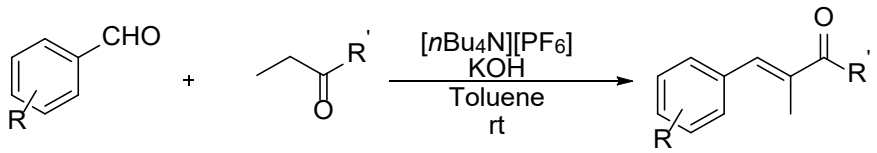
Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Table of Contents

General methods and general procedure for synthesis of substrates	S2
Optimization of the Reaction Conditions	S3-S4
General procedure for dual arylation reactions of α-Methylcinnamaldehyde (**3a**-**k**, **4a**-**l**)	S5-S14
Transformations of **3i**	S15-S17
X-Ray crystal structure of **3f**	S18
References	S19
Copies of NMR spectra	S20-S49

General Methods. Unless otherwise noted, all solvents were used directly without further purification. Palladium catalyst, Ag salt, and Aryl iodides were obtained from Aladdin, and TCI and used directly without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker instrument (400 MHz and 100 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protic solvent signals. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant (s) in Hz, integration). Data for ^{13}C NMR and ^{19}F NMR are reported in terms of chemical shift (δ, ppm).

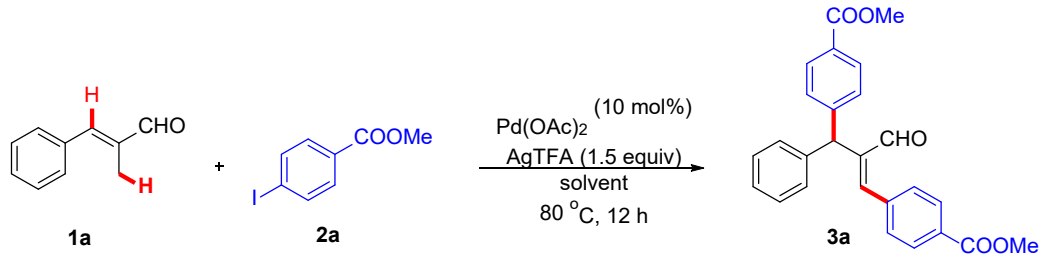
General procedure for the synthesis of substrates (1a-h)[1]



Solutions of substituted benzaldehyde (10 mmol) in benzene (5 mL) and then, dropwise, of propionaldehyde (12 mmol) or 3-pentanone (10 mmol) in benzene (5 mL) were added successively at 20 °C to vigorously stirred suspensions of the appropriate amounts of powdery KOH (15 mmol) and tetrabutylammonium hexafluorophosphate in benzene (5 mL). The reaction mixture was vigorously stirred at the same temperature until the condensation was complete (TLC monitoring). The organic solution was decanted from the wet PTC/KOH solid phase, and the residue was extracted with benzene (10 mL). The combined benzene extracts were washed with water(2×5 mL) and dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure, and the residue was distilled in vacuo or crystallized from hexane.

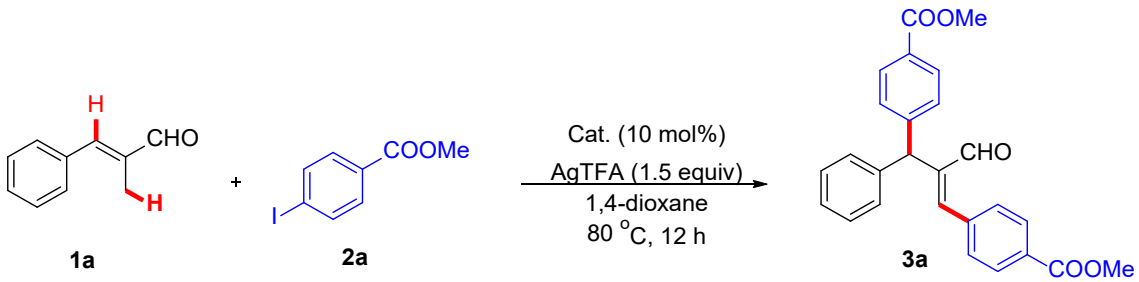
Optimization of the Reaction Conditions

Table S1 Screening of solvent using $Pd(OAc)_2$ as catalyst



Entry	Solvent	Yield (%)
1	HFIP	7
2	MeOH	20
3	EtOH	22
4	DMF	23
5	DMSO	NR
6	MeCN	10
7	DCE	35
8	toluene	34
9	1,4-dioxane	46

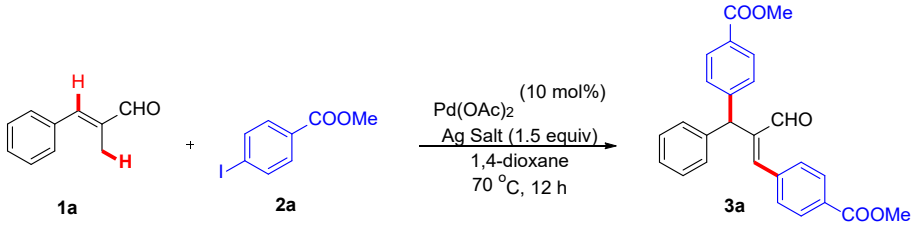
Table S2 Screening of catalyst using 1,4-dioxane as solvent[a,b]



Entry	Catalyst	Yield
1	$(PPh_3)_4Pd$	34
2	$PdCl_2(PPh_3)_2$	32
3	$Pd(OAc)_2$	46
4	$PdCl_2$	44
5	$Cu(OAc)_2$	NR
6	$Fe(OAc)_2$	NR
7	$Co(OAc)_2$	NR
8	**$Pd(OAc)_2$**	**55**[c]
9	$Pd(OAc)_2$	53[d]

[a] Reaction conditions: 1a (0.2 mmol), 2a (0.5 mmol), 1,4-dioxane (2 mL), air, 12 h. [b] Yields are based on 1a, determined by ^1H NMR using 1,3,5-trimethoxybenzene as the internal. [c] 70 °C. [d] 60 °C.

Table S3 Screening of Ag salts using 1,4-dioxane as solvent[a,b]

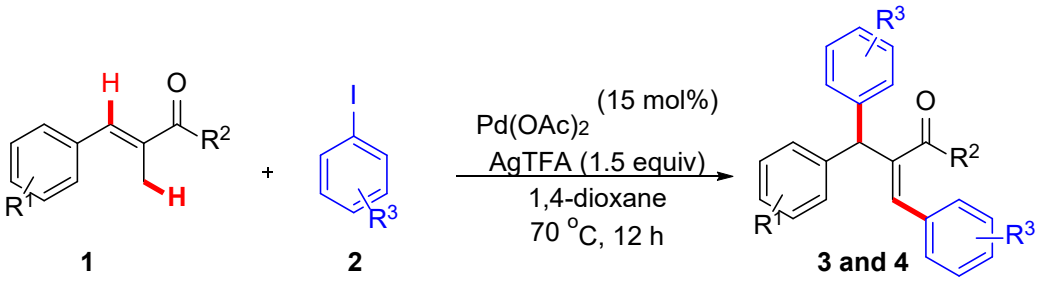


Entry	Ag Salt	Yield(%)
1	**AgTFA**	**55**
2	AgOAc	40
3	Ag_2CO_3	17
4	Ag_3PO_4	23
5	AgOTf	Trace
6	AgTFA	54[c]
7	AgTFA	55[d]

8	AgTFA	75 [e] (74) [f]
9	-	Trace
10	Na_2CO_3	Trace
11	K_3PO_4	Trace

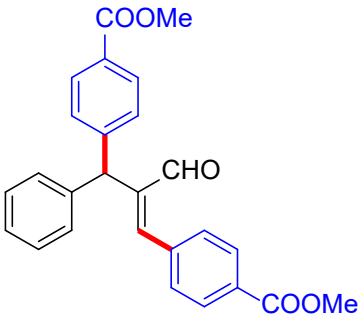
[a] Reaction conditions: 1a (0.2 mmol), 2a (0.5 mmol), $Pd(OAc)_2$ (10% mol), Ag. salt(1.5 equiv), 1,4-dioxane (2 mL), air, 70 °C, 12 h. [b] Yields are based on 1a, determined by ^1H NMR using 1,3,5-trimethoxybenzene as the internal. [c] $Pd(OAc)_2$ (20 mol%). [d] AgTFA (2.5 equiv). [e] $Pd(OAc)_2$ (15 mol%), AgTFA(2.5 equiv). [f] isolated yield.

General procedure for dual arylation reactions of α-Methylcinnamaldehyde (3a-k,4a-i)

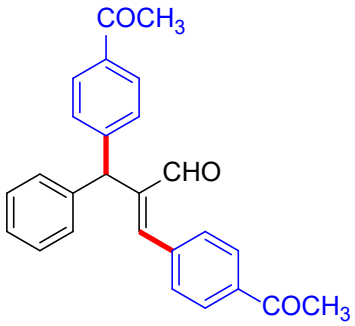


1 **2** **3 and 4**

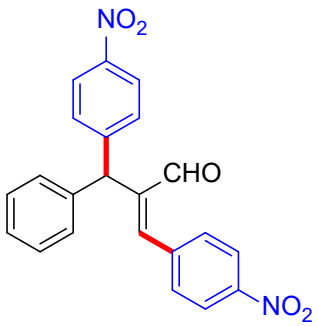
A 10 mL sealed tube equipped with a stir bar was charged with $Pd(OAc)_2$ (6.7 mg, 0.03 mmol, 0.15 equiv), AgTFA (110.4 mg, 0.5 mmol, 2.5 equiv) and Iodobenzene **2** (0.5 mmol, 2.5 equiv), followed by the addition of 1,4-dioxane (2.0 mL) and Cinnamaldehyde **1** (0.2 mmol, 1.0 equiv). The flask was then sealed and the mixture was stirred at 70 °C for 12 hours. After the reaction was complete (monitored by TLC), the reaction mixture was cooled to room temperature, filtrated via celite and the filtrate concentrated under reduced pressure. After the solvent was removed, the residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/60 to 1/5, v/v,) to afford desired product **3** and **4**.



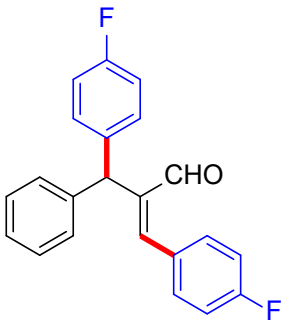
3a. Colorless oil (61.0 mg, 74% yield). Analytical data for **3a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.05 (d, *J* = 8.3 Hz, 2H), 8.00 (d, *J* = 8.4Hz, 2H), 7.37-7.32 (m, 4H), 7.28 – 7.26 (m, 3H), 7.23 (s, 1H), 7.16 (d, *J* = 7.1 Hz, 2H), 5.67 (s, 1H), 3.93 (s, 3H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 167.0, 166.5, 147.4, 146.9, 145.3, 140.7, 138.2, 131.0, 130.9, 130.1, 129.9, 129.8, 129.8, 129.3, 128.9, 127.2, 52.5, 52.2, 50.5. IR (film): 2952, 1717, 1674, 1434, 1274, 1102, 1018, 763, 701 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{23}O_5$ $[M+H]^+$: 415.1540, Found: 415.1537.



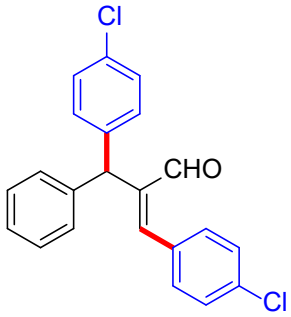
3b. Colorless oil (57.6 mg, 76% yield). Analytical data for **3b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 7.97 (d, *J* = 8.3 Hz, 2H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.35 – 7.26 (m, 5H), 7.24 (s, 1H), 7.16 (d, *J* = 7.2 Hz, 2H), 5.67 (s, 1H), 2.62 (s, 3H), 2.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 197.3, 191.1, 147.2, 147.1, 145.3, 140.5, 138.3, 137.4, 135.9, 130.1, 129.4, 129.2, 128.9, 128.8, 128.5, 127.3, 50.5, 26.8, 26.7. IR (film): 3000, 2855, 1733, 1675, 1601, 1356, 1264, 957, 700, 593 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{23}O_3$ $[M+H]^+$: 405.1462, Found: 405.1458.



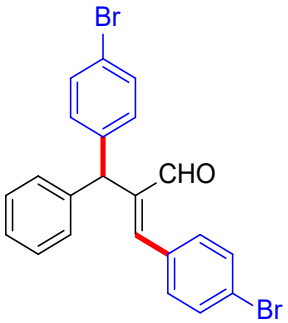
3c. Light yellow solid (51.0 mg, 66% yield). Analytical data for **3c**: m.p. = 167.2-167-9 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.27 (d, *J* = 8.3 Hz, 2H), 8.20 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.39-7.36 (m, 4H), 7.31 (t, *J* = 7.1 Hz, 1H), 7.23 (s, 1H), 7.15 (d, *J* = 7.5 Hz, 2H), 5.71 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 148.9, 148.3, 147.1, 146.0, 145.9, 139.9, 139.5, 130.7, 130.0, 129.3, 129.2, 127.8, 124.1, 123.9, 50.5. IR (film): 2349, 1667, 1516, 1342, 1107, 851, 701 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{16}N_2NaO_5$ $[M+Na]^+$: 411.0952, Found: 411.0953.



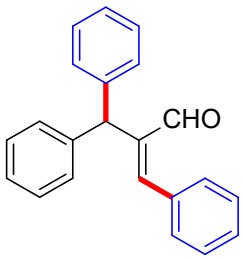
3d. Colorless oil (56.7 mg, 85% yield). Analytical data for **3d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 7.34 – 7.24 (m, 5H), 7.16 – 7.06 (m, 7H), 7.02-6.98 (m, 2H), 5.59 (s, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5, 163.5(d, J = 249.3), 161.8 (d, J = 244.0), 147.3, 144.6, 141.6, 137.2 (d, J = 3.2), 131.9 (d, J = 8.3), 130.7 (d, J = 7.7), 129.9 (d, J = 3.3), 129.2, 128.8, 127.0, 115.8 (d, J = 21.7), 115.6 (d, J = 21.3), 49.7. ^{19}F NMR (376 MHz, CDCl3) δ -110.9, -116.2. IR (film): 3020, 2330, 1670, 1480, 1080, 1009, 800, 680cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{16}F_2NaO$ $[M+Na]^+$: 357.1061, Found: 357.1032.



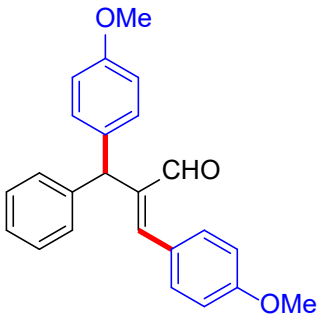
3e. Yellow solid (58.6 mg, 80% yield). Analytical data for **3e**: m.p. = 95.2 - 96.1°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.37 – 7.27 (m, 6H), 7.24-7.20 (m, 3H), 7.15 – 7.09 (m, 5H), 5.57 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 147.1, 144.7, 141.1, 140.2, 135.7, 132.7, 132.2, 131.3, 130.6, 129.2, 128.9, 128.9, 128.8, 127.1, 49.8. IR (film): 3019, 2872, 2336, 1668, 1485, 1089, 1013, 695 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{16}Cl_2NaO$ $[M+Na]^+$: 389.0471, Found: 389.0460.



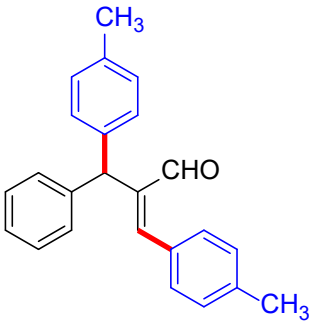
3f. White solid (74.0 mg, 82% yield). Analytical data for **3f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.52 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.34-7.30 (m, 2H), 7.27-7.25 (m, 1H), 7.16 (s, 1H), 7.14-7.12 (m, 4H), 7.05-7.03 (m, 2H), 5.55 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 147.2, 144.7, 141.0, 140.8, 132.7, 131.9, 131.8, 131.5, 131.0, 129.2, 128.7, 127.1, 124.0, 120.9, 50.0. IR (film): 3018, 1670, 1481, 1161, 1009, 805, 695 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{16}Br_2NaO$ $[M+Na]^+$: 478.9440, Found: 478.9445.



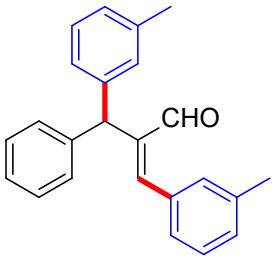
3g. White solid (54.4 mg, 92% yield). Analytical data for **3g**: m.p. = 111.1-111.8 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.39-7.36 (m, 4H), 7.34 – 7.27 (m, 6H), 7.23 (s, 1H), 7.22 – 7.18 (m, 3H), 7.17 (s, 2H), 5.63 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 148.7, 144.6, 141.9, 134.1, 131.3, 130.1, 129.4, 128.7, 128.6, 126.8, 50.4. IR (film): 3009, 2332, 1657, 1480, 1011, 755, 699, cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{18}NaO$ $[M+Na]^+$: 321.1250, Found: 321.1251.



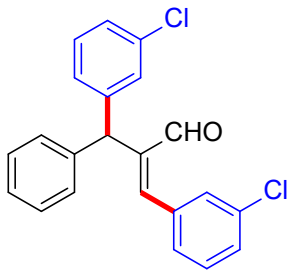
3h. Light yellow solid (37.1 mg, 52% yield). Analytical data for **3h**: m.p. = 117.5-118.8 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.31-7.28 (m, 2H), 7.26 – 7.20 (m, 3H), 7.19 – 7.12 (m, 3H), 7.08 (d, J = 8.6 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 5.56 (s, 1H), 3.82 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 160.8, 158.3, 148.3, 143.4, 142.5, 134.1, 131.8, 130.30, 129.2, 128.6, 126.6, 126.6, 114.0, 114.0, 55.5, 55.3, 49.6. IR (film): 2840, 2315, 1669, 1601, 1508, 1243, 1025, 750, 539 cm^{-1}. HRMS (ESI) calcd for $C_{24}H_{22}NaO_3$ $[M+Na]^+$: 381.1461, Found: 381.1458.



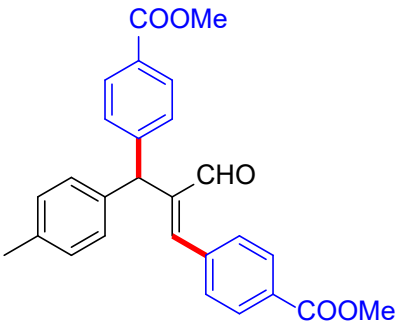
3i. White solid (62.4 mg, 90% yield). Analytical data for **3i**: m.p. = 108.1-109.3 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.31 – 7.21 (m, 4H), 7.18-7.13 (s, 6H), 7.12 – 7.05 (m, 4H), 5.58 (s, 1H), 2.36 (s, 3H), 2.31 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 148.6, 144.1, 142.3, 139.6, 139.0, 136.3, 131.2, 130.1, 129.3, 129.3, 129.2, 129.2, 128.6, 126.6, 50.0, 21.4, 21.2. IR (film): 2889, 1677, 1450, 1166, 788, 699 cm^{-1}. HRMS (ESI) calcd for $C_{24}H_{22}NaO$ $[M+Na]^+$: 349.1563, Found: 349.1571.



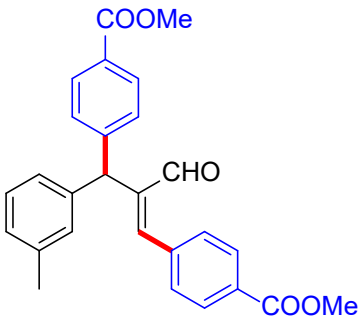
3j. White solid (47.0 mg, 72% yield). Analytical data for **3j**: m.p. = 97.9-99.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.31-7027 (m, 2H), 7.23-7.21 (m, 2H), 7.17-7.16 (m, 5H), 7.12-7.10 (m, 2H), 7.06-7.04 (m, 3H), 5.58 (s, 1H), 2.36 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 148.6, 144.1, 142.3, 139.6, 139.0, 136.2, 131.2, 130.1, 129.3, 129.84, 129.3, 129.2, 129.2, 129.11, 129.01, 128.90, 128.6, 126.6, 50.0, 21.4, 21.2. IR (film): 2854, 2229, 1657, 1449, 1160, 782, 700 cm^{-1}. HRMS (ESI) calcd for $C_{24}H_{22}NaO$ $[M+Na]^+$: 349.1563, Found: 349.1564.



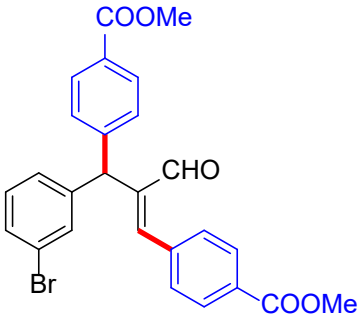
3k. White solid (61.4 mg, 84% yield). Analytical data for **3k**: m.p. = 104.2-105.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 7.39 – 7.27 (m, 6H), 7.25 – 7.20 (m, 2H), 7.19 – 7.12 (m, 5H), 7.09 – 7.03 (m, 1H), 5.58 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 147.0, 145.0, 143.7, 140.7, 135.5, 134.8, 134.7, 130.0, 129.9, 129.7, 129.5, 129.3, 129.3, 128.9, 128.2, 127.5, 127.2, 127.2, 50.1. IR (film): 2883, 1677, 1077, 892, 794, 693 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{16}Cl_2NaO$ $[M+Na]^+$: 389.0470, Found: 389.0470.



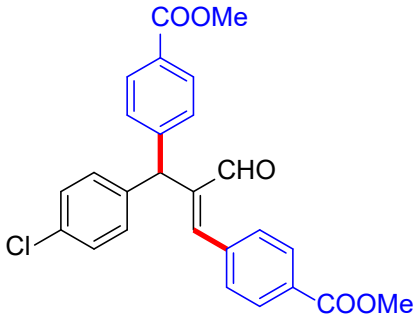
4a. Colorless oil (62.2 mg, 73% yield). Analytical data for **4a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.05 (d, J = 8.2 Hz, 2H), 7.99 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 8.2 Hz, 2H), 7.22 (s, 1H), 7.14 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 5.63 (s, 1H), 3.94 (s, 3H), 3.90 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3, 167.0, 166.5, 147.3, 147.2, 145.5, 138.3, 137.6, 136.9, 130.8, 130.0, 129.9, 129.8, 129.6, 129.2, 129.2, 128.8, 52.5, 52.2, 50.1, 21.2. IR (film): 2951, 1716, 1674, 1434, 1274, 1103, 1018, 733 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{25}O_5$ $[M+H]^+$: 429.1697, Found: 429.1699.



4b. Yellow oil (65.3 mg, 77% yield). Analytical data for **4b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.05 (d, J = 8.3 Hz, 2H), 8.00 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 7.27 – 7.20 (m, 4H), 7.07 (d, J = 7.6 Hz, 1H), 6.95 (d, J = 8.3 Hz, 2H), 5.63 (s, 1H), 3.93 (s, 3H), 3.90 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 167.0, 166.5, 147.3, 147.1, 145.4, 140.6, 138.6, 138.3, 130.8, 130.1, 130.0, 129.9, 129.8, 129.3, 128.9, 128.7, 128.0, 126.3, 52.5, 52.2, 50.5, 21.6. IR (film): 2951, 1717, 1434, 1274, 1103, 764, 707 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{24}NaO_5$ $[M+Na]^+$: 451.1516, Found: 451.1515.

