 124.6, 123.9 (d, *J* = 270.0 Hz), 120.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -62.6. M P: 215.5-216.5 °C. HRMS (ACPI): m/z $[M + H]^+$ calcd for $C_{28}H_{20}F_3NO$: 444.1560; found: 444.1566.

Product 24 (unknown compound)



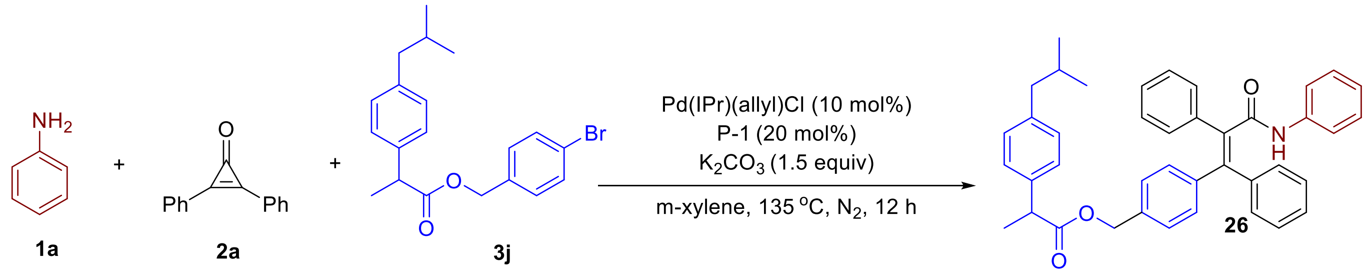
To an over dried bottle equipped with a magnetic stir bar, **1a** (18.6 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3h** (260 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol)were added. Then, m-xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 ^{o}C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) directly to give the desired product **24** in 75% isolated yield (71.4 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.74 (d, *J* = 7.6 Hz, 2H), 7.61 – 7.55 (m, 3H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.41 – 7.27 (m, 5H), 7.23 – 7.12 (m, 11H), 7.06 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 196.1, 168.0, 145.3, 143.5, 141.1, 138.5, 137.4, 136.3, 132.4, 130.8, 130.1, 130.0, 129.9, 129.7, 129.2, 128.8, 128.7, 128.7, 128.5, 128.3, 128.2, 128.0, 124.6, 120.1. M P: 181.5-182.5 ^{o}C. HRMS (ACPI): m/z $[M + H]^+$ calcd for $C_{34}H_{25}NO_2$: 480.1958; found: 480.1966.

Product 25 (unknown compound)



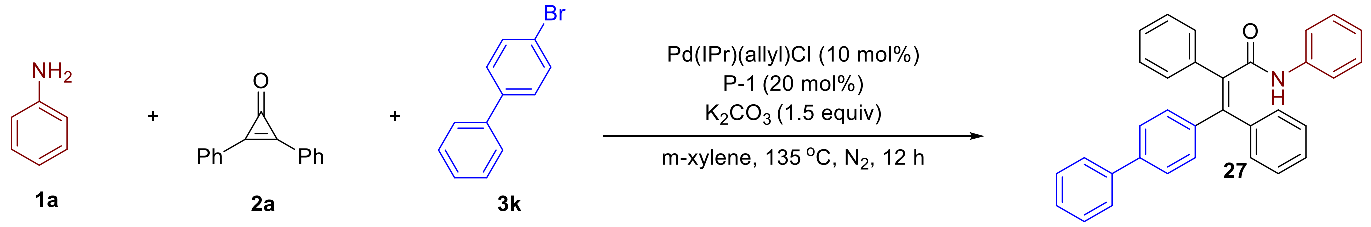
To an over dried bottle equipped with a magnetic stir bar, **1a** (18.6 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3i** (330 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) were added. Then, m-xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 ^{o}C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) directly to give the desired product **25** in 65% isolated yield (71.4 mg) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 7.35 (d, *J* = 7.8 Hz, 2H), 7.31 – 7.25 (m, 5H), 7.19 (d, *J* = 7.8 Hz, 8H), 7.16 – 7.11 (m, 5H), 7.09 – 7.06 (m, 2H), 7.06 – 7.00 (m, 3H), 5.07 (s, 2H), 2.55 – 2.52 (m, 1H), 1.96 – 1.93 (m, 1H), 1.64 – 1.60 (m, 1H), 1.35 – 1.32 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 173.1, 168.4, 144.0, 141.6, 140.8, 139.8, 137.8, 137.5, 137.4, 135.2, 131.1, 130.1, 129.2, 128.7, 128.6, 128.4, 128.4, 128.4, 127.6, 127.5, 126.5, 126.1, 124.4, 120.0, 66.0, 26.4, 24.1, 17.2. M P: 163.5-164.5 ^{o}C. HRMS (ACPI): m/z $[M + H]^+$ calcd for $C_{38}H_{31}NO_3$: 550.2377; found: 550.2386.

Product 26 (unknown compound)



To an over dried bottle equipped with a magnetic stir bar, **1a** (18.6 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3j** (374 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) were added. Then, m-xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 ^oC for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) directly to give the desired product **26** in 59% isolated yield (70.2 mg) as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.33 – 7.30 (m, 5H), 7.25 – 7.15 (m, 11H), 7.06 (q, *J* = 6.8 Hz, 4H), 6.96 (q, *J* = 8.1 Hz, 4H), 5.03 (s, 2H), 3.74 (q, *J* = 7.1 Hz, 1H), 2.43 (d, *J* = 7.2 Hz, 2H), 1.86 – 1.76 (m, 1H), 1.49 (d, *J* = 7.1 Hz, 3H), 0.87 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 174.4, 168.5, 144.2, 141.6, 140.6, 140.5, 137.8, 137.5, 137.4, 137.3, 135.5, 131.0, 130.2, 129.3, 129.2, 128.8, 128.6, 128.5, 128.4, 127.7, 127.2, 127.0, 124.5, 120.0, 65.7, 45.1, 45.0, 30.2, 22.3, 18.4. M P: 163.7-164.8 ^oC. HRMS (ACPI): m/z $[M + H]^+$ calcd for $C_{41}H_{39}NO_3$: 594.3003; found: 594.3009.

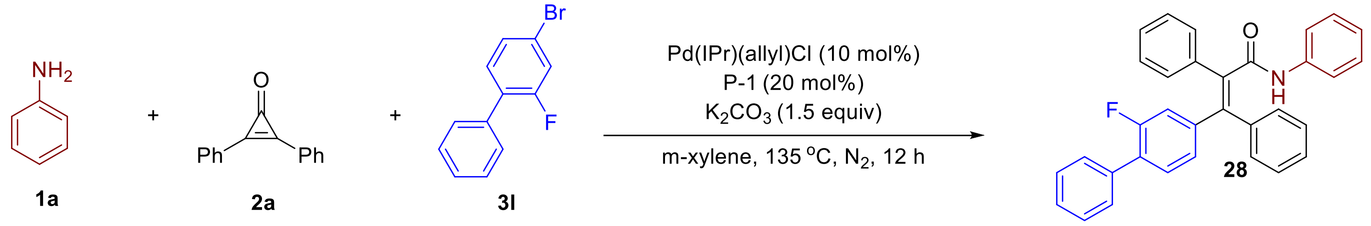
Product 27 (unknown compound)



To an over dried bottle equipped with a magnetic stir bar, **1a** (18.6 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3k** (232 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) were added. Then, m-xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 ^oC for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) directly to give the desired product **27** in 69% isolated yield (62.5 mg) as a white solid. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.55 (d, *J* = 7.4 Hz, 2H), 7.43 – 7.38 (m, 6H), 7.33 – 7.31 (m, 4H), 7.25 – 7.16 (m, 9H), 7.11 – 7.03 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$)

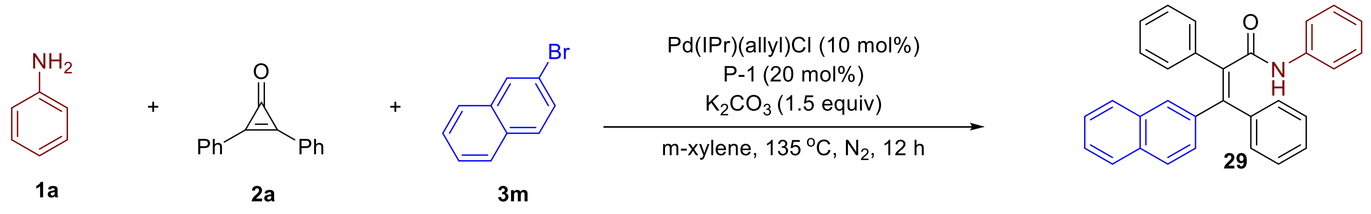
δ (ppm) = 168.6, 144.4, 141.8, 140.3, 140.2, 139.8 138.0, 137.5, 137.3, 131.5, 130.2, 129.3, 128.8, 128.7, 128.6, 128.5, 128.4, 127.7, 127.5, 126.9, 126.4, 124.4, 120.0. M P: 231.5-232.5 °C. HRMS (ACPI): m/z $[M + H]^+$ calcd for $C_{33}H_{25}NO$: 452.2009; found: 452.2017.

Product 28 (unknown compound)



To an over dried bottle equipped with a magnetic stir bar, **1a** (18.6 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3l** (250 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) were added. Then, m-xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 °C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) directly to give the desired product **28** in 63% isolated yield (59.5 mg) as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 7.51 (d, *J* = 7.9 Hz, 2H), 7.44 – 7.38 (m, 4H), 7.37 – 7.30 (m, 4H), 7.26 – 7.20 (m, 8H), 7.17 (d, *J* = 7.1 Hz, 2H), 7.11 – 7.04 (m, 2H), 6.86 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.81 (dd, *J* = 11.7, 1.7 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) = 168.2, 159.2 (d, *J* = 246 Hz), 143.1, 141.9 (d, *J* = 7.5 Hz), 141.2, 138.0, 137.5, 137.4, 135.1, 130.1, 130.0 (d, *J* = 4.5 Hz), 129.2, 128.9 (d, *J* = 3.0 Hz), 128.8, 128.70, 128.68, 128.6, 128.4, 128.1 (d, *J* = 13.5 Hz), 128.0, 127.8, 127.1 (d, *J* = 1.5 Hz), 124.5, 120.0, 118.6 (d, *J* = 24.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -118.2. M P: 229.5-230.5 °C. HRMS (ACPI): m/z $[M + H]^+$ calcd for $C_{33}H_{24}FNO$: 470.1915; found: 470.1908.

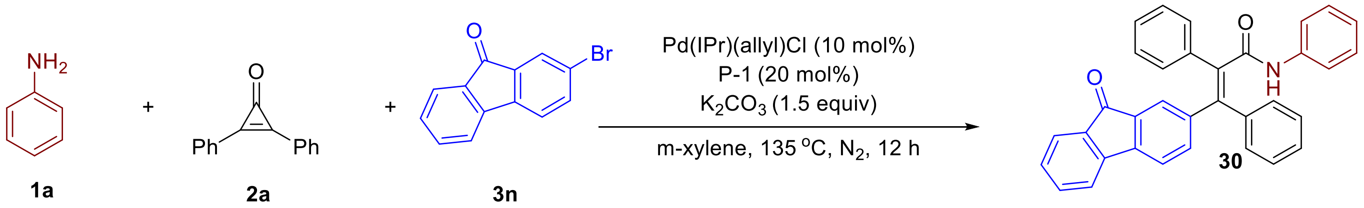
Product 29 (unknown compound)



To an over dried bottle equipped with a magnetic stir bar, **1a** (18.6 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3m** (206 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) were added. Then, m-xylene (1.5 mL) was added to the bottle in glovebox.

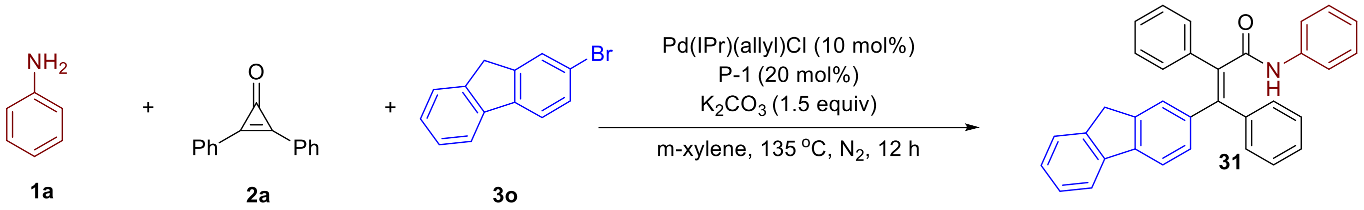
Then the mixture was stirred at 135 °C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) directly to give the desired product **29** in 69% isolated yield (59.1 mg) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.74 (d, *J* = 8.0 Hz, 1H), 7.64 – 7.55 (t, *J* = 9.7 Hz, 2H), 7.50 (s, 1H), 7.46 – 7.37 (m, 4H), 7.35 – 7.28 (m, 3H), 7.25 – 7.20 (m, 4H), 7.20 – 7.09 (m, 7H), 7.06 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 168.6, 144.5, 141.9, 138.5, 137.88, 137.6, 137.5, 132.9, 132.6, 130.7, 130.3, 129.4, 128.8, 128.6, 128.6, 128.5, 128.4, 128.1, 127.7, 127.5, 127.3, 126.4, 126.1, 124.4, 120.0. M P: 145.5-146.5 °C. HRMS (ACPI): m/z $[M + H]^+$ calcd for $C_{31}H_{23}NO$: 426.1852; found: 426.1847.

Product 30 (unknown compound)



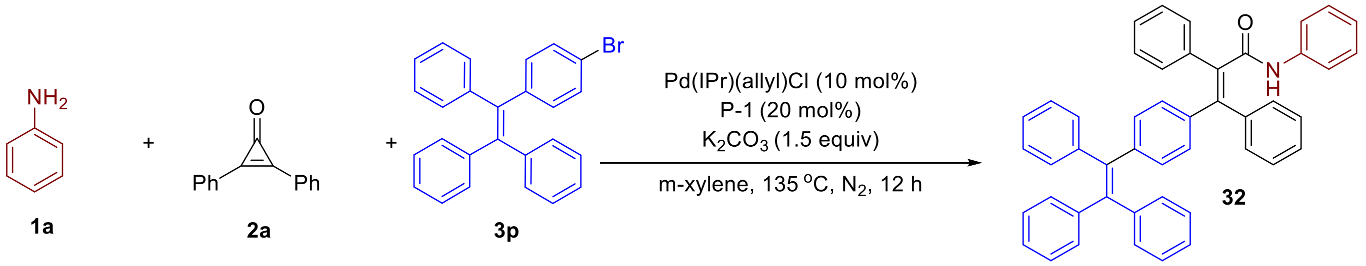
To an over dried bottle equipped with a magnetic stir bar, **1a** (18.6 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3n** (258 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) were added. Then, m-xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 °C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) directly to give the desired product **30** in 44% isolated yield (41.7 mg) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.58 (d, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 5.4 Hz, 2H), 7.37 (d, *J* = 5.0 Hz, 2H), 7.32 (t, *J* = 6.4 Hz, 4H), 7.27 – 7.10 (m, 12H), 7.05 (t, *J* = 7.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 193.4, 168.1, 143.9, 143.5, 143.4, 142.2, 140.9, 138.0, 137.5, 137.4, 137.3, 134.8, 134.4, 134.0, 130.1, 129.2, 129.2, 128.8, 128.7, 128.6, 128.0, 126.8, 124.5, 124.4, 120.4, 120.0, 119.8, 97.6. M P: 227.5-228.5 °C. HRMS (ACPI): m/z $[M + H]^+$ calcd for $C_{34}H_{23}NO_2$: 478.1802; found: 478.1810.

Product 31 (unknown compound)



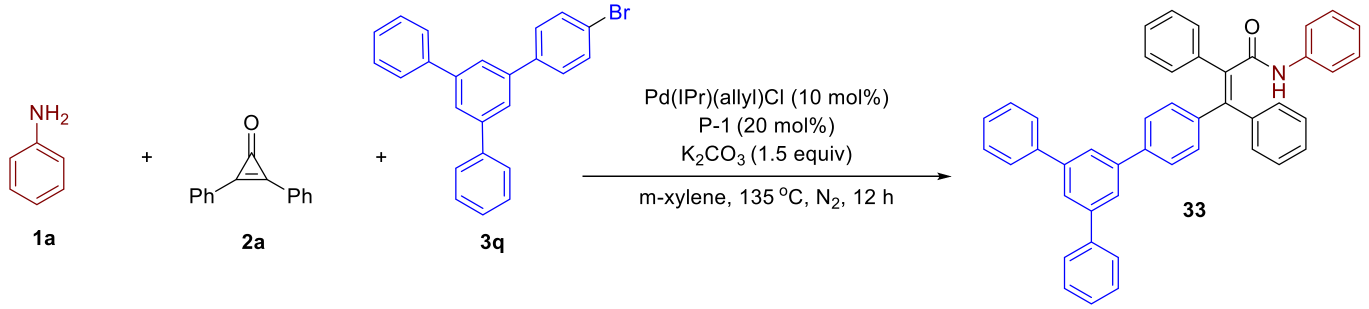
To an over dried bottle equipped with a magnetic stir bar, **1a** (18.6 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3o** (244 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) were added. Then, m-xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 °C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) directly to give the desired product **31** in (30.8 mg) 33% isolated yield as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.71 (d, *J* = 7.5 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.49 (d, *J* = 7.4 Hz, 1H), 7.42 (d, *J* = 7.3 Hz, 2H), 7.37 – 7.30 (m, 4H), 7.27 – 7.15 (m, 11H), 7.11 (s, 1H), 7.05 (t, *J* = 8.0 Hz, 2H), 3.73 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 168.7, 145.2, 143.6, 142.9, 142.1, 141.3, 141.2, 139.5, 138.3, 137.7, 137.2, 130.3, 130.0, 129.4, 128.8, 128.6, 128.5, 128.4, 127.7, 127.6, 127.0, 126.8, 125.0, 124.4, 120.0, 119.3, 36.8. M P: 237.5-238.5 °C. HRMS (ACPI): m/z $[M + H]^+$ calcd for $C_{34}H_{25}NO$: 464.2009; found: 464.2018.

Product 32 (unknown compound)



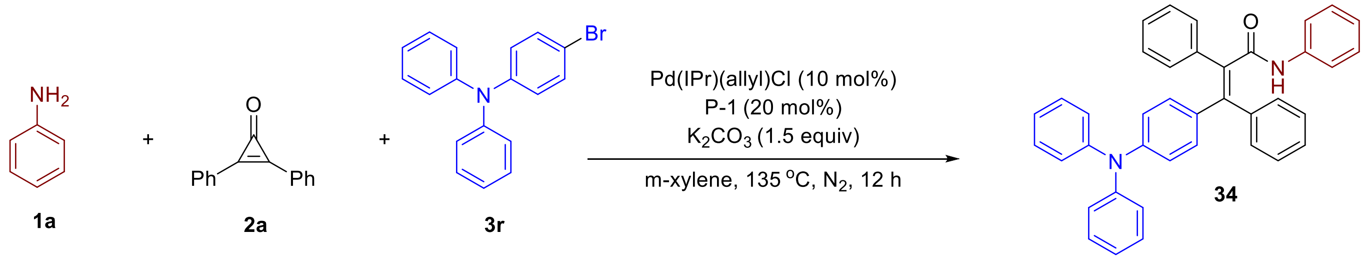
To an over dried bottle equipped with a magnetic stir bar, **1a** (18.6 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3p** (410 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) were added. Then, m-xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 °C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) directly to give the desired product **32** in 68% isolated yield (85.6 mg) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) = 10.09 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.18 (m, 10H), 7.18 – 7.04 (m, 11H), 7.02 – 6.90 (m, 7H), 6.80 (s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) = 168.1, 143.0, 142.9, 142.7, 142.1, 141.4, 140.8, 140.6, 140.1, 139.1, 138.7, 137.6, 137.3, 130.6, (overlap) 130.5, 130.2, 129.8, 129.2, 128.9, 128.4, 127.9, 127.9, 127.8, 127.7, 127.7, 127.6, 127.2, 126.6, 126.5, 123.4, 119.6 (overlap). M P: 259.5-260.5 °C. HRMS (ACPI): m/z $[M + H]^+$ calcd for $C_{47}H_{35}NO$: 630.2791; found: 630.2801.

Product 33 (unknown compound)



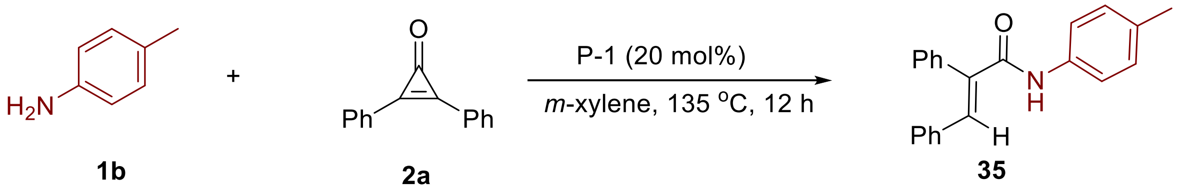
To an over dried bottle equipped with a magnetic stir bar, **1a** (18.6 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3q** (384 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol)were added. Then, m-Xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 ^{o}C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) directly to give the desired product **33** in (65.2 mg) 54% isolated yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.75 (d, *J* = 9.9 Hz, 3H), 7.68 (d, *J* = 7.6 Hz, 4H), 7.53 – 7.40 (m, 9H), 7.40 – 7.28 (m, 5H), 7.20 (dd, *J* = 17.2, 7.8 Hz, 7H), 7.12 (d, *J* = 8.0 Hz, 3H), 7.06 (t, *J* = 7.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 168.5, 144.3, 142.4, 141.8, 141.4, 141.0, 140.2, 140.1, 138.0, 137.6, 137.5, 131.6, 130.3, 129.4, 128.8, 128.8, 128.7, 128.5, 128.5, 127.7, 127.6, 127.3, 126.7, 125.4, 124.9, 124.5, 120.0. M P: 245.5-246.5 ^{o}C. HRMS (ACPI): m/z [M + H]$^+$ calcd for $C_{45}H_{33}NO$: 604.2635; found: 604.2644.

Product 34 (unknown compound)



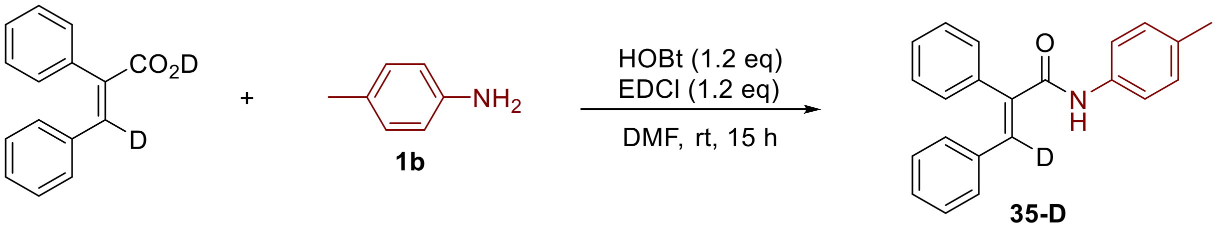
To an over dried bottle equipped with a magnetic stir bar, **1a** (18.6 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3r** (232 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) were added. Then, m-xylene (1.5 mL) was added to the bottle in glovebox. Then the mixture was stirred at 135 ^{o}C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) directly to give the desired product **34** in 96% isolated yield (104.4 mg) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.41 (d, *J* = 7.0 Hz, 2H), 7.36 – 7.28 (m, 3H), 7.25 – 7.17 (m, 10H), 7.15 (d, *J* = 7.9 Hz, 2H), 7.05 (d, *J* = 8.2 Hz, 6H), 7.00 (d, *J* = 7.6 Hz, 2H), 6.86 – 6.76 (m, 4H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) = ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.7, 147.2, 145.3, 144.8, 141.8, 138.5, 137.6, 136.4, 134.2, 131.9, 130.3, 129.4, 129.2, 128.8, 128.6, 128.4, 128.3, 127.5, 124.8, 124.3, 123.2, 121.7, 119.9. M P: 235.5-236.5 °C. HRMS (ACPI): m/z [M + H]$^+$ calcd for $C_{39}H_{30}N_2O$: 543.2431; found: 543.2436.

Product 35 (known compound, CAS: 344877-32-3)[5]



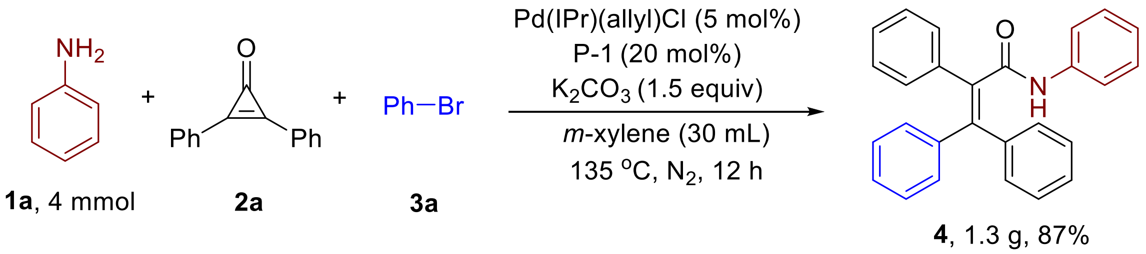
1b (21.4 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol) and **P-1** (12.2 mg, 0.04 mmol) were dissolved in *m*-xylene (1.5 mL) in the glovebox. Then the mixture was stirred at 135 °C for 12 h, as monitored by TLC analysis. The product was purified by flash chromatography on silica gel directly to give compound **35** in 97% yield (61.4 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm) = 7.96 (s, 1H), 7.49 (d, *J* = 7.4 Hz, 3H), 7.36 – 7.30 (m, 4H), 7.19 – 7.13 (m, 4H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 7.4 Hz, 2H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) = 164.8, 138.0, 135.8, 135.2, 134.8, 134.6, 134.1, 130.4, 130.0, 129.8, 129.4, 128.9, 128.7, 128.2, 119.9, 20.8.

Product 35-D



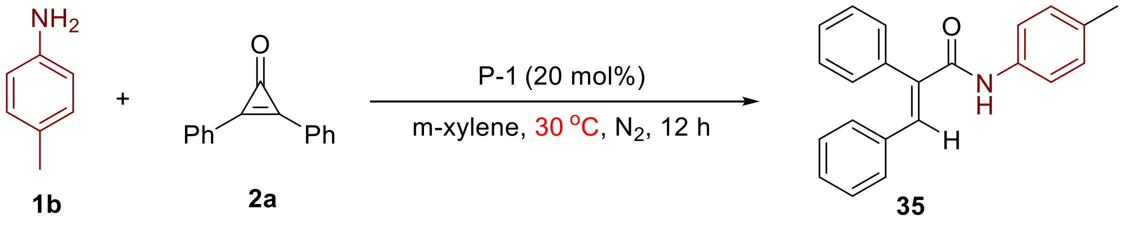
Add EDCl (230 mg, 1.2 mmol) in portions to a cool mixture at 0 ℃ of **B** (226.1 mg, 1 mmol), **1b** (214.3 mg, 2 mmol) and HOBt (162.1 mg, 1.2 mmol) in DMF (3 mL) under a dry, inert atmosphere. The mixture was stirred overnight at room temperature and concentrate under reduced pressure. After completion, the mixture was extracted with H_2O (6 mL) and EtOAc (10 mLx3), dried with anhydrous Na_2SO_4 and filtered. The collected filtrate was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography to obtain a product **35-D** (227 mg, 72 % yield, white solid). ^{1}H NMR (500 MHz, CDCl$_3$) δ (ppm) =7.95 (s, 2H), 7.48 (d, *J* = 7.3 Hz, 3H), 7.37 – 7.29 (m, 4H), 7.21 – 7.11 (m, 4H), 7.07 (d, *J* = 8.3 Hz, 2H), 7.01 (d, *J* = 7.1 Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) = 164.8, 137.6, 135.8, 135.2, 134.7, 134.5, 134.0, 130.4, 129.9, 129.8, 129.3, 128.8, 128.7, 128.2, 119.9, 20.8.

5. Large scale synthesis of 4

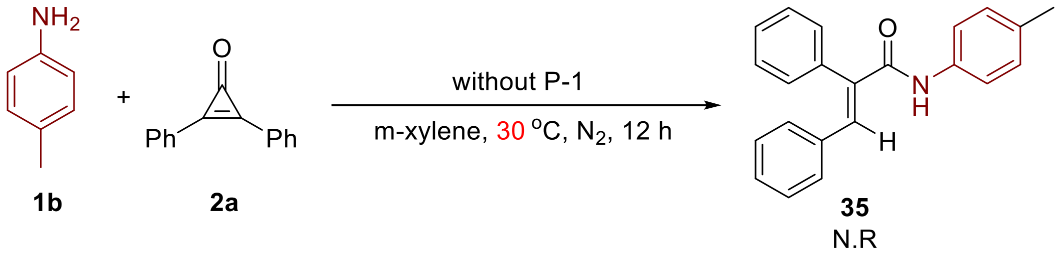


Under N_2 condition, **1a** (0.37 g, 4 mmol), **2a** (1.24 g, 6 mmol), **3a** (3.12 g, 2.1 mL, 20 mmol), P-1 (243.5 mg, 0.8 mmol), Pd(IPr)(allyl)Cl (114 mg, 0.2 mmol) and K_2CO_3 (829.2 mg, 6 mmol), enter were added into a three-necked flask. Then m-xylene (30 mL) was added into the flask. The mixture was stirred at 135 ^{o}C for 12 h. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 6:1) directly to give the desired product in 87% yield (1.3 g).

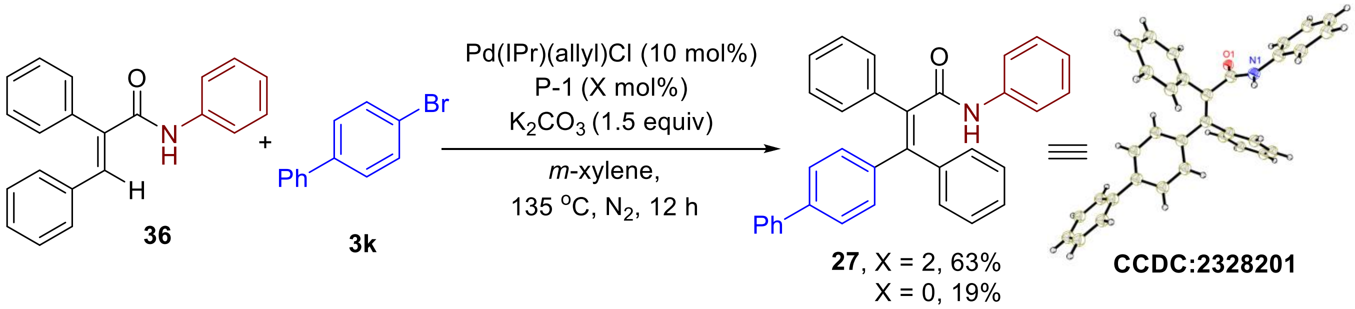
6. Mechanistic studies



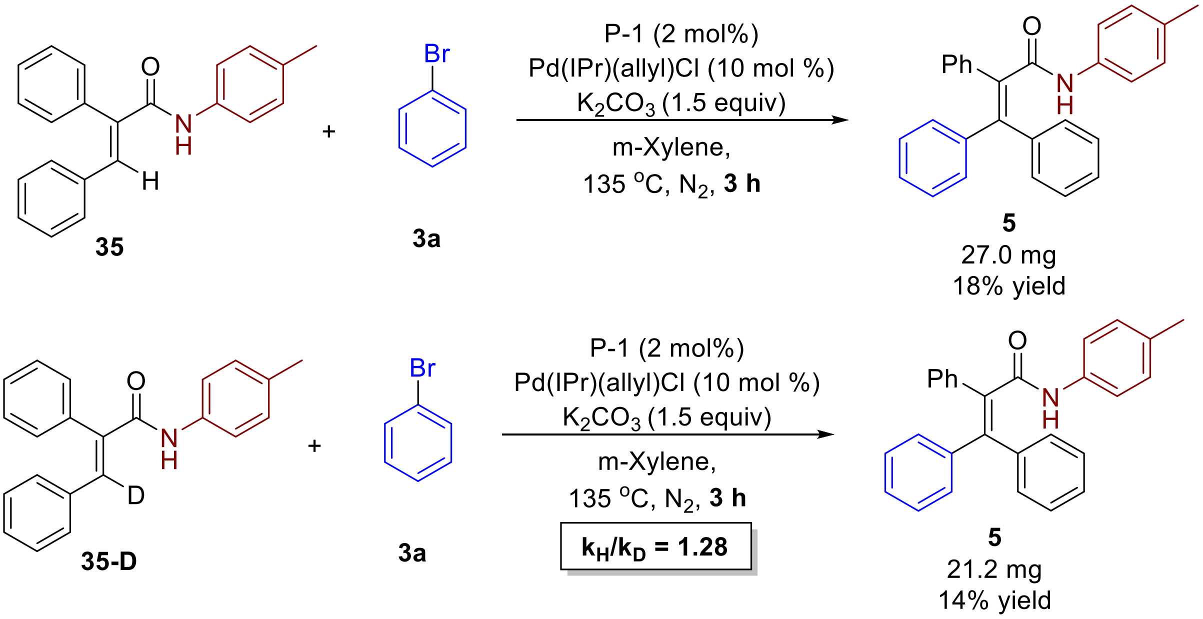
1b (21.4 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol) and **P-1** (12.2 mg, 0.04 mmol) were dissolved in m-xylene (1.5 mL) in the glovebox. Then the mixture was stirred at 30 ^{o}C for 12 h, as monitored by TLC analysis. The product was purified by flash chromatography on silica gel directly to give compound **35** in (59.6 mg) 95% yield.



1b (21.4 mg, 0.2 mmol) and **2a** (61.9 mg, 0.3 mmol) were dissolved in m-xylene (1.5 mL) in the glovebox. Then the mixture was stirred at 30 °C for 12 h. The analysis of the reaction mixture by TLC.



Compound **36** (59.8 mg, 0.2 mmol), **3k** (232 mg, 1 mmol), Pd(IPr)(allyl)Cl (11.4 mg, 0.02 mmol), **P-1** (1.2 mg, 0.004 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) were dissolved in m-xylene (1.5 mL) in the glovebox. Then the mixture was stirred at 135 °C for 12 h, as monitored by TLC analysis. The product was purified by flash chromatography on silica gel directly to give compound **27** in 63% yield (57.2 mg). However, in the absence of **P-1**, only 19% yield of **27** was obtained.



Compound **35** (125.2 mg, 0.4 mmol), **3a** (312 mg, 2 mmol), Pd(IPr)(allyl)Cl (22.9 mg, 0.04 mmol), **P-1** (2.4 mg, 0.008 mmol) and K_2CO_3 (82.9 mg, 0.6 mmol) were dissolved in m-xylene (3 mL) in the glovebox. Then the mixture was stirred at 135 °C for 3 h, as monitored by TLC analysis. The product was purified by flash chromatography on silica gel directly to give compound **5** in 18% yield (27.0 mg).

Compound **35-D** (125.6 mg, 0.4 mmol), **3a** (312 mg, 2 mmol), Pd(IPr)(allyl)Cl (22.9 mg, 0.04 mmol), **P-1** (2.4 mg, 0.008 mmol) and K_2CO_3 (82.9 mg, 0.6 mmol) were dissolved in m-xylene (3 mL) in the glovebox. Then the mixture was stirred at 135 °C for 3 h, as monitored by TLC analysis. The product was purified by flash chromatography on silica gel directly to give compound **5** in 14% yield (21.2 mg).

7. Fluorescent spectra of AIE luminogens

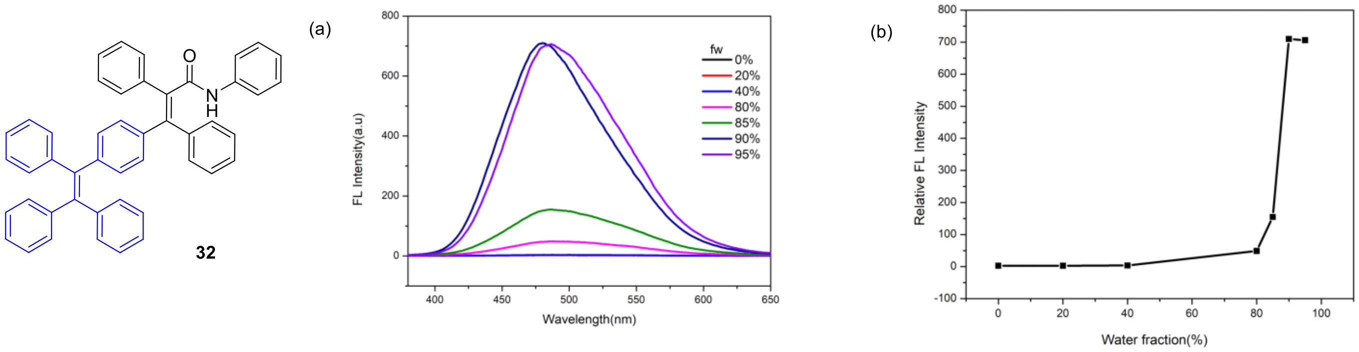

32

Figure 1. AIE effect of **32**. (a) Fluorescent spectra of **32** (10 μM) in tetrahydrofuran with different fractions of water. (b) Fluorescent intensity at 487 nm for **32** with changes of fractions of water. λex = 338 nm.

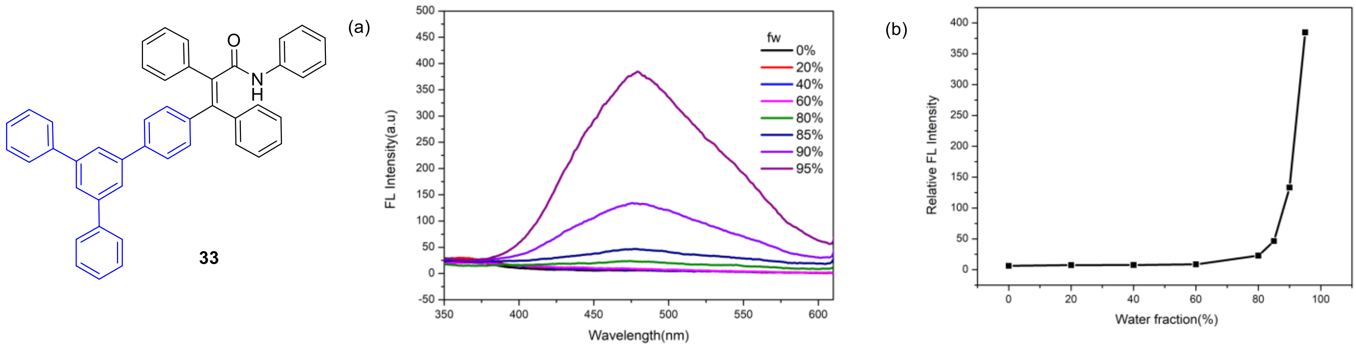

33

Figure 2. AIE effect of **33**. (a) Fluorescent spectra of **33** (10 μM) in tetrahydrofuran with different fractions of water. (b) Fluorescent intensity at 479 nm for **33** with changes of fractions of water. λex = 314 nm.

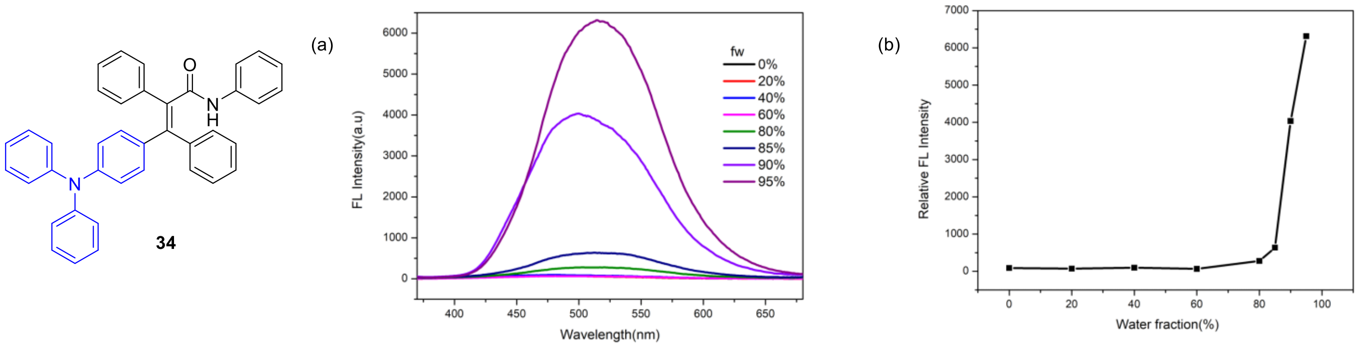
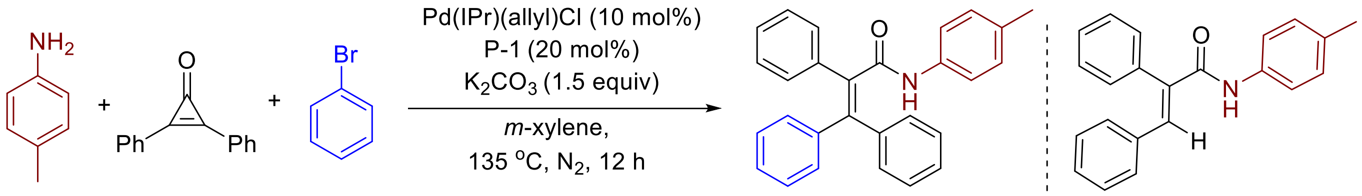
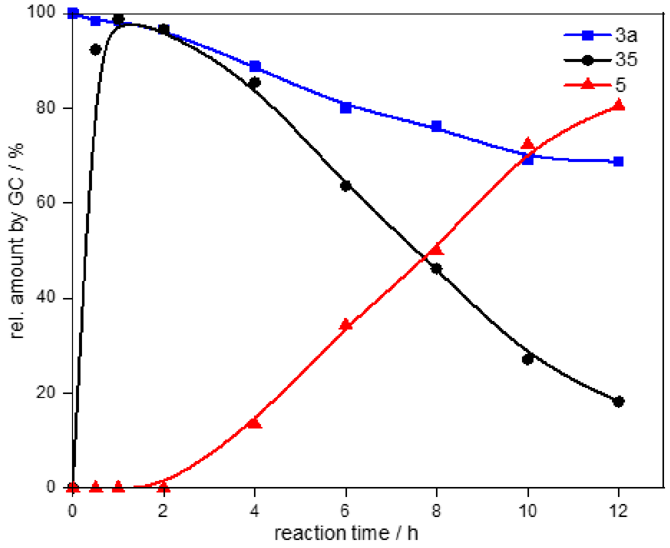

34

Figure 3. AIE effect of **34**. (a) Fluorescent spectra of **34** (10 μM) in tetrahydrofuran with different fractions of water. (b) Fluorescent intensity at 514 nm for **34** with changes of fractions of water. λex = 350 nm.

