Supplementary Material

Hydrogen bonding template enables remote *meta*-C–H alkenylation of nitroarenes

Bishal Dutta,[1] Mayank Mahajan,[2] Animesh Ghosh,[1] Maciej Dajek,[3] Rafal Kowalczyk,[3]* Bhaskar Mondal,[2]* Haibo Ge,[4]* and Debabrata Maiti[1]*

[1]Department of Chemistry, Indian Institute of Technology Bombay, Mumbai, India. *e-mail: dmaiti@iitb.ac.in
[2]School of Chemical Sciences, Indian Institute of Technology Mandi, Himachal Pradesh, India. *e-mail: bhaskarmondal@iitmandi.ac.in
[3]Wroclaw University of Science and Technology, Poland. *e-mail: rafal.kowalczyk@pwr.edu.pl
[4]Department of Chemistry and Biochemistry, Texas Tech University, USA, *e-mail: haibo.ge@ttu.edu

Supplementary Experimental Procedures

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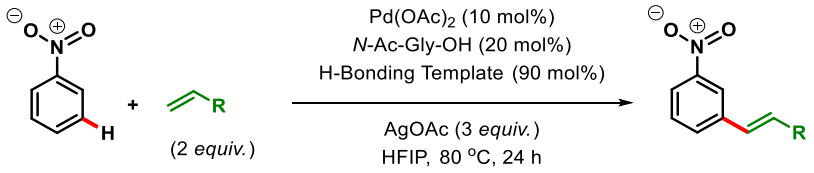
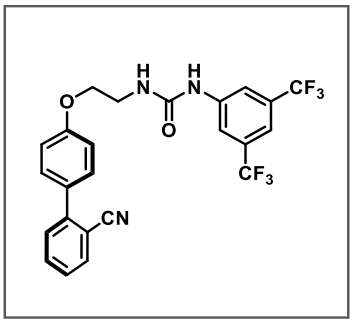
1. General Information:

1.1. Reagent Information. Unless otherwise stated, all reactions were carried out in screw cap reaction tubes. All the solvents were bought from commercial sources and were used without further purification. Palladium salts, silver salt and *N*-acetyl glycine were purchased from Aldrich. Silica gel (100–200 mesh) obtained from SRL Co. was used for column chromatography. A gradient elution using petroleum ether and ethyl acetate was performed, based on Merck aluminium TLC sheets (silica gel $60F_{254}$).

1.2. Analytical Information. All compounds are characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectroscopy and HR-MS. Copies of the ^{1}H NMR, ^{13}C NMR and ^{19}F NMR can be found in the Supporting Information. Unless otherwise stated, all Nuclear Magnetic Resonance spectra were recorded on a Bruker 500 MHz / 400 MHz instrument. All ^{1}H NMR experiments are reported in units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvent, unless otherwise stated. All ^{13}C NMR spectra were reported in ppm relative to deuterated chloroform (77.23 ppm), unless otherwise stated, and all were obtained with ^{1}H decoupling. High-resolution mass spectra (HRMS) were recorded on a micro-mass ESI TOF (time of flight) mass spectrometer.

2. General Procedure for palladium-catalyzed alkenylation of nitroarenes:





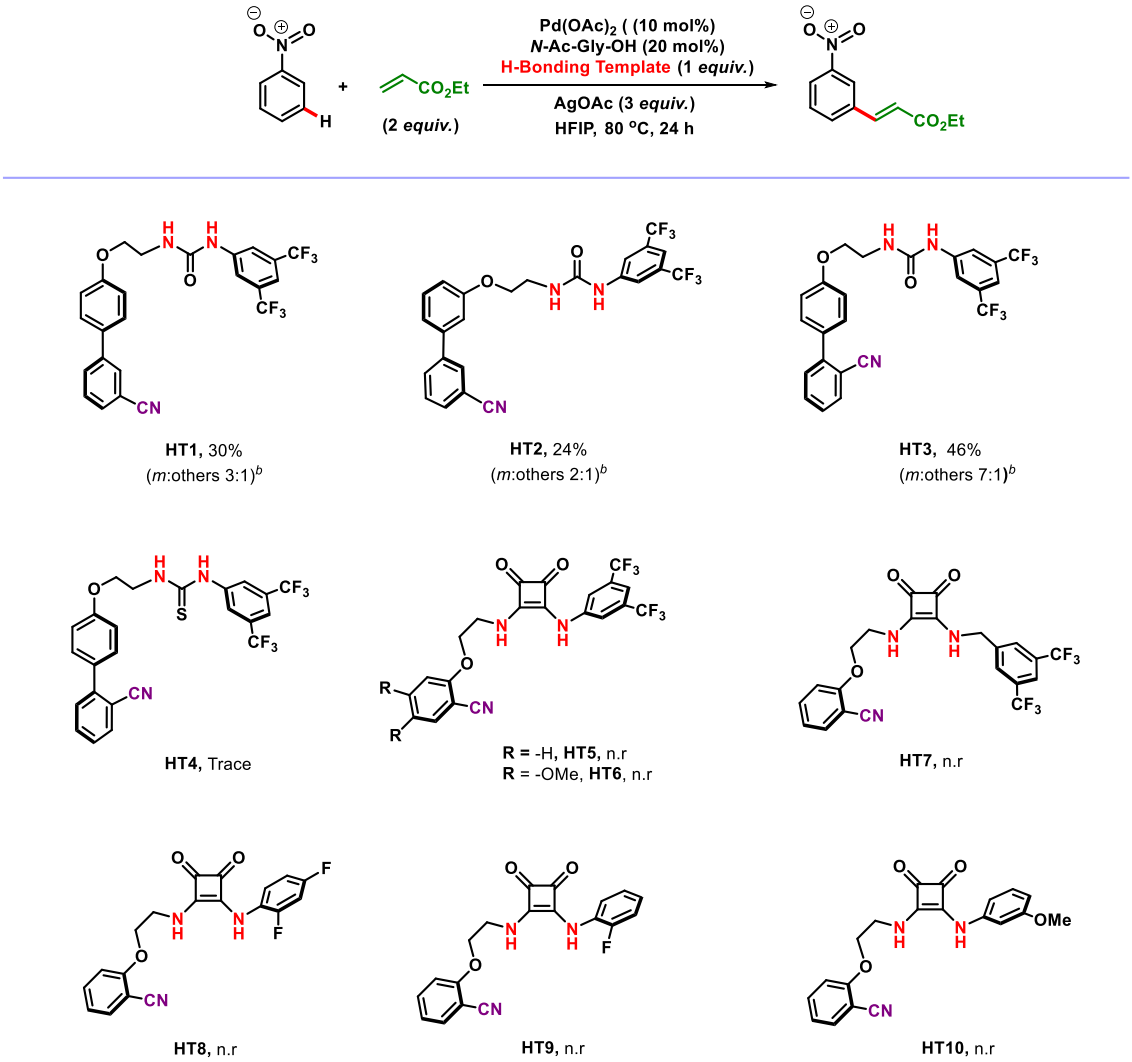
In an oven-dried screw capped reaction tube charged with magnetic stir-bar, substrate (nitroarene) (1 *equiv.*, 0.1 mmol), $Pd(OAc)_2$ (10 mol%, 2.24 mg), *N*-Ac-Gly-OH (20 mol%, 2.34 mg), H-bonding template (HTX) (0.9 *equiv.*, 45 mg), AgOAc (3 *equiv.*, 50.1 mg) in 1 mL of HFIP were added. After that, olefin (2 *equiv.*, 0.2 mmol) was added to that reaction mixture. The reaction tube was well capped and placed in a preheated oil bath at 80 ^{0}C with stirring (1000 rpm) for 24 h. Upon completion of the reaction, the mixture was diluted with

ethyl acetate and filtered through a celite pad. The filtrate was evaporated under reduced pressure and the crude mixture was purified by column chromatography using silica (100-200 mesh size) and petroleum ether/ethyl acetate as the eluent. The final *meta*-olefinated product was characterized by different spectroscopic techniques (^{1}H, ^{13}C, ^{19}F *etc*.).

3. Optimization details for *meta*-olefination of nitroarenes:

Yield was determined by ^{1}H NMR analysis of the crude product using TMB (1,3,5-trimethoxybenzene) as the internal standard.

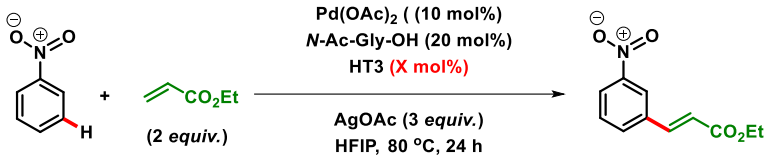
3.1. Optimization of Hydrogen-bonding templates:



[a]Yield and regioselectivity was determined by ^{1}H-NMR analysis with reference to TMB (1,3,5-trimethoxy benzene) as an internal standard.
[b]C–H olefination of the template was also observed. n.r : No reaction.

Table 1. Optimization of Hydrogen-bonding templates

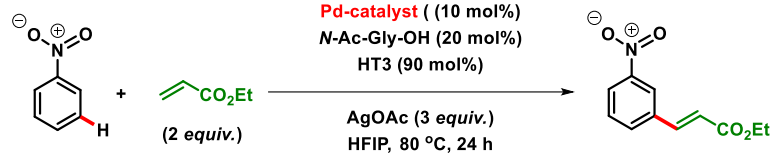
3.2. Optimization of Hydrogen-bonding template amount:



Entry	Amount of HT3 (mol%)	Yield of A (%)	Selectivity (*m:others*)
1	100	44	6.5:1
2	**90**	**46**	**7:1**
3	80	38	5:1
4	70	32	3:1
5	60	28	2.5:1
6	50	21	2.5:1

Table 2. H-bonding template amount optimization

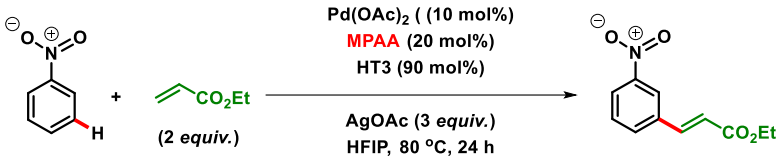
3.3. Optimization of palladium catalyst:



Entry	Pd Catalyst	Yield (%)	Selectivity (*m:others*)
1	**$Pd(OAc)_2$**	**46**	**7:1**
2	$Pd(TFA)_2$	15	4:1
3	$Pd(CH_3CN)_2Cl_2$	24	3:1
4	$Pd(acac)_2$	-	-
5	$PdCl_2$	18	2:1
6	$Pd(PhCN)_2Cl_2$	22	2.5:1
7	$Pd(COD)Cl_2$	12	1.8:1
8	$Pd(OPiv)_2$	33	3:1

Table 3: Optimization of palladium catalyst

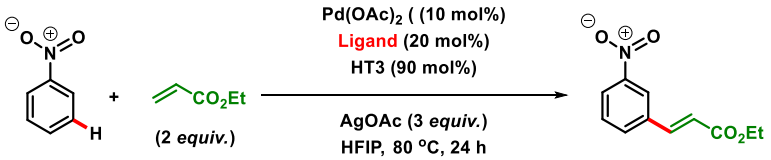
3.4. Optimization of MPAA ligands:



Entry	Ligand	Yield (%)	Selectivity (*m*:others)
1	***N*-Ac-Gly-OH**	**46**	**7:1**
2	*N*-Ac-Gly-Ethyl Ester	8	-
3	*N*-Ac-L-Val-OH	15	3:1
4	*N*-Ac-L-Phe-OH	36	4:1
5	*N*-Ac-L-Leu-OH	16	6:1
6	*N*-Boc-Gly-OH	25	4:1
7	*N*-Formyl-Gly-OH	30	2:1
8	*N*-Cbz-Gly-OH	-	-
9	*N*-Boc-L-Phe-OH	-	-
10	*N*-Boc-L-Val-OH	12	2:1
11	*N*-Boc-L-Ile-OH	-	-
12	*N*-Boc-L-Ala-OH	14	1:1
13	*N*-Boc-L-Tle-OH	-	-
14	Fmoc-L-Phe-OH	-	-
15	Fmoc-L-Phg-OH	6	-

Table 4. Optimization of MPAA ligands

3.5. Optimization of pyridine ligands:



Entry	Ligand	Yield (%)	Selectivity (*m:others*)
1	3-(Trifluoromethyl)-2-Pyridone	trace	-

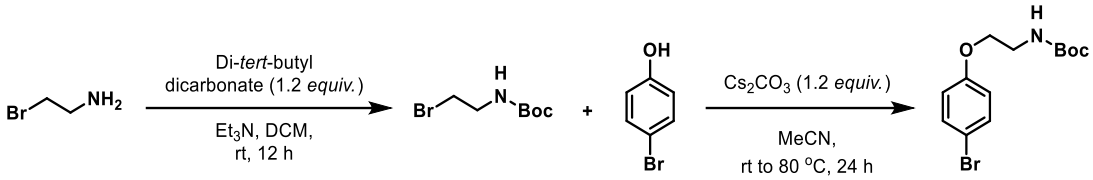
2	3-(Methyl)-2-Pyridone	trace	-
3	5-(Methyl)-3-(Nitro)-2-Pyridone	trace	-
4	6-(Methyl)-3-(Cyano)-2-Pyridone	4	1:1
5	3-(Nitro)-2-Pyridone	10	1:1

Table 5. Optimization of pyridone ligands

4. General procedure for the synthesis of hydrogen bonding template:

4.1. General procedure for the synthesis of HT1, HT3, HT4:

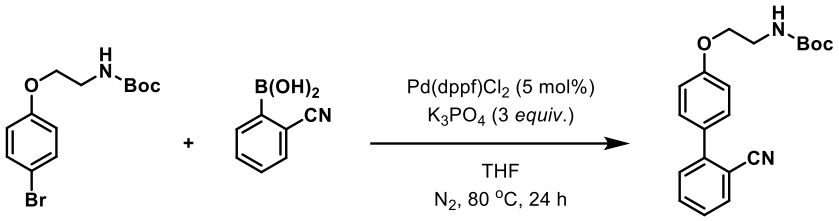
Step 1:



2-bromoethan-1-amine was taken in a clean, oven-dried 250 mL RB and was evacuated and backfilled with N_2. This procedure was continued for 3 times. The solid was dissolved in DCM and catalytic amount of Et_3N was added dropwise to the solution.[1] The reaction mixture was allowed to stir for 0.5 h in room temperature. After that, di-*tert*-butyl dicarbonate (1.2 *equiv.*) in DCM was added to that mixture and the resulting solution was allowed to stirred overnight in room temperature. Then the reaction mixture was diluted with DCM and quenched with saturated NH_4Cl solution and washed with saturated $NaHCO_3$ solution. The organic layer was extracted with DCM for three times. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. The crude product was allowed to proceed for the next step without further purification.

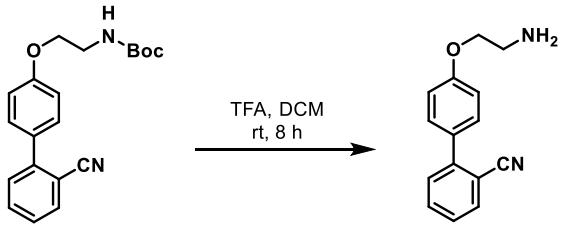
4-bromophenol was taken in a 20 mL clean, oven-dried reaction tube. Cesium carbonate was added to that reaction tube. The solids were allowed to dissolve in MeCN and stirred for 0.5 h at room temperature. Then Boc-protected compound (1.5 eq) was dissolved in MeCN and added dropwise to the previously placed reaction mixture. After addition, the reaction tube was shifted to a pre-heated oil bath at 80 ^oC for 12 h. The reaction mixture was allowed to cool to room temperature and the solvent was concentrated in *vacuo*. The mixture was quenched with water and the organic layer was extracted with EtOAc for three times. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. The crude product was purified through flash column chromatography using petroleum ether/EtOAc (85/15, v/v) as the eluent to give *tert*-butyl (2-(4-bromophenoxy)ethyl)carbamate with an overall yield of 85%.

Step 2:



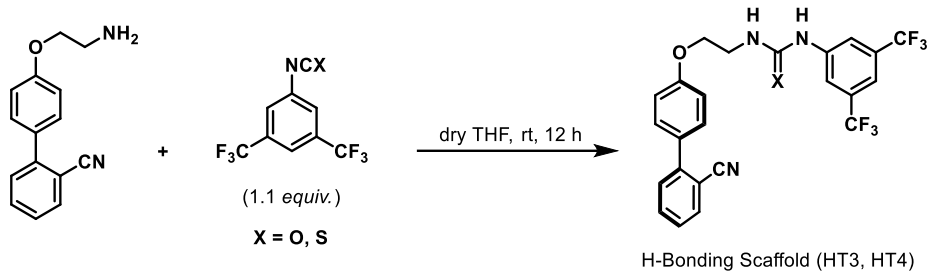
In an oven dried reaction tube, charged with stir-bar then $Pd(dppf)Cl_2$ (5 mol%), *tert*-butyl (2-(4-bromophenoxy)ethyl)carbamate (2.0 mmol), 2-cyanophenyl boronic acid (2.4 mmol) and K_3PO_4 (3.0 *equiv*.) were added. The reaction tubes were capped with Teflon cap and purged with N_2. THF was added to the reaction mixture (3 mL) and placed in a preheated 80 ^{0}C oil bath and allowed for vigorous stirring for 24 h. After 24 h, reaction mixture was allowed to cool and diluted with ethyl acetate and extracted with EtOAc for three times. The organic layer was dried over Na_2SO_4 and concentrated *via* evaporation. Concentrated organic part was purified by column chromatography. The solid compound tert-butyl(2-((2'-cyano-[1,1'-biphenyl]-4-yl)oxy)ethyl)carbamate was isolated in 75% yields using ethyl acetate and petroleum ether (20/80, v/v) as an eluent.

Step 3:



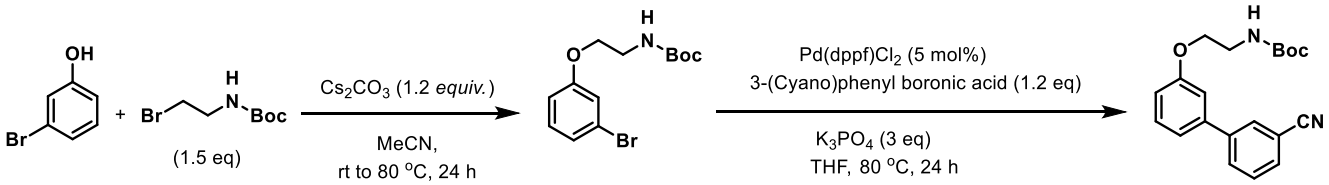
tert-butyl(2-((2'-cyano-[1,1'-biphenyl]-4-yl)oxy)ethyl)carbamate was taken in a 100 mL clean, oven-dried RB. The solid compound was dissolved with DCM. The reaction mixture was shifted to an ice bath at 0 ^{0}C. TFA was added dropwise to that solution. The reaction mixture was allowed to stir at room temperature for 8 h. The solution was quenched with saturated $NaHCO_3$ solution and the organic layer was extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. The crude product was purified through column chromatography using EtOAc/DCM as the eluent to give compound 4'-(2-aminoethoxy)-[1,1'-biphenyl]-2-carbonitrile with an overall yield of 70%.

Step 4:



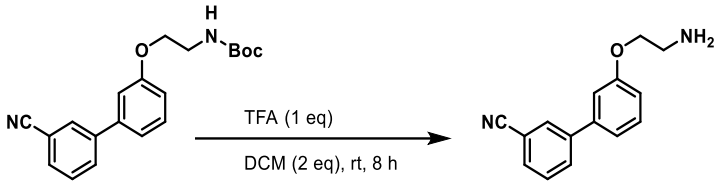
4'-(2-aminoethoxy)-[1,1'-biphenyl]-2-carbonitrile was taken in a 100 mL clean, oven-dried RB. The solid compound was dissolved in dry THF. 3,5-bis(trifluoromethyl)phenyl isocyanate/3,5-bis(trifluoromethyl)phenyl isothiocyanate was added dropwise to that solution. The reaction mixture was allowed to stir at room temperature for 12 h. After that, the resulting solution was concentrated by evaporation. The crude product was purified through column chromatography using petroleum ether/ethyl acetate (70/30, v/v) as the eluent to give the corresponding H-Bonded template with 85% yield.

4.2. General procedure for synthesis of HT2:

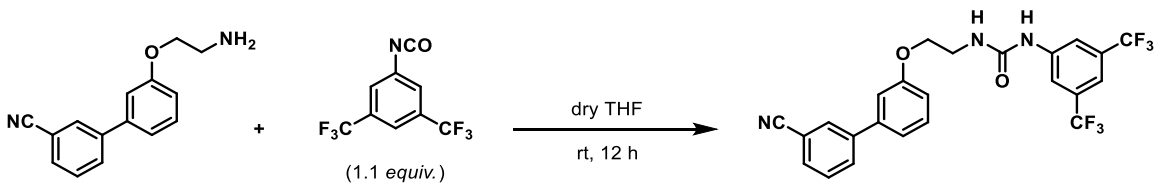


3-Bromophenol was taken in a 20 mL clean, oven-dried reaction tube. Cesium carbonate was added to that reaction tube. The solids were allowed to dissolve in MeCN and stirred for 30 minutes in room temperature. Boc-protected amine compound was then dissolved in MeCN and added dropwise to the previously placed reaction mixture. After addition, the reaction tube was shifted to a pre-heated oil bath at 80 ^{o}C for 12 h. The reaction mixture was allowed to cool to room temperature and the solvent was concentrated in *vacuo*. The mixture was quenched with water and the organic layer was extracted with EtOAc for three times. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. The crude product was purified through flash column chromatography using petroleum ether/EtOAc (85/15, v/v) as the eluent to give *tert*-butyl (2-(3-bromophenoxy)ethyl)carbamate with an overall yield of 95%.

In an oven dried reaction tube, charged with stir-bar, $Pd(dppf)Cl_2$ (5 mol%), *tert*-butyl (2-(3-bromophenoxy)ethyl)carbamate (2.0 mmol), 3-cyanophenyl boronic acid (2.4 mmol) and K_3PO_4 (3.0 *equiv*.) were added. The reaction tubes were capped with teflon cap and purged with N_2. THF was added to the reaction mixture (6 mL) and placed in a preheated 80 ^{0}C oil bath and allowed for vigorous stirring for 24 h. After 24 h, reaction mixture was allowed to cool and diluted with ethyl acetate and extracted with EtOAc for three times. The organic layer was dried over Na_2SO_4 and concentrated by evaporation. Concentrated organic part was purified by column chromatography. The solid tert-butyl (2-((3'-cyano-[1,1'-biphenyl]-3-yl)oxy)ethyl)carbamate was isolated in 85% yields using ethyl acetate and petroleum ether (20/80, v/v) as an eluent.



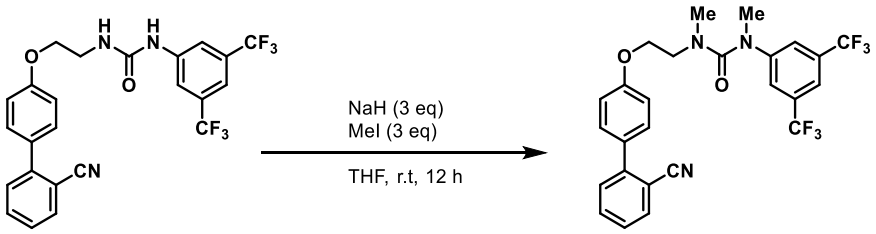
(2-((3'-cyano-[1,1'-biphenyl]-3-yl)oxy)ethyl)carbamate was taken in a 100 mL clean, oven-dried RB. The solid compound was dissolved with DCM. The reaction mixture was shifted to an ice bath at 0 ^{o}C. TFA was added dropwise to that solution. The reaction mixture was allowed to stirred at room temperature for 8 h. The solution was quenched with saturated $NaHCO_3$ solution and the organic layer was extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified through column chromatography using EtOAc/DCM as the eluent to give 3'-(2-aminoethoxy)-[1,1'-biphenyl]-3-carbonitrile with an overall yield of 70%.



3'-(2-aminoethoxy)-[1,1'-biphenyl]-3-carbonitrile was taken in a 100 mL clean, oven-dried RB. Then the RB was evacuated and backfilled with N_2. This procedure was continued for 3 times. The solid compound was dissolved in dry THF. 3,5-bis(trifluoromethyl)phenyl isocyanate was

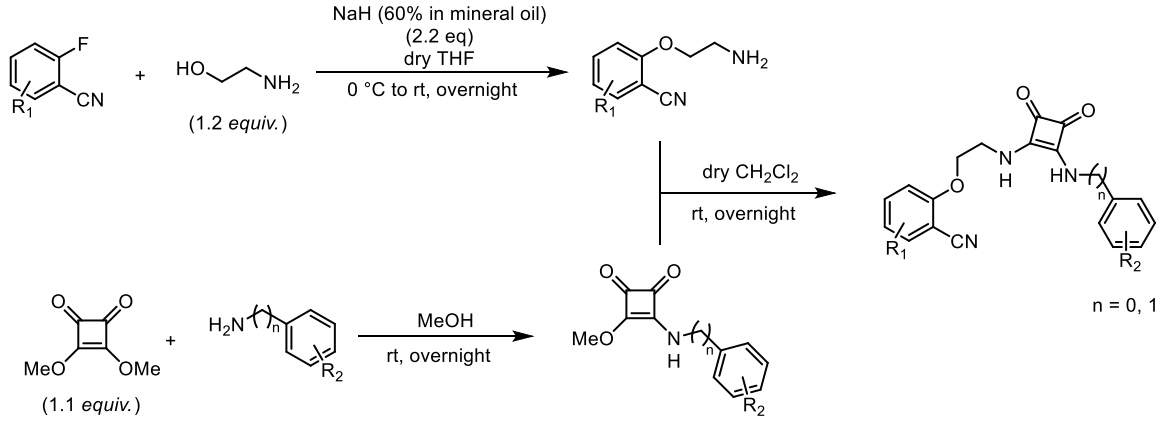
added dropwise to that solution. The reaction mixture was allowed to stir at room temperature for overnight. After that, the resulting solution was concentrated by evaporation. The crude product was purified through column chromatography using petroleum ether/ethyl acetate (70/30, v/v) as the eluent to give the corresponding urea motif with 80% yield.

4.3. General procedure for synthesis of HT11 template:



H-bonding template (HT3) was taken in a 100 mL clean, oven-dried RB. Then it was dissolved in THF solvent. The reaction mixture was shifted to an ice bath at 0 ^{o}C. Sodium hydride was added portionwise to that solution. The reaction mixture was stirred for 15 mins. After that, methyl iodide was added dropwise in the solution. The reaction mixture was allowed to stir at room temperature for 12 hrs. The reaction mixture was quenched with water. The organic layer was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified through flash column chromatography using petroleum ether/ethyl acetate as the eluent (70/30, v/v) to give di-methylated compound with an overall yield of 95%.

4.4. General procedure for the synthesis of squaramide based H-bonding templates (HT5-HT10):



2-(2-aminoethoxy)benzonitriles were obtained according to slightly modified procedure from literature[1]:

To a dry three-necked flask was added anhydrous THF (170 mL) and NaH (60% in mineral oil, 7.040 g, 176 mmol, 2.2 equiv.). The reaction flask was cooled to 0 °C and then 2-aminoethanol (5.8 mL, 96 mmol, 1.2 equiv.) was added slowly. After stirring for 20 min, to this reaction mixture was added slowly solution of substituted 2-fluorobenzonitrile (80 mmol, 1.0 equiv) in dry THF (40 mL). The mixture was stirred for 1h at 0 °C and then at room temperature overnight. After completion of reaction monitored by TLC analysis, the mixture was slowly quenched with 25 mL of water, extracted with 3 × 100 mL of diethyl ether and dried over anhydrous $MgSO_4$. Solvent was evaporated and the residue was subjected to silica gel flash column chromatography using CH_2Cl_2/MeOH (5% - 10% gradient) as eluent.

4.4.1. Preparation of monosquaramides:

Dimethoxycyclobut-3-ene-1,2-dione (3.126 g, 22 mmol, 1.1 equiv) was dissolved in 20 mL of methanol. Then the substituted amine or aniline (20 mmol, 1.0 equiv) was added dropwise as solution in 20 mL of methanol and the mixture was stirred for 48 h at room temperature. The mixture was cooled to -20 °C and precipitate was filtered and washed with cold methanol to give monosquaramide esters in various yields which were used in next step without further purification.

4.4.2. Preparation of squaramide based templates:

Monosquaramide ester (7.00 mmol, 1.0 equiv) was suspended in 37 mL of dry CH_2Cl_2. Then substituted 2-(aminoethoxy)benzonitrile (7.35 mmol, 1.05 equiv.) was added as solution in 5 mL of dry CH_2Cl_2 at once. The mixture was stirred overnight at room temperature. After completion the mixture was cooled to -20 °C and precipitate was filtered and washed with cold CH_2Cl_2 to obtain squaramides in various yields as white solids.

5. X-Ray crystal structure details

5.1. X-Ray structure of *Ethyl (E)-3-(2-methoxy-4-methyl-5-nitrophenyl)acrylate* (CCDC No **2209235):**

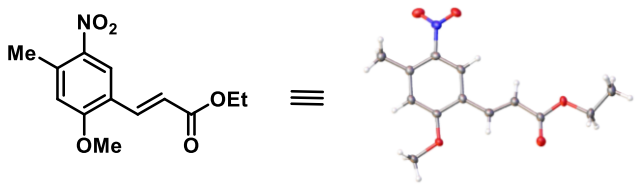


Figure 1: X-Ray crystal structure of **3j**

Crystallographic data

Identification code	DM_BD_218
Formula	$C_{13}H_{15}NO_5$
Formula weight(g/mol)	265.26
Temperature/K	109 K
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	12.8587 (7)
b/Å	13.2648 (5)
c/Å	7.9162 (4)
α/°	90
β/°	107.704 (5)
γ/°	90
Volume/Å^3	1286.30 (11)
Z	4
P_{calc}g/cm^3	1.370
μ/mm^{-1}	0.106
F(000)	560
Crystal size/mm^3	0.098 x 0.093x 0.089
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	2.263 to 24.987
Index ranges	-15<=h<=14, -15<=k<15, -9<=l<=9
Reflections collected / unique	14156/ 2257 [R(int) = 0.0975]
Data / restraints / parameters	2257 / 0 / 175
Goodness-of-fit on F^2	1.070
Final R indices [I>2σ(I)]	R1 = 0.0397, wR2 = 0.0987
Final R indices (all data)	R1 = 0.0465, wR2 = 0.1059
Largest diff. peak and hole/ e Å^{-3}	0.20 and -0.206

5.2. X-Ray structure of *Ethyl (E)-3-(2-ethoxy-5-nitrophenyl)acrylate* (CCDC No **2209236):**

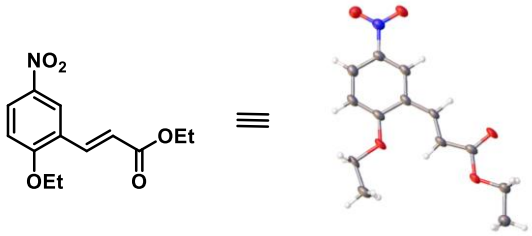


Figure 2: X-Ray crystal structure of **3e**

Crystallographic data

Identification code	DM_BD_237-2
Formula	$C_{13}H_{15}NO_5$
Formula weight(g/mol)	265.26
Temperature/K	120 K
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	12.0027(8)
b/Å	13.7374(5)
c/Å	8.0482(6)
α/°	90
β/°	107.968(7)
γ/°	90
Volume/Å^3	1262.31(14)
Z	4
P_{calc}g/cm^3	1.396
μ/mm^{-1}	0.108
F(000)	560
Crystal size/mm^3	0.110 x 0.098 x 0.093
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	1.784 to 24.997
Index ranges	-14<=h<=14, -16<=k<16, -9<=l<=9
Reflections collected / unique	21062 / 2223 [R(int) = 0.1152]
Data / restraints / parameters	2223/ 0 / 174
Goodness-of-fit on F^2	1.091
Final R indices [I>2σ(I)]	R1 = 0.0829, wR2 = 0.2115
Final R indices (all data)	R1 = 0.1034, wR2 = 0.2284
Largest diff. peak and hole/ e Å^{-3}	0.36 and -0.388

5.3. X-Ray structure of *Ethyl (E)-3-(4-methyl-3-nitrophenyl)acrylate* (CCDC No **2209234):**

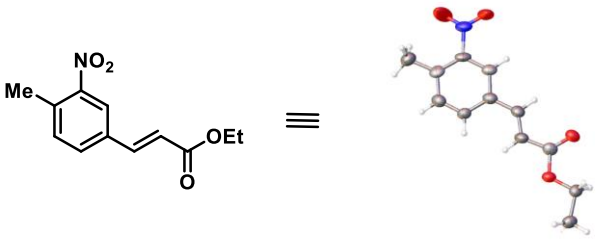


Figure 3: X-Ray crystal structure of **3b**

Crystallographic data

Identification code	DM_BD_213
Formula	$C_{13}H_{15}NO_5$
Formula weight(g/mol)	235.23
Temperature/K	106K
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	7.5661(8)
b/Å	21.261(3)
c/Å	7.2335(11)
α/°	90
β/°	94.876(14)
γ/°	90
Volume/Å^3	1159.4(3)
Z	4
P_{calc}g/cm^3	1.348
μ/mm^{-1}	0.102
F(000)	496
Crystal size/mm^3	0.108 x 0.098 x 0.095
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	1.916 to 24.994
Index ranges	-8<=h<=8, -25<=k<25, -8<=l<=8
Reflections collected / unique	19601/ 2036 [R(int) = 0.1583]
Data / restraints / parameters	2036/ 0 / 156
Goodness-of-fit on F^2	1.097
Final R indices [I>2σ(I)]	R1 = 0.1206, wR2 = 0.2823
Final R indices (all data)	R1 = 0.1772, wR2 = 0.3181
Largest diff. peak and hole/ e Å^{-3}	0.46 and -0.363

5.4. X-Ray structure of *1-(3,5-bis(trifluoromethyl)phenyl)-3-(2-((2'-cyano-[1,1'-biphenyl]-4-yl)oxy)ethyl)urea* (CCDC No **2209378):**

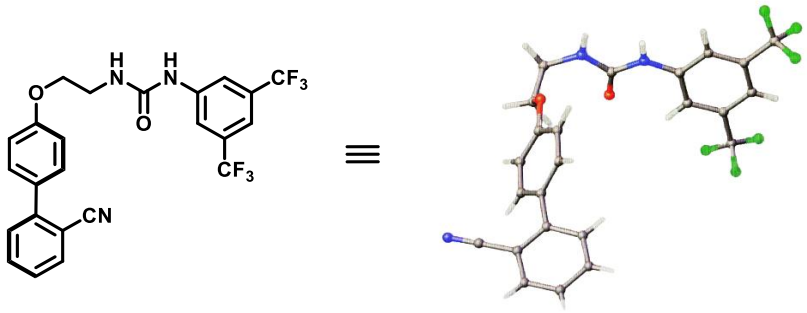


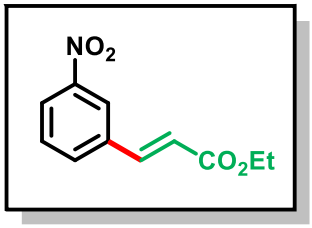
Figure 4: X-Ray crystal structure of **HT3**

Crystallographic data

Identification code	DM_AGJ_343_1
Formula	$C_{13}H_{15}NO_5$
Formula weight(g/mol)	493.40
Temperature/K	150K
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	18.9612(9)
b/Å	13.2965(7)
c/Å	9.0939(4)
α/°	90
β/°	102.475(5)
γ/°	90
Volume/Å^3	2238.60(19)
Z	4
P_{calc}g/cm^3	1.464
μ/mm^{-1}	0.129
F(000)	1008.0
Crystal size/mm^3	0.112 x 0.094 x 0.085
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.772 to 50
Index ranges	-22<=h<=22, -15<=k<15, -9<=l<=10
Reflections collected / unique	41191/ 3942 [R(int) = 0.1636]
Data / restraints / parameters	3942/81/381
Goodness-of-fit on F^2	1.061
Final R indices [I>2σ(I)]	R1 = 0.0575, wR2 = 0.1328
Final R indices (all data)	R1 = 0.0920, wR2 = 0.1586
Largest diff. peak and hole/ e Å^{-3}	0.23 and -0.290

6. Characterization data of olefinated nitroarenes:

Ethyl (E)-3-(3-nitrophenyl)acrylate **(3a):**



Physical appearance: Yellow solid.

Eluent: ethyl acetate/petroleum ether (05/95, v/v).

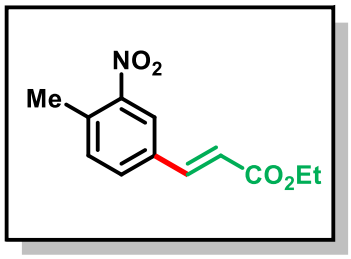
Column material: 100-200 mesh silica.

Yield: 46%

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.23 (ddd, *J* = 8.2, 2.3, 1.1 Hz, 1H), 7.82 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.72 (d, *J* = 16.0 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 6.56 (d, *J* = 16.0 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.35, 148.96, 141.89, 136.47, 133.80, 130.17, 124.70, 122.63, 121.74, 61.16, 14.49.

HRMS (ESI): Calculated mass for $C_{11}H_{11}NO_4$ $[M+H]^+$: 222.0766; observed mass: 222.0759.

Ethyl (E)-3-(4-methyl-3-nitrophenyl)acrylate **(3b):**



Physical appearance: Yellow crystalline solid.

Eluent: ethyl acetate/petroleum ether (06/94, v/v).

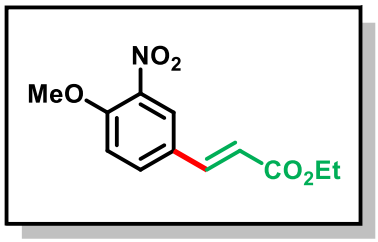
Column material: 100-200 mesh silica.

Yield: 51%

After purification by column chromatography, 3c was obtained in 51% yield as a mixture of regioisomers. Among them *meta* olefinated product was formed in major amount. The ratio of the product mixture was determined by ^{1}H NMR, *M*:others = 4:1, *m:m'* = 1.6:1. The characterization data of isomeric mixture:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 1.8 Hz, 1H), 7.97 (d, *J* = 15.9 Hz, 1H), 7.76 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.72 – 7.66 (m, 1H), 7.66 – 7.61 (m, 2H), 7.43 – 7.33 (m, 2H), 6.49 (d, *J* = 16.0 Hz, 1H), 4.61 – 3.94 (m, 5H), 2.62 (s, 4H), 2.51 (s, 2H), 1.37 – 1.30 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.52, 166.37, 165.90, 149.81, 142.00, 141.87, 140.90, 137.16, 135.48, 134.04, 133.64, 132.95, 132.54, 131.98, 131.24, 130.74, 130.60, 127.33, 126.97, 126.16, 125.62, 125.34, 125.12, 124.03, 123.57, 123.20, 122.29, 120.72, 120.69, 61.05, 20.66, 17.65, 15.51, 14.50. **HRMS (ESI):** Calculated mass for $C_{12}H_{13}NO_4$ $[M+H]^+$: 236.0923; observed mass: 236.0915.

***Ethyl (E)-3-(4-methoxy-3-nitrophenyl)acrylate* (3c):**



Physical appearance: Colourless oil.

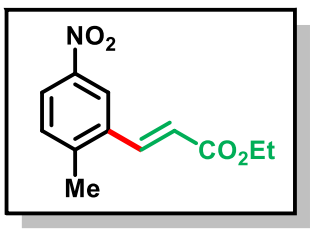
Eluent: ethyl acetate/petroleum ether (15/85, v/v).

Column material: 100-200 mesh silica.

Yield: 58%

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 2.3 Hz, 1H), 7.68 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.60 (d, *J* = 16.0 Hz, 1H), 7.11 (d, *J* = 8.8 Hz, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.68, 154.19, 141.71, 140.03, 133.67, 127.42, 125.15, 119.17, 114.07, 60.94, 56.96, 14.49. **HRMS (ESI):** Calculated mass for $C_{12}H_{13}NO_5$ $[M+H]^+$: 252.0872; observed mass: 252.0859.

***Ethyl (E)-3-(2-methyl-5-nitrophenyl)acrylate* (3d):**



Physical appearance: Yellow liquid.

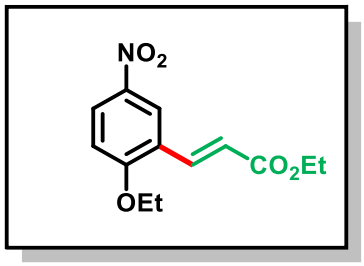
Eluent: ethyl acetate/petroleum ether (06/94, v/v).

Column material: 100-200 mesh silica.

Yield: 54%

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, *J* = 2.4 Hz, 1H), 8.11 (dd, *J* = 8.4, 2.5 Hz, 1H), 7.91 (d, *J* = 15.8 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 6.50 (d, *J* = 15.8 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.53 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.49, 144.95, 140.01, 135.09, 131.89, 129.90, 124.26, 122.64, 121.54, 61.14, 20.30, 14.49. **HRMS (ESI):** Calculated mass for $C_{12}H_{13}NO_4$ $[M+H]^+$: 236.0923; observed mass: 236.0909.

Ethyl (E)-3-(2-ethoxy-5-nitrophenyl)acrylate **(3e):**



Physical appearance: White crystaline solid.

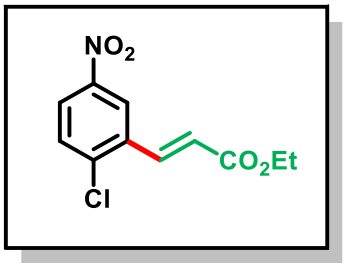
Eluent: ethyl acetate/petroleum ether (13/87, v/v).

Column material: 100-200 mesh silica.

Yield: 74%

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 2.8 Hz, 1H), 8.21 (dd, *J* = 9.1, 2.8 Hz, 1H), 7.94 (d, *J* = 16.2 Hz, 1H), 6.96 (d, *J* = 9.2 Hz, 1H), 6.61 (d, *J* = 16.2 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 4.21 (t, *J* = 7.0 Hz, 2H), 1.53 (t, *J* = 7.0 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.95, 162.16, 141.39, 137.81, 126.90, 124.39, 124.33, 121.60, 111.83, 65.42, 60.93, 14.72, 14.49. **HRMS (ESI):** Calculated mass for $C_{13}H_{15}NO_5$ $[M+H]^+$: 266.1028; observed mass: 266.1028.

Ethyl (E)-3-(2-chloro-5-nitrophenyl)acrylate **(3f):**



Physical appearance: White solid.

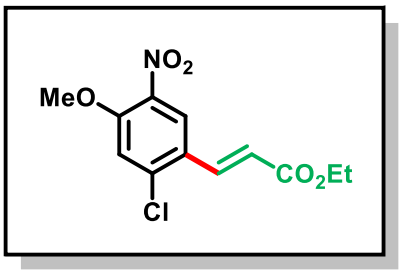
Eluent: ethyl acetate/petroleum ether (15/85, v/v).

Column material: 100-200 mesh silica.

Yield: 52%

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 2.6 Hz, 1H), 8.16 (dd, *J* = 8.8, 2.7 Hz, 1H), 8.04 (d, *J* = 15.9 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 4.31 (q, *J* = 7.0 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.93, 146.99, 141.34, 138.29, 134.54, 131.42, 125.19, 124.11, 122.75, 61.35, 14.47. **HRMS (ESI):** Calculated mass for $C_{11}H_{10}ClNO_4$ $[M+H]^+$: 256.0377; observed mass: 256.0370.

Ethyl (E)-3-(2-chloro-4-methoxy-5-nitrophenyl)acrylate **(3g):**



Physical appearance: Yellow oil.

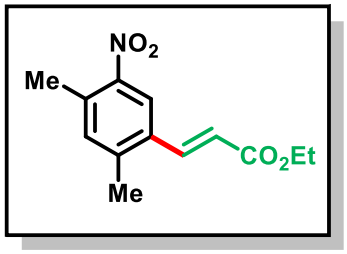
Eluent: ethyl acetate/petroleum ether (16/84, v/v).

Column material: 100-200 mesh silica.

Yield: 58%

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.95 (d, *J* = 16.0 Hz, 1H), 7.15 (s, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.28, 154.15, 140.68, 138.54, 137.95, 125.61, 124.90, 121.64, 115.29, 61.13, 57.30, 14.48. **HRMS (ESI):** Calculated mass for $C_{12}H_{12}ClNO_5$ $[M+H]^+$: 286.0482; observed mass: 286.0480.

Ethyl (E)-3-(2,4-dimethyl-5-nitrophenyl)acrylate **(3h):**



Physical appearance: Reddish liquid.

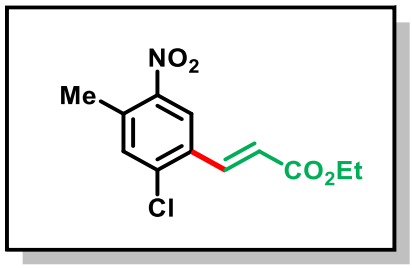
Eluent: ethyl acetate/petroleum ether (5/95 v/v).

Column material: 100-200 mesh silica.

Yield: 52%

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.86 (d, *J* = 15.9 Hz, 1H), 7.18 (s, 1H), 6.44 (d, *J* = 15.9 Hz, 1H), 4.77 – 4.11 (m, 2H), 2.60 (s, 3H), 2.47 (s, 3H), 1.35 (dd, *J* = 7.8, 6.6 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.67, 143.22, 139.90, 135.37, 135.23, 133.63, 132.71, 122.96, 121.61, 61.04, 20.79, 19.92, 14.49. **HRMS (ESI):** Calculated mass for $C_{13}H_{15}NO_4$ $[M+H]^+$: 249.0927; observed mass: 249.0921.

Ethyl (E)-3-(2-chloro-4-methyl-5-nitrophenyl)acrylate **(3i):**



Physical appearance: Yellowish oil.

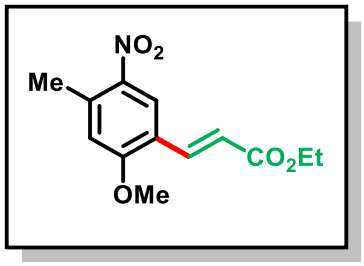
Eluent: ethyl acetate/petroleum ether (10/90, v/v).

Column material: 100-200 mesh silica.

Yield: 47%

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.98 (d, *J* = 16.0 Hz, 1H), 7.43 (s, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 2.62 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.11, 139.29, 138.16, 136.60, 134.33, 132.07, 128.17, 124.87, 124.03, 123.10, 61.24, 20.69, 14.48.

Ethyl (E)-3-(2-methoxy-4-methyl-5-nitrophenyl)acrylate **(3j):**



Physical appearance: White solid.

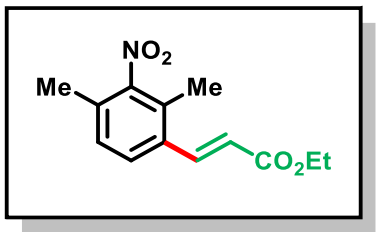
Eluent: ethyl acetate/petroleum ether (12/88, v/v).

Column material: 100-200 mesh silica.

Yield: 70%

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 1H), 7.86 (d, *J* = 16.2 Hz, 1H), 6.78 (s, 1H), 6.57 (d, *J* = 16.1 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.97 (s, 3H), 2.67 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ 166.09, 161.16, 142.19, 138.74, 137.64, 126.27, 122.41, 121.00, 114.71, 60.87, 56.41, 22.13, 14.50. **HRMS (ESI):** Calculated mass for $C_{13}H_{15}NO_5$ $[M+H]^+$: 266.1028; observed mass: 266.1006.

***Ethyl (E)-3-(2,4-dimethyl-3-nitrophenyl)acrylate* (3k):**



Physical appearance: White solid.

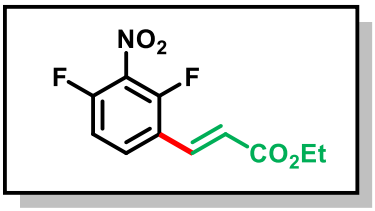
Eluent: ethyl acetate/petroleum ether (04/96, v/v).

Column material: 100-200 mesh silica.

Yield: 68%

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 15.8 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.35 (d, *J* = 15.8 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.31 (s, 3H), 2.30 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.62, 153.29, 140.52, 133.48, 130.94, 129.14, 128.45, 128.00, 121.77, 61.01, 17.59, 14.49, 14.34. **HRMS (ESI):** Calculated mass for $C_{13}H_{15}NO_4$ $[M+H]^+$: 250.1079; observed mass: 250.1067.

***Ethyl (E)-3-(2,4-difluoro-3-nitrophenyl)acrylate* (3l):**



Physical appearance: Yellow oil.

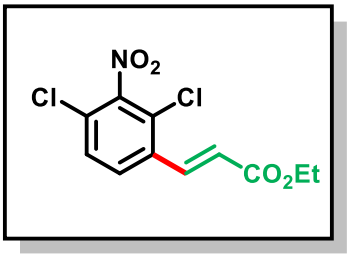
Eluent: ethyl acetate/petroleum ether (16/84, v/v).

Column material: 100-200 mesh silica.

Yield: 42%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.66 (m, 2H), 7.14 (td, *J* = 8.8, 1.9 Hz, 1H), 6.54 (d, *J* = 16.2 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.03, 165.32, 155.15 (d, $J_{C\text{-}F}$ = 194 Hz), 153.03 (d, $J_{C\text{-}F}$ = 196 Hz), 134.66, 133.99, 131.75, 131.71, 131.67, 131.64, 123.64, 113.55, 113.51, 113.39, 113.36, 61.93, 61.33, 14.46. **HRMS (ESI):** Calculated mass for $C_{11}H_9F_2NO_4$ $[M+H]^+$: 258.0578; observed mass: 258.0569.

***Ethyl (E)-3-(2,4-dichloro-3-nitrophenyl)acrylate* (3m):**



Physical appearance: White solid.

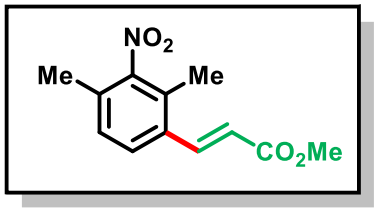
Eluent: ethyl acetate/petroleum ether (15/85, v/v).

Column material: 100-200 mesh silica.

Yield: 60%

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 16.0 Hz, 1H), 7.67 (d, *J* = 8.6 Hz, 1H), 7.46 (d, *J* = 8.6 Hz, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.76, 137.58, 134.67, 133.85, 129.14, 128.83, 127.44, 126.67, 124.24, 61.41, 14.46. **HRMS (ESI):** Calculated mass for $C_{11}H_9Cl_2NO_4$ $[M+H]^+$: 289.9987; observed mass: 289.9968.

***Methyl (E)-3-(2,4-dimethyl-3-nitrophenyl)acrylate* (3n):**



Physical appearance: White solid.

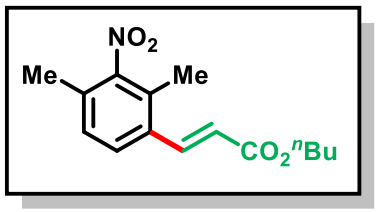
Eluent: ethyl acetate/petroleum ether (5/95 v/v).

Column material: 100-200 mesh silica.

Yield: 71%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 15.8 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 6.35 (d, *J* = 15.8 Hz, 1H), 3.82 (s, 3H), 2.31 (s, 3H), 2.30 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.05, 140.79, 133.38, 131.04, 129.16, 128.49, 127.99, 121.26, 52.13, 17.60, 14.35. **HRMS (ESI):** Calculated mass for $C_{12}H_{13}NO_4$ $[M+H]^+$: 236.0923; observed mass: 236.0909.

***Butyl (E)-3-(2,4-dimethyl-3-nitrophenyl)acrylate* (3o):**



Physical appearance: Yellow oil.

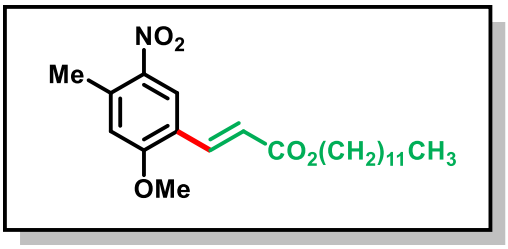
Eluent: ethyl acetate/petroleum ether (15/85 v/v).

Column material: 100-200 mesh silica.

Yield: 64%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 15.8 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 6.35 (d, *J* = 15.8 Hz, 1H), 4.22 (t, *J* = 6.7 Hz, 2H), 2.31 (s, 3H), 2.30 (s, 3H), 1.75 – 1.65 (m, 3H), 1.48 – 1.40 (m, 3H), 0.96 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.71, 153.29, 140.48, 133.49, 130.93, 129.13, 128.44, 128.00, 121.76, 64.93, 30.93, 19.40, 17.72, 17.59, 14.33, 13.94, 13.91.

***Dodecyl (E)-3-(2-methoxy-4-methyl-5-nitrophenyl)acrylate* (3p):**



Physical appearance: Yellow oil.

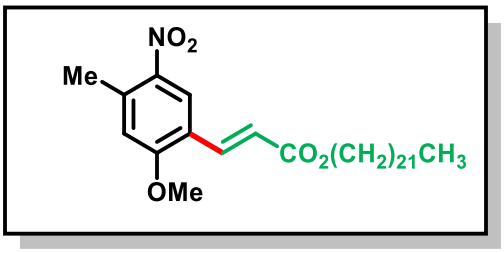
Eluent: ethyl acetate/petroleum ether (17/83 v/v).

Column material: 100-200 mesh silica.

Yield: 57%

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.86 (d, *J* = 16.2 Hz, 1H), 6.78 (s, 1H), 6.57 (d, *J* = 16.2 Hz, 1H), 4.19 (t, *J* = 6.7 Hz, 2H), 3.97 (s, 3H), 2.67 (s, 3H), 1.69 (dd, *J* = 14.5, 7.0 Hz, 2H), 1.25 (s, 18H), 0.87 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 167.15, 161.16, 142.22, 138.70, 137.58, 126.25, 122.48, 121.04, 114.70, 65.10, 56.43, 56.41, 32.12, 29.86, 29.83, 29.79, 29.74, 29.55, 29.49, 28.92, 26.18, 22.89, 22.14, 14.32. **HRMS (ESI):** Calculated mass for $C_{23}H_{35}NO_5$ $[M+H]^+$: 406.2593; observed mass: 406.2607.

***Docosyl (E)-3-(2-methoxy-4-methyl-5-nitrophenyl)acrylate* (3q):**



Physical appearance: Yellow solid.

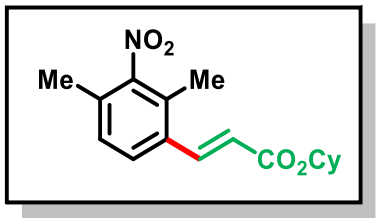
Eluent: ethyl acetate/petroleum ether (15/85, v/v).

Column material: 100-200 mesh silica.

Yield: 53%

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.87 (d, *J* = 16.2 Hz, 1H), 6.78 (s, 1H), 6.57 (d, *J* = 16.2 Hz, 1H), 4.20 (t, *J* = 6.8 Hz, 2H), 3.97 (s, 3H), 2.68 (s, 3H), 1.70 (dd, *J* = 8.1, 6.6 Hz, 2H), 1.25 (s, 38H), 0.87 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 167.14, 161.15, 142.23, 138.69, 137.57, 126.24, 122.48, 121.04, 114.69, 65.09, 56.41, 32.13, 29.91, 29.87, 29.83, 29.81, 29.78, 29.75, 29.73, 29.65, 29.57, 29.50, 29.46, 28.92, 28.70, 26.18, 26.14, 22.90, 22.13, 14.32. **HRMS (ESI):** Calculated mass for $C_{33}H_{55}NO_5$ $[M+H]^+$: 546.4158; observed mass: 546.4139.

