Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Cobalt-Catalyzed Direct Transformation of Aldehydes to Esters: The Crucial Role of an Enone as a Mediator

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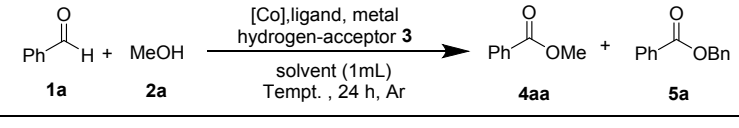
1. General Method

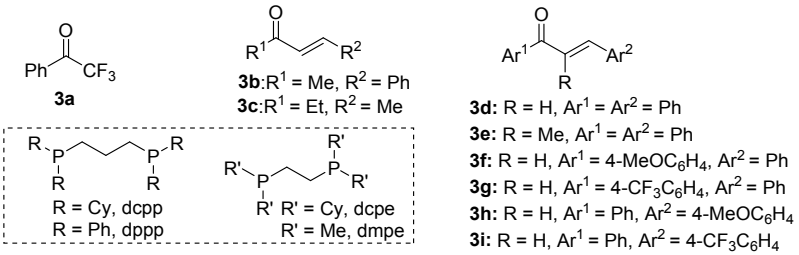
All reactions were prepared and sealed using a glass flask in a glove box filled with argon. Then the reactions were performed on a multi-zone reaction platform. NMR spectra were recorded on a Bruker ASCEND spectrometer (^{1}H, 600 MHz; ^{13}C{^{1}H}, 151 MHz) or a JEOL JNM-ECA600 spectrometer (^{1}H, 600 MHz; ^{13}C{^{1}H}, 151 MHz). ^{1}H NMR and ^{13}C{^{1}H} NMR, chemical shift is given relative to TMS and referenced to the solvent signal. GC analysis was performed using Aglient GC-7890B equipped with a DB-FFAP capillary column, 30 m×0.32 mm; FID detector. GC-MS analysis was performed using Shimadzu GCMS-QP2020 with HP-5MS column, FID detector. UV-visible spectroscopic studies were recorded with Shimadzu UV-2550. Column chromatography was performed using silica gel. Analytical TLC was done using pre-coated silica gel 60 F254 plates.

2. Optimization for Oxidative Esterification of Benzaldehyde with Methanol

Procedure: To a dry flask containing a 1,4-dioxane (1 mL) solution of cobaltous salt (0.02 mmol, 10 mol%), phosphine ligand (0.03 mmol, 15 mol%), reductive metal (0.08 mmol, 40 mol%) and oxidant (0.2 mmol, 1.0 equiv.), alcohol **2a** and aldehyde **1a** (0.2 mmol, 1.0 equiv.) were added in the glove box. The mixture was then stirred under the designated temperature. After reaction for 24 h, the mixture was cooled to room temperature and diluted with EtOAc, the mixture was filtered and then detected by GC with biphenyl as internal standard.

Table S1. Screening optimal conditions for oxidative esterification of benzaldehyde with methanol. [a]





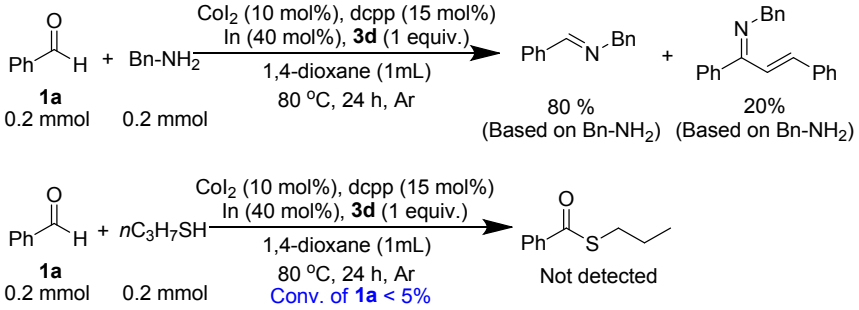
Entry	Deviation from "General conditions"	Conv. of **1a** [b] (%)	Yield [b] (%)	
			4aa	**5a**
1	**1a** instead of **3f**	38	6	0
2	**3a** instead of **3f**	78	34	9
3	**3b** instead of **3f**	35	12	0
4	**3c** instead of **3f**	57	11	0
5	**3d** instead of **3f**	98	69	15
6	**3e** instead of **3f**	62	33	13
7	**none**	95	73	14
8	**3g** instead of **3f**	99	67	17
9	**3h** instead of **3f**	98	69	15
10	**3i** instead of **3f**	97	65	15
11	dppp instead of dcpp	9	1	0
12	dcpe instead of dcpp	51	14	0
13	dmpe instead of dcpp	2	1	0
14	without In	17	8	0
15	Zn instead of In	99	66	13

16	Mn instead of In	99	63	17
17	$CoBr_2$ instead of CoI_2	94	56	19
18	5 mol% of CoI_2	98	67	19
19	20 mol% of CoI_2	98	65	17
20	THF instead of 1,4-dioxane	93	65	15
21	Toluene instead of 1,4-dioxane	98	31	52
22	DCE instead of 1,4-dioxane	4	2	0
23	60 ˚C	79	39	0
24	100 ˚C	95	70	14
25	2.5 equiv. of **2a**	97	82	5
26	5.0 equiv. of **2a**	95	83	4
27	2.5 equiv. of **2a**, 2.0 equiv. of **3f**	97	74	15

[a] General conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), **3f** (1.0 equiv.), In (40 mol%), dcpp (15 mol %), 1,4-dioxane (1 mL), 80 ˚C, under Ar atmosphere for 24 h. [b] yield determined by GC analysis with biphenyl as the internal standard. DCE=1, 2-dichloroethane.

3. Oxidative Cross-Coupling of Benzaldehyde with N- or S- Nucleophile

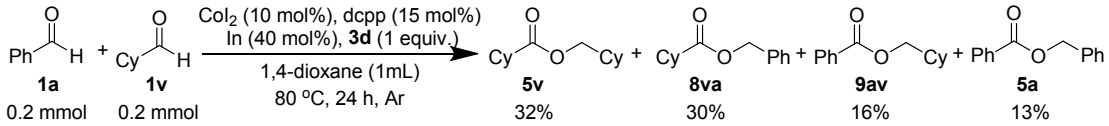
To investigate the compatibility of this new protocol toward other nucleophiles, aniline and propanethiol were employed as the substrates reacting with benzaldehyde **1a**. Both reactions leaded no target products were synthesized, imines were observed as the main product in the aniline case, and **1a** remained almost intact in the propanethiol case.



Scheme S1. Oxidative cross-coupling of **1a** with aniline and propanethiol

4. The Dimerization of Unsymmetrical Aldehydes

Benzaldehyde (**1a**) and cyclohexanealdehyde (**1v**) were reacted in the standard condition. This mixture reaction presented poor selectivity.

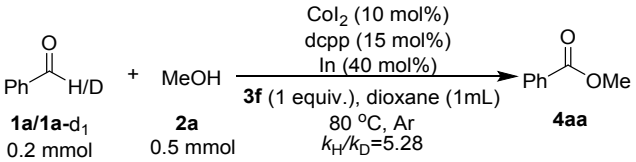


Scheme S2. Dimerization of mixture aldehydes **1a** and **1v**

5. Mechanistic Experiments

5.1 Kinetic Iotope Effect Experiments

Procedure: A mixture of CoI_2 (6.3 mg, 10 mol%), dccp (13.1 mg, 15 mol%), In (9.2 mg, 40 mol%) and **3f** (0.2 mmol) in dioxane (1.0 mL) was stirred at room temperature for 10 min in the glove box. Then, methanol (0.5 mmol) and aldehyde (0.2 mmol) or benzaldehyde-d_1 (0.2 mmol) were added into the resulting mixture. These reactions were conducted at 80 °C and monitored by GC. Using these independent rate measurements, a KIE of 5.28 was observed.



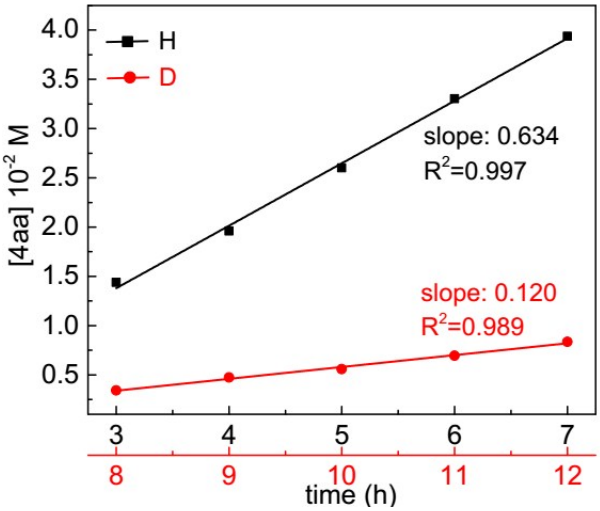
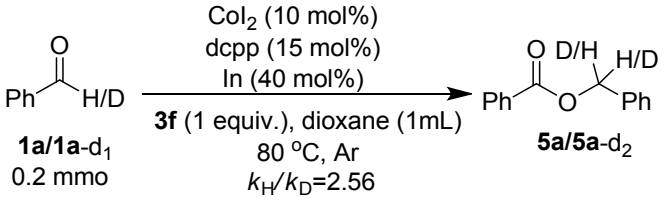


Figure S1. Initial reaction rate with respect to concentration of **4aa**.
Black: **1a** as substrate, Red: **1a**-d_1 as substrate.

Procedure: A mixture of CoI_2 (6.3 mg, 10 mol%), dccp (13.1 mg, 15 mol%), In powder (9.2 mg, 40 mol%) and **3f** (0.2 mmol) in dioxane (1.0 mL) was stirred at room temperature for 10 min in the glove box. Then, aldehyde (0.2 mmol) or benzaldehyde- d_1 (0.2 mmol) was added into the resulting mixture. These reactions were conducted at 80 °C and monitored by GC. Using these independent rate measurements, a KIE of 2.56 was observed.



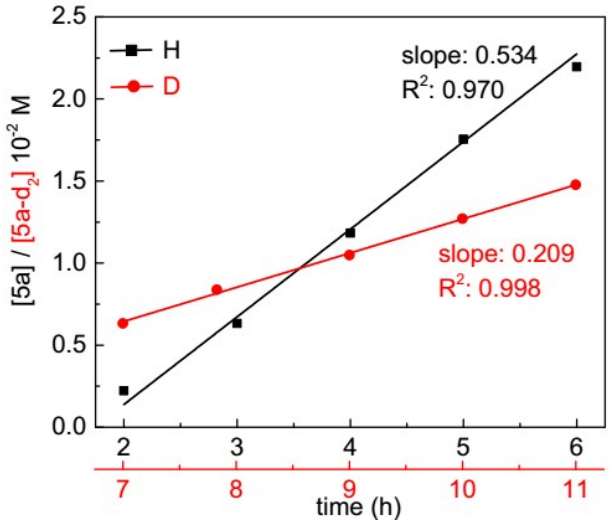
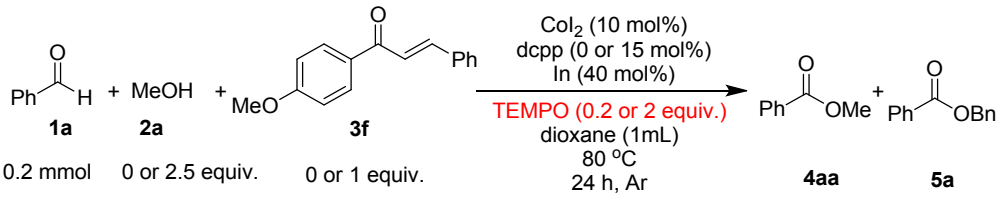


Figure S2. Initial reaction rate with respect to concentration of **5a**.
Black: **1a** as substrate, Red: **1a**-d_1 as substrate.

5.2 Effect of TEMPO on the Esterification

Table S2. Effect of TEMPO on the esterification



Entry	**2a** (equiv.)	**3f** (equiv.)	TEMPO (equiv.)	dcpp (mol%)	Yield (%)[a]	
					4aa	**5a**
1	0	1	2	15	0	0
2	0	1	0.2	15	0	0
3	2.5	1	2	15	79	8
4	2.5	0	2	0	0.8	0

Yield determined by GC analysis with biphenyl as the internal standard.

5.3 UV-visible Analysis

Procedure: To a dry flask containing a 1, 4-dioxane (1 mL) solution of CoI_2 (0.02 mmol, 1.0 equiv.), In (0.08 mmol, 4.0 equiv.), dcpp (0.03 mmol, 1.5 equiv.) and **3f** (0.04 mmol, 2.0 equiv.) or **1a** (0.04 mmol, 2.0 equiv.) were added in the glove box. The mixture was then stirred at 80 °C. TEMPO (0.04 mmol, 4.0 equiv.) or **2a** (0.1 mmol, 5.0 equiv.) was added into the mixture after reaction for 3 h. Aliquots (25 μL) removed immediately and diluted with dioxane (0.5 mL), and then 100 uL of this diluent was removed into 2.5 mL dioxane for UV analysis.

5.4 The Reduction of Chalcone in the Presence of Aldehyde and Alcohol

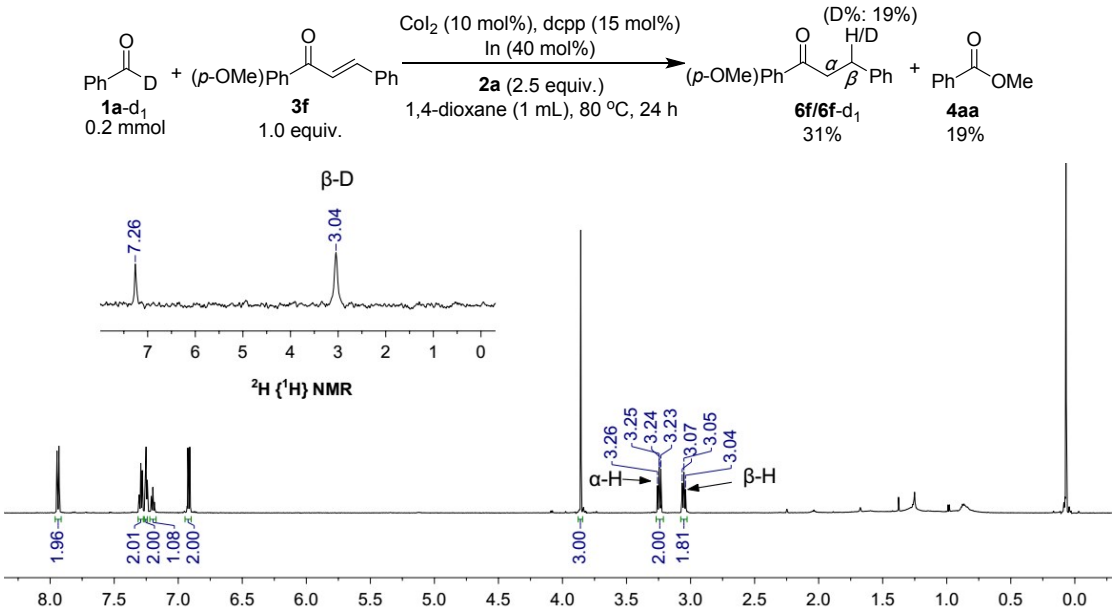
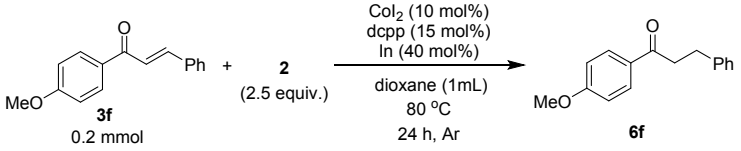


Figure S3. $^{2}H\{^{1}H\}$ NMR and **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K) of **6f/6f-**d_1

5.5 The Reduction of Chalcone by Using Alcohol as H-Source

5.5.1 Reduction of Chalcone (3f)

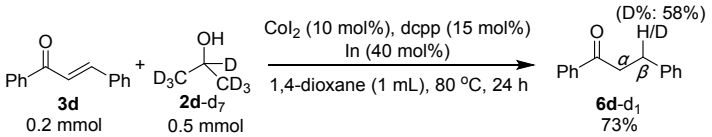
Table S3. Reduction of chalcone (**3f**)



Entry	**2**	Yield of **6f** (%)
1	MeOH	34
2	*i*PrOH	92

Yield determined by GC-MS through using areas of peak normalization method.