8. Conversion versus time plots

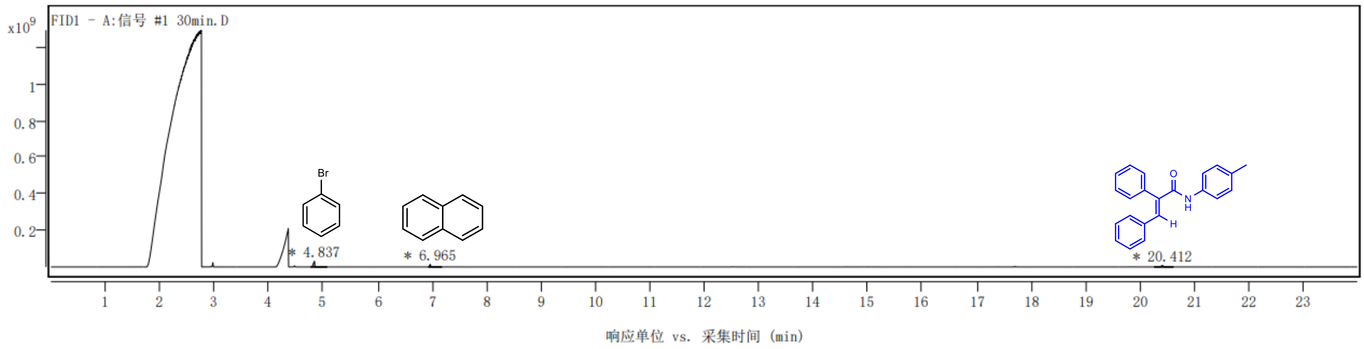


1b **2a** **3a** **5** **35**



1b (21.4 mg, 0.2 mmol), **2a** (61.9 mg, 0.3 mmol), **3a** (156 mg, 1 mmol), P-1 (12.2 mg, 0.04 mmol), Pd(IPr)(allyl)Cl (11 mg, 0.02 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) were added into a drying flask containing a magnetic stir bar. Naphthalene (0.208 mmol, 26.6 mg) was added as an internal standard. Then, m-xylene (1.5 mL) is added to the bottle in the glove box. Then the reaction mixture was stirred at 135 ℃, and analysis by GC tt 0.5h, 1 h, 2h, 4h, 6h, 8h, 10h, 12h.

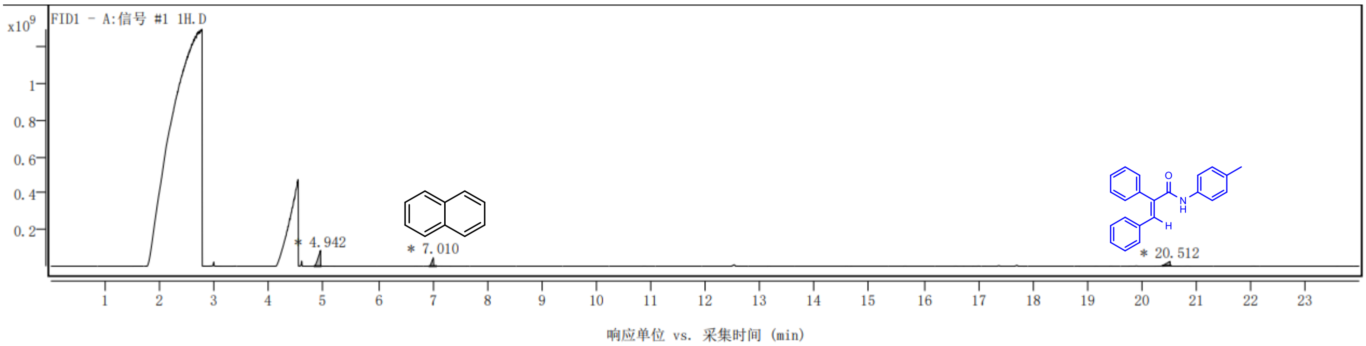
0.5 h (rel. amount by GC/%):**3a** = 98.3, **35** = 92.4, **5** = 0



色谱峰

峰	起始	RT	终止	峰高	面积	面积 %	SNR
1	4. 768	4. 837	5. 074	30869255	56520091	100. 00	
2	6. 928	6. 965	7. 183	14112912	20688735	36. 60	
3	20. 257	20. 412	20. 617	8052293	20360439	36. 02	

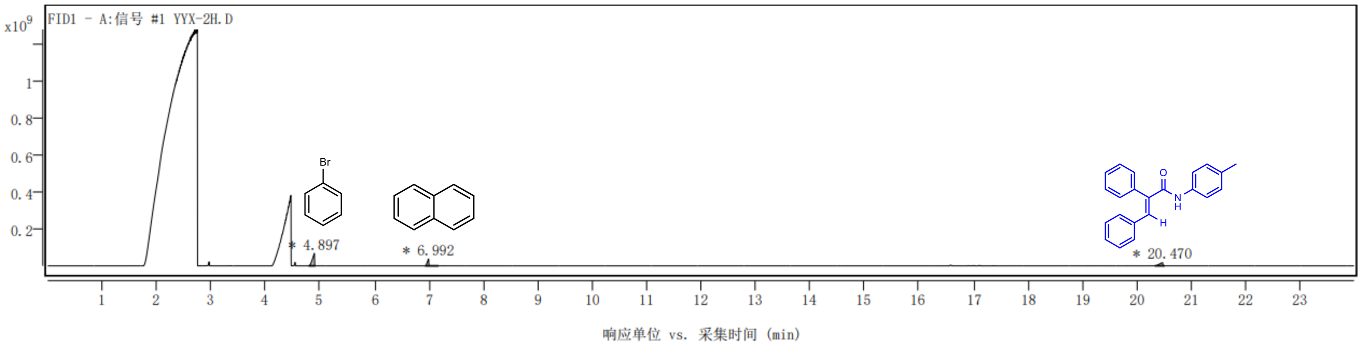
1 h (rel. amount by GC/%) : **3a** = 98.3, **35** = 98.8, **5** = 0



色谱峰

峰	起始	RT	终止	峰高	面积	面积 %	SNR
1	4.820	4.942	4.962	85546659	266916897	100.00	
2	6.928	7.010	7.076	45845403	97607652	36.57	
3	20.365	20.512	20.522	23008238	102754178	38.50	

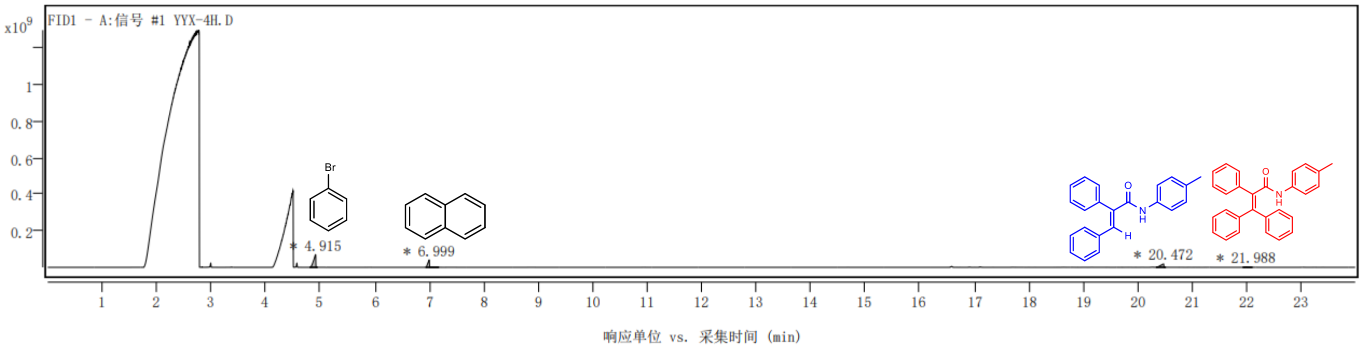
2 h (rel. amount by GC/%) : **3a** = 96.5, **35** = 96.6, **5** = 0



色谱峰

峰	起始	RT	终止	峰高	面积	面积 %	SNR
1	4.795	4.897	4.914	66795443	178762414	100.00	
2	6.932	6.992	7.178	36573444	69317816	38.78	
3	20.331	20.470	20.513	17745001	68670161	38.41	

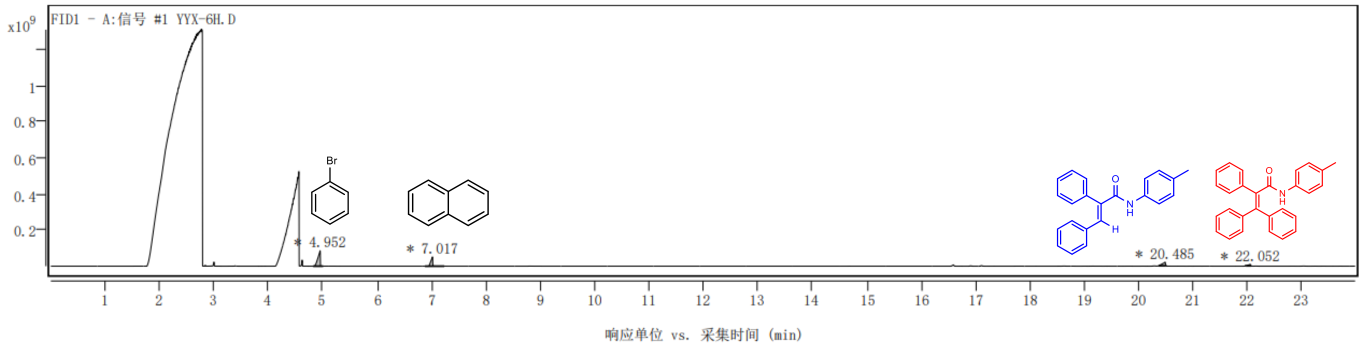
4 h (rel. amount by GC/%): **3a** = 88.8, **35** = 85.4, **5** = 13.5



色谱峰

峰	起始	RT	终止	峰高	面积	面积 %	SNR
1	4.806	4.915	4.953	69426635	194863458	100.00	
2	6.932	6.999	7.182	40561330	82120984	42.14	
3	20.332	20.472	20.517	19037929	71959185	36.93	
4	21.923	21.988	22.107	2256247	6312712	3.24	

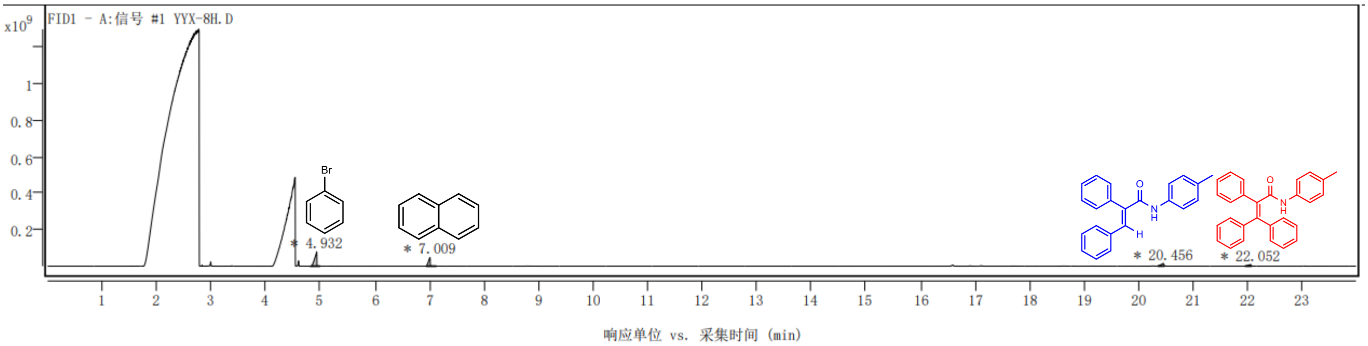
6 h (rel. amount by GC/%): **3a** = 80.1, **35** = 63.6, **5** = 34.3



色谱峰

峰	起始	RT	终止	峰高	面积	面积 %	SNR
1	4.824	4.952	5.006	84880739	254664025	100.00	
2	6.879	7.017	7.234	50835297	118892615	46.69	
3	20.367	20.485	20.501	19669894	77500745	30.43	
4	21.970	22.052	22.069	7980379	23171655	9.10	

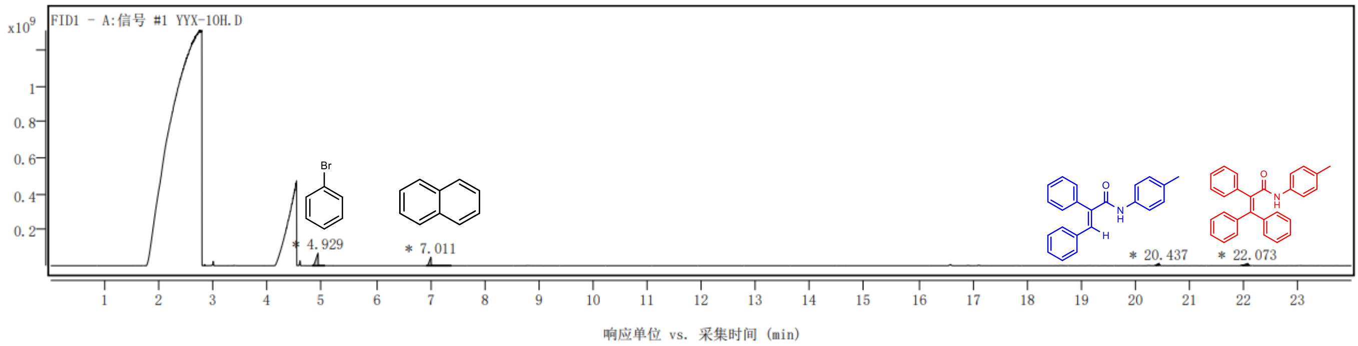
8 h (rel. amount by GC/%): **3a** = 76.2, **35** = 46.2, **5** = 50.0



色谱峰

峰	起始	RT	终止	峰高	面积	面积 %	SNR
1	4.827	4.932	4.996	76558025	214904271	100.00	
2	6.939	7.009	7.127	47091032	105516112	49.10	
3	20.351	20.456	20.475	14696753	50019796	23.28	
4	21.949	22.052	22.077	8692913	30028309	13.97	

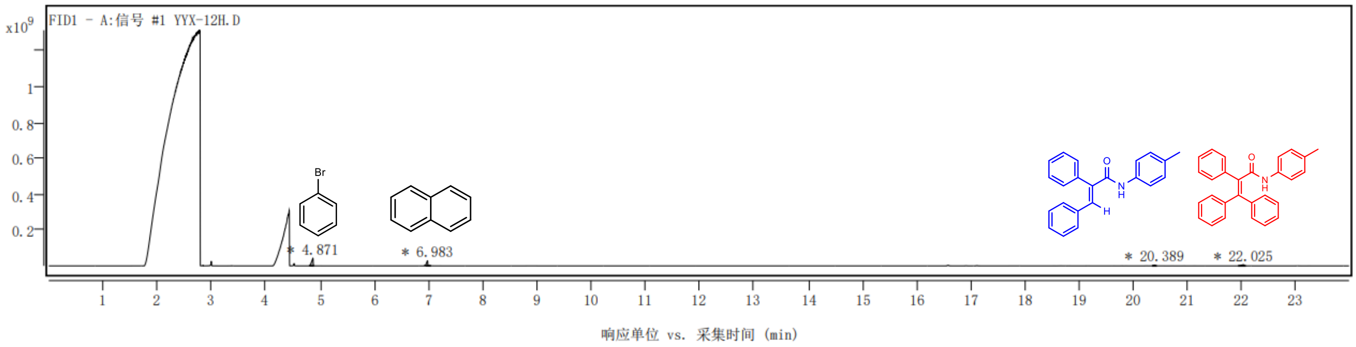
10 h (rel. amount by GC/%): **3a** = 69.1, **35** = 27.1, **5** = 72.4



色谱峰

峰	起始	RT	终止	峰高	面积	面积 %	SNR
1	4.820	4.929	5.057	68501929	190467918	100.00	
2	6.923	7.011	7.390	46918327	103038729	54.10	
3	20.365	20.437	20.452	11028872	28642620	15.04	
4	21.960	22.073	22.097	10868194	42394631	22.26	

12 h (rel. amount by GC/%): **3a** = 68.8, **35** = 18.2, **5** = 80.5

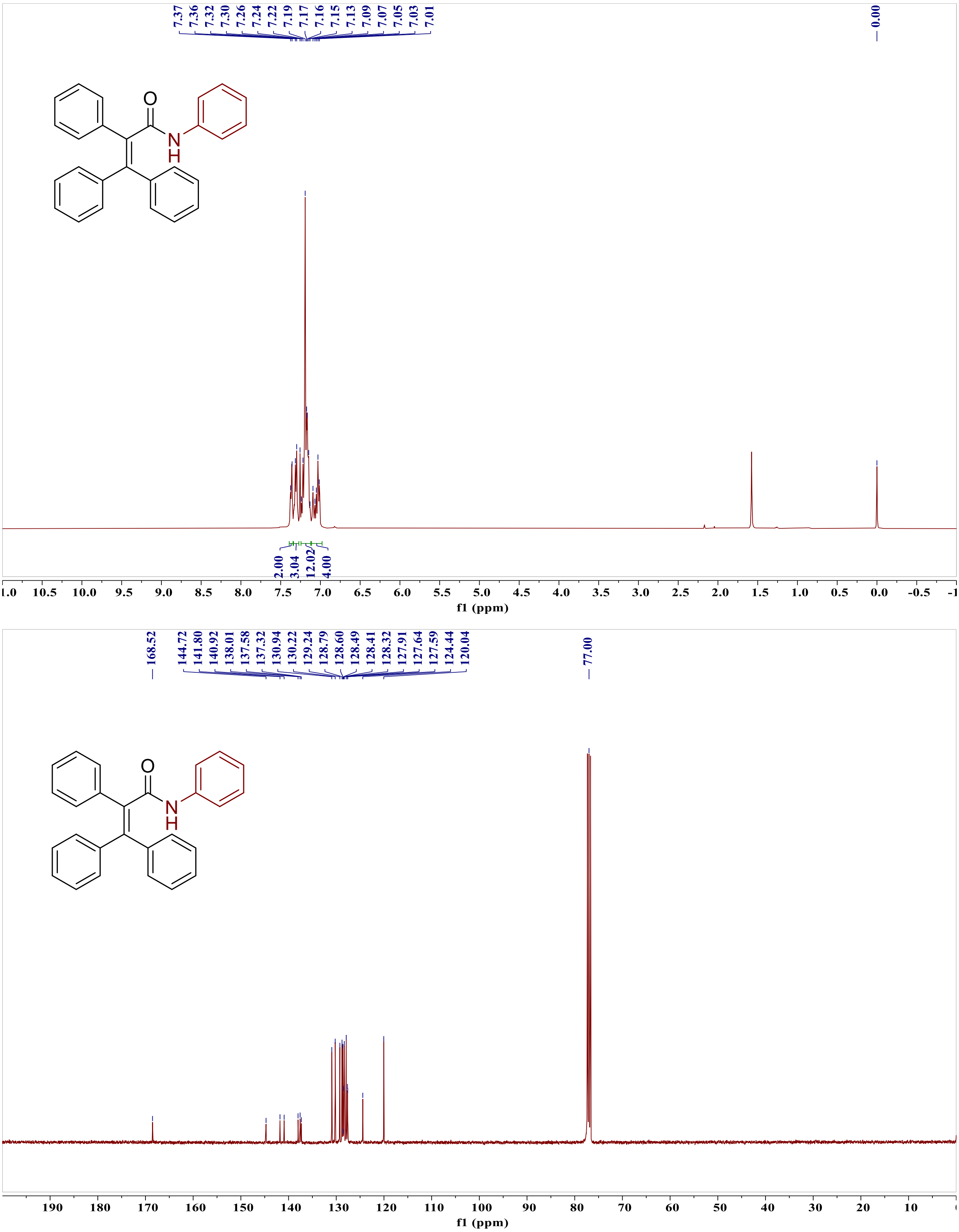


色谱峰

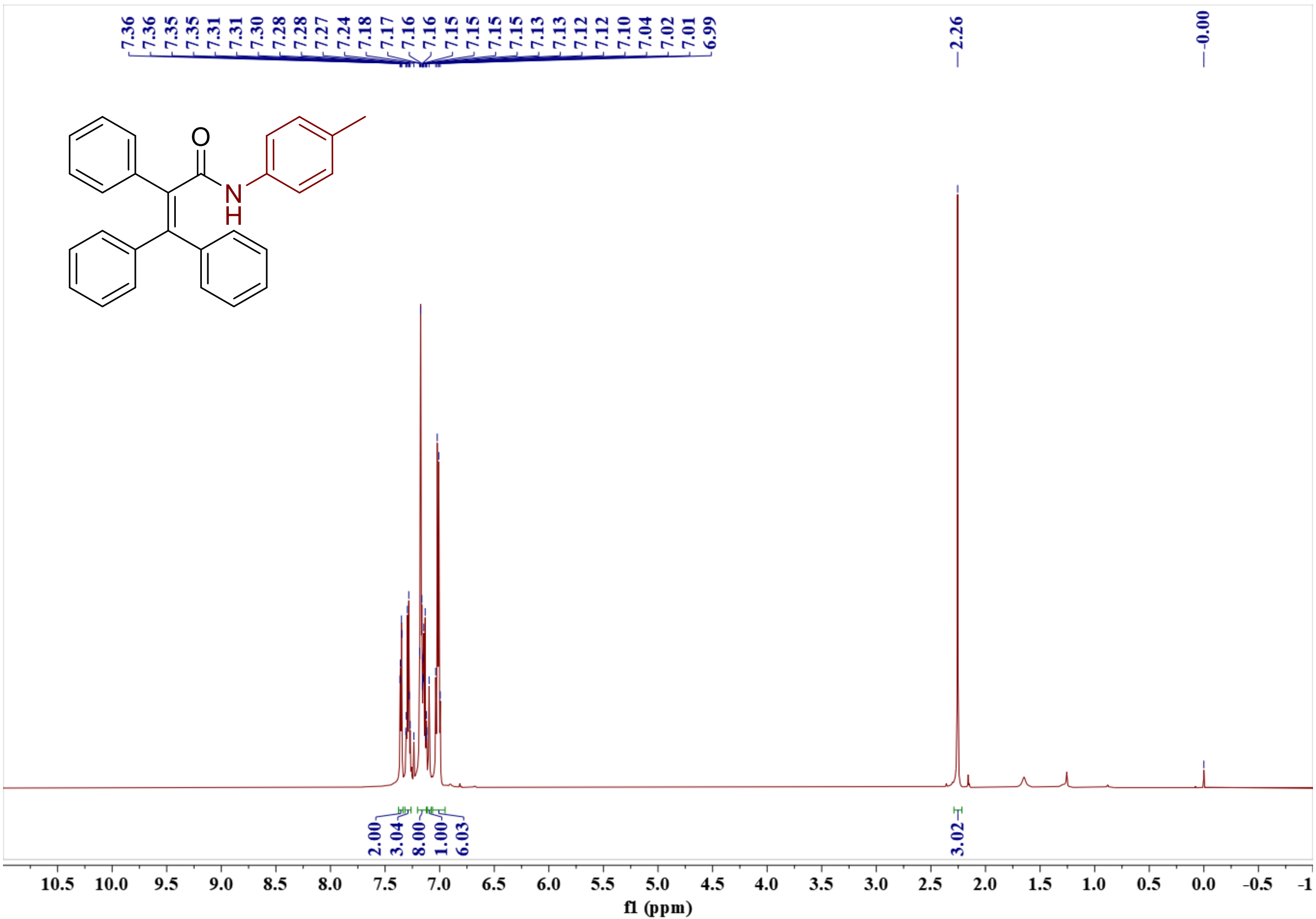
峰	起始	RT	终止	峰高	面积	面积 %	SNR
1	4.803	4.871	4.891	42913863	84996126	100.00	
2	6.935	6.983	7.048	28357557	46228290	54.39	
3	20.342	20.389	20.430	4101929	8648871	10.18	
4	21.928	22.025	22.072	6734312	21148823	24.88	

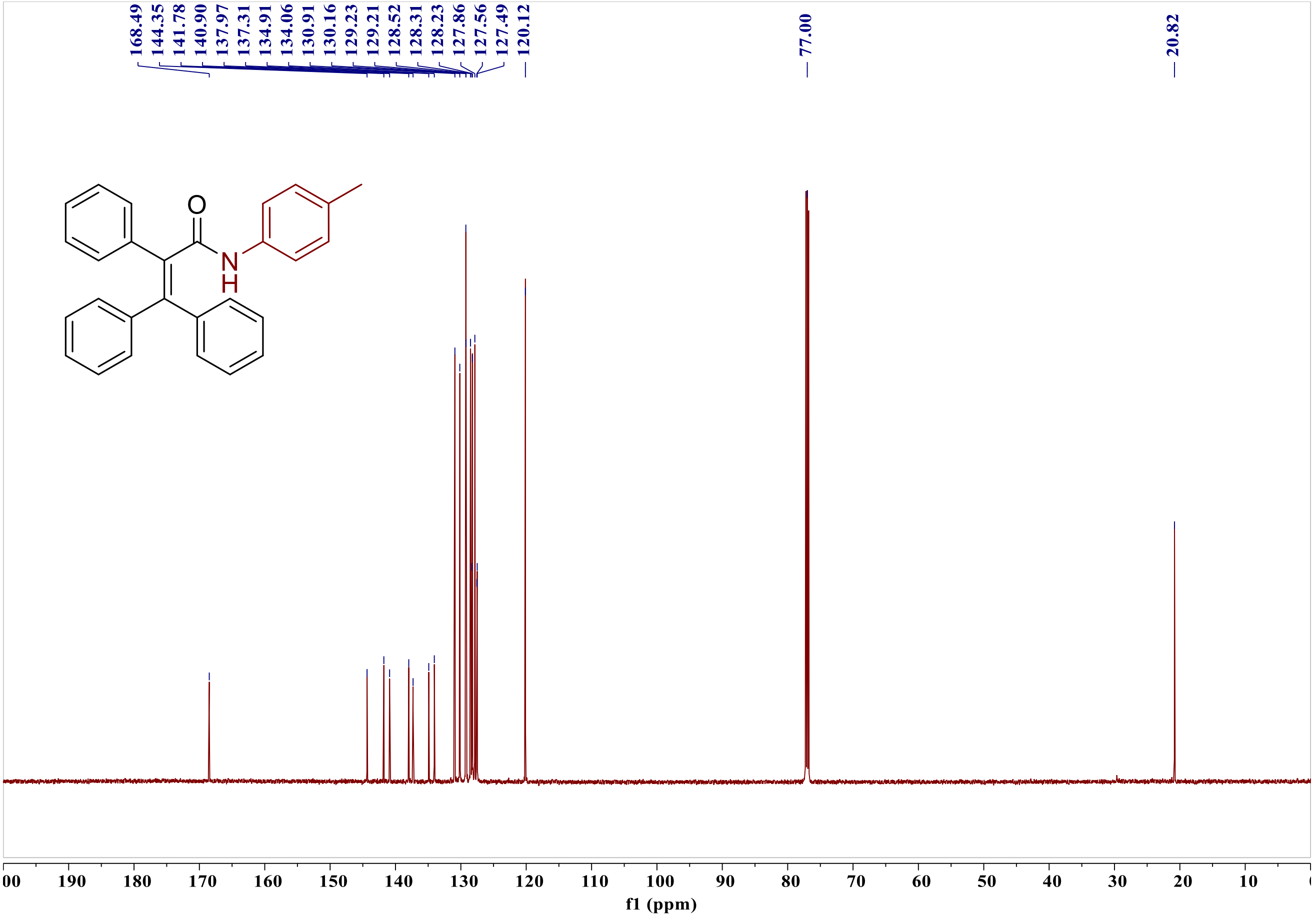
9. The NMR spectra of compounds 4-19 and 18-34

^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C NMR (100 MHz, CDCl$_3$) spectra of product 4

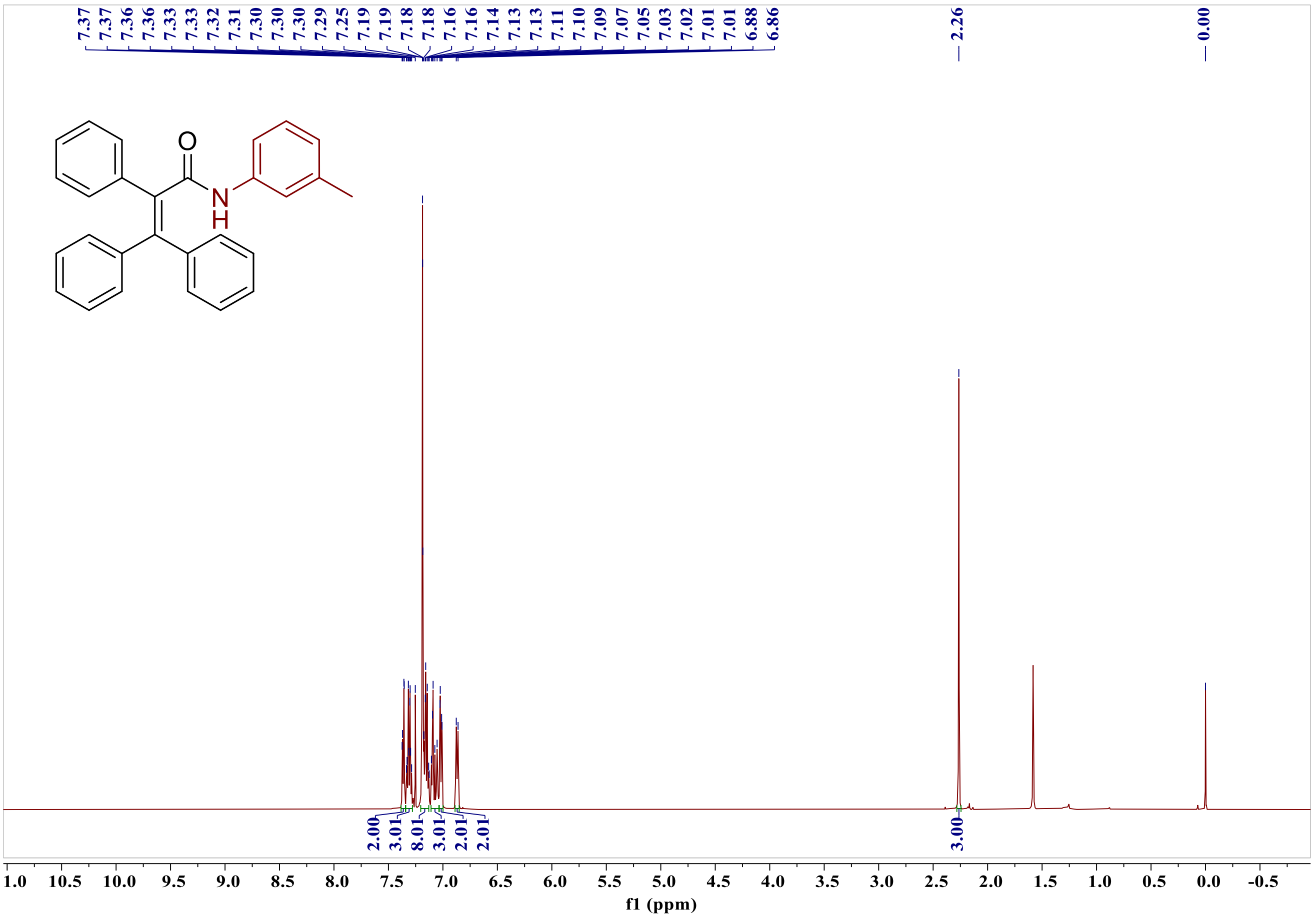


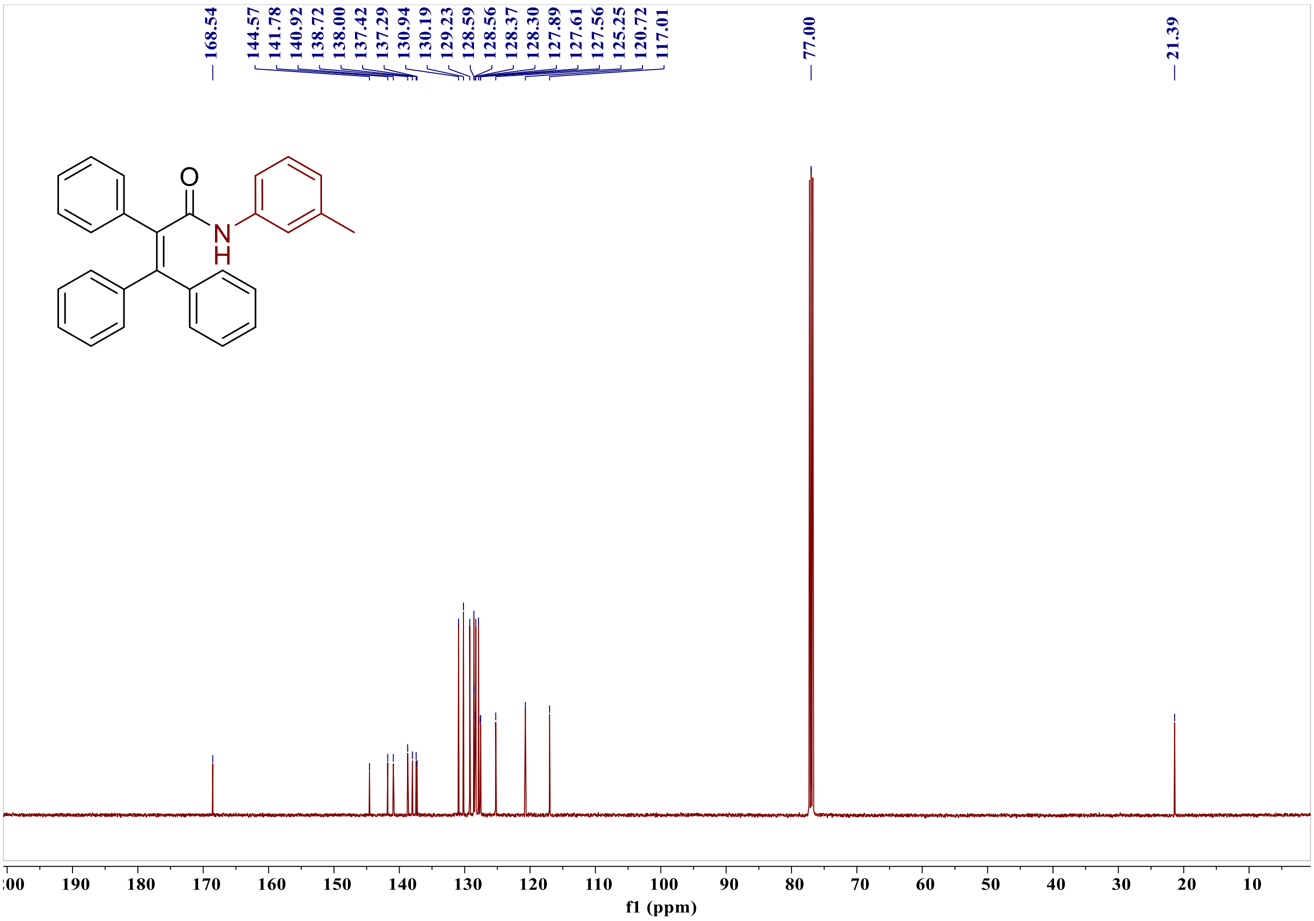
^{1}H NMR (600 MHz, CDCl$_3$) and ^{13}C NMR (150 MHz, CDCl$_3$) spectra of product 5



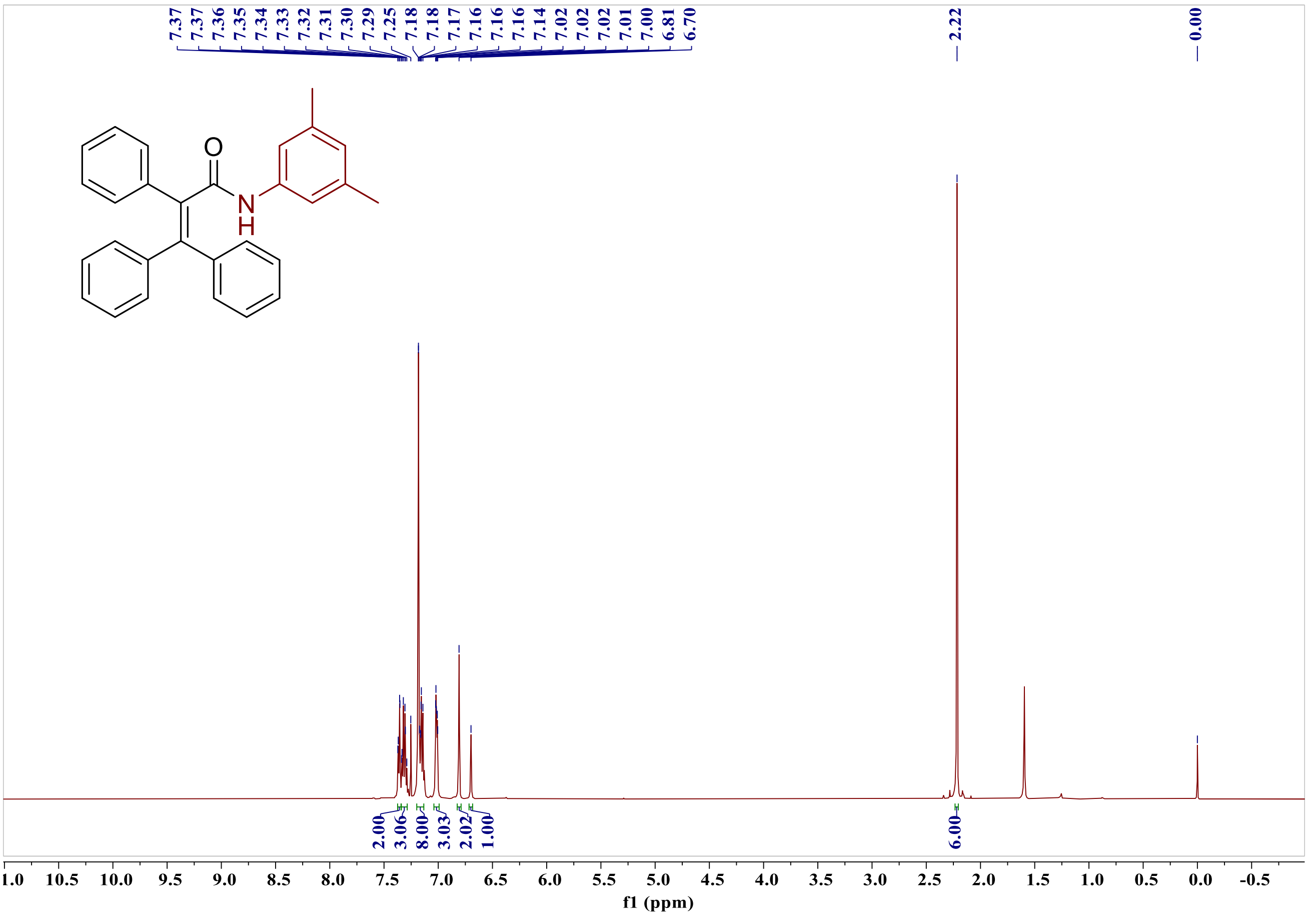


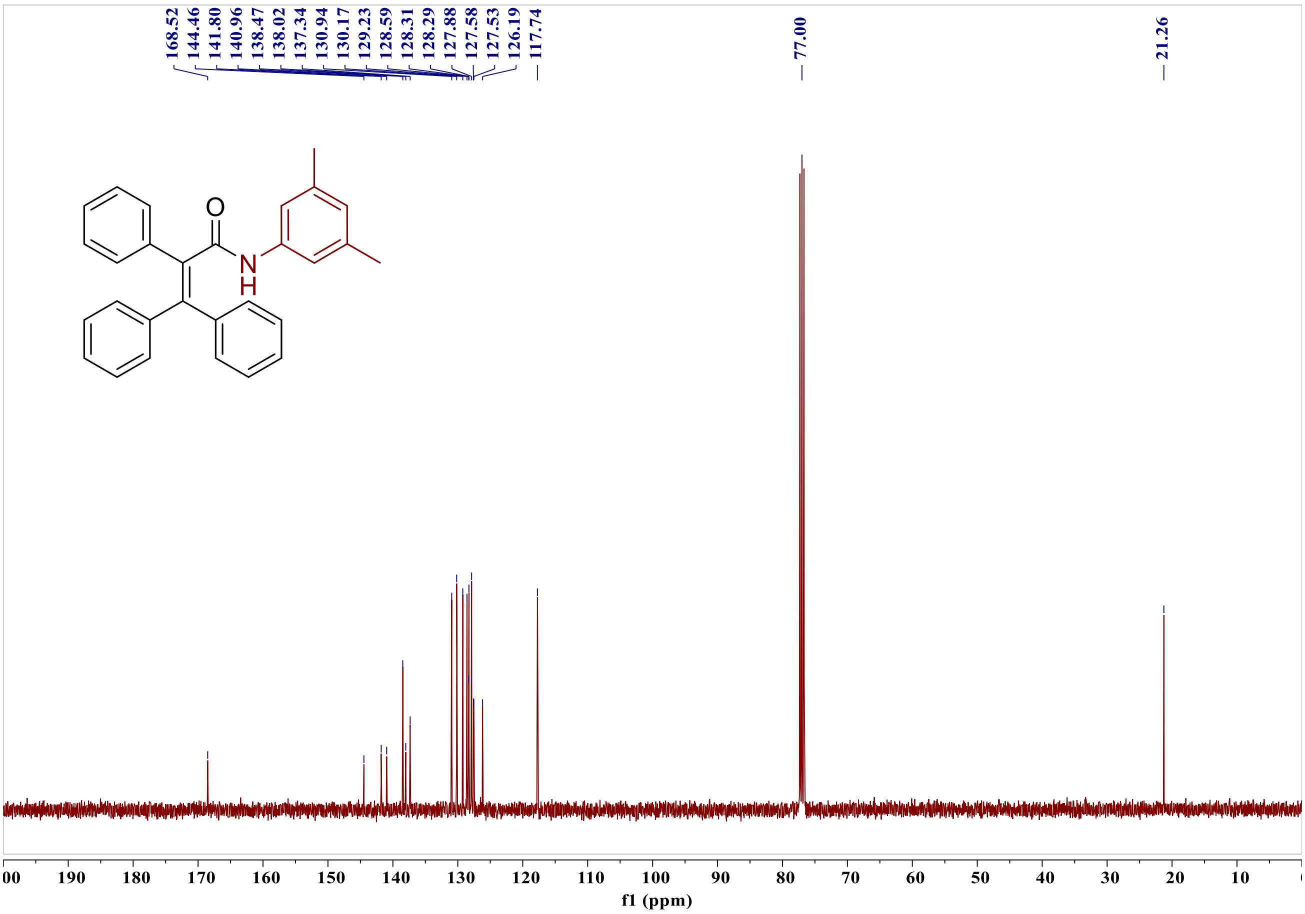
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra of product 6