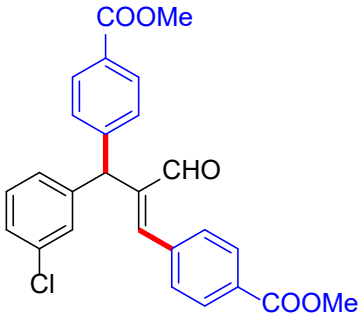


4c. Yellow oil (56.8 mg, 58% yield). Analytical data for **4c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.07 (d, J = 8.2 Hz, 2H), 8.01 (d, J = 8.4 Hz, 2H), 7.43 – 7.35 (m, 3H), 7.31 (s, 1H), 7.27 – 7.19 (m, 4H), 7.11-7.09 (m, 1H), 5.64 (s, 1H), 3.94 (s, 3H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 166.8, 166.4, 147.6, 146.0, 144.6, 143.1, 137.9, 132.2, 131.0, 130.4, 130.4, 130.2, 129.9, 129.8, 129.2, 129.2, 127.9, 123.1, 52.5, 52.3, 50.1. IR (film): 2951, 1717, 1434, 1273, 1103, 1018, 768, 705 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{21}BrNaO_5$ $[M+Na]^+$: 515.0465, Found: 515.0470.

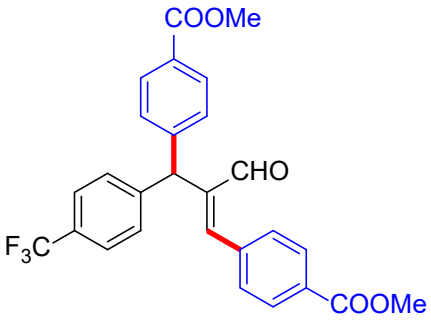


4d. White solid (57.6 mg, 65% yield). Analytical data for **4d**: m.p. = 97.2-99.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.06 (d, J = 8.3 Hz, 2H), 8.00 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 8.3 Hz, 2H), 7.20 (s, 1H), 7.10 (d, J = 8.5 Hz, 2H), 5.63 (s, 1H), 3.94 (s, 3H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 166.9, 147.5, 146.4, 144.9, 139.26, 137.9, 133.2, 131.1, 130.6, 130.2, 130.0, 129.8, 129.2, 129.2,

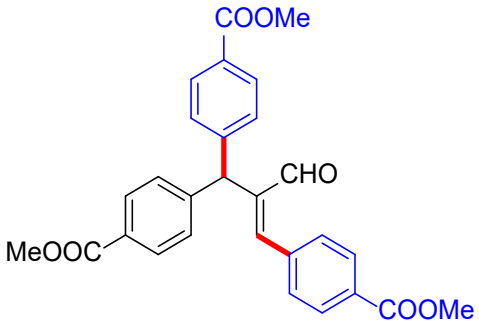
129.1, 52.5, 52.3, 49.9. IR (film): 2952, 1716, 1434, 1274, 1103, 1015, 766, 707 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{21}ClNaO_5$ $[M+Na]^+$: 471.0970, Found: 471.0967.



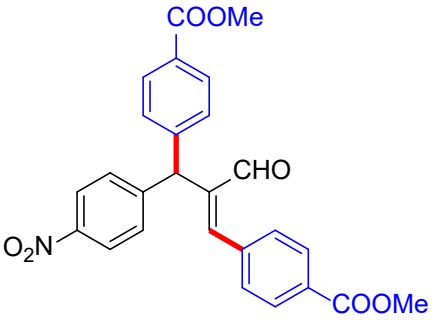
4e. Yellow oil (55.4 mg, 62% yield). Analytical data for **4e**: ^1H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.07 (d, J = 8.1 Hz, 2H), 8.01 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.29 – 7.22 (m, 5H), 7.15 (s, 1H), 7.06 (m, 1H), 5.64 (s, 1H), 3.94 (s, 3H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 166.8, 166.4, 147.6, 146.0, 144.6, 142.8, 137.9, 134.8, 131.0, 130.2, 130.1, 130.0, 129.8, 129.3, 129.2, 129.2, 127.5, 127.5, 52.5, 52.3, 50.11. IR (film): 2952, 1717, 1434, 1274, 1103, 768, 706 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{21}ClNaO_5$ $[M+Na]^+$: 471.0970, Found: 471.0972.



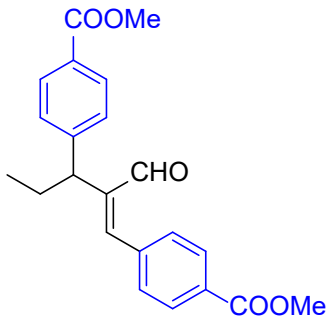
4f. Yellow solid (54.7 mg, 57% yield). Analytical data for **4f**: m.p. = 120.2-121.3 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 8.07 (d, J = 8.3 Hz, 2H), 8.02 (d, J = 8.3 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.26-7.23 (m, 3H), 5.73 (s, 1H), 3.94 (s, 3H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 166.8, 166.4, 147.7, 145.8, 144.9, 144.6, 137.8, 131.1, 130.2, 130.0, 129.9 (q, J = 32.7 Hz), 129.8, 129.6, 129.3, 129.3,126.8 (q, J = 270.5 Hz), 125.9 (q, J = 3.31 Hz), 52.5, 52.3, 50.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.5. IR (film): 2988, 1722, 1670, 1434, 1275, 1104, 709 cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{21}F_3NaO_5$ $[M+Na]^+$: 505.1233, Found: 505.1233.



4g. Light yellow solid (71.3 mg, 76% yield). Analytical data for **4g**: m.p. = 61.2-62.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 8.06 (d, *J* = 8.0 Hz, 2H), 8.01 (d, *J* = 8.1 Hz, 4H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 4H), 7.21 (s, 1H), 5.72 (s, 1H), 3.94 (s, 3H), 3.91 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 166.8, 166.4, 147.7, 146.0, 144.7, 137.9, 131.0, 130.2, 129.9, 129.8, 129.3, 129.2, 52.5, 52.3, 50.4. IR (film): 2329, 1719, 1434, 1276, 1104, 753, 666 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{24}NaO_7$ $[M+Na]^+$: 495.1414, Found: 495.1413.

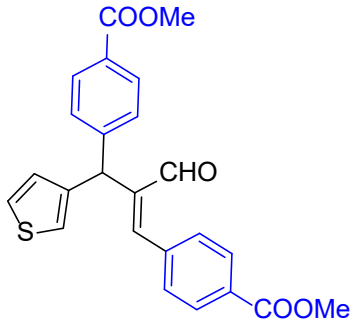


4h. Yellow solid (44.0 mg, 48% yield). Analytical data for **4h**: m.p. = 57.2-58.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 8.21 (d, *J* = 8.8 Hz, 2H), 8.08 (d, *J* = 8.3 Hz, 2H), 8.04 (d, *J* = 8.4 Hz, 2H), 7.39-7.36 (m, 4H), 7.25 (s, 1H), 7.23 (s, 2H), 5.75 (s, 1H), 3.94 (s, 3H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 166.7, 166.3, 148.4, 148.0, 147.2, 145.2, 144.1, 137.5, 131.3, 130.4, 130.1, 130.0, 129.9, 129.6, 129.3, 124.1, 52.5, 52.4, 50.4. IR (film): 2952, 1717, 1518, 1344, 1275, 1104, 847, 703 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{21}NNaO_7$ $[M+Na]^+$: 482.1210, Found: 482.1208.

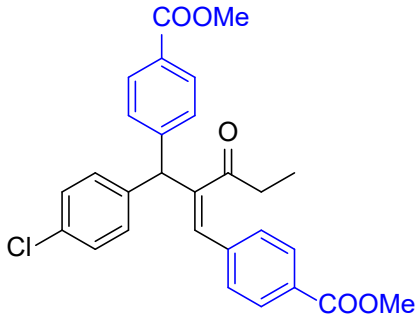


4i. Yellow oil (46.2 mg, 64% yield). Analytical data for **4i**: ^{1}H NMR (400 MHz, $CDCl_3$)δ 9.80 (s, 1H), 8.05 (d, *J* = 8.4 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.59 (s, 1H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.03 (t, *J*=7.2, 1H), 3.93 (s, 3H), 3.90 (s, 3H), 2.03 – 1.89 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 167.1, 166.5, 148.1, 145.5, 144.2, 138.5, 130.7, 130.0, 129.9, 129.7, 128.6, 128.3,

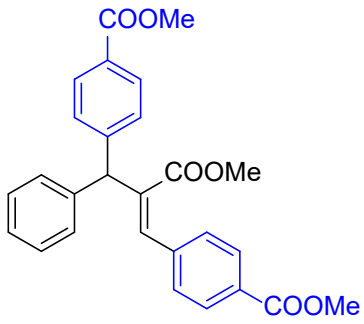
52.4, 52.1, 46.0, 27.1, 12.5. IR (film): 2954, 1717, 1435, 1274, 1104, 766, 704cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{23}O_5$ $[M+H]^+$: 367.1540, Found: 367.1541.



4j. Yellow oil (29.7mg, 36% yield). Analytical data for **4j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.06 (d, J = 8.3 Hz, 2H), 8.01 (d, J = 8.3 Hz, 2H), 7.38 – 7.30 (m, 6H), 6.91 (dd, J = 5.0, 1.3 Hz, 1H), 6.83 (dt, J = 2.9, 1.1 Hz, 1H), 5.68 (s, 1H), 3.93 (s, 3H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, CDCl3) δ 191.0, 167.0, 166.4, 146.8, 145.0, 141.7, 138.1, 130.8, 130.0, 129.9, 129.8, 129.0, 128.8, 128.3, 126.6, 123.4, 52.5, 52.2, 4. IR (film): 2951, 1716, 1672, 1607, 1434, 1274, 1179, 1101, 1018, 761, 644 cm^{-1}. HRMS (ESI) calcd for $C_{24}H_{21}O_5S$ $[M+H]^+$: 421.1104, Found: 421.1110.

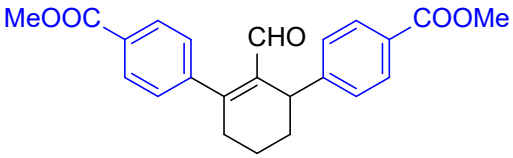


4k. Yellow oil (61.0 mg, 65% yield). Analytical data for **4k**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.92 (d, *J* = 8.1 Hz, 2H), 7.73 (s, 1H), 7.28-7.24 (m, 4H), 7.15 (d, J = 8.1 Hz, 2H), 7.03 (d, J = 8.2 Hz, 2H), 5.44 (s, 1H), 3.92 (s, 3H), 3.90 (s, 3H), 2.73 (q, J = 7.2 Hz, 2H), 0.99 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 167.1, 166.6, 147.2, 143.9, 139.9, 139.5, 139.4, 132.7, 132.0, 130.8, 130.5, 130.0, 129.7, 129.1, 128.8, 128.6, 128.6, 52.4, 52.2, 50.1, 32.9, 8.5. IR (film): 2952, 1719, 1435, 1275, 1103, 1016, 761, 517 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{26}ClO_5$ $[M+H]^+$: 477.1463, Found: 477.1462.

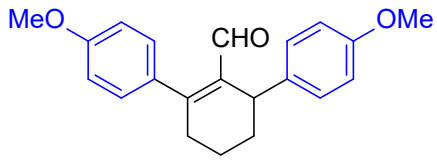


4l. Colorless oil (66.7 mg, 66% yield). Analytical data for **4l**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.93 (m, 5H), 7.32 – 7.24 (m, 5H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 7.1 Hz, 2H), 5.55 (s, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 3.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 167.1, 166.6, 147.6, 141.1, 140.6, 139.6, 135.8, 130.3,

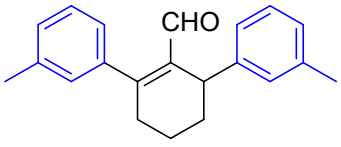
129.9, 129.6, 129.3, 129.2, 128.9, 128.5, 128.5, 127.0, 52.4, 52.2, 52.0, 50.0. IR (film): 2951, 1714, 1608, 1434, 1274, 1104, 699cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{25}O_6$ $[M+H]^+$: 445.1646, Found: 445.1651.



6a. Yellow solid (52.1 mg, 65% yield). Analytical data for **6a**: m.p. = 134.2-135.6 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.46 (s, 1H), 8.11 (d, *J* = 8.3 Hz, 2H), 7.97 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 4.18 (dr, 1H), 3.96 (s, 3H), 3.90 (s, 3H), 2.69 – 2.63 (m, 1H), 2.01 (m, 1H), 1.88 (m, 1H), 1.77 – 1.67 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 167.2, 166.6, 160.5, 150.2, 143.9, 137.2, 130.5, 129.8, 128.8, 128.3, 128.0, 52.5, 52.2, 37.9, 34.0, 30.6, 17.7. IR (film): 2952, 1710, 1600, 1433, 1270, 1104, 701cm^{-1}. HRMS (ESI) calcd for $C_{23}H_{22}NaO_5$ $[M+H]^+$: 401.1359, Found: 401.1358.

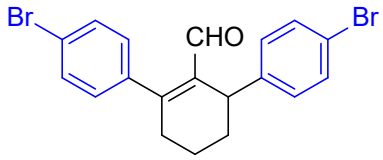


6b. Yellow solid (21.2 mg, 34% yield). Analytical data for **6b**: m.p. = 100.0-101.3 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.26 (d, *J* = 8.5 Hz, 2H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 4.10 (dr, 1H), 3.84 (s, 3H), 3.77 (s, 3H), 2.74 – 2.50 (m, 2H), 1.96 – 1.78 (m, 2H), 1.72-1.65 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 160.5, 160.1, 157.9, 137.3, 137.2, 131.6, 130.3, 128.9, 113.8, 113.8, 55.5, 55.3, 37.1, 34.0, 30.9, 17.7. IR (film): 2935, 1735, 1683, 1508, 1238, 1175, 1030, 828, 701 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{22}NaO_3$ $[M+Na]^+$: 345.1461, Found: 345.1460.



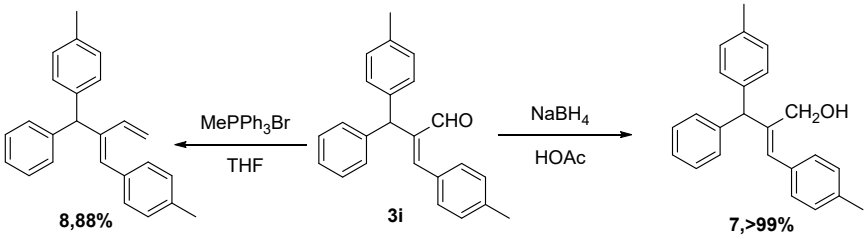
6c. Yellow oil (24.4 mg, 43% yield). Analytical data for **6c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (s, 1H), 7.31-7.28 (m, 1H), 7.21 – 7.12 (m, 4H), 7.02 – 6.93 (m, 3H), 4.10 (dr, 1H), 2.73 – 2.51 (m, 2H), 2.40 (s, 3H), 2.33 (s, 3H), 1.99 – 1.81 (m, 2H), 1.77 – 1.62 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 161.3, 144.9, 139.5, 138.2, 137.9, 137.1, 129.5, 129.4, 129.0, 128.3, 128.1, 127.0, 125.9, 124.9, 37.7, 34.2, 30.8, 21.7,

21.5, 17.7. IR (film): 2934, 1667, 1446, 1212, 1043, 781, 703 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{22}NaO$ $[M+Na]^+$: 313.1563, Found: 313.1564.



6d. Yellow solid (55.2 mg, 67% yield). Analytical data for **6d**: m.p. = 86.1-82.1 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 (s, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 4.07 (dr, 1H), 2.65 – 2.55 (m, 2H), 1.96-1.90 (m, 1H), 1.84-1.78 (m, 1H), 1.73-1.65 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 160.0, 143.8, 138.0, 137.3, 131.8, 131.5, 130.3, 129.7, 123.1, 120.1, 37.4, 34.0, 30.6, 17.6. IR (film): 2936, 1684, 1483, 1169, 1008, 814, 692 cm^{-1}. HRMS (ESI) calcd for $C_{19}H_{16}Br_2NaO$ $[M+Na]^+$: 442.9440, Found: 442.9440.

Transformation of 3i

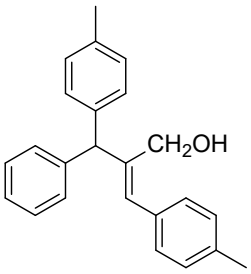


Reduction of 3i [2]

(*Z*)-2-(phenyl(p-tolyl)methyl)-3-(p-tolyl)prop-2-en-1-ol(7)

To a solution of **3i** (32.6 mg, 0.1 mmol) in 2 mL of acetic acid was added sodium borohydride (7.6 mg, 0.2 mmol) in portions at 0°C. The reaction was continued for another hour (monitored by TLC). Water (5 mL) was added, and then the mixture was neutralized with a saturated solution of potassium bicarbonate (5 mL).The aqueous

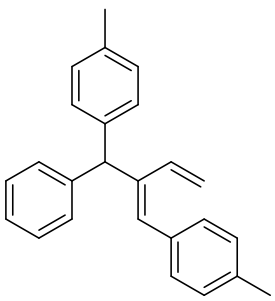
solution was extracted twice with 10 mL of ethyl acetate. The combined organic phase was washed with brine and dried over sodium sulfate. The solvent was removed under reduced pressure to give a crude residue. Further purification by preparative TLC gave compound **5** as a white solid (32.6mg, 99% yield).



Analytical data for **7:** m.p. = 87.9-88.8 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.23-7.22 (m, 3H), 7.16-7.10 (m, 8H), 6.17 (s, 1H), 5.22 (s, 1H), 4.28 (s, 2H), 2.32 (s, 3H), 2.32 (s, 3H), 1.38(s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 142.4, 139.2, 136.9, 136.3, 134.1, 132.3, 129.6, 129.5, 129.3, 129.0, 128.8, 128.6, 126.6, 61.4, 55.6, 21.3, 21.2. IR (film): 3388, 2921, 1510, 1297, 1007, 697, 523 cm^{-1}. HRMS (ESI) calcd for $C_{24}H_{24}NaO$ $[M+Na]^+$: 351.1719, Found: 351.1719.

(*E*)-4,4'-(3-phenyl-2-vinylprop-1-ene-1,3-diyl)bis(methylbenzene)(8) [3]

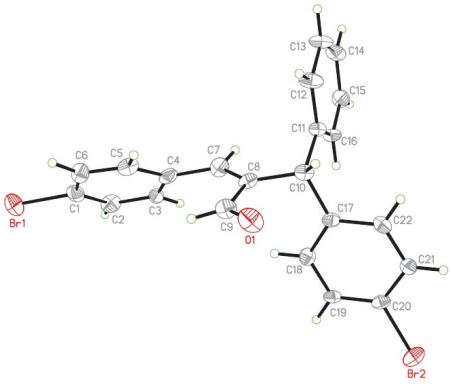
To a suspension of methyltriphenylphosphonium bromide (0.13 mmol, 1.3 equiv) in THF(1 mL) at 0 ºC was added dropwise *n*-butyllithium (2.5 M in hexane, 50 μ L, 0.125 mmol). The reaction mixture was stirred for 15 min and **3i** (32.6 mg, 0.1 mmol, 1 equiv) was added as solution in THF (1 mL). After 1 h the solution was warmed to room temperature and stirred for additional 6 hours. A saturated solution of NH_4Cl (5 mL) was added and the mixture was extracted with Et_2O (3 × 5 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, and the solvents were removed under reduced pressure. The residue was applied to a plug of silica, eluted with hexane, and the solvent was removed carefully under reduced pressure to obtain the desired compound (56.4 mg, 88%) as a colorless oil.



Analytical data for **8:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.28 (m, 2H), 7.20-7.18 (m, 3H), 7.11-7.09 (m, 8H), 6.88 (dd, J = 17.7, 11.2 Hz, 1H), 6.10 (s, 1H), 5.32 (s, 1H), 5.28 (d, J = 17.5 Hz, 1H), 5.09 (d, J = 11.0 Hz, 1H), 2.32 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 140.8, 140.1, 136.7, 135.9, 134.8,

134.6, 133.5, 129.6, 129.5, 129.2, 128.8, 128.4, 128.4, 126.4, 116.0, 53.7, 21.3, 21.2. IR (film): 3022, 1738, 1509, 1239, 905, 800, 699, 502 cm^{-1}. HRMS (ESI) calcd for $C_{25}H_{24}Na$ $[M+Na]^+$: 347.1770, Found: 347.1775.

X-Ray crystal structure of 3f (CCDC 2068405)




```
Bond precision:   C-C = 0.0127 A          Wavelength=0.71073

Cell:             a=5.7279(9)     b=9.0758(14)        c=17.852(3)
                  alpha=90        beta=94.135(5)      gamma=90
Temperature:      296 K

                  Calculated                  Reported
Volume            925.6(3)                    925.6(3)
Space group       P 21                        P 21
Hall group        P 2yb                       P 2yb
Moiety formula    C22 H16 Br2 O               C22 H16 Br2 O
Sum formula       C22 H16 Br2 O               C22 H16 Br2 O
Mr                456.15                      456.17
Dx,g cm-3         1.637                       1.637
Z                 2                           2
Mu (mm-1)         4.385                       4.385
F000              452.0                       452.0
F000'             451.05
h,k,lmax          6,10,21                     6,10,21
Nref              3365[ 1796]                 3332
Tmin,Tmax         0.225,0.416                 0.280,0.746
Tmin'             0.066

Correction method= # Reported T Limits: Tmin=0.280 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 1.86/0.99      Theta(max)= 25.348

R(reflections)= 0.0489( 3101)     wR2(reflections)= 0.1358( 3332)

S = 1.016                 Npar= 262
```

References

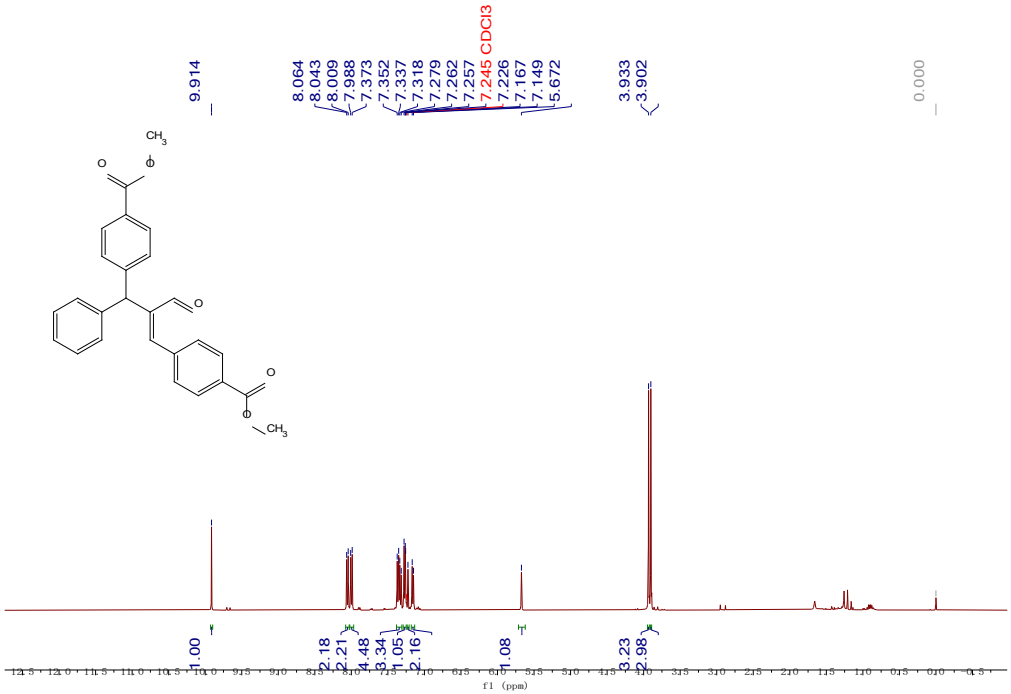
(1) Zlotin, S. G.; Kryshtal, G.V.; Zhdankina, G. M. *Eur. J. Org. Chem.* **2005**, *13* 2822–2827.

