Supporting Information

Cobalt Anion Couples Terminal Dienes with Trifuoroacetic Anhydride: A Direct Fluoroacylation of 1,3-Dienes

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I. General Procedures

All reactions were carried out under an atmosphere of argon. All glassware was either oven or flame-dried prior to use. Toluene, tetrahydrofuran (THF), and dichloromethane (CH_2Cl_2) were degassed with argon and then passed through two 4 x 36 inch columns of anhydrous neutral A-2 alumina (8 x 14 mesh; LaRoche Chemicals; activated under a flow of argon at 350 ºC for 12 h) to remove H_2O. Triethylamine (Et_3N) was distilled over CaH_2 under an argon atmosphere. ^1H NMR spectra were recorded on Varian Unity 300 (300 MHz ^1H, 75 MHz ^{13}C, 286 MHz ^{19}F) and Varian Unity 400 (400 MHz ^1H, 100 MHz ^{13}C, 381 MHz ^{19}F) spectrometers. Proton chemical shifts are reported in ppm (δ) relative to internal tetramethylsilane (TMS, δ 0.00) or relative to the respective solvent resonance as the internal standard (C_6D_6, δ 7.16 ppm). Data are reported as follows: chemical shift (multiplicity [singlet (s), broad singlet (brs), doublet (d), triplet (t), quartet (q), pentet (p), sextet (h), doublet of doublets (dd), doublet of doublet of doublets (ddd), triplet of doublets (td), doublet of triplets (dt), doublet of quartets (dq), doublet of pentets (dp), multiplet (m), apparent doublet (ad), and apparent triplet (at)], coupling constants [Hz], integration. Carbon chemical shifts are reported in ppm (δ) relative to the respective solvent resonance as the internal standard ($CDCl_3$, δ 77.23 ppm). Fluorine chemical shifts are reported in ppm (δ) relative to trifluorotoluene as the internal standard (δ -63.7 ppm). NMR data were collected at 25 ºC. Infrared spectra were obtained on a Nicolet Avatar 320 FT-IR spectrometer and Bruker Tensor 27 FT-IR spectrometer. Analytical thin-layer chromatography (TLC) was performed using Silica Gel 60 F254 precoated plates (0.25 mm thickness). Visualization was accomplished by irradiation with a UV lamp (254 nm) and/or staining with $KMnO_4$, solution. Flash chromatography was performed using Silica Gel 60A (170-400 mesh) from Silicycle Inc. Mass spectrometry was performed XXXX.

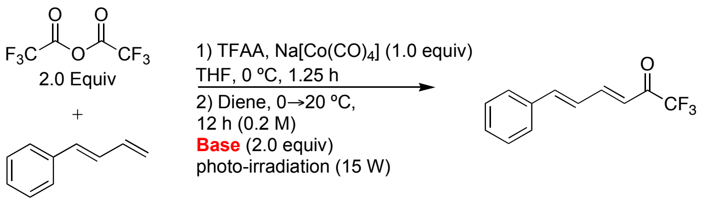
Na[Co(CO)$_4$] was made according to Edgell and Lyford in a glove box and was stored in the glovebox at 0 °C.[1] Trifluoroacetic anhydride was purchased from Oakwood Chemicals, distilled over P_2O_5, and stored under argon. 1,3-Dienes were stored at –10 °C and prepared by Wittig olefination of the commercially available α,β-unsaturated aldehyde or ketone using methyltriphenylphosphonium bromide and butyl lithium.[2] Compound **2a** (*E*,*Z*-mixture) was prepared from benzaldehyde and allyltriphenylphosphonium bromide.[2] The molarity of organolithium was determined by titration with menthol/bipyridine. $Co_2(CO)_8$ was purchased from Strem Chemicals, Inc. and used as received. Pentafluoropropionic anhydride and heptafluorobutyric anhydride were purchased from Oakwood Chemicals, used as received, and stored under argon in a desiccator. All other chemicals were purchased commercially and used as received from Sigma Aldrich, Alfa Aesar, or TCI America.

II. Representative procedure for fluoroacetylation reactions

In a glovebox, an oven-dried vial was charged with Na[Co(CO)$_4$] (34 mg, 0.10 mmol, 1.00 equiv) and dissolved into THF (0.50 mL). The reaction vial was sealed, removed from the glovebox, and cooled to 0 ºC under argon. Trifluoroacetic anhydride (27 μL, 0.20 mmol, 2.00 equiv) was added and stirred for 15 min. In a separate vial, 1,3-diene **2a** (0.10 mmol, 1.0 equiv) was dissolved into THF (0.50 mL) with 1,2,2,6,6-pentamethylpiperidine (36 μL, 0.20 mmol, 2.00 equiv). After the cobalt solution was stirred for 15 min. the diene and base solution was added to the cobalt reaction vial and irradiated with a 15 W lamp placed 2 inches above the reaction flask. The reaction was allowed to gradually warm to 20 ºC over 7 hours under an argon atmosphere. Upon reaction completion, the vial was opened to air and diluted with CH_2Cl_2 (2.5 mL), silica gel was added (1 mL), and the reaction was stirred open to air for 1 hour. The slurry was then passed through a 2 mL plug of silica gel and washed with CH_2Cl_2 (3 x 2 mL). The organics were concentrated and the organic residue was purified by flash column chromatography (3-10% Et_2O/Pentane) to give the desired ketone **3a** as a yellow oil (17.2 mg, 78% yield). Spectral data matches literature.[3]

III. Additional optimization reactions

The following base screen was run under standard conditions (section II above) for 12 hours.



Entry	Base	Yield (%)[a]
1	Et_3N	51
2	2,6-Lutidine	37
3	DABCO	23
4	*i*-Pr_2EtN	52
5	**1,2,2,6,6-pentamethylpiperidine**	**65**
6	DBU	0
7	Bu_3N	55
8	1,1,3,3-tetramethylguanidine	0
9	Quinuclidine	62

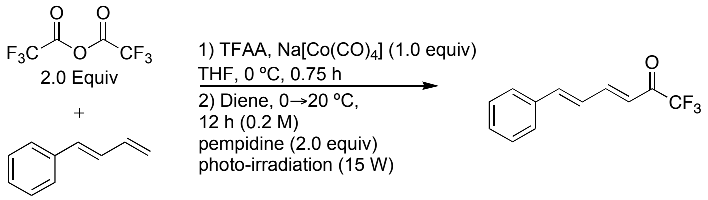
[a] Isolated yield after column chromatography.

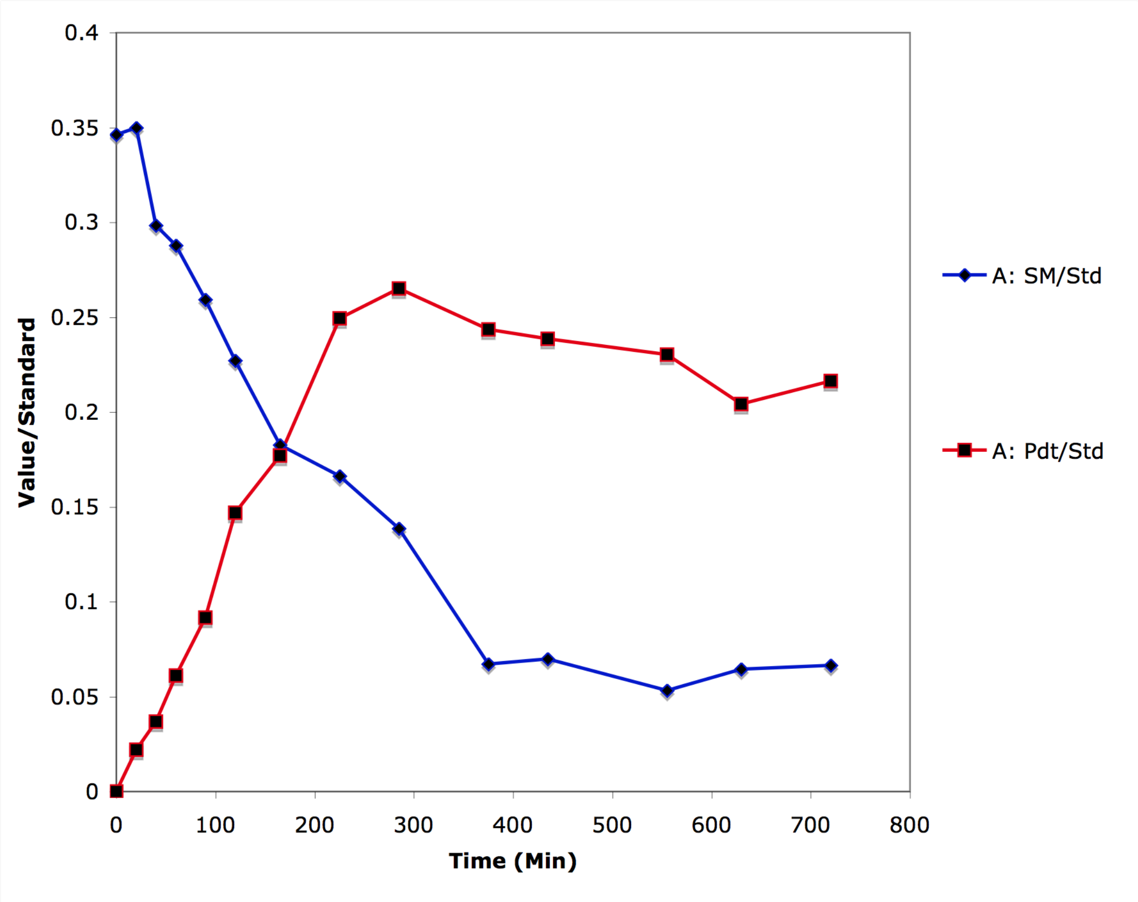
The optimal base was found to be 1,2,2,6,6-pentamethylpiperidine (pempidine). The yield is not subject to acidity alone, as bases that are both stronger (DBU) and weaker (DABCO) were ineffective in the reaction conditions.

IV. HPLC Time Point Experiments

HPLC Analysis:

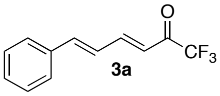
In a glovebox, an oven-dried vial was charged with $Na[Co(CO)_4]$ (34 mg, 0.10 mmol, 1.00 equiv) and dissolved into THF (0.50 mL). The reaction vial was sealed, removed from the glovebox, and cooled to 0 ºC under argon. Trifluoroacetic anhydride (27 μL, 0.20 mmol, 2.00 equiv) was added and stirred for 45 min. In a separate vial, 1,3-diene **2a** (0.10 mmol, 1.0 equiv) was dissolved into THF (0.50 mL) with 1,2,2,6,6-pentamethylpiperidine (36 μL, 0.20 mmol, 2.00 equiv) and 4,4'-di-tertbutyl-biphenyl (0.013 g, 0.05 mmol) and cooled to 0 ºC. After the cobalt solution had stirred for 45 min, the cobalt solution was added to the solution of diene and base and irradiated with a 15 W lamp placed 2 inches above the reaction flask. The reaction was allowed to gradually warm to 20 ºC. Aliquots (50 μL) were removed from the reaction at the designated time points, diluted with HPLC grade methanol (1.25 mL), and analyzed by HPLC comparing product and starting materials to the internal standard (4,4'-di-tertbutyl-biphenyl). HPLC method: C-18 column, solvent A = 0.1 % H_3PO_4/H_2O; solvent B = CH_3CN; gradient 10-95% B in 6 min and hold at 95% B for 2.5 minutes; flow rate 1.8 mL/min. R_f Starting material = 5.64 min.; R_f Product = 5.88 min.; R_f internal standard = 7.84 min.





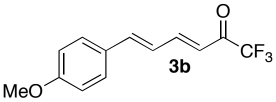
At approximately 300 minutes the reaction appears to reach maximum conversion of starting material to product. This is followed by a second reaction regime (after 300 minutes) that displays consumption of both starting material and product. This may be due to decomposition of both compounds through single electron or cationic polymerization pathways, or additional decomposition pathways.

