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Supporting Information

Organic bases-promoted enantioselective electrophilic cyanation of β-keto esters by chiral phase-transfer catalysts **

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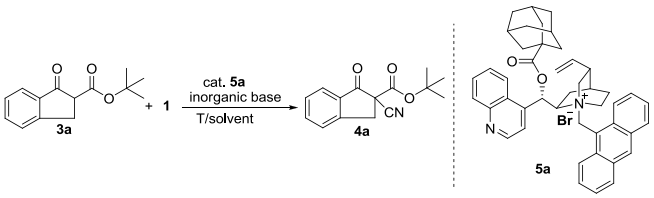
Content

1. General information

Unless specified noted, all reagents were purchased from commercial suppliers without further purification. All the solvents were treated according to general methods. Column chromatography was performed using 200-300 mesh silica gel (YanTai, China). ^{1}H NMR spectra were recorded on BRUKER 400 or 300 (400/300 MHz) spectrophotometer. ^{13}C NMR spectra were recorded on BRUKER 400 (100 MHz) with complete proton decoupling spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were internally referenced to tetramethylsilane signal or residual proton solvent signals. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, bs = broad singlet, m = multiplet), coupling constants (Hz) and integration. Mass spectra were measured on a Bruker Apex IV FTMS (ESI). IR spectrums were recorded on Perkin-Elmer-983 spectrometer. Optical rotations were measured with PerkinElmer 341 polarimeter. The enantiomeric excesses (*ee*) were determined by HPLC. HPLC analyses were performed on equipped with an indicated chiral column, using mixtures of *n*-hexane/isopropyl alcohol as mobile phase, at 25 ℃.

2. Optimization Enantioselective electrophilic cyanation of β-keto esters with inorganic bases and different cyanating reagents

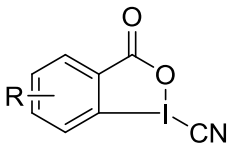
Table S1. The preliminary screening of asymmetric cyanation of β-keto esters with inorganic base



Entry[a]	1	Inorg. base	solvent	T [°C]	Conv.[b] [%]	ee[c] [%]
1	**1a**	Cs_2CO_3	THF	-40	100	21
2	**1a**	Cs_2CO_3	THF	-78	100	15
3	**1b**	Cs_2CO_3	THF	-78	91	35
4	**1b**	K_2HPO_4	THF	-78	83	34
5	**1b**	KOH	THF	-78	100	0
6	**1b**	Cs_2CO_3	Tol	-78	87	52
7	**1b**	Cs_2CO_3	Cl-Tol	-78	89	45

8[d]	**1b**	Cs_2CO_3	THF/Tol	-78	90	57(63)[g]
9[d]	**1c**	Cs_2CO_3	THF/Tol	-78	75	20
10[d]	**1d**	Cs_2CO_3	THF/Tol	-78	87	9
11[d]	**1e**	Cs_2CO_3	THF/Tol	-78	95	33
12[d]	**1f**	Cs_2CO_3	THF/Tol	-78	93	33
13[d]	**1g**	Cs_2CO_3	THF/Tol	-78	-[e]	-[f]
14[d]	**1h**	Cs_2CO_3	THF/Tol	-78	90	30

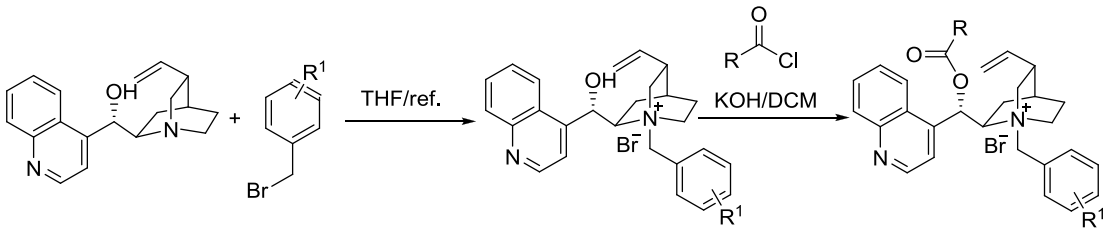
[a] Unless otherwise noted, the reaction was performed with 0.05 mmol of **3a**, 1.3 equiv. of **1** and 5equiv. of inorganic base in the presence of 5 mol% of catalyst in solvent (0.8 mL) for 6 h. [b] The conv. was determined by crude NMR. [c] The enantiomeric excess was determined by HPLC analysis of the product **3a** using a chiral column (DAICEL Chiralcel AS-H) with hexane/2-propanol (85:15) as the eluent. [d] THF/Tol=0.7 mL : 0.1 mL. [e] no product was obtained. [f] not determined. [g] isolated yield in parenthesis



R=H, **1a**
R=4-^{t}Bu, **1b**
R=4-OCH_3, **1c**
R=4,5- dimethyoxyl, **1d**
R=3-CH_3, **1e**
R=4-CF_3, **1f**
R=5-NO_2, **1g**
R=benzo, **1h**

3. Synthesis of chiral phase-transfer catalysts

3.1 general procedures for preparing *O*(9)-acyl-cinchoninium bromide

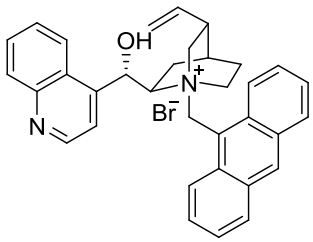


According to the known procedures[1,2] modified, to a flask equipped with a stirring bar and a reflux condenser was added cinchonine (3.4 mmol), benzyl bromide derivative (3.5 mmol). Then the system was evacuated 3 times and backfilled with Ar before solvent 50 ml THF were added by syringe. The mixture was heated to reflux within given time (mostly 5 hours) under Ar atmosphere and then cooled to room temperature, poured into Et_2O (150 mL) with vigorous stirring. The resulting suspension was aged for 15 minutes and the precipitation was isolated by suction filtration. And the pure cinchoninium bromide was obtained by recrystallized from MeOH/Et_2O at about 4 ^oC.

To the suspension of the cinchoninium bromide above (2 mmol) in DCM (20ml) was added 50% KOH solution (2g H_2O/2g KOH) and acyl chloride (4 mmol). The mixture was reacted for 1 hour with it becoming transparent, then water and additional DCM was added.

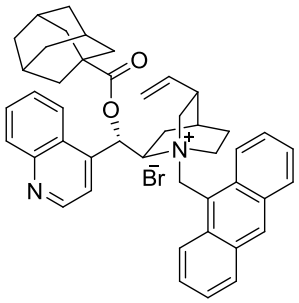
The aqueous phase was extracted with DCM twice (5 ml × 2). The organic phase was combined and washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with DCM and methanol as elute, which was concentrated to ~1 mL and poured onto Et_2O (20 mL). Then the precipitation was suction filtered and washed by Et_2O, providing the desired product as solid other than foam.

_N_-Anthracenylmethyl cinchoninium bromide 5b[1]



Prepared according to the general procedure, cinchonine (1.00 g, 3.4 mmol) and 9-bromomethyl anthracene (0.95 g, 3.5 mmol) gave the product as light yellow crystal 1. 67 g. Isolated yield 83%. $[\alpha]_D^{25}$ +290.6 (c 0.5, MeOH); mp 174-175℃; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.01(d, J = 8.6Hz, 1H), 8.78 (d, J = 8.0Hz, 2H), 8.54(d, J = 9.0Hz, 1H), 7.99(d, J = 4.4Hz, 1H), 7.85(s, 1H), 7.54(d, J = 8.0Hz, 1H), 7.47(t, J = 8.4Hz, 2H), 7.38(t, J = 7.6Hz, 1H), 7.24(d, J = 3.2Hz, 1H), 7.13(t, J = 7.4Hz, 1H), 7.00-7.04(m, 3H), 6.89-6.93(m, 2H), 6.42-6.48(m, 2H), 5.49-5.57(m, 1H), 4.98(d, J = 10.5Hz, 1H), 4.66-4.88(m, 2H), 4.30-4.41(m, 2H), 2.44(t, J = 11.6Hz, 1H), 2.30(dd, J = 10, 20Hz, 1H), 1.90(t, J = 12.5Hz, 1H), 1.61-1.71(m, 2H), 1.40-1.55(m, 1H), 1.31(bs, 1H), 1.14(t, J = 7Hz, 1H), 0.54-0.72(m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ149.5, 147.2, 145.1, 135.5, 133.2, 132.4, 131.2, 130.2, 130.1, 129.2, 128.9, 128.5, 128.1, 127.8, 127.4, 127.1, 126.4, 125.4, 124.81, 124.76, 124.1, 120.1, 117.7, 117.6, 67.6, 66.5, 57.6, 54.4, 54.2, 38.0, 26.3, 24.1, 22.7. HRMS (ESI+) calced for $[C_{34}H_{33}N_2OBr\text{-}Br]^+$: 485.2587, found: 485.2585.

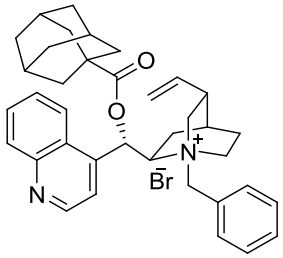
O-9-Adamantoyl-_N_-Anthracenylmethyl cinchoninium bromide 5a[3]



Prepared according to the general procedure, **5b** (2.0 mmol) and adamantonyl chloride (4.0 mmol) gave the product as light yellow powder 1.35 g. Isolated yield 92%. $[\alpha]_D^{25}$ +224.6 (c 0.5, $CHCl_3$); mp 114-115℃; v_{max} (film)/cm^{-1} 2908, 2853, 1740, 1509, 1452; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.78 (d, J = 9.2Hz, 1H), 8.96 (d, J = 4.8Hz, 2H), 8.50(s, 1H), 8.09(d, J = 8.2Hz, 2H), 8.03(t, J = 7.5Hz, 1H), 7.92(d, J = 8.0Hz, 2H), 7.78-7.84(m, 2H), 7.67-7.71(m, 2H), 7.50-7.58(m, 3H), 6.42(d, J = 13.3Hz, 1H), 5.81-5.90(m, 2H), 5.66(t, J = 10.8Hz, 1H), 5.40(d, J =

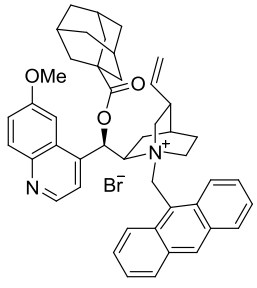
13.4Hz, 1H), 5.22-5.29(m, 1H), 5.00(d, *J* = 17.2Hz, 1H), 3.74(t, *J* = 10.3Hz, 1H), 3.06(t, *J* = 11.2Hz, 1H), 2.57(t, *J* = 12.0Hz, 1H), 2.47(dd, *J* = 9.8, 19.7Hz, 1H), 2.11-2.27(m, 11H), 1.82-1.97(m, 7H), 1.60-1.75(m, 1H), 1.41-1.61(m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ173.9, 147.4, 146.8, 138.9, 133.5, 132.1, 130.98, 130.95, 129.6, 129.1, 128.9, 128.7, 128.1, 127.5, 127.2, 127.0, 125.9, 125.2, 124.5, 123.5, 123.2, 123.0, 120.6, 117.1, 116.8, 115.2, 67.3, 63.9, 55.2, 53.5, 53.1, 39.7, 37.5, 36.3, 34.5, 29.2, 26.0, 24.1, 22.1, 21.6. HRMS (ESI+) calced for $[C_{45}H_{47}N_2O_2Br\text{-}Br]^+$: 647.3632, found: 647.3623.

O-9- Adamantoyl-*N*- benzylcinchoninium bromide 5c[4]



Prepared according to the general procedure, cinchonine (1.00 g, 3.4 mmol) and 9-bromomethyl benzene (0.598 g, 3.5 mmol) gave the product as white powder, isolated yield is 87% over two steps. $[\alpha]_D^{25}$ +91.2 (c 0.5, $CHCl_3$); mp 160-162℃; ν_{max} (film)/cm^{-1} 2915, 2853, 1742, 1600, 1455; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.15(s, 2H), 8.42(d, *J* = 8.0Hz, 1H), 8.10-8.11(m, 1H), 7.93-7.95(m, 1H), 7.75-7.81(m, 3H), 7.48-7.52(m, 4H), 6.42(d, *J* = 11.2Hz, 1H), 6.02-6.06 (m, 1H), 5.55(s, 1H), 5.39(d, *J* = 10.0Hz, 1H), 5.29(d, *J* = 17.2Hz, 1H), 5.02(bs, 1H), 4.16(d, *J* = 11.2Hz, 1H), 3.73-3.82(m, 2H), 2.93-2.95(m, 1H), 2.60-2.62(m, 1H), 2.41-2.47(m , 1H), 2.20(s, 3H), 2.10(s, 8H), 1.78-1.91(m, 7H), 1.48(bs, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ175.1, 146.3, 146.2, 143.0, 135.2, 134.1, 133.2, 131.1, 130.9, 129.6, 126.6, 125.9, 125.0, 119.2, 118.6, 68.7, 65.1, 62.7, 56.5, 54.9, 41.3, 39.1, 37.9, 36.3, 27.8, 26.9, 23.5, 23.3; HRMS (ESI+) calced for $[C_{37}H_{43}N_2O_2Br\text{-}Br]^+$: 547.3319, found: 547.3312.

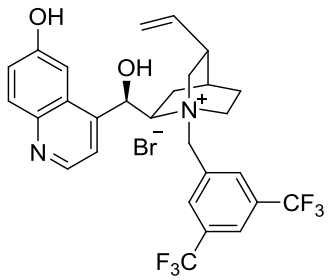
***O*-9- Adamantoyl-*N*- benzylquininium bromide 5d[4]**



Prepared according to the general procedure, quinine (1.10 g, 3.4 mmol) and 9-bromomethyl anthracene (0.95 g, 3.5 mmol) gave the product as yellow powder. Isolated yield is 93% over two steps. $[\alpha]_D^{25}$ -112.6 (c 0.5, $CHCl_3$); mp 123-124℃; ν_{max} (film)/cm^{-1} 2909, 2853, 1724, 1621, 1508, 1452; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.54(d, *J* = 8.8Hz, 1H), 8.77 (d, *J* = 4Hz, 1H), 8.59(s, 1H), 8.04(d, *J* = 7.6Hz, 1H), 7.89-7.98(m, 3H), 7.69-7.77(m, 3H), 7.63(s, 1H),

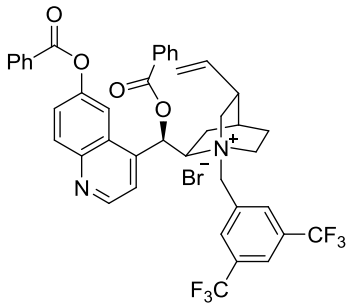
7.41-7.56(m, 3H), 7.29(d, *J* = 9.2Hz, 1H), 6.63(d, *J* = 13.4Hz, 1H), 6.32-6.44(m, 1H), 5.94-6.03(m, 1H), 5.78(d, *J* = 13.4Hz, 1H), 5.38-5.50(m, 1H), 5.22(d, *J* = 9.1Hz, 1H), 5.04(d, *J* = 10.4Hz, 1H), 4.12(bs, 3H), 3.79(t, *J* = 11.2Hz, 1H), 3.18(t, *J* = 11.6Hz, 1H), 2.48-2.55(m, 1H), 2.32-2.42(m, 2H), 2.19-2.31(m, 1H), 2.04-2.18(m, 4H), 1.84-2.03(m, 7H), 1.69-1.78(m, 7H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ176.6, 158.8, 147.0, 145.0, 139.4, 136.3, 134.3, 133.0, 132.7, 131.9, 131.6, 131.1, 130.4, 129.3, 129.0, 128.3, 128.0, 126.7, 126.3, 126.2, 125.2, 123.0, 122.9, 120.2, 118.8, 117.5, 102.0, 67.6, 66.4, 60.4, 56.3, 55.8, 50.9, 41.5, 39.0, 38.7, 36.3, 27.7, 26.9, 25.6, 23.0; HRMS (ESI+) calced for $[C_{46}H_{49}N_2O_3Br\text{-}Br]^+$: 677.3737, found: 677.3730.

***N*-(3,5-Ditrifluoromethyl)benzyl-6'-hydroxyquininium bromide (5g)[5]**



The staring material 6'-hydroxyquinine was prepared from the known procedures.[6] Then **5g** was obtained as white powder according to the general ways above, with 6'-hydroxyquinine (1.05 g, 3.4 mmol) and 3,5-ditrifluoromethylbenzyl bromide (1.075 g, 3.5 mmol) used, isolated yield is 48%. $[\alpha]_D^{25}$ -207.2 (c 0.5, CH_3OH); mp 241-243℃; v_{max} (film)/cm^{-1}, 1622, 1466; ^{1}H-NMR (400 MHz, MeOD): *δ*8.75(d, *J* =8.4Hz, 1H), 8.48(s, 2H), 8.28(s, 1H), 8.01(d, *J* =8.8Hz, 1H), 7.87(d, *J* =8.4Hz, 1H), 7.57(t, *J* =2.0Hz, 1H), 7.45(dd, *J* =8.8, 2.0Hz, 1H), 6.51(s, 1H), 5.71-5.80(m, 1H), 5.43(d, *J* =12.8Hz, 1H), 5.22-5.28(m, 2H), 5.08(d, *J* = 10.4Hz, 1H), 4.54-4.57(m, 1H), 4.05(t, *J* =8.8Hz, 1H), 3.78-3.81(m, 1H), 3.48-3.54(m, 1H), 3.38-3.44(m, 1H), 2.76(bs, 1H), 2.27-2.38(m, 2H), 2.13(s, 1H), 1.90-1.96(m, 1H), 1.48-1.54(m, 1H). ^{13}C-NMR (100 MHz, MeOD): *δ*156.9,147.6, 143.8, 143.7, 138.8, 135.5, 132.4, 132.2, 131.8, 131.5, 126.3, 125.4, 125.0, 122.7, 120.7, 117.4, 105.1, 69.0, 64.8, 61.6, 59.7, 51.4, 37.9, 26.8, 25.1, 21.5. HRMS (ESI+) calced for $[C_{28}H_{27}N_2O_2F_6Br\text{-}Br]^+$: 537.1968, found: 537.1971.

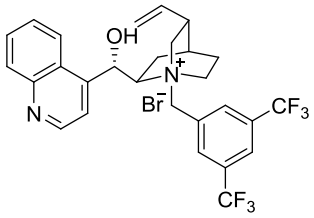
***O*-9- benzoyl-*N*-(3,5-Ditrifluoromethyl)benzyl-6'-benzoylquininium bromide (5h)**



Prepared according to the general procedure, **5g** (1.0 mmol) and benzoyl chloride (4.0 mmol) gave the product as white powder with isolated yield 82%. $[\alpha]_D^{25}$ -28.2 (c 0.5, $CDCl_3$); mp

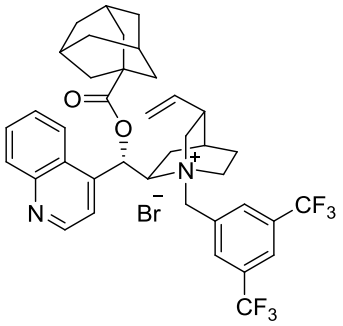
124-125℃; v_{max} (film)/cm^{-1} 2926, 1732; ^{1}H-NMR (400 MHz, MeOD): δ8.93(d, *J* =8.4Hz, 1H), 8.43(s, 2H), 8.39(d, *J* = 2.0Hz, 1H), 8.14-8.20(m, 4H), 7.90(d, *J* =7.6Hz, 2H), 7.60-7.69(m, 5H), 7.52(t, *J* =7.6Hz, 2H), 7.38(t, *J* =7.6Hz, 2H), 5.70-5.78(m, 2H), 5.11(d, *J* =12.8Hz, 1H), 4.99-5.05(m, 2H), 4.28-4.34(m, 1H), 4.17-4.24(m, 1H), 3.42-3.54(m, 3H), 2.68-2.75(m, 2H), 2.42-2.44(m, 1H), 2.21(s, 1H), 2.01-2.06(m, 1H), 1.83-1.98(m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ166.1, 165.1, 149.3, 148.1, 146.1, 140.8, 135.8, 134.5, 134.3, 133.1, 132.7, 132.3, 132.1, 130.9, 130.3, 129.1, 128.9, 128.7, 128.3, 124.5, 124.2, 124.1, 123.7, 121.5, 118.7, 114.6, 70.1, 69.7, 63.3, 61.2, 50.7, 37.5, 26.6, 24.8, 22.2. HRMS (ESI+) calced for $[C_{42}H_{35}N_2O_4F_6Br\text{-}Br]^+$: 745.2496, found: 745.2489.

_N_-(3,5-Ditrifluoromethyl)benzyl-cinchoninium bromide[7]



Prepared according to the general procedure, cinchonine (1.00 g, 3.4 mmol) and 3,5-ditrifluoromethylbenzyl bromide (1.075 g, 3.5 mmol) gave the product as colourless crystal 1.655 g with isolated yield 81%. $[\alpha]_D^{25}$ +101.2. (c 0.5, CH_3OH); mp 207-208℃; ^{1}H-NMR (400 MHz, MeOD): δ8.92(d, *J* = 4.4Hz, 1H), 8.80(s, 2H), 8.40-8.47(m, 2H), 8.20(s, 1H), 8.06-8.08(m, 1H), 8.92(d, *J* = 4.4Hz, 1H), 7.80(d, *J* = 4.0 Hz, 2H), 6.01-6.09(m, 1H), 5.45(d, *J* = 12.4Hz, 1H), 5.29-5.31(m, 3H), 4.53(t, *J* = 10.6Hz, 1H), 4.08-4.13 (m, 2H), 3.56(d, *J* =11.2Hz, 1H), 3.07-3.15(m, 1H), 2.63-2.69 (m, 1H), 2.48(t, *J* = 11.6Hz, 1H), 1.95(bs, 1H), 1.80-1.88(m, 2H), 1.04-1.10(m, 1H). ^{13}C-NMR (100 MHz, MeOD): δ151.0, 148.7, 147.1, 137.5, 135.6, 134.1, 133.8, 133.4, 133.1, 132.1, 131.1, 130.2, 129.3, 126.1, 125.9, 125.5, 124.7, 123.2, 121.2, 118.1, 69.7, 66.9, 62.7, 58.0, 56.4, 38.8, 28.4, 24.7, 22.3; HRMS (ESI+) calced for $[C_{28}H_{27}N_2OF_6Br\text{-}Br]^+$: 521.2022, found: 521.2015.

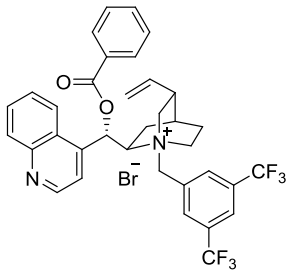
O-9- Adamantoyl-*N*- (3,5-Ditrifluoromethyl)benzylcinchoninium bromide (5i)



Prepared according to the general procedure, *N*-(3,5-Ditrifluoromethyl)benzyl-cinchoninium bromide (1.0 mmol) and adamantonyl chloride (2.0 mmol) gave the product as white powder 0.536g with isolated yield 76%. $[\alpha]_D^{25}$ +16.4 (c 0.5, $CHCl_3$); mp 150-151℃; v_{max} (film)/cm^{-1}

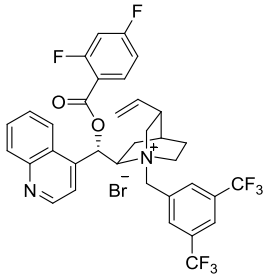
2925, 1732, 1511, 1452; ^{1}H-NMR (400 MHz, $CDCl_3$): δ8.92(d, *J* = 3.4Hz, 1H), 8.85(d, *J* = 8.4Hz, 1H), 8.42(s, 2H), 8.10(d, *J* =8.4Hz, 1H), 8.03(s, 1H), 7.88(t, *J* = 7.6Hz, 1H), 7.76(t, *J* = 7.6Hz, 1H), 7.43-7.55(m, 2H), 6.74(t, *J* = 12.0Hz, 1H), 5.97-6.05(m, 1H), 5.56(d, *J* = 10.0Hz, 1H), 5.40(d, *J* = 10.0Hz, 1H), 5.31(d, *J* = 17.2Hz, 1H), 4.94(t, *J* = 4.6Hz, 1H), 4.37(d, *J* = 12.0Hz, 1H), 3.85 (t, *J* = 9.6Hz, 1H), 3.62(t, *J* = 11.2Hz, 1H), 2.96-3.03 (m, 1H), 2.70-2.77 (s, 1H), 2.03-2.12(m, 7H), 1.77-1.88(m, 10H), 1.41-1.48(m, 1H).^{13}C-NMR (100 MHz, $CDCl_3$): 175.0, 149.1, 148.1, 140.3, 134.7, 134.0, 133.0, 132.6, 132.3, 130.6, 129.7, 129.0, 126.8, 124.9, 124.6, 124.3, 124.1, 121.3, 119.2, 117.9, 68.4, 65.9, 60.8, 56.6, 55.3, 41.2, 39.1, 37.6, 36.1, 27.6, 26.6, 23.2, 23.0. HRMS (ESI+) calced for $[C_{39}H_{41}N_2O_2F_6Br\text{-}Br]^+$: 683.3067, found: 683.3057.

_O_-9- benzoyl-_N_- (3,5-Ditrifluoromethyl)benzylcinchoninium bromide (5j)



Prepared according to the general procedure, *N*-(3,5-Ditrifluoromethyl)benzyl-cinchoninium bromide (1.0 mmol) and benzoyl chloride (2.0 mmol) gave the product as white powder 0.585g with isolated yield 83%. $[\alpha]_D^{25}$ +77.8 (c 0.5, $CHCl_3$); mp 146-147℃; v_{max} (film)/cm^{-1} 2917, 2854, 1744, 1593; ^{1}H-NMR (400 MHz, $CDCl_3$): δ9.08(d, *J* = 8.4Hz, 1H), 8.89(d, *J* = 4.4Hz, 1H), 8.90(bs, 2H), 8.24(d, *J* = 7.6Hz, 2H), 8.18(d, *J* = 8.4Hz, 1H), 8.03-8.06(m, 2H), 7.79-7.89(m, 3H), 7.65(t, *J* = 7.6Hz, 2H), 7.55(d, *J* = 4.4Hz, 1H), 7.05(t, *J* = 12.0Hz, 1H), 6.02-6.13(m, 2H), 5.47(d, *J* =10.4Hz, 1H), 5.24-5.32(m, 2H), 4.45(d, *J* = 12.0Hz, 1H), 3.83(t, *J* = 10.0 Hz, 1H), 3.45-3.55(m, 2H), 2.76-2.84(m, 1H), 2.63-2.69(m, 2H), 2.23(bs, 1H), 2.10-2.18(m, 1H), 1.57-1.63(m, 1H),. ^{13}C-NMR (100 MHz, $CDCl_3$): 164.2, 149.4, 148.5, 139.8, 135.3, 135.0, 134.3, 133.1, 132.7, 130.9, 130.1, 130.0, 129.9, 129.8, 129.6, 129.4, 128.0, 125.2, 124.3, 124.1. 121.4, 119.3, 118.1, 69.1, 66.1, 60.8, 56.5, 55.5, 37.6, 26.8, 23.5, 23.1; HRMS (ESI+) calced for $[C_{35}H_{31}N_2O_2F_6Br\text{-}Br]^+$: 625.2284, found: 625.2279.

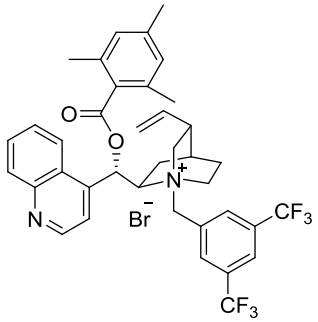
_O_-9-(2,4-difluorobenzoyl)-_N_- (3,5-Ditrifluoromethyl)benzylcinchoninium bromide (5k)



Prepared according to the general procedure, *N*-(3,5-Ditrifluoromethyl)benzyl-cinchoninium

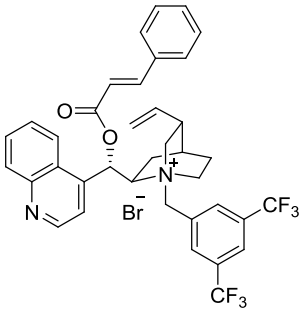
bromide (1.0 mmol) and 2,4-difluorobenzoyl chloride (2.0 mmol) gave the product as white powder 0.55g with isolated yield 74%. $[\alpha]_D^{25}$ +25.2 (c 0.5, $CHCl_3$); mp 143-145℃; v_{max} (film)/cm^{-1} 2925, 1730, 1615, 1500; ^{1}H-NMR (400 MHz, $CDCl_3$): δ9.09(d, *J* = 12.0Hz, 1H), 8.88(d, *J* = 4.5Hz, 1H), 8.52(s, 2H), 7.97-8.14(m, 4H), 7.83(t, *J* = 7.6Hz, 1H), 7.75(bs, 1H), 7.52(d, *J* = 4.6Hz, 1H), 7.10-7.16(m, 3H), 5.98-6.07(m, 2H), 5.34(d, *J* = 10.2Hz, 1H), 5.19-5.26(m, 2H), 4.35(d, *J* = 12.0Hz, 1H),3.87-3.92(m, 1H), 3.44-3.51(m, 1H), 2.76(dd, *J* = 21.0, 9.7Hz, 1H), 2.61(d, *J*=12.5Hz, 1H), 2.04-2.11(m, 2H), 1.46-1.53(m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 168.4, 165.9, 165.8, 164.1, 164.0, 162.03, 162.04, 149.4, 148.4, 139.7, 135.7, 135.6, 134.38, 134.35, 133.3, 133.0, 132.6, 132.3, 130.7, 129.3, 126.9, 124.2 121.4, 119.5, 118.4, 113.3, 113.2, 113.1, 106.2, 106.0, 105.7, 70.4, 66.1, 60.8, 56.8, 55.3, 38.4, 27.2, 23.5, 23.1; HRMS (ESI+) calced for $[C_{35}H_{29}N_2O_2F_8Br\text{-}Br]^+$: 661.2096, found: 661.2090.

_O_-9-(2,4,6-trimethylbenzoyl)-_N_- (3,5-Ditrifluoromethyl)benzylcinchoninium bromide (5l)



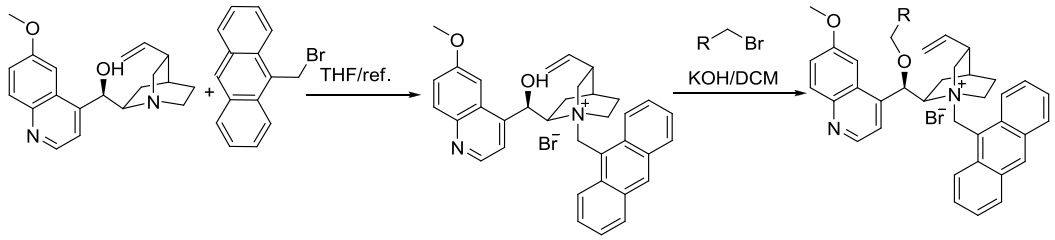
Prepared according to the general procedure, *N*-(3,5-Ditrifluoromethyl)benzyl-cinchoninium bromide (1.0 mmol) and 2,4,6-trimethylbenzoyl chloride (2.0 mmol) gave the product as white powder 0.55g with isolated yield 74%. $[\alpha]_D^{25}$ +53.8 (c 0.5, $CHCl_3$); mp 144-146℃; v_{max} (film)/cm^{-1} 2925, 1735, 1611, 1461; ^{1}H-NMR (400 MHz, $CDCl_3$): δ9.21(d, *J* = 8.0Hz, 1H), 9.06(bs, 1H), 8.33-8.35(m, 3H), 8.04-8.09(m, 2H), 7.93(t, *J* = 8.0Hz, 1H), 7.80(bs, 1H), 7.68(s, 1H), 7.23(d, *J* = 12.0Hz, 1H), 7.02(s, 2H), 5.96-6.00(m, 1H), 5.74-5.82(m, 1H), 5.24-5.27(m, 2H), 5.01(d, *J* =17.2Hz, 1H), 4.37(d, *J* =12.0Hz, 1H), 3.78-3.82(m, 1H), 3.44-3.50(m, 1H), 3.33(t, *J* = 10.8Hz, 1H), 2.79(bs, 1H), 2.51-2.58(m, 1H), 2.43(m, 6H), 2.37(s, 3H), 2.13(bs, 2H), 1.89(bs, 1H), 1.59(bs, 1H),. ^{13}C-NMR (100 MHz, $CDCl_3$): δ168.0, 149.0, 148.6, 141.6, 139.6, 135.3, 135.2, 134.7, 134.1, 133.6, 133.3, 132.9, 132.6, 130.9, 130.1, 129.8, 129.7, 129.4, 128.4, 126.8, 125.0, 124.4, 124.1, 121.4, 119.2, 118.7, 118.6, 70.3 66.0, 60.4, 56.4, 54.5, 37.4, 27.0, 23.4, 23.2, 21.3, 21.2; HRMS (ESI+) calced for $[C_{38}H_{37}N_2O_2F_6Br\text{-}Br]^+$: 667.2754, found: 667.2749.

_O_-9-cinamonyl-_N_- (3,5-Ditrifluoromethyl)benzylcinchoninium bromide (5m)



Prepared according to the general procedure, *N*-(3,5-Ditrifluoromethyl)benzyl-cinchoninium bromide (1.0 mmol) and cinamonyl chloride (2.0 mmol) gave the product as white powder 0.506g with isolated yield 69%. $[\alpha]_D^{25}$ -11.4 (c 0.5, $CHCl_3$); mp 151-152℃; v_{max} (film)/cm^{-1} 2925, 1725, 1632; ^{1}H-NMR (400 MHz, $CDCl_3$): δ8.90(d, *J* = 8.4Hz, 1H), 8.85(d, *J* = 4.5Hz, 1H), 8.53(s, 2H), 8.07(d, *J* = 8.4Hz, 1H),7.91-7.95(m, 2H), 7.86(d, *J* = 16.0Hz, 1H), 7.76(t, *J* = 7.6Hz, 1H), 7.58(m, 3H), 7.43-7.45(m, 4H), 6.79(d, *J* =12.0Hz, 1H), 6.67(d, *J* =16.0Hz, 1H), 6.00-6.08(m, 1H), 5.77(d, *J* = 10.8Hz, 1H), 5.44(d, *J* =9.6Hz, 1H), 5.32(d, *J* =8.6Hz, 1H), 5.06(t, *J* =9.6Hz, 1H), 4.40(t, *J* = 12.0Hz, 1H), 3.87(t, *J* = 9.8Hz, 1H), 3.52(t, *J* = 10.2Hz, 1H), 2.77(dd, *J* = 20.0, 10.0Hz, 1H), 2.64-2.68(m, 1H), 2.50(t, *J* =12.0Hz, 1H), 2.09-2.12(m, 1H), 1.97-2.05(m, 1H), 1.82-1.88(m, 1H), 1.37-1.47(m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ164.5, 149.5, 149.4, 148.5, 139.8, 135.4, 134.4, 133.4, 133.0, 132.7, 132.0, 130.8, 130.1, 129.9, 129.5, 129.4, 128.8, 125.0, 124.3, 124.2, 121.5, 119.0, 118.8, 118.2, 115.2, 68.9, 66.1, 60.9, 56.6, 55.5, 37.8, 27.0, 23.5, 22.9; HRMS (ESI+) calced for $[C_{37}H_{33}N_2O_2F_6Br\text{-}Br]^+$: 651.2441, found: 651.2434.

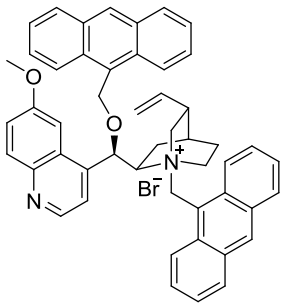
3.2 general procedures for preparing *O*(9)-alkyl-quininium bromide



To a flask equipped with a stirring bar and a reflux condenser was added quinine (3.4 mmol), 9-bromomethyl anthracene (0.95 g, 3.5 mmol). Then the system was evacuated 3 times and backfilled with Ar before solvent 50 ml THF were added by syringe. The mixture was heated to reflux within given time (mostly 5 hours) under Ar atmosphere and then cooled to room temperature, poured into Et_2O (150 mL) with vigorous stirring. The resulting suspension was aged for 15 minutes and the precipitation was isolated by suction filtration. And the pure quininium bromide was obtained by recrystallized from MeOH/Et_2O at about 4^{o}C. To the suspension of the quininium bromide above (1 mmol) in DCM (20ml) was added 50% KOH solution (2g H_2O/2g KOH) and alkyl bromide (4 mmol). The mixture was reacted for 48 hour, then water and additional DCM was added. The aqueous phase was extracted with DCM twice (5ml*2). The organic phase was combined and washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column

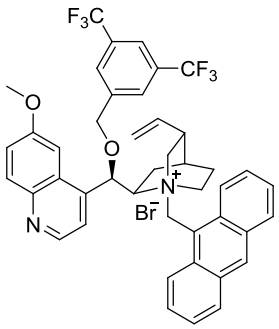
chromatography on silica gel with DCM and methanol as elute carefully, which was concentrated to ~1 mL and poured onto Et_2O (20 mL). then the precipitation was suction filtered and washed by Et_2O, providing the desired product as solid other than foam.

_O_-9- Anthracenylmethyl -_N_- Anthracenylmethyl quininium bromide (5e)



Isolated yield is 39% over two steps. $[\alpha]_D^{25}$ +19.0 (c 0.5, $CHCl_3$); mp 89-90℃; v_{max} (film)/cm^{-1} 2925, 2852,1619; ^{1}H-NMR (400 MHz, $CDCl_3$): δ8.78(d, J = 4.4Hz, 1H), 8.41-8.43(m, 3H), 8.23(s, 1H), 8.01-8.07(m, 3H), 7.92(d, J =8.4Hz, 2H), 7.82(d, J =8.4Hz, 2H), 7.47-7.52(m, 4H), 7.41(d, J = 2.8Hz, 1H), 7.34-7.38(m, 4H), 7.21-7.37(m, 2H), 5.72-5.82(m, 1H), 5.49(dd, J = 12.0, 18.6Hz, 2H), 5.08-5.11(m, 1H), 4.82-4.84(m, 1H), 4.80(m, 1H), 4.22-4.29(m, 2H), 3.50(s, 3H), 2.80(d, J =10.6Hz, 1H), 2.53(d, J =10.6Hz, 1H), 2.32(dd, J = 6.8, 2.4Hz, 1H), 2.00-2.05(m, 2H), 1.89-1.94(m, 2H), 1.27(t, J =7.2Hz, 1H), 1.11(bs, 1H), 0.95-0.99(m, 1H), 0.70-0.73(m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ158.1, 151.8, 147.8, 145.1, 141.9, 138.7, 131.65, 131.63, 131.61, 131.5, 131.5, 131.46, 131.1, 130.7, 129.13, 129.12, 129.0, 128.1, 127.7, 127.4, 126.2, 125.6, 125.5, 125.1, 125.1, 125.0, 124.4, 122.7, 122.0, 118.7, 115.6, 103.7, 64.0, 59.6(bs), 55.4, 55.4, 54.6, 54.1, 53.2(bs), 44.1, 39.5, 29.5, 27.9; HRMS (ESI+) calced for $[C_{50}H_{45}N_2O_2Br\text{-}Br]^+$: 705.3476, found: 705.3470.

_O_-9-(3,5-Ditrifluoromethyl)-_N_- Anthracenylmethyl quininium bromide (5f)

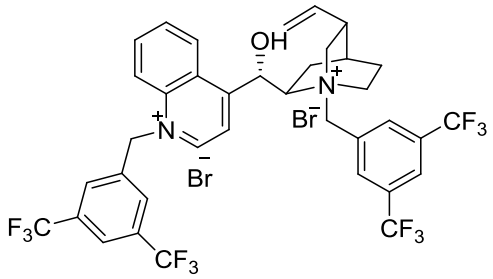


Isolated yield is 42% over two steps. $[\alpha]_D^{25}$ +15.8 (c 0.5, $CHCl_3$); mp 62-64℃; v_{max} (film)/cm^{-1} 2925, 2853,1620; ^{1}H-NMR (400 MHz, $CDCl_3$): δ8.74(d, J = 4.4Hz, 1H), 8.49(d, J = 8.4Hz, 2H), 8.40(s, 1H), 7.99-8.07(m, 3H), 7.81(s, 1H), 7.66-7.68(m, 2H), 7.44-7.52(m, 5H), 7.37-7.40(m, 1H), 7.23-7.26(m, 1H), 6.08-6.17(m, 1H), 5.17-5.21(m, 1H), 5.01-5.04(m, 1H), 4.99(s, 1H), 4.56-4.59(m, 2H), 4.34-4.40(m, 2H), 3.79(s, 3H), 2.96(d, J =10.6Hz, 1H), 2.86(d, J =10.6Hz, 1H), 2.54(dd, J = 11.0, 2.4Hz, 1H), 2.32-2.39(m, 1H), 2.18-2.31(m, 3H),

1.50-2.10(m, 2H), 1.38-1.49(m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ158.5, 151.4, 147.8, 144.9, 140.6, 140.2, 138.6, 132.1, 131.8, 131.7, 131.6, 130.4, 129.1, 127.8, 127.5, 125.55, 125.46, 125.0, 124.7, 122.7, 122.0, 121.9, 118.0, 116.0, 103.0, 69.8, 59.6(bs), 55.6, 54.8, 53.6, 45.4, 44.1, 39.7, 29.5, 28.5; HRMS (ESI+) calced for $[C_{44}H_{39}N_2O_2F_6Br\text{-}Br]^+$: 741.2910, found: 741.2907.

2.3 doubly-quaternized phase transfer catalysts

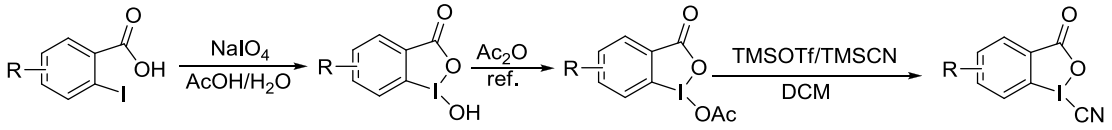
***N'*-(3,5-Ditrifluoromethyl)-*N*- (3,5-Ditrifluoromethyl) quininium dibromide (5n)**



According to the procedures[8] by N. Yasuda, to a flask equipped with a stirring bar and a reflux condenser was added cinchonine (3.4 mmol), benzyl bromide derivative (3.5 mmol). Then the system was evacuated 3 times and backfilled with Ar before solvent 50 ml THF were added by syringe. The mixture was heated to reflux within given time (mostly 5 hours) under Ar atmosphere and then cooled to room temperature, poured into Et_2O (150 mL) with vigorous stirring. The resulting suspension was aged for 15 minutes and the precipitation was isolated by suction filtration. And the pure cinchoninium bromide was obtained by recrystallized from MeOH/Et_2O at about 4^{o}C. To a flask equipped with a stirring bar and a reflux condenser was added *N*-(3,5-Ditrifluoromethyl)benzyl-cinchoninium bromide (1.0 mmol), 3,5-ditrifluoromethylbenzyl bromide (0.322 g, 1.05 mmol). Then the system was evacuated 3 times and backfilled with Ar before solvent 10 ml isoproponal and 1ml DMF were added by syringe. The mixture was heated to reflux within 5 hours under Ar atmosphere and then cooled to room temperature, poured into EA with vigorous stirring. The resulting suspension was aged for 15 minutes and the precipitation was isolated by suction filtration. washed by Et_2O, providing the desired product 0.73g as a light yellow solid. $[\alpha]_D^{25}$ +113.6 (c 0.5, CH_3OH); mp 241-242℃; v_{max} (film)/cm^{-1} 3437,1618; ^{1}H-NMR (400 MHz, DMSO): δ9.96(d, *J* =6.0Hz, 1H), 8.98(d, *J* = 8.4Hz, 1H), 8.67-8.71(m, 3H), 8.55(d, *J* = 6.0Hz, 1H), 8.29-8.34(m, 4H), 8.13-8.17(m, 2H), 7.33(d, *J* = 4.0Hz, 1H), 6.84(s, 1H), 6.65(s, 2H), 6.00-6.09(m, 1H), 5.71(d, *J* =12.4Hz, 1H), 5.35(d, *J* =12.4Hz, 1H), 5.26(d, *J* =12.8Hz, 2H), 4.32-4.41(m, 2H), 4.02-4.11(m, 1H), 3.50-3.56(m, 2H), 3.07-3.14(m, 1H), 2.64-2.71(m, 1H), 2.29(t, *J* =11.6.Hz, 1H), 1.90(s, 1H), 1.77-1.79(m, 2H), 1.16-1.23(m, 1H). ^{13}C-NMR (100 MHz, DMSO): δ159.0, 151.1, 138.1, 137.9, 137.6, 136.4, 135.6, 132.1, 131.8, 131.8, 131.7, 131.5, 131.4, 131.2, 130.1, 128.1, 128.0, 127.2, 125.4, 125.3, 125.0, 123.8, 122.7, 122.60, 122.56, 120.4, 120.0, 118.1, 68.2, 66.2, 60.9, 59.5, 56.6, 55.0, 37.7, 27.2, 23.9, 21.5. HRMS (ESI+) calced for $[C_{37}H_{32}N_2OF_{12}]/2^+$: 374.1156, found: 374.1152.

4. The procedures for the synthesis of cyanation-transfer reagents

Typical procedures

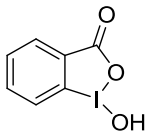


Following a reported procedure,[8] NaIO4 (4.04 mmol,) and 2-iodo benzoic acid derivatives (4mmol) were suspended in AcOH/H_2O (2.5ml:5.0ml) under air with vigorous stirring. The mixture was refluxed for 4 h, then diluted with cold water (50 mL). After vigorous stirring for 15 minutes, the precipitation was suction filtered and washed with ice water and cold acetone, respectively. The pure *1-Hydroxy-1,2-benziodoxol-3-(1H)-one derivatives* was obtained by vacuum desiccation at 50^{o}C as a white solid.

The *1-Hydroxy-1,2-benziodoxol-3-(1H)-one derivatives* (2 mmol) was put into 2 ml Ac_2O, then the suspension was heated at 140 ^{o}C, turning clear after several minutes when the reaction was over. The mixture was cooled and crystallized at -18^{o}C for 5 hours. The crystal was further dried by vacuum desiccation to provide the *1-Acetoxy-1,2-benziodoxol-3-(1H)-one derivatives.*

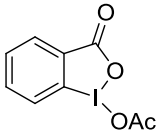
To the 5ml DCM solution of *1-Acetoxy-1,2-benziodoxol-3-(1H)-one derivatives* (1mmol) under Ar, added was 2 mmol TMSCN. Then TMSOTf (1 mol %) was added by syringe, with solid appearing. After 15-30 minutes stirring, the mixture was diluted with 15ml PE and filtered. And the collection was further washed by PE to give the desired product *1-Cyanyo-1,2-benziodoxol-3-(1H)-one derivative.*

1-Hydroxy-1,2-benziodoxol-3-(1H)-one[9]



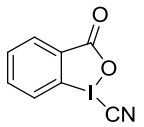
^{1}H-NMR (400 MHz, DMSO): δ 7.95-8.04(m, 3H), 7.86(d, J = 8.0Hz, 1H), 7.70-7.73(m, 1H). ^{13}C-NMR (100 MHz, DMSO): δ 168.2, 135.0, 132.0, 131.6, 130.9, 126.8, 120.9.

1-Acetoxy-1,2-benziodoxol-3-(1H)-one[9]



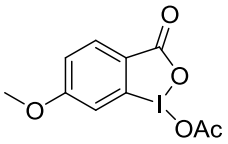
^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.16-8.18 (m, 1H), 7.95(d, J = 8.2Hz, 1H), 7.86-7.90(m, 1H), 7.66(t, J = 7.3Hz, 1H), 2.21(s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ176.4, 168.2, 136.2, 133.1, 131.3, 129.3, 129.0, 118.4, 20.3.

1-Cyano-1,2-benziodoxol-3-(1H)-one[10] (1a)



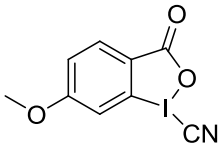
Isolated yield from 1-Acetoxy-1,2-benziodoxol-3-(1H)-one is 95% as white solid. ^{1}H-NMR (400 MHz, DMSO): δ 8.32 (d, J = 8.0Hz, 1H), 8.16(d, J = 8.0Hz, 1H), 8.02-8.07(m, 1H), 7.90-7.94(m, 1H). ^{13}C-NMR (100 MHz, DMSO): δ167.2, 137.0, 132.5, 132.3, 130.7, 128.3, 117.9, 88.4, NMR data correspond to the reported ones [10].

4-Metheoxyl-1-acetoxy-1,2-benziodoxol-3-(1H)-one



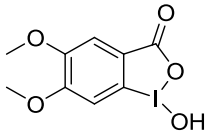
White solid. Isolated yield from 2-iodo-4-methoxybenzoic acid is 82%. M.p.171-172^{o}C, ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.10(d, J = 8.4Hz, 1H), 7.46(s, 1H), 7.17(d, J = 8.4Hz, 1H), 3.96(s, 3H), 2.24(s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ176.6, 168.3, 166.4, 134.2, 121.4, 120.6, 117.3, 114.8, 56.5, 20.6.

4-Metheoxyl-1-cyano-1,2-benziodoxol-3-(1H)-one (1c)



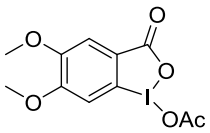
White solid. Yield 90%. M.p. 165-166^{o}C, v_{max} (KBr)/cm^{-1} 2163, ^{1}H-NMR (400 MHz, DMSO): δ 8.01(d, J = 8.4Hz, 1H), 7.72(s, 1H), 7.44(d, J = 8.4Hz, 1H), 3.94(s, 3H). ^{13}C-NMR (100 MHz, DMSO): δ 167.3, 166.2, 133.5, 123.3, 119.9, 118.4, 113.6, 89.6, 57.1; HRMS (ESI+) calced for $[C_9H_7O_3NI]^+$: 303.9465, found: 303.9465.

4,5-Dimetheoxyl-1-hydroxy-1,2-benziodoxol-3-(1H)-one[11]



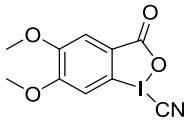
^{1}H-NMR (400 MHz, DMSO): δ 7.92(s, 1H), 7.44(s, 1H), 7.22(s, 1H), 3.88(bs, 6H). ^{13}C-NMR (100 MHz, DMSO): δ 168.8, 155.1, 151.6, 124.9, 113.4, 111.7, 108.4, 57.1, 56.9.

4,5-Dimetheoxyl-1-acetoxy-1,2-benziodoxol-3-(1H)-one



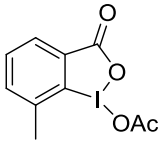
White solid. Yield 94%. M.p. 213-214^{o}C, ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.63(s, 1H), 7.35(s, 1H), 4.02(s, 3H), 4.00(s, 3H), 2.24(s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 176.6, 168.6, 156.2, 152.3, 122.1, 113.9, 110.3, 109.2, 56.9, 56.8, 20.6

4,5-Dimetheoxyl-1-cyano-1,2-benziodoxol-3-(1H)-one (1d)



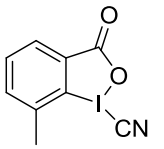
White solid. Yield 96%. M.p. 213-214^{o}C, v_{max} (KBr)/cm^{-1} 2164, ^{1}H-NMR (400 MHz, DMSO): δ 7.61(s, 1H), 7.51(s, 1H), 3.92(s, 3H), 3.90(s, 3H). ^{13}C-NMR (100 MHz, DMSO): δ 167.3, 155.9, 152.6, 123.8, 113.4, 109.9, 107.7, 89.4, 56.9, 55.6. HRMS (ESI+) calced for $[C_{10}H_9O_4NI]^+$: 333.9571, found: 333.9569.

3-Methyl-1-acetoxy-1,2-benziodoxol-3-(1H)-one



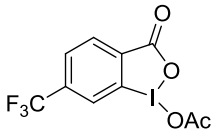
White solid. Yield 91%. M.p. 183-184^{o}C, ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.08(d, J = 7.6Hz, 1H), 7.67(d, J = 6.4Hz,1H), 7.57(t, J = 7.2Hz,1H), 2.65(s, 3H), 2.18(s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ176.7, 168.8, 140.7, 140.5, 132.3, 131.3, 129.8, 119.5, 23.0, 21.0.

3-Methyl-1-acetoxy-1,2-benziodoxol-3-(1H)-one (1e)



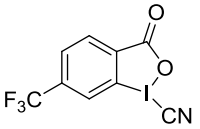
The reaction was conducted at 0 ^{o}C for 10mins to provide white solid. Yield 53%.(liable to decompose) M.p. 119-121^{o}C, v_{max} (KBr)/cm^{-1} 2164, ^{1}H-NMR (400 MHz, DMSO): δ 7.91(d, J = 7.6Hz, 1H), 7.85(d, J = 7.2Hz, 1H), 7.65(t, J = 7.4Hz, 1H), 2.76(s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 167.8, 140.7, 139.5, 132.3, 131.62, 131.58, 121.6, 89.3, 25.2. HRMS (ESI+) calced for $[C_9H_7O_2NI]^+$: 287.9516, found: 287.9517.

4-Trifluoromethyl-1-acetoxy-1,2-benziodoxol-3-(1H)-one



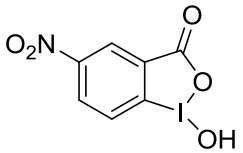
White solid. Yield 78% over two steps. M.p. 149-151°C, ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.37(d, J = 8.0Hz, 1H), 8.25(s, 1H), 7.97(d, J = 8.0 Hz, 1H), 2.29(s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 176.8, 166.9, 138.3, 137.9, 133.8, 132.6, 128.91, 128.87, 127.23, 127.19, 124.4, 121.7, 118.9, 20.5.

4-Trifluoromethyl-1-cyano-1,2-benziodoxol-3-(1H)-one (1f)



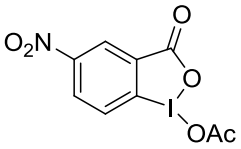
white solid. Yield 91%. M.p. 156-157°C, v_{max} (KBr)/cm^{-1} 2163, ^{1}H-NMR (400 MHz, DMSO): δ 8.46(s, 1H), 8.27-8.31(m, 2H). ^{13}C-NMR (100 MHz, DMSO): δ 166.6, 136.4, 136.0, 135.2, 133.6, 130.2, 125.91, 125.87, 125.4, 122.7, 119.9, 88.8. HRMS (ESI+) calced for $[C_9H_4O_2NIF_3]^+$: 341.9233, found: 341.9230.

5-Nitro-1-hydroxy-1,2-benziodoxol-3-(1H)-one[11]



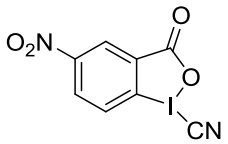
H-NMR (400 MHz, DMSO): δ 8.70(d, J = 2.4, 1H), 8.55(d, J = 2.4Hz, 1H), 8.51(s, 1H), 8.09(d, J = 8.8Hz, 1H). ^{13}C-NMR (100 MHz, DMSO): δ166.7, 150.5, 134.2, 129.0, 128.9, 128.5, 125.6.

5-Nitro-1-acetoxy-1,2-benziodoxol-3-(1H)-one[12]



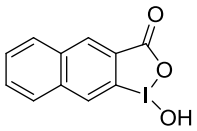
^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.03(d, J = 2.4Hz, 1H), 8.71(dd, J = 2.4, 8.8Hz, 1H), 8.27(d, J = 8.8Hz, 1H), 2.30(s, 3H). ^{13}C-NMR (100 MHz, DMSO): δ175.2, 166.7, 150.6, 132.5, 131.0, 130.3, 127.7, 126.2, 20.5.

5-Nitro-1-cyano-1,2-benziodoxol-3-(1H)-one (1g)



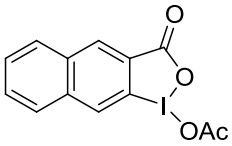
white solid. Yield 80%. M.p. 186-187°C, v_{max} (KBr)/cm^{-1} 2164, ^{1}H-NMR (400 MHz, DMSO): δ 8.77(d, J = 8.8Hz, 1H), 8.63(s, 1H), 8.54(d, J = 8.8Hz, 1H). ^{13}C-NMR (100 MHz, DMSO): δ165.7, 151.3, 133.0, 130.9, 130.8, 126.1, 125.2, 88.2; HRMS (ESI+) calced for $[C_8H_4O_2NI]^+$: 318.9210, found: 318.9209.

1-Hydroxy-1,2-napthiodoxol-3-(1H)-one[13]



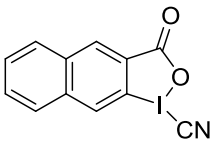
^{1}H-NMR (400 MHz, DMSO): δ8.67(s, 1H), 8.38(s, 1H), 8.28(d, J = 8.0Hz, 1H), 8.18-8.20(m, 2H), 7.71-7.78(m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ168.5, 136.6, 133.5, 132.5, 130.0, 129.6, 128.8, 128.7, 128.6, 127.1, 116.6.

1-Acetoxy-1,2-napthiodoxol-3-(1H)-one

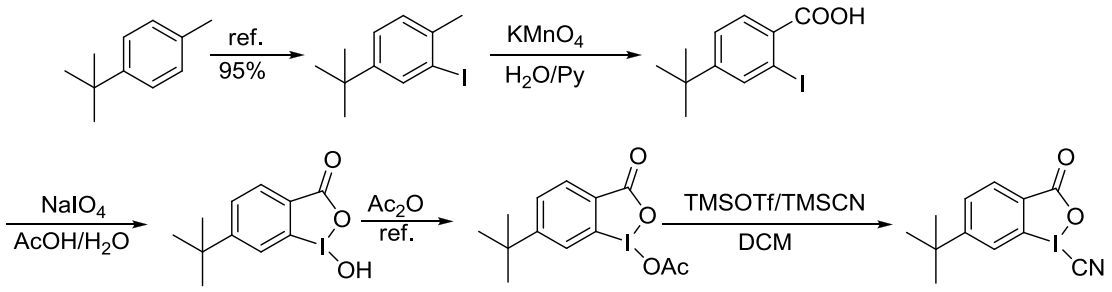


white solid. Yield 96%. M.p. 195-197°C, ^{1}H-NMR (400 MHz, $CDCl_3$): δ8.72(s, 1H), 8.35 (s, 1H), 8.05(d, J = 8.0Hz, 1H), 7.96(d, J = 8.0Hz, 1H), 7.68-7.77(m, 2H), 2.31(s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ176.7, 168.6, 137.7, 134.5, 133.6, 130.0, 129.9, 129.8, 129.2, 128.4, 124.6, 112.7, 20.7.

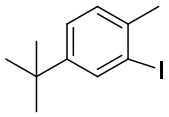
1-Cyano-1,2-napthiodoxol-3-(1H)-one (1h)



white solid. Yield 94%. M.p. 157-158°C, v_{max} (KBr)/cm^{-1} 2164, ^{1}H-NMR (400 MHz, DMSO): δ 8.73(d, J = 12.0Hz, 2H), 8.27(d, J = 7.6Hz, 1H), 8.19(d, J = 7.6Hz, 1H), 7.75-7.82(m, 2H). ^{13}C-NMR (100 MHz, DMSO): δ167.4, 137.5, 134.3, 133.4, 130.3, 130.2, 129.6, 128.8, 128.3, 126.7, 113.8, 88.8; HRMS (ESI+) calced for $[C_{12}H_7O_2NI]^+$: 323.9516, found: 323.9515.

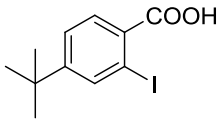


4-tert-butyl-2-iodo-1-methylbenzene[14]



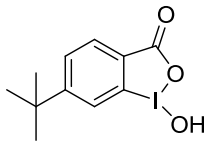
H-NMR (400 MHz, $CDCl_3$): δ7.85(s, 1H), 7.30(d, J = 8.0Hz, 1H), 7.19(d, J = 8.0Hz, 1H), 2.43(s, 3H), 1.32(s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ150.9, 138.5, 136.1, 129.5, 125.5, 101.6, 34.4, 31.5, 27.7.

4-tert-butyl-2-iodobenzoic acid



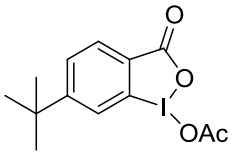
From a modification of known procedures[15], to the solution of 4-tert-butyl-2-iodo-1-methylbenzene (30mmol, 8.22g) in H_2O/pyridine(96ml:120 ml), was added KMnO4 (19g, 120mmol) and $^{n}BuN_4I$ (110mg, 1 mol%). The mixture was heated to reflux for 3 days when the solution turned clear. The hot solution was collected, while the black solid was extracted by EA. Then the former and latter was combined to get layered, the aqueous phase was further extracted by EA. The combined organic phase washed by 10 N HCl to adjust Ph 4. Then it was basified by 50% KOH solution to adjust Ph 10. The organic phase was collected, washed by brine and dried over anhydrous Na_2SO_4, and concentrated under reduced pressure, to provide the unreacted staring material 3.6g. While the aqueous phase was acidified by 2 N HCl to adjust Ph 10, it was extracted by EA, which was washed by brine and dried over anhydrous Na_2SO_4, and concentrated under reduced pressure, to provide the 4-tert-butyl-2-iodobenzoic acid 4.5g as a colorless solid. 49% yield. M.p. 162-163 ^{o}C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ8.04 (d, J = 1.8Hz, 1H), 7.97(d, J = 8.2Hz, 1H), 7.45(dd, J = 8.2, 1.8Hz, 1H), 1.31(s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 171.6, 158.0, 139.6, 132.3, 130.2， 125.5， 95.5，35.1，31.1.

4-^{t}Bu-1-hydroxy-1,2-benziodoxol-3-(1H)-one



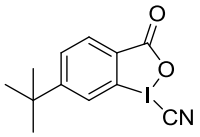
White solid. Yield 93% .M.p 190-193^{o}C. ^{1}H-NMR (400 MHz, DMSO): δ8.00(s, 1H), 7.92(d, *J* = 7.8Hz, 1H), 7.81(s, 1H), 7.74(d, *J* = 7.8Hz, 1H), 1.35(s, 9H). ^{13}C-NMR (100 MHz, DMSO): δ168.6, 158.8, 131.8, 130.0, 128.8, 123.3, 121.5, 36.5, 31.8.

4-^{t}Bu-1-Acetoxy-1,2-benziodoxol-3-(1H)-one



White solid. Yield 95% .M.p 150-153^{o}C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ8.14 (d, *J* = 8Hz, 1H), 7.94(d, *J* = 1.6Hz, 1H), 7.71(dd, *J* = 1.6, 8Hz, 1H), 2.26(s, 3H), 1.41(s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ176.4, 168.5, 161.2, 133.0, 129.1, 126.4, 125.8, 119.2, 36.4, 31.3, 20.5.

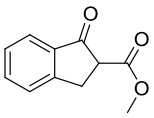
4-^{t}Bu-1-Acetoxy-1,2-benziodoxol-3-(1H)-one (1b)



white solid. Yield 93%. M.p. 176-177^{o}C, ν_{max} (KBr)/cm^{-1} 2162, ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.46(s, 1H), 8.25(d, *J* = 7.6Hz, 1H), 7.84(d, *J* = 8.0Hz, 1H), 1.44(s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ168.7, 162.1, 132.9, 130.0, 127.5, 124.9, 117.4, 85.6, 36.7, 31.3; HRMS (ESI+) calced for $[C_{12}H_{13}O_2NI]^+$: 329.9986, found: 329.9982.

5. Preparation of β-keto esters

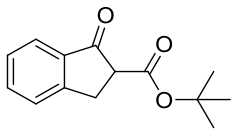
Methyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate[16] (3b)



Following the known procedure,[16] the product was obtained as light yellow solid in 86% yield. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.78(d, *J* =7.6Hz, 1H), 7.61-7.65(m, 1H), 7.51(d, *J* =7.6Hz, 1H), 7.38-7.42(m, 1H), 3.80(s, 3H), 3.74(dd, *J* =8.4, 4.0Hz, 1H), 3.55-3.60(m, 1H), 3.38(dd, *J* =8.4, 17.2Hz, 1H), Minor peaks due to enol observed at 3.86(s, 3H), 3.52(s, 2H);

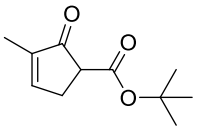
^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.6, 169.7, 153.8, 135.6, 135.4, 128.0, 126.7, 124.9, 53.3, 53.0, 30.4, Minor peaks due to enol observed at 129.6, 127.0, 124.9, 120.9, 51.4, 32.7; HRMS (ESI+) calced for $[C_{11}H_{10}O_2Na]^+$: 213.0522, found: 213.0525.

Tert-butyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate[3] (3a)



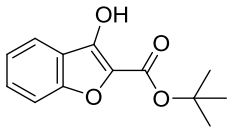
Following the known procedure,[3] the product was obtained as pink oil in 82% yield. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.74(d, J =7.6Hz, 1H), 7.57-7.61(m, 1H), 7.47(d, J =7.6Hz, 1H), 7.34-7.38(m, 1H), 3.60(dd, J =8.0, 2.0Hz, 1H), 3.55-3.60(m, 1H), 3.31(dd, J =8.0, 17.2Hz, 1H), 1.48(s, 9H), Minor peaks due to enol observed at 3.50-3.51(s, 2H), 1.56(s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 200.2, 168.5, 153.8, 135.6, 135.4, 127.8, 126.7, 124.7, 82.2, 54.5, 30.5, 28.2, Minor peaks due to enol observed at 129.2, 126.8, 124.8, 120.6, 81.1, 33.0, 28.6. HRMS (ESI+) calced for $[C_{14}H_{16}O_3Na]^+$: 255.0992, found: 255.0994.

Tert-butyl 3-methyl-2-oxocyclopent-3-enecarboxylate[17] (3q)



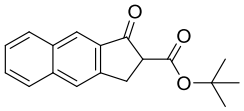
Following the known procedure,[17] the product was obtained as colorless oil in 93% yield. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.37(d, J =1.0Hz, 1H), 3.30(dd, J =2.1, 4.8Hz, 1H), 2.84-2.90(m, 1H), 2.71-2.78(m, 1H), 1.78(d, J =1.0Hz, 3H), 1.48(s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 203.3, 168.5, 157.7, 140.4, 81.8, 52.2, 30.9, 28.1, 10.4. HRMS (ESI+) calced for $[C_{11}H_{16}O_3Na]^+$: 219.0992, found: 212.0994.

