

Synthesis of 2,5-Dihydrofurans *via* a gold(I)-Catalyzed Formal [4+1] Cycloaddition of α -Diazoesters and Propargyl Alcohols

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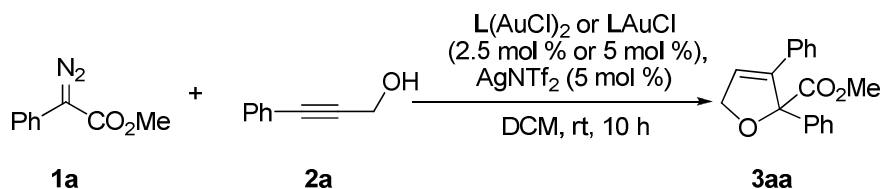
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General Information:

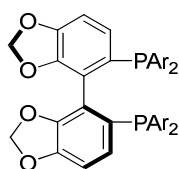
NMR spectra were recorded on a Bruker AM 400 spectrometers. Chemical shifts were referenced to residual solvent protons. Signal multiplicity as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). High resolution mass spectrometry (HRMS) was recorded using electron-spray ionization (ESI) technique. IR spectra were recorded on a Nicolet 170SX FT-IR spectrophotometer with KBr pellets. Thin-layer chromatography (TLC) was performed on silica gel 60 GF254 plate. The silica gel (size 200-300 mesh) used for the column chromatography was purchased from Qingdao Haiyang Chemistry Plant (China).

Propargyl alcohols¹ and α -diazoester² were prepared according literature procedures.

Chiral ligands for gold(I)-catalyzed formal [4+1] cycloaddition^a



entry	L	isolated yield (%)	ee (%)
1	L1	54	20
2 ^b	L1	49	20
3	L2	41	23
4	L3	44	20
5	L4	49	44
6	L5	43	35
7	L6	57	23
8	L7	39	16
9	L8	36	5



L1: (S)-SEGPHOS

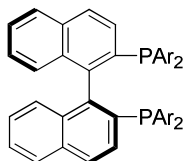
Ar = Ph

L2: (S)-DM-SEGPHOS

Ar = 3,5-(CH₃)₂C₆H₃

L3: (S)-DTBM-SEGPHOS

Ar = 3,5-(^tBu)₂-4-OCH₃C₆H₂



L4: (S)-BINAP

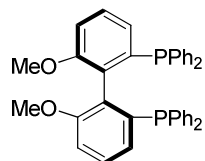
Ar = Ph

L5: (S)-T-BINAP

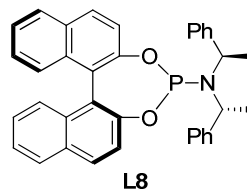
Ar = 4-CH₃C₆H₄

L6: (S)-DM-BINAP

Ar = 3,5-(CH₃)₂C₆H₃



L7: (S)-MeO-BIPHEP



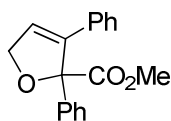
L8

^a General procedure: Chiral ligand (2.5 mol % or 5 mol %) and DMSAuCl (5 mol %) were dissolved in 1 mL of DCM and was stirred at rt for 1 h under argon. After that the solvent was removed under vacuum. AgNTf₂ (5 mol %) and 1 mL of DCM were added subsequently and the resulting solution was stirred at rt for another 5 min. To the solution, **2a** (0.3 mmol) was added, which was followed by the dropwise addition of **1a** (0.2 mmol). The resulting solution was allowed to stir at rt for 10 hours. When **1a** was consumed completely, the solvent was removed and the crude product was purified *via* column chromatography on silica gel (petroleum ether / ethyl acetate, 20:1 to 10:1) to yield **3aa**. The enantiomeric excess was determined by HPLC with a Lux 5u Cellulose-1, LC Column (90:10 hexane: 2-propanol, 1.0 mL/min, 254 nm); major enantiomer tr = 7.3 min, minor enantiomer tr = 6.8 min. ^b The reaction was carried out at 0 °C.

General procedure for gold(I)-catalyzed formal [4+1] cycloaddition of α -diazoesters (Procedure A)

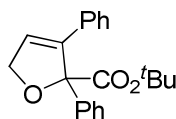
Propargyl alcohol (0.45 mmol) was added to a stirred suspension of JohnPhosAuCl (4.8 mg, 0.009 mmol) and AgSbF₆ (3.1 mg, 0.009 mmol) in 2 mL of 1,2-dichloroethane at room temperature. Subsequently, the solution of α -diazoester (0.3 mmol) in 1 mL of 1,2-dichloroethane was introduced into the reaction mixture by a syringe in 5 minutes. The resulting mixture was continually stirred at room temperature until α -diazoester was consumed completely determined by TLC analysis. After that the solvent was removed and the crude product was purified *via* column chromatography on silica gel (petroleum ether / ethyl acetate, 20:1 to 10:1) to yield 2,5-dihydrofuran in good yield.

Methyl 2,3-diphenyl-2,5-dihydrofuran-2-carboxylate(3aa)



3aa was obtained following the Procedure A from **1a** (52.9 mg, 0.3 mmol) and **2a** (59.5 mg, 0.45 mmol). Yield: 67.3 mg, 80%, yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.37\text{-}7.32$ (m, 5 H), $7.27\text{-}7.20$ (m, 5 H), 6.50 (t, 1 H, $J = 2$ Hz), 5.01-4.91 (m, 2 H), 3.78 (s, 3 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 171.9, 141.0, 139.3, 132.5, 128.3, 128.2, 127.9, 127.8, 127.8, 127.3, 126.8, 94.7, 74.7, 52.5$ ppm; IR (KBr): $\tilde{\nu} = 2949, 2850, 2029, 1625, 1392, 1249, 1078, 908, 757, 622, 482$ cm^{-1} ; HRMS (ESI): calculated for $\text{C}_{18}\text{H}_{16}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 303.0997, found 303.0975.

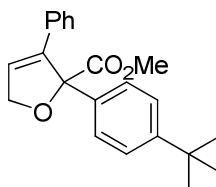
tert-Butyl 2,3-diphenyl-2,5-dihydrofuran-2-carboxylate(3ba)



3ba was obtained following the Procedure A from **1b** (65.5 mg, 0.3 mmol) and **2a** (59.5 mg, 0.45 mmol). Yield: 66.7 mg, 69%, yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.47\text{-}7.18$ (m, 10 H), 6.47 (s, 1 H), 4.97-4.88 (m, 2 H), 1.33 (s, 9 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 170.2, 141.3, 139.8, 133.1, 128.1, 128.07, 127.98, 127.7, 127.65, 127.60, 126.9, 95.0, 82.2, 74.6, 27.8$ ppm; IR (KBr): $\tilde{\nu} = 2977, 2850, 2029, 1625, 1382, 1257, 1161, 1082, 975, 622, 482$ cm^{-1} ; HRMS (ESI): calculated for $\text{C}_{21}\text{H}_{22}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 345.1467, found 345.1465.

For asymmetric catalysis, the enantiomeric excess was determined by HPLC with a Lux 5u Cellulose-1, LC Column (95:5 hexane: 2-propanol, 1.0 mL/min, 254 nm); major enantiomer $t_r = 12.6$ min, minor enantiomer $t_r = 11.6$ min; (20% ee).

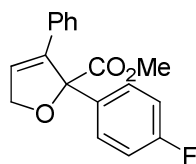
Methyl 2-(4-*tert*-butylphenyl)-3-phenyl-2,5-dihydrofuran-2-carboxylate(3ca)



3ca was obtained following the Procedure A from **1c** (69.7 mg, 0.3 mmol) and **2a**

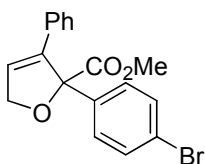
(59.5 mg, 0.45 mmol). Yield: 81.8 mg, 81%, yellow oil; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.34\text{--}7.20$ (m, 9 H), 6.49 (s, 1 H), 4.97–4.87 (m, 2 H), 3.74 (s, 3 H), 1.29 (s, 9 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 172.2, 151.1, 140.8, 136.2, 132.5, 127.9, 127.8, 127.7, 127.0, 126.8, 125.1, 94.5, 74.6, 52.4, 34.4, 31.2$ ppm; IR (KBr): $\tilde{\nu} = 2960, 2312, 1639, 1517, 686, 534$ cm^{-1} ; HRMS (ESI): calculated for $\text{C}_{22}\text{H}_{24}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 359.1623, found 359.1596.

Methyl 2-(4-fluorophenyl)-3-phenyl-2,5-dihydrofuran-2-carboxylate(3ea)



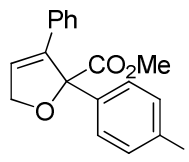
3ea was obtained following the Procedure A from **1e** (58.2 mg, 0.3 mmol) and **2a** (59.5 mg, 0.45 mmol). Yield: 63.5 mg, 71% , pale yellow oil; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.35$ (t, 2 H, $J = 5.6$ Hz), 7.23 (s, 5 H), 6.99 (t, 2 H, $J = 8.4$ Hz), 6.48 (s, 1H), 4.99–4.89 (m, 2 H), 3.77 (s, 3 H); ^{13}C NMR(100 MHz, CDCl_3): $\delta = 171.8, 162.5$ ($J_{\text{F-C}} = 247$ Hz), 141.0, 135.1 ($J_{\text{F-C}} = 3.1$ Hz), 132.3, 129.3 ($J_{\text{F-C}} = 8$ Hz), 128.1, 128.0, 127.7, 126.9, 115.0 ($J_{\text{F-C}} = 21$ Hz), 94.0, 74.8, 52.6 ppm; IR (KBr): $\tilde{\nu} = 2952, 2852, 2029, 1737, 1623, 1504, 1396, 1226, 1078, 831, 750, 621, 482$ cm^{-1} ; HRMS (ESI): calculated for $\text{C}_{18}\text{H}_{15}\text{FO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 321.0903, found 321.0902.

Methyl 2-(4-bromophenyl)-3-phenyl-2,5-dihydrofuran-2-carboxylate(3fa)



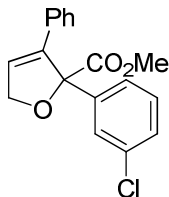
3fa was obtained following the Procedure A from **1f** (76.5 mg, 0.3 mmol) and **2a** (59.5 mg, 0.45 mmol). Yield: 82.9 mg, 77%, yellow oil; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.43$ (d, 2 H, $J = 8.4$ Hz), 7.25–7.22 (m, 7 H), 6.46 (s, 1 H), 5.00–4.89 (m, 2 H), 3.77 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 171.6, 140.8, 138.3, 132.3, 131.2, 129.1, 128.1, 128.0, 127.7, 127.0, 122.4, 94.0, 74.9, 52.6$ ppm; IR (KBr): $\tilde{\nu} = 3062, 2949, 2852, 1737, 1591, 1488, 1396, 1253, 1076, 906, 756, 696$ cm^{-1} ; HRMS (ESI): calculated for $\text{C}_{18}\text{H}_{15}\text{BrO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 381.0102, found 381.0076.

Methyl 2-(4-iodophenyl)-3-phenyl-2,5-dihydrofuran-2-carboxylate(3ga)



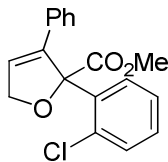
3ga was obtained following the Procedure A from **1g** (90.6 mg, 0.3 mmol) and **2a** (59.5 mg, 0.45 mmol). Yield: 97.5 mg, 80%, yellow oil; ^1H NMR (400 MHz, CDCl_3): δ = 7.63 (d, 2 H, J = 8.2 Hz), 7.23 (s, 5 H), 7.11 (d, 2 H, J = 8.2 Hz), 6.46 (s, 1 H), 4.99-4.89 (m, 2 H), 3.77 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 171.6, 140.8, 139.0, 137.2, 132.2, 129.3, 128.1, 128.0, 127.7, 127.1, 94.4, 94.1, 75.0, 52.7 ppm; IR (KBr): $\tilde{\nu}$ = 2850, 2029, 1625, 1392, 1253, 1078, 910, 622, 482 cm^{-1} ; HRMS (ESI): calculated for $\text{C}_{18}\text{H}_{15}\text{IO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 428.9964, found 428.9965.

Methyl 2-(3-chlorophenyl)-3-phenyl-2,5-dihydrofuran-2-carboxylate(3ha)



3ha was obtained following the Procedure A from **1h** (63.2 mg, 0.3 mmol) and **2a** (59.5 mg, 0.45 mmol). Yield: 64.2 mg, 68%, yellow oil; ^1H NMR (400 MHz, CDCl_3): δ = 7.40 (s, 1 H), 7.27-7.21 (m, 8 H), 6.46 (s, 1 H), 5.00-4.91 (m, 2 H), 3.77 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 171.4, 141.3, 140.8, 134.1, 132.2, 129.3, 128.4, 128.1, 128.1, 127.8, 127.5, 127.1, 125.5, 94.0, 75.0, 52.7 ppm; IR (KBr): $\tilde{\nu}$ = 2304, 1739, 1623, 1215, 1076, 767, 460 cm^{-1} ; HRMS (ESI): calculated for $\text{C}_{18}\text{H}_{15}\text{ClO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 337.0607, found 337.0583.

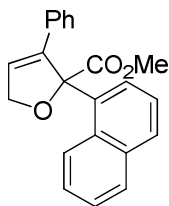
Methyl 2-(2-chlorophenyl)-3-phenyl-2,5-dihydrofuran-2-carboxylate(3ia)



3ia was obtained following the Procedure A from **1i** (63.2 mg, 0.3 mmol) and **2a** (59.5 mg, 0.45 mmol). Yield: 69.9 mg, 74%, yellow oil; ^1H NMR (400 MHz, CDCl_3): δ =

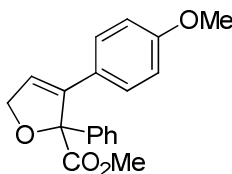
7.47-7.41 (m, 3 H), 7.33-7.25 (m, 5 H), 7.16 (t, 1 H, $J = 7.2$ Hz), 6.66 (s, 1 H), 5.06-4.81 (m, 2 H), 3.71 (s, 3 H); ^{13}C NMR(100 MHz, CDCl_3): $\delta = 171.7, 139.3, 137.2, 134.0, 131.9, 130.8, 130.2, 129.7, 128.6, 128.1, 128.0, 127.9, 126.3, 94.0, 74.9, 52.7$ ppm; IR (KBr): $\tilde{\nu} = 3064, 2854, 1714, 1587, 1438, 1247, 1091, 756, 529$ cm^{-1} ; HRMS (ESI): calculated for $\text{C}_{18}\text{H}_{15}\text{ClO}_3\text{Na} [\text{M}+\text{Na}]^+$: 337.0607, found 337.0582.

Methyl 2-(naphthalen-1-yl)-3-phenyl-2,5-dihydrofuran-2-carboxylate(3ja)



3ja was obtained following the Procedure A from **1j** (67.9 mg, 0.3 mmol) and **2a** (59.5 mg, 0.45 mmol). Yield: 74.0 mg, 75%, yellow oil; ^1H NMR (400 MHz, CDCl_3): $\delta = 8.03$ (d, 1 H, $J = 8.4$ Hz), 7.84-7.79 (m, 2 H), 7.53-7.40 (m, 5 H), 7.31-7.20 (m, 4 H), 6.68 (s, 1 H), 5.08-4.79 (m, 2 H), 3.64 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 173.4, 140.4, 135.2, 134.3, 132.4, 131.5, 129.6, 128.8, 128.1, 128.0, 127.7, 126.7, 126.1, 125.5, 125.2, 124.3, 94.5, 74.7, 52.5$ ppm; IR (KBr): $\tilde{\nu} = 3057, 2937, 2846, 1743, 1593, 1500, 1249, 1076, 912, 790, 536$ cm^{-1} ; HRMS (ESI): calculated for $\text{C}_{22}\text{H}_{18}\text{O}_3\text{Na} [\text{M}+\text{Na}]^+$: 353.1154, found 353.1127.

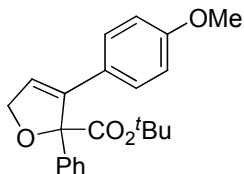
Methyl 3-(4-methoxyphenyl)-2-phenyl-2,5-dihydrofuran-2-carboxylate(3ab)



3ab was obtained following the Procedure A from **1a** (52.9 mg, 0.3 mmol) and **2b** (73.0 mg, 0.45 mmol). Yield: 68.9 mg, 74%, yellow oil; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.39$ -7.33 (m, 5 H), 7.26-7.22 (m, 2 H), 6.75 (d, 2 H, $J = 8.4$ Hz), 6.41 (s, 1 H), 4.99-4.90 (m, 2 H), 3.79 (s, 3 H), 3.76 (s, 3 H); ^{13}C NMR(100 MHz, CDCl_3): $\delta = 172.1, 159.1, 140.3, 139.4, 129.1, 128.2, 128.2, 127.4, 124.9, 124.9, 113.3, 94.6, 74.7, 55.1, 52.4$ ppm; IR (KBr): $\tilde{\nu} = 2950, 2310, 1737, 1612, 1512, 1355, 1255, 1078, 838, 698$ cm^{-1} ; HRMS (ESI): calculated for $\text{C}_{19}\text{H}_{18}\text{O}_4\text{Na} [\text{M}+\text{Na}]^+$: 333.1103, found

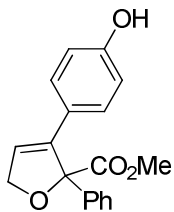
333.1079.

***tert*-Butyl 3-(4-methoxyphenyl)-2-phenyl-2,5-dihydrofuran-2-carboxylate(3bb)**



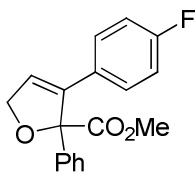
3bb was obtained following the Procedure A from **1b** (65.5 mg, 0.3 mmol) and **2b** (73.0 mg, 0.45 mmol). Yield: 75.1 mg, 71%, yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.40\text{-}7.19$ (m, 7 H), 6.72 (d, 2 H, $J = 8.0$ Hz), 6.39 (s, 1 H), 4.95-4.86 (m, 2 H), 3.75 (s, 3 H), 1.36 (s, 9 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 170.4, 159.1, 140.6, 139.9, 129.3, 128.1, 128.0, 127.7, 125.5, 125.1, 113.1, 94.9, 82.1, 74.6, 55.1, 27.8$ ppm; IR (KBr): $\tilde{\nu} = 2976, 2846, 2029, 1623, 1394, 1255, 1078, 838, 622, 482$ cm^{-1} ; HRMS (ESI): calculated for $\text{C}_{22}\text{H}_{24}\text{O}_4$ Na $[\text{M}+\text{Na}]^+$: 375.1572, found 375.1574.

Methyl 3-(4-hydroxyphenyl)-2-phenyl-2,5-dihydrofuran-2-carboxylate(3ac)



3ac was obtained following the Procedure A from **1a** (52.9 mg, 0.3 mmol) and **2c** (66.7 mg, 0.45 mmol). Yield: 37.3 mg, 42%, yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.34\text{-}7.25$ (m, 5 H), 7.12 (d, 2 H, $J = 8.4$ Hz), 6.61 (d, 2 H, $J = 8.4$ Hz), 6.38 (s, 1 H), 4.96-4.87 (m, 2 H), 4.35 (s, 1 H), 3.77 (s, 3 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 172.4, 155.7, 140.2, 139.2, 129.2, 128.4, 128.3, 127.4, 124.8, 124.7, 114.9, 94.7, 74.7, 52.6$ ppm; IR (KBr): $\tilde{\nu} = 3924, 2027, 1629, 1392, 1078, 621, 484$ cm^{-1} ; HRMS (ESI): calculated for $\text{C}_{18}\text{H}_{16}\text{O}_4$ Na $[\text{M}+\text{Na}]^+$: 319.0946, found 319.0946.

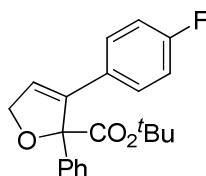
Methyl 3-(4-fluorophenyl)-2-phenyl-2,5-dihydrofuran-2-carboxylate(3ad)



3ad was obtained following the Procedure A from **1a** (52.9 mg, 0.3 mmol) and **2d**

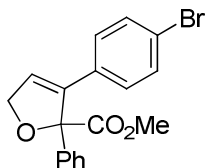
(67.6 mg, 0.45 mmol). Yield: 73.4 mg, 82% , yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.34$ (s, 5 H), 7.26-7.20 (m, 2 H), 6.90 (t, 2 H, $J = 8.8$ Hz), 6.43 (s, 1 H), 5.00-4.91 (m, 2 H), 3.79 (s, 3 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 171.9, 162.3$ ($J_{\text{F-C}} = 246$ Hz), 140.2, 139.1, 129.7 ($J_{\text{F-C}} = 8$ Hz), 128.7 ($J_{\text{F-C}} = 3$ Hz), 128.4, 128.3, 127.2, 126.7, 114.9 ($J_{\text{F-C}} = 22$ Hz), 94.7, 74.7, 52.5 ppm; IR (KBr): $\tilde{\nu} = 3172, 1685, 1583, 1064, 786, 734, 561$ cm^{-1} ; HRMS (ESI): calculated for $\text{C}_{18}\text{H}_{15}\text{FO}_3$ Na $[\text{M}+\text{Na}]^+$: 321.0903, found 321.0880.