V. Characterization data for products



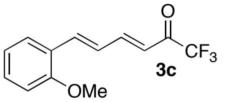
3a

Purified by flash column chromatography (3-6% Et_2O/Pentane) to give the desired ketone **3a** as a clear oil (17.2 mg, 78% yield). Spectral data matches literature.[3]



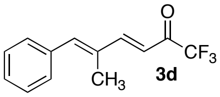
3b

Purified by flash column chromatography (5-10% Et_2O/Pentane) to give the desired ketone **3b** as a yellow solid (20.4 mg, 80% yield). Spectral data matches literature.[3]



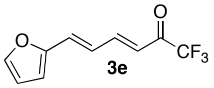
3c

Purified by flash column chromatography (5-10% Et_2O/Pentane) to give the desired ketone **3c** as a yellow oil (21.0 mg, 82% yield). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.75 (dd, *J* = 13.5, 12.7 Hz, 1H), 7.50 (bs, 1H), 7.49 (d, *J* = 22.2 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.04 (dd, *J* = 14.7, 12.2 Hz, 1H), 6.97 (t, *J* = 7.3 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 6.51 (d, *J* = 15.2 Hz, 1H), 3.89 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 180.0 (q, *J* = 291 Hz), 158.1, 151.1, 141.8, 131.6, 128.1, 126.5, 124.3, 120.8, 119.1, 116.5 (q, *J* = 35 Hz), 111.2, 55.5; **^{19}F NMR** ($CDCl_3$, 381 MHz): δ -77.4; **IR** (film, cm^{-1}) 3008, 2946, 1704, 1581, 1570; **GC-MS** (*m*): [M] 256; **TLC R_f** = 0.5 (10% Et_2O/Pentane, staining with $KMnO_4$).



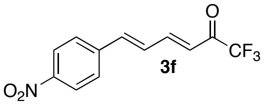
3d

Purified by flash column chromatography (3-6% Et_2O/Pentane) to give the desired ketone **3d** as a yellow oil (12.3 mg, 51% yield). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.78 (d, *J* = 15.5 Hz, 1H), 7.40 (s, 3H), 7.35 (d, *J* = 4.9 Hz, 1H), 7.08 (s, 1H), 6.53 (d, *J* = 15.5 Hz, 1H), 2.12 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 180.06 (q, *J* = 34.8 Hz), 155.3, 144.7, 136.0, 134.2, 129.8, 128.7, 128.5, 116.5 (q, *J* = 291 Hz), 116.0, 13.6; **^{19}F NMR** ($CDCl_3$, 381 MHz): δ -77.6; **IR** (film, cm^{-1}) 3062, 3028, 2927, 1701, 1576, 1566; **GC-MS** (*m*): [M] 240; **TLC R_f** = 0.6 (10% Et_2O/Pentane, staining with $KMnO_4$).



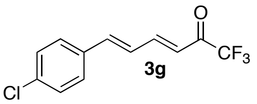
3e

Purified by flash column chromatography (3-10% Et_2O/Pentane) to give the desired ketone **3e** as a clear oil (13.6 mg, 63% yield). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.68-7.62 (m, 1H), 7.50 (d, *J* = 1.7 Hz, 1H), 6.92-6.81 (m, 2H), 6.60 (d, *J* = 3.4 Hz, 1H), 6.54 (s,), 6.51-6.48 (m, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 179.8 (q, *J* = 35.2 Hz), 151.7, 149.3, 145.0, 131.7, 124.1, 119.5, 115.2 (q, *J* = 219.0 Hz), 114.7, 112.7; **^{19}F NMR** ($CDCl_3$, 381 MHz): δ -77.5; **IR** (film, cm^{-1}) 2927, 1700, 1581; **GC-MS** (*m*): [M] 216; **TLC R_f** = 0.5 (10% Et_2O/Pentane, staining with $KMnO_4$).



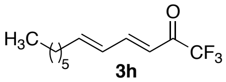
3f

Purified by flash column chromatography (3-10% Et_2O/Pentane) to give the desired ketone **3f** as a yellow solid (13.4 mg, 49% yield). Spectral data matches literature.[3]



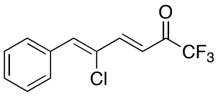
3g

Purified by flash column chromatography (3-10% Et_2O/Pentane) to give the desired ketone **3g** as a yellow oil (19.4 mg, 56% yield). Spectral data matches literature.[3]



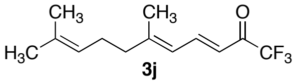
3h

Purified by flash column chromatography (0-2-5% Et$_2$O/Pentane) to give the desired ketone **3h** as a clear oil (22.2 mg, 76% yield). **^{1}H NMR** (CDCl$_3$, 400 MHz): δ 7.53 (dd, *J* = 15.3, 11.0 Hz, 1H), 6.43 (dt, *J* = 14.8, 7.3 Hz, 1H), 6.34 (d, *J* = 15.3 Hz, 1H), 6.28 (dd, *J* = 15.1, 11.0 Hz, 1H), 2.23 (q, *J* = 7.2 Hz, 2H), 1.48-1.41 (m, 2H), 1.34-1.23 (m, 6H), 0.87 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (CDCl$_3$, 100 MHz): δ 180.2 (q, *J* = 35 Hz), 151.8, 150.5, 128.6, 118.3, 116.3 (q, *J* = 291 Hz), 33.4, 31.5, 28.8, 28.3, 22.5, 14.0; **^{19}F NMR** (CDCl$_3$, 381 MHz): δ -77.6; **IR** (film, cm^{-1}) 2958, 2929, 2858, 1716, 1627, 1593; **GC-MS** (*m*): [M] 234; **TLC R$_f$** = 0.3 (100% Pentane, staining with KMnO$_4$).



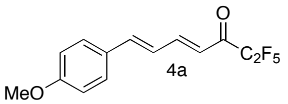
3i

Purified by flash column chromatography (5-10% Et$_2$O/Pentane) to give the desired ketone **3i** as a yellow solid (16.3 mg, 63% yield). **^{1}H NMR** (CDCl$_3$, 400 MHz): δ 7.83 (dt, *J* = 5.3, 2.1 Hz, 2H), 7.74 (d, *J* = 14.8 Hz, 1H), 7.45-7.41 (m, 3H), 7.18 (s, 1H), 6.91 (d, *J* = 14.8 Hz, 1H); **^{13}C NMR** (CDCl$_3$, 100 MHz): δ 179.8 (q, *J* = 36), 148.6, 140.7, 133.4, 130.7, 130.5, 129.2 (q, *J* = 48 Hz), 128.7, 118.8, 116 (q, *J* = 290.4); **^{19}F NMR** (CDCl$_3$, 381 MHz): δ -77.9; **IR** (film, cm^{-1}) 3031, 2926, 1717, 1603, 1583; **GC-MS** (*m*): [M] 260; **TLC R$_f$** = 0.7 (10% Et$_2$O/Pentane, staining with KMnO$_4$).



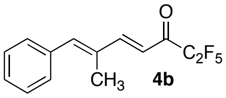
3j

Purified by flash column chromatography (2-4% Et$_2$O/Pentane) to give the desired ketone **3j** as a clear oil as a 1.3:1 mixture of Z,E and E,E isomers (25.2 mg, 51% yield). **^{1}H NMR** (CDCl$_3$, 400 MHz): δ 7.87 (ddd, *J* = 18.5, 15.0, 11.8 Hz, 1H), 6.33 (t, *J* = 15.7 Hz, 1H), 6.13 (d, *J* = 11.9 Hz, 1H), 5.09-5.03 (m, 1H), 2.37 (t, *J* = 7.5 Hz, 1H), 2.25-2.12 (m, 3H), 1.97 (s, 1H), 1.95 (s, 1H), 1.68 (s, 1H), 1.65 (s, 1H), 1.60 (s, 1H), 1.58 (s, 1H). ; **^{13}C NMR** (CDCl$_3$, 100 MHz): δ 180.4 (q, *J* = 34.5 Hz), 158.14, 158.09, 146.11, 145.92, 133.3, 132.7, 124.9, 124.0, 122.77, 122.58, 117.9, 117.6, 116.7 (q, *J* = 219 Hz), 40.7, 33.4, 29.7, 26.9, 26.2, 25.62, 25.57, 25.0, 18.0, 17.67, 17.63; **^{19}F NMR** (CDCl$_3$, 381 MHz): δ -77.5, -77.6; **IR** (film, cm^{-1}) 2968, 2930, 2859, 1716, 1700, 1616, 1587; **GC-MS** (*m*): [M] 246; **TLC R$_f$** = 0.7 (10% Et$_2$O/Pentane, staining with KMnO$_4$).



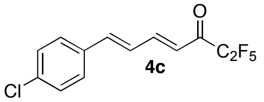
4a

Purified by flash column chromatography (5-10% Et$_2$O/Pentane) to give the desired ketone **4a** as a yellow oil (15.5 mg, 51% yield). **^{1}H NMR** (CDCl$_3$, 400 MHz): δ 7.76 (dd, *J* = 14.9, 11.4 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.13 (d, *J* = 15.3 Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.87 (dd, *J* = 15.4, 11.4 Hz, 1H), 6.61 (d, *J* = 15.1 Hz, 1H), 3.85 (s, 3H); **^{13}C NMR** (CDCl$_3$, 100 MHz): δ 161.8, 150.7, 147.0, 129.9, 128.4, 124.1, 118.9, 55.7; **^{19}F NMR** (CDCl$_3$, 381 MHz): δ -82.1, -123.8; **IR** (film, cm^{-1}) 3009, 2926, 2842, 1697, 1569, 1511; **GC-MS** (*m*): [M] 306; **TLC R$_f$** = 0.5 (10% Et$_2$O/Pentane, staining with KMnO$_4$).



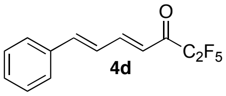
4b

Purified by flash column chromatography (3-10% Et$_2$O/Pentane) to give the desired ketone **4b** as a clear oil (26.6 mg, 48% yield). ^{1}**H NMR** (CDCl$_3$, 400 MHz): δ 7.81 (d, *J* = 15.2 Hz, 1H), 7.42 (s, 4H), 7.11 (s, 1H), 6.64 (d, *J* = 14.3 Hz, 1H), 2.14 (s, 3H); ^{13}**C NMR** (CDCl$_3$, 100 MHz): δ 180.3 (t, *J* = 26 Hz), 153.42, 153.35, 143.3, 141.2, 134.0, 132.3, 127.88, 127.75, 126.9, 126.6, 114.2, 11.7; ^{19}**F NMR** (CDCl$_3$, 381 MHz): δ -84.0, -125.6; **IR** (film, cm^{-1}) 3027, 2927, 1705, 1577; **GC-MS** (*m*): [M] 290; **TLC R$_f$** = 0.7 (10% Et$_2$O/Pentane, staining with KMnO$_4$).



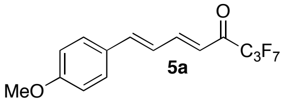
4c

Purified by flash column chromatography (3-8% Et$_2$O/Pentane) to give the desired ketone **4c** as a yellow solid (36.8 mg, 59% yield). ^{1}**H NMR** (CDCl$_3$, 400 MHz) δ 7.73(dd, *J* = 15.0, 11.2 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.12 (d, *J* = 15.5 Hz, 1H), 6.95 (dd, *J* = 15.4, 11.2 Hz, 1H), 6.67 (d, *J* = 15.1 Hz, 1H); ^{13}**C NMR** (CDCl$_3$, 100 MHz) δ 182.1 (t, *J* = 25.7 Hz), 149.5, 145.2, 136.5, 134.0, 129.5, 129.2, 126.6, 120.6, 118.0 (qt, *J* = 286.7, 34.7 Hz), 107.6 (tq, *J* = 265.83, 38.0 Hz); ^{19}**F NMR** (CDCl$_3$, 381): δ -82.1, -123.8; **IR** (film, cm^{-1}) 3079, 1695, 1608, 1573; **GC-MS** (*m*): [M] 260; **TLC R$_f$** = 0.75 (10% Et$_2$O/Pentane, staining with KMnO$_4$).