Tert-butyl 3-hydroxybenzofuran-2-carboxylate (3t)



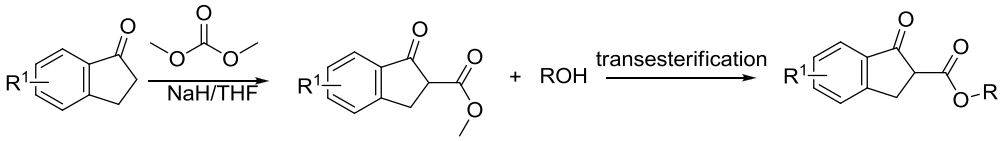
Following the known procedure,[18] the product was obtained as colorless solid in 90% yield. ^{1}H-NMR (400 MHz, $CDCl_3$): δ *enol form:* 8.27(bs, 1H), 7.71 (d, J =8.0Hz, 1H), 7.44-7.45(m, 2H), 7.25-7.28(m, 1H), 1.66(s, 9H), Minor peaks of ketone form observed at 1.52(s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 153.5, 129.1, 127.1, 125.0, 123.1, 120.6, 120.4, 113.8, 112.8, 83.6, 28.6. HRMS (ESI+) calced for $[C_{11}H_{16}O_3Na]^+$: 257.0784, found: 257.0785.

Tert-butyl 1-oxo-2,3-dihydro-1H-cyclopenta[b]naphthalene-2-carboxylate (3r)



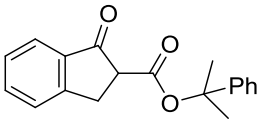
Following the known procedure,[3] the product was obtained as colorless solid in 76% yield from 2,3-dihydro-1H-cyclopenta[b]naphthalen-1-one. m.p. 99-100°C. ν_{max} (KBr)/cm^{-1} 2973, 2926, 1712, 1642, ^{1}H-NMR (400 MHz, $CDCl_3$): δ *keto form:* 8.32(s, 1H), 7.96(d, *J* =8.4Hz, 1H), 7.89(s, 1H), 7.83-7.85(m, 2H), 7.56-7.60(m, 1H), 3.71(dd, *J* =8.8, 4.8Hz, 1H), 3.63-3.68(m, 1H), 3.50(dd, *J* =8.8, 17.2Hz, 1H), 1.48(s, 9H), *enol form:* 8.06(s, 1H), 7.91-7.93(m,1H), 7.83-7.85(m, 1H), 7.46-7.50(m, 3H), 3.58(m, 2H), 1.58(s, 9H) ; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 200.4, 168.6, 146.1, 139.1, 137.5, 135.9, 134.3, 133.3, 132.5, 130.5, 129.0, 128.9, 128.0, 127.9, 126.5, 126.4, 125.8, 125.6, 124.8, 123.2, 120.1, 119.7, 112.0, 105.6, 82.2, 81.4, 55.2, 32.2, 30.0, 28.6, 28.2. HRMS (ESI+) calced for $[C_{18}H_{18}O_3Na]^+$: 305.1148, found: 305.1150.

General procedures by transesterification



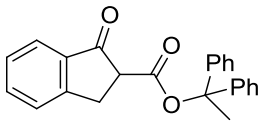
Following a literature procedure,[1] to a flask equipped with a Dean-Stark trap and reflux condenser was added β-keto methyl ester (3 mmol), corresponding alcohol, the transesterification catalyst DMAP or ZnO and toluene or cyclohexane. The mixture was refluxed under Ar until complete conversion was observed by TLC, then concentrated under reduced pressure and the crude residue was purified by column chromatography.

2-Phenylpropan-2-yl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate[1] (3c)



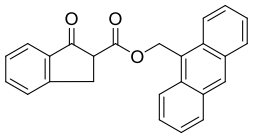
Following the general procedure, **3b** (3 mmol) was allowed to react with 2-phenylpropan-2-ol (653 mg, 4.8 mmol) in the presence of ZnO (48 mg, 0.6 mmol) and 25 mL of toluene overnight. the desired product was obtained as pink solid after column chromatography (silica gel, petroleum ether/ethyl acetate = 10/1) and recrystallization from PE and ether at -18°C (45% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* =7.6Hz, 1H), 7.56-7.60(m, 1H), 7.41-7.47(m, 3H), 7.31-7.39(m, 3H), 7.20-7.24(m, 1H), 3.72 (dd, *J* =4.0, 8.2Hz, 1H), 3.45-3.52(m, 1H), 3.31 (dd, *J* =17.2, 8.0Hz, 1H), 1.83(s, 3H), 1.80(s, 3H), Minor peaks due to enol observed at 3.61 (d, 2H), 1.89 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199. 8, 167.5, 153.8, 145.5, 135.5, 135.4, 128.4, 127.8, 127.2, 126.7, 124.7, 124.5, 83.4, 54.3, 30.2, 29.0, 28.4.HRMS (ESI+) calced for $[C_{19}H_{18}O_3Na]^+$: 317.1148, found: 317.1148.

1,1-diphenylethyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate[1] (3d)



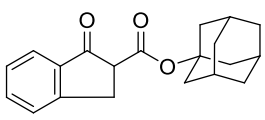
Following the general procedure, **3b** (3 mmol) was allowed to react with 1,1-diphenylethanol (951 mg, 4.8 mmol) in the presence of ZnO (48 mg, 0.6 mmol) and 25 mL of toluene overnight. The desired product was obtained as pink solid after column chromatography (silica gel, petroleum ether/ethyl acetate = 10/1) and recrystallization from ethanol and ether at -18°C (39% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* =7.6Hz, 1H), 7.60-7.63(m, 1H), 7.49 (d, *J* =7.6Hz, 1H), 7.20-7.44(m, 11H), 3.72 (dd, *J* =3.8, 8.0Hz, 1H), 3.50-3.55(m, 1H), 3.34 (dd, *J* =17.2, 8.0Hz, 1H), 1.83(s, 3H), 1.80(s, 3H), Minor peaks due to enol observed at 3.74 (s, 2H), 2.32 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.6, 167.0, 153.8, 145.6, 145.3, 135.5, 128.4, 128.3, 128.0, 127.5, 127.4, 126.8, 126.2, 126.2, 126.0, 124.8, 86.3, 54.5, 30.1, 26.9. HRMS (ESI+) calced for $[C_{24}H_{20}O_3Na]^+$: 379.1305, found: 379.1304.

Anthracen-9-ylmethyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate[1] (3e)



Following the general procedure, **3b** (3 mmol) was allowed to react with anthracen-9-ylmethanol (1374 mg, 3.75 mmol) in the presence of DMAP (48 mg, 0.6 mmol) and 25 mL of hexane overnight. The desired product was obtained as yellow solid after column chromatography (silica gel, PE/DCM = 1/1) and recrystallization from hot hexane (85% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ *keto form:*8.51(s, 1H), 8.38(d, *J* =8.8Hz, 2H), 8.05(s, *J* =8.8Hz, 2H), 7.76(d, *J* =7.6Hz, 1H), 7.56-7.61(m, 3H), 7.49-7.51(m, 2H), 7.43(d, *J* =7.6Hz, 1H), 7.35(bs, 1H), 6.33-6.35(m, 2H), 3.72(dd, *J* =8.0, 4.0Hz, 1H), 3.47-3.53(m, 1H), 3.30(dd, *J* =8.4, 17.2Hz, 1H), *enol form:* 8.53(s, 1H), 8.42(d, *J* =8.8Hz, 2H), 8.01-8.06(m, 2H), 7.56-7.61(m, 3H), 7.49-7.51(m, 2H), 7.37-7.39(m, 3H), 6.14-6.17(m, 2H), 3.39(s, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.5, 169.8, 153.7, 135.5, 131.6, 131.4, 129.6, 129.4, 129.3, 128.0, 127.0, 126.9, 126.7, 125.4, 124.9, 124.2, 60.5, 53.6, 30.6, Minor peaks due to enol observed at 143.6, 137.0, 135.5, 131.6, 129.5, 126.5, 125.9, 124.9, 121.0, 102.5, 58.7, 32.8. HRMS (ESI+) calced for $[C_{25}H_{18}O_3Na]^+$: 389.1148, found: 389.1149.

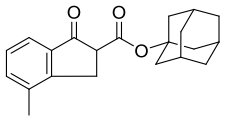
1-Adamantyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate[1] (3f)



Following the general procedure, **3b** (3 mmol) was allowed to react with 1-adamantanol (729

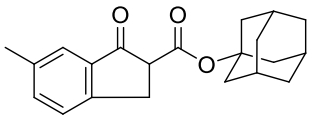
mg, 4.8 mmol) in the presence of ZnO (48 mg, 0.6 mmol) and 25 mL of toluene overnight. The desired product was obtained as pink solid after column chromatography (silica gel, PE/EA = 10/1) (42% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.76(d, J =7.6Hz, 1H), 7.59-7.63(m, 1H), 7.49(d, J =7.6Hz, 1H), 7.36-7.40(m, 1H), 3.61(dd, J =8.0, 4.0Hz, 1H), 3.47-3.52(m, 1H), 3.33(dd, J =8.0, 17.2Hz, 1H), 2.15(s, 9H), 1.66(s, 6H), Minor peaks due to enol observed at 3.47 (s, 2H), 2.23(s, 9H), 1.71(s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 200.2, 168.1, 153.9, 135.7, 135.3, 127.8, 126.7, 124.7, 82.3, 54.7, 41.4, 36.3, 31.0, 30.5, Minor peaks due to enol observed at 129.2, 126.8, 120.7, 45.5, 42.0, 36.4, 33.1, 30.9. HRMS (ESI+) calced for $[C_{20}H_{22}O_3Na]^+$: 333.1461, found: 333.1457.

1-Adamantyl 4-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3g)



Following the general procedure, Methyl 4-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3 mmol) was allowed to react with 1-adamantanol (912 mg, 6 mmol) in the presence of ZnO (48 mg, 0.6 mmol) and 25 mL of toluene overnight. The desired product was obtained as pink solid after column chromatography (silica gel, PE/EA = 10/1) (76% yield). m.p. 93-94^{o}C, v_{max} (film)/cm^{-1} 2914, 2852, 1712, 1646. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.60(d, J =7.6Hz, 1H), 7.41(d, J =7.2Hz, 1H), 7.26-7.32(m, 1H), 3.62(dd, J =8.4, 4.0Hz, 1H), 3.33-3.39(m, 1H), 3.21 (dd, J =17.2, 8.0Hz, 1H), 2.37(s, 3H), 2.15(s, 9H), 1.66(s, 6H), Minor peaks due to enol observed at 3.33-3.49(m, 2H), 2.24(s, 9H), 1.71(s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 200.5, 168.3, 152.9, 136.0, 135.8, 135.5, 128.1, 122.1, 82.3, 54.7, 41.4, 36.3, 31.1, 29.5, 17.9, Minor peaks due to enol observed at 130.3, 127.2, 118.4, 42.0, HRMS (ESI+) calced for $[C_{21}H_{24}O_3Na]^+$: 347.1618, found: 347.1616.

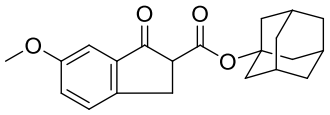
1-Adamantyl 6-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3h)



Following the general procedure, Methyl 6-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3 mmol) was allowed to react with 1-adamantanol (912 mg, 6 mmol) in the presence of ZnO (48 mg, 0.6 mmol) and 25 mL of toluene overnight. The desired product was obtained as pink solid after column chromatography (silica gel, PE/EA = 10/1) (48% yield). m.p. 102-104^{o}C, v_{max} (film)/cm^{-1} 2911, 2852, 1732, 1711, 1643. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.55(s, 1H), 7.36-7.43(m, 1H), 7.26-7.32(m, 1H), 3.60(dd, J =8.0, 4.0Hz, 1H), 3.40-3.45(m, 1H), 3.27 (dd, J =17.2, 8.0Hz, 1H), 2.40(s, 3H), 2.14(s, 9H), 1.65(s, 6H), Minor peaks due to enol observed at 3.40-3.45(m, 2H), 2.41(s, 3H), 2.23(s, 9H), 1.71(s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 200.3, 168.3,

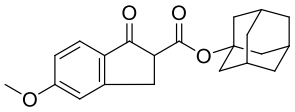
151.3, 137.8, 136.6, 135.8, 126.3, 124.6, 82.2, 55.1, 41.4, 36.3, 31.0, 30.2, 21.2, Minor peaks due to enol observed at 130.2, 124.5, 121.1, 45.5, 42.0, 36.4, 31.1 .HRMS (ESI+) calced for $[C_{21}H_{24}O_3Na]^+$: 347.1618, found: 347.1616.

1-Adamantyl 6-methoxyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate[1] (3i)



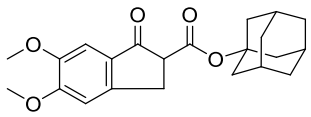
Following the general procedure, methyl 6-methoxyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3 mmol) was allowed to react with 1-adamantanol (912 mg, 6 mmol) in the presence of ZnO (48 mg, 0.6 mmol) and 25 mL of toluene overnight. The desired product was obtained as white solid after column chromatography (silica gel, PE/EA = 5/1) (53% yield). m.p. 122-124^{o}C, v_{max} (film)/cm^{-1} 2912, 2853, 1731, 1710, 1640. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.37(d, J =8.4Hz, 1H), 7.18-7.21(m, 2H), 3.83(s, 3H), 3.82(dd, J =8.0, 3.6Hz, 1H), 3.37-3.42(m, 1H), 3.25 (dd, J =16.8, 8.0Hz, 1H), 2.14(s, 9H), 1.66(s, 6H), Minor peaks due to enol observed at 3.85(s, 3H), 3.37-3.42(m, 2H), 2.23(s, 9H), 1.69(s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ200.2, 168.2, 159.8, 146.8, 136.8, 127.3, 124.8, 105.7, 82.2, 55.8, 55.4, 41.4, 36.3, 31.0, 29.9. HRMS (ESI+) calced for $[C_{21}H_{24}O_4Na]^+$: 363.1567, found: 363.1567.

1-Adamantyl 5-methoxyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate[19] (3j)



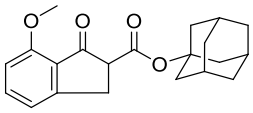
Following the general procedure, methyl 5-methoxyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3 mmol) was allowed to react with 1-adamantanol (912 mg, 6 mmol) in the presence of ZnO (48 mg, 0.6 mmol) and 25 mL of toluene overnight. The desired product was obtained as white solid after column chromatography (silica gel, PE/EA = 5/1) (98% yield), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.67(d, J =6.8Hz, 1H), 6.90(bs, 1H), 3.88(s, 3H), 3.59(s, 1H), 3.41-3.49(m, 1H), 3.24-3.28(m, 1H), 2.14(s, 9H), 1.65(s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 198.2, 168.4, 165.8, 156.9, 128.8, 126.3, 115.9, 109.6, 82.0, 55.8, 54.8, 45.4, 41.3, 36.2, 31.0. HRMS (ESI+) calced for $[C_{21}H_{24}O_4Na]^+$: 363.1567, found: 363.1566.

1-Adamantyl 4,5-Dimethoxyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate[1] (3k)



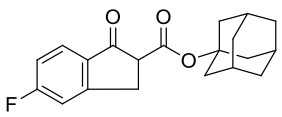
Following the general procedure, methyl 4,5-dimethoxyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3 mmol) was allowed to react with 1-adamantanol (912 mg, 6 mmol) in the presence of ZnO (48 mg, 0.6 mmol) and 25 mL of toluene overnight. The desired product was obtained as white solid after column chromatography (silica gel, PE/EA = 3/1) (84% yield), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.17(s, 1H), 6.90(s, 1H), 3.98(s, 3H), 3.90(s, 3H), 3.59(dd, J =7.6, 3.2Hz, 1H), 3.36-3.41(m, 1H), 3.59(dd, J =7.6, 16.8Hz, 1H), 2.15(s, 9H), 1.66(s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 198.8, 168.6, 156.1, 149.9, 149.4, 128.4, 107.5, 105.0, 82.2, 56.5, 56.3, 55.0, 41.4, 36.3, 31.1, 30.4. HRMS (ESI+) calced for $[C_{22}H_{26}O_5Na]^+$: 393.1673, found: 393.1673.

1-Adamantyl 7-methoxyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3l)



Following the general procedure, methyl 7-methoxyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3 mmol) was allowed to react with 1-adamantanol (912 mg, 6 mmol) in the presence of ZnO (48 mg, 0.6 mmol) and 25 mL of toluene overnight. The desired product was obtained as white solid after column chromatography (silica gel, PE/EA = 5/1) (95% yield), m.p. 102-103^{o}C, v_{max} (film)/cm^{-1} 2913, 2852, 1731, 1711, 1643. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.50-7.54(m, 1H), 7.01(d, J =7.6Hz, 1H), 6.78(d, J =8.0Hz, 1H), 3.93(s, 3H), 3.57(dd, J =8.0, 3.6Hz, 1H), 3.39-3.44(m, 1H), 3.23(dd, J =8.0, 17.2Hz, 1H), 2.15(s, 9H), 1.64(s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 197.5, 168.3, 158.8, 156.3, 137.0, 123.7, 118.3, 109.2, 82.0, 55.9, 55.0, 41.3, 36.2, 30.9, 30.0. HRMS (ESI+) calced for $[C_{21}H_{24}O_4Na]^+$: 363.1565, found: 363.1566.

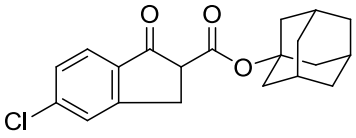
1-Adamantyl 5-fluoro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate[19] (3m)



Following the general procedure, methyl 5-fluoro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3 mmol) was allowed to react with 1-adamantanol (912 mg, 6 mmol) in the presence of ZnO (48 mg, 0.6 mmol) and 25 mL of toluene overnight. The desired product was obtained as pink solid after column chromatography (silica gel, PE/EA = 10/1) (93% yield), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.76(s, 1H), 7.08-7.16(m, 2H), 3.63-3.64(m, 1H), 3.46-3.51(m, 1H), 3.31 (dd, J =17.2, 8.0Hz,

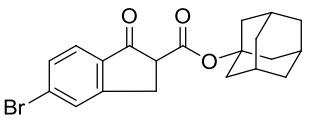
1H), 2.13(s, 9H), 1.65(s, 6H), Minor peaks due to enol observed at 3.46-3.51(m, 2H), 2.22(s, 9H), 1.70(s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 198.2, 168.9, 167.8, 166.3, 156.9, 156.8, 132.0, 127.1, 127.0, 116.3, 116.1, 113.5, 113.2, 82.5, 54.9, 41.9, 41.3, 36.3, 36.2, 31.0, 30.4. HRMS (ESI+) calced for $[C_{20}H_{21}O_3FNa]^+$: 351.1367, found: 351.1367.

1-Adamantyl 5-chloro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate[1] (3n)



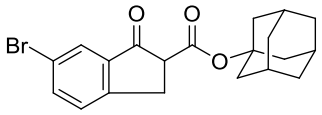
Following the general procedure, methyl 5-chloro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3 mmol) was allowed to react with 1-adamantanol (912 mg, 6 mmol) in the presence of ZnO (48 mg, 0.6 mmol) and 25 mL of toluene overnight. The desired product was obtained as pink solid after column chromatography (silica gel, PE/EA = 10/1) (39% yield), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J =8.0Hz, 1H), 7.49 (s, 1H), 7.36(d, J =8.0Hz, 1H), 3.62 (dd, J =4.0, 8.0Hz, 1H), 3.46-3.50(m, 1H), 3.30 (dd, J =17.2, 8.0Hz, 1H), 2.17(s, 3H), 2.14(s, 6H), 1.66(s, 6H), Minor peaks due to enol observed at 7.53 (d, J =8.0Hz, 1H), 7.42 (s, 1H), 7.36(d, J =8.0Hz, 1H), 3.45(s, 2H), 2.22(s, 9H), 1.70(s, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 198.6, 167.7, 155.3, 141.9, 134.1, 128.6, 126.9, 125.8, 82.5, 54.7, 41.3, 36.3, 36.2, 31.0, Minor peaks due to enol observed at 127.3, 125.2, 121.5, 41.9, 30.2. HRMS (ESI+) calced for $[C_{20}H_{21}O_3ClNa]^+$: 367.1071, found: 367.1073.

1-Adamantyl 5-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate[19] (3o)



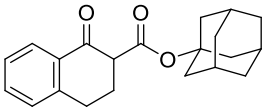
Following the general procedure, methyl 5-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3 mmol) was allowed to react with 1-adamantanol (912 mg, 6 mmol) in the presence of ZnO (48 mg, 0.6 mmol) and 25 mL of toluene overnight. The desired product was obtained as pink solid after column chromatography (silica gel, PE/EA = 10/1) (52% yield), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.68(s, 1H), 7.58-7.62(m, 1H), 7.50-7.53(m, 1H), 3.61(dd, J =8.0, 4.0Hz, 1H), 3.45-3.51(m, 1H), 3.30(dd, J =8.0, 17.2Hz, 1H), 2.17(s, 3H), 2.13(s, 6H), 1.65(s, 6H), Minor peaks due to enol observed at 3.44(s, 2H), 2.22(s, 9H), 1.70(s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 198.9, 167.7, 155.4, 134.5, 131.6, 130.8, 130.2, 130.0, 128.1, 125.9, 121.9, 82.6, 54.7, 42.0, 41.4, 36.4, 36.3, 33.0, 31.1, 30.2. HRMS (ESI+) calced for $[C_{20}H_{21}O_3BrNa]^+$: 411.0567, found: 411.0566.

1-Adamantyl 6-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate[1] (3p)



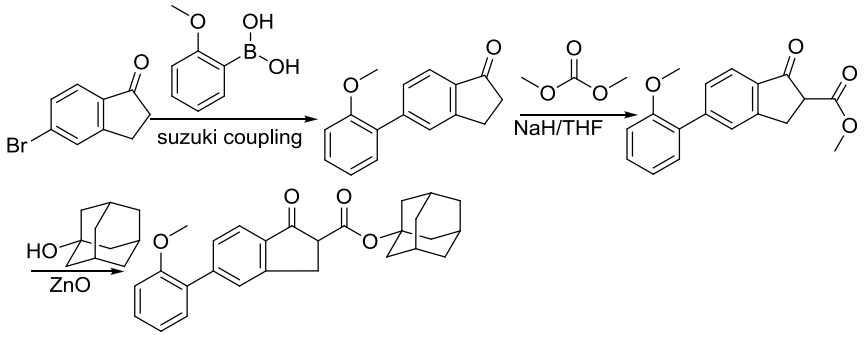
Following the general procedure, methyl 6-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3 mmol) was allowed to react with 1-adamantanol (912 mg, 6 mmol) in the presence of ZnO (48 mg, 0.6 mmol) and 25 mL of toluene overnight. The desired product was obtained as pink solid after column chromatography (silica gel, PE/EA = 10/1) (94% yield), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.87(s, 1H), 7.70-7.77(m, 1H), 7.38(d, J =8.0Hz, 1H), 3.63(dd, J =8.8, 4.0Hz, 1H), 3.41-3.46(m, 1H), 3.27(dd, J =8.8, 17.2Hz, 1H), 2.17(s, 3H), 2.13(s, 6H), 1.66(s, 6H), Minor peaks due to enol observed at 7.70-7.77(m, 1H), 7.47-7.50(m, 1H), 7.30(d, J =8.0Hz, 1H), 3.42(s, 2H), 2.22(s, 9H), 1.71(s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 198.7, 167.6, 152.4, 141.7, 139.5, 138.1, 137.5, 131.9, 128.2, 127.6, 126.2, 123.8, 122.0, 120.9, 105.6, 82.6, 81.7, 55.0, 42.0, 41.4, 36.4, 36.3, 32.9, 31.13, 31.08, 30.2. HRMS (ESI+) calced for $[C_{20}H_{21}O_3BrNa]^+$: 411.0567, found: 411.0563.

1-Adamantyl 1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate[1] (3s)



Following the general procedure, methyl 6-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3 mmol) was allowed to react with 1-adamantanol (912 mg, 6 mmol) in the presence of ZnO (48 mg, 0.6 mmol) and 25 mL of toluene overnight. The desired product was obtained as white solid after column chromatography (silica gel, PE/EA = 50/1) (92% yield), ^{1}H-NMR (400 MHz, $CDCl_3$): δ enol form: 12.61 (bs, 1H), 7.76-7.79 (m, 1H), 7.22-7.32(m, 2H), 7.15(d, J =6.8Hz, 1H), 2.76-2.80(m, 2H), 2.49-2.53(m, 2H), 2.21(s, 9H), 1.70(s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 172.6, 164.7, 139.5, 130.6, 130.4, 127.5, 126.7, 124.3, 98.6, 81.6, 41.8, 36.4, 31.1, 28.1, 21.2. HRMS (ESI+) calced for $[C_{21}H_{24}O_3Na]^+$: 347.1618, found: 347.1618.

1-Adamantyl 5-(2-methoxyphenyl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3u)



To a flask equipped with a stirring bar and a reflux condenser was added 5-bromoindan-1-one (1.055g, 5 mmol), the 2-methoxyphenylboronic acid (1.21g, 8 mmol), K_2CO_3(6.9g, 50mmol), $Pd(PPh_3)_4$ (288 mg, 5mol %). Then the system was evacuated 3 times and backfilled with Ar before solvent 75 ml THF and 25 ml H_2O were added by syringe. The mixture was heated to reflux overlight under Ar atmosphere. When it was cooled to room temperature, water and EA was added. The aqueous phase was extracted with EA twice (50ml*2). The organic phase was combined and washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA=20:1-5:1), providing 5-(2-methoxyphenyl)-2,3-dihydro-1H-inden-1-one as white solid of 1.04g. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.78(d, J =8.0Hz, 1H), 7.61(s, 1H), 7.53(d, J =8.0Hz, 1H), 7.31-7.39(m, 2H), 7.00-7.07(m, 2H), 3.82(s, 3H), 3.17(d, J =5.6Hz, 2H), 2.72(d, J =5.6Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 207.0, 156.6, 155.3, 145.5, 135.8, 131.0, 129.8, 129.7, 129.3, 127.8, 123.3, 121.1, 111.4, 55.7, 36.6, 26.01. The data was in accordance with reported ones.[20]

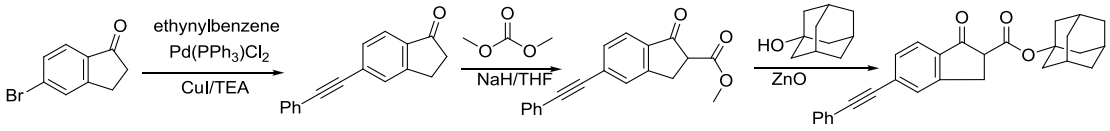
To a flask equipped with a stirring bar and a reflux condenser was added NaH(240mg, 6mmol, 60% in mineral oil), then the system was evacuated 3 times and backfilled with Ar before solvent 25 ml THF was added. A solution of 5-(2-methoxyphenyl)-2,3-dihydro-1H-inden-1-one (714mg, 3.0 mmol) in 10 ml THF was addded by syringe. After 10min when the evolution of H2 ceased, dimethyl carbonate (500 mg, 5.6 mmol) was added. Then the mixture was heated to reflux for 2 hours when the system solified. After it was cooled to room temperature, HCl (1M) and water was added to adjust pH

2. The aqueous phase was extracted with EA twice (25ml*2). The organic phase was combined and washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to furnish methyl 5-(2-methoxyphenyl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate without further purification.

Following the general procedure of transesterification above, methyl 7-methoxyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (all residue above) was allowed to react with 1-adamantanol (912 mg, 6 mmol) in the presence of ZnO (48 mg, 0.6 mmol) and 25 mL of toluene overnight. The desired product was obtained as white solid after column chromatography (silica gel, PE/EA = 10/1) (72% yield), m.p. 66-67^{o}C, v_{max} (film)/cm^{-1} 2917, 2852, 1733, 1712, 1604. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.78(d, J =8.0Hz, 1H), 7.62(s, 1H), 7.54(d, J =8.0Hz, 1H), 7.31-7.40(m, 2H), 7.00-7.07(m, 2H), 3.83(s, 3H), 3.64(dd, J =8.0, 4.0Hz, 1H), 3.47-3.51(m, 1H), 3.36(dd, J =8.4, 17.2Hz, 1H), 2.16(s, 9H), 1.62(s, 6H), Minor

peaks due to enol observed at 3.82(s, 3H), 3.55(m, 2H), 2.23(s, 9H), 1.70(s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.9, 168.3, 156.6, 153.8, 146.2, 134.2, 131.2, 131.0, 129.9, 129.7, 127.6, 124.2, 121.2, 111.5, 82.3, 55.8, 55.0, 41.5, 36.4, 31.1, 30.6. HRMS (ESI+) calced for $[C_{27}H_{28}O_4Na]^+$: 439.1880, found: 439.1878.

1-Adamantyl 1-oxo-5-(phenylethynyl)-2,3-dihydro-1H-indene-2-carboxylate (3w)



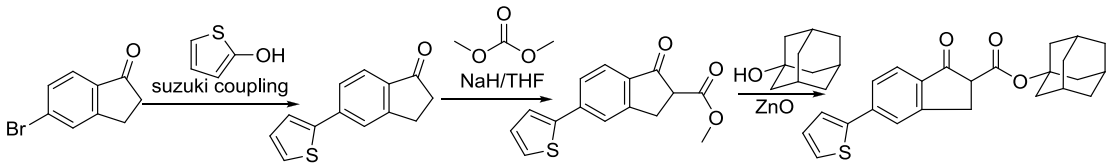
To a flask equipped with a stirring bar and a reflux condenser was added 5-bromoindan-1-one (844mg, 4 mmol), the ethynlbenzene (489mg, 4.8 mmol), $Pd(PPh_3)_2Cl_2$ (56mg, 8 mmol), CuI(30 mg, 0.16mmol). Then the system was evacuated 3 times and backfilled with Ar before solvent 75 ml THF and 1.20g ml TEA were added by syringe. The mixture was heated to reflux for 4 hours under Ar atmosphere. When it was cooled to room temperature, water and EA was added. The aqueous phase was extracted with EA twice (50ml*2). The organic phase was combined and washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA=100:0-5:1), providing 5-(phenylethynyl)-2,3-dihydro-1H-inden-1-one as white solid of 560mg. H-NMR (400 MHz, $CDCl_3$): δ 7.74(d, J =8.0Hz, 1H), 7.64(s, 1H), 7.50-7.57(m, 3H) , 7.37-7.39(m, 3H), 3.16(d, J =6.0Hz, 2H), 2.73(d, J =6.0Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 206.2, 155.1, 136.6, 131.9, 130.9, 129.8, 129.1, 128.6, 125.1, 123.8, 122.8, 92.9, 89.1, 36.5, 25.8 . The data was in accordance with reported ones.[21]

To a flask equipped with a stirring bar and a reflux condenser was added NaH(160mg, 4mmol, 60% in mineral oil), then the system was evacuated 3 times and backfilled with Ar before solvent 15 ml THF was added. A solution of 5-(phenylethynyl)-2,3-dihydro-1H-inden-1-one (404mg, 2.0 mmol) in 10 ml THF was addded by syringe. After 10min when the evolution of H_2 ceased, dimethyl carbonate (244 mg, 2.72 mmol) was added. Then the mixture was heated to reflux for 2 hours when the system solified. After it was cooled to room temperature, HCl (1M) and water was added to adjust pH 2. The aqueous phase was extracted with EA twice (25ml*2). The organic phase was combined and washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to furnish methyl 1-oxo-5-(phenylethynyl)-2,3-dihydro-1H-indene-2-carboxylate without further purification.

Following the general procedure of transesterification above, methyl 7-methoxyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (all residue above) was allowed to react with 1-adamantanol (608 mg, 4 mmol) in the presence of ZnO (32 mg, 0.4 mmol) and 15mL of toluene overnight. The desired product was obtained as white solid after column chromatography (silica gel, PE/EA = 10/1) (70% yield), m.p. 139-140^{o}C, v_{max} (film)/cm^{-1} 2912, 2853, 1732, 1711, ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.73(d, J =8.0Hz, 1H), 7.64(s, 1H),

7.53-7.57(m, 3H), 7.34-7.38(m, 2H), 3.63(dd, *J* =8.0, 4.0Hz, 1H), 3.51-3.52(m, 1H), 3.32(dd, *J* =8.0, 17.2Hz, 1H), 2.17(s, 3H), 2.15(s, 6H), 1.66(s, 6H), Minor peaks due to enol observed at 3.47-3.48(s, 2H), 2.23(s, 9H), 1.71(s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.3, 168.0, 153.7, 135.0, 132.0, 131.8, 131.3, 129.6, 129.2, 128.7, 128.6, 124.6, 93.4, 89.0, 82.4, 54.8, 41.4, 36.3, 31.1, 30.3. HRMS (ESI+) calced for $[C_{28}H_{26}O_4Na]^+$: 433.1774, found: 433.1775.

1-Adamantyl 1-oxo-5-(thiophen-2-yl)-2,3-dihydro-1H-indene-2-carboxylate (3v)



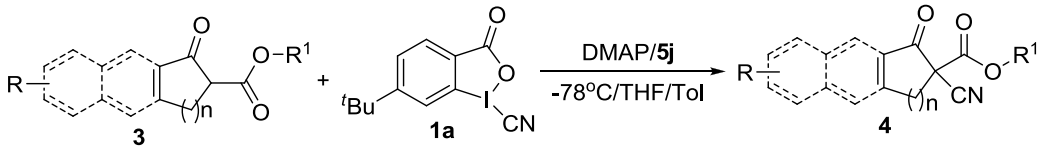
To a flask equipped with a stirring bar and a reflux condenser was added 5-bromoindan-1-one (1.055g, 5 mmol), the 2-methoxyphenylboronic acid (1.00g, 8 mmol), K_2CO_3(6.9g, 50mmol), $Pd(PPh_3)_4$ (288 mg, 5mol %). Then the system was evacuated 3 times and backfilled with Ar before solvent 75 ml THF and 25 ml H_2O were added by syringe. The mixture was heated to reflux overlight under Ar atmosphere. When it was cooled to room temperature, water and EA was added. The aqueous phase was extracted with EA twice (50ml*2). The organic phase was combined and washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA=5:1), providing 5-(thiophen-2-yl)-2,3-dihydro-1H-inden-1-one as white solid of 960mg. m.p. 149-150^{o}C, v_{max} (film)/cm^{-1} 2920, 1698. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.73(d, *J* =8.0Hz, 1H), 7.67(s, 1H), 7.60(d, *J* =8.0Hz, 1H), , 7.43(d, *J* =3.6Hz, 1H), 7.37(d, *J* =4.8Hz, 1H), 7.10-7.12(m, 1H), 3.15(d, *J* =6.0Hz, 2H), 2.70(d, *J* =6.0Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 206.3, 156.2, 143.3, 140.5, 136.1, 128.6, 126.8, 125.3, 125.1, 124.4, 123.4, 36.6, 25.9. HRMS (ESI+) calced for $[C_{13}H_{10}NOSNa]^+$: 237.0344, found: 237.0344.

To a flask equipped with a stirring bar and a reflux condenser was added NaH(240mg, 6mmol, 60% in mineral oil), then the system was evacuated 3 times and backfilled with Ar before solvent 25 ml THF was added. A solution of 5-(thiophen-2-yl)-2,3-dihydro-1H-inden-1-one (642mg, 3.0 mmol) in 10 ml THF was addded by syringe. After 10min when the evolution of H2 ceased, dimethyl carbonate (500 mg, 5.6 mmol) was added. Then the mixture was heated to reflux for 2 hours when the system solified. After it was cooled to room temperature, HCl (1M) and water was added to adjust Ph 2. The aqueous phase was extracted with EA twice (25ml*2). The organic phase was combined and washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to furnish methyl 5-(2-methoxyphenyl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate without further purification.

Following the general procedure of transesterification above, methyl 7-methoxyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (all residue above) was allowed to react with 1-adamantanol (912 mg, 6 mmol) in the presence of ZnO (48 mg, 0.6 mmol) and 25 mL of toluene overnight. The desired product was obtained as yellow solid after column chromatography (silica gel, PE/EA = 15/1) and then recrystallization from Et_2O and DCM (89%

yield), m.p. 147-148°C, v_{max} (film)/cm^{-1} 2914, 2849, 1733, 1707, 1604. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.74(d, *J* =8.0Hz, 1H), 7.68(s, 1H), 7.64(d, *J* =8.0Hz, 1H), 7.45(bs, 1H), 7.39(d, *J* =8.0Hz, 1H), 7.10-7.13(m, 1H), 3.63-3.65(m, 1H), 3.49-3.53(m, 1H), 3.33(dd, *J* =8.0, 17.2Hz, 1H), 2.16(s, 9H), 1.67(s, 6H), Minor peaks due to enol observed at 3.75(s, 2H), 2.24(s, 9H), 1.71(s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.2, 168.1, 154.7, 143.1, 141.1, 134.5, 128.6, 127.1, 125.7, 125.3, 125.3, 123.2, 82.3, 54.9, 41.4, 36.3, 31.0, 30.5, Minor peaks due to enol observed at 68.1, 41.9, 36.4, 31.1, 25.8. HRMS (ESI+) calced for $[C_{24}H_{24}O_3SNa]^+$: 415.1338, found: 415.1338.

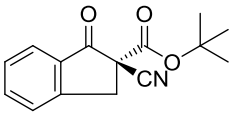
6. Enantioselective Electrophilic Cyanation of β-keto Esters



General procedure for the cyanation of cyclic-keto esters.

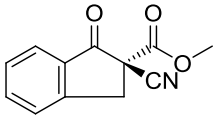
The cyclic-keto ester **3** (0.2 mmol, 1 equiv.), DMAP (1.1 equiv.) and chiral phase transfer catalyst **5j** (0.1equiv.) was dissolved in a tube in toluene/tetrahydrofuran (0.3ml/0.6ml). After the mixture was stirred for 10mins when it was cooled to -78°C, **1a** (1.1 equiv) was added in one portion. The reaction was monitored by TLC until complete consumption of the starting material within given time. when the mixture was warmed to r.t., the solvent was removed under vacuum. The residue was purified by flash chromatography with EA/PE as elute to give compound **4**.

(S)-Tert-butyl 2-cyano-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4a)



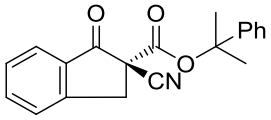
Reaction time 1h, white solid, 96% yield, m.p. 49-50°C, v_{max} (film)/cm^{-1} 2982, 2934, 2248, 1731, 1606, $[\alpha]_D^{25}$ +27.2 (c 0.5, $CDCl_3$, 82% ee), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.74(d, *J* =7.6Hz, 1H), 7.62-7.66(m, 1H), 7.47(d, *J* =7.6Hz, 1H), 7.38-7.42(m, 1H), 3.80(d, *J* =17.2Hz, 1H), 3.57(d, *J* =17.2Hz, 1H), 1.40(s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 191.4, 162.9, 151.8, 136.9, 132.3, 128.9, 126.6, 126.1, 116.2, 85.8, 55.3, 37.6, 27.7; HRMS (ESI+) calced for $[C_{15}H_{15}O_3NNa]^+$: 280.0944, found: 280.0942; HPLC conditions: Chiralcel AS-H column, hexane/*i*-PrOH = 85/15, 1 mL/min, 254nm, t_R(minor) = 9.0 min, t_R(major) = 10.7 min.

(S)-methyl 2-cyano-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4b)



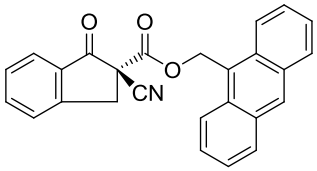
Reaction time 1h, colorless oil, 94% yield, , v_{max} (film)/cm^{-1} 2956, 2249, 1752, 1732, $[\alpha]_D^{25}$ +47.8 (c 0.5, $CDCl_3$, 75% ee), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.86(d, J =7.6Hz, 1H), 7.73-7.77(m, 1H), 7.56(d, J =7.6Hz, 1H), 7.49-7.52(m, 1H), 3.96(d, J =17.2Hz, 1H), 3.88(s, 3H), 3.71(d, J =17.2Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 190.8, 164.8, 151.7, 137.2, 132.2, 129.2, 126.7, 126.5, 115.9, 54.8, 54.4, 37.7 ; HRMS (ESI+) calced for $[C_{12}H_9O_3NNa]^+$: 238.0475, found: 238.0474; HPLC conditions: Chiralcel AS-H column, hexane/*i*-PrOH = 85/15, 1 mL/min, 254nm, t_R(minor) = 18.9 min, t_R(major) = 29.3 min.

(S)-2-phenylpropan-2-yl 2-cyano-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4c)



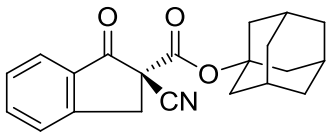
Reaction time 1h, white solid, 88% yield, m.p. 88-89°C, v_{max} (film)/cm^{-1} 2983, 2928, 2248, 1731, 1604, $[\alpha]_D^{25}$ +7.2 (c 0.5, $CDCl_3$, 63% ee), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J =7.6Hz, 1H), 7.66-7.60(m, 1H), 7.43-7.49(m, 2H), 7.24-7.37(m, 5H), 3.85 (d, J =17.2Hz, 1H), 3.62 (d, J =17.2Hz, 1H), 1.84(s, 3H), 1.81(s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 191.1, 162.2, 151.8, 144.3, 137.0, 132.5, 129.1, 128.7, 127.9, 126.6, 126.4, 124.4, 116.3, 86.9, 55.3, 37.5, 28.5, 28.1; HRMS (ESI+) calced for $[C_{20}H_{17}O_3NNa]^+$: 342.1100, found: 342.1098; HPLC conditions: Chiralcel AS-H column, hexane/*i*-PrOH = 85/15, 1 mL/min, 254nm, t_R(minor) = 12.4 min, t_R(major) = 15.1 min.

(S)-anthracen-9-ylmethyl 2-cyano-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4e)



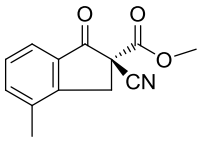
Reaction time 1h, yellow solid, 93% yield, m.p. 126-128°C, v_{max} (film)/cm^{-1} 2925, 2250, 1748, 1730, $[\alpha]_D^{25}$ +26.4 (c 0.5, $CDCl_3$, 65% ee), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.38(s, 1H), 8.22(d, J =8.8Hz, 2H), 7.92(s, J =8.4Hz, 2H), 7.73(d, J =7.6Hz, 1H), 7.32-7.57(m, 5H), 7.2-7.36(m, 2H), 6.21(s, 2H), 3.70(d, J = 17.2 Hz, 1H), 3.50(d, J =17.2Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 190.7, 164.5, 151.5, 136.9, 132.1, 131.2, 131.1, 130.0, 129.2, 128.9, 127.1, 126.5, 126.2, 125.2, 124.3, 123.6, 115.7, 62.6, 54.6, 37.6; HRMS (ESI+) calced for $[C_{26}H_{17}O_3NNa]^+$: 414.1101, found: 414.1096; HPLC conditions: Chiralcel AS-H column, hexane/*i*-PrOH = 60/40, 1 mL/min, 254nm, t_R(minor) = 24.7 min, t_R(major) = 35.4min.

(S)-1-Adamantyl 2-cyano-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4f)



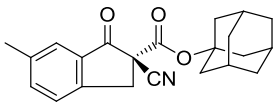
Reaction time 1h, white solid, 97% yield, m.p. 117-118°C, ν_{max} (film)/cm^{-1} 2915, 2855, 2247, 1729, $[\alpha]_D^{25}$ +32.8 (c 0.5, $CDCl_3$, 87% ee), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.84(d, J =7.6Hz, 1H), 7.70-7.74(m, 1H), 7.54(d, J =7.6Hz, 1H), 7.46-7.40(m, 1H), 3.88(d, J =17.2Hz, 1H), 3.65(d, J =17.2Hz, 1H), 2.18(s, 3H), 2.12(s, 6H), 1.64(s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 191.5, 162.5, 151.8, 136.9, 132.5, 129.0, 126.6, 126.3, 116.3, 86.0, 55.5, 41.0, 37.7, 36.0, 31.1; HRMS (ESI+) calced for $[C_{21}H_{21}O_3NNa]^+$: 358.1414, found: 358.1410; HPLC conditions: Chiralcel AS-H column, hexane/*i*-PrOH = 85/15, 1 mL/min, 254nm, t_R(minor) = 11.0 min, t_R(major) = 15.3min.

(S)-1-Adamantyl 2-cyano-4-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4g)



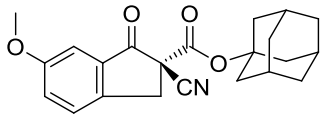
Reaction time 1h, white solid, 87% yield, m.p. 97-99°C, ν_{max} (film)/cm^{-1} 2911, 2247, 1730, $[\alpha]_D^{25}$ +44.0 (c 0.5, $CDCl_3$, 82% ee), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.67(d, J =7.6Hz, 1H), 7.52(d, J =7.2Hz, 1H), 7.26-7.32(m, 1H), 3.77(d, J =17.2Hz, 1H), 3.52 (d, J =17.2, Hz, 1H), 2.39(s, 3H), 2.18(s, 3H), 2.13(s, 6H), 1.65(s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ191.7, 162.6, 150.8, 137.4, 136.1, 132.3, 129.1, 123.6, 116.4, 85.9, 55.4, 40.9, 36.7, 36.0, 31.1, 17.8; HRMS (ESI+) calced for $[C_{22}H_{23}O_3NNa]^+$: 327.1570, found: 372.1565; HPLC conditions: Chiralcel AS-H column, hexane/*i*-PrOH = 85/15, 1 mL/min, 254nm, t_R(minor) = 10.0 min, t_R(major) = 20.6min.

(S)-1-Adamantyl 2-cyano-6-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4h)



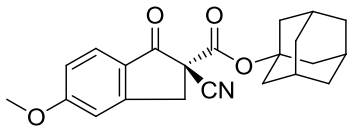
Reaction time 1h, colorless oil, 98% yield, ν_{max} (film)/cm^{-1} 2915, 2864, 2247, 1744, 1728 , $[\alpha]_D^{25}$ +23.4 (c 0.5, $CDCl_3$, 86% ee), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.62(s, 1H), 7.53(d, J =8.0Hz, 1H), 7.42(d, J =8.0Hz, 1H), 3.82(d, J =17.2Hz, 1H), 3.59 (d, J =17.2Hz, 1H), 2.42(s, 3H), 2.18(s, 3H), 2.12(s, 6H), 1.64(s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 191.5, 162.6, 149.3, 139.2, 138.2, 132.7, 126.2, 126.0, 116.4, 85.8, 55.8, 40.9, 37.4, 36.0, 31.1, 21.2; HRMS (ESI+) calced for $[C_{22}H_{23}O_3NNa]^+$: 372.1570, found: 372.1566; HPLC conditions: Chiralcel AS-H column, hexane/*i*-PrOH = 85/15, 1 mL/min, 254nm, t_R(minor) = 11.4 min, t_R(major) = 12.1min.

(S)-1-Adamantyl 2-cyano-6-methoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4i)



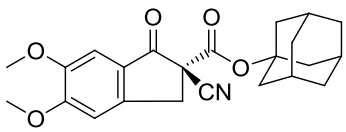
Reaction time 12h, colorless oil, 90% yield, ν_{max} (film)/cm^{-1} 2911, 2248, 1728, $[\alpha]_D^{25}$ +9.6 (c 0.25, $CDCl_3$, 88% ee), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.42(d, J =4.4Hz, 1H), 7.27-7.30(m, 1H), 7.22 (s, 1H), 3.84(s, 3H), 3.78(dd, J =17.2Hz, 1H), 3.57(dd, J =17.2Hz, 1H), 2.18(s, 3H), 2.11(s, 6H), 1.64(s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 191.4, 162.5, 160.4, 144.7, 133.7, 127.2, 126.3, 116.2, 106.8, 85.7, 56.1, 55.8, 40.9, 37.1, 35.9, 31.0; HRMS (ESI+) calced for $[C_{22}H_{23}O_4NNa]^+$: 388.1519, found: 388.1513; HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 80/20, 1 mL/min, 254nm, t_R(minor) = 10.3 min, t_R(major) = 13.7min.

(S)-1-Adamantyl 2-cyano-5-methoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4j)



Reaction time 12h, white solid, m.p. 103-104°C, 90% yield, ν_{max} (film)/cm^{-1} 2914, 2853, 2246, 1742, 1724, $[\alpha]_D^{25}$ +73.2 (c 0.5, $CDCl_3$, 93% ee), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.75(d, J =8.8Hz, 1H), 6.98(d, J =8.8Hz, 1H), 6.94(s, 1H), 3.92(s, 3H), 3.82(d, J =17.2Hz, 1H), 3.57(d, J =17.2Hz, 1H), 2.18(s, 3H), 2.13(s, 6H), 1.65(s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 189.3, 167.0, 162.8, 155.1, 127.9, 125.3, 117.2, 116.6, 109.6, 85.7, 56.1, 55.7, 40.9, 37.5, 36.0, 31.0; HRMS (ESI+) calced for $[C_{22}H_{23}O_4NNa]^+$: 388.1519, found: 388.1514; HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 80/20, 1 mL/min, 254nm, t_R(minor) = 13.5 min, t_R(major) = 15.6min.

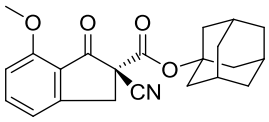
(S)-1-Adamantyl 2-cyano-5,6-dimethoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4k)



Reaction time 12h, white solid, m.p. 162-163°C, 94% yield, ν_{max} (film)/cm^{-1} 2915, 2854, 2246, 1739, 1719, $[\alpha]_D^{25}$ +52.8 (c 0.5, $CDCl_3$, 93% ee), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.19(s, 1H), 6.94(s, 1H), 4.01(s, 3H), 3.92(s, 3H), 3.77(d, J =17.2Hz, 1H), 3.55(d, J =17.2Hz, 1H), 2.18(s,

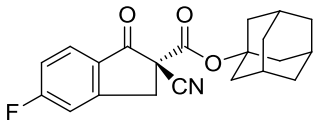
3H), 2.13(s, 6H), 1.65(s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 189.7, 162.8, 157.2, 150.5, 147.9, 125.0, 116.6, 107.2, 105.7, 85.6, 56.6, 56.3, 55.7, 40.9, 37.3, 35.9, 31.0; HRMS (ESI+) calced for $[C_{23}H_{25}O_5NNa]^+$: 418.1625, found: 418.1620; HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 80/20, 1 mL/min, 254nm, t_R(minor) = 12.7 min, t_R(major) = 16.1min.

(S)-1-Adamantyl 2-cyano-7-methoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4l)



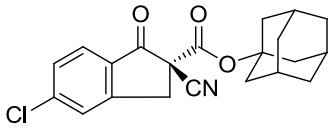
Reaction time 12h, white solid, m.p. 102-103°C, 92% yield, ν_{max} (film)/cm^{-1} 2914, 2247, 1724, $[\alpha]_D^{25}$ +56.8 (c 0.5, $CDCl_3$, 66% ee), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.62-7.66(m, 1H), 7.05(d, *J* =7.6Hz, 1H), 6.88(d, *J* =8.0Hz, 1H), 3.97(s, 3H), 3.80(d, *J* =17.2Hz, 1H), 3.55(dd, *J* =8.0, 17.2Hz, 1H), 2.17(s, 3H), 2.13(s, 6H),1.64(s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 188.3, 162.7 ,159.8, 153.8, 138.8, 120.5, 118.0, 116.5, 110.3, 85.6, 56.1, 55.8, 40.9, 37.0, 35.9, 31.0; HRMS (ESI+) calced for $[C_{22}H_{23}O_4NNa]^+$: 388.1519, found: 388.1519; HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 80/20, 1 mL/min, 254nm, t_R(minor) = 14.1 min, t_R(major) = 19.6min.

(S)-1-Adamantyl 2-cyano-5-fluoro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4m)



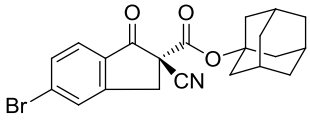
Reaction time 1h, white solid, m.p. 146-147°C, 93% yield, ν_{max} (film)/cm^{-1} 2916, 2855, 2249, 1732, $[\alpha]_D^{25}$ +46.6 (c 0.5, $CDCl_3$, 80% ee), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.86(dd, *J* =4.2, 8.4Hz, 1H), 7.17-7.22(m, 2H), 3.88 (d, *J* =17.2Hz, 1H), 3.63 (d, *J* =17.2Hz, 1H), 2.19(s, 3H), 2.12(s, 6H), 1.65(s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 189.5, 169.6, 167.0, 162.2, 154.9, 154.8, 128.9, 128.8, 128.7, 117.7, 117.4, 116.0, 113.7, 113.4, 86.2, 55.7, 41.0, 37.4, 36.0, 31.1; HRMS (ESI+) calced for $[C_{21}H_{20}O_4NFNa]^+$: 376.1319, found: 376.1316; HPLC conditions: Chiralcel AS-H column, hexane/*i*-PrOH = 85/15, 1 mL/min, 254nm, t_R(minor) = 12.3 min, t_R(major) = 15.4min.

(S)-1-Adamantyl 2-cyano-5-chloro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4n)



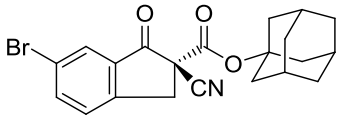
Reaction time 1h, white solid, m.p. 138-139°C, 99% yield, v_{max} (film)/cm^{-1} 2916, 2855, 2249, 1743, 1735, 1599, $[\alpha]_D^{25}$ +29.6 (c 0.25, $CDCl_3$, 80% ee), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* =8.0Hz, 1H), 7.54 (s, 1H), 7.46(d, *J* =8.0Hz, 1H), 3.86 (d, *J* =17.2Hz, 1H), 3.62 (d, *J* =17.2Hz, 1H), 2.19(s, 3H), 2.11(s, 6H), 1.64(s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 190.0, 162.1, 153.2, 143.7, 131.0, 129.8, 127.2, 126.8, 115.9, 86.2, 55.6, 40.9, 37.2, 35.9, 31.1; HRMS (ESI+) calced for $[C_{21}H_{20}O_4NClNa]^+$: 392.1024, found: 392.1018, HPLC conditions: Chiralcel AS-H column, hexane/*i*-PrOH = 85/15, 1 mL/min, 254nm, t_R(minor) = 11.5 min, t_R(major) = 15.1min.

(S)-1-Adamantyl 2-cyano-5-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4o)



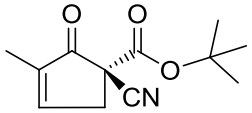
Reaction time 1h, white solid, m.p. 124-125°C, 93% yield, v_{max} (film)/cm^{-1} 2914, 2854, 2249, 1731, 1595, $[\alpha]_D^{25}$ +40.4 (c 0.5, $CDCl_3$, 81% ee), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.69-7.73(m, 2H), 7.62(d, *J* =8.4Hz, 1H), 3.86(d, *J* =17.2Hz, 1H), 3.62(d, 17.2Hz, 1H), 2.19(s, 3H), 2.12(s, 6H), 1.65(s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 190.3, 162.1, 153.2, 132.8, 132.7, 131.4, 130.0, 127.3, 115.9, 86.4, 55.5, 41.0, 37.2, 36.0, 31.1; HRMS (ESI+) calced for $[C_{21}H_{20}O_4NBrNa]^+$: 436.0519, found: 436.0514, HPLC conditions: Chiralcel AS-H column, hexane/*i*-PrOH = 85/15, 1 mL/min, 254nm, t_R(minor) = 13.1 min, t_R(major) = 17.9 min.

(S)-1-Adamantyl 2-cyano-6-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4p)



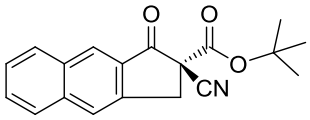
Reaction time 1h, white solid, m.p. 88-90°C, 99% yield, v_{max} (film)/cm^{-1} 2915, 2855, 2249, 1734, $[\alpha]_D^{25}$ +17.0 (c 0.5, $CDCl_3$, 78% ee), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.95(s, 1H), 7.81(d, *J* =8.0Hz, 1H), 7.44(d, *J* =8.0Hz, 1H), 3.83(d, *J* =17.2Hz, 1H), 3.59(d, *J* =17.2Hz, 1H), 2.19(s, 3H), 2.11(s, 6H), 1.64(s, 6H),; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 190.1, 162.0, 150.4, 139.7, 134.3, 128.9, 128.1, 123.0, 115.8, 86.3, 55.8, 40.9, 37.3, 35.9, 31.1; HRMS (ESI+) calced for $[C_{21}H_{20}O_4NBrNa]^+$: 436.0519, found: 436.0515, HPLC conditions: Chiralcel AS-H column, hexane/*i*-PrOH = 85/15, 1 mL/min, 254nm, t_R(minor) = 12.4 min, t_R(major) = 13.7 min.

(S)-tert-butyl 1-cyano-3-methyl-2-oxocyclopent-3-enecarboxylate (4q)



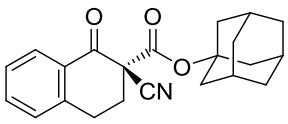
Reaction time 1h, white solid, m.p. 76-78°C, 76% yield, ν_{max} (film)/cm^{-1} 2926, 2855, 2248, 1728; $[\alpha]_D^{25}$ +3.2 (c 0.5, $CDCl_3$, 57% ee), H-NMR (400 MHz, $CDCl_3$): δ 7.47(d, J =1.0Hz, 1H), 3.30(dd, J =2.1, 4.8Hz, 1H), 2.84-2.90(m, 1H), 2.71-2.78(m, 1H), 1.78(d, J =1.0Hz, 3H), 1.48(s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 203.3, 168.5, 157.7, 140.4, 81.8, 52.2, 30.9, 28.1, 10.4; HRMS (ESI+) calced for $[C_{12}H_{15}O_3NNa]^+$: 244.0944, found: 244.0940, HPLC conditions: Chiralcel AS-H column, hexane/*i*-PrOH = 85/15, 1 mL/min, 254nm, t_R(minor) = 11.1 min, t_R(major) = 15.3 min.

(S)-tert-butyl 2-cyano-1-oxo-2,3-dihydro-1H-cyclopenta[b]naphthalene-2-carboxylate (4r)



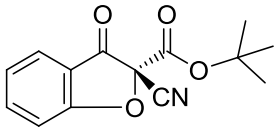
Reaction time 1h, white solid, m.p. 151-152°C, 93% yield, ν_{max} (film)/cm^{-1} 2245, 1745, 1732; $[\alpha]_D^{25}$ +32.2 (c 0.5, $CDCl_3$, 80% ee), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.40(s, 1H), 7.86-7.98(m, 3H), 7.63-7.67(m, 1H), 7.52-7.56(m, 1H), 4.05(d, J =17.2Hz, 1H), 3.80(d, J =17.2Hz, 1H), 1.50(s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 191.6, 163.2, 143.2, 138.0, 132.8, 130.6, 130.2, 129.8, 128.1, 128.0, 127.2, 125.0, 116.4, 85.9, 56.1, 37.3, 27.8; HRMS (ESI+) calced for $[C_{19}H_{17}O_3NNa]^+$: 333.1101, found: 333.1097, HPLC conditions: Chiralcel IC-H column, hexane/*i*-PrOH = 80/20, 1 mL/min, 254nm, t_R(minor) = 20.2 min, t_R(major) = 16.9 min.

(S)-1-Adamantly-2-cyano-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (4s)



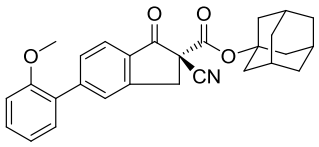
Reaction time 6 days, white solid, m.p. 123-124°C, 83% yield, ν_{max} (film)/cm^{-1} 2912, 2846, 2242, 1739, 1686, 1600; $[\alpha]_D^{25}$ +17.4 (c 0.5, $CDCl_3$, 66% ee), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.04(d, J =8.0Hz, 1H), 7.76-7.56 (m, 1H), 7.33-7.37(m, 1H), 7.24-7.27(m, 1H), 3.16-3.24(m, 1H), 3.04-3.11(m, 1H), 2.76-2.83(m, 1H), 2.56-2.62(m, 1H), 2.16(s, 3H), 2.11(s, 6H), 1.63(s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 185.8, 163.3, 142.6, 135.0, 130.0, 129.1, 129.0, 127.7, 115.5, 85.8, 56.5, 41.1, 36.1, 31.7, 31.1, 25.6; HRMS (ESI+) calced for $[C_{22}H_{23}O_3NNa]^+$: 372.1570, found: 372.1507, HPLC conditions: Chiralcel AS-H column, hexane/*i*-PrOH = 85/15, 1 mL/min, 254nm, t_R(minor) = 10.2 min, t_R(major) = 10.8 min.

(R)-tert-butyl 2-cyano-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (4t)



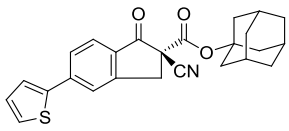
Reaction time 1 hour, colorless oil, 96% yield, v_{max} (film)/cm^{-1} 2925, 2855, 2255, 1763, 1748, 1612; $[\alpha]_D^{25}$ +9.0 (c 0.5, $CDCl_3$, 28% ee), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.73-7.80(m, 2H), 7.25-7.31(m, 2H), 1.54(s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 186.5, 172.3, 158.4, 140.2, 126.2, 124.6, 116.8, 114.1, 111.8, 87.8, 79.8, 27.7; HRMS (ESI+) calced for $[C_{14}H_{13}O_4NNa]^+$: 282.0737, found: 282.0737, HPLC conditions: Chiralcel AS-H column, hexane/*i*-PrOH = 85/15, 1 mL/min, 254nm, t_R(minor) = 7.4 min, t_R(major) = 6.7 min.

(S)-1-Adamantyl-2-cyano-5-(2-methoxyphenyl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4u)



Reaction time 1 hour, white solid, m.p. 146-147°C, 90% yield, v_{max} (film)/cm^{-1} 2915, 2854, 2247, 1729, 1604; $[\alpha]_D^{25}$ +44.6 (c 0.5, $CDCl_3$, 78% ee), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.83(d, *J* =8.0Hz, 1H), 7.62-7.66(m, 2H), 7.38-7.41(m, 1H), 7.32(d, *J* =6.8Hz, 1H), 7.00-7.08(m, 2H), 3.91(d, *J* =12.0Hz, 1H), 3.83(s, 3H), 3.66(d, *J* =17.2Hz, 1H), 2.18(s, 3H), 2.14(s, 6H), 1.64(s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 191.0, 162.7, 156.5, 151.7, 147.9, 130.9, 130.8, 130.7, 130.3, 128.8, 127.3, 125.5, 121.2, 116.4, 111.5, 85.8, 55.7, 55.6, 40.9, 37.6, 36.0, 31.0; HRMS (ESI+) calced for $[C_{28}H_{27}O_4NNa]^+$: 464.1832, found: 464.1829, HPLC conditions: Chiralcel AS-H column, hexane/*i*-PrOH = 85/15, 1 mL/min, 254nm, t_R(minor) = 13.4 min, t_R(major) = 17.1 min.

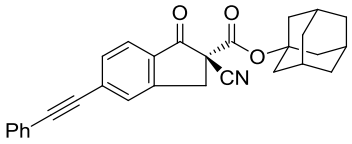
(S)-1-Adamantyl -2-cyano-1-oxo-5-(thiophen-2-yl)-2,3-dihydro-1H-indene-2-carboxylate (4v)



reaction time 1 hour, white solid, m.p. 152-153°C, 67% yield, v_{max} (film)/cm^{-1} 2911, 2852, 2245, 1736, 1727, 1603; $[\alpha]_D^{25}$ +58.0 (c 0.1, $CDCl_3$, 86% ee), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.82(d, *J* =8.4Hz, 1H), 7.70-7.72(m, 2H), 7.50(d, *J* =3.2Hz, 1H), 7.45(d, *J* =4.8Hz, 1H), 7.15-7.17(m, 1H), 3.90(d, *J* =17.2Hz, 1H), 3.64(d, *J* =17.2Hz, 1H), 2.19(s, 3H), 2.14(s, 6H), 1.65(s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 190.4, 162.6, 152.8, 142.7, 142.4, 131.1, 128.9, 128.1, 126.9, 126.7, 126.2, 122.9, 116.4, 86.1, 55.8, 41.0, 37.6, 36.1, 31.2; HRMS

(ESI+) calced for $[C_{25}H_{27}O_3NSNa]^+$: 440.1291, found: 440.1286, HPLC conditions: Chiralcel AS-H column, hexane/*i*-PrOH = 85/15, 1 mL/min, 254nm, t_R(minor) = 21.8 min, t_R(major) = 36.8 min.

(S)-1-Adamantyl-2-cyano-1-oxo-5-(phenylethynyl)-2,3-dihydro-1H-indene-2-carboxylate (4w)



reaction time 1 hour, white solid, m.p. 108-109°C, 80% yield, ν_{max} (film)/cm^{-1} 2912, 2853, 2247, 2207, 1728, 1603; $[\alpha]_D^{25}$ +84.6 (c 0.5, $CDCl_3$, 85% ee), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.78(d, *J* =8.0Hz, 1H), 7.64(s, 1H), 7.54-7.59(m, 3H), 7.38-7.39(m, 3H), 3.85(d, *J* =17.2Hz, 1H), 3.61(d, *J* =17.2Hz, 1H), 2.17(s, 3H), 2.11(s, 6H), 1.63(s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 190.4, 162.3, 151.6, 132.1, 132.0, 131.5, 129.4, 129.2, 128.6, 125.9, 122.2, 116.1, 95.0, 88.4, 85.9, 55.5, 40.9, 37.3, 35.9, 31.0; HRMS (ESI+) calced for $[C_{29}H_{25}O_3NNa]^+$: 458.1727, found: 58.1720, HPLC conditions: Chiralcel AS-H column, hexane/*i*-PrOH = 90/10, 1 mL/min, 254nm, t_R(minor) = 18.0 min, t_R(major) = 21.1 min.

7. The reference

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8. X-Ray Structure of 4p

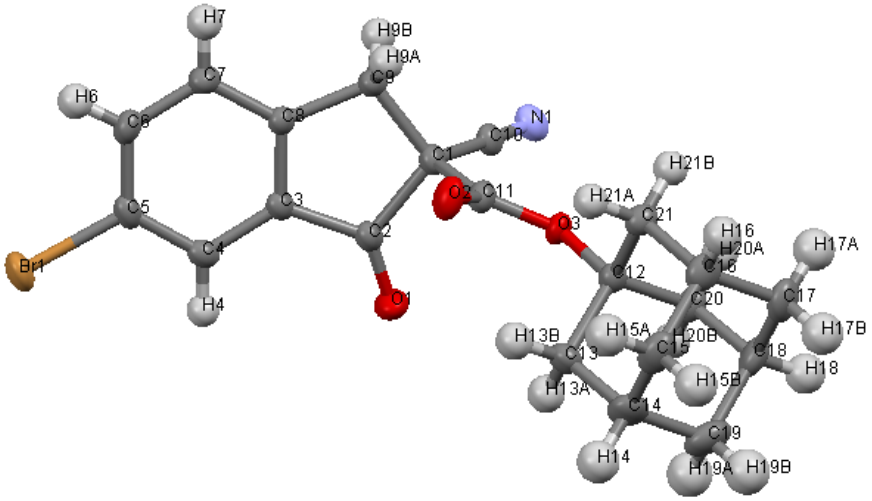


Table 1. Crystal data and structure refinement for **4p**.

