Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Indium Controlled Regioselective 1,4-Alkylarylation of 1,3-Dienes with *α*-Carbonyl Alkyl Bromides and *N*-Heterocycles

Chang-Cheng Gu[†], Xuan-Hui Ouyang[†], Ren-Jie Song[*,†], and Jin-Heng Li[*,†,‡,§]

[†]Key Laboratory of Jiangxi Province for Persistent Pollutants Control and Resources Recycle, Nanchang Hangkong University, Nanchang 330063, China

‡State Key Laboratory of Chemo/Biosensing and Chemometrics, Hunan University, Changsha 410082, China

[§]State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China

E-mail: srj0731@hnu.edu.cn and jhli@hnu.edu.cn

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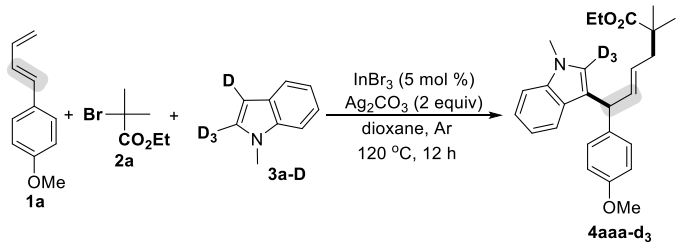
(A) Typical experimental procedure

(a) Typical Experimental Procedure for the Indium Controlled Regioselectivity: 1,4-Alkylarylation of 1,3-Dienes with α-Carbonyl Alkyl Bromides and *N*-Heterocycles:

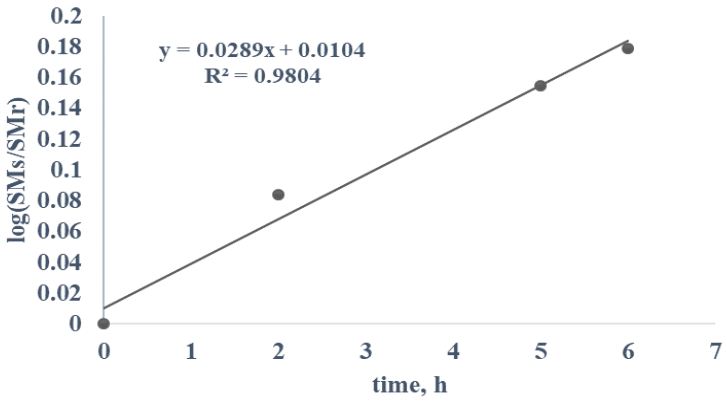
To a Schlenk tube were added substrates **1a** (0.2 mmol), **2a** (2 equiv), **3a** (2 equiv), $InBr_3$ (5%), Ag_2CO_3 (2 equiv), and dioxane (1 mL), the tube was then charged with argon. The mixture was stirred at 120 ℃ until complete consumption of starting material as monitored by TLC and/or GC-MS analysis (about 5 h). After the reaction was finished, the reaction mixture was concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired product **4aaa** and **5aaa**.

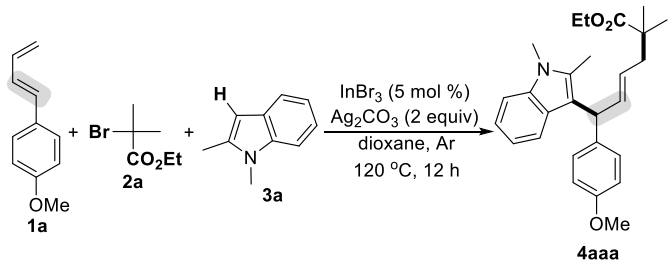
(b) Scheme S1. The kinetic isotope effect (KIE) experiments



1-methyl-2-(methyl-d_3)-1*H*-indole-3-*d*

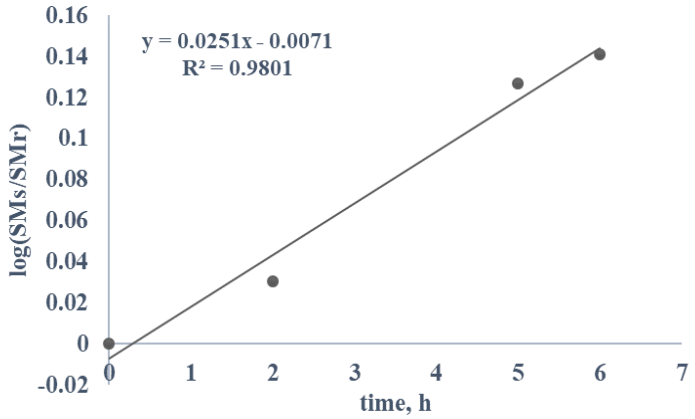
t, hour	SMs	SMr	log(SMs/SMr)
0	0	0	0
2	0.379	0.312	0.084
4	0.379	0.265	0.155
6	0.406	0.269	0.179





1,2-dimethyl-1*H*-indole

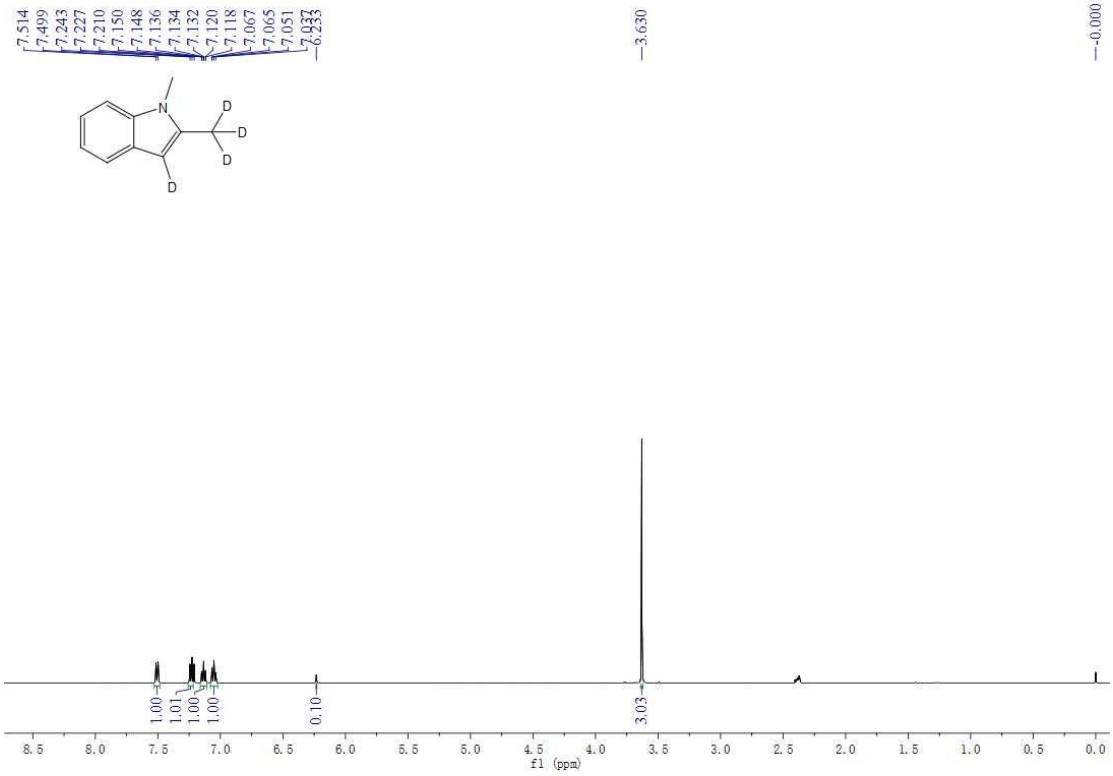
t, hour	SMs	SMr	log(SMs/SMr)
0	0	0	0
2	0.414	0.386	0.03
4	0.414	0.309	0.127
6	0.414	0.299	0.141



Scheme S1. The kinetic isotope effect (KIE) experiments.

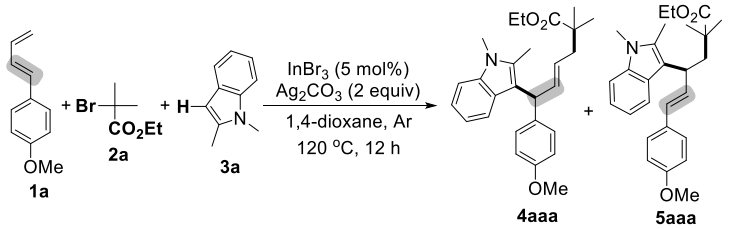
Calculation: k_H/k_D = 0.0251/0.0289 = 0.87

1-methyl-2-(methyl-*d*$_3$)-1*H*-indole-3-*d* (3a-D)



(B) Control experiments and mechanistic insights

Table S1. Control experiments[a]



Entry	Variation from the Standard Conditions	Isolated yield(%)		**4aaa:5aaa**
		4aaa	**5aaa**	
1	none	86	3	>20:1
2	without $InBr_3$	32	11	3:1
3	$InBr_3$ (2 mol%)	13	6	2:1
4	$InBr_3$ (10 mol%)	41	20	2:1
5	$InCl_3$ instead of $InBr_3$	58	13	4.5:1

6	$In(OAc)_3$ instead of $InBr_3$	51	13	4:1
7	$In(NO_3)_3 \cdot 4H_2O$ instead of $InBr_3$	34	10	3:1
8	In_2O_3 instead of $InBr_3$	55	11	5:1
9	$Zn(OTf)_2$ instead of $InBr_3$	54	18	3:1
10	$Yb(OTf)_2$ instead of $InBr_3$	45	20	2:1
11	$CeCl_3$ instead of $InBr_3$	28	6	4.5:1
12	$Cu(OAc)_2$ instead of $InBr_3$	52	10	5:1
13	$FeCl_2$ instead of $InBr_3$	62	12	5:1
14	$Co(acac)_2$ instead of $InBr_3$	39	5	8:1
15	$Ni(COD)_2$ instead of $InBr_3$	57	15	4:1

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), **3a** (0.4 mmol), catalyst (5 mol%), Ag_2CO_3 (2 equiv), 1,4-dioxane (1 mL), argon, 120 °C, and 12 h.

In order to investigate the role of the Lewis acid in the regiochemical outcome of the reaction, we performed some control experiments. First of all, the loading of $InBr_3$ was tested for the reactivity and regioselectivity, four relevant experiments was performed and the results showed that the 5 mol% of catalyst was generally enough for an excellent regioselectivity of **4aaa** and **5aaa** (>20:1 ratio) (entries 1-4).

Subsequently, other Lewis acid including $InCl_3$, $In(OAc)_3$, $In(NO_3)_3$ $CeCl_3$ $Cu(OAc)_2$ and In_2O_3, were performed, they exhibited high catalytic activity and provided moderate yields but with a lower regioselectivity (entries 5-8). The results were showed a mixture of **4aaa**/**5aaa** with 4.5:1 ratio, 4:1 ratio, 3:1 ratio, 5:1 ratio, respectively.

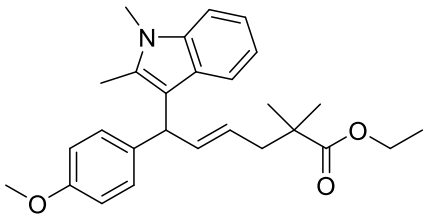
Finally, other types of Lewis acids, such as $Zn(OTf)_2$, $Yb(OTf)_2$, $CeCl_3$, $Cu(OAc)_2$, $FeCl_2$, $Co(acac)_2$ and $Ni(COD)_2$ were tested, the results showed a low

regioselectivity as we expected based on the report of the manuscript "*Adv. Synth. Catal.*, 2018, **360**, 1296" (entries 9-15).

In conclusion, by comparing the effects of different Lewis acids, we found $InBr_3$ as a Lewis acid not only promoted a high regioselectivity, but also gave the best yield.

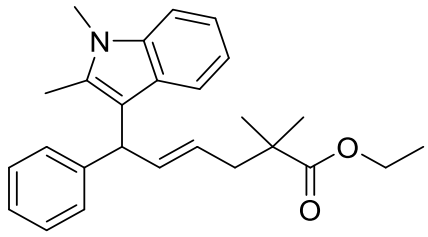
(C) Analytical data

Ethyl (*E*)-6-(1,2-dimethyl-1*H*-indol-3-yl)-6-(4-methoxyphenyl)-2,2-dimethylhex-4-enoate (4aaa):



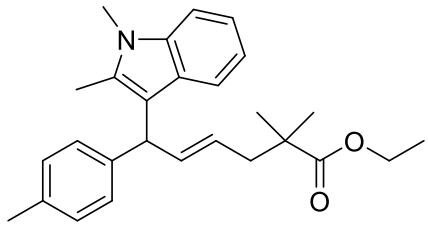
76.1 mg, 86%; Yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.27 (d, *J* = 10.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 8.5 Hz, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.95-6.92 (m, 1H), 6.79-6.76 (m, 2H), 6.06 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.45-5.39 (m, 1H), 4.90 (d, *J* = 7.5 Hz, 1H), 4.03-3.99 (m, 2H), 3.76 (s, 3H), 3.66 (s, 3H), 2.32 (s, 3H), 2.28 (d, *J* = 7.5 Hz, 2H), 1.17 (s, 3H), 1.15 (s, 3H), 1.13 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.6, 157.7, 136.7, 136.0, 135.6, 133.0, 129.0, 126.8, 126.3, 120.3, 119.5, 118.6, 113.4, 112.7, 108.5, 60.2, 55.2, 44.3, 43.5, 42.6, 29.5, 25.0, 14.1, 10.7; LRMS (EI, 70eV) *m/z* (%): 419 (M^+, 100), 145 (88), 201 (26), 290 (64), 304 (48); HRMS *m/z* (ESI) calcd for $C_{27}H_{33}NO_3$ ($[M+H]^+$) 420.2533, found 420.2530.

Ethyl (*E*)-6-(1,2-dimethyl-1*H*-indol-3-yl)-2,2-dimethyl-6-phenylhex-4-enoate (4baa):



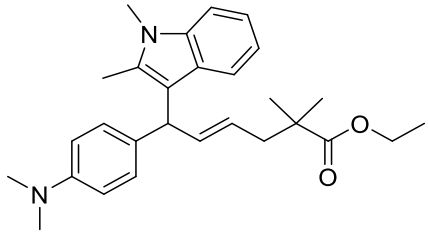
62.5 mg, 68%; Yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.28-7.22 (m, 6H), 7.16-7.14 (m, 1H), 7.12-7.09 (m, 1H), 6.95-6.92 (m, 1H), 6.09 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.47-5.41 (m, 1H), 4.95 (d, *J* = 7.5 Hz, 1H), 4.03-3.99 (m, 2H), 3.66 (s, 3H), 2.32 (s, 3H), 2.29 (d, *J* = 7.0 Hz, 2H), 1.17 (s, 3H), 1.16 (s, 3H), 1.12 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.6, 143.9, 136.7, 135.2, 133.1, 128.0, 128.0, 126.7, 126.6, 125.8, 120.3, 119.4, 118.6, 112.5, 108.5, 60.2, 45.1, 43.5, 42.5, 29.5, 25.0, 24.9, 14.1, 10.7; LRMS (EI, 70eV) *m/z* (%): 389 (M^+, 52), 145 (100), 182 (11), 274 (26), 312 (10); HRMS *m/z* (ESI) calcd for $C_{26}H_{31}NO_2$ ($[M+H]^+$) 390.2428, found 390.2439.

Ethyl (*E*)-6-(1,2-dimethyl-1*H*-indol-3-yl)-2,2-dimethyl-6-(*p*-tolyl)hex-4-enoate (4caa):



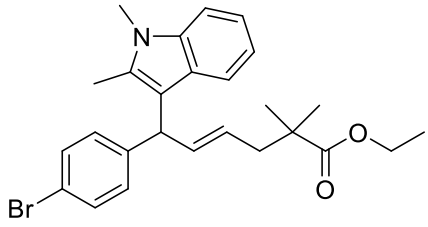
49.2 mg, 50%; Yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.29 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 8.5 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.10 (t, *J* = 7.5 Hz, 1H) 7.04 (d, *J* = 7.5 Hz, 2H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.08 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.46-5.40 (m, 1H), 4.91 (d, *J* = 7.5 Hz, 1H), 4.04-3.98 (m, 2H), 3.65 (s, 3H), 2.32 (s, 3H), 2.29-2.28 (m, 5H), 1.16 (s, 3H), 1.15 (s, 3H), 1.13 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.6, 140.8, 136.7, 135.5, 135.2, 133.1, 128.7, 127.9, 126.8, 126.4, 120.3, 119.5, 118.5, 112.6, 108.5, 60.2, 44.7, 43.5, 42.6, 29.5, 25.0, 20.9, 14.1, 10.7; LRMS (EI, 70eV) *m/z* (%): 403 (M^+, 63), 145 (100), 248 (15), 264 (18), 288 (28); HRMS *m/z* (ESI) calcd for $C_{27}H_{33}NO_2$ ($[M+H]^+$) 404.2584, found 404.2574.

Ethyl (*E*)-6-(1,2-dimethyl-1*H*-indol-3-yl)-6-(4-(dimethylamino)phenyl)-2,2-dimethylhex-4-enoate (4daa):



80.4 mg, 75%; Brown oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.31 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 8.5 Hz, 1H), 7.13-7.08 (m, 3H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.65 (d, *J* = 9.0 Hz, 2H), 6.06 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.45-5.40 (m, 1H), 4.87 (d, *J* = 7.5 Hz, 1H), 4.05-3.98 (m, 2H), 3.65 (s, 3H), 2.88 (s, 6H), 2.32 (s, 3H), 2.29-2.27 (m, 2H), 1.17 (s, 3H), 1.16 (s, 3H), 1.13 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.7, 148.9, 136.7, 135.9, 133.0, 132.0, 128.6, 126.9, 125.9, 120.2, 119.6, 118.4, 112.9, 112.6, 108.4, 60.2, 44.2, 43.5, 42.5, 40.8, 29.5, 25.0, 14.1, 10.7; LRMS (EI, 70eV) *m/z* (%): 432 (M^+, 78), 134 (41), 158 (62), 303 (100), 317 (27); HRMS *m/z* (ESI) calcd for $C_{28}H_{36}N_2O_2$ ($[M+H]^+$) 433.2850, found 433.2872.

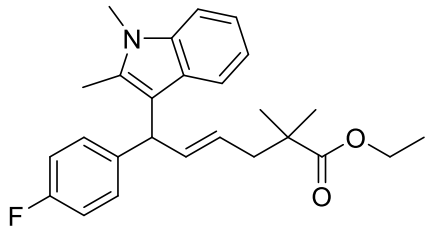
Ethyl (*E*)-6-(4-bromophenyl)-6-(1,2-dimethyl-1*H*-indol-3-yl)-2,2-dimethylhex-4-enoate (4eaa):



79.2 mg, 83%; Yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.35-7.33 (m, 2H), 7.23 (d, *J* = 10.0 Hz, 2H), 7.14-7.10 (m, 3H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.03 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.47-5.41 (m, 1H), 4.88 (d, *J* = 7.5 Hz, 1H), 4.04-3.98 (m, 2H), 3.66 (s, 3H), 2.32 (s, 3H), 2.28 (d, *J* = 7.5 Hz, 2H), 1.16 (s, 3H), 1.15 (s, 3H), 1.13 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.5, 142.9,

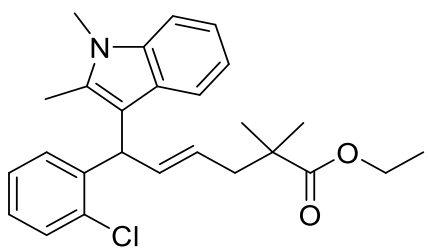
136.7, 134.6, 133.2, 131.0, 129.8, 127.1, 126.5, 120.5, 119.6, 119.2, 118.7, 111.9, 108.6, 60.3, 44.6, 43.5, 42.5, 29.5, 25.0, 24.9, 14.1, 10.6; LRMS (EI, 70eV) *m/z* (%): 469 (M^++2, 24), 467 (M^+, 25), 145 (100), 182 (13), 290 (30), 352 (14); HRMS *m/z* (ESI) calcd for $C_{26}H_{30}BrNO_2$ ($[M+H]^+$) 468.1533, found 468.1528.

Ethyl (*E*)-6-(1,2-dimethyl-1*H*-indol-3-yl)-6-(4-fluorophenyl)-2,2-dimethylhex-4-enoate (4faa):



63.7 mg, 70%; Yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.24-7.20 (m, 4H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.96-6.90 (m, 3H), 6.05 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.45-5.41 (m, 1H), 4.91 (d, *J* = 7.5 Hz, 1H), 4.03-3.98 (m, 2H), 3.66 (s, 3H), 2.32 (s, 3H), 2.29 (d, *J* = 7.5 Hz, 2H), 1.17 (s, 3H), 1.16 (s, 3H), 1.12 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.5, 161.2 (d, J_{C-F} = 237.5 Hz), 139.5 (d, J_{C-F} = 3.0 Hz), 136.7, 135.1, 133.1, 129.4 (d, J_{C-F} = 7.8 Hz), 126.8, 126.5, 120.4, 119.3, 118.6, 114.7 (d, J_{C-F} = 20.9 Hz), 112.2, 108.6, 60.2, 44.4, 43.5, 42.5, 29.5, 25.0, 24.9, 14.1, 10.6; ^{19}F NMR (500 MHz, $CDCl_3$) δ: -117.9; LRMS (EI, 70eV) *m/z* (%): 407 (M^+, 54), 145 (100), 252 (14), 278 (22), 292 (32); HRMS *m/z* (ESI) calcd for $C_{26}H_{30}FNO_2$ ($[M+H]^+$) 408.2333, found 408.2324.

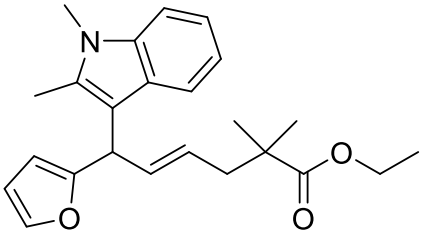
Ethyl (*E*)-6-(2-chlorophenyl)-6-(1,2-dimethyl-1*H*-indol-3-yl)-2,2-dimethylhex-4-enoate (4gaa):



44.9 mg, 44%; Yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.47 (d, *J* = 8.0 Hz, 1H), 7.43-7.42 (m, 1H), 7.31-7.30 (m, 1H), 7.24 (d, *J* =

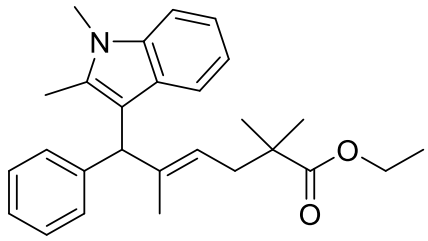
8.0 Hz, 1H), 7.17-7.14 (m, 1H), 7.12-7.09 (m, 2H), 6.99-6.95 (m, 1H), 6.03 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.31 (d, *J* = 5.0 Hz, 1H), 5.26-5.19 (m, 1H), 4.03-3.98 (m, 2H), 3.65 (s, 3H), 2.34 (s, 3H), 2.30 (d, *J* = 7.0 Hz, 2H), 1.13 (s, 3H), 1.12 (s, 3H), 1.11-1.09 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.6, 141.4, 136.6, 134.5, 133.9, 133.8, 130.1, 129.4, 127.3, 126.8, 126.5, 120.2, 119.4, 118.7, 110.8, 108.5, 60.2, 43.3, 42.5, 29.5, 24.9, 24.8, 14.1, 10.7; LRMS (EI, 70eV) *m/z* (%): 425 (M^++2, 14), 423 (M^+, 38), 145 (100), 182 (11), 264 (9), 308 (23),; HRMS *m/z* (ESI) calcd for $C_{26}H_{30}{}^{35}ClNO_2$ ($[M+H]^+$) 424.2038, found 424.2041.

Ethyl (*E*)-6-(1,2-dimethyl-1*H*-indol-3-yl)-6-(furan-2-yl)-2,2-dimethylhex-4-enoate (4haa):



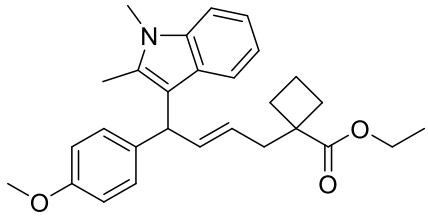
47.5 mg, 60%; Brown oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.30-7.29 (m, 1H), 7.27-7.22 (m, 2H), 7.12-7.09 (m, 1H), 6.98-6.95 (m, 1H), 6.30-6.29 (m, 1H), 6.09-6.08 (m, 1H), 5.97 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.49-5.43 (m, 1H), 4.94 (d, *J* = 7.0 Hz, 1H), 4.04-3.97 (m, 2H), 3.66 (s, 3H), 2.33 (s, 3H), 2.27-2.24 (m, 2H), 1.14-1.11 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.6, 157.0, 141.2, 136.6, 133.2, 132.6, 126.9, 126.5, 120.4, 119.0, 118.8, 110.0, 108.6, 105.9, 60.2, 43.2, 42.5, 39.6, 29.5, 25.0, 24.8, 14.1, 10.4; LRMS (EI, 70eV) *m/z* (%): 379 (M^+, 66), 145 (100), 224 (29), 250 (47), 264 (81); HRMS *m/z* (ESI) calcd for $C_{24}H_{29}NO_3$ ($[M+H]^+$) 380.2220, found 380.2209.

Ethyl (*E*)-6-(1,2-dimethyl-1*H*-indol-3-yl)-2,2,5-trimethyl-6-phenylhex-4-enoate (4jaa):



43.5 mg, 53%; Yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.31 (d, *J* = 8.0 Hz, 1H), 7.24-7.21 (m, 5H), 7.16-7.13 (m, 1H), 7.12-7.09 (m, 1H), 6.96-6.93 (m, 1H), 5.08 (t, *J* = 7.5 Hz, 1H), 4.92 (s, 1H), 4.02-3.98 (m, 2H), 3.65 (s, 3H), 2.37-2.30 (m, 2H), 2.27 (s, 3H), 1.66 (s, 3H), 1.14-1.11 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.8, 143.0, 139.7, 136.5, 134.0, 129.0, 127.9, 127.7, 125.7, 123.1, 120.1, 119.7, 118.6, 111.4, 108.4, 60.2, 51.5, 42.8, 38.8, 29.5, 25.0, 24.9, 16.8, 14.1, 10.6; LRMS (EI, 70eV) *m/z* (%): 403 (M^+, 57), 145 (71), 207 (12), 234 (100), 274 (19); HRMS *m/z* (ESI) calcd for $C_{27}H_{33}NO_2$ ($[M+H]^+$) 404.2584, found 404.2597.