***Cyclohexyl (E)-3-(2,4-dimethyl-3-nitrophenyl)acrylate* (3r):**



Physical appearance: White solid.
Eluent: ethyl acetate/petroleum ether (5/95 v/v).

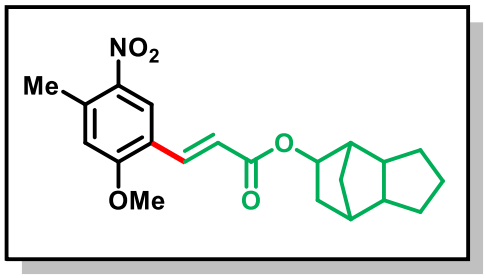
Column material: 100-200 mesh silica.

Yield: 60%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 15.8 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.15 (d, *J* = 8.1 Hz, 1H), 6.35 (d, *J* = 15.8 Hz, 1H), 4.89 (ddt, *J* = 13.1, 9.0, 3.9 Hz, 1H), 2.31 (s, 3H), 2.30 (s, 3H), 2.08 – 1.84 (m, 2H), 1.86 – 1.68 (m, 2H), 1.48 (ddd, *J* = 12.8, 9.7, 2.8 Hz, 3H), 1.42 – 1.26 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.08, 140.20, 133.56, 130.83, 129.10, 128.51, 128.40, 128.00, 122.34, 73.34, 31.90, 31.57, 25.59, 23.98, 17.72, 17.59, 14.34.

HRMS (ESI): Calculated mass for $C_{17}H_{21}NO_4$ $[M+H]^+$: 304.1549; observed mass: 304.1539.

***Octahydro-1H-4,7-methanoinden-5-yl(E)-3-(2-methoxy-4-methyl-5- nitrophenyl)acrylate* (3s):**



Physical appearance: Colourless oil.

Eluent: ethyl acetate/petroleum ether (15/85 v/v).

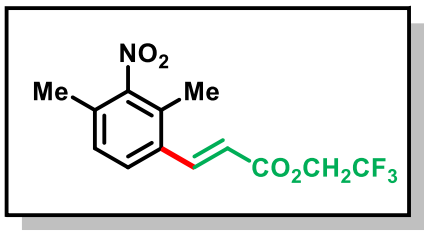
Column material: 100-200 mesh silica.

Yield: 58%

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.83 (d, *J* = 16.2 Hz, 1H), 6.77 (s, 1H), 6.54 (d, *J* = 15.9 Hz, 1H), 4.69 (dd, *J* = 7.2, 2.4 Hz, 1H), 3.97 (s, 3H), 2.67 (s, 3H), 2.14 (s, 1H), 2.06 (d, *J* = 4.6 Hz, 1H), 1.95 – 1.82 (m, 3H), 1.81 – 1.65 (m, 4H), 1.49 (ddd, *J* = 13.4, 4.5, 2.5 Hz, 1H), 1.31 – 1.17 (m, 2H), 1.02 – 0.90 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.89, 161.15,

142.20, 138.63, 137.26, 126.24, 122.55, 121.57, 114.69, 56.42, 49.55, 47.50, 47.38, 46.41, 43.45, 43.23, 42.07, 39.91, 39.83, 39.35, 32.24, 32.19, 31.89, 29.67, 28.78, 28.03, 27.94, 22.15. **HRMS (ESI):** Calculated mass for $C_{21}H_{25}NO_5$ $[M+H]^+$: 372.1811; observed mass: 372.1813.

***2,2,2-trifluoroethyl (E)-3-(2,4-dimethyl-3-nitrophenyl)acrylate* (3t):**



Physical appearance: Brown liquid.

Eluent: ethyl acetate/petroleum ether (10/90 v/v).

Column material: 100-200 mesh silica.

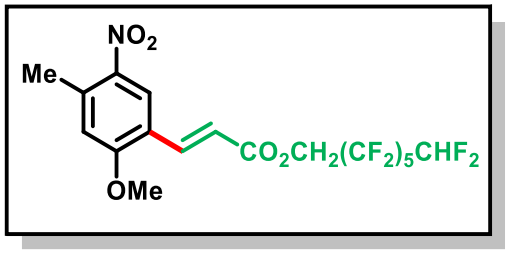
Yield: 51%

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 15.8 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 1H), 6.42 (d, *J* = 15.8 Hz, 1H), 4.60 (q, *J* = 8.4 Hz, 2H), 2.33 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.86, 153.35, 142.99, 132.78, 131.74, 130.71, 129.31, 128.85, 128.11, 124.29, 122.09, 119.29, 118.61, 60.77 (q, $J_{C\text{-}F}$ = 29 Hz), 17.68, 14.34.

^{19}F NMR (471 MHz, $CDCl_3$) δ -73.69. **HRMS (ESI):** Calculated mass for $C_{13}H_{12}F_3NO_4$ $[M+H]^+$: 303.0797; observed mass: 303.0733.

***2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl(E)-3-(2-methoxy-4-methyl-5-nitrophenyl)acrylate* (3u):**



Physical appearance: Yellow liquid.

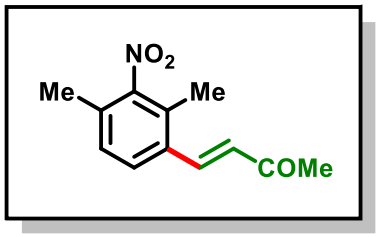
Eluent: ethyl acetate/petroleum ether (15/85 v/v).

Column material: 100-200 mesh silica.

Yield: 44%

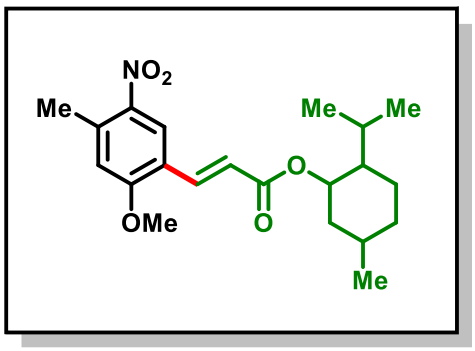
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.97 (d, *J* = 16.2 Hz, 1H), 6.81 (s, 1H), 6.63 (d, *J* = 16.2 Hz, 1H), 6.22 – 5.88 (m, 1H), 4.90 – 4.65 (m, 2H), 3.99 (s, 3H), 2.69 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 165.37, 165.34, 161.37, 142.32, 140.35, 140.34, 139.54, 139.49, 133.98, 133.03, 130.41, 130.10, 128.41 (d, J_{C-F} = 3 Hz), 127.47, 126.76, 126.74, 121.82, 121.79, 119.68, 118.57, 118.55, 114.91, 114.88, 113.89, 107.79 (t, J_{C-F} = 25 Hz), 66.63, 59.91 (t, J_{C-F} = 22 Hz), 56.55, 56.53, 22.25, 22.19. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -63.02, -73.56, -119.35, -119.39, -122.12, -123.39, -129.41, -136.97, -137.00. **HRMS (ESI):** Calculated mass for $C_{18}H_{13}F_{12}NO_5$ $[M+H]^+$: 551.0602; observed mass: 551.0600.

***(E)-4-(2,4-dimethyl-3-nitrophenyl)but-3-en-2-one* (3v):**



Physical appearance: Yellow liquid.
Eluent: ethyl acetate/petroleum ether (15/85 v/v).
Column material: 100-200 mesh silica.
Yield: 45%
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 16.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 1H), 6.64 (d, *J* = 16.0 Hz, 1H), 2.39 (s, 3H), 2.33 (s, 3H), 2.31 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.92, 176.09, 141.15, 138.89, 133.41, 131.21, 129.89, 129.22, 129.17, 128.73, 127.98, 101.97, 17.62, 14.34. **HRMS (ESI):** Calculated mass for $C_{12}H_{13}NO_3$ $[M+H]^+$: 220.0929; observed mass: 220.0964.

***2-isopropyl-5-methylcyclohexyl (E)-3-(2-methoxy-4-methyl-5-nitrophenyl)acrylate* (3w):**



Physical appearance: Yellow liquid.

Eluent: ethyl acetate/petroleum ether (5/95 v/v).

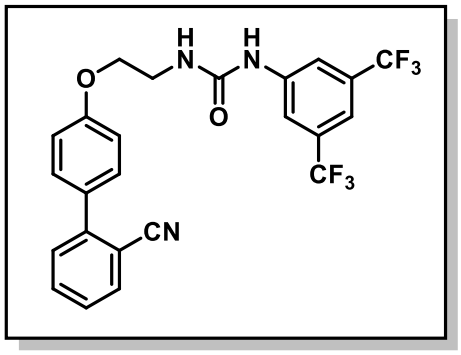
Column material: 100-200 mesh silica.

Yield: 64%

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.86 (d, *J* = 16.2 Hz, 1H), 6.78 (s, 1H), 6.57 (d, *J* = 16.1 Hz, 1H), 4.82 (td, *J* = 10.8, 4.4 Hz, 1H), 3.98 (s, 3H), 2.68 (s, 3H), 2.14 – 1.99 (m, 1H), 1.93 (pt, *J* = 7.0, 3.5 Hz, 1H), 1.76 – 1.64 (m, 2H), 1.58 (s, 3H), 1.46 (ddt, *J* = 12.4, 10.7, 3.1 Hz, 2H), 1.14 – 0.99 (m, 2H), 0.92 (dd, *J* = 6.8, 2.9 Hz, 7H), 0.79 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.67, 161.16, 142.19, 138.67, 137.44, 126.28, 122.55, 121.48, 114.68, 74.66, 56.42, 47.37, 41.19, 34.49, 31.64, 26.52, 23.70, 22.26, 22.18, 21.00, 16.61. **HRMS (ESI):** Calculated mass for $C_{21}H_{29}NO_5$ $[M+H]^+$: 376.2124; observed mass: 376.2044.

7. Characterization of spectral data of H-bonding templates:

1-(3,5-bis(trifluoromethyl)phenyl)-3-(2-((2'-cyano-[1,1'-biphenyl]-4-yl)oxy)ethyl)urea:



Physical appearance: White crystalline solid.

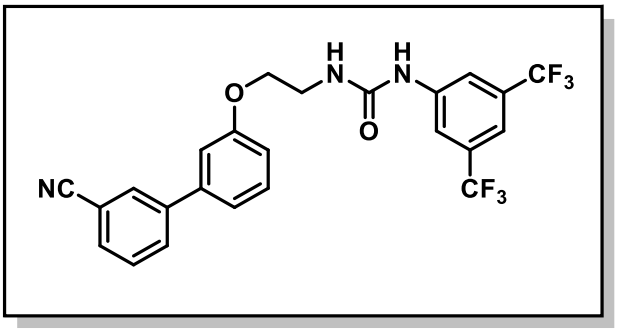
Eluent: ethyl acetate/petroleum ether (30/70 v/v).

Column material: 100-200 mesh silica.

Yield: 85%

^{1}H NMR (400 MHz, Acetone-d_6) δ 8.76 (s, 1H), 8.17 (d, *J* = 1.6 Hz, 2H), 7.85 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.75 (td, *J* = 7.7, 1.4 Hz, 1H), 7.65 – 7.47 (m, 5H), 7.24 – 7.03 (m, 2H), 6.47 (t, *J* = 5.9 Hz, 1H), 4.22 (t, *J* = 5.4 Hz, 2H), 3.69 (q, *J* = 5.5 Hz, 2H). **^{13}C NMR (101 MHz, Acetone-d_6)** δ 160.44, 156.01, 145.89, 143.73, 134.79, 134.18, 132.55 (q, $J_{C\text{-}F}$ = 32.30 Hz), 131.95, 131.19, 131.06, 128.59, 124.70 (q, $J_{C\text{-}F}$ = 272.70 Hz), 119.56, 118.69, 118.64, 115.73, 115.08, 115.04, 115.00, 111.92, 68.22, 40.32.
HRMS (ESI): Calculated mass for $C_{24}H_{17}F_6N_3O_2$ $[M+H]^+$: 494.1303; observed mass: 494.1306.

1-(3,5-bis(trifluoromethyl)phenyl)-3-(2-((3'-cyano-[1,1'-biphenyl]-3-yl)oxy)ethyl)urea:



Physical appearance: Yellowish solid.

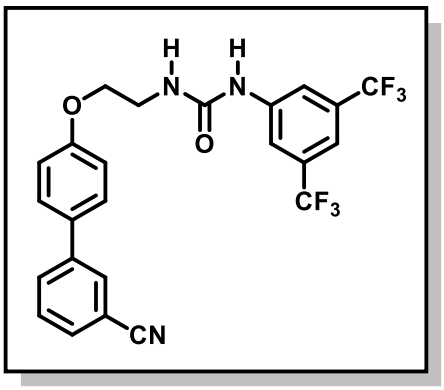
Eluent: ethyl acetate/petroleum ether (30/70 v/v).

Column material: 100-200 mesh silica.

Yield: 90%

^{1}H NMR (500 MHz, Acetone-*d*$_6$) δ 8.77 (s, 1H), 8.16 (s, 3H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.77 (t, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.52 (s, 1H), 7.44 (t, *J* = 7.9 Hz, 2H), 7.29 – 7.13 (m, 3H), 7.08 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.48 (t, *J* = 6.8 Hz, 1H), 4.22 (t, *J* = 5.5 Hz, 3H), 3.68 (t, *J* = 5.5 Hz, 3H). **^{13}C NMR (126 MHz, Acetone-*d*$_6$)** δ 160.33, 156.20, 156.13, 146.26, 144.02, 143.93, 141.12, 135.05, 134.45, 132.81 (q, $J_{C\text{-}F}$ = 32.76 Hz), 131.49, 131.19, 129.43, 126.05, 123.89, 122.63, 119.59, 118.91, 118.87, 116.36, 116.20, 115.25, 112.42, 68.53, 40.58. **HRMS (ESI):** Calculated mass for $C_{24}H_{17}F_6N_3O_2$ $[M+H]^+$: 494.1303; observed mass: 494.1303.

1-(3,5-bis(trifluoromethyl)phenyl)-3-(2-((3'-cyano-[1,1'-biphenyl]-4-yl)oxy)ethyl)urea:



Physical appearance: Brown crystalline solid.

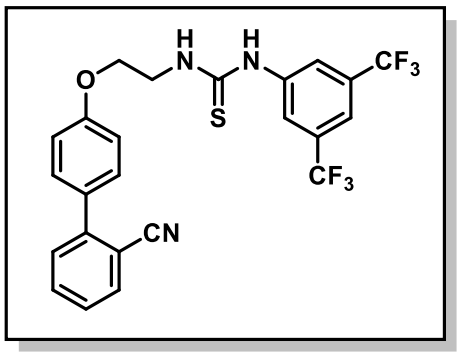
Eluent: ethyl acetate/petroleum ether (35/65 v/v).

Column material: 100-200 mesh silica.

Yield: 95%

^{1}H NMR (500 MHz, Acetone-*d_6*) δ 8.77 (s, 1H), 8.16 (d, *J* = 1.7 Hz, 3H), 7.99 (s, 1H), 7.96 – 7.89 (m, 1H), 7.73 – 7.66 (m, 4H), 7.63 (t, *J* = 7.7 Hz, 1H), 7.53 (s, 1H), 7.09 (d, *J* = 8.8 Hz, 2H), 6.46 (t, *J* = 5.8 Hz, 1H), 4.20 (t, *J* = 5.5 Hz, 3H), 3.68 (t, *J* = 5.5 Hz, 2H). **^{13}C NMR (126 MHz, Acetone-*d_6*)** δ 159.53, 155.13, 142.87, 141.99, 131.73 (q, $J_{C\text{-}F}$ = 32.76 Hz), 131.48, 131.08, 130.33, 130.30, 130.18, 130.00, 128.46, 128.42, 123.86 (q, $J_{C\text{-}F}$ = 272.2 Hz), 118.77, 117.84, 117.81, 115.35, 114.29, 114.26, 114.23, 114.19, 113.10, 67.38, 39.49, 39.37. **HRMS (ESI):** Calculated mass for $C_{24}H_{17}F_6N_3O_2$ $[M+H]^+$: 494.1303; observed mass: 494.1304.

1-(3,5-bis(trifluoromethyl)phenyl)-3-(2-((2'-cyano-[1,1'-biphenyl]-4-yl)oxy)ethyl)thiourea:



Physical appearance: Brown solid.

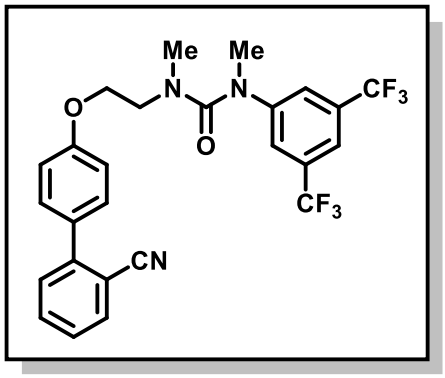
Eluent: ethyl acetate/petroleum ether (25/75 v/v).

Column material: 100-200 mesh silica.

Yield: 90%

^{1}H NMR (500 MHz, Acetone-*d_6*) δ 8.78 (s, 1H), 8.17 (s, 2H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.79 – 7.70 (m, 1H), 7.65 – 7.43 (m, 6H), 7.12 (d, *J* = 8.7 Hz, 2H), 6.47 (t, *J* = 5.7 Hz, 1H), 4.22 (t, *J* = 5.4 Hz, 2H), 3.71 – 3.68 (m, 2H). **^{13}C NMR (126 MHz, Acetone-*d_6*)** δ 160.60, 156.13, 146.07, 143.87, 134.92, 134.29, 132.75 (q, $J_{C\text{-}F}$ = 32.76 Hz), 132.14, 131.33, 131.21, 128.72, 124.85 (q, $J_{C\text{-}F}$ = 272.2 Hz), 119.67, 118.83, 115.91, 115.21, 115.18, 115.15, 112.14, 79.60 - 79.08 (m), 68.42, 40.50. **HRMS (ESI):** Calculated mass for $C_{24}H_{17}F_6N_3OS$ $[M+H]^+$: 510.1075; observed mass: 510.1080.

1-(3,5-bis(trifluoromethyl)phenyl)-3-(2-((2'-cyano-[1,1'-biphenyl]-4-yl)oxy)ethyl)-1,3-dimethylurea:



Physical appearance: Brown gummy liquid.

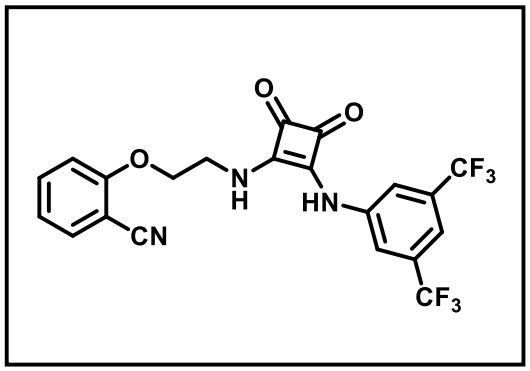
Eluent: ethyl acetate/petroleum ether (20/80 v/v).

Column material: 100-200 mesh silica.

Yield: 90%

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.66 (m, 2H), 7.61 (tt, *J* = 7.9, 1.5 Hz, 1H), 7.53 – 7.45 (m, 7H), 7.39 (td, *J* = 7.6, 1.2 Hz, 1H), 7.11 – 6.97 (m, 2H), 4.24 (t, *J* = 5.2 Hz, 2H), 3.73 (t, *J* = 5.2 Hz, 2H), 3.29 (s, 3H), 2.83 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 160.71, 158.96, 147.56, 145.20, 133.85, 132.94, 131.18, 130.21, 130.03, 127.29, 124.28, 122.11, 120.96, 120.93, 119.05, 116.47, 116.44, 116.41, 114.81, 114.75, 111.18, 65.80, 49.46, 38.52, 37.92. **HRMS (ESI):** Calculated mass for $C_{26}H_{21}F_6N_3O_2$ $[M+H]^+$: 522.1616; observed mass: 522.1610.

2-{2-[(2-{[3,5-bis(trifluoromethyl)phenyl]amino}-3,4-dioxocyclobut-1-en-1-yl)amino]ethoxy}benzonitrile:

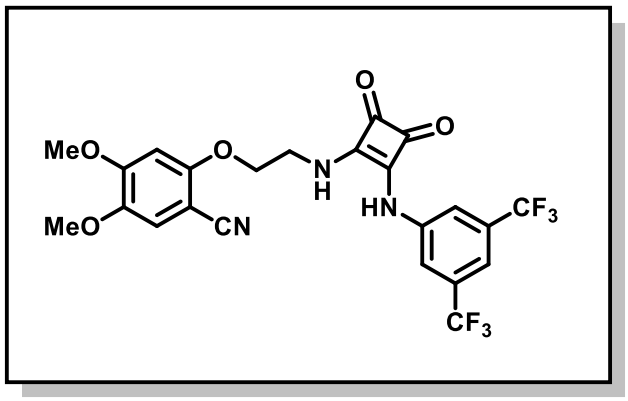


Physical appearance: White solid.

Yield: 93%

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.07 (s, 1H), 8.00 (d, *J* = 1.5 Hz, 2H), 7.88 (s, 1H), 7.77 – 7.63 (m, 2H), 7.60 (s, 1H), 7.30 (d, *J* = 8.5 Hz, 1H), 7.10 (td, *J* = 7.6, 0.9 Hz, 1H), 4.37 (t, *J* = 5.2 Hz, 2H), 4.07 (t, *J* = 5.2 Hz, 2H); **^{13}C NMR (126 MHz, DMSO-*d6*)** δ 184.95, 180.95, 170.22, 162.58, 159.79, 141.12, 135.27, 135.22, 133.87, 133.83, 131.46 (q, J_{C-F} = 35.28 Hz), 123.25 (q, J_{C-F} = 274.68 Hz), 121.59, 118.14, 116.31, 114.78, 113.28, 100.87, 79.24, 79.21, 68.36, 43.18. **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ –61.76 (s, 6F); **HRMS (ESI-TOF)** calculated mass for $[C_{21}H_{13}F_6N_3O_3+H]^+$ 470.0934 found 470.0947.

2-{2-[(2-{[3,5-bis(trifluoromethyl)phenyl]amino}-3,4-dioxocyclobut-1-en-1-yl)amino]ethoxy}-4,5-dimethoxybenzonitrile:

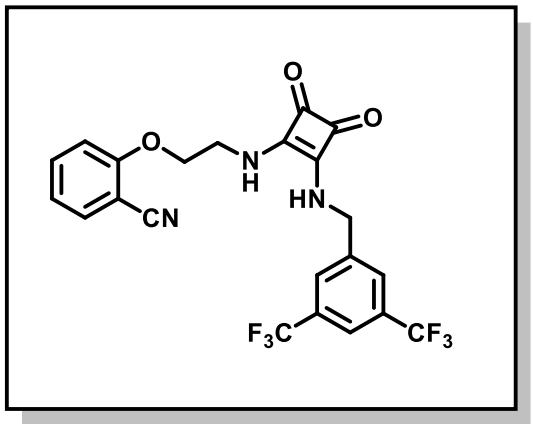


Physical appearance: White solid.

Yield: 89%

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.07 (s, 1H), 8.00 (s, 2H), 7.90 (s, 1H), 7.60 (s, 1H), 7.18 (s, 1H), 6.89 (s, 1H), 4.36 (t, *J* = 5.3 Hz, 2H), 4.04 (t, *J* = 5.5 Hz, 2H), 3.89 (s, 3H), 3.73 (s, 3H). **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ 184.81, 180.70, 170.07, 162.38, 155.87, 154.22, 143.28, 140.93, 131.13 (q, $J_{C\text{-}F}$ = 33.3 Hz), 122.93 (q, $J_{C\text{-}F}$ = 274.7 Hz), 117.99, 116.32, 115.19, 114.37 (m), 99.16, 90.93, 68.87, 56.22, 55.99, 43.00. **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ -61.72.
HRMS (ESI-TOF) Calculated mass for $[C_{23}H_{17}F_6N_3O_5+H]^+$ 530.1145 found 530.1160.

2-{2-[(2-{[3,5-bis(trifluoromethyl)benzyl]amino}-3,4-dioxocyclobut-1-en-1-yl)amino]ethoxy}benzonitrile:



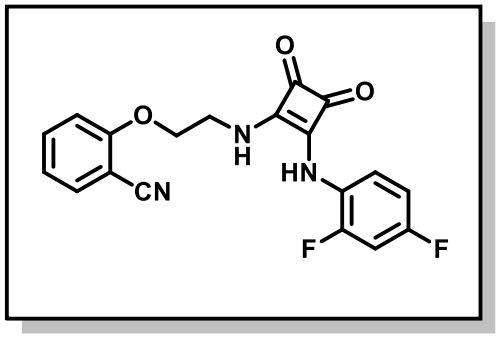
Physical appearance: White solid.

Yield: 92%

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.05 (s, 2H), 7.98 (s, 1H), 7.91 (s, 1H), 7.71 – 7.54 (m, 3H), 7.27 (d, *J* = 8.5 Hz, 1H), 7.10 (td, *J* = 7.6, 0.9 Hz, 1H), 4.91 (d, *J* = 5.4 Hz, 2H), 4.30 (t, *J* = 5.4 Hz, 2H), 3.94 (q, *J* = 5.5 Hz, 2H). **^{13}C NMR (126 MHz, DMSO-*d6*)** δ 183.04, 182.88, 168.45, 167.41, 159.86, 142.70, 135.21, 133.84, 130.57 (q, $J_{C\text{-}F}$ = 32.76 Hz), 128.67,

126.67, 124.50, 122.33, 121.54, 121.28, 120.16, 116.28, 113.27, 100.84, 79.25, 68.50, 45.89, 42.70. **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ –61.31 (s, 6F); **HRMS (ESI-TOF)** Calculated mass for $[C_{22}H_{16}F_6N_3O_3+H]^+$ 484.1090 found 484.1084.

2-[2-({2-[(2,4-difluorophenyl)amino]-3,4-dioxocyclobut-1-en-1-yl}amino)ethoxy]benzonitrile:

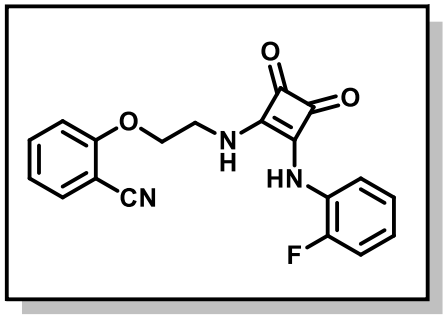


Physical appearance: White solid.

Yield: 72%

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.07 (s, 1H), 7.88 (td, *J* = 9.5, 5.8 Hz, 1H), 7.79 – 7.60 (m, 2H), 7.40 – 7.20 (m, 2H), 7.18 – 6.99 (m, 2H), 4.37 (t, *J* = 5.3 Hz, 2H), 4.05 (t, *J* = 5.3 Hz, 2H). **^{13}C NMR (126 MHz, DMSO-*d6*)** δ 184.66, 180.57, 169.79, 163.31, 159.82, 158.68, 156.75, 153.27, 151.21, 135.29, 134.06, 133.91, 123.82, 123.79, 123.72, 122.31, 122.24, 121.78, 121.61, 116.48, 116.39, 113.34, 113.25, 111.78, 111.60, 104.57, 104.39, 104.35, 104.17, 100.82, 79.25, 68.55, 42.99.
^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ –116.89 (br. s, 1F), –123.59 (br. s, 1F); **HRMS (ESI-TOF)** Calculated mass for $[C_{19}H_{13}F_2N_3O_3+H]^+$ 370.0998 found 370.1013.

2-[2-({2-[(2-fluorophenyl)amino]-3,4-dioxocyclobut-1-en-1-yl}amino)ethoxy]benzonitrile:



Physical appearance: White solid.

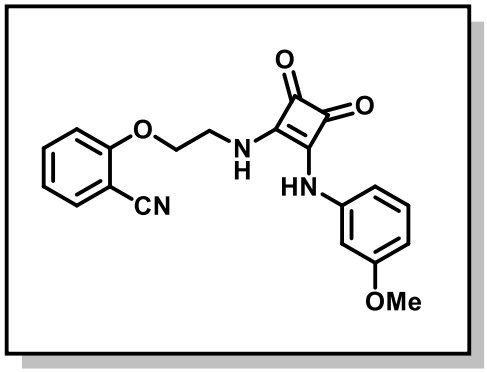
Yield: 98%

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.50 (s, 1H), 8.15 (t, *J* = 6.1 Hz, 1H), 7.91 (td, *J* = 8.4, 1.6 Hz, 1H), 7.79 – 7.61 (m, 2H), 7.31 (d, *J* = 8.5 Hz, 1H), 7.24 (ddd, *J* = 11.7, 8.1, 1.4 Hz, 1H), 7.17 (td, *J* = 7.8, 1.5 Hz, 1H), 7.11 (td, *J* = 7.6, 0.9 Hz, 1H), 7.05 (tdd, *J* = 7.8, 5.0, 1.7 Hz, 1H), 4.37 (t, *J* = 5.3 Hz, 2H), 4.05 (q, *J* = 5.6 Hz, 2H). **^{13}C NMR (126 MHz, DMSO-*d6*)** δ 184.81, 180.42, 169.87, 163.29, 159.77, 152.32 (d, J_{C-F} = 242 Hz), 135.21, 133.85, 126.97 (d,

J_{C-F} = 10.08 Hz), 124.94, 123.78, 121.55, 121.27, 116.31, 115.56 (d, J_{C-F} = 18.90 Hz), 113.32, 100.80, 68.53, 42.94.

HRMS (ESI-TOF) Calculated mass for $[C_{19}H_{14}FN_3O_3+H]^+$ 352.1092 found 352.1111.

2-[2-({2-[(3-methoxyphenyl)amino]-3,4-dioxocyclobut-1-en-1-yl}amino)ethoxy]benzonitrile:



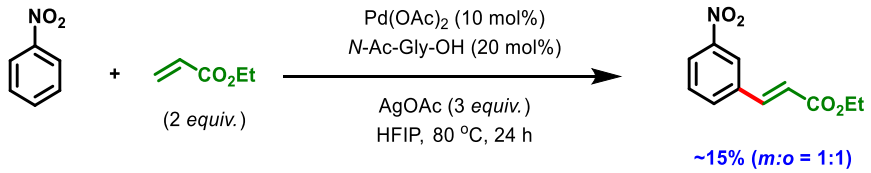
Physical appearance: White solid.

Yield: 93%

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 9.60 (s, 1H), 7.75 – 7.58 (m, 3H), 7.31 (d, *J* = 8.5 Hz, 1H), 7.26 – 7.15 (m, 2H), 7.11 (td, *J* = 7.6, 1.0 Hz, 1H), 6.89 (ddd, *J* = 7.9, 2.2, 0.9 Hz, 1H), 6.60 (ddd, *J* = 8.2, 2.5, 0.9 Hz, 1H), 4.37 (t, *J* = 5.3 Hz, 2H), 4.05 (q, *J* = 5.5 Hz, 2H), 3.76 (d, *J* = 0.9 Hz, 3H). **^{13}C NMR (126 MHz, DMSO-*d*$_6$)** δ 184.11, 180.70, 169.41, 163.73, 160.26, 159.77, 140.22, 135.20, 133.84, 130.24, 121.53, 116.31, 113.28, 110.30, 108.50, 103.89, 100.79, 68.52, 55.11, 42.97.
HRMS (ESI-TOF) Calculated mass for $[C_{20}H_{17}N_3O_4+H]^+$ 364.1292 found 364.1316.

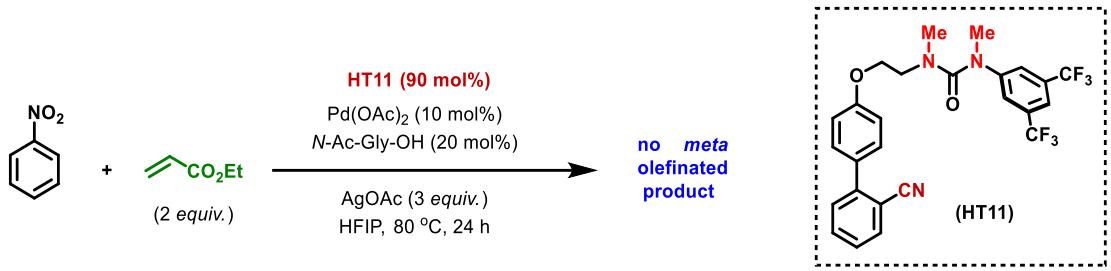
8. MECHANISTIC STUDIES

8.1. Control reactions



Reaction was performed with 0.05 mmol nitrobenzene substrate according to the general procedure for Pd-catalysed alkenylation of nitroarenes in absence of **HT3**. The reaction mixture was mixed with 0.05 mmol of 1,3,5-trimethoxybenzene to be considered as internal standard. The resulting solution was diluted with ethyl acetate, filtered on celite pad and ^{1}H NMR was recorded for the crude reaction mixture. Alkenylated product was formed with 15% yield with

equimolar mixture of regio-isomers. Hence, the presence of H-bonding template is playing a crucial role in this protocol.

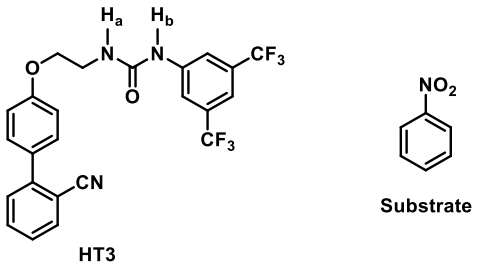


Reaction was performed with 0.05 mmol nitrobenzene substrate according to the general procedure for Pd-catalyzed alkenylation of nitroarenes in presence of **HT11**. The reaction mixture was mixed with 0.05 mmol of 1,3,5-trimethoxybenzene to be considered as internal standard. The resulting solution was diluted with ethyl acetate, filtered on celite pad and NMR was recorded for the crude reaction mixture. The *meta*-olefinated product was not formed suggesting the role of H-bonding template in guiding regioselectivity.

8.2. NMR experiment:

To justify hydrogen bonding interaction, we have performed two set of NMR experiment using acetone-d6 as solvent.[5]

Procedure 1: In a clean and oven dried NMR tube template **HT3** (25 mg, 0.05 mmol) was taken followed by 0.6 ml of acetone-d6. Then the ^{1}H NMR of the template was recorded (Fig 5). The value of H_a and H_b proton was noted. In the same nmr tube nitrobenzene substrate was added in equimolar ratio with HT3 (6.3 µL, 0.05 mmol). After some time ^{1}H NMR was recorded of this 1:1 mixture of substrate and HT3. A clear downfield shift of the two characteristic N–H peaks (H_a, H_b) was observed indicating possibility of hydrogen bonding. In this case both the –NH peaks shift equally with a value of 15 Hz indicating both the hydrogens of urea template is participating in H-bonding with nitro group.



HT3 (mM)	Substrate (mM)	HT3 : Substrate	H_a (ppm)	H_b (ppm)
83	0	1:0	6.45	8.73
83	83	1:1	6.48	8.76

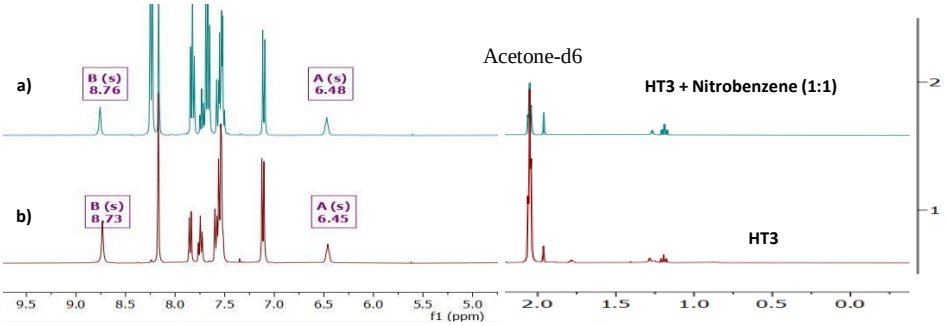


Figure 5. NMR experiment as a proof of hydrogen bonding. a) ^{1}H NMR of an equimolar mixture of HT3 and nitrobenzene; b) ^{1}H NMR of HT3 in acetone-d6.

Procedure 2: A clean and oven dried nmr tube was charged with an equimolar mixture of HFIP (5.25 µL, 0.05 mmol) and HT3 (25 mg, 0.05 mmol). Then 0.6 ml of acetone d6 was added and ^{1}H NMR spectra was recorded. The peaks (H_a and H_b) were shifted to downfield region. After that nitrobenzene substrate was added (6.3 µL, 0.05 mmol) in the same nmr tube and spectra was recorded. It was observed that the characteristic N–H peaks are shifted further to the downfield region. This time the peaks shifts unequally (35 Hz and 10 Hz) shows participation of HFIP in H-bonding interaction. The results are as follows:

HT3 (mM)	Substrate (mM)	HFIP (mM)	HT3:Substrate:HFIP	H_a (ppm)	H_b (ppm)
83	0	83	1:0:1	6.49	8.76
83	83	83	1:1:1	6.51	8.83

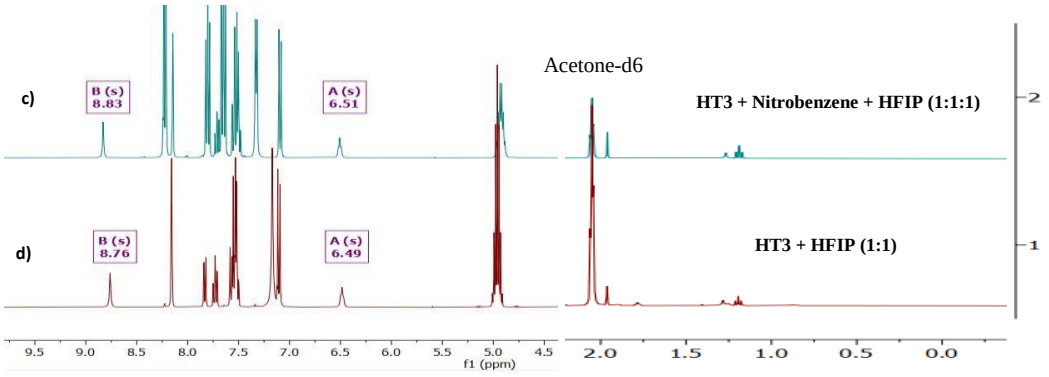
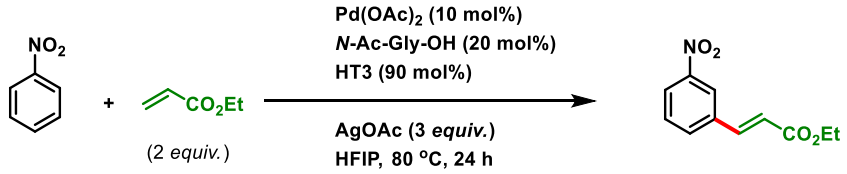


Figure 6. NMR experiment as a proof of hydrogen bonding. c) ^{1}H NMR of an equimolar mixture of HT3, nitrobenzene and HFIP; d) ^{1}H NMR of HT3 and HFIP (1:1) in acetone-d6.

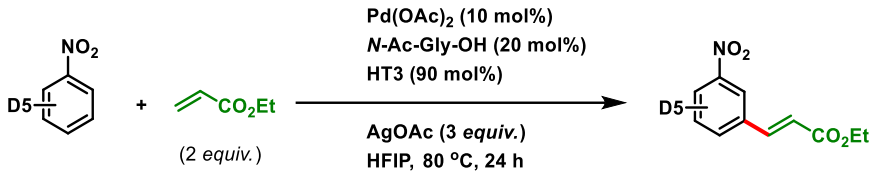
9. Kinetics study:

To decide the rate-determining step of this alkenylation reaction we performed kinetic isotope effect (k_H/k_D) study. Simple nitrobenzene and d5-nitrobenzene were taken and reaction progress was monitored at every 5 mins time interval. The results of both set of reactions are as follows:



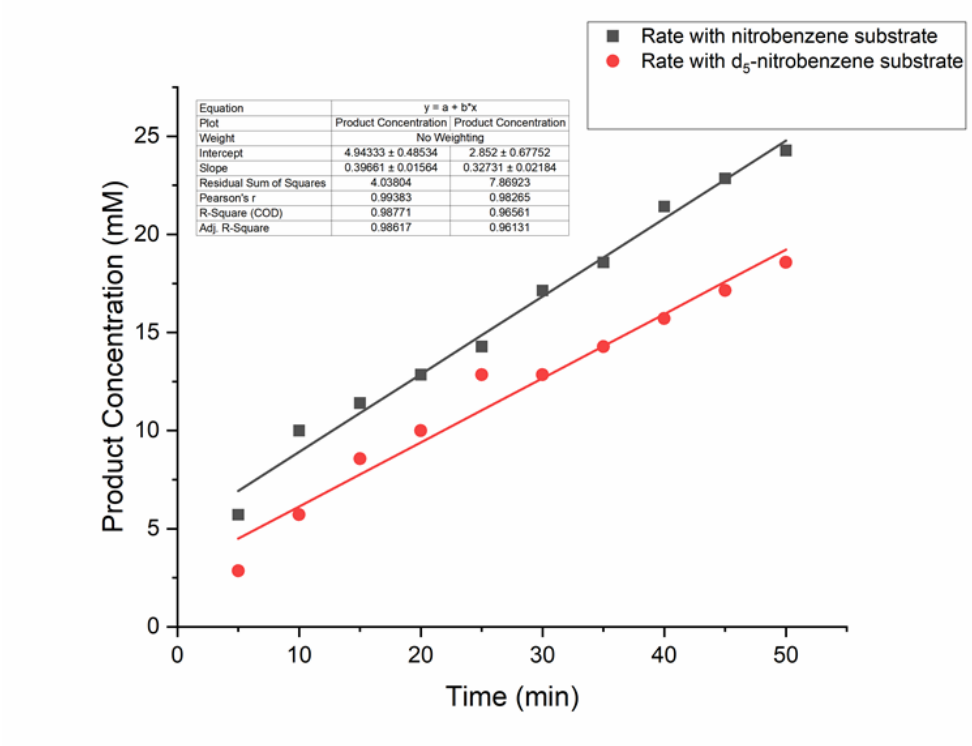
Set-I: Rate of the reaction with nitrobenzene

Sl. No.	Time (min.)	Product concentration (mM)
1	5	5.71
2	10	10
3	15	11.4
4	20	12.85
5	25	14.28
6	30	17.14
7	35	18.57
8	40	21.42
9	45	22.85
10	50	24.28



Set-II: Rate of the reaction with d5-nitrobenzene

Sl. No.	Time (min.)	Product concentration (mM)
1	5	2.85
2	10	5.71
3	15	8.57
4	20	10
5	25	12.85
6	30	12.85
7	35	14.28
8	40	15.71
9	45	17.14
10	50	18.57



K_H/K_D= slope of line 1/ slope of line 2

= 0.39661/0.32731

= 1.211

- **K_H/K_D = 1.2**

10. Computational Details:

The mechanism of *meta*-C–H alkenylation of nitroarenes assisted by the hydrogen bonding template was investigated by employing density functional theory (DFT) calculations using the Gaussian 16 suite of quantum chemistry programs.[6] The geometry optimization was performed using hybrid B3LYP[7] functional in conjunction with the basis set combination of 6-31G(d)[8] for main group elements and LANL2DZ[9] basis set and associated effective core potential (ECP) for the Pd center. The dispersion corrections were accounted for using Grimme's D3[10] dispersion formalism. The solvent effect of HFIP was included implicitly using a solution model based on density (SMD)[11] (ε = 16.7). The transition state (TS) was confirmed to be a first-order saddle point with only one imaginary corresponding to the reaction coordinate. The intrinsic reaction coordinate (IRC) calculation was performed to confirm that TS(s) are connected to the correct minima. The single point correction to electronic energies was done using B3LYP functional with quadrupole-ζ def2-QZVPP[12] basis set for all atoms. Non-covalent hydrogen-bonding interactions (NCI) were evaluated using the Multiwfn[13] program and visualized using VMD[14] software.

10.1 Different modes of C–H Activation pathways

The possibilities of different C–H activation modes were investigated and the C–H activation pathway featuring assistance from the O-atom of *N*-acetyl glycine ligand in activating the *meta*-C–H bond appeared to be most facile as it holds the plane containing Pd–C–O–C atoms in an almost coplanar fashion (φ_{1234} = 2.0°, Figure S6) enabling efficient deprotonation of the C–H bond. The other two pathways distort the planarity of these atoms as the dihedral angle is increased to 9.7° and 18.5° leading to the observed higher barriers. Moreover, with ligand assisting C–H activation, the bite angle of *N*-acetyl glycine with Pd(II) is relatively smaller (82.5°) as compared to other two scenarios (86.7° and 87.5°), which also offers lower steric hinderance towards hydrogen-bonding template coordination to the Pd(II) centre.

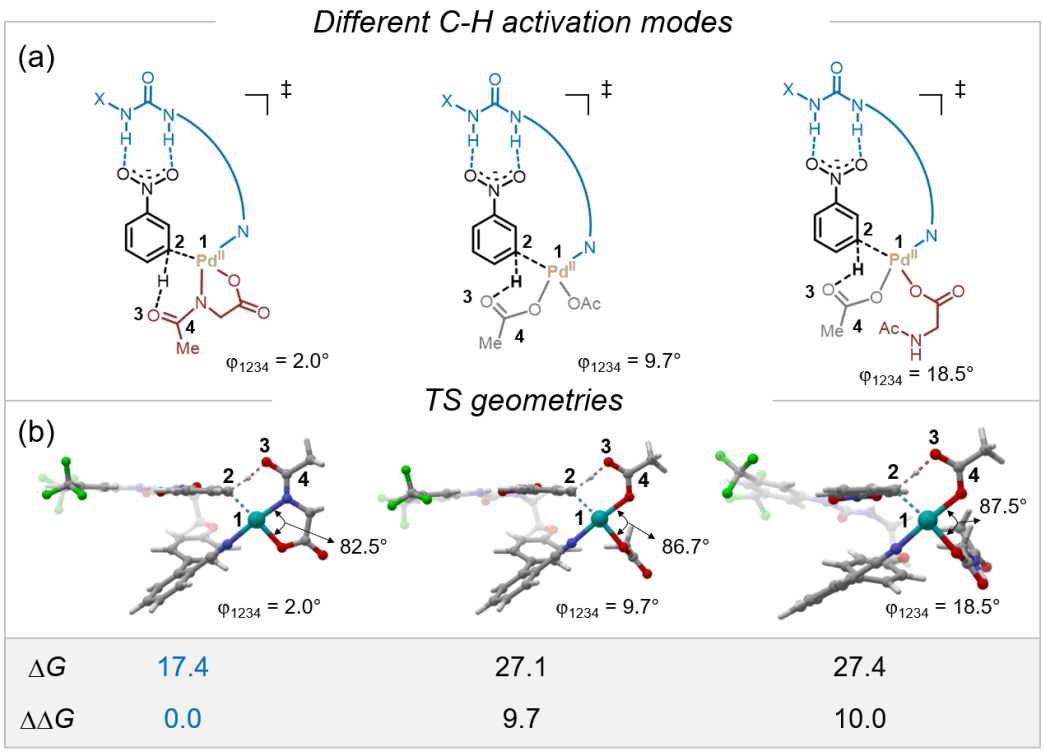


Figure S6: (a) Different C–H activation pathways and (b) TS geometries of the corresponding C–H activation pathways. The dihedral angle between atoms 1,2,3, and 4 is represented by φ_{1234}.

10.2 *meta*-selective olefination reaction without hydrogen bonding template:

To investigate the role of hydrogen bonding template HT3 in assisting of olefination of nitrobenzene the catalytic cycle was modelled in absence of HT3. The absence of hydrogen bonding template results in enhancement in reaction barrier of C–H activation, 1,2-migratory insertion, and β-hydride elimination steps. Moreover, the C–H activation step was calculated to possess the highest barrier of 32.1 kcal/mol which is ~10 kcal/mol higher than the barrier of RDS of reaction in the presence of HT3. This clearly suggests that the hydrogen bonding interactions between the O-atom of nitrobenzene and NH groups of hydrogen bonding template HT3 helps in the stabilisation of transition states generated in the catalytic cycle, thereby accelerating the reaction.

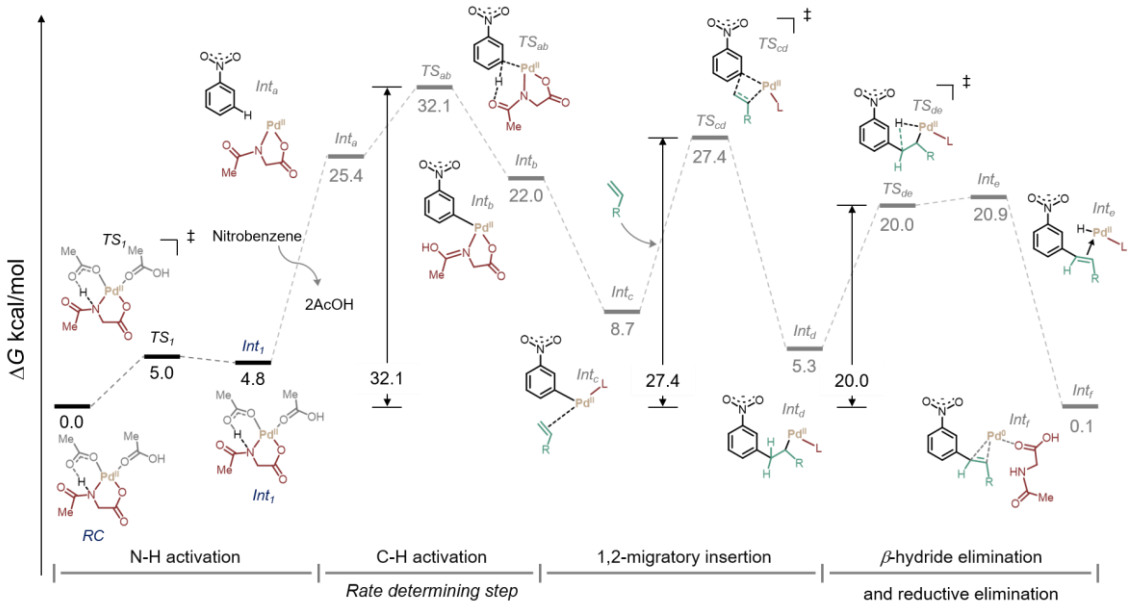


Figure S7: Reaction free energy profile for *meta*-C–H alkenylation of nitrobenzene without hydrogen-bonding template evaluated at DFT-B3LYP/Def2-QZVPP/SMD level of theory.

10.3 Effect of hydrogen-bonding templates on C–H activation Step

The extent of hydrogen bonding interactions by different HTs has a noticeable effect in activating the *meta*-C–H bond of nitrobenzene. Since the C–H activation step involves Pd^{II} as the reaction center, the distortion of the Pd–C–O–C system from planarity will also affect the deprotonation of the H atom from the C–H bond. The HT1 with φ_{1234} = –27.6° and HT2 φ_{1234} = –11.8° both deviating from the ideal requirement of coplanarity required for the efficient abstraction of the H-atom from the C–H bond by O atom of the *N*-acetyl glycine ligand hinders the C–H activation step. Collectively, the higher extent of hydrogen bonding interactions and planarity of the Pd–C–O–C (φ_{1234} = 2.0°) system favors the HT3 over HT1 and HT2 which is also reflected in relatively higher barrier 5.8 and 4.5 kcal/mol respectively.

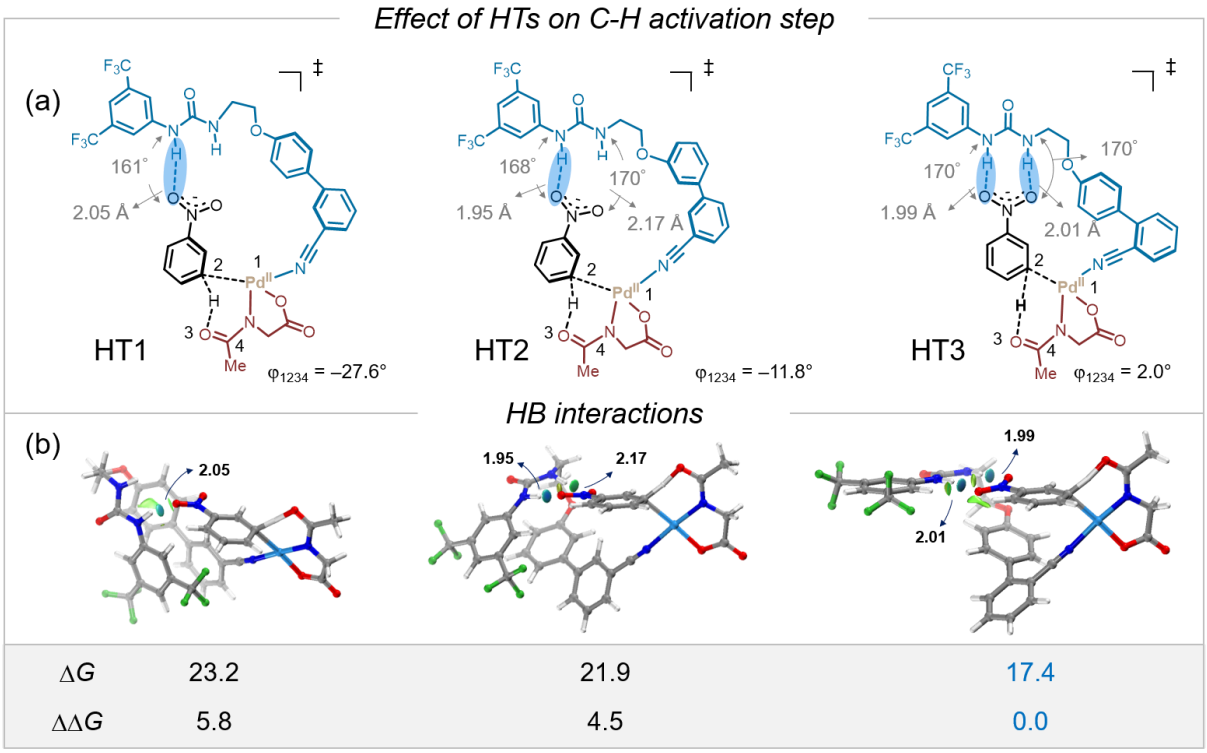


Figure S8. (a) Key hydrogen bonding parameters and (b) NCI plot depicting hydrogen-bonding interactions for C-H activation step with HT1, HT2, and HT3 hydrogen bonding templates. The dihedral angle between atoms 1,2,3 and 4 is represented by φ_{1234}.

10.4 Effect of hydrogen-bonding templates on the RDS:

The different hydrogen bonding templates also affect the rate determining 1,2-migratory insertion TS3. The HT3 orients itself in such a way that the two N–H groups are colinear (∠N–H···O =170°) with the O atom of the nitro group of the nitrobenzene substrate thereby facilitating two strong hydrogen bonding interactions and imposing maximum stabilisation in olefin insertion TS3. The HT1 have a similar orientation of two NH groups and two O atoms but features one strong hydrogen bond with ∠NHO =161° and NH group and acceptor O atom distance of 1.99Å while the other hydrogen bond is very weak as donor and acceptor distance is sufficiently larger (2.42Å) and additionally the linearity of the hydrogen bond is lost with ∠NHO =153° making only one effective hydrogen bond in this case. HT2 have different orientation of N–H group and nitrobenzene wherein there is only one hydrogen bond with ∠NHO = 161° and donor and acceptor distance of 2.01Å. The result of maximum stabilisation due to hydrogen bonds with HT3 in TS3 lowers the barrier of this step (22.2 kcal/mol), in

comparison to the HT1 and HT2 coordinated Pd-catalyst with higher barrier of 25.6 kcal/mol and 23.5 kcal/mol respectively as depicted in Figure S9.