5.5.2 Reduction of Chalcone (3d) by Using C_3D_7OH as H/D-source



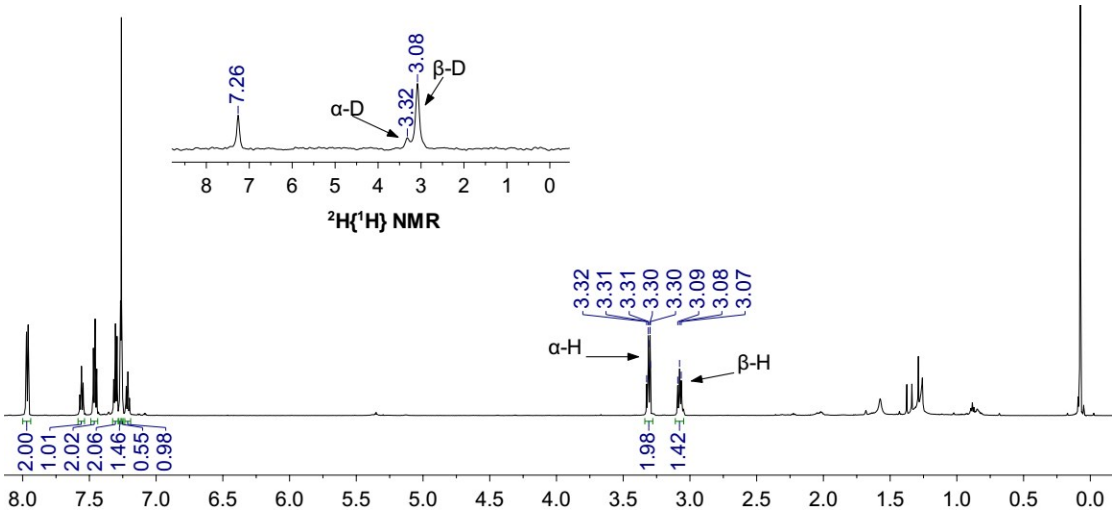
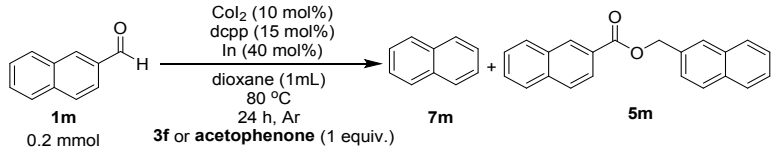


Figure S4. $^2H\{^1H\}$ NMR and **^1H NMR** (600 MHz, $CDCl_3$, 298 K) of **6d-**d_1

5.6 Effect of Ketone on the Dimerization of Aldehyde

When the carbonyl compound acetophenone was used as the mediator, the esterification was inefficient, moreover, the decarbonylation product (**7m**) of aldehyde **1m** was observed.

Table S4. Effect of α, β-unsaturated ketone on the esterification of aldehyde



Entry	**3f**/ acetophenone	Yield of **7m** (%)	Yield of **5m** (%)
1	**3f**	0	86
2	acetophenone	24	4

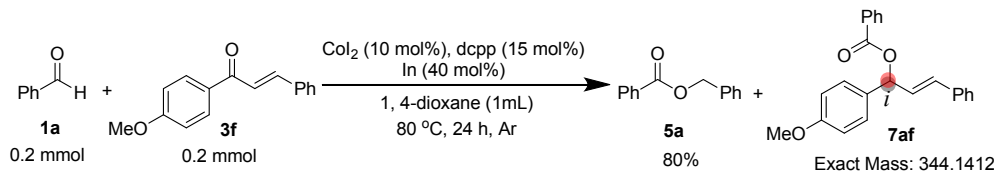
Yield determined by GCMS through using areas of peak normalization method.

5.7 Efforts on the Observing of Heterodimer Product of Aldehyde and Chalcone

In the mechanism study of dimerization of aldehyde mediated by chalcone, we suspected that the reaction may produce some amount of ester derived from chalcone by reductive elimination of species. To verify whether such an ester product (**7af**, Equation 1 or **7af**-d_1, Equation 2) was formed in the reaction, the ^{1}H NMR (Figure S5.), ^{2}H NMR (Figure S6.) and GCMS analysis (Figure S7 and S8.) toward the reaction mixture were performed after the reaction was completed, respectively. Initially, we chose the benzyl-H (*i*-position, **7af**) as the characteristic H. Unfortunately, we just can assign the shift of the benzyl-H would locate between 6.0 and 5.0, since no relevant literatures could be referenced to get an accurate identify (maybe this kind of ester is unsteady). Coincidentally, the signal was intervened by the benzyl-H of **5a** (at the root of peak 5.36, some weak signals were also observed, moreover, the broad peak at 2.64 maybe from the -OH that degraded from the **7af** as the instability of it). In the deuterated experiment (Equation 2), as the dimerization was so poor that no deuterated signal was observed in the ^{2}H NMR spectra excepted the benzyl-D of **5a**-d_2 (**1a**-d_1 could be removed during the vacuum rotary evaporation). Consistent with the ^{1}H NMR, **5a** and **3f** were detected as the main compounds in the GCMS analysis (Figure S7-a.). However, after magnification of baseline, we found a weak peak 8 at around 13.1 min (Figure S7-b.). Interesting, the mass data of 8 was equal to the exact mass (344.1412) of **7af** that predicted by ChemDraw. According to the observation of above, we suspected that an ester derived from aldehyde and chalcone by reductive

elimination like **7af** was indeed given by our protocol, however, the yield of this kind of ester is too low to isolate.

Equation 1:



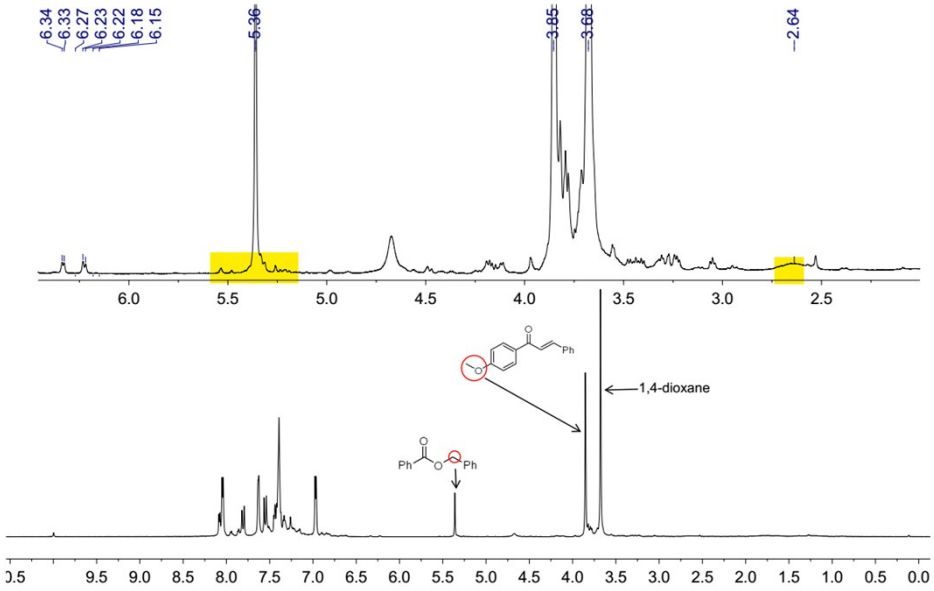
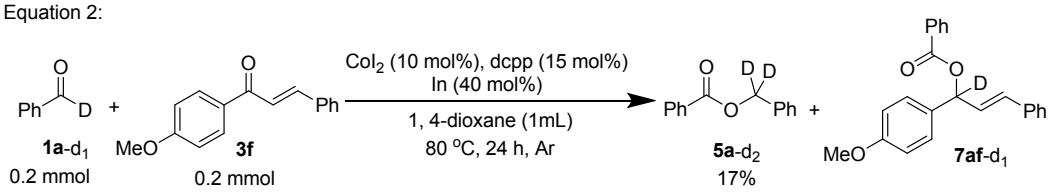


Figure S5. ^{1}H NMR of Equation 1 reaction mixture

Equation 2:



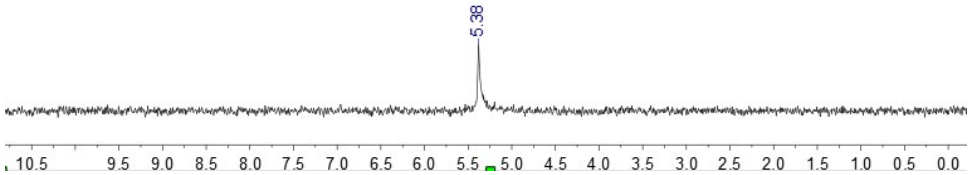


Figure S6. ^{2}H NMR of Equation 2 reaction mixture

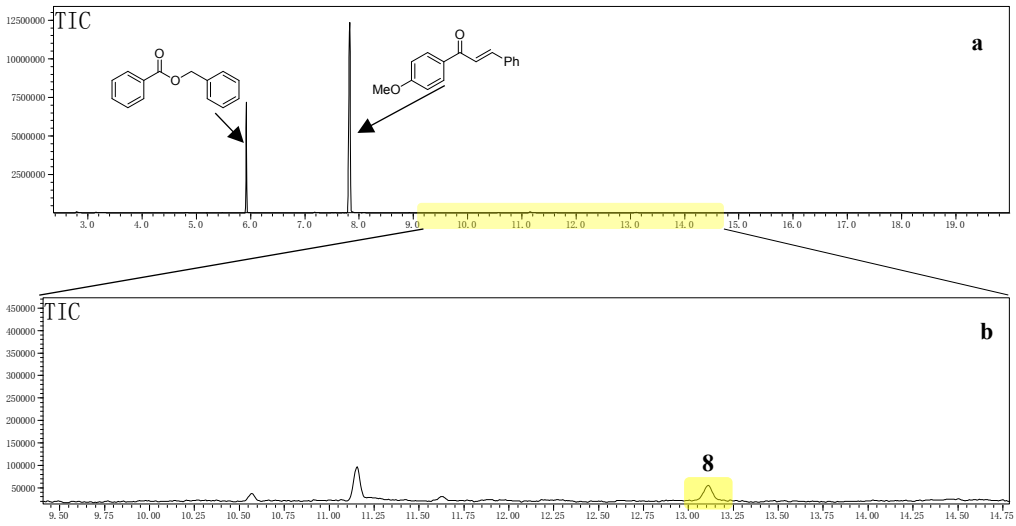


Figure S7. GC-MS analysis of the reaction mixture of Equation 1

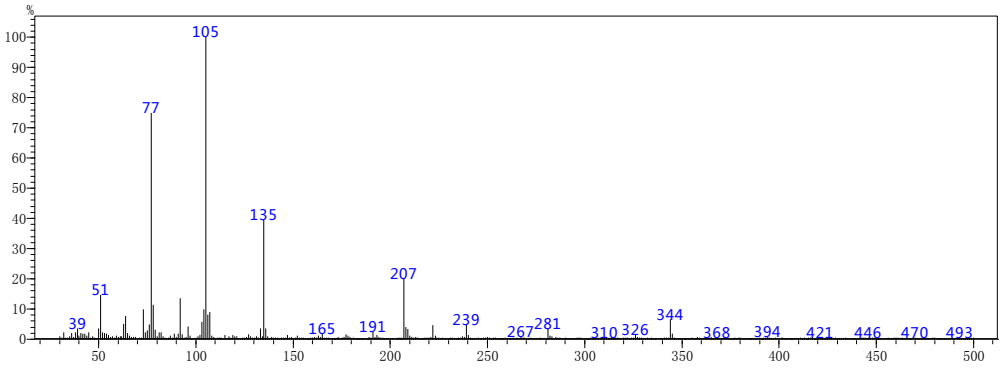
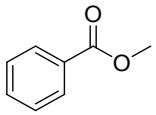


Figure S8. MS analysis of peak 8

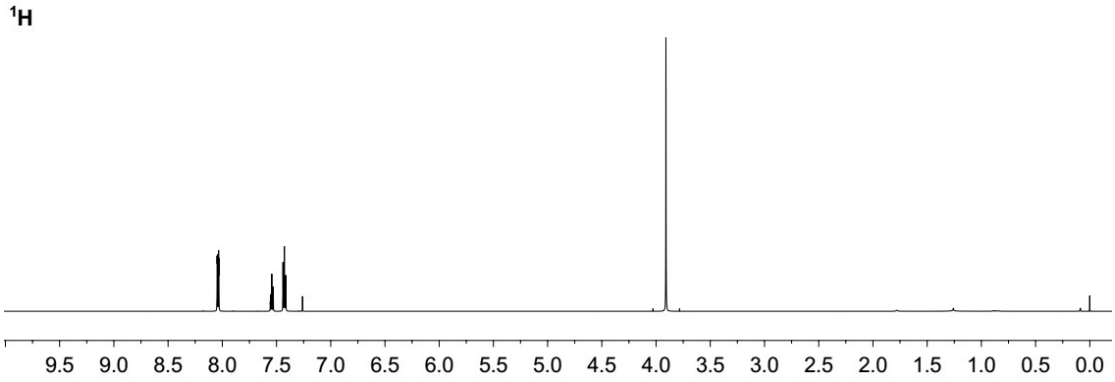
It's difficult to provide an accurate assignment for the formation of **7af** (Equation 1) upon reductive elimination of species like **G** (Scheme 8 in the text). The difficulties include the following three aspects: (a) **7af** is an unknown product as far as we know and there was no characterization data could be referred. (b) ^{1}H NMR spectrum of the reaction solution (Figure S5) demonstrated the aldehyde substrate (**1a**) has been fully converted but it contains several minor products besides the ester product $PhC(O)_2Bn$ (**5a**) and the recovered enone (**3f**). A set of peaks assigned to the typical *i*-CH, vinyl and -OMe group was detected. But it's unclear if it's **7af** or not. It makes the situation worse that the signal of *i*-CH and the benzyl-H of **5a** overlaps at 5.36 ppm, thus the clear integration and comparison cannot be conducted. Besides, we also found a broad peak at 2.64 ppm assigned to secondary -OH group, probably suggesting the C=O bond of **3f** was reduced as a minor product. But it's again not unambiguous. (c) In line with the ^{1}H NMR, **5a** and **3f** were detected as the main compounds during the GC-MS analysis (Figure S7-a). Besides, two minor eluents at 11.2 min and

13.1 min (Figure S7-b) were also obtained, wherein the later provide a corresponding MS value at 344 (**7af**, calculated: 344.1412, Figure S8).