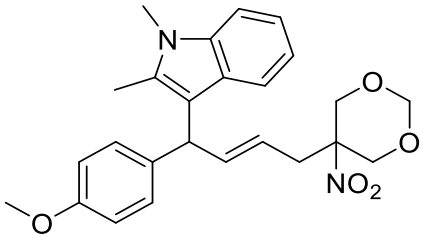
Ethyl (*E*)-1-(4-(1,2-dimethyl-1*H*-indol-3-yl)-4-(4-methoxyphenyl)but-2-en-1-yl)cyclobutane-1-carboxylate (4aba):



81.2 mg, 89%; Yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.27 (d, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 9.5 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.78-6.76 (m, 2H), 6.08 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.44-5.38 (m, 1H), 4.88 (d, *J* = 7.5 Hz, 1H), 4.06-3.99 (m, 2H), 3.75 (s, 3H), 3.65 (s,3H), 2.51 (d, *J* = 7.0 Hz, 2H), 2.42-2.39 (m, 2H), 2.31 (s, 3H), 1.92-1.82 (m, 4H), 1.15-1.12 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 176.9, 157.7, 136.7, 135.9,

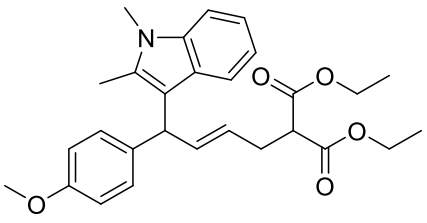
135.3, 133.1, 129.0, 126.8, 125.9, 120.3, 119.5, 118.5, 113.4, 112.7, 108.5, 60.2, 55.2, 47.4, 44.3, 40.6, 29.5, 29.3, 15.3, 14.1, 10.6; LRMS (EI, 70eV) *m/z* (%): 431 (M^+, 99), 145 (98), 158 (85), 290 (85), 303 (80); HRMS *m/z*(ESI) calcd for $C_{28}H_{33}NO_3$ ($[M+H]^+$) 432.2533, found 432.2546.

(*E*)-3-(1-(4-methoxyphenyl)-4-(5-nitro-1,3-dioxan-5-yl)but-2-en-1-yl)-1,2-dimethyl-1*H*-indole (4aca):



72.7 mg, 70%; Yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.23 (t, *J* = 8.3 Hz, 2H), 7.11 (t, *J* = 8.0 Hz, 3H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 8.5 Hz, 2H), 6.16 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.25-5.19 (m, 1H), 4.92 (d, *J* = 6.0 Hz, 2H), 4.65 (d, *J* = 6.0 Hz, 1H), 4.62-4.57 (m, 2H), 3.78-3.73 (m, 5H), 3.65 (s, 3H), 2.49 (d, *J*= 7.5 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 157.8, 139.6, 136.7, 134.7, 133.3, 128.9, 126.5, 120.4, 119.9, 119.2, 118.7, 113.5, 111.5, 108.7, 93.7, 85.6, 70.2, 55.2, 44.0, 36.8, 29.5, 10.6; HRMS *m/z* (ESI) calcd for $C_{25}H_{28}N_2O_5$ ($[M+H]^+$) 437.2071, found 437.2073.

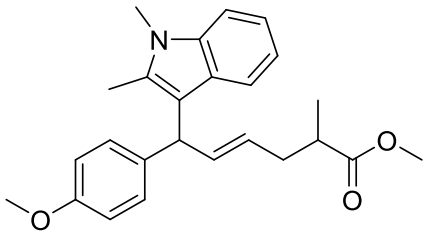
Diethyl (*E*)-2-(4-(1,2-dimethyl-1*H*-indol-3-yl)-4-(4-methoxyphenyl)but-2-en-1-yl) malonate (4ada):



114.9 mg, 71%; Yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.27-7.22 (m, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 9.0 Hz, 2H), 6.15 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.48-5.42 (m, 1H), 4.88 (d, *J* = 7.5 Hz, 1H), 4.18-4.07 (m, 4H), 3.75 (s, 3H), 3.65 (s, 3H), 3.41 (t, *J*=

7.5 Hz, 1H), 2.66 (t, *J*= 7.5 Hz, 2H), 2.30 (s, 3H), 1.22-1.16 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 169.0, 157.7, 136.7, 135.7, 135.4, 133.1, 128.9, 126.7, 126.1, 120.3, 119.4, 118.6, 113.4, 112.4, 108.5, 61.3, 55.2, 52.1, 44.1, 31.7, 29.5, 14.0, 10.6; LRMS (EI, 70eV) *m/z* (%): 463 (M^+, 68), 145 (100), 264 (41), 288 (73), 448 (16); HRMS *m/z* (ESI) calcd for $C_{28}H_{33}NO_5$ ($[M+H]^+$) 464.2431, found 464.2441.

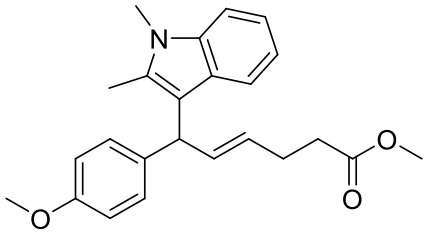
Methyl (*E*)-6-(1,2-dimethyl-1*H*-indol-3-yl)-6-(4-methoxyphenyl)-2-methylhex-4-enoate (4aea):



d.r. = 1:1 ;

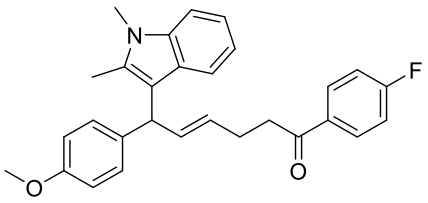
64.3 mg, 72%; Yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.29-7.27 (m, 1H), 7.24-7.22 (m, 1H), 7.17-7.16 (m, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.94 (t, *J* = 7.3 Hz, 1H), 6.79-6.77 (m, 2H), 6.08 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.45-5.39 (m, 1H), 4.89 (d, *J* = 7.0 Hz, 1H), 3.75 (s, 3H), 3.64 (s, 3H), 3.61 (s, 1.53H), 3.57 (s, 1.53H), 2.54-2.50 (m, 1H), 2.43-2.38 (m, 1H), 2.31 (s, 3H), 2.23-2.17 (m, 1H), 1.15 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 176.7, 157.6, 136.7, 135.9 (2C), 134.6 (2C), 133.0, 128.9, 127.5 (2C), 126.7 (2C), 120.3, 119.4 (2C), 118.5, 113.4, 112.6 (2C), 108.5, 55.2, 51.5 (2C), 44.1 (2C), 39.6 (2C), 36.7 (2C), 29.5, 16.8 (2C), 10.6 (2C); LRMS (EI, 70eV) *m/z* (%): 391 (M^+, 82), 145 (100), 264 (24), 290 (61), 376 (20); HRMS *m/z* (ESI) calcd for $C_{25}H_{29}NO_3$ ($[M+H]^+$) 392.2220, found 392.2213.

Methyl (*E*)-6-(1,2-dimethyl-1*H*-indol-3-yl)-6-(4-methoxyphenyl)hex-4-enoate (4afa):



66.2 mg, 77%; Yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.30 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 10.5 Hz, 1H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 8.5 Hz, 2H), 6.09 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.50-5.46 (m, 1H), 4.89 (d, *J* = 7.5 Hz, 1H), 3.76 (s, 3H), 3.66 (s, 3H), 3.63 (s, 3H), 2.40-2.38 (m, 4H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 173.7, 157.7, 136.7, 136.0, 133.4, 133.1, 128.9, 128.7, 126.8, 120.3, 119.4, 118.6, 113.4, 112.7, 108.6, 55.2, 51.5, 44.1, 34.0, 29.5, 27.8, 10.7; LRMS (EI, 70eV) *m/z* (%): 377 (M^+, 79), 145 (100), 264 (25), 290 (65), 362 (23); HRMS *m/z* (ESI) calcd for $C_{24}H_{27}NO_3$ ($[M+H]^+$) 378.2064, found 378.2055.

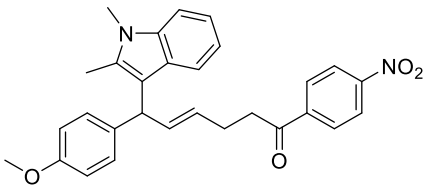
(*E*)-6-(1,2-dimethyl-1*H*-indol-3-yl)-1-(4-fluorophenyl)-6-(4-methoxyphenyl)hex-4-en-1-one (4aga):



73.9 mg, 62%; Yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.95-7.93 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 9.0 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.12-7.07 (m, 3H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 8.5 Hz, 2H), 6.11 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.57-5.51 (m, 1H), 4.89 (d, *J* = 7.5 Hz, 1H), 3.75 (s, 3H), 3.65 (s, 3H), 3.01 (t, *J* = 7.5 Hz, 2H), 2.53-2.48 (m, 2H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 198.2, 165.6 (d, J_{C-F} = 253.0 Hz), 157.7, 136.7, 136.0, 133.4,

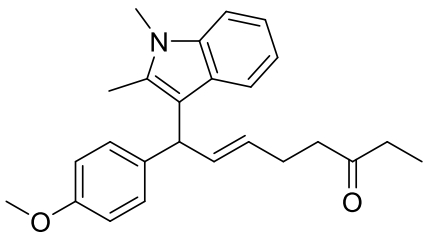
133.0 (d, J_{C-F} = 2.6 Hz), 130.6 (d, J_{C-F} = 9.2 Hz), 129.1, 128.9, 127.2, 126.8, 120.3, 119.4, 118.6, 115.6 (d, J_{C-F} = 21.6 Hz), 113.8, 113.4, 112.7, 108.6, 55.2, 44.2, 38.2, 29.5, 27.2, 10.6; ^{19}F NMR (500 MHz, $CDCl_3$) δ: -105.5; HRMS *m/z* (ESI) calcd for $C_{29}H_{28}FNO_2$ ($[M+H]^+$) 442.2177, found 442.2162.

(*E*)-6-(1,2-dimethyl-1*H*-indol-3-yl)-6-(4-methoxyphenyl)-1-(4-nitrophenyl)hex-4-en-1-one (4aha):



69.3 mg, 66%; Yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.25 (d, *J* = 8.0 Hz, 2H), 8.03 (d, *J* = 9.0 Hz, 2H), 7.29-7.25 (m, 2H), 7.16-7.10 (m, 3H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 9.0 Hz, 2H), 6.11 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.57-5.51 (m, 1H), 4.89 (d, *J* = 7.5 Hz, 1H), 3.76 (s, 3H), 3.66 (s, 3H), 3.09 (t, *J* = 7.5 Hz, 2H), 2.56-2.52 (m, 2H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 198.3, 157.7, 150.1, 141.3, 136.7, 135.8, 133.9, 133.1, 129.0, 128.9, 128.5, 126.7, 123.8, 120.4, 119.4, 118.6, 113.4, 112.6, 108.6, 55.2, 44.2, 38.8, 29.5, 26.9, 10.7; HRMS *m/z* (ESI) calcd for $C_{29}H_{28}N_2O_4$ ($[M+H]^+$) 469.2122, found 469.2119.

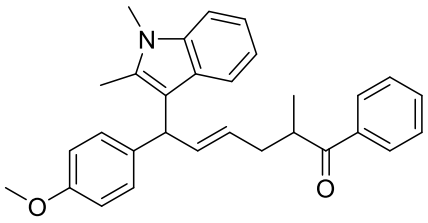
(*E*)-8-(1,2-dimethyl-1*H*-indol-3-yl)-8-(4-methoxyphenyl)oct-6-en-3-one (4aia):



43.2 mg, 56%; Yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.30 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 1H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 8.5 Hz, 2H), 6.05 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.49-5.43 (m, 1H), 4.88 (d, *J* = 7.5 Hz, 1H), 3.76 (s, 3H), 3.66 (s, 3H), 2.49 (t, *J* = 7.5 Hz, 2H), 2.40-2.34 (m, 4H), 2.32 (s, 3H), 1.02 (t, *J* = 7.5 Hz, 3H); ^{13}C

NMR (125 MHz, $CDCl_3$) δ: 211.2, 157.6, 136.7, 136.0, 133.1, 129.2, 128.9, 128.6, 126.8, 120.3, 119.4, 118.6, 113.4, 112.7, 108.6, 55.2, 44.1, 42.0, 36.0, 29.5, 26.8, 10.7, 7.7; LRMS (EI, 70eV) *m/z* (%): 375 (M^+, 22), 121 (11), 145 (32), 182 (10), 290 (100); HRMS *m/z* (ESI) calcd for $C_{25}H_{29}NO_2$ ($[M+H]^+$) 376.2271, found 376.2268.

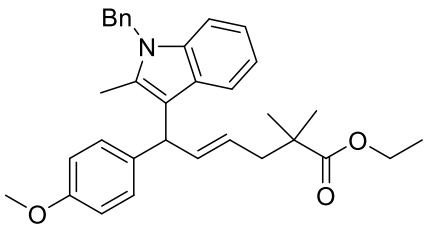
(*E*)-6-(1,2-dimethyl-1*H*-indol-3-yl)-6-(4-methoxyphenyl)-2-methyl-1-phenylhex-4-en-1-one (4aja):



d.r.= 1.2:1;

52.9 mg, 51%; Yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.93-7.89 (m, 2H), 7.55-7.52 (m, 1H), 7.45-7.40 (m, 2H), 7.24-7.21 (m, 2H), 7.12-7.09 (m, 3H), 6.94-6.88 (m, 1H), 6.75-6.72 (m, 2H), 6.06 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.49-5.40 (m, 1H), 4.85 (t, *J* = 7.5 Hz, 1H), 3.75 (s, 1.63H), 3.74 (s, 1.38H), 3.63 (s, 3H), 3.56-3.51 (m, 1H), 2.59-2.53 (m, 1H), 2.27 (s, 1.62H), 2.25 (s, 1.38H), 2.24-2.19 (m, 1H), 1.22-1.18 (m, 3H); ^{13}CNMR (125 MHz, $CDCl_3$) δ: 204.0, 157.6, 136.6, 136.5 (2C), 135.9, 134.7, 134.5, 133.0 (2C), 132.8 (2C), 128.9, 128.6 (2C), 128.3 (2C), 127.9, 127.8, 120.3, 119.4 (2C), 118.5 (2C), 113.3, 108.5, 55.1, 44.1, 40.8 (2C), 36.7 (2C), 29.5, 17.1 (2C), 10.6; HRMS *m/z* (ESI) calcd for $C_{30}H_{31}NO_2$ ($[M+H]^+$) 438.2428, found 438.2423.

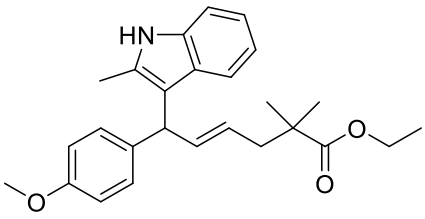
Ethyl (*E*)-6-(1-benzyl-2-methyl-1*H*-indol-3-yl)-6-(4-methoxyphenyl)-2,2-dimethylhex-4-enoate (4aab):



57.7 mg, 52%; Yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.30-7.28 (m, 1H), 7.25-7.18 (m, 6H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.97-6.94 (m, 3H),

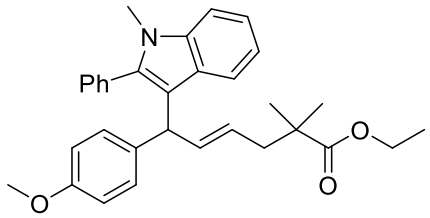
6.80 (d, *J* = 9.0 Hz, 2H), 6.09 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.46-5.40 (m, 1H), 5.31 (s, 2H), 4.93 (d, *J* = 7.5 Hz, 1H), 4.03-3.96 (m, 2H), 3.77 (s, 3H), 2.30 (d, *J* = 7.0 Hz, 2H), 2.25 (s, 3H), 1.16 (s, 3H), 1.15 (s, 3H), 1.12 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.6, 157.7, 138.0, 136.9, 136.6, 135.8, 135.5, 133.0, 129.0, 128.7, 127.2, 127.0, 126.4, 125.9, 120.6, 119.6, 118.9, 113.4, 109.0, 60.2, 55.2, 46.4, 44.3, 43.5, 42.5, 25.0, 24.9, 14.1, 10.6; LRMS (EI, 70eV) *m/z* (%): 495 (M^+, 27), 91 (71), 207 (45), 281 (13), 366 (100); HRMS *m/z* (ESI) calcd for $C_{33}H_{37}NO_3$ ($[M+H]^+$) 496.2846, found 496.2840.

Ethyl (*E*)-6-(4-methoxyphenyl)-2,2-dimethyl-6-(2-methyl-1*H*-indol-3-yl)hex-4-en oate (4aac):



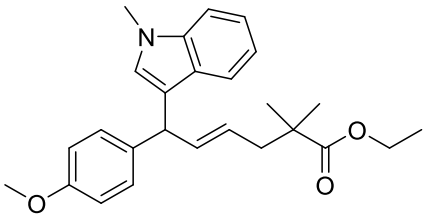
24.4 mg, 29%; Yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.80 (s, 1H), 7.25-7.24 (m, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 8.5 Hz, 2H), 6.05 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.46-5.40 (m, 1H), 4.87 (d, *J* = 7.5 Hz, 1H), 4.03-3.96 (m, 2H), 3.77 (s, 3H), 2.32 (s, 3H), 2.29 (d, *J* = 7.5 Hz, 2H), 1.16 (s, 3H), 1.15 (s, 3H), 1.12 (t, *J* = 7.0 Hz, 3H); 13C NMR (125 MHz, CDCl3) δ: 177.6, 157.7, 135.7, 135.4, 135.3, 131.2, 129.0, 127.8, 126.4, 120.7, 119.5, 119.0, 113.5, 113.4, 110.1, 60.2, 55.2, 44.0, 43.5, 42.6, 25.0, 24.9, 14.1, 12.3; LRMS (EI, 70eV) m/z (%): 405 (M+, 100), 121 (41), 145 (59), 276 (81), 290 (63); HRMS m/z (ESI) calcd for $C_{26}H_{31}NO_3$ ([M+H]+) 406.2377, found 406.2373.

Ethyl (*E*)-6-(4-methoxyphenyl)-2,2-dimethyl-6-(1-methyl-2-phenyl-1*H*-indol-3-yl) hex-4-enoate (4aad):



48.1 mg, 50%; Yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.48-7.42 (m, 3H), 7.36 (d, *J* = 6.5 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.21-7.18 (m, 1H), 7.13 (d, *J* = 9.0 Hz, 2H), 7.00-6.97 (m, 1H), 6.76-6.74 (m, 2H), 6.08 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.36-5.30 (m, 1H), 4.71 (d, *J* = 7.5 Hz, 1H), 4.01-3.94 (m, 2H), 3.75 (s, 3H), 3.59 (s, 3H), 2.26 (d, *J* = 7.5 Hz, 2H), 1.15 (s, 3H), 1.13 (s, 3H), 1.09 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.6, 157.5, 138.2, 137.4, 136.1, 135.7, 131.9, 130.8, 128.9, 128.3, 128.2, 126.6, 126.3, 121.4, 120.9, 119.0, 114.6, 113.3, 109.3, 60.2, 55.2, 44.5, 43.5, 42.6, 30.8, 25.0, 24.9, 14.0; LRMS (EI, 70eV) *m/z* (%): 481 (M^+, 100), 121 (24), 159 (28), 207 (36), 352 (77); HRMS *m/z* (ESI) calcd for $C_{32}H_{35}NO_3$ ($[M+H]^+$) 482.2690, found 482.2691.

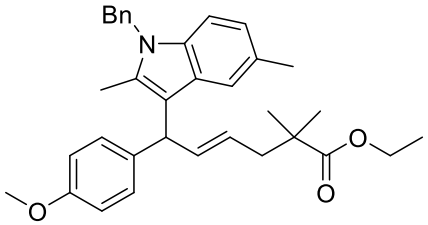
Ethyl (*E*)-6-(4-methoxyphenyl)-2,2-dimethyl-6-(1-methyl-1*H*-indol-3-yl)hex-4-en oate (4aae):



55.2 mg, 64%; Yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.35 (d, *J* = 7.5 Hz, 1H), 7.27-7.24 (m, 1H), 7.19-7.16 (m, 3H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 8.5 Hz, 2H), 6.68 (s, 1H), 5.94 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.45-5.39 (m, 1H), 4.85 (d, *J* = 7.0 Hz, 1H), 4.04-4.00 (m, 2H), 3.77 (s, 3H), 3.72 (s, 3H), 2.28 (d, *J* = 7.5 Hz, 2H), 1.18-1.12 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.6, 157.9, 137.3, 136.3, 136.1, 129.2, 127.1, 127.0, 126.2, 121.5, 120.0, 118.6,

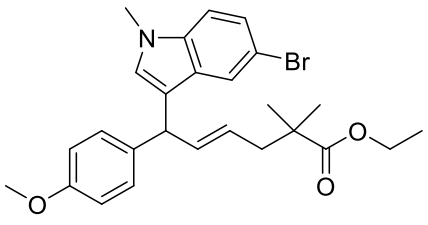
117.7, 113.6, 109.0, 60.2, 55.2, 45.1, 43.4, 42.6, 32.6, 24.9, 14.1; LRMS (EI, 70eV) *m/z* (%): 405 (M^+, 98), 159 (43), 276 (82), 250 (22), 290 (100); HRMS *m/z* (ESI) calcd for $C_{26}H_{31}NO_3$ ($[M+H]^+$) 406.2377, found 406.2377.

Ethyl (*E*)-6-(1-benzyl-2,5-dimethyl-1*H*-indol-3-yl)-6-(4-methoxyphenyl)-2,2-dim ethylhex-4-enoate (4aaf):



76.1 mg, 59%; Red oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.27-7.22 (m, 3H), 7.19 (d, *J* = 9.0 Hz, 2H), 7.12 (s, 1H), 7.08 (d, *J* = 8.5 Hz, 1H), 6.94 (d, *J* = 7.5 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 2H), 6.09 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.46-5.40 (m, 1H), 5.28 (s, 2H), 4.91 (d, *J* = 7.5 Hz, 1H), 4.04-3.98 (m, 2H), 3.77 (s, 3H), 2.35 (s, 3H), 2.30 (d, *J* = 6.5 Hz, 2H), 2.22 (s, 3H), 1.17 (s, 3H), 1.16 (s, 3H), 1.13 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.6, 157.6, 138.1, 135.9, 135.6, 135.0, 133.0, 129.0, 128.7, 128.0, 127.3, 127.1, 126.4, 125.8, 122.1, 119.3, 113.4, 112.9, 108.7, 60.2, 55.2, 46.4, 44.2, 43.5, 42.6, 25.0, 24.9, 21.5, 14.1, 10.7; LRMS (EI, 70eV) *m/z* (%): 509 (M^+, 75), 91 (100), 235 (100), 394 (27), 380 (29); HRMS *m/z* (ESI) calcd for $C_{34}H_{39}NO_3$ ($[M+H]^+$) 510.3003, found 510.3017.

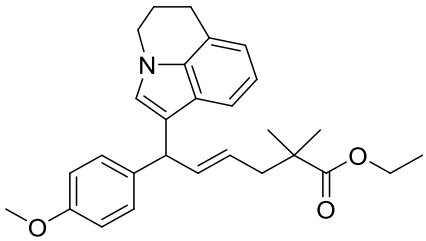
Ethyl (*E*)-6-(5-bromo-1-methyl-1*H*-indol-3-yl)-6-(4-methoxyphenyl)-2,2-dimethy lhex-4-enoate (4aag):



68.4 mg, 58%; Yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.49 (d, *J* = 7.0 Hz, 1H), 7.24 (d, *J* = 6.5 Hz, 1H), 7.15-7.12 (m, 3H), 6.84-6.82 (m, 2H), 6.66 (s, 1H), 5.90 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.43-5.36 (m, 1H), 4.78 (d, *J* = 7.0

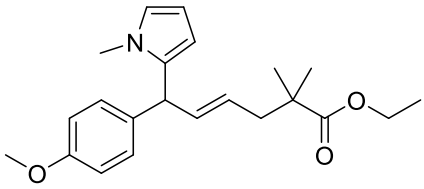
Hz, 1H), 4.06-4.01 (m, 2H), 3.79 (s, 3H), 3.70 (s, 3H), 2.29 (d, *J* = 7.0 Hz, 2H), 1.16-1.13 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.6, 158.0, 136.0, 135.8, 135.5, 129.1, 128.7, 128.3, 126.6, 124.3, 122.4, 117.4, 113.7, 112.1, 110.6, 60.2, 55.2, 44.8, 43.4, 42.5, 32.8, 24.9, 24.8, 14.1; LRMS (EI, 70eV) *m/z* (%): 485 (M^++2, 99), 483 (M^+, 99), 121 (43), 159 (77), 275 (62), 368 (100); HRMS *m/z* (ESI) calcd for $C_{26}H_{30}BrNO_3$ ($[M+H]^+$) 484.1482, found 484.1472.

Ethyl (*E*)-6-(5,6-dihydro-4H-pyrrolo[3,2,1-*ij*]quinolin-1-yl)-6-(4-methoxyphenyl) -2,2-dimethylhex-4-enoate (4aah):



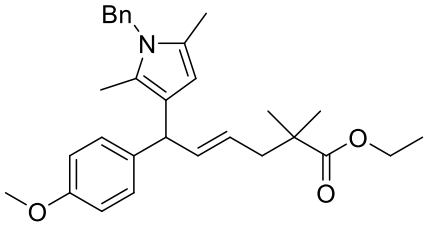
93.1 mg, 65%; Yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.18 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 1H), 6.91-6.85 (m, 2H), 6.82 (d, *J* = 9.0 Hz, 2H), 6.71 (s, 1H), 5.95 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.47-5.41 (m, 1H), 4.83 (d, *J* = 7.5 Hz, 1H), 4.08 (t, *J* = 5.5 Hz, 2H), 4.05-4.01 (m, 2H), 3.78 (s, 3H), 2.96 (t, *J* = 6.0 Hz, 2H), 2.28 (d, *J* = 7.5 Hz, 2H), 2.24-2.19 (m, 2H), 1.16-1.13 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.6, 157.8, 136.4, 136.3, 134.8, 129.2, 126.0, 124.6, 124.3, 121.5, 119.0, 118.4, 117.8, 117.5, 113.5, 60.2, 55.2, 45.5, 43.9, 43.4, 42.5, 25.0, 24.9, 24.7, 22.8, 14.1; LRMS (EI, 70eV) *m/z* (%): 431 (M^+, 97), 159 (27), 276 (22), 302 (69), 316 (100); HRMS *m/z* (ESI) calcd for $C_{28}H_{33}NO_3$ ($[M+H]^+$) 432.2533, found 432.2531.