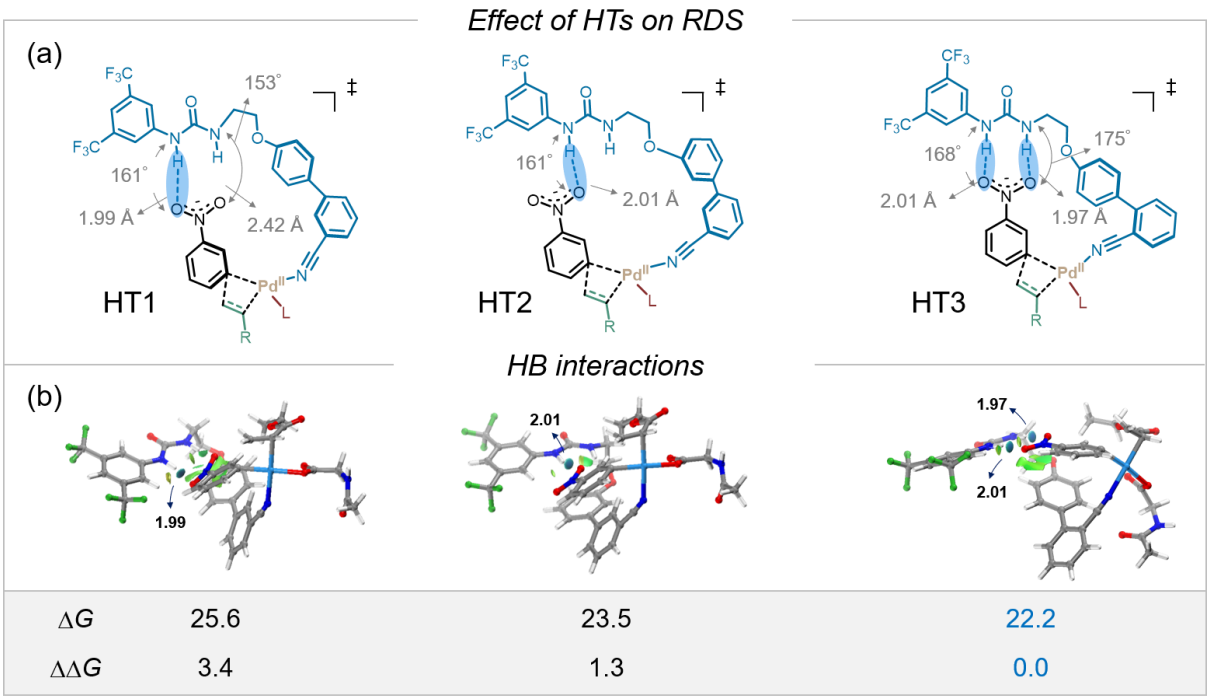


Figure S9: (a) Key hydrogen bonding parameters and (b) NCI plot depicting hydrogen-bonding interactions for TS3 with HT1, HT2, and HT3 hydrogen bonding templates.

10.5 Hydrogen bonding interactions in the key TSs of *meta*-selective olefination reaction:

The hydrogen bonds are formed in the transition states between donor NH group of the hydrogen boding template HT3 and acceptor O atom of nitrobenzene (Figure S10). The strength of hydrogen bonds depends on the distance between donor and acceptor group and angle formed between them. The shorter the distance and more linear the angle (~180°) the stronger will be the hydrogen bonding interaction[15]. The scale shown in Figure S10 depicts the colour of the non-covalent interactions with red colour representing strong repulsive interactions while the blue colour representing strong attractive hydrogen bonds. The blue discs that can be viewed in panel c of Figure S10 for *meta*-TS2 and *meta*-TS3 signifies that there are strong hydrogen bonds present while the greenish colour in *meta*-TS4 implies that the hydrogen bonding interaction has weakened due to increase in distance between donor and acceptor group.

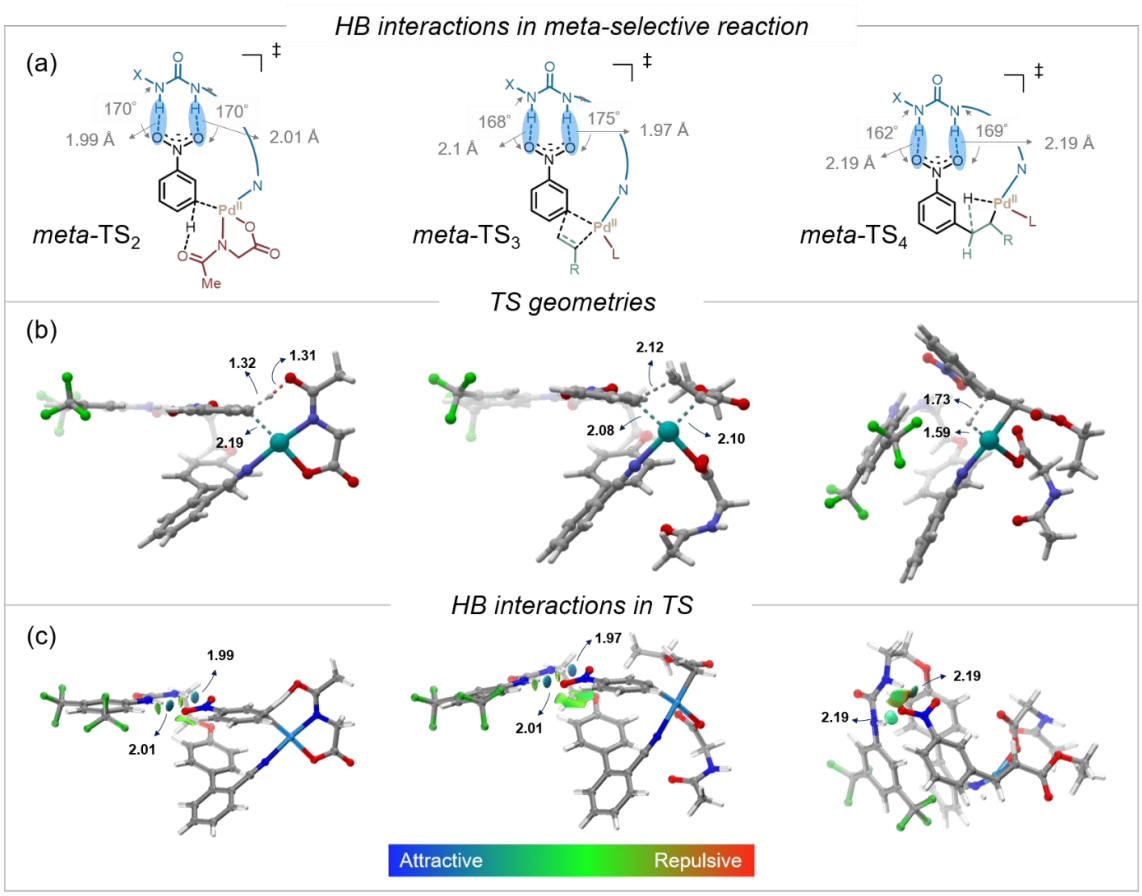


Figure S10: Geometries and hydrogen-bonding interactions in the key transition states of the *meta*-C–H alkenylation of nitroarenes.

10.6 Steric bulk of *N*-acetyl glycine ligand affecting the C-H activation step:

The introduction of steric bulk on the *N*-acetyl glycine ligand have a pronounced effect on the rate of C-H activation step. The least sterically hindered *N*-acetyl glycine ligand (L1) places O atom of the ligand in an almost coplanar arrangement (φ_{1234} / $\varphi_{Pd\text{-}C\text{-}O\text{-}C}$ = 2.0°) with the *meta*-C–H bond of nitrobenzene providing a facile mode for the deprotonation of H atom from the C–H bond. The introduction of the steric bulk on the ligand by substitution on the carbon chain on the ligand L2, L3 and L4, disturbs the coplanarity required for the Pd–C–O–C system. The almost coplanar φ_{1234} angle deviates to –12.6° in L2, 14.1° in L3 and 10.8° in L4 making the deprotonation from *meta*-C–H bond sluggish which is also reflected in observed relatively higher barrier compared to L1 (Figure S11).

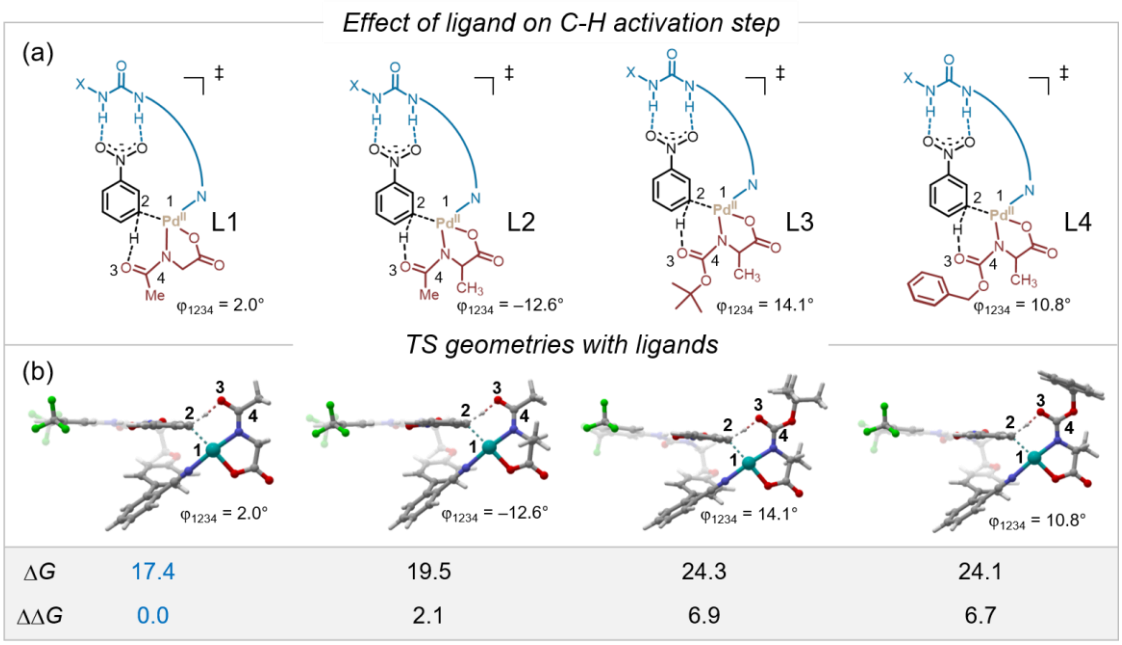


Figure S11: DFT optimised geometries of the C–H activation transition states with different ligands attached to Pd^{II} center. The dihedral angle between atoms 1,2,3 and 4 is represented by φ_{1234}.

10.7 Effect of steric bulk of ligand on the RDS:

The steric effect of the ligand has comparatively smaller effect on rate-determining olefin insertion step (TS3) as can be seen in Figure S12. This smaller effect on the barrier with the increase in steric bulk on the *N*-acetyl glycine ligand can be attributed to the fact that in the TS the ligand orientation is in such a way that the steric substitution on the ligand is present far away from the reaction center, thereby having a slight effect on the extent of 1,2-migratory insertion step.

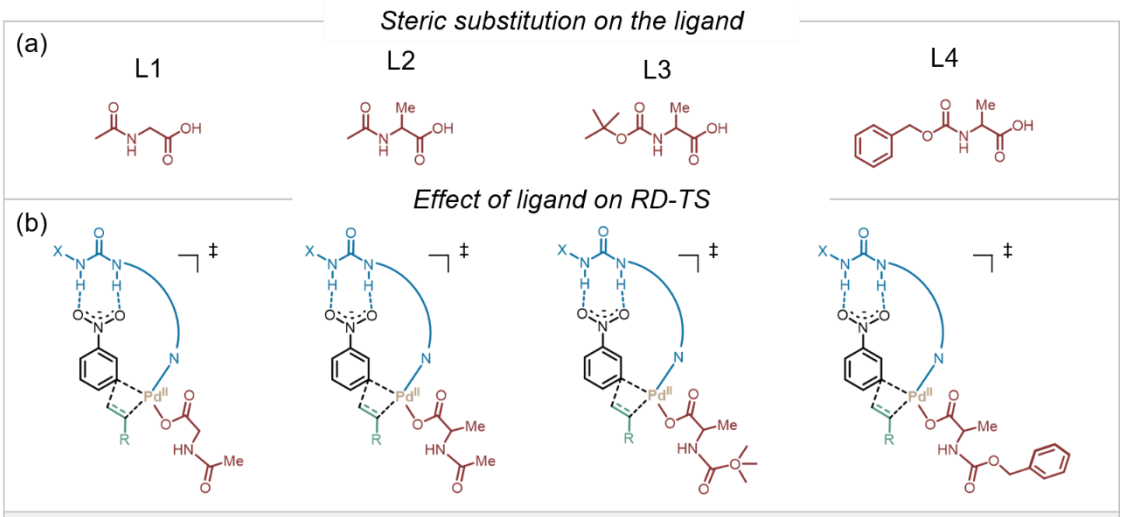


Figure S12: Depiction of 1,2-migratory insertion TS3 with different ligands attached to Pd^{II} center.

11. Optimised cartesian coordinates:

RC

46	0.093337000	0.188507000	-0.025878000
8	-2.213384000	1.735215000	-1.497492000
6	-2.108745000	3.853142000	-0.372405000
6	-1.658077000	2.425848000	-0.628931000
8	-0.672879000	2.050385000	0.136858000
6	-1.300885000	-1.964371000	-1.292461000
6	0.074369000	-2.527192000	-0.908300000
8	0.831882000	-1.697636000	-0.201430000
8	0.430433000	-3.636363000	-1.253238000
1	-2.057420000	-2.749843000	-1.243042000
1	-1.235677000	-1.624011000	-2.330358000
1	-2.909150000	3.830487000	0.378125000
1	-1.295227000	4.473212000	0.012387000
1	-2.514261000	4.284451000	-1.291420000
7	-1.694015000	-0.780419000	-0.476865000
1	-2.150127000	-0.025834000	-1.026330000
6	-2.420909000	-0.976540000	0.768233000
8	-3.217965000	-0.131839000	1.109380000
6	-2.088321000	-2.218125000	1.552703000
1	-2.572314000	-2.156285000	2.528565000
1	-2.451003000	-3.110979000	1.029664000
1	-1.005838000	-2.321858000	1.679243000
6	3.088059000	0.453648000	0.322970000

6	4.356993000	1.215949000	0.549860000
1	4.948437000	1.201018000	-0.373108000
1	4.137893000	2.246332000	0.831166000
1	4.945924000	0.724012000	1.330639000
8	1.982708000	1.033367000	0.357489000
8	3.254865000	-0.822652000	0.084411000
1	2.382047000	-1.305794000	-0.056667000

TS1

46	0.250895000	0.239918000	0.066223000
8	-2.460268000	1.382810000	-1.051013000
6	-2.281796000	3.703846000	-0.556503000
6	-1.737540000	2.301603000	-0.525851000
8	-0.613039000	2.112805000	0.028132000
6	-1.110038000	-1.897443000	-1.127318000
6	0.269568000	-2.464840000	-0.759334000
8	1.027102000	-1.625022000	-0.050696000
8	0.649477000	-3.565814000	-1.105613000
1	-1.850379000	-2.699286000	-1.137546000
1	-1.035929000	-1.508469000	-2.149889000
1	-2.790271000	3.887615000	-1.506788000
1	-3.021607000	3.801794000	0.247792000
1	-1.486156000	4.433912000	-0.398191000
7	-1.497049000	-0.775036000	-0.248337000
1	-2.054644000	0.314317000	-0.773789000
6	-2.188193000	-1.023556000	0.968677000
8	-2.413660000	-0.091006000	1.724928000
6	-2.669296000	-2.428945000	1.255955000
1	-3.166024000	-2.429848000	2.227650000
1	-3.375439000	-2.766733000	0.488663000
1	-1.832207000	-3.136733000	1.272053000
6	3.255146000	0.610739000	0.265268000
6	4.514981000	1.405992000	0.417465000
1	5.084411000	1.353903000	-0.517743000
1	4.283113000	2.444947000	0.653187000
1	5.132166000	0.965066000	1.207186000
8	2.138178000	1.163413000	0.327983000
8	3.442425000	-0.669884000	0.061138000
1	2.572436000	-1.174241000	-0.029488000

Int1

46	0.257251000	0.210895000	0.055659000
8	-2.495786000	1.451349000	-1.062024000
6	-2.275634000	3.748537000	-0.521504000
6	-1.731616000	2.353171000	-0.508715000
8	-0.621623000	2.111342000	0.013080000
6	-1.057694000	-2.014990000	-1.051252000
6	0.334237000	-2.532309000	-0.663180000
8	1.074874000	-1.634648000	-0.007713000
8	0.745097000	-3.639999000	-0.948158000

1	-1.778183000	-2.832672000	-0.997526000
1	-0.998855000	-1.702180000	-2.101342000
1	-3.071831000	3.815060000	0.230308000
1	-1.490452000	4.466313000	-0.281093000
1	-2.716381000	3.970189000	-1.497705000
7	-1.446714000	-0.852031000	-0.236627000
1	-2.123912000	0.508110000	-0.886842000
6	-2.229834000	-1.001285000	0.908260000
8	-2.311111000	-0.090058000	1.729177000
6	-3.036937000	-2.278042000	1.069406000
1	-3.689554000	-2.161341000	1.936611000
1	-3.643571000	-2.489290000	0.182036000
1	-2.372450000	-3.135075000	1.232592000
6	3.276080000	0.640134000	0.251035000
6	4.526693000	1.454063000	0.384617000
1	5.113922000	1.362976000	-0.536243000
1	4.281518000	2.500593000	0.567795000
1	5.133487000	1.057583000	1.205655000
8	2.151919000	1.175894000	0.304825000
8	3.481651000	-0.643041000	0.074341000
1	2.617755000	-1.159607000	0.001629000

Int1’

6	2.146792000	2.961604000	-2.521614000
6	3.410062000	2.513143000	-2.882707000
6	3.722297000	1.134438000	-2.832375000
6	2.756515000	0.211679000	-2.397498000
6	1.491214000	0.706539000	-2.014422000
6	1.171734000	2.055230000	-2.077036000
1	2.935890000	-0.851229000	-2.493429000
7	0.493123000	-0.236128000	-1.539591000
8	-0.656504000	0.176771000	-1.340033000
8	0.833517000	-1.408407000	-1.355254000
1	4.161253000	3.216319000	-3.228575000
1	4.657946000	0.747251000	-3.219049000
1	0.190505000	2.399824000	-1.773793000
1	1.902861000	4.017792000	-2.571003000
8	0.718734000	-3.195212000	2.063773000
6	-0.430447000	-4.056869000	1.992819000
1	-1.291678000	-3.614156000	2.503197000
1	-0.138960000	-4.961075000	2.536618000
6	-0.773183000	-4.429478000	0.549843000
1	0.124206000	-4.809839000	0.052364000
1	-1.521273000	-5.226593000	0.566707000
7	-1.293231000	-3.322113000	-0.236652000
1	-0.615870000	-2.640990000	-0.566527000
6	-2.609441000	-2.954022000	-0.123735000
8	-3.467316000	-3.668393000	0.397222000
7	-2.864290000	-1.692629000	-0.655851000
1	-2.054201000	-1.145441000	-0.937749000

6	-4.064955000	-0.982930000	-0.620908000
6	-5.304551000	-1.553241000	-0.286834000
6	-4.015747000	0.384149000	-0.955184000
6	-6.451349000	-0.757182000	-0.284628000
6	-5.174525000	1.152977000	-0.945948000
6	-6.410797000	0.597357000	-0.609035000
1	-5.359388000	-2.600765000	-0.029761000
1	-3.068649000	0.844692000	-1.214514000
1	-7.309337000	1.202467000	-0.600406000
6	-5.109719000	2.597083000	-1.361178000
9	-5.971378000	3.365104000	-0.654631000
9	-3.874879000	3.125930000	-1.199192000
9	-5.433662000	2.757550000	-2.668719000
6	-7.753061000	-1.377810000	0.145389000
9	-7.853878000	-2.671149000	-0.238845000
9	-7.891307000	-1.364366000	1.495448000
9	-8.824044000	-0.724268000	-0.360350000
6	0.607500000	-1.842697000	2.143852000
6	-0.578897000	-1.104283000	2.015608000
6	1.812566000	-1.158718000	2.378795000
6	-0.543925000	0.287306000	2.094987000
6	1.833421000	0.226456000	2.465001000
6	0.655348000	0.985557000	2.311740000
1	-1.527930000	-1.591447000	1.843264000
1	2.723925000	-1.732085000	2.514777000
1	-1.470336000	0.837155000	1.954966000
1	2.783371000	0.708890000	2.666647000
6	0.653049000	2.466065000	2.390202000
6	-0.353377000	3.144267000	3.096025000
6	1.639160000	3.272733000	1.756129000
6	-0.376587000	4.536279000	3.179904000
6	1.624064000	4.676975000	1.846606000
6	0.613902000	5.308413000	2.562057000
1	-1.116505000	2.563906000	3.605079000
6	2.628703000	2.642183000	0.953131000
1	-1.168828000	5.022504000	3.742152000
1	2.396661000	5.251910000	1.346092000
1	0.596047000	6.391126000	2.636458000
7	3.376599000	2.060566000	0.283833000
46	4.320628000	0.348496000	-0.431758000
8	4.995069000	0.017432000	1.432645000
6	5.344296000	-1.232488000	1.680064000
8	5.571602000	-1.624445000	2.815233000
1	6.449716000	-2.592242000	0.483239000
6	5.444353000	-2.154442000	0.471070000
1	4.733143000	-2.978556000	0.627628000
7	5.177604000	-1.431436000	-0.769684000
6	5.434031000	-1.973759000	-1.981294000
6	6.040285000	-3.377154000	-1.995995000
1	5.429224000	-4.091162000	-1.432166000

1	6.110660000	-3.702736000	-3.035738000
1	7.043480000	-3.379243000	-1.553025000
8	5.204459000	-1.397281000	-3.058257000

TS2

6	1.971405000	2.255270000	-2.385520000
6	3.243482000	1.678287000	-2.345117000
6	3.445163000	0.358406000	-1.880673000
6	2.317777000	-0.390587000	-1.497837000
6	1.056046000	0.199349000	-1.548027000
6	0.862935000	1.519575000	-1.973392000
1	2.424483000	-1.412763000	-1.153608000
7	-0.103450000	-0.582334000	-1.145333000
8	-1.198407000	-0.010767000	-1.061368000
8	0.050105000	-1.783955000	-0.908069000
1	4.101824000	2.259396000	-2.672104000
1	4.350333000	-0.340100000	-2.532873000
1	-0.132850000	1.945539000	-1.992338000
1	1.837751000	3.274438000	-2.734798000
8	-0.101805000	-3.500596000	2.227424000
6	-1.401329000	-4.113041000	2.321356000
1	-2.100885000	-3.470453000	2.865923000
1	-1.245440000	-5.025545000	2.906513000
6	-1.949801000	-4.490147000	0.945976000
1	-1.195052000	-5.072153000	0.407148000
1	-2.833927000	-5.117682000	1.083432000
7	-2.324459000	-3.347888000	0.130234000
1	-1.565165000	-2.779448000	-0.233754000
6	-3.589318000	-2.823003000	0.189209000
8	-4.544324000	-3.408600000	0.701716000
7	-3.673543000	-1.561739000	-0.396462000
1	-2.798028000	-1.130244000	-0.684673000
6	-4.803843000	-0.759308000	-0.546776000
6	-6.108437000	-1.167886000	-0.218807000
6	-4.610810000	0.533683000	-1.068519000
6	-7.174947000	-0.290150000	-0.414935000
6	-5.693217000	1.388679000	-1.251696000
6	-6.992208000	0.992801000	-0.929347000
1	-6.272764000	-2.156505000	0.183415000
1	-3.611561000	0.869379000	-1.325964000
1	-7.831039000	1.662782000	-1.073738000
6	-5.461919000	2.739846000	-1.870250000
9	-6.374729000	3.649993000	-1.460885000
9	-4.238016000	3.235984000	-1.573157000
9	-5.541181000	2.692253000	-3.223924000
6	-8.552978000	-0.722201000	0.007686000
9	-8.729208000	-2.058513000	-0.103559000
9	-8.800738000	-0.405395000	1.304126000
9	-9.521587000	-0.127051000	-0.726471000
6	0.066928000	-2.156226000	2.334215000

6	-0.941443000	-1.192736000	2.180920000
6	1.377820000	-1.733277000	2.613262000
6	-0.632791000	0.160634000	2.303723000
6	1.671804000	-0.382012000	2.741038000
6	0.672164000	0.599475000	2.585613000
1	-1.956347000	-1.481201000	1.943311000
1	2.149019000	-2.484729000	2.752808000
1	-1.423990000	0.888515000	2.149367000
1	2.684153000	-0.094036000	3.006588000
6	0.953275000	2.045492000	2.745359000
6	0.048841000	2.869226000	3.435924000
6	2.116265000	2.674373000	2.224214000
6	0.282603000	4.232796000	3.608391000
6	2.359567000	4.050275000	2.406026000
6	1.441472000	4.829101000	3.099353000
1	-0.842064000	2.421810000	3.865004000
6	3.057220000	1.942551000	1.444334000
1	-0.440011000	4.832165000	4.155029000
1	3.260307000	4.490655000	1.990287000
1	1.625977000	5.889396000	3.240706000
7	3.823402000	1.364771000	0.793573000
46	5.061309000	0.219375000	-0.404925000
8	6.507566000	0.136069000	1.030419000
6	7.571362000	-0.564749000	0.718237000
8	8.522351000	-0.715616000	1.475082000
1	8.483134000	-0.850633000	-1.195060000
6	7.589520000	-1.212240000	-0.670903000
1	7.707608000	-2.294672000	-0.533174000
7	6.373232000	-0.904134000	-1.421782000
6	6.181924000	-1.334316000	-2.654983000
6	7.232891000	-2.179791000	-3.338455000
1	7.423282000	-3.092802000	-2.763249000
1	6.890933000	-2.445093000	-4.339699000
1	8.178312000	-1.630342000	-3.409485000
8	5.120780000	-1.061783000	-3.315558000

Int2

6	2.556400000	-1.713877000	-3.235786000
6	3.257637000	-0.931020000	-2.310696000
6	2.862724000	-0.854632000	-0.960475000
6	1.759693000	-1.610112000	-0.547118000
6	1.082521000	-2.396809000	-1.485361000
6	1.449766000	-2.455157000	-2.832518000
1	1.397535000	-1.573237000	0.473447000
7	-0.082969000	-3.144207000	-1.048390000
8	-0.841502000	-3.613906000	-1.914282000
8	-0.300639000	-3.266272000	0.160940000
1	4.124984000	-0.370891000	-2.650248000
1	4.292892000	-2.163800000	-0.140144000
1	0.892439000	-3.069574000	-3.528582000

1	2.876341000	-1.747946000	-4.273023000
8	-2.269445000	-3.188556000	3.000106000
6	-3.564513000	-3.806444000	2.909343000
1	-4.363041000	-3.066352000	2.972828000
1	-3.644692000	-4.464641000	3.780483000
6	-3.695036000	-4.651021000	1.633758000
1	-3.053232000	-5.532900000	1.710573000
1	-4.732172000	-4.990747000	1.550865000
7	-3.306939000	-3.956843000	0.414798000
1	-2.308956000	-3.937565000	0.228561000
6	-4.066234000	-2.951986000	-0.113299000
8	-5.170640000	-2.623061000	0.318780000
7	-3.449290000	-2.329520000	-1.213636000
1	-2.622439000	-2.811230000	-1.557100000
6	-3.414097000	-0.939028000	-1.395884000
6	-4.475748000	-0.093897000	-1.036433000
6	-2.242038000	-0.371825000	-1.922034000
6	-4.324556000	1.287508000	-1.158392000
6	-2.113568000	1.011008000	-2.028446000
6	-3.148064000	1.862122000	-1.641365000
1	-5.385440000	-0.520568000	-0.637740000
1	-1.415029000	-1.009730000	-2.214224000
1	-3.035628000	2.937599000	-1.699158000
6	-0.820749000	1.575317000	-2.552746000
9	-0.646545000	2.869200000	-2.202498000
9	0.251149000	0.888003000	-2.084295000
9	-0.750184000	1.518445000	-3.904874000
6	-5.416387000	2.185789000	-0.648098000
9	-6.638544000	1.617773000	-0.737653000
9	-5.230299000	2.494398000	0.666956000
9	-5.465750000	3.362743000	-1.310322000
6	-2.102015000	-1.871036000	2.700441000
6	-3.107660000	-1.009190000	2.241991000
6	-0.806922000	-1.356117000	2.891932000
6	-2.808984000	0.319945000	1.961995000
6	-0.523012000	-0.022568000	2.614699000
6	-1.518834000	0.850169000	2.128867000
1	-4.111469000	-1.359831000	2.047341000
1	-0.033693000	-2.018231000	3.269127000
1	-3.601050000	0.943954000	1.567292000
1	0.480534000	0.341388000	2.810523000
6	-1.283558000	2.271571000	1.780127000
6	-2.300284000	3.219461000	2.001534000
6	-0.098180000	2.756408000	1.164930000
6	-2.167746000	4.551762000	1.618359000
6	0.039978000	4.107402000	0.781142000
6	-0.996283000	5.003967000	1.001466000
1	-3.212503000	2.903057000	2.494337000
6	1.017205000	1.921840000	0.870755000
1	-2.983671000	5.243227000	1.808899000

1	0.959846000	4.429780000	0.303678000
1	-0.891225000	6.041652000	0.700978000
7	1.982049000	1.328145000	0.623922000
46	3.781725000	0.432883000	0.291445000
8	4.825157000	1.832590000	1.480690000
6	6.099393000	1.863251000	1.241912000
8	6.893214000	2.684808000	1.697528000
1	6.831323000	1.277024000	-0.693855000
6	6.646433000	0.790726000	0.272674000
1	7.603671000	0.434219000	0.658261000
7	5.684190000	-0.304043000	0.081139000
6	6.077241000	-1.529276000	-0.034137000
6	7.507620000	-1.983165000	-0.065878000
1	7.982533000	-1.802308000	0.905117000
1	7.548506000	-3.050793000	-0.287113000
1	8.069613000	-1.431159000	-0.825181000
8	5.205619000	-2.530517000	-0.133345000

Int2'

6	-1.527768000	-0.563180000	4.617563000
6	-2.657299000	-0.626068000	3.788353000
6	-2.528390000	-0.684921000	2.393334000
6	-1.255369000	-0.681585000	1.826205000
6	-0.142506000	-0.611678000	2.673506000
6	-0.251360000	-0.551494000	4.066533000
1	-1.113271000	-0.715913000	0.752993000
7	1.183540000	-0.601098000	2.080041000
8	2.170376000	-0.447937000	2.799402000
8	1.268681000	-0.746570000	0.846115000
1	-3.643341000	-0.628800000	4.245590000
1	0.635978000	-0.501346000	4.685261000
1	-1.649287000	-0.521058000	5.696027000
8	-0.214840000	-2.379433000	-2.606963000
6	0.985738000	-2.840715000	-3.252791000
1	1.521594000	-2.010585000	-3.722976000
1	0.655347000	-3.528666000	-4.039015000
6	1.879260000	-3.592438000	-2.270633000
1	1.304777000	-4.403443000	-1.810453000
1	2.715894000	-4.033333000	-2.817544000
7	2.421839000	-2.748597000	-1.220300000
1	1.760467000	-2.360198000	-0.559749000
6	3.673564000	-2.193195000	-1.319733000
8	4.495603000	-2.532974000	-2.171837000
7	3.911864000	-1.225348000	-0.349503000
1	3.131141000	-0.991428000	0.260382000
6	5.081810000	-0.499186000	-0.130012000
6	6.239875000	-0.612304000	-0.918517000
6	5.085091000	0.397376000	0.955456000
6	7.359272000	0.162394000	-0.612979000
6	6.215226000	1.159707000	1.234300000

6	7.369379000	1.057927000	0.455372000
1	6.255244000	-1.302918000	-1.748540000
1	4.206233000	0.479034000	1.587403000
1	8.249130000	1.647619000	0.682997000
6	6.170368000	2.153226000	2.362586000
9	5.333016000	1.768555000	3.352967000
9	7.388473000	2.347335000	2.918271000
9	5.738816000	3.369291000	1.941558000
6	8.567428000	0.068115000	-1.504649000
9	8.702359000	-1.157742000	-2.060179000
9	8.501587000	0.953151000	-2.531736000
9	9.714847000	0.335214000	-0.838550000
6	-0.418522000	-1.055030000	-2.338818000
6	0.598256000	-0.101379000	-2.189315000
6	-1.758622000	-0.666438000	-2.185570000
6	0.267082000	1.215874000	-1.874305000
6	-2.077895000	0.653609000	-1.888724000
6	-1.068553000	1.620620000	-1.710431000
1	1.641207000	-0.379906000	-2.273548000
1	-2.552416000	-1.395206000	-2.308887000
1	1.069162000	1.932897000	-1.722018000
1	-3.125424000	0.931446000	-1.836024000
6	-1.382854000	3.025390000	-1.353544000
6	-0.714358000	4.091224000	-1.976470000
6	-2.345553000	3.366812000	-0.366027000
6	-0.988206000	5.418748000	-1.648007000
6	-2.628136000	4.703967000	-0.035304000
6	-1.948166000	5.731268000	-0.679095000
1	0.016580000	3.869223000	-2.747834000
6	-3.023440000	2.333550000	0.340898000
1	-0.455545000	6.215732000	-2.159270000
1	-3.371125000	4.920027000	0.725380000
1	-2.163273000	6.765338000	-0.428402000
7	-3.538232000	1.465123000	0.912723000
46	-4.137712000	-0.534654000	1.192917000
6	-4.664009000	-2.688132000	0.749171000
6	-4.780169000	-2.494496000	2.109669000
1	-4.011317000	-2.841848000	2.791089000
1	-5.738195000	-2.215313000	2.542334000
1	-5.518682000	-2.549583000	0.100026000
8	-3.752056000	-4.068776000	-0.947205000
6	-3.563387000	-3.455014000	0.085321000
8	-2.405930000	-3.440463000	0.757555000
6	-1.327308000	-4.223960000	0.169643000
1	-1.131869000	-3.839050000	-0.834857000
1	-1.661388000	-5.263018000	0.085576000
1	-0.349456000	-4.426309000	2.090291000
6	-0.121084000	-4.088062000	1.073761000
1	0.213931000	-3.049189000	1.118830000
1	0.699923000	-4.697760000	0.680891000

8	-5.844807000	-0.071789000	-0.006227000
8	-4.902659000	-1.011050000	-1.832856000
6	-5.717169000	-0.263580000	-1.276534000
6	-6.727644000	0.516551000	-2.144851000
1	-7.653401000	-0.061903000	-2.225706000
1	-6.296817000	0.620174000	-3.142999000
7	-7.056334000	1.827470000	-1.611518000
1	-7.872019000	1.901863000	-1.017071000
6	-6.069892000	2.752582000	-1.455956000
8	-4.950854000	2.603728000	-1.955250000
1	-5.873939000	4.834853000	-0.991922000
1	-7.498829000	4.184369000	-0.621897000
1	-6.114838000	3.782600000	0.415323000
6	-6.425721000	3.967697000	-0.620877000

TS3

6	-1.108964000	1.191155000	3.891659000
6	-2.413927000	0.748640000	3.640925000
6	-2.652296000	-0.238037000	2.673996000
6	-1.579149000	-0.842436000	2.013712000
6	-0.292747000	-0.370684000	2.271919000
6	-0.031928000	0.647834000	3.195132000
1	-1.741787000	-1.638308000	1.297759000
7	0.814856000	-0.972702000	1.547421000
8	1.922457000	-0.422328000	1.594700000
8	0.602587000	-2.010335000	0.911922000
1	-3.246115000	1.191814000	4.179947000
1	0.982539000	0.984748000	3.369526000
1	-0.933654000	1.970068000	4.627433000
8	0.058486000	-2.589670000	-2.387827000
6	1.253896000	-3.086031000	-3.016762000
1	1.826808000	-2.269287000	-3.467087000
1	0.918120000	-3.755575000	-3.817279000
6	2.107046000	-3.873340000	-2.026108000
1	1.494222000	-4.656808000	-1.567670000
1	2.928001000	-4.351221000	-2.566390000
7	2.669908000	-3.048352000	-0.971911000
1	2.012379000	-2.670131000	-0.296035000
6	3.908285000	-2.477416000	-1.096880000
8	4.722668000	-2.799038000	-1.963733000
7	4.146136000	-1.501432000	-0.130258000
1	3.374714000	-1.271410000	0.492261000
6	5.304319000	-0.750437000	0.065245000
6	6.473193000	-0.891167000	-0.703151000
6	5.288332000	0.199062000	1.105026000
6	7.583913000	-0.095655000	-0.420428000
6	6.411353000	0.977831000	1.365005000
6	7.576683000	0.845743000	0.607603000
1	6.501937000	-1.617532000	-1.501603000
1	4.398482000	0.319391000	1.713830000

1	8.450806000	1.449539000	0.820539000
6	6.355361000	2.022572000	2.445645000
9	5.431486000	1.738205000	3.391875000
9	7.545141000	2.163191000	3.074940000
9	6.036993000	3.243223000	1.945719000
6	8.804020000	-0.217103000	-1.292710000
9	8.934068000	-1.451552000	-1.829127000
9	8.763787000	0.655260000	-2.331821000
9	9.944144000	0.047214000	-0.612544000
6	-0.124409000	-1.253816000	-2.176283000
6	0.909127000	-0.332512000	-1.947984000
6	-1.455598000	-0.811728000	-2.162943000
6	0.603171000	1.011390000	-1.737444000
6	-1.750926000	0.530576000	-1.956153000
6	-0.724702000	1.472553000	-1.744215000
1	1.941775000	-0.655435000	-1.910455000
1	-2.261513000	-1.518572000	-2.326194000
1	1.414232000	1.707987000	-1.543358000
1	-2.787439000	0.846983000	-2.010752000
6	-1.016950000	2.915801000	-1.570938000
6	-0.239117000	3.883455000	-2.227373000
6	-2.078103000	3.393747000	-0.757741000
6	-0.504858000	5.246510000	-2.098944000
6	-2.355420000	4.767195000	-0.634170000
6	-1.568831000	5.694320000	-1.308299000
1	0.571463000	3.553259000	-2.869668000
6	-2.857718000	2.477321000	0.005584000
1	0.114815000	5.963579000	-2.630239000
1	-3.178697000	5.089655000	-0.004407000
1	-1.780883000	6.755110000	-1.216820000
7	-3.459532000	1.720275000	0.645479000
46	-4.308279000	-0.094911000	1.417110000
6	-5.121632000	-1.854774000	2.222534000
6	-4.142107000	-1.635332000	3.228902000
1	-3.333308000	-2.348750000	3.332597000
1	-4.447272000	-1.139263000	4.145661000
1	-6.154037000	-1.579892000	2.426567000
8	-5.923017000	-3.472849000	0.659979000
6	-4.977614000	-2.947503000	1.215964000
8	-3.690439000	-3.284884000	1.013910000
6	-3.433832000	-4.194098000	-0.086776000
1	-3.851188000	-3.741570000	-0.990377000
1	-3.953544000	-5.138178000	0.107723000
1	-1.532184000	-4.785387000	0.759691000
6	-1.932917000	-4.382527000	-0.177669000
1	-1.424297000	-3.441135000	-0.402342000
1	-1.703358000	-5.089285000	-0.983391000
8	-5.786526000	0.092502000	-0.069405000
8	-4.541219000	-1.302368000	-1.344756000
6	-5.431188000	-0.457169000	-1.182890000

6	-6.241794000	0.016897000	-2.407688000
1	-7.119055000	-0.626870000	-2.527195000
1	-5.607874000	-0.099042000	-3.289017000
7	-6.694705000	1.394154000	-2.308016000
1	-7.592956000	1.553544000	-1.869476000
6	-5.779052000	2.401289000	-2.245733000
8	-4.589302000	2.225400000	-2.521619000
1	-5.734732000	4.542189000	-2.296336000
1	-7.374718000	3.881978000	-2.016945000
1	-6.159432000	3.847891000	-0.721514000
6	-6.308616000	3.752362000	-1.804872000

Int3

6	-2.343772000	0.575736000	4.240462000
6	-3.626528000	0.259299000	3.797243000
6	-3.838852000	-0.746140000	2.818909000
6	-2.712676000	-1.387930000	2.259569000
6	-1.434701000	-1.051643000	2.733836000
6	-1.230609000	-0.085830000	3.715825000
1	-2.840484000	-2.191563000	1.545818000
7	-0.294129000	-1.731921000	2.156051000
8	0.820516000	-1.555223000	2.669247000
8	-0.478816000	-2.466567000	1.179410000
1	-4.488704000	0.768730000	4.217518000
1	-0.228445000	0.153351000	4.049896000
1	-2.203931000	1.341290000	4.996445000
8	0.401598000	-3.331957000	-2.477912000
6	1.425163000	-4.337519000	-2.425161000
1	2.393567000	-3.942641000	-2.740275000
1	1.118631000	-5.099413000	-3.148553000
6	1.519702000	-4.982745000	-1.038055000
1	0.560857000	-5.444097000	-0.784923000
1	2.279105000	-5.770040000	-1.078632000
7	1.843692000	-4.051117000	0.035140000
1	1.060295000	-3.537248000	0.427262000
6	3.079927000	-3.466193000	0.086190000
8	4.025717000	-3.827675000	-0.616483000
7	3.151902000	-2.412297000	1.000034000
1	2.307341000	-2.232073000	1.538586000
6	3.998528000	-1.304492000	0.886807000
6	5.215359000	-1.325074000	0.186911000
6	3.576853000	-0.099399000	1.477243000
6	5.958041000	-0.149759000	0.061355000
6	4.340494000	1.055805000	1.343743000
6	5.538676000	1.053145000	0.627765000
1	5.555715000	-2.244155000	-0.267161000
1	2.630329000	-0.058058000	2.005044000
1	6.122268000	1.958268000	0.513980000
6	3.864928000	2.320130000	2.004709000
9	4.266907000	2.394497000	3.298766000

9	4.335687000	3.427774000	1.388268000
9	2.513709000	2.409397000	2.017536000
6	7.204092000	-0.178708000	-0.780789000
9	7.864874000	-1.354782000	-0.676821000
9	6.917653000	-0.012058000	-2.097265000
9	8.073764000	0.801641000	-0.446118000
6	0.677957000	-2.022097000	-2.213866000
6	1.955311000	-1.482983000	-1.999176000
6	-0.435014000	-1.166052000	-2.182069000
6	2.092936000	-0.136499000	-1.666890000
6	-0.283369000	0.179166000	-1.872758000
6	0.982494000	0.717905000	-1.566219000
1	2.844205000	-2.098714000	-2.037937000
1	-1.423885000	-1.556846000	-2.393865000
1	3.086734000	0.237042000	-1.442062000
1	-1.158307000	0.816501000	-1.905344000
6	1.162848000	2.121025000	-1.127892000
6	2.283445000	2.861585000	-1.540730000
6	0.257670000	2.774887000	-0.249298000
6	2.497141000	4.171288000	-1.114881000
6	0.465382000	4.101981000	0.171226000
6	1.585183000	4.801177000	-0.261471000
1	2.991267000	2.402036000	-2.223291000
6	-0.882134000	2.097648000	0.275765000
1	3.377967000	4.706569000	-1.458144000
1	-0.251688000	4.565014000	0.842052000
1	1.748721000	5.823190000	0.066062000
7	-1.806578000	1.561236000	0.730646000
46	-3.703700000	0.443727000	0.830092000
6	-5.448668000	-0.612819000	0.971298000
6	-5.243958000	-1.176674000	2.382968000
1	-5.321794000	-2.267783000	2.410846000
1	-5.981119000	-0.759252000	3.073252000
1	-6.262770000	0.106396000	0.883466000
8	-6.245529000	-1.479560000	-1.122166000
6	-5.481804000	-1.566212000	-0.177865000
8	-4.552145000	-2.541087000	-0.056333000
6	-4.295738000	-3.342093000	-1.235946000
1	-4.217210000	-2.665133000	-2.089817000
1	-5.142945000	-4.018391000	-1.396782000
1	-3.090382000	-4.751175000	-0.113413000
6	-3.004428000	-4.099087000	-0.990542000
1	-2.171921000	-3.406376000	-0.832025000
1	-2.770392000	-4.721471000	-1.861848000
8	-4.347730000	1.428263000	-0.879859000
8	-3.503351000	-0.267318000	-2.120879000
6	-3.989531000	0.859481000	-1.985687000
6	-4.237399000	1.729593000	-3.235756000
1	-5.242736000	1.521685000	-3.615274000
1	-3.512681000	1.424853000	-3.993731000

7	-4.125249000	3.156246000	-2.989272000
1	-4.972000000	3.654632000	-2.746100000
6	-2.941117000	3.664525000	-2.544268000
8	-1.898729000	3.005960000	-2.570313000
1	-2.041009000	5.582116000	-2.231710000
1	-3.821481000	5.664640000	-2.395494000
1	-3.081491000	5.029217000	-0.909221000
6	-2.984251000	5.079823000	-2.001514000

TS4

6	0.925904000	-5.103007000	-2.241984000
6	1.955801000	-4.168093000	-2.375077000
6	2.218924000	-3.231127000	-1.363984000
6	1.428233000	-3.226984000	-0.206940000
6	0.397471000	-4.157786000	-0.109282000
6	0.124886000	-5.101819000	-1.105651000
1	1.580643000	-2.492955000	0.579362000
7	-0.483278000	-4.099261000	1.052278000
8	-0.220646000	-3.308129000	1.961373000
1	2.561000000	-4.160562000	-3.277303000
1	-0.693966000	-5.800375000	-0.989163000
1	0.740209000	-5.822797000	-3.032426000
8	-1.813216000	-0.630632000	4.126303000
6	-3.043541000	-1.047732000	4.736696000
1	-3.867809000	-0.387535000	4.470482000
1	-2.892871000	-0.981741000	5.819638000
6	-3.373210000	-2.502181000	4.362503000
1	-2.706083000	-3.184278000	4.895920000
1	-4.399990000	-2.716171000	4.676537000
7	-3.210736000	-2.794891000	2.946047000
1	-2.277859000	-3.087334000	2.677180000
6	-3.989418000	-2.193167000	1.999797000
8	-4.977147000	-1.507100000	2.259550000
7	-3.550925000	-2.444969000	0.688255000
1	-2.846634000	-3.168974000	0.598432000
6	-3.524602000	-1.484609000	-0.333222000
6	-4.503183000	-0.487967000	-0.468493000
6	-2.457071000	-1.520599000	-1.246537000
6	-4.384139000	0.458729000	-1.487470000
6	-2.365685000	-0.569903000	-2.258354000
6	-3.323268000	0.436717000	-2.392426000
1	-5.330461000	-0.454788000	0.226255000
1	-1.684636000	-2.275802000	-1.151417000
1	-3.240318000	1.183242000	-3.173468000
6	-1.237229000	-0.649518000	-3.249213000
9	-1.610034000	-1.287433000	-4.386774000
9	-0.803815000	0.577523000	-3.622252000
9	-0.169061000	-1.323922000	-2.760629000
6	-5.392586000	1.571157000	-1.573723000
9	-5.000078000	2.665405000	-0.864476000

9	-5.579138000	1.992684000	-2.845118000
9	-6.600047000	1.211396000	-1.085514000
6	-1.798858000	0.282028000	3.112038000
6	-2.930440000	0.881815000	2.540032000
6	-0.526269000	0.642103000	2.634926000
6	-2.778397000	1.824186000	1.527286000
6	-0.386256000	1.598568000	1.633504000
6	-1.514622000	2.215712000	1.054668000
1	-3.931375000	0.589806000	2.823540000
1	0.352142000	0.161178000	3.053214000
1	-3.672478000	2.232569000	1.070412000
1	0.614170000	1.905562000	1.351133000
6	-1.429775000	3.254344000	-0.000015000
6	-2.330432000	4.335132000	0.009179000
6	-0.500650000	3.221672000	-1.075335000
6	-2.319761000	5.315771000	-0.980210000
6	-0.483371000	4.216505000	-2.074159000
6	-1.394794000	5.262925000	-2.028697000
1	-3.042384000	4.414488000	0.823839000
6	0.440862000	2.163699000	-1.213432000
1	-3.033656000	6.133090000	-0.927077000
1	0.242151000	4.145885000	-2.878643000
1	-1.383880000	6.028543000	-2.798230000
7	1.227676000	1.323447000	-1.354104000
46	2.678623000	-0.113905000	-0.953675000
8	3.174450000	1.021465000	0.758172000
8	2.548401000	-0.644737000	2.159900000
6	2.972461000	0.496016000	1.912587000
6	3.259623000	1.428314000	3.109799000
1	3.851229000	0.875789000	3.844924000
1	2.295134000	1.667021000	3.567300000
7	3.930664000	2.669427000	2.780387000
1	4.921225000	2.605135000	2.581238000
6	3.250487000	3.706824000	2.207616000
8	2.021182000	3.779222000	2.207256000
1	3.622279000	5.744922000	1.652842000
1	5.119911000	4.833386000	2.008666000
1	4.229583000	4.541192000	0.500708000
6	4.119450000	4.775239000	1.567512000
6	3.315794000	-2.249686000	-1.567742000
1	3.824853000	-2.307531000	-2.527729000
6	4.042835000	-1.668871000	-0.501119000
1	3.824805000	-1.924173000	0.530624000
6	5.370305000	-1.053412000	-0.776428000
8	5.853232000	-0.897303000	-1.886216000
8	5.949968000	-0.671569000	0.372836000
6	7.134962000	0.161383000	0.268219000
1	7.808287000	-0.261097000	-0.482767000
1	7.601752000	0.084489000	1.252598000
6	6.748204000	1.595048000	-0.059892000

1	5.995871000	1.954617000	0.648597000
1	6.330157000	1.662153000	-1.069072000
1	7.631999000	2.240887000	-0.004398000
1	2.425751000	-0.949040000	-2.285852000
8	-1.490167000	-4.822582000	1.063840000

Int4

6	-1.294843000	4.982998000	-2.495055000
6	-2.324882000	4.040441000	-2.525614000
6	-2.531179000	3.153266000	-1.455224000
6	-1.681473000	3.211318000	-0.338837000
6	-0.639680000	4.134691000	-0.355366000
6	-0.426390000	5.029851000	-1.410358000
1	-1.793185000	2.519415000	0.492953000
7	0.324222000	4.115687000	0.740395000
8	0.116671000	3.377045000	1.705783000
1	-2.976165000	3.983055000	-3.393488000
1	0.402090000	5.726221000	-1.378411000
1	-1.156398000	5.665080000	-3.327536000
8	1.736638000	0.951524000	4.100398000
6	2.951153000	1.453544000	4.677871000
1	3.794995000	0.795414000	4.473748000
1	2.792881000	1.474944000	5.761308000
6	3.242140000	2.879629000	4.182421000
1	2.546449000	3.583464000	4.646739000
1	4.257281000	3.152834000	4.487936000
7	3.091601000	3.040906000	2.744090000
1	2.151246000	3.263772000	2.436088000
6	3.916789000	2.397792000	1.866696000
8	4.933828000	1.791353000	2.202143000
7	3.487971000	2.505091000	0.533404000
1	2.735352000	3.165453000	0.372888000
6	3.558561000	1.470612000	-0.408983000
6	4.588467000	0.517636000	-0.424421000
6	2.530884000	1.380200000	-1.364231000
6	4.556039000	-0.514641000	-1.363700000
6	2.526732000	0.346051000	-2.294812000
6	3.535522000	-0.619394000	-2.307331000
1	5.384455000	0.580353000	0.303722000
1	1.721838000	2.103616000	-1.357908000
1	3.517762000	-1.433301000	-3.022638000
6	1.433642000	0.271612000	-3.325071000
9	1.837348000	0.756060000	-4.525411000
9	1.034801000	-1.005411000	-3.542965000
9	0.336909000	0.979729000	-2.968895000
6	5.607153000	-1.588298000	-1.304365000
9	5.220785000	-2.626645000	-0.511024000
9	5.866203000	-2.118994000	-2.520707000
9	6.777453000	-1.138047000	-0.801337000
6	1.755530000	-0.009871000	3.132948000

6	2.905586000	-0.614891000	2.605669000
6	0.496888000	-0.420111000	2.659786000
6	2.784261000	-1.606963000	1.637265000
6	0.386755000	-1.426151000	1.704409000
6	1.534571000	-2.045964000	1.167742000
1	3.897367000	-0.291504000	2.887469000
1	-0.392392000	0.066851000	3.045807000
1	3.692560000	-2.017086000	1.211615000
1	-0.605543000	-1.762185000	1.425793000
6	1.487709000	-3.129894000	0.157310000
6	2.424138000	-4.178765000	0.214745000
6	0.567596000	-3.172276000	-0.925905000
6	2.457507000	-5.195019000	-0.737295000
6	0.596060000	-4.202706000	-1.888354000
6	1.543138000	-5.213358000	-1.796353000
1	3.130543000	-4.203839000	1.037483000
6	-0.410223000	-2.158159000	-1.118944000
1	3.198861000	-5.984084000	-0.646756000
1	-0.122175000	-4.186364000	-2.702241000
1	1.567899000	-6.006059000	-2.537533000
7	-1.227487000	-1.359725000	-1.315304000
46	-2.693036000	0.051496000	-1.082503000
8	-3.073246000	-0.862378000	0.810516000
8	-2.595965000	0.933190000	2.103336000
6	-2.945215000	-0.247027000	1.927190000
6	-3.230251000	-1.103843000	3.179843000
1	-3.807907000	-0.500855000	3.885692000
1	-2.265681000	-1.332093000	3.642604000
7	-3.918246000	-2.352768000	2.926092000
1	-4.900657000	-2.283751000	2.691895000
6	-3.247549000	-3.454106000	2.475679000
8	-2.020837000	-3.553769000	2.520621000
1	-3.674092000	-5.531173000	2.159007000
1	-5.150385000	-4.530191000	2.292185000
1	-4.152454000	-4.467966000	0.824715000
6	-4.122320000	-4.563613000	1.917452000
6	-3.611439000	2.154596000	-1.577963000
1	-4.079240000	2.085866000	-2.556969000
6	-4.247777000	1.510938000	-0.527273000
1	-3.997458000	1.728975000	0.505723000
6	-5.497542000	0.734107000	-0.775320000
8	-5.996391000	0.538914000	-1.870593000
8	-5.984569000	0.270191000	0.385028000
6	-7.065992000	-0.697081000	0.305934000
1	-7.822476000	-0.335540000	-0.396090000
1	-7.486171000	-0.706096000	1.313880000
6	-6.528130000	-2.062896000	-0.091672000
1	-5.696208000	-2.344608000	0.560205000
1	-6.168514000	-2.052671000	-1.125094000
1	-7.321213000	-2.814367000	-0.005123000

1	-2.464534000	0.487457000	-2.556707000
8	1.341544000	4.816688000	0.639191000

Int5

6	0.340306000	-3.998351000	-2.900802000
6	1.520425000	-3.249346000	-2.888713000
6	2.111058000	-2.817727000	-1.685568000
6	1.475980000	-3.164160000	-0.481786000
6	0.291992000	-3.893571000	-0.517381000
6	-0.298758000	-4.330044000	-1.710722000
1	1.866451000	-2.822574000	0.468285000
7	-0.393083000	-4.146783000	0.741823000
8	0.135258000	-3.815511000	1.799523000
1	1.992610000	-2.982700000	-3.830500000
1	-1.221945000	-4.894937000	-1.698138000
1	-0.088271000	-4.316330000	-3.846297000
8	-2.102696000	-1.393636000	4.025368000
6	-3.384471000	-1.864619000	4.470020000
1	-4.169088000	-1.136871000	4.264655000
1	-3.309308000	-1.981122000	5.556430000
6	-3.731263000	-3.228166000	3.848208000
1	-3.108383000	-4.007405000	4.294753000
1	-4.777121000	-3.453321000	4.084057000
7	-3.507210000	-3.297926000	2.413698000
1	-2.622608000	-3.693925000	2.117763000
6	-4.219432000	-2.541105000	1.531474000
8	-5.227031000	-1.905226000	1.844224000
7	-3.684519000	-2.549220000	0.232229000
1	-2.887515000	-3.164638000	0.100305000
6	-3.683194000	-1.438687000	-0.624710000
6	-4.706700000	-0.478769000	-0.643045000
6	-2.580515000	-1.274258000	-1.481327000
6	-4.588978000	0.635355000	-1.476013000
6	-2.492845000	-0.159465000	-2.309157000
6	-3.490835000	0.816506000	-2.315066000
1	-5.558587000	-0.593350000	0.011354000
1	-1.776042000	-2.001855000	-1.471880000
1	-3.404908000	1.697029000	-2.940408000
6	-1.305959000	-0.002295000	-3.219544000
9	-1.564100000	-0.458141000	-4.471170000
9	-0.941250000	1.296472000	-3.351321000
9	-0.223340000	-0.678855000	-2.775526000
6	-5.626282000	1.719365000	-1.389089000
9	-5.299484000	2.648076000	-0.446148000
9	-5.764296000	2.394116000	-2.552449000
9	-6.844882000	1.243989000	-1.049939000
6	-2.001529000	-0.365434000	3.134401000
6	-3.080108000	0.297747000	2.532602000
6	-0.695443000	0.055902000	2.825632000
6	-2.846285000	1.337250000	1.637312000