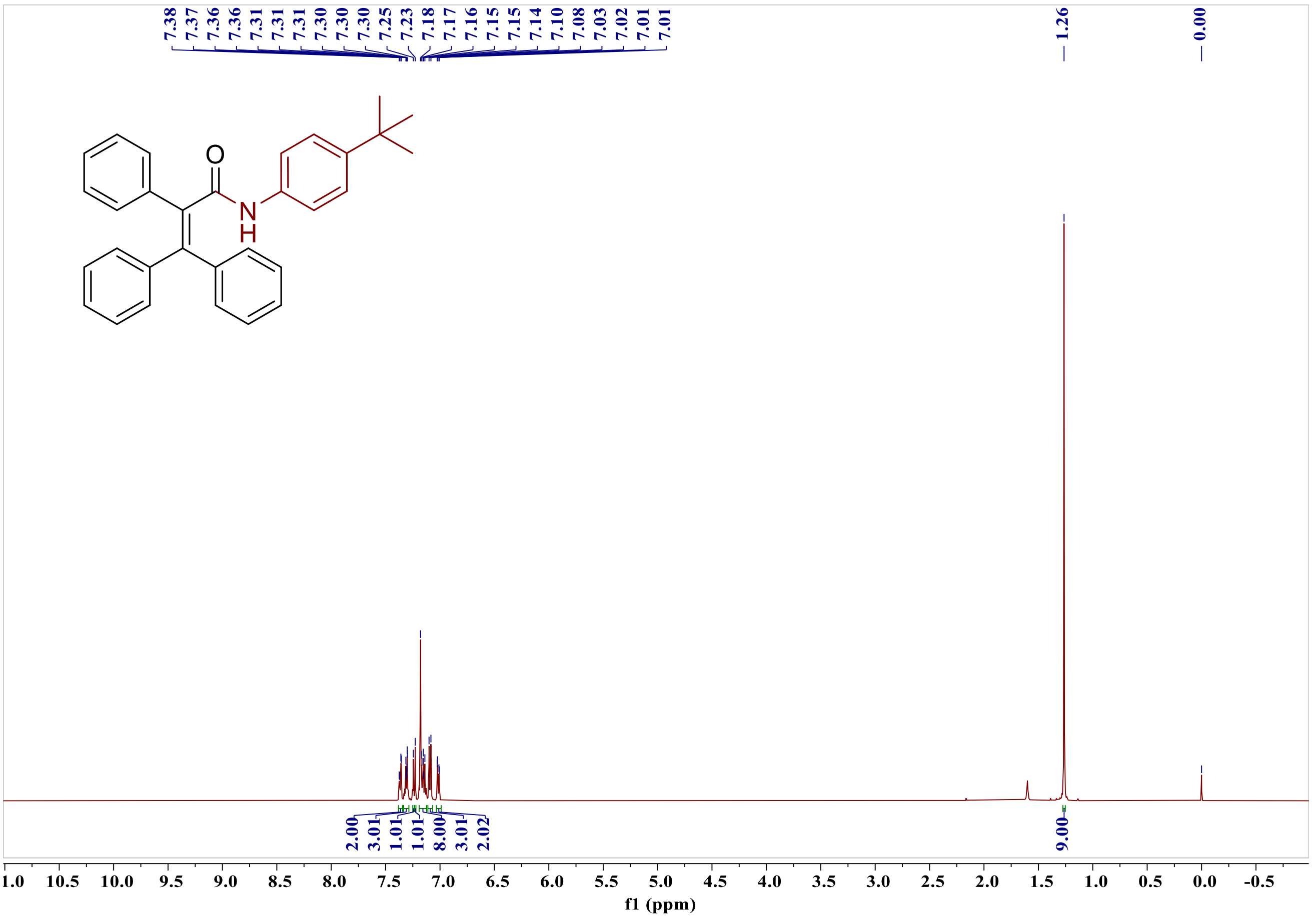


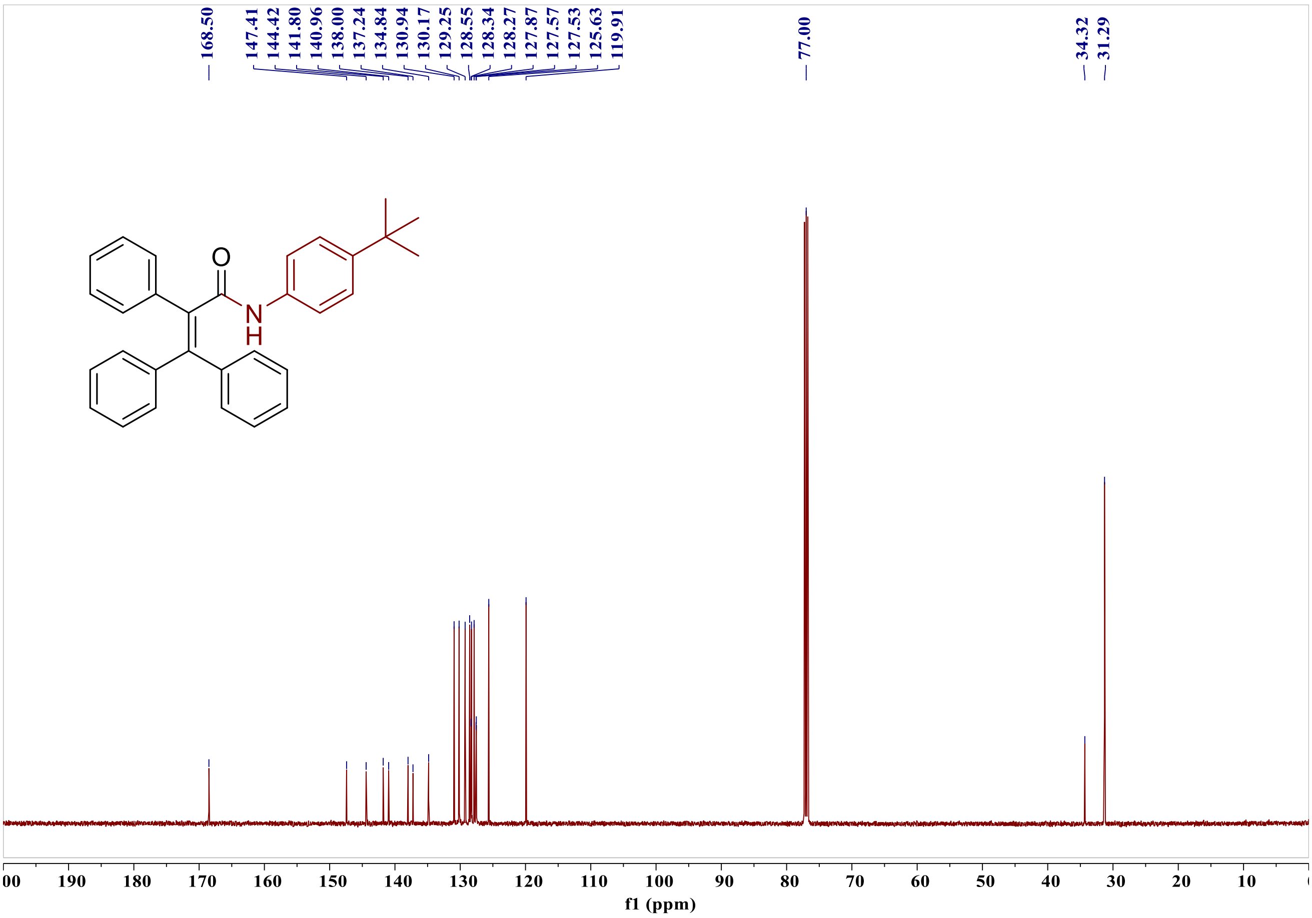
^{1}H NMR (500 MHz, CDCl$_3$) and ^{13}C NMR (100 MHz, CDCl$_3$) spectra of product 7



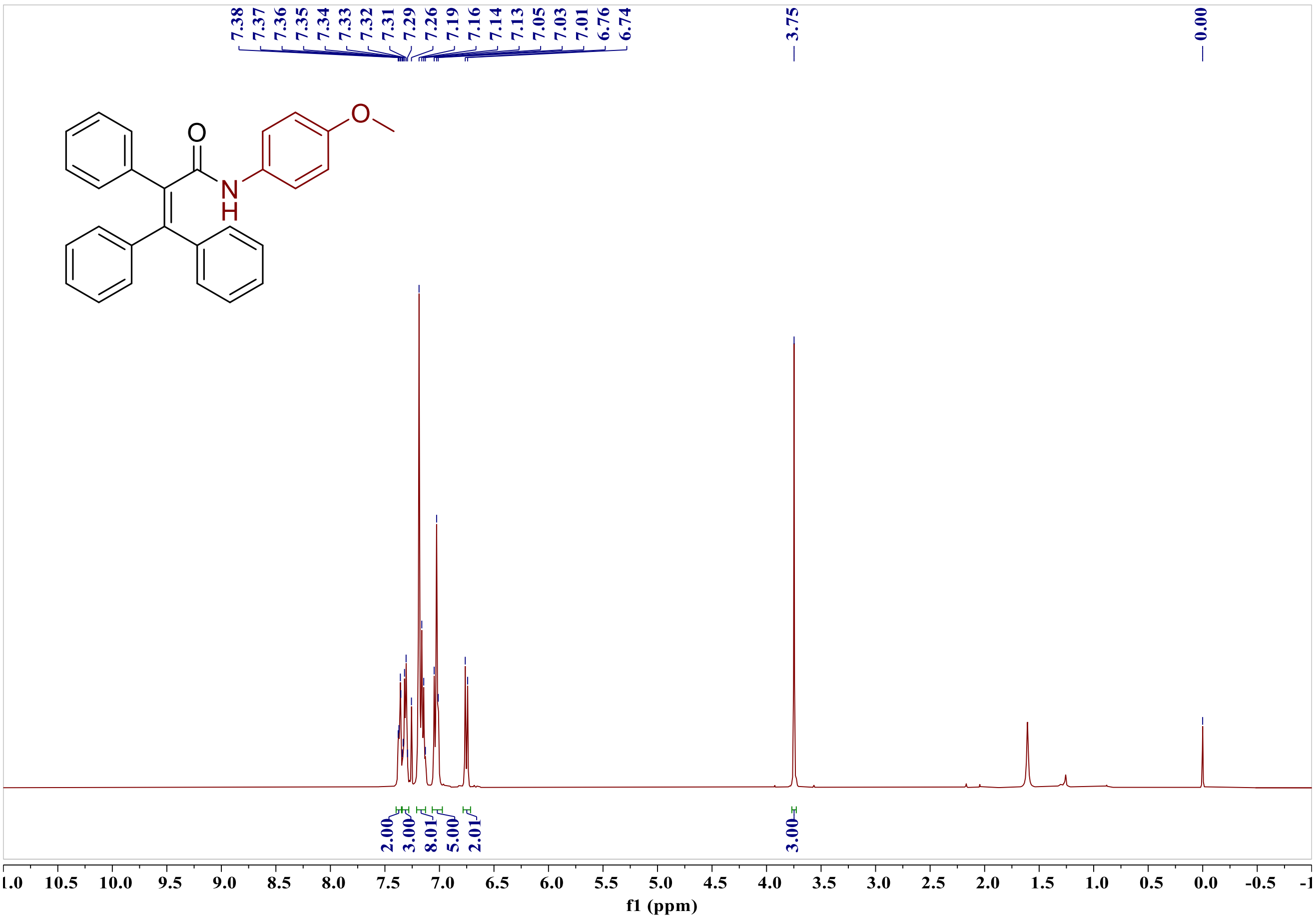


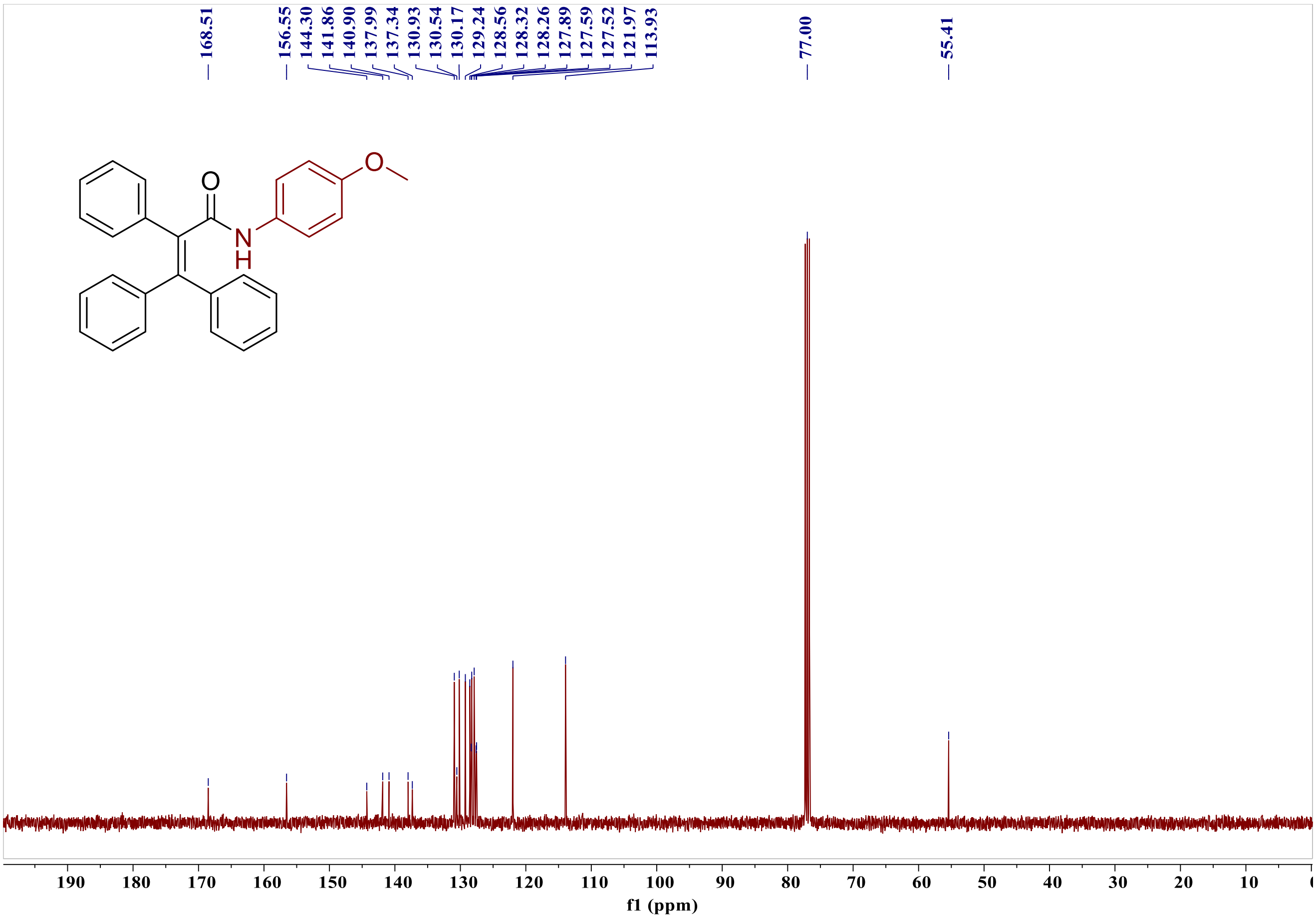
^{1}H NMR (500 MHz, CDCl$_3$) and ^{13}C NMR (125 MHz, CDCl$_3$) spectra of product 8



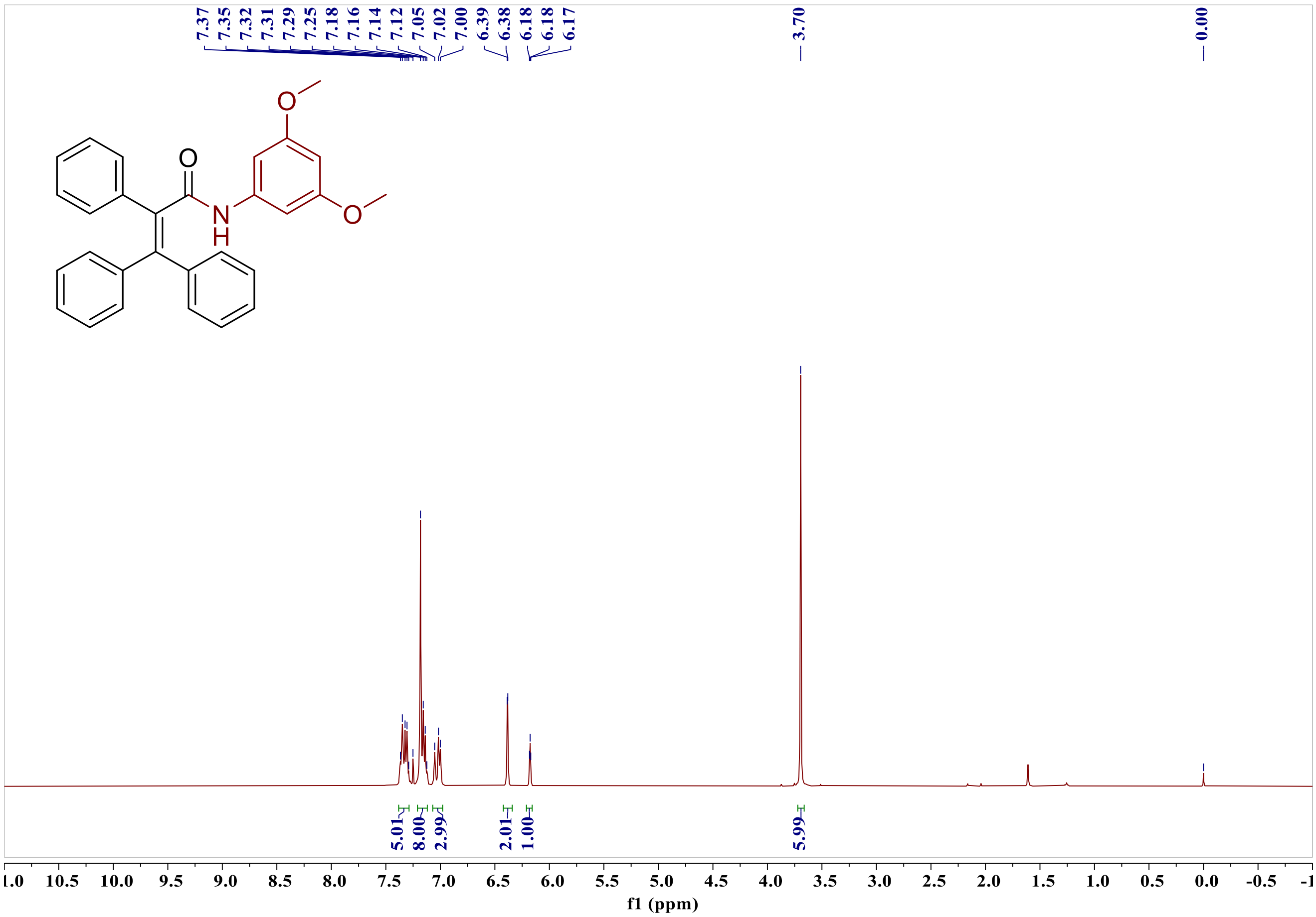


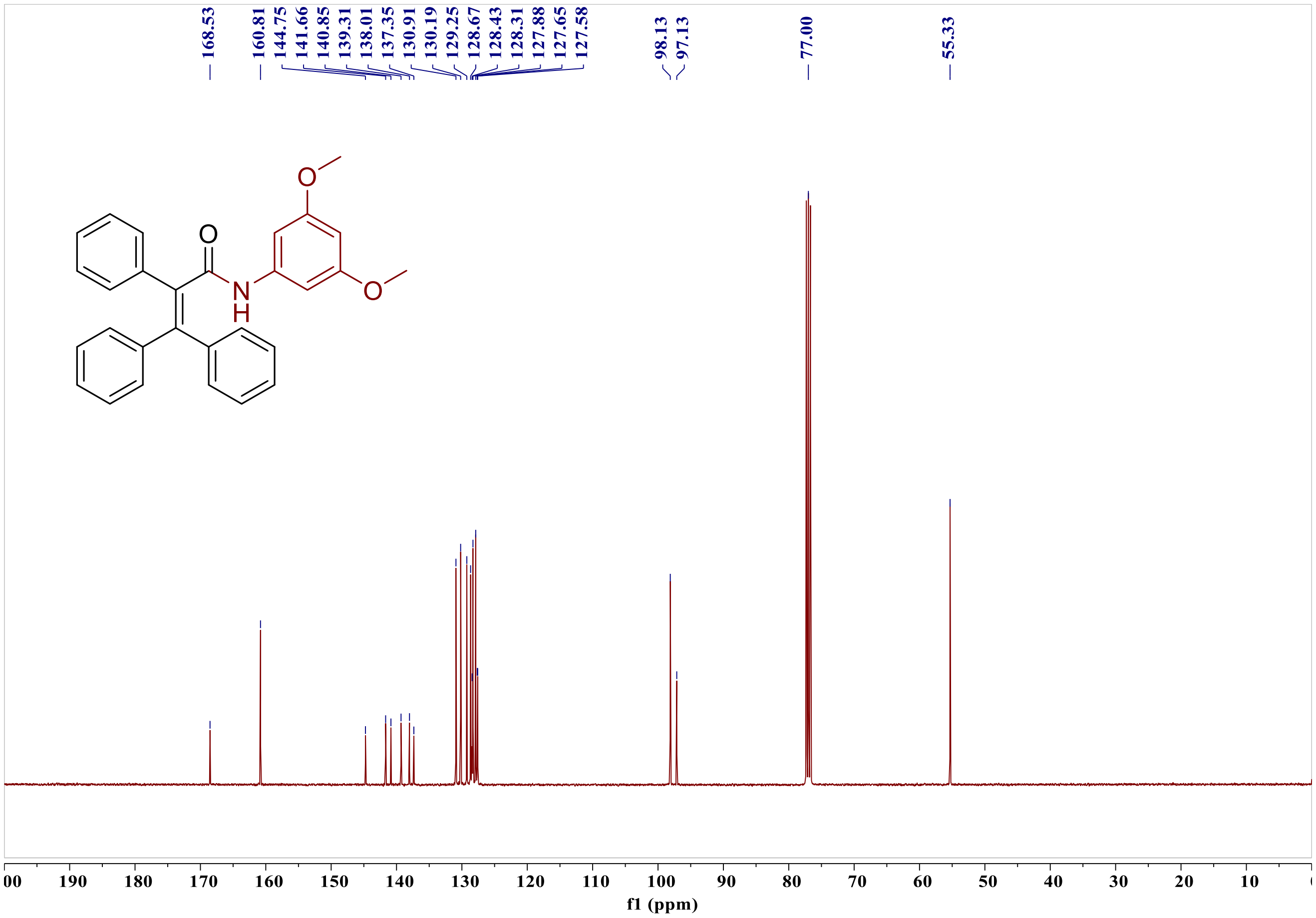
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 9



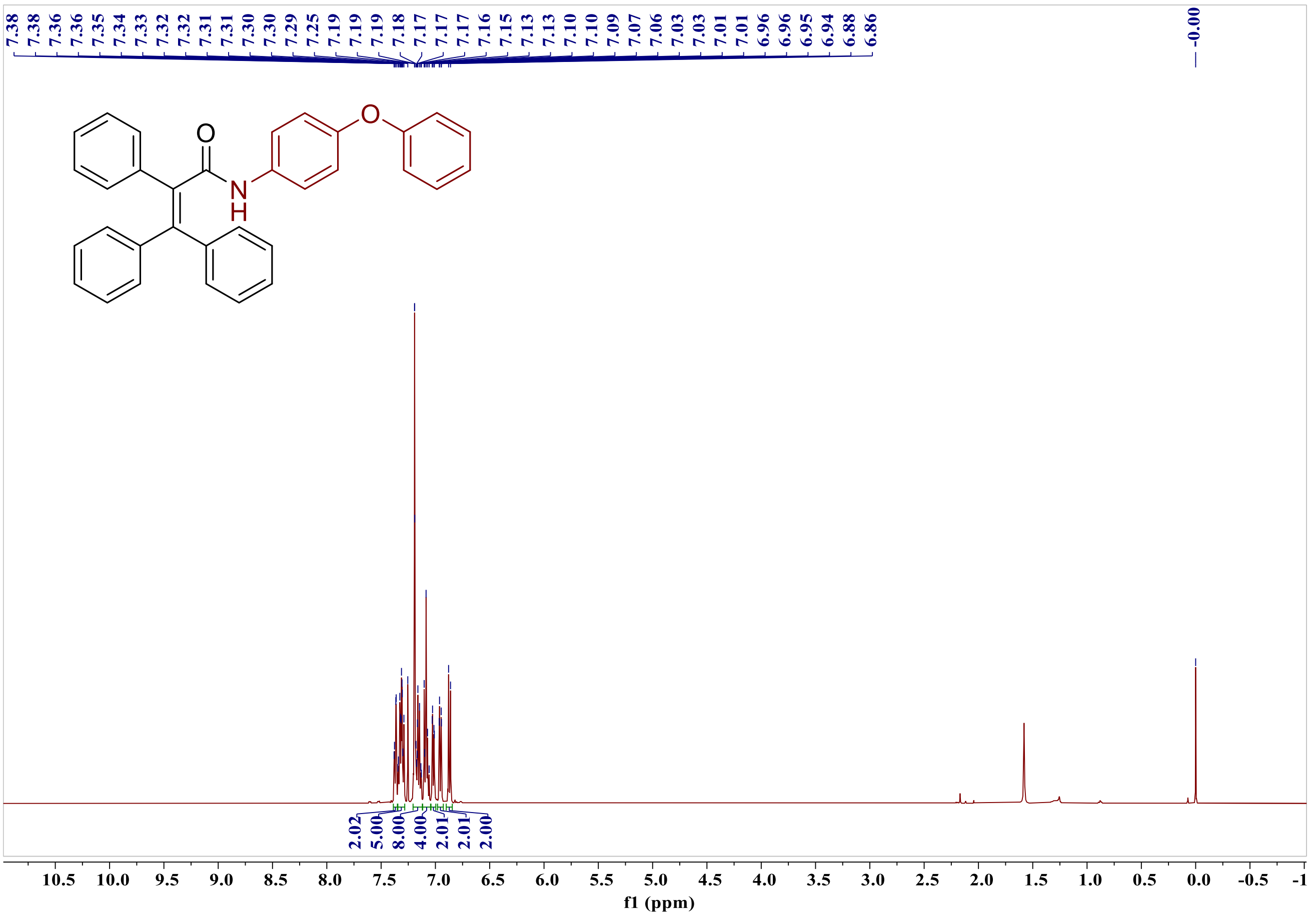


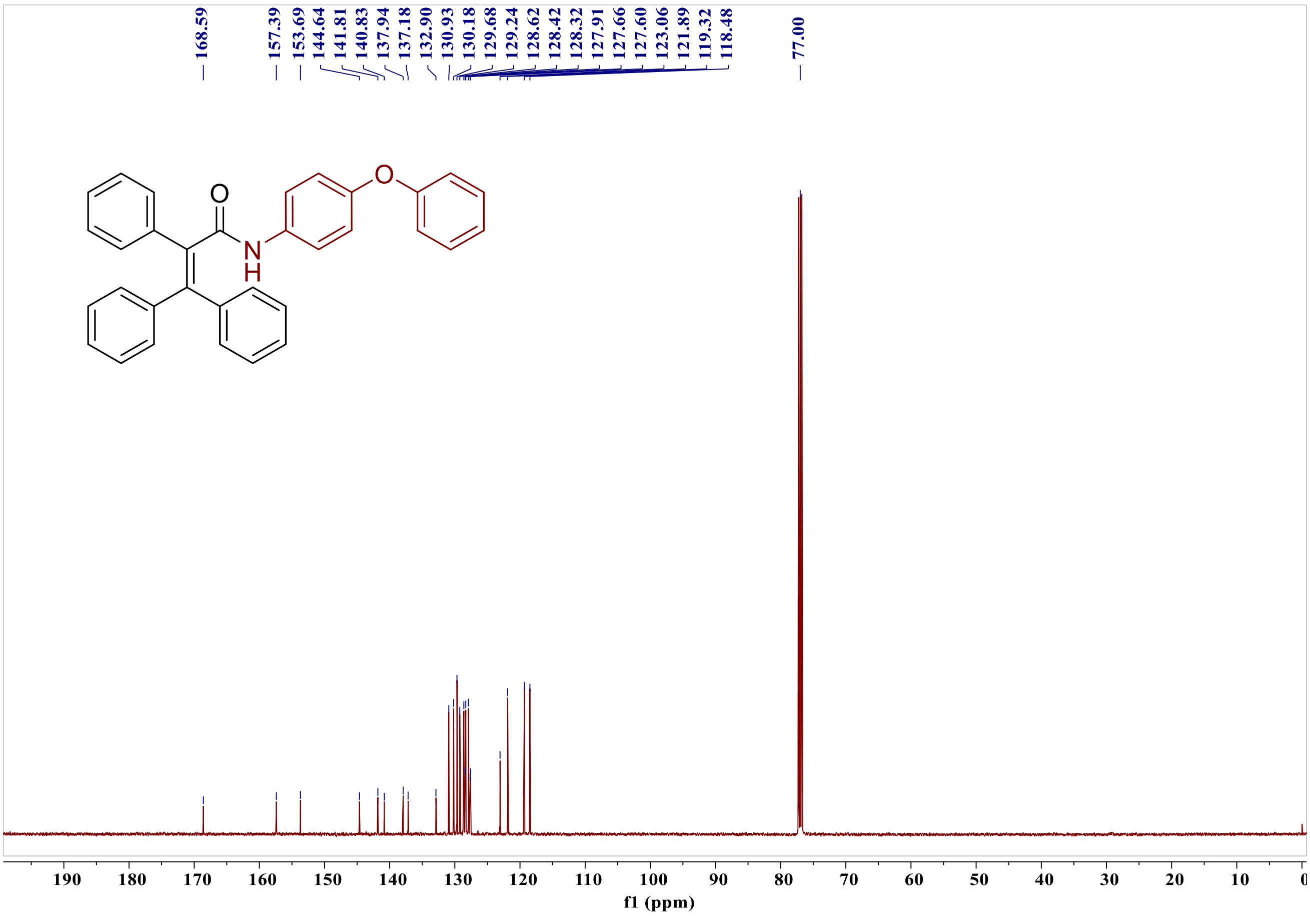
^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C NMR (100 MHz, CDCl$_3$) spectra of product 10



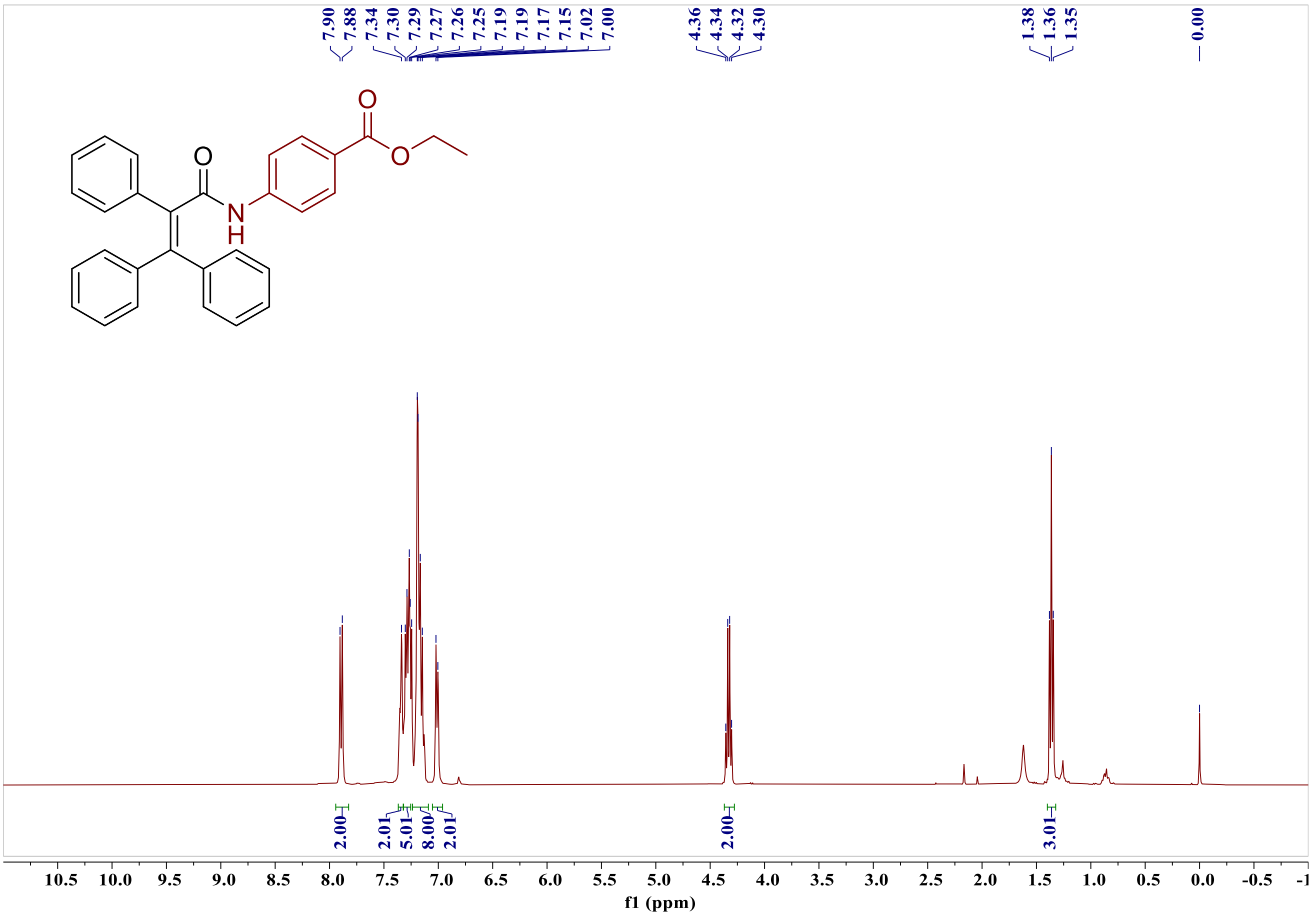


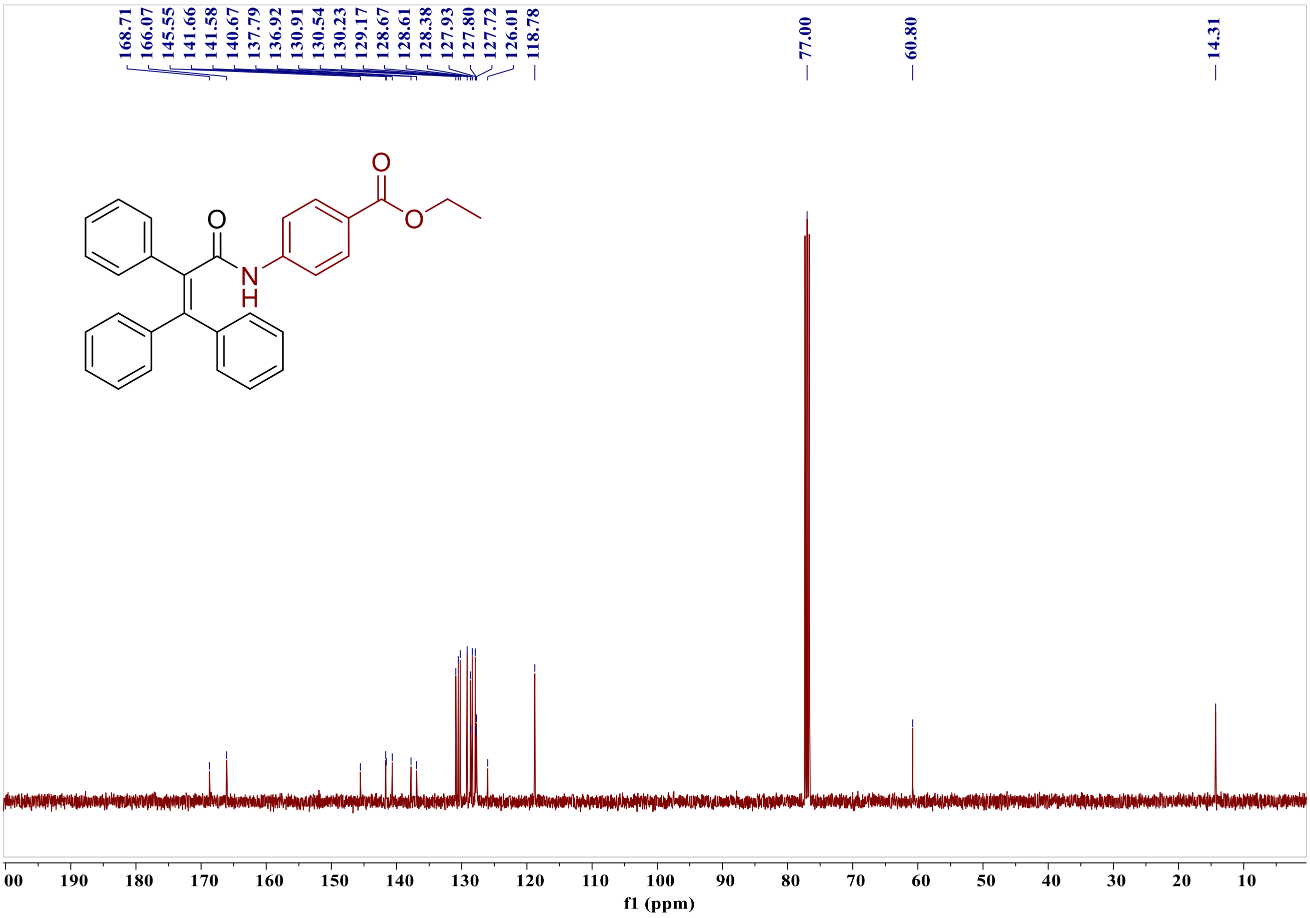
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra of product 11



