Supplementary Material (ESI) for Chemical Communications

A *N*-heterocyclic carbene derived highly regioselective ambident C-C-S and C-C-N 1,3-dipolar system

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Melting points are uncorrected. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) were recorded in $CDCl_3$ otherwise as indicated. *N, N'*-Dialkylbenzimidazolium salts were prepared by alkylation of benzimidazole with alkyl halides,[1] while *N, N'*-dialkylimidazolium salts were prepared from *N, N'*-dialkylethylenediamine and triethyl orthoformate according to the method described in the literature.[2]

(1). O. V. Starikova, G. V. Dolgushin, L.I. Larina, T. N, Komarova, V. A. Lopyrev, *ARKIVOC* 2003, **13**, 119.
(2). A. J. Arduengo, III, R. Krafczyk, R. Schmutzler, *Tetrahedron* **1999**, **55**, 14523.

1. General procedure for the preparation of 2-thiocarbamoyl benzimidazolium inner salts 1 and 2-thiocarbamoyl imidazolinium inner salts 2

At ambient temperature, a *N, N'*-dialkylbenzimidazolium bromide or imidazolinium chloride (5 mmol) was mixed with phenyl isothiocyanate (5 mmol) in dry THF (50 cm^3). Under nitrogen atmosphere, NaH (6 mmol, 50% in mineral oil) was added in portions to the mixture at 10-20 ^oC. The resulting mixture was then stirred for 2-5 h (for benzimidazolium salts) or 18-24 h (for imidazolinium salts) at 10-20 ^oC. After the reaction, the remaining sodium hydride was quenched by adding water (10 cm^3) dropwise. The solvent was removed and the residue was extracted with dichloromethane (50×3 cm^3). The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated to give 2-thiocarbamoyl benzimidazolium inner salts **1** as yellow crystals or the crude 2-thiocarbamoyl imidazolinium inner salts as sticky oil. The products **1** were further purified by recrystallization from dichloromethane and petroleum ether (30-60 ^oC), while the pure 2-thiocarbamoyl imidazolinium inner salts **2** were obtained by column chromatography on silica gel eluting with a mixture of petroleum ether (30-60 ^oC) and dichloromethane (1:1).

1,3-Diethyl-2-*N*-phenylthiocarbamoyl benzimidazolium inner salt (1a).

63 %, mp 168-169 ^oC; IR *v* (cm^{-1}) 1589, 1502, 1477, 1468; ^{1}H NMR (CD_3OD) δ (ppm): 7.93-7.94 (m, 2H), 7.67-7.68 (m, 2H), 7.35-7.40 (m, 4H), 7.12 (t, *J* 6.7 Hz, 1H), 4.62 (q, *J* 7.3 Hz, 4H), 1.63 (t, *J* 7.3 Hz, 6H); ^{13}C NMR δ (ppm): 166.1, 150.3, 149.7, 130.2, 128.6, 127.1, 126.2, 124.0, 122.5, 112.5, 41.3, 14.5; MS (ESI): 310 [M+1]. Found: C 70.31, H 6.35, N 13.56. Calcd. for $C_{18}H_{19}N_3S$: C 69.87, H 6.19, N 13.58.

1,3-Dibutyl-2-*N*-phenylthiocarbamoyl benzimidazolium inner salt (1b).

69%, mp 149-150 ^oC; IR *v* (cm^{-1}) 1588, 1539, 1502, 1471; ^{1}H NMR δ (ppm): 7.62 (brs, 2H), 7.59 (brs, 2H), 7.45 (brs, 4H), 7.14 (brs, 1H), 4.57 (brs, 4H), 2.09 (qt, *J* 7.7 Hz, 4H), 1.50-1.54 (m, 4H), 1.02 (t, *J* 7.3 Hz, 6H); ^{13}C NMR δ (ppm) 166.3, 150.7, 150.0, 130.5, 129.2, 128.6, 126.1, 123.7, 122.8, 122.2, 45.9, 31.3, 20.3, 13.7; MS (ESI): 366 (M+1). Found: C 72.36, H 7.40, N 11.34. Calcd. for $C_{22}H_{27}N_3S$: C 72.29, H 7.45, N 11.50.

1,3-Dibenzyl-2-*N*-phenylthiocarbamoyl benzimidazolium inner salt (1c).

89%, mp 233-234 ^{o}C (lit.[3] mp 203-205 ^{o}C); IR *v* (cm^{-1}) 1591, 1523, 1497, 1464; ^{1}H NMR δ (ppm) 7.62 (brs, 4H), 7.37-7.43 (m, 14H), 7.17 (brs, 1H), 5.81 (brs, 4H); ^{13}C NMR δ (ppm) 165.7, 150.8, 150.4, 133.4, 130.5, 129.2, 128.8, 128.6, 128.4, 126.2, 124.0, 122.4, 113.4, 50.2; MS (ESI): 434 (M^{+}).

(3) Cetinkaya, B.; Cetinkaya, E.; Chamizo, J. A.; Hitchcock, P. B.; Jasim, H. A.; Kücükbay, H.; Lappert, M. F. *J. Chem. Soc., Perkin Trans. I* **1998**, 2047.

1-Butyl-3-ethyl-2-*N*-phenylthiocarbamoyl benzimidazolium inner salt (1d).

65%, mp 148-149 ^{o}C; IR *v* (cm^{-1}) 1591, 1537, 1504, 1480, 1469; ^{1}H NMR (CD_3OD) δ (ppm) 9.26 (dd, *J* 6.0 and 3.2 Hz, 2H), 8.93 (dd, *J* 6.0 and 3.0 Hz, 2H), 8.74 (d, *J* 7.6 Hz, 2H), 8.58 (t, *J* 7.7 Hz, 2H), 8.29 (t, *J* 7.3Hz, 1H), 5.88-5.96 (m, 4H), 3.30-3.37 (m, 2H), 2.89 (t, *J* 7.2 Hz, 3H), 2.75 (sx, *J* 7.5 Hz, 2H), 2.23 (t, *J* 7.4Hz, 3H); ^{13}C NMR δ (ppm) 166.3, 150.4, 149.7, 130.5, 130.0, 128.7, 126.2, 123.9, 122.3, 112.6, 112.4, 45.9, 41.3, 31.3, 20.3, 14.6, 13.7; MS (ESI) 338 (M+1). Found:C 71.12, H 7.11, N 12.31. Calcd for $C_{20}H_{23}N_3S$: C 71.18, H 6.87, N 12.45.

Butyl-3-isopropyl-2-*N*-phenylthiocarbamoyl benzimidazolium inner salt (1e).

67%, mp 131-132 ^{o}C; IR *v* (cm^{-1}) 1535, 1508, 1467, 1443; ^{1}H NMR δ (ppm) 7.79 (d, *J* 7.7 Hz, 1H), 7.61 (d, *J* 7.7 Hz, 1H), 7.50-7.57 (m, 4H), 7.43 (t, *J* 7.5 Hz, 2H), 7.13 (t, *J* 7.1 Hz, 1H), 5.40-5.46 (m, 1H), 4.49 (t, *J* 7.1 Hz, 2H), 2.09 (qt, *J* 7.6 Hz, 2H), 1.81 (d, *J* 6.9 Hz, 6H), 1.53 (sx, *J* 7.5 Hz, 2H), 1.02 (t, *J* 7.4 Hz, 3H); ^{13}C NMR δ (ppm) 166.7, 150.6, 149.7, 131.2, 128.8, 128.6, 125.7, 125.6, 123.8, 122.4, 114.6, 112.8, 51.8, 45.9, 31.2, 20.9, 20.3, 13.7; MS (ESI) 352 (M+1). Found: C 71.37, H 7.00, N 11.63. Calcd. for $C_{21}H_{25}N_3S$: C 71.75, H 7.17, N 11.95.

Benzyl-3-ethyl-2-*N*-phenylthiocarbamoyl benzimidazolium inner salt (1f).

78%, mp 186-187 ^{o}C; IR *v* (cm^{-1}) 1588, 1529, 1504, 1473, 1466; ^{1}H NMR δ (ppm) 7.59-7.64 (m, 3H), 7.55 (t, *J* 7.7 Hz, 2H), 7.40-7.45 (m, 5H), 7.35-7.39 (m, 3H), 7.16 (brs, 1H), 5.77 (s, 2H), 4.66 (q, *J* 7.3 Hz, 2H), 1.73 (t, *J* 7.3 Hz, 3H); ^{13}C NMR δ (ppm) 166.0, 150.2, 133.5, 130.5, 130.2, 129.1, 128.8, 128.6, 128.4, 126.2, 124.0, 122.5, 113.5, 112.4, 50.0, 41.5, 14.6; MS (ESI) 372 (M+1). Found: C 74.11, H 6.05, N 11.26. Calcd. for $C_{23}H_{21}N_3S$: C 74.36, H 5.70, N 11.31.

Benzyl-3-butyl-2-*N*-phenylthiocarbamoyl benzimidazolium inner salt (1g).

76%, mp 165-166 ^{o}C; IR *v* (cm^{-1}) 1590, 1499, 1476, 1467; ^{1}H NMR δ (ppm) 7.59-7.62 (m, 3H), 7.53 (t, *J* 8.0 Hz, 1H), 7.40-7.49 (m, 5H), 7.33-7.37 (m, 3H), 7.15 (brs, 1H), 5.78 (s, 2H), 4.61 (t, *J* 7.6 Hz, 2H), 2.12 (qt, *J* 7.7 Hz, 2H), 1.54 (sx, *J* 7.6 Hz, 2H), 1.03 (t, *J* 7.3 Hz, 3H); ^{13}C NMR δ (ppm) 166.0, 150.7, 150.3, 133.6, 130.5, 130.3, 129.1, 128.8, 128.6, 128.5, 126.2, 123.8, 122.4, 113.4, 112.6, 49.9, 46.1, 31.2, 20.3, 13.7; MS (ESI) 400 (M+1). Found: C 75.19, H 6.51, N 10.39. Calcd. for $C_{25}H_{25}N_3S$: C 75.15, H 6.31, N 10.52.

1,3-Diethyl-2-*N*-phenylthiocarbamoyl imidazolinium inner salt (2a).

63%, mp 147-148 ^{o}C; IR *v* (cm^{-1}) 1586, 1523.; ^{1}H NMR δ (ppm) (CD_3COCD_3): 7.33 (d, *J* 7.9 Hz, 2H), 7.26 (t, *J* 7.6 Hz, 2H), 6.98 (t, *J* 7.3 Hz, 1H), 3.98 (s, 4H), 3.58 (q, *J* 7.2 Hz, 4H), 1.29 (t, *J* 7.2 Hz, 6H). ^{13}C NMR δ (ppm) 166.9, 163.6, 150.3, 128.5, 123.5, 122.4, 46.3, 42.0, 12.7; MS (ESI) 262 (M+1). Found: C 64.27, H 7.07, N 16.06. Calcd for $C_{14}H_{19}N_3S$: C 64.33, H 7.33, N 16.08.

1,3-Dibutyl-2-*N*-phenylthiocarbamoyl imidazolinium inner salt (2b).

67%, mp 96-97 ^{o}C; IR *v* (cm^{-1}) 1585, 1516; ^{1}H NMR δ (ppm) 7.36-7.39 (m, 4H), 7.09 (t, *J* 6.5 Hz, 1H), 3.86 (s, 4H), 3.62 (br, 4H), 1.72 (br, 4H), 1.42 (sx, *J* 7.5 Hz, 4H), 0.97 (t, *J* 7.4 Hz, 6H). ^{13}C NMR δ (ppm) 167.0, 163.9, 150.4, 128.5, 123.4, 122.2, 47.0 (d), 29.4, 9.9, 13.7; MS (ESI): 318 (M+1). Found: C 67.87, H 8.24, N 13.15. Calcd for $C_{18}H_{27}N_3S$: C 68.10, H 8.57, N 13.24.

1,3-Di-*tert*-butyl-2-*N*-phenylthiocarbamoyl imidazolinium inner salt (2c).
70%, mp 200-201 ^{o}C; IR ν (cm^{-1}) 1592, 1529, 1514, 1496; ^{1}H NMR δ (ppm) 7.53 (d, *J* 7.2 Hz, 2H), 7.38 (t, *J* 7.6 Hz, 2H), 7.09 (t, *J* 7.2 Hz, 1H), 3.82 (s, 4H), 1.67 (s, 18H); ^{13}C NMR δ (ppm) 170.3, 163.3, 149.6, 128.4, 123.6, 122.3, 60.2, 44.5, 28.4; MS (ESI) 318 (M+1). Found: C 67.82, H 8.41, N 13.10. Calcd for $C_{18}H_{27}N_3S$: C 68.10, H 8.57, N 13.24.

1,3-Dibenzyl-2-*N*-phenylthiocarbamoyl imidazolinium inner salt (2d).
68%, mp 185-187 ^{o}C; IR ν (cm^{-1}) 1592, 1578, 1518; ^{1}H NMR δ (ppm) 7.55 (d, *J* 6.9 Hz, 4H), 7.45 (d, *J* 7.6 Hz, 2H), 7.36-7.42 (m, 8H), 7.10 (t, *J* 7.3 Hz, 1H), 4.82 (s, 4H), 3.60 (s, 4H); ^{13}C NMR δ (ppm) 166.6, 163.6, 150.4, 133.3, 129.1 (d), 128.8, 128.6, 123.7, 122.4, 51.3, 46.2; MS (ESI) 386 (M+1). Found: C 74.65, H 6.37, N 10.63. Calcd for $C_{24}H_{23}N_3S$: C 74.77, H 6.01, N 10.90.

1,3-Di(p-methoxy)benzyl-2-*N*-phenylthiocarbamoyl imidazolinium inner salt (2e).
73%, mp 177-179 ^{o}C; IR ν (cm^{-1}) 1611, 1578, 1511; ^{1}H NMR δ (ppm) 7.48 (d, *J* 8.2 Hz, 6H), 7.41 (t, *J* 7.5 Hz, 2H), 7.12 (t, *J* 7.3 Hz, 1H), 6.92 (d, *J* 8.3 Hz, 4H), 4.76 (s, 4H), 3.83 (s, 6H), 3.59 (s, 4H); ^{13}C NMR δ (ppm) 166.8, 163.3, 160.0, 150.2, 130.6, 128.6, 125.2, 123.6, 122.4, 114.4, 55.3, 50.7, 46.0; MS (ESI) 446 [M+1]. Found: C 69.62, H 6.08, N 9.31. Calcd for $C_{26}H_{27}N_3O_2S$: C 70.09, H 6.11, N 9.43.

2. General procedure for the reaction of 2-thiocarbamoyl benzimidazolium inner salts 1 or 2-thiocarbamoyl imidazolinium inner salts 2 with dimethyl acetylenedicarboxylate (DMAD).
At ambient temperature (20-30 ^{o}C), the solution of DMAD (1 mmol) in solvent (10 cm^3) was added dropwise to the yellow solution of benzimidazolium salts **1** (1 mmol) or imidazolinium salts **2** (1 mmol) in solvent (20 cm^3). The reaction mixture turned into a dark solution immediately. The mixture was then stirred at room temperature or at the refluxing temperature of the solvent for a period of time. After removal of the solvent, the residue was chromatographied on silica gel eluting with a mixture of petroleum ether (30-60 ^{o}C) and ethyl acetate (5:1). The red purple crystals **3** along with tiny amount of green products **4**, or pale yellow crystalline products **5** and a tiny amount of orange crystals **6** were isolated.

Table 1 The chemical yields of products from the reaction between **1** or **2** and DMAD under the optimal conditions.

Starting materials	R^1 R^2	**1, 2** : DMAD	Solvent	Temp. (^oC)	Time (h)	Products	Yield (%)
1a	Et	1:1	$ClCH_2CH_2Cl$	20-30	0.5	**3a**	93
	Et					**4a**	-*
1b	*n*-Bu	1:1	$ClCH_2CH_2Cl$	20-30	0.5	**3b**	90
	n-Bu					**4b**	4
1c	Bz	1:1	$ClCH_2CH_2Cl$	20-30	0.5	**3c**	95
	Bz					**4c**	-*
1d	Et	1:1	$ClCH_2CH_2Cl$	20-30	0.5	**3d**	92
	n-Bu					**4d**	-*
1e	*i*-Pr	1:1	$ClCH_2CH_2Cl$	20-30	0.5	**3e**	90
	n-Bu					**4e**	-*
1f	Et	1:1	$ClCH_2CH_2Cl$	20-30	0.5	**3f**	91
	Bz					**4f**	-*
1g	*n*-Bu	1:1	$ClCH_2CH_2Cl$	20-30	0.5	**3g**	94
	Bz					**4g**	4
2a	Et	1:1	$ClCH_2CH_2Cl$	20-30	0.5	**5a**	95
	Et					**6a**	-*
2b	*n*-Bu	1:1	$ClCH_2CH_2Cl$	20-30	0.5	**5a**	93
	n-Bu					**6a**	-*
2c	*t*-Bu	1:1	$ClCH_2CH_2Cl$	20-30	0.5	**5b**	94
	t-Bu					**6b**	-*
2d	Bz	1:1	$ClCH_2CH_2Cl$	20-30	0.5	**5c**	92
	Bz					**6c**	3
2e	MeOBz	1:1	$ClCH_2CH_2Cl$	20-30	0.5	**5d**	93
	MeOBz					**6d**	2

* A tiny amount of minor product was observed.

Table 2 The optimization of reaction between **1** and dimethyl acetylenedicarboxylate.

Starting materials	R^1 R^2	**1** : DMAD	Solvent	Temp. (oC)	Time (h)	Product	Yield (%)
1b	*n*-Bu	1:1	$ClCH_2CH_2Cl$	20-30	0.5	**3b**	90
	n-Bu					**4b**	4
1b	*n*-Bu	1:1	$ClCH_2CH_2Cl$	50-60	0.5	**3b**	90
	n-Bu					**4b**	5
1b	*n*-Bu	1:1	$ClCH_2CH_2Cl$	50-60	18	**3b**	21
	n-Bu					**4b**	-*
1b	*n*-Bu	1:1	CH_3COCH_3	50-60	0.5	**3b**	85
	n-Bu					**4b**	6
1b	*n*-Bu	1:1	THF	50-60	0.5	**3b**	64
	n-Bu					**4b**	8
1b	*n*-Bu	1:1	CH_3CN	50-60	0.5	**3b**	78
	n-Bu					**4b**	-*

*A tiny amount of minor product was observed.

Dimethyl 1,3-diethyl-2'-phenylimino-2',3'-dihydrospiro[benzimidazoline-2,3'-thiophene]-4',5'-dicarboxylate (3a). 91%, mp 103-104 ^oC, IR ν (cm^{-1}) 1739, 1719, 1648, 1594, 1494; ^1H NMR (C_6D_6) δ (ppm) 7.19 (t, *J* 7.8 Hz, 2H), 7.00-7.03 (m, 3H), 6.87 (dd, *J* 4.4 and 3.3 Hz, 2H), 6.45 (dd, *J* 4.3 and 3.3 Hz, 2H), 3.44 (s, 3H), 3.32-3.40 (m, 4H), 3.30 (s, 3H), 1.35 (t, *J* 7.2 Hz, 6H); ^{13}C NMR δ (ppm) 166.0, 163.9, 161.5, 150.9, 139.3, 132.1, 129.3, 126.1, 125.9, 119.3, 118.2, 122.7, 103.3, 53.4, 52.8, 39.4, 14.2; MS (ESI) 452 [M+1]. Found: C 64.03, H 5.75, N 9.32. Calcd for $C_{24}H_{25}N_3O_4S$: C 63.84, H 5.58, N 9.31.

Dimethyl 1,3-dibutyl-2'-phenylimino-2',3'-dihydrospiro[benzimidazoline-2,3'-thiophene]-4',5'-dicarboxylate (3b). 90% mp 70-71 ^oC, IR ν (cm^{-1}) 1740, 1720, 1644, 1593, 1501; ^1H NMR (C_6D_6) δ (ppm) 7.21 (t, *J* 7.8 Hz, 2H), 7.14 (d, *J* 7.6 Hz, 2H), 7.02 (t, *J* 7.3 Hz, 1H), 6.89 (dd, *J* 5.2 and 3.1 Hz, 2H), 6.51 (dd, *J* 5.1 and 3.2 Hz, 2H), 3.39-3.49 (m, 4H), 3.43 (s, 3H), 3.30 (s, 3H), 1.79-1.93 (m, 4H), 1.36-1.41 (m, 4H), 0.93 (t, *J* 7.3 Hz, 6H); ^{13}C NMR δ (ppm) 166.5, 163.8, 161.6, 150.9, 139.6, 132.4, 131.5, 129.3, 125.9, 119.3, 118.2, 112.8, 103.3, 53.4, 52.6, 45.1, 31.2, 20.6, 14.0; MS (TOF) 506 (M-1)/507 (M^+)/508 (M+1). Found C 66.32, H 6.43, N 8.20. Calcd for $C_{28}H_{33}N_3O_4S$: C 66.25, H 6.55, N 8.28.

Dimethyl 1,3-dibutyl-1'-phenyl-2',3'-dihydrospiro[benzimidazoline-2,3'-pyrrole]-2'-thione-4',5'-dicarboxylate (4b). 5%, 122-123 ^oC, IR ν (cm^{-1}) 1755, 1702, 1646, 1595, 1497; ^1H NMR δ (ppm) 7.47-7.55 (m, 3H), 7.28 (d, *J* 7.3 Hz, 2H), 6.61 (dd, *J* 5.4 and 3.2Hz, 2H), 6.32 (dd, *J* 5.4 and 3.2Hz, 2H), 3.74 (s, 3H), 3.67 (s, 3H), 3.15 (qt, *J* 7.3 Hz, 2H), 3.02 (qt, *J* 7.2 Hz, 2H), 1.60 (qt, *J* 7.4 Hz, 4H), 1.38 (m, 4H), 0.94 (t, *J* 7.3 Hz, 6H); ^{13}C NMR δ (ppm) 208.5, 161.5, 160.9, 147.1, 140.0, 135.7, 129.8, 127.4, 117.8, 113.6, 103.1, 97.6, 53.5, 52.0, 44.8, 31.0, 20.5, 14.0; MS (TOF) 506 [M-1]. Found C 66.41, H 6.85, N 8.38. Calcd for $C_{28}H_{33}N_3O_4S$: C 66.25, H 6.55, N 8.28.

Dimethyl 1,3-dibenzyl-2'-phenylimino-2',3'-dihydrospiro[benzimidazoline-2,3'-thiophene]-4',5'-dicarboxylate (3c). 95%, mp 123-124 ^oC; IR ν (cm^{-1}) 1739, 1734, 1640, 1495; ^1H NMR (C_6D_6) δ (ppm) 7.63 (d, *J* 7.4 Hz, 4H), 7.23 (t, *J* 7.6 Hz, 4H), 7.11-7.18 (m, 4H), 6.98 (t, *J* 7.4 Hz, 1H), 6.75 (d, *J* 7.6 Hz, 2H), 6.66 (dd, *J* 5.4

and 3.2Hz, 2H), 6.32 (dd, *J* 5.4 and 3.2 Hz, 2H), 4.74 (d, *J* 16.2 Hz, 2H), 4.60 (d, *J* 16.2 Hz, 2H), 3.42 (s, 3H), 3.30 (s, 3H); ^{13}C NMR δ (ppm) 165.4, 163.7, 161.6, 150.6, 139.5, 137.6, 134.8, 129.8, 129.1, 128.7, 128.1, 127.6, 127.3, 125.8, 119.3, 118.8, 113.5, 104.9, 53.4, 52.7, 49.1; MS (ESI) 576 (M+1). Found C 70.92, H 5.19, N 7.59. Calcd for $C_{34}H_{29}N_3O_4S$: C 70.94, H 5.08, N 7.30.

Dimethyl 1-butyl-3-ethyl-2'-phenylimino-2',3'-dihydrospiro[benzimidazoline-2,3'-thiophene]-4',5'-dicarboxylate (3d). 92%, mp 67-68 °C; IR *ν* (cm^{-1}) 1740, 1728, 1644, 1493; ^{1}H NMR (C_6D_6) δ (ppm) 7.20 (t, *J* 7.8 Hz, 2H), 7.07 (d, *J* 7.7 Hz, 2H), 7.02 (t, *J* 7.4 Hz, 1H), 6.88-6.89 (m, 2H), 6.50-6.52 (m, 1H), 6.45-6.46 (m, 1H), 3.43 (t, *J* 7.6 Hz, 2H), 3.43 (s, 3H), 3.46 (q, *J* 7.2 Hz, 2H), 3.29 (s, 3H), 1.83-1.89 (m, 2H), 1.32-1.40 (m, 2H), 1.34 (t, *J* 7.1 Hz, 3H), 0.95 (t, *J* 7.3 Hz, 3H); ^{13}C NMR δ (ppm) 166.3, 163.8, 161.6, 150.9, 139.7, 139.1, 132.3, 129.3, 125.9, 119.3, 118.2, 112.8, 112.6, 103.4, 103.2, 53.4, 52.7, 45.0, 39.4, 31.1, 20.6, 14.2, 14.0. HRMS (FAB) 480.1944 (M+1). Found C 65.18, H 6.48, N 8.64. Calcd for $C_{26}H_{29}N_3O_4S$: C 65.11, H 6.09, N 8.76.

Dimethyl 1-butyl-3-isopropyl-2'-phenylimino-2',3'-dihydrospiro[benzimidazoline-2,3'-thiophene]-4',5'-dicarboxylate (3e). 90%, mp 91-92 °C, IR *ν* (cm^{-1}) 1739, 1642, 1593, 1490; ^{1}H NMR (C_6D_6) δ (ppm) 7.21 (t, *J* 8.0 Hz, 2H), 7.10 (d, *J* 7.5 Hz, 2H), 7.02 (t, *J* 7.4 Hz, 1H), 6.84-6.87 (m, 2H), 6.57 (d, *J* 8.1 Hz, 1H), 6.52 (d, *J* 8.1 Hz, 1H), 3.60 (qt, *J* 6.8 Hz, 1H), 3.37-3.42 (m, 2H), 3.43 (s, 3H), 3.31 (s, 3H), 1.82-1.91 (m, 2H), 1.54 (d, *J* 6.8 Hz, 3H), 1.49 (d, *J* 6.8 Hz, 3H), 1.36 (sx, *J* 7.5 Hz, 2H), 0.93 (t, *J* 7.3 Hz, 3H); ^{13}C NMR (C_6D_6) δ (ppm) 166.0, 163.2, 161.8, 150.8, 140.9, 136.6, 134.0, 131.3, 129.4, 125.9, 119.7, 118.2, 117.7, 105.4, 103.5, 102.0, 52.5, 51.9, 47.1, 45.1, 31.2, 20.8, 20.7, 19.0, 13.9; MS (ESI) 494 (M+1). Found: C 65.67, H 6.58, N 8.51. Calcd for $C_{27}H_{31}N_3O_4S$: C 65.70, H 6.33, N 8.51.

Dimethyl 1-benzyl-3-ethyl-2'-phenylimino-2',3'-dihydrospiro[benzimidazoline-2,3'-thiophene]-4',5'-dicarboxylate (3f). 91%, mp 125-126 °C, IR *ν* (cm^{-1}) 1744, 1732, 150, 1490; ^{1}H NMR (C_6D_6) δ (ppm) 7.56 (d, *J* 7.4 Hz, 2H), 7.15-7.21 (m, 5H), 7.01 (t, *J* 7.2 Hz, 1H), 6.89 (d, *J* 7.9 Hz, 2H), 6.84 (t, *J* 7.6 Hz, 1H), 6.69 (t, *J* 7.5 Hz, 1H), 6.45 (d, *J* 7.4 Hz, 1H), 6.29 (d, *J* 7.4 Hz, 1H), 4.69 (d, *J* 16.2 Hz, 1H), 4.57 (d, *J* 16.2 Hz, 1H), 3.43 (s, 3H), 3.36-3.41 (m, 2H), 3.30 (s, 3H), 1.37 (t, *J* 7.1 Hz, 3H); ^{13}C NMR δ (ppm) 166.0, 163.9, 161.5, 150.8, 139.4, 139.3, 137.6, 133.2, 131.2, 129.2, 128.5, 127.5, 127.2, 125.9, 119.3, 118.9, 118.2, 104.9, 103.4, 102.1, 53.5, 52.8, 48.9, 39.6, 14.3; HRMS (FAB): 514.1791 (M+1). Found: C 67.96, H 5.60, N 8.23. Calcd for $C_{29}H_{27}N_3O_4S$: C 67.82, H 5.30, N 8.18.