***tert*-Butyl 3-(4-fluorophenyl)-2-phenyl-2,5-dihydrofuran-2-carboxylate(3bd)**



3bd was obtained following the Procedure A from **1b** (65.5 mg, 0.3 mmol) and **2d** (67.6 mg, 0.45 mmol). Yield: 67.4 mg, 66%, yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.37$ -7.33 (m, 5 H), 7.22-7.19 (m, 2 H), 6.88 (t, 2 H, $J = 9.2$ Hz), 6.43 (s, 1 H), 4.96-4.88 (m, 2 H), 1.35 (s, 9 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 170.1, 162.3$ ($J_{\text{F-C}} = 247$ Hz), 140.4, 139.6, 129.8 ($J_{\text{F-C}} = 8$ Hz), 129.3 ($J_{\text{F-C}} = 3$ Hz), 128.3, 128.2, 127.5, 126.8, 114.7 ($J_{\text{F-C}} = 21$ Hz), 94.9, 82.4, 74.5, 27.8 ppm; IR (KBr): $\tilde{\nu} = 2979, 2852, 2025, 1625, 1392, 1240, 1082, 973, 840, 622, 482$ cm^{-1} ; HRMS (ESI): calculated for $\text{C}_{21}\text{H}_{21}\text{FO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 363.1372, found 363.1371.

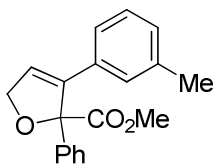
Methyl 3-(4-bromophenyl)-2-phenyl-2,5-dihydrofuran-2-carboxylate(3ae)



3ae was obtained following the Procedure A from **1a** (52.9 mg, 0.3 mmol) and **2e** (95.0 mg, 0.45 mmol). Yield: 79.7 mg, 74%, yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.33$ -7.32 (m, 7 H), 7.12 (d, 2 H, $J = 8.0$ Hz), 6.50 (s, 1 H), 4.98-4.91 (m, 2 H), 3.79 (s, 3 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 171.8, 140.2, 139.0, 131.5, 131.1, 129.5, 128.5, 128.4, 127.4, 127.2, 122.1, 94.7, 74.7, 52.6$ ppm; IR (KBr): $\tilde{\nu} = 2947, 2852, 2312, 1737, 1595, 1496, 1361, 1251, 1076, 900, 756, 696$ cm^{-1} ; HRMS(ESI):

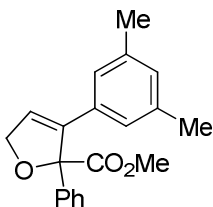
calculated for $C_{18}H_{15}BrO_3 Na$ $[M+Na]^+$: 381.0102, found 381.0074.

Methyl 2-phenyl-3-*m*-tolyl-2,5-dihydrofuran-2-carboxylate(3ag)



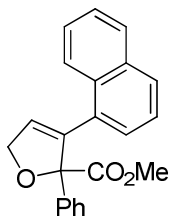
3ag was obtained following the Procedure A from **1a** (52.9 mg, 0.3 mmol) and **2g** (65.8 mg, 0.45 mmol). Yield: 57.4 mg, 65%, yellow oil; 1H NMR (400 MHz, $CDCl_3$): δ = 7.38-7.32 (m, 5 H), 7.11-6.99 (m, 4 H), 6.47 (s, 1 H), 5.00-4.91 (m, 2 H), 3.79 (s, 3 H), 2.27 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.0, 141.2, 139.4, 137.5, 132.5, 128.7, 128.5, 128.2, 128.1, 127.8, 127.3, 126.6, 125.0, 94.7, 74.7, 52.5, 21.4 ppm; IR (KBr): $\tilde{\nu}$ = 2312, 1739, 1616, 1502, 1253, 1078, 757, 696, 561 cm^{-1} ; HRMS (ESI): calculated for $C_{19}H_{18}O_3 Na$ $[M+Na]^+$: 317.1154, found 317.1133.

Methyl 3-(3,5-dimethylphenyl)-2-phenyl-2,5-dihydrofuran-2-carboxylate(3ah)



3ah was obtained following the Procedure A from **1a** (52.9 mg, 0.3 mmol) and **2h** (72.1 mg, 0.45 mmol). Yield: 55.5 mg, 60%, yellow oil; 1H NMR (400 MHz, $CDCl_3$): δ = 7.41-7.32 (m, 5 H), 6.90-6.88 (m, 3 H), 6.45 (s, 1 H), 5.00-4.92 (m, 2 H), 3.81 (s, 3 H), 2.23 (s, 6 H); ^{13}C NMR(100 MHz, $CDCl_3$): δ = 172.0, 141.3, 139.4, 137.3, 132.5, 129.5, 128.1, 128.0, 127.3, 126.4, 125.6, 94.6, 74.7, 52.5, 21.2 ppm; IR (KBr): $\tilde{\nu}$ = 2310, 1739, 1627, 1255, 613 cm^{-1} ; HRMS (ESI): calculated for $C_{20}H_{20}O_3Na$ $[M+Na]^+$: 331.1310, found 331.1284.

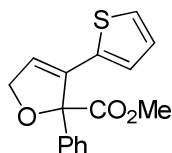
Methyl 3-(naphthalen-1-yl)-2-phenyl-2,5-dihydrofuran-2-carboxylate(3ai)



3ai was obtained following the Procedure A from **1a** (52.9 mg, 0.3 mmol) and **2i** (82.0

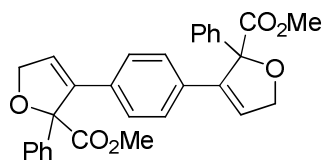
mg, 0.45 mmol). Yield: 44.6 mg, 45%, yellow oil; ^1H NMR (400 MHz, CDCl_3): δ = 7.78 (t, 2 H, J = 7.4 Hz), 7.60 (d, 1 H, J = 8.4 Hz), 7.40 (t, 1 H, J = 7.2 Hz), 7.33-7.18 (m, 7 H), 6.89 (d, 2 H, J = 7.4 Hz), 6.14 (s, 1 H), 5.25-5.16 (m, 2 H), 3.65 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 171.3, 134.0, 138.9, 133.3, 132.8, 131.1, 129.5, 128.2, 128.0, 127.9, 127.8, 126.9, 126.3, 125.7, 125.5, 124.5, 95.6, 75.5, 52.4 ppm; IR (KBr): $\tilde{\nu}$ = 3153, 2927, 2312, 1737, 1589, 1348, 1251, 1072, 898, 779, 669, 518, 437 cm^{-1} ; HRMS (ESI): calculated for $\text{C}_{22}\text{H}_{18}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 353.1154, found 353.1130.

Methyl 2-phenyl-3-(thiophen-2-yl)-2,5-dihydrofuran-2-carboxylate(3aj)



3aj was obtained following the Procedure A from **1a** (52.9 mg, 0.3 mmol) and **2j** (55.9 mg, 0.45 mmol). Yield: 44.7 mg, 52%, yellow oil; ^1H NMR (400 MHz, CDCl_3): δ = 7.40-7.33 (m, 5 H), 7.15 (d, 1 H, J = 4.8 Hz), 6.85-6.81 (m, 2 H), 6.44 (s, 1 H), 4.99-4.90 (m, 2 H), 3.82 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 171.7, 138.7, 135.1, 135.08, 128.5, 128.2, 127.6, 127.3, 126.0, 125.1, 94.7, 74.7, 52.6 ppm; IR (KBr): $\tilde{\nu}$ = 2029, 1623, 1392, 1078, 622, 482 cm^{-1} ; HRMS (ESI): calculated for $\text{C}_{16}\text{H}_{14}\text{O}_3\text{SNa}$ $[\text{M}+\text{Na}]^+$: 309.0561, found 309.0565.

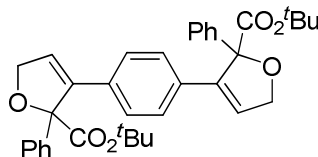
Dimethyl 3,3'-(1,4-phenylene)bis(2-phenyl-2,5-dihydrofuran-2-carboxylate) (3ak)



3ak was obtained following the Procedure A from **1a** (105.7 mg, 0.6 mmol) and **2k** (37.2 mg, 0.2 mmol). Yield: 70.4 mg, 73%, yellow solid; m.p. 140.6°C; ^1H NMR (400 MHz, CDCl_3): δ = 7.33 (s, 10 H), 7.15 (s, 4 H), 6.50 (s, 2 H), 4.97-4.88 (m, 4 H), 3.77 (s, 6 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 171.9, 140.3, 139.1, 131.8, 128.3, 128.2, 127.3, 127.1, 94.5, 74.6, 52.4 ppm; IR (KBr): $\tilde{\nu}$ = 2947, 2852, 1730, 1629, 1438, 1257, 1078, 894, 757, 696, 480 cm^{-1} ; HRMS (ESI): calculated for $\text{C}_{30}\text{H}_{26}\text{O}_6\text{Na}$ $[\text{M}+\text{Na}]^+$: 505.1627, found 505.1626.

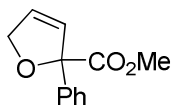
tert-Butyl 3,3'-(1,4-phenylene)bis(2-phenyl-2,5-dihydrofuran-2-carboxylate)

(3bk)



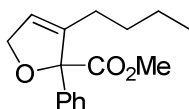
3bk was obtained following the Procedure A from **1b** (131.0 mg, 0.6 mmol) and **2k** (37.2 mg, 0.2 mmol). Yield: 80.5 mg, 71%, yellow oil; ^1H NMR (400 MHz, CDCl_3): δ = 7.33-7.30 (m, 10 H), 7.12 (d, 4 H, J = 13.6 Hz), 6.51 (s, 1 H), 6.44 (s, 1 H), 4.94-4.84 (m, 4 H), 1.34 (s, 9 H), 1.31 (s, 9 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 170.24, 170.19, 140.8, 140.4, 139.62, 139.59, 132.4, 132.0, 129.1, 128.6, 128.13, 128.08, 127.61, 127.57, 127.4, 127.3, 127.12, 127.07, 94.82, 94.79, 82.24, 82.19, 74.56, 74.5, 27.79, 27.77 ppm; IR (KBr): $\tilde{\nu}$ = 2029, 1625, 1392, 1080, 622, 482 cm^{-1} ; HRMS (ESI): calculated for $\text{C}_{36}\text{H}_{38}\text{O}_6\text{Na}$ $[\text{M}+\text{Na}]^+$: 589.2566, found 589.2565.

Methyl 2-phenyl-2,5-dihydrofuran-2-carboxylate(3al)



3al was obtained following the Procedure A from **1a** (52.9 mg, 0.3 mmol) and **2l** (25.2 mg, 0.45 mmol). Yield: 34.3 mg, 56%, yellow oil; ^1H NMR (400 MHz, CDCl_3): δ = 7.49-7.46 (m, 2 H), 7.38-7.28 (m, 3 H), 6.27-6.24 (m, 1 H), 6.11-6.09 (m, 1 H), 4.94-4.79 (m, 2 H), 3.74 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 172.3, 140.4, 128.8, 128.5, 128.1, 125.4, 93.8, 76.0, 52.6 ppm; IR (KBr): $\tilde{\nu}$ = 2029, 1625, 1392, 1244, 1076, 622, 482 cm^{-1} ; HRMS (ESI): calculated for $\text{C}_{12}\text{H}_{12}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 227.0684, found 227.0687.

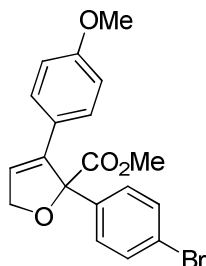
Methyl 3-butyl-2-phenyl-2,5-dihydrofuran-2-carboxylate(3am)



3am was obtained following the Procedure A from **1a** (52.9 mg, 0.3 mmol) and **2m** (50.5 mg, 0.45 mmol). Yield: 46.9 mg, 60%, yellow oil; ^1H NMR (400 MHz, CDCl_3): δ = 7.38-7.26 (m, 5 H), 5.76 (s, 1 H), 4.82 (s, 2 H), 3.80 (s, 3 H), 2.32-2.25 (m, 1 H), 1.93-1.86 (m, 1 H), 1.51-1.36 (m, 4 H), 0.85 (t, 3 H, J = 7.3 Hz); ^{13}C NMR (100 MHz,

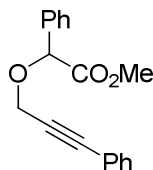
CDCl₃): δ = 172.0, 142.8, 139.6, 128.2, 128.0, 126.1, 121.9, 95.1, 75.0, 52.3, 29.9, 26.4, 22.4, 13.9 ppm; IR (KBr): $\tilde{\nu}$ = 2952, 1731, 1616, 1446, 1255, 1078, 754, 698, 617, 478 cm⁻¹; HRMS (ESI): calculated for C₁₆H₂₀O₃Na [M+Na]⁺: 283.1310, found 283.1312.

Methyl 2-(4-bromophenyl)-3-(4-methoxyphenyl)-2,5-dihydrofuran-2-carboxylate. (3fb)



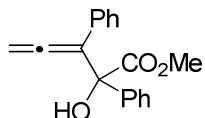
3fb was obtained following the Procedure A from **1f** (76.5 mg, 0.3 mmol) and **2b** (73.0 mg, 0.45 mmol). Yield: 91.1 mg, 78%, yellow oil; ¹H NMR (400 MHz, CDCl₃): δ = 7.43 (d, 2 H, *J* = 8.0 Hz), 7.26-7.18 (m, 4 H), 6.75 (d, 2 H, *J* = 8.4 Hz), 6.38 (s, 1 H), 4.97-4.86 (m, 2 H), 3.77 (s, 3 H), 3.75 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ = 171.7, 159.3, 140.0, 138.4, 131.2, 129.2, 129.0, 125.1, 124.5, 122.4, 113.5, 94.0, 74.9, 55.1, 52.6 ppm; IR (KBr): $\tilde{\nu}$ = 2950, 2846, 2029, 1622, 1394, 1255, 1076, 829, 619, 482 cm⁻¹; HRMS (ESI): calculated for C₁₉H₁₇BrO₄Na [M+Na]⁺: 411.0208, found 411.0203.

Methyl 2-phenyl-2-(2-phenylethynoxy)acetate(4a)



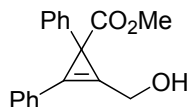
4a was obtained following the Procedure A from **1a** (52.9 mg, 0.3 mmol) and **2a** (59.5 mg, 0.45 mmol). Yield: 57.2 mg, 68%, yellow oil; ¹H NMR (400 MHz, CDCl₃): δ = 7.51-7.30 (m, 10 H), 5.29 (s, 1 H), 4.56-4.36 (m, 2 H), 3.73 (s, 3 H); ¹³C NMR (400 MHz, CDCl₃): δ = 170.9, 135.6, 131.8, 129.0, 128.7, 128.6, 128.3, 127.6, 122.3, 87.4, 83.8, 78.8, 57.1, 52.4 ppm; IR (KBr): $\tilde{\nu}$ = 2027, 1629, 1392, 1078, 621, 484 cm⁻¹; HRMS (ESI): calculated for C₁₈H₁₆O₃Na [M+Na]⁺: 303.0997, found 303.1005.

Methyl 2-hydroxy-2,3-diphenylpenta-3,4-dienoate(5a)



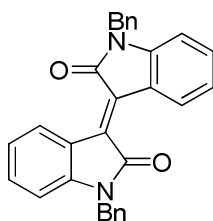
5a was obtained following the Procedure A from **1a** (52.9 mg, 0.3 mmol) and **2a** (59.5 mg, 0.45 mmol) by the use of Cu(OTf)₂ as catalyst in stead of JohnPhosAuCl/AgSbF₆. Yield: 16.8 mg, 20%, yellow oil; ¹H NMR (400 MHz, CDCl₃): δ = 7.63 (d, 2 H, *J* = 7.6 Hz), 7.36-7.12 (m, 8 H), 5.12 (s, 2 H), 4.25 (s, 1 H), 3.70 (s, 3 H); ¹³C NMR(400 MHz, CDCl₃): δ = 209.1, 174.4, 139.5, 133.3, 131.8, 128.11, 128.06, 127.9, 127.1, 126.9, 108.7, 81.3, 79.7, 53.3; HRMS (ESI): calculated for C₁₈H₁₆O₃Na [M+Na]⁺: 303.0997, found 303.1007.

Methyl 2-(hydroxymethyl)-1,3-diphenylcycloprop-2-enecarboxylate(6a)



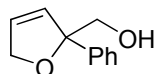
6a was obtained following the Procedure A from **1a** (52.9 mg, 0.3 mmol) and **2a** (59.5 mg, 0.45 mmol) by the use of Cu(OTf)₂ as catalyst in stead of JohnPhosAuCl/AgSbF₆. Yield: 10.1 mg, 12%, yellow oil; ¹H NMR (400 MHz, CDCl₃): δ = 7.61 (d, 2 H, *J* = 7.2 Hz), 7.43-7.35 (m, 5 H), 7.29-7.20 (m, 3 H), 4.92-4.79 (m, 2 H), 3.72 (s, 3 H), 2.62 (s, 1 H); ¹³C NMR(400 MHz, CDCl₃): δ = 175.2, 140.3, 129.8, 129.5, 128.9, 128.18, 128.17, 126.6, 125.7, 113.4, 110.9, 56.7, 52.3, 36.7 ppm; IR (KBr): $\tilde{\nu}$ = 2029, 1625, 1392, 1078, 622, 484 cm⁻¹; HRMS (ESI): calculated for C₁₈H₁₆O₃Na [M+Na]⁺: 303.0997, found 303.1002.

Dimerization product (7)³



7 was obtained following the Procedure A from **1m** (74.7 mg, 0.3 mmol) and **2a** (59.5 mg, 0.45 mmol). Yield: 59.7 mg, 45%, yellow oil; ¹H NMR (400 MHz, CDCl₃): δ = 9.22 (d, 2 H, *J* = 8.0 Hz), 7.33-7.25 (m, 12 H), 7.04 (t, 2 H, *J* = 7.8 Hz), 6.71 (d, 2 H, *J* = 7.8 Hz), 5.0 (s, 4 H).