Ethyl (*E*)-6-(4-methoxyphenyl)-2,2-dimethyl-6-(1-methyl-1*H*-pyrrol-3-yl)hex-4-enoate (4aai):



33.7 mg, 45%; Yellow oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.01-6.98 (m, 2H), 6.82-6.80 (m , 2H) 6.56 (t, *J* = 2.3 Hz, 1H), 6.06 (t, *J* = 8.0 Hz, 1H), 5.88-5.87 (m, 1H), 5.84 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.28-5.22 (m, 1H), 4.57 (d, *J* = 7.0 Hz, 1H), 4.06-4.02 (m, 2H), 3.78 (s, 3H), 3.33 (s, 3H), 2.27-2.25 (m, 2H), 1.17 (t, *J* = 7.0 Hz, 3H), 1.14 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.5, 158.0, 135.2, 134.4, 134.3, 129.1, 126.8, 121.9, 113.7, 107.2, 106.3, 60.3, 55.2, 45.7, 43.3, 42.5, 33.8, 25.0, 24.8, 14.1; LRMS (EI, 70eV) *m/z* (%): 355 (M^+, 60), 94 (21), 159 (36), 226 (41), 240 (100); HRMS *m/z* (ESI) calcd for $C_{22}H_{29}NO_3$ ($[M+H]^+$) 356.2220, found 356.2217.

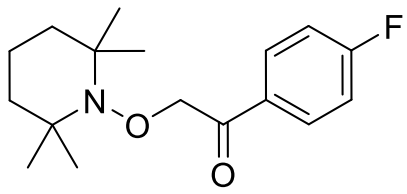
Ethyl (*E*)-6-(1-benzyl-2,5-dimethyl-1*H*-pyrrol-3-yl)-6-(4-methoxyphenyl)-2,2-dimethylhex-4-enoate (4aaj):



49.8 mg, 47%; Brown oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.30-7.27 (m, 2H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 9.0 Hz, 2H), 6.86 (d, *J* = 7.0 Hz, 2H), 6.83-6.81 (m, 2H), 5.85 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.66 (s, 1H), 5.36-5.30 (m, 1H), 4.98 (s, 2H), 4.51 (d, *J* = 7.0 Hz, 1H), 4.07-4.03 (m, 2H), 3.78 (s, 3H), 2.28 (d, *J* = 7.5 Hz, 2H), 2.09 (s, 3H), 1.98 (s, 3H), 1.18 (t, *J* = 7.0 Hz, 3H), 1.15 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.7, 157.5, 138.7, 137.3 (2C), 129.0, 128.6, 126.9, 126.7, 125.6, 125.2, 123.6, 120.8, 113.4, 105.8, 60.2, 55.2, 46.7, 45.1, 43.4,

42.5, 24.9, 24.8, 14.1, 12.3, 10.1; LRMS (EI, 70eV) *m/z* (%): 459 (M^+, 64), 91 (100), 185 (25), 344 (80), 345 (21); HRMS *m/z* (ESI) calcd for $C_{30}H_{37}NO_3$ ($[M+H]^+$) 460.2846, found 460.2833.

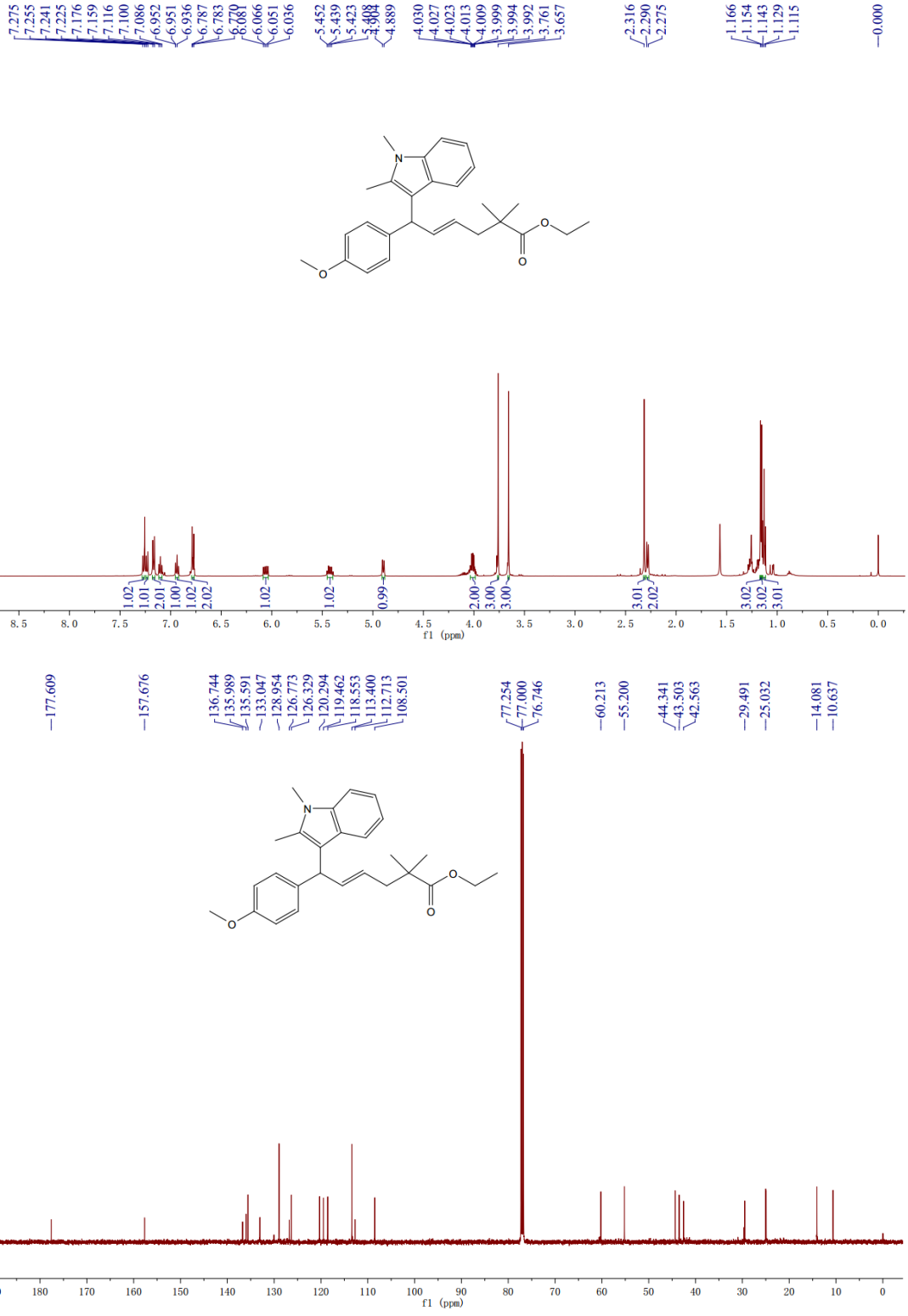
1-(4-Fluorophenyl)-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethan-1-one (6):



66.0 mg, 52%; Colorless oil liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.00-7.98 (m, 2H), 7.14 (t, *J* = 8.5 Hz, 2H), 5.06 (s, 2H), 1.64-1.63 (m, 2H), 1.49-1.46 (m, 4H), 1.17 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 194.4, 165.8 (d, J_{C-F} = 253.3 Hz), 131.8 (d, J_{C-F} = 2.8 Hz), 130.8 (d, J_{C-F} = 9.3 Hz), 115.7 (d, J_{C-F} = 21.6 Hz), 81.4, 60.1, 39.7, 32.8, 20.2, 17.0; ^{19}F NMR (500 MHz, $CDCl_3$) δ: -104.7; LRMS (EI, 70eV) *m/z* (%): 293 (M^+, 74), 133 (16), 186 (25), 277 (15), 292 (100); HRMS *m/z* (ESI) calcd for $C_{17}H_{24}FNO_2$ ($[M+H]^+$) 294.1864, found 294.1875.

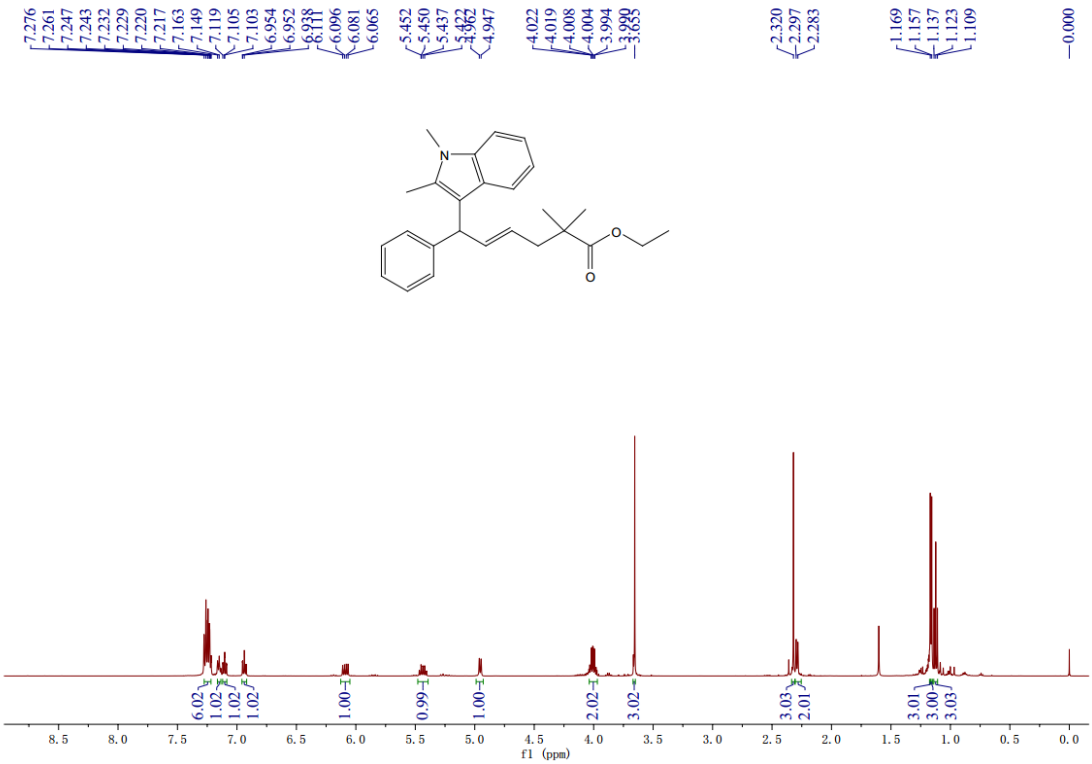
(D) Spectra

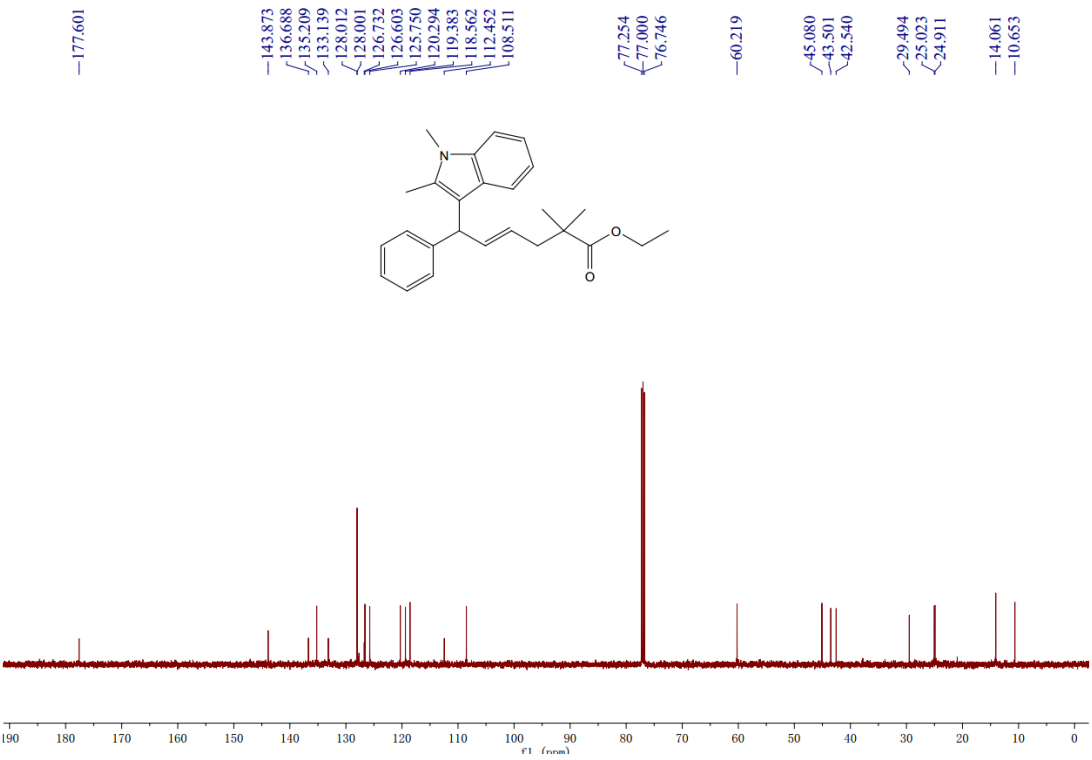
Ethyl (*E*)-6-(1,2-dimethyl-1*H*-indol-3-yl)-6-(4-methoxyphenyl)-2,2-dimethylhex-4-enoate (4aaa)



Ethyl (*E*)-6-(1,2-dimethyl-1*H*-indol-3-yl)-2,2-dimethyl-6-phenylhex-4-enoate

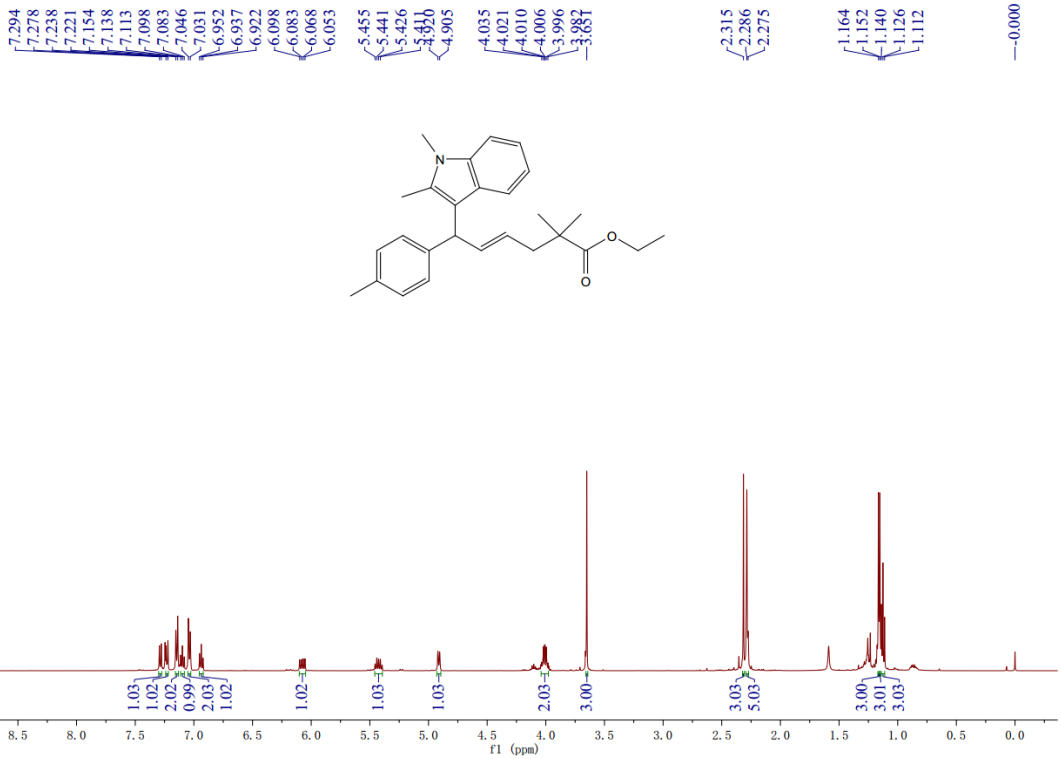
(4baa)

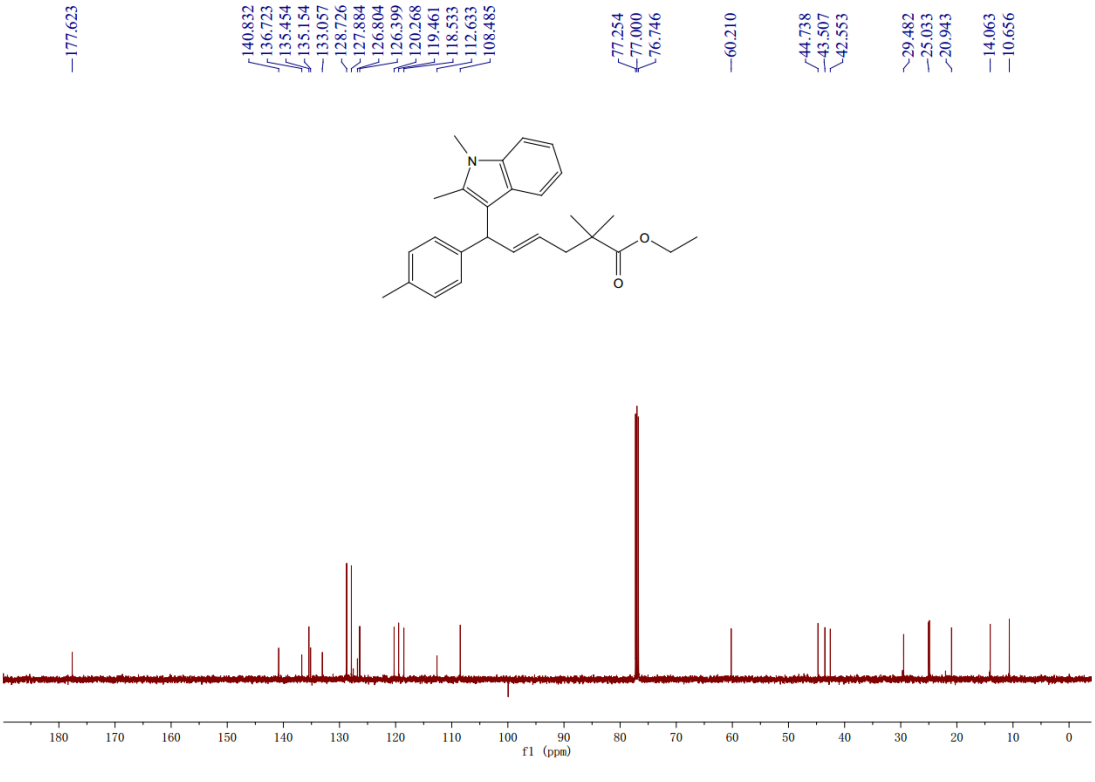




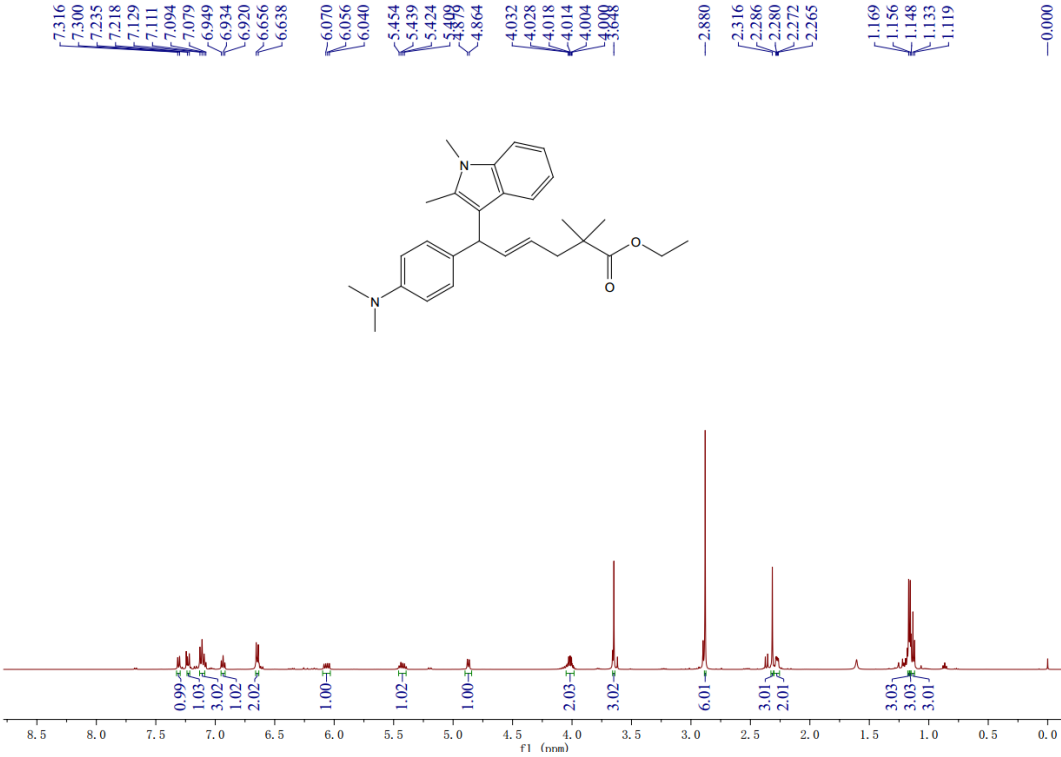
Ethyl (*E*)-6-(1,2-dimethyl-1*H*-indol-3-yl)-2,2-dimethyl-6-(*p*-tolyl)hex-4-enoate

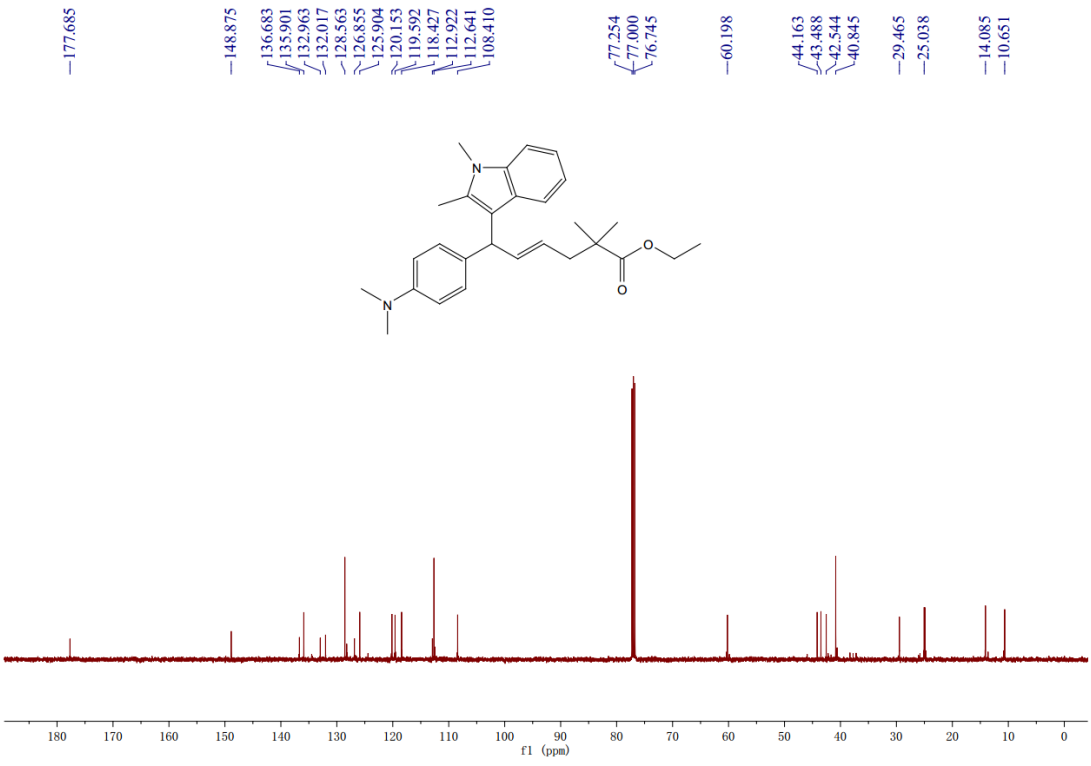
(4caa)