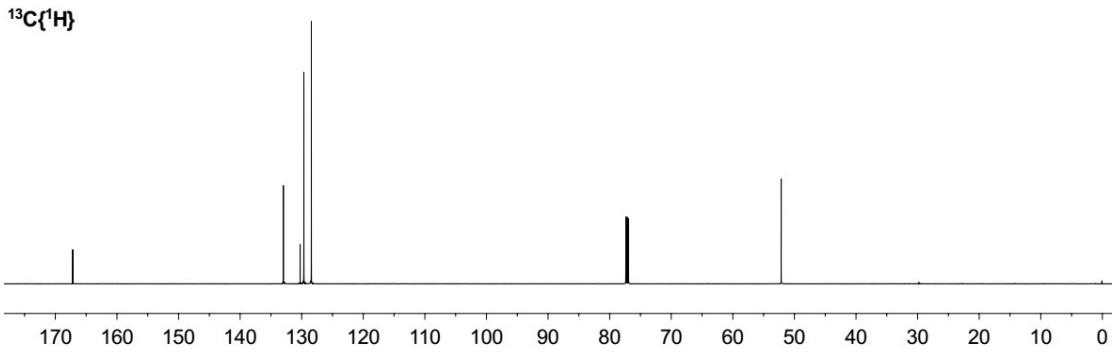
6. Characterization of Products



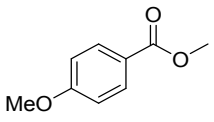
Methyl benzoate (4aa). Yield 21.7 mg, 80%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 8.04 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.3 Hz, 2H, Ph), 7.56-7.53 (m, 1H, Ph), 7.44-7.14 (m, 2H, Ph), 3.91 (s, 3H, OCH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 167.2 (C=O), 133.0, 130.3, 129.7, 128.4 (Ph), 52.2 (OCH_3).



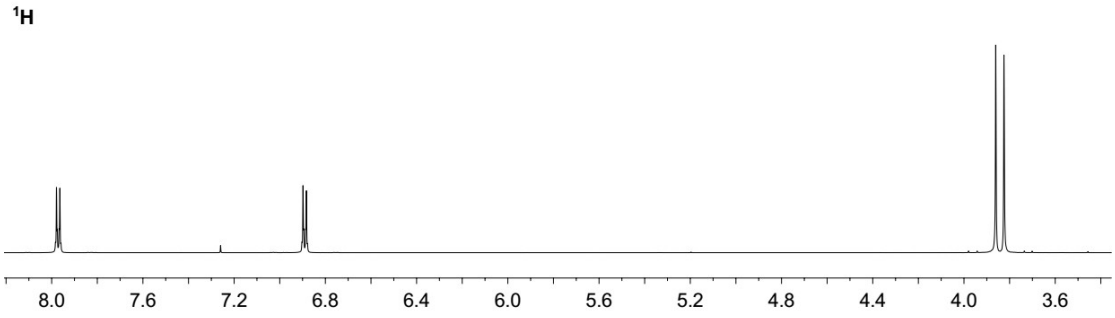
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4aa**



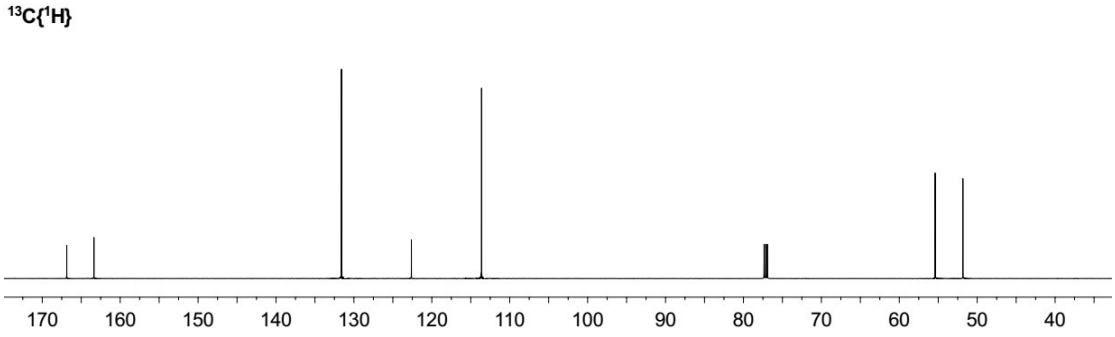
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **4aa**



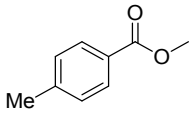
Methyl *p*-methoxy benzoate (4ba). Yield 28.9 mg, 87%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.97 (dt, $^3J_{HH}$ = 8.9, $^4J_{HH}$ = 2.3 Hz, 2H, Ph), 6.89 (dt, $^3J_{HH}$ = 8.9, $^4J_{HH}$ = 2.3 Hz, 2H, Ph), 3.86, 3.83 (each s, each 3H, OCH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ = 166.9 (C=O), 163.4, 131.6, 122.6, 113.6 (Ph), 55.4, 51.9 (each OCH_3).



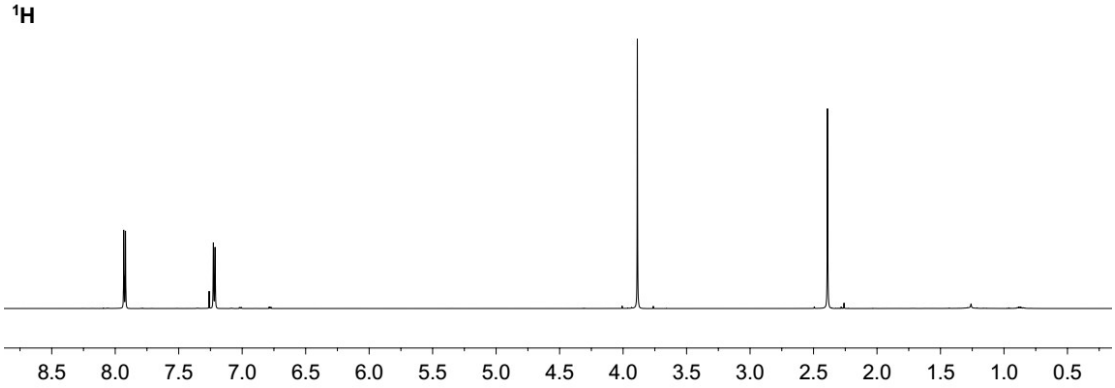
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4ba**



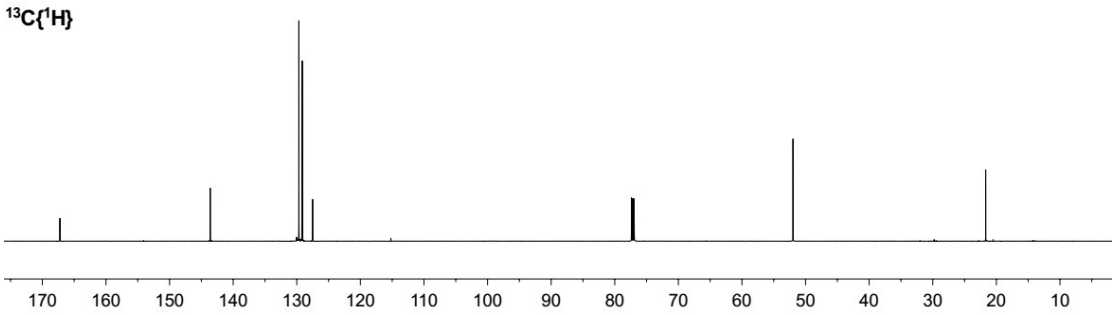
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **4ba**



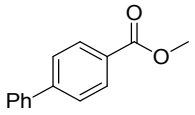
Methyl *p*-methyl benzoate (4ca). Yield 25.8 mg, 86%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.93 (dm, $^3J_{HH}$ = 8.2 Hz, 2H, Ph), 7.22 (dm, $^3J_{HH}$ = 8.2 Hz, 2H, Ph), 3.89 (s, 3H, OCH_3), 2.39 (s, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 167.2 (C=O), 143.6, 129.7, 129.1, 127.51 (Ph), 52.0 (OCH_3), 21.7 (CH_3).



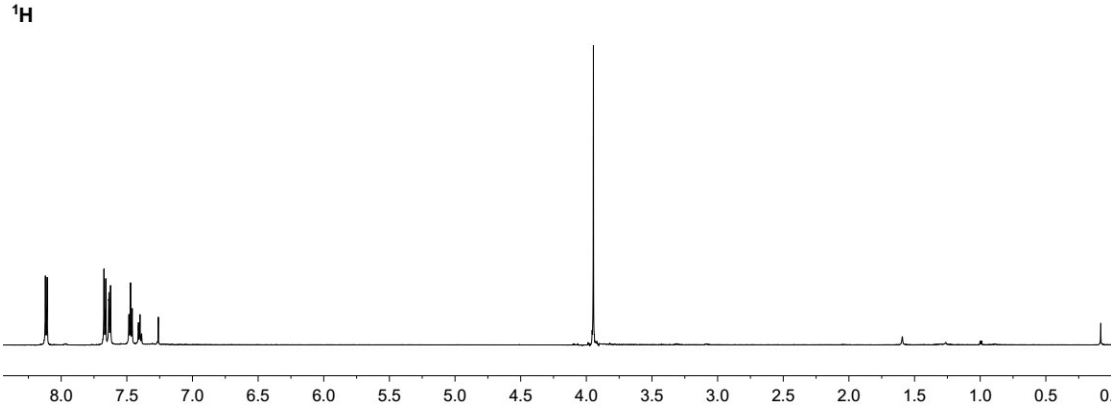
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4ca**



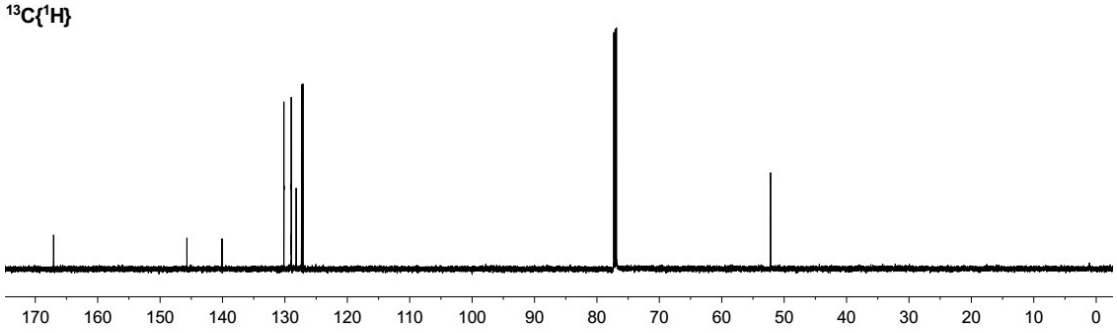
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **4ca**



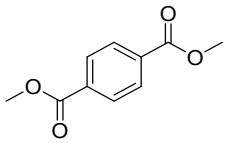
Methyl *p*-phenyl benzoate (4da). Yield 33.1 mg, 78%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 8.12-8.11 (m, 2H, Ph), 7.67-7.66 (m, 2H, Ph), 7.64-7.62 (m, 2H, Ph), 7.48-7.46 (m, 2H, Ph), 7.41-7.39(m, 1H, Ph), 3.95 (s, 3H, OCH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ = 167.1 (C=O), 145.7, 140.1, 130.1, 129.0, 128.2, 127.3, 127.1(Ph), 52.2 (OCH_3).



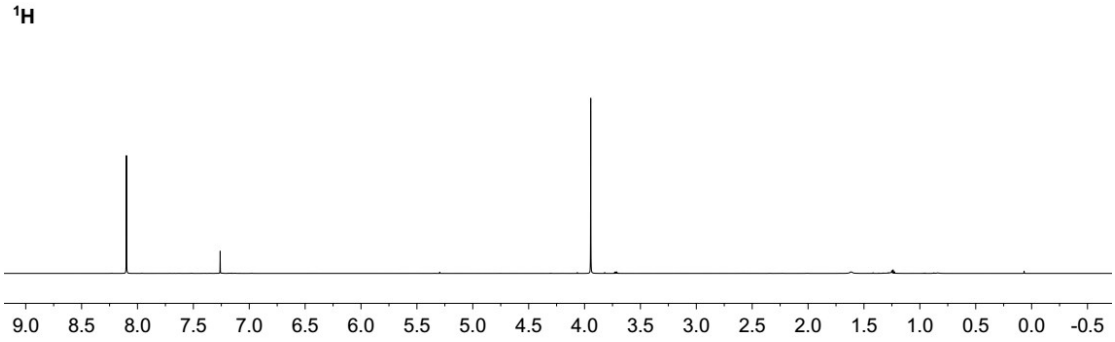
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4da**



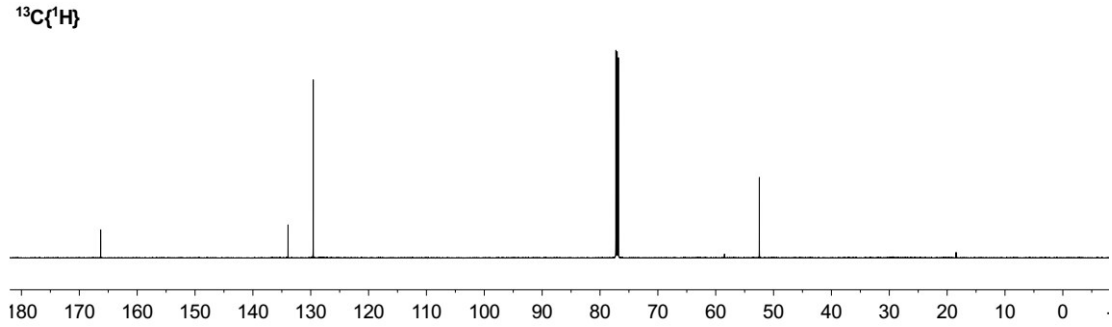
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **4da**



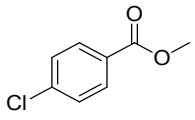
Dimethyl terephthalate (4ea). Yield 31.0 mg, 80%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 8.10 (s, 4H, Ph), 3.94 (s, 6H, OCH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$) δ = 166.3 (C=O), 133.9 (Ph), 129.6 (Ph), 52.5 (OCH_3).