Identification code	sa3912	
Empirical formula	C21 H20 Br N O3	
Formula weight	414.29	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 6.4981(19) Å	α= 90°.
	b = 11.985(4) Å	β= 90°.
	c = 23.813(7) Å	γ = 90°.
Volume	1854.6(9) $Å^3$	
Z	4	
Density (calculated)	1.484 Mg/m^3	
Absorption coefficient	2.237 mm^{-1}	
F(000)	848	
Crystal size	0.23 x 0.13 x 0.06 mm^3	
Theta range for data collection	3.078 to 27.482°.	
Index ranges	-8<=h<=8, -15<=k<=15, -30<=l<=30	
Reflections collected	14635	
Independent reflections	4250 [R(int) = 0.0474]	
Completeness to theta = 26.000°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.7499	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4250 / 0 / 235	
Goodness-of-fit on F^2	1.131	
Final R indices [I>2sigma(I)]	R1 = 0.0407, wR2 = 0.0733	
R indices (all data)	R1 = 0.0445, wR2 = 0.0747	

Absolute structure parameter	0.006(6)
Extinction coefficient	n/a
Largest diff. peak and hole	0.289 and -0.266 e.Å $^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å ^{2}x 10^3)

For **4p**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br1	7778(1)	9057(1)	5966(1)	35(1)
O1	1982(4)	5377(2)	6061(1)	33(1)
O2	6048(4)	3295(3)	6301(1)	33(1)
O3	2797(4)	2667(2)	6151(1)	22(1)
N1	1078(6)	3411(3)	4886(2)	31(1)
C1	4105(6)	4030(3)	5532(2)	22(1)
C2	3532(6)	5192(3)	5807(2)	22(1)
C3	5271(5)	5939(3)	5688(1)	20(1)
C4	5525(6)	7031(3)	5881(2)	23(1)
C5	7312(7)	7569(3)	5728(1)	23(1)
C6	8782(6)	7063(3)	5394(2)	27(1)
C7	8491(6)	5985(4)	5197(2)	26(1)
C8	6711(6)	5421(3)	5352(2)	21(1)
C9	6115(6)	4242(3)	5203(2)	25(1)
C10	2397(6)	3660(3)	5177(2)	23(1)
C11	4463(6)	3258(3)	6042(2)	24(1)
C12	2677(6)	1969(3)	6666(1)	22(1)
C13	2903(7)	2679(3)	7192(2)	30(1)
C14	2565(8)	1930(4)	7703(2)	38(1)
C15	4186(7)	994(5)	7702(2)	39(1)
C16	3959(7)	300(4)	7171(2)	32(1)
C17	1799(7)	-206(4)	7156(2)	37(1)
C18	207(6)	721(4)	7151(2)	34(1)

C19	408(8)	1421(5)	7686(2)	44(1)
C20	535(6)	1477(4)	6637(2)	27(1)
C21	4277(6)	1047(4)	6654(2)	26(1)

Table 3. Bond lengths [Å] and angles [°] for **4p**.

Br1-C5	1.896(3)
O1-C2	1.196(4)
O2-C11	1.202(5)
O3-C11	1.320(4)
O3-C12	1.485(4)
N1-C10	1.141(5)
C1-C2	1.583(5)
C1-C9	1.545(5)
C1-C10	1.465(5)
C1-C11	1.543(5)
C2-C3	1.469(5)
C3-C4	1.396(5)
C3-C8	1.379(5)
C4-H4	0.9300
C4-C5	1.378(5)
C5-C6	1.383(6)
C6-H6	0.9300
C6-C7	1.387(6)
C7-H7	0.9300
C7-C8	1.390(5)
C8-C9	1.508(5)
C9-H9A	0.9700
C9-H9B	0.9700
C12-C13	1.522(5)
C12-C20	1.514(5)
C12-C21	1.518(5)
C13-H13A	0.9700

C13-H13B	0.9700
C13-C14	1.529(5)
C14-H14	0.9800
C14-C15	1.539(7)
C14-C19	1.529(7)
C15-H15A	0.9700
C15-H15B	0.9700
C15-C16	1.521(6)
C16-H16	0.9800
C16-C17	1.530(6)
C16-C21	1.536(5)
C17-H17A	0.9700
C17-H17B	0.9700
C17-C18	1.518(6)
C18-H18	0.9800
C18-C19	1.530(7)
C18-C20	1.538(6)
C19-H19A	0.9700
C19-H19B	0.9700
C20-H20A	0.9700
C20-H20B	0.9700
C21-H21A	0.9700
C21-H21B	0.9700

C11-O3-C12	120.6(3)
C9-C1-C2	105.3(3)
C10-C1-C2	109.1(3)
C10-C1-C9	113.4(3)
C10-C1-C11	112.7(3)

C11-C1-C2	103.8(3)
C11-C1-C9	111.7(3)
O1-C2-C1	124.7(3)
O1-C2-C3	129.2(4)
C3-C2-C1	106.0(3)
C4-C3-C2	126.8(3)
C8-C3-C2	111.1(3)
C8-C3-C4	122.2(4)
C3-C4-H4	121.6
C5-C4-C3	116.8(3)
C5-C4-H4	121.6
C4-C5-Br1	119.7(3)
C4-C5-C6	122.0(3)
C6-C5-Br1	118.3(3)
C5-C6-H6	119.7
C5-C6-C7	120.6(4)
C7-C6-H6	119.7
C6-C7-H7	120.8
C6-C7-C8	118.4(4)
C8-C7-H7	120.8
C3-C8-C7	120.0(4)
C3-C8-C9	112.6(3)
C7-C8-C9	127.4(4)
C1-C9-H9A	110.8
C1-C9-H9B	110.8
C8-C9-C1	104.6(3)
C8-C9-H9A	110.8
C8-C9-H9B	110.8
H9A-C9-H9B	108.9

N1-C10-C1	177.1(4)
O2-C11-O3	128.4(4)
O2-C11-C1	120.8(3)
O3-C11-C1	110.7(3)
O3-C12-C13	111.1(3)
O3-C12-C20	103.4(3)
O3-C12-C21	111.0(3)
C20-C12-C13	110.1(3)
C20-C12-C21	110.2(3)
C21-C12-C13	110.9(3)
C12-C13-H13A	110.0
C12-C13-H13B	110.0
C12-C13-C14	108.3(3)
H13A-C13-H13B	108.4
C14-C13-H13A	110.0
C14-C13-H13B	110.0
C13-C14-H14	109.3
C13-C14-C15	109.2(4)
C13-C14-C19	110.1(4)
C15-C14-H14	109.3
C19-C14-H14	109.3
C19-C14-C15	109.7(4)
C14-C15-H15A	109.8
C14-C15-H15B	109.8
H15A-C15-H15B	108.2
C16-C15-C14	109.5(4)
C16-C15-H15A	109.8
C16-C15-H15B	109.8
C15-C16-H16	109.5

C15-C16-C17	108.9(4)
C15-C16-C21	109.6(4)
C17-C16-H16	109.5
C17-C16-C21	109.7(4)
C21-C16-H16	109.5
C16-C17-H17A	109.8
C16-C17-H17B	109.8
H17A-C17-H17B	108.2
C18-C17-C16	109.6(3)
C18-C17-H17A	109.8
C18-C17-H17B	109.8
C17-C18-H18	109.3
C17-C18-C19	109.7(4)
C17-C18-C20	110.1(4)
C19-C18-H18	109.3
C19-C18-C20	109.1(4)
C20-C18-H18	109.3
C14-C19-C18	108.7(4)
C14-C19-H19A	110.0
C14-C19-H19B	110.0
C18-C19-H19A	110.0
C18-C19-H19B	110.0
H19A-C19-H19B	108.3
C12-C20-C18	108.8(3)
C12-C20-H20A	109.9
C12-C20-H20B	109.9
C18-C20-H20A	109.9
C18-C20-H20B	109.9
H20A-C20-H20B	108.3

C12-C21-C16	108.5(3)
C12-C21-H21A	110.0
C12-C21-H21B	110.0
C16-C21-H21A	110.0
C16-C21-H21B	110.0
H21A-C21-H21B	108.4

Symmetry transformations used to generate equivalent atoms:

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

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br1	45(1)	21(1)	38(1)	-5(1)	-4(1)	-7(1)
O1	27(2)	32(2)	41(2)	-5(1)	12(2)	0(1)
O2	24(2)	36(2)	39(2)	11(1)	-8(1)	-7(1)
O3	22(1)	22(1)	23(1)	5(1)	0(1)	-4(1)
N1	37(2)	23(2)	33(2)	-2(2)	-4(2)	1(2)
C1	25(2)	17(2)	25(2)	1(2)	0(2)	-1(2)
C2	27(2)	20(2)	21(2)	0(2)	-1(2)	-1(2)
C3	25(2)	18(2)	18(2)	2(2)	-1(1)	2(2)
C4	29(2)	21(2)	19(2)	0(2)	0(2)	5(2)
C5	31(2)	18(2)	21(2)	1(1)	-6(2)	-1(2)
C6	26(2)	26(2)	28(2)	5(2)	1(2)	-6(2)
C7	28(2)	23(2)	27(2)	1(2)	6(2)	4(2)
C8	24(2)	18(2)	20(2)	3(2)	2(2)	0(2)
C9	30(2)	21(2)	25(2)	-1(2)	7(2)	-1(2)
C10	28(2)	15(2)	25(2)	2(1)	-1(2)	0(2)
C11	24(2)	21(2)	28(2)	3(2)	1(2)	-1(2)
C12	24(2)	22(2)	19(2)	2(1)	-1(2)	-1(2)
C13	35(2)	28(2)	27(2)	-7(2)	2(2)	-2(2)
C14	49(3)	47(3)	19(2)	-2(2)	4(2)	-3(2)
C15	39(2)	51(3)	27(2)	11(2)	-5(2)	-10(3)
C16	34(2)	32(2)	31(2)	12(2)	-1(2)	3(2)
C17	43(3)	33(2)	35(2)	15(2)	-2(2)	-10(2)
C18	24(2)	39(3)	38(2)	13(2)	1(2)	-9(2)
C19	44(3)	57(3)	32(3)	13(2)	13(2)	5(3)

C20	23(2)	31(2)	27(2)	5(2)	-3(2)	-5(2)
C21	25(2)	27(2)	26(2)	4(2)	2(2)	3(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å ^{2}x 10^{-3}) for **4p**.

	x	y	z	U(eq)
H4	4535	7378	6103	27
H6	9976	7448	5301	32
H7	9465	5648	4966	32
H9A	7179	3721	5316	30
H9B	5887	4169	4802	30
H13A	1897	3277	7189	36
H13B	4266	3008	7206	36
H14	2715	2374	8046	46
H15A	5555	1315	7718	47
H15B	4003	523	8029	47
H16	4986	-299	7171	39
H17A	1645	-665	6823	45
H17B	1595	-676	7483	45
H18	-1174	393	7135	41
H19A	-618	2009	7686	53
H19B	189	956	8014	53
H20A	379	1046	6295	33
H20B	-481	2069	6635	33
H21A	5649	1366	6660	31
H21B	4131	609	6313	31

Table 6. Torsion angles [°] for **4p**.

Br1-C5-C6-C7	-178.4(3)
O1-C2-C3-C4	4.0(7)
O1-C2-C3-C8	-176.5(4)
O3-C12-C13-C14	174.8(3)
O3-C12-C20-C18	179.7(3)
O3-C12-C21-C16	-175.4(3)
C1-C2-C3-C4	-175.2(3)
C1-C2-C3-C8	4.3(4)
C2-C1-C9-C8	6.2(4)
C2-C1-C11-O2	-78.6(4)
C2-C1-C11-O3	97.2(4)
C2-C3-C4-C5	178.4(3)
C2-C3-C8-C7	-179.2(3)
C2-C3-C8-C9	-0.3(4)
C3-C4-C5-Br1	179.6(3)
C3-C4-C5-C6	0.6(5)
C3-C8-C9-C1	-4.0(4)
C4-C3-C8-C7	0.3(5)
C4-C3-C8-C9	179.3(3)
C4-C5-C6-C7	0.5(6)
C5-C6-C7-C8	-1.3(6)
C6-C7-C8-C3	0.9(5)
C6-C7-C8-C9	-178.0(4)
C7-C8-C9-C1	174.9(4)
C8-C3-C4-C5	-1.1(5)
C9-C1-C2-O1	174.3(4)
C9-C1-C2-C3	-6.5(4)

C9-C1-C11-O2	34.4(5)
C9-C1-C11-O3	-149.8(3)
C10-C1-C2-O1	52.2(5)
C10-C1-C2-C3	-128.6(3)
C10-C1-C9-C8	125.5(3)
C10-C1-C11-O2	163.5(4)
C10-C1-C11-O3	-20.8(5)
C11-O3-C12-C13	60.2(4)
C11-O3-C12-C20	178.3(3)
C11-O3-C12-C21	-63.6(4)
C11-C1-C2-O1	-68.2(5)
C11-C1-C2-C3	111.0(3)
C11-C1-C9-C8	-105.8(4)
C12-O3-C11-O2	3.1(6)
C12-O3-C11-C1	-172.2(3)
C12-C13-C14-C15	60.1(5)
C12-C13-C14-C19	-60.3(5)
C13-C12-C20-C18	-61.6(4)
C13-C12-C21-C16	60.6(4)
C13-C14-C15-C16	-60.6(5)
C13-C14-C19-C18	60.6(5)
C14-C15-C16-C17	-59.9(5)
C14-C15-C16-C21	60.1(5)
C15-C14-C19-C18	-59.6(5)
C15-C16-C17-C18	60.7(5)
C15-C16-C21-C12	-59.5(4)
C16-C17-C18-C19	-61.2(5)
C16-C17-C18-C20	58.8(5)
C17-C16-C21-C12	60.1(5)

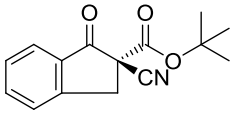
C17-C18-C19-C14	60.3(5)
C17-C18-C20-C12	-59.4(5)
C19-C14-C15-C16	60.1(5)
C19-C18-C20-C12	60.9(4)
C20-C12-C13-C14	61.0(4)
C20-C12-C21-C16	-61.5(4)
C20-C18-C19-C14	-60.2(5)
C21-C12-C13-C14	-61.3(4)
C21-C12-C20-C18	61.0(4)
C21-C16-C17-C18	-59.2(5)

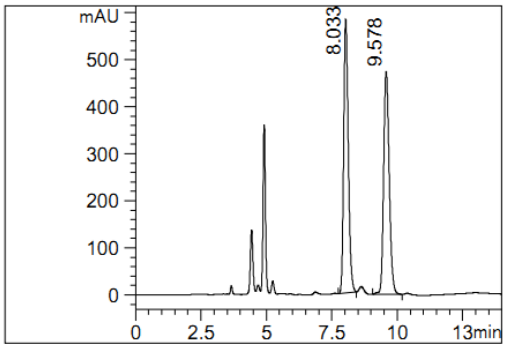
Symmetry transformations used to generate equivalent atoms:

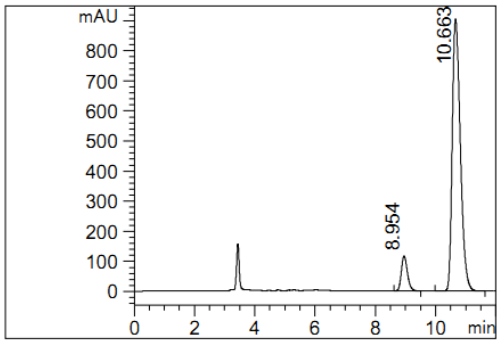
Table 7. Hydrogen bonds for **4p** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

9. HPLC spectra





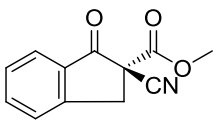


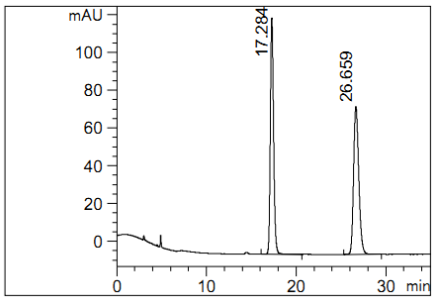
Signal 1: VWD1 A, Wavelength=254 nm

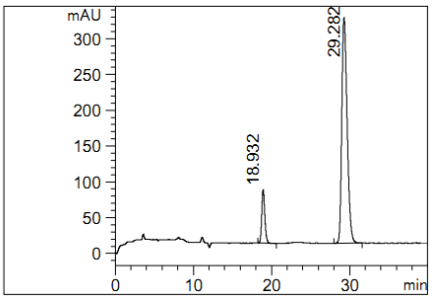
Peak #	RT [min]	Area %	Area
1	8.033	50.235	7.091e3
2	9.578	49.765	7.024e3

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Area %	Area
1	8.954	8.757	1.619e3
2	10.663	91.243	1.687e4





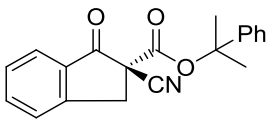


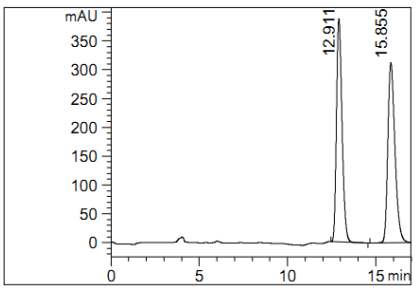
Signal 1: VWD1 A, Wavelength=254 nm

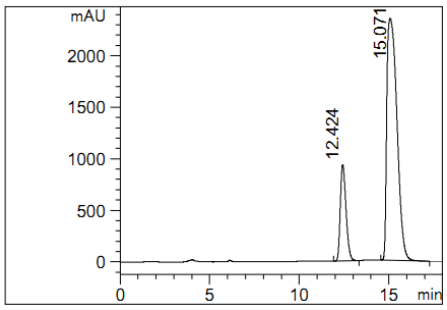
Peak #	RT [min]	Area %	Area
1	17.284	50.139	3.163e3
2	26.659	49.861	3.145e3

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Area %	Area
1	18.932	11.958	2.039e3
2	29.282	88.042	1.501e4





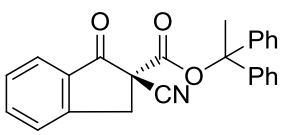


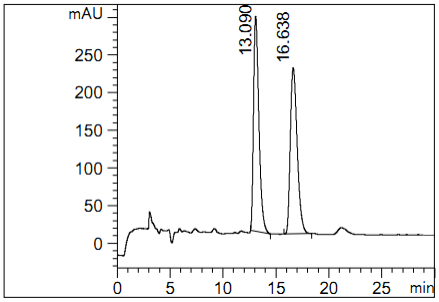
Signal 1: VWD1 A, Wavelength=254 nm

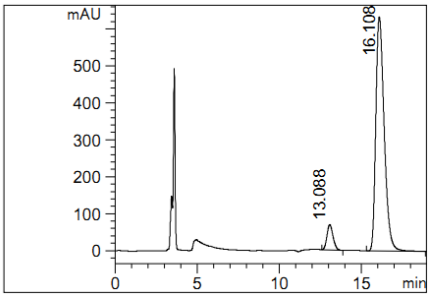
Peak #	RT [min]	Area %	Area
1	12.911	49.217	8.519e3
2	15.855	50.783	8.790e3

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Area %	Area
1	12.424	18.301	2.068e4
2	15.071	81.699	9.230e4





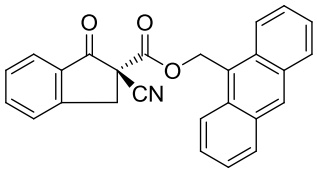


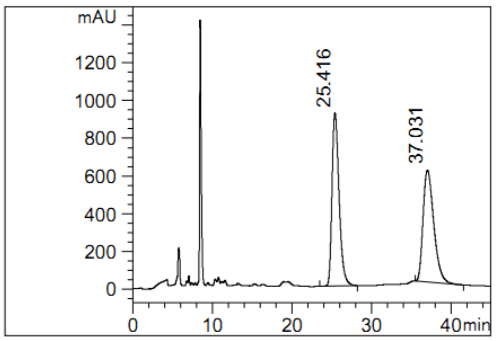
Signal 1: VWD1 A, Wavelength=254 nm

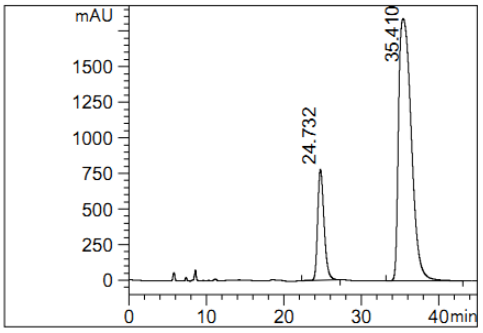
Peak #	RT [min]	Area %	Area
1	13.090	50.096	1.004e4
2	16.638	49.904	9.999e3

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Area %	Area
1	13.088	7.278	1.764e3
2	16.108	92.722	2.248e4





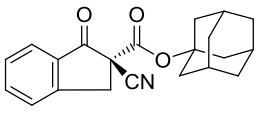


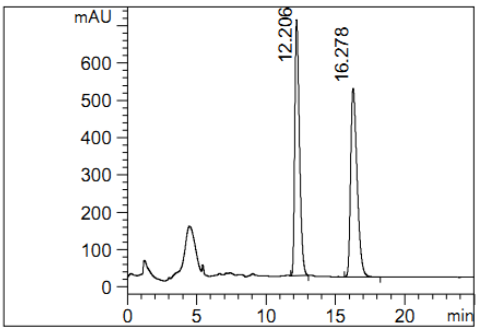
Signal 1: VWD1 A, Wavelength=254 nm

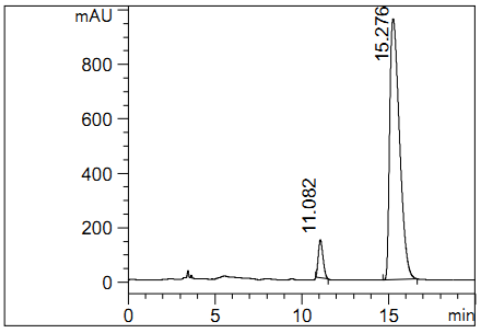
Peak #	RT [min]	Area %	Area
1	25.416	50.507	5.691e4
2	37.031	49.493	5.577e4

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Area %	Area
1	24.732	17.543	4.465e4
2	35.410	82.457	2.099e5





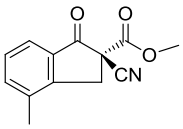


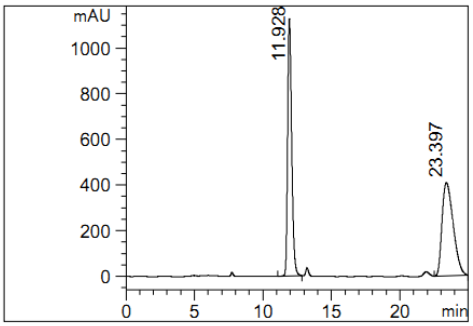
Signal 1: VWD1 A, Wavelength=254 nm

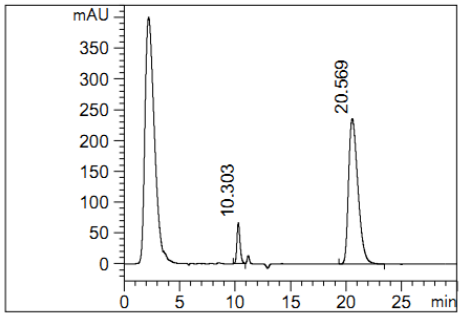
Peak #	RT [min]	Area %	Area
1	12.206	49.630	1.610e4
2	16.278	50.370	1.634e4

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Area %	Area
1	11.082	6.477	2.603e3
2	15.276	93.523	3.758e4





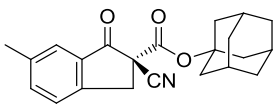


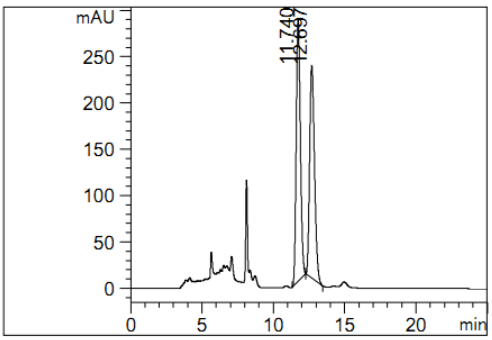
Signal 1: VWD1 A, Wavelength=254 nm

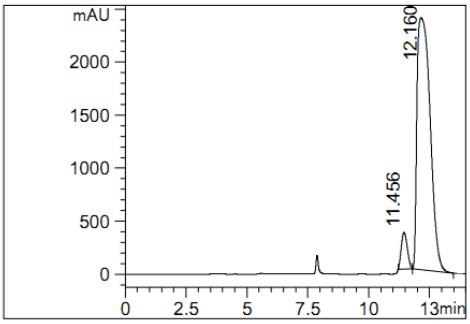
Peak #	RT [min]	Area %	Area
1	11.928	50.121	2.323e4
2	23.397	49.879	2.312e4

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Area %	Area
1	10.303	8.547	1.292e3
2	20.569	91.453	1.383e4





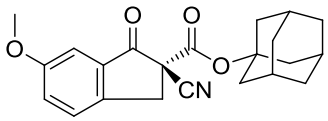


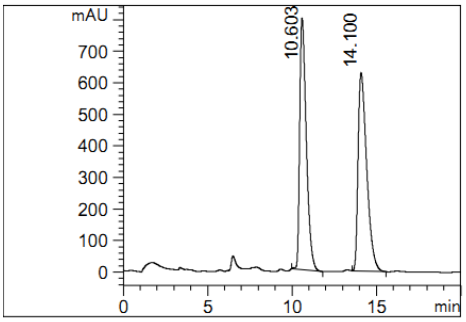
Signal 1: VWD1 A, Wavelength=254 nm

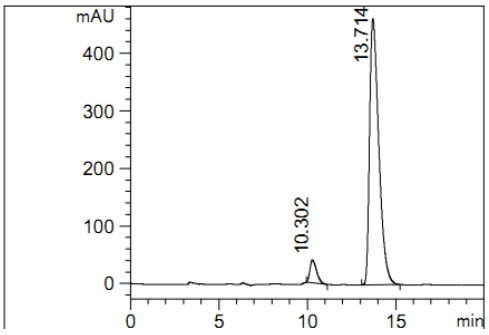
Peak #	RT [min]	Area %	Area
1	11.740	51.196	5.704e3
2	12.697	48.804	5.437e3

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Area %	Area
1	11.456	6.194	5.891e3
2	12.160	93.806	8.922e4





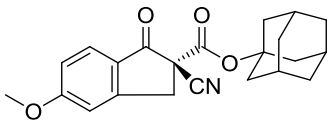


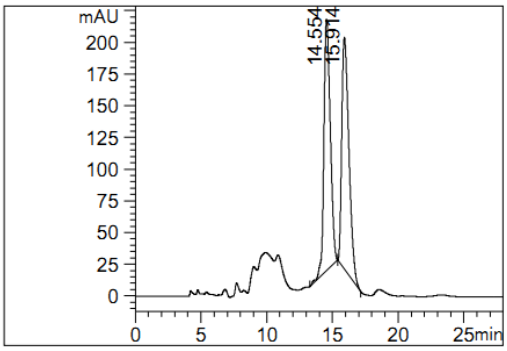
Signal 1: VWD1 A, Wavelength=254 nm

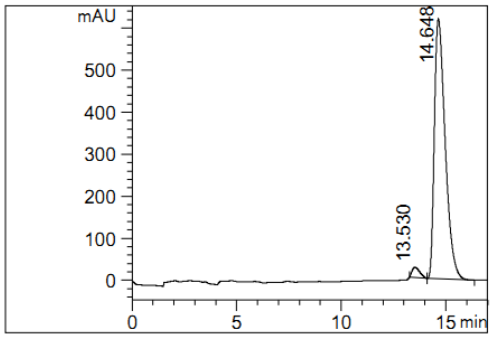
Peak #	RT [min]	Area %	Area
1	10.603	49.264	2.173e4
2	14.100	50.736	2.238e4

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Area %	Area
1	10.302	5.847	1.039e3
2	13.714	94.153	1.673e4





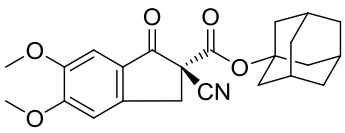


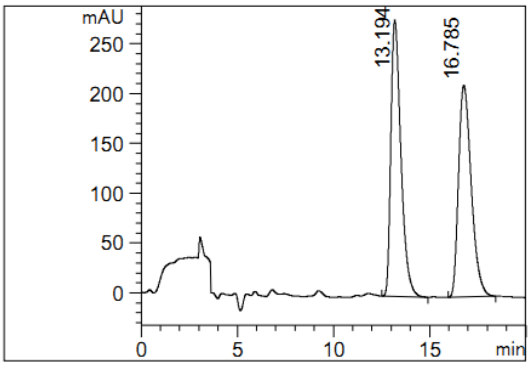
Signal 1: VWD1 A, Wavelength=254 nm

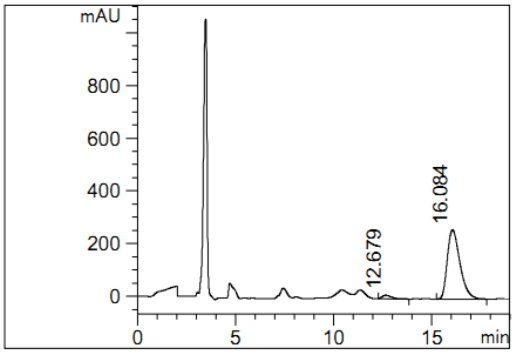
Peak #	RT [min]	Area %	Area
1	14.554	49.239	6.707e3
2	15.914	50.761	6.914e3

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Area %	Area
1	13.530	2.641	604.050
2	14.648	97.359	2.227e4





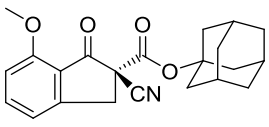


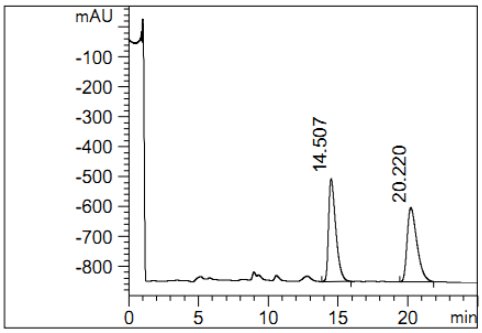
Signal 1: VWD1 A, Wavelength=254 nm

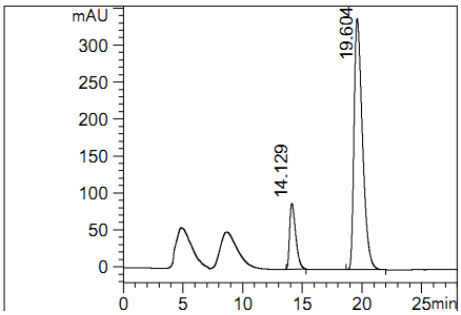
Peak #	RT [min]	Area %	Area
1	13.194	50.776	1.008e4
2	16.785	49.224	9.770e3

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Area %	Area
1	12.679	3.495	424.856
2	16.084	96.505	1.173e4





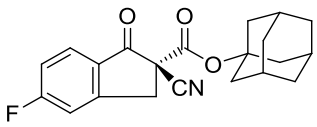


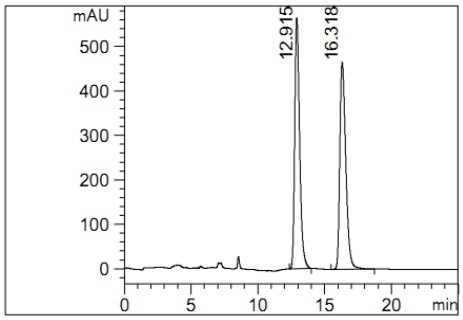
Signal 1: VWD1 A, Wavelength=254 nm

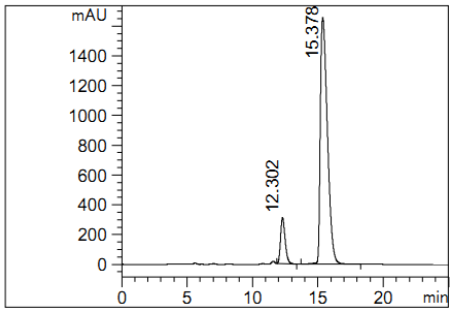
Peak #	RT [min]	Area %	Area
1	14.507	50.429	1.232e4
2	20.220	49.571	1.212e4

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Area %	Area
1	14.129	15.945	3.158e3
2	19.604	84.055	1.665e4





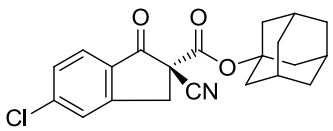


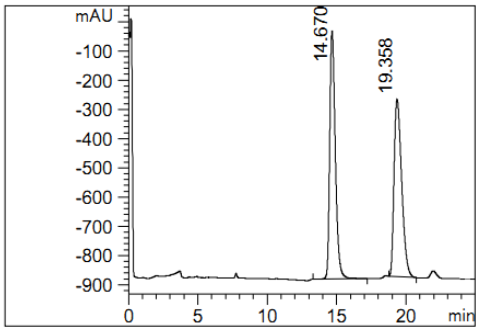
Signal 1: VWD1 A, Wavelength=254 nm

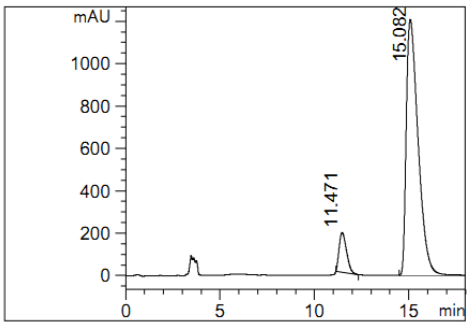
Peak #	RT [min]	Area %	Area
1	12.915	49.852	1.441e4
2	16.318	50.148	1.449e4

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Area %	Area
1	12.302	10.813	7.576e3
2	15.378	89.187	6.249e4





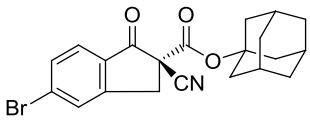


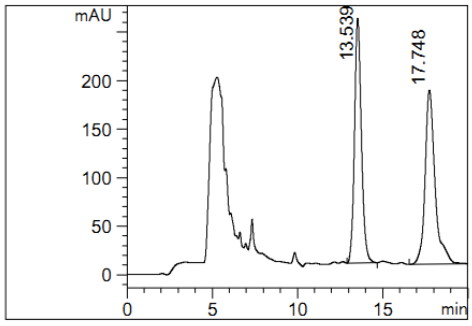
Signal 1: VWD1 A, Wavelength=254 nm

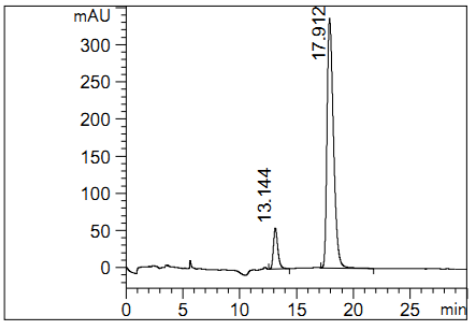
Peak #	RT [min]	Area %	Area
1	14.670	50.743	2.390e4
2	19.358	49.257	2.320e4

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Area %	Area
1	11.471	8.861	5.099e3
2	15.082	91.139	5.245e4





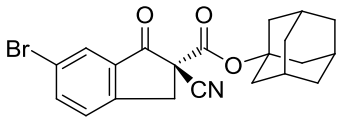


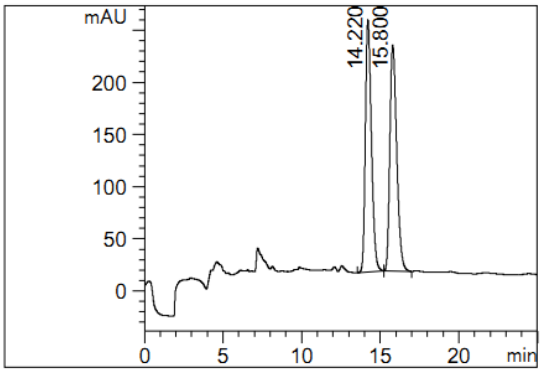
Signal 1: VWD1 A, Wavelength=254 nm

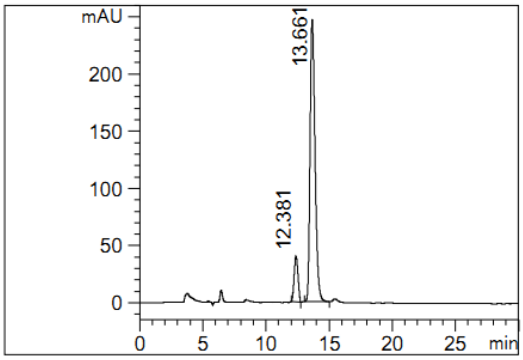
Peak #	RT [min]	Area %	Area
1	13.539	49.283	7.099e3
2	17.748	50.717	7.306e3

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Area %	Area
1	13.144	10.061	1.478e3
2	17.912	89.939	1.321e4





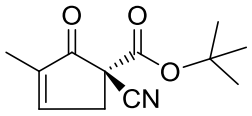


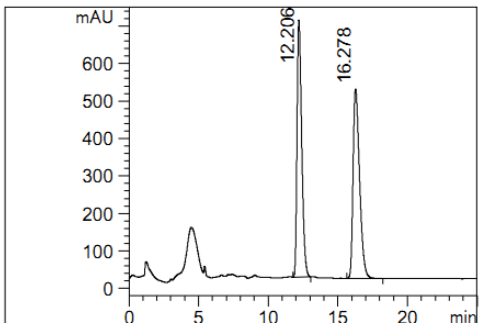
Signal 1: VWD1 A, Wavelength=254 nm

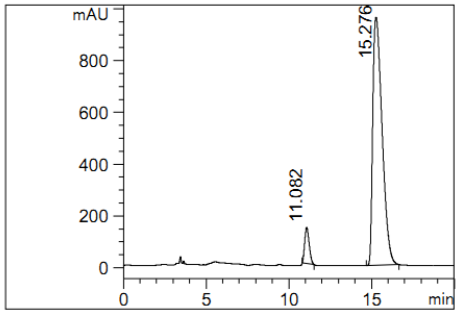
Peak #	RT [min]	Area %	Area
1	14.220	49.644	6.507e3
2	15.800	50.356	6.600e3

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Area %	Area
1	12.381	11.110	844.183
2	13.661	88.890	6.754e3





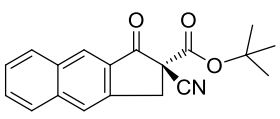


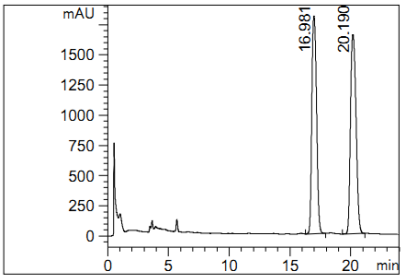
Signal 1: VWD1 A, Wavelength=254 nm

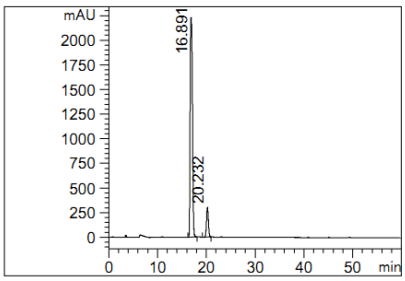
Peak #	RT [min]	Area %	Area
1	12.206	49.630	1.610e4
2	16.278	50.370	1.634e4

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Area %	Area
1	11.082	6.477	2.603e3
2	15.276	93.523	3.758e4





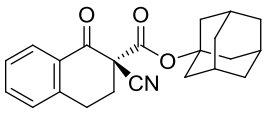


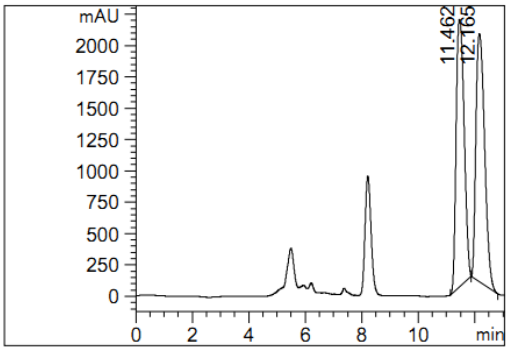
Signal 1: VWD1 A, Wavelength=254 nm

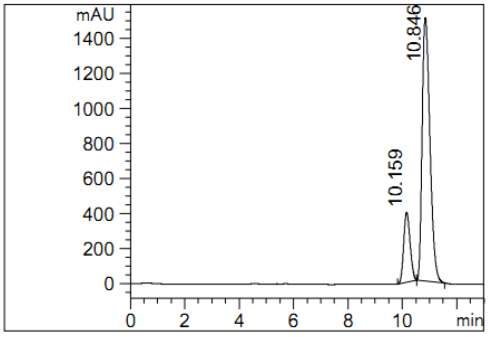
Peak #	RT [min]	Area %	Area
1	16.981	48.366	4.904e4
2	20.190	51.634	5.235e4

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Area %	Area
1	16.891	89.951	7.296e4
2	20.232	10.049	8.151e3





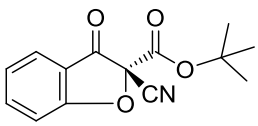


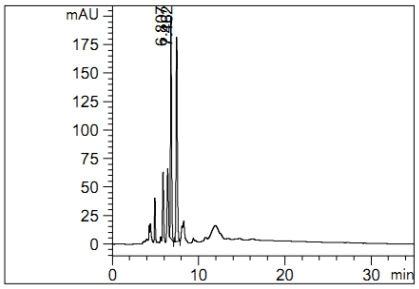
Signal 1: VWD1 A, Wavelength=254 nm

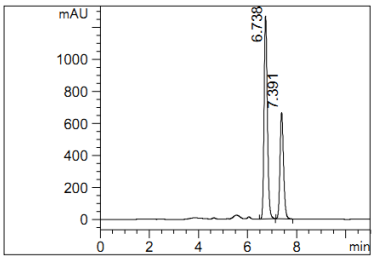
Peak #	RT [min]	Area %	Area
1	11.462	49.801	4.193e4
2	12.165	50.199	4.227e4

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Area %	Area
1	10.159	17.886	6.487e3
2	10.846	82.114	2.978e4





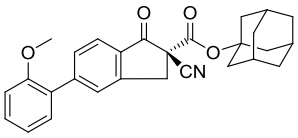


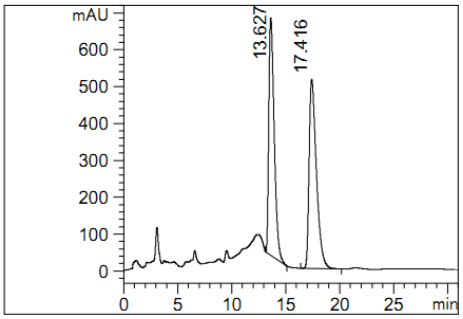
Signal 1: VWD1 A, Wavelength=254 nm

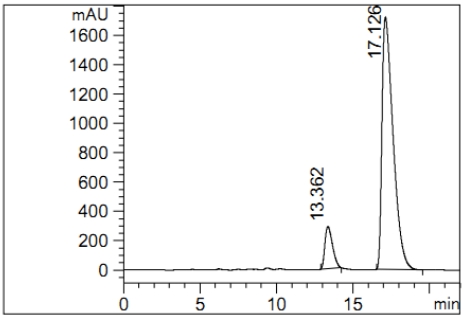
Peak #	RT [min]	Area %	Area
1	6.807	49.032	1.707e3
2	7.462	50.968	1.774e3

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Area %	Area
1	6.738	64.001	1.178e4
2	7.391	35.999	6.624e3





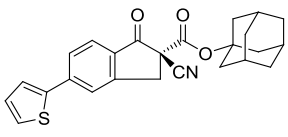


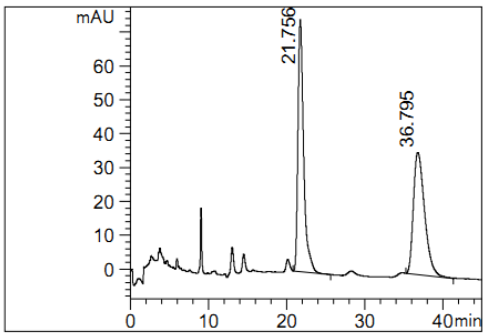
Signal 1: VWD1 A, Wavelength=254 nm

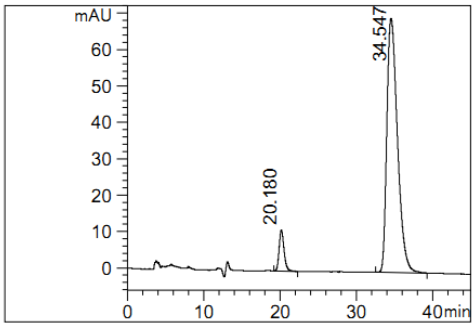
Peak #	RT [min]	Area %	Area
1	13.627	48.146	2.235e4
2	17.416	51.854	2.408e4

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Area %	Area
1	13.362	10.332	9.978e3
2	17.126	89.668	8.659e4





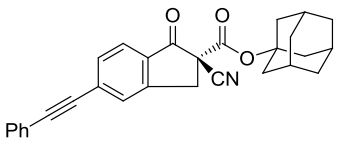


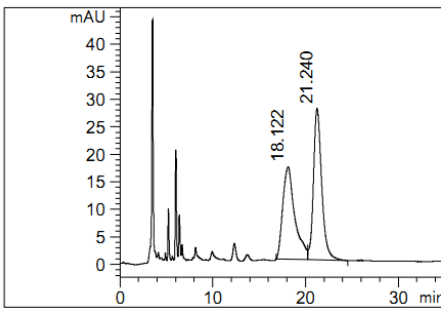
Signal 1: VWD1 A, Wavelength=254 nm

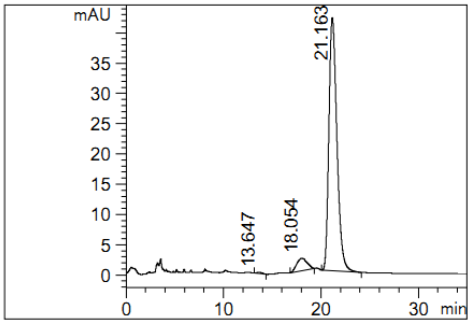
Peak #	RT [min]	Area %	Area
1	20.180	6.952	504.164
2	34.547	93.048	6.748e3

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Area %	Area
1	21.756	51.350	3.788e3
2	36.795	48.650	3.589e3







Signal 1: VWD1 A, Wavelength=254 nm

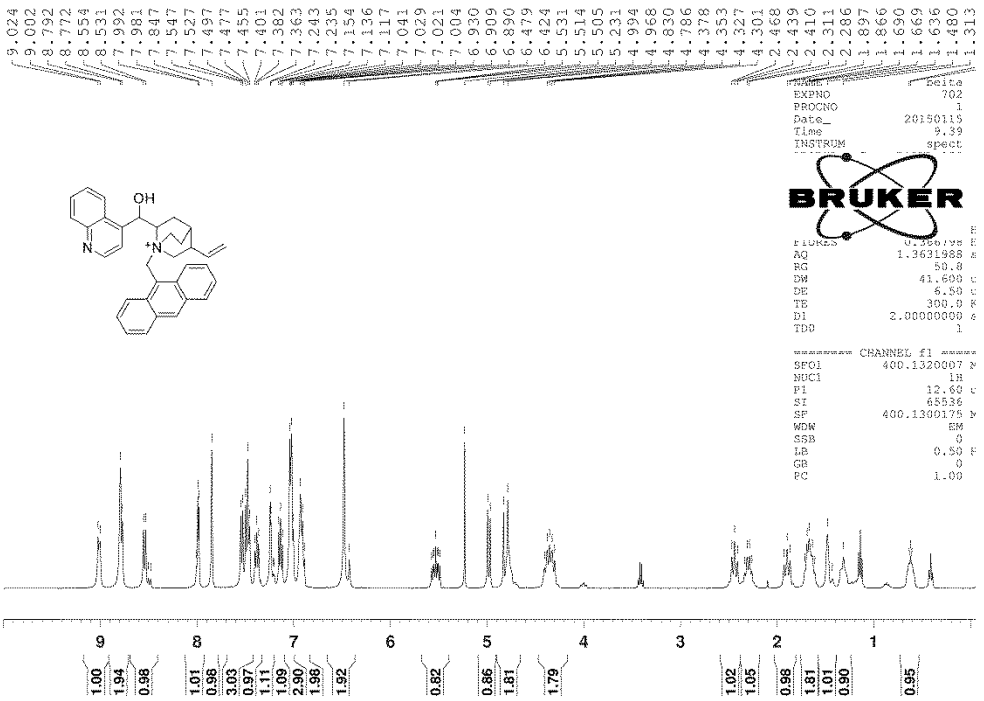
Peak #	RT [min]	Area %	Area
1	18.122	46.937	1.511e3
2	21.240	53.063	1.708e3

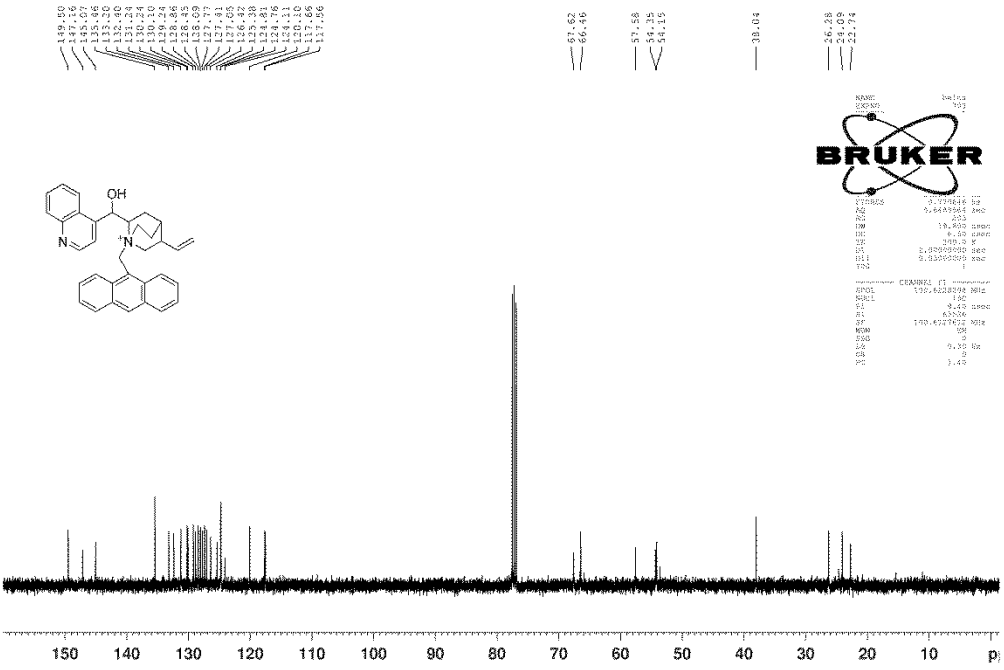
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RT [min]	Area %	Area
1	13.647	0.261	6.669
2	18.054	5.809	148.265
3	21.163	93.929	2.397e3

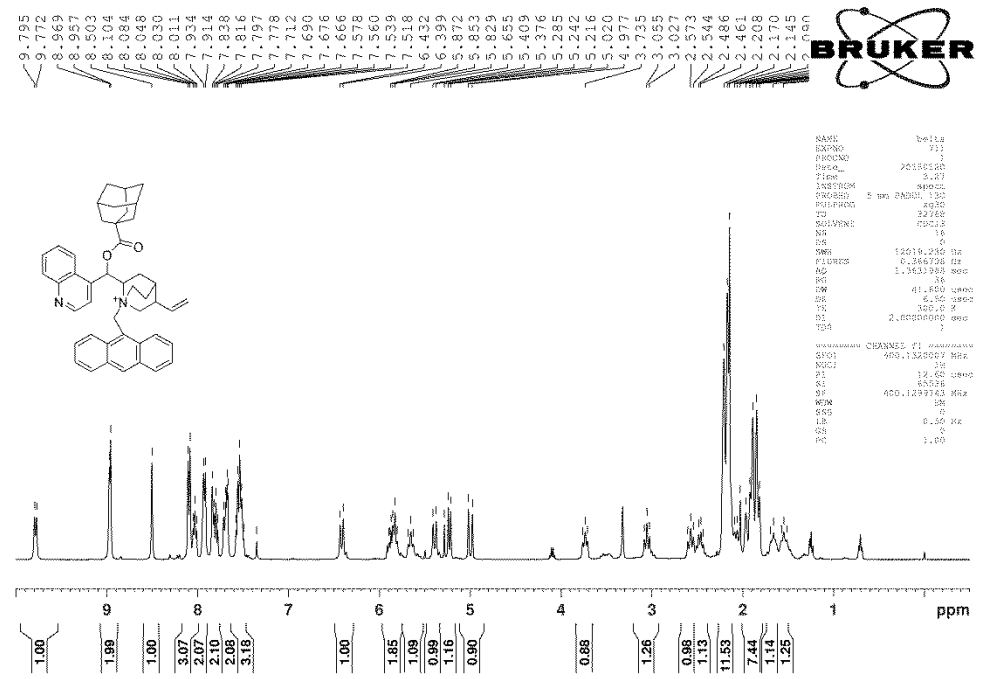
10. Copies of ^{1}H, ^{13}C NMR spectra

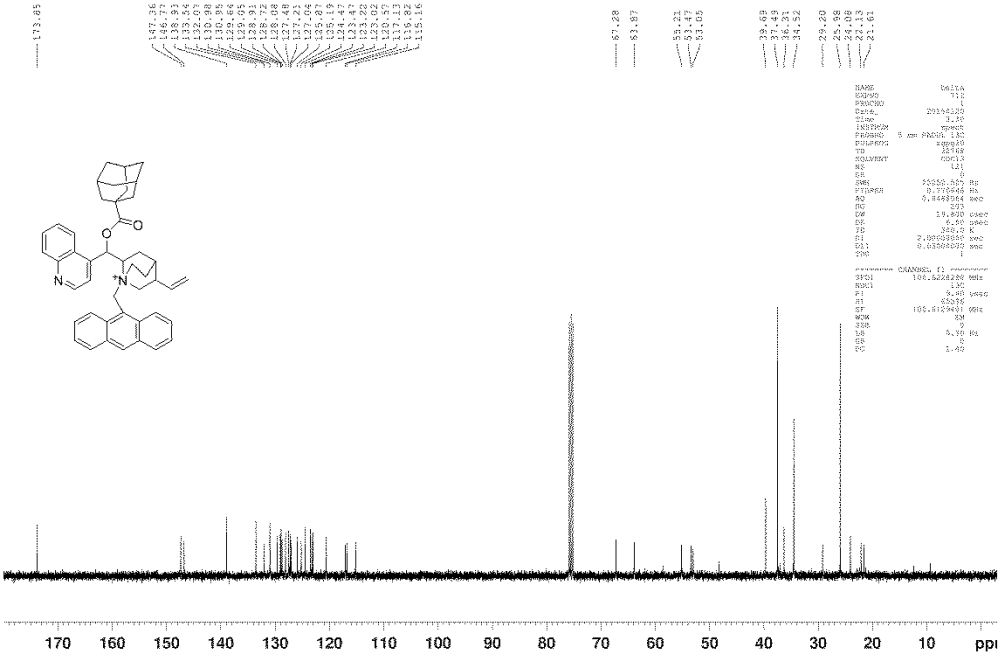
N-Anthracenylmethyl cinchoninium bromide (5b)



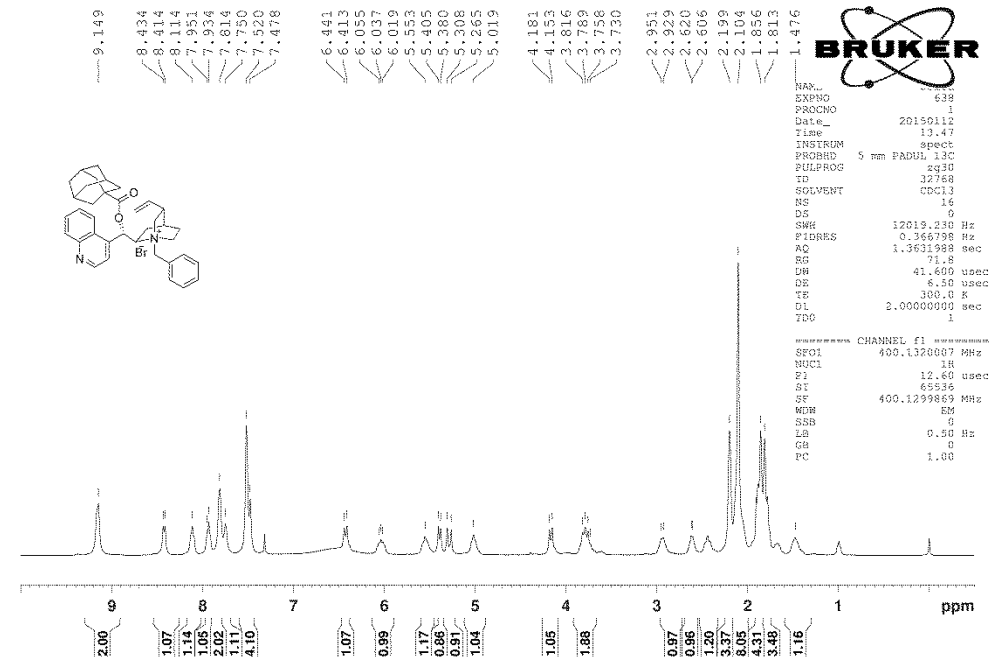


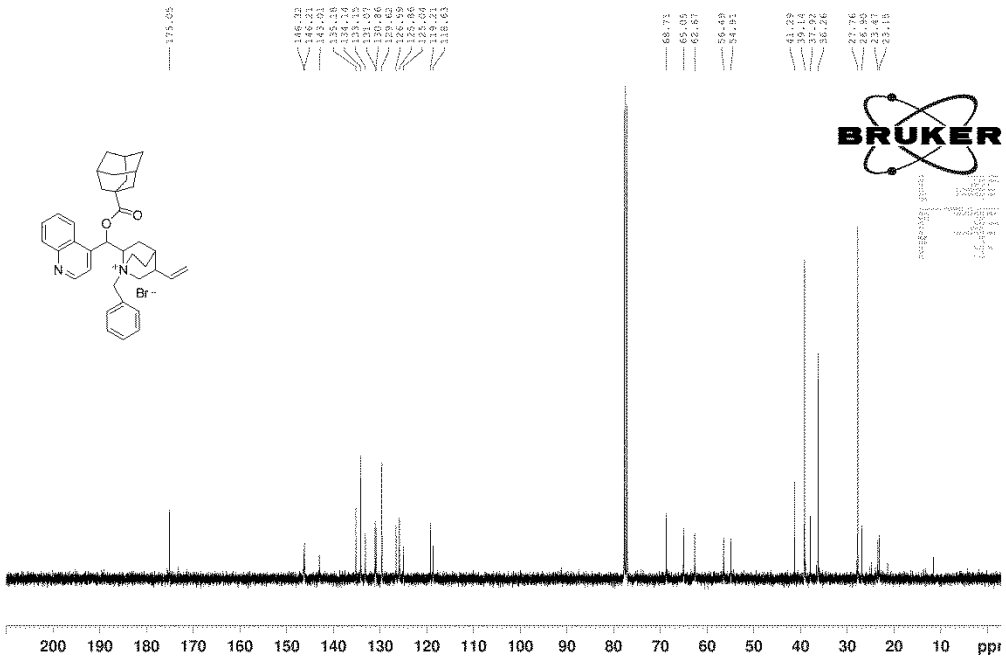
O-9-Adamantoyl-*N*-Anthracenylmethyl cinchoninium bromide (5a)



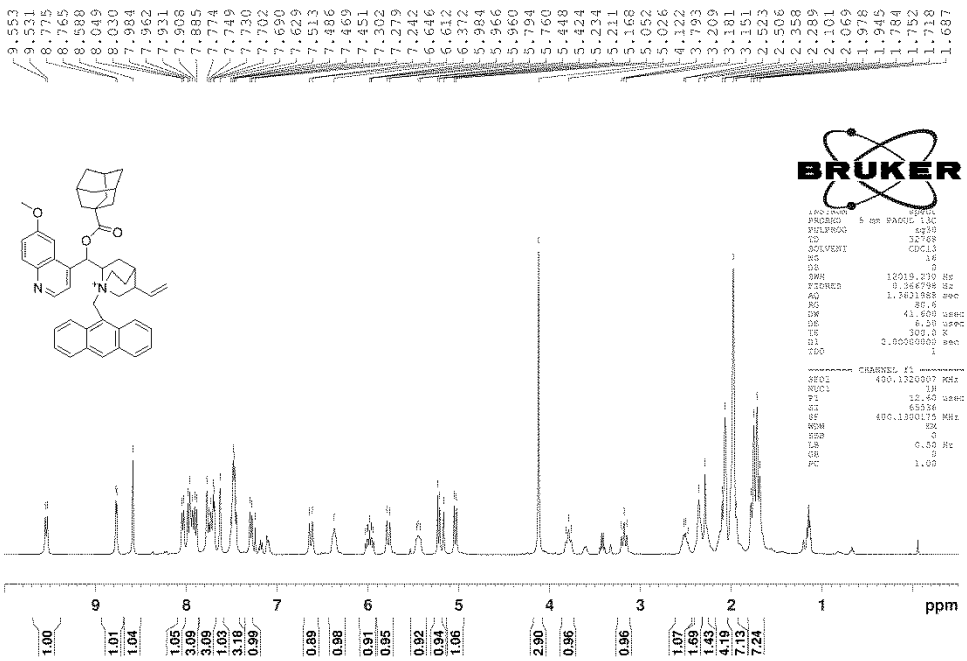


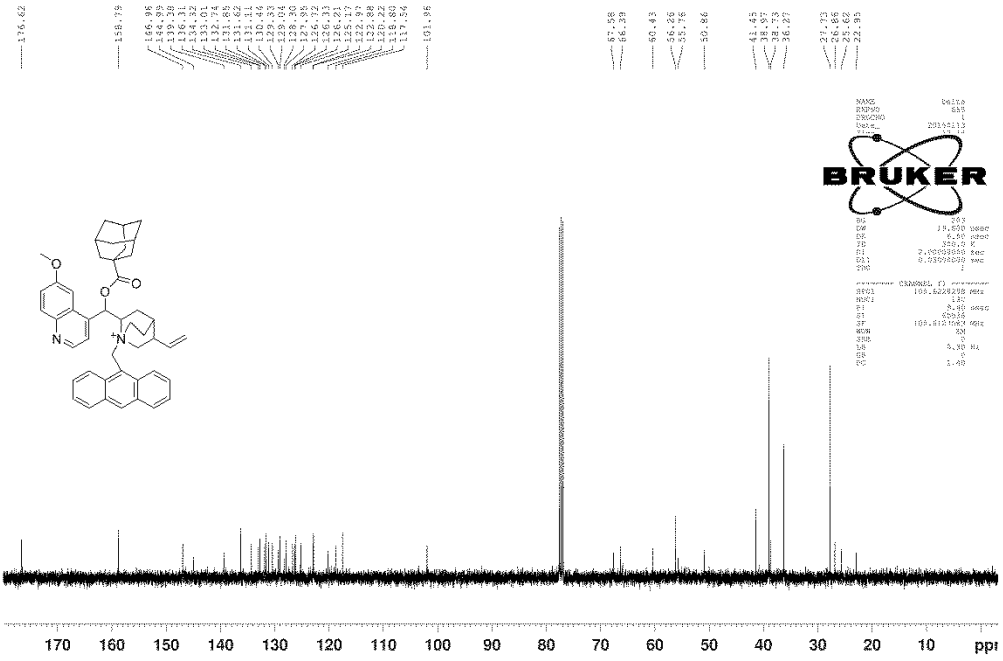
O-9- Adamantoyl-*N*- benzylcinchoninium bromide (5c)



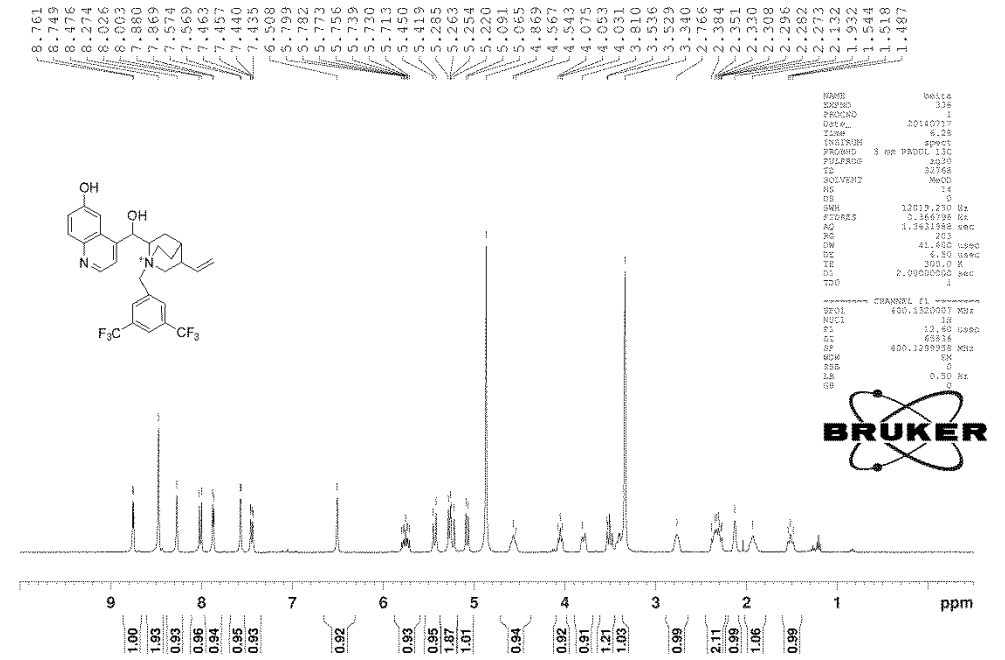


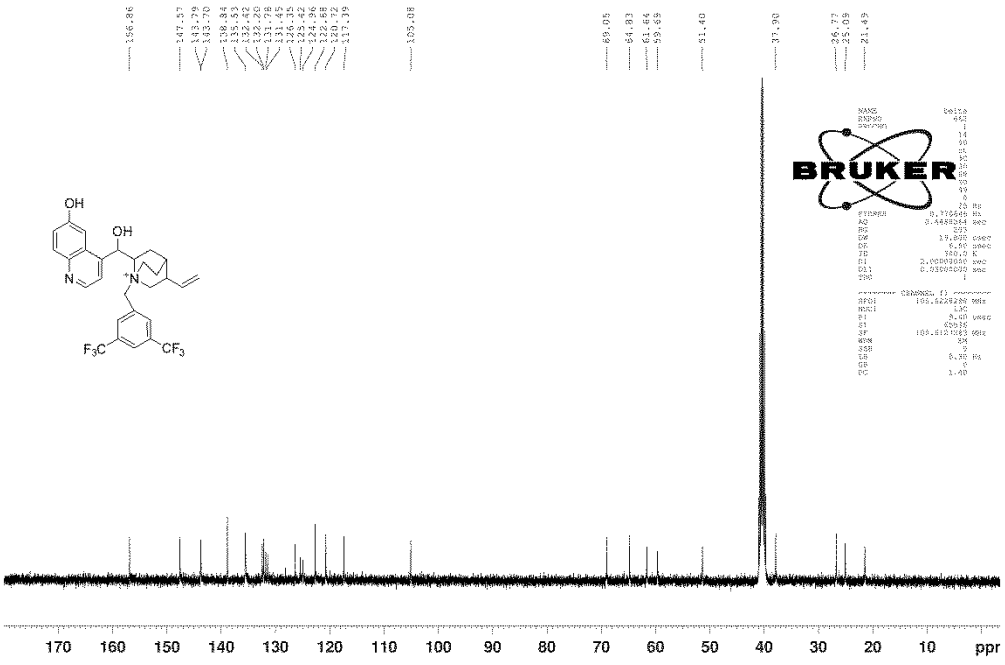
O-9- Adamantoyl-*N*- benzylquininium bromide (5d)