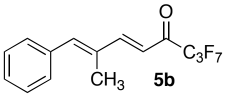
4d

Purified by flash column chromatography (3-10% Et$_2$O/Pentane) to give the desired ketone **4d** as a clear oil (21.3 mg, 56% yield). Spectral data matches literature.[4]



5a

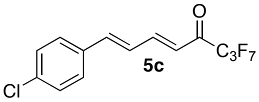
Purified by flash column chromatography (5-10% Et$_2$O/Pentane) to give the desired ketone **5a** as a yellow oil (48.5 mg, 68% yield). ^{1}**H NMR** (CDCl$_3$, 400 MHz) δ 7.74 (dd, *J* = 14.9, 11.4 Hz, 1H), 7.46 (ad, *J* = 8.8 Hz, 2H), 7.11 (d, *J* = 15.3 Hz, 1H), 6.91 (dt, *J* = 9.1, 2.2 Hz, 2H), 6.86 (dd, *J* = 15.4, 11.4 Hz, 1H), 6.59 (d, *J* = 14.9 Hz, 1H), 3.84 (s, 3H) ; ^{13}**C NMR** (CDCl$_3$, 100 MHz) δ 181.7 (t, *J* = 25.3 Hz), 161.6, 150.4, 146.8, 130.1, 129.6, 128.1, 123.8, 118.8, 114.5, 55.4; ^{19}**F NMR** (CDCl$_3$, 381 MHz**)** δ -80.6 (t, *J* = 8.8 Hz), -121.8 (q, *J* = 8.7 Hz), -126.8; **IR** (film, cm^{-1}) 3010, 2963, 1698, 1568, 1512; **GC-MS** (*m*): [M] 356; **TLC R$_f$** = 0.5 (10% Et$_2$O/Pentane, staining with KMnO$_4$).



5b

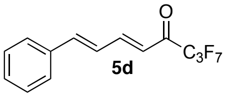
Purified by flash column chromatography (4-8% Et$_2$O/Pentane) to give the desired ketone **5b** as a clear oil (31.2 mg, 46% yield). ^{1}**H NMR** (CDCl$_3$, 400 MHz): δ 7.80 (d, *J* = 15.3 Hz, 1H), 7.40 (s, 4H), 7.35 (d, *J* = 4.3 Hz, 1H), 7.10 (s, 1H), 6.61 (d, *J* = 15.3 Hz, 1H), 2.12

(s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 182 (t, *J* = 25.3 Hz), 155.2, 145.3, 135.9, 134.2, 129.8, 128.8, 128.5, 116.3, 13.6; **^{19}F NMR** ($CDCl_3$, 381 MHz): δ -80.6 (t, *J* = 8.7 Hz), -121.8 (q, *J* = 8.5 Hz), -126.7; **IR** (film, cm^{-1}) 2928, 3028, 2928, 1705, 1578; **GC-MS** (*m*): [M] 340; **TLC R$_f$** = 0.75 (10% Et_2O/Pentane, staining with $KMnO_4$).



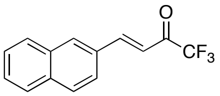
5c

Purified by flash column chromatography (4-8% Et_2O/Pentane) to give the desired ketone **5c** as a yellow solid (39.4 mg, 55% yield). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.71 (dd, *J* = 15.0, 11.2 Hz, 1H), 7.43 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.10 (d, *J* = 15.5 Hz, 1H), 6.94 (dd, *J* = 15.4, 11.2 Hz, 1H), 6.65 (d, *J* = 15.0 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 181.9 (t, *J* = 25.4 Hz), 149.2, 145.0, 136.2, 133.7, 129.3, 128.9, 126.3, 120.5; **^{19}F NMR** ($CDCl_3$, 381 MHz): δ -80.6 (t, *J* = 8.8 Hz), -121.9 (q, *J* = 8.7 Hz), -126.8; **IR** (film, cm^{-1}) 3031, 1697, 1608, 1572; **GC-MS** (*m*): [M] 310; **TLC R$_f$** = 0.75 (10% Et_2O/Pentane, staining with $KMnO_4$).



5d

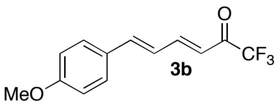
Purified by flash column chromatography (4-8% Et_2O/Pentane) to give the desired ketone **5d** as a clear oil (14.4 mg, 44% yield). **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.76 (dd, *J* = 14.7, 11.4 Hz, 1H), 7.55 (dd, *J* = 16.0, 2.6 Hz, 2H), 7.40 (d, *J* = 3.1 Hz, 3H), 7.23 (d, *J* = 16.0 Hz, 1H), 6.99 (dd, *J* = 15.3, 11.4 Hz, 1H), 6.67 (d, *J* = 14.9 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 181.9 (t, *J* = 24.6 Hz), 149.7, 146.7, 135.3, 130.3, 129.0, 127.8, 125.9, 120.1; **^{19}F NMR** ($CDCl_3$, 381 MHz): δ -80.6, -121.9, -126.8; **IR** (film, cm^{-1}) 3066, 3031, 1701, 1600, 1581; **GC-MS** (*m*): [M] 326; **TLC R$_f$** = 0.7 (10% Et_2O/Pentane, staining with $KMnO_4$).



10

Purified by flash column chromatography (3-10% Et_2O/Pentane) to give the desired ketone **10** as a white solid (13.0 mg, 48% yield). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.14 (d, *J* = 15.9 Hz, 1H), 8.08 (s, 1H), 7.89 (q, *J* = 7.3 Hz, 3H), 7.75 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.62-7.53 (m, 2H), 7.13 (d, *J* = 16.0 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 179.9 (q, *J* = 35.1 Hz), 150.2, 135.1, 133.1, 132.6, 130.8, 129.13, 128.98, 128.4, 127.9, 127.1, 123.3, 116.6, 116.5 (q, *J* = 291.7 Hz); **^{19}F NMR** ($CDCl_3$, 381 MHz): δ -77.6; **IR** (film, cm^{-1}) 3064, 1715, 1607, 1594; **GC-MS** (*m*): [M] 250; **TLC R$_f$** = 0.7 (10% Et_2O/Pentane, staining with $KMnO_4$).

VI. Crystal Structure Data for 3b



3b

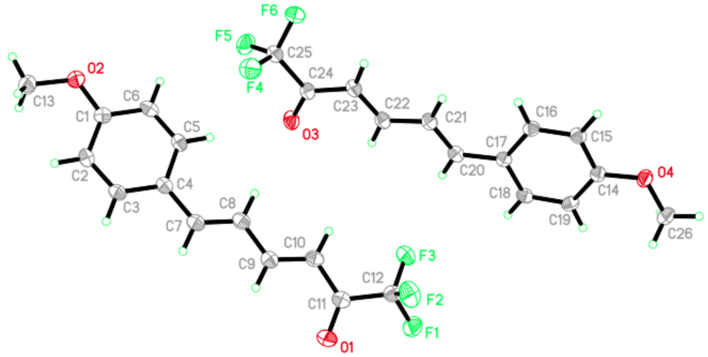


Table 1. Crystal data and structure refinement for **3b**.

Identification code	rovis169_0m	
Empirical formula	$C_{13}H_{11}F_3O_2$	
Formula weight	256.22	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	*a* = 7.6763(3) Å	α= 81.300(2)°.
	b = 10.0446(4) Å	β= 82.163(2)°.
	c = 15.7356(6) Å	γ = 86.148(2)°.
Volume	1186.79(8) Å^3	
Z	4	
Density (calculated)	1.434 Mg/m^3	
Absorption coefficient	0.127 mm^{-1}	
F(000)	528	
Crystal size	0.27 x 0.23 x 0.05 mm^3	
Theta range for data collection	2.05 to 28.32°.	
Index ranges	-9<=h<=10, -13<=k<=13, -20<=l<=20	
Reflections collected	20906	
Independent reflections	5867 [R(int) = 0.0324]	
Completeness to theta = 28.32°	99.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9937 and 0.9666	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5867 / 0 / 327	
Goodness-of-fit on F^2	1.016	

Final R indices [I>2sigma(I)]	R1 = 0.0417, wR2 = 0.0829
R indices (all data)	R1 = 0.0794, wR2 = 0.0951
Largest diff. peak and hole	0.228 and -0.246 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for Rovis169_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	-2160(2)	4728(1)	9594(1)	23(1)
C(2)	-1454(2)	3416(1)	9711(1)	25(1)
C(3)	-491(2)	2895(1)	9017(1)	24(1)
C(4)	-197(2)	3648(1)	8198(1)	22(1)
C(5)	-956(2)	4966(1)	8089(1)	25(1)
C(6)	-1915(2)	5494(1)	8771(1)	26(1)
C(7)	857(2)	3059(1)	7491(1)	25(1)
C(8)	1295(2)	3665(1)	6677(1)	26(1)
C(9)	2298(2)	2996(1)	6016(1)	25(1)
C(10)	2753(2)	3578(1)	5198(1)	27(1)
C(11)	3682(2)	2822(1)	4545(1)	25(1)
C(12)	4404(2)	3638(1)	3676(1)	28(1)
C(13)	-3352(2)	4611(2)	11080(1)	34(1)
C(14)	6692(2)	9482(1)	798(1)	21(1)
C(15)	6548(2)	10223(1)	1491(1)	23(1)
C(16)	5450(2)	9841(1)	2240(1)	23(1)
C(17)	4448(2)	8697(1)	2332(1)	21(1)
C(18)	4595(2)	7987(1)	1625(1)	23(1)
C(19)	5693(2)	8359(1)	867(1)	24(1)
C(20)	3304(2)	8232(1)	3117(1)	23(1)
C(21)	3070(2)	8758(1)	3865(1)	25(1)
C(22)	1920(2)	8202(1)	4602(1)	24(1)
C(23)	1642(2)	8688(1)	5366(1)	25(1)
C(24)	498(2)	8025(1)	6085(1)	22(1)
C(25)	310(2)	8597(1)	6947(1)	26(1)
C(26)	8049(2)	9222(1)	-630(1)	28(1)
F(1)	4439(1)	2943(1)	3017(1)	44(1)
F(2)	6059(1)	3950(1)	3705(1)	43(1)
F(3)	3494(1)	4794(1)	3474(1)	39(1)
F(4)	1380(1)	7882(1)	7471(1)	41(1)
F(5)	-1316(1)	8511(1)	7360(1)	40(1)

F(6)	723(1)	9884(1)	6864(1)	36(1)
O(1)	3994(1)	1611(1)	4631(1)	32(1)
O(2)	-3106(1)	5358(1)	10229(1)	30(1)
O(3)	-299(1)	7013(1)	6093(1)	28(1)
O(4)	7862(1)	9937(1)	100(1)	26(1)

Table 3. Bond lengths [Å] and angles [°] for Rovis169_0m.