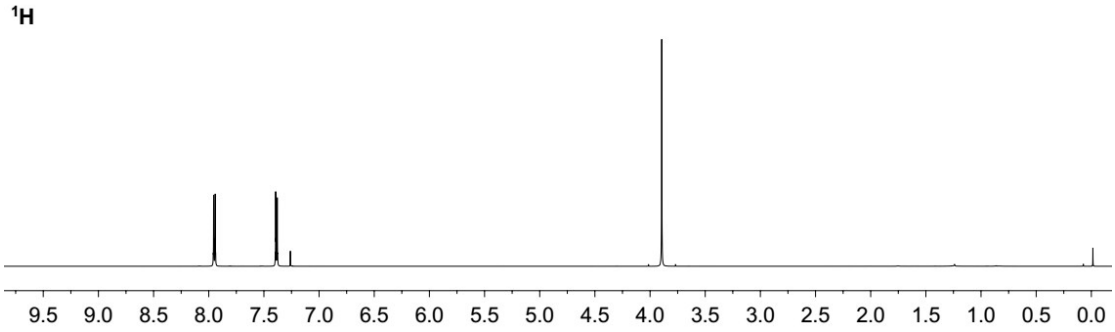
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4ea**



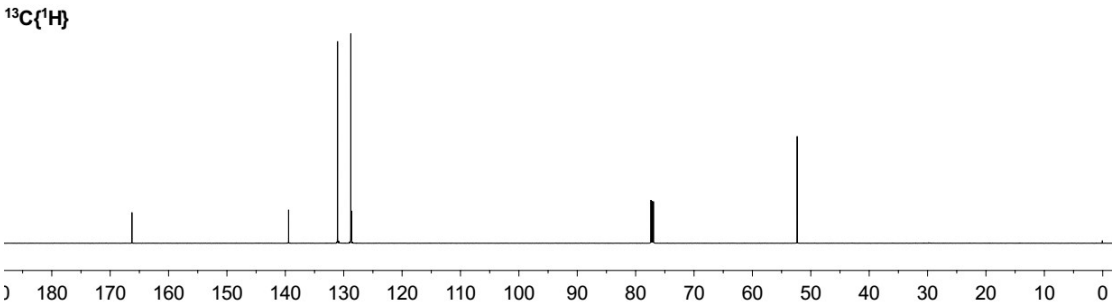
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **4ea**



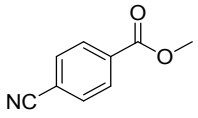
Methyl *p*-chloro benzoate (4fa). Yield 24.8 mg, 73%.**^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.95 (dm, $^3J_{HH}$ = 8.5 Hz, 2H, Ph), 7.39 (dm, $^3J_{HH}$ = 8.5 Hz, 2H, Ph), 3.89 (s, 3H, OCH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 166.3 (C=O), 139.4, 131.1, 128.8, 128.7 (Ph), 52.3 (OCH_3).



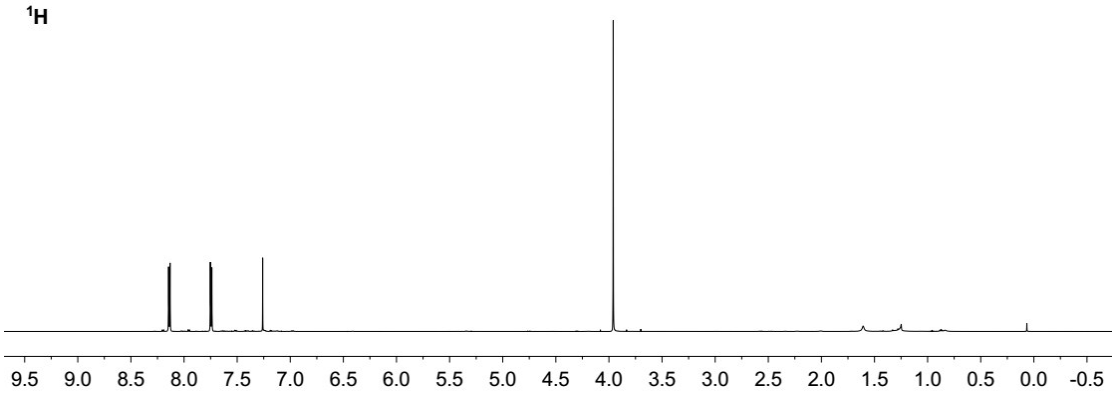
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4fa**



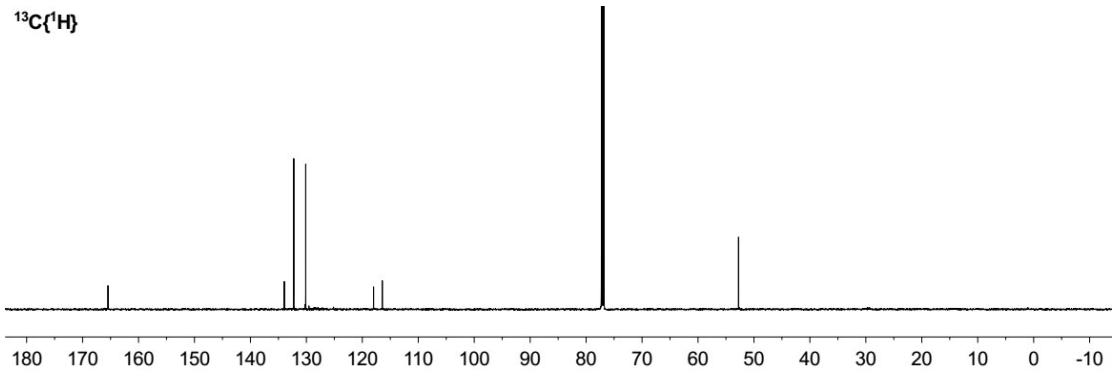
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **4fa**



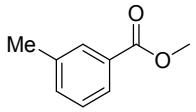
Methyl 4-cyano benzoate (4ha). Yield 22.9 mg, 71%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 8.14 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ph), 7.75 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ph), 3.96 (s, 3H, OCH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 165.5 (C=O), 134.0 (Ph), 132.3, 130.1 (Ph), 118.0 (CN), 116.4 (Ph), 52.8 (OCH_3).



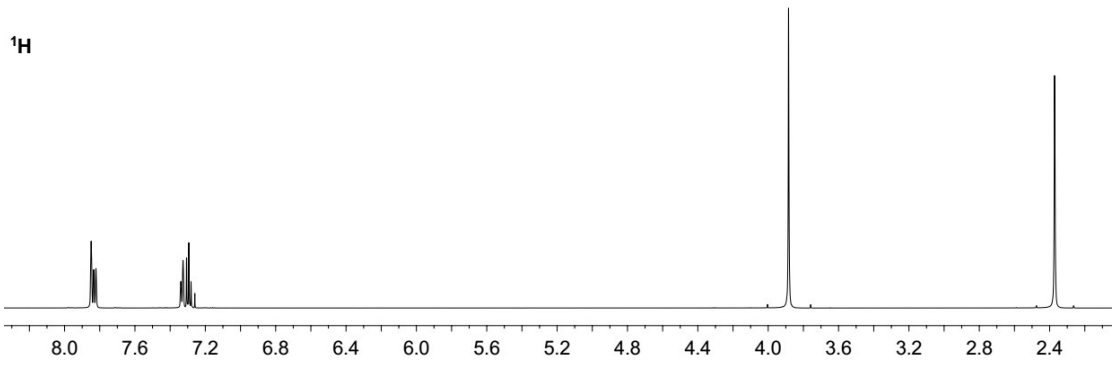
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4ha**



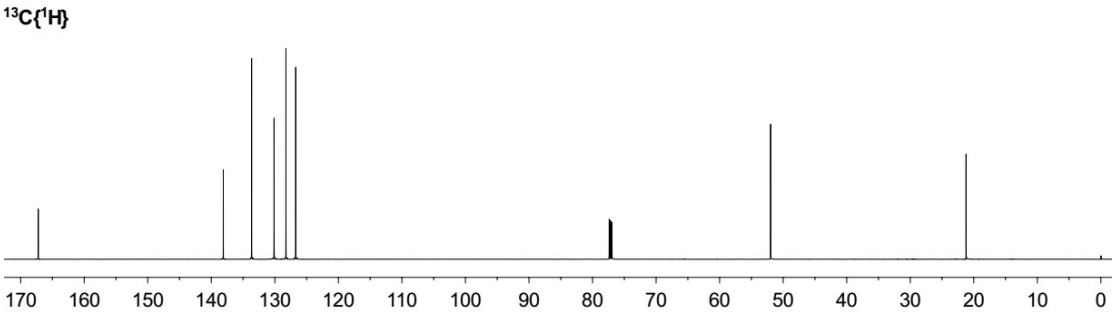
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **4ha**



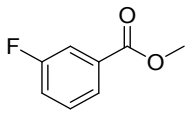
Methyl *m*-methyl benzoate (4ja). Yield 24.0 mg, 80%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K) δ = 7.85 (br s, 1H, Ph), 7.83 (dm, $^3J_{HH}$ = 7.5 Hz, 1H, Ph), 7.33 (dm, $^3J_{HH}$ = 7.8 Hz, 1H, Ph), 7.30 (tm, $^3J_{HH}$ = 7.5 Hz, 1H, Ph), 3.89 (s, 3H, OCH_3), 2.37 (s, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 167.1 (C=O), 138.0, 133.6, 130.1, 128.2, 126.7 (Ph), 51.9 (OCH_3), 21.1 (CH_3).



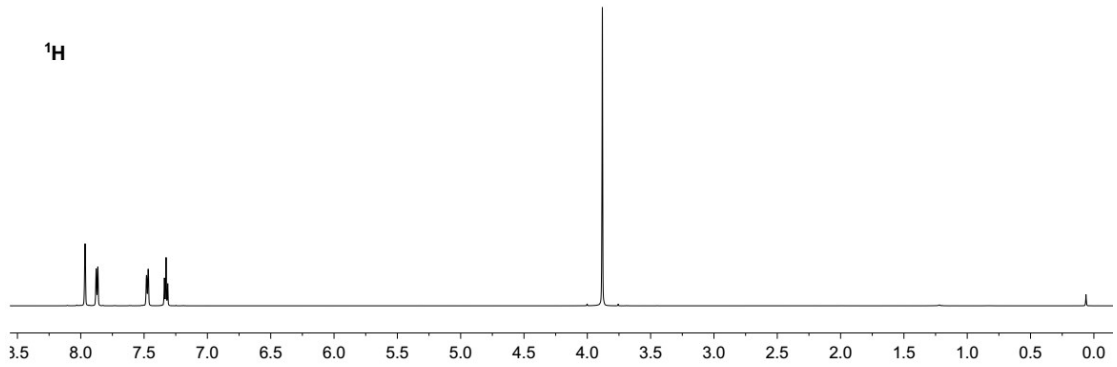
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4ja**



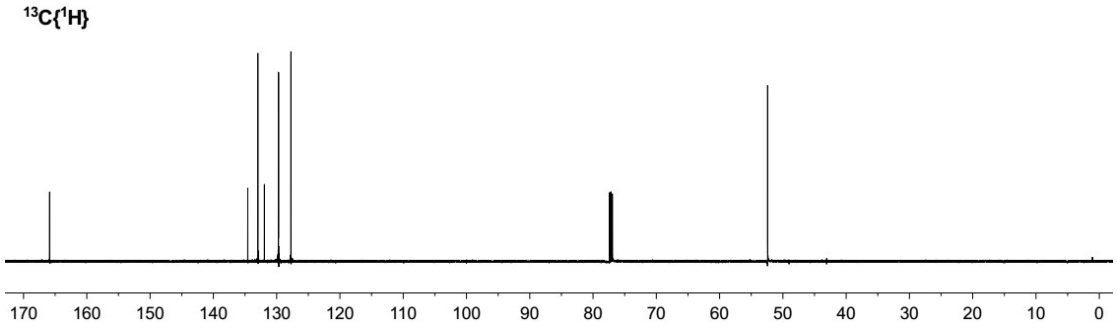
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **4ja**



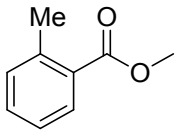
Methyl *m*-fluoro benzoate (4ka). Yield 21.6 mg, 70%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K) δ = 7.98 (s, 1H, Ph^F), 7.89-7.88 (d, $^3J_{HH}$ = 7.8 Hz, 1H, Ph), 7.49-7.48 (d, $^3J_{HH}$ = 8.4 Hz, 1H, Ph), 7.35-7.33 (t, $^3J_{HH}$ = 7.8 Hz, 1H, Ph), 3.89 (s, 3H, OCH_3), 2.37 (s, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 165.9 (C=O), 134.6, 133.0, 131.9, 129.7, 127.7(Ph), 52.4 (OCH_3).