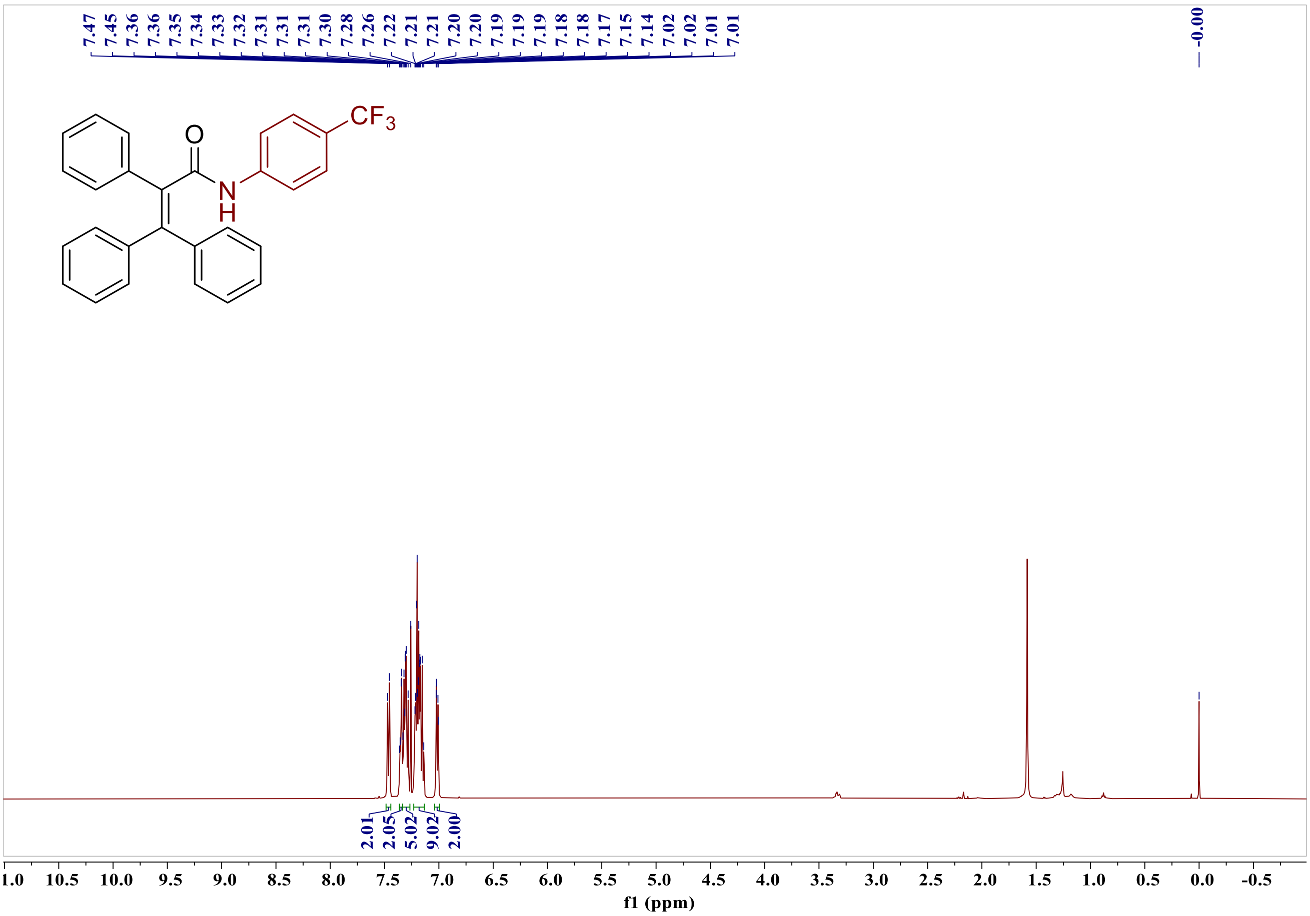


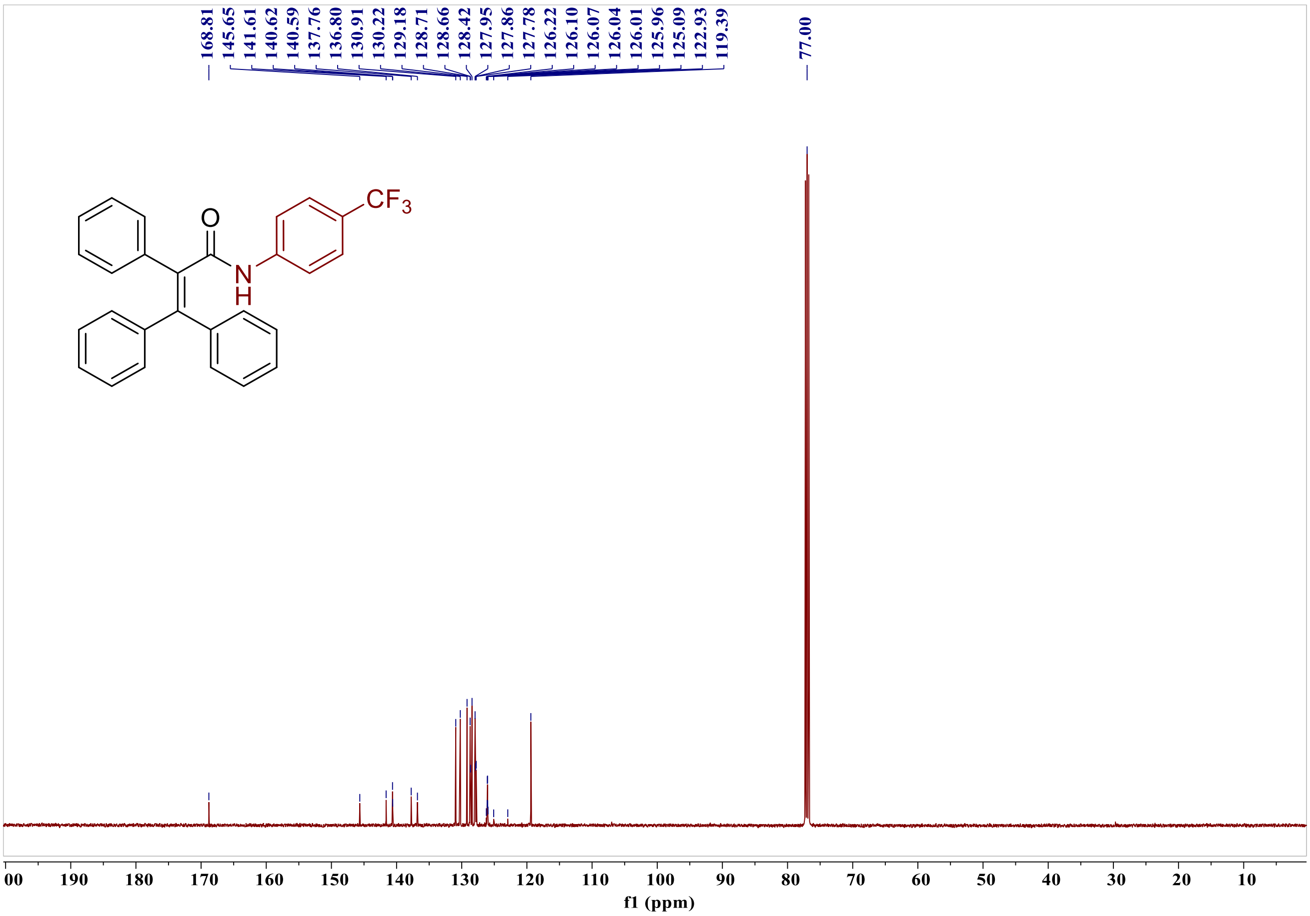
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 12

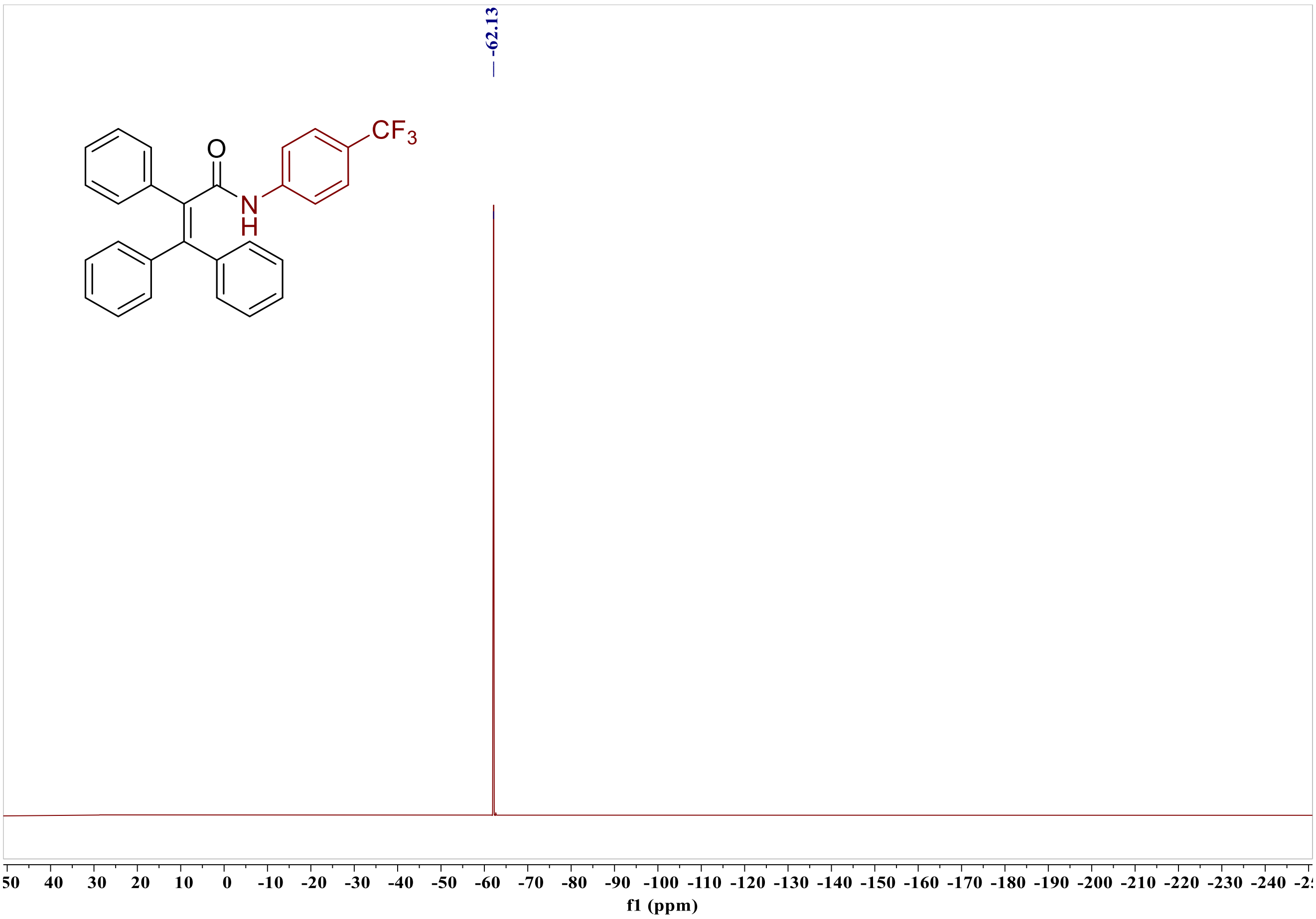




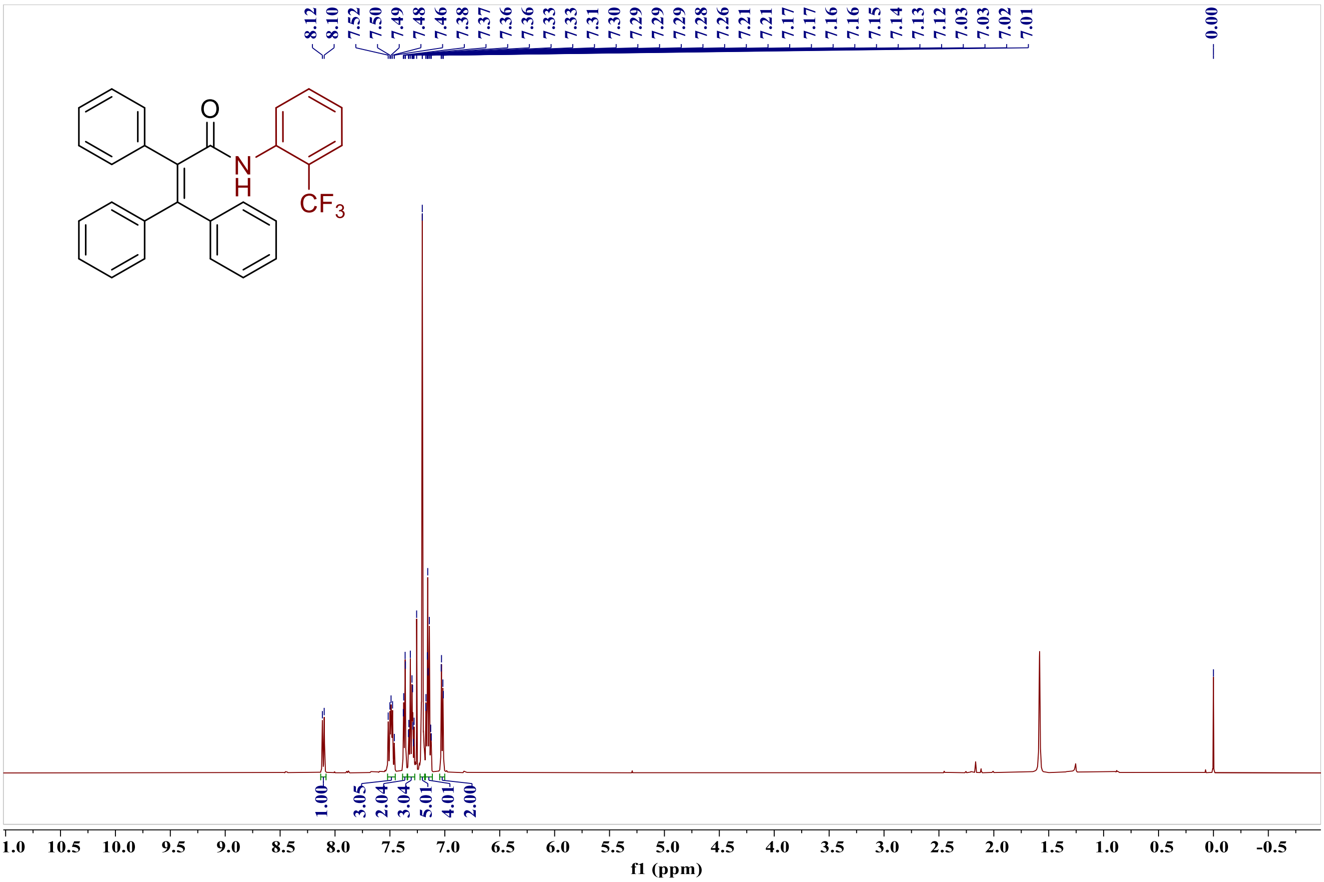
^{1}H NMR (500 MHz, CDCl$_3$), ^{13}C NMR (125 MHz, CDCl$_3$) and ^{19}F NMR (376 MHz, CDCl$_3$) spectra of product 13

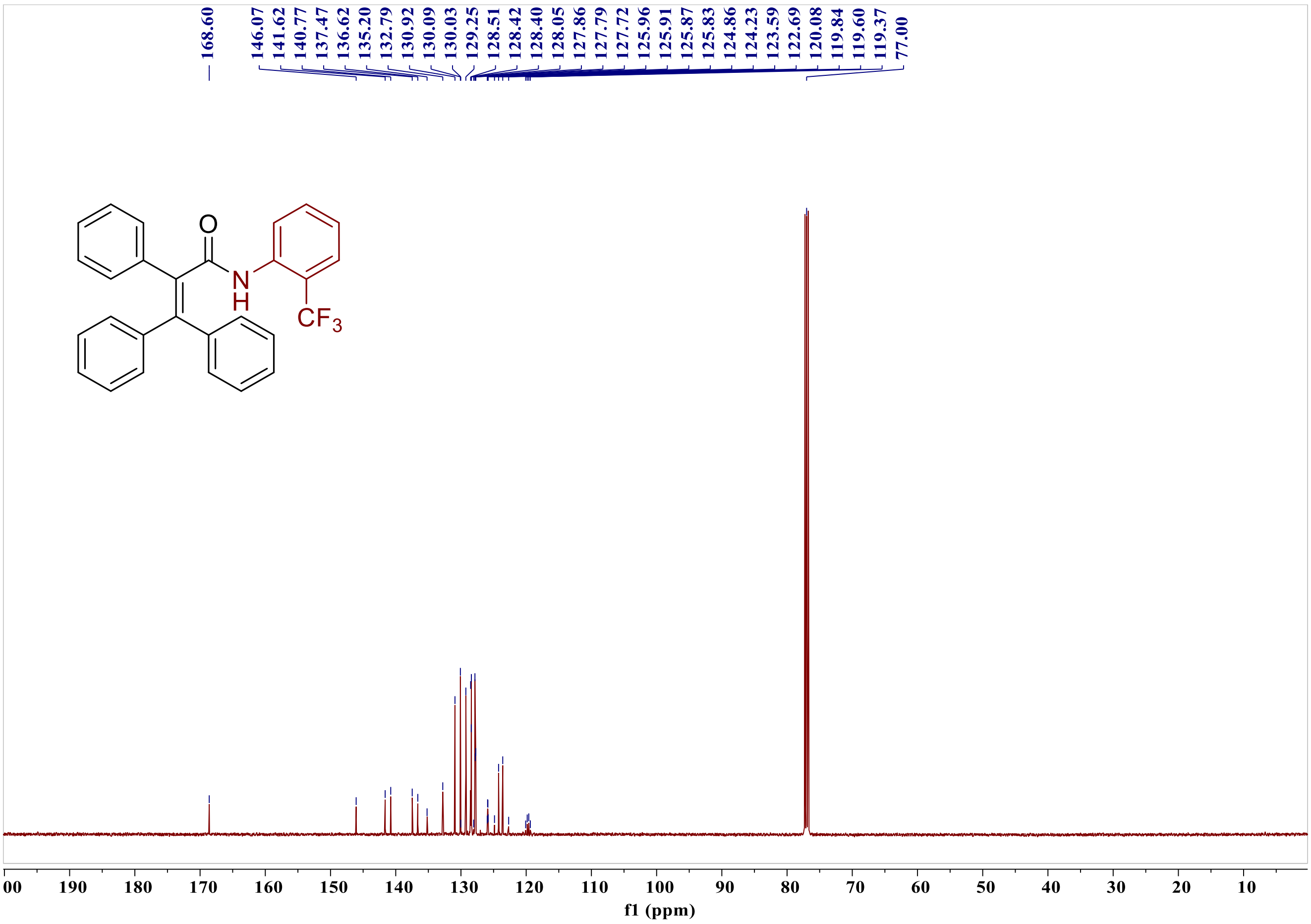






^{1}H NMR (500 MHz, CDCl$_3$), ^{13}C NMR (125 MHz, CDCl$_3$) and ^{19}F NMR (376 MHz, CDCl$_3$) spectra of product 14

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127.72
125.96
125.91
125.87
125.83
124.86
124.23
123.59
122.69
120.08
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119.60
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77.00
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N
H
CF3
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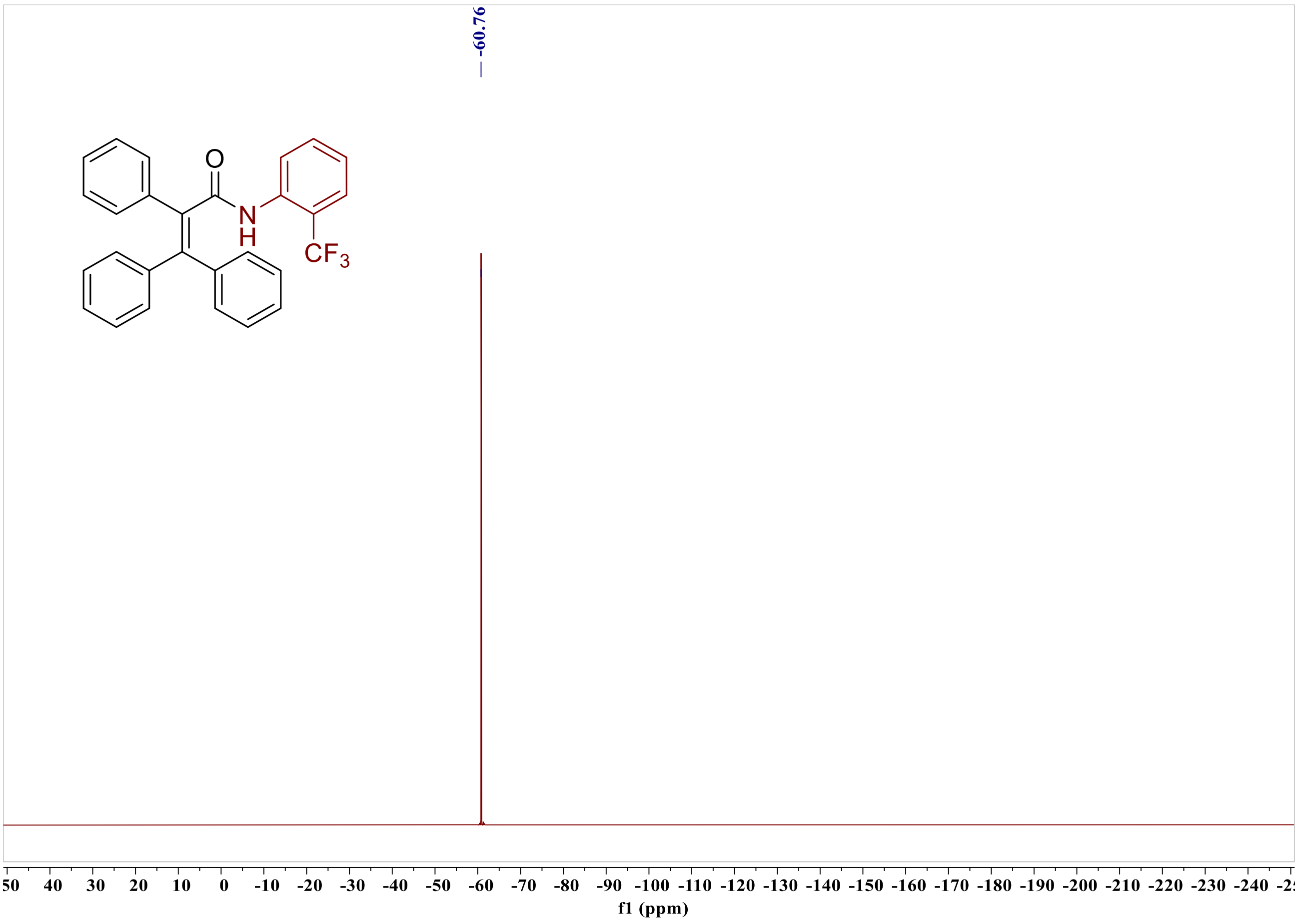
f1 (ppm)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O
N
H
CF3
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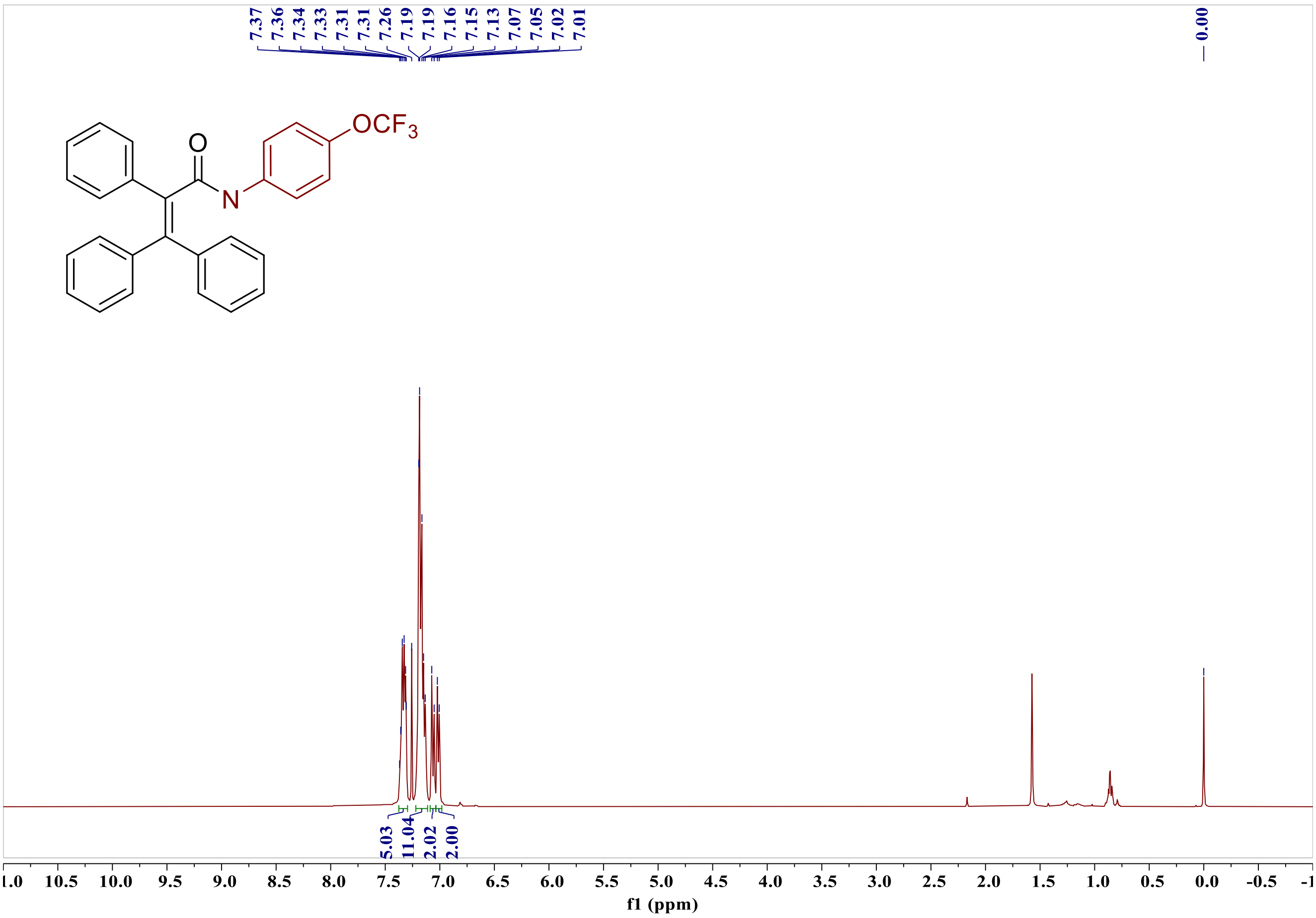
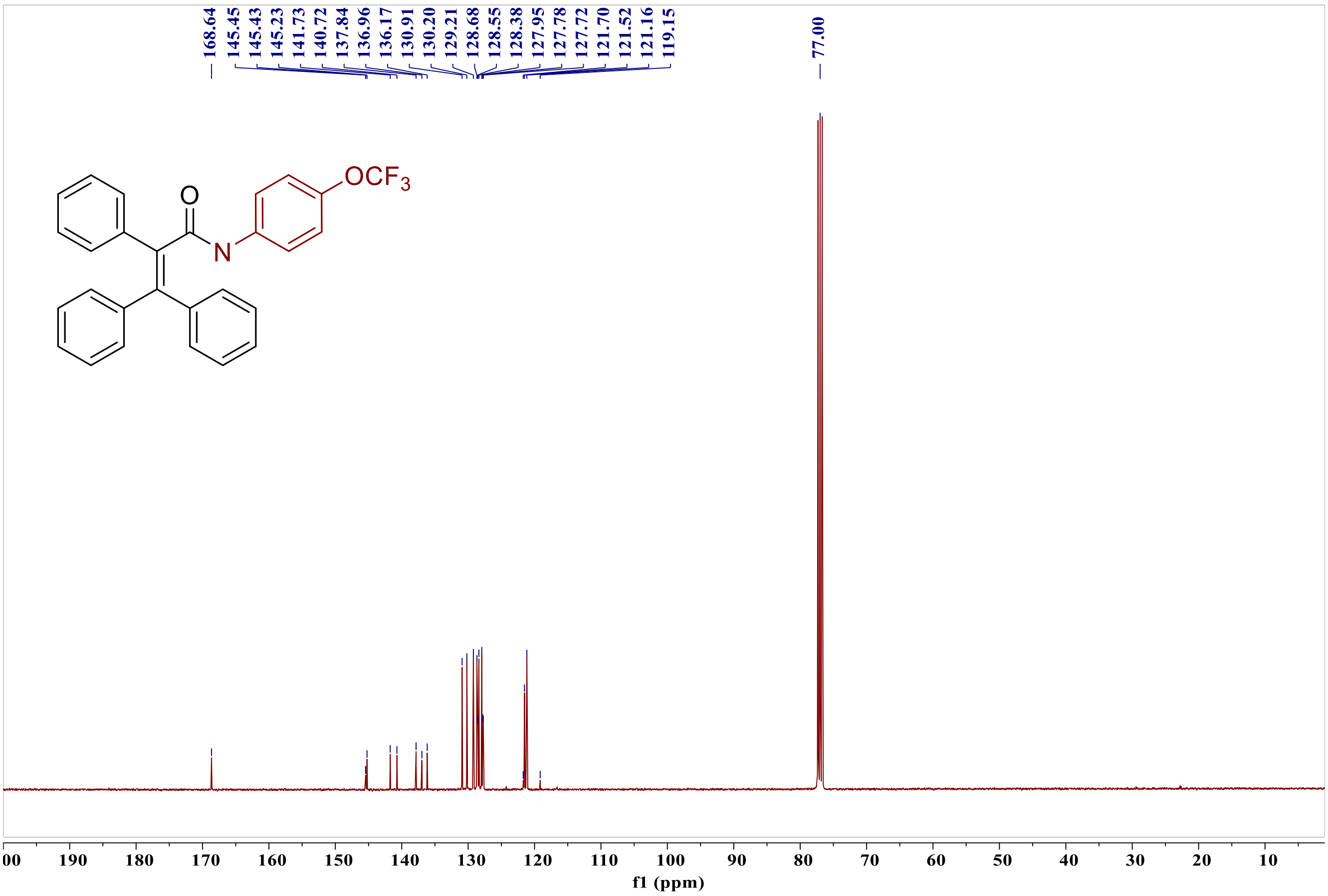
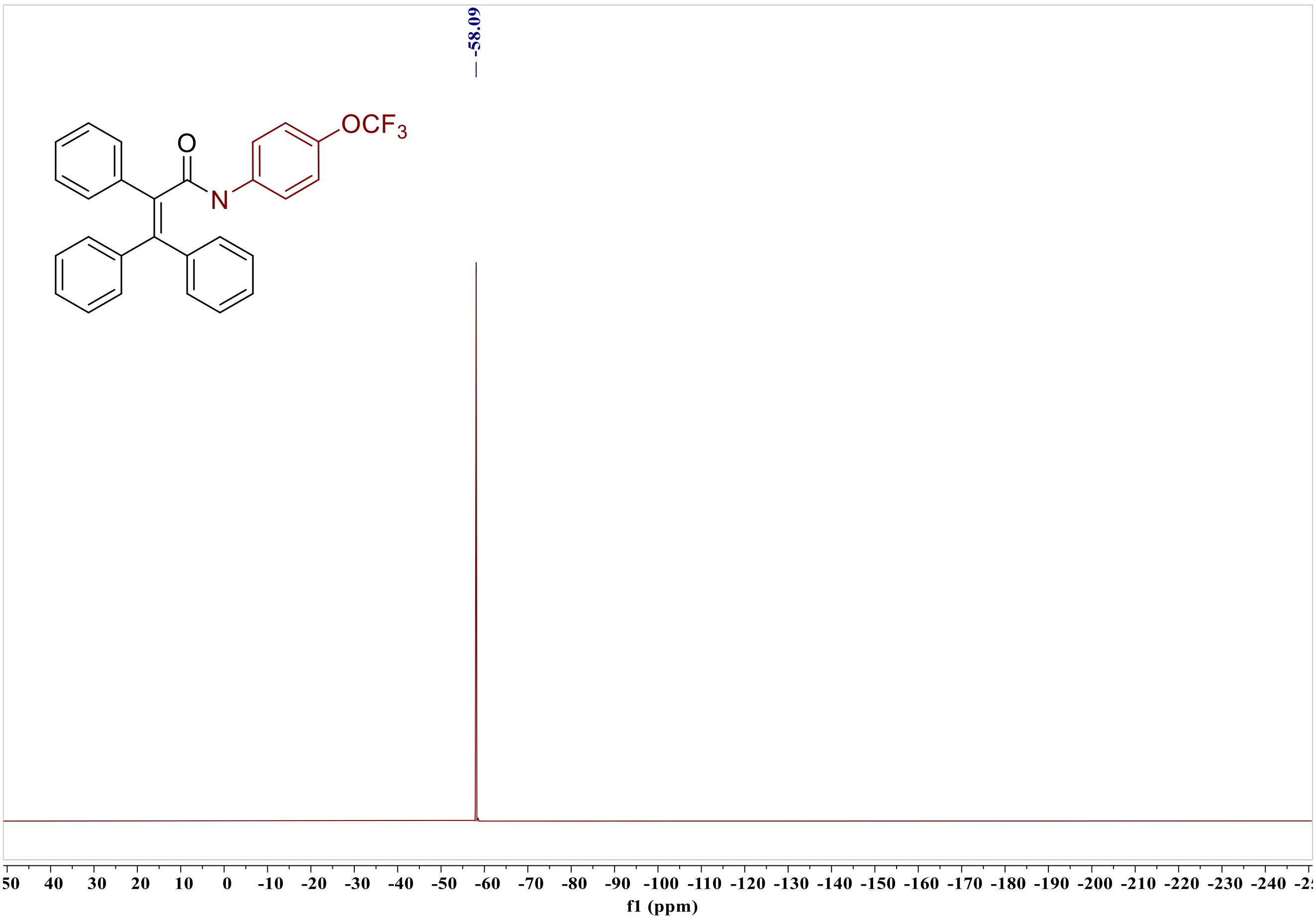
f1 (ppm)

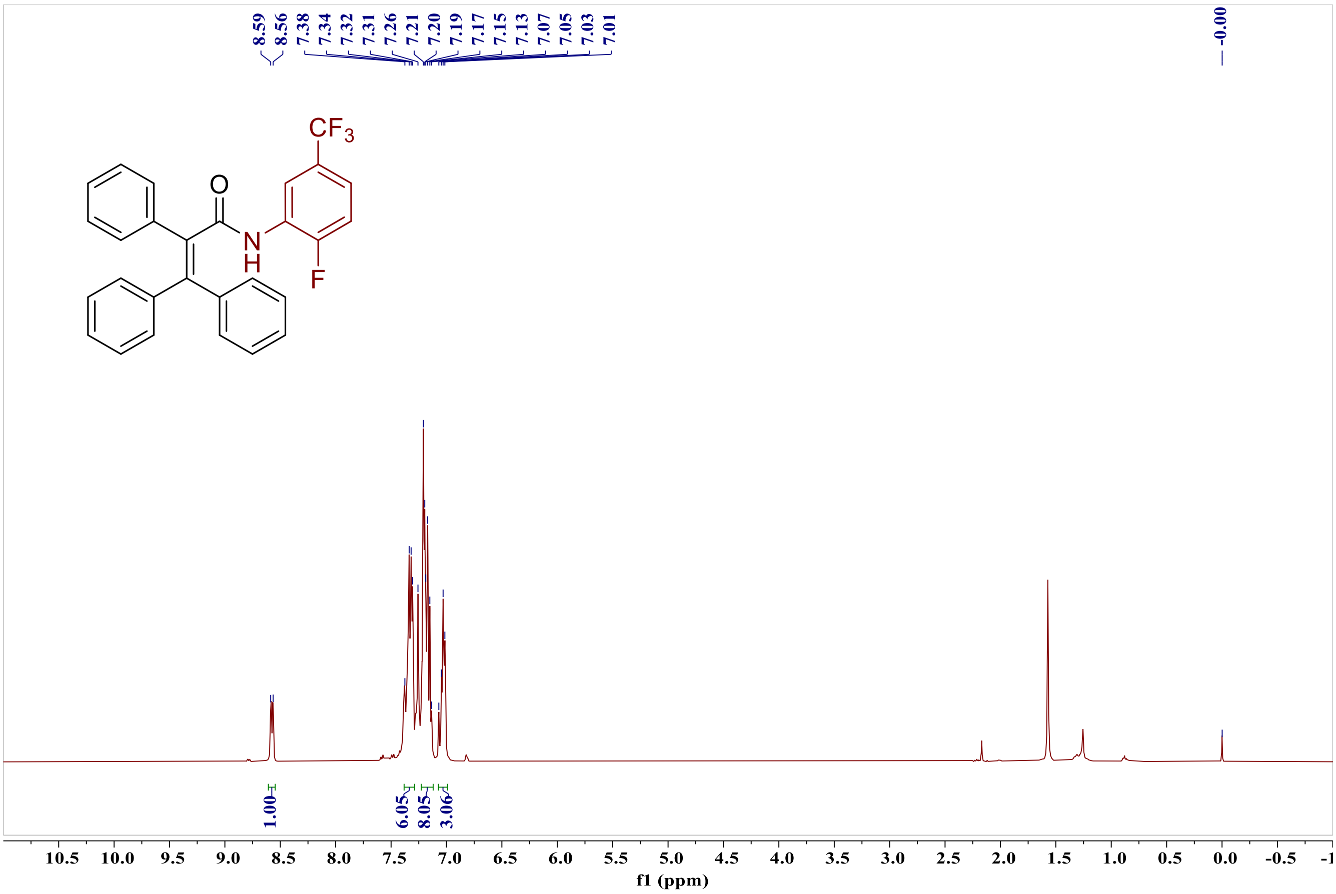
^{1}H NMR (400 MHz, CDCl$_3$), ^{13}C NMR (100 MHz, CDCl$_3$)and ^{19}F NMR (376 MHz, CDCl$_3$) spectra of product 15

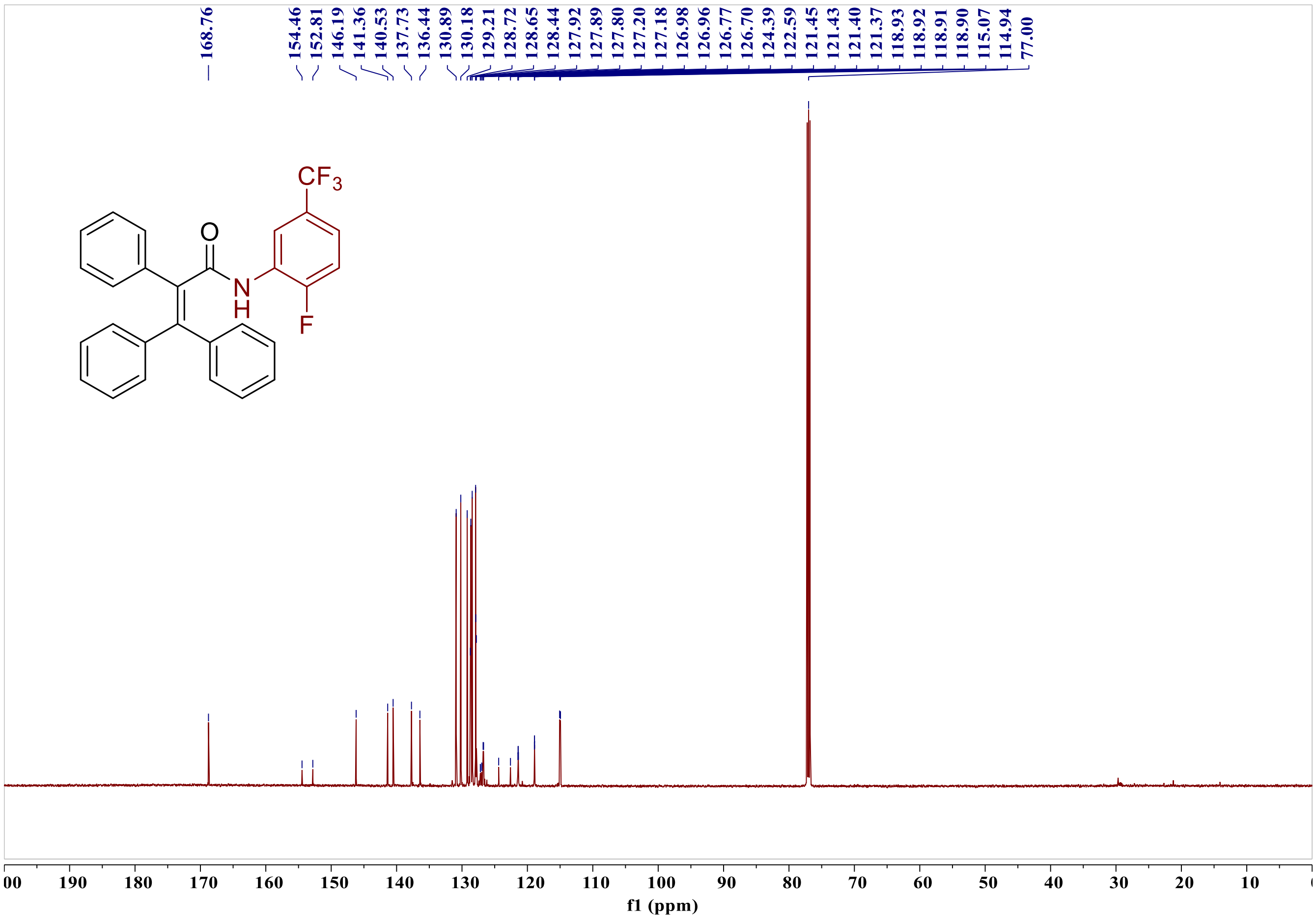






^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (150 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 16