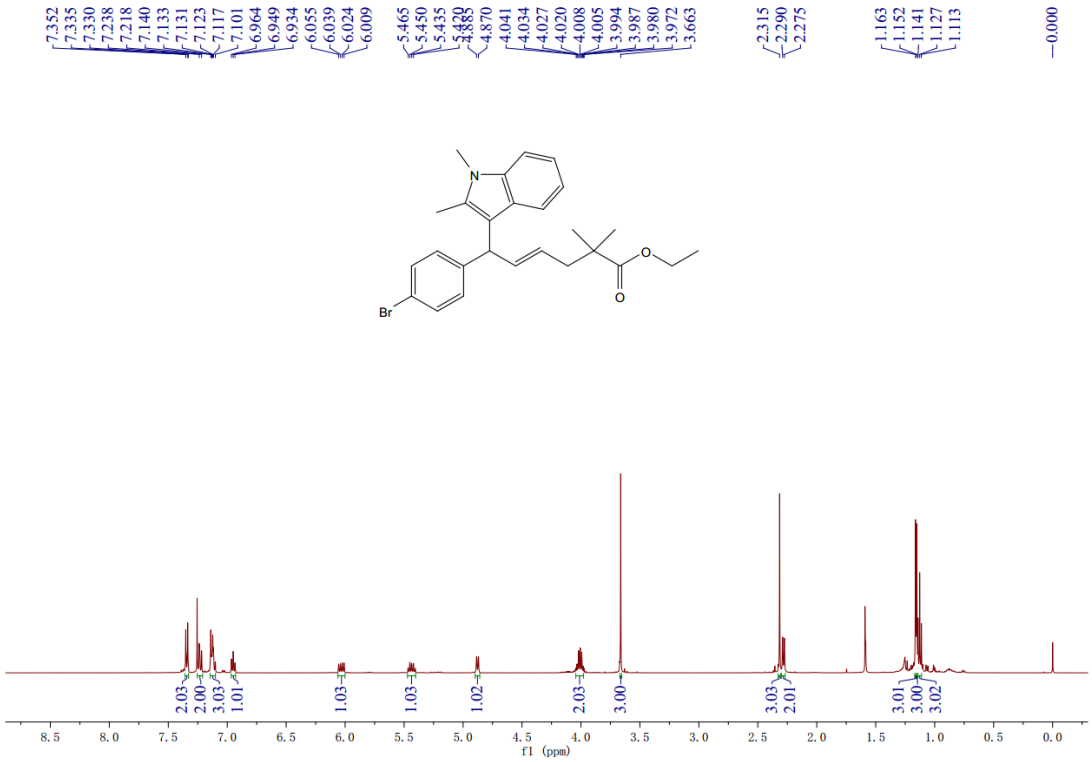


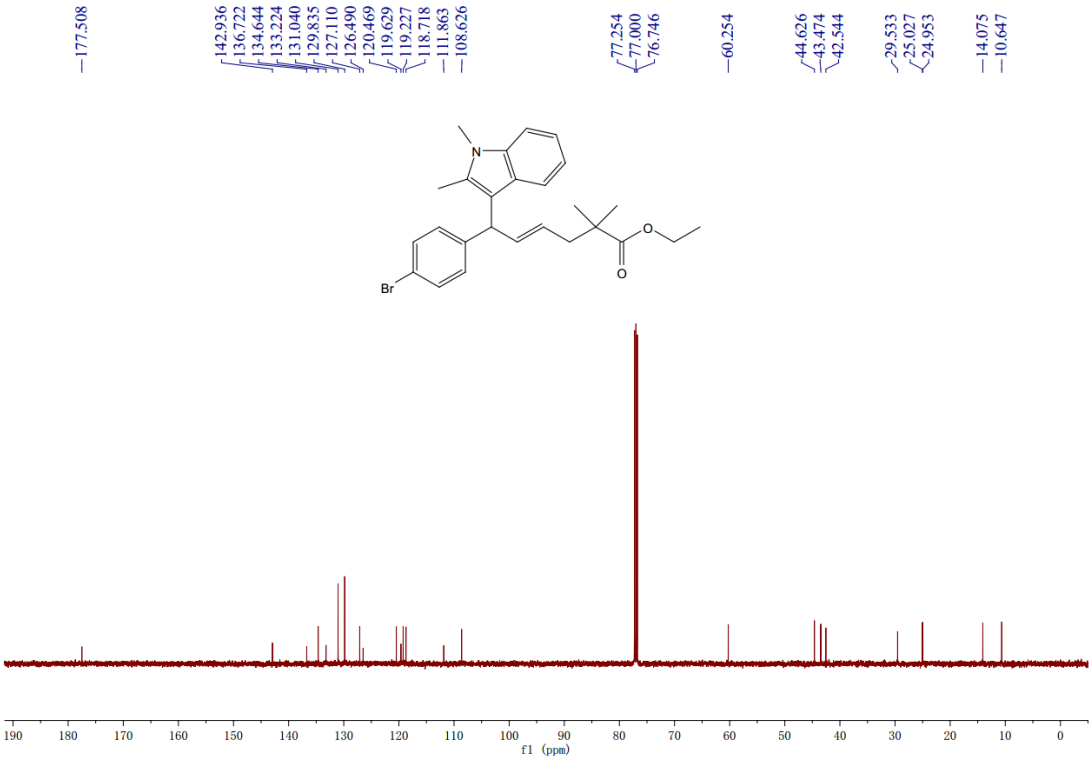
Ethyl (*E*)-6-(1,2-dimethyl-1*H*-indol-3-yl)-6-(4-(dimethylamino)phenyl)-2,2-dimethylhex-4-enoate (4daa)





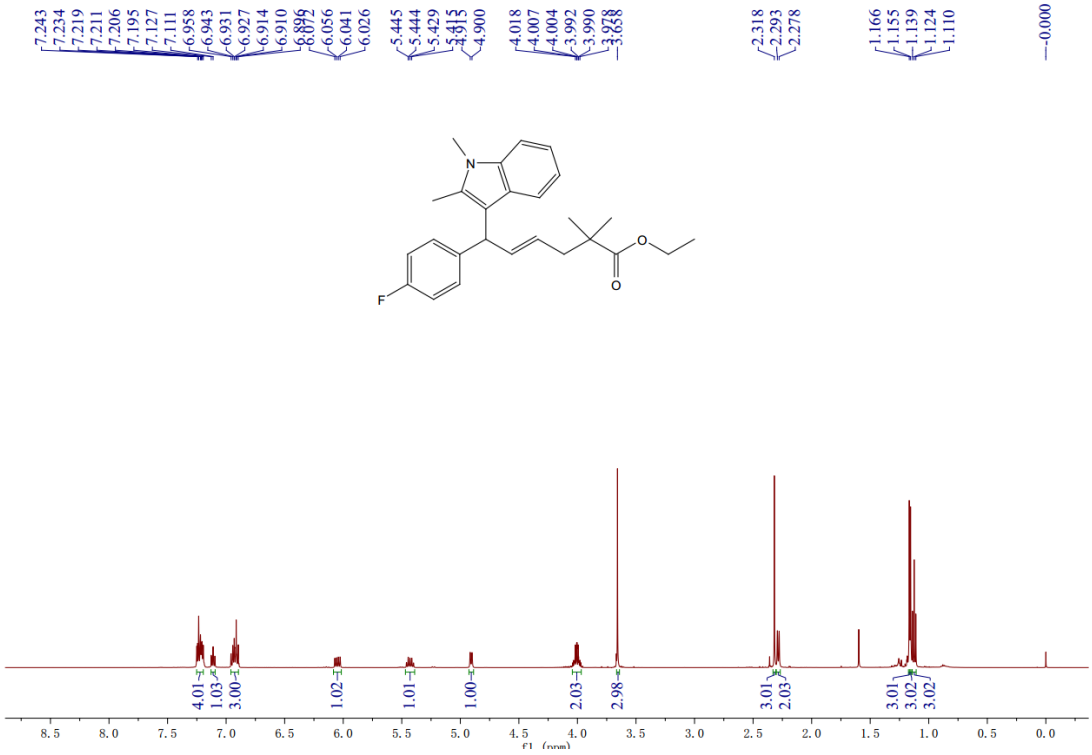
Ethyl (*E*)-6-(4-bromophenyl)-6-(1,2-dimethyl-1*H*-indol-3-yl)-2,2-dimethylhex-4-enoate (4eaa)

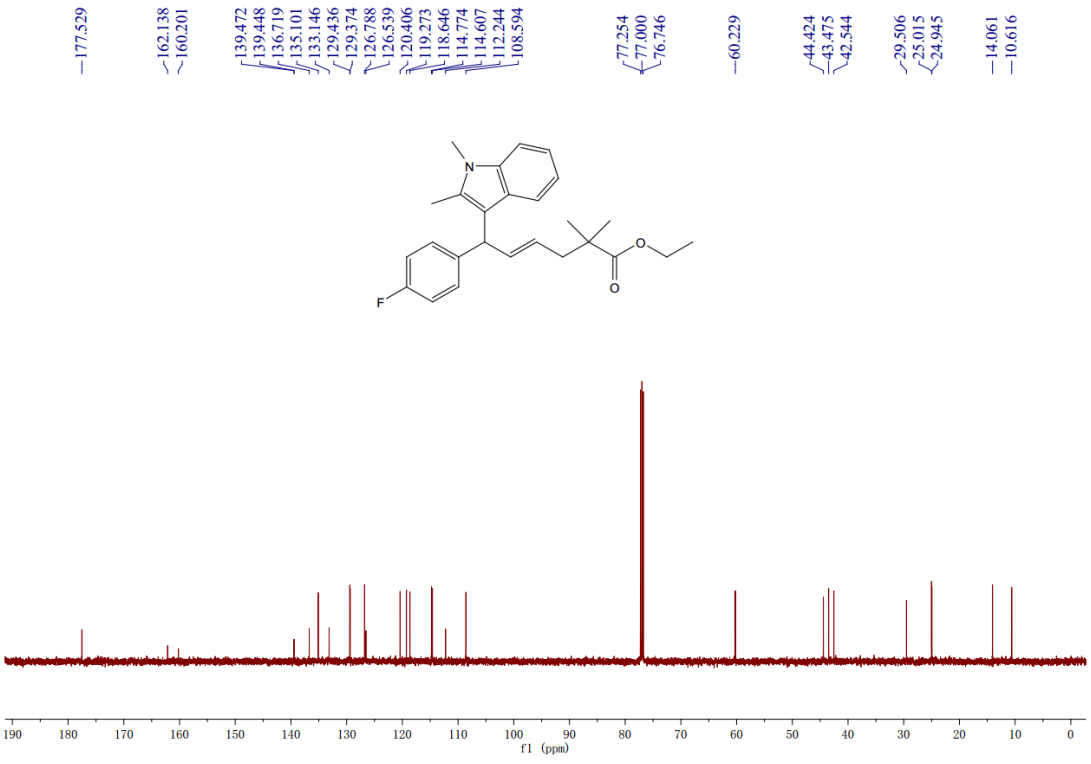


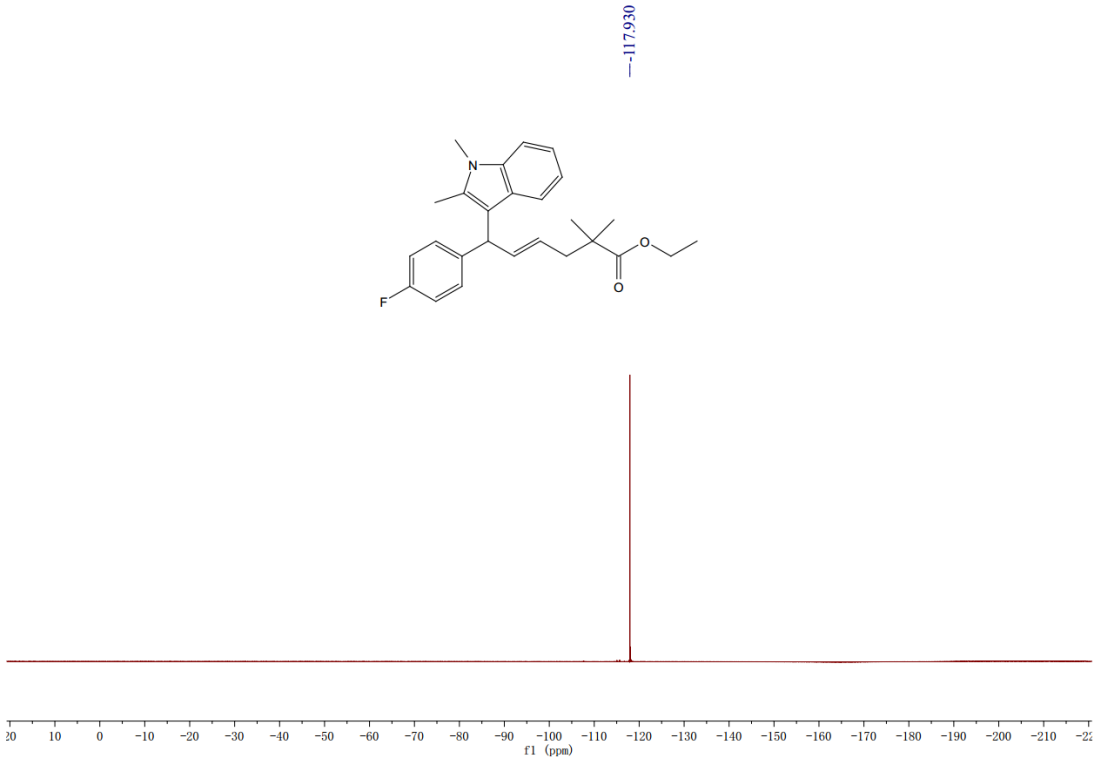


Ethyl (*E*)-6-(1,2-dimethyl-1*H*-indol-3-yl)-6-(4-fluorophenyl)-2,2-dimethylhex-4-e

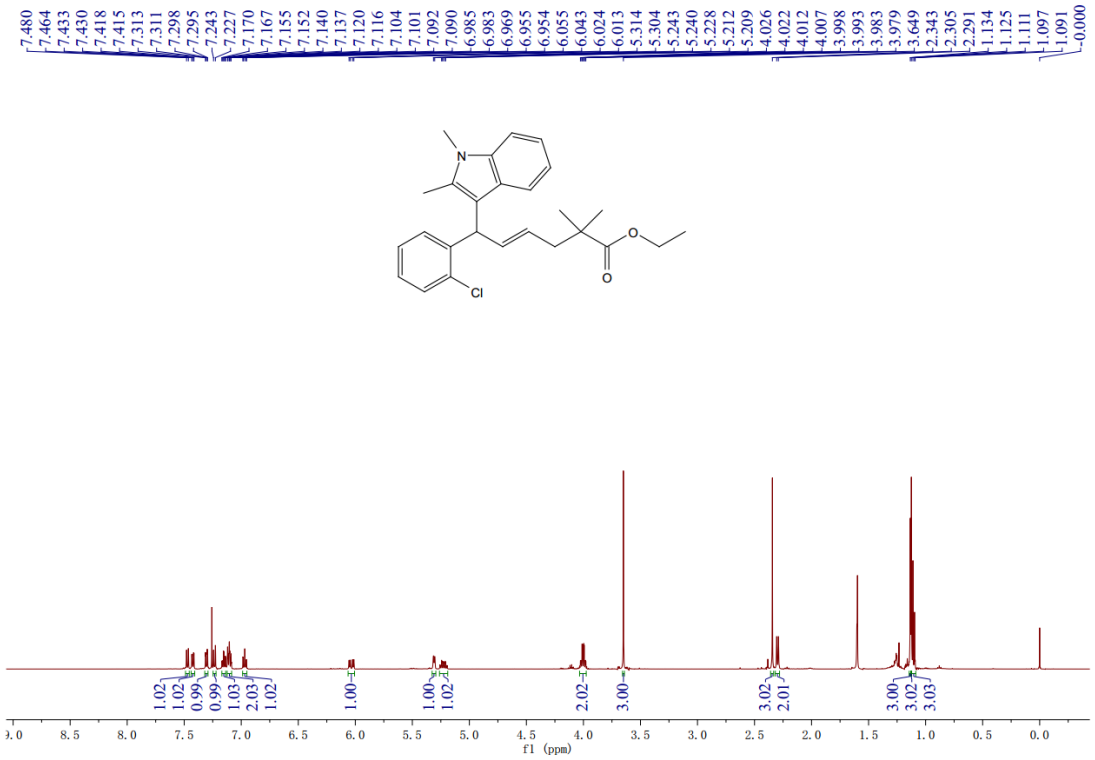
noate (4faa)

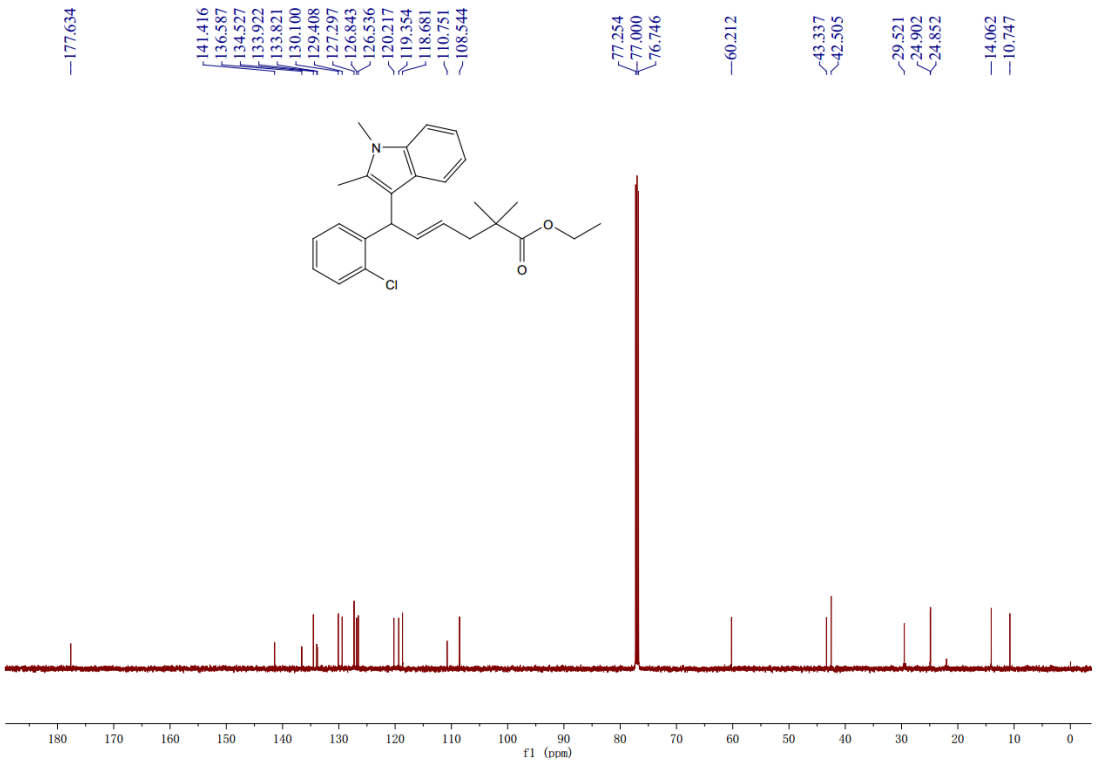





-117.930
N
F
O
O
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

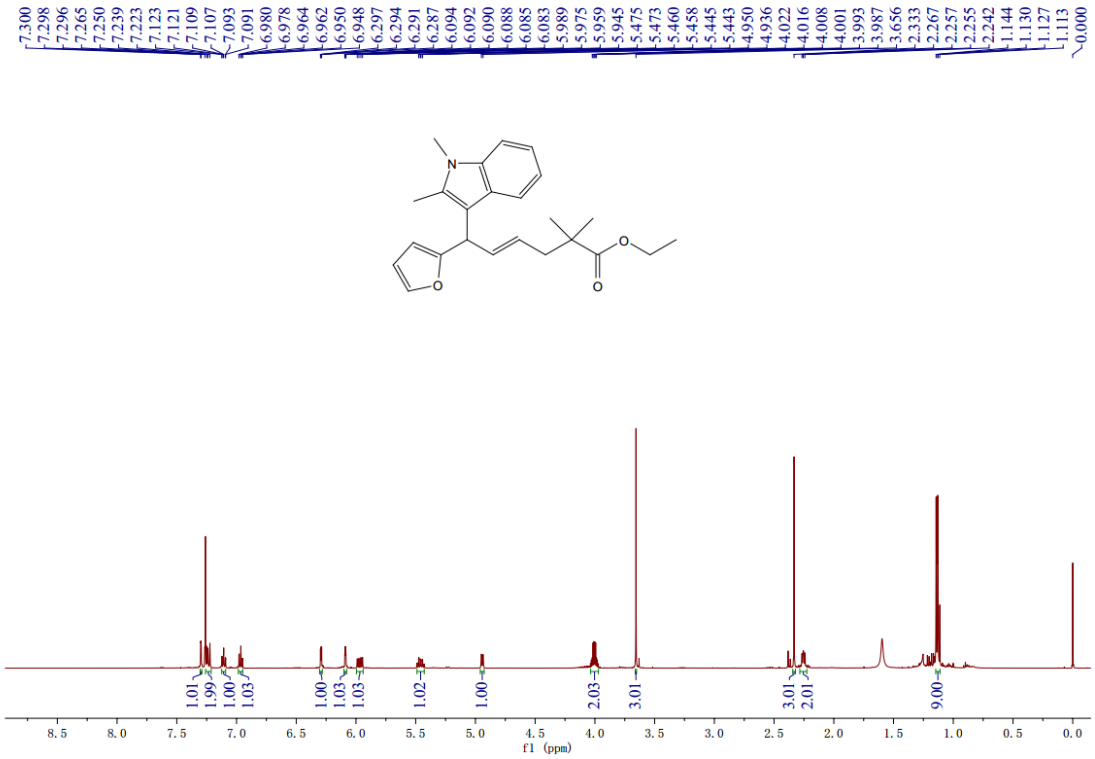
Ethyl (*E*)-6-(2-chlorophenyl)-6-(1,2-dimethyl-1*H*-indol-3-yl)-2,2-dimethylhex-4-enoate (4gaa)

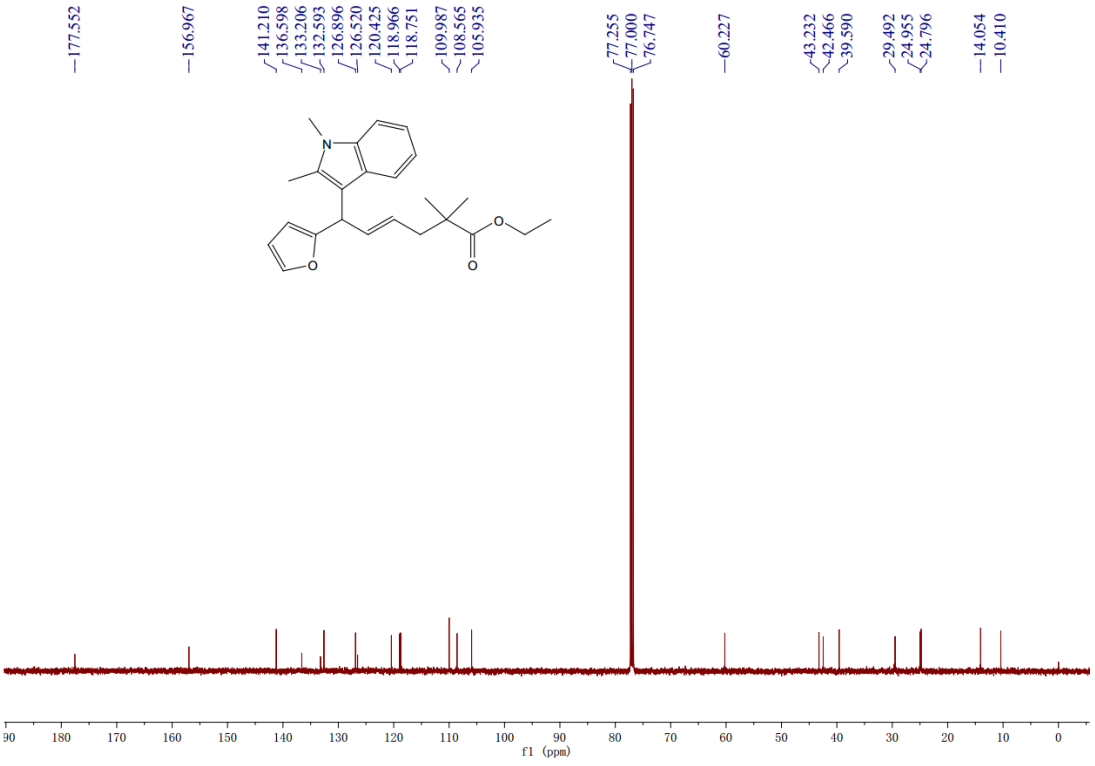




Ethyl (*E*)-6-(1,2-dimethyl-1*H*-indol-3-yl)-6-(furan-2-yl)-2,2-dimethylhex-4-enoate

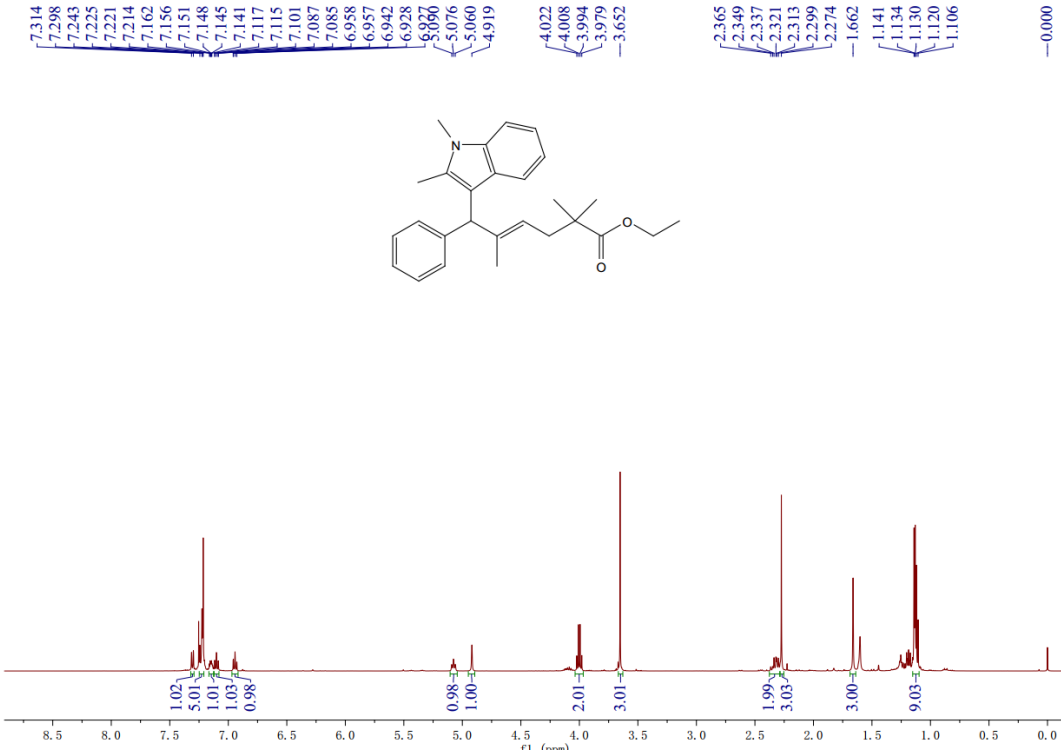
(4haa)