Dimethyl 1-benzyl-3-butyl-2'-phenylimino-2',3'-dihydrospiro[benzimidazoline-2,3'-thiophene]-4',5'-dicarboxylate (3g). 94%, mp 128-129 °C; IR *ν* (cm^{-1}) 1741, 1644, 1496; ^{1}H NMR δ (ppm) 7.48 (d, *J* 7.3 Hz, 2H), 7.25-7.33 (m, 5H), 7.16 (t, *J* 7.4 Hz, 1H), 6.74 (d, *J* 7.7 Hz, 2H), 6.61 (t, *J* 6.9 Hz, 1H), 6.48 (t, *J* 7.4 Hz, 1H), 6.35 (d, *J* 7.3 Hz, 1H), 6.05 (d, *J* 7.4 Hz, 1H), 4.51 (d, *J* 16.1 Hz, 1H), 4.34 (d, *J* 15.7 Hz, 1H), 3.86 (s, 3H), 3.64 (s, 3H), 3.30 (br, 1H), 3.19 (br, 1H), 1.69-1.78 (m, 2H), 1.43 (sx, *J* 7.3 Hz, 2H), 0.97 (t, *J* 7.3 Hz, 3H); ^{13}C NMR δ (ppm) 166.1, 163.8, 161.6, 150.8, 139.8, 139.3, 137.7, 133.5, 130.7, 129.2, 128.5, 127.5, 127.2, 125.9, 119.3, 118.9, 118.2, 104.7, 103.5, 102.1, 53.4, 52.7, 49.0, 45.3, 31.3, 20.6, 14.0; MS (ESI) 542 (M+1). Found C 69.01, H 6.13, N 7.95. Calcd for $C_{31}H_{31}N_3O_4S$: C 68.74, H 5.77, N 7.76.

Dimethyl 1-benzyl-3-butyl-1'-phenyl-2',3'-dihydrospiro[benzimidazoline-2,3'-pyrrole]-2'-thione-4',5'-dicarboxylate (4g). 6%, mp 126-127 °C; IR *ν* (cm^{-1}) 1750, 1707, 1641, 1596, 1496; ^{1}H NMR δ (ppm) 7.46-7.51 (m, 3H), 7.42 (d, *J* 7.0 Hz, 2H), 7.30-7.34 (m, 3H), 7.16 (d, *J* 6.9 Hz, 2H), 6.64 (t, *J* 7.5 Hz, 1H), 6.53 (t, *J*

7.5 Hz, 1H), 6.36 (d, *J* 7.4 Hz, 1H), 6.15 (d, *J* 7.3 Hz, 1H), 4.32 (d, *J* 15.6 Hz, 1H), 4.22 (d, *J* 15.7 Hz, 1H), 3.70 (s, 3H), 3.66 (s, 3H), 3.15-3.19 (m, 1H), 3.01-3.05 (m, 1H), 1.61 (qt, *J* 7.5 Hz, 2H), 1.37-1.42 (m, 2H), 0.95 (t, *J* 7.3 Hz, 3H); ^{13}C NMR δ (ppm) 206.7, 161.2, 160.6, 147.5, 140.3, 139.9, 137.3, 135.6, 129.7, 129.6, 128.4, 128.1, 127.4, 118.6, 117.8, 113.1, 104.7, 103.4, 97.6, 53.2. 51.8, 49.2, 44.8, 31.0, 20.5, 13.9; MS (TOF) 540 (M-1)/541 (M^+)/542 (M+1). Found C 68.71, H 6.06, N 7.82. Calcd for $C_{31}H_{31}N_3O_4S$: C 68.74, H 5.77, N 7.76.

Dimethyl

1,3-diethyl-2'-phenylimino-2',3'-dihydrospiro[imidazolidine-2,3'-thiophene]-4',5'-dicarboxylate (5a). 95%, mp 140-141 °C; IR *v* (cm^{-1}) 1740, 1644, 1593; ^{1}H NMR δ (ppm) 7.38 (t, *J* 7.7 Hz, 2H), 7.19 (t, *J* 7.4 Hz, 2H), 6.98 (d, *J* 7.4 Hz, 2H), 3.89 (s, 3H), 3.82 (s, 3H), 3.45-3.46 (m, 2H), 3.19-3.21 (m, 2H), 2.80-2.86 (m, 2H), 2.63-2.68 (m, 2H), 1.16 (t, *J* 7.1 Hz, 6H); ^{13}C NMR δ (ppm) 167.3, 164.6, 161.0, 151.2, 138.7, 131.7, 129.3, 125.4, 119.7, 98.1, 53.1, 52.6, 47.9, 43.3, 14.2; MS (EI) 241 (80), 300 (100), 404 (M+1, 45%). Anal. Calcd for $C_{20}H_{25}N_3O_4S$: C 59.53, H 6.25, N 10.41. Found: C 59.54, H 6.55, N 10.37.

Dimethyl

1,3-dibutyl-2'-phenylimino-2',3'-dihydrospiro[imidazolidine-2,3'-thiophene]-4',5'-dicarboxylate (5b).

93%, mp 80-81 °C; IR *v* (cm^{-1}) 1739, 1726, 1637; ^{1}H NMR δ (ppm) 7.39 (t, *J* 7.7 Hz, 2H), 7.20 (t, *J* 7.4 Hz, 1H), 6.99 (d, *J* 7.6 Hz, 2H), 3.86 (s, 3H), 3.83 (s, 3H), 3.40 (brs, 2H), 3.21 (brs, 2H), 2.73-2.79 (m, 2H), 2.60-2.64 (m, 2H), 1.53 (qt, *J* 7.3 Hz, 4H), 1.41-1.46 (m, 2H), 1.33-1.39 (m, 2H), 0.94 (t, *J* 7.3 Hz, 6H) ^{13}C NMR δ (ppm) 167.4, 164.5, 161.2, 151.3, 138.3, 132.2, 129.3, 125.4, 119.6, 98.2, 53.1, 52.3, 48.9. 48.3, 31.1, 20.4, 14.2; MS (ESI): 460 (M+1). Found: C 62.86, H 7.43, N 9.06. Calcd for $C_{24}H_{33}N_3O_4S$: C 62.72, H 7.24, N 9.14.

Dimethyl

1,3-di-*tert*-butyl-2'-phenylimino-2',3'-dihydrospiro[imidazolidine-2,3'-thiophene]-4',5'-dicarboxylate (5c). 94 %, mp 86-87 °C; IR *v* (cm^{-1}) 1736, 1725, 1637, 1591; ^{1}H NMR δ (ppm) 7.41 (t, *J* 7.7 Hz, 2H), 7.20 (t, *J* 7.4 Hz, 1H), 7.05 (d, *J* 7.7 Hz, 2H), 3.85 (s, 3H), 3.82 (s, 3H), 3.41 (t, *J* 5.8 Hz, 2H), 3.21 (t, *J* 5.4 Hz, 2H), 1.32 (s, 18H); ^{13}C NMR δ (ppm) 173.0, 164.6, 162.5, 151.4, 142.7, 131.7, 129.4, 125.4, 119.2, 94.5, 54.5, 52.9, 52.0, 44.1, 28.8; MS (ESI) 460 (M+1). Found: C 62.50, H 7.25, N 9.12. Calcd for $C_{24}H_{33}N_3O_4S$: C 62.72, H 7.24, N 9.14.

Dimethyl

1,3-dibenzyl-2'-phenylimino-2',3'-dihydrospiro[imidazolidine-2,3'-thiophene]-4',5'-dicarboxylate (5d).

92%, mp 177 °C (decomposed); IR *v* (cm^{-1}) 1737, 1725, 1640; ^{1}H NMR δ (ppm) 7.46-7.49 (m, 6H), 7.35 (t, *J* 7.3 Hz, 4H), 7.26-7.29 (m, 3H), 7.14 (d, *J* 7.5 Hz, 2H), 4.16 (d, *J* 12.7 Hz, 2H), 3.99 (s, 3H), 3.85 (s, 3H), 3.69 (d, *J* 12.7 Hz, 2H), 3.20-3.21 (m, 2H), 3.11-3.12 (m, 2H); ^{13}C NMR δ (ppm) 166.7, 164.6, 161.0, 151.0, 138.6, 137.6, 133.4, 129.5, 128.7, 128.2, 127.1, 125.8, 119.9, 97.8, 53.5, 53.2, 52.6, 48.3; MS (ESI): 528 (M+1). Found: C 68.00, H 5.90, N 7.86. Calcd for $C_{30}H_{29}N_3O_4S$: C 68.29, H 5.54, N 7.96.

Dimethyl

1,3-dibenzyl-1'-phenyl-2',3'-dihydrospiro[imidazolidine-2,3'-pyrrole]-2'-thione-4',5'-dicarboxylate (6d). 3%, mp 147-148 °C; IR *v* (cm^{-1}) 1751, 1724, 1639, 1495; ^{1}H NMR (C6D6) δ (ppm) 7.60 (d, *J* 7.4 Hz, 4H), 7.31 (t, *J* 7.4 Hz, 4H), 7.22 (t, *J* 7.3 Hz, 2H), 7.12-7.16 (m, 4H), 7.06-7.09 (m, 1H), 4.23 (d, *J* 13.2 Hz, 2H), 4.06 (d, *J* 13.2 Hz, 2H), 3.64 (s, 3H), 3.53-3.55 (m, 2H), 3.25-3.27 (m, 2H), 3.25 (s, 3H); ^{13}C NMR (C6D6) δ (ppm) 209.2, 161.8, 160.5, 147.0, 139.1, 136.7, 129.1, 129.0, 128.9,128.4, 127.2, 116.5, 95.1,

53.5, 52.2, 51.3, 47.9; MS (ESI) 528 (M+1). Found: C 68.21, H 5.62, N 7.99. Calcd for $C_{30}H_{29}N_3O_4S$: C 68.29, H 5.54, N 7.96.

Dimethyl 1,3-di-(p-methoxy)benzyl-2'-phenylimino-2',3'-dihydrospiro[imidazolidine-2,3'-thiophene]-4',5'-dicarboxylate (5e). 93%, mp174-180 ^oC (decomposed); IR ν (cm^{-1}) 1736, 1726, 1640, 1613, 1512; ^1H NMR δ (ppm) 7.46 (t, *J* 7.8 Hz, 2H), 7.38 (d, *J* 8.3 Hz, 4H), 7.26 (t, *J* 7.5 Hz, 1H), 7.13 (d, *J* 7.7 Hz, 2H), 6.87 (d, *J* 8.1 Hz, 4H), 4.08 (d, *J* 12.4 Hz, 2H), 4.00 (s, 3H), 3.84 (s, 3H), 3.82 (s, 6H), 3.64 (d, *J* 12.4Hz, 2H), 3.18 (brs, 2H), 3.10 (brs, 2H); ^{13}C NMR($CDCl_3$): 166.7, 164.6, 161.0, 158.8, 151.1, 137.8, 133.1, 130.7, 129.9, 129.5, 125.7, 119.9, 113.6, 97.7, 55.3, 53.2, 52.8, 52.6, 48.1; MS (ESI): 588 (M+1). Found: C 65.14, H 5.71, N 7.07. Calcd for $C_{32}H_{33}N_3O_6S$: C 65.40, H 5.66, N 7.15.

Dimethyl 1,3-di-(p-methoxy)benzyl-1'-phenyl-2',3'-dihydrospiro[imidazolidine-2,3'-pyrrole]-2'-thione-4',5'-dicarboxylate (6e). 2%, mp 98-99 ^oC; IR ν (cm^{-1}) 1748, 1718, 1635, 1612, 1512; ^1H NMR (C6D6) δ (ppm) 7.53 (d, *J* 8.4 Hz, 4H), 7.14-7.18 (m, 4H), 7.07-7.09 (m, 1H), 6.94 (d, *J* 8.5 Hz, 4H), 4.23 (d, *J* 12.9 Hz, 2H), 4.07 (d, *J* 12.9 Hz, 2H), 3.66 (s, 3H), 3.59-3.62 (m, 2H), 3.45 (s, 6H), 3.32-3.35 (m, 2H), 3.27 (s, 3H). ^{13}C NMR (C6D6) δ (ppm) 209.4, 161.9, 160.6, 159.3, 146.6, 136.8, 131.0, 130.2, 129.1, 128.8, 117.0, 113.9, 94.9, 54.6, 52.9, 52.1, 51.3, 48.0; MS(ESI) 588 (M+1).

3. General procedure for the reaction of 2-thiocarbamoyl benzimidazolium inner salts 1 or 2-thiocarbamoyl imidazolinium inner salts 2 with ethyl propiolate.

At ambient temperature (20-30 ^oC), ethyl propiolate (1-5 mmol) was mixed with benzimidazolium salts **1** (1 mmol) or imidazolinium salts **2** (1 mmol) in solvent (20 cm^3). The reaction mixture was stirred at room temperature or at the refluxing temperature of the solvent for a period of time. After removal of the solvent, the residue was chromatographied on silica gel eluting with a mixture of petroleum ether (30-60 ^oC) and ethyl acetate (5:1). The green crystalline products **7** and red by-products **8,** or orange crystalline products **9** and colorless crystalline by-products **10** were isolated.

Table 3 The chemical yield of products between **1** or **2** and ethyl propiolate under optimal conditions.

Starting materials	R^1 R^2	**1, 2** : ethyl propiolate	Solvent	Temp. (^oC)	Time	Product	Yield (%)
1a	Et	1:5	$ClCH_2CH_2Cl$	Refluxing	40 min	**7a**	84
	Et					**8a**	-*
1b	*n*-Bu	1:5	$ClCH_2CH_2Cl$	Refluxing	30 min	**7b**	80
	n-Bu					**8b**	-*
1c	Bz	1:5	$ClCH_2CH_2Cl$	Refluxing	50 min	**7c**	82
	Bz					**8c**	8
1d	Et	1:5	$ClCH_2CH_2Cl$	Refluxing	30 min	**7d**	87
	n-Bu					**8d**	-
1e	*i*-Pr	1:5	$ClCH_2CH_2Cl$	Refluxing	45 min	**7e**	86
	n-Bu					**8e**	-*
1f	Et	1:5	$ClCH_2CH_2Cl$	Refluxing	40 min	**7f**	85
	Bz					**8f**	7
1g	*n*-Bu	1:5	$ClCH_2CH_2Cl$	Refluxing	50 min	**7g**	82
	Bz					**8g**	-*
2d	Bz	1:5	THF	Refluxing	1.5 h	**9d**	73
	Bz					**10d**	15
2e	MeOBz	1:5	THF	Refluxing	1.5 h	**9e**	71
	MeOBz					**10e**	15

*A tiny amount of minor product was observed.

Table 4 The optimization of reaction of **1** or **2** with ethyl propiolate.

Starting materials	R^1 R^2	**1, 2** : ethyl propiolate	Solvent	Temp. (^oC)	Time (h)	Product	Yield (%)
1b	*n*-Bu	1:5	$ClCH_2CH_2Cl$	Refluxing	0.5	**7b**	80
	n-Bu					**8b**	3
1b	*n*-Bu	1:3	$ClCH_2CH_2Cl$	Refluxing	1	**7b**	72
	n-Bu					**8b**	4
1b	*n*-Bu	1:1	$ClCH_2CH_2Cl$	Refluxing	7	**7b**	52
	n-Bu					**8b**	2
1b	*n*-Bu	1:1	$ClCH_2CH_2Cl$	20-30	48	**7b**	23
	n-Bu					**8b**	4
1b	*n*-Bu	1:1	CH_3COCH_3	Refluxing	28	**7b**	67
	n-Bu					**8b**	2
1b	*n*-Bu	1:1	$CH_3CH_2COCH_3$	Refluxing	5	**7b**	59
	n-Bu					**8b**	-*
1b	*n*-Bu	1:1	1,4-dioxane	Refluxing	28	**7b**	52
	n-Bu					**8b**	-*
1b	*n*-Bu	1:1	THF	Refluxing	35	**7b**	59
	n-Bu					**8b**	4
2d	Bz	1:5	$ClCH_2CH_2Cl$	Refluxing	1	**9d**	34
	Bz					**10d**	12
2d	Bz	1:1	$ClCH_2CH_2Cl$	Refluxing	22	**9d**	38
	Bz					**10d**	9
2d	Bz	1:5	THF	Refluxing	1.5	**9d**	73
	Bz					**10d**	15
2d	Bz	1:1	THF	Refluxing	18	**9d**	55
	Bz					**10d**	13
2d	Bz	1:1	CH_3COCH_3	Refluxing	12	**9d**	57
	Bz					**10d**	16

*A tiny amount of minor product was observed.

Ethyl 1,3-diethyl-1'-phenyl-2',3'-dihydrospiro[benzimidazoline-2,3'-pyrrole]-2'-thione-4'-carboxylate (7a). 84%, 111-112 ^oC; IR *v* (cm^{-1}) 3104, 3057, 1701, 1640, 1594, 1502; ^1H NMR δ (ppm) 7.72 (s, 1H), 7.51-7.57 (m, 4H), 7.46 (t, *J* 7.0 Hz, 1H), 6.59 (dd, *J* 5.3 and 3.2 Hz, 2H), 6.29 (dd, *J* 5.3 and 3.2 Hz, 2H), 4.09 (q, *J* 7.1 Hz, 2H), 3.12-3.18 (m, 2H), 3.07-3.12 (m, 2H), 1.17 (t, *J* 7.2 Hz, 6H), 0.98 (t, *J* 7.1 Hz, 3H); ^{13}C NMR δ (ppm) 211.1, 161.7, 143.8, 139.4, 138.0, 129.6, 128.7, 124.9, 118.3, 117.5, 102.5, 60.3, 38.6, 13.8, 13.7; MS (TOF) 406 (M-1)/407 (M^+)/ 408 (M+1). Found: C 67.99, H 6.47, N 10.43. Calcd for: $C_{23}H_{25}N_3O_2S$: C 67.79, H 6.18, N 10.31.

Ethyl 1,3-dibutyl-1'-phenyl-2',3'-dihydrospiro[benzimidazoline-2,3'-pyrrole]-2'-thione-4'-carboxylate (7b).

80%, mp 135-136 ^oC; IR *v* (cm^{-1}) 3081, 1692, 1629, 1596, 1507; ^1H NMR δ (ppm) 7.74 (s, 1H), 7.56 (t, *J* 7.9 Hz, 2H), 7.49 (d, *J* 7.4 Hz, 2H), 7.46 (t, *J* 7.3 Hz, 1H), 6.58 (dd, *J* 5.4 and 3.2 Hz, 2H), 6.28 (dd, *J* 5.5 and 3.2 Hz, 2H), 4.11 (q, *J* 7.1 Hz, 2H), 3.05-3.08 (m, 2H), 2.97-3.04 (m, 2H), 1.53-1.59 (m, 4H), 1.33-1.37

(m, 4H), 1.02 (t, *J* 7.1 Hz, 3H), 0.92 (t, *J* 7.4 Hz, 6H); ^{13}C NMR δ (ppm) 209.8, 161.7, 144.3, 140.1, 138.0, 129.7, 128.7, 125.0, 118.2, 117.6, 102.7, 98.1, 60.4, 44.7, 30.9, 20.6, 13.9, 13.8; MS (TOF) 462 (M-1)/463 (M^+)/ 464 (M+1). Found: C 70.13, H 7.46, N 9.18. Calcd for $C_{27}H_{33}N_3O_2S$: C 69.95, H 7.17, N 9.06.

Ethyl

1,3-dibenzyl-1'-phenyl-2',3'-dihydrospiro[benzimidazoline-2,3'-pyrrole]-2'-thione-4'-carboxylate (7c).

82%, mp 162-163 ^{o}C; IR *v* (cm^{-1}) 3083, 3058, 1695, 1627, 1598, 1495; ^{1}H NMR δ (ppm) 7.53 (s, 1H), 7.48 (t, *J* 7.4 Hz, 2H), 7.41-7.43 (m, 5H), 7.27-7.32 (m, 8H), 6.53 (dd, *J* 5.4 and 3.2 Hz, 2H), 6.14 (dd, *J* 5.4 and 3.2 Hz, 2H), 4.31 (d, *J* 15.7 Hz, 2H), 4.18 (d, *J* 15.7 Hz, 2H), 4.14 (q, *J* 7.1 Hz, 2H), 1.13 (t, *J* 7.1 Hz, 3H); ^{13}C NMR δ (ppm) 204.8, 161.3, 145.5, 145.4, 140.4, 137.5, 129.5, 128.7, 128.4, 127.9, 127.3, 124.9, 118.4, 117.3, 104.9, 98.3, 60.4, 49.2, 14.0; MS (TOF) 531 (M^+). Found: C 74.68, H 5.69, N 7.98. Calcd for $C_{33}H_{29}N_3O_2S$: C 74.55, H 5 50, N 7.90.

Ethyl

1,3-dibenzyl-2'-phenylimino-2',3'-dihydrospiro[benzimidazoline-2,3'-thiophene]-4'-carboxylate (8c).

8%, mp135-136 ^{o}C; IR *v* (cm^{-1}) 3060, 1702, 1654, 1578, 1560; ^{1}H NMR δ (ppm) 7.80 (s, 1H), 7.47 (d, *J* 7.2 Hz, 4H), 7.27-7.37 (m, 7H), 7.15 (t, *J* 7.4 Hz, 1H), 6.60 (d, *J* 7.5 Hz, 2H), 6.54 (dd, *J* 5.4, 3.2 Hz, 2H), 6.15 (dd, *J* 5.4, 3.2 Hz, 2H), 4.38 (d, *J* 16.2 Hz, 2H), 4.44 (d, *J* 16.2 Hz, 2H), 4.12 (q, *J* 7.1 Hz, 2H), 1.02 (t, *J* 7.1 Hz, 3H); ^{13}C NMR δ (ppm) 168.0, 161.3, 150.8, 140.5, 140.0, 138.1, 129.1, 128.4, 127.5, 127.2, 125.5, 124.4, 119.3, 118.3, 103.8, 97.3, 60.8, 48.8, 13.7; MS (ESI) 532 (M+1). Found: C 74.15, H 5.82, N 7.78. Calcd for $C_{33}H_{29}N_3O_2S$: C 74.55, H 5.50, N 7.90.

Ethyl

1-butyl-3-ethyl-1'-phenyl-2',3'-dihydrospiro[benzimidazoline-2,3'-pyrrole]-2'-thione-4'-carboxylate (7d).

87%, mp 74-75 ^{o}C; IR *v* (cm^{-1}) 3088, 1692, 1633, 1596, 1509; ^{1}H NMR δ (ppm) 7.73 (s, 1H), 7.56 (t, *J* 7.4 Hz, 2H), 7.51 (d, *J* 7.3 Hz, 2H), 7.46 (t, *J* 7.2 Hz, 1H), 6.57-6.60 (m, 2H), 6.28 (m, 2H), 4.08-4.14 (m, 2H), 3.13-3.20 (m, 1H), 3.05-3.10 (m, 2H), 2.99-3.03 (m, 1H), 1.53-1.59 (m, 2H), 1.33-1.59 (m, 2H), 1.18 (t, *J* 7.2 Hz, 3H), 1.00 (t, *J* 7.1 Hz, 3H), 0.91 (t, *J* 7.3 Hz, 3H); ^{13}C NMR δ (ppm) 210.4, 161.7, 144.1, 140.1, 139.4, 138.0, 129.6, 128.7, 125.0, 118.2, 117.6, 117.5, 102.7, 102.4, 97.9, 60.3, 44.6, 38.7, 30.9, 20.6, 13.9, 13.8; MS (TOF) 434 (M-1)/435 (M^+)/ 436 (M+1). Found: C 69.05, H 6.95, N 9.61. Calcd for: $C_{25}H_{29}N_3O_2S$: C 68.93, H 6.71, N 9.65.

Ethyl

1-butyl-3-isopropyl-1'-phenyl-2',3'-dihydrospiro[benzimidazoline-2,3'-pyrrole]-2'-thione-4'-carboxylate (7e).

86%, mp 120-121 ^{o}C; IR *v* (cm^{-1}) 3085, 1692, 1633, 1595, 1506; ^{1}H NMR δ (ppm) 7.69 (s, 1H), 7.51-7.58 (m, 4H), 7.46 (t, *J* 7.2 Hz, 1H), 6.54 (m, 2H), 6.38 (m, 1H), 6.27 (m, 1H), 4.09 (q, *J* 7.1 Hz, 2H), 3.24 (qt, *J* 6.9 Hz, 1H), 3.01 (t, *J* 7.5 Hz, 1H), 1.54 (qt, *J* 7.3 Hz, 2H), 1.38 (d, *J* 6.9 Hz, 3H), 1.35 (q, *J* 7.3 Hz, 2H), 1.29 (d, *J* 6.8 Hz, 3H), 0.95 (t, *J* 7.1 Hz, 3H), 0.90 (t, *J* 7.3 Hz, 3H); ^{13}C NMR δ (ppm) 211.6, 161.9, 143.4, 140.8, 138.2, 136.5, 129.6, 128.7, 124.9, 118.4, 117.3, 116.7, 104.2, 102.6, 97.8, 60.3, 46.3, 44.4, 30.8, 20.6, 20.1, 19.5, 13.9, 13.6; MS (ESI): 450 (M+1). Found: C 69.46, H 6.95, N 9.30. Calcd for $C_{26}H_{31}N_3O_2S$: C 69.46, H 6.95, N 9.35.

Ethyl 1-benzyl-3-ethyl-1'-phenyl-2',3'-dihydrospiro[benzimidazoline-2,3'-pyrrole]-2'-thione-4'-carboxylate (7f).

85%, mp 116-117 ^{o}C; IR *v* (cm^{-1}) 3081, 1696□1631□1598□1499; ^{1}H NMR δ (ppm) 7.62 (s, 1H), 7.51 (t, *J* 7.6 Hz, 2H), 7.36-7.44 (m, 5H), 7.26-7.31 (m, 3H), 6.64 (t, *J* 7.5Hz, 1H), 6.51 (t, *J* 7.5 Hz, 1H), 6.34 (d, *J* 7.3 Hz, 1H), 6.12 (d, *J* 7.3 Hz, 1H), 4.27 (d, *J* 15.7 Hz, 1H), 4.20 (d, *J* 15.7 Hz, 1H), 4.10-4.16 (m, 2H), 3.16-3.22 (m, 1H), 3.07-3.12 (m, 1H), 1.20 (t, *J* 7.2 Hz, 3H), 1.06 (t, *J* 7.1, 3H); ^{13}C NMR δ (ppm) 208.0, 161.5, 144.7, 140.0, 139.8, 137.8, 137.6, 129.5, 128.7, 128.3, 127.9, 127.3, 125.0, 118.5, 117.8, 117.5, 104.5, 102.8, 98.0, 60.4, 49.1, 38.8, 13.9; MS (TOF): 468 (M-1)/469 (M^{+})/ 470 (M+1). Found: C 71.47, H 5.62, N 8.85. Calcd for: $C_{28}H_{27}N_3O_2S$: C 71.61, H 5.80, N 8.95.

Ethyl 1-benzyl-3-ethyl-2'-phenylimino-2',3'-dihydrospiro[benzimidazoline-2,3'-thiophene]-4'-carboxylate (8f).

7%, mp 102-103 ^{o}C; IR *v* (cm^{-1}) 3064, 1694, 1658, 1585, 1509; ^{1}H NMR δ (ppm) 7.81 (s, 1H), 7.44 (d, *J* 7.2 Hz, 2H), 7.25-7.34 (m, 6H), 7.16 (t, *J* 7.4 Hz, 1H), 6.74 (d, *J* 7.5 Hz, 2H), 6.62 (t, *J* 7.4 Hz, 1H), 6.50 (t, *J* 7.4 Hz, 1H), 6.32 (d, *J* 7.3 Hz, 1H), 6.10 (d, *J* 7.3 Hz, 1H), 4.36 (d, *J* 16.3 Hz, 1H), 4.28 (d, *J* 16.3 Hz, 1H), 4.10 (q, *J* 7.0 Hz, 2H), 3.19-3.31 (m, 2H), 1.26 (t, *J* 7.2 Hz, 3H), 0.98 (t, *J* 7.1 Hz, 3H); ^{13}C NMR δ (ppm) 169.0, 161.5, 151.0, 139.7, 139.5, 138.2, 129.1, 128.4, 127.4, 127.1, 125.6,124.9, 119.2, 118.3, 117.4, 103.5, 102.3, 60.7, 48.5, 38.7, 14.2, 13.7; MS (ESI): 470 (M+1). Found: C 71.55, H 6.02, N 8.78. Calcd for: $C_{28}H_{27}N_3O_2S$: C 71.61, H 5.80, N 8.95.