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140.53
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136.44
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128.65
128.44
127.92
127.89
127.80
127.20
127.18
126.98
126.96
126.77
126.70
124.39
122.59
121.45
121.43
121.40
121.37
118.93
118.92
118.91
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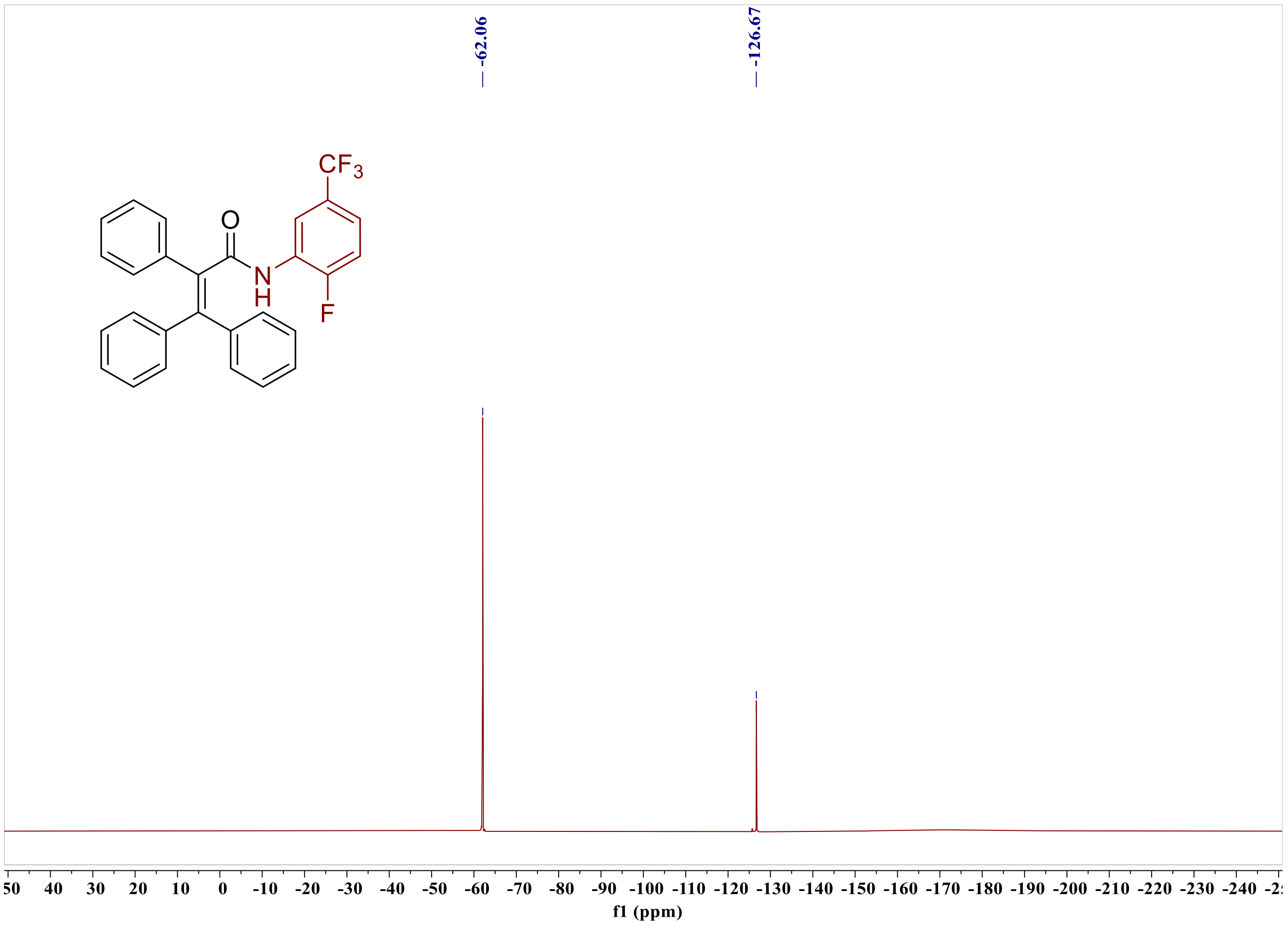
CF3
O
N
H
F
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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N
H
F
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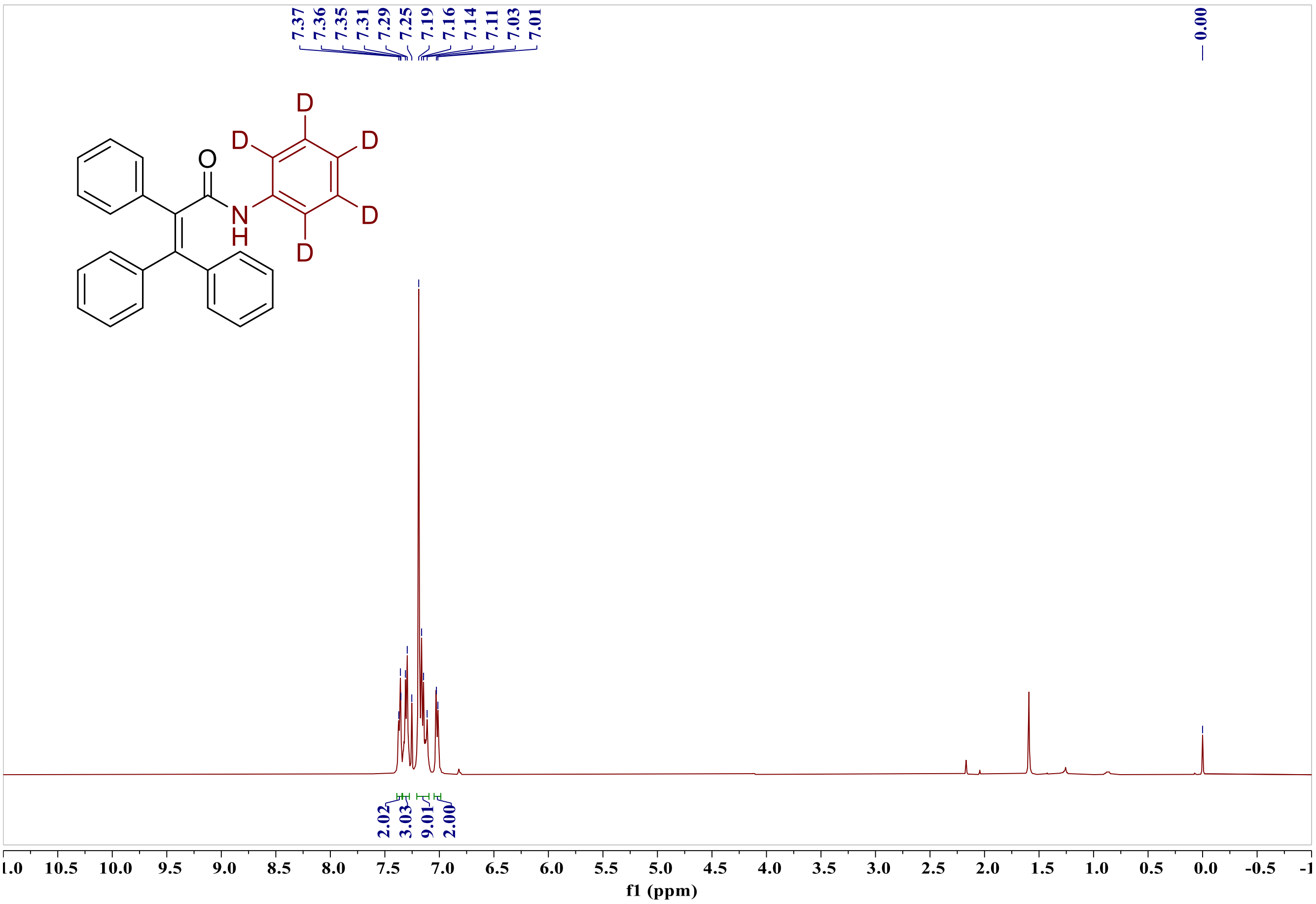
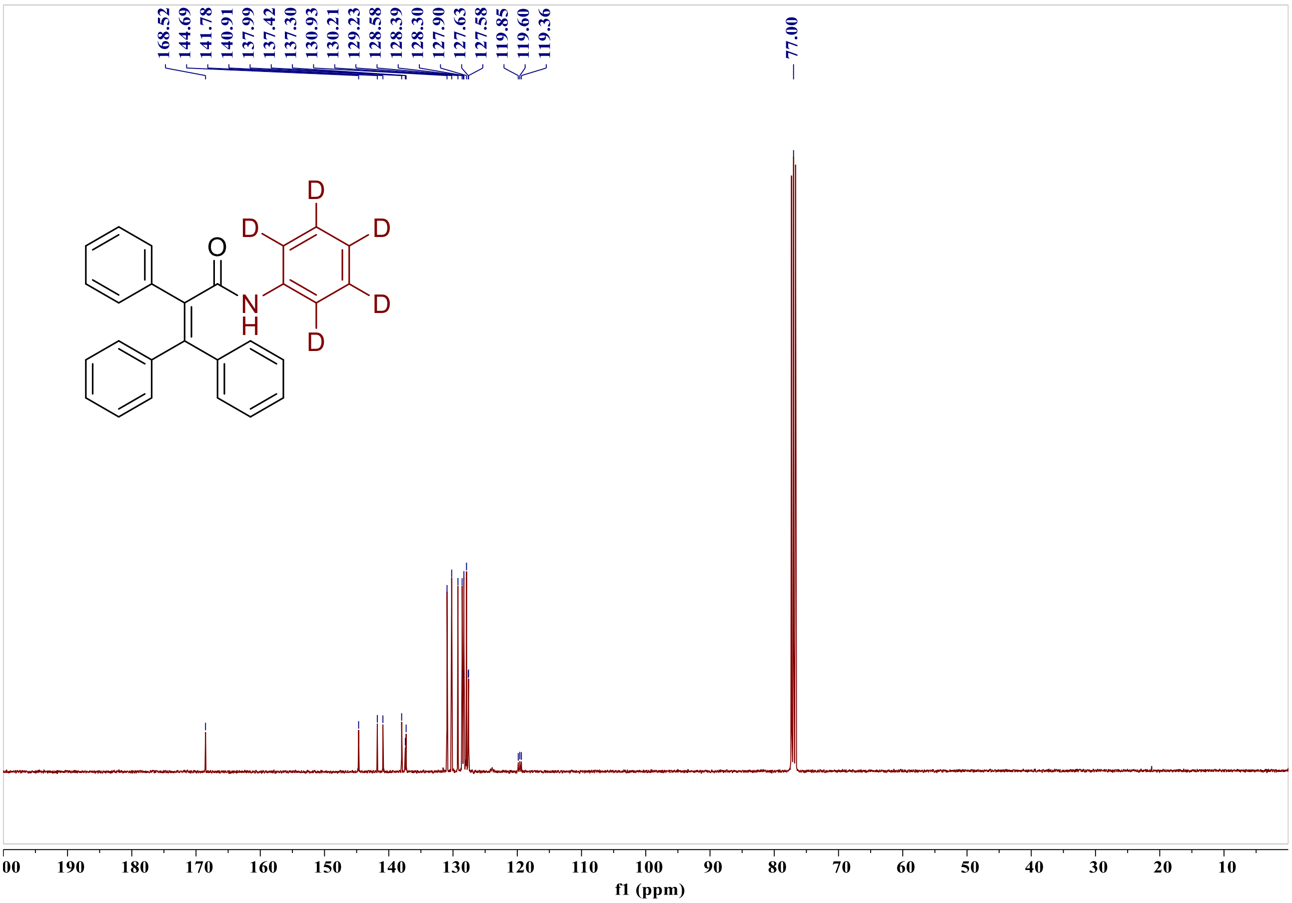
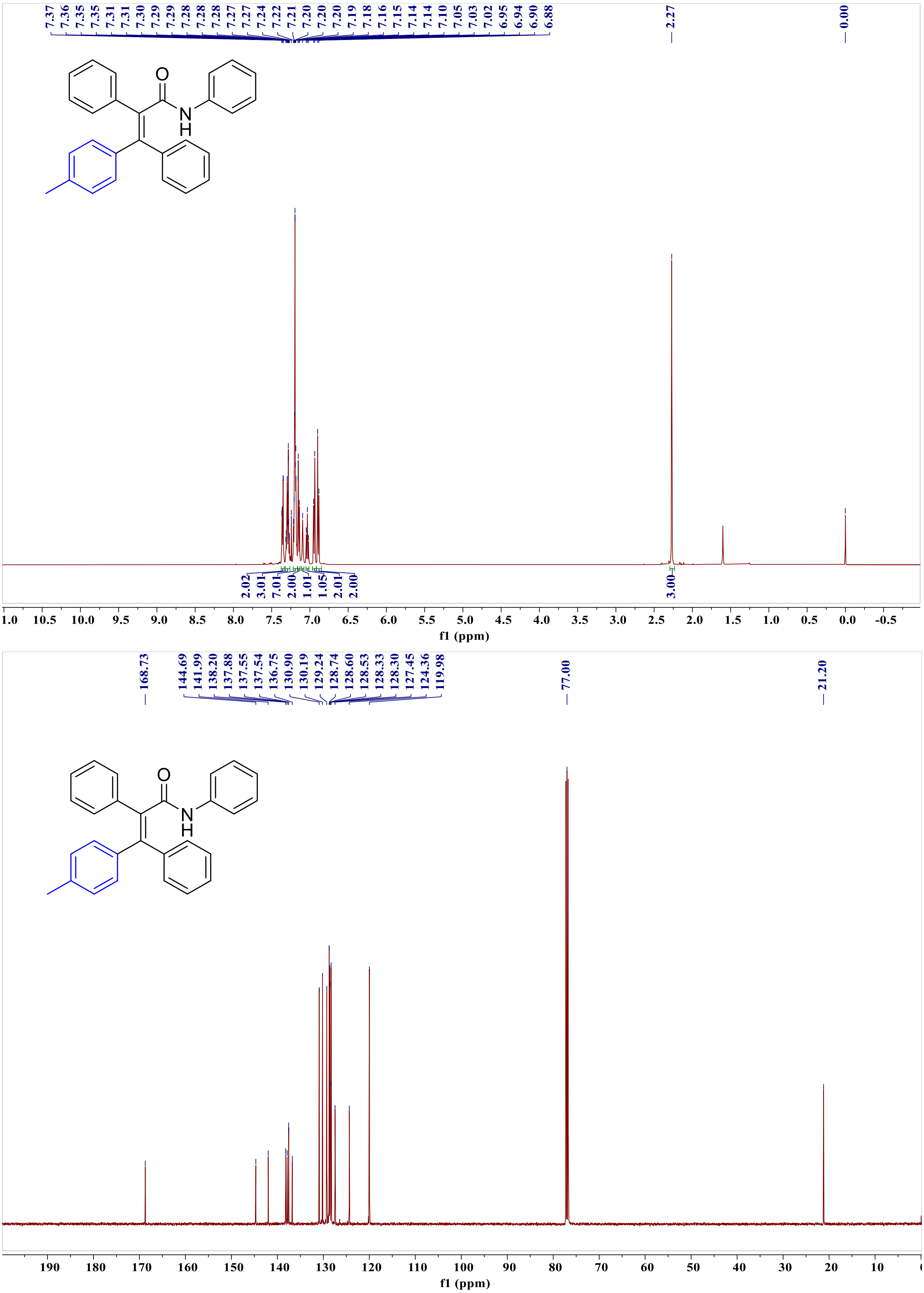
f1 (ppm)

^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C NMR (100 MHz, CDCl$_3$) spectra of product 17

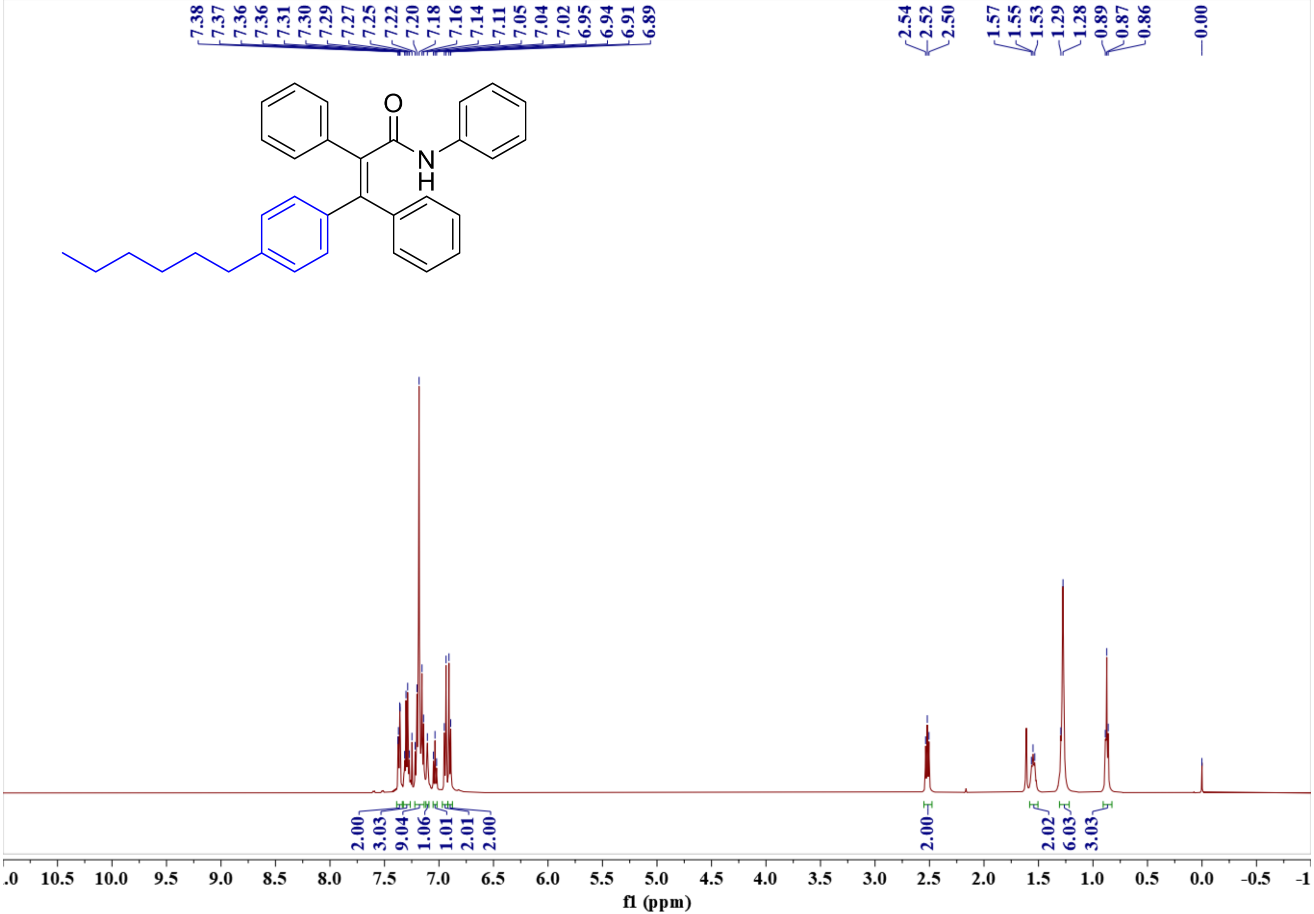


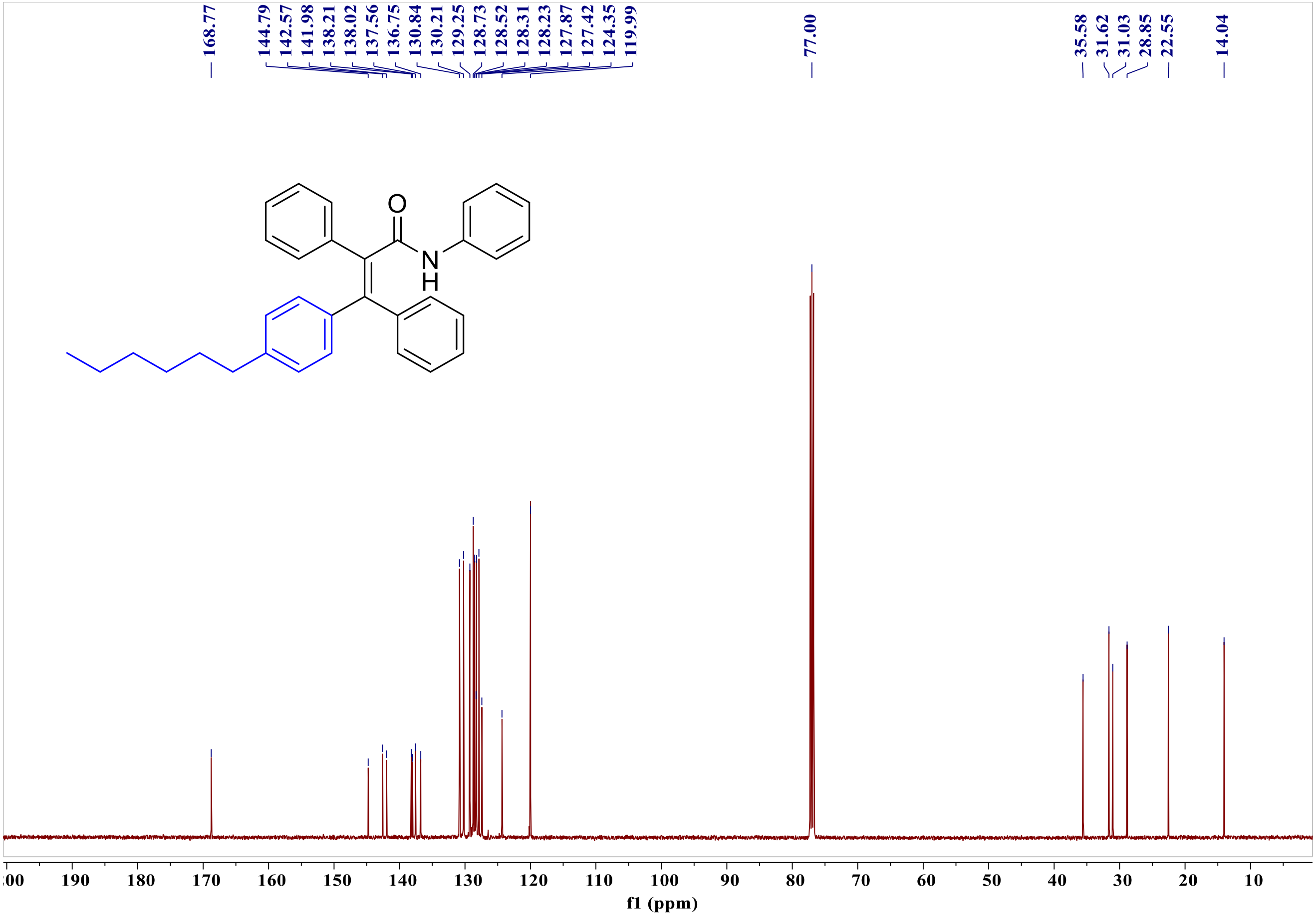


^{1}H NMR (500 MHz, CDCl$_3$) and ^{13}C NMR (125 MHz, CDCl$_3$) spectra of product 18

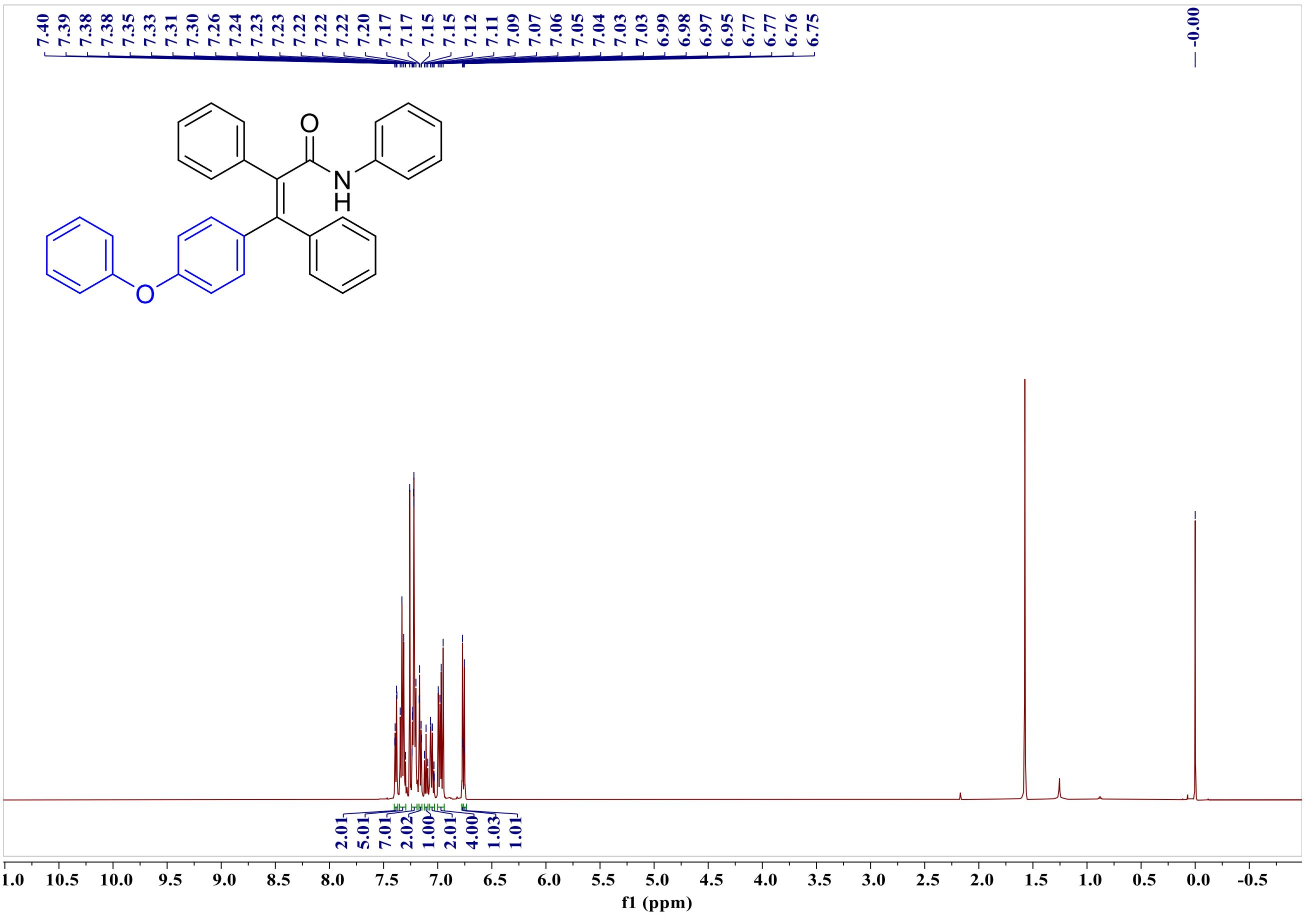


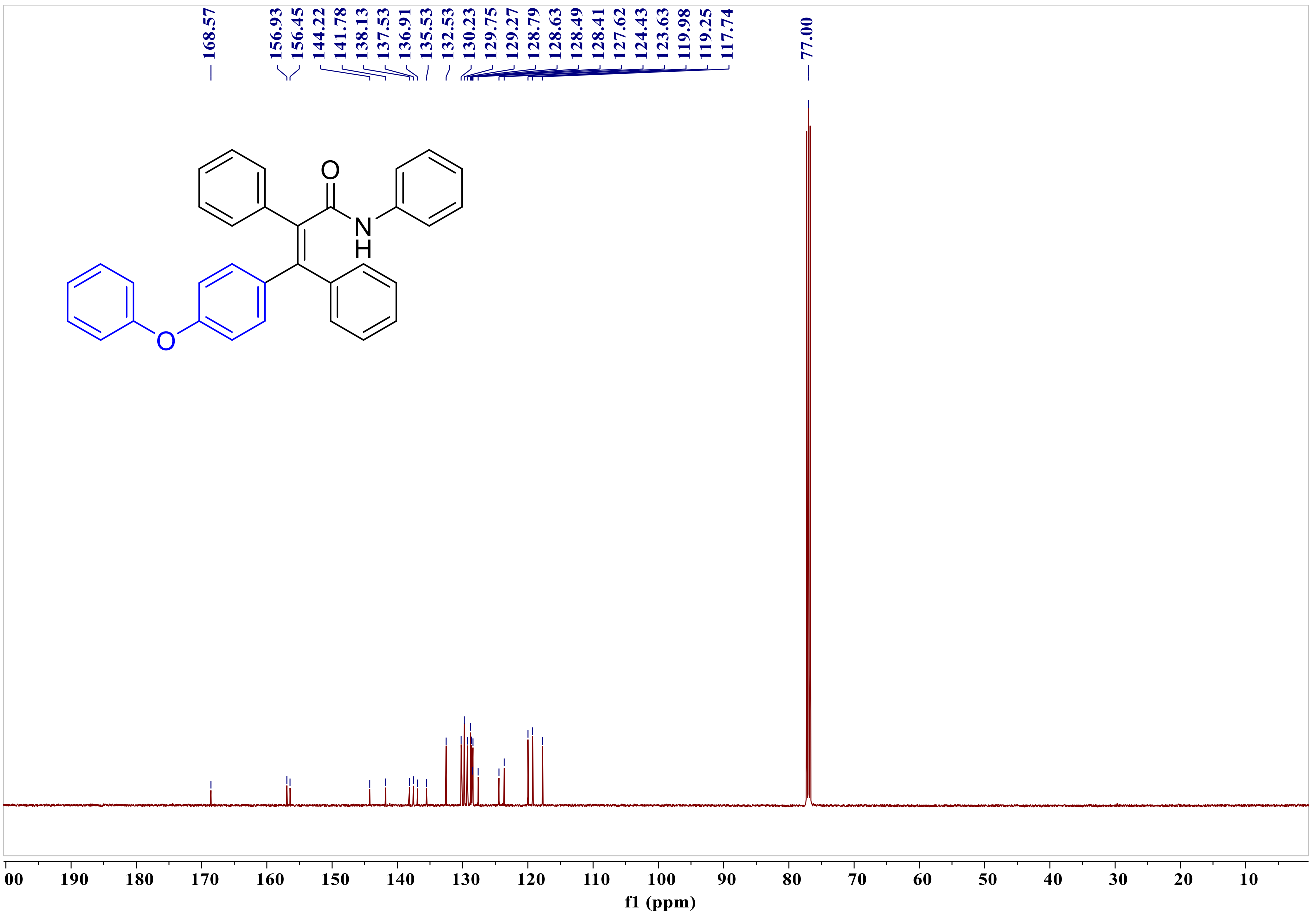
^1H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra of product 19



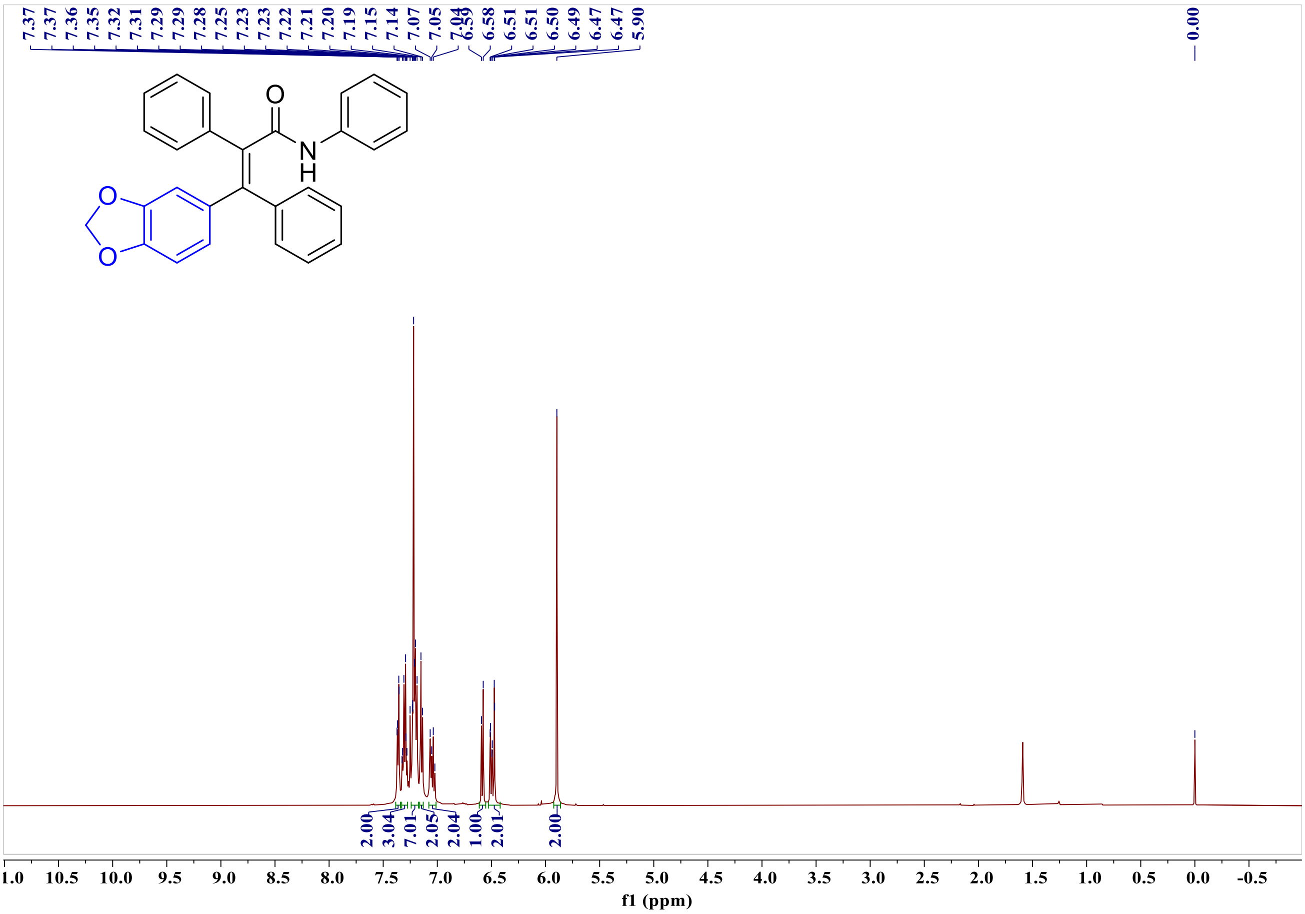


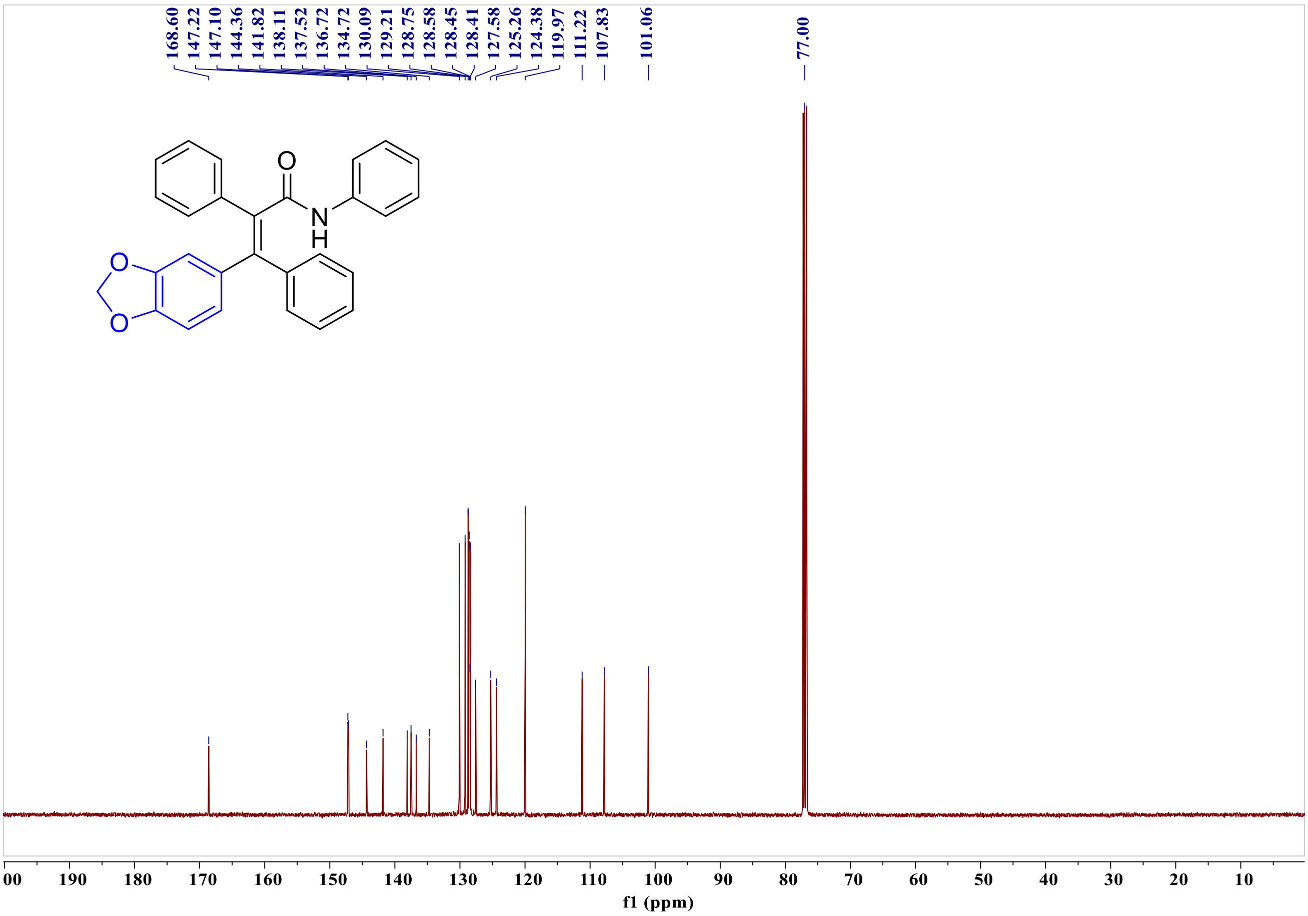
^{1}H NMR (500 MHz, CDCl$_3$) and ^{13}C NMR (125 MHz, CDCl$_3$) spectra of product 20



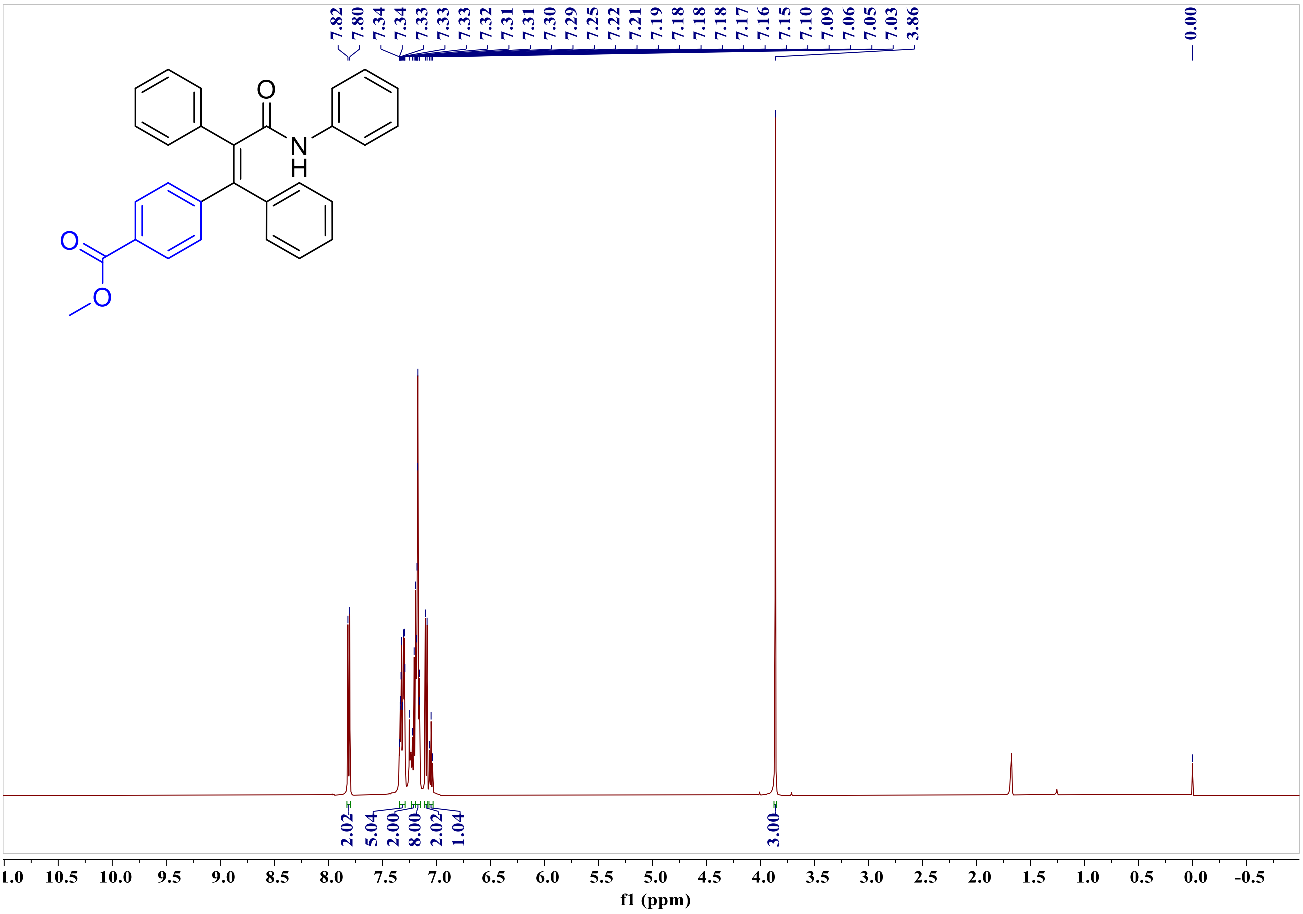


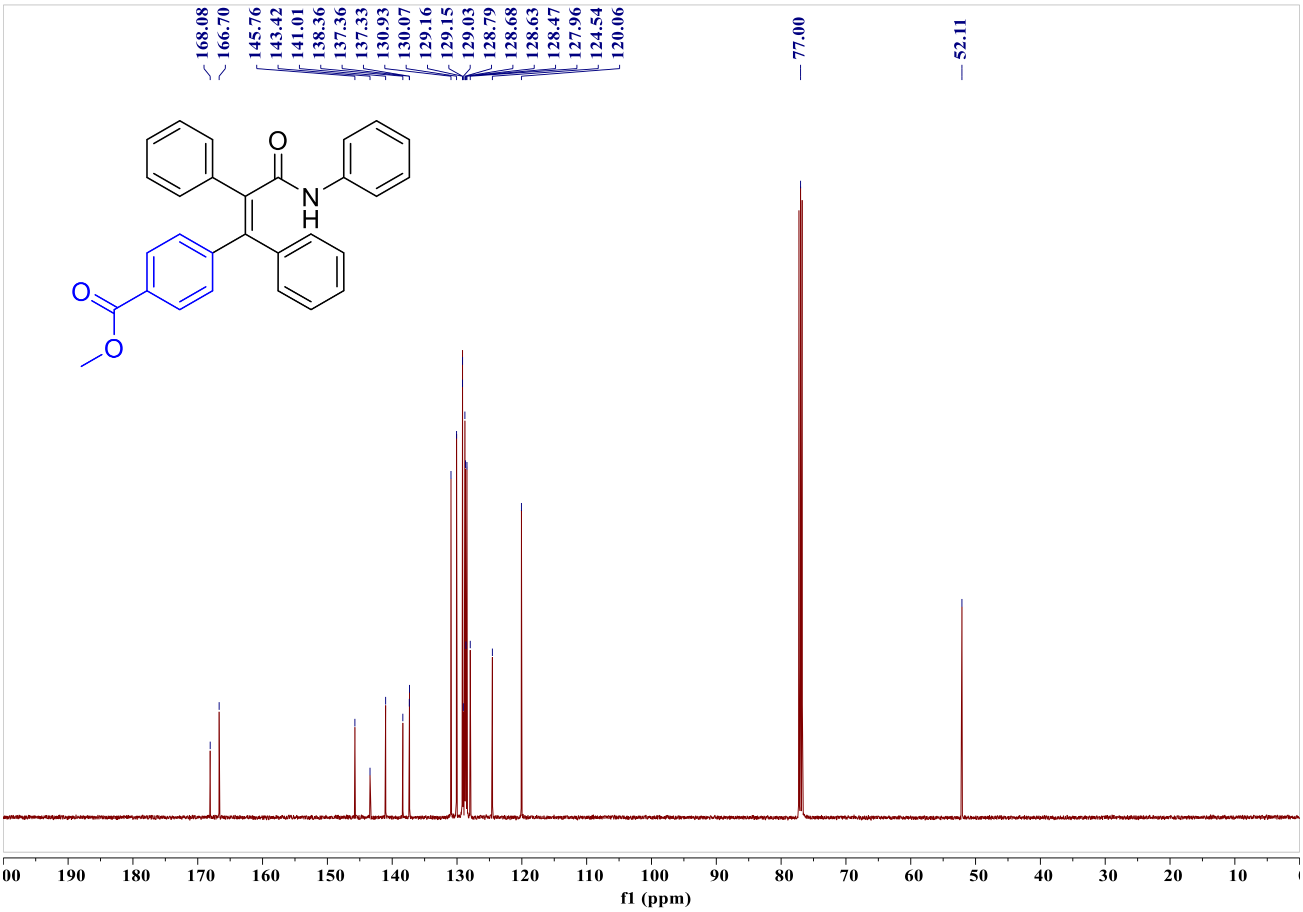
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra of product 21