C(1)-O(2)	1.3627(17)
C(1)-C(2)	1.3864(18)
C(1)-C(6)	1.399(2)
C(2)-C(3)	1.384(2)
C(3)-C(4)	1.390(2)
C(4)-C(5)	1.4059(18)
C(4)-C(7)	1.460(2)
C(5)-C(6)	1.371(2)
C(7)-C(8)	1.341(2)
C(8)-C(9)	1.431(2)
C(9)-C(10)	1.342(2)
C(10)-C(11)	1.451(2)
C(11)-O(1)	1.2154(15)
C(11)-C(12)	1.537(2)
C(12)-F(1)	1.3315(17)
C(12)-F(3)	1.3330(15)
C(12)-F(2)	1.3375(17)
C(13)-O(2)	1.4273(18)
C(14)-O(4)	1.3623(17)
C(14)-C(19)	1.389(2)
C(14)-C(15)	1.3986(19)
C(15)-C(16)	1.372(2)
C(16)-C(17)	1.4039(19)
C(17)-C(18)	1.3970(19)
C(17)-C(20)	1.450(2)
C(18)-C(19)	1.381(2)
C(20)-C(21)	1.3460(19)
C(21)-C(22)	1.424(2)
C(22)-C(23)	1.350(2)
C(23)-C(24)	1.440(2)
C(24)-O(3)	1.2186(16)
C(24)-C(25)	1.538(2)
C(25)-F(5)	1.3283(17)
C(25)-F(6)	1.3340(15)

C(25)-F(4)	1.3407(16)
C(26)-O(4)	1.4305(17)

O(2)-C(1)-C(2)	124.91(13)
O(2)-C(1)-C(6)	115.73(12)
C(2)-C(1)-C(6)	119.37(13)
C(3)-C(2)-C(1)	119.55(13)
C(2)-C(3)-C(4)	122.06(12)
C(3)-C(4)-C(5)	117.43(13)
C(3)-C(4)-C(7)	119.92(12)
C(5)-C(4)-C(7)	122.65(13)
C(6)-C(5)-C(4)	121.10(14)
C(5)-C(6)-C(1)	120.47(13)
C(8)-C(7)-C(4)	126.93(13)
C(7)-C(8)-C(9)	123.16(13)
C(10)-C(9)-C(8)	124.36(13)
C(9)-C(10)-C(11)	121.69(13)
O(1)-C(11)-C(10)	126.07(14)
O(1)-C(11)-C(12)	116.99(13)
C(10)-C(11)-C(12)	116.89(12)
F(1)-C(12)-F(3)	106.94(12)
F(1)-C(12)-F(2)	107.15(12)
F(3)-C(12)-F(2)	106.93(12)
F(1)-C(12)-C(11)	112.06(12)
F(3)-C(12)-C(11)	113.87(12)
F(2)-C(12)-C(11)	109.54(12)
O(4)-C(14)-C(19)	125.21(13)
O(4)-C(14)-C(15)	115.31(12)
C(19)-C(14)-C(15)	119.47(14)
C(16)-C(15)-C(14)	120.73(13)
C(15)-C(16)-C(17)	120.93(13)
C(18)-C(17)-C(16)	117.21(13)
C(18)-C(17)-C(20)	119.73(13)
C(16)-C(17)-C(20)	123.05(13)
C(19)-C(18)-C(17)	122.56(13)
C(18)-C(19)-C(14)	119.09(13)

C(21)-C(20)-C(17)	127.39(14)
C(20)-C(21)-C(22)	122.42(14)
C(23)-C(22)-C(21)	124.72(14)
C(22)-C(23)-C(24)	120.54(14)
O(3)-C(24)-C(23)	126.53(14)
O(3)-C(24)-C(25)	115.77(13)
C(23)-C(24)-C(25)	117.64(13)
F(5)-C(25)-F(6)	107.20(11)
F(5)-C(25)-F(4)	107.03(12)
F(6)-C(25)-F(4)	107.02(12)
F(5)-C(25)-C(24)	111.79(12)
F(6)-C(25)-C(24)	114.02(12)
F(4)-C(25)-C(24)	109.44(11)
C(1)-O(2)-C(13)	117.06(11)
C(14)-O(4)-C(26)	117.58(11)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for Rovis169_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	18(1)	24(1)	28(1)	-6(1)	-6(1)	-2(1)
C(2)	24(1)	26(1)	24(1)	2(1)	-5(1)	-2(1)
C(3)	24(1)	20(1)	29(1)	-1(1)	-8(1)	0(1)
C(4)	20(1)	22(1)	25(1)	-2(1)	-7(1)	-5(1)
C(5)	26(1)	22(1)	27(1)	1(1)	-5(1)	-5(1)
C(6)	25(1)	19(1)	35(1)	-1(1)	-7(1)	0(1)
C(7)	24(1)	22(1)	30(1)	-3(1)	-7(1)	-4(1)
C(8)	25(1)	22(1)	30(1)	-3(1)	-6(1)	-5(1)
C(9)	24(1)	24(1)	28(1)	-4(1)	-6(1)	-6(1)
C(10)	27(1)	23(1)	32(1)	-6(1)	-6(1)	-3(1)
C(11)	21(1)	24(1)	30(1)	-5(1)	-8(1)	-4(1)
C(12)	27(1)	26(1)	31(1)	-8(1)	-4(1)	-4(1)
C(13)	35(1)	36(1)	28(1)	-4(1)	1(1)	2(1)
C(14)	18(1)	23(1)	22(1)	-2(1)	-3(1)	2(1)
C(15)	24(1)	22(1)	24(1)	-5(1)	-5(1)	-5(1)
C(16)	25(1)	23(1)	21(1)	-6(1)	-5(1)	-1(1)
C(17)	19(1)	21(1)	23(1)	-3(1)	-5(1)	0(1)
C(18)	22(1)	20(1)	29(1)	-5(1)	-6(1)	-4(1)
C(19)	23(1)	25(1)	24(1)	-8(1)	-5(1)	1(1)
C(20)	21(1)	22(1)	26(1)	-1(1)	-6(1)	-2(1)
C(21)	24(1)	24(1)	26(1)	-1(1)	-3(1)	-4(1)
C(22)	22(1)	24(1)	25(1)	0(1)	-5(1)	-2(1)
C(23)	26(1)	24(1)	26(1)	0(1)	-4(1)	-5(1)
C(24)	20(1)	24(1)	22(1)	0(1)	-6(1)	-1(1)
C(25)	27(1)	23(1)	27(1)	-1(1)	-4(1)	-3(1)
C(26)	30(1)	34(1)	22(1)	-8(1)	-1(1)	2(1)
F(1)	62(1)	39(1)	31(1)	-13(1)	3(1)	-11(1)
F(2)	28(1)	48(1)	53(1)	2(1)	-4(1)	-16(1)
F(3)	47(1)	30(1)	36(1)	4(1)	-3(1)	4(1)
F(4)	58(1)	38(1)	30(1)	-6(1)	-24(1)	5(1)
F(5)	38(1)	44(1)	37(1)	-11(1)	12(1)	-9(1)

F(6)	48(1)	25(1)	36(1)	-8(1)	-2(1)	-10(1)
O(1)	38(1)	22(1)	38(1)	-5(1)	-6(1)	-1(1)
O(2)	32(1)	28(1)	28(1)	-5(1)	-1(1)	3(1)
O(3)	32(1)	30(1)	24(1)	-1(1)	-5(1)	-11(1)
O(4)	27(1)	29(1)	21(1)	-6(1)	1(1)	-3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for Rovis169_0m.

	x	y	z	U(eq)
H(2)	-1630	2879	10264	30
H(3)	-15	1994	9103	29
H(5)	-801	5499	7534	30
H(6)	-2417	6387	8683	32
H(7)	1278	2150	7622	30
H(8)	921	4583	6532	31
H(9)	2667	2079	6168	30
H(10)	2460	4509	5042	32
H(13A)	-4022	3816	11074	51
H(13B)	-4000	5180	11482	51
H(13C)	-2203	4323	11267	51
H(15)	7217	10999	1442	27
H(16)	5366	10358	2703	27
H(18)	3914	7219	1669	28
H(19)	5764	7853	399	28
H(20)	2646	7470	3103	28
H(21)	3695	9527	3902	30
H(22)	1304	7433	4553	29
H(23)	2205	9474	5430	30
H(26A)	8400	8277	-448	43
H(26B)	8951	9629	-1077	43
H(26C)	6924	9269	-865	43

VII. References

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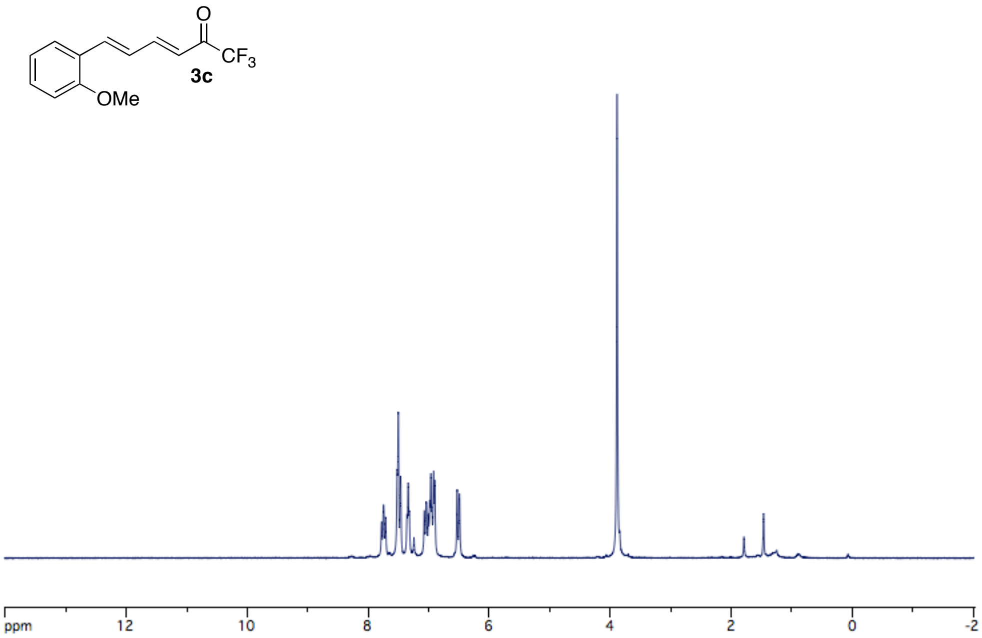
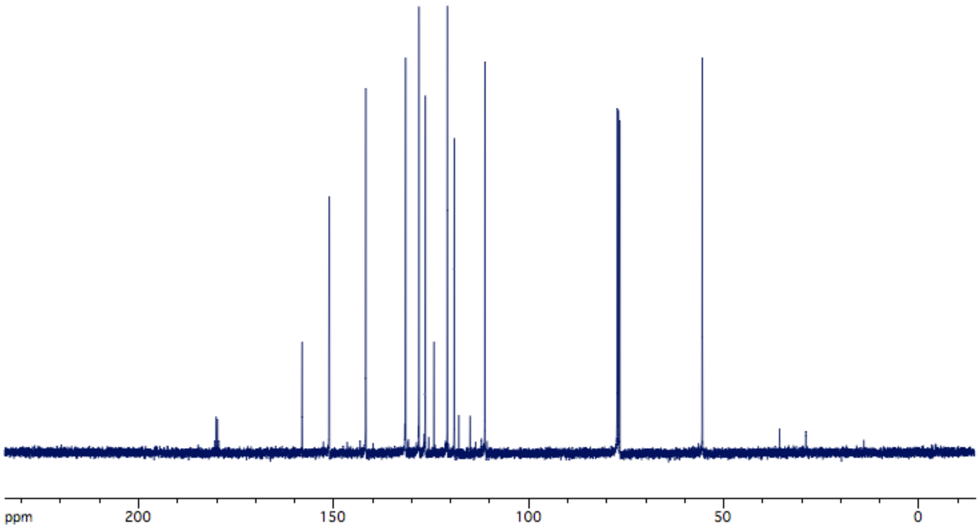
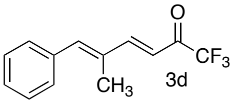
VIII. NMR Spectra







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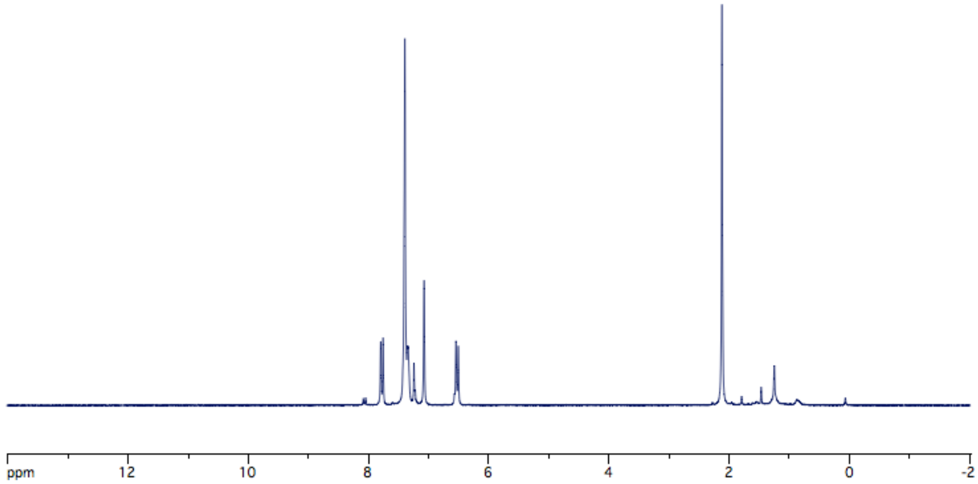