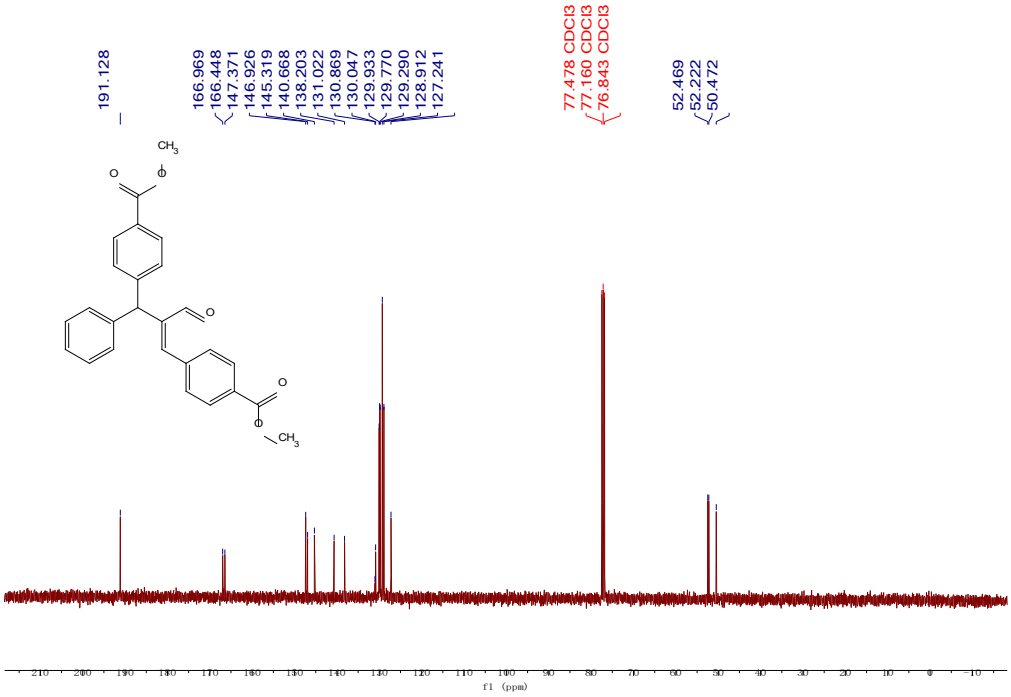
(2) L.-L. Ding, X. –W. Sui, Z.-H. Gu. *ACS Catal.* **2018**, *8*, 5630-5635.

(3) Liu, Q.; Wu, L. Z.; Wei, X. *J.*; Yang, D. T.; Wang, L.; Song, T. *Org. Lett.* **2013**, *15*, 6054–6057.

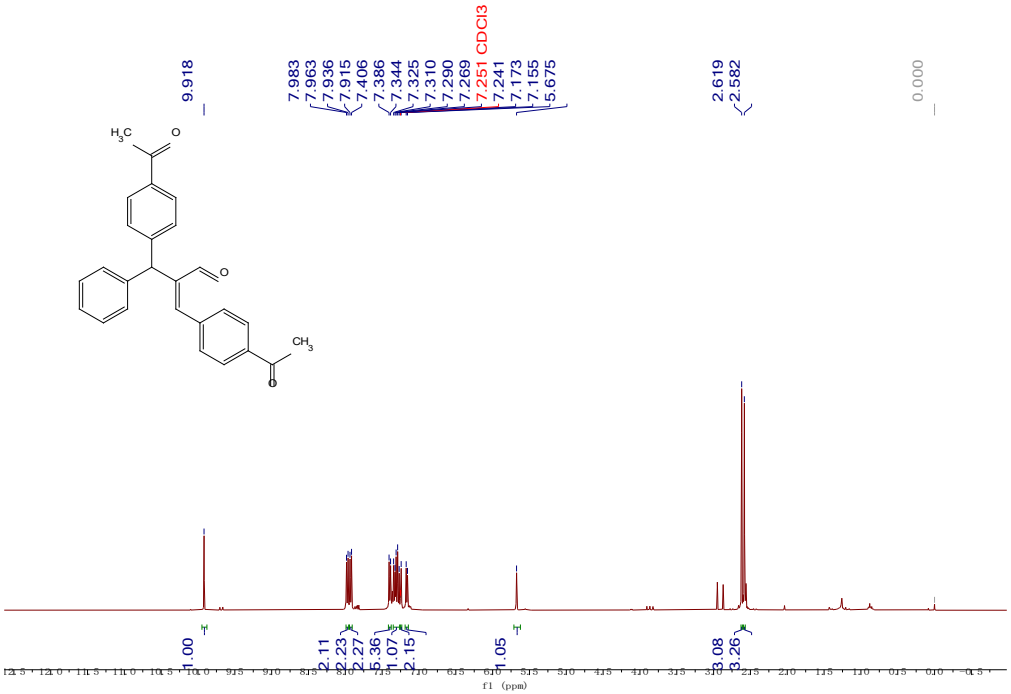
NMR Spectra of products

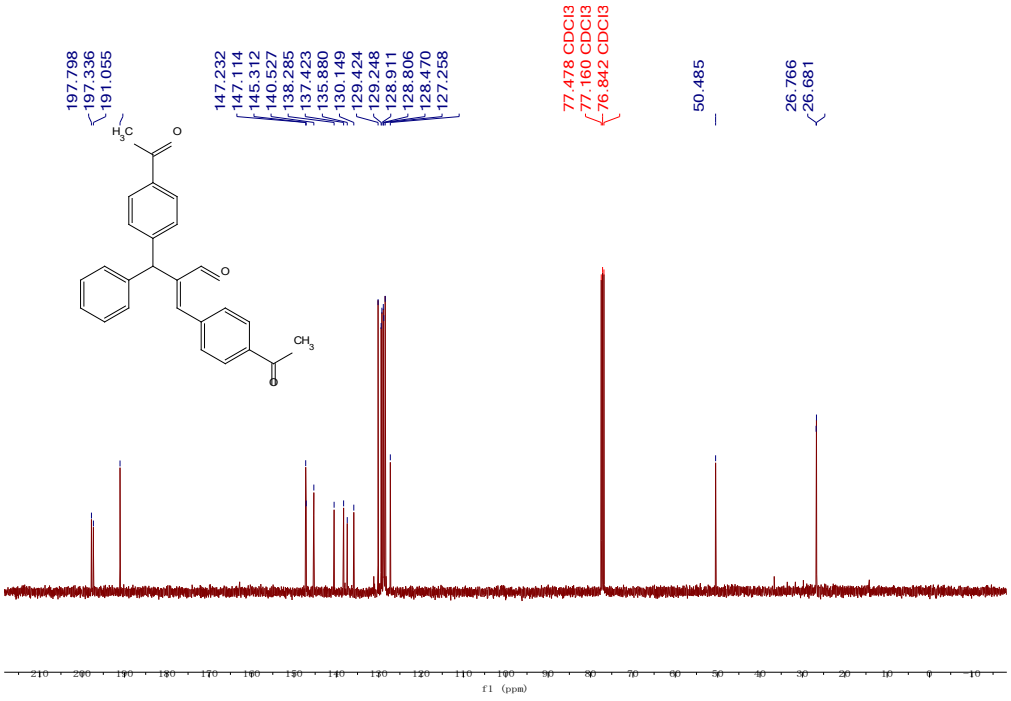
^{1}H NMR and ^{13}C NMR spectra of 3a



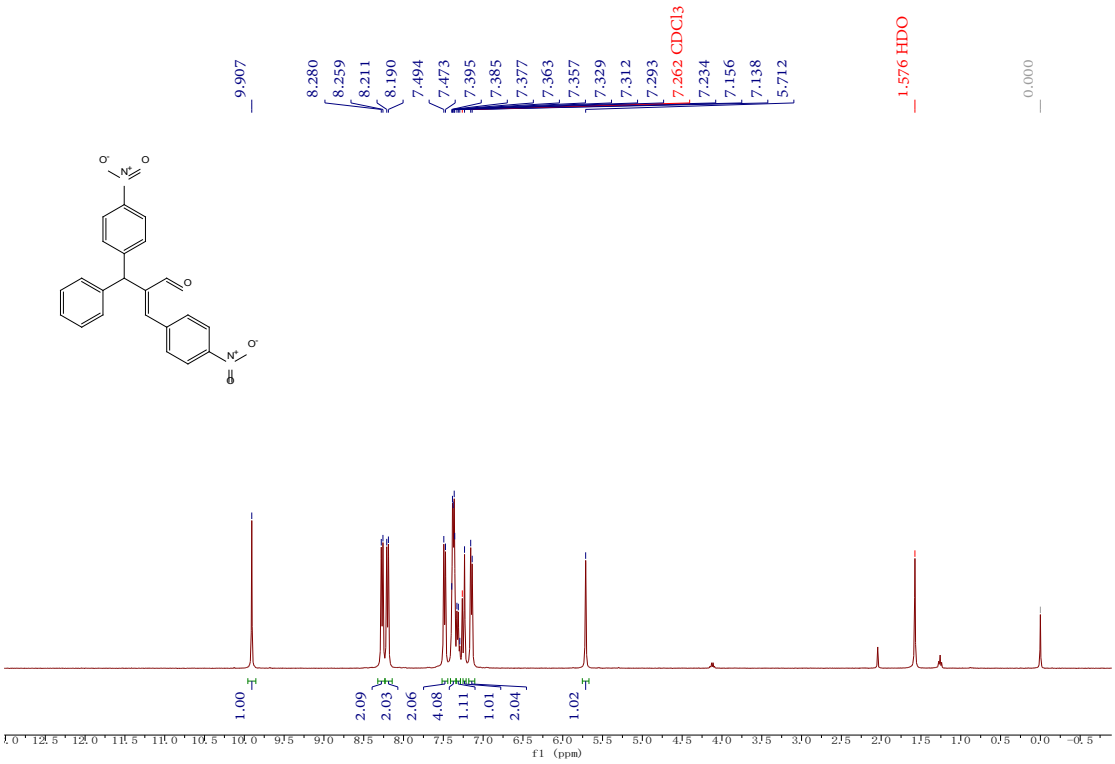


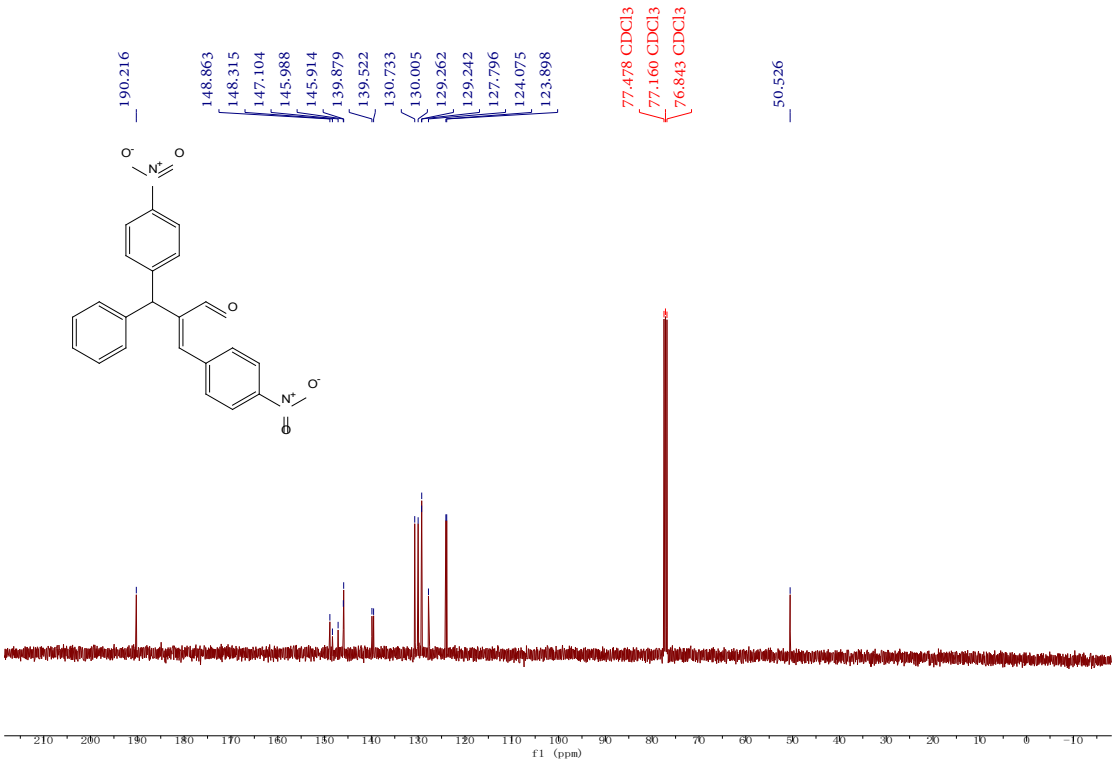
^{1}H NMR and ^{13}C NMR spectra of 3b



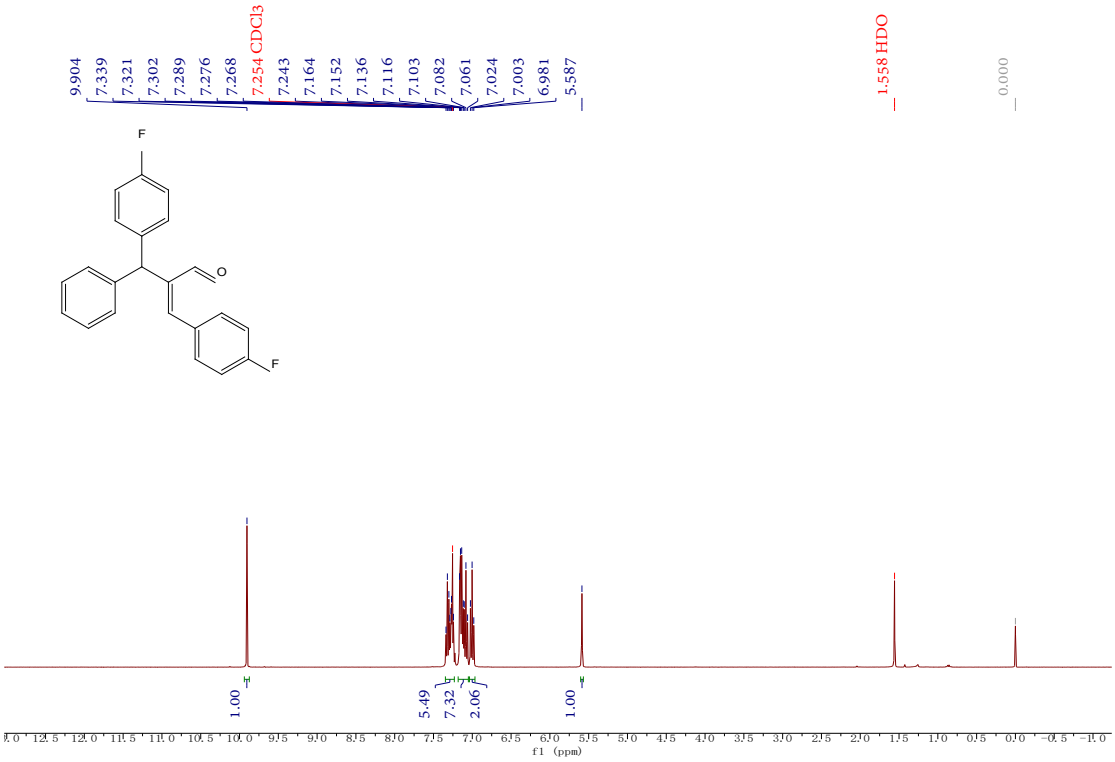


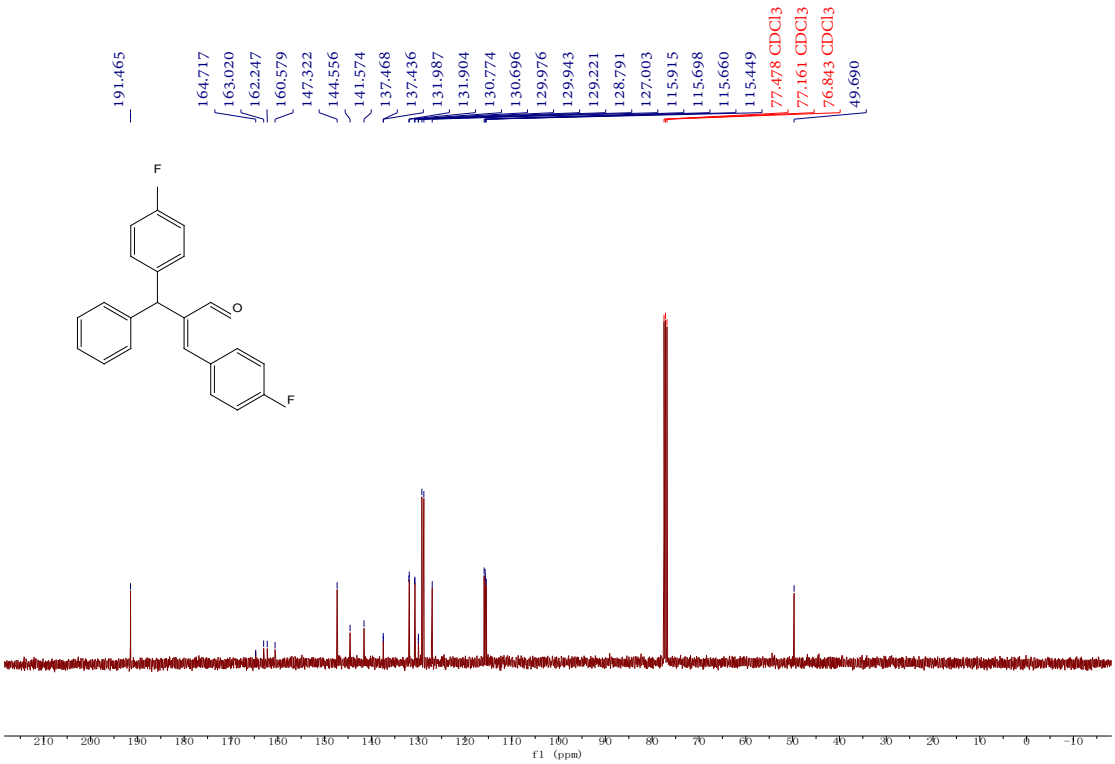
^{1}H NMR and ^{13}C NMR spectra of 3c

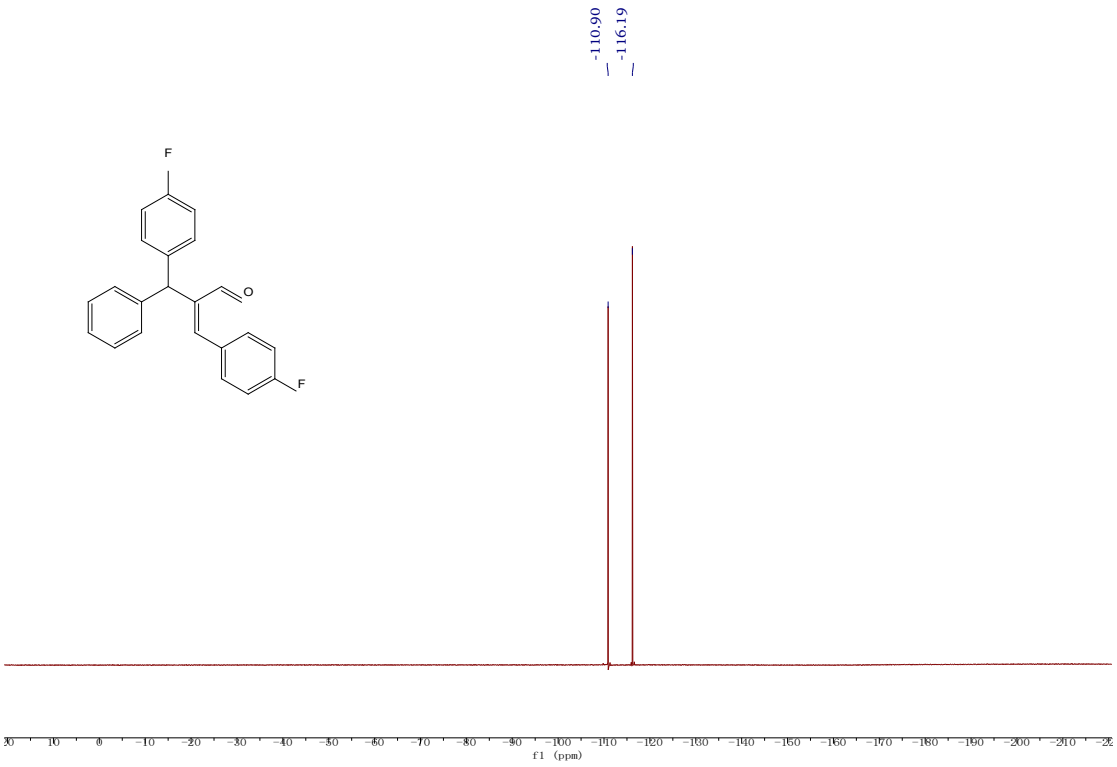




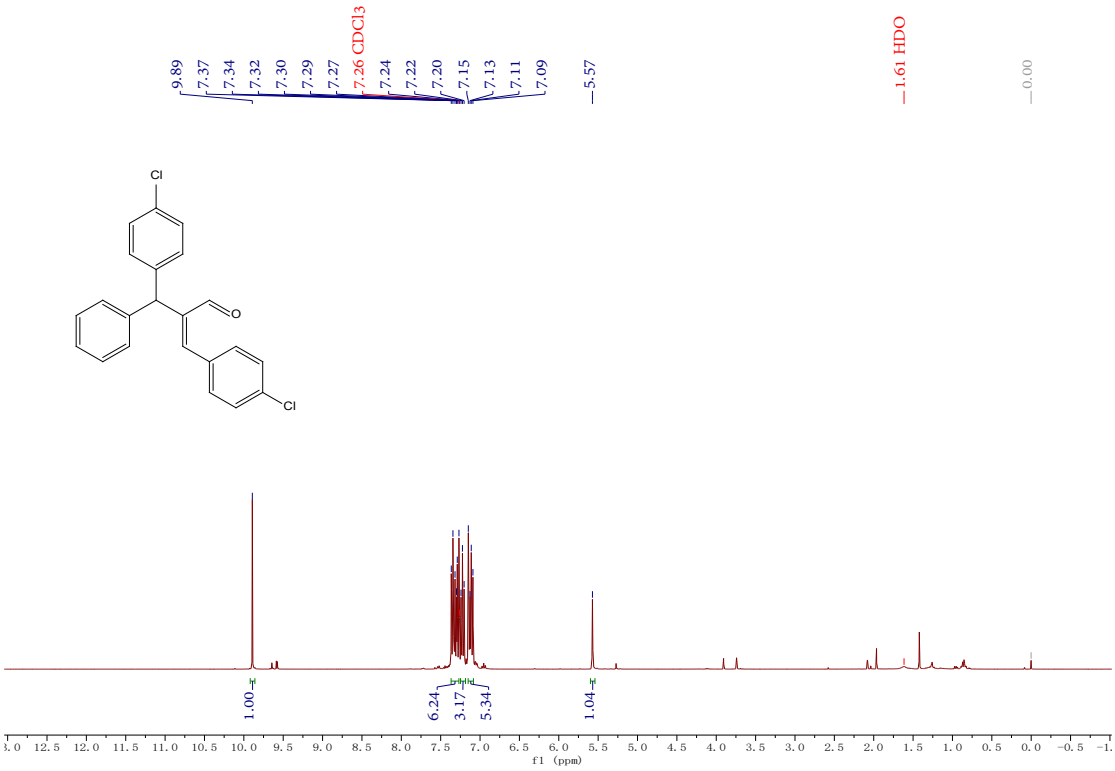
^{1}H NMR, ^{13}C NMR and ^{19}F NMRspectra of 3d