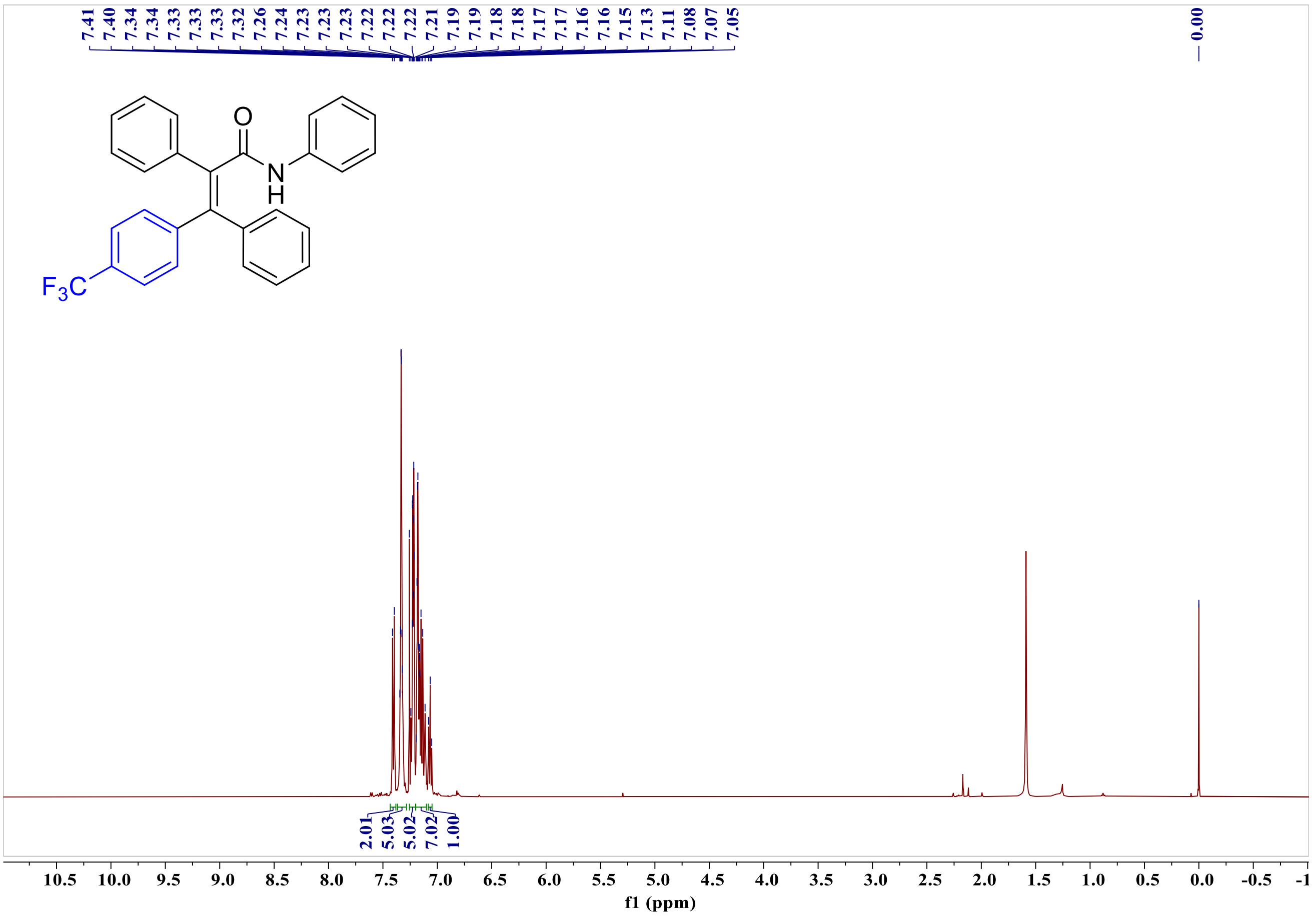


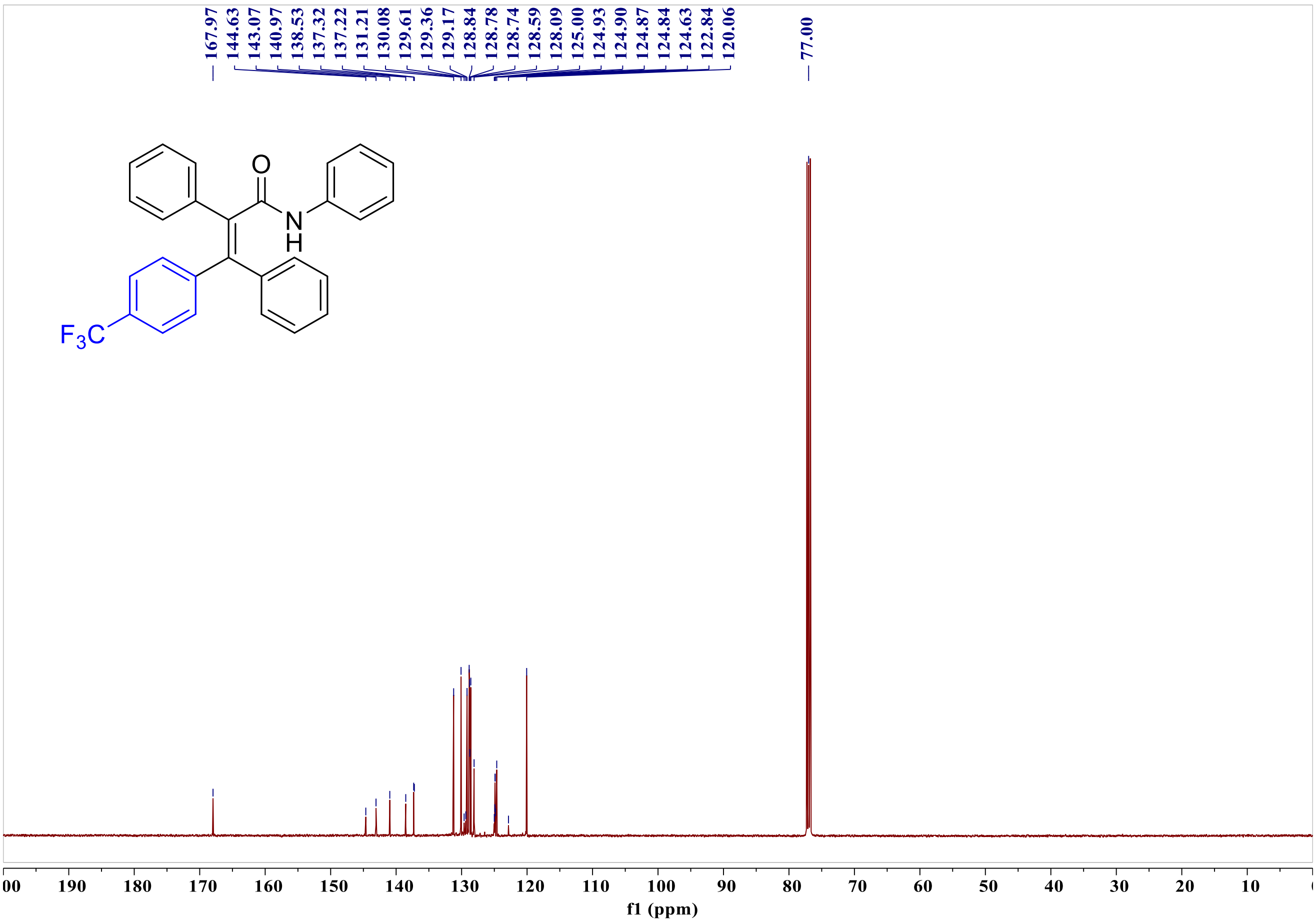
^{1}H NMR (500 MHz, CDCl$_3$) and ^{13}C NMR (125 MHz, CDCl$_3$) spectra of product 22

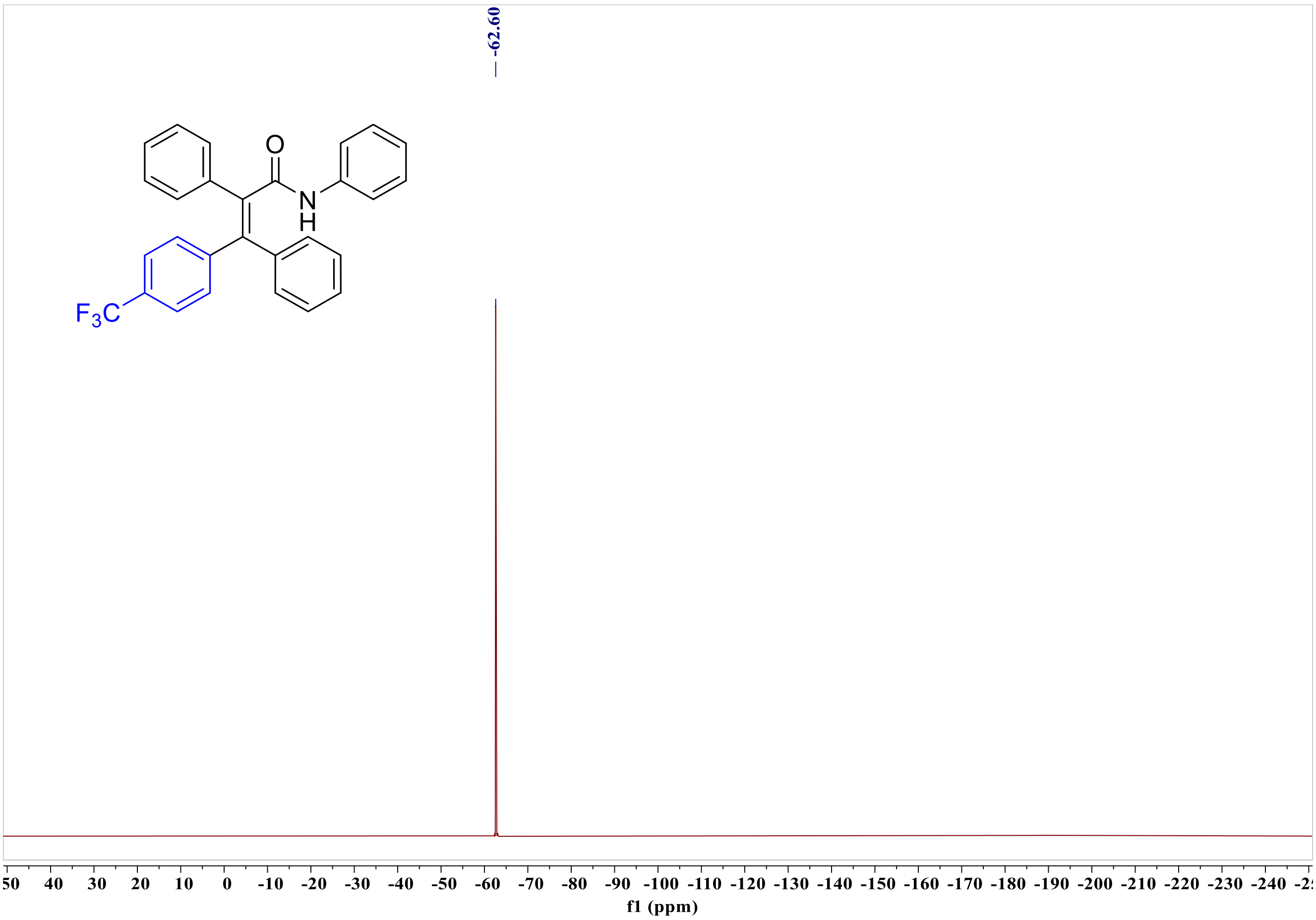




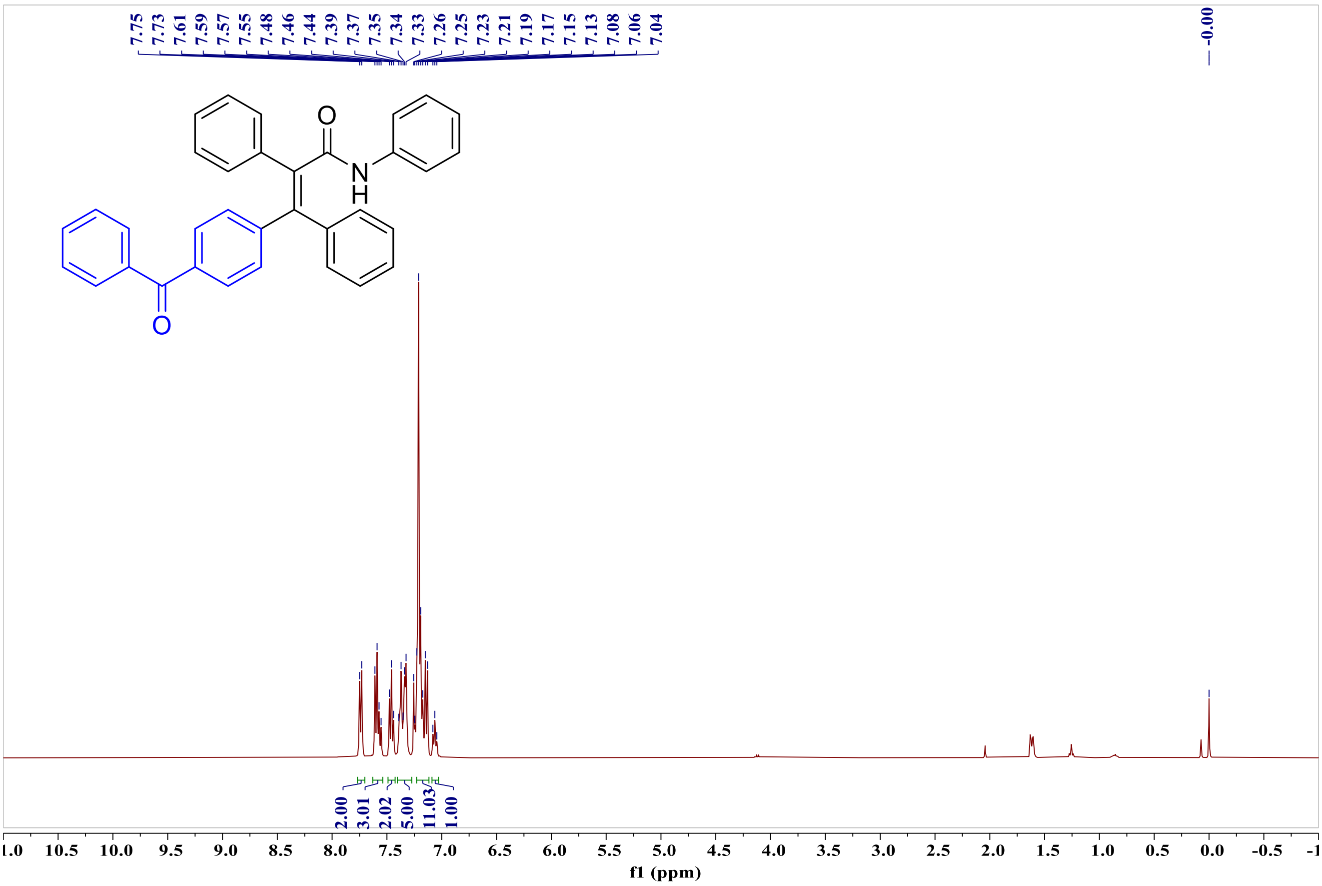
^{1}H NMR (500 MHz, CDCl$_3$), ^{13}C NMR (125 MHz, CDCl$_3$) and ^{19}F NMR (376 MHz, CDCl$_3$) spectra of product 23

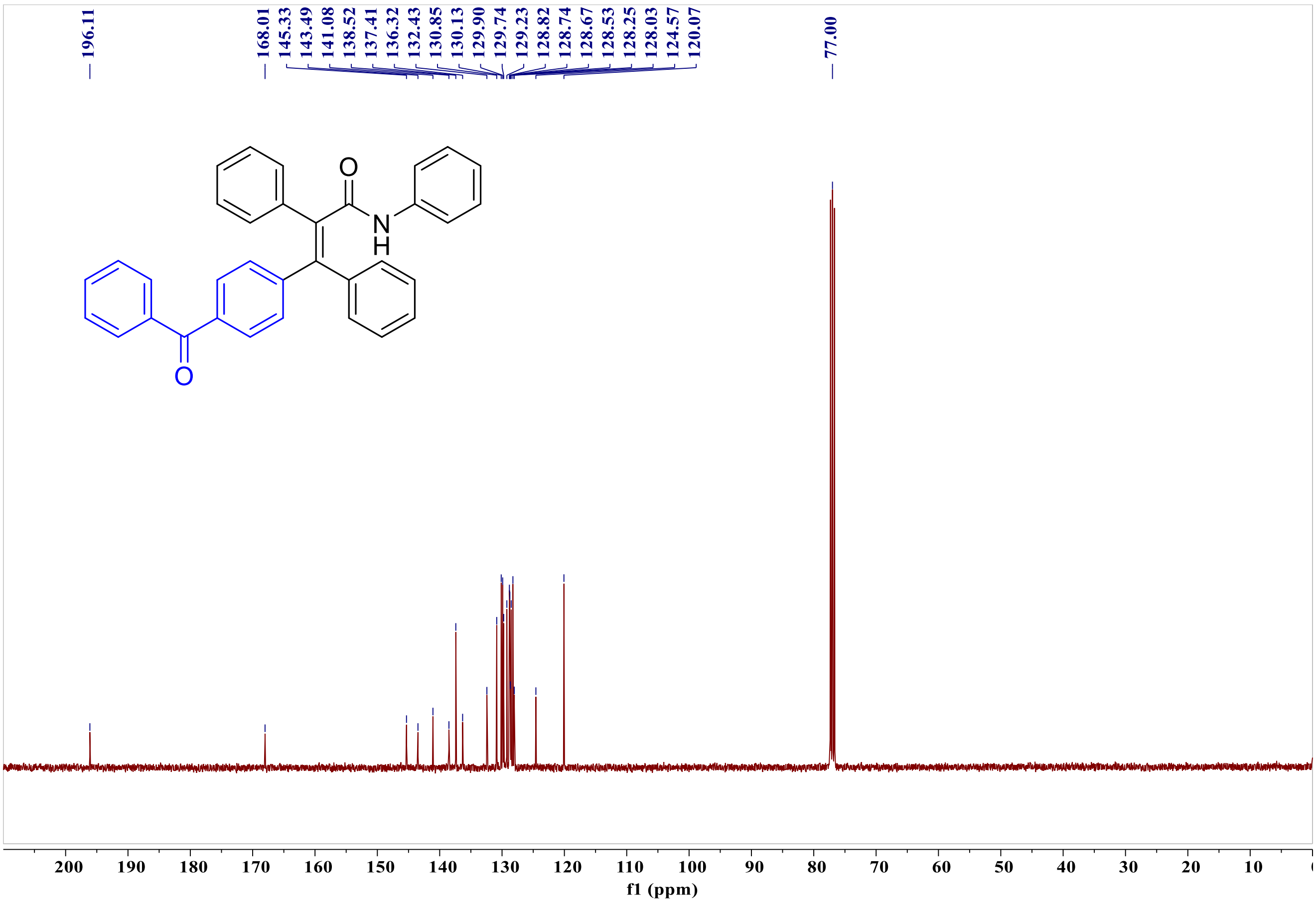




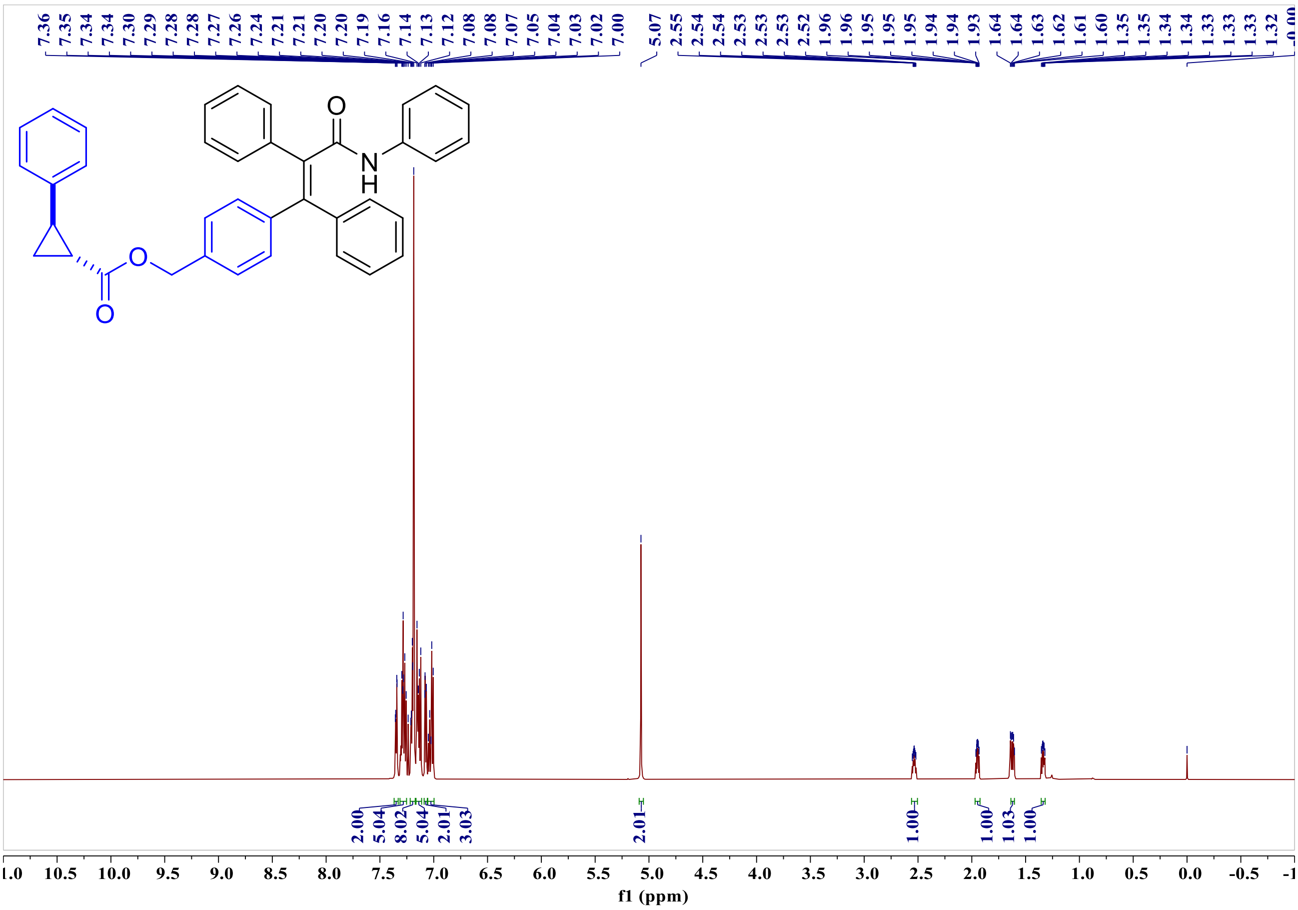


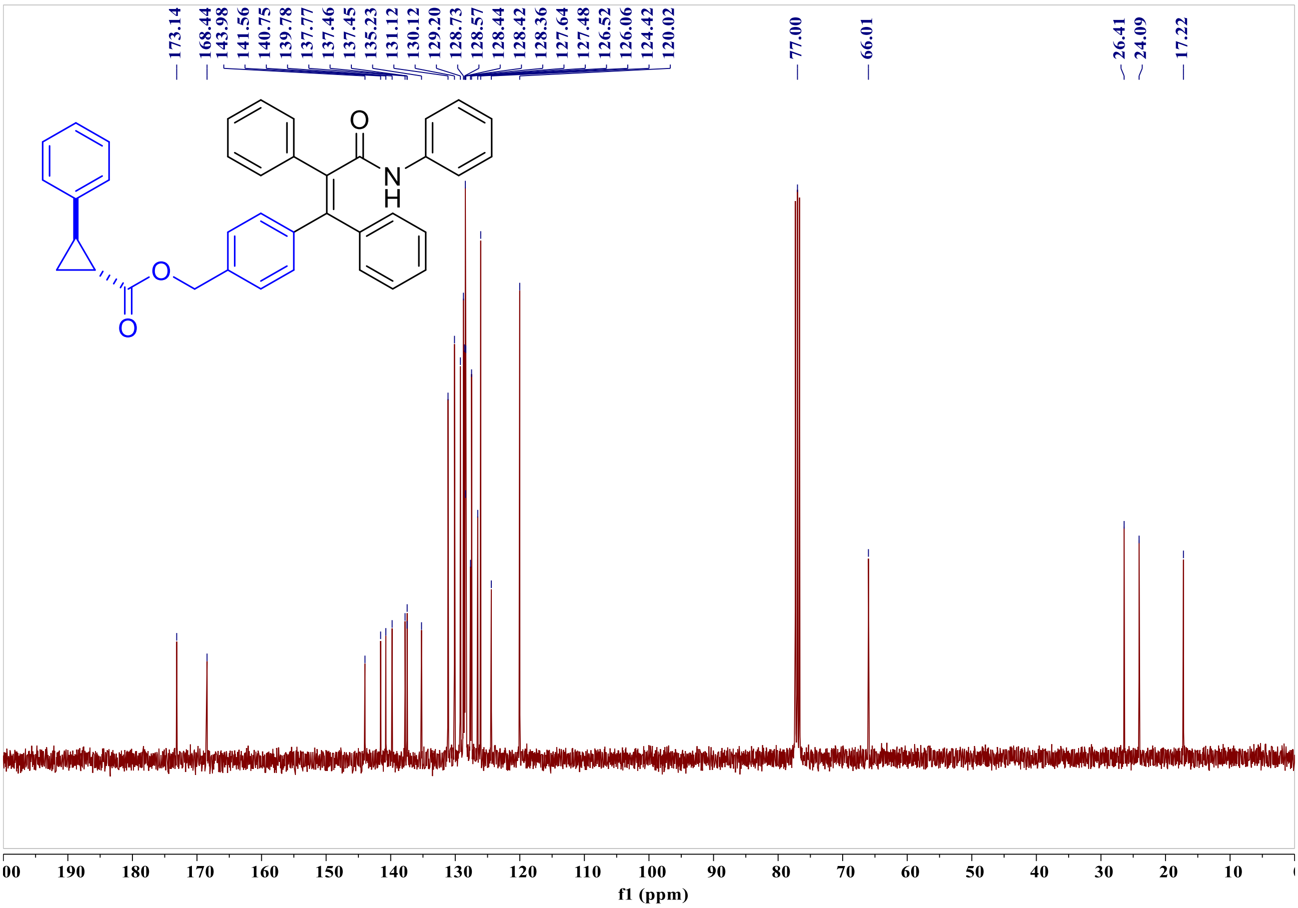
H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 24



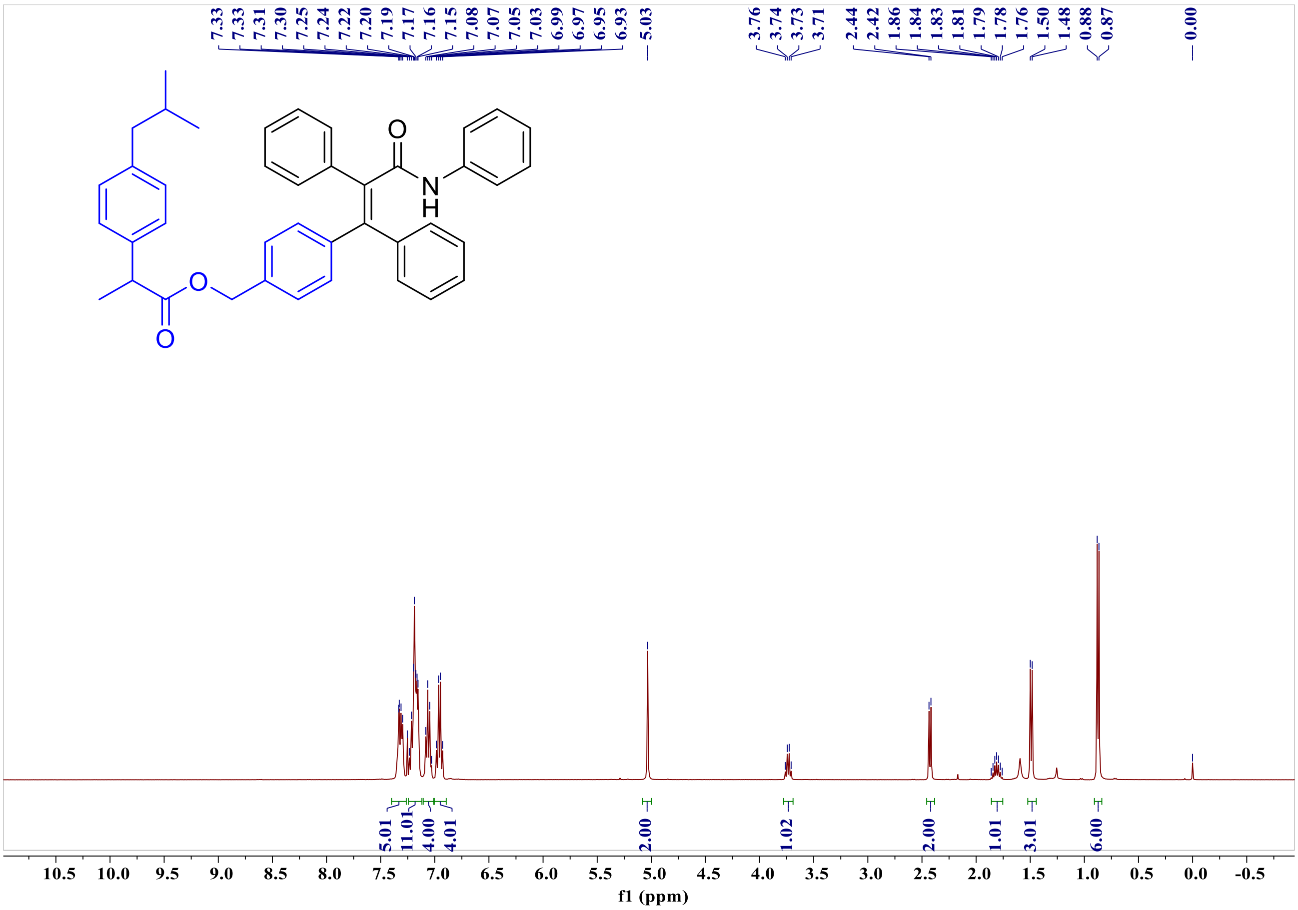


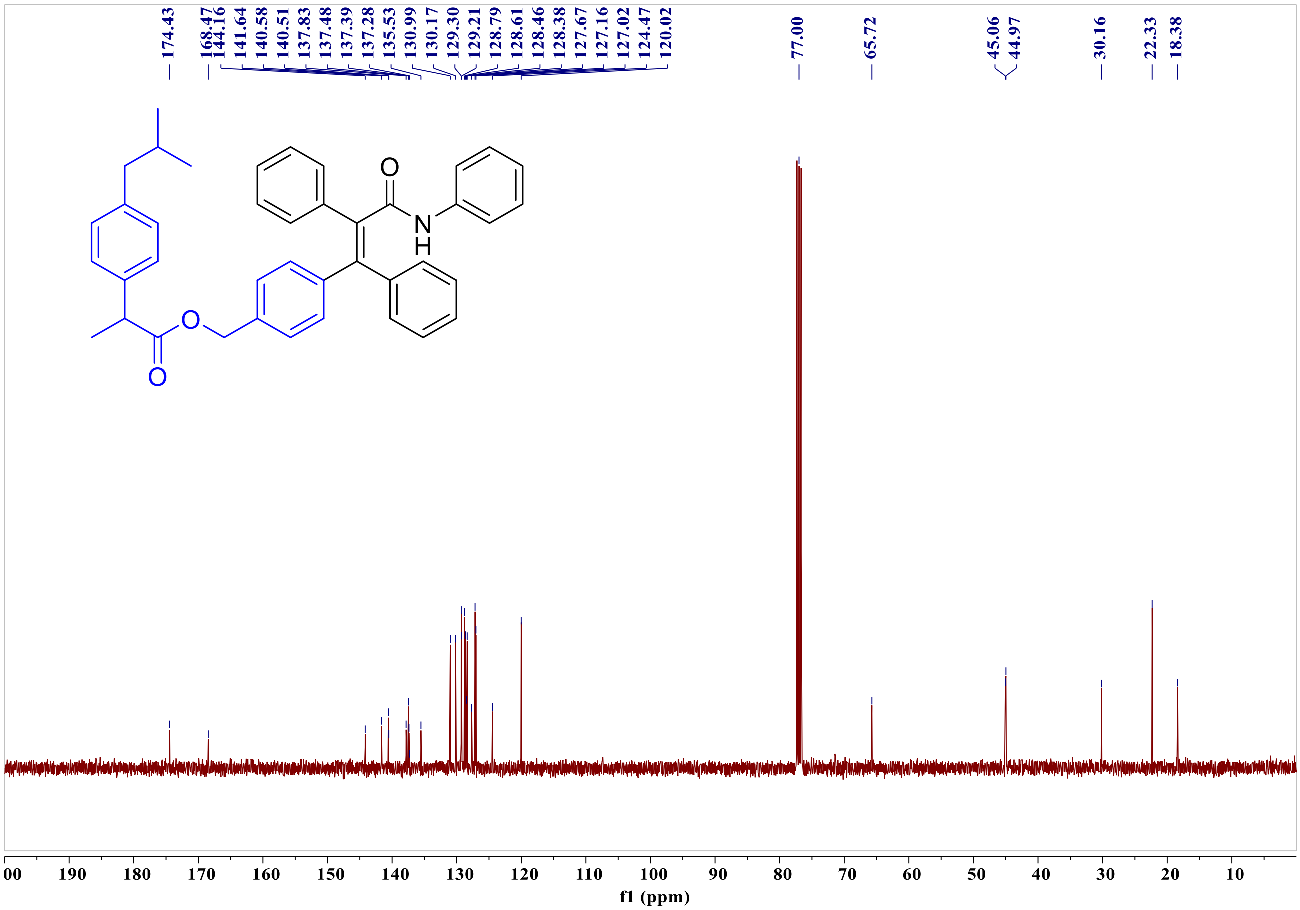
^{1}H NMR (600 MHz, CDCl$_3$) and ^{13}C NMR (100 MHz, CDCl$_3$) spectra of product 25



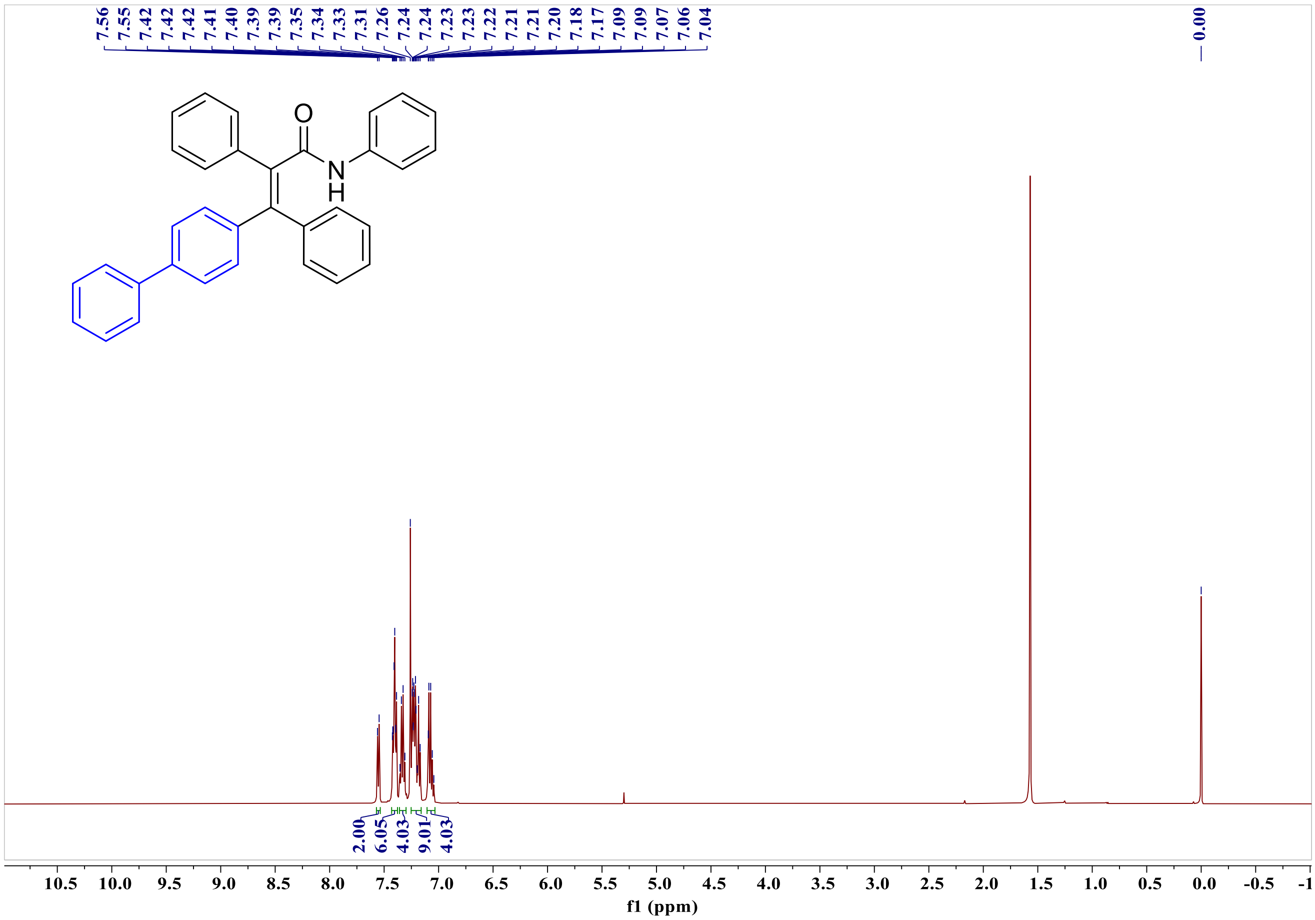


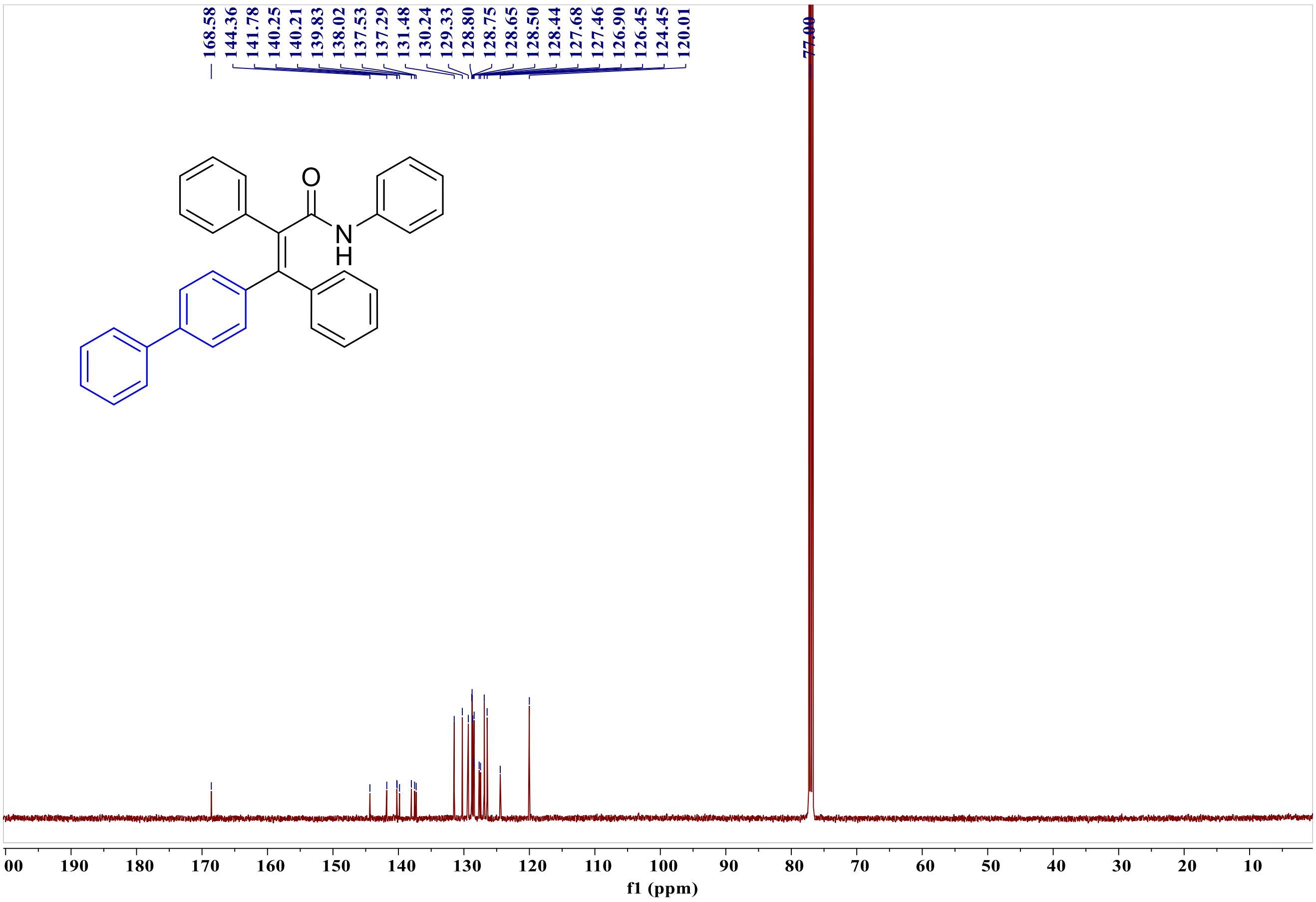
^{1}H NMR (600 MHz, CDCl$_3$) and ^{13}C NMR (100 MHz, CDCl$_3$) spectra of product 26