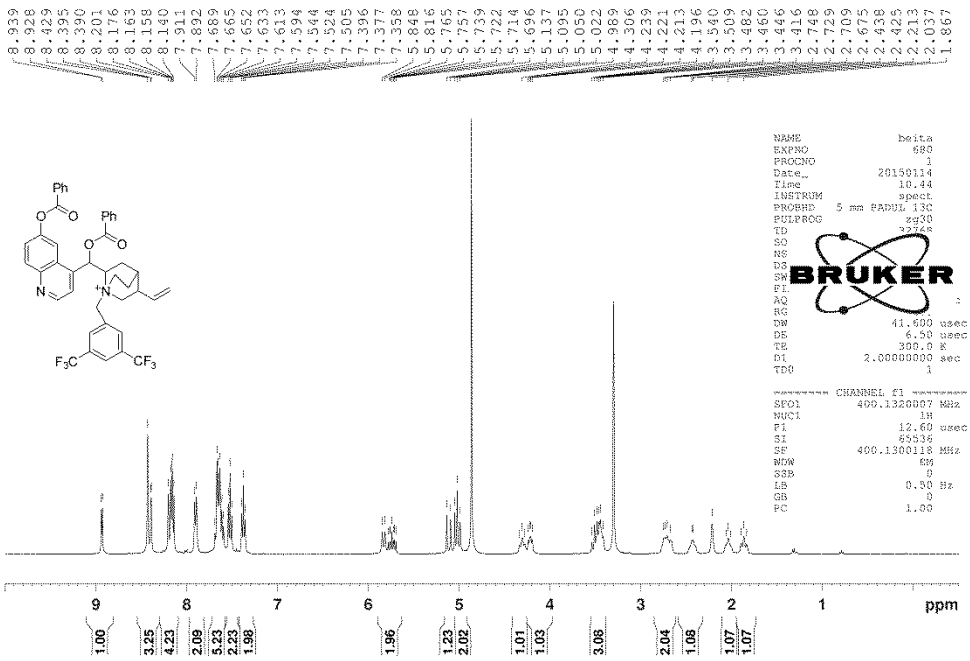


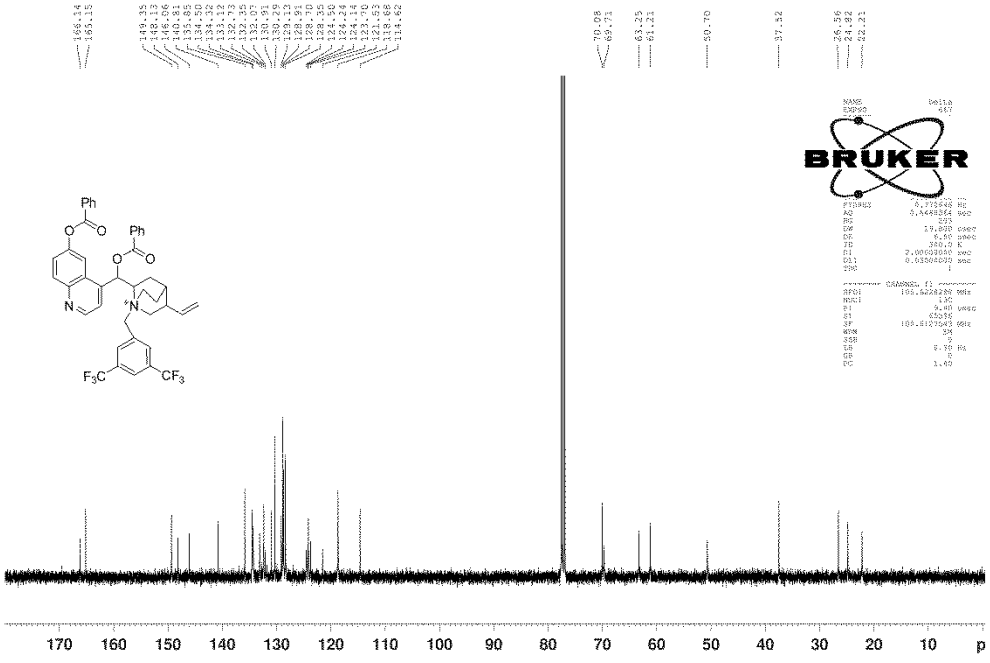
***N*-(3,5-Ditrifluoromethyl)benzyl-6'-hydroxyquininium bromide (5g)**



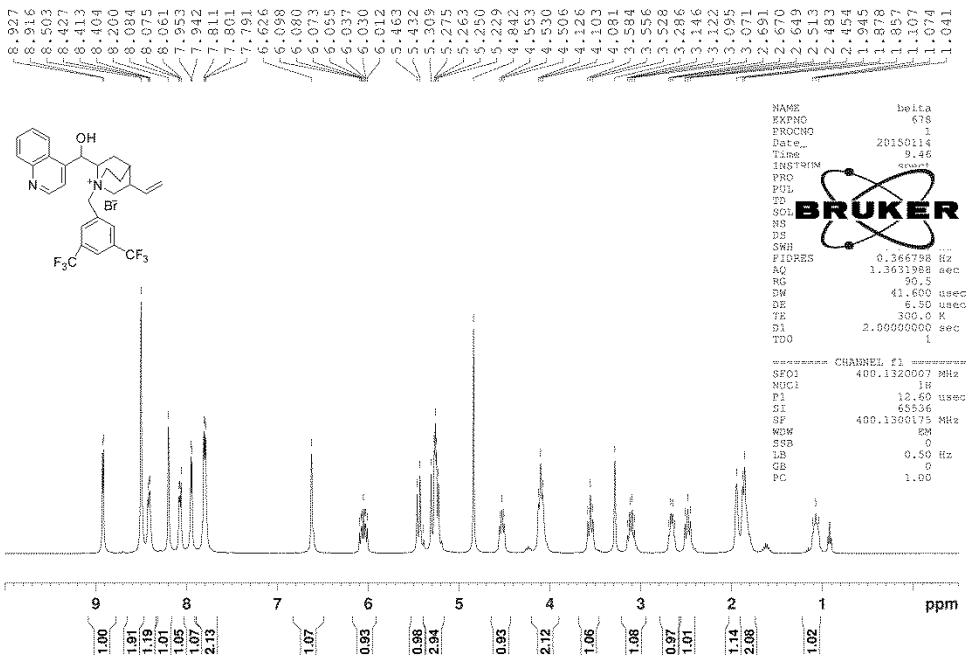


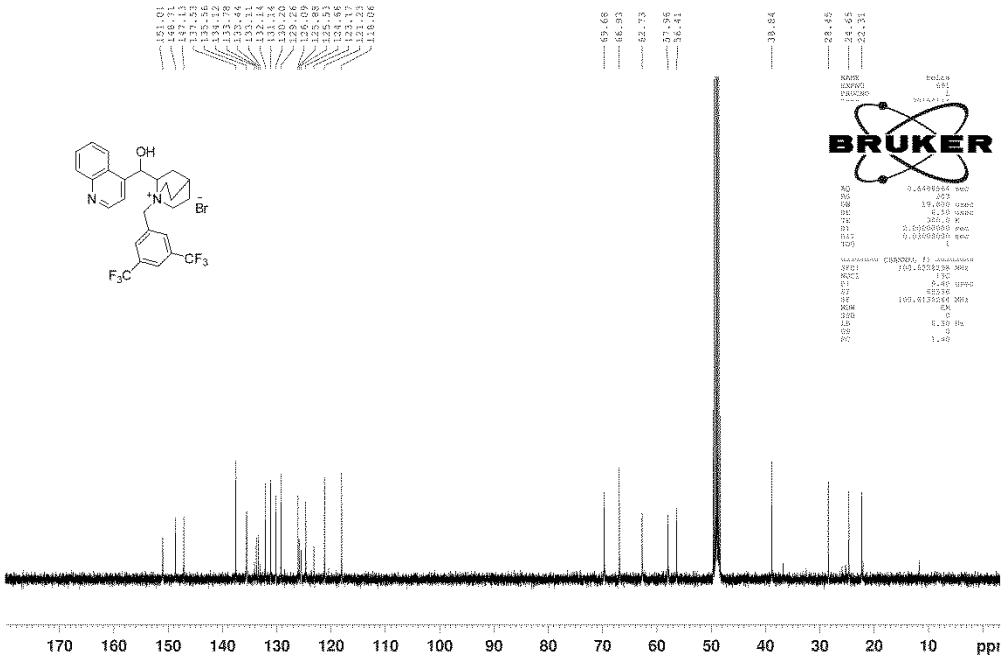
***O*-9- benzoyl-*N*-(3,5-Ditrifluoromethyl)benzyl-6'-benzoylquininium bromide (5h)**



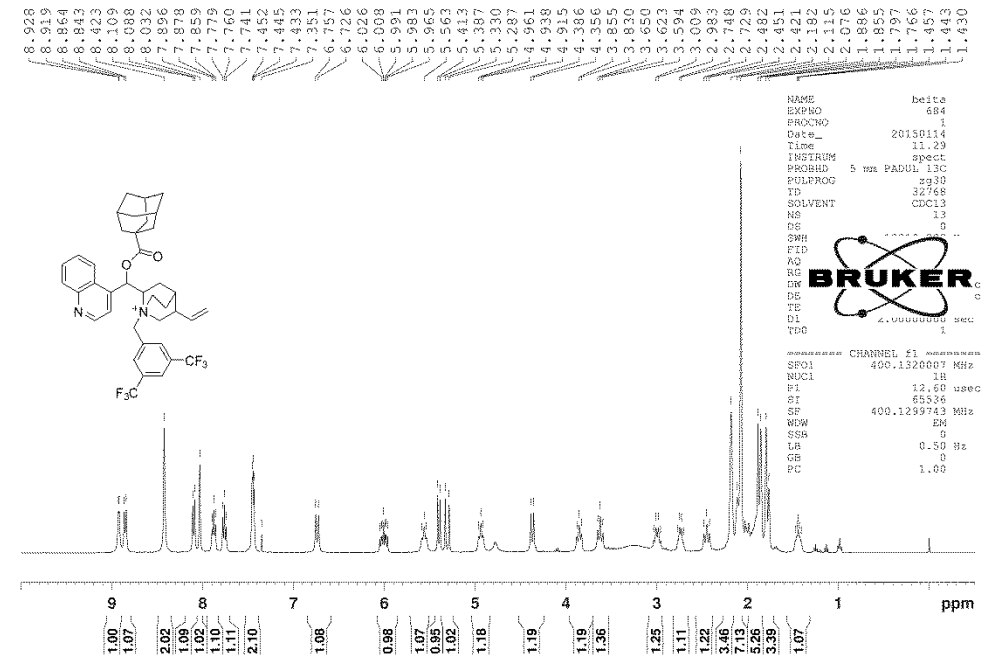


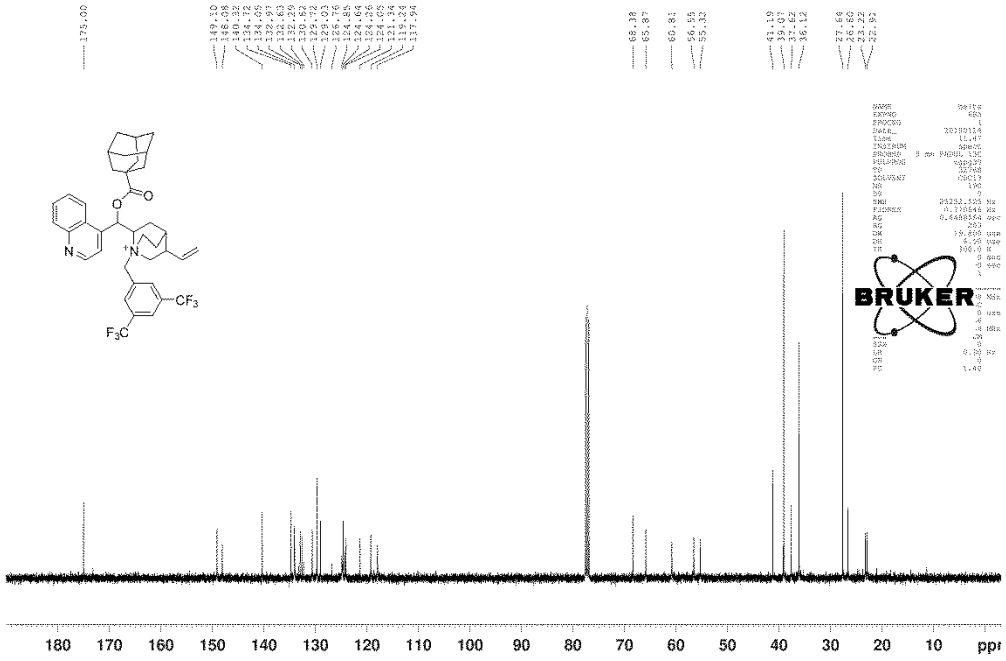
N-(3,5-Ditrifluoromethyl)benzyl-cinchoninium bromide



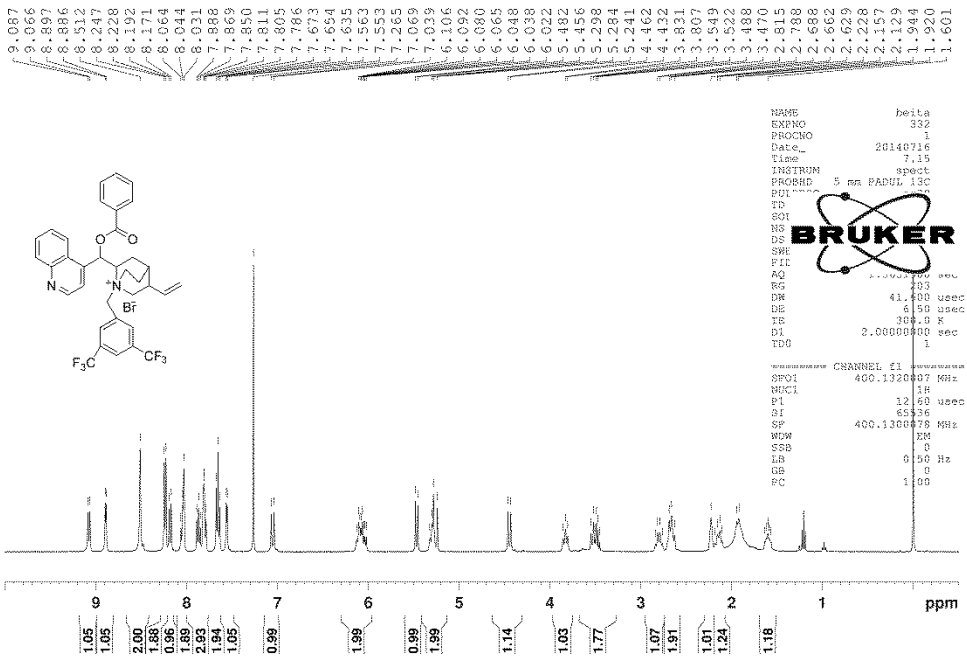


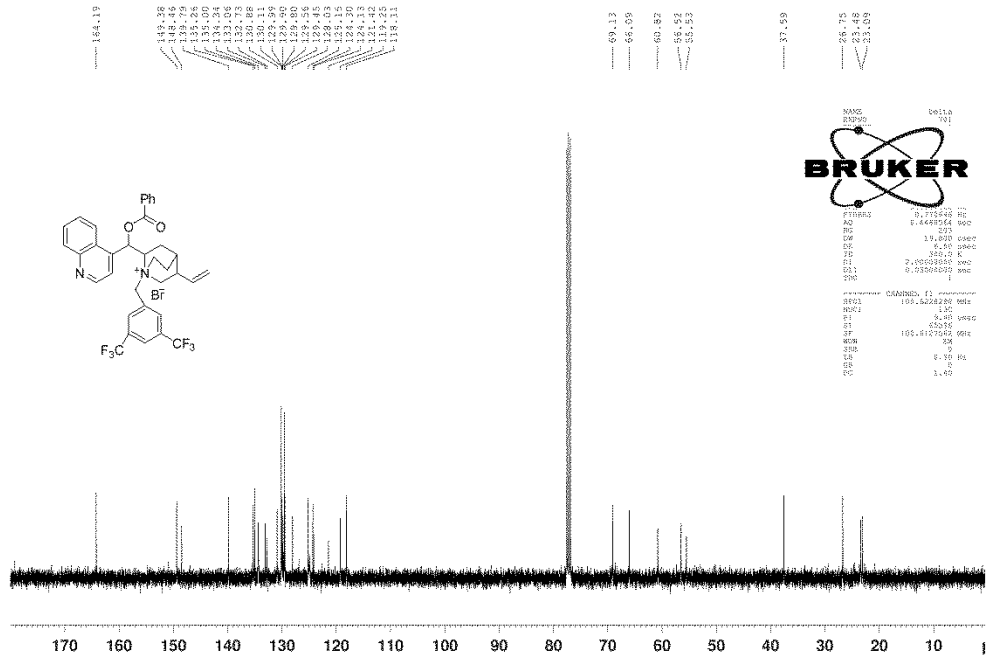
O-9- Adamantoyl-*N*- (3,5-Ditrifluoromethyl)benzylcinchoninium bromide (5i)



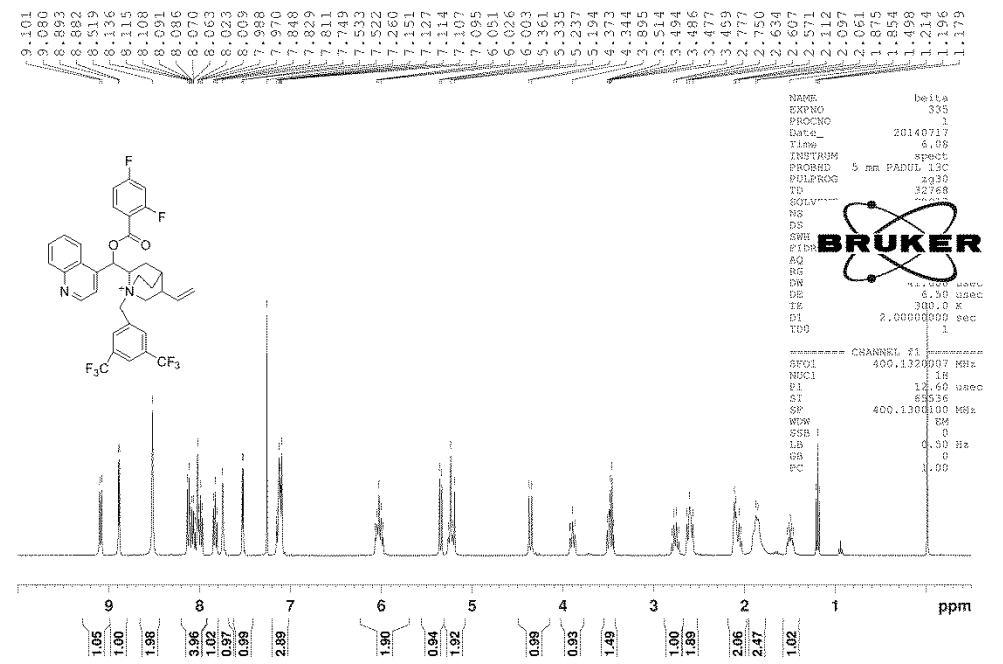


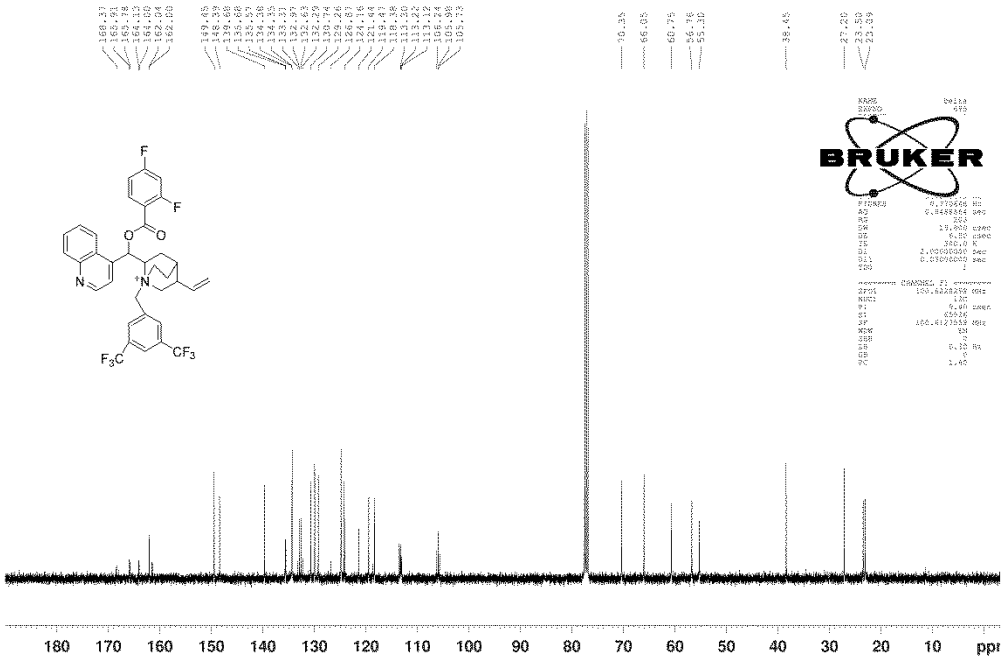
***O*-9- benzoyl-*N*- (3,5-Ditrifluoromethyl)benzylcinchoninium bromide (5j)**



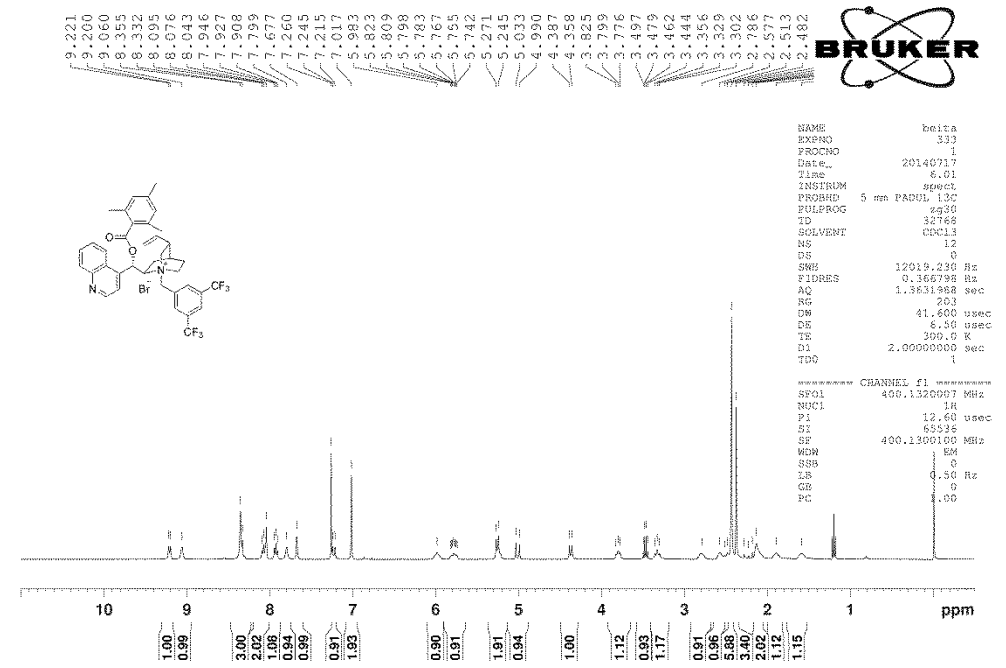


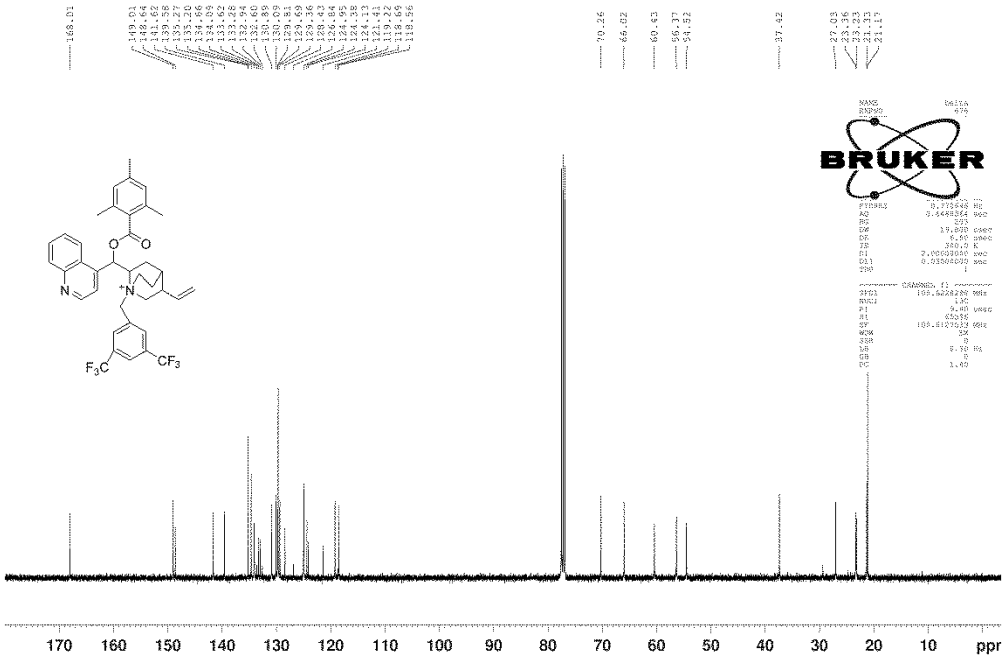
***O*-9-(2,4-difluorobenzoyl)-*N*- (3,5-Ditrifluoromethyl)benzylcinchoninium bromide (5k)**



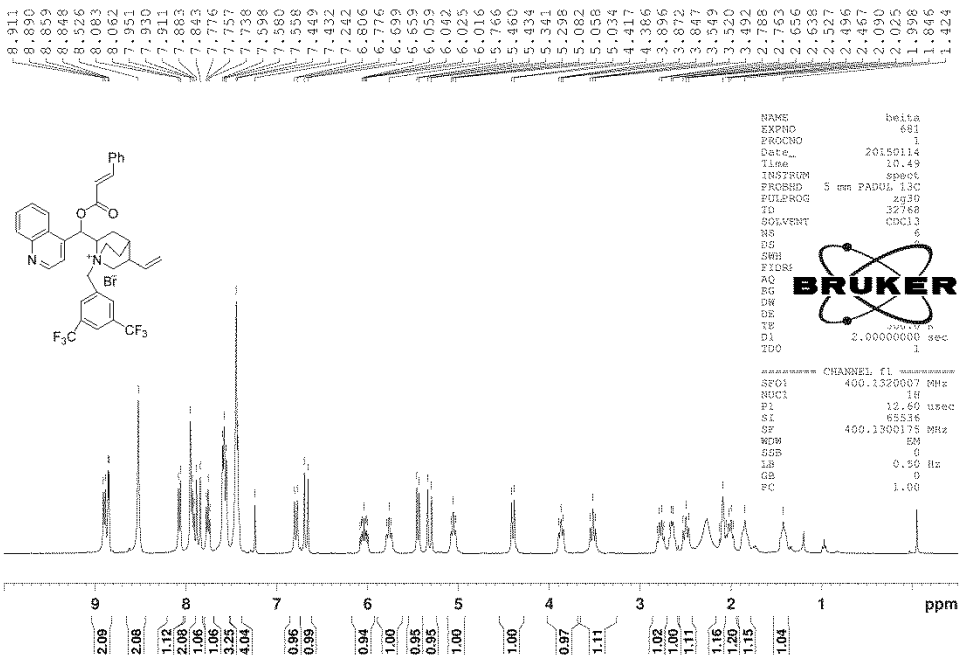


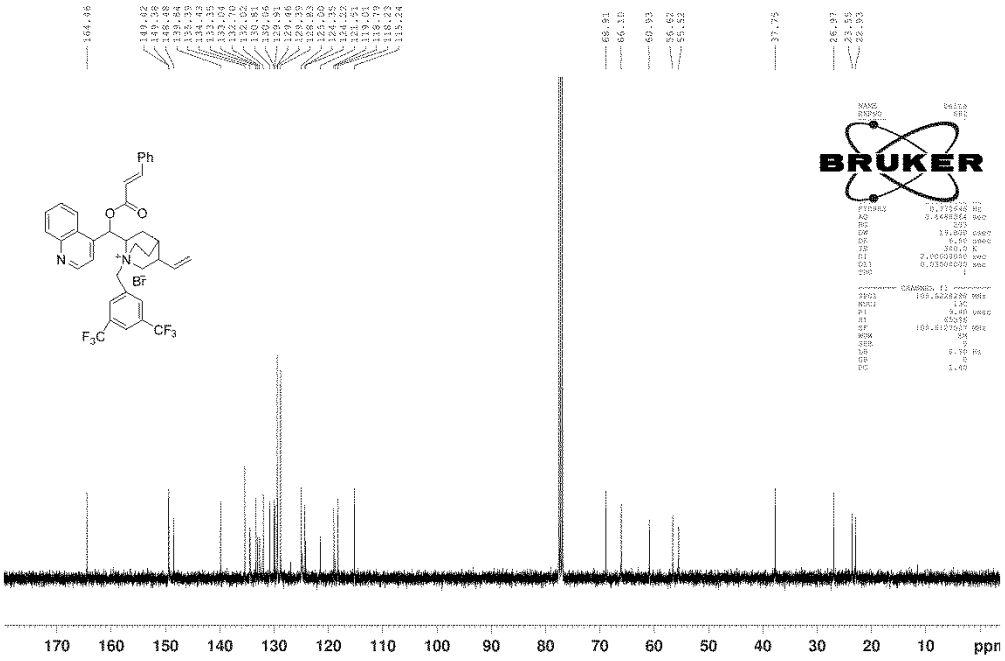
_O_-9-(2,4,6-trimethylbenzoyl)-_N_- (3,5-Ditrifluoromethyl)benzylcinchoninium bromide 5l



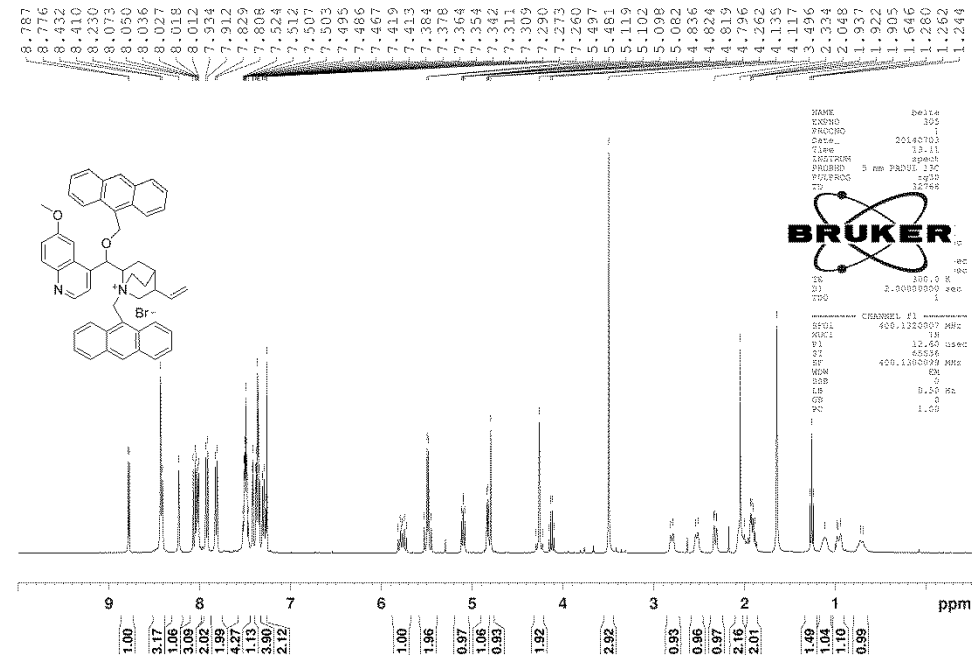


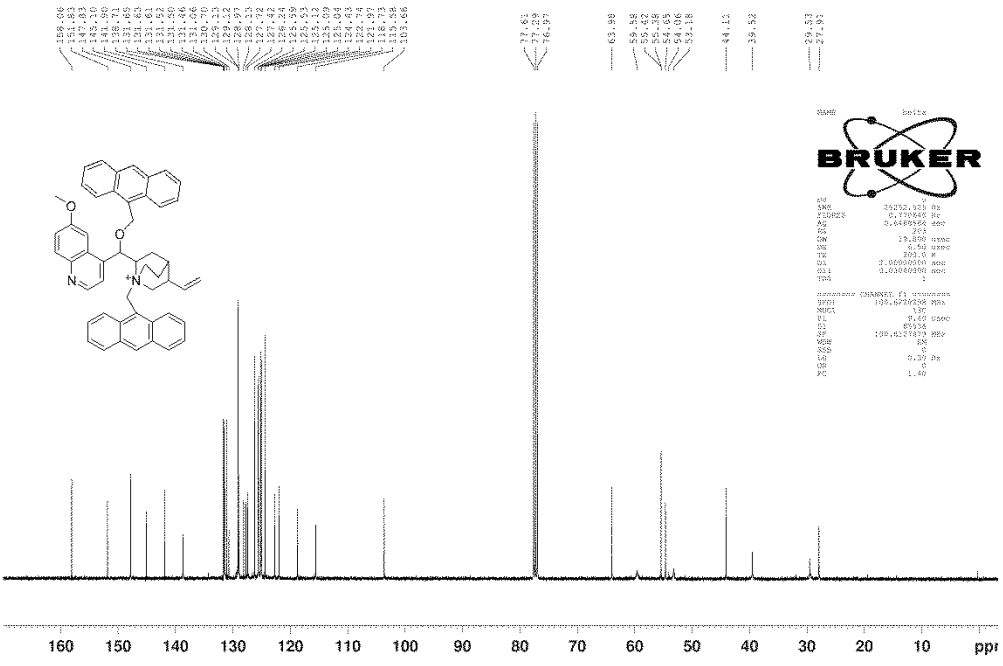
***O*-9-cinamonyl-*N*- (3,5-Ditrifluoromethyl)benzylcinchoninium bromide 5m**



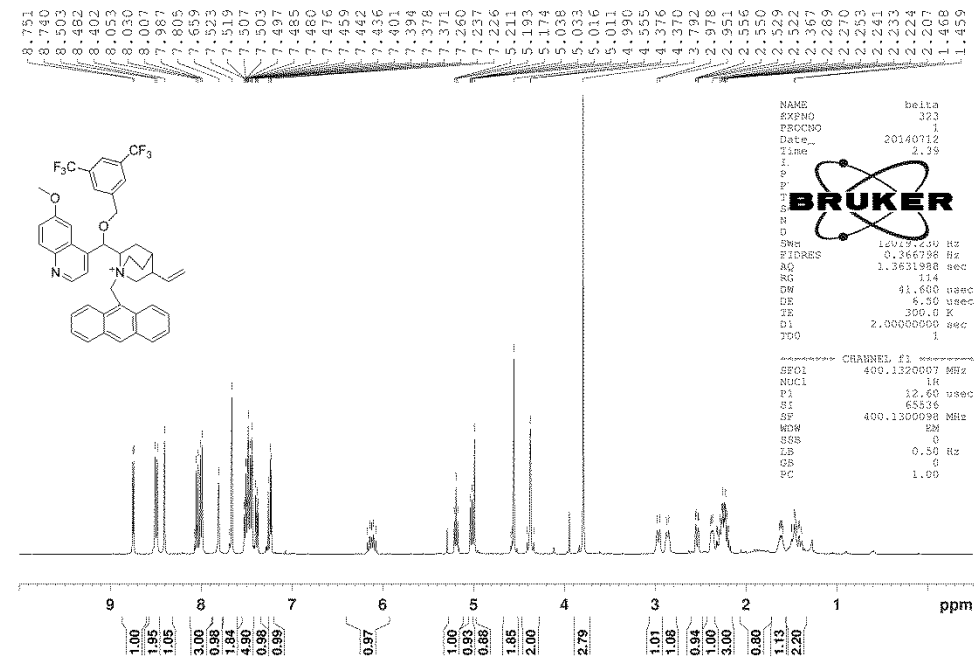


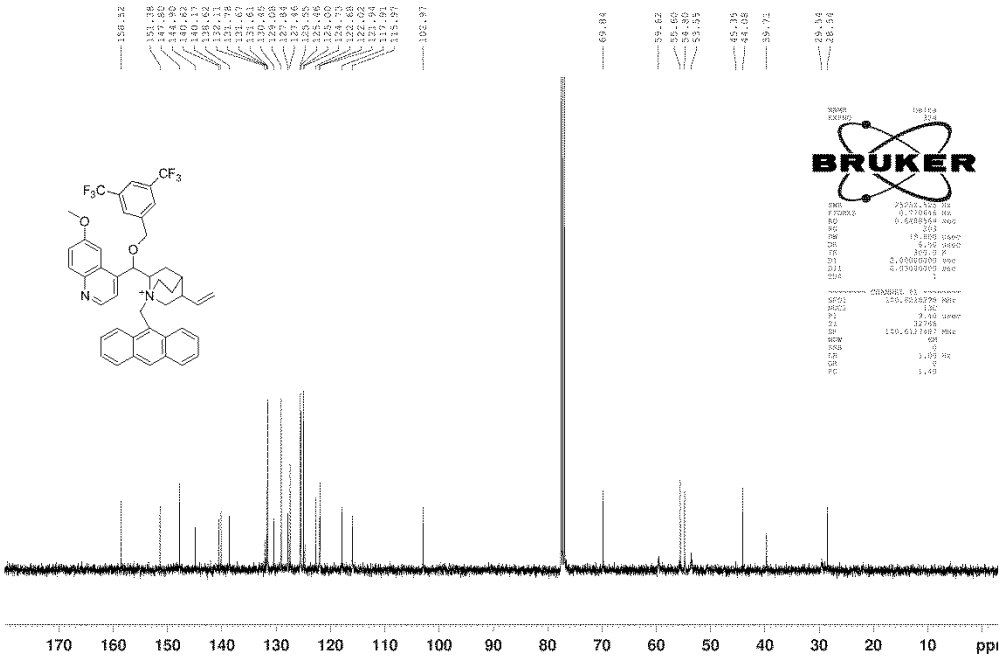
***O*-9- Anthracenylmethyl -*N*- Anthracenylmethyl quininium bromide 5e**



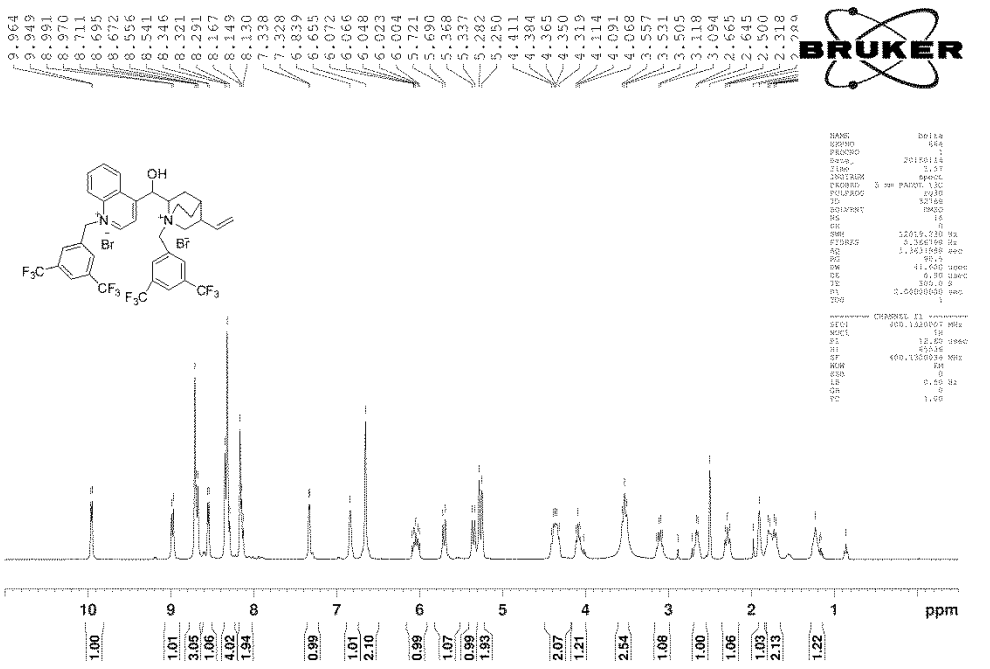


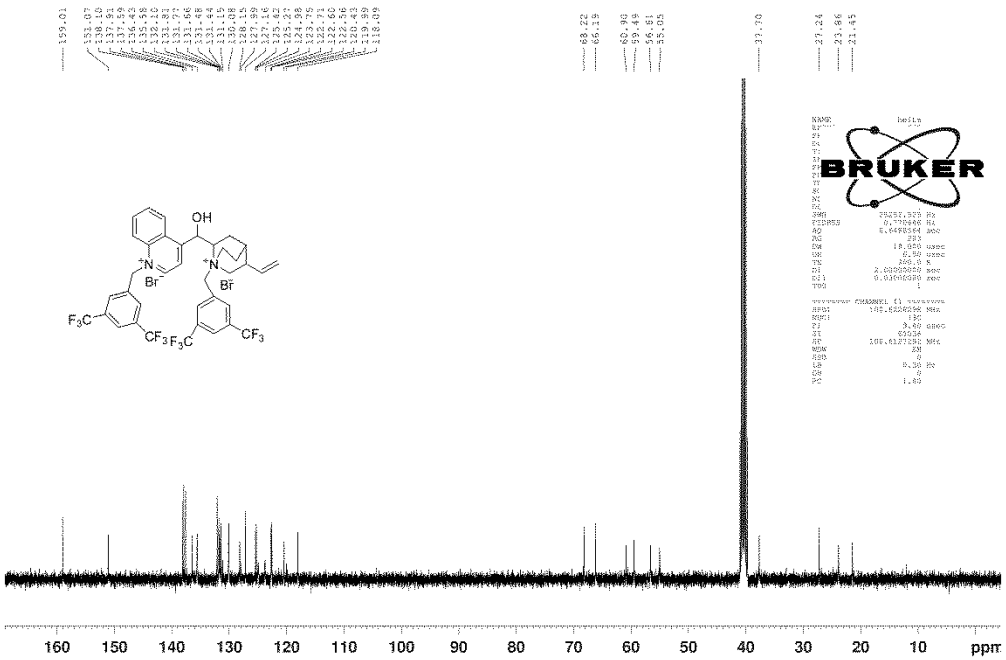
***O*-9-(3,5-Ditrifluoromethyl)-*N*- Anthracenylmethyl quininium bromide 5f**



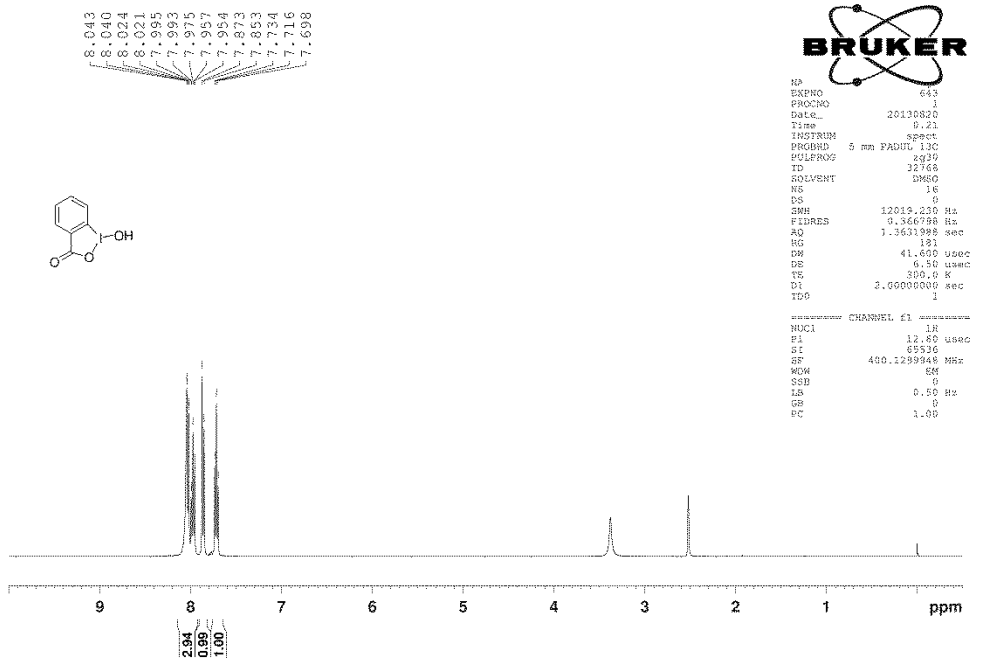


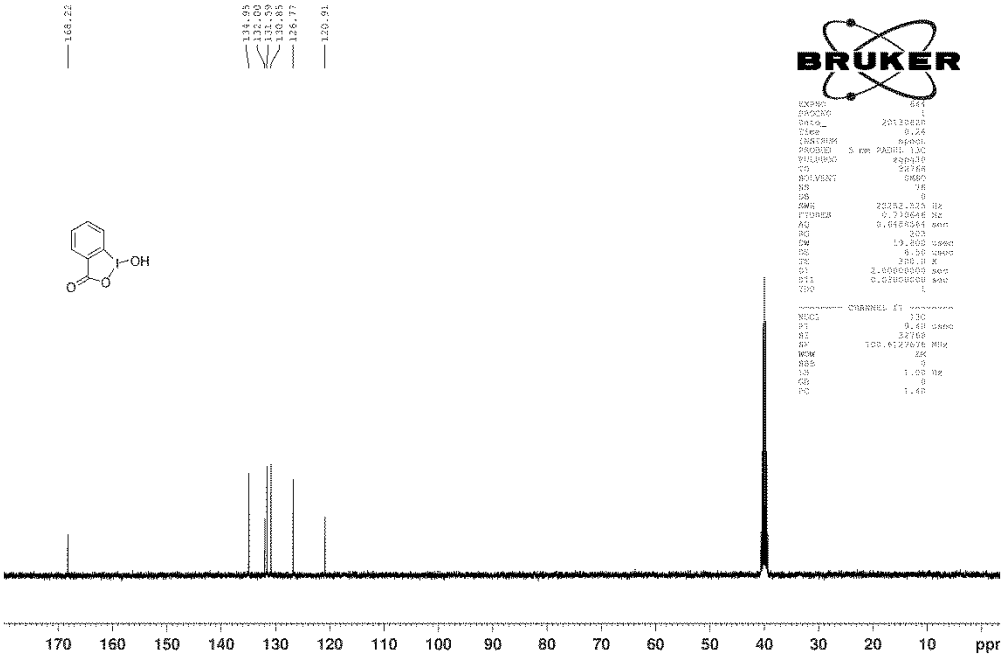
***N'*-(3,5-Ditrifluoromethyl)-*N*- (3,5-Ditrifluoromethyl) quininium dibromide 5n**



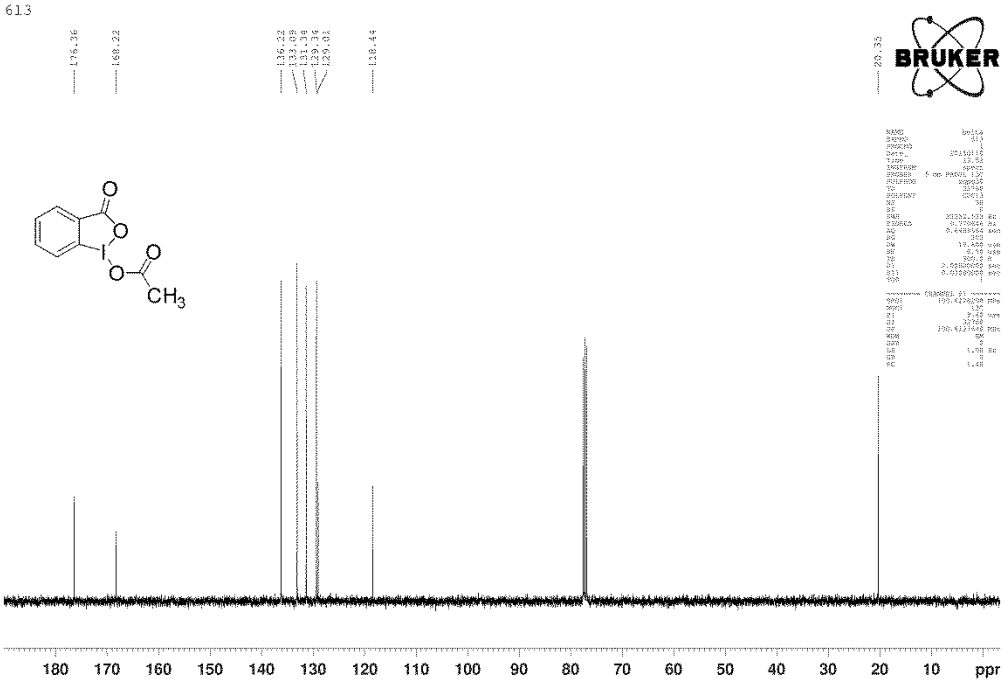


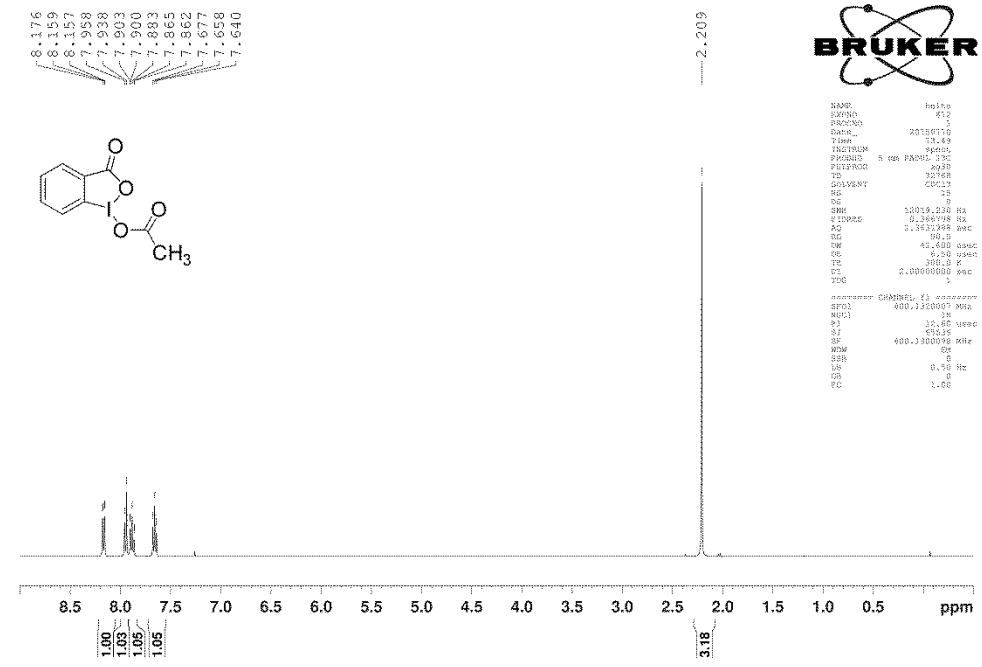
1-Hydroxy-1,2-benziodoxol-3-(1H)-one



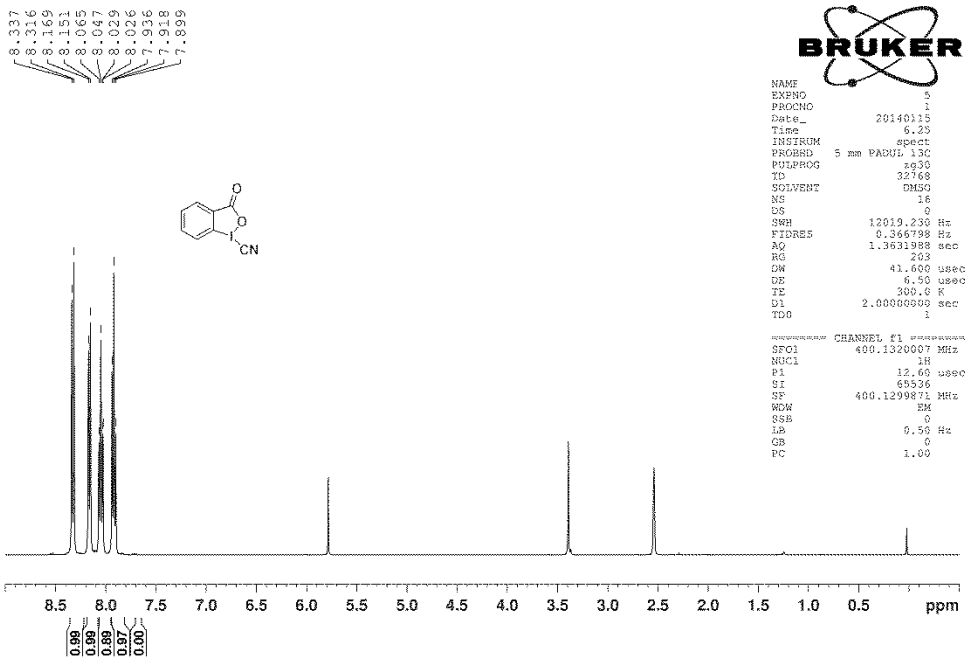


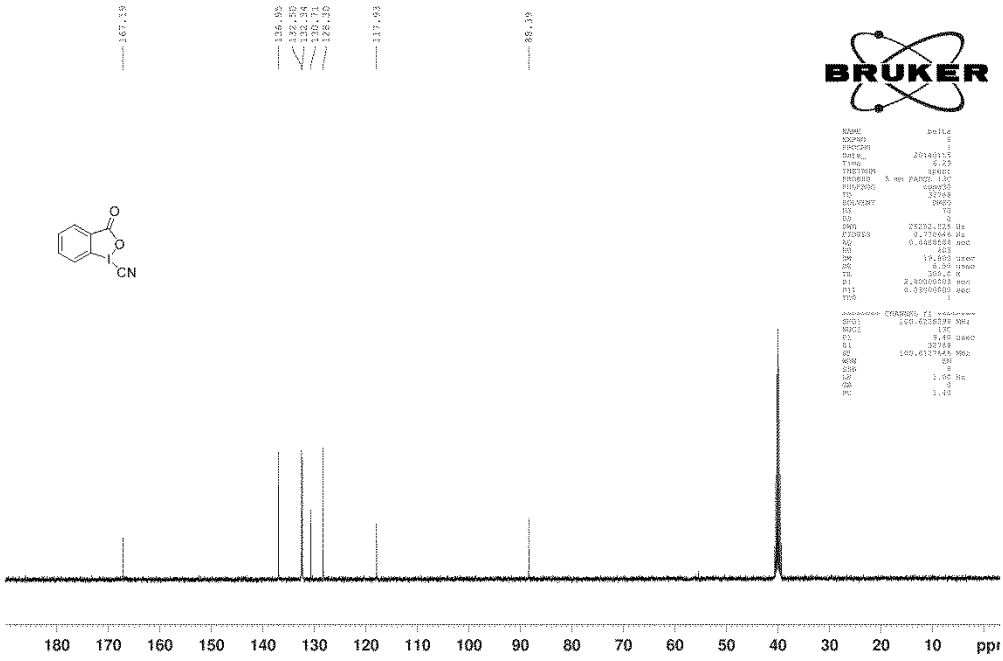
1-Acetoxy-1,2-benziodoxol-3-(1H)-one



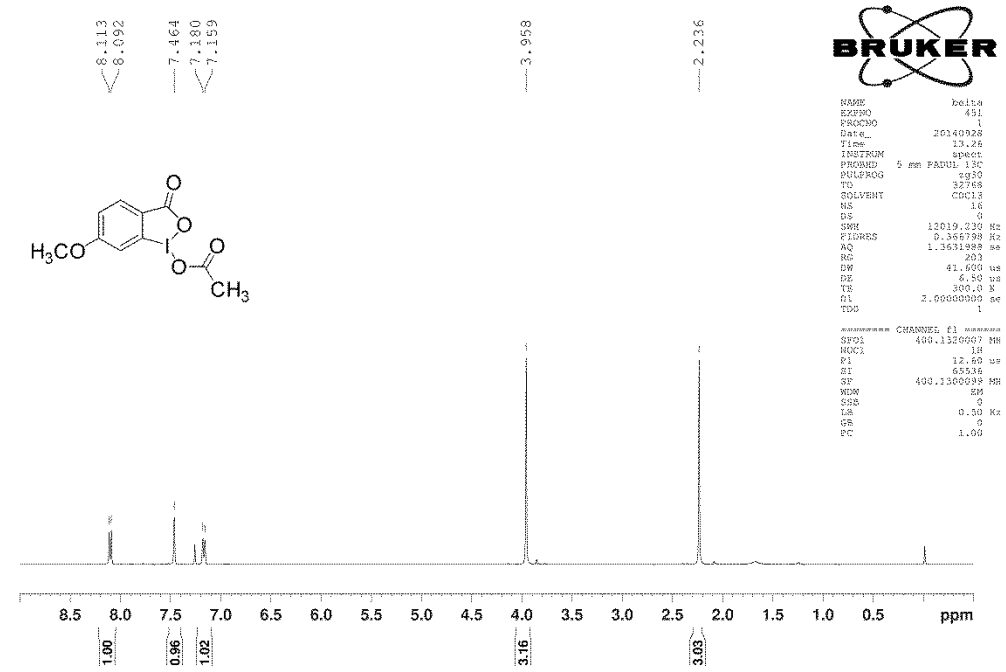


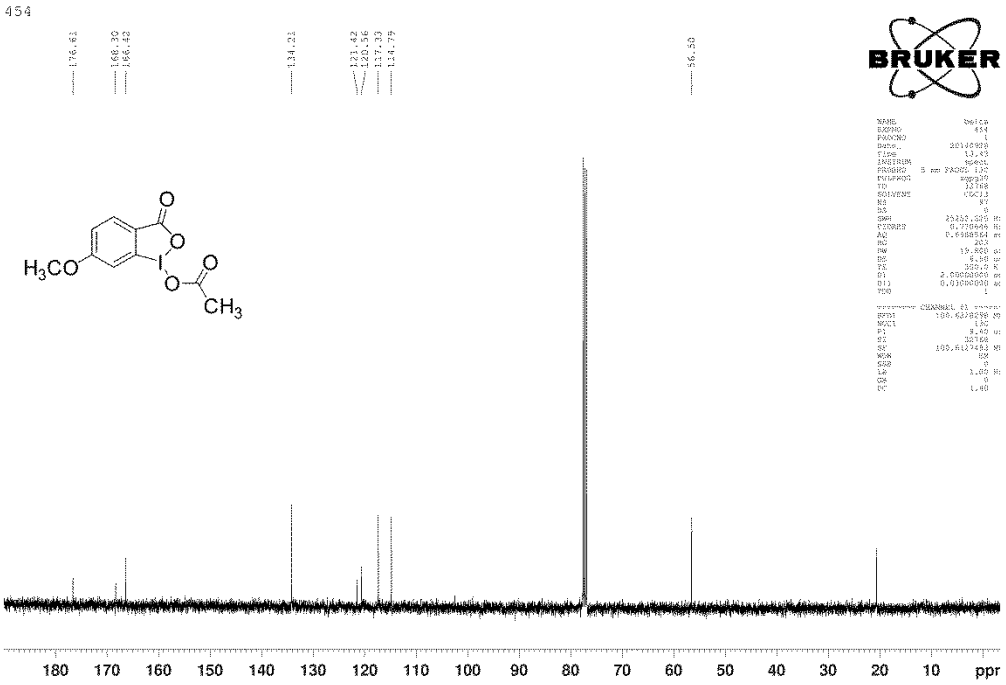
1-Cyano-1,2-benziodoxol-3-(1H)-one



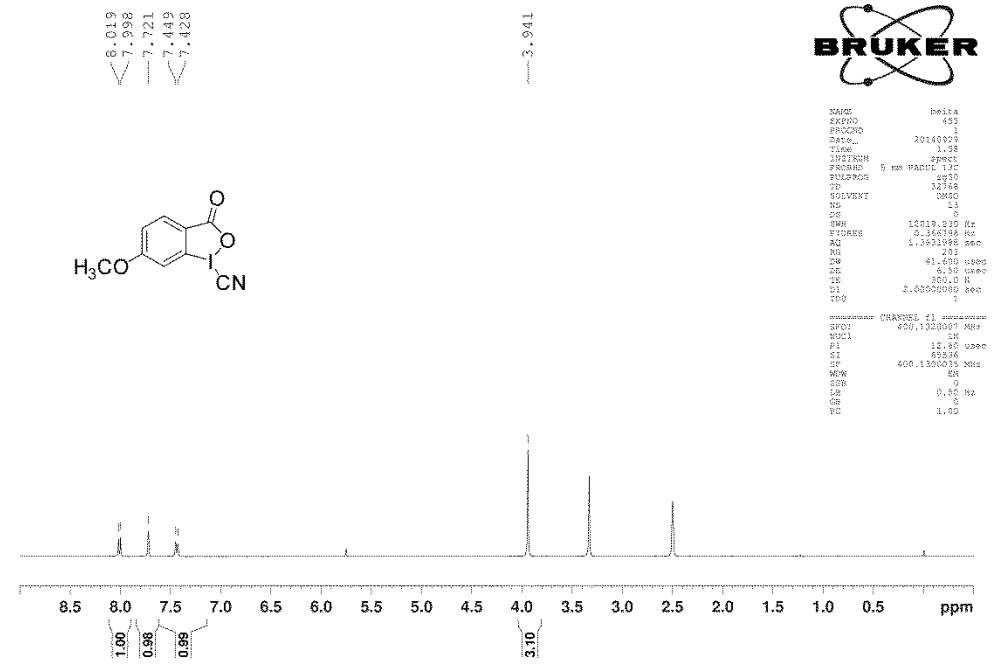


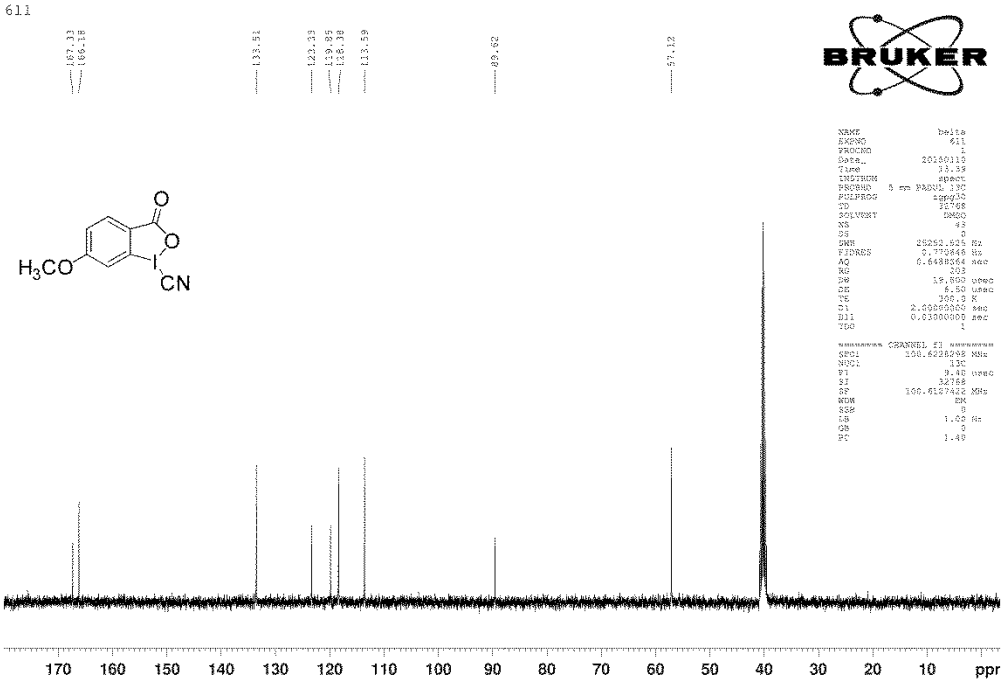
4-Metheoxyl-1-acetoxy-1,2-benziodoxol-3-(1H)-one