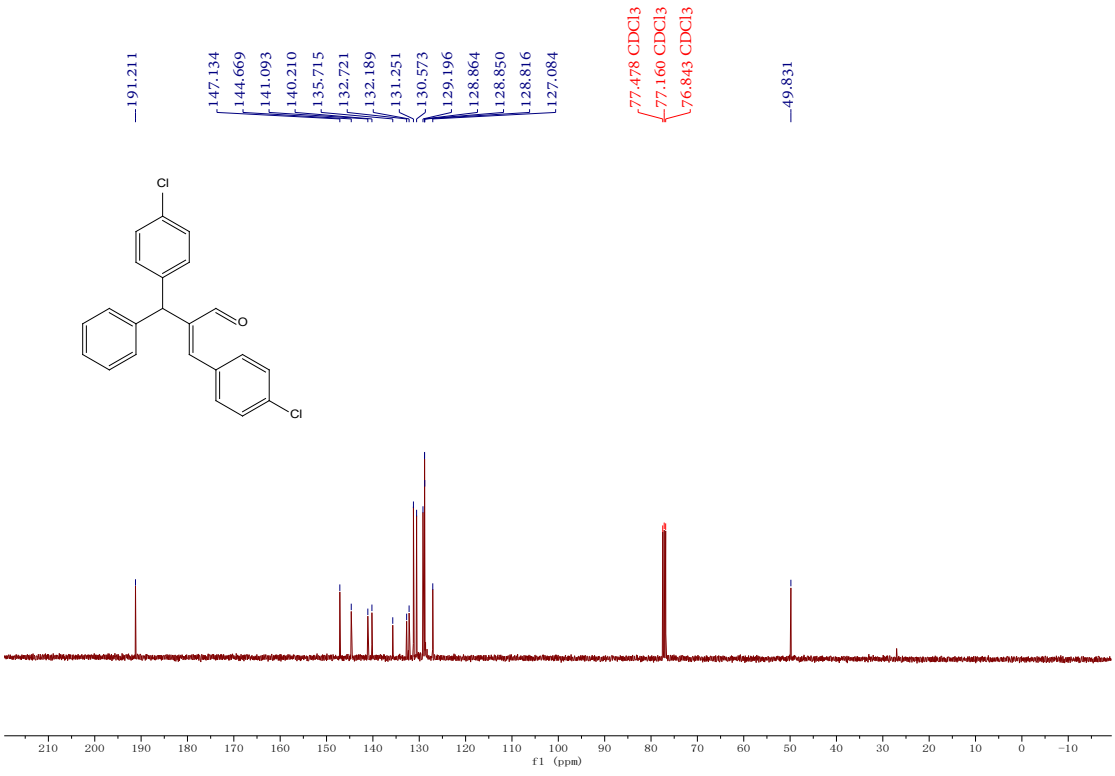




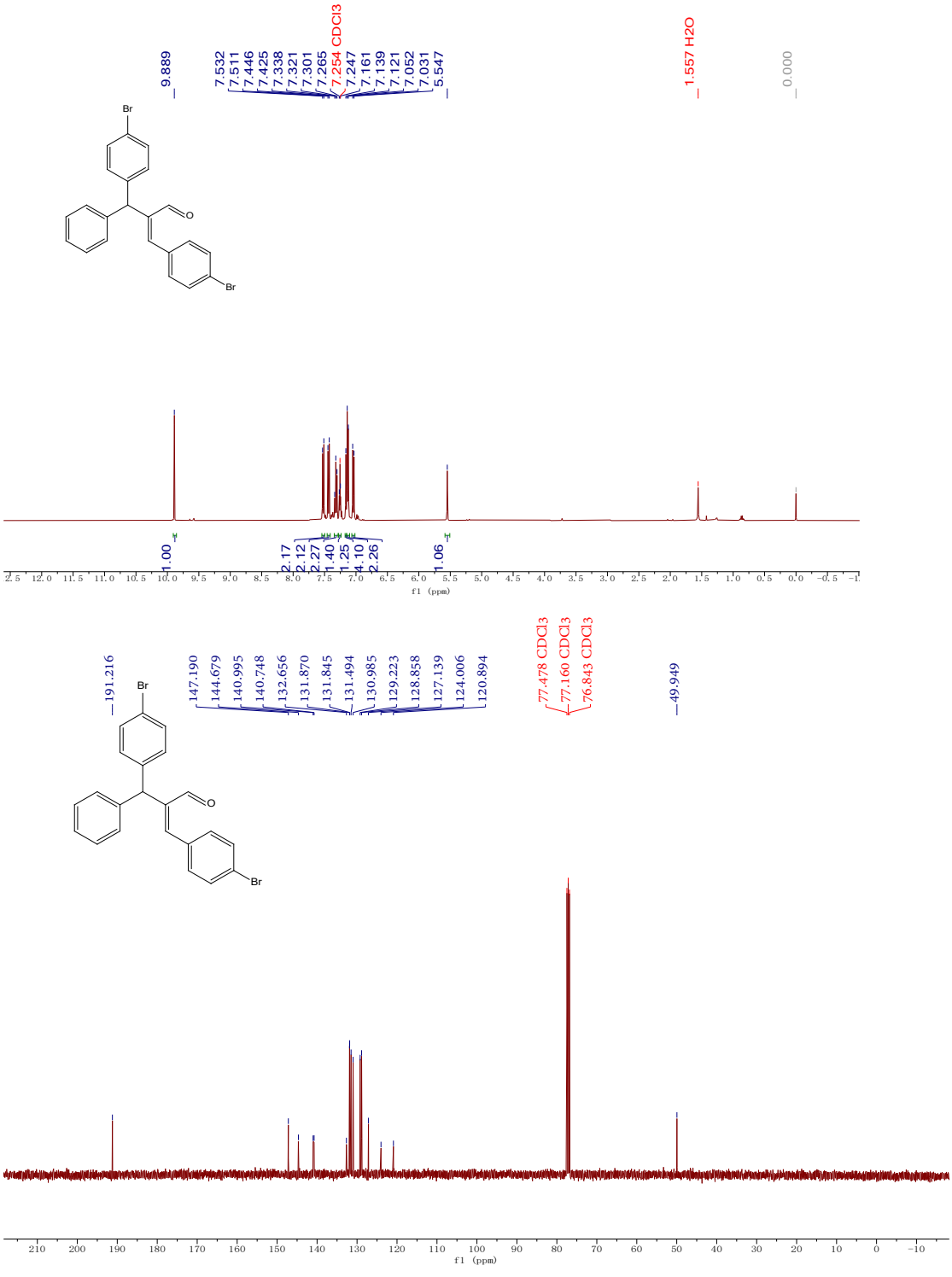

-110.90
-116.19
F
O
F
f1 (ppm)