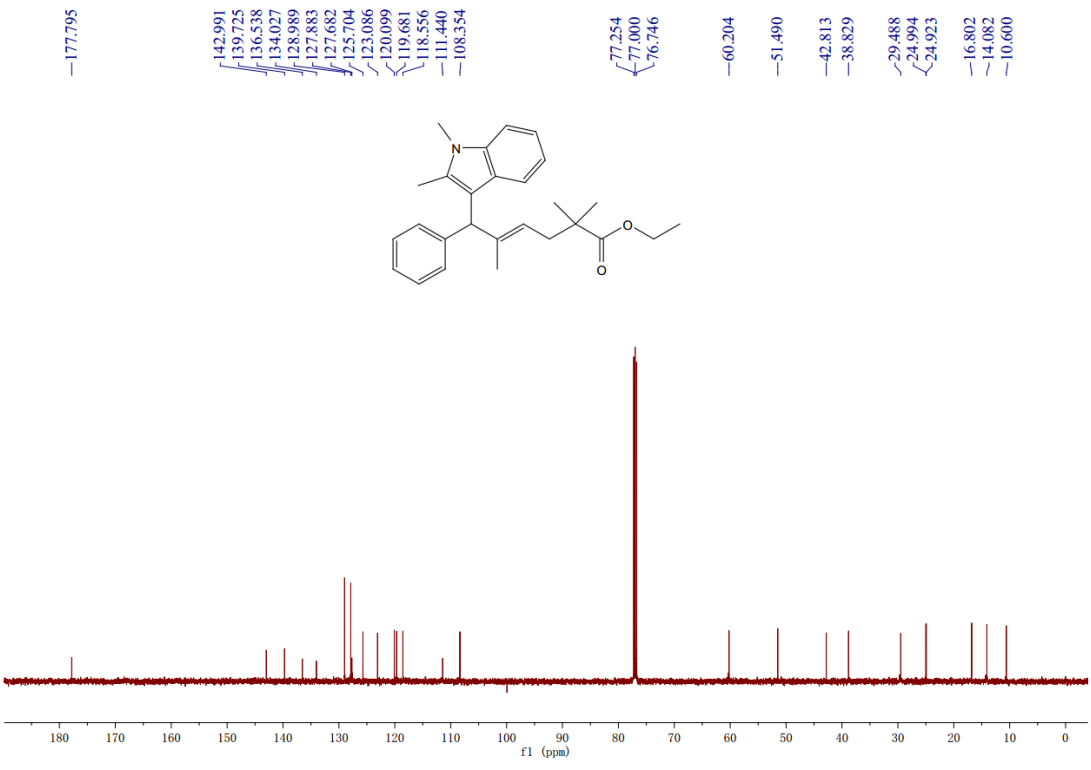




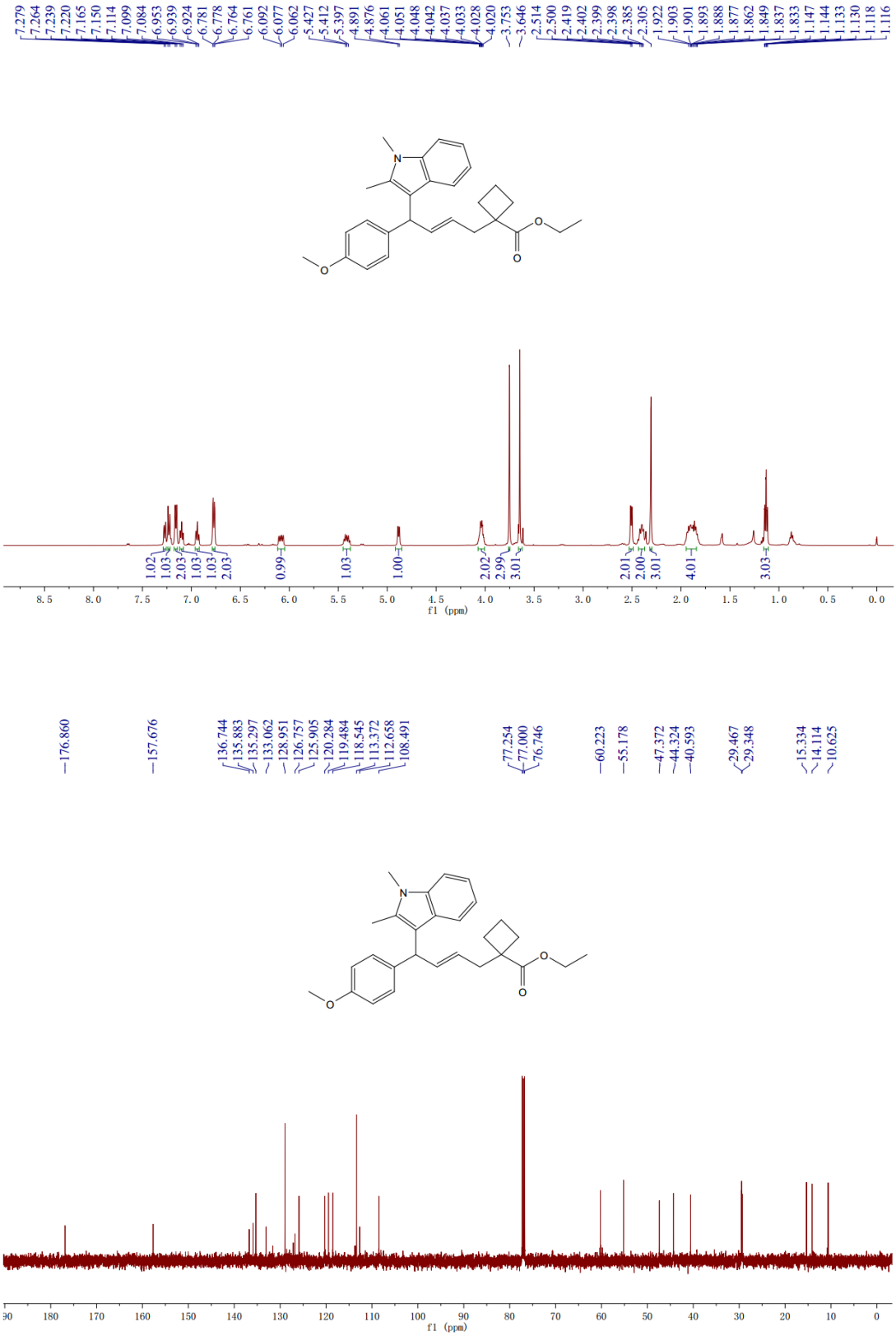
Ethyl (*E*)-6-(1,2-dimethyl-1*H*-indol-3-yl)-2,2,5-trimethyl-6-phenylhex-4-enoate

(4jaa)



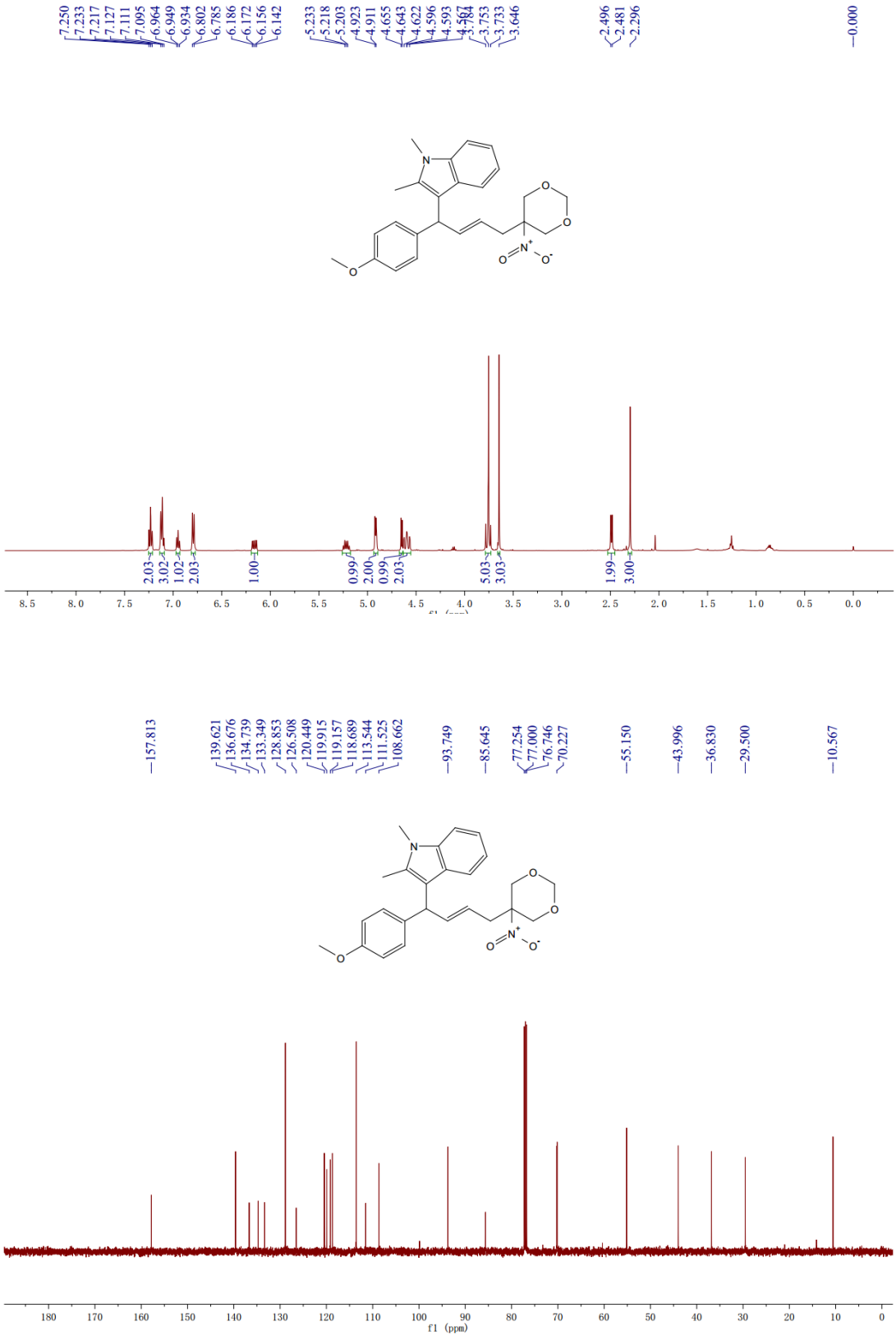


Ethyl (*E*)-1-(4-(1,2-dimethyl-1*H*-indol-3-yl)-4-(4-methoxyphenyl)but-2-en-1-yl) cyclobutane-1-carboxylate (4aba)

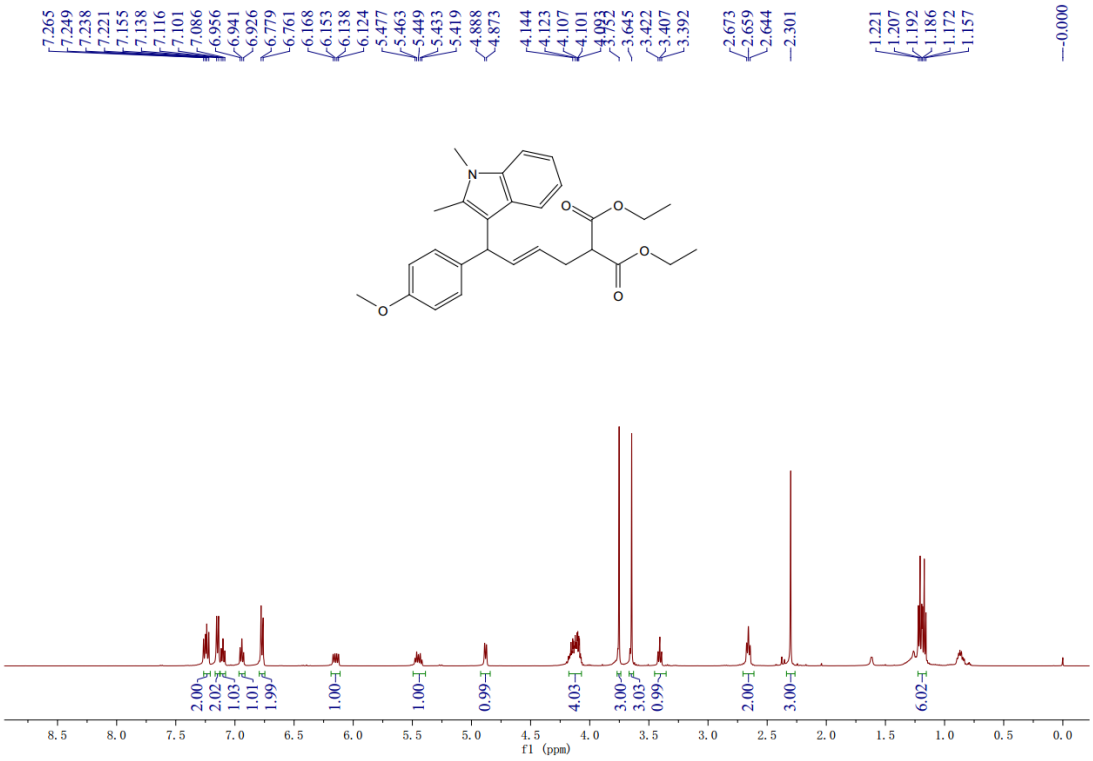


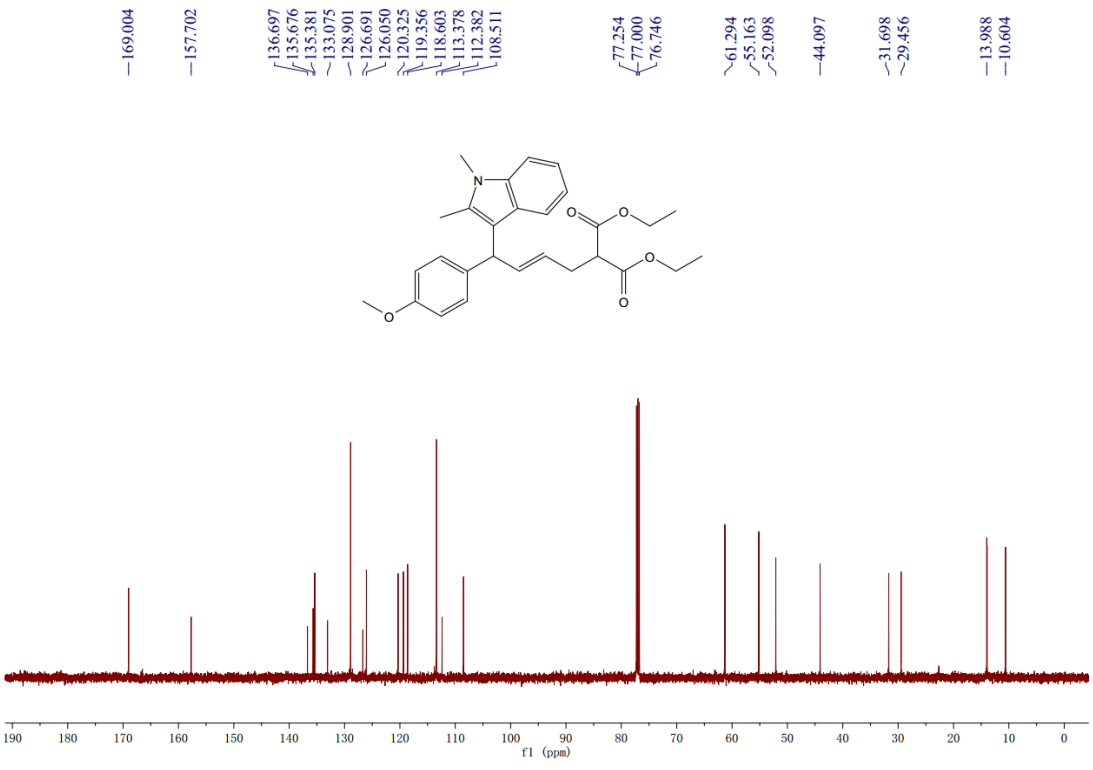
(*E*)-3-(1-(4-methoxyphenyl)-4-(5-nitro-1,3-dioxan-5-yl)but-2-en-1-yl)-1,2-dimethy

l-1*H*-indole (4aca)

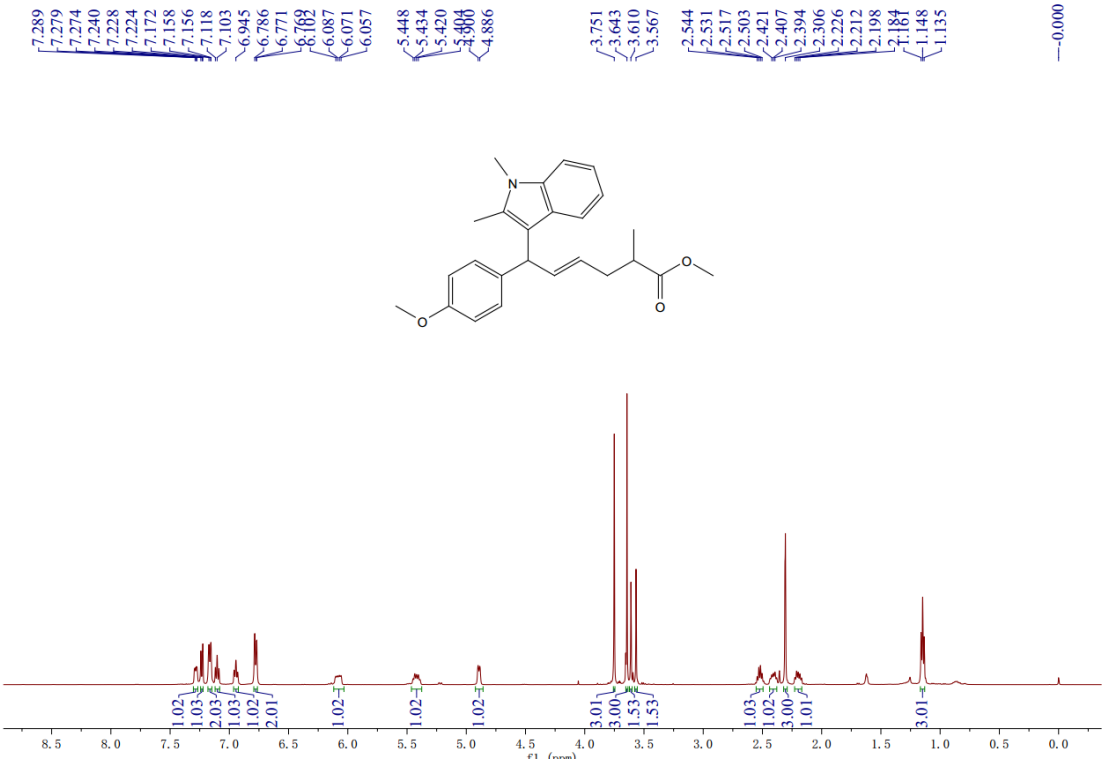


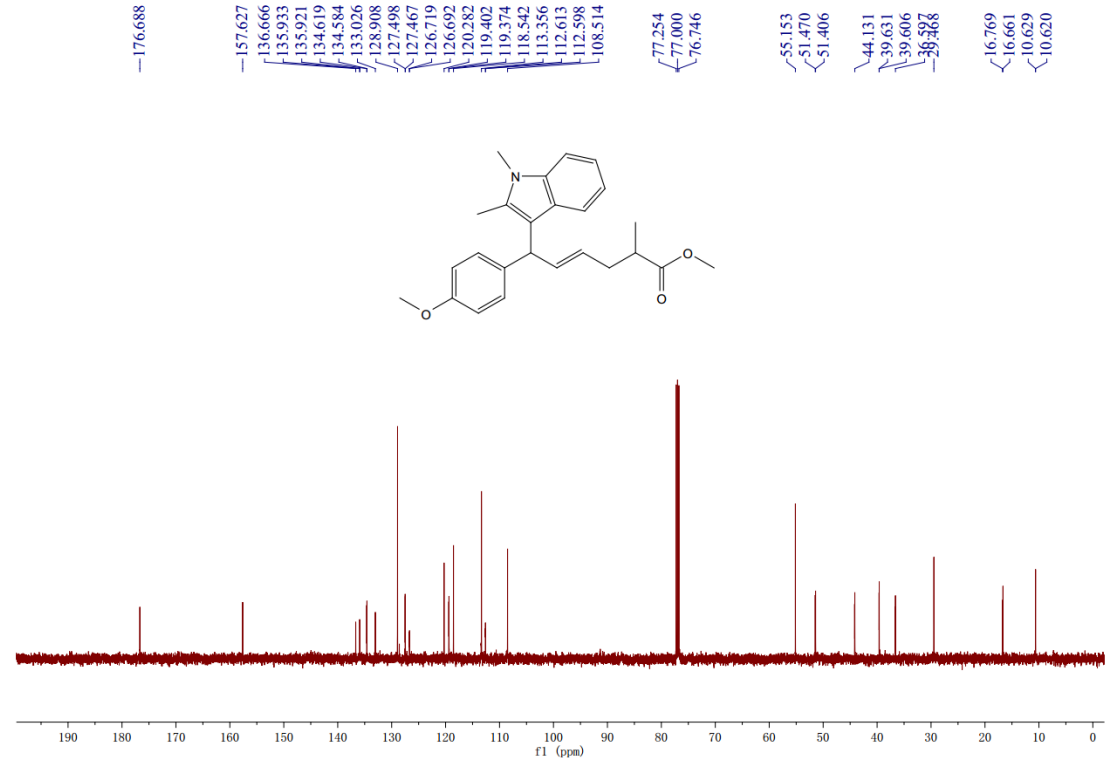
Diethyl (*E*)-2-(4-(1,2-dimethyl-1*H*-indol-3-yl)-4-(4-methoxyphenyl)but-2-en-1-yl) malonate (4ada)





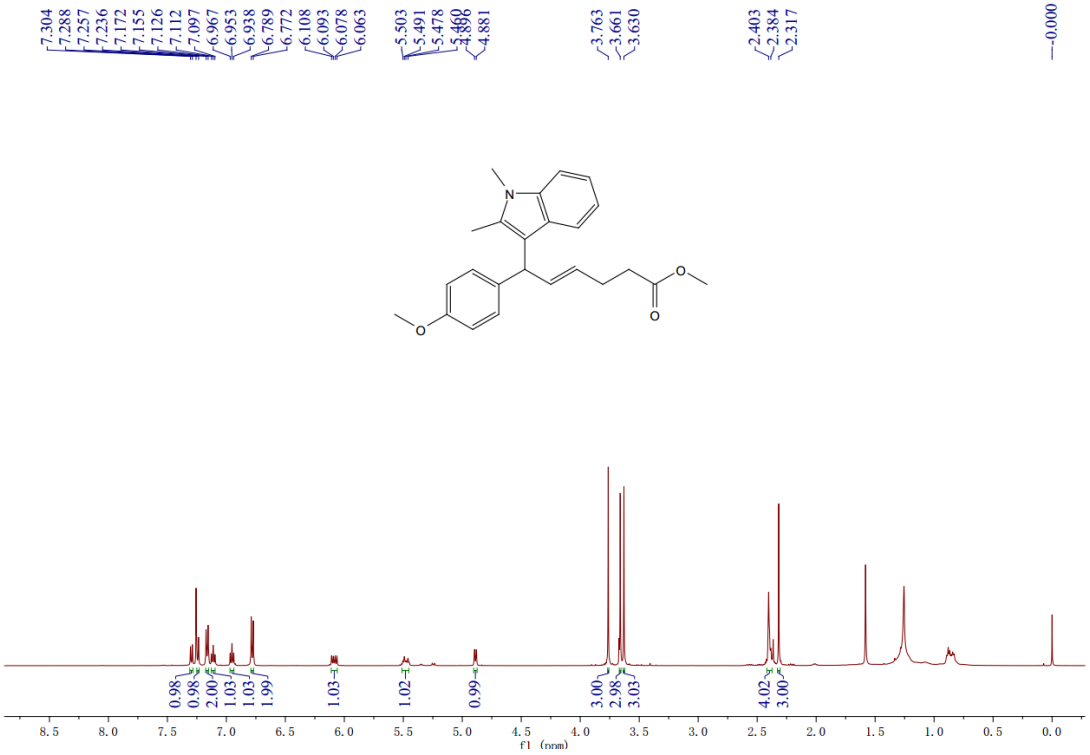
Methyl (*E*)-6-(1,2-dimethyl-1*H*-indol-3-yl)-6-(4-methoxyphenyl)-2-methylhex-4-enoate (4aea)