Ethyl 1-benzyl-3-butyl-1'-phenyl-2',3'-dihydrospiro[benzimidazoline-2,3'-pyrrole]-2'-thione-4'-carboxylate (7g). 82%, mp 139-140 ^{o}C; IR *v* (cm^{-1}) 3083, 3054, 1718, 1620, 1597, 1497; ^{1}H NMR δ (ppm) 7.63 (s, 1H), 7.51 (t, *J* 7.6 Hz, 2H), 7.37-7.45 (m, 5H), 7.26-7.31 (m, 3H), 6.63 (t, *J* 7.5 Hz, 1H), 6.51 (t, *J* 7.5 Hz, 1H), 6.34 (d, *J* 7.4 Hz, 1H), 6.11 (d, *J* 7.3 Hz, 1H), 4.28 (d, *J* 15.7 Hz, 1H), 4.19 (d, *J* 15.7 Hz, 1H), 4.14 (q, *J* 7.1 Hz, 2H), 3.08-3.14 (m, 1H), 2.95-3.01 (m, 1H), 1.56-1.60 (m, 2H), 1.34-1.39 (m, 2H), 1.08 (t, *J* 7.1 Hz, 3H), 0.92 (t, *J* 7.3, 3H); ^{13}C NMR δ (ppm) 207.3, 161.5, 145.0, 140.6, 140.0, 137.8, 137.6, 129.6, 128.7, 128.3, 127.9, 127.3, 125.0, 118.5, 117.8, 117.6, 104.5, 103.1, 98.2, 60.4, 49.2, 44.8, 31.0, 20.6, 13.9; MS (TOF) 496 (M-1)/497 (M^{+})/ 498 (M+1). Found: C 72.59, H 6.54, N 8.49. Calcd for $C_{30}H_{31}N_3O_2S$: C 72.40, H 6.28, N 8.44.

Ethyl 1,3-dibenzyl-1'-phenyl-2',3'-dihydrospiro[imidazolidine-2,3'-pyrrole]-2'-thione-4'-carboxylate (9d).

73%, mp 134-135 ^{o}C; IR *v* (cm^{-1}) 1692, 1628, 1589; ^{1}H NMR δ (ppm) 7.48 (s, 1H), 7.48 (t, *J* 8.2 Hz, 2H), 7.37-7.41 (m, 6H), 7.28-7.30 (m, 5H), 7.24 (d, *J* 7.1 Hz, 2H), 4.36 (q, *J* 7.1 Hz, 2H), 3.84 (d, *J* 13.6 Hz, 2H), 3.78 (d, *J* 13.6 Hz, 2H), 3.42-3.45 (m, 2H), 3.23-3.26 (m, 2H), 1.41 (t, *J* 7.1 Hz, 3H); ^{13}C NMR (C6D6) δ (ppm) 209.7, 161.4, 145.4, 139.6, 138.1, 128.9, 128.8, 128.3, 128.0, 127.0, 125.3, 118.0, 95.2, 59.7, 53.4, 48.2, 14.4; MS (ESI): 484 (M+1). Found: C 72.10, H 6.11, N 8.71. Calcd for $C_{29}H_{29}N_3O_2S$: C 72.02, H 6.04, N 8.69.

Eethyl 1,3-dibenzyl-2'-phenylimino-2',3'-dihydrospiro[imidazolidine-2,3'-thiophene]-4'-carboxylate (10d).

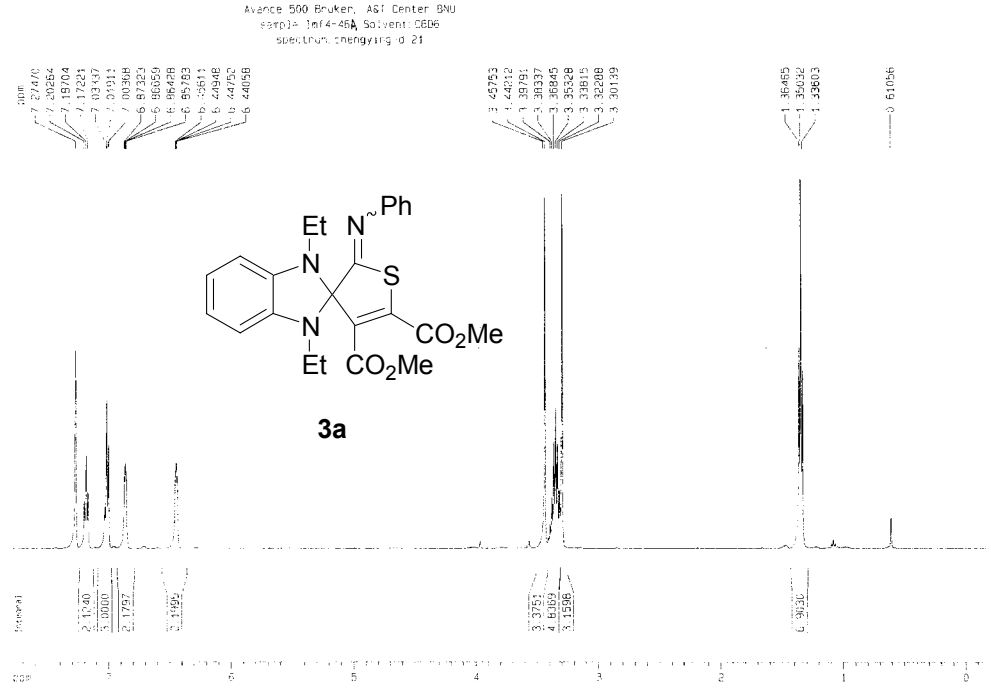
15%, mp 102-103 ^{o}C; IR *v* (cm^{-1}) 3057, 1696, 1640, 1582; ^{1}H NMR δ (ppm) 7.78 (s, 1H), 7.41-7.45 (m, 6H), 7.32 (t, *J* 7.2 Hz, 4H), 7.24-7.27 (m, 3H), 7.08 (d, *J* 7.6 Hz, 2H), 7.37 (q, *J* 7.1 Hz, 2H), 3.94 (d, *J* 13.6 Hz, 2H), 3.80 (d, *J* 13.4 Hz, 2H), 3.29 (brs, 4H), 1.42 (t, *J* 7.1 Hz, 3H); ^{13}C NMR δ (ppm) 170.2, 161.7, 151.4,

140.7, 139.4, 129.3, 128.4, 128.2, 127.5, 126.9, 125.4, 119.8, 93.1, 60.4, 53.4, 48.9, 14.5; MS (ESI): 484 (M+1). Found: C 72.00, H 6.00, N 8.62. Calcd for $C_{29}H_{29}N_3O_2S$: C 72.02, H 6.04, N 8.69.

Ethyl 1,3-di(p-methoxy)benzyl-1'-phenyl-2',3'-dihydrospiro[imidazolidine-2,3'-pyrrole]-2'-thione-4'-carboxylate (9e). 71%, mp 116-117 ^{o}C; IR ν (cm^{-1})1717, 1616, 1512; ^{1}H NMR (C_6D_6) δ (ppm) 7.54 (d, *J* 8.4 Hz, 4H), 7.26 (s, 1H), 7.06-7.14 (m, 5H), 6.92 (d, *J* 8.4 Hz, 4H), 4.36 (q, *J* 7.1 Hz, 2H), 4.03 (d, *J* 13.2 Hz, 2H), 3.99 (d, *J* 13.2 Hz, 2H), 3.65 (brs, 2H), 3.42 (s, 8H), 1.27 (t, *J* 7.1 Hz, 3H); ^{13}C NMR (C6D6) δ (ppm) 209.9, 161.5, 159.2, 145.3, 138.2, 131.5, 130.0, 128.9, 127.7, 125.4, 118.2, 113.8, 95.1, 59.7, 54.6, 52.9, 48.3, 14.5; MS (ESI): 544 (M+1). Found: C 68.66, H 6.53, N 8.12. Calcd for $C_{31}H_{33}N_3O_4S$: C 68.48, H 6.12, N 7.73.

Eethyl 1,3-di(p-methoxy)benzyl-2'-phenylimino-2',3'-dihydrospiro[imidazolidine-2,3'-thiophene]-4'-carboxylate (10e). 15%, mp 119-120 ^{o}C; IR ν (cm^{-1}) 1726, 1634, 1610, 1579; ^{1}H NMR δ (ppm) 7.76 (s, 1H), 7.44 (t, *J* 7.7 Hz, 2H), 7.30 (d, *J* 8.3 Hz, 4H), 7.24 (t, *J* 7.3 Hz, 1H), 7.07 (d, *J* 7.5 Hz, 2H), 6.85 (d, *J* 8.4 Hz, 4H), 4.35 (q, *J* 7.0 Hz, 2H), 3.86 (d, *J* 13.3 Hz, 2H), 3.82 (s, 6H), 3.72 (d, *J* 13.2 Hz, 2H), 3.24 (brs, 4H), 1.41 (t, *J* 7.1 Hz, 3H); ^{13}C NMR δ (ppm) 170.2, 161.7, 158.7, 151.4, 140.4, 140.4, 131.5, 129.5, 129.3, 125.3, 119.8, 113.6, 92.9, 60.4, 55.3, 52.7, 48.8, 14.5; MS (ESI): 544 (M+1). Found: C 68.23, H 6.24, N 7.69. Calcd for $C_{31}H_{33}N_3O_4S$: C 68.48, H 6.12, N 7.73.

4. The NMR spectra of products 3-10.



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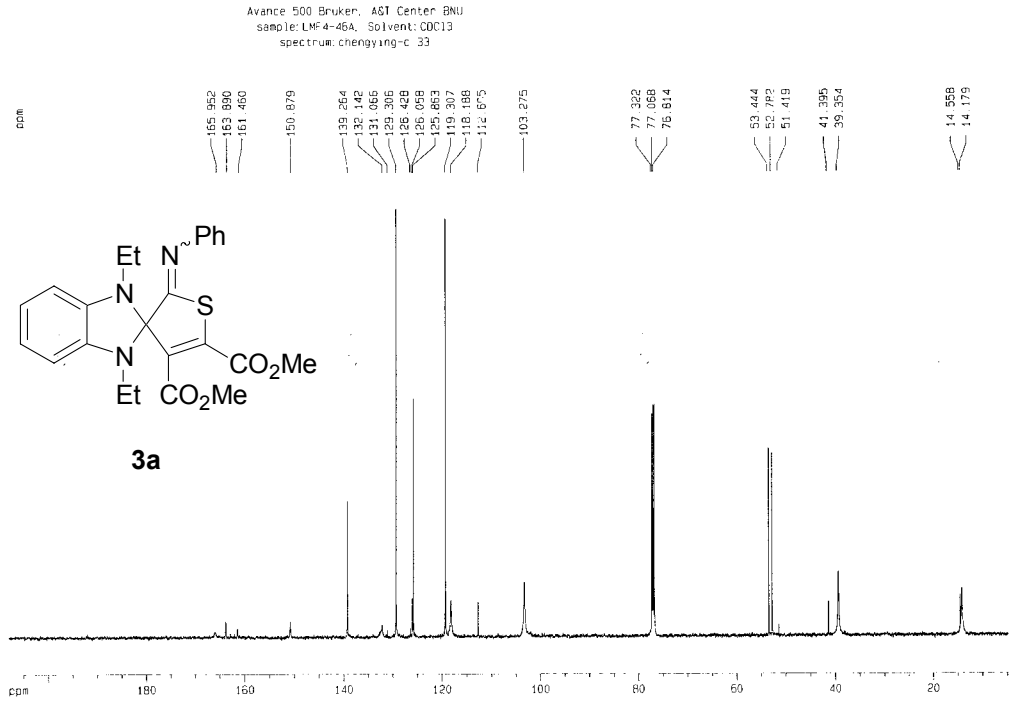

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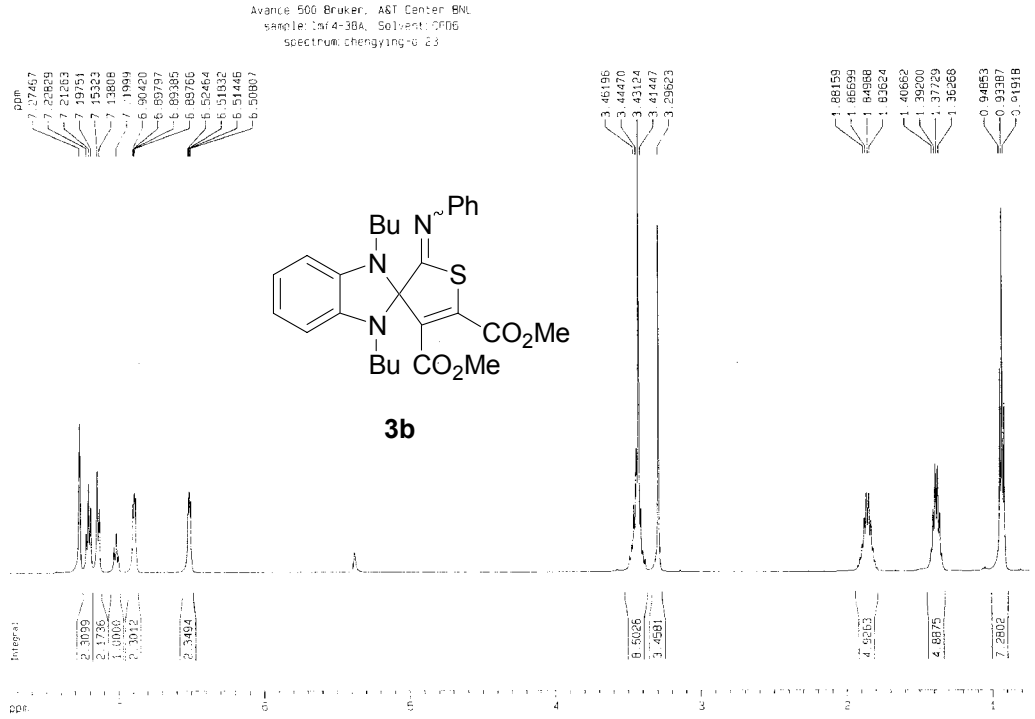
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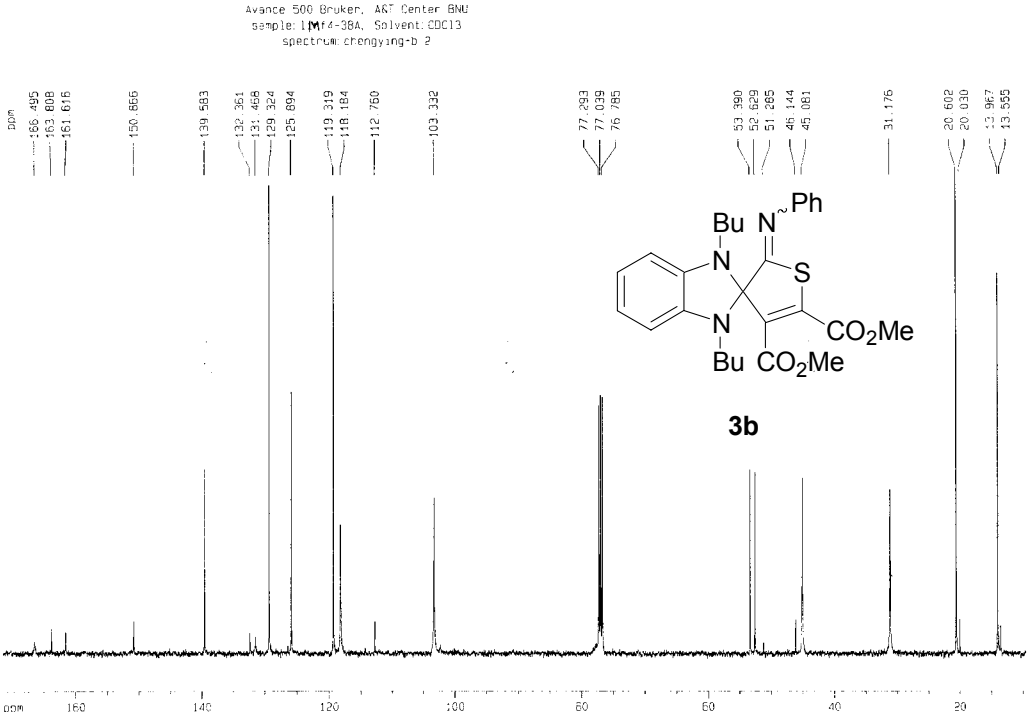
N
CO2Me
Bu CO2Me
3b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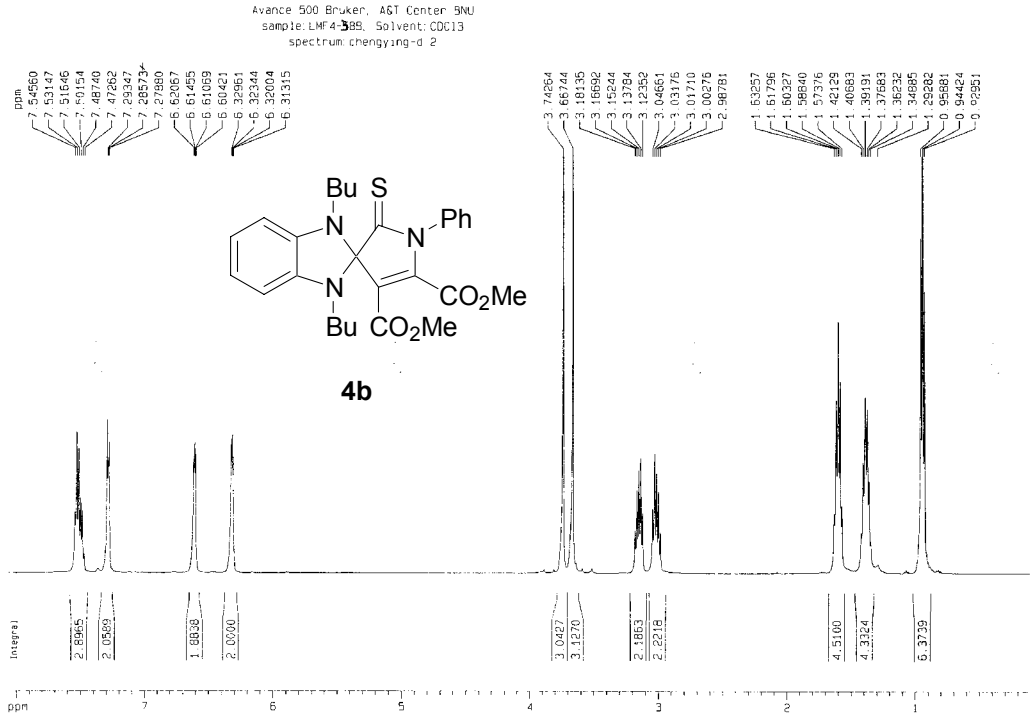
N
S
N
CO2Me
Bu CO2Me
3b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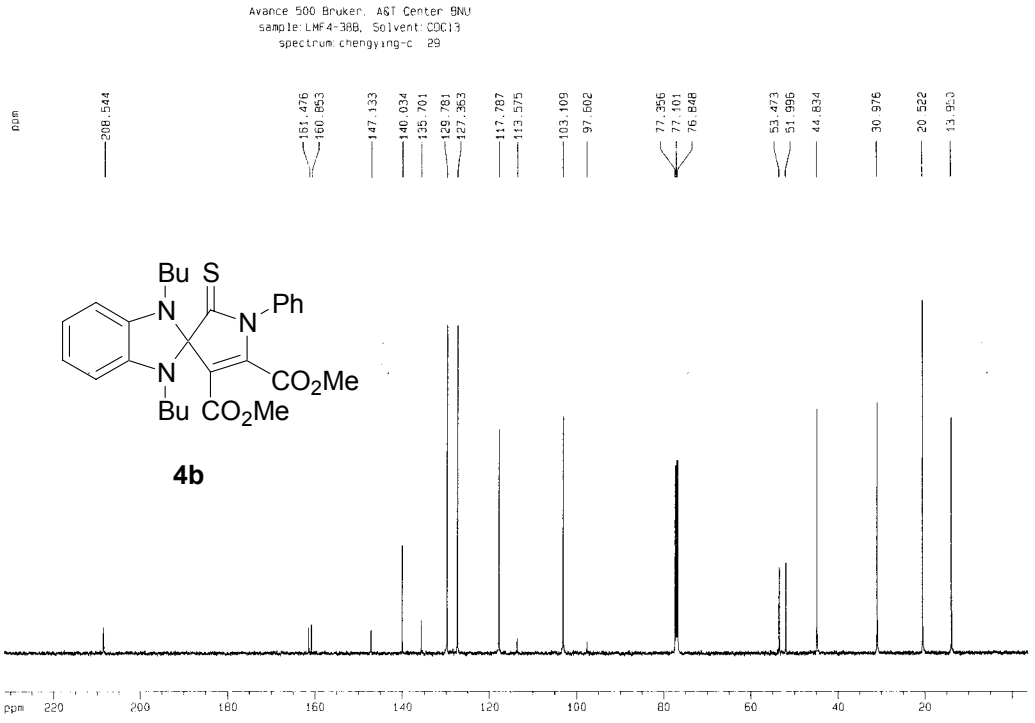
Ph
N
N
CO2Me
Bu CO2Me
4b
Integral
ppm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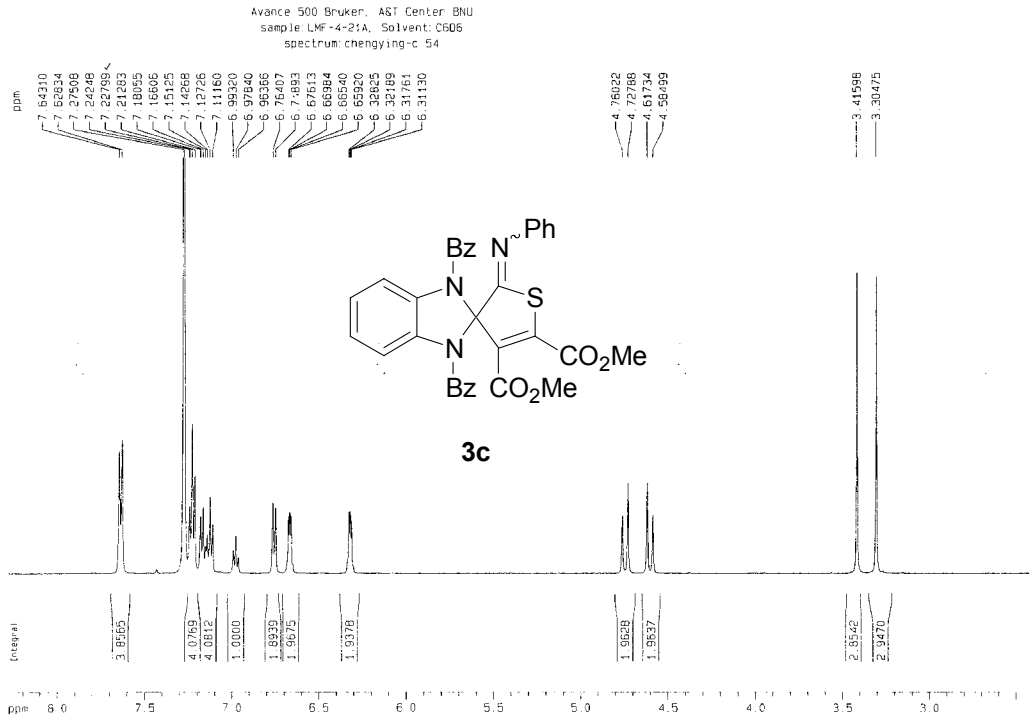
N
Ph
N
N
CO2Me
Bu CO2Me
4b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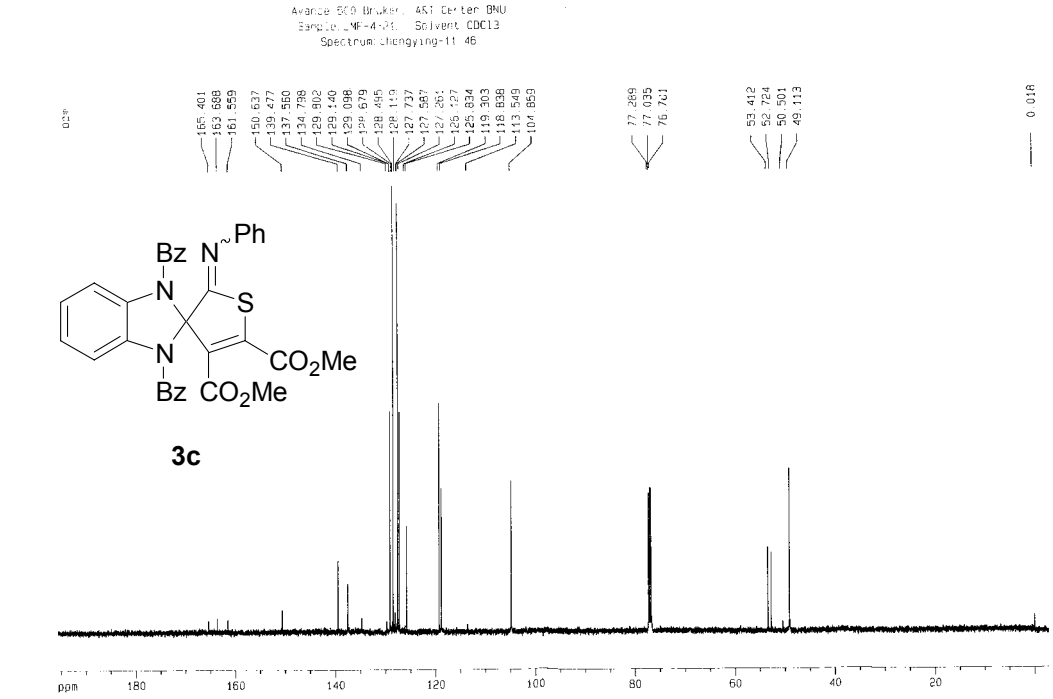
3c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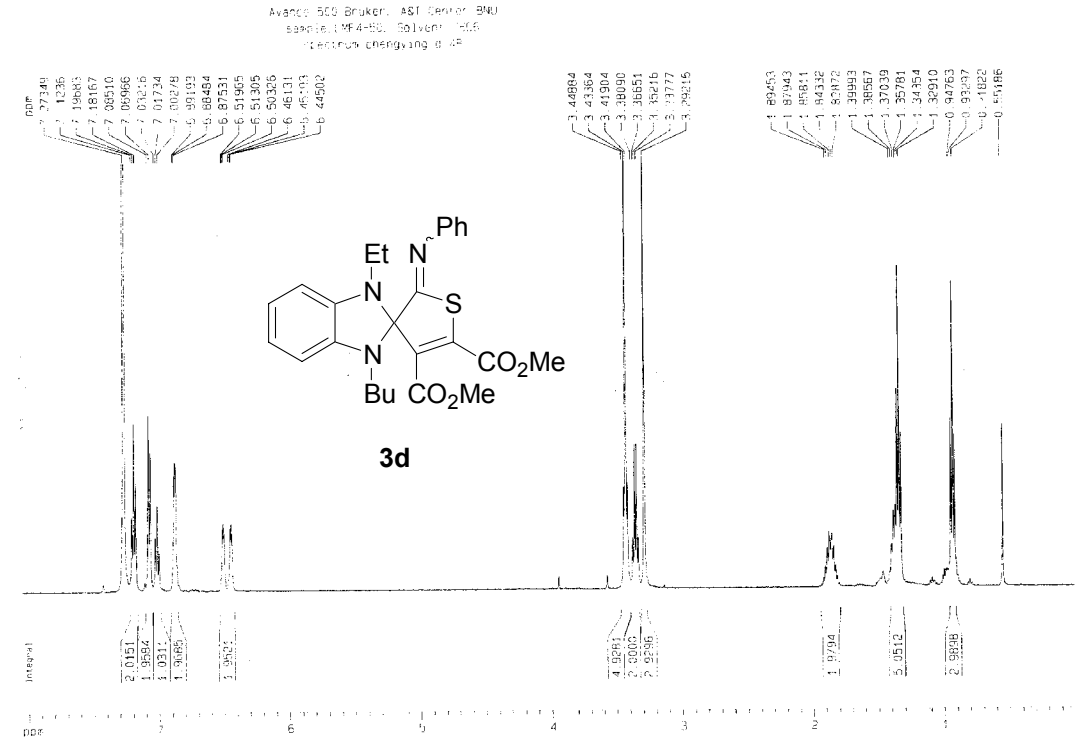
CO2Me
Bz CO2Me
3c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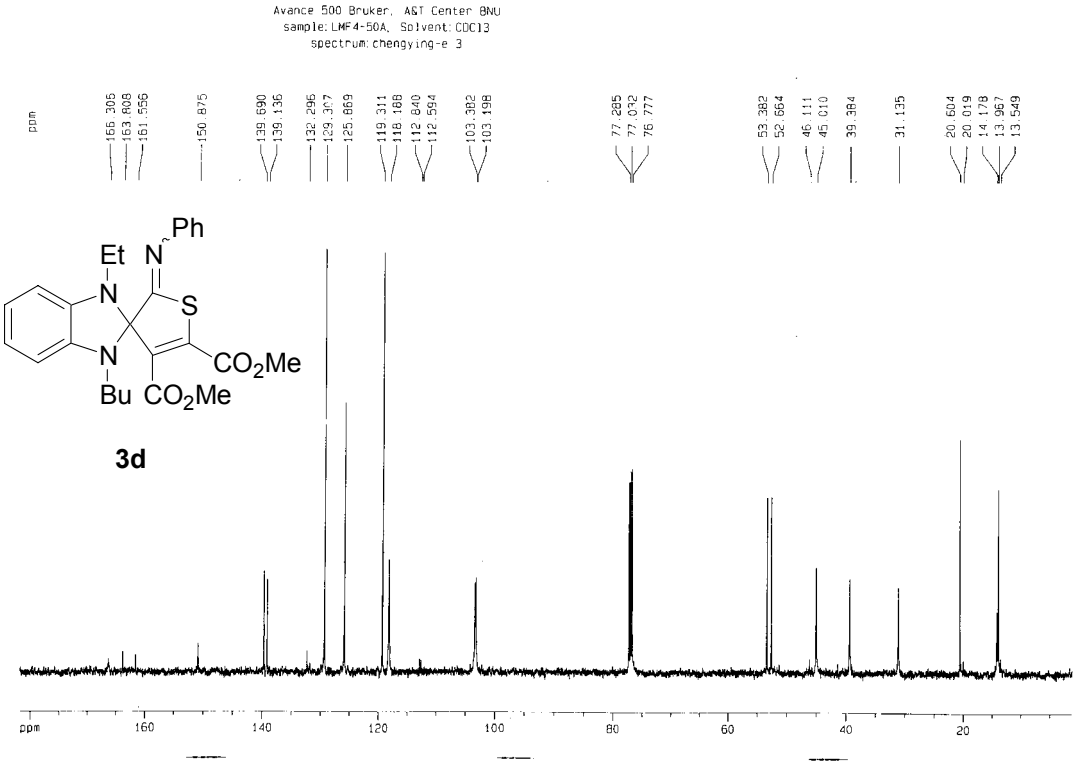
CO2Me
Bu
CO2Me