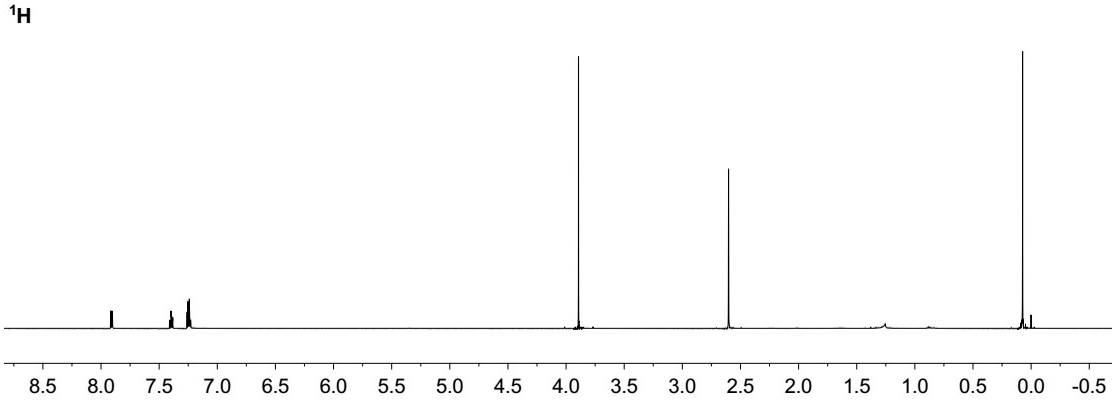
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4ka**



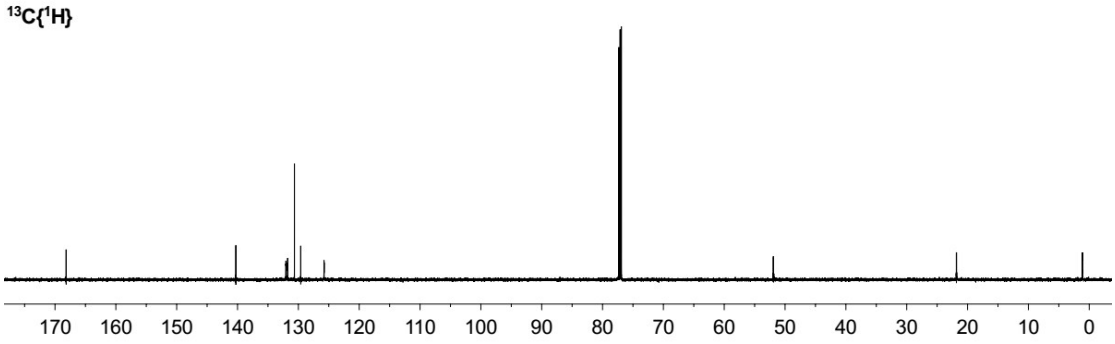
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **4ka**



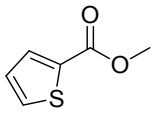
Methyl *o*-methyl benzoate (4la). Yield 21.9 mg, 73%.**^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.90 (dd, $^{3}J_{HH}$ = 7.8, $^{4}J_{HH}$ = 1.7 Hz, 1H, Ph), 7.39 (td, $^{3}J_{HH}$ = 7.5, $^{4}J_{HH}$ = 1.4 Hz, 1H, Ph), 7.24 (m, 2H, Ph), 3.90 (s, 3H, OCH_3), 2.60 (s, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 168.2 (C=O), 140.3, 132.0, 131.8, 130.7, 129.6, 125.8 (Ph), 51.9 (OCH_3), 21.8 (CH_3).



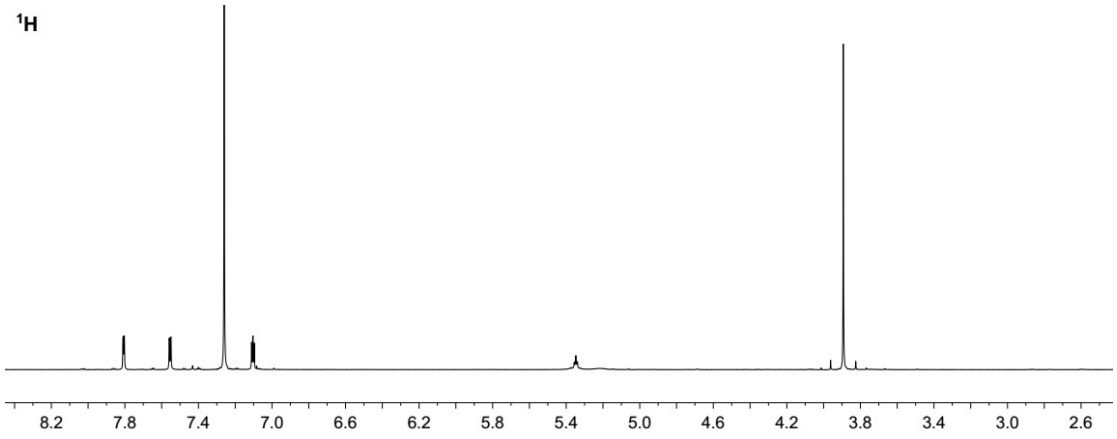
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4la**



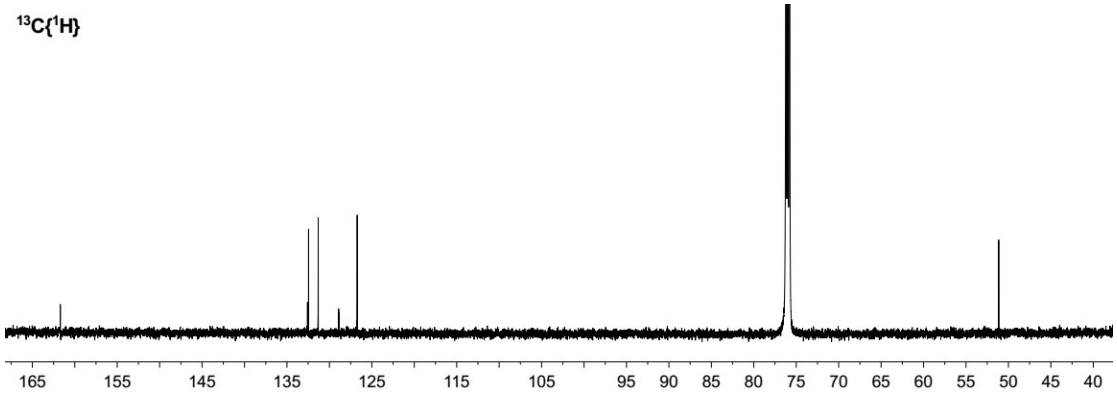
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **4la**



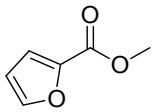
Methyl thiophene-*o*-carboxylate (4ma). Yield 21.6 mg, 76%.**^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.81 (dd, $^{3}J_{HH}$ = 3.7, $^{4}J_{HH}$ = 0.9 Hz, 1H, thiophen), 7.55 (dd, $^{3}J_{HH}$ = 4.9, $^{4}J_{HH}$ = 0.9 Hz, 1H, thiophen), 7.10 (dd, $^{3}J_{HH}$ = 4.9, $^{4}J_{HH}$ = 3.7 Hz, 1H, thiophene), 3.89 (s, 3H, OCH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 162.9 (C=O), 133.6, 132.5, 130.1, 127.9 (thiophene), 52.3 (OCH_3).



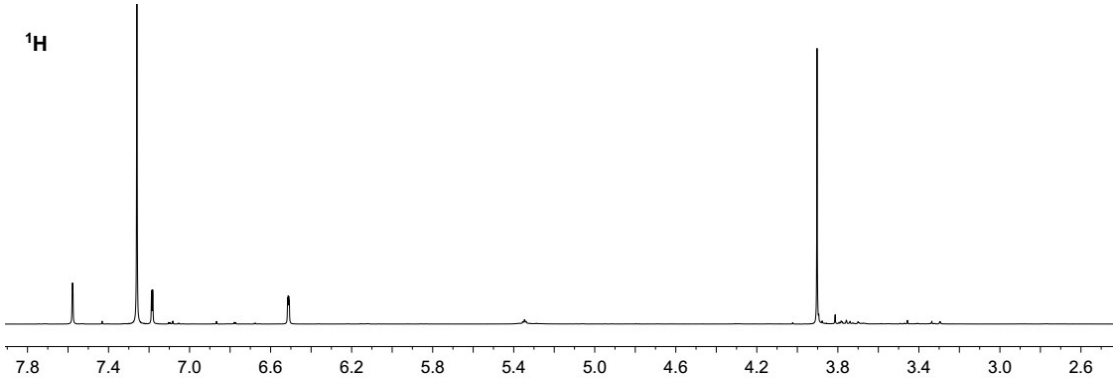
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4ma**



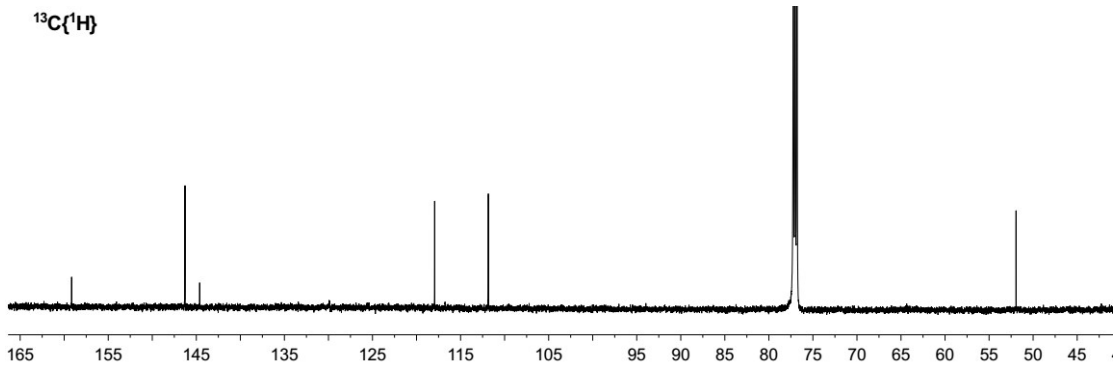
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **4ma**



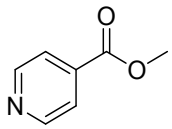
Methyl furan-*o*-carboxylate (4na). Yield 18.4 mg, 73%.**^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.58 (m, 1H, furyl), 7.18 (d, $^3J_{HH}$ = 3.4 Hz, 1H, furyl), 6.51 (dd, $^3J_{HH}$ = 3.4, $^4J_{HH}$ = 1.7 Hz, 1H, furyl), 3.90 (s, 3H, OCH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 159.3 (C=O), 146.4, 144.8, 118.1, 112.0 (furyl), 52.1 (OCH_3).



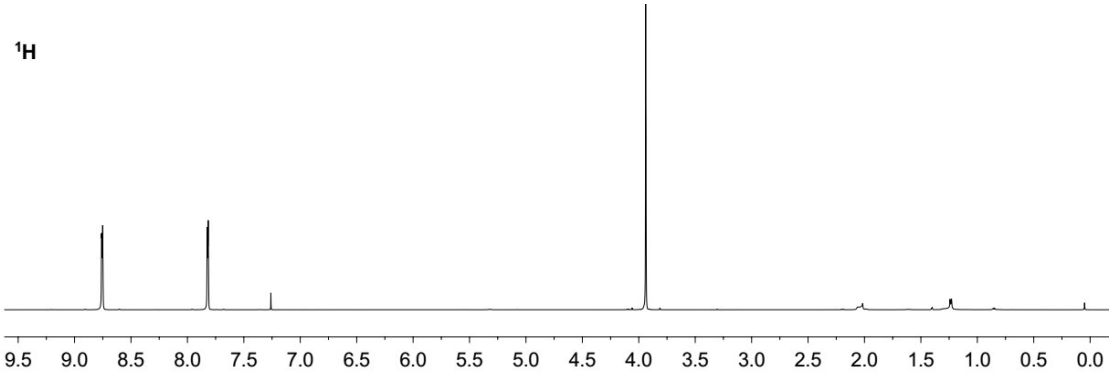
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4na**



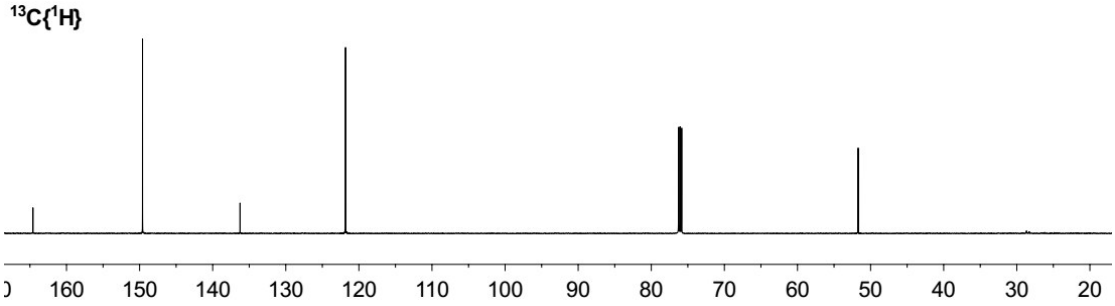
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **4na**



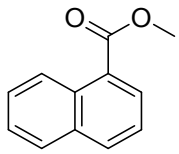
Methyl Pyridine-4-carboxylate (4oa). Yield 22.2 mg, 81%.**^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 8.76 (m, 2H, Py), 7.82 (m, 2H, Py), 3.94 (s, 3H, OCH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 164.7 (C=O), 149.7, 136.4, 121.9 (Py), 51.8 (OCH_3).



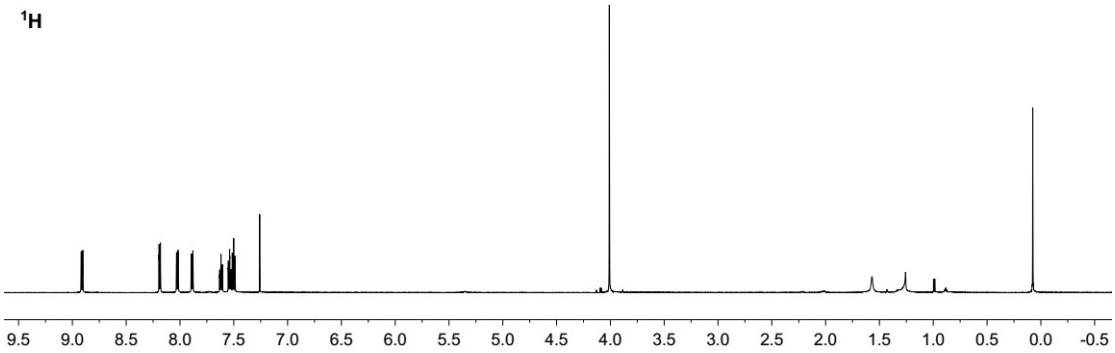
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4oa**



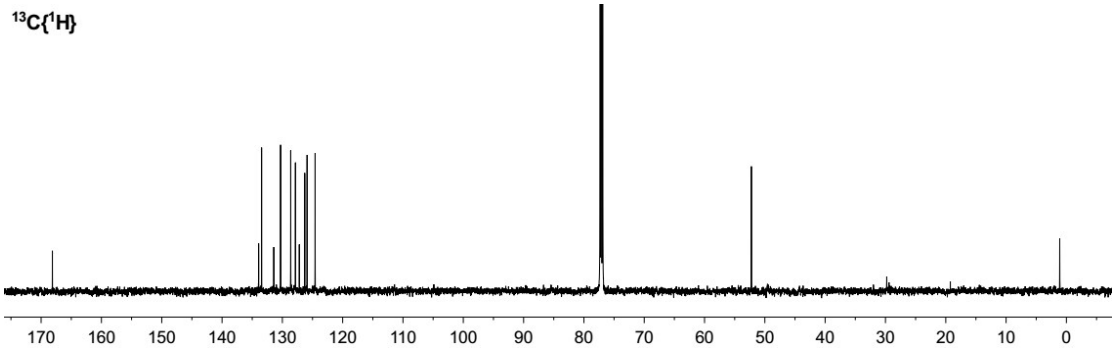
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **4oa**



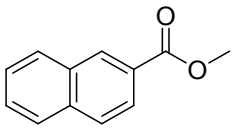
Methyl 1-naphthoate (4 pa). Yield 26.4 mg, 71%.**^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 8.91 (d, $^3J_{HH}$ = 8.4 Hz, 1H, Nap), 8.19 (dd, $^3J_{HH}$ = 7.2, $^4J_{HH}$ = 1.2 Hz, 1H, Nap), 8.03 (d, $^3J_{HH}$ = 8.4 Hz, 1H, Nap), 7.89 (d, $^3J_{HH}$ = 8.4 Hz, 1H, Nap), 7.63-7.61(m, 1H, Nap), 7.55-7.49 (m, 2H, Nap), 4.01 (s, 3H, OCH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 168.1 (C=O), 133.9, 133.4, 131.4, 130.3, 128.6, 127.8, 127.2, 126.3, 125.9, 124.6 (Nap), 52.2 (OCH_3).