(2-Phenyl-2,5-dihydrofuran-2-yl)methanol (8**)⁴**

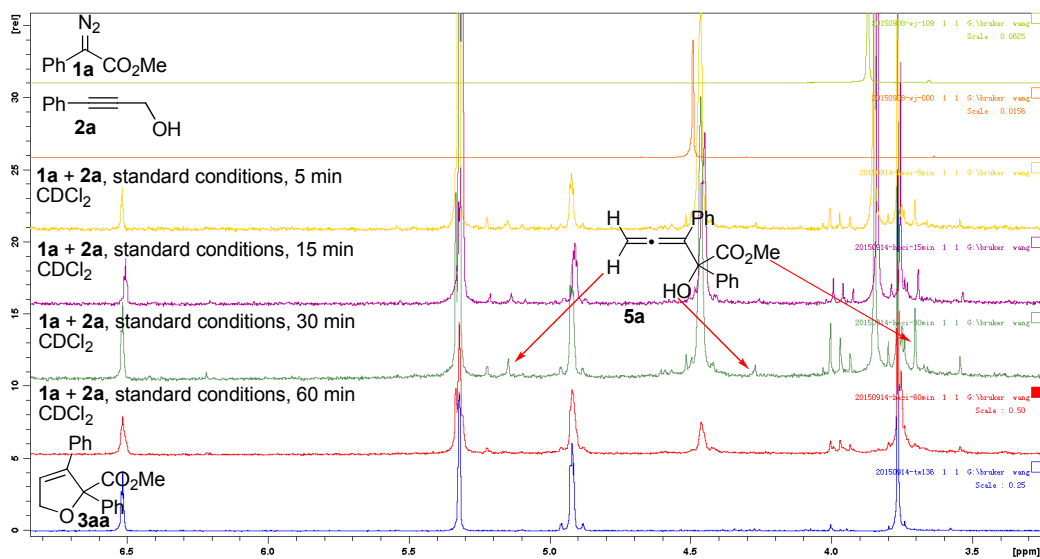
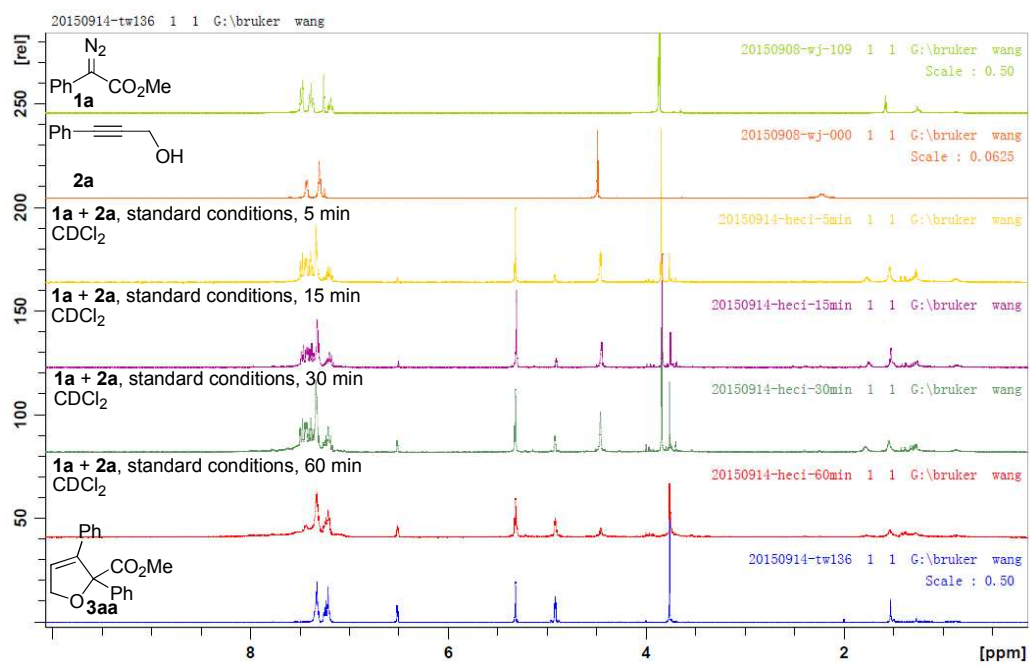


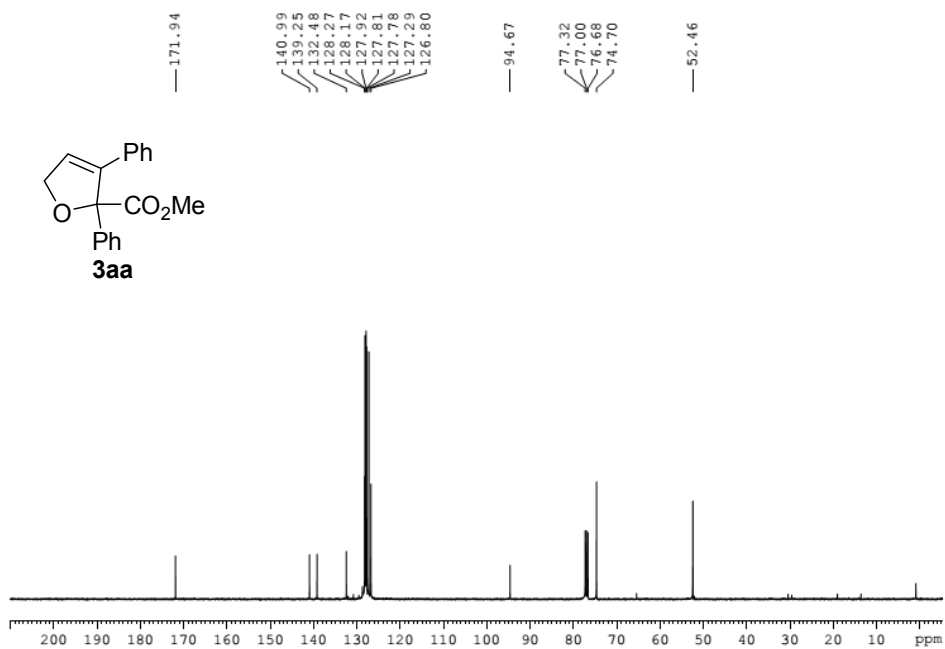
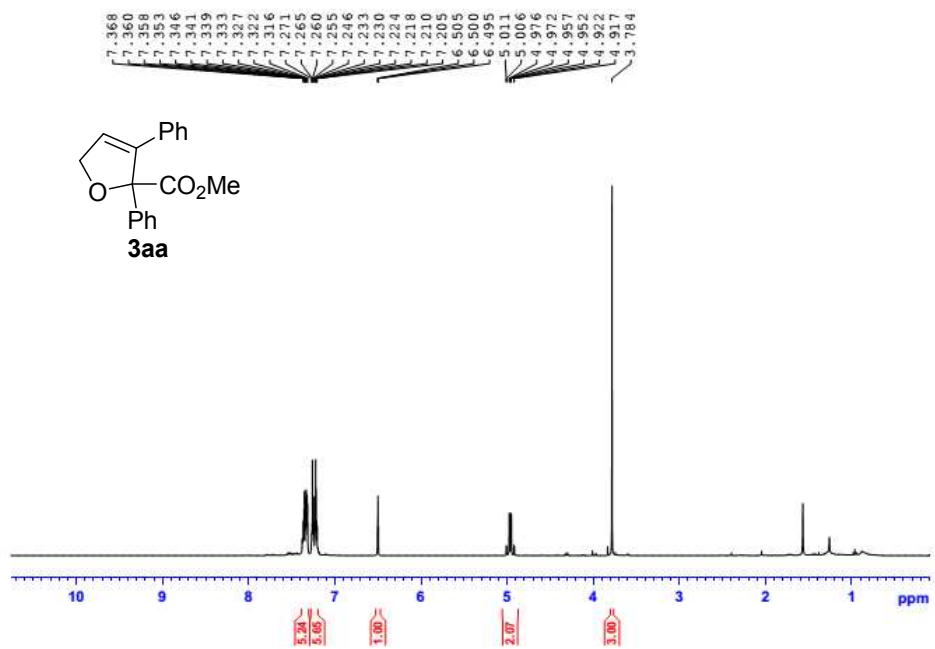
To a solution of LiAlH₄ (0.2 mL, 2.5 M in THF) in dry THF (2.5 mL) at 0 °C, a solution of **3aa** (40.8mg, 0.2 mmol) in 2.5 mL of THF was added dropwise. The resulting solution was stirred at 0 °C for 20 min. After that the solution was warmed up to room temperature and was stirred for 1 h. The mixture was quenched with water (10 mL), and extracted with EtOAc (2 × 10 mL). The organic layers were collected, dried over MgSO₄, concentrated and purified by column chromatography (petroleum ether / ethyl acetate, 10:1 to 5:1) to afford 20.1 mg of **8**. Yield: 57%, yellow oil; ¹H NMR (400 MHz, CDCl₃): δ = 7.39-7.25 (m, 5 H), 6.04 (s, 2 H), 4.86-4.73 (m, 2 H), 3.80 (s, 2 H), 1.60 (sbr, 1 H).

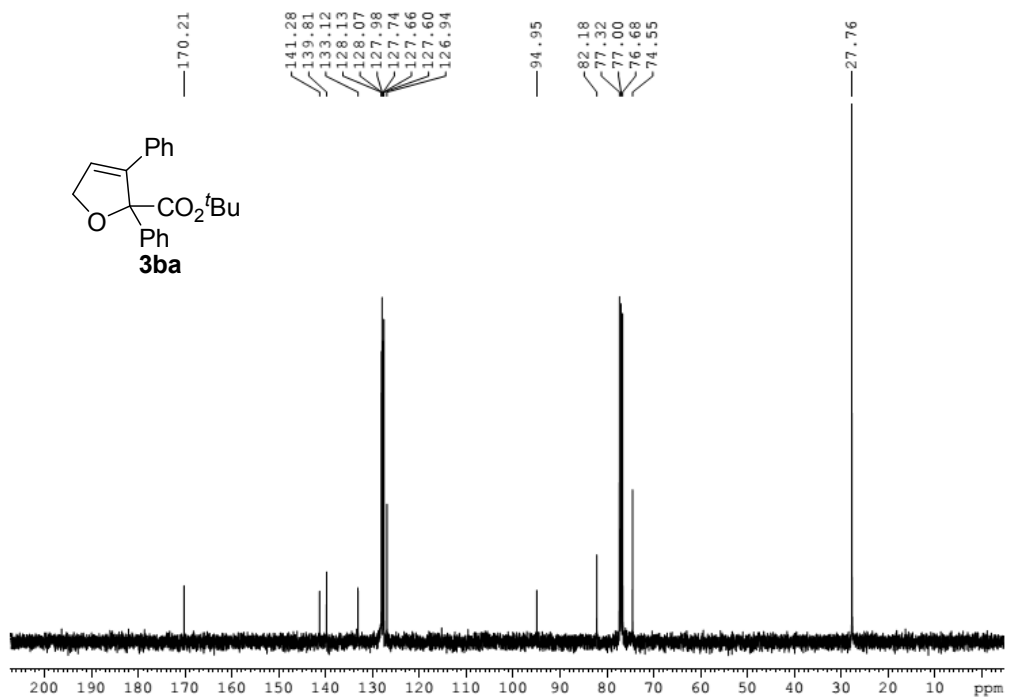
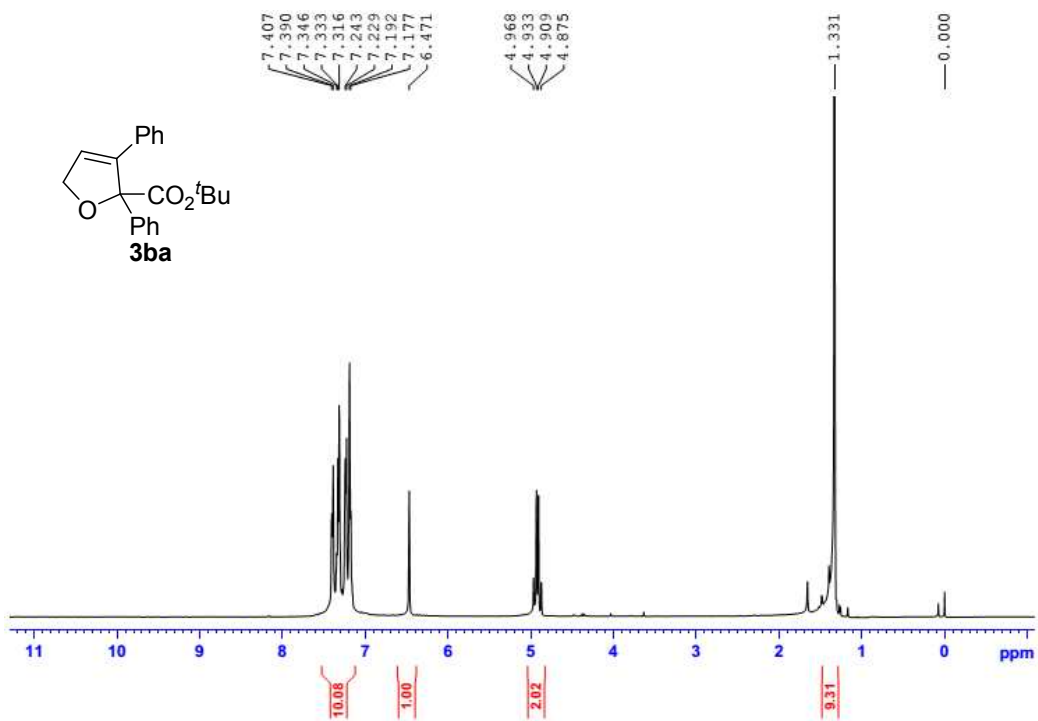
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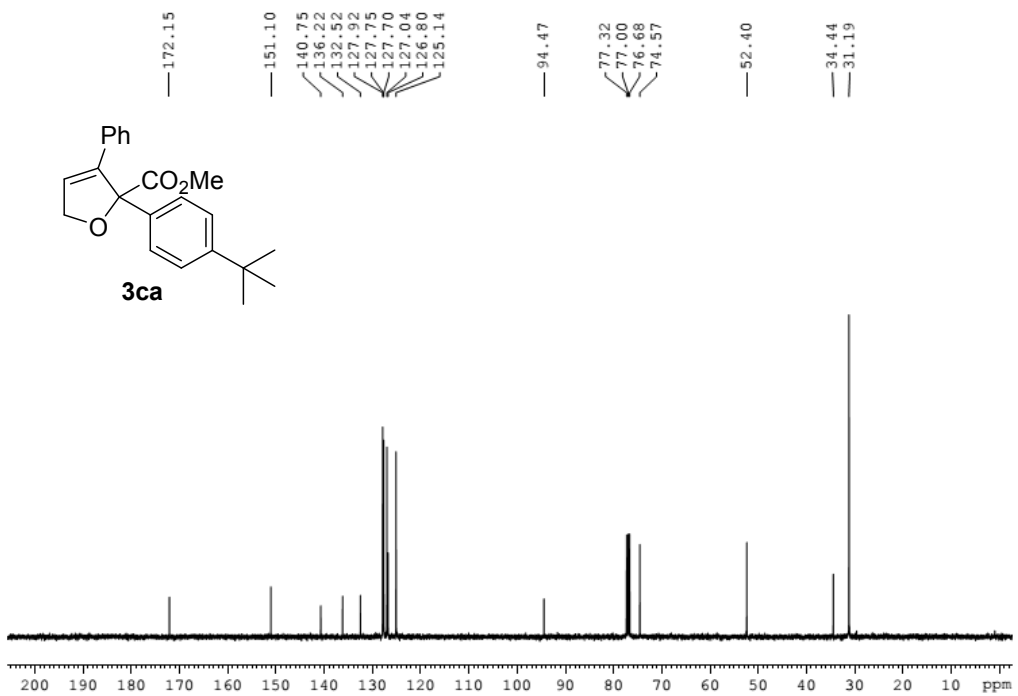
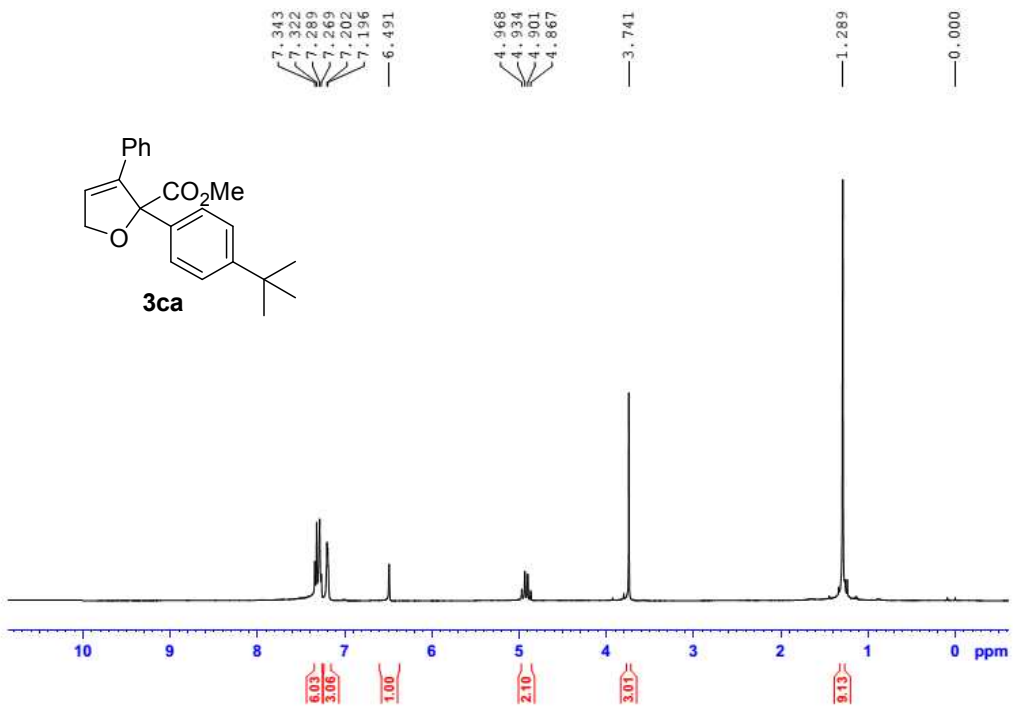
1. Tietze, L. F.; Vock, C. A.; Krimmelbein, I. K.; Wiegand, J. M.; Nacke, L.; Ramachandar, T.; Islam, K. M. D.; Ga, C. *Chem.–Eur. J.*, **2008**, *14*, 3670-3679.
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4. Trost, B. M.; Brown, B. S.; McEachern, E. J.; Kuhn, O. *Chem. Eur. J.* **2003**, *9*, 4442-4451.

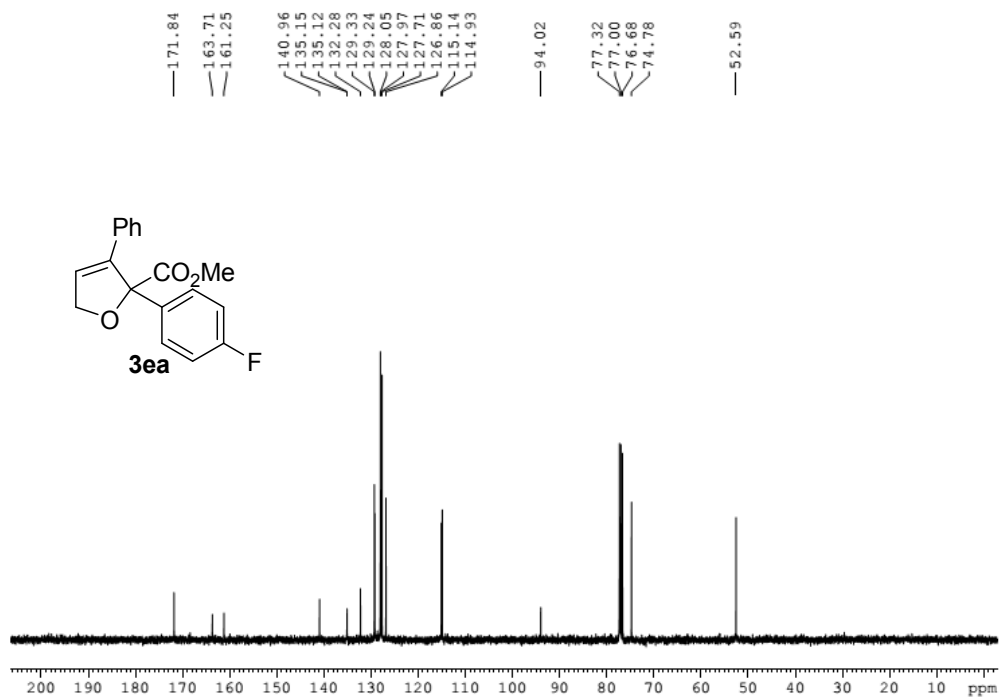
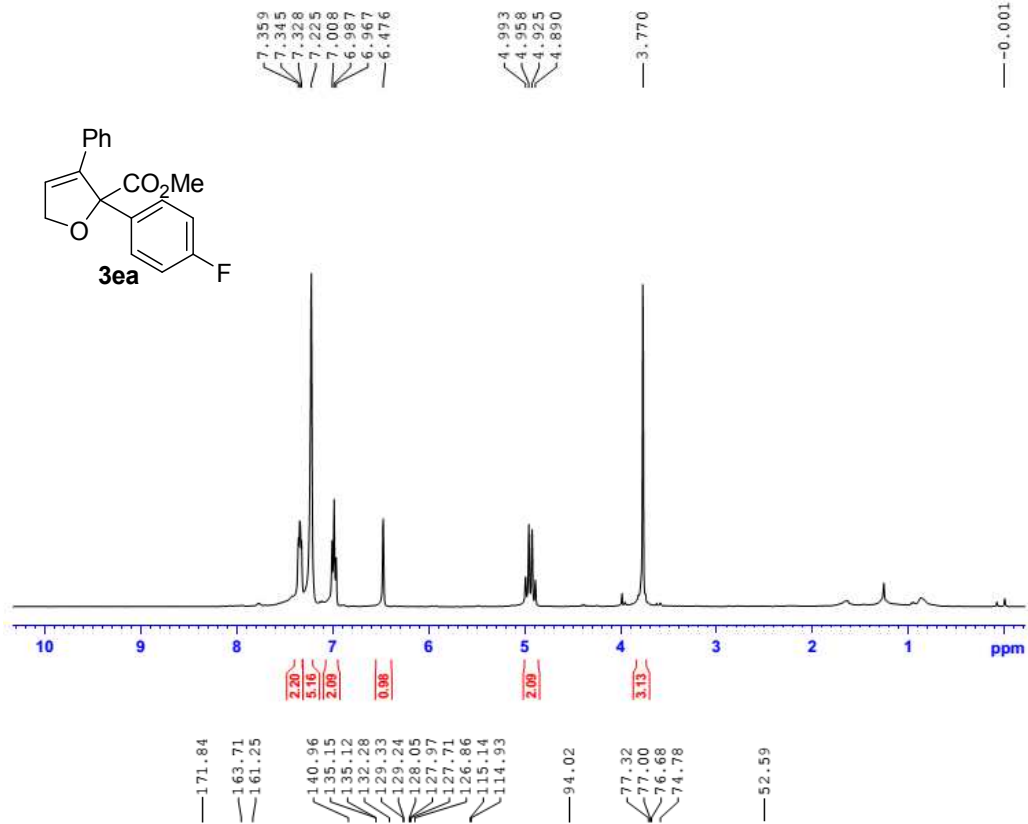
Spectrum for NMR investigations