3d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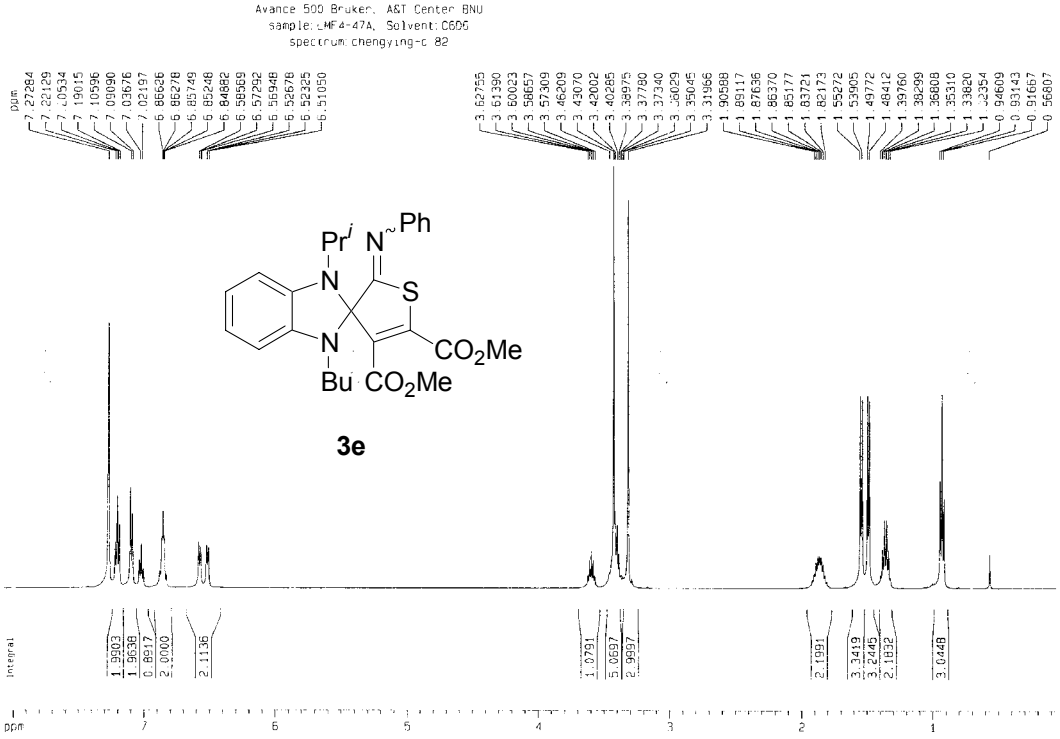
3d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Ph
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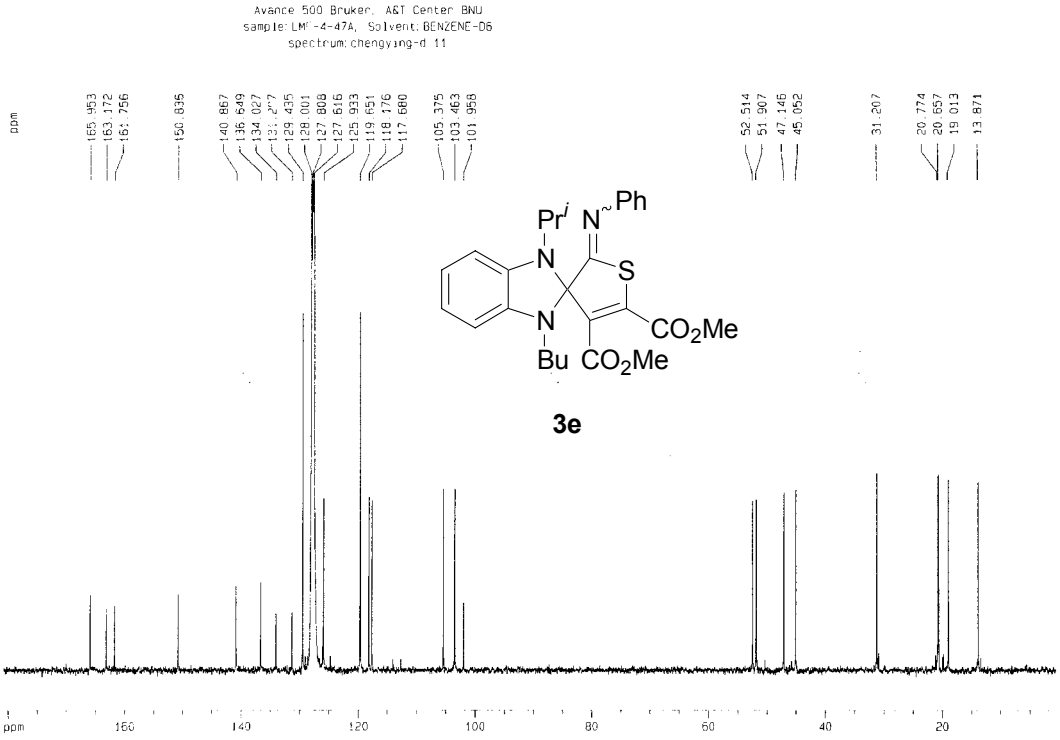
Bu
CO2Me
3e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Ph
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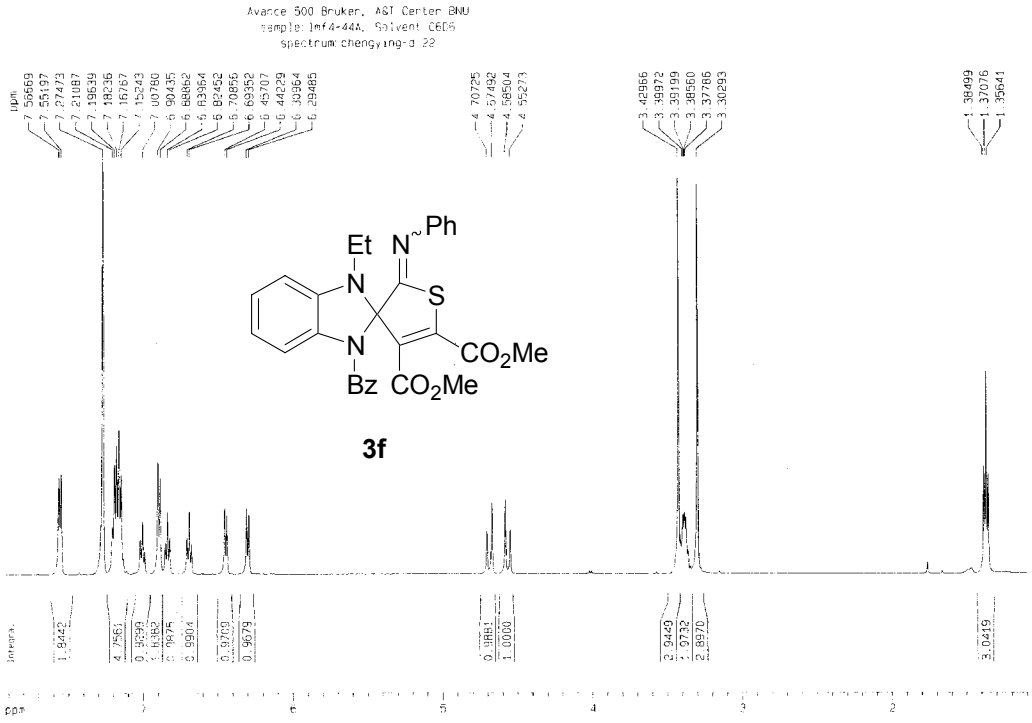
3e



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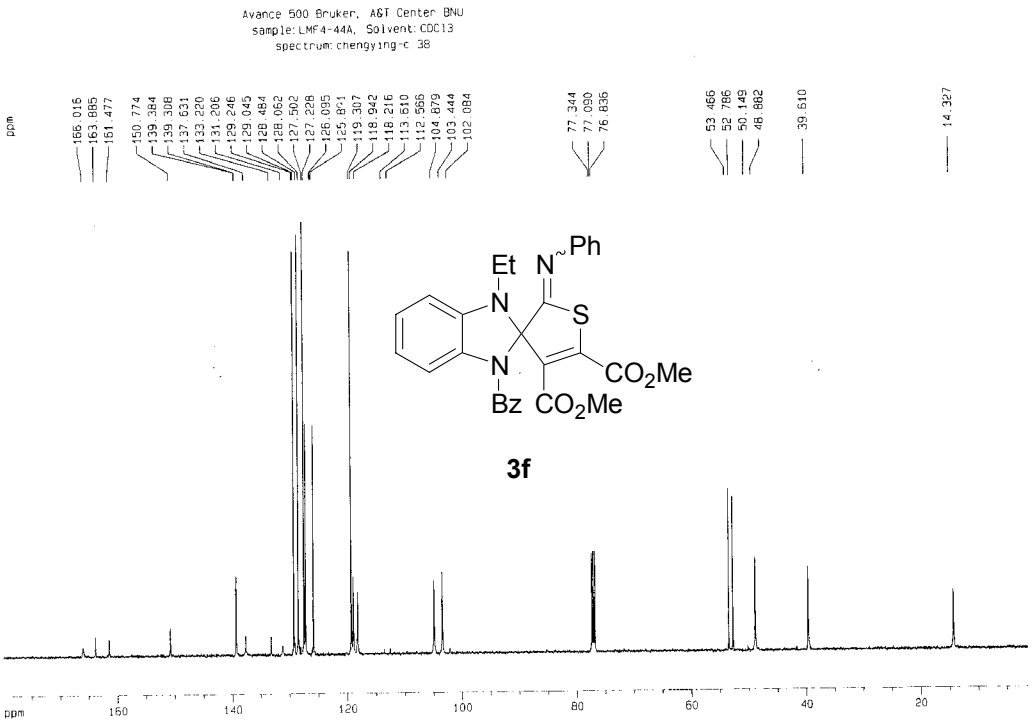

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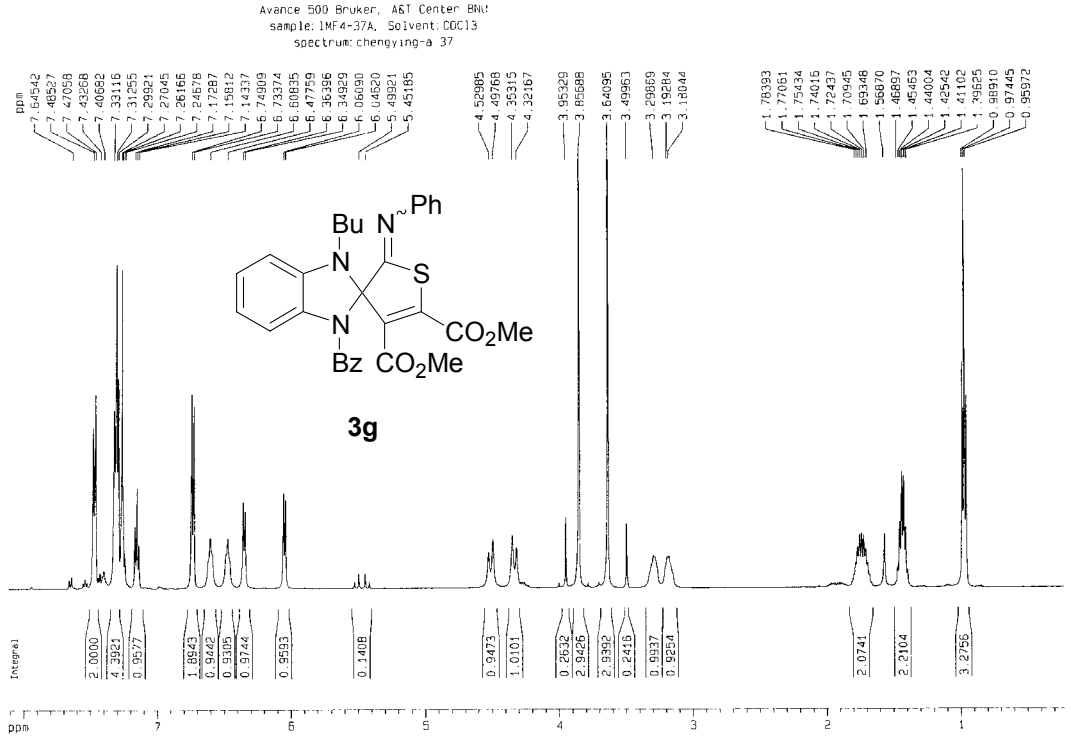
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Ph
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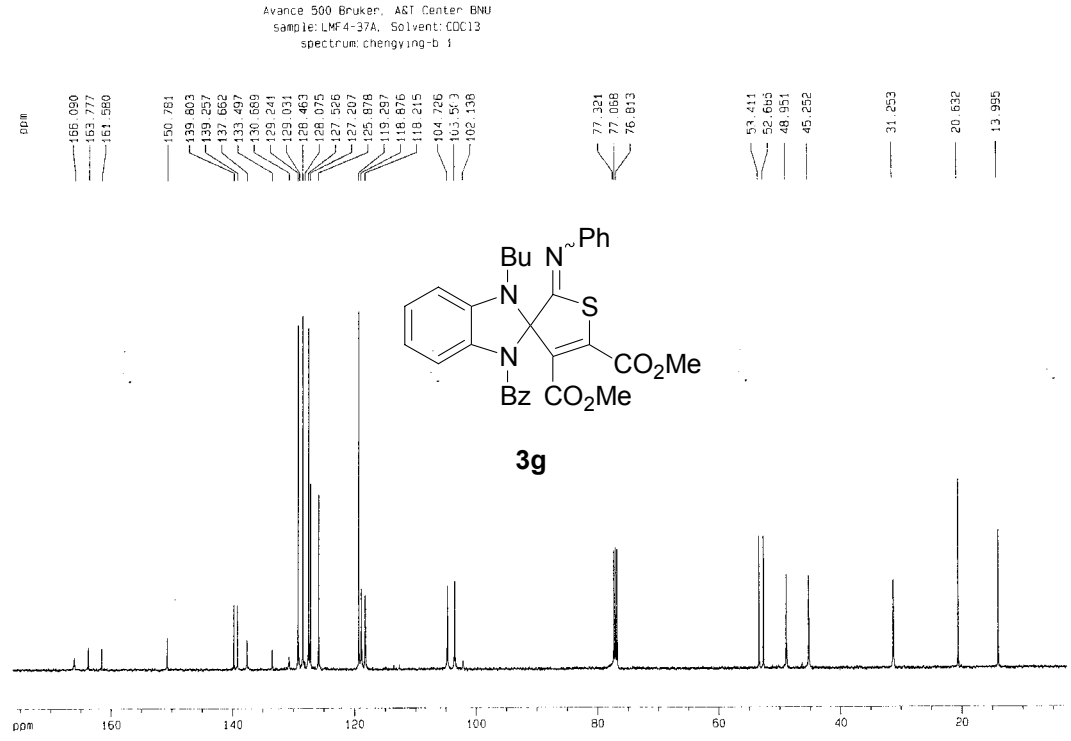
CO2Me
Bz
CO2Me
3g
Integral
ppm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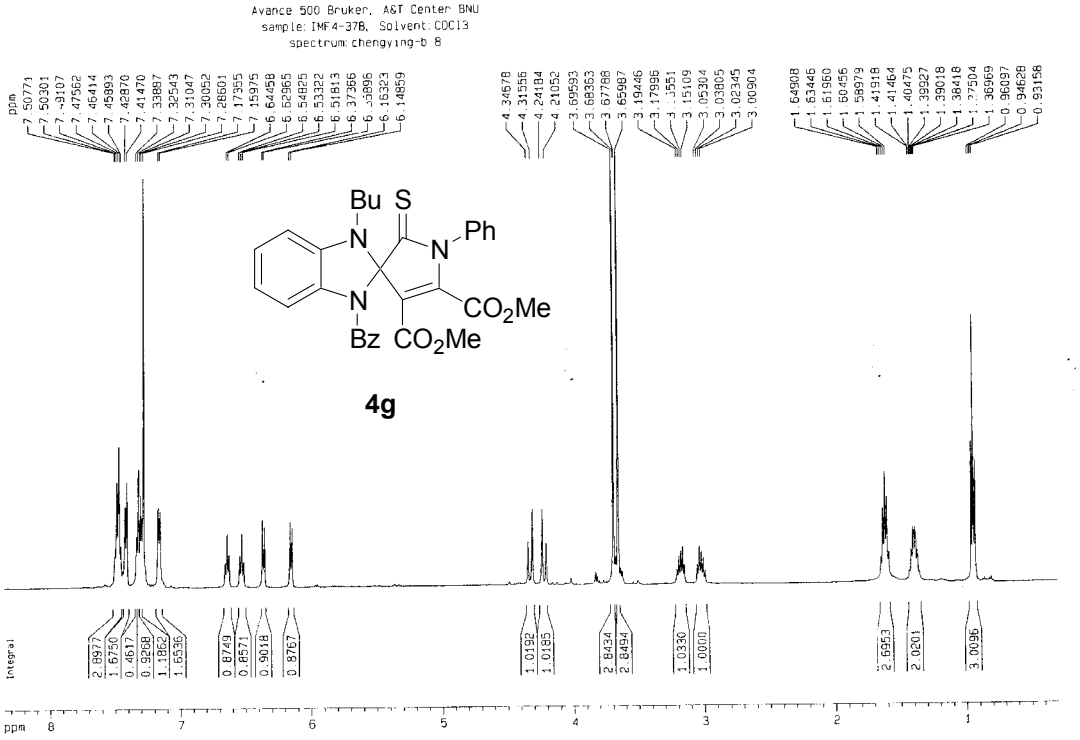
S
CO2Me
Bz
CO2Me
3g
ppm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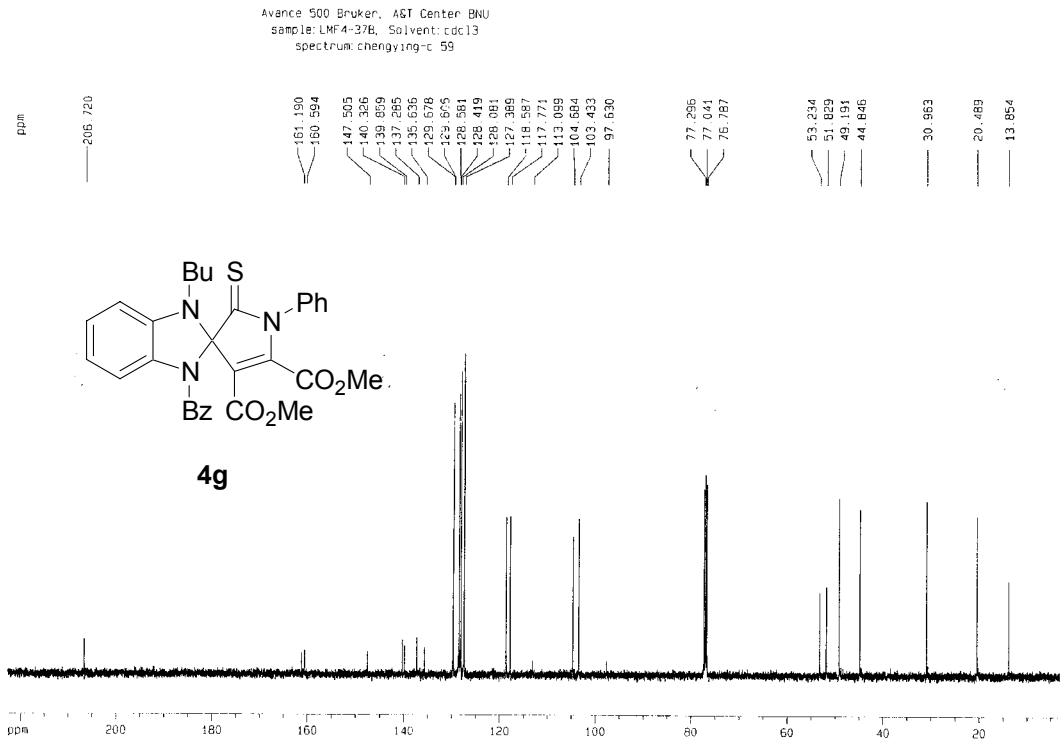
N
Ph
N
CO2Me
Bz CO2Me
4g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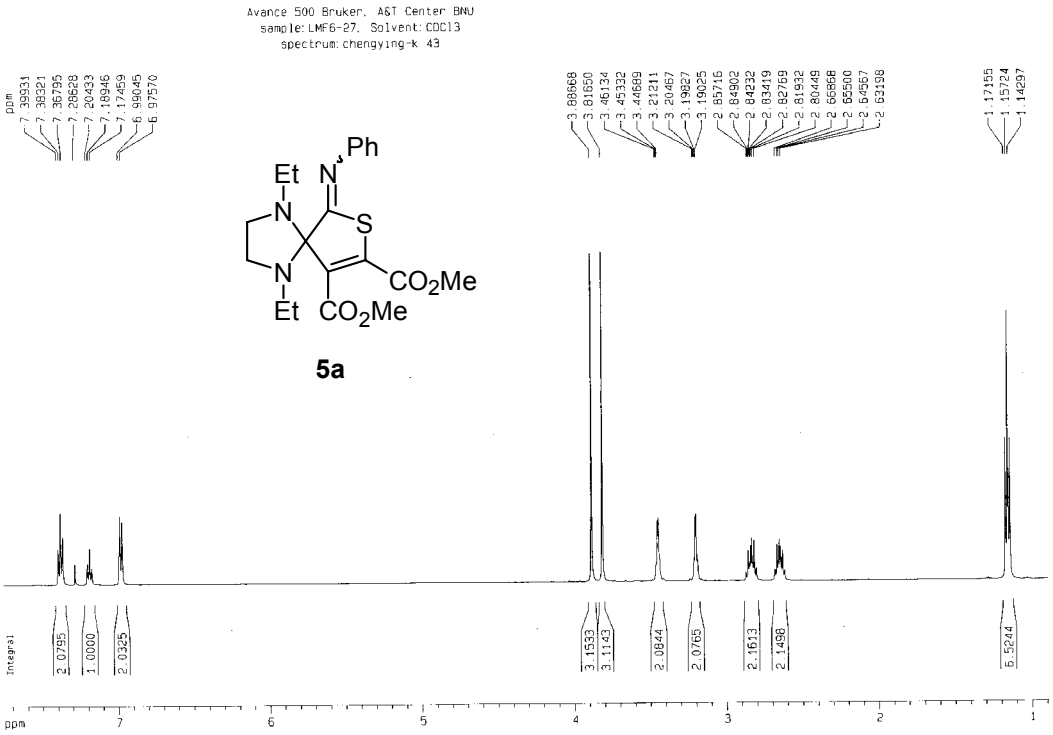
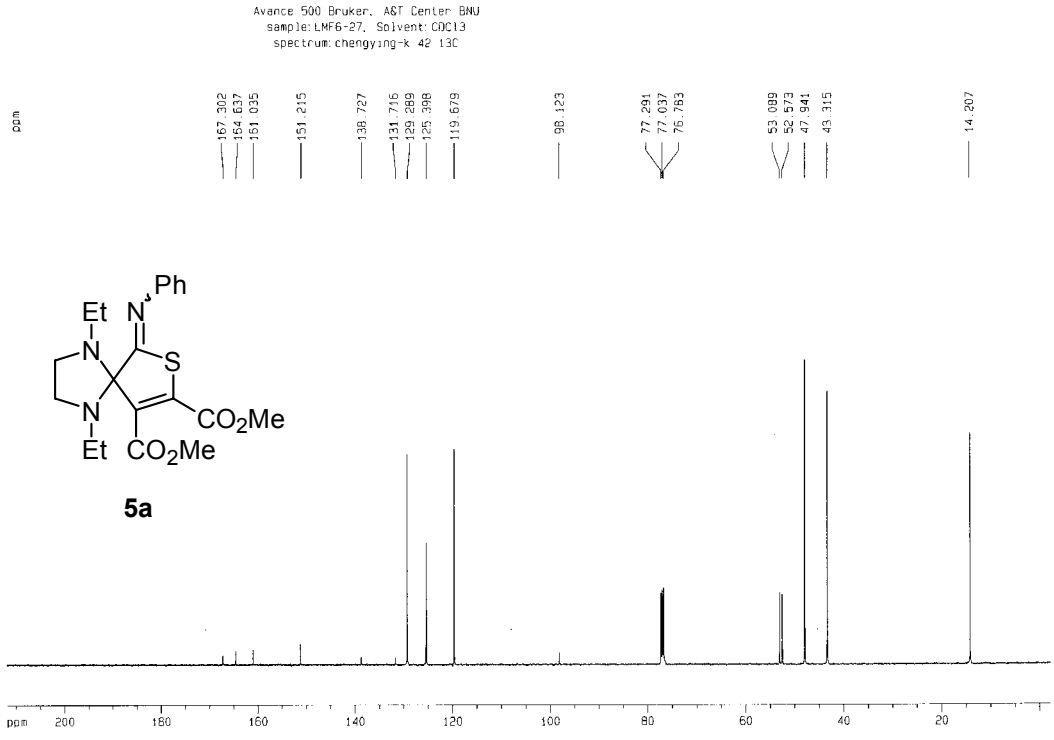
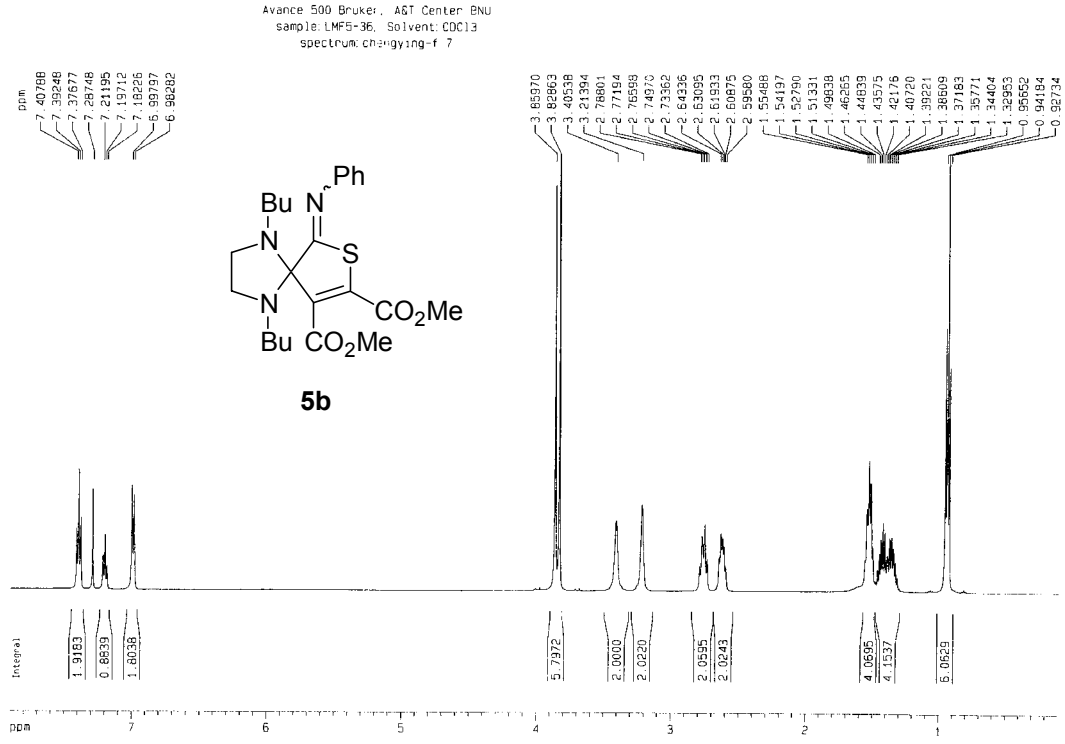
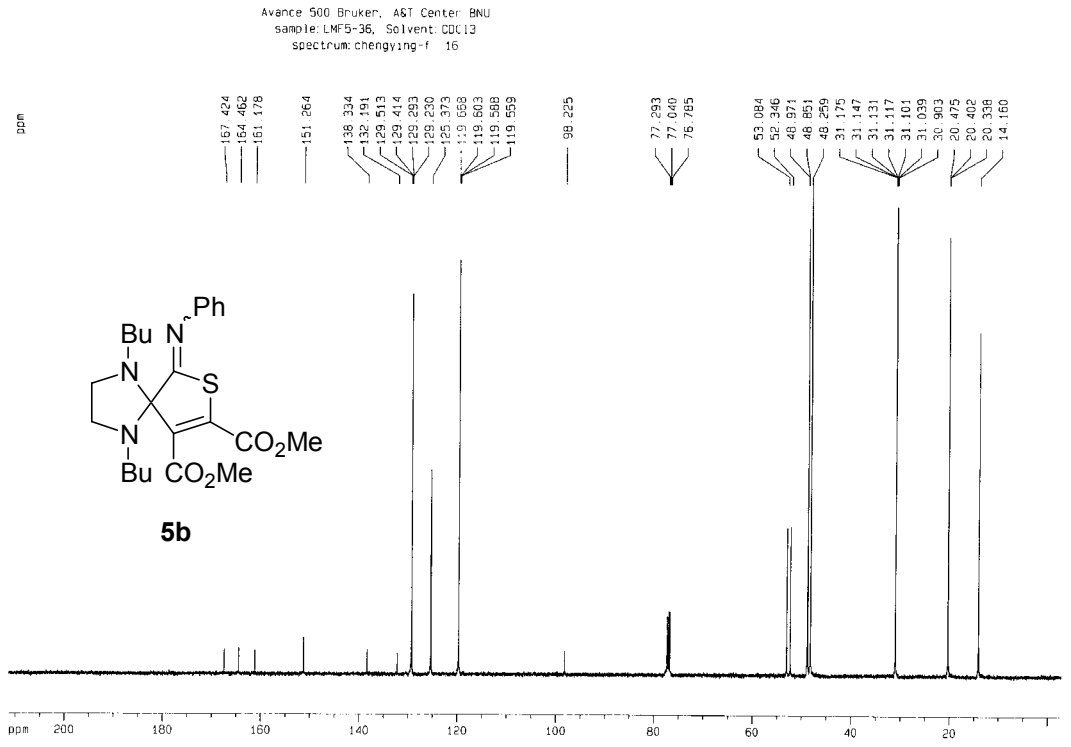
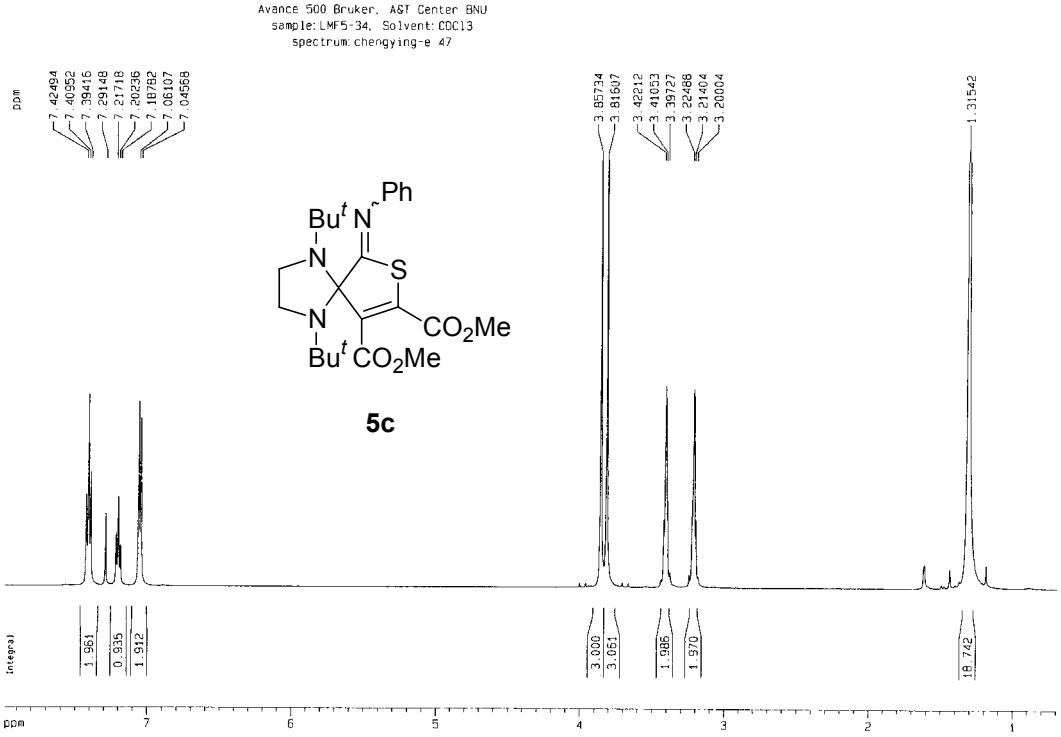
4g