^{1}H NMR and ^{13}C NMR spectra of 3e

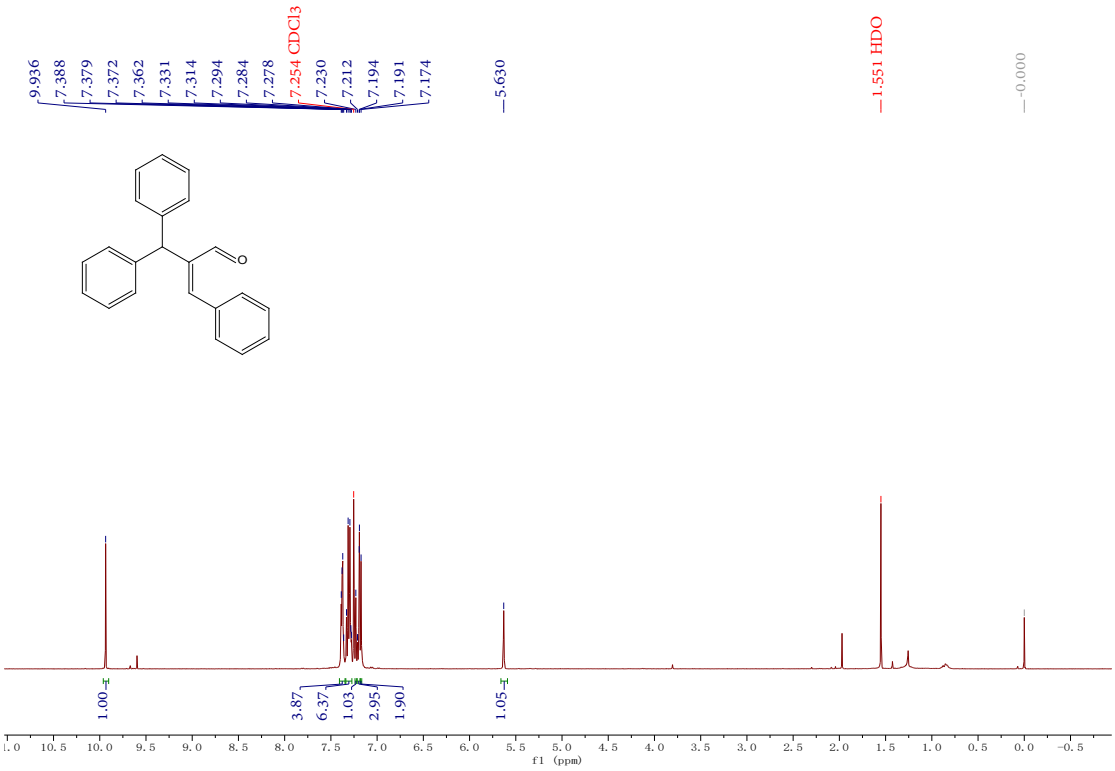


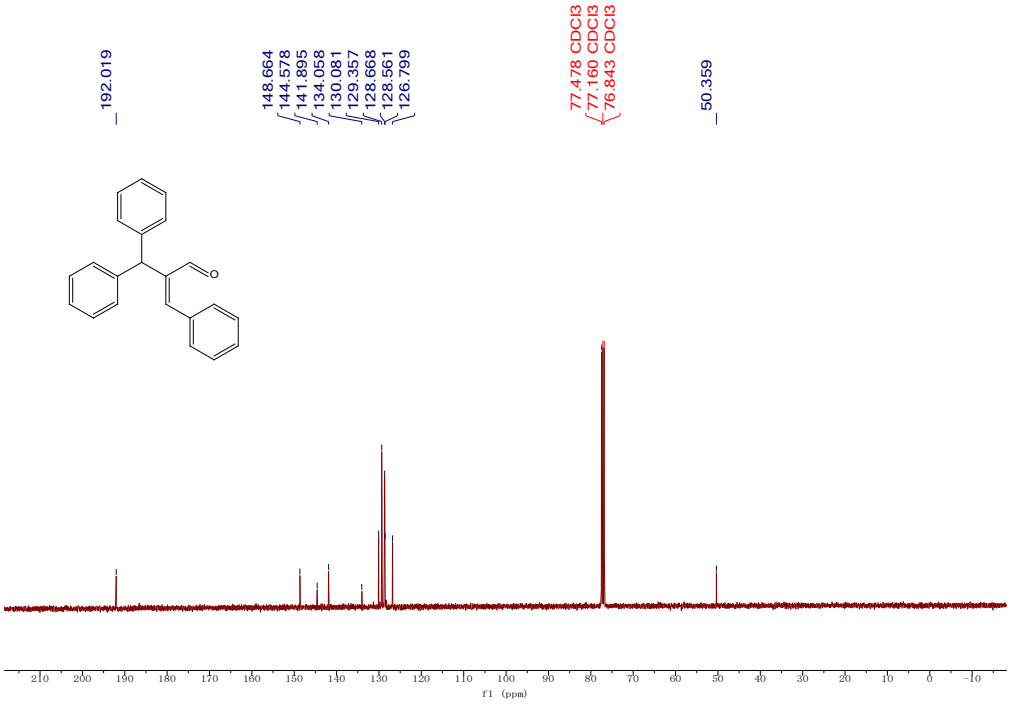


^{1}H NMR and ^{13}C NMR spectra of 3f

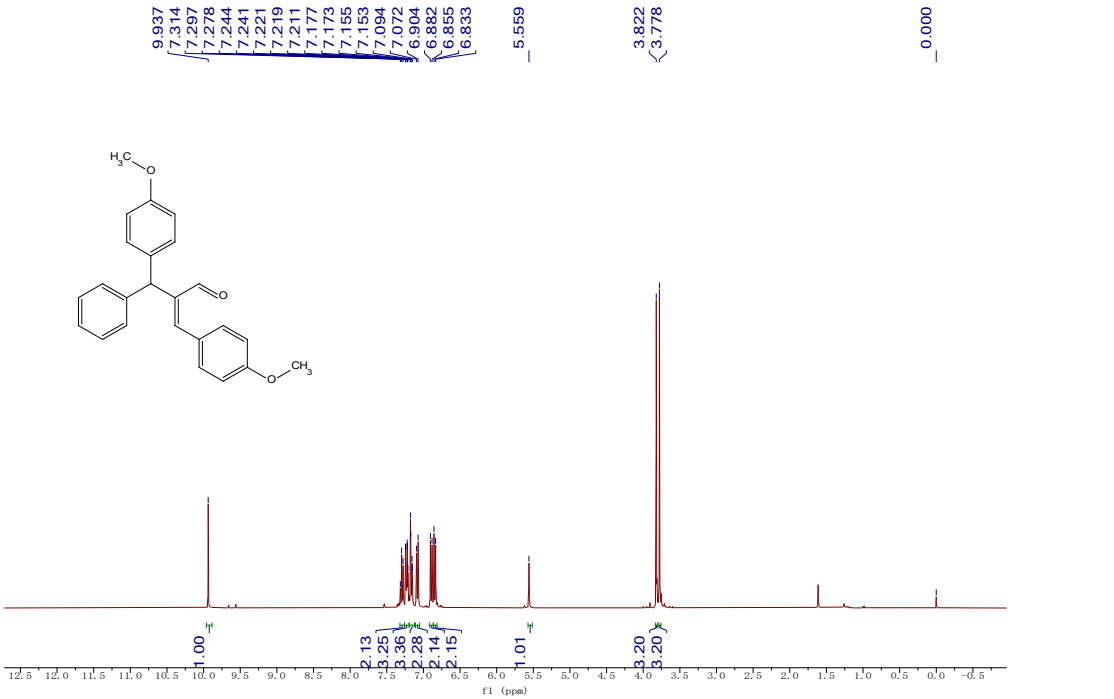


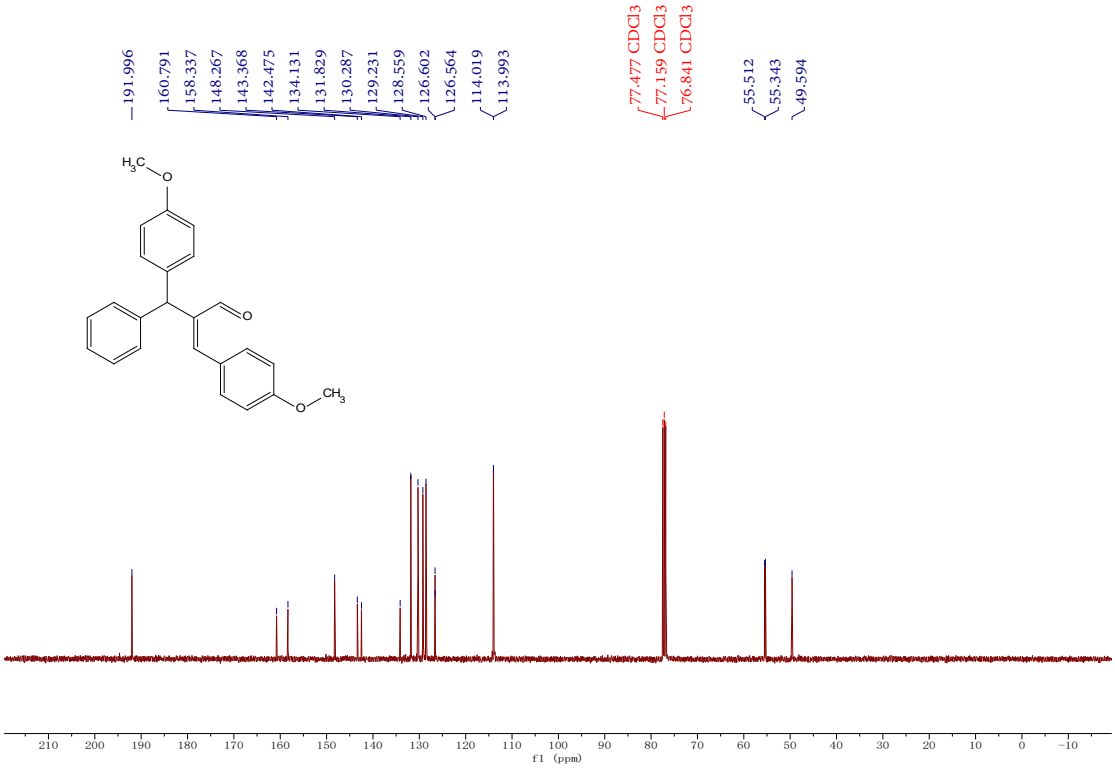
^{1}H NMR and ^{13}C NMR spectra of 3g



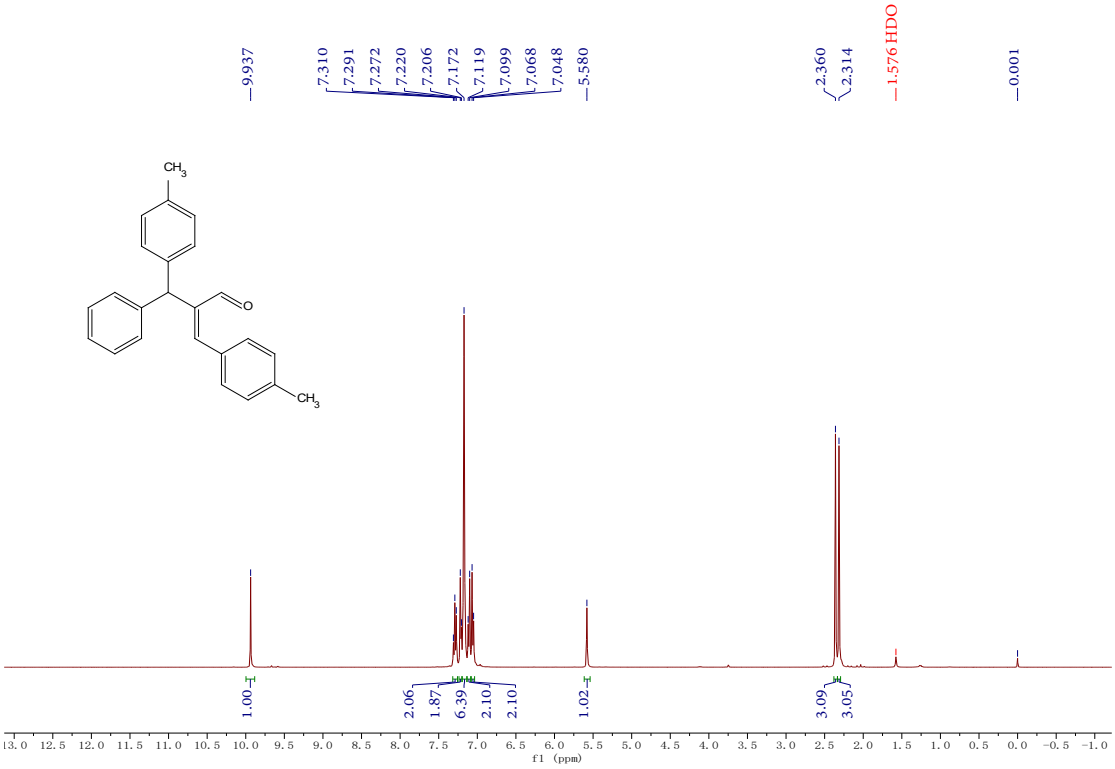


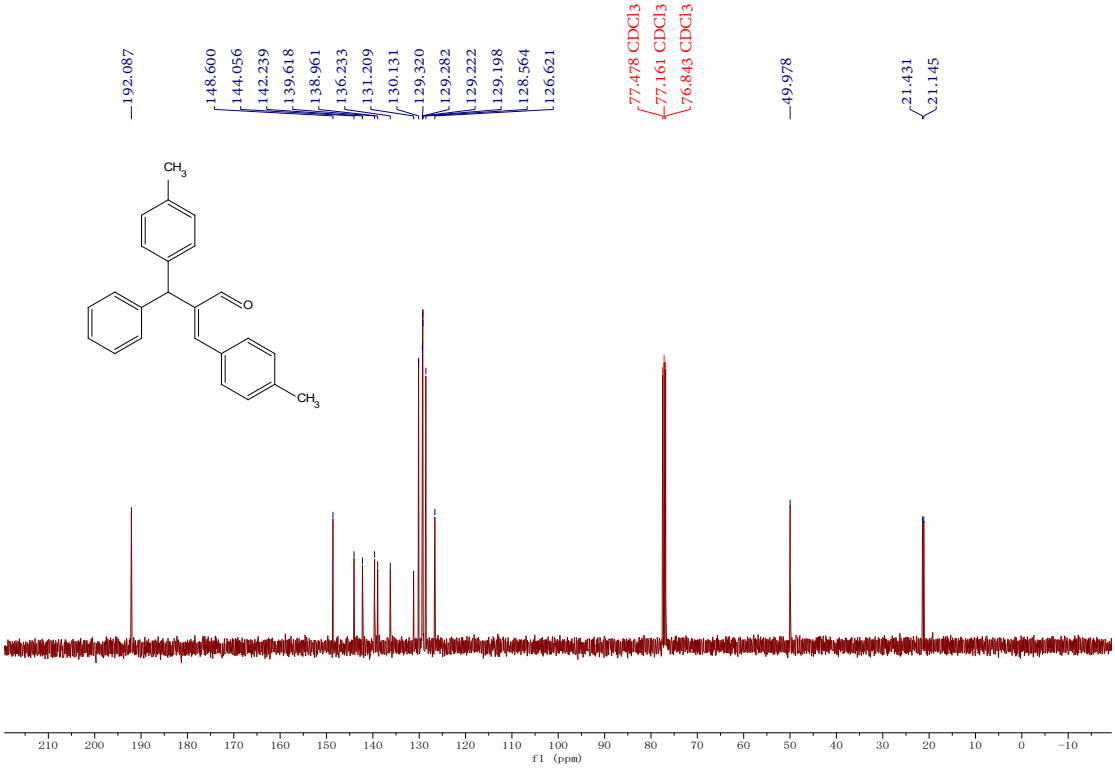
^{1}H NMR and ^{13}C NMR spectra of 3h



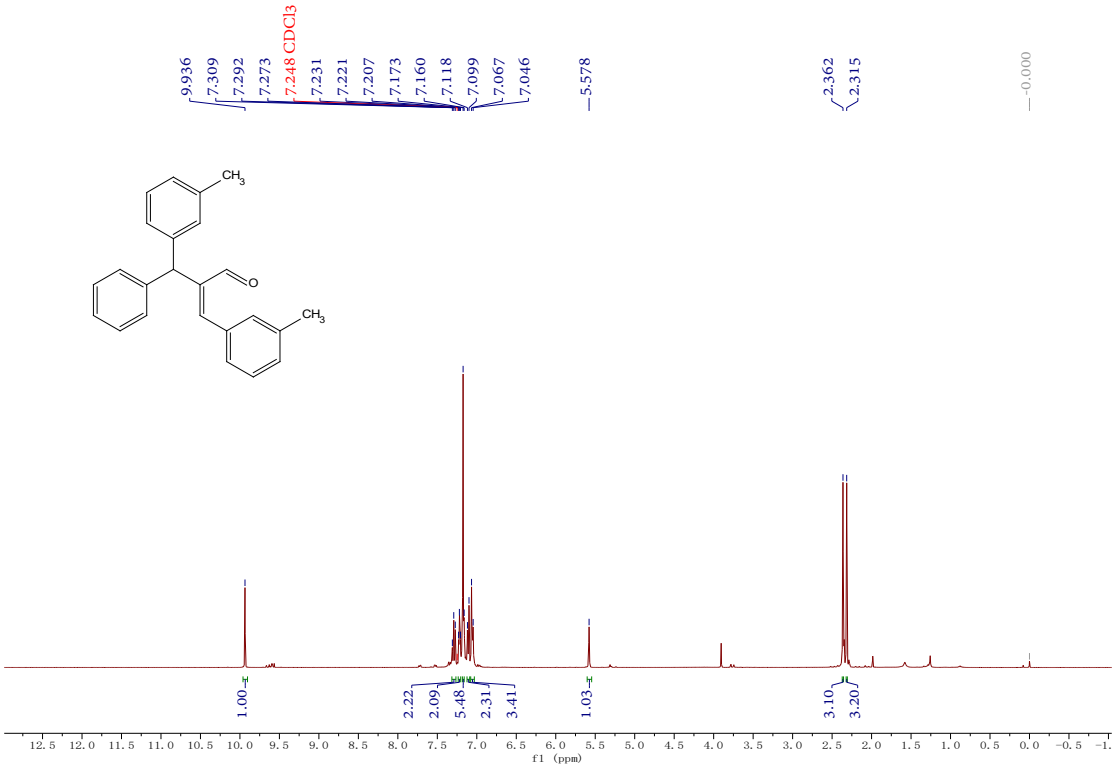


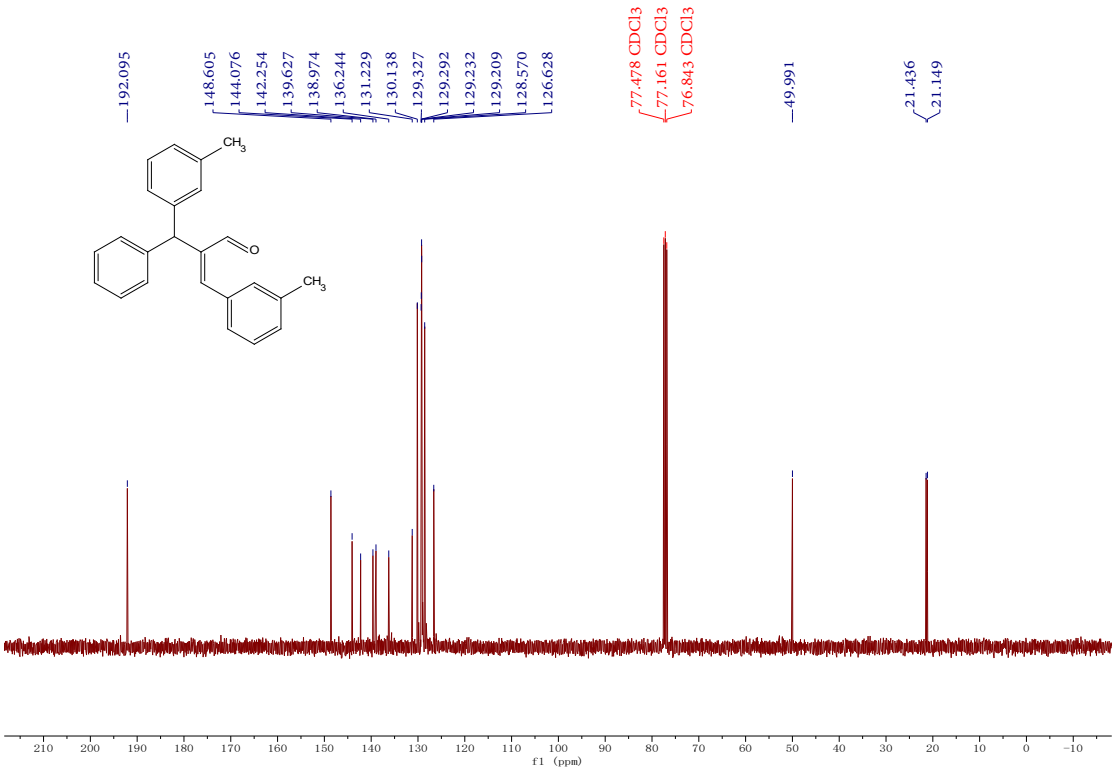
^{1}H NMR and ^{13}C NMR spectra of 3i



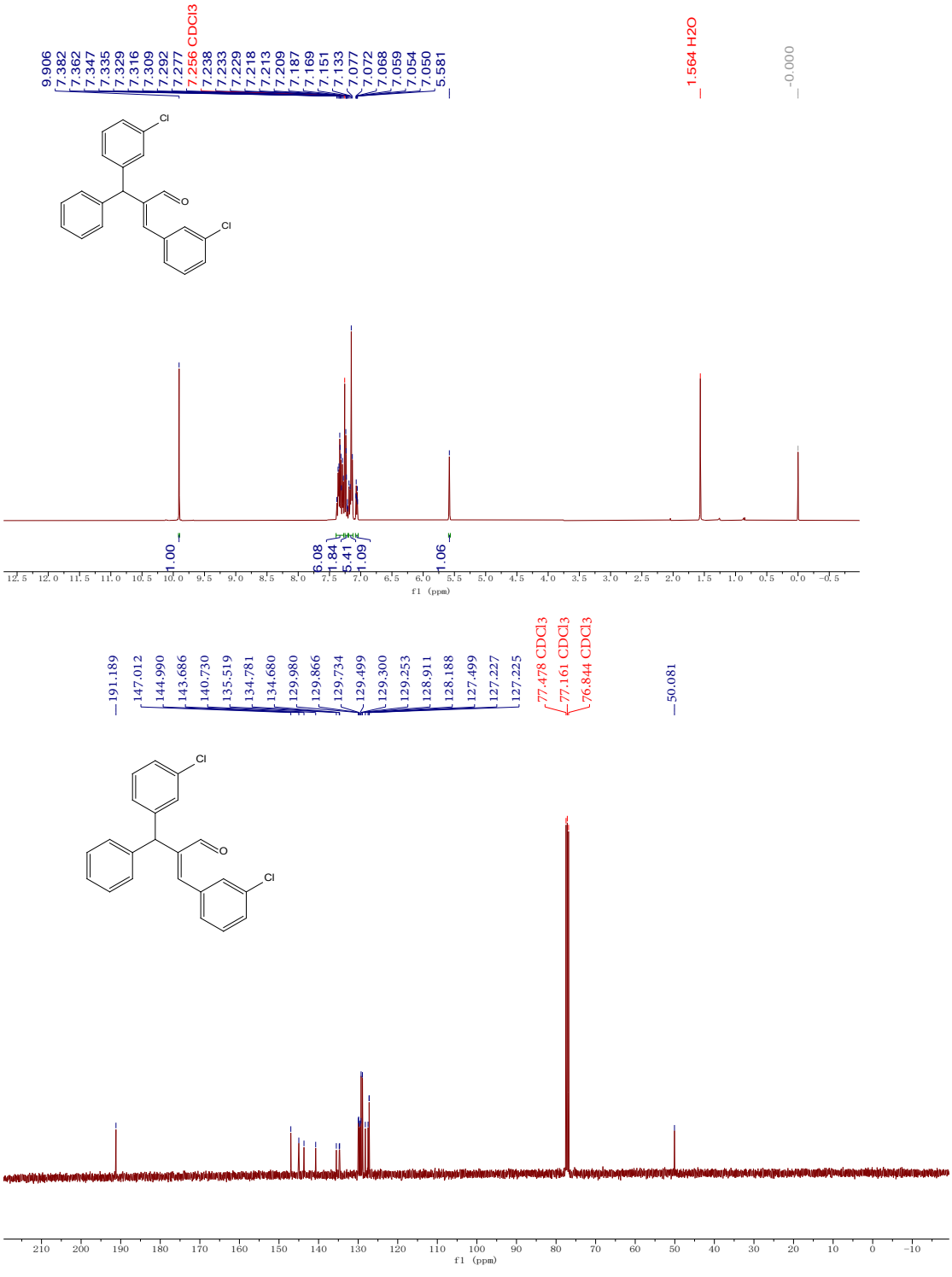


^{1}H NMR and ^{13}C NMR spectra of 3j

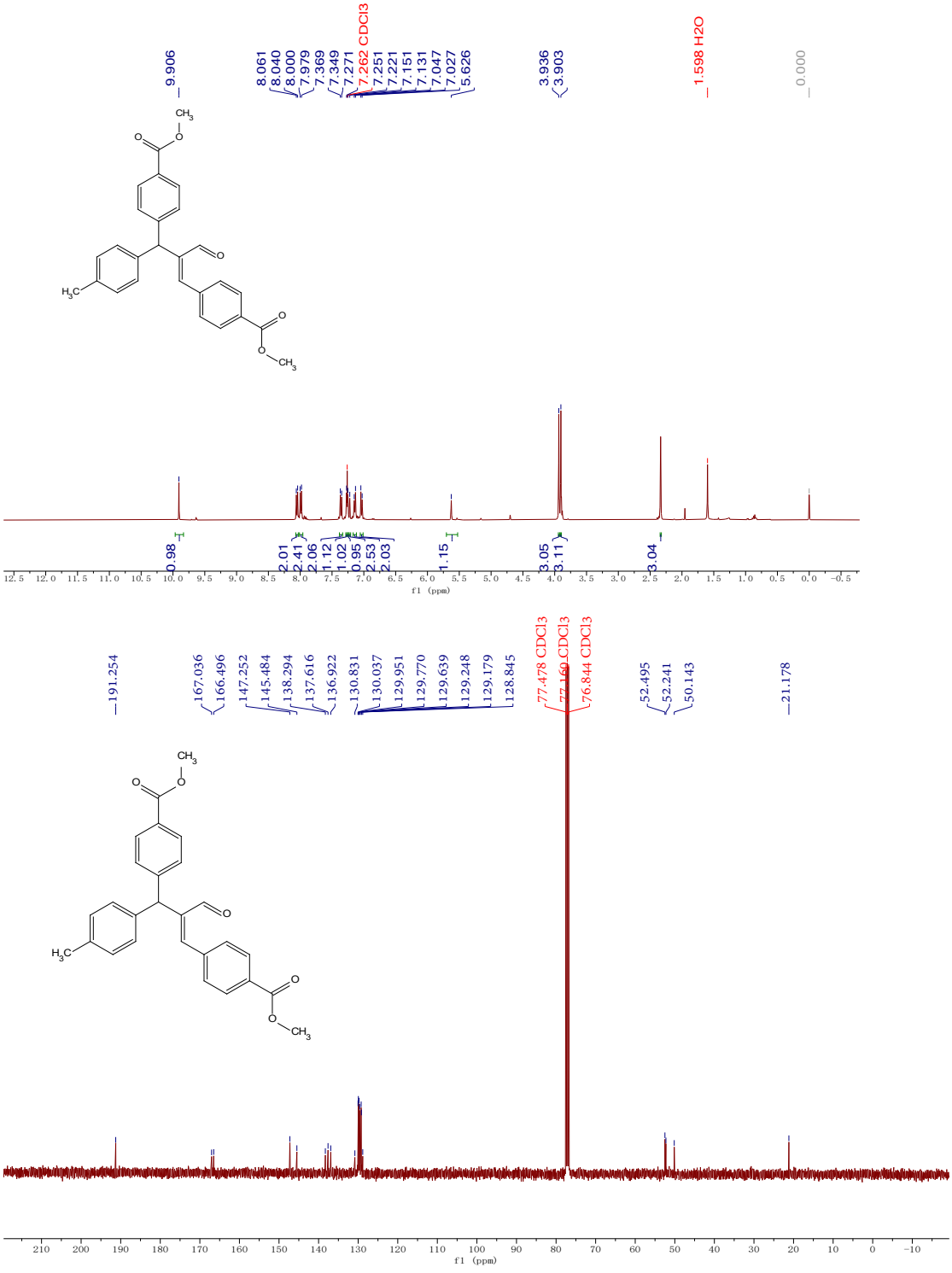




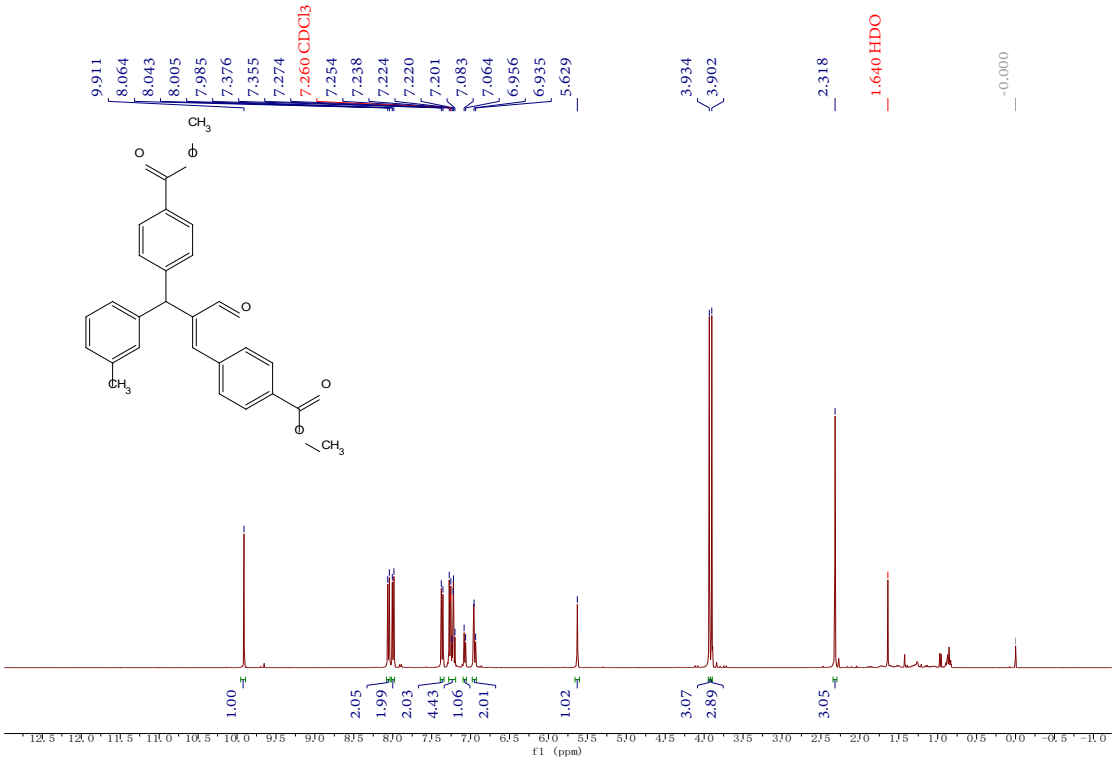
^{1}H NMR and ^{13}C NMR spectra of 3k

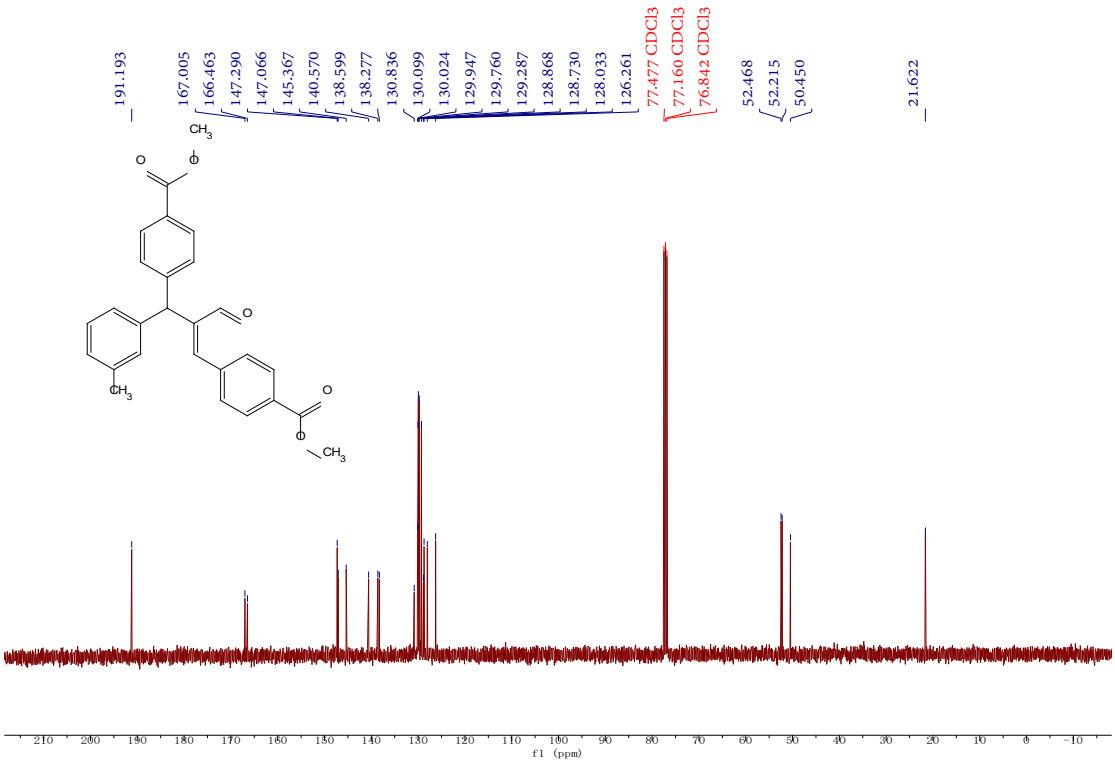