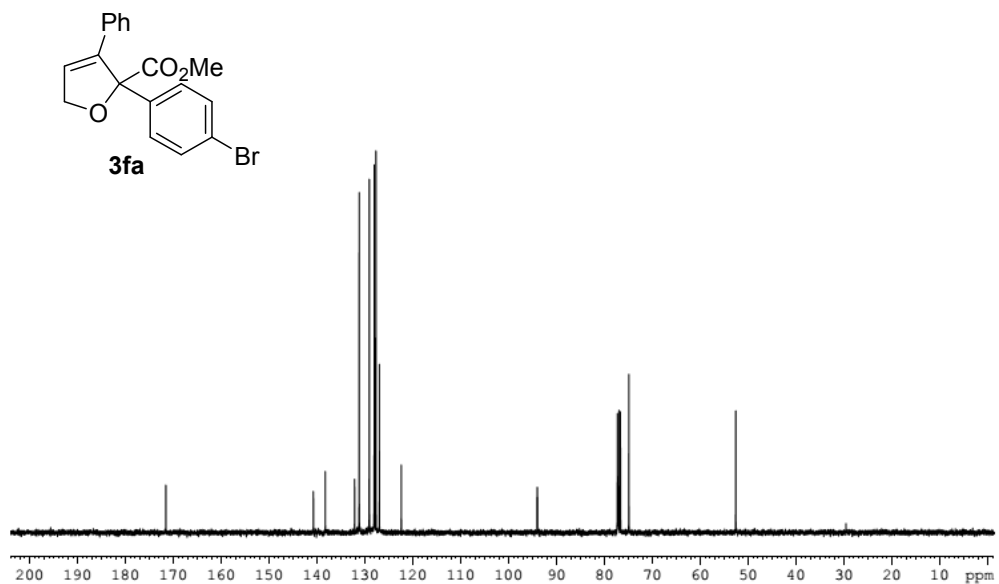
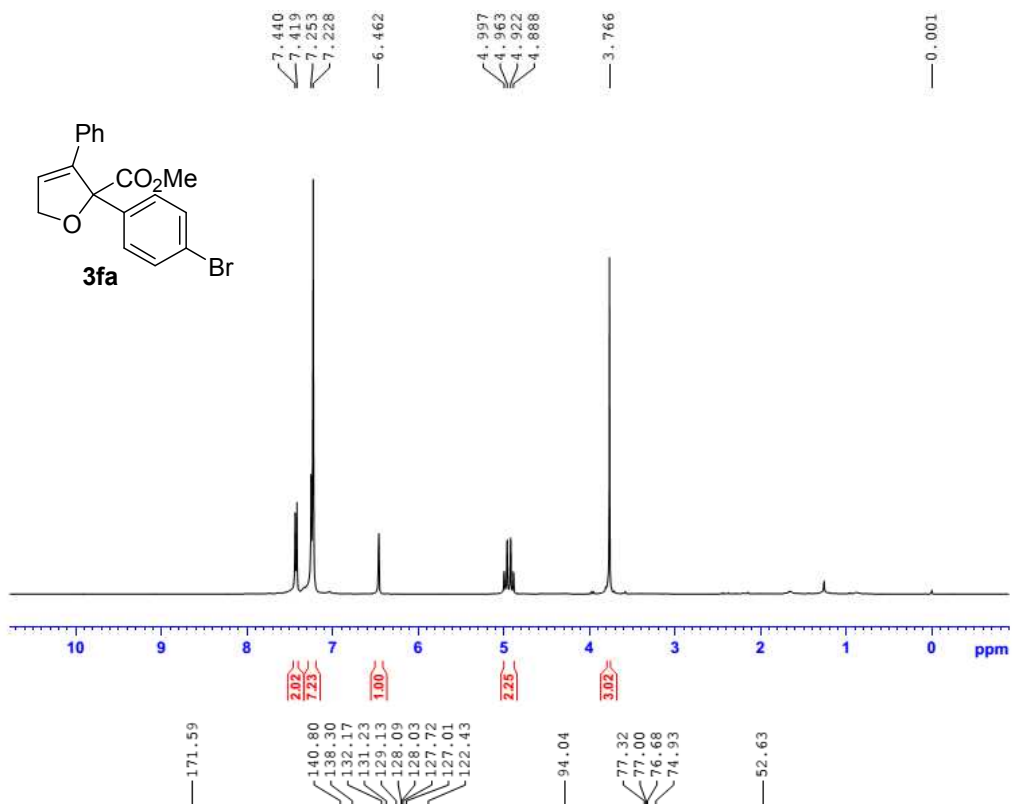


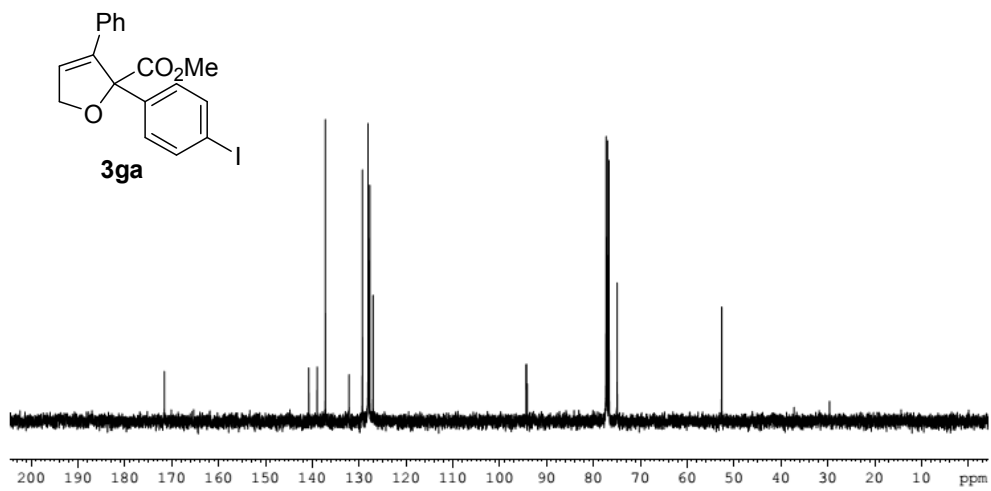
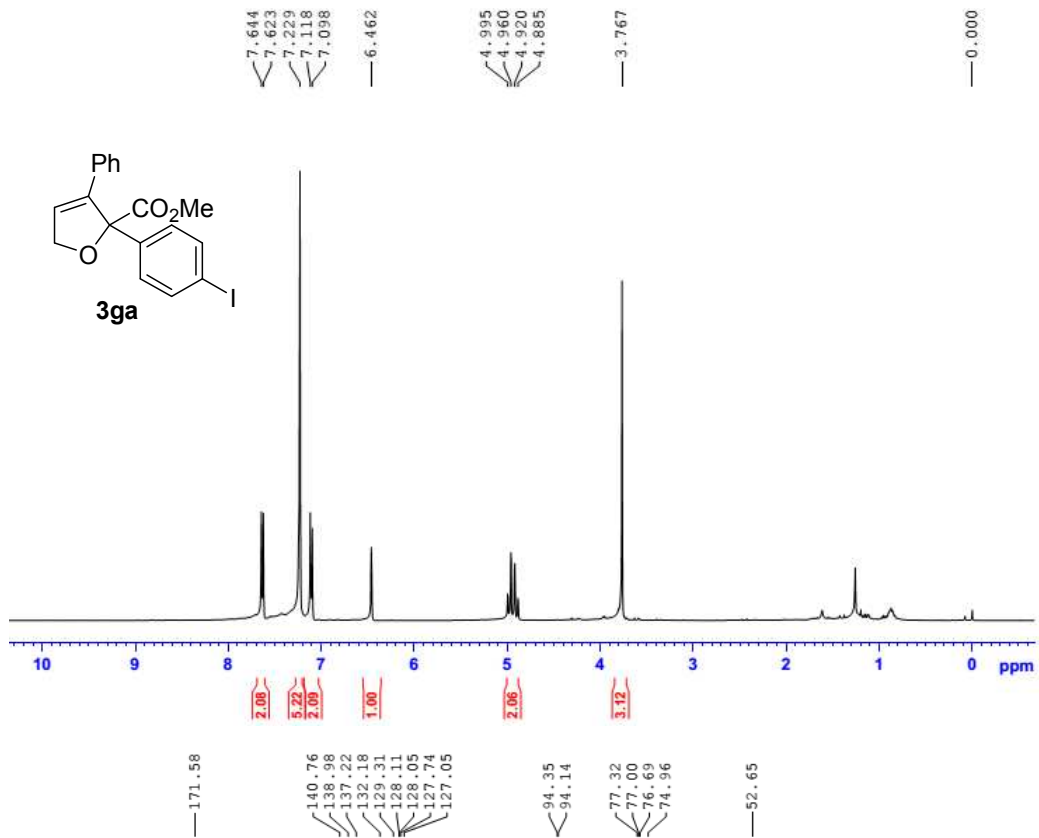


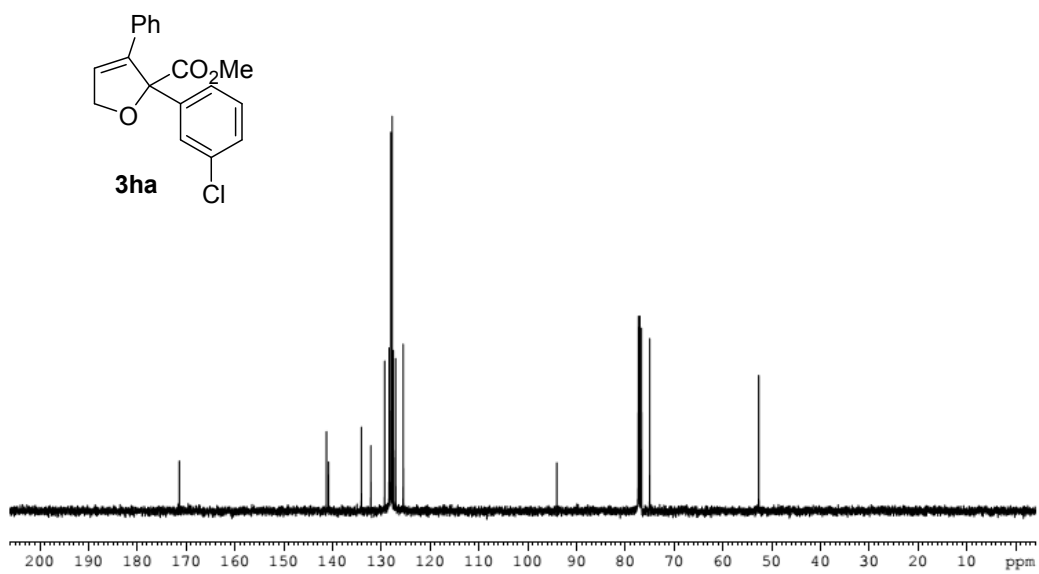
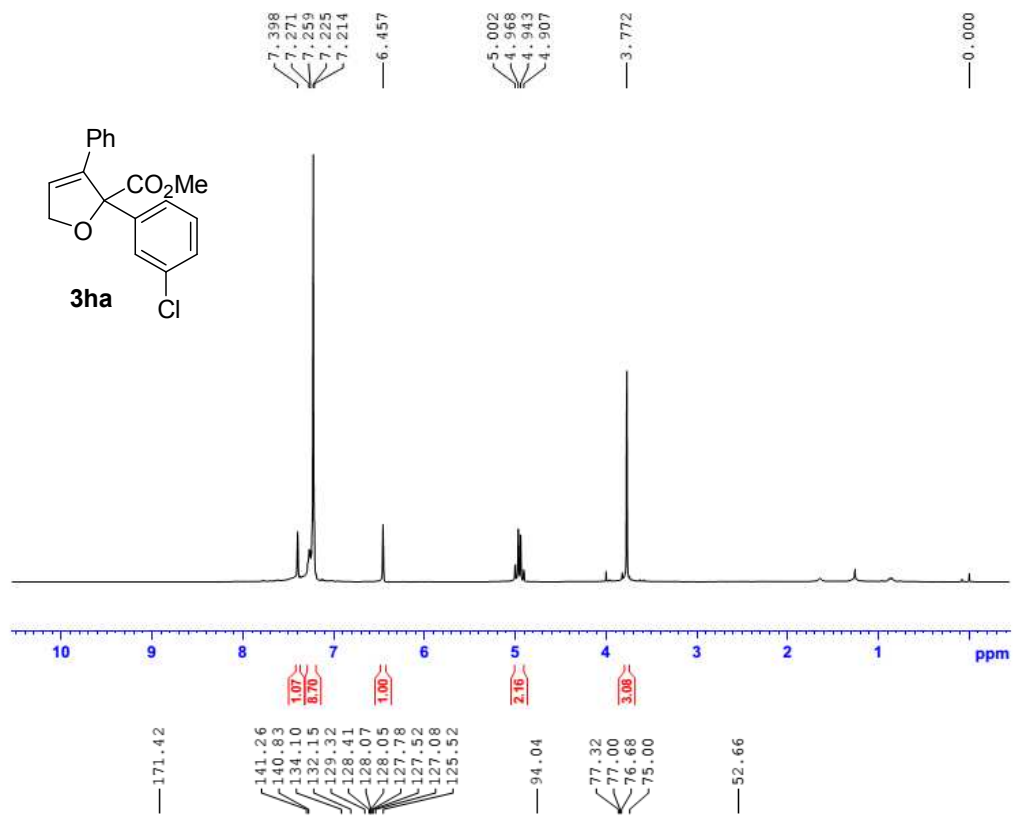


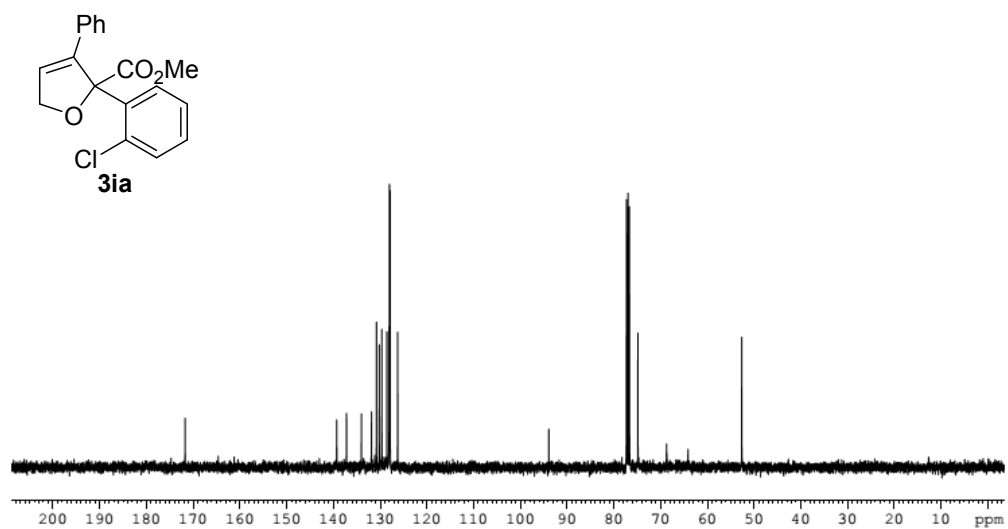
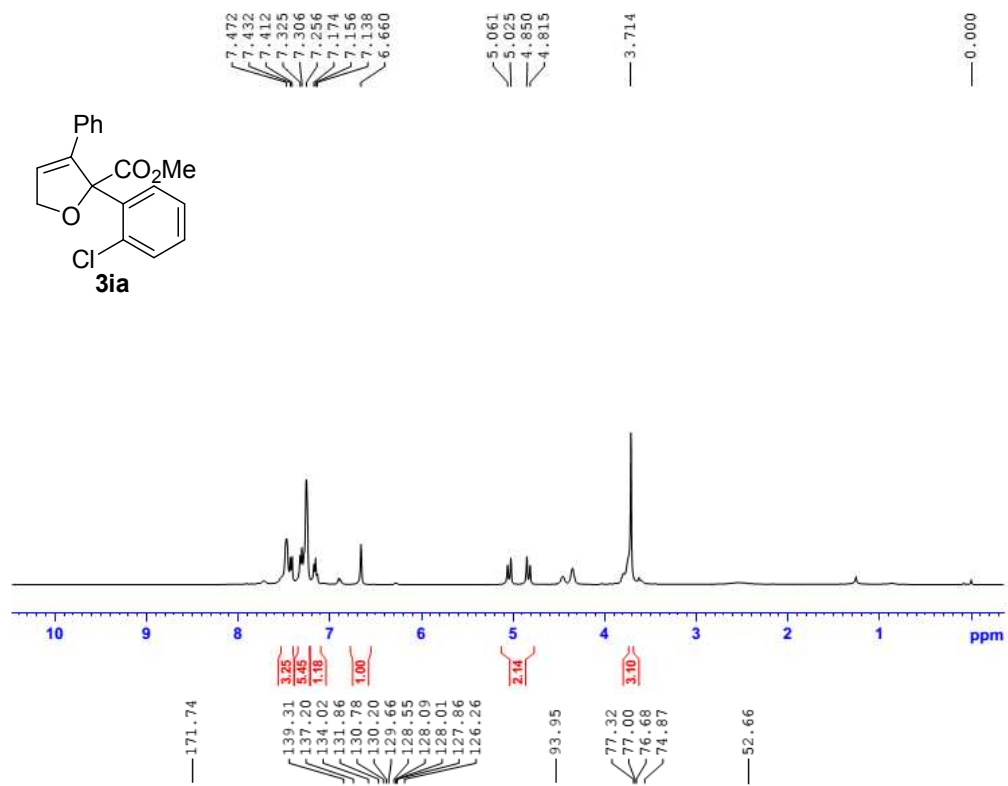


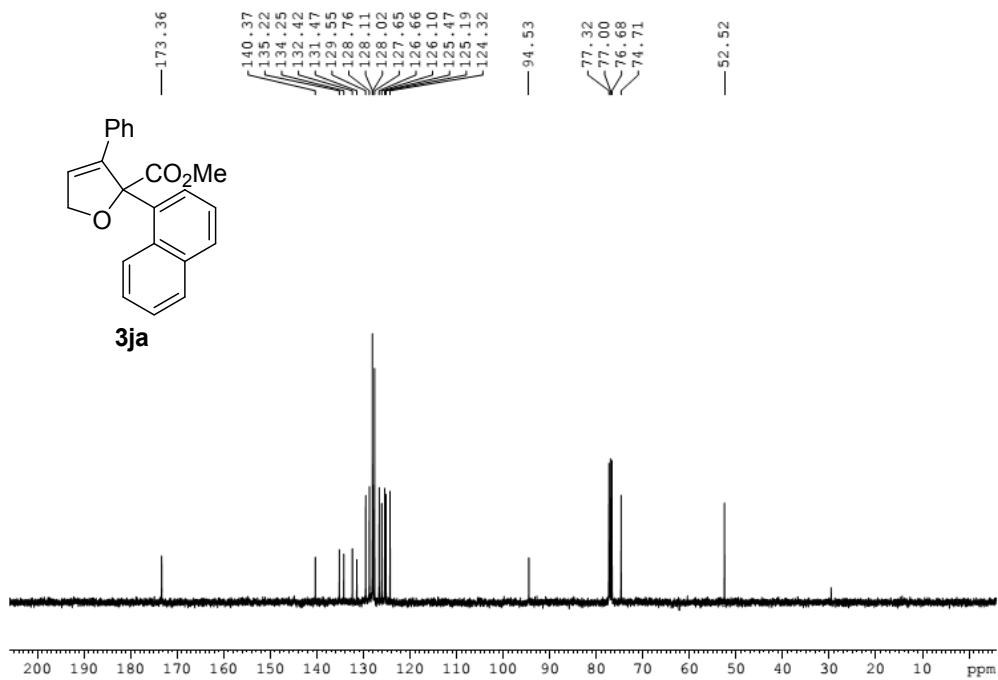
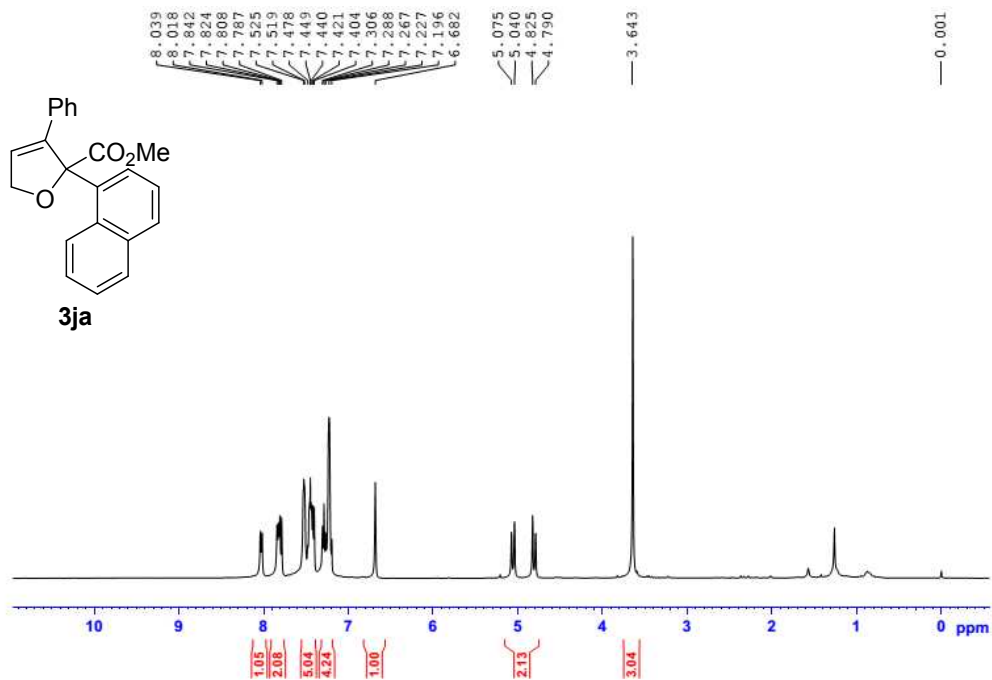