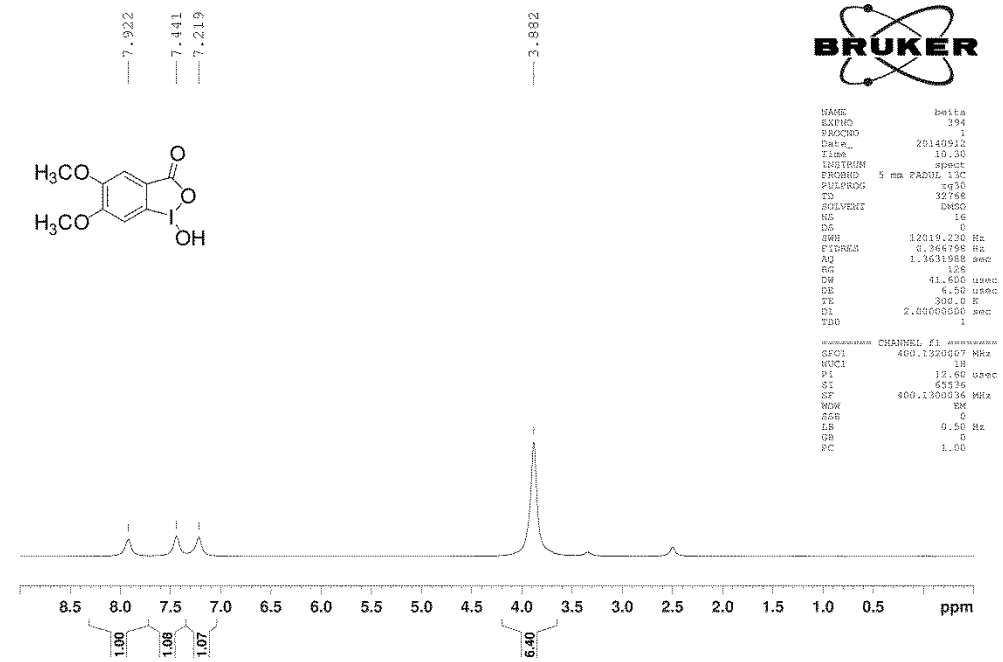


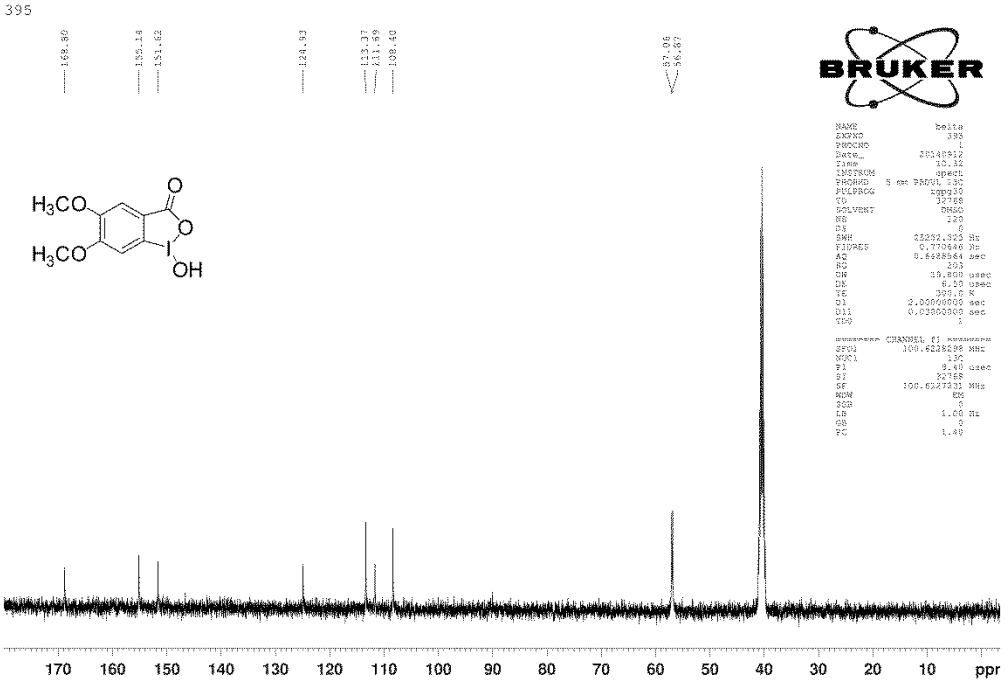
4-Metheoxyl-1-cyano-1,2-benziodoxol-3-(1H)-one



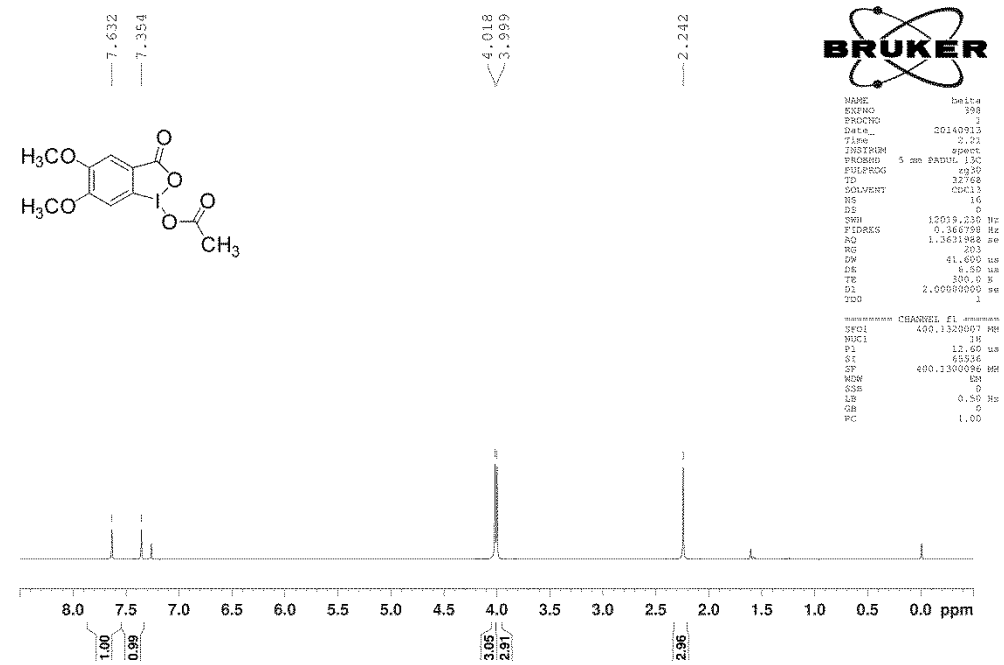


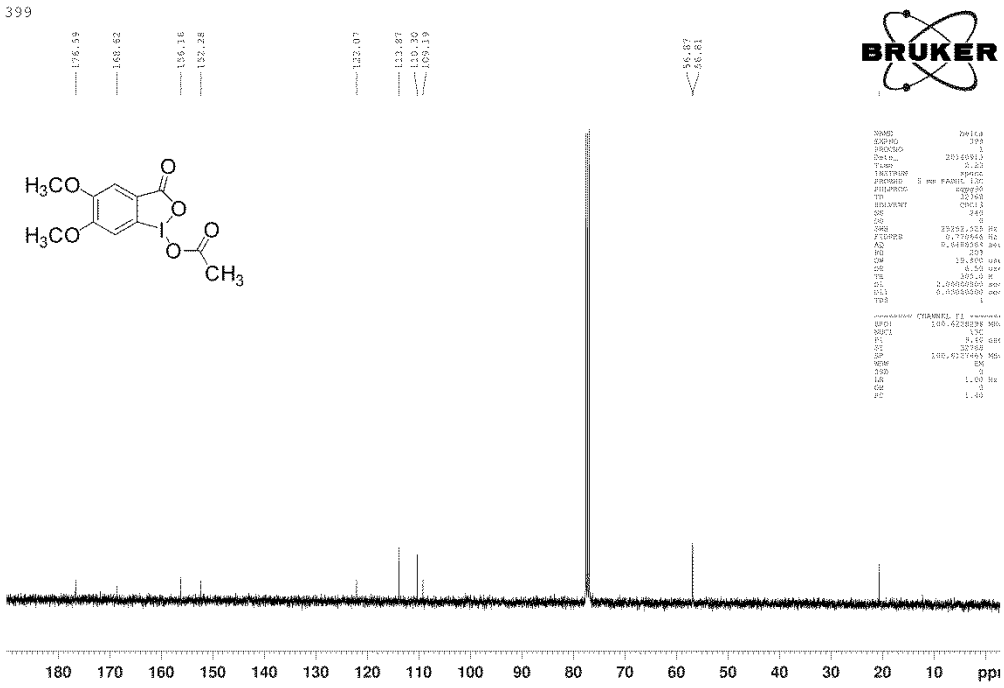
4,5-Dimetheoxyl-1-hydroxy-1,2-benziodoxol-3-(1H)-one



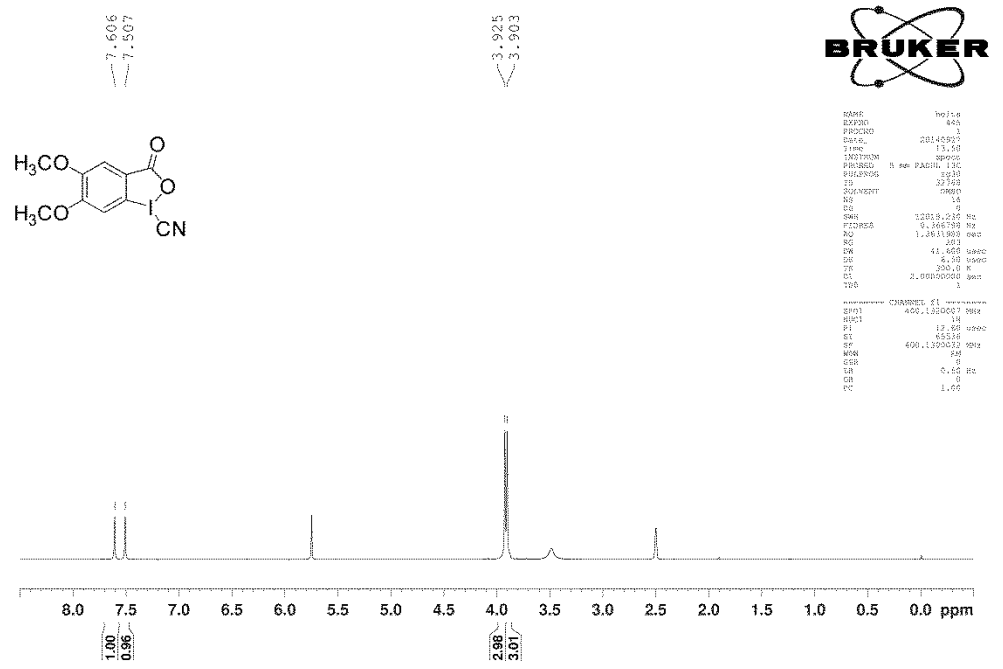


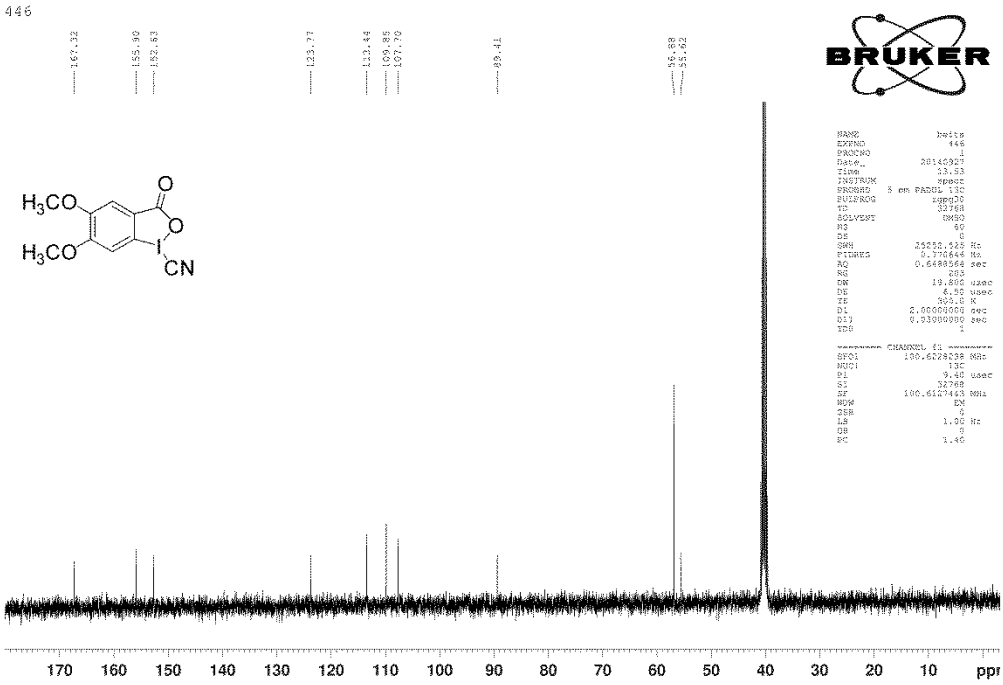
4,5-Dimetheoxyl-1-acetoxy-1,2-benziodoxol-3-(1H)-one



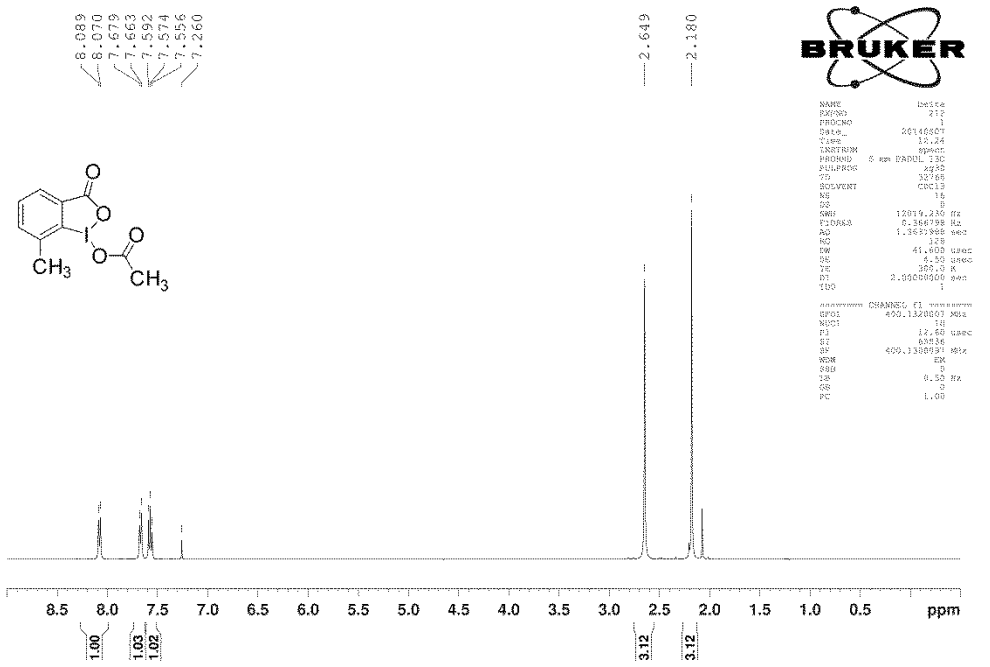


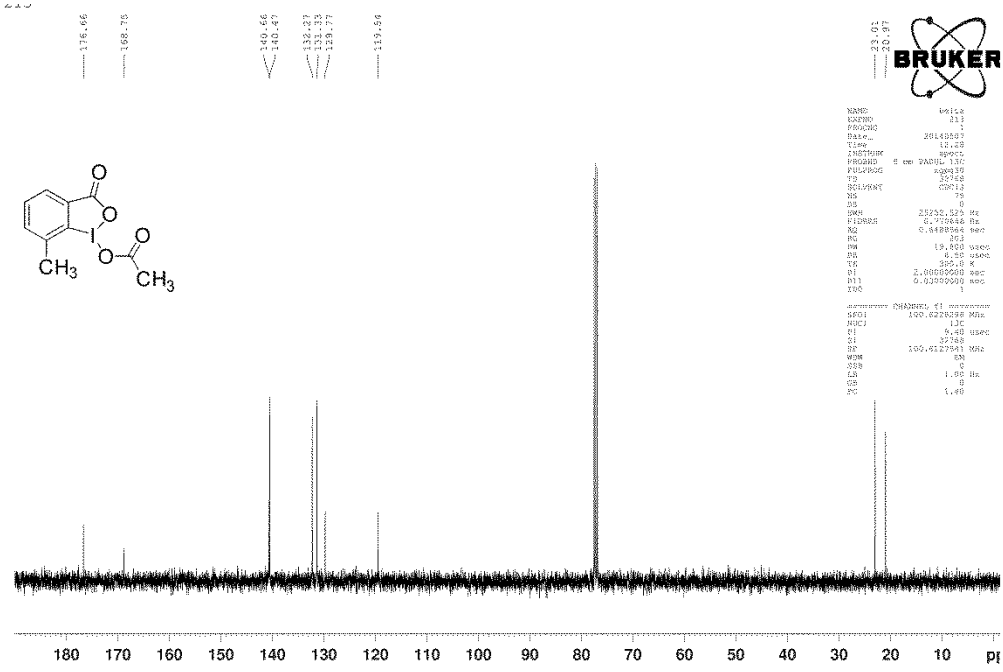
4,5-Dimetheoxyl-1-cyano-1,2-benziodoxol-3-(1H)-one (1d)



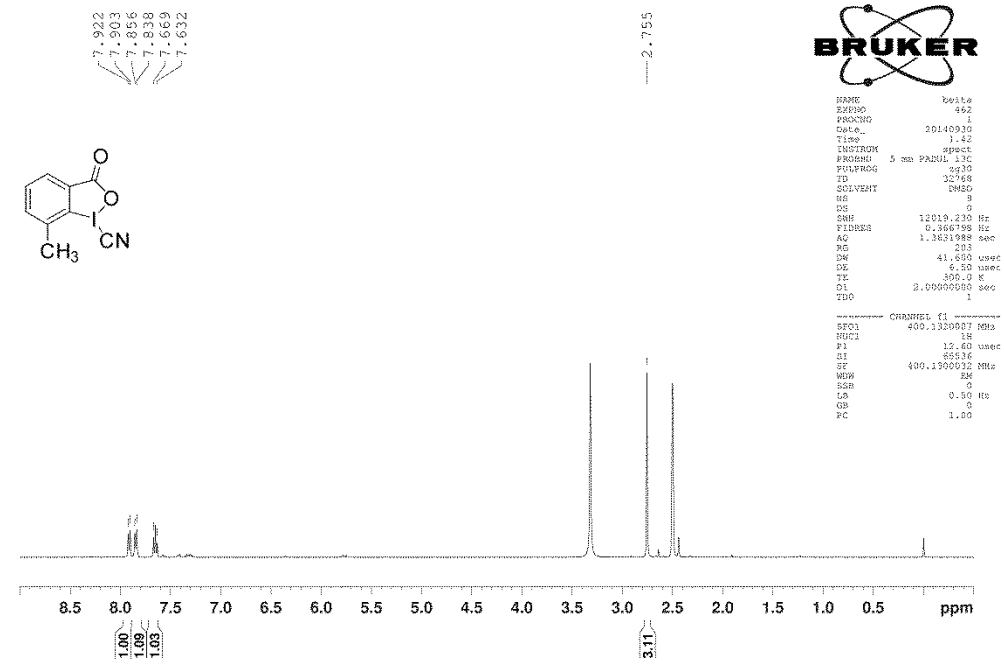


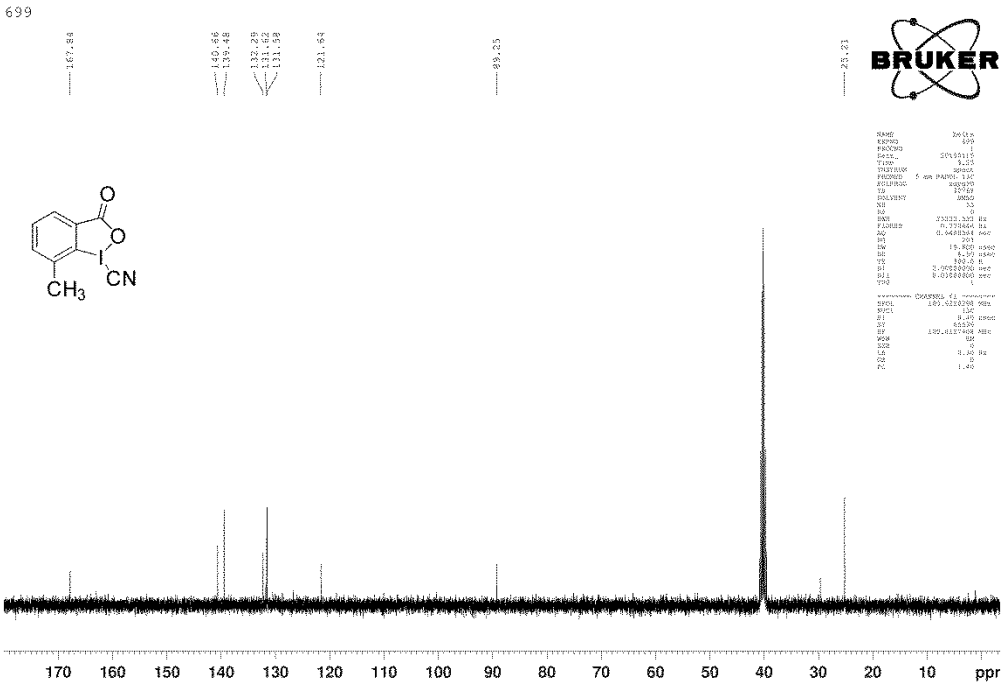
3-Methyl-1-acetoxy-1,2-benziodoxol-3-(1H)-one



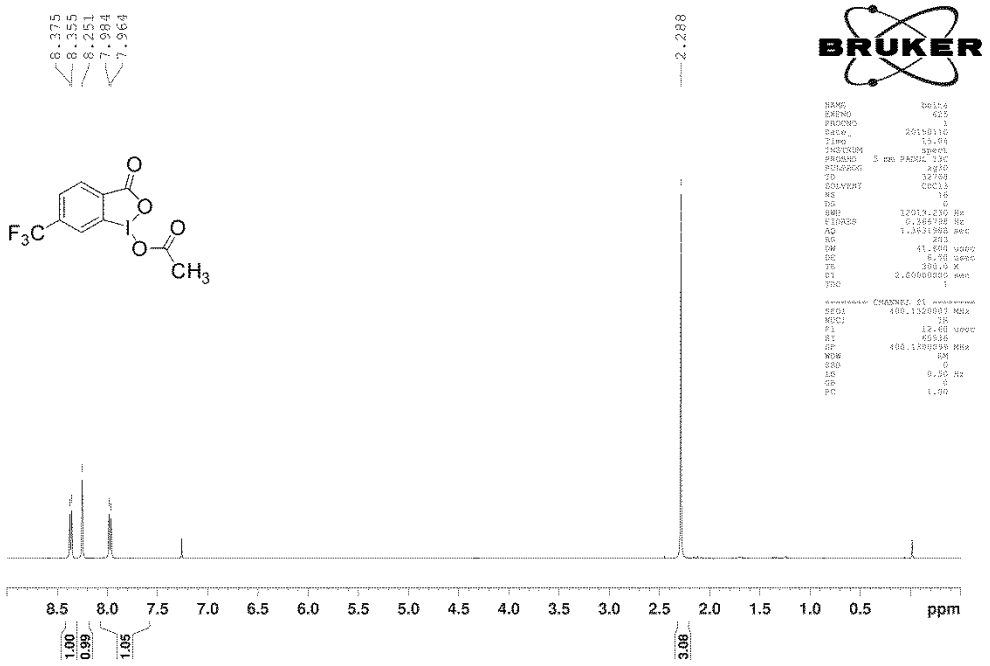


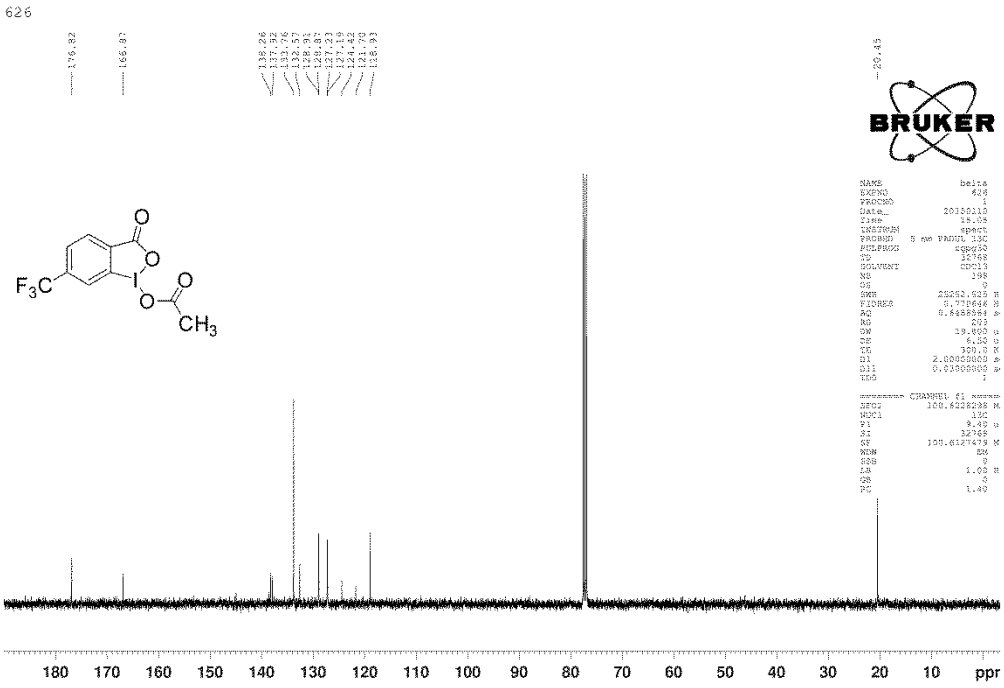
3-Methyl-1-acetoxy-1,2-benziodoxol-3-(1H)-one (1e)



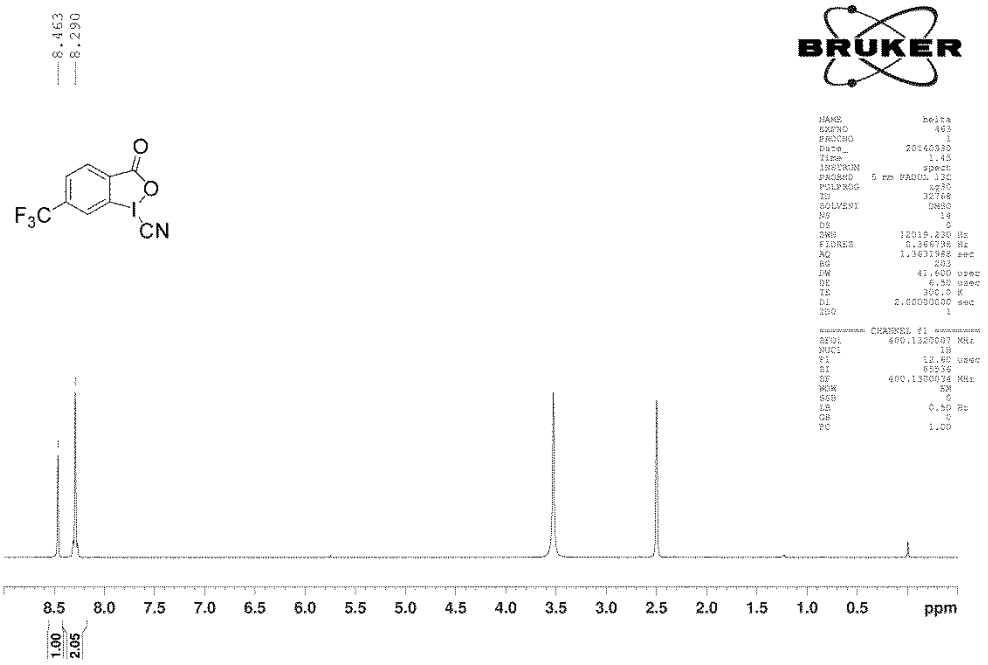


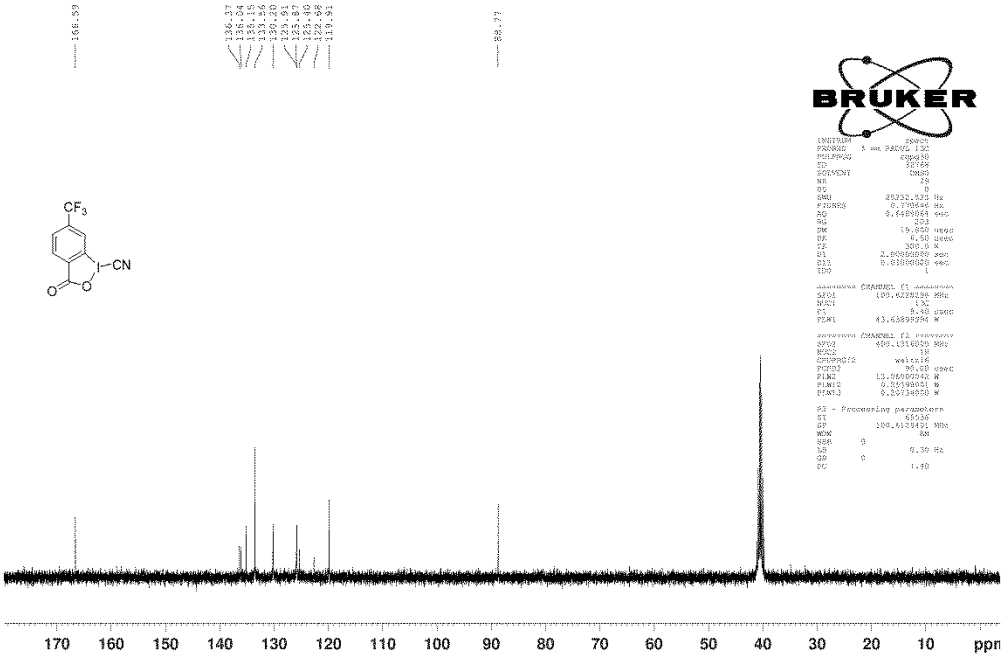
4-Trifluoromethyl-1-acetoxy-1,2-benziodoxol-3-(1H)-one



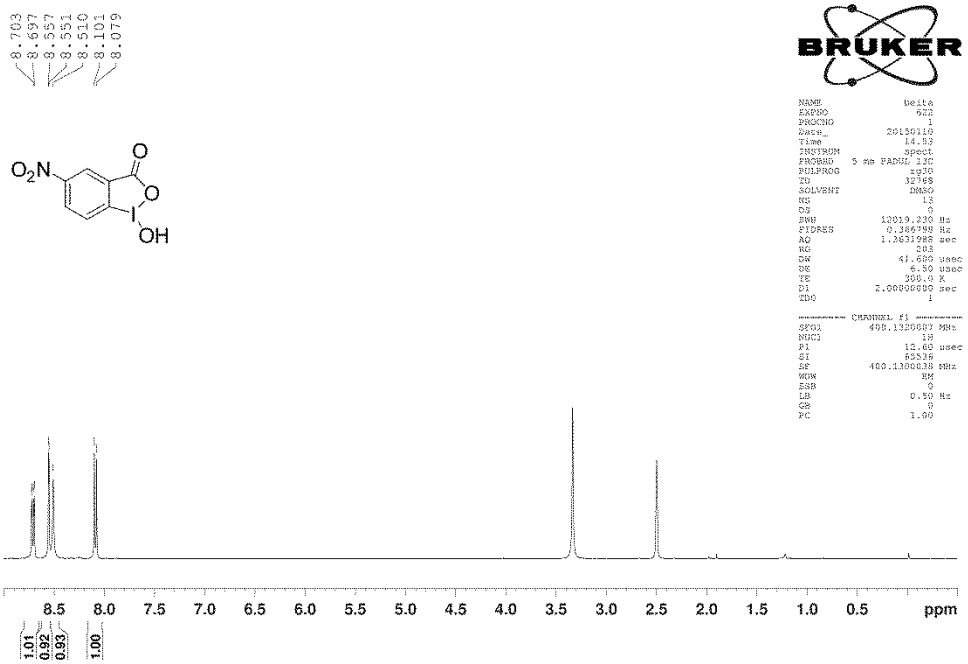


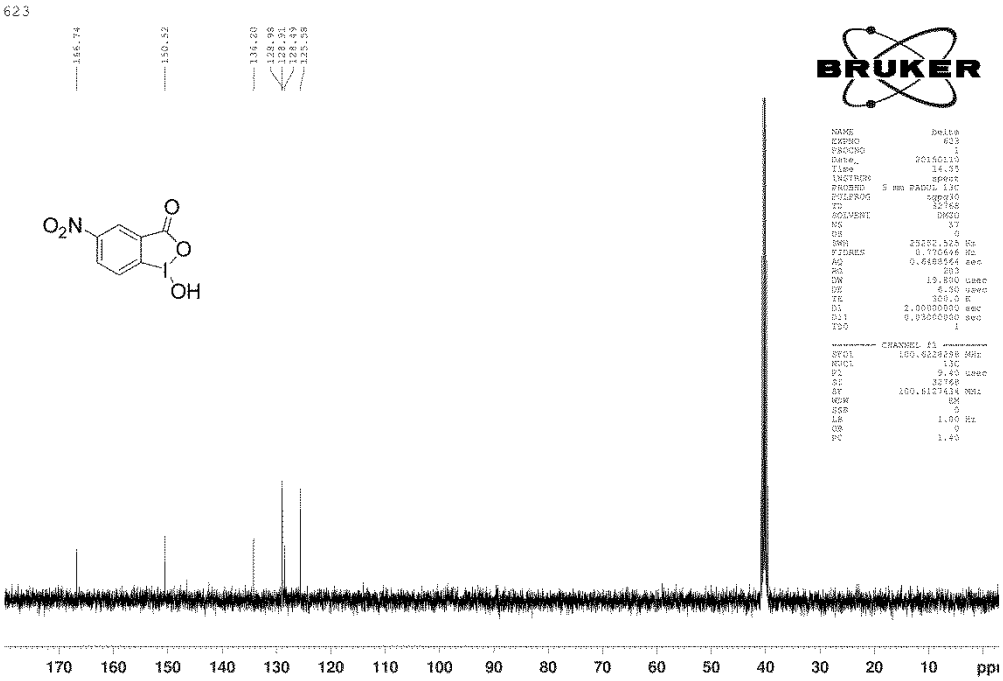
4-Trifluoromethyl-1-cyano-1,2-benziodoxol-3-(1H)-one (1f)



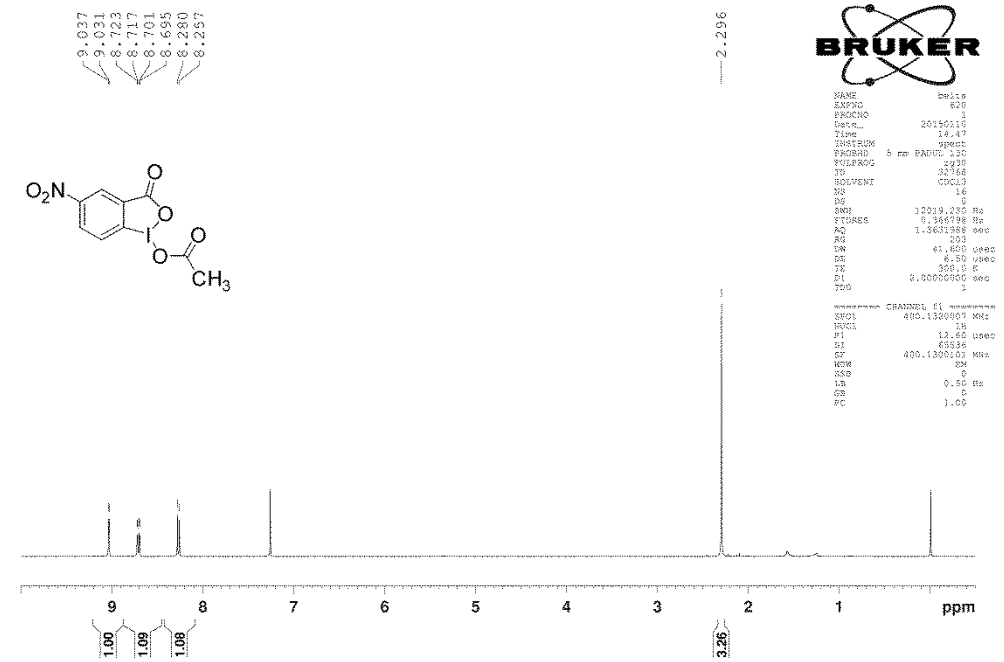


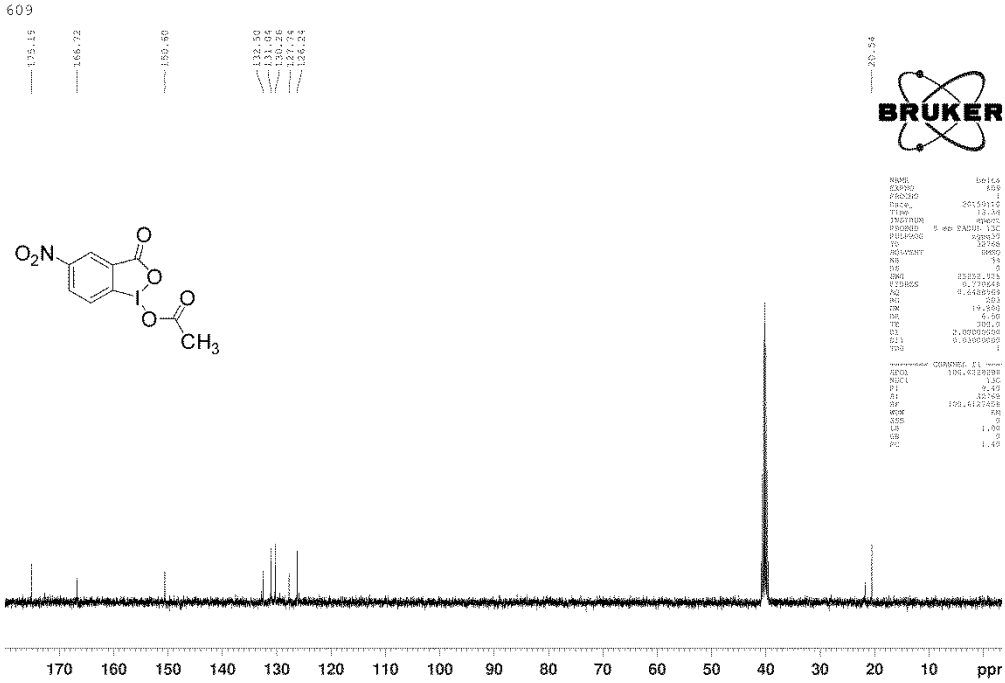
5-Nitro-1-hydroxy-1,2-benziodoxol-3-(1H)-one



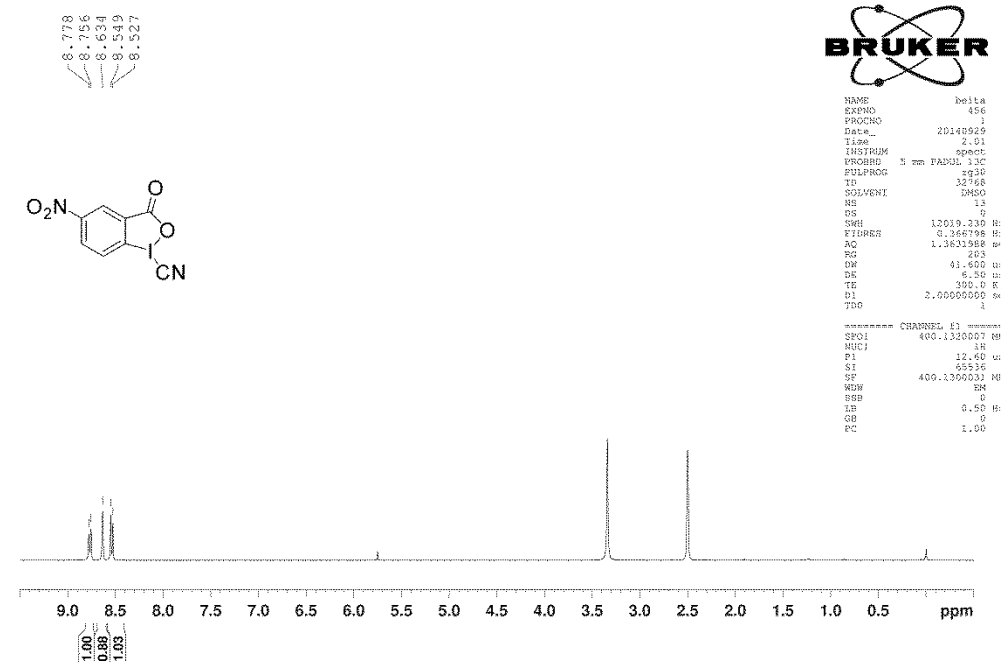


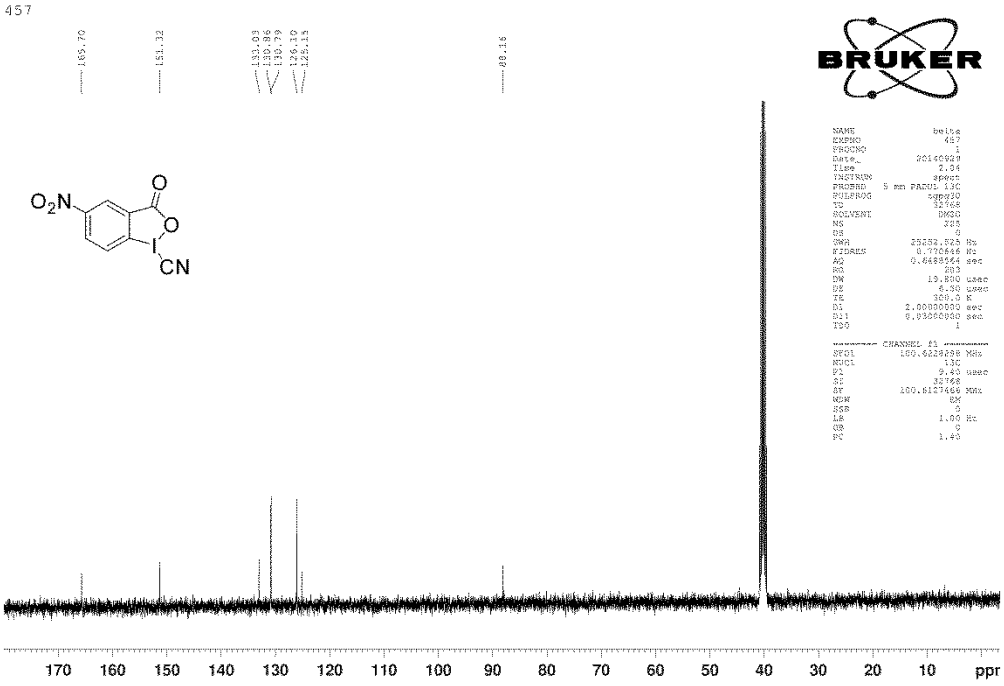
5-Nitro-1-acetoxy-1,2-benziodoxol-3-(1H)-one



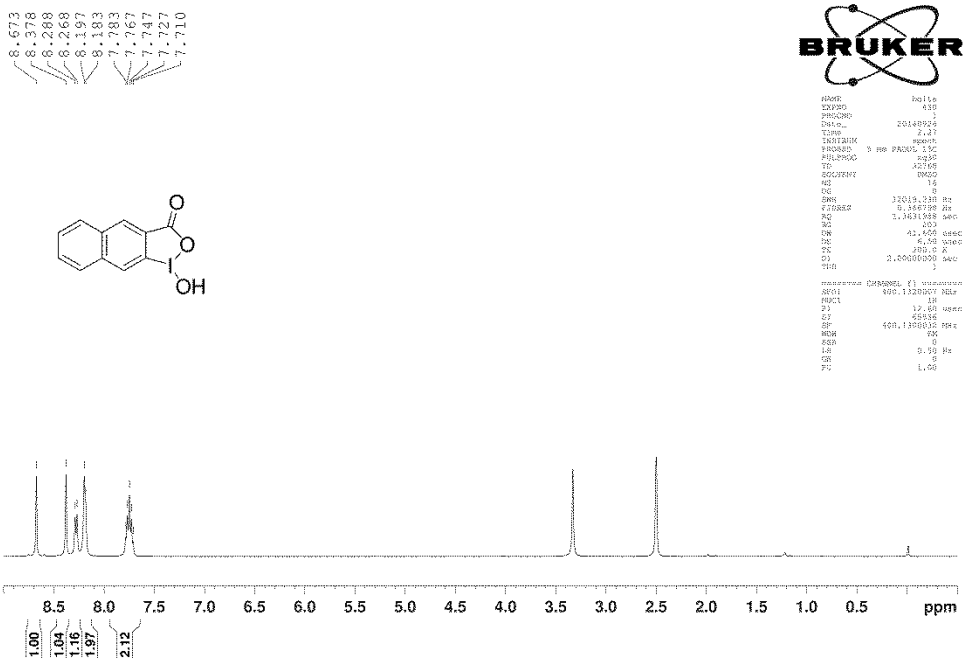


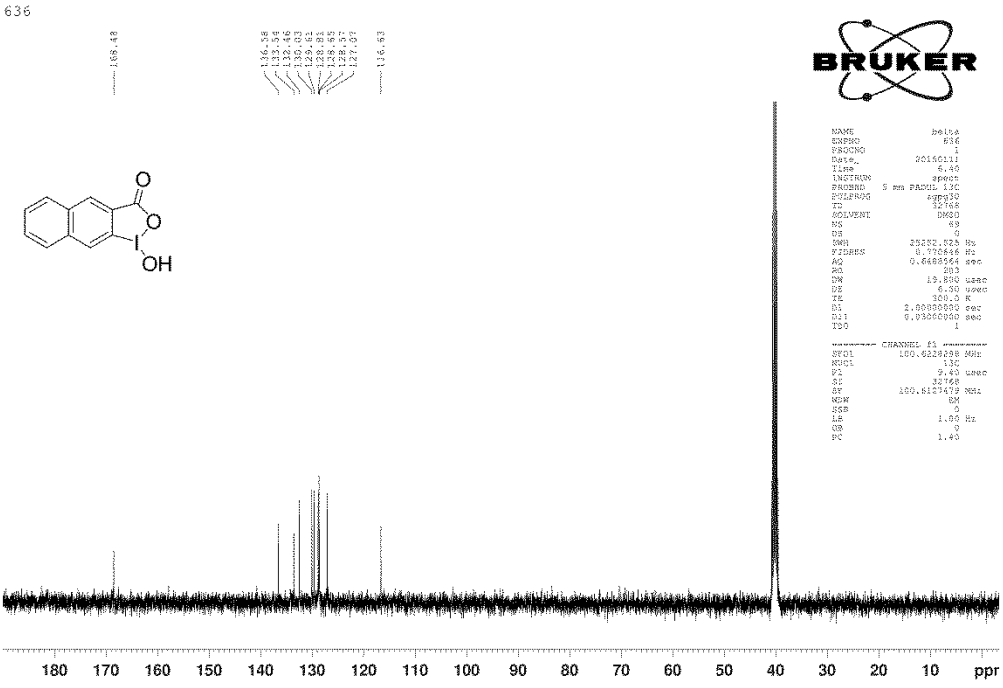
5-Nitro-1-cyano-1,2-benziodoxol-3-(1H)-one (1g)



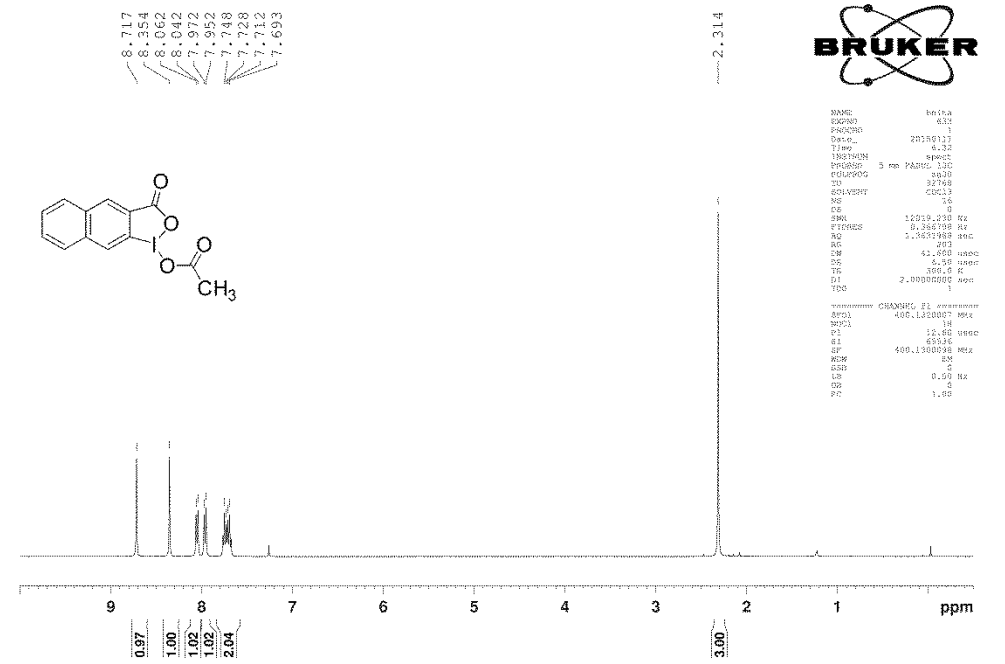


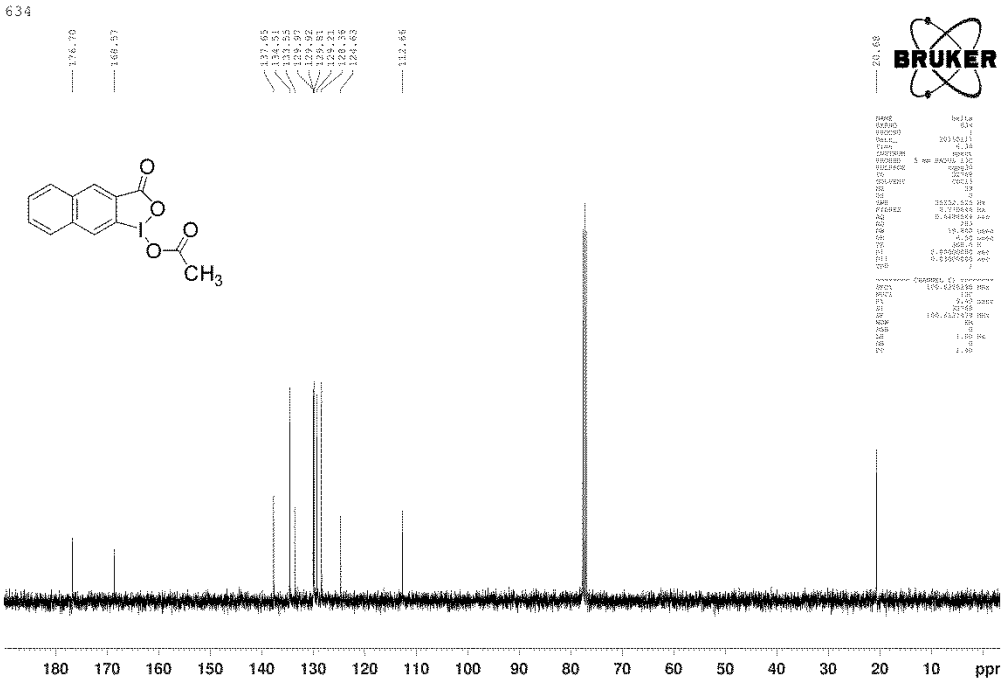
1-**Hydroxy-1,2-napthiodoxol-3-(1H)-one**



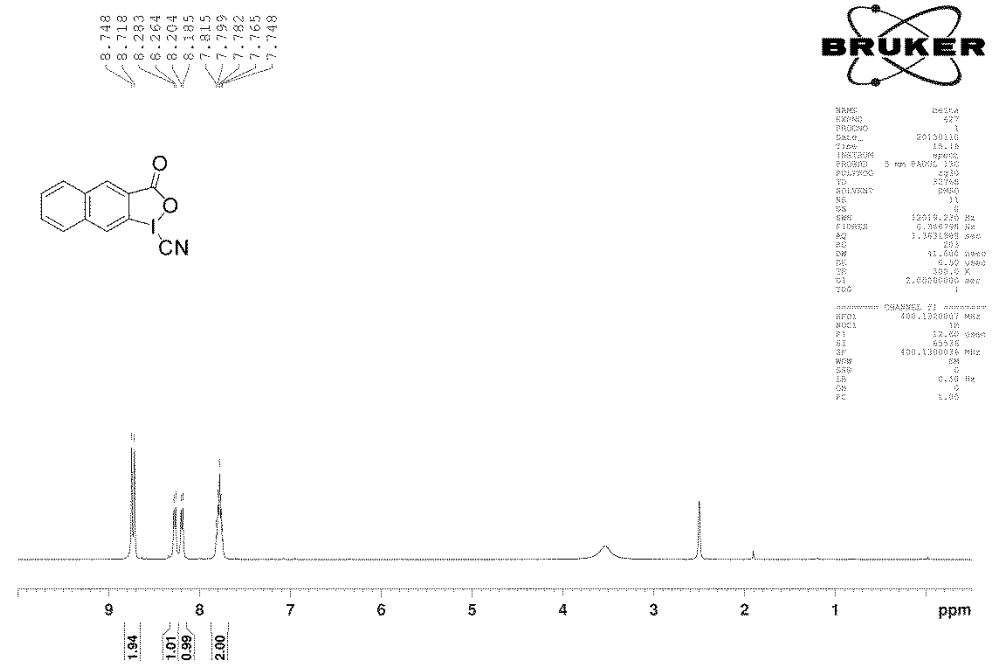


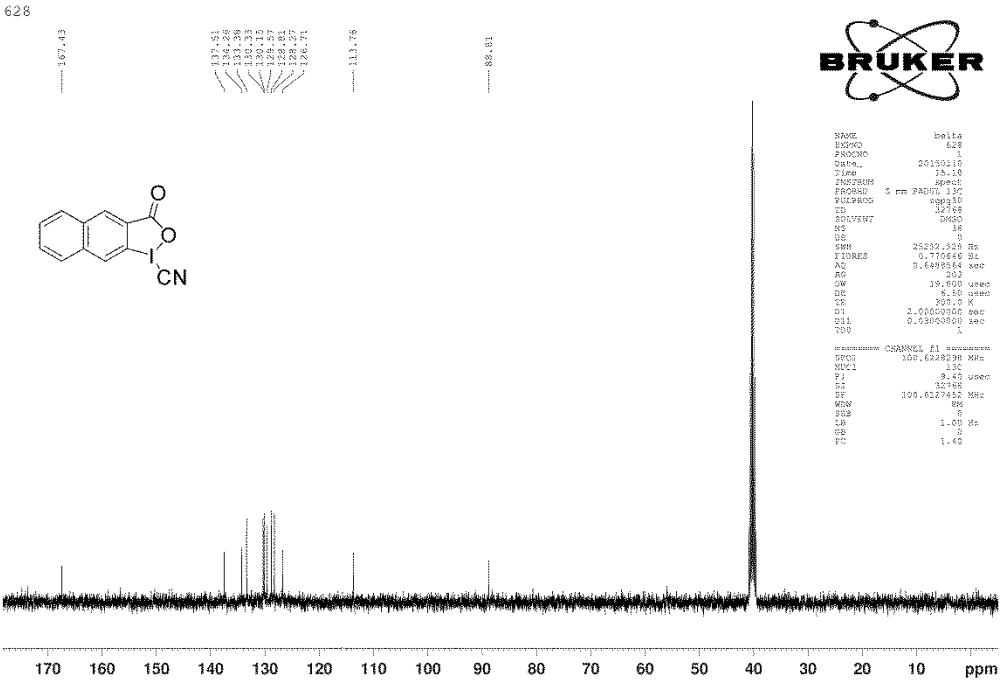
1-Acetoxy-1,2-napthiodoxol-3-(1H)-one



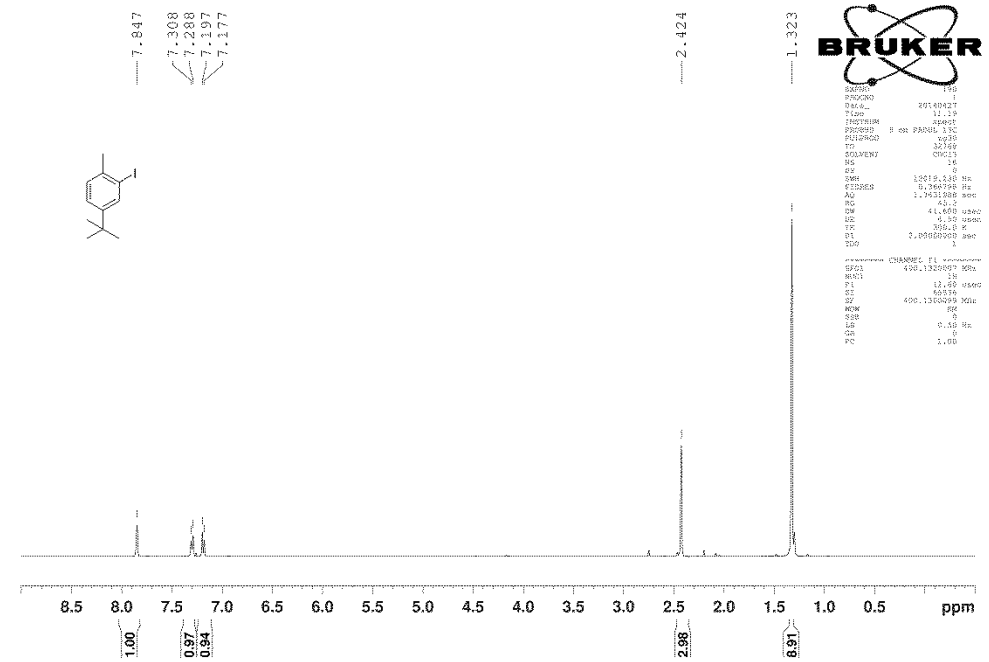


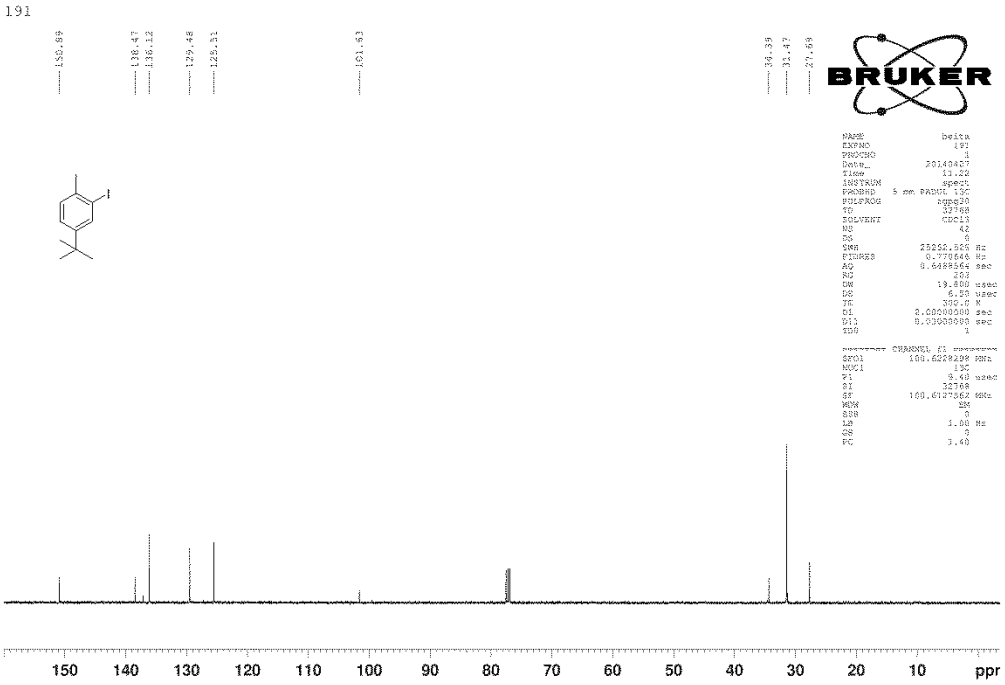
1-Cyano-1,2-napthiodoxol-3-(1H)-one (1h)



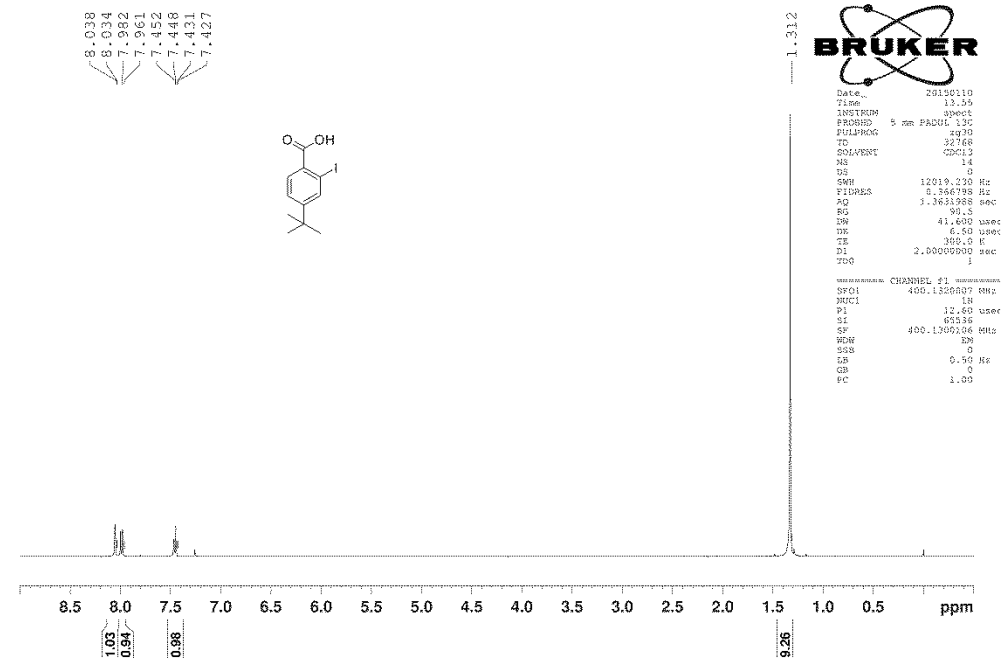


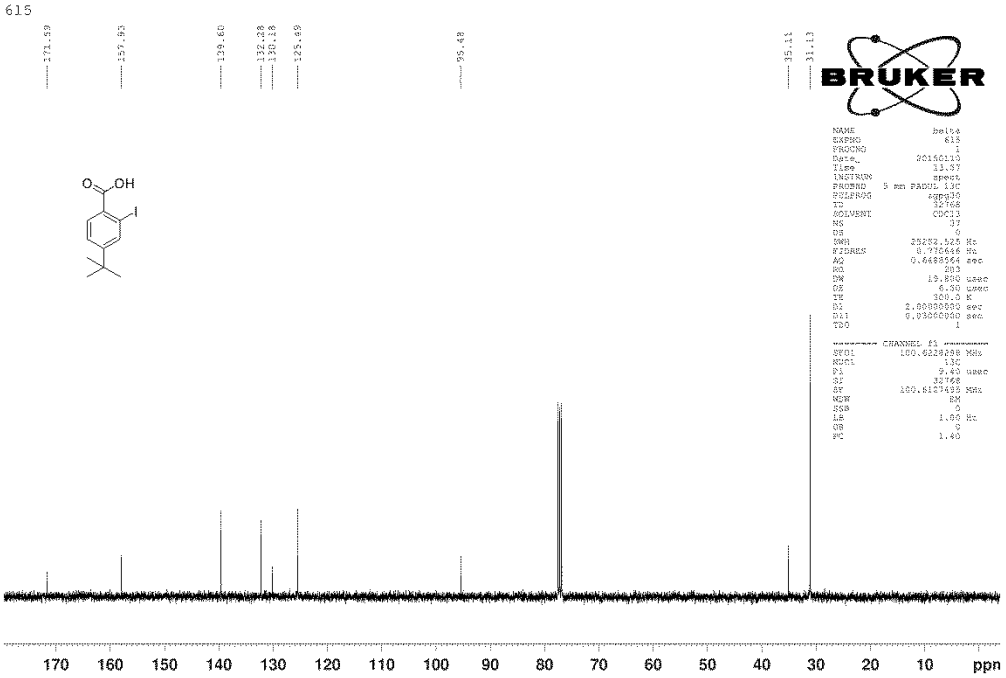
4-tert-butyl-2-iodo-1-methylbenzene



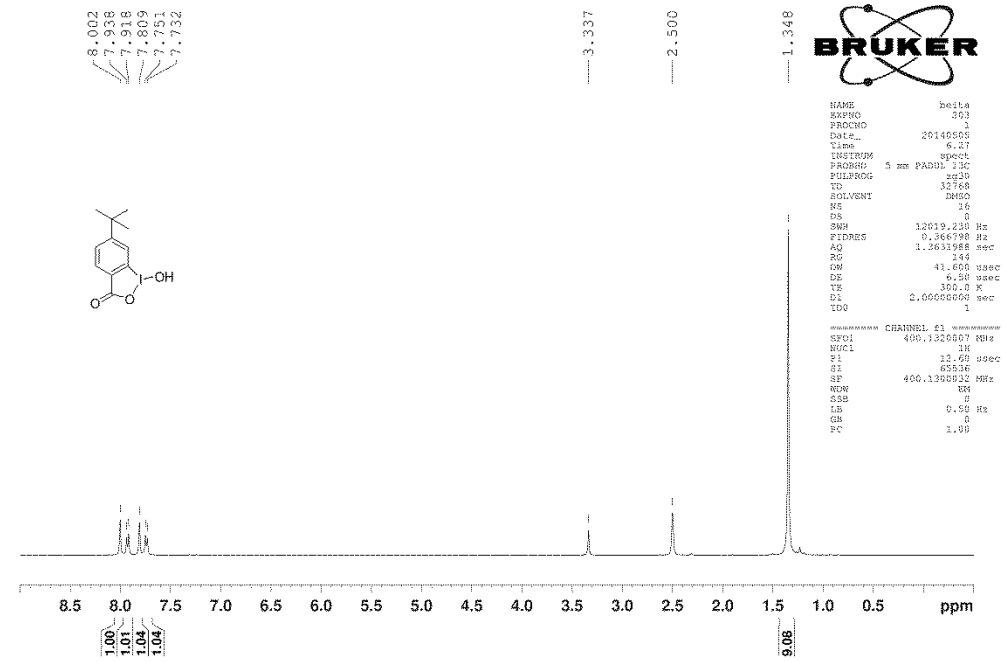


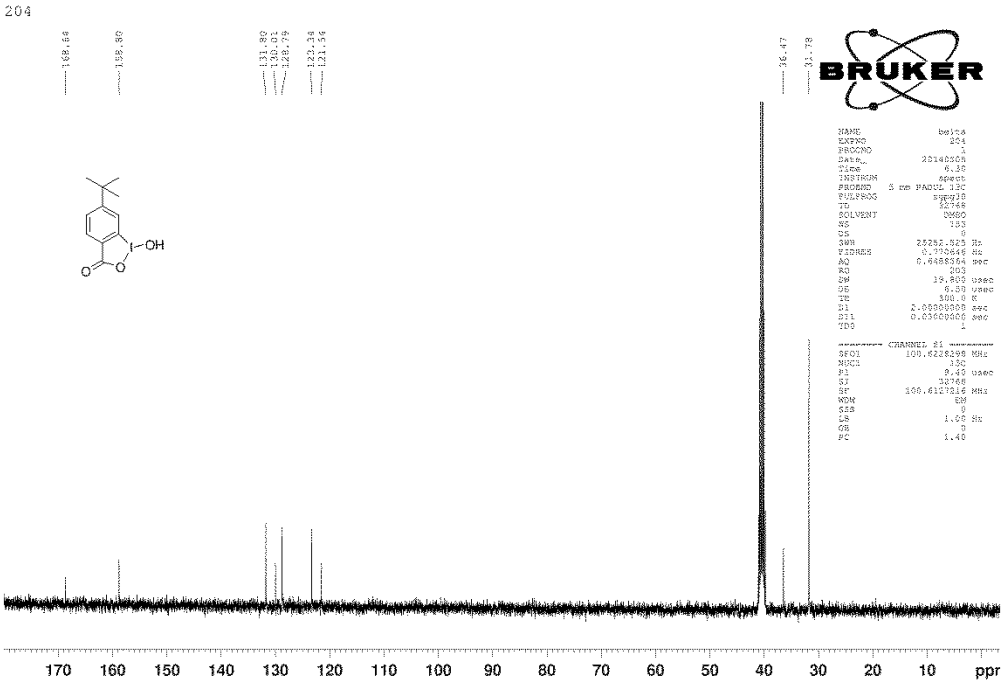
4-tert-butyl-2-iodobenzoic acid



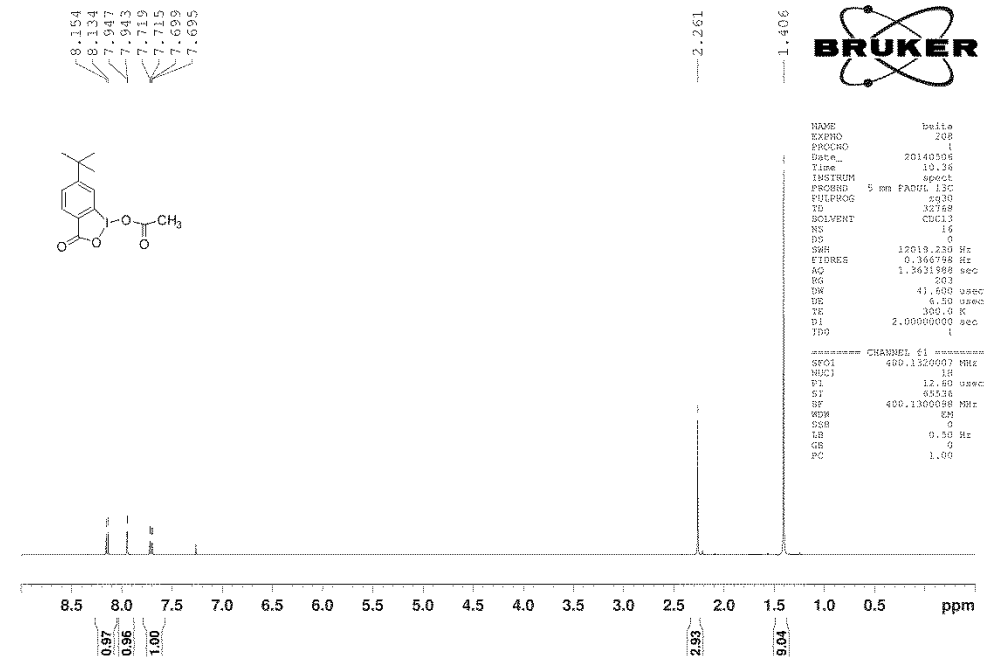


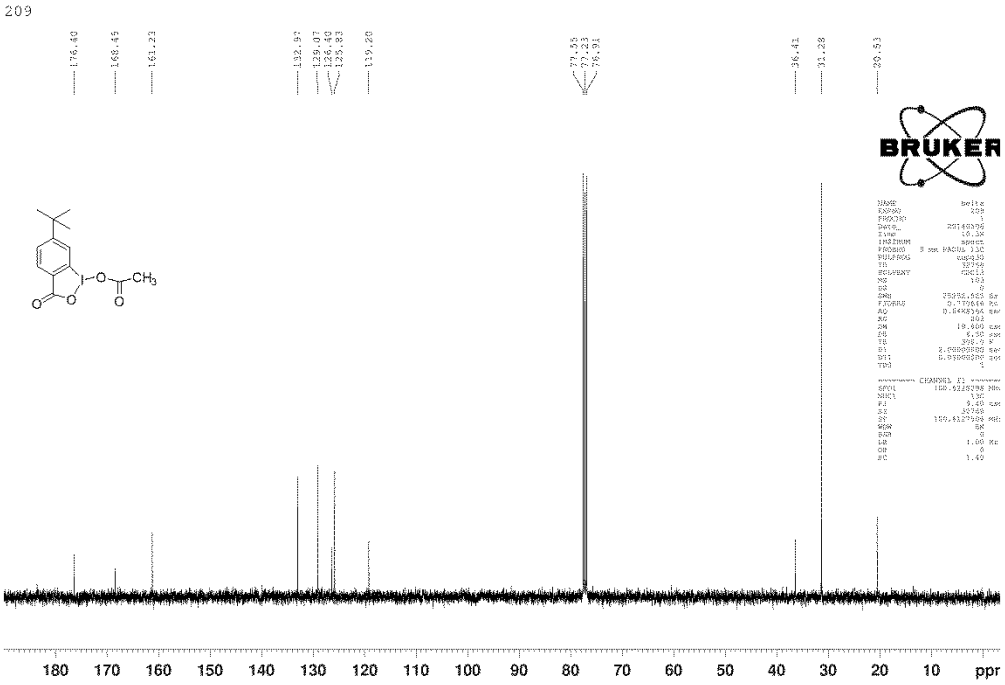
4-^{t}Bu-1-hydroxy-1,2-benziodoxol-3-(1H)-one