^{1}H NMR and ^{13}C NMR spectra of 4a

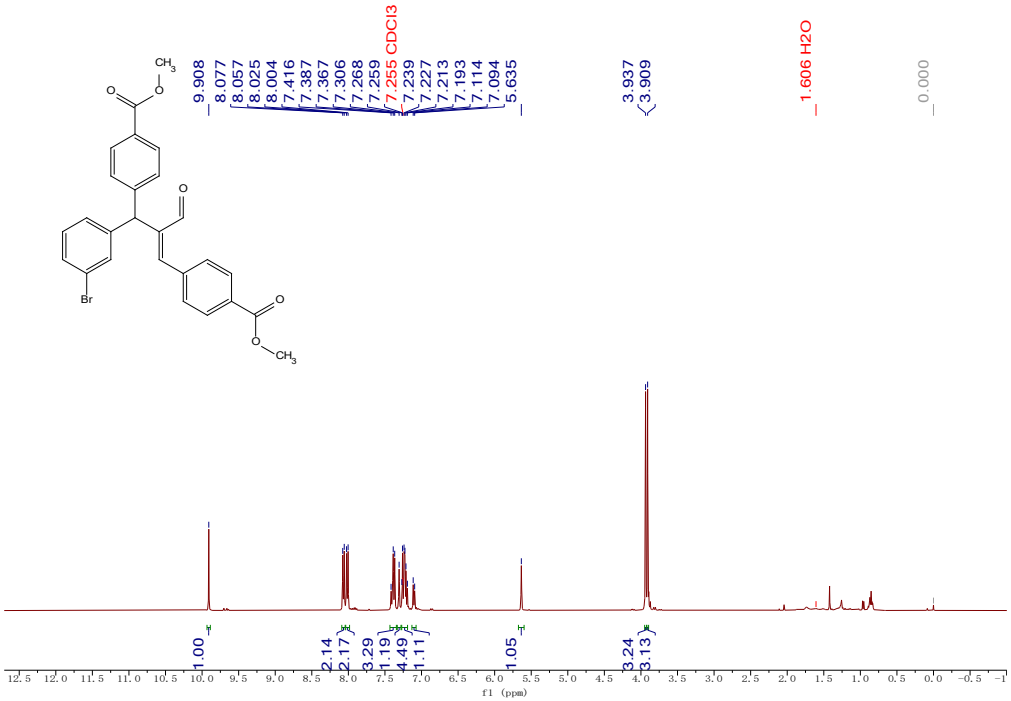


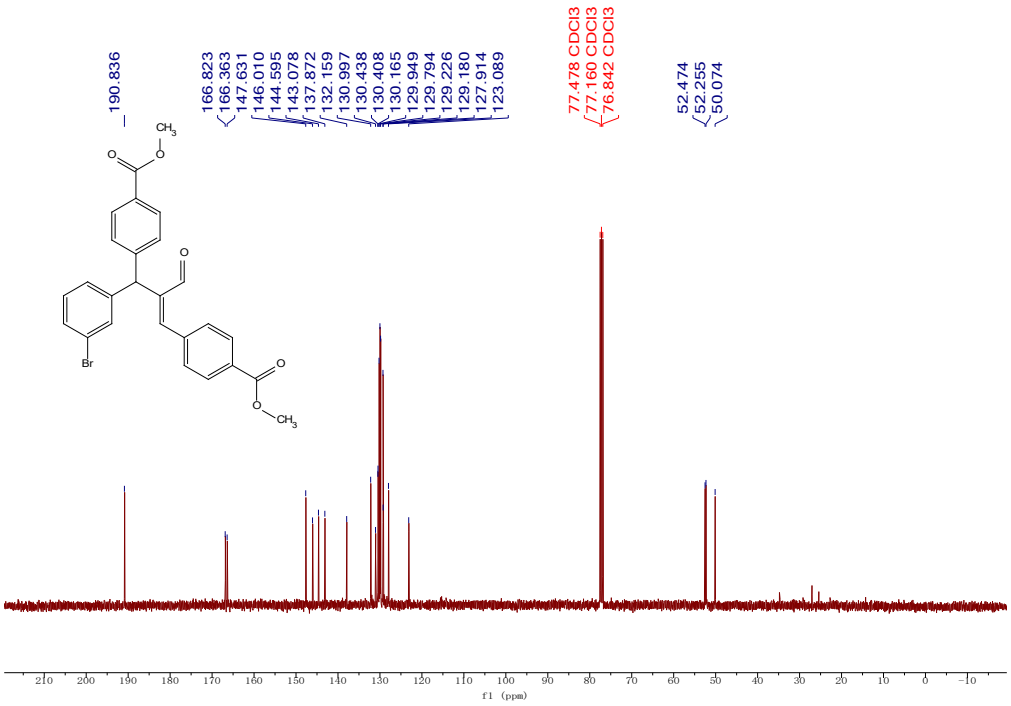
^{1}H NMR and ^{13}C NMR spectra of 4b



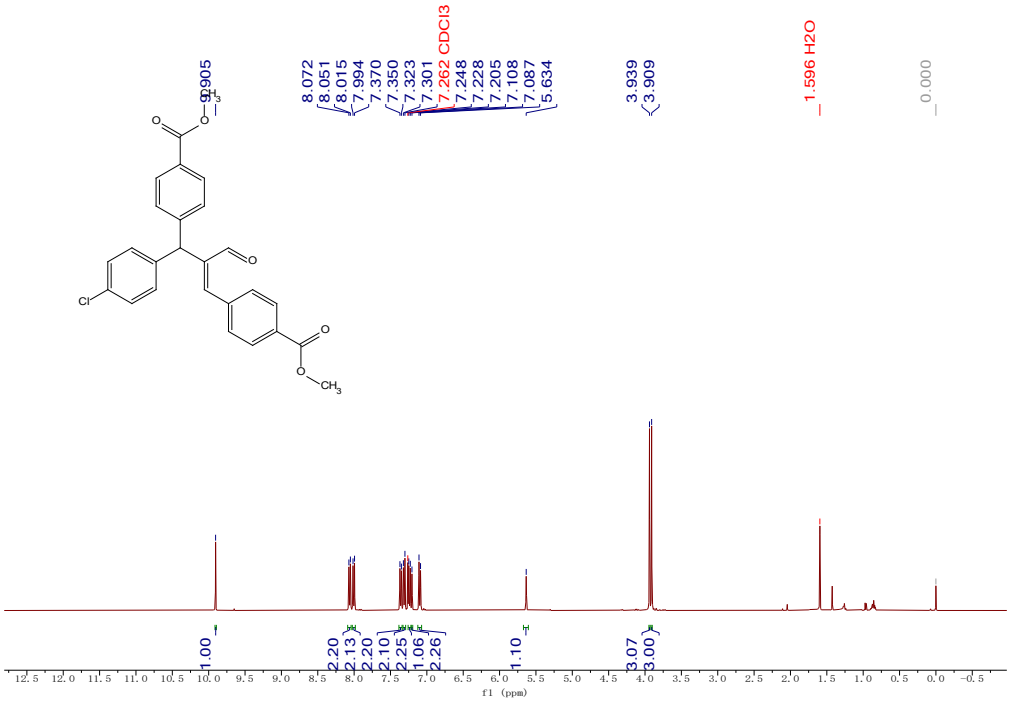


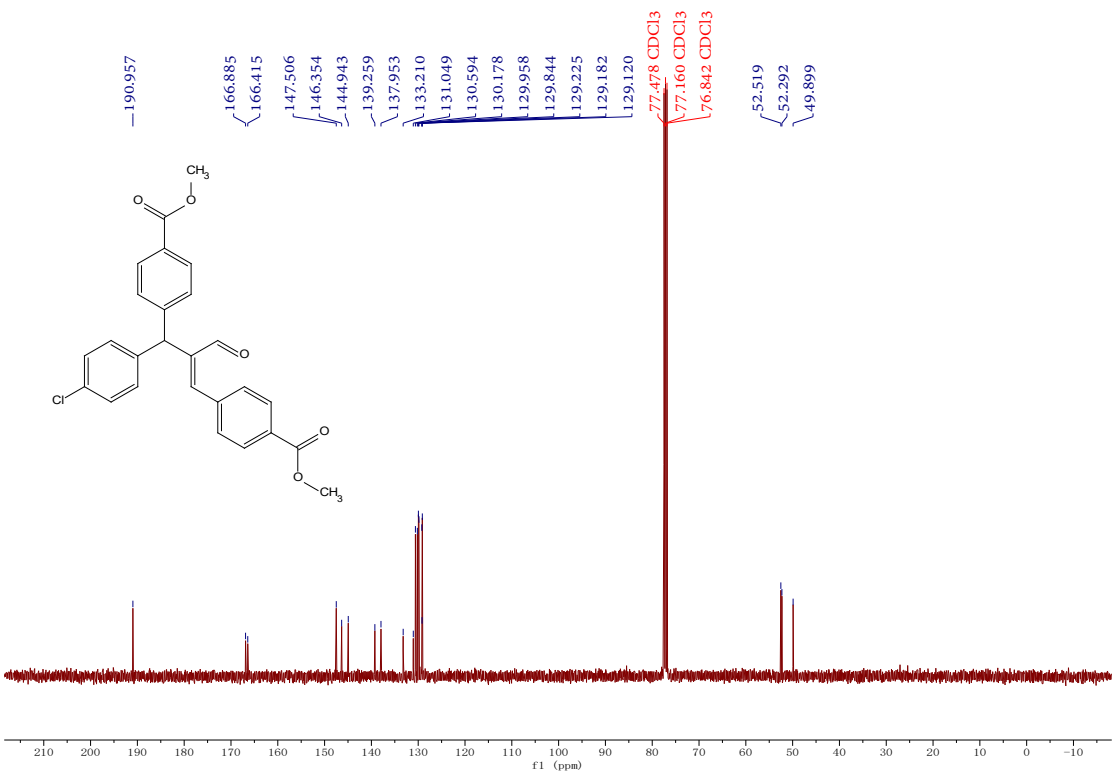
^{1}H NMR and ^{13}C NMR spectra of 4c



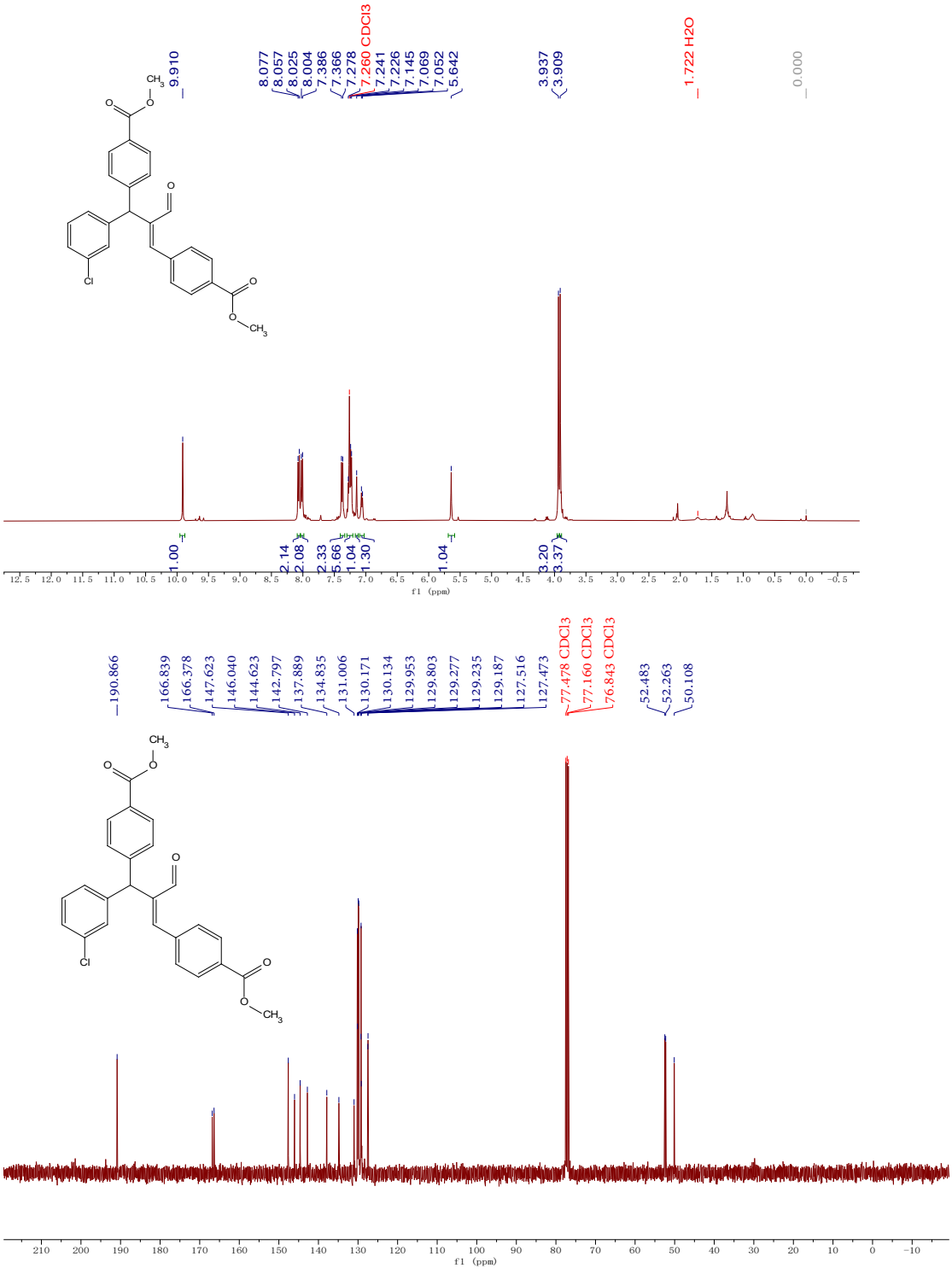


^{1}H NMR and ^{13}C NMR spectra of 4d

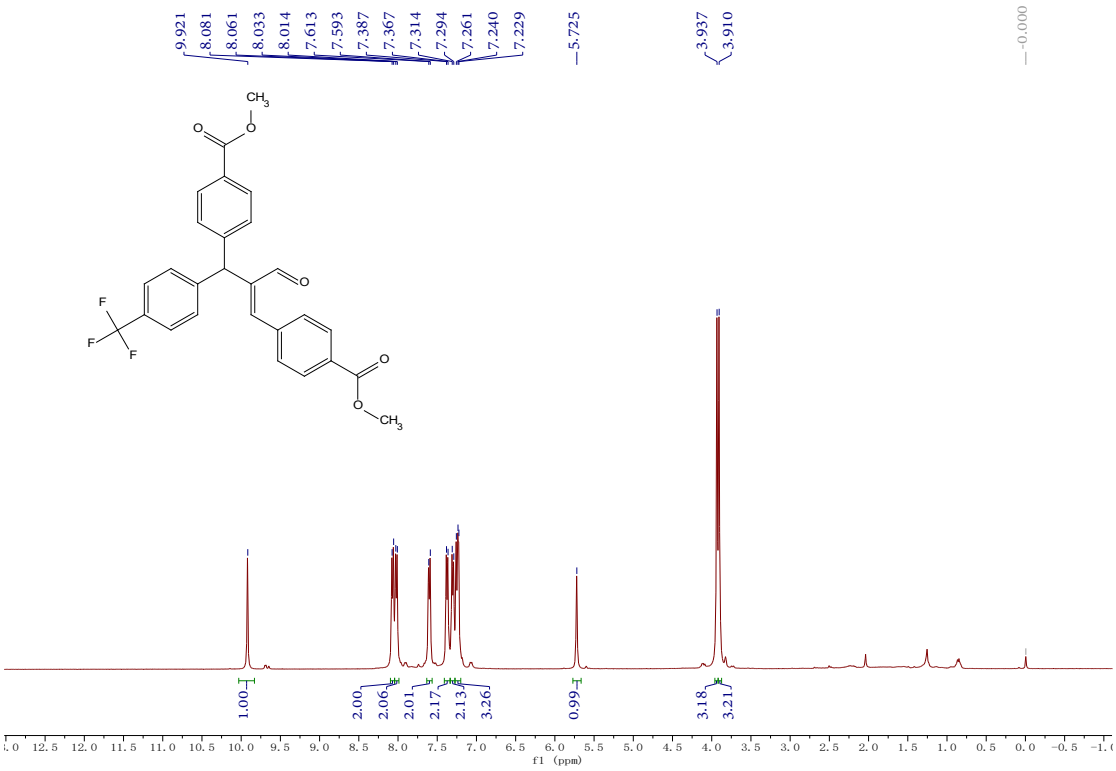


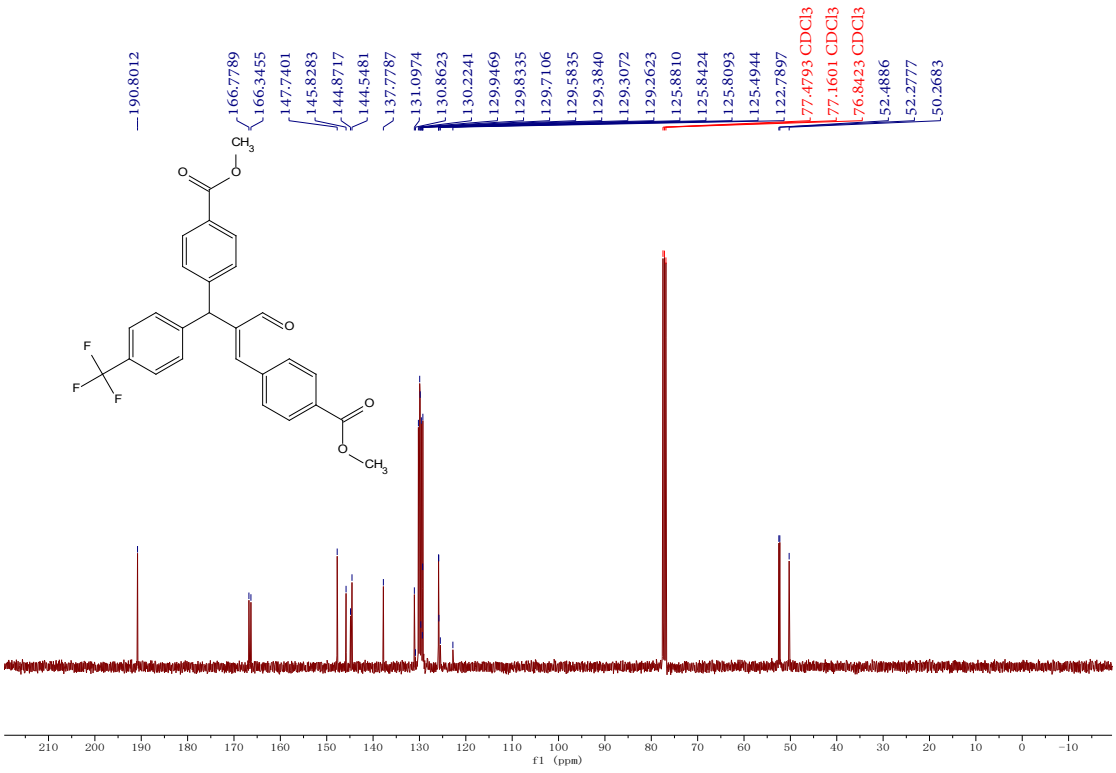


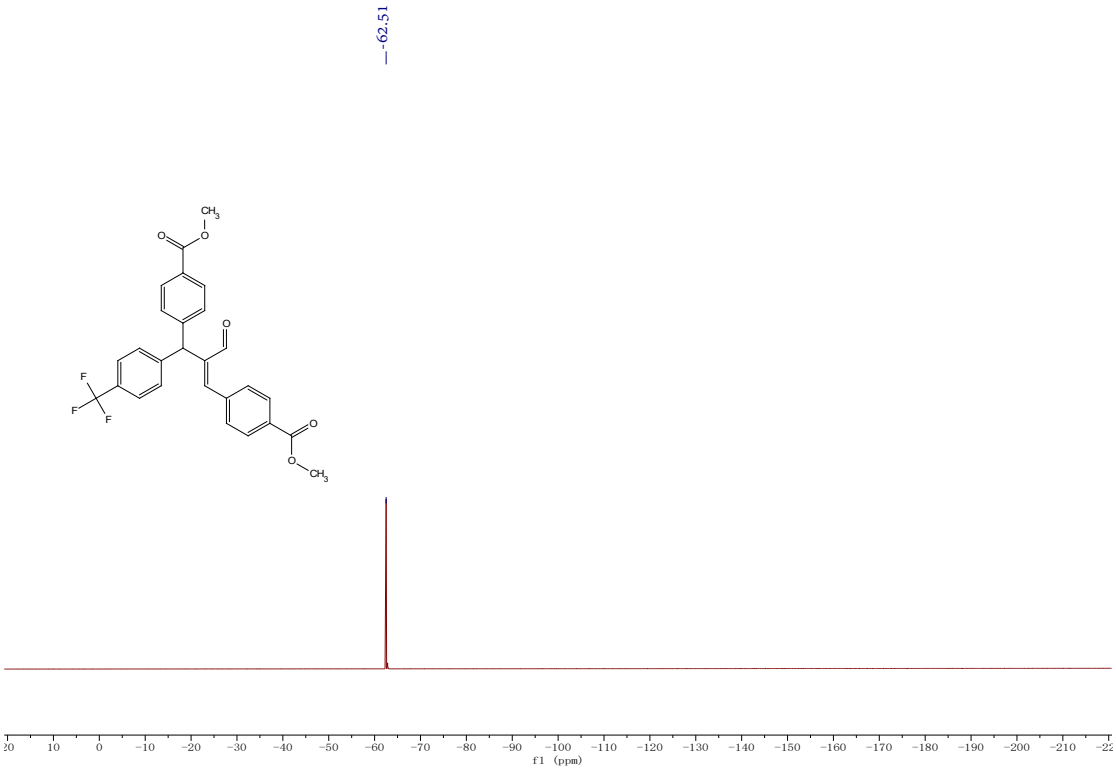
^{1}H NMR and ^{13}C NMR spectra of 4e



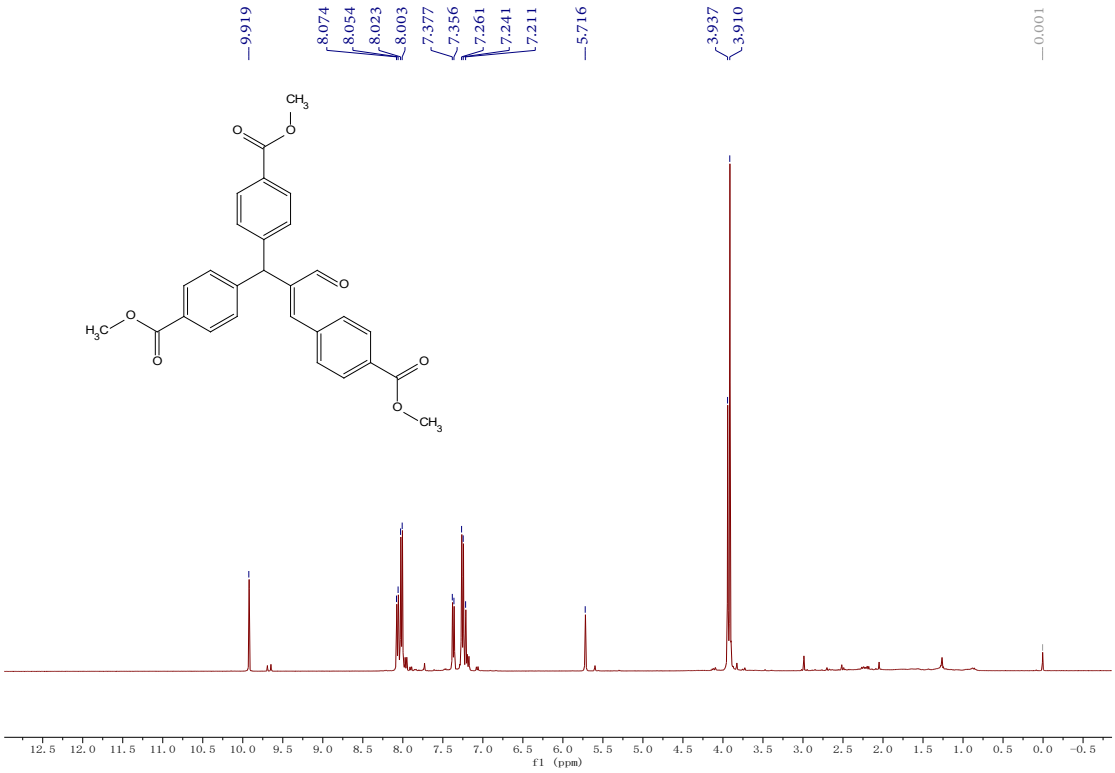
^{1}H NMR ,^{13}C NMR and ^{19}F spectra of 4f

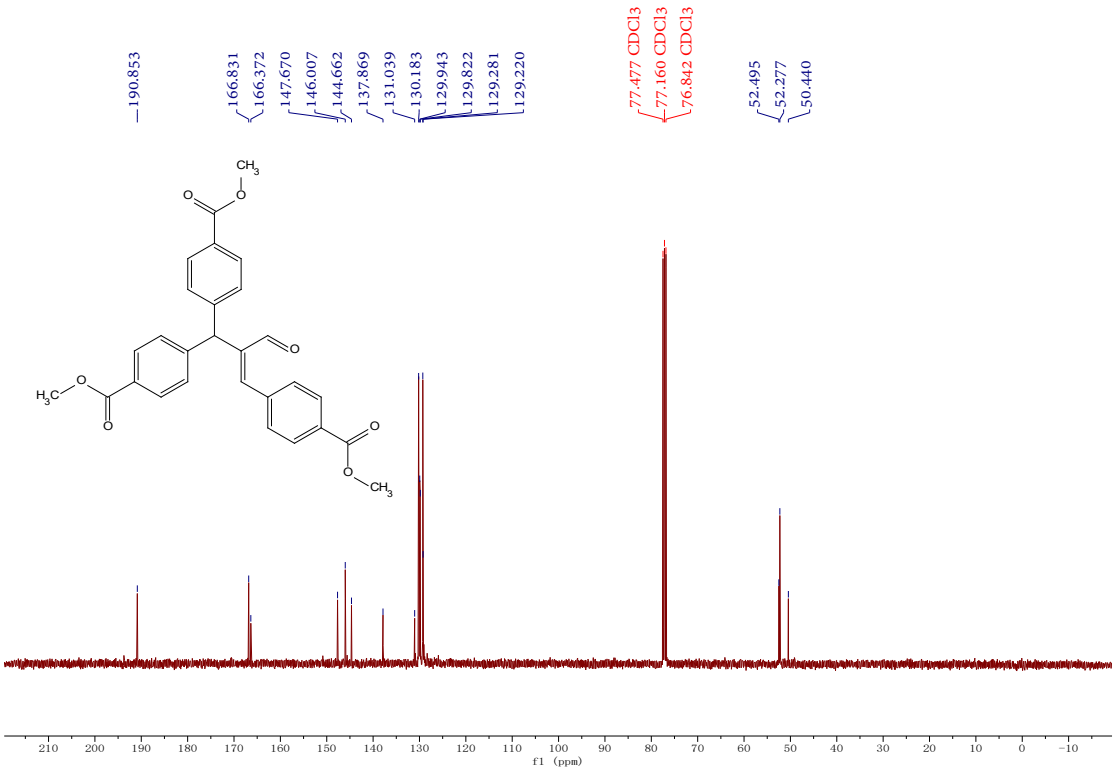




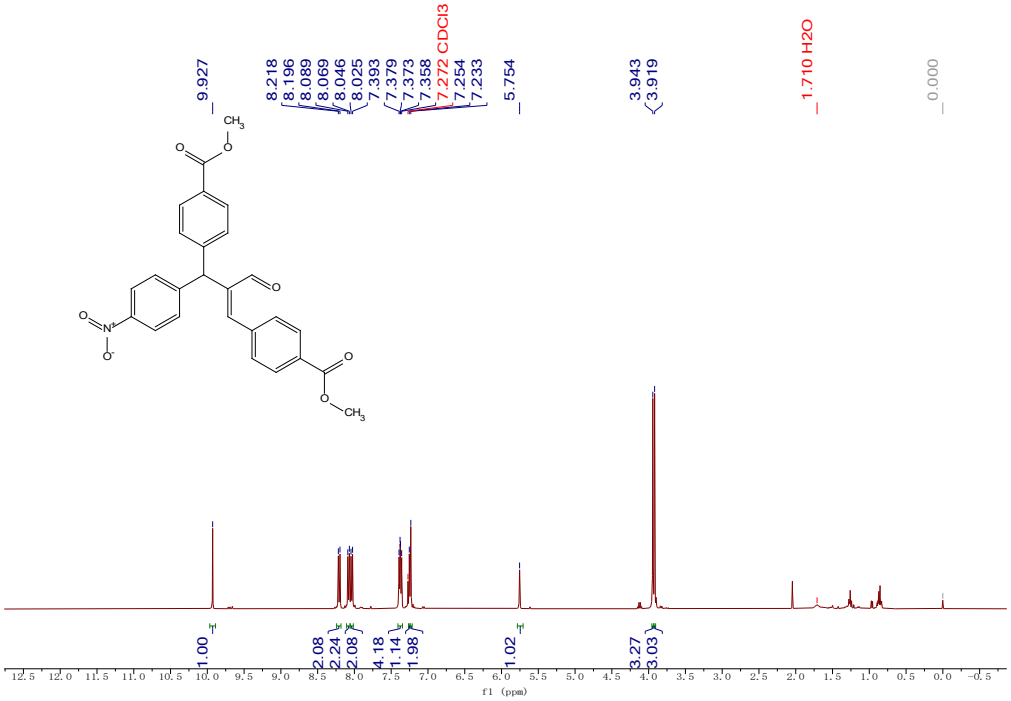

-62.51
CH3
O
O
O
F
F
F
O
O
CH3
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