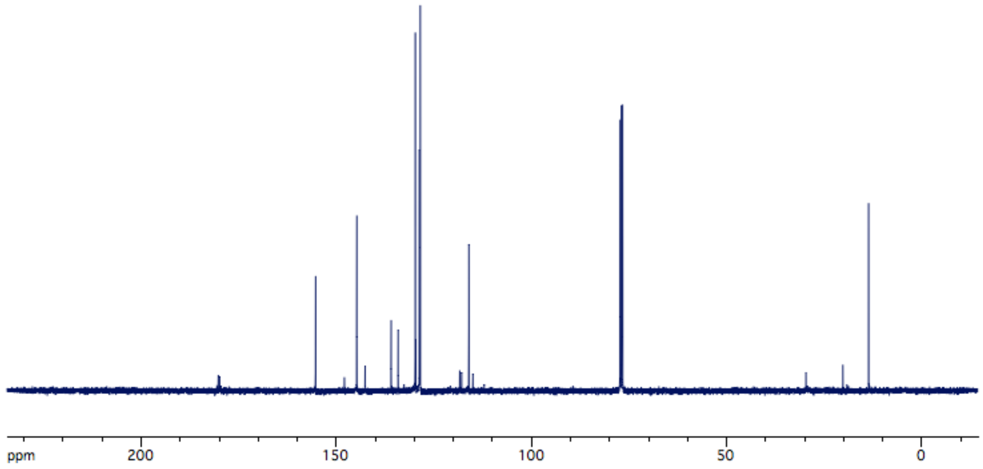

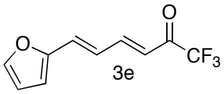

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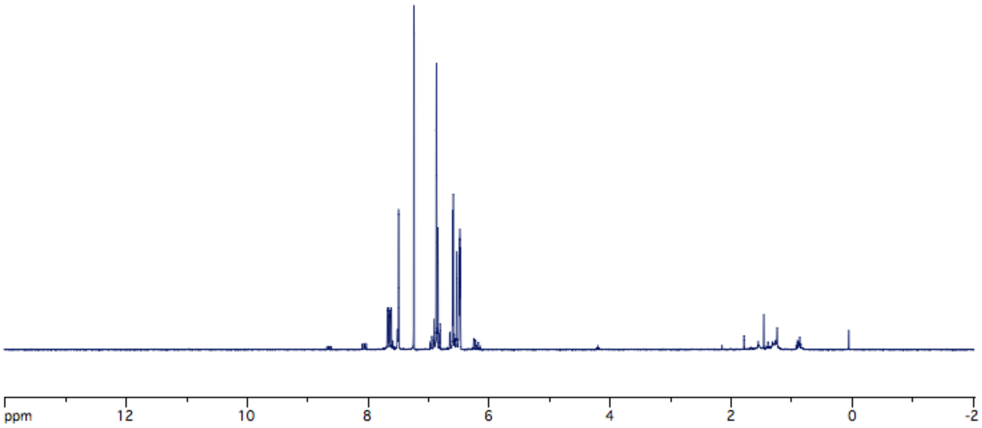

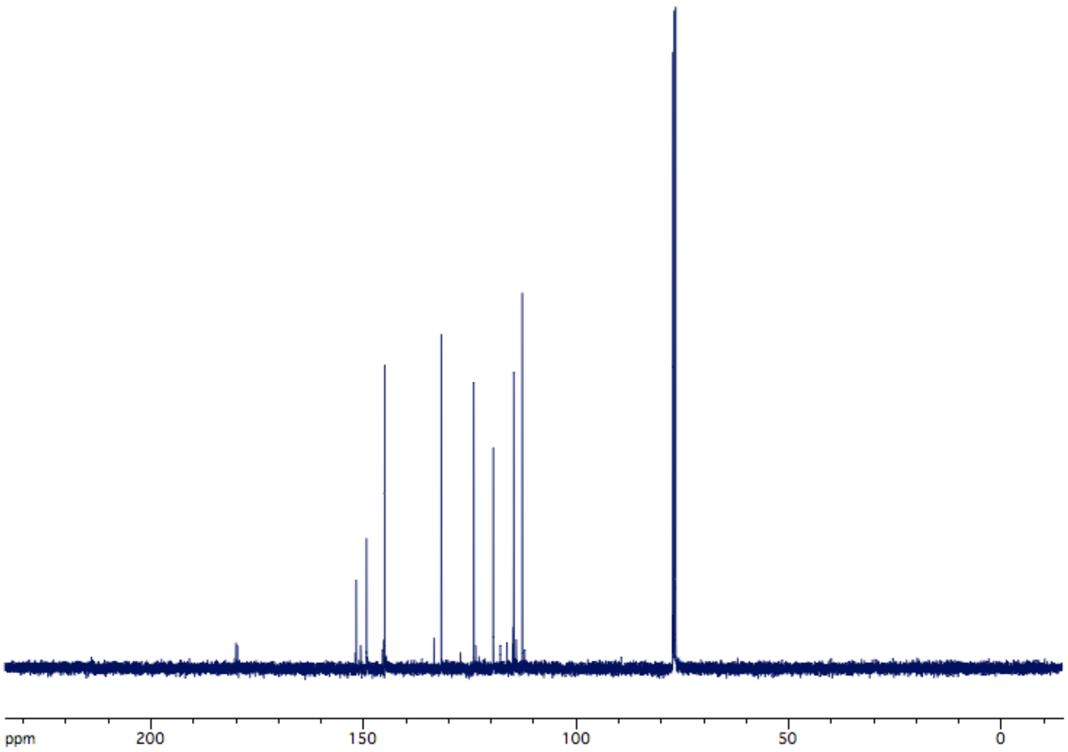

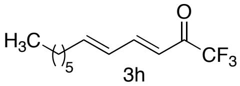

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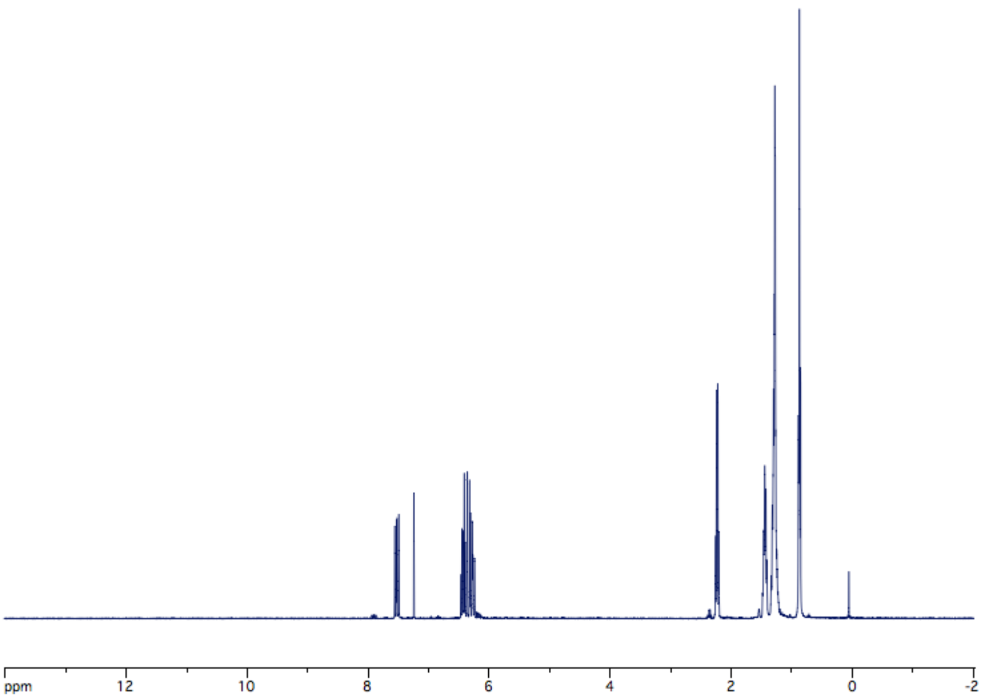

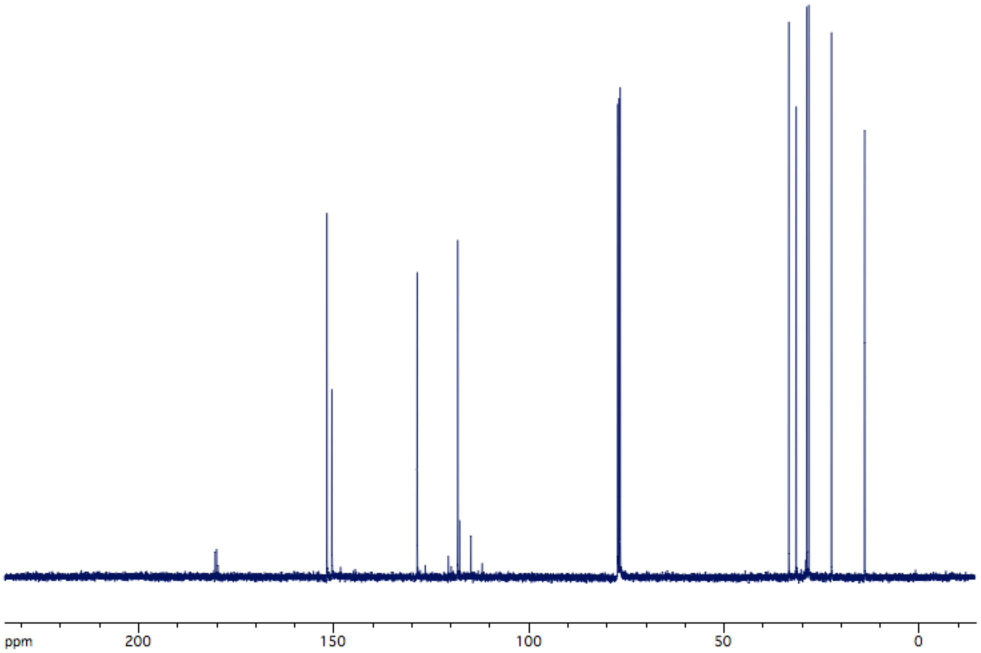

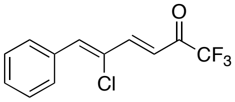

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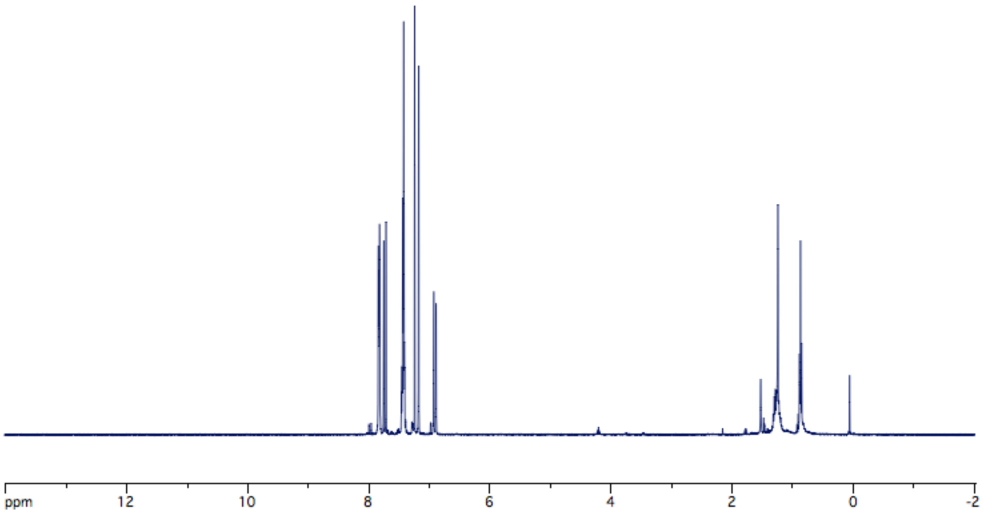