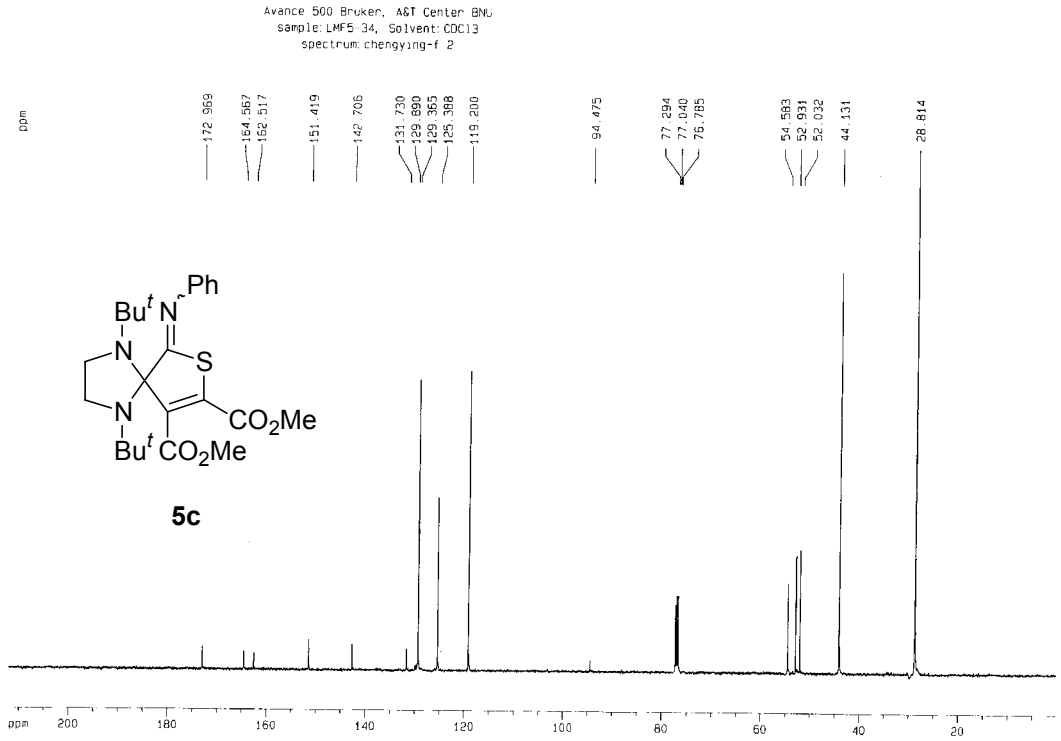

Avance 500 Bruker, A&T Center BNU
sample: LMF6-27, Solvent: CDCl3
spectrum: chengying-k 43
ppm
7.39931
7.38321
7.36795
7.28628
7.20433
7.18946
7.17459
6.99045
6.97570
3.88868
3.81650
3.46134
3.45332
3.44689
3.21211
3.20467
3.19927
3.19025
2.85716
2.84902
2.84232
2.83419
2.82769
2.81932
2.80449
2.66868
2.65500
2.64567
2.63198
1.17155
1.15724
1.14297
Et
N
Ph
S
CO2Me
Et
CO2Me
5a
Integral
2.0795
1.0000
2.0325
3.1533
3.1143
2.0844
2.0765
2.1613
2.1498
6.5244
ppm
7
6
5
4
3
2
1

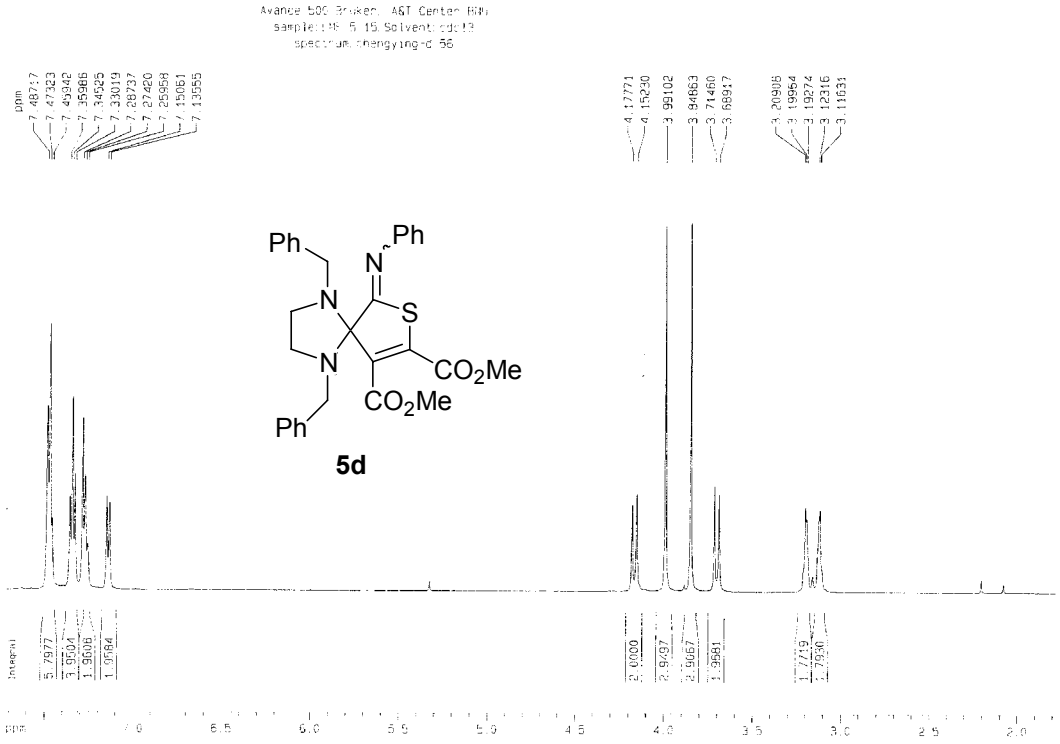

Avance 500 Bruker, A&T Center BNU
sample: LMF6-27, Solvent: CDCl3
spectrum: chengying-k 42 13C
ppm
167.302
164.637
161.035
151.215
138.727
131.716
129.289
125.398
119.679
98.123
77.291
77.037
76.783
53.089
52.573
47.941
43.315
14.207
Et
N
Ph
S
CO2Me
Et
CO2Me
5a
ppm
200
180
160
140
120
100
80
60
40
20


Avance 500 Bruker, A&T Center BNU
sample: LMF5-36, Solvent: CDCl3
spectrum: chengying-f 7
Ph
Bu N
N
S
N
CO2Me
Bu CO2Me
5b
Integral
ppm

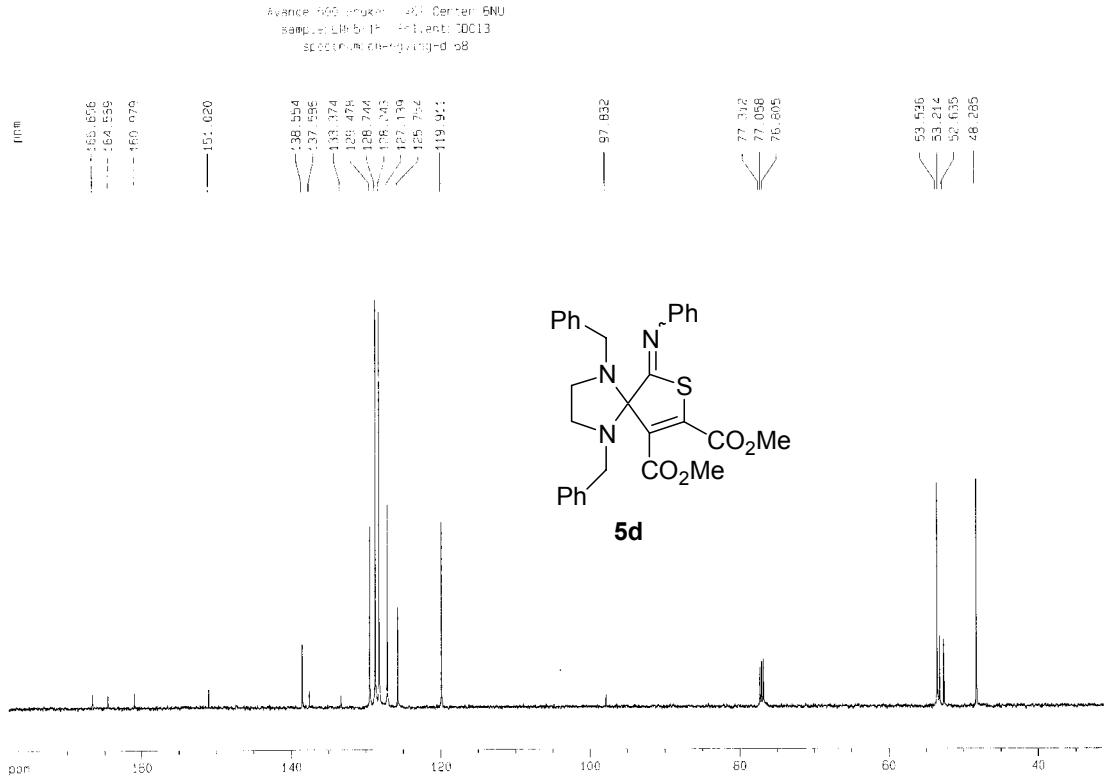

Avance 500 Bruker, A&T Center BNU
sample: LMF5-36, Solvent: CDCl3
spectrum: chengying-f 16
Ph
Bu N
N
S
N
CO2Me
Bu CO2Me
5b
ppm


Avance 500 Bruker, A&T Center BNU
sample: LMF5-34, Solvent: CDCl3
spectrum: chengying-e 47
ppm
7.42494
7.40952
7.39416
7.29148
7.21718
7.20236
7.18782
7.06107
7.04568
3.85734
3.81607
3.42212
3.41053
3.39727
3.22468
3.21404
3.20004
1.31542
Integral
1.961
0.935
1.912
3.000
3.061
1.986
1.970
18.742
ppm
7
6
5
4
3
2
1
Ph
Bu^t N
N
S
N
CO2Me
Bu^t CO2Me
5c

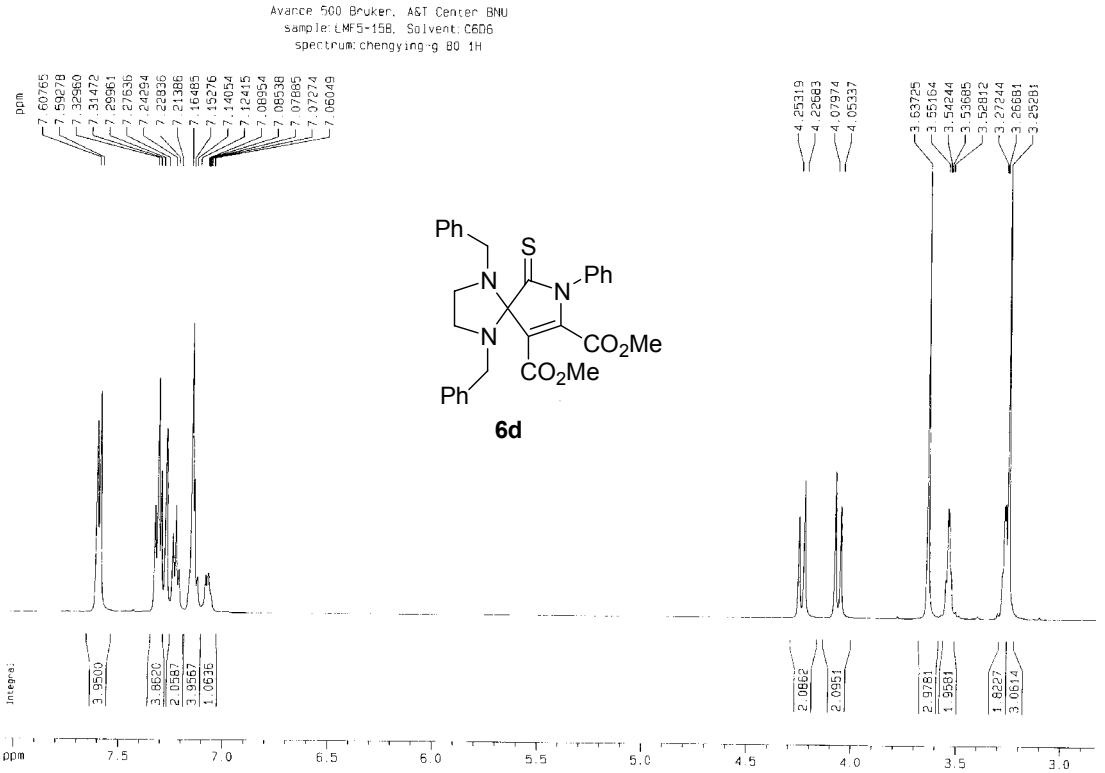

Avance 500 Bruker, A&T Center BNU
sample: LMF5-34, Solvent: CDCl3
spectrum: chengying-f 2
ppm
172.969
164.567
162.517
151.419
142.706
131.730
129.890
129.365
125.388
119.200
94.475
77.294
77.040
76.785
54.583
52.931
52.032
44.131
28.814
ppm
200
180
160
140
120
100
80
60
40
20
Ph
Bu^t N
N
S
N
CO2Me
Bu^t CO2Me
5c