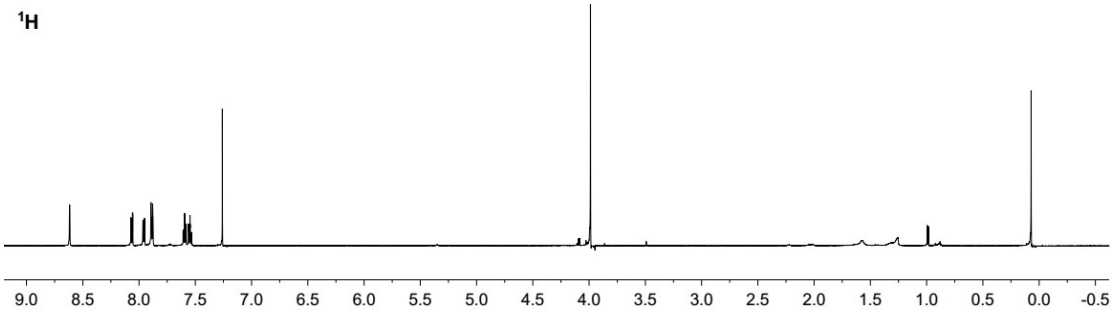
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4pa**



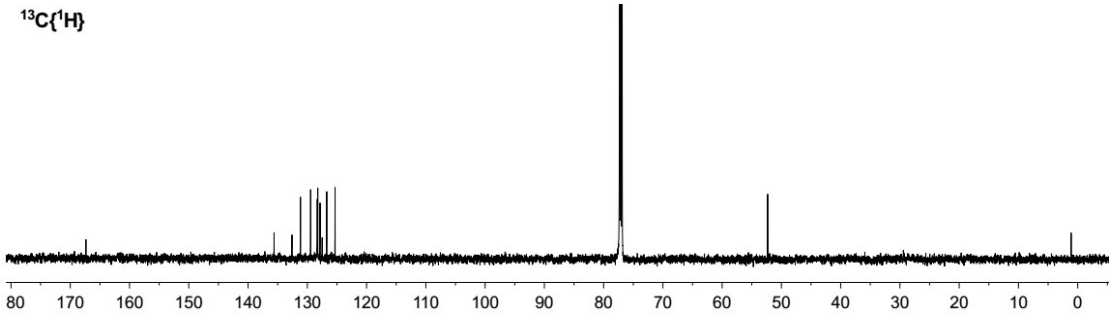
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **4pa**



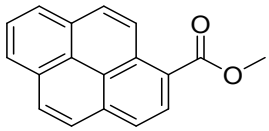
Methyl 2-naphthoate (4qa). Yield 30.5 mg, 82%.**^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 8.62 (d, 1H, Nap), 8.06 (dd, $^3J_{HH}$ = 8.4, $^4J_{HH}$ = 1.2 Hz, 1H, Nap), 7.96 (m, 1H, Nap), 7.89-7.88 (m, 2H, Nap), 7.61-7.58(m, 1H, Nap), 7.56-7.53(m, 1H, Nap), 3.99 (s, 3H, OCH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 167.4 (C=O), 135.6, 132.6, 131.2, 129.4, 128.3, 128.2, 127.8, 127.5, 126.7, 125.3 (Nap), 52.3 (OCH_3).



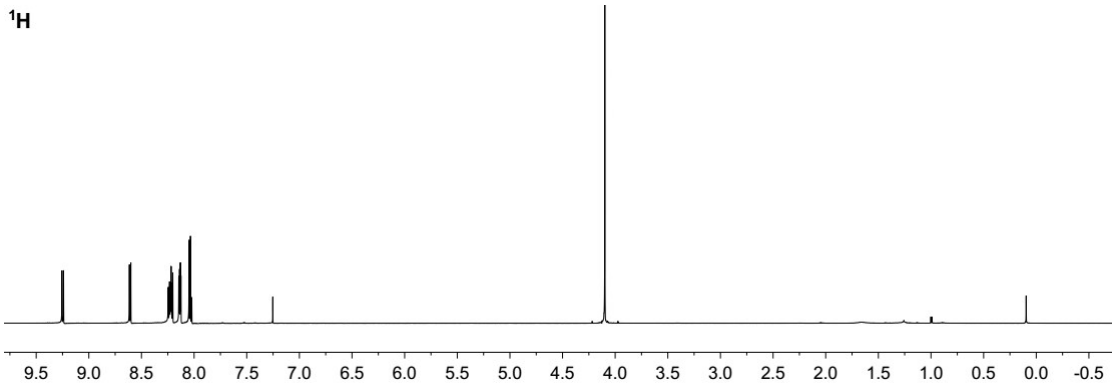
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4qa**



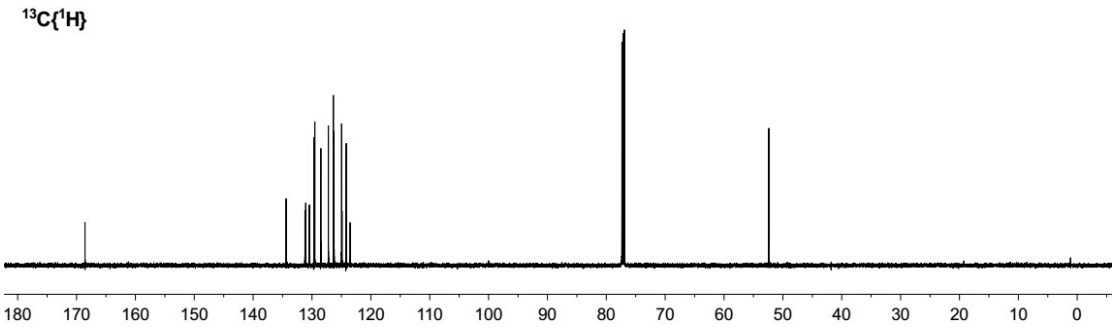
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **4qa**



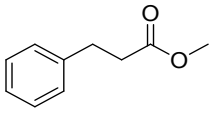
Methyl pyrene-1-carboxylate (4ra). Yield 35.4 mg, 68%.**^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 9.26 (d, $^3J_{HH}$ = 9.6Hz, 1H, pyrene), 8.62 (d, $^3J_{HH}$ = 9.0, 1H, pyrene), 8.25-8.21 (m, 3H, pyrene), 8.15-8.13 (m, 2H, pyrene), 8.06-8.03(m, 2H, pyrene), 4.11 (s, 3H, OCH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 168.6 (C=O), 134.4, 131.2, 131.1, 130.5, 129.7, 129.5, 128.5, 127.2, 126.37, 126.36, 126.25, 124.97, 124.89, 124.3, 124.2, 123.5 (pyrene), 52.4 (OCH_3).



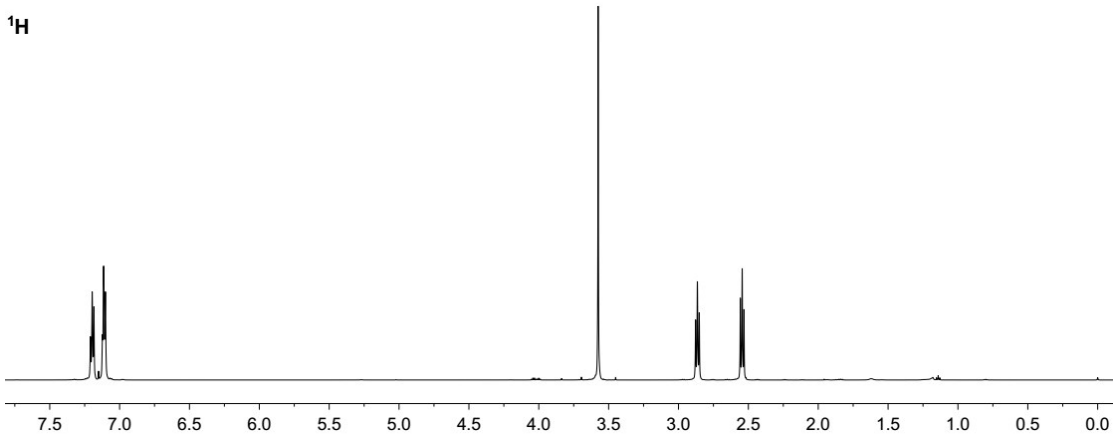
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4ra**



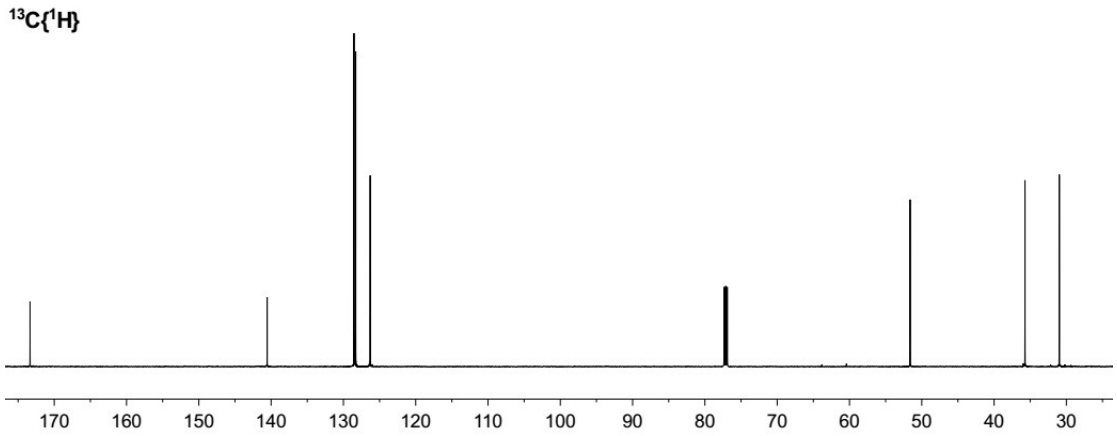
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **4ra**



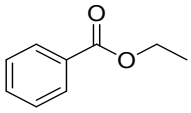
Methyl 3-phenyl propanoate (4sa). Yield 27.9 mg, 85%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.32-7.29 (m, 2H, Ph), 7.23-7.21 (m, 3H, Ph), 3.68 (s, 3H, OCH_3), 2.97 (t, $^3J_{HH}$ = 8.1 Hz, 2H, CH_2), 2.65 (t, $^3J_{HH}$ = 8.1 Hz, 2H, CH_2). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 173.4 (C=O), 140.6, 128.6, 128.35, 126.35, 51.7 (OCH_3), 35.77, 31.02 (each CH_2).



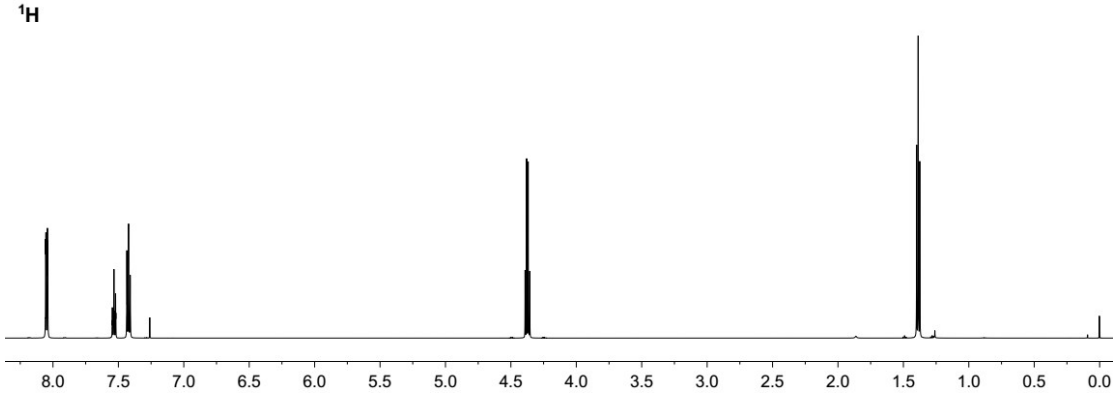
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4sa**



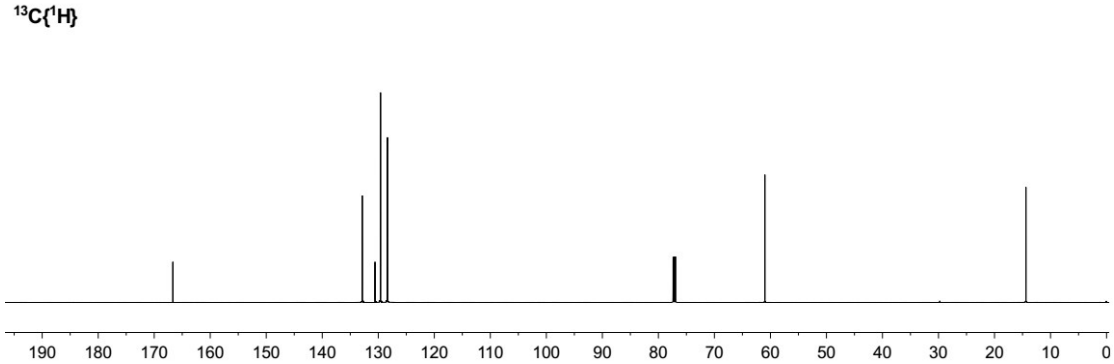
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **4sa**



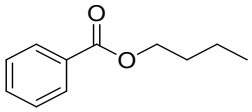
Ethyl benzoate (4ab). Yield 24.0 mg, 80%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 8.05 (dm, $^3J_{HH}$ = 8.4 Hz, 2H, Ph), 7.53 (tm, $^3J_{HH}$ = 7.5 Hz, 1H, Ph), 7.42 (ddm, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 7.5 Hz, 2H, Ph), 4.37 (q, $^3J_{HH}$ = 7.1 Hz, 2H, CH_2), 1.39 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 166.7 (C=O), 132.9, 130.6, 129.6, 128.4, 61.0 (CH_2), 14.4 (CH_3).