6	-0.475124000	1.108852000	1.942394000
6	-1.550247000	1.773667000	1.317545000
1	-4.100775000	-0.016089000	2.696461000
1	0.141144000	-0.449307000	3.299343000
1	-3.701993000	1.787466000	1.147805000
1	0.538643000	1.450117000	1.776466000
6	-1.385728000	2.890680000	0.354011000
6	-2.317469000	3.944918000	0.348065000
6	-0.358325000	2.951603000	-0.623906000
6	-2.249903000	4.988990000	-0.572235000
6	-0.288582000	4.006450000	-1.554628000
6	-1.233736000	5.024686000	-1.532227000
1	-3.104186000	3.952917000	1.094971000
6	0.647353000	1.947477000	-0.735215000
1	-2.991734000	5.782020000	-0.534330000
1	0.508814000	4.007544000	-2.291327000
1	-1.177775000	5.835742000	-2.251893000
7	1.497811000	1.165967000	-0.867949000
46	3.111140000	-0.199957000	-0.569358000
8	3.792005000	1.347255000	1.101044000
8	2.895929000	0.242496000	2.801962000
6	3.438280000	1.345136000	2.264876000
6	3.612145000	2.556155000	3.183403000
1	4.522217000	2.410023000	3.774371000
1	2.763065000	2.610568000	3.872498000
7	3.715299000	3.781398000	2.431396000
1	4.638458000	4.110393000	2.177630000
6	2.635596000	4.191009000	1.698268000
8	1.541711000	3.638856000	1.821837000
1	1.968985000	5.943727000	0.674789000
1	3.728952000	5.952722000	1.007716000
1	3.055896000	4.906540000	-0.263035000
6	2.871922000	5.330621000	0.732255000
6	3.329326000	-1.982495000	-1.717973000
1	3.679052000	-1.734465000	-2.719401000
6	4.298511000	-1.945245000	-0.676523000
1	4.185224000	-2.546751000	0.223078000
6	5.670118000	-1.489809000	-0.969576000
8	6.085258000	-1.079741000	-2.045216000
8	6.446448000	-1.569008000	0.143914000
6	7.772291000	-1.000447000	0.053920000
1	8.219370000	-1.270516000	-0.907106000
1	8.334273000	-1.484866000	0.856867000
6	7.730031000	0.509271000	0.238121000
1	7.262522000	0.768314000	1.194898000
1	7.157730000	0.976583000	-0.569499000
1	8.747765000	0.917281000	0.225873000
8	-1.522085000	-4.676542000	0.694769000
1	2.634555000	0.397668000	3.731303000

Int_a

6	-2.988804000	-1.101012000	1.602523000
6	-2.028238000	-0.415027000	2.332459000
6	-1.265200000	0.610591000	1.717277000
6	-1.491753000	0.941155000	0.365397000
6	-2.502043000	0.242868000	-0.335329000
6	-3.237309000	-0.769845000	0.253631000
1	-0.999479000	1.798106000	-0.074170000
7	-2.743288000	0.585598000	-1.740622000
8	-3.683027000	0.037034000	-2.318411000
8	-1.985754000	1.401821000	-2.268691000
1	-1.856677000	-0.654016000	3.377088000
1	-0.577433000	1.221435000	2.289348000
1	-3.992673000	-1.297112000	-0.316663000
1	-3.569987000	-1.891507000	2.066386000
46	0.305957000	-0.632222000	0.375483000
8	1.620639000	-2.001658000	-0.240847000
6	2.754702000	-1.541068000	-0.734732000
8	3.608251000	-2.276433000	-1.203887000
1	3.883378000	0.181832000	-0.200771000
6	2.925081000	-0.027989000	-0.689454000
1	2.998946000	0.330511000	-1.725578000
7	1.814150000	0.609436000	0.019900000
6	1.833216000	1.909133000	0.406558000
6	3.079921000	2.700465000	0.004441000
1	3.283821000	2.627553000	-1.069092000
1	2.907378000	3.744553000	0.272523000
1	3.964391000	2.334653000	0.539081000
8	0.928748000	2.467406000	1.041591000

TS_{ab}

6	-2.758996000	0.158755000	2.245697000
6	-1.431757000	0.449781000	1.920106000
6	-1.002833000	0.491687000	0.574184000
6	-1.950979000	0.280049000	-0.445314000
6	-3.268862000	-0.007180000	-0.098814000
6	-3.688269000	-0.075939000	1.232945000
1	-1.667553000	0.343791000	-1.489692000
7	-4.253477000	-0.238391000	-1.165798000
8	-5.418906000	-0.470895000	-0.838901000
8	-3.863597000	-0.188592000	-2.334055000
1	-0.716997000	0.652358000	2.713597000
1	-0.099484000	1.417264000	0.296079000
1	-4.723115000	-0.300169000	1.461955000
1	-3.075963000	0.120285000	3.283429000
46	0.775295000	-0.657395000	0.259969000
8	2.346208000	-1.916605000	0.017116000
6	3.485621000	-1.351307000	-0.307702000
8	4.520481000	-1.975923000	-0.493286000
1	4.209354000	0.590403000	0.246291000

6	3.471338000	0.175558000	-0.450739000
1	3.795155000	0.426254000	-1.468214000
7	2.137984000	0.714779000	-0.180214000
6	1.843402000	2.002480000	-0.216601000
6	2.927551000	2.998410000	-0.565286000
1	3.338735000	2.779518000	-1.556736000
1	2.507848000	4.004857000	-0.556485000
1	3.747730000	2.935937000	0.158367000
8	0.674800000	2.452165000	0.029634000

Int_b

6	-2.747632000	-0.102644000	2.249914000
6	-1.387799000	-0.196834000	1.931231000
6	-0.962185000	-0.268376000	0.589455000
6	-1.921989000	-0.189335000	-0.431509000
6	-3.272913000	-0.094266000	-0.087925000
6	-3.705333000	-0.052830000	1.238436000
1	-1.637645000	-0.201101000	-1.477961000
7	-4.274062000	-0.025156000	-1.162484000
8	-5.462580000	0.054887000	-0.844221000
8	-3.877070000	-0.051064000	-2.329545000
1	-0.655823000	-0.215698000	2.735321000
1	-0.276240000	1.533797000	0.378586000
1	-4.761637000	0.027073000	1.463977000
1	-3.061453000	-0.061063000	3.288902000
46	0.896230000	-0.890142000	0.155334000
8	2.751912000	-1.722598000	-0.269701000
6	3.719418000	-0.875374000	-0.445624000
8	4.886889000	-1.169315000	-0.690074000
1	3.978826000	1.049360000	0.464272000
6	3.365162000	0.616490000	-0.334183000
1	3.652882000	1.102009000	-1.273318000
7	1.935694000	0.862148000	-0.055870000
6	1.504680000	2.081597000	0.018839000
6	2.377010000	3.287983000	-0.165096000
1	2.817764000	3.284118000	-1.168143000
1	1.786060000	4.195110000	-0.031546000
1	3.198422000	3.276005000	0.559341000
8	0.237137000	2.370527000	0.266346000

Int_c

6	-2.244315000	-1.923488000	2.172629000
6	-1.105996000	-1.173628000	1.848064000
6	-0.964259000	-0.635004000	0.563934000
6	-1.953521000	-0.833827000	-0.396578000
6	-3.083497000	-1.575371000	-0.041006000
6	-3.247739000	-2.131404000	1.228577000
1	-1.878425000	-0.418294000	-1.394495000
7	-4.151968000	-1.744155000	-1.033040000
8	-5.087783000	-2.497793000	-0.758853000

8	-4.066392000	-1.117136000	-2.093717000
1	-0.339402000	-1.014861000	2.601397000
1	-4.139895000	-2.697578000	1.465317000
1	-2.349640000	-2.339381000	3.170399000
46	0.708029000	0.303205000	0.071118000
6	-0.163661000	2.356583000	0.027159000
6	0.149595000	2.048302000	1.338433000
1	-0.622702000	1.752640000	2.041414000
1	1.118746000	2.319106000	1.750955000
1	0.560384000	2.852298000	-0.615491000
8	-1.764637000	2.514139000	-1.730641000
6	-1.547098000	2.344276000	-0.544656000
8	-2.488151000	2.131481000	0.380465000
6	-3.856449000	2.007119000	-0.099168000
1	-3.880288000	1.257694000	-0.895489000
1	-4.162258000	2.969070000	-0.522713000
1	-4.666717000	2.360739000	1.875755000
6	-4.708778000	1.603447000	1.085374000
1	-4.371095000	0.646159000	1.495778000
1	-5.750416000	1.494848000	0.763370000
8	2.869810000	0.554039000	-0.646796000
8	1.844588000	-1.407670000	-0.508208000
6	2.892167000	-0.703090000	-0.752641000
6	4.147323000	-1.442103000	-1.201406000
1	4.046878000	-1.674551000	-2.266583000
1	4.195323000	-2.386781000	-0.654015000
7	5.359277000	-0.681262000	-0.996093000
1	5.698108000	-0.111063000	-1.760204000
6	5.756751000	-0.378621000	0.275848000
8	5.210167000	-0.877706000	1.259557000
1	7.517851000	0.345414000	1.253933000
1	7.527194000	0.639976000	-0.509913000
1	6.491626000	1.611238000	0.558073000
6	6.903376000	0.608305000	0.388866000

TS_{cd}

6	3.383807000	-2.806172000	-0.942342000
6	2.234539000	-2.166769000	-1.420491000
6	1.841279000	-0.939786000	-0.864922000
6	2.634048000	-0.302459000	0.096575000
6	3.773143000	-0.965841000	0.549142000
6	4.162548000	-2.211173000	0.049296000
1	2.375505000	0.676120000	0.483870000
7	4.601325000	-0.319249000	1.578023000
8	5.611428000	-0.910737000	1.963404000
8	4.243953000	0.781271000	2.002665000
1	1.646213000	-2.623576000	-2.210964000
1	5.060061000	-2.688680000	0.422173000
1	3.677996000	-3.767605000	-1.352296000
46	-0.161534000	-0.612044000	-0.633137000

6	-0.245464000	0.855983000	-2.122377000
6	1.094425000	0.433135000	-2.336127000
1	1.901736000	1.100835000	-2.057477000
1	1.293800000	-0.231927000	-3.170541000
1	-1.022877000	0.516684000	-2.803331000
8	-1.666694000	2.673107000	-1.511365000
6	-0.581569000	2.132237000	-1.413502000
8	0.435718000	2.584378000	-0.667150000
6	0.129338000	3.678273000	0.239186000
1	-0.731597000	3.374899000	0.840628000
1	-0.139200000	4.559770000	-0.352234000
1	2.226279000	4.170179000	0.458474000
6	1.364162000	3.913046000	1.084048000
1	1.609262000	3.019823000	1.669093000
1	1.181171000	4.741206000	1.777963000
8	-2.190289000	-0.442410000	-0.141718000
8	-1.499295000	1.028259000	1.424487000
6	-2.381361000	0.416462000	0.805189000
6	-3.851123000	0.711281000	1.150695000
1	-4.066520000	1.732585000	0.819522000
1	-3.950748000	0.684045000	2.237861000
7	-4.820891000	-0.189851000	0.562122000
1	-5.046790000	-0.038128000	-0.413136000
6	-4.957813000	-1.461674000	1.043631000
8	-4.473928000	-1.816425000	2.118467000
1	-6.275593000	-3.133438000	0.786759000
1	-6.475666000	-1.883552000	-0.476869000
1	-5.058922000	-2.953629000	-0.490381000
6	-5.753913000	-2.406119000	0.159309000

Int_d

6	2.762039000	-2.859102000	-0.873807000
6	2.130864000	-1.977798000	-1.759761000
6	2.083522000	-0.587016000	-1.492517000
6	2.649211000	-0.110686000	-0.286629000
6	3.273637000	-1.011987000	0.574450000
6	3.344098000	-2.379948000	0.298226000
1	2.625009000	0.946417000	-0.055510000
7	3.857102000	-0.500673000	1.819254000
8	4.451713000	-1.296734000	2.548169000
8	3.722978000	0.698852000	2.072863000
1	1.701665000	-2.350664000	-2.685019000
1	3.837859000	-3.047691000	0.993644000
1	2.801352000	-3.919390000	-1.100852000
46	0.038452000	-0.714689000	-0.482662000
6	0.024981000	0.636071000	-2.001720000
6	1.453444000	0.397422000	-2.490282000
1	2.036236000	1.321548000	-2.520867000
1	1.446753000	-0.049369000	-3.487340000
1	-0.766893000	0.312829000	-2.676986000

8	-1.414116000	2.480261000	-1.464752000
6	-0.320562000	1.951928000	-1.373788000
8	0.711551000	2.470410000	-0.684772000
6	0.415492000	3.609951000	0.164351000
1	-0.438123000	3.341790000	0.792188000
1	0.139922000	4.460032000	-0.468743000
1	2.512229000	4.124410000	0.331223000
6	1.661729000	3.887023000	0.980439000
1	1.922871000	3.018106000	1.594492000
1	1.484867000	4.740988000	1.644054000
8	-1.959329000	-0.415183000	-0.030201000
8	-1.290453000	1.087939000	1.523656000
6	-2.156311000	0.497351000	0.869419000
6	-3.629084000	0.879746000	1.099522000
1	-3.731501000	1.931632000	0.813715000
1	-3.831671000	0.801085000	2.169839000
7	-4.606079000	0.092451000	0.378096000
1	-4.689172000	0.274173000	-0.614488000
6	-4.965440000	-1.150082000	0.819069000
8	-4.681657000	-1.562083000	1.943820000
1	-6.450800000	-2.626961000	0.362024000
1	-6.288510000	-1.382162000	-0.911817000
1	-5.047244000	-2.637425000	-0.720579000
6	-5.747000000	-1.988502000	-0.178347000

TS_{de}

6	-5.167101000	-1.165840000	-0.622267000
6	-3.906890000	-1.764852000	-0.650803000
6	-2.765025000	-1.066751000	-0.222680000
6	-2.892517000	0.259341000	0.222518000
6	-4.160646000	0.831438000	0.237488000
6	-5.306352000	0.144485000	-0.173798000
1	-2.026618000	0.839306000	0.529676000
7	-4.306242000	2.221074000	0.701137000
8	-3.290476000	2.832753000	1.031552000
1	-3.803049000	-2.787408000	-1.003040000
1	-6.272591000	0.632184000	-0.144416000
1	-6.040553000	-1.719962000	-0.950720000
46	0.217109000	-0.567535000	-1.248729000
8	1.718093000	0.614936000	-0.401467000
8	0.287305000	1.633885000	1.025474000
6	1.414899000	1.422895000	0.557975000
6	2.598279000	2.198057000	1.171615000
1	2.544772000	2.082692000	2.258252000
1	2.451748000	3.256860000	0.941937000
7	3.911416000	1.805183000	0.706819000
1	4.265762000	0.919610000	1.046515000
6	4.405151000	2.259582000	-0.483738000
8	3.909783000	3.208622000	-1.090610000
1	6.227194000	2.177891000	-1.612904000
1	6.227473000	1.079537000	-0.201179000

1	5.273682000	0.681418000	-1.643249000
6	5.617190000	1.505487000	-1.004558000
6	-1.470464000	-1.779662000	-0.228390000
1	-1.502243000	-2.809963000	-0.574409000
6	-0.363920000	-1.421512000	0.578512000
1	-0.421150000	-0.580828000	1.262586000
6	0.712716000	-2.423409000	0.847681000
8	0.772842000	-3.536521000	0.355675000
8	1.609813000	-1.902136000	1.697197000
6	2.857033000	-2.627391000	1.872720000
1	2.641739000	-3.692773000	1.990333000
1	3.262709000	-2.236411000	2.807991000
6	3.786354000	-2.359785000	0.699386000
1	3.901863000	-1.282034000	0.546042000
1	3.386188000	-2.798782000	-0.220160000
1	4.770030000	-2.800949000	0.896212000
1	-0.791549000	-1.535041000	-1.979591000
8	-5.441221000	2.701581000	0.735428000

Int_e

6	-4.853438000	-1.323289000	-0.925823000
6	-3.578731000	-1.882701000	-0.842876000
6	-2.524109000	-1.195954000	-0.212113000
6	-2.760169000	0.080129000	0.332968000
6	-4.040878000	0.612684000	0.230799000
6	-5.097722000	-0.063290000	-0.386041000
1	-1.963941000	0.653713000	0.801744000
7	-4.299114000	1.949650000	0.792178000
8	-3.362887000	2.548078000	1.320614000
1	-3.391882000	-2.865048000	-1.267848000
1	-6.078365000	0.392792000	-0.438786000
1	-5.656921000	-1.867639000	-1.411438000
46	0.320259000	-0.622566000	-1.261121000
8	0.994009000	1.197221000	-0.475544000
8	0.037628000	1.511142000	1.545342000
6	0.948542000	1.674566000	0.721508000
6	2.163588000	2.541686000	1.107647000
1	2.222579000	2.588837000	2.198388000
1	2.007082000	3.553883000	0.722622000
7	3.411452000	2.051960000	0.554423000
1	3.694028000	1.122506000	0.843852000
6	3.903197000	2.504708000	-0.638570000
8	3.502012000	3.531650000	-1.183963000
1	5.606316000	2.240333000	-1.917320000
1	5.634222000	1.177427000	-0.479566000
1	4.530190000	0.829467000	-1.822826000
6	4.995649000	1.636572000	-1.242009000
6	-1.216786000	-1.866534000	-0.145354000
1	-1.198829000	-2.881750000	-0.532291000
6	-0.117333000	-1.471940000	0.638584000

1	-0.177784000	-0.605845000	1.292990000
6	1.002144000	-2.427534000	0.911324000
8	1.080332000	-3.565311000	0.487875000
8	1.914053000	-1.824406000	1.692675000
6	3.166075000	-2.526538000	1.923037000
1	2.962755000	-3.592820000	2.049292000
1	3.536921000	-2.115499000	2.864245000
6	4.126324000	-2.263283000	0.774924000
1	4.285387000	-1.186476000	0.646017000
1	3.733909000	-2.675372000	-0.160725000
1	5.092918000	-2.735741000	0.983653000
1	0.169080000	-1.979519000	-1.991460000
8	-5.443156000	2.401355000	0.702600000

Int$_f$

6	4.404791000	-1.024108000	-1.836203000
6	3.134312000	-0.472302000	-2.010327000
6	2.490854000	0.234118000	-0.975086000
6	3.168299000	0.379769000	0.246974000
6	4.434417000	-0.175871000	0.397364000
6	5.075896000	-0.882770000	-0.623670000
1	2.717692000	0.908582000	1.076656000
7	5.122875000	-0.013569000	1.685569000
8	4.541219000	0.595937000	2.586407000
1	2.623325000	-0.590552000	-2.962341000
1	6.061751000	-1.301332000	-0.465695000
1	4.876203000	-1.565223000	-2.651046000
46	-0.348094000	-0.328603000	-0.161722000
8	-1.354325000	-2.228751000	0.278067000
8	-1.982749000	-3.143300000	-1.634632000
6	-2.240916000	-2.746353000	-0.389335000
6	-3.639937000	-3.010070000	0.164191000
1	-3.683210000	-4.048998000	0.507081000
1	-4.370593000	-2.891728000	-0.643838000
7	-3.951500000	-2.130430000	1.261247000
1	-3.901719000	-2.495458000	2.203583000
6	-3.948531000	-0.780220000	1.057331000
8	-3.814207000	-0.313745000	-0.076995000
1	-4.843202000	0.862511000	2.090407000
1	-4.387553000	-0.478841000	3.179423000
1	-3.140523000	0.583070000	2.477138000
6	-4.099224000	0.085832000	2.287979000
6	1.142759000	0.787607000	-1.213781000
1	0.834148000	0.793991000	-2.258536000
6	0.438343000	1.638561000	-0.338519000
1	0.860447000	1.966899000	0.608030000
6	-0.674567000	2.465361000	-0.861954000
8	-1.096773000	2.455148000	-2.008293000
8	-1.171184000	3.256586000	0.120676000
6	-2.376520000	4.006419000	-0.168634000

1	-2.443768000	4.179095000	-1.245105000
1	-2.246565000	4.965965000	0.339861000
6	-3.588308000	3.253489000	0.357995000
1	-3.524304000	3.133535000	1.445194000
1	-3.657696000	2.256780000	-0.091030000
1	-4.503836000	3.811325000	0.125926000
8	6.251710000	-0.495710000	1.805052000
1	-2.777436000	-3.532015000	-2.052412000

***para*-TS3**

6	-1.847732000	-1.083716000	3.306534000
6	-2.512468000	-1.395341000	2.109147000
6	-1.822291000	-2.031590000	1.060744000
6	-0.469858000	-2.309165000	1.179422000
6	0.183227000	-1.951767000	2.364803000
6	-0.484901000	-1.337452000	3.430266000
1	0.067721000	-2.762901000	0.357780000
7	1.599459000	-2.228755000	2.491026000
8	2.257440000	-1.628212000	3.339117000
8	2.097121000	-3.077631000	1.725372000
1	0.053840000	-1.077987000	4.334278000
1	-2.385743000	-0.623951000	4.129406000
8	-0.146660000	-2.403032000	-2.658509000
6	0.938310000	-3.021448000	-3.371649000
1	1.624596000	-2.272248000	-3.771364000
1	0.481734000	-3.552391000	-4.214733000
6	1.686832000	-4.040135000	-2.512138000
1	0.981920000	-4.786299000	-2.136079000
1	2.409166000	-4.550906000	-3.159715000
7	2.371180000	-3.480075000	-1.356014000
1	1.971939000	-3.640050000	-0.440989000
6	3.478699000	-2.693485000	-1.493846000
8	3.949768000	-2.402719000	-2.597656000
7	3.994529000	-2.236800000	-0.285999000
1	3.528153000	-2.559459000	0.558223000
6	4.897212000	-1.190674000	-0.088869000
6	5.642888000	-0.590479000	-1.115945000
6	5.049983000	-0.718334000	1.228961000
6	6.510245000	0.460834000	-0.811929000
6	5.926955000	0.325406000	1.502954000
6	6.670739000	0.933223000	0.488402000
1	5.534543000	-0.941471000	-2.131930000
1	4.471219000	-1.163675000	2.033182000
1	7.351219000	1.746654000	0.708029000
6	6.020418000	0.861012000	2.905369000
9	5.726401000	-0.076206000	3.834503000
9	7.257264000	1.332700000	3.186500000
9	5.159725000	1.890893000	3.105642000
6	7.334203000	1.042496000	-1.928330000
9	6.622490000	1.162566000	-3.073777000

9	7.818908000	2.268337000	-1.627287000
9	8.403212000	0.259809000	-2.221139000
6	-0.080514000	-1.088670000	-2.290927000
6	1.110204000	-0.374558000	-2.090224000
6	-1.310878000	-0.446819000	-2.079696000
6	1.058178000	0.939049000	-1.625921000
6	-1.351754000	0.868578000	-1.633758000
6	-0.164931000	1.578882000	-1.367305000
1	2.074437000	-0.827076000	-2.279189000
1	-2.238727000	-0.977629000	-2.263371000
1	1.991795000	1.460187000	-1.431096000
1	-2.318048000	1.348563000	-1.522498000
6	-0.184042000	2.951751000	-0.809295000
6	0.670417000	3.947390000	-1.307041000
6	-1.037145000	3.316015000	0.265627000
6	0.672490000	5.238266000	-0.778345000
6	-1.039562000	4.616690000	0.799000000
6	-0.184509000	5.579372000	0.273816000
1	1.326879000	3.704948000	-2.137195000
6	-1.899284000	2.338681000	0.843202000
1	1.341505000	5.985439000	-1.196225000
1	-1.706487000	4.855535000	1.621147000
1	-0.184461000	6.585573000	0.681398000
7	-2.579889000	1.515804000	1.297804000
46	-3.980973000	-0.125091000	1.354371000
6	-5.391243000	-1.663940000	1.536560000
6	-4.391863000	-2.223541000	2.386599000
1	-3.942364000	-3.167440000	2.100354000
1	-4.486535000	-2.062601000	3.456682000
1	-6.236616000	-1.154057000	1.993255000
8	-6.766297000	-2.077425000	-0.368750000
6	-5.697094000	-2.231421000	0.190764000
8	-4.667394000	-2.932967000	-0.316534000
6	-4.791196000	-3.336181000	-1.704304000
1	-4.964123000	-2.432537000	-2.294964000
1	-5.660093000	-3.995047000	-1.803745000
1	-3.323909000	-4.905055000	-1.441714000
6	-3.505345000	-4.040483000	-2.090604000
1	-2.642466000	-3.368813000	-2.029285000
1	-3.584096000	-4.397661000	-3.123951000
8	-5.291430000	1.119945000	0.263639000
8	-4.556747000	-0.046912000	-1.528516000
6	-5.164705000	0.896249000	-1.001319000
6	-5.873158000	1.923574000	-1.905849000
1	-6.914694000	1.616330000	-2.043420000
1	-5.376446000	1.904238000	-2.878382000
7	-5.863185000	3.274634000	-1.372813000
1	-6.666832000	3.575322000	-0.836214000
6	-4.672560000	3.894279000	-1.140771000
8	-3.606736000	3.437401000	-1.562114000

1	-3.922467000	5.833051000	-0.624647000
1	-5.695622000	5.691958000	-0.429119000
1	-4.600774000	4.919069000	0.735326000
6	-4.738251000	5.171223000	-0.324017000
1	-2.348859000	-2.300203000	0.152754000

***ortho*-TS3**

6	0.672973000	-2.440065000	4.409381000
6	1.800584000	-3.084506000	3.886398000
6	2.650226000	-2.413136000	3.007725000
6	2.367801000	-1.107134000	2.568660000
6	1.235369000	-0.482380000	3.123706000
6	0.400585000	-1.126430000	4.047438000
7	0.851995000	0.859426000	2.710860000
8	0.037383000	1.473257000	3.427038000
8	1.308705000	1.339185000	1.673045000
1	-0.462665000	-0.609398000	4.447460000
1	0.011841000	-2.954933000	5.098749000
8	-0.202416000	4.323525000	-1.859545000
6	-1.021776000	5.311773000	-1.220964000
1	-2.079913000	5.166478000	-1.442257000
1	-0.713201000	6.270828000	-1.648363000
6	-0.788871000	5.350966000	0.295206000
1	0.239715000	5.657080000	0.500476000
1	-1.460312000	6.105486000	0.720226000
7	-0.990778000	4.079721000	0.977481000
1	-0.174270000	3.490098000	1.095898000
6	-2.225449000	3.494710000	1.049463000
8	-3.249809000	4.007741000	0.598710000
7	-2.195244000	2.260600000	1.703439000
1	-1.349191000	2.064017000	2.233448000
6	-2.987990000	1.148844000	1.417732000
6	-4.188239000	1.210690000	0.689425000
6	-2.528076000	-0.106666000	1.847140000
6	-4.859981000	0.030748000	0.371170000
6	-3.222514000	-1.269028000	1.525004000
6	-4.395698000	-1.222755000	0.774703000
1	-4.564343000	2.168591000	0.359064000
1	-1.606308000	-0.182018000	2.408832000
1	-4.922929000	-2.128180000	0.502927000
6	-2.648754000	-2.577342000	1.994571000
9	-2.667986000	-2.679301000	3.347885000
9	-3.312123000	-3.644536000	1.503358000
9	-1.347261000	-2.713756000	1.629586000
6	-6.056689000	0.111671000	-0.533854000
9	-6.767281000	1.246836000	-0.352566000
9	-5.683651000	0.096962000	-1.845196000
9	-6.903853000	-0.927858000	-0.366928000
6	-0.651046000	3.039734000	-2.003963000
6	-1.998434000	2.649532000	-1.989601000

6	0.338184000	2.069561000	-2.222540000
6	-2.328920000	1.301163000	-2.101094000
6	-0.003516000	0.727349000	-2.339664000
6	-1.344260000	0.308684000	-2.243187000
1	-2.791851000	3.365726000	-1.824768000
1	1.381015000	2.359364000	-2.276113000
1	-3.373090000	1.018531000	-2.027960000
1	0.781099000	0.005615000	-2.533269000
6	-1.737021000	-1.119474000	-2.232608000
6	-2.915339000	-1.541372000	-2.872347000
6	-1.004968000	-2.112712000	-1.528463000
6	-3.348904000	-2.864674000	-2.817502000
6	-1.440916000	-3.450294000	-1.473216000
6	-2.613612000	-3.826830000	-2.116495000
1	-3.496710000	-0.813943000	-3.428964000
6	0.173995000	-1.791033000	-0.792099000
1	-4.265723000	-3.146909000	-3.327747000
1	-0.861755000	-4.174253000	-0.909409000
1	-2.952301000	-4.857148000	-2.069840000
7	1.124117000	-1.569333000	-0.164406000
46	3.005683000	-0.849533000	0.584286000
6	4.775151000	0.018614000	1.301984000
6	4.070558000	0.036440000	2.544410000
1	3.611045000	0.970322000	2.850560000
1	4.459972000	-0.579196000	3.346937000
1	5.577594000	-0.705579000	1.178563000
8	5.932340000	1.413475000	-0.249253000
6	4.995617000	1.273197000	0.515184000
8	4.077428000	2.210426000	0.783996000
6	4.075238000	3.388279000	-0.057850000
1	4.182395000	3.062305000	-1.093915000
1	4.934390000	4.013371000	0.212583000
1	2.636445000	4.367282000	1.232492000
6	2.757023000	4.100287000	0.176360000
1	1.921055000	3.463994000	-0.124769000
1	2.724619000	5.018137000	-0.421308000
8	3.756137000	-1.089063000	-1.347099000
8	3.260022000	1.021959000	-1.988086000
6	3.589997000	-0.146838000	-2.211497000
6	3.866293000	-0.577909000	-3.668544000
1	4.889397000	-0.291053000	-3.931879000
1	3.181133000	-0.021056000	-4.311224000
7	3.710836000	-2.002639000	-3.904180000
1	4.520850000	-2.584919000	-3.730931000
6	2.485629000	-2.578314000	-3.737920000
8	1.451173000	-1.910746000	-3.665667000
1	1.547011000	-4.473389000	-4.077803000
1	3.334097000	-4.562092000	-4.116142000
1	2.475373000	-4.365103000	-2.572360000
6	2.470668000	-4.091164000	-3.635470000

1	3.553095000	-2.903454000	2.654554000
1	2.026704000	-4.106812000	4.175706000

HT1-TS2

6	-2.661320000	-1.647701000	3.008197000
6	-3.710623000	-1.403400000	2.119875000
6	-3.561134000	-1.576312000	0.723895000
6	-2.317623000	-2.024792000	0.241341000
6	-1.279847000	-2.260591000	1.141901000
6	-1.431598000	-2.082397000	2.522495000
1	-2.157640000	-2.177332000	-0.819517000
7	0.025554000	-2.669678000	0.632063000
8	0.913765000	-2.935963000	1.458825000
8	0.204020000	-2.718751000	-0.584646000
1	-4.673983000	-1.085754000	2.510064000
1	-4.630439000	-2.112906000	0.193360000
1	-0.602127000	-2.277768000	3.190749000
1	-2.796295000	-1.503417000	4.075634000
8	5.852496000	-3.158478000	-2.042830000
6	6.743843000	-3.186038000	-0.912429000
1	7.089234000	-2.182624000	-0.655481000
1	7.605809000	-3.784004000	-1.222021000
6	6.076217000	-3.838666000	0.303932000
1	5.851197000	-4.886430000	0.088176000
1	6.779809000	-3.805353000	1.142480000
7	4.819174000	-3.209352000	0.696922000
1	3.992002000	-3.554757000	0.224971000
6	4.798121000	-1.910918000	1.140631000
8	5.817742000	-1.278506000	1.414950000
7	3.510387000	-1.392643000	1.260220000
1	2.732955000	-2.042984000	1.172035000
6	3.159380000	-0.045548000	1.375648000
6	4.052889000	1.007607000	1.123143000
6	1.823301000	0.264018000	1.683387000
6	3.588945000	2.322305000	1.124789000
6	1.386368000	1.585852000	1.684532000
6	2.257538000	2.635997000	1.394486000
1	5.087457000	0.791667000	0.902715000
1	1.126093000	-0.532685000	1.909766000
1	1.907909000	3.660783000	1.374482000
6	-0.040911000	1.896218000	2.040490000
9	-0.524613000	2.941494000	1.326543000
9	-0.866335000	0.845876000	1.814547000
9	-0.179553000	2.224595000	3.347664000
6	4.540251000	3.407692000	0.705845000
9	5.795345000	3.196483000	1.161453000
9	4.635845000	3.483954000	-0.652371000
9	4.154266000	4.629928000	1.131243000
6	4.964103000	-2.117734000	-2.127088000
6	5.329501000	-0.777846000	-1.939619000

6	3.636404000	-2.428724000	-2.446528000
6	4.358920000	0.219648000	-1.985700000
6	2.675669000	-1.423567000	-2.500404000
6	3.009085000	-0.082015000	-2.235765000
1	6.357742000	-0.513343000	-1.718942000
1	3.367764000	-3.466753000	-2.618877000
1	4.653171000	1.240046000	-1.765894000
1	1.651604000	-1.693232000	-2.737465000
6	1.963924000	0.965912000	-2.140973000
6	2.229837000	2.317580000	-2.435615000
6	0.675512000	0.635416000	-1.698212000
6	1.252919000	3.304823000	-2.289115000
6	-0.308062000	1.629042000	-1.572198000
6	-0.028771000	2.976644000	-1.856752000
1	3.213474000	2.603365000	-2.792143000
1	1.494877000	4.337790000	-2.519910000
1	-0.796933000	3.732991000	-1.737767000
46	-4.508964000	0.063935000	-0.398019000
8	-5.436285000	1.681961000	-1.228402000
6	-6.744070000	1.685766000	-1.118912000
8	-7.445320000	2.625442000	-1.471892000
1	-7.891095000	0.732496000	0.422175000
6	-7.390484000	0.433563000	-0.508634000
1	-8.165201000	0.089700000	-1.202274000
7	-6.391166000	-0.601386000	-0.255303000
6	-6.685862000	-1.884887000	-0.151708000
6	-8.124979000	-2.348341000	-0.202497000
1	-8.525225000	-2.213636000	-1.214517000
1	-8.172146000	-3.405875000	0.061161000
1	-8.750059000	-1.768420000	0.483921000
8	-5.780007000	-2.775872000	-0.006601000
6	-1.602244000	1.236210000	-1.124615000
7	-2.639228000	0.863508000	-0.765236000
1	0.432290000	-0.384241000	-1.422555000

HT1-TS3

6	-0.393285000	-3.391124000	0.073071000
6	-1.630180000	-3.222428000	-0.560566000
6	-2.044341000	-1.949861000	-0.981487000
6	-1.182571000	-0.856240000	-0.842159000
6	0.035909000	-1.051089000	-0.193084000
6	0.449102000	-2.301268000	0.280570000
1	-1.459943000	0.125186000	-1.207684000
7	0.915143000	0.095769000	-0.006099000
8	1.807895000	0.007815000	0.850192000
8	0.747578000	1.099434000	-0.701168000
1	-2.279180000	-4.080162000	-0.711279000
1	1.410990000	-2.420155000	0.763594000
1	-0.085276000	-4.377179000	0.407422000
8	2.210991000	5.637566000	0.454724000

6	3.513917000	5.461360000	-0.126427000
1	4.250854000	5.145353000	0.620613000
1	3.788949000	6.460729000	-0.475344000
6	3.498492000	4.498107000	-1.316958000
1	2.645611000	4.742063000	-1.959379000
1	4.415447000	4.644423000	-1.893219000
7	3.430724000	3.091058000	-0.954140000
1	2.541680000	2.714603000	-0.646824000
6	4.556014000	2.314692000	-0.893248000
8	5.659807000	2.688633000	-1.294314000
7	4.321194000	1.059765000	-0.335861000
1	3.418364000	0.909740000	0.108655000
6	5.188359000	-0.032722000	-0.295652000
6	6.475098000	-0.041061000	-0.863161000
6	4.723851000	-1.203500000	0.331836000
6	7.248645000	-1.200946000	-0.802040000
6	5.514074000	-2.347233000	0.373748000
6	6.790194000	-2.367379000	-0.190217000
1	6.851702000	0.848331000	-1.346367000
1	3.736093000	-1.220543000	0.776328000
1	7.400305000	-3.261719000	-0.162043000
6	4.985210000	-3.560247000	1.088177000
9	3.643637000	-3.699976000	0.932487000
9	5.557300000	-4.703188000	0.650398000
9	5.209221000	-3.496166000	2.423899000
6	8.643126000	-1.164063000	-1.366294000
9	8.741284000	-0.343889000	-2.437821000
9	9.540391000	-0.714564000	-0.452693000
9	9.069307000	-2.387338000	-1.757128000
6	1.638236000	4.611570000	1.155196000
6	2.340038000	3.749323000	2.010444000
6	0.252058000	4.465726000	1.013910000
6	1.660721000	2.728799000	2.672724000
6	-0.416740000	3.449626000	1.687333000
6	0.276307000	2.548651000	2.515545000
1	3.412236000	3.849633000	2.137057000
1	-0.281972000	5.150481000	0.362006000
1	2.225781000	2.040387000	3.294106000
1	-1.492327000	3.356252000	1.566143000
6	-0.427444000	1.407550000	3.147307000
6	-0.095327000	0.928099000	4.429152000
6	-1.443792000	0.749514000	2.445295000
6	-0.755041000	-0.168686000	4.989231000
6	-2.099818000	-0.356636000	3.010661000
6	-1.763819000	-0.828475000	4.288806000
1	0.680755000	1.429573000	4.999908000
1	-0.480410000	-0.510416000	5.982642000
1	-2.276121000	-1.686593000	4.710413000
46	-4.065212000	-1.444204000	-0.819865000
6	-4.244773000	-1.336564000	-2.910136000

6	-2.978124000	-1.975523000	-2.890159000
1	-2.112338000	-1.430183000	-3.245587000
1	-2.941919000	-3.052207000	-3.025039000
1	-5.132913000	-1.927860000	-3.119588000
8	-5.416836000	0.602157000	-3.669092000
6	-4.389628000	0.113288000	-3.238241000
8	-3.263462000	0.805417000	-2.987236000
6	-3.376581000	2.252356000	-3.023946000
1	-4.228377000	2.532368000	-2.398959000
1	-3.571176000	2.564934000	-4.055338000
1	-1.222731000	2.480094000	-3.101893000
6	-2.072076000	2.815953000	-2.496752000
1	-1.903519000	2.506335000	-1.459928000
1	-2.106820000	3.910993000	-2.527173000
8	-6.064239000	-0.816855000	-0.603803000
8	-5.201882000	1.265507000	-0.434896000
6	-6.145873000	0.462466000	-0.463125000
6	-7.575651000	1.026445000	-0.359632000
1	-7.785567000	1.560752000	-1.292281000
1	-7.588348000	1.754057000	0.454343000
7	-8.618443000	0.046231000	-0.133240000
1	-8.911289000	-0.498571000	-0.934697000
6	-8.773010000	-0.523032000	1.099043000
8	-8.229643000	-0.073406000	2.108280000
1	-10.209692000	-1.768032000	2.090120000
1	-10.382836000	-1.783418000	0.310287000
1	-9.041177000	-2.647905000	1.090017000
6	-9.669204000	-1.749185000	1.139953000
1	-1.711054000	1.064179000	1.442923000
6	-3.056652000	-1.000849000	2.171448000
7	-3.756979000	-1.442633000	1.355781000

HT2-TS2

6	-2.955571000	-0.923038000	-3.326181000
6	-4.136000000	-0.563661000	-2.669626000
6	-4.143903000	0.377594000	-1.615146000
6	-2.924659000	0.979582000	-1.252618000
6	-1.755816000	0.604491000	-1.913164000
6	-1.749285000	-0.341926000	-2.947149000
1	-2.885198000	1.713990000	-0.456483000
7	-0.489198000	1.193733000	-1.505546000
8	0.515847000	0.936283000	-2.181791000
8	-0.459387000	1.920953000	-0.505720000
1	-5.074987000	-1.016187000	-2.977952000
1	-5.201871000	1.162970000	-1.628119000
1	-0.819969000	-0.609838000	-3.434917000
1	-2.969455000	-1.654232000	-4.128535000
8	2.201337000	3.320855000	2.617136000
6	2.864718000	4.433185000	1.994033000
1	3.937571000	4.259324000	1.902221000

1	2.706130000	5.291454000	2.653871000
6	2.262195000	4.729210000	0.614269000
1	1.225255000	5.058125000	0.721813000
1	2.833819000	5.543670000	0.156037000
7	2.245973000	3.572744000	-0.273686000
1	1.408165000	3.001243000	-0.237100000
6	3.416517000	2.966657000	-0.647641000
8	4.526987000	3.454685000	-0.440407000
7	3.210434000	1.741754000	-1.287685000
1	2.240244000	1.497229000	-1.471531000
6	4.076163000	0.646979000	-1.226264000
6	5.456690000	0.763777000	-1.007600000
6	3.509846000	-0.635441000	-1.337268000
6	6.228558000	-0.389059000	-0.858287000
6	4.303888000	-1.767472000	-1.193861000
6	5.674124000	-1.664376000	-0.944207000
1	5.901909000	1.743951000	-0.917322000
1	2.441073000	-0.742059000	-1.490121000
1	6.284342000	-2.550201000	-0.814225000
6	3.658366000	-3.123479000	-1.159034000
9	4.442623000	-4.078449000	-1.707999000
9	3.413969000	-3.518340000	0.121563000
9	2.471378000	-3.153400000	-1.804006000
6	7.673346000	-0.234156000	-0.476017000
9	8.242717000	0.856164000	-1.037085000
9	7.810366000	-0.089193000	0.871193000
9	8.420487000	-1.304965000	-0.825490000
6	4.047293000	1.727077000	2.378833000
6	4.424641000	0.395186000	2.196621000
6	2.684212000	2.052774000	2.416912000
6	3.472256000	-0.613365000	2.064180000
6	1.725064000	1.039214000	2.313149000
6	2.101918000	-0.300979000	2.131865000
1	5.479878000	0.150009000	2.122336000
1	3.792195000	-1.628432000	1.858115000
1	0.681775000	1.326590000	2.388577000
6	1.069757000	-1.363332000	1.997290000
6	1.335675000	-2.694653000	2.375786000
6	-0.207838000	-1.069090000	1.502439000
6	0.367853000	-3.694894000	2.270717000
6	-1.188064000	-2.073689000	1.427567000
6	-0.909933000	-3.398146000	1.804792000
1	2.308222000	-2.950009000	2.782385000
1	0.608348000	-4.709374000	2.573441000
1	-1.678795000	-4.160637000	1.738897000
46	-5.287697000	-0.354687000	0.110665000
8	-6.328324000	-1.164776000	1.664556000
6	-7.595560000	-0.830952000	1.727154000
8	-8.362994000	-1.265624000	2.576519000
1	-8.909357000	-0.341175000	0.108712000

6	-8.104212000	0.153303000	0.667674000
1	-8.548069000	1.006878000	1.193933000
7	-7.027939000	0.579221000	-0.225775000
6	-7.187912000	1.543230000	-1.113291000
6	-8.527033000	2.230225000	-1.259866000
1	-8.772826000	2.776449000	-0.341677000
1	-8.485853000	2.930237000	-2.095431000
1	-9.322234000	1.497247000	-1.432342000
8	-6.236244000	1.935239000	-1.873361000
6	-2.493597000	-1.703591000	0.989847000
7	-3.540809000	-1.338655000	0.652029000
1	-0.456317000	-0.067261000	1.170909000
1	4.807037000	2.493671000	2.474034000

HT2-TS3

6	1.663021000	3.851284000	-1.870741000
6	2.742236000	3.016162000	-2.184967000
6	2.669272000	1.638877000	-1.931964000
6	1.488030000	1.083933000	-1.428799000
6	0.435588000	1.941284000	-1.108307000
6	0.499399000	3.323092000	-1.317075000
1	1.396514000	0.016376000	-1.271443000
7	-0.775145000	1.373863000	-0.524127000
8	-1.695910000	2.130613000	-0.219680000
8	-0.822067000	0.144105000	-0.362326000
1	3.646802000	3.441876000	-2.609474000
1	-0.339913000	3.955548000	-1.056325000
1	1.733839000	4.919402000	-2.052440000
8	-1.448431000	-2.774004000	3.586181000
6	-2.079037000	-3.852600000	2.875284000
1	-3.168344000	-3.751863000	2.873934000
1	-1.817838000	-4.756442000	3.433254000
6	-1.554174000	-3.963404000	1.441704000
1	-0.465273000	-4.057961000	1.452776000
1	-1.974495000	-4.863456000	0.983369000
7	-1.885548000	-2.809862000	0.610996000
1	-1.268387000	-2.011210000	0.693314000
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7	-3.433821000	-1.303035000	-0.209505000
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6	-4.732313000	0.665941000	-0.609931000
6	-7.039861000	-0.817128000	-1.008219000
6	-5.934520000	1.300116000	-0.911212000
6	-7.107466000	0.572387000	-1.111288000
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1	-8.039578000	1.070709000	-1.347699000

6	-5.963153000	2.803019000	-0.950633000
9	-4.835137000	3.318571000	-1.493294000
9	-7.007377000	3.279382000	-1.664998000
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9	-8.058477000	-2.871703000	-1.628494000
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9	-9.177570000	-1.042074000	-2.012220000
6	-3.211034000	-1.103672000	3.276855000
6	-3.524034000	0.241000000	3.066375000
6	-1.865156000	-1.488028000	3.351901000
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6	-0.857826000	-0.524205000	3.244551000
6	-1.171923000	0.827670000	3.041813000
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6	2.122725000	2.457508000	2.100271000
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6	8.451484000	-0.775630000	1.488511000
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6	9.715125000	-0.022690000	1.108312000
1	1.237605000	0.515214000	1.809955000
6	3.255894000	2.083779000	1.320232000
7	4.090747000	1.709595000	0.603016000
1	-4.003474000	-1.838288000	3.370010000

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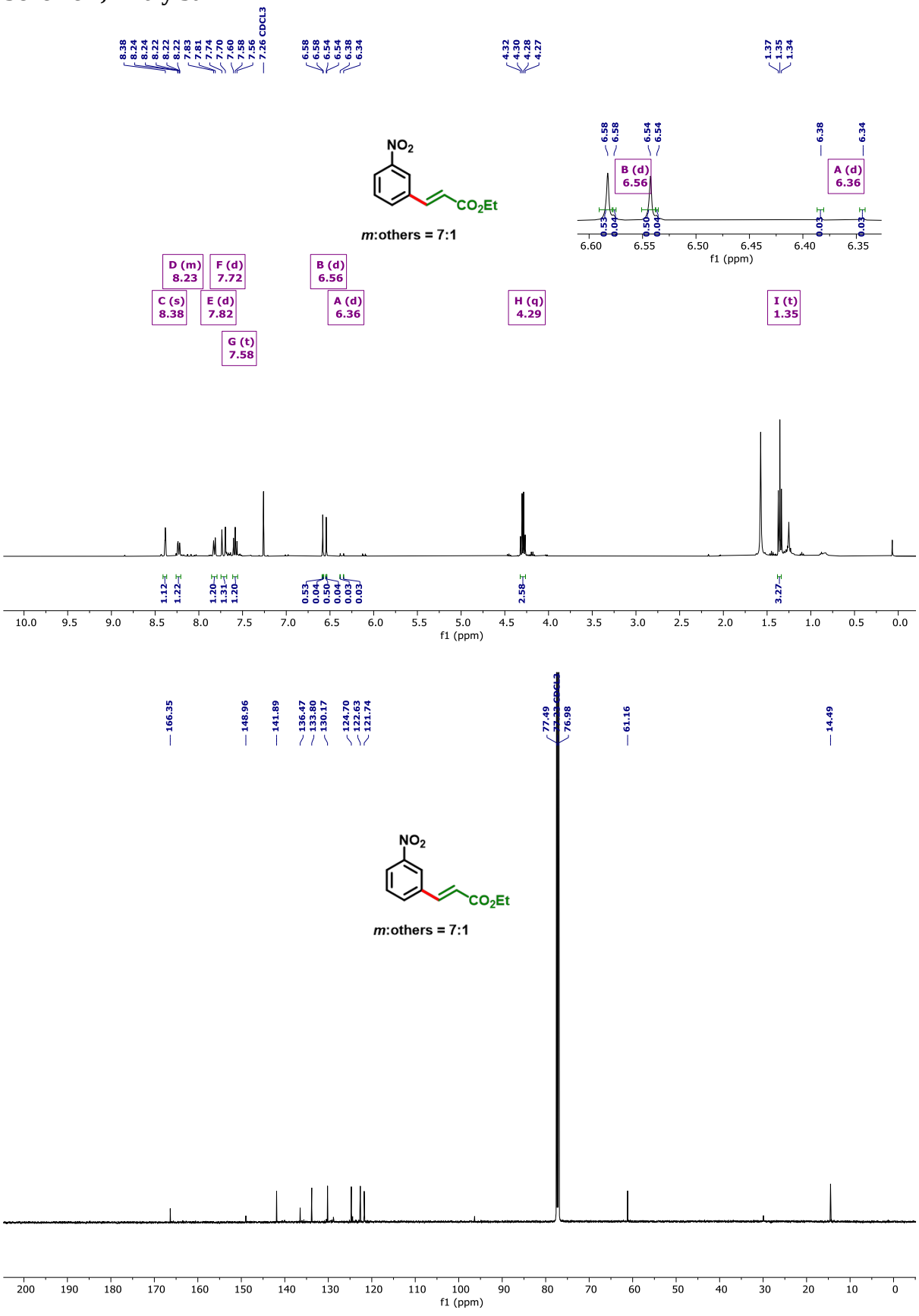
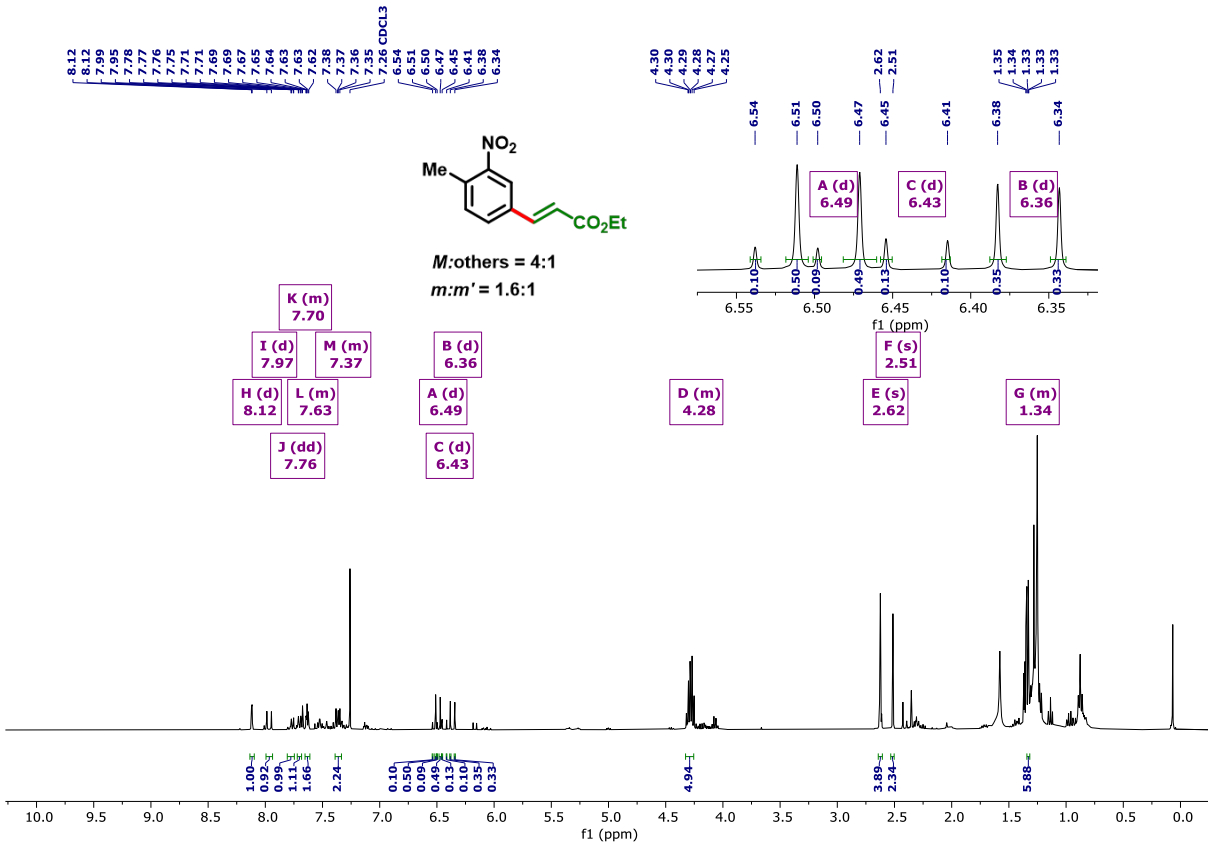
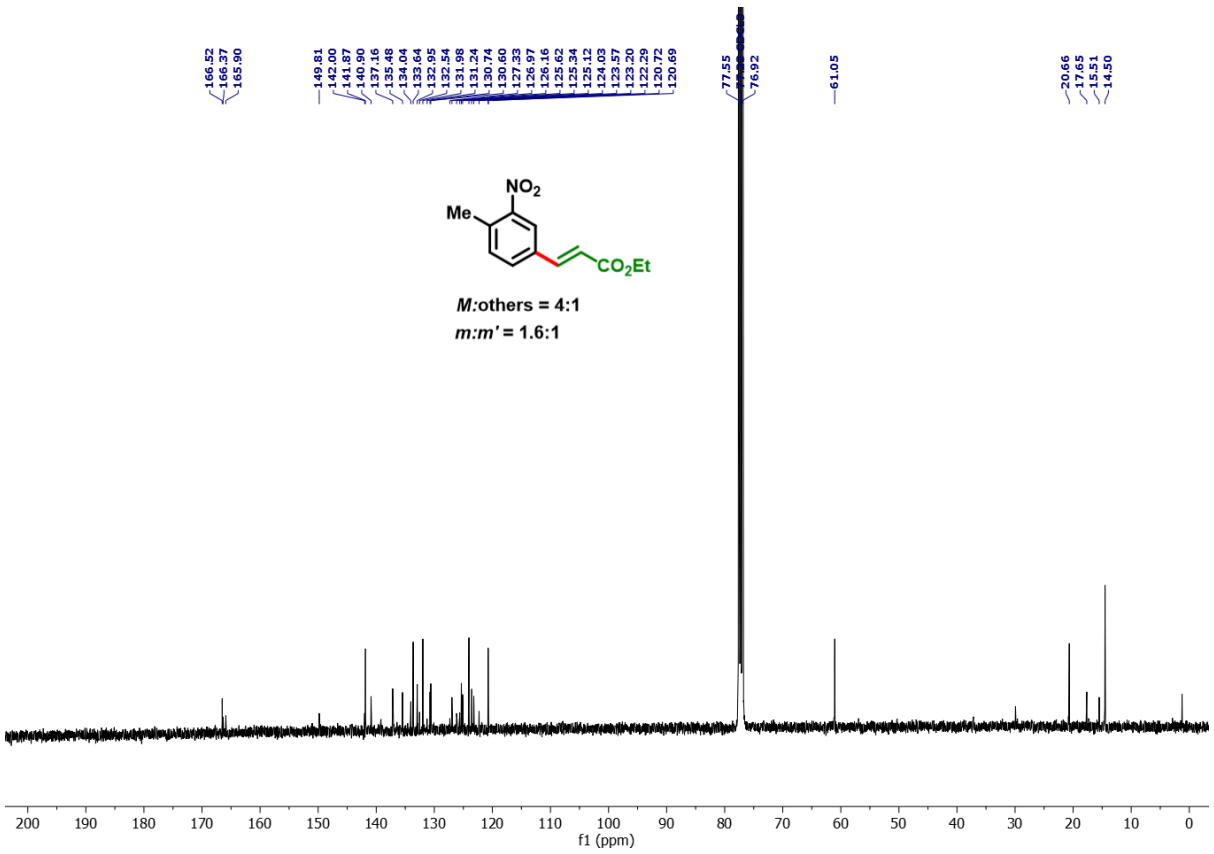
NMR SPECTRA