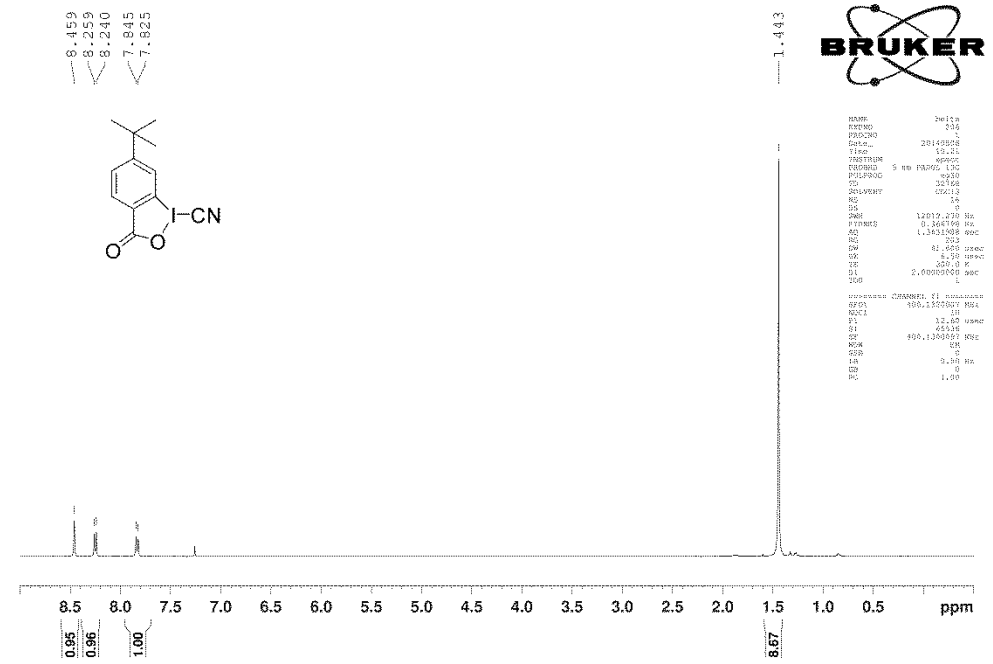


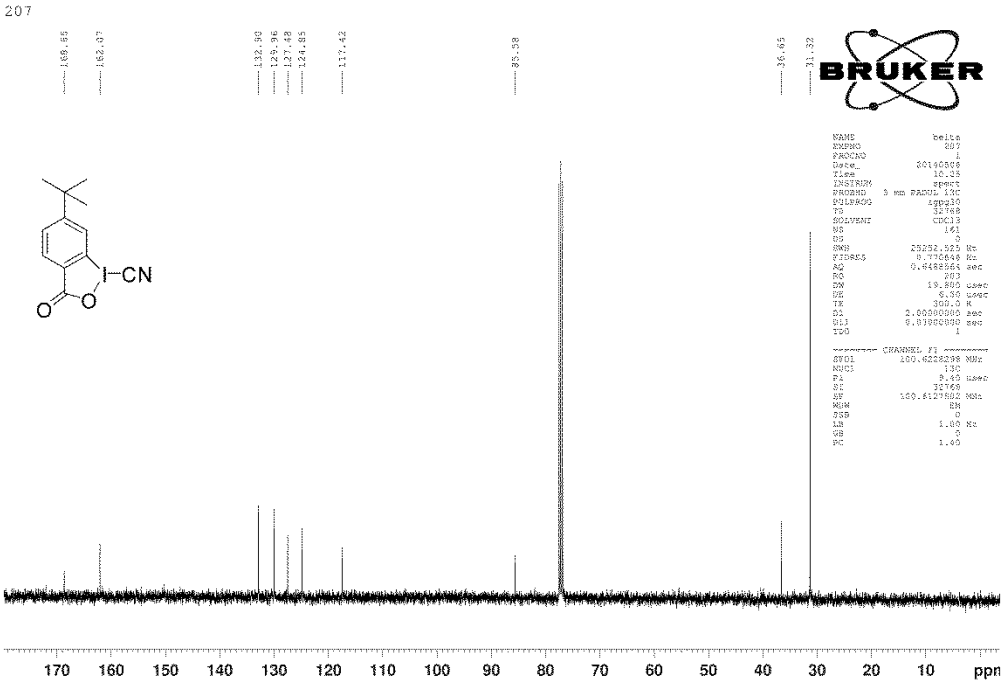
4-^{t}Bu-1-aetoxy-1,2-benziodoxol-3-(1H)-one



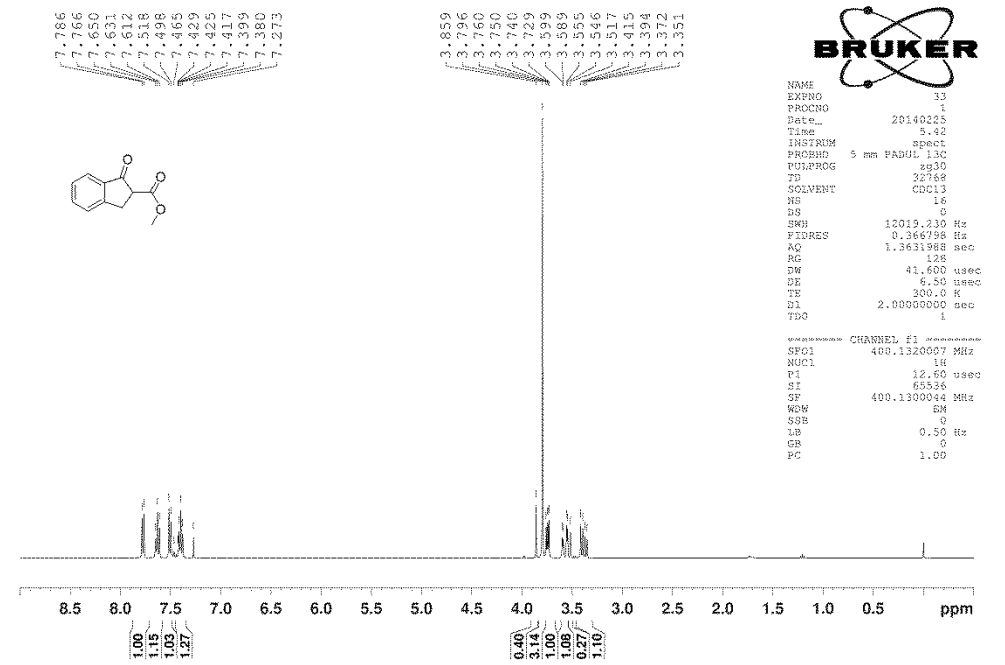


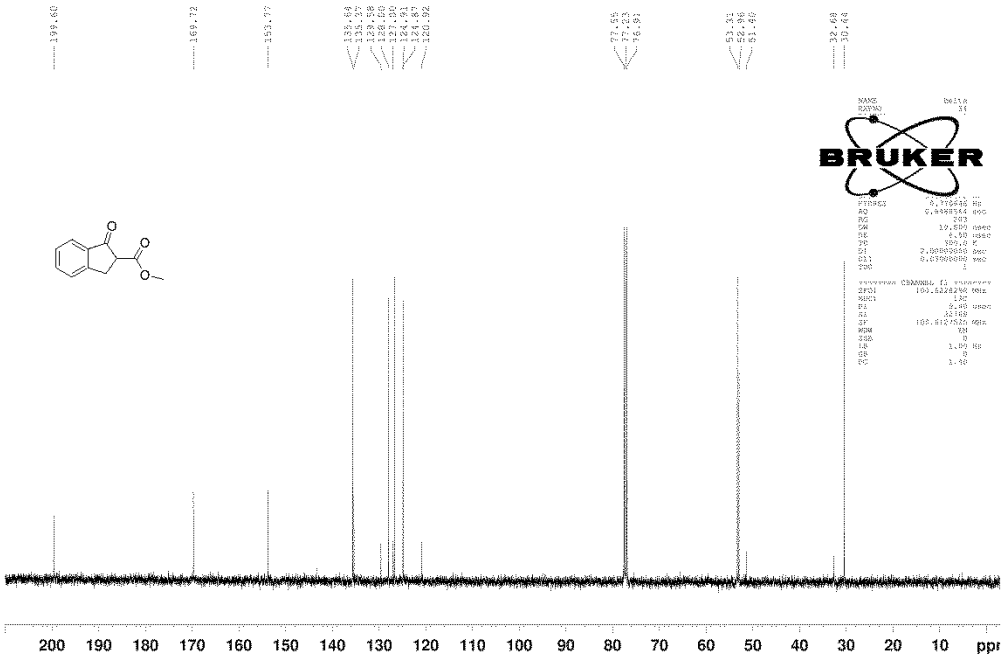
4-^{t}Bu-1-aetoxy-1,2-benziodoxol-3-(1H)-one (1b)



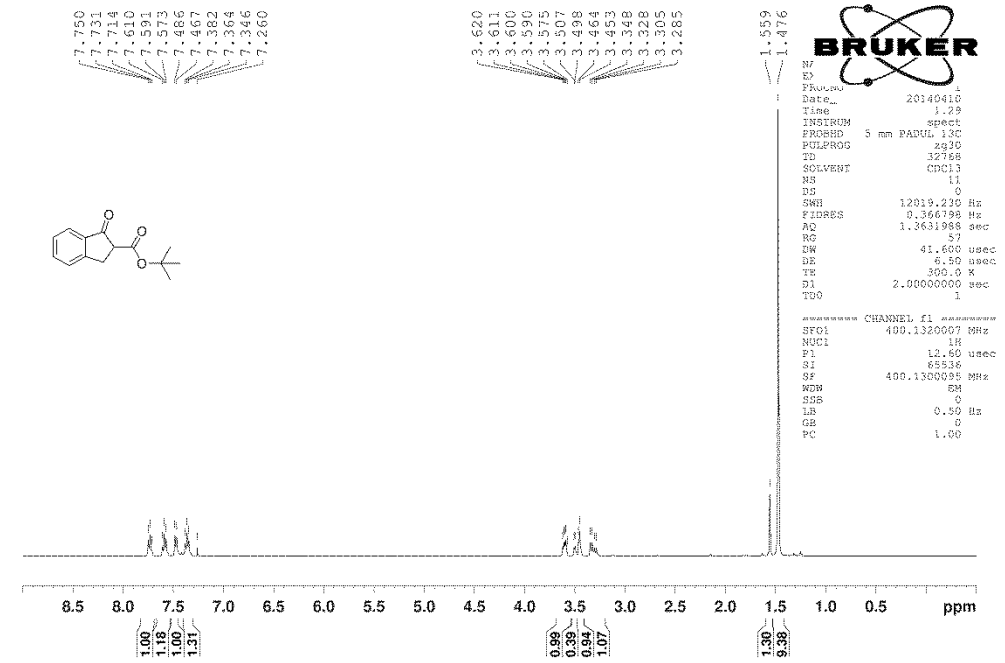


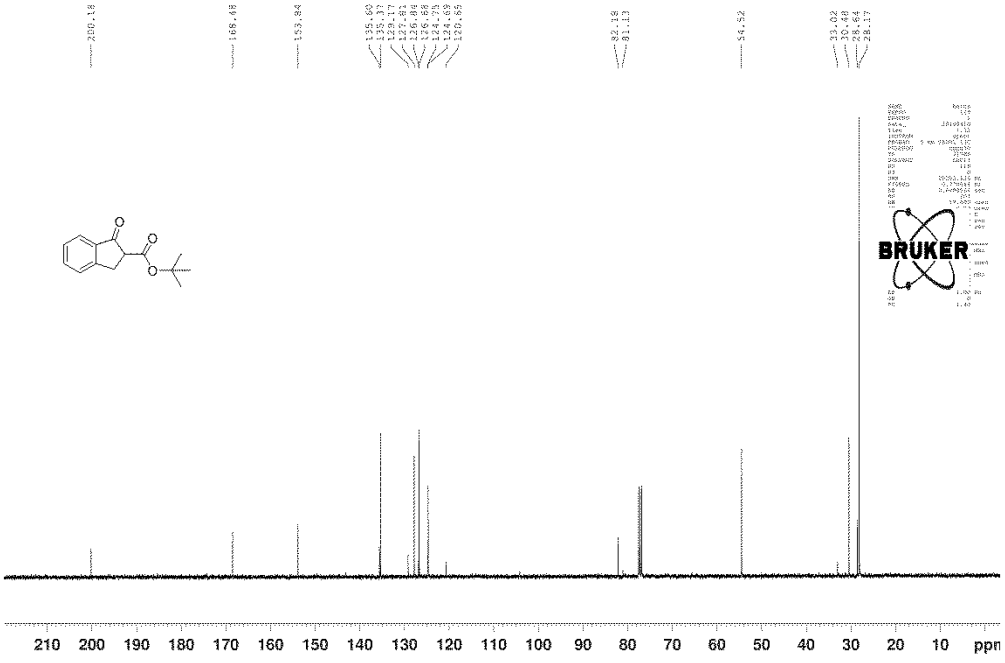
Methyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3b)



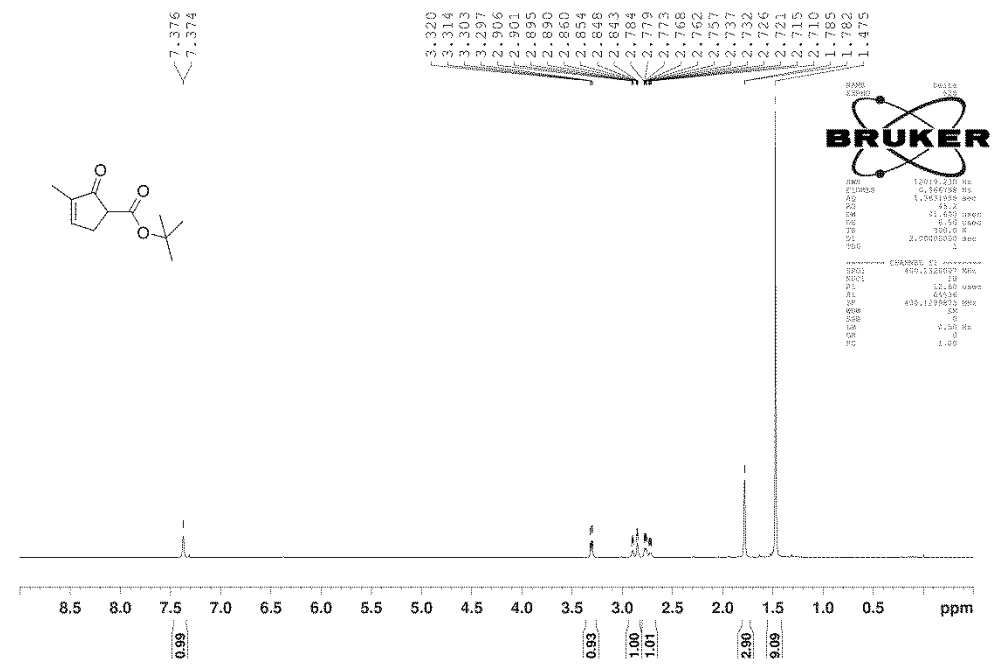


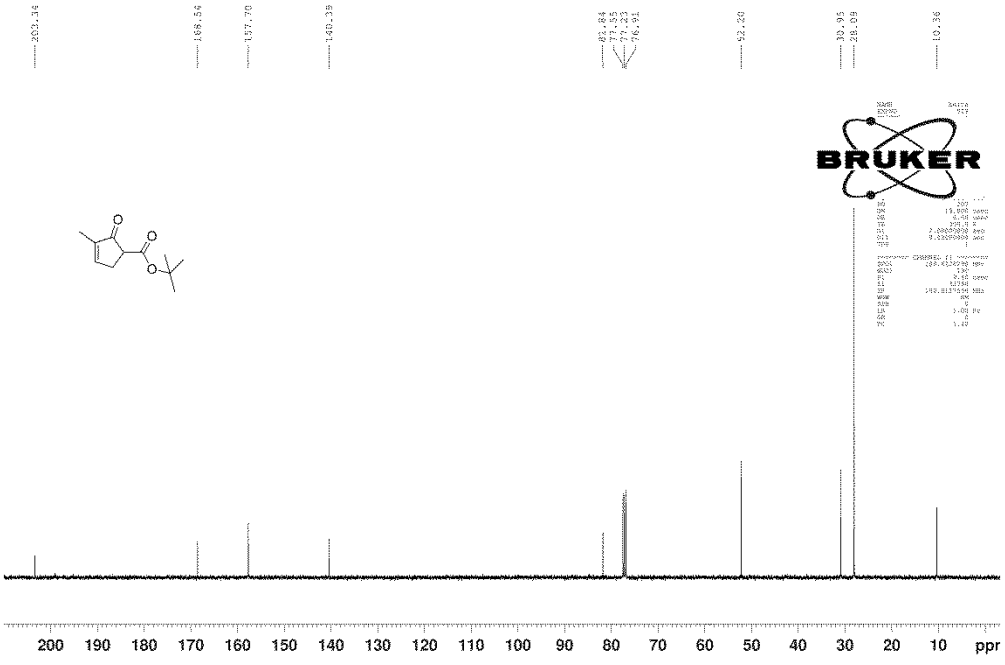
Tert-butyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3a)



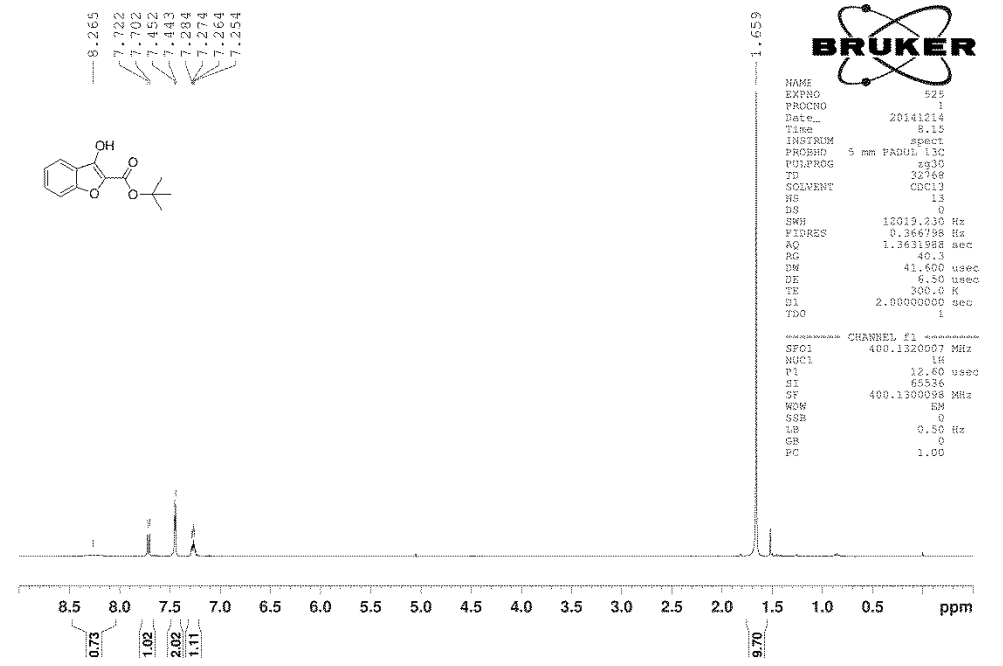


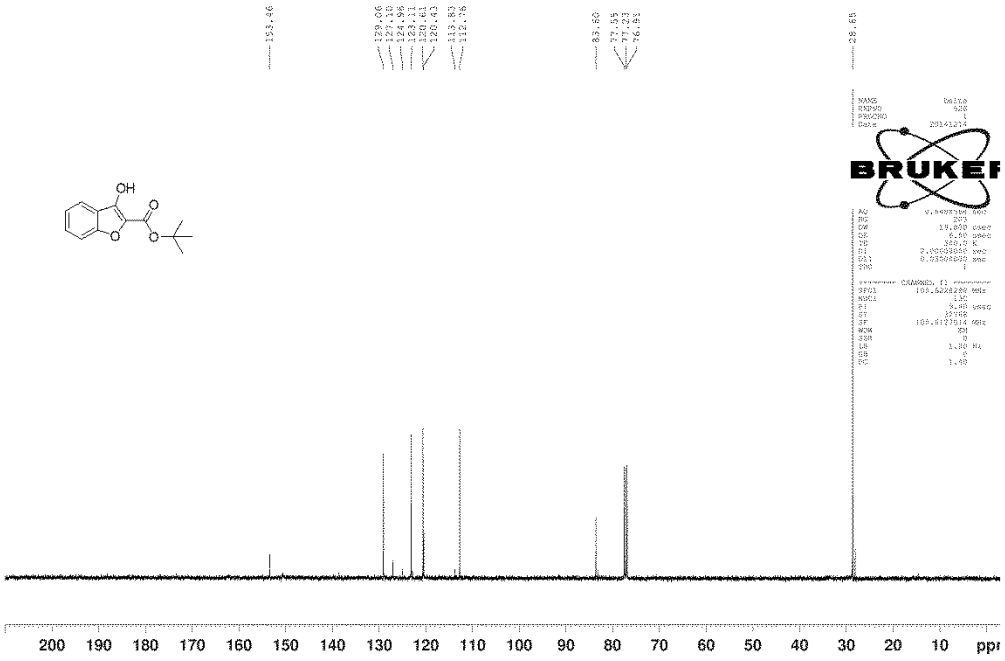
Tert-butyl 3-methyl-2-oxocyclopent-3-enecarboxylate (3q)



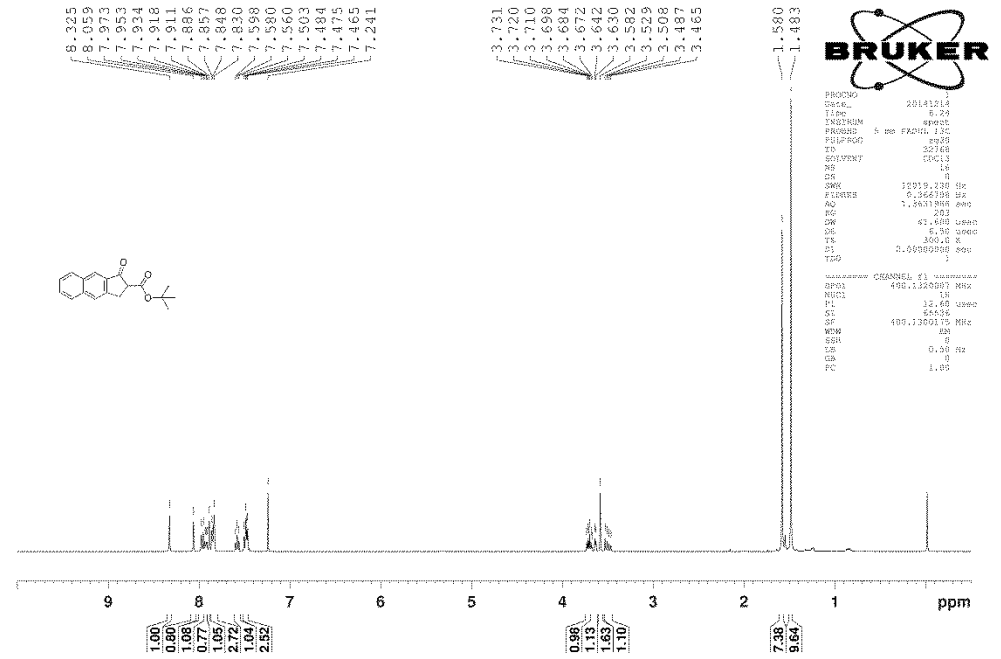


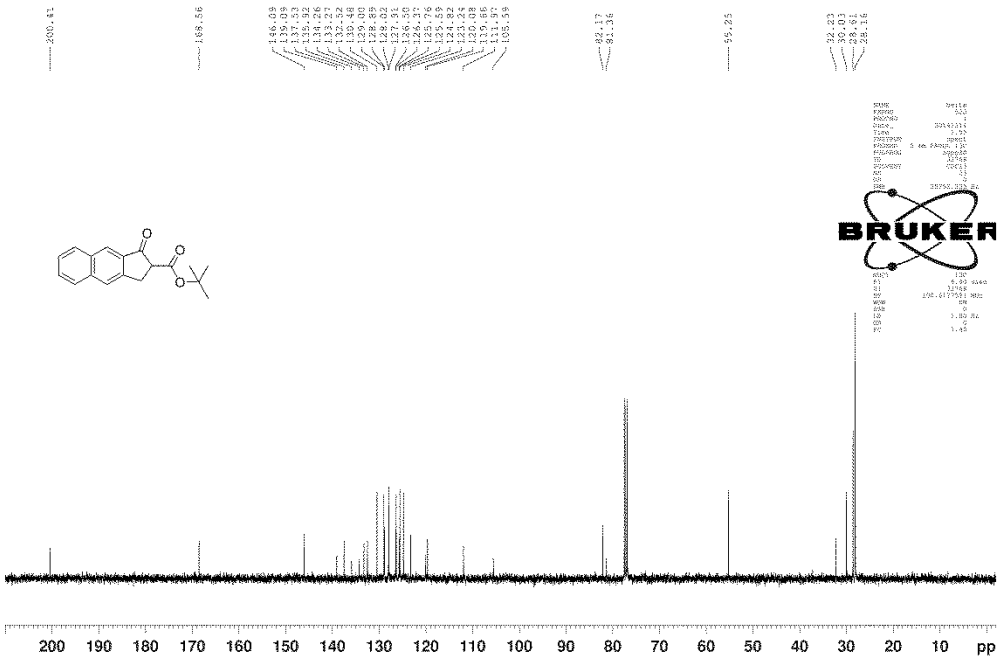
Tert-butyl 3-hydroxybenzofuran-2-carboxylate (3t)



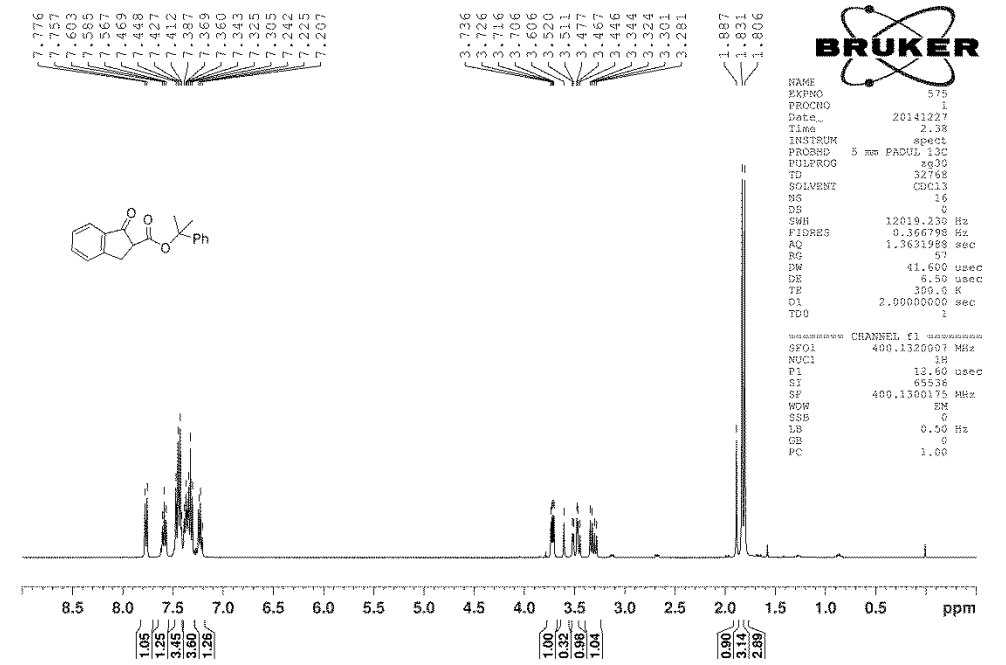


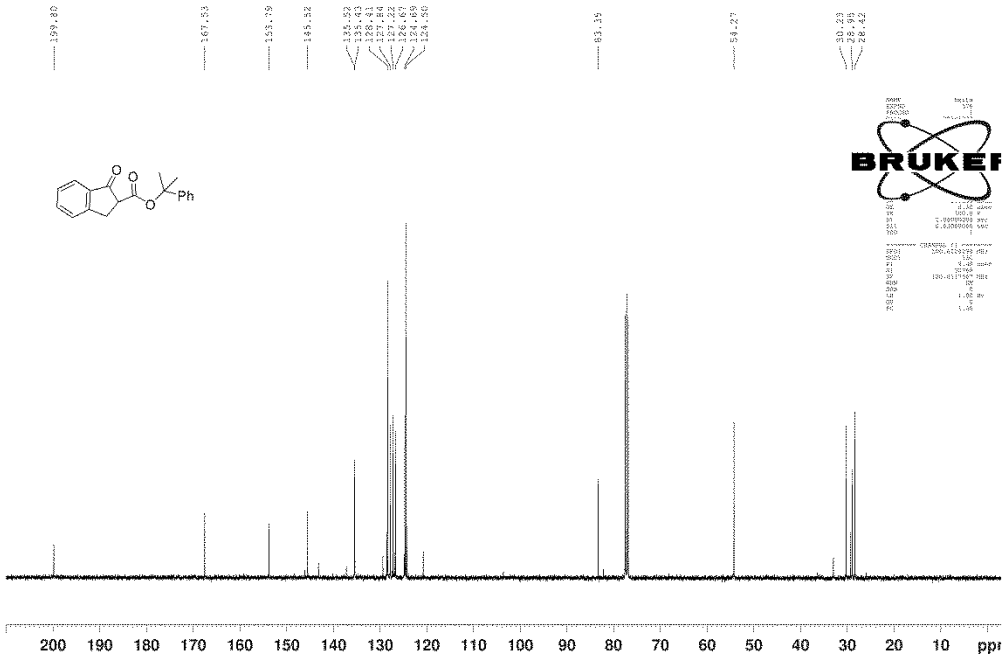
Tert-butyl 1-oxo-2,3-dihydro-1H-cyclopenta[b]naphthalene-2-carboxylate (3r)



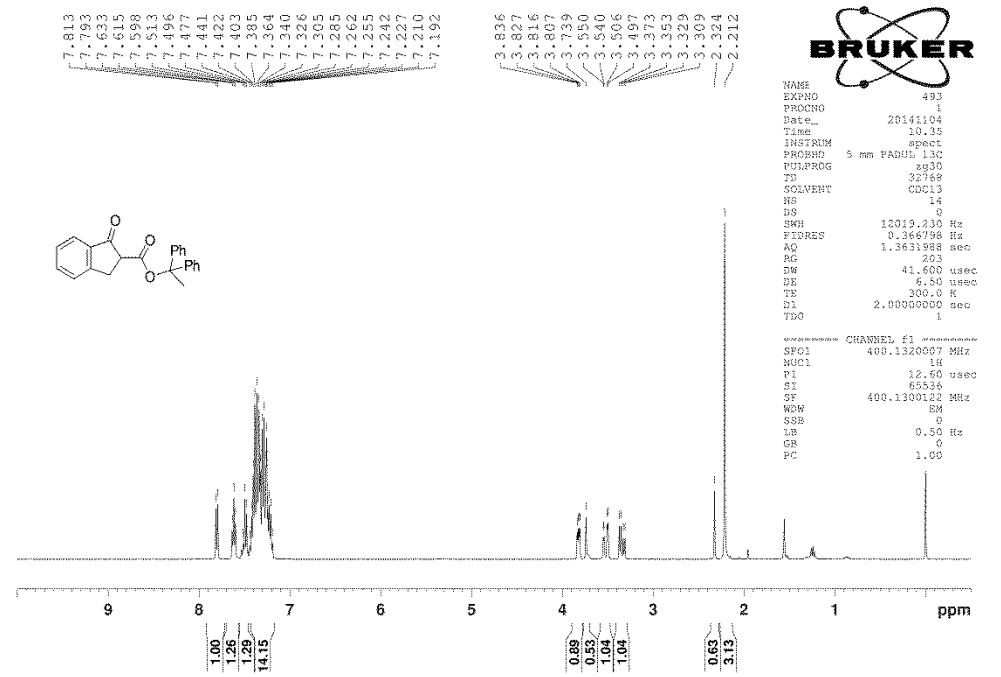


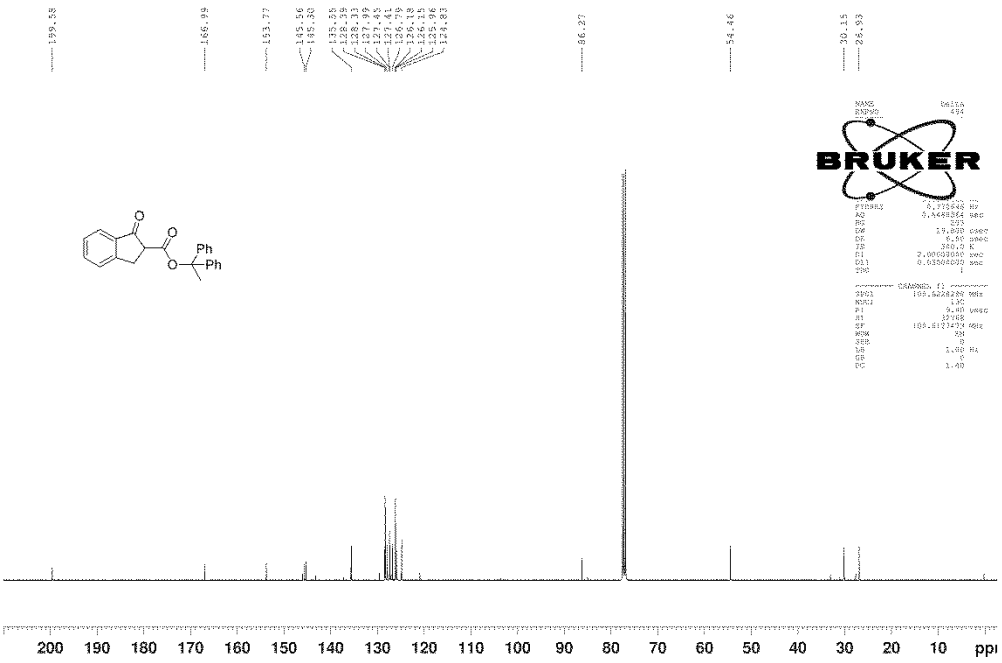
2-Phenylpropan-2-yl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3c)



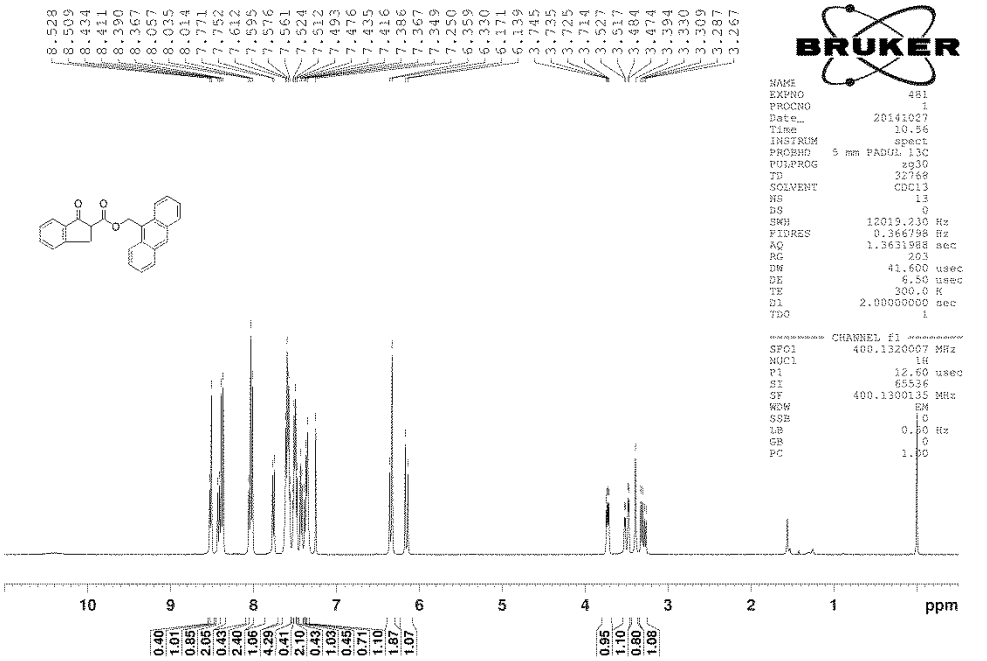


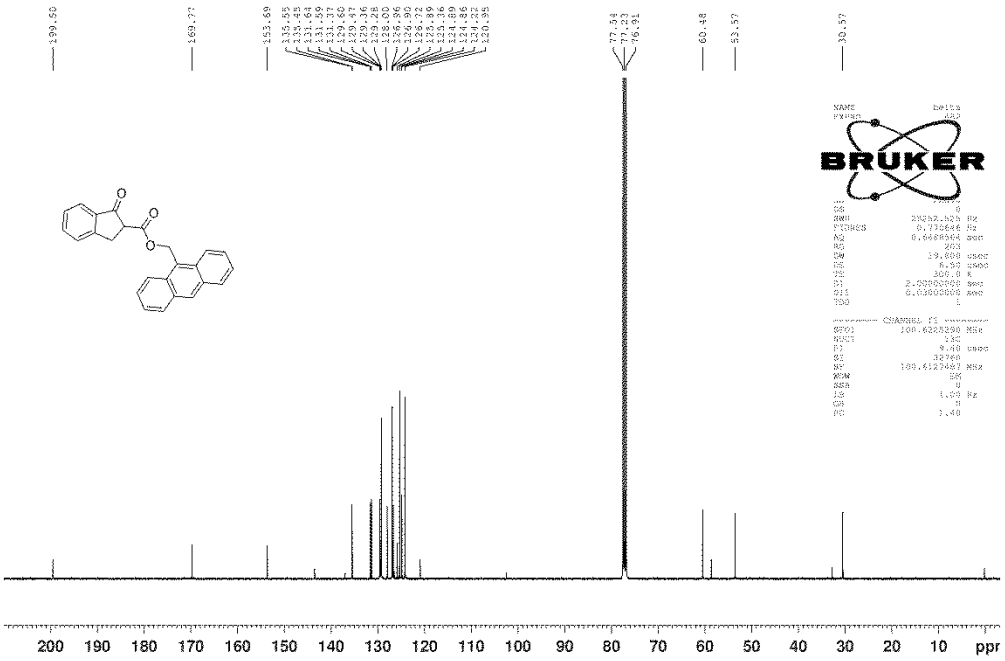
1,1-diphenylethyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3d)



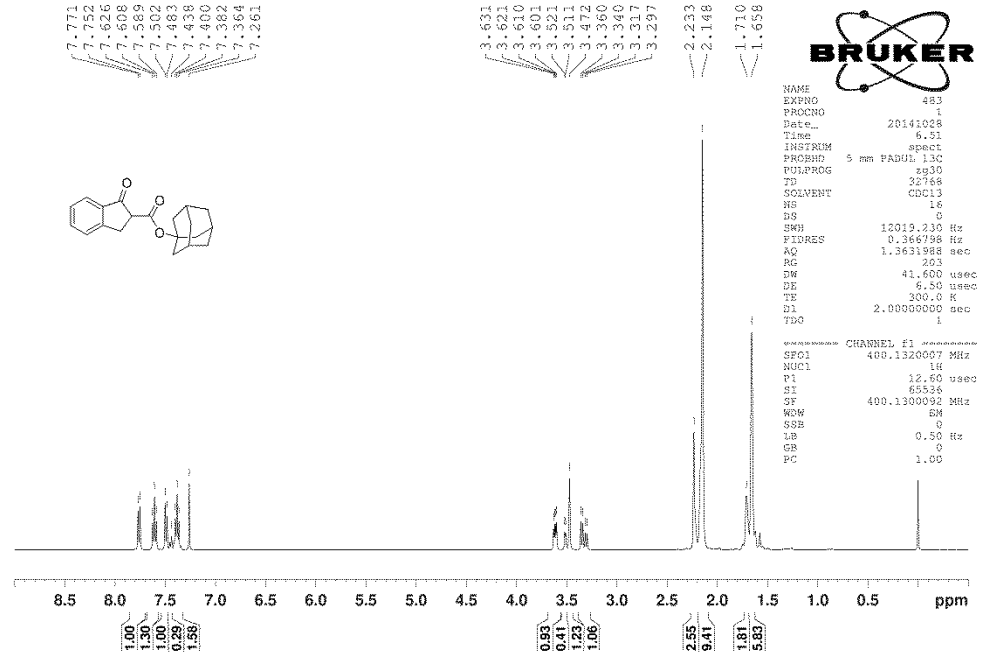


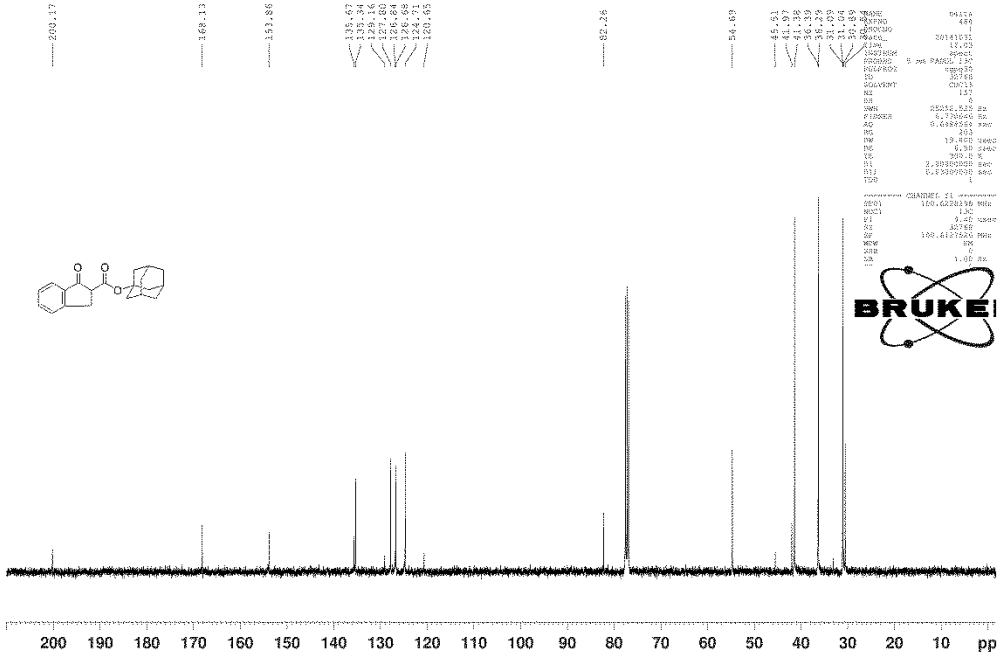
Anthracen-9-ylmethyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3e)



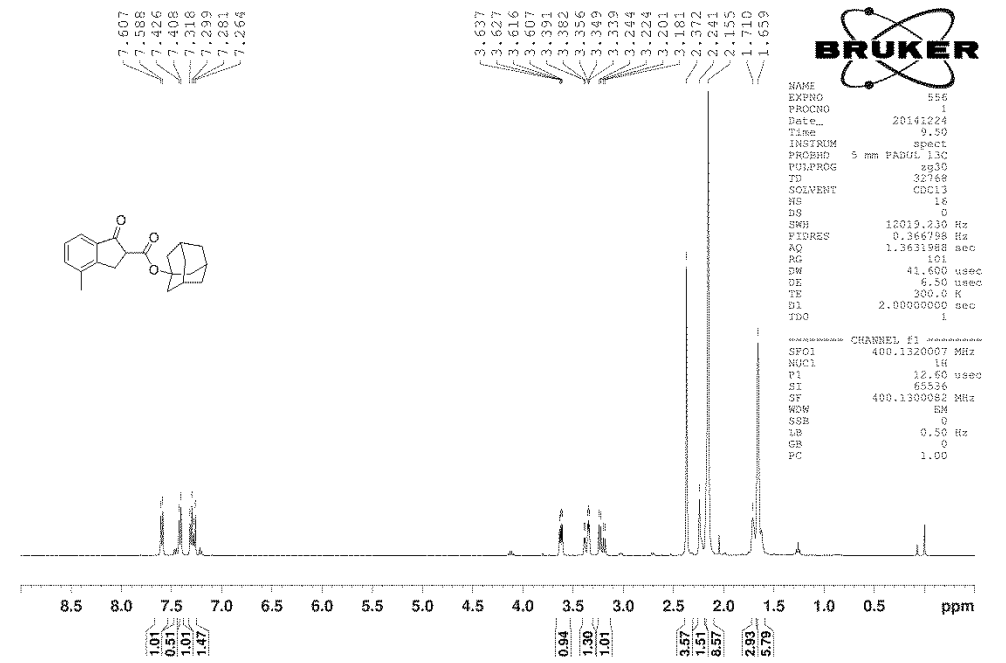


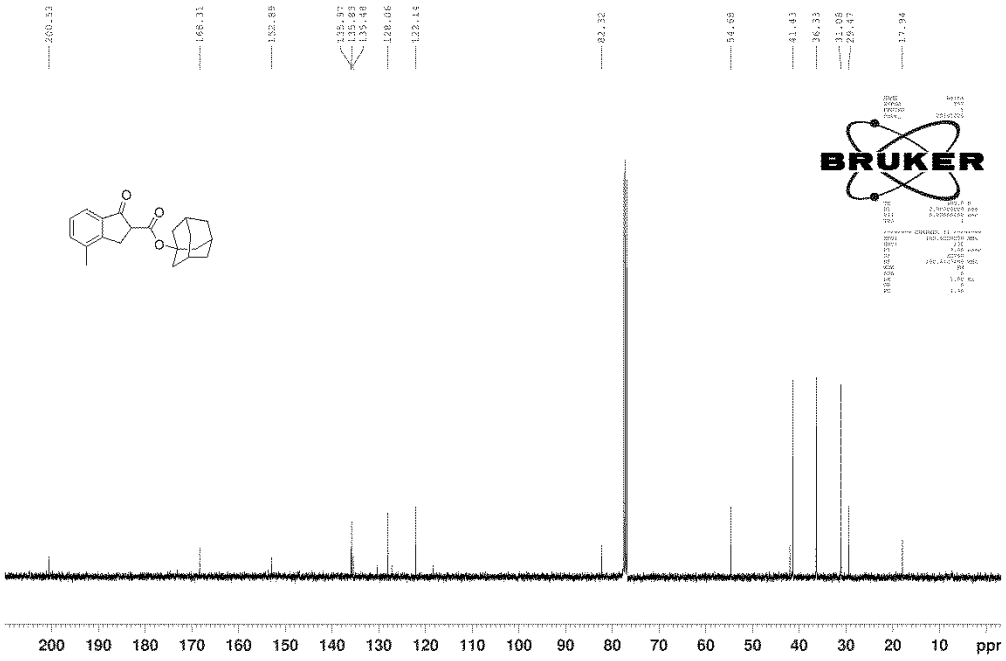
1-Adamantyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate[1] (3f)



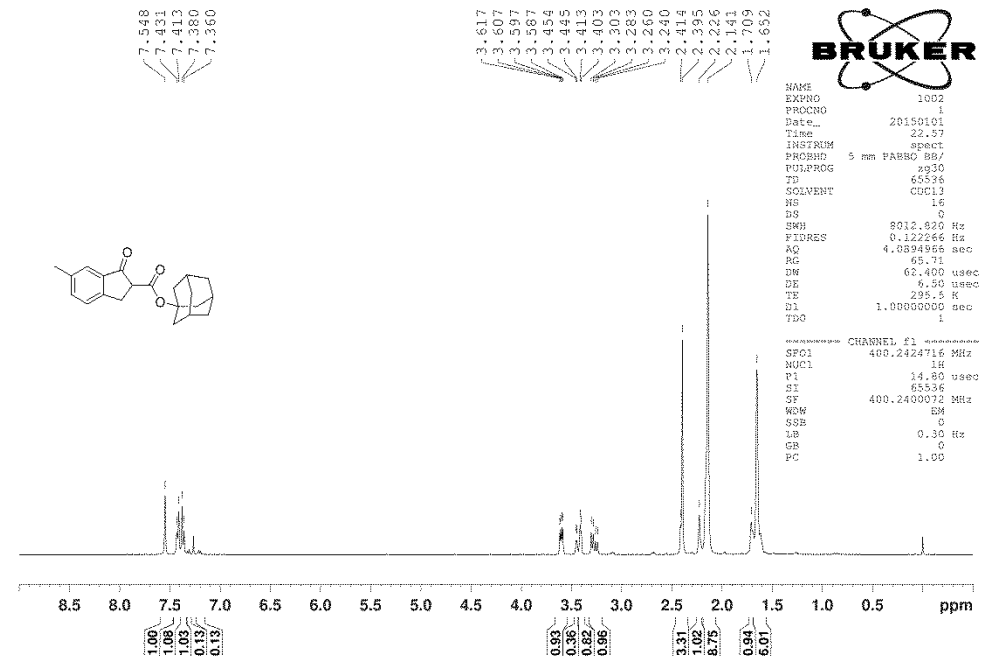


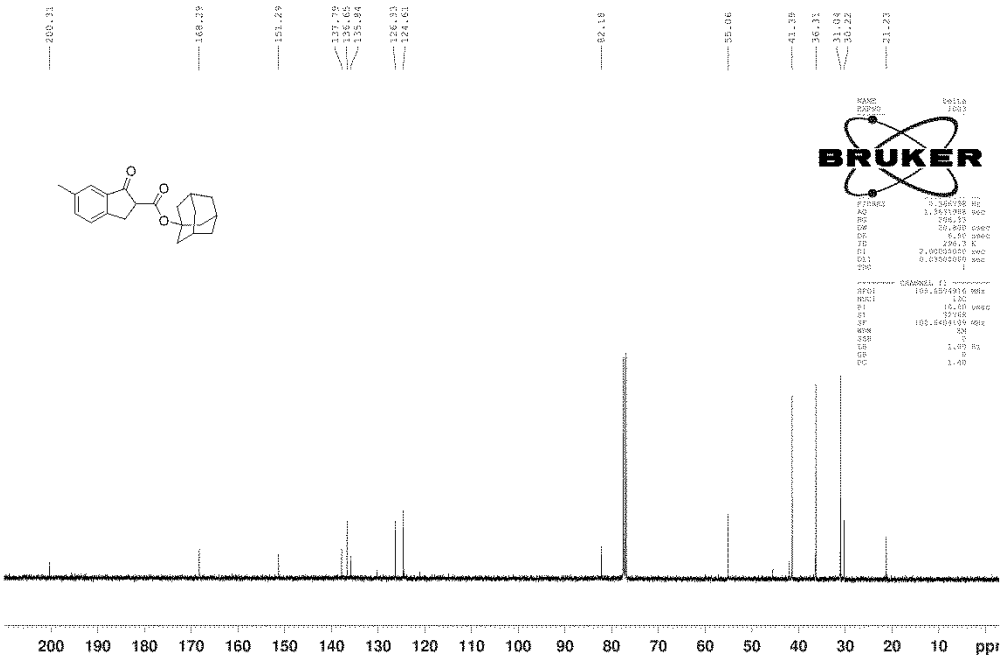
1-Adamantyl 4-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3g)



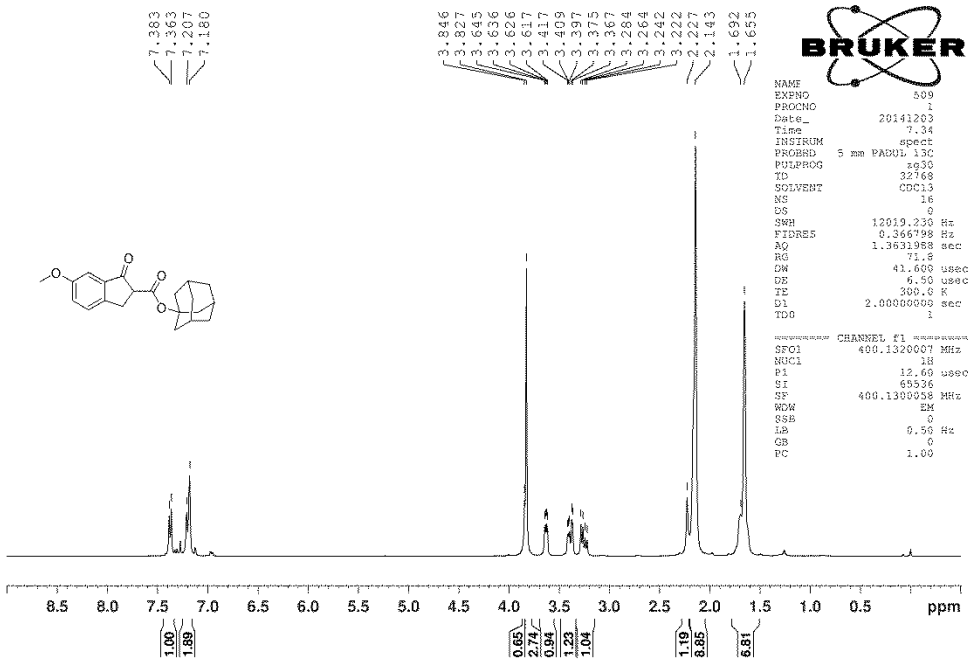


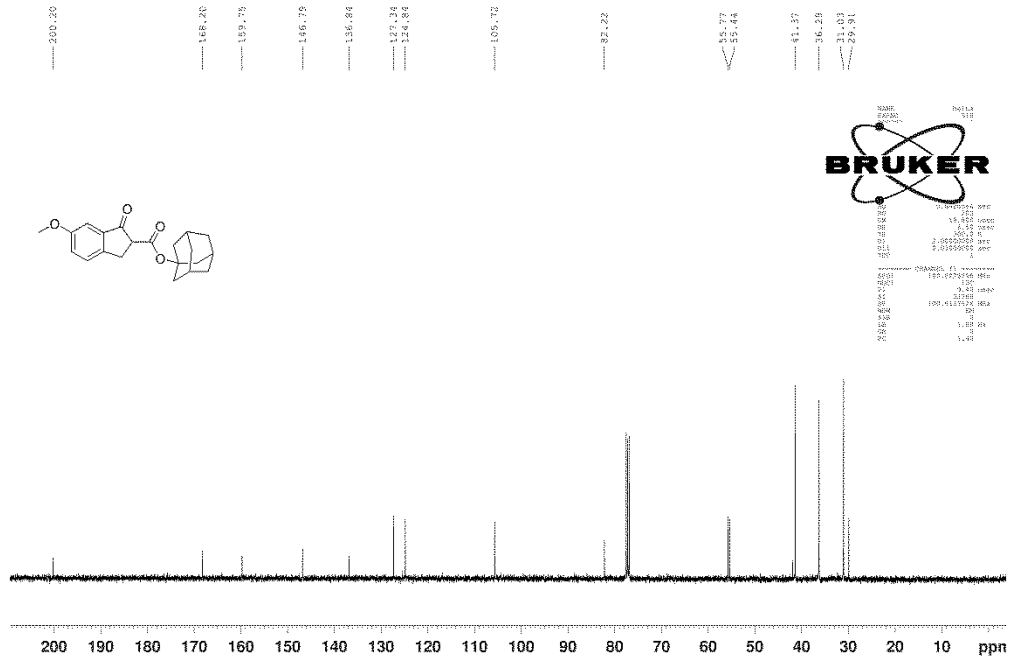
1-Adamantyl 6-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3h)



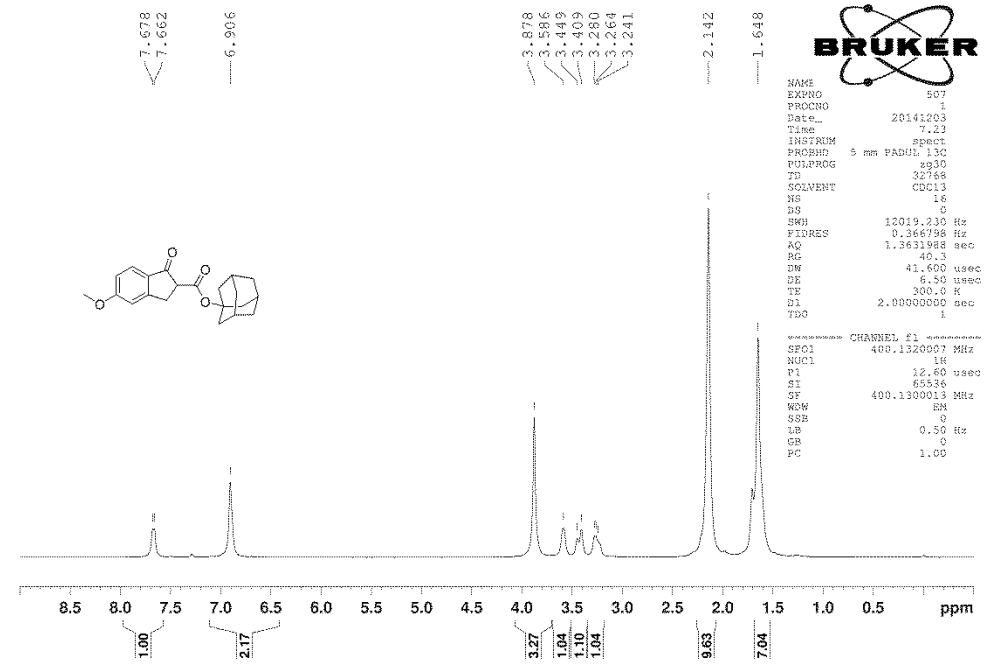


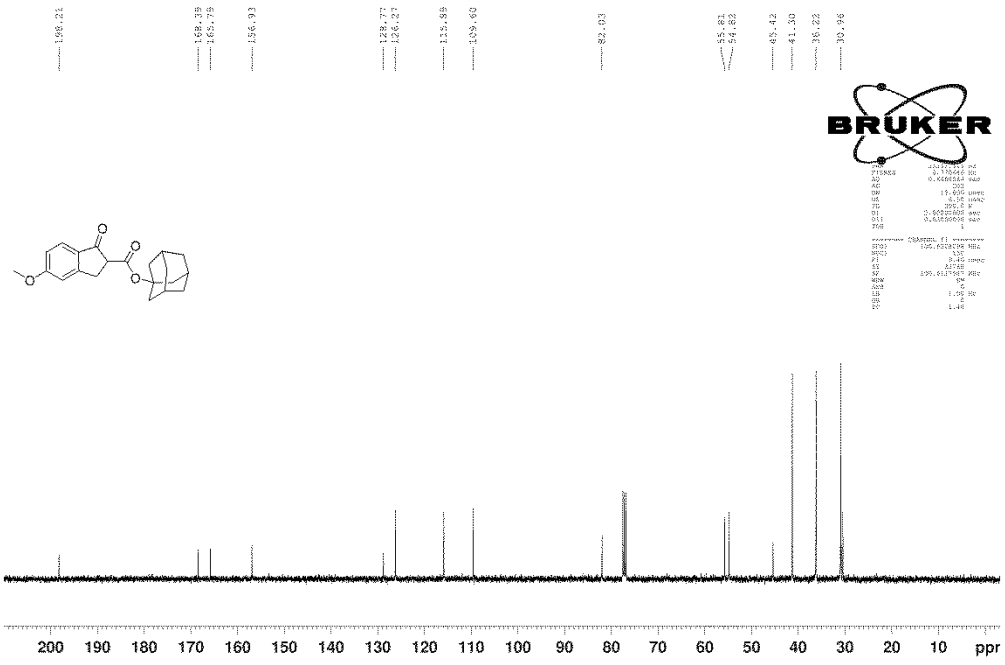
1-Adamantyl 6-methoxyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3i)