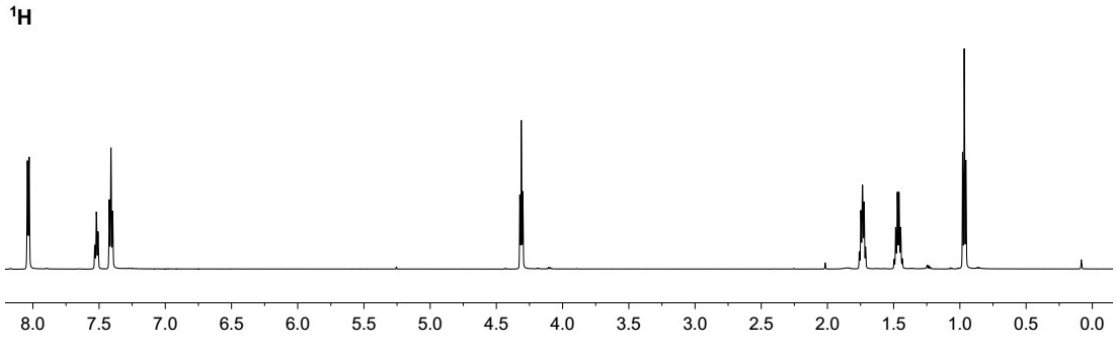
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4ab**



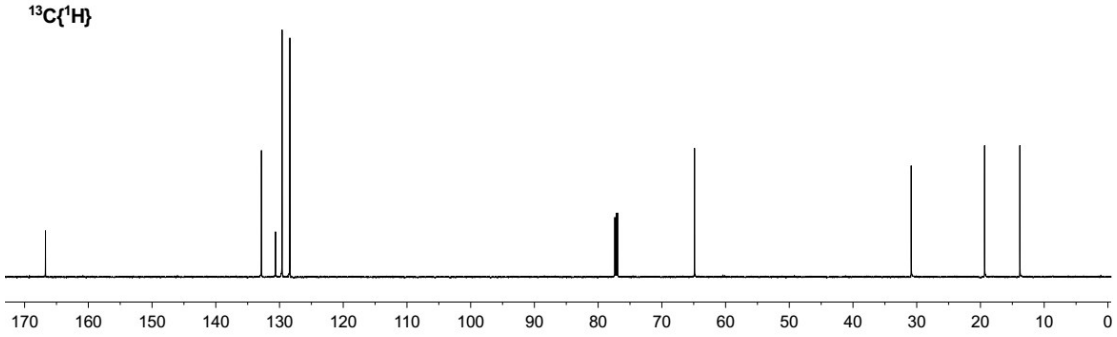
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **4ab**



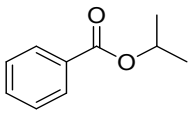
***n*-Butyl benzoate (4ac).** Yield 29.5 mg, 83%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 8.05 (dm, $^3J_{HH}$ = 7.5 Hz, 2H, Ph), 7.54 (tm, $^3J_{HH}$ = 7.4 Hz, 1H, Ph), 7.43 (ddm, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.4 Hz, 2H, Ph), 4.33 (t, $^3J_{HH}$ = 6.6 Hz, 2H, OCH_2), 1.75 (m, 2H, CH_2), 1.48 (m, 2H, CH_2), 0.98 ($^3J_{HH}$ = 7.3 Hz, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 166.7 (C=O), 132.8, 130.6, 129.6, 128.4 (Ph), 64.9 (OCH_2), 30.9, 19.4 (each CH_2), 13.8 (CH_3).



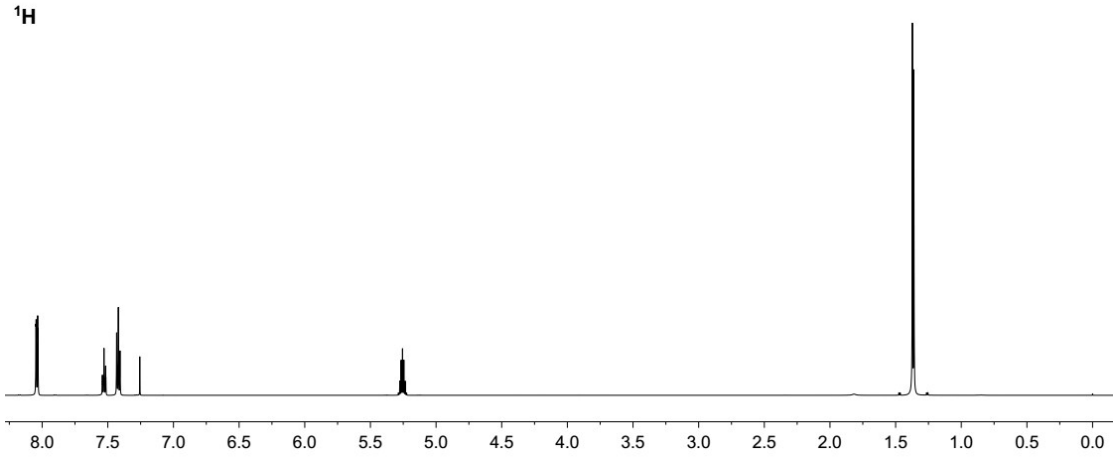
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4ac**



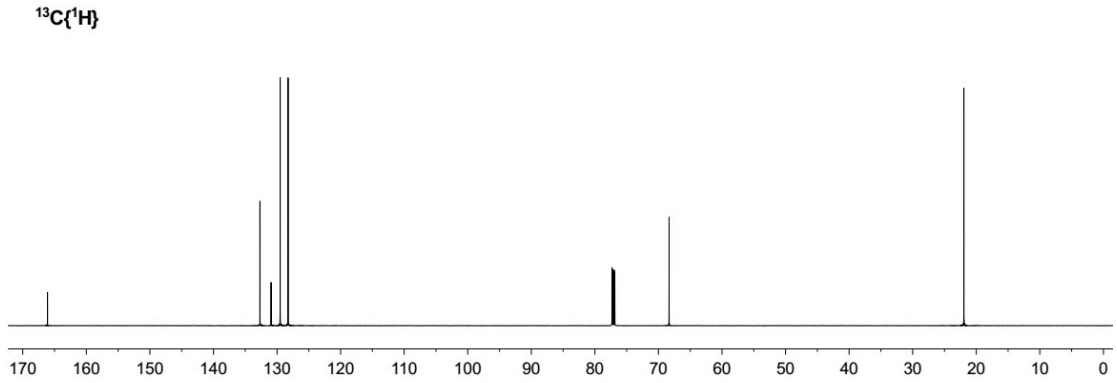
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **4ac**



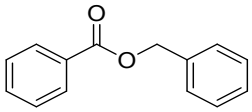
Isopropyl benzoate (4ad). Yield 23.6 mg, 72%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 8.05 (dm, $^3J_{HH}$ = 7.6 Hz, 2H, Ph), 7.53 (tm, $^3J_{HH}$ = 7.4 Hz, 2H, Ph), 7.42 (ddm, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 7.4 Hz, 2H, Ph), 5.26 (hept, $^3J_{HH}$ = 6.3 Hz, 1H, CH), 1.37 (d, $^3J_{HH}$ = 6.3 Hz, 6H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 166.2 (C=O), 132.7, 131.0, 129.6, 128.3 (Ph), 68.4 (CH), 22.0 (CH_3).



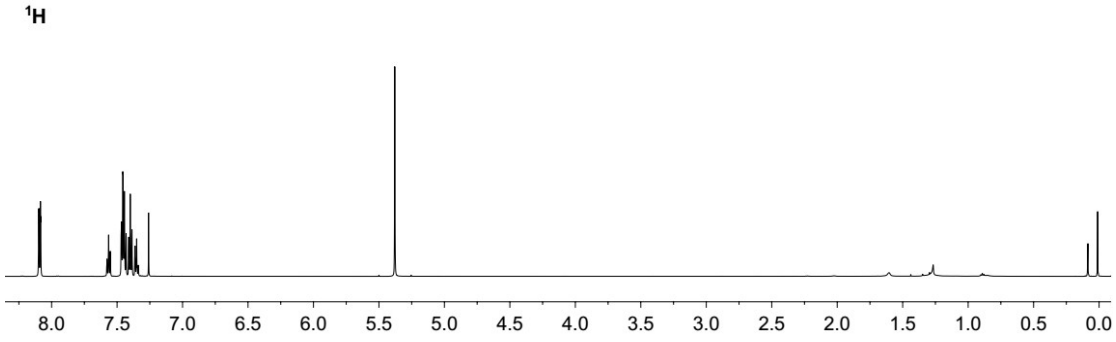
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4ad**



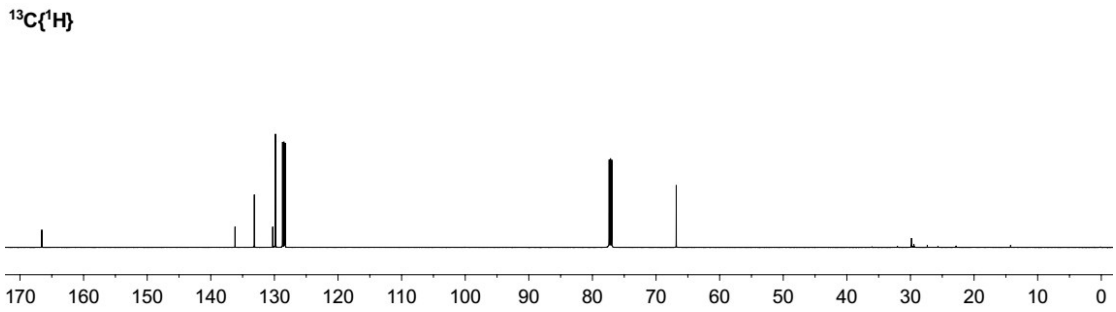
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **4ad**



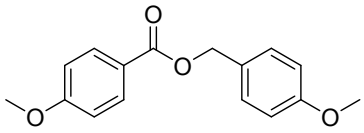
Benzyl benzoate (5a). Yield 33.9 mg, 80%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 8.09 (dm, $^3J_{HH}$ = 7.1 Hz, 2H, Ph), 7.56 (m, 1H, Ph), 7.46 (dm, $^3J_{HH}$ = 7.5 Hz, 2H, Ph), 7.44 (m, 2H, Ph), 7.40 (m, 2H, Ph), 7.36 (m, 1H, Ph), 5.38 (s, 2H, CH_2). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298K): δ = 166.6 (C=O), 136.2, 133.2, 130.3, 129.8, 128.7, 128.5, 128.4, 128.3 (Ph), 66.8 (CH_2).



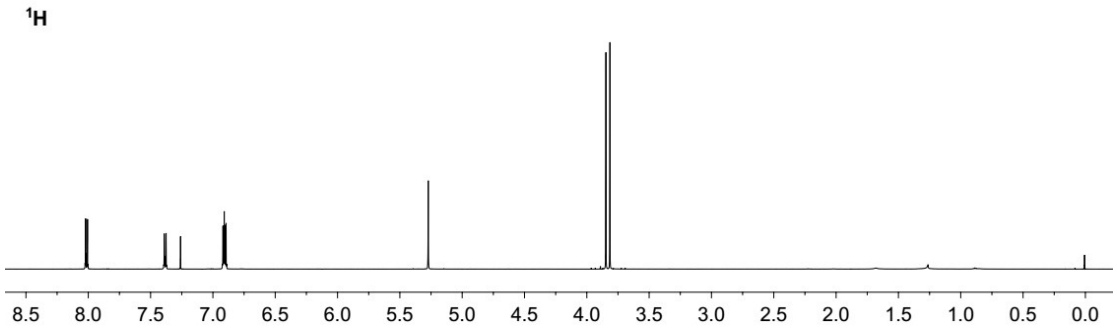
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **5a**



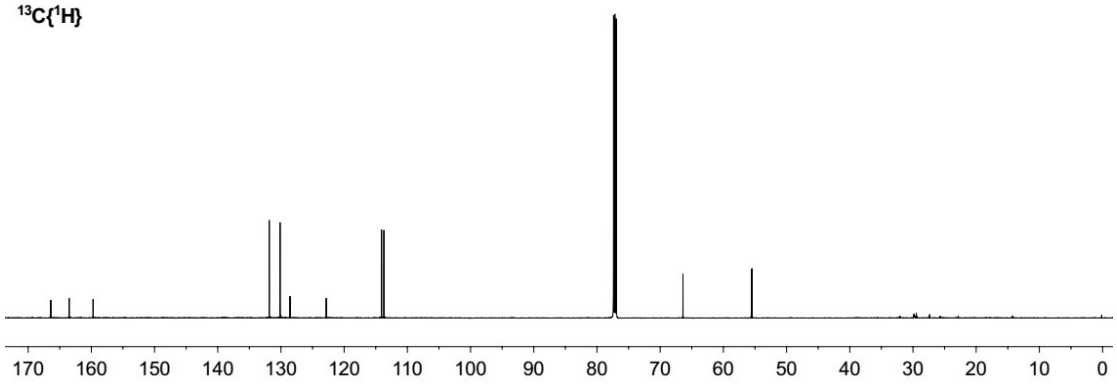
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **5a**



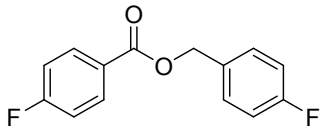
4-Methoxybenzyl 4-methoxy benzoate (5b). Yield 26.7 mg, 49%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 8.02 (dm, $^3J_{HH}$ = 9.0 Hz, 2H, Ph), 7.38 (dm, $^3J_{HH}$ = 8.8 Hz, 2H, Ph), 6.91 (dm, $^3J_{HH}$ = 8.8 Hz, 2H, Ph), 6.91 (dm, $^3J_{HH}$ = 9.0 Hz, 2H, Ph), 5.27 (s, 2H, CH_2), 3.85 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298K): δ = 166.4 (C=O), 163.5, 159.7, 131.8, 130.1, 128.6, 122.8, 114.1, 113.7 (Ph), 66.4 (CH_2), 55.6 (OCH_3), 55.4 (OCH_3).