Scheme 2, Entry 3a

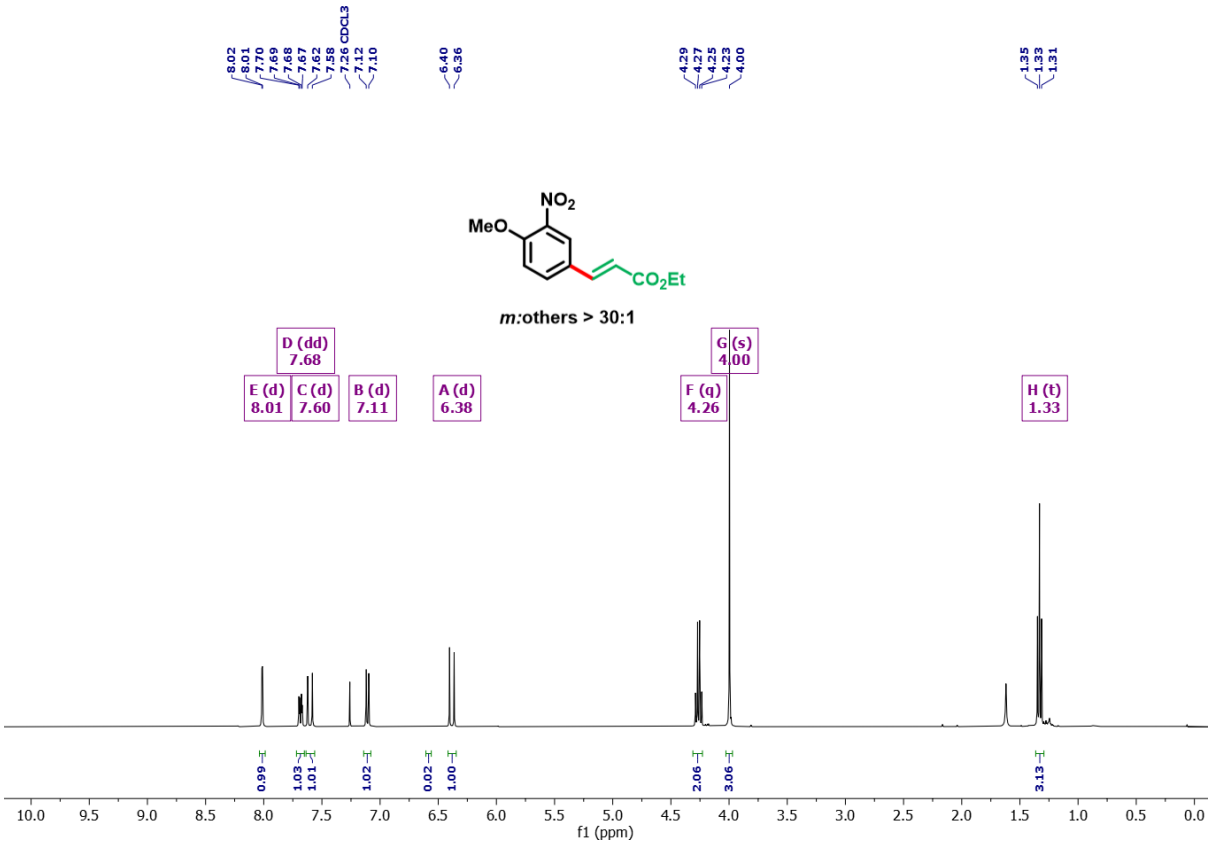


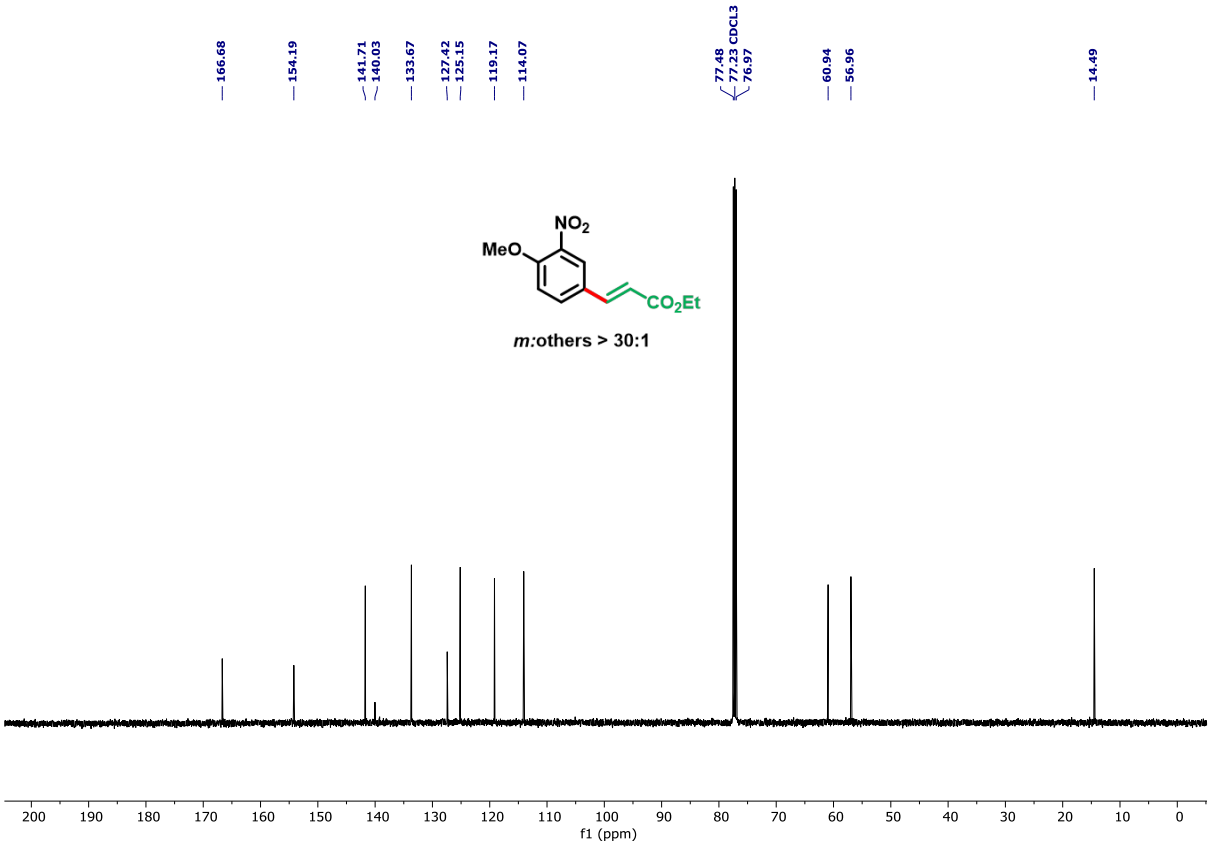
Scheme 2, Entry 3b



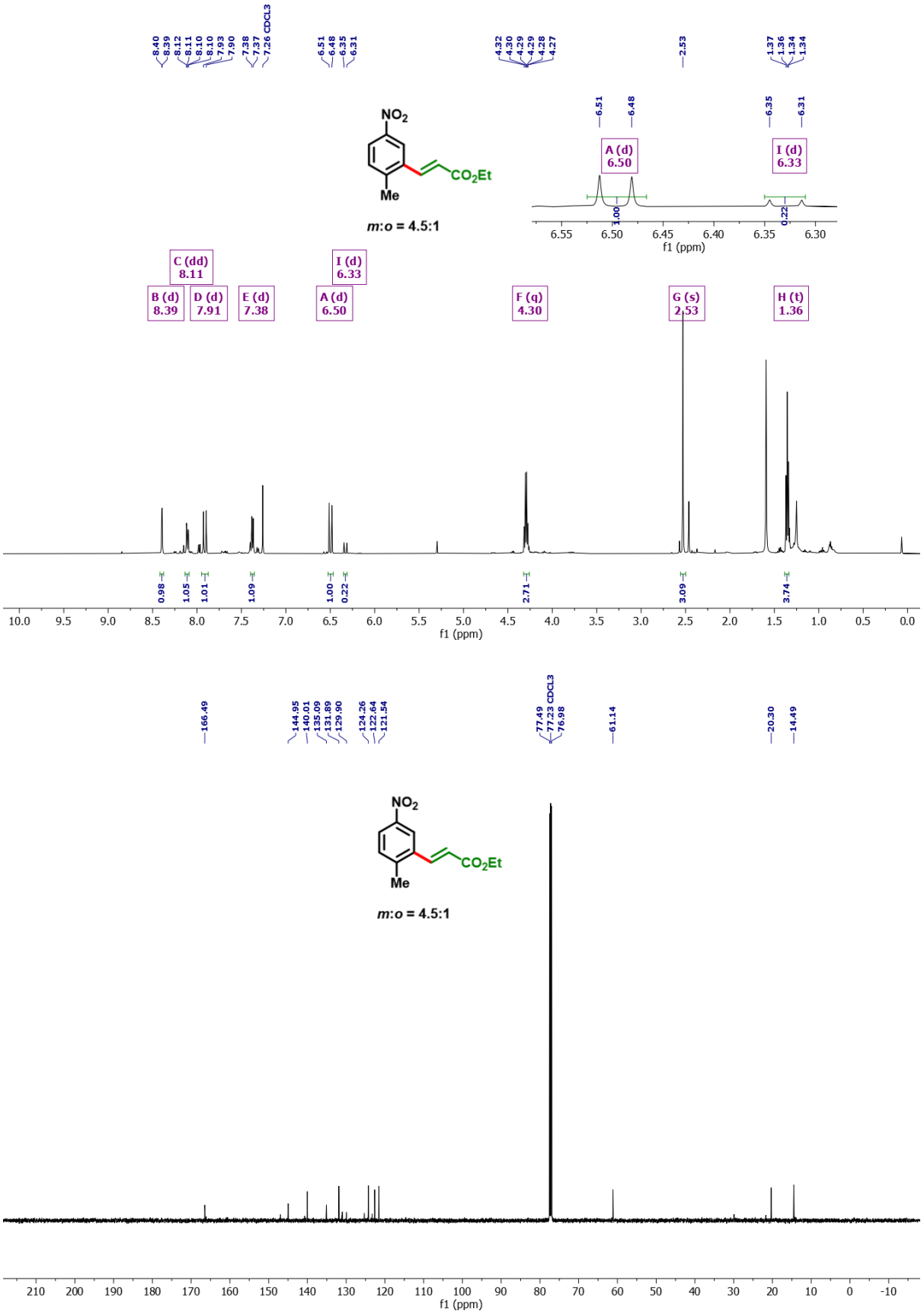


Scheme 2, Entry 3c

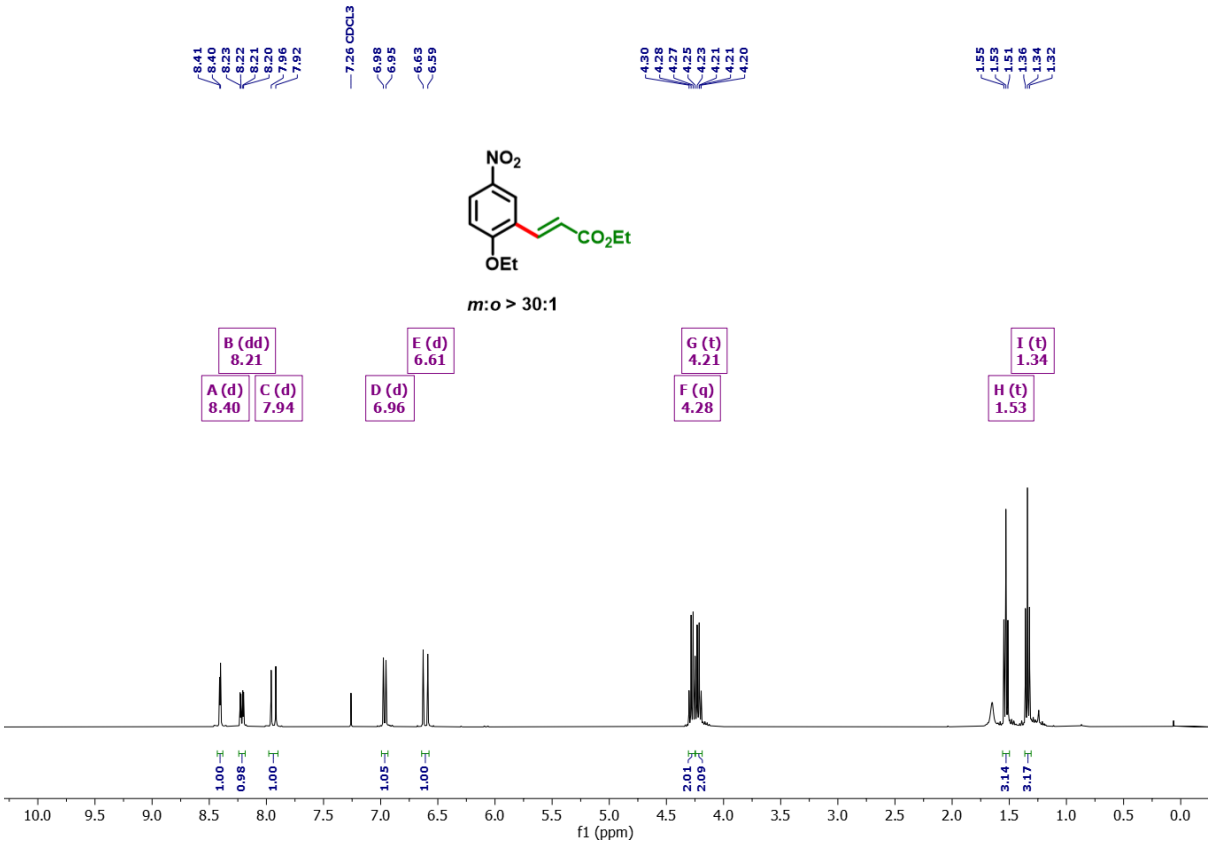


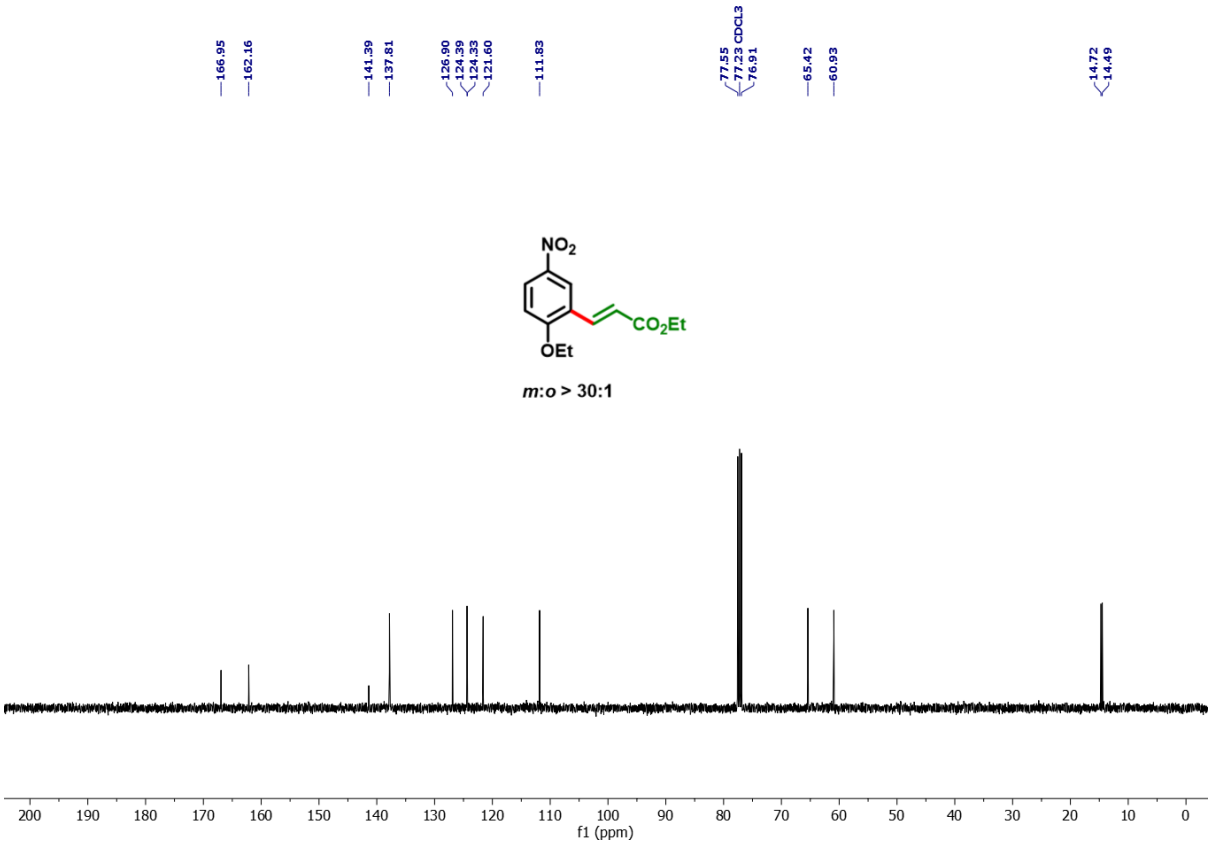


Scheme 2, Entry 3d

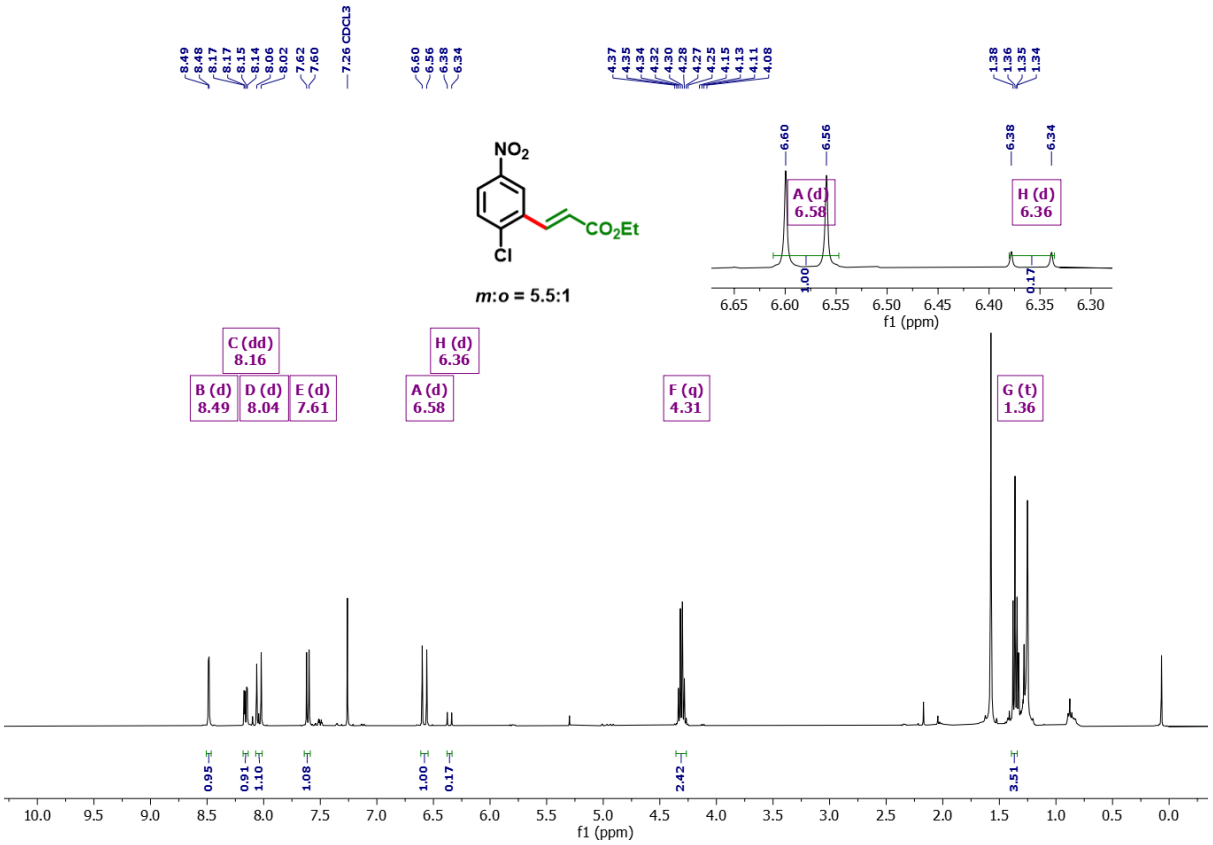


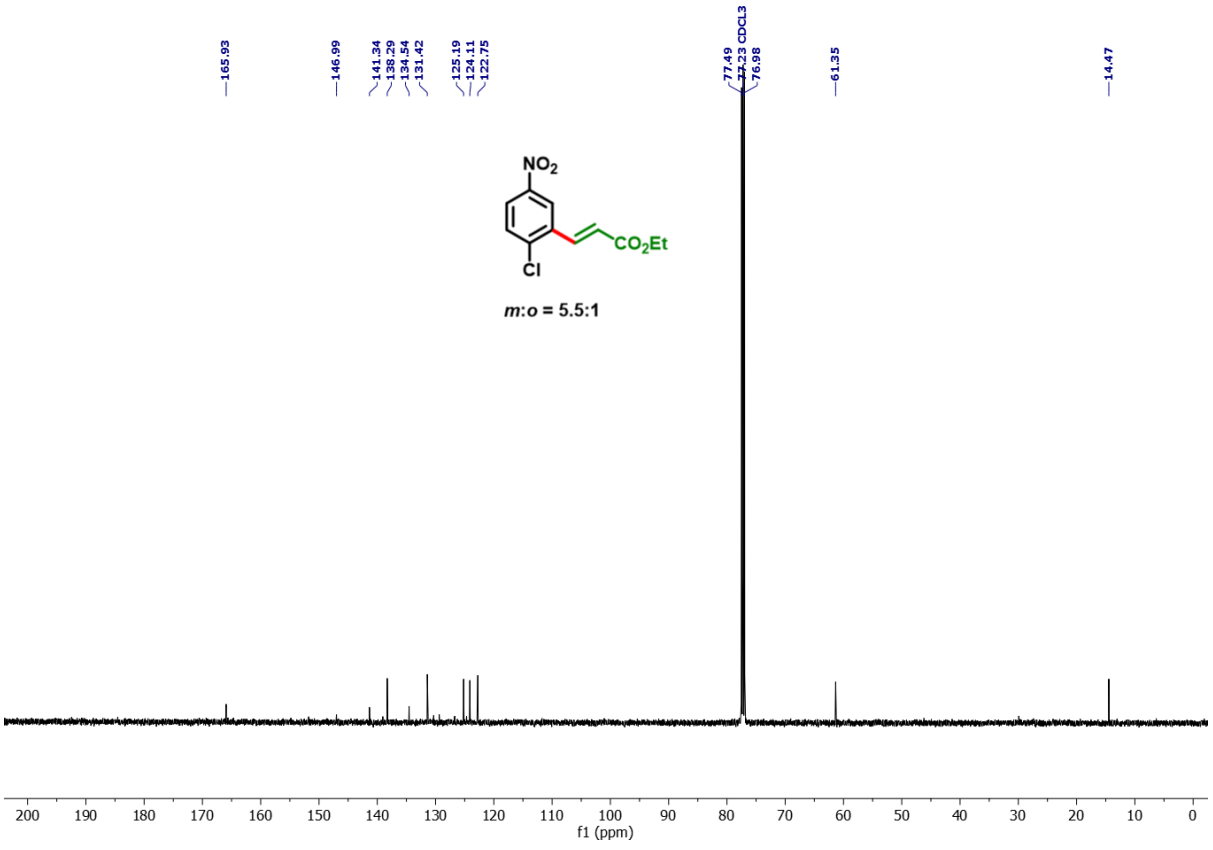
Scheme 2, Entry 3e



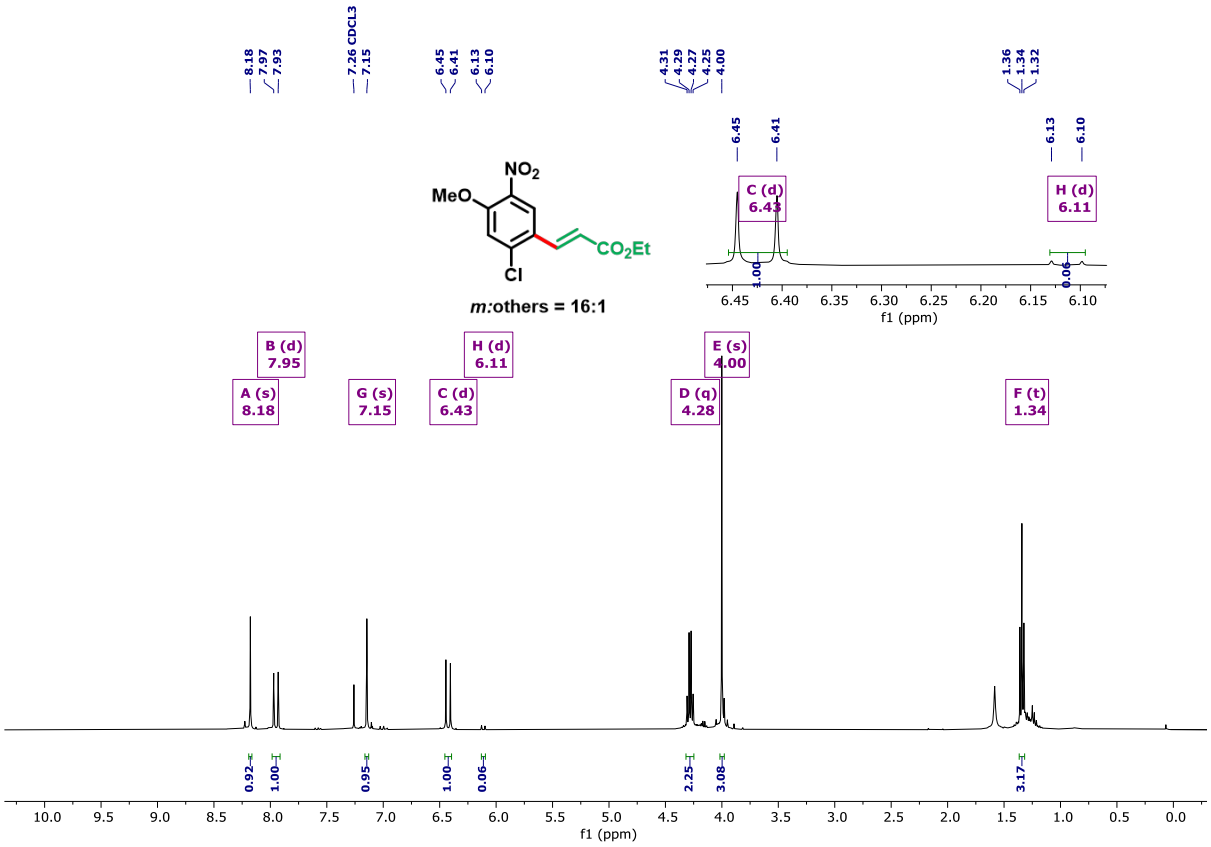


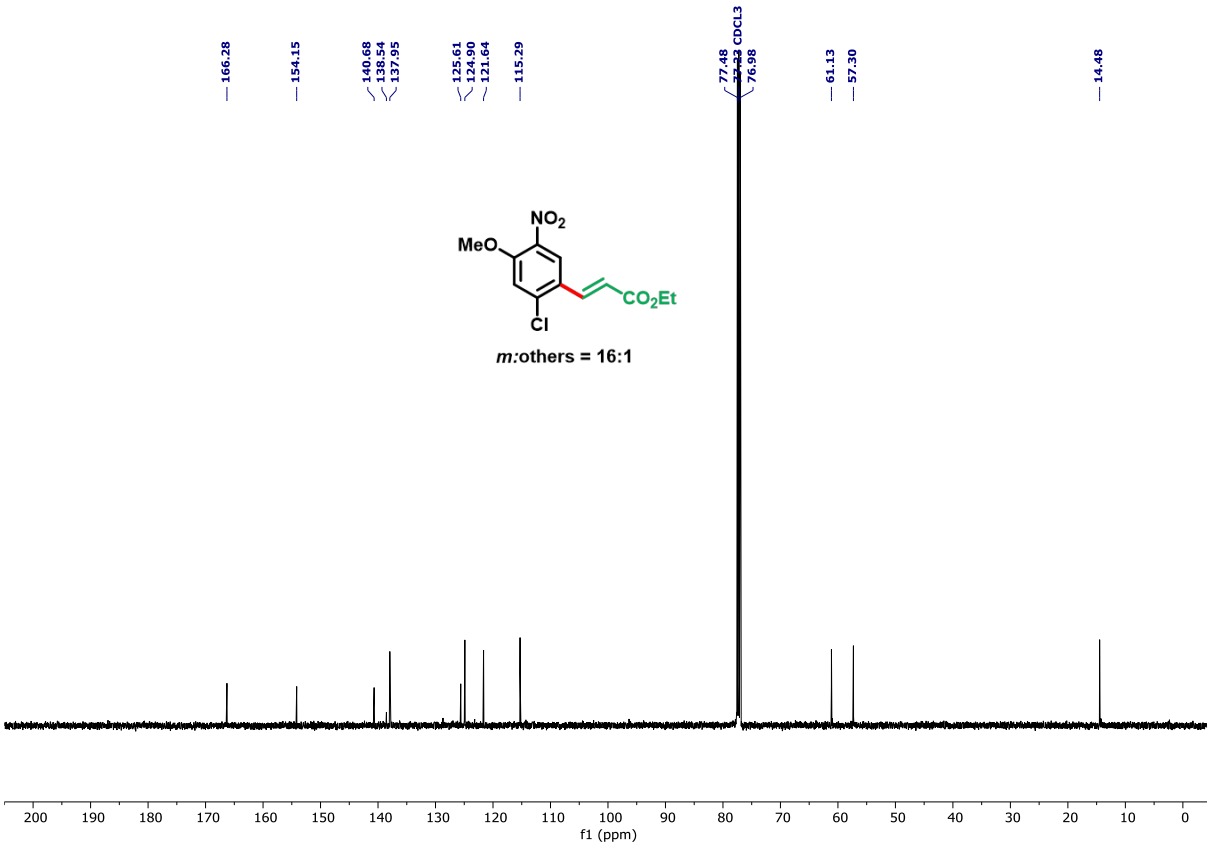
Scheme 2, Entry 3f



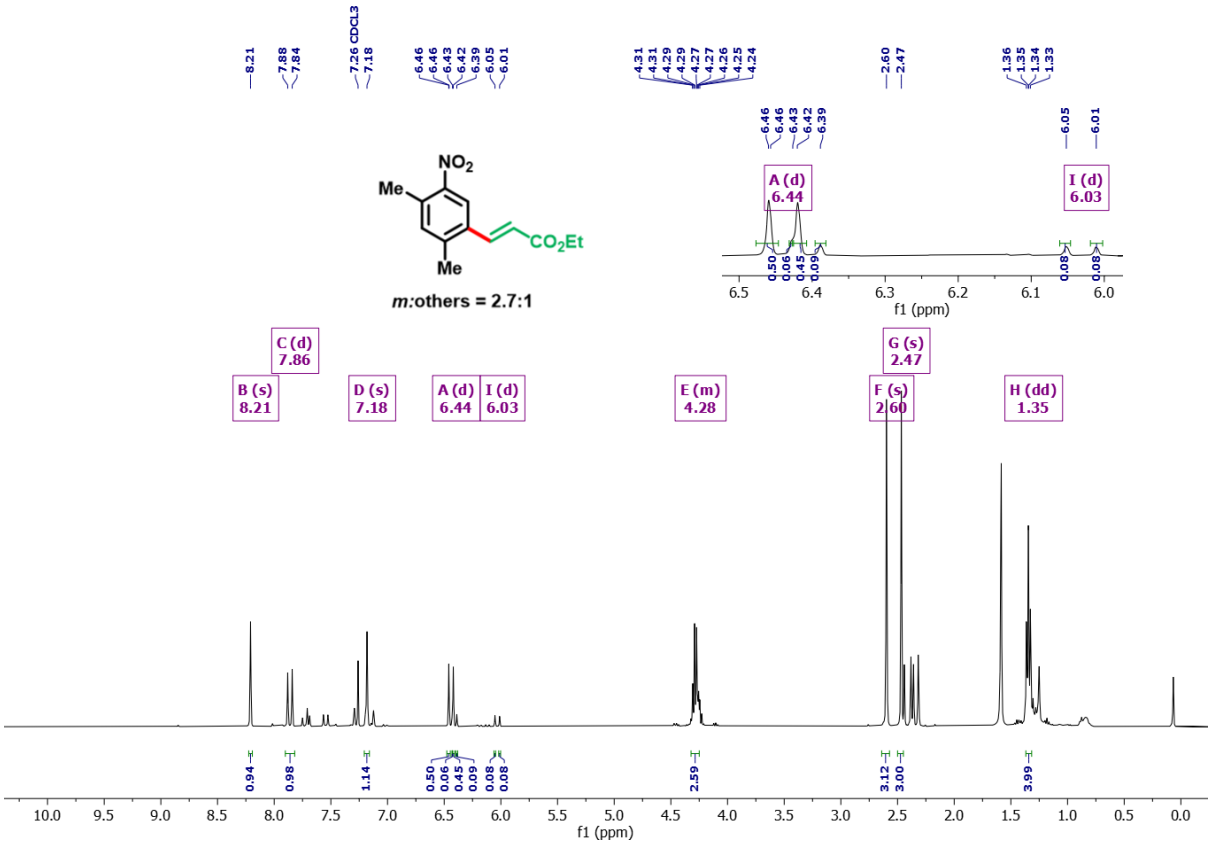


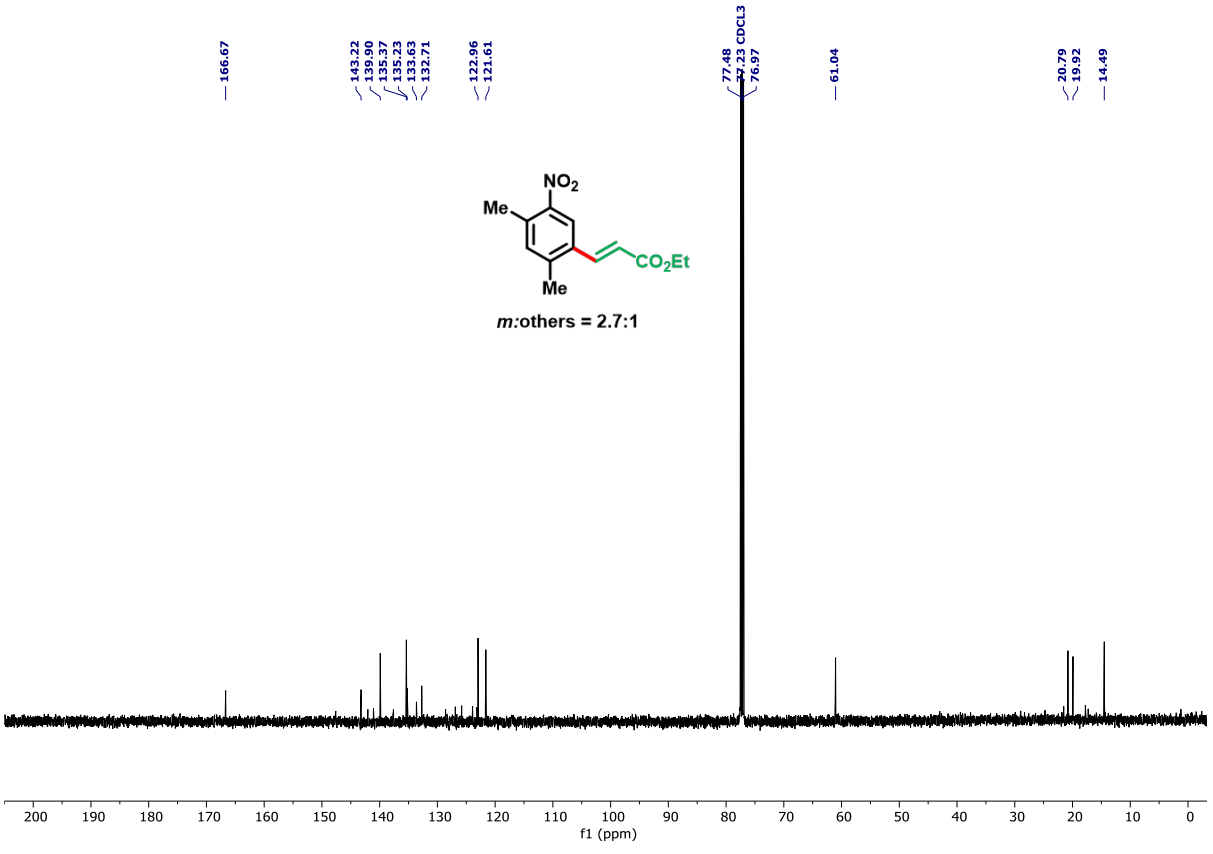
Scheme 2, Entry 3g



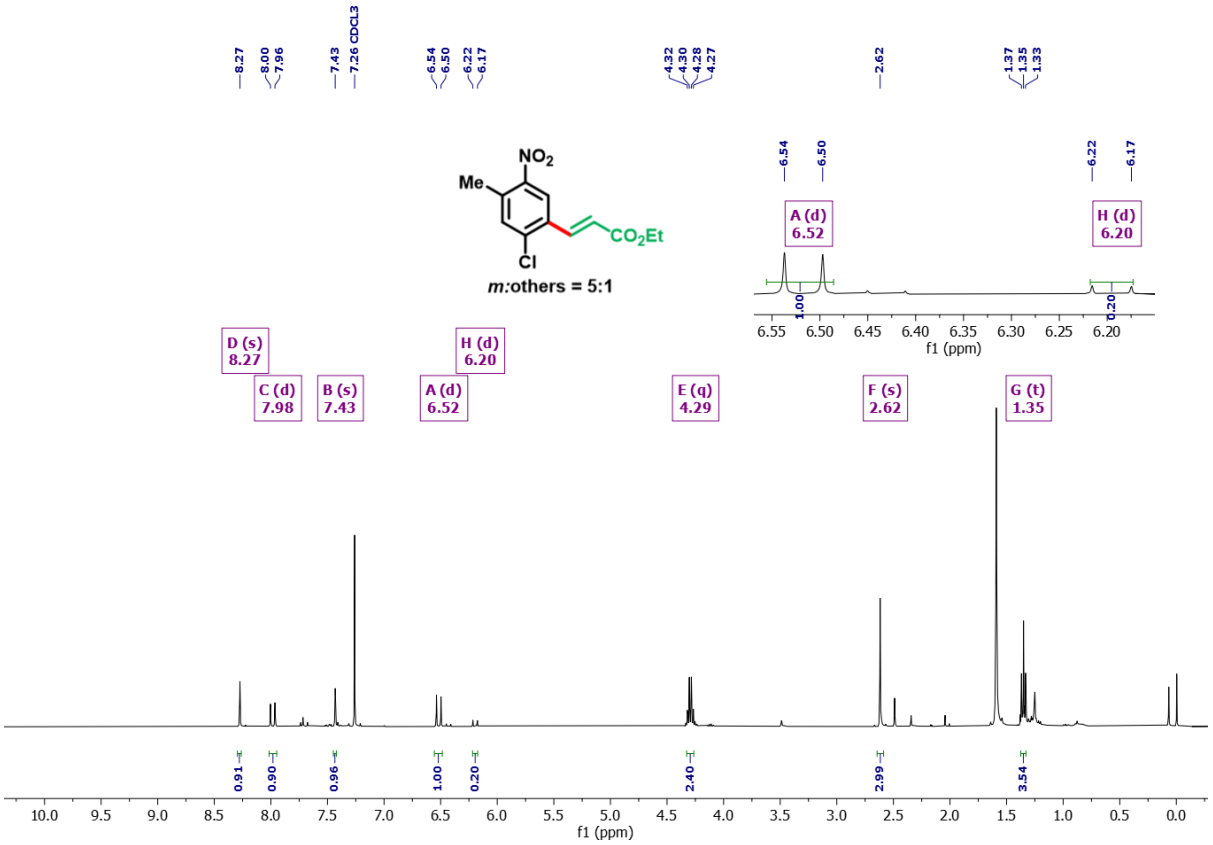


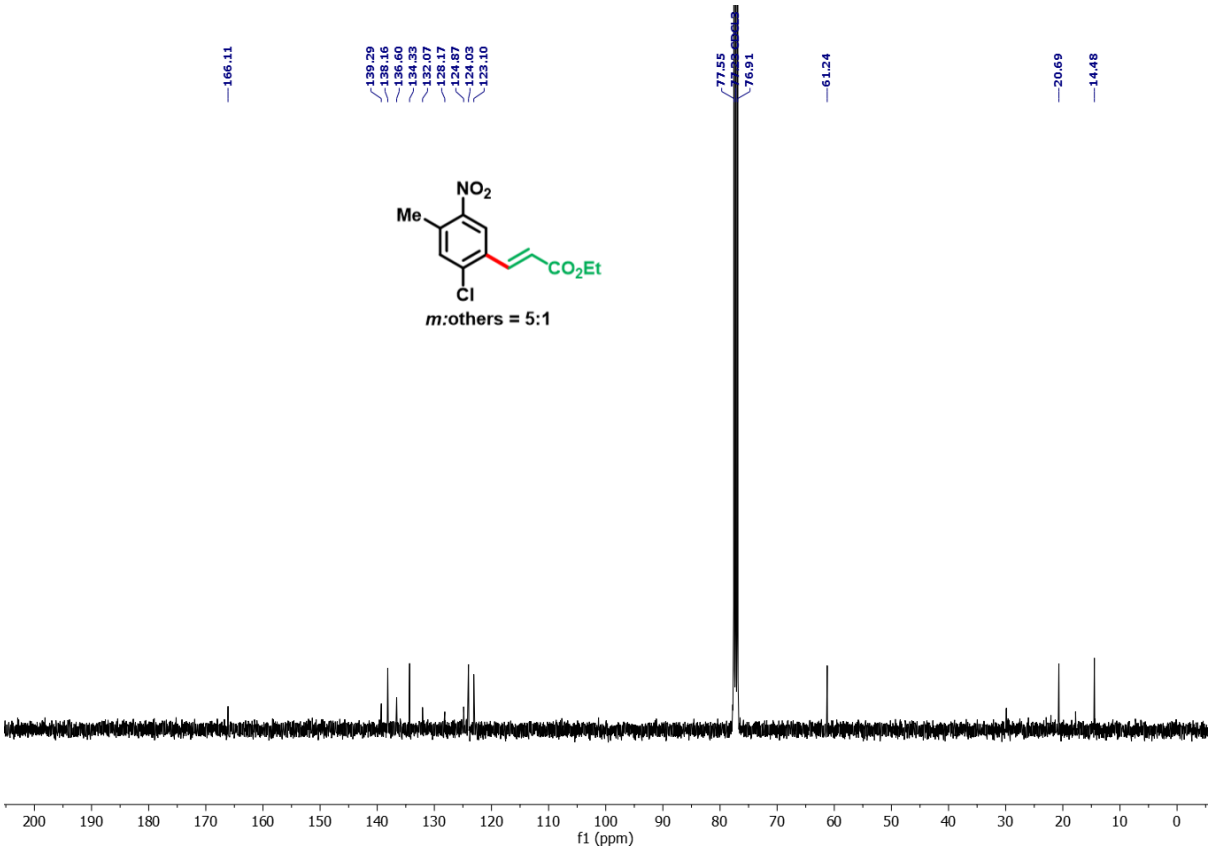
Scheme 2, Entry 3h



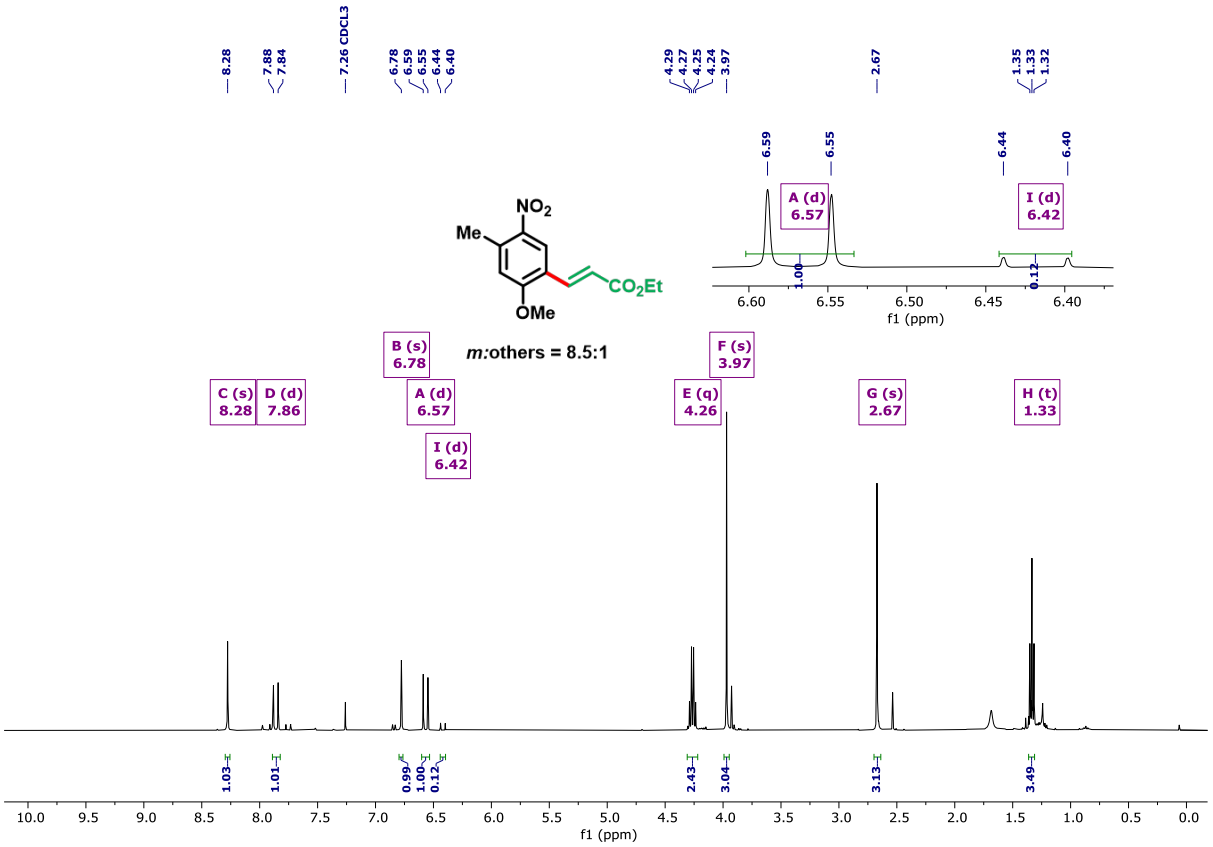


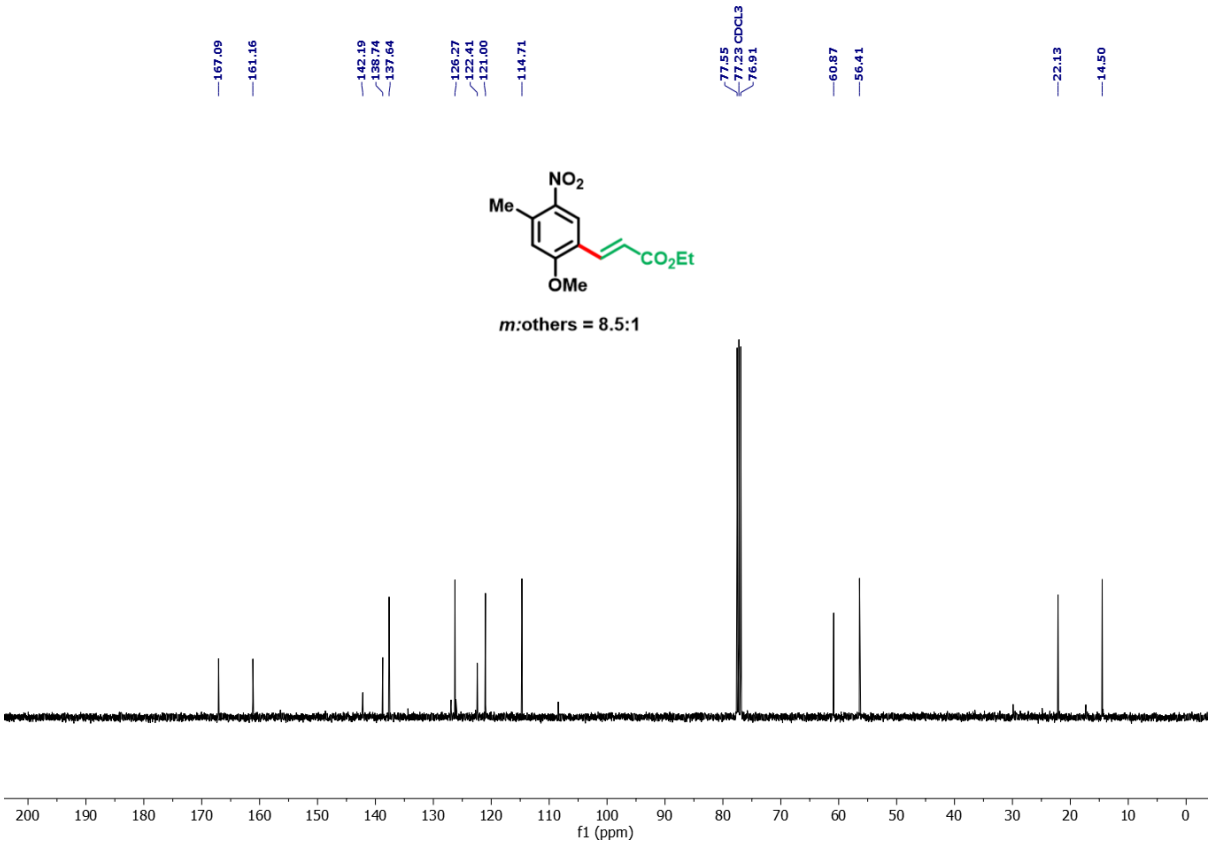
Scheme 2, Entry 3i



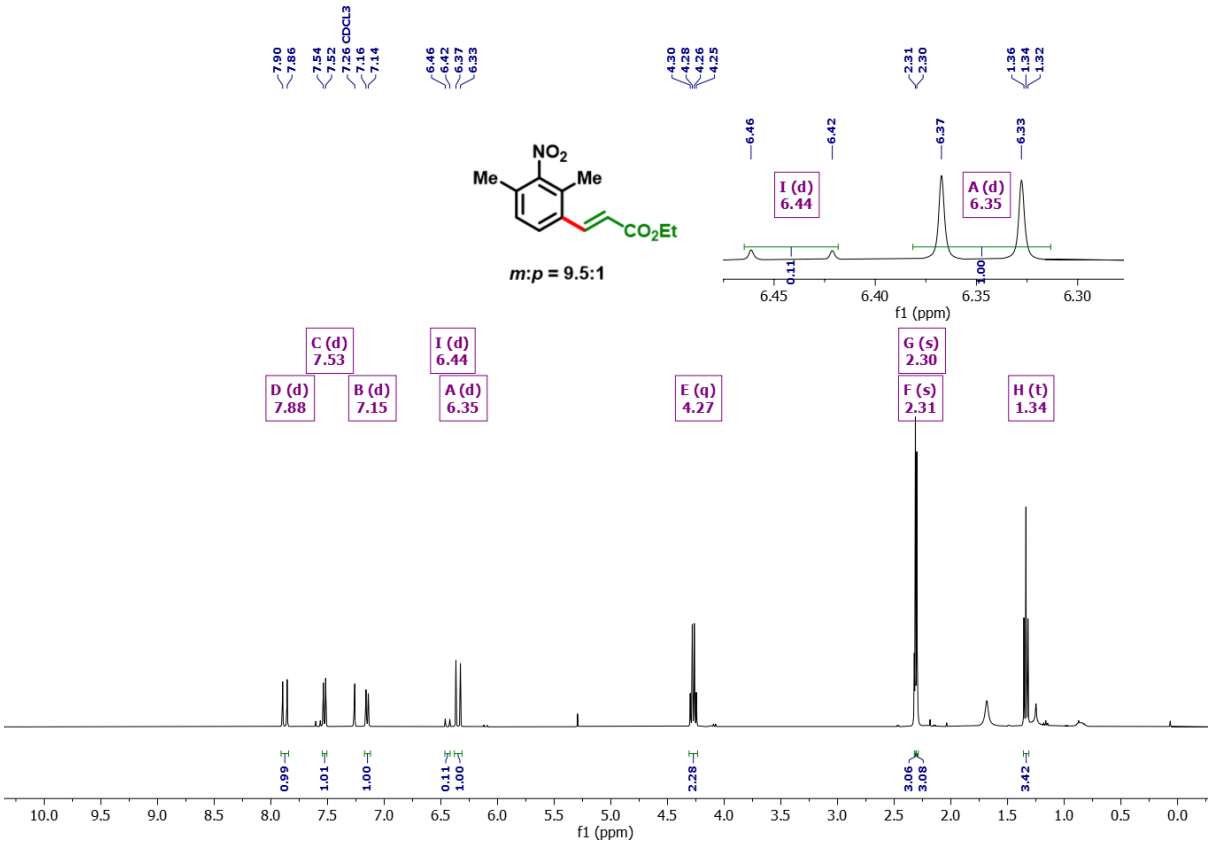


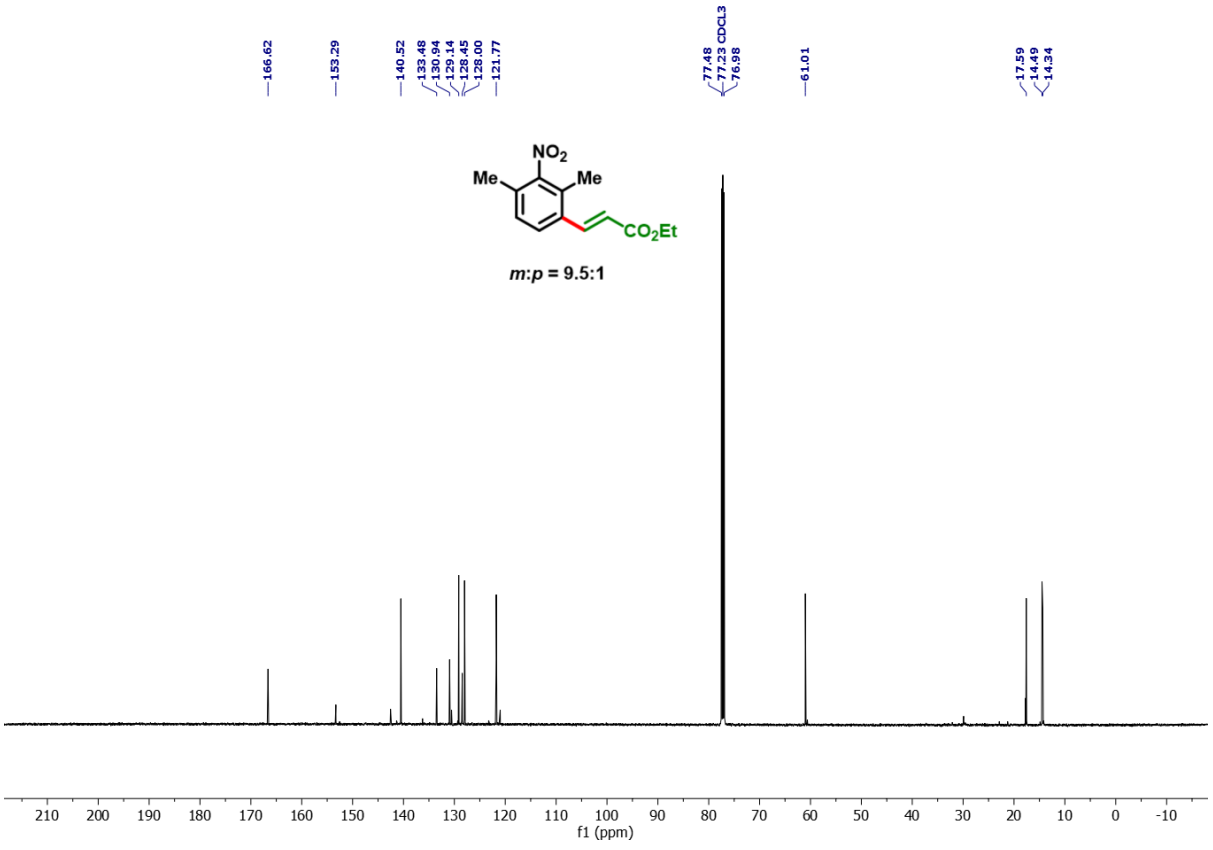
Scheme 2, Entry 3j





Scheme 2, Entry 3k





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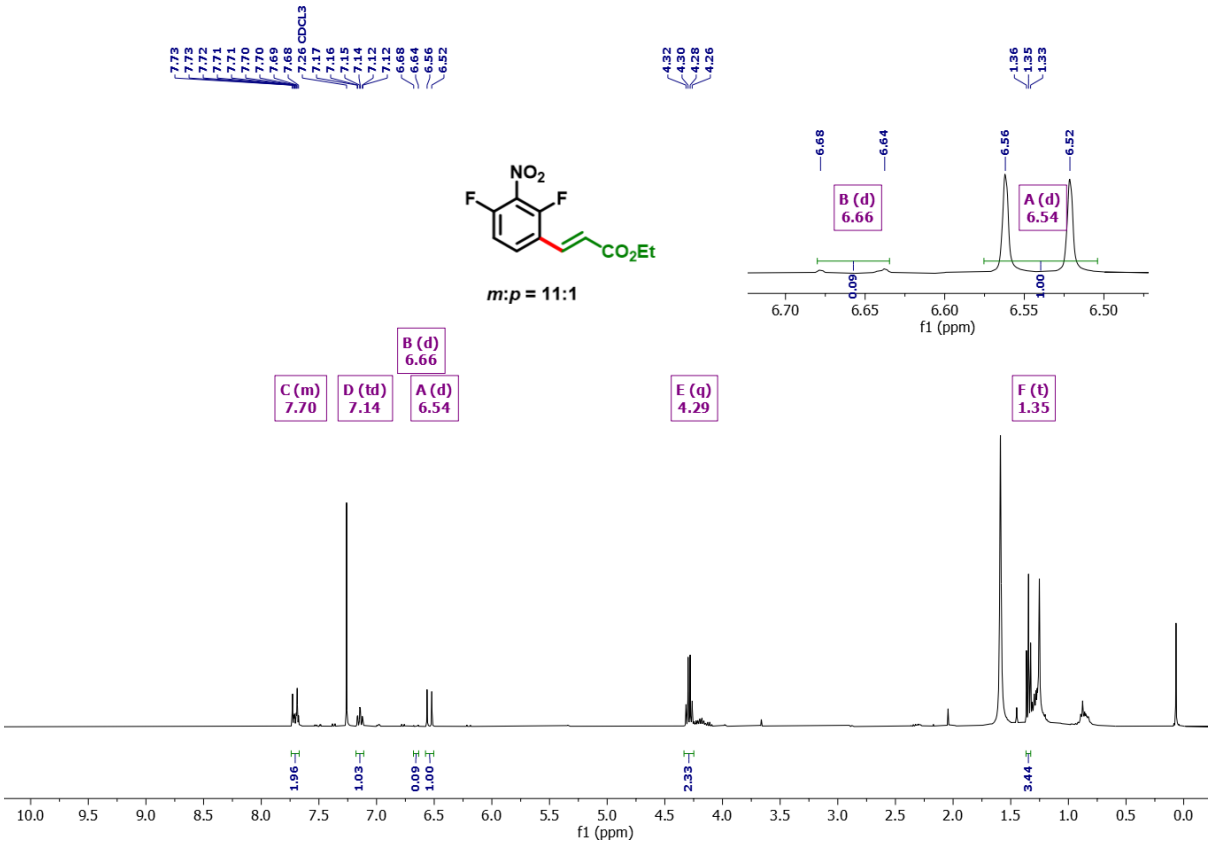
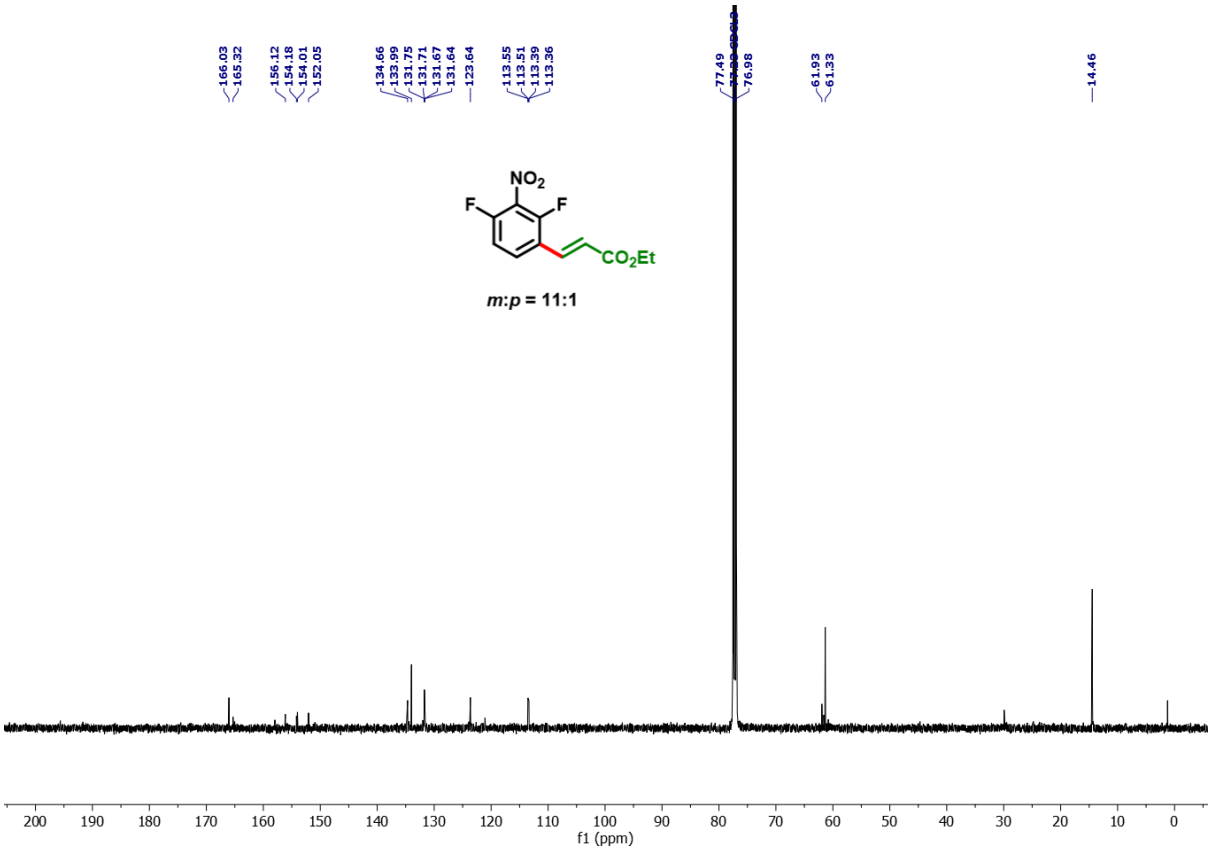
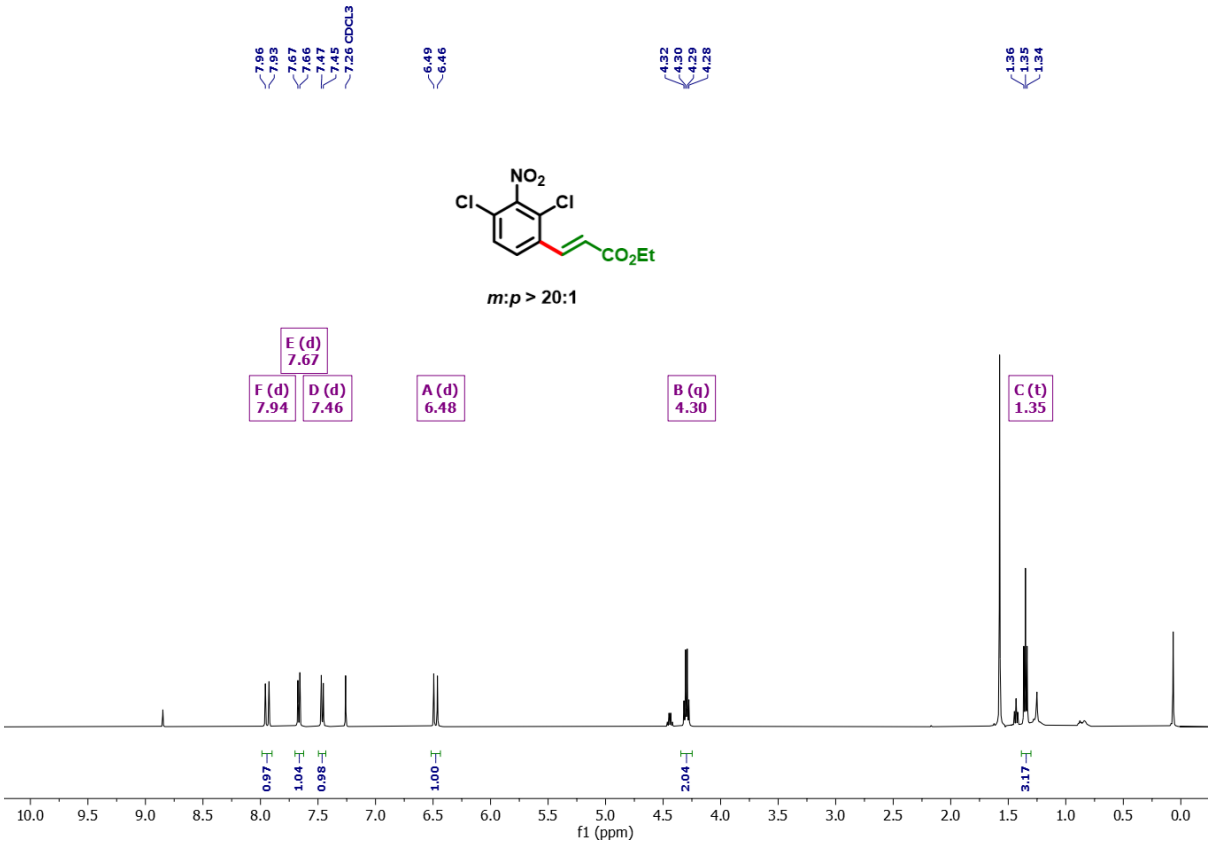
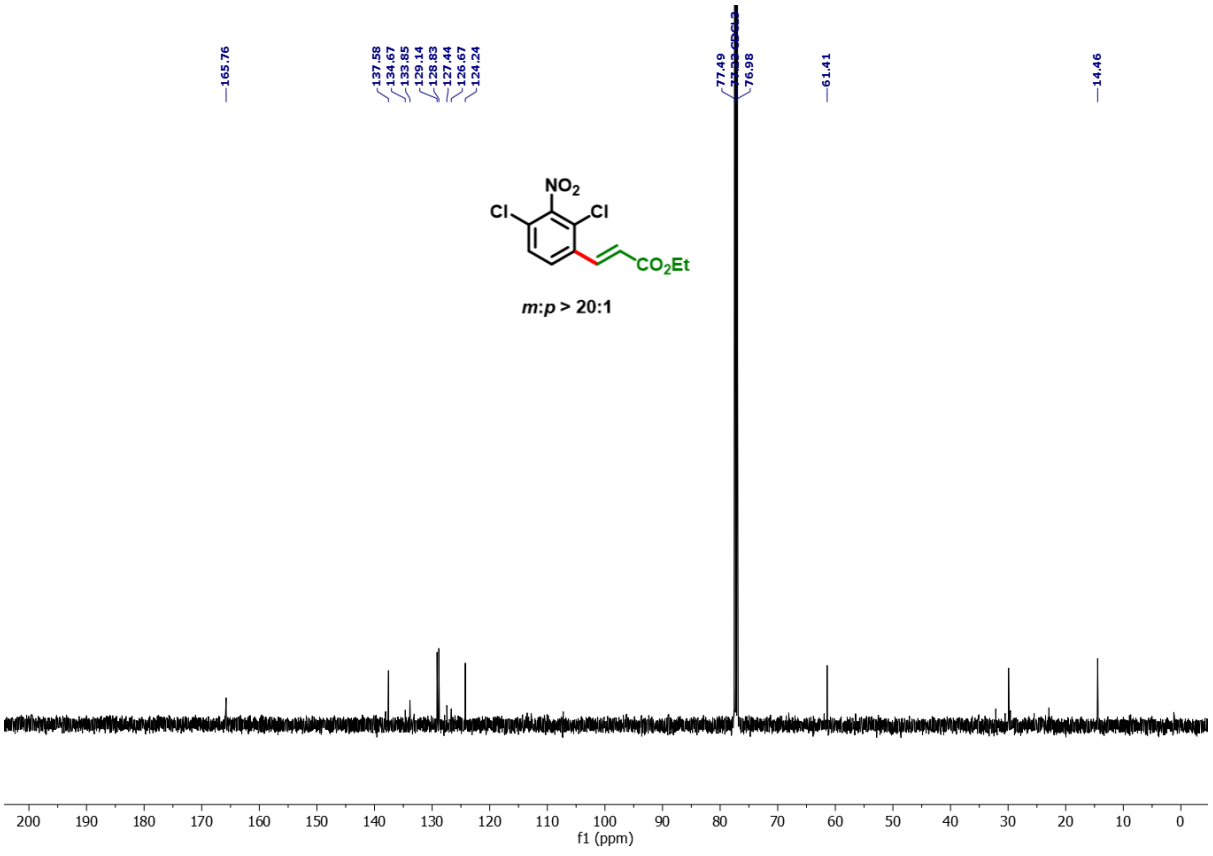