^{1}H NMR and ^{13}C NMR spectra of 4g



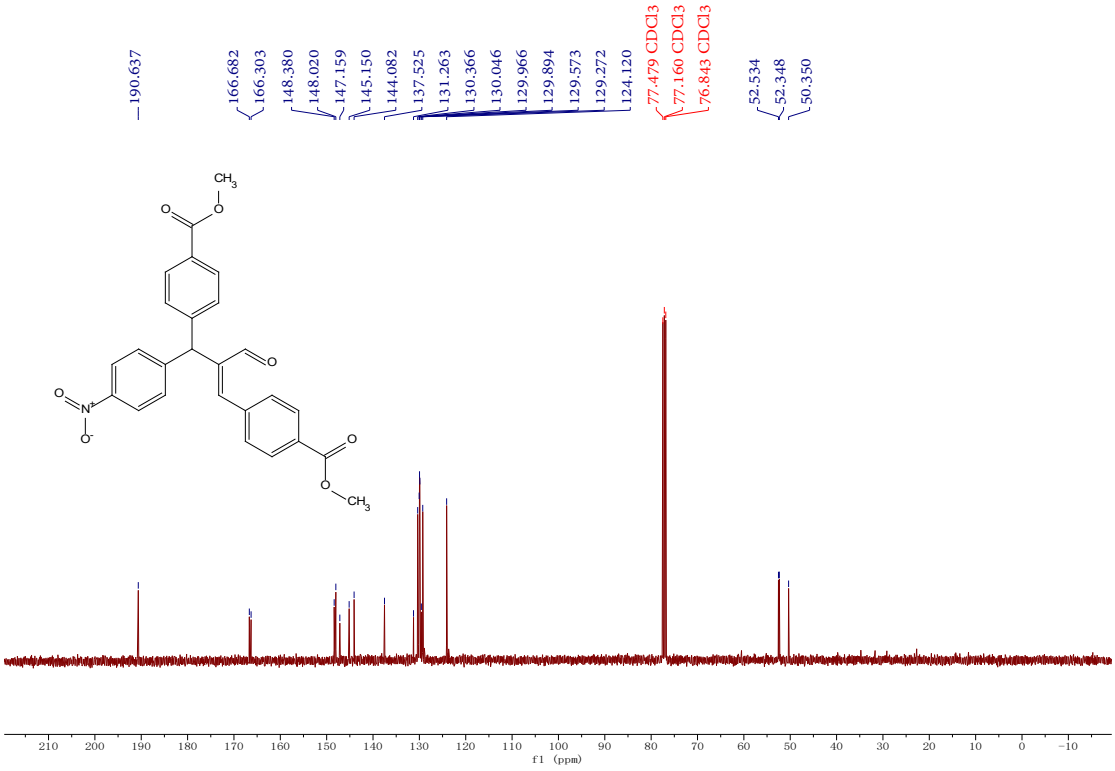


^{1}H NMR and ^{13}C NMR spectra of 4h

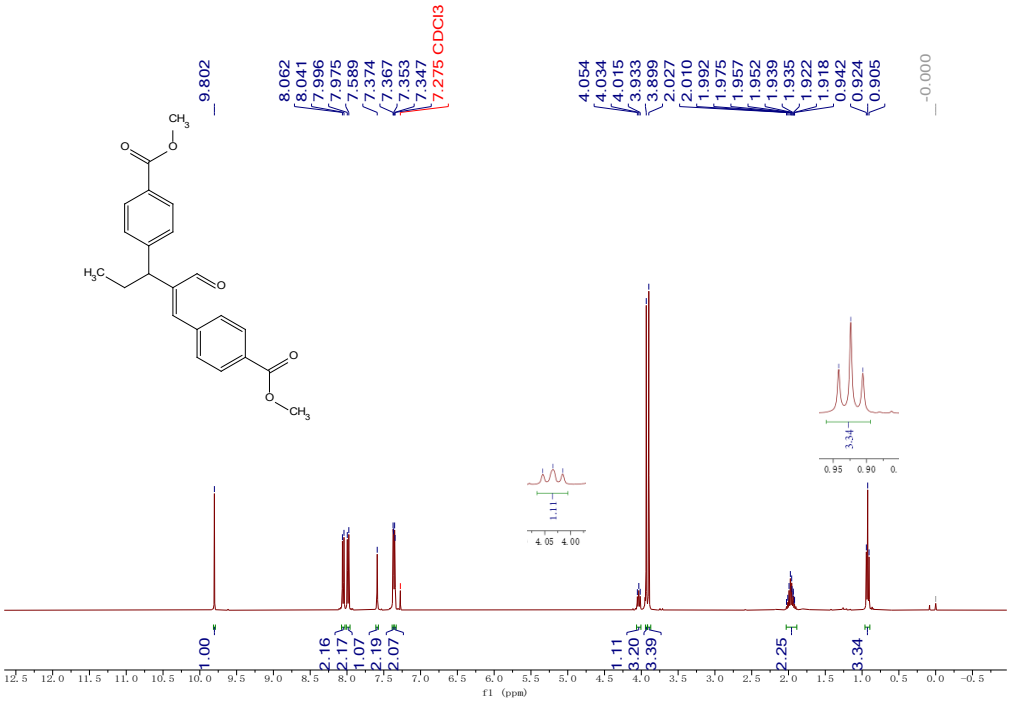


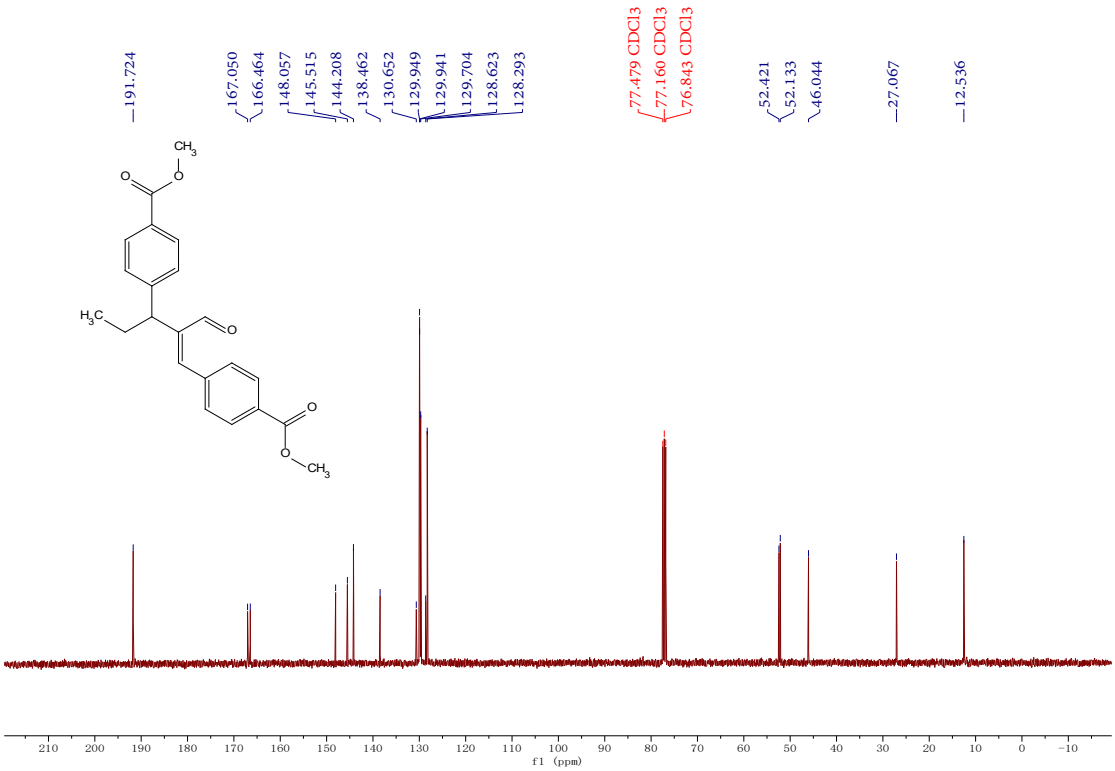
.....

.....