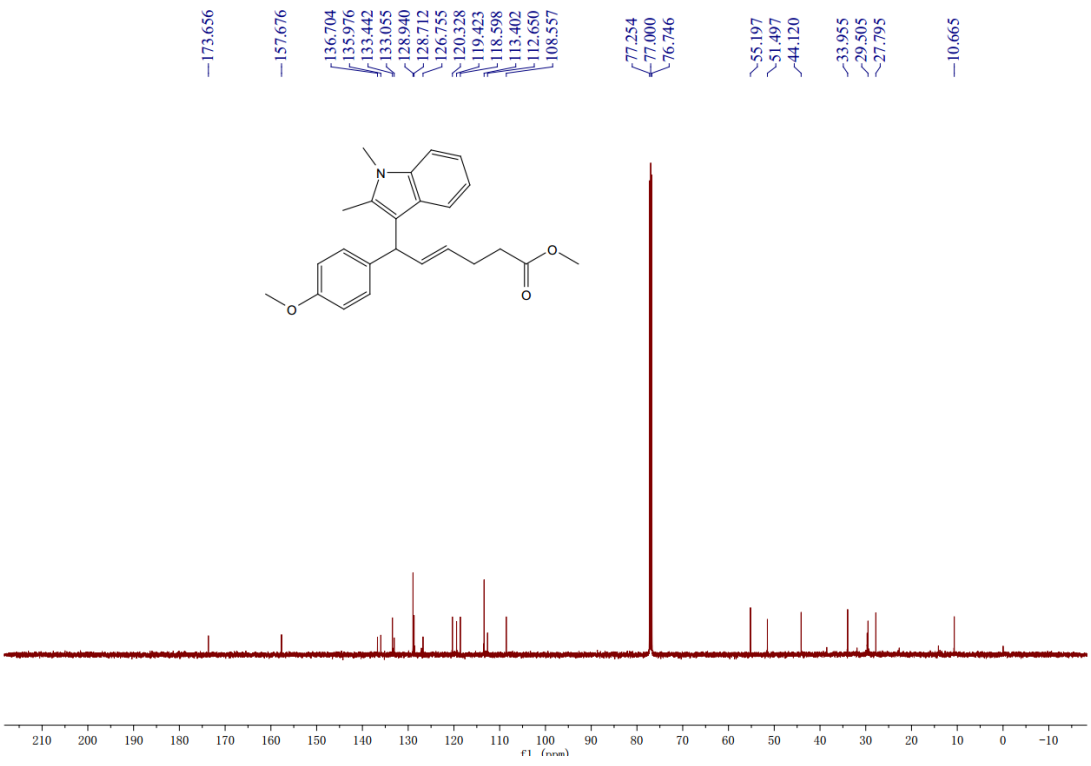




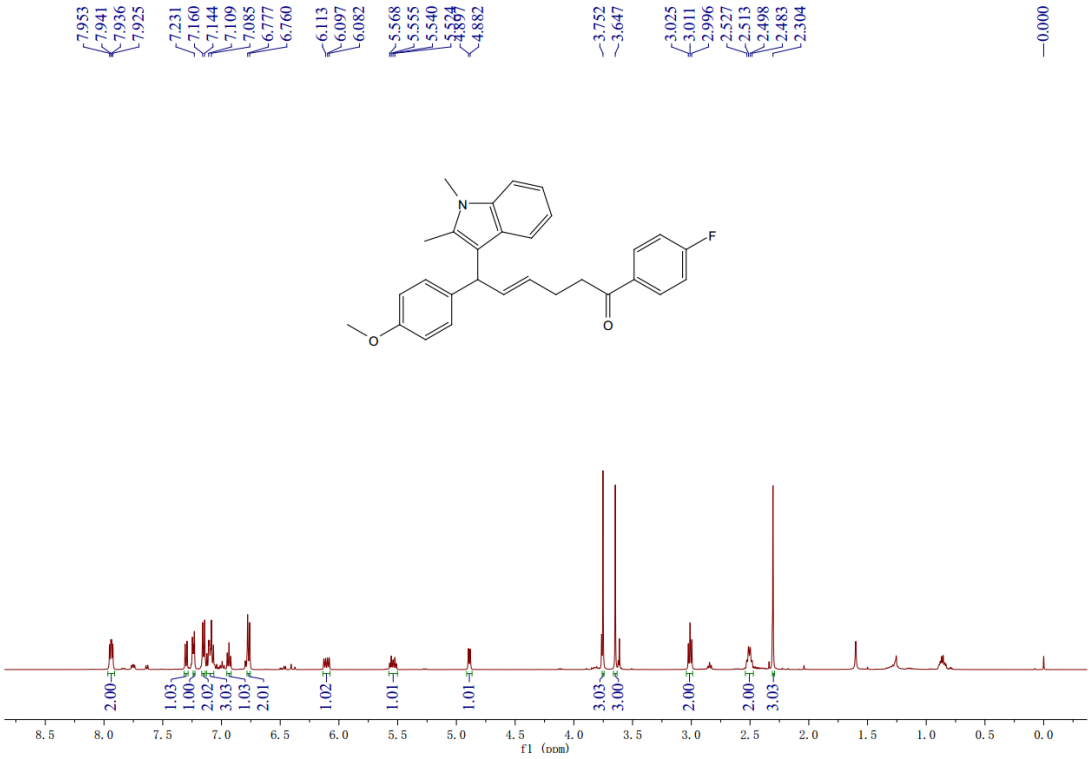
Methyl (*E*)-6-(1,2-dimethyl-1*H*-indol-3-yl)-6-(4-methoxyphenyl)hex-4-enoate

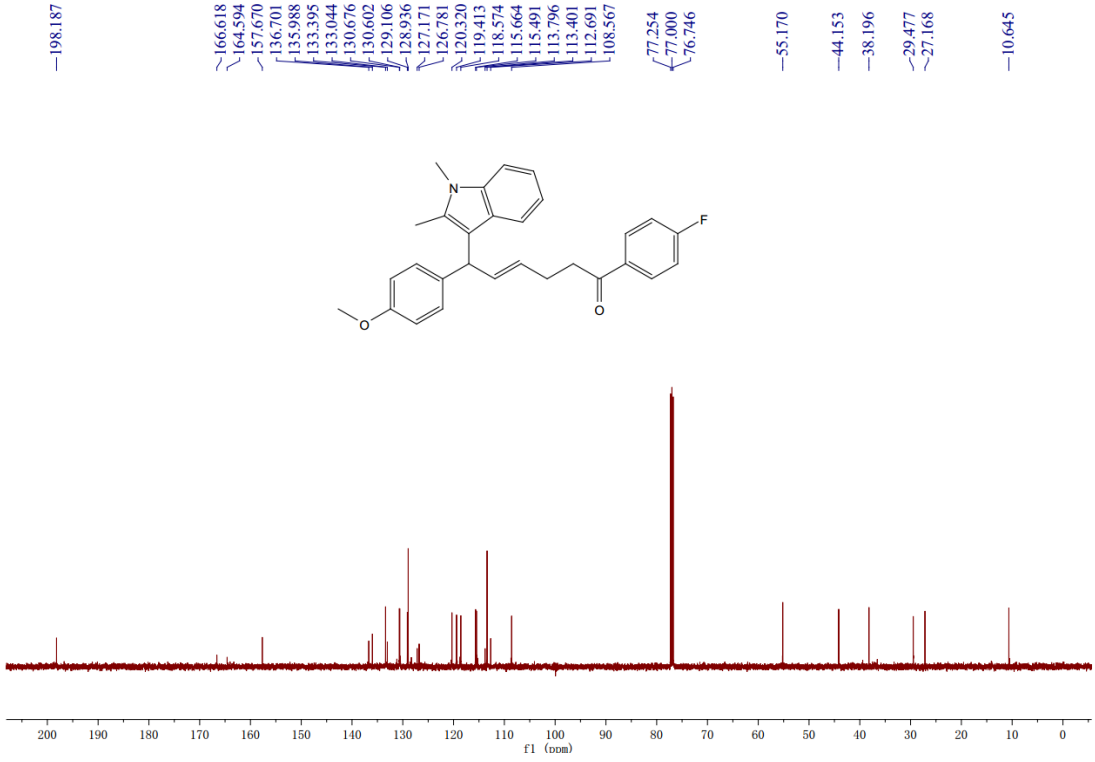
(4afa)

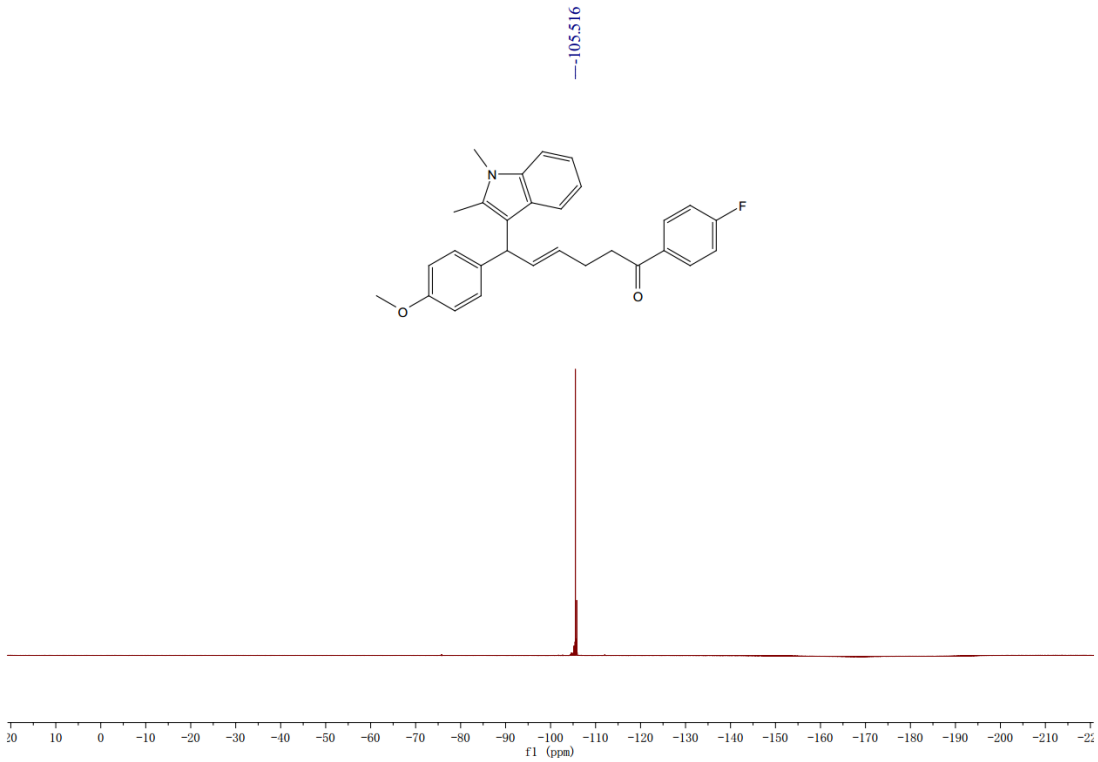




(*E*)-6-(1,2-dimethyl-1*H*-indol-3-yl)-1-(4-fluorophenyl)-6-(4-methoxyphenyl)hex-4-en-1-one (4aga)



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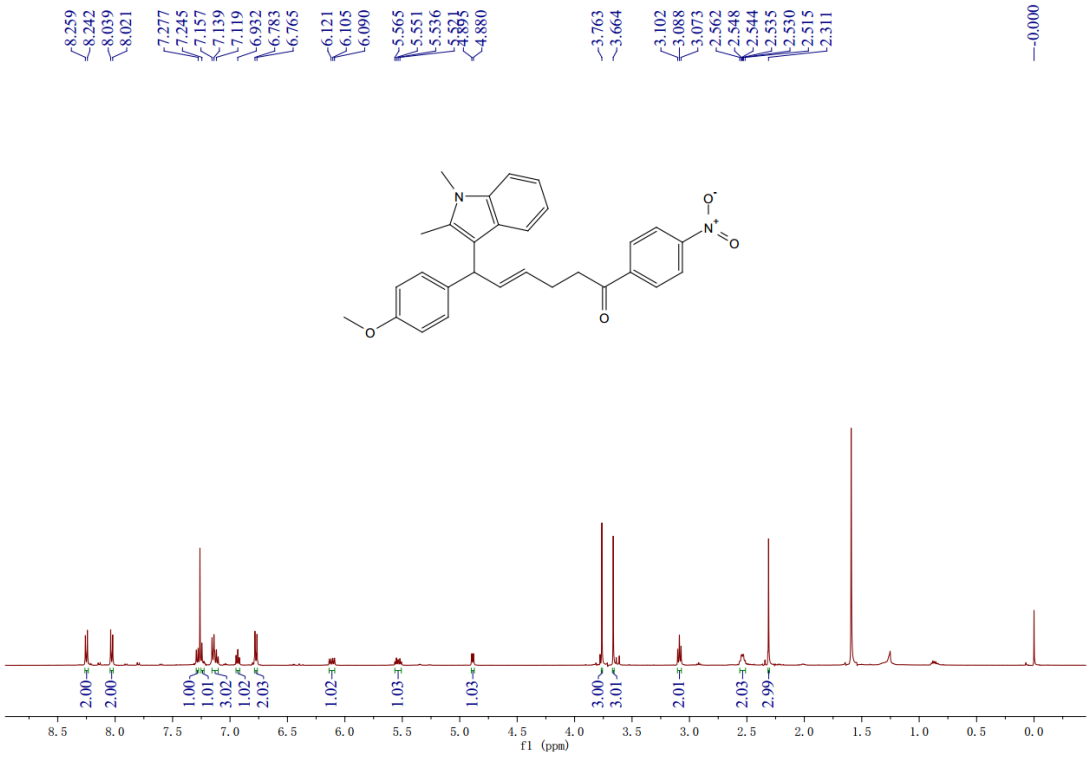
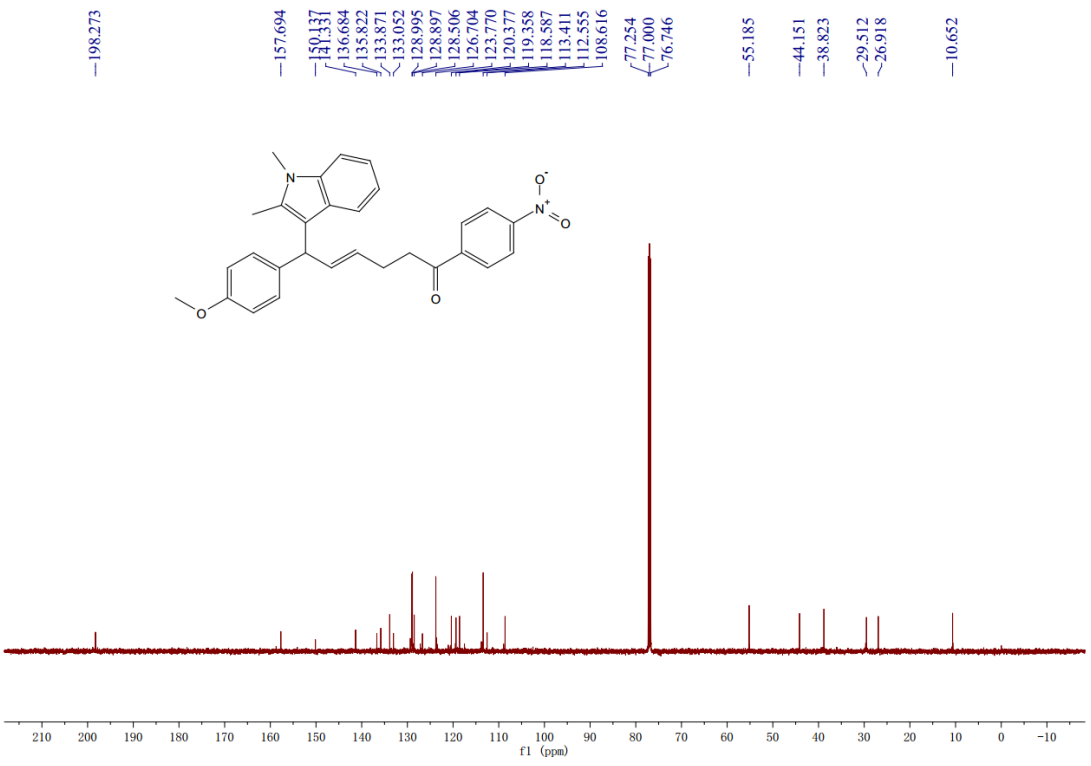
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

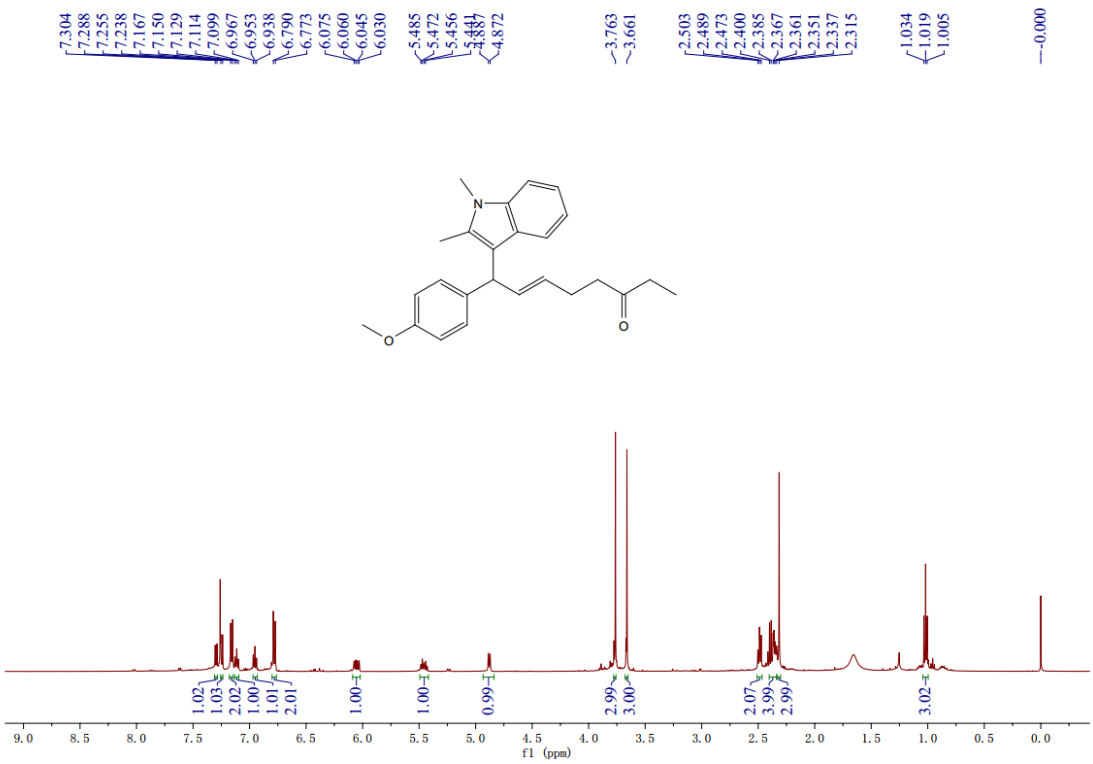
(*E*)-6-(1,2-dimethyl-1*H*-indol-3-yl)-6-(4-methoxyphenyl)-1-(4-nitrophenyl)hex-4-e

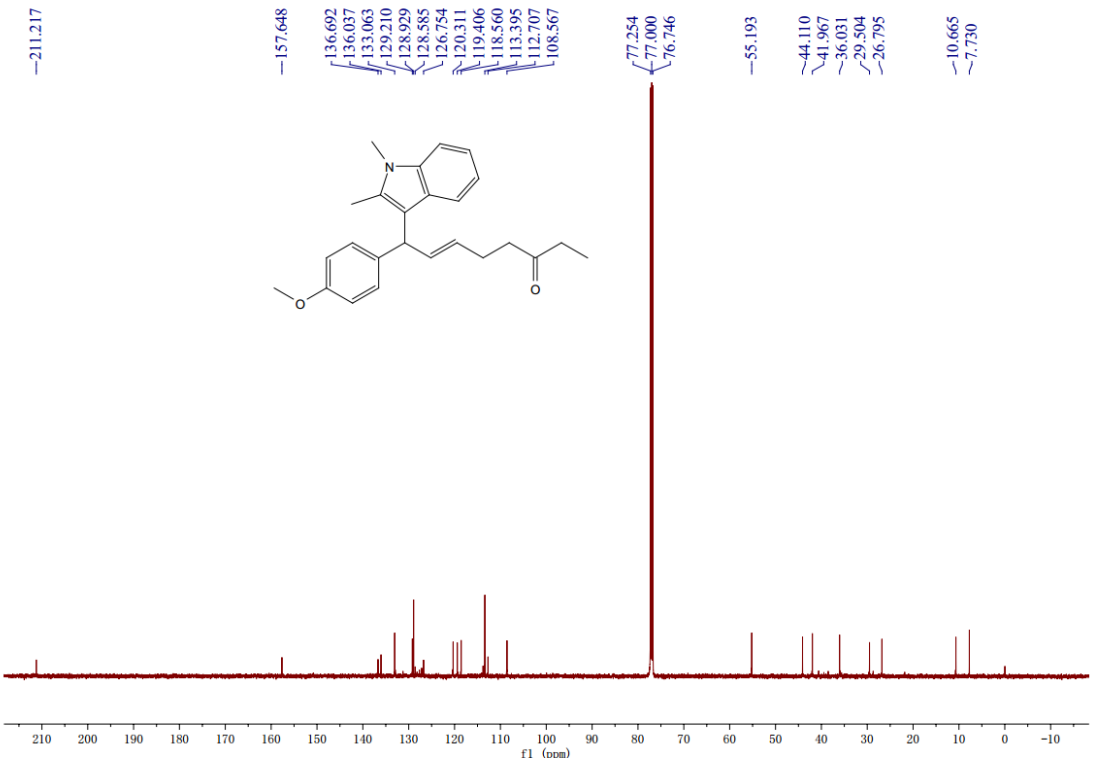
n-1-one (4aha)



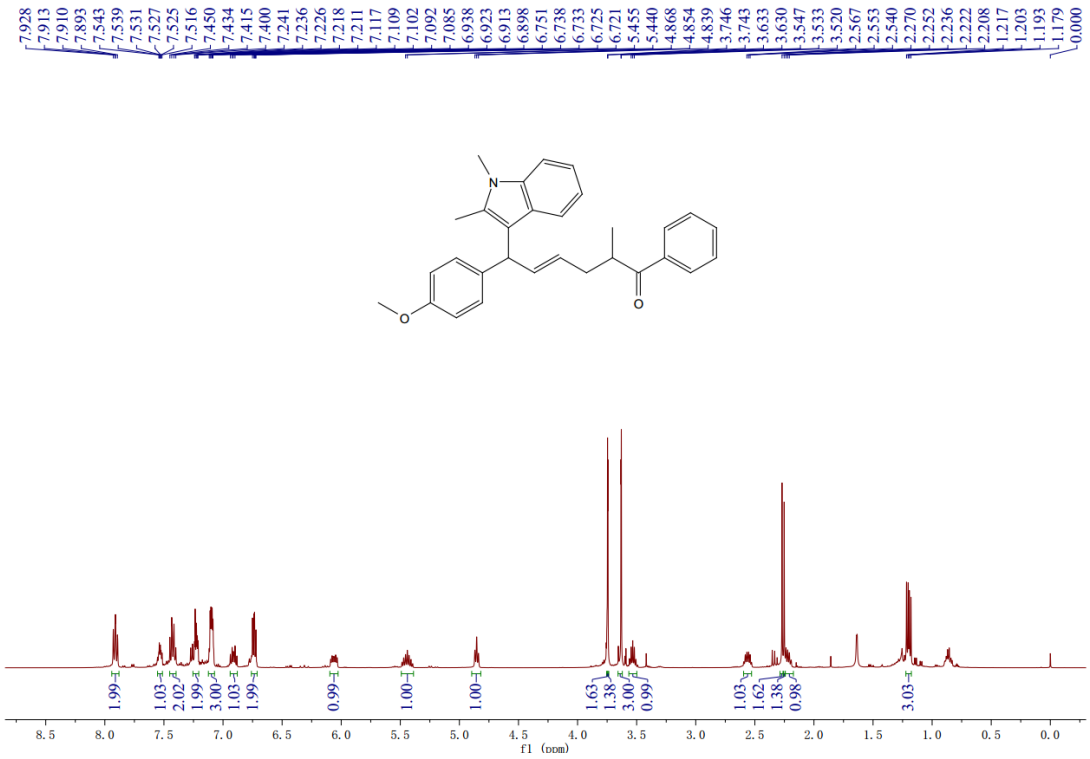


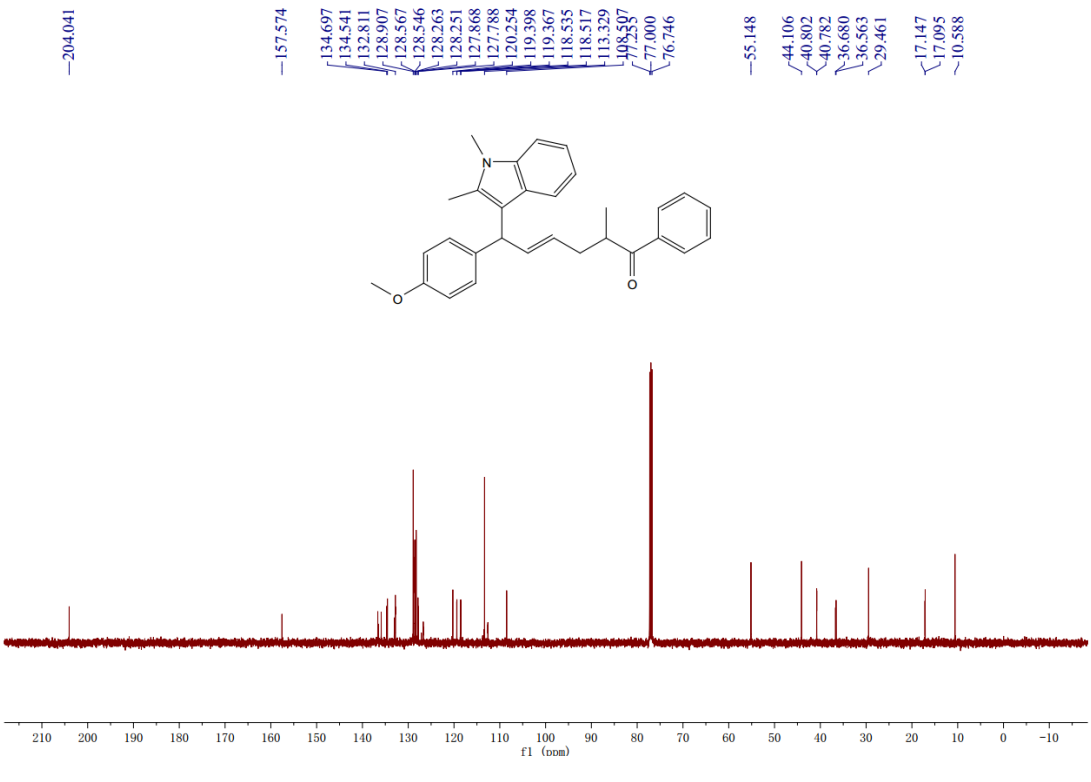
(*E*)-8-(1,2-dimethyl-1*H*-indol-3-yl)-8-(4-methoxyphenyl)oct-6-en-3-one (4aia)