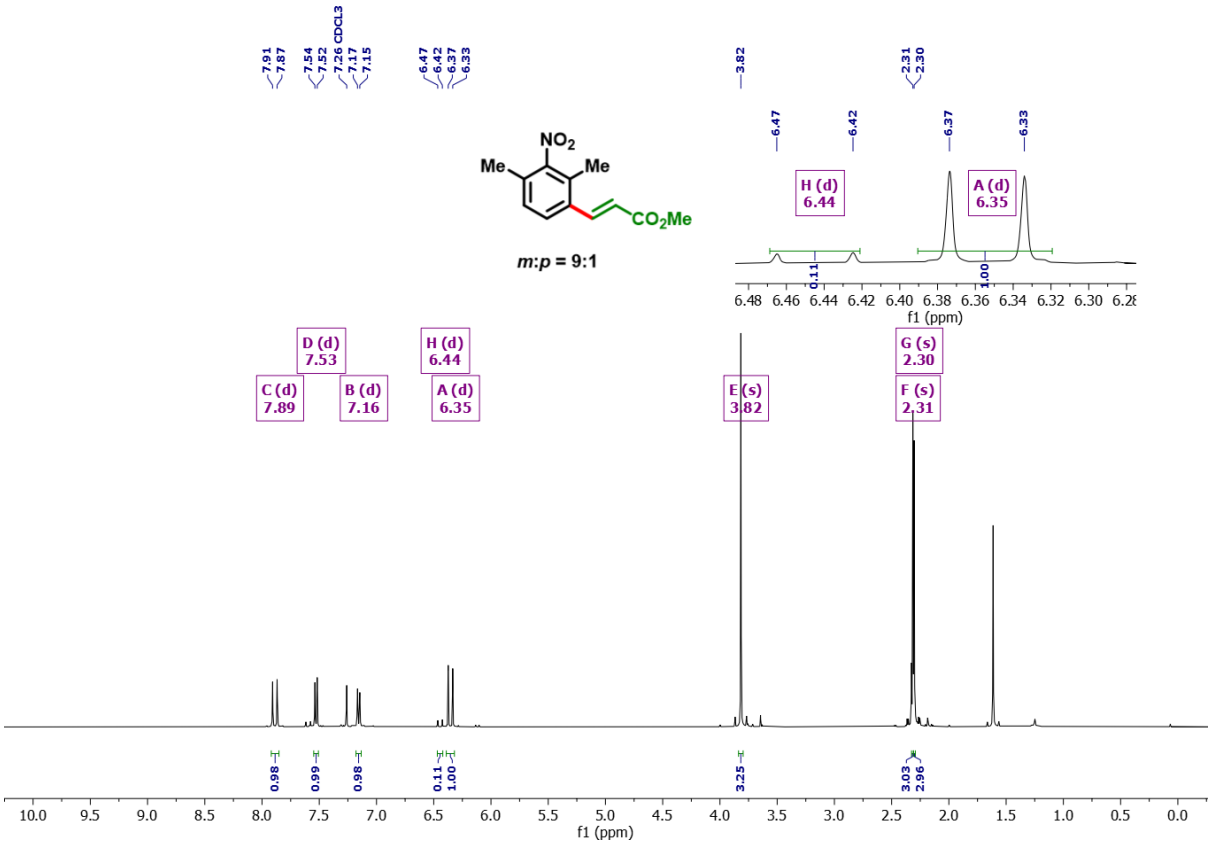


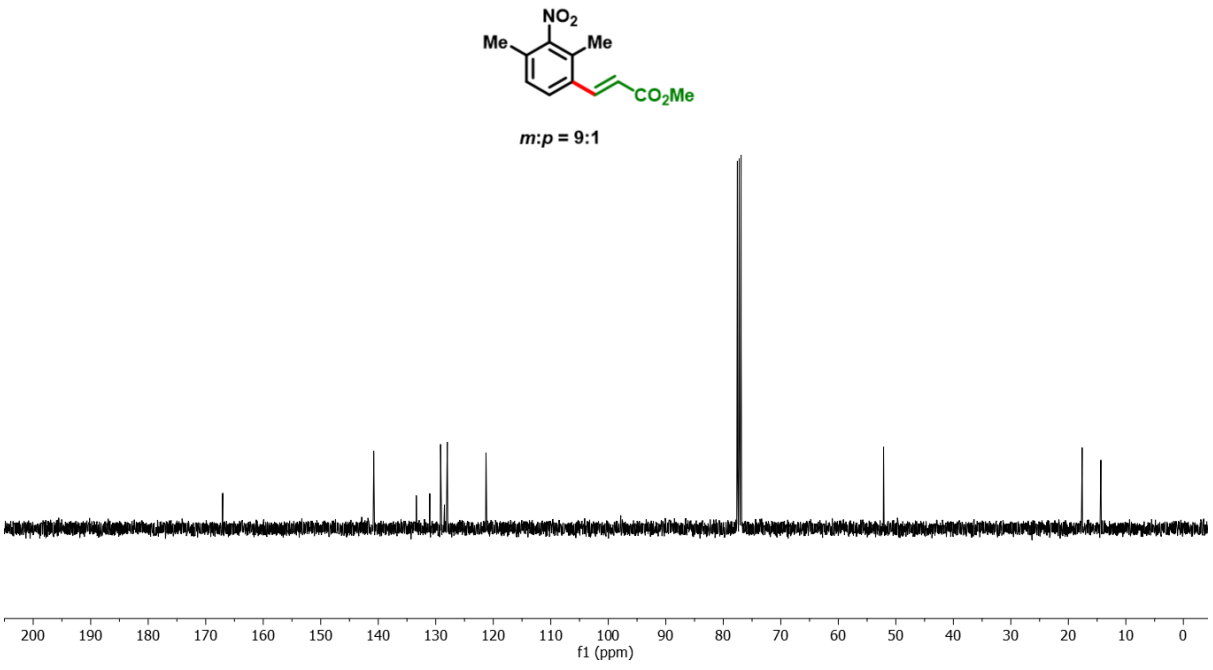
Scheme 2, Entry 3m



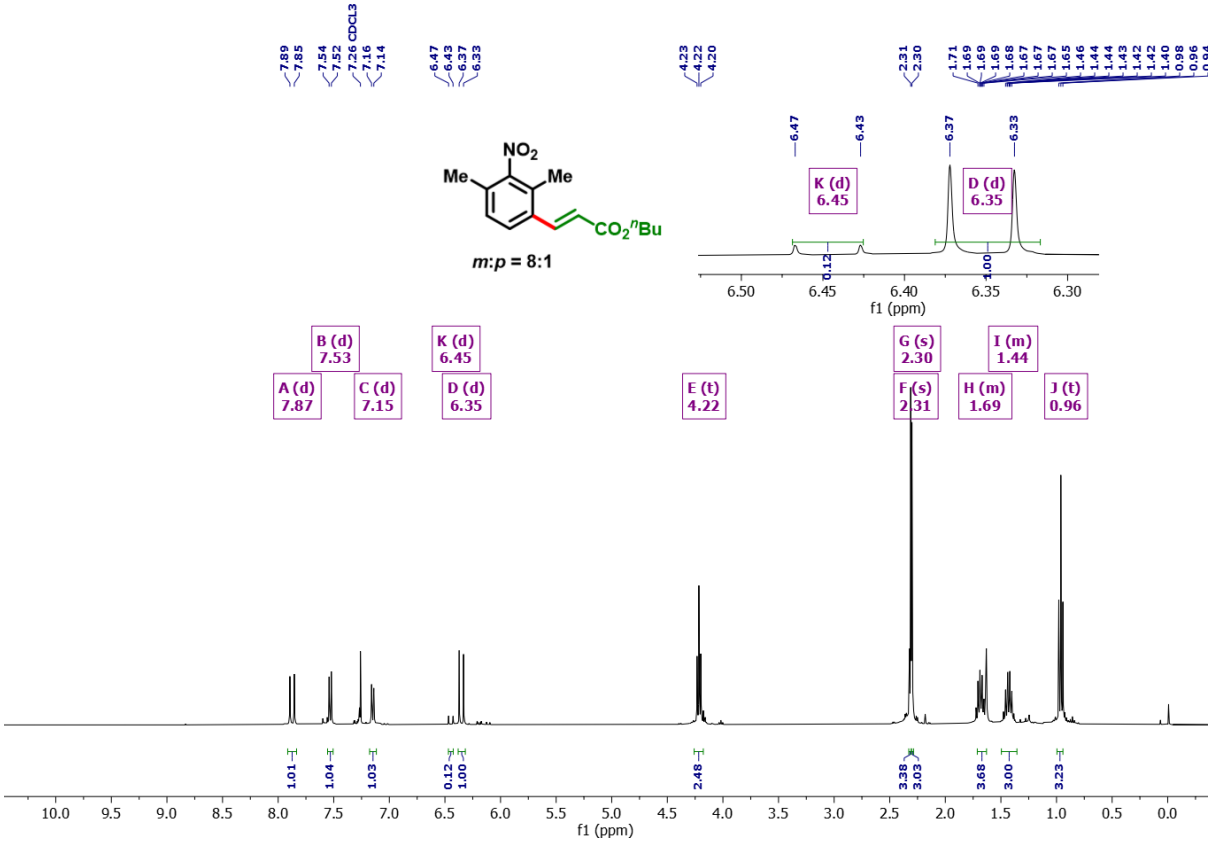


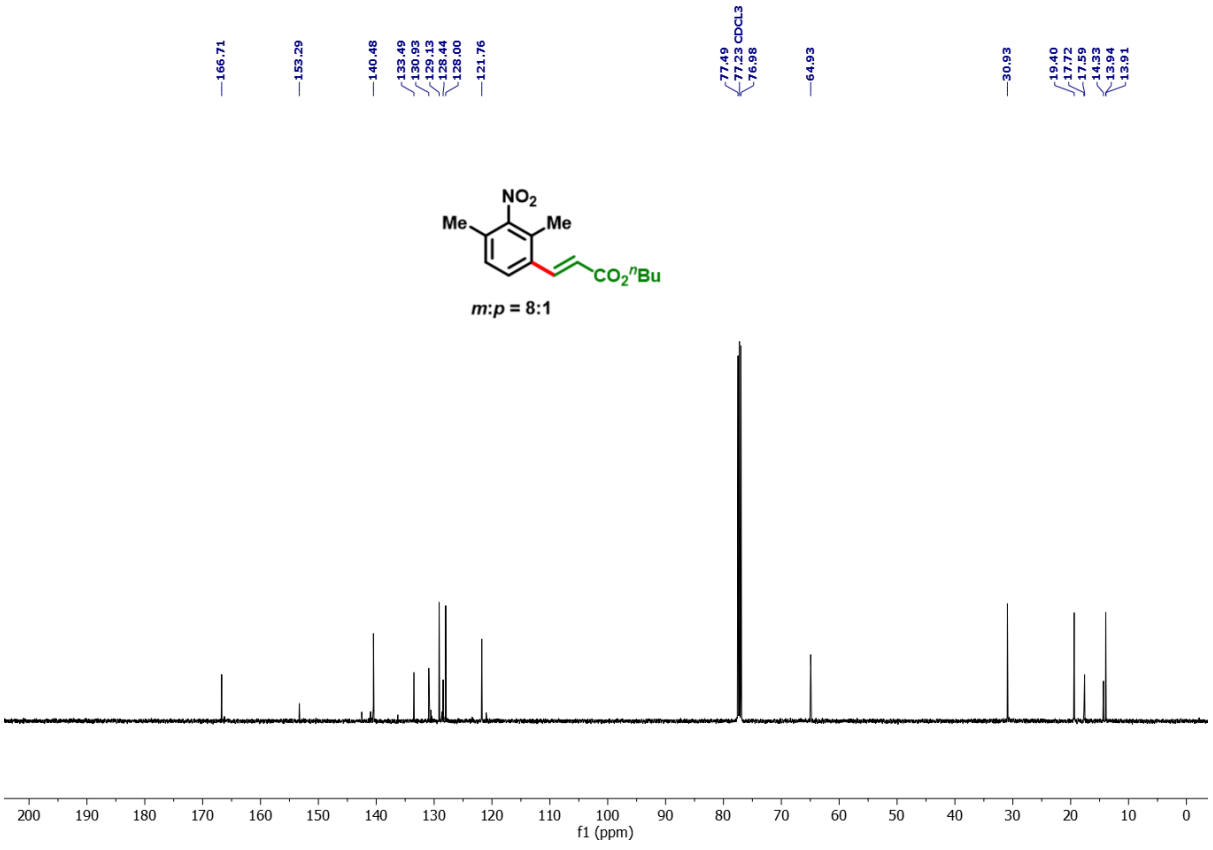
Scheme 3, Entry 3n



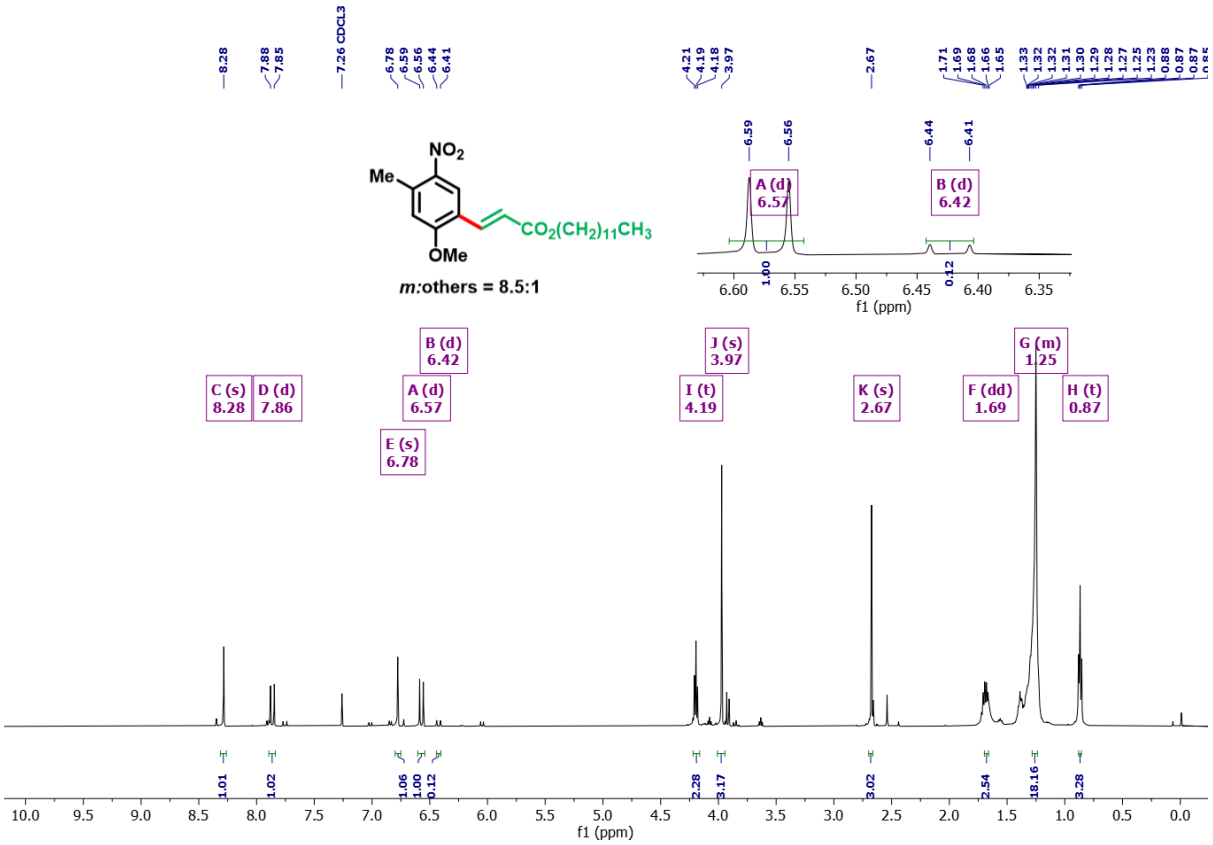


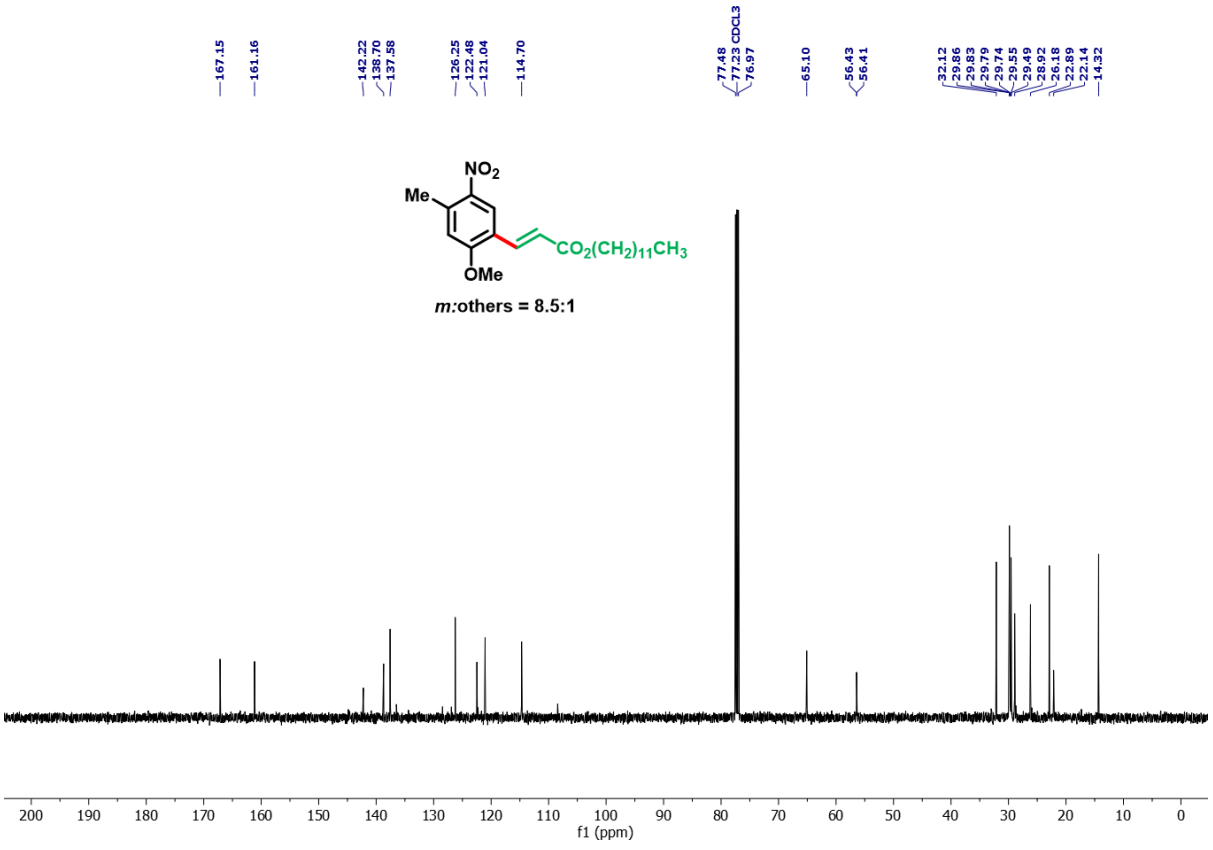
Scheme 3, Entry 3o



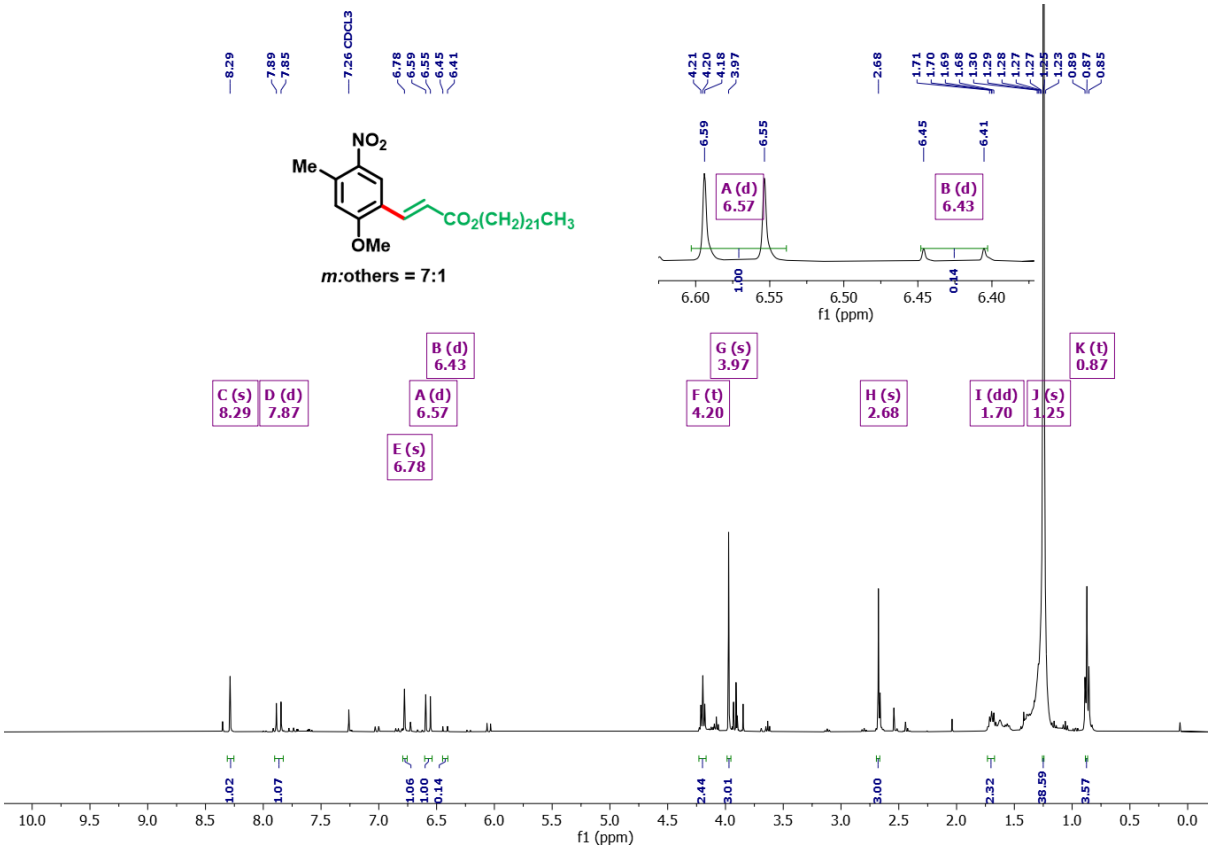


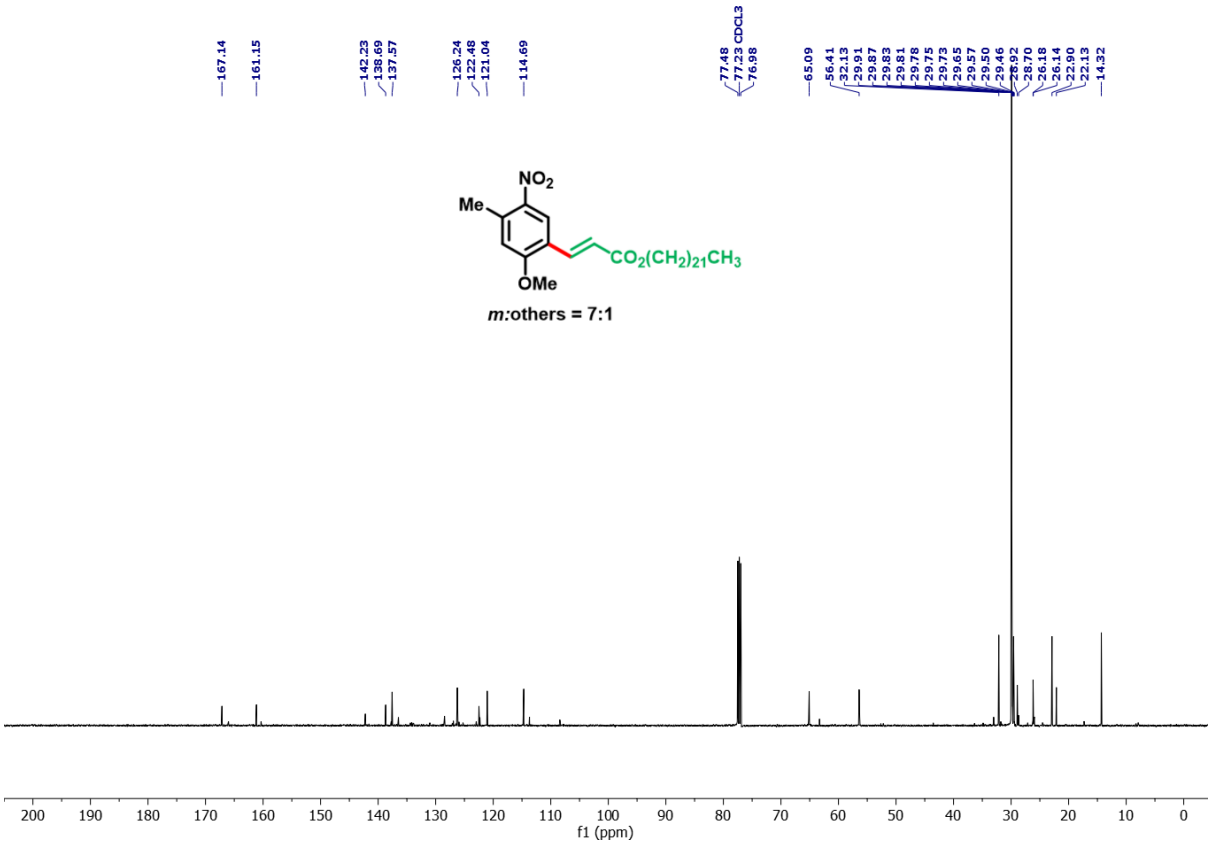
Scheme 3, Entry 3p



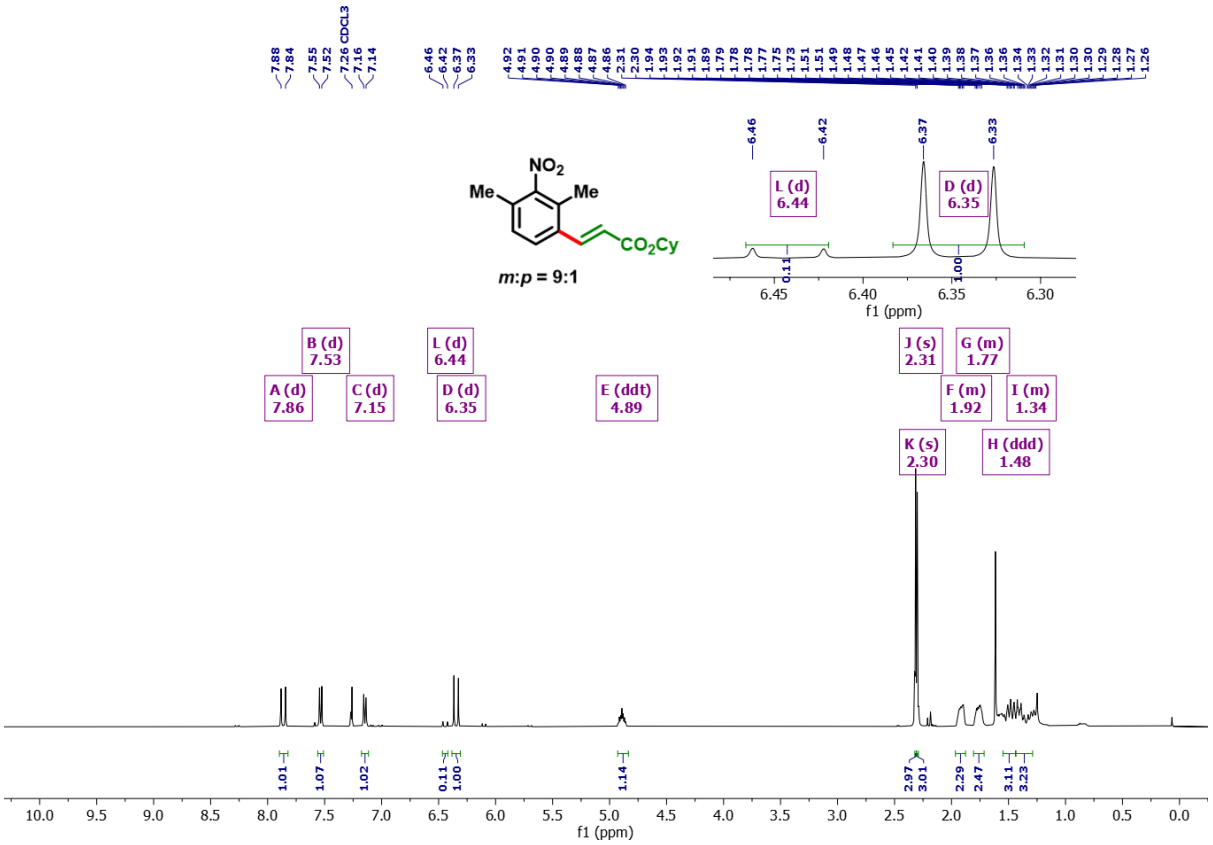


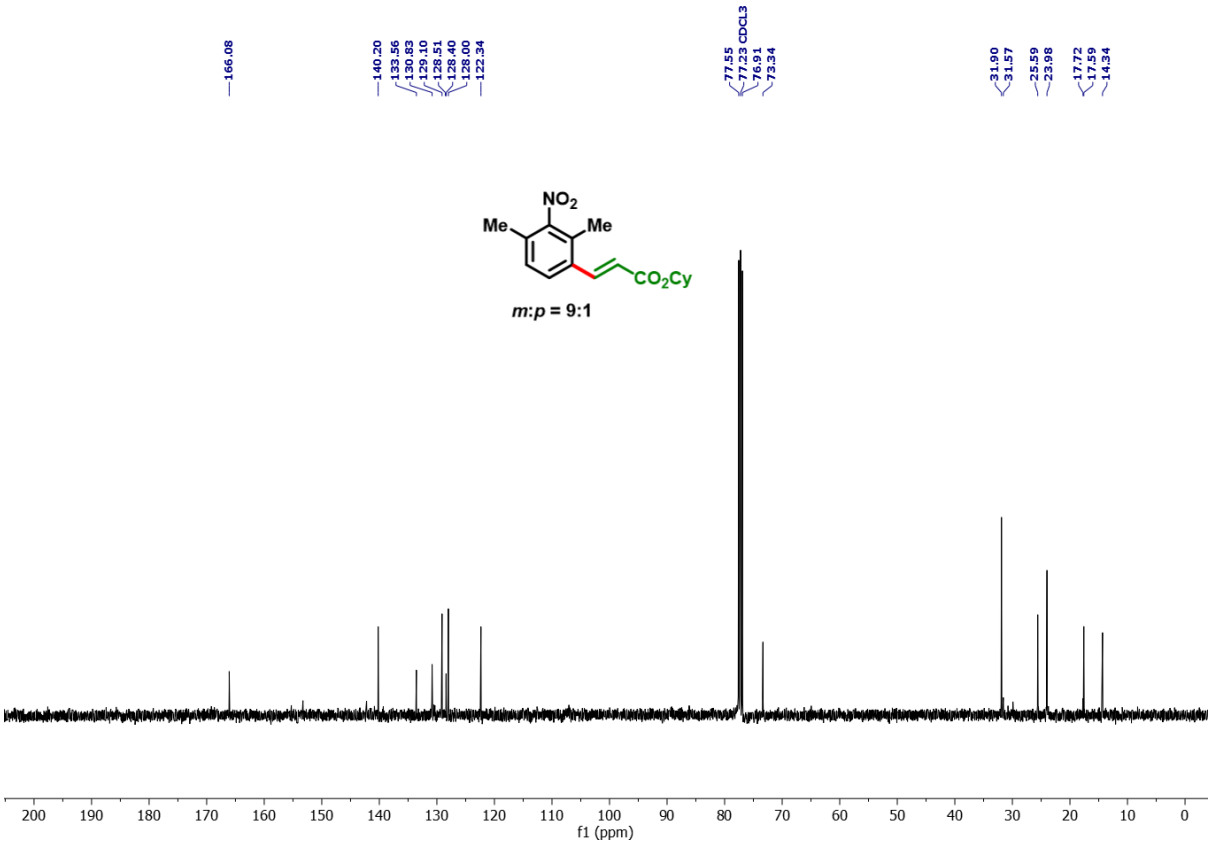
Scheme 3, Entry 3q



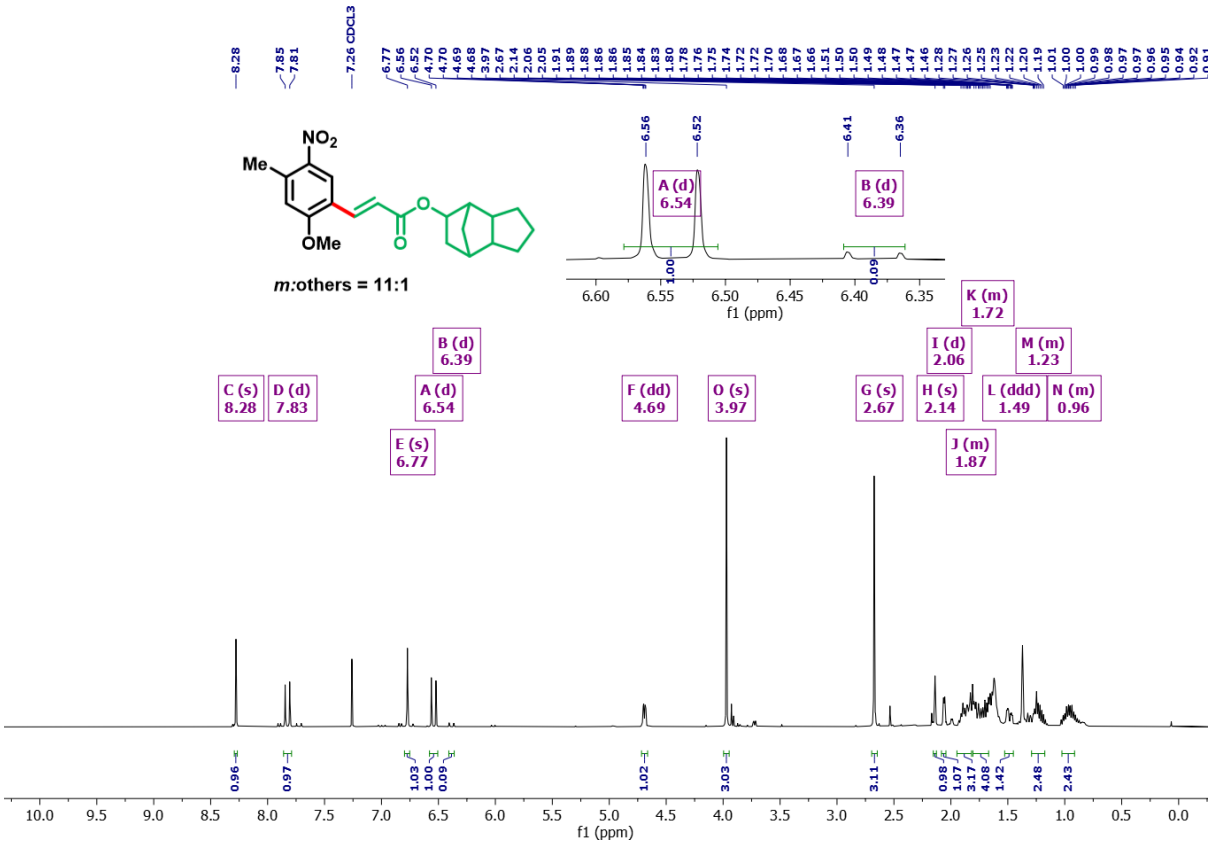


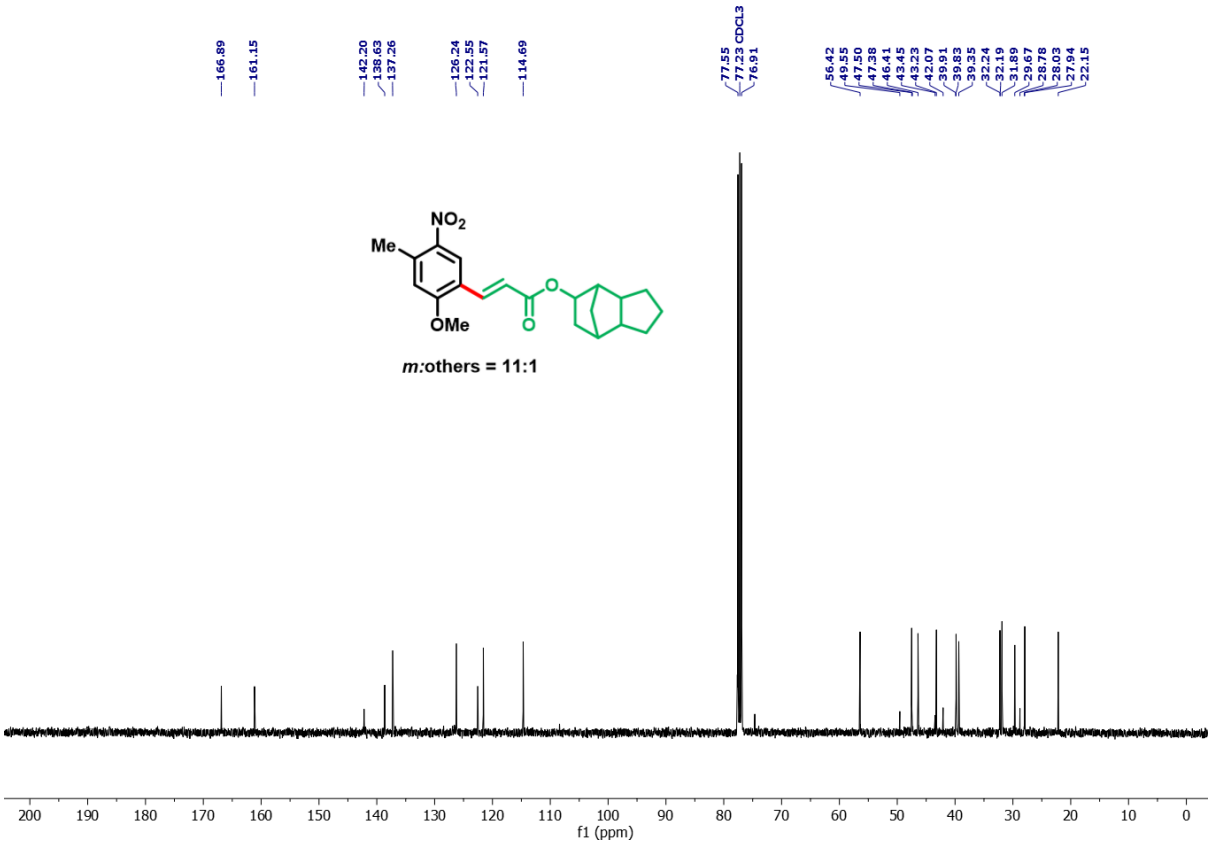
Scheme 3, Entry 3r



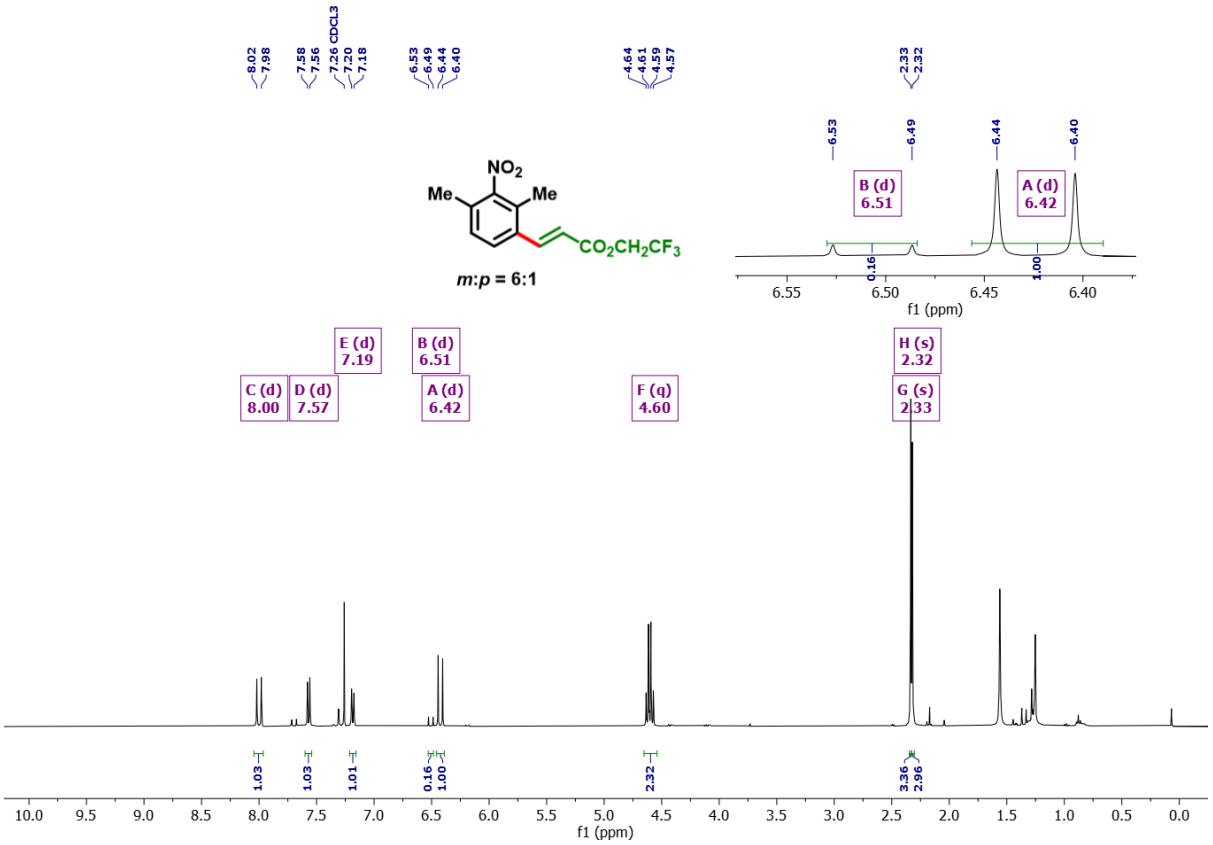


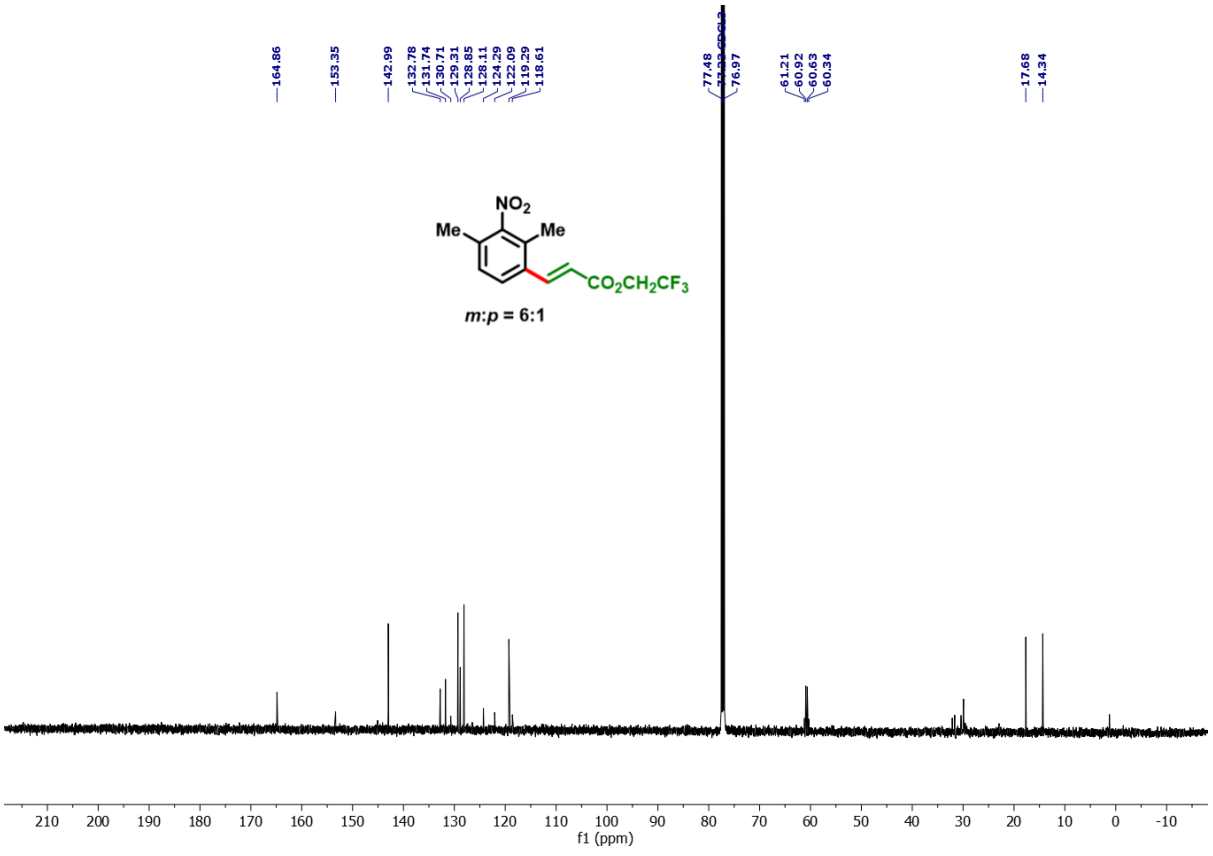
Scheme 3, Entry 3s

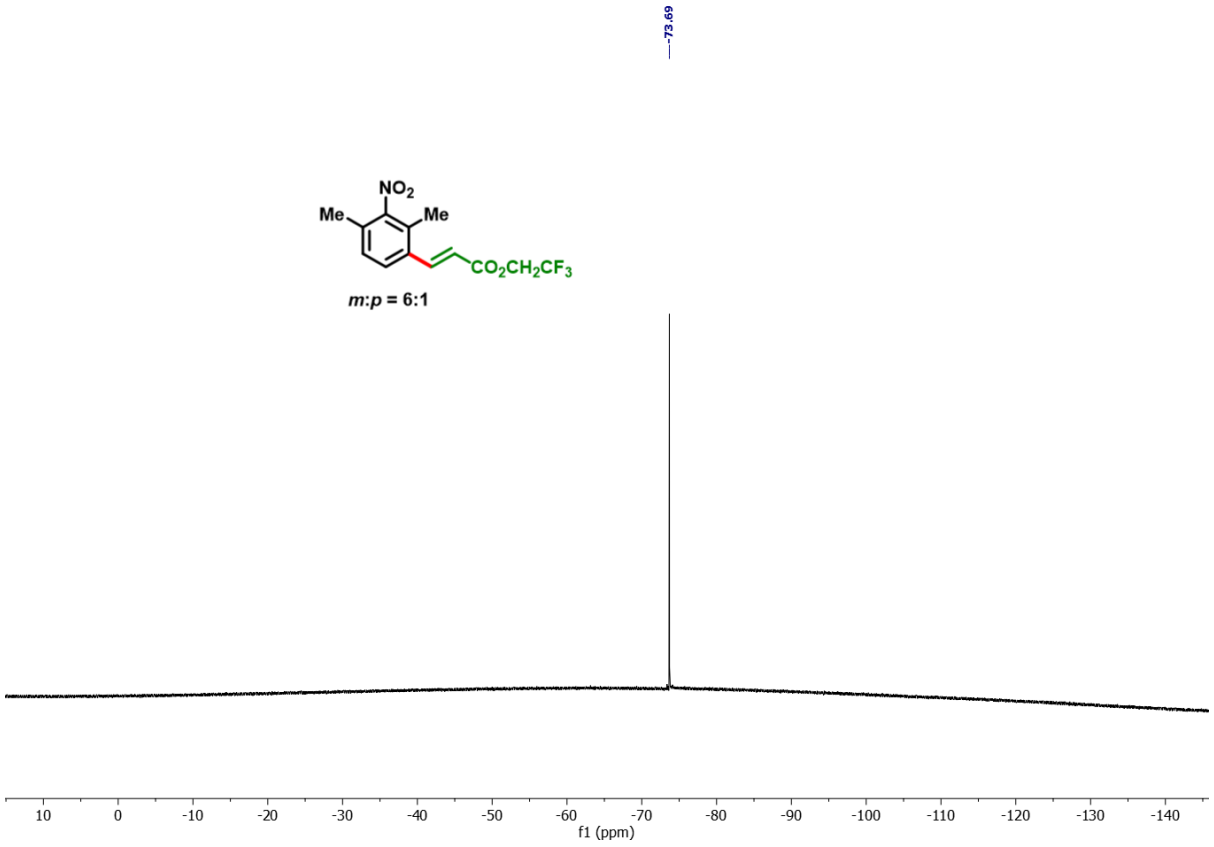




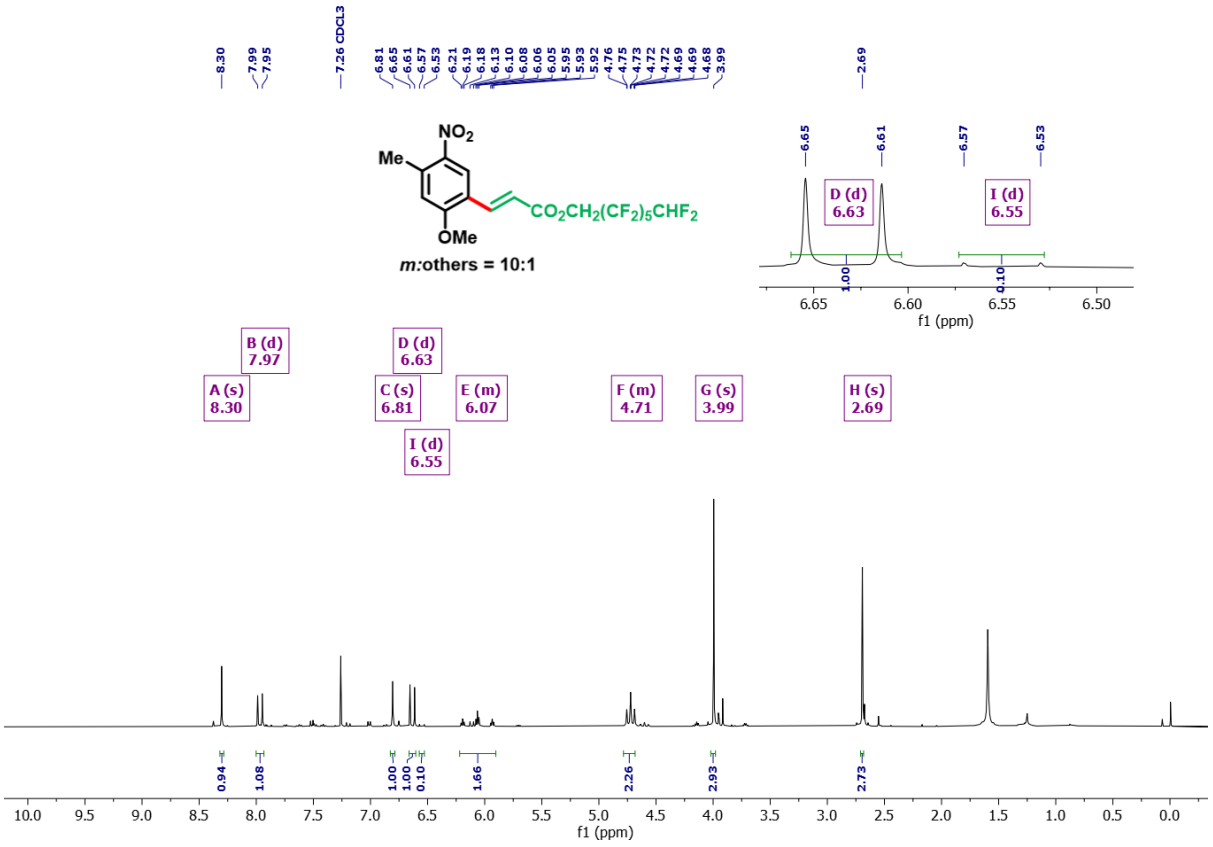
Scheme 3, Entry 3t

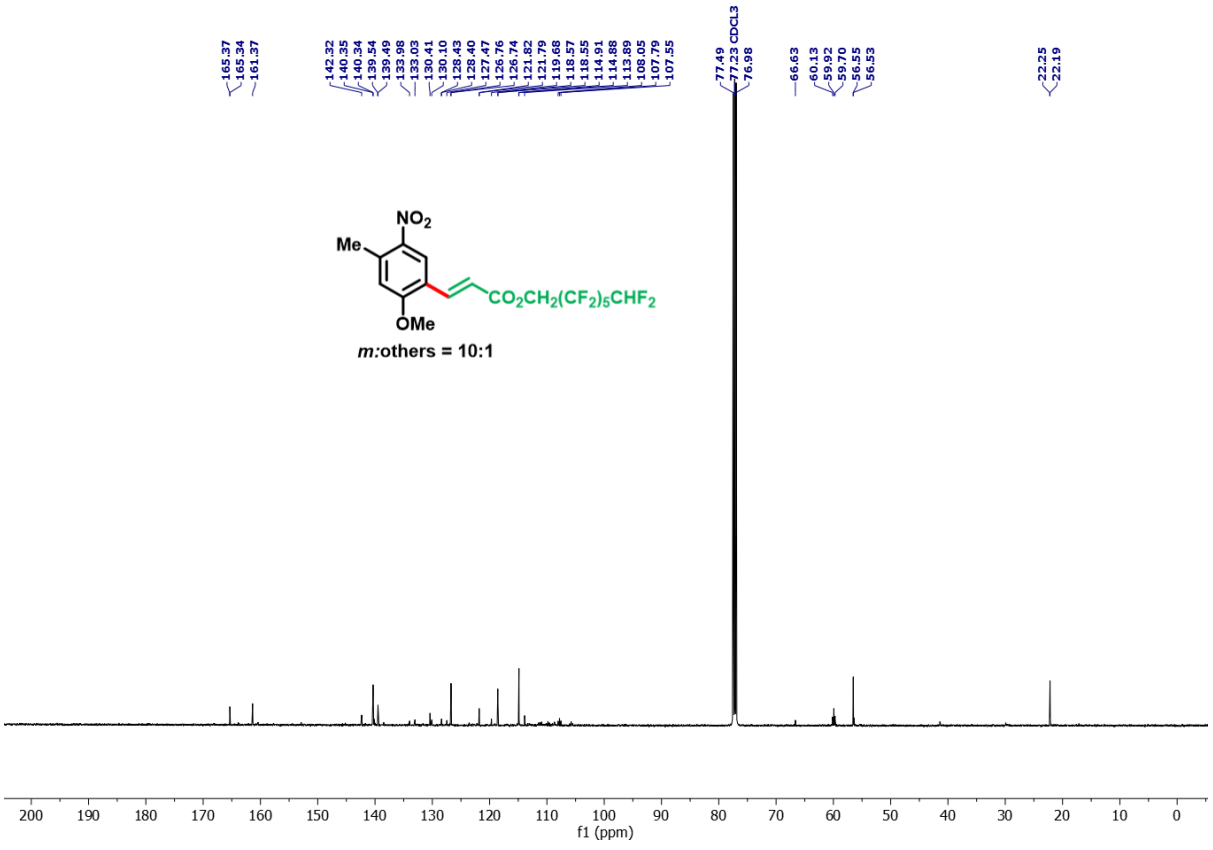


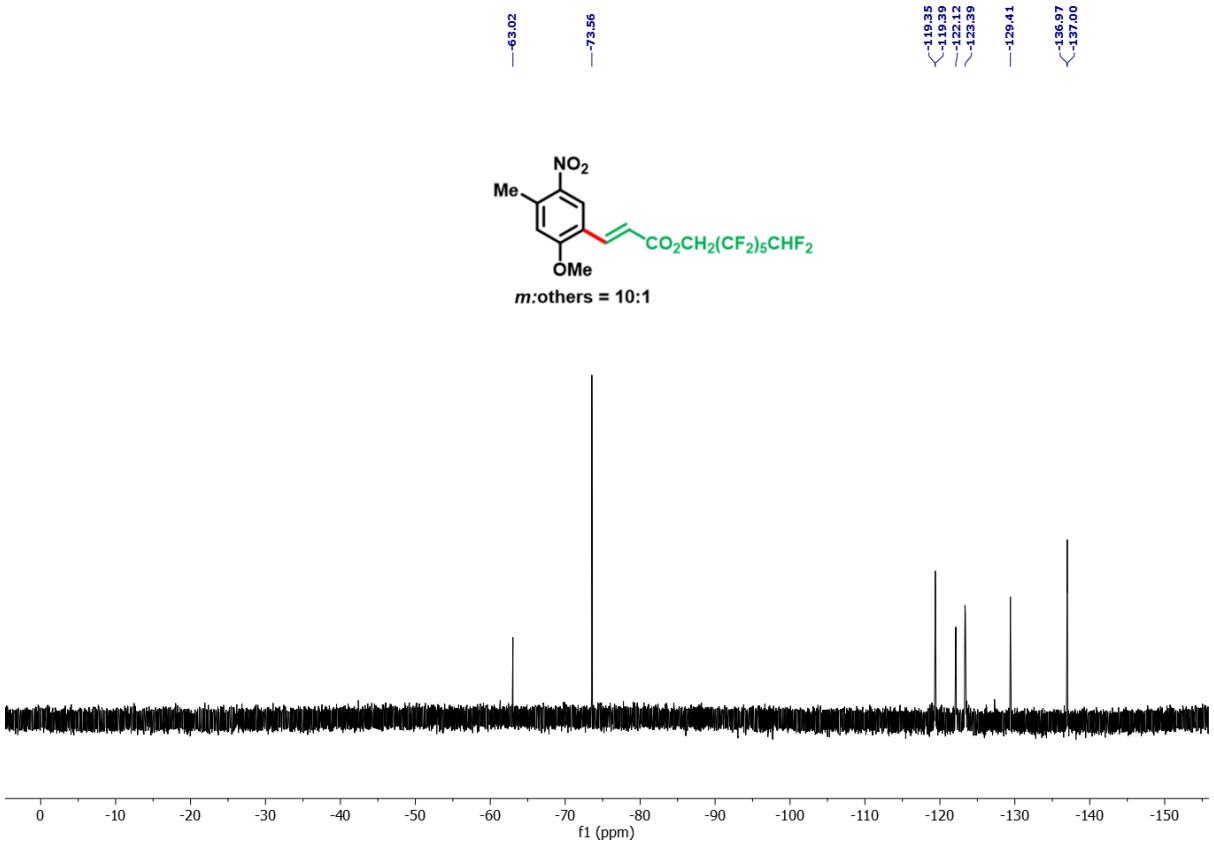



-73.69
NO2
Me
Me
CO2CH2CF3
m:p = 6:1
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
f1 (ppm)

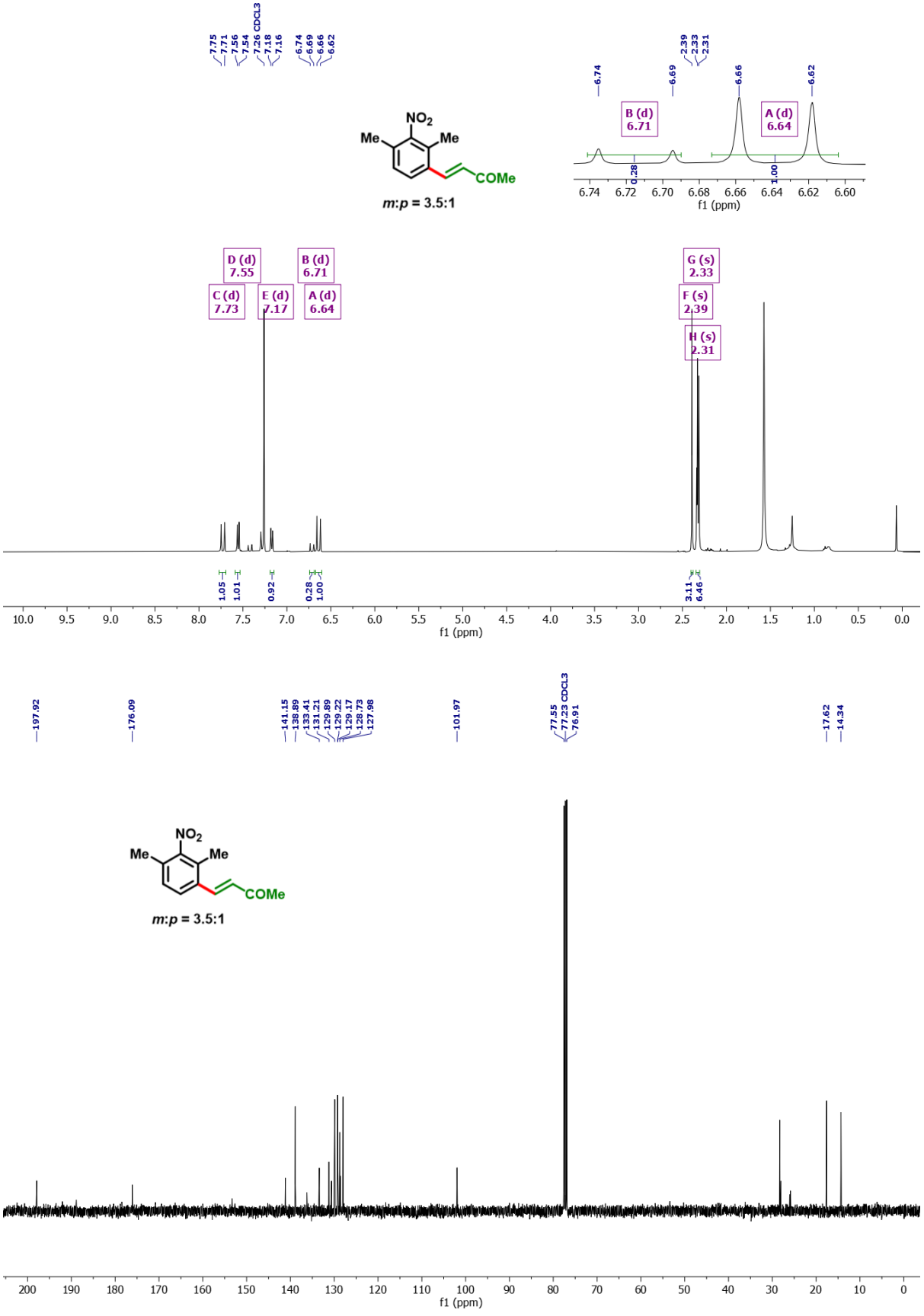
Scheme 3, Entry 3u



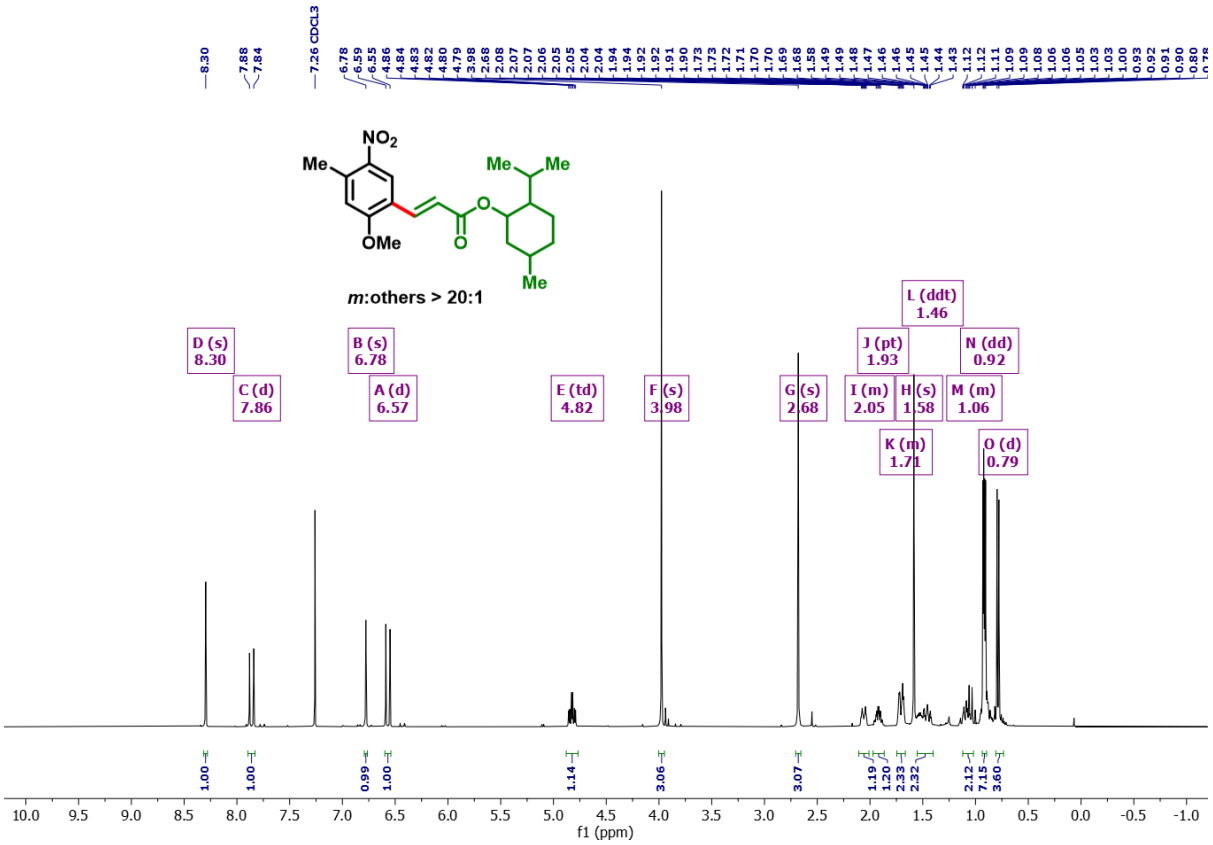


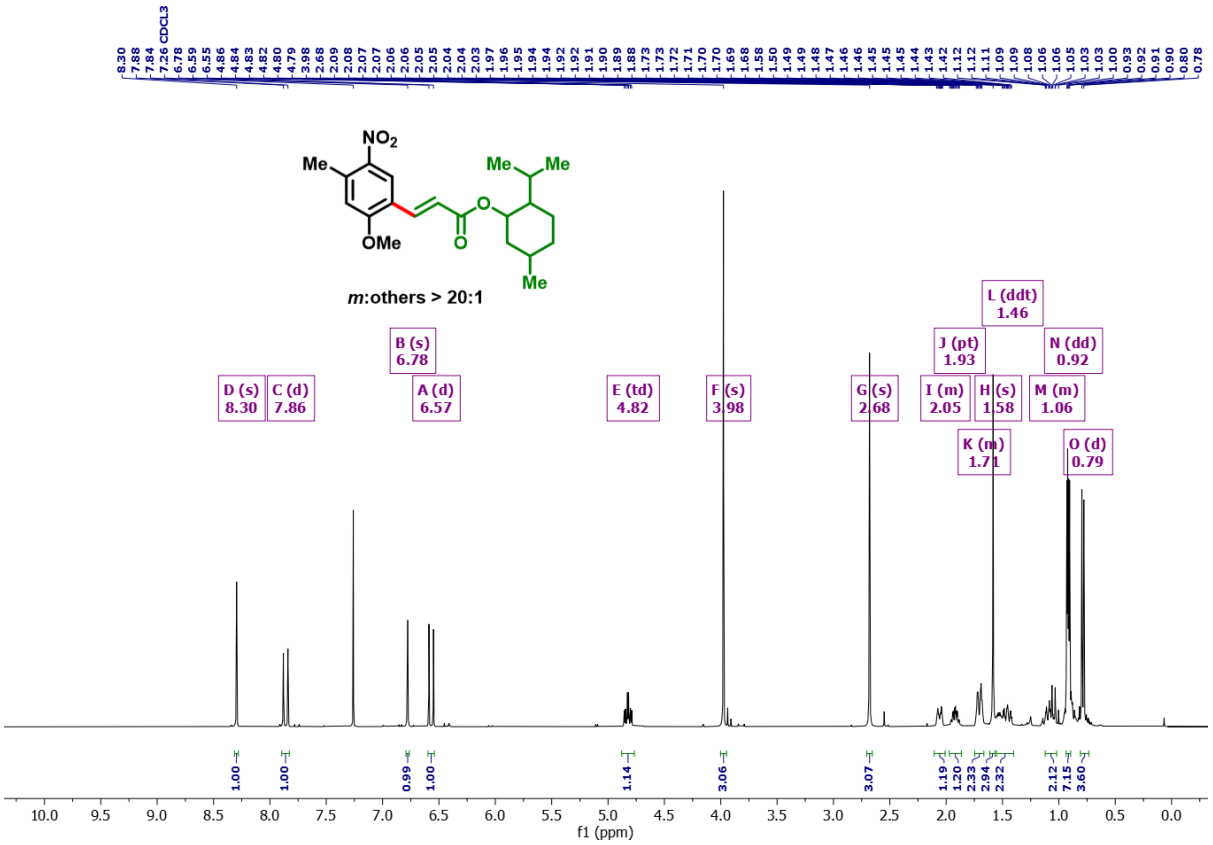

-63.02
-73.56
-119.35
-119.39
-122.12
-123.39
-129.41
-136.97
-137.00
NO2
Me
OMe
CO2CH2(CF2)5CHF2
m:others = 10:1
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)

Scheme 3, Entry 3v

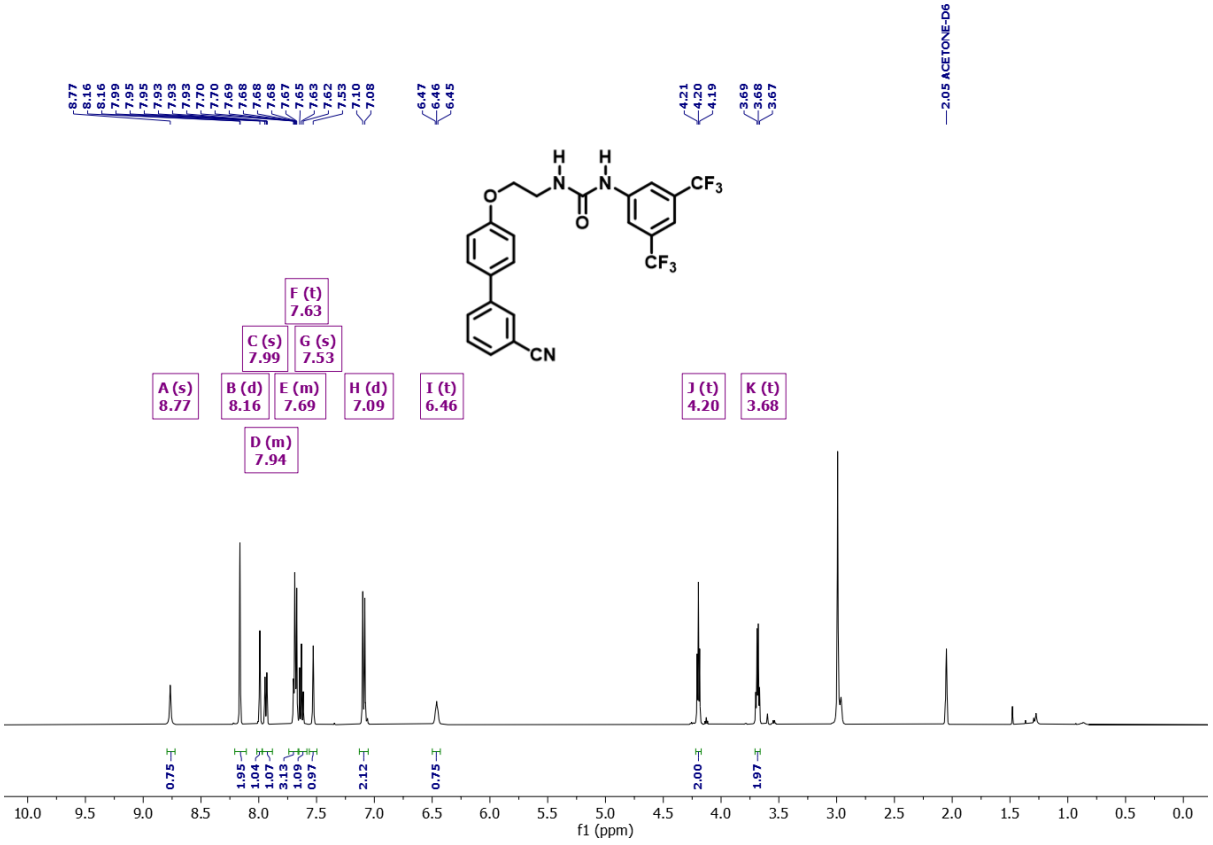


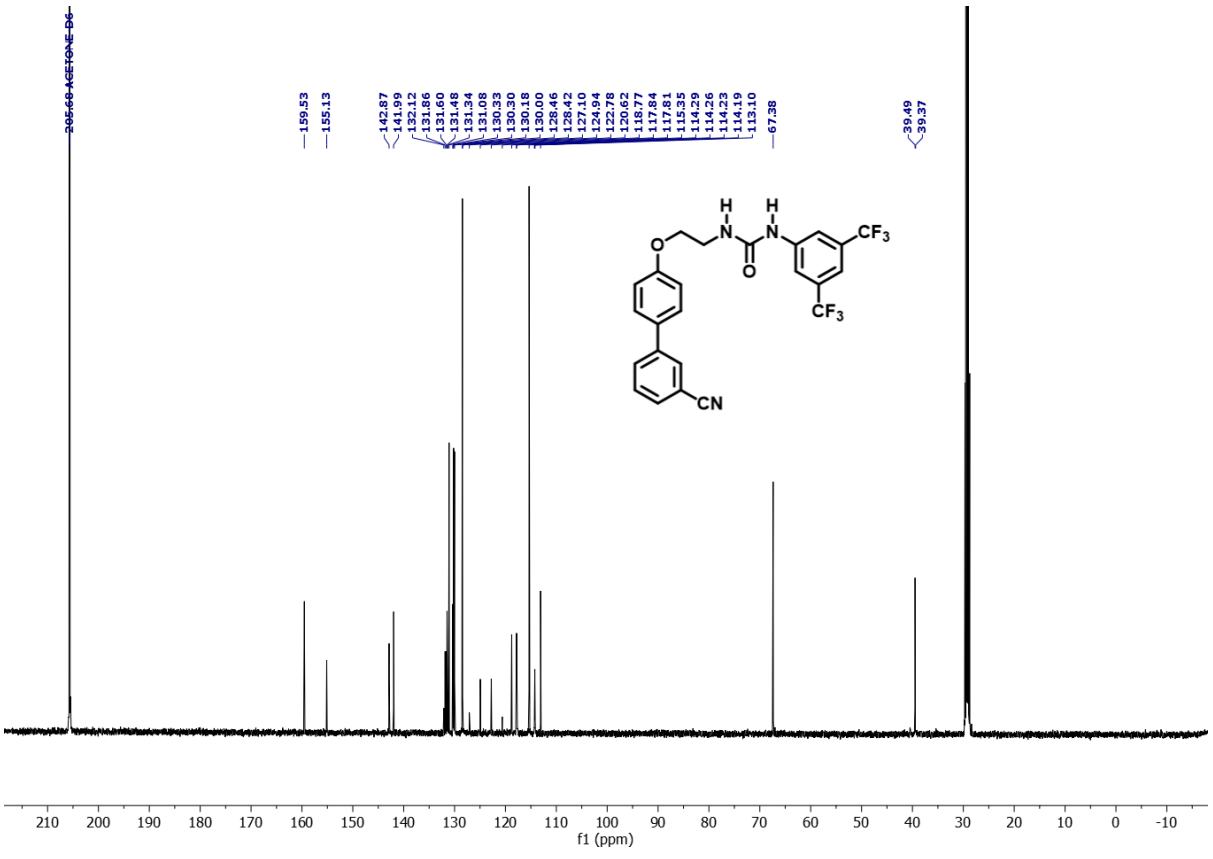
Scheme 3, Entry 3w