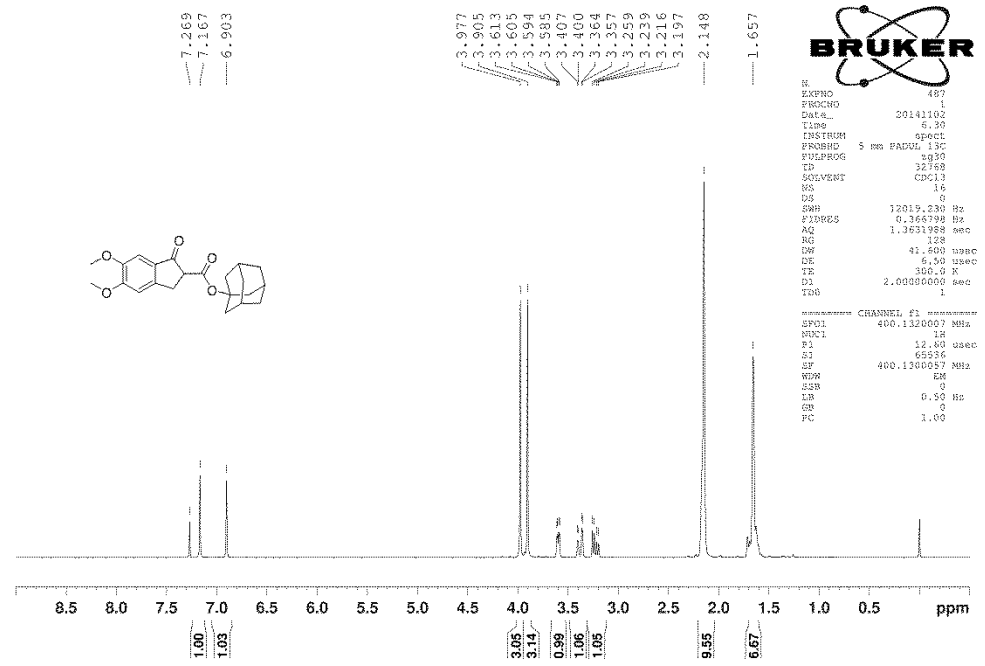


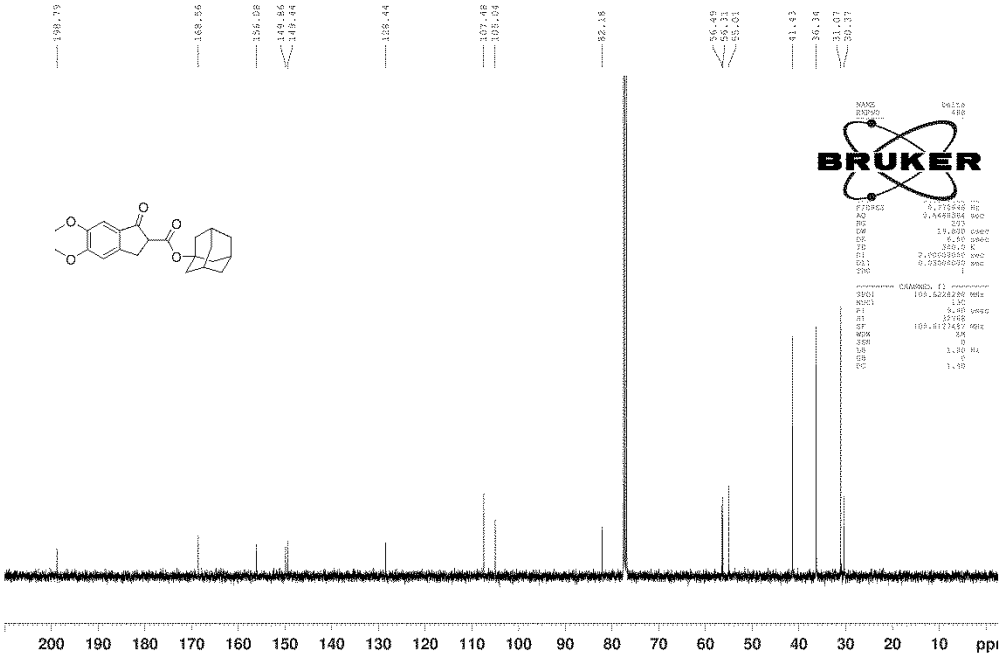
1-Adamantyl 5-methoxyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate(3j)



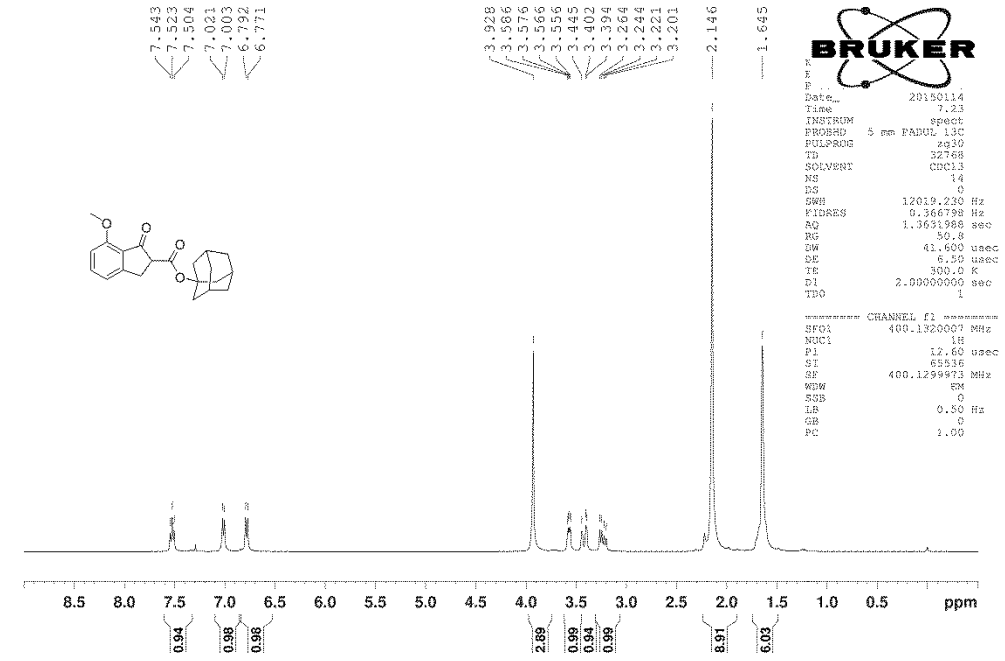


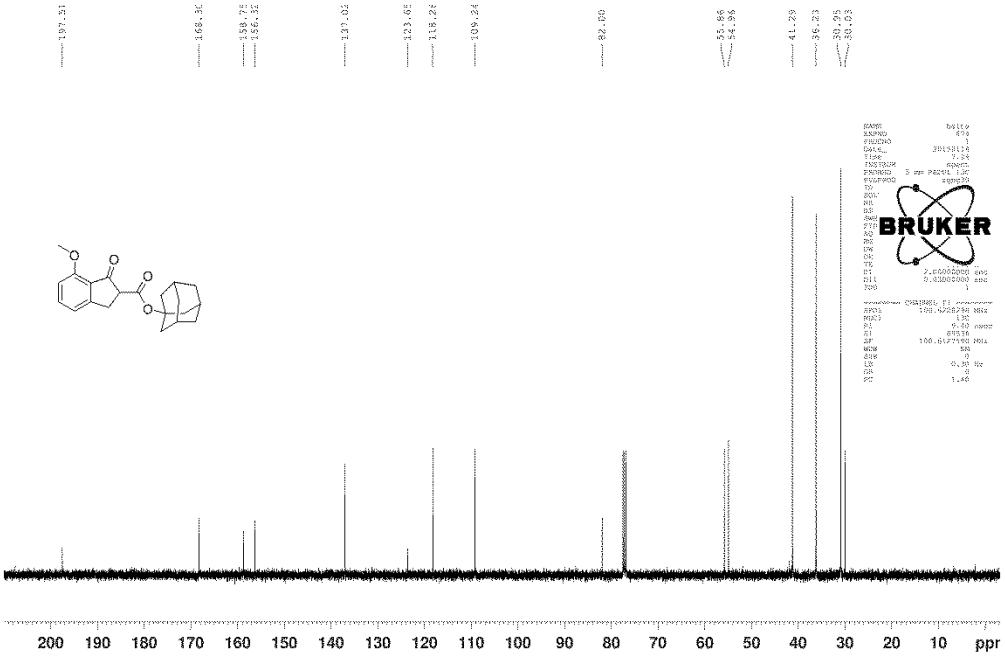
1-Adamantyl 4,5-Dimethoxyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3k)



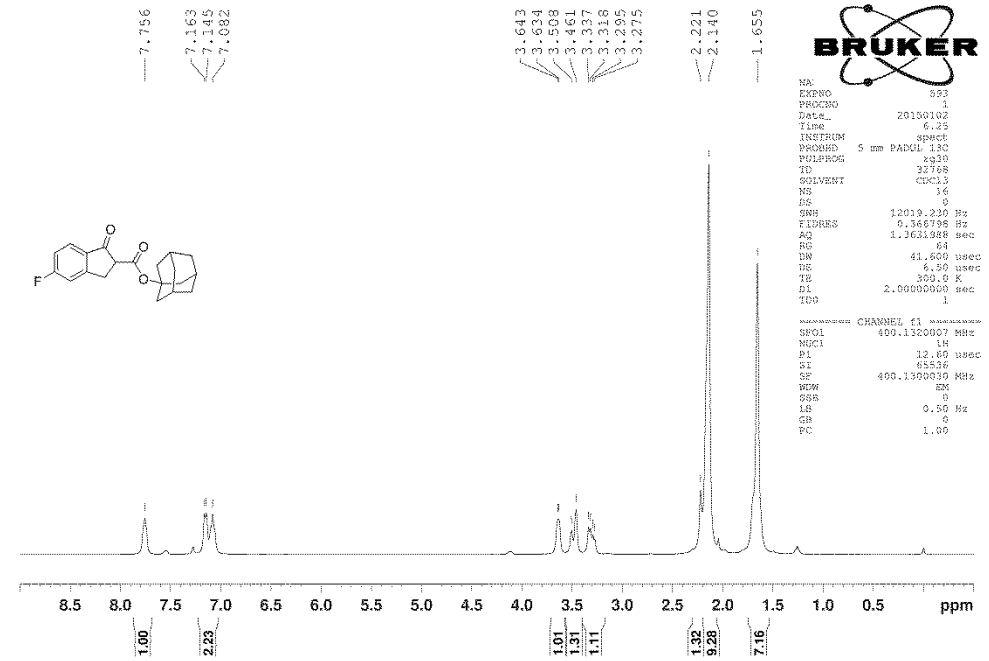


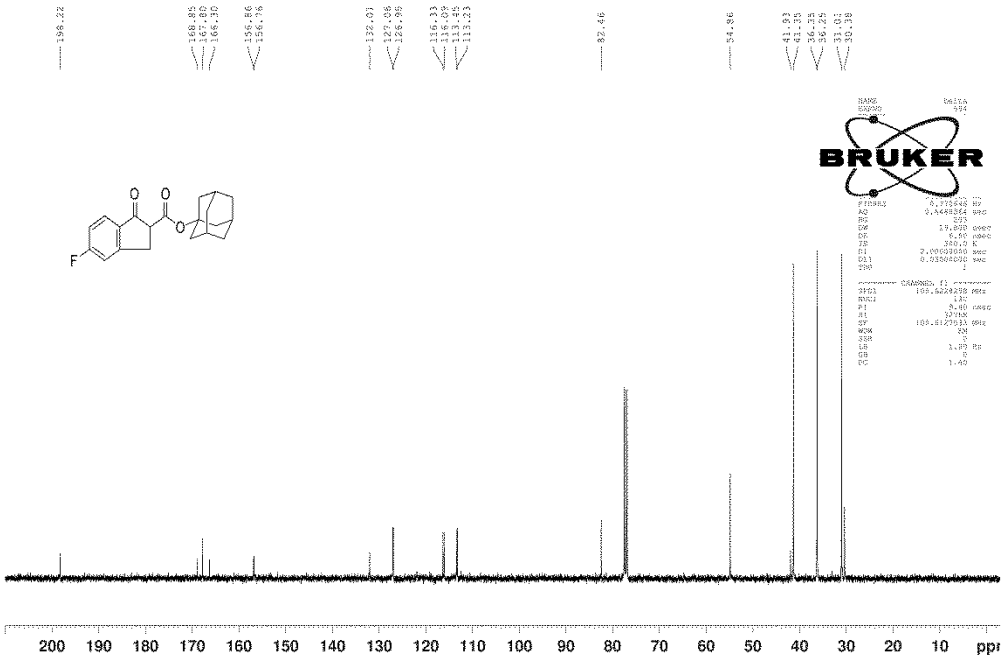
1-Adamantyl 7-methoxyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3l)



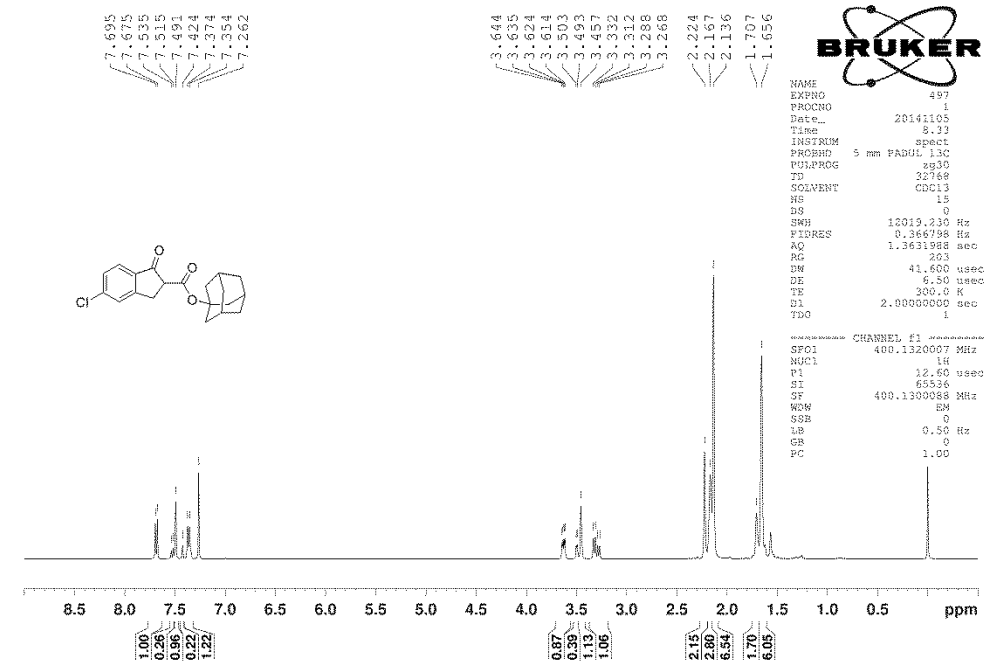


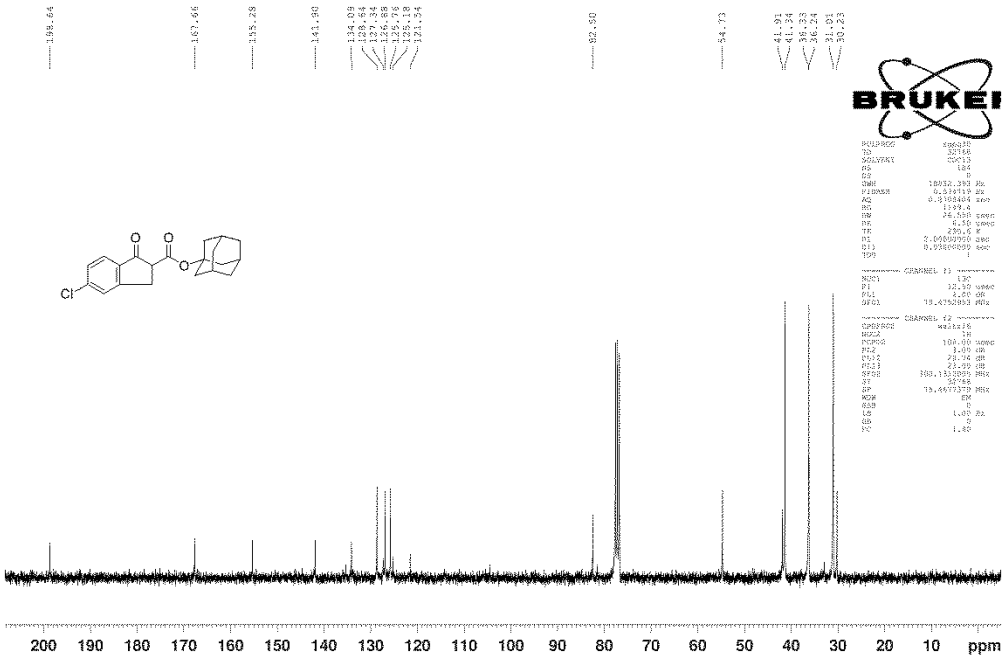
1-Adamantyl 5-fluoro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate(3m)



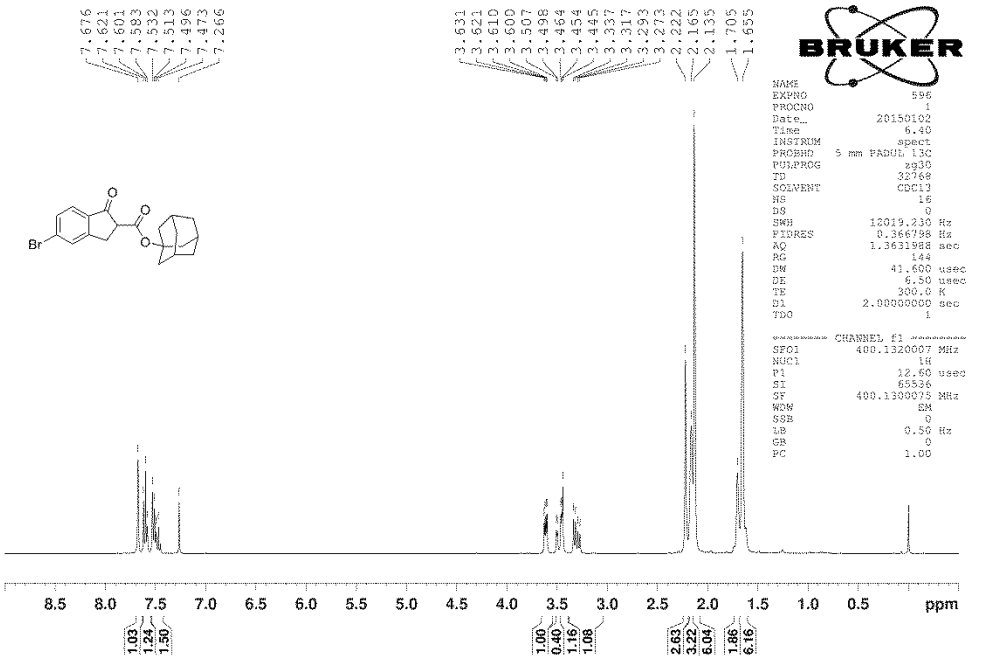


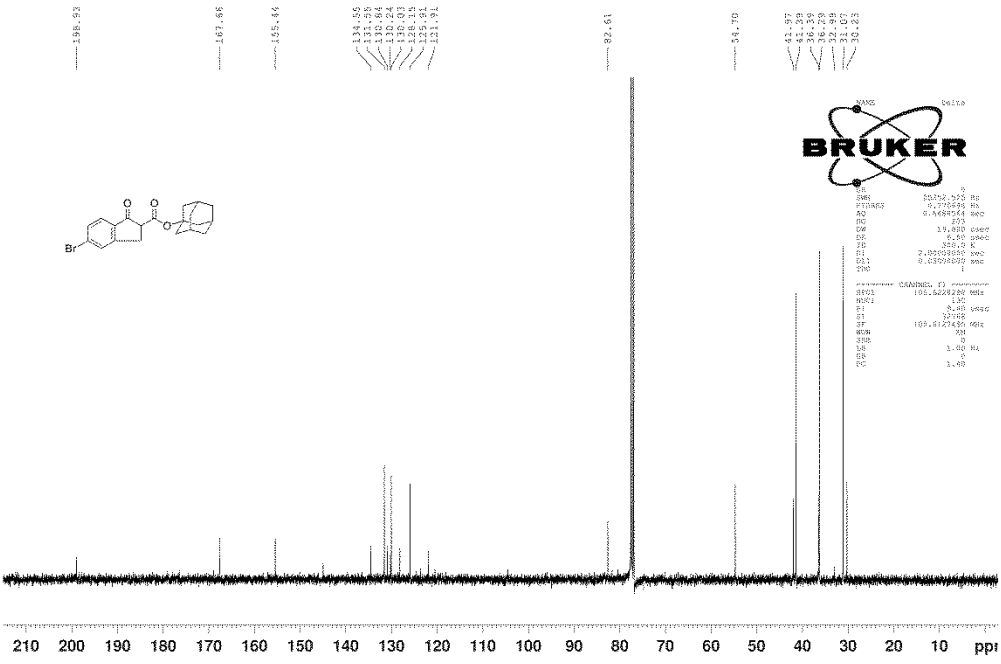
1-Adamantyl 5-chloro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate(3n)



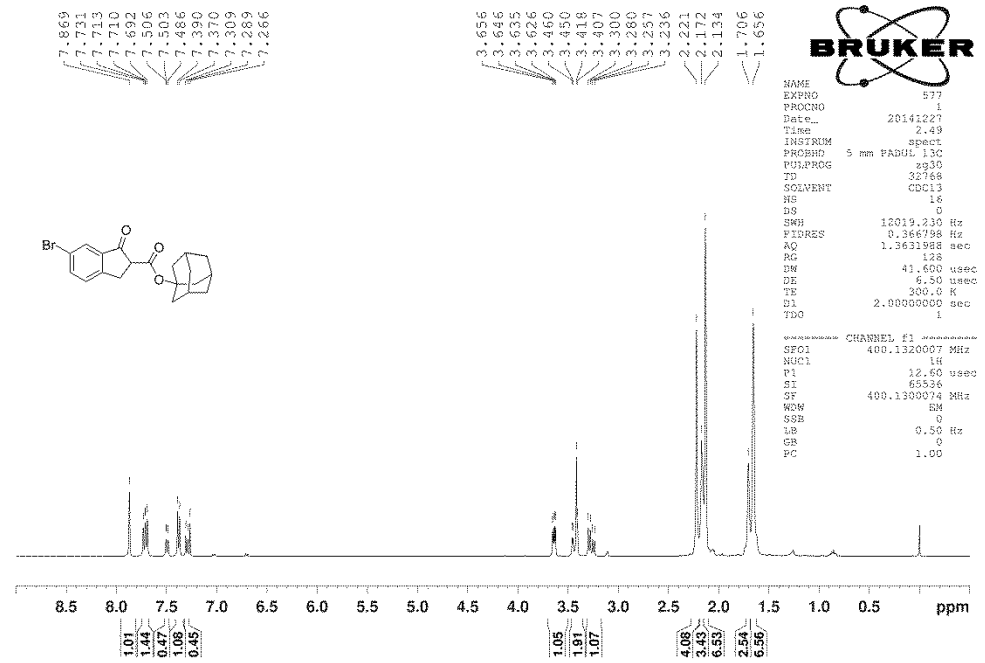


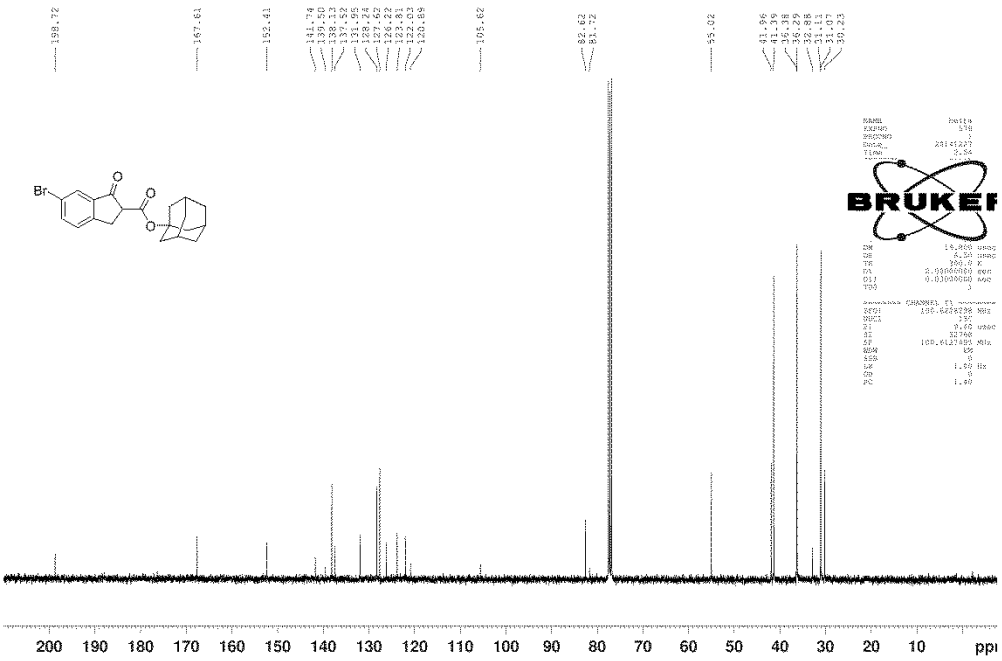
1-Adamantyl 5-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3o)



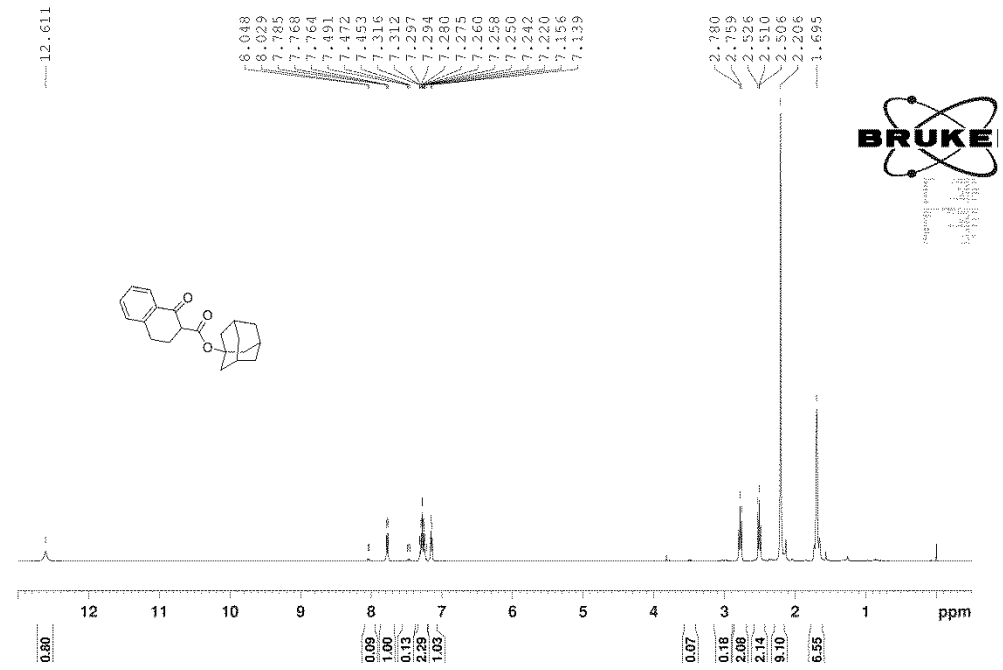


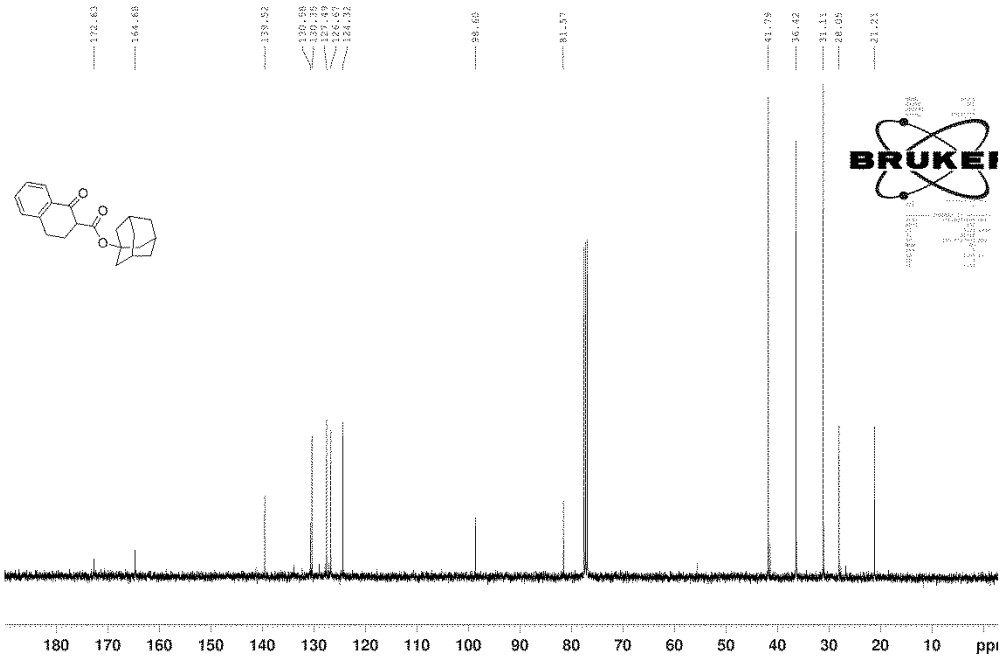
1-Adamantyl 6-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3p)



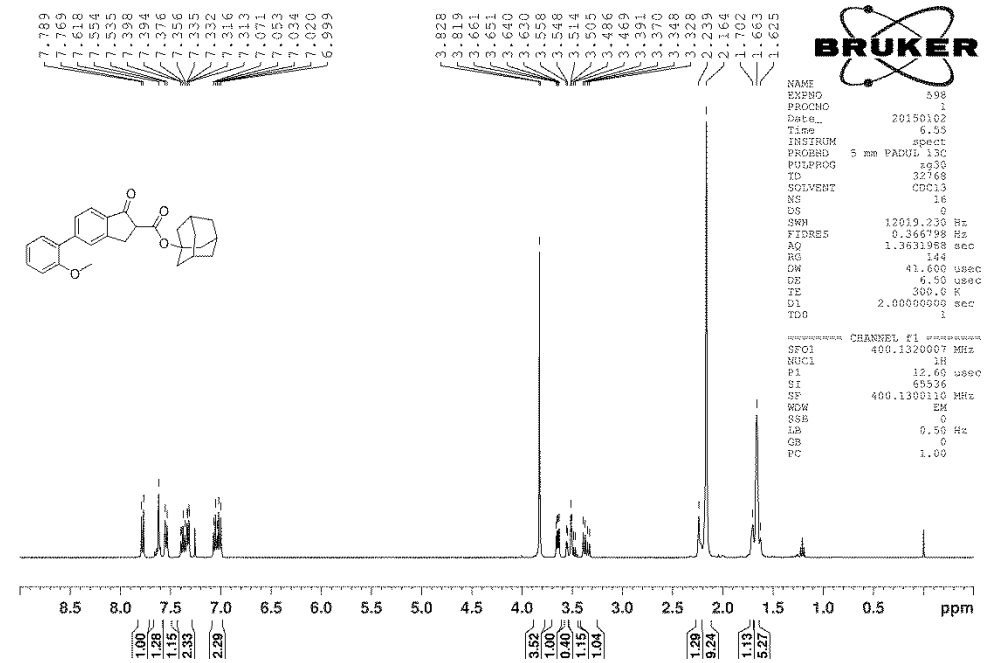


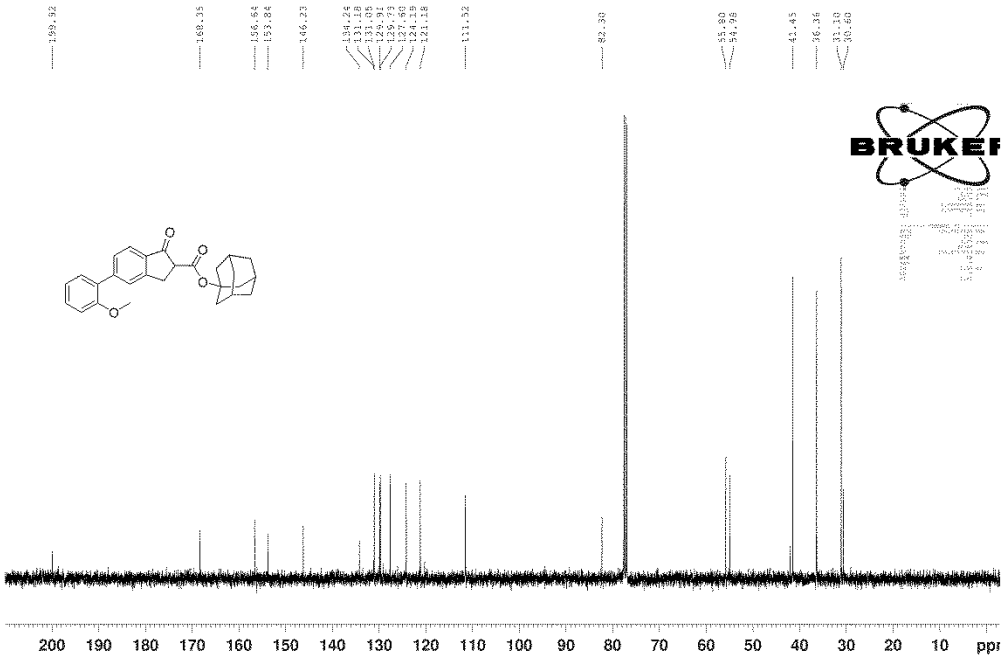
1-Adamantyl 1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (3s)



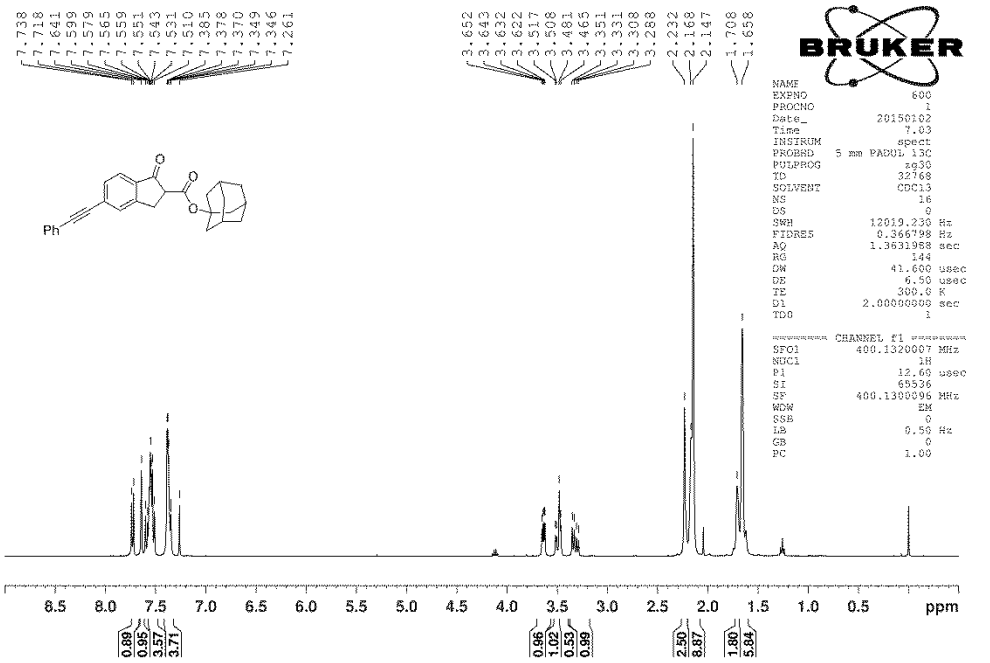


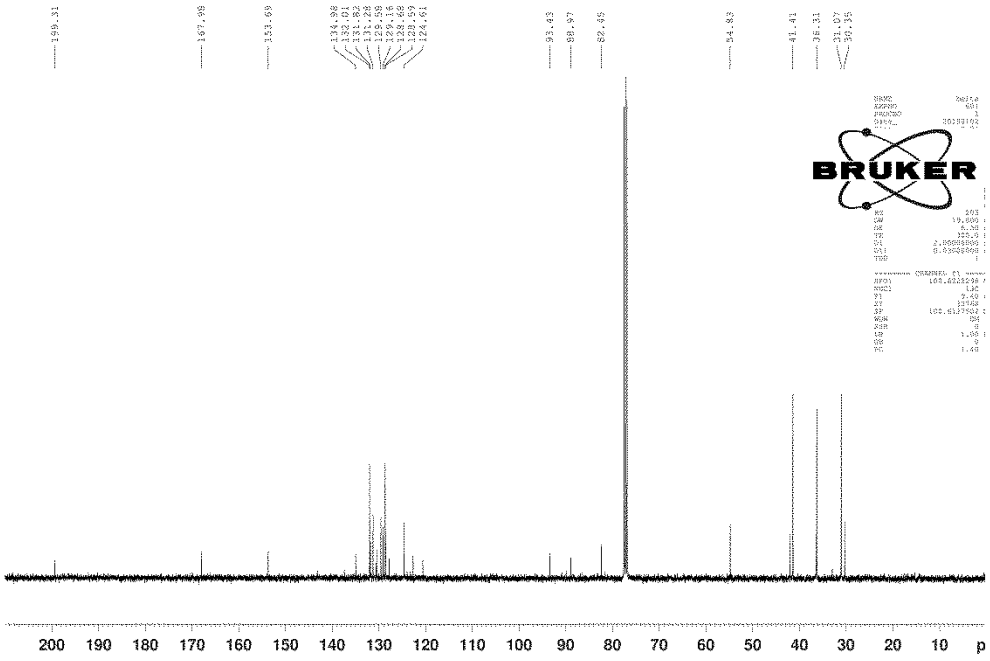
1-Adamantyl 5-(2-methoxyphenyl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (3u)



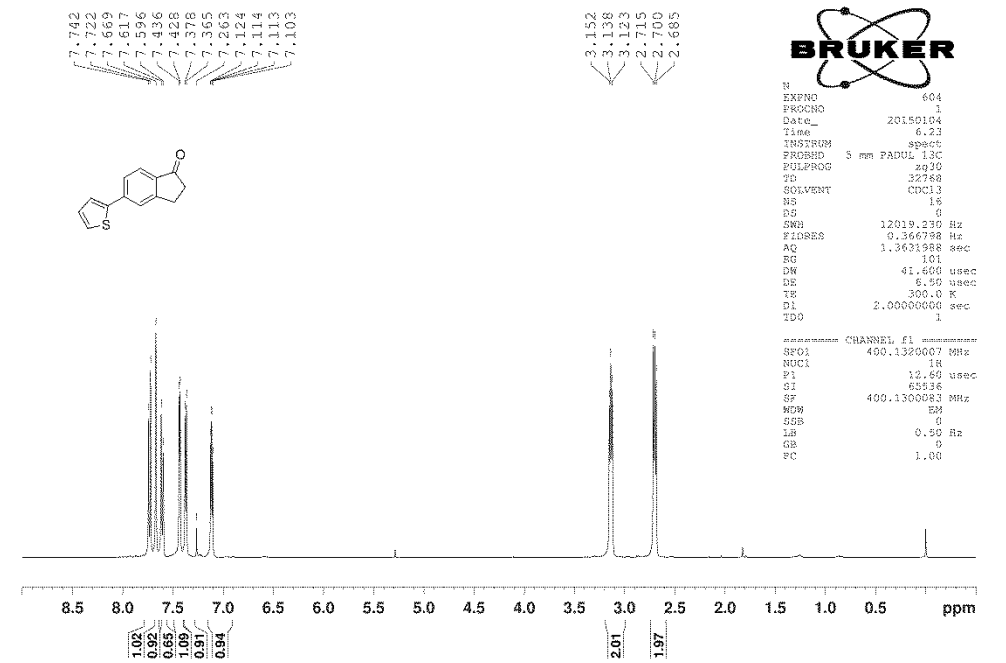


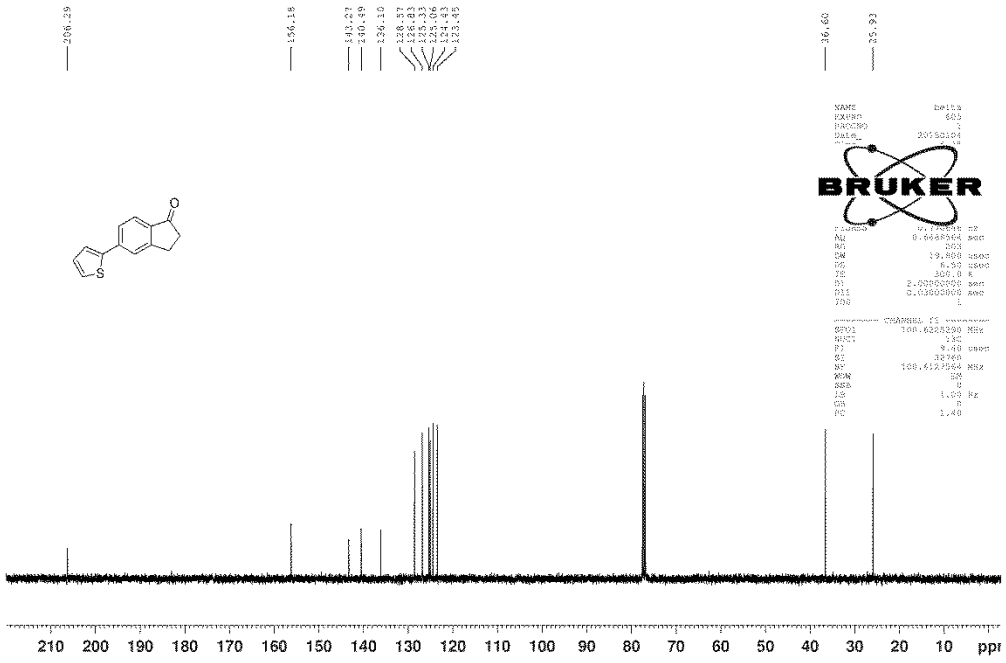
1-Adamantyl 1-oxo-5-(phenylethynyl)-2,3-dihydro-1H-indene-2-carboxylate (3w)



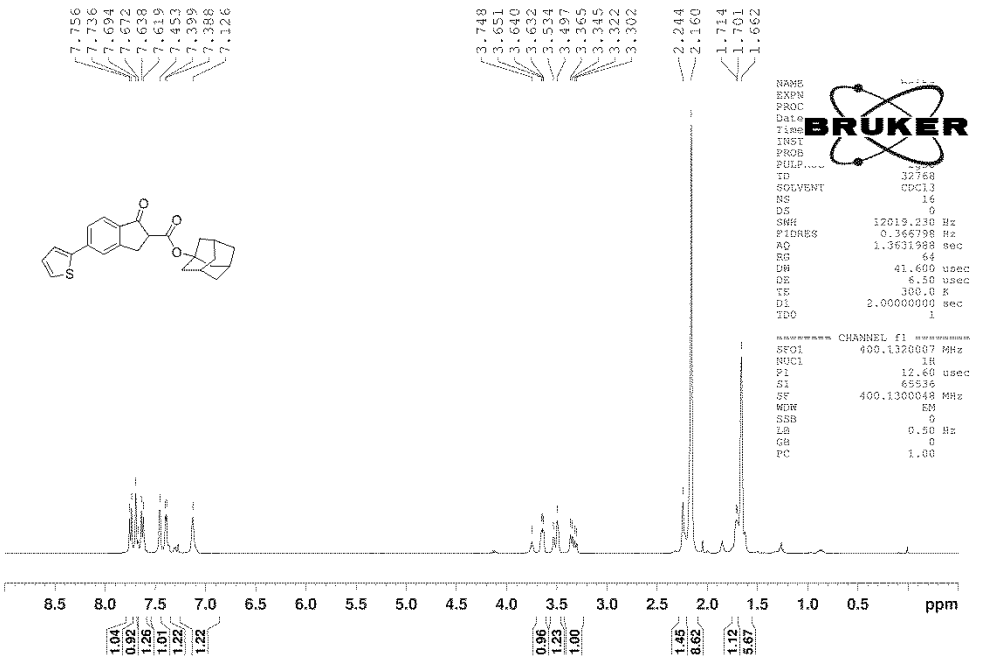


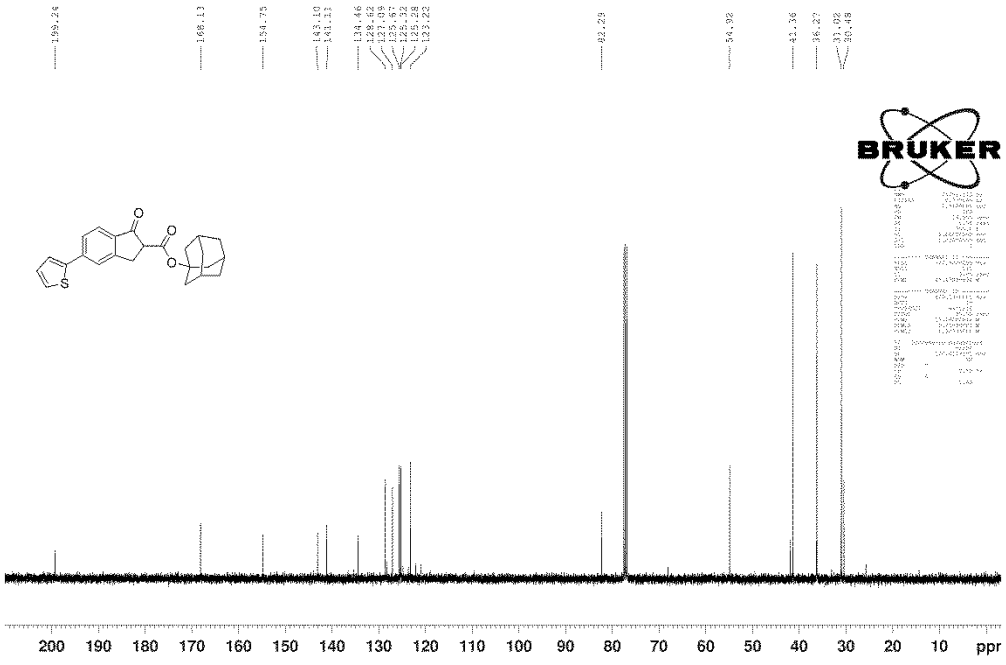
5-(thiophen-2-yl)-2,3-dihydro-1H-inden-1-one



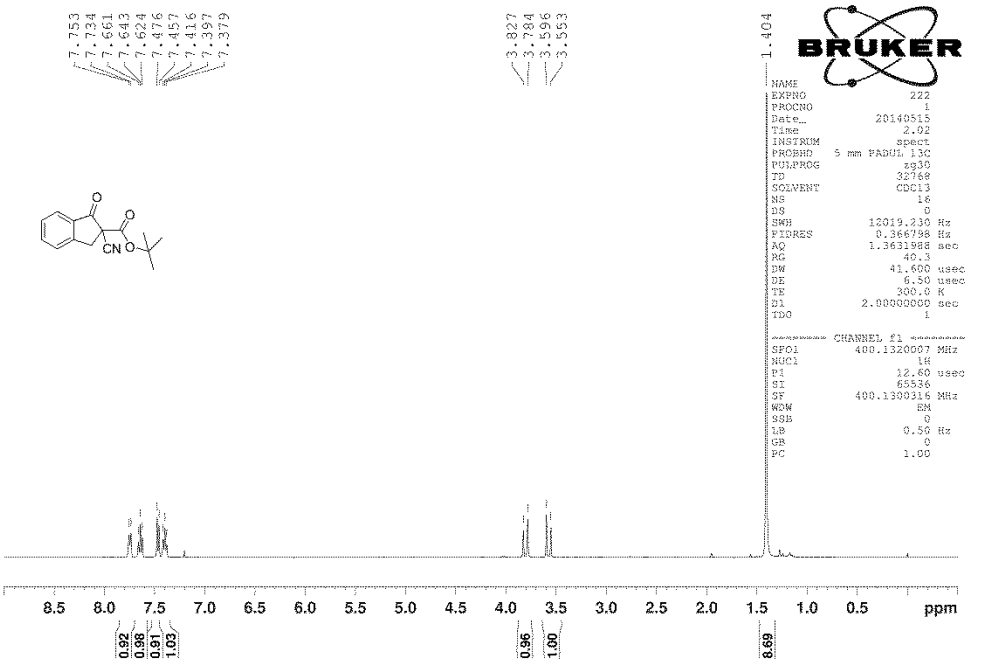


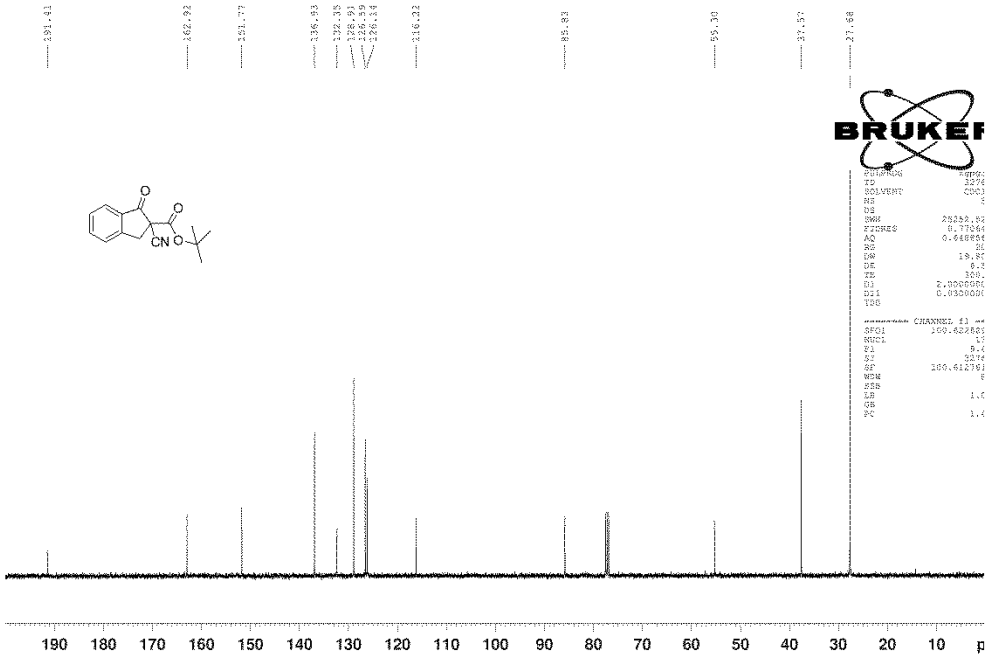
1-Adamantyl 1-oxo-5-(thiophen-2-yl)-2,3-dihydro-1H-indene-2-carboxylate (3v)



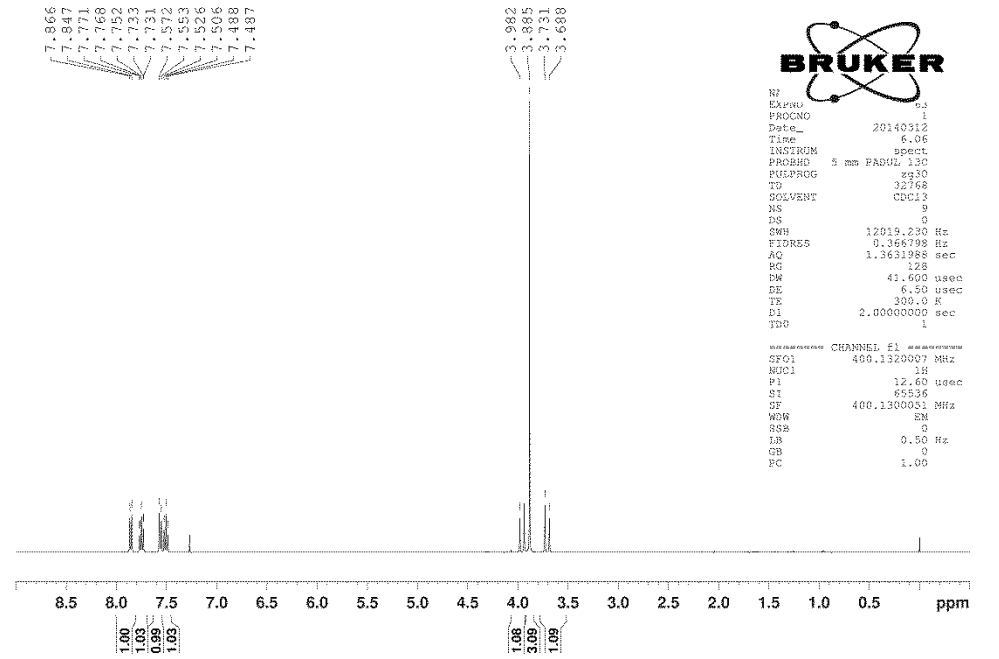


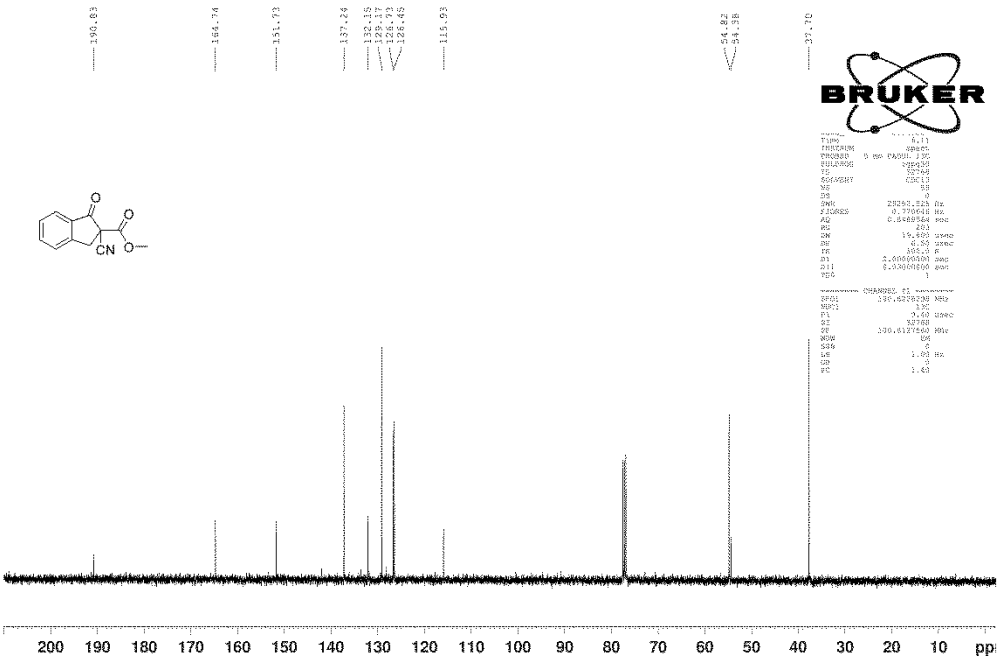
(S)-Tert-butyl 2-cyano-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4a)



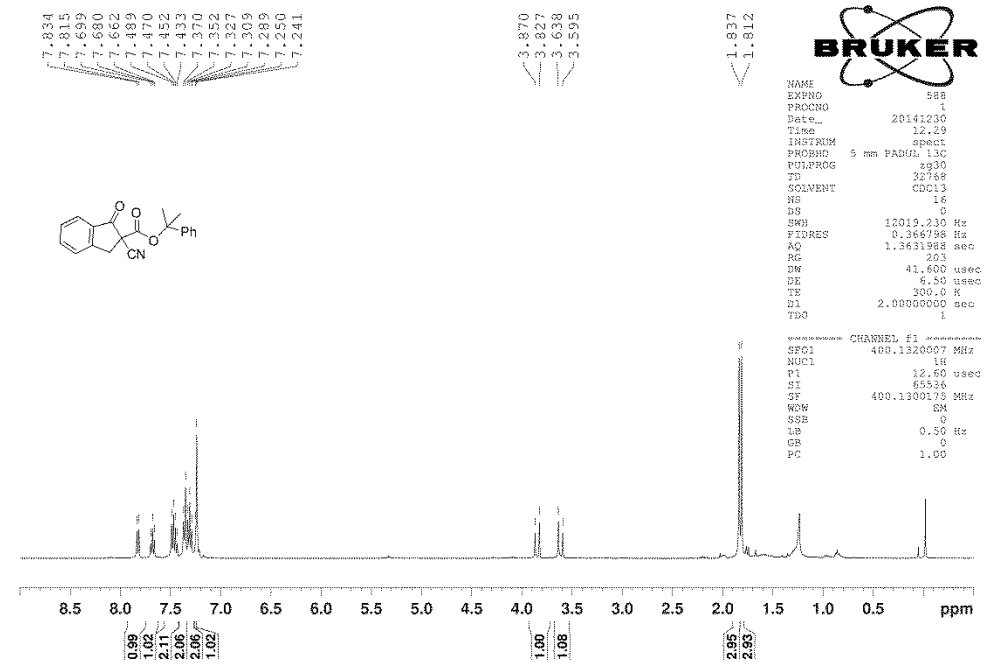


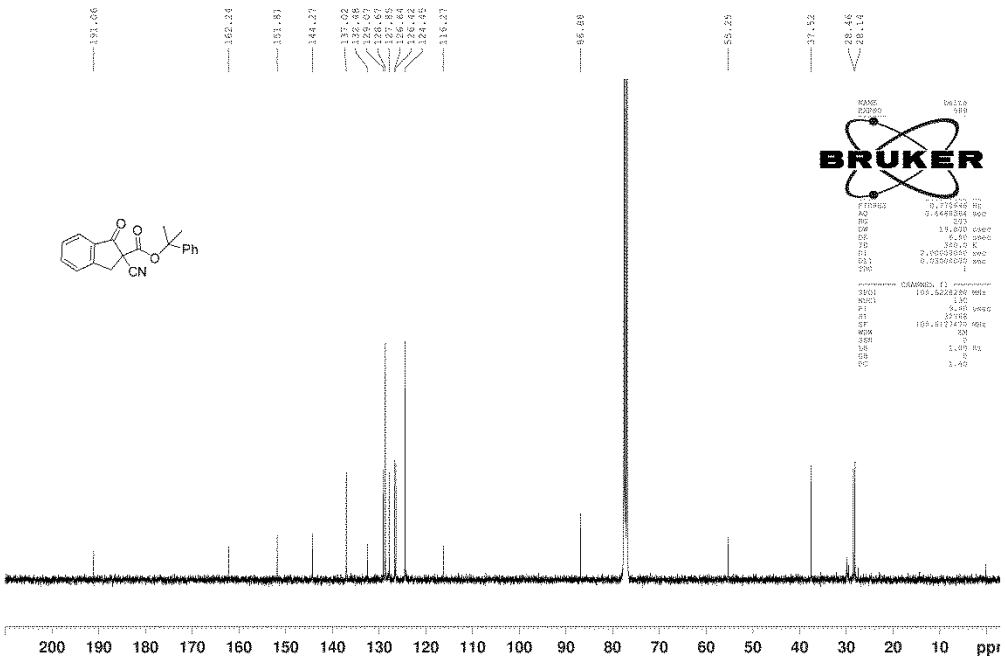
(S)-methyl 2-cyano-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4b)



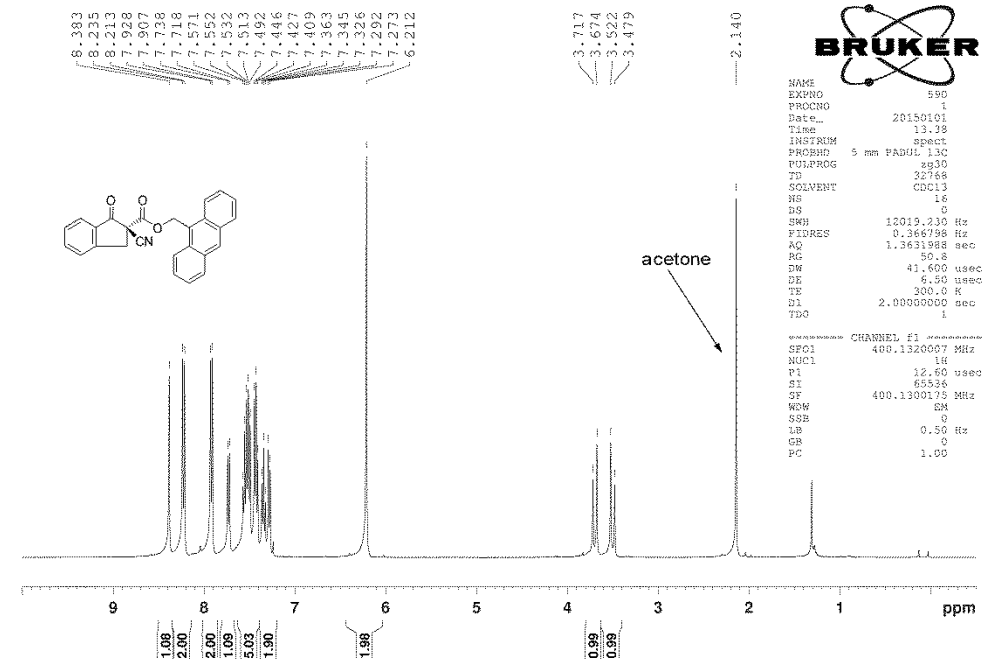


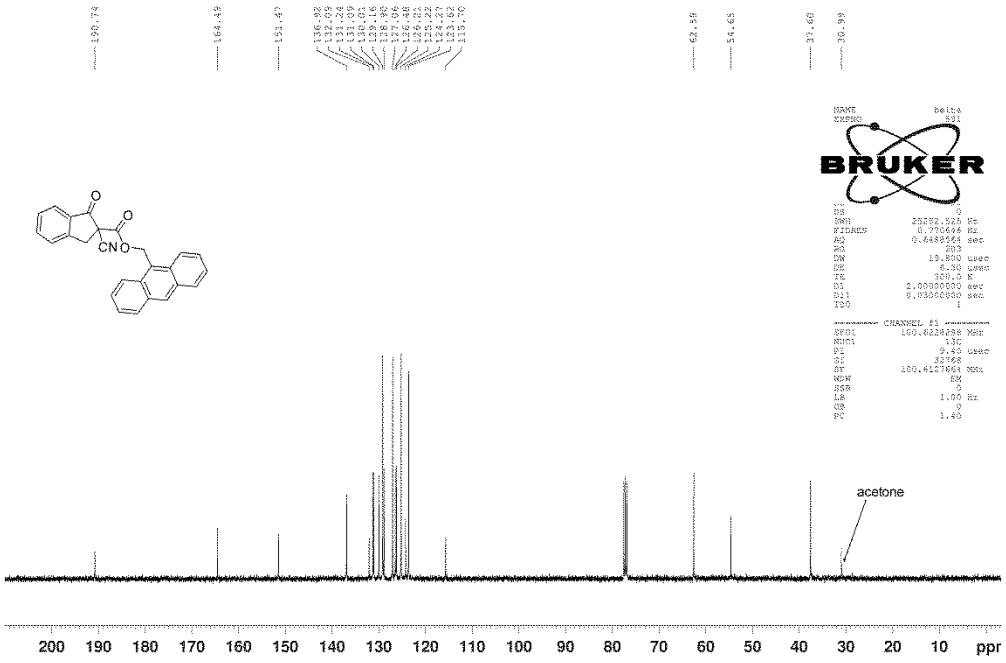
(S)-2-phenylpropan-2-yl 2-cyano-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4c)



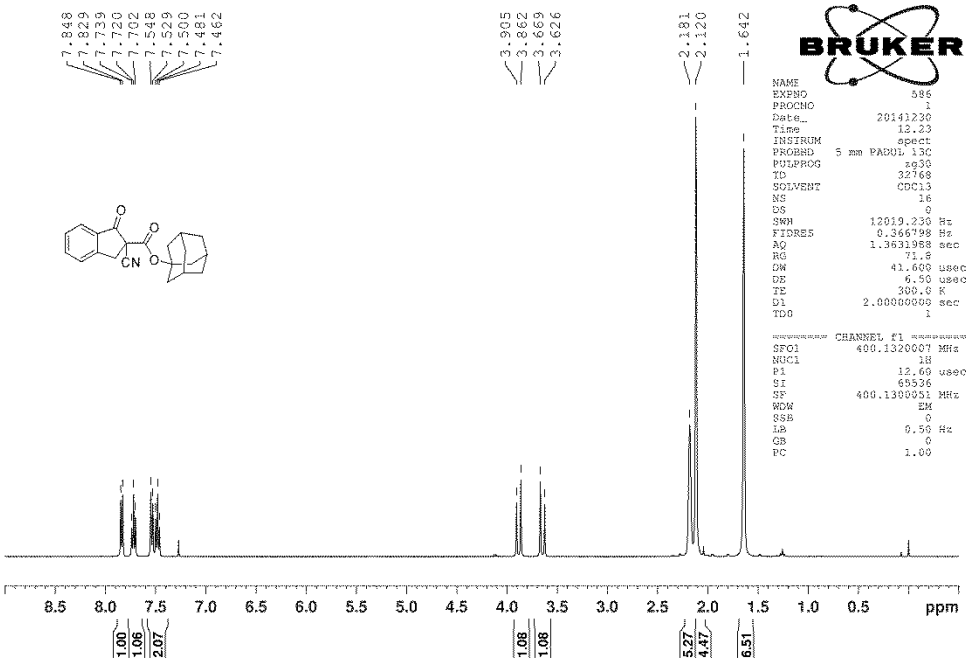


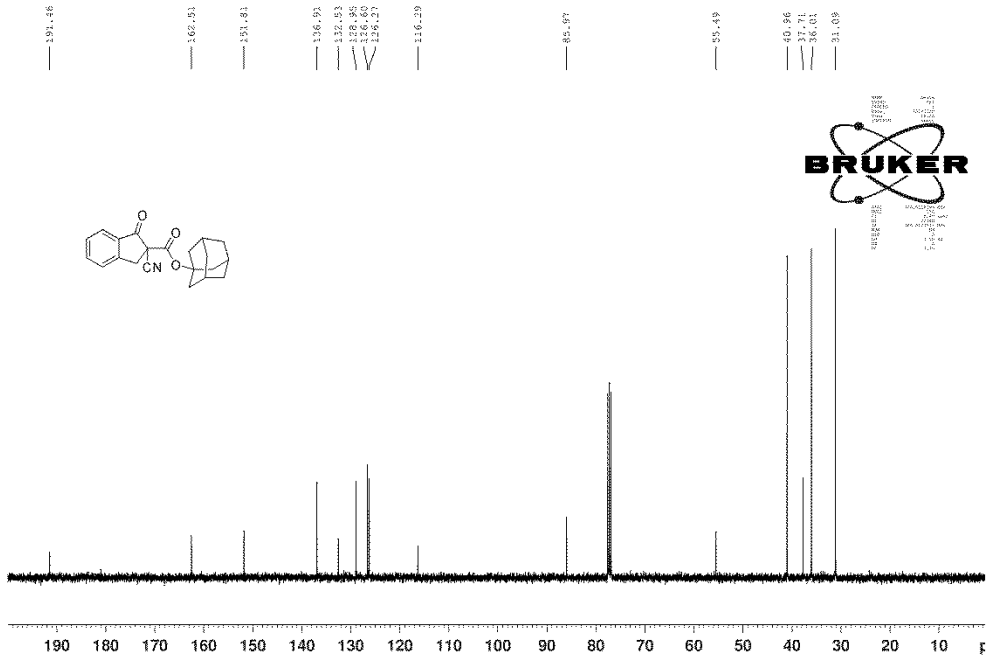
(S)-anthracen-9-ylmethyl 2-cyano-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4e)