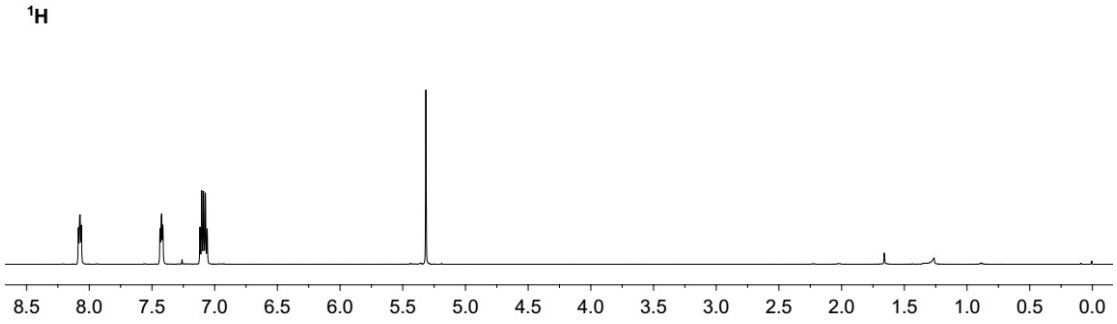
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **5b**



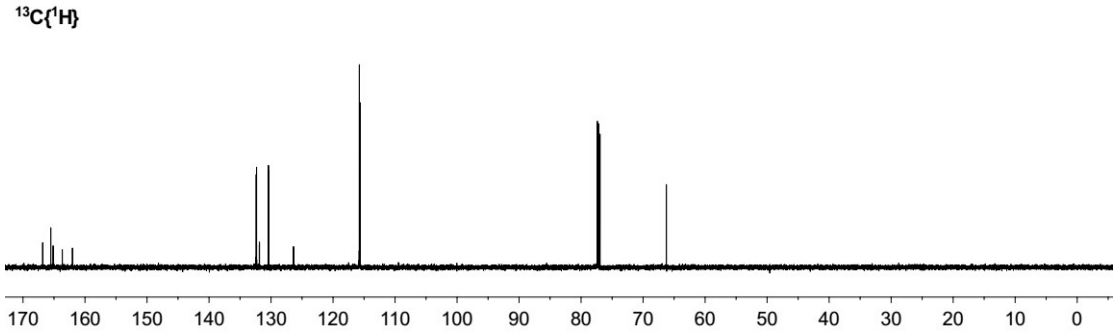
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **5b**



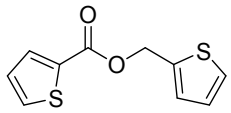
4-Fluorobenzyl 4-fluoro benzoate (5w). Yield 32.2 mg, 65%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 8.07 (m, 2H, Ph), 7.43 (m, 2H, Ph), 7.10 (m, 2H, Ph), 7.07 (m, 2H, Ph), 5.32 (s, 2H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298K): δ = 166.0 (dm, $^1J_{FC}$ ~ 254 Hz, *i*-Ph^F), 165.5 (C=O), 162.8, 132.4, 131.9, 130.4, 126.4, 126.4, 115.8, 115.6 (Ph), 66.2 (CH_2).



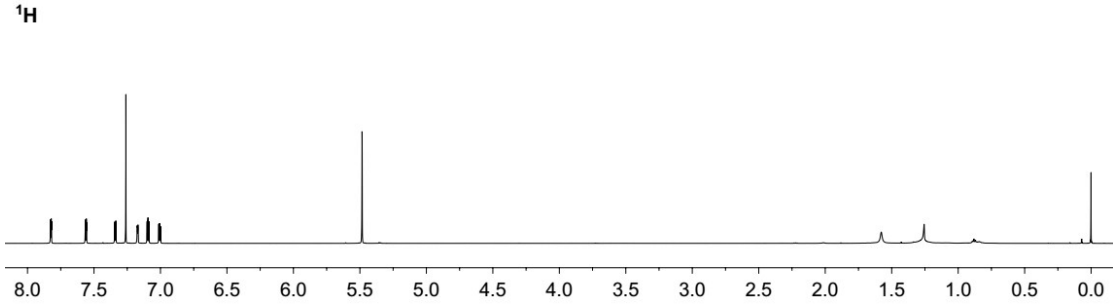
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **5w**



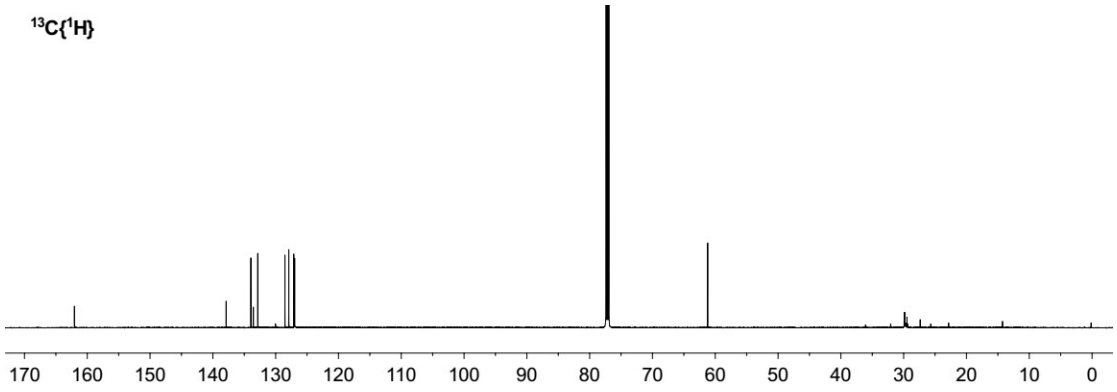
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **5w**



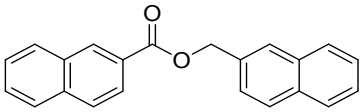
Thiophen-2-ylmethyl thiophene-2-carboxylate (5m). Yield 9.0 mg, 20%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.82 (m, 1H, Thio), 7.56 (m, 1H, Thio), 7.34 (m, 1H, Thio), 7.17 (m, 1H, Thio), 7.09 (m, 1H, Thio), 7.01 (m, 1H, Thio), 5.48 (s, 2H, CH_2). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298K): δ = 162.0 (C=O), 137.9, 133.9, 133.6, 132.8, 128.5, 127.9, 127.1, 127.0 (Thio), 61.2 (CH_2).



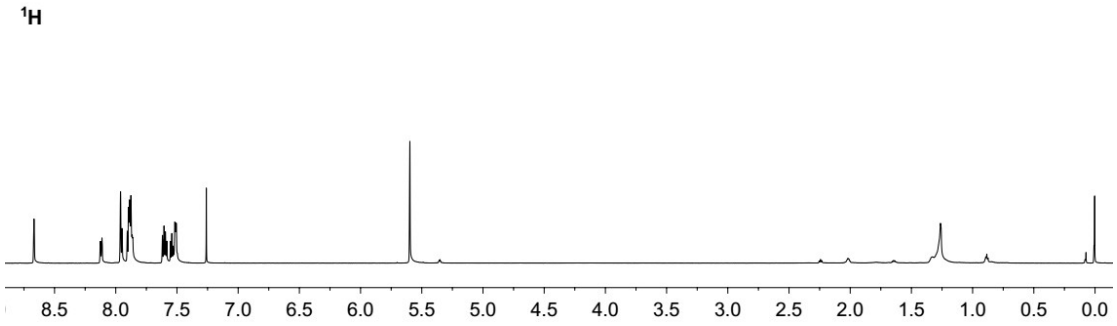
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **5m**



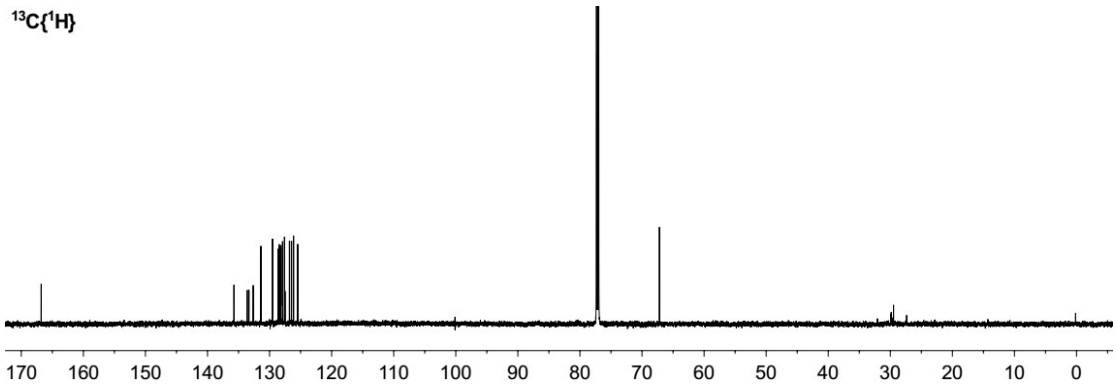
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **5m**



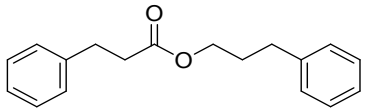
Naphthalen-2-ylmethyl 2-naphthoate (5q). Yield 51.2 mg, 82%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 8.67 (s, 1H, Nap), 8.12 (dm, $^3J_{HH}$ = 8.5 Hz, 1H, Nap), 7.96 (s, 1H, Nap), 7.95 (dm, $^3J_{HH}$ = 8.9 Hz, 1H, Nap), 7.91 (m, 2H, Nap), 7.89 (m, 2H, Nap), 7.87 (m, 1H, Nap), 7.61 (m, 1H, Nap), 7.59 (m, 1H, Nap), 7.54 (m, 1H, Nap), 7.51 (m, 2H, Nap), 5.60 (s, 2H, CH_2). **^{13}C{^{1}H} NMR** (176 MHz, $CDCl_3$, 298K): δ = 166.8 (C=O), 135.7, 133.6, 133.4, 133.3, 132.6, 131.4, 129.5, 128.6, 128.4, 128.3, 128.2, 127.9, 127.8, 127.6, 127.5, 126.8, 126.4, 126.4, 126.1, 125.5 (Nap), 67.2 (CH_2).



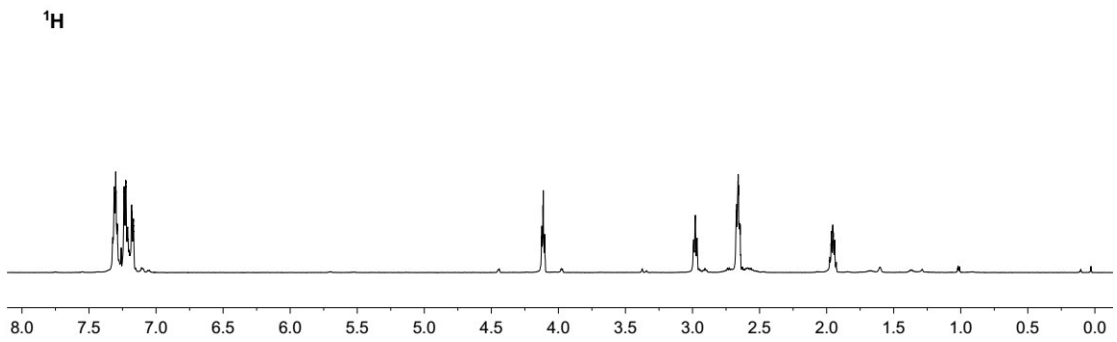
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **5q**



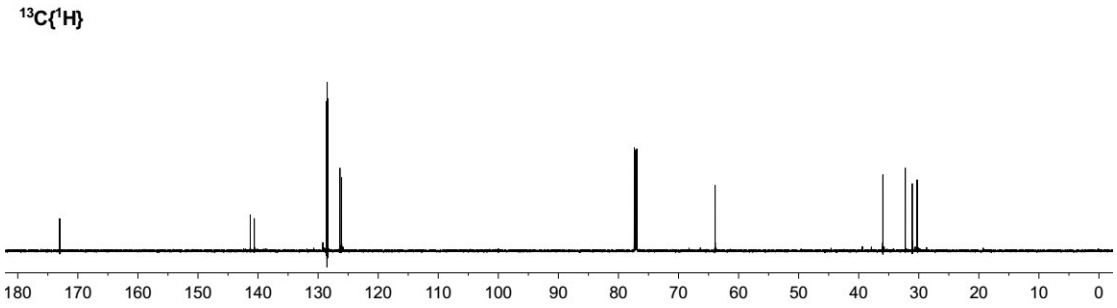
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **5q**



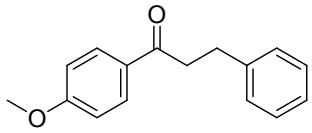
3-Phenylpropyl 3-phenyl propanoate (5s). Yield 39.1 mg, 73%. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.32-7.27 (m, 4H, Ph), 7.24-7.18 (m, 4H, Ph), 7.17 (m, 2H, Ph), 4.11 (m, 2H, OCH_2), 2.97 (m, 2H, $CH_2^{C=O}$), 2.67-2.64 (m, 4H, CH_2), 1.98-1.94 (m, 2H, CH_2). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298K): δ = 173.0 (C=O), 141.3, 140.6, 128.6, 128.5, 128.5, 128.4, 126.4, 126.1 (Ph), 63.9(OCH_2), 36.0 ($CH_2^{C=O}$), 32.2, 31.1, 30.3 (CH_2).



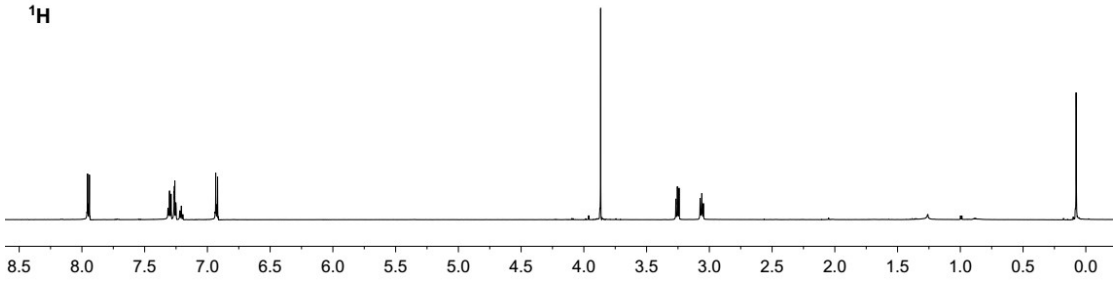
^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **5s**



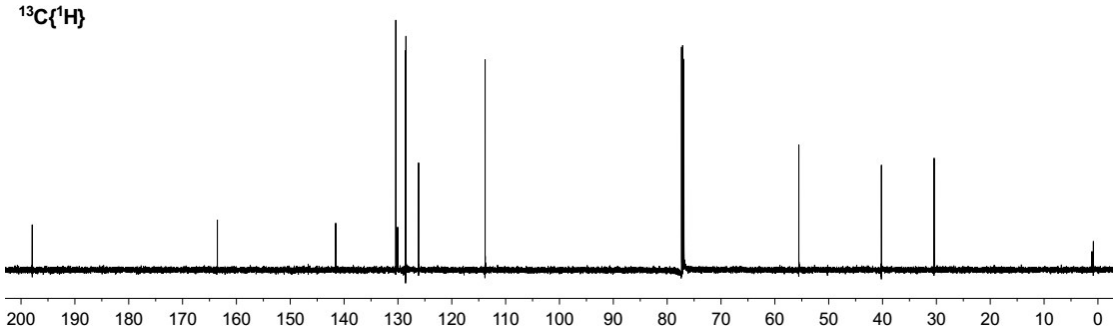
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **5s**



1-(4-methoxyphenyl)-3-phenyl propan-1-one (6f). **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.95 (m, 2H, Ph), 7.30 (m, 2H, Ph), 7.26 (m, 2H, Ph), 7.22 (m, 1H, Ph), 6.94-6.92 (m, 2H, Ph), 3.86 (s, 3H, OCH_3), 3.25 (m, 2H, CH_2) , 3.06 (t, $^{3}J_{HH}$ = 7.2 Hz, 2H, CH_2). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298K): δ = 197.9 (C=O), 163.5, 141.6, 130.4, 130.1, 128.6, 128.51, 126.2, 113.8(Ph), 55.6(CH_3), 40.2, 30.4(CH_2).



^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **6f**



^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 298 K) of **6f**