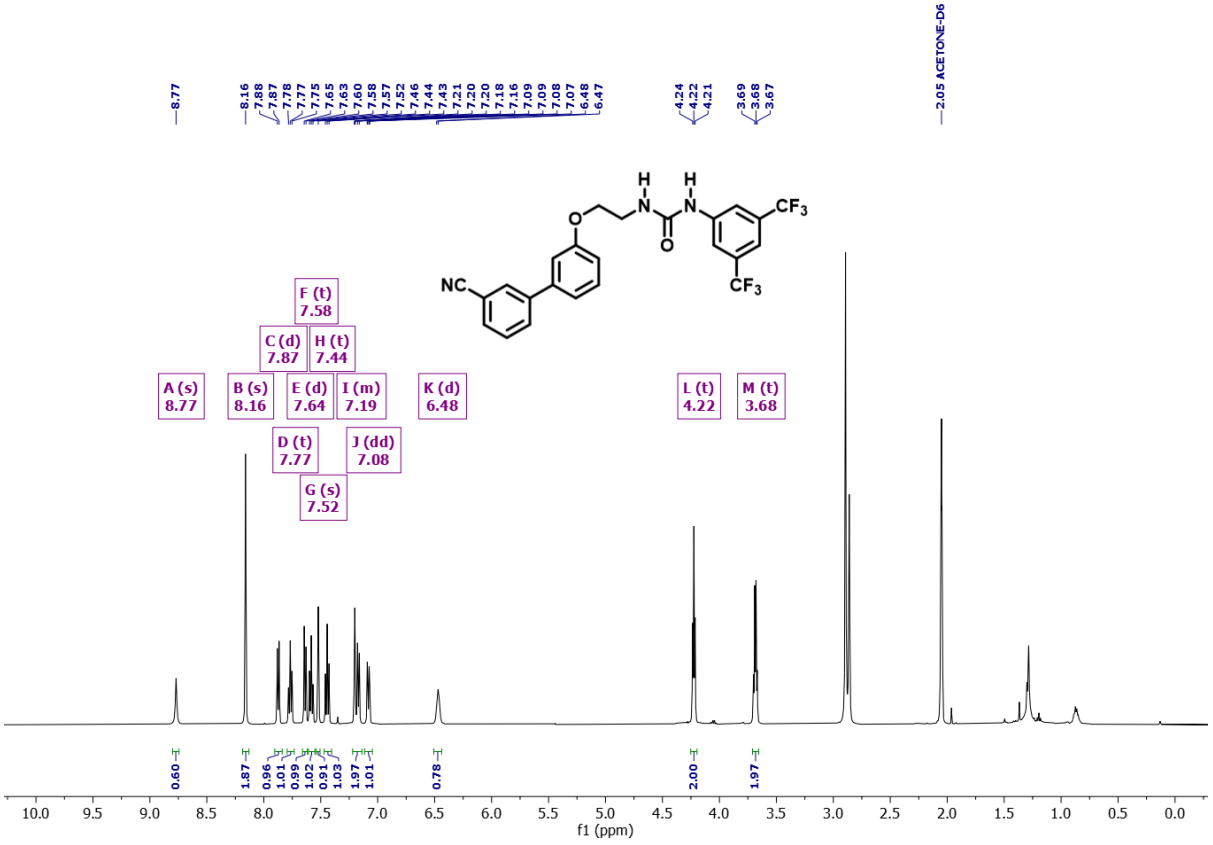


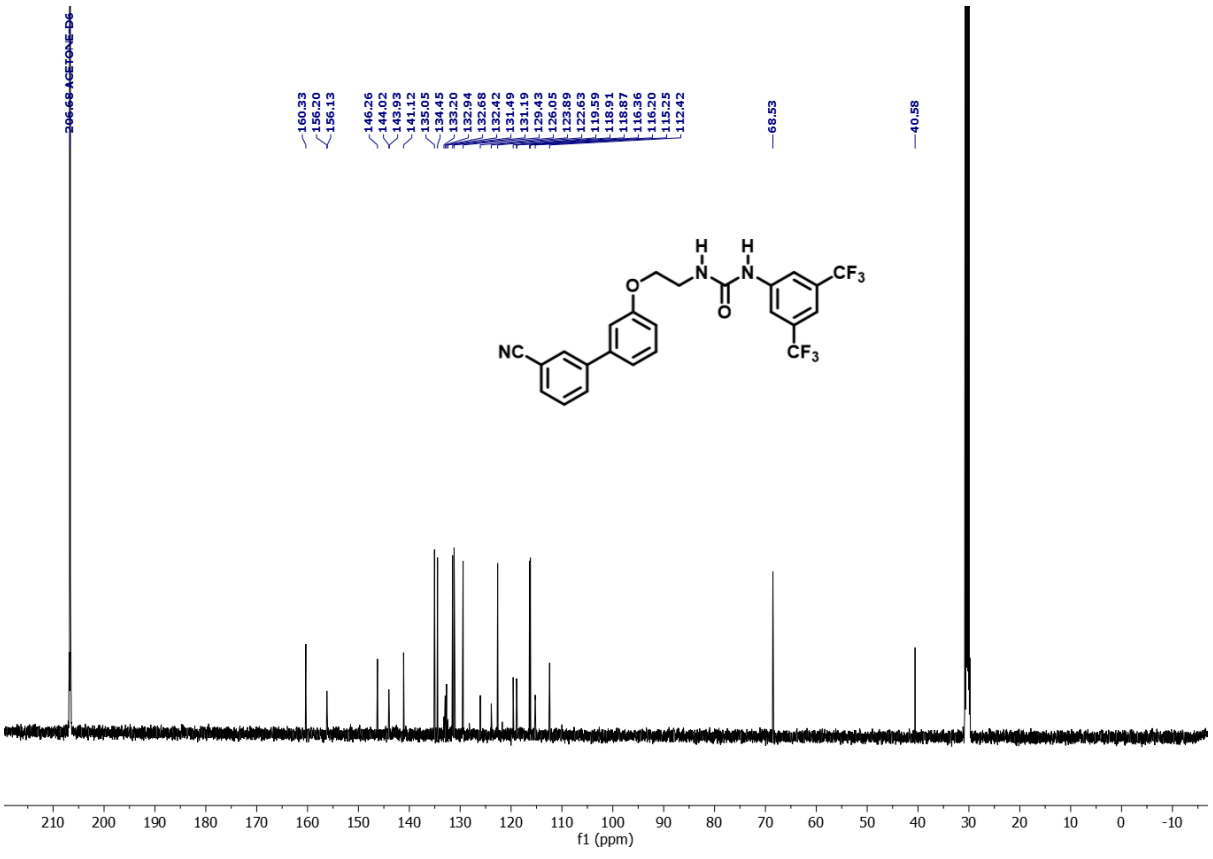
Scheme 1, HT1


A (s) 8.77
B (d) 8.16
C (s) 7.99
D (m) 7.94
E (m) 7.69
F (t) 7.63
G (s) 7.53
H (d) 7.09
I (t) 6.46
J (t) 4.20
K (t) 3.68
f1 (ppm)

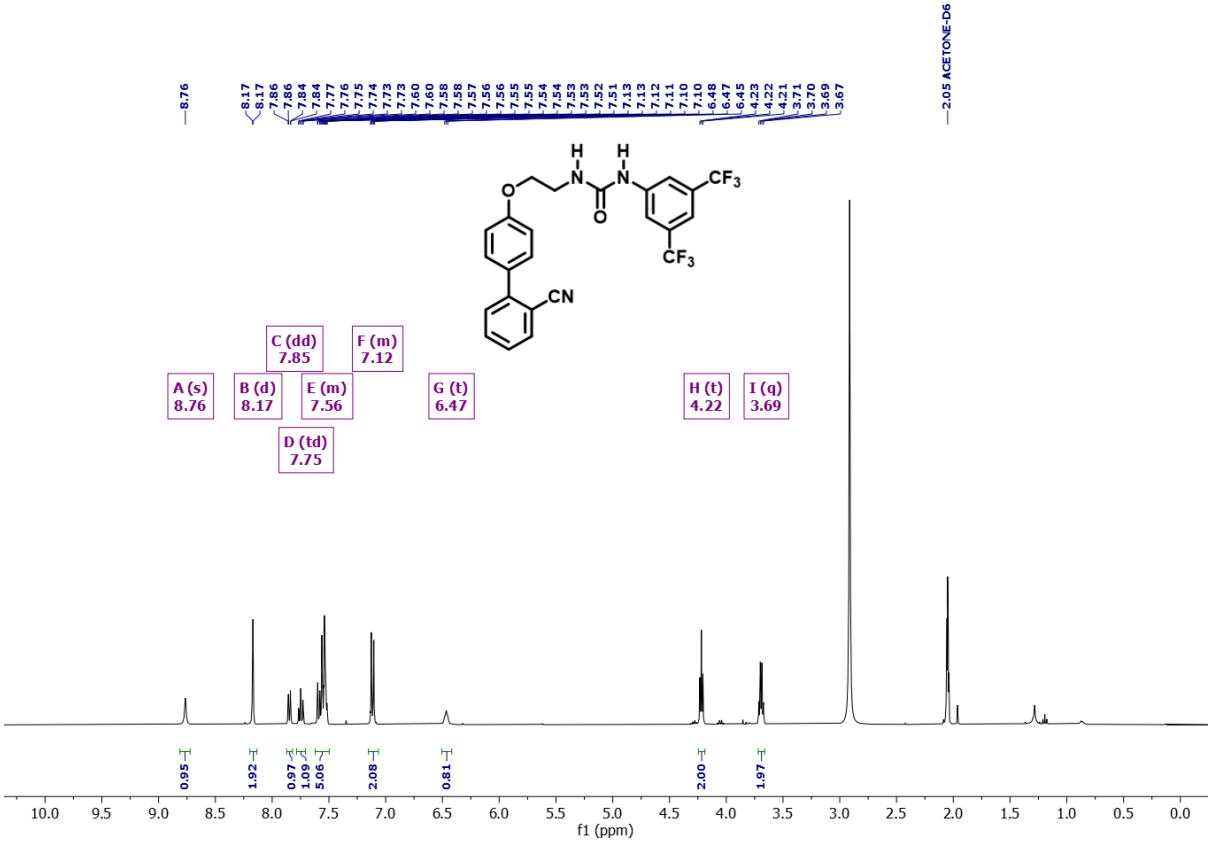

f1 (ppm)

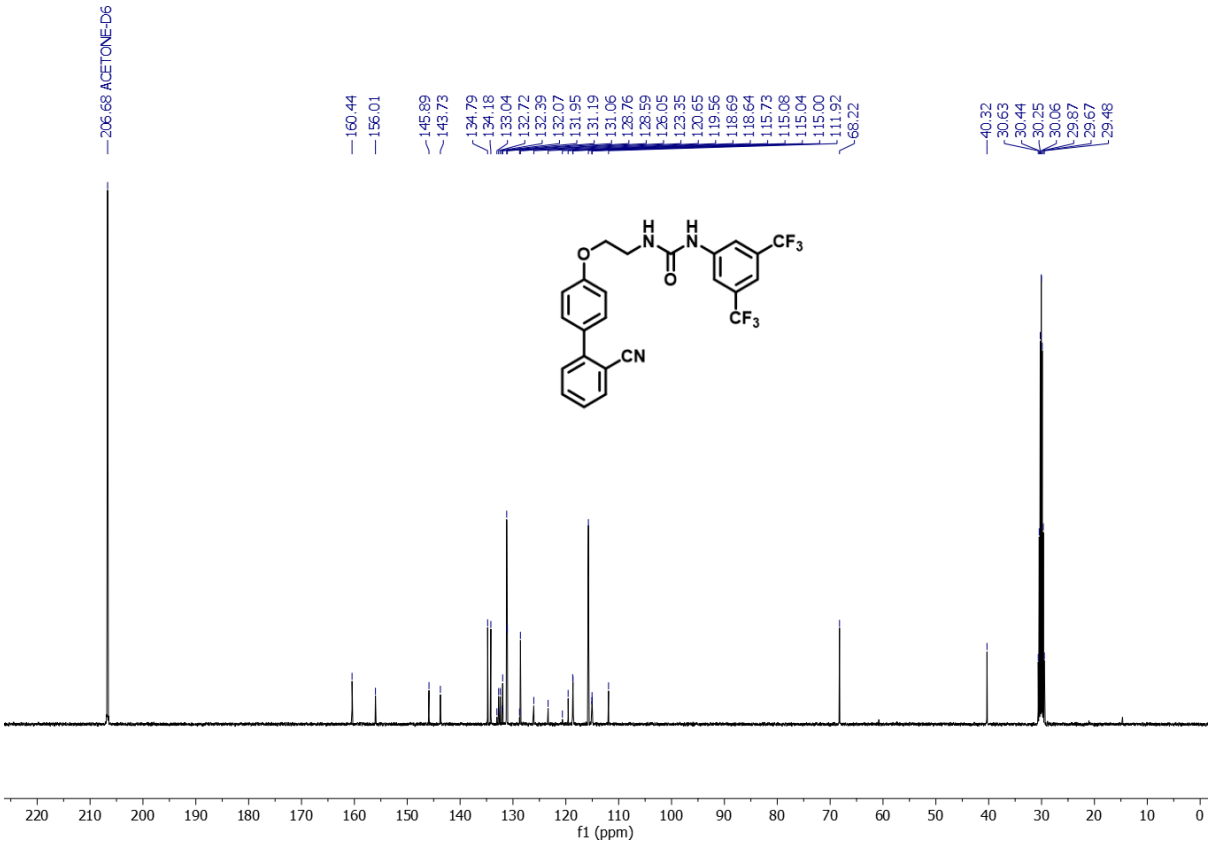
Scheme 1, HT2


8.77
8.16
7.88
7.87
7.78
7.77
7.75
7.65
7.63
7.60
7.58
7.57
7.52
7.46
7.44
7.43
7.21
7.20
7.20
7.18
7.16
7.09
7.09
7.08
7.07
6.48
6.47
4.24
4.22
4.21
3.69
3.68
3.67
2.05 ACETONE-D6
F (t) 7.58
C (d) 7.87
H (t) 7.44
A (s) 8.77
B (s) 8.16
E (d) 7.64
I (m) 7.19
K (d) 6.48
L (t) 4.22
M (t) 3.68
D (t) 7.77
J (dd) 7.08
G (s) 7.52
0.60
1.87
0.96
1.01
0.99
1.02
0.91
1.03
1.97
1.01
0.78
2.00
1.97
f1 (ppm)

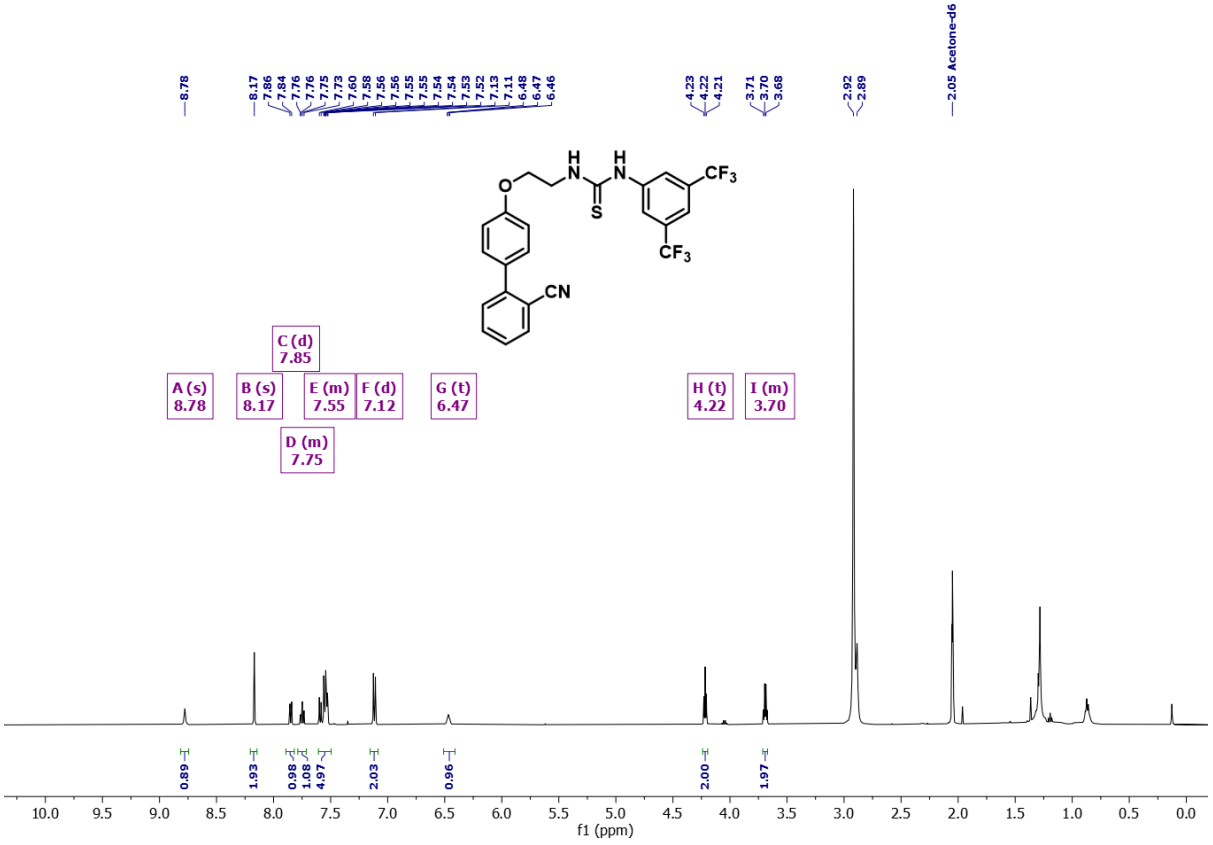

206.68 ACETONE-D6
160.33
156.20
156.13
146.26
144.02
143.93
141.12
135.05
134.45
133.20
132.94
132.68
132.42
131.49
131.19
129.43
126.05
123.89
122.63
119.59
118.91
118.87
116.36
116.20
115.25
112.42
68.53
40.58
f1 (ppm)

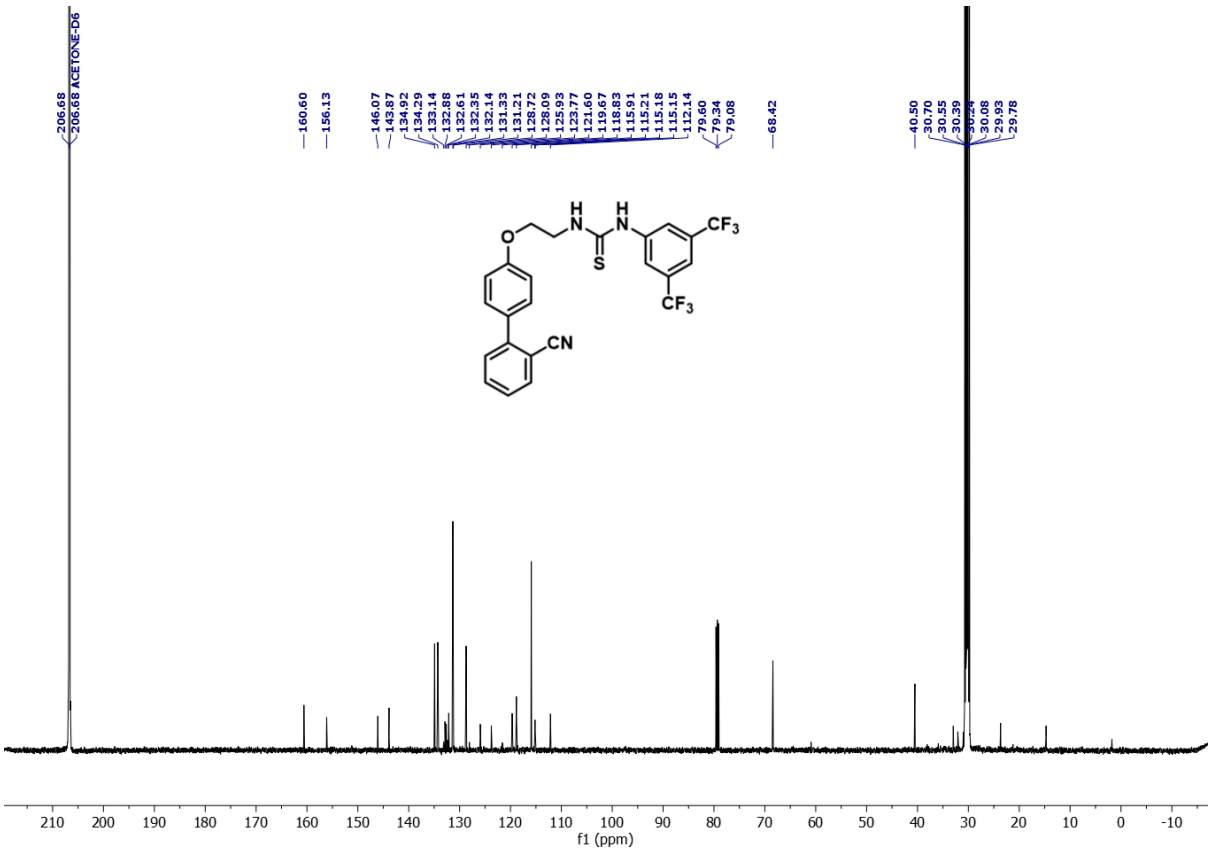
Scheme 1, HT3


8.76
8.17
8.17
7.86
7.86
7.84
7.84
7.77
7.76
7.75
7.74
7.73
7.73
7.60
7.58
7.58
7.57
7.56
7.56
7.55
7.55
7.54
7.54
7.53
7.53
7.52
7.51
7.13
7.13
7.12
7.11
7.10
7.10
6.48
6.47
6.45
4.23
4.22
4.21
3.71
3.70
3.69
3.67
2.05 ACETONE-D6
CF3
CF3
CN
C (dd) 7.85
F (m) 7.12
A (s) 8.76
B (d) 8.17
E (m) 7.56
G (t) 6.47
H (t) 4.22
I (q) 3.69
D (td) 7.75
0.95
1.92
0.97
1.09
5.06
2.08
0.81
2.00
1.97
f1 (ppm)