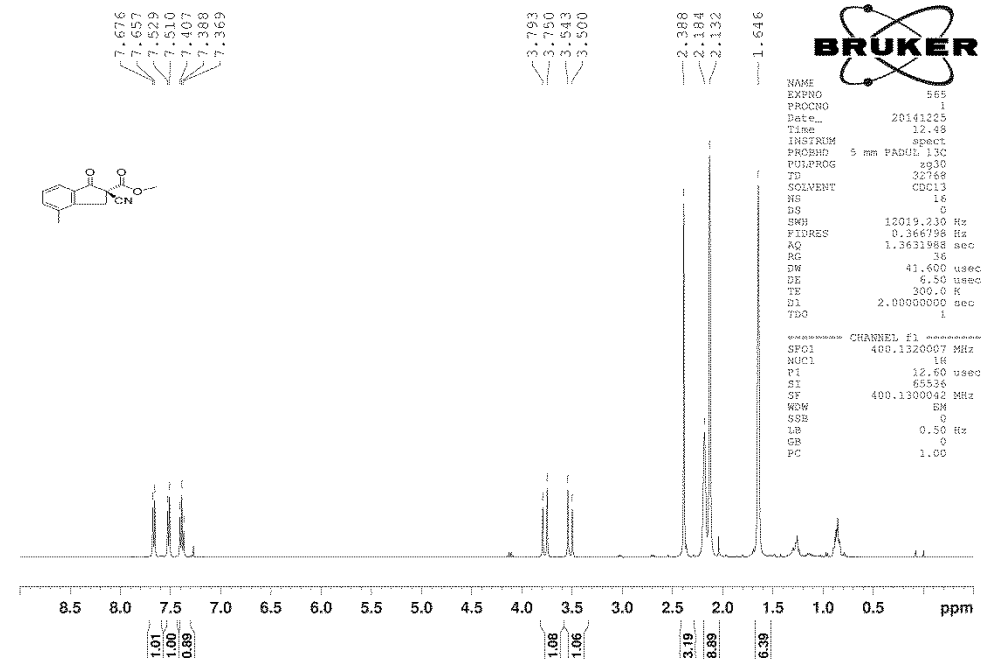


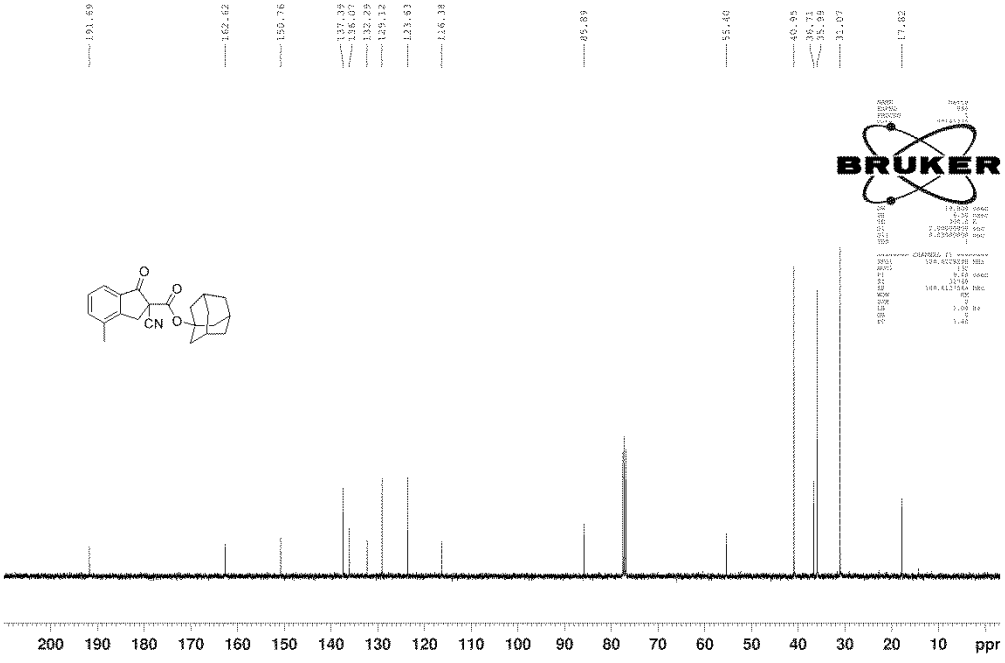
(S)-1-Adamantyl 2-cyano-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4f)



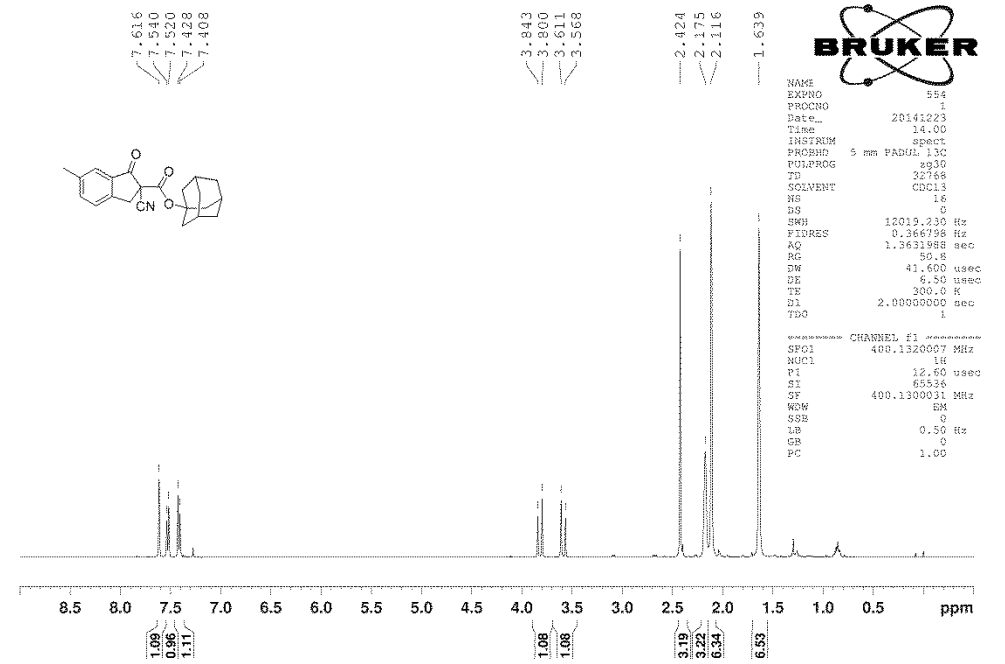


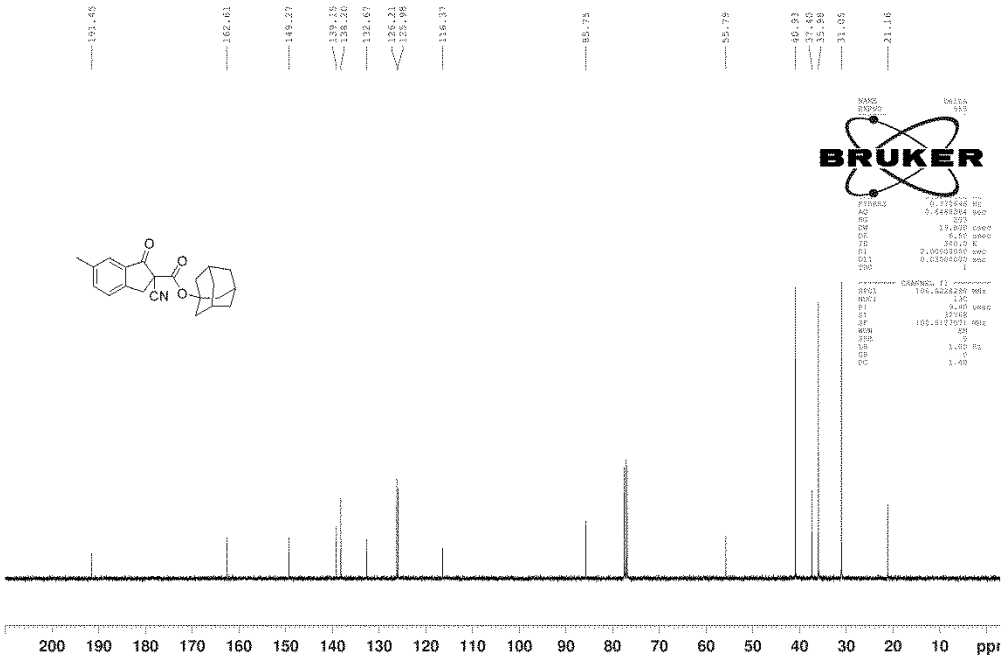
(S)-1-Adamantyl 2-cyano-4-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4g)



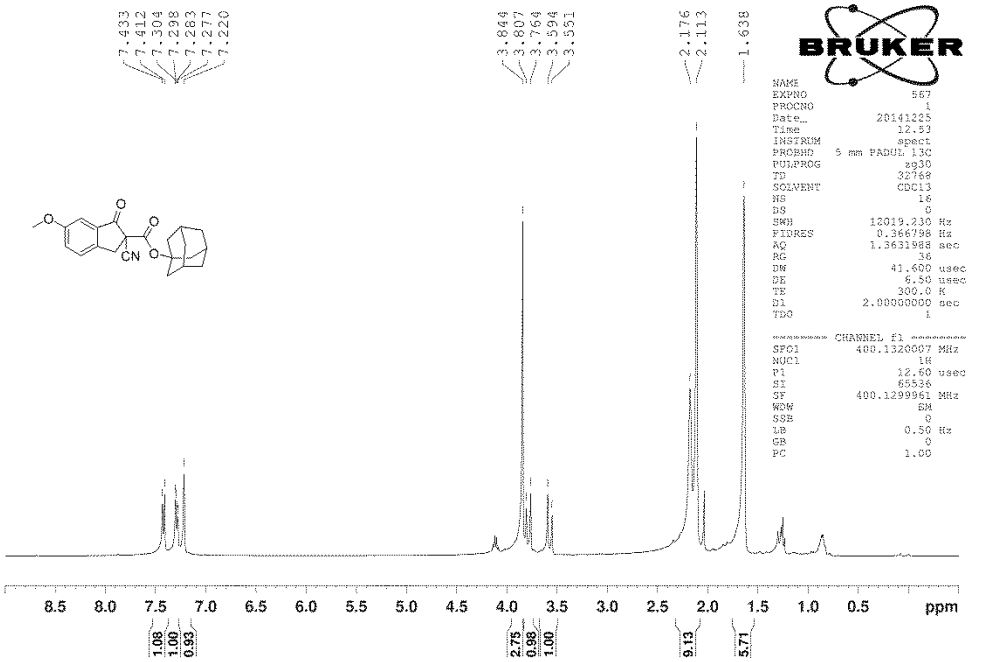


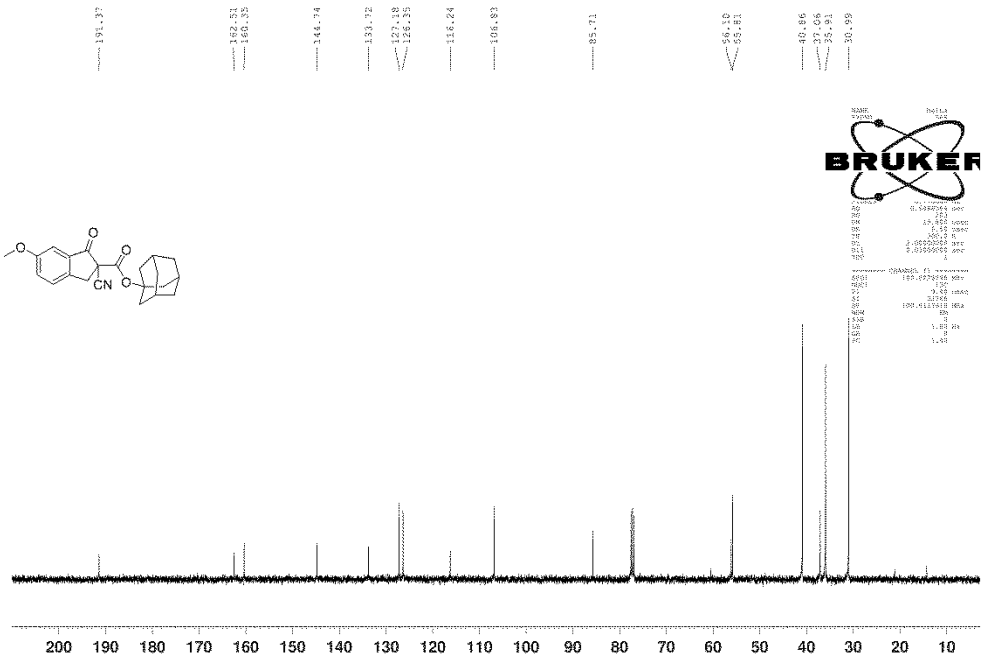
(S)-1-Adamantyl 2-cyano-6-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4h)



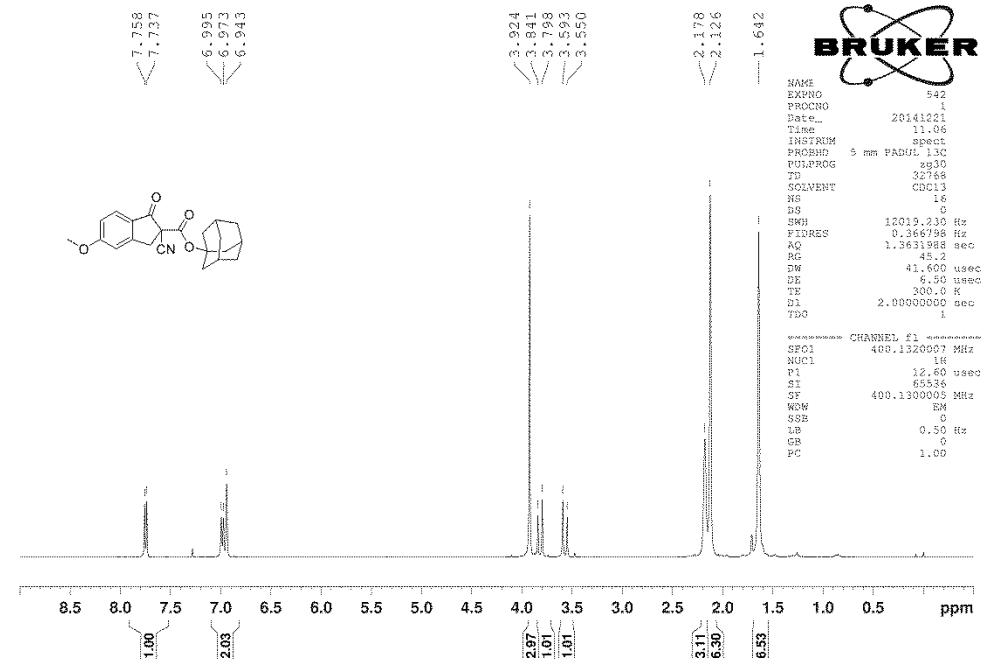


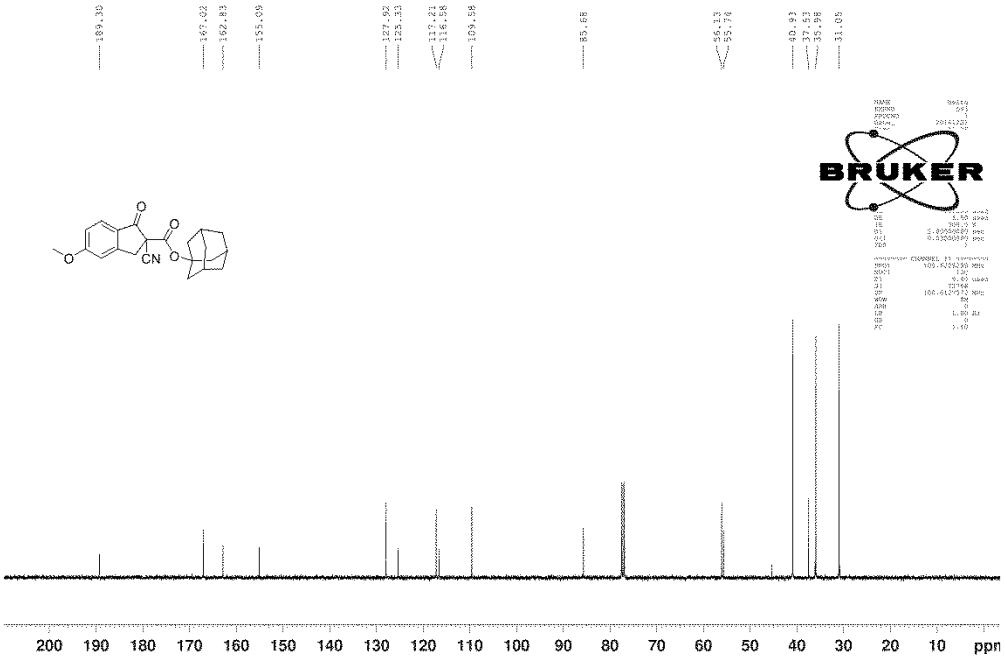
(S)-1-Adamantyl 2-cyano-6-methoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4i)



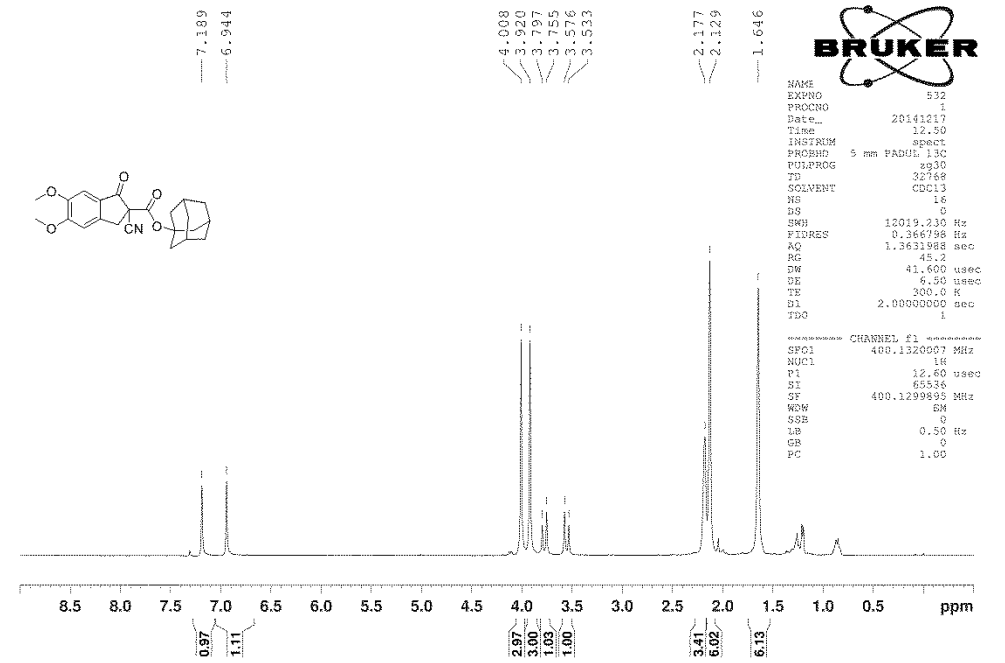


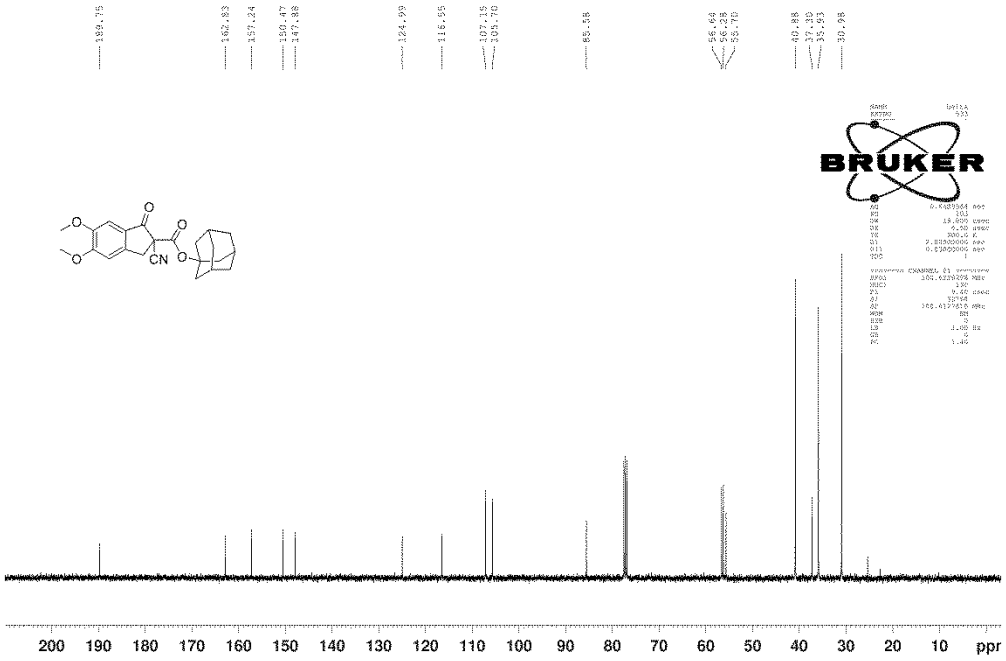
(S)-1-Adamantyl 2-cyano-6-methoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4j)



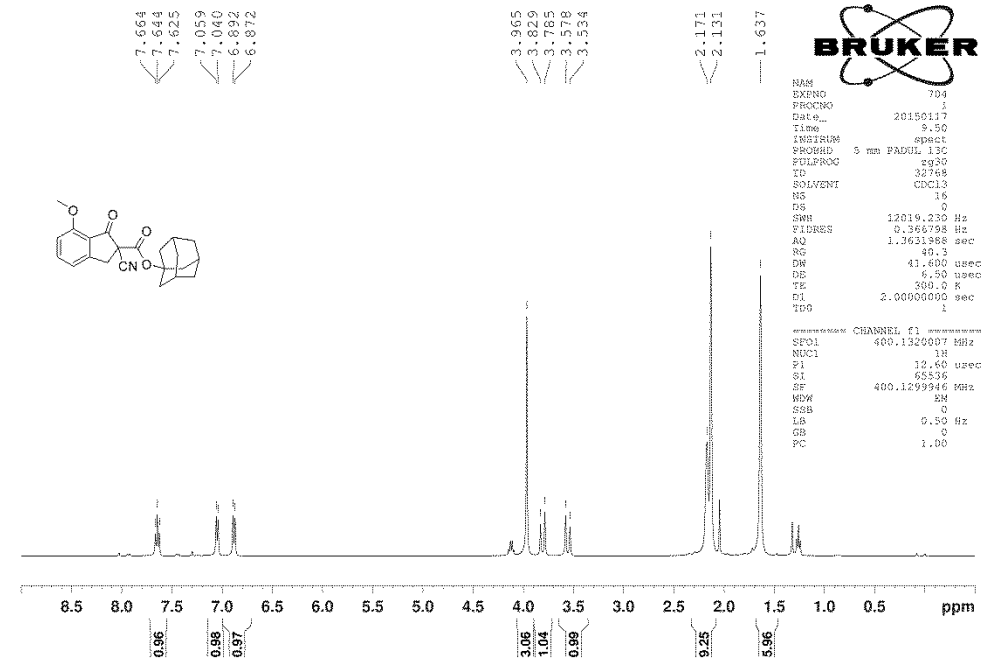


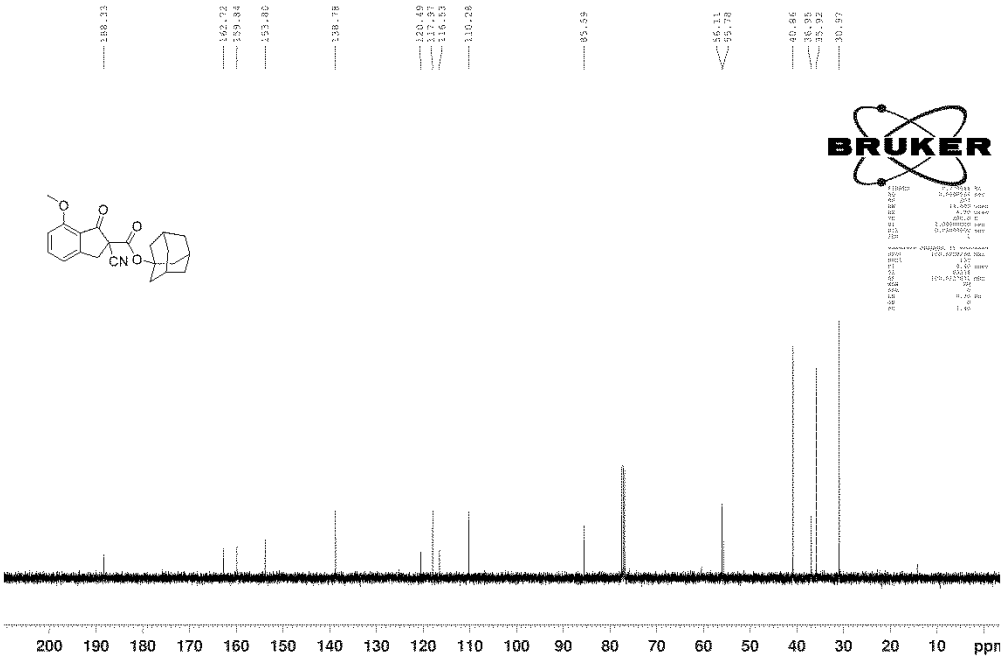
(S)-1-Adamantyl 2-cyano-5,6-dimethoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4k)



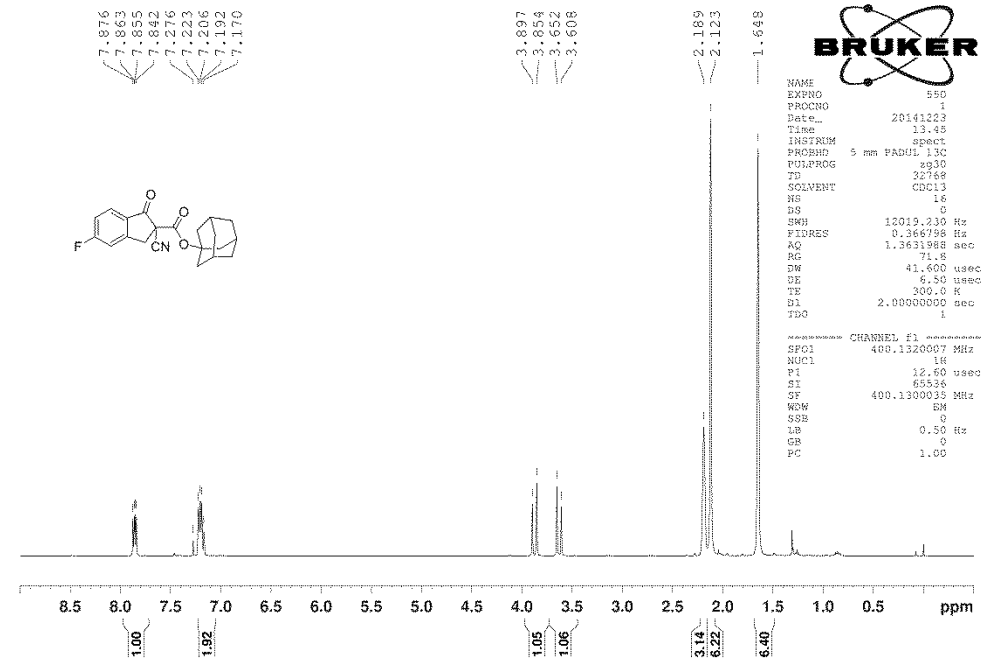


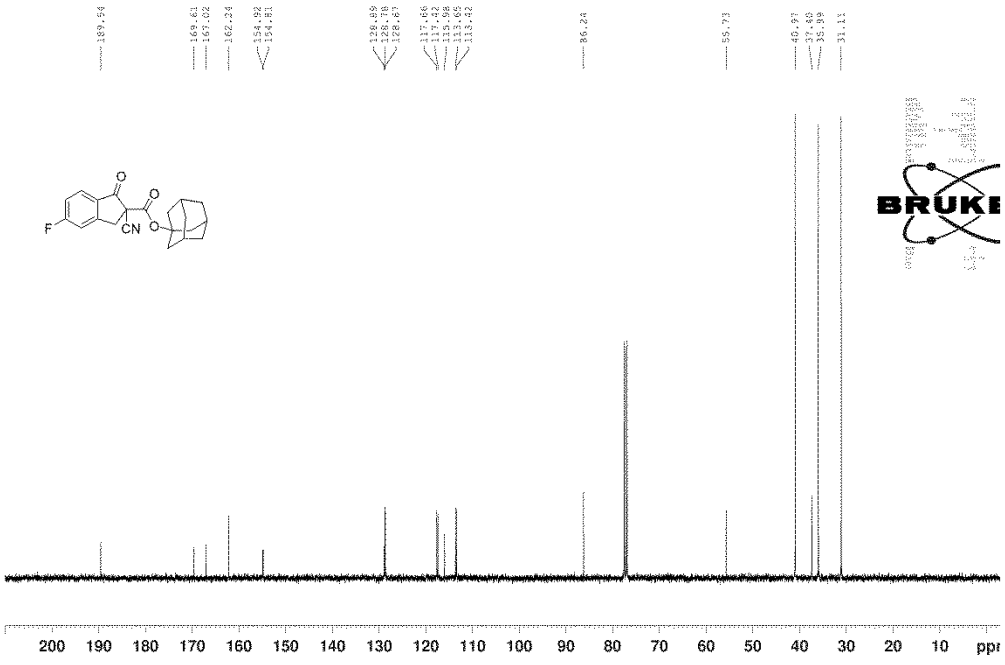
(S)-1-Adamantyl 2-cyano-7-methoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4l)



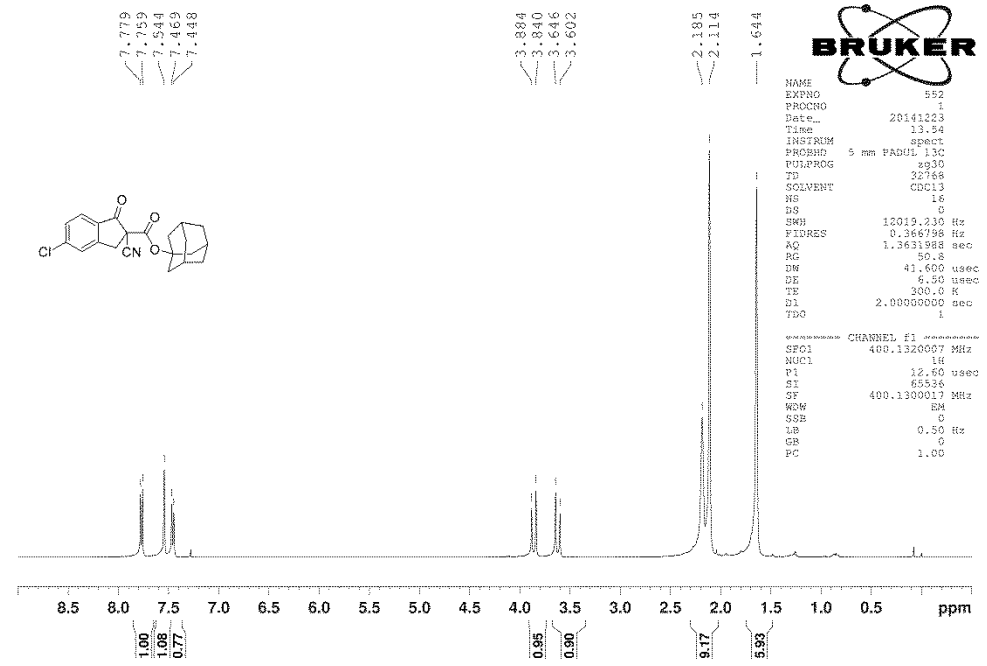


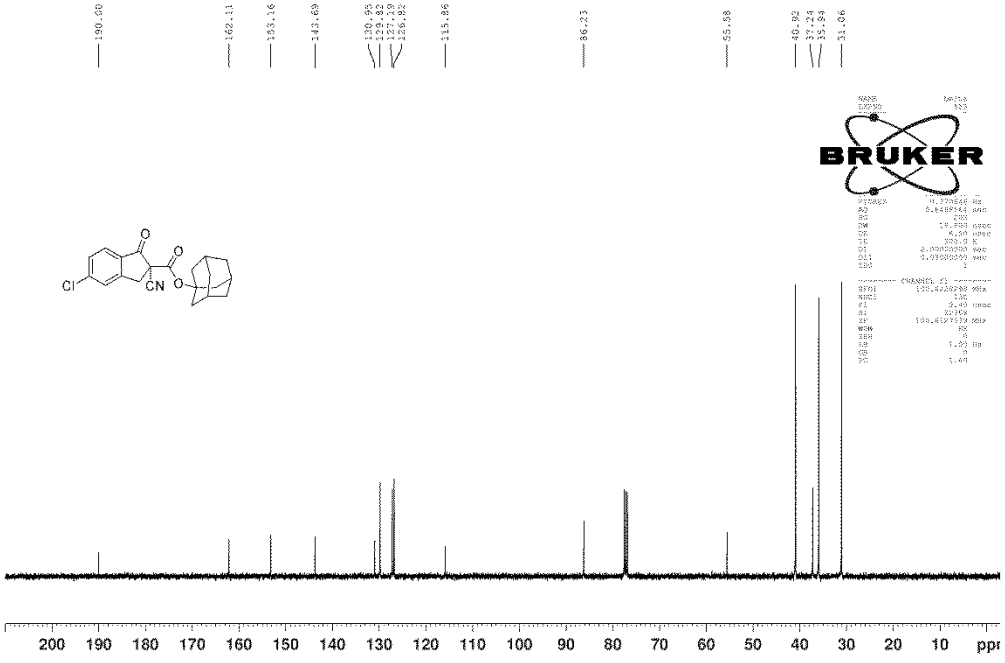
(S)-1-Adamantyl 2-cyano-5-fluoro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4m)



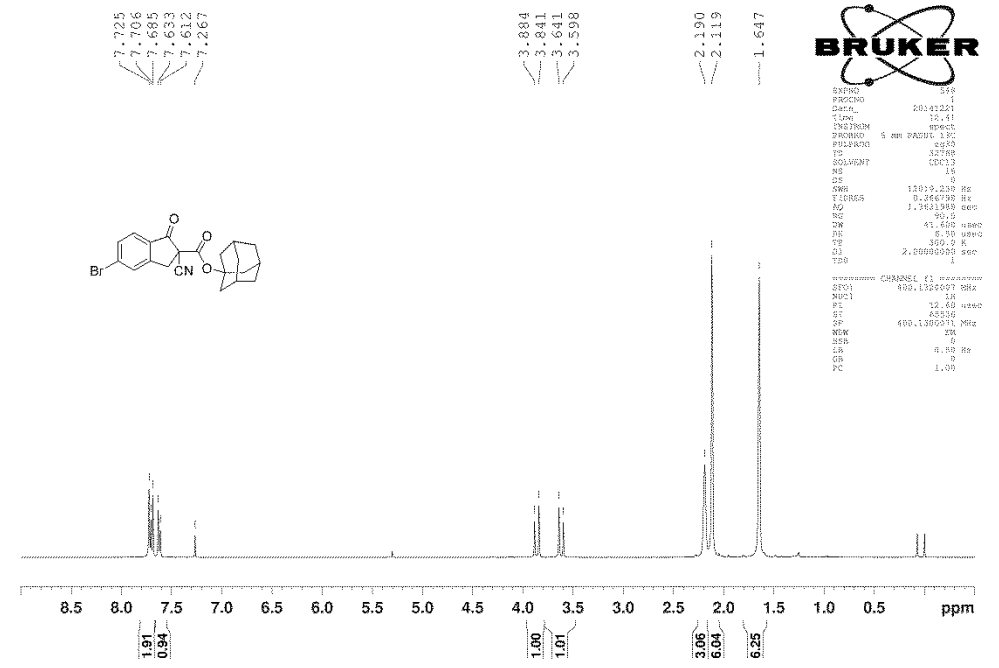


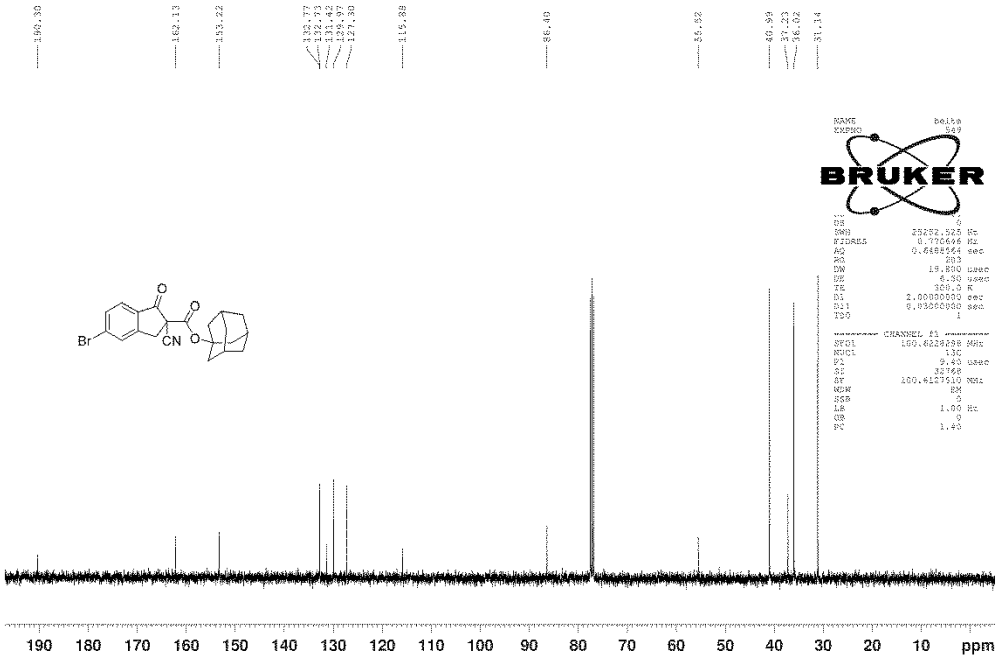
(S)-1-Adamantyl 2-cyano-5-chloro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4n)



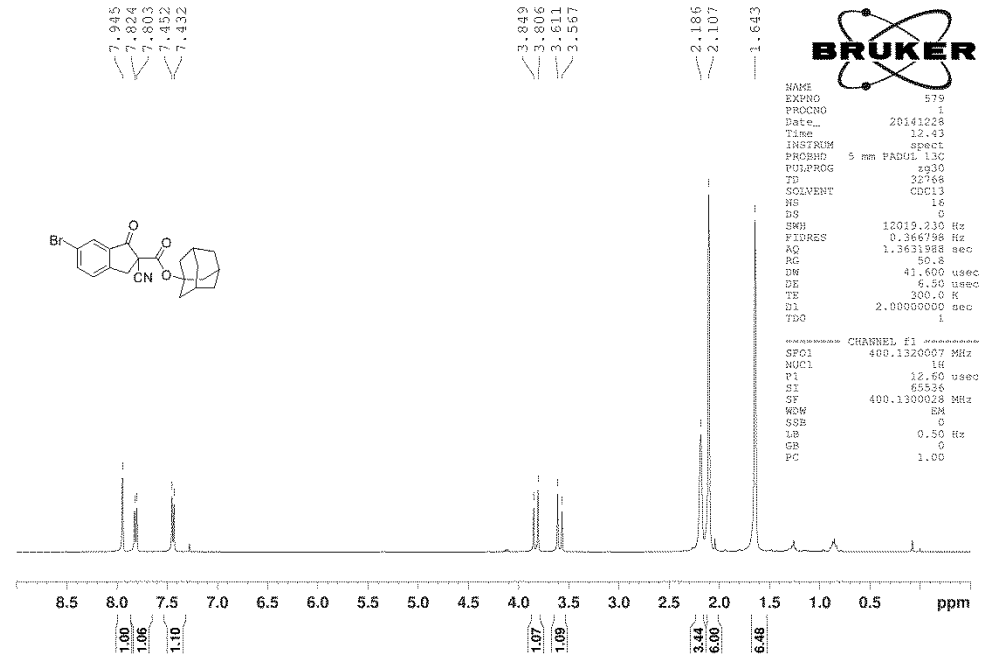


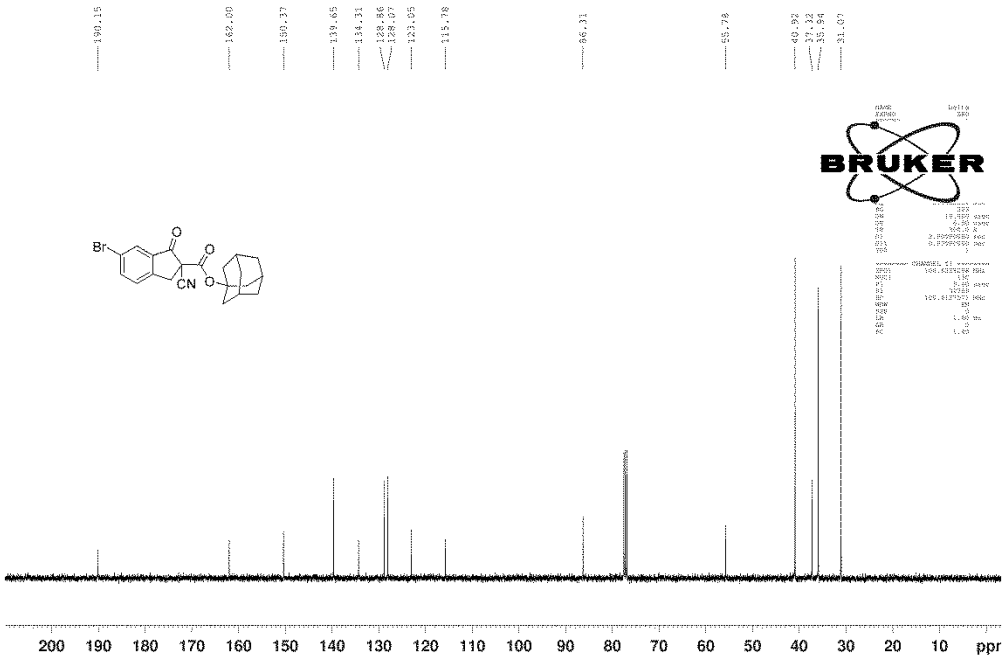
(S)-1-Adamantyl 2-cyano-5-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4o)



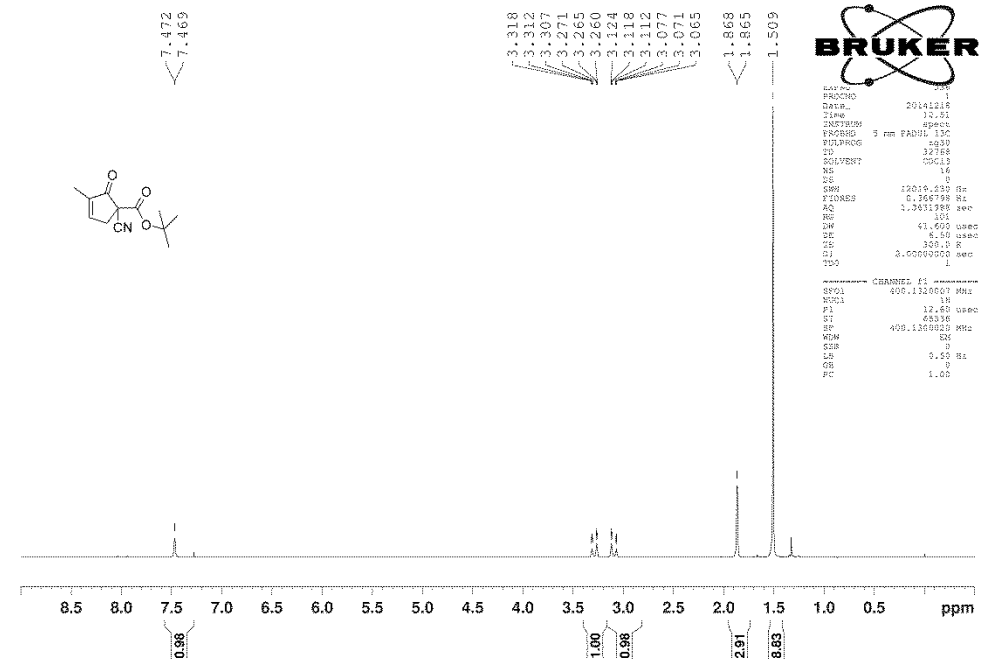


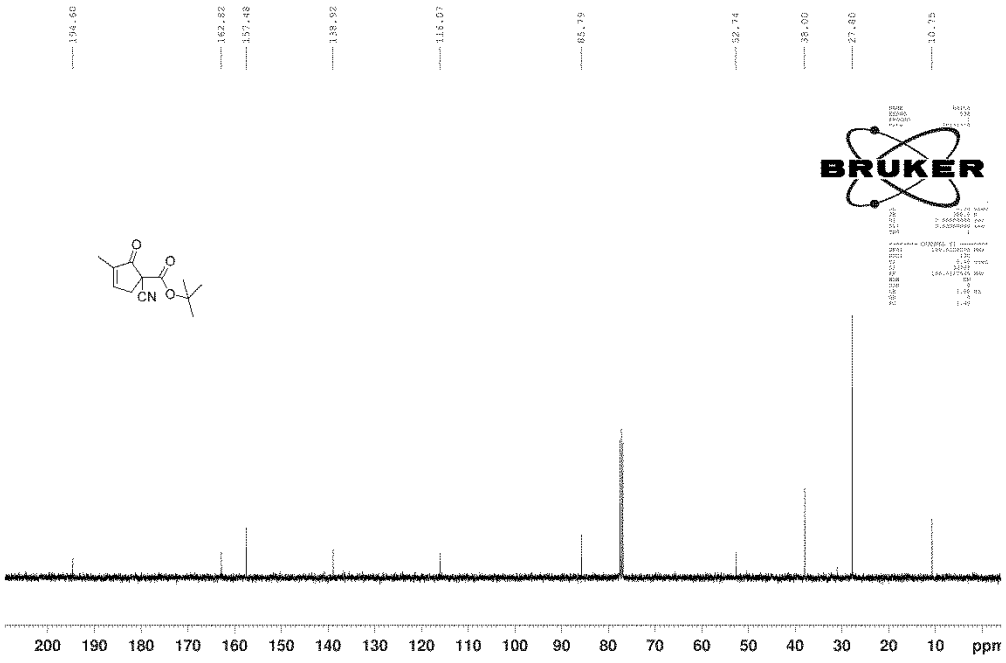
(S)-1-Adamantyl 2-cyano-6-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4p)



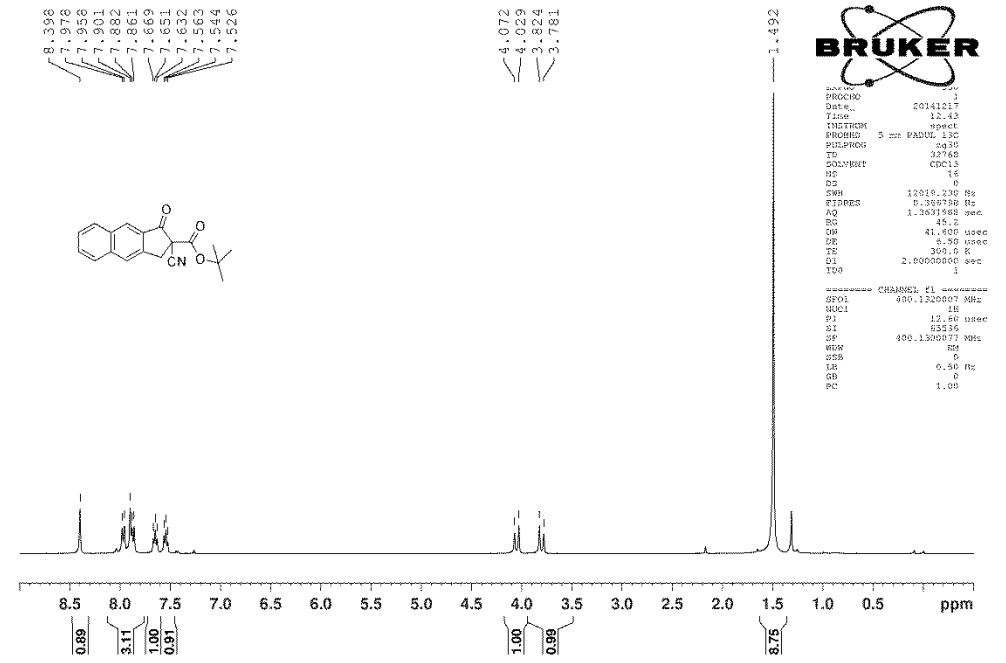


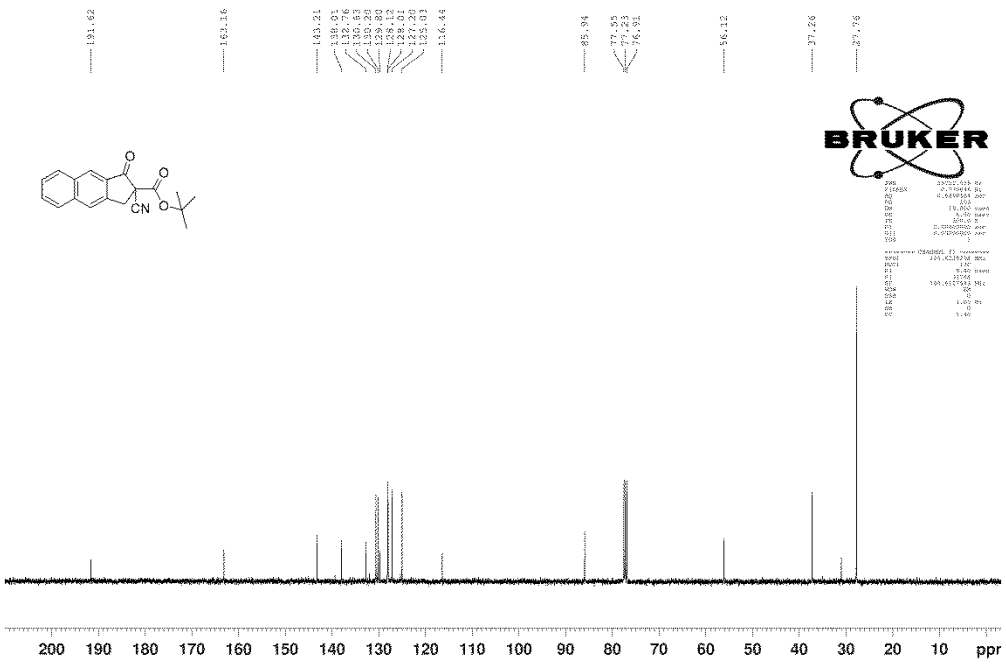
(S)-tert-butyl 1-cyano-3-methyl-2-oxocyclopent-3-enecarboxylate (4q)



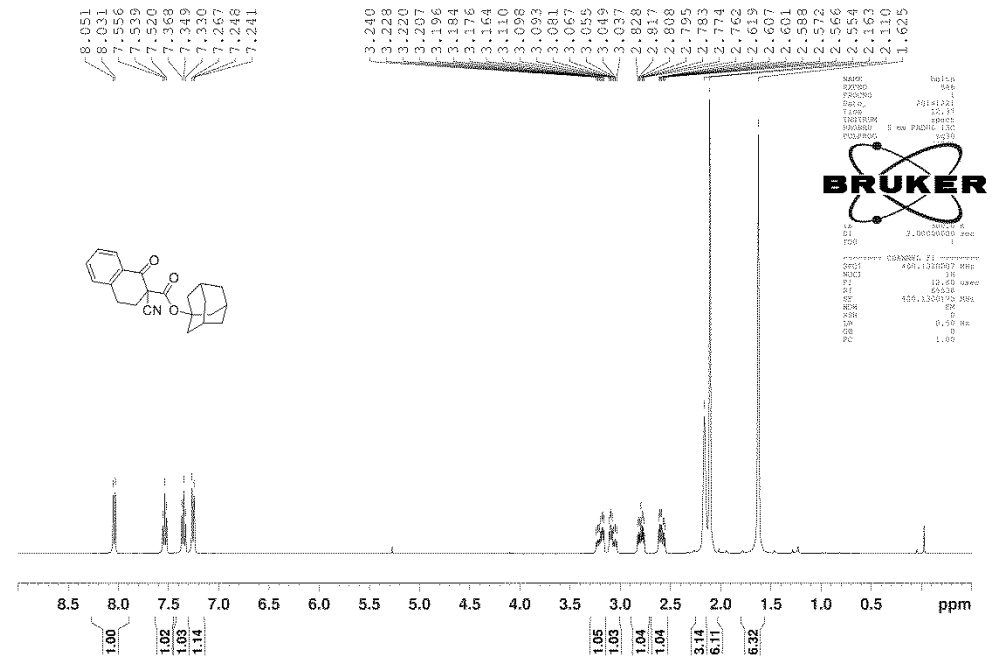


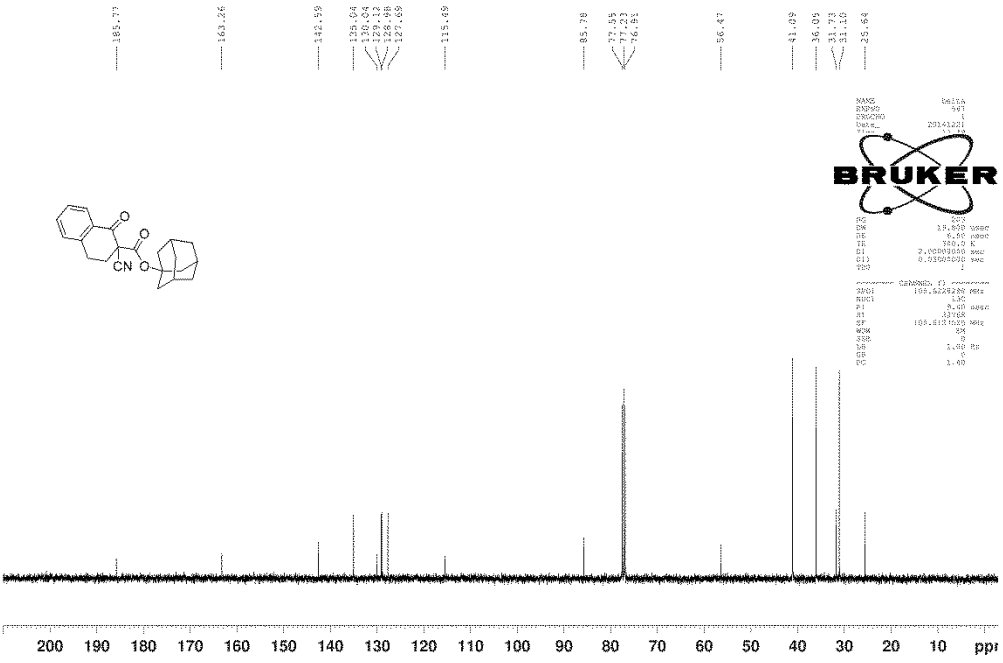
(S)-tert-butyl 2-cyano-1-oxo-2,3-dihydro-1H-cyclopenta[b]naphthalene-2-carboxylate (4r)



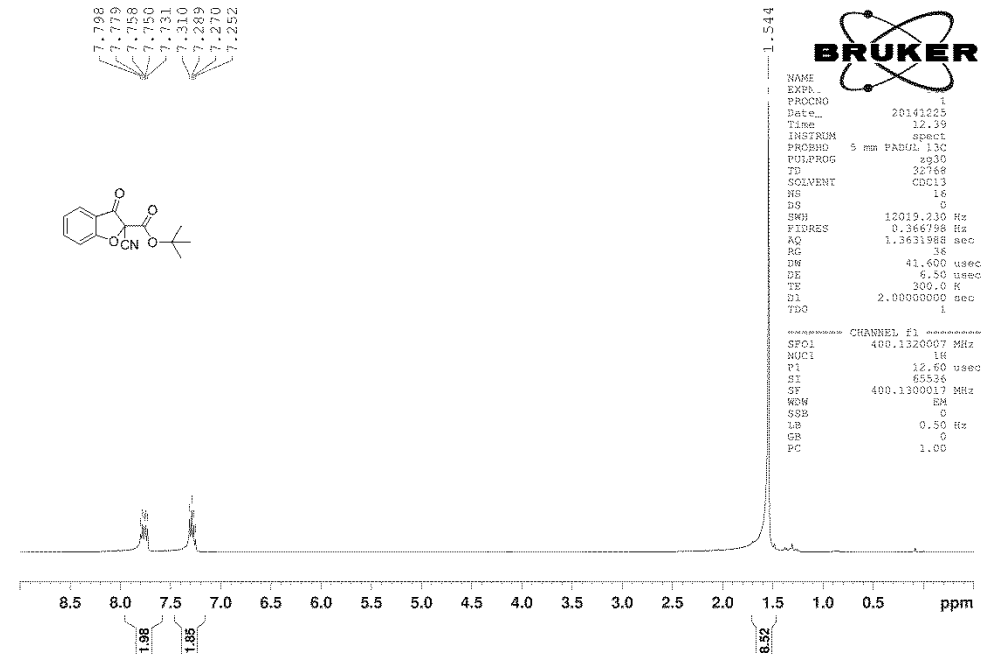


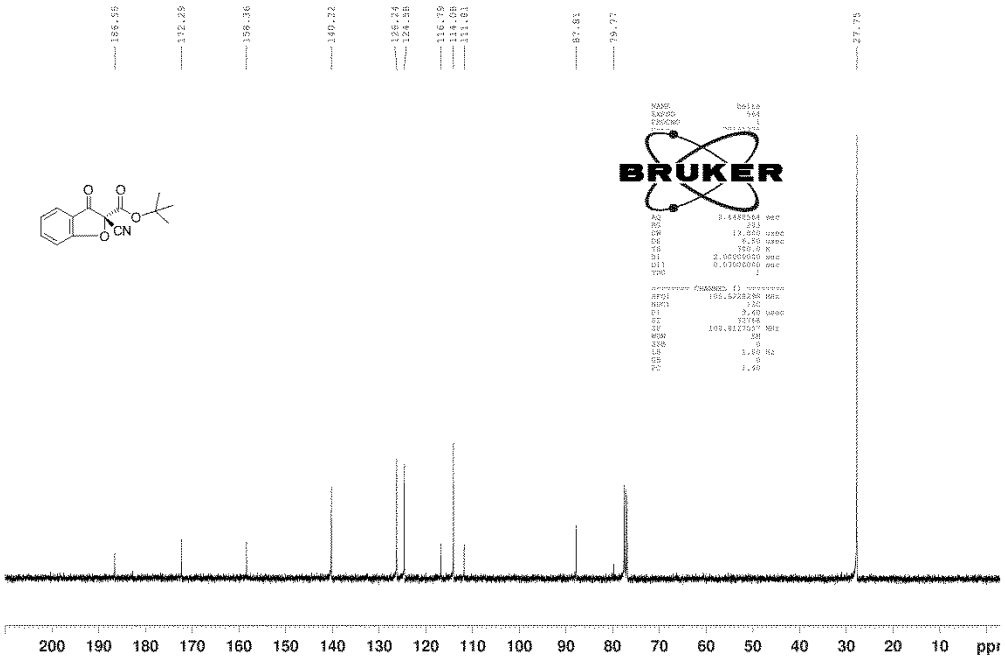
(S)-1-Adamantly-2-cyano-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (4s)



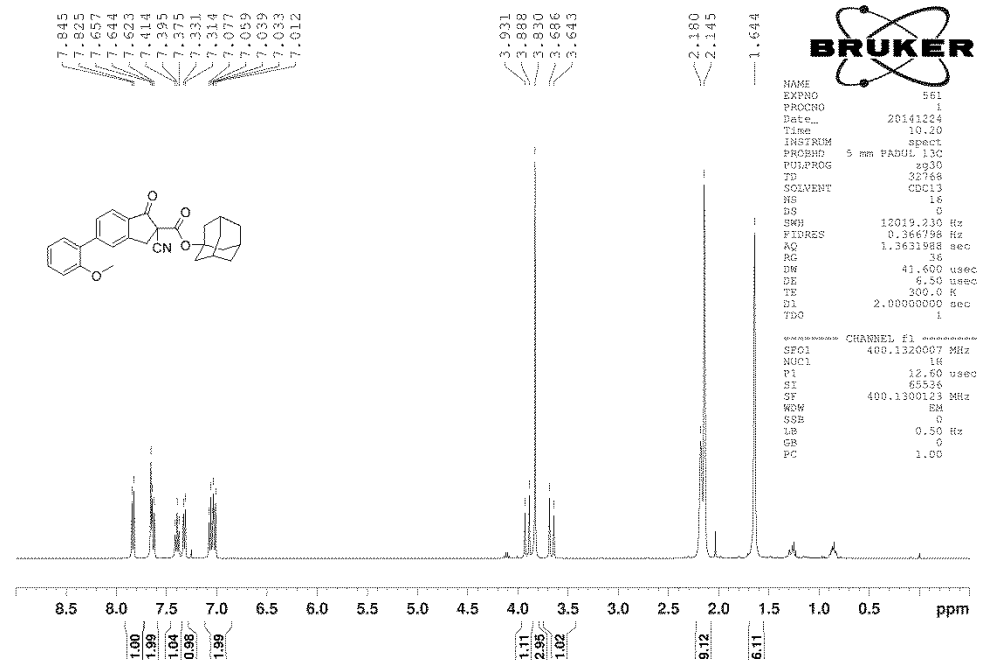


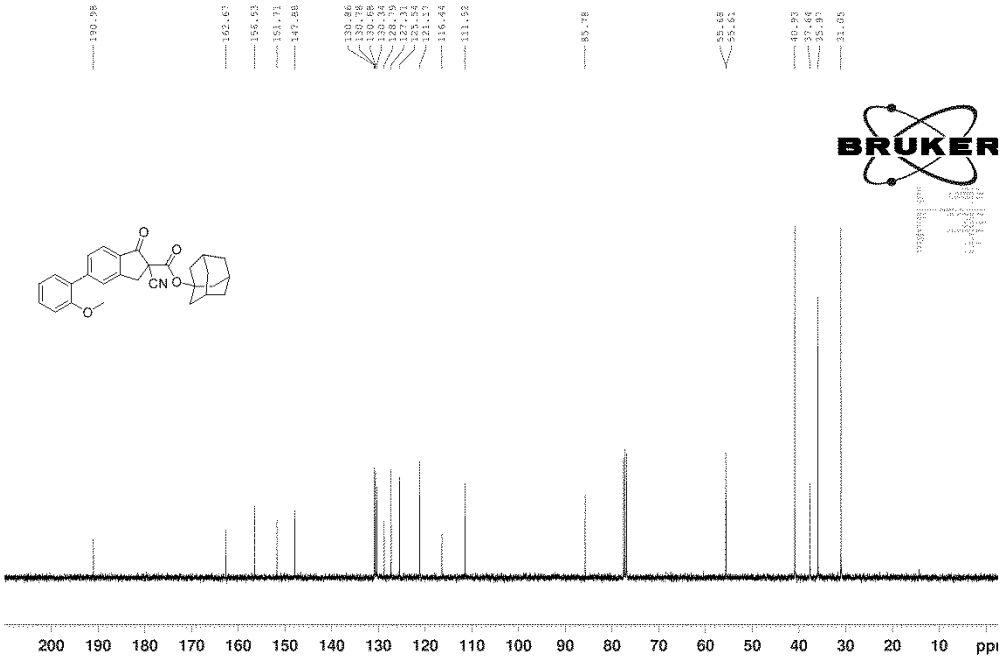
(R)-tert-butyl 2-cyano-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (4t)



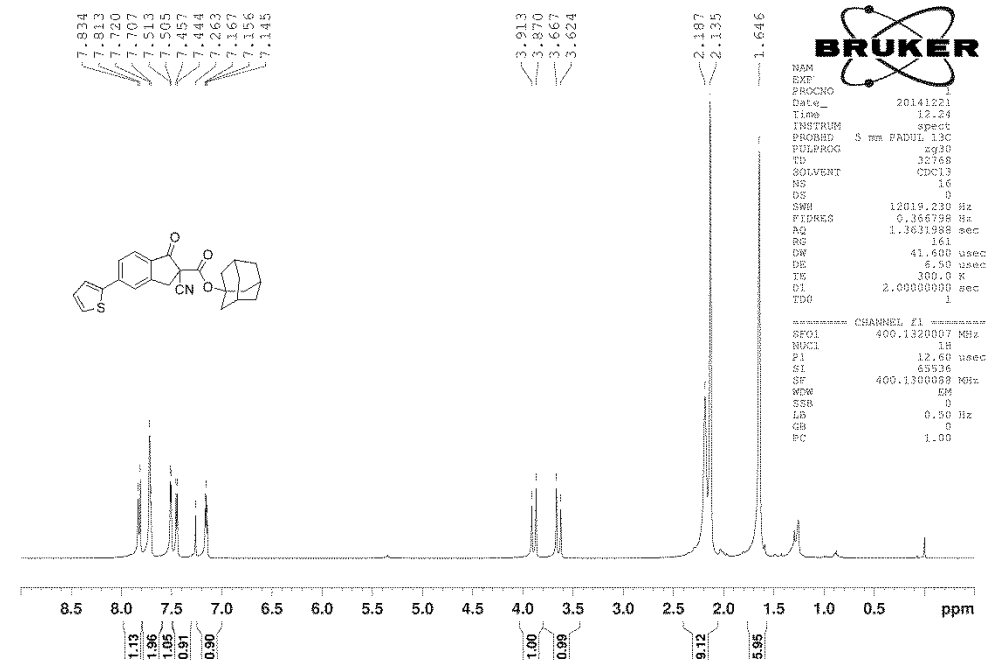


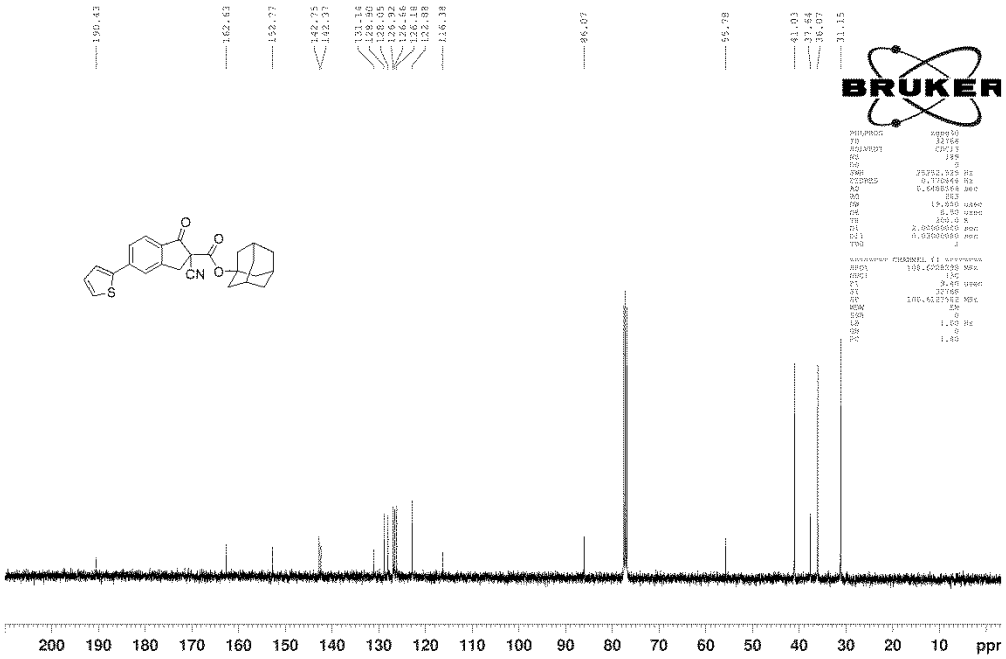
(S)-1-Adamantyl-2-cyano-5-(2-methoxyphenyl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (4u)





(S)-1-Adamantyl -2-cyano-1-oxo-5-(thiophen-2-yl)-2,3-dihydro-1H-indene-2-carboxylate (4v)





(S)-1-Adamantyl-2-cyano-1-oxo-5-(phenylethynyl)-2,3-dihydro-1H-indene-2-carboxylate (4w)