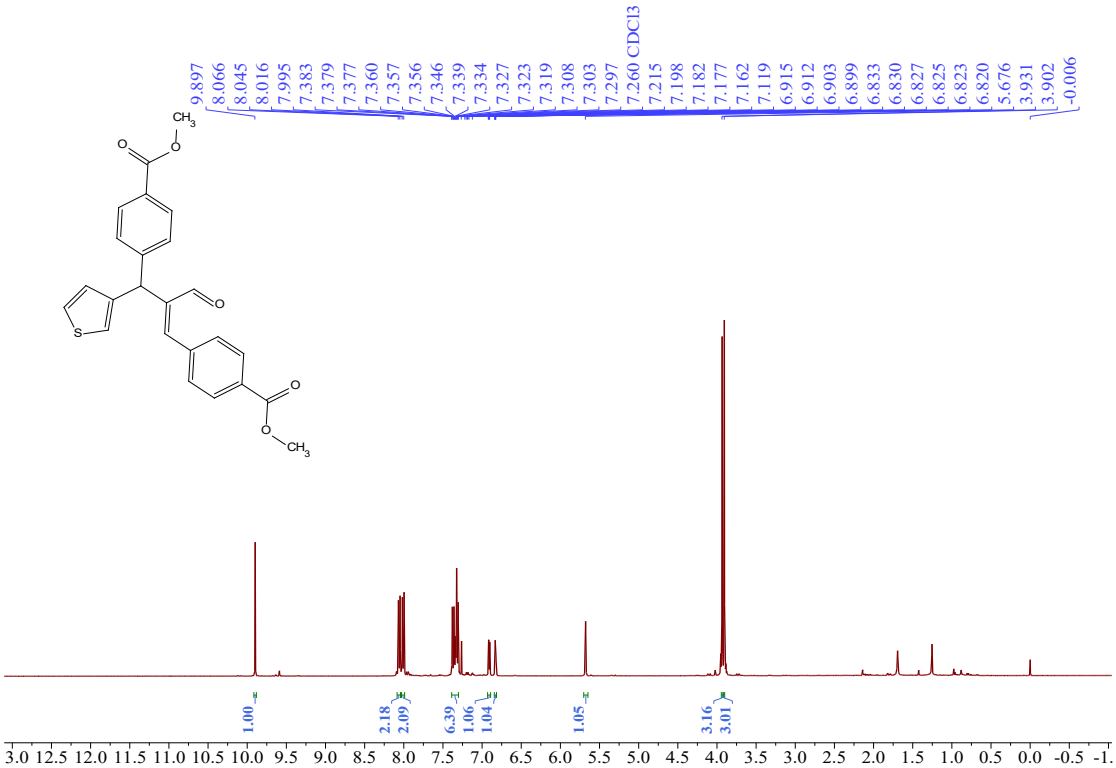


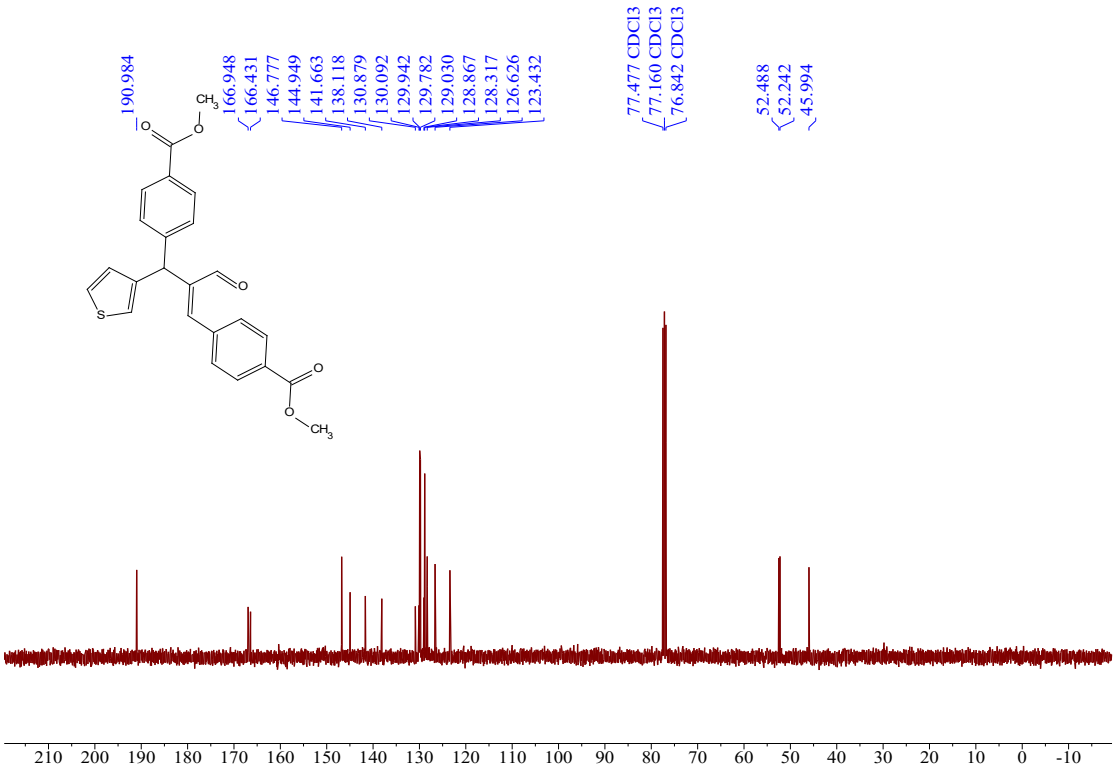
^{1}H NMR and ^{13}C NMR spectra of 4i



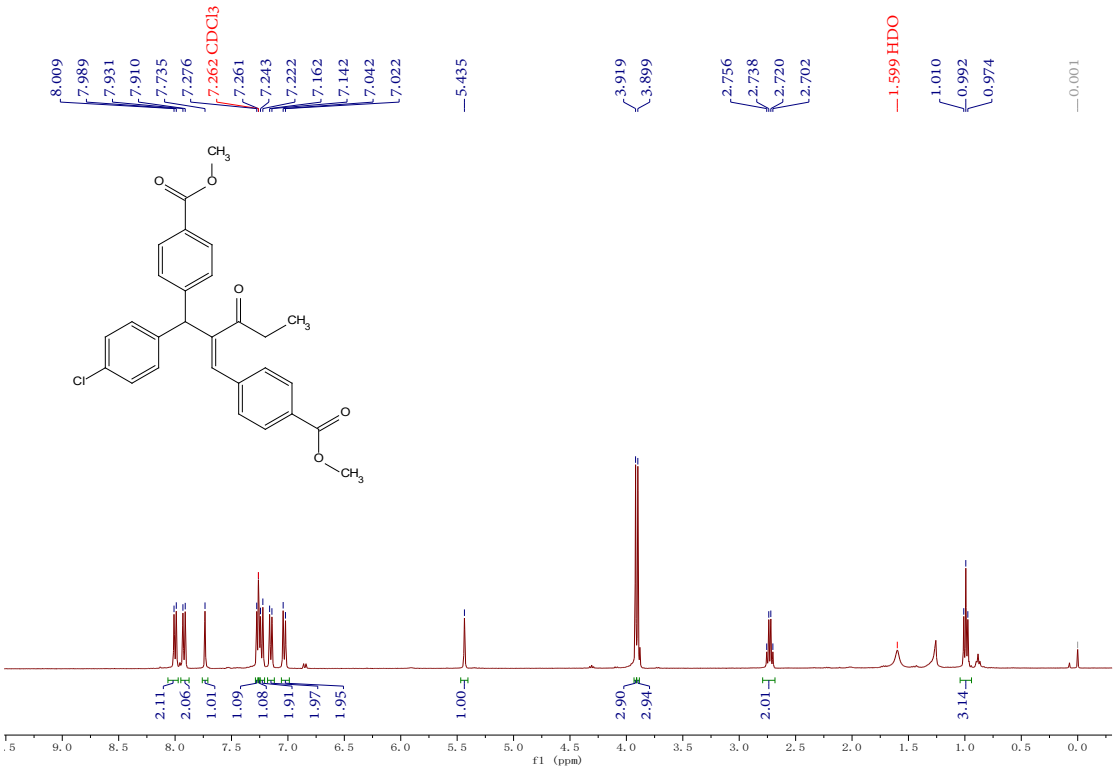


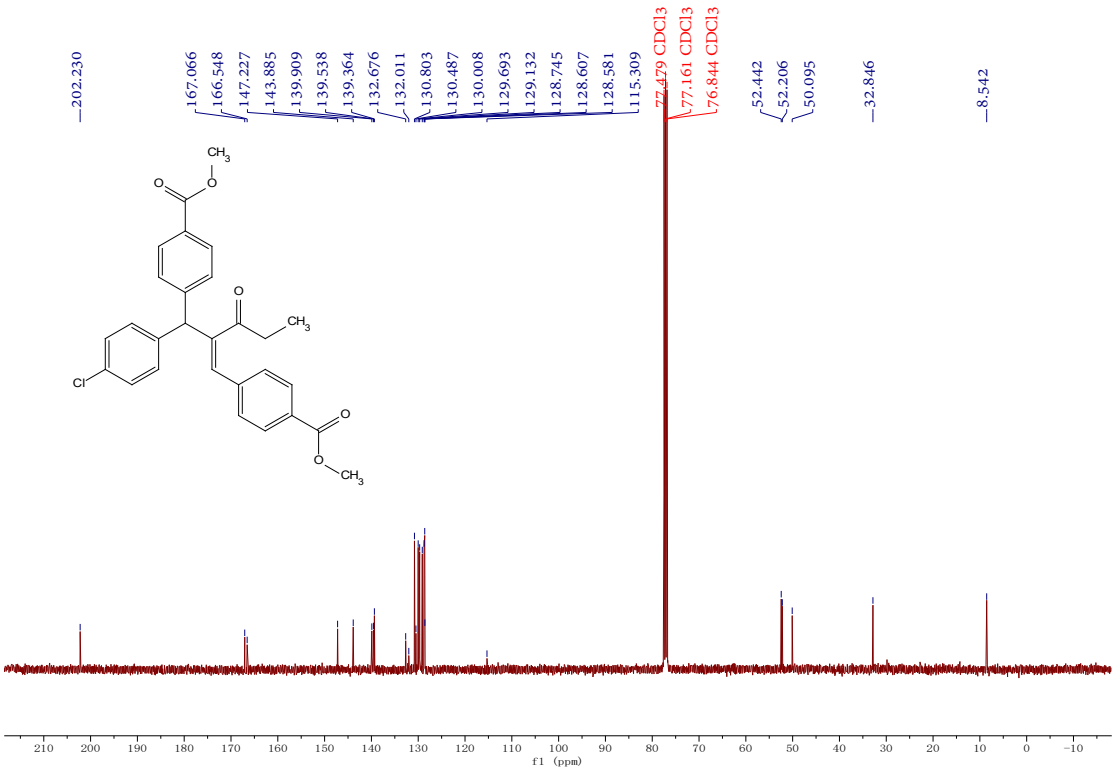
^{1}H NMR and ^{13}C NMR spectra of 4j



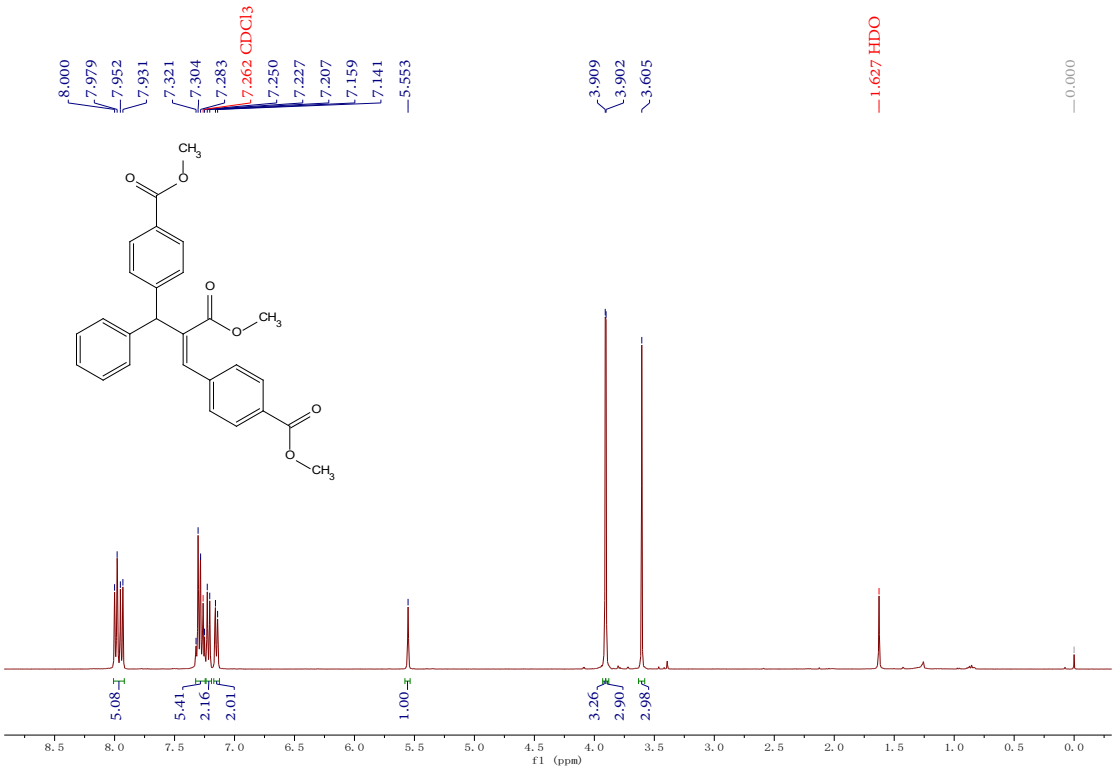


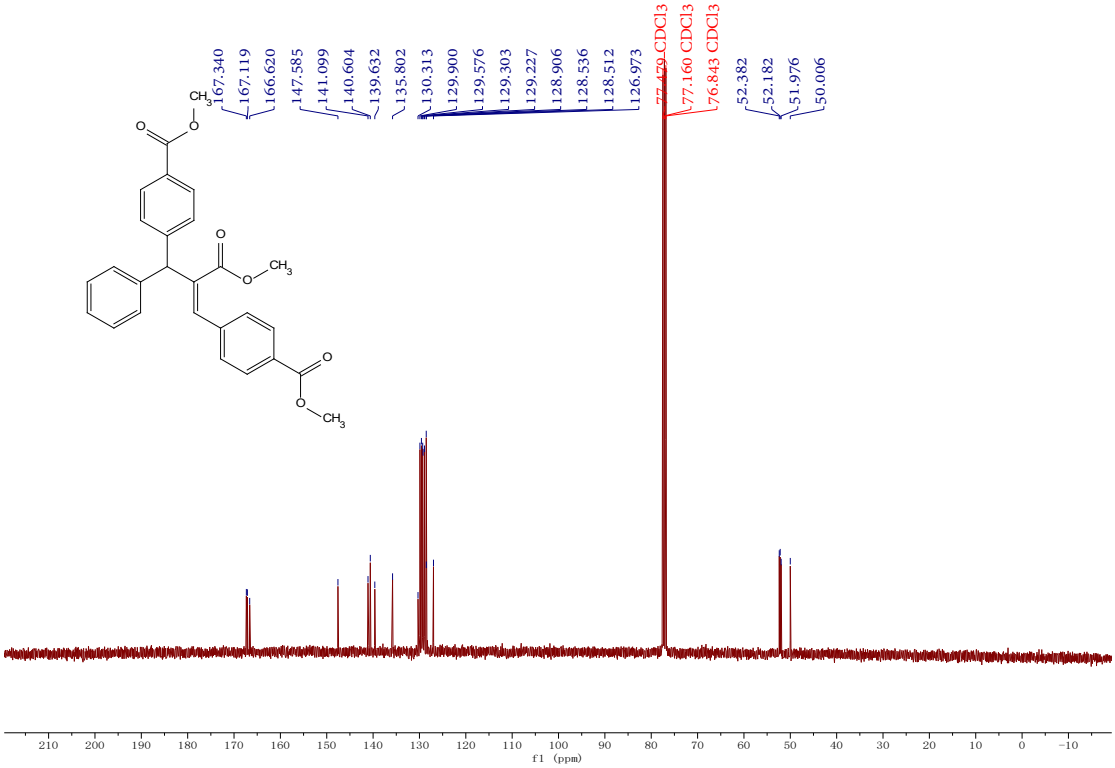
^{1}H NMR and ^{13}C NMR spectra of 4k



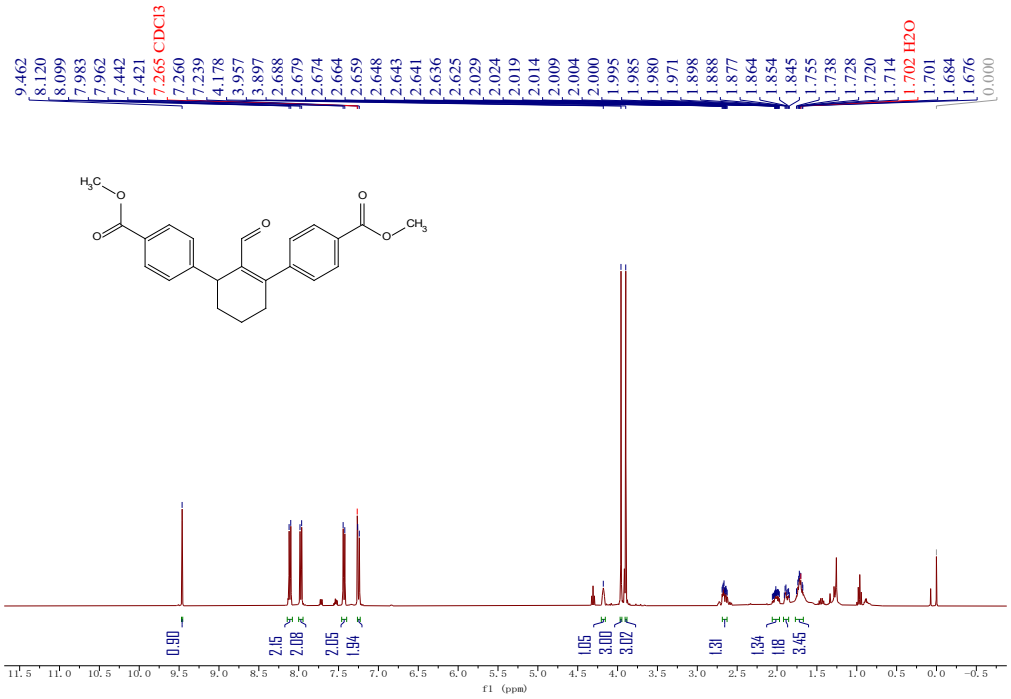


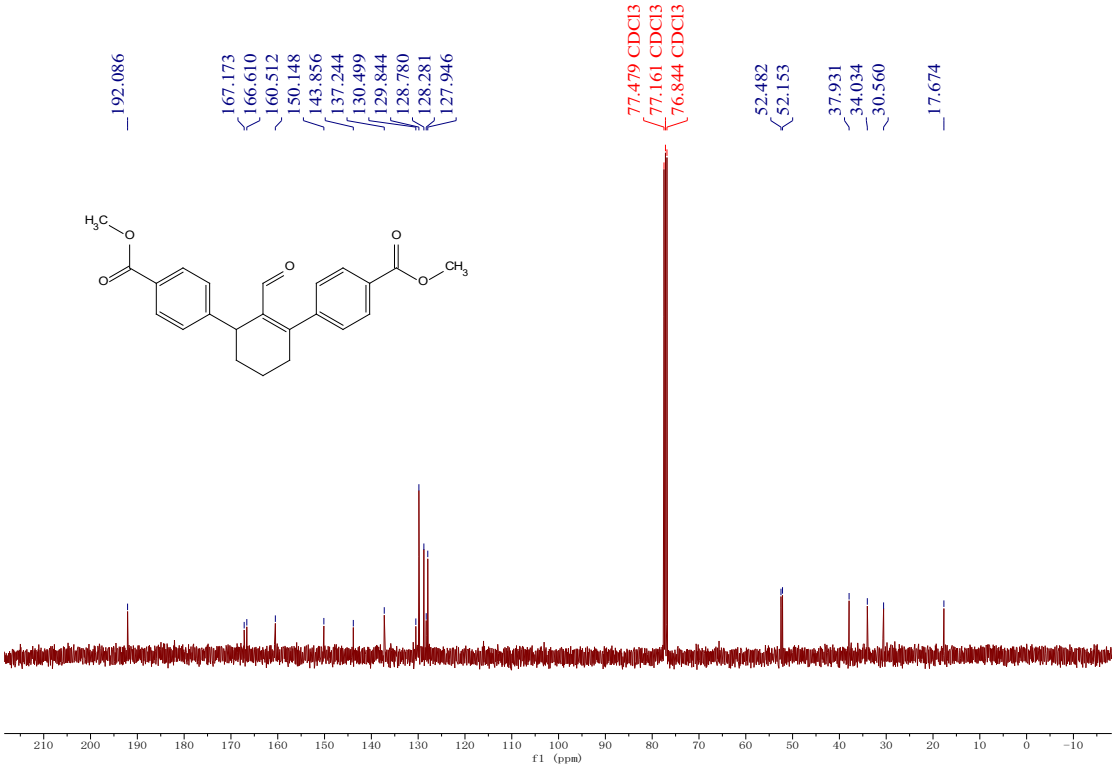
^{1}H NMR and ^{13}C NMR spectra of 4l



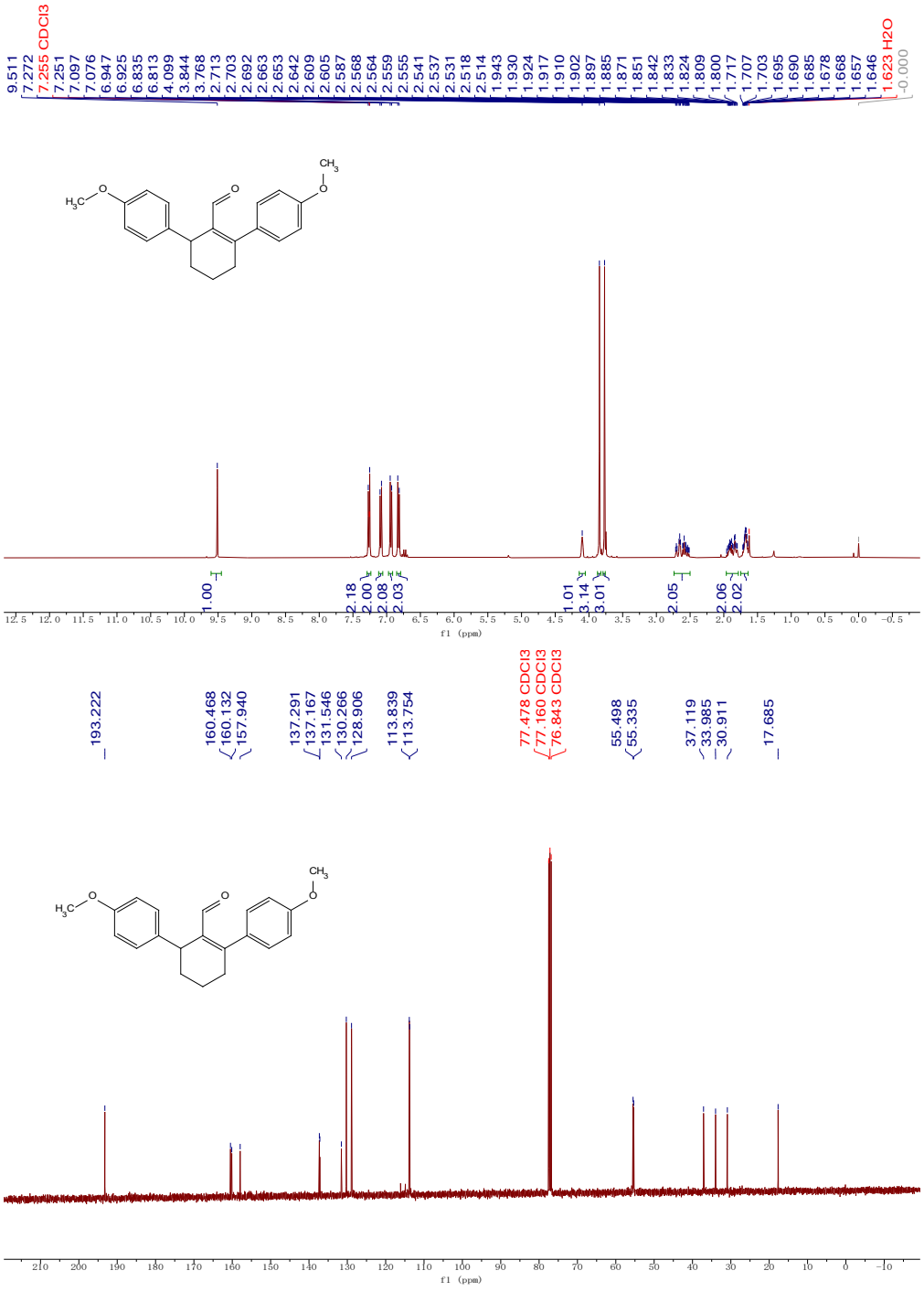


^{1}H NMR and ^{13}C NMR spectra of 6a

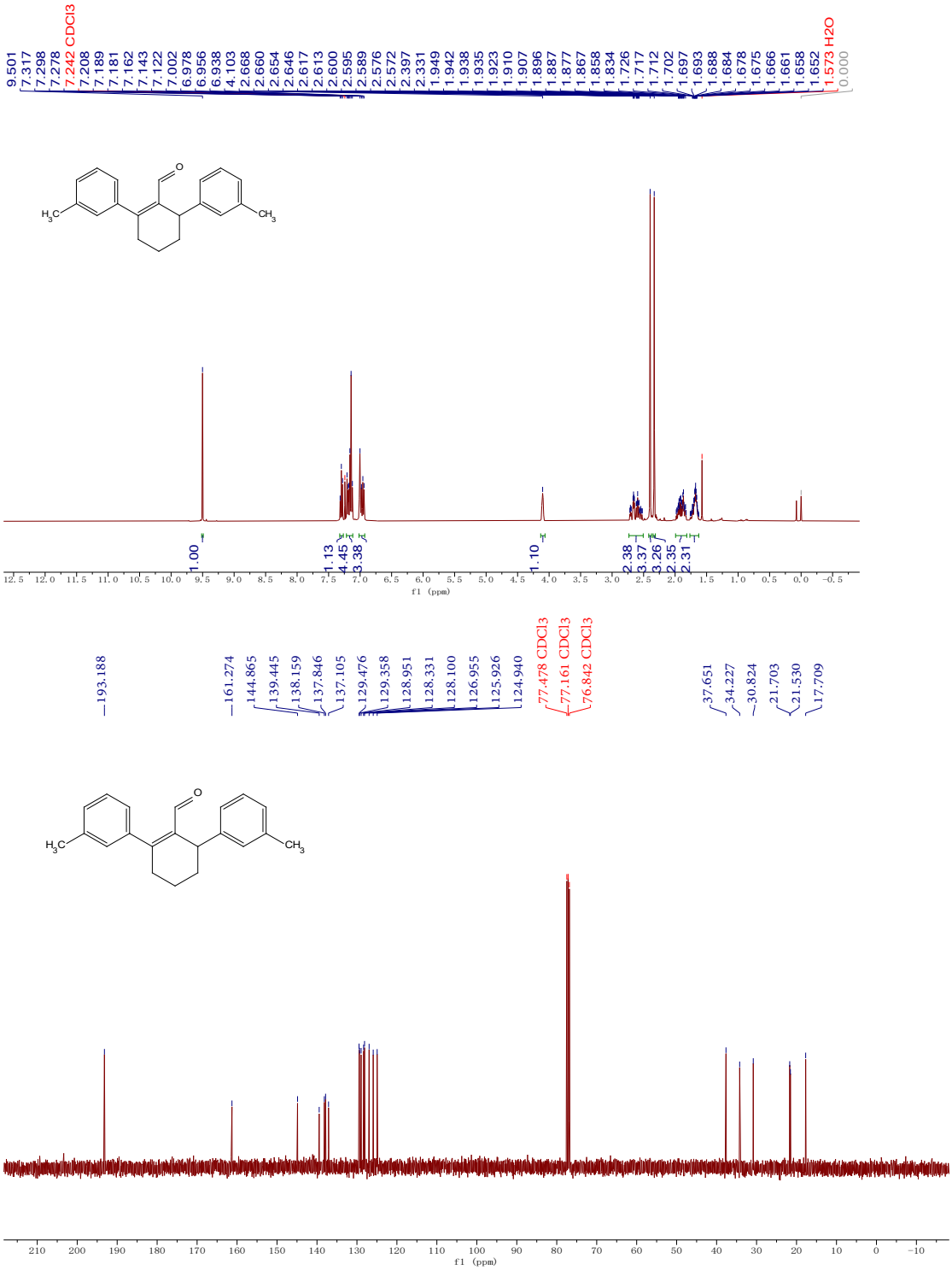




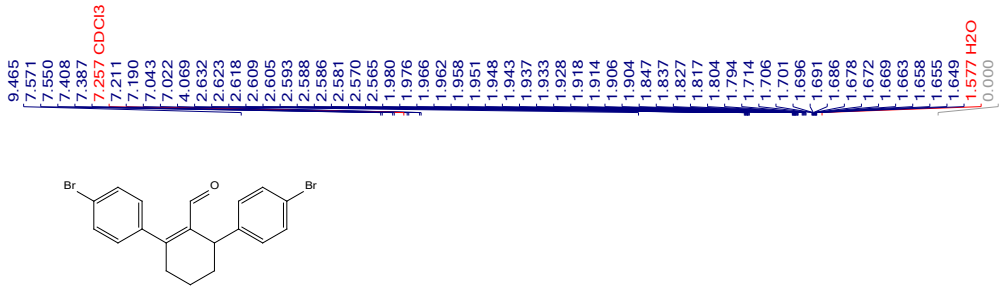
^{1}H NMR and ^{13}C NMR spectra of 6b

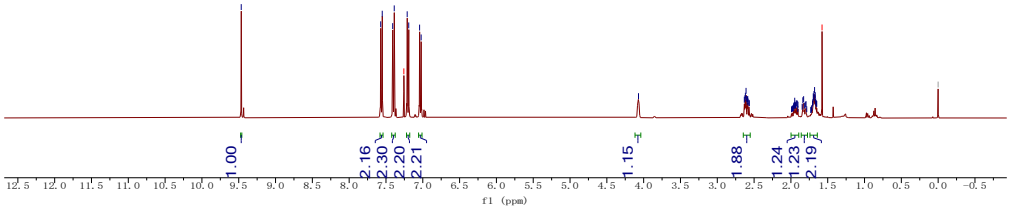


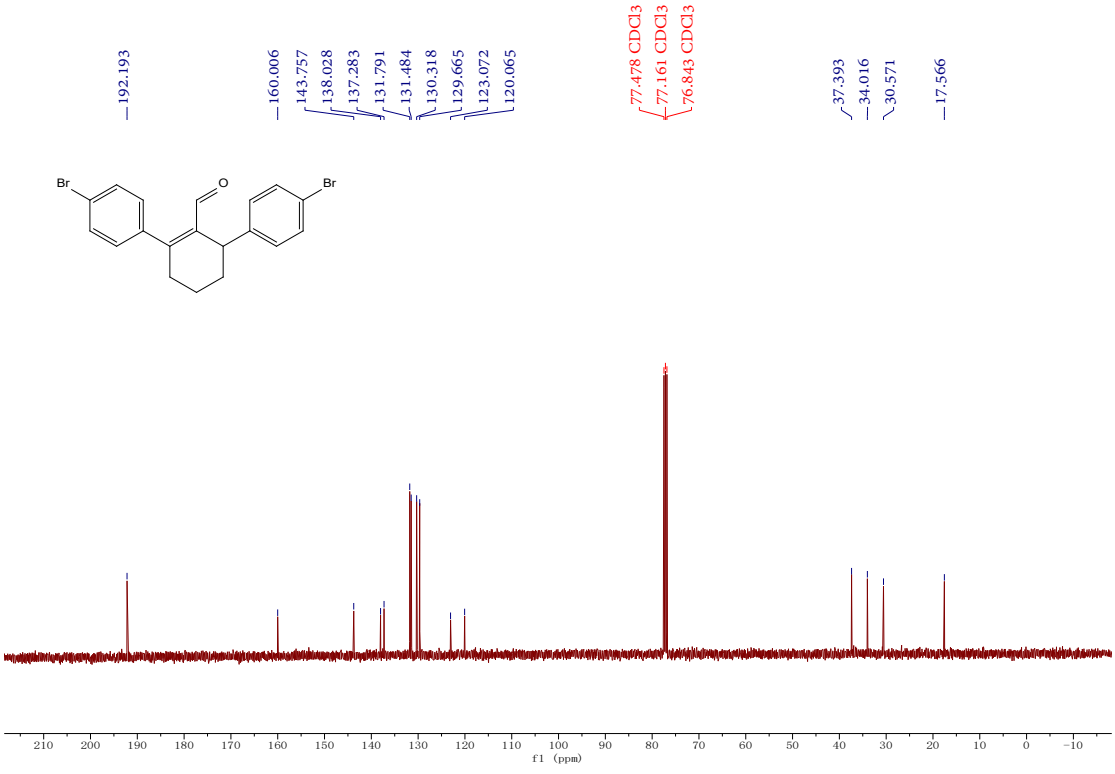
^{1}H NMR and ^{13}C NMR spectra of 6c



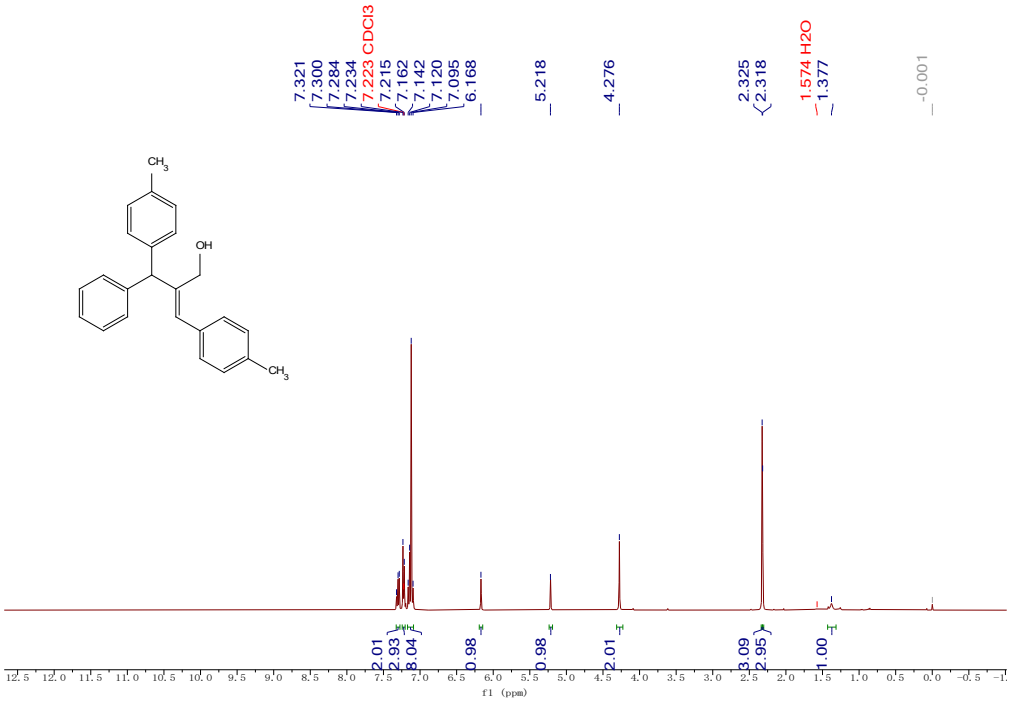
^{1}H NMR and ^{13}C NMR spectra of 6d

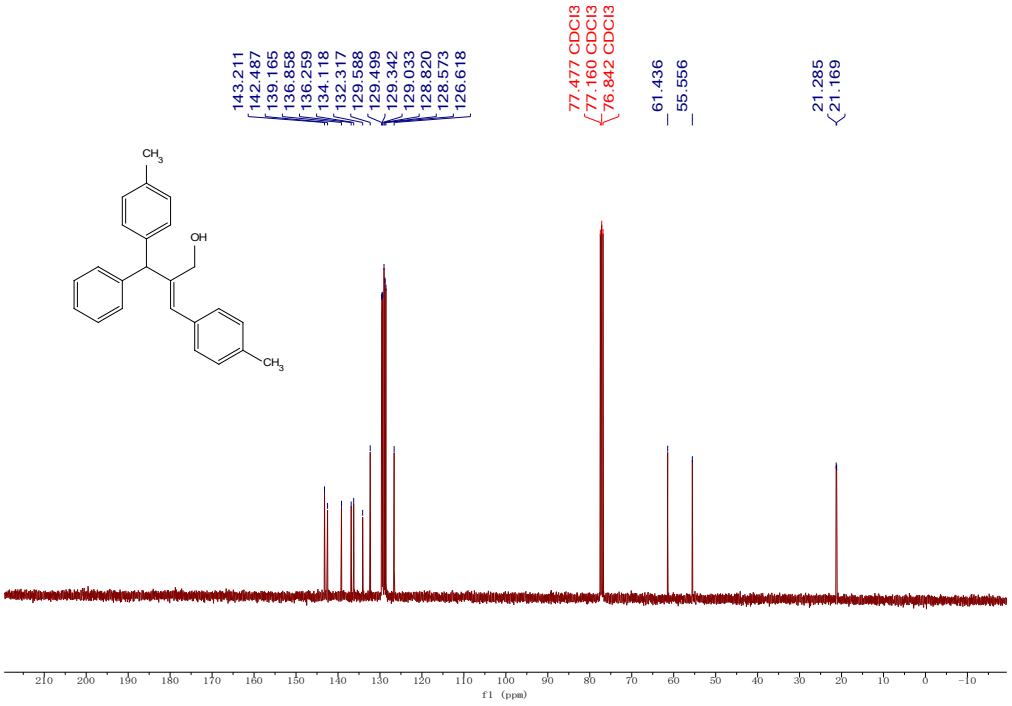






^{1}H NMR and ^{13}C NMR spectra of 7





^{1}H NMR and ^{13}C NMR spectra of 8