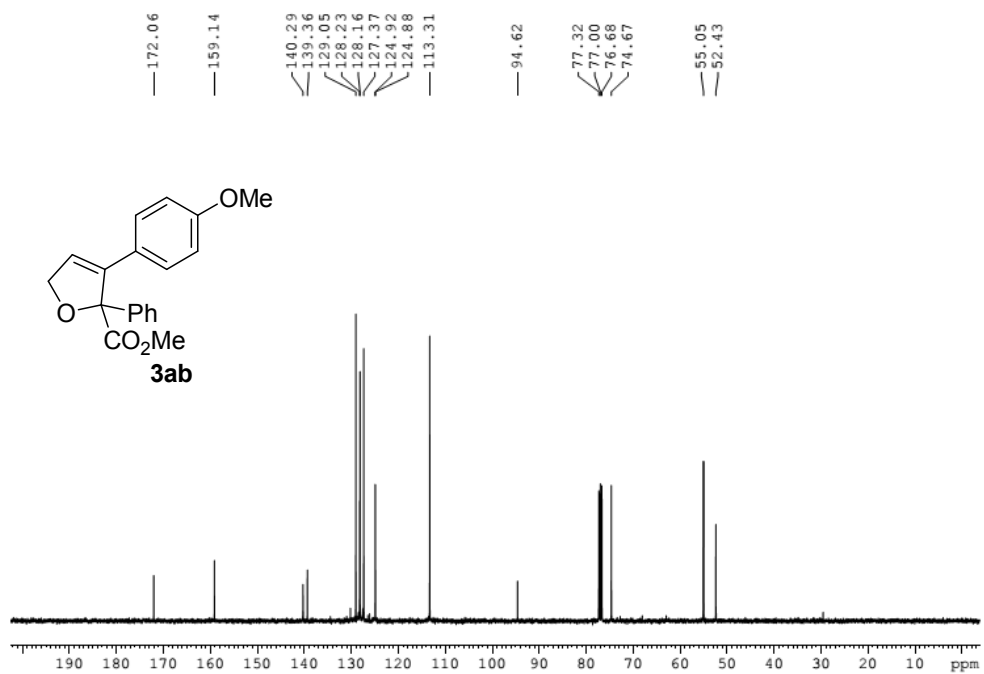
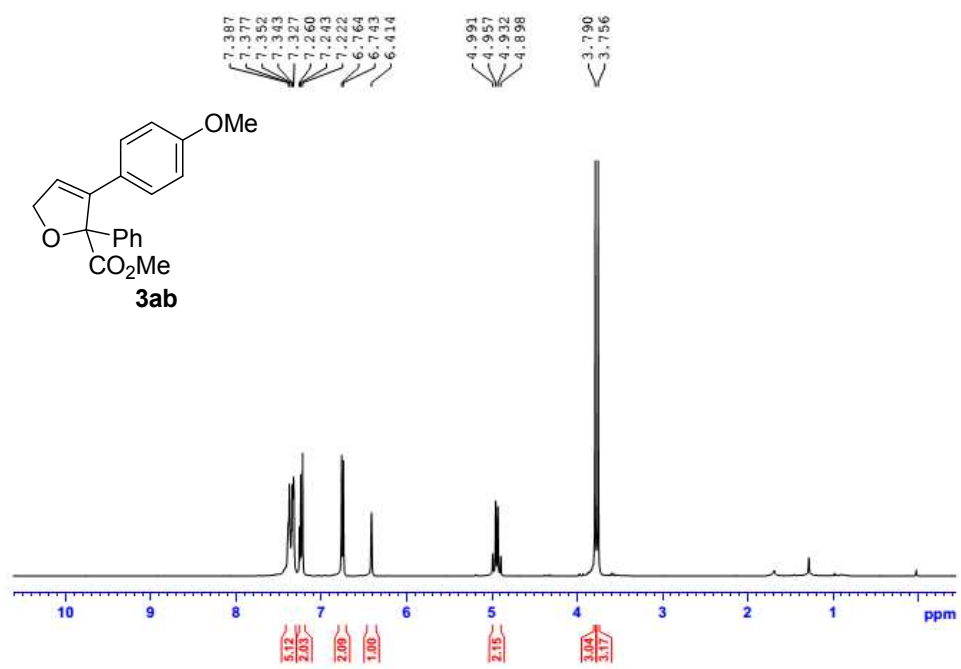


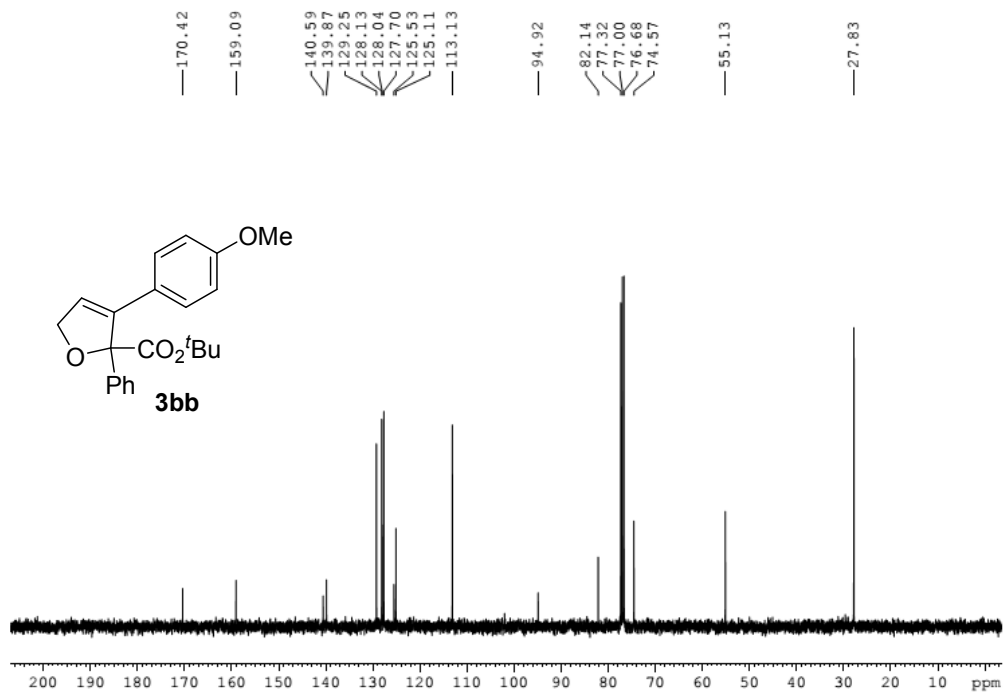
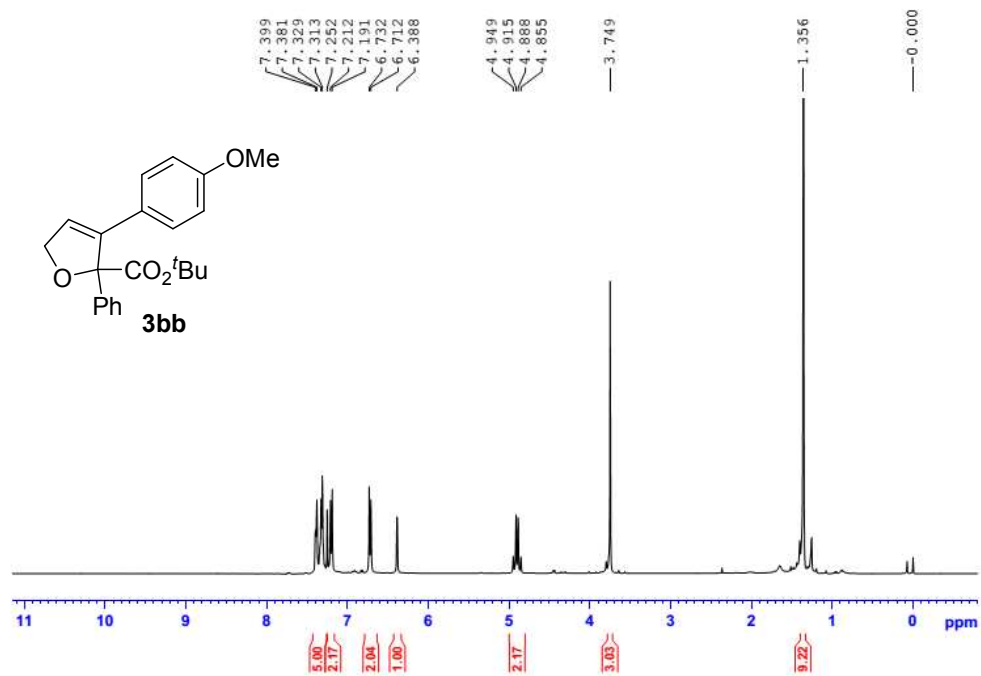


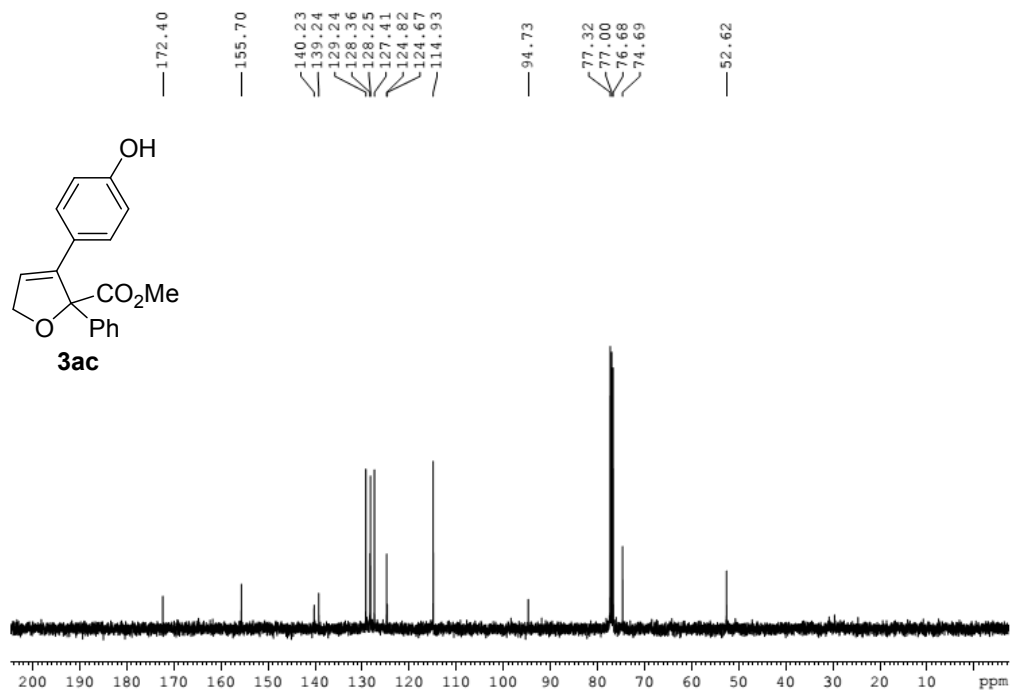
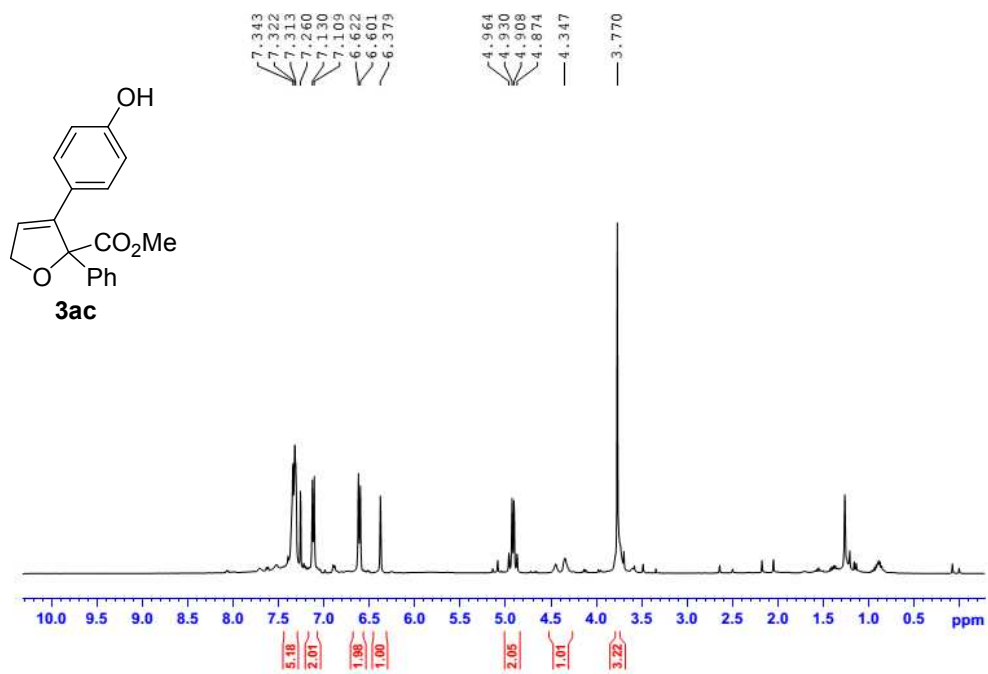


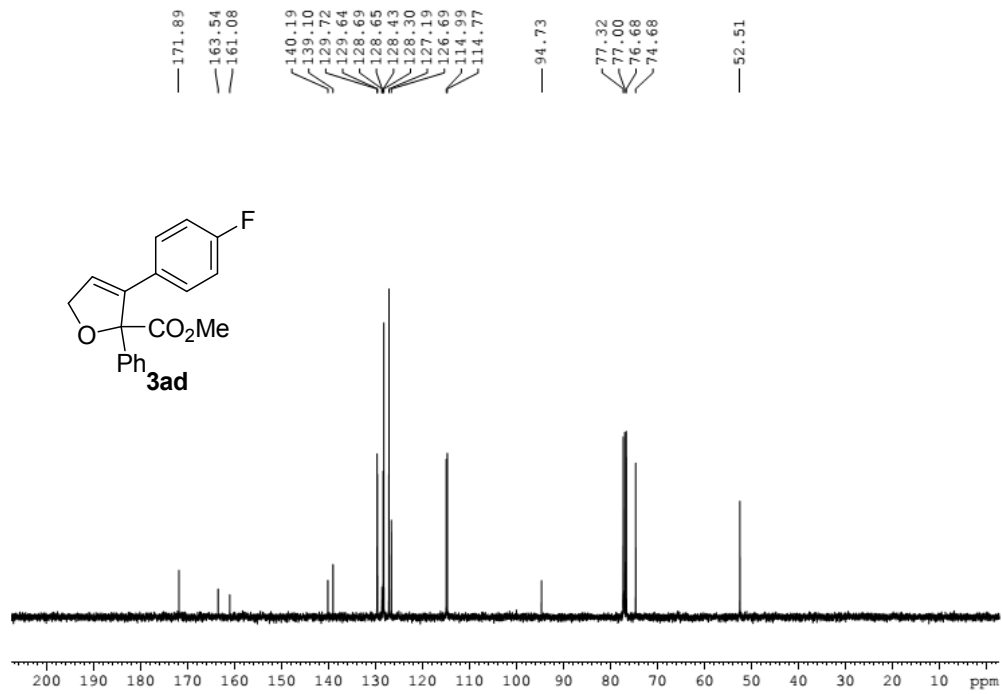
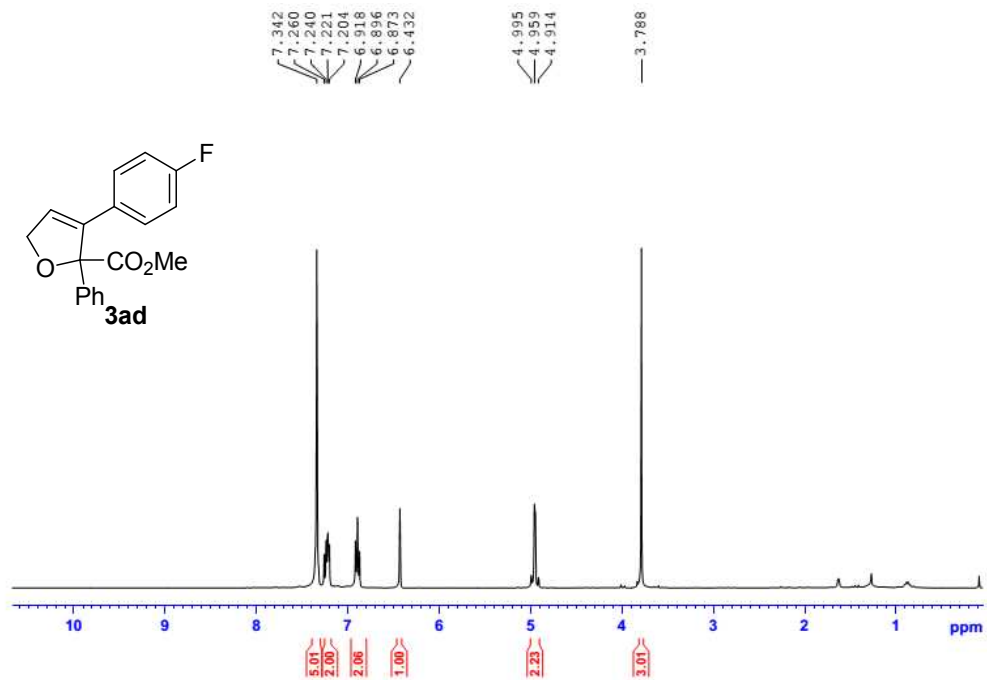


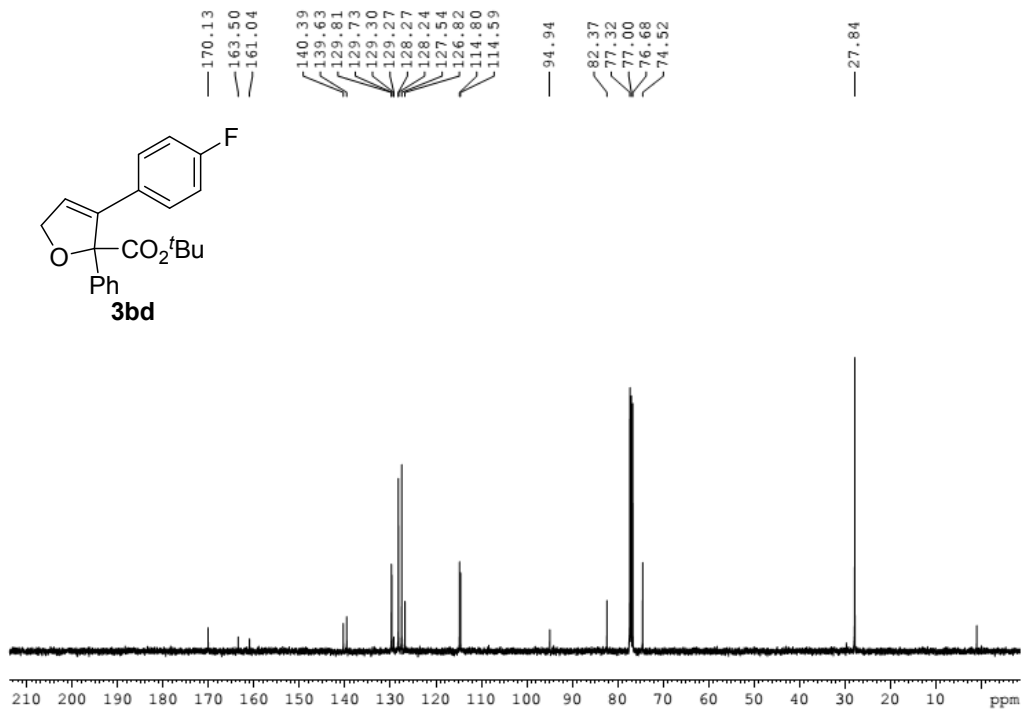
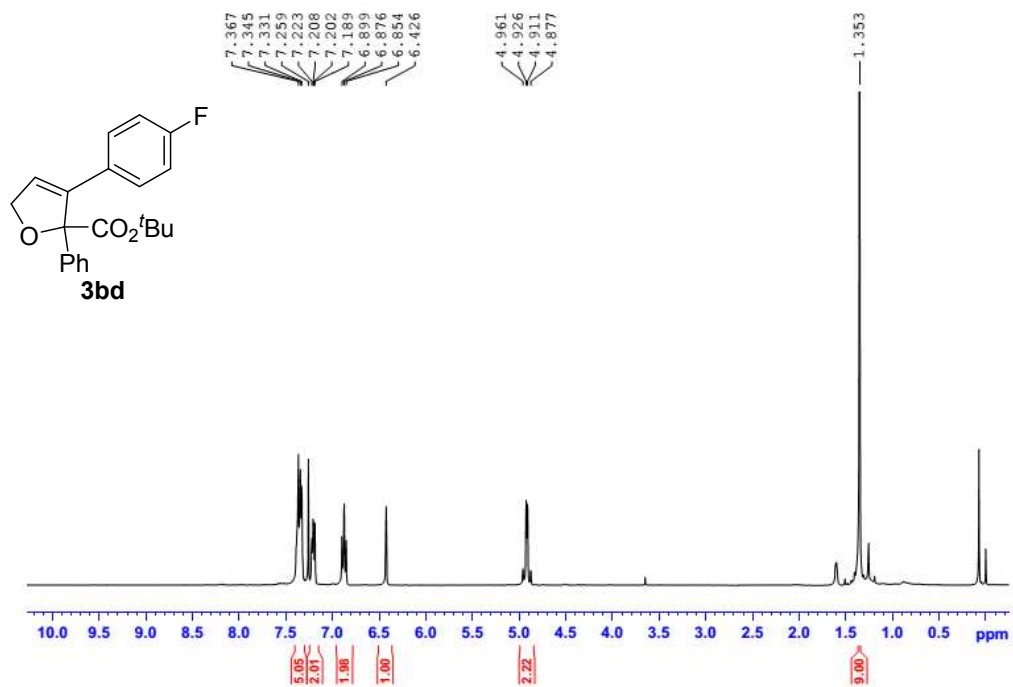