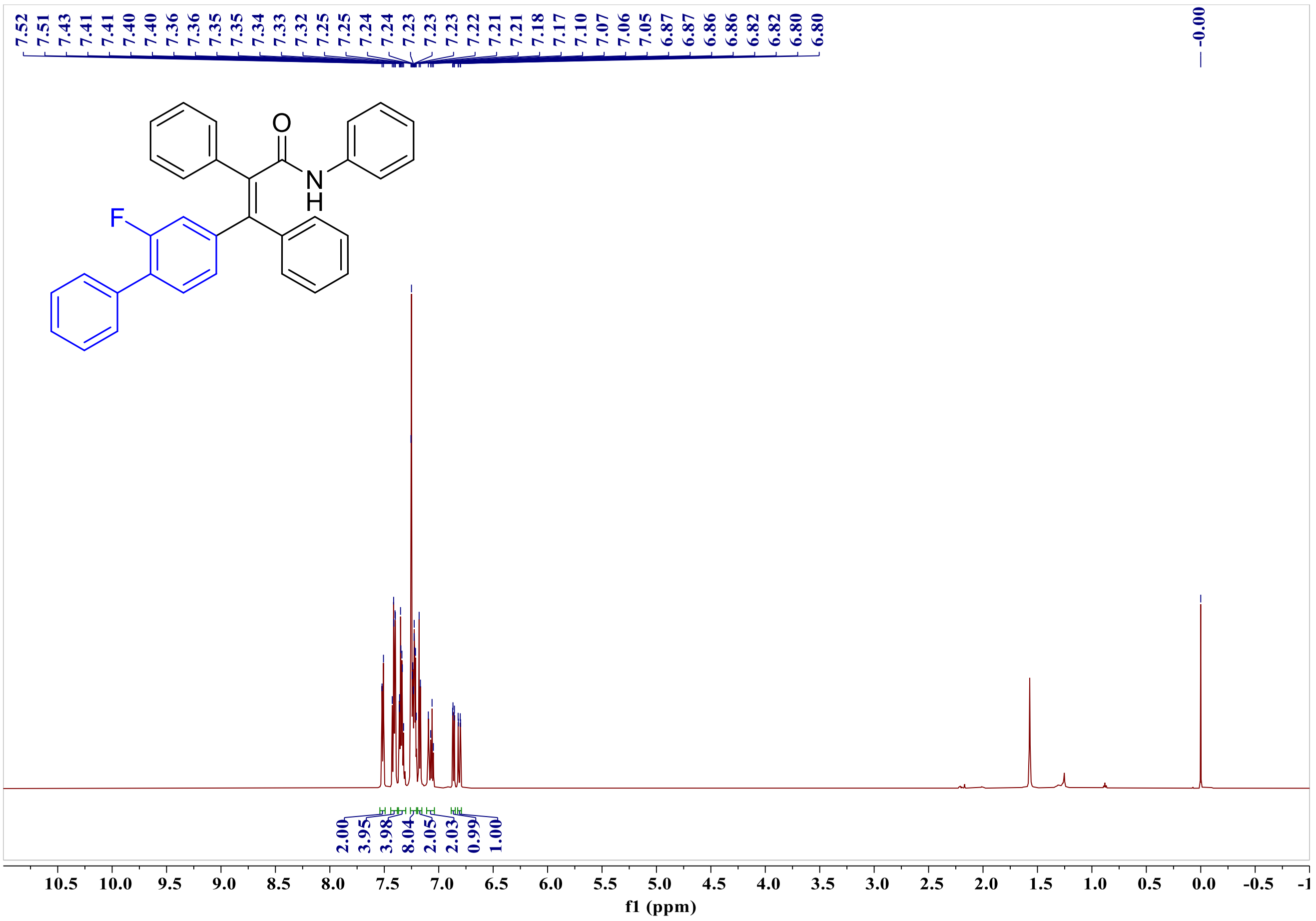


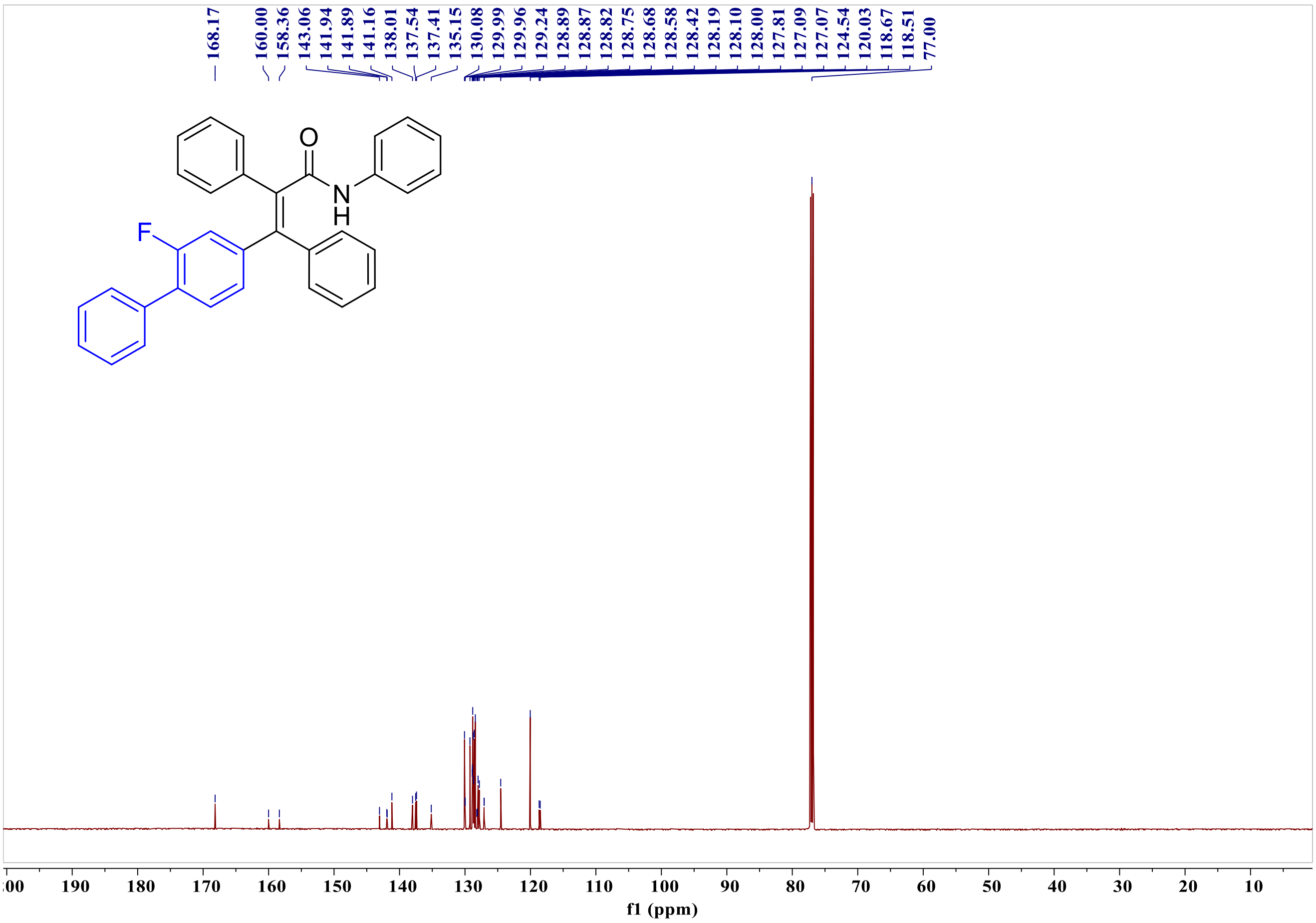
^{1}H NMR (500 MHz, CDCl$_3$) and ^{13}C NMR (125 MHz, CDCl$_3$) spectra of product 27





^{1}H NMR (600 MHz, CDCl$_3$), ^{13}C NMR (150 MHz, CDCl$_3$) and ^{19}F NMR (376 MHz, CDCl$_3$) spectra of product 28

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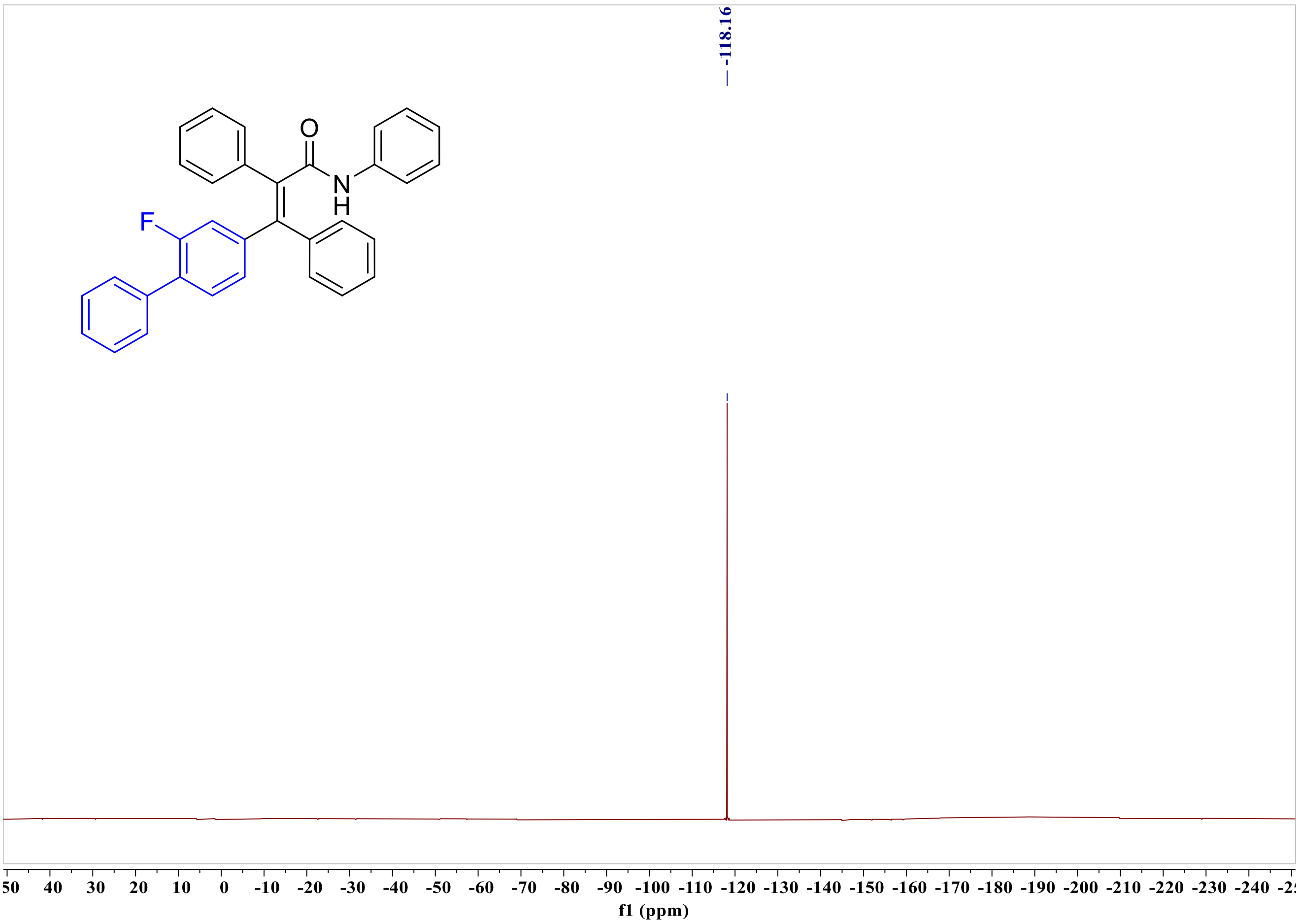
160.00
158.36
143.06
141.94
141.89
141.16
138.01
137.54
137.41
135.15
130.08
129.99
129.96
129.24
128.89
128.87
128.82
128.75
128.68
128.58
128.42
128.19
128.10
128.00
127.81
127.09
127.07
124.54
120.03
118.67
118.51
77.00
O
N
H
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


-118.16
O
N
H
F
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40
30
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10
0
-10
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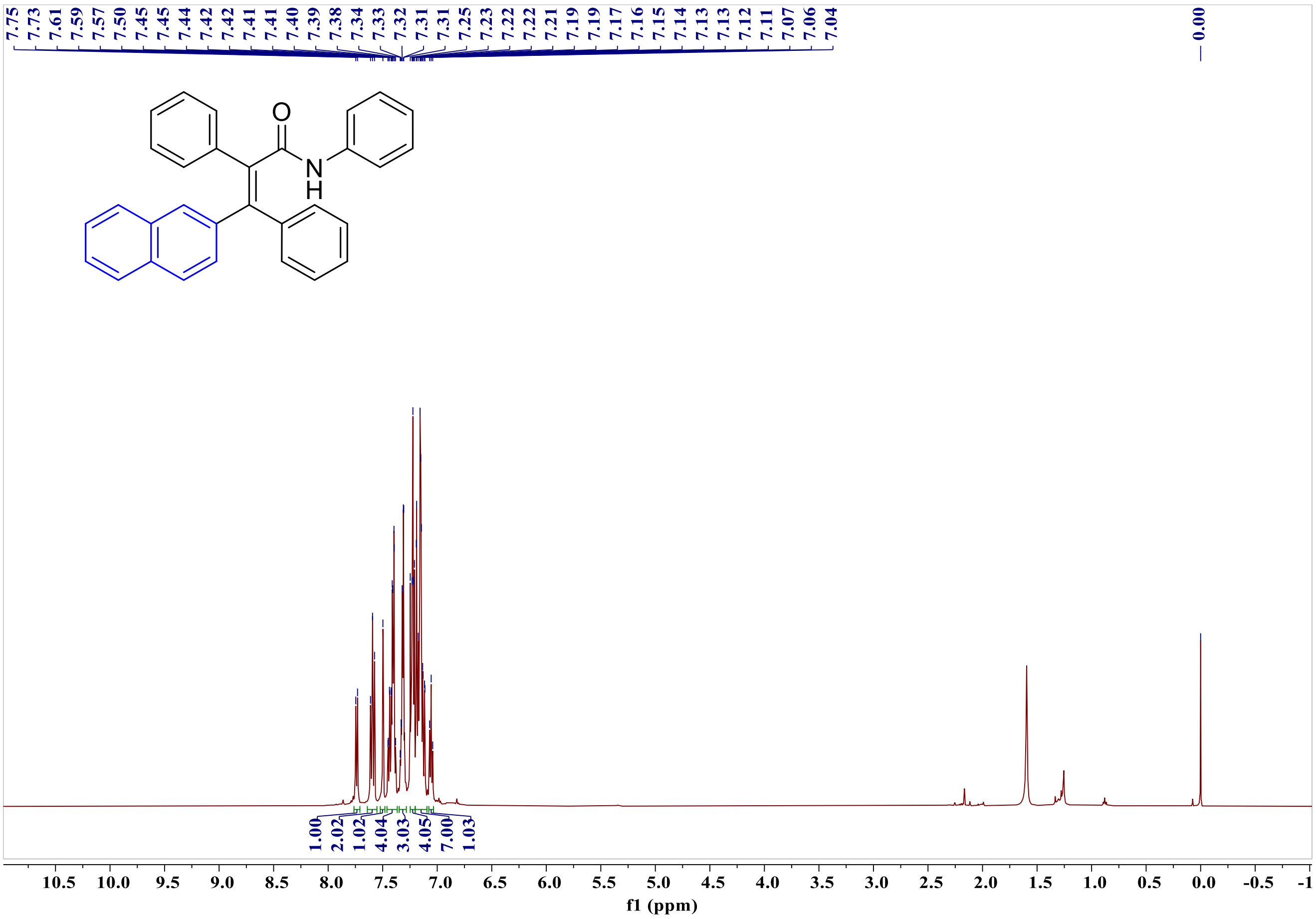
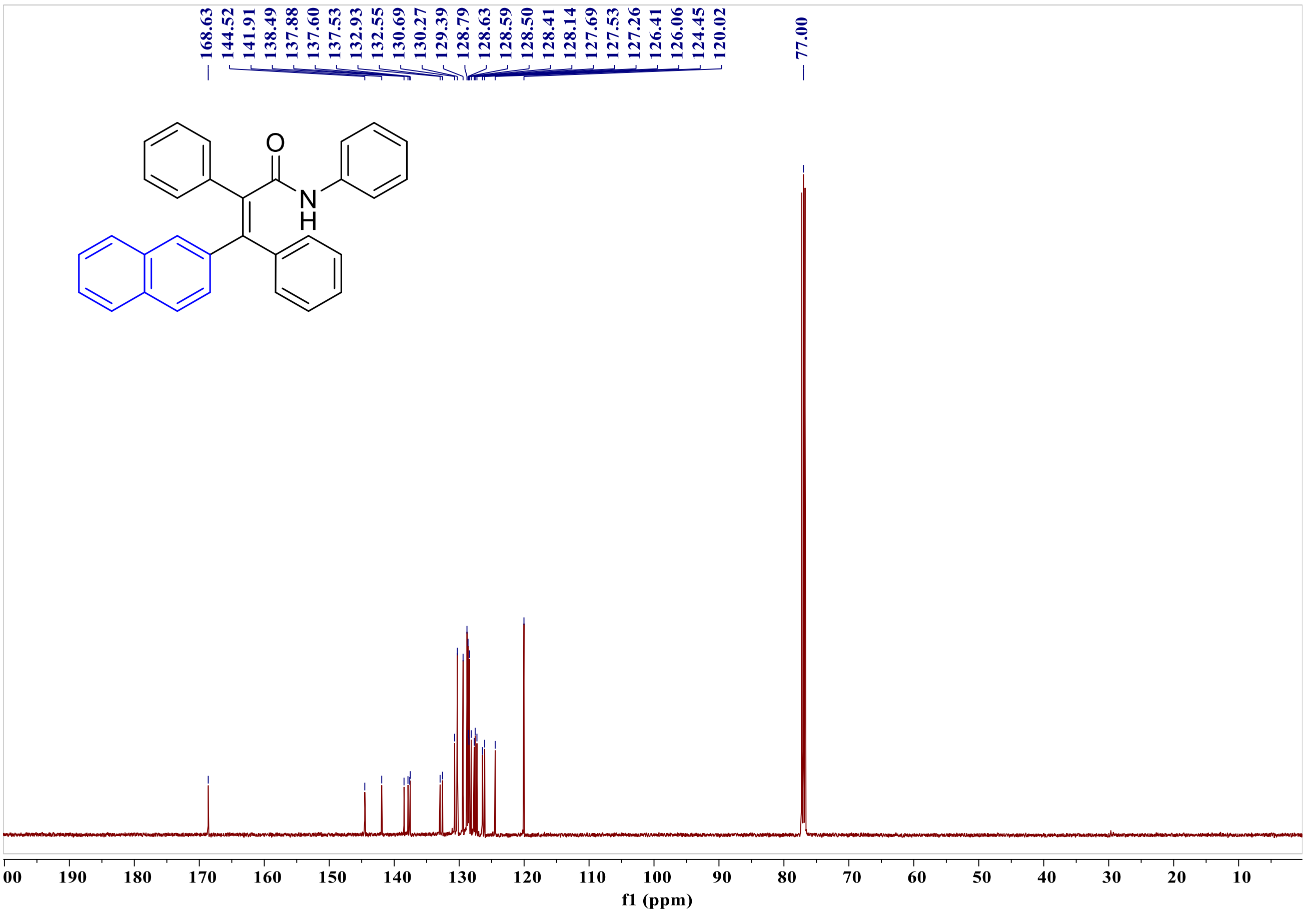
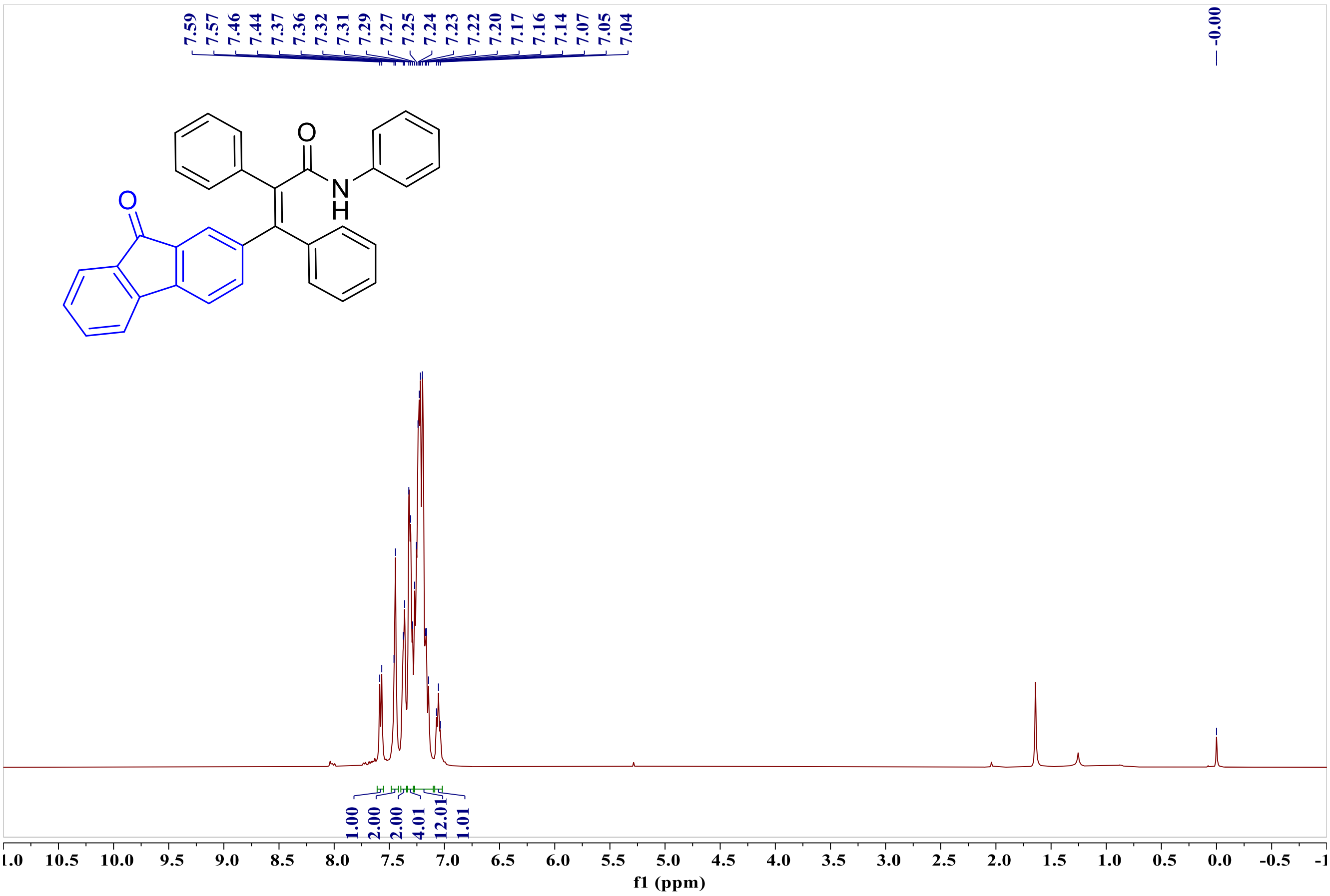
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
f1 (ppm)

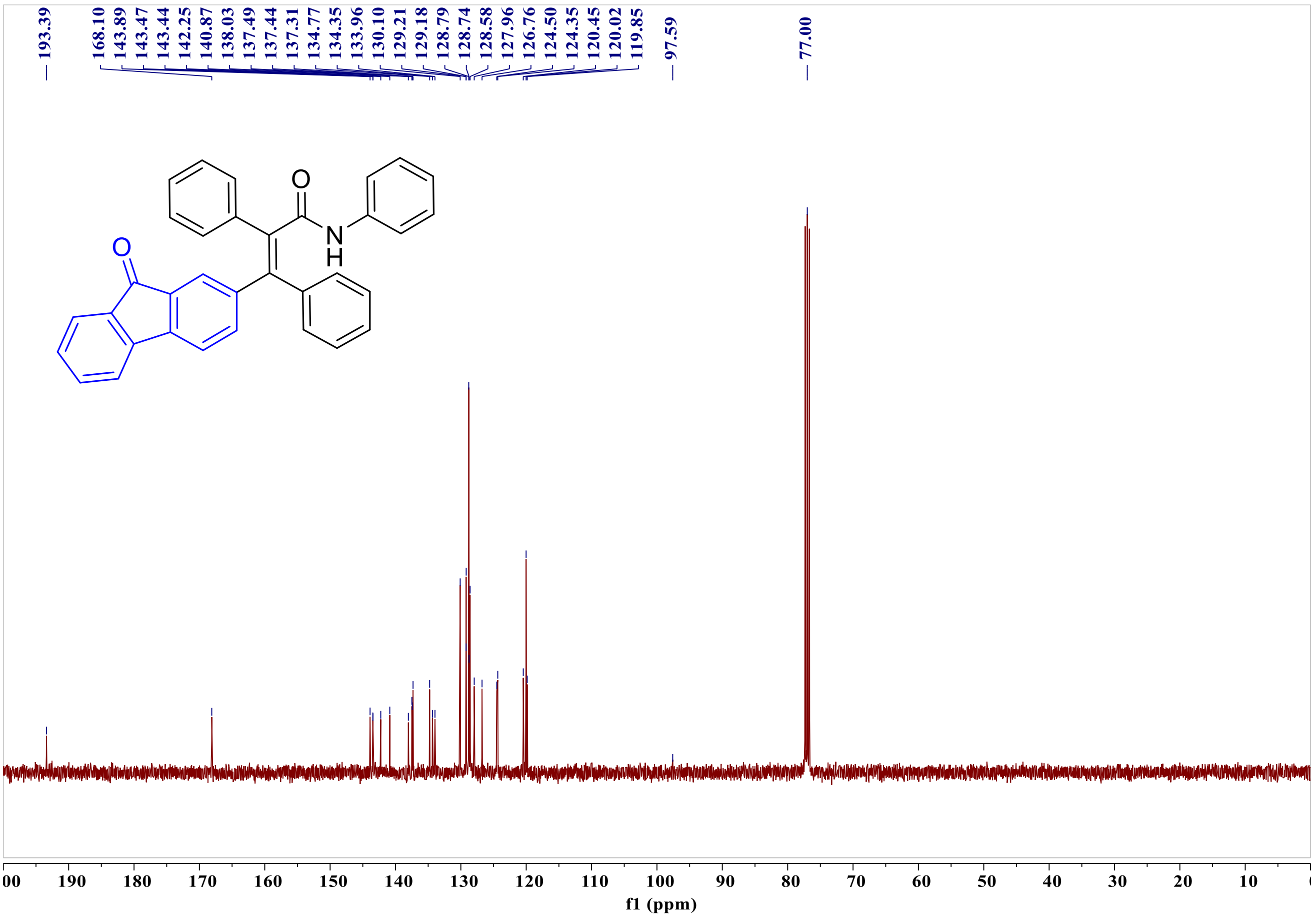
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) spectra of product 29



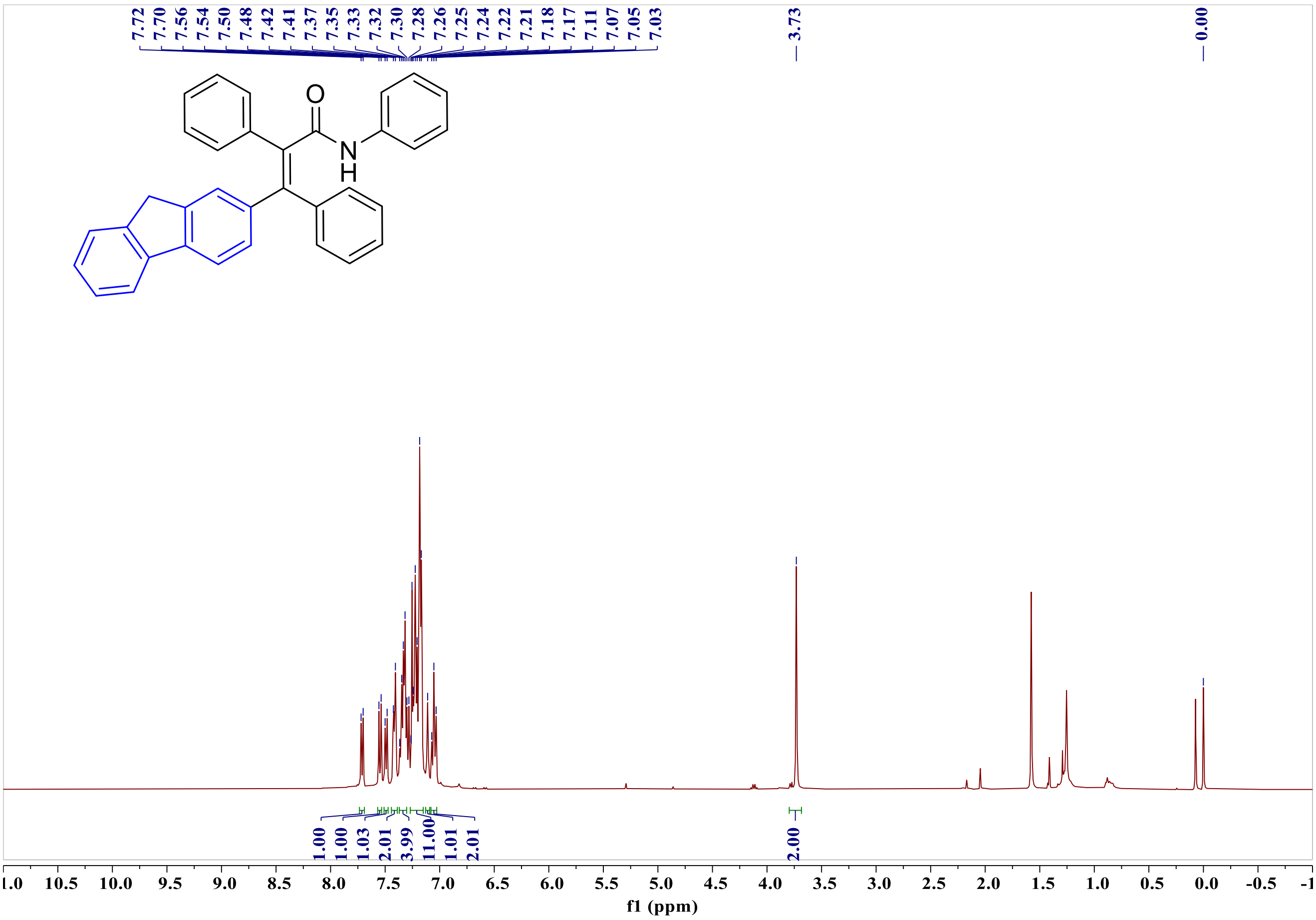


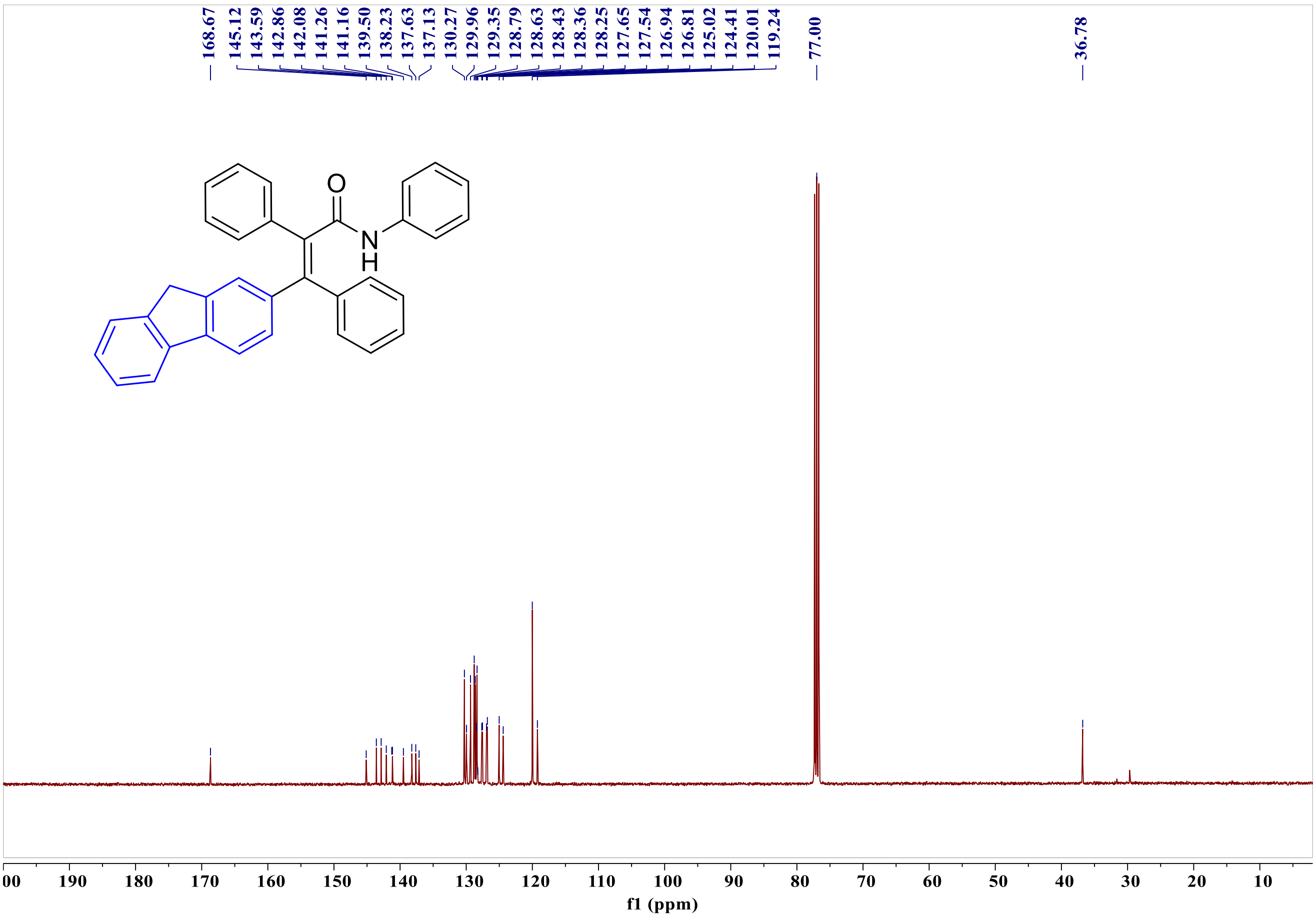
^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C NMR (100 MHz, CDCl$_3$) spectra of product 30