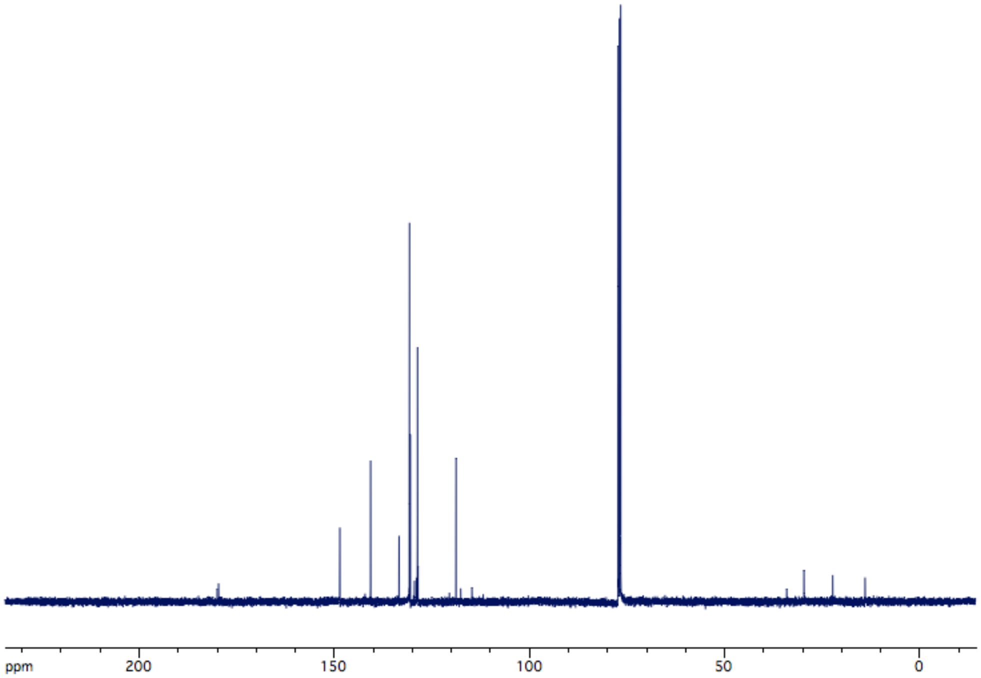

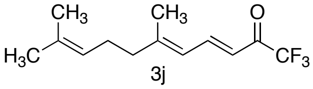

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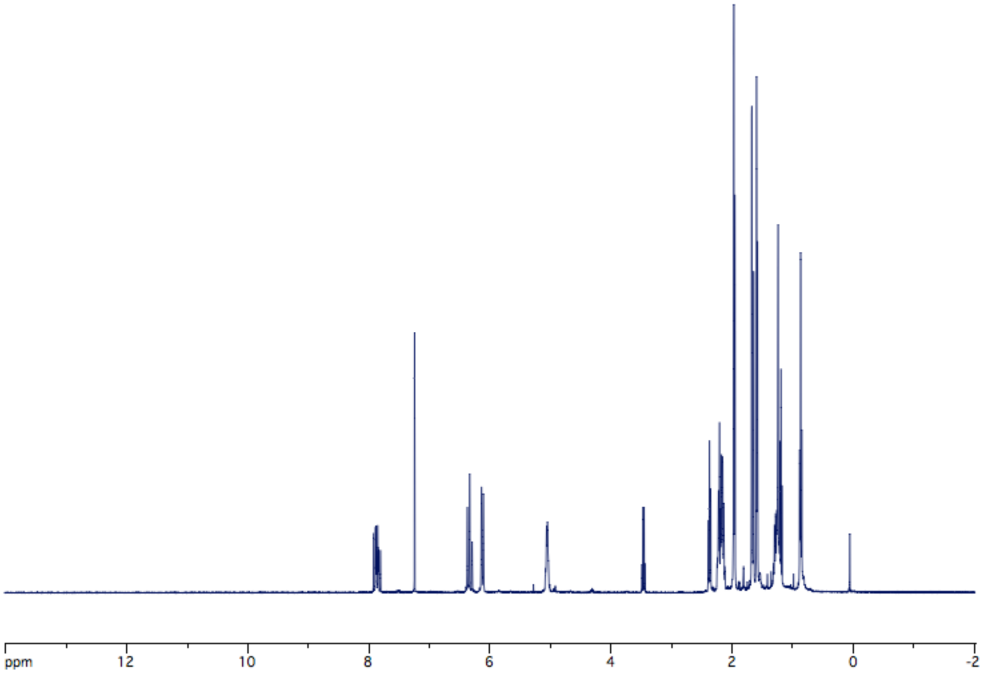

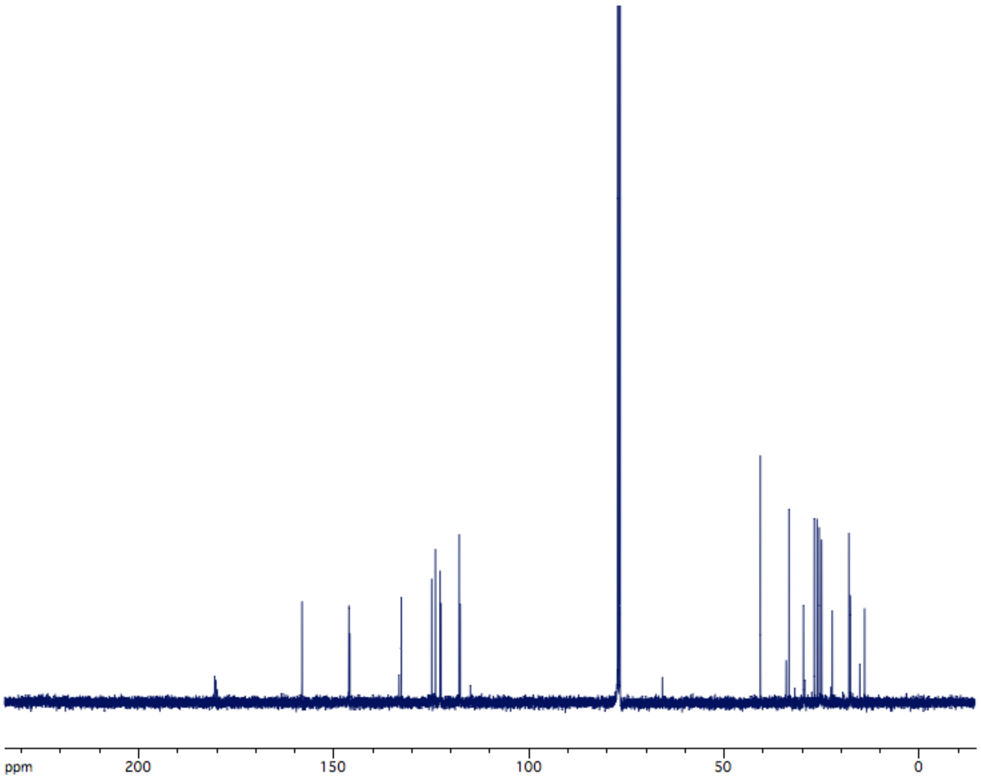

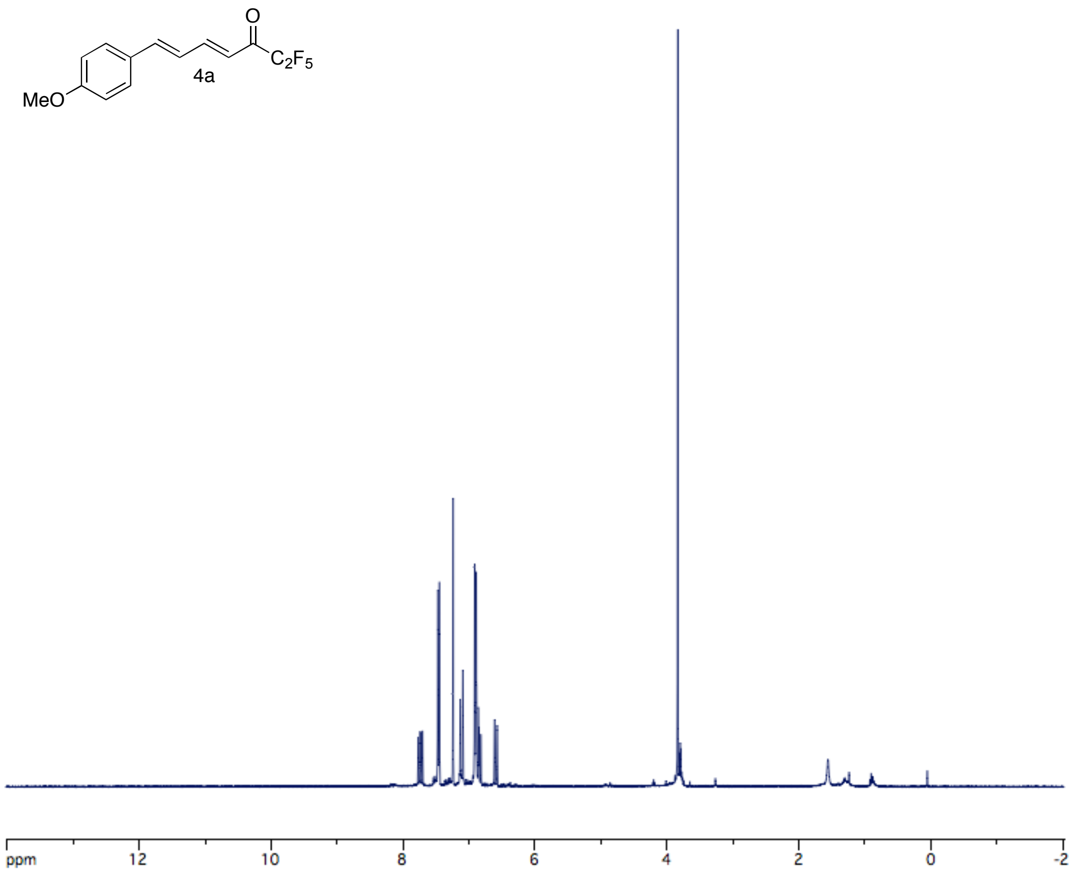
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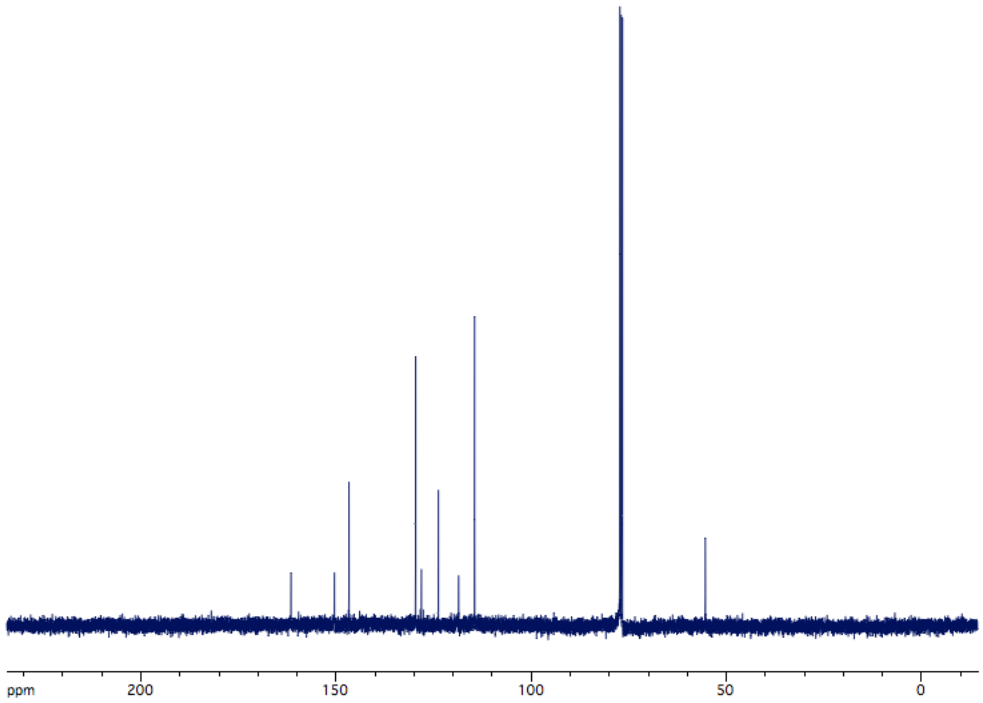
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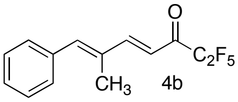