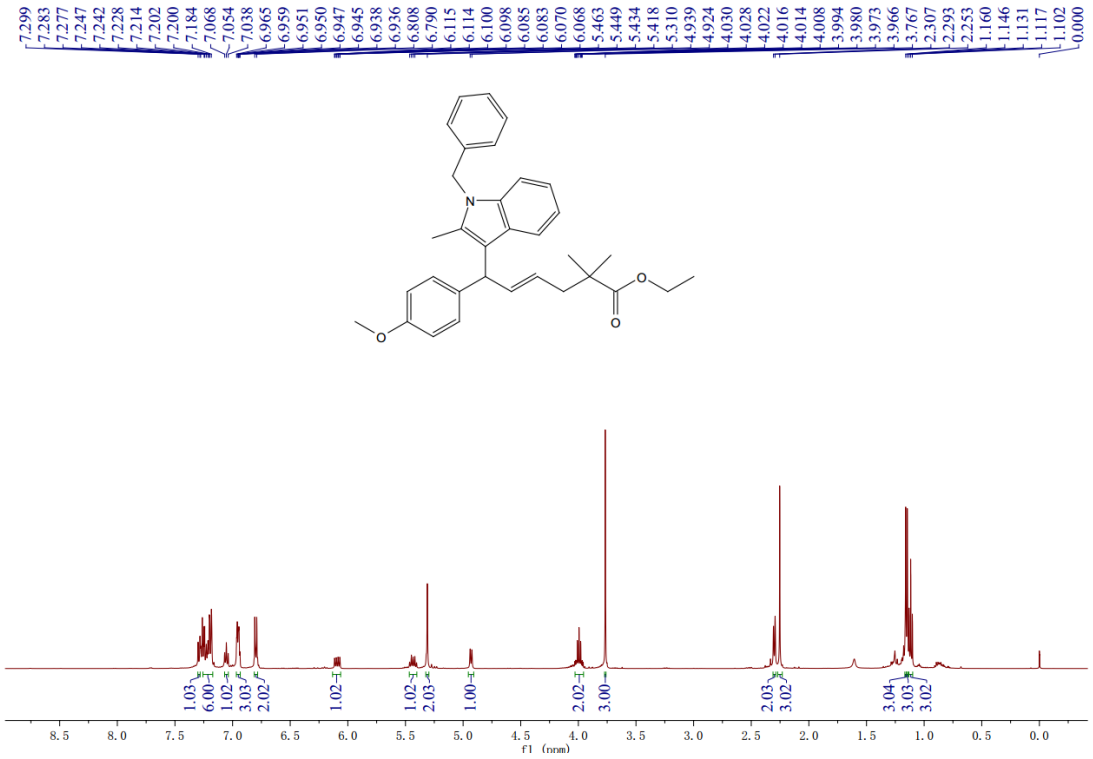


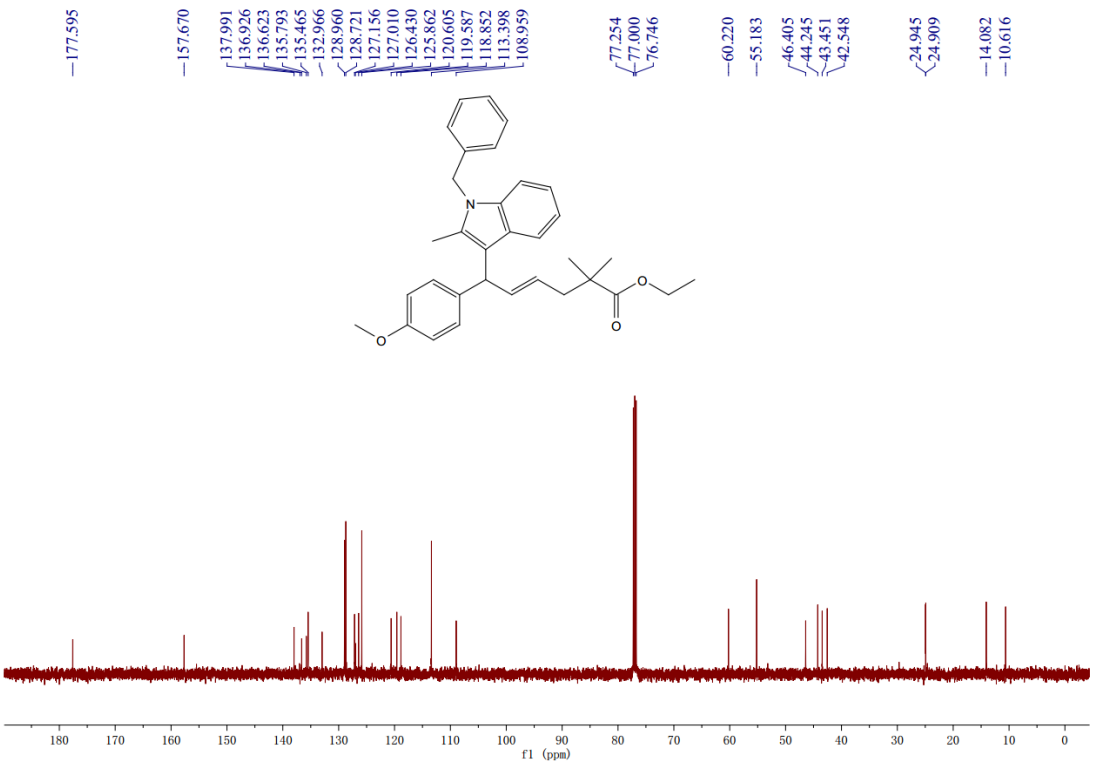
(*E*)-6-(1,2-dimethyl-1*H*-indol-3-yl)-6-(4-methoxyphenyl)-2-methyl-1-phenylhex-4-en-1-one (4aja)



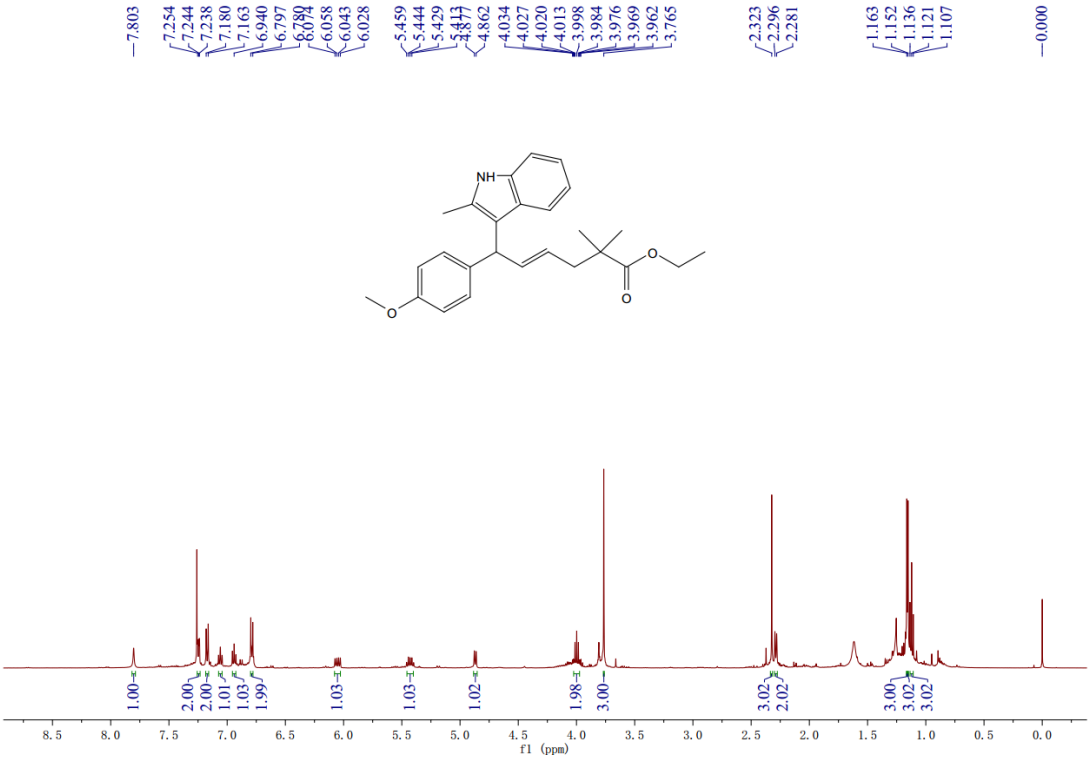


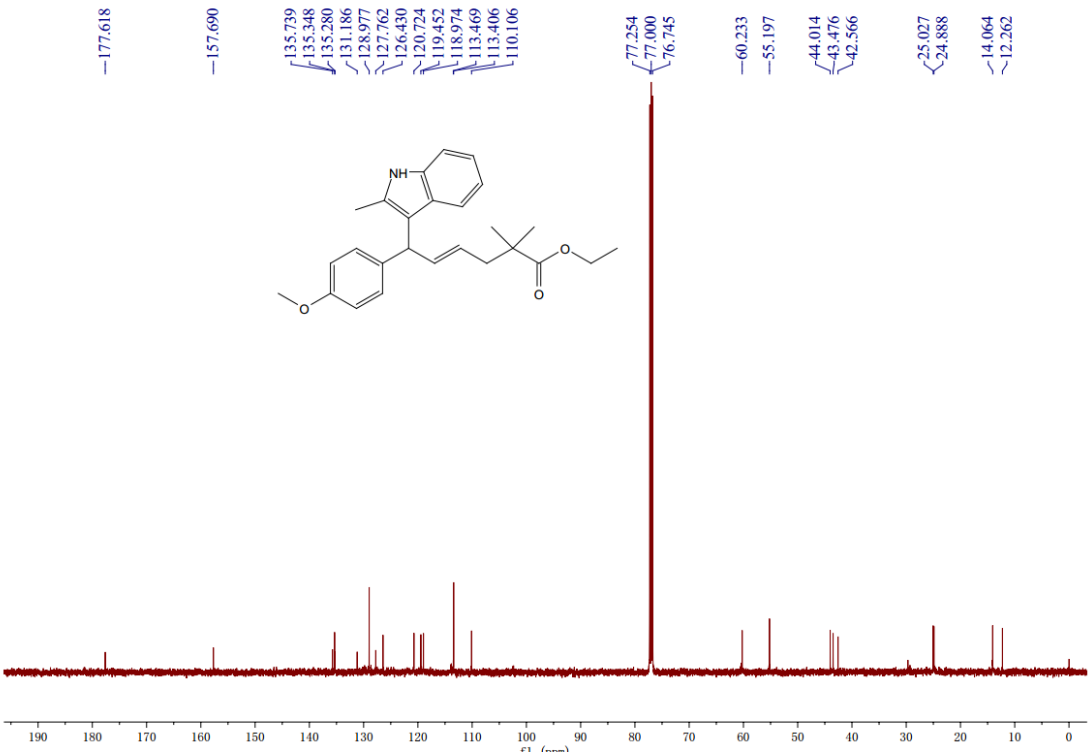
Ethyl (*E*)-6-(1-benzyl-2-methyl-1*H*-indol-3-yl)-6-(4-methoxyphenyl)-2,2-dimethylhex-4-enoate (4aab)



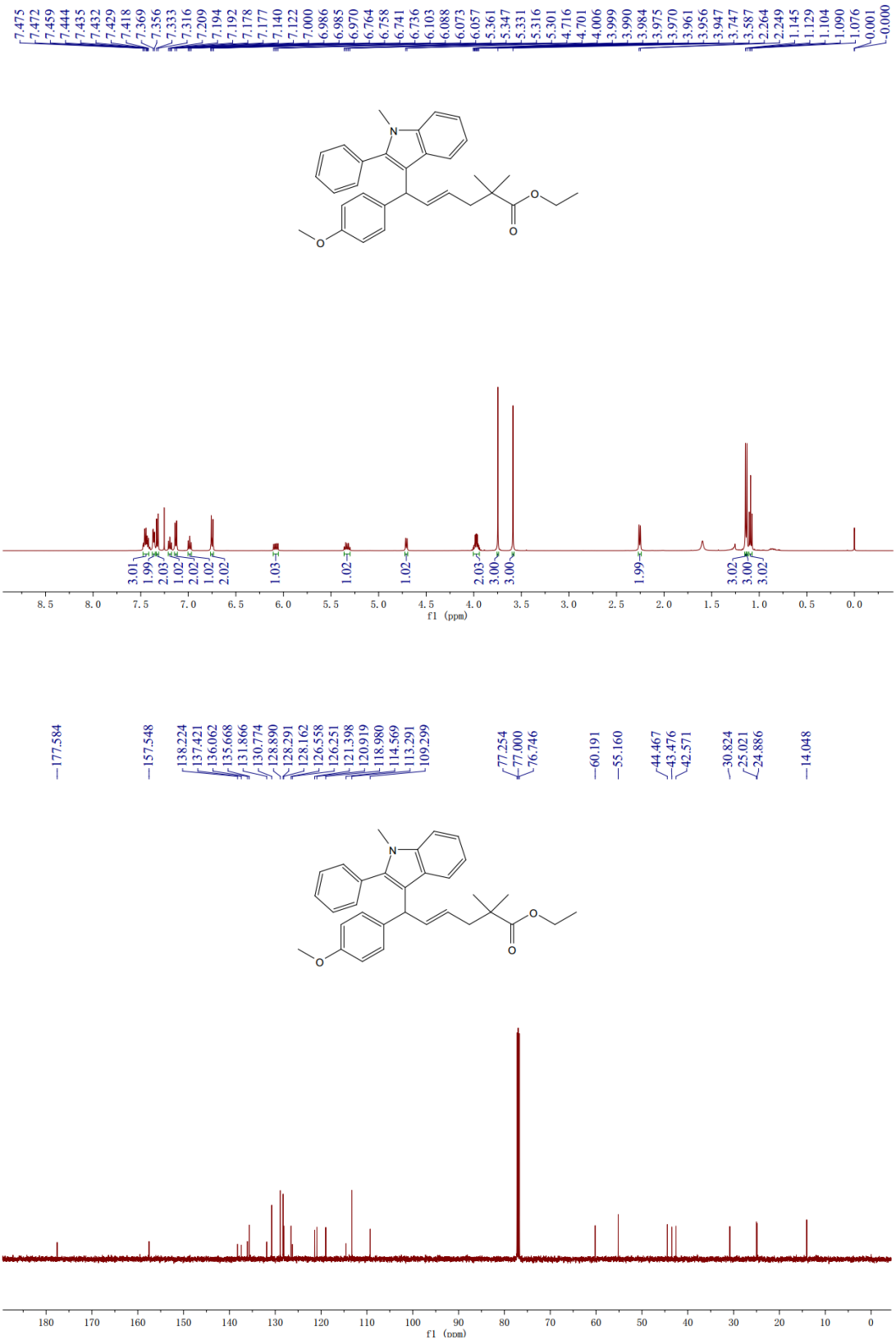


Ethyl (*E*)-6-(4-methoxyphenyl)-2,2-dimethyl-6-(2-methyl-1*H*-indol-3-yl)hex-4-en oate (4aac)

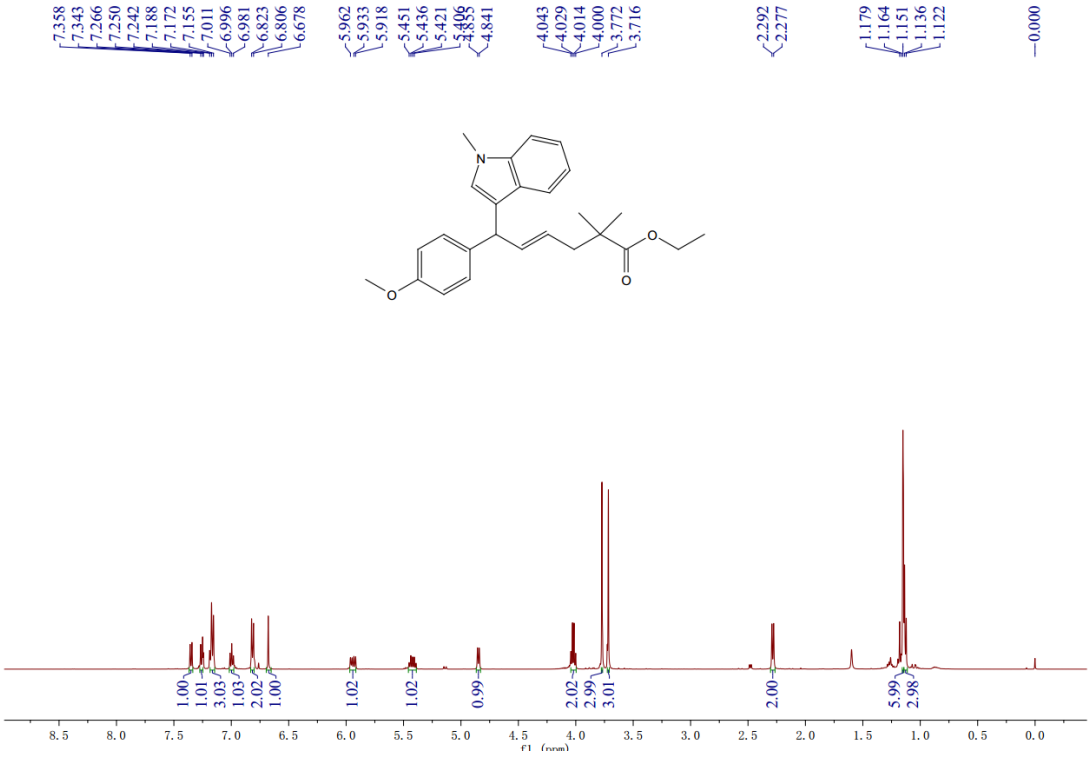


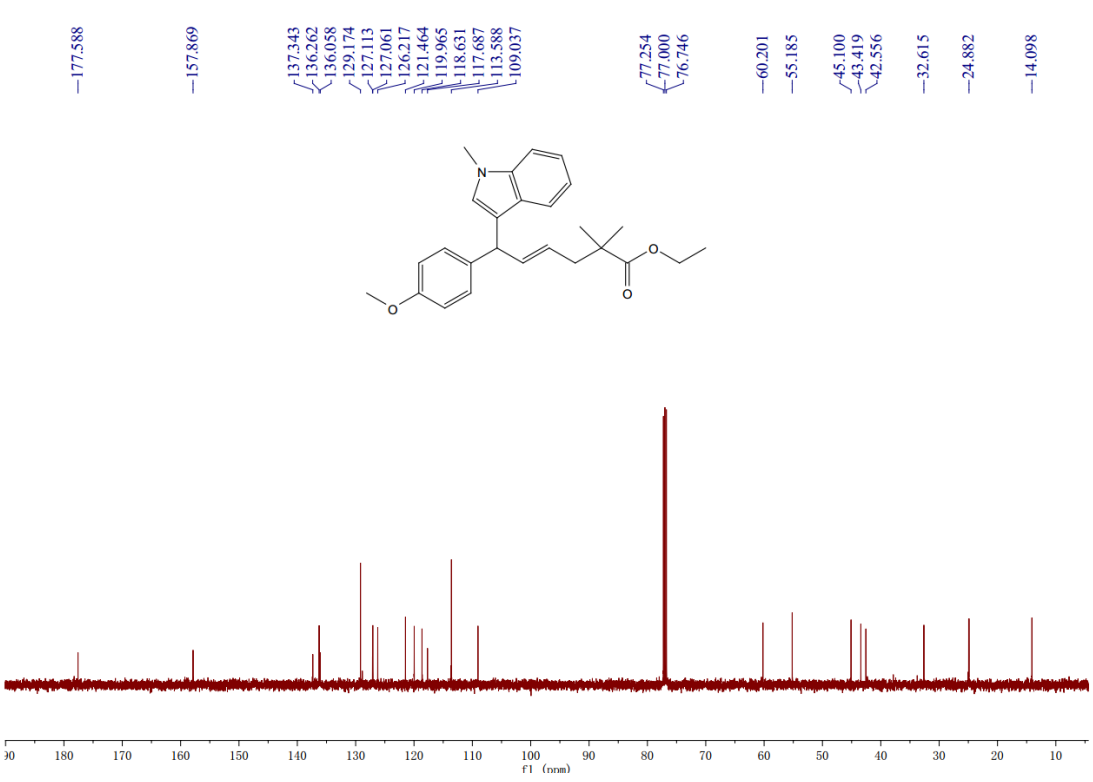


Ethyl (*E*)-6-(4-methoxyphenyl)-2,2-dimethyl-6-(1-methyl-2-phenyl-1*H*-indol-3-yl) hex-4-enoate (4aad)



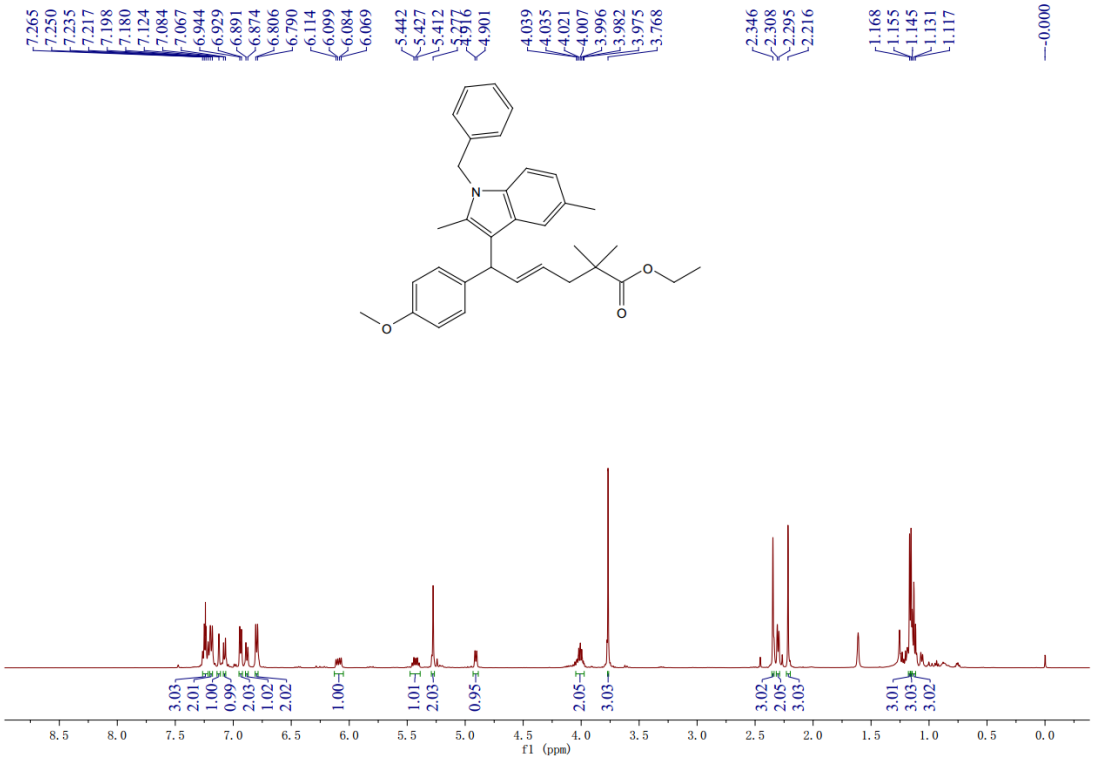
Ethyl (*E*)-6-(4-methoxyphenyl)-2,2-dimethyl-6-(1-methyl-1*H*-indol-3-yl)hex-4-en oate (4aae)

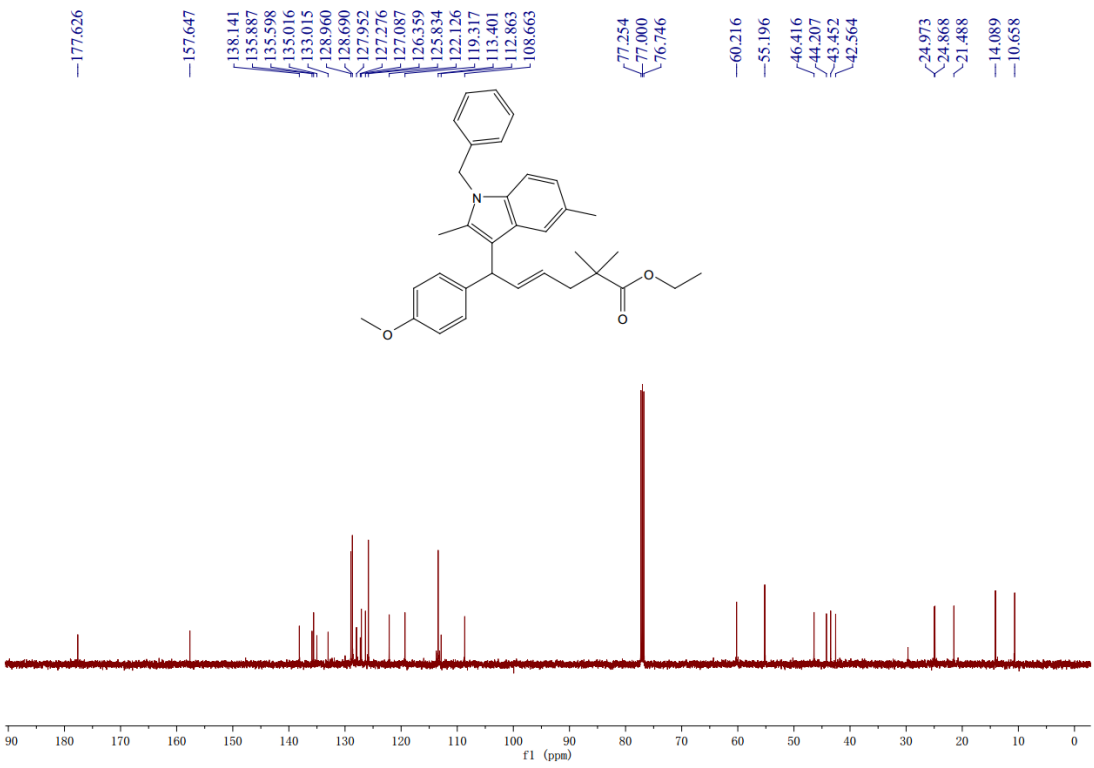




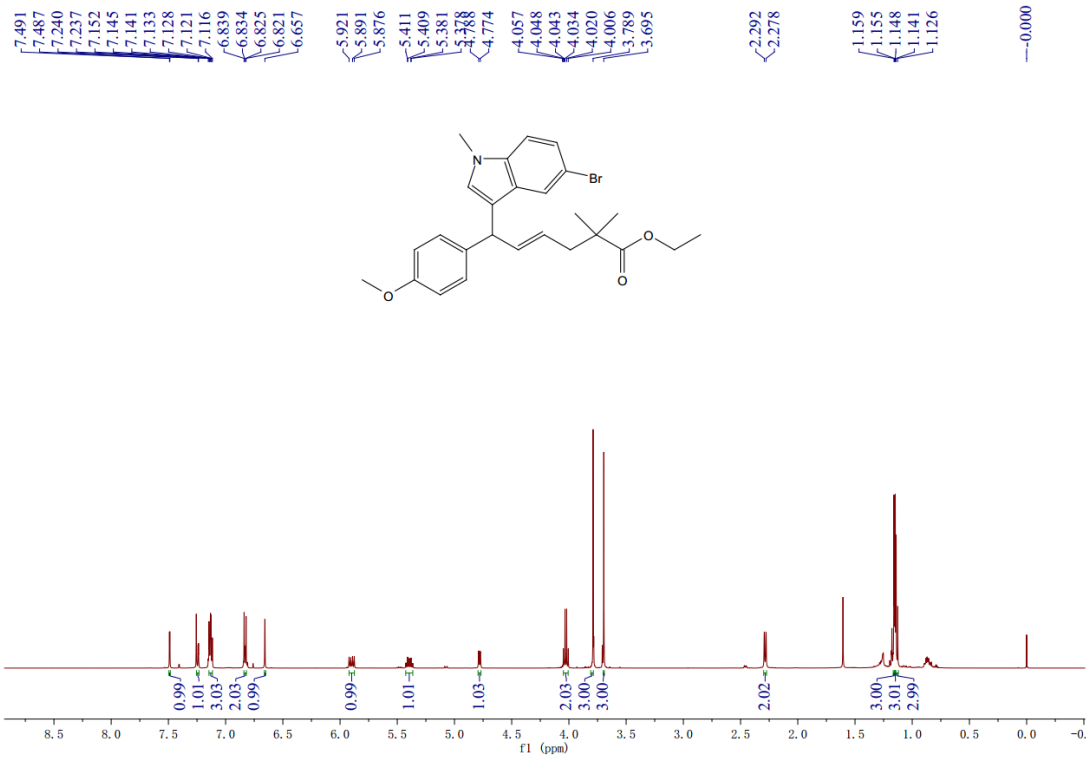
Ethyl (*E*)-6-(1-benzyl-2,5-dimethyl-1*H*-indol-3-yl)-6-(4-methoxyphenyl)-2,2-dim