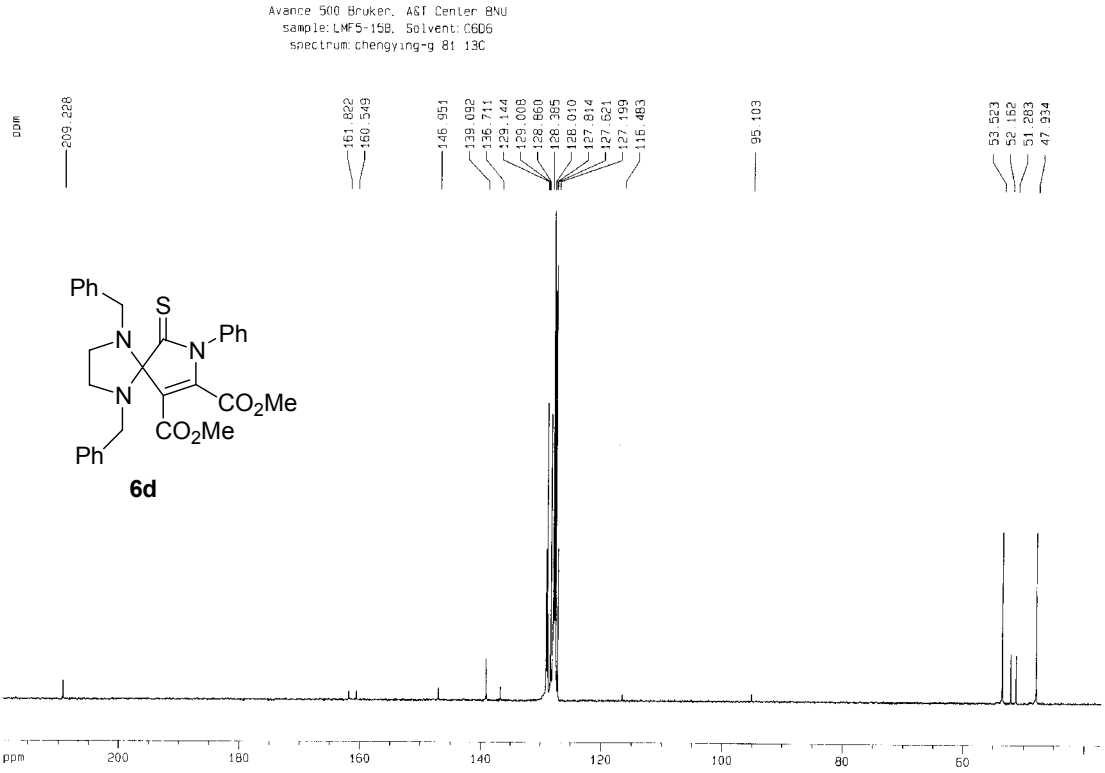


5d

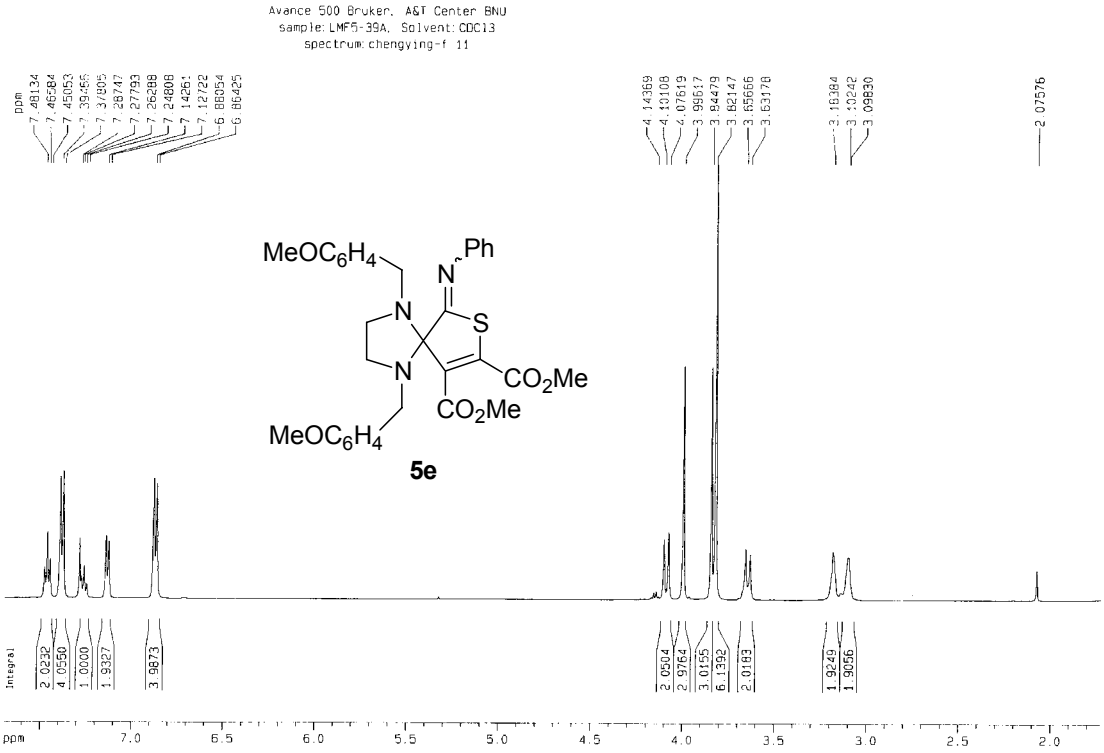


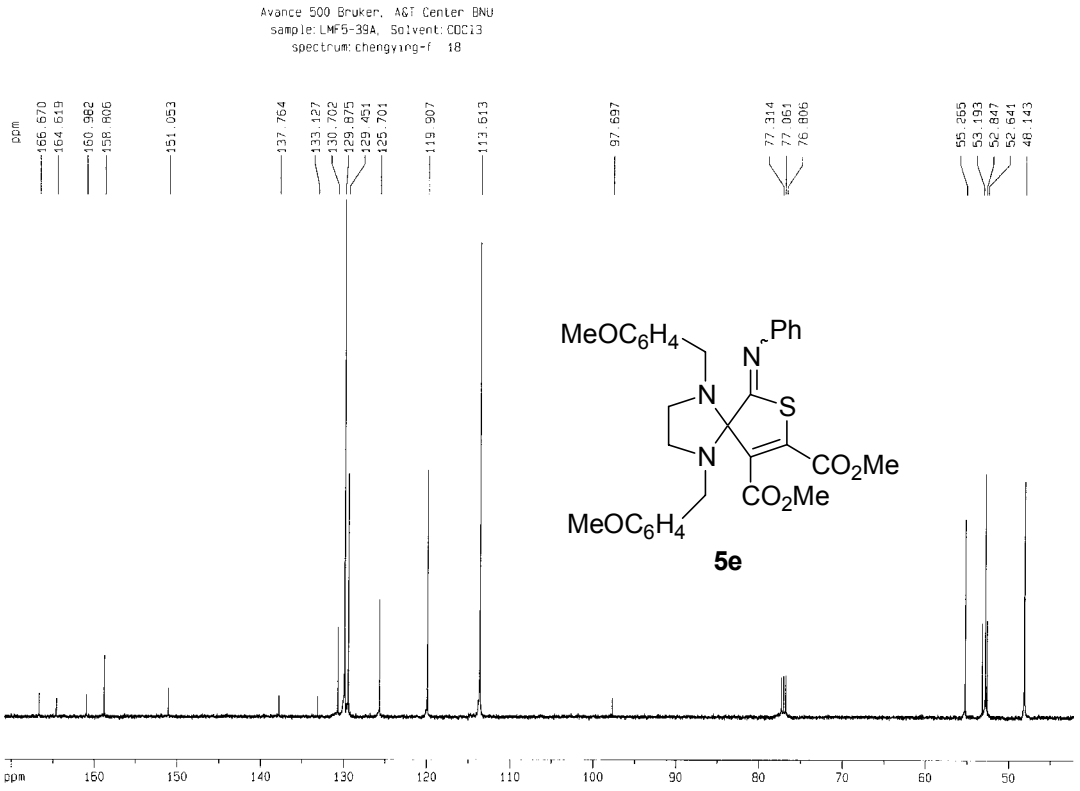
5d

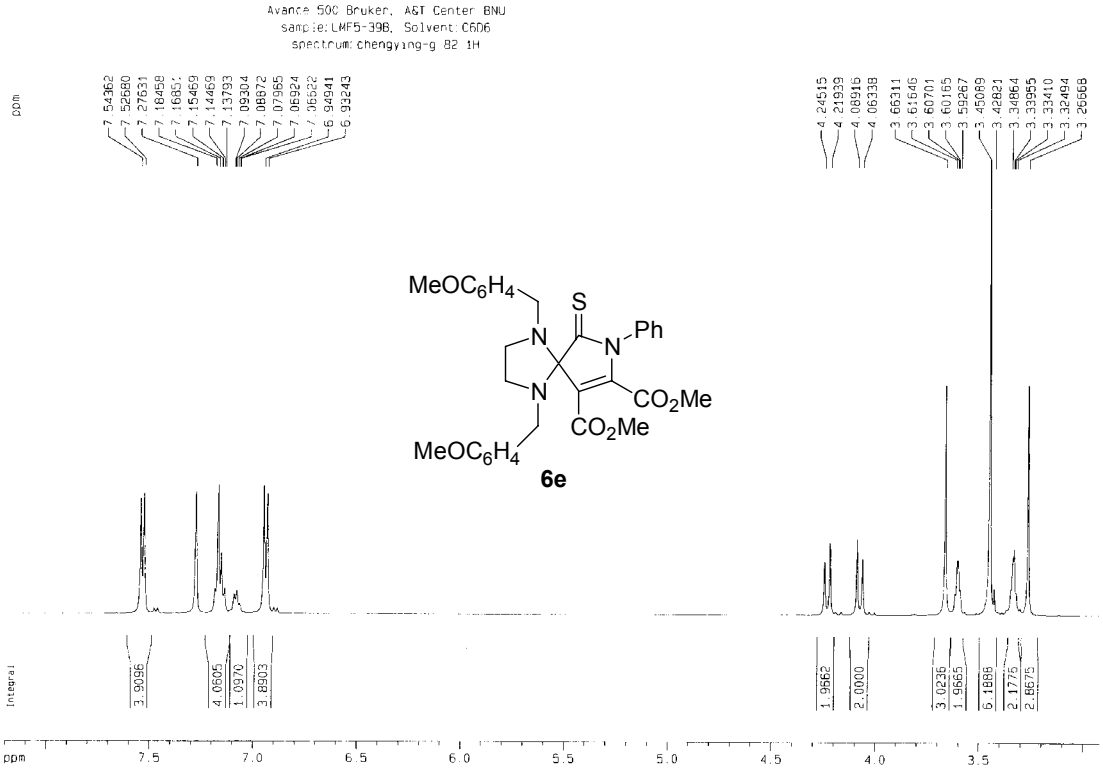


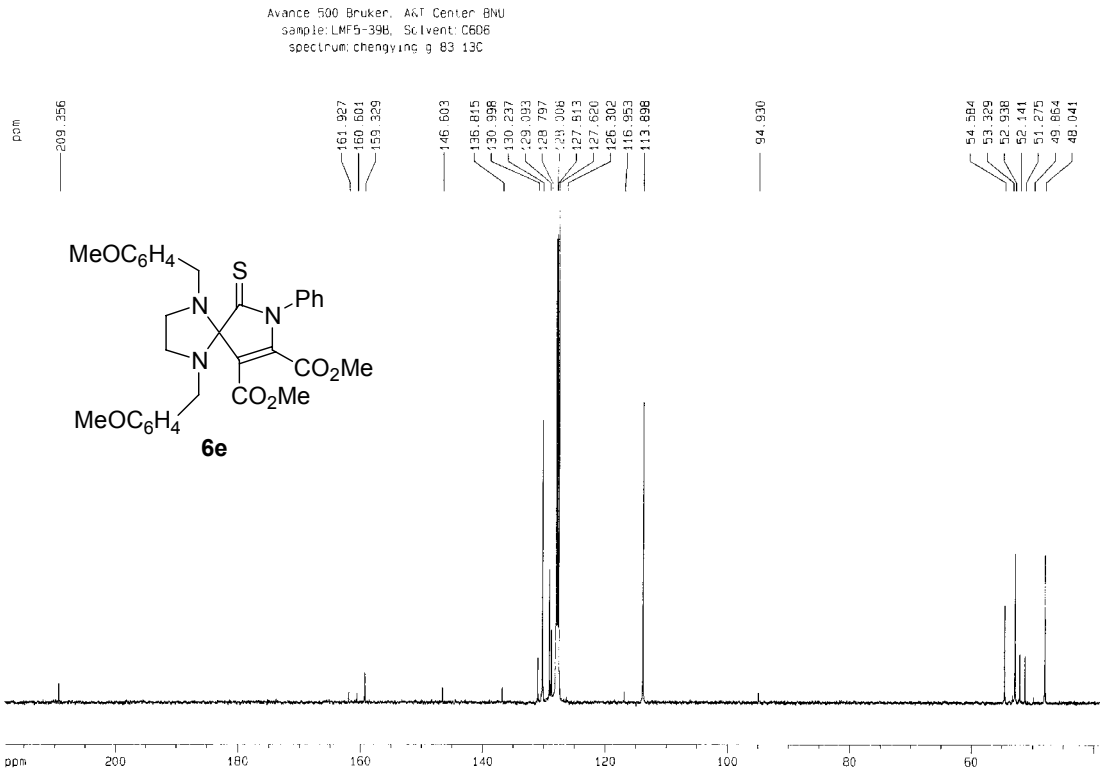


Solvent□C_6D_6

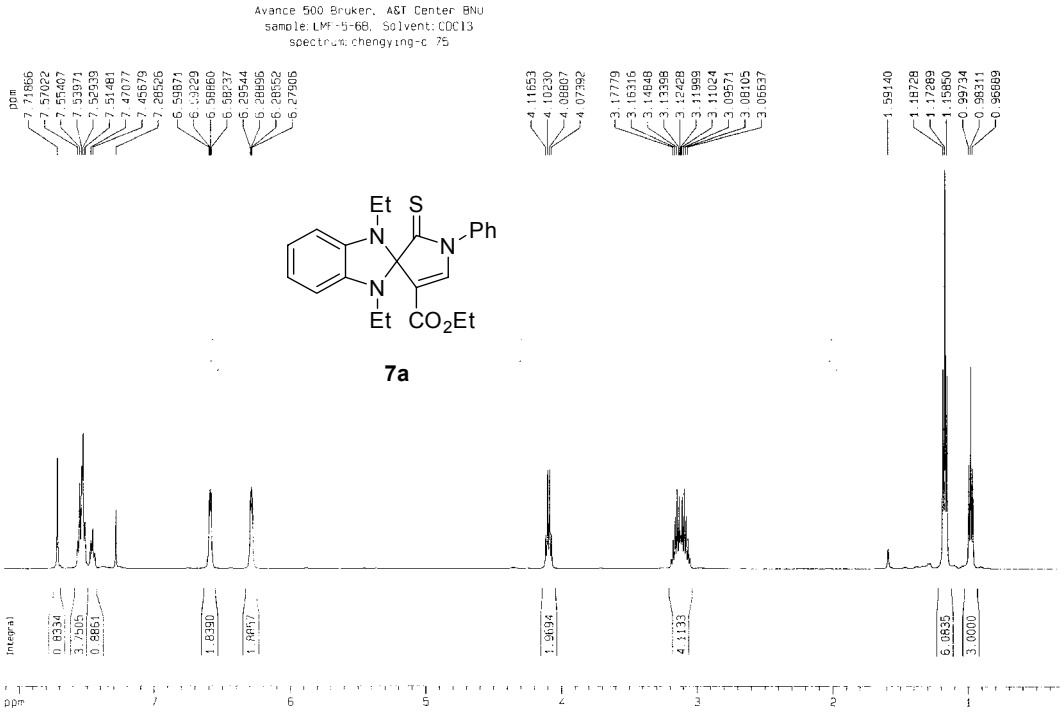

Avance 500 Bruker, A&T Center BNU
sample: LMF5-39A, Solvent: CDCl3
spectrum: chengying-f 11
MeOC6H4
Ph
N
N
S
N
CO2Me
CO2Me
MeOC6H4
5e
ppm
Integral


Avance 500 Bruker, A&T Center BNU
sample: LMF5-39A, Solvent: CDCl3
spectrum: chengying-f 18
MeOC6H4
Ph
N
N
S
N
CO2Me
CO2Me
MeOC6H4
5e
ppm

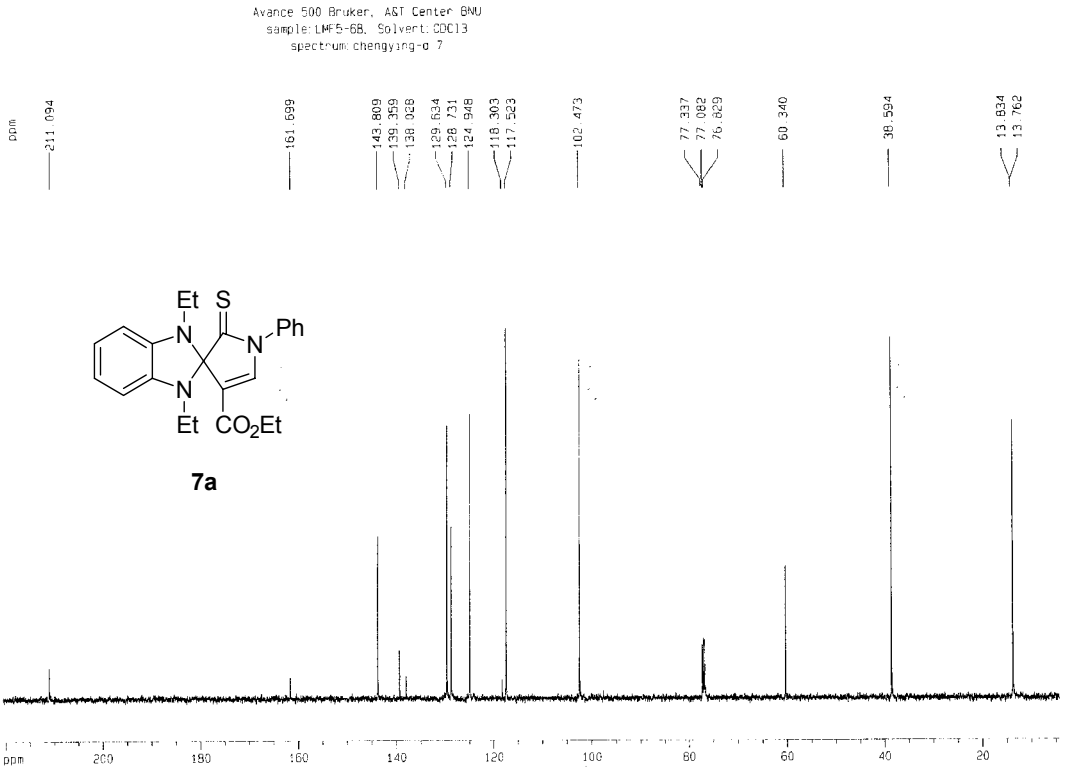




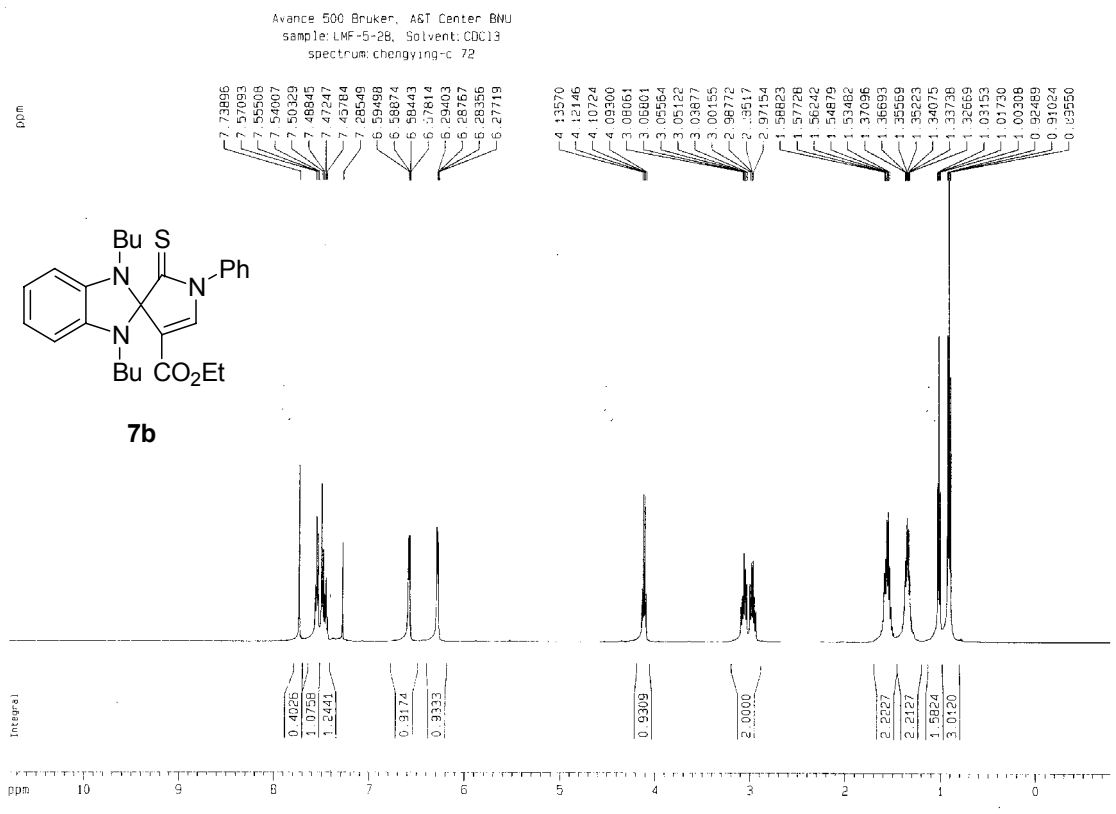
Solvent□C_6D_6


Avance 500 Bruker, A&T Center BNU
sample: LMF-5-6B, Solvent: CDCl3
spectrum: chengying-c 75
ppm
7.71866
7.57022
7.55407
7.53971
7.52939
7.51481
7.47077
7.45679
7.28526
6.59871
6.59229
6.58960
6.58737
6.29544
6.28895
6.28552
6.27905
4.11653
4.10230
4.08807
4.07392
3.17779
3.16316
3.14848
3.13398
3.12428
3.11999
3.11024
3.09571
3.08105
3.06537
1.59140
1.18728
1.17289
1.15850
0.99734
0.98311
0.96889
Et S
N
Ph
N
N
Et CO2Et
Integral
0.8334
3.7505
0.8861
1.8390
1.8857
1.9694
4.1133
6.0835
3.0000
ppm

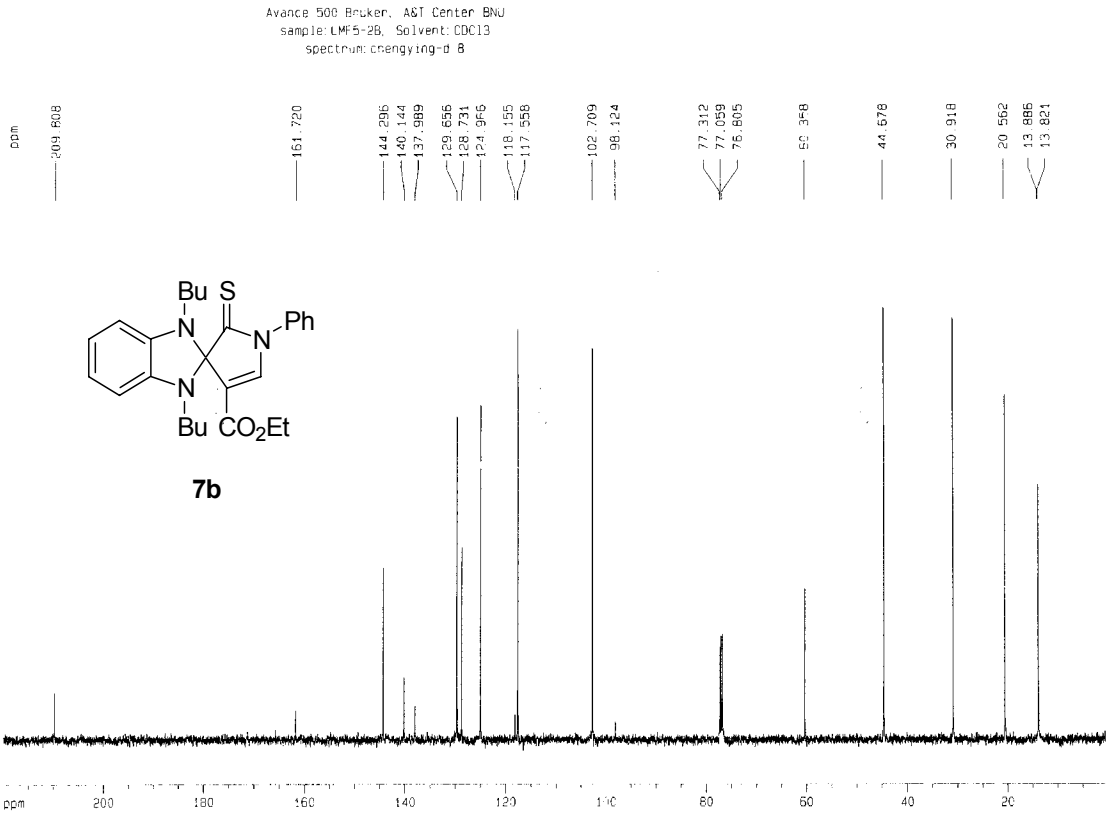
7a


Avance 500 Bruker, A&T Center BNU
sample: LMF5-6B, Solvent: CDCl3
spectrum: chengying-c 7
ppm
211.094
161.699
143.809
139.359
138.028
129.634
128.731
124.948
118.303
117.523
102.473
77.337
77.082
76.829
60.340
38.594
13.834
13.762
Et S
N
Ph
N
N
Et CO2Et
ppm

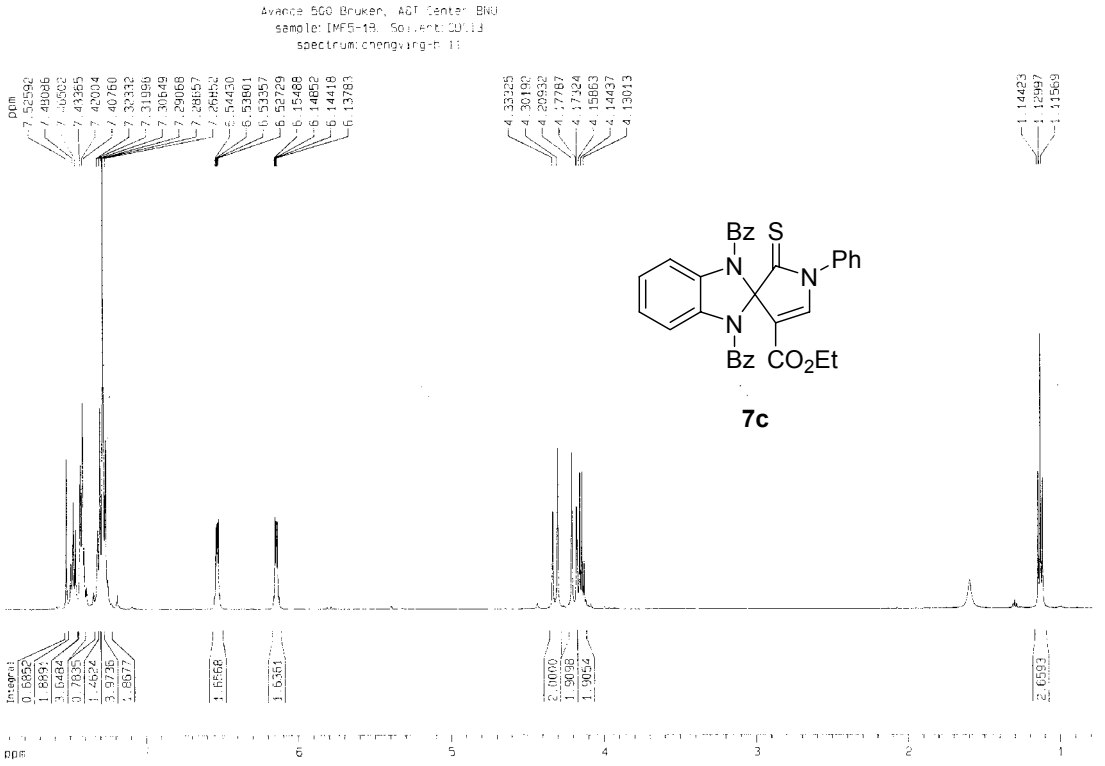
7a

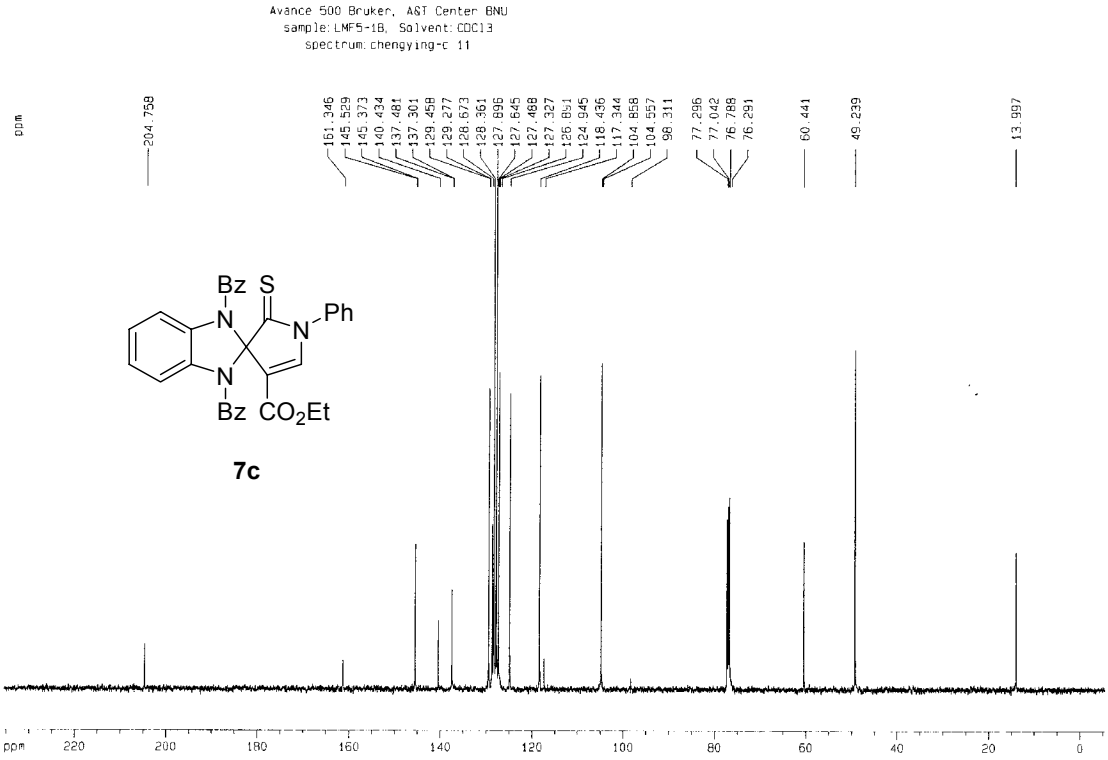

Avance 500 Bruker, A&T Center BNU
sample: LMF-5-2B, Solvent: CDCl3
spectrum: chengying-c 72
ppm
Integral
0.4026
1.0758
1.2441
0.9174
0.9333
0.9309
2.0000
2.2227
2.2127
1.5824
3.0120
ppm

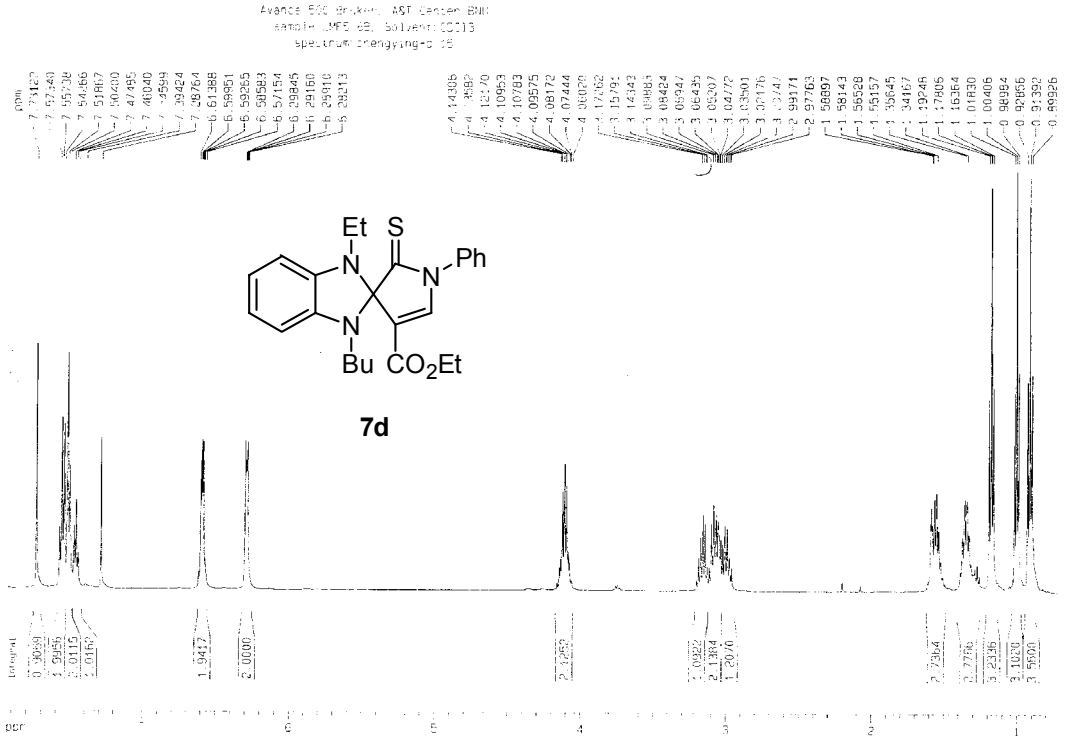
7b


Avance 500 Bruker, A&T Center BNU
sample: LMF5-2B, Solvent: CDCl3
spectrum: chengying-d 8
ppm
209.808
161.720
144.296
140.144
137.989
129.656
128.731
124.966
118.155
117.558
102.709
98.124
77.312
77.059
76.805
50.358
44.678
30.918
20.562
13.886
13.821
ppm