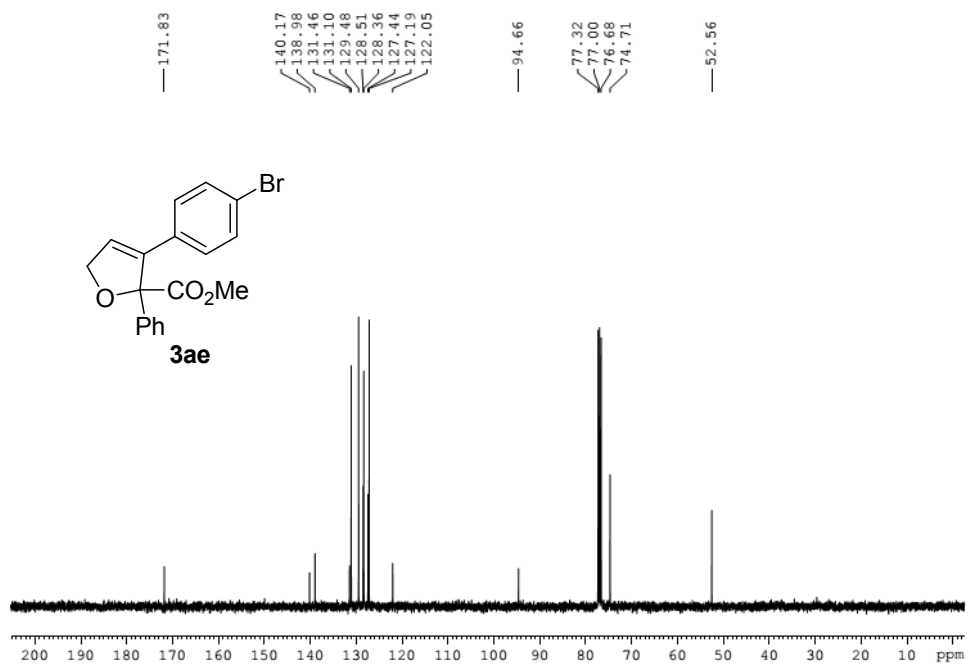
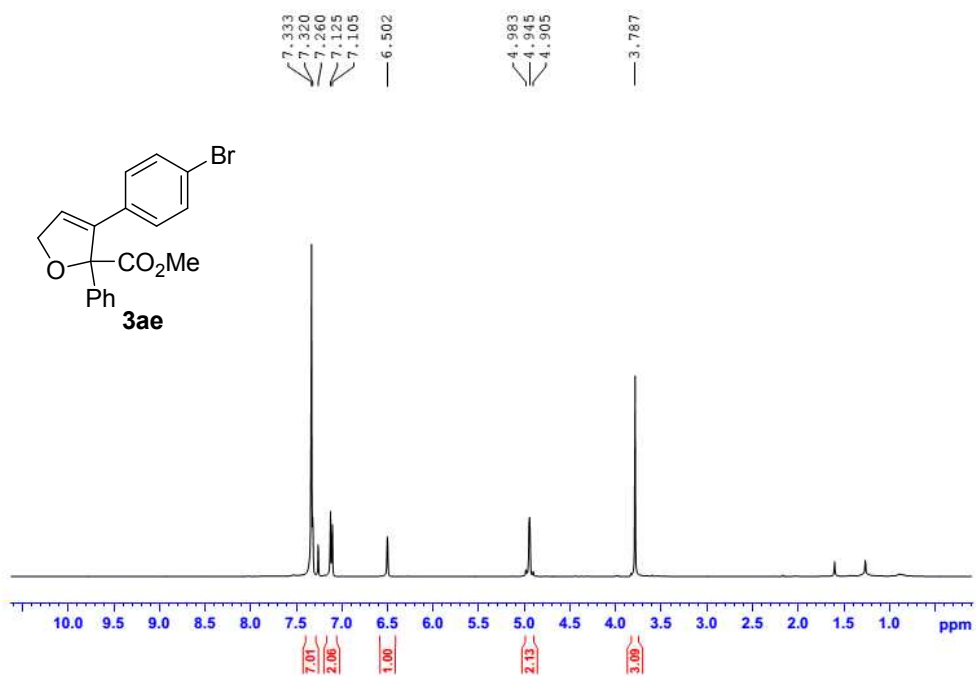


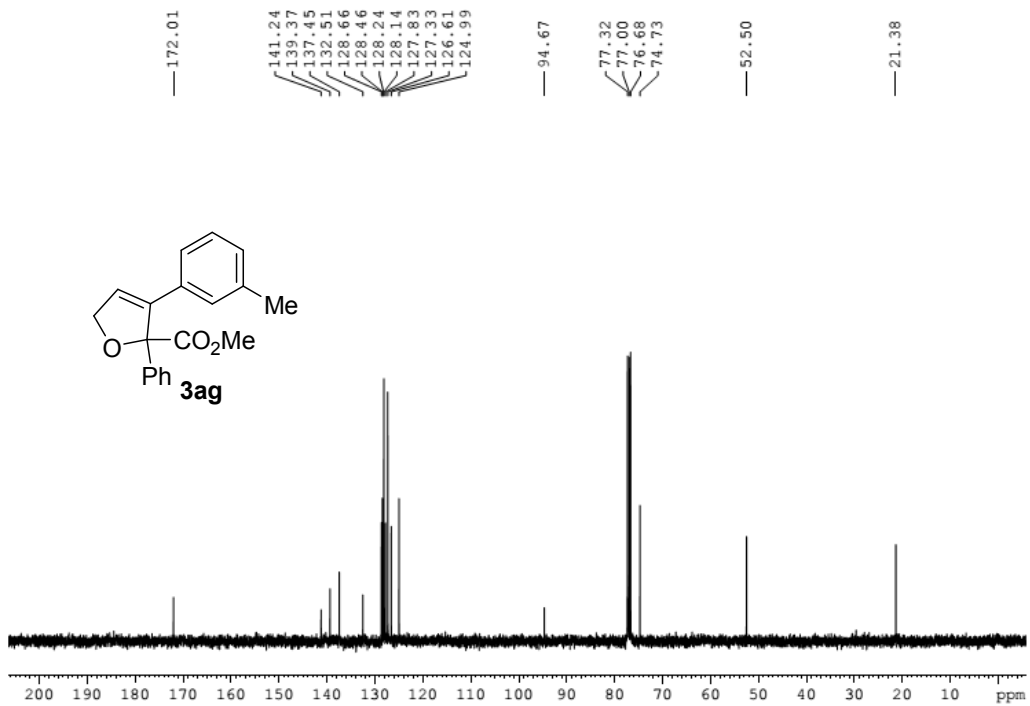
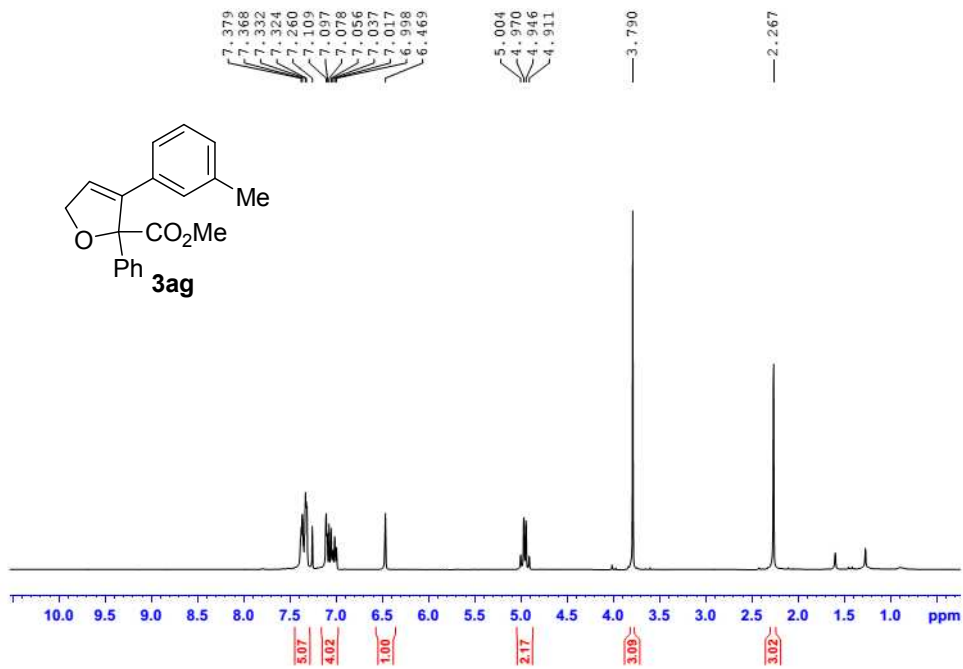


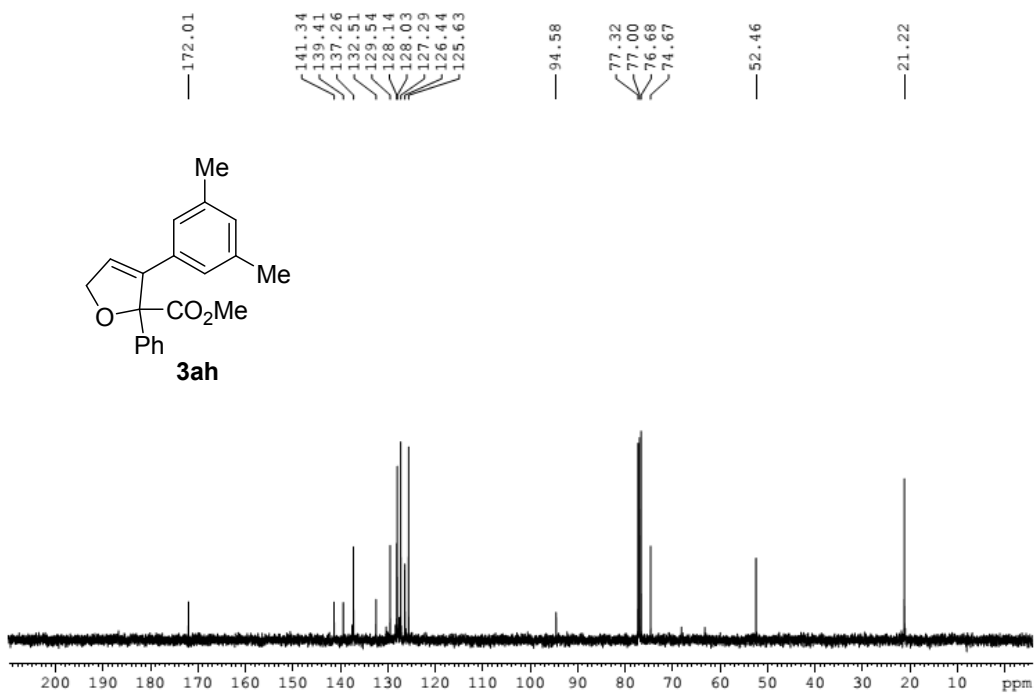
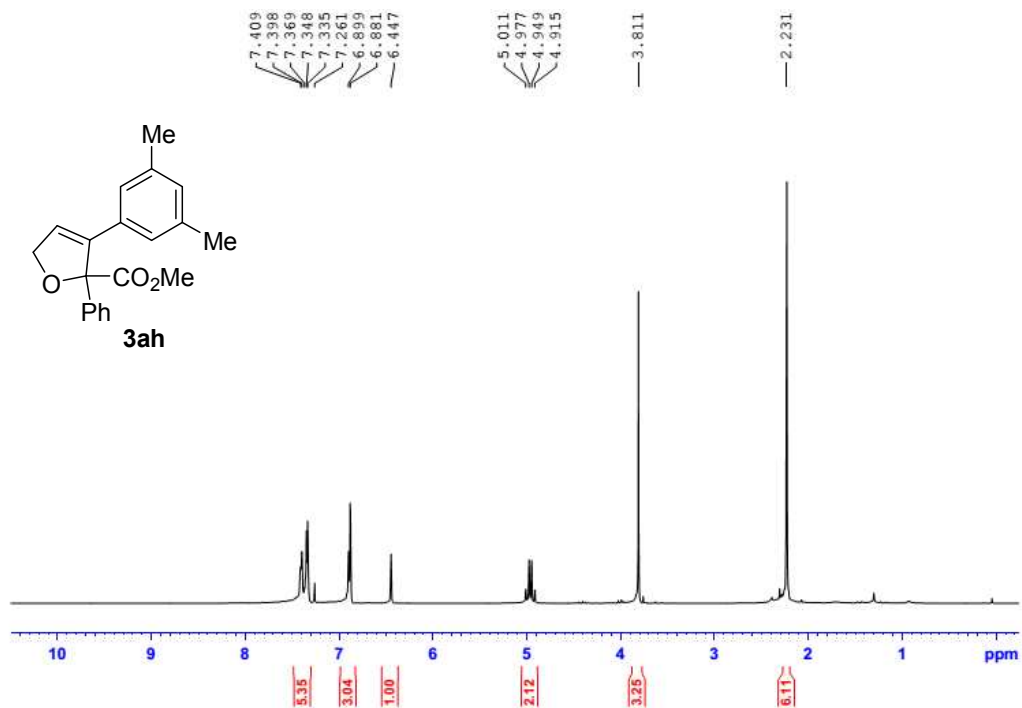


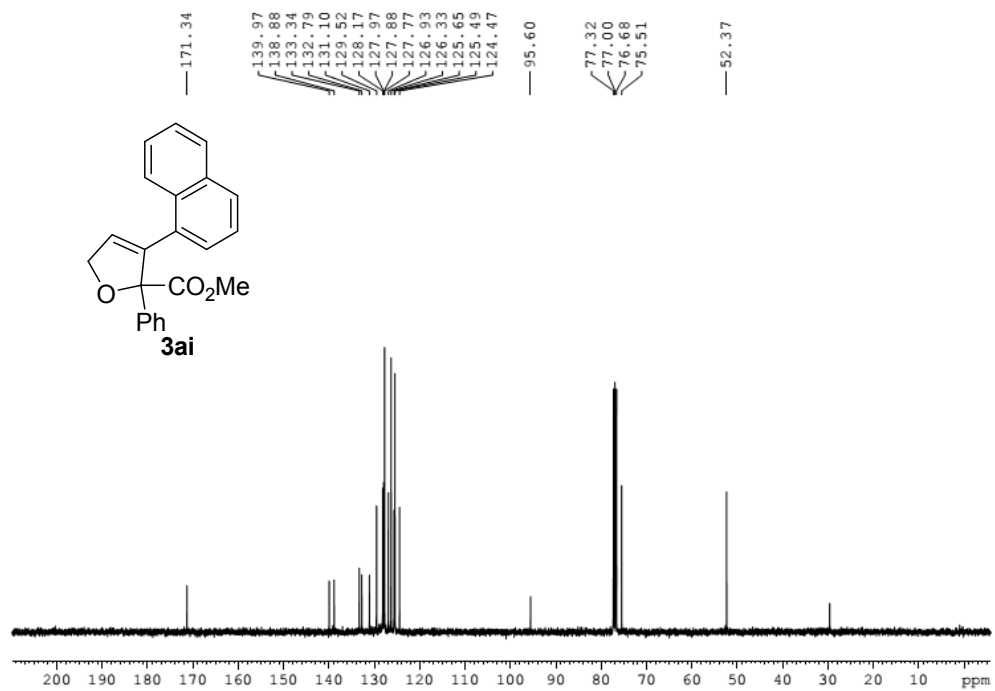
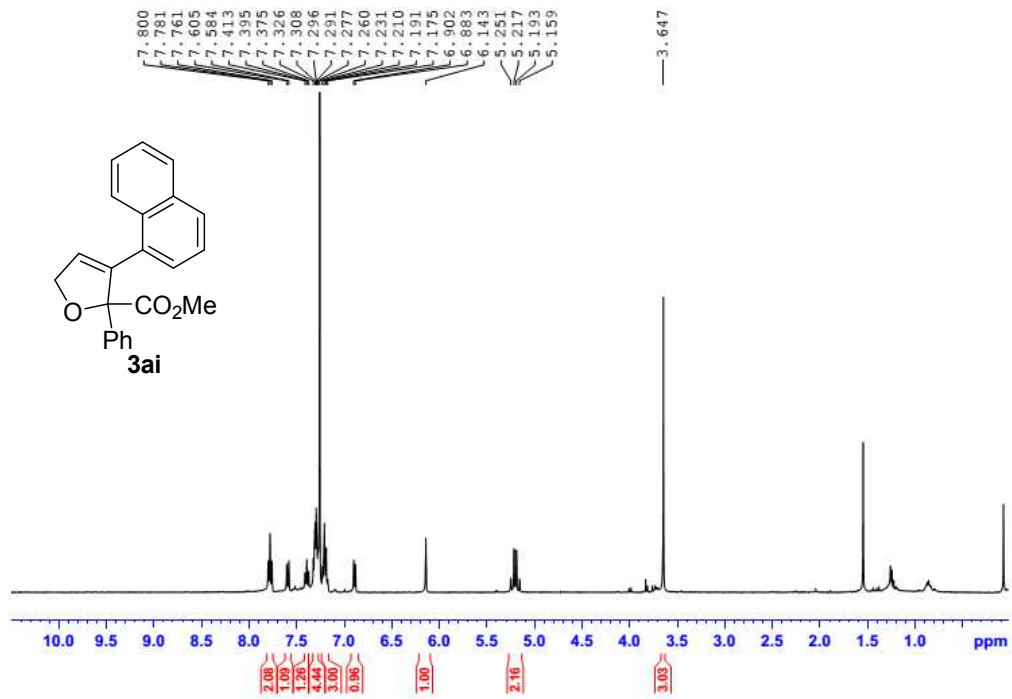