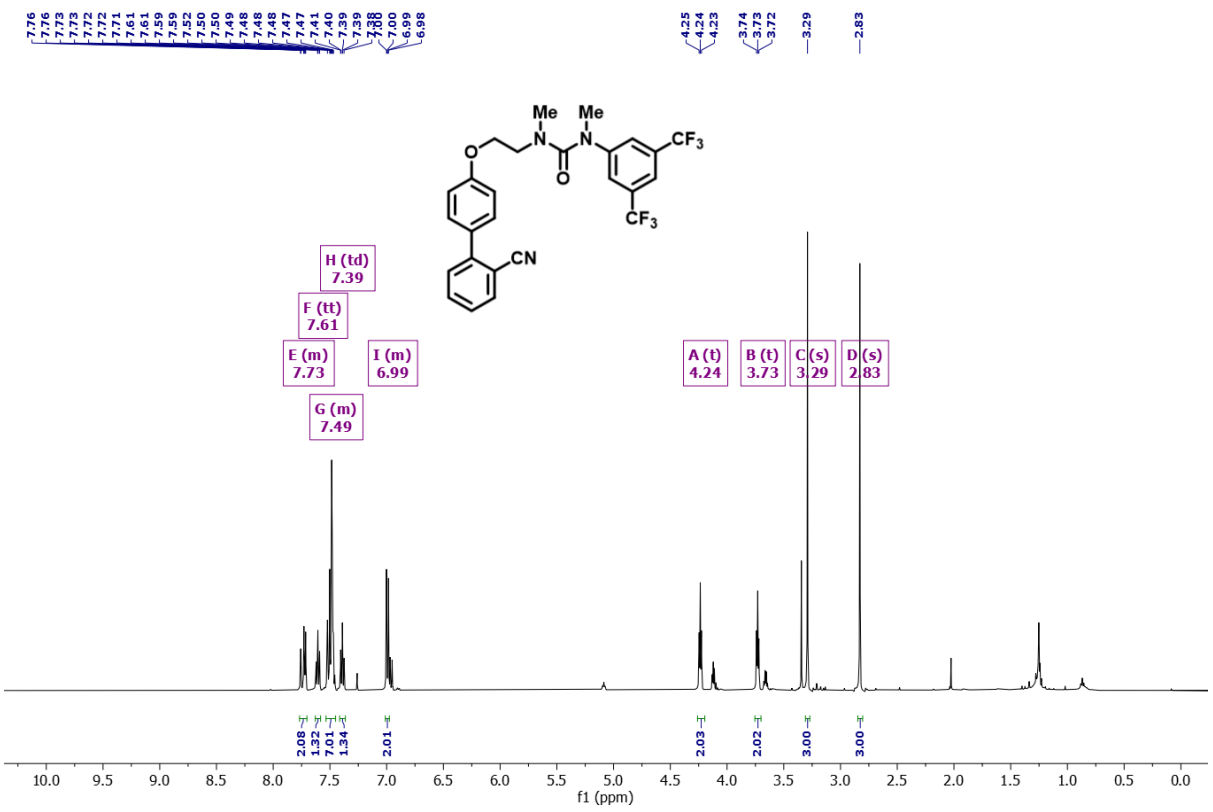

206.68 ACETONE-D6
160.44
156.01
145.89
143.73
134.79
134.18
133.04
132.72
132.39
132.07
131.95
131.19
131.06
128.76
128.59
126.05
123.35
120.65
119.56
118.69
118.64
115.73
115.08
115.04
115.00
111.92
68.22
40.32
30.63
30.44
30.25
30.06
29.87
29.67
29.48
CF3
CF3
CN
f1 (ppm)

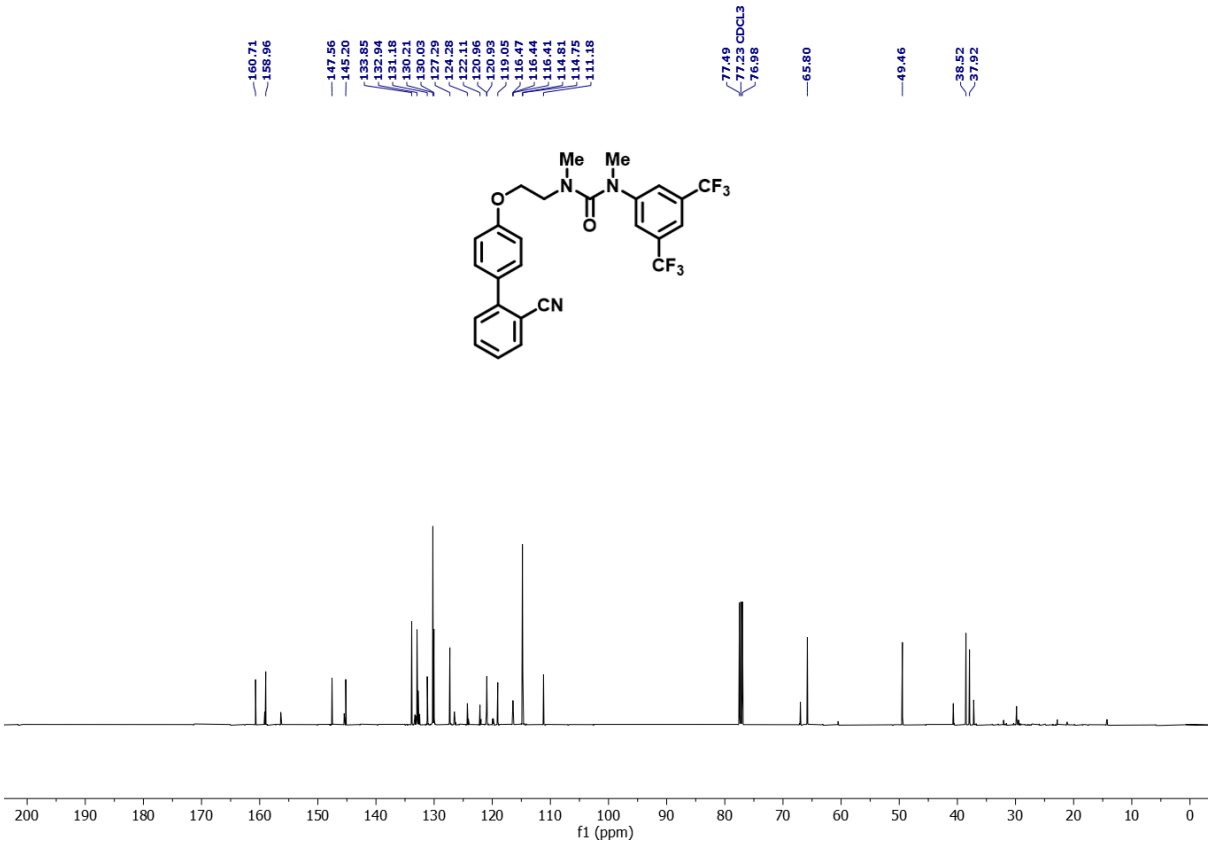
Scheme 1, HT4


8.78
8.17
7.86
7.84
7.76
7.75
7.73
7.60
7.58
7.56
7.55
7.54
7.53
7.52
7.13
6.48
6.47
6.46
4.23
4.22
4.21
3.71
3.70
3.68
2.92
2.89
2.05 Acetone-d6
A (s) 8.78
B (s) 8.17
C (d) 7.85
D (m) 7.75
E (m) 7.55
F (d) 7.12
G (t) 6.47
H (t) 4.22
I (m) 3.70
0.89
1.93
0.98
1.08
4.97
2.03
0.96
2.00
1.97
f1 (ppm)

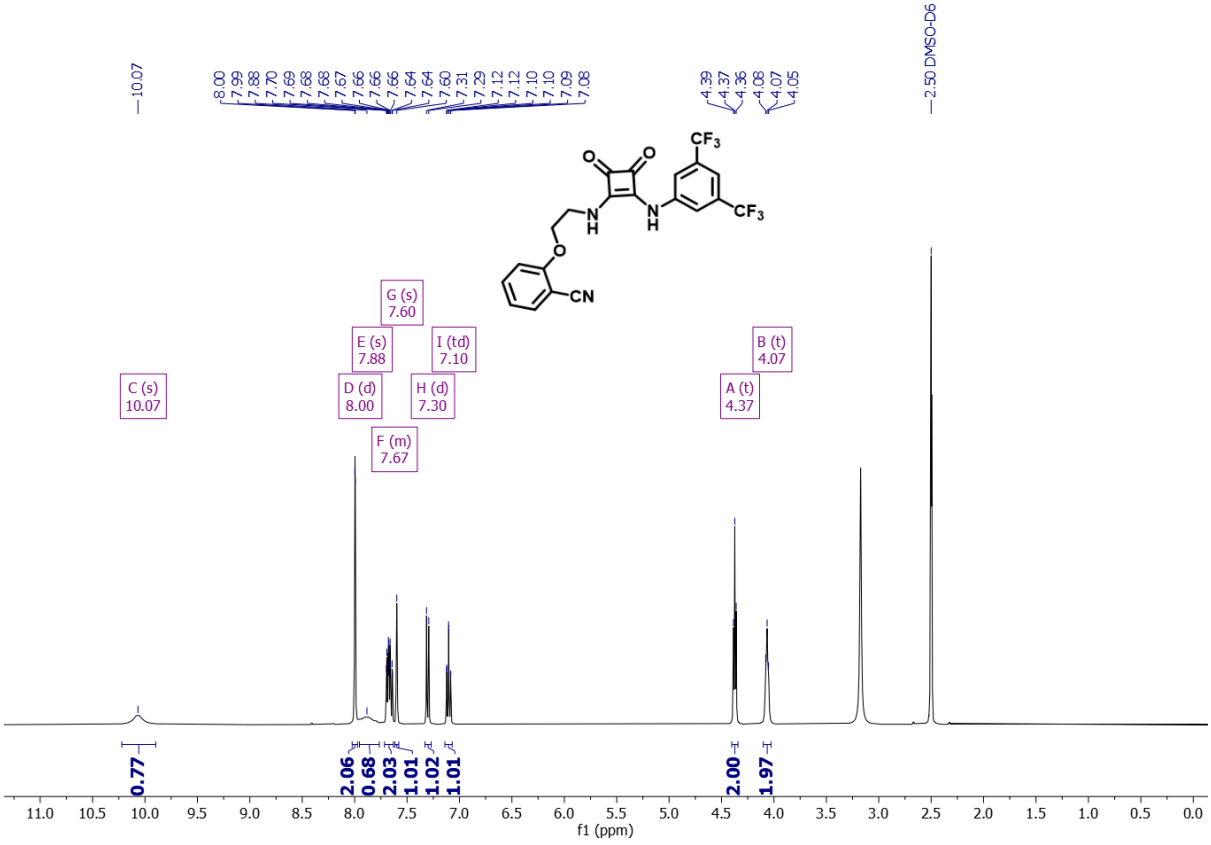

206.68
206.68 ACETONE-D6
160.60
156.13
146.07
143.87
134.92
134.29
133.14
132.88
132.61
132.35
132.14
131.33
131.21
128.72
128.09
125.93
123.77
121.60
119.67
118.83
115.91
115.21
115.18
115.15
112.14
79.60
79.34
79.08
68.42
40.50
30.70
30.55
30.39
30.24
30.08
29.93
29.78
f1 (ppm)

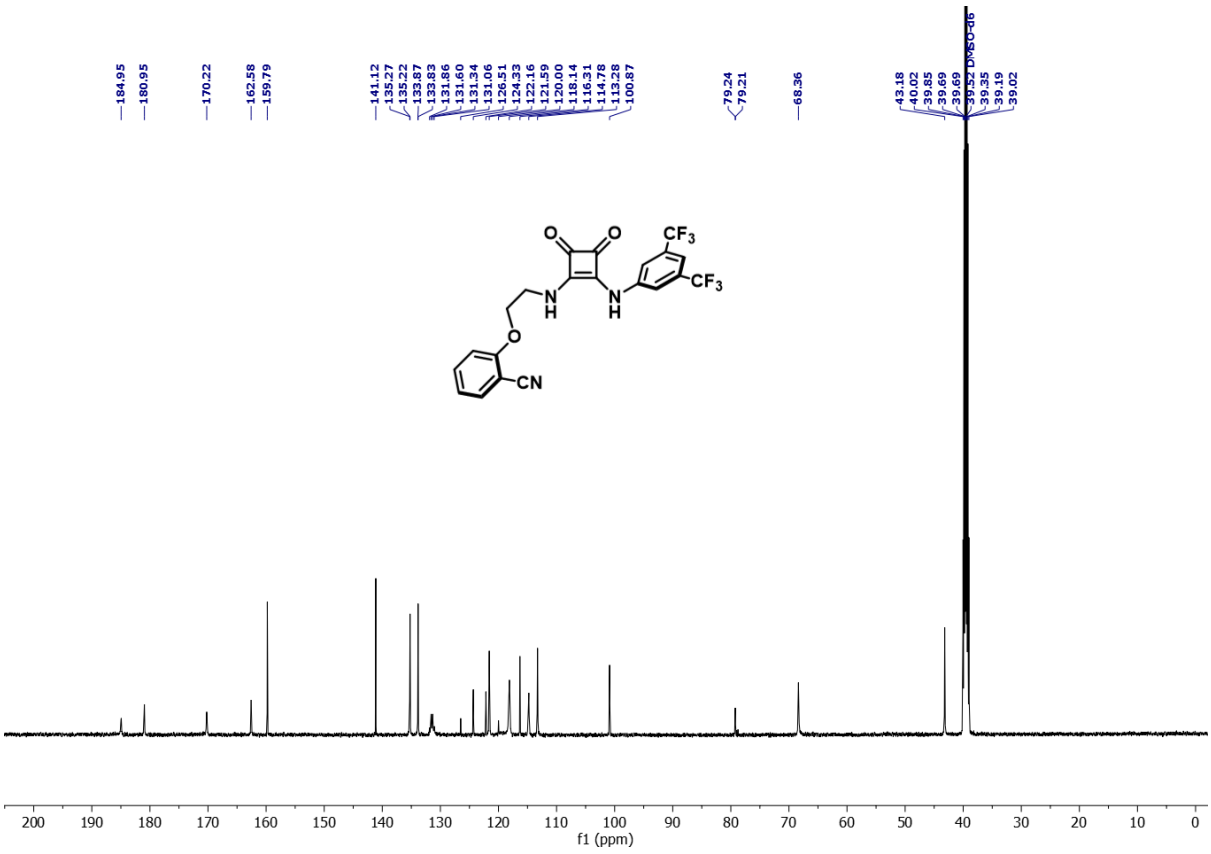
Scheme 4A, HT11

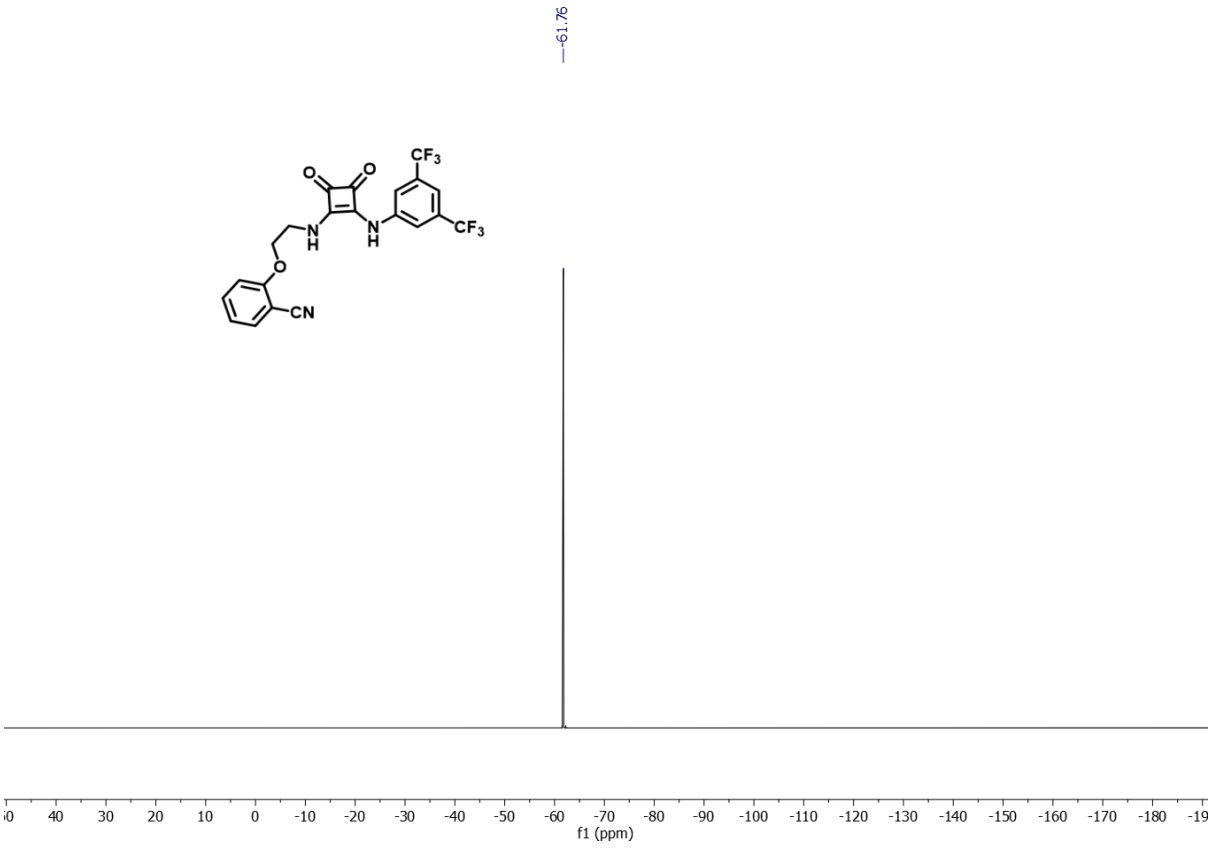




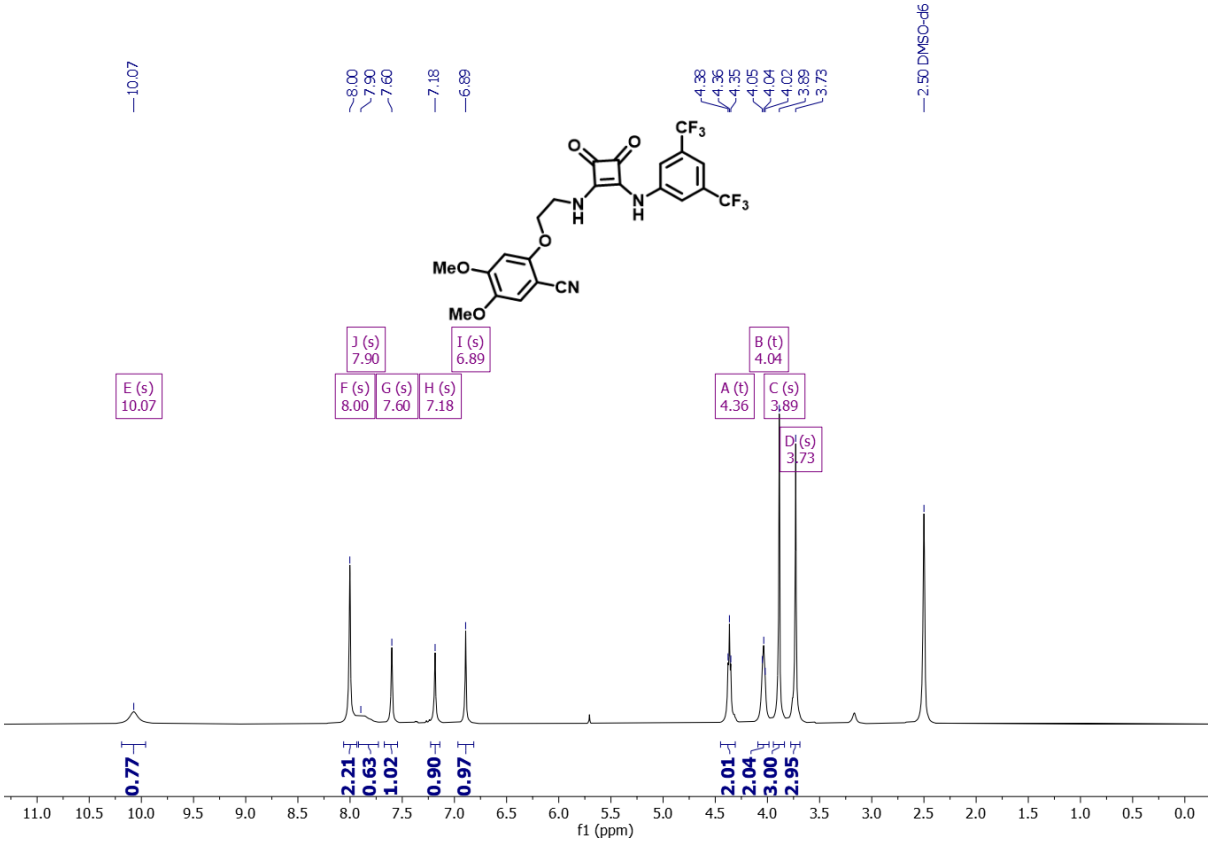
Scheme 1, HT5

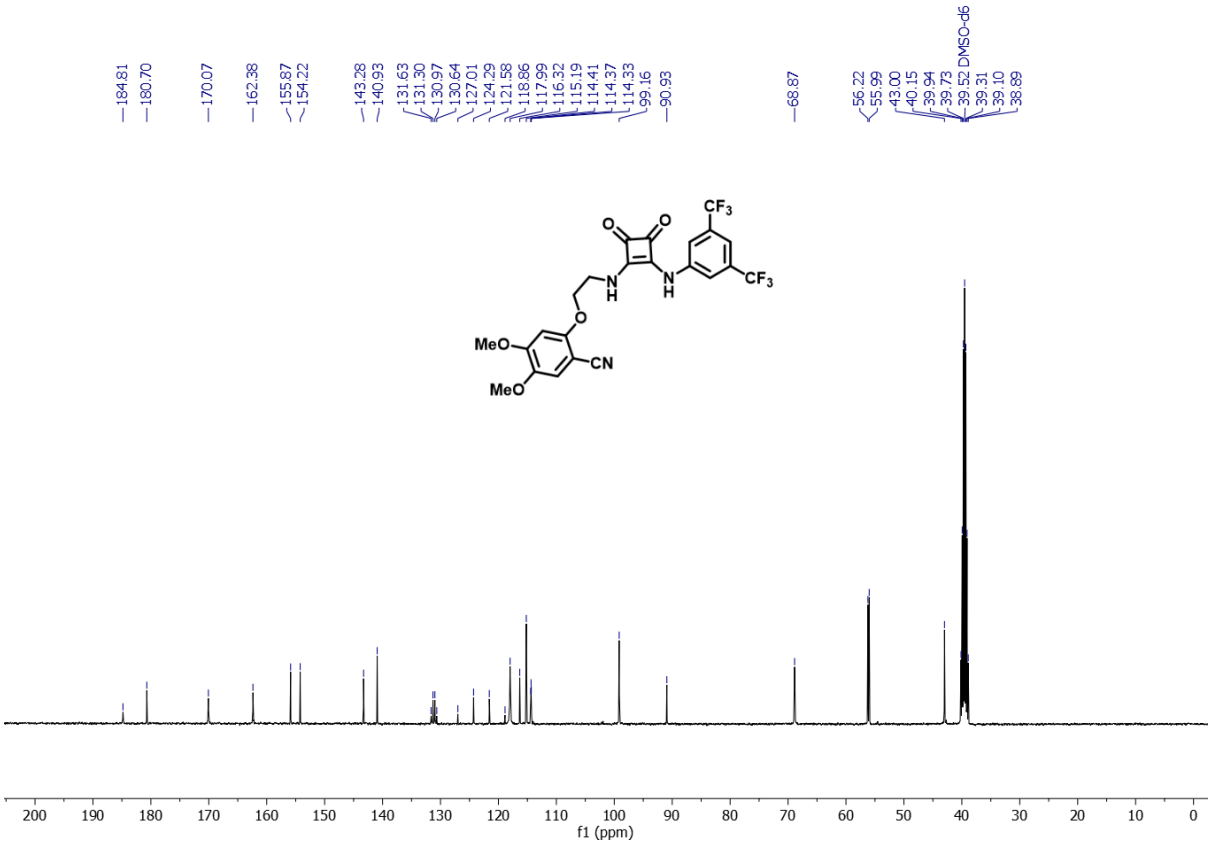

10.07
8.00
7.99
7.88
7.70
7.69
7.68
7.68
7.67
7.66
7.66
7.66
7.64
7.64
7.60
7.31
7.29
7.12
7.10
7.10
7.09
7.08
4.39
4.37
4.36
4.08
4.07
4.05
2.50 DMSO-D6
CF3
CF3
O
O
N
H
N
H
O
CN
G (s) 7.60
E (s) 7.88
I (td) 7.10
B (t) 4.07
C (s) 10.07
D (d) 8.00
H (d) 7.30
A (t) 4.37
F (m) 7.67
0.77
2.06
0.68
2.03
1.01
1.02
1.01
2.00
1.97
f1 (ppm)

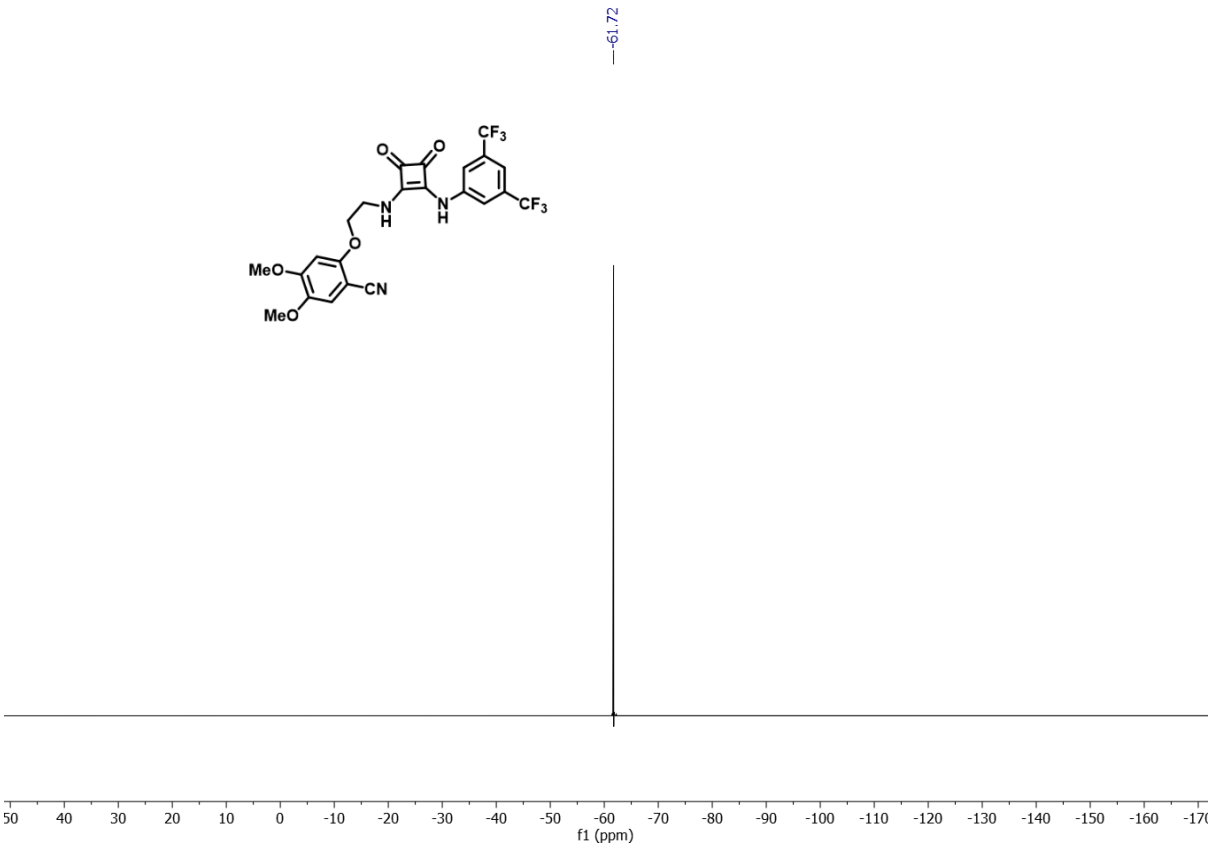

184.95
180.95
170.22
162.58
159.79
141.12
135.27
135.22
133.87
133.83
131.86
131.60
131.34
131.06
126.51
124.33
122.16
121.59
120.00
118.14
116.31
114.78
113.28
100.87
79.24
79.21
68.36
43.18
40.02
39.85
39.69
39.69
39.52 DMSO-D6
39.35
39.19
39.02
CF3
CF3
O
O
N
H
N
H
O
CN
f1 (ppm)


-61.76
O
O
N
H
N
H
CF3
CF3
O
CN
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

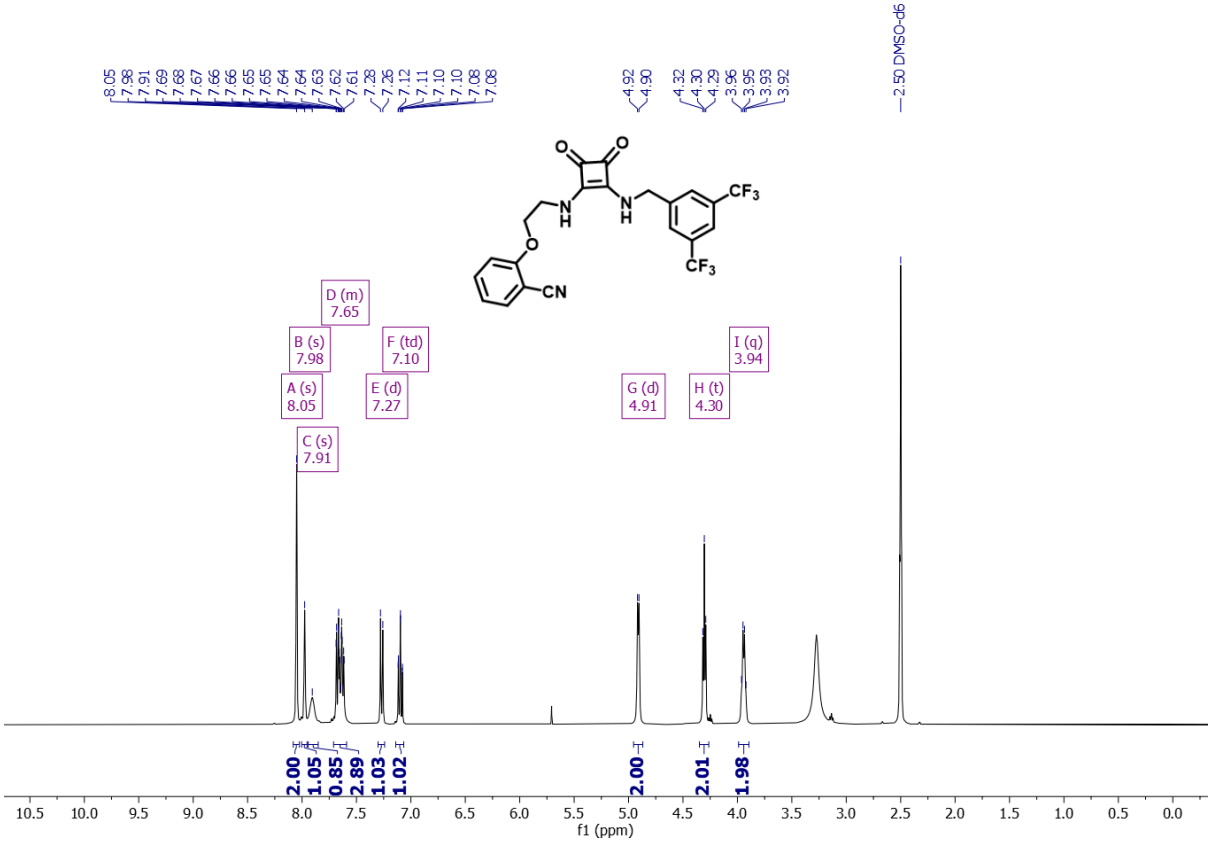
Scheme 1, HT6

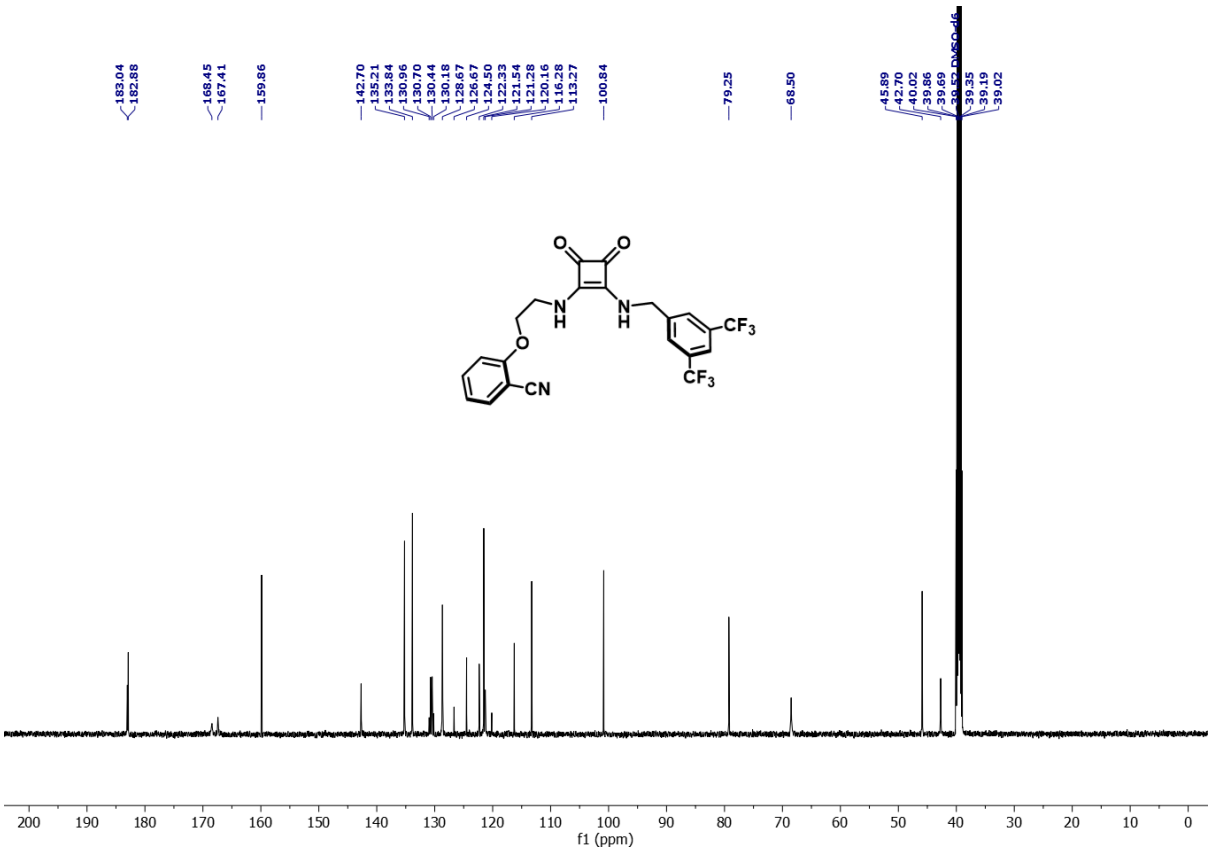

10.07
8.00
7.90
7.60
7.18
6.89
4.38
4.36
4.35
4.05
4.04
4.02
3.89
3.73
2.50 DMSO-d6
E (s) 10.07
F (s) 8.00
G (s) 7.60
H (s) 7.18
J (s) 7.90
I (s) 6.89
A (t) 4.36
C (s) 3.89
B (t) 4.04
D (s) 3.73
0.77
2.21
0.63
1.02
0.90
0.97
2.01
2.04
3.00
2.95
f1 (ppm)

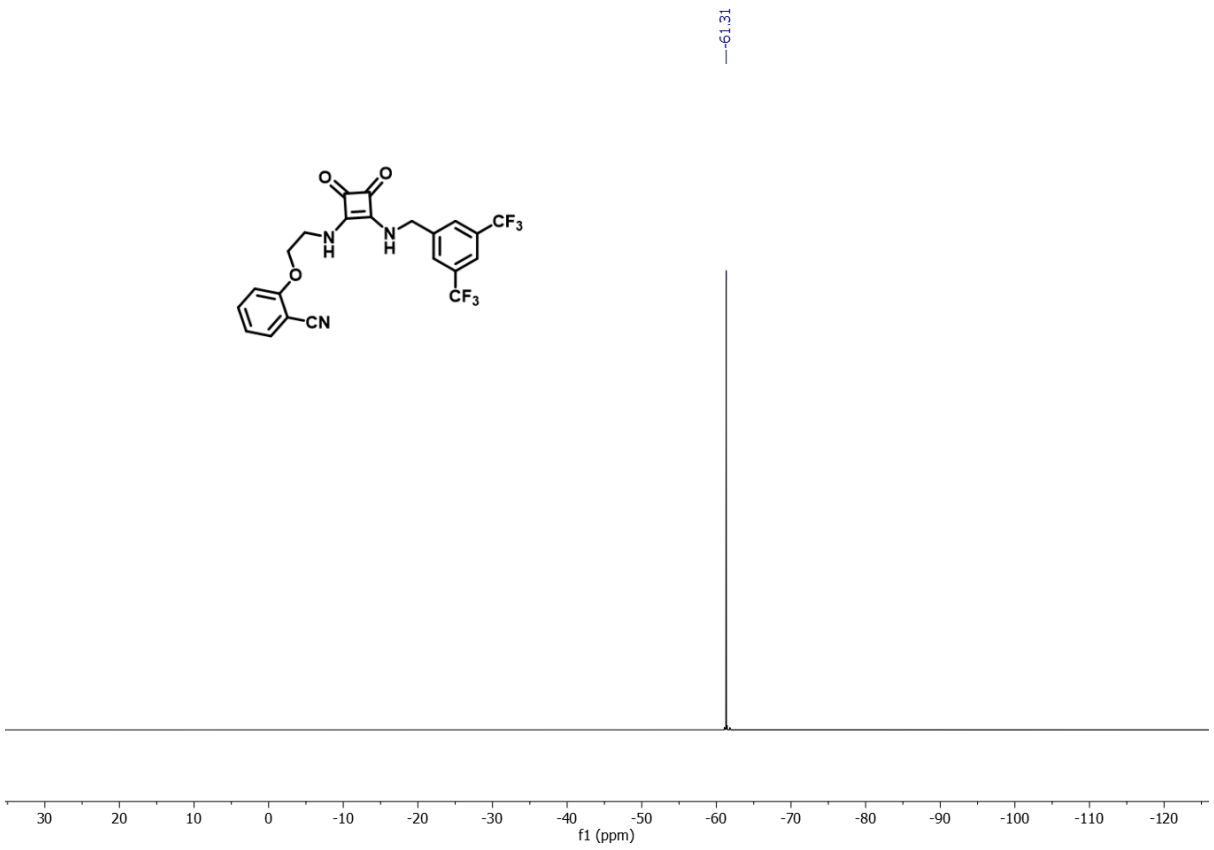

184.81
180.70
170.07
162.38
155.87
154.22
143.28
140.93
131.63
131.30
130.97
130.64
127.01
124.29
121.58
118.86
117.99
116.32
115.19
114.41
114.37
114.33
99.16
90.93
68.87
56.22
55.99
43.00
40.15
39.94
39.73
39.52 DMSO-d6
39.31
39.10
38.89
f1 (ppm)


-61.72
CF3
CF3
O
O
N
H
N
H
O
MeO
MeO
CN
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -17
f1 (ppm)

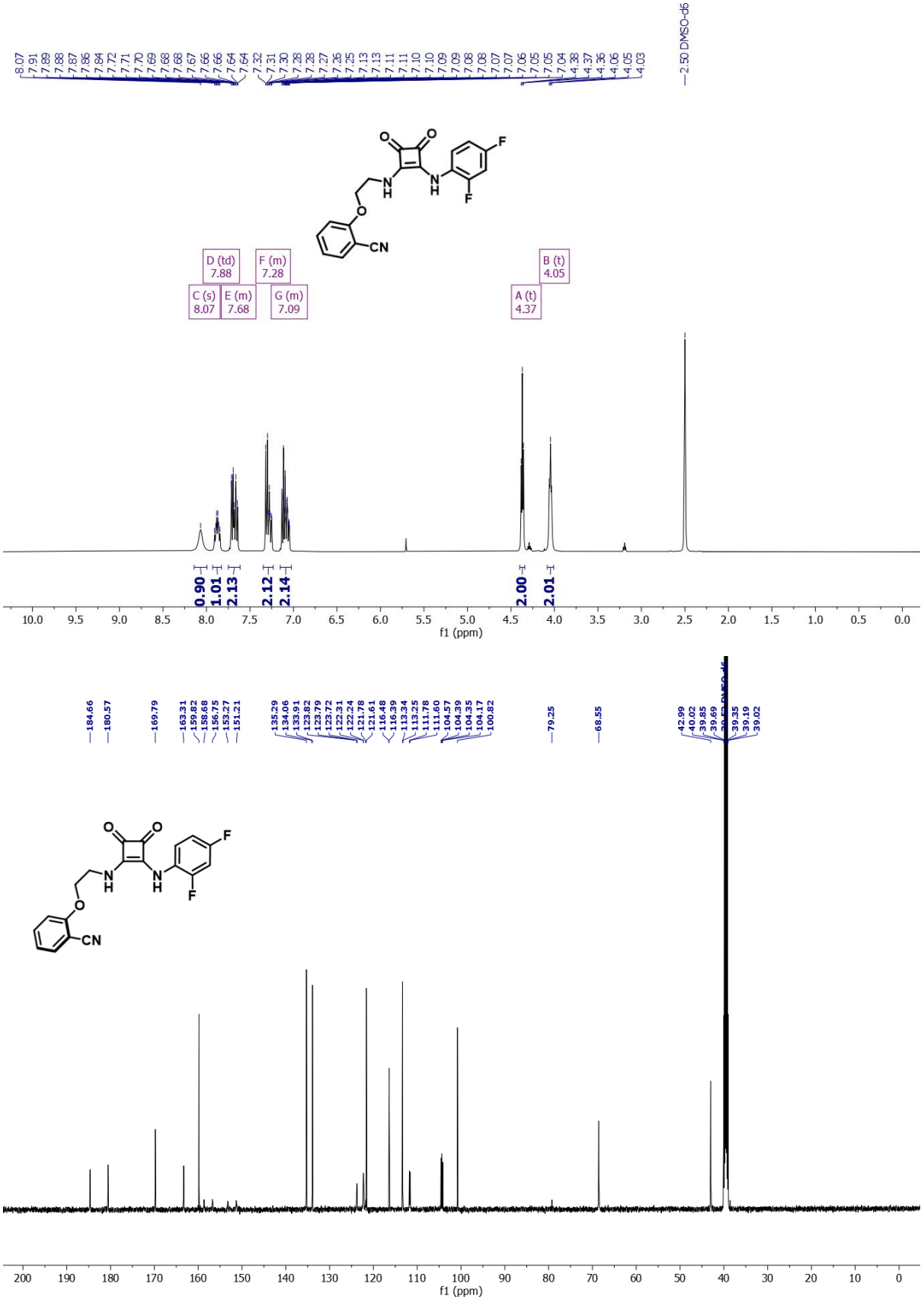
Scheme 1, HT7

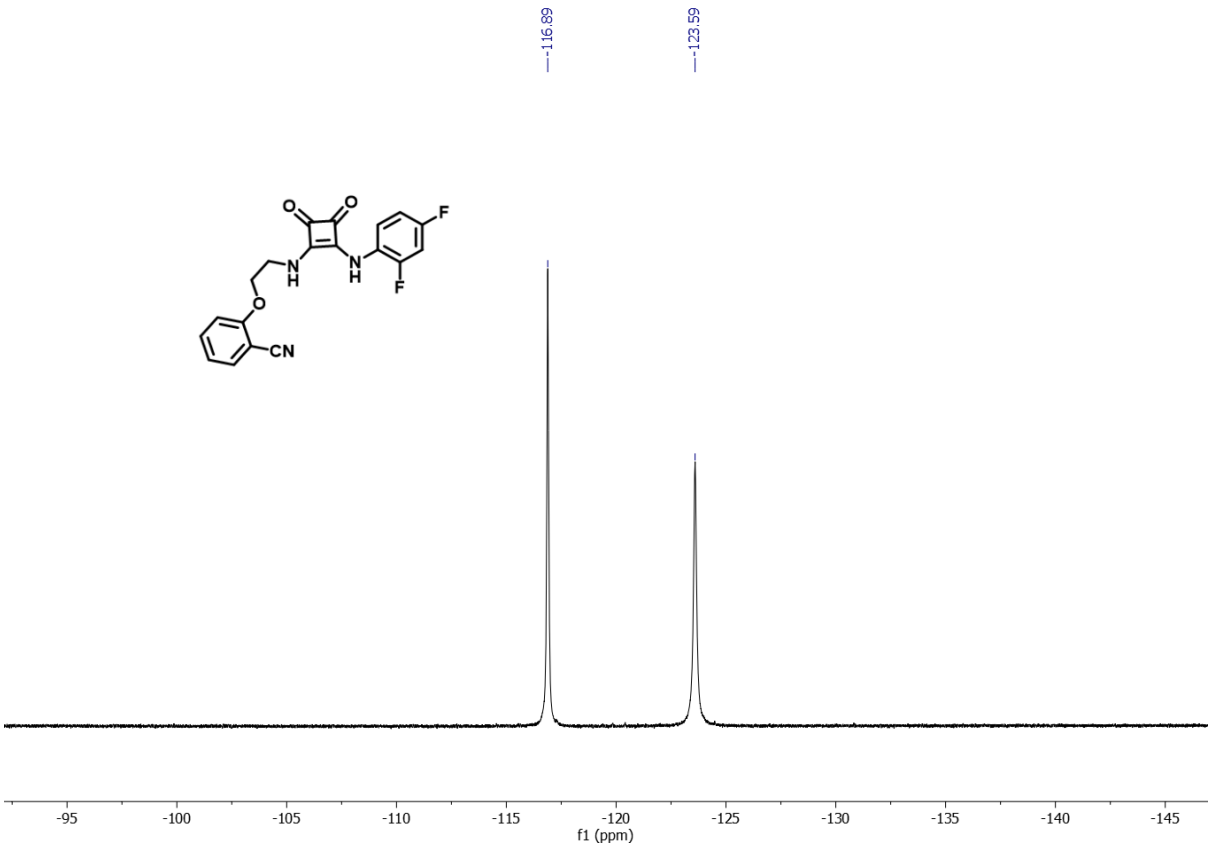

8.05
7.98
7.91
7.69
7.68
7.67
7.66
7.66
7.65
7.65
7.64
7.64
7.63
7.62
7.61
7.28
7.26
7.12
7.11
7.10
7.10
7.08
7.08
4.92
4.90
4.32
4.30
4.29
3.96
3.95
3.93
3.92
2.50 DMSO-d6
D (m) 7.65
B (s) 7.98
F (td) 7.10
I (q) 3.94
A (s) 8.05
E (d) 7.27
G (d) 4.91
H (t) 4.30
C (s) 7.91
2.00
1.05
0.85
2.89
1.03
1.02
2.00
2.01
1.98
f1 (ppm)


183.04
182.88
168.45
167.41
159.86
142.70
135.21
133.84
130.96
130.70
130.44
130.18
128.67
126.67
124.50
122.33
121.54
121.28
120.16
116.28
113.27
100.84
79.25
68.50
45.89
42.70
40.02
39.86
39.69
39.52 DMSO-d6
39.35
39.19
39.02
f1 (ppm)

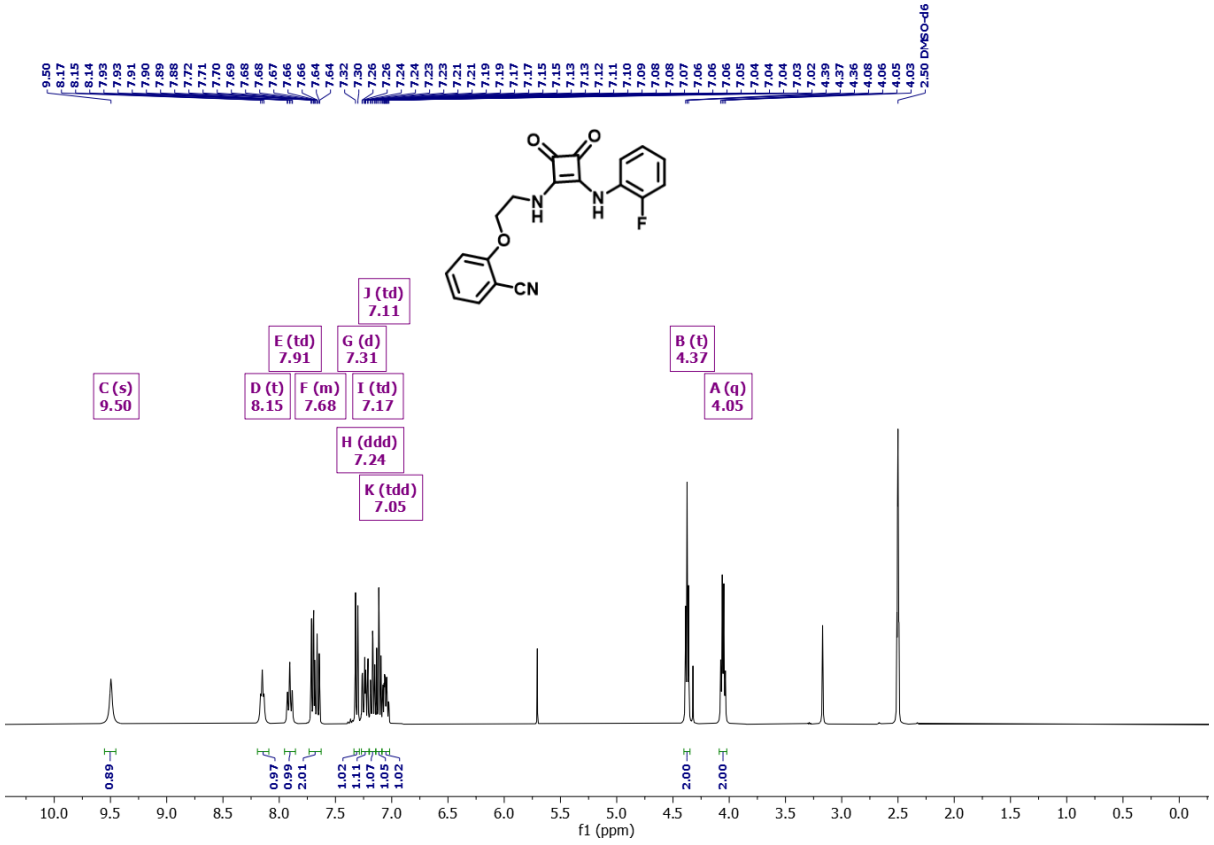

-61.31
O
O
N
H
N
H
O
CN
CF3
CF3
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
f1 (ppm)

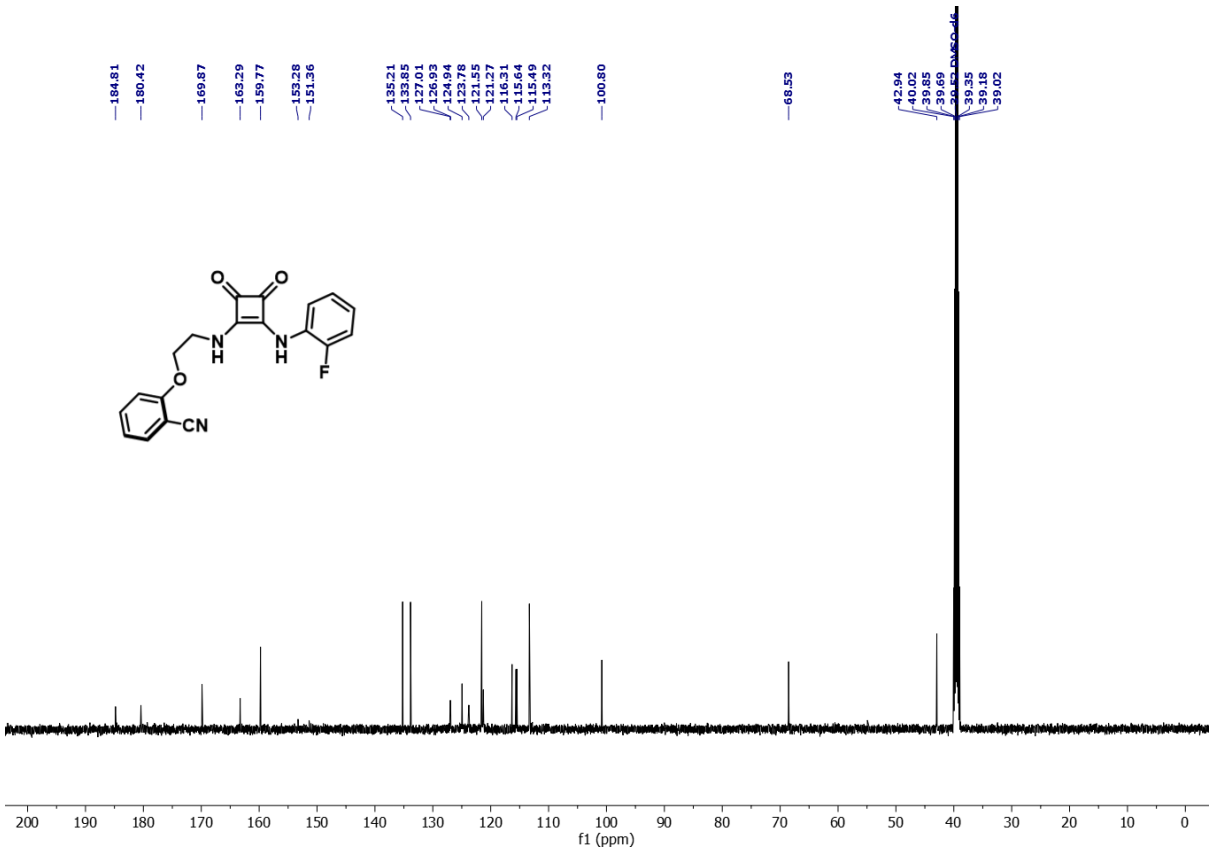
Scheme 1, HT8


8.07
7.91
7.89
7.88
7.87
7.86
7.84
7.72
7.71
7.70
7.69
7.68
7.68
7.67
7.66
7.66
7.64
7.64
7.32
7.31
7.30
7.28
7.28
7.27
7.26
7.25
7.13
7.13
7.11
7.11
7.10
7.10
7.09
7.09
7.08
7.08
7.07
7.07
7.06
7.05
7.05
7.04
4.38
4.37
4.36
4.06
4.05
4.03
2.50 DMSO-d6
D (td) 7.88
F (m) 7.28
B (t) 4.05
C (s) 8.07
E (m) 7.68
G (m) 7.09
A (t) 4.37
0.90
1.01
2.13
2.12
2.14
2.00
2.01
f1 (ppm)
184.66
180.57
169.79
163.31
159.82
158.68
156.75
153.27
151.21
135.29
134.06
133.91
123.82
123.79
123.72
122.31
122.24
121.78
121.61
116.48
116.39
113.34
113.25
111.78
111.60
104.57
104.39
104.35
104.17
100.82
79.25
68.55
42.99
40.02
39.85
39.69
39.35
39.19
39.02
f1 (ppm)


-116.89
-123.59
O
O
F
N
H
N
H
F
O
CN
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
f1 (ppm)

Scheme 1, HT9


J (td) 7.11
E (td) 7.91
G (d) 7.31
B (t) 4.37
C (s) 9.50
D (t) 8.15
F (m) 7.68
I (td) 7.17
A (q) 4.05
H (ddd) 7.24
K (tdd) 7.05
f1 (ppm)


f1 (ppm)

Scheme 1, HT10