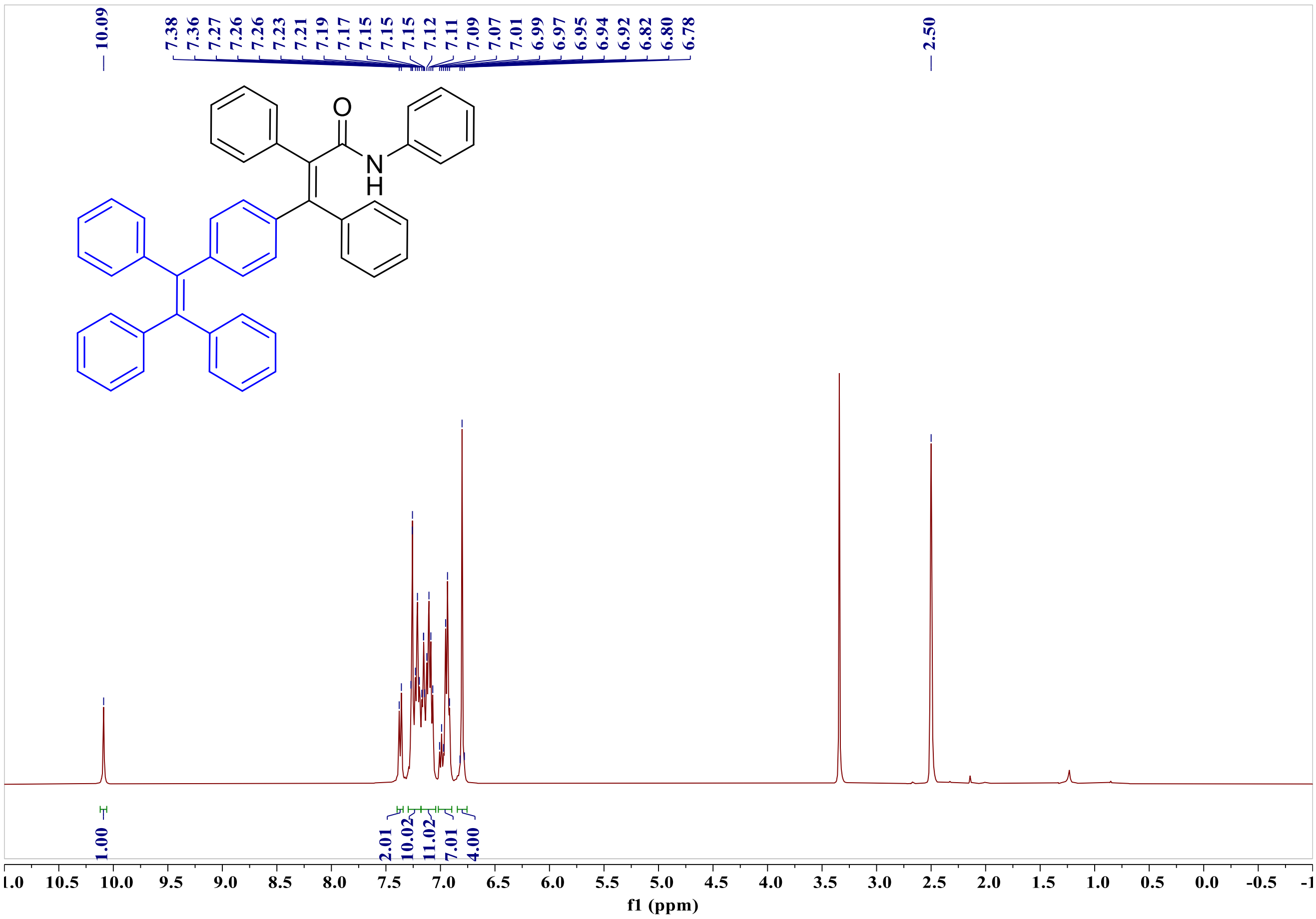


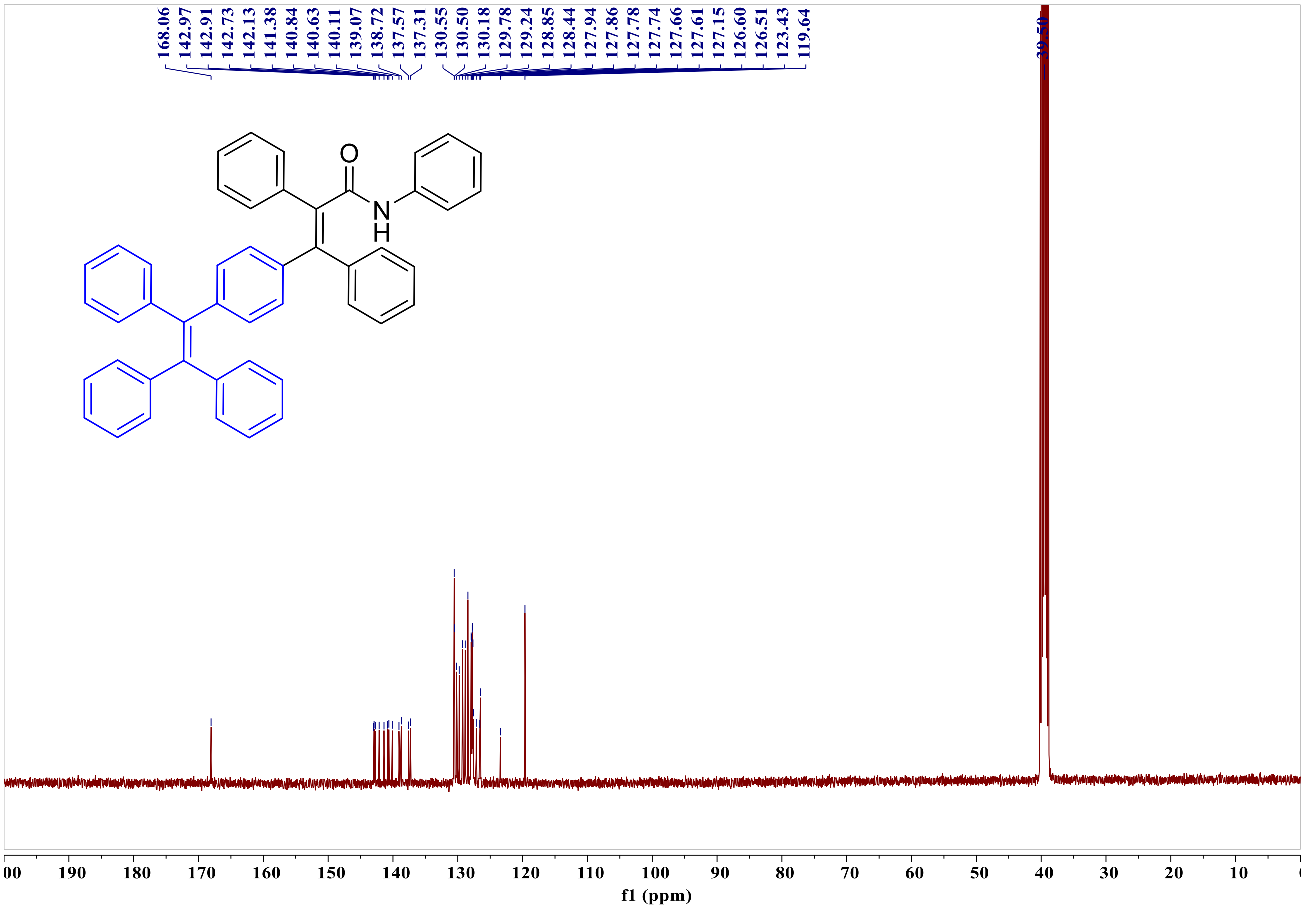
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 31



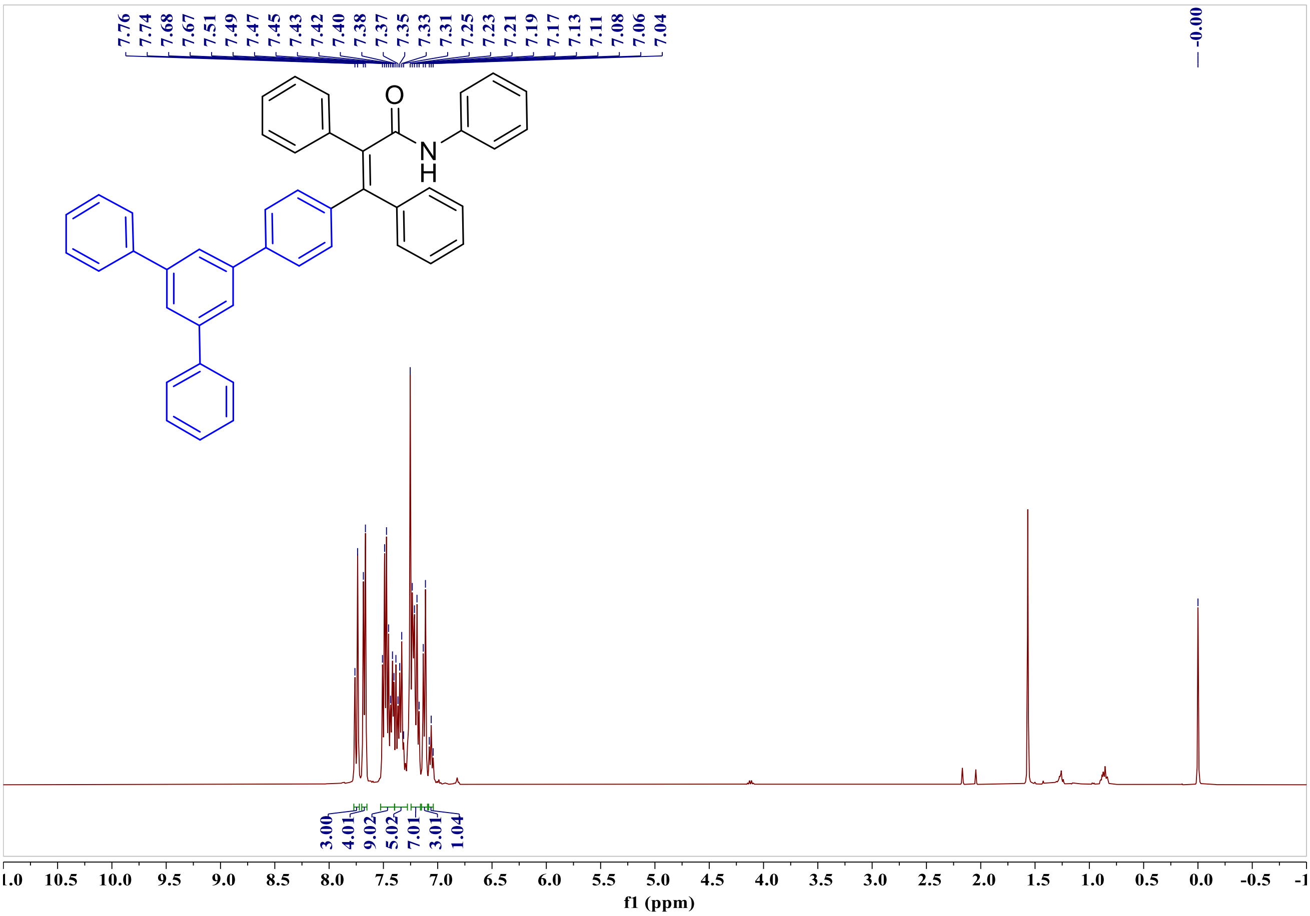


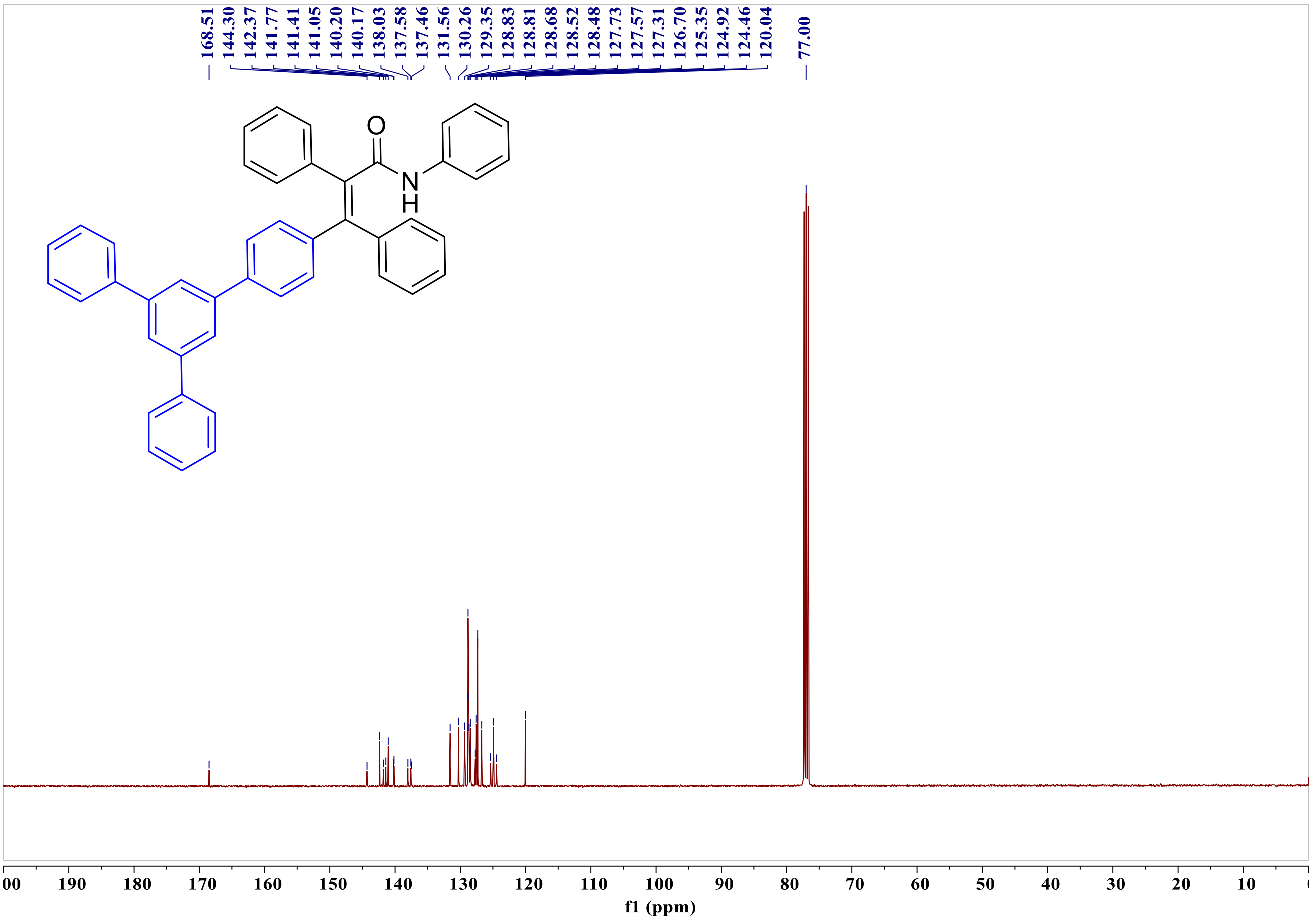
^{1}H NMR (400 MHz, DMSO-d$_6$) and ^{13}C NMR (100 MHz, DMSO-d$_6$) spectra of product 32



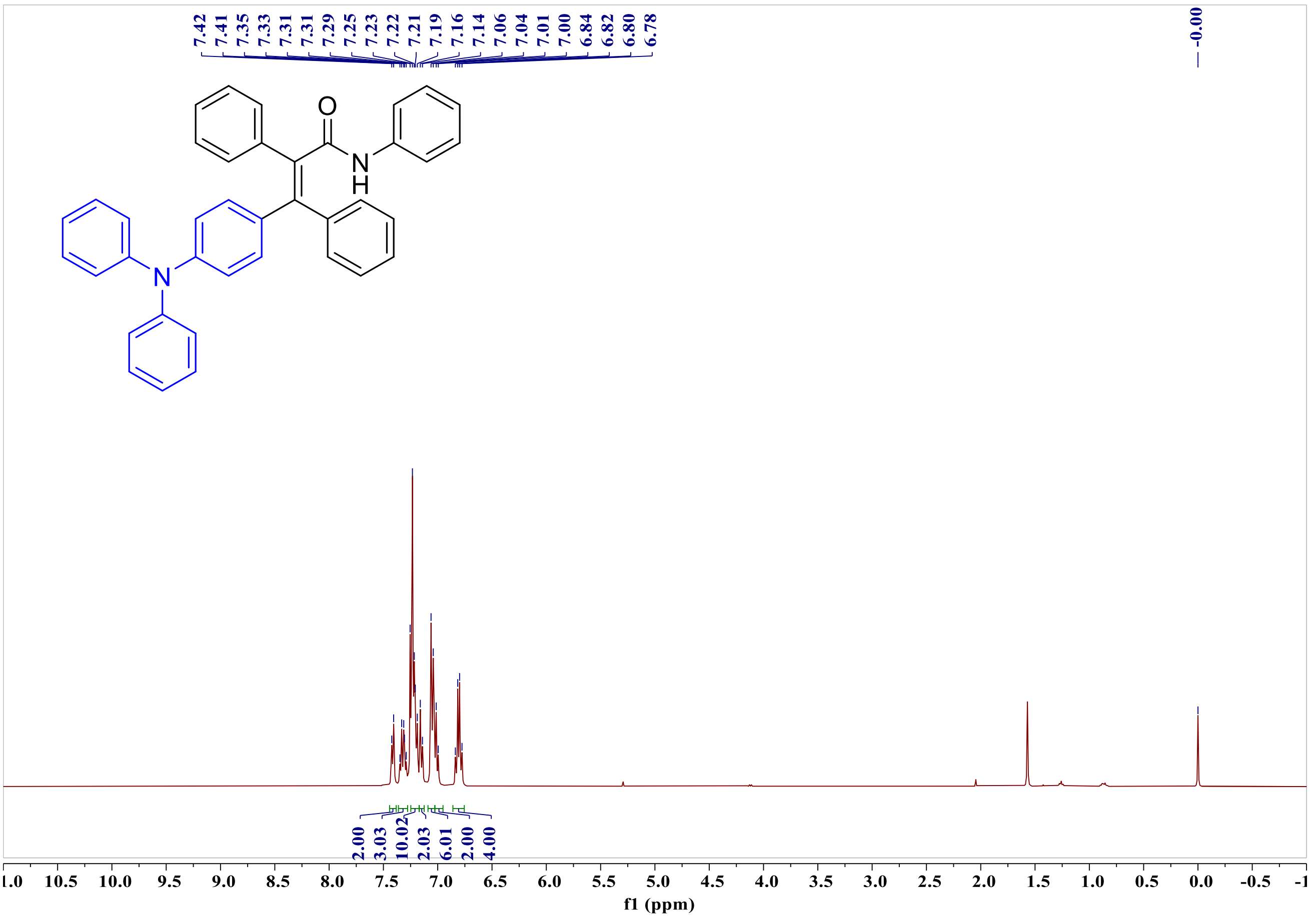


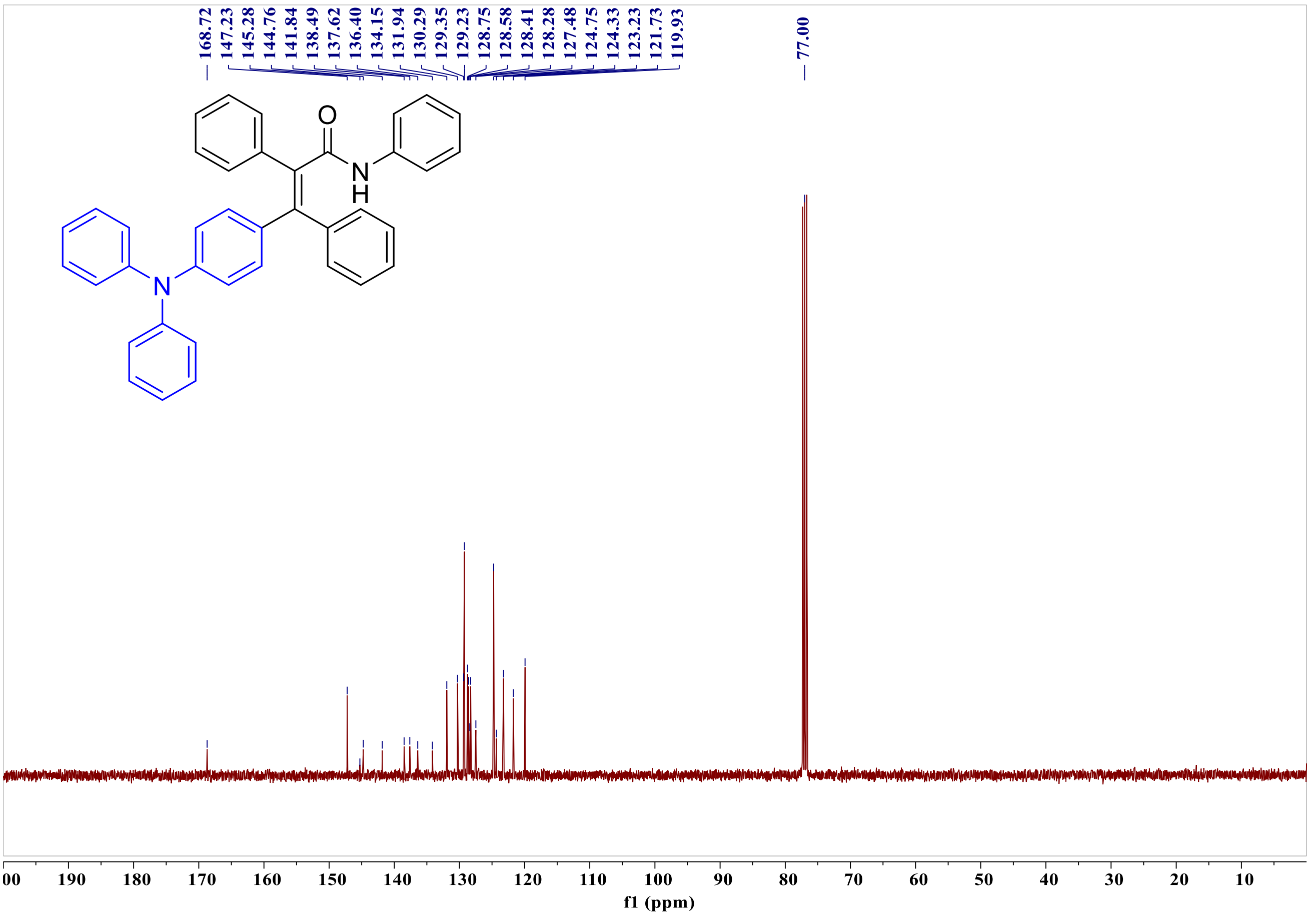
^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C NMR (100 MHz, CDCl$_3$) spectra of product 33



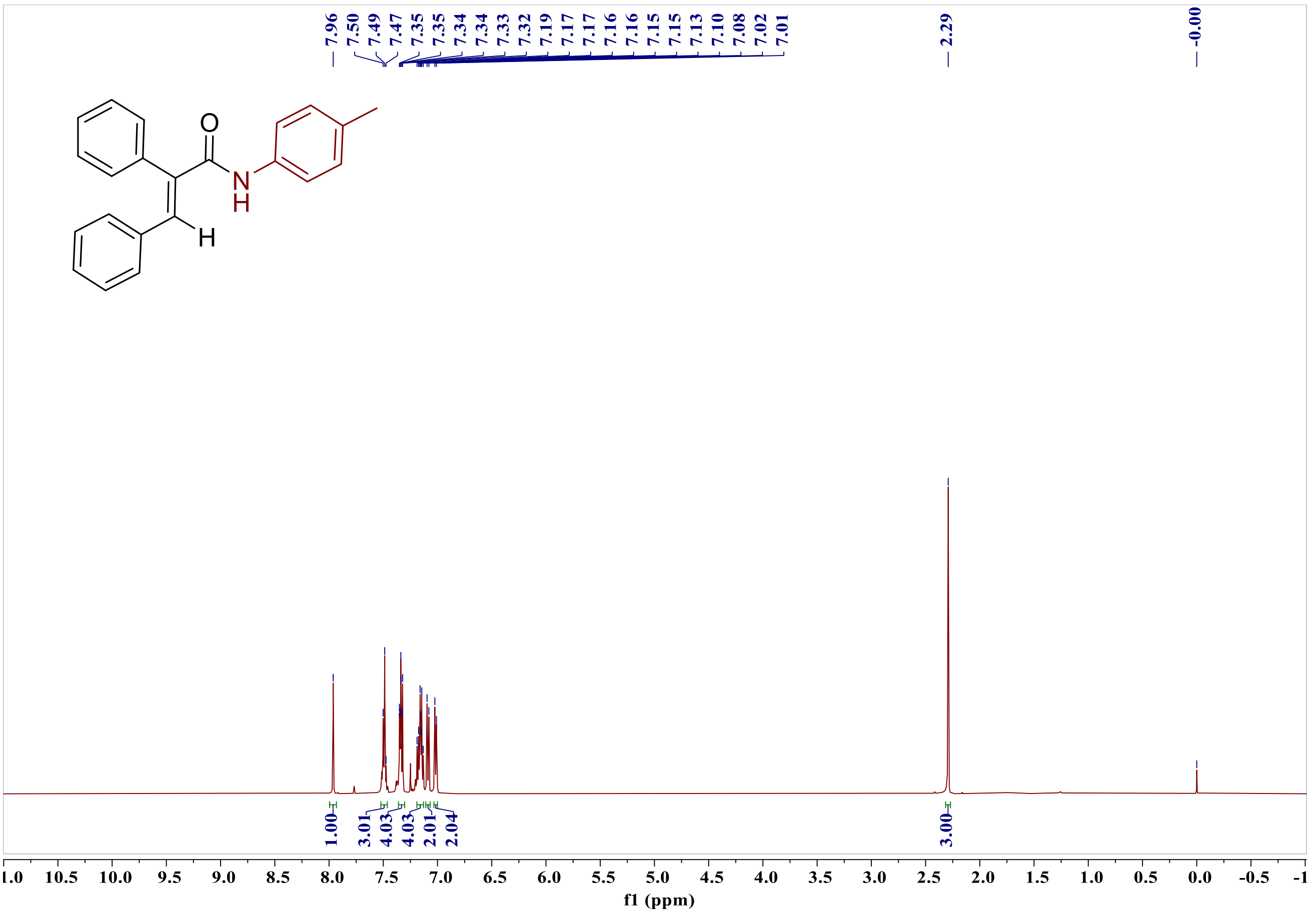


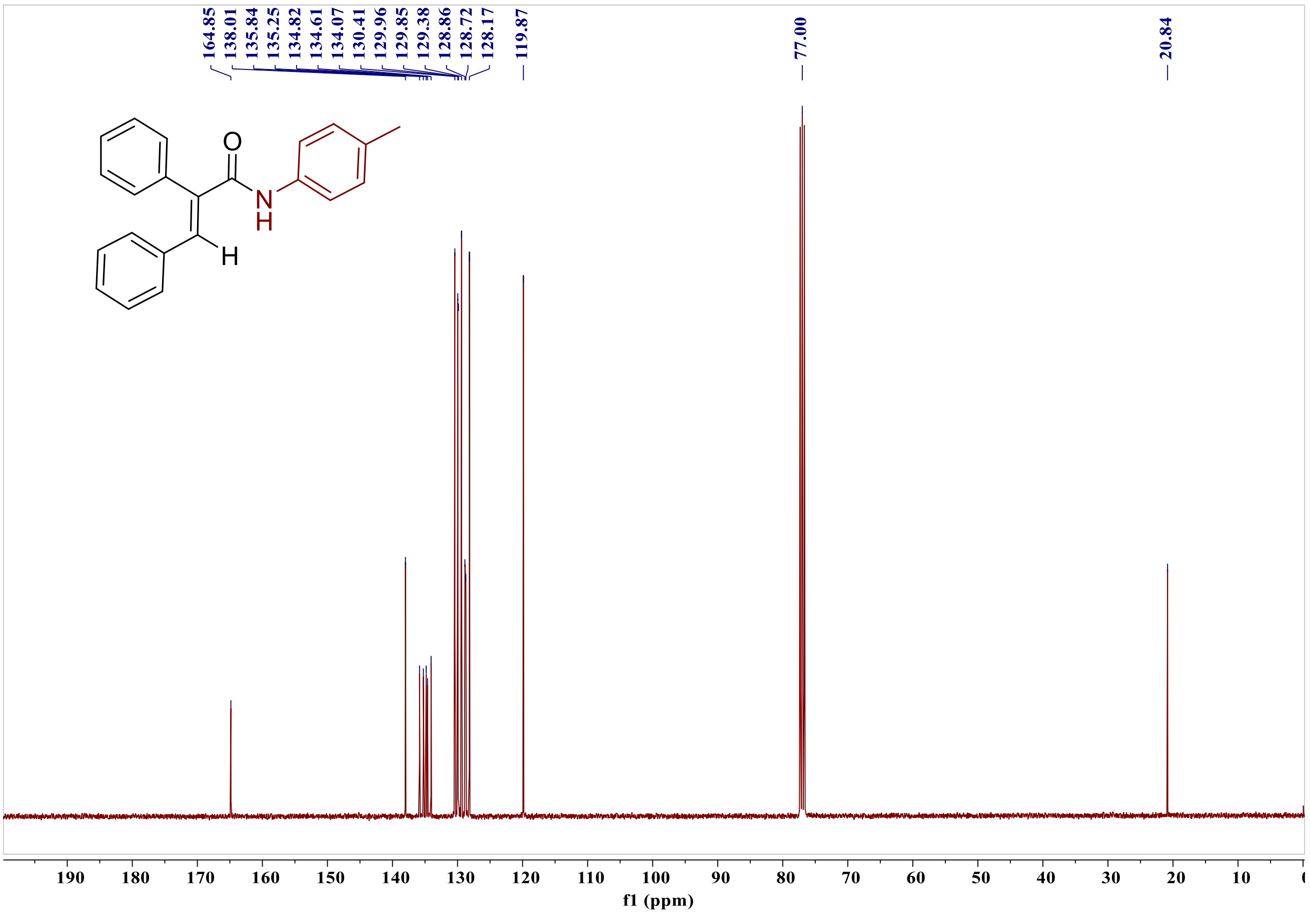
^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C NMR (100 MHz, CDCl$_3$) spectra of product 34



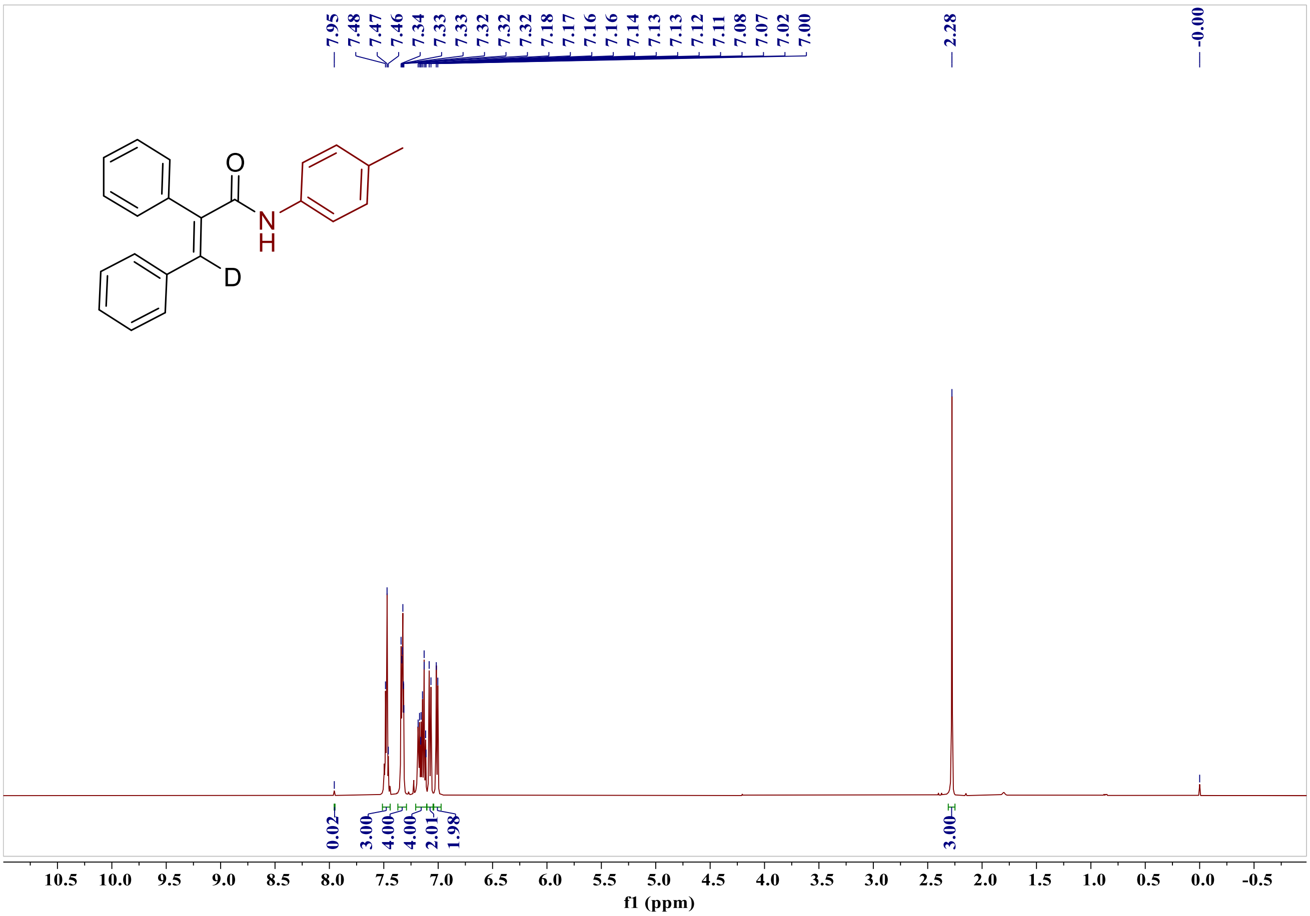


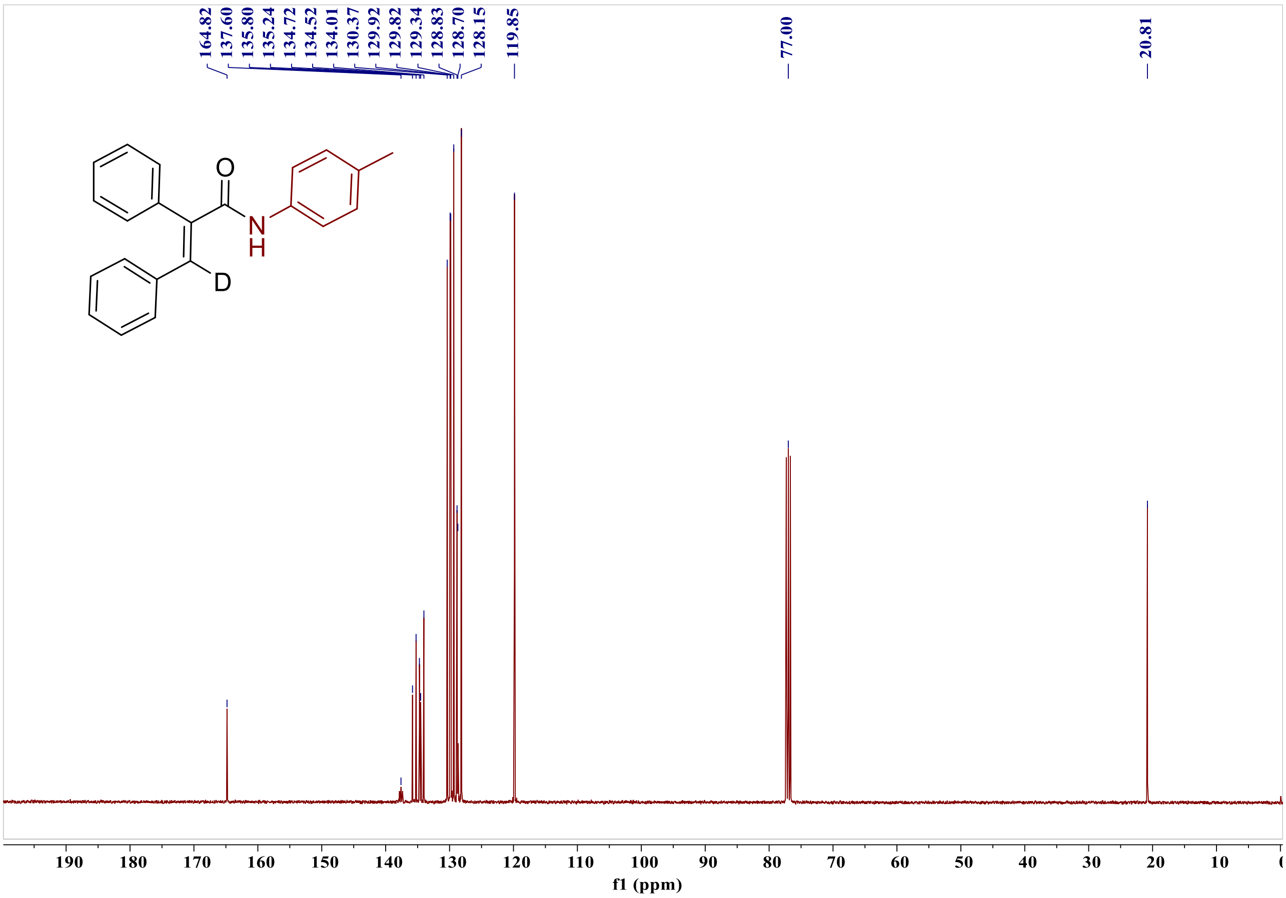
^{1}H NMR (400 MHz, CDCl$_3$) and ^{13}C NMR (100 MHz, CDCl$_3$) spectra of intermediate 35





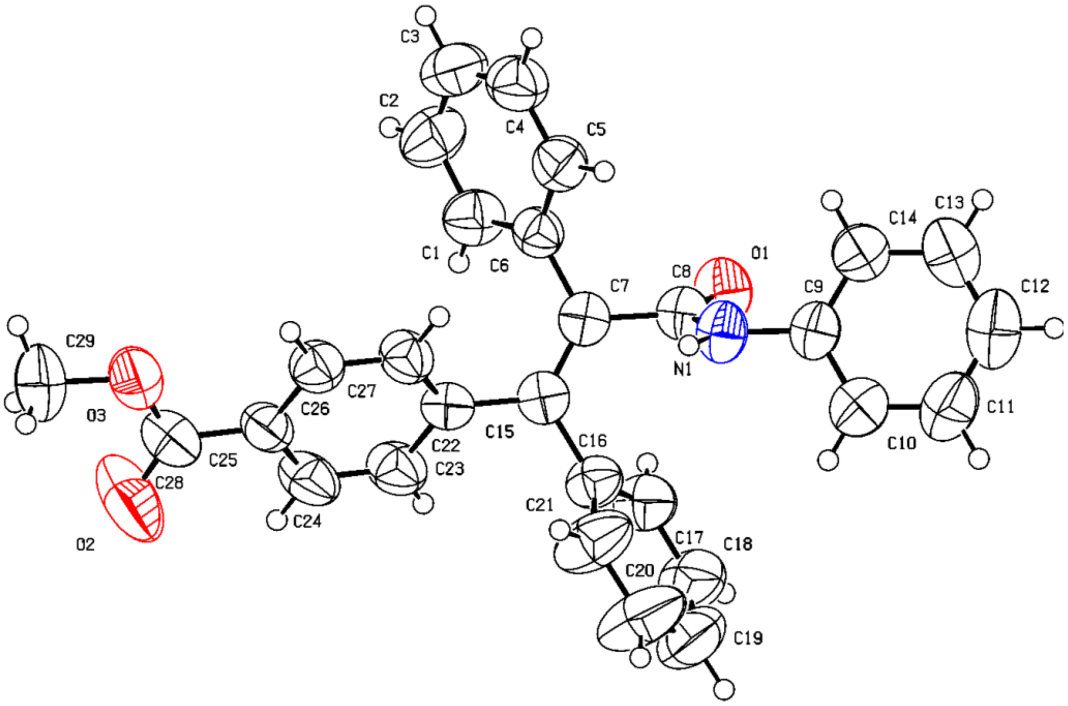
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of intermediate 35-D



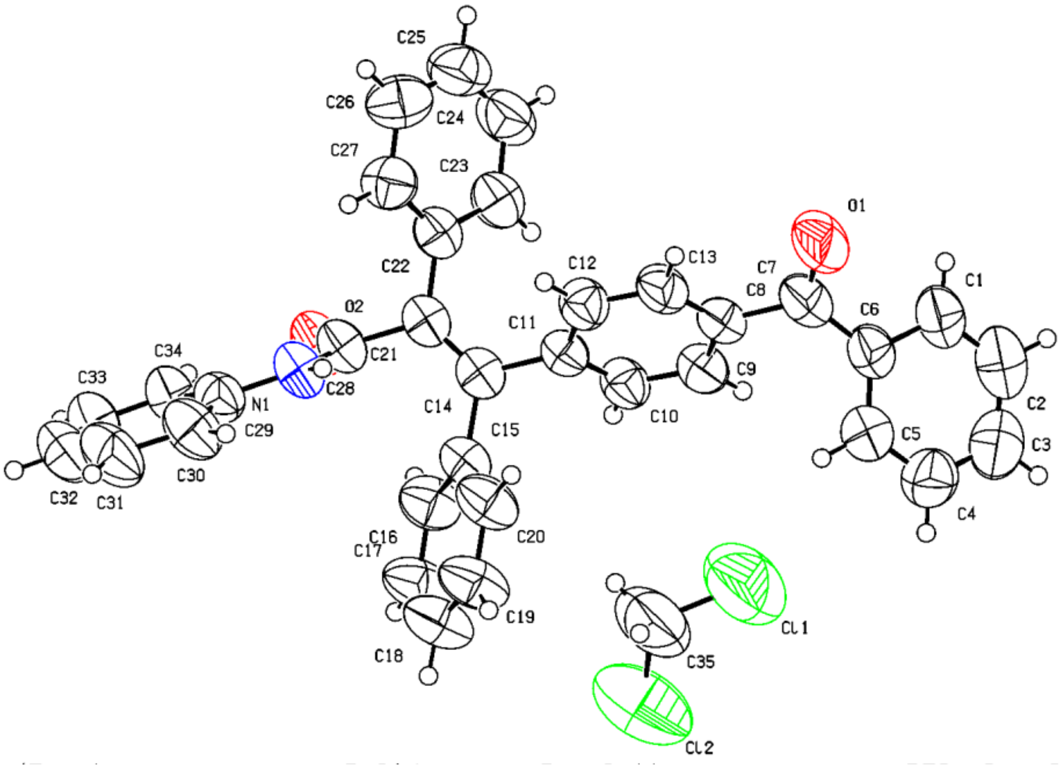


10. X-Ray data of 22, 24, 27.

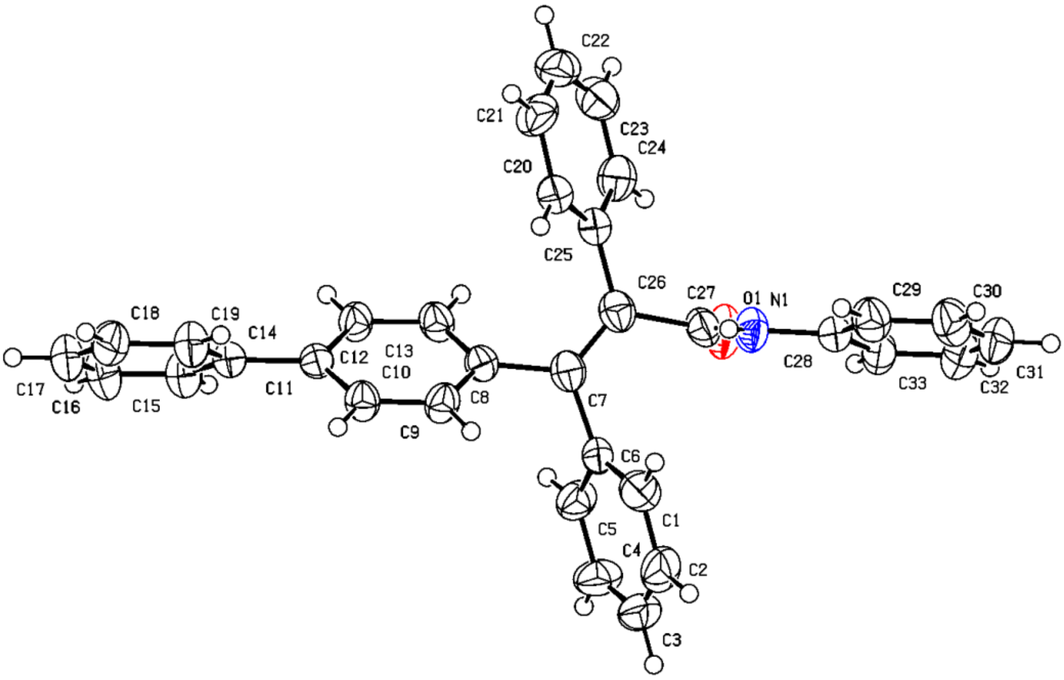
22 : CCDC : 2328203



24 : CCDC : 2328202



27 : CCDC : 2328201



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