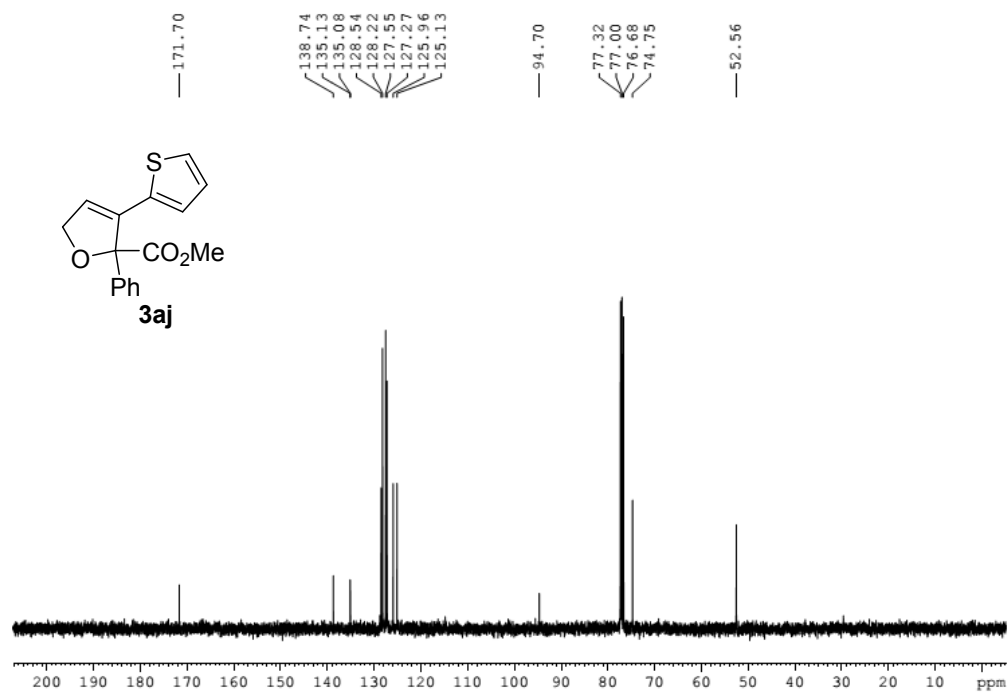
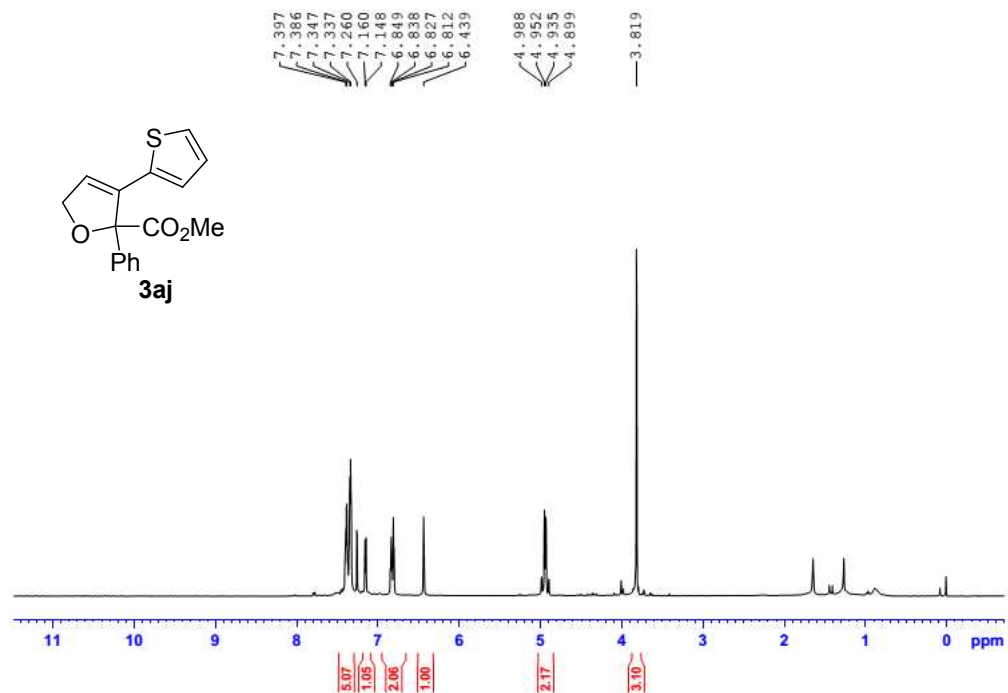


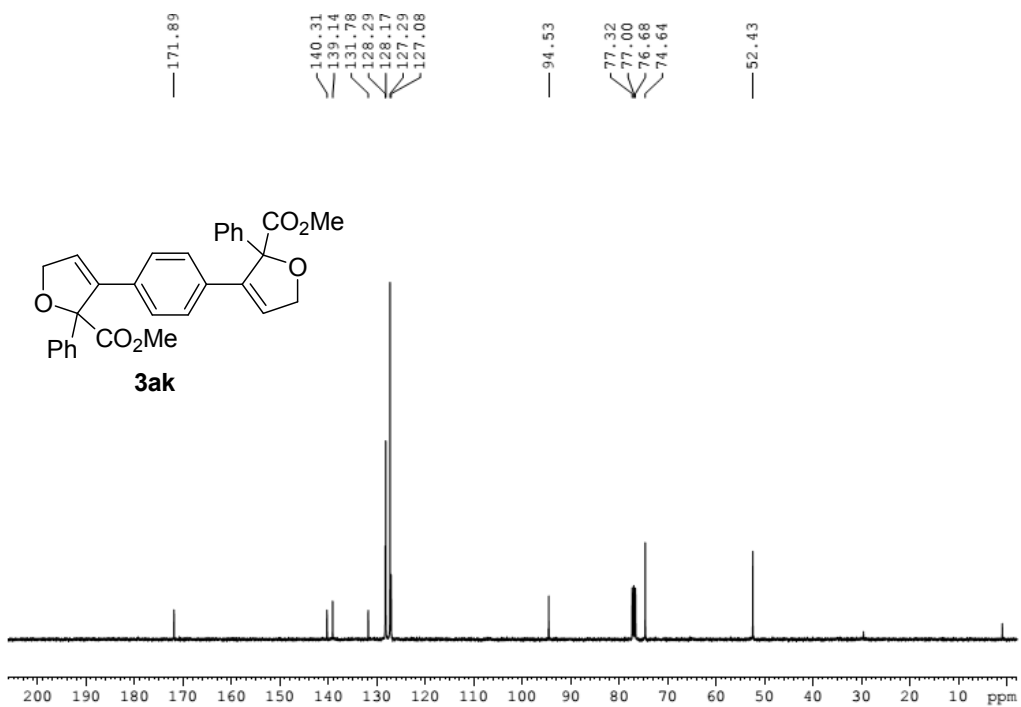
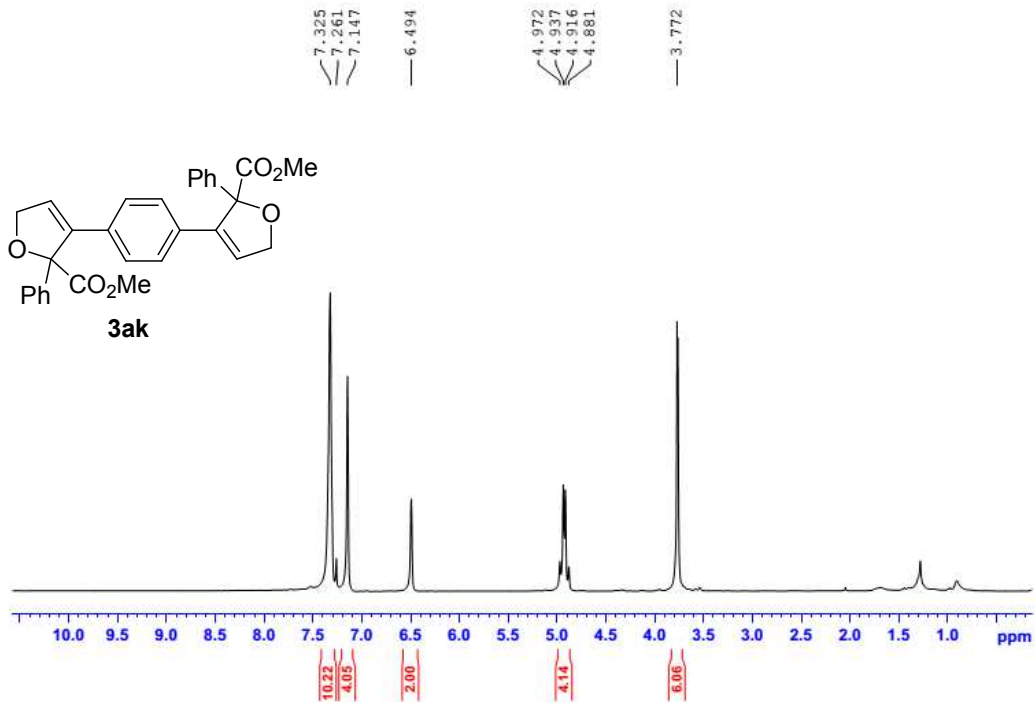


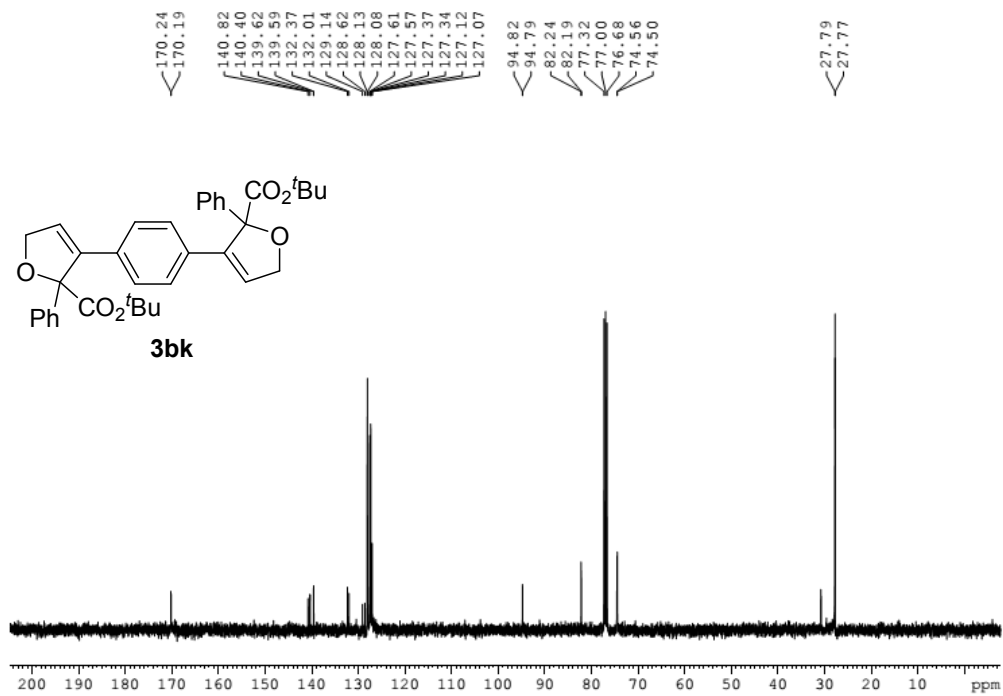
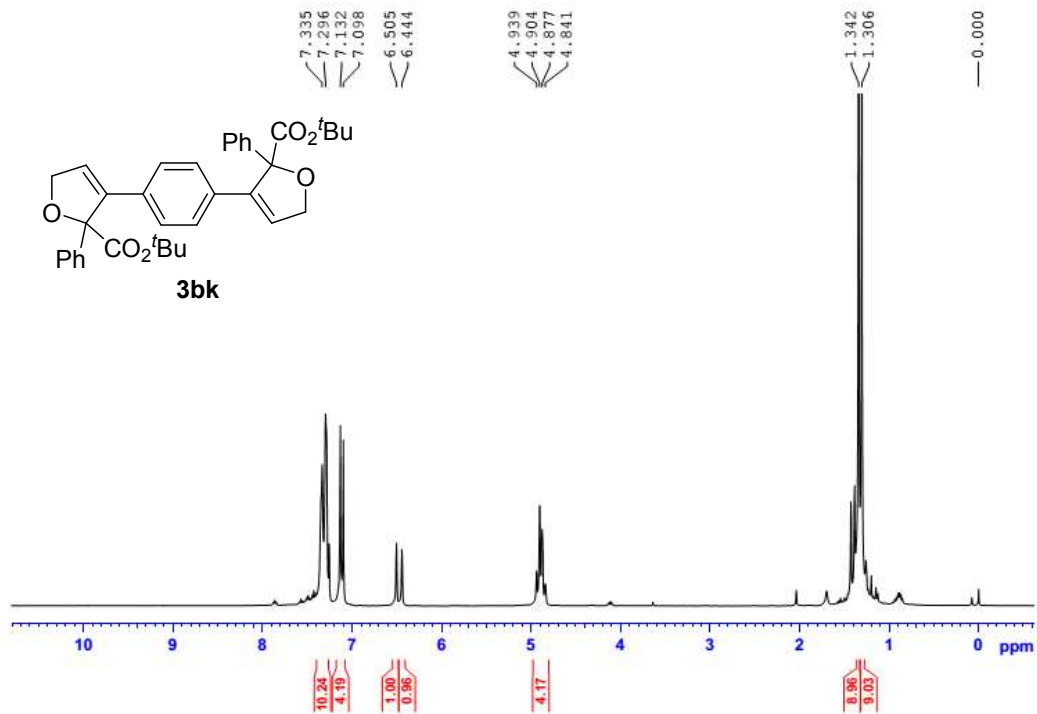


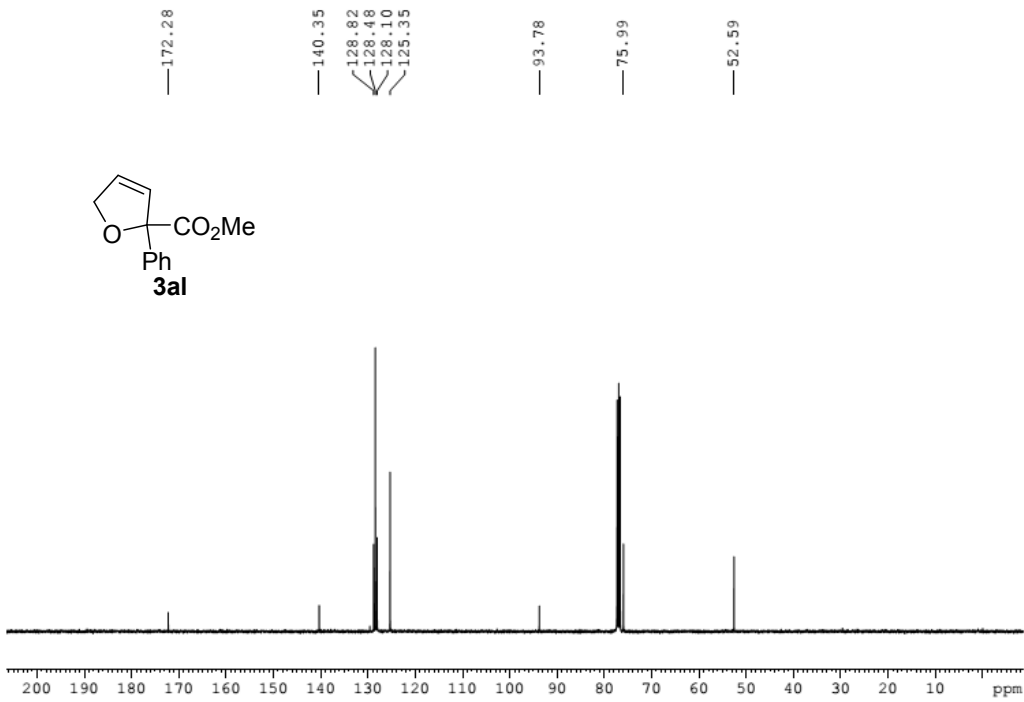
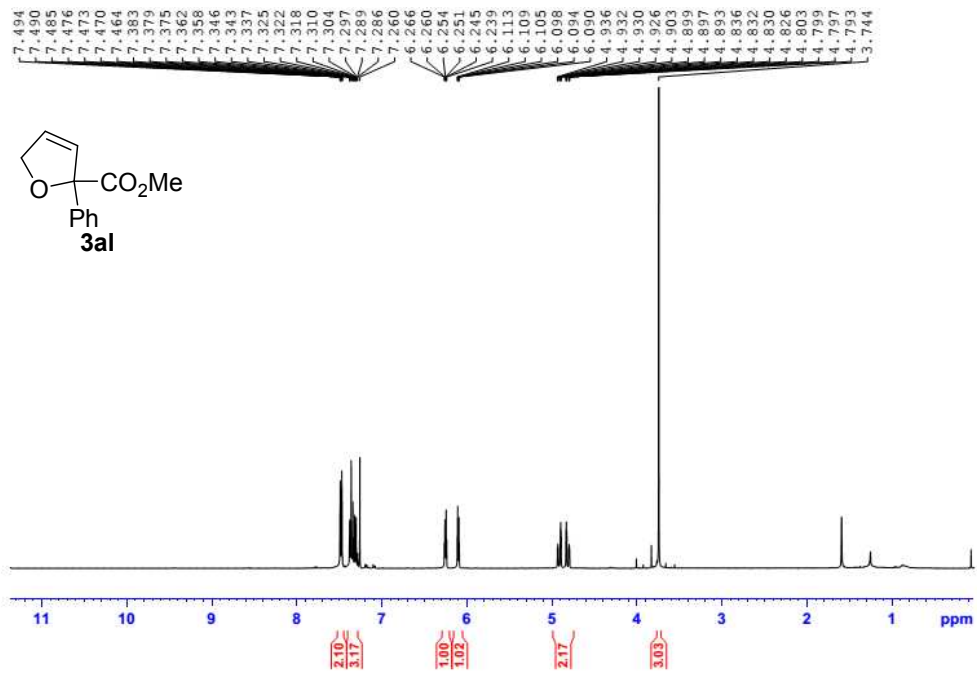


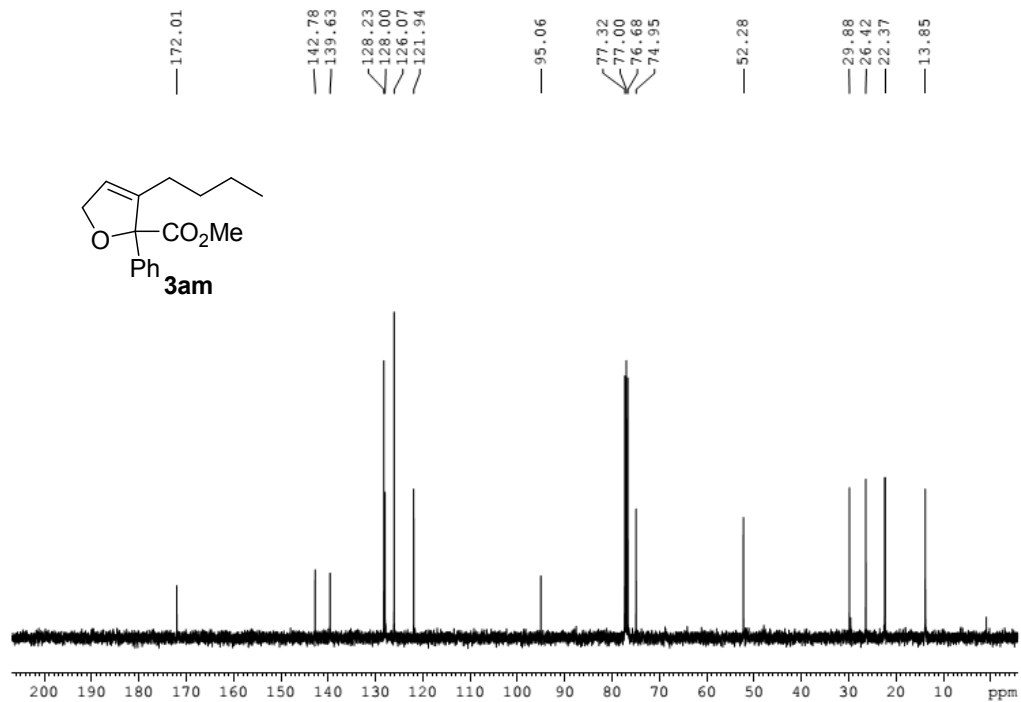
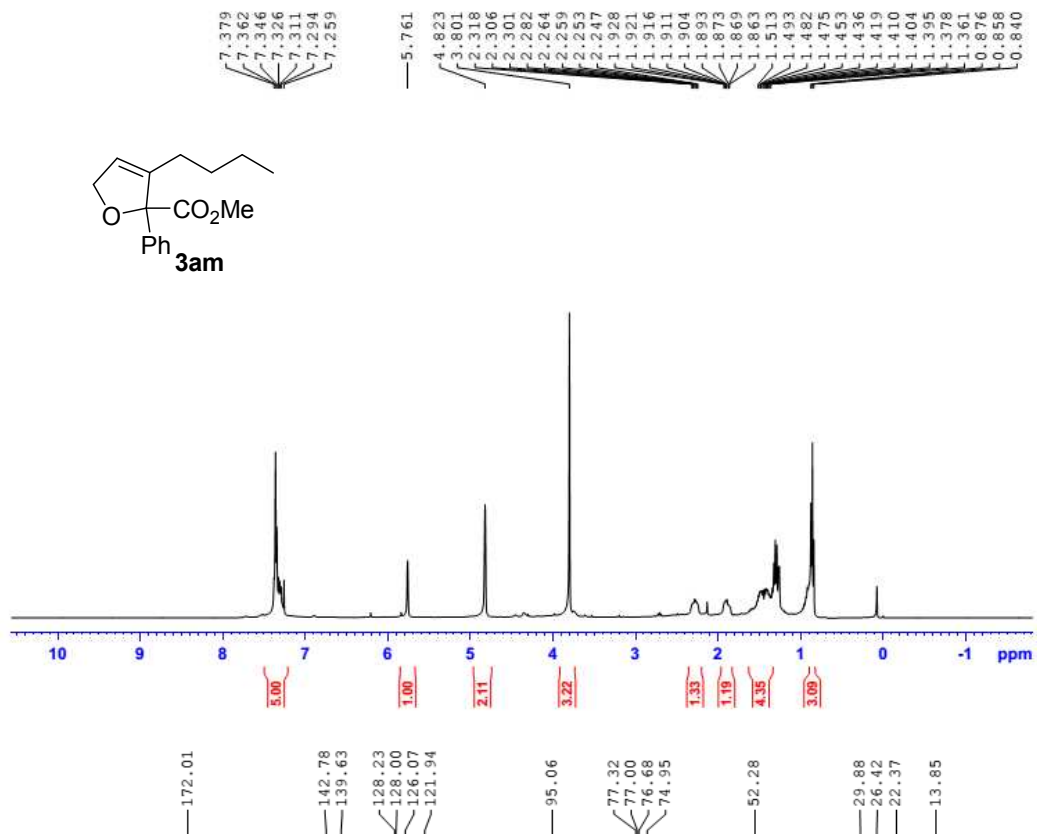