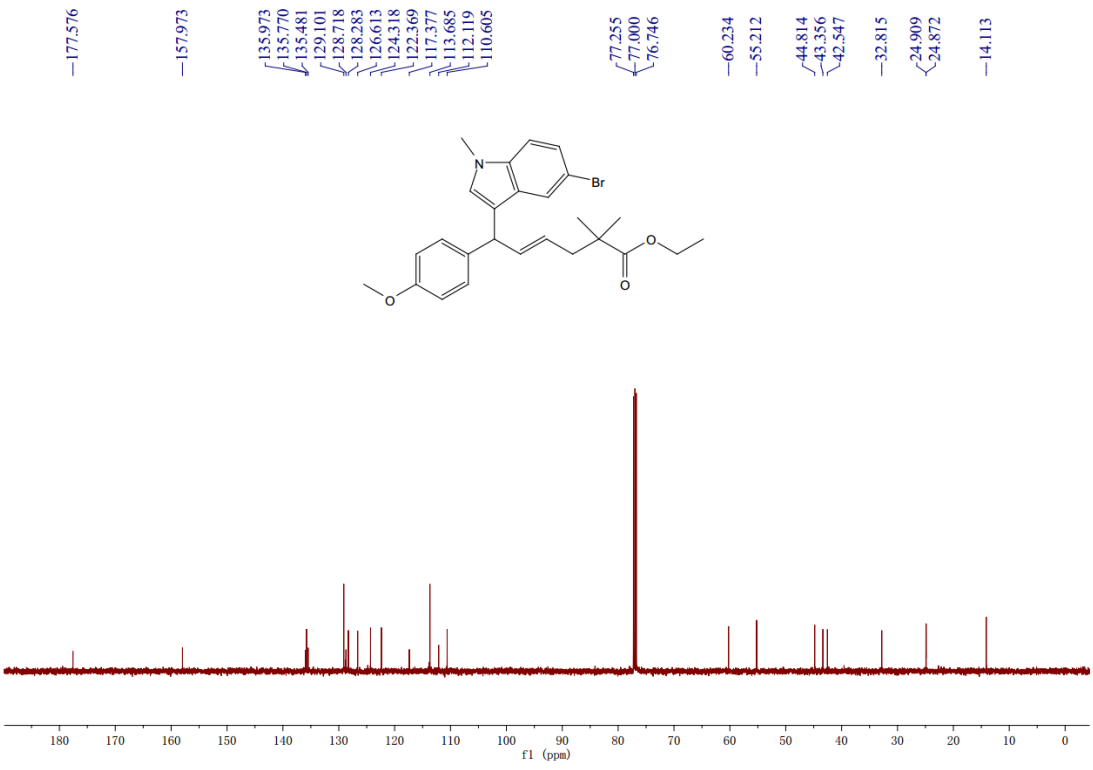
ethylhex-4-enoate (4aaf)



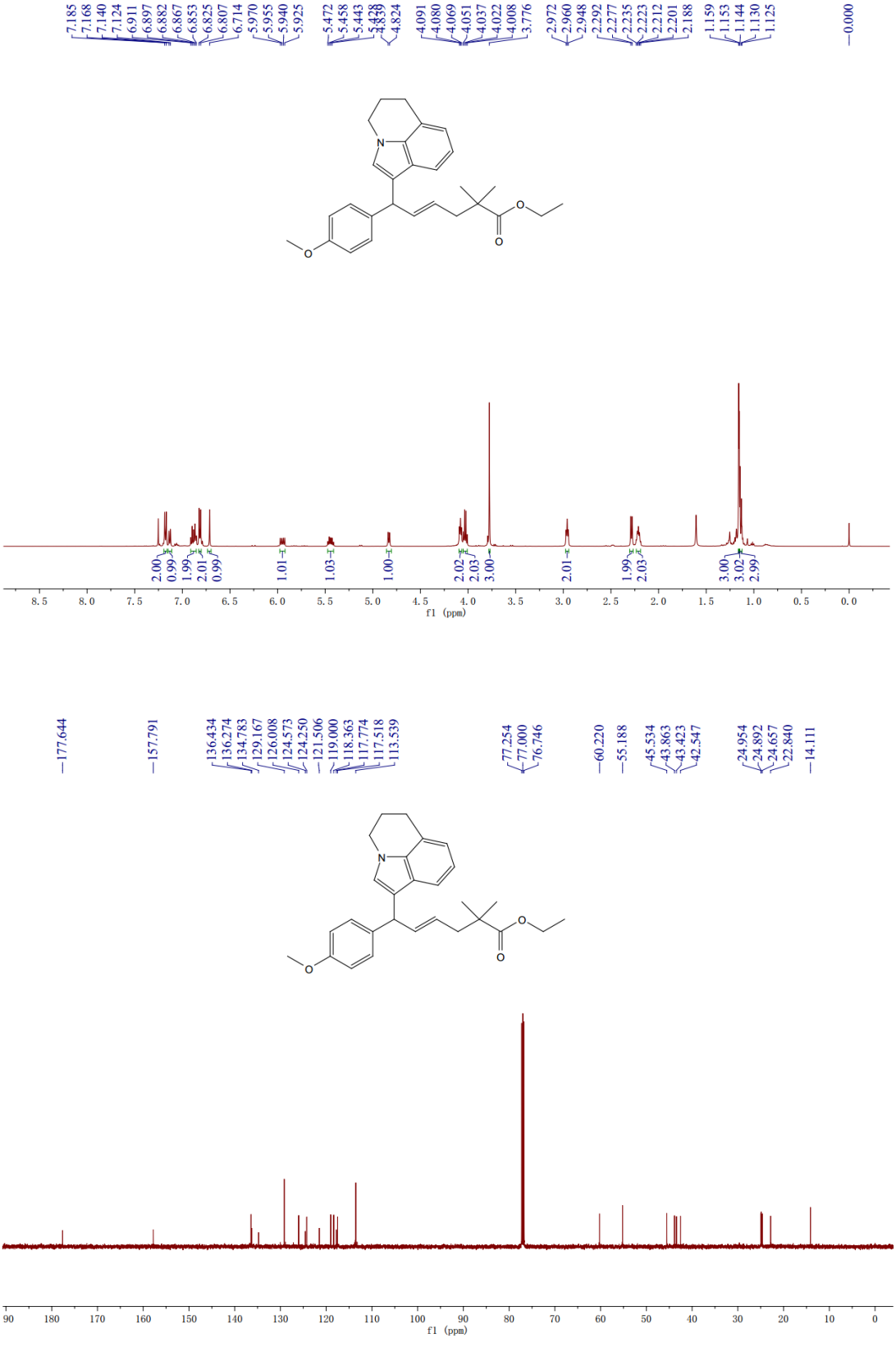


Ethyl (*E*)-6-(5-bromo-1-methyl-1*H*-indol-3-yl)-6-(4-methoxyphenyl)-2,2-dimethylhex-4-enoate (4aag)



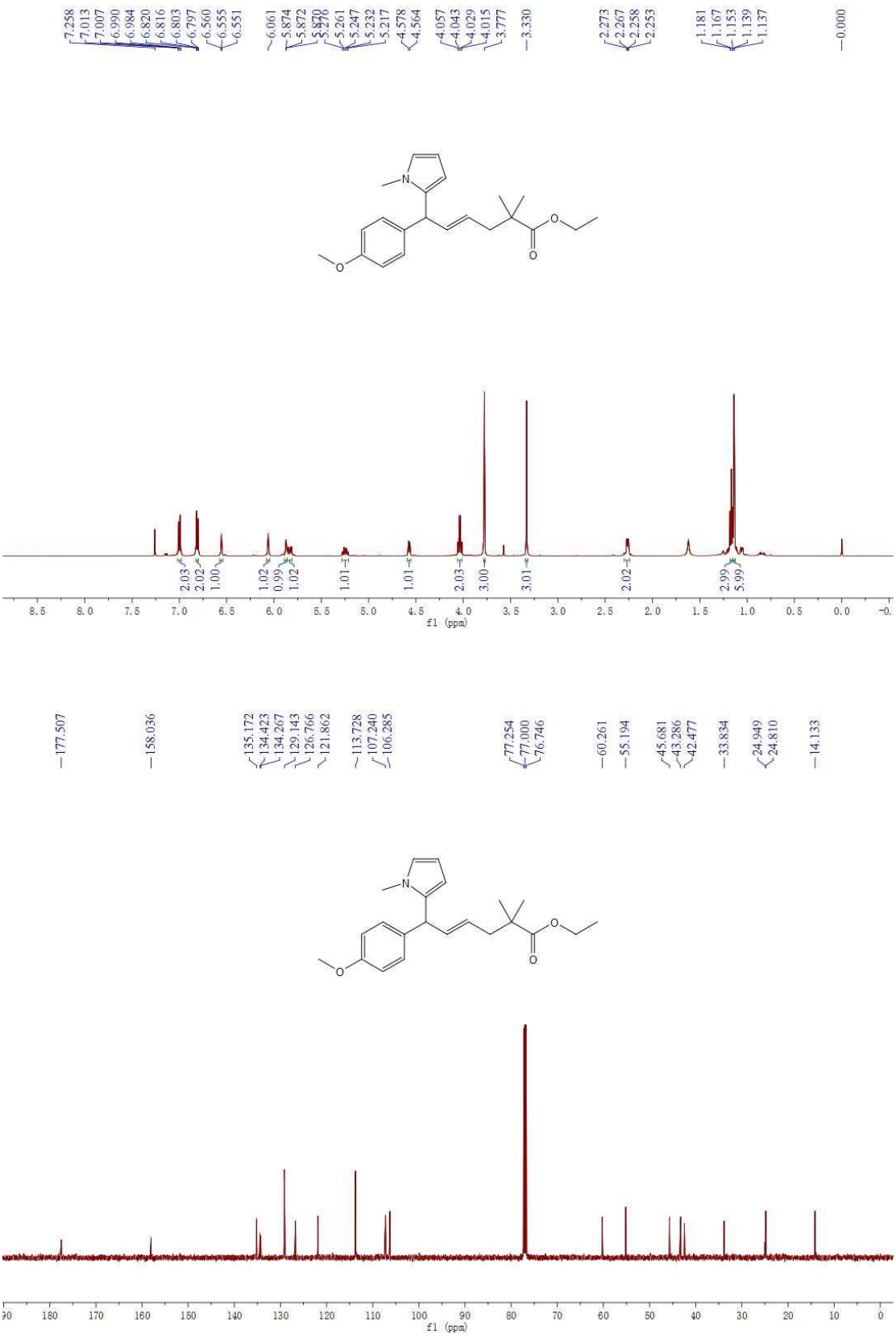


Ethyl (*E*)-6-(5,6-dihydro-4H-pyrrolo[3,2,1-*ij*]quinolin-1-yl)-6-(4-methoxyphenyl)-2,2-dimethylhex-4-enoate (4aah)

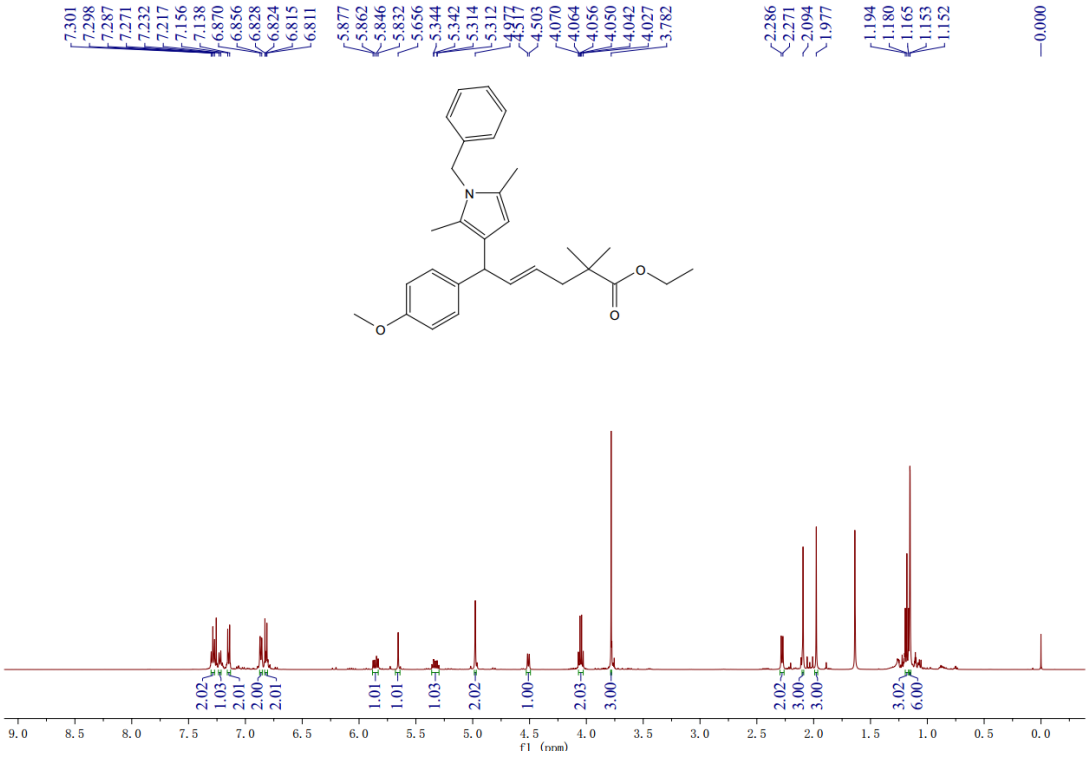


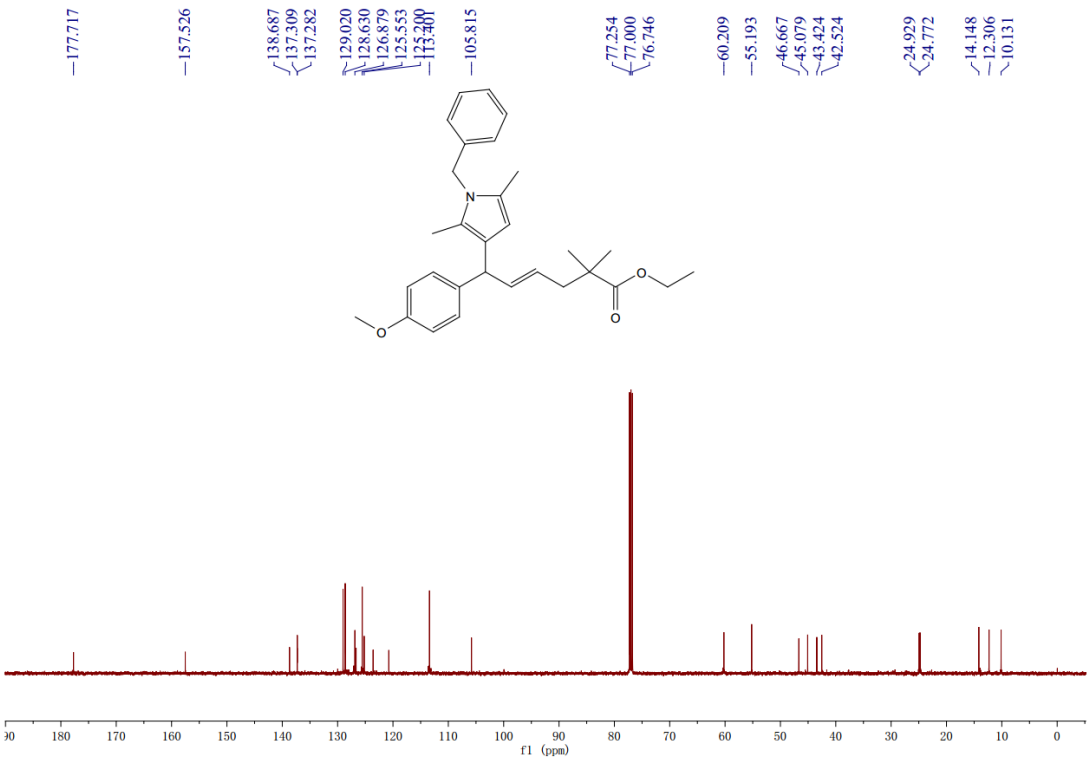
Ethyl (*E*)-6-(4-methoxyphenyl)-2,2-dimethyl-6-(1-methyl-1*H*-pyrrol-3-yl)hex-4-e

noate (4aai)

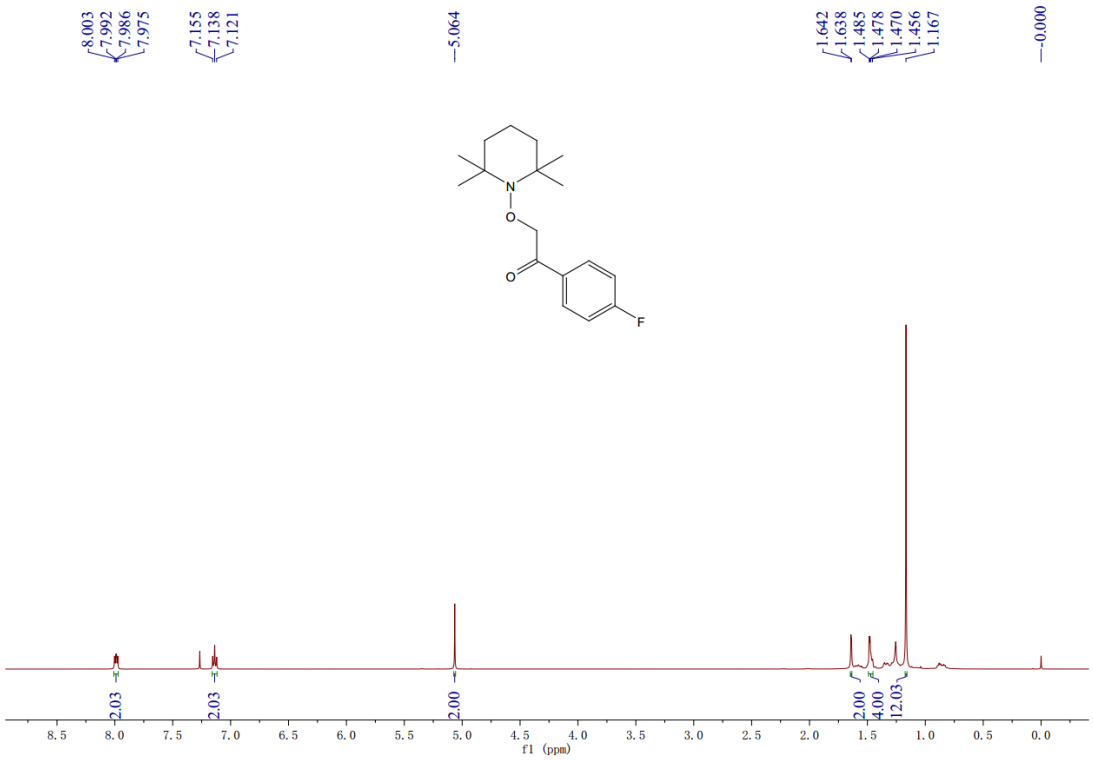


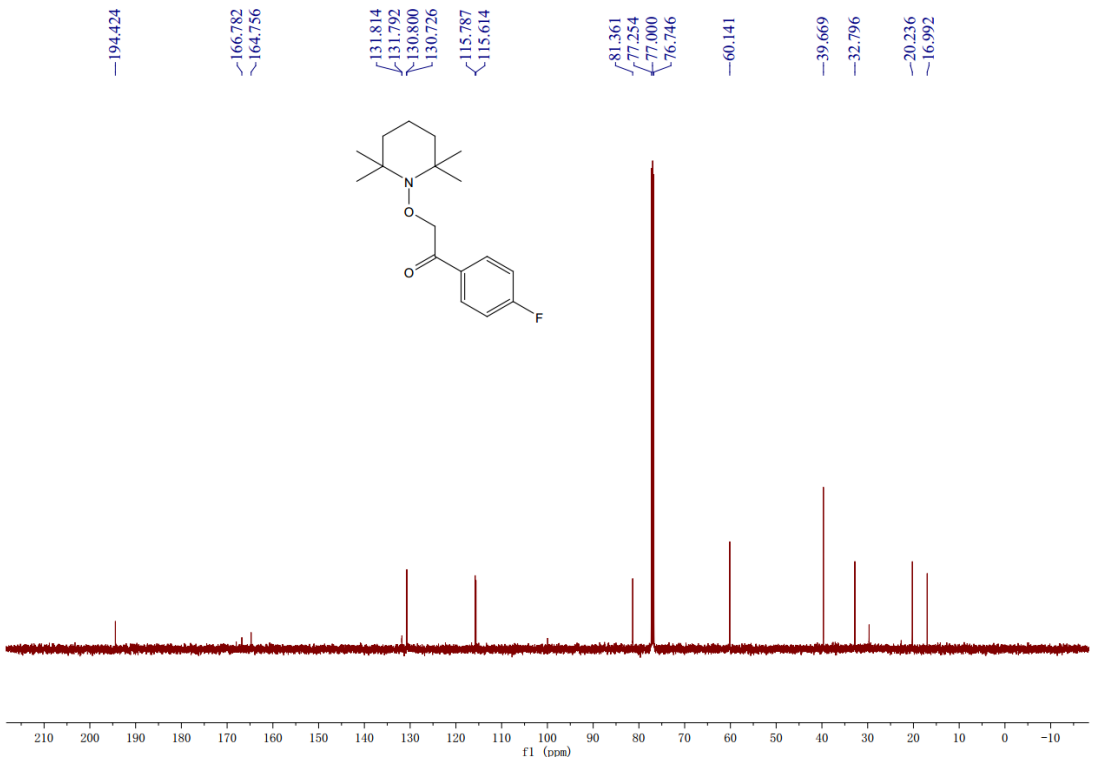
Ethyl (*E*)-6-(1-benzyl-2,5-dimethyl-1*H*-pyrrol-3-yl)-6-(4-methoxyphenyl)-2,2-dimethylhex-4-enoate (4aaj)

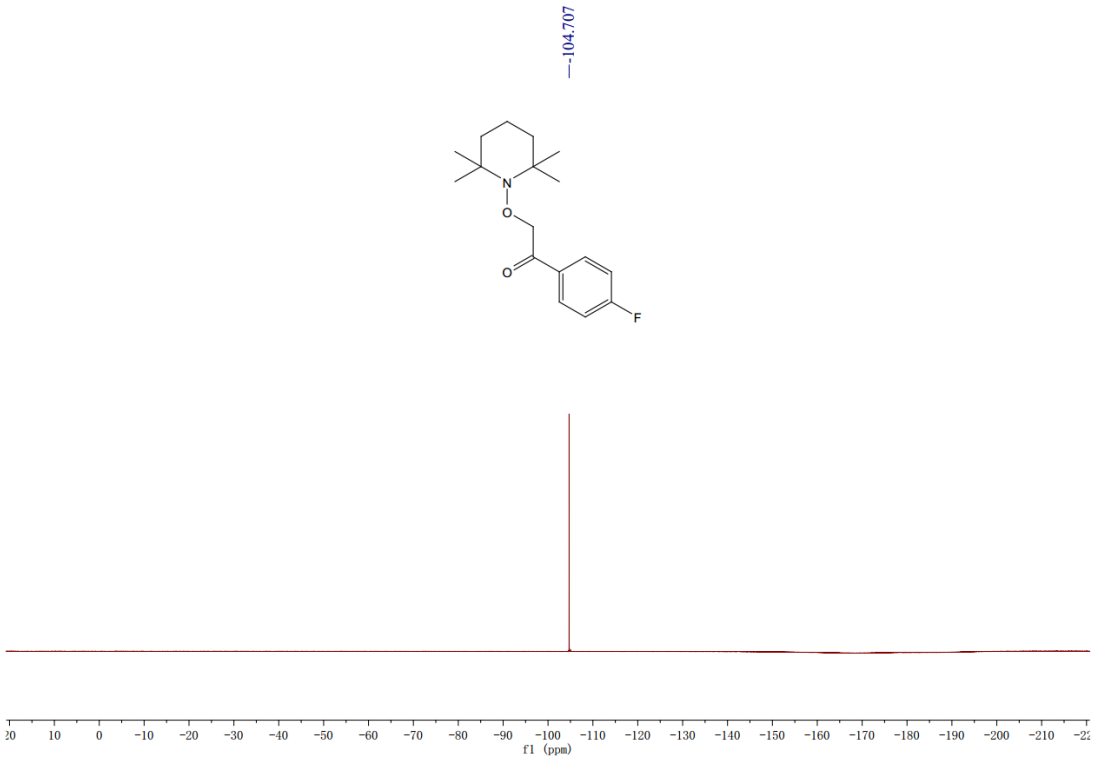




1-(4-Fluorophenyl)-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethan-1-one (6)



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O
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-210
f1 (ppm)