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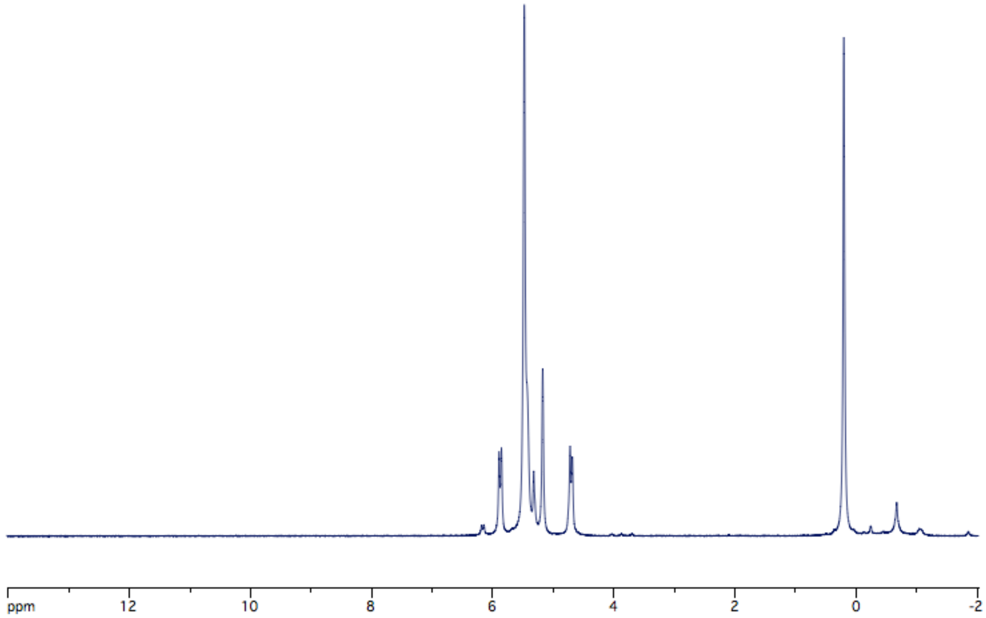

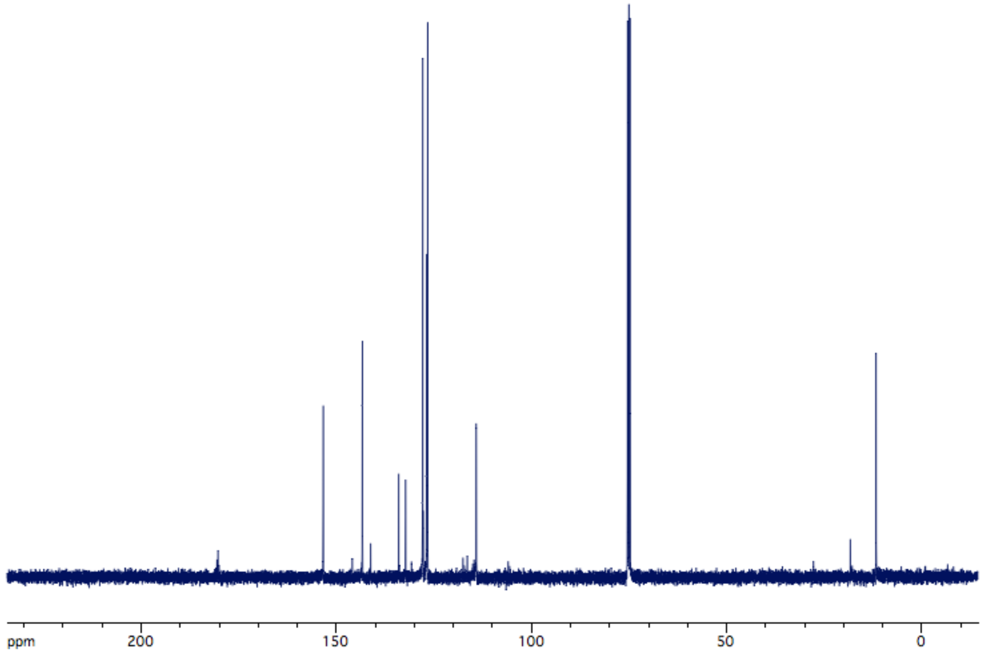

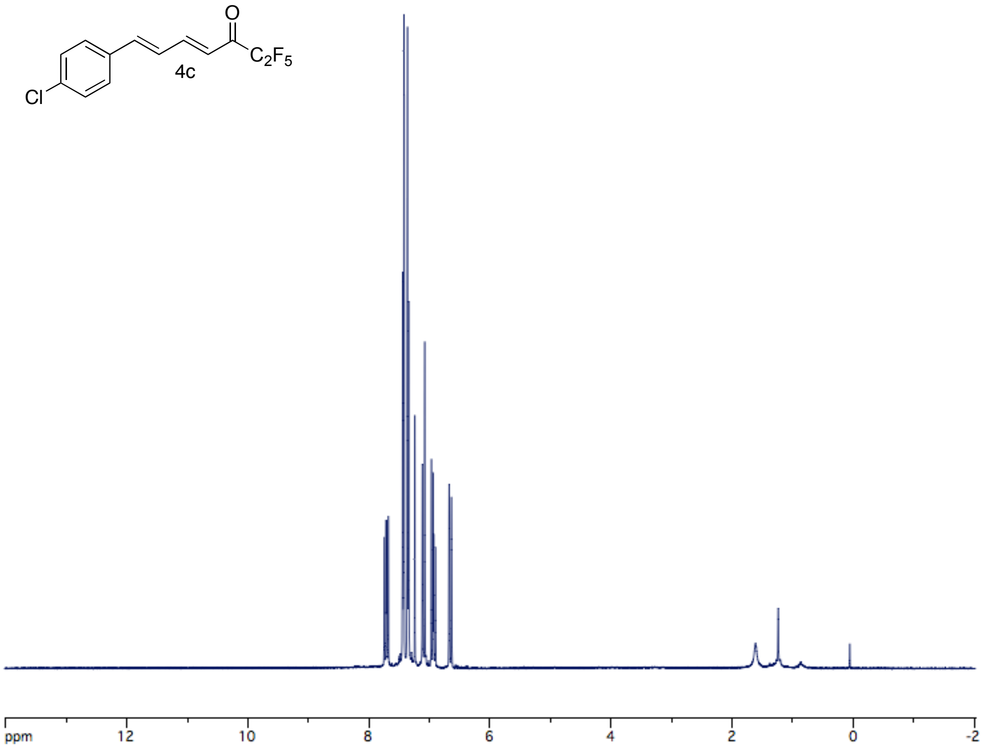

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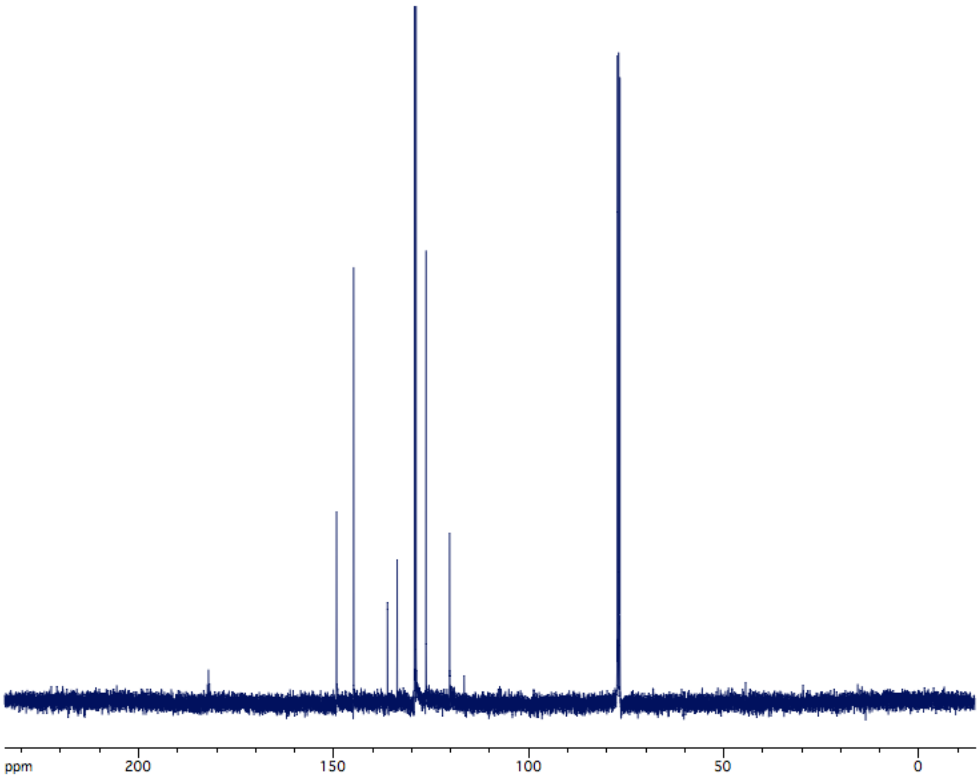

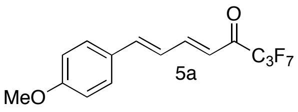

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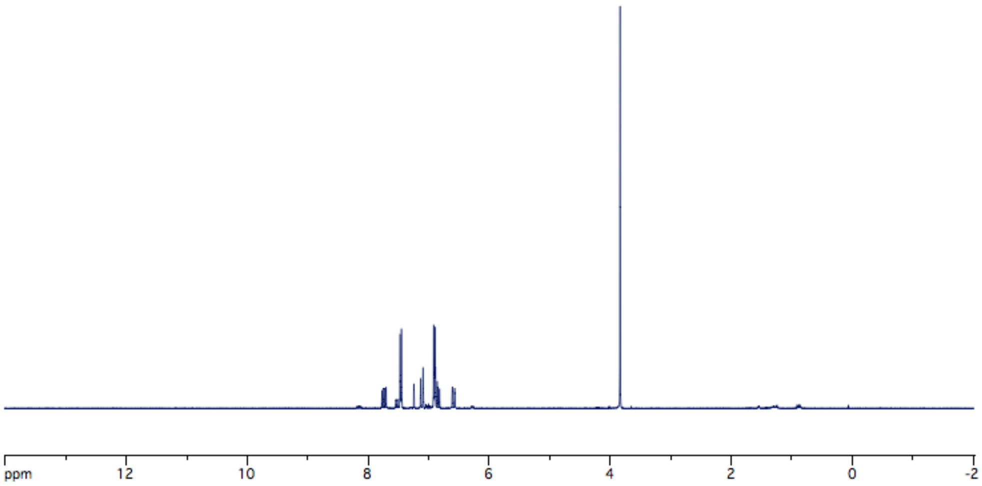