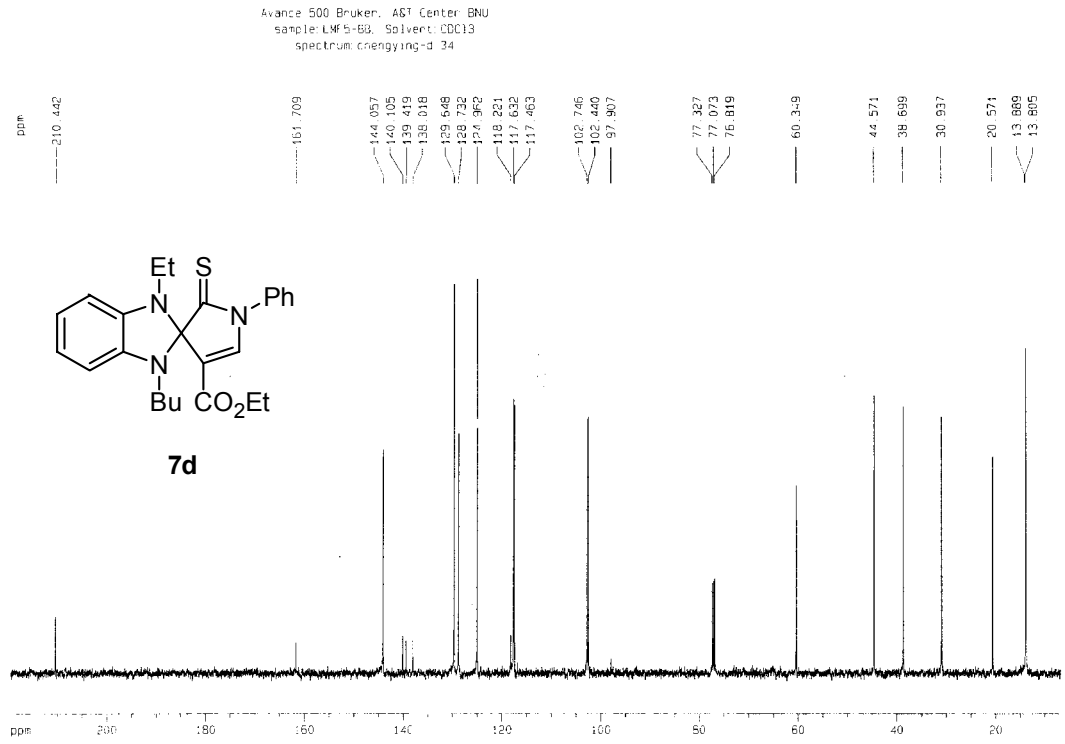
7b


Avance 500 Bruker, A&T Center BNU
sample: LMF5-1B, Solvent: CDCl3
spectrum: chengying-c 11
Bz S
N
Ph
N
N
Bz CO2Et
7c

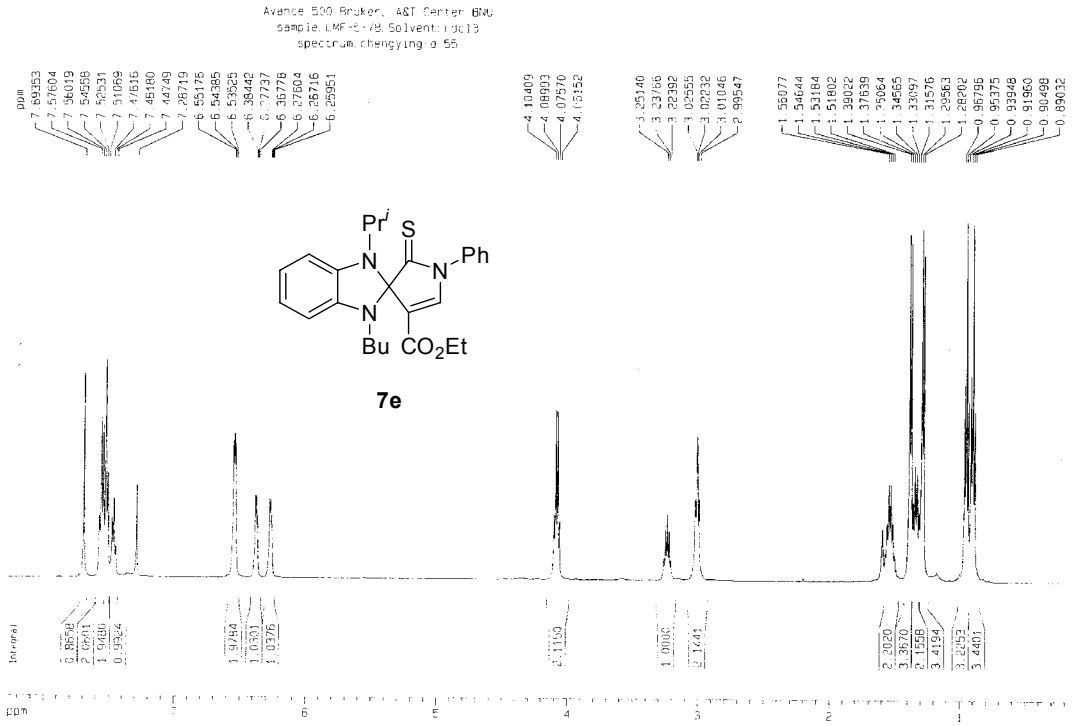

Avance 500 Bruker, A&T Center BNU
sample: LMF5-1B, Solvent: CDCl3
spectrum: chengying-c 11
Bz S
N
Ph
N
N
Bz CO2Et
7c



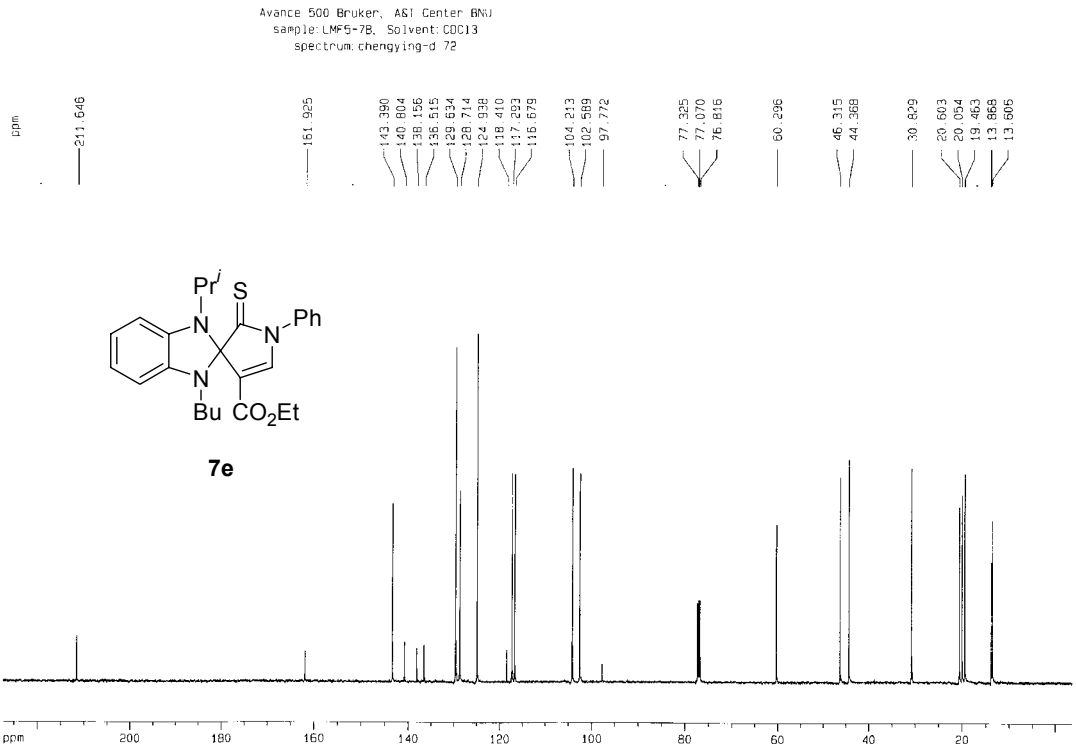
7d



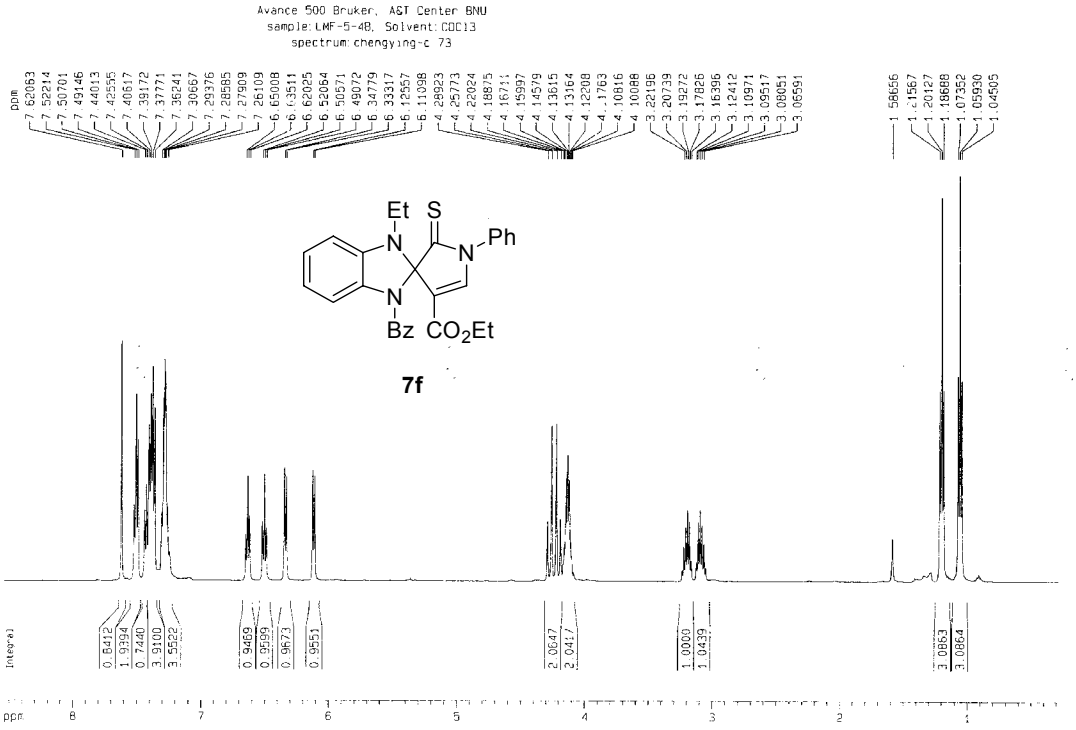
7d

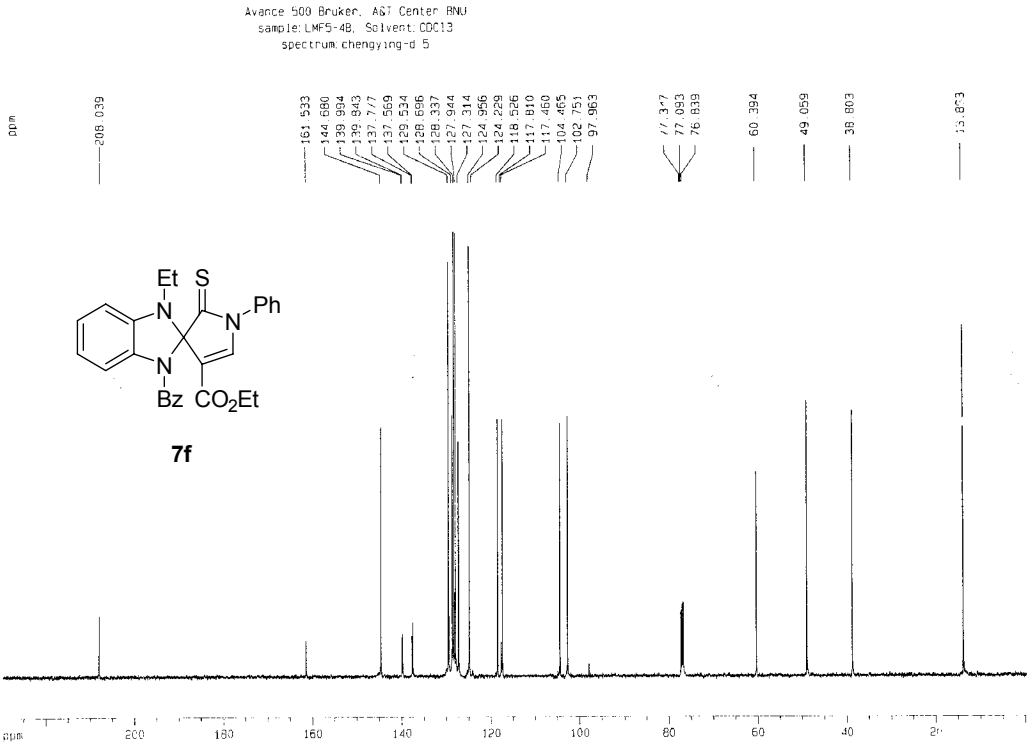

Avance 500 Bruker, A&I Center BNU
sample: LMF5-7B, Solvent: cdcl3
spectrum: chengying-d 55
ppm
Integral
Pr^i
S
N
Ph
Bu
CO2Et

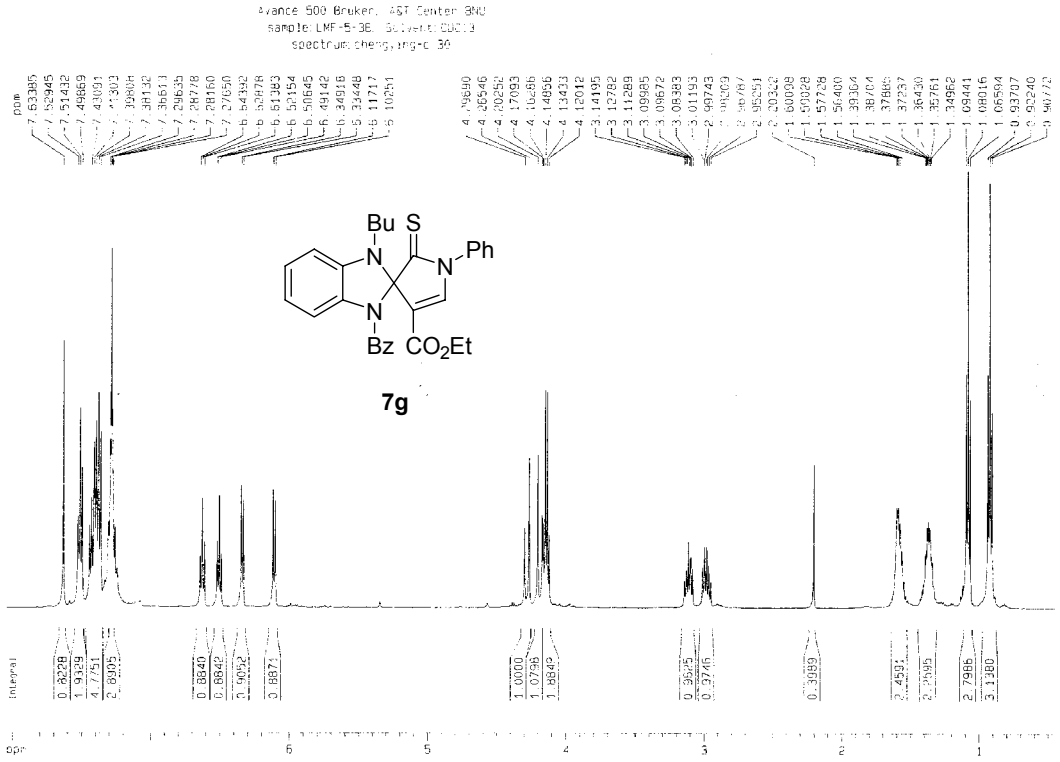
7e

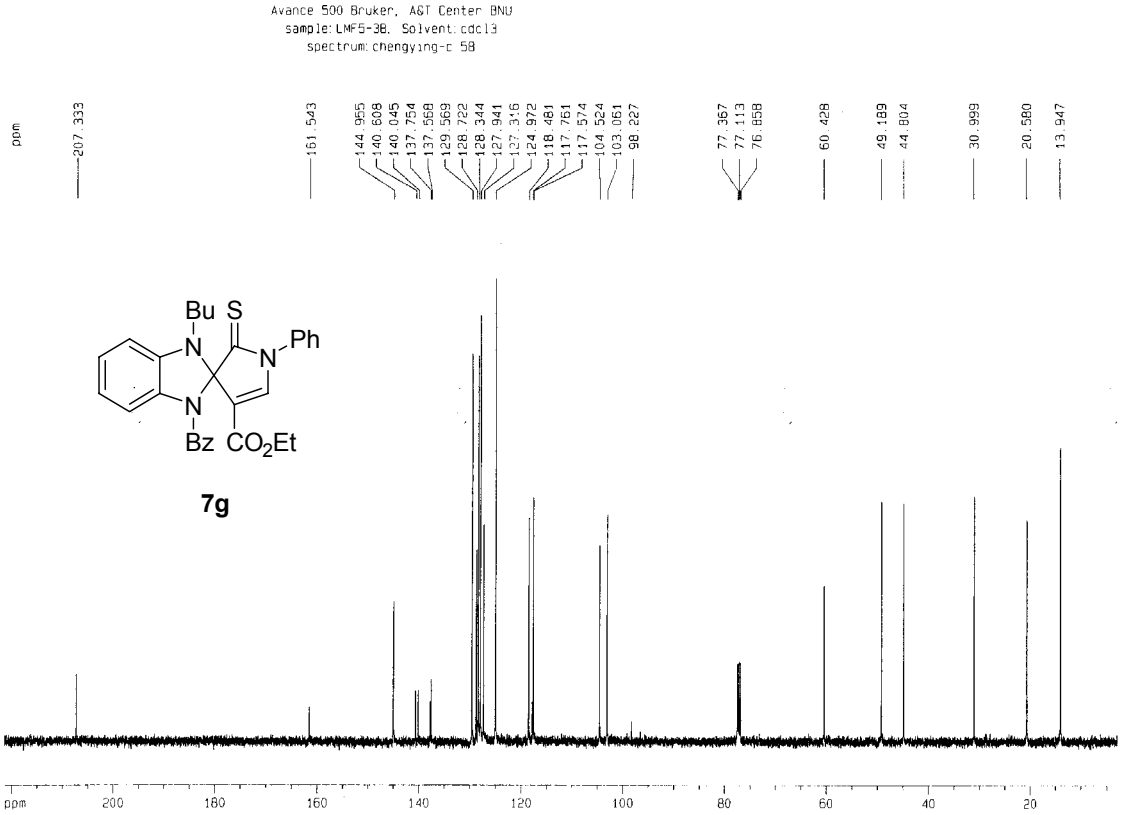

Avance 500 Bruker, A&I Center BNU
sample: LMF5-7B, Solvent: CDCl3
spectrum: chengying-d 72
ppm
211.646
161.925
143.390
140.804
138.156
136.515
129.634
128.714
124.938
118.410
117.293
116.679
104.213
102.589
97.772
77.325
77.070
76.816
60.296
46.315
44.368
30.829
20.603
20.054
19.463
13.868
13.606
Pr^i
S
N
Ph
Bu
CO2Et

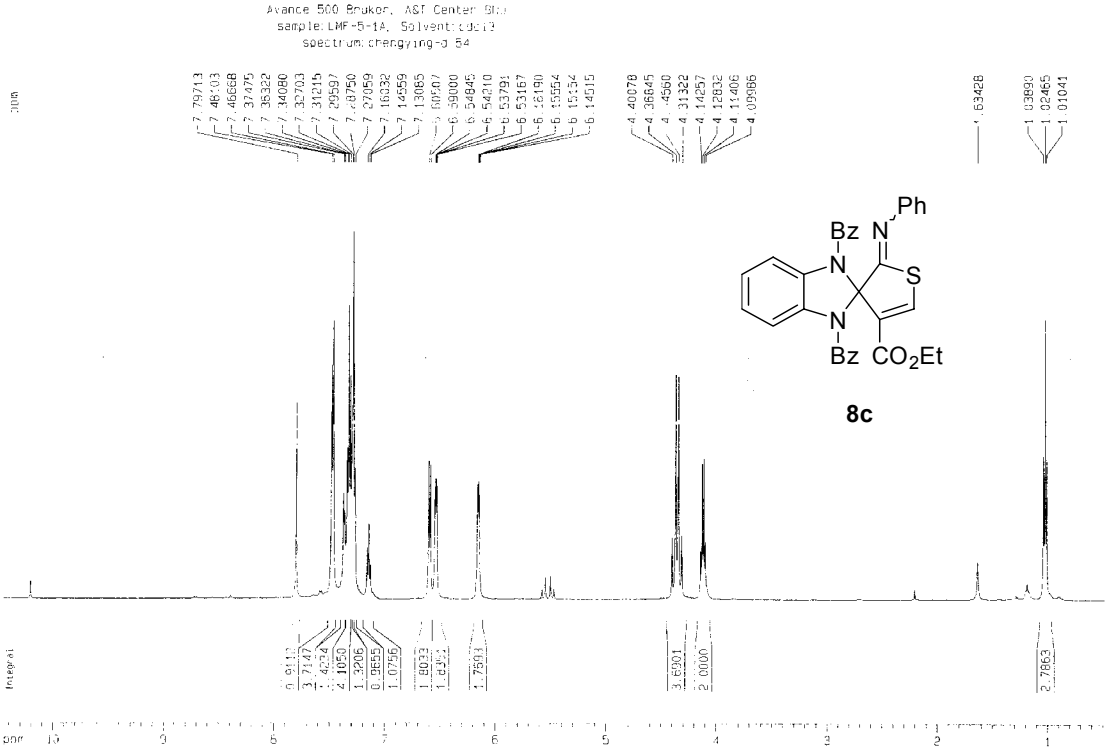
7e

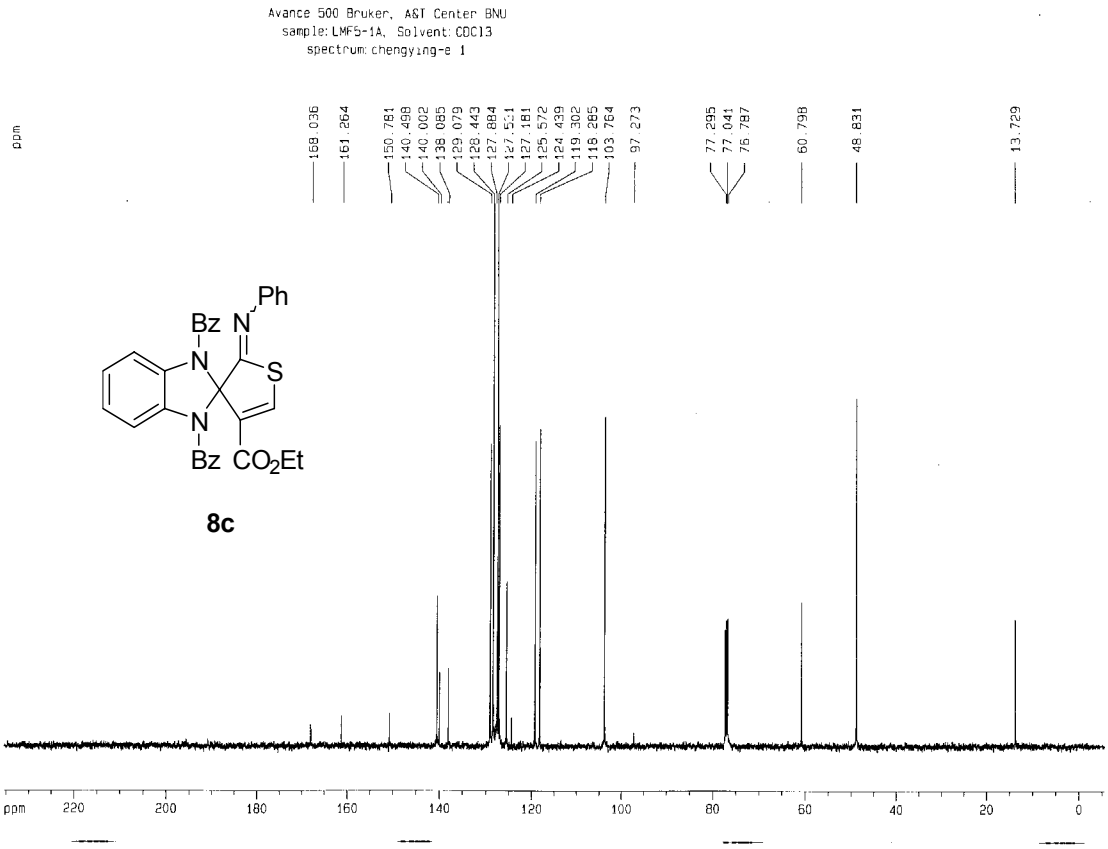

Avance 500 Bruker, A&T Center BNU
sample: LMF-5-4B, Solvent: CDCl3
spectrum: chengying-c 73
Et S
N
Ph
N
N
Bz CO2Et
7f
Integral
ppm

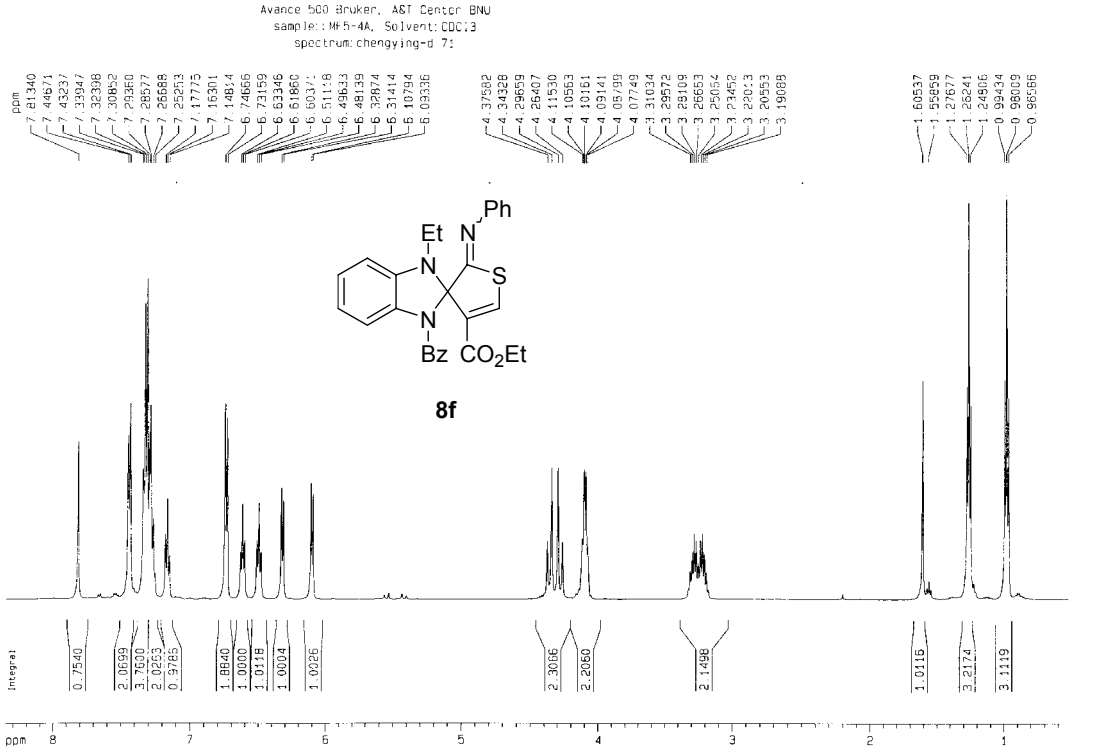

Avance 500 Bruker, A&T Center BNU
sample: LMF5-4B, Solvent: CDCl3
spectrum: chengying-d 5
ppm
Et S
N
Ph
N
N
Bz CO2Et
7f