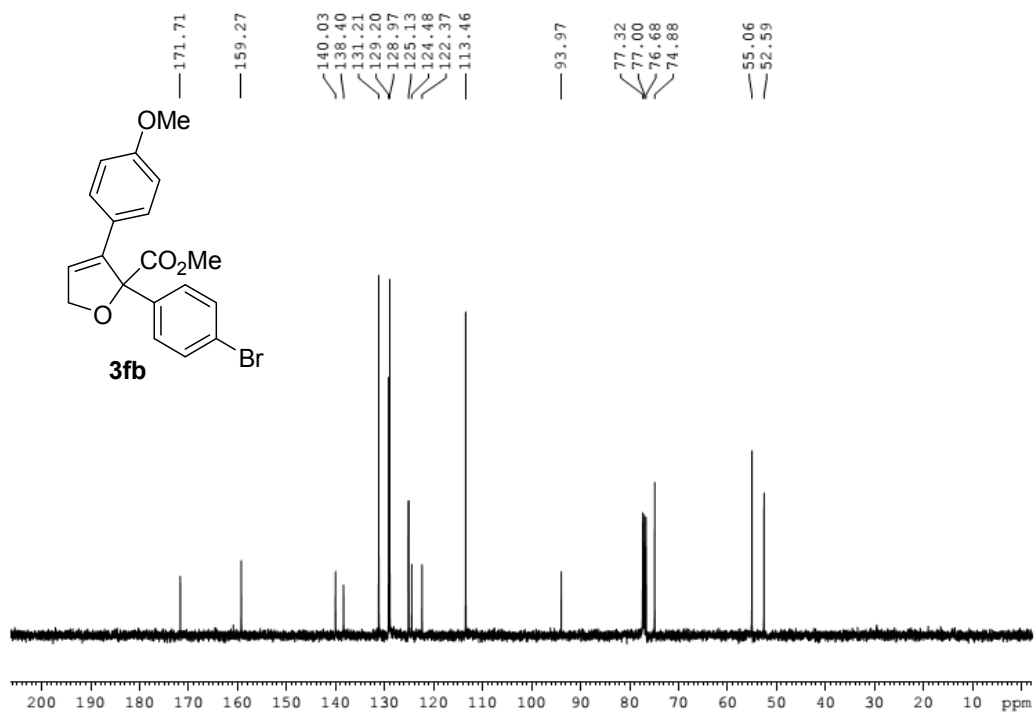
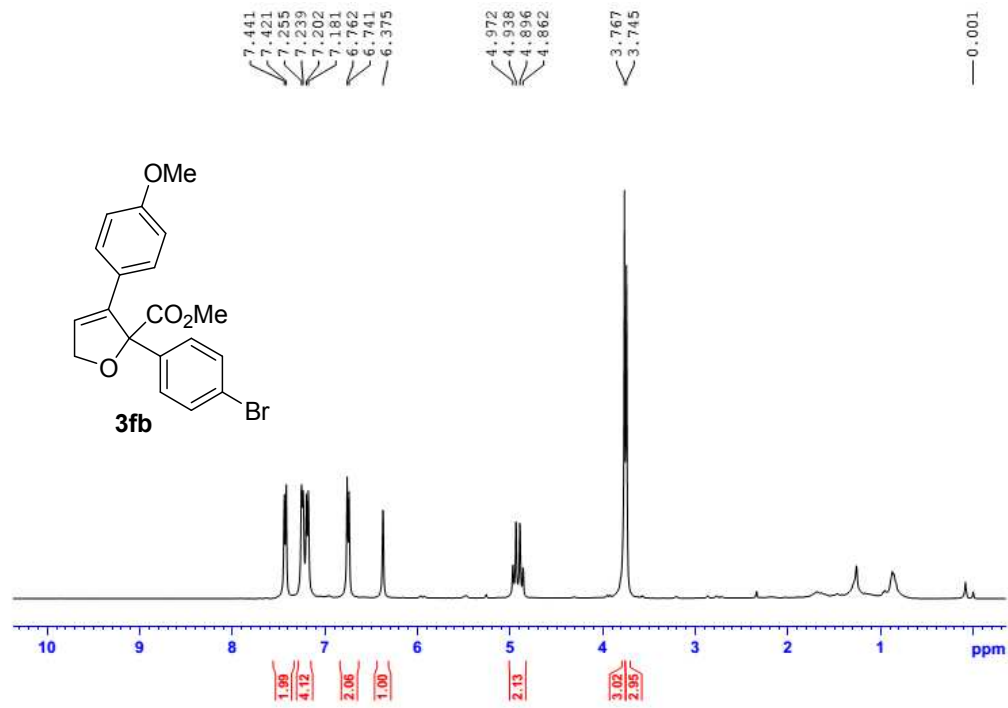


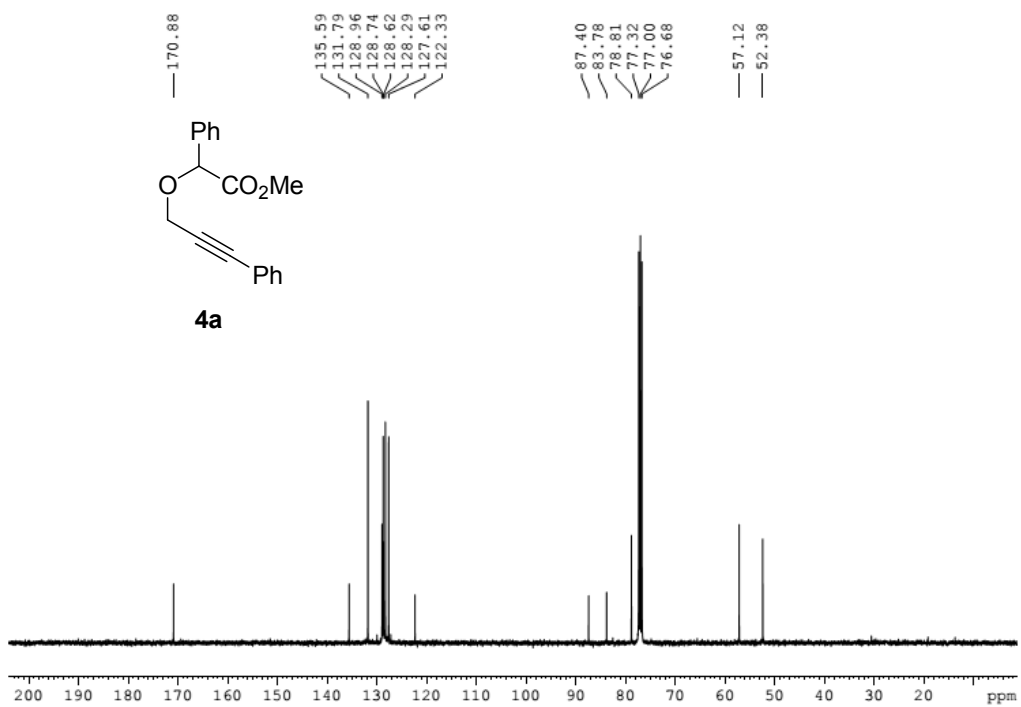
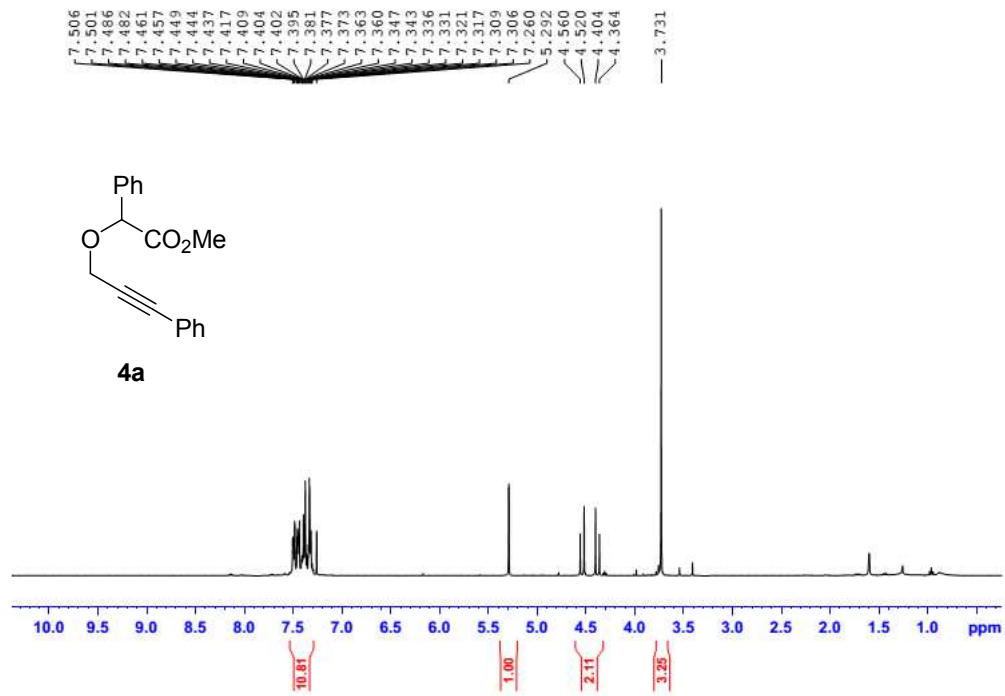


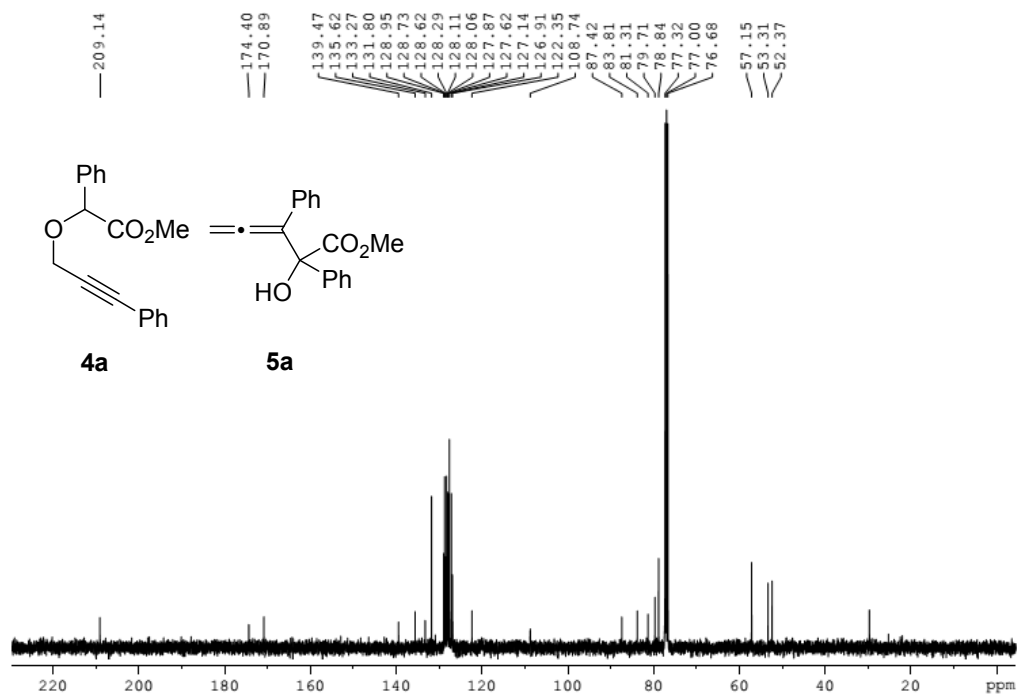
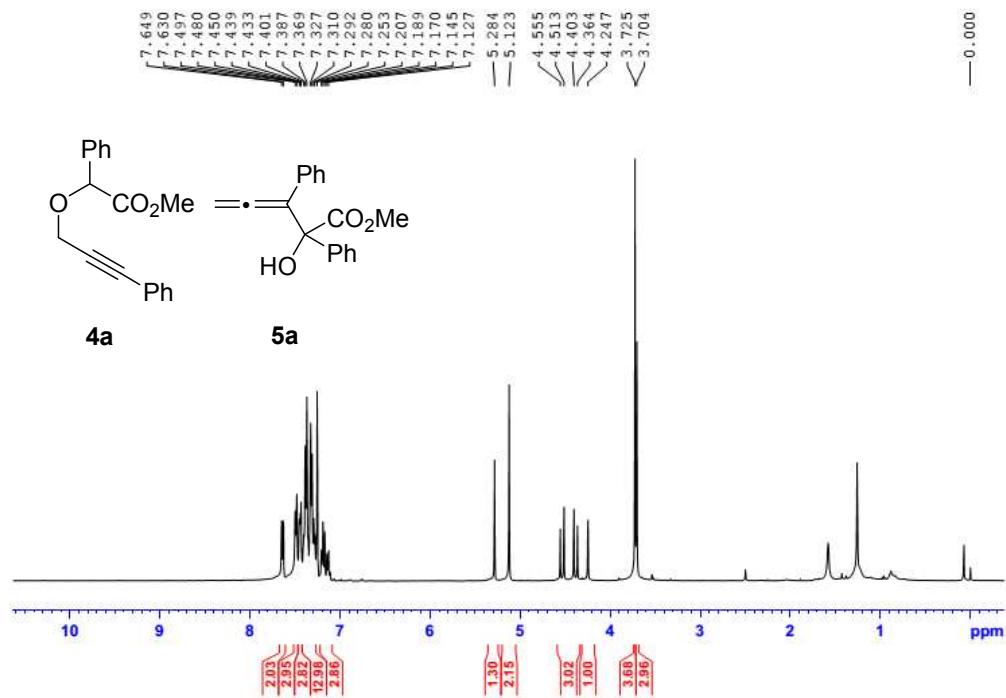


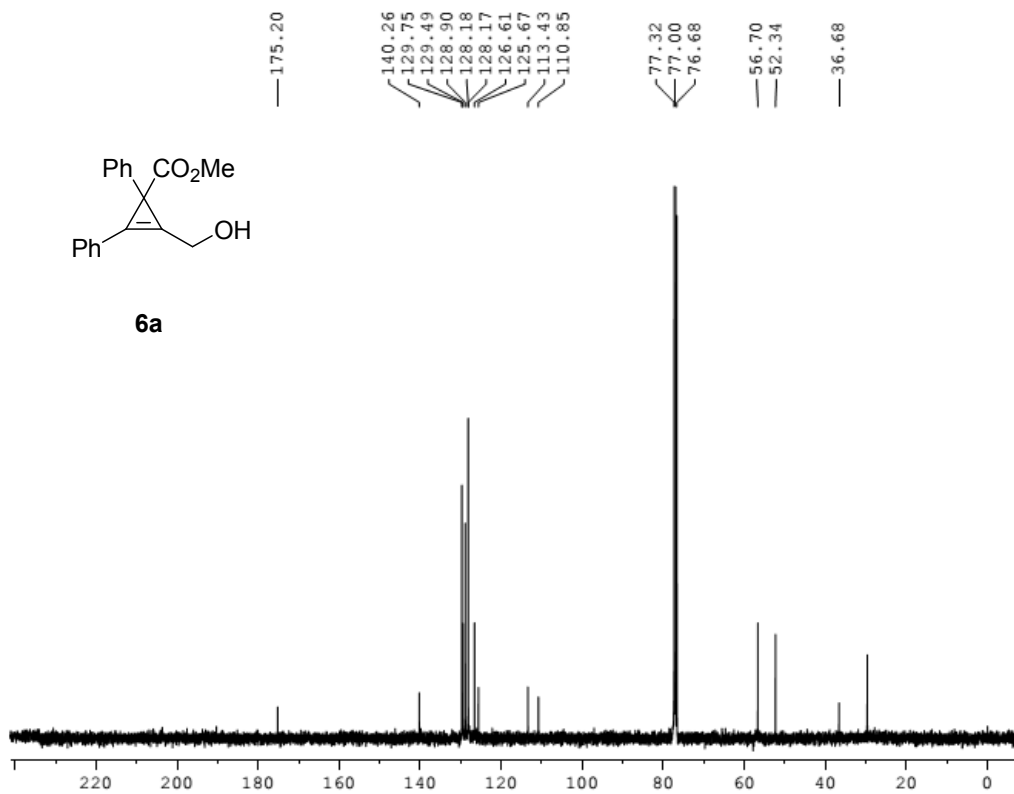
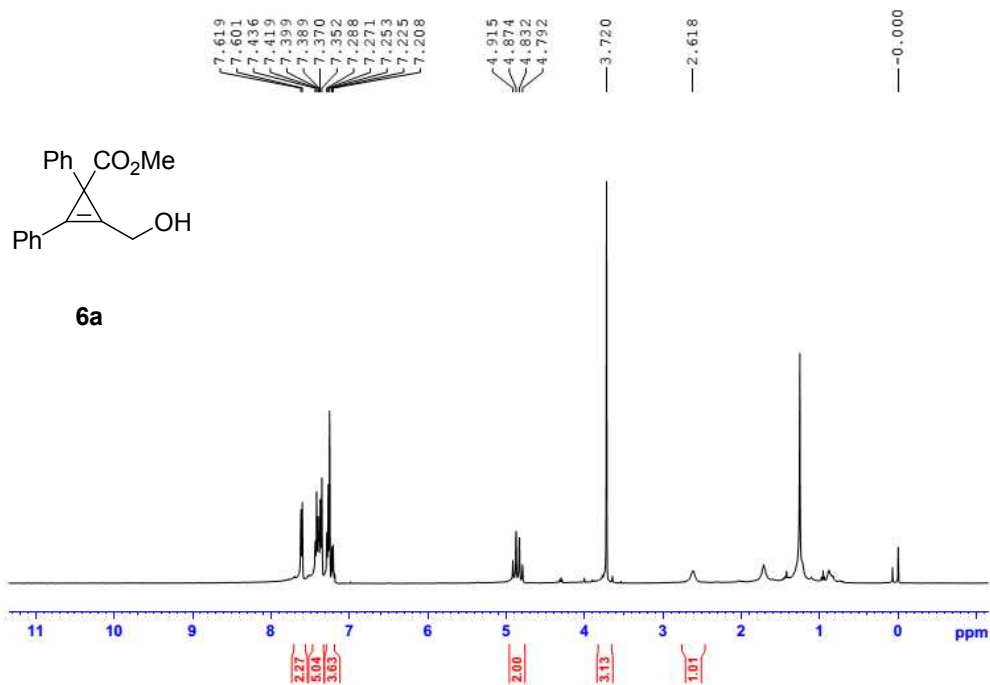


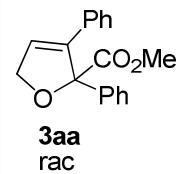
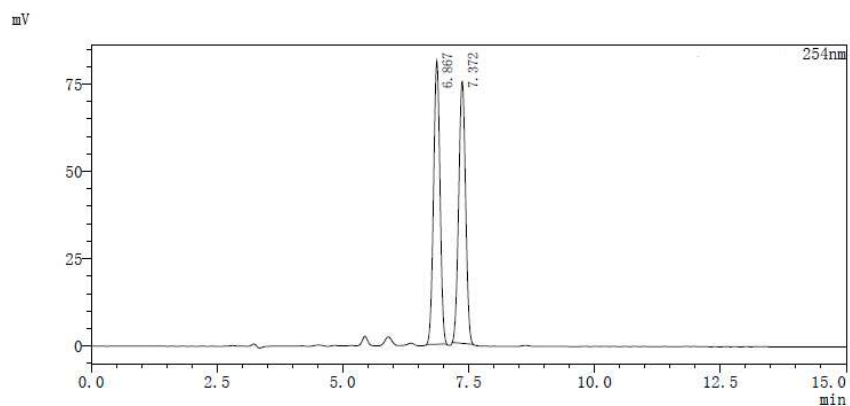




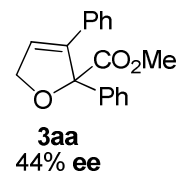
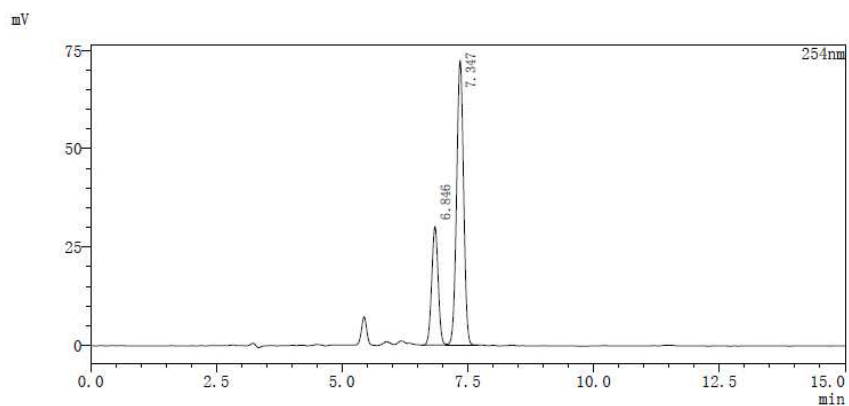








Time (min)	Area (mV*min)	Area (%)
6.867	722334	50.215
7.372	716143	49.785
	1438477	100.000



Time (min)	Area (mV*min)	Area (%)
6.846	269449	27.864
7.347	697575	72.136
	967024	100.000