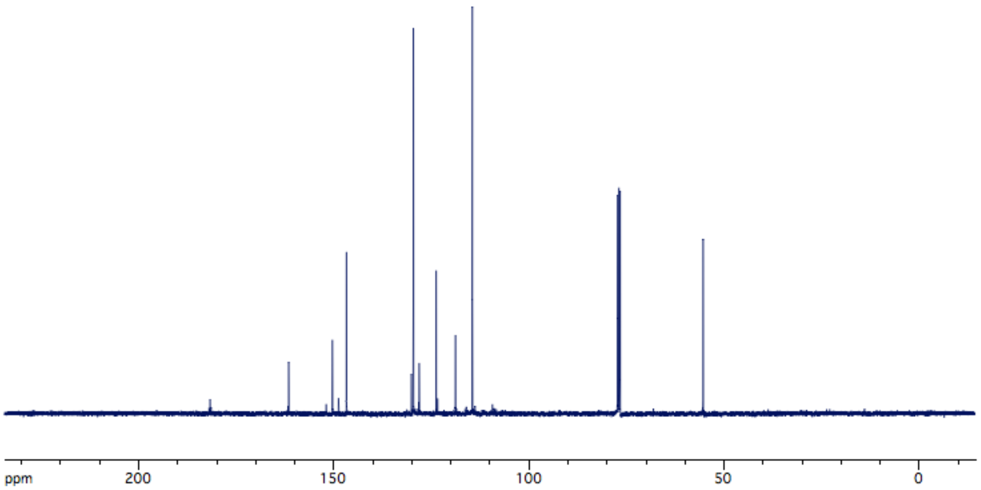

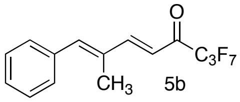

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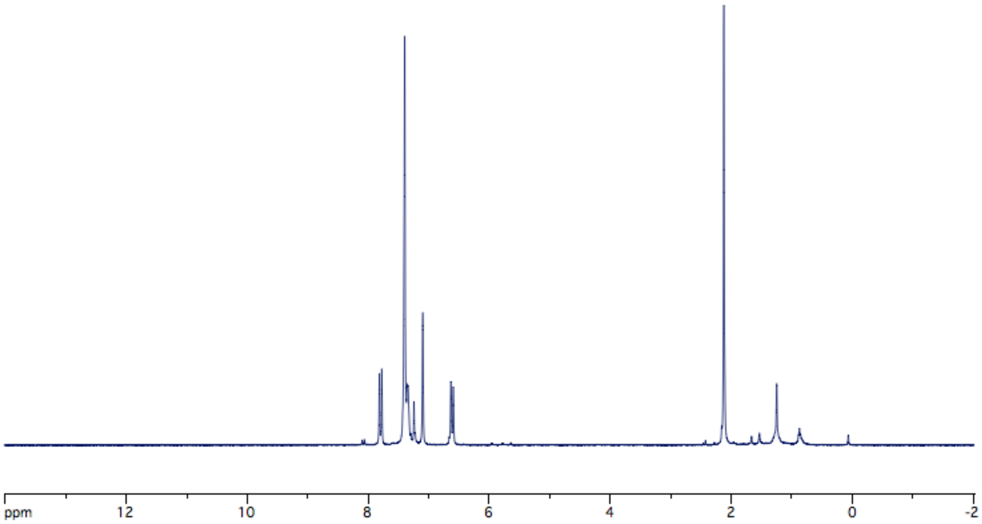

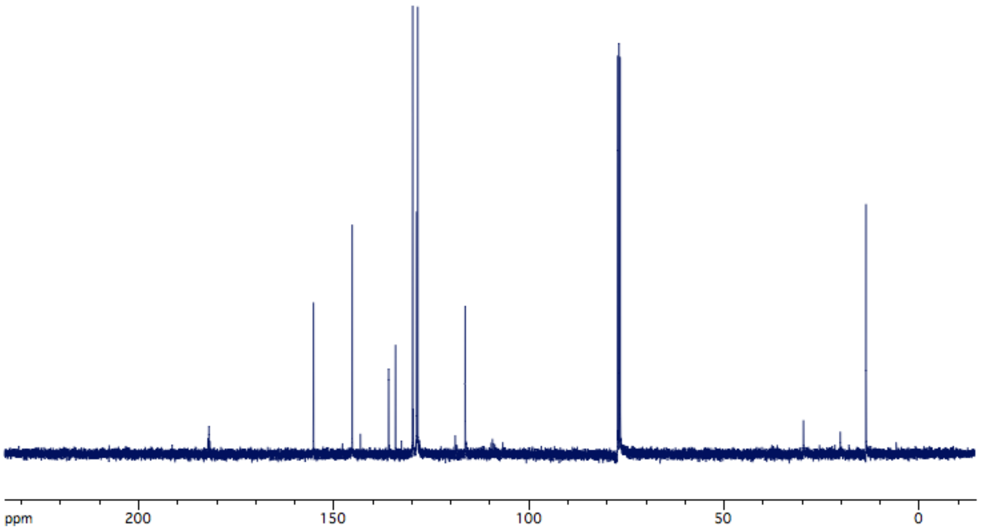

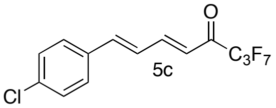

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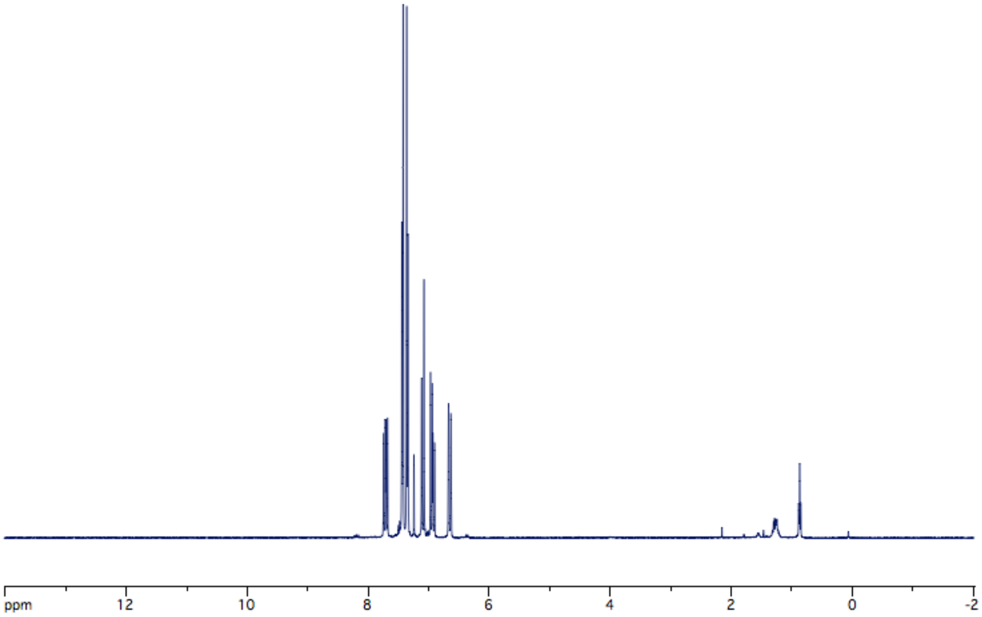

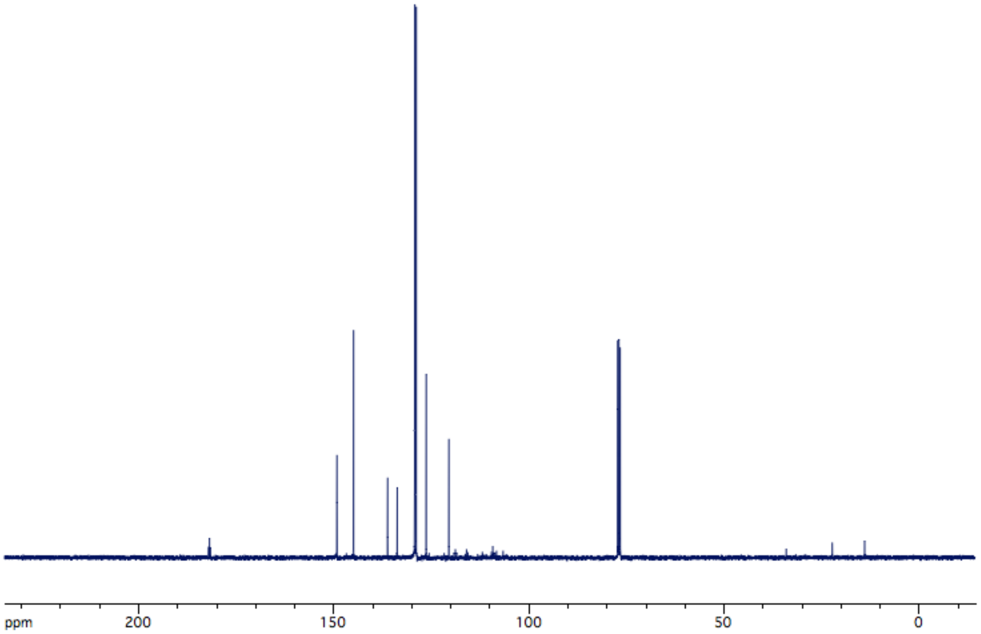

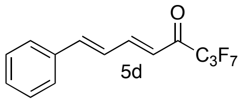

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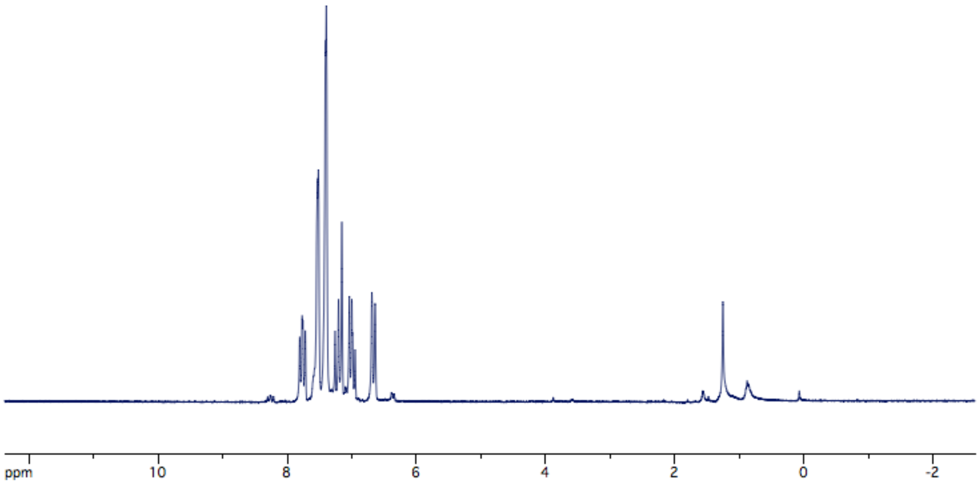

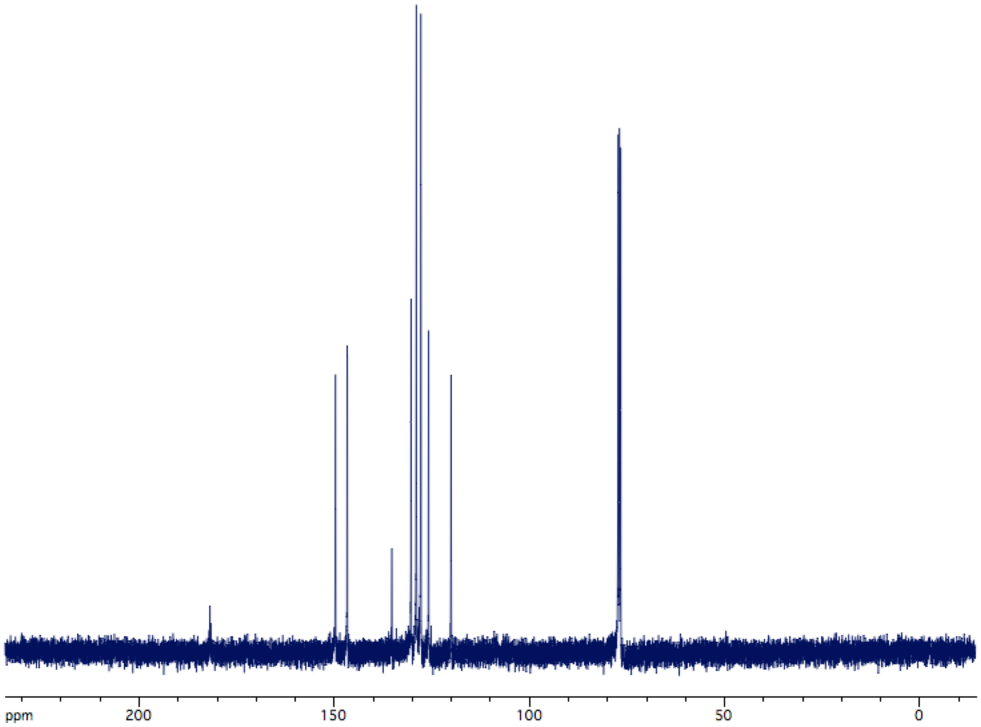

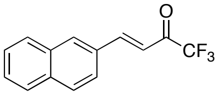

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