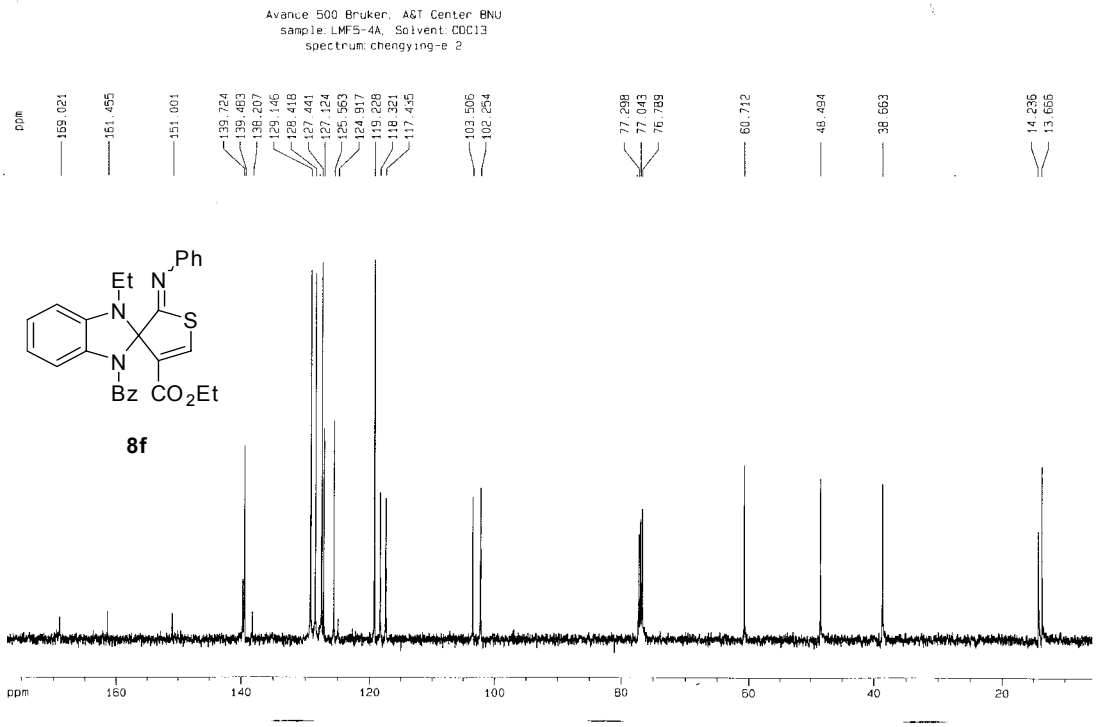

Avance 500 Bruker, A&T Center BNU
sample: LMF5-3B, Solvent: CDCl3
spectrum: chengying-c 39
Bu S
N
Ph
N
N
Bz CO2Et
7g
Integral
ppm

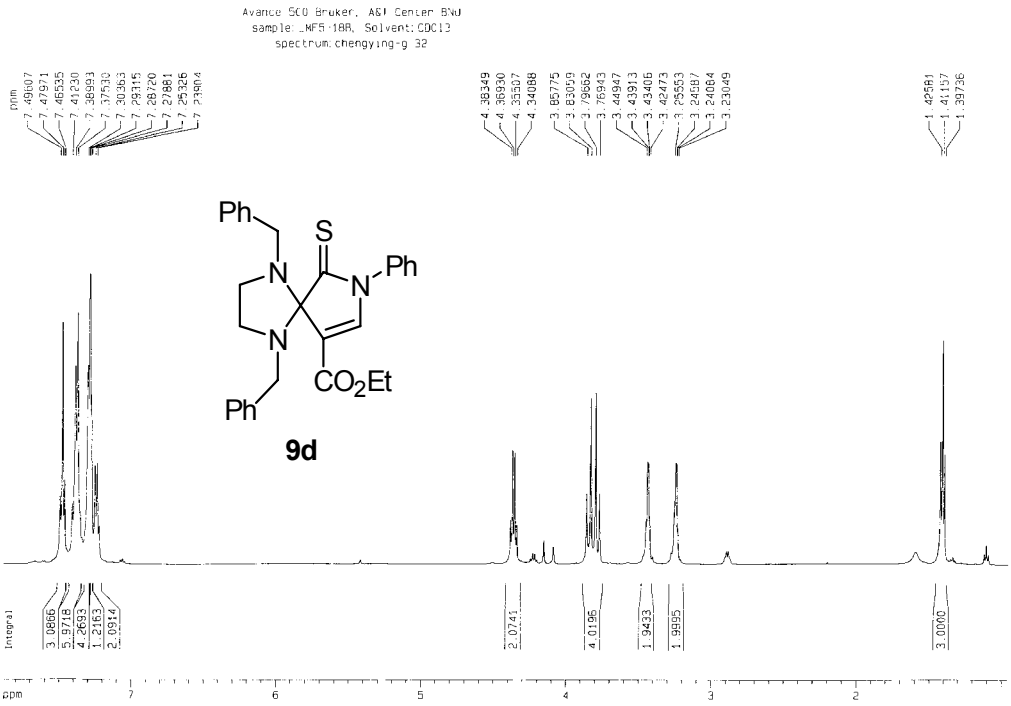

Avance 500 Bruker, A&T Center BNU
sample: LMF5-3B, Solvent: cdcl3
spectrum: chengying-c 58
ppm
207.333
161.543
144.955
140.608
140.045
137.754
137.568
129.569
128.722
128.344
127.941
127.316
124.972
118.481
117.761
117.574
104.524
103.061
98.227
77.367
77.113
76.858
60.428
49.189
44.804
30.999
20.580
13.947
Bu S
N
Ph
N
N
Bz CO2Et
7g
ppm

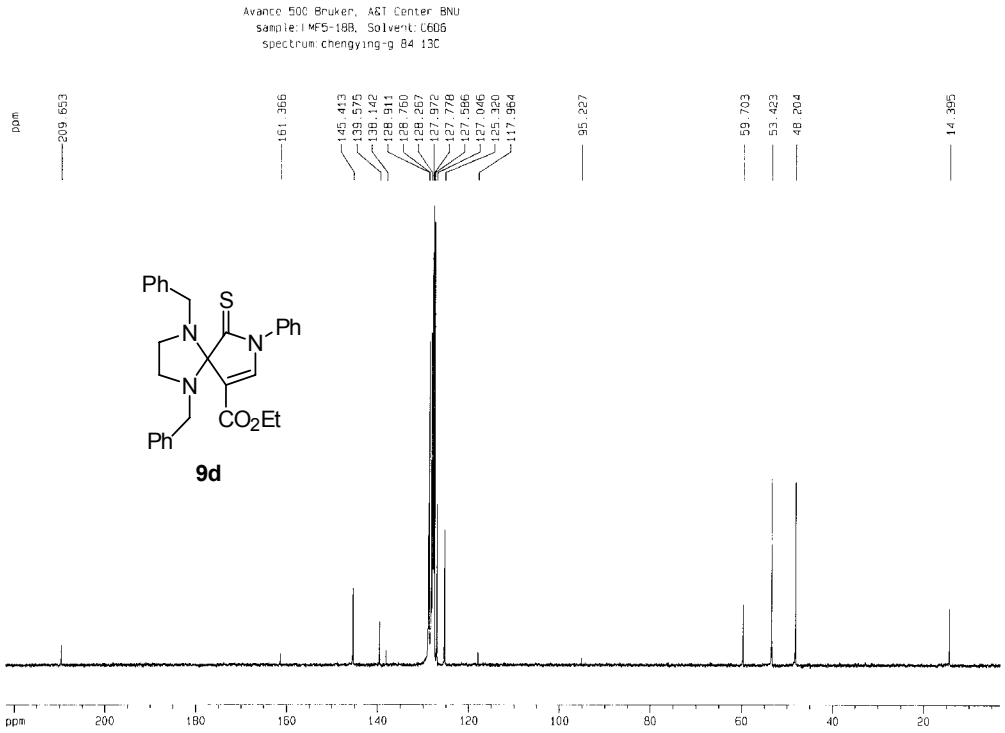

Avance 500 Bruker, A&T Center BNU
sample: LMF5-1A, Solvent: CDCl3
spectrum: chengying-h 54
Ph
Bz N
N
S
N
Bz CO2Et
8c


Avance 500 Bruker, A&T Center BNU
sample: LMF5-1A, Solvent: CDCl3
spectrum: chengying-c 1
Ph
Bz N
N
S
N
Bz CO2Et
8c

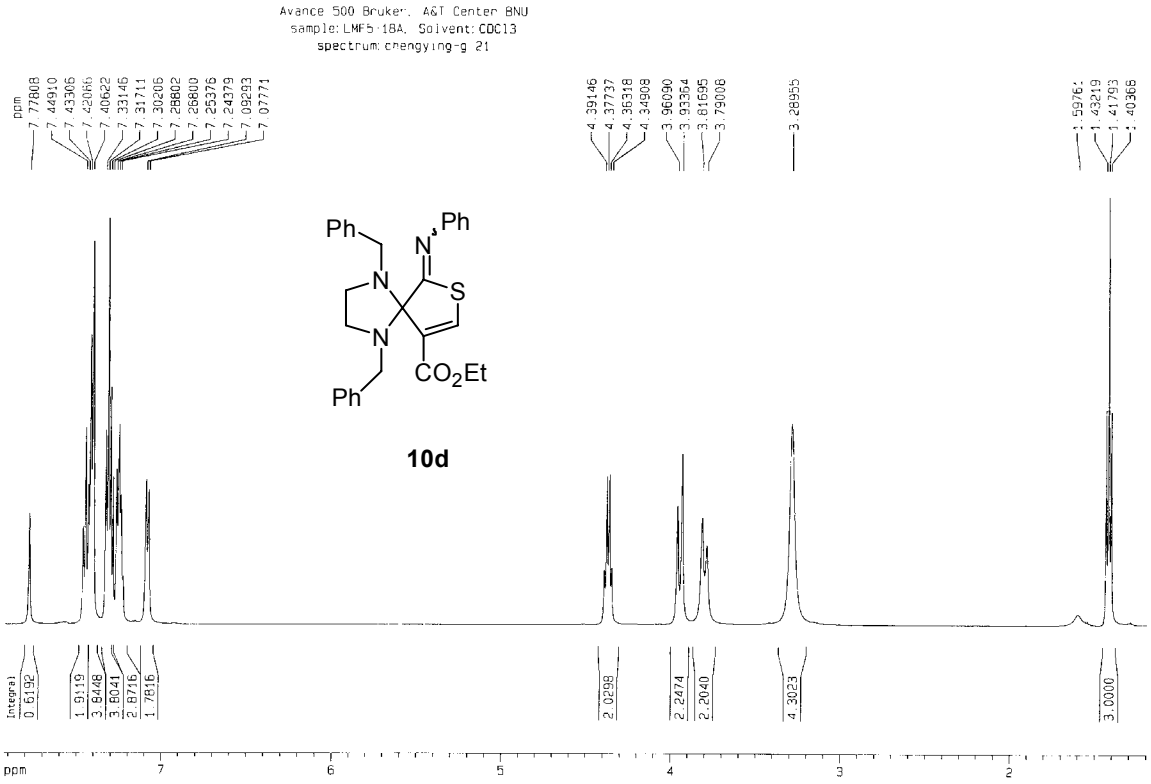

Avance 500 Bruker, A&T Center BNU
sample: : MF5-4A, Solvent: CDCl3
spectrum: chengying-d 71
Et
N
Ph
S
Bz
CO2Et
8f
Integral
ppm

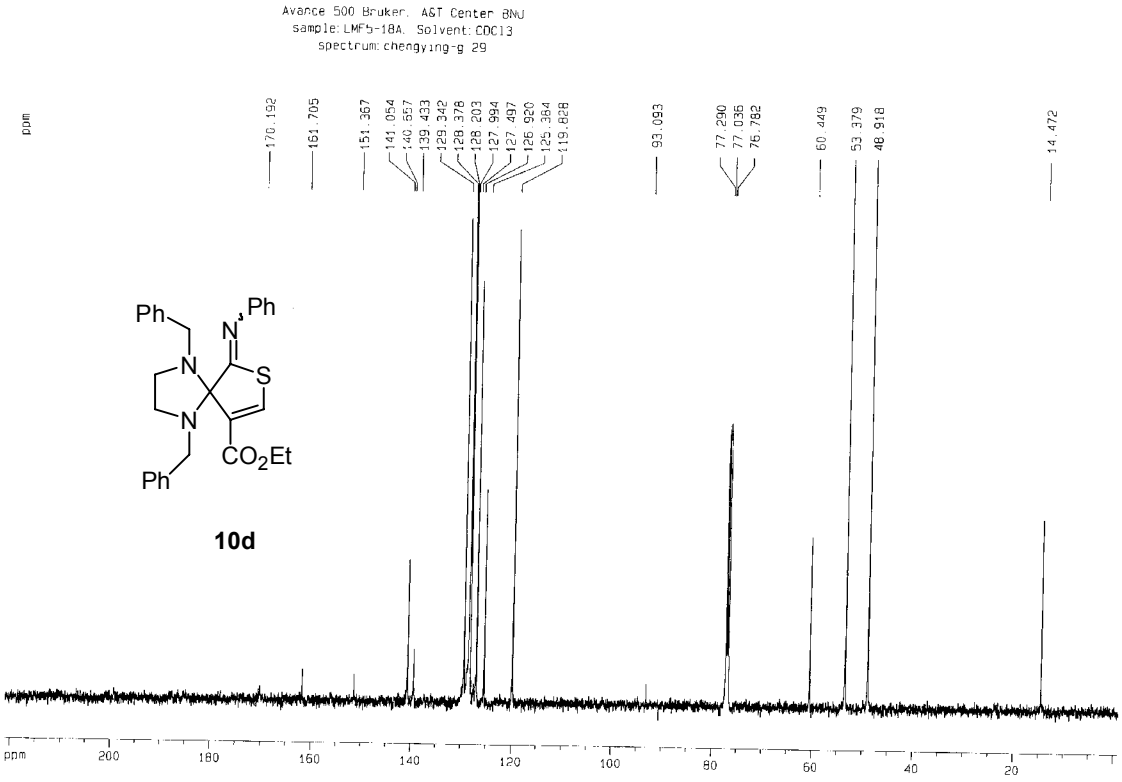

Avance 500 Bruker, A&T Center BNU
sample: LMF5-4A, Solvent: CDCl3
spectrum: chengying-e 2
Et
N
Ph
S
Bz
CO2Et
8f
ppm

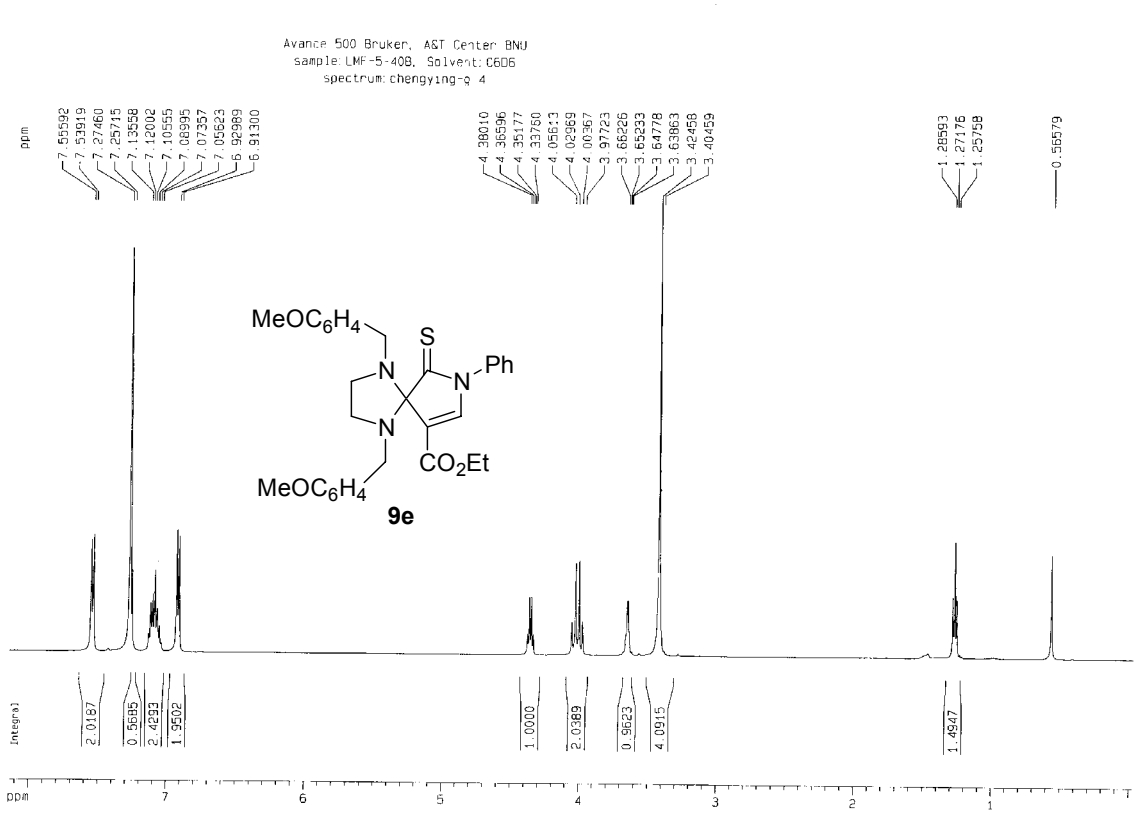


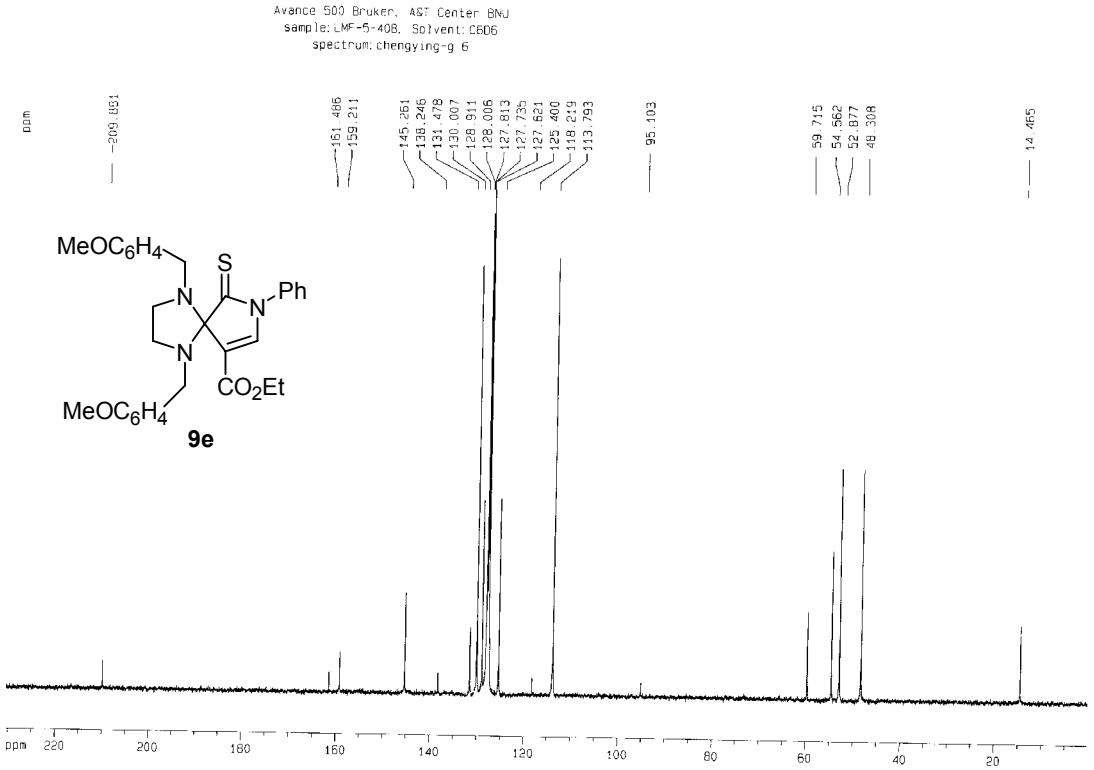


Solvent□C_6D_6

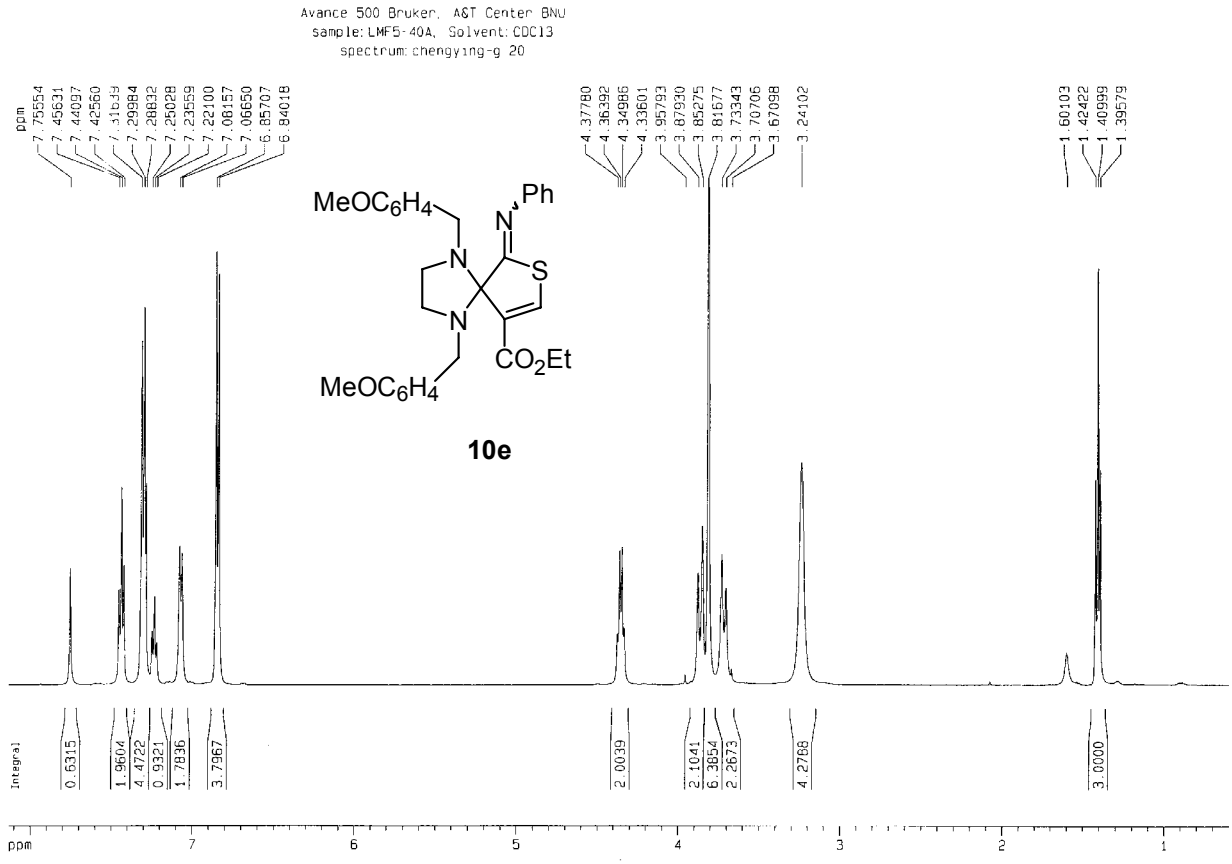

Avance 500 Bruker. A&T Center BNU
sample: LMF5-18A. Solvent: CDCl3
spectrum: chengying-g 21
ppm
7.78081
7.49101
7.43365
7.42066
7.40622
7.33146
7.31711
7.30206
7.28802
7.26800
7.25376
7.24379
7.09293
7.07771
4.39146
4.37737
4.36318
4.34908
3.96090
3.93354
3.81695
3.79006
3.28955
1.59767
1.43219
1.41793
1.40366
Ph
N
Ph
N
S
N
CO2Et
Ph
10d
Integral
0.6192
1.9119
3.8448
3.8041
2.8716
1.7816
2.0298
2.2474
2.2040
4.3023
3.0000
ppm
7
6
5
4
3
2

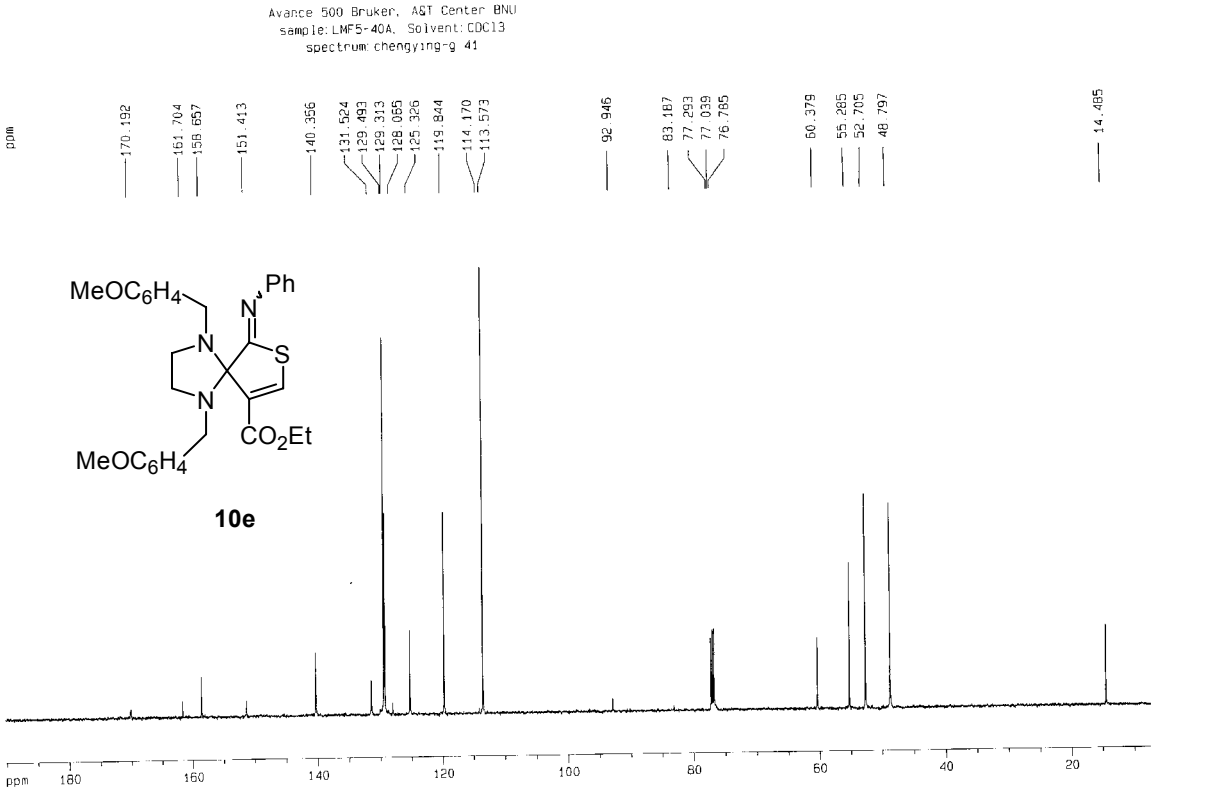

Avance 500 Bruker. A&T Center BNU
sample: LMF5-18A. Solvent: CDCl3
spectrum: chengying-g 29
ppm
170.192
161.705
151.367
141.054
140.557
139.433
129.342
128.378
128.203
127.994
127.497
126.920
125.384
119.828
93.093
77.290
77.036
76.782
60.449
53.379
48.918
14.472
Ph
N
Ph
N
S
N
CO2Et
Ph
10d
ppm
200
180
160
140
120
100
80
60
40
20





Solvent□C_6D_6


Avance 500 Bruker, A&T Center BNU
sample: LMF5-40A, Solvent: CDCl3
spectrum: chengying-g 20
ppm
7.75554
7.45631
7.44097
7.42560
7.29984
7.28832
7.25028
7.23559
7.22100
7.08157
7.06650
6.85707
6.84018
4.37780
4.36392
4.34986
4.33601
3.95793
3.87930
3.85275
3.81677
3.73343
3.70706
3.67098
3.24102
1.60103
1.42422
1.40999
1.39579
MeOC6H4
Ph
N
N
S
N
CO2Et
MeOC6H4
10e
Integral
0.6315
1.9604
4.4722
0.9321
1.7836
3.7967
2.0039
2.1041
6.3654
2.2673
4.2768
3.0000
ppm
7
6
5
4
3
2
1


Avance 500 Bruker, A&T Center BNU
sample: LMF5-40A, Solvent: CDCl3
spectrum: chengying-g 41
ppm
170.192
161.704
158.657
151.413
140.356
131.524
129.493
129.313
128.065
125.326
119.844
114.170
113.573
92.946
83.187
77.293
77.039
76.785
60.379
55.285
52.705
48.797
14.485
MeOC6H4
Ph
N
N
S
N
CO2Et
MeOC6H4
10e
ppm
180
160
140
120
100
80
60
40
20